

Assignment 9

Due: *In Lab*, Tuesday, February 26/Thursday, February 28

1. This week you will be synthesizing a unique class of polymer: a block copolymer, focus of a significant amount of basic and applied research here at the University of Minnesota. One of the most interesting characteristics of block copolymers is their tendency to segregate into microphases—in which, essentially, chemically different polymer blocks attached to the same molecule do their best to stay away from each other. A good review on the physics of block copolymer segregation can be found at:

Bates, F. S.; Frederickson, G. H. "Block Copolymers—Designer Soft Materials." *Physics Today*, February 1999, pp. 32-38. (<http://dx.doi.org/10.1063/1.882522>)

The physical properties of block copolymers are very much unlike those of statistical copolymers. In Lab 2, you determined that statistical copolymers of styrene and butylacrylate had physical properties that were intermediate between polystyrene and poly(butylacrylate) homopolymers. However, unlike statistical copolymers, a combined block copolymer often simultaneously retains properties of *both* of the component blocks. For example, polystyrene is a rigid material with a high glass transition temperature ($T_g = 100\text{ }^\circ\text{C}$), and polyisoprene is a viscous material with a low glass transition temperature ($T_g = -73\text{ }^\circ\text{C}$). A statistical P(SI) copolymer would likely show a T_g somewhere between $100\text{ }^\circ\text{C}$ and $-73\text{ }^\circ\text{C}$. But PS-PI block copolymers actually show *both* T_g s, corresponding to the melting of each of the physically segregated portions of the polymer. On the face of it, this might not make much sense; how could a polymer be simultaneously glassy and molten? In PS-PI copolymers, this simply means that there are regions of glassy and molten polymer throughout the material. These regions are incredibly small—on the order of nanometers—and together they have a dramatic effect on the physical properties of the copolymer material.

This unique characteristic of block copolymers has been utilized in thermoplastic elastomers. In a typical elastomer (rubber), polymer chains are chemically crosslinked into a networked structure. This network is responsible for the elastic behavior of the rubber, but also means that the material cannot be reformed into a new shape once it has been set. In a thermoplastic elastomer, "crosslinks" in the material are formed not by chemical bonds, but rather by triblock (PS-PI-PS) copolymer chains that stretch from one glassy PS region to another. As a result, melting the glassy PS regions releases the elastomer and allows it to be re-formed and, if desired, recycled. Technologically, thermoplastic elastomers are obviously unsuitable for high-temperature applications (such as auto tires), because the rubber melts. But they are ideal for finely molded objects such as garden tool handles and shoe soles.

A good source of reading on these materials:

Holden, G. *Understanding Thermoplastic Elastomers* (Hanser Gardner, Cincinnati, 2000), pp. 1-52. (*On reserve, Walter Library.*)

You can also read more about commercial PS-PI-PS triblock elastomers at Kraton (<http://www.kraton.com/>) and Dexco (<http://www.dexcopolymers.com/>), two companies that specialize in block copolymer materials.

Draw a cartoon that best illustrates the structural difference between chemically crosslinked and thermoplastic elastomers, representing the polymer chains as lines and squiggles. In both cases, also draw cartoons that show how the elastomer responds to elongation.

2. You will be synthesizing your polymers by living, anionic polymerization, a method which is exceptional for its control over molecular weight and monodispersity. You may want to review a text chapter on anionic polymerization (e.g., Odian) before doing Lab 4.

One of the great characteristics of anionic polymerization is its relative predictability; because initiation and polymerization are perfectly efficient, it is easy to target a particular molecular weight product and then achieve that molecular weight. In this lab, you will synthesize your first polystyrene homopolymer/block with a target molecular weight determined by your pair number:

pair number	PS block length (g/mol)
1,2,9,10	4,000
3,4,11,12	5,000
5,6,13,14	6,000
7,8,15,16	7,000

Before you come to lab, you will need to calculate the amounts of styrene and isoprene (in mL) you will need to obtain your target molecular weight.

For ideal anionic polymerization, once polymerization is complete, the degree of polymerization

$$\overline{DP} = \frac{[M]_0}{[I]_0}$$

So, molecular weight is determined solely by the amounts of initiator and monomer used. In this lab, you will use 2.0 mL of 1.4 M *sec*-butyllithium solution in cyclohexane as an initiator. Assuming $M_x = M_n$ (a symmetrical distribution of polymer molecular weights) how much styrene will you need to syringe into your polymerization flask to achieve your target M_n for your initial homopolymer?

3. You will also be synthesizing PS-PI diblock copolymers with the same polystyrene block length as in your PS homopolymer. However, we will only be using *half* the amount of initiator (1.0 mL of 1.4 M *sec*-butyllithium) in the diblock synthesis. How much styrene (in mL) should you use in the diblock synthesis?

4. We will synthesize diblock copolymers with a range of polyisoprene block lengths:

pair number	PI block length (g/mol)
1,3,13,15	3,000
5,7,9,11	4,000
2,4,14,16	6,000
6,8,10,12	7,000

Given your answer to problem 3, how much isoprene (in mL) will you need to will you need to syringe into your polymerization flask to achieve your target PI block length?