

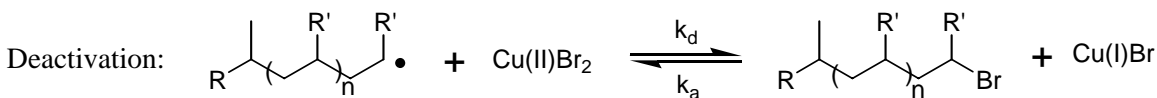
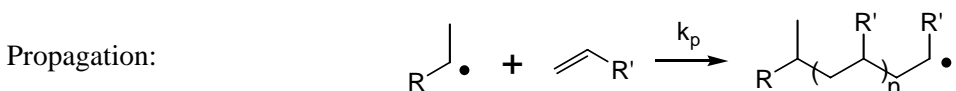
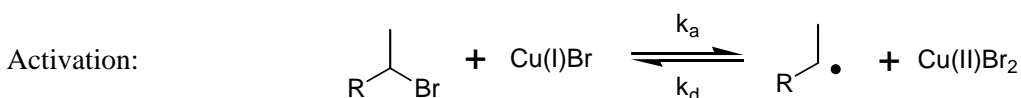
Lab 5

Controlled Radical Polymerization (ATRP)

Introduction

In Lab 4, you were exposed to living polymerization—polymer synthesis in which there were no termination or transfer reactions and in which initiation was much faster than polymerization. Recently, researchers have developed a number of alternative radical polymerizations which, while not strictly living, suppress termination and transfer enough that they can be termed “controlled” radical polymerizations. Controlled free-radical polymerizations offer good control over molecular weight and polydispersity. (This is in obvious contrast to normal radical polymerizations, which are characterized by poor control over molecular weight.) In addition, controlled free-radical polymerizations retain the advantage of all radical polymerizations, that they are relatively insensitive to monomer functionality or reaction impurities such as water.

Controlled radical polymerizations have been reported using metal-mediated homolytic bond cleavage of alkyl halides and related compounds. This process has been termed Atom Transfer Radical Polymerization (ATRP).¹ The alkyl halide reacts reversibly with the metal catalyst; abstraction of the halide produces a radical, and an oxidized metal catalyst. Propagation of the monomeric species can then occur at the radical, but chain growth is modulated by deactivation of the radical back to the alkyl halide.

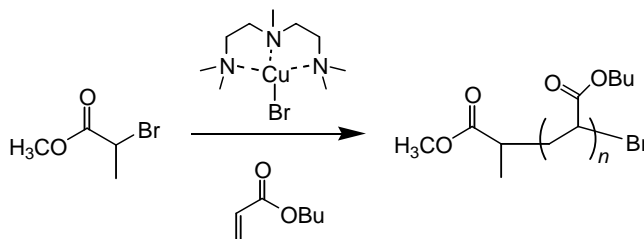


In a successful ATRP reaction, enough activation occurs to allow for chain propagation to useful molecular weights, but frequent deactivation by the metal halide maintains the concentration of radicals at low enough levels that termination involving two radicals does not occur. The rates of radical termination and disproportionation are very fast (near the diffusion controlled limit), so the concentration of the activated radical species must be limited in order to prepare polymers with controlled structures. For this reason, in successful ATRP reactions the metal-alkyl halide equilibria favors the deactivated species.

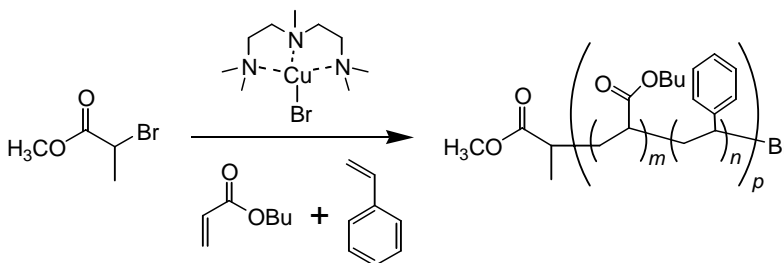
¹ Patten, T.E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901.

In this experiment, you will be synthesizing two polymers via ATRP—a homopolymer of *n*-butyl acrylate and a statistical copolymer of *n*-butyl acrylate and styrene—using a chelated copper bromide as the catalyst, and α -bromoesters as initiators.

Homopolymer:



Random copolymer:



Because ATRP is less sensitive to reaction impurities than anionic polymerization, you should be able to obtain monodisperse polymers with less trouble than in Lab 4. However, ATRP polymerization kinetics and catalyst stability both depend on the monomer being polymerized. As a result, part of your task for Lab 5 will be to evaluate the effect of styrene on the success of your ATRP polymerization.

The polymers you will make in this lab will differ from your previous materials in that they will be extremely viscous liquids rather than solids at room temperature. This is actually more common than you might think; $T_g < 298$ K for many polymers, including poly(*n*-butyl acrylate) ($T_g = 218$ K). The viscosities (η) of bulk polymers and of polymer solutions depend on molecular weight and, for solutions, polymer concentration. Molecular weight control in polymer synthesis, as a result, is important for the development of viscosity-modifying polymer additives in products such as motor oil, foods, and personal care products.

Experimental

Polymerization of *n*-butyl acrylate and statistical copolymerization of *n*-butyl acrylate and styrene via ATRP (March 9/10)

- Check out from the stockroom:
 - 2 50 mL round bottom centrifuge tubes
 - 2 NS 14/20 rubber septa

- Heat/stirplate

In addition, pick up 2 NS 14/20 rubber septa, a blank purge needle and two argon balloons from the TA's.

- Set up a 70 °C water bath in a beaker at your bench, immediately next to a clamp support. The beaker should be large enough to accommodate both of your centrifuge tubes, and not overflow when you insert the tubes into the bath.
- To each centrifuge tube, add a small stirbar, the quantities of *n*-butyl acrylate and styrene you calculated in Assignment 16, and 0.05 g of Cu(I)Br. Cap each tube with a septum. As you did in Lab 4, use one argon balloon to purge the headspace above the monomer, and then use another to maintain positive argon pressure. (ATRP is tolerant of water, but oxygen can oxidize the copper(I) catalyst to inactive copper(II).)
- Immerse your reaction in a heated water bath at 70 °C, and start the stirring.
- Via syringe, add 0.08 mL *N,N,N',N'',N'''*-pentamethyldiethylenetriamine to each tube, and then the amount of methyl 2-bromopropionate initiator you calculated. Allow the mixture to stir at 70 °C for 2 hours. Make sure to note any changes you observe in the reactions.
- Allow the flask to cool to room temperature, and remove the argon balloon. If the reaction has solidified during this time (highly unlikely), add discrete volumes of methyl ethyl ketone (MEK) until your reaction product dissolves. Make sure you record how much MEK you've added.

Isolation of polymers (March 9/10)

- Check out from the stockroom:
 - A fritted filter funnel. The porosity of the filter frit should be *coarse*; this will be marked on the side of the funnel (pore size 40-60 microns, type "C" for coarse).
- Dilute each polymer sample in 50 mL acetone. (As is usual for dissolving polymers, this may take a while.) Then, add ~5 g solid silica gel to the solution, with stirring, until the silica suspension turns bright blue. Pack the fritted filter funnel with a centimeter or so of solid Celite, and vacuum-filter your silica suspension through the Celite into a filter flask. (The Celite has very poor binding properties, but packs well; it is intended to keep the fritted funnel from being plugged with silica.)
- After the silica step, some green color may still remain in your solution. If so, add 2 g of DOWEX MSC-1 ion-exchange resin beads to the flask. Stir for 30 minutes, or until the green color disappears, and then decant the solution from the beads.
- Estimate the volume of your current solution, multiply by 10, and prepare a 1:1 methanol/ice mixture with the calculated volume. With rapid stirring, pour your polymer into this mixture. If your mixture is cold enough, your polymer should precipitate as a white goop or glob. As best you can, decant the supernatant off the goop. Prepare another 1:1 methanol ice mixture, and use this to wash the polymer product. Again, decant the supernatant, and collect your polymer in a tared screw-top vial. Place foil over the vial, with some very small holes punched in it to allow solvent to escape, and place your product in the vacuum oven at 80 °C overnight.

Characterization (March 23/24)

- Remove your samples from the vacuum oven, and determine the yield for each. Physically, how do they compare?
- Make up an NMR sample of your P(nBA-co-S) sample (20 mg polymer/mL CDCl₃), and submit it to the TA's for NMR.
- Make up GPC samples for each of your polymers (10 mg polymer/mL THF), and run GPC on them.

There is no Lab Report due for this Lab. Instead, you will analyze your results in Assignments 16 (due *By Lecture*, Wednesday, March 29) and 18 (due *In Lecture*, Wednesday, April 5).