Plastics, General Survey, 1. Definition, Molecular Structure and Properties

Hans-Georg Elias, Michigan Molecular Institute, Midland, United States

Rolf Mülhaupt, Institute for Macromolecular Chemistry, Freiburg, Germany

10.1002/14356007.a20_543.pub2

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, also termed macromolecules (Greek: *macro* = large), are not synonyms. Polymers or prepolymers are raw materials for plastics; they become plastics only after processing. The same polymers may be used as plastics or as fibers, paints, rubbers, coatings, adhesives, thickeners, surfactants, and ion-exchange membranes. Properties of polymers are engineered by varying the molecular architecture or the formulation, combining them with different materials in multicomponent and multiphase systems. Typically, plastics contain additives that are needed to enhance their stability and to tune their properties. Unparalleled by any other material, polymers are exceptional regarding their attractive combination of facile processing with low mass and high versatility in terms of properties, applications, flexible choice of feedstocks, and recycling. The system integration of functional polymers represents the key to the development of advanced technologies with applications ranging from lightweight engineering to packaging, construction, aerospace and automotive industries, as well as biomedical engineering. Whereas most plastics are passive, advanced functional plastics are rendered interactive and capable of responding to environmental stimuli. Today, highly cost-, resource-, eco-, and energy-efficient polymers play a prominent role in sustainable development of advanced materials and technologies.

1.1. Polymers

1.1.1. Fundamental Terms [1–16]

The term polymer refers to macromolecules composed of many units (Greek: *poly* = many, *meros* = parts). As first proposed by HERMANN STAUDINGER in 1920, who was awarded the Nobel Price of Chemistry for his groundbreaking concept in 1953, macromolecules consist of many atoms, usually a thousand or more, thereby having high molar masses. Prior to STAUDINGER, the term polymer was not related to high molar mass. For example, benzene was originally called a polymer which was "polymerized" from three acetylene molecules. What is now called a polymer consists of molecules with hundreds and thousands of such units; it was therefore termed "high polymer" in the ancient 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 monomer units in the polymer molecule is called the degree of polymerization X. There are, however, many polymer molecules (especially biopolymer molecules) with very different types of monomers per molecule, such as protein molecules $H(NH–CHR–CO)_nOH$ with up to 20 different R substituents. In accordance with STAUDINGER's view, a less constraining and more general term for polymer molecule is thus macromolecule. However, there is no sharp dividing line with respect to the number of units per molecule between macromolecules and low molar mass compounds. In principle, linear thermoplastic polymers are considered polymers when entanglement occurs, thus accounting for the viscoelastic properties typical for polymeric thermoplastics.

It was HERMANN STAUDINGER who recognized that polymers in industry and in nature are synthesized according to the same blueprint. Similar to pearls in a pearl necklace, monomer molecules are linked together by covalent bond formation. In the early days of polymer sciences and engineering, all polymers were bio-based, because efficient synthetic polymerization processes were not at hand. Prominent examples of biopolymers include proteins, polynucleotides, *cis*-1,4-polyisoprene as natural rubber, polysaccharides (carbohydrates) with cellulose as the most abundant polymer and major component of biomass. Wood is a composite of two biopolymers, i.e., cellulose and lignin. As pointed out by STAUDINGER and others, most silicates are inorganic polymers derived by polymerization of silicic acid and its derivatives. Some of these naturally occurring polymers are used by man without further chemical transformation (e.g., cellulose for paper and cardboard). Yet, the chemical transformation of natural polymers with retention of their chain structures leads to solution and even melt processable 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 produce galalith (plastic) or the vulcanization of *cis*-1,4-polyisoprene (natural rubber) to afford an elastomer.

Today, most polymers are synthesized chemically from synthetic monomers. Examples include 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. Whereas the majority of monomers are derived from oil and gas in petrochemistry, the progress in biotechnology and the quest for green economy are stimulating the production of bio-based synthetic monomers, such as butadiene, ethylene, propene, acrylic acid, glycol, and lactic acid in biorefineries using biomass as feedstock. Some industrial polymers result from the chemical conversion of other synthetic polymers, for example, poly(vinyl alcohol) from poly(vinyl acetate). In contrast to natural polymer syntheses and biotechnology, most large scale commercial synthetic polymers are produced in the absence of water either in bulk or gas phase. Moreover, compared to biopolymers, synthetic polymers, including the synthetic bio-based polymers derived from renewable feedstocks, are much easier to tailor with respect to their molar mass distribution, short- and long-chain branching and stereochemistry, thus meeting the demands of polymer melt processing and polymer applications. In contrast to protein synthesis, where polypeptide chains are produced with identical molar mass and comonomer sequence distribution, is rather problematic to produce thermoplastics with shear thinning resulting from long chain branching and multimodal molar mass distribution with enzyme-catalyzed reactions.

1.1.2. Nomenclature [1, 5, 17–19]

The nomenclature of individual polymers and plastics is as confusing as their classification according to properties. Various systems of nomenclature are used simultaneously. Abbreviations and acronyms abound, sometimes with different meanings for the same letter combinations and other times without explanation. In addition, many thousands of trade names are used worldwide for plastics, fibers, elastomers, and polymeric additives. 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. 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, styrene to polystyrene, vinyl chloride to poly(vinyl chloride), and lactic acid to a polylactic acid. 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 polyisocyanates 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), abbreviated as POM. 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 poly(ethylene terephthalate) and poly(ethylene glycol terephthalate). It is also known 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.

With exception of POM, 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 [20–56]

Early plastics resembled natural resins. 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 enabling chain entanglement. Examples are melting temperatures and the moduli of elasticity. Other properties, however, increase with increasing molar mass and entanglement (e.g., melt viscosities).

Thermosets are usually generated from fairly low molar mass polymers, called oligomers (science) or prepolymers (industry). Oligomers containing functional endgroups are named telechelics, and telechelics containing polymerizable endgroups are termed macromonomers. High molar masses are unnecessary here because chemical reactions between prepolymer molecules lead to an interconnection of these molecules (cross-linking or advancement, respectively) and thus to a giant molecule with 100% conversion of the prepolymer. 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 an oxygen 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 at low cost; hence, the terms bulk plastics or standard plastics. Engineering plastics possess improved mechanical properties and improved dimensional stability as compared to commodity plastics. Such improved properties may be higher moduli of elasticity, higher heat distortion temperature, 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), abbreviated as PVC, high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE), isotactic polypropylene (PP), polystyrene (PS), polystyrene foam as expanded polystyrene (EPS) and poly(ethylene terephthalate) (PET).

Engineering Plastics. Polypropylene (PP), poly (ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), polyamides (aliphatic, amorphous, aromatic) (PA), polycarbonate (PC), polyoxymethylenes (POM), poly(methyl methacrylate) (PMMA), some modified polystyrenes such as styrene–acrylonitrile (SAN) and acrylonitrile–butadiene–styrene (ABS) copolymers, and high-impact polystyrenes (HIPS), as well as various blends such as poly (phenylene oxide)–polystyrene (PPO–PS), polyoxymethylene–polyurethane (POM–PUR), polypropylene–poly(ethylene-co-propene-co-diene) rubber (PP–EPDM), and polycarbonate–ABS (PC–ABS).

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

1.2.2. Designations [57–61]

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 1–4): 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 [61].

Tables 1–4 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). "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 chemical structures nor with those of elastomers containing the same monomer units; some of these also deviate from those recommended for recyclable plastics. Several abbreviations have different meanings in either two or more of the ASTM, DIN, ISO and IUPAC systems and/or the technical literature.

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 3). 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 polymer 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 =

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-propene-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
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™
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+propene		E/P	E/P		PEP
Ethylene+propene (+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$^{\#}$	

Table 1. (*Continued*)

Polymers of	ASTM	DIN	ISO	IUPAC	Other
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				
Hexafluoropropene+tetrafluoroethylene	FEP	FEP	FEP		
Hexamethylenediamine+sebacic acid		PA 610			PA 6.10
p-Hydroxybenzoic acid	POB				PHB[#]
3-Hydroxybutyric acid					PHB[#]
2-Hydroxyethylmethacrylate					PHEMA
Isobutene	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		
Octyl acrylate+vinyl chloride		VC/OA	VC/OA		
Perfluoroalkoxyalkane	PFA	PFA			
Phosphoric acid					PPA[#]
Propene	PP	PP	PP	PP	
Oriented polymer					OPP
Oriented biaxially					BOPP
Propene+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		

[#] Abbreviation with more than one meaning.

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				

[*] Saran coated polymer film.
[**] Metallized polymer film.
[#] Abbreviation with more than one meaning.

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 = mass (weight); X = cross-linked. The technical literature also uses BO = biaxially oriented and O = oriented (usually in one direction).

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) [57, 58]. 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.

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

- Chemical structure data, such as content of vinyl acetate (VAC) or acrylonitrile

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	

* Saran coated polymer film.

units (AN), isotacticity (IT), or density (D) as a measure of branching

- Molar mass data, such as intrinsic viscosity (IV) or Fikentscher's K value (FK)
- Bulk density (BD)
- Rheological data, such as melt flow rate (MFR) (melt flow index)
- Thermal data, such as Vicat temperature (VT) or torsional stiffness temperature (TST)
- Mechanical properties, such as modulus of elasticity (*E*), tensile stress at 100% strain (TS), shore hardness (SH), or impact strength (notched) (ISN)

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 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. *Data block 1.* 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 [59, 60]. A typical ASTM designation, for example, would read "Molding material ASTM D-4000 PI 000 G 42 360"; this material is a polyimide (PI). Because 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 3 500 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 [13–16, 62–67]

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 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. Because 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" because 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 unsuccessful. 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 [66].

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 and Celanese were necessary before it became an engineering plastic in 1956.

Vinyl chloride was synthesized by H. V. REGNAULD in 1838, who also observed the formation of resins. Vinyl chloride was polymerized by KLATTE in Germany and OSTROMUISLENSKY in England in 1912, 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, NATTA employed ZIEGLER'S catalysts to polymerize α-olefins, such as propene, thus producing solid, crystalline stereoregular polymers. The commercial production of isotactic polypropylene (PP) began in Italy, 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. Progress in heterogeneous polymerization catalysis enabled morphology control in olefin polymerization, thus producing spherical pellet-sized polyolefin particles without requiring pelletizing extrusion.

1.4. Economic Importance [68–73]

The rapid growth of plastics production is a result of three factors: (i) growth of world population with surging demand for cost-, resource-, eco-, and energy-efficient advanced materials, (ii) average increase in standard of living, and (iii) replacement of metal, wood, ceramics, and environmentally less friendly materials by plastics. The growth pattern may be economy driven [determined by the price of materials (substitutes); shortages (substitution), or governmental regulations; or technology driven (determined by technological requirements, internal knowhow, and accidental discoveries). At present, the expected declining supply of fossil resources, and public concerns relating to global warming and climate change, are stimulating the quest for polymers based on renewable resources. The world population grew from 2.532×10^9 in 1950 to 7.159×10^9 in 2014, and is expected to reach 9×10^9 in

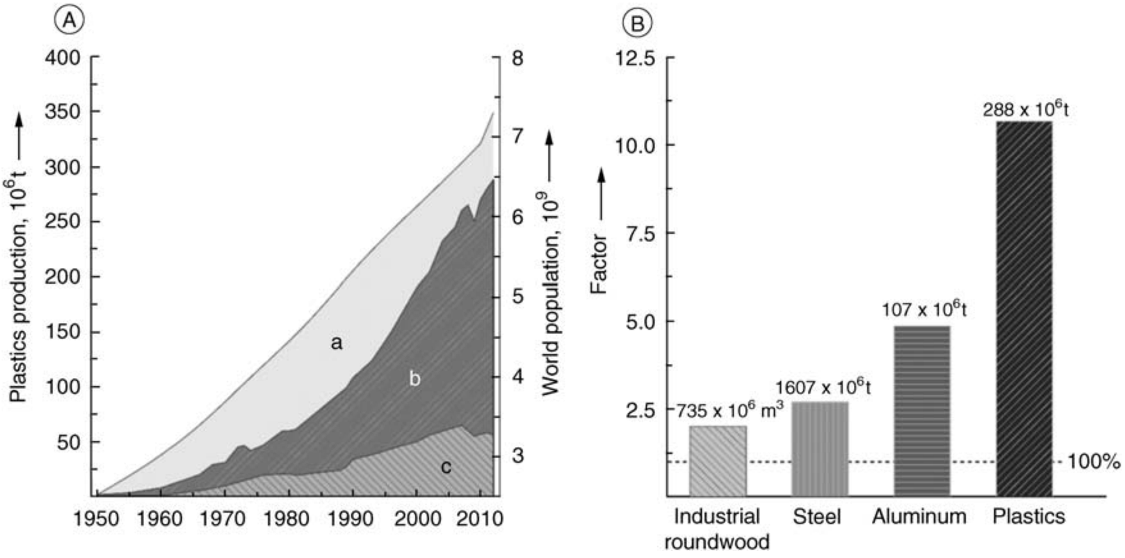


Figure 1. A) Growth of world plastics production and world population (data taken from [73, 74]); B) Production growth (1970–2012) of other materials
a) Population Growth; b) World plastic production; c) European production

2050. Because more people aspire the high living standards of the Western World, the rapid growing world population is accompanied by a surging demand for polymeric materials. Hence, the world plastics production (approximately equal to consumption) climbed from 0.6 kg per capita (1950) to ca. 42 kg per capita in 2014 (see Fig. 1).There are great differences in plastics consumption between various countries: Whereas plastic production is slowing down in Europe, it continues to grow rapidly in Asia and India.

According to a survey conducted by PlasticsEurope (the association of plastics manufacturers in Europe) in 2012, the European plastics industry producers, plastics converters, and plastics machinery with more than 62 000 companies accounted for approximately 1.4 million jobs in the European Union's 27 member states and had a combined turnover of around 3×10^9 Euro. By 2014, the world plastics production will pass the 300×10^6 t/a mark. In 2012, China was the leading plastics producer with 23.9% share of the world plastics production, followed by the rest of Asia, including Japan, (20.4%), Europe (20.4%), NAFTA (19.9%), Middle East/Africa (7.2%). In 2013, the world's plastic consumption was close to 300×10^6 t, of which commodity polymers, such as PE, PP, PVC, PS, and PET claim a major share of around 80% (Fig. 2). The growth of the plastics production during the first decade of the 21st century is unparalleled by any other class of materials including wood, aluminum and steel (Fig. 1). Close to half of the world's plastics production are polyolefins, such as PE and PP. Plastics serve the needs of a variety

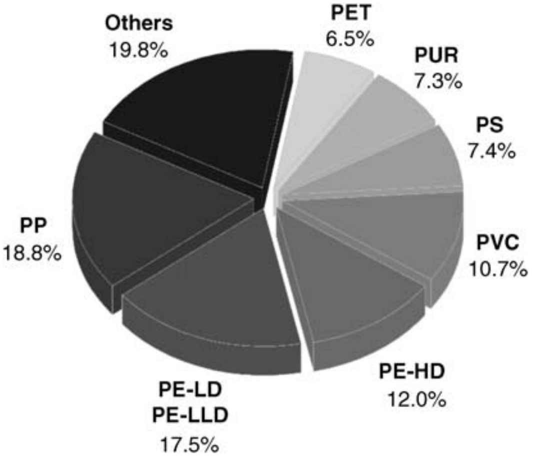


Figure 2. Industrially important polymers [73]

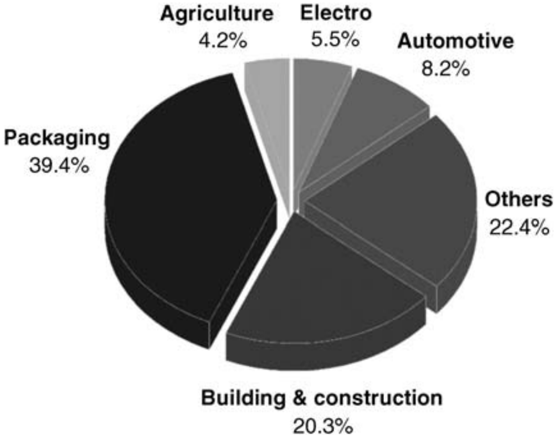


Figure 3. Application areas of plastics [73]

of markets (Fig. 3). In 2012, the largest plastic application area in Europe was packaging (39.4%), followed by building and construction (20.3%), automotive (8.2%), electrical and electronics (5.2%), agricultural applications (4.2%), and other diversified sectors (22.4%) including consumer and household products, furniture, sports, safety, as well as medical applications (see Fig. 3). Today, plastics wastes are recognized as very valuable source of raw materials and energy. Upon thermal treatments, commodity plastics are converted back into oil and gas, thus substituting fossil resources. In 2012, the plastics recycling and energy recovery reached 61.9% in Europe. The recycling of plastics and polymer products, ranging from lightweight engineering to membranes for water purification, offer great prospects for sustainable development, protecting resources, such as oil and water, for future generations, reducing carbon footprint, and securing the supply of energy and food.

2. Molecular Structure of Polymers [1–12]

2.1. Constitution

2.1.1. Homopolymers

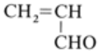
A homopolymer is defined as a polymer derived from one type of monomer. The term homopolymer thus refers to the origin of the monomers in a polymer and not to the actual constitutional units. The polymerization of a monomer $CH_2{=}CHR$ leads to constitutional units $–CH_2CHR–$. These units may be connected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

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

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

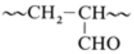
The proportion of head-to-head regioisomeric units increases with decreasing size of substituents R and with reduced resonance stabilization of the growing species. Free-radical polymerization of vinyl acetate [$CH_2{=}CH(OOCCH_3)$] leads to 1–2%, of vinyl fluoride ($CH_2{=}CHF$) to 6–10%, and of vinylidene fluoride ($CH_2{=}CF_2$) to 10–12% tail-to-tail connections. Head-to-head connection is detrimental to thermal stability, because the steric hindrance of the substituents reduces the bond strength of the C–C bonds.

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**):



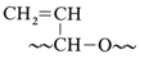
$$CH_2{=}\underset{\underset{CHO}{|}}{CH}$$

1



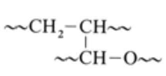
$$\sim\!CH_2-\underset{\underset{CHO}{|}}{CH}\!\sim$$

2



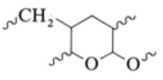
$$CH_2{=}\underset{\underset{\sim CH-O\sim}{|}}{CH}$$

3



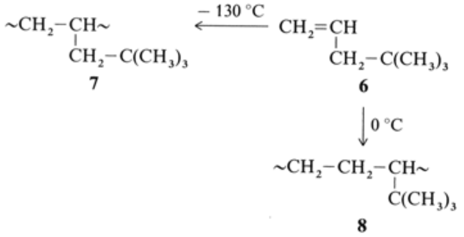
$$\sim\!CH_2-\underset{\underset{\sim CH-O\sim}{|}}{CH}\!\sim$$

4



5

Monomers may also isomerize during polymerization, especially cationic polymerization. 4,4-Dimethyl-pentene-1 (**6**) polymerizes at low 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 (→ Plastics, General Survey, 2. Production of Polymers and Plastics); these reactions lead to branched polymers.

The groups at the ends of polymer chains are 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

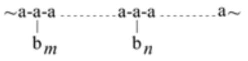
Copolymers are generated from more than one type of monomer; they are called bipolymers, terpolymers, quaterpolymers, etc., according to the number of monomer types. The copolymerization of ethylene ($CH_2{=}CH_2$) and propene [$CH_2{=}CH(CH_3)$] thus leads to the bipolymer poly(ethylene-*co*-propene). 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 $-CH_2{-}CH(OH)-$. Thus, the term copolymer 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 5), 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;

Table 5. Types of copolymers from monomers A, B, and C (monomeric units are characterized by lower-case letters)

Name	Structure	Shorthand name
Copolymer without specified squende	∼(a/b)∼	poly(A-co-B)
Statistical copolymer (example)	∼a-b-b-b-a-a-b-a-a-a-a-b∼	poly(A-stat-B)
Random copolymer (with Bernoulli statistics of sequence)	ditto	poly(A-ran-B)
Alternating copolymer	∼a-b-a-b-a-b-a-b-a-b-a-b∼	poly(A-alt-B)
Periodic copolymer	∼a-b-b-a-b-b-a-b-b-a-b-b∼	poly(A-per-B-per-B)
	∼a-b-c-a-b-c-a-b-c-a-b-c∼	poly(A-per-B-per-C)
Diblock copolymer	∼a . . . . .a-b . . . . .b∼	poly(A)-block-poly(B)
Triblock copolymer	∼a . . . . a-b . . . . b-c . . . . c∼	poly(A)-block-poly(B)-block-poly(C)
Graft copolymer		poly(A)-graft-poly(B)

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 possess n monomeric “m” units and two R end groups. They are also called linear chains (Fig. 4, 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. 4, R) consist of linear polymer molecules that are joined via their ends. They do not have end groups and are not called macrocycles because 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. 4, S).
2. *Dendrimers* (dendritic polymers) are tree-like star polymers in which the subchains are themselves starlike branched (Fig. 4, D). They are also called cascade polymers (because of the cascade-like sequence of branching points), isotropically branched polymers, or isobranched polymers (because each generation of newly added monomer molecules is “isotropically” arranged around the central core), or much more poetically, starburst polymers. Whereas ideal dendrimers require tedious multistep syntheses, a more industrially viable synthesis is to produce less perfect cascade macromolecules, which are known as hyperbranched polymers.
3. *Comb polymers* have “long” side chains, whose chemical structures usually differ from those of the main chains (Fig. 4, 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.

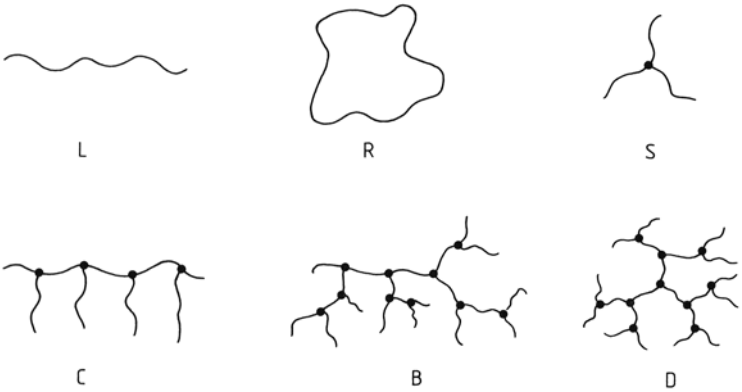
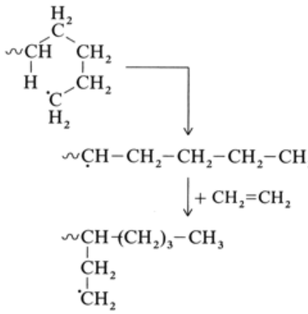
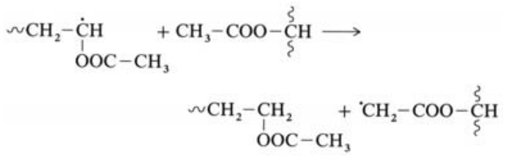


Figure 4. Schematic representation of linear and branched marcomolecules
L = Linear (unbranched) chain in almost extended state; R = ring molecule; S = starlike molecule with three subchains, C = comblike molecule with four branching points of functionality 3; B = randomly branched chain with subsequent branching; D = dendrimer with three-functional branch points and three generations of subchains

4. *Randomly branched polymers* have a random distribution of branching points (Fig. 4, 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.



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

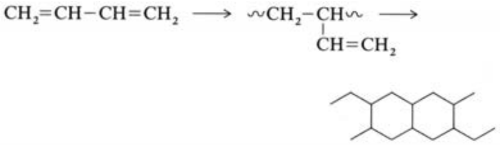
Such side-chain radicals are also formed by radical transfer from certain initiator radicals. Side chains introduced by the inherent structure of a (co)monomer are not called branches in polymer science. Neither linear poly(vinyl acetate) nor the low-crystallinity, low-density polymers formed by copolymerization 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. Although short-chain branching significantly reduces melting temperature and crystallinity of polyethylene, as reflected by reduced density, the incorporation of a few long chain branches greatly improves melt processing, such as shear thinning and melt strengthening in blow molding of polyolefin films.

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. 5, 1), phyllo (Fig. 5, 2) and tecto (Fig. 5, 3) compounds.

Linear polymers are catena polymers in this nomenclature because the fully extended chains extend in only one direction (Fig. 5, 1). Spiro polymers possess two chains with connecting atoms shared by both of them (Fig. 5, S).

Ladder polymers consist of two chains joined by bonds in regular intervals (Fig. 5, 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



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 5 but to a pearl-string-like polymer P (Fig. 5, P). Many silicates are ladder polymers or double-ladder polymers.

Phyllo polymers are also called layer or parquet polymers (Fig. 5, 2). Graphite and the silicates montmorillonite, bentonite, and mica are well-known examples. Cell walls of bacteria consist of bag-shaped polymers (i.e., layer polymers). Diamond and quartz are

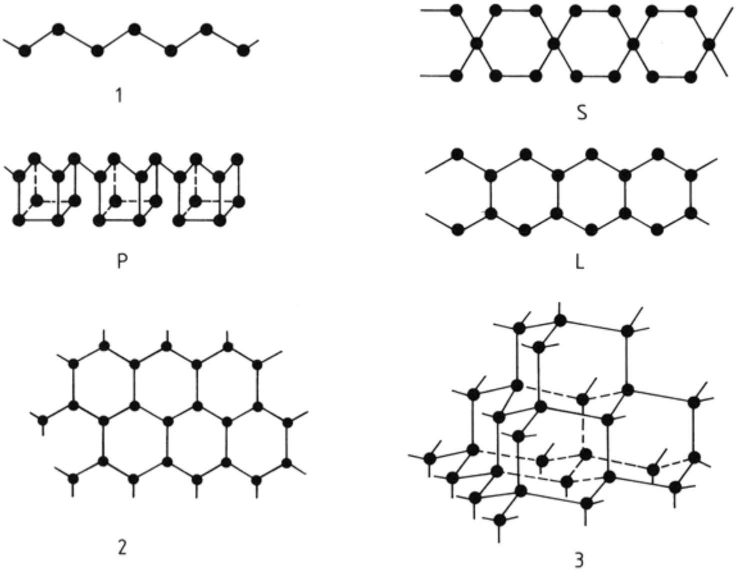


Figure 5. Schematic representation of some ordered chain assemblies
1 = Catena polymer in all-*trans* conformation; S = Spiro polymer; P = Pearl-stringlike polymer; L = Ladder polymer; 2 = Phyllo polymer; 3 = Tecto polymer

examples of tecto polymers (Fig. 5, 3). Two-dimensional carbon polymers, consisting of planar honeycomb-like sp^2-hybridzed carbons, are known as graphene which is equivalent to a single carbon layer of the graphite lattice.

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. 6, 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. 6, MN).

In principle, two chemically different networks poly (a) and poly (b) can coexist independently of each other in interpenetrating

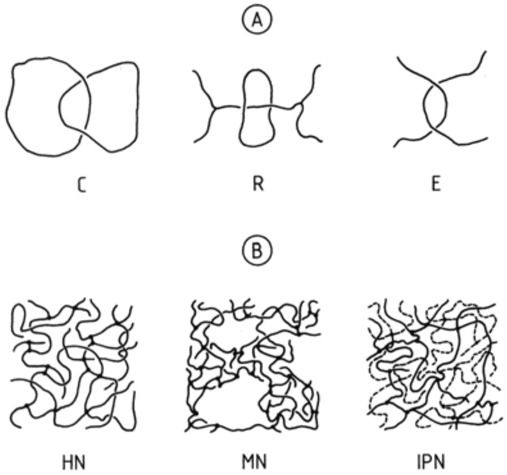


Figure 6. Schematic representation of cross-linked polymers
A) Physical cross-links; B) Chemical networks
C = catenane; E = entanglement; HN = homogeneous network; IPN = interpenetrating network; MN = macroreticular network; R = rotaxane
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

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).

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. 6, 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. 6, C) and rotaxanes (Fig. 6, 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.

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 [75].

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 $Z_i \equiv z_i/\Sigma_i z_i = w_i M_i/\bar{M}_w = x_i M_i^2/(\bar{M}_n M_w)$. The number-, mass-, and z-average molar masses are defined as

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

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

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

Each of these three average moments is essentially a single moment of the distribution of molar masses present. There are, however, molar mass averages that 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

Number-Average Molar Masses. 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 $R_o = K \cdot c \cdot \bar{M}_{w,\mathrm{app}}$, at very low angles relative to the incident light beam, where K is an optical constant and $M_{w,\mathrm{app}}$ an apparent mass-average molar mass that 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 $\eta_{red} = (\eta - \eta_o)/(\eta_o \cdot c)$. 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 because 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. Because 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:

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

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. Because $m \sim M$ 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

$$[\eta] = K \cdot M^a \tag{1}$$

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

Viscometry delivers a peculiar molar mass average, such as can be derived from Equation (1):

$$\bar{M}_n = ([\eta]/K)^{1/a} = \left(K^{-1}\dot{c}\Sigma_i w_i [\eta]_i\right)^{1/a} = \left(\Sigma_i w_i M_i^a\right)^{1/a}$$

Numerical values of viscosity-average molar masses $\bar{M}_\eta$ lie between number and mass

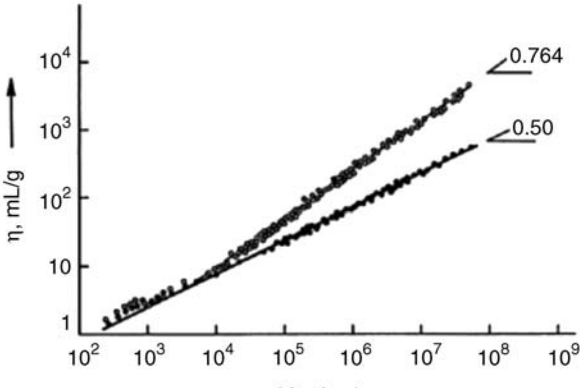


Figure 7. Molar mass dependence of intrinsic viscosities of flexible, coillike molecules: polystyrene in the theta solvent cyclohexane at 34.5°C (●) and in the thermodynamically good solvent benzene at 25°C (○)
The slopes at high molar masses adopt the theoretical values of 0.764 (good solvent) and 0.500 (theta solvent)

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. 8). 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 because 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 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

$$w_i = \frac{(k/\bar{X}_n)^k \cdot X_i^k \cdot \exp(-kX_i/\bar{X}_n)}{\Gamma(k+1)} \qquad (2)$$

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 (2) reduces for $k = 1$ and high degrees of polymerization to

$$w_i = (1/\bar{X}_n)^2 \cdot X_i \cdot [1 - (1/\bar{X}_n)]^{xi}$$

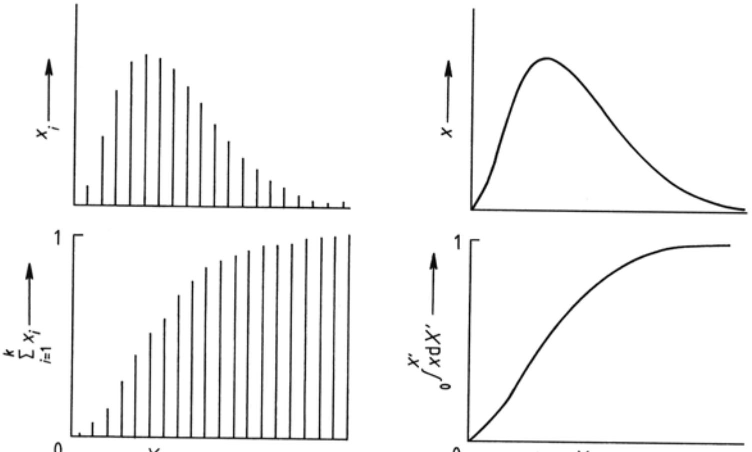


Figure 8. Distributions of mole fractions x of degrees of polymerization X
Left: discontinuous (discrete); right: continuous; top: differential; bottom: integral (cumulative)
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

The various average degrees of polymerization are connected via

$$\bar{X}_n/k = \bar{X}_w/(k+1) = \bar{X}_z/(k+2)$$

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

$$w_i = \frac{X_i \cdot (\bar{X}_n - 1)^{X_i - 1} \cdot [\exp(1 - \bar{X}_n)]}{(X_i - 1)!(X_n)}$$

and the interrelationship between the various averages by

$$\bar{X}_w/\bar{X}_n = 1 + (1/\bar{X}_n) - (1/\bar{X}_n)^2$$

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 $\bar{X}_w/\bar{X}_n$ 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:

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

This expression converts to the Schulz–Zimm distribution if $\gamma = 1$, $\varepsilon = k$, and $\beta = k\,\bar{X}_n$. 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 9. Note that only the logarithmic normal distribution shows a maximum in the distribution of mole fractions and that none of the maxima in the distributions of the mass fractions correspond to simple molar mass averages.

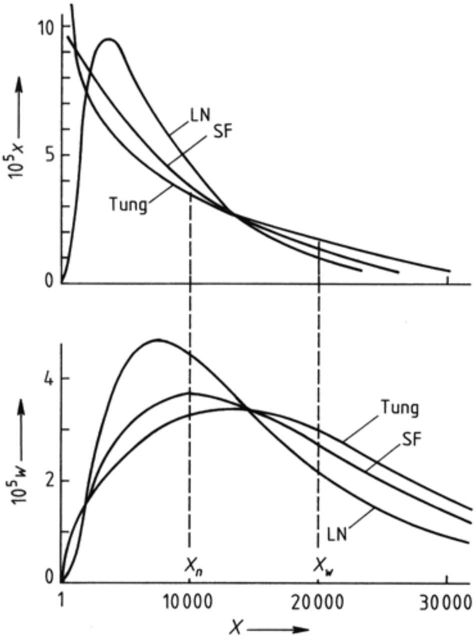


Figure 9. Continuous differential distributions of degrees of polymerization X for a) the logarithmic normal distribution (LN); b) the Schulz–Flory distribution (SF); and c) the Tung distribution (Tung), shown as distributions of mole fractions (top) and corresponding mass fractions (bottom) for a polymer with $\bar{X}_n = 10\,000$ and $\bar{X}_w = 20\,000$
The Poisson distribution is so narrow that it is practically identical with the vertical line for $\bar{X}_n = 10\,000$.
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

2.2.4. Determination of Molar Mass Distributions

Molar mass distributions can be determined by preparative *fractionation* of polymers from solutions because 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), also being referred to as gel permeation chromatography (GPC). 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. 10). 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.

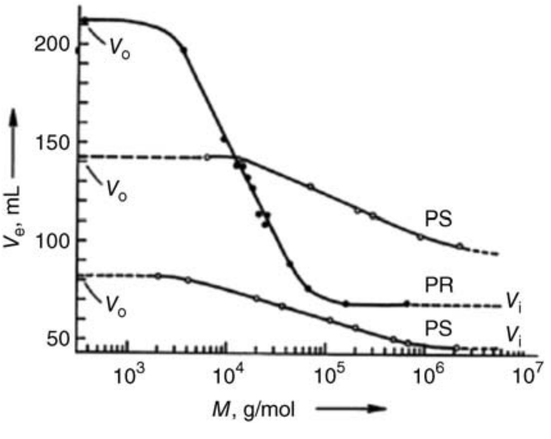
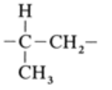


Figure 10. Molar mass dependence of elution volumes V_e
a) Coil-like linear polystyrenes PS with two different SEC columns from cross-linked polystyrenes; b) Various spheroidal proteins PR with cross-linked dextran
V_o = total volume; V_i = interstitial volume

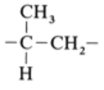
Elution volumes depend to a first approximation on the logarithms of molar masses (Fig. 10). A function $V_e = K \cdot \ln M$ is thus often used to determine unknown molar masses with the help of a constant K derived from calibrations with narrow-distribution polystyrene standards. This procedure does 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 $V_e = f\ (\log\ [\eta] \cdot M)$ because $[\eta]$ measures the specific hydrodynamic volume of the solute molecules and $[\eta] \cdot M$ has the physical unit of a molar volume.

2.3. Configurations

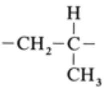
Polymers with symmetric repeating units, such as $—CH_2—CH_2—(—CH_2—CH_2—)$, $—CH_2—CF_2—$, and $—NH—CO(CH_2)_5—$ do not possess configurational isomers. Such isomers do exist, however, for polymer molecules with nonsymmetric repeating units, such as $—CH(CH_3)—CH_2—$(polypropylene) and $—NH—CO—CH(CH_3)—$(polyalanine).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


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

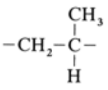
9a


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

9b

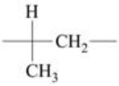

$-CH_2-\overset{H}{\underset{CH_3}{C}}-$

10a


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

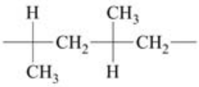
10b

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



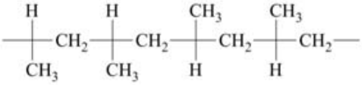
$$-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{+}}-\mathrm{CH_2}-$$

it



$$-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{+}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{+}}-\mathrm{CH_2}-$$

st



$$-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{+}}-\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{+}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{+}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{+}}-\mathrm{CH_2}-$$

ht

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 because 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 substituents 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. 11), that is $\sim(\mathrm{CHR{-}CH_2})\sim$.

Real polymer chains of the types $\sim\mathrm{CHR}\sim$, $\sim\mathrm{CHR{-}CH_2}\sim$, $\sim\mathrm{X{-}CHR{-}CH_2}\sim$, 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 11 thus shows five diads, four triads, three tetrads, etc., for $\sim\mathrm{CHR}\sim$. The sum of the mole fractions of all J-ads of given J must equal 1 ($x_\mathrm{i} + x_\mathrm{s} \equiv 1, x_\mathrm{ii} + x_\mathrm{is} + x_\mathrm{si} + x_\mathrm{ss} \equiv 1$, 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, $x_\mathrm{i} = x_\mathrm{ii} + (1/2)(x_\mathrm{is} + x_\mathrm{si})$, etc. The number-average sequence length of isotactic sequences is thus given by $(\bar{X}_i)_n = 2\,x_\mathrm{i}/(x_\mathrm{is} + x_\mathrm{si})$.

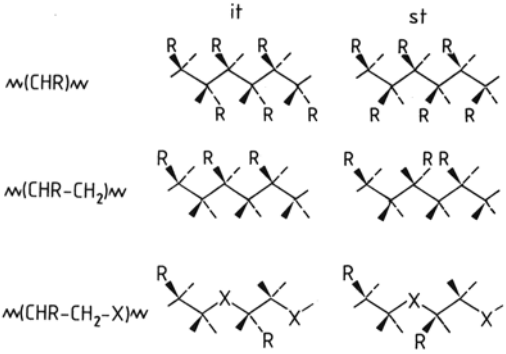
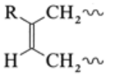


Figure 11. Isotactic (it) and syndiotactic (st) polymers with monomeric units –CHR–, –CHR–$\mathrm{CH_2}$–, and –CHR–$\mathrm{CH_2}$–X– in *trans* conformations
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

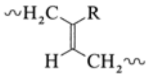
The presence and/or fraction of tactic J-ads can be investigated by a number of experimental methods. 2D-NMR spectroscopy allows absolute determination of the types of J-ads and their amounts up to pentads, whereas conventional high-resolution NMR spectroscopy requires prior knowledge of the J-ad type 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-polybutene-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.

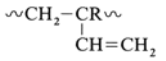
Polymers with different geometric isomerism are also tactic. Depending on the configuration of the chain segments relative to the double bonds in the chain *cis*-tactic (ct) and *trans*-tactic (tt) structures are distinguished. The ct structure of 1,4-polyprenes[$\sim(CH_2—CR{=}CH—CH_2)_n \sim$] from 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, i.e., the macroconformation (in statistical mechanics, the configuration).

In principle, an infinite number of conformations are 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. 12). On rotation by 360° around the C—C axis, three energetically equivalent eclipsed and three energetically equivalent staggered positions may be occupied as 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.

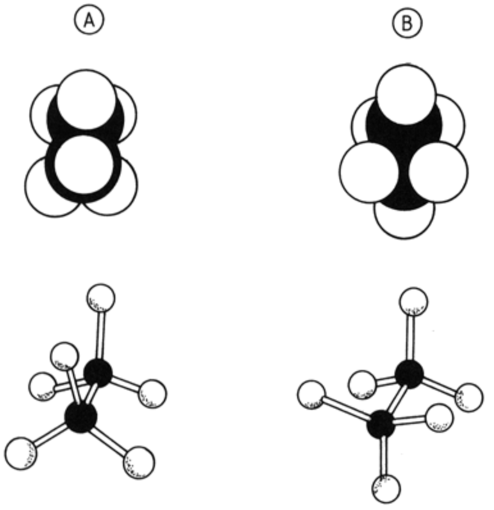


Figure 12. Microconformations of ethane
A) Eclipsed position (*cis* or synperiplanar); B) Staggered position (*trans* or antiperiplanar)
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

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

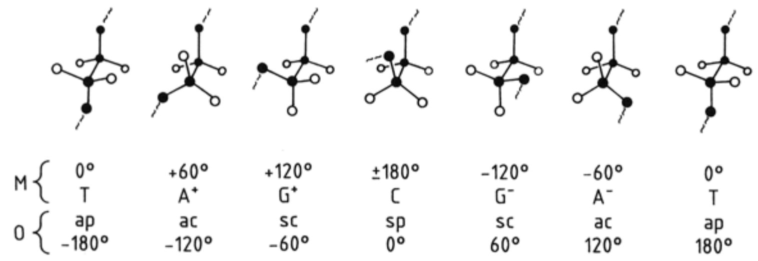


Figure 13. Chain conformations and their names and symbols in macromolecular (M) and organic (O) chemistry
● Chain atoms; ○ substituents; T = *trans*, A = *anti*; G = *gauche*; C = *cis*; ap = antiperiplanar; ac = anticlinal; sc = synclinal; sp = synperiplanar

gauche and each *anti* position can occur in two spatially different positions that are energetically equivalent (plus and minus) if two of the three bonded atoms are equivalent. These (micro)conformers have different names in macromolecular and in organic chemistry (Fig. 13).

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. 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 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 $\sim CH_2—CO—O—CH_2\sim$. Because 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 (e. g., the chain in Fig. 5, 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. 13). All *gauche* conformations must be alike for steric reasons; conformational diads G^+G^- and G^-G^+ are forbidden (Fig. 13). The chain thus adopts either a . . . $TG^+TG^+TG^+$ . . . or a $TG^-TG^-TG^-$ . . . macroconformation, i.e., 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 propene units per one turn (3_1 helix, Fig. 14 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. 14 B), and poly(3-methylbutene-1) (P3MB) has four units per one turn (4_1 helix, Fig. 14 C). The conformational angles are not

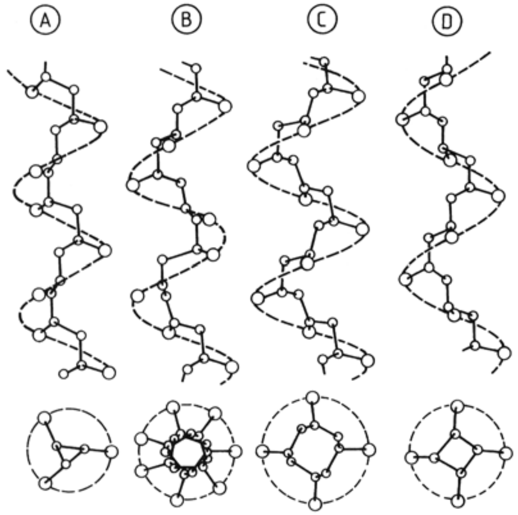


Figure 14. Helix types of poly(α-olefins) ~CH_2—CHR~ A) 3_1 Helix; B) 7_2 Helix; C), D) Different types of 4_1 helices Reprinted with permission by Societa Italiana di Fisica, Bologna, from [76]

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.

The R substituents of syndiotactic vinyl polymers [~(CH_2—CHR)$_n$~] are farther apart than those of their isotactic counterparts (see Fig. 11). 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. Because 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:

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. 15).

Figure 15. Electron micrograph of the double helix molecules of deoxyribonucleic acid chains showing two-dimensional random coils
Reprinted with permission by Academic Press, London, from [77]

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, r^2_∞, of such a coil is given by the number N of its unspecified segments with segment lengths b:

$$\langle r^2_{oo} \rangle = N \cdot b^2$$

Real chains possess 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

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

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

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:

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

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; $r_{\text{cont}} = X \cdot b_{\text{eff}} = N_K \cdot L_K$)

$$\langle r_o^2 \rangle = N_K \cdot L_K^2$$

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

$$\langle s_o^2 \rangle = \langle r_o^2 \rangle / 6$$

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 (Fig. 15). 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 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

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

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

$$\langle r_o^2 \rangle / 6 = \langle s_o^2 \rangle = a \cdot r_{\text{cont}} / 3 = a \cdot N_K \cdot L_K / 3$$

For infinitely stiff chains,

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

which 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. Thermal Properties [78]

3.1. Molecular Motion

3.1.1. 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.

3.1.2. 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 $1.22\,\mathrm{J\,K^{-1}\,g^{-1}}$ and a molar heat capacity (per monomeric unit) of $146.4\,\mathrm{J\,K^{-1}mol^{-1}}$. The molar heat capacity (per mole of atoms) is thus $146.4\,\mathrm{J\,K^{-1}mol^{-1}}/17 = 8.61\,\mathrm{J\,K^{-1}mol^{-1}}$ (i.e., approximately $1\,R = 8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}$).

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.

3.1.3. 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.

3.2. Thermal Transitions and Relaxations

3.2.1. 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 16 shows a typical thermogram.

Many methods are available for the study of molecular motions and thus *thermal relaxations*. These methods work with frequencies ν that 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 ($10^{-12} < t_c/\text{s} < 10^{-8}$), NMR spin-lattice relaxation ($10^{-12} < t_c/\text{s} < 10^{-5}$), dielectric relaxation ($10^{-10} < t_c/\text{s} < 10^{-5}$), and photon correlation spectroscopy ($10^{-4} < t_c/\text{s} < 10^2$). Thermal relaxations furthermore manifest themselves in sudden changes of mechanical properties, such as rebound elasticity ($t_c/\text{s} \approx 10^{-5}$), penetrometry ($t_c/\text{s} \approx 10^2$), mechanical loss ($10^3 < t_c/\text{s} < 10^7$), and thermal expansion ($t_c/\text{s} \approx 10^4$). 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. 17). They often cannot be correlated with 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:

$$\nu = (k_B T / 2\pi h) \exp(-\Delta H^{\neq}/RT) \exp(\Delta S^{\neq}/R) \tag{3}$$

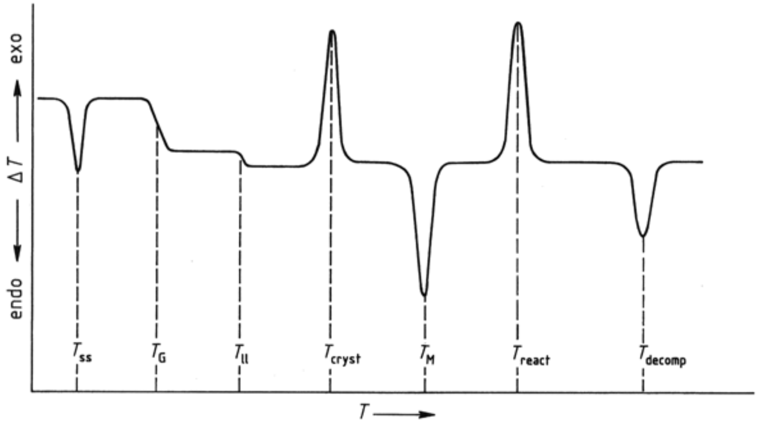


Figure 16. Idealized thermogram of a partially crystalline polymer with solid–solid transition T_{ss}, glass transition temperature T_G, liquid–liquid transition T_{ll}, maximum crystallization temperature T_{cryst}, melting temperature T_M, maximum temperature T_{react} of a chemical transformation, and maximum temperature T_{decomp} of chemical degradation
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

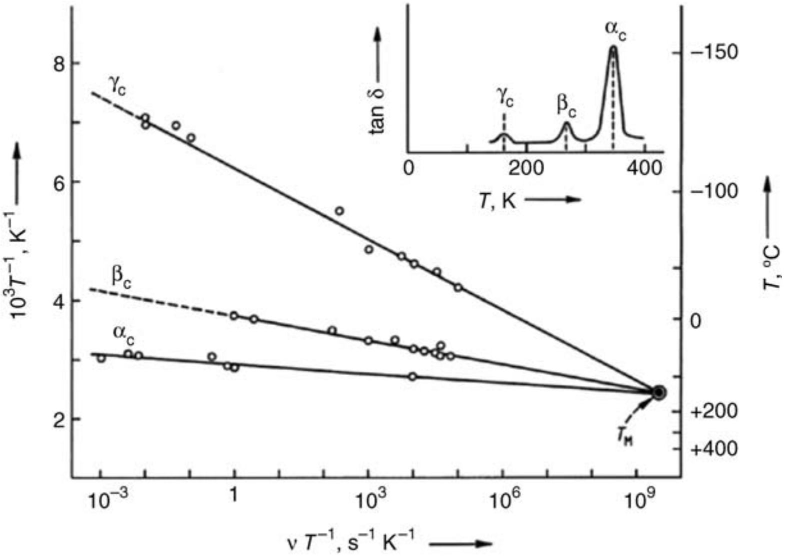


Figure 17. Dependence of inverse relaxation temperature $1/T$ on the logarithm of reduced frequency ν/T for various relaxation processes of a low-density polyethylene
Insert shows the mechanical relaxation spectrum at $\nu = 1\ 000$ Hz.
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

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 (3) leads to

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

In a $(1/T) = f\,[\ln(\nu/T)]$ plot, lines for various processes intersect at the melting temperature ($T_M = 131$ °C in Fig. 17). Such common intersects seem to be general for nonhelical polymers.

3.2.2. Crystallization

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

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 agents. Such nuclei must have minimum sizes of 2–10 nm. Their concentrations can range from ca. 1 nucleus per cubic centimeter

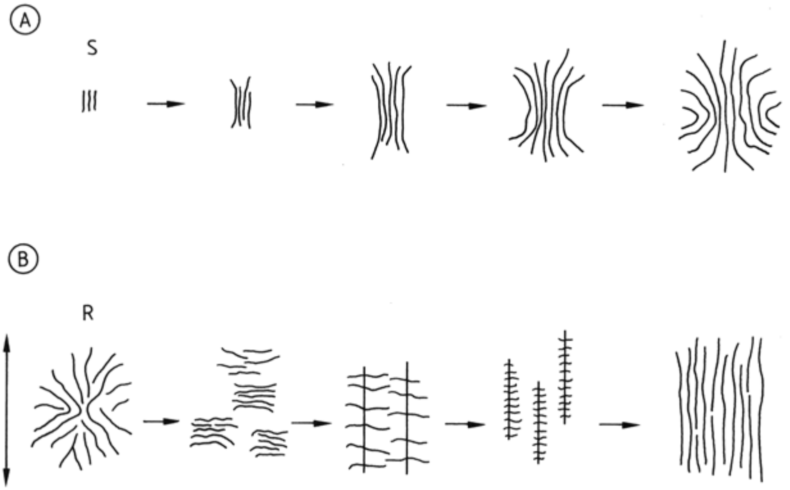


Figure 18. A) Formation of spherulites from lamellae on crystallization of melts at rest; B) Transformation of spherulites into row structures by shearing or drawing in ↕ direction.
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

(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 after-crystallization, lamellae may thicken, lattices become more perfect, etc.

Primary crystallization can be characterized by the Avrami equation:

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

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.

3.2.3. 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:

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

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_M^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

$$({}^*V\mathrm{u}^\mathrm{m}/{}^*V1^\mathrm{m})[(1 - \phi_2) - \chi(1 - \phi_2)^2] \text{ (solvent)}$$

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

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

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 $\sim$(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 packed helices [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. 19).

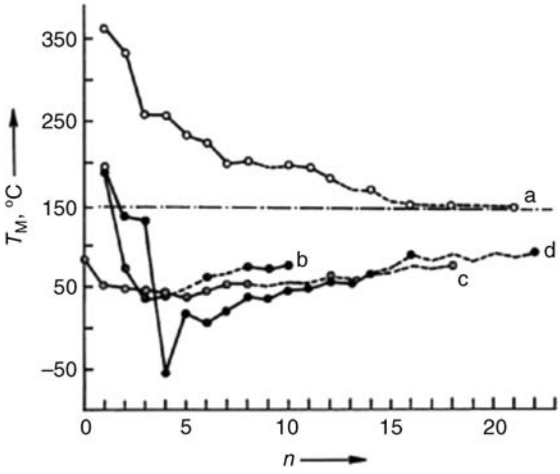


Figure 19. Melting temperatures of (○, ⊙, ⊕) aliphatic polymers ~[X-$(CH_2)_n$]~ and (●) isotactic poly(α-olefins) ~{CH_2—CH[$(CH_2)_n$H]}~ as function of the length *n* of methylene sequences
a) X = NHCO (polyamides); b) X = O (polyoxides); c) X = COO$(CH_2)_3$OOC (aliphatic polyesters of trimethylene glycol)
– ·—· theoretical melting temperature of polyethylene

3.2.4. 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_{cs}, $T_{cn} < T_{ni}$); they are called *enantiotropic phases*.

Mesophases form dispersions in supercooled isotropic melts if clearing temperatures are lower than melting temperatures (T_{cs}, $T_{cn} > T_{ni}$). 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: $1/T_{trans} = f(1/X)$. 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 $\Delta S_{sn} < \Delta S_{ni}$.

3.2.5. 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 6):

$$f_{exp} \approx (\beta_L - \beta_G) \cdot T_G \approx 0.11 \pm 0.02 \tag{4}$$

The Williams–Landel–Ferry (WLF) approach relates a free-volume fraction f_{WLF} to the probability of segment movements. Empirically, values of $f_{WLF} \approx 0.025 \pm 0.01$ were found; these values can be calculated, for example, from $K = f_{WLF}/(\beta_L - \beta_G)$ and $K' = \log e/f_{WLF}$ of the semiempirical WLF equation

Table 6. 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	
Polyisobutene	−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

(Eq. 5) where $-\log a_t = \Delta(\log t)$ is a shift factor

$$T = T_G + \frac{K \cdot \log a_t}{K' - \log a_t} = T_G + \frac{51.6 \cdot \log a_t}{17.4 - \log a_t} \tag{5}$$

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

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 $N_{seg} <$ 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 $T_G \approx (2/3)T_M$, which holds reasonably well for many polymers except for chains such as polyethylene and polyoxyethylene for which $T_G/T_m \approx 1/2$.

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 carbon, carbon–oxygen, or carbon–nitrogen chains (another measure of segment flexibilities). The three lines intersect at $A = 0.17\ \text{nm}^2$ 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, $\sim[\text{O—Si(CH}_3)_2]_n\sim$.

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

3.2.6. 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).

3.2.7. 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.

3.3. Transport

3.3.1. 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. 20). 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. 20).

The resulting topological restraints make the polymer chain move through the maze of other

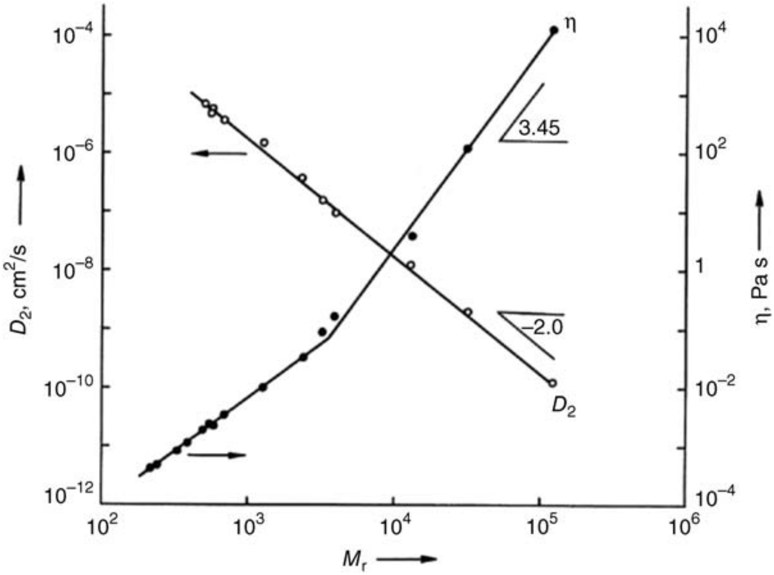


Figure 20. Segmental self-diffusion coefficients D_2 (○) and Newtonian melt viscosities η of alkanes and narrow-distribution polyethylenes (●) as function of the relative molecular mass M_r at 175°C
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

Figure 21. Reptation of a test chain (black) through the segments of a matrix (white). The "walls" of the tube are indicated by dotted lines.
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

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. 21). The theory 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 ($M_{\mathrm{test}} \ll M_{\mathrm{matrix}}$); the molar mass of the matrix exerts no influence. If however $M_{\mathrm{test}} \gg M_{\mathrm{matrix}}$, then a function $D_{\mathrm{test}} = f\ [(M_{\mathrm{test}})^{-1/2} \cdot (M_{\mathrm{matrix}})^{-1}]$ is predicted and observed.

3.3.2. 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:

$$P = D \cdot S = \frac{Q \cdot L}{A \cdot \Delta p \cdot t} \tag{6}$$

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 (6), 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 · mm)/(24 h m^2 atm). If like units are used, then the unit of P is of course length^2 · time^{-1} · 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.

Table 7. Permeation coefficients of gases (P) and water vapor (P^*) through polymers at 30 °C [a]: $P = 1 \times 10^{-14}\,\mathrm{cm^2\,s^{-1}\,Pa^{-1}}$ corresponds to $P^* = 1 \times 10^{-9}\,\mathrm{cm^2/s}$ at normal pressure ($p = 1 \times 10^5$ Pa)

Polymer	$\frac{10^{14} P}{\mathrm{cm^2\,s^{-1}\,Pa^{-1}}}$		$\frac{10^{9} P^*}{\mathrm{cm^2\,s^{-1}}}$
	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, required for bottles	0.002	0.02	0.02
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.

Permeation coefficients of gases in polymers vary widely; for example, oxygen permeates 10 million times faster through polydimethylsiloxane than through polyacrylonitrile (Table 7). 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.

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 ($1/2 < n < 1$).

4. Rheological Properties [79, 80]

4.1. Introduction

Materials exhibit two limiting types of behavior against deformation. Typical 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.

4.2. Shear Viscosities at Rest

4.2.1. 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);

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

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_0 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.

4.2.2. 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. 20). 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.

4.2.3. 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

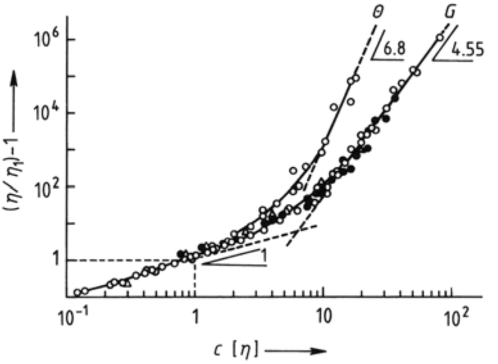


Figure 22. Relative viscosity increment ("specific viscosity") as function of $c \cdot [\eta]$ for (○) polystyrenes in *trans*-decalin (theta solvent) or toluene (good solvent G) at 25 °C; (●) *cis*-1,4-polyisoprene in toluene at 34°C; and (Δ) hyaluronates in water at 25°C
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

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. 22), 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, because $[\eta] \sim M^a$, $\eta_i \sim c^q \cdot M^{aq}$. 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. 22). In good solvents, $a \rightarrow 0.764$ and $q = 4.55$. These relationships are independent of the chemical nature of polymers and solvents.

4.3. Non-Newtonian Shear Viscosities

4.3.1. Overview

The shear stress σ_{21} is directly proportional to the shear gradient γ 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. 23). *Plastic bodies* (Bingham bodies) exhibit a yield value *y*, i.e., shear stresses have finite values σ_o at $\dot{\gamma} \rightarrow 0$. 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.

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 plug-like flow results (e.g., tooth pastes). An additional complication may result from the onset of turbulence, which usually occurs at much

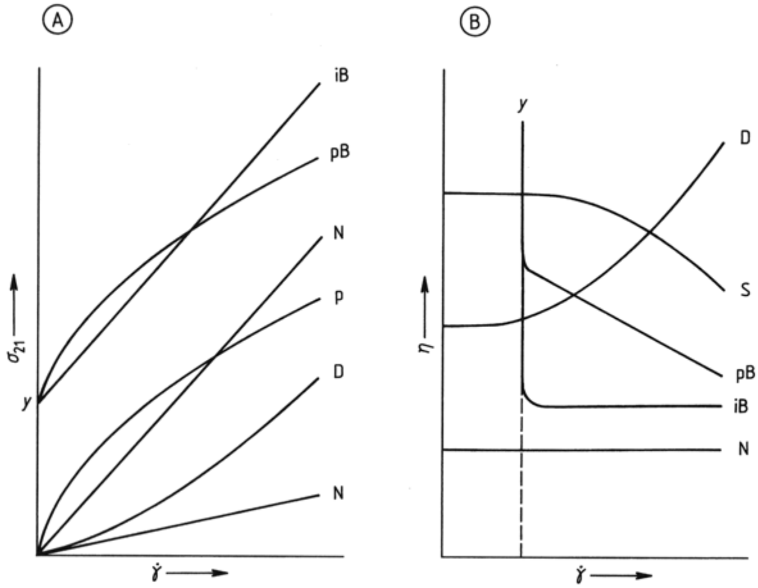


Figure 23. A) Shear stress σ_{21} and B) shear viscosity η as a function of shear rate $\dot{\gamma}$ for Newtonian (N), dilatant (D), and pseudoplastic (P) liquids and for ideal (iB) and pseudoplastic (pB) Bingham bodies (y = yield)
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

lower Reynolds numbers in non-Newtonian than in Newtonian liquids.

4.3.2. 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. Because 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. 24).

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

$\dot{\gamma} = a \cdot (\sigma_{21})^m$ Ostwald – de Waele
$\dot{\gamma} = b \cdot \sinh(\sigma_{21}/d)$ Prandtl – Eyring
$\dot{\gamma} = f \cdot \sigma_{21} + g \cdot (\sigma_{21})^3$ Rabinowitsch – Weissenberg

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.

4.3.3. Melt Viscosities

Polymers below the critical molar masses M_c for entanglements show extended Newtonian

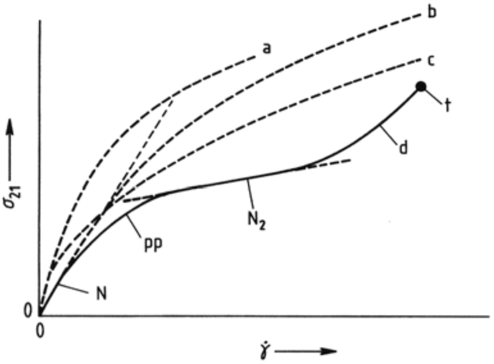


Figure 24. Generalized flow curve with first Newtonian region (N), pseudoplasticity (pp), second Newtonian region (N_2), dilatancy (d), and onset of turbulence (t)
- - - Schematic representations of various viscosity "laws": a) Prandtl—Eyring; b) Rabinowitsch—Weissenberg; c) Ostwald–de Waele
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

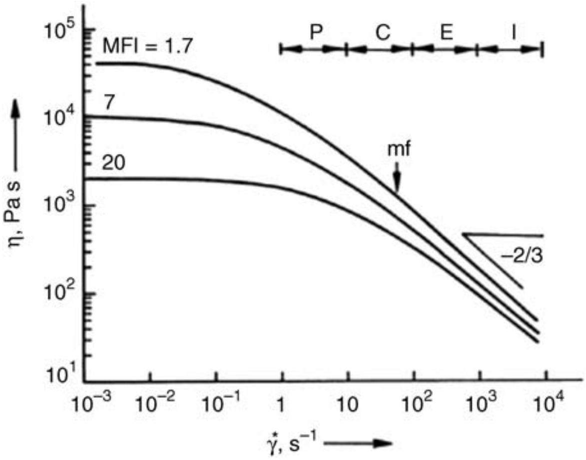


Figure 25. Dependence of melt viscosities of polyethylenes with different melt flow indices (MFI, inversely proportional to molar mass) on shear rates (mf = onset of melt fracture for the highest molar mass polyethylene)
The ranges of the various processing regimes overlap: P = compression molding, C = calendering, E = extrusion, I=injection molding. Shear rates refer to those at orifices and are much lower in the mold (tool, die).
Reprinted with permission by BASF AG, Ludwigshafen [81]

ranges. For $M > M_c$, non-Newtonian behavior appears at lower shear rates as molar mass increases (lower melt flow index) (Fig. 25). At high shear rates, a constant exponent q is approached for the function $\eta = f(\dot{\gamma}^q)$. 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.

Shear thinning, i.e., 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 roughness 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. 26). For $M > M_c$, segments can no longer slip from each other at 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

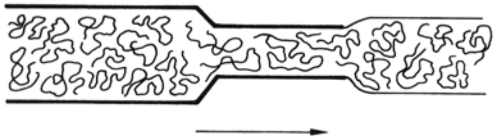


Figure 26. Parison swell upon extrusion (Barus effect)
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

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 $p = 2\sigma_{21}(L/R) = 2\eta \cdot \dot{\gamma}(L/R)$ because $\sigma_{21} = \eta \cdot \dot{\gamma}$. In the Bagley diagram, pressure p is accordingly plotted at constant shear rate against die geometry L/R (Fig. 27). For non-Newtonian liquids, a relationship

$$p = p_o + K \cdot (L/R)$$

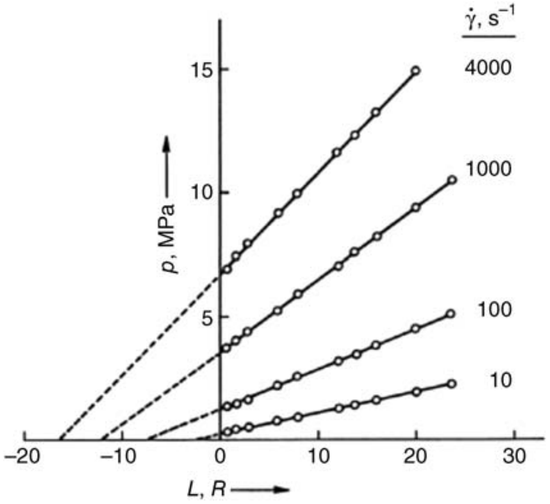


Figure 27. Bagley diagram for a high-impact polystyrene at 189°C and different shear rates
The intercept at $L/R \rightarrow 0$ is the pressure correction; the intercept at $p \rightarrow 0$, the Bagley correction a) $\dot{\gamma} = 4000\,\mathrm{s}^{-1}$; b) $\dot{\gamma} = 1000\,\mathrm{s}^{-1}$; c) $\dot{\gamma} = 100\,\mathrm{s}^{-1}$; d) $\dot{\gamma} = 10\,\mathrm{s}^{-1}$
Reprinted with permission by BASF AG, Ludwigshafen [81]

is found. The intercept p_o at $L/R \rightarrow 0$ 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 be the applied pressure. Die lengths should thus be as short as possible.

4.4. Extensional Viscosities

4.4.1. 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.

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 $\dot{\varepsilon}$

$$\eta_e = \sigma_{11}/\dot{\varepsilon} \tag{7}$$

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 (7) is the true strain $\varepsilon' = \ln(L/L_o)$ (Hencky strain) and not the nominal strain $\varepsilon = (L - L_0)/L_0$ (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.

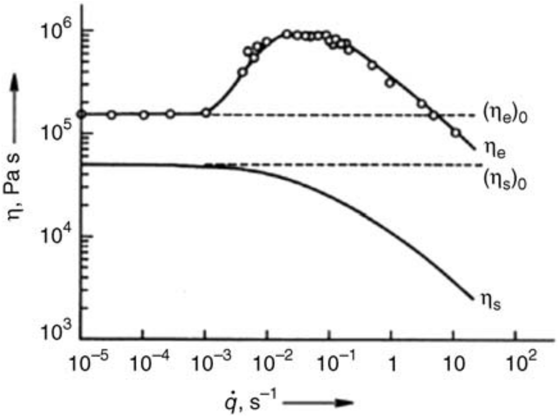


Figure 28. Shear viscosity η_s as function of shear rate $\dot{q} = \dot{\gamma}$, and extensional viscosity η_e as function of the uniaxial extensional rate $\dot{q} = \dot{\varepsilon}$ of a polyethylene at 150 °C Reprinted with permission by Steinkopff Verlag, Darmstadt [82]

4.4.2. Melts

Extensional and shear viscosities depend very differently on deformation rates. At low rates, extensional viscosities are independent of the rate of extension (Fig. 28). The uniaxial extensional viscosity at rest (historically called "Trouton viscosity") is three times the Newton viscosity [$(\eta_e)_0 = 3(\eta_s)_0$], 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.

4.4.3. 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.

5. Mechanical Properties [78, 83, 84]

5.1. Introduction

5.1.1. 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 ($T < T_G$). All mechanical deformations recover for $M > M_{\mathrm{ent}}$ and $T < T_G$ because 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.

5.1.2. 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) $\lambda = L/L_o$, or tensile strain (elongation) $\varepsilon = (L—L_o)/L_o = \lambda - 1$. If a specimen is extended to $L = 2.5\ L_o$ 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. 29). Typical *thermoplastics* (and most fibers) follow Hooke’s law

$$\sigma_{11} = (F/A_o) \cdot \varepsilon = E \cdot \varepsilon$$

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 $\sigma_S/E \approx 0.025$ 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

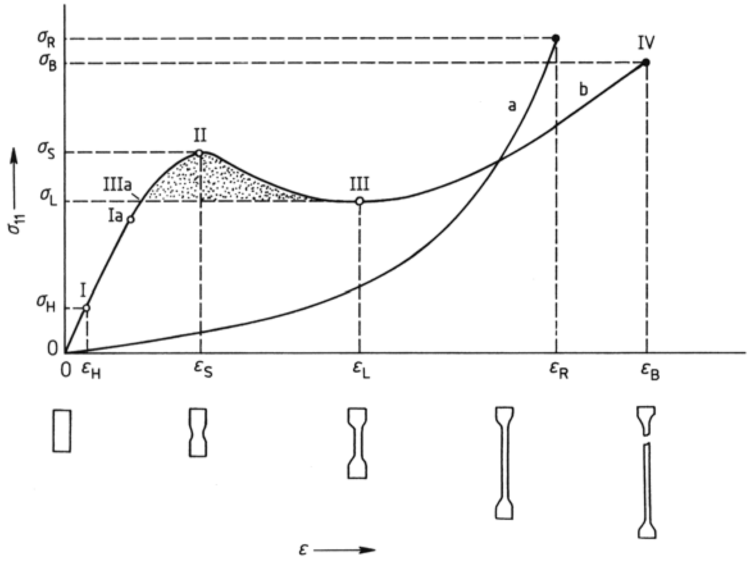


Figure 29. Stress–strain curves of an elastomer (a) and a partially crystalline thermoplastic (b) (schematic) (for further explanation, see text)
The necking effect shown below is characteristic for conventional thermoplastics; it is not found for elastomers and hard-elastic thermoplastics.
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

relative to the actual cross section instead of the initial one.

The region between points IIIa—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 hard polymers are phenolics [phenol–formaldehyde (PF)], polyacetals [polyoxymethylene (POM)], polycarbonates (PC), and poly(ethylene terephthalates) (Fig. 30). 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). 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. 30, insert). Rubber modification of PS leads to high-impact polystyrene (HIPS), which behaves quite differently from PS under tension (see Section 5.6.4).

No yield value is found if drawn polymers are further subjected to tensile tests. In biaxially stretched poly(ethylene terephthalate) (PET-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

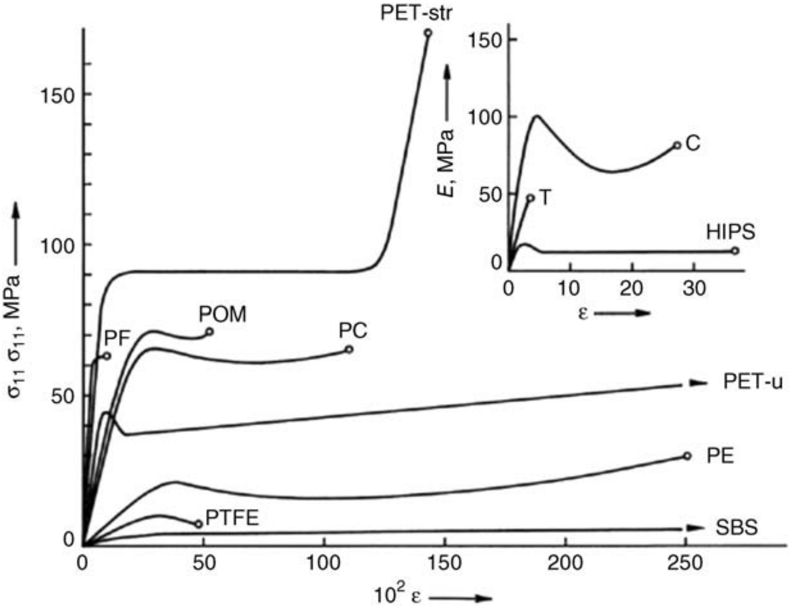


Figure 30. Stress–strain curves of polymers at room temperature (see text for explanation)

temperature, chain segments become more mobile. Molecules attempt to attain their unperturbed dimensions and the films shrink, covering the goods tightly.

5.1.3. 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
$E = \sigma_{11}/\varepsilon$	$D = 1/E$
$G = \sigma_{21}/\gamma$	$J = 1/G$
$K = p/(-\Delta V/V_o)$	$B = 1/K$

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

$$E = 2G \cdot (1 + \mu) = 3K \cdot (1 - 2\mu) \qquad (8)$$

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 (8) 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 8). Ultradrawn and self-reinforcing polymers may, however, exhibit tensile moduli that exceed those of steel (see below).

5.2. Energy Elasticity

5.2.1. Theoretical Moduli

The tensile moduli of common polymers are far lower than the theoretical moduli deduced from their chemical and physical structures (Table 9). Such theoretical moduli can be calculated from bond lengths, valence angles, and force constants for the deformation of these quantities. The theoretical moduli agree well with the microscopic lattice constants, which are

Table 8. 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	2 000	1 000	667

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. 31). 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 ($E_{\|} = 1\,160$ 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 $90 \mathrel{\widehat{=}}$ N/tex, 1 tex = 1 g per 1 000 m).

Table 9. Modulus of elasticity

Polymer	$E_{\|}$, 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

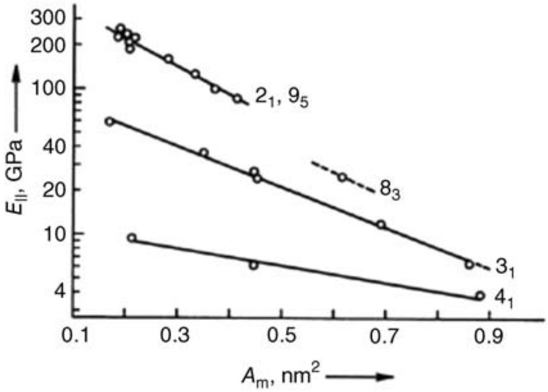


Figure 31. Longitudinal lattice moduli $E_{\|}$ as function of cross-sectional area A_m of polymer chains in all-*trans* (2_1) or helical conformations (9_5, 8_3, 3_1, 4_1) of their main chains Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

5.2.2. 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 10, 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-orienting polymers possess much higher moduli in the longitudinal direction than conventionally processed flexible polymers (Table 9). Their transverse moduli are

Table 10. 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	1 000	?	74
PET	19	?	0.13	1 400	?	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	?	2 800	?	?
LT PPBT[d]	120	17	62	1 500	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).

also higher because of intermolecular dipole–dipole interactions.

5.2.3. Temperature Dependence

Young's moduli change characteristically with temperature for the various classes of polymers (Fig. 32). 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 and thus behave like cross-linked thermoplastics above the T_G 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 because their amorphicity

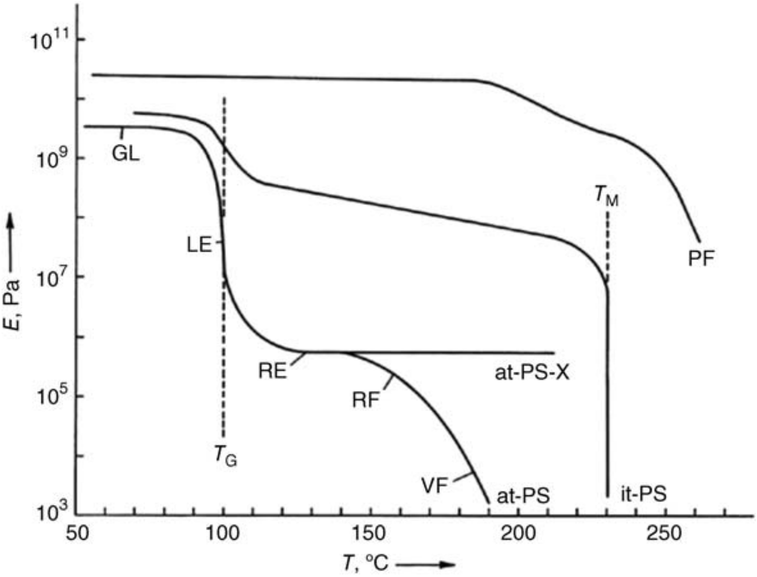


Figure 32. Temperature dependence of Young's moduli for conventional polymers
at-PS = amorphous (atactic) polystyrene ($M > M_c$); at-PS-X = its slightly cross-linked product; it-PS = partially crystalline (isotactic) polystyrene; PF = hardened phenol–formaldehyde resin; GL = glasslike; LE = leatherlike; RE = rubber (entangled); RF = viscoelastic; VF = viscous flow
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

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. The subsequent rubbery region is not very marked because the cross-linking density is high.

5.3. 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

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

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 ($V_o/V = 1$):

$$\begin{aligned} RT \cdot [M_c] &= lim_{\lambda \rightarrow 1}[\sigma_{11}/(\lambda - \lambda^{-2})] \\ &= \sigma_{11}/[3(\lambda - 1)] = \sigma_{11}/(3\varepsilon) = E_o \end{aligned} \tag{9}$$

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

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

They are, however, non-Hookean for elongations because $E_o \neq \sigma_{11}/\varepsilon$ (Eq. 9).

5.4. Viscoelasticity (→ Plastics, Properties and Testing)

5.4.1. Fundamentals

Most polymers do not revert "instantaneously" to their initial states after the removal of loads; they are neither ideal energy elastic (Section 5.2) nor ideal entropy elastic (Section 5.3). 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. 33). The Maxwell element combines spring and dashpot 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 11). 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 $d\gamma/dt = 0$,

$$\sigma = \sigma_o \cdot \exp(-G \cdot t_e/\eta) = \sigma_o \cdot \exp(-t_e/\tau)$$

The relaxation time $\tau = \eta/G$ indicates the time after which the stress has fallen to the e−1th 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-

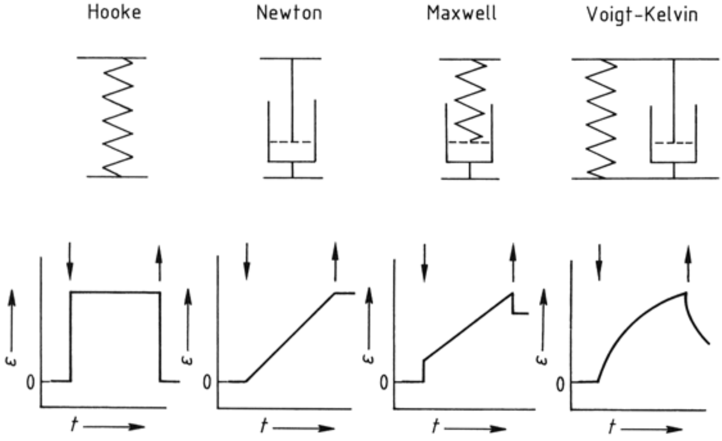


Figure 33. Time dependence of deformations according to various models. Loads are added at ↓ and removed at ↑ Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

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. 33), which yields for the deformation γ_r at constant stress σ_o after indexation for retardations r

$$\gamma_r = (\sigma_o/G_r) \cdot [1 - \exp(-G_r \cdot t_r/\eta)] \tag{10}$$

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.

Table 11. Simple mechanical models for the deformation of polymers

Model	Function	Behavior*	
		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.

The term "viscoelasticity" is sometimes used to describe the reversible deformation according to Equation (10). However, it is often applied to the total deformation, which is composed of the contributions by Equation (10), a Hookean body with $\gamma_e = \sigma_o/G_o$, and a Newtonian liquid $[\gamma_\eta = (\sigma_o/\eta_o) \cdot t]$:

$$\begin{aligned}\gamma_{tot} &= \{(1 - G_o) + (t/\eta_o) + (1/G_r) \cdot [1 - \exp(-t/\tau)]\} \cdot \sigma_o \\ &= \gamma_e + \gamma_\eta + \gamma_r\end{aligned}$$

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:

$$\gamma_{tot} = \gamma_e + \gamma_c = \gamma_e + \gamma \cdot t^n$$

5.4.2. Time—Temperature Superposition

Deformations, shear moduli, and shear compliances are time and temperature dependent

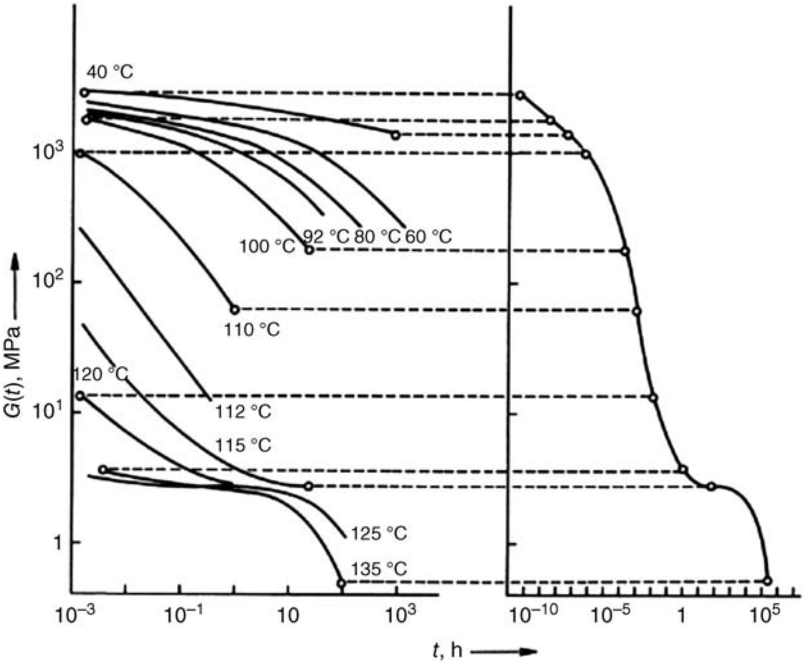


Figure 34. Time dependence of the shear modulus from measurements of the stress relaxation of a poly(methyl methacrylate) ($\bar{M}_n = 3\ 600\ 000$ g/mol) at various temperatures (left) and the resulting time–temperature superpositions for a reference temperature of 115°C (right) (circles represent equivalent positions)
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

(Fig. 34). 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. 34) and the G values are shifted horizontally with the help of a shift factor from the WLF equation (Eq. 5).

5.5. Dynamic Behavior

5.5.1. 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 ($\gamma_{\mathrm{t}} = \gamma_{\mathrm{o}} \cdot \sin \omega \cdot t$) 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 ($\sigma' = \sigma_o \cdot \cos \theta$); the other is not ($\sigma'' = \sigma_o \cdot \sin \cos \theta$).

Each of these two components possesses a modulus. The *real modulus* (*shear storage*

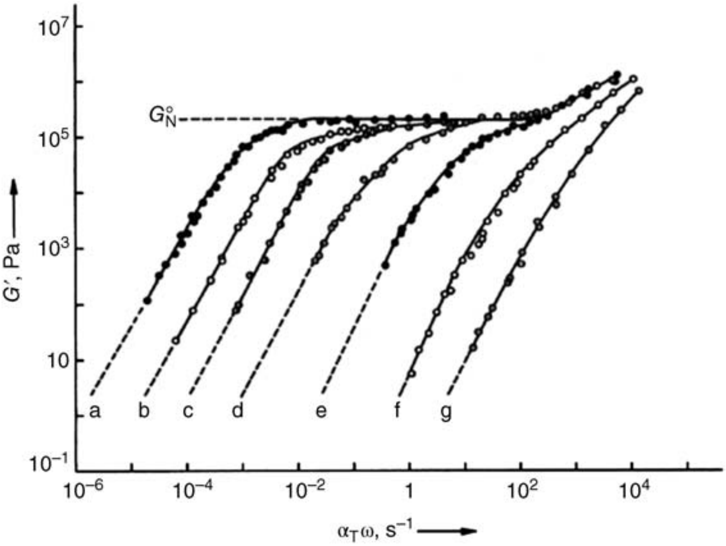


Figure 35. Frequency dependence of the shear storage modulus G' for narrow-distribution polystyrene melts of different molar masses M. A shift factor α_T was used to convert to 160°C data measured at various temperatures
a) $M = 581\,000$ g/mol; b) $M = 351\,000$ g/mol; c) $M = 215\,000$ g/mol; d) $M = 113\,000$ g/mol; e) $M = 46\,900$ g/mol; f) $M = 14\,800$ g/mol; g) $M = 8\,900$ g/mol
Reprinted with permission by Hüthig and Wepf Publ., Basel [5] after data of [85]

modulus) G' measures the stiffness and shape stability of the specimen:

$$G' = \sigma'/\gamma_o = (\sigma_o/\gamma_o) \cdot \cos\theta = G^* \cdot \cos\theta$$

whereas the *imaginary modulus* (*shear loss modulus*) G'' describes the loss of usable mechanical energy by dissipation into heat:

$$G'' = \sigma''/\gamma_o = G^* \cdot \sin\theta$$

The same quantities can also be derived if complex variables are introduced

$$G^* = G' + i \cdot G'' = [(G')^2 + (G'')^2]^{-1/2}$$

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

$$\Delta = \tan\theta = G''/G' = E''/E' < K''/K'$$

5.5.2. Molecular Interpretations

The *shear storage moduli* of low molar mass polymer melts with narrow molar mass distributions increase continually with increasing frequency (Fig. 35). At high normalized frequencies $\alpha_T\omega$, all storage moduli asymptotically 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. 32 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

Table 12. 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		
Polyisobutene	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

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

$$M_e = RT \cdot r_p \cdot \phi_p / G_N^o$$

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 12).

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.

5.6. Fracture [83]

5.6.1. 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 1 000%.

Two fracture modes can be distinguished, brittle and tough (ductile). Brittle polymers fracture perpendicularly to the stress direction, tough polymers longitudinally (Fig. 36). 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. 36).

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

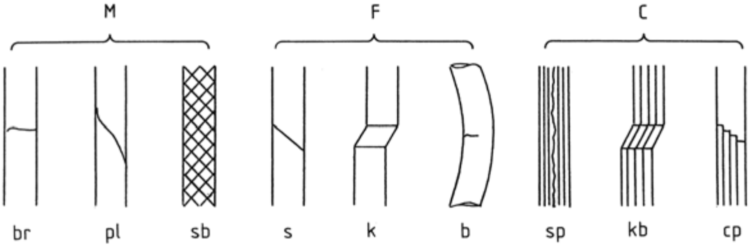


Figure 36. Failure modes of polymers (matrix M), fibers (F), and fiber-reinforced polymer composites (C) by brittle failure (br), plastic flow (pl), shear band formation (sb), shearing (s), kink formation (k), bending (b), longitudinal splicing (sp), formation of kink bands (kb), and step formation by compression (cp)
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

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.

5.6.2. 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 $\sigma^o_{\|}$ is given by [5].

$$\sigma^o_{\|} = \frac{E^o_{\|} \cdot (L_b - L_o)}{\pi L_o} = K \cdot E^o_{\|} \qquad (11)$$

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 $\sigma^o_{\|}$ should be ca. one-tenth of the theoretical tensile modulus $E^o_{\|}$ in the chain direction, regardless of the chemical nature of the polymer. Polyethylene with a theoretical modulus of 340 GPa (Table 9) 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 (11) 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. 37). 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

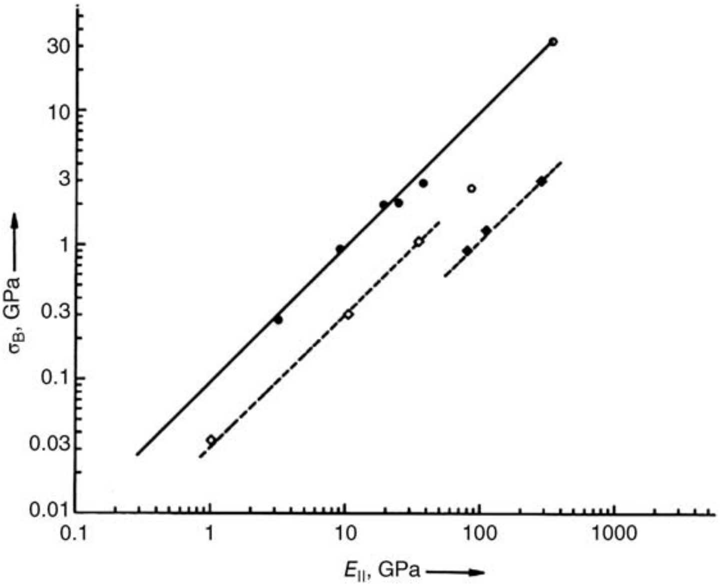
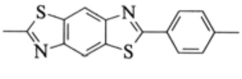
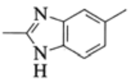


Figure 37. Tensile strength at break as function of tensile modulus: (•) Experimentally ultradrawn ultra-high-modulus polyethylenes; (○) Industrially manufactured ultradrawn polyethylene (Dyneema); (⊙) Theory for perfectly aligned polyethylene; (◆) Heterogeneous molecular composites of ABPBI fibers or PBT fibers or films in ABPBI matrix; (◆) Homogeneous molecular composites of PBT fibers or PBT fibers for films in ABPBI. Solid line corresponds to $\sigma_B = 0.095 \cdot E_{\|}$

proportionality constant. In other ultradrawing experiments, a power dependence $\sigma = K' \cdot E^{n}$ was found, however.



PPBT



ABPBI

5.6.3. Real Fracture Strength

The lower than theoretical fracture strengths of most polymers (see Tables 9 and 10) 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

$$\sigma_{\mathrm{a}}^{\mathrm{o}} = (E \cdot \gamma_{\mathrm{lv}}/L_{\mathrm{o}})^{1/2} \tag{12}$$

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 (12). The ratios $\sigma_{a}^{0}/\sigma_{\mathrm{exp}}$ of molded (unoriented) plastics decrease with increasing elongation ε_{b} at break (Fig. 38), 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:

$$\sigma_{\mathrm{B}} = [(2E \cdot \gamma_{\mathrm{lv}})/(\pi \cdot L)]^{1/2} \tag{13}$$

This functionality is indeed observed for artificially introduced long cracks. The

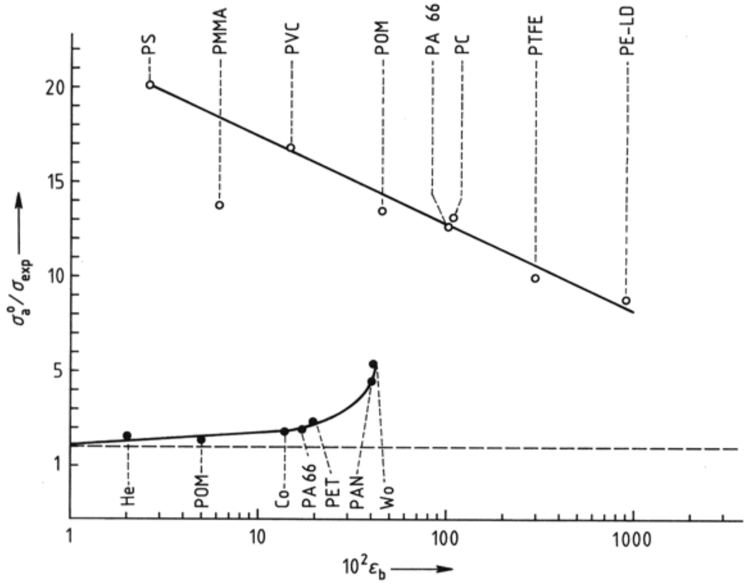


Figure 38. Ratio $\sigma_{a}^{0}/\sigma_{\mathrm{exp}}$ of theoretical [Eq. (12)] and experimental fracture strengths as function of elongation at break ε_{b} for (○) nonoriented (molded plastics) and (●) oriented (fibers) polymers
He = hemp, Co = cotton, Wo = wool (for other abbreviations see Tables 1–4)

predicted fracture strengths are however much lower than those found by experiment. Furthermore, deviations from Equation (13) 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. 29). 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. 36). Chain segments are arranged at angles between shear bands and stress directions.

All polymers with upper yield values form crazes upon stress softening (Fig. 39), 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.

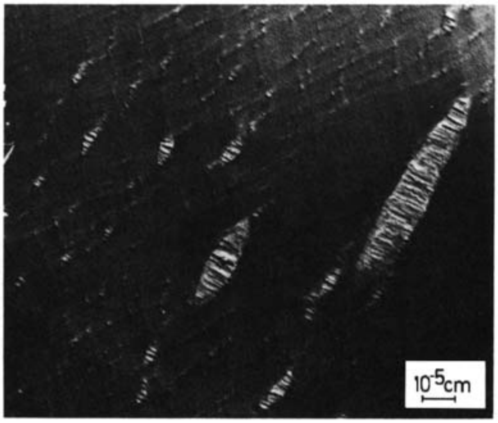


Figure 39. Crazes in a polystyrene drawn to 25% [86]

The formation of crazes is the primary mechanism for the dissipation of stress energy. It is utilized in the rubber reinforcement of polystyrene. Rubber-modified polypropylene, on the other hand, deforms mainly by shear flow.

5.6.4. 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 → Plastics, General Survey, 4. Polymer Composites).

5.6.5. 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.

5.6.6. 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. 40). Partially crystalline polymers show a bend in these lines after certain times, which indicates a change from tough fracture (short times) to brittle fracture (long times), probably caused by recrystallization phenomena.

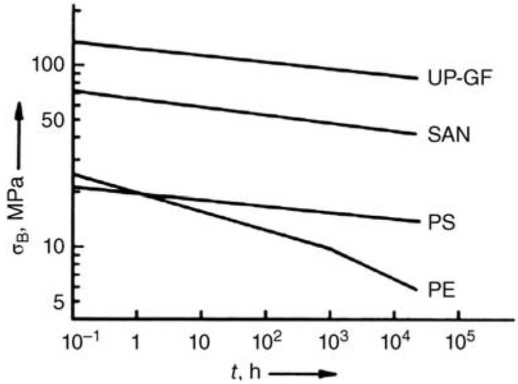


Figure 40. Time dependence of tensile fracture strengths after static loading during time t. UP-GF = glass-fiber-reinforced unsaturated polyester; SAN = styrene–acrylonitrile copolymer (impact polystyrene); PS = polystyrene; PE = polyethylene
Reprinted with permission by BASF AG, Ludwigshafen [81]

5.7. Surface Mechanics

5.7.1. 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).

5.7.2. 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 13).

Table 13. 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

5.7.3. Abrasion and Wear

Abrasion is the loss of material from surfaces by friction. It is thus affected by both friction properties 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 14).

Table 14. 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

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).

6. Electric Properties [78, 80, 87, 88]

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 6.1), but certain polymers are intrinsic semiconductors and some may even be conductors after doping (Section 6.2).

6.1. Dielectric Properties

6.1.1. Relative Permittivity

Groups within a molecule and entire molecules of an insulator are polarized by applied electric fields. Polarization is usually measured by the

Table 15. Electrical properties of plastics

Polymer	Δw [a]		ρ_v [c]	ρ_s [d]	S [f]		
	%	ε_r [b]	$\Omega \cdot cm$	Ω	$\tan\delta$ [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] $\Delta w =$ water absorption (at 50% relative humidity).
[b] $\varepsilon_r =$ relative permittivity ("dielectric constant").
[c] $\rho_v =$ volume resistivity (inverse specific electrical conductivity).
[d] $\rho_S =$ surface resistivity (inverse surface conductivity).
[e] $\tan\delta =$ 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).

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 15).

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).

6.1.2. 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'):

$$N_v/N_b = \tan\delta = \sin\delta/\cos\delta = \varepsilon''/\varepsilon'$$

Sometimes power factors sinδ 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 fields; PVC is an example. Polymers with low loss factors [PE, PS, polyisobutene (PIB)], on the other hand, are excellent insulators for high-frequency conductors.

Real and imaginary relative permittivities depend on the frequencies ν of the alternating

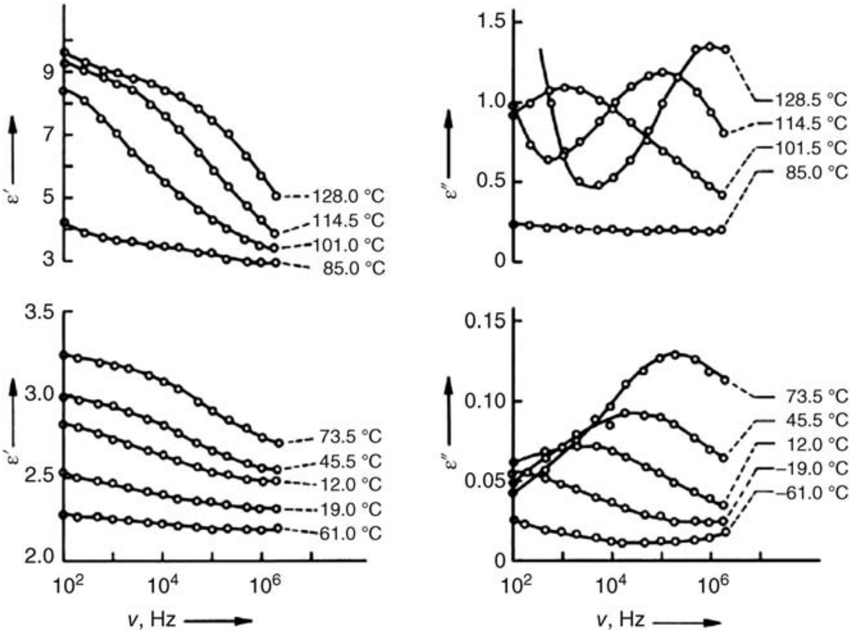


Figure 41. Frequency dependence of real (ε′) and imaginary relative permittivities (ε″) of a poly(vinyl chloride) at various temperatures
Upper: β-dispersion; lower: γ-dispersion.
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

current (Fig. 41). The function $\varepsilon' = f(\nu)$ corresponds to a dispersion and the function $\varepsilon'' = f(\nu)$ 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.

6.1.3. 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 15).

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 15). 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 has a poor tracking resistance although it is a good insulator.

6.1.4. 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 15). 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 3 000 V/cm (POM vs. PA 6) and – 1 700 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.

6.2. Electrical Conductivity (→ Polymers, Electrically Conducting) [80, 87–91]

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

$$\sigma = (N/V) \cdot \mu \cdot e$$

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.

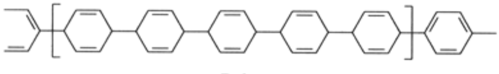
Polymers with conjugated chains [e.g., *trans*-polyacetylene $\sim$(CH=CH)$_n$$\sim$] are, for these reasons, merely semiconductors and insulators even if the chains are planar. These low conductivities can be increased substantially, however, if the polymers are doped with substances such as I_2, AsF_5, BF_3, etc.: Doping with AsF_5 increases the specific electrical conductivity of *trans*-polyacetylene from 10^{-9} to 1 200 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.

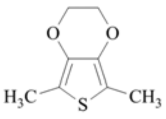
Solitons can move only along the chain; there is no tunnel effect between chains. Because of this anisotropic behavior, doped polymers (and conducting low molar mass organic molecules) are called low-dimensional conductors, synthetic metals, or organic metals.

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.

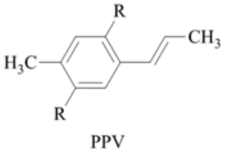
Electrically conducting polymers are presently used in small batteries, for example, a complex of poly(2-vinylpyridine)/I_2 as cathode in Li/I_2 batteries for pacemakers ($\sigma = 10^{-3}$ S/cm). Other possible applications of electrically conducting polymers are in solar cells, electrolysis membranes, microwave shielding, and integrated circuits.

One prime example of an electrically conducting polymer is poly-3,4-ethylendioxythiophene (PEDOT), which consists of 2,5-coupled 3,4-ethylendioxythiophene repeat units and is made by oxidative coupling. In its oxidized form, PEDOT is an almost transparent, light-blue conductor, and, depending on the application, several counterions can be employed. The most common form of PEDOT is the commercially available blend with polystyrene sulfonate (PSS) in aqueous suspension (PEDOT:PSS, Baytron P). High conductivities up to 1 000 S/cm allow to apply this material as thin film for electrode coatings in solar cells or sensor devices to replace the traditionally used indium tin oxide.

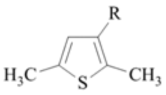
Although high electrical conductivities of conjugated polymers obtained by chemical doping are important for e.g., electrode applications, conjugated absorber materials in organic photovoltaics are required to exhibit semiconducting behavior. An appropriate design of conjugated polymers for organic photovoltaics is of critical importance, as several parameters, such as absorption, energy levels, charge carrier mobility, molar mass, or solubility have to be considered simultaneously and are mutually dependent. Consequently, numerous new conjugated polymer structures have been prepared by transition metal-catalyzed cross coupling since the 1990s, whereby the most successful materials have moved from the class of polyphenylene–vinylenes (PPV) and poly(3-alkylthiophene)s (P3ATs) to donor–acceptor polymers with alternating electron-rich and electron-deficient repeat units. The photovoltaic performance of the best donor–acceptor copolymers are now approaching 10%, which is considered an important threshold value to commercialization. Two successful copolymers DPPTT and PTB7 are shown below:



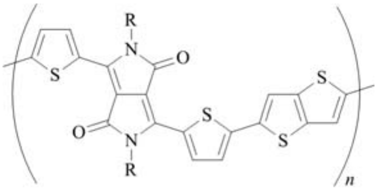
PEDOT



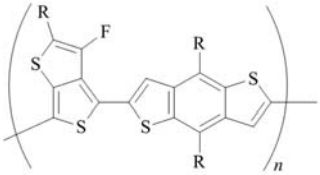
PPV



P3AT



DPPTT



PTB7

6.3. 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.

7. Optical Properties [78]

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

$$(n^2-1)/(n^2-2) = (4/3)\pi Q = (4/3)\pi(N/V)\cdot\alpha$$

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. Because the contributions of the latter can be neglected and because 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:

$$R = \frac{I_r}{I_0} = \frac{1}{2}\left[\frac{\sin^2(\alpha-\beta)}{\sin^2(\alpha+\beta)} + \frac{\tan^2(\alpha-\beta)}{\tan^2(\alpha+\beta)}\right] \tag{14}$$

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°).

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 (14). It increases with increasing refractive index of the specimen and with increasing angle of incidence (Fig. 42). The maximum theoretical gloss is almost never achieved because of surface roughness.

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 $\alpha \rightarrow 0$ and $\beta \rightarrow 0$. They can have values between 98.0% ($n = 1.33$) and

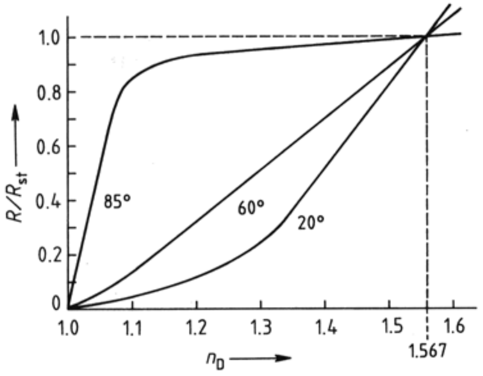


Figure 42. Maximum theoretical gloss as a function of the refractive index of specimen for various angles of incidence α and a standard with $n_D = 1.567$
Reprinted with permission by Hüthig and Wepf Publ., Basel [5]

92.8% ($n = 1.73$) for polymers, (i.e., between 2 and 7.2% of the incident 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 1 100 nm (theory 96.1%). Transparencies decrease above wavelengths of ca. 1 150 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 ($\tau_i < 0.90$) 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.

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 L. Mandelkern: *An Introduction to Macromolecules*, 2nd ed., Springer, New York 1972, 1982.
7 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.
8 F.A. Bovey, F.H. Winslow (eds.): *Macromolecules*, Academic Press, New York 1979.
9 R.B. Seymour, C.E. Carraher, Jr.: *Polymer Chemistry*, 2nd ed., Dekker, New York 1989.
10 A. Rudin: *The Elements of Polymer Science and Engineering*, Academic Press, New York 1982.
11 P.C. Hiemenz: *Polymer Chemistry*, Dekker, New York 1984.
12 P. Munk: *Introduction to Macromolecular Science*, Wiley, New York 1989.
13 H. Morawetz (eds.): *Polymers: The Origins and Growth of a Science*, John Wiley & Sons, New York 1985.
14 Y. Furukawa (ed.): *Inventing Polymer Science, Staudinger, Carothers, and the Emergence of Macromolecular Chemistry*, University of Pennsylvania Press, Philadelphia 1998.
15 H. Ringsdorf, *Angew. Chem. Int. Ed.* **43** (2004) 1064.
16 R. Mülhaupt, *Angew. Chem. Int. Ed.* **43** (2004) 1054.
17 International Union of Pure and Applied Chemistry: *Compendium of Macromolecular Nomenclature (Purple Book)*, Blackwell Sci. Publ., Oxford 1991.
18 R.C. Hiorns, R.J. Boucher, R. Duhlev, K.-H. Hellwich, P. Hodge, A.D. Jenkins, R.G. Jones, J. Kahovec, G. Moad, C. K. Ober, D.W. Smith, R.F.T. Stepto, J.-P. Vairon, J. Vohlídal, *Pure Appl. Chem.* **84** (2012) 2167.
19 J. Brandrup, H.E. Immergut, E.A. Grulke (eds.): *Polymer Handbook*, John Wiley & Sons, New York 1999.

20 J. Schultz: *Polymer Materials Science*, Prentice-Hall, Englewood Cliffs, N.J., 1974.

21 J.A. Brydson: *Plastics Materials*, 3rd ed., Butterworth, London 1975.

22 S. Rosen: *Fundamental Principles of Polymeric Materials for Practicing Engineers*, Cahners Books, Boston 1973.

23 J.H. DuBois, F.W. John: *Plastics*, 5th ed., Van Nostrand-Reinhold, New York 1976.

24 W.E. Driver: *Plastics Chemistry and Technology*, Van Nostrand-Reinhold, Cincinnati 1974.

25 *Houben-Weyl*, 5th ed., vol. 20; *Science of Synthesis*, vol. 1, Georg Thieme, Stuttgart 2001, p. 57; *Science of Synthesis*, vol. 2, Georg Thieme, Stuttgart 2002, p. 291; *Science of Synthesis*, vol. 2, Georg Thieme, Stuttgart 2002, p. 906.

26 G.W. Becker et al. (eds.): *Kunststoff-Handbuch*, 2nd ed., Hanser, München 1983 ff. (many vols.).

27 H. Mark, C. Overberger, G. Menges, N.M. Bikales (eds.): *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Wiley, New York 1985–1990.

28 W.A. Kargin (ed.): *Enciklopedia Polimerov*, 3 vols., Sovietskaya Enciklopedia Publ., Moscow 1972.

29 G. Allen, J.C. Bevington (eds.): *Comprehensive Polymer Science*, Pergamon, Oxford 1989.

30 *Chemiefasern auf dem Weltmarkt*, 7th ed., Deutsche Rhodiaceta, Freiburg/Br., 1969, Supplement 1976 (trade names of fibers).

31 The International Plastics Selector, *Commercial Names and Sources*, Cordura Publ., San Diego 1978.

32 Fachinformationszentrum Chemie: *Index of Polymer Trade Names (Parat)*, VCH, Weinheim 1987.

33 J. Brandrup, E.H. Immergut (eds.): *Polymer Handbook*, 3rd ed., Wiley, New York 1989.

34 O. Griffin Lewis: *Physical Constants of Linear Homopolymers*, Springer, Berlin 1968.

35 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.

36 P.A. Schweitzer: *Corrosion Resistance Tables (Metals, Plastics, Nonmetallics, Rubbers)*, Dekker, New York 1976.

37 The International Plastics Selector, San Diego 1977.

38 H. Saechtling: *Kunststoff-Taschenbuch*, 24th ed., Hanser, Munich 1989; *International Plastics Handbook*, 2nd ed., Hanser, München 1989.

39 *Modern Plastics Encyclopedia*, McGraw-Hill, New York (annually in October as issue 10 A).

40 *Encyclopedie Francaise des Matieres Plastiques*, Les Publicateurs Techniques Association, Paris, annually.

41 J.E. Williams (ed.): *Computer-Readable Databases*, American Library Association, Chicago 1985.

42 German Plastics Institute, Plastics Databank POLYMAT, Darmstadt; Fachinformationszentrum Chemie, Berlin (6000 polymers from 80 manufacturers).

43 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.

44 E.R. Yescombe: *Plastics and Rubbers: World Sources of Information*, 2nd ed., Appl. Sci. Publ., Barking 1976.

45 G.J. Patterson: *Plastics Book List*, Technomic Publ., Westport 1975.

46 P. Eyerer: *Informationsführer Kunststoffe*, VDI-Verlag, Düsseldorf 1976.

47 J. Schrade: *Kunststoffe (Hochpolymere): Bibliographie aus dem deutschen Sprachgebiet*, 1st ed., Schweiz. Aluminium AG., Zürich 1976; 2nd ed., Zürich 1980.

48 O.A. Battista, *The Polymer Index*, McGraw Hill, New York 1976.

49 S.M. Kaback: "Literature of Polymers," *Encycl. Polym. Sci. Technol.* **8** (1968) 273; J.T. Lee, *Encycl. Polym. Sci. Eng.* **9** (1987) 62.

50 W.J. Roff, J.R. Scott: *Handbook of Common Polymers*, Butterworths, London 1971.

51 M. Ash, I. Ash: *Encyclopedia of Plastics, Polymers and Resins*, Chem. Publ. Co., New York 1982–1988.

52 M.S.M. Alger: *Polymer Science Dictionary*, Elsevier Applied Sci. Publ., Barking 1989.

53 American Society for Testing Materials, ASTM D-1600–86 a; D-1418–67; D-4020–81.

54 German Industrial Standards DIN 7723; 7728 (1988); 16 913; 55 950; 60 001.

55 European Textile Characterization Law.

56 International Organization for Standardization, ISO 1043–1978, ISO 1629–1980.

57 Guide for the Harmonisation of Designations of Thermoplastic Materials, ISO/TC 61/SC 9 N 435, April 1981; ASTM D 4000.

58 K. Wiebusch, *Kunststoffe-German Plastics* **72** (1982) 22, 167.

59 F.O. Swanson, *Plastics Engng.* (1983) Jan. 31.

60 R.H. Wehrenberg, II, *Mat. Engng.* (1984) Feb. 48.

61 H. Elias et al., *Polymer News* **9** (1983) 101; **10** (1985) 169.

62 J.H. DuBois: *Plastics History–U.S.A.*, Cahners, Boston 1971.

63 J.K. Craver, R.W. Tess (eds.): Applied Polymer Science, *Am. Chem. Soc.*, Washington, D.C., 1975.

64 F.M. McMillan: *The Chain Straigtheners: Fruitful Innovation. The Discovery of Linear and Stereoregular Polymers*, MacMillan, London 1981.

65 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.

66 R. Friedel: *Pioneer Plastic. The Making and Selling of Celluloid*, University of Wisconsin Press, Madison 1983.

67 W. Glenz (ed.): *Kunststoffe–Ein Werkstoff macht Karriere*, Hanser, München 1985.

68 United Nations, Statistical Yearbooks. United Nations, http://esa.un.org/unpd/wpp/Excel-Data/population.htm accessed March 7, 2015

69 Calculated from data in *Kunststoffe* **73** (1983) no. 10.

70 H.-G. Elias, F. Vohwinkel: *New Commercial Polymers*, Gordon and Breach, New York 1986; *Neue polymere Werkstoffe*, Hanser, München 1983.

71 H.-G. Elias, *Grosse Moleküle*, Springer, Berlin 1985; *Mega Molecules*, Springer, Berlin 1987; *Megamolekuly*, Khimiya, Leningrad 1990.

72 United States, Statistical Abstracts (annually).

73 Plastics Europe, http://www.plasticseurope.org/Document/plastics-the-facts-2013 (accessed April 26, 2014).

74 United Nations: *World population to 2300*, United Nations, New York 2004, http://www.un.org/esa/population/publications (accessed August 5, 2014).

75 D. Tomalia, A.M. Naylor, W.A. Goddard III, *Angew. Chem.* **102** (1990) 119; *Angew. Chem. Intern. Ed.* **29** (1990) 138.

76 G. Natta, P. Corradini, *Nuovo Cimento, Suppl.* **15** (1960) 11.

77 D. Lang, H. Bujard, B. Wolff, D. Russell, *J. Mol. Biol.* **23** (1967) 163.

78 D.W. Van Krevelen, K. Te Nijenhuis (eds.): *Properties of Polymers*, Elsevier, Amsterdam 2009.

79 Y.G. Yanovsky (ed.): *Polymer Rheology: Theory and Practice*, Springer, Berlin 2014.

80 E. Riande, R. Diaz-Celleja (eds.): *Electrical Properties of Polymers*, Marcel Dekker, New York 2004.

81 *Kunststoff-Physik im Gespräch*, 8th ed., BASF, Ludwigshafen 1988.

82 H.M. Laun, H. Münstedt, *Rheol. Acta* **17** (1978) 415.

83 G.H. Michler, F.J. Balta-Calleja (eds.): *Nano- and Micromechanics of Polymers*, Hanser Publ., Munich 2012.

84 R.F. Landel, L.E. Nielsen (eds.): *Mechanical Properties of Polymers and Composites*, CRC Press, Boca Raton 1993.

85 S. Onogi, T. Matsuda, K. Kitagawa, *Macromolecules* **3** (1970) 109.

86 S. Wellinghoff, E. Baer, private communication.

87 T.A. Skotheim, R.L. Elsenbaumer, J.R. Reynolds (eds.): *Handbook of Conducting Polymers*, New York 1998.

88 T.A. Skotheim, J. Reynolds (eds.): *Conjugated Polymers: Theory, Synthesis, Properties and Characterization*, CRC Press, Boca Raton 2006.

89 J.-F. Morin, M. Leclerc (eds.): *Design and Synthesis of Conjugated Polymers*, Wiley-VCH, Weinheim 2010.

90 C. Brabec, V. Dyakonov, U. Scherf (eds.): *Organic Photovoltaics*, Wiley-VCH, Weinheim 2008.

91 G. Hadziioannou, G.G. Maliaras (eds.): *Simconducting Polymers*, Wiley-VCH, Weinheim 2006.

Further Reading

P.C. Painter, M.M. Coleman (eds.): *Essentials of Polymer Science and Engineering*, DEStech Publication, Lancaster 2009.

E.S. Guerra, E.V. Lima (eds.): *Handbook of Polymer Synthesis, Characterization and Processing*, John Wiley & Sons, Hoboken 2013.

H.G. Elias (ed.): *Macromolecules: Industrial Polymers and Synthesis*, Wiley-VCH, Weinheim 2007.

H.G. Elias (ed.): *Macromolecules*, vols. 1-4, Wiley-VCH, Weinheim 2008.

K. Matyjaszewski, M. Möller (eds.): *Polymer Science: A Comprehensive Reference*, Elsevier, Amsterdam 2012.

G.H. Michler, F.J. Balta-Calleja (eds.): *Nano- and Micromechanics of Polymers*, Hanser Publ., Munich 2012.

N. Rudolph, T. Osswald (eds.): *Polymer Rheology: Fundamentals and Applications*, Hanser Publ. Munich 2014.