POLYMER CHEMISTRY

David Whisnant
Wofford College

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David Whisnant

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Licensing

A detailed breakdown of this resource's licensing can be found in ***Back Matter/Detailed Licensing****.*

CHAPTER OVERVIEW

1: Chemical Composition

The chemical composition of a polymer influences the forces of attractions between polymer chains and how closely the chains can pack. These can have an important effect on the physical properties of the polymer.

1.1: Intermolecular Forces
1.2: Pendant Groups
1.3: Polymerization Reactions
1.4: Stiffening Groups

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- David Whisnant (Wofford College). Partial support for this work was provided by the National Science Foundation's Division of Undergraduate Education through grants DUE #9950809 and DUE #9950296. Additional support was provided by the Camille and Henry Dreyfus Foundation.

1.1: Intermolecular Forces

The intermolecular forces for polymers are the same as for small molecules. Because polymer molecules are so large, though, the magnitude of their intermolecular forces can vastly exceed those between small molecules. The presence of strong intermolecular forces is one of the main factors leading to the unique physical properties of polymers.

Dispersion Forces

Dispersion forces are due to instantaneous dipoles that form as the charge clouds in the molecules fluctuate. Dispersion forces, the weakest of the intermolecular forces, are present in all polymers. They are the only forces possible for nonpolar polymers such as polyethylene.

Dispersion forces depend on the polarizability of a molecule. Larger molecules generally are more polarizable, so large polymers with high molecular weights can have significant dispersion forces. Ultra high molecular weight polyethylene (UHMWPE), which has a molecular weight in excess of 3,000,000 g/mole, is used to make bulletproof vests.

Dipole-Dipole Forces

Dipole-dipole forces result from the attraction between polar groups, such as those in polyesters and vinyl polymers with chlorine pendant groups.

Hydrogen Bonding

Hydrogen bonding can take place when the polymer molecule contains -OH or -NH groups. Hydrogen bonding is the strongest of the intermolecular forces. Polymers such as poly(vinyl alcohol) and polyamides are hydrogen bonded.

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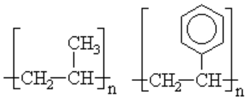
1.2: Pendant Groups

A group attached to the polymer backbone and present in the repeating unit is called a **pendant group**. Examples of pendant groups are the methyl group in polypropylene and the benzene ring in polystyrene.



Common Pendant Groups: (left) polypropylene and (right) polystyrene

Polymers with pendant groups still are designated as linear polymers. The presence of pendant groups modifies the properties of a polymer.

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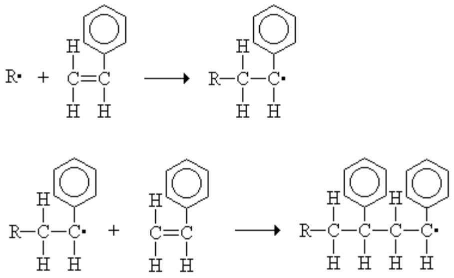
1.3: Polymerization Reactions

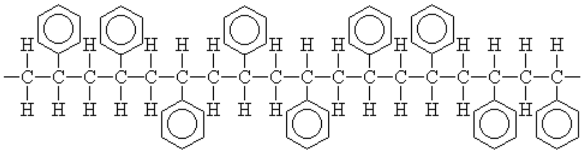
For polymerization to take place, the monomers must be capable of being linked to two (or more) other monomer molecules[2] . Most of these reactions can be placed in one of two classifications: chain-reaction polymerization and step-reaction polymerization.

Chain-Reaction Polymerization

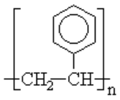
Chain-reaction polymerization, sometimes called addition polymerization, requires an **initiator** to start the growth of the reaction. The largest family of polymers [3], vinyl polymers, are produced by chain polymerization reactions. A good example is the free-radical polymerization of styrene, which is initiated by a free radical (R) that reacts with styrene. The compound that is formed still is a free radical, which can react again.



This reaction eventually leads to the formation of **polystyrene**, a portion of which is shown below. Polystyrene prepared by free-radical polymerization is



Polystyrene can be represented using a shorthand notation.



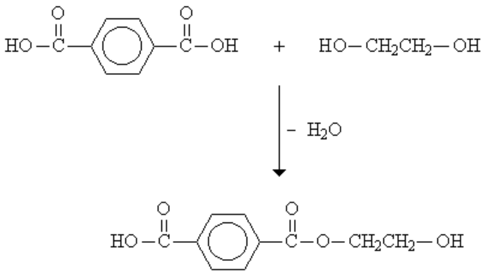
Styrene is an example of a vinyl monomer - a small molecules containing carbon-carbon double bonds. A few other important vinyl monomers are listed below[4]. Some of these polymers are synthesized by methods involving initiators other than free radicals - carboanions, carbocations, or coordination compounds, for instance. Vinyl polymers are **addition polymers**, which have the same atoms as the monomer in their repeat units.

Monomer		Polymer	
ethylene		polyethylene	
propylene		polypropylene	
vinyl chloride		poly(vinyl chloride) (PVC)	
vinylidene chloride		poly(vinylidene chloride) (Saran)	
methylmethacrylate		poly(methylmethacrylate) (PMMA)	
Produced by hydrolysis of poly(vinyl acetate)		poly(vinyl alcohol) (PVA)	

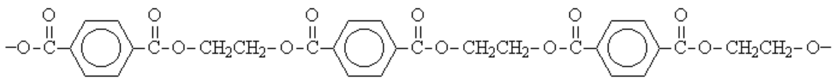
Step-Reaction Polymerization

In a step-reaction polymerization reaction, sometimes called condensation polymerization, the polymer chains grow by reactions that occur between two molecular species. An example is the polymerization reaction involving terephthalic acid and ethylene glycol, both of which are **bifunctional**.

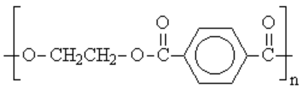
Polymer formation begins with one diacid molecule reacting with one dialcohol molecule to eliminate a water molecule and form an ester. The ester unit has an alcohol on one end and acid on the other, which are available for further reactions.



The eventual result is a **polyester** called poly(ethylene terephthalate) or more commonly, **PET**.



PET is the plastic in soda bottles. It can be represented with a shorthand notation.



Polyesters are condensation polymers, which contain fewer atoms within the polymer repeat unit than the reactants because of the formation of byproducts, such as H_2O or NH_3, during the polymerization reaction. Most synthetic fibers are condensation polymers.

A few types of condensation polymers are listed below. In the table, R and R' stand for organic groups.

Typical Monomers		Polymer Type	
		polyester	
		polyamide (nylon)	
		polyurethane	
		polycarbonate	

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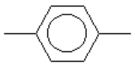
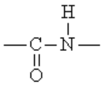
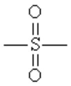
1.4: Stiffening Groups

The flexibility of a polymer chain depends on the groups present in the polymer backbone. Groups such as the following are called *stiffening groups* because they decrease the flexibility of the polymer chain.

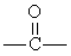

p-phenylene


$-\underset{\underset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-$

amide

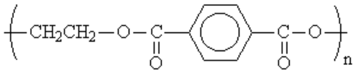
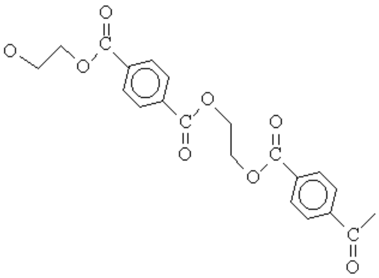
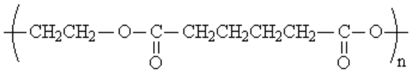
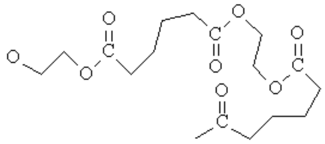

$-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-$

sulfone


$-\overset{\overset{O}{\|}}{C}-$

carbonyl

As an example, poly(ethylene terephalate) is a stiffer molecule than poly(ethylene adipate) because a benzene ring is not as flexible as a chain of CH_2 groups.

 poly(ethylene terephthalate)	
 $\left(CH_2CH_2-O-\underset{\underset{O}{\|}}{C}-CH_2CH_2CH_2CH_2-\underset{\underset{O}{\|}}{C}-O\right)_n$ poly(ethylene adipate)	

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CHAPTER OVERVIEW

2: Experimental Methods

There is a wide range of methods available for testing and characterizing polymers.

2.1: Polymer Density
2.2: Tensile Testing
2.3: Differential Scanning Calorimetry

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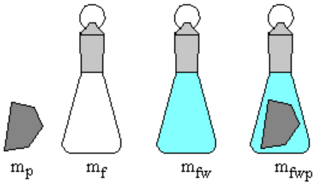
2.1: Polymer Density

Polymer samples usually are irregular in shape, making it difficult to measure their volume directly. There are four routine methods for determining the density of a polymer. One of these methods is called *pycnometry*. The density can be used to calculate the percent of a polymer that is crystalline.

Density by Pycnometry

In a pycnometer, the volume of the polymer is determined by the displacement of a liquid or gas. A special container, made of soda glass to avoid static charges, typically is used for the experiment. For our purposes a ground-glass stoppered 25.00-mL Erlenmeyer flask will suffice. We will use water as the liquid.



Four measurements are made ($\pm 0.0001\ g$):

- m_p = mass of polymer
- m_f = mass of dry empty flask
- m_{fw} = mass of flask filled with water
- m_{fwp} = mass of flask filled with polymer and water

The temperature of the water also is measured (). The density of water at this temperature can be found in the *International Critical Table*s and other reference books.

It is important to make sure that all air bubbles have been excluded from the flask when m_{fw} and m_{fwp} are measured. The flask should be filled to the rim and the glass stopper gently dropped into place. It is particularly important to watch for bubbles clinging to the polymer. It is best to use a degassed liquid[55], although this may be difficult in our experiments.

The volume of the flask, V_f, is calculated from m_f, m_{fw}, and the density of water.

When the polymer is in the flask, the water occupies a smaller volume, V_{fp}. This volume is calculated from m_{fwp}, m_f, m_p, and the density of water.

The volume of the polymer is calculated from V_f and V_{fp}.

Once the volume of the polymer is known, its density can be calculated.

Percent Crystallinity

We will assume that a semi-crystalline polymer is a simple two-phase system and that the volume of the polymer is a sum of the volumes of the crystalline and amorphous phases.

$$V = V_a + V_c \tag{2.1.1}$$

Let m, m_a, and m_c be the masses of the polymer, amorphous phase, and crystalline phase. Let D, D_a, and D_c be the corresponding densities. Then we can write this equation.

$$\frac{m}{D} = \frac{m_a}{D_a} + \frac{m_c}{D_c} \tag{2.1.2}$$

Divide through by the mass of the polymer.

$$\frac{1}{D} = \frac{m_a/m}{D_a} + \frac{m_c/m}{D_c} \tag{2.1.3}$$

The mass ratios are the percent by mass of the amorphous and crystalline phases, expressed as decimal fractions.

$$\frac{1}{D}=\frac{P_a}{D_a}+\frac{P_a}{D_c} \tag{2.1.4}$$

Assuming that the polymer is a two-phase system, the sum of the percents should be 1.

$$\frac{1}{D}=\frac{1-P_c}{D_a}+\frac{P_c}{D_c} \tag{2.1.5}$$

This equation can be solved for the *percent crystallinity:*

$$P_c=\frac{\frac{1}{D}-\frac{1}{D_a}}{\frac{1}{D_c}-\frac{1}{D_a}} \tag{2.1.6}$$

Amorphous and Crystalline Densities

Determination of the percent crystallinity using densities assumes a knowledge of the densities of 100% amorphous and 100% crystalline polymers. The crystalline density usually is obtained from the unit-cell derived from X-ray diffraction experiments. A reliable value of the amorphous density is much more difficult to obtain[55]. Often the amorphous density is obtained by extrapolating data taken in the melt, from x-ray scattering, or from the fact that the ratio of the crystalline/amorphous densities is roughly 1.08. Densities of 100% crystalline and 100% amorphous phases are tabulated below for a few common polymers[55].

Polymer	D_a (g/cm^3)	D_c (g/cm^3)
polyethylene	0.853	1.004
poly(vinyl alcohol)	1.291	1.350
poly(vinyl chloride)	1.412	1.477
poly(vinylidene chloride)	1.775	1.957
poly(ethylene terephthalate)	1.336	1.514

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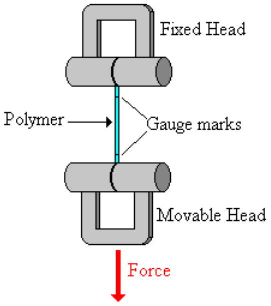
2.2: Tensile Testing

In a tensile test, a sample of known dimensions (including thickness) is held between two clamps.



As the sample is stretched, the force exerted by the instrument and the length (and sometimes cross-sectional area) of the sample are measured. This data can be used to construct a stress-strain curve and to calculate several mechanical properties of the polymer.

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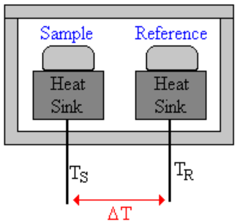
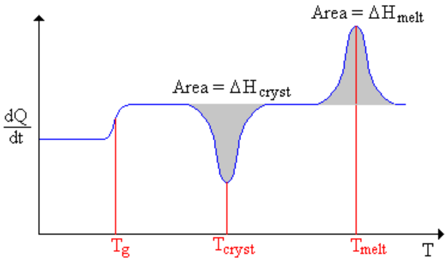
2.3: Differential Scanning Calorimetry

In a Differential Scanning Calorimeter (DSC) a sample and a reference (often a piece of Indium metal) are contained in small aluminum pans with crimped tops. The pans are placed on individual heaters in a furnace in a nitrogen atmosphere. A diagram of a heat flux DSC furnace is shown below.[58]



The furnace is heated and the temperature difference between the sample and reference is monitored so that the DSC can keep the temperatures the same. If an exothermic phase transition occurs, the temperature of the sample will tend to surge ahead of the reference. In this case the DSC doesn't need to furnish as much heat to the sample. If an endothermic transition occurs, the DSC must furnish more heat to the sample. The electrical power difference between the sample and reference measures the heat flow (dQ/dt) in the sample.

Data are plotted as heat flow (dQ/dt) against temperature, giving a graph called a thermogram. An example thermogram is shown at the right.



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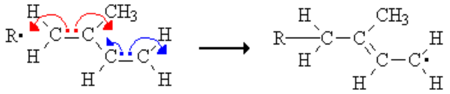
3: Isomerism

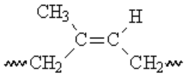
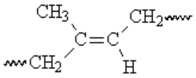
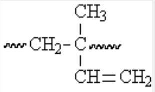
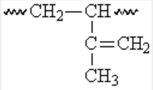
It is a general rule that for a polymer to crystallize, it must have highly regular polymer chains. Highly irregular polymers are almost inevitably amorphous. Polymer chains can have isomeric forms that decrease the regularity of the chains. There are three important forms of isomerism in polymers.

Structural Isomerism

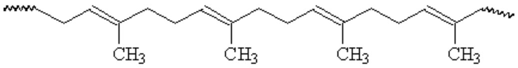
Double bonds in the polymer chain can show *cis*- or *trans*-isomerism. When a monomer with two conjugated double bonds, such as isoprene, undergoes chain polymerization one double bond can remain in the chain.



This segment of the polyisoprene chain can have four different isomers.

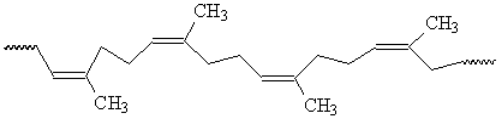
	
	

The difference between the properties of the cis- and trans-isomers is apparent for naturally-occurring polyisoprenes[13]. *Gutta percha* is predominantly *trans*-1,4-polyisoprene, which has a regular structure that allows crystallization. As a result, *gutta percha* is hard and rigid. Natural rubber is *cis*-1,4-polyisoprene, which has a less symmetrical structure that does not allow easy crystallization.



Gutta Percha (trans-1,4-polyisoprene)

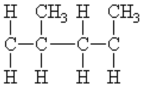
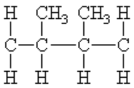
Natural rubber is an amorphous rubbery material.



Natural Rubber (cis-1,4-polyisoprene)

Sequence Isomerism (Head-to-Tail or Head-to-Head)

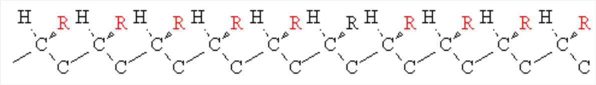
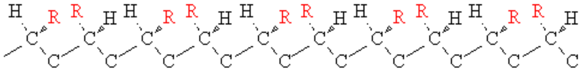
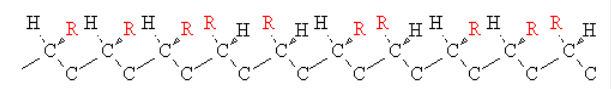
In chain polymerization monomers with pendant groups can attach in two ways.

	
head-to-tail	head-to-head

The usual arrangement is head-to-tail with the pendant groups on every other carbon atom in the chain

Stereoisomerism (Tacticity)

When a chiral center is present in a polymer molecule, different configurations or optical isomers are possible. Three of them are shown below for a monosubstituted vinyl polymer.

Name	Arrangement
isotactic	
syndiotactic	
atactic	

Stereochemistry can have an important effect on chain packing. Isotactic polypropylene (PP), for instance, is highly crystalline because the regular chains can pack closely together. Isotactic PP has a melting point of 160^{o}C. Atactic PP, on the other hand is a soft noncrystalline polymer with a melting point of only 75^{o}C.

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4: Mechanical Properties

The mechanical properties of polymers are one of the features that distinguishes them from small molecules.. The mechanical properties of a polymer involve its behavior under stress. These properties tell a polymer scientist or engineer many of the things he or she needs to know when considering how a polymer can be used.

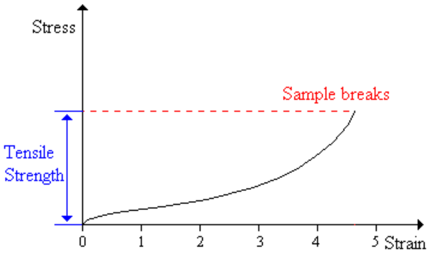
- How strong is the polymer? How much can you stretch it before it breaks?
- How stiff is it? How much does it bend when you push on it?
- Is it brittle? Does it break easily if you hit it hard?
- Is it hard or soft?
- Does it hold up well under repeated stress?

Tensile Strength

The tensile strength is the stress needed to break a sample[45]. It is expressed in Pascals or psi (pounds per square inch).

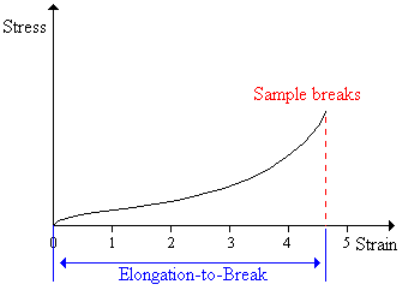
$$1\ \text{MPa} = 145\ \text{psi}$$

The tensile strength is an important property for polymers that are going to be stretched. Fibers, for instance, must have good tensile strength.



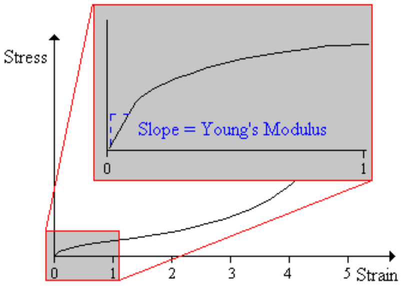
% Elongation to Break

The elongation-to-break is the strain on a sample when it breaks - this usually is expressed as a percent. The elongation-to-break sometimes is called the *ultimate elongation*. Fibers have a low elongation-to-break and elastomers have a high elongation-to-break[47].



Young's Modulus

Young's modulus is the ratio of stress to strain. It also is called the *modulus of elasticity* or the *tensile modulus*. Young's modulus is the slope of a stress-strain curve. Stress-strain curves often are not straight-line plots, indicating that the modulus is changing with the amount of strain. In this case the initial slope usually is used as the modulus, as is illustrated in the diagram at the right.



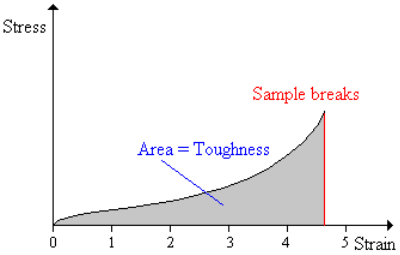
Rigid materials, such as metals, have a high Young's modulus. In general, fibers have high Young's modulus values, elastomers have low values, and plastics lie somewhere in between.

Toughness

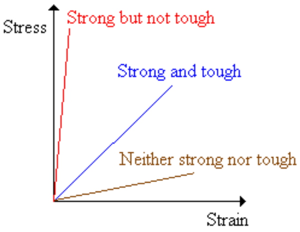
The toughness of a material is the area under a stress-strain curve. The stress is proportional to the tensile force on the material and the strain is proportional to its length. The area under the curve then is proportional to the integral of the force over the distance the polymer stretches before breaking.

$$Area \propto \int F(L)dL \tag{4.1}$$

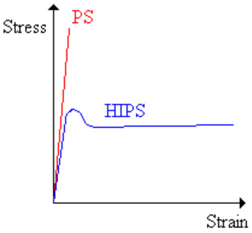
This integral is the work (energy) required to break the sample. The toughness is a measure of the energy a sample can absorb before it breaks.



There is a difference between toughness and strength, as is illustrated in the three plots below.



A material that is strong but not tough is said to be brittle. Brittle substances are strong, but cannot deform very much. Polystyrene (PS) is brittle, for example. High impact polystyrene (HIPS), a blend of polystyrene and polybutadiene (a rubbery polymer above its glass transition temperature) is said to be rubber-toughened.



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5: Molecular Weight Averages

The molecular weights of polymers are much larger than the small molecules usually encountered in organic chemistry. Most chain reaction and step reaction polymerizations produce chains with many different lengths, so polymers also differ from small molecules in that the polymer molecular weights are average values. You may refer elsewhere for a discussion of the different methods of measuring the average molecular weight of polymers. Of the key parameters influencing the physical properties of polymers, the molecular weight distribution usually is the dominant factor, often influencing the other parameters.

Degree of Polymerization

The degree of polymerization (DP) in a polymer molecule is the number, n, of repeating units in the polymer chain.

$$-\!\!\left[CH_2 - CH_2 \right]_n$$

The molecular weight of a particular polymer molecule is a product of the degree of polymerization and the molecular weight of the repeating unit. For instance a particular polyethylene molecule with $DP = 1000$ will have a molecular weight of 28,000. Because polymeric materials do not consist of strictly identical molecules, but instead are a mixture of many species having different values of DP, the DP of the material only is an average value, $\overline{DP}$.

> *Hence, measured polymer molecular weights are only average values.*

Molecular Weight Averages

Unless they have been purified, synthetic polymers have a distribution of molecular weights. Different methods of measuring the molecular weight yield different types of averages. Two of the most important are the number-average and the weight-average molecular weights. Suppose that you have a set of values $\{x_1, x_2, ..., x_n\}$ for which you calculate an average value. If the probability of each value occurring are given by $\{P_1, P_2, ..., P_n\}$ then the average is given by the sum below.

$$\sum_{i=0}^{\infty} P_i x_i \tag{5.1}$$

The type of average depends on the formula used for the probability, P_i.

Number-Average Molecular Weight

Suppose that you have a mixture of polymer molecules with different molecular weights in which the number of molecules having a particular *molecular weight*, M_i, is given by N_i. The "number-average" probability of a given mass being present is

$$P_i = \frac{N_i}{\sum_{j=0}^{\infty} N_j} \tag{5.2}$$

and the number-average molecular weight (Equation 5.1) is given by

$$\overline{M}_n = \sum_{j=0}^{\infty} \left(\frac{N_i}{\sum_{j=0}^{\infty} N_j} \right) M_i = \frac{\sum_{i=0}^{\infty} N_i M_i}{\sum_{j=0}^{\infty} N_j} \tag{5.3}$$

The number average is the simple arithmetic mean, representing the total weight of the molecules present divided by the total number of molecules. Most thermodynamic measurements are based on the number of molecules present and hence depend on the number-average molecular weight: examples are the colligative properties, osmotic pressure and freezing point depression. End-group analysis also produces a value for $\overline{M}_n$.

Weight-Average Molecular Weight

The probability factor in a weight-average emphasizes the mass of the molecules so that the heavier molecules are more important.

$$P_i = \frac{N_i M_i}{\sum_{j=0}^{\infty} N_j M_j} \tag{5.4}$$

The weight-average formula (Equation 5.1) then is the following:

$$\overline{M}_w = \sum_{j=0}^{\infty} \left(\frac{N_i M_i}{\sum_{j=0}^{\infty} N_j M_j} \right) M_i = \frac{\sum_{i=0}^{\infty} N_i M_i^2}{\sum_{j=0}^{\infty} N_j M_j} \tag{5.5}$$

Molecular weight measurements that depend on the contributions of molecules according to their sizes give weight-average molecular weights. Light scattering and ultracentrifuge methods are examples of this type of technique.

The weight-average molecular weight is larger than or equal to the number-average molecular weight. The ratio of the weight-average and number-average molecular weights,

$$\frac{\overline{M}_w}{\overline{M}_n} \tag{5.6}$$

is a measure of the polydispersity of a polymer mixture - how widely distributed the range of molecular weights are in the mixture. A ratio that is around 1.0 indicates that the range of molecular weights in the mixture is narrow; a high ratio indicates that the range is wide. With rare exceptions, all synthetic polymers are polydisperse.

Comparison of Number- and Weight-Averages

Suppose that you want to travel from Atlanta to Los Angeles, visiting your friends along the way. Unfortunately your friends live only on the eastern and western coasts, leading to a somewhat unconventional journey.

Start	Destination	Miles
1: Atlanta, GA	2: Columbia, SC	210
2: Columbia, SC	3. Charlotte, NC	90
3: Charlotte, NC	4. New York, NY	620
4. New York, NY	5. Los Angeles, CA	2790

- The number-average of the miles traveled in the four legs of the journey is 928 miles. This is the average distance travelled in each leg of the journey. It places equal emphasis on each leg.
- The mass-average of the miles traveled in the four legs of the journey is 2216 miles. This average places a greater emphasis on the leg of the journey with the largest "mass" - that is the fourth leg in which you travel 2790 miles. It is more representative of the major part of your journey.
- This mass-average/number-average ratio for this journey is 2.4, indicating that the trip is polydisperse with widely different mileages for the separate legs of the journey.

Viscosity Average

One of the oldest methods of measuring the average molecular weight of polymers is by solution viscosity. The viscosity-average molecular weight, $\overline{M}_v$, lies somewhere between the number average and the weight average.

Chain Entanglement

Small molecules, even relatively large hydrocarbons such as the paraffins, do not have long enough chains to become entangled and do not exhibit polymer properties. Polymer molecules are long chains, which can become entangled with one another. Along with intermolecular forces, chain entanglement is an important factor contributing to the unique physical properties of polymers. The difficulty in untangling their chains makes polymers strong and resilient.

At some critical degree of polymerization a polymer will begin to show the mechanical properties, such as strength and toughness, that are characteristic of polymers. The value of the critical degree of polymerization that is necessary for a oligomer to show polymer properties is dependent on the intermolecular forces between polymer chains and on the amount of chain entanglement. All polymers exhibit no strength below DP = 30. The strength also does not change much above DP's in the 600 range. As the chains become very long, molecular entanglements and intermolecular forces become so great that the chains no longer slip along each other. At this point, further lengthening of the chains doesn't make much difference[22].

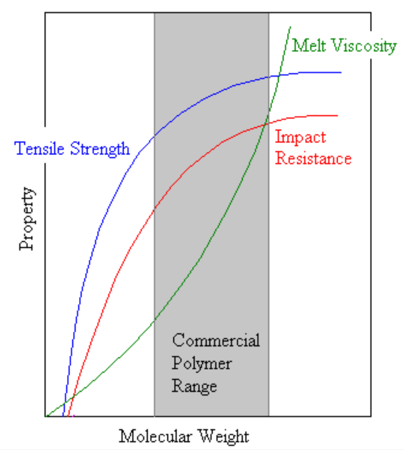
Threshold Molecular Weight

Polymer chemists sometimes refer to the threshold molecular weight below which an oligomer will not display the properties needed *for a particular application*. The value of the threshold molecular weight depends on the application. If the polymer is to be used as an adhesive, the required molecular weight may be relatively low. If the polymer is to be used in a trash barrel on the other hand, a high molecular weight is required.

Commercial Polymer Range

Beyond the critical degree of polymerization, as molecular weight grows larger polymer strength increases rapidly. Eventually, as is shown in the diagram at the right, the strength levels off.

The threshold molecular weight is a lower limit for the molecular weight required for a given commercial application. As the molecular weight increases the chains also entangle more, which increases the viscosity of the polymer melt. In most industrial applications a polymer is melted as it is processed so that it will flow into a mold or through an orifice. Eventually the viscosity gets so high that the polymer cannot be processed easily, establishing an upper molecular weight beyond which it is prohibitively expensive to process the polymer.



Thus we see that for a particular application only a certain molecular weight range is practical for a given polymer. This range is a compromise between optimum properties and ease of processing. Most of the practically useful polymers have a DP between 200 to 2000, corresponding to a molecular weight range from 20,000 to 200,000.

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CHAPTER OVERVIEW

6: Morphology

Polymer morphology is the overall form of polymer structure, including crystallinity, branching, molecular weight, cross-linking, and so on. Small molecules usually have crystalline solids, which are highly-ordered 3-dimensional arrays of the molecules. Solid polymers can be crystalline or amorphous (disordered arrangements of randomly coiled and entangled chains). Thermoplastics usually are semicrystalline - a combination of crystalline and amorphous regions. The properties of thermoplastics are strongly influenced by their morphology.

6.1: Classification of Polymers
6.2: Crystallization Tendency
6.3: Polymer Crystallinity

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6.1: Classification of Polymers

The most common way of classifying polymers is to separate them into three groups - *thermoplastics*, *thermosets*, and *elastomers*. The thermoplastics can be divided into two types - those that are crystalline and those that are amorphous.

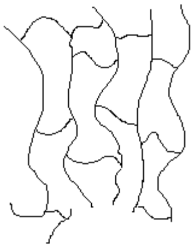
Thermoplastics

Molecules in a thermoplastic are held together by relatively weak intermolecular forces so that the material softens when exposed to heat and then returns to its original condition when cooled. Thermoplastic polymers can be repeatedly softened by heating and then solidified by cooling - a process similar to the repeated melting and cooling of metals. Most linear and slightly branched polymers are thermoplastic. All the major thermoplastics are produced by chain polymerization.

Thermoplastics have a wide range of applications because they can be formed and reformed in so many shapes. Some examples are food packaging, insulation, automobile bumpers, and credit cards.

Thermosets

A thermosetting plastic, or thermoset, solidifies or "sets" irreversibly when heated; they cannot be reshaped by heating. Thermosets usually are three-dimensional networked polymers in which there is a high degree of cross-linking between polymer chains. The cross-linking restricts the motion of the chains and leads to a rigid material. A simulated skeletal structure of a network polymer with a high cross-link density is shown below.



Thermosets are strong and durable. They primarily are used in automobiles and construction. They also are used to make toys, varnishes, boat hulls, and glues.

Elastomers

Elastomers are rubbery polymers that can be stretched easily to several times their unstretched length and which rapidly return to their original dimensions when the applied stress is released. Elastomers are cross-linked, but have a low cross-link density. The polymer chains still have some freedom to move, but are prevented from permanently moving relative to each other by the cross-links. To stretch, the polymer chains must not be part of a rigid solid - either a glass or a crystal. An elastomer must be above its glass transition temperature, T_g, and have a low degree of crystallinity. Rubber bands and other elastics are made of elastomers.

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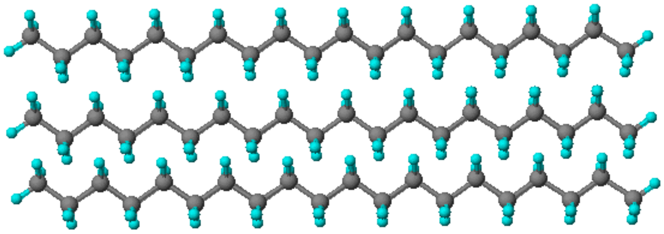
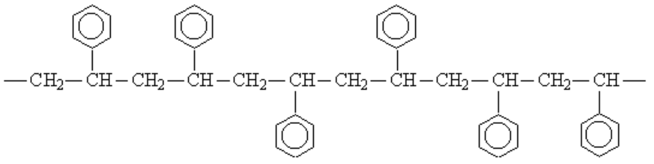
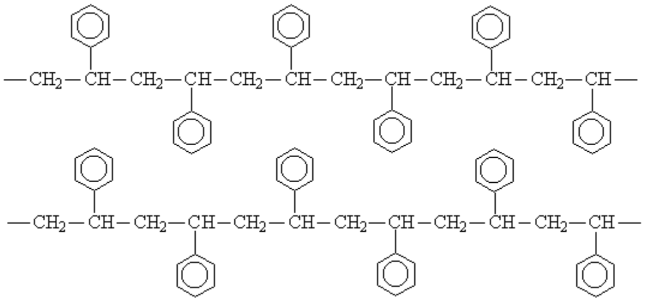
6.2: Crystallization Tendency

Some polymers form more crystalline solids than others. It will be useful for us to relate the tendency to crystallize to the chemical composition and structural details of particular polymers. Six factors favor a polymer with a high percent crystallinity: a regular and symmetrical linear chain, a low degree of polymerization, strong intermolecular forces, small and regular pendant groups, a slow rate of cooling, and oriented molecules.

Structural Regularity

To crystallize a polymer chain must be linear, although limited crystallization can take place if a small number of branches are present. Crystallization is favored by a regular arrangement along the polymer chain giving the structure a high degree of symmetry.

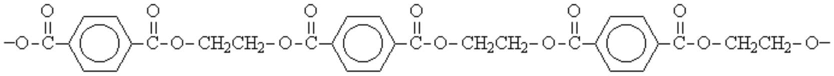
Linear polyethylene for example can form a solid with over 90% crystallinity in some cases. This is made possible by the planar zig-zag structure easily assumed by the molecule.	
Normal polystyrene is atactic with no regular order in the position of the benzene rings along the chain. The irregularity prevents the chains from packing closely to each other. Atactic polystyrene, is amorphous. It is comparatively soft, low melting, and becomes swollen in solvents.	 Atactic Polystyrene
In syndiotactic polystyrene the benzene rings are on alternate sides of the chain. This allows the chains to pack into crystals. Syndiotactic polystyrene is crystalline. It is rigid, high melting, and not penetrated readily by solvents.	 Syndiotactic Polystyrene (two chains shown)

Degree of Polymerization

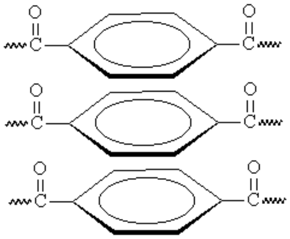
Relatively short polymer chains form crystals more readily than long chains, because the long chains tend to be more tangled. High crystallinity generally means a stronger material, but low molecular weight polymers usually are weaker in strength even if they are highly crystalline. Low molecular weight polymers have a low degree of chain entanglement, so the polymer chains can slide by each other and cause a break in the material.

Intermolecular Forces

Crystallinity is favored by strong interchain forces. The presence of polar and hydrogen bonding groups favors crystallinity because they make possible dipole-dipole and hydrogen bonding intermolecular forces. A polyester, such as poly(ethylene terephalate), contains polar ester groups. Dipole-dipole forces between the polar groups hold the PET molecules in strong crystals.

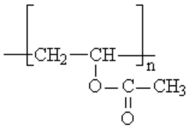
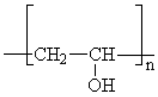


Crystallinity in poly(ethylene terephalate) also is favored by the structural regularity of the benzene rings in the chain[24]. The benzene rings stack together in an orderly fashion.



Pendant Groups

Regular polymers with small pendant groups crystallize more readily than do polymers with large, bulky pendant groups. Poly(vinyl alcohol) (PVA) is made by the hydrolysis of poly(vinyl acetate) (PVAc).

	→	
PVAc		PVA

PVA crystallizes more readily than PVAc because of the bulky acetate groups in PVAc. The -OH groups in PVA also form strong hydrogen bonds.

Processing

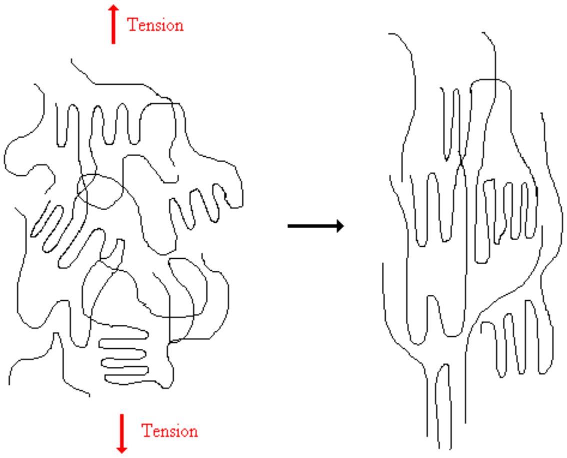
A major difference between small molecules and polymers is that the morphology of a polymer is dependent on its thermal history. The crystallinity of a polymer can be changed by cooling the polymer melt slowly or quickly, and by "pulling" the bulk material either during its synthesis or during its processing

A. Cooling Rate

When they are processed industrially, polymers often are cooled rapidly from the melt[31]. In this situation, crystallization is controlled by kinetics rather than thermodynamics. There may not be time for the chains, which are entangled in the melt, to separate enough to form crystals, so the amorphous nature of the melt is "frozen into" the solid. A polymer is more likely to have a higher percent crystallinity if it is cooled slowly from the melt.

B. Orientation

Crystallinity can be enhanced by pulling the bulk material either when it is synthesized or during its processing. This is common for both films and fibers. When a film is formed the small crystallites tend to be randomly oriented relative to each other. Drawing (stretching) the film pulls the individual chains into a roughly parallel organization as is shown in the schematic diagram at the right. Films can either be uniaxially oriented (oriented in only one direction) or biaxially oriented (oriented in two directions).



Fibers normally are drawn so that they are oriented in one direction. Unstretched nylon fibers are brittle, for example, when the fibers are stretched the oriented fibers are strong and tough. Polyethylene can be unentangled by forming a gel with a low molecular weight solvent. When the gel is drawn, the resulting fibers are highly oriented. Ultra-oriented PE formed in this way is used in bullet-proof vests.

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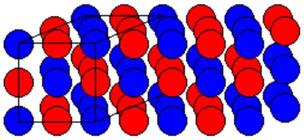
6.3: Polymer Crystallinity

Most small molecule behavior can be understood in terms of three states: gas, liquid, and solid. Polymers are large molecules with strong intermolecular forces and tangled chains, and do not have a vapor phase - they decompose before the temperature gets high enough to form a vapor. The length of polymer molecules also makes it difficult for the large crystals found in the solid phases of most small molecules to form. Instead solid polymers can be modeled in terms of two phases - crystalline and amorphous. Thus the behavior of polymers can better be understood in term of the three phases: melt, crystalline, and amorphous[15].

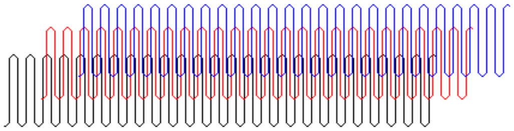
Crystalline Polymers

Highly crystalline polymers are rigid, high melting, and less affected by solvent penetration. Crystallinity makes a polymers strong, but also lowers their impact resistance. As an example, samples of polyethylene prepared under high pressure (5000 atm) have high crystallinities (95 - 99%), but are extremely brittle[21]. Small molecules and ions form a three-dimensional lattice with an extended regular structure that makes large crystals possible. A small portion of the NaCl lattice is modeled in the diagram below.



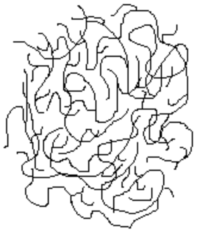
We usually describe such lattices with a unit cell - the smallest repeating unit in the lattice . In the case of NaCl, the unit cell is said to be **face-centered cubic**.

Polymer molecules are *very* large so it might seem that they could not pack together regularly and form a crystal. It now is known that regular polymers may form lamellar (plate-like) crystals with a thickness of 10 to 20 nm in which the parallel chains (shown in different colors in the simulated structure at the right) are perpendicular to the face of the crystals[18].



Amorphous Polymers

Polymer chains with branches or irregular pendant groups cannot pack together regularly enough to form crystals. These polymers are said to be amorphous. A two-dimensional schematic of an amorphous polymer is shown below.



Amorphous regions of a polymer are made up of a randomly coiled and entangled chains. They have been compared to a bucket containing a large number of entangled worms - each one 20-feet long and of 1/4-inch thickness[1]. The worms are so tangled that an entire worm cannot slide past the others, but small portions of the worms can twist around within the mass. Amorphous polymers are softer, have lower melting points, and are penetrated more by solvents than are their crystalline counterparts.

Glassy and Rubber States

At low temperatures molecular motion in an amorphous region is restricted to molecular vibrations, but the chains cannot rotate or move in space (the worms are frozen and cannot move). This form is the glassy state of the amorphous region. The glassy state can be thought of as being a supercooled liquid where the molecular motions have been frozen in. The glassy state is *hard, rigid, and brittle like a crystalline solid, but retains the molecular disorder of a liquid*[33].

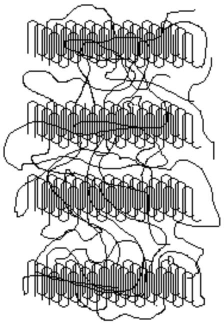
When the material is heated the polymer will reach a temperature at which segments (20 - 50 atoms long) of the entangled chains can move (small portions of the entangled worms can move around so the mass in the bucket writhes). At this temperature, called the glass transition temperature, the amorphous region becomes rubbery. When an amorphous polymer is in its rubbery state it is *soft and flexible*.

Semi-Crystalline Polymers

Semi-crystalline polymers have both crystalline and amorphous regions. Semi-crystallinity is a desirable property for most plastics because they combine the strength of crystalline polymers with the flexibility of amorphous. Semi-crystalline polymers can be tough with an ability to bend without breaking.

Isolated lamellar single crystals are obtained by crystallization from dilute solution. When crystals are formed from the melt, chain entanglements are extremely important[19]. In this case the solid is more irregular with polymer chains meandering in and out of ordered crystalline portions. The crystalline portion is in the lamellae; the amorphous portion is outside the lamallae.

Polymers such as this are said to be *semi-crystalline*. The crystals are small and connected to the amorphous regions by polymer chains so there may be no sharp well-defined boundaries between the two types of regions. For some polymers, such as polyvinyl alcohol, there is a fairly distinct separation between the crystalline and amorphous regions, though. In other cases (e.g., HDPE) the structure basically is crystalline with uniformly-distributed flaws and imperfections[20].



If we model a polymer as having distinct crystalline and amorphous regions then the percentage of the polymer that is crystalline is called the percent crystallinity. The percent crystallinity has an important influence on the properties of the polymer.

Spherulites

When a molten crystallizable polymer cools, the crystals grow from individual nuclei[25] and radiate out like the spokes of a bicycle wheel as is illustrated in the schematic diagram at the right. The crystalline portions actually radiate out in in three dimensions, forming spheres that are called spherulites. In a sample of a crystalline polymer there are billions of spherulites.

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7: Topology

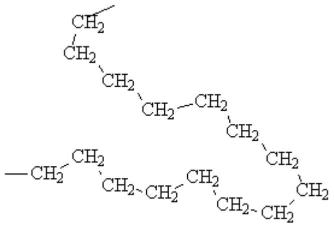
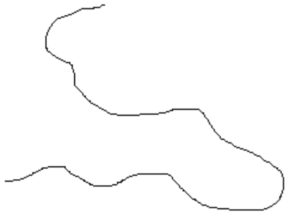
Polymers are very large molecules with unusual physical properties that depend on the interactions between its chains. An important factor in these interactions is the shape of the chain making up the backbone of the molecule.

Linear Polymers

Some polymer molecules are linear, similar to a normal alkane such as n-decane. An example is high density polyethylene (HDPE), which can contain more than 1000 CH_2 groups.

$$\left[-CH_2-CH_2-\right]_n$$

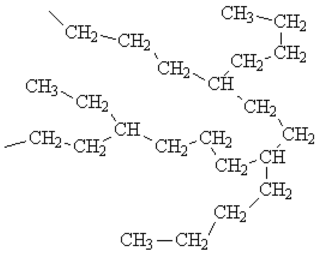
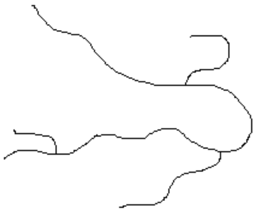
Simulated structures of HDPE are shown below. The skeletal structure shows only the polymer backbone.

Polymer	Simulated Structure	Simulated Skeletal Structure
Linear	 High Density Polyethylene (HDPE)	

HDPE has a high density because the linear molecules can pack closely.

Nonlinear (Branched) Polymers

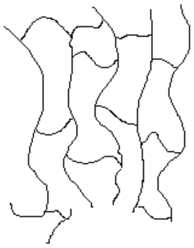
Some polymers, such as low density polyethylene (LDPE), have branches of different sizes irregularly spaced along the chain. Such polymers are said to be nonlinear. Polymers with pendant groups, such as the methyl group in polypropylene, are considered to be linear.

Polymer	Simulated Structure	Simulated Skeletal Structure
Nonlinear	 Low Density Polyethylene (LDPE)	

The branches prevent the nonlinear molecules from packing as closely as the linear, reducing their density.

Network Polymers

Some polymers have cross-links between polymer chains creating three-dimensional networks. A high density of cross-linking restricts the motion of the chains and leads to a rigid material. A simulated skeletal structure of a network polymer with a high cross-link density is shown below.



A simulated skeletal structure of a network polymer

Contributors and Attributions

- David Whisnant (Wofford College). Partial support for this work was provided by the National Science Foundation's Division of Undergraduate Education through grants DUE #9950809 and DUE #9950296. Additional support was provided by the Camille and Henry Dreyfus Foundation.

CHAPTER OVERVIEW

8: Transitions

Transition regions are narrow temperature intervals over which the properties of a polymer change by a large amount. The most important examples are the glass transition and the crystal melting transition. Most semicrystalline polymers exhibit their most useful properties between the temperatures of the glass transition, T_g, and the crystal melting point, T_m

8.1: Crystal Melting Transition
8.2: Factors Influencing Tg
8.3: The Glass Transition

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8.1: Crystal Melting Transition

Melting is the transition between a crystalline solid and a liquid. The melting point of a small molecule is very well-defined at a given pressure. Water, for instance, melts at 0^{o}C when P = 1 atm.

Polymers, on the other hand, do not have a single well-defined melting point. When a polymer "melts" it slowly becomes "leathery," then "tacky," and then liquid over a fairly broad temperature range[42]. The crystalline portion of the polymer is a nonequilibrium distribution of a large number of crystallites of different sizes and in different environments. They all do not melt at exactly the same temperature.

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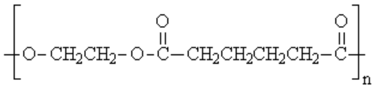
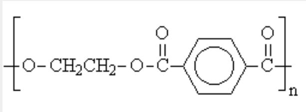
8.2: Factors Influencing Tg

The value of T_g depends on the mobility of the polymer chain - the more immobile the chain, the higher the value of T_g. In particular, anything that restricts rotational motion within the chain should raise T_g. A polymer chain that can move easily will change from a glass to a rubber at a low temperature. If the polymer chains don't move as easily, then it will require a relatively high temperature to change the compound into a rubbery form.

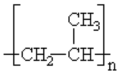
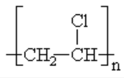
Chain Stiffness

Stiffening groups in the polymer chain reduce the flexibility of the chain and raise the value of T_g .

poly(ethylene adipate)	T_g = -70 °C		 $\left[-O-CH_2CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-\right]_n$
poly(ethylene terephthalate)	T_g = 69 °C		

Intermolecular Forces

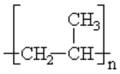
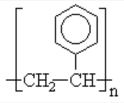
Stronger intermolecular forces lead to a higher T_g. PVC has stronger intermolecular forces than polypropylene because of the dipole-dipole forces from the C-Cl bond.

Atactic Polypropylene	T_g = -20 °C		 $\left[-CH_2-\overset{CH_3}{\overset{\|}{CH}}-\right]_n$
Atactic Poly(vinyl chloride)	T_g = 81 °C		 $\left[-CH_2-\overset{Cl}{\overset{\|}{CH}}-\right]_n$

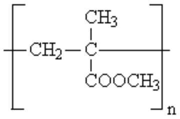
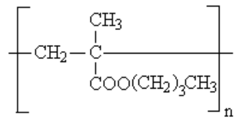
Pendant Groups

The influence of pendant groups on the glass transition temperature is somewhat more complicated.

Bulky pendant groups, such as a benzene ring, can catch on neighboring chains like a "fish hook" and restrict rotational freedom. This increases T_g.

Atactic Polypropylene	T_g = -20 °C		 $\left[-CH_2-\overset{CH_3}{\overset{\|}{CH}}-\right]_n$
Atactic Polystyrene	T_g = 100 °C		

Flexible pendant groups, such as aliphatic chains, tend to limit how close chains can pack. This increases rotational motion and lowers T_g.

Poly(methyl methacrylate)	T_g = 105 °C		 $\left[-CH_2-C(CH_3)(COOCH_3)-\right]_n$
Poly(butyl methacrylate)	T_g = 20 °C		 $\left[-CH_2-C(CH_3)(COO(CH_2)_3CH_3)-\right]_n$

Cross-Linking

The presence of cross-links between chains restricts rotational motion and raises Tg.

Plasticizers

Plasticizers are low molecular weight compounds added to plastics to increase their flexibility and workability. They weaken the intermolecular forces between the polymer chains and decrease T_g. Plasticizers often are added to semi-crystalline polymers to lower the value of T_g below room temperature. In this case the amorphous phase of the polymer will be rubbery at normal temperatures, reducing the brittleness of the material.

Plasticizers are added to the plastic used for automobile upholstery. In older automobiles, the plasticizer may be distilled from the upholstery during hot weather so that it becomes brittle over time. Some plasticizers have been identified as major health and environmental problems. Before 1977, Polychlorinated biphenyls (PCBs) were used as plasticizers in paints and plastics. Because they are toxic and possible endocrine disrupters, PCBs no longer are used.

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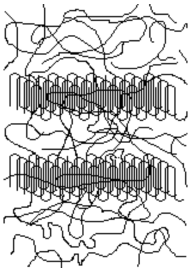
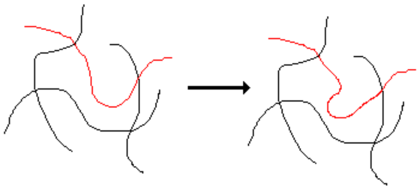
8.3: The Glass Transition

Semi-crystalline solids have both amorphous and crystalline regions. According to the temperature, the amorphous regions can be either in the glassy or rubbery state. The temperature at which the transition in the amorphous regions between the glassy and rubbery state occurs is called the *glass transition temperature*.



The Glass Transition

The glass transition is a property of only the amorphous portion of a semi-crystalline solid. The crystalline portion remains crystalline during the glass transition. At a low temperature the amorphous regions of a polymer are in the glassy state. In this state the molecules are frozen on place. They may be able to vibrate slightly, but do not have any segmental motion in which portions of the molecule wiggle around. In the glassy state, the motion of the red molecule in the schematic diagram below would NOT occur. When the amorphous regions of a polymer are in the glassy state, it generally will be hard, rigid, and brittle.



If the polymer is heated it eventually will reach its **glass transition temperature**. At this temperature portions of the molecules can start to wiggle around as is illustrated by the red molecule in the diagram above. The polymer now is in its **rubbery state**. The rubbery state lends softness and flexibility to a polymer.

You may have experienced the glass transition of chewing gum. At body temperature the gum is soft and pliable, which is characteristic of an amorphous solid in the rubbery state. If you put a cold drink in your mouth or hold an ice cube on the gum, it becomes hard and rigid. The glass transition temperature of the gum is somewhere between 0 °C and 37 °C.

Comparison with Melting

The glass transition is NOT the same as melting.

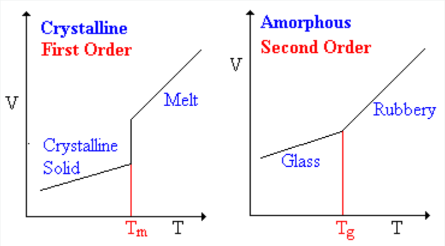
Glass Transition

- Property of the amorphous region
- Below T_g: Disordered amorphous solid with immobile molecules
- Above T_g: Disordered amorphous solid in which portions of molecules can wiggle around
- A second order transition (see below)

Melting

- Property of the crystalline region
- Below T_m: Ordered crystalline solid
- Above T_m: Disordered melt
- A first-order transition (see below)

Thermodynamic transitions are classified as being first- or second-order. In a **first-order transition** there is a transfer of heat between system and surroundings and the system undergoes an abrupt volume change. **In a second-order transition**, there is no transfer of heat, but the heat capacity does change. The volume changes to accommodate the increased motion of the wiggling chains, but it does not change discontinuously. Illustrative plots of specific volume vs. temperature are shown at the right for amorphous and crystalline polymers.



Glass Transition Temperature

When an amorphous polymer is heated, the temperature at which it changes from a glass to the rubbery form is called the **glass transition temperature, T_g**. *A given polymer sample does not have a unique value of T_g* because the glass phase is not at equilibrium. The measured value of T_g will depend on the molecular weight of the polymer, on its thermal history and age, on the measurement method, and on the rate of heating or cooling. Approximate glass transition temperatures of a few polymers are shown below.

Table: Glass Transition Temperatures

Polymer	T_g (°C)
Polyethylene (LDPE)	-125
Polypropylene (atactic)	-20
Poly(vinyl acetate) (PVAc)	28
Poly(ethyleneterephthalate) (PET)	69
Poly(vinyl alcohol) (PVA)	85
Poly(vinyl chloride) (PVC)	81
Polypropylene (isotactic)	100
Polystyrene	100
Poly(methylmethacrylate) (atactic)	105

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