# <u>Polymers- A Guided Inquiry Exercise</u>

**<u>Excerpted from "An Introduction to Materials Science and Engineering"- A Guided Inquiry by</u>**

**Elliot P. Douglas, Pearson Inc. 2014.**

Polymers are high molar mass compounds or macromolecules many of which have molecular weights exceeding one million.

The process of formation of these large molecules from smaller units ( called monomers) is called polymerization, Monomers may be alike or different. When there are two or more monomers, the macromolecule is known as a co-polymer. Starch, glycogen, DNA, cellulose and proteins are examples of naturally occuring polymers. Man made polymers include polyethylene, nylon, Dacron, Lucite and Polyvinyl chloride ( PVC) etc.

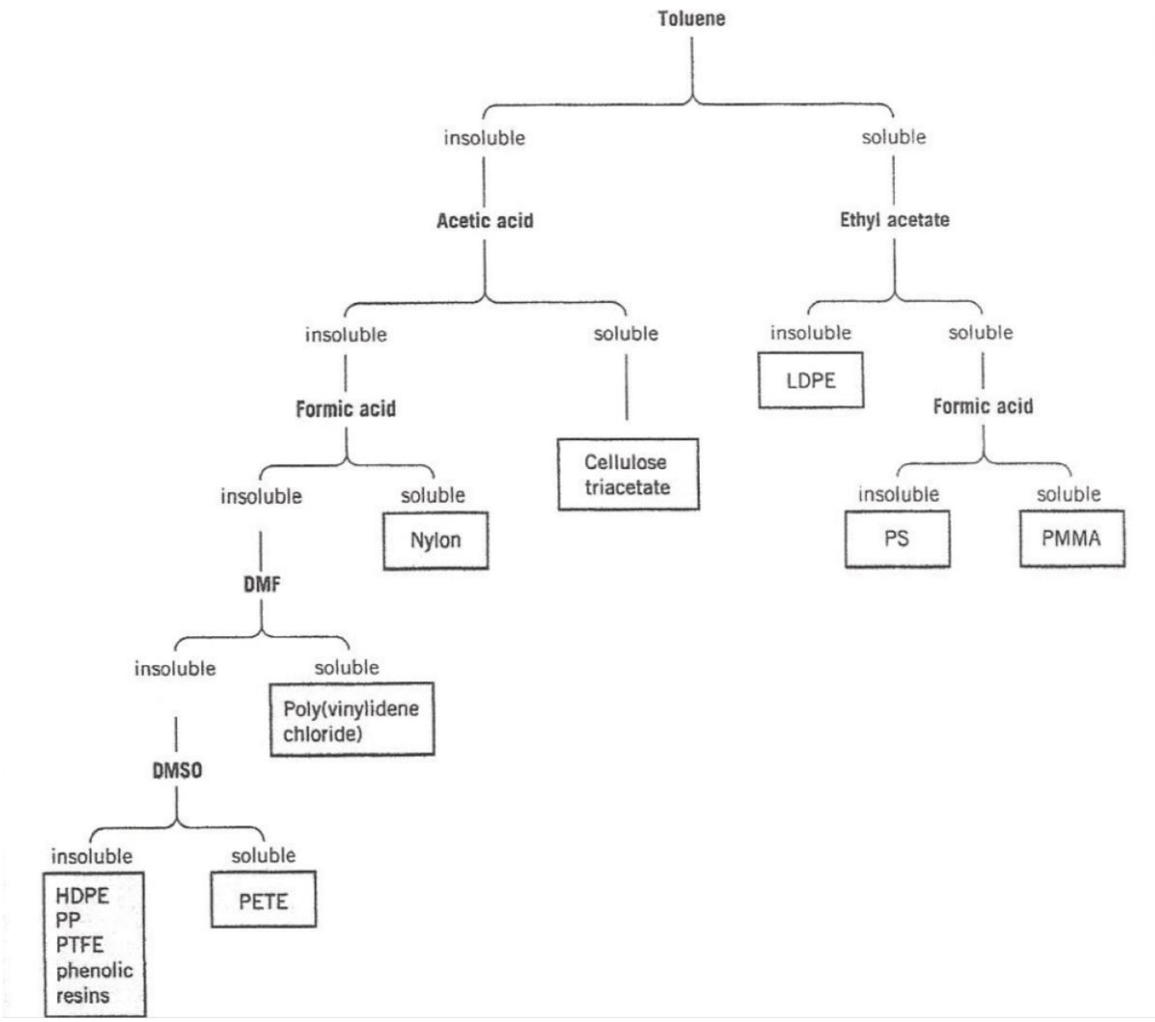
Alkenes or substituted alkenes are among the most common monomers for making synthetic polymers For example ethylene can be polymerized to polyethylene.

$$n\ CH_2{=}CH_2 \rightarrow \text{--}CH_2CH_2\text{--}(CH_2CH_2\text{-})_n\text{-}CH_2CH_2\text{—}$$

Polymers that soften on heating and therefore can be changed into different usable shapes are known as thermoplastic polymers. Polymers that set to infusible solids and do not soften on reheating are known as thermosetting polymers. Polymers can be classified as addition polymers or condensation polymers. An addition polymer is formed by successive addition of repeating monomer units. A condensation polymer is formed from monomers with elimination of water or some small molecule like methanol or water.

**Identification of Polymers by Solubility ( Courtesy- Daniel Palleros, Experimental Organic Chemistry, John Wiley & Sons, Inc. 2000)**

To identify polymers via solubility a flow chart shown below can be followed. One can start by checking solubility of polymer in toluene. If the polymer is soluble, follow branch on the right side; if it is insoluble, follow the branch on the left side. For example, if you were to try the solubility of an unknown polymer in toluene and you find out it is soluble. Then you will check its solibility in ethyl acetate using a fresh sample of polymer. If the polymer dissolves, then try its solubility in 96% ( w/w) formic acid with a fresh sample. If it dissolves in this solvent, your unknown is likely to be PMMA ( poly( methylmethacrylate) . You can use this solubility scheme shown below to identify the most commonly used polymers such as PTFE, nylon, PETE, cellulose acetate, saran ( polyvinylidene chloride), HDPE, LDPE, PP, PS and PMMA.




The solubility of a polymer in a given solvent depends on the physical state of the polymer. Powders dissolve much more quickly than solids or films.

**Identification of plastics by Density**.

Density of polymers can be estimated by placing a small sample of polymer in a series of solvents of known density and observing whether the polymer floats or sinks. If the polymer sinks, you will try its buoyancy in the next solvent of higher density. You will start with the solvent of lower density ( ethanol-water, 4:1_ and stop when you find a solvent in which your sample floats. *The density of the polymer will be **in between the densities** of the two solvents where the transition between sinking and floating occurs.* Use the table below as a guideline:

**<u>Solvents for the Determination of Polymer Density</u>**

| Solvent | Density (g/mL) | Solvent | Density ( g/mL) |
|---|---|---|---|
| Ethanol -water ( 4:1) (v/v) | 0.86 | 10% NaCl ( w/w) | 1.06 |
| Ethanol- water (10:7)(v/v) | 0.91 | Dilute light cornsyrup (4:1) w/v) | 1.29 |
| Ethanol-water (1:1) (v/v) | 0.92 | Light corn syrup | 1.41 |
| Water | 1.00 | | |

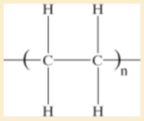
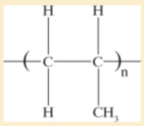
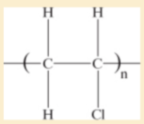
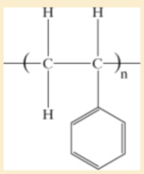
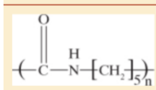
## Nylon

Nylon 6,6 is a condensation polymer mae from two different monomers, **adipic acid and 1,6-diaminohexane**. In the name, Nylon 6-6, the first 6- refers to the number of carbons ( methylene group carbons) in the diamine and the second "6" refers to the total number of carbon sinteh di-acid or diacid chloride, including the carbonyl carbons and methylene carbons. Thus, **Nylon 5-10 may be synthesized from polymerizign 1,5- diamino pentane [$NH_2(CH_2)_5NH_2$] with sebacoyl chloride [ ClCO ( $CH_2)_8$COCl].**

**n HOOC-($CH_2)_4$-COOH + n $H_2N$-($CH_2)_6$-$NH_2$ → [-OC-( $CH_2)_4$-CO-NH-($CH_2)_6$-NH-]$_n$ + (2n-1) $H_2O$**

**Nylon 6-6**

The value of "***n***" is called the degree pf polymerization or DP. Typical values for the degree of polymerization range from 100 to hundreds of thousands.

| | | |
|---|---|---|
|  | Polyethylene | PE |
|  | Polypropylene | PP |
|  | Poly(vinyl chloride) | PVC |
|  | Polystyrene | PS |
|  | Polycaprolactam | Polyamide 6 or Nylon 6 |

The table above provides the repeat units for a few polymers.

Use this table to answer the following:

**A) For polypropylene with a DP of 3500, what is the polymer molecular weight?**

Ans. The predicted molecular weight of propylene is 42, so in propylene, there are two hydrogen molecules present, one at first and last. Therefore, the molecular weight is 40. For the 3499, the additional 1 DP, it is 42.

So, the molecular weight = (3499*40)+ (1*42) = 140,002 g/mol.

**B) For Nylon 6 with a polymer molecular weight of 150,000 g/mol what is the DP?**

Ans. The repetitive unit of the molecular weight of Nylon 6 is 113.16 g/mol

$$DP = \frac{150{,}000}{113.16} = 1326$$

**C) What is the DP for polypropylene with a molecular weight of 35,000g/mol. What are the units of DP?**

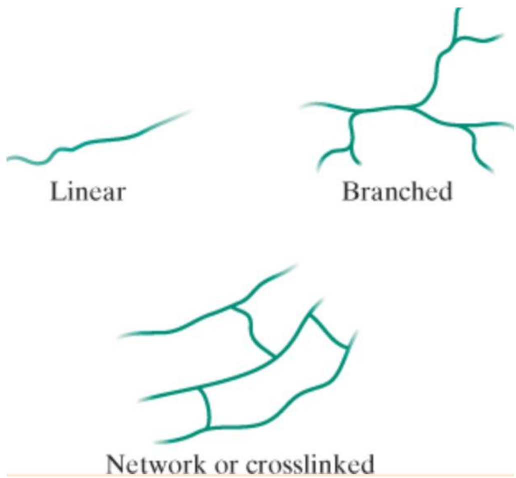
Ans. Polypropylene molecular weight for a single monomer is 40, so the DP is given as:

$$DP = \frac{35{,}000}{40} = 875$$

Degree of polymerization has no specific unit because the formula cancels the polymer and monomer unit.

**Chain Shape**

A way to change the properties of polymer is to change it's overall shape. The 3 main shapes are shown below: In a *linear* polymer the repeat units are all lined up in a straight chain. In a *branched polymer* there are branches off the main chain. These branches are made of the same repeat units of the main chain. In a network or cross linked polymer, individual linear polymer molecules are connected via *covalent* bonds.




Answer the following with respect to the above:

**A) In which type of structure are chains connected by non-bonding interactions? In which are they connected by covalent bonds?**

Ans. Generally, the cross linked polymers are connected by the utilization of non-bonding interactions. This include branched chains which have covalent bonds.

**B) Of the 3 shapes, shown above, which can be recycled? Why?**

Ans. The linear structure of chain can be recycled. This is due to its easy to melt characteristics and chains that can be molded into chains.

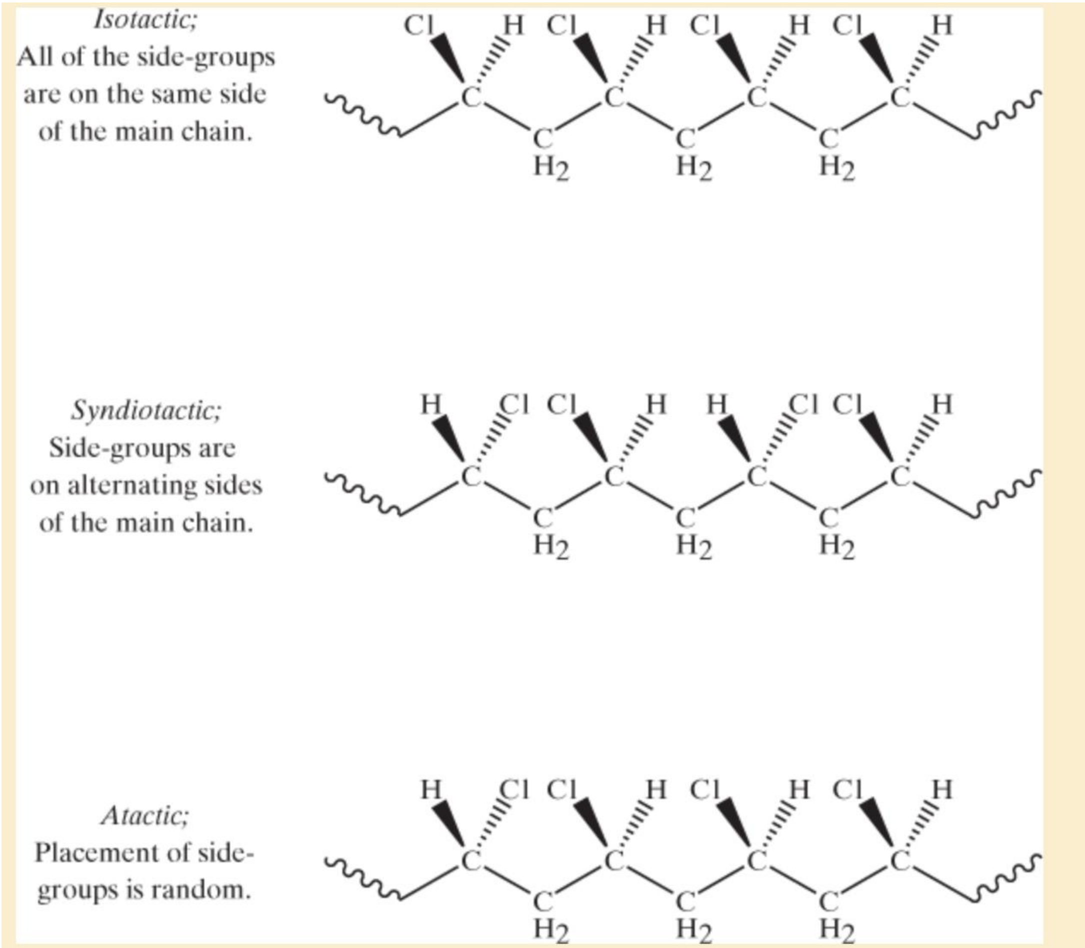
**C) Which polymer will more easily form a crystal – linear or branched?**

Ans. The linear polymer structure can form the crystal because of their arrangement in a crystal lattice.

**Tacticity**

Another important aspect of of the shape of polymers is their *tacticity*. Tacticity occurs in polymers

that have all carbon -carbon single bonds in their main chain, such as polypropylene, polystyrene and poly ( vinylchloride). Tacticity refers to the arrangement of side groups as shown below:




A) **In which structure is the chlorine atom always on the same side of the chain? In which is the chlorine atom on the alternating sides?**

Ans. The structure in which the side groups remains on the similar side of the chain is isotactic structure. In this framework, the chlorine atoms are attached on the same side. On the other hand, the structure which side groups present on the alternating position is syndiotactic structure. Here also, the chlorine atoms remain on same alternating sides.

B) **Of the three tacticities, which least easily forms a crystal. Why?**

Ans. The easy-to-form tactic structure is the isotactic crystal because the packing of crystals is very high in this case due to symmetry of polymer.

**Molecular Weight**

We can calculate the molecular weight of polymer by knowing molecular weight of a **repeat unit** and the **degree of polymerization**. But in reality a piece of plastic contains a mixture of polymeric molecules with different molecular weights. Therefore, we need to be able to calculate an **average molecular weight for a mixture of polymer chains**. First we need to do a simple weighted average.

**Sample problem**: If you have a sample of plastic which you know contains 10 moles of chains that have a molecular weight of 5,000g /mol and 5 mols of chains with a molecular weight of 50,000g/mol. What is the average molecular weight of this mixture?

So, the average molecular weight is called the *number average molecular weight*, because the average is weighted by the number of molecules that are present for each molecular weight. Mathematically this average can be written as follows:

$$\overline{M_n} = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

Where $\boldsymbol{N_i}$ is the number of moles of chains with molecular weight $\boldsymbol{M_i}$ .
So the average molecular weight of the mixture would be:

$$\mathbf{\frac{(10x\ 5000) + (5\ x\ 50{,}000)}{10 + 15} = 20{,}000g/mol}$$

Problem:

**a) So, if you have a sample of plastic which you know is 15 mol% polymer molecules with molecular weight 500,000g/mol and 85 mol% polymer molecules with molecular weight 150,000 g/mol.**

**i) For this mixture, what numerical values will you use for N to calculate the average molecular weights?**

Ans. The value of n that we will use is 100.

**ii) What is the number average molecular weight for the mixture?**

Ans. The overall number of molecular weight of the given sample can be calculated as:

$$\frac{15 * 500{,}000 + 85 * 150{,}000}{(15 + 85)} = 202{,}500 \frac{gm}{mol}$$

The number average molecular weight is not the only average that one can calculate . The *weight average molecular weight* is calculated by weighting the average based on the mass of the molecules that are present for each molecular weight. Mathematically, this average can be written as follows:

$$\overline{M_w} = \frac{\sum_i w_i M_i}{\sum_i w_i} = \frac{\sum_i \left(N_i M_i\right) M_i}{\sum_i \left(N_i M_i\right)} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

Where ***wi*** is the total mass of all chains with moelcular weight $M_{i.}$

The molecular weight of a polymer has an important effect on its properties. This can be conceptualized by considering a bowl of cooked spaghetti. If we compare a regular sized spaghetti versus a bowl of spaghetti cut into short pieces, this difference is analogous to polymers with different molecular weights. It is harder to pull apart "chopped spaghetti" compared to "regular sized long spaghetti" is it not?

So, let us consider these questions:

**a) Which would you expect to be *stronger*; a polymer with a high molecular weight OR one with low molecular weight?**

Ans. The mechanical properties of the polymer is dependent on the molecular weight, especially when the specimen is treated above glass transition temperature. Therefore, higher the molecular weight, greater will be its mechanical property.

**b) Which *would flow more easily*? A polymer with high molecular weight OR one with low molecular weight?**

Ans. Usually polymeric compounds with low molecular weight flow easily compared to higher molecular weight. This is due to less frictional effect of the molecules and less entanglement of the polymeric chains.

**c) So, you are working at a plastics company, and your boss wants you to modify an existing polymer so it will be stronger and flow more easily for processing. How would you change the molecular weight distribution to meet both of these requirements?**

Ans. First, we will compare the two polymer compounds and analyze their molecular weights. The polymer that comprises of high molecular weight should have longer chains and vice versa. Therefore, the longer chain polymer should have high mechanical property compared to short chains. The polymeric compounds with the short chain is usually lesser than the viscosity of the long chain polymer. Therefore, the viscosity of the low molecular weight polymer will also be shallow. Therefore, in order to attain high strength and flow, we can add the long chain polymer and short chain polymer in the existing compounds.