Kirk-Othmer Encyclopedia of Chemical Technology.

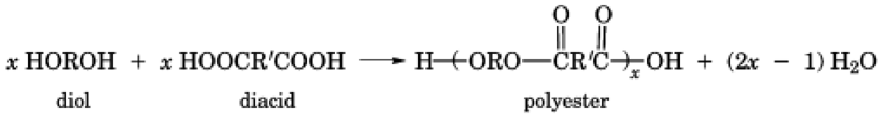
POLYMERS

Polymers are very large molecules made by covalently binding many smaller molecules. The word polymer is derived from the Greek *poly* (many) and *meros* (part). The size of polymer molecules imparts many interesting and useful properties not shared by low molecular weight materials. Polymers are the fundamental materials of plastics, rubbers and most fibers, and surface coatings and adhesives, and as such are essential to modern society. Also, many important constituents of living organisms, eg, proteins (qv) and cellulose (qv), are biopolymers (qv).

1. Classification and Nomenclature

Polymers were initially classified according to their response to temperature. Those that are softened (plasticized) reversibly by heat are known as thermoplastics. By analogy, wax behaves as a thermoplastic. Others, though they might initially be liquid or soften once upon heating, undergo a curing (setting) reaction that solidifies them, and further heating leads only to degradation. These are known as thermosets. Again by analogy, an egg behaves as a thermoset. The ability of polymers to soften and flow at least once is one of their most valuable assets, as it allows them to be formed into complex shapes easily and inexpensively.

In general, polymers are formed by two types of reactions: condensation and addition. The formation of a polyester by polycondensation may be illustrated as follows.

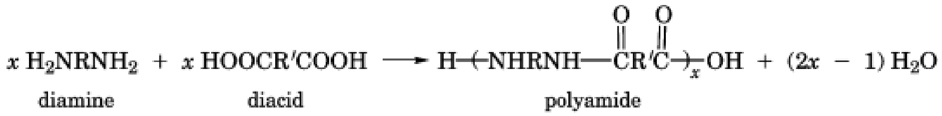


$$x\,\mathrm{HOROH} + x\,\mathrm{HOOCR'COOH} \longrightarrow \mathrm{H}\!\left(\mathrm{ORO}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{R'}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\right)_{x}\mathrm{OH} + (2x-1)\,\mathrm{H_2O}$$

In the polyester formula shown, parentheses enclose the repeating unit. The quantity x is the degree of polymerization, sometimes also called the chain length, the number of repeating units strung together like identical beads on a string. Neglecting the ends of the molecule, which is usually justified for large x, the molecular weight M of the polymer molecule is given by $M = mx$, where m is the molecular weight of the repeating unit. Since x can easily be in the thousands, it is not surprising that the term macromolecules is also used to describe these materials.

The ester linkage in the repeating unit characterizes polyesters. R and R′ represent portions of the monomer molecule that do not participate in the polymerization. They may vary widely, giving rise to many different polyesters. Poly(ethylene terephthalate) (PET), made from ethylene glycol ($R = (CH_2)_2$) and terephthalic acid ($R' =$ ), is familiar in the form of soda bottles, recording tape, and polyester fiber (see Fibers, polyester).

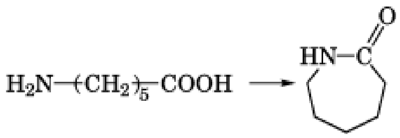
Another common polycondensation involves reaction of diamines and diacids to form polyamides, commonly called nylons:



$$x\,H_2NRNH_2 + x\,HOOCR'COOH \longrightarrow H\!\left(NHRNH-\overset{\overset{O}{\|}}{C}R'\overset{\overset{O}{\|}}{C}\right)_{x}\!OH + (2x-1)\,H_2O$$

The amide linkage characterizes nylons. In the first commercial nylon, nylon-6,6, $R = (CH_2)_6$ and $R' = (CH_2)_4$. Nylon-6,6 is familiar as a textile fiber (nylon stockings) and a molded plastic (see Polyamides).

The two complementary functional groups that react to form condensation polymers may also occur in a single monomer, eg, a hydroxy acid, HO–R–COOH, or an amino acid, H_2N–R–COOH. In some cases, such monomers self-condense to a cyclic structure, which is what actually polymerizes. For example, ϵ-caprolactam (**1**) can be thought of as the self-condensation product of an amino acid. Caprolactam undergoes a ring-opening polymerization to form another



(1)

important nylon, nylon-6 (see Caprolactam). Even though no water is eliminated in the actual polymerization step, the polymer is usually considered a condensation polymer. Table 1 illustrates some other important condensation polymers.

$$x\,(\mathbf{1}) \longrightarrow -\!\left(NH(CH_2)_5\overset{\overset{O}{\|}}{C}\right)_{x}\!-$$

Addition or chain-growth polymerization involves the opening of a double bond to form new bonds with adjacent monomers, as typified by the polymerization of ethylene to polyethylene:

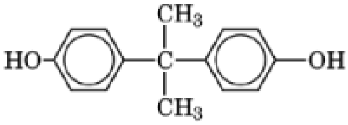
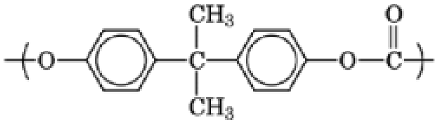
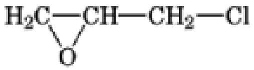
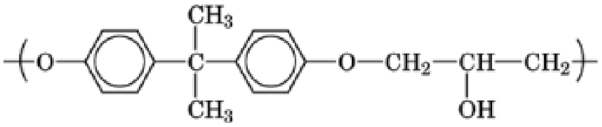
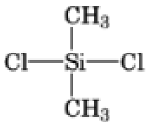
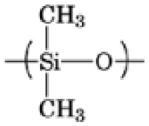
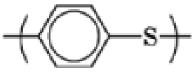
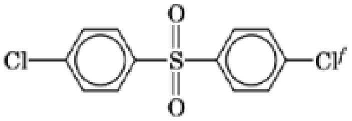
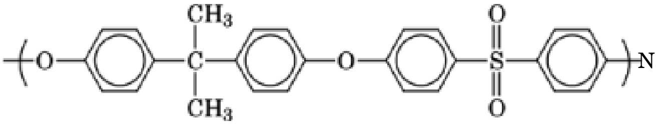
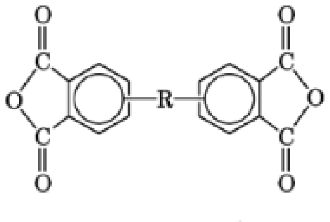
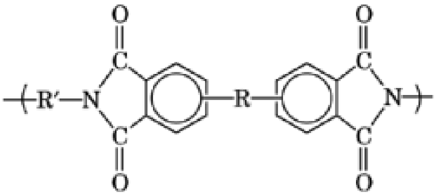
$$xH_2C{=}CH_2 \longrightarrow -\!\left(CH_2{-}CH_2\right)_x\!-$$

Because no molecule is split out, the molecular weight of the repeating unit is identical to that of the monomer. Vinyl monomers, $H_2C{=}CHR$ (Table 2) undergo addition polymerization to form many important and familiar polymers. Diene (two double bonds) monomers also undergo addition polymerization. Normally, one double bond remains, leaving an unsaturated polymer, with one double bond per repeating unit. These double bonds provide sites for subsequent reaction, eg, vulcanization.

In terms of molecular structure, there are three principal categories of polymers, illustrated schematically in Figure 1. If each monomer is difunctional, that is, can react with other monomers at two points, a linear polymer is formed. All the examples given above are linear polymers. Polymers that contain two different repeating units, say A and B, are known as copolymers (qv). A linear polymer with a random (AABBABAAABABB) arrangement of the repeating units is a random or statistical copolymer, or just copolymer. It is termed poly(A–*co*–B), with the primary constituent listed first. A molecule in which the two repeating units are arranged in long, contiguous blocks ($[A]_x$———$[B]_y$) is a block (*b*) copolymer, poly(A–*b*–B).

A few points of tri- or higher functionality introduced along the polymer chains, either intentionally or through side reactions, give a branched polymer. A branched structure with the backbone consisting of one repeating unit (A) and the branches of another (B), is a graft (*g*) copolymer, poly(A–*g*–B). Dendrimers are a

Table 1. Some Commercial Condensation Polymers

Polymer	Monomers	Repeating unit	Eliminated molecule[a]
polycarbonate	 **bisphenol A**[b] [a]		HCl
epoxy resin	 **epichlorohydrin**[c] [a]		HCl
polydimethylsiloxane (silicone rubber)	 **dimethyl dichlorosilane**[d] [a]		HCl
poly(phenylene sulfide)			NaCl
polysulfone[e]	[f] [a]		NaCl
polyimide	 **dianhydride**[g]		H_2O

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[a] A true condensation reaction is characterized by elimination of a small molecule when the monomers condense to form the repeating unit.

[b] Reacts with phosgene $COCl_2$ to form the repeat unit shown (see Polycarbonates).

[c] Reacts with bisphenol A to form the repeat units shown (see Epoxy resins).

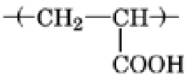
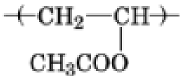
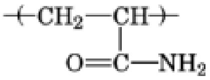
[d] Reacts with H_2O to form the repeat units shown (see Silicon compounds, silicones).

[e] See Polymers containing sulfur.

[f] Reacts with the disodium salt of bisphenol A.

[g] Reacts with diamine $H_2N–R'–NH_2$ (see Polyimides).

Table 2. Some Vinyl Monomers, $\mathrm{CH_2{=}CHR}$

R	Common name	Polymer repeating unit	*Encyclopedia* reference
Cl	vinyl chloride	$\mathrm{-\!\!(CH_2-CHCl)\!\!-}$	Vinyl polymers, vinyl chloride polymers
C_6H_5	styrene	$\mathrm{-\!\![CH_2-CH(C_6H_5)]\!\!-}$	Styrene plastics
CH_3	propylene	$\mathrm{-\!\![CH_2-CH(CH_3)]\!\!-}$	Olefin polymers, polypropylene
C≡N	acrylonitrile	$\mathrm{-\!\!(CH_2-CH_2CN)\!\!-}$	Acrylonitrile polymers
COOH	acrylic acid	 $\mathrm{-\!\!(CH_2-\underset{COOH}{CH})\!\!-}$	Acrylic acid and derivatives
$OOCCH_3$	vinyl acetate	 $\mathrm{-\!\!(CH_2-\underset{CH_3COO}{CH})\!\!-}$	Vinyl polymers, vinyl acetate polymers
$CONH_2$	acrylamide	 $\mathrm{-\!\!(CH_2-\underset{O=C-NH_2}{CH})\!\!-}$	Acrylamide polymers

more recent development. They are molecules that branch repeatedly as they grow outward from a central core (1–3).

As the length and frequency of branches increase, they may ultimately reach from chain to chain. If all the chains are connected together, a cross-linked or network polymer is formed. Cross-links may be built in during the polymerization reaction by incorporation of sufficient tri- or higher functional monomers, or may be created chemically or by radiation between previously formed linear or branched molecules (curing or vulcanization). For example, a liquid epoxy (Table 1) oligomer (low molecular weight polymer) with $x \approx 6 - 8$ is cured to a cross-linked solid by reaction of the hydroxyl and terminal epoxide groups with a diamine or acid anhydride. In a fully cross-linked polymer, all the atoms are connected to one another by covalent bonds, so the entire macroscopic polymer mass is literally a single molecule. Thus, the cross-linked polyester in a bowling ball has a molecular weight on the order of 10^{27} g/mol.

2. Structure and Properties

Various levels of structure ultimately determine the properties of a polymer. The characterization of structure and how it influences properties is outlined in the following.

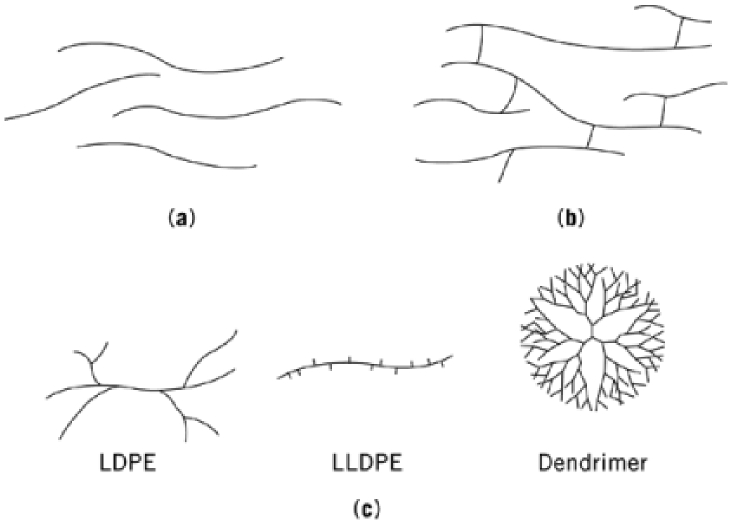


Fig. 1. Schematic diagram of polymer structures: (**a**) linear; (**b**) cross-linked; and (**c**) branched, where LDPE = low density polyethylene and LLDPE=linear low density polyethylene.

2.1. Molecular Weights

With the exception of some naturally occurring polymers, all linear and branched polymers consist of molecules with a distribution of molecular weights. Two average molecular weights are commonly defined; the number-average, $\overline{M}_n$, and the weight-average, $\overline{M}_w$:

$$\overline{M}_n = \frac{W}{N} = \frac{\sum_{x=1}^{\infty} n_x M_x}{\sum_{x=1}^{\infty} n_x}$$

$$\overline{M}_w = \frac{\sum w_x M_x}{\sum w_x} = \frac{\sum n_x M_x^2}{\sum n_x M_x}$$

where

W = total sample weight = $\sum_{x=1}^{\infty} w_x = \sum_{x=1}^{\infty} n_x M_x$;
w_x = total weight of x−mer;
N = total number of moles in the sample (of all sizes) = $\sum_{x=1}^{\infty} n_x$;
n_x = number of moles of x−mer;
M_x = molecular weight of x−mer.

It may be shown that $\overline{M}_w \geq \overline{M}_n$. The two are equal only for a monodisperse material, in which all molecules are the same size. The ratio $\overline{M}_w/\overline{M}_n$ is known as the polydispersity index and is a measure of the breadth of the molecular weight distribution. Values range from about 1.02 for carefully fractionated samples or certain polymers produced by anionic polymerization, to 20 or more for some commercial polyethylenes.

Colligative property techniques that measure the moles of polymer in solution give $\overline{M}_n$. These include membrane and vapor-pressure osmometry and freezing-point depression. Procedures which, in effect, determine the mass of polymer at each size level give $\overline{M}_w$. These include light scattering and sedimentation in an ultracentrifuge. Another technique, intrinsic viscosity, makes use of the large increase in viscosity caused by relatively small amounts of polymeric solute. Intrinsic viscosity gives yet another average molecular weight, $\overline{M}_v$ (viscosity-average), which is between $\overline{M}_n$ and M_w, but is closer to the latter. Unlike the other techniques mentioned, it must be calibrated with monodisperse samples of known molecular weight. Still, because much calibration data are available in the literature (4), the necessary equipment is inexpensive, and the measurements are precise, straightforward, and rapid, it is used frequently.

In the 1990s, most molecular weight characterization is done by size-exclusion chromatography (sec) (5), also known as gel-permeation chromatography (gpc). Sec makes use of a column packed with particles of a porous substrate, most commonly a cross-linked polystyrene gel (hence gpc). Solvent is pumped through the column at a constant rate. A small amount of polymer solution is injected ahead of the column. The solvent flow carries the polymer through the column. The smaller molecules have easy access to the substrate pores and diffuse in and out, following a circuitous route as they progress through the column. Larger molecules cannot fit into the smaller pores and are swept more directly through the interstices between the substrate particles. Thus, a separation is obtained, the largest molecules leaving the column first, followed by successively smaller ones. A detector, for example a differential refractometer, records the concentration of the solution leaving the column. Until recently, calibration with monodisperse samples of known molecular weight was necessary. However, as of 1995, a laser light-scattering photometer may be added to the differential refractometer, giving an on-line $\overline{M}_{\mathrm{w}}$ determination and eliminating the need for calibration.

Size-exclusion chromatography (sec) easily and rapidly gives the complete molecular weight distribution and any desired average (6). Thus, it has become the technique of choice for determining molecular weights despite its relatively high initial cost.

2.2. Secondary Bonding

The atoms in a polymer molecule are held together by primary covalent bonds. Linear and branched chains are held together by secondary bonds: hydrogen bonds, dipole interactions, and dispersion or van der Waal's forces. By copolymerization with minor amounts of acrylic ($CH_2{=}CHCOOH$) or methacrylic acid followed by neutralization, ionic bonding can also be introduced between chains. Such polymers are known as ionomers (qv).

$$\sim\!\sim\mathrm{COOH} + \mathrm{M(OH)_2} + \mathrm{HOOC}\sim\!\sim\ \longrightarrow\ \sim\!\sim\ \mathrm{COO}]^{-+}[\mathrm{M}]^{+-}[\ \mathrm{OOC}\sim\!\sim + 2\mathrm{H_2\,O}$$

Secondary bonds are considerably weaker than the primary covalent bonds. When a linear or branched polymer is heated, the dissociation energies of the secondary bonds are exceeded long before the primary covalent bonds are broken, freeing up the individual chains to flow under stress. When the material is cooled, the secondary bonds reform. Thus, linear and branched polymers are generally thermoplastic. On the other hand, cross-links contain primary covalent bonds like those that bond the atoms in the main chains. When a cross-linked polymer is heated sufficiently, these primary covalent bonds fail randomly, and the material degrades. Therefore, cross-linked polymers are thermosets. There are a few exceptions such as cellulose and polyacrylonitrile. Though linear, these polymers are not thermoplastic because the extensive secondary bonds make up for in quantity what they lack in quality.

Similarly, polymers dissolve when a solvent penetrates the mass and replaces the interchain secondary bonds with chain-solvent secondary bonds, separating the individual chains. This cannot happen when the chains are held together by primary covalent cross-links. Thus, linear and branched polymers dissolve in appropriate solvents, whereas cross-linked polymers are insoluble, although they may be swelled considerably by absorbed solvent. The extent of swelling is inversely related to the degree of cross-linking.

2.3. Stereoisomerism

Vinyl monomers, $CH_2{=}CHR$, generally polymerize in a head-to-tail fashion, placing the R group on every other carbon atom in the chain backbone. If a chain is conceptually stretched out, the carbon atoms in the backbone will lie in a plane (Fig. 2). The arrangement in which the R groups are all on one side of that plane

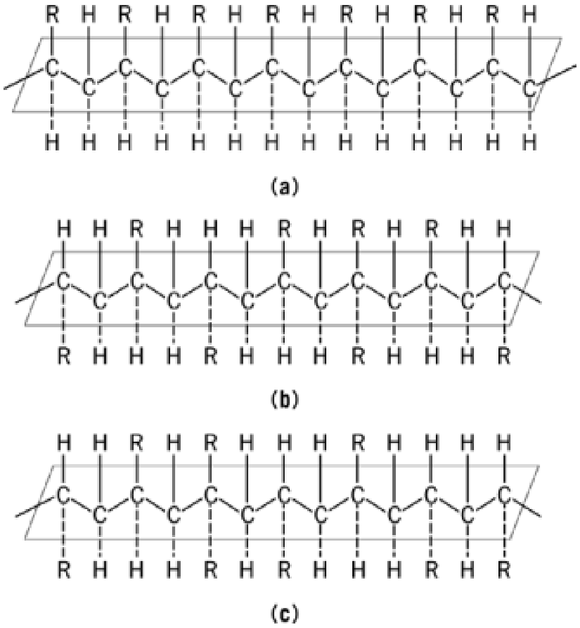


Fig. 2. Stereoisomerism in vinyl polymers: (**a**) isotactic; (**b**) syndiotactic; and (**c**) atactic.

is the isotactic stereoisomer. Regular alternation of the R groups from side to side is the syndiotactic form. Random placement of the R groups is the atactic (without order) polymer. Stereoisomers are formed during polymerization, and cannot be altered subsequently by rotation about the bonds. It is important to note that isotactic and syndiotactic chains are regular, whereas atactic chains are irregular (7).

2.4. Crystallinity

Crystals are an ordered, regular arrangement of units in a repeating, three-dimensional lattice structure. Small molecules, which in the liquid state have three-dimensional mobility, crystallize readily when cooled. It is not so easy for polymers, because a repeating unit cannot move independently of its neighbors in the chain. Nevertheless, some polymers can and do crystallize, though never completely. Not surprisingly, a regular chain structure is required if the chains are to fit into a regular crystal lattice. Thus, isotactic and syndiotactic polypropylenes crystallize, but atactic polypropylene does not. Similarly, branches protruding from a chain sterically inhibit crystallization in their vicinity.

Polymer crystals most commonly take the form of folded-chain lamellae. Figure 3 sketches single polymer crystals grown from dilute solution and illustrates two possible modes of chain re-entry. Similar structures exist in bulk-crystallized polymers, although the lamellae are usually thicker. Individual lamellae are held together by tie molecules that pass irregularly between lamellae. This explains why it is difficult to obtain a completely crystalline polymer. Tie molecules and material in the folds at the lamellae surfaces cannot readily fit into a lattice.

In bulk-crystallized polymers, lamellae are often organized into spherulites, spherical structures which grow outward from a point of nucleation, typically to about 0.01 mm in diameter. Spherulites are in some ways similar to the grain structure in metals. They can make a polymer brittle and also reduce transparency.

Linear polyethylene fibers containing extended-chain crystals, in which the chains are arranged parallel to one another over great distances with a minimum of folding, are produced by using a flow field to align the

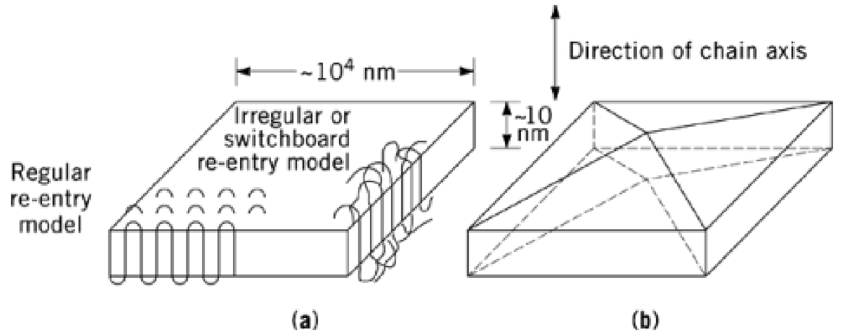


Fig. 3. Polymer single crystals: (**a**) flat lamellae; and (**b**) pyramidal lamellae. Two concepts of chain re-entry are illustrated (6).

Table 3. Comparison of Some Properties of PE[a] and Steel

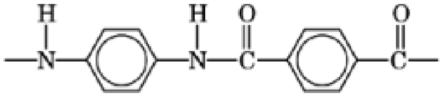
Property	Extended-chain PE	Ordinary PE	Steel
tensile modulus, GPa[b]	44	1.2	206
tensile strength, GPa[b]	1.8	0.04	0.8
density, g/cm^3	0.97	0.97	7.6

[a] Extended-chain linear PE and ordinary linear PE.

[b] To convert GPa to psi, multiply by 145,000.

molecules in solution just prior to crystallization. The resulting fibers are then drawn (stretched) to enhance orientation further. These fibers (Spectra, by AlliedSignal) are impressively strong, particularly on a strength-to-weight basis, because the chains are oriented most efficiently, in the fiber direction, to resist stress (see Fibers, olefin; olefin polymers). Table 3 compares some properties of extended-chain linear polyethylene (8) with quiescently crystallized linear polyethylene.

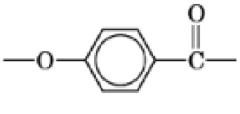
Similarly, liquid-crystal polymers exhibit considerable order in the liquid state, either in solution (lyotropic) or melt (thermotropic). When crystallized from solution or melt, they have a high degree of extended-chain crystallinity, and thus have superior mechanical properties. Kevlar (Du Pont) is an aromatic polyamide (aramid) with the repeating unit designated as (**2**). It is spun into



(**2**)

fibers from a lyotropic liquid-crystal solution in concentrated H_2SO_4. The solution is extruded through small holes into a bath which leaches out the acid, forming the fibers (wet spinning). Because the molecules are oriented prior to crystallization, the fibers maintain a high degree of extended-chain crystalline order in the fiber direction, imparting remarkable strength. The fibers are used in antiballistic armor, as a tire cord (qv), and as a reinforcement in high strength composites (see Polyamides, fibers).

The thermotropic liquid-crystal polyester Vectra A (Hoechst-Celanese) is reported to have the repeating units **3** and **4** and Xydar (Dartco) the repeating units **5** and (**3**).



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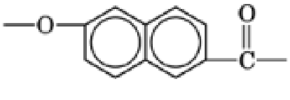

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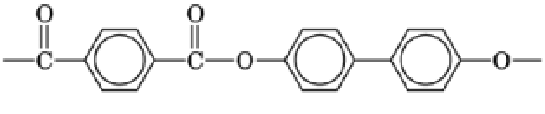


(5)

The macroscopic orientation of their extended-chain crystals depends on the orientation imparted by flow during molding. Because of the fibrous nature of the extended-chain crystals, these materials behave as self-reinforcing composites, with excellent mechanical properties.

The crystalline melting point is governed by $\Delta G = \Delta H - T\Delta S$. At the equilibrium crystalline melting point, T_m, $\Delta G = 0$, and $T_m = \Delta H_m/\Delta S_m$, where ΔH_m is the heat (enthalpy) of melting and ΔS_m is the entropy of melting. ΔH_m represents the secondary bond energy holding the chains in the crystal lattice. Thus, polymers which form strong and/or extensive secondary bonds, eg, hydrogen bonds, between chains have high crystalline melting points, other things being equal. ΔS_m characterizes the degree of randomness the chains gain upon melting. The highly aromatic liquid crystalline polymers shown above have stiff, rigid chains, and stackable, nearly planar aromatic rings, causing them to maintain a high degree of order in the liquid state. This results in a low ΔS_m and therefore a high T_m in addition to good mechanical strength.

Because shorter chains randomize more upon melting, they have a larger ΔS_m than longer chains. Therefore, T_m decreases as the molecular weight is reduced, though this effect becomes important only at relatively low molecular weights.

2.5. The Amorphous Phase and T_g

Not all polymers crystallize, and even those that do are not completely crystalline. Noncrystalline polymer is termed amorphous. Four types of molecular motion have been identified in amorphous polymers. Listed in order of decreasing activation energy, they are (*1*) translational motion of entire molecules, (*2*) coiling and uncoiling of 40–50 C-atom segments of chains, (*3*) motion of a few (five to six) atoms along the main chain or on side groups, and (*4*) vibrations of individual atoms. Type 1 motions are responsible for flow. Type 2 motions give rise to rubber elasticity. The temperature below which type 1 and 2 motions are frozen out is known as the glass-transition temperature, T_g. Below its T_g, an amorphous polymer is a glass; hard, rigid, and often brittle. Above T_g, it becomes rubbery, and at still higher temperatures, if it is not cross-linked, it flows easily. Consider the demonstration in which a rubber ($T_g = -70°C$) ball bounces at room temperature, but when cooled in liquid nitrogen ($-196°C$), shatters when dropped. Thus amorphous polymers intended for use as plastics, which require mechanical rigidity, must be below their T_g at use temperature. Rubber polymers must be amorphous, at least in their unstretched state, because crystallinity inhibits type 1 and 2 motions. They also must be above their T_g to permit type 2 motions, and are usually lightly cross-linked (vulcanized) to eliminate the type 1 motions which lead to irrecoverable deformation.

In general, things that impede type 1 and 2 motions raise T_g. These include strong secondary forces between chains and steric hindrance to rotation about main-chain bonds. Chemists take advantage of these to design plastics that maintain rigidity at higher temperatures. Too high a T_g may make a polymer difficult to process, however. A good way of viewing linear polymers that are not thermoplastic, eg, cellulose and polyacrylonitrile, is that their T_g and/or T_m exceeds their thermal decomposition temperature. Similarly, even light cross-linking eliminates type 1 motions. Increasing degrees of cross-linking begin to inhibit type 2 motions as well, raising T_g. Highly cross-linked polymers maintain their rigidity until they degrade, ie, their T_g is above their decomposition temperature.

The T_g of random copolymers varies with composition between the T_g of the corresponding homopolymers. Thus, random copolymerization with a monomer whose homopolymer has a low T_g provides internal plasticization. Addition of an external plasticizer, a liquid with a molecular weight on the order of several hundred, displaces the secondary bonds between polymer chains, reducing the T_g and softening the polymer mass. This is most often practiced with poly(vinyl chloride) (PVC) which has $T_g = 86°\text{C}$. At room temperature, nearly unplasticized PVC is a rigid material used for pipe, window frames, siding, etc. Addition of a plasticizer, commonly di-2-ethylhexyl phthalate (DEHP), also known as dioctyl phthalate (DOP), reduces its T_g and converts it into a material suitable for flexible tubing (Tygon, by Norton), wire insulation, refrigerator door gaskets, and a leather-like upholstery material (Naugahyde, by Uniroyal Engineered Products) (see Leather-like materials; Plasticizers).

2.6. Effects of Crystallinity on Properties

In polymers that can crystallize, the ratio of crystalline to amorphous material has a profound effect on properties. Because the chains are packed more tightly and efficiently in the crystalline areas than in the amorphous, the crystalline phase has a higher density and greater mechanical strength. In fact, density is a common measure of degree of crystallinity. The mechanical differences are greater if the amorphous phase is above its T_g, giving rigid crystallites in a rubbery matrix, as is the case for polyethylene ($T_m = 135°\text{C}$, $T_g = -120°\text{C}$) at room temperature. Table 4 illustrates how the strength and stiffness increase with the degree of crystallinity for several polyethylenes. In polyethylenes, crystallinity is sterically reduced by branching (see Fig. 1). High density PE (HDPE) (eg, milk jugs) has little branching. Side reactions during polymerization give rise to long, branched branches which lead successively to low density polyethylene (LDPE) (eg, squeeze bottles). In the newer linear, low density polyethylenes (LLDPE), short branches are introduced by random copolymerization with α-olefins, $\text{CH}_2{=}\text{CHC}_n\text{H}_m$, such as butene, hexene, or octene. Isotactic polypropylene ($T_m = 165°\text{C}$, $T_g = -30°\text{C}$) is highly crystalline and an important plastic. The atactic form does not crystallize, however, and is above T_g at room temperature. It is used as a caulking compound, pressure-sensitive adhesive, etc.

Similarly, the random introduction by copolymerization of sterically incompatible repeating unit B into chains of crystalline A reduces the crystalline melting point and degree of crystallinity. If T_m is reduced to T_g, crystals cannot form. Isotactic polypropylene and linear polyethylene homopolymers are each highly crystalline plastics. However, a random 65% ethylene–35% propylene copolymer of the two, poly(ethylene-*co*-propylene) is a completely amorphous ethylene–propylene rubber (EPR). On the other hand, block copolymers of the two, poly(ethylene-*b*-propylene) of the same overall composition, are highly crystalline. X-ray studies of these materials reveal both the polyethylene lattice and the isotactic polypropylene lattice, as the different blocks crystallize in their own lattices.

The stiffest polymers are both crystalline and have a glassy amorphous phase, ie, are below both T_m and T_g. They are often useful as engineering (structural) plastics. Nylon-6,6 and crystalline poly(ethylene terephthalate) are examples of this class of materials, as is the newly developed syndiotactic polystyrene. Traditional polystyrene is atactic, and therefore cannot crystallize. It has $T_g = 100°\text{C}$ and so is rigid at room

Table 4. Influence of Crystallinity on Properties of Polyethylene[a, b]

Commercial product	Low density	Medium density	High density
density range, g/cm^3	0.910–0.925	0.926–0.940	0.941–0.965
approximate crystallinity, %	42–53	54–63	64–80
branching, equivalent CH_3 groups/1000 carbon atoms	15–30	5–15	1–5
crystalline melting point, °C	110–120	120–130	130–136
hardness, Shore D	41–46	50–60	60–70
tensile modulus, MPa[c]	97–260	170–380	410–1240
tensile strength, MPa[c]	4.1–16	8.3–24	21–38
flexural modulus, MPa[c]	34–410	410–790	690–1800

[a] Ref. 6 (see Olefin polymers, polyethylene).

[b] It must be kept in mind that mechanical properties are influenced by factors other than the degree of crystallinity (molecular weight, in particular).

[c] To convert MPa (N/mm^2) to psi, multiply by 145.

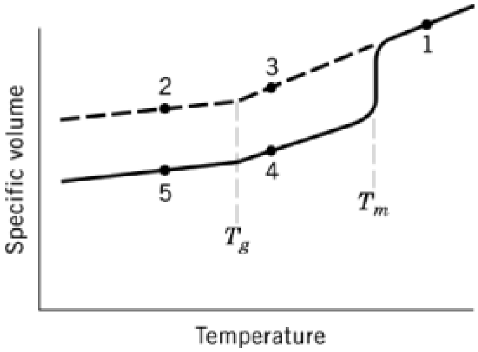


Fig. 4. Specific volume vs temperature for a crystallizable polymer. The dashed line represents amorphous material (6). Numbers refer to individual states. See text.

temperature, but is brittle and not particularly strong, limiting its structural applications (see Styrene plastics). The syndiotactic form does crystallize, providing greater strength and a higher heat-distortion temperature.

Crystalline polymers undergo a discontinuous decrease in volume when cooled through T_m (Fig. 4). This can lead to nonuniform shrinkage and warping in molded objects. On the other hand, it also causes the polymer to “lock on” to reinforcing fibers, eg, glass (qv), so that crystalline thermoplastics benefit much more than amorphous thermoplastics from fiber reinforcement.

Crystallinity also influences optical properties. In a crystalline polymer, the denser crystalline areas generally have a higher refractive index than the amorphous areas and have dimensions comparable to the wavelength of visible light (0.4–0.7 μm) or greater. Thus, light is scattered as it passes between phases, so crystalline polymers have a characteristic white, translucent-to-opaque appearance, depending on the thickness of the specimen, its degree of crystallinity, and the size of the crystallites. Large spherulites scatter considerable light, so nucleating agents are used to promote smaller spherulites and enhance clarity. Isotactic poly(4-methylpentene) is the only polymer known which is both transparent and highly crystalline, because the refractive indexes of the crystalline and amorphous phases are almost identical (see Olefin polymers, polymers of higher olefins).

Pure amorphous polymers, being homogeneous materials, are transparent. Atactic polystyrene is a good example. The crystalline syndiotactic form is not transparent. A lack of transparency does not necessarily indicate crystallinity, however. It can also be caused by inorganic fillers, pigments, gas bubbles (as in a foam), a second polymer phase, etc.

Even though a polymer is capable of crystallizing, it may not. Long, entangled polymer chains cannot rearrange instantaneously from the disordered amorphous state into a regular crystal lattice. Some polymers, if cooled rapidly enough from above T_m to below T_g, where the chains lose the mobility to rearrange (Fig. 4, state 2), persist indefinitely in a metastable amorphous state as long as they are maintained below T_g. If heated above T_g (state 3) for a while, such a material anneals to the crystalline form (state 4), and goes from transparent to opaque in the process. The metastable amorphous state (state 2) is easily obtained with poly(ethylene terephthalate) ($T_m = 267°C$, $T_g = 69°C$), with its bulky, aromatic repeating unit. It has important commercial applications (eg, soda bottles) in state 2 and also in crystalline state 5, eg, fibers, molded plastic (see Polyester, thermoplastic; Fibers, polyester).

Transitions such as T_g and T_m are rapidly and conveniently studied using differential scanning calorimetry (dsc). This technique monitors changes in enthalpy that accompany the transitions as a sample is heated at a constant rate.

2.7. Solubility

Cross-linking eliminates polymer solubility. Crystallinity sometimes acts like cross-linking because it ties individual chains together, at least well below T_m. Thus, there are no solvents for linear polyethylene at room temperature, but as it is heated toward its T_m (135°C), it dissolves in a variety of aliphatic, aromatic, and chlorinated hydrocarbons. A rough guide to solubility is that like dissolves like, ie, polar solvents tend to dissolve polar polymers and nonpolar solvent dissolve nonpolar polymers.

Solubility is thermodynamically feasible if the sign of the Gibbs free energy ($\Delta G = \Delta H - T\Delta S$) for the process is negative. Distributing the solute molecules throughout the solvent molecules represents a decrease in order (positive ΔS), so the entropy term favors solubility. The difference between polymeric and low molecular weight solutes lies in the magnitude of the entropy term. Because a repeating unit in a polymer chain is confined between its neighbors in the chain whereas low molecular weight solutes are free to move anywhere, the entropy of solution for high molecular weight polymers is much smaller than for equivalent masses or volumes of monomeric solutes. The higher the molecular weight, the lower the entropy of solution, which accounts for the observed decrease in solubility with molecular weight.

Because the magnitude of the entropy term is so small for high molecular weight polymers, one of the schemes for predicting polymer solubility concentrates only on the enthalpy term. If ΔH is negative, solubility is assured. Negative ΔH arises from strong polymer–solvent secondary bonds, eg, hydrogen bonds. In the more common situation, where ΔH is positive, it must be quite small, smaller than $-T\Delta S$ for solution to occur. Regular solution theory predicts equation 1 where the subscripts 1 and 2 refer to solvent and solute, respectively;

$$\Delta H \approx \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \qquad (1)$$

φ represents volume fractions; and δ represents solubility parameters as defined by equation 2, where ΔE_v is the energy of vaporization and v the molar volume.

$$\delta = (\Delta E_v / v)^{1/2} \qquad (2)$$

The solubility parameter is therefore a measure of the energy density holding the molecules in the liquid state. Note that regular solution theory can only predict positive ΔH. Thus, with this approach, prediction of solubility involves matching the solute and solvent solubility parameters as closely as possible to minimize ΔH. As a very rough rule of thumb $|\delta_1 - \delta_2|$ must be less than 2 $(J/cm^3)^{1/2}$ for solubility.

The practical utility of the solubility parameter approach was enhanced considerably by Hansen (9–11), who reasoned that ΔE_v was made up of hydrogen bonding, h; permanent dipole interaction, p; and dispersion, d, contributions, so that equation 3 holds where $\delta_j = (\Delta E_j/v)^{1/2};\ j = d, p, h$. This equation is

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (3)$$

reminiscent of the relation between the magnitude of a vector and its components. Hansen observed empirically that if the solvent components δ_{j1} and the solute components δ_{j2} are plotted in three dimensions, using a δ_d scale twice the size of the others, solvents that fall within a sphere of radius R from the polymer point dissolve the polymer. Thus, equation 4 states the solubility condition:

$$\left[\left(\delta_{p1} - \delta_{p2}\right)^2 + \left(\delta_{h1} - \delta_{h2}\right)^2 + 4\left(\delta_{d1} - \delta_{d2}\right)^2\right]^{1/2} < R \quad \text{for solubility} \qquad (4)$$

Because values of δ_d cover a rather small range, the three-dimensional scheme is often reduced to two dimensions, with polymers and solvents represented on $\delta_h - \delta_p$ coordinates with a solubility circle of radius R.

Values of solubility parameters, their three-dimensional components, and R are available (9, 10, 12). Not surprisingly, the three-dimensional scheme, with more constants to adjust, does a better job of predicting solubility.

More fundamental treatments of polymer solubility go back to the lattice theory developed independently and almost simultaneously by Flory (13) and Huggins (14) in 1942. By imagining the solvent molecules and polymer chain segments to be distributed on a lattice, they statistically evaluated the entropy of solution. The enthalpy of solution was characterized by χ, the Flory-Huggins interaction parameter, which is related to solubility parameters by equation 5. For high molecular weight polymers in monomeric solvents, the Flory-Huggins solubility criterion is $\chi \leq 0.5$.

$$\chi = \frac{v\left(\delta_1 - \delta_2\right)^2}{RT} \qquad (5)$$

Experimental values of χ have been tabulated for a number of polymer-solvent systems (4, 12). Unfortunately, they often turn out to be concentration and molecular weight dependent, reducing their practical utility. The Flory-Huggins theory qualitatively predicts several phenomena observed in solutions of polymers, including molecular weight effects, but it rarely provides a good quantitative fit of data. Considerable work has been done subsequently to modify and improve the theory (15, 16).

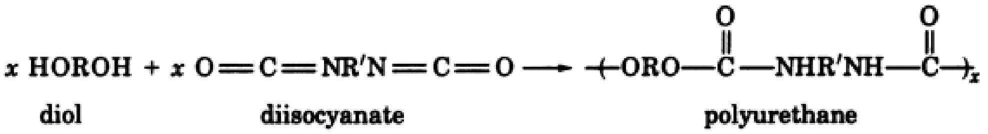
A newer approach uses group-contribution methods to predict solubility. It has been remarkably successful when applied to nonpolymer solutions and there are indications that it will be equally successful for treating polymer solutions (17).

Polymer solutions are often characterized by their high viscosities compared to solutions of nonpolymeric solutes at similar mass concentrations. This is due to the mechanical entanglements formed between polymer chains. In fact, where entanglements dominate flow, the (zero-shear) viscosity of polymer melts and solutions varies with the 3.4 power of weight-average molecular weight.

3. Polymer Synthesis

3.1. Step-Growth Polymerization

Step-growth polymerization is characterized by the fact that chains always maintain their terminal reactivity and continue to react together to form longer chains as the reaction proceeds, ie, $x\text{–mer} + y\text{–mer} \longrightarrow (x + y)\text{–mer}$. Because there are reactions that follow this mechanism but do not produce a molecule of condensation, eg, the formation of polyurethanes from diols and diisocyanates (eq. **6**), the terms step-growth and polycondensation are not exactly synonymous (6, 18, 19).



$$x\,\mathrm{HOROH} + x\,\mathrm{O{=}C{=}NR'N{=}C{=}O} \longrightarrow \left(\mathrm{ORO}-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{NHR'NH}-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\right)_x \qquad (6)$$

For linear step-growth, the number-average degree of polymerization, $\bar{x}_n$, is given by equation 7, where $r = N_A/N_B$, the stoichiometric ratio of the

$$\bar{x}_n = \frac{\overline{M}_n}{m} = \frac{1+r}{1+r-2rp} \qquad (7)$$

complementary functional groups A and B, and p is the fractional conversion of the limiting functional group, A. Here, $\bar{x}_n$ refers to the number of monomer residues rather than repeating units in the chain. This equation reveals that even with perfect stoichiometry ($r = 1$), a conversion $p = 0.99$ is required to achieve an $\bar{x}_n = 100$ (a modest value). A stoichiometric imbalance further lowers $\bar{x}_n$ at any value of p. Thus, producing high molecular weight, linear condensation polymers requires both high conversions and a close approach to stoichiometric equivalence. On the other hand, molecular weights can be limited when desired by a deliberate stoichiometric imbalance.

High conversions are promoted by efficient removal of a molecule of condensation. This may be done with a vacuum if the molecule of condensation is sufficiently volatile, by carrying out the reaction in a refluxing organic solvent, condensing the vapors and decanting the water of condensation before returning the solvent to the reactor, by having a molecule of condensation that is insoluble in the reaction medium, or by a secondary reaction that consumes the molecule of condensation as it is formed. An example of the last is the production of a polycarbonate from bisphenol A and phosgene (see Table 1). By carrying out this reaction in a basic medium, the HCl is consumed as it is formed (see Polycarbonates).

If a step-growth polymerization batch includes some monomer with a functionality greater than two, and if the reaction is carried to a high enough conversion, a cross-linked network or gel may be formed. In the production of thermosetting molding compounds, the reaction must be terminated short of the conversion at which a gel is formed, or the material could not be molded (cross-linking is later completed in the mold). Flory worked out the statistics of gelation, relating the gel-point conversion to the stoichiometry of the reactor charge (6, 20).

3.2. Chain-Growth Polymerization

Chain-growth polymerizations are characterized by chains that propagate by adding one monomer molecule at a time, ie, $x-\mathrm{mer} + \mathrm{monomer} \longrightarrow (x+1)-\mathrm{mer}$. There are, however, several mechanisms by which this occurs.

3.2.1. Free-Radical Addition

In free-radical addition polymerization, the propagating species is a free radical. The free radicals, $\mathrm{R}\cdot$, are most commonly generated by the thermal decomposition of a peroxide or azo initiator, I (see Initiators, free-radical):

$$\textit{Decomposition} \qquad \mathrm{I} \xrightarrow{k_d} 2\,\mathrm{R}\cdot$$

The radicals then initiate chain growth by adding an unsaturated monomer molecule, M, to form growing chain $P_1^{\cdot}$.

Addition $\quad R\cdot + M \xrightarrow{k_a} P_1$

$P_1^{\cdot}$ is a growing polymer chain with one monomer unit. The chain end remains an active radical and propagates by the sequential addition of monomer.

Propagation $\quad P_x^{\cdot} + M \xrightarrow{k_p} P_{(x+1)}^{\cdot}$

Chains terminate by either of two mechanisms: combination or disproportionation. Two chain radicals may combine to form a single bond between them:

Combination $\quad P_x^{\cdot} + P_y^{\cdot} \xrightarrow{k_{tc}} P_{(x+y)}$

Alternatively one chain radical may abstract a proton from the penultimate carbon atom of the other, giving one saturated and one unsaturated dead chain:

Disproportionation $\quad P_x^{\cdot} + P_y^{\cdot} \xrightarrow{k_{td}} P_x + P_y$

Chain transfer may also occur:

Transfer $\quad P_x^{\cdot} + R'X \xrightarrow{k_{tr}} P_x + R'\cdot$

Addition $\quad R'\cdot + M \xrightarrow{k_{a'}} P_1^{\cdot}$

The compound R′X is a chain-transfer agent, with X usually H or Cl. The net effect of chain transfer is to kill a growing chain and start a new one in its place, thus shortening the chains. Mercaptan chain-transfer agents are often used to limit molecular weight, but under appropriate conditions, almost anything in the reaction mass (solvent, dead polymer, initiator) can act as a chain-transfer agent to a certain extent.

The above mechanism, together with the assumptions that initiator decomposition is rate controlling and that a steady state in chain radicals exists, results in the classical expressions (eqs. 8 and 9) for polymerization rate, r_{p}, and number-average degree of polymerization, $\overline{x}_{\mathrm{n}}$, in a homogeneous, free-radical polymerization (6).

$$r_p = k_p \left(\frac{f k_d}{k_t} \right)^{1/2} [I]^{1/2} [M] \tag{8}$$

$$\overline{x}_n = \frac{k_p [M]}{\zeta \left(f k_d k_t [I] \right)^{1/2} + k_{tr} \left[R'X \right]} \tag{9}$$

In equations 8 and 9, f is the initiator efficiency, the fraction of initiator radicals that actually initiates chain growth, $k_t = k_{tc} + k_{td}$, and ζ is the number of dead chains formed per termination reaction; $\zeta = 2$ for disproportionation, $\zeta = 1$ for combination.

Unlike step-growth polymerization, free-radical chains do not continue to grow as the reaction proceeds. Typically, the monomer half-life is many hours, but the average lifetime of a growing chain, from initiation to termination, is less than a second. Thus, high molecular weight polymer is produced right from the beginning; high conversions are not required.

The minimum polydispersity index from a free-radical polymerization is 1.5 if termination is by combination, or 2.0 if chains are terminated by disproportionation and/or transfer. Changes in concentrations and temperature during the reaction can lead to much greater polydispersities, however. These concepts of polymerization reaction engineering have been introduced in more detail elsewhere (6).

3.2.2. Polymerization Processes

Free-radical polymerization is carried out in a variety of ways. One of the practical problems that must be dealt with is runaway reactions which can result from autoacceleration, an increase in rate of polymerization caused by diffusion-limited termination (reduced k_t) at high conversions. The effects of autoacceleration are compounded by large, exothermic heats of polymerization, typically 42–84 kJ/mol (-10 to -20 kcal/mol), and the great increase in polymerization rate with temperature. Also, the low heat capacities and thermal conductivities of organic reaction masses and the very high viscosities of the reaction mass at high conversions limit heat removal and make temperature control difficult.

3.2.2.1. Bulk Polymerization. This involves only monomer, initiator, and perhaps chain-transfer agent. It gives the greatest polymer yield per unit of reactor volume and a very pure polymer. However, in large-scale batch form, it must be run slowly or in continuous form with a lot of heat-transfer area per unit of conversion to avoid runaway. Objects are conveniently cast to shape using batch bulk polymerization. Poly(methyl methacrylate) glazing sheets are produced by batch bulk polymerization between glass plates. They are also made by continuous bulk polymerization between polished stainless steel belts. Polystyrene and other thermoplastic molding compounds are produced by continuous bulk polymerization processes (6).

3.2.2.2. Solution Polymerization. In this process an inert solvent is added to the reaction mass. The solvent adds its heat capacity and reduces the viscosity, facilitating convective heat transfer. The solvent can also be refluxed to remove heat. On the other hand, the solvent wastes reactor space and reduces both rate and molecular weight as compared to bulk polymerization. Additional technology is needed to separate the polymer product and to recover and store the solvent. Both batch and continuous processes are used.

3.2.2.3. Suspension Polymerization. In this process the organic reaction mass is dispersed in the form of droplets 0.01–1 mm in diameter in a continuous aqueous phase. Each droplet is a tiny bulk reactor. Heat is readily transferred from the droplets to the water, which has a large heat capacity and a low viscosity, facilitating heat removal through a cooling jacket.

Agitation is critical to carrying these reactions out successfully. It is used, along with suspending agents in the aqueous phase, to control droplet size and maintain dispersion. If it fails or weakens before the particles become sufficiently rigid (the polymer must be below its T_g), the particles coalesce, leading to a runaway bulk reaction, which not only can be dangerous, but may require the use of mining tools to clear a commercial reactor. For this reason also, it has not been possible to run suspension polymerization continuously, since any flow system has some stagnant corners where polymer would accumulate, nor can it be used to produce rubbers. Commercially, the reactions are carried out in jacketed, stainless steel or glass-lined stirred tanks of up to 75.5 m^3 (20,000 gal) capacity.

The product of a successful suspension polymerization is small, uniform polymer spheres. For certain applications, they are used directly, eg, as the precursors for ion-exchange resins or bead foams. For others, they may be extruded and chopped to form larger, more easily handled molding pellets.

3.2.2.4. Emulsion Polymerization. When the U.S. supply of natural rubber from the Far East was cut off in World War II, the emulsion polymerization process was developed to produce synthetic rubber. In this complex process, the organic monomer is emulsified with soap in an aqueous continuous phase. Because of the much smaller ($\leq 0.1\ \mu m$) dispersed particles than in suspension polymerization and the stabilizing action of the soap, a proper emulsion is stable, so agitation is not as critical. In classical emulsion polymerization, a water-soluble initiator is used. This, together with the small particle size, gives rise to very different kinetics (6, 21–23).

The product of an emulsion polymerization is a latex; ie, polymer particles on the order of 0.5–0.15 μm stabilized by the soap. These form the basis for the popular latex paints. Solid rubber is recovered by coagulating the latex with ionic salts and acids (see Latex technology).

The original wartime process was run batchwise in reactors similar to those used for suspension polymerization. Since then, in many plants, the reactors have been hooked together as a series of continuous stirred tanks.

3.2.3. Ionic Polymerization

3.2.3.1. Anionic Polymerization. Addition polymerization may also be initiated and propagated by anions (23–26), eg, in the polymerization of styrene with n-butyllithium. The Li^+ gegen ion, held electrostatically in

$$[n\text{–}C_4H_9{:}]^-\,Li^+ + CH_2{=}CHC_6H_5 \longrightarrow [n\text{–}C_4H_9\text{—}CH_2\text{—}CHC_6H_5{:}]^-\,Li^+$$

$$[n\text{–}C_4H_9\text{—}\!\left(CH_2CHC_6H_5\text{—}\right)_x CH_2CHC_6H_5{:}]^-Li^+ + CH_2{=}CHC_6H_5 \longrightarrow$$

$$[n\text{–}C_4H_9\text{—}\!\left(CH_2CHC_6H_5\text{—}\right)_{x+1} CH_2CHC_6H_5$$

the vicinity of the propagating chain end, can exert a steric influence on the addition of monomer molecules to the chain. Growing chains are terminated immediately by proton-donating impurities, eg, water:

$$[n\text{–}C_4H_9\text{—}\!\left(CH_2CHC_6H_5\text{—}\right)_x CH_2CHC_6H_5{:}]^-Li^+ + H_2O \longrightarrow$$

$$n\text{–}C_4H_9\text{—}\!\left(CH_2CHC_6H_5\text{—}\right)_x CH_2CH_2C_6H_5 + LiOH$$

There are some important differences between anionic and free-radical addition. First, unlike free-radical initiators, which decompose and start chains randomly throughout the course of the reaction, anionic initiators ionize readily in fairly polar organic solvents (eg, tetrahydrofuran) or at low concentrations ($<10^{-4}$ molar) in hydrocarbons, and chains are started immediately, one for each molecule of initiator. Second, in the absence of impurities, there is no termination. Thus, in a batch reactor, all chains are initiated at the same time, the number of propagating chains remains constant, and the propagating chains continue to grow, competing for monomer on an even basis. This gives rise to an essentially monodisperse polymer, with $x = M_oX/I_o$, where M_o is the moles monomer charged, I_o the moles initiator charged, and X the fractional conversion of monomer to polymer. In practice, polydispersity indexes of less than 1.1 can be achieved with reasonable care.

When the initial monomer supply is exhausted, the anionic chain ends retain their activity. Thus, these anionic chains have been termed living polymers. If more monomer is added, they resume propagation. If it is a second monomer, the result is a block copolymer.

Anionic polymerization provided, for the first time, a convenient means of synthesizing nearly monodisperse polymers and block copolymers. It also can provide chains with useful terminal functionality. For example, bubbling CO_2 through a batch of living chains, followed by exposure to water, gives carboxyl-terminated chains. Substituting ethylene oxide for the CO_2 gives hydroxyl-terminated chains. By using multifunctional initiators or reagents which couple the living chains, star polymers can be produced.

3.2.3.2. Cationic Polymerization. For decades cationic polymerization has been used commercially to polymerize isobutylene and alkyl vinyl ethers, which do not respond to free-radical or anionic addition (see Elastomers, synthetic-butyl rubber). More recently, development has led to the point where living cationic chains can be made, with many of the advantages described above for anionic polymerization (27, 28).

3.2.3.3. Group-Transfer Polymerization. Du Pont has patented (29) a technique known as group-transfer polymerization and applied it primarily to the polymerization of acrylates and methacrylates. It is mechanistically similar to anionic polymerization, giving living chains, except that chain transfer can occur (30).

Ionic polymerizations are almost exclusively solution processes. To produce monodisperse polymers or block copolymers, they must be run batchwise, so that all chains grow for the same length of time under identical conditions.

3.3. Heterogeneous Stereospecific Polymerization

In the early 1950s, Ziegler observed that certain heterogeneous catalysts based on transition metals polymerized ethylene to a linear, high density material at modest pressures and temperatures. Natta showed that these catalysts also could produce highly stereospecific poly-α-olefins, notably isotactic polypropylene, and polydienes. They shared the 1963 Nobel Prize in chemistry for their work.

A typical Ziegler-Natta catalyst might be made from $TiCl_4$ or $TiCl_3$ and $Al(C_2H_5)_3$. Vanadium and cobalt chlorides are also used, as is $Al(C_2H_5)_2Cl$. When these substances are mixed in an inert solvent, a crystalline solid is obtained. Early catalysts consisted of the finely divided solid alone, but in modern catalysts, it is often supported on SiO_2 or $MgCl_2$.

Polymerization occurs at active sites formed by interaction of the metal alkyl with metal chloride on the surface of the metal chloride crystals. Monomer is chemisorbed at the site, thus accounting for its orientation when added to the chain, and propagation occurs by insertion of the chemisorbed monomer into the metal–chain bond at the active site. The chain thus grows out from the surface (31). Hydrogen is used as a chain-transfer agent. Chain transfer with the metal alkyl also occurs.

$$\text{site}—P_x + M \longrightarrow \text{site}—P_{x+1}$$

$$\text{site}—P_x + H_2 \longrightarrow H + H—P_x$$

$$\text{site}—P_x + Al\,(R)_3 \longrightarrow \text{siteR} + Al\,(R)_2 —P_x$$

Because initiation and transfer occur randomly in these systems, they have much more in common with free-radical addition than they have with anionic addition. Based on this randomness, a polydispersity index of two would be expected. Much greater values, up to 20 or more, are observed in practice. This results mainly from sites of widely differing activity on the catalyst surface (32). More recently, single-site metallocene catalysts have been introduced which can give polydispersity indexes approaching the theoretical minimum of two, allowing closer control over polymer properties (33). They also have been used to produce two promising new polymers, syndiotactic (crystalline) polystyrene and syndiotactic polypropylene, and they are reported to give a more uniform distribution of comonomer in the production of linear low density polyethylenes (LLDPE) (34–36).

Modern catalysts produce a much higher percentage of isotactic polypropylene than in the past, eliminating the need for a costly extraction step to remove an atactic fraction. Yields are high enough ($>10,000$ g polymer/g catalyst) so that a catalyst removal (de-ashing) step is no longer required.

These heterogeneous catalysts are used either in solution or gas-phase bulk processes. When a rubber is produced in a solution process, it remains in solution. Crystalline polymers such as polyethylene and isotactic polypropylene may be made at temperatures high enough so that they remain in solution. More commonly, the temperatures are low enough so that solid polymer coats the catalyst particle as it forms. These are known as slurry processes. In the popular Unipol gas-phase process (37), polymer grows on the catalyst particles which are suspended in a fluidized bed by circulating monomer. The heat of polymerization is removed from the monomer in external heat exhangers, and polymer particles are discharged from the reactor looking like laundry detergent powder.

Great care must be exercised in the preparation and use of Ziegler-Natta catalysts. They are easily poisoned by moisture, among other things. They are pyrophoric and are used in conjunction with large amounts of flammable monomer and solvent, and so can present a significant safety hazard.

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