Conducting A Reversible-Deactivation Radical Polymerization (RDRP)

**Aim:** To Prepare Block Copolymers of Methyl Methacrylate (MMA) and Styrene.

Polymers are ubiquitous in the modern world. They provide tremendous value because the chemical and physical properties of these materials are determined by the monomers that are used to put them together. One of the most powerful methods to construct polymers is radical-chain polymerization and this method is used in the commercial synthesis of polymers everyday. Methyl methacrylate is polymerized to form poly(methyl methacrylate) (PMMA) which is also known as acrylic glass or Plexiglas (about 2 billion pounds per year in the US). This material is lightweight, strong and durable. The polymer chains are rigid due to the tetrasubstituted carbon atom in the polymer backbone and they have excellent optical clarity. As a consequence, these materials are used in aircraft windows, glasses, skylights, signs and displays. Polystyrene (PS), which can also be synthesized from radical chain polymerization, has found extensive use as a material (also approximately 2 billion pounds per year in the US). One of the forms of PS, Styrofoam, is used extensively to make disposable cups, thermal insulation, and cushion for packaging.

**Scheme 1. Radical polymerization of methyl methacrylate or styrene.**

![Methyl Methacrylate](O=O \rightarrow R' \rightarrow O=O\_n) \quad \text{PMMA}

![Styrene](\text{Ph} \rightarrow R' \rightarrow H\_n) \quad \text{PS}

While there are extensive uses for these polymers, when synthesizing any material using a free-radical polymerization, samples are obtained with limited control over molecular weight and molecular weight distribution. New methods have been developed directly at Carnegie Mellon ([https://www.cmu.edu/maty/](https://www.cmu.edu/maty/)) which lead to improved control in this process. This new method is a reversible-deactivation of the polymerization reaction where highly reactive radicals toggle back and forth between an active state, where the polymer chain is growing, and a dormant state, where the polymer chain is capped (Scheme 2). This is termed atom-transfer radical polymerization (ATRP), and is achieved by a copper catalyst bearing a polydentate nitrogen ligand, which can cleave a C-Br bond to form the radical responsible for polymerization. This process is reversible so the Br can be transferred back from the copper to the polymer, producing the dormant chain. This equilibrium between active and dormant chains is influenced by the copper complex used and in this experiment N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) will be used as the ligand.

**Scheme 2. Simplified depiction of ATRP (ligand not shown).**

\[
P - \text{Br} + \text{CuBr} \xleftrightarrow{M} \text{P}^\prime + \text{CuBr}_2
\]

You will use a new technique in ATRP to produce block copolymers of PMMA and PS. One of the advantages of these controlled radical polymerizations is the ability to access polymers that could not be prepared using conventional polymerization. Block copolymers consist of
two different polymer chains, linked by a covalent bond. You will start from \((\text{PMDETA})\text{CuBr}_2\) which can be reduced by Cu wire to form the desired \((\text{PMDETA})\text{CuBr}\) activator for polymerization (Scheme 3). This reaction is a comproportionation reaction where two metals with different oxidation states combine to produce a metal with the same oxidation state. This will all be conducted during polymerization and the polymerization will follow the expected pathway outlined in Scheme 2. A starting bromide reagent (ethyl bromophenylacetate: EBPA), will be used to initiate polymerization.

**Scheme 3. Active formation of \((\text{PMDETA})\text{CuBr}\) and the radical initiator for polymerization.**

![Scheme 3](image)

Before starting the lab, draw the first two steps of propagation: i.e., the initiator reacting with two equivalents of methyl methacrylate. Remember that monomer can be added to the growing polymer chain and reversible-deactivation will incorporate a Br atom at the polymer chain end to produce a dormant chain.

**Homopolymerization of MMA**

Purify 25 mL (enough for 2-3 people) of methyl methacrylate (MMA) by running it through a column with a short alumina plug (about two inches high). To prepare the column, plug the column with a small piece of cotton and add about ½ cm of sand to cover the cotton and create a flat surface. Add the alumina and tap the column gently with a cork ring to level the surface. Pour the MMA into the column and drain to the top of the alumina.

Make precomplexed \(\text{CuBr}_2/\text{PMDETA}\) by placing approximately 20 mg of \(\text{CuBr}_2\), 0.06 mL of PMDETA, and 1 mL of dimethylformamide (DMF) in a small vial. Let stir for a few minutes. When not in use, seal with electrical tape and store in locker.

![CuBr2/PMDETA solution](image)

Place the following in a 40 mL glass vial: 6 mL of uninhibited MMA, 0.02 mL of the EBPA initiator, 0.08 mL of the precomplexed \(\text{CuBr}_2/\text{PMDETA}\), 6 mL of anisole, a small
egg-shaped stir bar, and a small piece of copper wire (a few inches long, twisted into a ring shape). Seal the vial and degas for 30 minutes. The degassing is critical to the reaction. This can be accomplished via freeze-pump-thaw cycle, or by  After degassing, stir the vial in a 60 °C oil bath for an hour.

Remove the vial from the heat and open to air. Dilute reaction mixture with a few mL of acetone if too viscous. Place 350 mL of methanol and a large stir bar into a 500 mL Erlenmeyer flask and start stirring rapidly. Pipette the reaction mixture dropwise into the flask. Let stir for five more minutes after all of the reaction mixture has been added.

Collect the precipitated PMMA by vacuum filtration. Wash the solids on the filter with methanol. Dry the solids under vacuum for several minutes. Weigh dried product.
Prepare a GPC sample by dissolving about 1 mg of the PMMA in 1-2 mL of tetrahydrofuran (THF) in a small vial. Filter approx. 1.2 mL using a syringe filter into a GPC sample vial. $^1$H NMR spectroscopy can also be employed for analysis.

**Chain extension of PMMA**

Purify 10 mL of either monomer (styrene or butyl acrylate) by running it through a column with a short alumina plug. To a 20 mL glass vial, add 0.5 g of the PMMA, 1 mL of the uninhibited monomer, 15 μL of CuBr$_2$/PMDETA, 1 mL of anisole, a stir bar, and a small piece of copper wire (can reuse piece from polymerization of PMMA). Seal and degas for 30 minutes. If monomer is styrene, stir in 80 °C oil bath overnight. If monomer is butyl acrylate (BA), stir in a 60 °C oil bath overnight.

Dilute reaction mixture with acetone if too viscous. For PMMA-b-PS, follow the same precipitation method as for PMMA. Weigh dried product. Prepare a GPC sample.
For PMMA-b-PBA, precipitate using 50/50 (v/v) methanol/water as the solvent. Instead of precipitating as a solid, PMMA-b-PBA should precipitate as gooey oil. Pour out the solvent, leaving the oil in the flask. Dissolve the oil in a minimum amount of acetone and transfer to a small flask. Remove the acetone by directing a stream of air into the flask. Weigh dried product. Prepare a GPC sample.

**Casting a film**

Dissolve 300 mg of either block copolymer in 10 mL of dichloromethane. Plug the tip of a disposable pipet with a small piece of a Kimwipe and filter through the pipet into a small Petri dish. Let the solvent evaporate by placing the Petri dish under a glass dish that is propped up slightly with paper towels to allow air in.

After about half an hour, once solvent is completely evaporated, peel film off with tweezers. If film is difficult to remove, cover with a thin layer of water and let soak.