

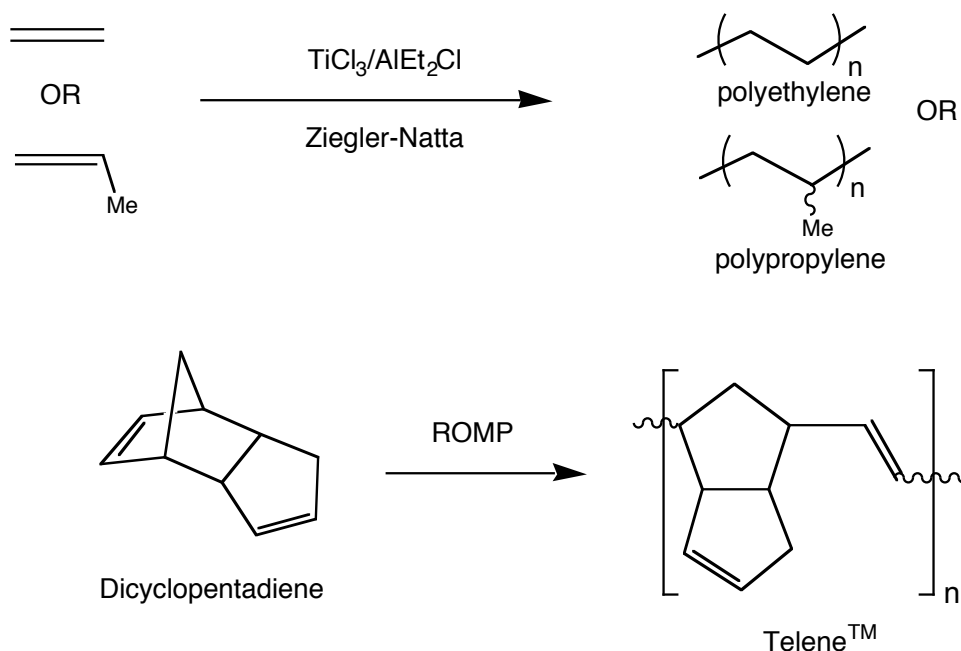
EXPERIMENT D

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 NosorexTM. NosorexTM 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 (C₁₀H₁₂) and the materials are known commercially as TeleneTM (B. F. Goodrich) or MettonTM (Hercules).

In this experiment you will polymerize norbornene using a tungsten catalyst that is generated in situ and cast a film of the resulting polynorbornene.



Useful references:

(1) Petasis and Fu, *J. Am. Chem. Soc.* **1993**, *115*, 7208-7214. (2) Nguyen, Grubbs and Ziller, *J. Am. Chem. Soc.* **1993**, *115*, 9858-9859.

PART 2. ATOM TRANSFER RADICAL POLYMERIZATION (ATRP)

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 ($\Delta[M]/[I]_0$), assuming that initiation is quantitative.

The most commonly applied mediator systems in ATRP include a transition metal compound Mt^n , 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'',N'''*-pentamethyldiethylenetriamine (PMDETA), which is oxidized to Cu(II)X₂ upon homolytic cleavage of the carbon-halogen bond (Figure 1). The exchange equilibrium ($K_{eq} = k_a/k_d$, where k_a is the rate constant of activation of the polymer chain end and k_d 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, $[R-M_n]$, that leads to a suppression of irreversible termination reactions (k_t) relative to propagation (k_p).

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). 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.

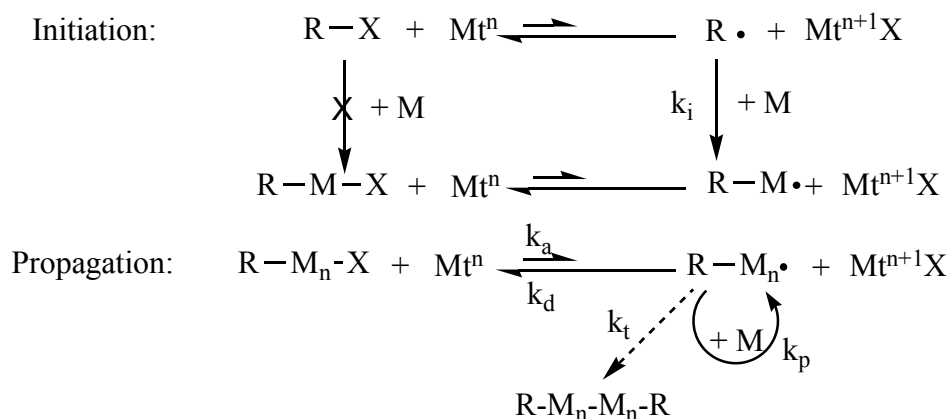


Figure 1. General mechanism of atom transfer radical polymerization

In this experiment, you will polymerize styrene using the ATRP method and compare the results with that of an uncontrolled polymerization. The resulting polymers will be analyzed by gel permeation chromatography (GPC), ^1H NMR spectroscopy, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

Useful references:

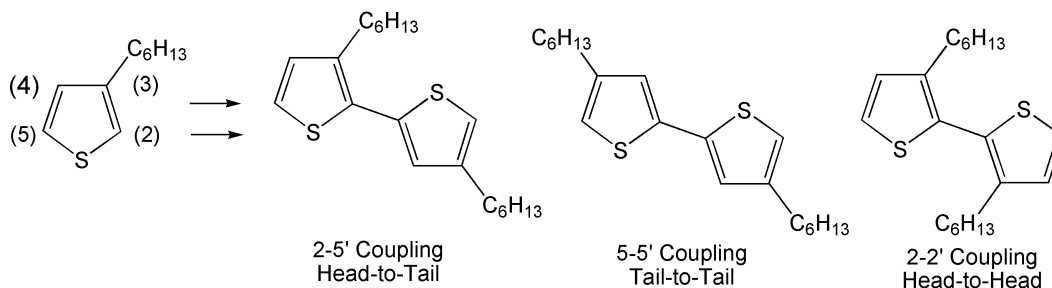
- (1) K. Davis, K. Matyjaszewski, *Macromolecules* **2000**, 33, 4039
- (2) K. Davis, K. H.-J. Paik, K. Matyjaszewski, *Macromolecules* **1999**, 32, 1767
- (3) J. Xia, K. Matyjaszewski, *Macromolecules* **1997**, 30, 7697

PART 3. GRIGNARD METATHESIS POLYMERIZATION (GRIM)¹

- Controlled Synthesis of a Conjugated Polymer -

Conducting Polymers. Most people view organic materials (i.e. plastics) as being insulators rather than conductors of electrical current. For example, copper wire (an inorganic material) conducts electricity while being insulated by a plastic coating (an organic material). Advances in the later half of the 20th century, however, have shown that plastics are capable of conducting electricity. The discovery in the late 1970's that conjugated polymers can be made highly electrically conducting has opened up many new possibilities for devices combining unique optical, electrical, and mechanical properties of plastics and conventional inorganic materials. In certain applications, organic materials may compete with conventional inorganic electronic materials. These plastics are attractive due to their low density, flexibility, and processibility over large coverage areas.

The polymers you will investigate in this experiment, poly(3-hexylthiophene) and related derivatives, have been among the most studied conducting polymers for their use in applications such as thin film transistors and solar cells.² After preparing this polymer, you will investigate its regiochemistry and the conformational effects on its physical properties. As is evident from its structure, 3-hexylthiophene is not a symmetric molecule. As the monomer polymerizes to form the polymer, three unique couplings are possible as seen below:

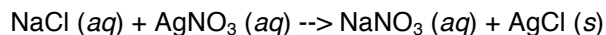


Polymers that contain a mixture of these couplings are referred to as regiorandom (or irregular). The head-to-head couplings in regiorandom poly(3-alkylthiophenes) cause adjacent thiophene rings to twist due to steric interactions of the alkyl groups. This twisting of rings results in decreased conjugation of the polymer. On the other hand, polymers that contain ONLY head-to-tail couplings are referred to as regioregular. Regioregular poly(3-alkylthiophenes) can easily access a low energy planar conformation, leading to highly conjugated polymers. An increase of the torsion angles between thiophene rings leads to greater bandgaps, with a decrease in conductivity and other desirable properties.

Synthetic methods have been developed to form both regioregular and regiorandom poly(3-alkylthiophenes). In this experiment, you will prepare poly(3-hexylthiophene) using Grignard Metathesis Polymerization (GRIM), analyze the regioregularity of your synthesized polymer and compare it to a polymer prepared by an alternative synthetic method. You will use a variety of spectroscopic methods to determine the regioregularity of your isolated polymer.

In this experiment, you will attempt to polymerize the 2,5-dibromo-3-alkylthiophene that you prepared in Experiment B, in the presence of the nickel catalyst, Ni(dppp)Cl₂. Before the polymerization can occur, however, you will utilize a powerful Grignard reagent (*tert*-butylmagnesium chloride) in a Grignard metathesis reaction. Metathesis reactions are prevalent in many areas of chemistry including inorganic and organometallic chemistry. In a metathesis reaction, components of salts

or molecules simply exchange partners. In the case of salts, anions and cations exchange partners. For example, in general chemistry, you likely performed one of the most classical metathesis reactions:

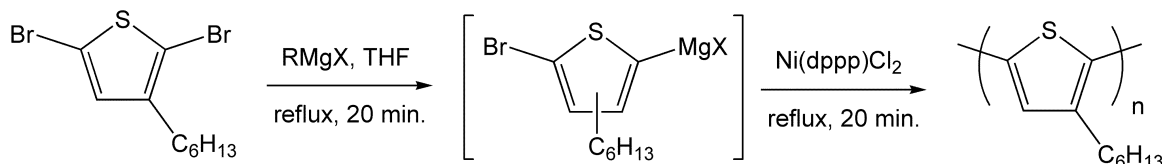


Metathesis reactions are also applicable to Grignard chemistry. Let's take a closer look at the formation of the intermediate in the polymerization reaction shown previously. If a metathesis takes place, there is most certainly an additional product as a result of the exchange of partners:



Notice the Grignard reagent and aromatic halide exchanged partners to form a new organic halide and, most notably, a new Grignard intermediate. This process is known as Grignard metathesis (commonly abbreviated as GRIM). Even better is the fact that just about any common alkyl Grignard works in this particular metathesis reaction, thus we can use whatever Grignard reagent we have available at the time.

The actual polymerization reaction occurs after you add the nickel catalyst (see scheme below). Nickel catalysis produces the “coupled product” poly(3-hexylthiophene); the mechanism is similar to the Kumada coupling that you used to prepare the 3-alkylthiophene precursor, except for that the coupling occurs many times (n times), producing a polymer with an average number of n repeating units.

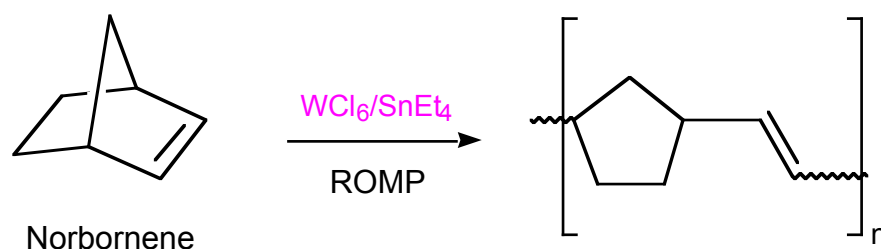


Q. Based on the mechanism (Kumada coupling), what groups do you expect at the polymer chain ends?

1. **Adapted from:** Ted M. Pappenfus, David L. Hermanson, Stuart G. Kohl, Jacob H. Melby, Laura M. Thoma, and Nancy E. Carpenter, Demetrio A. da Silva Filho and Jean-Luc Bredas *J. Chem. Educ.* **2010**, *87*, 522-525. Loewe, R. S., Khersonsky, S. M., McCullough, R. D. *Advanced Materials*, **1999**, *11*, 250.
2. Jeffries-El, M.; McCullough, R. D. In *Handbook of Conducting Polymers*, 3rd ed.; Skotheim, T. A., Reynolds, J. R., Eds.; CRC Press: New York, 2007.

Session 1

Transition-Metal-Catalyzed Polymerization of Norbornene.



In this session a very reactive and air-sensitive catalyst is prepared from WCl_6 and tetraethyltin, SnEt_4 . The catalyst preparation and the polymerization 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.

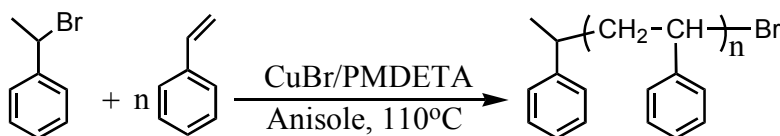
Weigh 0.4 g of WCl_6 and 0.15 mL of SnEt_4 into a vial with a micro stir bar and add 20 mL of dry toluene. Allow this mixture to age for 15 minutes. This is the catalyst solution. Mix the catalyst solution up and add about 5 mL to a solution of 1.0 g of norbornene in 5 mL of dry toluene in a large vial containing a micro stirbar. Seal the vial and remove it from the dry box. 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 approx. 60 min. in the fumehood** for the catalyst to be destroyed (by air). Filter off the blue/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 an insoluble polymer. The crude polymer may also be blue in color due to tungsten impurities, which should disappear before the next period.

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

Important Note: A well-defined catalyst system that can also be used for the polymerization of norbornene is pentacarbonyl{phenyl(ethoxy)carbene}tungsten(0) / AlCl_3 . The ^1H (Dspectrum2.pdf) and ^{13}C NMR (Dspectrum3.pdf) spectra of this carbene complex can be downloaded from the website and should be assigned. Also postulate the structure of the active species for the WCl_6 / SnEt_4 system and compare it with the structure of pentacarbonyl{phenyl(ethoxy)carbene}tungsten(0) (*Fischer vs. Schrock carbene!*).

Session 2

1. Copper-Mediated Homopolymerization of Styrene



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. **The temperature has to be controlled very carefully, otherwise you will not get a well-defined product!** Remove the needle and close the stopcock to the flask containing the ATRP polymerization mixture. (remember to carefully clean the needle with a small amount of THF and then acetone). Then cool the reaction mixture of both polymerizations to room temperature in a cold water bath. You will do the workup of your polymer in the last session.

2. Workup of Polynorbornene. (*Perform this work while heating the styrene solutions*)

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). Obtain a ¹H NMR spectrum of your norbornene polymer in CDCl₃ and compare it to the spectrum of the monomer ([Dspectrum1.pdf](#)). 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. Preparation of a Poly(3-alkylthiophene) by GRIM Polymerization.

Assemble the reaction apparatus using a 100 mL Schlenk flask, stir bar, and rubber septum. Use the glassware from the oven and work quickly in setting up the apparatus to minimize exposure to the atmosphere. While the flask is still warm, place the apparatus under vacuum and then refill with nitrogen.

Remove the rubber septum from the round bottom flask and under positive nitrogen pressure, quickly add 3 mmol (_____ g) of your 2,5-dibromo-3-alkylthiophene via pipet while minimizing the time the system is open to the atmosphere. Add distilled THF (20 mL) through the septum via syringe so that the final monomer concentration is 0.15 M and begin stirring the solution.

Now add 1 equivalent of Grignard solution (_____ mL) with respect to the 2,5-dibromo-3-hexylthiophene via syringe. Heat to 50 °C and stir the reaction for 30 minutes. Then allow to **COMPLETELY** cool to room temperature.

Add enough Ni catalyst to make the Ni catalyst final concentration 3.0×10^{-3} M (_____ mg) [Note any color changes after adding the Ni-catalyst]. Heat to 50 °C again and stir the reaction for another 20 minutes, then allow to cool to room temperature.

Workup: Precipitate the polymer by dropwise addition to an Erlenmeyer flask containing ~100 mL of methanol (with stirring, add the polymer solution to the vortex). Collect the precipitate on a filter paper and wash with some more methanol. You typically get a pasty solid; let the polymer dry on the filter paper until the next lab period. Then collect the product in a pre-weighed labeled vial for further studies.

2. Cast a Film of the Norbornene Polymer Obtained from $\text{WCl}_6/\text{SnEt}_4$ Catalyzed Reaction.

Cast a film 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).**

Session 4

1. Workup of Polystyrene.

Dilute the reaction mixture from the styrene ATRP polymerization with 10 ml of THF and suction filter the solution through a short plug of neutral alumina that has been wet with ca. 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 flask and concentrate on a rotary evaporator to ca. 10-20 ml. Recover the polymer by precipitation into a large excess of rapidly stirring methanol (~200 ml), suction filtration, and washing three times with ca. 20 ml methanol.

Transfer the polymer into a 100 ml Schlenk flask with wide opening and dry it under high vacuum at 50 °C (warm water bath) for at least 1 h. Determine the yield of your polymer and submit samples for GPC and ¹H NMR analysis.

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) ¹H NMR end group analysis (*you need to correctly choose your end group signal !*)
- (iii) GPC analysis

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

2. Data Collection for Poly(3-alkylthiophene).

- Obtain ¹H NMR data in CDCl₃ of your polymer Use ~5 mg (no more or it may not dissolve!!!). *In your report, compare the results to those for a polymer prepared by the “FeCl₃ method” (spectrum provided).*¹
- Obtain GPC data of your polymer in THF and determine the average number of repeating units. *Did you obtain a polymer with a “narrow” molecular weight distribution ?*
- Obtain both solid state and solution absorption spectra (in chloroform) of your polymer and compare to data for polymer prepared using the “FeCl₃ method” (*data provided*). For solid state UV-Vis: add dropwise your chloroform solution onto a microscope slide until entire slide is covered, let solvent evaporate, should end up with a nice film on the microscope slide. *In your report discuss the differences!*
- Obtain solution emission spectra of the two polymers using the procedure above. *In your report discuss the differences!*

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¹ The “FeCl₃ method” involves preparing poly(3-alkylthiophene)s by the oxidative polymerization of 3-alkylthiophene with FeCl₃.