Plastics, General Survey

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1. Introduction

Plastics are commercially used materials that are based on polymers or prepolymers. The name plastics refers to their easy processibility and shaping (Greek: *plastein* = to form, to shape).

Plastics and polymers are not synonyms. Polymers or prepolymers are raw materials for plastics; they become plastics only after physical compounding and/or chemical hardening. The same polymers may be used not as plastics but as fibers, in paints, or in other applications. Other polymers may be utilized as fibers, elastomers, thickeners, ion-exchange resins, etc., but not as plastics.

1.1. Polymers

1.1.1. Fundamental Terms [1–5, 8–14]

Polymers are chemical substances (chemical compounds) composed of polymer molecules. The term polymer refers to molecules composed of many units (Greek: *poly* = many, *meros* = parts). Polymer molecules may thus consist of many atoms, usually a thousand or more, thereby having high molar masses ("molecular weights"). Benzene can, for example, be "polymerized" from three acetylene molecules and was originally called a polymer. What is now called a polymer consists of molecules with hundreds and thousands of such units; it was therefore termed "high polymer" in the older literature.

The term polymer carries with it the connotation of molecules composed of many equal "mers",such as the ethylene units in polyethylene, $R'(CH_2CH_2)_nR''$. The number n of mers in a polymer molecule is called the degree of polymerization X. There are, however, many polymer molecules (especially biopolymer molecules) with very different types of mers per molecule, such as protein molecules $H(NH-CHR-CO)_nOH$ with up to 16 different R substituents in irregular sequence. A less constraining and more general term for polymer molecule is thus macromolecule. No sharp dividing line with respect to the number of units per molecule exists, however, between macromolecules and low molar mass compounds (micromolecules).

Macromolecules constitute the simplest individual chemical constituents of a polymer. A macromolecule may exist as an individual entity (in linear and branched polymers) or may be thought of as the primary molecule before chemical cross-linking.

Macromolecules exist in nature; examples are nucleic acids, proteins, polysaccharides, polyprenes, and lignins. Some of these naturally occurring polymers are used by man without further chemical transformation (e.g., cellulose for paper and cardboard). The chemical transformation of natural polymers with retention of their chain structures leads to semisynthetic materials, for example, cellulose acetates from cellulose. Chains of other natural polymers are cross-linked before commercial use. Examples are the hardening of casein (a protein) by formaldehyde to galalith (plastic) or the vulcanization of *cis*-1,4-polyisoprene (natural rubber) to an elastomer.

Most polymers are, however, synthesized chemically from molecules with low molar masses, the so- called monomers. Examples are the preparations of polyethylene from ethylene, poly(vinyl chloride) from vinyl chloride, nylon 6 from ε- caprolactam, or nylon 66 from adipic acid and hexamethylenediamine. Some industrial polymers result from the chemical conversion of other synthetic polymers, for example, poly (vinyl alcohol) from poly(vinyl acetate).

1.1.2. Nomenclature [1], [5], [15]

The nomenclature of individual polymers and plastics is as confusing as their classification according to properties. Various systems of nomenclature are used simultaneously, often by the same author. Abbreviations and acronyms abound, sometimes with different meanings for the same letter combinations and other times without explanation. In addition, about 25 000 trade names are used worldwide for plastics, fibers, and elastomers. Furthermore, a polymer from a certain company may come in many different grades depending on the processibility and application, sometimes up to 100 per polymer type. Some of these grades may even bear different trade names for various applications. On the other hand, the same trade name is occasionally used for plastics based on very different polymer types. An example is Bexloy of Du Pont, which may be an amorphous polyamide (Bexloy C), a high-impact polyester (Bexloy J), an ionomer (Bexloy W), or a thermoplastic elastomer (Bexloy V).

The following nomenclature systems are commonly used for polymers:

Long-Known Natural Polymers Often have Trivial Names. Examples are cellulose, the polymeric sugar (-ose) of the plant cell; casein, the most important protein of milk and cheese (Latin: *caseus* = cheese); nucleic acids, the acids found in the cell nucleus; catalase, a catalyzing enzyme.

Synthetic Polymers are Often Named after Their Monomers. Polymers of ethylene thus lead to polyethylene, those of styrene to polystyrene, those of vinyl chloride to poly(vinyl chloride), and those of a lactam to a polylactam. This "polymonomer" nomenclature has the disadvantage that the constitution of monomeric units of the polymer molecules is not identical with the constitution of the monomers themselves. For example, the polymerization of ethylene, $CH_2{=}CH_2$, leads to $\sim(CH_2-CH_2)_n\sim$, a saturated compound and thus a polyalkane, not an unsaturated "ene" as the name polyethylene may suggest. The polymerization of lactams (cyclic amides) does not give macromolecules with intact lactam rings in the polymer chains but gives open-chain polyamides, etc. This polymonomer scheme is also ambiguous if a monomer can lead to more than one characteristic unit in a polymer. An example is acrolein, $CH_2{=}CH(CHO)$, which can polymerize via the ethylenic double bond to give $\sim[CH_2-CH(CHO)]_n\sim$, via the aldehyde group to $\sim[O-CH(CH{=}CH_2)]_n$, or via both to give six-membered rings in polymer chains.

For trade purposes, certain polymer names may denote not only homopolymers but also copolymers, contrary to what the "chemical" names imply. For example, the copolymers of ethylene with up to 10 % butene-1, hexene-1, or octene-1 are known as linear low-density polyethylenes (LLDPEs). The commonly used chemical names of plastics thus often do not indicate the true chemical structure of the monomeric units of the polymers on which they are based.

Polymers are Often Named after Characteristic Groups in Their Repeating Units. Polyamides are thus polymers with amide groups $-NHCO-$ in their repeating units; for example $\sim[NHCO(CH_2)_5]_n\sim$ = polyamide 6 = nylon 6 = poly(ε-caprolactam). Other examples are polyesters with ester groups $-COO-$ or polyurethanes with urethane groups $-NH-CO-O-$ in the chains. A disadvantage is that this naming scheme is identical with that of organic chemistry where a polyisocyanate denotes a low molar mass compound with more than one isocyanate group per molecule [e.g., $C_6H_3(NCO)_3$]. A macromolecular polyisocyanate would thus be a polymer with many intact isocyanate groups per chain, for example, poly(vinyl isocyanate) $\sim[CH_2-CH(NCO)]_n\sim$. The poly(isocyanate)s of polymer chemistry, on the other hand, possess polymerized isocyanate groups as, for example, in $\sim(NR-CO)_n\sim$. Such compounds are unfortunately also often called polyisocyanates.

IUPAC Names. IUPAC recommends the use of constitutive names, similar to those used in inorganic and organic chemistry. The nomenclature of low and high molar mass inorganic molecules follows the additivity principle; those of low molar mass organic molecules the substitution principle. The nomenclature of organic macromolecules is a hybrid of both principles: the smallest repeating units are thought of as biradicals according to the substitution principle; then their names are added according to the additivity principle, put in parentheses, and prefixed with "poly." Names of repeating units are written without spaces between words. The polymer $\sim[O-CH_2]_n\sim$ from formaldehyde, $H_2C{=}O$, is thus called poly(oxymethylene). The polycondensation of ethylene glycol $HO-CH_2-CH_2-OH$ with terephthalic acid $HOOC-(p\text{-}C_6H_4)-COOH$ leads to a polymer $\sim[O-CH_2CH_2-O-OC(p\text{-}C_6H_4)CO]_n\sim$ with the systematic name poly(oxyethyleneoxyterephthaloyl). The trivial names of this polymer are polyethylene terephthalate, and poly(ethylene glycol terephthalate), poly(ethylene terephthalate). It is also known as "saturated polyester" (although it is only one of the many possible saturated polyesters), as PET (an acronym) or PETP (an abbreviation) in the plastics literature, by the acronym PES in the fiber literature, and as PETE for recycling purposes.

IUPAC names are rarely used in the plastics literature. They are however important for systematic searches in *Chemical Abstracts* and other literature services.

1.2. Plastics

1.2.1. Fundamental Terms [16–39, 41–53]

Early plastics resembled natural resins. These natural resins are organic solids that break with a conchoidal fracture in contrast to the planar surfaces created upon the fracture of crystalline materials or the drawn-out zones formed upon the breaking of gums and waxes. Natural resin refers mainly to oleoresins from tree sap but is also used for shellac, insect exudations, and mineral hydrocarbons (→ Resins, Natural).

Early plastics were thus sometimes called synthetic resins. The word resin is today occasionally used for any organic chemical compound with medium to high molar mass that serves as a raw material for plastics (for a definition of the term resin according to current standards, see → Resins, Synthetic). Resin is not to be confused with rosin, which refers to mixtures of C_{20} fused-ring monocarboxylic acids such as pine oil, tall oil, and kauri resin. Rosin is the main component of naval stores (→ Resins, Natural).

Plastics are usually divided into two groups according to their hardening processes. Those that yield solid materials by simple cooling of a polymer melt (a physical process) and soften while being heated are called *thermoplastics*. *Thermosets*, on the other hand, harden through chemical cross-linking reactions between polymer molecules; when heated, they do not soften but decompose chemically (→ Thermosets). The shaping of a thermoplastic is thus a reversible process: the same material can be melted and processed again. A thermoset cannot be remelted and reshaped; its formation is irreversible.

Thermoplastics are normally composed of fairly high molar mass molecules because many physical properties effectively become molar mass independent only above a certain molar mass. Examples are melting temperatures and the moduli of elasticity. Other properties, however, increase with increasing molar mass (e.g., melt viscosities).

Thermosets are usually generated from fairly low molar mass polymers, called oligomers (science) or prepolymers (industry). High molar masses are unnecessary here because chemical reactions between prepolymer molecules lead to an interconnection of these molecules (cross-linking) and thus to a giant molecule, with 100 % conversion of the prepolymer. The properties of these giant polymer molecules are obviously independent (or nearly so) of the molar mass of the primary molecules. Prepolymers are thus thermosetting materials and become true thermosets only after the hardening reaction.

Plastics are usually divided into four groups: commodity plastics (also called standard plastics or bulk plastics), engineering plastics (sometimes referred to as technical plastics or technoplastics), high-performance plastics, and functional plastics (or specialty plastics). A commodity, engineering, or high-performance plastic may have many different applications, whereas a functional plastic has one very specific application. Polyethylene, a commodity plastic, may according to its type or grade be used for containers, as packaging film, as agricultural mulch, etc. Poly(ethylene – co – vinyl alcohol) with a high content of vinyl alcohol units, on the other hand, is a functional plastic that is used only as a barrier resin. Other functional plastics are employed in optoelectronics, as resists, as piezoelectric materials, etc. Functional plastic is not synonymous with functional polymer or functionalized polymer, because the latter terms refer to polymers with functional chemical groups (i.e., groups with specific chemical reactivities).

Commodity plastics are manufactured in great amounts, hence the terms bulk plastics or standard plastics. Engineering plastics possess improved mechanical properties compared to commodity plastics. Such improved properties may be higher moduli of elasticity, smaller cold flows, higher impact strengths, etc. Engineering plastics are also often defined as those thermoplastics that maintain dimensional stability and most mechanical properties above 100 °C or below 0 °C. High-performance plastics, on the other hand, are engineering plastics with even more improved mechanical properties.

No sharp dividing lines exist between commodity plastics and engineering plastics on the one hand or engineering plastics and high-performance plastics on the other; nor are there generally agreed upon property levels beyond which polymers are designated as engineering or high-performance plastics. The three groups of plastics, in general, include the following:

Commodity Plastics. Poly(vinyl chloride), polyethylenes (high density, low density, very low density), isotactic polypropylene, standard polystyrene.

Engineering Plastics. Poly(ethylene terephthalate), poly(butylene terephthalate), polyamides (aliphatic, amorphous, aromatic), polycarbonates, polyoxymethylenes, poly(methyl methacrylate), some modified polystyrenes such as styrene – acrylonitrile (SAN) and acrylonitrile – butadiene – styrene (ABS) copolymers, and high-impact polystyrenes (SB), as well as various blends such as poly(phenylene oxide) – polystyrene and polycarbonate – ABS.

High-Performance Plastics. Liquid crystalline polymers (LCPs), polyetheretherketone (PEEK), various polysulfones, polyimides, etc.

Some *thermosets* are also classified as engineering or high-performance plastics. In general, thermosets are, however, considered a separate group of plastics. They comprise alkyd (→ Alkyd Resins), phenolic (→ Phenolic Resins), and amino resins (→ Amino Resins) (melamine and urea resins), epoxides (epoxies) (→ Epoxy Resins), unsaturated polyesters (including so-called vinyl esters) (→ Polyester Resins, Unsaturated), polyurethanes (→ Polyurethanes), and allylics (→ Allyl Compounds, Chap. 3.).

1.2.2. Designations [54–58]

The plastics trade and technical literature indulges in trivial names, abbreviations, and acronyms. Acetal polymer is, for example, the name given to polymers with $-OCH_2-$ as the major repeating unit. Polymers of methacryl esters $\sim[CH_2 - C(CH_3)\ (COOR)]_n\sim$ are known as methacrylics (or often only acrylics), but polyacrylonitrile $\sim[CH_2 - CH(CN)]_n\sim$ is not considered an "acrylic" in the plastics literature (the textile literature calls it an acrylic fiber). Styrenics comprise homopolymers of styrene as well as copolymers of styrene with other monomers. Nylon, originally a protected trade name, is now a generic term for polyamides, especially aliphatic ones.

Abbreviations often have more than one meaning (Tables 1, 2, 3, 4): PBT may, for example, denote poly(butylene terephthalate), but it is also used for poly(*p*-phenylenebenzbisthiazole). Exhaustive lists of commonly used abbreviations of polymers and additives as recommended by various organizations have been compiled [58].

Table 1. Polymers by chain polymerization (addition polymerization), copolymerization, polycondensation (condensation polymerization), and polyaddition which are characterized by abbreviations based on the poly(monomer) nomenclature

Polymers of	ASTM	DIN	ISO	IUPAC	Other
Acrylester+acrylonitrile+butadiene	ABA	A/B/A			
Acrylester+acrylonitrile+styrene	ASA	A/S/A	A/S/A		
Acrylester+ethylene	EEA$^{\#}$		E/EA		EAA
Acrylic acid	PAA				PAS$^{\#}$
Acrylonitrile	PAN	PAN		PAN	
Acrylonitrile+butadiene	PBAN				
Acrylonitrile+butadiene+methyl methacrylate+styrene					MABS
Acrylonitrile+butadiene+styrene	ABS	ABS	ABS	ABS	ABS
Acrylonitrile+ethylene-propylene-diene + styrene		A/EPDM/S		AES	
Acrylonitrile+methyl methacrylate	AMMA	A/MMA	A/MMA		
Acrylonitrile+styrene	SAN	SAN	SAN	SAN	PSAN
Acrylonitrile+styrene+chlorinated polyethylene		A/PE-C/S			
Adipic acid+hexamethylenediamine	PA 6.6	PA 66	PA 6.6	PA 6.6	
Adipic acid+tetramethylene glycol					PTMA
Allyldiglycol carbonate	ADC				
p-Aminobenzoic acid					PAB
Aminotriazol					PAT
11-Aminoundecanoic acid		PA 11			
Azelaic anhydride					PAPA
Bisphenol A+phosgene	PC$^{\#}$	PC$^{\#}$	PC$^{\#}$	PC$^{\#}$	
Bitumen+ethylene				ECB	
Butadiene+methyl methacrylate + styrene		MBS			
Butadiene+styrene (thermoplastic)	SB	S/B	S/B	S/B	PASB
Butene-1	PB	PB	PB		BT
Butyl acrylate		PBA		PBA	
Butylene glycol+terephthalic acid	PBT	PBT	PBT		PTMT
Butyl methacrylate					PBMA
ε-Caprolactam	PA 6	PA 6	PA 6	PA 6	
Chlorotrifluoroethylene	PCTFE	PCTFE	PCTFE	PCTFE	
Chlorotrifluoroethylene+ethylene					ECTFE

Table 1 (*Continued*)

Polymers of	ASTM	DIN	ISO	IUPAC	Other
Cresol+formaldehyde	CF	CF	CF	CF	
1,4-Cyclohexanedimethylol+terephthalic acid					PCDT
Diallyl chloroendate (=diallyl ester of 4,5,6,7,7-hexachlorobicyclo-[2,2,1] 5-heptane-2,3-dicarbonic acid)	PDAC				
Diallyl fumarate	PDAF				
Diallyl isophthalate	PDAIP				
Diallyl maleate	PDAM				
Diallyl phthalate	PDAP	PDAP	PDAP	PDAP	DAP
1,4-Dichlorobenzene+disodium sulfide	PPS	PPS			
2,6-Dimethylphenol+oxygen	POP				PPO$^{\text{TM}}$
Dodecanolactam (laurolactam)	PA 12	PA 12	PA 12	PA 12	
Ethyl acrylate					PEA
Ethyl acrylate+ethylene		E/EA			EEA$^{\#}$
Ethylene	PE	PE	PE	PE	PL
Cross-linked polymer		VPE			XLPE
High-density polymer	HDPE	PE-HD	PE-HD		
Low-density polymer	LDPE	PE-LD	PE-LD		
Low-density polymer, linear	LLDPE				
Medium density polymer	MDPE				
Ultra-high molar mass polymer	UHMW-PE				
Ethylene+methyl acrylate+vinyl chloride		VC/E/MA	VC/E/MA		
Ethylene+methyl methacrylate	EMA	E/MA			
Ethylene+propylene		E/P	E/P		PEP
Ethylene+propylene (+diene)		EPDM			
Ethylene+tetrafluoroethylene	ETFE	E/TFE			
Ethylene+vinyl acetate	EVA	E/VA E/VAC	EVA E/VAC		VAE
Ethylene+vinyl acetate+vinyl chloride		VC/E/VAC	VC/E/VAC		
Ethylene+vinyl chloride		VC/E	VC/E		
Ethylene glycol					PEG
Ethylene glycol+maleic anhydride	UP$^{\#}$				
Ethylene glycol+terephthalic acid (ester)	PET	PET	PETP	PETP	PETE
Fast crystallizing polymer					CPET
Oriented polymer					OPET
Ethylene oxide	PEO	PEOX	PEOX	PEO	
Formaldehyde (or trioxane)	POM$^{\#}$	POM$^{\#}$	POM$^{\#}$	POM$^{\#}$	
Formaldehyde+furan	FF				
Formaldehyde+melamine	MF	MF	MF	MF	
Formaldehyde+melamine+phenol		MPF	MPF		
Formaldehyde+phenol	PF	PF	PF	PF	
Formaldehyde+urea	UF	UF	UF	UF	
Furfural+Phenol	PFF				
Hexafluoropropylene+tetrafluoroethylene	FEP	FEP	FEP		
Hexamethylenediamine+sebacic acid		PA 610			PA 6.10
p-Hydroxybenzoic acid	POB				PHB$^{\#}$
3-Hydroxybutyric acid					PHB$^{\#}$
2-Hydroxyethylmethacrylate					PHEMA
Isobutylene	PIB	PIB	PIB	PIB	IM
Laurolactam (dodecanolactam)	PA 12	PA 12	PA 12	PA 12	
Linseed oil, epoxidized		ELO	ELO		
Maleic anhydride+ styrene	SMA	S/MA			
Methacrylimide		PMI			
Methyl acrylate					PMA
Methyl acrylate+vinyl chloride		VC/MA	VC/MA		
Methyl α-chloromethacrylate	PMCA				
Methyl methacrylate	PMMA	PMMA	PMMA	PMMA	
Methyl methacrylate+vinyl chloride			VC/MMA		
1,4-Methylpentene	PMP	PMP	PMP		TPX
α-Methylstyrene		PMS			PAMS
α-Methylstyrene+styrene	SMS	S/MS	S/MS		

(*Continued*)

Table 1 (*Continued*)

Polymers of	ASTM	DIN	ISO	IUPAC	Other
Octyl acrylate+vinyl chloride		VC/OA	VC/OA		
Perfluoroalkoxyalkane	PFA	PFA			
Phosphoric acid					PPA#
Propylene	PP	PP	PP	PP	
Oriented polymer					OPP
Oriented biaxially					BOPP
Propylene+tetrafluoroethylene (alt.)					TFE-P
Propylene oxide	PPOX	PPOX	PPOX		
Soybean oil, epoxidized		ESO	ESO		
Styrene	PS	PS	PS	PS	
Expanded (foamed) polymer					EPS
High-impact polymer					HIPS
Impact resistant polymer	SRP	IPS			
Oriented polymer					OPS
Tetrafluoroethylene	PTFE	PTFE	PTFE	PTFE	
Tetrahydrofuran					PTHF
Polymer with hydroxy endgroups					PTMEG
Triallyl cyanurate	PTAC				
Trifluoroethylene				P 3 FE	
Trioxane (+comonomers)	POM#	POM#	POM#	POM#	
Vinyl acetate	PVAC	PVAC	PVAC	PVAC	PVA
Vinyl acetate+vinyl chloride	PVCA	VC/VAC	VC/VAC		
N-Vinylcarbazole	PVK	PVK	PVK		
Vinyl chloride	PVC	PVC	PVC	PVC	PCU, V
Polymerized in bulk					M-PVC
Polymerized in emulsion					E-PVC
Polymerized in suspension					S-PVC
Polymer as flexible film					FPVC
Polymer as oriented film					OPVC
Polymer as rigid film					RPVC
Vinyl chloride and vinylidene chloride		VC/VDC	VC/VDC		
Vinyl fluoride	PVF	PVF	PVF	PVF	
Vinylidene chloride	PVDC	PVDC	PVDC	PVDC	
Vinylidene fluoride	PVDF	PVDF	PVDF	PVDF	
Vinyl methyl ether					PVME
N-Vinylpyrrolidone	PVP	PVP	PVP		

Tables 1, 2, 3, and 4 give the recommendations for abbreviations of names of thermoplastics and thermosets by ASTM/ANSI (American Society for the Testing of Materials/American National Standards Institute [D 1600–86 a]), DIN (German Industrial Standards [7728]), ISO (International Standardization Organization [1043 – 1986 (ε)]), IUPAC (International Union of Pure and Applied Chemistry [Pure Appl. Chem. 59 (1987) 691]). "Other" means other abbreviations used in the field but not recommended by ASTM, DIN, ISO, or IUPAC. The recommended abbreviations are often neither identical with those of fibers of the same chemial structures nor with those of elastomers containing the same monomer units; some of these also deviate from those recommended for recycleable plastics. Several abbreviations have different meanings in either two or more of the ASTM, DIN, ISO and IUPAC systems and/or the technical literature, resp.; symbols with more than one meaning are characterized by # in Tables 1–4.

The abbreviations are in part based on the poly (monomer) nomenclature, i.e., on the names of the monomers used in the manufacture of polymers, sometimes, however, without a prefix "P" for "poly" (Table 1). The names of monomers for copolymers are given in alphabetical order without regard to their prevalence.

Other abbreviations are based on characteristic groups of polymers (Table 2) or indicate polymers synthesized by chemical transformation of base polymers (Table 4). Special abbreviations apply to blends, reinforced polymers, etc. (Table 4).

Special properties of polymers are symbolized by up to four additional letters. These letters are arranged after the symbol for the base poly-

Table 2. Abbreviations for polymers named after a characteristic polymer group

Characteristic group	ASTM	DIN	ISO	IUPAC	Other
Amide	PA	PA	PA	PA	
Amide, aromatic	PARA				
Metal coated films	PA**				
Saran coated films	PA*				
Amide – imide	PAI	PAI			
Aryl amide	PARA				
Aryl sulfone					PAS#
Benzimidazole					PBI
Carbodiimide					PCD
Carbonate, aromatic	PC#	PC#	PC#	PC#	
Epoxide (epoxy)	EP	EP	EP	EP	
Glass-fiber reinforced					GEP
Epoxide – ester			EPE		
Ester, saturated		SP			
Ester, thermoplastic	TPES				
Metallized polymer film					MPE
Ester, unsaturated	UP#	UP#	UP#	UP#	
Glass fiber reinforced					FRP
Ester – alkyd	PAK				
Ester – ether (thermoplastic elastomer)	TEEE				
Ester – imide	PEI				
Ether – block-amide	PEBA	PEBA			
Etheretherketone	PEEK				
Ether – imide		PEI			
Ether sulfone	PES PESU	PES			
Imide	PI	PI			
Isocyanurate		PIR			
Parabanic acid					PPA#
Phenylene ether	PPE	PPE			
Phenylene sulfone	PPSU	PPSU	PPSU		PSU
Silicone	SI	SI	SI		
Sulfone	PSUL	PSU			
Urethane	PUR	PUR	PUR	PUR	
Thermoplastic	TPUR				
Thermoset	TSUR				

mer according to ISO and DIN; in the technical literature, they are, however, commonly placed in front of the base symbol, following ASTM. DIN recommends the following letters for special properties: C = chlorinated; D = density; E = expanded, expandable; F = flexible, liquid; H = high; I = impact resistant; L = linear, low; M = molar mass, average (mean), molecular; N = normal, novolac; P = plasticized; R = raised (enhanced), resol; U = ultra, plasticizer-free (unplasticized); V = very; W = weight (mass); X = cross-linked. The technical literature also uses BO = biaxially oriented and O = oriented (usually in one direction). In the ASTM scheme, an asterisk (*) denotes a saran coated polymer film, two asterisks (**) a metallized polymer film.

Table 3. Abbreviations for polymers produced by chemical transformation of other polymers

Resulting polymer	ASTM	DIN	ISO	IUPAC	Other
Carboxymethyl cellulose	CMC	CMC	CMC	CMC	
Carboxymethyl hydroxyethyl cellulose					CMHEC
Casein, cross-linked with formaldehyde	CS	CS	CS	CS	
Cellulose, as Cellophan	C				
Ditto, coated with Saran	C*				
Cellulose acetate	CA	CA	CA	CA	
Cellulose acetobutyrate	CAB	CAB	CAB	CAB	
Cellulose acetopropionate	CAP	CAP	CAP	CAP	
Cellulose nitrate	CN	CN	CN	CN	NC
Cellulose plastics, unspecified	CE				
Cellulose propionate	CP	CP	CP	CP	
Cellulose triacetate	CTA	CTA			TA
Ethyl cellulose	EC	EC	EC	EC	
Hydroxyethyl cellulose					HEC
Hydroxypropyl cellulose					HPC
Hydroxypropyl methyl cellulose					HPMC
Methyl cellulose		MC			
Polyethylene, chlorinated	CPE	PE-C	PEC		
Chlorosulfonated	CSM				CSR
Poly(ethylene-co-vinyl alcohol)		E/VAL			EVAL
					EVOH
Polypropylene, chlorinated		PPC			
Polyvinyl alcohol	PVAL	PVAL	PVAL	PVAL	PVOH
Polyvinyl butyral	PVB	PVB	PVB		
Polyvinyl chloride, chlorinated	CPVC	PVC-C	PVCC		PC#, PeCe
Polyvinyl formal	PVFM	PVFM	PVFM	PVFM	

Companies have long used internal classification systems, and the military has issued plastics specifications. An industry-wide classification system for thermoplastic materials introduced by ISO is based on an alphanumeric "line call-out," a special code (see below) [54], [55]. A material is characterized by several data blocks that indicate its composition and certain property data or ranges. These property data refer to essential criteria. Since different thermoplastics have different applications, property data are restricted to different "leading properties" for each type of thermoplastic.

Table 4. Abbreviations for blends, reinforced polymers, etc

Resulting polymer	ASTM	DIN	ISO	IUPAC	Other
Elastomers, thermoplastic					
Containing ester and ether groups	TEEE				
Olefin-based	TEO				
Styrene-based	TES				
Epoxide, glass-fiber reinforced					GEP
Plastic, carbon-fiber reinforced		KEK			CFP
Glass-fiber reinforced					GFK
Man-made fiber reinforced					CFK
Metal fiber reinforced					MFK
Poly(acrylonitrile-co-styrene)+ chlorinated polyethylene					ACS
Sheet molding compound					SMC
with high glass fiber content					HMC

The property data covered by this classification scheme are thus not comprehensive. Rather, various plastics types are characterized by one to three sets of leading criteria, selected from

1. Chemical structure data such as content of vinyl acetate (VAC) or acrylonitrile units (AN), isotacticity (IT), or density (D) as a measure of branching
2. Molar mass data such as intrinsic viscosity (IV) or Fikentscher's K value (FK)
3. Bulk density (BD)
4. Rheological data such as melt flow rate (MFR) (melt flow index)
5. Thermal data such as Vicat temperature (VT) or torsional stiffness temperature (TST)
6. Mechanical properties such as modulus of elasticity (E), tensile stress at 100 % strain (TS), Shore hardness (SH), or impact strength (notched) (ISN)

The following leading criteria are used:

Polyethylene	D, MFR
Polypropylene	I, MFR
Polystyrene and acrylonitrile – styrene copolymers	VT, MFR
Styrene – butadiene, acrylonitrile – butadiene – styrene, and acrylonitrile – styrene – acrylic acid copolymers	VT, MFR, ISN
Ethylene – vinyl acetate copolymers	VAC, MFR
Poly(vinyl chloride)	IV, FK, BD
Poly(vinyl chloride), unplasticized	VT, E, ISN
Poly(vinyl chloride), plasticized	TS, SH, TST
Polyamides	IV, E
Polycarbonates	IV, MFR, E
Poly(methyl methacrylate)	IV, VT
Poly(ethylene terephthalate)	IV

The standard designation of a thermoplastic material consists of a description block, a standard number block, and a series of data blocks.

Designation Block. The designation block gives the type of material (e.g., thermoplastic, molding, etc.).

Standard Number Block. The standard number block consists of the number of the ISO (or DIN or other national) standard, followed by a hyphen and *data block 1*. This data block contains the abbreviation of the chemical name of the material [e.g., PE = polyethylene, PVC = poly(vinyl chloride)]. This may be followed by analytical data such as the vinyl acetate content of ethylene – vinyl acetate copolymers (EVAC). However, these are not the exact analytical data but rather code numbers for the range (called "cell") in which this material can substitute for a similar one. Separated by a hyphen, supplemental information on this material may be given (e.g., H = homopolymer, P = plasticized, U = unplasticized, E = polymerized in emulsion).

Data Block 2 may contain up to four letters that give qualitative information. The first letter denotes the intended application (e.g., B = blow molding, G = general purpose, P = paste resin, Y = textile yarn). The following one to three letters can code up to three essential additives or supplemental information, for example, A = antioxidant, D = powder (dry blend), L = light and weather stabilizer, S = slip agent.

Data Block 3. Quantitative information about the designated properties is contained in data block 3. The encoding of these data is different for each plastic material and each testing standard. For example, the code 20 – D 050 in data block 3 for a polyethylene tested according to DIN 16 776 means a material with a density of 0.918 g/cm^3 (cell 020) and a melt flow rate of 4.2 g/min (cell 050) measured at 190 °C under a load of 2.16 kg (D). On the other hand, a third data block 22 – 030 for a polyamide 12 means a polymer with an intrinsic viscosity of 210 cm^3/g (cell 22) and a modulus of elasticity of 280 MPa (cell 030). The definition of the cells can be found in special cell tables.

Data Block 4 gives information about the type and content of fillers or reinforcing materials; these codes are independent of the types of polymers. The first letter gives the type of filler, for example, C = carbon or G = glass. The second letter indicates the shape of the filler (e.g., F = fiber, S = sphere). The letters are followed by a code for the mass content of the filler; 15 for the range 12.5 – 17.5 wt %, 60 for the range 57.5 – 62.5 wt %.

Data Block 5 is reserved for specifications based on individual agreements between supplier and customer. It may code additional requirements, restrictions, or supplemental information.

A thermoplastic may thus carry the designation "Molding material DIN 7744-PC, XF, 55 – 045, GF 30," which indicates a polycarbonate (PC) with no special indication of its application (X) but with special burning characteristics (F), an intrinsic viscosity in a coded range of 55 (here for $[\eta] = 56\ cm^3/g$), and a melt flow rate of 5.5 g/(10 min) (coded as 045), which contains 30 % (30) of glass (G) fibers (F).

A designation system similar to the above ISO – DIN system has been recommended by ASTM [56], [57]. A typical ASTM designation, for example, would read "Molding material ASTM D-4000 PI 000 G 42 360"; this material is a polyimide (PI). Since no individual property table has been specified for polyimides, the cell table G of ASTM D-4000 has been used to characterize the properties of PI. This particular cell table identifies five different properties by designating cell limits to the five digits following the letter G. The first digit characterizes the minimum tensile strength, here "4", which according to cell table G means at least 85 MPa. The second digit gives the cell value for the flexural modulus (here "2" for 3500 MPa). The third digit denotes the Izod impact strength (50 J/m →"3"), and the fourth digit the heat deflection temperature (300 °C→"6"). The fifth digit is undetermined; the "0" indicates an unspecified property.

1.3. History of Plastics [59–64]

The first plastics were prepared long before their macromolecular nature was discovered. Decorative coatings based on polymers such as egg white or blood proteins were used in the cave paintings of Altamira, Spain, as early as 15 000 B.C. Later painting methods utilized gelatin and the polymers resulting from naturally drying vegetable oils. The use of these materials resulted from the eternal desire of artists for easy-to-handle materials that give an optimal artistic effect and have infinite stability.

These requirements were not restricted to surface coatings, which are two dimensionally applied plastics. Cow horns were used in the Middle Ages to prepare windows for lanterns and intarsia in wood. To this purpose, the horns had to be flattened by steaming, a very difficult process. The flattened horns also tended to curl up after a while. An early, easy-to-process substitute for natural horn was reported by the Bavarian monk WOLFGANG SEIDEL (1492 – 1562); it undoubtedly derived from far older recipes. This imitation horn was based on the protein casein, the white material from skim milk. Casein was extracted from skim milk with hot water, treated with warm lye, and shaped while being warmed; the desired shape was then fixed by immersion in cold water. Unknown inventors later discovered that the addition of inorganic fillers increased the mechanical stability of this early thermoplastic. The same material was used later for children's building blocks by the German aviation pioneer OTTO LILIENTHAL (1848 – 1896) and his brother GUSTAV. In 1885 a patent based on the same physical process was granted to the American EMERY EDWARD CHILDS. The properties of these plastics were improved markedly by the chemical reaction of casein with formaldehyde, as described in 1897 by the German inventors WILHELM KRISCHE and ADOLF SPITTELER. The resulting thermoset was called galalith (Greek: *gala* = milk, *lithos* = stone); it is still used today for haberdashery.

Another early thermoset used natural rubber as the raw material. In 1839 the American CHARLES GOODYEAR discovered the cross-linking (vulcanization) of natural rubber to an elastomer by sulfur under the action of "white lead" (basic lead carbonate) and heat. His brother NELSON used larger amounts of sulfur and in 1851 invented ebonite, a hard, black thermoset.

The first fully synthetic thermoset was invented in 1906 by the Belgian-born American chemist Leo H. Baekeland, who heated various phenols with formaldehyde under pressure and produced insoluble hard masses. These "bakelites" were recognized in 1909 as excellent electrical insulators and thus became one of the foundations of the modern electrical industry. Baekeland was not the first to prepare phenolic resins though; they were first observed by Adolf von Baeyer in 1872. Baeyer's substances were merely resinous materials, and Baekeland's "heat and pressure" process was necessary before commercially useful materials could be produced.

The first *semisynthetic thermoplastics* originated from cotton. Cotton fibers consist of cellulose; they have been used by man since prehistoric times. Since cotton is relatively easily grown, many attempts have been made to improve its textile properties. The Englishman John Mercer discovered in 1844 that the treatment of cotton with aqueous solutions of caustic soda (sodium hydroxide) leads to fibers with increased strength, higher luster, and improved dyeability. The Frenchman L. Figuier demonstrated in 1846 that cellulose paper was strengthened in a manner similar to cotton when it was treated with sulfuric acid. In 1853 W. E. Gaine received an English patent for the same process, which delivered a parchment-like material. An English patent by Thomas Taylor described the formation of very resistant materials from layers of paper sheets by the combined action of zinc chloride and pressure. These products were called "vulcanfiber" since they resembled the vulcanization products of natural rubber.

Mercerized cotton, artificial parchment, and vulcanized paper result from physical transformations of cellulose. If, however, cellulose materials are treated not by sulfuric acid alone but by a mixture of sulfuric and nitric acids, a chemical reaction to cellulose nitrate (nitrocellulose, gun cotton) occurs. This chance discovery by the German Christian Friedrich Schönbein in 1846 paved the way for the invention of the first semisynthetic thermoplastic. In 1862 Alexander Parkes found an easy method for processing cellulose nitrate into thermoplastic masses by the addition of castor oil, camphor, and dyes. The manufacture of the resulting "parkesine" was difficult, however, and production ceased in 1867. The use of alcoholic solutions of camphor by Daniel W. Spill was equally unsuccesful. In 1869 a patent was granted to the American John Wesley Hyatt for the use of camphor without camphor oil or alcohol. The resulting "celluloid" is generally considered the pioneering thermoplastic [63].

Other early, fully synthetic thermoplastics have a far longer history, albeit not as industrial materials. Polymers of formaldehyde were found by Justus von Liebig in 1839; yet extensive scientific investigations by Hermann Staudinger in the 1920s and 1930s and major industrial development work by Du Pont were necessary before it became an engineering plastic in 1956.

Vinyl chloride was synthesized in 1838 by H. V. Regnauld, who also observed the formation of resins. Vinyl chloride was polymerized in 1912 by Klatte in Germany and Ostromuislensky in England, but not until 1931 was the first poly(vinyl chloride) produced commercially in Germany by I. G. Farben.

Styrene was discovered by a chemist called Neuman as reported in W. Nicholson's 1786 *Dictionary of Practical and Theoretical Chemistry*. The conversion of styrene to a solid mass was discovered by E. Simon in 1839, who considered it a styrene oxide. A. W. von Hofmann and J. Blyth showed in 1845 that the alleged styrene oxide was an isomer of styrene; they called it metastyrene. It was however only in 1920 that the polymeric nature of polystyrene was recognized by H. Staudinger; it was first produced commercially by I. G. Farben (Germany) in 1930.

A highly branched polyethylene is found in nature as the "mineral" elaterite. Lightly branched synthetic polyethylene was first obtained in 1933 by high-pressure polymerization of ethylene at ICI (England); its commercial production began in 1939. Linear polyethylenes were first synthesized in 1953 by low-pressure polymerization using catalysts based on transition metals (Ziegler), chromium oxide (Phillips Petroleum), and molybdenum oxide (Standard Oil of Indiana). For the first time, Ziegler – Natta catalysts also enabled the polymerization of α-olefins such as propylene to solid, stereoregular polymers; the commercial production of isotactic polypropylene (PP) began in Italy, the Federal

Table 5. World production of polymers (in 10^6 t/a)

Type	1940	1950	1960	1970	1980	1990
Plastics	0.36	1.62	6.7	31.0	59.0	100
Fibers						
Synthetic	0.005	0.069	0.70	5.0	11.5	15.7
Semisynthetic	1.1	1.6	2.6	3.4	3.3	3.2
Natural**	8.7	8.0	12.8	14.0	17.7	18*
Elastomers						
Synthetic	0.043	0.54	1.94	5.9	8.7	9.1*
Natural	1.44	1.9	2.02	3.1	3.9	4.9*

*Estimated.

**Textile fibers only.

Republic of Germany, and the United States in 1957. The use of these catalysts and the availability of inexpensive feedstocks from petroleum refining led to rapid growth of the polymer industry (Table 5).

Plastics are the leader in this growth, followed by synthetic fibers and synthetic elastomers. The world production of semisynthetic fibers (rayon and cellulose acetate) (→ Cellulose Esters) has, however, declined, mainly because of cost and environmental concerns in the developed countries and despite increased production of semisynthetic fibers in the developing countries.

1.4. Economic Importance [65–69]

The rapid growth of plastics production is a result of three factors: growth of world population, average increase in standard of living, and replacement of older materials by plastics. The growth pattern may be economy driven [determined by the price of materials (substitutes); shortages ("ersatz"), or government intervention (environmental concerns)], or technology driven (determined by technological requirements, internal knowhow, accidental discoveries).

The world population grew from 2.532×10^9 in 1950 to 5.32×10^9 in 1980, while the world plastics production (approximately equal to consumption) climbed from 0.6 kg per capita (1950) to ca. 18.8 kg per capita (1990) (Table 6).

These numbers are approximate because statistics are incomplete and may differ considerably from source to source. For example, 1987 world plastics production is given as either 37.5×10^6 t ([65], excluding South Africa and the People's Republic of China) or 55.4×10^6 t [66].

Table 6. Production of plastics, world population, and consumption per capita

Region/country	Production in 10^6 t/a				
	1950	1960	1970	1980	1990
European Community	0.3	2.3	11.5	19.7	30
United States	1.1	2.8	9.1	16.1	30
Japan	0.04	0.7	5.3	7.5	13
Eastern Europe	0.1	0.5	4.0	6.9	13
Other	0.07	0.3	1.1	8.8	14
Total	1.6	6.7	31.0	59.0	100
World population, $\times10^{-6}$	2532	3062	3730	4498	5320
Per capita consumption in kg	0.6	2.2	8.3	13.1	18.8

Great differences in plastics consumption exist between various countries. In 1988, the apparent annual per capita consumption as calculated from production plus import minus export (i.e., including stockpiling) was 128 kg in the Federal Republic of Germany; 104 kg in the United States of America, 95 kg in Switzerland; and 81 kg in Japan and the United Kingdom but in 1978 only 1.2 kg in Black Africa, 1.1 kg in Bolivia, and 0.4 kg in India [67] and has not much changed since. Since world population continues to grow and people in less developed countries justifiably aspire to higher living standards, the world plastics production is most likely to increase further despite some environmental concerns in highly industrialized countries (see below). Although all regions will share in this growth, it will be most pronounced in "other" countries (e.g., Saudi Arabia, countries in Central and South America, Southeast Asia, and the Indian subcontinent) and, if planned economies are replaced by free-market types, also in the former Comecon countries.

The replacement of other materials by plastics is more difficult to judge. Since developing countries possess a great and unsatisfied need for goods that have long been taken for granted in more affluent societies, an analysis cannot be based on world production of materials but only on that in highly developed countries such as the United States (Table 7).

Table 7 gives the apparent consumption of selected important materials, calculated from production plus import minus export i.e., including stockpiling but excluding the import – export of manufactured goods such as machinery

Table 7. Per capita consumption of selected materials in the United States in 1983 (estimated population: 234×10^6) [68]

Materials	Source	Consumption in kg/a	Imports in % of consumption
Nonmetallic minerals			
Sand, gravel	N[a]	2576	0
Stone	N[a]	3322	0
Cement	MN[b]	287	6
Clay	MN[b]	270	0
Gypsum	N[a]	81	39
Metals			
Raw steel	S[c]	421	15
Aluminum, primary	S[c]	15.0	6
Copper	S[c]	6.4	31
Lead	S[c]	4.8	10
Zinc	S[c]	3.8	39
Polymers			
Wood, wood products			
Lumber	N[a]	466	22
Plywood	MN[b]	29.6	4
Paper	MN[b]	277	6
Other	?	35	?
Fibers (excluding export – import of fabrics and garments)			
Cotton	N[a]	5.5	(50)[e]
Rayon, acetate	MN[b]	3.6	66
Wool, silk	N[a]	1.6	92
Synthetic fibers	S[c]	16.9	?
Elastomers (excluding exported rubber goods)			
Natural rubber	MN[b]	2.6	100
Synthetic rubber	S[c]	6.7	(12)[e]
Plastics (excluding manufactured goods)			
Plastics, resins	S[c]	71	(9)[e]
	MN[b]	0.2[d]	?
Leather	MN[b]	6.4	?

[a] Natural product.

[b] MN = physically or chemically modified natural product.

[c] S = synthetic product.

[d] Estimated.

[e] Net exports.

(metals), garments (fibers), tires (cars), newsprint (paper), etc. The highest per capita consumption is in construction materials (nonmetallic minerals, lumber, partly steel and aluminum), followed by packaging materials (partly steel, aluminum, paper).

Plastics constitute a fairly small percentage of all consumed materials (Table 7). However, they have the highest growth rate (Fig. 1). The data in Figure 1 are given on a volume basis because materials are used by volume although they are sold by mass. Although the share of plastics in terms of total materials produced (and mainly disposed) is quite low, it causes environmental concern because of its very visible proportion in household refuse (see Chap. 12).

Since construction and packaging are major applications for lumber, steel, and aluminum, it can be expected that plastics are important replacements for these materials. Packaging and building – construction are indeed the most important applications of plastics (Table 8); they also show the highest growth rates (ca. 15 % per year).

Plastics are consumed in far lesser amounts in electric – electronics applications, transportation, toys, housewares, appliances, and furniture; the U.S. use in agriculture and paints and coatings has not been reported. Plastics are critical and irreplaceable components in certain fields such as the electric – electronics industry. Consumption patterns are similar for nations with comparable affluence; the United States and West German applications of plastics do not differ significantly when the fact is considered that ca. 53 % of U.S. applications are not accounted for.

2. Molecular Structure of Polymers [1–5, 8–14]

2.1. Constitution

2.1.1. Homopolymers

A homopolymer is defined as a polymer derived from one type of monomer. The term homopolymer thus refers to the origin of the monomers in a polymer and not to the actual constitutional units. The polymerization of a monomer $CH_2{=}CHR$ leads to constitutional units $-CH_2CHR-$. These units may be connected to each other not only in head-to-tail positions but also in head-to-head and tail-to-tail arrangements:

$$\underset{\text{Head-to-tail}}{-CH_2-CHR-CH_2-CHR-} \qquad \underset{\text{Tail-to-tail}}{-CH_2-CHR-CHR-CH_2-}$$

$$\underset{\text{Head-to-head}}{-CHR-CH_2-CH_2-CHR-}$$

The proportion of head-to-head regioisomeric units increases with decreasing size of substituents R and with reduced resonance stabilization

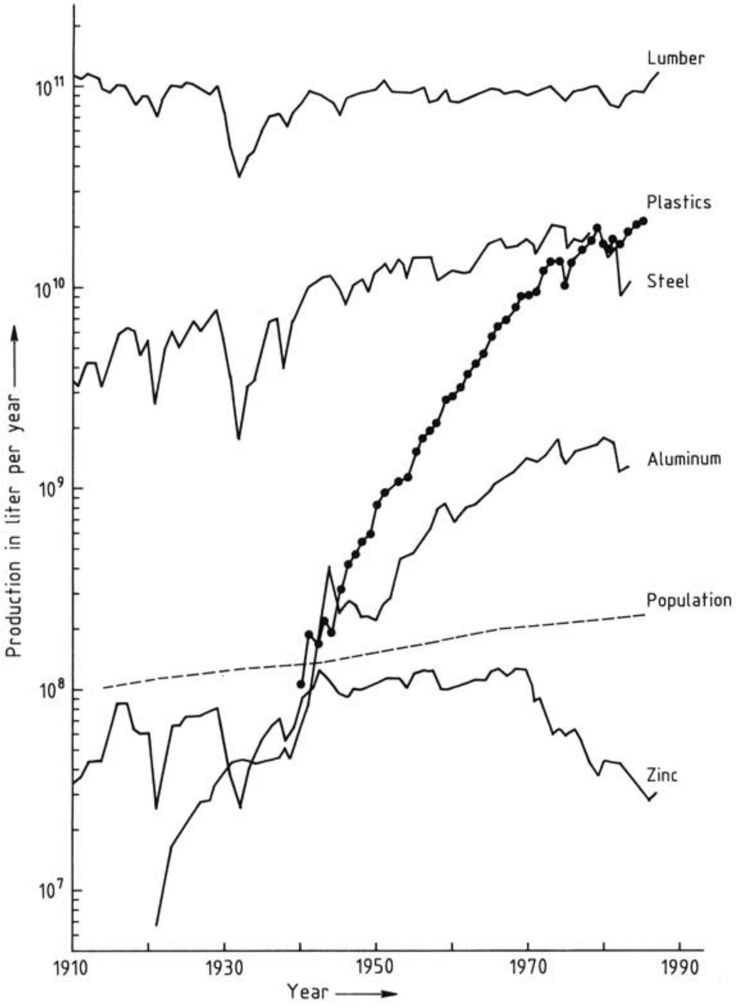
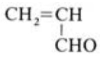


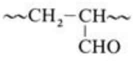
Figure 1. Production of important materials (in liters per year) in the United States during 1910 – 1990.
All metals are on smelter basis; - - - U.S. population (numbers). Reported commercial data were converted as follows: 1 board foot lumber = 2.36 L, 1 short ton ≈ 907 kg, 1 lb ≈ 0.454 kg; densities of steel (7.85 g/cm^3), aluminum (2.70 g/cm^3), zinc (7.13 g/cm^3), and plastics (1.1 g/cm^3) (average, weighted according to market shares of major plastics). Data from [69].

of the growing species. Free-radical polymerization of vinyl acetate [$CH_2{=}CH(OOCCH_3)$] leads to 1 – 2 %, of vinyl fluoride ($CH_2{=}CHF$) to 6 – 10 %, and of vinylidene fluoride ($CH_2{=}CF_2$) to 10 – 12 % tail-to-tail connections.

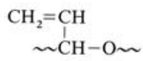
Monomer molecules can also polymerize to a lesser or greater extent via “wrong” groups. The amount of such isomeric units depends on the constitution of the monomer and the mode of polymerization. Acrolein (**1**), for example, polymerizes free radically via the carbon – carbon double bond (**2**) and the aldehyde group (**3**); it forms branched (**4**) or cross-linked units and even intramolecular rings (**5**) from two units of (**4**):


$CH_2{=}\underset{\displaystyle CHO}{\underset{|}{C}}H$

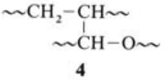
1


$\sim CH_2{-}\underset{\displaystyle CHO}{\underset{|}{C}}H\sim$

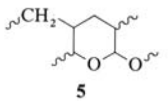
2


$CH_2{=}\underset{\displaystyle \sim CH{-}O\sim}{\underset{|}{C}}H$

3


$\sim CH_2{-}\underset{\displaystyle \sim CH{-}O\sim}{\underset{|}{C}}H\sim$

4


5

Monomers may also isomerize during polymerization, especially cationic polymerization. 4,4-Dimethyl-pentene-1 (**6**) polymerizes at low

Table 8. U.S. plastics sales and applications in 1988 (in 1000 t)

Polymer	Domestic sales	Domestic applications [a]								
		A	B	E	F	H	P	T	Y	U
PE-HD	3 743	9	251	53	5	143	1 692	19	77	1 494
PE-LD	4 479		127	168	4	191	1 092	20	74	2 803
PP	3 316	67	18	21	30	92	470	170	18	2 430
PS	2 329	77	127	186	55	115	108		108	1 553
SAN	62	10		2		10	8			32
ABS	562	91	69	53	2		2	95	17	233
Other styrenics	553									553
PPO alloys	82	20	2	1						59
PVC	3 779	64	2 301	232	41	29	199	101	15	809
Other vinyls [b]	435		2				53			380
PMMA	316	4	110					25		177
POM	58	5	7	2				12		32
PA	253	8		36			25	69		115
PC	195	16	52	25				28		74
PETP, PBT	911	3	3	20			450	20		415
Fluoropolymers	13									13
Cellulosics	41	1	2	2			3		1	32
Thermoplastic elastomers	225									225
UP [c]	623	30	132	17	9			64		371
EP	213	4	19	25			15	45		105
PF [d]	1 376	15	411	45	77	18	6	10		794
UF, MF [d]	688		121	14	10	6	3			534
PUR [e]	1 319	73	309		257				331	349
Alkyds	145									145
Other [f]	500	16		21	3	29	86	52	41	252
Total	26 216	513	4 063	923	493	633	4 212	730	682	13 979
% of accounted		4.2	33.2	7.6	4.0	5.1	34.4	6.0	5.5	
% of U.S. total	100	2.0	15.5	3.5	1.9	2.4	16.0	2.8	2.6	53.3
% of FRG [g]	100		21.0	15.0	5.0	2.5	25.0	7.0		10.5

[a] A=appliances, B=building/construction, E=electrical/electronic, F=furniture, H=household goods, P=packaging, T=transportation, Y=toys, U=unaccounted; 1982 FRG percentages (bottom line) are given for comparison.

[b] Poly(vinyl acetate), poly(vinyl butyral), ethylene – vinyl alcohol copolymers, etc.

[c] Without glass fibers.

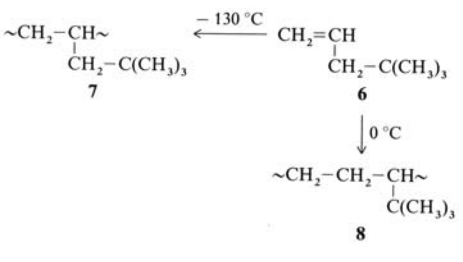
[d] Resin in plywood assumed as 20 %.

[e] Raw materials.

[f] Coumarones, high-performance resins, etc.

[g] Plus paints etc. (10 %) and agricultural (4.0 %).

temperature (≈−130 °C) via the carbon – carbon double bond (**7**), but at higher temperature (≈0 °C) leads to a "phantom polymer" (**8**) with three carbon atoms per monomeric unit:



Irregular structures may also be created by chain-transfer reactions to polymer molecules (see Chap. 3); these reactions lead to branched polymers.

The presence of such isomeric units can often be neither proved nor disproved. Polymer structures are therefore generally depicted by their most common constitutional repeating units; they are idealized structures.

The groups at the ends of polymer chains are likewise not shown, in part because they are often unknown and in part because their structure does not influence most of the polymer properties. End groups may be initiator or catalyst residues or groups that are generated by transfer reactions. These groups rarely affect mechanical properties; they may, however, negatively influence the thermal or photochemical stability of polymers.

2.1.2. Copolymers

Copolymers are generated from more than one type of monomer; they are called bipolymers, terpolymers, quaterpolymers, etc., according to the number of monomer types. The copolymerization of ethylene ($CH_2{=}CH_2$) and propylene [$CH_2{=}CH(CH_3)$] thus leads to the bipolymer poly(ethylene-*co*-propylene). Polymers of butadiene ($CH_2{=}CH{-}CH{=}CH_2$) with 1,4-units $-CH_2-CH{=}CH-CH_2-$ and 1,2-units $-CH_2-CH(CH{=}CH_2)-$ are not called copolymers because they are generated from only one monomer type. Rather, they are pseudocopolymers such as the ones that result from partial saponification of poly(vinyl acetate), $\sim[CH_2{-}CH(OOCCH_3)]_n\sim$, to a pseudocopolymer with vinyl acetate units and vinyl alcohol units $-CH_2-CH(OH)-$. The term copolymer thus does not refer to the chemical structure of the resulting polymer, but to the monomers from which it derives.

The succession of monomeric units in copolymer chains is known as their sequence. Monomer units "a" and "b" alternate in *alternating copolymers* (Table 9), which are limiting cases of periodic copolymers $\sim(abb)_n\sim$, $\sim(aabb)_n\sim$, $\sim(abc)_n\sim$, etc.

The sequence of monomeric units in *statistical copolymers* is determined by the statistics of copolymerization (Markov statistics of zeroth, first, etc., order). *Random copolymers* are special cases of statistical copolymers: the sequence follows Bernoulli statistics (i.e., zeroth-order Markov statistics).

Graded copolymers (i.e., tapered copolymers) exhibit a compositional gradient along the chain: one chain end is enriched in "a" units, the other in "b" units. *Block copolymers* are extreme cases of such graded copolymers; they consist of blocks of homosequences that are joined via their ends. Linear multiblock copolymers with short blocks are called *segment(ed) copolymers*. In *graft copolymers*, "b" blocks are connected to "a" chains via center monomeric units.

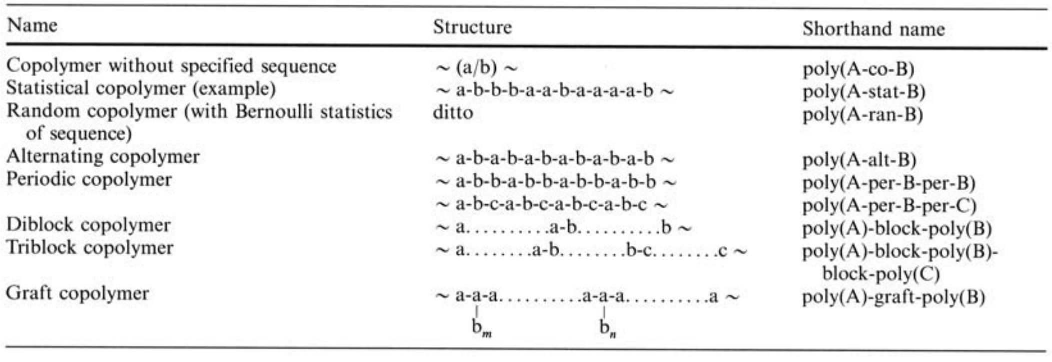
Copolymers poly(A-co-B) of monomers A and B possess properties quite different from blends of homopolymers A and B.

2.1.3. Branched Polymers

Open chains of the type $R-m_n-R$ exhibit the simplest structures. They posses n monomeric "m" units and two R end groups. They are also called linear chains (Fig. 2, L) because of their one-dimensional connectivity or their unbranched structures and because they were originally (and wrongly) assumed to be completely extended (stretched out). Spiropolymers and ladder polymers (see below) are also linear polymers because they are not "branched" in the macromolecular sense.

Cyclic Polymers (ring polymers; Fig. 2, R) consist of linear polymer molecules that are joined via their ends. They do not have end groups and are not called macrocycles because

Table 9. Types of copolymers from monomers A, B, and C (monomeric units are characterized by lower-case letters)



Name	Structure	Shorthand name
Copolymer without specified sequence	$\sim$ (a/b) $\sim$	poly(A-co-B)
Statistical copolymer (example)	$\sim$ a-b-b-b-a-a-b-a-a-a-a-b $\sim$	poly(A-stat-B)
Random copolymer (with Bernoulli statistics of sequence)	ditto	poly(A-ran-B)
Alternating copolymer	$\sim$ a-b-a-b-a-b-a-b-a-b-a-b $\sim$	poly(A-alt-B)
Periodic copolymer	$\sim$ a-b-b-a-b-b-a-b-b-a-b-b $\sim$ $\sim$ a-b-c-a-b-c-a-b-c-a-b-c $\sim$	poly(A-per-B-per-B) poly(A-per-B-per-C)
Diblock copolymer	$\sim$ a..........a-b..........b $\sim$	poly(A)-block-poly(B)
Triblock copolymer	$\sim$ a........a-b........b-c........c $\sim$	poly(A)-block-poly(B)-block-poly(C)
Graft copolymer	$\sim$ a-$\underset{b_m}{\underset{\vert}{a}}$-a..........a-$\underset{b_n}{\underset{\vert}{a}}$-a..........a $\sim$	poly(A)-graft-poly(B)

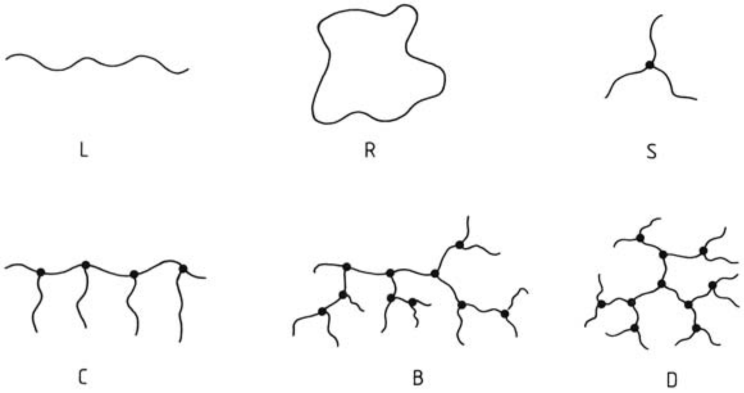
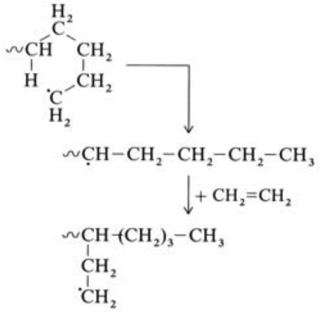


Figure 2. Schematic representation of linear and branched marcomolecules
L = Linear (unbranched) chain in almost extended state; R = ring molecule; S = starlike molecule with three subchains, C = comblike molecule with four branching points of functionality 3; B = randomly branched chain with subsequent branching; D = dendrimer with three-functional branch points and three generations of subchains

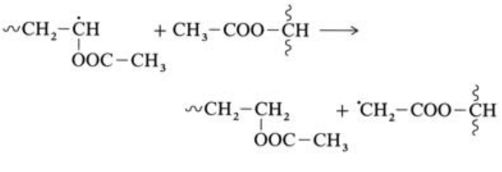
that term is traditionally reserved for "big rings" of ca. 15 – 20 chain atoms.

Branched polymers contain branch points that connect three or more subchains (sometimes called subunits). The following types of branched polymers are distinguished:

1. *Star polymers* possess one branching point from which three or more subchains radiate (Fig. 2, S).
2. *Dendrimers* (dendritic polymers) are star polymers in which the subchains are themselves starlike branched (Fig. 2, D). They are also called cascade polymers (because of the cascade-like sequence of branching points), isotropically branched polymers, or isobranched polymers (since each generation of newly added monomer molecules is "isotropically" arranged around the central core), or much more poetically, starburst polymers.
3. *Comb polymers* have "long" side chains, whose chemical structures usually differ from those of the main chains (Fig. 2, C). The term *graft copolymer* refers to comb polymers into which branches have been introduced by subsequent grafting onto a primary chain. Comb polymers whose side chains exhibit liquid crystalline (LC) behavior are called LC side-chain polymers.
4. *Randomly branched polymers* have a random distribution of branching points (Fig. 2, B); the subchains may be further branched (Christmas tree branching) or not. Short-chain and long-chain branching are distinguished. *Short-chain branches* are often generated by intramolecular transfer reactions, for example, the butyl side chain of polyethylene is formed during free-radical polymerization of ethylene:



Long-Chain Branches are usually generated by intermolecular transfer reactions. In the polymerization of vinyl acetate, side-chain radicals formed by transfer reactions may initiate the polymerization of additional vinyl acetate monomers.



$$\sim CH_2-\underset{OOC-CH_3}{\dot{C}H} + CH_3-COO-CH \longrightarrow \sim CH_2-\underset{OOC-CH_3}{CH_2} + \dot{C}H_2-COO-CH$$

Such side-chain radicals are also formed by radical transfer from certain initiator radicals.

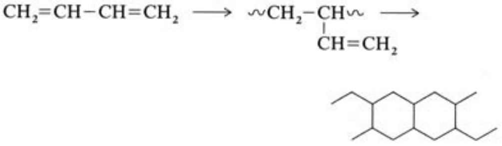
Side chains introduced by the inherent structure of a (co)monomer are not called branches in polymer science. Neither linear poly(vinyl acetate) nor the low- crystallinity, low-density polymers formed by copolymerization of ethylene with small amounts of α-olefins (butene-1, hexene-1, octene-1) are considered branched; the latter are known as linear low-density polyethylenes.

2.1.4. Ordered Chain Assemblies

Two or more chains may also be joined at more than two points by chemical bonds in an ordered way. The chains are thought to be fully extended for classification purposes; a distinction is made among one-, two-, and three-dimensional assemblies or, according to IUPAC, among catena (Fig. 3 –1), phyllo (Fig. 3 –2) and tecto (Fig. 3 –3) compounds.

Linear polymers are catena polymers in this nomenclature since the fully extended chains extend in only one direction (Fig. 3 –1). Spiro polymers possess two chains with connecting atoms shared by both of them (Fig. 3-S).

Ladder polymers consist of two chains joined by bonds in regular intervals (Fig. 3-L); they are also called double-strand polymers. Such ladder polymers are generated by first forming a linear chain with pendant side groups that are subsequently polymerized. An example is the polymerization of 1,3-butadiene to 1,2-polybutadiene with subsequent cyclization to cyclopolybutadiene



$$CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \sim CH_2{-}\underset{\displaystyle CH{=}CH_2}{\underset{|}{CH}}\sim \longrightarrow$$

Ladder polymers may also be synthesized by two-step polycondensation or polyaddition reactions; in general, however, only fairly short ladderlike units are formed in this way (see below). One-step ladder syntheses are very rare. Polymerization of the silicon analogue of cubane, $(C_6H_5)_8Si_8O_{12}$, does not lead to a ladder polymer of type L in Figure 3 but to a pearl-string-like polymer P (Fig. 3-P). Many silicates are ladder polymers or double-ladder polymers.

Phyllo polymers are also called layer or parquet polymers (Fig. 3). Graphite and the silicates montmorillonite, bentonite, and mica are well-known examples. Cell walls of bacteria consist of

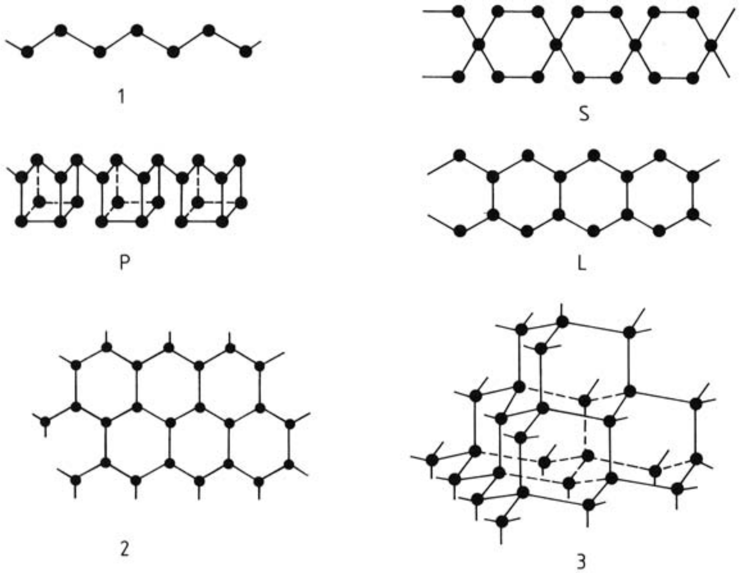


Figure 3. Schematic representation of some ordered chain assemblies
1 = Catena polymer in all-*trans* conformation; S = Spiro polymer; P = Pearl-stringlike polymer; L = Ladder polymer; 2 = Phyllo polymer; 3 = Tecto polymer

bag-shaped polymers (i.e., layer polymers). Diamond and quartz are examples of tecto polymers (Fig. 3).

2.1.5. Unordered Networks

Multifunctional oligomer and polymer molecules can be interconnected via chain groups or end groups to cross-linked polymers (networks). The cross-linking points must be at least trifunctional; that is, the cross-linkable groups must be at least bifunctional. The cross-linking bridges between chains can be short or long; the distribution of cross-linking points, at random or in clusters. Both chemical and physical bonds can be employed for cross-linking; chemically and physically cross-linked polymers are thus distinguished.

Chemical Networks. The structure of chemical networks depends on the relative amount of cross-linking sites and the state of the reactants during the cross-linking reaction. The network structure is to a first approximation independent of the chemical structure of the cross-linking sites. The relative amount of cross-linking sites determines the cross-link density. Light cross-linking does not change the mobility of chain segments between cross-links, and the resulting networks behave as elastomers if the chain segments are above the glass transition temperature. Networks with strong cross-linking or chain segments below the glass transition temperature are employed for thermosets.

Networks are fairly *homogeneous* with respect to the distribution of cross-links if they are prepared by polymerization in bulk or from homogeneous solutions and if the corresponding linear chains are soluble in their own monomers or in the applied solvent (Fig. 4, HN). Inhomogeneous networks are formed if phase separation occurs during polymerization; for example, if the low molar mass polymers generated early are insoluble in the applied solvent or the remaining monomer. The resulting *macroreticular networks* exhibit cavities (Fig. 4, MN).

In principle, two chemically different networks poly (a) and poly (b) can coexist independently of each other in interpenetrating networks (IPNs). In reality, these networks are not molecularly interdispersed; rather, each network forms interconnected domains with higher cross-link densities. Semi-interpenetrating networks consist of cross-linked poly (a) in uncross-linked poly (b).

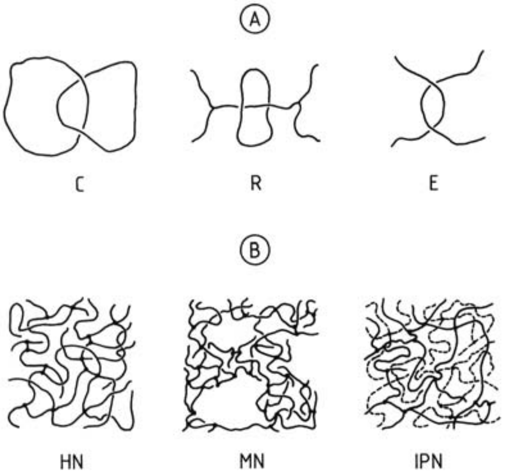


Figure 4. Schematic representation of cross-linked polymers
A) Physical cross-links; B) Chemical networks
C = catenane; E = entanglement; HN = homogeneous network; IPN = interpenetrating network; MN = macroreticular network; R = rotaxane
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Chemical cross-links are in most cases irreversible. These cross-linked polymers do not dissolve in solvents. With an increase in temperature, subchains decompose rather than revert to the original monomers. Chemically reversible cross-linked networks are being investigated because they would be of value in the recycling of thermosets.

Physical Networks. Physically cross-linked polymers, on the other hand, are in most cases reversibly cross-linked. Examples are microdomains in block copolymers, ion clusters in ionomers, or even crystallites in partly crystallized polymers. Physically cross-linked polymers often dissolve in suitable solvents.

Entanglements (Fig. 4, E) behave under strain as physical cross-links because the two chains cannot diffuse away rapidly enough; the chains disentangle, however, if sufficient time is allowed. Catenanes (Fig. 4, C) and rotaxanes (Fig. 4, R) have irreversible physical cross-links. Catenanes consist of two intertwined rings. Such structures are well known for deoxyribonucleic acids; they have also been observed for some synthetic polymers. Rotaxanes are rings on chains that are sealed on both ends by branched or cross-linked structures in such a way that the ring cannot slip out. Such structures are suspected to exist in some cross-linked polydimethylsiloxanes.

2.2. Molar Masses and Molar Mass Distributions

Molar masses of polymers can be varied over a wide range; they may extend from several hundreds to several millions, albeit not for every polymer type. The molar mass ranges used industrially depend on the limitations of the available polymerization procedures, the restrictions imposed by processing methods, and the desired properties of the plastics.

Presently available polymerization methods all employ statistical approaches to initiation and propagation of growing chains, as well as to termination and transfer, where applicable. The resulting polymer molecules thus show a distribution of molar masses; they are not molecularly uniform, and the experimentally determined molar masses represent averages. Synthetic copolymers are, in addition, nonhomogeneous with respect to the distribution of different types of monomer units; they are polydisperse with respect to both constitution and molar mass.

In contrast, biopolymers are synthesized via matrix polymerization. Many (if not all) biopolymers are monodisperse in their biological environments: each macromolecule of a polymer has the same constitution and the same molar mass. Examples are nucleic acids and enzymes. Upon isolation from living cells and further processing, some degradation may occur. Industrially employed celluloses thus exhibit molar mass distributions.

The recently discovered starburst dendrimers are synthetic polymers that are molecularly uniform. Their molecular homogeneity approaches that of isotopic distributions in atoms and molecules. It is caused by a self-limitation of molecular growth due to surface crowding after a certain number of growth generation steps [70].

2.2.1. Molar Mass Average

Many polymer properties depend on the type and range of molar mass distributions. In many cases, molar mass averages are determined instead, in part because it is experimentally easier and in part because a number is simpler to grasp than a function.

The averages employed in polymer science are usually arithmetic averages. The polymer molecules of size i (degree of polymerization X_i, molar mass M_i) are counted according to their statistical weight g_i, which may be their mole fraction $x_i \equiv n_i/\Sigma_i n_i$, their mass fraction $w_i \equiv m_i/\Sigma_i m_i = x_i M_i/\bar{M}_n$, or their z-fraction defined as $Z_i \equiv z_i/\Sigma_i z_i = w_i M_i/\bar{M}_w = x_i M^2{}_i/(\bar{M}_n M_w)$. The number-, mass-, and z-average molar masses are defined as

$$\mathrm{M}_n \equiv \Sigma_i x_i M_i = \frac{\Sigma_i w_i}{\Sigma_i (w_i/M_i)} \tag{1}$$

$$\mathrm{M}_w \equiv \Sigma_i w_i M_i = \frac{\Sigma_i x_i M_i^2}{\Sigma_i x_i M_i} \tag{2}$$

$$\mathrm{M}_z \equiv \Sigma_i Z_i M_i = \frac{\Sigma_i w_i M_i^2}{\Sigma_i w_i M_i} = \frac{\Sigma_i x_i M_i^3}{\Sigma_i x_i M_i^2} \tag{3}$$

Each of these three average moments is essentially a single moment of the distribution of molar masses present. There are, however, molar mass averages which are composed of more than one moment, for example, molar masses from sedimentation and diffusion coefficients for certain types of molecular shapes and solvent interactions.

2.2.2. Determination of Molar Mass

Many methods exist for the determination of molar masses. Most important for the *number-average molar mass* is *osmometry*, which measures the osmotic pressure Π of polymer solutions at various polymer concentrations c against the solvent. Solution and solvent are separated by a semipermeable membrane that is permeable to the solvent but not to the polymer molecules.

Older osmometers determined osmotic pressure in true thermodynamic equilibrium, which was reached only after days and weeks because large volumes of solvent had to be moved through the membrane. Modern osmometers compensate for the increase in pressure difference between solution and solvent caused by the flow of solvent into the solution chamber via a servomechanism by a change of solvent pressure; equilibrium pressures are established after 10 – 30 min. Reduced osmotic pressures, Π/c, determined at various concentrations, are extrapolated to zero concentration to give the number-average molar mass according to the van't Hoff equation, $\bar{M}_n = RT/[\lim_{c\to 0} (\Pi/c)]$. Number-average molar masses may be determined by osmometry in the range of 10^4 g/mol (lower limit of semipermeability of membranes) to ca. 10^6 g/mol (upper limit of sensitivity).

Mass-average Molar Masses are determined mainly via static *light scattering* of dust-free dilute solutions. Modern instruments measure the so- called Rayleigh ratio $R_o = K \cdot c \cdot \bar{M}_{w,\,\text{app}}$, at very low angles relative to the incident light beam, where K is an optical constant and $M_{w,\,\text{app}}$ an apparent mass average molar mass which is calculated from R_o, c, and K. Values of $K \cdot c/R_o$ are measured at various polymer concentrations and extrapolated to zero concentration. The limiting value $\lim_{c\to 0} (K \cdot c/R_o)$ delivers the inverse mass-average molar mass, $1/\bar{M}_w$. Molar masses from several hundred to several million grams per mole can be determined by light scattering, the upper limit being given by experimental problems such as multiple scattering. If measurements are performed over a wide range of scattering angles, important additional information about the radii of gyration of the molecules can be gained from the angular dependence of the Rayleigh ratio.

The *viscometric method* is fast and simple and therefore the most often applied method. From solvent viscosity η_o and viscosities η of dilute solutions of various concentrations c (measured at low shear rates), reduced viscosities (i.e., viscosity numbers) are calculated via $\eta_{\text{red}} = (\eta - \eta_o)/(\eta_o \cdot c)$. The reduced viscosities are extrapolated to zero concentration to give the *intrinsic viscosity* (limiting viscosity number) $[\eta]$ (DIN recommends the symbol J_o). This quantity has the physical unit of a specific volume since the concentration c is measured as mass per volume. The recommended units are milliliters per gram (cubic centimeters per gram), but data in 100 mL/g are still found in the literature; in the older literature, $[\eta]$ was given as Z_η in liters per gram.

Intrinsic viscosities measure the volume occupied by 1 g polymer at $c \to 0$, that is, the specific volumes (inverse densities) of isolated polymer molecules. Since molecular density varies with size for most molecule shapes, intrinsic viscosities can be used to measure molar masses for a homologous series of polymer molecules.

The viscosity increment η_i of unsolvated, compact spheres is, according to EINSTEIN:

$$\eta_i = (\eta - \eta_o)/\eta_o = (5/2)\phi = (5/2)(N_A V_H c/M) \qquad (4)$$

where N_A is the Avogadro number, ϕ the volume fraction, $V_H = \rho_H/m$ the hydrodynamic volume, ρ_H the density, and m the mass of a sphere. Hard spheres from the same material have the same density. Since $m \sim M$ and $\eta_i/c \approx [\eta]$, intrinsic viscosities of spheres are independent of their molar masses (i.e., $[\eta] = K \cdot M^0$).

The hydrodynamic densities of other particle shapes such as rods and coils change, however, with the molar mass

$$[\eta] = K \cdot M^a \qquad (5)$$

The exponent $a = 2$ for rigid rods of infinite length. Theory and experiment indicate a value of $a = 1/2$ for random coils in the unperturbed state (see below); this is a limiting case for very flexible chains in theta solvents. A theta solvent is a solvent being at a temperature at which a polymer adopts the theta state, i.e., where coil molecules are in their unperturbed state with a Gaussian distribution of segments (no excluded volumes). A theta solvent is a thermodynamically bad solvent. Theory predicts $a = 0.764$ for nondraining coils of high molar mass in thermodynamically good solvents (Fig. 5). Experimentally, values of $0.5 < a < 0.764$ are often found for flexible chains (such as most thermoplastics in solution) because their molar masses are not high enough for the assumptions of the theory to be fulfilled.

Wormlike molecules may adopt values of $0 < a < 2$ because they resemble spheres and ellipsoids at low molar masses, rigid rods at medium ones, and random coils at very high molar masses. This behavior is found for stiff molecules such as the double helices of deoxyribonucleic acids in aqueous solutions or certain poly(α-

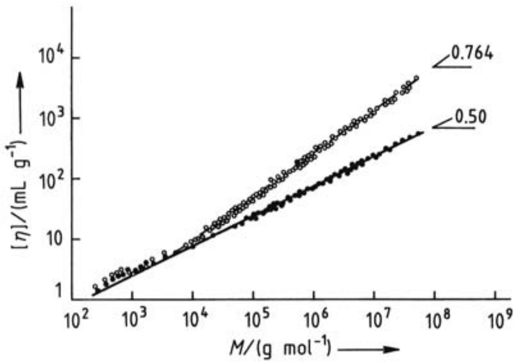

Figure 5. Molar mass dependence of intrinsic viscosities of flexible, coillike molecules: polystyrene in the theta solvent cyclohexane at 34.5 °C (•) and in the thermodynamically good solvent benzene at 25 °C (o)
The slopes at high molar masses adopt the theoretical values of 0.764 (good solvent) and 0.500 (theta solvent)

amino acids) in helicogenic solvents (see Chap. 5).

Viscometry delivers a peculiar molar mass average, such as can be derived from equation (5):

$$M_\eta = ([\eta]/K)^{1/a} = (K^{-1}\cdot\Sigma_i w_i[\eta]_i)^{1/a} = (\Sigma_i w_i M_i^a)^{1/a} \tag{6}$$

Numerical values of viscosity-average molar masses $\bar{M}_\eta$ lie between number and mass averages for $0<a<1$ and become identical with mass averages if $a = 1$.

2.2.3. Molar Mass Distributions

The types and characteristic parameters of molar mass distributions of polymers are determined thermodynamically or kinetically by the synthesis conditions and, to a smaller extent, by the processing of plastics. The molar mass distributions are mathematically described by distribution functions, which may be discontinuous (discrete) or continuous and differential or integral (cumulative) (Fig. 6). In these functions, polymer molecules of size i (molar mass M_i,degree of polymerization X_i) are considered according to their statistical weights, which may be mole fractions x_i, mass fractions w_i, etc.

All molar mass distributions are discrete because successive polymer molecules of a homologous series differ from each other by a degree of polymerization of 1 and the molar mass M_u of one monomeric unit. The discrete distribution functions can normally be replaced by continuous ones since so many different degrees of polymerization exist and the difference in molar masses between molecules with M_i and M_{i+1} is small compared to the average molar mass.

The various types of distribution functions are usually named after their discoverers. The *Schulz – Zimm distribution* function derives from processes in which reactive chains add other monomer or polymer molecules until the chains are deactivated. Such deactivation

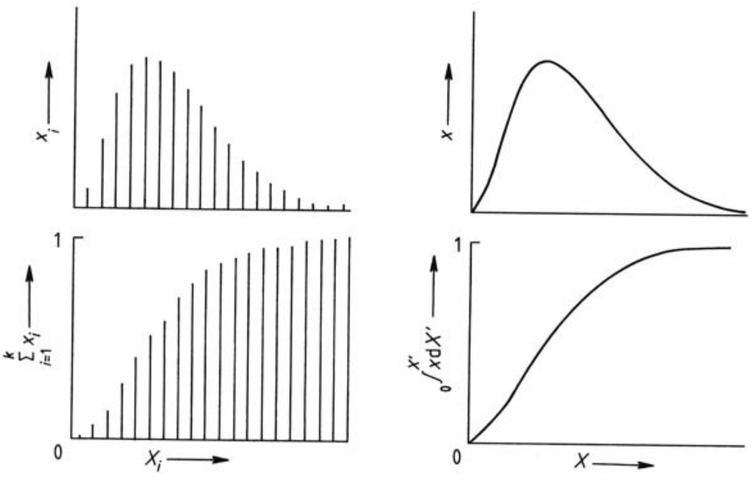

Figure 6. Distributions of mole fractions x of degrees of polymerization X
Left: discontinuous (discrete); right: continuous; top: differential; bottom: integral (cumulative)
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processes may be chain termination reactions (chain polymerization, polyelimination) or the decrease of reactivity by lowering of temperature (polycondensation, polyaddition). The mass fraction of polymer molecules with degree of polymerization X_i is given by

$$w_i = \frac{(k/X_n)^k \cdot X_i^k \cdot \exp(-kX_i/X_n)}{\Gamma(k+1)} \tag{7}$$

where k is the degree of coupling of chains (e.g., $k = 2$ for recombination of two growing chains to one dead chain and $k = 1$ if two growing chains react by disproportionation to two dead chains) and γ ($k = 1$) the gamma function of ($k = 1$). This function is called *Schulz – Flory* or *Flory distribution* for the special case of $k = 1$ (polycondensation, radical chain polymerization with termination by disproportionation). Equation (34 reduces for $k = 1$ and high degrees of polymerization to

$$w_i = (1/X_n)^2 \cdot X_i \cdot [1-(1/X_n)]^{xi} \tag{8}$$

The various average degrees of polymerization are connected via

$$X_n/k = X_w/(k+1) = X_z/(k+2) \tag{9}$$

Poisson distributions are formed if a constant number of chains starts to grow simultaneously and if monomer molecules are added to the chains at random and independent of previous additions. The mass fraction of molecules of degree of polymerization X_i is given by

$$w_i = \frac{X_i \cdot (X_n-1)^{X_i-1} \cdot [\exp(1-X_n)]}{(X_i-1)!(X_n)} \tag{10}$$

and the interrelationship between the various averages by

$$X_w/X_n = 1+(1/X_n)-(1/X_n)^2 \tag{11}$$

The ratio of mass to number average approaches 1 at infinitely high molar masses. The Poisson distribution is thus a very narrow distribution, in contrast to the Schulz – Zimm distribution where the ratio $\overline{X}_w/\overline{X}_n$ equals 2 for $k = 1$ and 3/2 for $k = 2$.

The *Schulz – Zimm distribution* is a special case of the *Kubin distribution*, an empirical, generalized exponential distribution (GEX distribution) with three empirical, adjustable parameters γ, ε, and β:

$$w_i = \frac{\gamma \cdot \beta^{(\varepsilon+1)/\gamma} \cdot X_i^{\varepsilon} \cdot \exp(-\beta X_i^{\gamma})}{\Gamma[(\varepsilon+1)/\gamma]} \tag{12}$$

This expression converts to the Schulz – Zimm distribution if $\gamma = 1$, $\varepsilon = k$, and $\beta = k/\overline{X}_n$. The Kubin distribution also includes the *Tung distribution* ($\varepsilon = \gamma - 1$) and the logarithmic normal distribution ($\gamma = 0$; $\varepsilon = \infty$), both of which frequently describe molar mass distributions of polymers from Ziegler – Natta polymerizations. The Kubin distribution is a very adaptable distribution because it contains a "stretched exponential" (i.e., a variable X with an exponent γ in the exponential term).

Some of these distribution functions are compared in Figure 7. Note that only the logarithmic normal distribution shows a maximum in the distribution of mole fractions and that none of

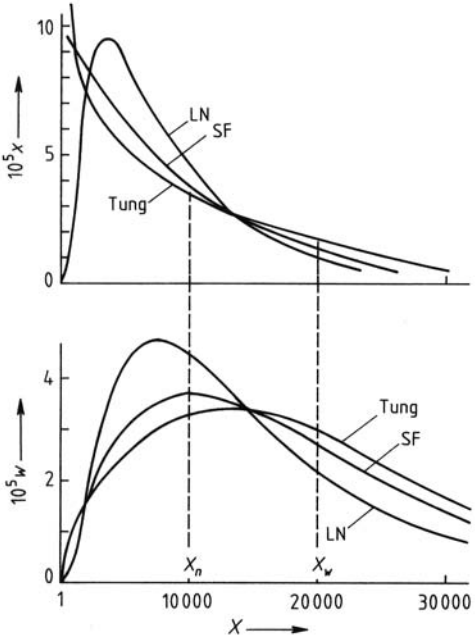

Figure 7. Continuous differential distributions of degrees of polymerization X for a) the logarithmic normal distribution (LN); b) the Schulz – Flory distribution (SF); and c) the Tung distribution (Tung), shown as distributions of mole fractions (top) and corresponding mass fractions (bottom) for a polymer with $\overline{X}_n = 10\,000$ and $\overline{X}_w = 20\,000$

The Poisson distribution is so narrow that it is practically identical with the vertical line for $\overline{X}_n = 10\,000$.

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the maxima in the distributions of the mass fractions correspond to simple molar mass averages.

2.2.4. Determination of Molar Mass Distributions

Molar mass distributions can be determined by preparative *fractionation* of polymers from solutions since the various species of a polymer-homologous series exhibit small differences in solubility. Fractionation occurs upon change of temperature or addition of a nonsolvent. The molar masses of the resulting fractions are determined in separate experiments. Fractionations are inexpensive but time consuming.

The method of choice for the fast determination of molar mass distribution is *size exclusion chromatography* (SEC). Dilute polymer solutions are placed on the top of a column filled with a porous carrier. Low molar mass molecules can enter the pores, but high molar mass molecules cannot. Medium-sized molecules enter with difficulty and remain for shorter times than low molar mass molecules. Higher molar masses are thus eluted first, and elution curves are observed that give the concentration of eluted molecules as a function of the eluted volume V_e. The maximum of the elution curve is called the retention volume.

The retention volumes depend on the SEC system (carrier, solvent, temperature) and the polymer being investigated. The carrier may consist of rigid porous materials (e.g., porous glass beads) or swollen, cross-linked polymers (e.g., cross-linked polystyrenes or dextrans). In the latter case, the method is called gel permeation chromatography (synthetic polymers) or gel filtration (biopolymers).

Retention volumes are constant below and above certain molar masses of the polymers (Fig. 8). The volume V_o at lower molar masses gives the total volume available for the flow of solvent; the volume V_i at upper molar masses indicates the interstitial volume between carrier particles. Polymer molecules can thus be separated only in the range $V_i < V_e < V_o$, where V_e is the elution volume.

Elution volumes depend to a first approximation on the logarithms of molar masses (Fig. 8). A function $V_e = K \cdot \ln M$ is thus often used to determine unknown molar masses with the help of a constant K derived from calibrations with narrow-distribution polystyrene standards. This procedure does not give absolute molar masses because polystyrenes and test polymers with the same molar masses possess different chromatographically effective volumes. A frequently used "universal" calibration method thus employs a function $V_e = f(\log [\eta] \cdot M)$ since $[\eta]$ measures the specific hydrodynamic volume of the solute molecules and $[\eta] \cdot M$ has the physical unit of a molar volume.

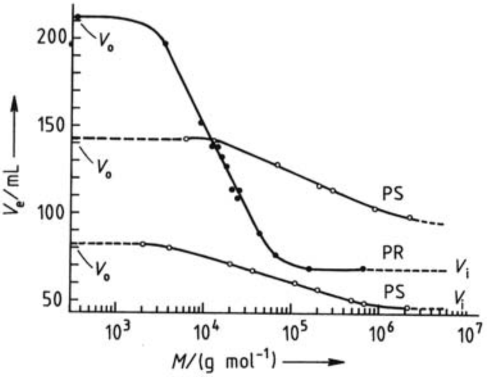
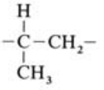


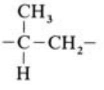
Figure 8. Molar mass dependence of elution volumes V_e
a) Coil-like linear polystyrenes PS with two different SEC columns from cross-linked polystyrenes; b) Various spheroidal proteins PR with cross-linked dextran
V_o = Total volume; V_i = Interstitial volume

2.3. Configurations

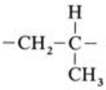
Polymers with symmetric repeating units, such as $-CH_2-CH_2-$ $(-CH_2-CH_2-)$, $-CH_2-CF_2-$, and $-NH-CO-(CH_2)_5-$, do not possess configurational isomers. Such isomers do exist, however, for polymer molecules with nonsymmetric repeating units, such as $-CH(CH_3)-$ (polymethylmethylene), $-CH(CH_3)-CH_2-$ (polypropylene), and $-NH-CO-CH(CH_3)-$ (polyalanine). Polypropylene, for example, has two configurational repeating units **9** and **10** with two different monomeric units each:


$-\overset{H}{\underset{CH_3}{C}}-CH_2-$

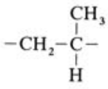
9a


$-\overset{CH_3}{\underset{H}{C}}-CH_2-$

9b

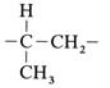

$-CH_2-\overset{H}{\underset{CH_3}{C}}-$

10a


$-CH_2-\overset{CH_3}{\underset{H}{C}}-$

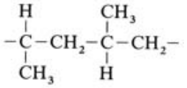
10b

The configurational units **9a** and **9b** are enantiomeric; they belong to the same constitutional unit – $CH(CH_3) – CH_2$ –. The configurational units **9a** and **10a**, on the other hand, are based on two different constitutional units. Several configurational units may be joined to give steric repeating units; the three simplest steric repeating units for polypropylene are



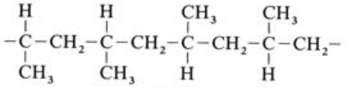
$-\underset{CH_3}{\overset{H}{C}}-CH_2-$

IT



$-\underset{CH_3}{\overset{H}{C}}-CH_2-\underset{H}{\overset{CH_3}{C}}-CH_2-$

ST



$-\underset{CH_3}{\overset{H}{C}}-CH_2-\underset{CH_3}{\overset{H}{C}}-CH_2-\underset{H}{\overset{CH_3}{C}}-CH_2-\underset{H}{\overset{CH_3}{C}}-CH_2-$

HT

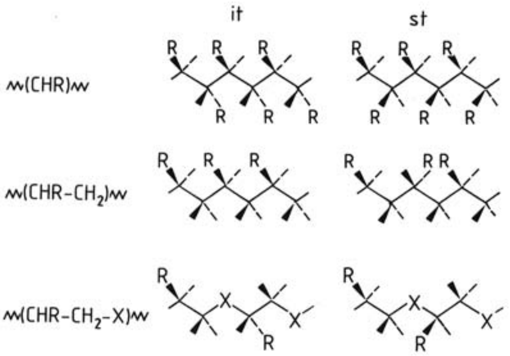


Figure 9. Isotactic (it) and syndiotactic (st) polymers with monomeric units – CHR –, – CHR – CH_2 –, and – CHR – CH_2–X– in *trans* conformations
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The repetition of these units leads to polymer chains that are called isotactic (IT), syndiotactic (ST), and heterotactic (HT). A *heterotactic unit* ht in a polymer chain consists of three monomeric units (the first or last three of HT), but the repetition of such ht-triads does not lead to a completely heterotactic polymer HT because it would consist of alternating heterotactic and syndiotactic triads. Whether **9a** or **10a** is used as the simplest configurational repeating unit is immaterial since infinitely long polypropylene chains of **9a** differ from those of **10a** only by the orientation of these units.

The term *tacticity* thus refers to the relative arrangements of configurational units in a chain. Relative configurations are classified by starting at one end of the polymer chain and considering the configuration around a central atom relative to the preceding one. This classification is different from that of the absolute configuration of organic chemistry where the configuration of each central atom is determined relative to the ligand with the lowest seniority.

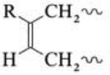
The ligands R of *isotactic polymer* molecules are always "on the same side" if these molecules are shown in Fischer projections or in other stereo formulas with hypothetical *cis* conformations of the chains. In stereo formulas based on *trans* conformations, ligands are only on the same side for isotactic molecules consisting of two chain atoms per monomeric unit (Fig. 9), that is $\sim(CHR – CH_2)\sim$.

Real polymer chains of the types $\sim CHR\sim$, $\sim CHR – CH_2\sim$, $\sim X – CHR – CH_2\sim$, etc., contain configurational mistakes; they are neither 100 % isotactic nor 100 % syndiotactic. The tacticity of such chains is expressed by the fraction X_J of their isotactic or syndiotactic diads, triads, etc. A diad consists of two monomeric units, a triad, of three; etc. Each monomeric unit of a polymer chain belongs to two tactic diads, three tactic triads, four tactic tetrads, and so on. Figure 9 thus shows five diads, four triads, three tetrads, . . . , etc., for $\sim$ CHR $\sim$. The sum of the mole fractions of all J-ads of given J must equal 1 ($x_i + x_s \equiv 1,\ x_{ii} + x_{is} + x_{si} + x_{ss} \equiv 1$, etc.), where i=isotactic diad, s=syndiotactic diad, ii=isotactic triad of two isotactic diads, etc. The mole fraction of isotactic diads is given by the mole fraction of isotactic triads plus 1/2 of the mole fraction of the sum of the two heterotactic triads, that is, $x_i = x_{ii} + (1/2)\ (x_{is} + x_{si})$, etc. The number-average sequence length of isotactic sequences is thus given by $(X_I)_n = 2\ x_i/(x_{is} + x_{si})$.

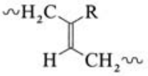
The presence and/or fraction of tactic J-ads can be investigated by a number of experimental methods. 2 D-NMR spectroscopy allows absolute determination of the types of J-ads and their amounts up to pentads, whereas conventional high-resolution NMR spectroscopy requires prior knowledge of the J-ad type by X-ray crystallography or other methods. Infrared spectroscopy detects only diads, whereas crystallinity, solubility, glass and melt temperatures, and chemical reactions may or may not indicate the presence of shorter or longer tactic sequences.

Highly isotactic polymers can be produced by Ziegler – Natta polymerization of α-olefins (e.g., it-polypropylene or it-polybutylene-1). Special Ziegler – Natta catalysts lead to st-polypropylene and st-polystyrene; these syndiotactic polymers have no commercial use thus far. Highly syndiotactic polymers are also generated by most very low-temperature free-radical polymerizations of vinyl and acryl monomers. Conventional vinyl and acryl polymers are, however, synthesized at ambient temperature or above, and consist, at best, of slightly syndiotactic polymers; in general, they are considered atactic polymers.

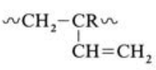
Polymers with different geometric isomerism are also tactic. Depending on the configuration of the chain segments relative to the double bonds in the chain *cis*-tactic (ct) and *trans*-tactic (tt) structures are distinguished. The ct structure of 1,4-polyprenes[$\sim (CH_2 - CR{=}CH - CH_2)_n \sim$] from the polymerization of 1,3-dienes $CH_2{=}CR - CH{=}CH_2$ via both double bonds corresponds to an E isomer; the tt structure, to a Z isomer. If the polymerization proceeds via one double bond only, 1,2-polydienes are formed that may be isotactic, syndiotactic, atactic, etc.



cis-1,4 (E)



trans-1,4 (Z)



1,2 (it or st)

2.4. Conformations

2.4.1. Microconformations

Rotations of atoms or groups of atoms around single bonds create spatial arrangements called conformations (organic chemistry) or microconformations (macromolecular chemistry). The sequence of these microconformations determines the shape of the macromolecule – the macroconformation (in statistical mechanics, the configuration).

In principle, an infinite number of conformations is possible around each single bond. In practice, certain positions are energetically preferred; only these are called (micro)conformations. In two joined tetrahedrons, such as ethane ($H_3C - CH_3$), two extremes of energetically different positions are possible: the staggered position corresponds to a minimum of energy and the eclipsed position to a maximum of energy if repulsive forces are prevalent (Fig. 10). On rotation by 360° around the C – C axis, three energetically equivalent eclipsed and three energetically equivalent staggered positions may be occupied since the three H atoms bound to the same C atom ("bonded atoms") are equivalent. Small molecules, such as ethane, can be considered as definite species in conformations with energy minima; they are called conformers, rotamers, or rotational isomers.

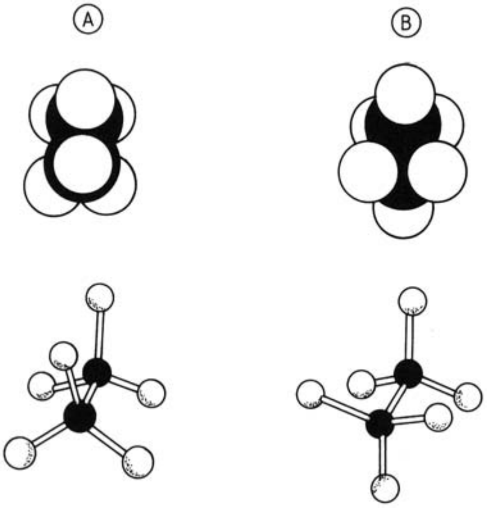


Figure 10. Microconformations of ethane
A) Eclipsed position (*cis* or synperiplanar); B) Staggered position (*trans* or antiperiplanar)
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The number of types of conformers increases if the three bonded atoms are not equivalent, for example, in butane ($CH_3 - CH_2 - CH_2 - CH_3$) (one CH_3 group and two H atoms bonded to each carbon atom participating in the central C – C bond). In polymer chains, one of the bonded atoms is never equivalent because it is part of the chain; in polyethylene ($\sim CH_2 - CH_2 \sim$), the bonded atoms are two H atoms and the chain. There are two energetically different eclipsed positions (*cis* and *anti*) and two energetically different staggered ones (*trans* and *gauche*). Each *gauche* and each *anti* position can occur in two spatially different positions that are energetically equivalent (plus and minus) if two of the

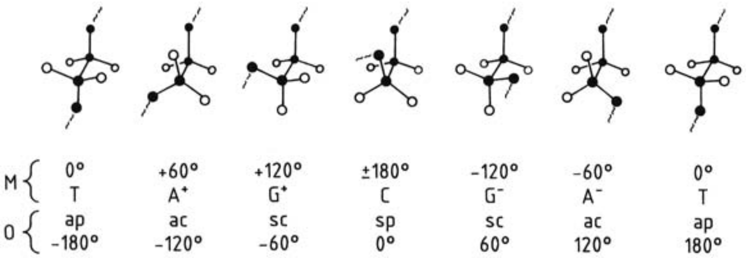

Figure 11. Chain conformations and their names and symbols in macromolecular (M) and organic (O) chemistry
• Chain atoms; ○ substituents; T = *trans*, A = *anti*; G = *gauche*; C = *cis*; ap = antiperiplanar; ac = anticlinal; sc=synclinal; sp = synperiplanar

three bonded atoms are equivalent. These (micro)conformers have different names in macromolecular and in organic chemistry (Fig. 11).

All eclipsed positions are sterically hindered in polymer chains and therefore only *trans* and *gauche* positions must be considered. The conformational energy is the energy difference between the energies of the *trans* and *gauche* conformations. An activation energy (potential energy) is necessary to overcome the rotational barrier between *trans* and *gauche* conformations. This rotational barrier increases with decreasing length of the central bond and with increasing number and increasing size of bonded atoms. Its value is, for example, 12.1 kJ/(mol bond) for the C – C bonds in polyethylene chains $\sim(CH_2 - CH_2)_n\sim$ but only 2.1 kJ/mol for the $CH_2 - CO$ bonds in polyester chains with units $\sim CH_2 - CO - O - CH_2\sim$. Since these bond energies can easily be overcome by thermal energy, (hindered) rotations are possible around the chain bonds and the molecules may adopt many chain conformations (Section 2.4.3). Isolated aliphatic polyester chains $\sim OOC(CH_2)_x\sim$ (with $x>3$) are thus more flexible than carbon chains; such polymers are used as polymeric plasticizers.

Two different types of flexibility are distinguished. A chain molecule is said to be *statically flexible* if it possesses many accessible conformational minima. *Dynamic flexibilities* are characterized by low barriers between conformational minima.

2.4.2. Conformations in Ideal Polymer Crystals

A regular sequence of microconformations leads to regular macroconformations of polymer chains. The chains are linearly extended; the end-to-end distance is commonly called the contour length r_{cont} of the chain (this term originally referred to the contour of the chain along the individual chain bonds). Chains in all-*trans* microconformations are said to be fully extended, for example, the chain in Figure 3-1.

Polyethylene crystallizes ideally in an all-*trans* conformation because the shortest distance between nonbonded hydrogen atoms (0.254 nm) is greater than the sum of the van der Waals radii of H atoms (0.24 nm). The size of substituents R in isotactic poly(α-olefins) $(\sim(CH_2 - CHR)_n\sim)$, however, forces the microconformation around each second chain bond to adopt a *gauche* position (see Fig. 11). All *gauche* conformations must be alike for steric reasons; conformational diads G^+G^- and G^-G^+ are forbidden (Fig. 11). The chain thus adopts either a . . . $TG^+TG^+TG^+$ . . . or a $TG^-TG^-TG^-$ . . . macroconformation; that is, it becomes helical. The number of monomeric units per complete turn is determined mainly by the size of the immediate substituents. it-Polypropylene $\sim (CH_2 - CH(CH_3))_n \sim$ has three propylene units per one turn (3_1 helix, Fig. 12 A), it-poly(4-methylpentene-1) (P4MP) $\sim (CH_2 - CH(CH_2CH(CH_3)_2))_n \sim$ has seven units per two turns (7_2 helix = 3.5 helix, Fig. 12 B), and poly(3-methylbutene-1) (P3MB) has four units per one turn (4_1 helix, Fig. 12 C). The conformational angles are not necessarily the ideal ones of 0° for *trans* and 120° for *gauche* as found for it-polypropylene; they are rather −13°/110° for P4MP and −24°/96° for P3MB. Conformational positions with deviations up to ± 30° from the ideal conformational angles are still named after the ideal microconformations.

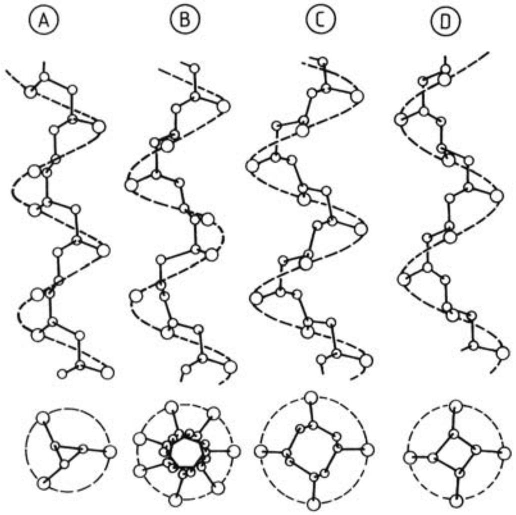

Figure 12. Helix types of poly(α-olefins) ~ CH_2–CHR~ A) 3_1 Helix; B) 7_2 Helix; C), D) Different types of 4_1 helices Reprinted with permission by Societa Italiana di Fisica, Bologna, from [71]

The R substituents of syndiotactic vinyl polymers [~$(CH_2 - CHR)_n$~] are farther apart than those of their isotactic counterparts (see Fig. 9). In general, *trans* conformations thus have the lowest energy in those st-polymers where only repulsive forces operate. Attractive forces, such as intramolecular hydrogen bonds between neighboring OH groups in poly(vinyl alcohol) (~$[CH_2 - CH(OH)]_n$~, PVAL), lead to different conformational sequences: isotactic PVAL exists in all-*trans* conformations, whereas syndiotactic PVAL forms helices.

Chain atoms with free electron pairs lead to *gauche* effects. The chains of crystallized polyoxymethylene [~$(O - CH_2)_n$~] exist in all-*gauche* conformation (9_5 helix). Polyoxyethylene [~$(O - CH_2 - CH_2)_n$~] and polyglycine [~$(NH - CO - CH_2)_n$~], on the other hand, possess the conformational sequence TTG. The resulting 7_2 helices of polyglycine are stabilized by intramolecular hydrogen bonds between the first, fourth, seventh, etc., peptide bonds of a chain.

Polypeptides [~$(NH - CO - CHR)_n$~] are based on chiral monomeric units. An L-polymer may thus form two different helices: a right-handed and a left-handed one. These helices are diastereomers with different energy contents. In general, one "handedness" is preferred over the other in polymers with chiral base units. Poly (L-α-amino acids) generally form right-handed helices, whereas poly([*S*]-α-olefins) and most polysaccharides from D-sugars exist as left-handed ones.

2.4.3. Conformations in Polymer Solutions

Helices can survive melting and dissolution processes only if the helical structure is stabilized by intramolecular attractive forces. Examples are the hydrogen bonds in helices of poly α-amino acids or hydrogen bonds plus base stacking in double helices of deoxyribonucleic acids. These forces may be so strong that the molecules decompose rather than melt on heating. A delicate balance between intramolecular bonding and solvation of substituents is necessary to preserve helical structures in solution; examples are poly(α-amino acids) in helicogenic solvents.

Helices that are generated in crystals by packing of chains whose microconformations originate from repulsive forces do not survive the melting process intact. Each macromolecule can form many macroconformers that equilibrate rapidly. Only very short helical sequences in very low concentrations may thus exist in melts.

Two extreme cases must be considered for the dissolution of polymers. Only weak interactions (or none at all) exist between monomeric units of apolar polymers and apolar solvent molecules. Conformational changes are thus entropy driven; the sequence of microconformations is irregular, and the polymer molecule adopts the macroconformation of a coil.

In apolar enantiomeric polymers in apolar solvents, long conformational sequences are conserved, although fast conformational transformations from left- to right-handed helices and vice versa may occur in enantiomeric polymers. On average, few microconformations are converted into other ones. These helical sequences may be stabilized by association processes.

Polar solvents, on the other hand, interact strongly with polar polymers; these solvents cause strong changes in microconformations. Since the ligands around each chain bond can adopt various microconformations and these microconformations can change rapidly, a given macromolecule may exist in time in many macroconformations, similar to those of simple apolar polymers in apolar solvents:

Figure 13. Electron micrograph of the double helix molecules of deoxyribonucleic acid chains showing two-dimensional random coils
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A polymethylene [$\sim(CH_2)_n\sim$] with degree of polymerization $n = 20\,001$ possesses 20 000 chain bonds, each of which can adopt three microconformations: *trans*, *gauche* (plus), and *gauche* (minus). According to statistics, such chain can exist in $3^n = 3^{20\,000} \approx 10^{9542}$ different macroconformations. Conversely, a collection of chains may have many macroconformations at any given time. None of these macroconformations adopts a simple geometric shape, not even instantaneously. Rather, the chains form rapidly changing coil structures that can be made visible by electron microscopy as two-dimensional projections of the three-dimensional coil shape for chains of sufficiently long chain diameter (Fig. 13).

2.4.4. Unperturbed Coils

The instantaneous shapes of coils cannot be determined by presently known methods. Their radius of gyration can be measured, however, by light scattering, small-angle X-ray scattering, and small-angle neutron scattering. The end-to-end distances of coiled linear chains can be modeled for various types of chains and calculated for individual chains via the rotational isomeric state method.

The simplest model is that of a freely jointed chain (no fixed bond angles) that assumes infinitely thin segments without interactions. The mean square end-to-end distance, $\langle r_{oo}^2 \rangle$, of such a coil is given by the number N of its unspecified segments with segment lengths b:

$$\langle r_{oo}^2 \rangle = N \cdot b^2 \tag{13}$$

Real chains posses fixed bond angles τ between chain atoms and finite torsion (or dihedral) angles θ ($\theta = 0°$ for *trans* conformations). The mean square end-to-end distance for such a chain in the unperturbed state (zero net polymer – polymer and polymer – solvent interactions) is given by

$$\langle r_o^2 \rangle = N \cdot b^2 \cdot \left(\frac{1-\cos\tau}{1+\cos\tau}\right) \cdot \left(\frac{1+\cos\theta}{1-\cos\theta}\right) \tag{14}$$

$$\langle r_o^2 \rangle = N \cdot b^2 \cdot \left(\frac{1-\cos\tau}{1+\cos\tau}\right) \cdot \sigma^2 \tag{15}$$

The factor σ is called the *hindrance parameter* or steric factor. Often the hindrance parameter and the bond angle are combined to give the *characteristic ratio* C_N:

$$\begin{aligned} C_N &= \langle r_o^2 \rangle / (N^2 \cdot b^2) \\ &= (1-\cos\tau) \cdot (1+\cos\tau)^{-1} \cdot \sigma^2 \end{aligned} \tag{16}$$

The characteristic ratio becomes approximately constant for chains with more than 100 atoms. A chain can also be characterized by its *Kuhn length* L_K, which can be calculated from its unperturbed mean square end-to-end distance, its degree of polymerization, and the effective length b_{eff} of monomeric units (i.e., length of units in chain direction projected on a plane; $r_{cont} = X \cdot b_{eff} = N_K \cdot L_K$)

$$\langle r_o^2 \rangle = N_K \cdot L_K^2 \tag{17}$$

End-to-end distances can rarely be measured directly. They are however related to the experimentally accessible radii of gyration s via

$$\langle s_o^2 \rangle = \langle r_o^2 \rangle / 6 \tag{18}$$

This relationship applies to all chains with random flight statistics (e.g., unperturbed chains and freely jointed chains). It is not valid for perturbed chains (Section 2.4.5).

Coil densities are very low (cf. Fig. 13). The volume fraction of monomeric units is, for example, only 0.012 at the center of gyration for a polyethylene chain with a molar mass of 1.19×10^6 g/mol; 99.8 % of the space of these polyethylene coils is occupied by solvent molecules (in very dilute solutions) or by units of other polymer chains (in melts).

A chain in a melt cannot distinguish between its own segments and segments of other chains. Because the interactions between the segments of various chains are also the same, such chains adopt their unperturbed dimensions, which has been confirmed by small-angle neutron scattering. Most of the coil volume is filled by segments of other chains to avoid empty space. Chains of sufficient length may thus become entangled, which manifests itself in properties such as diffusion and melt viscosity.

2.4.5. Perturbed Coils

Coils adopt their unperturbed dimensions in melts or in certain solvents at certain temperatures (so-called theta solvents). In such theta solvents, polymer – solvent and polymer – polymer interactions cancel each other and the chain behaves as if it is infinitely thin. In thermodynamically good solvents, polymer – solvent interactions dominate and the coil is swollen. The volume requirements of such coils must thus lead to interpenetrations by other coils even at very low concentrations. Because segments are not infinitely thin, however, a part of the total space is excluded for segments of other chains (and also for other segments of the same chain).

2.4.6. Wormlike Chains

Real polymer chains are not totally flexible. Their finite thickness and the partially hindered rotation around chain bonds prevent them from adopting all possible positions in space. Such chains can be described by the model of the wormlike chain (Kratky – Porod model).

The characteristic parameter of this model is the *persistence length a*. This parameter is defined as the average of the projection of the end-to-end-distance of an infinitely long and infinitely thin chain in the direction of the first segment. It can be calculated from the radius of gyration and the conventional contour length via

$$\langle s_o^2 \rangle = a^2\{(y/3)-1+(2-y)-(2/y^2)[1-\exp(-y)]\} \qquad (19)$$

where $y = r_{\mathrm{cont}}/a$. For flexible chains, it is related to the unperturbed radius of gyration via

$$\langle r_o^2 \rangle/6 = \langle s_o^2 \rangle = a \cdot r_{\mathrm{cont}}/3 = a \cdot N_K \cdot L_K/3 \qquad (20)$$

For infinitely stiff chains,

$$\langle s_o^2 \rangle = a^2 \cdot y^2/12 = (r_{\mathrm{cont}})^2/12 \qquad (21)$$

that is an infinitely stiff chain behaves like an infinitely thin rod. Wormlike chains thus describe the whole transition from rodlike molecules (small y) to random coils (large y). The model is strictly valid for infinitely thin chains, but the error produced by this assumption is negligible if the persistence length is much greater than the chain diameter.

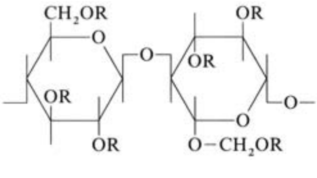
3. Polymer Manufacture

3.1. Raw Materials

The raw materials for most industrially used plastics are synthetic polymers and prepolymers; only a few are derived from naturally occurring polymers or monomers. The overwhelming majority of polymers for plastics are organic materials; very few are semiorganics (i.e., inorganic polymer chains with organic substituents). Raw materials for polymers include wood, coal, petroleum, natural gas, and certain natural oils.

3.1.1. Wood

Wood (→ Wood) is a naturally occurring composite of oriented cellulose fibers in a continuous matrix of cross-linked lignin; it is plasticized by water and “foamed” by air (vacuoles). The water content varies from 40 – 60 % for green wood to 10 – 20 % for air-dried wood. Solids include cellulose (42 %); hemicelluloses (28 – 38 %); lignin (19 – 28 %); and proteins, resins, and waxes (2 – 3 %), depending on the type and age of the plant. Most of the wood is used directly as fuel or for construction purposes, but one-sixth is converted into wood pulp or cellulose pulp for the manufacture of paper, cardboard, or rayon. A very small amount of wood is filled with monomers that are subsequently polymerized to give polymer wood.



Repeating unit (cellobiose) of cellulose (R=H) and cellulose derivates

Cellulose pulp is chemically transformed into cellulose derivatives (→ Cellulose; → Cellulose Esters; → Cellulose Ethers):

1. 2,5-Acetate with 2,5 acetate groups, R=OOC–CH_3, per glucose residue (fibers, cigarette filters)
2. Cellulose triacetate with three acetate groups per glucose residue (fibers)
3. Cellulose acetobutyrate with R = 29 – 6 mol % acetyl and 17 – 48 mol % butyryl groups (a thermoplastic for tubes, packaging)
4. Cellulose nitrate (R = NO_2; various degrees of substitution; gun cotton, films, lacquers, celluloid)
5. Cellulose ethers with R = CH_3, C_2H_5, $CH_2CH_2OR^1$, or CH_2 – $CHOR^2$ – CH_3, where R^1 may be $CH_2CH_2OR^1$ or CH_2CH_2OH and R^2 = CH_2–$CHOR^2$–CH_3 or CH_2 – CHOH–CH_3 (thickeners, binders, suspension agents, injection molding materials, etc.)

Huge amounts of *lignin sulfonates* (→ Lignin, Chap. 5.) are generated during wood pulp production, most of which are burned. Small amounts are used for street pavement, as binders for foundry sand, or as drilling agents, and even smaller amounts as raw materials for organic intermediates (→ Lignin, Chap. 7.). Degradation products of lignin have been utilized for the synthesis of ion-exchange resins and other polymers.

3.1.2. Coal

Coals (→ Coal) are polymerized and partly cross-linked hydrocarbons with average compositions between $C_{75}H_{140}O_{56}N_2S$ (peat) and $C_{240}H_{90}O_4NS$ (anthracite). They were the primary raw materials for acetylene-based monomers during the first half of this century but have since been replaced in most countries by oil and natural gas as monomer sources.

Coals deliver coke and coal tar. A number of aliphatic monomers are produced from coke via acetylene, such as chloroprene, various vinyl monomers, acrylonitrile, and hexamethylenediamine. Coal tar delivers aromatics such as benzene, xylene, phenol, and phthalic anhydride, which lead subsequently to polystyrene, phenolic resins, and glyptal resins, to name a few.

3.1.3. Natural Gas

Natural gas (→ Natural Gas) is a gas with a high proportion of aliphatic hydrocarbons. European gas is rich in methane, whereas American and Saudi Arabian gases are relatively rich in higher hydrocarbons. Natural gas is processed to synthesis gas, ethylene, and acetylene. These gases are used to produce a variety of monomers for polymers.

3.1.4. Petroleum

Petroleum (crude oil) (→ Oil Refining) is the main feedstock for monomers. It consists of 95 – 98 % hydrocarbons and 2 – 5 % oxygen, nitrogen, and sulfur compounds. The hydrocarbons are largely aliphatic, partly naphthenic, and to a small extent aromatic, depending on the source. Petroleum distillation leads to saturated hydrocarbons (gas, naphtha, gasoline, kerosene, diesel fuel, heating oil, etc.). For monomer production, these hydrocarbons are subsequently cracked to mixtures of olefins that are fractionated by distillation. The resulting compounds are used as such or are converted further into the desired monomers.

The polymer industry is a major petrochemical customer: about 60 % of the cracking and subsequent products of naphtha are used to produce polymers (ca. 50 % for plastics – elastomers, ca. 10 % for fibers). However, the final yields of polymers and converted plastics, respectively, are fairly small: 1000 kg of petroleum delivers only 30 kg of polyethylene and subsequently 16 kg of polyethylene film, in addition to 360 kg of useful byproducts [liquid gas, gasoline, propylene, etc.].

3.1.5. Other Natural Raw Materials

Vegetable oils are a relatively large source of raw materials. They consist of mixtures of fatty acid triglycerides and are usually subdivided into drying oils with high linolenic and linoleic acid content, semidrying oils with high linoleic and oleic acid content, and nondrying oils with high oleic acid content (→ Fats and Fatty Oils). Some oils are used directly for paints; others are chemically converted into monomers.

Castor Oil is converted into methyl ricinoleate, which is thermally cracked into methyl undecenate and heptanal. Methyl undecenate is the raw material for 11-aminoundecanoic acid, which is subsequently polycondensed to form polyamide 11. Alkali scission of castor oil or ricinoleic acid produces sebacic acid, a monomer used to prepare polyamide (PA) 610.

Soybean Oil is converted by a series of chemical reactions into the methyl ester of the C_{10} amino acid $H_2N(CH_2)_9COOCH_3$, which is the monomer for PA 10. The plant *Crambe abyssinica* contains about 55 % of erucic acid, which leads to the C_{13} amino acid and subsequently to PA 13 ($\sim[NH(CH_2)_{12}CO]_n\sim$).

Corn husks and other agricultural waste are rich in *pentosans*, which can be converted into tetrahydrofuran and further into polytetrahydrofuran [$HO(CH_2CH_2CH_2CH_2O)_nH$], which serves as a soft block in certain polyurethanes.

The supply of raw materials from vegetable sources is relatively small. It is also fairly uncertain because quality and quantity may depend on weather conditions or be influenced by political turmoil. Most monomers for the polymer industry are thus obtained from fossil feedstocks.

3.2. Polymer Syntheses: Overview

3.2.1. Classifications

Polymers may be synthesized from monomers by polymerization or from other polymers by chemical transformations. The nomenclature and classification of these reactions have grown and changed with the times; they are not very systematic and are sometimes confusing.

All reactions of small molecules to macromolecules are called *polymerizations*. Polymerizations are classified according to the

1. Origin of polymers (biopolymerizations, synthetic polymerizations)
2. Chemical structure of monomers (vinyl polymerizations, diene polymerizations, ring-opening polymerizations, etc.)
3. Chemical structure of resulting polymers (linear, branching, cross-linking, isomerizing, ring-forming, etc., polymerizations)
4. Relative composition of monomers and monomer units (addition polymerization, condensation polymerization, etc.)
5. Formation of low molar mass byproducts (polycondensation vs. polyaddition, etc.)
6. Type of polymerization initiation (thermal, catalytic, photochemical, enzymatic, etc.)
7. Type of propagating species (free radical, anionic, cationic, etc.)
8. Type of mechanism (equilibrium, addition, insertion, living, stepwise, etc.)
9. Reaction media (bulk, solution, emulsion, suspension, crystal, mesophase, etc.)
10. State of matter (gaseous, homogeneous, heterogeneous, etc.)

The most common classification is according to (4) the relative chemical composition of monomer vs. monomeric unit and (5) the type of molecules that may react with the growing polymer chain. The resulting four types of polymerization can be depicted schematically as

$$P_n + P_m \rightarrow P_{n+m} \qquad\qquad P_n + M \rightarrow P_{n+1}$$

Polyaddition Chain polymerization

$$P_n + P_m \rightarrow P_{n+m} + L \qquad\qquad P_n + M \rightarrow P_{n+1} + L$$

Polycondensation Polyelimination

where M denotes monomer; P_n, P_m, P_{n+m}, P_{n+}, denote polymers and L leaving molecules (e.g., water in polyesterifications of diacids and diols).

The names of three of these four types have been used with different meanings by different researchers over the past 70 years. The following discussion thus centers around the present nomenclature recommendations by IUPAC.

Chain Polymerization. Polymer chains grow by repeated addition of monomer molecules M to polymer molecules P_i, consisting of *i* monomeric units m, an initiator end group R, and an “active center *,” without the formation of leaving molecules:

$$R(m_n)m* + M \rightarrow R(m_{n+1})m* \tag{23}$$

An example is the polymerization of vinyl monomers ($CH_2{=}CHR$) by chain carriers Y*, which may be free radicals $Y^{\cdot}$, anions Y^-, or cations Y^+:

$$\begin{aligned}&Y—CH_2—CHR* + CH_2 = CHR \rightarrow\\ &Y—CH_2—CHR—CH_2—CHR*\end{aligned} \qquad (24)$$

A *living polymerization* is a chain polymerization consisting only of fast initiating reactions ($Y^* + CH_2{=}CHR \rightarrow Y - CH_2 - CHR^*$) and propagation reactions [$Y -(CH_2 - CHR)_n^* + CH_2{=}CHR \rightarrow Y -(CH_2 - CHR)_{n+1}^*$] without termination of the growing chains and without side reactions. In such reactions, the degree of polymerization is directly proportional to the conversion u of monomer molecules or p of functional groups, respectively (Fig. 14, curve CP – L). An example is the polymerization of styrene $CH_2{=}CH(C_6H_5)$ by the butyl anion $C_4H_9^-$ from lithiumbutyl (butyllithium) LiC_4H_9.

The variation of the degree of polymerization with monomer conversion is quite different for *radical polymerizations* such as the polymerization of styrene by benzoyloxy radicals $C_6H_5COO^\cdot$ from the thermal decomposition of dibenzoyl peroxide, $C_6H_5COO-OOCC_6H_5$. Radicals are here formed successively and not "at once" as are the butyl anions in living polymerizations. Growing chains are terminated by reaction with other radicals. Many side reactions may occur because of the high and fairly indiscriminate reactivity of radicals. Depending on reaction conditions, the degree of polymerization may remain constant (primarily at low conversions) or increase with monomer conversion (so-called gel effect) (Fig. 14, curve CP – FR).

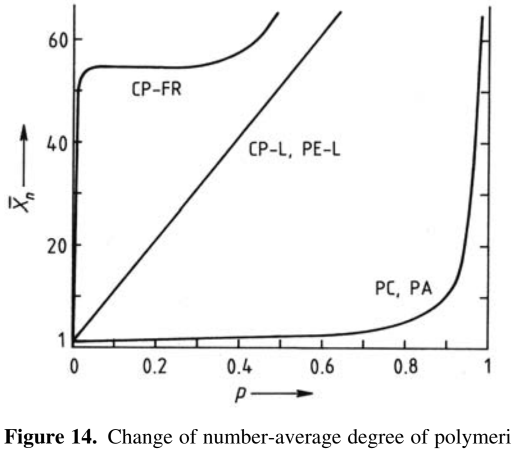


Figure 14. Change of number-average degree of polymerization $\bar{X}_n$ with the extent of reaction of functional monomer groups p for living chain polymerizations CP-L and living polyeliminations PE-L (with initial monomer – initiator ratio 100 : 1 mol/mol), free-radical chain polymerizations CP-FR with gel effect (schematic for high initiator concentrations), and equilibrium polycondensations PC and polyadditions PA (numerically exact)

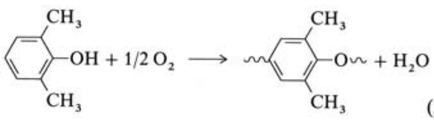
Chain polymerizations have generally been called *addition polymerizations* in the literature. Addition polymerization is not to be confused with polyaddition (see below).

Condensative Chain Polymerization. This is the name recommended by IUPAC for a polymerization by repeated addition of monomer molecules with elimination of low molar mass molecules L; this polymerization has thus also been called *polyelimination* [5]:

$$R(m_n)m* + M \rightarrow R(m_{n+1})m* + L \qquad (25)$$

Biological polymerizations to polysaccharides seem to proceed exclusively through polyeliminations. Cellulose of cotton, for example, is formed by polymerization of guanosine diphosphate D-glucose attached to a lipid matrix. The reaction proceeds via insertion of the glucose moiety into the chain with elimination of guanosine diphosphate.

Synthetic polymers are rarely formed by polyelimination. Examples are the polymerizations of α-amino acid *N*- carboxyanhydrides (Leuchs anhydrides) and the "oxidative polymerization" of 2,6-dimethylphenol to polyphenylene oxide (PPO, PPE):



(26)

Polycondensations. In polycondensation, polymer growth proceeds by reaction between molecules of all degrees of polymerization (not just between a polymer molecule and a monomer molecule as in chain polymerization and polyelimination), with the formation of molecules having low molar mass. Many polymers with hetero atoms in the chains are generated by polycondensation. An example is the polycondensation of 11-aminoundecanoic acid to polyamide 11:

$$n\,H_2N(CH_2)_{10}COOH \rightarrow H[NH(CH_2)_{10}CO]_nOH + (n-1)H_2O \qquad (27)$$

In these reactions, dimers ($n = 2$) are formed first, which may then react with monomers to form trimers ($n = 3$) or with other dimers to form tetramers ($n = 4$), etc. The reaction is thus statistical with respect to the size of the molecules to which the functional groups are attached. The degree of polymerization of the polymer is a number average $\overline{X}_n$ over all degrees of polymerizations of the polymer molecules.

All amino groups have the same chance to react if their reactivity is independent of molecule size. The reaction of amino groups attached to molecules with higher molar mass adds, however, considerably more to the increase of the degree of polymerization than the reaction of lower molar mass molecules: the degree of polymerization snowballs with increasing extent of reaction of functional groups (Fig. 14, curve PC).

The term polycondensation was used in the past as a synonym for condensation polymerization. The latter term included both the current concepts of polycondensation and polyelimination (condensative chain polymerization).

Polyaddition. This is a polymerization by reaction among molecules of all degrees of polymerization but without the formation of leaving molecules. The number-average degree of polymerization of the resulting polymers varies with the extent of reaction of functional groups in the same way as it does in polycondensation. An example of polyaddition is the polymerization of a diisocyanate with a diol to form a polyurethane:

$$\begin{aligned} &n\,\mathrm{OCN{-}R{-}NCO} + n\,\mathrm{HO{-}R'{-}OH} \rightarrow \\ &\mathrm{OCN(R{-}NH{-}CO{-}O{-}R'O)_nH} \end{aligned} \qquad (28)$$

These polymerizations have also been called "polyadduct formations." Polyaddition is not to be confused with addition polymerization, the term used in the literature for chain polymerization and occasionally also for polyaddition.

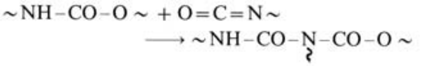
3.2.2. Functionality

Polymerizable monomers must be at least bifunctional under reaction conditions so that they can connect to the growing chains on one hand and generate new coupling sites on the other. Ethylene and other monomers with ethylenic double bonds are such bifunctional monomers under all polymerization conditions (e.g., see Eq. 24). Divinyl compounds, such as the divinylbenzenes $CH_2{=}CH - C_6H_4 - CH{=}CH_2$, are thus tetrafunctional compounds in free-radical polymerizations, leading first to branched and later to cross-linked polymers. The second vinyl group of a divinylbenzene possesses, however, a different reactivity after polymerization of the first one. The two reactivities may differ so strongly in certain ionic polymerizations of divinylbenzenes that linear polymers, and not cross-linked ones, result (e.g., in the cationic polymerization of 1,4-divinylbenzene by acetyl perchlorate in dichloromethane).

The isocyanate group $-N{=}C{=}O$ is a monofunctional group under the conditions of polyaddition reactions (Eq. 28). It may, however, undergo a chain polymerization to polyisocyanates via the N=C double bond

$$n\,\mathrm{R{-}N{=}C{=}O} \rightarrow \sim\mathrm{(NR{-}CO)}_n\sim \qquad (29)$$

and it thus reacts as a bifunctional group under these conditions. It may even behave as a half-functional group because urethane groups formed according to Equation (28) may react further to allophanate groups by the addition of isocyanate groups



$$\begin{aligned} &\sim\mathrm{NH{-}CO{-}O}\sim + \mathrm{O{=}C{=}N}\sim \\ &\qquad \longrightarrow \sim\mathrm{NH{-}CO{-}\underset{\wr}{N}{-}CO{-}O}\sim \end{aligned} \qquad (30)$$

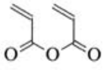
The functionality f of polymer molecules is given by the functionality f_o of the monomer molecules and the number X of mers if no intramolecular rings are formed between functional groups.

$$\begin{aligned} f &= 2(f_o - 1) + (X - 2)(f_o - 2) \\ &= 2 + X(f_o - 2) \end{aligned} \qquad (31)$$

A monomer with functionality $f_o = 3$ thus gives a dimer ($X = 2$) with a functionality $f = 4$ and a 100-mer ($X = 100$) with a functionality $f = 102$. Since the molecule needs to be bifunctional only for the formation of linear molecules, the "extra" functionalities lead to interconnections between various molecules (branching) and thus finally to cross-linked, "infinitely large" molecules.

3.2.3. Cyclopolymerizations

Polymerizations of multifunctional molecules may proceed not only intermolecularly to produce branched and cross-linked molecules but also intra/intermolecularly with the formation of rings in chains. These polymerizations are called cyclopolymerizations. They occur especially with monomers having carbon – carbon double bonds in the 1,5- or 1,6-position. An example is acrylic anhydride (**11**), $CH_2{=}CH{-}CO-O-OC-CH{=}CH_2$, which polymerizes free-radically even at high monomer concentrations to soluble polymers with 90 – 100 % six-membered (**12**) and five-membered (**13**) ring structures, and only 0 – 10 % "linear" monomeric units **14** (R symbolizes a polymer chain and * an active chain end):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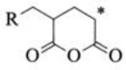
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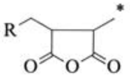
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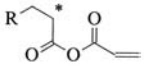
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3.3. Chain Polymerizations and Polyeliminations

Chain polymerization and polyelimination (condensative chain polymerization) agree in their polymerization kinetics, molar mass distributions, etc., if similar polymerization mechanisms are compared. They differ in the formation of low molar mass byproducts and thus in the design of industrial polymerization reactors.

3.3.1. Thermodynamics

Polymerizations occur only if their molar standard Gibbs energies ΔG_p^o are negative. Since the Gibbs energy

$$\Delta G_p^o = \Delta H_p^o - T \cdot \Delta S_p^o = -RT \cdot \ln K \qquad (32)$$

is determined by both the polymerization enthalpy ΔH_p^o and the polymerization entropy ΔS_p^o, four different cases are possible:

Case 1. Both enthalpy and entropy are negative; the entropy term $-T \cdot \Delta S_p^o$ becomes more positive with increasing temperature. At a certain temperature, the enthalpy and entropy terms balance each other; no polymerization to high molar mass molecules is possible above this *ceiling temperature*. Oligomers may be formed at the ceiling temperature, however, since polymerization equilibria consist of a series of consecutive equilibria between monomer and growing chains of different degrees of polymerization.

Case 1 is the most common case. It is found for monomers with polymerizable double and triple bonds, such as C=C, C=O, C=S, or C=N. The polymerization entropies of such monomers are practically determined only by the loss of translational entropy; they are thus almost independent of the chemical structure of the monomers. The polymerization enthalpy of α-olefins $CH_2{=}CHR$ is influenced little by resonance stabilization and is practically independent of the size of the substituent R. Steric hindrance, however, strongly decreases the polymerization enthalpy of 1,1-disubstituted compounds $CH_2{=}CRR'$. Styrene and α-methylstyrene, have practically the same polymerization entropies ($-$ 105 J K^{-1} mol^{-1}) but very different polymerization enthalpies ($-$ 71 vs. -35 kJ/mol, respectively) for the polymerization of liquid monomers to condensed polymers. The ceiling temperatures in bulk are 303 °C (styrene) and 60 °C (α-methylstyrene), (i.e., the latter cannot be homopolymerized to high molar mass compounds above 60 °C).

σ-Bonds are opened and formed again in ring-opening polymerization of cyclic monomers. Differences of bond energies in monomers and polymers are thus practically zero, and the polymerization enthalpy is determined by delocalization and strain energies. Polymerization enthalpies are very negative for ring-opening polymerization of three-membered rings, increase to about zero for five- or six-membered rings, drop again to negative values, and return almost to zero for very large rings. The polymerization entropies of very small rings are very negative due to the release of rotational entropy upon polymerization. They become less negative with increasing ring size.

Case 2. The polymerization enthalpy is negative (or zero) and the polymerization entropy positive. Polymerization is possible at all temperatures in this rare case, the polymerization of cyclooctamethyltetrasiloxane being an example.

Case 3. The polymerization enthalpy is positive (or zero) and the polymerization entropy is negative. No polymerization is possible at any temperature. This case seems to apply to the polymerization of acetone.

Case 4. Both polymerization enthalpy and polymerization entropy are positive. A *floor temperature* exists below which no polymerization is possible. This rare case is fulfilled for the polymerization of tightly packed cyclic monomers such as cyclooctasulfur or oxacycloheptane (oxepane) since the number of rotatory degrees of freedom increases strongly upon polymerization to open chains.

Polymerization enthalpies and entropies are influenced by the state of monomers and polymers (gaseous, liquid, crystalline, etc.); the physical interaction between reactants themselves or reactants and solvents; and pressure. Especially important for industrial polymerizations is the fact that most (but not all, see above) chain polymerizations are exothermic. The heat of polymerization can be considerable: adiabatic polymerization of gaseous ethylene to crystalline polyethylene would result in a temperature increase of 1800 K for complete monomer conversion. Polymerization reactors must be designed in such a way that the heat of polymerization can be removed rapidly because, otherwise, inhomogeneous charges may result or the reactor may even explode.

3.3.2. Free-Radical Polymerizations

Free-radical polymerizations are initiated and propagated by free radicals. Such polymerizations are relatively insensitive to impurities in the reaction mixture and fairly easy to control. They are thus the methods of choice for the industrial production of plastics if the monomers can be subjected to free-radical polymerizations. This is true for ethylene and many ethylene derivatives: most commodity plastics are thus obtained from free-radical polymerizations (Table 10).

Other industrial polymers formed by free-radical homopolymerizations include poly(vinyl acetate) (for coatings and adhesives), poly(acryl ester) (for adhesives), polyacrylamide (for thickeners), polyacrylonitrile (for fibers), polychloroprene (for elastomers), poly(acryl acid) (for thickeners), and poly(*N*-vinylpyrrolidone) (for various applications).

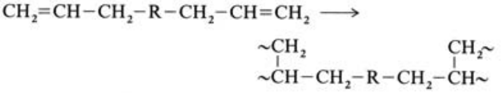
Polymerizations may be carried out in the gas phase, bulk, suspension, emulsion, solution, or under precipitation. Most monomers are bifunctional; they lead to linear or slightly branched polymers and thus to thermoplastics. The only thermosets obtained from free-radical homopo-

Table 10. Plastics by free-radical chain polymerizations*

Monomers	Polymerization in						Monomeric units
	Gas phase	Bulk	Suspension	Emulsion	Solution	Precipitation	
Living polymerization							
p-Xylylene	+						$-CH_2-(p\text{-}C_6H_4)-CH_2-$
Irreversible polymerization to linear or slightly branched polymers							
Ethylene		+	+	(+)	(+)	(+)	$-CH_2-CH_2-$
Styrene		+	+	(+)	(+)		$-CH_2-CH(C_6H_5)-$
p-Methylstyrene			+	+			$-CH_2-CH(p\text{-}CH_3C_6H_4)-$
Vinyl acetate		(+)	(+)	+	(+)		$-CH_2-CH(OOCCH_3)-$
Vinyl chloride	+	(+)	(+)	+	(+)		$-CH_2-CHCl-$
Vinyl fluoride		+					$-CH_2-CHF-$
Vinylidene fluoride			+	+			$-CH_2-CF_2-$
Trifluorochloroethylene			+				$-CF_2-CFCl-$
Tetrafluoroethylene			+				$-CF_2-CF_2-$
Methyl methacrylate		+	+	+	+		$-CH_2-C(CH_3)(COOCH_3)-$
Cross-linking polymerization							
Diallyl phthalate		+					see Equation (32)

[*] + = major processes; (+) = minor processes. Other industrial polymers by free radical homopolymerizations include poly(vinyl acetate) (for coatings and adhesives), poly(acryl ester) (for adhesives), polyacrylamide (for thickeners), polyacrylonitrile (for fibers), polychloroprene (for elastomers), poly(acrylic acid) (for thickeners), and poly(*N*-vinyl pyrrolidone) (for various applications).

lymerizations are diallyl and triallyl compounds that cross-link under polymerization conditions:



$$CH_2{=}CH{-}CH_2{-}R{-}CH_2{-}CH{=}CH_2 \longrightarrow \sim CH(CH_2\sim){-}CH_2{-}R{-}CH_2{-}CH(CH_2\sim)\sim$$

(33)

where R may be $COO(CH_2)_2O(CH_2)_2OOC$ [diethylene glycol bis(allyl carbonate], o-$C_6H_4(COO)_2$ (diallyl phthalate), or m-$C_6H_4(COO)_2$ (diallyl isophthalate). Other allyl compounds are used as cross-linking comonomers (diallyl fumarate, diallyl maleate, triallyl cyanurate).

Most free-radical polymerizations follow the kinetics of true chain reactions. In initiating (start) reactions (Eq. 35), radicals $R^\bullet$ formed from the decomposition (Eq. 34) of initiator molecules I react with monomer molecules M. The resulting "monomer radicals" $R-M^\bullet$ add further monomer molecules in the propagation reaction (Eq. 36) until the growing polymer radicals $R{\sim}{\sim}{\sim}M^\bullet$ are terminated by recombination (Eq. 37) or disproportionation (Eq. 38) with other polymer radicals or by addition of initiator radicals (Eq. 39):

$$I \to 2\,R^\bullet \tag{34}$$

$$R^\bullet + M \to R-M^\bullet \tag{35}$$

$$R-M^\bullet + M \to R-M-M^\bullet, \text{etc.} \to R-M_{n-1}-M^\bullet \tag{36}$$

$$R-M_{n-1}-M^\bullet + {}^\bullet M-M_{m-1}-R \to R-M_{n+m}-R \tag{37}$$

$$\begin{aligned} &R-M_{n-1}-M^\bullet + {}^\bullet M-M_{m-1}-R \to \\ &R-M_{n-2}-M=M+X-M_m-R \end{aligned} \tag{38}$$

$$R-M_{n-1}-M^\bullet + R^\bullet \to R-M_n-R \tag{39}$$

In Equation (38), X is an atom or a group that is transferred from the ultimate monomeric unit of one polymer radical to another polymer radical, for example, the H atom in the reaction

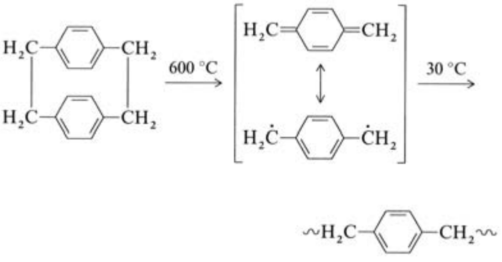
$$\sim CH_2-C^\bullet HR + {}^\bullet CHR-CH_2\sim \;\to\; \sim CH_2-CH_2R + CHR=CH_2\sim$$

These reactions are kinetically classified as termination reactions and not as transfers because they lead to dead chains. The term "transfer" is rather reserved for chemical transfers that generate new propagating radicals, such as

$$\sim CH_2-C^\bullet HR + AX \to \sim CH_2-CHRX + A^\bullet \tag{40}$$

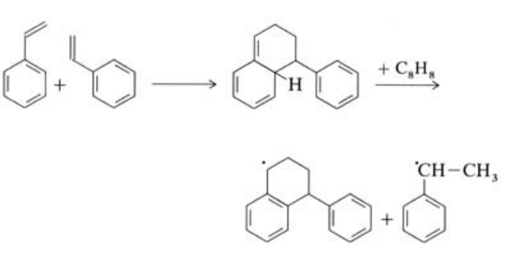
Initiation. Free-radical polymerizations can be initiated thermally by thermal initiators, by redox initiators, by photoinitiators, or electrolytically.

Thermal Initiation is utilized in the polymerization of p- cyclophane to poly(p-xylylene):



Propagation proceeds by addition of biradicals of various sizes (i.e., by polyaddition and not by chain polymerization). The resulting polymer is cross-linked since radicals also attack methylene groups, which generates more than two radical sites per reactant and thus cross-linking sites. The reaction is utilized for the formation of thin coatings.

Styrene is the only monomer that is polymerized commercially by thermal initiation through monoradicals. The primary Diels – Alder adduct of two styrene molecules reacts with another styrene molecule to give two different starter radicals:



Only relatively small amounts of styrene are, however, polymerized commercially by this method. Most styrene polymerizations, like many other commercial free-radical polymerizations, are started by radicals from *thermal initiators*. These thermal initiators dissociate homolytically into two radicals at elevated temperature, usually 60 – 80 °C. For the bulk polymerization of styrene, high-temperature initiators such as 1,2-dimethyl-1,2-diethyl-1,1-diphenyl-ethane or vinylsilane triacetate are preferred. For styrene polymerization in suspension, dibenzoyl peroxide (BPO) ($C_6H_5CO - O - O - OCC_6H_5$) and *tert*-butyl perbenzoate [$C_6H_5CO - O - O - C(CH_3)_3$] are used.

Many other bulk polymerizations employ diisopropyl peroxydicarbonate (IPP), which decomposes according to

$$\begin{aligned}&(CH_3)_2CHO - COO - OOC - OCH(CH_3)_2 \rightarrow\\&2(CH_3)_2CHO - COO^\bullet\end{aligned} \tag{41}$$

Water-soluble initiators such as dipotassium persulfate ($K_2S_2O_8$) and certain redox initiators are used in emulsion polymerizations. *Redox initiators* generate radicals by reaction of a reducing agent with an oxidizing agent (e.g., $Fe^{2+} + H_2O_2$). These systems need far less activation energy for the formation of radicals, and polymerization can thus be initiated at low temperature.

Photochemical Initiations are utilized for the production of lithographic plates (→ Imaging Technology, 3. Imaging in Graphic Arts) and for hardening lacquers but not in the manufacture of plastics. *Electrolytic polymerizations* find applications in the coating of metal sheets by plastics.

Only initiator radicals are formed at the early stages of free-radical polymerizations. These radicals are successively converted into monomer radicals by addition of initiator radicals to monomer molecules and into polymer radicals by further addition of monomers. At the same time, some polymer radicals are removed by termination reactions. Finally, a steady state is established in which as many radicals are formed as are removed by termination. This state of constant total radical concentration (ca. 10^{-8} mol/L) is in general observed within seconds at monomer conversions of $10^{-2} - 10^{-4}$ %.

Propagation. Monomer molecules are usually added head-to-tail to growing polymer radicals:

$$\begin{aligned}&\sim CH_2 - CHR^\bullet + CH_2 = CHR \rightarrow\\&\sim CH_2 - CHR - CH_2 - CHR^\bullet\end{aligned} \tag{42}$$

but tail-to-tail additions do occur (see Section 2.1).

Free-radical polymerizations lead in general to atactic or predominantly syndiotactic polymers. The syndiotacticity increases with decreasing polymerization temperature.

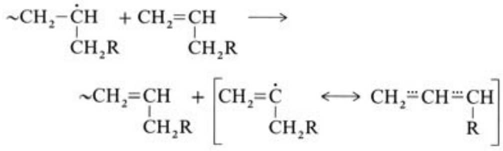
Termination. Termination reactions by recombination, disproportionation, and (at higher initiator concentrations) addition of initiator radicals, cannot be avoided. Since initiator radicals and thus also polymer radicals are formed successively and are deactivated at random by different termination reactions, distributions of molar masses are formed. The width of these distributions is given by the relative proportion of the different types of termination reactions.

Chain Transfer. The transfers of radicals to monomers, solvents, and initiators terminate polymer chains and generate others (Eq. 40). The ratios of rate constants k_{tr} of transfer to rate constants k_p of propagation are called transfer constants, $C_{tr} = k_{tr}/k_p$; at 60 °C they possess values between ca. 2×10^{-6} for the transfer of polystyryl radicals to benzene and 5700 for the transfer of poly(vinyl acetate) radicals to carbon tetrabromide.

Chain transfers often lead to new radicals that have approximately the same reactivity as the disappearing ones. In this case, the rate of polymerization is not decreased by chain transfer, but the degree of polymerization is lowered. Certain transfer agents with high transfer constants (such as thiols) are thus often employed to regulate molar mass.

Retardation occurs if the new radical is more sluggish in adding monomers than the transferring polymer radical; *inhibition*, if a new chain does not start at all. Chain transfers to polymers lead to branched polymers; most radically polymerized polymers are thus slightly branched.

The chain transfer to nonionic allyl monomers generates resonance-stabilized allyl radicals. The addition of monomer molecules to these radicals produces radicals



$$\sim CH_2-\overset{\bullet}{C}H(CH_2R) + CH_2=CH(CH_2R) \longrightarrow \sim CH_2=CH(CH_2R) + \left[CH_2=\overset{\bullet}{C}(CH_2R) \longleftrightarrow CH_2\overset{...}{=}CH\overset{...}{=}CH(R)\right]$$

(43)

that are more stabilized by resonance than their precursors and thus do not start a polymer chain. The polymerization of noncharged monoallyl monomers thus leads to oligomers with degrees of polymerization of ca. 10 – 20.

Polymerization Kinetics. Initiator radicals are generated by initiator decomposition (Eq. 34) with a rate of $2\,f \cdot k_d \cdot [I]$ where f is the radical yield (i.e., the fraction of radicals that start the polymerization). Initiator radicals disappear in the start reaction with a rate of $k_{st}[I^\bullet]$ [M]. In the steady state, the rate of the start reaction equals the rate of the termination reaction(s), thus $R_{st} = R_t$, and for terminations through deactivation by other polymer radicals,

$$d[P]/dt = R_{st} - R_t = 2f \cdot k_d \cdot [I] - k_t[P]^2 = 0 \qquad (44)$$

Since monomer is practically consumed only by the propagation reaction with a rate of $R_p = -\,d[M]/dt = k_p[P^\bullet]\,[M]$, the propagation rate at diminishing initiator consumption is obtained from Equation (44)

$$R_p = -d[M]/dt = k_p(2f \cdot k_d/k_t)^{1/2} \cdot [I]_o^{1/2}[M] \qquad (45)$$

The polymerization rate is directly proportional to the monomer concentration; bulk polymerization is thus always faster than solution polymerization. The monomer concentration decreases with increasing monomer conversion as does the rate R_p.

A "self-acceleration" of the polymerization and a concomitant increase in the degree of polymerization are observed at higher monomer conversion, especially in bulk and in concentrated solutions. This *gel effect* or *Trommsdorff – Norrish* effect is caused by a changing diffusion control of the termination by mutual reaction of two polymer radicals (i.e., a decrease of termination reactions), which in turn comes from an increasing entanglement of polymer chains. Because neither the rate of the initiator decomposition nor the rate of monomer addition is affected by increasing entanglements, both overall polymerization rates and molar masses increase. The gel effect broadens molar mass distributions.

Cross-Linking Polymerizations. Free-radical chain polymerizations are employed commercially in the manufacture of diallyl thermosets and in styrene – divinylbenzene copolymerizations for polymer beads. Primary macromolecules produced at very low monomer conversions are almost linear and carry pendant polymerizable groups. The likelihood of an attack at these groups increases with increasing mass average molar mass. Branched molecules are formed that convert to cross-linked polymers at the gel point. Monomer conversion at the gel point cannot at present be predicted theoretically for such free-radical polymerizations.

Process Engineering. Free-radical polymerizations may be performed in the gas phase, in bulk, solution, emulsion, suspension, or under precipitation (Table 10). Each method has advantages and disadvantages.

Bulk Polymerizations. Industrial bulk polymerizations are performed in *liquid monomers*, occasionally with the addition of 5 – 15 vol % solvent as a polymerization aid. The process leads to very pure products. However, much heat is generated per unit volume and, in addition, by the gel effect. Local overheating may cause multimodal molar mass distributions, branching, polymer degradation, discoloring, or explosion. Bulk polymerizations are thus often terminated at 40 – 60 % monomer conversion. The remaining monomer is distilled and recovered. Alternatively, polymerizations may be performed in two steps: first in large batch reactors, then in thin layers. Residual monomer is usually removed by steam.

Suspension Polymerization is a "water-cooled" bulk polymerization. Water-insoluble monomers are suspended as small droplets of 0.001 – 1-cm diameter with the help of suspending agents. The polymerization is initiated by oil-soluble initiators. The droplets are converted by polymerization into pearls, and the process is also called *pearl polymerization*. Suspension polymerization allows easy control of the reaction and delivers the polymer as easy-to-handle beads. A disadvantage is the cost of water removal and cleaning, along with the sometimes deleterious effects of incorporated suspension agents.

Emulsion Polymerization. In emulsion polymerizations, water-insoluble monomers are solubilized in water by micelles of surfactant molecules (4 – 10-nm diameter); the monomers are also suspended in a few droplets (ca. 1000-nm diameter). Water-soluble initiators decompose into radicals that travel through the water to the micelles where polymerization begins. Diffusion of monomer from the droplets to the micelles replenishes the monomer that has been used up by reaction in the micelles. The micelles finally grow into latex particles of 500 – 5000-nm diameter. Since the reaction volume is very small in micelles (and in growing latex particles), termination reactions are rare and polymerization proceeds in a quasi-living manner, leading to much higher molar masses than bulk polymerization. In terms of reaction control, emulsion polymerizations have advantages similar to suspension polymerizations. In addition, they offer higher polymerization rates by redox initiators and higher molar masses (which can be regulated by transfer agents). The resulting latex can furthermore be used directly for paints, adhesives, and coatings.

Gas-Phase Polymerization. Gas-phase polymerizations can be initiated photochemically. Each growing particle contains only one radical and the polymerization is thus quasi-living. The polymerization rate is determined by the rate of monomer adsorption in the precipitating particles and later by monomer diffusion to the occluded polymer radicals. The resulting polymers are very clean.

Solution Polymerization. Solution polymerizations decrease polymerization rates by monomer dilution and allow easy removal of the heat of polymerization. Solvents are however costly to remove, and the process is used only if the resulting polymer solutions can be used directly or if monomers and polymers decompose in melts.

3.3.3. Anionic Polymerizations

Anionic polymerizations are initiated by bases or Lewis bases such as alkali metals, alkoxides, amines, phosphines, Grignard compounds, and sodium naphthalene, very often in solution. The initiators dissociate "instantaneously" into the initiating species. These dissociations and the subsequent start reactions need little activation energy; anionic polymerizations thus often proceed with high speed even at −100 °C.

The initiating species and the growing macroions are rarely completely dissociated into anions and counterions. They are rather in equi-librium with various types of ion pairs (nondissociated species contact ion pair solvent-separated ion pair free ions; plus associates of these species). The type and amount of initiating species strongly affect the polymerization rates and the tacticity of polymers.

The initiating species are present in their effective concentrations at the beginning of polymerization; they are not formed one after another as in free-radical polymerization. Termination reactions are fairly rare; anionic polymerizations are often "living." Very low initiator concentrations are required for living polymerizations to high molar masses (see Section 3.2.1); however, high monomer – initiator ratios are difficult to control and may lead to low polymerization rates. In general, polymers from living polymerizations have very narrow molar mass distributions of the Poisson type if diffusion effects are avoided during the mixing of monomer and initiator solutions.

Very few anionic polymerizations are therefore employed for the production of thermoplastics, most notably those of formaldehyde, ε- caprolactam (also for reaction injection molding), and laurolactam (Table 11). Anionic polymerizations are however the method of choice for the syntheses of block copolymers (e.g., thermoplastic elastomers of the styrene – butadiene – styrene type).

3.3.4. Cationic Polymerizations

Three groups of monomers can be polymerized cationically: olefin derivatives $CH_2{=}CHR$ with electron-rich substituents, monomers with double bonds containing heteroatoms or heterogroups Z (e.g., $CH_2{=}Z$), and rings with heteroatoms. Initiators are Brønsted acids (perchloric acid, trichloroacetic acid, trifluoromethanesulfonic acid, etc.); Lewis acids ($AlCl_3$, $TiCl_4$, etc.)

Table 11. Industrial anionic homopolymerizations

Monomer	Repeating unit	Application
Butadiene	$\sim CH_2-CH=CH-CH_2\sim$	elastomer (1,4-*cis*)
Isoprene	$\sim CH_2-C(CH_3)=CH-CH_2\sim$	elastomer (1,4-*cis*)
Methyl cyanoacrylate	$\sim CH_2C(CN)(COOCH_3)\sim$	adhesive
Formaldehyde	$\sim O-CH_2\sim$	engineering plastics
Ethylene oxide	$\sim O-CH_2-CH_2\sim$	thickener
Glycolide	$\sim O-CO-CH_2\sim$	surgical threads
ε-Caprolactone	$\sim O-CO-(CH_2)_5\sim$	polymer plasticizer
ε-Caprolactam	$\sim NH-CO-(CH_2)_5\sim$	fiber, thermoplastic
Lauryllactam	$\sim NH-CO-(CH_2)_{11}\sim$	fiber, film
Hexamethyl-cyclotrisiloxane	$\sim O-Si(CH_3)_2\sim$	elastomer

with “coinitiators” such as water; and carbenium salts (acetyl perchlorate, tropylium hexachloroantimonate, etc.). The propagating macrocations are thermodynamically and kinetically unstable. They attempt to stabilize themselves by addition of nucleophilic species, which leads to very fast polymerization on one hand and to a host of transfer and termination reactions on the other. Very few monomers are thus polymerized cationically on an industrial scale (Table 12).

3.3.5. Ziegler – Natta Polymerizations

Ziegler – Natta polymerizations are chain polymerizations that are initiated and propagated by Ziegler catalysts, a vast group of coordination compounds from transition-metal compounds and metal alkyls. These polymerizations are also called coordination polymerizations or anionic – coordination polymerizations, although coordination of a monomer to an initiator need not lead to a Ziegler – Natta type of polymerization and no anions are involved at all.

Table 12. Industrial cationic polymerizations

Monomer		Application**
Name	Structure*	
Isobutene	$CH_2=C(CH_3)_2$	elastomers, adhesives, VI improvers
Vinyl ethers	$CH_2=CHOR$	adhesives, textile aids, plasticizers
Formaldehyde	$CH_2=O$	engineering plastic
Ethyleneimine	c-$(NHCH_2CH_2)$	paper additive, flocculant
Tetrahydrofuran	c-$[O(CH_2)_4]$	soft segment for polyurethanes or polyether – ester elastomers

*c=cyclo.

**VI=viscosity index.

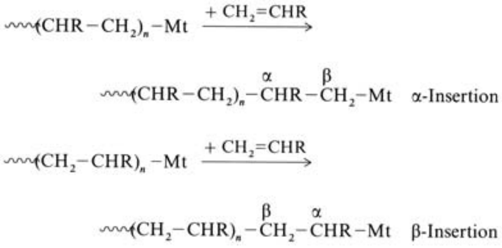
Table 13. Important industrial polymerizations with transition-metal catalysts

Monomer	Initiator	Application
Ethylene	$TiCl_3-AlR_3$; Cr – silica	thermoplastic
Propene	$TiCl_3-R_2AlCl$	thermoplastic
Ethylene+propene+ nonconjugated diene	$VOCl_3-R_2AlCl$	elastomer
Butadiene	TiI_4-AlR_3; $R_3Al_2Cl_3-Co(OOCR')_2$	elastomer
Isoprene	$TiCl_3-AlR_3$	elastomer
Butene-1	$TiCl_3-Et_2AlCl$	thermoplastic
4-Methylpentene-1	?	thermoplastic

Typical Ziegler catalysts for industrial polymerizations are shown in Table 13. The so- called third-generation catalysts for ethylene polymerizations are composed of $TiCl_3 + AlR_3 + MgCl_2$; their high catalyst yield of more than 50 000 g of polyethylene produced per 1 g of $TiCl_3$ makes removal of catalyst residues from the polymer unnecessary.

Various complexes between transition-metal compounds and metal alkyls are known to be formed, but which of these are polymerization active and to what extent are rarely known. In any case, the transition-metal atoms of these complexes are bound to the growing chains; Ziegler catalysts are thus not catalysts but initiators.

Propagation proceeds via insertion of the monomer molecule between the already existing chain and the bound transition metal Mt:



$$\sim\!\!\sim\!\!\sim(\text{CHR}-\text{CH}_2)_n-\text{Mt} \xrightarrow{+\,\text{CH}_2=\text{CHR}} \sim\!\!\sim\!\!\sim(\text{CHR}-\text{CH}_2)_n-\overset{\alpha}{\text{CHR}}-\overset{\beta}{\text{CH}_2}-\text{Mt} \quad \alpha\text{-Insertion}$$

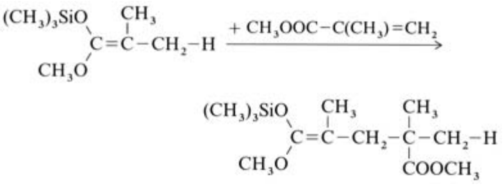
$$\sim\!\!\sim\!\!\sim(\text{CH}_2-\text{CHR})_n-\text{Mt} \xrightarrow{+\,\text{CH}_2=\text{CHR}} \sim\!\!\sim\!\!\sim(\text{CH}_2-\text{CHR})_n-\overset{\beta}{\text{CH}_2}-\overset{\alpha}{\text{CHR}}-\text{Mt} \quad \beta\text{-Insertion}$$

The isospecific polymerization of propene with $TiCl_4-AlR_3$ is an α-insertion; the syndiospecific polymerization of the same monomer is very probably a β-insertion. The ability of Ziegler catalysts to regulate the stereocontrol of such polymerizations to a very high degree makes Ziegler – Natta polymerizations extremely useful industrially. Propene, for example, polymerizes free-radically or cationically to highly branched, atactic, low molar mass polymers that do not crystallize and have low glass transition temperatures. They can be used only for hotmelt adhesives. Ziegler – Natta polymerizations (Table 13) lead, however, to stereoregular polymers with high melting temperatures; isotactic polypropylenes find extensive use as thermoplastics.

Similar catalysts are used in *metathesis polymerizations*. Metatheses are exchange and disproportionation reactions of double bonds, mainly carbon – carbon double bonds in olefins and cycloolefins. A low molar mass example is the metathesis of pentene-2 to butene-2, pentene-2, and hexene-3 (in the ratio 1 : 2 : 1) by the catalyst system $WCl_6 – C_2H_5AlCl_2 – C_2H_5OH$. Industrially, cyclooctene, norbornene, and dicyclopentadiene are polymerized by metathesis polymerization. Cyclooctene gives polyoctenamer $\sim CH{=}CH–(CH_2)_6 \sim$; both the *cis* and the *trans* isomers are elastomers (→ Rubber, 6. Synthesis by Radical and Other Mechanisms, Chap. 4.). Norbornene polymerizes to a thermoplastic polymer

that is plasticized with mineral oil to give an elastomer (→ Rubber, 6. Synthesis by Radical and Other Mechanisms, Chap. 3.). Dicyclopentadiene is considered as a monomer for reaction injection molding (RIM) processes.

Group transfer polymerizations are also insertion polymerizations because a monomer molecule is inserted into the bond between the active center and the remaining polymer chain. Depending on the monomer, these polymerizations may proceed by either α- or β-insertions and with the help of nucleophilic or electrophilic catalysts. Only a small-scale polymerization of alkyl methacrylates to low molar mass polymers by silylketene acetals and nucleophilic catalysts ($[(CH_3)_3SiF_2]^-$, $[HF_2]^-$, CN^-, etc.) is utilized industrially at present:



3.3.6. Copolymerizations

Copolymerizations are joint polymerizations of two or more monomers; they were also called interpolymerizations in the older literature. In the simplest case, both active chain ends ∼a* and ∼b* react irreversibly with the two monomers A and B:

$$\sim a * + A \rightarrow \sim a{-}a*; R_{aA} = k_{aA}[a*][A]$$

$$\sim a * + B \rightarrow \sim a{-}b*; R_{aB} = k_{aB}[a*][B]$$

$$\sim b * + A \rightarrow \sim b{-}a*; R_{bA} = k_{bA}[b*][A]$$

$$\sim b * + B \rightarrow \sim b{-}b*; R_{bB} = k_{bB}[b*][B] \qquad (46)$$

Four rates R_{ij} and four rate constants k_{ij} are to be considered in this terminal model, which corresponds to Markov first-order statistics. At high molar masses, monomers are consumed only by the four propagation reactions. The relative monomer conversion is given by

$$\frac{-d[A]/dt}{-d[B]/dt} = \frac{R_{aA}+R_{bA}}{R_{bB}+R_{aB}} = \left(\frac{k_{bA}+k_{aA}([a^*]/[b^*])}{k_{bB}+k_{aB}([a^*]/[b^*])}\right)\cdot\frac{[A]}{[B]} = \frac{d[A]}{d[B]} \qquad (47)$$

The ratios of rate constants of homopropagations and cross-propagations are called copolymerization parameters

$$r_A \equiv k_{aA}/k_{aB};\ r_B \equiv k_{bB}/k_{bA} \qquad (48)$$

Five different cases can be distinguished for each copolymerization parameter:

$r = 0$	The rate constant of homopropagation is zero; the active center adds only the other monomer.
$r < 1$	The other monomer is added preferentially.
$r = 1$	Both monomers are added in the same amounts.
$r > 1$	The own monomer is added preferentially but not exclusively.

Table 14. Types of copolymerization of monomers A and B

Types	Copolymerization parameters				
	Azeotropic		Nonazeotropic		
	r_A	r_B	r_A	r_B	r_Ar_B
Alternating	0	0	0	> 0	0
Statistical	< 1	< 1	$< 1/r_B$	> 1	< 1
Ideal	1	1	$1/r_B$	$1/r_A$	1
Block forming	> 1	> 1	$> 1/r_B$	< 1	> 1
Blend forming	∞	∞	∞	$< \infty$	∞

$r = \infty$ No copolymerization, only homopolymerization.

Depending on the relative numerical value of the two copolymerization parameters, five different types of copolymerization can be distinguished (Table 14).

In general, one of the monomers is consumed preferentially during copolymerization ($r_A \neq r_B$). This drift of copolymer composition can be avoided if the more reactive monomer is fed into the reactor according to its consumption. A conversion-independent polymer composition also results if copolymerization is performed under azeotropic conditions, which are defined by

$$d[A]/d[B] \equiv [A]/[B] \tag{49}$$

i.e., the relative rate of monomer consumption equals the ratio of monomer concentrations at any time: The monomer and the polymer compositions do not drift with the progress of polymerization.

This equation is a special case of the Lewis – Mayo equation, which describes the instantaneous composition of the copolymer as a function of the ratio of instantaneous monomer concentrations:

$$\frac{d[A]}{d[B]} = \frac{1+r_A([A]/[B])}{1+r_B([B]/[A])} = \frac{x_a}{x_b} \tag{50}$$

All types of copolymerization can in principle occur with the same monomer pair if various initiators are used. All copolymerizations of styrene and methyl methacrylate shown in Figure 15 are, for example, statistical. The free-radical-initiated copolymerization is, however, azeotropic, and the cationic and anionic ones are nonazeotropic. Initiation by $Et_3Al_2Cl_3$ and traces of oxygen leads to almost alternating copolymers, whereas cationic polymerization generates long styrene sequences and anionic polymerization produces long methyl methacrylate ones. The sequence length determines many polymer properties, most notably glass and melting temperatures.

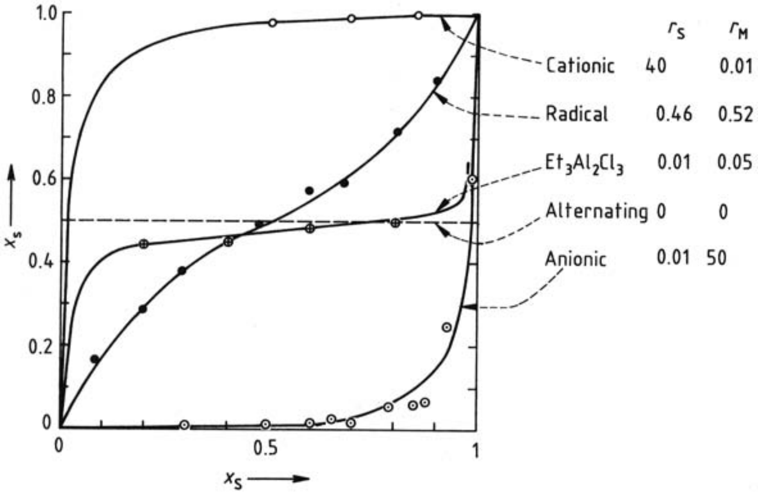


Figure 15. Instantaneous mole fraction x_s of styrene units in the polymer formed as a function of the instantaneous mole fraction x_s of styrene in the copolymerization of styrene with methyl methacrylate initiated by (o) cations; (•) free radicals; (⊕) $Et_3Al_2Cl_3$; (⊙) Anions

Solid lines: calculated with copolymerization parameters shown to the right; dotted line: theory for alternating copolymerizations.

Table 15. Industrial copolymerizations

Monomers	Polymerization	Application
Free radical, linear (or slightly branched)		
Ethylene+10 % vinyl acetate	bulk	shrink films
Ethylene+10 – 35 % vinyl acetate	bulk	thermoplastics
Ethylene+35 – 40 % vinyl acetate	under precipitation [a]	films
Ethylene+>60 % vinyl acetate	emulsion	elastomers
Ethylene+<10 % methacrylic acid	bulk	extrusion coating
Ethylene+trifluorochloroethylene		thermoplastics
Butadiene+styrene	emulsion	multipurpose elastomers
Butadiene+37 % acrylonitrile	emulsion	oil-resistant elastomers
Vinyl chloride+3 – 20 % vinyl acetate	solution [b]	paints
Vinyl chloride+15 % vinyl acetate	solution [b]	Hi-fi records
Vinyl chloride+3 – 10 % propene	bulk	thermoplastics
Acryl esters+5 – 15 % acrylonitrile		oil-resistant elastomers
Acrylonitrile+4 % different monomers	under precipitation [c]	fibers with improved dyeability
Acrylonitrile+styrene		thermoplastics
Acrylonitrile+butadiene+styrene		thermoplastics
Tetrafluoroethylene+propene	emulsion	thermoplastics
Methacrylic acid+methacrylonitrile		hard foams (after cyclization)
Free radical, cross-linking		
Glycol methacrylate+2 – 4 % glycol dimethacrylate		contact lenses
Unsaturated polyesters+styrene or methyl methacrylate	bulk	glass-fiber-reinforced thermosets
Anionic		
Styrene+butadiene	solution	elastomers
Cationic		
Isobutene+2 % isoprene	solution	butyl rubber
Trioxane+ethylene oxide	solution	thermoplastics
Ethylene oxide+propylene oxide	solution	thickener, detergents
Ziegler – Natta polymerization		
Propylene oxide+nonconjugated dienes	solution	elastomers
Ethylene+propene+nonconjugated dienes		elastomers

[a] In *tert*-butanol.

[b] In acetone, 1,4-dioxane or hexane.

[c] In water.

Ionic copolymerizations very often lead to long block sequences, whereas free-radical copolymerizations tend in general to produce more random copolymers. Free-radical copolymerizations are thus the method of choice for industrial purposes if allowed by monomer structures (Table 15).

3.4. Polycondensations and Polyadditions

3.4.1. Bifunctional Polycondensations

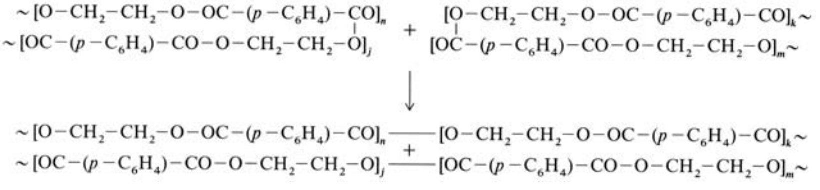
Polycondensations and polyadditions are generally divided into bifunctional reactions (two functional groups per reactant) and multifunctional ones (three or more functional groups per monomer molecule). Bifunctional reactions lead to linear macromolecules; multifunctional ones, to branched and finally cross-linked polymers. Bifunctional reactions are further subdivided into AB reactions (e.g., that of $H_2N-R-COOH$) and AA/BB reactions (e.g., $H_2N-R-NH_2 + HOOC-R'-COOH$).

All reactants, from monomer to high polymer, may react to form macromolecules in bifunctional polycondensations and polyadditions. Only monomers are present at the beginning of the reaction; later, oligomers are present. If the reactivity of the functional groups is independent of molecule size, then the greater number of smaller molecules leads first to low molar mass polymers and only at high conversions to chemical compounds with high molar masses (see Fig. 14). In equilibrium, the number-average degree of polymerization of polymers from AB and stoichiometric AA – BB reactions is dictated by the extent of functional group reaction p:

$$X_n = 1/(1-p) \tag{51}$$

At 50 % conversion ($p = 0.5$), the number-average degree of polymerization of reactants is only 2 (this includes monomer molecules), and the number-average degree of polymerization of polymers ($2 < X_i < \infty$) is only 3. Industrial polycondensations rarely deliver number-average degrees of polymerization greater than 100 – 200 (i.e., $p = 0.99 – 0.995$ in equilibrium). The endgroups of these equilibrium polymers may condense further during processing by, e.g., extrusion or injection molding. The accompanying strong increase in viscosity is undesirable and these endgroups are therefore blocked against further polycondensation by "sealing" them with monofunctional reagents.

Equilibria are established not only by retroreactions (reversal of polycondensations and polyadditions) but also by catalyzed exchange reactions between chain segments. In these trans reactions, number-average molar masses remain constant, but mass-average molar masses increase if the initial ratio of mass to number-average molar mass was smaller than dictated by equilibrium conditions. An example is the transesterification of poly(ethylene terephthalate):



Higher degrees of polymerization at lower extents of reaction can be obtained by irreversible "activated reactions" and especially by heterogeneous reactions of fast reacting monomers. An example is the Schotten – Baumann reaction of diamines in water with diacid dichlorides in chloroform, for example. A polyamide film is formed at the interface of the two solutions. Functional groups of this polymer are buried in the interior of the film; they cannot react with each other. Exchange reactions and retroreactions are also absent. Only surface groups can react; the resulting irreversible reaction leads to high molar masses. Industrially, this reaction is utilized for one of the two industrial syntheses of polycarbonates, i.e., from the sodium salt of bisphenol A and phosgene (Table 16).

Most industrial polycondensations are of the AA – BB type (Table 16); they can be described by

$$n\,\mathrm{A{-}V{-}A} + n\,\mathrm{B{-}W{-}B} \rightarrow \mathrm{A{-}(V{-}W)}_n\mathrm{{-}B} + (2n-1)\mathrm{AB} \tag{52}$$

where A– and B– are leaving groups, AB represents leaving molecules, –V– and –W– are monomeric units, and –V–W– are repeating units.

Industrial AB polycondensations are fairly rare. Examples are the formation of polyamide 11 (nylon 11) (Eq. 27), the polycondensation of carbodiimides

$$\begin{aligned}&\mathrm{O=C=N{-}R{-}N=C=O} \rightarrow\\ &\sim\mathrm{R{-}N=C=N}\sim + \mathrm{CO_2}\end{aligned} \tag{53}$$

and the synthesis of certain polysulfones

$$\begin{aligned}&\mathrm{C_6H_5O(}p\mathrm{\text{-}C_6H_4)SO_2Cl} \rightarrow\\ &\sim (p\mathrm{\text{-}C_6H_4}){-}\mathrm{O}{-}(p\mathrm{\text{-}C_6H_4}){-}\mathrm{SO_2} \sim + \mathrm{HCl}\end{aligned} \tag{54}$$

3.4.2. Multifunctional Polycondensations

Multifunctional polycondensations are condensation reactions with the participation of monomers having higher functionality ($f_o > 2$). At low conversions, branched molecules are formed with increasingly higher number of functional end groups per molecule (i.e., increased functionality f) :

$$f = 2(f_o - 1) + (X - 2)(f_o - 2) = 2 + X(f_o - 2) \tag{55}$$

Only one such group is however needed to link two molecules; the probability of such a linkage thus increases dramatically with increasing degree of polymerization X. At a certain degree of conversion of functional groups, molecules are linked throughout the volume of the reactor. The viscosity increases strongly, and the mass-average molar mass of the cross-linked polymer approaches infinity at this "gel point." Not all reactants are linked at the gel point; some are still soluble up to

Table 16. Industrially important linear AA – BB polycondensations following Equation (52)

Polymer	Chemical structure				Remarks
	A	V	W	B	
Poly(ethylene terephthalate)	H	$O(CH_2)_iO$	CO – *p*-Ph – CO	OH	*i*=2 (ethylene) or 4 (butene)
	H	$O(CH_2)_iO$	CO – *p*-Ph – CO	OCH_3	
Unsaturated polyesters	H	$O(CH_2)_2O$	CO – CH=CH – CO	$O_{1/2}$	from maleic anhydride (isomerizes mainly to fumaric acid residues)
Polycarbonate	H	O – *p*-Ph – $C(CH_3)_2$ – *p*-Ph – O	CO	OC_6H_5	
	Na	O – *p*-Ph – $C(CH_3)_2$ – *p*-Ph – O	CO	Cl	
Polyarylates	Na	O – Ar – O	CO – Ar – CO	Cl	different Ar
Poly(phenylene sulfide)	Na	S	*p*-Ph	Cl	
Polysulfides	Na	S	R	Cl	different R
Polysulfones	K	O – *p*-Ph – O	SO_2 – *p*-Ph – O – *p*-Ph – SO_2	Cl	different V and W units
Polyamides	H	$NH(CH_2)_iNH$	$CO(CH_2)_jCO$	OH	PA 66 (*i*=6; *j*=4) PA 610 (*i*=6; *j*=8) PA 46 (*i*=4; *j*=4)
Polyetheretherketone	K	O – *p*-Ph – CO – *p*-Ph – O	*p*-Ph – CO – *p*-Ph	F	

Ar=aromatic residue,
p-Ph=*para*-substituted phenylene group,
R=organic residue.

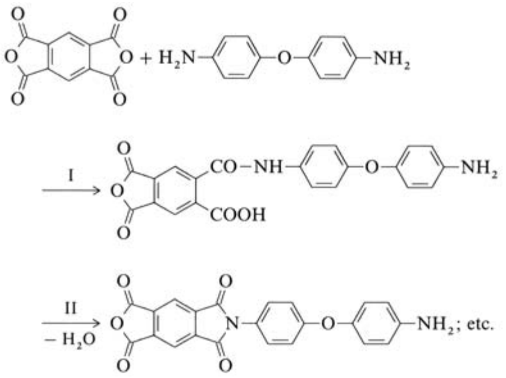
high conversions. The number-average degrees of polymerization of reactants are thus fairly low at the gel point, usually in the range $10<\overline{X}_n<50$.

Knowledge of the gel point is technically very important. Polymers cannot, or can only with difficulty, be processed beyond the gel point and must thus be shaped before or during the cross-linking reaction. The gel point can be calculated from the functionality and relative amounts of reactive groups if intramolecular cyclizations are assumed absent. In practice, such cyclizations are often present and cross-linking occurs at higher extents of reaction than calculated. The theoretical calculations thus provide a safety margin.

Chemical cross-linking reactions are utilized for thermosets, certain leathers, and the preparation of elastomers from rubber. Thermosetting polycondensation reactions allow the hardening of phenol, amino, and alkyd resins. In the reaction of phenol(s) with formaldehyde, methylene, formal, and ether bridges are formed between the *ortho* and *para* positions of the phenols; the hardening of novolacs with hexamethylenetetramine (urotropin) also leads to imine structures (→ Phenolic Resins). Amino plastics result from the reaction of urea or melamine with formaldehyde (→ Amino Resins), and alkyd resins from multifunctional alcohols with bifunctional organic acids or their anhydrides (→ Alkyd Resins).

Cross-linking also occurs inadvertently during cyclopolycondensations. In such reactions, rings are formed during the polycondensation. An example is the formation of polyimides from pyromellitic acid dianhydride with aromatic diamines.

Step I is a polyaddition to a polyamic acid. Step II may occur as shown but also by intermolecular reaction. To prevent such cross-linking reactions, step I is performed at 10 – 15 % solids content and conversion is limited to 50 %. Polyimide films are formed from the cross-linking of polyamic films. Polybenzimidazoles and ladder polymers are similarly obtained through such cyclopolycondensations.



3.4.3. Polyaddition

No leaving molecules have to be removed during polyadditions, an important advantage for process engineering. Practically all industrially important polyadditions are thus performed with thermosetting resins. Polyurethanes are formed from diisocyanates (or triisocyanates) and polyols (see Eq. 28 for diols). Polyurethane formation may be so rapid that cross-linking and shaping can be performed in one step through reaction injection molding with short cycle times. Epoxides (epoxy resins) contain two or more epoxy groups per prepolymer molecule and are cured with either difunctional or multifunctional amines or with anhydrides of organic acids.

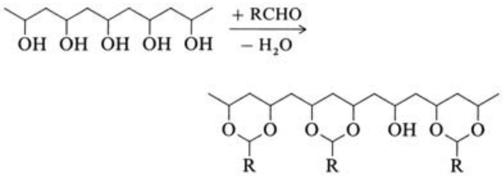
3.5. Polymer Reactions

3.5.1. Polymer Transformations

Several polymers are chemically transformed into industrially useful polymers by polymeranalogous reactions of their substituents (Table 17).

These reactions per group are chemically identical to their low molar mass analogues. They differ in the effect of side reactions, which do not lead to removable byproducts as in micromolecules but to "wrong" structures in the polymer chain. In most cases, such structures decrease the desired polymer properties. Polymer transformations that are prone to side reactions are thus generally avoided. This is one reason why only five types of polymer-analogous reactions are utilized commercially: transesterification – saponification, chlorination – sulfochlorination, etherification, hydrogenation, and cyclization.

The reaction of poly(vinyl alcohol) with butyraldehyde leads to acetals. For statistical reasons, however, not all hydroxyl groups can be transformed:



The resulting poly(vinyl butyral) is used as an intermediate layer in safety glass and for wash primers.

Heating of methacrylic acid – methacrylonitrile copolymers with ammonia produces polymethacrylimide structures that are hard foams:

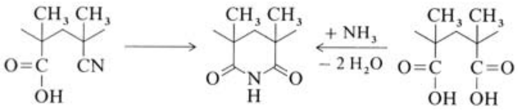


Table 17. Industrial polymer transformations (for ring formations see text)

Base units in primary polymer	Reagent	Conversion, %	Base units in final polymer	Application
$CH_2CH(OOCCH_3)$	ROH	98	$CH_2 - CHOH$	thickener
$CH_2CH_2CH_2CH(OOCCH_3)$	CH_3OH	99	$CH_2 - CHOH/CH_2 - CH_2$	engineering plastics
Cellulose – $NHCOCH_3$	H_2O	?	Cellulose NH_2	paper additive
Cellulose OH	CH_3COOH	83 – 100	Cellulose $OOCCH_3$	fibers, films
Cellulose OH	HNO_3	67 – 97	Cellulose – ONO_2	plastics, fibers
Cellulose ONa	oxirane	53 – 87	Cellulose – OCH_2CHRCH_3	thickener
Cellulose OH	oxirane	100 – 400 [a]	Cellulose – $OCH_2CH(OR')CH_3$	thickener
$CH_2 - CH_2$	Cl_2	25 – 40 [b]	$CH_2 - CHCl$	elastomer
		>40 [b]	$CH_2 - CHCl/CHCl - CHCl$	impact improver for PVC
$CH_2 - CHCl$	Cl_2	64 [b]	$CH_2 - CHCl/CHCl - CHCl$	adhesives, paints
$CH_2 - CH_2$	Cl_2/SO_2	<42 [b]; <2 [c]		coatings
$CH_2CH{=}CHCH_2/CH_2 - CHCN$	H_2	?	$(CH_2)_4/CH_2 - CHCN$	elastomer
$CH_2 - CH(C_6H_5)$	SO_3	low	$CH_2 - CH(C_6H_4SO_3H)$	ion exchangers
$N{=}PCl_2$	RONa	?	$N{=}P(OR)_2$	elastomer

[a] Further reaction of primary reaction products may lead to more than one monomeric unit of reagent per hydroxyl group of cellulose.
[b] Chlorine content in %.
[c] Ether groups per glucose unit.

3.5.2. Block and Graft Formations

Reactive chain ends can either initiate the polymerization of other monomers or couple with other preformed macromolecules to give block polymers:

$$A_n^* + m\,B \rightarrow A_nB_m^* \qquad (56)$$

$$A_n^* + {}^*B_m \rightarrow A_nB_m \qquad (57)$$

Both methods are used industrially with a variety of strategies for the synthesis of diblock polymers A_nB_m as compatibilizing agents for polymer blends, triblock polymers $A_nB_mA_n$ as thermoplastic elastomers, and various multiblock polymers for different purposes, especially for thermoplastic elastomers. Anionic living polymerizations are used for the syntheses of poly(styrene – block-butadiene – block-styrene) and poly(styrene – block-isoprene – block-styrene). Polycondensations serve for the preparation of multi[{poly(butylene terephthalate)} – block-poly{(polytetrahydrofuran) – terephthalate}], and various polyesteramide and polyetheramide segmented block polymers.

Graft copolymers result from the grafting of monomers on chemically different polymer chains. Grafts of isobutene – isoprene on polyethylenes, vinyl chloride on poly(ethylene-stat-vinyl acetate), ethylene – propylene on poly(vinyl chloride), or styrene – acrylonitrile on saturated acryl rubber also yield thermoplastic elastomers.

3.5.3. Cross-Linking Reactions

Cross-linking of preformed polymers is used for vulcanizing unsaturated rubbers with sulfur, vulcanizing saturated rubbers with peroxides, hardening unsaturated polyester chains with styrene or methyl methacrylate via copolymerization, or tanning collagen with certain reagents to leather.

3.5.4. Degradation Reactions

Degradation of polymers is undesirable for their application and often desirable for their disposal after use. The term degradation includes the decrease in degree of polymerization with preservation of the chemical structure of monomeric units (depolymerization), the unwanted chemical transformation of some monomeric units with preservation of the degree of polymerization (decomposition), and a combination of both. The terms degradation, depolymerization, and decomposition are sometimes used with the same meaning as in this article, but other times with broader or more restricted meanings; no accepted usage exists.

Depolymerizations involve chain scissions. They are retroreactions (i.e., the reverse of chain polymerizations, polyeliminations, polycondensations, or polyadditions). Chain scissions may be at random as in retropolycondensations and retropolyadditions or may be unzipping reactions as in retro-chain polymerizations and retropolyeliminations.

Unzipping can occur only with activated chains above their ceiling temperatures, that is, with living polymers, chain ends comprising certain functional groups, or radical ends generated by a prior chain scission.

Unzipping at higher temperature results in gaseous monomers that lead to voids in molded parts. This can be prevented or reduced by shorter sequence lengths of the unzippable polymer blocks. This strategy is utilized, for example, in the formation of acetal copolymers by copolymerization of trioxane (gives unzippable oxymethylene sequences $\sim OCH_2\sim$) with ethylene oxide (oxyethylene sequences $\sim OCH_2CH_2\sim$ do not unzip).

Decomposition can be caused by heat, light, oxygen, water, or other environmental agents as well as mechanical forces such as extensional flow, ultrasound, or a combination of these. It may lead to undesirable changes of mechanical, electrical, or optical properties. Unstabilized poly(vinyl chloride) $\sim(CH_2CHCl)_n\sim$ discolors on decomposition because HCl is eliminated and colored polyene sequences $\sim(CH{=}CH)_i\sim$ are formed. The polymer ultimately becomes brittle.

Decomposition is the primary degradation process in the pyrolysis of polymers, which may be desirable (rocket fuels, waste disposal) or not (fires), and often produces toxic fumes or smoke at lower flame temperatures. The risk of pyrolysis is enhanced for polymers with branching points, electron-accepting groups, long methylene sequences, and all groups capable of forming five- or six-membered rings. Thermostability is enhanced by aromatic rings, ladder structures, fluorine as a substituent, and low hydrogen content.

4. Plastics Manufacture

4.1. Homogenization and Compounding

Polymerization reactors do not deliver polymers that can be used directly as raw materials for plastics. Polymer melts must be filtered; melts, powders, beads, pellets, and granulates must be degassed; and all particulates must be dried or conditioned to environmental surroundings. Beads from suspension polymerization are washed and polymer solutions concentrated.

Batchwise polymerizations often lead to slightly different products, which are mixed (blended) to guarantee customers polymer grades according to specifications (microhomogenization). Granulates and pellets are sometimes similarly blended by macrohomogenization.

Compounding is the mixing of polymers and additives. This process can be performed either by adding single additives one at a time, by using additive systems, or by employing master batches. Additive systems are carefully adjusted mixtures of additives that are formulated to avoid mutually synergistic or antagonistic effects. Master batches are concentrates of additives in polymers; they facilitate the dosage of small amounts of additives.

The properties of compounds depend very much on the compounding process. Only heterogeneous compounds result when poly(vinyl chloride) is mixed with additives in regular mixers; these compounds cannot be processed directly to end-use products. High-performance mixers deliver free-flowing powders; these "dry blends" can be extruded and injection molded. Compounding is often carried out by specialized companies (compounders).

4.2. Additives [5], [73] (→ Plastics, Additives)

4.2.1. Overview

Polymers are rarely used directly as materials. They do not fulfill per se all technological requirements and become commercially useful only after they have been mixed with certain additives. These additives average ca. 23 % of the total weight of plastics (Table 18) but may range for individual plastics from 0 % (packaging films for food) to 90 % (barium ferrite-filled ethylene – vinyl acetate copolymers for magnetizable sealing strips). Their economic value approximates that of plastics because some additives command prices that are a hundred times those of the plastics themselves.

Table 18. Annual U.S. consumption of polymer additives for plastics, 1980 (plastics production: 16 076 000 t/a)

Additive	Consumption in t/a
Process additives	
Processing stabilizers	
Heat stabilizers (PVC)	43 000
Antioxidants	18 000
Processing aids	
Lubricants, slip agents, etc.	50 000
Polymeric processing aids	<1 000
Mold-release agents	<1 000
Nucleating agents	<1 000
Radical initiators for thermosets	15 000
Functional additives	
Stabilizing additives	
Antioxidants	see above
Metal deactivators	<1 000
Light stabilizers	2 400
Flame retardants	220 000
Biostabilizers	<1 000
Modifiers	
Colorants	150 000
Fillers and reinforcing agents	
Mineral-based	1730 000
Glass	462 000
Natural organic	133 000
Synthetic organic	2 000
Plasticizers	1 000 000
Blowing agents (without gases)	7 000
Impact modifiers	<5 000
Antistatic agents	2 000
Total	3 844 400

Polymer additives are to be distinguished from *polymer auxiliaries*; the former are added to polymers after the polymerization process, whereas the latter are used for the manufacture of polymers (e.g., polymerization catalysts, emulsifiers, initiators). The free-radical initiators used for the hardening of unsaturated polyesters are sometimes considered additives (added to the solution of unsaturated polyester molecules in monomers such as styrene) and sometimes auxiliaries (promoting the thermosetting reaction).

Additives are usually subdivided according to their application into process additives and functional additives. Process additives aid the processing of plastics by either stabilizing the chemical composition of polymers (processing stabilizers) or facilitating the processing itself (processing aids). Functional additives stabilize the chemical composition against attacks by environmental agents (stabilizing additives) or improve certain end-use properties (modifiers). Additives may also be classified according to their primary mode of action (chemical or physical). Some additives act in more than one way: a filler or colorant may also be a nucleating agent for crystallization, a pigment may enhance discoloration, etc.

4.2.2. Chemofunctional Additives

Polymers can be attacked by oxygen and ozone during processing and use. The attack generates radicals that cause chain reactions to produce even more radicals. Ultimately, changed chemical compositions, degradation, or cross-linking result. Oxidation is reduced if the accessibility of the oxidizable groups is limited or if radical formation is prevented. Oxygen diffusion into the polymer is slowed by certain coatings that act as mechanical barriers or by additives that diffuse into surface layers and are preferentially oxidized there.

Antioxidants (→ Antioxidants) prevent radical formation, at least during processing and for the targeted lifetime of the plastic. They are subdivided into deinitiators and chain terminators.

Deinitiators prevent the formation of radicals (therefore: preventive antioxidants) and are always used in combination with chain terminators (therefore also called secondary antioxidants). They are further subdivided into peroxide deactivators, metal deactivators, and UV absorbers. Peroxide deactivators (tertiary amines, tertiary phosphines, sulfides) convert hydroperoxides into harmless compounds before they can form radicals. Metal deactivators are chelating agents that form inactive complexes with catalytically active metal species (mainly from Ziegler – Natta polymerizations).

Chain Terminators, such as hindered phenols, amines, and anellated hydrocarbons, react with already formed radicals and terminate the kinetic chain (chain-breaking or primary antioxidants). A combination of deinitiators and chain terminators often leads to synergistic effects. Antagonistic effects are also known (e.g., with carbon black as filler).

Light-induced degradation reactions can be prevented by the reduction of light absorption or by the addition of *UV absorbers* and quenchers. Less light is absorbed by the plastic if the surfaces are reflective or if certain pigments are added (e.g., carbon black). Ultraviolet absorbers either convert the incident light into harmless infrared radiation or are transformed into other chemical compounds. Quenchers deactivate excited states and themselves become excited.

Heat Stabilizers prevent chemical transformations of plastics at higher temperature; their main application is for the stabilization of poly (vinyl chloride) against HCl elimination during processing.

Flame Retardants either prevent oxygen access to burning plastics by formation of nonburning gases or by "poisoning" radicals generated by the burning. Some plastics are selfextinguishing because either CO_2 (polycarbonates) or water vapor and a protecting carbon layer are formed (vulcanized fiber: a $ZnCl_2$-treated cellulose) during burning. Chlorine and bromine compounds generate radicals during burning; these radicals combine with radicals from the degradation of plastics and stop the kinetic chain. Phosphorus compounds are oxidized during the burning to nonvolatile phosphor oxides, which either form a protective layer or are converted by water into phosphorus acids that catalyze the elimination of water.

The flammability of plastics is often characterized by the limiting oxygen index (LOI). The LOI value indicates the limiting value of the volume fraction of oxygen in an oxygen – nitrogen mixture that just allows the polymer to burn after ignition with a flame. Materials with LOI>0.225 are called flame retardant; those with LOI>0.27, self-extinguishing. Low LOI values (high flammabilities) are exhibited by polyoxymethylenes (0.14), polyolefins (0.17 – 0.18), saturated polyesters (0.20), and cellulose (0.20). High LOI values are exhibited by poly (vinyl chloride) (0.32), polybenzimidazole

(0.48), and polytetrafluoroethylene (0.95). However, LOI values are not absolute measures of the flammability or combustibility of plastics because these properties also depend on flame temperatures, heat capacities, heat conductivities, melting temperatures, and melt viscosities. The hazard of burning plastics is also determined by smoke formation and the toxicity of the evolving gases.

4.2.3. Processing Aids

Processing aids facilitate the processing of plastics by enhancing either transport rates to the processing machines, flow behavior in these machines, achievement of final properties during processing, or removal of shaped articles from the machines or from each other.

Easy-flow grades of powdered polystyrenes, for example, often contain 3 – 4 % mineral oil, which forms a low-viscosity film on the surface of the particles and thus reduces friction in polar polymers; amphiphilic compounds such as metal stearates or fatty acid amides are used for this purpose. Such *external lubricants* also reduce the friction between polymer particles and the walls of the processing machine and the friction of polymer melts at such walls; they also prevent the cleavage of particles to smaller flow units. External lubricants are always incompatible with polymers and are thus found predominantly at polymer surfaces. They are related to *release agents*, which facilitate the separation of shaped articles from the tools (molds), and *slip agents*, which prevent the sticking together of shaped articles. Slip agents are thus sometimes also called lubricants.

Internal lubricants improve the flow behavior and homogeneity of polymer melts; they also reduce the Barus effect (see Section 7.3.2) and the melt fracture. Internal lubricants probably act by desegregating larger units (aggregates), which were probably formed during polymerization and are still present shortly after the melting of the polymer to a macroscopically homogeneous material. Typical internal lubricants are amphipolar compounds, e.g., modified esters of long- chain fatty acids.

Nucleating agents promote the crystallization of crystallizable polymers by generating many nuclei for crystallites. They prevent the formation of larger spherulites and thus improve the mechanical properties of plastics.

4.2.4. Extending and Reinforcing Fillers

Fillers are solid inorganic or organic materials. Some fillers are added mainly to improve the economics of expensive polymers; they are *extenders*. Extenders are usually particulate materials of corpuscular nature, such as chalk and glass spheres (aspect ratio ca. 1). Other fillers are *reinforcing agents* (“active fillers”); they improve certain mechanical properties. Reinforcing agents possess aspect ratios higher than 1; they may be short fibers, platelets (e.g., kaolin, talc, mica) (→ Reinforced Plastics), or long fibers (continuous filaments). Active fillers are sometimes subdivided into property enhancers (aspect ratio < 100) and true reinforcing fillers (aspect ratio > 100). No sharp dividing line exists between fillers and reinforcing agents, nor can the term “reinforcement” be unambiguously defined (e.g., it may denote an increase in breaking or impact strength or a decrease of brittleness).

A variety of fillers are used for plastics (Table 19).

Glass-fiber-reinforced polymers often carry the abbreviation GRP (or FRP); those reinforced by synthetic organic fibers, CRP. Syntactic plastics are polymers reinforced with hollow glass spheres. The amounts of fillers added vary widely: in general, industry standards are about 30 wt % for thermoplastics and 60 wt % for thermosets.

Fillers act very differently in polymers. Some fillers form chemical bonds with polymers; an example is carbon black, which acts as a chemical cross-linker in elastomers. Other fillers can adsorb polymers on their surfaces: that is, physical bonds are introduced between fillers and polymers. On impact, adsorbed chain segments may take up energy and slip from the surface, which increases impact strength. Still other fillers act as nucleating agents in crystallizable polymers. Fillers furthermore constitute impenetrable walls to polymer coils. They restrict the number of conformational positions of chain segments near the filler surface; chains become less flexible, and tensile strengths and moduli of elasticity increase.

Table 19. Fillers for thermoplastics (T), thermosets (D), and elastomers (E). For definition of other acronyms see Tables 1–4

Filler	Application in	Concentration in %	Improved property
Inorganic fillers			
Chalk	PE, PVC, PPS, PB, UP	< 33 in PVC	price, gloss
Potassium titanate	PA	40	dimensional stability
Heavy spar	PVC, PUR	< 25	density
Talc	PUR, UP, PVC, EP, PE, PS, PP		white pigment, impact strength, plasticizer uptake
Mica	PUR, UP	< 25	dimensional stability, stiffness, hardness
Kaolin	UP, vinyls	< 60	demolding
Glass spheres	T, D	< 40	modulus of elasticity, shrinkage, compressive strength, surface properties
Glass fibers	T, D	< 40	fracture strength, impact strength
Fumed silica	T, D	< 3	tear strength, viscosity (increase)
Quartz	PE, PMMA, EP	< 45	heat stability, fracture
Sand	EP, UP, PF	< 60	shrinkage (decrease)
Al, Zn, Cu, Ni, etc.	PA, POM, PP	< 100	conductivity (heat and electricity)
MgO	UP	< 70	stiffness, hardness
ZnO	PP, PUR, UP, EP	< 70	UV stability, heat conductivity
Organic fillers			
Carbon black	PVC, HDPE, PUR, PI, PE, E	< 60	UV stability, pigmentation, cross-linking
Graphite	EP, MF, PB, PI, PPS, UP, PMMA, PTFE	< 50	stiffness, creep
Wood flour	PF, MF, UF, UP	< 5	shrinkage (decrease), impact strength
Starch	PVAL, PE	< 7	biological degradation

4.2.5. **Plasticizers** (→ Plasticizers)

Plasticizers are added to polymers to improve their flexibility, processibility, or foamability. About 500 different types of plasticizers are marketed. They are generally low molar mass liquids; polymer plasticizers are used in much smaller amounts. Of all plasticizers for thermoplastics, 80 – 85 % are used for poly(vinyl chloride); the most important plasticizer is di-2-ethylhexyl phthalate (“dioctyl phthalate,” DOP). The main plasticizer for elastomers is mineral oil; tires contain up to 40 %. Polymer plasticizers are mainly aliphatic polyesters and polyethers. The former are prepared by polycondensation; they thus possess fairly broad molar mass distributions and also contain monomeric and oligomeric molecules. Since their number-average molar mass is low (ca. 4000 g/mol), they are called oligomer plasticizers. Plasticization can also be achieved by copolymerization of the parent monomer with certain other monomers; this effect is called internal plasticization, in analogy to external plasticization by added high and low molar mass plasticizers.

External plasticizers are subdivided into primary and secondary ones. Primary plasticizers interact directly with chains by way of solvation. Secondary plasticizers are merely extenders; they can be used only in combination with a primary plasticizer. A certain plasticizer may thus be a primary or a secondary one, depending on the chemical constitution of the polymer. Mineral oils are, for example, primary plasticizers for polydienes but extenders for poly(vinyl chloride).

4.2.6. **Colorants**

Colorants are subdivided into dyes (soluble in polymer matrix) and pigments (insoluble). Textile fibers are dyed mainly with dyes. Pigments are preferred for plastics because they have a higher lightfastness and are more stable against migration than dyes. Colorants for plastics are dominated by titanium dioxide (60 – 65 %) and carbon black (20 %); only 2 % are dyes.

Pigment particles generally possess diameters of 0.3 – 0.8 μm, which allows the pigmentation of films and fibers of > 20-μm thickness. Very thin films and fibers are colored exclusively by organic pigments because these can be ground to much smaller diameters than inorganic ones. The hiding power of pigments increases with increasing difference between refractive indices of pigment and polymer.

Pigments need not have a special affinity for polymers. They must be wettable by the polymer melt, however, which can be achieved by treating them with surfactants. The aggregation of pigments is mainly the result of air inclusions; it can be removed by the application of vacuum. Pigments can be metered into plastics via master batches (in plastics), color concentrates (in plasticizers), or electric charging of the surface of polymer particles in granulate mixers. Up to 1 wt % of pigment can be mixed in by the last method.

4.2.7. Blowing Agents

Foamed plastics (plastic foams, cellular plastics, expanded plastics) are blends of polymers with gases (→ Foamed Plastics). They may be rigid (glass transition or melting temperature higher than use temperature) or flexible; their cell structure can be open or closed. The gases may be air, nitrogen, carbon dioxide, fluorinated hydrocarbons, etc.

Plastic foams can be produced by mechanical means (whipping, stirring), physical methods (shock volatilization of liquids, washing-out of solids), or chemical foaming either by internal foaming during the polymerization or by external foaming with chemical blowing agents. Chemical blowing agents are chemical compounds that decompose at elevated temperature with release of gases. The most widely used agent for natural rubber is *N,N′*-azobisisobutyronitrile $(CH_3)_2C(CN)-N{=}N-C(CN)(CH_3)_2$ (AIBN); for plasticized PVC, *N,N′*-dinitroso dimethyl terephthalamide $CH_3-N(NO)-CO-(p\text{-}C_6H_4)-CO-N(NO)-CH_3$ (NTA); and for other plastics, 1,1′-azobisformamide $H_2N-CO-N{=}N-CO-NH_2$ (ABFA). Blowing agents are used in amounts of ca. 0.1 % to eliminate sinks in injection molding; 0.2 – 0.8 % for injection-molded structural foams; 0.3 % for extended profiles; 1 – 15 % for vinyl plastisol foaming; and 5 – 15 % for compression-molded foam products.

4.3. Processing

Many different types of processes exist to convert monomers, prepolymers, or polymers into plastics. In general, four procedures can be distinguished for processing raw materials into shaped plastics:

1. From monomers to polymers by direct polymerization with simultaneous shaping
2. From monomers by oligomerization to prepolymers, followed by simultaneous polymerization and shaping
3. From monomers by polymerization to polymers, followed by separate shaping
4. From monomers by polymerization to polymers, shaping to semifinished product, and finally to the end product

In all four cases, end products must sometimes be aftertreated (degated, polished, etc.).

Procedure 1 has only one process step and should be the most economical. It is widely used for wire coatings. However, technological problems are often encountered for shaped articles because the process involves the conversion of a low-viscosity liquid into a high-viscosity body. Since very high polymerization rates are required for this process to achieve high cycle times (phase sequences) in molding (i.e., number of articles produced per unit time), very few monomers, types of polymerization, and shaping methods are suitable. The method is utilized industrially in the RIM process, mainly for the polyaddition of diisocyanates with polyols. The anionic polymerization of lactams and the Diels – Alder polymerization of dicyclopentadienes and related compounds are also (in principle) suitable for RIM.

Procedure 2 is typical for thermosets. Oligomerizations are conducted to conversions shortly before the gel point. Additives are added, and the final processing step consists of a simultaneous cross-linking polymerization and shaping. Typical processing methods include molding, compression molding, cavity compression molding (hot pressing), injection – compression molding, injection molding, and extrusion.

Procedure 3 is generally chosen for thermoplastics. Polymers from the polymerization process are isolated before shaping and stored (e.g., as granulate) for a shorter or longer period of time. The stored polymers must be dried before further processing; otherwise, steam produced at higher processing temperatures may lead to voids and cavities in shaped articles. After compounding, the plastic raw material must be weighed out accurately for each cycle in discontinuous processing procedures. The filling factor (= raw material density/bulk density) must be known.

The choice of a processing technique is influenced technically by the rheological properties of the material and the form or shape of the desired article. The cost of processing machines and the cycle time are economically important. Commodity articles are produced by casting, centrifugal casting, hot pressing, injection – compression molding, coating, spraying, roll milling, extrusion, injection molding, cold forming, press forming, stretch forming, blowing, extrusion blowing, sintering, fluidized-bed sintering, flame spraying, or hot blast sprinkling, and specialty articles by molding.

Procedure 4 is the method of choice for difficult-to-manufacture articles. Procedures such as welding, stamping, cutting, forging, sawing, boring, turning, milling (in the metalworking sense), sintering, and baking are employed for both thermoplastics and thermosets. The surfaces of plastics are sometimes treated further for technical (surface hardness, friction) or aesthetic reasons (gloss, color) by polishing, painting, metallizing, coating, etc.

5. Supermolecular Structures
(→ Plastics, Properties and Testing)

Polymer properties are influenced not only by the chemical structure (constitution, molar mass, configuration, microconformation) but also by the physical structure of polymers. These structures may range from totally irregular arrangements of chain segments over shorter or longer parallelizations of chains, to voids and other defects in otherwise highly organized assemblies of polymer molecules. Two possible ideal structures exist in the solid state: perfect crystals and totally amorphous polymers. Polymer molecules are perfectly ordered in ideal crystals. They convert at the thermodynamic melting temperature into melts, which ideally are totally disordered. Amorphous polymers can be viewed as frozen-in polymer melts. They are polymer glasses that convert to melts at the glass transition temperature.

5.1. Noncrystalline States

5.1.1. Structure

Isolated polymer coils possess approximately a Gaussian distribution of chain segments; their segment density decreases with increasing chain length. However, the macroscopic densities of polymer melts do not change with chain lengths if end group effects on small molar mass molecules are neglected. Coils must therefore overlap considerably in polymer melts. At the glass transition temperature, cooperative segmental movements freeze in, and the physical structure of the melt is conserved. Small-angle neutron scattering studies have shown that the radii of gyration of amorphous polymers are indeed essentially identical for their melts, glasses, and solutions in theta solvents.

The absence of long-range order in melts and amorphous polymers does not exclude the presence of short-range order in these states. Because of the persistence of polymer chains, a parallelization of short segments seems probable, as is found, for example, for alkanes according to X-ray investigation. This local order does not exceed 1 nm in each direction.

The packing of chain segments cannot be perfect. Amorphous polymers thus possess “free volumes”, which are regions of approximately atomic diameters. The volume fraction of this free volume is ca. 2.5 % at the glass transition temperature and is independent of polymer constitution. Polymer segments in melts can move more freely than in the glassy state; the densities of melts are thus higher than the densities of glasses at the same temperature.

5.1.2. Orientation

Polymer segments, polymer molecules, and crystalline domains may be oriented along the machine direction by drawing or other mechanical processes. The orientation of chain segments need not necessarily lead to crystallization, however. An example is injection-molded polystyrene, which shows optical birefringence due to the orientation of segments but no X-ray crystallinity.

The degree of orientation of segments or crystallites can be measured by wide-angle X-ray or small-angle light scattering, infrared dichroism, optical birefringence, polarized fluorescence, and ultrasound velocity. The orientation is usually characterized for each of the three directions *a*, *b*, and *c* by a *Hermans orientation factor* f_i, where β is the angle between the draw direction and the principal axis of the segments:

$$f_i = (1/2)(3\langle\cos^2\beta\rangle - 1) \qquad (58)$$

The orientation factor becomes 1 for a complete orientation of that axis in the draw direction ($\beta = 0°$), $-1/2$ for a complete orientation perpendicular to the draw direction ($\beta = 90°$), and 0 for a random orientation.

Since methods to determine orientation factors are often expensive, time consuming, or difficult to perform, the easy-to-calculate *draw ratio* (length after drawing/length before drawing) is often used to characterize orientation. The draw ratio is, however, not a good measure of the degree of orientation because it depends on the history of the specimen. Drawing may also lead to viscous flow of the polymer without any orientation of segments and crystallites.

5.2. Polymer Crystals [74]

5.2.1. Introduction

Spheres and other geometrically simple entities can be arranged in crystal lattices irrespective of whether they are atoms, small molecules, large molecules such as enzyme, or latex particles. The centers of gravity of these entities occupy lattice sites that are regularly spaced in three dimensions. Lattices are called *superlattices* if the distances between lattice points significantly exceed atomic dimensions. The existence of three-dimensional order on the atomic level is called crystallinity.

Chain molecules can also be arranged in crystal lattices. The whole chain may be completely parallel to other chains as in the case of truly extended chain crystals; the microconformation of the chain can be all *trans* or helical (Fig. 16), and the chains may have a directional sense as in polyamide 6 or an inversion center as in polyamide 66 (Fig. 17). In other cases, only sections of the chains may be parallel to each other, either sections of a single chain as in folded chain crystals or those of neighboring chains as in

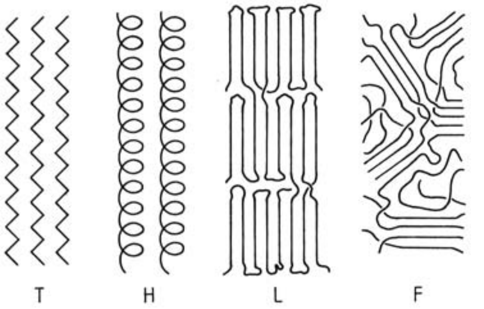


Figure 16. Schematic representation of crystalline polymers as extended chain crystals with chains in all-*trans* (T) or helical conformation (H), (L) lamellae of chains interconnected by tie molecules, and (F) fringed micelles. No bond angles are shown for H, L, and F

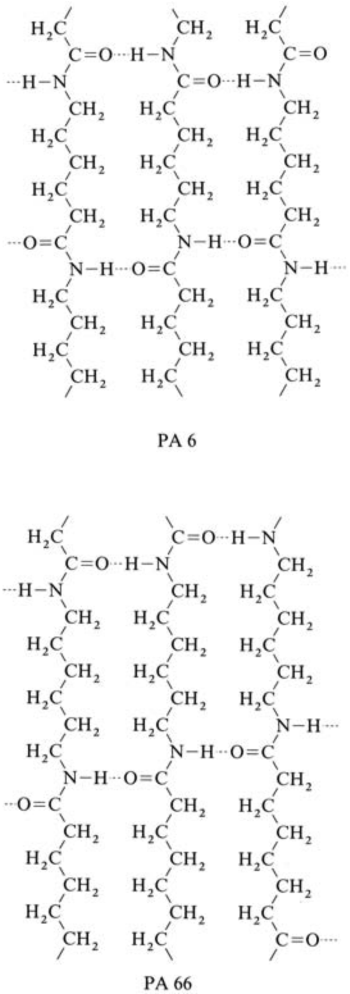


Figure 17. Pleated-sheet structures of polyamides 6 (anticlinal) and 66 (isoclinal)

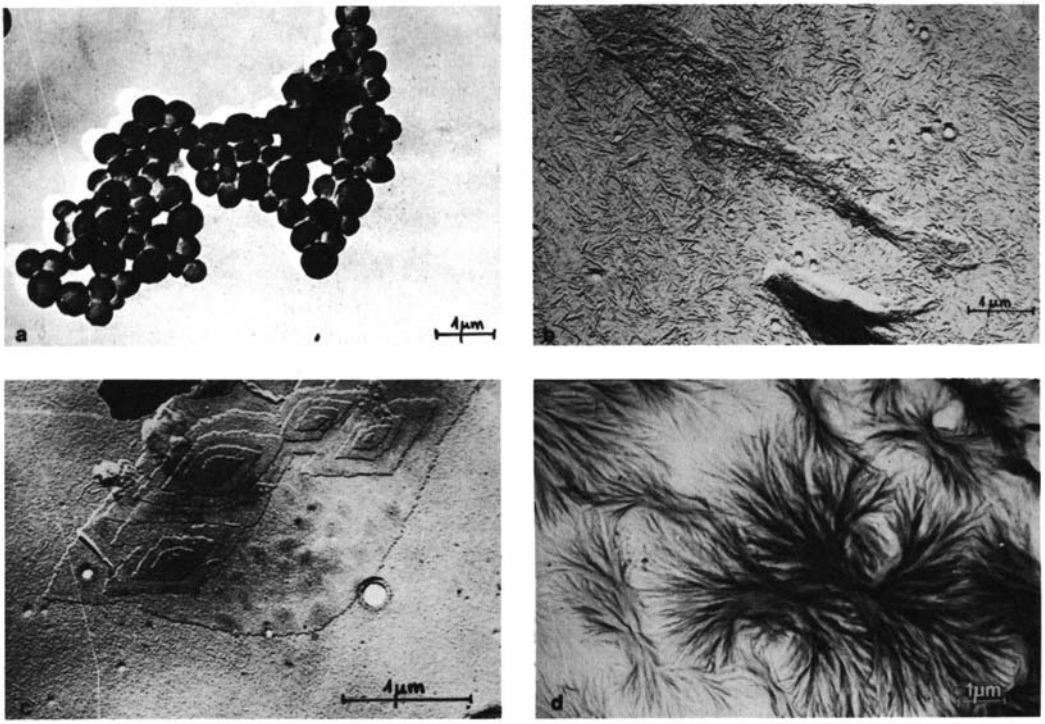


Figure 18. Electron micrographs of different morphologies of a polyamide 6
a) From a 260 °C solution in glycerol quenched into 20 °C glycerol; b) Same solution fast cooled (40 K/min); c) Same solution slowly cooled (1 – 2 K/min); d) Slow evaporation of formic acid solution at room temperature [75]

fringed micelles. These ordered segments form crystalline regions in otherwise less ordered (though not necessarily completely disordered) polymers.

Crystalline regions may be assembled into greater entities, which themselves may be more or less ordered. The types and degrees of order – disorder depend on external conditions such as temperature, pressure, cooling and heating rates, and presence of solvents. A variety of morphologies may thus exist for any crystallizable polymer [73], for example, spherical, platelet-like, fibrillar, and sheaflike structures of a polyamide 6 (Fig. 18).

5.2.2. Crystal Structures

The unit cell describes the smallest, regularly repeating structure of a parallelepiped that generates a crystal by parallel displacements in three directions. The parallelepipeds are characterized by three lattice constants (distances between lattice points in three directions) and three lattice angles (Table 20).

Lattice constants reflect the microconformations of chains in crystal lattices. The *c*-direction is normally assigned to the chain direction; a value of $c = 0.254$ nm thus gives the distance between repeating units $-CH_2-CH_2-$ in all-*trans* conformation (bond distance 0.154 nm, bond angle 112°). The *c*-values in carbon chains that are nonmultiples of 0.254 indicate the presence of non-all-*trans* conformations (e.g., helical structures in it-polypropylene and it-polybutylene-1). The *a* and *b* values reflect physical bonds (such as van der Waals or hydrogen bonds) that are longer than the chemical bonds in the *c*-direction. The anisotropy of bond lengths in the three spatial directions prevents the existence of cubic lattices for chain molecules. The other six lattice types are however found [hexagonal, tetragonal, trigonal, (ortho)rhombic, monoclinic, triclinic].

Most polymers form polymorphs (i.e., polymers of the same constitution and configuration

Table 20. Crystal structure of some polymers

Polymer			N_u	Lattice constants			Angles of unit cell			Helix type	Crystal system
				a nm	b nm	c nm	α °	β °	γ °		
PE		I [a]	2	0.742	0.495	0.254	90	90	90	2_1	R
		II [a]	2	0.809	0.479	0.253	90	90	107.9	2_1	M
PP,	st	8	1.450	0.560	0.74	90	90	90	2_1	R	
	it	α [a]	12	0.665	2.09	0.495	90	99.6	90	3_1	M
	it	β [a]	3	0.638	0.638	0.633	90	90	120	3_1	VI
	it	γ [a]	12	0.647	2.140	6.50	89	100	99	3_1	T
PB,	it	I [a]	18	1.769	1.769	0.650	90	90	90	3_1	VI
		II [a]	44	1.485	1.485	2.060	90	90	90	11_3	IV
		III [a]	8	1.238	0.892	0.745	90	90	90	4_1	R

[a] N_u=Number of monomeric units per unit cell.

[b] Crystal modification.

[c] R=(ortho)rhombic; M=monoclinic; VI=hexagonal; T=triclinic; IV=tetragonal.

can possess various energetically different crystal modifications). *Polymorphism* may be caused by different microconformations of polymer chains (e.g., polybutylene-1) or by different packing of chains with identical chain conformations (e.g., it-polypropylene). Such differences can be generated by small changes in processing conditions (e.g., different crystallization temperatures) or by stretching.

Copolymers can furthermore show *isomorphism* if different monomeric units can replace each other without change of lattice structure. Isomorphism of chains is also possible if the two corresponding homopolymers have analogous crystal modifications, similar lattice constants, and the same helix types. An example is a mixture of the γ-modification of it-polypropylene and the modification I of it-polybutylene-1 (Table 20). This phenomenon is sometimes also called allomerism. One company calls its crystalline copolymers from two or more olefinic monomers *polyallomers* because the monomeric units are isomorphic.

5.2.3. Crystallinity

Perfect crystal lattices should give sharp X-ray reflections and sharp melting points. Polymers do not exhibit these features, even if they show a crystallike appearance in electron micrographs. In addition, X-ray patterns of polymers frequently exhibit continuous, diffuse scattering. These findings can be interpreted by either a one-phase model (voids in crystals) or a two-phase model (coexistence of completely crystalline and completely amorphous regions). Crystallinity is defined as the presence of three-dimensional order on the level of atomic dimensions.

In reality, segments are ordered to various degrees. Since most experimental methods are sensitive to different types and degrees of order, various "degrees of crystallinities" are found depending on the experiment. The degree of crystallinity is the fractional amount of crystallinity. Stretched poly(ethylene terephthalate) has, for example, a degree of crystallinity of 59 % by IR spectroscopy, 20 % by density determination, and 2 % by X-ray diffraction.

5.2.4. Morphology

Earlier experimental findings were interpreted in terms of the two-phase model of partially crystalline polymers: the coexistence of crystalline reflexes and amorphous halos in X-ray diagrams, the independence of X-ray short periodicities on molar masses, the disappearance of X-ray long periodicities with increasing molar masses, lower macroscopic densities than predicted by X-ray densities of unit cells, broad melting ranges, optical birefringence of oriented polymers, and heterogeneity of partially crystalline polymers against chemical reactions.

In 1957, however, three different groups found that rhombic platelets are obtained if very dilute solutions of polyethylene are cooled. Similar platelets of 5 – 20-nm thickness are now known from many other crystallizable polymers (e.g., see Fig. 18). Electron diffraction showed sharp reflections typical of single crystals and chain directions perpendicular to the surface of the platelets. Since the contour lengths of the chains are greater than the thicknesses of the platelets, chains must be folded back as shown in Fig. 16 – L.

Crystallization from polyethylene melts similarly shows stacked single crystals. These lamellae are 75 – 80 % X-ray crystalline. After oxidation of the surface, a 100 % crystalline material remains. The folds or the interface between lamellae must thus be "amorphous." Various models have been suggested for the surface layers: loose folds with adjacent reentry of the chains, a switchboard-like structure, adsorbed chains not involved in chain folding, loose or entangled cilia (tangling chain ends), and crystal bridges composed of tie molecules (Fig. 19). Electron microscopy has shown that crystal bridges exist in crystallized mixtures of high and low molar mass polyethylenes. Such interlamellar connections are responsible for some remarkable properties of partially crystalline polymers (see below). Highly crystalline polymers result if tie molecules and surface layers are removed (e.g., by grinding); these fairly low molar mass materials are called microcrystalline polymers.

Crystallization of melts sometimes delivers spherical, polycrystalline entities (Fig. 20). These spherulites exhibit radial symmetry. They consist of lamellae with tangential chain axes (Fig. 21 A); radial chain axes seem to be unknown (Fig. 21 B). The formation of spherulites can be controlled by the crystallization temperature, the cooling rate, and the addition of nucleating agents.

Spherulites lead to opaque plastics if their diameters are greater than one-half the wavelength of incident light and their densities and refractive indices are different for crystalline and noncrystalline regions. The numbers and sizes of such spherulites are important for the fracture behavior of polymers.

Spherulites develop in a viscous environment if crystallization nuclei are present and if equal crystallization rates prevail in all three directions.

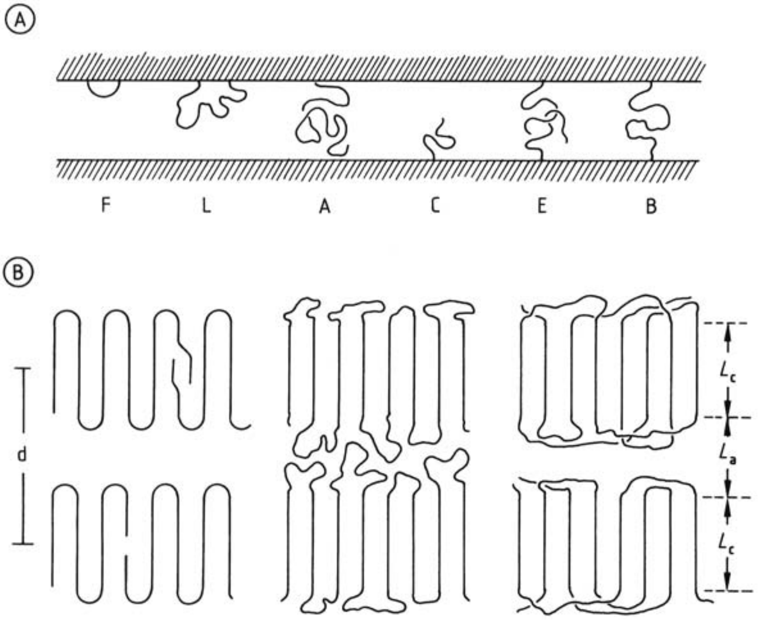


Figure 19. Models for the fine structure of lamellae of single crystals
A) Chains between two adjacent lamellae: F = sharp folds, L = loose loops, A = adsorbed chain, C = cilium, E = entangled cilium, B = crystal bridge or tie segment; B) Structures of lamellae: R=Regular lamellae with sharp folds, adjacent chain reentry, void from chain ends (below) and dislocation (above); L = lamellae with loose loops and adjacent reentry; S = switchboard model; d = crystallographic long period; L_c=thickness of lamella; L_a = thickness of "amorphous" surface layer ($d = L_c + L_a$)
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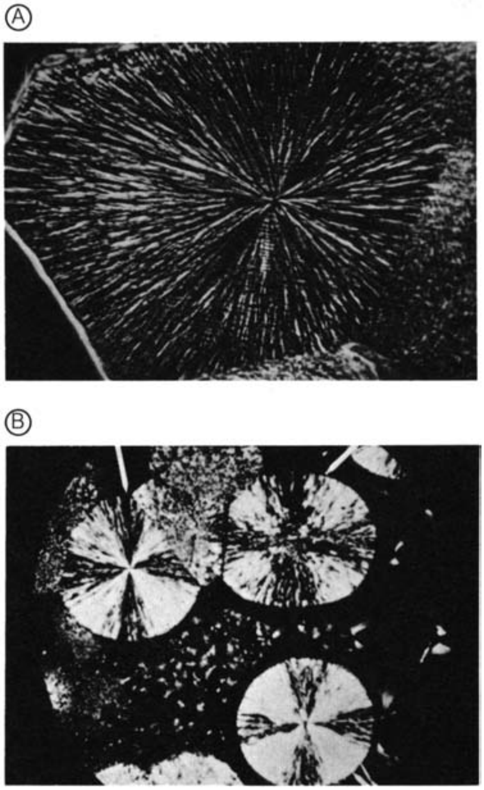


Figure 20. Spherulites of it-polypropylene under the phase contrast microscope (A) and the polarization microscope (B) 76

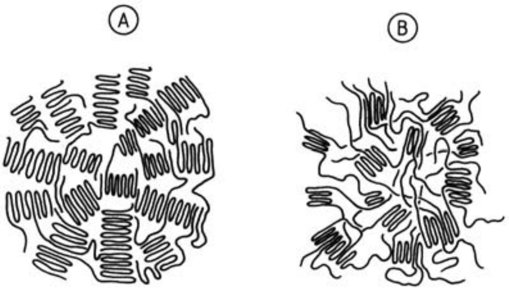


Figure 21. Schematic representation of spherulite structures A) Tangential chain axes; B) Radial chain axes (hypothetical) Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

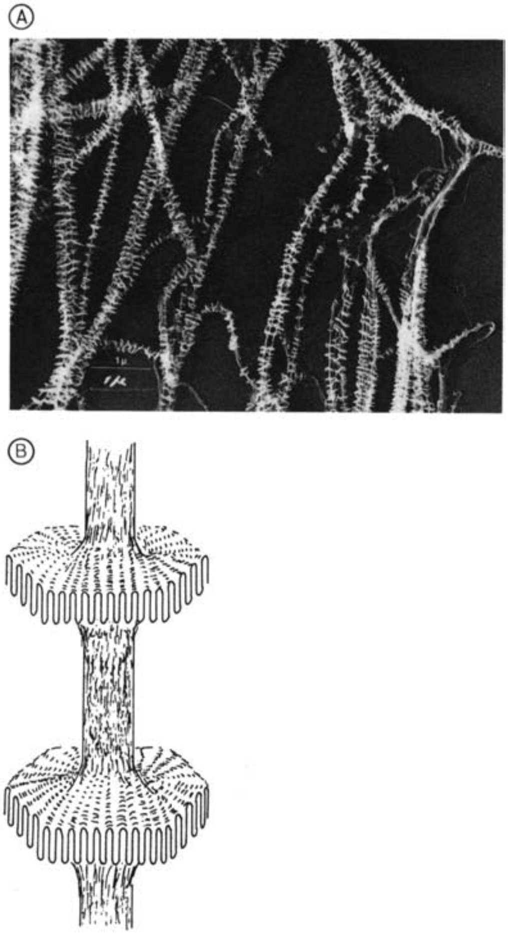


Figure 22. Shish kebab structures of linear polyethylene crystallized from rapidly stirred 5 % solutions in toluene [71] A) Electron micrograph; B) Schematic draw\ing of chain arrangements

Different crystallization rates exist in strongly stirred dilute solutions. Polymer chains then try to orient themselves along the flow gradients and crystallize in an extended (nonfolded) conformation. The resulting fibrils are organized in bundles with chains parallel to the fibril axes. These bundles act as nuclei – substrate for the epitaxial growth of the remaining chains. Since the shear rate is strongly reduced between bundles, crystallization leads to lamellae with folded chains whose axes are parallel to the fibril axes (Fig. 22). The resulting extended-chain structures are responsible for the remarkable properties of some ultraoriented polymers.

5.3. Mesophases

5.3.1. Introduction

Mesomorphic chemical compounds exhibit microscopic structures (mesophases) that are intermediate between crystals with long-range three-dimensional order and liquids without long-range order (Greek: *mesos* = middle, *morphe* = shape, form). Three types of mesophases are distinguished: liquid crystals, plastic crystals, and condis crystals. Since liquid crystals were discovered first and are furthermore the most common of the three classes, the term mesophase is often used as a synonym for liquid crystal.

Liquid Crystals (LCs) (→ Liquid Crystals) possess a certain ordered structure like crystals, but they flow like liquids. *Thermotropic liquid crystals* exhibit this phenomenon in the pure state above a certain solid – mesophase transition temperature, where the solid may be a crystal or a glass. *Lyotropic liquid crystals* exhibit mesophase behavior in certain solvents above critical concentrations. Liquid crystalline behavior is present in both cases if the molecules contain "mesogens", that are short rodlike sections that comprise the whole molecule as in low molar mass LCs, or segments thereof as in polymer liquid crystals (LCPs). Mesogens are anisotropic; they are oriented with respect to their mesogen axes but not with respect to their positions.

Plastic Crystals exhibit order of positions but disorder of orientations of molecules. They are found for certain spherical low molar mass molecules packed in cubic lattices (i.e., they are isotropic). The absence of strong attractive forces between molecules and the presence of slip planes lead to easy deformabilities of plastic crystals, sometimes even under their own weight. No polymers are known that form plastic crystals.

Condis Crystals are *con*formationally *dis*ordered crystals containing several conformational isomers in more or less ideal crystalline positions with respect to position and orientation of segments (conformational isomorphs). An example is the hexagonal high-pressure phase of polyethylene extended- chain crystals. It is often difficult to determine whether polymer crystals are normal or condis crystals.

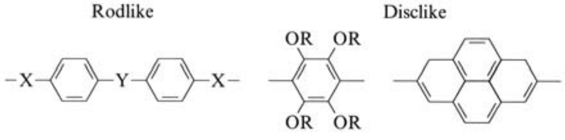
On cooling, thermotropic liquid crystals either crystallize or solidify to "mesomorphic glasses" with retention of their liquid crystal structures. These glasses do not carry special names, but since "liquid crystalline glass" and similar names are oxymorons, the terms "LC glass," "PC glass," and "CD glass" have been suggested for the three classes of mesomorphic materials. The LCPs are used mainly as LC glasses not as liquid crystals per se, except in processing.

Condensed matter can thus exist in several of the five possible classes of pure phases: completely ordered crystal oC, mesomorphic glass mG, amorphous glass aG, ordered mesophase oM, and isotropic melt (liquid) iL. Seven types of biphasic materials exist: oC + mG, oC + aG, oC + oM, oC + iL, mG + aG, mG + iL, oM + iL, and three types of triphasic materials: oC+mG+aG, oC + mG+iL, oC + oM + iL. Since each class can be subdivided further, many physical structures (and thus properties) are possible for the same polymer.

Mesophasic polymers are characterized by domains of microscopic size (see below). "Microdomains" of similar size are also exhibited by certain block copolymers and, in much smaller sizes, by ionomers.

5.3.2. Types of Liquid Crystals

Liquid crystals and LC glasses are generated by rod- or disclike mesogens, which either comprise the whole molecule (as in low molar mass LCs) or sections of it (LCPs). Examples are



where X = O, OOC, COO, etc.; Y = COO, p-C_6H_4, CH=CH, N=N, etc.; R = CO $(CH_2)_nCH_3$, etc.; and phenylene residues may be replaced by 1,4- cyclohexane rings. The lengths of polymer mesogens are often comparable to those of repeating units; they seem to be identical with respect to persistence lengths.

Rodlike mesogens are also called calamitic (Greek: *calamos* = reed) and disclike ones discotic. Calamitic liquid crystals are further subdivided into smectic, nematic, and cholesteric mesophases. Smectic LCs show fan-shaped structures under the polarization microscope; they feel like soaps (Greek: *smegma* = soap).

Nematic LCs form threadlike schlieren (Greek: *nema* = thread). Cholesteric LCs exhibit beautiful reflective colors, which were first discovered with cholesterol.

The birefringence of LCs originates from the anisotropy of mesogens, which are more or less aligned in microscopic domains with diameters in the micrometer range. These alignments lead to different refractive indices parallel and perpendicular to the direction of polarization of incident light. The domains themselves are arranged randomly. The presence of birefringence however is not proof for the existence of mesogens; it may also result from higher-melting crystallites in partially molten polymers or from crystallites in partially molten polymers or from crystallites in gels or concentrated solutions.

Liquid crystals are turbid because their domains are anisotropic structures whose dimensions are greater than the wavelength of incident light. At a certain "clearing temperature," these domains melt to a transparent (isotropic) liquid.

The soaplike character of *smectic LCs* is due to two-dimensional, layerlike arrangements of mesogens (Fig. 23). At present, twelve different smectic types are known: four with the average direction of the long axes perpendicular to layer planes and seven with tilted axes. Examples are type S-A with mesogens perpendicular to the layer planes; type S-B, the same but with perfect hexagonal packing of mesogens; type S-C, with mesogen axes at an angle to the planes, etc.

Nematic Mesophases (Fig. 23, N) are one-dimensionally ordered. The principal axes of mesogens are more or less parallel to each other; the centers of mass are however distributed at random.

Cholesteric Mesophases (Fig. 23, N – C) are observed only with chiral mesogens. They consist of layers of nematically ordered mesogens. These layers have a sense of rotation relative to each other due to the presence of chirality centers in mesogens. Cholesteric mesophases are thus screwlike nematics.

Discotic Mesophases may exist in many different structures. The disclike mesogens are randomly arranged in nematic-discotic types (Fig. 23, N – D) but stacked like coins in columnar-discotic ones (Fig. 23, C – D).

5.3.3. Mesogens

Mesogens of polymers can be contained in main chains (MC-LCPs) or in side chains (SC-LCPs). Thermotropic MC-LCP glasses are used as engineering plastics; lyotropic MC-LCP glasses, for fibers. Thermotropic SC-LCPs are not used commercially at present but may find use in optical recording devices.

Mesogens usually constitute the whole molecule in low molar mass LC molecules. In macromolecules, this is true only for dissolved helices up to certain molar masses. Such helicogenic macromolecules are rigid rods at small molar masses but become coillike at very high degrees of polymerization (cf. the behavior of short and very long garden hoses). This behavior is demonstrated by the molar mass dependence of their intrinsic viscosities, which are measures of the molecule volume per unit mass (Fig. 24). Rodlike molecules are characterized by their axial ratio (aspect ratio) Λ (length/diameter).

All other polymer chains form either flexible or semiflexible coils in dilute solution or in their isotropic melts (see examples in Fig. 25). Semiflexible (wormlike) chains SF allow rotations around some of their chain bonds. The rodlike character of their segments is however preserved in melts or concentrated solutions if the chain axes remain linear or if the segment linearity can

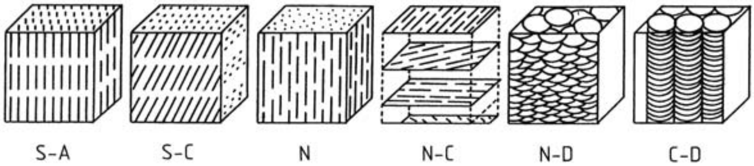


Figure 23. Schematic representation of mesogens in different types of mesophases
S = smectic (types A and C); N = nematic; N–C = nematic cholesteric; C–D = columnar discotic; N–D = nematic discotic
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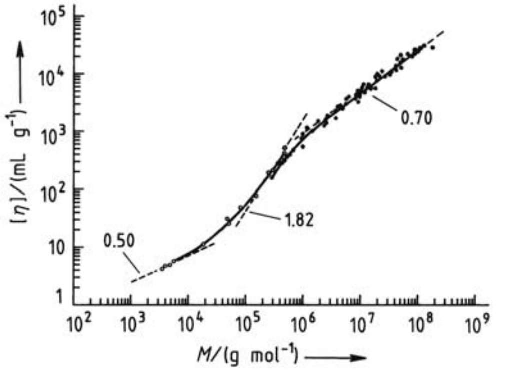

Figure 24. Molar mass dependence of intrinsic viscosities of wormlike chains
(○) Helices of poly(γ-benzyl-L-glutamate) (PLBG) in *N,N*-dimethylformamide at 25 °C; (•) double helices of deoxyribonucleic acids in dilute aqueous NaCl solutions at 20 °C. The two polymers are comparable because the helix diameters are similar (1.5 nm for PLBG, 2.0 nm for DNA). Numbers indicate exponents *a* in Equation (5)
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be restored by a crankshaft motion. Conjugated bond structures are helpful but not necessarily required for mesogens since, for example, 1,4-phenylene rings may be replaced by 1,4-cyclohexylene units.

Linear chain axes are present in poly(*p*-phenylene) (PPP) or poly(*p*-phenylene benzoxazole) (PBO). Crankshaft motions around the chain axes are possible in the conjugated chains of poly(*p*-phenylene vinylene) (PPV), the partially conjugated chains of poly(*p*-hydroxybenzoic acid) (PHB), and even in the nonconjugated poly(*p*-phenylene alkylenes) as long as even numbers of methylene groups are present between phenylene rings as in poly(*p*-phenylene ethylene). Semiflexible molecules are characterized by their persistence lengths *a* or their Kuhn lengths $L_K = 2\,a$.

Rodlike molecules and semiflexible molecules with long persistence lengths form many physical bonds between parallel chains. The total energy of such assemblies is so high that individual intramolecular chemical bonds rather than all of the physical bonds are broken upon heating: these molecules decompose instead of producing thermotropic mesophases. They may however form lyotropic mesophases in suitable solvents. An example is poly(*p*-phenylene bisbenzoxazole).

The "stiffness" of the chain segments can be removed or reduced by several means (Fig. 26).

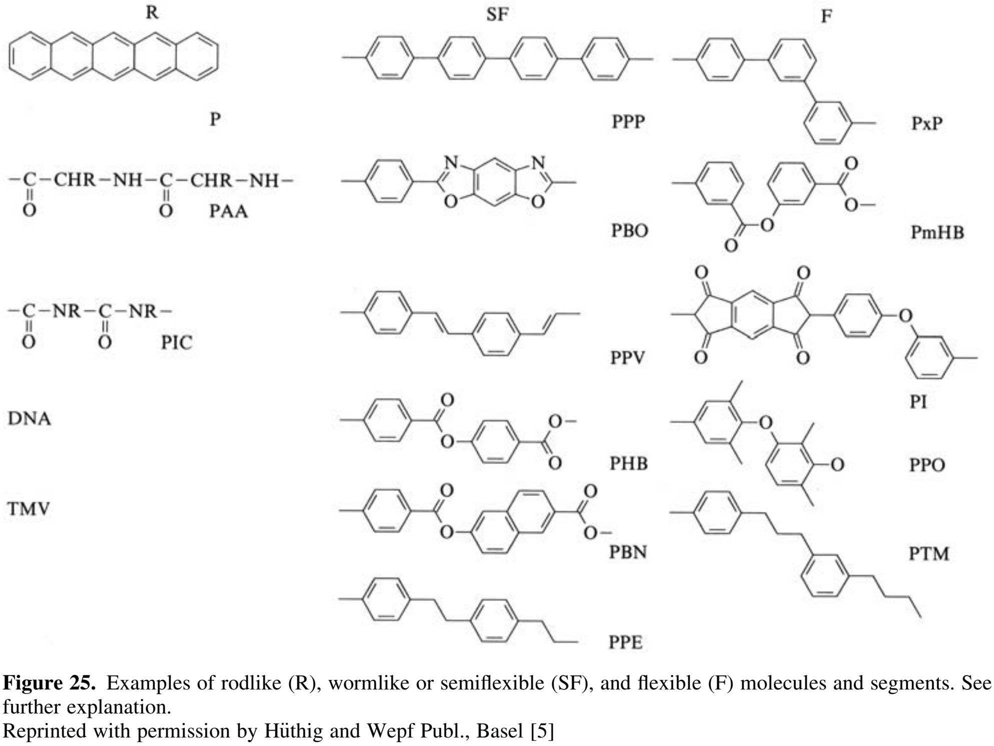

Figure 25. Examples of rodlike (R), wormlike or semiflexible (SF), and flexible (F) molecules and segments. See text for further explanation.
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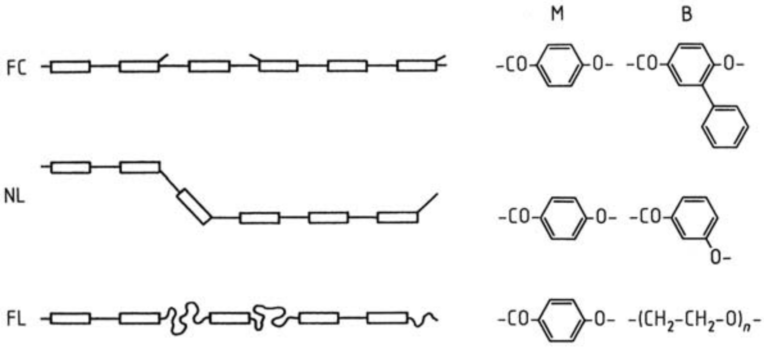

Figure 26. Flexibilization of rigid chain segments by frustrated crystallization (FC), nonlinear chains (NL), or flexible chain elements (FL); M = mesogen-forming monomeric units; B = stiffness-breaking units
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Bulky substituents prevent the parallelization of chains; they "frustrate" crystallization. Nonlinear chain elements (such as *ortho* and *meta* substituents) work in the same way. Flexible chain segments reduce the persistence lengths of the chains.

5.3.4. Lyotropic Liquid Crystalline Polymers

Molecule axes of low molar mass rodlike molecules are disordered in isotropic melts, whereas mesogen axes are more or less parallel to each other in nematic and smectic mesophases. Very short rods resemble spheroids. They can arrange themselves in various stable ways, but the parallel ordering need not be much more stable than other arrangements. Therefore, a critical axial ratio exists above which the simple geometric anisotropy is sufficient to stabilize a mesophase.

This critical axial ratio has been calculated with the lattice theory of polymer solutions as $\Lambda_{\text{crit}} \approx 6.42$. A geometric stabilization by repulsion is insufficient for $\Lambda < \Lambda_{\text{crit}}$ and the mesogens must exert additional orientation-dependent attractive forces.

In solution, repulsive forces between mesogens can act only at sufficiently high mesogen concentrations. At a critical volume fraction ϕ_p^*, phase separation occurs into a polymer-rich mesophase and a dilute isotropic phase. The dependence of ϕ_p^* on Λ can be described to a first approximation by [77]

$$\phi_p^* \approx 8(1-2L^{-1})/L \qquad (59)$$

The axial ratio Λ is the molar mass-dependent true axial ratio of rodlike molecules (i.e., helices) and the molar mass-independent Kuhn length of semiflexible molecules. Equation (59) is remarkably well fulfilled for both helical and semiflexible molecules (Fig. 27). An exception is the tobacco mosaic virus, probably because of additional charge effects that are not considered by the theory.

Lyotropic mesophases are formed by the helices of tobacco mosaic virus (c>2 %) and deoxyribonucleic acids (c>6 %) in dilute aqueous salt solutions as well as by poly(α-amino acids) in helicogenic solvents, e.g., poly(γ-methyl L-glutamate) in dichloromethane – ethyl acetate

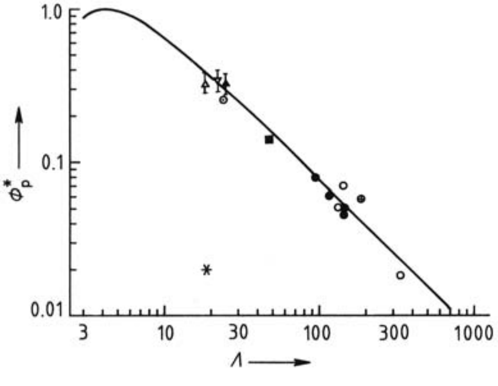

Figure 27. Critical volume fractions ϕ_p^* for phase separations of isotropic solution → nematic mesophase as function of Λ [i.e., the axial ratio of helical (rigid) molecules (circles) and the Kuhn length of semiflexible molecules (triangles, square)]
*Tobacco mosaic virus; solid line: prediction of Equation (59)
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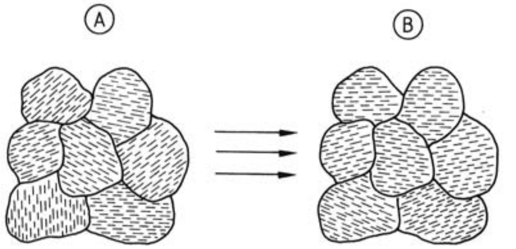
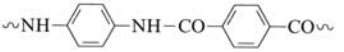


Figure 28. Alignment of mesogen axes upon shearing
A) Mesophase domains in liquid crystalline state at rest; B) During shearing or as LC glass with "frozen in sheared state"

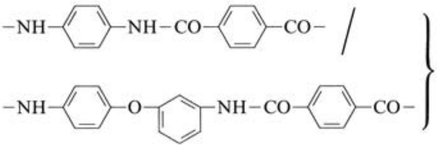
(12 : 5) ($c > 15\,\%$). Hydroxypropyl cellulose (HPC) forms a cholesteric mesophase at room temperature in water at $w_{\mathrm{HPC}} > 0.41$.

On shearing, mesophase domains become oriented with respect to the mesogen axes (Fig. 28). This alignment becomes frozen-in on rapid quenching of thermotropic LCs or by precipitation of lyotropic ones into baths (half-lifes of orientation between a few seconds and a few hundredths seconds). The resulting LC glasses possess good orientations of mesogen axes in the shear direction (e.g., fiber direction), high tensile strengths, and low extensibilities.

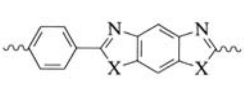
A number of LC fibers are produced commercially. Poly(*p*-phenylene terephthalamide) (PPB – T) was originally spun from concentrated sulfuric acid solutions, whereas chlorinated *N*-methyl pyrrolidine is now used:


Kevlar; PPB − T

A similar copolyamide is also on the market


Technora

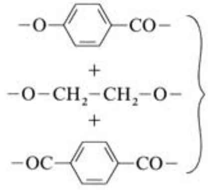
Even better LC fibers are produced from poly (*p*-phenylene-2,6-benzoxazoles) and poly(*p*-phenylene-2,6-benzthiazoles) (PBT), which are spun from poly(phosphoric acid) solutions, at present on a bench scale. Both "*cis*" (shown) and "*trans*" (X and N exchanged at one ring) structures are known:

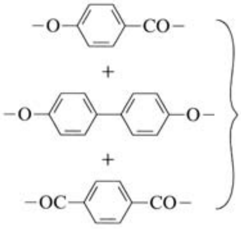

PBO (X = O); PBT (X = S)

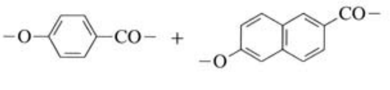
5.3.5. Thermotropic Liquid Crystal Polymers

Non-Newtonian shear viscosities of liquid crystal polymers drop drastically with increasing shear rates due to the orientation of mesogen axes upon shearing. Less energy is thus needed for processing thermotropic LCPs than isotropic thermoplastics. The high orientation times permit a freezing-in of the mesogen orientation in injection molding, for example. Because of the higher than usual moduli of elasticity and tensile strengths, such LCPs are also called *self-reinforcing polymers.*

The first self-reinforcing polymer was the copolyester X7 G with 60 mol % *p*-hydroxybenzoyl and 40 mol % terephthaloyl glycol units. It is no longer produced because the less expensive glass-fiber-reinforced saturated polyesters possess similar properties. Xydar and Vectra are, however, industrially produced:


X7G


Xydar


Vectra

Polymeric side-chain LCs can serve for the thermooptical storage of information. A guided laser beam increases the temperature locally, whereupon phase transformations occur. The change of order can then be frozen-in on cooling below the glass transition temperature. The resolution is ca. 0.3 µm.

5.3.6. Block Copolymers

Block copolymers consist of two and more blocks of constitutionally or configurationally different monomeric units (e.g., $A_n - B_m$, $A_n - B_m - A_n$). In most cases these blocks are thermodynamically or kinetically immiscible because their homopolymers A_n, B_m, etc., are not miscible. The demixing of block copolymers cannot proceed, however, to macroscopic phase separations because the blocks are chemically coupled. Similar blocks of different block copolymer molecules can thus only aggregate and form domains in a matrix of the other blocks. This phenomenon is called microphase separation.

Three different *applications* of block copolymers are known: polymeric detergents, thermoplastic elastomers, and compatibilizers for blends. *Polymeric detergents* consist of hydrophilic and hydrophobic blocks. Examples are the multiblock copolymers from watersoluble ethylene oxide blocks $[-(OCH_2CH_2)_n-]$ and water-insoluble propylene oxide blocks $-[OCH_2CH(CH_3)]_n-$. The hydrophobic blocks associate in water, which produces high viscosities.

A similar action is exerted by *compatibilizers* for nonmiscible blends of A_n and B_m polymers. These polymers are $A_p - B_q$ diblock copolymers: the A_p block resides in the A_n phases and the B_q block in the B_m ones. Compatibilizers thus anchor the two types of phases (Fig. 29).

Thermoplastic Elastomers consist of tri- or multiblock copolymers. Triblock copolymers $S_n - B_m - S_n$ possess a soft center polybutadiene block $- B_m -$ (glass transition temperature below use temperature) and two hard end polystyrene blocks $S_n -$ (glass transition temperature above use temperature). Below certain *m/n* ratios, styrene blocks form spherical microdomains in a continuous matrix of butadiene blocks. These spherical domains thus act as cross-linking units in an elastomer (Fig. 29, S). The hard domains "melt" above their glass transition temperatures, and the block copolymers can then be processed like thermoplastics.

The morphology of *diblock copolymers* is governed mainly by the relative spatial requirements of the blocks. Both blocks, if independent, would form unperturbed random coils. If the unperturbed volumes of both blocks are of equal size, all A_n blocks would line up in one layer and all B_m blocks in another because the blocks are (1) coupled to each other and (2) incompatible. The A_n layer faces another A_n layer, where the A_n blocks are coupled to B_m blocks, etc. (Fig. 29, L). The diblock polymers thus form lamellae with a thickness of two coil diameters. Similar structures result for triblock polymers $A_r - B_m - A_r$, where $r = n/2$.

If the volume of the A_n blocks is much lower than the volume of the B_m blocks, then the A_n blocks can no longer be packed into layers without violating the demand for tightest packing or deviating from the shape of unperturbed coils. Both possibilities are energetically unfavorable, and the smaller A_n blocks thus cluster together and form spherical domains in a continuous matrix of the larger B_m blocks. If the A_n blocks are somewhat larger (but not big enough to form lamellae), then cylinders would result (Fig. 30).

A great number of thermoplastic elastomers of both the triblock and the multiblock type is known [67]. Their chemical structures range from $(\text{styrene})_n - (\text{butadiene})_m - (\text{styrene})_n$ triblock copolymers to polyether − urethane multi-

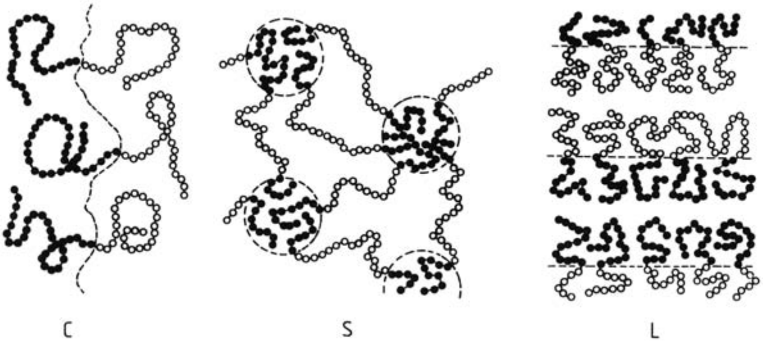


Figure 29. Arrangement of A_n blocks (with A units •) and B_m blocks (with B units ○) in diblock (C, L) and triblock copolymers (S)
C: compatibilizers at an interface - - -; S: spherical A_n domains in continuous matrix B_m; L: lamellae of A_n and B_m

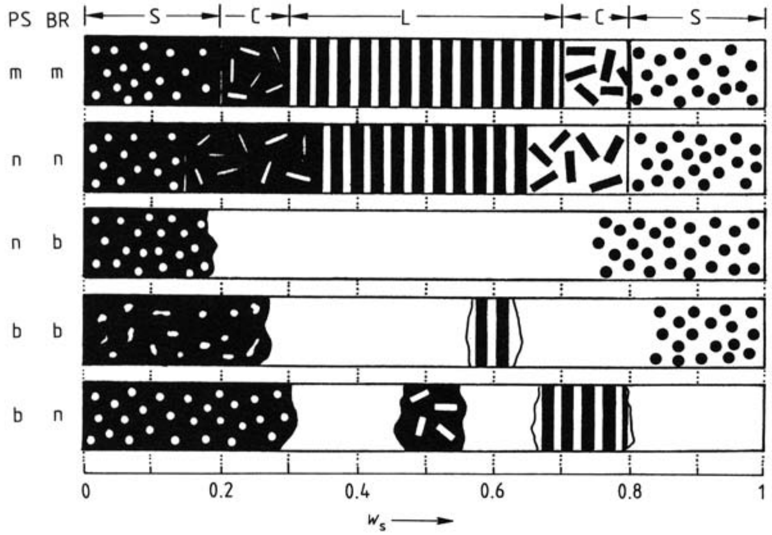


Figure 30. Morphology of styrene – butadiene diblock copolymers as a function of the mass fraction of the styrene units. White: polystyrene blocks (PS); black: polybutadiene blocks (BR). The block length distribution may be (m) molecularly homogeneous (theory), (n) narrow, or (b) broad
S = Spherical domains, C = cylinders (rods), L = lamellae (layers). Upper row: predictions of Meier theory; rows 2 – 5: schematic after experimental results of many authors
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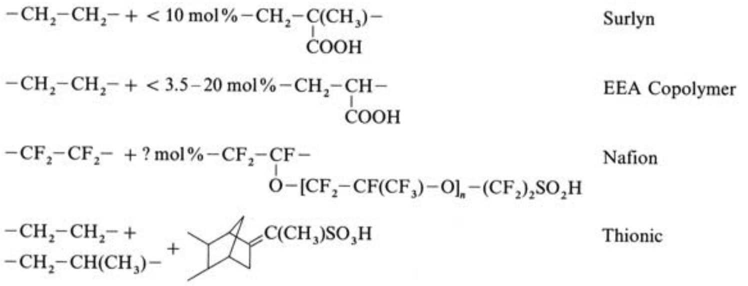
block polymers, ethylene – propylene copolymer – polyolefin blends, polyether – esters, and graft copolymers of butyl rubber on polyethylenes.

5.3.7. Ionomers

Ionomers are copolymers from primarily hydrophobic monomers with small amounts of ionic comonomers. The ionic groups may be in the main chain or in substituents. Four different types of ionomers are produced commercially.



$-CH_2-CH_2- + < 10\,\text{mol\%}-CH_2-\underset{COOH}{C}(CH_3)-$ Surlyn

$-CH_2-CH_2- + < 3.5-20\,\text{mol\%}-CH_2-\underset{COOH}{CH}-$ EEA Copolymer

$-CF_2-CF_2- + ?\,\text{mol\%}-CF_2-\underset{O-[CF_2-CF(CF_3)-O]_n-(CF_2)_2SO_2H}{CF}-$ Nafion

$-CH_2-CH_2- + -CH_2-CH(CH_3)- +$ $C(CH_3)SO_3H$ Thionic

Surlyn, EEA, and Nafion are synthesized by direct copolymerization of the corresponding monomers. Thionic results from the postpolymerization sulfonation (< 5 %) of the diene units (usually 5-ethylidene-2-norbornene) of the primary ethylene – propylene – diene (EPDM) rubber. Both EEA and Nafion are used as acids, whereas Surlyn and Thionic are obtained by aftertreatment that leads to sodium or zinc salts.

The introduction of ionic groups into hydrophobic polymers leads to ion associations and subsequently to microphase separations. The ion association is controlled by the coordination number of the ions; that is, sodium ions with valence 1 and coordination number 6 are as good cross-linkers as zinc ions with valence 2. Cross-linking by ions does not occur via ion pairs but via clusters and domains of many ions. These ionic bonds dissociate at higher temperature, and the ionomers can then be processed like thermoplastics. At lower temperature, they behave either as thermoplastic elastomers (T_G of polymer segments lower than use temperature) or as "reversible" thermosets (T_G of segments higher than use temperature).

5.4. Gels

Chemically lightly cross-linked polymers swell upon addition of solvent to form gels. The maximum degree of swelling results from the attempt of segments located between cross-linking sites to attain their energetically most favored coil dimensions which in turn is counteracted by the elastic retraction due to cross-links. Physically cross-linked polymers behave in the same way if the physical cross-links (crystallites, ion clusters, etc.) survive the dissolution process.

The latter phenomenon is utilized in poly (vinyl chloride) pastes. The strong dipole – dipole interactions between C–Cl bonds leads to associations of chain segments, which at room temperature resist dissolution by plasticizers such as phthalates, adipates, sebacates, or citrates. Heating of PVC with these plasticizers and subsequent cooling leads to gelation by formation of a lightly physically cross-linked network. Plasticized PVC thus behaves like an elastomeric material. The physical cross-links dissociate at higher temperature, and the resulting PVC paste can be processed with extruders or roll mills.

5.5. Polymer Surfaces

5.5.1. Structure

Outer layers of solid or liquid polymers do not exhibit – against air, water, metal surfaces, etc. – the same average composition as the interiors of these polymers. Groups or segments with the lowest Gibbs interfacial energy will reside preferentially at the surface or interface. Surface structures may also be altered by chemical attack during processing or on prolonged use (e.g., by oxidation) or by physical processes such as transcrystallization.

This behavior can be studied by a wide variety of new spectroscopic methods, for example, the concentration of immediate surface groups by Fourier transform infrared spectroscopy (FT-IR); the composition of the upper 0.3 – 0.5-nm layer by ion scattering spectroscopy (ISS, LEIS); of the upper 1 – 10 nm by photoelectron spectroscopy [UPS, PE (S)], electron spectroscopy for chemical analysis (ESCA, XPES, XPS, IEE), and Auger spectroscopy (AES).

These methods have shown that poly-(2-vinylpyridine) and poly(4-vinylpyridine) have much more hydrophobic surfaces than their chemical structure indicates: CH_2 and CH groups face the surface; pyridine residues (C_5H_4N), the interior. Imide – carbonyl residues of polyimides, on the other hand, are preferentially found at the surface and aromatic rings in the interior. The surface is enriched by siloxane residues in polycarbonate – polydimethylsiloxane block copolymers but by styrene units in polystyrene – poly(ethylene oxide) block copolymers. Since the surface energy depends on the contact (air, water, metals, etc.) and also on kinetic effects (thermal history, solvents, etc.), one and the same polymer may possess various surface compositions and thus also surface properties.

5.5.2. Interfacial Tension

Interfacial tension is the force that acts at the interface between two phases; it is called surface tension for the interface condensed phase – gas phase.

Surface tensions γ_{lv} of liquid polymers against air decrease with the two-third power of the molar mass according to

$$\gamma_{lv} = \gamma_{lv}^{\infty} + K_e \cdot M^{-2/3} \qquad (60)$$

They do not vary markedly with temperature. Typical values (at 150 °C) range from 13.6 mN/m (polydimethylsiloxane), 22.1 mN/m (it-polypropylene), 28.1 mN/m (polyethylene), and 33.0 mN/m poly(ethylene oxide). At present, no correlation of these surface tensions with chemical constitution is possible because the surface structures of liquid polymers are unknown.

Interfacial tensions between two liquid polymers are always lower than surface tensions. They are low for two apolar polymers but higher if one polymer or both of them are polar. For example, the interfacial tension of polyethylene – it-polypropylene is only 1.1 mN/m, but that of polyethylene – poly(ethylene oxide) is 9.5 mN/m and poly(ethylene oxide) – polydimethylsiloxane 9.8 mN/m.

The interfacial tensions between solid polymer and air are generally unknown. They do not differ markedly, however, from the critical surface tensions determined by the *Zisman method*. In this method, the liquid – air surface tensions of various liquids are plotted against the cosine of contact angles ϑ of these liquids against air and extrapolated to $\cos \vartheta \rightarrow 0$. The resulting "critical" surface tensions of polymers are always lower than the surface tension of water: polytetrafluoroethylene, 18.5; polyethylene, 33; poly (vinyl alcohol), 37; polyamide 66, 46; and urea – formaldehyde resins, 61 mN/m. Fluorinated polymers have especially low critical surface tensions. They are not wetted by water (72 mN/m) or oils and fats (20 – 30 mN/m) and are therefore used as surface coatings to prevent sticking.

5.5.3. Adsorption

Macromolecules possess many adsorbable groups and segments. The type of adsorption depends on the adsorption energy per segment (group), the concentration of adsorbable macromolecules, and the duration of the experiment.

"Adsorption equilibria" are established in minutes to hours at smooth surfaces but may take days to attain at rough surfaces or powders. The adsorption time increases with the concentration and molar mass of the polymer.

Polymer coils tend to overlap even in fairly dilute solutions: the adsorbed polymer layers are almost always multilayers, except for the adsorption of oligomers (X<10 – 100) or from very dilute solutions (volume fractions $<10^{-4} - 10^{-3}$). At higher concentrations or molar masses, adsorbed amounts and structures of polymer layers are mainly kinetically controlled. Reorganization may occur with time: for example, the adsorption of polar polymers at polar surfaces can change from an initial loose loop structure to a more compact, flat covering. The layer of poly (ethylene oxide) adsorbed on chromium surfaces is only ca. 2 nm thick and so tightly packed that the refractive index of the adsorbed layer is identical with that of the crystalline polymer. The thickness of the surface layer of polystyrene of $M = 176\ 000$ g/mol adsorbed from a 5 mg/mL solution in the thermodynamically bad solvent cyclohexane is however about 27 nm (i.e., identical with the end-to-end distance in the unperturbed state). The physical structures of adsorbed polymers obviously play an important, yet widely unknown, role in many technological applications of polymers.

6. Thermal Properties

6.1. Molecular Motion

6.1.1. Thermal Expansion

Isotropic bodies expand upon heating equally in all three spatial directions because of the increasing thermal motions of atoms, groups, and molecules. The expansion is characterized by the cubic expansion coefficient $\beta = V^{-1} (\partial V / \partial T)_p$, which is usually converted by $\beta = 3\ \alpha$ into the linear expansion coefficient $\alpha = L^{-1} (\vartheta L / \vartheta T)_p$. Such isotropic materials are, for example, diamond ($\alpha = 1.06 \times 10^{-6}\ \mathrm{K}^{-1}$), iron ($12 \times 10^{-6}\ \mathrm{K}^{-1}$), water ($70 \times 10^{-6}\ \mathrm{K}^{-1}$), and carbon disulfide ($380 \times 10^{-6}\ \mathrm{K}^{-1}$) (all data at 25 °C). All of these materials exhibit the same types of bonds in the three directions: all covalent bonds between carbon atoms in diamond, all metallic bonds between iron atoms, all hydrogen bonds between water molecules, and all dispersion forces between CS_2 molecules.

Polymer chains are however anisotropic: the intramolecular bonds along the chain are chemical (almost always covalent); the intermolecular bonds perpendicular to the chain, physical (dispersion forces, dipole – dipole interactions). On thermal expansion of polymer crystals, chains contract because of the increasing amplitude of the lateral motions. The thermal expansion coefficient in the chain direction is thus zero to negative, whereas the overall expansion coefficient is positive. The linear thermal expansion coefficients of polymers are thus averages over the three spatial directions; they lie between those of metals and liquids. Typical values are $\alpha = 60 \times 10^{-6}\ \mathrm{K}^{-1}$ (polyamide 6) and $80 \times 10^{-6}\ \mathrm{K}^{-1}$ [poly(vinyl chloride)].

Significant problems may thus arise due to different expansion coefficients for polymer – metal composites upon thermal stress. Another problem is the low dimensional stability of polymers on temperature change. This problem may be aggravated by a concomitant change of the water content of polymers or by recrystallization phenomena, both of which can lead to warping.

6.1.2. Heat Capacity

The molar heat capacity can be 3 R per atom according to the law of equal distribution of energy. In reality, degrees of freedom are always frozen in and the molar heat capacity is lowered. Empirically, a value of ca. 1 R has been found for solid polymers at room temperature. Poly(2,6-dimethylphenylene oxide) $[(C_8H_8O)_n]$ at 25 °C has a specific heat capacity of $1.22\ J\ K^{-1}\ g^{-1}$ and a molar heat capacity (per monomeric unit) of $146.4\ J\ K^{-1}\ mol^{-1}$. The molar heat capacity (per mole of atoms) is thus $146.4\ J\ K^{-1}\ mol^{-1}/17 = 8.61\ J\ K^{-1}\ mol^{-1}$ (i.e., approximately $1\ R = 8.314\ J\ K^{-1}\ mol^{-1}$).

Below the glass transition temperature T_G, heat capacities are not influenced by the degree of crystallinity of the polymer. At T_G, a stepwise increase is observed. The heat capacity passes through a maximum a few degrees below the macroscopic melting temperature; that is, the true melting temperature is given by the upper end of the melting range where the largest and most perfect crystals melt.

6.1.3. Heat Conductivity

Conventional polymers are electrical insulators. Heat is thus not transported by electrons but by elastic waves (phonones in the corpuscular model). The free path length of phonones is defined as the distance at which the intensity of elastic waves has decreased to 1/e. This free path length is about 0.7 nm for glasses, amorphous polymers, and liquids; it is practically independent of temperature. The slight decrease of heat conductivities (thermal conductivities) of amorphous plastics and elastomers below their glass transition temperatures must thus be caused by the decrease of heat capacities with decreasing temperature. For crystalline polymers, a strong decrease of heat capacities is observed at their melting points because packing densities decline drastically at these temperatures.

6.2. Thermal Transitions and Relaxations

6.2.1. Overview

Thermal transitions and relaxations are characterized by large changes of physical properties at the corresponding temperatures. In a true thermal transition, chemical compounds are in equilibrium on both sides of the transition temperature. An example is the melting transition.

Thermal Relaxations, on the other hand, are kinetic effects. They depend on the frequency of the experimental method and thus on the time scale. Typical thermal relaxations are caused by the onset of translations and rotations of charges, dipoles, and chemical groups (i.e., by atomic motions).

Some experimental methods work at frequencies that such relaxations appear to be thermal transitions. The best-known example is the glass transition temperature at which hard, glassy polymers convert to soft, rubbery materials and vice versa. In many cases, a thermal effect cannot be unambiguously classified as either transition or relaxation.

Thermal transitions and relaxations can be detected and determined by many different experimental methods. The most commonly applied methods for the determination of *thermal transitions* are differential thermoanalysis (measures temperature differences between specimen and standard on heating or cooling with constant rate), differential scanning calorimetry (does the same for enthalpy differences), thermomechanical analysis (deformation of specimen under load), dynamical – mechanical analysis (either free or forced vibration of specimen), and torsional braid analysis (specimen on vibrating support). Figure 31 shows a typical thermogram.

Many methods are available for the study of molecular motions and thus *thermal relaxations.* These methods work with frequencies ν which correspond to correlation times t_c of $10^{-12}\ s < 1/\nu < 10^6\ s$ (11.5 d). Typical methods include quasi-elastic neutron scattering $(10^{-12} < t_c/$

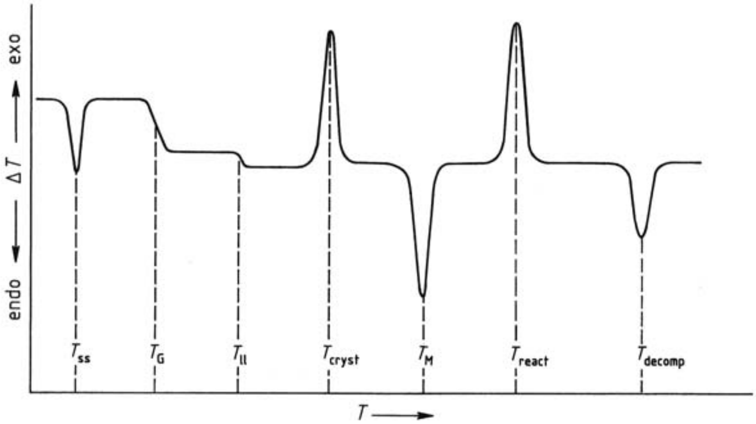


Figure 31. Idealized thermogram of a partially crystalline polymer with solid – solid transition T_{ss}, glass transition temperature T_G, liquid – liquid transition T_{ll}, maximum crystallization temperature T_{cryst}, melting temperature T_M, maximum temperature T_{react} of a chemical transformation, and maximum temperature T_{decomp} of chemical degradation
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$s<10^{-8}$), NMR spin-lattice relaxation ($10^{-12} < t_c/s<10^{-5}$), dielectric relaxation ($10^{-10} < t_c/s<10^{-5}$), and photon correlation spectroscopy ($10^{-4}<t_c/s<10^{2}$). Thermal relaxations furthermore manifest themselves in sudden changes of mechanical properties, such as rebound elasticity ($t_c/s\approx10^{-5}$), penetrometry ($t_c/s\approx10^{2}$), mechanical loss ($10^{3}<t_c/s<10^{7}$), and thermal expansion ($t_c/s\approx10^{4}$). Slow methods (high t_c) are called "static" methods; fast ones, "dynamic." Transition – relaxation phenomena are also detected by several empirical, standardized methods that measure the resistance of specimens against flow under various loads (Vicat temperature, heat distortion temperature, Martens temperature, etc.).

Various characteristic signals are observed at a fixed temperature for a given frequency (see insert in Fig. 32). They often cannot be correlated with

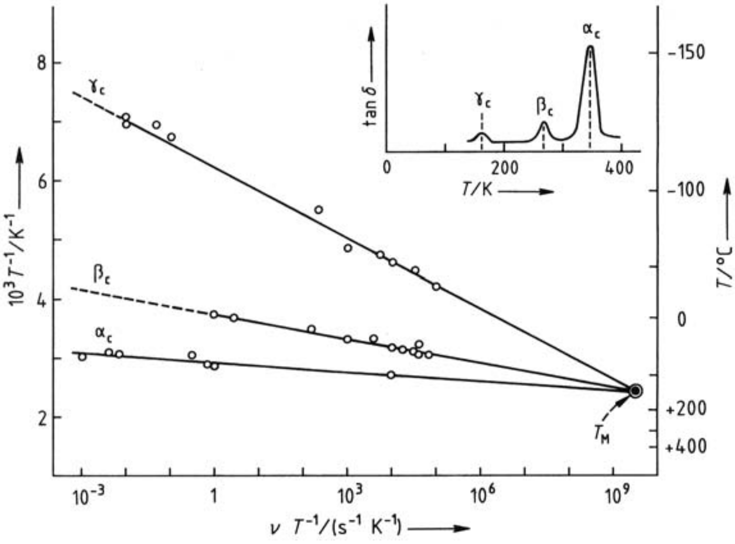

Figure 32. Dependence of inverse relaxation temperature $1/T$ on the logarithm of reduced frequency ν/T for various relaxation processes of a low-density polyethylene
Insert shows the mechanical relaxation spectrum at $\nu = 1000$ Hz.
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molecular processes and are commonly indicated with descending temperature by letters in the sequence of the Greek alphabet, starting with the melting temperature (crystalline polymers, subscript c) or glass transition temperature (amorphous polymers, subscript a).

The various methods work at different frequencies and thus give different relaxation temperatures for the same molecular process. The frequency dependence of relaxation temperatures can be described by the Eyring equation for rate processes:

$$\nu = (k_B T/2\pi h)\exp\left(-\Delta H^{\neq}/RT\right)\exp\left(\Delta S^{\neq}/R\right) \tag{61}$$

where k_B is the Boltzmann constant, h the Planck constant, $\Delta H^{\neq}$ the activation enthalpy, and $\Delta S^{\neq}$ the activation entropy. Transformation of Equation (61) leads to

$$\frac{1}{T} = \frac{R}{\Delta H^{\neq}}\cdot\left[\left(\frac{\Delta S^{\neq}}{R} + \ln\frac{k_B}{2\pi h}\right) - \ln\frac{\nu}{T}\right] \tag{62}$$

In a $(1/T) = f\,[\ln(\nu/T)]$ plot, lines for various processes intersect at the melting temperature ($T_M = 131$ °C in Fig. 32). Such common intersects seem to be general for nonhelical polymers.

6.2.2. Crystallization

The crystallization of coillike polymers from dilute solutions leads to platelets (Fig. 18) in which folded polymer chains are arranged with their stems perpendicular to the fold surface (Fig. 19). From concentrated solutions and melts at rest, lamellae are organized into spherulites (Fig. 21), which may be transformed to row structures by shearing or drawing (Fig. 33).

Crystallization can be subdivided into two elementary processes: primary nucleation and crystal growth (secondary nucleation). Both processes determine the crystallization rates, which depend strongly on both temperature and polymer structure. At 30 K below the melt temperature, the linear crystallization rate may, for example, range between 5000 μm/min for polyethylene and 0.01 μm/min for poly(vinyl chloride). Symmetrically structured polymers usually crystallize rapidly; polymers with bulky groups or low tacticities, only slowly. Quenching of poly(ethylene terephthalate) melts leads, for example, to amorphous polymers, whereas quenching of polyethylene melts never gives amorphous polymers, even if liquid nitrogen is used.

Primary Nucleation may be homogeneous (spontaneous, sporadic, thermal) or heterogeneous (simultaneous, athermal). Homogeneous nuclei are formed from segments of the crystallizing polymer molecules; they are very rare. Heterogeneous nuclei result from extraneous materials such as additives, dust particles, container walls, or specially added nucleation

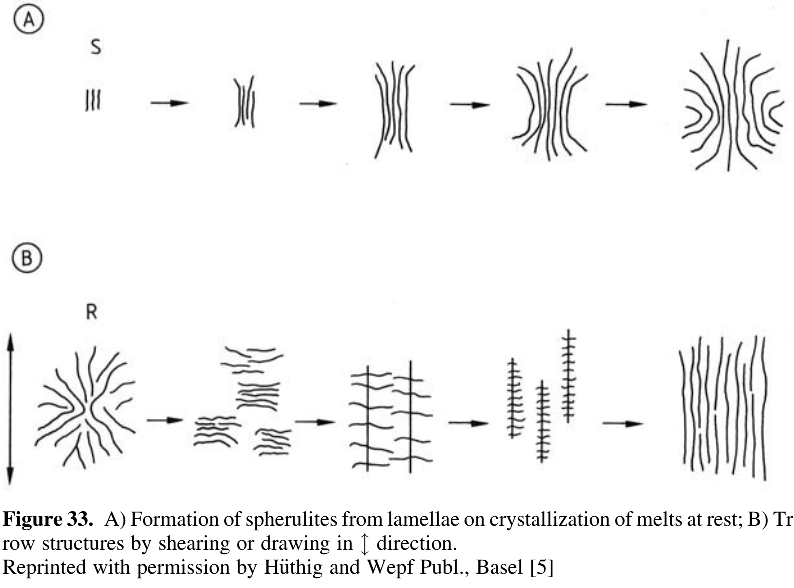

Figure 33. A) Formation of spherulites from lamellae on crystallization of melts at rest; B) Transformation of spherulites into row structures by shearing or drawing in ↕ direction.
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agents. Such nuclei must have minimum sizes of 2 – 10 nm. Their concentrations can range from ca. 1 nucleus per cubic centimeter (polyoxyethylene) to ca. 10^{12} nuclei per cubic centimeter (polyethylene).

Above the melting temperature, fragments of crystallites may survive for certain time periods. These fragments act as athermal primary nucleation agents on subsequent cooling. They are responsible for the "memory effect" (i.e., the reappearance of spherulites at the same locations after and before the melting), which occurs because of low diffusion rates at very high melt viscosities.

Growth of primary nuclei occurs by a *secondary nucleation process*. The growth rate is low just below the melting temperature because secondary nuclei are formed and dissolved rapidly. About 50 K below the glass transition temperature, on the other hand, motions of molecule segments are practically zero and the crystal growth rate is therefore low as well. Crystallization rates must thus exhibit a maximum between the melting and glass transition temperatures; the maximum crystallization rates are usually at (0.80 – 0.87) T_{M} (in kelvin).

In addition, the entire crystallization process can be subdivided into a primary and a secondary phase. The *primary phase* comprise the conversion of the total volume to a solid. At the end of this phase, the volume may be filled (e.g., with spherulites), but not all polymer segments between spherulites or between the lamellae of the spherulites may have crystallized. The polymer has not attained its maximal crystallinity (the crystallizability). Crystallization may thus continue during the *second phase*. In this aftercrystallization, lamellae may thicken, lattices become more perfect, etc.

Primary crystallization can be characterized by the Avrami equation:

$$\phi/\phi_{\infty} = 1 - \exp(-z \cdot t^{n}) \tag{63}$$

where ϕ = fraction of crystallized volume, ϕ_{∞} fraction of maximal attainable crystallinity for a given entity (e.g., spherulite), and z and n are constants that depend on both the nature of the nucleation process (homogeneous, heterogeneous) and the type of growing entity (rod, disk, sphere, sheaflet, etc.). The exponents n range between 1 and 7; empirically, they may assume fractional values.

6.2.3. Melting

Melting is defined as the thermal transition of a crystal to an isotropic melt. The melting temperature T_{M} (fusion temperature) is defined as the temperature at which crystallites are in equilibrium with the melt. Melting starts at the corners and edges of crystal surfaces; in contrast to crystallization, no nuclei are needed.

Segments of about 60 – 100 chain atoms participate in the melting process. During heating, segments are redistributed continuously between crystalline and noncrystalline regions; a melting range exists and no sharp melting point is observed. The melting temperature is defined as the upper end of the melting range because the biggest and most perfect crystals melt there. Published melting temperatures often refer to the maxima of $\Delta T = f(T)$ curves, however. Observed melting temperatures are in general lower than the thermodynamic melting temperatures of perfect crystals but may be occasionally higher because of overheating effects.

Melting temperatures increase with molar mass and become practically constant at molar masses of ca. 50 000 – 150 000 g/mol. The melt can be considered as a dilute solution of end groups in monomeric units, and the reduction of the melting temperature with decreasing molar mass (i.e., increasing concentration of end groups) can be described by the thermodynamic law for the lowering of freezing temperatures:

$$\frac{1}{T_{\mathrm{M}}} = \frac{1}{T_{\mathrm{M}}^{0}} + \left(\frac{2R}{\Delta H_{\mathrm{M,u}}^{\mathrm{m}}}\right) \cdot \frac{1}{\mathrm{X}_{n}} \tag{64}$$

where $\Delta H_{\mathrm{M,u}}^{\mathrm{m}}$ is the molar melt enthalpy per monomeric unit, $\bar{X}_n$ the number-average degree of polymerization, and T_{M} and $T_{\mathrm{M}}^{\mathrm{o}}$ are the thermodynamic melting temperatures at finite and infinite molar masses. Similar depression of the melting point is caused by addition of low molar mass solvents and amorphous polymers or by statistical copolymerization; in all these cases, the term $2/\bar{X}_n$ must be replaced by

$$({}^{*}V_{\mathrm{u}}^{\mathrm{m}}/{}^{*}V_{1}^{\mathrm{m}})[(1-\phi_2)-\chi(1-\phi_2)^2] \text{ (solvent)} \tag{65}$$

$$({}^{*}V_{\mathrm{u}}^{\mathrm{m}}/{}^{*}V_{\mathrm{A}}^{\mathrm{m}})-\chi(1-\phi_2)^2] \text{ (amorphous polymer)} \tag{66}$$

$$[-\ln x_{\mathrm{u}}-\chi(1-\phi_2)^2] \text{ (statistical copolymer)} \tag{67}$$

where $*V^{\mathrm{m}}$ is the partial molar volume of solvent 1, amorphous polymer A, or monomeric units u of copolymer; x_{u} the mole fraction of units u; ϕ_2 the volume fraction of crystallizable polymer 2; and χ an interaction parameter.

Melting temperatures $T_{\mathrm{M}} = \Delta H_{\mathrm{M}}^{\mathrm{m}} / \Delta S_{\mathrm{M}}^{\mathrm{m}}$ are determined by the changes in molar melting enthalpies $\Delta H_{\mathrm{M}}^{\mathrm{m}}$ and molar melting entropies $\Delta S_{\mathrm{M}}^{\mathrm{m}}$. The *melting entropy* results from conformational changes and volume changes upon melting. The melting entropy theoretically adds $R \cdot \ln 3 = 9.12$ J K^{-1} mol^{-1} for the formation of three conformers with equal energy and 7.41 J K^{-1} mol^{-1} for one *trans* and two *gauche* conformers in the case of polymethylene $\sim (\mathrm{CH_2})_n \sim$. The entropy change due to the volume change should add another 10.9 J K^{-1} mol^{-1} so that the theoretical melt entropy of polymethylene should be ca. 18.3 – 20.0 J K^{-1} mol^{-1}. Experimentally, only 9.9 J K^{-1} mol^{-1} is observed, which points toward either the existence of local order in melts or a high segment mobility below the melting temperature. The latter was found experimentally by broad-line NMR for *cis*-1,4-polyisoprene ($\Delta S_{\mathrm{M}}^{\mathrm{m}} = 4.8$ J K^{-1} mol^{-1}).

Melting Enthalpies are usually between 1 and 5 kJ per mole of chain atom. Low values are to be expected for polymers with high chain mobilities below the melting temperature (*cis*-1,4-polyisoprene, aliphatic polyesters and polyethers). High values are found for polymers with strong interactions between chains and tight packing of chains in crystals (polyoxymethylene, it-polystyrene). Some of these strong interactions may survive the melting process; for example, most of the hydrogen bonds of polyamides are still detected by IR spectroscopy above the melting temperature.

Thus the primary factors for high melting temperatures are not intermolecular interactions (e.g., cohesive energies) but reduced flexibilities of chains. Low melting temperatures are found for polymers with low rotational barriers (ester, oxygen, sulfide groups in chains), high melting temperatures for tightly packedhelices [polyoxymethylene, it-poly(3-methylbutene)] and for ladder and ladderlike polymers [poly(*p*-phenylene), polybenzimidazole, etc.]. Such factors are responsible for the variation of melting temperatures with the number of methylene units in aliphatic polymer chains of the type $\sim$X–(CH$_2$)$_n$$\sim$ (Fig. 34).

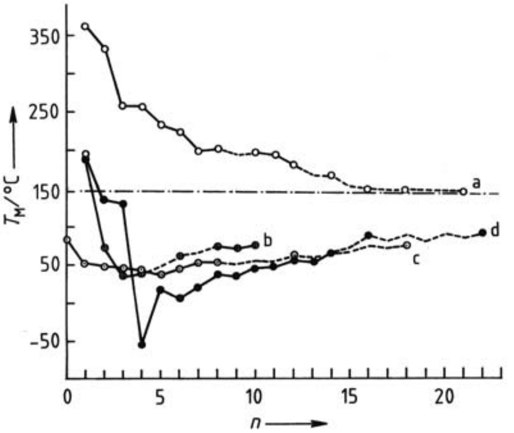

Figure 34. Melting temperatures of (○, ⊙, ⊕) aliphatic polymers $\sim [\mathrm{X\text{-}(CH_2)}_n]\sim$ and (•) isotactic poly(α-olefins) $\sim \{\mathrm{CH_2–CH[(CH_2)}_n\mathrm{H]}\}\sim$ as function of the length n of methylene sequences
a) X = NHCO (polyamides); b) X = O (polyoxides); c) X = COO(CH$_2$)$_3$OOC (aliphatic polyesters of trimethylene glycol)
–·–·–· theoretical melting temperature of polyethylene

6.2.4. Liquid Crystal Transitions

Thermal transitions of thermotropic LC polymers from their crystals to smectic (T_{cs}) or nematic phases (T_{cn}), from smectic to nematic mesophases (T_{sn}), and from nematic phases to isotropic melts (T_{ni}, clearing temperature) are thermodynamic first-order transitions. They exhibit steplike changes in volume, enthalpy, and entropy, just like the melting of three-dimensional crystals to isotropic melts. Thermodynamically stable phases can exist only between melting and clearing temperatures ($T_{\mathrm{cs}}, T_{\mathrm{cn}} < T_{\mathrm{ni}}$); they are called *enantiotropic phases*.

Mesophases form dispersions in supercooled isotropic melts if clearing temperatures are lower than melting temperatures ($T_{\mathrm{cs}}, T_{\mathrm{cn}} > T_{\mathrm{ni}}$). Such phases are thermodynamically unstable compared to the crystalline; they are called *monotropic*.

Mesophases may be supercooled below T_{M} T_{cs} to smectic liquids sL* and below T_{sn} to nematic liquids nL* if crystallization can be suppressed. At even lower temperatures T_{gn} and T_{gs}, these supercooled liquids may yield anisotropic glasses nG and sG, respectively. Some of these transition temperatures cannot be measured directly, but their existence can be deduced from extrapolations of transition temperatures of copolymers to 100 % of the pure mesogenic compound (virtual transition temperatures).

The transition temperatures T_{trans} (i.e., T_{cs}, T_{gs}, T_{sn}, T_{cn}, T_{gn}, T_{ni}) depend on the degree of polymerization X in the same way the melting temperature does: $1/T_{\text{trans}} = f\,(1/X)$. The transition enthalpy ΔH_{ni} is always lower than the transition enthalpies ΔH_{gs} and ΔH_{sn} because the n → i transition is from order to disorder, whereas the g → s and s → n transitions are from order to less order. Transition entropies of mesophases are lower than melt entropies; they usually have values of ca. 0.5 – 1.5 J K^{-1} mol^{-1}, with $\Delta S_{\text{sn}} < \Delta S_{\text{ni}}$.

6.2.5. Glass Transitions

Glass transitions are phenomenologically characterized by a change from a "hard," noncrystalline, glasslike material to a rubbery to highly viscous "melt." The viscosities at glass transitions are ca. 10^{12} Pa · s, independent of chemical structures. Glass transitions were thus thought to be "isoviscous" phenomena. Today, glass transitions are considered to occur at that physical state where all materials exhibit the same "free volume."

Various free-volume fractions are discussed in the literature. The empirical Boyer – Simha rule relates a free-volume fraction f_{exp} to the cubic expansion coefficients β of liquid (L) and amorphous, glasslike (G) polymers and their glass transition temperatures T_{G} (see Table 21):

$$f_{\text{exp}} \approx (\beta_{\text{L}} - \beta_{\text{G}}) \cdot T_{\text{G}} \approx 0.11 \pm 0.02 \tag{68}$$

The Williams – Landel – Ferry (WLF) approach relates a free-volume fraction f_{WLF} to the probability of segment movements. Empirically, values of $f_{\text{WLF}} \approx 0.025 \pm 0.01$ were found; these values can be calculated, for example, from $K = f_{\text{WLF}}/(\beta_{\text{L}} - \beta_{\text{G}})$ and $K' = \log e/f_{\text{WLF}}$ of the semiempirical WLF equation (Eq. 69) where $-\log a_t = \Delta(\log t\,)$ is a shift factor

$$T = T_G + \frac{K \cdot \log a_t}{K' - \log a_t} = T_{\text{G}} + \frac{51.6 \cdot \log a_t}{17.4 - \log a_t} \tag{69}$$

The Williams – Landel – Ferry equation applies to all relaxation processes; its use is restricted to temperatures in the range $T_{\text{G}} < T < (T_{\text{G}} + 100\ \text{K})$.

Table 21. Glass transition temperatures and free-volume fractions of polymers (for explanation of symbols, see text)

Polymer	T_{G} °C	f_{exp}	f_{WLF}	f_{fluc}
Polyethylene	− 80	0.098	0.025	
Polyisobutylene	− 73	0.079	0.026	0.0017
Poly(butyl methacrylate)	20	0.13	0.026	0.0010
Poly(vinyl acetate)	27	0.128	0.028	0.0023
Polystyrene	100	0.133	0.025	0.0035
Poly(methyl methacrylate)	105	0.118	0.025	0.0015

The WLF equation allows calculation of the static glass transition from the various dynamic glass transition temperatures if the deformation times (inverse effective frequencies) of the methods are known. The glass transition temperatures of poly(methyl methacrylate) (PMMA) are given as 105 °C (thermal expansion, "static"), 120 °C (penetrometry), and 160 °C (rebound elasticity). The same polymer may thus exhibit very different mechanical properties if subjected to different stresses; at 140 °C, PMMA behaves as either a glass (rebound elasticity) or an elastomer (penetrometry).

The glass transition temperature indicates the onset of cooperative movements of chain segments of 25 – 50 chain atoms, which can be deduced from the ratio of molar activation energies and melt energies. These cooperative movements very probably involve *trans – gauche* transitions that proceed cooperatively along greater distances since only small changes of chain axes are involved according to deuterium NMR. The participation of segments of 25 – 50 chain atoms is also indicated by cross-linking experiments: as long as the average segment length N_{seg} between two cross-linking points is less than 25 – 50 chain atoms, no change of glass transition temperatures is observed. At $N_{\text{seg}} < 25 - 50$, T_{G} increases with the inverse molar mass of the segments.

Since both glass transition and melt temperatures depend on segmental motions, close relationship between these two temperatures can be expected. The empirical Beaman – Boyer rule states that $T_{\text{G}} \approx (2/3) T_{\text{M}}$, which holds reasonably well for many polymers except for chains such as polyethylene and polyoxyethylene for which $T_{\text{G}}/T_{\text{m}} \approx 1/2$.

A vast literature exists about effects of constitution on T_{G}. Cyclic macromolecules possess no end groups, and thus no free-volume effects from these. Small rings are furthermore strained (less possible microconformations). The greater the molar mass, the more microconformations can be adopted, the greater is the chain flexibility and the lower is T_G. The same is true for segment flexibilities of star-branched polymers and long side chains in comblike molecules (side- chain "crystallization").

Linear relationships are found between the logarithms of glass transition temperatures T_G and the logarithms of cross-sectional areas A of either carbon, carbon – oxygen, or carbon –nitrogen chains (another measure of segment flexibilities). The three lines intersect at $A=0.17$ nm^2 and $T_G=141$ K, which should be the lowest glass transition temperature possible. The lowest experimentally found glass transition temperature (150 K) is that of polydimethylsiloxane, $\sim$ (O – Si(CH$_3$)$_2$)$_n$ $\sim$.

Glass transitions can be decreased (or increased) by copolymerization with suitable monomers (internal plasticization) and by addition of external plasticizers (see Section 4.2.5).

6.2.6. Other Transitions and Relaxations

Experimentally, a number of other transition – relaxation temperatures are observed, mostly of unknown origin. Amorphous polymers exhibit weak "liquid – liquid" transitions at ca. $T_{ll} \approx 1.2\ T_G$. Below the critical molar mass for entanglements, transition temperatures T_{ll} equal flow temperatures T_F at which polymers start to flow under their own weight. At higher molar masses, $T_F > T_{ll}$.

Another transition temperature $T_U \approx 1.2\ T_M$ seems to exist for crystalline polymers. This transition has been interpreted as the dissolution of smectic structures.

Few β-relaxations have been correlated with molecular phenomena. An example is the frequency-dependent boat – chair transition of cyclohexane rings, which occurs at e.g., − 125 °C (10^{-4} Hz) and + 80 °C (10^5 Hz).

6.2.7. Technical Methods

The technical testing on thermal transitions and relaxations of plastics is usually performed with simple methods under standardized conditions and always under load. *Martens numbers* measure temperatures at which the specimen has experienced a certain bend, *Vicat softening temperatures* give the temperatures for a certain penetration of a rod into the plastics, and the *heat distortion temperatures* (heat deflection temperatures) indicate the temperatures for a certain bending with a three-point method. The temperatures from these three methods do not only depend on transitions or relaxations but also on the elasticity of the specimen; Vicat and heat distortion temperatures are in addition affected by the surface hardness. The resulting softening temperatures are neither identical with glass transition nor with melting temperatures; they are often also not a good measure of the continuous service temperature of a plastic.

6.3. Transport

6.3.1. Self-Diffusion

Brownian movements cause molecules and their segments to interchange positions in fluid phases. If all entities are of the same type, such interchanges lead to a "self-diffusion", which involves no net transport of polymers. Self-diffusions can be measured by pulsed field-gradient spin-echo NMR (segments) and radioactive tracers (molecules).

Coiled molecules behave in their melts as unperturbed coils with low coil densities, which are filled with segments of other coils. Self-diffusion of a segment must therefore occur by interchanging position with a segment of another molecule.

Self-diffusion coefficients decrease with the squares of molar masses (Fig. 35). According to *reptation theory*, this functionality is caused by temporary (but fairly long-lived) entanglements of polymer chains. Such entanglements cause the sudden change of molar mass dependences of melt viscosities above a critical molar mass M_c (Fig. 35).

The resulting topological restraints make the polymer chain move through the maze of other segments like a reptile through brush. According to the Doi – Edwards theory, the test chain reptates in a tube of ca. 5-nm diameter, which is formed by other segments (Fig. 36). The theory

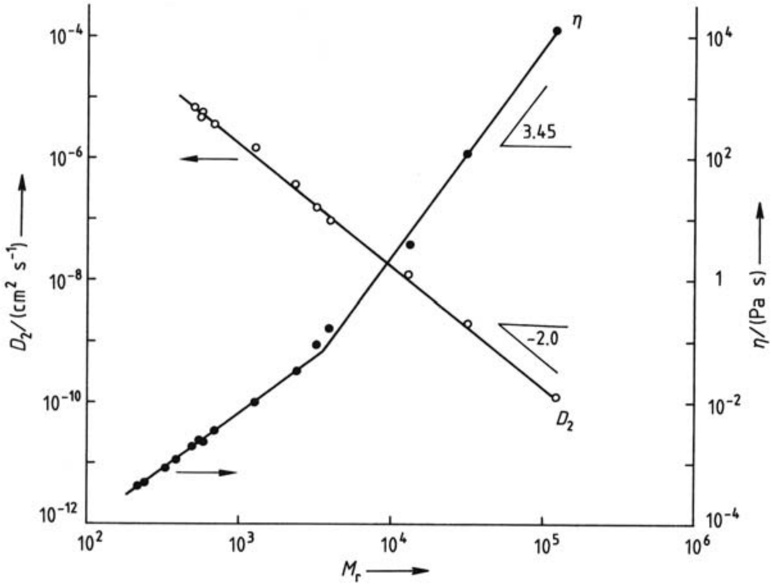

Figure 35. Segmental self-diffusion coefficients D_2 (○) and Newtonian melt viscosities η of alkanes and narrow-distribution polyethylenes (•) as function of the relative molecular mass M_r at 175 °C
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predicts the experimentally found function $D_2 = f(M^{-2})$ albeit only for $M > M_c$. Experimentally, the same function is also observed for $M < M_c$, probably because end groups cause successively greater free-volume fractions, which are assumed by the reptation theory to be molar mass independent.

The same dependence of self-diffusion coefficients of test chains on the squares of their molar masses is theoretically predicted and experimentally found for test chains in higher molar mass matrices of the same constitution and configuration ($M_{\text{test}} << M_{\text{matrix}}$); the molar mass of the matrix exerts no influence. If however $M_{\text{test}} \gg M_{\text{matrix}}$, then a function $D_{\text{test}} = f\,[(M_{\text{test}})^{-1/2} \cdot (M_{\text{matrix}})^{-1}]$ is predicted and observed.

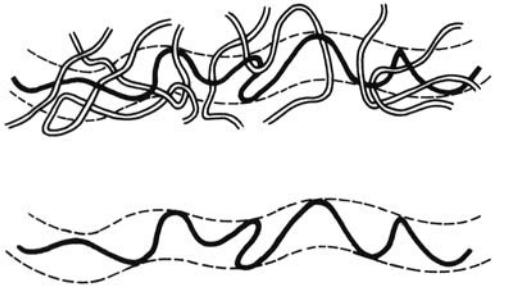

Figure 36. Reptation of a test chain (black) through the segments of a matrix (white). The "walls" of the tube are indicated by dotted lines.
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6.3.2. Permeation

The transport of extraneous material through polymers is called permeation. The resulting net flow of mass is caused by differences in chemical potentials, that is, concentration differences (at constant temperature) or thermal gradients (at constant concentration). Permeation may be desirable as in the dyeing of textiles or the controlled transdermal delivery of pharmaceuticals, or undesirable as in the loss of carbon dioxide from plastic bottles for carbonated soft drinks or in migration of plasticizers.

Permeation of chemical compounds through amorphous polymers below their glass transition temperatures or through crystalline polymers below their melting temperatures can occur either by flow through pores or by molecular transport. Pores have diameters much greater than the diameters of permeating substances (diameter of spheres, cross section of coillike chains); the interactions of permeants and pore walls are negligible. Molecular transport, on the other hand, depends on such interactions between permeant and matrix (i.e., on the solubility of the former in the latter). Both types of transport can be distinguished by their temperature dependence: permeation coefficients of gases decrease with temperature at pore membranes; they increase with temperature at solubility membranes.

The counteraction of the two types of permeation can be utilized in lamination. Oxygen permeates through pores in aluminum films but by molecular transport through polyethylene films. At 1 bar, permeation rates decrease from 5×10^{-5} cm^3/s for 0.025-mm-thick aluminum films to 5×10^{-13} cm^3/s for the same films laminated with 0.025-mm-thick PE films.

The permeation coefficient P is given by the product of the diffusion coefficient D and the solubility coefficient S of the permeant in the matrix and, in the steady state, by the expression to the right of the second equality sign:

$$P = D{\cdot}S = \frac{Q{\cdot}L}{A{\cdot}\Delta p{\cdot}t} \tag{70}$$

where Q = permeated amount, L = thickness of film (membrane, etc.), A = area, Δp = pressure difference, and t = time. The literature often uses different "practical units" for the various quantities of Equation (70), for example, Q in cm^3, L in mm, A in m^2, Δp in atm, and t in 24 h; P is then given in (cm$^3\cdot$ mm)/(24 h m^2 atm). If like units are used, then the unit of P is of course length$^2\cdot$ time$^{-1}\cdot$ pressure^{-1} and the unit of S is pressure^{-1}. Permeation coefficients P^* of liquids are usually measured without a pressure differential; their unit is cm^2/s and the unit of S is 1.

Permeation Coefficients of Gases in polymers vary widely; for example, oxygen permeates 10 million times faster through polydimethylsiloxane than through polyacrylonitrile (Table 22). Gases in general, have lower permeation coefficients in thermoplastics than in elastomers because segmental movements of the former are frozen-in below the glass transition temperature. Bulky substituents, orientation of polymer segments, crystalline domains, and added fillers all increase the pathway for a gas molecule through a polymer matrix; these tortuosity factors decrease permeation coefficients.

Table 22. Permeation coefficients of gases (P) and water vapor (P^*) through polymers at 30 °C [a]: $P=1\times10^{-14}$ cm^2 s^{-1} Pa^{-1} corresponds to $P^*=1\times10^{-9}$ cm^2/s at normal pressure ($p=1\times10^5$ Pa)

Polymer	$\frac{10^{14}P}{\text{cm}^2\text{s}^{-1}\text{Pa}^{-1}}$		$\frac{10^9P^*}{\text{cm}^2\text{s}^{-1}}$
	O_2	CO_2	H_2O
Polydimethylsiloxane	25 000	85 000	40
cis-1,4-Polyisoprene	2 000	10 000	0.3
Butyl rubber	100	500	0.1
Polystyrene			
Regular	200	1 000	1
Biaxially oriented	0.1	100	0.5
Poly(ethylene terephthalate)			
Regular	4	20	0.2
Biaxially oriented	0.2	1	0.2
Poly(vinylidene chloride)	0.05	0.15	0.02
Cellulose	0.03	0.1	10
Polyacrylonitrile	0.002	0.02	0.02
Required for bottles			
Cola	1	0.5	0.14
Beer	0.05	0.5	0.14

[a] Literature values vary widely because polymers are often not identical with respect to crystallinity, orientation, water absorption, etc.

The *permeation of nondissolving liquids* through a polymer is proportional to t^n. The exponent n depends on the ratio of the relaxation time of the polymer – solvent system to the diffusion time of the solvent (i.e., on the Deborah number DB).

Three different regimes are normally considered. In the regime denoted as *Case I*, the mobility of the permeant is much smaller than the relaxation of the polymer segments ($DB<0.1$). The movement of the permeant causes "instantaneous" conformational changes of the polymer segments. Both permeant and polymer behave as viscous liquids: the system can be described by Fickian diffusion laws (i.e., $n=1/2$).

In the *Case II* regime, the mobility of the permeant is much higher than the relaxation of the polymer segments ($DB>10$). The physical structure of the polymer does not change during the permeation; the polymer appears to the permeant as an elastic body. Case II is characterized by a sharp demarcation line between the glassy inner polymer core and the swollen zone advancing with constant speed. The permeating amount is directly proportional to time (i.e., $n=1$).

Relaxation and permeation become comparable for $0.1<DB<10$. This *third regime* is usually called anomalous diffusion or viscoelastic diffusion ($1/2<n<1$).

7. Rheological Properties

7.1. Introduction

Materials exhibit two limiting types of behavior against deformation. Typicial liquids such as water flow under their own weight and are irreversibly deformed (viscous behavior). Typical solids such as iron resist deformation; they return from small deformations to their former states after removal of loads (elastic behavior). Polymers commonly combine both types of behavior: they are viscoelastic materials. Their melts exhibit viscous behavior at small deformations and elastic properties at larger ones. Polymer solids respond elastically at small deformations but begin to flow at larger ones.

Polymer melts and solutions have extremely high viscosities which may, in addition, be dependent on deformation rates and duration of the experiment. Air has, for example, a viscosity of 10^{-5} Pa · s; water, 10^{-3} Pa · s; and glycerol, 1 Pa · s, whereas polymer melts exhibit viscosities of ca. 10^2–10^8 Pa · s.

Three types of viscosity are usually distinguished:

1. Shear viscosity describes the rate of shear flow as function of the applied stress.
2. Extensional viscosity measures the rate of extensional (elongational) flow as function of tensile stress.
3. Bulk viscosity relates the rate of deformation of volume to the applied hydrostatic pressure.

Shear Viscosities are the most often studied rheological properties of polymers; they are of great importance for the processing of plastics by extrusion or injection molding, for example. Much less is known about *extensional viscosities* (important for blow forming and fiber spinning) and practically nothing about the *bulk viscosities* of polymers.

7.2. Shear Viscosities at Rest

7.2.1. Fundamentals

Nine different shear stresses may be assigned to a three-dimensional body: one parallel to each of the three spatial directions (σ_{11}, σ_{22}, σ_{33}) and six perpendicular to these (σ_{12}, σ_{13}, etc.). A body is by definition sheared in the 2 – 1 direction. The ratio of shearing force K to contact area is called the shear(ing) stress $\sigma_{21}=K/A$; it produces a shear strain γ. The ratio $G=\sigma_{21}/\gamma$ is the shear modulus. Between layers of distance y moving parallel to each other with different rates v, a shear gradient $\dot{\gamma}=\mathrm{d}\,v/\mathrm{d}\,y$ thus exists. The ratio of shear stress to shear rate is the (dynamic) viscosity (Newton's law);

$$\eta = \sigma_{21}/\dot{\gamma} \tag{71}$$

its inverse $1/\eta$ is called fluidity.

Viscosities are independent of shear rates for Newtonian liquids ($\eta=\eta_o$); these viscosities are also called zero-shear viscosities, viscosities at rest, or stationary viscosities. For Newtonian liquids, the shear modulus G_o is independent of the extent of deformation. η_o and G_o are true material constants, whereas η and G depend on shear rates and sometimes also on shearing time.

Shear stresses and shear gradients (and thus viscosities) can be measured with a variety of instruments that usually belong to one of three groups: capillary, rotatory, and cone – plate viscometers. A number of industrially used instruments provide viscometric indicators (but neither shear stress, shear gradient, nor viscosity); this group includes Höppler viscometers, Cochius tubes, Ford beakers, and instruments that measure melt flow indices or Mooney values (Mooney viscosities).

Thermoplastics are usually characterized by their *melt flow indices* $\mathrm{MFI}_{T/F}$. The melt flow index measures the mass of polymer extruded in 10 min by a standard load F from a standard plastometer at temperature T. It is a measure of the (usually non-Newtonian) fluidity. The higher the melt flow indices, the lower are the molar masses of polymers of the same constitution.

The Mooney "viscosity" is really a measure of elasticity; it is used mainly for elastomers but also for polymer melts. A polymer is deformed in a standardized cone – plate viscometer at constant rotational speed and constant temperature T; after t minutes, the force to recover is read.

7.2.2. Molar Mass Dependence

Newtonian viscosities exhibit two different regimes for their (mass-average) molar mass dependencies $\eta_o = K \cdot M^a$: a weaker dependency (a=1/2 – 1) for low molar masses and a stronger one ($a \approx 3.4$) at higher molar masses (Fig. 35). The transition from one to the other is thought to be caused by the onset of molecular entanglements that cause the molecules to behave as physically cross-linked networks.

The number of entanglements can be assumed to be constant at low shear rates. The elasticity of such a network is described by its shear modulus G (unit of pressure). Because shear viscosities have the unit pressure · time, $\eta_o = G_o \cdot t$. The reptation model identifies the time t as the time required for a chain to leave the tube. This time is proportional to the third power of the number of segments per molecule (i.e., the viscosity should be proportional to the third power of the molar mass). The deviation between the theoretically predicted $\alpha = 3$ and the experimental value of $\alpha = 3.4$ is thought to be due to “breathing” of the tube. Breathing pushes nonentangled chain loops back into the surrounding matrix; chain ends cause additional relaxations and the tube length decreases.

7.2.3. Concentrated Solutions

Newtonian viscosities of concentrated solutions increase with both solute concentrations c and molar masses M or, since $[\eta] = K \cdot M^a$, with intrinsic viscosity $[\eta]$ as well. The concentration c measures the mass of polymer per unit volume of solution; the intrinsic viscosity, the volume of polymer molecules per unit mass of polymer. The product $c \cdot [\eta]$ is thus a measure of the volume fraction of polymer molecules that would be occupied by isolated polymer coils. At higher concentrations, coils start to overlap and the total occupied volume is smaller than the one demanded by isolated coils (i.e. $c \cdot [\eta] > 1$).

At low values of $c \cdot [\eta]$, η_i (the “specific viscosity”) and $c \cdot [\eta]$ are proportional (Fig. 37), where $\eta_i = (\eta/\eta_1) - 1$, η is the viscosity of the polymer solution at rest, and η_1 the viscosity of the solvent. At higher $c \cdot [\eta]$ values, $\eta_i \sim (c \cdot [\eta])^q$ or, since $[\eta] \sim M^a$, $\eta_i \sim c^q \cdot M^{aq}$. Because at very high concentrations $\eta_i \approx \eta/\eta_1$ and η approaches the Newtonian melt viscosity $\eta_o \sim M^{3.4}$ for high molar masses, $a \cdot q = 3.4$ is obtained. In theta solvents and melts, coils are unperturbed (a = 1/2) and q=6.8 (Fig. 37). In good solvents, a 0.764 and q=4.55. These relationships are independent of the chemical nature of polymers and solvents.

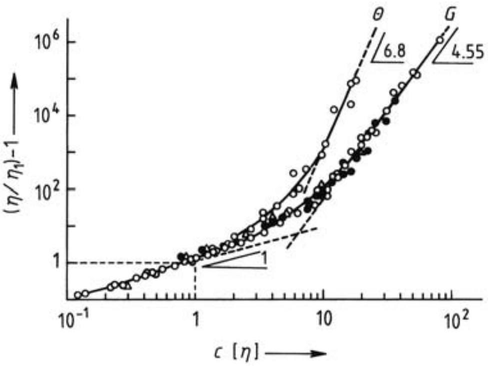

Figure 37. Relative viscosity increment (“specific viscosity”) as function of $c \cdot [\eta]$ for (○) polystyrenes in *trans*-decalin (theta solvent) or toluene (good solvent G) at 25 °C; (•) *cis*-1,4-polyisoprene in toluene at 34 °C; and (Δ) hyaluronates in water at 25 °C
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7.3. Non-Newtonian Shear Viscosities

7.3.1. Overview

The shear stress σ_{21} is directly proportional to the shear gradient $\dot{\gamma}$ for Newtonian liquids; these relationships and thus the viscosities η are moreover, independent of the duration of the experiments. Non-Newtonian viscosities (apparent viscosities), on the other hand, vary with shear rate and sometimes even with time.

Various dependencies of (apparent) viscosity on shear rate are found for time-independent non-Newtonian liquids (Fig. 38). *Plastic bodies* (Bingham bodies) exhibit a yield value y, i.e., shear stresses have finite values σ_o at $\dot{\gamma} \to 0$. Above σ_o, such bodies may behave in a Newtonian (ideal Bingham bodies) or non-Newtonian (pseudoplastic Bingham bodies) manner. This behavior seems to be due to the disappearance of aggregates. An example for a Bingham body is tomato ketchup.

In *dilatant liquids*, the shear stress increase is more than linearly proportional to shear rate; viscosities increase with shear rate (shear thickening). This behavior occurs frequently in polymer dispersions.

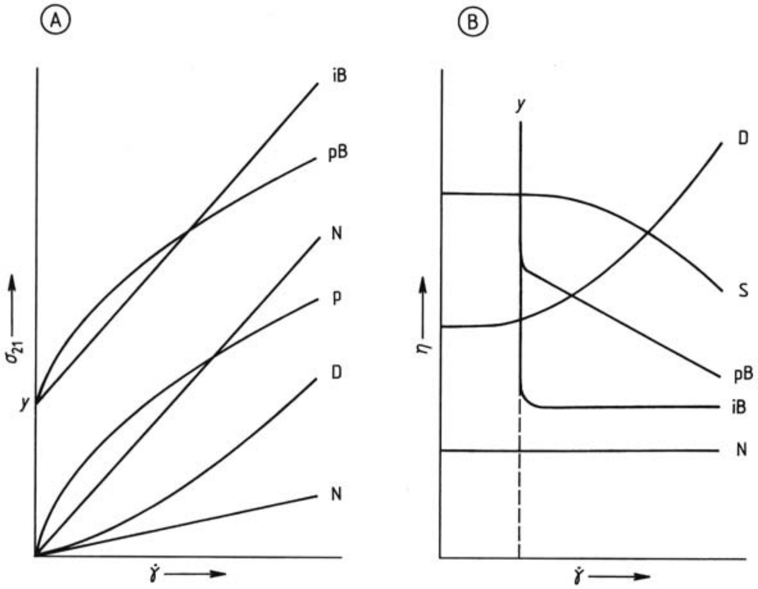

Figure 38. A) Shear stress σ_{21} and B) shear viscosity η as a function of shear rate $\dot{\gamma}$ for Newtonian (N), dilatant (D), and pseudoplastic (P) liquids and for ideal (iB) and pseudoplastic (pB) Bingham bodies (y=yield)
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A decrease of apparent viscosity with shear rate is most common for polymer melts. Because such behavior resembles that of pseudoplastic Bingham bodies, it is called *pseudoplasticity* in the English literature ("structural viscosity" in German), although such "pseudoplastic" materials do not possess a yield value. Pseudoplastic behavior eases polymer processing from melts and reduces the energy required (e.g., lower pressures can be applied in injection molding). It is usually accompanied by an orientation of chain segments that is most pronounced in the processing of liquid crystalline polymers with rigid mesogens and the ultradrawing of flexible polymers.

Dilatant and pseudoplastic liquids are characterized by "instantaneous" adoption of shear rates on application of shear stresses (i.e., by time-independent apparent viscosities). *Thixotropic materials* exhibit a decrease of apparent viscosity with time at constant shear rate; examples are dispersions of bentonite and other platelet-like silicates. *Rheopectic* or *antithixotropic* materials show an increase of apparent viscosity with time at constant shear rate. The flow behavior may be further complicated by wall effects. Certain dispersions and gels exude liquid on application of a shear stress. The liquid acts as an external lubricant and a pluglike flow results (e.g., tooth pastes). An additional complication may result from the onset of turbulence, which usually occurs at much lower Reynolds numbers in non-Newtonian than in Newtonian liquids.

7.3.2. Flow Curves

A plot of log $\dot{\gamma}=f\,(\sigma_{21})$ or vice versa is usually called a flow curve. A generalized flow curve may contain an initial Newtonian region, followed by pseudoplasticity and a second Newtonian regime. Since experiments are difficult to conduct at high shear rates, many rheologists doubt the existence of true second Newtonian regions. Dilatancy may or may not be present. Finally, turbulence sets in and melt fracture occurs (Fig. 39).

Several empirical laws have been suggested for the description of flow curves, all of which usually apply only to limited ranges of shear rates. Examples include

$$\dot{\gamma} = a\cdot(\sigma_{21})^m \text{ Ostwald–de Waele} \qquad (72)$$

$$\dot{\gamma} = b\cdot\sinh(\sigma_{21}/d) \text{ Prandtl–Eyring} \qquad (73)$$

$$\dot{\gamma} = f\cdot\sigma_{21}+g\cdot(\sigma_{21})^3 \text{ Rabinowitsch–Weissenberg} \qquad (74)$$

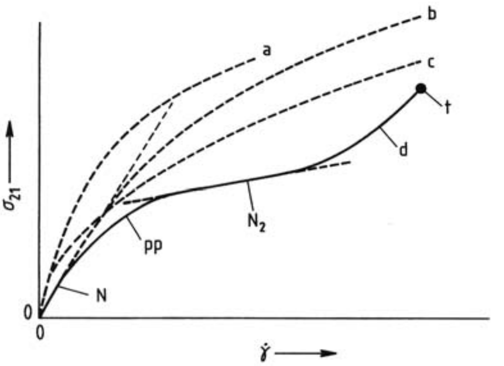

Figure 39. Generalized flow curve with first Newtonian region (N), pseudoplasticity (pp), second Newtonian region (N_2), dilatancy (d), and onset of turbulence (t)
- - - Schematic representations of various viscosity "laws": a) Prandtl – Eyring; b) Rabinowitsch – Weissenberg; c) Ostwald – de Waele
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where *a, b, d, f, g*, and *m* are empirical constants. The exponent *m* is known as the "flow exponent"; it takes a value of 1 (Newtonian liquid) and < 1 (pseudoplasticity). No constitutive equations are known that cover the entire range of rheological phenomena.

7.3.3. Melt Viscosities

Polymers below the critical molar masses M_c for entanglements show extended Newtonian ranges. For $M>M_c$, non-Newtonian behavior appears at lower shear rates as molar mass increases (lower melt flow index) (Fig. 40). At high shear rates, a constant exponent q is approached for the function $\eta=f(\gamma^q)$. The non-Newtonian viscosities are no longer proportional to the mass-average molar masses; the broader the molar mass distribution, the more the number average seems to be the correct corresponding quantity.

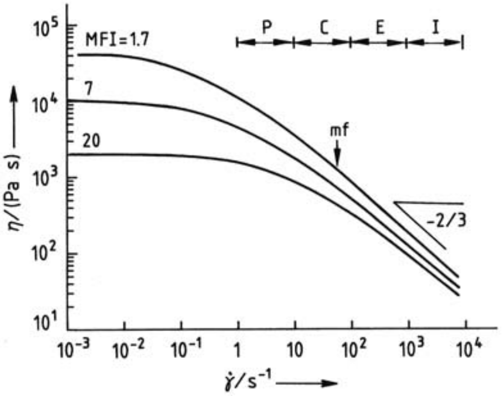

Figure 40. Dependence of melt viscosities of polyethylenes with different melt flow indices (MFI, inversely proportional to molar mass) on shear rates (mf=onset of melt fracture for the highest molar mass polyethylene)
The ranges of the various processing regimes overlap: P=compression molding, C= calendering, E=extrusion, I=injection molding. Shear rates refer to those at orifices and are much lower in the mold (tool, die).
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The decrease of apparent viscosity with shear rate is very important for plastics processing. Viscosities describe a frictional behavior: the higher the viscosity, the higher is the internal friction of the melt and the greater is the proportion of energy provided that is converted into heat. Strong non-Newtonian behavior thus saves energy. Polymer melts are therefore processed at the highest possible shear rates. The upper range is given by the processing method (calendering, extrusion, etc.), and the polymer properties (thermal degradation, melt fracture, etc.).

Surface roughnesses of barrel walls, diameter changes, etc., create additional rate components in extrusion that are dampened by the viscosity of the liquid. These disturbances become stronger with increasing flow rate and can no longer be dampened at high shear rate. Finally, turbulence sets in. In entangled polymer melts, additional elastic vibrations occur due to the presence of physical cross-links. The resulting elastic turbulences lead to rough surfaces of the extrudate, which are subsequently frozen-in upon exit from the orifice. The polymer surface appears "fractured"; "melt fracture" thus does not refer to a breakage of the extrudate strand.

Molecular coils are deformed if their melt is pressed through an orifice (Fig. 41). For $M>M_c$, segments can no longer slip from each other at

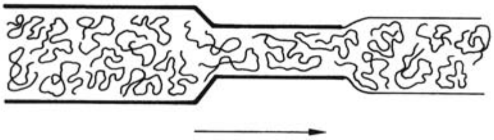

Figure 41. Parison swell upon extrusion (Barus effect)
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high stresses and short times because of entanglements; a "normal" stress builds up perpendicular to the stress direction. At the die exit, this stress is relieved and the coil returns to the thermodynamically more favorable shape of an unperturbed coil. The melt expands perpendicular to the flow direction. This phenomenon is known as Barus effect or memory effect (melts), the Weissenberg effect (solutions), parison swell (extrusion), swelling (blow molding), etc. It is especially pronounced for high molar mass tails in polymers with $M > M_c$ because of the 3.4 power dependence of η on $\bar{M}_w$.

Negative Barus effects are known for solutions of rodlike molecules or LCPs with rodlike mesogens (diameter of strand smaller than diameter of orifice). If such molecules crystallize after exiting from the die, the strand contracts perpendicular to the extrusion direction and the strand diameter becomes smaller than the diameter of the orifice.

The effect of normal stress can be determined by the Bagley equation. A force $F_f = \pi R^2 p$ is exerted on a liquid during the flow through a capillary with radius R and length L under a pressure p. It is counteracted by a frictional force $F_r = 2\pi RL\sigma_{21}$. In steady state, $F_f = F_r$; thus $p = 2\sigma_{21}(L/R) = 2\eta \cdot \dot{\gamma} \cdot (L/R)$ since $\sigma_{21} = \eta \cdot \dot{\gamma}$. In the Bagley diagram, pressure p is accordingly plotted at constant shear rate against die geometry L/R (Fig. 42). For non-Newtonian liquids, a relationship

$$p = p_o + K \cdot (L/R) \tag{75}$$

is found. The intercept p_o at $L/R \to 0$ is identified with the pressure loss caused by the elastically stored energy of the flowing melt and the formation of a steady-state flow profile at both ends of the capillary (die). The higher L/R is, the higher must the applied pressure be. Die lengths should thus be as short as possible.

7.4. Extensional Viscosities

7.4.1. Fundamentals

Polymer liquids can be elongated considerably without being broken. This extensibility allows fiber spinning from melts and solutions, blow molding of hollow bodies, vacuum forming of parts, etc.

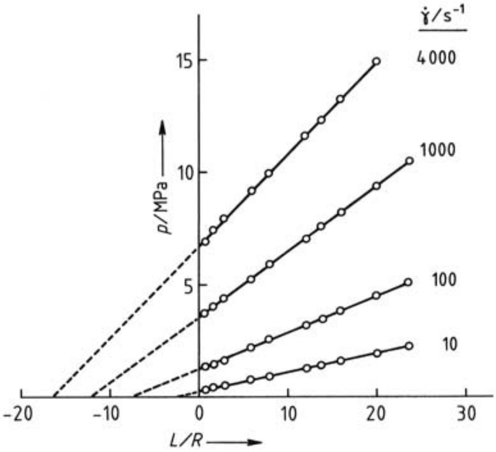

Figure 42. Bagley diagram for a high-impact polystyrene at 189 °C and different shear rates
The intercept at $L/R \to 0$ is the pressure correction; the intercept at $p \to 0$, the Bagley correction.a) $\dot{\gamma} = 4000\ s^{-1}$; b) $\dot{\gamma} = 1000\ s^{-1}$; c) $\dot{\gamma} = 100\ s^{-1}$; d) $\dot{\gamma} = 10\ s^{-1}$
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The extensional viscosity η_e (elongational viscosity) is given by the ratio of tensile stress σ_{11} in draw direction 11 to the elongational rate $\dot{\varepsilon}$

$$\eta_e = \sigma_{11}/\dot{\varepsilon} \tag{76}$$

The type of deformation must always be indicated for extensional viscosities, contrary to shear viscosities. The three principal deformation rates can be defined in such a way that $\dot{\varepsilon}_{11} \geq \dot{\varepsilon}_{22} \geq \dot{\varepsilon}_{33}$. The ratio $m = \dot{\varepsilon}_{22}/\dot{\varepsilon}_{11}$ characterizes the special type of elongational flow: theory gives $m = -1/2$ for uniaxial elongation, $m = 1$ for equal-biaxial, and $m = 0$ for planar (pure shear). Uniaxial elongational viscosities are important for fiber spinning; they are the only ones used to characterize fluids. Biaxial elongational viscosities play an important role in blow and vacuum forming; very little is known about them.

The elongation in Equation (76) is the true strain $\varepsilon' = \ln(L/L_o)$ (Hencky strain) and not the nominal strain $\varepsilon = (L - L_o)/L_o$ (Cauchy strain, engineering strain). The rate of elongation is thus $\dot{\varepsilon} = \mathrm{d}\varepsilon/\mathrm{d}t = \mathrm{d}\ln L/\mathrm{d}t = L^{-1}(\mathrm{d}L/\mathrm{d}t)$.

Extensional viscosities are very difficult to measure. Elastomers and melts of entangled polymer coils can be stretched between rotating rollers. Extensional viscosities of solutions can be determined if two liquid jets streaming toward each other are redirected by rollers or siphoned off.

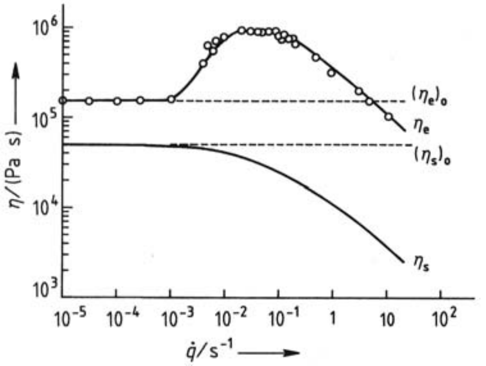

Figure 43. Shear viscosity η_s as function of shear rate $\dot{q}=\dot{\gamma}$, and extensional viscosity η_e as function of the uniaxial extensional rate $\dot{q}=\dot{\varepsilon}$ of a polyethylene at 150 °C
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7.4.2. Melts

Extensional and shear viscosities depend very differently on deformation rates. At low rates, extensional viscosities are independent of the rate of extension (Fig. 43). The uniaxial extensional viscosity at rest (historically called "Trouton viscosity") is three times the Newton viscosity $[(\eta_e)_o=3\ (\eta_s)_o]$, whereas the biaxial extensional viscosity at rest is six times its shear counterpart.

Above a critical deformation rate, shear thinning is observed for the shearing and extension of melts of linear coil molecules. At the same rate, melts of branched coil molecules become dilatant on extension. The apparent extensional viscosities then pass through a maximum and decrease with further increase of extension rates. The maximum of the extensional viscosity increases with broader molar mass distribution and increased long chain branching, which indicates the strong influence of entanglements on extensional viscosities.

7.4.3. Solutions

Rodlike Molecules and Segments are increasingly oriented in the extensional direction with increasing elongational rates. The molecular axes are no longer distributed at random, and the solution becomes anisotropic and thus birefringent. A limiting value is asymptotically reached if all molecular axes are completely aligned in the flow direction.

Flexible Molecules in solution are only slightly deformed and oriented at comparable extension rates because elastic (entropic) forces cause the chains to return to the thermodynamically favored coil shape. At high critical extension rates, these retraction forces can be overcome and the chain axes become oriented in the flow direction. Only an incremental increase of extension rates is needed to orient the chains completely. Molecules are stressed more and more above the critical extension rates until they finally break. This fracture occurs primarily in the middle of the molecule so that degradation products possess 1/2, 1/4, 1/8, etc., of the initial molar mass. Such degradation occurs under very low deformation rates for rigid macromolecules, for example, during pipetting of dilute solutions of high molar mass deoxyribonucleic acids.

These degradations by extensional flow are not caused by turbulence because they happen at lower Reynolds numbers than those of pure solvents. Chain degradations by turbulence do occur on shearing of very dilute solutions of flexible coil molecules (e.g., 10^{-4} g/mL aqueous solutions of polyoxyethylenes). The degradation reduces the frictional resistance of liquids up to 75 %. This "Toms effect" by added small amounts of such polymers eases the flow of crude oil through pipelines and increases the distance and height to which water can be directed at fires.

8. Mechanical Properties

8.1. Introduction

8.1.1. Deformation of Polymers

Mechanical properties of a polymer include the deformation of bulk polymers or their surfaces, the resistance to such deformation, and the fracture under static or dynamic loads. Deformations may be reversible or irreversible; they can be caused by drawing, shearing, compression, bending, and torsion, as well as by combinations of these.

Reversible deformations are due to the presence of elasticity. Irreversible deformations are also called inelastic; they are further subdivided into deformation by viscous flow, plasticity, phase transformations, craze formation, cracking, viscoelasticity, creep, etc. An inelastic deformation of metals by viscoelasticity is known as anelasticity; in polymer physics, anelasticity denotes a reversible elasticity with retardation, which does not lead to energy dissipation. Deformation of the upper layers of a polymer body is characterized by its "hardness," which influences friction and abrasion.

The term elasticity may refer to either energy or entropy elasticity. These elasticities differ in their molecular mechanisms and the resulting phenomenological behavior. In *energy-elastic bodies* (steel, plastics, and elastomers at low strains), torsion and bond angles are changed and bond distances are enlarged on deformation, whereas the macroconformations of chains, for example, remain basically the same. A deformation of *entropy-elastic bodies* (elastomers at high strains), on the other hand, leads to entropically unfavorable positions of chain segments which, however, cannot slip irreversibly from each other because of their cross-linking ("rubber elasticity"). The deformation thus changes the macroconformation (molecular picture), decreases entropy (thermodynamics), and creates normal stresses (mechanics).

These molecular changes are reflected in the properties of energy- and entropy-elastic materials:

	Energy-elastic	Entropy-elastic
Elastic moduli	large	small
Reversible deformation	small	large
Temperature change on deformation	cooling	warming
Length change on heating	expansion	contraction

The deformation behavior of plastics depends on the molar mass of their constituting polymers and on the testing temperature: That is, whether the molar mass is greater than the one needed for the establishment of entanglements between chains ($M > M_{\mathrm{ent}}$) and whether the testing temperature is lower than the glass transition temperature of the polymers ($T < T_{\mathrm{G}}$). All mechanical deformations recover for $M > M_{\mathrm{ent}}$ and $T < T_{\mathrm{G}}$ since chain entanglements cannot reorganize below the glass transition temperature (memory effect). Yielded plastics and crazed plastics recover on (not too long) heating above the glass transition temperature. These plastics thus do not show true plastic flow.

8.1.2. Tensile Tests

Mechanical properties of polymers are most commonly evaluated by tensile tests in which a specimen is drawn with constant speed. The tensile stress σ_{11} is recorded as a function of time t, draw ratio (strain ratio) $\lambda = L/L_{\mathrm{o}}$, or tensile strain (elongation) $\varepsilon = (L{-}-L_{\mathrm{o}})/L_{\mathrm{o}} = \lambda - 1$. If a specimen is extended to $L = 2.5\ L_{\mathrm{o}}$ of the original length L_{o}, then it is said to have been drawn by 150 %.

The tensile stress of *elastomers* increases continuously with increasing tensile strain until the polymer finally ruptures at σ_{R} and ε_{R} (Fig. 44). Typical *thermoplastics* (and most fibers) follow Hooke's law

$$\sigma_{11} = (F/A_{\mathrm{o}})\cdot\varepsilon = E\cdot\varepsilon \tag{77}$$

for small strains (up to point I), where A_{o} is the original cross section of the specimen, F is the force, and E is the tensile modulus (Young's modulus). Point I is thus called the proportionality limit or elastic limit; it is defined for a remaining strain of 0.1 % after removal of the stress.

The maximum of the stress – strain curve is called the upper yield (point II), and the subsequent minimum is the lower yield (point III). The ratio of upper yield stress σ_{S} to tensile modulus E is practically constant for all polymers; the numerical value of $\sigma_{\mathrm{S}}/E \approx 0.025$ suggests that van der Waals bonds are broken and molecule segments begin to move more freely.

Brittle polymers break at the upper yield. Tough polymers continue to extend and the stress either remains constant (see below) or decreases. The latter phenomenon is called stress softening. It is typical for polymers with neck formation (telescope effect) and is nominal since it disappears if the stress is given relative to the actual cross section instead of the initial one.

The region between points III a – II – III is known as the ductile region; its area describes the absorbed energy and thus the toughness of the specimen. The subsequent increase of stress with strain is called stress hardening. At point IV, the ultimate strength (tensile strength, tenacity at break) σ_{B} and ultimate elongation (elongation at break) ε_{B} occur.

Stress – strain curves may differ considerably for plastics. Polymers with high Young's moduli (steep initial slopes) are called hard polymers; those with low moduli, soft; this hardness should not be confused with surface hardness. Typical

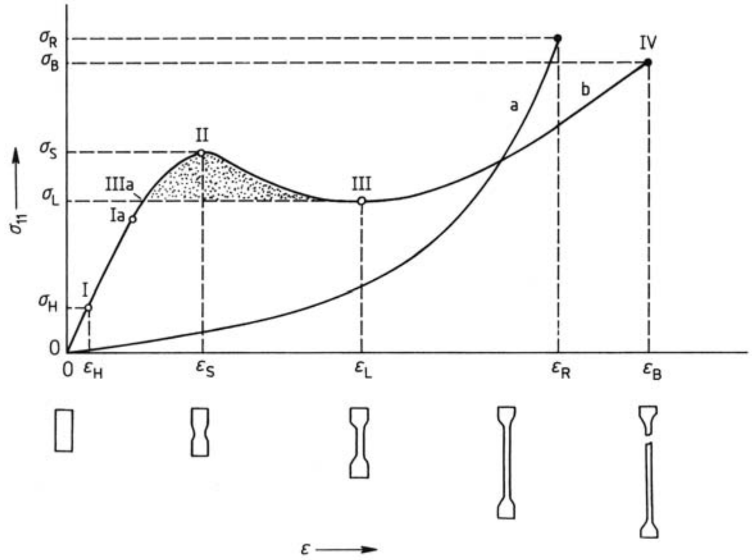

Figure 44. Stress – strain curves of an elastomer (a) and a partially crystalline thermoplastic (b) (schematic) (for further explanation, see text)
The necking effect shown below is characteristic for conventional thermoplastics; it is not found for elastomers and hard-elastic thermoplastics.
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hard polymers are phenolics [phenol – formaldehyde (PF)], polyacetals [polyoxymethylene (POM)], polycarbonates (PC), and poly(ethylene terephthalates) (Fig. 45). Polymers are further characterized by their stress – strain behavior between upper yield and failure. Polymers without yield cannot absorb energy and thus break easily; they are hard-brittle polymers (e.g., PF).

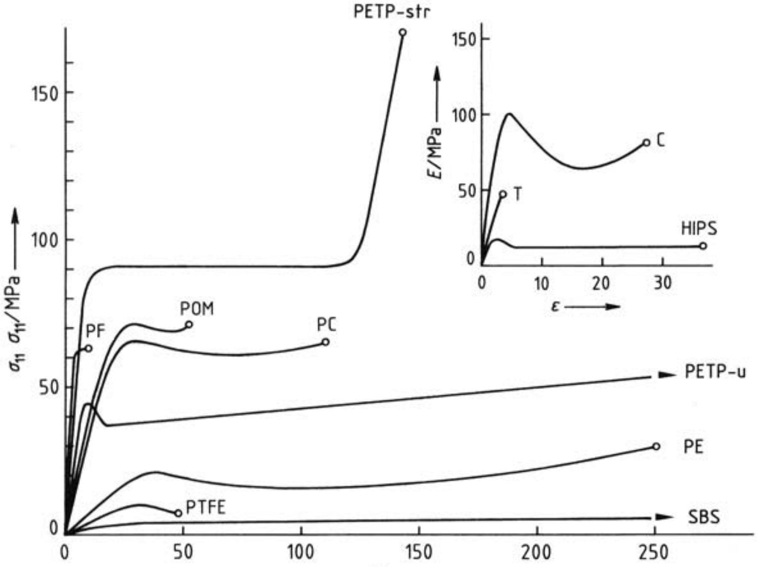

Figure 45. Stress – strain curves of polymers at room temperature (see text for explanation)

Polycarbonates, on the other hand, show an extended ductile region and a fairly high fracture strain; they are called hard-tough. Polyethylene is similar with respect to ductile behavior and strain hardening; the modulus is however much lower, and PE is considered soft-tough.

The stress – strain behavior described above is typical for tensile experiments. Tensile stresses lead to strong deformations in neck zones and cause microscopic voids at which fracture originates. Atactic polystyrene (PS) is such a hard-brittle polymer under tension *T*. No voids can be formed, however, under compression *C*, and PS appears as a hard-tough material (Fig. 45, insert). Rubber modification of PS leads to high-impact polystyrene (HIPS), which behaves quite differently from PS under tension (see Section 8.6.4).

No yield value is found if drawn polymers are further subjected to tensile tests. In biaxially stretched poly(ethylene terephthalate) (PETP-str) some chain segments are already oriented, whereas other remain in their original positions. Biaxially stretched films are thus under stress, which is utilized in shrink films. Such films are used for the packaging of goods. On heating semicrystalline polymers above the glass transition temperature and below the melting temperature, chain segments become more mobile. Molecules attempt to attain their unperturbed dimensions and the films shrink, covering the goods tightly.

8.1.3. Moduli and Poisson Ratios

Elasticities can be described by three elastic moduli: tensile modulus or Young's modulus *E*, shear modulus *G*, and bulk modulus or compressive modulus *K*. Their values are inversely proportional to the corresponding compliances for static deformations (but not for dynamic ones):

Moduli	Compliances
$E=\sigma_{11}/\varepsilon$	$D=1/E$
$G=\sigma_{21}/\gamma$	$J=1/G$
$K=p/(-\Delta V/V_o)$	$B=1/K$

Table 23. Poisson ratios and elastic constants of various materials

Material	μ	E/GPa	G/GPa	K/GPa
Water	0.50	≈ 0	≈ 0	≈ 2
Gelatin (80 % water)	0.50	0.002		
Natural rubber	0.495	0.0009	0.0003	≈ 2
Polyethylene, LD	0.49	0.20	0.070	3.3
Polystyrene	0.38	3.4	1.2	5.0
Granite	0.30	30	12	25
Steel	0.28	211	80	160
Glass	0.23	60	25	37
Quartz	0.07	101	47	39
Aluminum oxide fibers	0	2000	1000	667

The three simple moduli are related to each other for small deformations of simple isotropic bodies:

$$E = 2G\cdot(1+\mu) = 3K\cdot(1-2\mu) \qquad (78)$$

where $\mu=(\Delta\, d/d_o)/(\Delta\, L/L_o)$ is the Poisson ratio (Poisson number), *d* is the diameter, and *L* is the length of the specimen. Poisson ratios can only adopt values $0<\mu<1/2$ for isotropic bodies but may assume $\mu>1/2$ for anisotropic ones. Equation (78) is invalid for anisotropic bodies and viscoelastic materials; $E/3<G<E/2$ and $0<K<E/3$, are however, still valid for these materials.

Common polymers behave with respect to μ, *E*, *G*, and *K* more like liquids than like metals (Table 23). Ultradrawn and self-reinforcing polymers may however exhibit tensile moduli that exceed those of steel (see below).

8.2. Energy Elasticity

8.2.1. Theoretical Moduli

The tensile moduli of common polymers are far lower than the theoretical moduli deduced from their chemical and physical structures (Table 24). Such theoretical moduli can be calculated from bond lengths, valence angles, and force constants for the deformation of these quantities. The

Table 24. Modulus of elasticity

Polymer	$E_{\parallel}$/GPa			$E_{\perp}$/GPa
	Theory	Lattice	Tensile	Lattice
Polyethylene	340	325	< 1	3.4
Polypropylene, it	50	42	< 3	2.9
Polyoxymethylene				
Orthorhombic	220	189	< 2	7.8
Trigonal	48	54	2	
Poly(*p*-phenylene terephthalamide)	182	200	132	10
Poly(4-methylpentene)	6.7		1	2.9

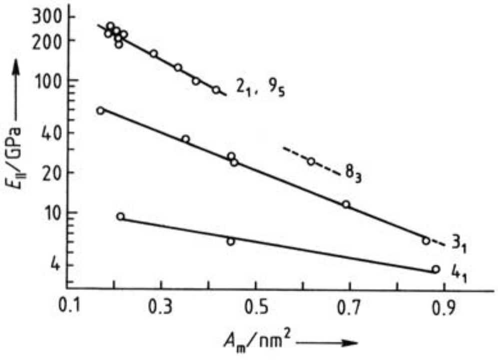

Figure 46. Longitudinal lattice moduli $E_{\|}$ as function of cross-sectional area A_m of polymer chains in all-*trans* (2_1) or helical conformations (9_5, 8_3, 3_1, 4_1) of their main chains Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

theoretical moduli agree well with the microscopic lattice constants, which are determined experimentally by X-ray diffraction (change of Bragg reflexes), Raman spectroscopy, or inelastic neutron scattering under load. The longitudinal theoretical moduli $E_{\|}$ are far greater than the transverse moduli $E_{\perp}$ because the former are controlled by covalent bonds and the latter by van der Waals forces.

The larger the cross-section of the single polymer chain, the larger is the force distributed to fewer chains per unit area and the smaller are the moduli (Fig. 46). Chains in the all-*trans* conformation always exhibit higher theoretical moduli than do helical chains since the elongation of the former changes bond angles, whereas the extension of the latter involves only lower-energy torsion angles.

Polyethylene has the highest theoretical modulus of all one-dimensional chains ($E_{\|}=340$ GPa), about one-third that of diamond ($E_{\|}$ 1160 GPa) with its "naked" carbon chains. Polypropylene has the highest theoretical modulus of helical chains ($E_{\|}=50$ GPa).

Moduli approaching these theoretical values have been realized by ultradrawing of mats of polyethylene single crystals, giving polymers with $E_{\|}=240$ GPa. Industrially, high-modulus polyethylene fibers are manufactured by gel spinning of ultra-high molecular polyethylene ($E_{\|}=$ 97 GPa$\triangleq$90 N/tex, 1 tex=1 g per 1000 m).

8.2.2. Real Moduli

The much lower tensile moduli of conventionally processed polymers result from their disordered physical structures. In amorphous polymers, chain segments are oriented at random. Even in partially crystallized polymers, amorphous layers exist and chain axes (stems of lamellae) are distributed at random. The moduli of flexible polymers can be increased somewhat by processing under external force fields, for example, by partial orientation of chain segments during fiber spinning (Table 25, column L). Extrusion of solid polymers is a particularly effective method: the longitudinal modulus of polyoxymethylene increased to 24 GPa from 2 GPa on hydrostatic extrusion.

Rodlike mesogens of liquid semiflexible polymers align in mesophase domains. The domains orient themselves in shear fields; the orientations can be frozen-in to LCP glasses. Such self-or-

Table 25. Moduli and fracture strengths of conventional polymers as isotropic molding masses (I) or in draw direction of fibers (L) and of thermotropic (TT) and lyotropic (LT) glasses longitudinal (L) and transverse (T) to draw direction compared to isotropic polymers (I)

Polymer	*E*/GPa			σ_B/MPa		
	L	T	I	L	T	I
PE-LD	?	?	0.15	?	?	23
PA 6.6	13	?	2.5	1000	?	74
PETP	19	?	0.13	1400	?	54
TT X 7 G [a]	54	1.4	2.2	151	10	63
TT Vectra [b]	11	2.6	5.0	144	54	97
LT Kevlar [c]	138	7	?	2800	?	?
LT PPBT [d]	120	17	62	1500	680	700

[a] X 7 G=poly(*p*-hydroxybenzoate-*co*-ethylene terephthalate).

[b] Vectra=poly(*p*-hydroxybenzoate-*co*-2-hydroxy-6-naphthalate).

[c] Kevlar 49=poly(*p*-phenylene terephthalamide).

[d] PPBT=30 % poly(*p*-phenylene benzbisthiazole) in poly(2,5-benzimidazole).

ienting polymers possess much higher moduli in the longitudinal direction than conventionally processed flexible polymers (Table 24). Their transverse moduli are also higher because of intermolecular dipole – dipole interactions.

8.2.3. Temperature Dependence

Young's moduli change characteristically with temperature for the various classes of polymers (Fig. 47). Five characteristic ranges can be distinguished: glassy (GL), leatherlike (LE), rubbery (RE), viscoelastic (RF), and viscous (VF).

Amorphous Polymers. Moduli (0.1 – 1 GPa) are practically independent of temperature below the glass transition temperature T_G but drop to 10^5–10^6 Pa at $T = T_G$; the polymer appears leathery around T_G and rubbery above the glass transition temperature. The rubbery region is maintained for entangled (high molar mass) polymers but is nonexistent for low molar masses ($M < M_c$). Moduli decrease on further temperature increase until the polymers behave like viscous liquids ($E \approx 10^3$ Pa).

Elastomers. At use temperatures, these polymers are above their T_G's and thus behave like cross-linked thermoplastics above the T_G's of the latter. The decrease in modulus at T_G is limited by (and a measure of) the degree of cross-linking. At higher temperatures, elastomers decompose and the moduli decrease drastically.

Crystalline Polymers have only a weak leathery region around T_G since their amorphicity is slight and their crystallites act as physical cross-linkers. The modulus at the beginning of the rubbery plateau is a measure of the degree of crystallinity. The moduli decrease slowly during the rubbery "plateau" because more and more crystallites are molten. The remaining crystallites practically disappear at the melt temperature: the moduli drop drastically and the polymers behave like viscous liquids.

Thermosets. Thermosets are highly cross-linked polymers. They have high Young's moduli below T_G, usually one decade higher than thermoplastics. A very weak glass transition is accompanied by a somewhat leathery behavior.

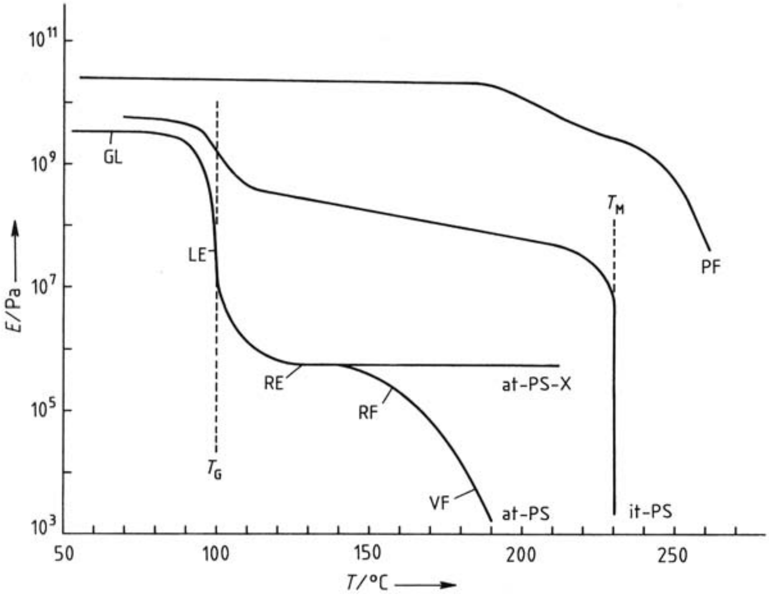

Figure 47. Temperature dependence of Young's moduli for conventional polymers
at-PS=Amorphous (atactic) polystyrene ($M > M_c$); at-PS-X=Its slightly cross-linked product; it-PS=Partially crystalline (isotactic) polystyrene; PF=Hardened phenol – formaldehyde resin; GL=glasslike; LE=leatherlike; RE=rubber (entangled); RF=viscoelastic; VF=viscous flow
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The subsequent rubbery region is not very marked because the cross-linking density is high.

8.3. Entropy Elasticity

Elastomers show pronounced entropy elasticities. They exhibit simultaneously some characteristics of solids, liquids, and gases. Like solids, they display Hookean behavior at not too high deformations (i.e., they show no permanent deformation after removal of the load). Moduli and expansion coefficients, on the other hand, resemble those of liquids. Like compressed gases, stresses increase with increasing temperature for elastomers at $T>T_G$.

The elastic behavior can be modeled with various theories. In the simplest case, dislocations of network junctions are assumed to be affine to the macroscopic deformation of the network. The tensile stress σ_{11} varies with the elongation $\lambda = L/L_o$ according to

$$\sigma_{11} = RT \cdot [M_c] \cdot (V_o/V)^{-1/3} (\lambda - \lambda^{-2}) \tag{79}$$

It depends on the volumes before (V_o) and after (V) deformation and on the molar concentration $[M_c]$ of network junctions. True Young's moduli can be obtained from the limiting value of $\sigma_{11}/(\lambda - \lambda^{-2})$ at $\lambda \rightarrow 1$, for example, for volume-constant deformations ($V_o/V = 1$):

$$\begin{aligned} RT \cdot [M_c] &= \lim_{\lambda \to 1} [\sigma_{11}/(\lambda - \lambda^{-2})] \\ &= \sigma_{11}/[3(\lambda - 1)] = \sigma_{11}/(3\varepsilon) = E_o \end{aligned} \tag{80}$$

The Young's modulus is thus directly proportional to the molar concentration of network junctions (cross-linking sites), independent of the nature of the latter. On shearing, elastomers behave like Hookean bodies because

$$RT \cdot [M_c] = \sigma_{21}/\gamma = G \tag{81}$$

They are, however, non-Hookean for elongations because $E_o \neq \sigma_{11}/\varepsilon$ (Eq. 80).

8.4. **Viscoelasticity** (→ Plastics, Properties and Testing)

8.4.1. Fundamentals

Most polymers do not revert "instantaneously" to their initial states after the removal of loads; they are neither ideal energy elastic (Section 8.2) nor ideal entropy elastic (Section 8.3). These processes take certain times, (i.e., time-independent elastic and time-dependent viscous properties work together to produce a viscoelastic behavior). If stress, strain, and strain rate can be combined linearly, then the process is said to be linear elastic. In addition, some polymers may be irreversibly deformed.

The two ideal cases of response to deformations can be well described by mechanical models: a spring for a Hookean body (instantaneous response) and a dashpot for a Newtonian liquid (linear time dependence of response) (Fig. 48). The Maxwell element combines spring and dash-

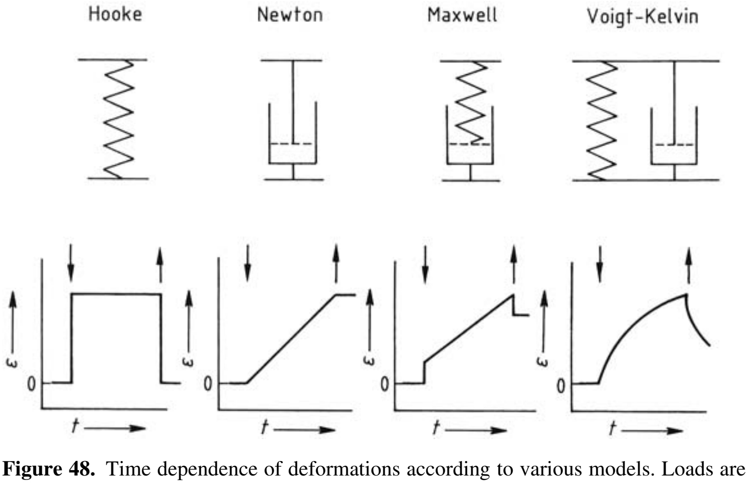

Figure 48. Time dependence of deformations according to various models. Loads are added at ↓ and removed at ↑ Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

Table 26. Simple mechanical models for the deformation of polymers

Model	Function	Behavior [a]	
		Initial	Final
Newtonian liquid	$\sigma = \eta\cdot\dot{\gamma}$	L	L
Voigt – Kelvin element	$\sigma = G\cdot\gamma+\eta\cdot\dot{\gamma}$	L	S
Maxwell element	$\sigma+(\eta/G)\cdot\dot{\sigma} = \eta\cdot\dot{\gamma}$	S	L
Hookean body	$\sigma = G\cdot\gamma$	S	S
Jeffrey's body	$\sigma+(\eta/G)\cdot\dot{\sigma} = G\cdot\gamma+\eta\cdot\dot{\gamma}$	S	S

[*] S=solid-like behavior; L=liquid-like.

pot in a series; the Voigt – Kelvin element, in a parallel manner.

The Maxwell element describes a *relaxation* (i.e., the decrease of stress at constant deformation; Table 26). Linear combination of elastic deformation rates $d\gamma_e/dt=(1/G)\ (d\sigma/dt)$ and viscous deformation rates $d\gamma_\eta/dt=\sigma/\eta$ yields, after integration of the resulting expression and indexing the time for this particular behavior for $d\gamma/dt=0$,

$$\sigma = \sigma_0\cdot\exp(-G\cdot t_e/\eta) = \sigma_o\cdot\exp(-t_e/\tau) \tag{82}$$

The relaxation time $\tau=\eta/G$ indicates the time after which the stress has fallen to the e_{-1}th fraction of its initial value. The ratio τ/t_e of the relaxation time τ to the time scale t_e of the experiment is called the Deborah number ($DB=\tau/t_e$); it is 0 for liquids, ∞ for ideal-elastic solids, and approximately 1 for polymers near their glass transition temperatures.

Retardation is defined as the increase of deformation with time at constant stress. It is characterized by a "creep" of the material. Since this phenomenon was first observed on seemingly solid polymers at room temperature, it is also called "cold flow." In principle, retardation phenomena can be described by a Maxwell element. Because of mathematical difficulties in the solution of the equations, a special model is prefered (Voigt – Kelvin element) (Fig. 48), which yields for the deformation γ_r at constant stress σ_o after indexation for retardations r

$$\gamma_r = (\sigma_o/G_r)\cdot[1-\exp(-G_r\cdot t_r/\eta)] \tag{83}$$

where G_r is the retardation modulus, also often called the relaxation modulus. The retardation time t_r indicates the time at which the deformation has reached $(1-1/e)=0.632$ of the final deformation σ_o/G_r. Retardation times and relaxation times are of the same magnitude, but not equal because they rely on different models.

The term "viscoelasticity" is sometimes used to describe the reversible deformation according to Equation (83). However, it is often applied to the total deformation, which is composed of the contributions by Equation (83), a Hookean body with $\gamma_e=\sigma_o/G_o$, and a Newtonian liquid [$\gamma_\eta=(\sigma_o/\eta_o)\cdot t$]:

$$\begin{aligned}\gamma_{tot} &= \{(1-G_o)+(t/\eta_o)+(1/G_r)\cdot[1-\exp(-t/\tau)]\}\cdot\sigma_o \\ &= \gamma_e+\gamma_\eta+\gamma_r\end{aligned} \tag{84}$$

The three deformation terms γ_e (elastic), γ_η (viscous), and γ_r (viscoelastic) are often not explicitly evaluated. The time-dependent viscous and viscoelastic parts are rather combined into a new parameter $\gamma_c=\gamma\cdot t^n$ (Findlay law). The resulting function for the creep curve allows an extrapolation to long-time behavior from short-time experiments:

$$\gamma_{tot} = \gamma_e+\gamma_c = \gamma_e+\gamma\cdot t^n \tag{85}$$

8.4.2. Time – Temperature Superposition

Deformations, shear moduli, and shear compliances are time and temperature dependent (Fig. 49). The moduli vary about one decade for six decades in time at constant temperature, and up to one decade for each 10 K at constant frequency. Since no single experimental method can cover the 15 – 20 decades of frequency that are required for good characterization of a polymer, time – temperature data from various techniques are usually combined with the help of the Boltzmann superposition principle.

This principle states that the deformation (or recovery) caused by an additional load (or removal thereof) is independent of previous loads or their removal. The $G=f\,(t, T)$ curves can be combined if (1) the relaxation time spectrum is temperature independent and (2) the thermal activation is the same over the entire time and temperature range (no transition or relaxation temperatures). A reference temperature is chosen close to the static glass transition temperature (115 vs. 105 °C in Fig. 49) and the G values are shifted horizontally with the help of a shift factor from the WLF equation (Eq. 69).

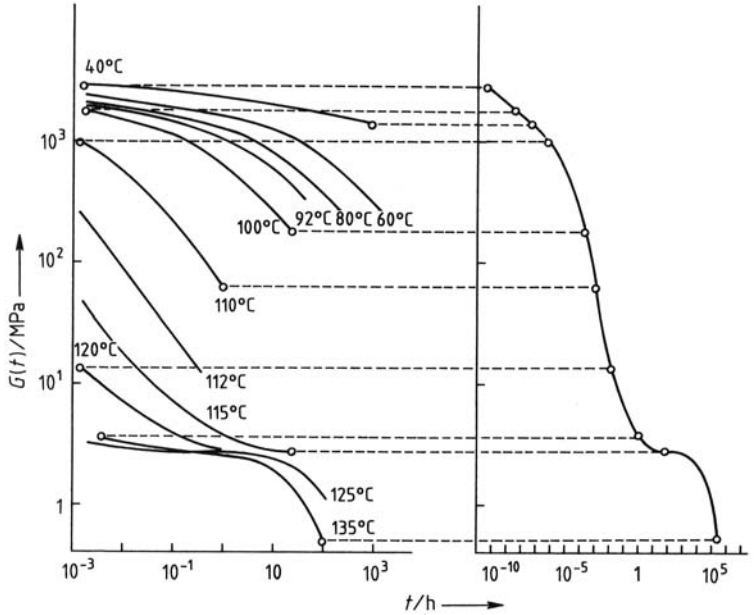

Figure 49. Time dependence of the shear modulus from measurements of the stress relaxation of a poly(methyl methacrylate) ($\bar{M}_v$=3 600 000 g/mol) at various temperatures (left) and the resulting time – temperature superpositions for a reference temperature of 115 °C (right) (circles represent equivalent positions)
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8.5. Dynamic Behavior

8.5.1. Fundamentals

Dynamic – mechanical methods expose the specimen to periodic stresses. The polymer either is put under torsion once and then oscillates freely (torsion pendulum) or is subjected continuously to forced oscillations (e.g., Rheovibron). In addition, ultrasound, dielectric, and NMR methods can be used to study the dynamic properties of polymers.

In the simplest case, the applied stress is sinusoidal with a frequency ω ($\sigma_t = \sigma_o \cdot \sin \omega \cdot t$). The deformation of ideal-elastic bodies follows the stress instantaneously ($\gamma_t = \gamma_o \cdot \sin \omega \cdot t$) but that of viscoelastic polymers experiences a delay ($\gamma_t = \gamma_o \cdot \sin(\omega \cdot t - \vartheta)$). The stress vector is assumed to be a sum of two components: one component is in phase with the deformation ($\sigma' = \sigma_o \cdot \cos \vartheta$); the other is not ($\sigma'' = \sigma_o \cdot \sin \vartheta$).

Each of these two components possesses a modulus. The *real modulus* (*shear storage modulus*) G' measures the stiffness and shape stability of the specimen:

$$G' = \sigma'/\gamma_o = (\sigma_o/\gamma_o) \cdot \cos\theta = G^* \cdot \cos\theta \qquad (86)$$

whereas the *imaginary modulus* (*shear loss modulus*) G'' describes the loss of usable mechanical energy by dissipation into heat:

$$G'' = \sigma''/\gamma_o = G^* \cdot \sin\vartheta \qquad (87)$$

The same quantities can also be derived if complex variables are introduced

$$G^* = G' + i \cdot G'' = [(G')^2 + (G'')^2]^{-1/2} \qquad (88)$$

The loss factor δ is the ratio of imaginary to real modulus. It is the same for shear and Young's moduli but not for compression moduli

$$\Delta = \tan\vartheta = G''/G' = E''/E' < K''/K' \qquad (89)$$

8.5.2. Molecular Interpretations

The *shear storage moduli* of low molar mass polymer melts with narrow molar mass distributions increase continually with increasing frequency (Fig. 50). At high normalized frequencies $\alpha_T\omega$, all storage moduli asymptotically

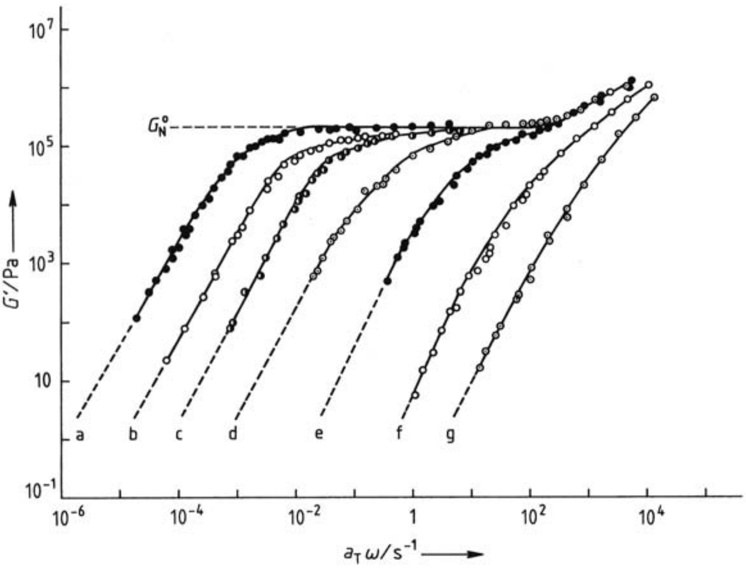

Figure 50. Frequency dependence of the shear storage modulus G' for narrow-distribution polystyrene melts of different molar masses M. A shift factor α_T was used to convert to 160 °C data measured at various temperatures
a) M=581 000 g/mol; b) M=351 000 g/mol; c) M=215 000 g/mol; d) M=113 000 g/mol; e) M=46 900 g/mol; f) M=14 800 g/mol; g) M=8900 g/mol
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approach a limiting line, regardless of molar mass. This part of the relaxation spectrum thus originates from the mobility of chain segments; it is called the transition range.

High molar mass polymers show a corresponding frequency dependence of *loss moduli* at very low frequencies (called end range), followed by a plateau at higher frequencies (plateau modulus G_N^o), and finally the transition range. The end ranges of these spectra are molar mass dependent; this behavior must come from long-range conformational changes. Since the transition range characterizes viscous behavior, and the end range viscoelastic behavior, the plateau range must reflect rubbery behavior (see Fig. 47 for the temperature dependence).

The *rubbery behavior* of polymer melts can be described by the theories of entropy elasticity according to which the shear modulus of chemically cross-linked polymers depends on the molar concentration of network junctions. The plateau modulus G_N^o of melts thus indicates the concentration of temporary junctions (entanglements). The molar mass M_e of segments between such junctions of polymers with volume fractions ϕ_p in solution (ϕ_p=1 for melts) and polymer melt densities ρ_p is given by

$$M_e = RT \cdot r_p \cdot \phi_p / G_N^o \tag{90}$$

These dynamic entanglement molar masses M_e are a factor 2.0±0.2 lower than the corresponding molar masses M_c from rest viscosities (Table 27).

The plateau is not well developed or may even be absent for polymers with broad molar mass distributions; a complicated dependence of shear compliances on higher molar mass averages has been predicted by reptation theory.

Table 27. Critical molar masses for entanglement from shear moduli (M_e) and rest viscosities (M_c)

Polymer	T °C	M_c g/mol	M_e g/mol	M_c/M_e
Polyethylene	190	3 800	1 790	2.1
Polypropylene, it	190	7 000		
Polyisobutylene	25	15 200	8 800	1.7
Polydimethylsiloxane	25	24 500	10 500	2.4
Poly(vinyl acetate), at	57	24 500	12 000	2.0
Poly(α-methylstyrene), at	100	28 000	13 500	2.1
Polystyrene, at	190	35 000	18 100	1.9

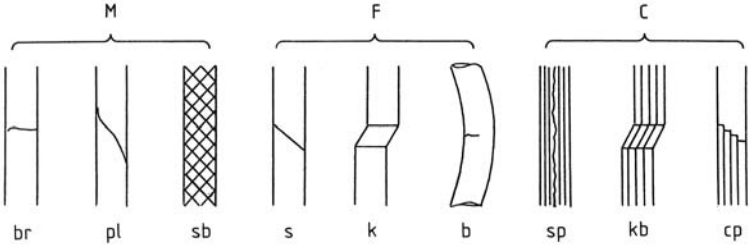

Figure 51. Failure modes of polymers (matrix M), fibers (F), and fiber-reinforced polymer composites (C) by brittle failure (br), plastic flow (pl), shear band formation (sb), shearing (s), kink formation (k), bending (b), longitudinal splicing (sp), formation of kink bands (kb), and step formation by compression (cp)
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8.6. Fracture

8.6.1. Overview

Polymers break very differently depending on their chemical and physical structure; environment (humidity, solvents, temperature); and the type, duration, and frequency of deformation. Some polymers break immediately; others are unchanged even after months. The fracture surface can be smooth or splintery; the elongation at fracture, less than 1 % or greater than 1000 %.

Two fracture modes can be distinguished: brittle and tough (ductile). Brittle polymers fracture perpendicularly to the stress direction, tough polymers longitudinally (Fig. 51). A polymer is defined as brittle if its elongation at break is less than 20 %.

Brittle Fractures are rare for ideal solids since many bonds must be severed simultaneously. Real polymers however contain many small imperfect regions that act as "nuclei" for the formation of microcracks. Brittle polymers usually possess "natural" microvoids, which may also appear in drawn amorphous polymers or through separation of crystal lamellae in hard-tough polymers.

Tough Failures (ductile fractures) are caused by viscous flow ("plastic flow"). This process may involve the slipping of chain segments past each other (amorphous polymers) or the movement of crystalline domains (partly crystalline polymers). Polymer chains may also de-entangle at long times and under small stresses. The same processes and additional ones may occur on failure of composites (Fig. 51).

Polymers are subjected to very different stress conditions in typical applications; they thus experience different failure modes. Test methods try to simulate complex real-life situations by standardized procedures. They include long-term experiments such as static deformations under constant load by tension, compression, or bending; short-term methods such as tensile tests under various speeds or impact tests with unnotched or notched specimens; dynamic testing with variation of the number of loadings – unloadings, impacts, vibrations, etc.

8.6.2. Theoretical Fracture Strength

The fracture of brittle polymers generates free radicals. Since the probabilities of such homolyses depend on bond strengths, which also determine tensile moduli, relationships must exist between the theoretical moduli and the theoretical fracture strengths of polymers.

Bonds are severed if atoms are separated from each other by certain distances L_b greater than their equilibrium distances L_o. The necessary theoretical strength $\sigma^o{}_{\parallel}$ is given by [5].

$$\sigma^o_{\parallel} = \frac{E^o_{\parallel} \cdot (L_b - L_o)}{\pi L_o} = K \cdot E^o_{\parallel} \qquad (91)$$

Polymer main-chain bonds break at approximately the same relative distance ($L_b \approx 1.3\ L_o$) because bond lengths and strengths are not too different for bonds such as C–C, C–O, and C–N. Thus, $K \approx 0.095$ and the theoretical fracture strength $\sigma^o{}_{\parallel}$ should be ca. one-tenth of the theoretical tensile modulus $E^o{}_{\parallel}$ in the chain direction, regardless of the chemical nature of

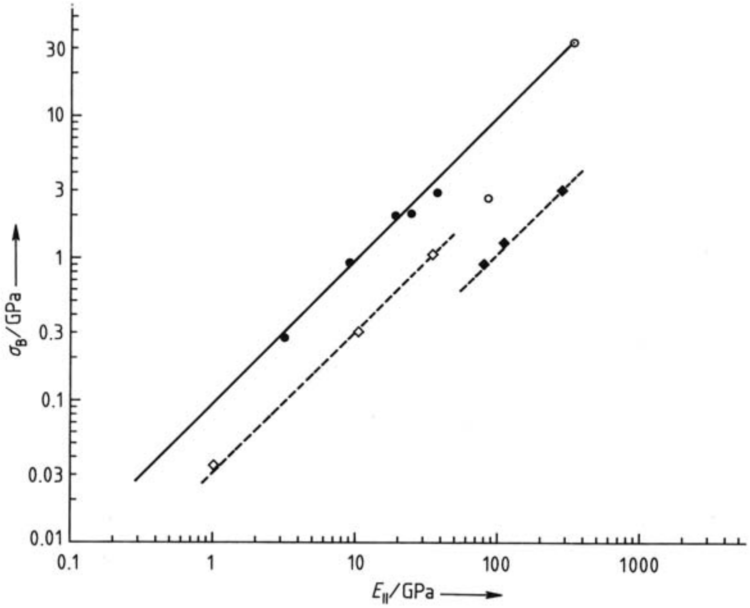
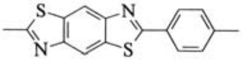


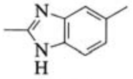
Figure 52. Tensile strength at break as function of tensile modulus: (•) experimentally ultradrawn ultra-high-modulus polyethylenes; (○) industrially manufactured ultradrawn polyethylene (Dyneema); (⊙) theory for perfectly aligned polyethylene; (♦) heterogeneous molecular composites of ABPBI fibers or PBT fibers or films in ABPBI matrix; (♦) homogeneous molecular composites of PBT fibers or PBT fibers for films in ABPBI. Solid line corresponds to σ_B=0.095 · $E_\parallel$

the polymer. Polyethylene with a theoretical modulus of 340 GPa (Table 24) should thus have a theoretical fracture strength of ca. 32 GPa [i.e., much higher than the theoretical strength of steel (ca. 20 GPa)]. Industrially manufactured ultradrawn polyethylene fibers have higher experimental fracture strengths than steel (2.9 GPa=2.7 N/tex vs. 2.5 GPa).

The theoretical fracture strength – tensile modulus relationship of Equation (91) has been realized for certain ultradrawn polyethylenes in which both the predicted proportionality constant K=0.095 and the first power of E were found (Fig. 52). The type of same relationship is also observed for molecular composites of poly (*p*-phenylene-2,6-bisbenzthiazole) (PPBT) with rodlike mesogens in coillike polybenzimide (ABPBI), albeit with a lower proportionality constant. In other ultradrawing experiments, a power dependence $\sigma=K' \cdot E^n$ was found, however.



PPBT



ABPBI

8.6.3. Real Fracture Strength

The lower than theoretical fracture strengths of most polymers (see Tables 24 and 25) are caused by many factors. Theoretical fracture strengths relate to infinitely long, completely aligned, immobile polymer chains. End groups and chain folds act as disturbances: fracture strengths of conventional polymers increase with increasing molar mass and become practically constant above a "critical" molar mass.

At the latter molar mass range, chain segments of amorphous polymers are distributed at random. A brittle fracture across such polymers will create two new surfaces with a total surface energy of 2 γ_{lv}. The theoretical fracture strength for brittle, energy-elastic bodies

$$\sigma_a^o = (E\cdot\gamma_{lv}/L_o)^{1/2} \tag{92}$$

now depends on the product of modulus and surface energy (Ingles theory). The Ingles theory works well for silicate glasses.

The experimentally found fracture strengths σ_b of plastics are however much lower than the strengths predicted by Equation (92). The ratios σ_a^o/σ_{exp} of molded (unoriented) plastics decrease

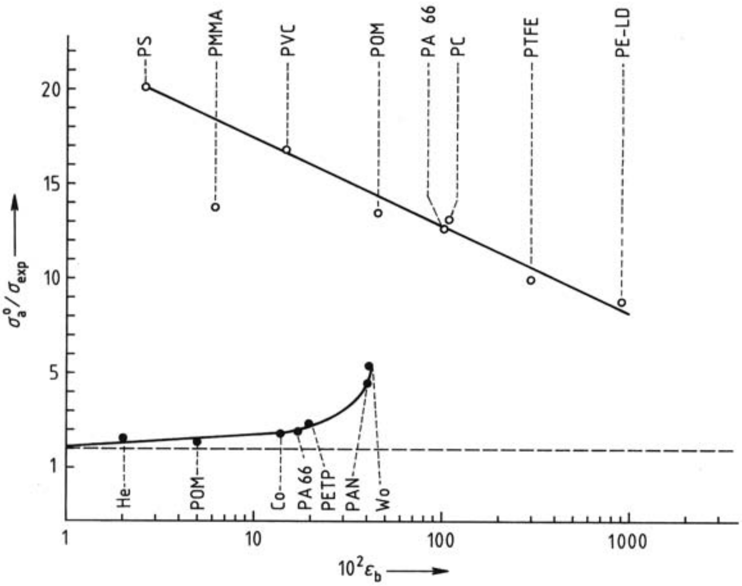


Figure 53. Ratio σ_a^0/σ_{exp} of theoretical [Eq. (92)] and experimental fracture strengths as function of elongation at break ε_b for (○) nonoriented (molded plastics) and (•) oriented (fibers) polymers
He=hemp, Co=cotton, Wo=wool (for other abbreviations see Tables 1–4)

with increasing elongation ε_b at break (Fig. 53), whereas those of drawn fibers (partially oriented chain segments) increase.

The reason for the lower than expected fracture strengths of amorphous polymers is the presence of microvoids, which act on drawing as nuclei for cracks. According to the Griffith theory, a crack can grow only if the energy required for the fracture of chemical bonds is just surpassed by the stored elastic energy. This theory predicts a dependence of the fracture strength on crack length *L*:

$$\sigma_B = [(2E \cdot \gamma_{lv})/(\pi \cdot L)]^{1/2} \tag{93}$$

This functionality is indeed observed for artificially introduced long cracks. The predicted fracture strengths are however much lower than those found by experiment. Furthermore, deviations from Equation (93) occur at small crack lengths because the fracture behavior of plastics is not dominated by the cleavage of chemical bonds but by other types of energy absorption (crazing; shear flow).

On drawing, stresses are imposed on microvoids. The polymer reaches its upper yield stress at sufficiently high stress concentrations at the tip of such a void and relieves the stress by stress softening (Fig. 44). The induced cooperative movements of chain segments cause long-range changes of macroconformations. In partially crystalline polymers, these changes can occur only in amorphous domains; spherulitic polymers break accordingly either between spherulites or in the radial spherulite direction.

The cooperative movements of segments lead to either shear or normal stress yielding. On shearing, the whole specimen yields either homogeneously or heterogeneously (localized). In the latter case, shear bands are formed at angles of 38 – 45° to the stress direction (Fig. 51). Chain segments are arranged at angles between shear bands and stress directions.

All polymers with upper yield values form crazes upon stress softening (Fig. 54), regardless of whether they are amorphous, crystalline, linear, or cross-linked. Crazes can be up to 100 μm long and 10 μm wide; their long axes are parallel to the stress direction. They are not voids since their interior is filled with amorphous microfibrils of 0.6 – 30 nm diameter; these microfibrils are oriented in the stress direction (i.e., perpendicular to the craze long axes). On further deformation, microvoids are formed.

The formation of crazes is the primary mechanism for the dissipation of stress energy. It is

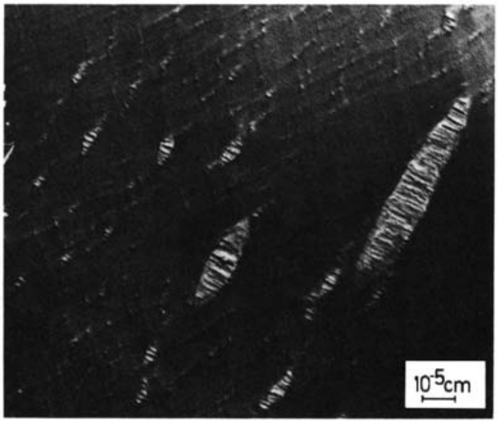


Figure 54. Crazes in a polystyrene drawn to 25 % [81]

utilized in the rubber reinforcement of polystyrene. Rubber-modified polypropylene, on the other hand, deforms mainly by shear flow.

8.6.4. Impact Resistance

Impact strength is the resistance of a material to impact. It is one of the many quantities used to characterize the strength of a material under (the usually complex) use conditions; all test methods are thus standardized. Most test methods measure the energy required to break a notched or unnotched specimen (Izod, Charpy, high-speed tensile). Impact speeds range from 10^{-5}–10^{-1} m/s in conventional tensile tests to 20 – 240 m/s for high-speed tensiles; elongation speeds are usually from 10^{-3} to 10^{4} s^{-1}.

Impact strengths depend on experimental conditions. The smaller the radius of the notch, the higher is the stress concentration at the tip and the lower is the impact strength. At very low temperature, all polymers are brittle. The mobility of chain segments increases with increasing temperature, allowing stresses to be relieved by shear-band or craze formation: impact strengths increase with temperature, especially near the glass transition temperature. Polymers with additional transition temperatures below the glass transition temperatures are for the same reason almost always more impact resistant than polymers without such transitions. Nonentangled polymers exhibit very low impact strengths because no crazes can be formed. The impact behavior of polymers can be improved considerably by modification with rubber (see Section 11.4.3).

8.6.5. Stress Cracking

Stress cracking (stress corrosion, stress crazing) is the formation of crazes under the physical action of chemicals, especially surfactants. Stress corrosion starts at polymer surfaces and proceeds into the interior until the polymer finally cracks. The appearance and the extent of stress cracking depend on the polymer – reagent interaction and the magnitude of the stress.

Effects are weak in nonwetting liquids but strong in polymer – liquid systems with solubility parameters of polymers and liquids matching each other and even more dramatic under tension in the presence of surfactants. Stress cracking decreases with increasing molar mass of the polymer since entanglements allow stresses to relax elastically. Cross-linked polymers are less prone to stress cracking for the same reason. Stress cracking is also reduced if polymer plasticizers are present in plastics because these additives increase the mobility of chain segments and thus the ability to relieve stresses. The same action is responsible for the fact that no stress corrosions are observed above glass transition temperatures.

8.6.6. Fatigue

Materials may be damaged not only "instantaneously" (i.e., on impact) but also by static or periodic loads after certain times or number of loadings. This fatigue is characterized by the *fatigue limit* (endurance) at which the plastics are not damaged even after infinite time and the *fatigue strength*, which indicates the load at which damage sets in after a certain time.

Plastics may be subjected to static loads for certain times t, after which their fracture strengths σ_B are measured by tensile tests. The logarithms of strength of amorphous polymers usually decrease linearly with logarithms of time due to viscous flow (Fig. 55). Partially crystalline polymers show a bend in these lines after certain times, which indicates a change from tough fracture (short times) to brittle fracture

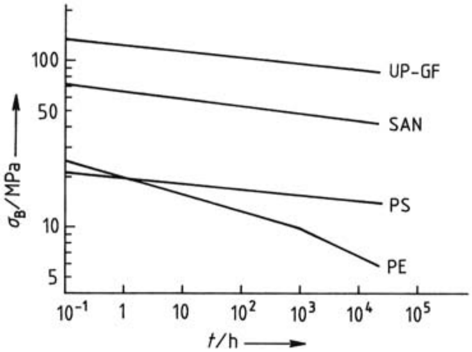


Figure 55. Time dependence of tensile fracture strengths after static loading during time *t*. UP-GF=Glass-fiber-reinforced unsaturated polyester; SAN=Styrene – acrylonitrile copolymer (impact polystyrene); PS=Polystyrene; PE=Polyethylene
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(long times), probably caused by recrystallization phenomena.

8.7. Surface Mechanics

8.7.1. Hardness

The hardness of a material is its resistance to penetration by another body. Hardness is a very complex quantity; it depends on Young's modulus, yield stress, and stress hardening. A general definition of hardness, applicable to all materials, does not exist; neither does a universally applicable testing method. The various technical test methods thus emphasize one or another factor that contributes to the hardness of a specific class of materials.

The hardness of *hard plastics* is normally characterized by various Rockwell (ISO, ASTM) or ball indentation hardnesses (DIN, ISO). These methods measure the indentation of a polymer by a steel sphere under load and thus the compression set and the recoverable deformation. The plastic deformations of polymers increase with time (creep), whereas those of metals are time independent. Because of the short duration of the hardness test polymers exhibit relatively high Rockwell hardnesses.

The hardness of *soft plastics* is characterized by their durometer (ASTM) or various Shore hardnesses (ISO, DIN). These methods measure the resistance to penetration by a truncated cone (static methods). Hardness properties of metals and hard plastics are evaluated by another Shore hardness that uses the rebound of a small steel sphere (dynamic method).

All methods measure the hardness of surfaces, not of the interior of the specimen. The surface may, for example, be plasticized by the humidity of the air. Crystallizable polymers may have lower surface hardnesses than interior hardnesses (if the plastic had been injected into a cold mold) or the reverse may be true (if transcrystallization occurred).

8.7.2. Friction

Friction, the resistance against the relative movement of two bodies contacting each other is measured by the friction coefficient $\mu = R/L$ (i.e., the ratio of friction R to total load L). Friction depends in a complex and not understood way on both the surface roughness of the specimen and its mechanical properties.

The rolling of *hard bodies on soft materials* is determined almost exclusively by the deformation of the soft base (i.e., its viscoelastic properties). Elastomers thus have fairly high friction coefficients of $0.5 < \mu < 3.0$, depending on the contacting body and its type of movement (rolling, sliding).

The sliding of *hard bodies on other hard bodies* occurs on the tops of the microscopic surfaces: the true contact area is much smaller than the geometric one. The applied load thus acts on very small effective areas. Local stresses are high and the tops are leveled. Large adhesion forces exist between chemical groups of the resulting effective contact areas of both bodies, which must be overcome by breaking the bonds or by shearing one of the materials. The adhesive friction $R = A_w \cdot \sigma_b$ is given by the effective contact surface A_w and the shear strength σ_b. Soft materials possess high effective surfaces (large A_w) and are easily sheared (small σ_b), whereas the opposite is true for hard materials. Plastics, metals, and ceramics therefore often exhibit very similar friction coefficients (Table 28).

8.7.3. Abrasion and Wear

Abrasion is the loss of material from surfaces by friction. It is thus affected by both friction prop-

Table 28. Friction coefficients of various sliding bodies

Plastic	Friction coefficient of		
	Plastic on plastic	Plastic on steel	Steel on plastic
Poly(methyl methacrylate)	0.8	0.5	0.45
Polystyrene	0.5	0.3	0.35
Polyethylene, high density	0.1	0.15	0.20
Polyethylene, low density	0.3		0.80
Polytetrafluoroethylene	0.04	0.04	0.10

erties and hardnesses of the specimens. The abrasion coefficient K is given by the applied force F, the linear speed v of the contacting body, the total time t, and the volume loss ΔV of the abraded material: $K = \Delta V/(F \cdot v \cdot t)$.

Abrasion coefficients vary widely with polymer type and state (resting, mobile) (Table 29).

The best resistance against abrasion is shown by polyureas, followed by polyamides and polyacetals. It can be enhanced greatly by addition of certain fillers (e.g., short fibers).

9. Electric Properties

Matter is subdivided according to its specific electrical conductivity σ into insulators ($\sigma = 10^{-14}$–10^{-22} S/cm), semiconductors (10^{2} – 10^{-9} S/cm), conductors ($> 10^{3}$ S/cm), and superconductors ($\approx 10^{20}$ S/cm). Most plastics are insulators (Section 9.1), but certain polymers are intrinsic semiconductors and some may even be conductors after doping (Section 9.2).

Table 29. Abrasion coefficients K for moving plastics against resting materials

Resting material	10^{10} K MPa^{-1}	Moving polymer	10^{10} K MPa^{-1}
Polycarbonate A	200 000	polyamide 66	11 000
Polyamide 66	250	polycarbonate A	9 800
Polyamide 66	220	polyamide 66	510
Polyamide 66	10	polyacetal	12
Polyacetal	11	polyamide 66	15
Steel		polyamide 66	8 600
Steel		polyamide 66 with 30 % glass fibers	1

9.1. Dielectric Properties

9.1.1. Relative Permittivity

Groups within a molecule and entire molecules of an insulator are polarized by applied electric fields. Polarization is usually measured by the ratio of capacitances of a condensor in vacuo and in the specimen (i.e., the relative permittivity ε_r of the specimen; formerly called the dielectric constant). Relative permittivities are low for apolar polymers [polytetrafluoroethylene (PTFE); PE], higher for polymers with polarizable groups (PS, PC), and still higher for polar materials [dry polyamide (PA)] (Table 30).

The relative permittivity thus increases with increasing water content of plastics ($\varepsilon_r = 81$ for water). It also increases with increased segmental mobility ($\varepsilon_r = 13.0$ for *cis*-1,4-polyisoprene); rubber-modified plastics have higher relative permittivities than conventional plastics. Expanded plastics and elastomers are composites with air ($\varepsilon_r = 1.00058$) and subsequently have low relative permittivities of ca. 1 – 2. Fillers increase the relative permittivities to values up to 170 (filled thermoplastics) and up to 18 000 (filled elastomers).

9.1.2. Dielectric Loss

Dipoles try to follow the direction of an electric field if an alternating current is applied. The required adjustment times correspond to the orientation times of groups and molecules. The faster the alternation, the longer the orientation lags behind the field and the greater is the electrical energy consumed. Available output power is decreased because electric power is lost by conversion into thermal energy.

The ratio of power loss N_v to total power output N_b is called the dielectric dissipation factor or loss tangent tan δ, which can also be expressed as the ratio of imaginary relative permittivity (ε'') to real relative permittivity (ε'):

$$N_v/N_b = \tan\delta = \sin\delta/\cos\delta = \varepsilon''/\varepsilon' \qquad (94)$$

Sometimes power factors sin δ are given instead of loss tangents tan δ.

Polymers with high loss factors $\varepsilon \cdot \tan\delta$ can be heated and thus welded by high-frequency

Table 30. Electrical properties of plastics

Polymer	Δw^{a}		$\rho_v{}^{c}$ $\Omega \cdot$cm	$\rho_s{}^{d}$ Ω	S^{f}		
	%	$\varepsilon_r{}^{b}$			tan δ^{e}	kV^{-1}mm^{-1}	U^{g}/V
PTFE	0	2.15	10^{18}		0.0001	40	> 600
PE	0.05	2.3	10^{17}	10^{13}	0.0007	70	600
PS	0.1	2.5	10^{18}	10^{15}	0.0002	140	500
SAN		3			0.0070	100	
ABS		3.2	10^{15}	10^{13}	0.02	15	600
PVC	$< 1.8^{h}$	$< 3.7^{h}$	10^{15}	10^{13}	0.015	< 50	< 600
PA 6							
Dry	0	3.7	10^{15}		0.03	< 150	600
Conditioned	9.5	7	10^{12}		0.3	80	600
CA	4.7	5.8	10^{13}		0.03	35	
UP		3.4	10^{13}	10^{12}	0.01	50	500
PUR		4	10^{13}		0.05	30	
PF		8	10^{14}		0.05	12	
With inorganic fillers			10^{10}		< 0.5	14	< 150
Without inorganic fillers			10^{9}		< 0.5	10	125
UF		6	10^{11}		0.1	10	

[a] Δw=water absorption (at 50 % relative humidity.

[b] ε_r=relative permittivity (“dielectric constant”).

[c] ρ_v=volume resistivity (inverse specific electrical conductivity).

[d] ρ_S=surface resistivity (inverse surface conductivity).

[e] tan δ=dissipation factor (loss tangent, at 1 MHz).

[f] S=dielectric strength.

[g] U=tracking resistance (method KC).

[h] Depends on impurities from polymerization (e.g., emulsifier residues).

fields; PVC is an example. Polymers with low loss factors [PE, PS, polyisobutylene (PIB)], on the other hand, are excellent insulators for high-frequency conductors.

Real and imaginary relative permittivities depend on the frequencies v of the alternating current (Fig. 56). The function $\varepsilon' = f(v)$ corresponds to a dispersion and the function $\varepsilon'' = f(v)$ to an absorption of energy. Transitions and relaxations consume energy and therefore inflection points (ε'-curves) and maxima (ε''-curves) are found at appropriate temperatures and frequencies.

9.1.3. Dielectric Strength and Tracking Resistance

The imaginary part of the relative permittivity is caused by the dissociation of polar groups that may be either inherent to the polymer or introduced by extraneous impurities. These polar groups must be of ionic nature since the electrical conductivities of conventional plastics are strongly temperature dependent (electronic conductivities are far less temperature dependent).

Heat is caused to develop by the imaginary part of the relative permittivity. The low thermal conductivities of plastics do not allow this heat to dissipate, and the temperature increases. Ionic conductivities are thus increased until a breakdown (arcthrough) finally occurs. The resistance against such a breakdown is measured by the electric strengths S of a plastic (“dielectric strength”) (Table 30).

A breakdown can also occur through tracking on the surface of a plastic. The tracking resistance is difficult to measure because surface resistivities are 2 – 3 decades lower than volume resistivities (Table 30). The tracking resistance is thus measured by standardized methods, such as the maximal voltage that does not cause tracking if 50 drops of an aqueous 0.1 wt % NH_4Cl solution are applied between two platinum electrodes that are under an alternating current and 4 mm apart on the specimen surface. A polymer has a good tracking resistance if it forms volatile products and no carbon upon degradation (volatile monomer by depolymerization of PMMA, volatile oligomers by degradation of PE or PA). Poly(*N*-vinyl carbazole) does not form volatile products and thus

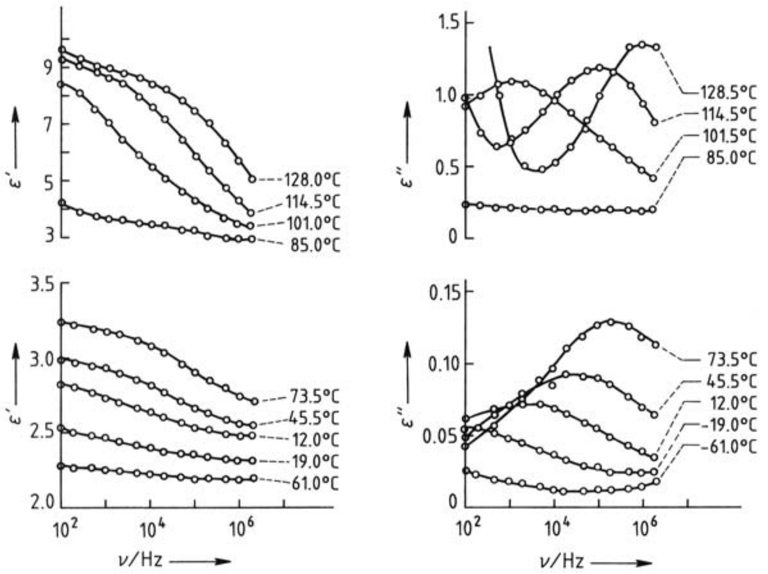

Figure 56. Frequency dependence of real (ε^{+}) and imaginary relative permittivities (ε'') of a poly(vinyl chloride) at various temperatures
Upper: β-dispersion; lower: γ-dispersion.
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has a poor tracking resistance although it is a good insulator.

9.1.4. Electrostatic Charging

Static electricity originates from an excess or a deficiency of electrons on isolated or ungrounded surfaces. It can be created by rubbing two surfaces against each other (triboelectric charging) or by contact of a surface with ionized air. Matter is charged electrostatically if specific conductivities are lower than ca. 10^{-8} S/cm and relative humidities lower than ca. 70 %. All conventional plastics can thus be electrostatically charged (Table 30). Charge densities may vary between, e. g., 8.2 C/g for polychlorotrifluoroethylene (PCTFE) and − 13.9 C/g for phenolic resins, and charges may vary between 3000 V/cm (POM vs. PA 6) and − 1700 V/cm (ABS vs. PA 6).

Static charging can be reduced by incorporation of conducting fillers into the plastics, such as carbon black or metal powders (internal antistatics). External antistatics reduce surface resistivities by increasing the polarity of the surface via application of humidity-absorbing additives or by reducing friction through lubricants or coating with PTFE.

9.2. Electrical Conductivity
(→ Polymers, Electrically Conducting)

Electrical conductivities in metals are caused by $N/V = 10^{21}$–10^{22} (quasi) free electrons per cubic centimeter with electric charges $e \equiv 1.6 \times 10^{-19}$ C and mobilities $\mu = 10 - 10^{6}$ cm^2 V^{-1} s^{-1}. According to

$$\sigma = (N/V) \cdot \mu \cdot e \tag{95}$$

specific electrical conductivities of metals are therefore between ca. 630 000 (Ag) and 10 400 (Hg) S/cm. Graphite exhibits $\sigma = 10^{4}$ S/cm in plane direction and 1 S/cm perpendicular to it. Semiconductors possess carrier mobilities similar to metals but at far lower carrier concentrations.

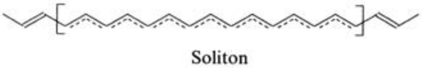
Charge transfer occurs fairly easily in metals and semimetals because atoms are tightly packed. Chain atoms of polymer molecules are also close in the chain direction because of covalent bonds. Only van der Waals and/or dipole forces act between chains, however, resulting in large intermolecular atomic distances and very difficult charge transfers. All electrons are furthermore localized in covalent polymer chains. Conventional polymers are thus insulators.

Polymers with conjugated chains [e.g., *trans*-polyacetylene $\sim$(CH=CH)$_n\sim$] are, for these reasons, merely semiconductors and insulators even if the chains are planar. These low conductivities can be increased substantially, however, if the polymers are doped with substances such as I_2, AsF_5, BF_3, etc.: doping with AsF_5 increases the specific electrical conductivity of *trans*-polyacetylene from 10^{-9} to 1200 S/cm and of poly(*p*-phenylene) from 10^{-15} to 500 S/cm. Such doped polymers can be processed like thermoplastics to any shape desired, which together with their light weight makes them attractive for many applications.

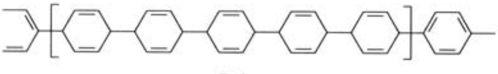
The action of these dopants is quite different from those of small amounts of dopants in inorganic semiconductors. The doping of inorganic semiconductors such as GaP, InSb, or Ge generates quasi-free electrons (*n*- carriers) or defect electrons (*p*- carriers), whereas the doping of suitable organic polymers leads to oxidation (*p*-doping) or reduction (*n*-doping) reactions. Sizable effects in organics are thus achieved only if large amounts of dopants are used, often up to 1 : 1 molar ratios of dopants to repeating units.

Doped polymers exhibit neither Curie paramagnetism (localized charge carriers) nor Pauli paramagnetism (electrons delocalized over the entire system). Thus the electrical conductivity of such systems is assumed to be due to solitons or polarons.

Double and single bonds alternate in *trans*-polyacetylene. Since these bonds are exchangeable, two low-energy states A and B with equal energy must exist. A *soliton* is a kind of topological kink that separates the A state from the B state with opposite bond alternation. *Polarons* are similar kinks between aromatic and quinoid structures:



Soliton



Polaron

The kink is small (about 14 chain atoms in *trans*-polyacetylene) and thus very mobile. Two types of solitons and polarons exist. Neutral solitons and polarons possess radicals that are produced as defects during isomerization of the polymers. Charged solitons and polarons are created by doping, either as carbonium ions or as carbanions.

Solitons can move only along the chain; there is no tunnel effect between chains. Because of this anisotropic behavior, doped polymers (and conducting low molar mass organic molecules) are called low-dimensional conductors, synthetic metals, or organic metals.

The most important condition for the existence of electrical conductivity in organic polymers seems to be the ability to form overlapping orbitals. The planar structure of *trans*-polyacetylene promotes the overlapping of its π and *p* orbitals. In poly(*p*-phenylene sulfide) (PPS) $\sim$[S – (*p*-C_6H_4)]$_n\sim$, *p* and *d* orbitals of sulfur atoms probably overlap with the π systems of phenylene groups; PPS – AsF_5 shows an electrical conductivity of 10 S/cm, although the chain is not planar and the phenylene residues are arranged at angles of 45 °C to the planar zigzag chain of the sulfur atoms.

Electrically conducting polymers are presently used in small batteries, for example, a complex of poly(2-vinylpyridine)/I_2 as cathode in Li/I_2 batteries for pacemakers ($\sigma = 10^{-3}$ S/cm). Other possible applications of electrically conducting polymers are in solar cells, electrolysis membranes, microwave shielding, and integrated circuits.

9.3. Photoconductivity

Light generates radical ions and thus photoconductivities in certain systems. This effect is used in xerography to generate pictures of objects (e.g., copies of documents). The early photoconducting material As_2Se_3 has since been replaced by poly(*N*-vinylcarbazole), which absorbs UV light and forms an exciton, which is ionized by an electric field. The polymer is nonconducting in visible light; upon sensibilization by certain electron donors, charge-transfer complexes are formed, however. Another photoconducting system consists of polycarbonate A and triphenylamine.

10. Optical Properties

Many optical properties of plastics depend on their *refractive index n*, for example, reflection, gloss, transparency, and hiding power. Refractive indices are in turn determined by the polarizabilities Q according to the Lorenz – Lorentz relationship

$$(n^2-1)/(n^2-2) = (4/3)\pi Q = (4/3)\pi(N/V)\cdot\alpha \qquad (96)$$

where N/V is the number concentration of molecules with polarization α. The polarization is a function of the dipole moments of all groups in a molecule (i.e., the mobility and the number of electrons per molecule). Contributions to the refractive index are thus much higher for carbon atoms than for hydrogen atoms. Since the contributions of the latter can be neglected and since carbon atoms dominate the structures of polymers, all polymers possess approximately the same refractive index of 1.5 (e.g., PMMA 1.492, PP-it 1.53, PS 1.59). Deviations from this rule exist for strongly polarizable polymers (PTFE 1.37), polymers with bulky conjugated substituents (PVK 1.69), or polymers with a high content of noncarbon atoms (PDMS 1.40). According to the molecular structure of all known polymers, their refractive indices should be between ca. 1.33 and 1.73.

Molecules are more tightly packed in crystalline polymers than in amorphous ones. Refractive indices thus increase with increasing crystallinity. Because crystalline polymers are always anisotropic, different polarizabilities and refractive indices are exhibited in the chain direction and perpendicular to it.

A part of the light falling on a homogeneous, transparent body is reflected. *Reflectivity* is defined as the ratio of the intensities of reflected and incident light $R=I_r/I_o$, which according to Fresnel's law depends on the angles of incidence α and refraction β:

$$R = \frac{I_r}{I_0} = \frac{1}{2}\left[\frac{\sin^2(\alpha-\beta)}{\sin^2(\alpha+\beta)} + \frac{\tan^2(\alpha-\beta)}{\tan^2(\alpha+\beta)}\right] \qquad (97)$$

The reflectivity is low at small incident angles (R=0.040 for n=1.5 at 10°) and rises sharply at higher ones (R=0.388 for n=1.5 at 80°).

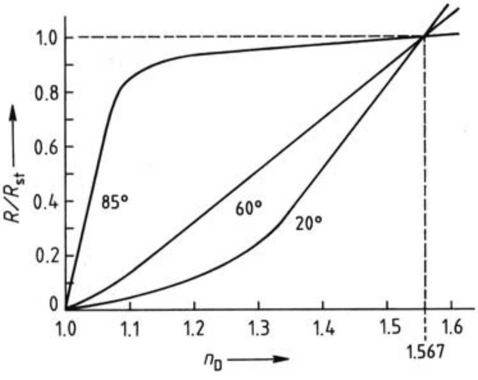


Figure 57. Maximum theoretical gloss as a function of the refractive index of specimen for various angles of incidence α and a standard with n_D=1.567
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Gloss is the ratio of the reflection of the specimen to that of a standard, for example, a body with n_D=1.567 in the paint industry. The maximum theoretical gloss R_o is given by Equation (97). It increases with increasing refractive index of the specimen and with increasing angle of incidence (Fig. 57). The maximum theoretical gloss is almost never achieved because of surface roughnesses.

The maximum *transparencies* $\tau_i=1-R_o$ can be calculated from $R_o=(n-1)^2/(n+1)^2$ by Fresnel's law for $\alpha\rightarrow0$ and $\beta\rightarrow0$. They can have values between 98.0 % (n=1.33) and 92.8 % (n=1.73) for polymers, (i.e., between 2 and 7.2 % of the indicent light is maximally reflected at the polymer – air interface). These ideal transparencies are rarely achieved for polymers because a small portion of the light is always absorbed and/or scattered. Poly(methyl methacrylate), one of the most transparent plastics, never exceeds a transparency of ca. 93 % between wavelengths of 430 and 1100 nm (theory 96.1 %). Transparencies decrease above wavelengths of ca. 1150 nm and (rapidly) below 380 nm. All polymers except halogenated polyethylenes absorb infrared radiation.

A distinction is usually made between transparent and translucent polymers. *Transparent* polymers have transparencies > 90 %; they look clear even at greater thicknesses. *Translucent* polymers (τ_i<0.90) appear clear only as thin films. They are also called contact clear because films look clear in contact with packaged goods but turbid when viewed alone.

An additional loss of clarity is caused by light scattering. Electromagnetic waves lose part of their energy by scattering in inhomogeneous systems. The loss of contrast by forward scattering is called *haze*. The combined loss by forward and backward scattering makes a specimen milky. A body appears opaque if local fluctuations of refractive indices or orientations of anisotropic volume elements are present. The different volume elements must also be larger than the wavelength of incident light. The clarity of a material can thus be increased considerably if the size of the different volume elements (e.g., microdomains) is decreased. Diminished differences in refractive indices improve the clarity to only a small extent. Lamellar structures are optically less heterogeneous than spherulites of approximately the same diameter. Under certain conditions, clear polyethylene films can be produced by quenching and orientation, although crystalline lamellae with dimensions greater than the wavelength of light are present in these films.

11. Polymer Composites

(→ Composite Materials)

11.1. Introduction

11.1.1. Overview

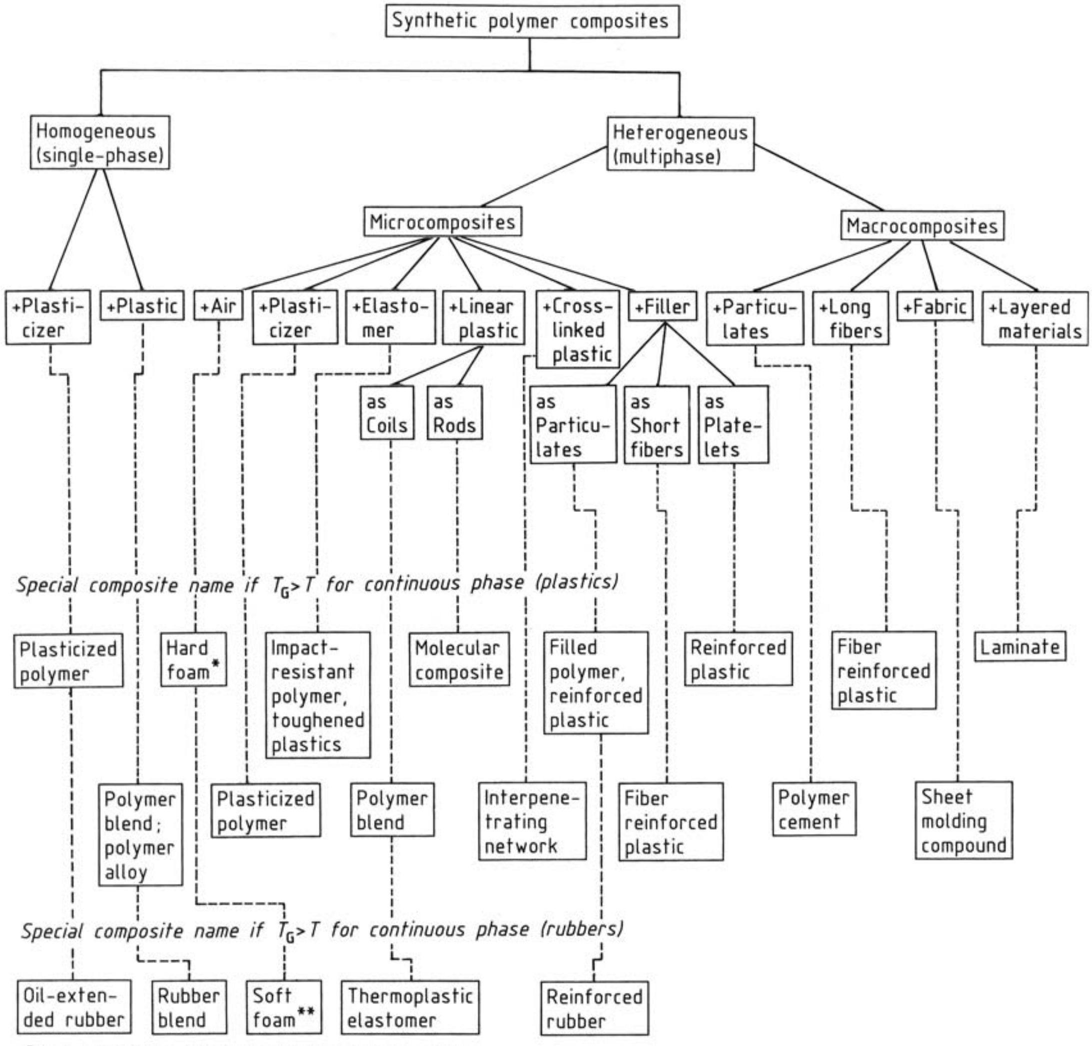
The term composite has various meanings. In general, it denotes a complex material in which two or more distinct substances combine to produce some properties not present in any individual component. In biomaterials, it means any two joined materials (e.g., polymer- coated titanium parts). In engineering, composites are more narrowly defined as physical admixtures of various materials that are present as distinct phases. The term "phase" is used here in the descriptive sense, not in the thermodynamic one. The engineering term "composite" thus includes only heterogeneous composites. Heterocomposites can be further subdivided into microcomposites (dispersed phase in the micrometer to millimeter range) and macrocomposites. Typical nonpolymer heteromicrocomposites are metal alloys; a typical heteromacrocomposite is steel-reinforced concrete.

Polymer composites are defined as composites in which at least one component is of a polymeric nature. In accordance with the general definition of a composite and in contrast to the engineering use of the word, the term "polymer composite" is often used to cover not only heterogeneous mixtures of a polymer and another material (minerals, fibers, other plastics, elastomers, etc.), but also homogeneous (singlephase) materials of two polymers (homogeneous polymer blends). Such polymer composites are a subgroup of "multicomponent polymer systems", which also include copolymers (two or more types of monomeric units chemically bound together).

Polymer composites occur naturally (wood, bamboo, lobster shells, bone, muscle tissue, etc.) or are manufactured synthetically. Synthetic polymer composites can also be subdivided into single-phase (homogeneous) and multiphase (heterogeneous) composites. Further subdivisions may be according to the second component's size (microcomposites, macrocomposites), chemical nature (air, low molar mass plasticizer, elastomer, plastic, mineral), geometry (particulate, fiber, platelet, fabric), and macroconformation (if polymeric: coil, rod), etc. (see Fig. 58). Most of these subclasses have different technical names depending on whether the glass transition temperature of the continuous phase is above (plastics) or below (rubbers) the use temperature. The same name is often given to various subtypes.

A mixture of two (or more) different polymers is often called a *blend* when both polymers are either above (rubber) or below (plastics) their glass transition temperatures. Blends are distinguished from composites of two polymers such as polymer – fiber-reinforced or rubber-toughened plastics. The term blend is sometimes restricted to mean only "incompatible polymer mixtures", whereas compatible polymer mixtures are called polymer alloys. The latter term is, however, occasionally more narrowly used for mixtures of two crystallizable polymers.

The term *miscibility* refers to admixtures on the molecular level (nanometer range), that is true thermodynamic solubility. It is sometimes used more loosely for any polymer mixture that exhibits only one glass transition temperature. *Compatibility* denotes the ability of admixtures to be blended to heterogeneous microcomposites that do not separate into macroscopic phases.



*Also: rigid foam, expanded plastics, cellular plastics
**Also: flexible foam, foamed rubber, cellular rubber

Figure 58. Classification of polymer composites of a base polymer (matrix polymer) with other materials (plasticizer, plastic, air, long fiber, layered materials). Some of these materials have their molecules in different shapes (coils, rods) or have various outer shapes (particulates, short fibers, platelets). Adopted from [1].

11.1.2. Mixture Rules

The composition dependence of properties Q of composites can often be described by mixture rules. The *generalized simple mixing law* relates Q to the fractions $f_A = 1 - f_B$ of components A and B with properties Q_A and Q_B:

$$Q^n = Q_A^n \cdot f_A + Q_B^n \cdot f_B \qquad (98)$$

The generalized simple mixing law is usually applicable to single-phase composites without specific interactions of its components and to two-phase systems with regularly dispersed discrete phases of "infinite" dimensions. It includes three special cases that are known by different names in different fields (Table 31) and are illustrated in Figure 59.

The *rule of mixtures* ($n = 1$) applies, for example, to various moduli if both components behave elastically. An example is Young's modulus parallel to the fiber direction for epoxide resins reinforced with long glass fibers (see below). The

Table 31. Names of simple mixing rules

Field	Property exponent in generalized mixing law		
	$n=1$	$n=0$	$n=-1$
Mathematics	arithmetic mean	harmonic mean	geometric mean
Chemical engineering	rule of mixtures	logarithmic mixture rule	inverse rule of mixtures
Mechanical engineering	Voigt model		Reuss model
Electrical engineering	parallel		series
Materials science	upper bound		lower bound

same composites follow the *inverse rule of mixtures* ($n=-1$) if the modulus is measured perpendicular to the fiber direction and no slippage occurs. The *logarithmic mixture rule*

$$\log Q = f_A \cdot \log Q_A + f_B \cdot \log Q_B \quad (99)$$

is obtained from Equation (98) for $n=0$ after some mathematical manipulation. The only known case concerns the permeation of oxygen through ABS resins. The proper fraction f_i in Equations (98) and (99) is always the volume fraction. If weight fractions are used instead, deviations from the curves shown in Figure 59 occur, which may be confused with either deviations from additivity or specific interactions.

True deviations from the upper bound S and lower bound I (Fig. 59) may be caused by irregularities in phase distributions (discrete phases) or phase continuities (continuous phases), phase alignments (anisotropic phases), bonding (adhesion), or nonuniform stresses. The resulting functions always lie between the upper and the lower bound if specific interactions are absent. Many empirical, semiempirical, and theoretical expressions have been proposed for such composites. A widely used function is the Halpin – Tsai equation

$$Q = Q_B \cdot \frac{1+K_1K_2f_A}{1-K_2f_A}; K_2 = \frac{Q_A-Q_B}{Q_A+K_1Q_B} \quad (100)$$

where K_1 is an adjustable constant. The Halpin – Tsai equation gives the lower bound for $K_1 \to 0$ and the upper bound for $K_1 \to \infty$. Particulate fillers often have $K_1 \approx 0$, and fiber-reinforced plastics $K_1 \approx 2\ L/d$, where $2\ L/d$ is the aspect ratio of the fiber.

Specific interactions between components can be considered by an additional interaction term. This term is differently defined, for example:

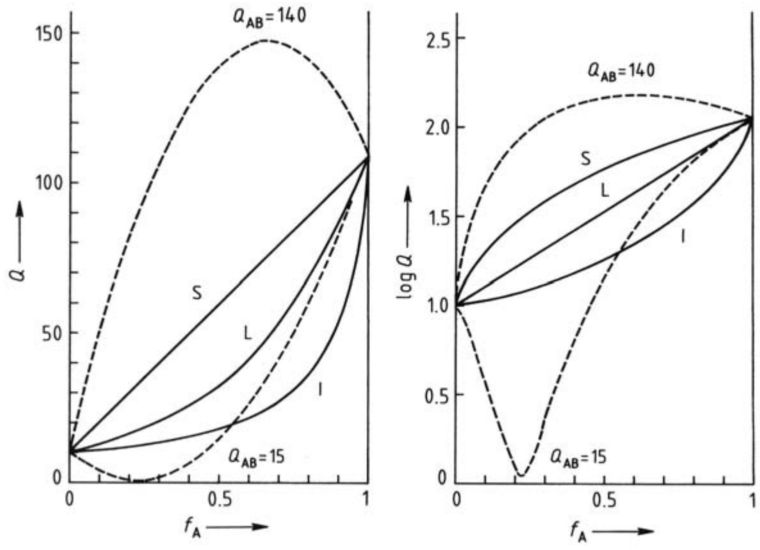


Figure 59. Mixing laws for composites with $Q_A=110$ and $Q_B=10$: left: $Q=f(f_A)$; right: log $Q=f(f_A)$
Simple mixing laws with interaction parameter
$Q_{AB}=0$ (S=simple mixing law; L=logarithmic mixing law; I=inverse mixing law
- - - Composites with interaction parameters $Q_{AB}=140$ and 15, as indicated

$$Q = Q_A f_A + Q_B f_B + K_i f_A f_B; \quad K_i = 2(2Q_{AB} - Q_A - Q_B) \tag{101}$$

where the property term Q_{AB} is taken at $f_A = f_B = 1/2$. The value Q_{AB} may be an interaction parameter between components A and B in homogeneous mixtures or the property of the interphase between A and B phases in heterogeneous mixtures. The upper bound for absent interactions or interphases is retrieved for the condition $Q_{AB} = (Q_A + Q_B)/2$. The functions for $Q_{AB} \neq (Q_A + Q_B)/2$ may lie fully or partially outside the range between upper and lower bounds (Fig. 59); that is synergistic effects (above the upper bound) or antagonistic effects (below the lower bound) may be present. They may also show maxima and minima, depending on the relative magnitudes of Q_{AB}, Q_A, and Q_B. Maxima or minima that exceed the highest property value (either Q_A or Q_B) are sometimes considered the true criteria for synergistic and antagonistic effects, respectively.

11.2. Filled Polymers

11.2.1. Microcomposites

The addition of fillers (low thermal expansion) to polymers (high thermal expansion) reduces the proportion of the latter and thus the shrinkage of plastics on processing (Table 32).

Table 32. Effect of fillers on some properties of amorphous (A) and crystalline (C) thermoplastics [(↑) weak increase, ↑ increase, ↑↑ strong increase, (↓) weak decrease, ↓ decrease, ↓↓ strong decrease]

Property	Extenders		Reinforcing agents	
	A	C	A	C
Shrinkage	↓	↓	↓	↓
Heat deflection temperature		(↑ ↓)		↑
Melt flow	↓	↓	↓	↓
Young's modulus	(↑)	(↑)	↑	↑
Flexural modulus	↑	↑	↑	↑ ↑
Fracture strength	↓	↓	↑	↑
Brittleness	↑	↑	↑ ↓ [a]	↑ ↓ [a]

[*] Tough plastics become more brittle and brittle plastics become tough.

The melt flow is also lower.

Heat deflection temperatures (HDT) of amorphous polymers are either the same as those of unfilled plastics or no more than ca. 10 K higher (Fig. 60), group a), probably because of the increased viscosity of the filled plastic. The HDTs of amorphous thermoplastics are almost identical with glass transition temperatures.

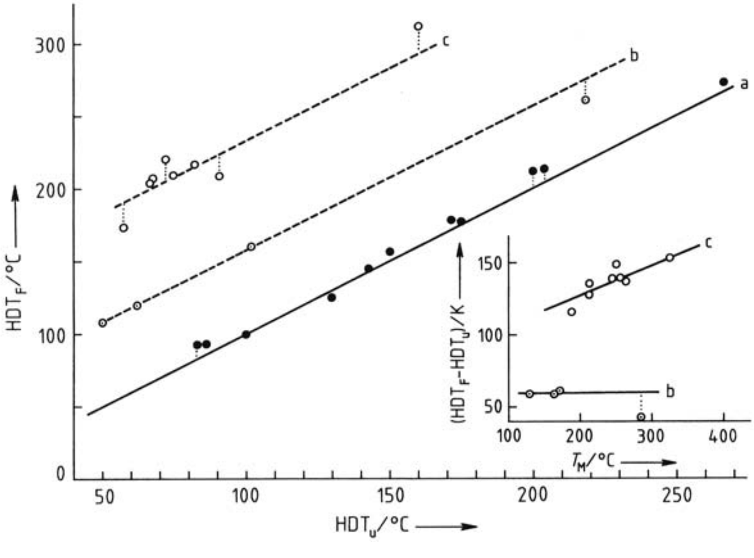


Figure 60. Heat deflection temperatures HDT_F of thermoplastics filled with 30 wt % short glass fibers as a function of heat deflection temperatures HDT_u of the corresponding unfilled polymers, both at 1.85 N/mm^2 (ISO/R 75 A)
(•) Amorphous polymers; (⊙, ○) crystalline polymers; solid line: $HDT_F = HDT_u$; broken lines: empirical
a) Amorphous polymers; b) Apolar crystalline polymers; c) Polar crystalline polymers
Insert: difference $HDT_F - HDT_u$ as function of melting temperatures T_M of unfilled crystalline polymers

The HDTs of crystalline polymers depend on a number of factors. Unfilled or particulate-filled crystalline polymers show HDTs that are often considerably lower than their melting temperature. Upon fiber-filling, HDTs of crystalline polymers increase strongly; they may reach values near the melting temperatures. This behavior is thought to be due to additional polymer crystallization near, or polymer adsorption on, the fiber surface, epitaxial layers have been found to extend from the filler up to 150 nm into the matrix. The surface layers overlap; the resulting physical network reduces creep.

Two groups of HDTs of glass-fiber-filled crystalline polymers can be distinguished (Fig. 60). The HDTs of group b are about 50 – 60 K above those of their unfilled counterparts. This group comprises apolar polymers such as polyethylene, polypropylene, and poly(phenylene sulfide); polyoxymethylene also belongs to group b because its oxygen groups are buried deep inside compact helical structures, which are thus apolar on their surfaces. The difference in HDTs of filled and unfilled group b polymers does not vary with melting temperature. Group c includes polar crystalline polymers (polyesters, polyamides, etc.). For this group, the difference in HDTs of filled and unfilled polymers increases with the melting temperature of the unfilled polymer.

Young's moduli of thermoplastics increase with filler content (Fig. 61). The increase is small for spheroidal fillers (glass spheres, chalk), stronger for platelets (kaolin, talc), and strongest for fibers (glass). Short fibers are usually added in amounts of ca. 30 wt %, which corresponds to ca. 17 vol % for glass fibers ($\rho=2.55$ g/cm^3) in an average polymer ($\rho\approx1.2$ g/cm^3). Higher fiber content often leads to packing problems since the maximum volume fraction of three-dimensional randomly packed rods with $L/d=20$ is already ca. 25 % (glass fibers typically have diameters $d=10-20$ μm and lengths of ca. 0.2 mm after injection molding). Particulate fillers can be added in far greater amounts without sacrificing properties (see Table 19) because maximum packing densities of spheres are, for example, 0.745 for the hexagonally most dense and 0.637 for the randomly most dense packing.

Young's moduli E of filled materials can be described by a modified mixing law

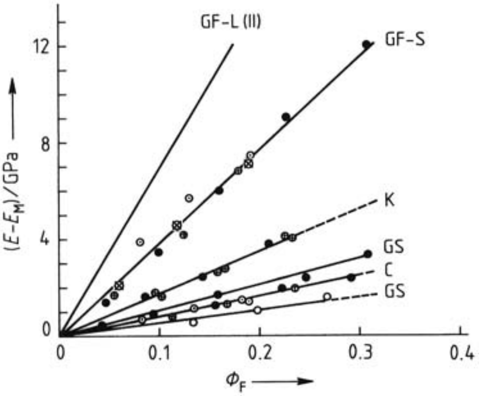


Figure 61. Influence of the volume fraction ϕ_F of fillers on the difference in Young's moduli of filled thermoplastics (E) and their polymer matrices (E_M)
GS=glass spheres; C=chalk; K=kaolin; GF=glass fibers; (S=short; L=long)
○=polyethylene; ⊙=polypropylene; ⊗=polyoxymethylene; ⊕=poly(butylene terephthalate); •=polyamide 6
The solid line for GF-L (||) corresponds to the simple mixing law. From data of [82]

$$E = E_M\phi_M + f\,E_F\phi_F = E_M + (f\,E_F - E_M)\cdot\phi_F \qquad (102)$$

where f is an adjustable parameter. The data in Figure 61 can be described with $f=0.39\pm0.03$ (chalk), 0.66 ± 0.04 (kaolin), and 1.61 (talc). The effect of 30 wt % of short glass fiber was tested in 14 thermoplastics, and f was found to be 0.57 ± 0.04. These numbers increase with the specific area of the fillers, which are given as 0.3 – 2.2 (ground limestone), 0.5 – 1 (glass fibers), 6 – 22 (kaolin), and 6 – 17 m^2/g (talc) [83]. Composites obviously increase in stiffness as the contact between filler and polymer segments increases. Good adhesion is not necessary, since E is measured for strains approaching zero.

The adjustable parameter f of Equation (102) adopts a physical meaning for short fiber reinforced plastics. In such composites, forces are transferred to the hard fiber from the soft matrix if (1) the Young's modulus of the fiber is greater than the Young's modulus of the matrix ($E_F>E_M$), (2) the fiber length L_F exceeds a certain critical value $L_{F,\,crit}$, and (3) the shear strength in the matrix is smaller than the shear strength between fiber and matrix (the fiber would be otherwise pulled out of the matrix unless the fiber breaks). In this case, $f=1-[L_{F,\,crit}/(2\,L_F)]$.

Fracture strengths are, however, measured for maximum strains. The failure mode of filled thermoplastics is matrix dominated. Electron micrographs show that at low fiber contents, planar cracks spread through the matrices and debonded fibers are pulled out of either surface; the matrix must thus adhere well to the filler.

The tensile strength σ_B at break is given by the rule of mixtures ($\sigma_B=\sigma_F\,\phi_F+\sigma'_{M'}\,\phi_M$) where $\sigma'_{M'}$ is the tensile stress of the matrix upon application of a load σ_B to the composite. This relationship applies if (1) the tensile strength σ_B is greater than the contribution $\sigma_M\,\phi_M$ of the matrix component to the total tensile strength σ_B (that is $\sigma_B>\sigma_M\,\phi_M$), and (2) the volume fraction ϕ_F of the fiber exceeds a certain minimum value ($\phi_F>\phi_{F,\,\min}$).

Particulate Fillers usually strongly reduce the fracture strengths of composites of amorphous thermoplastics, whereas those of crystalline polymers are reduced less or not at all. *Short fibers* generally increase the fracture strengths by factors of 1.5 – 2 for amorphous and crystalline polymers alike. Rigid PVC is an exception because its fracture strength is reduced on fiber-filling. The moduli and strengths can be further enhanced if coupling agents are used, which improves the bonding between fiber and matrix (e.g., silanes for glass-fiber-filled polymers).

11.2.2. Molecular Composites

The problem of insufficient bonding between fiber and matrix can be dramatically reduced if so-called molecular composites are used. These materials are dispersions of semiflexible (rod-like) polymer molecules with mesogenic units in chemically similar polymer matrices, e.g., poly(*p*-phenylenebenzobisthiazoles) in polybenzimides (see Fig. 52). The mesogens are not truly molecularly dissolved; rather, they form microdomains in the matrix. The segment axes are randomly distributed in these domains if the molecular composites are formed from polymer solutions with total polymer concentrations c below the critical isotrope phase – mesophase concentration $c_{i/n}$. Microdomains show mesophase behavior if films or fiber are formed at $c>c_i/_n$. Such microcomposites have excellent moduli and fracture strengths (Fig. 52).

11.2.3. Macrocomposites

Polymer macrocomposites are heterogeneous composites of polymers and "macro"-sized additives. Examples are polymer concrete, composition board, long fiber-reinforced polymers, and plywood.

Polymer Concrete is composed of polymer [usually polyester or poly(methyl methacrylate)], aggregate (sand, ground limestone, etc.), and other additives (dyes, etc.); it does not contain cement. *Polymer-concrete hybrids* include polymer – cement hybrids (cement is partially replaced by polymers) and polymer-impregnated concrete (conventional concrete saturated with a monomer that is polymerized in place). Polymer concretes have higher moduli and higher tensile and compressive strengths than ordinary concretes. They are not vulnerable to damage by freeze-thaw cycles.

Composition Boards are panel products. They include particleboard, fiberboard, hard board from flakes or shearings, etc. The fillers are mainly wood products; the resins, urea – formaldehyde (interior applications), and polyurethanes or phenolic resins (exterior).

Long-fiber-filled polymer macrocomposites range in structure from polymers filled with "long" fibers 6 – 12 mm in length to fiber strands and mats filled with polymers. The filler content can often reach 65 wt %. Upon application of tensile stress, local stress concentrations are transferred by shear forces onto the plastic – fiber interface and distributed over the much greater fiber surface area. The fibers must therefore bond well to the plastic (use of coupling agents) and must have a certain length to avoid slipping.

Young's moduli of long glass-fiber-reinforced epoxide resins follow the simple mixing law if the tensile stress is in the fiber direction (Fig. 62). The inverse mixing law is not observed as well for stresses perpendicular to the fiber direction since some fibers bend under stress.

The simple mixing law corresponds to $f=1$ in Equation (102). For long fibers, f has the meaning of an orientation factor. It becomes 1/6 for fibers distributed three-dimensionally at random, 1/2 for 90° cross-plies measured in either fiber direction, and 3/8 for a uniform, planar distribution of fibers.

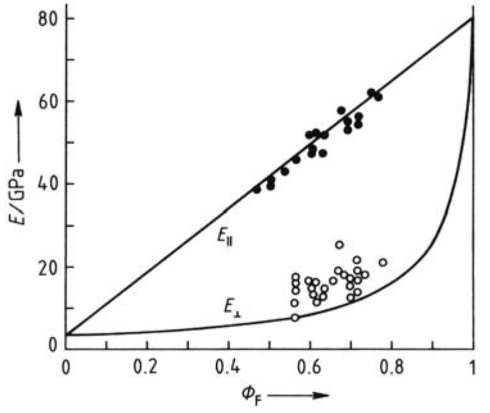


Figure 62. Young's moduli of epoxy – glass-fiber composites parallel (||) and perpendicular (⊥) to the fiber direction.

This group of macrocomposites also includes prepregs (fiber mats soaked with unsaturated polyester resins) and the composites generated by filament winding (wound filaments saturated with epoxies or unsaturated polyesters), both of which are subsequently polymerized.

11.3. Homogeneous Blends

Mixtures of polymers with other polymers are called polymer blends (→ Polymer Blends). Such blends may be composed of two thermoplastics (plastic blends), two elastomers (rubber blends), a plastic filled with an elastomer as the dispersed phase (rubber-modified plastics), an elastomer with a plastic as the dispersed phase (polymer-filled elastomer), or a plastic filled with a polymer melt or a low molar mass liquid (plasticized polymers). Whether or not these blends are truly miscible on a molecular level depends on the thermodynamics of the systems.

11.3.1. Thermodynamics

If two components 1 and 2 are mixed, entropy *S*, enthalpy *H*, and volume *V* change. In many cases, volume changes can be neglected and the Gibbs energy of mixing is given by the changes in enthalpy and entropy: $\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\cdot S_{\mathrm{mix}}$. These changes can be calculated by the Flory – Huggins theory, which assumes that the mixture can be modeled by a three-dimensional lattice on which the monomeric units (or solvent molecules) can be placed. Each monomeric unit experiences the same force field; the theory is thus a mean-field theory. The assumption of a constant force field is fairly well fulfilled for polymer blends and concentrated polymer solutions but not for dilute solutions.

The entropy and enthalpy of mixing are calculated separately. *Entropies* are calculated for ideal solutions (zero mixing enthalpy); all environment-dependent entropy changes are thus zero (translational, vibrational, and inner rotational entropies do not change). Units can however be arranged relative to each other in many ways; however, there is a combinatorial entropy that is also called "configurational entropy" in statistical mechanics.

The mixing of two components is modeled as a quasi- chemical reaction. The *mixing enthalpy* is thus determined by the change in interaction energies and the number and type of nearest neighbors. Enthalpy and entropy terms are added to give the molar Gibbs energy of mixing:

$$(\Delta G_{\mathrm{mix}})^{\mathrm{m}}/RT = \chi\cdot\phi_1\phi_2+\phi_1\cdot\ln\phi_1+(X_1/X_2)\cdot\phi_2\cdot\ln\phi_2 \qquad (103)$$

which, on differentiation with respect to the molar amounts of the components, yields the chemical potentials, for example, of component 1

$$\Delta\mu_1 = RT\{\chi\cdot\phi_2^2+\ln(1-\phi_2)+[1-(X_1/X_2)]\cdot\phi_2^2\} \qquad (104)$$

where χ is the parameter for the interaction between component 1 and component 2 (usually with numerical values between 0 and 2), also called the Flory – Huggins parameter. All three terms in braces must be considered if a polymer 2 is mixed with a solvent 1, for example, a plasticizer ($X_1 \ll X_2$). If both components are polymers however, then $X_1 \approx X_2$ and the entire entropy contribution comes from the relatively small logarithmic term. Thus little combinatorial entropy is gained on mixing two polymers, and the miscibility is determined mainly by the mixing enthalpy, that is, by the term $\chi\,\phi_2^2$.

Phase separation occurs if the curve $(\Delta G_{\mathrm{mix}})^{\mathrm{m}} = f(\phi_2)$ (at T=const.) has a shape that can be touched at two points by a tangent. The compositions at these points are ϕ_2' and ϕ_2'' (with $\phi_2' < \phi_2''$). Two phases exist for the unstable range $\phi_2' < \phi_2 < \phi_2''$, which is separated from the stable ranges $\phi_2 < \phi_2'$ and $\phi_2'' > \phi_2$ by the so- called binodal. The unstable range itself is subdivided by the spinodal into two metastable ranges and one unstable one. Spinodals are characterized by inflection points in the Gibbs energy – composition functions and extremal values in the chemical potential – composition functions. Maximum, minimum, and inflection point become identical at the critical point, which is defined by a zero value of the second derivative of the chemical potential

$$\partial^2\Delta\mu_1/\partial\phi_2^2 = RT\cdot[2\chi-(1-\phi_2)^{-2}] = 0 \qquad (105)$$

This critical point is characterized by a critical volume fraction $\phi_{2,\mathrm{crit}} = 1/(1+X_2^{1/2})$ and a critical interaction parameter $\chi_{\mathrm{crit}} \approx (1/2) + (1/X_2)^{1/2}$.

The temperature dependence of χ is approximately

$$\chi \approx A+(B/T) \qquad (106)$$

where A and B are system-dependent constants; B is positive for endothermal mixtures [i.e., χ increases with increasing temperature and a homogeneous solution exists above an "upper critical solution temperature" (UCST)]. Other systems are homogeneous only below a "lower critical solution temperature" (LCST). The demixing is correspondingly either enthalpy (UCST) or entropy (LCST) induced.

The terms UCST and LCST do not indicate the absolute position of demixing temperatures since some systems show LCST>UCST (Fig. 63). Depending on the system, either an hourglass-type diagram or a closed miscibility gap is shown.

11.3.2. Plastification

Plastification of a plastic is the flexibilization of the material either by added plasticizers (external plastification) or by incorporated flexibilizing comonomer units (internal plastification).

The molecular action of plasticizers consists of a flexibilization of chain segments, which can have various causes. *Polar plasticizers* increase the proportion of *gauche* conformations in polar chains, thus decreasing rotational barriers. *Primary plasticizers* can dissolve helical structures and crystalline regions if they are thermodynamically good solvents. Furthermore both *primary and secondary plasticizers* are diluents; their addition increases the distance between polymer segments and thus decreases the activation energy needed for cooperative movement of segments. Solvation does not per se increase chain flexibility, however, because

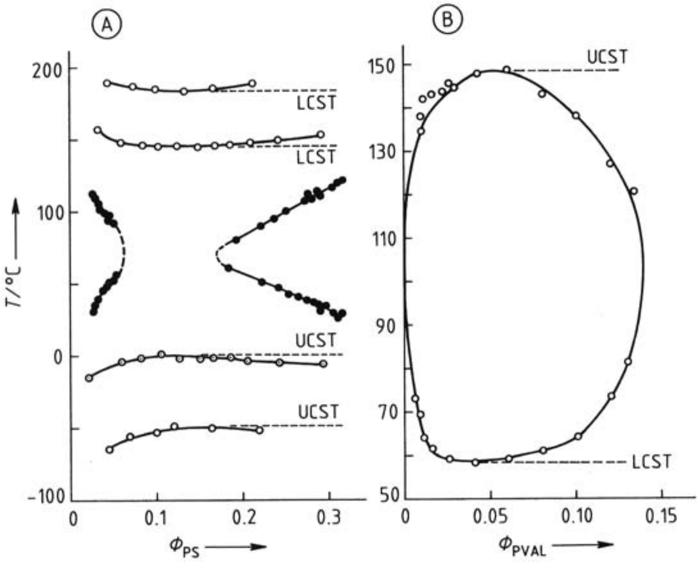


Figure 63. Phase separation temperature as function of polymer – solvent composition
A) Polystyrenes with various molar masses in acetone; B) Poly(vinyl alcohol-*co*-vinyl acetate) (93 : 7) in water
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

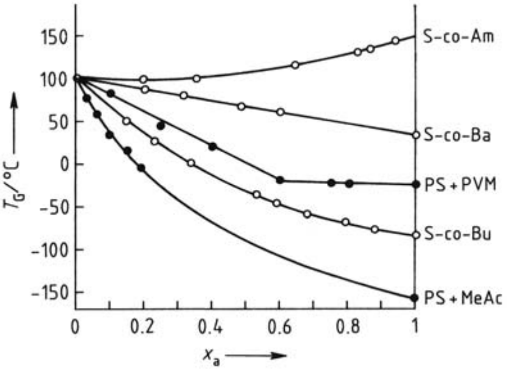


Figure 64. Glass transition temperatures of (•) polystyrene plasticized with methyl acetate (MeAc) or poly(vinyl methyl ether) (PVM) and (○) copolymers of styrene with butadiene (Bu), butyl acrylate (Ba), or acryl amide (Am)

solvent shells act as substituents and increase the rotational barriers.

The molecular effect of an increase in chain flexibility by plasticization is measured as a decrease of glass transition temperatures (Fig. 64). Small molecules are better plasticizers than bigger ones of similar chemical constitution. The plasticizer efficiency decreases with increasing thermodynamic "goodness" of the plasticizer for the polymer (greater interaction, i.e., bigger solvation). Good plasticizers with respect to lowering glass transition temperatures are thus small molecules that act as theta solvents. These plasticizers are however bad for technological applications because they bleed (transport of plasticizer to the surface of the plastic), migrate (transport of plasticizer into another contacting material), or are extractable (e.g., transport into packaged foods). These transport phenomena can be reduced if polymer plasticizers are used. Increasing molar masses lead to decreasing thermodynamic compatibility, however (see below). Technical plasticizers are therefore in most cases a compromise between thermodynamic plasticizer efficiency and kinetically hindered plasticizer transport.

Plastification can also be followed by the changes of certain mechanical properties such as lowering of fracture strength, increase of elongation, and decrease of tensile moduli. Such methods sometimes show "antiplasticizations" at low plasticizer concentrations (Fig. 65) (e.g., increases of moduli). Glass transition temperatures are not increased, however. The effect thus cannot be the result of increased segment mobility. It may be due to a healing of microvoids in amorphous polymers such as polystyrene or to additional crystallization of slightly crystalline polymers such as poly(vinyl chloride).

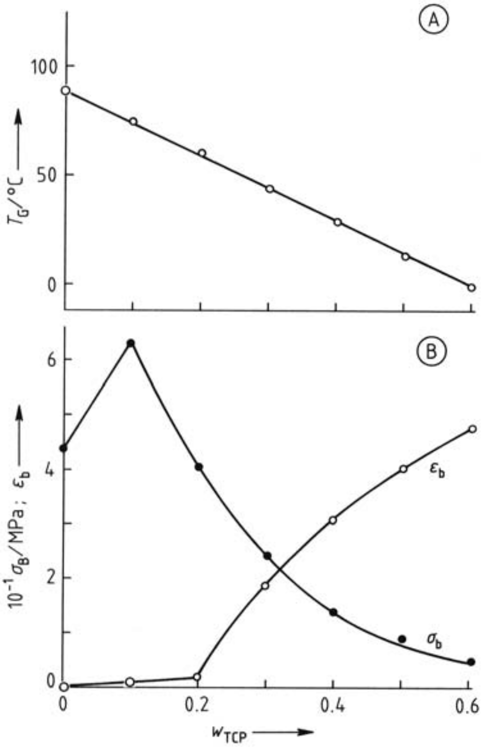


Figure 65. A) Glass transition temperature T_G and B) fracture strength σ_B and elongations ε_B at break of a poly(vinyl chloride) plasticized with tricresyl phosphate (TCP). Reprinted with permission by Hüthig and Wepf Publ., Basel [7]

11.3.3. Rubber Blends

About 75 % of all elastomers are employed as blends. Heterogeneous blends of natural (rubber – styrene) – butadiene rubber or (*cis*-butadiene rubber – styrene) – butadiene rubber are used mainy for tire treads since they reduce abrasion. Homogeneous blends are more rare. They possess only one glass transition temperature which, for 50 – 50 blends, is an average of the glass transition temperatures of the two parent polymers. Heterogeneous blends exhibit two glass transition temperatures, both practically identical to those of the parent polymers.

Homogeneous blends are usually formed if the difference in solubility parameters is smaller than 0.7 $cal^{1/2}\ cm^{-3/2}$ (1.44 $J^{1/2}\ cm^{-3/2}$).

11.3.4. Plastic Blends

Plastic blends are usually immiscible because the combinatorial entropy of mixing is too small (high molar masses) and the enthalpy changes on mixing are often positive. Miscibility is observed for three types of systems:

1. Chemically similar polymers, for example, polystyrene – poly(*o*- chlorostyrene), showing both LCST and UCST
2. Systems having specific interactions between different components, for example, polystyrene – poly(vinyl methyl ether); these systems show only LCSTs
3. Systems consisting of oligomers, for example, oligo(ethylene oxide) – oligo(propylene oxide); these systems possess only UCSTs

Homogeneous polymer blends show only single glass transition temperatures; the composition dependence of these T_G's can be described by the simple rule of mixtures. Two-phase systems always show two glass transition temperatures if the phase diameters are greater than ca. 3 nm. Transparency, on the other hand, is no indication of a single-phase blend since opacity can be observed only if the refractive indices of the two phases are sufficiently different and if the phase diameters are greater than ca. one-half the wavelength of incident light. The presence of two phases in clear specimens can often be detected with electron microscopy by special staining techniques.

Modified PPO, a blend of poly(2,6-dimethylphenylene oxide) and polystyrene, is the industrially leading *homogeneous blend*. Blends of poly (vinyl chloride) with poly(methyl methacrylate), poly(ethylene-co-vinyl acetate) or chlorinated polyethylene are also said to be one-phase systems.

11.4. Heterogeneous Blends

11.4.1. Compatible Polymers

Two polymers may be thermodynamically immiscible but still mechanically compatible. These compatible blends are two- or multiphase systems that show multiple glass transition temperatures, which do not change with composition. The components do not separate, however, under mechanical stress during the expected life of the product. Such mechanical compatibilities can be improved or introduced by the addition of diblock polymers. One block of these diblock polymers is compatible with one phase type of the heterogeneous blend and the other one with the other type (see Section 5.3.6). The two blocks need not necessarily be chemically identical with the two parent polymers, that is, a compatibility of poly (A) and poly (B) can be achieved not only by addition of poly (A)-*block*-poly (B) but also by poly (A)-*block*-poly (C) if the C block is either miscible with poly (B) or can form mixed crystals with poly (B).

11.4.2. Blend Formation

Heterogeneous polymer blends can be produced by mixing together two polymers (as melts, lattices, or in solution) or by in situ polymerization of a monomer in the presence of a dissolved polymer.

The energy taken up during *melt mixing* is used for flow processes and for the generation of surfaces of new microdomains. After some time, a steady state is established and the domain size becomes constant. No macroscopic demixing occurs because of the low diffusion coefficients resulting from the high viscosities.

Latex Blending consists of the mixing of aqueous dispersions of two polymers. Far lower temperatures and lower shear fields can be employed compared to melt blending. The good mixing of the latex particles remains after coagulation. The domain size is, however, restricted to the size of the latex particles themselves; it is not altered by subsequent melting of the coagulate.

Solution Blending involves the mixing of two polymer solutions. Miscible polymers can be blended to domains of molecular size. Solutions of immiscible polymers demix, however, at very low concentrations, sometimes under fractionation with respect to molar masses. Domains grow further on solvent removal by distillation or freeze drying.

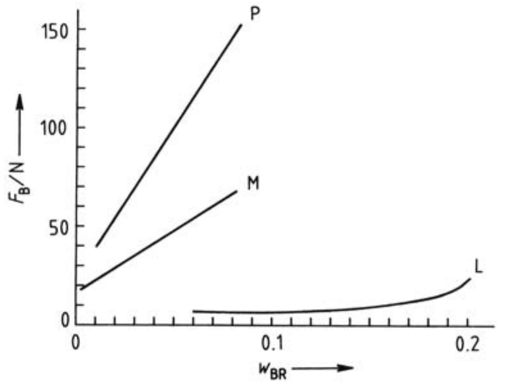


Figure 66. Impact strength with notch F_B as function of the mass concentration w_{BR} of *cis*-1,4-polybutadiene in its blends with polystyrene. P=In situ polymerization of styrene; M=Melt blending; L=Latex blending
Reprinted with permission by Plenum, New York [84]

In situ polymerization involves solutions or gels of polymers in monomers, which are subsequently polymerized. The in situ polymerization of styrene in a styrenic polydiene solution, which leads to rubber-toughened polystyrene (HIPS) is most important industrially. The polymerization of a cross-linkable monomer in a gel of a cross-linked rubber in the very same monomer results in interpenetrating networks.

Various blending processes produce blends with very different properties (Fig. 66). The high notched impact strengths of the polymerization-blended materials (line P) are caused by a strong anchoring of phases due to the formation of graft copolymers of styrene on polybutadiene and cross-linking within the rubber domains, both caused by free-radical initiators. Such processes are less prevalent during melt blending (radical formation by high shearing at elevated temperature) (line M) and latex blending (low shearing at ambient temperature) (line L). In situ polymerization is thus the method of choice for unsaturated rubber (easy cross-linking and grafting by chain transfer) and monomer – rubber pairs with favorable *Q*, *e*-values for copolymerizations. In all other cases, blends are formed by melt mixing.

11.4.3. Toughened Plastics

Rubber-modified plastics (toughened plastics, high-impact plastics) consist of rubber domains dispersed in plastic matrices. The domain size varies with the blending process. Typical values are ca. 0.1 μm for melt-blended poly(vinyl chloride) – acryl rubber and 1 μm for polystyrene – polybutadiene. The domains are often multiphased; small plastic domains are imbedded in the rubber domains (Fig. 67). The morphologies depend strongly on the blending process. During stirred in situ polymerizations, phase inversions often occur if the amount of newly formed plastic approaches that of the incipient rubber. During phase inversion, already present plastic particles may be embedded in the newly formed rubber domains.

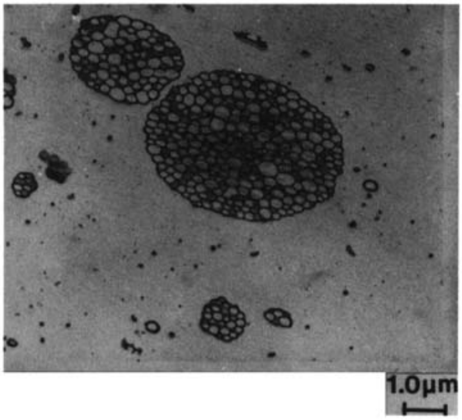


Figure 67. Rubber domains in high-impact polystyrene by in situ free-radical polymerization of styrenic polybutadiene solutions
Reprinted with permission by Society of Plastics Engineers [85]

Rubber-toughened plastics are valued because of their improved impact strength. On impact, very many crazes are formed near the equators of the rubber particles. The crazes propagate until they encounter an obstacle (e.g., rubber particle or shear band) or until the stress concentration at the tip of the craze becomes very low. Many small crazes result, and the stress is evenly distributed if the rubber phase is cross-linked and binds well to the thermoplast phase [e.g., by in situ formed graft copolymers (HIPS)]. In contrast, stress peaks concentrate at a few defect points in normal thermoplasts.

11.4.4. Thermoplastic Elastomers

(→ Thermoplastic Elastomers)

Thermoplastic elastomers (elastoplastics, thermoplastics, plastomers) are processed like thermoplastics but applied like elastomers. Their unique properties follow from their molecular structures; their chains consist of "soft" and "hard" segments in block, graft, or segmented copolymers composed of monomeric units A and B. The A and B segments are mutually incompatible and form locally separated regions. With a well-designed molecular architecture, domains of the "hard" A segments (transition temperature>service temperature) act as physical cross-links in the continuous matrix of the "soft" B segments (transition temperature<service temperature) (Section 5.3.6). Such transition temperatures may be glass transition temperatures in amorphous polymers or melting temperatures in partially crystalline polymers. The A segments attain mobility above these transition temperatures and the elastoplasts become processible.

Thermoplastic elastomers comprise linear triblock polymers of the polystyrene – *block*-polydiene – *block*-polystyrene type; radial, star, or "teleblock" polymers of the same monomeric units; urethane segment or block copolymers with polyester or polyether soft segments; polyesteramides and polyesteretheramides; graft copolymers of butyl rubber on polyethylene, vinyl chloride on poly(ethylene-co-vinyl acetate), styrene – acrylonitrile on saturated acryl rubbers, and various ionomers.

Thermoplastic elastomers can also be produced by "dynamic vulcanization." The mastication of blends of conventional rubbers and crystalline poly(α-olefins) leads to chain scissions. The resulting macroradicals cross-link the rubber domains.

The mechanical properties of thermoplastic elastomers are determined mainly by their morphologies. In styrene – butadiene – styrene triblock polymers, for example, morphologies are governed by the spatial requirements of the various blocks (Section 5.3.6). With a low content of hard styrene segments, small spherical polystyrene microdomains are formed in the soft polybutadiene matrix. These microdomains act as physical cross-linkers. The distances between the domains are large, and the polymer behaves as a weakly linked elastomer with correspondingly high extension (Fig. 68). The domains are larger and their distances are shorter at 28 % styrene units and the polymer strengthens (stiffens). The stiffening becomes stronger for rodlike styrene domains (39 % S). Lamellar morphologies (53 % S) show an "unruly" behavior initially because of reorientation of

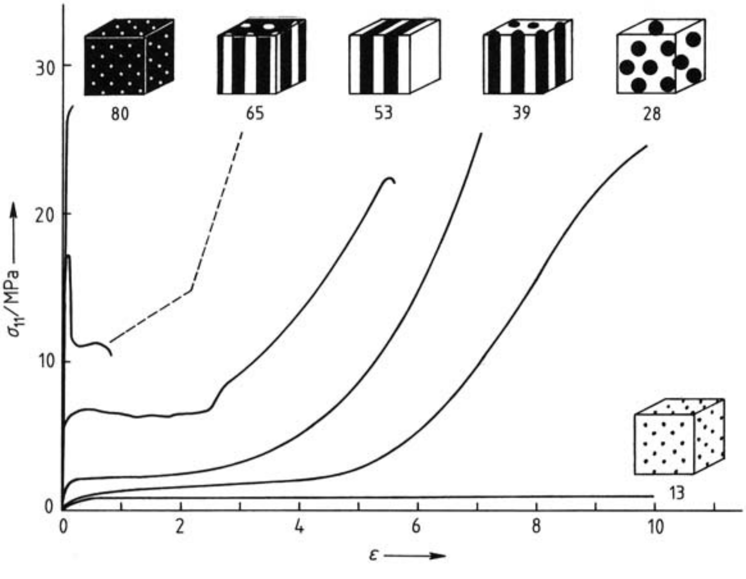


Figure 68. Stress – strain curves and morphologies of styrene – butadiene – styrene triblock polymers with various styrene contents
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

lamellae. At even higher styrene content, the polymer behaves as a plasticized tough thermoplast (65 % S) or almost like polystyrene itself (80 % S).

11.5. Expanded Plastics (→ Foamed Plastics)

Expanded plastics (foams, foamed plastics, cellular plastics) are blends of plastics with air. They are subdivided according to their rigidity, their cell structure, and the nature of the parent plastics. Rigid expanded plastics are used mainly for thermal insulation, and flexible foams for damping and cushioning materials.

The rigidity ("hardness") of expanded plastics follows the properties of the parent polymers. Phenolic and urea resins thus yield brittle-rigid plastics; polystyrene and hard poly(vinyl chloride), tough-rigid; and polyethylenes, polyurethanes, and plasticized PVC, semirigid to flexible foams. The elastic moduli of expanded plastics decrease approximately proportional to their polymer content (simple mixing law). Since, however, the stiffness of an article increases with the third power of the wall thickness, the gases in expanded plastics work as enhancers that reduce material costs and weights.

Tensile strengths of foamed plastics also follow the simple mixing law. Because the tensile strengths of gases are diminishingly small, tensile strengths σ_B of foamed plastics are determined by the volume fraction ϕ_p and strengths $\sigma_{B,p}$ of the plastics themselves [i.e., $\sigma_B \approx \sigma_{B,p} \cdot \phi_p = \sigma_{B,p} \cdot (\rho/\rho_p)$] (Fig. 69). Compression strengths follow a similar simple mixing law.

The cell structure can be open, closed, or mixed. Open-celled foams are always air filled, regardless of the blowing or expanding gases used for foam manufacture. The trapped gases in closed-cell structures can be exchanged with the surrounding air only by slow diffusion through the polymer matrix. Since thermal conductivities of low-density foams ($\rho_p < 0.3$) obey, to a first approximation, a logarithmic mixing law, they are considerably affected by the thermal conductivities of trapped gases [(λ=93 J m^{-1} h^{-1} K^{-1} (nitrogen), 56 J m^{-1} h^{-1} K^{-1} (CO_2), 26.4 J m^{-1} h^{-1} K^{-1} (CCl_3F)]. The gas exchange is considerably reduced in integral skin foams (dense skin, low-density core) and in syntactic foams (plastics filled with hollow

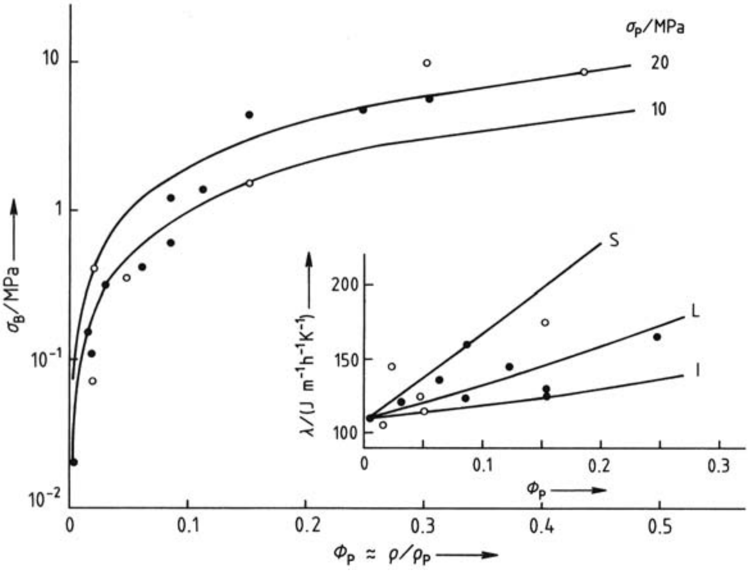


Figure 69. Tensile strengths of expanded plastics as a function of the volume fraction of the rigid (•) or flexible (○) parent polymers P

Solid lines indicate a) Simple mixing law for σ_p=20 MPa; b) Simple mixing law for σ_p=10 MPa;Insert: Thermal conductivities (for λ_p=700 and λ_{air}=110 J (m^{-1} h^{-1} K^{-1}) of rigid (•) and flexible (o) plastic foams S: Simple mixing law; L: Logarithmic mixing law; I: Inverse mixing law spheres; spheres may be made of glass, ceramics, or plastics and contain either gases or a vacuum).

12. Waste Disposal (→ Plastics, Recycling)

Four different, although frequently interconnected, aspects must be considered in the disposal of plastic waste: (1) technological demands, (2) economic considerations, (3) energy consumption, and (4) environmental concerns.

Modern technology demands certain material properties for certain applications that can be delivered only by polymers and not by other materials such as metals or ceramics. Examples range from rubber tires to high-tech applications such as polymer resists in electronic chip production. The desirability of polymers for technology-driven demands is usually undisputed; the discussion centers rather around the desirability of commodity plastics, especially for packaging purposes.

It is also not much disputed, at least among people that are well-versed in technology, that polymeric materials are very economical compared to other materials in terms of production and use. However, the ecological costs are questioned: the hidden costs of the "free" use of air, water, and land in the production and disposal of polymers and the suspected high energy consumption in the use of polymers.

Energy consumption has been studied by consumer agencies (e.g., NATO Science Committee), industry (e.g., BASF), and government (e.g., Swiss Environmental Protection Agency). Although differences exist, newer data all agree that the energy consumed in plastics production agrees favorably with that of other materials (Table 33) if use (on a volume basis) rather than sale (on a weight basis) is considered.

Energy considerations must however be based on specific applications of materials. For example, these considerations must take into account for a certain good the current possible use of different materials for its manufacture, its use (including cleaning), possible recycling, and/or disposal by landfill or incineration (with partial use of heat). This is shown for the example of 1000 1-L milk packages (in Table 34).

Energy data are again favorable for plastics, as are the critical amounts of air and water employed in their production, use, and disposal (i.e., volumes to which air and water can be maximally charged without exceeding Swiss environmental laws). It must be mentioned in this context that only ca. 5 % of the world petroleum production is used for the manufacture of polymers; the remainder is burned (as gasoline, heating oil, etc.), often with very low energy efficiency (ca. 30 % in cars) and large amounts of harmful byproducts (exhaust gases).

Environmental concerns include possible harmful effects by plastic articles, plastics themselves, polymers, incineration products, and byproducts of polymer and plastics manufacture. Environmentalists estimate the amount

Table 33. Energy consumption for the production of various materials according to various sources

Material	Consumption, kJ/cm^3		
	NATO	BASF	SEPA*
Lumber	2.0		
PE-HD		63	68
PVC	11	73	84
ABS		89	87
PET		113	
PS, expanded		1.4	
PUR, expanded		3.0	
Paper (kraft, unbleached)	40		63
Tin plate			210
Aluminum	< 460		750
Glass	< 125		> 26

[*] Swiss Environmental Protection Agency.

Table 34. Energy consumption and critical environmental data for 1000 1-L packages of milk [86]

	PE		Paper carton	Glass bottle
	Tube	Bottle		
Use cycle (life)	1	1	1	40
Weight per life in kg	7.0	22.0	25.0	40.0
Energy consumption in MJ*	400	1510	1770	650
Environmental impacts				
Air, 10^6 m^3	5.9	20.5	30.9	5.4
Water, m^3	3.0	17.2	154	9.3
Solids (landfill), L	2.3	9.8	8.3	6.8
Solids, (average Swiss disposal), L**	0.35	3.0	1.3	3.3

[*] For average Swiss disposal: 23 % landfill and 77 % incineration (55 % with use of energy).

[**] Solid waste from PE (ash from production processes), paper (ash from production and paper), glass (with 60 % recycling assumed), aluminum and tin plate (100 %, no recycling).

of plastics discarded annually into the high seas as 1×10^6 t. Certain plastics articles are undoubtedly harmful to wildlife, for example, six-pack rings and old fishing nets to fish and other animals. Since man is notoriously careless, the use of biodegradable plastics for such articles may be justified.

Biodegradable plastics either contain biodegradable polymers themselves or are compounds of conventional polymers with biodegradable polymers such as starch. Biodegradation may occur via hydrolysis (starch, polyesters) or UV radiation (polymers containing carbonyl groups) or both. The degradation however is slow, taking from several months under laboratory conditions to several years in landfills. Biodegraded products may no longer be visible, but whether biodegradation proceeds to small molecules and whether these molecules are harmful to living organisms are still not known. Harmful polymer additives may be released during biodegradation. Conventional polymer molecules, on the other hand, are not harmful to living beings, at least not to higher ones, because they can be neither resorbed nor digested. The energy content of plastics is of course wasted during biodegradation.

Biodegradable polymers thus do not seem to be the general solution to the plastic waste problem. Contrary to popular opinion, the amount of plastics in household refuse is relatively small, ca. 7 wt% vs. ca. 50 % paper, and almost constant over at least 25 years according to archaeological studies of landfills. Weight fractions and not volume fractions of plastics must be used for comparison with other materials because hollow plastic containers and expanded plastics are compressed by the weight of the landfill (glass bottles are not compressed). Biodegradation processes are very slow in landfills (absence of light, air, and even microorganisms); some buried papers could be read after 25 years in a landfill.

Table 35. Recycling of plastics in the United States (1988)

Polymer	Mass in 1000 t		% Recycled
	Consumed	Recycled	
Polyolefins	11 538	343	3.0
PVC	3 779	34	0.9
Styrenics	3 516	39	1.1
PETP (bottles)	911	54	5.9
PA	253	27	10.7
Other	6 219	< 1	< 0.01
Total	26 216	498	1.9

This leaves recycling and incineration as possible ways for disposing of plastics. Most industrial plastic waste is already recycled or incinerated. The problem is the collection, cleaning, and recycling of household refuse. Only ca. 2 % of all plastics consumed were recycled in the United States (Table 35) and the Federal Republic of Germany in 1988.

Since unsorted recycled polymers represent mixtures of different grades and even different polymers, they can be used only for low-value articles. For comparison: the gross discards recovered in the United States were 25 % of aluminum, 23 % of paper and paperboard, and 9 % of glass.

The sorting of discarded plastics articles is made more easy by recently introduced codes which are stamped on the bottom of containers or other inconspicuous places. The codes consist of three broken arrows, arranged in a triangle, and a number, sometimes also combined with letters and/or bar code (Fig. 70). The numbers and letter combinations indicate the type of plastics. The letter combinations are not always identical with the acronyms and abbreviations recommended by ISO, ASTM, DIN, IUPAC, etc. for the same polymers. The following number and letter codes are used: 1=PETE [for poly (ethylene terephthalate)], 2=HDPE (for high-density polyethylene), 3=V (for vinyl chloride polymers), 4=LDPE (for low-density polyeth-

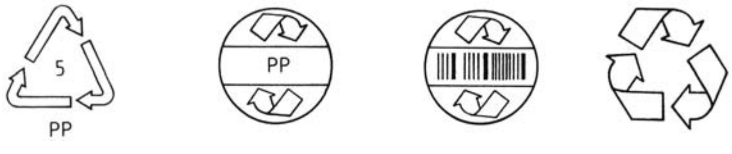


Figure 70. Symbols for recyclable plastics. Left: U.S. symbol with code number and code letters. All others: various symbols used by European manufacturers.

ylene), 5=PP (for polypropylene), 6=PS (for polystyrene), 7 (for all other plastics, including multilayered materials).

Incineration is the present method of choice in many European communities: 77 % of all household refuse is incinerated in densely populated Switzerland and 30 % in West Germany, but only 10 % in the United States where 80 % of the refuse is accumulating rapidly in landfills. Furthermore, concerns exist about the emission of HCl from the burning of PVC, the generation of dioxins, and the disposal of heavy-metal-containing ash. In the Federal Republic of Germany, only 18 % of the HCl comes from the incineration of refuse (and not more than half of it from PVC); the primary sources of HCl are power plants (1978 data). This HCl is removed by scrubbing, etc., and may be used to bind heavy metals in compost from incineration. Generation of dioxins can be reduced significantly by high-temperature incinerators, which of course command higher investment costs.

References

1 H.-G. Elias: “Technologie,” *Makromoleküle*, vol. 2, Hüthig and Wepf, Basel 1992.
2 F. W. Billmeyer, Jr.: *Textbook of Polymer Science*, 3rd ed., Wiley, New York 1984.
3 F. Rodriguez: *Principles of Polymer Systems*, 3rd ed., Hemisphere Publ., New York 1989.
4 G. Champetier, R. Buvet, J. Néel, P. Sigwalt, (eds.): *Chimie Macromolèculaire*, 2 vols., Hermann, Paris 1970 – 1972.
5 H.-G. Elias: “Grundlagen,” *Makromoleküle*, 5th ed., vol. 1, Hüthig and Wepf, Basel 1989.
6 *Macromolecules*, 2nd ed., 2 vols., Plenum, New York 1984.
7 *Makromoleküle*, 4th ed., Hüthig and Wepf, Basel 1981.
8 L. Mandelkern: *An Introduction to Macromolecules*, 2nd ed., Springer, New York 1972, 1982.
9 J. M. G. Cowie: *Polymers: Chemistry and Physics of Modern Materials*, Intext Educational Publ., New York 1974; *Polymers: Chemistry and Physics of Modern Materials*, 2nd ed., Routledge, Chapman and Hall, New York 1991.
10 F. A. Bovey, F. H. Winslow (eds.): *Macromolecules*, Academic Press, New York 1979.
11 R. B. Seymour, C. E. Carraher, Jr. *Polymer Chemistry*, 2nd ed., Dekker, New York, 1989.
12 A. Rudin: *The Elements of Polymer Science and Engineering*, Academic Press, New York 1982.
13 P. C. Hiemenz: *Polymer Chemistry*, Dekker, New York 1984.
14 P. Munk: *Introduction to Macromolecular Science*, Wiley, New York 1989.
15 International Union of Pure and Applied Chemistry: *Compendium of Macromolecular Nomenclature (Purple Book)*, Blackwell Sci. Publ., Oxford 1991.
16 J. Schultz: *Polymer Materials Science*, Prentice-Hall, Englewood Cliffs, N.J., 1974.
17 J. A. Brydson: *Plastics Materials*, 3rd ed., Butterworth, London 1975.
18 S. Rosen: *Fundamental Principles of Polymeric Materials for Practicing Engineers*, Cahners Books, Boston 1973.
19 J. H. DuBois, F. W. John: *Plastics*, 5th ed., Van Nostrand-Reinhold, New York 1976.
20 W. E. Driver: *Plastics Chemistry and Technology*, Van Nostrand-Reinhold, Cincinnati 1974.
21 *Houben-Weyl*, 5th ed., **20**; *Science of Synthesis*, vol. 1, 2001, p. 57; *Science of Synthesis*, vol. 2, 2002, p. 291; *Science of Synthesis*, vol. 2, 2002, p. 906.
22 G. W. Becker, D. Braun et al. (eds.): *Kunststoff-Handbuch*, 2nd ed., Hanser, München, 1983 ff. (many vols.).
23 H. Mark, C. Overberger, G. Menges, N. M. Bikales (eds.): *Encyclopedia of Polymer Science and Engineering*, 2nd ed., 19 vols., Wiley, New York 1985 – 1990.
24 W. A. Kargin (ed.): *Enciklopedia Polimerov*, 3 vols., Sovietskaya Enciklopedia Publ., Moscow 1972.
25 G. Allen, J. C. Bevington (eds.): *Comprehensive Polymer Science*, 7 vols., Pergamon, Oxford 1989.
26 *Chemiefasern auf dem Weltmarkt*, 7th ed., Deutsche Rhodiaceta , Freiburg/Br., 1969, Supplement 1976 (trade names of fibers).
27 The International Plastics Selector, *Commercial Names and Sources*, Cordura Publ., San Diego 1978.
28 *Parat (Fachinformationszentrum Chemie*, Berlin), Index of Polymer Trade Names, VCH, Weinheim, Germany 1987.
29 J. Brandrup, E. H. Immergut (eds.): *Polymer Handbook*, 3rd ed., Wiley, New York 1989.
30 O. Griffin Lewis: *Physical Constants of Linear Homopolymers*, Springer, Berlin 1968.
31 R. E. Schramm, A. F. Clark, R. P. Reeds (eds.): *A Compilation and Evaluation of Mechanical, Thermal, and Electrical Properties of Selected Polymers*, U.S. National Bureau of Standards , Washington, D.C., 1973.
32 P. A. Schweitzer: *Corrosion Resistance Tables (Metals*, Plastics, Nonmetallics, Rubbers), Dekker, New York 1976.
33 The International Plastics Selector, San Diego 1977.
34 H. Saechtling: *Kunststoff-Taschenbuch*, 24th ed., Hanser, Munich 1989; International Plastics Handbook, 2nd ed., Hanser, München 1989.
35 *Modern Plastics Encyclopedia*, McGraw-Hill, New York (annually in October as issue 10 A).
36 *Encyclope* die Francaise des Matieres Plastiques, Les Publicateurs Techniques Association , Paris, annually.
37 J. E. Williams (ed.): *Computer-Readable Databases*, American Library Association, Chicago 1985.

38 German Plastics Institute, Plastics Databank POLYMAT, Darmstadt; Fachinformationszentrum Chemie, Berlin (6000 polymers from 80 manufacturers).
39 Plastics Databank CAMPUS (= Computer Aided Material Preselection by Uniform Standards), (5000 thermoplastics with 50 most important properties each), issued for their company products by 17 European companies.
40 Polymer Materials Database, Fachinformationszentrum Berlin (continuously updated).
41 E. R. Yescombe: *Plastics and Rubbers: World Sources of Information*, 2nd ed., Appl. Sci. Publ., Barking 1976.
42 G. J. Patterson: *Plastics Book List*, Technomic Publ., Westport 1975.
43 P. Eyerer: *Informationsführer Kunststoffe*, VDI-Verlag, Düsseldorf 1976.
44 J. Schrade: *Kunststoffe (Hochpolymere), Bibliographie aus dem deutschen Sprachgebiet, Erste Folge* 1911 – 1969, I. Schrade, Schweiz. Aluminium AG., Zürich 1976, Zweite Folge, Zürich 1980.
45 O. A. Battista, *The Polymer Index*, McGraw Hill, New York 1976.
46 S. M. Kaback: "Literature of Polymers, " *Encycl. Polym. Sci. Technol.* **8** (1968) 273; J. T. Lee, *Encycl. Polym. Sci. Eng.*, 2nd ed., **9** (1987) 62.
47 W. J. Roff, J. R. Scott: *Handbook of Common Polymers*, Butterworths, London 1971.
48 M. Ash, I. Ash: *Encyclopedia of Plastics, Polymers and Resins*, 4 vols., Chem. Publ. Co., New York 1982 –1988.
49 M. S. M. Alger: *Polymer Science Dictionary*, Elsevier Applied Sci. Publ., Barking 1989.
50 American Society for Testing Materials, ASTM D-1600–86 a; D-1418–67; D-4020–81.
51 German Industrial Standards DIN 7723; 7728 (1988); 16 913; 55 950; 60 001.
52 European Textile Characterization Law.
53 International Organization for Standardization, ISO 1043 – 1978, ISO 1629 – 1980.
54 Guide for the Harmonisation of Designations of Thermoplastic Materials, ISO/TC 61/SC 9 N 435, April 1981; ASTM D 4000.
55 K. Wiebusch, *Kunststoffe-German Plastics* **72** (1982) 22, 167.
56 F. O. Swanson, *Plastics Engng.* (1983) Jan. 31.
57 R. H. Wehrenberg, II, *Mat. Engng.* (1984) Feb. 48.
58 H.-Elias *et al.*, *Polymer News* **9** (1983) 101; **10** (1985) 169.
59 J. H. DuBois: *Plastics History – U.S.A.*, Cahners, Boston 1971.
60 J. K. Craver, R. W. Tess (eds.): *Applied Polymer Science*, Am. Chem. Soc., Washington, D.C., 1975.
61 F. M. McMillan: *The Chain Straigtheners: Fruitful Innovation. The Discovery of Linear and Stereoregular Polymers*, MacMillan, London 1981.
62 R. B. Seymour (ed.): *History of Polymer Science and Technology*, Dekker, New York 1982 (Reprint of articles in *J. Macromol. Sci.-Chem.* A 17 (1982) 1065 –1460.
63 R. Friedel: *Pioneer Plastic. The Making and Selling of Celluloid*, University of Wisconsin Press, Madison, 1983.
64 W. Glenz (ed.): *Kunststoffe – Ein Werkstoff macht Karriere*, Hanser, München 1985.
65 United Nations, Statistical Yearbooks.
66 Calculated from data in *Kunststoffe* **73** (1983) no. 10.
67 H.-G. Elias, F. Vohwinkel: *New Commercial Polymers*, Gordon and Breach, New York 1986; Neue polymere Werkstoffe, Hanser, München 1983.
68 H.-G. Elias, *Grosse Moleküle*, Springer, Berlin 1985 *Mega Molecules*, Springer, Berlin 1987. *Megamolekuly*, Khimiya, Leningrad 1990.
69 United States, Statistical Abstracts (annually).
70 D. Tomalia, A. M. Naylor, W. A. Goddard III, *Angew. Chem.* **102** (1990) 119; *Angew. Chem. Intern. Ed.* **29** (1990) 138.
71 G. Natta, P. Corradini, *Nuovo Cimento, Suppl.* **15** (1960) 11.
72 D. Lang, H. Bujard, B. Wolff, D. Russell, *J. Mol. Biol.* **23** (1967) 163.
73 R. Gächter, H. Müller (eds.): *Plastics Additives Handbook* 3rd ed., Hanser, München 1989.
74 A. E. Woodward, *Atlas of Polymer Morphology*, Hanser, München 1988.
75 C. Ruscher, E. Schulz, private communication.
76 R. J. Samuels, private communication.
77 P. J. Flory, *Adv. Polym. Sci.* **59** (1984) 1.
78 *Kunststoff-Physik im Gespräch*, 8th ed., BASF, Ludwigshafen 1988.
79 H. M. Laun, H. Münstedt, *Rheol. Acta* **17** (1978) 415.
80 S. Onogi, T. Matsuda, K. Kitagawa, *Macromolecules* **3** (1970) 109.
81 S. Wellinghoff, E. Baer, private communication.
82 G. E. Ehrenstein, R. Wurmb, *Angew. Makromol. Chem.* **60/61** (1977) 157.
83 T. H. Ferrigno, in S. Katz, J. V. Milewski (eds.): *Handbook of Fillers and Reinforcements for Plastics*, Van Nonstrand, New York 1978, p. 11.
84 J. A. Manson, L. H. Sperling: *Polymer Blends and Composites*, Plenum, New York 1976.
85 S. L. Aggarwal, R. L. Livigni, *Polym. Eng. Sci.* **17** (1977) 498.
86 Bundesamt für Umweltschutz, Oekobilanzen von Packstoffen (Schriftenreihe Umweltschutz), no. 24, Bern 1984.

Further Reading

C. A. Harper: *Handbook of plastics technologies*, McGraw-Hill, New York, NY 2006.
E. Lokensgard: *Industrial plastics*, 5th ed., Delmar Cengage Learning, Clifton Park NY 2009.