

EXPERIMENT #5 – POLYMERS

Background

Polymers are *macromolecules* – large molecules – which contain one or two *repeating units*. The repeating unit is a group of atoms which is covalently bonded to another repeating unit and so on. Polystyrene, polyvinyl chloride, and high density polyethylene are examples of polymers. Sections of these polymers, the repeating unit, and the *monomers*, from which they are made, are shown in Figure 1.

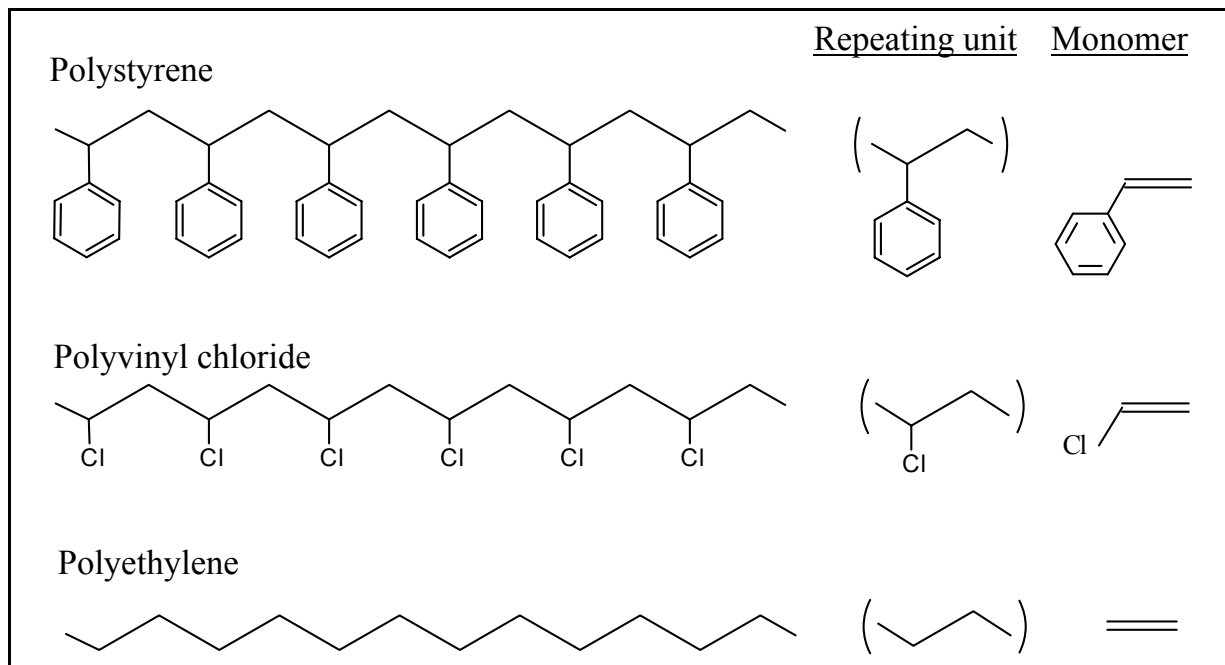


Figure 1: Unbranched Polymers

The polymers shown are called *unbranched* because there are no branches off the chain, except, perhaps, for small groups of atoms. The chains may be quite long. For example, polyvinyl chloride could easily be composed of polymer chains which average 10,000 repeating units per chain. The properties exhibited by unbranched polymers are partly the result of attractions among the chains (which may be van der Waals, dipole-dipole, hydrogen bonding, or ionic, depending on the structure), partly the result of physical entanglement of the chains and partly due to other factors. With respect to entanglement, a sample of an unbranched polymeric material is sometimes compared to a bowl of spaghetti. However, this is a flawed analogy. Even the thin “angel hair” pasta, which has a typical diameter of 1 mm and a typical length of 230 mm, is much shorter, relative to its thickness, than a typical polymer. A typical high density polyethylene molecule might contain 20 or 30 thousand CH_2 units. For a piece of angel hair pasta to have the same aspect ratio as the polyethylene it would have to be about 20 meters long!

Unbranched polymers are generally *thermoplastic*. This means that they are glasses at room temperature (perhaps containing microcrystalline domains) and soften as they are warmed. As one of these polymers is warmed it will remain solid until the *glass transition temperature* (T_g), at which point it becomes soft. If the polymer is *crystalline* (ie, it does contain microcrystalline domains) it will become a liquid at the *melting temperature* (T_m). If the polymer is *amorphous* (does not contain microcrystalline domains) as it is warmed above T_g it will gradually become softer and finally liquefy. Thermoplastic polymers can be extruded, molded, pressed, *etc.* In other words, these polymers can be shaped when heated.

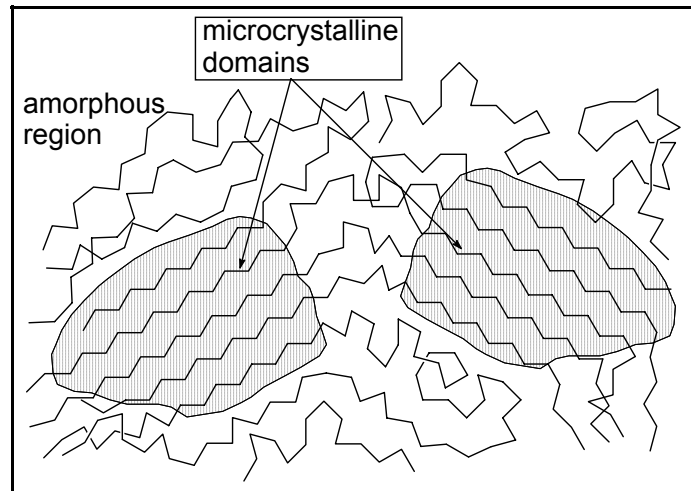


Figure 2: Unbranched Crystalline Polymer

Branched polymers have similar characteristics to those which are unbranched, except that they are more likely to be amorphous, owing to their irregular shape. Figure 2 shows a representation of an unbranched crystalline polymer, while Figure 3 shows a branched amorphous polymer.

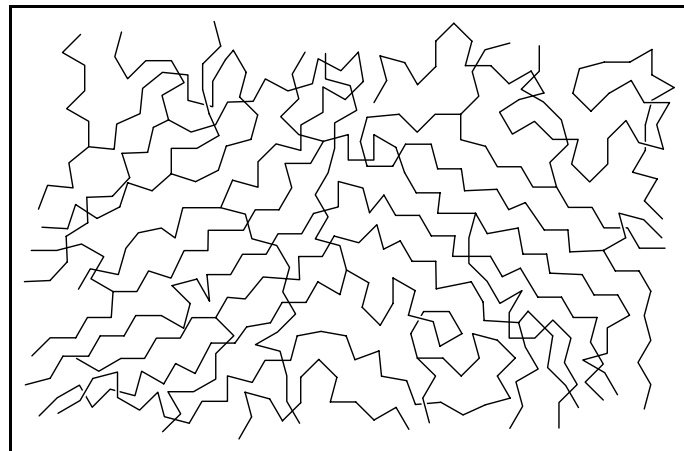


Figure 3: Branched Amorphous Polymer

A third type of polymer is one which is *crosslinked*. In this type of polymer all the atoms are joined together by covalent bonds; the whole polymer is one giant molecule. Diamond is an example of this type of polymer. Crosslinked polymers are not thermoplastic, they are *thermosetting*. They do not soften or melt when heated. A schematic diagram of a crosslinked polymer appears in Figure 4.

Unbranched and branched polymers soften at a glass transition temperature, T_g , mainly because of increased opportunity for conformational changes in the chains at the elevated temperature and possibly also because of increased translational freedom. Some polymers become liquid at the still higher melting temperature, T_m , meaning that the molecules become sufficiently independent of each other that they are able to slide past one another (in a crystalline polymer the crystallites would melt at this temperature in much the same way ordinary crystals melt). On the other hand, crosslinked polymers are

fairly rigid without much conformational flexibility so they do not soften at a T_g , and since one part of the macromolecule cannot free itself from the covalent bonds which hold it to the other parts, they certainly cannot melt.

Unbranched and branched polymers tend to be soluble in solvents which have properties similar to themselves. Thus, non-polar polymers are most soluble in non-polar solvents, polar polymers are most soluble in polar solvents, and polymers which exhibit intermolecular hydrogen bonding are most soluble in solvents which hydrogen bond. Thus, toluene (non-polar, non hydrogen bonding) is a good solvent for polystyrene (non-polar, non hydrogen bonding) while ethanol (polar, hydrogen bonding) is not. Crosslinked polymers are insoluble although they may swell through solvent absorption if placed in a solvent with similar properties.

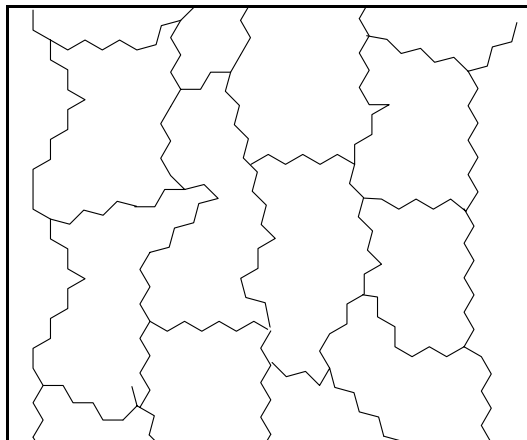


Figure 4: Crosslinked Polymer

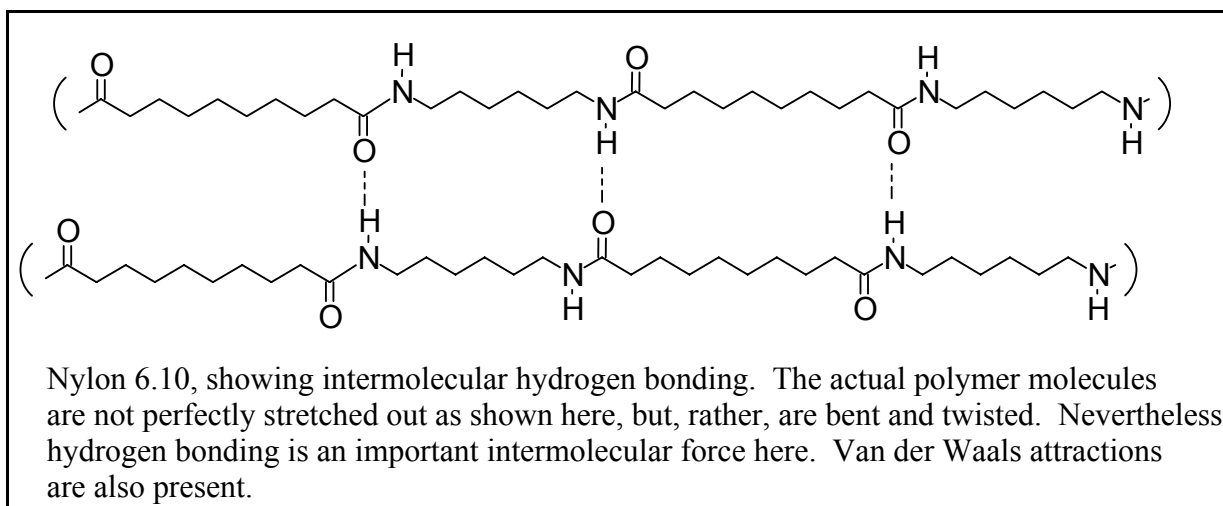


Figure 5: Nylon 6.10

Nylon 6.10

Nylon is an unbranched polymer which can be prepared by a condensation reaction between a diamine, $\text{H}_2\text{N}-(\text{CH}_2)_m-\text{NH}_2$, and a diacid, $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$, or between a diacid dichloride, $\text{Cl}-\text{CO}-(\text{CH}_2)_n-\text{CO}-\text{Cl}$, and a diamine. [The Nylon which results is named Nylon m.n.] Condensation reactions are those which occur between molecules resulting in the molecules becoming covalently bonded to each other with the concomitant elimination of a small molecule such as H_2O or HCl . Thus, the following reaction between an acid chloride and an amine to give an amide is a condensation reaction: $\text{R}-\text{CO}-\text{Cl} + \text{H}_2\text{N}-\text{R}' \longrightarrow \text{R}-\text{CO}-\text{NH}-\text{R}' + \text{HCl}$. When the acid is a diacid and the amine is a diamine, the formation of an unbranched polymer is possible.

Preparation of Nylon 6.10

Place 10 ml of a 5% aqueous 1,6-hexanediamine solution and 2 ml of a 20% aqueous sodium hydroxide solution in a 50 ml beaker and stir. *Slowly and carefully* pour 10 ml of a 5% sebacyl chloride in cyclohexane solution down the inside wall of the beaker so that this solution floats on the aqueous solution already in the beaker. Almost immediately, you should notice a film of Nylon forming at the interface between the two immiscible liquids. Hook the disc of Nylon at its center using a piece of wire which is bent at one end. *Slowly and steadily* pull the film upward out of the beaker so that a strand of Nylon extends from the interface to the wire. As you continue to raise the wire the Nylon at the interface will join the strand and, as the Nylon is removed from the interface, more will form there. Continue to draw out the Nylon until no more forms at the interface, or until you have a substantial amount and you tire of the process. Using a glass stirring rod, stir the material left in the beaker to cause unreacted material to react and form Nylon on the rod. Dry all the Nylon by pressing it between layers of paper towel. Soak the paper towels with water to wash the Nylon, transfer the Nylon to dry paper towels and

allow the Nylon to dry until next week in order to examine its melting and solubility properties. *Wash your hands to remove any hexanediamine or sebacyl chloride as these compounds may cause irritation.*

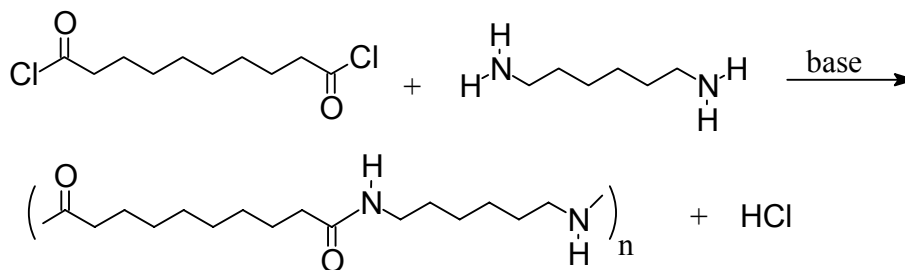


Figure 6: Formation of Nylon 6.10

Polystyrene

Polystyrene is that ubiquitous polymer which is used to make crystal-clear, brittle, drinking glasses, white foam insulation (disposable coffee cups, cheap beer coolers, insulation in appliances and homes), and other items, including some flexible ones, such as automobile upholstery, when a *plasticizer* is mixed with the polymer. Its structure is shown in Figure 1 and it is formed by a free radical addition reaction from styrene. In this experiment, benzoyl peroxide is the initiator.

Preparation of Polystyrene

Caution!

Benzoyl peroxide may decompose violently if heated by itself. Keep it away from heat until it is dispersed in the styrene.

Clamp a Pasteur pipet in the vertical position with the tip down. Place a *small* loose wad of glass wool inside the pipet and, using a thin glass rod, push it toward the tip until it enters the part of the pipet where the diameter decreases. Add enough alumina to fill about one-third of the pipet; it will be supported by the glass wool. Place a *10x75 mm* test tube under the tip of the pipet and add 1.5-2 ml of styrene to the

pipet. Collect at least 1 ml of styrene which has passed through the alumina. [The styrene contains a free radical inhibitor that is removed by the chromatography process.] Dispose of the Pasteur pipet and alumina in the appropriate container under the hood. Add 50 mg (0.050g) of benzoyl peroxide to the test tube, insert a thin glass stirring rod, and *mix the contents of the tube until the benzoyl peroxide is thoroughly dispersed in the styrene*. Heat the tube in the BB bath. When the temperature reaches about 135°C, polymerization begins and, owing to its exothermicity, the temperature rises. The viscosity of the material in the tube also increases as polymerization occurs. If bubbles form in the liquid remove the tube from the heat until things calm down a bit, then reinsert. When you find that the polymer is so viscous that it is difficult to stir with the glass rod, allow the tube to cool. Place the tube, with your name attached, into an 85°C oven so that polymerization will go to completion.

You will examine the solubility and melting behavior of this polymer next week.

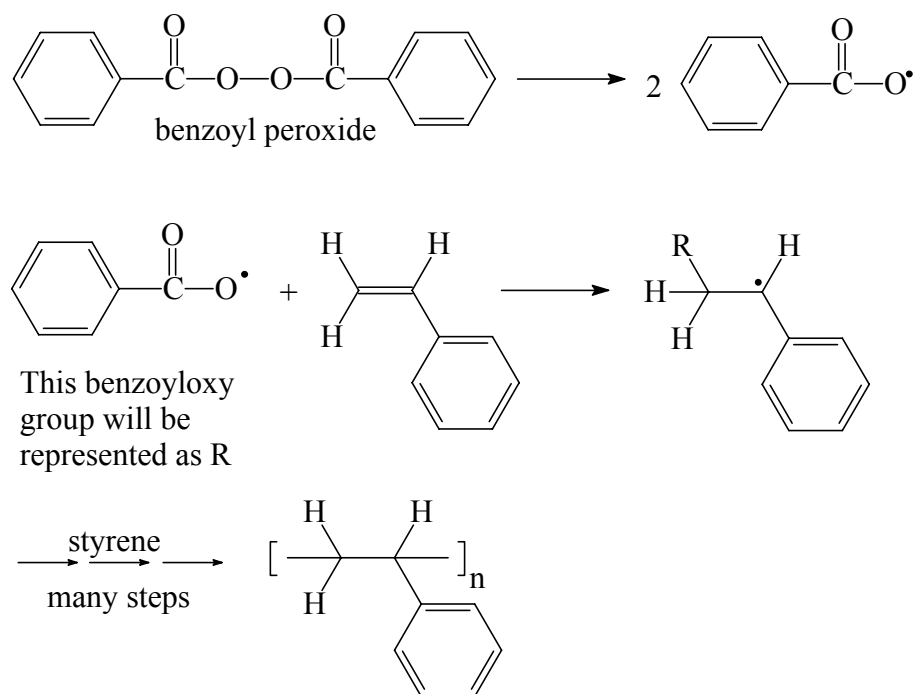


Figure 8: Preparation of Polystyrene

