

Introduction to Polymer Chemistry

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Polymers are extremely large molecules that are essential to our very existence. They are a main constituent of our food (starch, protein, etc.), our clothes (polyester, nylons, etc.), our houses (wood cellulose, alkyd paints, etc.), and our bodies (poly(nucleic acids), proteins, etc.). Hence, it is reasonable to assume the education of every chemist should, at least, include an introduction to their chemistry and properties. The objectives of this paper are (1) to introduce the reader to the types of chemical reactions that are used to prepare polymers and (2) to acquaint him or her with the structural parameters that result in the unusual physical properties displayed by these molecules.

Polymer Synthesis

There are two major types of polymerization methods used to convert small molecules (monomers) into polymers. These methods were originally referred to as addition and condensation polymerization. Depending on the author, addition polymerization is now called chain, chain-growth, or chain-reaction polymerization. Condensation polymerization is now referred to as step-growth or step-reaction polymerization. The major distinctions between these two methods, which, hopefully, will become apparent from the following discussion, result from the differences in the kinetics of the polymerization reactions.

Chain-Reaction A Polymerization (Addition)

The monomers normally employed in this type of polymerization contain a carbon-carbon double bond that can participate in a chain reaction. As in the chain reactions studied in organic chemistry, e.g., the free-radical halogenation of alkanes, the mechanism of the polymerization consists of three distinct steps. In the Initiation Step an initiator molecule(s) is thermally decomposed or allowed to undergo a chemical reaction to generate an "active species." This "active species," which can be a free radical, a cation, an anion, or a coordination complex, then initiates the polymerization by adding to the monomer's carbon-carbon double bond. The reaction occurs in such a manner that a new free radical, cation, anion, or complex is generated. The initial monomer becomes the first repeat unit in the incipient polymer chain. In the Propagation Step, the newly generated "active species" adds to another monomer in the same manner as in the Initiation Step. This procedure is repeated over and over again until the final step of the process, Termination, occurs. In this step, the growing chain terminates through reaction with another growing chain, by reaction with another species in the polymerization mixture, or by the spontaneous decomposition of the active site. Under certain conditions, anionic and coordination polymerizations can be carried out without the Termination Step to generate so-called "living" polymers.

The following are several general characteristics of this type of polymerization:

- 1) Once initiation occurs, the polymer chain forms very quickly, i.e., 10^{-1} to 10^{-6} sec.
- 2) The concentration of "active species" is very low. For example, in free radical polymerizations the concentration of free radicals is approximately 10^{-8} M. Hence, the polymerization mixture consists primarily of newly-formed polymer and unreacted monomer.
- 3) Since the carbon-carbon double bonds in the monomers are, in effect, converted to two single carbon-carbon bonds in the polymer,

Table 1. Typical Polymers Produced by Chain-Reaction Polymerizations

Chemical Name	Repeat Unit	Applications
Polyethylene	$\text{-(CH}_2\text{)-CH}_2\text{-}$	film, housewares
Polypropylene	$\text{-(CH}_2\text{)-CH(CH}_3\text{)-}$	rope, automotive and appliance parts
Polystyrene	$\text{-(CH}_2\text{)-CH(C}_6\text{H}_5\text{)-}$	packaging, insulation
Poly(vinyl chloride)	$\text{-(CH}_2\text{)-CH(Cl)-}$	floor covering, wire and cable insulation
Poly(methyl methacrylate)	$\text{-(CH}_2\text{)-CH(CO}_2\text{CH}_3\text{)-}$	automotive parts (tail and signal-light lenses, etc.), display signs
Poly(vinyl alcohol)	$\text{-(CH}_2\text{)-CH(OH)-}$	water-soluble thickening agent

Table 2. Typical Copolymers Produced by Chain Reaction Copolymerizations

Common Name	Comonomers	Applications
SBR rubber	$\text{CH}_2=\text{CH-CH=CH}_2$, $\text{C}_6\text{H}_5\text{CH=CH}_2$	tires, shoe soles
ABS resins	$\text{CH}_2=\text{CH-CN}$, $\text{CH}_2=\text{CH-CH=CH}_2$, $\text{C}_6\text{H}_5\text{CH=CH}_2$	appliance housings
Modacrylics	$\text{CH}_2=\text{CH-CN}$, $\text{CH}_2=\text{CH-Cl}$	clothing
Ionomers	$\text{CH}_2=\text{CH}_2$, $\text{CH}_2=\text{C(CO}_2\text{H)-}$ (acid group converted to metal salt in polymer)	packaging

energy is released making the polymerization exothermic with cooling often required.

- 4) Chain-reactions normally afford polymers with high molecular weights, i.e., 10^4 – 10^7 .
- 5) Polymers can be obtained that contain secondary chains (branches) attached to the main chain (backbone). For example, free radicals sometimes abstract hydrogens from a formed polymer chain, thereby generating new free radicals along the backbone which initiate secondary polymerizations.
- 6) Crosslinked systems can form where all the primary chains are interconnected with secondary chains. For example, growing free-radical branches sometimes terminate by coupling reactions with other growing branches to form a continuous network.

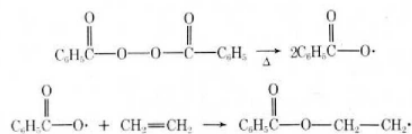
Two or more different monomers are often employed in a chain-reaction polymerization to yield a polymer containing the corresponding repeat units. Such a process is referred to as copolymerization, and the resulting product is called a copolymer. By varying the copolymerization technique and the amounts of each monomer, one can use as few as two monomers to prepare a series of copolymers with considerably different properties. The amount of different materials that can be prepared increases dramatically as the number of monomers employed increases. Thus, it is not too surprising that the majority of synthetic polymers used today are copolymers.

The following are four different types of copolymer structures that have been prepared:

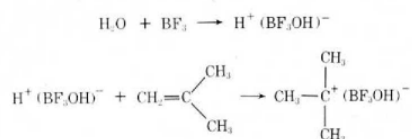
CHAIN REACTION A POLYMERIZATION

Initiation

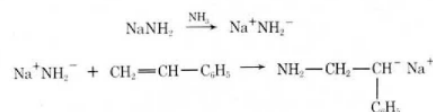
Free radical



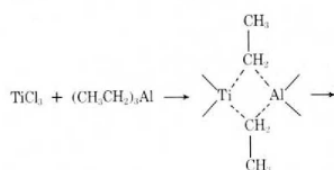
Cationic



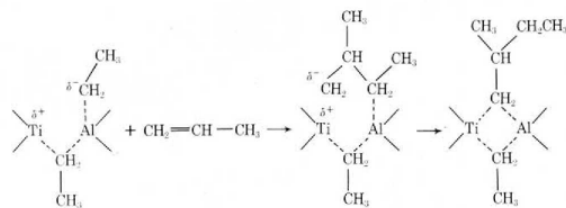
Anionic



Coordination Complex

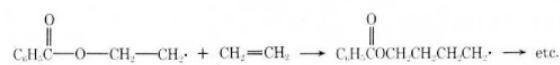


Complex Precipitate

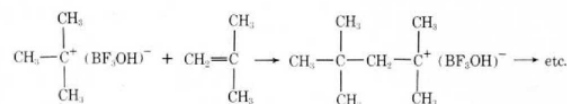


Propagation

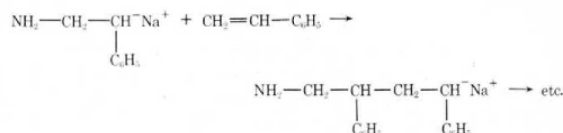
Free Radical



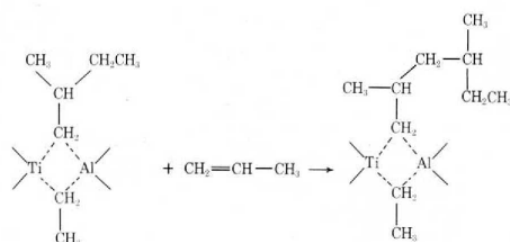
Cationic



Anionic

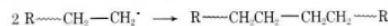


Coordination Complex

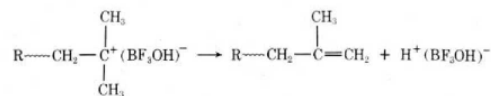


Termination

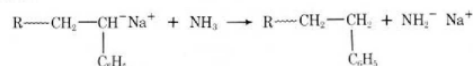
Free Radical



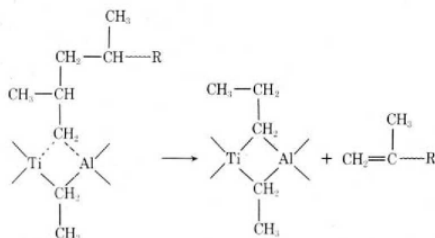
Cationic



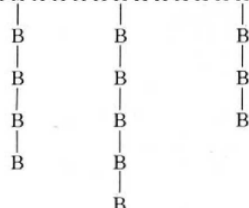
Anionic



Coordination Complex



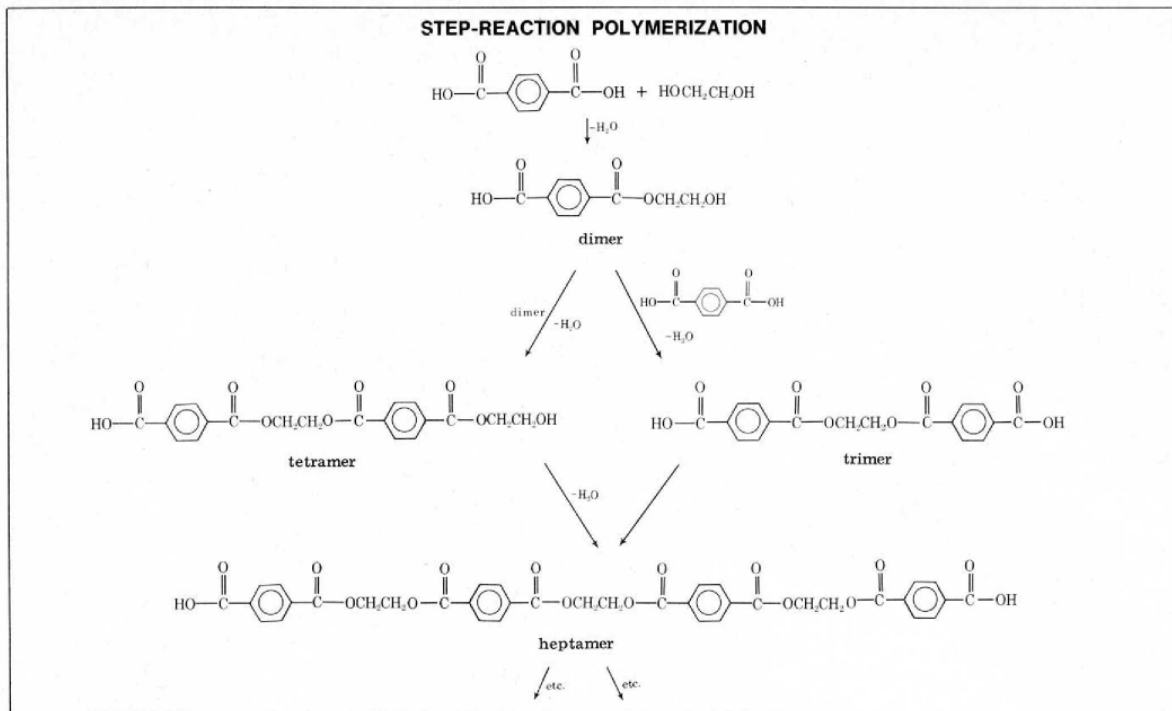
- 1) Random copolymer. The repeat units are randomly distributed along the polymer backbone.
-A-A-B-B-B-A-A-B-B-B-B-A-A-B-A-A-A-B-A-
- 2) Alternating copolymer. The repeat units are located in alternating positions along the backbone.
-A-B-A-B-A-B-A-B-A-B-A-B-
- 3) Block copolymer. The repeat units are located in long alternating segments.
-A-A-A-A-A-A-B-B-B-B-B-B-B-B-B-B-A-A-A-A-A-A-
- 4) Graft copolymer. Branches containing one repeat unit are attached to the main chain, which contains the other unit.
-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-



Step-Reaction Polymerization (Condensation)

This type of polymerization normally employs two difunctional monomers that are capable of undergoing typical organic reactions. For example, a diacid can be allowed to react with a diol in the presence of an acid catalyst to afford a polyester. In this case, chain growth is initiated by the reaction of one of the diacid's carboxyl groups with one of the diol's hydroxyl groups. The free carboxyl or hydroxyl group of the

STEP-REACTION POLYMERIZATION



resulting dimer can then react with an appropriate functional group in another monomer or dimer. This process is repeated throughout the polymerization mixture until all of the monomers are converted to low molecular weight species, such as dimers, trimers, tetramers, etc. These molecules, which are called oligomers, can then further react with each other through their free functional groups. Polymer chains that have moderate molecular weights can be built in this manner. The high molecular weights common to chain-reaction polymerizations are usually not reached. This is due to the fact that as the molecular weight increases the concentration of the free functional groups decreases dramatically. In addition, the groups are attached to the ends of chains and, hence, are no longer capable of moving freely through the viscous reaction medium.

The following are several general characteristics of this type of polymerization.

- 1) The polymer chain forms slowly, sometimes requiring several hours to several days.
- 2) All of the monomers are quickly converted to oligomers, thus, the concentration of growing chains is high.
- 3) Since most of the chemical reactions employed have relatively high energies of activation, the polymerization mixture is usually heated to high temperatures.
- 4) Step-reaction polymerizations normally afford polymers with moderate molecular weights, i.e., <100,000.
- 5) Branching or crosslinking does not occur unless a monomer with three or more functional groups is used.

Chemical Properties of Polymers

The chemical properties of polymers are very similar to those of analogous small molecules. A functional group attached to a polymer chain generally reacts the same way it would if present in a monomer. For example, an acid group can be esterified, an aromatic ring can be sulfonated, and an allylic hydrogen can be abstracted by free radicals. The rates at which these pendant groups undergo reactions, however, can be quite different. For example, due to steric effects and the hydrophobicity of its surroundings, the ester group in poly(methyl methacrylate) (Table 1) is considerably more resistant to hydrolysis than the ester group in methyl propionates.

Conversely, the reactivity of pendant functional groups can be substantially increased by the presence of suitable neighboring groups. For example, the rate of transesterification of pendant phenyl-ester groups surrounded by pendant carboxyl groups is many orders of magnitude faster than that of analogous phenyl acetates (7).

Physical Properties of Polymers

All of us are well aware that polymers display unique physical properties for non-metals. Some are tough undergoing large permanent deformations without breaking, some are stiff and strong, some are soft and flexible, and others can withstand considerable impact without breaking. All of these "mechanical properties" are peculiar to the polymer and are not characteristic of the monomer from which it was prepared. Ethylene gas, for example, does not form very good films! Why? What makes polymers so "different"? A polymer's unusual physical behavior is due to the tremendous amount of interactions between its chains. These interactions consist of various types of intermolecular bonds and physical entanglements. The magnitude of these interactions is dependent upon the nature of the intermolecular bonding forces, the molecular weight, the manner in which the chains are packed together, and the flexibility of the polymer chain. Thus, the amount of interaction is different in different polymers and quite often different in different samples of the same polymer (1).

Nature of Intermolecular Bonding Forces

The secondary bonding forces present in polymers, e.g., van der Waals and dipole-dipole, are identical to those present in small molecules. In polymers, however, all the types of electrostatic forces can be present and acting between different parts of the same molecule. The strength of these bonds increases with increasing polarity and decreases sharply with increasing distance. Although the individual energies are low, ranging between 0.5 and 10 kcal/mole, the cumulative effect of thousands of these bonds along the polymer chain results in large electrostatic fields of attraction.

Van der Waals forces are the weakest type of intermolecular

bonds found in polymers. These bonds arise from extremely short-lived dipoles, which result from the motion of electrons in the molecules. Linear, nonpolar polymers, such as polyethylene, that have only van der Waals attractions between the chains, must have relatively high molecular weights and be packed very close together to have useful mechanical properties.

It should not be too surprising that many commercial polymers contain polar functional groups that provide stronger dipole-dipole interactions between the chains (Fig. 1). Ester groups, nitro groups, cyano groups and halogens are common pendant substituents. Polar ether and ester linkages are also incorporated in many polymer chains. Since dipole-dipole interactions are dependent on the alignment of the dipoles, the interactions between polar polymer molecules can be enhanced considerably by properly orienting the chains.

The strongest type of dipole-dipole interaction, i.e., hydrogen bonding, is also present in many important polymer systems (Fig. 1). In fact, polymers that contain functionality that results in hydrogen bonding between the chains have mechanical properties superior to those of analogous polar systems. For example, aliphatic polyamides (nylons) have properties that permit them to be used in many applications. Whereas, the properties of aliphatic polyesters do not warrant their commercial production. Other polymers that display hydrogen bonding include poly(vinyl alcohol) and cellulose, with their pendant hydroxyl groups, and polyurethanes, with their carbamate linkages.

A relatively new class of polymers called ionomers actually have ionic interactions between the chains (Fig. 1) (8). These polyolefins contain pendant carboxylate groups associated with free Group I and Group II metallic cations. Since ionic bond energies are on the order of 100 kcal/mole, the amount of interactions between the chains is extremely large. This results in outstanding strength and impact resistance.

Molecular Weight

Before the effect of molecular weight on intermolecular interaction is discussed, it should be pointed out that most

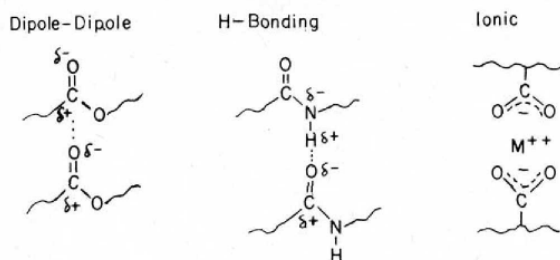


Figure 1. Intermolecular bonds found in polymers.

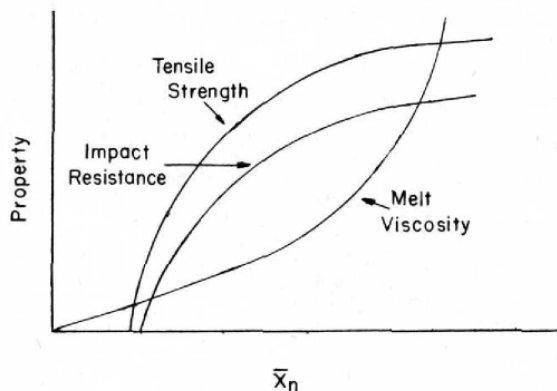


Figure 2. Plot of selected properties versus $\bar{X}_n$ for a hypothetical polymer.

chain-reaction and step-reaction polymerizations afford chains with many different lengths. Hence, one must talk in terms of average chain lengths and average molecular weights. The number-average degree of polymerization ($\bar{X}_n$) is defined as the average number of repeat units in the polymer chains. Closely associated with $\bar{X}_n$ is the number-average molecular weight ($\bar{M}_n$) which is equal to $\bar{X}_n$ multiplied by the molecular weight of the repeat unit. For example, a polyethylene sample with an $\bar{X}_n = 10,000$ has a $\bar{M}_n$ of 280,000 ($10,000 \times 28$). Both $\bar{X}_n$ and $\bar{M}_n$ are, of course, dependent on the sample's molecular weight distribution, i.e., the amount of each molecular weight species present.

If the intensity of electrostatic forces per unit length for a collection of molecules is the same, such as in the homologous series, then the total amount of attractive force increases as the molecular weight increases. The increase in interaction results first in changes in physical state. For example, as the molecular weight increases in the alkane series (C_nH_{2n+2}), the molecules change successively from gases to volatile liquids to nonvolatile liquids to nonvolatile solids. The solids then become progressively harder changing from soft waxes to hard resins. At a molecular weight of approximately 1,000, the molecules begin to decompose before boiling. This means that the total bonding force between the nonpolar molecules has become stronger than their covalent intramolecular bonds. None of the relatively low molecular weight hydrocarbons, however, display the mechanical properties of polyethylene.

The question then becomes: How high must the molecular weight be before the molecule exhibits "polymer properties"? Oligomers have relatively no strength until a critical $\bar{X}_n$ is reached (Fig. 2). At this point, which depends on the type of secondary bonding forces present, the molecule begins to develop mechanical properties, such as tensile strength, elongation to break and impact strength. For polymers containing hydrogen bonding, e.g., polyamides, the value of this critical $\bar{X}_n$ can be as low as 40. Polyhydrocarbons, however, must reach degrees of polymerization of greater than 100 before the process begins. Above this $\bar{X}_n$ the mechanical properties increase rapidly with increasing molecular weight until a second critical $\bar{X}_n$ is reached. After this point further increases in molecular weight result in very little change in a particular property. The value of this second critical $\bar{X}_n$ is also very dependent upon the type of intermolecular bonding present. For polyamides this point occurs near degrees of polymerization of 200. Polyhydrocarbons require $\bar{X}_n$ values of greater than 500. The properties of most other polymers level off at degrees of polymerization between these two. Although the second critical point is also slightly different for different properties, once the $\bar{X}_n$ is reached, the property becomes characteristic of the polymer. Polymer chemists

Table 3. Typical Polymers Produced by Step-Reaction Polymerizations

Common Name	Repeat Unit	Applications
Nylon 66	$\text{--}[\text{NH--C(=O)--CH}_2\text{--C(=O)--NH--CH}_2\text{--}]_n\text{--}$	clothing, tire cord
Polyester	$\text{--}[\text{O--C(=O)--C}_6\text{H}_4\text{--C(=O)--OCH}_2\text{--CH}_2\text{--}]_n\text{--}$	clothing, tire cord
Polyurethane	$\text{--}[\text{O--C(=O)--NH--C}_6\text{H}_4\text{--CH}_3\text{--NH--C(=O)--O--R--}]_n\text{--}$	flooring, wood and fabric coatings
Polycarbonates	$\text{--}[\text{O--C}_6\text{H}_4\text{--C(CH}_3\text{)}_2\text{--C}_6\text{H}_4\text{--O--C(=O)--}]_n\text{--}$	appliance parts, machinery housings

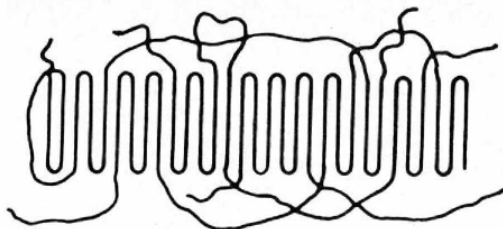


Figure 3. Schematic two-dimensional representation of lamellae model.

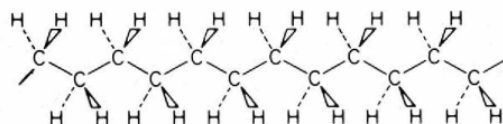


Figure 4. Extended, planar, zig-zag conformation of polyethylene.

sometimes refer to a "threshold molecular weight," which is the minimum molecular weight a polymer must possess to display the properties needed for a particular application.

It is tempting to conclude that chemists simply prepare polymers with as high a molecular weight as possible in order to maximize their properties. This is usually not the case, however, because polymers also become much harder to process as the molecular weight increases. In most industrial processing operations the polymer must undergo considerable flow, which is dependent on the melt viscosity, another property that increases with increasing molecular weight. Fortunately, the rate at which the melt viscosity increases is low until a critical molecular weight is reached (Fig. 2). After this point the melt viscosity increases rapidly. This behavior is due to the fact that low-molecular-weight polymers are free to flow as single molecules. As the chain length increases, the chains begin to entangle and "network flow" occurs. As the molecules become still larger the flow network and, hence, the resistance to flow, rapidly increases. In fact, the resistance to flow eventually will become so high that the polymer cannot be worked mechanically ($\bar{M}_n \approx 10^7$). In practice, the upper limit on the polymer's molecular weight is usually set by the flow requirements of the processing operation employed. The final product often reflects a compromise between optimum properties and ease of processing.

It should be pointed out that not all physical properties are dependent on molecular weight or, for that matter, on the magnitude of intermolecular interactions. For example, a polymer's refractive index, color, hardness, density, and electrical properties are all independent of molecular weight.

Nature of the Chain Packing

Linear polymer chains pack together in both disordered (amorphous) and ordered (crystalline) fashions. Although these two types of packing are analogous to the amorphous and crystalline forms of small molecules, the microstructure in polymers is considerably more complex. For example, small molecules are usually either totally amorphous or totally crystalline. Polymers, however, quite often contain both crystalline and amorphous regions. In fact, polymers can be divided into two classes: those which are completely amorphous under all conditions and those which are semicrystalline.

Totally amorphous polymers, such as atactic polystyrene and poly(methyl methacrylate), are generally assumed to consist of randomly coiled and entangled chains. A good analogy of what this must look like on the molecular level is to imagine a bucket of worms (2). In order to have the same

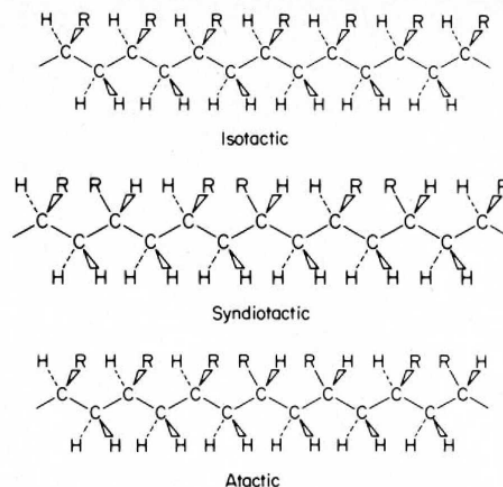


Figure 5. Stereochemical configurations of monosubstituted vinyl polymers.

relative dimensions of a typical polymer, however, a $\frac{1}{4}$ -in. thick worm would have to be over 20 feet long. Physically entangled worms of such length could still show considerable motion, but they would not be free to move as independent moieties. Only segments of any one worm could be in motion at any one time. This is exactly the type of behavior displayed by entangled polymer chains. The intensity of the motion of the segments, which are 20 to 50 atoms long, is dependent upon the temperature. Below a critical temperature called the glass transition temperature (T_g) the polymer segments do not have sufficient energy to move past one another. At this point segmental motion ceases and the material changes from a rubbery solid to a brittle glass-like state. A polymer above its T_g or a ball of living worms can withstand considerable impact, but the same polymer below its T_g or a ball of frozen worms will shatter when struck. For example, compare the results of throwing a rubber ball against a wall before and after it has been cooled in liquid nitrogen to below its T_g .

In semicrystalline systems, the crystalline order exists in crystalline domains called crystallites or lamellae, which are surrounded by an amorphous matrix. The crystallites do not have the regular shape of most organic crystals. They are also much smaller in size, typically $100 \text{ \AA} \times 100 \text{ \AA} \times 200 \text{ \AA}$, and contain many more imperfections. Although the individual polymer molecules are several thousand Angstroms long, the chains are aligned normal to the crystalline surfaces (Fig. 3). This means that a molecule can remain in crystalline order for only $\approx 100 \text{ \AA}$ before it reaches the surface of the crystal. It then usually folds back on itself and reenters the crystal at some other point. Some chains do not reenter the crystal but instead enter the surrounding amorphous region where they may become part of another crystallite. These small crystallites also tend to aggregate in larger three-dimensional regions called spherulites. Since there are normally no sharp boundaries between the crystalline regions and the amorphous parts of the system, it is sometimes useful to consider them as one-phase systems with varying degrees of order. Excellent detailed discussions of crystallinity in polymers are available (9, 10).

The regularity and close packing of the molecules in a crystallite maximizes the electrostatic forces operating between the chains. Since the crystalline and amorphous regions are continuous, the crystallites enhance the cohesiveness of the entire sample. In fact, they act very much like covalent crosslinks that are stable to time but not to temperature. Semicrystalline polymers are stiffer, stronger, and generally more useful than their amorphous counterparts.

Associated with the crystalline regions is another important

thermal parameter, the crystalline melting point (T_m). This is somewhat of a misnomer as polymers tend to melt over ranges of 2 to 10°C. This is due primarily to the fact that each sample contains more than one crystal size. Of course, once melting occurs the cohesiveness described above is lost. Keeping in mind the earlier discussion of T_g , it is not surprising that most semicrystalline polymers exhibit their most useful properties at temperatures above their T_g and below their T_m .

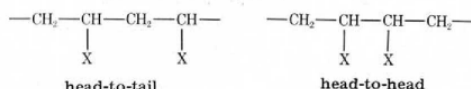
What then determines whether a polymer will crystallize readily or remain amorphous under all conditions? Although there are many contributing factors, the following are the most important: the polymer's conformation, the polymer's configuration, and the size of the pendant substituents.

Polymer Conformation

In order for a polymer to crystallize it must be able to assume a regular conformation, i.e., the three-dimensional arrangement of the polymer backbone as produced by rotation about the bonds must be regular. Polyethylene, for example, crystallizes in a fully-extended, planar zig-zag conformation (Fig. 4). Polymers with short, bulky substituents that are regularly spaced along the chain often assume a helical conformation in the crystalline phase. This allows the substituents to pack closely together without any appreciable distortion of the chain bonds. Amorphous polymers, on the other hand, tend to exist in completely random conformations.

Polymer Configuration

For a substituted polymer chain to crystallize it must also possess a regular configuration, i.e., the succession and spatial arrangements of the atoms as set by the chemical bonds must be regular. There are two principal types of structural regularity: recurrence regularity and stereoregularity. Recurrence regularity refers to the regularity with which the repeat unit occurs along the chain. For example, most monosubstituted vinyl monomers ($\text{CH}_2=\text{CHX}$) polymerize to afford a head-to-tail configuration, where the head or substituted end of one monomer is attached to the tail of another. Another less prevalent configuration is the head-to-head.



The presence of a high degree of recurrence regularity, however, does not generally guarantee crystallizability. Spatial regularity, i.e., stereoregularity, is also extremely important. For example, monosubstituted vinyl polymers can exist in three different spatial configurations. These configurations can be illustrated by drawing the backbone in the extended, planar, zig-zag conformation and then examining the possible spatial arrangements of the substituent group (Fig. 5). There are: the isotactic form, where the substituents are all attached to the same side of the main chain; the syndiotactic form, where each successive substituent is attached on opposite sides of the main chain; and the atactic form, where the attachment of substituents is completely random. The isotactic and syndiotactic forms are stereoregular structures, which exhibit strong tendencies to crystallize. Except for poly(vinyl alcohol), the atactic forms of monosubstituted vinyl polymers are amorphous.

The importance of stereoregularity can be illustrated by examining the history of polypropylene. Prior to 1957, the polymer could be produced only in the atactic form. This material has very poor mechanical properties at ambient temperature and, hence, was not produced commercially. In the late 1950's new coordination catalysts were discovered that made the production of isotactic polypropylene possible. The semicrystalline material possesses high tensile strength, stiffness, and hardness. Its high strength-to-weight ratio makes it useful for many applications, such as the production of ropes used in water-skiing.

Size of the Pendant Substituents

As long as the substituent is short and bulky, such as a methyl or phenyl group, and is attached in a stereoregular manner to the polymer backbone, it will not prevent the development of crystallinity in the polymer. In fact, it can enhance the intermolecular interactions in the crystallites by stiffening the chain (discussed below). As the length of the substituent increases, however, the distance between the chains in the crystalline regions increases. This results in considerably less electrostatic interaction between the chains. Eventually the main chains will no longer be able to crystallize. If the long substituents have regular structures, they may crystallize to form a comb-like structure.

Chain Flexibility

Linear polymer chains that meet the requirements of conformation and configuration tend to crystallize considerably faster and more easily than polymers with rigid backbones. Flexible chains, however, generally do not develop as strong electrostatic force fields between the chains as do stiffer chains. The latter polymers, once crystallized, form an extended intermolecular bonding network that is extremely difficult to break. For example, cellulose, which is a very rigid crystalline polymer with hydrogen bonds between the chains, is infusible, insoluble in all but a few solvent systems, and has an unusual modulus of rigidity for an organic polymer.

The effect of chain flexibility can be qualitatively visualized by comparing (1) the peeling of a leather strap from a wall to which it is nailed to (2) the peeling of a nailed wooden board (2). In the first case, one nail at a time may be broken loose, while in the second all the nails must be stressed simultaneously. The molecular analogy for a nail is the intermolecular bond.

The term flexibility, as used here, refers to the ease with which chain segments can undergo vibrational and rotational motions to assume different conformations. Chain flexibility is controlled primarily by the chemical structure of the polymers backbone and by the size and shape of the pendant substituents. For example, the energy barriers to rotation for carbon-carbon or carbon-oxygen single bonds are very low, permitting segments containing these linkages to undergo facile conformational changes. The energy barrier to rotation for large cyclic structures, such as phenyl rings, is relatively high. Thus, the incorporation of such structures in the backbone stiffens the chain dramatically. Short bulky substituents also increase the stiffness of the chain by inhibiting rotation.

Cohesive Energy Density (Solubility Parameters)

In order to quantitatively describe the magnitude of interaction between polymer chains, the polymer chemist makes use of a parameter that can be used to indicate such interactions between small molecules. The cohesive energy density (CED) of a liquid is defined as the molar energy of vaporization (ΔE_v) divided by the molar volume (V_1). One can determine CED experimentally by measuring the liquid's molar heat of vaporization (ΔH_v) and its density (d). These values are then used in the following equation:

$$\text{CED} = \frac{\Delta E_v}{V_1} = \frac{\Delta H_v - RT}{M/d}$$

where M is equal to molecular weight.

An associated parameter that is used quite often in polymer chemistry is the solubility parameter (δ), which is defined as the square root of the CED. Of course, when using these terms, one must also give the appropriate units. CED and δ are often expressed in cal/cm^3 and $(\text{cal/cm}^3)^{1/2}$, respectively.

Although amorphous polymers closely resemble liquids in behavior, they do not boil, thus, their δ cannot be determined directly. Several indirect methods have been developed that make use of the fact that linear polymers are only soluble in

Table 4. Typical Polymer Transition Temperatures and Solubility Parameters⁽¹²⁾

Polymer	$T_g(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$	Solubility Parameter (cal/cm ³) ^{1/2}
Polyethylene	-125	135	7.9
Polypropylene	0	171 ^a	9.2
Polystyrene	100	240 ^a	9.1
Poly(vinyl chloride)	81	212 ^b	9.7
Poly(methyl methacrylate)	105	>200 ^b	9.5
Poly(ethylene terephthalate)	69	250-265	10.7
Poly(hexamethylene adipamide)	50	250-260	13.6

a = isotactic; b = syndiotactic

solvents that have δ 's very close to their own (like dissolves like). Crosslinked systems, which are insoluble in all solvents, will only swell in solvents with similar δ 's. The thermodynamic explanation for this behavior is the following (6): In order for the polymer to dissolve, the free energy of solution must be negative. The factors that contribute to this value (temperature, enthalpy and entropy) are related by the familiar equation:

$$\Delta G = \Delta H - T\Delta S$$

Since there are many degrees of local motion associated with an amorphous polymer, the entropy of solution has only a small positive value. Thus, the enthalpy of solution must be very small for the free energy change to be negative. The enthalpy of mixing (ΔH_m) for two liquids is given by the Scatchard-Hildebrand equation:

$$\frac{\Delta H_m}{V\theta_1\theta_2} = \left[\left(\frac{\Delta E_{v1}}{V_1} \right)^{1/2} - \left(\frac{\Delta E_{v2}}{V_2} \right)^{1/2} \right]^2 = (\delta_1 - \delta_2)^2$$

where V is the total volume of the mixture, ΔE_{v1} and ΔE_{v2} are the vaporization energies of components 1 and 2, V_1 and V_2 their molar volumes, and θ_1 and θ_2 their volume fractions. Hence, the probability that a polymer and a solvent will be miscible increases as the difference between their δ 's decreases. Although solvents are generally miscible if this difference is ± 3.5 (cal/cm³)^{1/2}, the difference between the δ 's of a polymer and solvent can usually be no larger than ± 1.5 (cal/cm³)^{1/2} for solution to occur.

The solubility parameter for a mixture of solvents (δ_{sm}) is approximated by the following equation:

$$\delta_{sm} = \frac{X_1V_1\delta_1 + X_2V_2\delta_2}{X_1V_1 + X_2V_2}$$

where X is the mole fraction and V the molar volume of each component of the mixture. Polymers are often dissolved in

solvent mixtures where the amounts of the components have been adjusted to bring the δ_{sm} close to the δ of the polymers. In fact, some polymers can be dissolved in a mixture of two non-solvents, e.g. cellulose nitrate is soluble in a 50:50 mixture of ethanol and ether but insoluble in either solvent alone.

Solvent mixtures are also employed in turbidimetric titrations, which are used to determine the solubility parameter spectrum of polymers. In this procedure, the solubility of the polymer is tested in different solvents until a suitable solvent is found. Two non-solvents for the polymer that are miscible with the solvent are then selected. One of these non-solvents should have a δ larger than the solvent's and the other's should be smaller. A solution of the polymer is then titrated with one of the non-solvents until the polymer begins to precipitate causing the mixture to become turbid. The δ of the mixture at that point is calculated using the expression for δ_{sm} . A similar titration is also carried out with the other non-solvent. In this manner, both the high and low value of δ that will affect solution of the polymer is determined. The mid-point of the range is sometimes reported as the δ of the polymer.

Although the solubility parameter concept is extremely useful to the polymer chemist, it still does not completely characterize the complex intermolecular interactions that occur in a polymer sample. This is demonstrated by the fact that inconsistencies sometimes arise when polymer properties are correlated with solubility parameters. One difficulty in the solubility parameter concept is that it involves the resolution of the composite influences of van der Waals, polar, and hydrogen-bonding forces. More advanced treatments subdivided solvents into non-polar (δ_n), polar (δ_p), and hydrogen-bonding (δ_h) classes (11). Separate parameters are then determined in solvents in each class and the composite solubility parameter (δ_0) calculated from the following expression:

$$\delta_0^2 = \delta_n^2 + \delta_p^2 + \delta_h^2$$

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