The Polymer Primer

A Modular Introduction to Polymer Science

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January 2005
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Introduction

One of the most meaningful achievements of the twentieth century was the development of polymer science. The century began with the use of natural polymers such as cotton, wool, and natural rubber, and ended with most manufactured products made from or at least containing natural or synthetic polymers. Today most of the objects we come in contact with, if not metallic, are at least partially composed of polymers; from throw-away packaging to artificial hearts, from Silly Putty® to stealth airplanes. While the basic laws of chemistry apply equally to simple and “macro” molecules, the sheer size of polymer molecules presents new chemical and physical challenges and attributes.

With the myriad of polymer applications in today’s world, it is not surprising that a large number of chemists and chemical engineers are involved in some aspect of polymer chemistry. For that reason, all baccalaureate chemists and chemical engineers should have a basic knowledge of polymer terminology, theory, and technology. Historically, this need has not been met with mainstream chemistry texts. The Polymer Primer is meant to address this need. For more in-depth coverage a list of introductory polymer texts appears in Appendix A. In addition students are strongly encouraged to visit Macrogalleria, on the University of Southern Mississippi School of Polymers and High Performance Materials home page (www.psrc.usm.edu/macrog/).

I would like to thank Amanda Ely, of the class of 2004, for her assistance in proof reading this document.
Unit 1 – Polymer Chemistry

What is a polymer?

The word polymer was derived from two Greek words, *poly* meaning many and *meres* meaning parts. A polymer is a *macromolecule* composed of a large number of identical or near identical repeat units. Natural polymers include starch, cellulose, cotton, wool, protein, natural rubber, and DNA. Some examples of synthetic polymers are polyethylene, nylon, polyester, PVC, and latex paint.

The identical or nearly identical repeat unit in a polymer is referred to as a *monomeric unit*. A monomeric unit is normally derived from one or two relatively small molecules called *monomers*. Two monomeric units bonded together are referred to as a *dimer*, three a *trimer*, etc. Small polymeric sections, often between ten and twenty monomeric units in length, are referred to as oligomers. Polymers normally contain hundreds if not thousands of monomeric units.

The relative number of monomeric units in a polymer is referred to as its *dispersity*. If all the polymer molecules have the same number of monomeric units, the polymer is referred to as being *mono-dispersed*. A specific DNA or protein is mono-dispersed. If the number of monomeric units is not the same, the polymer is referred to as *poly-dispersed*. Most natural and all synthetic polymers are poly-dispersed.

The number of monomeric units in a mono-dispersed polymer is known as its *degree of polymerization*. The degree of polymerization *n* can be used in writing the chemical formula of the polymer,

\[ \text{[formula of monomeric unit]}_n \]

*Terminal groups represent such a small fraction of the total mass of a polymer molecule they are usually ignored.* With a poly-dispersed polymer, \( \bar{n} \) becomes the *average degree of polymerization*. For a mono-dispersed polymer the product of the degree of polymerization and mass of the monomeric unit is the *molar mass* (M). Note: *molecular weight* rather than molar mass is still commonly used in polymer chemistry.

\[ M = n \text{ (mass of monomeric unit)} \]

For a poly-dispersed polymer one gets the *average molar mass*.

\[ \bar{M} = \bar{n} \text{ (mass of monomeric unit)} \]

There are a number of different molecular weights used in polymer science. The average molar mass as defined above is referred to as the *number average molecular weight*. It can be defined as

\[ M_n = \frac{\sum N_i M_i}{\sum N_i} \]

where the summation is over all individual molar masses (\( M_i \)) and \( N_i \) is the number of molecules, moles, fraction or percentage with that molar mass. Let us analyze the following simplified example.

Consider the following poly-dispersed polymer population:

<table>
<thead>
<tr>
<th>Molar Mass (( M_i ) in grams/moles)</th>
<th>Number of Molecules in the Group (( N_i ) in moles)</th>
<th>( M_i N_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>800,000</td>
<td>0.0010</td>
<td>800</td>
</tr>
<tr>
<td>850,000</td>
<td>0.0020</td>
<td>1,700</td>
</tr>
<tr>
<td>900,000</td>
<td>0.0050</td>
<td>4,500</td>
</tr>
<tr>
<td>950,000</td>
<td>0.0030</td>
<td>2,850</td>
</tr>
<tr>
<td>1,000,000</td>
<td>0.0020</td>
<td>2,000</td>
</tr>
<tr>
<td>1,050,000</td>
<td>0.0010</td>
<td>1,050</td>
</tr>
</tbody>
</table>
The Polymer Primer

\[\sum N_i = 0.0140 \quad \sum M_i N_i = 12,900\]

\[
\overline{M_n} = \frac{\sum_{i=1}^{\infty} M_i N_i}{\sum_{i=1}^{\infty} N_i} = \frac{12,900 \text{ g mol}^{-2}}{0.0140 \text{ mol}^{-1}} = 921,400 \text{ g mol}^{-1}
\]

There are many polymer properties that are heavily influenced by the more massive polymer molecules. To reflect these properties two additional molecular weights are in use. The first is the **weight average molecular weight** \((M_w)\). If the number average molecular weight is considered the first moment (in a mathematical sense) the weight average molecular weight is the second moment and is defined as:

\[
\overline{M_w} = \frac{\sum_{i=1}^{\infty} M_i^2 N_i}{\sum_{i=1}^{\infty} M_i N_i}
\]

The weight average molecular weight increases the weighting of the larger molecules and as such is more relevant to those properties that are dependent on the larger molecules. The third moment is also used and is referred to as the **z-average molecular weight** \((M_z)\).

\[
\overline{M_z} = \frac{\sum_{i=1}^{\infty} M_i^3 N_i}{\sum_{i=1}^{\infty} M_i^2 N_i}
\]

Going back to the above example:

<table>
<thead>
<tr>
<th>(M_i)</th>
<th>(N_i)</th>
<th>(M_i N_i)</th>
<th>(M_i^2 N_i)</th>
<th>(M_i^3 N_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800,000</td>
<td>0.0010</td>
<td>800</td>
<td>6.400x10^8</td>
<td>5.120x10^{14}</td>
</tr>
<tr>
<td>850,000</td>
<td>0.0020</td>
<td>1,700</td>
<td>1.445x10^9</td>
<td>1.228x10^{15}</td>
</tr>
<tr>
<td>900,000</td>
<td>0.0050</td>
<td>4,500</td>
<td>4.050x10^9</td>
<td>3.645x10^{15}</td>
</tr>
<tr>
<td>950,000</td>
<td>0.0030</td>
<td>2,850</td>
<td>2.708x10^9</td>
<td>2.572x10^{15}</td>
</tr>
<tr>
<td>1,000,000</td>
<td>0.0020</td>
<td>2,000</td>
<td>2.000x10^9</td>
<td>2.000x10^{15}</td>
</tr>
<tr>
<td>1,050,000</td>
<td>0.0010</td>
<td>1,050</td>
<td>1.103x10^9</td>
<td>1.158x10^{15}</td>
</tr>
<tr>
<td>Summing</td>
<td>0.0140</td>
<td>12,900</td>
<td>1.195x10^{10}</td>
<td>1.112x10^{16}</td>
</tr>
</tbody>
</table>

Thus,

\[\overline{M_w} = 926,400 \text{ g mol}^{-1} \quad \text{and} \quad \overline{M_z} = 930,500 \text{ g mol}^{-1}\]

The larger the molar mass range the greater the deviation between the molecular weights. The corollary is also true: the smaller the range the closer the molecular weights. The ultimate is a mono-dispersed polymer. In such a case all three molecular weights are the same. The homogeneity of a polymer can be evalu-
ated by calculating the **polydispersity index**. The polydispersity index is defined as the ratio of the weight average to the number average molecular weights (i.e., \( M_w / M_n \)). Our example polymer would have a polydispersity index of

\[
\text{Polydispersity Index} = \frac{M_w}{M_n} = \frac{926,400 \text{ g mol}^{-1}}{921,400 \text{ g mol}^{-1}} = 1.005
\]

or the polymer is fairly homogeneous. A fourth molecular weight, the **viscosity molecular weight** \( (M_v) \), is determined from the viscosity of polymer solutions (to be covered in Unit 3). The distribution of molecular weights is given in Figure 1.1.

![Molecular Weight Distribution](image)

**Figure 1.1 Molecular Weight Distribution**

**Augmentation**: The number average molecular weight (molar mass) can be determined by colligative properties (i.e., boiling point elevation, freezing point depression, osmotic pressure). The weight average and z-average molecular weights can be determined by light scattering and centrifugation techniques.

**How are polymers prepared?**

There are two primary modes by which polymers are synthesized, **chain growth or addition polymerization** and **step growth or condensation polymerization**. The two modes require different monomer and polymerization conditions and yield different molar mass distributions. We shall begin by considering chain growth or addition polymerization.

**Chain Growth or Addition Polymerization**

Many commercial chain growth or addition polymers are prepared using a **free radical mechanism**. The polymerization process is initiated by the introduction of a free radical \((R^*)\) **initiator** into the liquid or gaseous monomer or monomer solution (Figure 1.2).
The free radical reacts with one of the sp$^2$ hybridized carbons causing the pi bond to break. This results in the formation of sp$^3$ hybridization at the reacted carbon and the formation of a new free radical to perpetuate the reaction. At each step a monomer is added to the polymer chain, thus the name addition polymerization. In the formation of a polymer this process occurs hundreds if not thousands of times.

Often students confuse initiators with catalysts. They are not the same; a catalyst is not consumed by the reaction whereas an initiator is. Three representative initiators are given in Figure 1.3.

**General Reaction**

\[ \text{In} - \text{In} \rightarrow 2 \text{In} \cdot \]

**Examples**

- **Benzoyl Peroxide**
  
  \[
  \begin{array}{c}
  \text{O} \\
  \text{C} - \text{O} - \text{O} - \text{C} \\
  \text{O}
  \end{array}
  \]
  
  \[
  \begin{array}{c}
  \text{O} \\
  \text{S} - \text{O} - \text{S} - \text{O} \\
  \text{O}
  \end{array}
  \]

- **Persulfate**

- **2,2'-azobis(isobutyronitrile) (AIBN)**

**Figure 1.3 Free Radical Initiators**

With a limited amount of initiator, chain growth or addition polymerization produces long polymer chains (i.e., chain growth polymerization). Figure 1.4 represents the early stage of a chain growth or addition polymerization. The separate lines represent unreacted monomer whereas the connected lines represent a polymer molecule. Thus during the early stages of polymerization, the reaction media is composed of long and growing polymers and unreacted monomers. The size of the polymer is a function of the
relative concentrations of initiator to monomer. This can be modified by the addition of a **free radical transfer agent**. The purpose of the free radical transfer agent is to terminate the polymerization in one chain and initiate a new chain.

![Initial stage of polymerization](image)

**Figure 1.4 Chain Growth or Addition Polymerization**

Chain growth or addition polymerization can also proceed by anionic or cationic mechanisms (*i.e.*, the transfer of both electrons involved in the pi bond). These methods tend to be more expensive but yield a more controlled, higher quality polymer. Industrially, the most important is the anionic polymerization using a Ziegler-Natta catalyst. A Ziegler-Natta catalyst has two components: a group IV to VIII transition metal compound such as dialkyl titanium dichloride and a group I to III organometallic compound such as dialkyl aluminum chloride. Normally, the catalyst needs to be aged before it reaches its maximum activity. During this aging period it appears that rearrangement occurs. While the mechanism is not well understood, it appears that the resultant complex has an unoccupied d-orbital on the transition metal complex. During polymerization this unoccupied d-orbital π-bonds to an olefin monomer. Consider the polymerization of ethylene in Scheme 1.1. As the bonding changes from π to σ a cyclic mechanism inserts the ethylene to the lead position on the adjacent growing polymer. The structural complexity of the mechanism leads to a highly ordered linear polymer.

![Scheme 1.1 Ziegler-Natta Polymerization of Ethylene](image)

The most common chain growth or addition monomers are alkenes, vinyl compounds, or conjugated dienes. Considering Figure 1.2, what is X? Some common side or pendant groups are given in Figure 1.5.

<table>
<thead>
<tr>
<th>X</th>
<th>Polymer Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>CH₃</td>
<td>Polypropylene</td>
</tr>
</tbody>
</table>
When X in Figure 1.5 is not hydrogen, there are two orientations that each monomer can take in adding to the polymer chain. The two configurations are referred to as **head-to-head** or **head-to-tail**. If X is small, a random configuration may result. On the other hand, if X is large, the head-to-tail configuration normally occurs. This shall be considered further in the next Unit.

**Step Growth or Condensation Polymerization**

Alternatively, polymers can be produced by the reaction of difunctional molecules. Consider a di-carboxylic acid reacting with a di-alcohol, Figure 1.6(a) or a di-carboxylic acid reacting with a di-amine, Figure 1.6(b).

---

**Figure 1.5 Alkene and Vinyl Monomers**

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Monomer Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_6H_5</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>Cl</td>
<td>polyvinylchloride (PVC)</td>
</tr>
<tr>
<td>OCOCH_3</td>
<td>Poly(vinyl acetate)</td>
</tr>
<tr>
<td>CN</td>
<td>Polyacrylonitrile</td>
</tr>
</tbody>
</table>

---

**Figure 1.6  Step Growth or Condensation Polymerization**
During step growth or condensation polymerization a small secondary product molecule is usually produced. In the above examples the second product is water. As the reaction proceeds, steam is produced. This steam must be removed from the reaction vessel to force the reaction to completion, thus the name \textit{condensation polymerization}. Usually two monomers are involved in a chain growth or condensation polymerization, however, this not always the case. Consider nylon-6 (Figure 1.7).

\[
\begin{align*}
\text{H}_2\text{N}-(\text{CH}_2)_6\text{C-}&\text{OH} \quad \text{H}_2\text{N}-(\text{CH}_2)_6\text{C-}&\text{OH} \\
\downarrow & \\
\text{H}_2\text{N}-(\text{CH}_2)_6\text{C-}&\text{N}-(\text{CH}_2)_6\text{C-}&\text{OH} \quad \text{H}_2\text{O} \\
\downarrow & \\
\left[\text{N-(CH}_2)_6\text{C-}\right]_n
\end{align*}
\]

\textit{Figure 1.7 Preparation of Nylon-6}

During a step growth or condensation polymerization reaction the size of the oligomers increase as the reaction progresses, thus \textit{step growth polymerization}, see Figure 1.8. It is not until the end of the reaction that large polymer molecules are produced.

\textit{Addition polymerization} and \textit{condensation polymerization} were used in early polymer literature. Even though their use persists, \textit{chain growth} and \textit{step growth polymerization} are now favored. In the remainder of this document \textit{chain growth} and \textit{step growth polymerization} will be used.

Some common polymers are given in Appendix B.
Copolymers

Copolymers are macromolecules with more than one monomeric unit. In most cases two competing monomers are used in preparing the polymerizing solution. In the polymer they can be distributed randomly or in some cases in mostly alternating positions. The alternating configuration is normally a result of steric factors. Copolymers can also be produced by partially reacting pendant groups.

Augmentation: In some ionic chain growth polymerization the monomeric solution can be changed during polymerization leading to blocked polymers (i.e., regions of different monomeric units).

General References


The Macrogalleria, Department of Polymer Science, University of Southern Mississippi, Web Page (www.psrc.usm.edu/macrog/)


Important Terms

addition polymerization
average degree of polymerization
chain growth polymerization
condensation polymerization
copolymer
degree of polymerization
dimter
dispersity
free radical mechanism
free radical transfer agent
head-to-head linkage
head-to-tail linkage
initiator
macromolecule
molar mass
molecular weight
mono-dispersed
monomer
monomeric unit
number average molecular weight
oligomer
poly-dispersed
polydispersity index
polymer
step growth polymerization
trimer
viscosity molecular weight
weight average molecular weight
Questions

1. Name five polymers you come in contact with on a daily basis.

2. What is a pentamer?

3. Give a specific example of a mono-dispersed polymer.

4. What is the molar mass of the polypropylene molecule \( H(CH_3CH_2)_100H \)?

5. Consider the following:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Molar Mass (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.200</td>
<td>1,000,000</td>
</tr>
<tr>
<td>0.300</td>
<td>500,000</td>
</tr>
<tr>
<td>0.300</td>
<td>100,000</td>
</tr>
<tr>
<td>0.200</td>
<td>10,000</td>
</tr>
</tbody>
</table>

Calculate \( M_n \), \( M_w \), \( M_z \) and the polydispersity index.

6. Why is it a free radical initiator while it is a Ziegler-Natta catalyst?

7. In your own words explain the difference between chain growth polymerization and step growth polymerization.

8. Name three chain growth polymers that do not appear in Figure 1.5.

9. What is the difference between a monomer and a monomeric unit? Give a specific example.

10. If \( M_n \) for polyethylene is 1,000,000 what is \( DPM \) ?

11. How many free carboxyl groups are present per molecule of nylon 6.6, which was prepared with excess adipic acid?

Unit 2 - Morphology

According to Webster’s New World Dictionary, morphology is defined as “the study of form and structure”. In this Unit we shall examine the molecular structure of polymers and its influence on macroscopic behavior. In general we can divide polymers into three structural categories: linear, branched, and cross-linked or network polymers. According to Figure 2.1, linear polymers are one-dimensional. They are single strands of bonded monomers. Unlike Figure 2.1, they are not straight.

- Most likely, the polymer molecule is composed of \( sp^3 \) hybridized carbon, oxygen and nitrogen atoms, and as such contains bonding angles of approximately 109.5°. The arrangement of the atoms in the polymer molecule is known as its conformation.
- Without mechanical alignment, polymer molecules clump together much like a number of chains dropped together in a pile. Normally the two ends of the linear polymer molecule are relatively close together.

To complete our picture, the polymer molecules are in constant vibrational motion. Excuse the analogy, but our polymer sample would look much like a mass of very long shivering earthworms.

The simplest linear polymer is polyethylene; a very long chain of \( CH_2 \) groups. All other vinyl or alkene type monomers will have at least one side group (X from Figure 1.2). This side group will normally occur in each monomeric unit and thus will be repeated at set intervals along the polymer chain. These regularly spaced side groups are referred to as pendant groups.
Often in a free radical polymerization the free radical end of one polymer chain will bond with the side of another polymer. This will produce a branch on the second polymer chain. Under vigorous reaction conditions branching can be quite common. The end result is a **branched polymer**. Since branched polymers cannot pack as closely together as linear polymers, they tend to form materials of lower density and mechanical strength.

Sometimes compounds are added to polymers that form covalent bridges between adjacent polymer chains. This process is referred to as **cross-linking**. Cross-linkage inhibits significant motion between adjacent chains and thus produces a covalent network throughout the object. In reality, a heavily cross-linked object becomes a single molecule. Tires and older black bowling balls are examples of single molecules. That shoots the h ___ out of what we learned in general chemistry. One mole of twelve pound bowling balls would have a mass better than half that of the earth. It is not surprising that cross-linked polymers cannot easily be recycled.

The physical characteristic of the polymer is also a function of the polymer’s composition. Oxygen (\(-\text{O}\)-) and methylene (\(-\text{CH}_2\)-) groups tend to make the polymer more flexible while more bulky groups such as amides, carboxyls, \(p\)-phenylene and sulfones stiffen the polymer.

**Isomerism**

Isomerism occurs when two different compounds have the same chemical formula. There are a number of significant examples of isomerism in polymer chemistry.

**Structural Isomerism**

One of the most significant examples of structural isomerism in polymer chemistry involves the orientation of the monomeric unit. As noted in Unit 1, in chain growth polymerization, a non-symmetrical monomer can add to the polymer chain in one of two orientations, **head-to-tail or head-to-head**.

If the steric effects and polarity of the two ends of the monomer are approximately the same the distribution can be random. This is not usually the case. Usually the head-to-tail orientation predominates. The head-to-tail or head-to-head orientation of the monomeric units can significantly alter both the chemical and physical properties of the polymer.
**Stereoisomerism or Cis-Trans Isomerism**

When conjugated dienes are involved in chain growth polymerization, a carbon-to-carbon double bond remains. The orientation around this bond could be either *cis* or *trans*. In free radical preparations, where steric effects are not significant, a random distribution results.

\[ n \text{R}_2\text{C} = \text{CH} - \text{CH} = \text{CR}_2 \rightarrow [ - \text{CR}_2 - \text{CH} = \text{CH} = \text{CR}_2 - ]_n \text{ cis or trans} \]

![Figure 2.3 Cis and Trans Configurations](image)

In nature both the cis and trans conformations of polyisoprene exist, Figure 2.4. The cis conformation is known as natural rubber whereas the trans is known as gutta-percha.

![Figure 2.4 The Synthetic Polymerization of Isoprene](image)

In the trans conformation, the polymer molecules stack closely together forming a dense hard polymer, which has been used as a covering for golf balls. In the cis conformation the polymer molecules cannot stack. They form loose coils, which produce a less-dense stretchy material, natural rubber.

Ionic chain growth polymerizations have been used to prepare stereospecific or optical isomers such as polypropylene, Figure 2.5.

![Figure 2.5 Optically active carbon in Polypropylene](image)

If all of the asymmetric centers are the same arrangement, DDDD or LLLL, the polymer is called *isotactic*. If the asymmetric centers alternate, DLDL, the polymer is called *syndiotactic*. If the order is random the polymer is referred to as *atactic*. Free radical polymers are atactic whereas ionic polymers are often isotactic or syndiotactic.
Intermolecular Forces and Molecular Alignment

Intermolecular forces are the same in polymer chemistry as in chemistry in general. The weakest intermolecular forces are London forces caused by the pulsating charge centers in atoms and yield a weak attractive force. The closer the atoms are together the stronger the resultant London forces. Next are the dipole-dipole attractions followed by hydrogen bonding.

Intermolecular attraction is dependent on molecular contact, the greater the contact, the greater the attraction. As a result:

- Polymer alignment strengthens intermolecular attraction, see Figure 2.6.

\[
\begin{array}{c|c}
\text{Not Aligned} & \text{Aligned} \\
\end{array}
\]

Figure 2.6 Molecular Alignment

- While bulky pendant groups may mechanically inhibit slippage (see below) they hold the polymer chains apart and thus decrease intermolecular attraction. It should be noted that lack of close packing is not necessarily bad. A large number of polymer applications require polymers, which stretch and/or bend.

Such alignment can occur naturally in the solidification process or can be done mechanically. Let us first consider mechanical alignment. Fibers are prepared by forcing melted polymer or viscous polymers solution through a small hole. After passing through the hole the polymer cools or the solvent evaporates to form a polymer fiber. The molecules in this fiber are not aligned. To align the molecules, the fiber is heated to just below its melt temperature, stretched, and cooled. The stretching aligns the molecules much like using your hands to stretch a pile of cooked spaghetti. This produces alignment in one direction. For films or sheet plastic, two-dimensional alignment is usually desired. The hot polymer is blown or rolled to give it two-dimensional alignment.

Most linear polymers, if allowed to cool slowly, form crystalline regions. These regions, called lamella or crystallites, can be produced by the folding of a single polymer chain, a linear segment involving many chains or more commonly a combination of both, see Figure 2.7. Typically, the lamella aggregate into larger structures called spherulites.

Figure 2.7 Crystal Formation

If there is no crystal formation, the polymer is said to be amorphous. Amorphous polymers contain only one phase and are therefore transparent. If crystallization has occurred the polymer is a mixture of crystal-
lites surrounded by amorphous regions. As such it is composed of two-phases and appears cloudy. To make transparent objects, a polymer which does not crystallize easily is selected. An example of such a polymer is polystyrene (PS). In addition, the object should be cooled rapidly so that crystallization does not have an opportunity to occur.

**Entanglement**

If one has a pile of string segments two centimeters in length, it is not at all difficult to extract a one string segment. If, on the other hand, one has a comparable pile of string segments twenty centimeters long, extraction of a single string can be much more difficult. The reason for the increased difficulty is that the two-centimeter segments are too short for entanglement whereas the twenty-centimeter segments are not. A comparable situation exists with linear polymers. Each polymer has a critical entanglement length beyond which entanglement occurs. However polymers, unlike strings, are not static. Molecular vibration can in time free entangled polymers. We shall consider this point further in Unit 4.

**Glass Transition Temperature and Melting Point**

Most pure solids expand on heating. This increase in volume is the result of increased atomic and molecular vibration. In General Chemistry we learned that this expansion and resultant decrease in intermolecular attraction continues until the solid melts. At the melt temperature ($T_m$) the atoms or molecules have sufficient energy to break free of the crystalline lattice. This process is more complicated with polymers. Amorphous polymers contain the random molecular configuration found in the liquid state and as such do not have a melt temperature. Simply, as the temperature increases so does their ability to flow.

If the temperature is sufficiently low linear polymer molecules, either amorphous or crystalline, are locked into position by intermolecular forces. If an expansive or compressive stress is applied, the molecules comply with a distortion of their bonding angles. See Figure 2.8(a). As the temperature increases molecular motion pushes the polymer molecules apart. At some point in this expansion, there is sufficient room for stressed polymer chains to slide past each other, Figure 2.8(b). This point of segmental motion is known as the glass transition temperature ($T_g$). Below the glass transition temperature polymers tend to be hard and brittle. As the polymer passes through the glass transition temperature it becomes flexible and leathery. As the temperature continues to increase the polymer becomes stretchy and elastic. Eventually, upon heating the melt or flow temperature will be reached and the polymer becomes a liquid.

![Figure 2.8 Glass Transition Point]

Linear polymers, either partially crystalline or amorphous, are known as thermoplastics. They can be melted and cast into different shapes (i.e., they can be recycled). Cross-linked polymers cannot melt. If heated to a sufficiently high temperature, they simply decompose. Cross-linked polymers are known as thermoset plastics. Obviously, thermoset plastics cannot be conveniently recycled.

**Plastics, Fibers and Elastomers**
**Plastics** are non-aligned linear polymers below $T_g$. **Fibers** are composed of strands of aligned polymers below $T_g$. For fibers to have a high “tensile” strength strong intermolecular attraction must be present. As noted above, elastomers are polymers well above $T_g$.

**General References**


*The Macrogalleria*, Department of Polymer Science, University of Southern Mississippi, Web Page (www.psrc.usm.edu/macrog/)


**Important Terms**

amorphous
atactic
branched polymer
cis-trans isomerism
conformation
cross-linkage
dipole-dipole attraction
entanglement
fiber
glass transition temperature
head-to-head linkage
head-to-tail linkage
hydrogen bonding
isomerism
isotactic
lamella
linear polymer
London forces
melt temperature
network polymer
pendant groups
spherulite
stereoisomerism
structural isomerism
syndiotactic
thermoplastics
thermoset plastics

**Questions**

1. Why do polymers, prepared by a free radical mechanism, tend to be branched?
2. Which polymer is softer, LDPE or HDPE? LDPE is low density polyethylene prepared by free radical polymerization and thus containing a considerable amount of branching. HDPE is high density polyethylene prepared by a Ziegler-Natta ionic polymerization. HDPE has no branching.

3. What is the difference between pendant groups and branching?

4. What is the difference between hydrogen bonding and cross-linking?

5. Do LDPE and HDPE differ by conformation or configuration?

6. Why do fibers need strong intermolecular forces?

7. Why are partially crystalline polymers translucent while amorphous polymers are clear?

8. How could one increase the clarity of a polymer that tends to crystallize?

9. Why doesn’t an amorphous polymer have a distinct melt temperature?

10. What physical changes in a polymer would you expect as it goes through its glass transition point?

11. What polymer is primarily dependent on London forces for intermolecular attraction?

12. What polymer is primarily dependent on dipole – dipole forces for intermolecular attraction?

13. What polymer is primarily dependent on hydrogen bonding for intermolecular attraction?
Polymer Solubility

As a family of compounds, polymers are not particularly soluble. It is probably easier to note characteristics that hinder as opposed to favor solubility.

1. **Cross-linkage eliminates solubility.**
2. **Crystallinity normally eliminates solubility.**
   
   *To dissolve a polymer with significant crystallinity either a very good solvent (see below) must be used or the mixture must be heated to near the crystal melt temperature.*
3. **Compact polymers if they dissolve, dissolve very slowly.**
   
   *Polymers with bulky pendant groups or short branches tend to dissolve more rapidly since solvent can more easily penetrate the solid polymer.*
4. **Polymer solubility decreases with increased molar mass.**

On the positive side the same rule of thumb applies to polymers as to the rest of chemistry.

*Like dissolves like.*

Polar solvents work best for dissolving polar polymers, while non-polar solvents work best for dissolving non-polar polymers. A solvent that is very effective in dissolving a polymer is referred to as a *good solvent* while one that does not dissolve, or marginally dissolves a polymer, is referred to as a *poor solvent.*

It may be of interest to examine the thermodynamics of solution. If a solid substance is to dissolve it must be accompanied by a negative change in the Gibbs free energy of solution, or

\[
\Delta_{\text{sol}}G = \Delta_{\text{sol}}H - T\Delta_{\text{sol}}S
\]

where \(\Delta_{\text{sol}}H\) is the enthalpy of solution and \(\Delta_{\text{sol}}S\) is the entropy of solution. Since \(T\) is always positive and \(\Delta_{\text{sol}}S\) is positive for the solution process, the entropy term \(\Delta_{\text{sol}}S - T\Delta_{\text{sol}}S\) must favor solution. The only question is the size of the term. For polymers the size of the entropy term is surprisingly small. Recall that entropy is a measure of disorder. Figure 3.1 (a) represents the disorder in a non-polymer solution whereas Figure 3.1 (b) represents that for a comparable polymer. Since polymer segments must be connected, the number of permutations, and thus the entropy, is dramatically reduced.

Consequently, the sign and magnitude of the free energy term is primarily dependent on the sign and magnitude of the enthalpy term. It has been shown that simple dispersion forces yield a positive enthalpy and no solution. For \(\Delta_{\text{sol}}H\) to be negative, strong intermolecular forces must be present. Thus for the free energy to be negative and for solution to occur there must be strong polar or hydrogen bonding between the solvent and the polymer.
The Solubility Parameter

The cohesive energy density (CED) is a measure of the energy necessary to completely remove a molecule from a pure solid or liquid. For a solvent this is approximately equal to the internal energy of vaporization, \( \Delta U \), per cubic centimeter.

\[
CED = \frac{\Delta_v U}{V} = \frac{J}{\text{mol cm}^3} = \frac{J}{\text{cm}^3}
\]

Here

\[
\Delta U = \Delta H - RT
\]

where \( R \) is the ideal gas constant and \( T \) the absolute temperature. Some representative solvent cohesive energy densities are appear in Table 3.1.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CED (J/cm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>219</td>
</tr>
<tr>
<td>Toluene</td>
<td>335</td>
</tr>
<tr>
<td>Acetone</td>
<td>396</td>
</tr>
<tr>
<td>Methanol</td>
<td>882</td>
</tr>
<tr>
<td>Water</td>
<td>2,294</td>
</tr>
</tbody>
</table>

* (Collins (1973)) Billmeyer

The CED’s for polymers are determined empirically. Table 3.2 lists a few examples.
The solubility parameter ($\delta$) is defined as the square root of the CED. As noted above the guiding rule in selecting a solvent for a polymer is

"Like dissolves like".

Consequently in selecting a solvent, choose one with a comparable solubility parameter. As a general rule of thumb,

$$|\delta_s - \delta_p| < 4.0$$

where the subscript $s$ stands for solvent and $p$ for polymer. Some typical solubility parameters appear in Table 3.3.

### Table 3.3 Selected Solubility Parameters for Solvents and Polymers ($J/cm^3^{1/2}$)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta_s$</th>
<th>Polymer</th>
<th>$\delta_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>14.8</td>
<td>Polyethylene</td>
<td>16.2</td>
</tr>
<tr>
<td>Toluene</td>
<td>18.3</td>
<td>Polystyrene</td>
<td>17.6</td>
</tr>
<tr>
<td>Acetone</td>
<td>19.9</td>
<td>Poly(vinyl acetate)</td>
<td>21.7</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>20.3</td>
<td>Poly(vinyl formal)</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>25.5</td>
<td>Poly(vinyl alcohol)</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>29.7</td>
<td>Nylon 66</td>
<td>27.8</td>
</tr>
<tr>
<td>Water</td>
<td>47.9</td>
<td>Polyacrylonitrile</td>
<td>31.5</td>
</tr>
</tbody>
</table>

When solvent mixtures are used the resultant solubility parameter is the weighted average of the individual solubility parameters. Since the solubility parameter is a function of the CED, which in turn is molar mass dependent, at least in theory, a polymer can be partitioned using a turbidimetric titration. In a turbidimetric titration a polymer is dissolved in a good solvent and the resultant solution titrated with a poor solvent. At the limit of solubility the solution turns turbid as the largest polymer molecules precipitate. After removal, more poor solvent is added and a second molar mass fraction is precipitated and removed. This process is continued until the entire polymer has precipitated.
Even though cross-linked polymers and polymers containing crystallites will not dissolve they will swell in a good solvent. This swelling separates polymer chains thus decreasing the intermolecular attraction of the polymer. This yields a softer more pliable polymer. An example is adding water to a dry sponge. A solvent used to soften a polymer is called a plasticizer. A commercial plasticizer must

- have a solubility parameter within 4.0 \((J/cm^3)^{1/2}\) of the polymer
- be small enough to be absorbed by the polymer
- have a very low volatility.

An example of a commercial plasticizer is dioctyl phthalate (DOP).

\[
\begin{align*}
\text{O} & \quad \text{CH}_3 \\
\text{C-CH}_2-\text{CH-CH}_2-\text{CH}_2-\text{CH}_3 \\
\text{O} & \quad \text{CH}_2 \\
\text{C-CH}_2-\text{CH-CH}_2-\text{CH}_2-\text{CH}_3 \\
\end{align*}
\]

**Dioctyl Phthalate (DOP)**

A plasticizer in essence decreases the glass transition point of a plastic.

**Polymer Solutions**

In solution the conformation of a linear polymer depends on the intermolecular attraction between the solvent and the polymer. In a poor solvent the polymer chains are more attracted to themselves than the solvent. In such a case, the polymer’s intramolecular attraction squeezes out the solvent thus producing a compact conformation (Figure 3.2 (a)). If, on the other hand, it is dissolved in a good solvent the conformation will maximize the solvent – polymer interaction. This will result in a very open conformation (Figure 3.2 (b)). The conformation of the polymer in solution impacts the viscosity of the solution where viscosity is defined as the resistance to flow. The more extended the polymer the greater the likelihood of entanglement. Thus a polymer should have a higher viscosity in a good solvent than a poor solvent. In cases where the mixing of polymer solutions is involved (e.g., the oil based paint industry), the use of a poor solvent requires less energy and as a result less cost.

![Figure 3.2](image-url)  
(a) Polymer in "Poor" Solvent  
(b) Polymer in "Good" Solvent
Viscosity

In Unit 1 it was noted that viscosity measurements of polymer solutions could be used to determine the *viscosity molecular weight*. The viscosity molecular weight lies between the number average and weight average molecular weights. Since viscosity molecular weights can be determined rather quickly and with a minimum cost, they are routinely used in approximate determinations. Since viscosity is not only solvent dependent but also temperature dependent, viscosity readings are made under constant temperature conditions. This is normally accomplished by placing a viscometer (Figure 3.3) in a constant temperature bath. Since viscosity readings are dependent on gravity flow of the solution through the viscometer, it is important to use the same volume of solution for each determination. A rubber bulb is used to push the solution from the bottom reservoir to the upper reservoir. For a determination, the flow time of the solution meniscus between the two lines is recorded. This is done for the pure solvent and for a number of dilutions of the polymer solution. The ratio of the time for a polymer solution over that of the solvent is known as the *relative viscosity* or

\[
\frac{t}{t_0} = \frac{\eta}{\eta_0} = \eta_r = \text{Relative Viscosity}
\]

![Figure 3.3 Ostwald Viscometer](Image)

The relationship between the relative viscosity and other viscosity terms is given in Table 3.4.

### Table 3.4 Common Viscosity Terms

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Viscosity</td>
<td>( \eta_r )</td>
<td>( \frac{t}{t_0} )</td>
</tr>
<tr>
<td>Specific Viscosity</td>
<td>( \eta_{sp} )</td>
<td>( \eta_r - 1 )</td>
</tr>
<tr>
<td>Reduced Viscosity</td>
<td>( \eta_{red} )</td>
<td>( \frac{\eta_{sp}}{C} )</td>
</tr>
<tr>
<td>Inherent Viscosity</td>
<td>( \eta_{inh} )</td>
<td>( \frac{\ln(\eta_r)}{C} )</td>
</tr>
<tr>
<td>Intrinsic Viscosity</td>
<td>( [\eta] )</td>
<td>( \lim(\eta_{red})<em>{c \to 0} ) or ( \lim(\eta</em>{inh})_{c \to 0} )</td>
</tr>
</tbody>
</table>
It is the intrinsic viscosity that we will be using to calculate the viscosity molecular weight. The second intrinsic viscosity relationship is obtained by using the Taylor expansion of the ln term and neglecting higher power terms as the concentration (in g/dL) approaches zero (c→0)

$$\lim_{c \to 0} \left\{ \frac{\eta_{inh} - \eta}{c} \right\} = \lim_{c \to 0} \left\{ \frac{\ln(\eta)}{c} \right\} \approx \lim_{c \to 0} \left\{ \frac{\eta_{sp} - \cdots}{c} \right\} = \lim_{c \to 0} \left\{ \frac{\eta}{c} \right\} = [\eta]$$

Thus, the intrinsic viscosity [\eta] can be determined by either extrapolating the reduced viscosity or the inherent viscosity back to zero concentration. Normally both extrapolations are used, see Figure 3.4.

**Concentration in g/dL**

**Figure 3.4 The Determination of Intrinsic Viscosity**

The Mark-Houwink equation relates the intrinsic viscosity and the viscosity molecular weight, $M_v$.

$$[\eta] = KM_v^a$$

where both $K$ and $a$ are empirically determined constants. $K$ is a proportionality constant whereas $a$ is dependent on the “goodness” of the solvent. A poor solvent will have an a-value of about 0.5 whereas a good solvent will have an a-value of about 1.0. Empirically determined $K$ and $a$-values are also available for the number average and the weight average molecular weights, see Table 3.5.

**Table 3.5 Mark-Houwink Parameters for Poly(Vinyl Acetate) in Acetone**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$K$</th>
<th>$a$</th>
<th>Type of Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>$5.6 \times 10^4$</td>
<td>0.625</td>
<td>Viscosity</td>
</tr>
<tr>
<td>30</td>
<td>$1.76 \times 10^4$</td>
<td>0.63</td>
<td>Number Average</td>
</tr>
<tr>
<td>30</td>
<td>$1.01 \times 10^4$</td>
<td>0.73</td>
<td>Weight Average</td>
</tr>
</tbody>
</table>

**Augmentation:** In polymer science reference is often made to $Q$-solvents and $\Theta$ $Q$-temperature. A $\Theta$-solvent is a poor solvent where the bulk conformation has not been altered by the solvent. The $\Theta$-temperature is the temperature at which a polymer of infinite molar mass will begin to precipitate (on cooling).
Polymer Emulsions

Emulsion polymers, or latexes, are of great economic importance. Among their attributes are

- they do not use volatile petroleum based solvents thus avoiding higher costs and environmental problems
- they generally have a much lower viscosity thus decreasing the cost of preparation
- they are easy to clean up after
- water is cheap

Before discussing the specifics of latexes, let us first consider emulsions in general.

An emulsion consists of an immiscible non-continuous phase dispersed in a continuous phase. Latexes contain a non-continuous hydrocarbon phase dispersed in a continuous aqueous phase. The non-continuous phase or micelle exists as tiny droplets surrounded by a surfactant. A surfactant is a “dysfunctional” molecule with both organic and ionic components. Since it is neither purely organic nor ionic, it concentrates at the organic/aqueous interface, see Figure 3.5.

![Figure 3.5 Stable Micelle](image)

The negative charge on the micelle is countered by the mono-charged cations in solution. In addition since all of the micelles have a negative charge they repel each other and thus stabilize the emulsion. If a multi-charged cation is added, the negative micelle charge is effectively cancelled allowing the micelles to coalesce and thus coagulate, see Figure 3.6.
The following ingredients are normally used in the preparation of latex. It should be noted that oxygen reacts with the free radical and terminates the polymerization reaction. All solutions must be de-oxygenated with nitrogen and the reaction must be run under a nitrogen atmosphere.

- Continuous Phase - water
- Non-continuous Phase - monomer (e.g., styrene, vinyl acetate, etc.)
- Surfactant - sodium dodecyl sulfate (sodium lauryl sulfate)
- Initiator – potassium persulfate
- Free Radical Transfer Agent – n-dodecyl mercaptan

The emulsion is prepared by stirring a water solution of monomer, surfactant and free radical transfer agent. Once the emulsion is established an initiator solution is added. The micelle initially contains mostly monomer with the initiator in the aqueous solution. Some initiator, with great difficulty, will cross into the micelle initiating the free radical polymerization reaction. The reaction will continue until all the monomer has been used. Without the free radical transfer agent the polymers can grow to extreme lengths. Extremely large polymers are very difficult to work with and thus expensive to handle.

**General References**


The Macrogalleria, Department of Polymer Science, University of Southern Mississippi, Web Page (www.psrc.usm.edu/macrog/)


**Important Terms**
Questions

1. Why aren’t cross-linked polymers soluble?
2. What does “like dissolves like” mean?
3. Why is the entropy of solution so low for polymers?
4. What conditions produce a high enthalpy of solution?
5. For polymers, why is the CED based on J/cm$^3$ rather than J/mol?
6. How does a plasticizer lower the glass transition temperature?
7. Why should a polymer’s viscosity be molar mass dependent?
8. In a latex paint what is the continuous phase and what is the non-continuous phase?
9. What is a better solvent for poly(vinyl acetate), n-hexane or acetone? Explain your answer.
Unit 4 – Rheology

Typical chemistry curriculums provide the basics for understanding polymer chemistry, morphology and solubility. The same cannot be said for polymer rheology. **Rheology** is a field of engineering which deals with material deformation and flow. Before proceeding it would be beneficial to examine some engineering basics.

**Hookean Behavior**

Hooke’s Law is covered in introductory physics. It states that if the end of a spring is displaced by a distance $x$ with the application of a force $F$, then

$$F = -kx$$

where $k$ is the force constant of the spring. If polymers are being considered rather than a spring the amount of polymer must be quantified. *Are we talking about the stretching of a rubber band or an inner tube?* This ambiguity can be address by considering the force per unit area or stress ($s$). Engineers refer to the resultant elongation as strain ($\gamma$). Thus, in engineering stress and strain are related by

$$s = E \gamma$$

where $E$ is Young’s modulus of elasticity. A polymer that obeys Hooke’s Law is said to have **Hookean** behavior, which yields a linear relationship between stress and strain. The Hookean spring is represented in Figure 4.1.

![Figure 4.1 Hookean Spring and Stress-Strain Plot](image)

**Newtonian Dashpot**

Engineers represent the flow behavior of a material with a **Newtonian dashpot**, see Figure 4.2. The dashpot is a cylindrical tube capped at one end. It is fitted with a piston (or plunger) that either does not fit tightly or alternatively has a hole. As stress is applied, fluid moves slowly into or out of the enclosed volume. The stress remains constant as the strain increases. A tube of toothpaste could be considered a Newtonian dashpot where squeezing the tube represents pushing the plunger.
the viscoelastic behavior of polymers can be modeled by combinations of Hookean springs and Newtonian dashpots. We shall examine two simple models. In the first the Hookean spring and the Newtonian dashpot are combined in series. This is known as a Maxwell model, see Figure 4.3.

Maxwell behavior is very time dependent. If the stress is applied and released quickly relative to the movement of the dashpot, the system behaves simply as a Hookean spring and returns to its original position. As such this system has memory. This is what happens when bouncing a silly putty ball or stretching and releasing a rubber band. If, however, there is time for dashpot movement, on release, the system does not return to its original position. Here the system does not have memory. The polymer is said to creep or experience creepage. The time for dashpot motion is very short for silly putty since it can be easily deformed by hand. On the other hand it is much longer for a rubber band. Nevertheless if a rubber band is stretch around a book or the back of a chair over night, it will not return to its original length when released and as such it too has experienced creepage.
The second or Voigt-Kelvin model for viscoelastic behavior has the Hookean spring and the Newtonian dash-pot in parallel, see Figure 4.4.

The Hookean spring, in this viscoelastic model, in time returns the model back to its original length. This restoring force is called memory, see below. Objects, that normally exhibit Voigt-Kelvin behavior, are pillows and seat cushions.

The above models were considered to facilitate discussion concerning viscoelastic behavior. While we will use them in a qualitative sense in engineering they can be incorporated into a very elaborate and complex system that quantitatively represents the behavior of a particular polymer.

**What is Memory?**

Viscoelastic *memory* is permanent or near permanent linkages that bring the material back to its original shape after segmental motion has occurred. The most common linkages are cross-linkage, entanglement, and crystallite formation. These linkages are noted as black circles in Figure 4.5.
While cross-linkage and crystallite formation tend to be permanent under ambient conditions, entanglement is not. With molecular vibration, entangled molecules under stress and time can untangle. This would be an example of creepage at the molecular level.

General References


*The Macrogalleria*, Department of Polymer Science, University of Southern Mississippi, Web Page (www.psrc.usm.edu/macrog/)


Important Terms

creep
creepage
Hookean behavior
Maxwell behavior
memory
Newtonian behavior
Newtonian dashpot
rheology
strain
stress
stress-stain behavior
viscoelastic
Voigt-Kelvin model

Questions

1. What is the difference between stress and force? Why is stress used in polymer science?
2. Describe the behavior of a Newtonian dashpot.
3. Fully describe what happens to a polymer that exhibits Maxwell behavior. In answering this question consider both rapidly and slowly applied stress.

4. Fully describe what happens to a polymer that exhibits Voigt-Kelvin behavior. In answering this question consider both rapidly and slowly applied stress.

5. What “real world” products exhibit viscoelastic behavior? Is their behavior Maxwell or Voigt-Kelvin?

6. What is the difference between rheology and morphology?
Polymer technology is as varied as polymer properties and applications. In this Unit we shall examine some of the more common processes by which synthetic polymer products are prepared. Let us begin with the polymerization process.

**Industrial Polymerization**

Polymers can be prepared as a pure polymer, as a solution, or as we observed in the last Unit, as an emulsion. Pure polymers can be prepared in a batch or continuous process. In the *batch process* the ingredients are added to some type of vessel and the reaction initiated. Usually the reaction must be carefully monitored and controlled. Since free radical reactions are exothermic, heat may need to be removed. In step growth reactions heat may be required to drive off production generated water or other bi-products. Generally air or oxygen must be excluded. After the batch is completed it can be used directly or converted into chips or pellets for subsequent use. In the *continuous process* the ingredients are continuously fed into a reactor and polymer continuously produced. Here again the polymer can be used directly or converted into chips or pellets.

Solution and emulsion polymers can be prepared by either a batch or continuous process. The resultant polymer may be used as an emulsion or separated from the liquid phase. It is important to realize that the polymerization process affects molar mass, branching, and possibly the stereo specificity of the resultant polymer. Often the applications dictate the polymerization process.

**Polymer Additives**

Polymer *additives* may be dictated by aesthetics, cost or use. Colorants are common additives. *Colorants* are materials that are used to color the polymer. The colorant must be miscible with the polymer. Non-polar colorants are used with non-polar polymers while polar colorants are used with polar polymers. *Often “dye sites” are incorporated into the polymer*. An example is aminoterephthalic acid which is added to the terephthalic acid in the condensation polymerization polyester. The amino group provides dye sites comparable to those found in wool and silk. Other common additives are *antioxidants*, *UV stabilizers*, *flame-retardants*, *fillers* and *composites*.

While fillers can be added to decrease costs, most fillers (or reinforcements) impart positive properties to the product. Common fillers are wood flour, fibers such as cotton, glass, or graphite, carbon black, sand, glass spheres, metallic dust, alumina, and pulverized limestone. Additives such as carbon black and metallic dust dissipate heat and electrical charge while others impart strength. Polymers with strength enhancing additives are called *composites*.

Composites can be one, two, or three-dimensional. While fibers are usually one-dimensional, glass spheres are three-dimensional. In addition fibers can be aligned or woven into a two-dimensional or three-dimensional arrays.

**Fabrication Techniques**

Elastomers are often prepared by producing covalent cross-links between polymer molecules. *Vulcanized rubber* is produced when natural rubber is heated with sulfur, etc. The sulfur produces covalent bridges between polymer molecules. The more sulfur the more linkages and the more rigid the resultant polymer. In the case of tires, a mixture of rubber, carbon black, and sulfur are injected into a mold containing the reinforcing mesh (belts) and heated. Other materials can also be used to cross-link polymers.

Let us now examine some common fabrication techniques.
**Melt Extrusion**

In the melt extrusion process, polymer chips or pellets are heated and compressed to form a high-pressure melt, see Figure 5.1. The chip is fed through the extruder via a rotating auger. As the polymer is pushed through, the extruder is heated to its melt temperature. As the polymer moves through the displacement of the auger blades decrease thus increasing the pressure. Normally, heated polymer must be maintained in an inert nitrogen atmosphere to inhibit decomposition.

![Figure 5.1 Melt Extrusion](image)

**Extrusion Film**

The extrusion film process is used to produce a cylindrical film tube, see Figure 5.2. The extruder melt is fed through a circular orifice while air is blown through the center. In operation the tube is pulled upward by the drive rollers. By the time the tube has reached the top the polymer has solidified. After the drive rollers, the tube can be cut to produce a sheet polymer or rolled as a tube for subsequent processing into trash bags, *etc*.

![Figure 5.2 Extrusion Film](image)

**Fiber Formation**
In fiber extrusion, a polymer is extruded through a plate called a spinneret. The spinneret contains a large number of very small shaped holes; see Figure 5.3. The filaments are grouped together into a fiber. At this point the molecules in the fibers have no directionality and as such are weak and stretchy. To align the molecules, the fiber is heated to near its melt temperature and stretched. The stretching is accomplished by passing the hot fiber over a set of rollers, the second of which is rotating more rapidly than the first. After cooling the fiber can be passed through a solution for surface treatment.

![Figure 5.3 Fiber Formation](image)

The fibers can be used as is or further processed. Synthetic fibers can be used in lieu of or blended with natural fibers. However for this to occur the fiber must be textured and cut. The texturing is accomplished by crimping. The synthetic fiber is again heated to near its melt temperature and then passed through a crimping unit where a small, tight wave is imparted to the fiber. The fiber is then cut to the appropriate length for the natural fiber (i.e., wool for nylon and cotton for polyester). The resultant fibers can be spun directly into a thread or blended with natural fiber, before spinning.

**Injection Molding**

In injection molding the melted polymer is forced into a mold and allowed to cool. Subsequently the mold is opened and the plastic object removed.

![Figure 5.4 Injection Molding](image)

**Pultrusion Process**

The pultrusion process is used to coat or embed a fibrous material with polymer. It can be used to produce fiberglass rods or for coating a wire with insulation.
Vacuum Thermoforming

Vacuum thermoforming is used to prepare a multitude of products from bottles to dishpans. The objects normally start as molded precasts. The heated precast is placed in or above a mold and a vacuum is used to expand the precast into the mold.

Foams

Foams are prepared by one of two basic processes. In the first a volatile compound, a foaming agent, is dissolved in the polymer melt under pressure. When the pressure is released the volatile compound vaporizes producing a foam. The foam is injected into a mold where it solidifies. In the past Freon was used as a foaming agent. Its use has now been banned for environmental reasons. It has been replaced by other compounds such as carbon dioxide.

In the second process the foaming agent is produced by a polymerization process. This is the case with polyurethane foams. Urethanes are produced by the reaction of a diisocyanate and a glycol. If excess diisocyanate is present it breaks down to produce carbon dioxide, the foaming agent. See Unit 6.

General References


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Important Terms

additives
batch process
chips
colorants
composites
continuous process
crimping
extrusion film
fiber
foam
foaming agent
injection molding
melt extrusion
pellets
pultrusion process
spinneret
vacuum thermoforming
vulcanized rubber

Questions

1. What is the difference between batch and continuous processes?
2. List and describe some polymer products that contain additives.
3. Why can’t thermoset polymers be pelletized prior to use?
4. Commercially how should each of the following products be prepared?
   a) trash bags
   b) handles for graphite golf clubs
   c) belts for tires
   d) pail
   e) beer cooler
   f) polymer coated cable
   g) contact lenses
   h) clothing
   i) pillow
Unit 6 – Some Commercial Polymers

There are hundreds of polymers, copolymers and polymer blends on the market. In this Unit we will examine some of the more common polymers and correlate their structure with their use. Before proceeding however, let us reexamine some polymer properties.

1. A polymer’s physical characteristics are a function of its glass transition temperature (T$_g$). Specifically,
   • polymers below T$_g$ tend to be hard and brittle.
   • plasticizers can effectively lower T$_g$.
   • stressed polymers above T$_g$ creep unless the adjacent polymer chains are periodically locked together. This lockage can be a result of entanglement, crystallinity, or cross-linkage. These locks give the polymer memory.

2. With increasing molar mass a polymer’s
   • solubility decreases.
   • tensile (pulling) strength increases.
   • ability to withstand abuse, its toughness, increases.
   • viscosity increases and as a result, increasing processing cost.

3. Intermolecular attraction
   • increases with molecular alignment.
   • decreases with pendant groups and/or branching.

4. Crystalline polymers
   • are insoluble
   • contain amorphous regions between crystallites.
   • are translucent since two phases are present. (Amorphous polymers are clear.)
   • have a distinct melting point or temperature.

5. Flexibility of amorphous polymers
   • increases and density decreases with the presence of pendant groups.
   • is enhanced by methylene and oxygen links.
   • is decreased with p-phenylene, amide, carbonyl, and sulfone stiffening groups.

6. Elastomers contain two primary components
   • an amorphous chain containing flexible links such as methylene and oxygen
   • a lock to periodically fasten adjacent chains together such as entanglement, crossing-linkage and crystallites.
Consider the following polymers.

**Polyethylene** (LDPE, HDPE, UHMWPE)  
Monomer: ethylene

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

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Polymerization</th>
<th>Morphology</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>amorphous</td>
<td>free radical</td>
<td>branched</td>
<td>thermoplastic</td>
</tr>
<tr>
<td>linear</td>
<td>Ziegler-Natta</td>
<td>highly crystalline fiber</td>
<td></td>
</tr>
</tbody>
</table>

Melting Temperature: 137°C  
Glass Transition Temperature: -125°C

Polyethylene was originally prepared by a free radical process. This product was highly branched and as such had a relatively low density and strength. While in many applications the branched nature of the polymer would be a disadvantage, that is not the case with films. In the extrusion film process the polymer melt is stretched in two directions forcing the polymer into a flat, intertwined conformation. Low-density polyethylene (LDPE) is still used for plastic bags and sheets.

Linear polyethylene can be prepared by ionic polymerization processes. Since linear molecules pack more closely, the resultant polymer has a higher density and when aligned, linear strength. Most high-density polyethylene (HDPE) is prepared using the Ziegler-Natta catalytic process. Linear polyethylene crystallizes easily thus producing a translucent polymer. High-density polyethylene is injection molded into durable products such as storage containers and wastebaskets. While the melt temperature of HDPE is approximately 137°C, the polymer begins to deform at about 100°C. That means that HDPE containers are neither microwave oven nor dishwasher proof.

Fibers require strong intermolecular attraction and as a result, most commercial polymers utilize hydrogen bonding. However, even with relatively weak London bonding, strong fibers can be produced if the molecules are very long. Ultra high molecular weight polyethylene (UHMWPE) is now being prepared with molar masses in the 200,000 to 500,000 range. If sufficiently aligned, extremely strong fibers can be produced. Such fibers are now being used in the production of bulletproof vests.

**Polypropylene** (PP)  
Monomer: propylene

\[ \left[ CH_2-CH-CH_3 \right]_n \]

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Polymerization</th>
<th>Morphology</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear (isotactic)</td>
<td>Ziegler-Natta</td>
<td>highly crystalline fiber, thermoplastic</td>
<td></td>
</tr>
</tbody>
</table>

Melting Temperature: 174°C  
Glass Transition Temperature: -17°C (isotactic)

Isotactic polypropylene has several advantages over polyethylene. First, with a melt temperature of 174°C, polypropylene containers are both microwave oven and dishwasher proof. Most “refrigerator” containers are made from polypropylene. Polypropylene also has many medical and scientific uses since it can be sterilized. However, with a glass transition temperature of -17°C polypropylene containers can crack under freezer conditions. To minimize this defect, small amounts of ethylene are sometimes added as a copolymer with the propylene to lower the glass transition temperature.

Isotactic polypropylene can also be used as a fiber. For many applications it’s decreased strength, relative to nylon, is more than compensated for by its dye ability, ease of production and impermeability to water. Polypropylene is used for indoor-outdoor carpeting.
Polycyanoacrylates (Super Glue ®, etc.)

\[
\begin{align*}
H & \quad \text{CN} \\
C & \quad \text{O} \\
H & \quad \text{O} \\
R = \text{CH}_3, \ C_2\text{H}_5, \text{etc.}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Polymerization</th>
<th>Morphology</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>anionic</td>
<td>linear</td>
<td>adhesive</td>
</tr>
</tbody>
</table>

A thin coating of the monomer is spread on the surfaces to be glued. The presence of both a cyano and an ester group on each monomeric unit produces strong adhesion to the surface and moisture initiates the polymerization reaction.

Poly(vinyl acetate) (PVAc)

Monomer: vinyl acetate

\[
\begin{align*}
\left[ \text{CH}_2=\text{CH} \right]_n \\
\text{O} \quad \text{C} \quad \text{CH}_3 \\
\text{O}
\end{align*}
\]

Melting Temperature: None  
Glass Transition Temperature: 32°C

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Polymerization</th>
<th>Morphology</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>free radical</td>
<td>amorphous</td>
<td>adhesive, chewing gum, polyvinyl alcohol</td>
</tr>
</tbody>
</table>

Poly(vinyl acetate) can be prepared by either the direct polymerization of the monomer in a batch or continuous flow process or by emulsion polymerization. Its low glass transition temperature eliminates its use as a thermoplastic. However, low molar mass PVAc works well as an adhesive either in the form of an Elmer’s Glue® latex or as a hot-melt.

Poly(vinyl acetate) has been very important in the production of latex paint. Early latex paints were primarily PVAc latexes with white filler such as lime (CaCO$_3$) and colorant. With acrylic latexes, a partially saponified PVAc is used as an emulsifier, see *Macrogalleria*, [www.psrc.usm.edu/macrog/](http://www.psrc.usm.edu/macrog/).

The major use of poly(vinyl acetate) is for the production of poly(vinyl alcohol), see below.

Poly(vinyl alcohol) (PVA)

Monomer: NA (made by the alcoholysis of PVAc)

\[
\begin{align*}
\left[ \text{CH}_2=\text{CH} \right]_n \\
\text{OH}
\end{align*}
\]
Poly(vinyl alcohol) is a water soluble polymer. It dissolves slowly in cold water but more rapidly upon heating. A major use of PVA is as a thickening agent for emulsions and suspensions. Poly(vinyl alcohol) is also spun into a fiber and then partially converted to poly(vinyl formal) (PVF) by treatment with sulfuric acid and formaldehyde. The conversion of approximately 30% of the PVA to PVF makes the resultant polymer highly absorbent but insoluble.

Poly(vinyl chloride) is a very versatile plastic. It is used for plumbing and numerous “vinyl” products such as vinyl flooring, siding, table cloths, shower curtains, etc.

Pure PVC is not stable at elevated temperatures and therefore requires stabilizing additives. Normally PVC products contain a plasticizer. Rigid PVC contains about 10% plasticizer while flexible PVC contains up to 40% plasticizer. The plasticizer is often a diethylene glycol – adipic acid polyester. Such additives make PVC that is resistant to cracking for many years.

### Poly(vinyl alcohol)

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Polymerization</th>
<th>Morphology</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>NA</td>
<td>amorphous</td>
<td>adhesive, water soluble thickening agent</td>
</tr>
</tbody>
</table>

Since vinyl alcohol is unstable and isomerizes to acetaldehyde, poly(vinyl alcohol) must be synthesized by an indirect method. Poly(vinyl alcohol) is prepared by alcoholysis of poly(vinyl acetate).

\[
\left[\text{CH}_2\text{CH}_2\right]_n + n \text{CH}_3\text{OH} \rightarrow \left[\text{CH}_2\text{CH}_2\right]_n + n \text{CH}_3\text{COCH}_3
\]

\[
\begin{array}{c}
\text{O} \\
\text{C} \equiv \text{O} \\
\text{CH}_3
\end{array}
\]

\[
\begin{array}{c}
\text{O} \\
\text{CH}_3
\end{array}
\]

Poly(vinyl chloride) is a very soluble polymer. It dissolves slowly in cold water but more rapidly upon heating. A major use of PVA is as a thickening agent for emulsions and suspensions. Poly(vinyl alcohol) is also spun into a fiber and then partially converted to poly(vinyl formal) (PVF) by treatment with sulfuric acid and formaldehyde. The conversion of approximately 30% of the PVA to PVF makes the resultant polymer highly absorbent but insoluble.

### Poly(vinyl chloride) (PVC)

Monomer: vinyl chloride

\[
\left[\text{CH}_2\text{CH}_2\right]_n
\]

Melting Temperature: None

Glass Transition Temperature: 84°C

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Polymerization</th>
<th>Morphology</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>free radical</td>
<td>amorphous</td>
<td>thermoplastic - sheet, floor covering, seat covers, food wrap, wire covering</td>
</tr>
</tbody>
</table>

### Polystyrene (PS)

Monomer: styrene

Melting Temperature: Decomp. 150°C

Glass Transition Temperature: 85°C

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Polymerization</th>
<th>Morphology</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>NA</td>
<td>amorphous</td>
<td>adhesive, water soluble thickening agent</td>
</tr>
</tbody>
</table>
Polystyrene is a rather inert, inexpensive polymer that is easily injection molded. It is used for appliance cases, toys, and molded parts for auto interiors. While easily produced, polystyrene products tend to be brittle and UV sensitive. Polystyrene products were very common during the infancy of the synthetic polymer era. Their lack of durability helped give plastics a negative image.

The polystyrene melt is also mixed with a foaming agent under pressure. When the pressure is reduced, a molten foam is produced which can be used for injection molding objects such as Styrofoam® cups or cast into rigid foam sheets.

Polystyrene is an important cross-linking agent. See Polyester below.

**Poly(methyl methacrylate) (PMMA)**

Monomer: methyl methacrylate

Melting Temperature: None

Glass Transition Temperature: 120°C

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Polymerization</th>
<th>Morphology</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>free radical</td>
<td>amorphous</td>
<td>clear thermoplastic, acrylic paints</td>
</tr>
<tr>
<td>(syndiotactic)</td>
<td>Ziegler-Natta</td>
<td>syndiotactic</td>
<td>toys, appliance cases, foam insulation</td>
</tr>
</tbody>
</table>

Poly(methyl methacrylate) (PMMA) is an extremely clear strong amorphous thermoplastic. It is used as a glass replacement (Plexiglas® and Lucite®). PMMA is much clearer than glass and has been used for windows as thick as 13 inches. It is also used with poly(vinyl acetate) for acrylic latex paints.

**Teflon®, Polytetrafluoroethylene (PTFE)**

Monomer: tetrafluoroethylene
Polytetrafluoroethylene (PTFE) exists as long $sp^3$ hybridized chains of carbon saturated with fluorine atoms. The carbon–fluorine bonds are very strong and the carbon-to-carbons bonds are almost totally shielded by the fluorine atoms. PTFE has a very low coefficient of friction. Commercial PTFE has a number-average molecular weight of several million. This makes polytetrafluoroethylene extremely inert.

In forming articles of PTFE the cold powder is pressure molded to the proper shape and then heated to its melt temperature. PTFE’s ability to cold flow under pressure is utilized in Teflon® tape, used as a pipe sealant and as a lubricant. PTFE is used for nonlubricated bearings, gaskets, valve and pump packing. It has a low dielectric constant and finds many uses in electrical components. Linearly aligned PTFE is now being used as fibers.

**Polyurethane**

Monomers: a di-isocyanate and a di-alcohol

$$\left[ \begin{array}{c}
\text{O} \\
\text{H}
\end{array} \text{-C-N} \begin{array}{c}
\text{H}
\end{array} \right]_n$$

Melting Temperature: NA Glass Transition Temperature: NA

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Polymerization</th>
<th>Morphology</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>step-growth</td>
<td>crystalline</td>
<td>sealant, fibers, foam, wire covering</td>
</tr>
</tbody>
</table>

Linear polyurethanes are produced by the reaction of a di-isocyanate and a di-alcohol. Consider the following example.

$$n \text{ O}=\text{C}=\text{N}-\text{N}=\text{C}=: + n \text{ HO-CH}_2\text{-CH}_2\text{-OH}$$

$$\left[ \begin{array}{c}
\text{O} \\
\text{H}
\end{array} \text{-C-N} \begin{array}{c}
\text{H}
\end{array} \right]_n$$

If an elastomer is desired a polyether or something comparable can be used instead of the di-alcohol. Consider the following.
Since both methylene and oxygen are flexing groups, the polyether is very flexible. When this is coupled with the easily crystallizable polyurethane blocks, the two elastomer components are present (i.e., flexible chain and locks). Spandex® is a urethane - polyether blocked polymer.

Cross-linking occurs when tri- or poly-alcohols or polymeric units are used. As a coating, polyurethane is impact resistant and resists abrasions. It is relatively inert to solvents and weathering.

Polyurethanes are commonly used in the form of foams. To produce foam excess di-isocyanate is used. When water is present

\[ RNCO + H_2O \rightarrow RNH_2 + CO_2 \]

Carbon dioxide serves as a foaming agent. Supplemental foaming agents are often used. If flexible foam is desired, di-alcohol polyethers can be used. Flexible foams are used for pillows and cushions. For rigid foams poly-alcohols are used. Rigid foams are routinely used for insulation such as RMAX®.

**Polyester poly(ethylene terephthalate) PET or PETE**

Monomers: ethylene glycol and p-dimethyl terephthalate

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{CH}_2-\text{CH}_2-\text{O} = \text{C} < \text{C} - \text{C} \\
\text{CH}_2-\text{CH}_2-\text{O} = \text{C} < \text{C} - \text{C}
\end{array}
\]

Melting Temperature: 265°C  
Glass Transition Temperature: 74°C

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Polymerization</th>
<th>Morphology</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>step-growth</td>
<td>crystalline</td>
<td>fibers, thermoplastic</td>
</tr>
</tbody>
</table>

Aliphatic polyesters have too low a melting point to be useful for fibers. (They would melt during ironing.) Aromatics in the polymer chain not only stiffen the polymer, they raise the melting point. (See Nomex® and Kevlar® below.) The introduction of the p-terephthalate group increases the melting point to the range necessary for fibers.

You may have noticed that the methyl ester of p-terephthalic acid was used rather than the dicarboxylic acid. The use of esters rather than carboxylic acid is fairly common in step growth polymerization for two reasons, both of which are important here. First of all esters are usually much easier to purify than carboxylic acids. Impurities often interfere with the polymerization process and as a result decrease the degree of polymerization. For useful polyesters, a high degree of polymerization is required.

Second, the free energy of the esterification reaction favors the reactants rather than the products. This is not good for the production of polyester. By using an ester the polymerization reaction is transesterification rather than esterification. The transesterification reaction involves the equilibrium interchange of alcoholic groups in the ester

\[
\begin{array}{c}
\text{R} - \text{C} - \text{O} - \text{R'} + \text{R''} - \text{O} - \text{H} \rightleftharpoons \text{R} - \text{C} - \text{O} - \text{R'} \rightleftharpoons \text{R} - \text{C} - \text{O} - \text{R''} + \text{R'} - \text{O} - \text{H} \\
\text{O} \cdot \text{H} \\
\text{R''}
\end{array}
\]

The reaction is run at a sufficiently high temperature to vaporize the methanol (R’OH) and thus shift the equilibrium to the right. For more details see (www.psrc.usm.edu/macrog/petsyn.htm).
Poly(ethylene terephthalate) or polyester is used in fabrics blended with cotton, as a thermoplastic in MYLAR® sheets, and clear plastic soda bottles and other containers. Unsaturated polyesters are involved in most fiberglass production to date. Specifically, the continuous phase for the production of fiberglass products can be prepared with a low molecular weight unsaturated polyesters blended with a vinyl monomer(s) such as styrene and/or methyl methacrylate. The low molecular weight unsaturated polyester can be prepared from maleic anhydride and a glycol.

\[
\text{O} \quad + \quad n \text{HO-CH}_2\text{-CH}_2\text{OH} \quad \rightarrow \quad \left[ \text{C} \quad \text{HC-CH-C} \quad \text{O-CH}_2\text{-CH}_2\text{-O} \right]_n
\]

The vinyl monomer is used for cross-linking. Such a reaction, yield one carbon-carbon double bond per monomeric unit. With such a high concentration of double bonds, the cross-linked product would be very hard and brittle. It can be made less brittle by replacing some-to-much of the maleic anhydride with a saturated anhydride such as phthalic anhydride. Typically a one-to-one blend is used. Overall, the blend is about 60% polyester and 40% vinyl monomer.

The cross-linking polymerization can be initiated with a free radical initiator such as methyl ethyl ketone peroxide (MEKP). MEKP is prepared from methyl ethyl ketone and hydrogen peroxide in a 93% dimethyl phthalate solution.

\[
\begin{align*}
2 \quad \text{CH}_3\text{-C-C}_2\text{H}_5 + \quad \text{HO-\text{OH}} \quad \rightarrow \quad \text{CH}_3\text{-C-O-O-C}\text{-CH}_3 \\
\quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\
\text{MEKP}
\end{align*}
\]

**Nylon 6.6**

Monomers: adipic acid and hexamethylenediamine

\[
\left[ \text{NH-(CH}_2\text{)_6-NH-C-(CH}_2\text{)_4-C} \right]_n
\]

Melting Temperature: 280°C Glass Transition Temperature: 50°C

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Polymerization</th>
<th>Morphology</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>step-growth</td>
<td>crystalline</td>
<td>fibers, thermoplastic</td>
</tr>
</tbody>
</table>

Nylon is a name coined by Dupont for its step growth polymer formed from hexamethylenediamine and adipic acid. Since the name was not registered it has evolved to a general term for polyamides. Polyamides can be separated into two categories, the alkyiamides and the aramides (aromatic amides). The alkyiamides are named according to their constituent monomers. If two numbers follow the word nylon, the first gives the number of carbons in the di-amine and the second the number of carbons in the di-carboxylic acid. Thus with nylon 6,6 both the di-amine and the di-carboxylic acid have six carbons. If the word nylon is followed by only one number the polymer is formed from a single cyclic amino acid, a lactam. Thus, nylon 6 is formed from caprolactam (see below). The aramides are composed primarily of phenylene groups that give the resultant polymers some unique properties. See Nomex® and Kevlar® below.

The first step in the manufacture of nylon 6,6 is the production of the 1:1 salt of adipic acid and hexamethylenediamine. When the two components are dissolved in methanol and mixed, the salt precipi-
tates. Nylon 6,6 is produced by dissolving the 1:1 salt in water with a small amount of acetic acid. The acetic acid is a terminating group and is used to regulate the average molar mass of the polymer. Originally the solution was pumped into an autoclave where the temperature was raised to approximately 275°C and maintained under a pressure of 250 psi. Nitrogen was pumped through the autoclave to flush out the water vapor and force the reaction to completion. Nylon 6,6 is now prepared primarily by a continuous flow process.

Hydrogen bonding and the resulting crystallization produce an incredibly strong fiber. Nylon 6,6 fiber is used for clothing, carpeting, rope and numerous other products. Nylon 6,6 is also used as a tough durable thermoplastic.

**Nylon 6**
Monomer: caprolactam

\[
\begin{align*}
\text{Nylon 6 Dimer} & \quad \left[ \text{NH}-(\text{CH}_2)_6-\text{NH}-\left(\text{CH}_2\right)_4-\text{C}\right] \\
\text{Nylon 6,6 Monomeric Unit} & \quad \left[ \text{NH}-(\text{CH}_2)_6-\text{NH}-\left(\text{CH}_2\right)_4-\text{C}\right]
\end{align*}
\]

Nylon 6 was developed and marketed in Europe to circumvent the Dupont patent on nylon 6,6. Comparing the nylon 6 dimer with the nylon monomeric unit it is not surprising that their properties are very similar.

Nylon 6 is prepared by the step growth polymerization of caprolactam.
**Nomex®**  
Monomers: isophthaloyl chloride and m-phenylenediamine  

Melting Temperature: 500°C  
Glass Transition Temperature: °C  

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Polymerization</th>
<th>Morphology</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>step-growth</td>
<td>crystalline</td>
<td>fibers</td>
</tr>
</tbody>
</table>

Nomex®, like all polyamides, has strong hydrogen bonding and thus forms very strong fibers. However being composed primarily of meta-phenylene groups it has an extremely high melt temperature. Nomex® clothing is used by firemen, oil refinery workers, racecar drivers, and others who have the potential of coming in contact with fire.

**Kevlar®**  
Monomers: Terephthaloyl chloride and p-phenylenediamine  

Melting Temperature: decompose > 500°C  
Glass Transition Temperature: °C  

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Polymerization</th>
<th>Morphology</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>step-growth</td>
<td>crystalline</td>
<td>fibers</td>
</tr>
</tbody>
</table>

Kevlar®, like Nomex®, has a very high melt temperature. In addition Kevlar® with its p-phenylene groups is sterically forced to take a linear conformation. The combination of high melt temperature, strong hydrogen bonding, and a linear conformation makes Kevlar® fibers extremely strong. It has been used for bulletproof vests, brake friction parts, ropes, and cables. It is used as a composite fiber in tires and in structural elements.

**Epoxy resins**  
Monomers: a di-epoxide and a di-alkylamine
<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Polymerization</th>
<th>Morphology</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>cross-linked</td>
<td>step-growth</td>
<td>amorphous</td>
<td>resin</td>
</tr>
</tbody>
</table>

Epoxy resins come in two containers. The first contains a low molar mass polymer containing epoxy groups on each end. The second is an alkyl di-amine. On mixing a single di-amine bonds with four epoxy groups resulting in a cross-linked or network polymer.

General References


[The Macrogalleria](http://www.psrc.usm.edu/macrog/), Department of Polymer Science, University of Southern Mississippi, Web Page


Important Terms

epoxy resins
HDPE
Kevlar®
LDPE
Nomex®
Nylon
Nylon 6
Nylon 6,6
PET or PETE
PMMA
poly(ethylene terephthalate)
poly(methyl methacrylate)
poly(vinyl acetate)
poly(vinyl alcohol)
poly(vinyl chloride)
polyester
polyethylene
polypropylene
polystyrene
polytetrafluoroethylene
polyurethane
PS
PTFE
PVA
PVAc
PVC
Teflon®
UHMWPE

Questions

1. Why can ultra high molecular weight polyethylene be used for bulletproof vests?
2. Which fiber would have the highest tensile strength, polypropylene or nylon and why?
3. When does a crystalline polymer become an elastomer?
4. Why does intermolecular attraction increase with alignment?
5. Which is more flexible amorphous or isotactic polypropylene?
6. Why is the poly(vinyl alcohol) – poly(vinyl formal) copolymer fiber better for diapers than pure poly(vinyl alcohol) fibers?
7. Why is PMMA a better glass substitute than PET?
8. Why is Kevlar® a better bulletproof fiber than Nomex®?
Polymer chemistry is not a spectator sport. The learning process can be greatly enhanced if laboratory work is included. In this Unit we shall give a number of experiments that can be performed with a minimum of equipment and danger. We have selected the poly(vinyl acetate) – poly(vinyl alcohol) – poly(vinyl formal) preparations and experiments due to the benign nature of the reactant and product compounds. There are two exceptions, vinyl acetate and formalin. The MSDS forms for these chemicals in particular should be examined before use. Both of these chemicals should only be used in a well-ventilated hood. Formalin can be avoided by skipping the preparation of poly(vinyl formal). Vinyl acetate is a suspected carcinogen.

I would like to thank my two senior research students (Spring 2002) Erica Kiss and Sidney Hankerson for their effort in refining the following laboratory experiences.
The Emulsion Polymerization of Vinyl Acetate

Purpose: This exercise is designed to give the student experience in preparing an emulsion polymer.

Reference Reading:
- Poly(vinyl acetate): page 43
- Emulsion polymerization: pages 27-28

Two approaches have been used.
A. Team or Small Group Preparation
B. Pilot Plant Class Preparation

A. Team or Small Group Preparation

Equipment Setup: *This reaction should be conducted in the hood.*
- A one-liter reactor (4 opening head) with a stirrer (center neck), a Snyder, floating ball, reflux column, and two septa. The septa are perforated for a thermometer and a syringe needle. A heating mantle is used to initially heat the flask to 50°C. One also needs an ice bath and long syringe needles (10 and 25 cm), a micro-pipette, a 25 mL graduated cylinder for deoxygenating the persulfate solution, and a 30 mL syringe for the persulfate solution. The system is deoxygenated using nitrogen and maintained under a nitrogen atmosphere.

Chemicals:
- 500 mL of distilled water, 110 mL of vinyl acetate, 0.50 g of sodium lauryl sulfate, and 0.625 g of potassium persulfate dissolved in 20 mL of water (deoxygenated), and 1.5 mL of n-dodecyl mercaptan, a free-radical transfer agent.

Procedure:
1) Add 0.625 g of potassium persulfate to a 25 mL graduated cylinder and add 20 mL of water. Using a syringe needle, bubble nitrogen into the solution for about 10 minutes. Deoxygenate a 30 mL syringe and then fill with the persulfate solution (cap the end of the needle with a pencil eraser).
2) Add 500 mL of water, 110 mL of vinyl acetate, 0.50 g of lauryl sulfate (a surfactant), and the 1.5 mL n-dodecyl mercaptan to the reactor. Insert the stirrer, thermometer, and long syringe needle. At this point, the syringe needle should be at the bottom of the flask. Bubble nitrogen through the solution for about 30 minutes. While the solution is being deoxygenated adjust the temperature of the solution to 50°C.
3) Partially retract the syringe needle so that it will not interfere with the stirrer. Start the stirrer. **This is an exothermic reaction.** Have an ice bath ready to cool the reaction mixture, if needed. Maintain at 50°C. After the stirrer is running, inject the 20 mL of persulfate solution. The reaction should be complete in about 40 minutes.

B. Pilot Plant or Class Preparation Since our students have never worked at the macroscale we used a small (5 liter) pilot plant setup for the preparation of the poly(vinyl acetate).

Equipment Setup:
- A five-liter reactor (5 opening head) with a stirrer (center neck), a Snyder, floating ball, reflux column with an exhaust hose to the hood, a 500 mL addition funnel, a gas bubbling tube extending to the (near) bottom of the reactor, and a thermometer. Two stirring hotplates with two 2-liter beakers were used to preheat the water to about 55°C. A heating gun was initially used to maintain the flask at 50°C. A large stainless steel bowl was placed under the reactor for future use as an ice bath. 25 mL and 500 mL graduated cylinders, parafilm, an approximately 15 cm syringe needle, a large funnel and a 250 mL Erlenmeyer flask for the persulfate solution. The system is deoxygenated using nitrogen and maintained under a nitrogen atmosphere.

Chemicals:
3500 mL of water, 800 mL of vinyl acetate, 3.50 g of sodium lauryl sulfate, and 4.40 g of potassium persulfate dissolved in 140 mL of water (deoxygenated), 10.5 mL of n-dodecyl mercaptan, a free-radical transfer agent, and ice.

Procedure:
1) Add 4.40 g of potassium persulfate to a 250 mL Erlenmeyer flask and add 140 mL of distilled water. Using a 15 cm syringe needle, bubble nitrogen through the solution for about 10 minutes. Cover the flask with parafilm.

2) Add 3500 mL of water, 300 mL of vinyl acetate, 3.50 g of lauryl sulfate (a surfactant), and the 10.5 mL n-dodecyl mercaptan to the reactor and stir. Add 500 mL of vinyl acetate to the addition funnel and briefly degas with nitrogen. **Note:** vinyl acetate fumes must be exhausted to the hood. Bubble nitrogen through the solution for about 30 minutes. While the solution is being deoxygenated adjust the temperature of the solution to 50°C.

3) **Note: this is a large scale exothermic reaction, be careful.** Have lots of ice ready to cool the reaction mixture. Quickly remove the Snyder column and pour the persulfate solution into the reaction. Let it react for about ten minutes.

The rate of the reaction is controlled by the drip rate of the vinyl acetate into the reactor. Add the vinyl acetate slowly. If the temperature starts to increase stop the addition of vinyl acetate and add ice and water to the stainless steel bowl (ice bath). Maintain the temperature at 50-53°C. After all the vinyl acetate has been added let the reaction continue for about 30 minutes.

Concerns:
1) Potassium persulfate is a very reactive material. Carefully read the MSDS form.
2) Vinyl acetate is a suspected carcinogen. Carefully read the MSDS form.

Reference:
The Separation of Poly(vinyl acetate)

Purpose:
This exercise is designed to show the student how to separate the polymer from a polymer emulsion.

Reference Reading:
Emulsions: pages 27-28

Equipment Setup:
A 600 mL beaker, a blender, a magnetic stirrer, stirring bar, filter flask, a large course fritted glass filter, and a flat polypropylene (kitchen) storage container.

Chemicals:
200 mL of poly(vinyl acetate) emulsion and 250 mL of saturated aluminum potassium sulfate (alum) solution.

Procedure:
1) **Rapidly** stir the saturated alum solution on the magnetic stirrer.
2) **Slowly** pour 200 mL of the emulsion into the saturated alum solution.
3) Decant the liquid leaving the polymer. Wash with "lots" of water.
4) If necessary, decant the liquid phase and place the polymer in a blender with 250 mL of water. Blend to cut polymer into small pieces.
   Filter the poly(vinyl acetate) using a fritted glass filter.
5) Air dry the polymer by spreading it in pieces over the bottom of the polypropylene storage container.
6) After air drying, re-chop the dry polymer in the blender if necessary.

Concerns:
1) None.

* Suggested by Michael Scott (Class of 2001)
The Viscosity Determination of Molecular Weight of Poly(vinyl acetate)

Purpose:
To determine the average molecular weight of the prepared poly(vinyl acetate) using viscosity measurements.

**NOTE:** It is best to do steps 1 through the first part of 3 the lab period prior to this experiment. This will allow the polymer to dissolve.

Reference Reading:
Viscosity: pages 24-26

Equipment Setup:
An Ostwald Viscometer (ASTM size 150), a stopwatch, five 50-mL volumetric flasks, 25-mL pipet, 10 mL pipet, rubber bulb, 3-decimal place top-loading balance, and a 30°C constant temperature bath.

Chemicals:
1 gram of poly(vinyl acetate) and acetone.

Procedure:
1) Number (1 through 5) and weigh five volumetric flasks.
2) Place approximately 1 gram of poly(vinyl acetate) in volumetric flask 1. Weigh the flask and polymer to get the mass of the polymer.
3) Add about 25 mL of acetone. Swirl the flask until the polymer dissolves and then fill the volumetric flask to the mark. Invert flask many times(*) to get a homogeneous solution. Weigh the filled flask.

* IMPORTANT - In preparing a homogeneous solution let the bubble do the stirring. Invert the flask until the bubble rises to the flask bottom and then right the flask until the bubble rises to its original position in the neck. Rotate the flask about 15° and repeat. To get a homogeneous solution this procedure needs to be repeated about thirty (30) times.

4) Pipet 25 mL of the solution from flask 1 and put it into flask 2. Weigh flask 2. Dilute to the mark. Make the solution homogeneous. Weigh the filled flask.
5) Repeat the process with flasks 3 through 5, taking 25 mL from flask 2 and placing it in flask 3; 3 to 4; and 4 to 5.
6) Use the masses of the polymer, initial solution, and final solution to determine the polymer concentration in each flask in units of grams per 100 mL (i.e., dL) of solution.
7) Use 10 mL aliquots of the solvent and the solutions in the Ostwald viscometer in the 30°C bath. Determine the time needed for the solutions to move between the two marks.
8) Calculate the intrinsic viscosity of your poly(vinyl acetate) in acetone.
9) Calculate the number average and mass average molecular weight for your polymer.
Mark-Houwink Parameters for Acetone*

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>K</th>
<th>a</th>
<th>Type of Molecular Weight</th>
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</thead>
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<tr>
<td>20</td>
<td>5.6 X 10^{-4}</td>
<td>0.625</td>
<td>Viscosity</td>
</tr>
<tr>
<td>30</td>
<td>1.76 X 10^{-4}</td>
<td>0.63</td>
<td>Number Average</td>
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<tr>
<td>30</td>
<td>1.01 X 10^{-4}</td>
<td>0.73</td>
<td>Weight Average</td>
</tr>
</tbody>
</table>

Concerns:
1) Acetone is a flammable liquid.


The Preparation of a Sheet of Poly(vinyl acetate)

Purpose:
This exercise demonstrates how crude poly(vinyl acetate) can be heat-pressed into a polymer sheet.

Reference Reading:
Fabrication Techniques: pages 44-47

Equipment Setup:
Heated press and two sheets of mylar approximately the size of the heated plates.
For the mylar sheets we use overhead transparencies.

Chemicals:
Approximately 5 grams of solid poly(vinyl acetate).

Procedure:
1) Heat the press heads to approximately 175°C (350°F).
2) Place 5 grams of the poly(vinyl acetate) in the center of one of the mylar sheets. Cover with the second sheet.
3) Place the mylar-PVAc-mylar sandwich in the press and slowly press the sample tightly.
4) After about 5 seconds release and open the press.
5) Carefully remove the sandwich and let cool.
6) Peel the mylar sheets off the poly(vinyl acetate).
7) Bend the poly(vinyl acetate) sheet. What happens?

NOTE: The glass transition temperature for PVAc is about 28 °C. Check it’s behavior both above and below this temperature.

Concerns:
1) Be careful of the heated press. It is hot enough to cause burns.
The Testing of the Poly(vinyl acetate) Emulsion

Purpose:
This exercise demonstrates some of the properties of a poly(vinyl acetate) emulsion. It will be used as glue and as paint. In making the paint, food coloring is being used as a colorant and flour as filler. The flour gives a white base to the paint.

Reference Reading:
Poly(vinyl acetate): page 43-44

Equipment Setup:
Blender, 50mL graduated cylinder, a Pasture pipet, two sheets of porous paper, a piece of white poster board, food coloring, 200 mL beaker, a scoop, and a paint brush.

Chemicals:
Approximately 50 mL of poly(vinyl acetate) emulsion, flour, food coloring.

Procedure:

1) Glue
   a) Using the Pasture pipet place one drop of the emulsion in the center of one sheet of porous paper and using a book press the second sheet on top.
   b) The next laboratory period, examine the two sheets of paper. Are they glued together?

2) Latex Paint
   a) Add 50 mL of latex to the blender.
   b) Add food coloring to produce the desired color and intensity.
   c) Add 1 gram of flour and blend to incorporate the flour.
   d) Paint a section of the poster board with your "latex paint". Set it aside until the next laboratory period.
   e) Next laboratory period wash the painted surface. What are your observations?

Concerns:
1) None.
Cross-linking the Poly(vinyl acetate)

Purpose:
In this exercise both the student’s poly(vinyl acetate) and Elmer’s Glue-All® will be cross-linked using borax.

![Borax Structure](image)

Reference Reading:
Morphology: page 12-17

Equipment Setup:
A 25 mL graduated cylinder, a 250 mL beaker, and a quart Ziplock® bag.

Chemicals:
Approximately 25 mL of poly(vinyl acetate) emulsion, 25 mL of Elmer’s Glue-All®, and 10 grams of borax (Na₂B₄O₇·10H₂O).

Procedure:
1) Dissolve 10 grams of borax in 400 mL of water.
2) Transfer 25 mL of poly(vinyl acetate) to the Ziplock® bag.
3) Add 5 mL of borax solution to the Ziplock® bag and seal.
4) Mix the contents of the bag by squeezing.
5) Remove the cross-linked polymer from the bag and examine.
6) The borax replaces acetates on adjacent poly chains forming a bridge. Draw the cross-linked structure.
7) Repeat steps 2 through 6 using Elmer’s Glue-All®

Concern:
1) None

Reference:
http://www.niagara.edu/chemistry/fun.html
The Preparation of Poly(vinyl alcohol)

Purpose:
This exercise demonstrates the alcoholysis of poly(vinyl acetate) to poly(vinyl alcohol).

Reference Reading:
Poly(vinyl alcohol) (PVA): page 44

Equipment Setup:
A 1-Liter reactor with at least a 2-hole head, a stirring motor; bearing for the head, and blade; stoppers for the reactor head; a heating mantle; blender; reflux column; a large ice bath; a Lab Jack; and a large course fritted glass filter setup.

Chemicals:
Approximately 12 grams of pulverized poly(vinyl acetate), 300 mL of methanol, and 3 pellet of sodium hydroxide.

Procedure:
1) Put 300 mL of methanol in the 1-Liter reactor.
2) Fit the reactor with the stirrer, heating mantle, and reflux condenser.
3) Vigorously stir the methanol solution while adding 12 grams of pulverized poly(vinyl acetate). The PVAc will gel along the sides of the reactor. Continue vigorous stirring while gradually bringing the solution to reflux. The gel should dissolve within a half hour. Note: over heating will cause the gel to cross-link. You do not want that.
4) Add three sodium hydroxide pellets to the refluxing solution and continue the stirred reflux for an hour.
5) Remove the heating mantle and bring the ice bath up round the reactor using the Lab Jack. Continue stirring until chilled.
6) Collect the precipitate in a large course fritted glass filter and wash with methanol.
8) Dry by pulling air through the filter.
9) If chunky blend (chop) the dry precipitate to a powder.

NOTE: Make sure that you save a small amount of the PVA for the IR spectra.

Concerns:
1) Methanol is flammable, explosive when mixed with air, and toxic. Read the MSDS form before doing this experiment.
Head-to-Head Contacts in Polyvinyl Alcohol

Purpose:
To determine the average number of head-to-head contacts in the prepared poly(vinyl alcohol). For steric reasons, when vinyl acetate polymerizes the smaller CH= group of the monomer attaches to the bulkier acetate end of the growing polymer chain. This produces a polymer chain with acetate groups on alternate carbons or a head-to-tail conformation. However, sometimes by accident or as when two polymer free radicals bond together, a head-to-head (acetate carbon-to-acetate carbon bond) is formed. When this occurs the resultant polyvinyl alcohol contains a glycol linkage. This experiment is based on the fact that KIO₄ cleaves glycol linkages thus producing a larger number of shorter polymers.

NOTE: It is best to put the polyvinyl alcohol in water the period prior to this experiment. This will allow the polymer to partially dissolve.

Reference Reading:
Viscosity: pages 24-26

Equipment Setup:
An Ostwald Viscometer (ASTM size 100); a stopwatch; a 250-mL volumetric flask; eight 100-mL volumetric flasks, 50-mL pipet, two 200 mL beakers; a hotplate; thermometer; a 10 mL pipet, rubber ball, and a 25°C constant temperature bath.

Chemicals:
4 gram of poly(vinyl alcohol); 0.25 grams of KIO₄; and distilled water.

Procedure:
1) Clean a viscometer and immerse in a 25 °C constant temperature bath.
2) Place approximately 4.00 grams of dry, pulverized poly(vinyl alcohol) in a 400 mL beaker and add about 200 mL of distilled water. Gently warm (on a hotplate) and stir until the polymer dissolves. (If the polymer does not completely dissolve filter the solution through a course sintered glass filter.) Cool to room temperature and transfer to a 250 mL volumetric flask. Dilute to the line. Stir the solution to make it homogeneous(*). Label this flask “uncleaved stock solution”.

* IMPORTANT - In preparing a homogeneous solution let the bubble do the stirring. Invert the flask until the bubble rises to the flask bottom and then right the flask until the bubble rises to its original position in the neck. Rotate the flask about 15° and repeat. To get a homogeneous solution this procedure needs to be repeated about thirty (30) times.

3) Pipet 50.0 mL of the “uncleaved stock solution” to a 400 mL beaker and add 25 mL of distilled water and 0.25 grams of KIO₄. With stirring, warm the solution to about 70°C. After cooling, quantitatively transfer the solution to a 100 mL volumetric flask and dilute to the line. Label this flask “cleaved #1”. Stir until homogeneous.

4) Pipet 50 mL of the “uncleaved stock solution” into a second clean 100 mL volumetric flask and dilute to the line. Label this 100 mL volumetric flask “uncleaved #1”. Stir until homogeneous.

5) Pipet 50 mL of the “uncleaved #1” solution to another 100 mL volumetric flask, fill to the line and label “uncleaved #2”. Likewise prepare a “cleaved #2” from “cleaved #1”. Using 50 mL of “uncleaved #2” prepare an “uncleaved #3” and likewise for “cleaved #3”, and likewise for an “uncleaved #4” and a “cleaved #4”. Stir all until homogeneous before extracting any solution.

6) Use the Ostwald viscometer in the 25°C bath and determine the time necessary for the solvent (water) and the eight polymer solutions to move between the two marks.

7) Calculate the intrinsic viscosity of “uncleaved” and “cleaved” polymers.

8) Calculate the viscosity average molecular weight for the two polymers.
9) Calculate the average number of head-to-head contacts in the prepared poly(vinyl alcohol).

**Mark-Houwink Parameters for Water**

<table>
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<th>Temperature (°C)</th>
<th>K</th>
<th>a</th>
<th>Type of Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>$2.0 \times 10^{-4}$</td>
<td>0.76</td>
<td>Viscosity</td>
</tr>
</tbody>
</table>


**Concerns:**

1) KIO₄ is a very strong oxidizing agent. Read the MSDS sheet for KIO₄ before using.

**References:**

The Preparation of Poly(vinyl formal)

Purpose:
To prepare poly(vinyl formal) from poly(vinyl alcohol)

Reference Reading:
Poly(vinyl alcohol): Page 44

Equipment Setup:
400 mL beaker, magnetic stirrer with stirring bar, a watch glass to cover the 400 mL beaker, a 50- or 100-mL graduated cylinder, a 10 mL graduated pipet, a pipet bulb, and an ice bath

Chemicals:
1.0 grams of poly(vinyl alcohol), 40 mL of glacial acetic acid, 4.0 grams (2 mL) of concentrated sulfuric acid, and 20 mL of formalin (37% formaldehyde solution).

Procedure:
1) Place the 400 mL beaker on the stirring hotplate and add 10 mL of water and 1.0 grams of poly(vinyl alcohol). Cover the beaker with the watch glass. Carefully stir the solution with mild heating (i.e., less 100 °C) until the polymer dissolves.
2) Cool to room temperature and then add 40 mL of glacial acetic acid and 20 mL of formalin with stirring.
3) Carefully add 2 mL of concentrated sulfuric acid to the stirred solution.
4) Stir the reaction mixture overnight.
5) Place the beaker in an ice bath and then add about 40 mL of water to precipitate poly(vinyl formal). Collect the polymer on filter paper using a Büchner funnel. Remove from the filter paper before it strongly adheres.
6) Using gloves, transfer the polymer mass to a beaker of water. Squeeze and release until most of the acetic acid is removed. Blot dry with paper towels.
7) Place the polymer in a small beaker and cover with a tissue or Kimwipe® secured with a rubber band to completely dry.

Concerns:
1) Formaldehyde is a carcinogen. Read the MSDS forms before doing the experiment.

Reference:
The Preparation and Characterization of IR Spectra

Purpose:
To prepare infrared spectra for poly(vinyl acetate), poly(vinyl alcohol), and poly(vinyl formal).

Equipment Setup:
Three test tubes and three disposable or Teflon covered IR slide holders.

Chemicals:
Three small polymer solutions (1 – 2 mL)
1) poly(vinyl acetate) in acetone.
2) poly(vinyl alcohol) in water. Heat to dissolve.
3) poly(vinyl formal) in methylene chloride. Dissolves very slowly.
   NOTE: It is best to make these solutions in advance.

Procedure:
1) Coat each of three slides with a polymer solution and let the solvent evaporate. Recoat as necessary.
2) Use a new slide as a blank.
3) Scan each of the three polymer slides (minus blank).
4) Analyze and compare the three spectra.

Question: Based on the IR spectra, is the PVF pure?

Concerns:
1) None
Appendix A – Polymer Textbooks

The *Polymer Primer* is meant as a supplement to an advanced lecture, laboratory or combined course. It is not intended as a textbook for a polymer course. If the student is interested in learning more about polymer science the following textbook are respected introductory polymer texts. Books noted with (*) appear in *Books in Print* as of this writing.

(*) **An Introduction to Polymer Physics**, D.I. Bower, Cambridge University Press, USA, 2002

(*) **An Introduction to Polymer Science**, H. Elias, John Wiley & Sons Inc., USA, 1997


(*) **Introduction to Physical Polymer Science**, L.H. Sperling, John Wiley & Sons, New York, USA, 1986

**Introductory Polymer Chemistry**, G. Misra, Halsted Press, New York, USA, 1993


(*) **Polymer Physics**, M. Rubinstein, Oxford University Press, Inc. USA, 2003

(*) **Polymer Science and Technology**, R. Ebewele, C R C Press LLC, Boca Raton, USA, 2000


Appendix B – Common Polymers

Polyacrylonitrile

\[
\left[ CH_2 - \left( CH - CN \right) \right]_n
\]

Polybutadiene

\[
\left[ CH_2 - CH = CH - CH_2 \right]_n
\]

Polyethylene

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

Poly(ethylene terephthalate) PET

\[
\left[ O - CH_2 - CH_2 - O \cdot \text{Cyclic} \cdot O \right]_n
\]

Poly(hexamethyleneadipamide) Nylon 66

\[
\left[ \text{NH} - (CH_2)_6 - \text{NH} - C - (CH_2)_4 - C \right]_n
\]

Polyisoprene

\[
\left[ CH_2 - \left( CH - CH \right) \right]_n
\]
Polypropylene

\[
\left[ \begin{array}{c}
\text{CH}_2\text{-CH} \\
\text{CH}_3
\end{array} \right]_n
\]

Polystyrene

\[
\left[ \begin{array}{c}
\text{CH}_2\text{-CH} \\
\text{C}_6\text{H}_5
\end{array} \right]_n
\]

Polytetrafluororthylene (Teflon)

\[
\left[ \begin{array}{c}
\text{CF}_2\text{-CF}_2 \\
\text{C}_6\text{H}_5
\end{array} \right]_n
\]

Poly(vinyl acetate) PVAc

\[
\left[ \begin{array}{c}
\text{CH}_2\text{-CH} \\
\text{O}\text{-C}-\text{CH}_3
\end{array} \right]_n
\]

Poly(vinyl alcohol) PVA

\[
\left[ \begin{array}{c}
\text{CH}_2\text{-CH} \\
\text{O}\text{-H}
\end{array} \right]_n
\]

Polyvinyl chloride) PVC

\[
\left[ \begin{array}{c}
\text{CH}_2\text{-CH} \\
\text{Cl}
\end{array} \right]_n
\]

Poly(vinyl formal) PVF

\[
\left[ \begin{array}{c}
\text{CH}_2\text{-CH} \\
\text{O}\text{-C}-\text{CH}
\end{array} \right]_n
\]

Appendix C – Glossary of Terms
addition polymerization – monomers add to the end of polymer chain by free radical or ionic mechanism, same as chain growth polymerization

additives - something added to the polymer melt such as colorants, UV stabilizers, antioxidants, etc.

amorphous – random conformation of polymer with no crystallization. Pure amorphous polymers are transparent.

atactic – a non-stereospecific polymer

average degree of polymerization – average number of repeat or monomeric units in a polymer

batch process – all ingredients placed in a vessel where the reaction takes place, as opposed to a continuous process

branched polymer – a polymer with a significant number of side polymer off-shoots

chain growth polymerization - monomers add to end of polymer chain by free radical or ionic mechanism, same as addition polymerization

chips – small pieces of polymer produced for subsequent use

cis-trans isomerism – main chains on the same side (cis) or opposite sides (trans) of a carbon-to-carbon double bond

cohesive energy density (CED) – energy required to remove a molecule from is pure liquid or solid state

colorants – a material which gives color to a polymer

composites – a one, two, or three dimensional solid embedded in a polymer to give strength to the polymer

condensation polymerization – a polymer composed of difunctional monomers, also known as step growth polymerization

Configuration - arrangement of a molecule due to chemical bonds

conformation - a normal arrangement of atoms in a polymer chain or arrangement due to rotation around a single bond.

continuous process – ingredients continuously flowing into a reaction chamber while product is flowing out, as opposed to a batch process

copolymer – polymer containing two different monomeric units

creep – the process by which a polymer is permanently distorted, see creepage

creepage – permanent distortion in a polymer caused by a stress

crimping – putting small tight waves into the polymer fiber to keep it from slipping

cross-linkage – the formation of a covalent bond between adjacent polymer chains

degree of polymerization – the number of repeat or monomeric units in a polymer

dimmer - two monomeric units bonded together

dipole-dipole attraction – electrostatic attraction between molecules or components which have a permanent charge separation or dipole

dispersity - relative number of monomeric units in a polymer

entanglement – The tangling of polymer chains
**enthalpy of solution** – under ambient conditions the energy change associated with a solute being solvated

**entropy of solution** – a measure of the increase in randomness of a solute going into solution

**extrusion film** – a film or membrane produced by inflating a polymer melt

**fiber** – a group of filaments each of which contains aligned polymer molecules. Fibers are usually made from linear polymer with strong intermolecular attraction.

**Foam** – A plastic containing a large number of small bubbles. The bubbles can be joined like a sponge or separate

**foaming agent** – a volatile compound dissolve in a plastic under high pressure. The compound vaporizes when the pressure is reduced forming bubbles.

**free radical mechanism** – a polymerization mechanism dependent on the propagation of a free radical from one monomer linkage to the next

**free radical transfer agent** – a compound which terminates the free radical polymerization in one chain and initiates a new chain

**Gibbs free energy of solution** – the free energy change under constant pressure conditions associated with the dissolving of a solute (here a polymer)

**Glass transition temperature** – the temperature at which segmental motion begins

**good solvent** – a solvent which strongly solvates the polymer molecule. This normally causes the polymer molecule to extend into the solvent.

**head-to-head linkage** – A segment of a polymer chain where the comparable monomer ends of a chain growth polymer bond together

**head-to-tail linkage** – A segment of a polymer chain where the opposite monomer ends of a chain growth polymer bond together

**Hookean behavior** – a polymer that obeys Hooke’s Law

**hydrogen bonding** – Intermolecular attraction resulting from a hydrogen atom bonded to a very electronegative atom and a second electronegative atom.

**Inherent viscosity** – The natural logarithm of the relative viscosity divided by the concentration

**Initiator** – a compound which will break down to free radicals under reaction conditions

**Injection molding** – a polymer is injected into a mold where it solidifies

**Intrinsic viscosity** – the limit of the reduced viscosity extrapolated to zero concentration and the limit of the inherent viscosity extrapolated to zero concentration. It is used in the Mark-Houwink equation to calculate the viscosity molecular weight

**Isomerism** – different compounds having the same formula

**Isotactic** – a stereospecific polymer with a DDDDD or LLLLL arrangement

**Lamella** – a small crystalline region resulting from folding of a single polymer chain, a linear segment involving many chains or a combination of both

**linear polymer** – a single strand of bonded monomers
London forces – an attractive force produced by pulsating charge centers

Macromolecule – a very large molecule

Maxwell behavior – an engineering model for a viscoelastic material involving a Hookean spring in series with a Newtonian dashpot

melt extrusion – an instrument which convert polymer chip to high pressure polymer melt

melt temperature – the temperature at which a polymer melts

memory – a structural feather in a polymer which allows the polymer to return to its original shape and size

micelle – a small organic droplet surrounded by a surfactant in an aqueous media

molar mass – at the nanoscale the mass of a molecule in amu’s or at the macroscale the mass in grams of one mole of material

molecular weight – an older term for molar mass

mono-dispersed – a polymer in which all the polymers have the same length and molar mass

monomer – a molecular building block from which polymer are built

monomeric unit – identical or nearly identical repeat unit

network polymer – a cross-linked polymer

Newtonian behavior – the permanent distortion of a viscoelastic material

Newtonian dashpot – a cylindrical tube capped at one end fitted with a plunger that either does not fit tightly or alternatively has a hole

number average molecular weight – the molar mass

oligimer – ten to twenty monomeric units

ostwald viscometer – an instrument used to determine the viscosity of a liquid

pellets – a small cylindrical piece of polymer produced for subsequent use

pendant groups – a “smallish” side group which is part of the monomer molecule

plasticizer – a solvent that swells a cross-linked or partially crystallized polymer.

poly-dispersed – a polymer without a uniform molar mass

polydispersity index – a measure of the molar mass uniformity within a polymer. A mono-dispersed polymer has a polydispersity index of one, the larger the index the greater the variation.

polymer – a macromolecule with hundreds to thousands of monomeric units

poor solvent – a solvent that does not solvate the polymer

pultrusion process – a technology used embed polymer into a pours material or to coat wires

reduced viscosity – equals the specific viscosity divided by the concentration

relative viscosity – equals the viscometer time for the solution over that of the solvent
rheology – a field of engineering which deals with material deformation and flow

solubility parameter – a relative measure of the solvent – polymer solubility. The closer the solubility parameters the more likely a solution will occur.

Specific viscosity – equals the relative viscosity minus one

Spherulite – a crystalline region in a polymer

Spinneret – a metal plate containing small shaped holes through which fibers are formed

step growth polymerization - – a polymer composed of difunctional monomers, also known as condensation polymerization

stereoisomerism – optical isomers

strain – elongation of a stressed polymer

stress – force per unit area of polymer

stress-stain behavior – the interrelationship between stress and strain

structural isomerism – different compounds with the same formula

syndiotactic – a stereospecific polymer with a DLDL arrangement

thermoplastics – a polymer which can be melted and recycled

thermoset plastics – cross-linked polymer which cannot be melted and recycled

trimer – three monomeric units bonded together

turbidimetric titration – titration of a polymer dissolved in a good solvent with a poor solvent until the solution turns turbid

vacuum thermoforming – a technology by which a heated polymer is pulled into a mold by reduced pressure

viscoelastic polymer – a polymer which experiences Hookean and/or Newtonian motion

viscometer – am instrument used to measure the viscosity of a liquid

viscosity – the resistance to flow

viscosity molecular weight – a molecular weight between the number average and the mass average molecular weight. It is determined with the Mark-Houwink equation using the intrinsic viscosity

Voigt-Kelvin model – a viscoelastic model which contains a Hookean spring and a Newtonian dashpot in parallel

vulcanized rubber – rubber cross-linked with sulfur

weight average molecular weight – a second moment molecular weight stressing heavier molecules

z-average molecular weight - – a third moment molecular weight stressing heavier molecules

Ziegler-Natta catalyst – a catalyst that has two components a group IV to VIII transition metal compound such as titanium chloride and a group I to III organometallic compound such as diethyl aluminum chloride
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