EXPERIMENT D

TRANSITION-METAL-MEDIATED POLYMERIZATION REACTIONS

Part 1. Ring-Opening Metathesis Polymerization (ROMP)

Transition metal complexes are widely used in industry as catalysts. One application is their use in polymerization reactions such as the preparation of polyethylene and polypropylene, (Ziegler-Natta polymerization). This experiment demonstrates the Ring-Opening Metathesis Polymerization (ROMP) of cyclic olefins catalyzed by transition-metal complexes. A typical strained cyclic olefin is norbornene (bicyclo[2.2.1]hept-2-ene). The polymer that results from the ROMP of norbornene is a commercially available material called Norsorex™. Norsorex™ can absorb 5-10 times its weight in oil and pads of this material are used for oil spill recovery, or when filled with oil, the material is used for noise damping. The ROMP of other strained cyclic olefins leads to many commercial products through “Reaction Injection Molding” (RIM). Typically, the two reactants that form the catalyst are separately dissolved in solutions of the monomer along with fillers and coloring agents. The two solutions are then simultaneously injected into a mold. The catalyst forms and polymerizes the monomer in the mold. The finished product can then be removed from the mold with the catalyst trapped inside. Products like plastic car bumpers and golf carts are made this way from the monomer dicyclopentadiene (C\textsubscript{10}H\textsubscript{12}) and the materials are known commercially as Telene™ (B. F. Goodrich) or Metton™ (Hercules).

In this experiment you will polymerize norbornene using the Grubb’s second generation catalyst and cast a film of the resulting polynorbornene. The Grubb’s catalyst is a Ruthenium complex containing chloro, benzylidene, N-heterocyclic carbene and tricyclohexylphosphine ligands.

Useful references:

As of 1998, above 100 billion pounds of synthetic polymers were produced each year in the United States alone. Of that amount, chain growth polymerization accounts for approximately 80% and radical polymerization is by far the most commonly used method in this area. In a traditional radical polymerization process, the initiator, for example a peroxide (e.g. benzoyl peroxide, BPO) or a dialkyldiazene (e.g. 2,2'-azobisisobutyronitrile, AIBN), decomposes to generate radicals that add quickly across double bonds to form long chains. The initiator decomposes slowly compared to the rate of polymerization such that chains are continuously generated and terminated. This process leads to a statistical distribution of molecular weights since the conditions change to favor longer or shorter chains and the resulting polymers typically have a polydispersity of 2.0 or higher. Another problem with radical polymerization is that radical chain ends react with each other to terminate chains with either saturated alkane or hindered alkene chain ends, which makes further transformation of the chain ends into other types of chemical groups or extension with other monomers difficult.

Atom transfer radical polymerization (ATRP) mediated by metal complexes represents one solution to this problem (other methods are “Stable Free Radical Polymerization”, SFRP, and Reversible Addition-Fragmentation Chain Transfer, RAFT). ATRP was developed at Carnegie Mellon University by Professor Matyjaszewski and utilizes reversible halogen atom exchange between the propagating radical chain end and a redox-active inorganic species to reduce the radical concentration and suppress the contribution of irreversible bimolecular termination reactions that pervade conventional radical polymerization (Figure 1). This, combined with fast initiation from a small organic halide, R–X, with a sufficiently reactive C–X bond, leads to a polymer sample of fairly uniform molecular weight chains, which retain the halogen end group, X. Molecular weights can be predicted and controlled by the molar ratio of consumed monomer to initiator (Δ[M]/[I]₀), assuming that initiation is quantitative.

The most commonly applied mediator systems in ATRP include a transition metal compound Mtⁿ, for example a Cu(I)X salt where X = Cl or Br, complexed by bidentate or tridentate nitrogen ligands such as 2,2'-dipyridyl-based ligands and N,N',N″,N‴-pentamethyldiethylenetriamine (PMDETA), which is oxidized to Cu(II)X₂ upon homolytic cleavage of the carbon–halogen bond (Figure 1). The exchange equilibrium (Kₑq = kₘ/k₃d, where kₘ is the rate constant of activation of the polymer chain end and k₃d is the rate constant of deactivation) necessarily favors the dormant organic halide species in order to maintain a low steady-state concentration of radical chain ends. It is the greatly reduced concentration of propagating radicals, [R-Mₙ], that leads to a suppression of irreversible termination reactions (kₜ) relative to propagation (kₚ).

One consequence of regulating the growth of chains is that the molecular weight increases steadily with conversion. The result is a well-defined polymer sample with low polydispersity (sometimes as low as 1.05, which approaches the limit of most commonly used detection methods). The other big advantage is that virtually all chains have a halogen atom on the end when the reaction is finished. These polymers can then be extended...
with another monomer to generate block copolymers, or the end groups can be transformed into something else such as an azido, amino, or hydroxyl group using standard organic synthesis techniques. This gives the polymer functionality that can then be manipulated in a number of ways including tethering to surfaces or incorporating into other polymers.

**Initiation:**
\[
R-X + M^a \xrightarrow{k_i} R + M^a + M
\]
\[
R-M-X + M^a \xrightarrow{k_i} R-M^+ + M^a + M
\]

**Propagation:**
\[
R-M_n^a + M^a \xrightarrow{k_a, k_d} R-M_n^+ + M^a + M
\]
\[
R-M_n-M_n^-R + M \xrightarrow{k_p} \]

![Figure 1. General mechanism of atom transfer radical polymerization](attachment:figure1.png)

In this experiment, you will polymerize styrene using the ATRP method and extend it with methyl methacrylate to make a diblock copolymer PS-block-PBA. The resulting polymers will be analyzed by gel permeation chromatography (GPC), \(^1\)H NMR spectroscopy, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

**Useful references:**
Session 1

Transition-Metal-Catalyzed Polymerization of Norbornene.

In this session the polymerization of norbornene using Grubb’s second generation catalyst will be performed inside an inert-atmosphere glove box under an atmosphere of dry nitrogen gas. The T.A. will instruct you as to how to use the glove box.

Weigh out approx. 1.0 g of norbornene into a large vial containing a micro stirbar and add 5 ml of dry toluene (provided in the box). Add 1 mL of the catalyst solution (ca. 2 mg/mL of the Grubb’s catalyst) by syringe with stirring. Seal the vial and remove it from the dry box, note that the reaction is very exothermic and the vial may be quite hot. After 10-30 minutes the solution will become immobile. Open the vial and add about 5-10 mL of toluene to help remove the polymer solution and precipitate it into methanol (ca. 100 mL) in a beaker. Precipitation is best achieved by slowly adding the toluene solution dropwise to the vortex of the rapidly stirred methanol. Let it stand for in the fumehood for a few minutes for the catalyst to be destroyed (by air) and filter off the white polymer solid. Let it dry and dissolve it in a minimum of THF for purification in the next period. The solution may be extremely viscous and the polymer may simply swell rather than dissolve. This is an indication of very high molecular weight and a fairly insoluble polymer.

Q1. What would be a likely end group of your polymer?

Q2. Draw a mechanism for the polymerization of cyclopentene instead of norbornene using the Grubb’s catalyst.

NMR Assignment: A well-defined catalyst system that can also be used for the polymerization of norbornene is pentacarbonyl{phenyl(ethoxy)carbene}tungsten(0) activated with AlCl₃. The $^1$H (Dspectrum6.pdf) and $^{13}$C NMR (Dspectrum5.pdf) spectra of this carbene complex can be downloaded from the website and should be fully assigned.
**Session 2**

1. Copper-Mediated Homopolymerization of Styrene

\[
\begin{align*}
\text{Br} & \quad \text{CuBr/PMDETA} \\
\text{C}_6\text{H}_5 & \quad \text{Anisole, 110°C} \\
\text{CH}_2-\text{CH} & \quad \text{Br}
\end{align*}
\]

Before the experiment starts, setup a magnetic stir/hot plate beside the nitrogen line with an oil bath at 110 °C. In the dry box, add 0.13 g CuBr (0.875 mmol), 0.16 g PEB (phenyl ethylbromide, 0.875 mmol – via syringe), and a large magnetic stir bar into a 100 ml Schlenk flask. Seal the flask with a rubber septum and take it outside to the magnetic stir plate. Under nitrogen protection add 10 ml styrene (9.09 g, 87.5 mmol), 5 ml anisole, and 0.2 ml PMDETA (0.875 mmol) to the flask using plastic syringes. Fix a long needle to the nitrogen line (place the thick end inside the hose), purge the needle with N₂, and then insert the sharp end into the flask through the septum. Connect the closed stopcock outlet of the Schlenk flask to an oil bubbler using a clean piece of rubber tubing. Slowly start to open the stopcock (only partially!) and adjust it to such a speed that you can clearly see 3 or 4 bubbles per second in the oil bubbler. Then place the tip of the needle in the reaction mixture but out of the way of the stir bar. After purging for 30 minutes lift up the needle and lower the N₂ flow to ca. 1 bubble per 3 seconds. Immerse the flask in the 110 °C oil bath and keep the mixture stirring for 2.5 hours. Remove the needle and close the stopcock (remember to carefully clean the needle with a small amount of THF and then acetone). Then cool the reaction mixture to room temperature in a cold water bath. You will do the workup of your polymer in the next session.

2. Workup of Polynorbornene.

Add the THF solution from the previous period to methanol to reprecipitate the polymer as before. Dry the purified polymer under high vacuum for 1 h (warm water bath) and calculate the yield. Obtain a \(^1\text{H NMR}\) spectrum of your norbornene polymer in CDCl₃. Note: it will likely take a few minutes (or hours) to dissolve the sample in the solvent due to its high molecular weight and extensive chain entanglement. Submit a sample in THF to the TA for GPC analysis. GPC is Gel Permeation Chromatography and gives an estimate of the polymer molecular weight. Include your GPC of the sample in your lab report. Also submit a sample of your precipitated product with your report.

Redissolve the remainder of your polymer in a vial with 10 ml THF. You will cast films from the THF solution in the next period.
Session 3

1. Workup of Polystyrene.

Dilute the reaction mixture from the styrene polymerization with 10 ml of THF and suction filter the solution through a short plug of neutral alumina that has been wet with 20 mL of THF (approximately 3 cm high, packed into a short column or Buchner funnel). Wash the column twice with 20 ml THF and combine the solutions. Transfer your polymer solution to a Schlenk flask and concentrate it under high vacuum to ca. 10-20 ml. Recover the polymer by precipitation into a large excess of rapidly stirring methanol (~200 ml), suction filtration, and washing twice with ca. 20 ml methanol. Air-dry and then redissolve your polymer in ca. 5-10 ml THF, reprecipitate into methanol, and wash again twice with methanol. Transfer your polymer into a 100 ml Schlenk flask with wide opening and dry it under high vacuum for at least 1 h. Determine the yield of your polymer and submit samples for GPC and \(^1\)H NMR analysis. Also save a small amount of polymer for differential scanning calorimetry (DSC) (see the TA for instructions). Weigh 4.0 g of your polymer into the 100 ml Schlenk flask (for your report calculate the moles of polystyrene using the molecular weight result from GPC analysis). Add a large stir bar, evacuate the flask and bring it into the dry box. In the glove box add 0.10 g CuBr (0.70 mmol) and seal the flask with a rubber septum. Leave the flask in the glove box until the next period when you will use your polymer as the initiator for the polymerization of n-butyl methacrylate.

**Calculations:** For your report determine the theoretical and actual number of repeating units of your polystyrene polymer from

(i) the ratio of monomer/initiator and the actual monomer conversion (estimated from polymer yield)
(ii) \(^1\)H NMR end group analysis
(iii) GPC analysis

Q3. Compare and interpret your results; which method is most reliable?

2. Cast a film of the Norbornene polymer obtained from WCl\(_6\)/SnEt\(_4\) catalyzed reaction.

Cast films of the norbornene polymer from THF by allowing a concentrated viscous solution to evaporate on a glass slide or a petri dish or in the bottom of a small beaker. Allow the cast film to dry until it can be peeled from the container. Note and explain the properties of the newly cast films and the properties of aged films (a few days later). Compare the spectrum of the polymer with that of the monomer (Dspectrum4.pdf). You must assign the spectra of both monomer and polymer.
Session 4

Formation of a Block Copolymer with \( n\)-butyl methacrylate

\[
\begin{align*}
\text{CH}_2\text{-CH}_n\text{Br} + \text{m} \text{CH}_2\text{-CH}_m\text{OBu} & \xrightarrow{\text{CuBr/PMDETA}} \text{CH}_2\text{-CH}_n\text{OBu} + \text{CH}_2\text{-CH}_m\text{Br}
\end{align*}
\]

Start on time, this experiment is lengthy! Work in the hood, the acrylate is very smelly!

Before the experiment starts, setup a magnetic stir plate beside the nitrogen line and an oil bath at 80 \(^\circ\)C. Take the Schlenk flask containing your polystyrene and CuBr outside the glove box and add under nitrogen protection 10 ml \( n\)-butyl methacrylate, 10 ml anisole and 0.15 ml PMDETA (0.72 mmol) through syringes. Stir well to dissolve all the polystyrene. Purge the reaction mixture with nitrogen for 30 minutes as you have done for the styrene polymerization. Immerse the flask in the 80 \(^\circ\)C oil bath and keep it stirring for 1 hour.

Cool the reaction mixture to room temperature in a cold water bath, dilute the reaction mixture with 10 ml THF and work up your polymer in the fumehood by filtration through alumina, concentration of the resulting block copolymer solution, and one precipitation into methanol (see workup of polystyrene). Transfer your polymer to a Schlenk flask and dry it for 30 min under high vacuum. Submit samples for GPC (in THF) and \(^1\text{H}\) NMR (in CDCl\(_3\)) analysis. If it can be transferred to a vial submit your final block copolymer with your report.

Note: Do not attempt to determine a yield for your block copolymer. Only determine the product mass.

Calculations: Determine number of repeating units of methyl methacrylate in your block copolymer from

(ii) \(^1\text{H}\) NMR analysis: compare the number of methyl methacrylate (m) versus styrene (n) repeating units – use the GPC results from the polystyrene homopolymer for the number n. Do not perform an end group analysis!

(iv) GPC analysis – use the GPC results from the polystyrene homopolymer for the number n.

Q4. Compare and interpret your results; which method is more reliable here?

Chemicals and Hazards

All of the reactions in this experiment should be carried out in well-ventilated fume hoods or in the dry box. All chemicals should be handled in fume hoods with protective clothing including lab coats, protective gloves and eyewear. Liquid waste should be collected and labeled as halogenated organic waste containing copper salts, although only trace amounts of either are present in the liquid waste. The initiation from the organic halides is near quantitative, incorporating the halogens into the polymers, which can be disposed of as solid waste. The copper salts (along with the triamine ligand) are reduced to ppm quantities in the liquid waste by filtration through alumina, transferring the heavy metal salts into solid waste as well. Both of the monomers used in this experiment, styrene and methyl methacrylate, are flammable, toxic irritants. Styrene is a suspected carcinogen and methyl methacrylate is a suspected teratogen. The ligand, pentamethyldiethylenetriamine, is combustible, flammable, toxic, and is readily absorbed through the skin and lungs, but is used in small quantities and should only be handled in syringes.

FJ/JBS

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