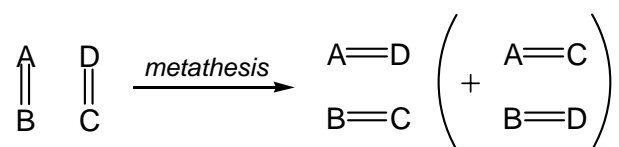
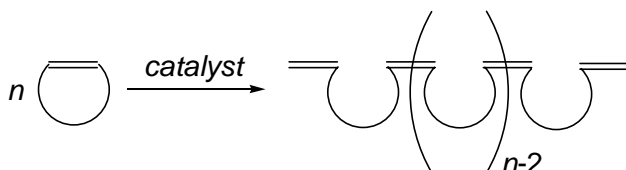


Lab 7Crosslinked, Thermoset Elastomers via Ring-Opening
Metathesis Polymerization**Introduction**

Ring-opening metathesis polymerization (ROMP) allows for the preparation of high molecular-weight polymers starting from cyclic olefin monomers.^{1,2} Olefin metathesis essentially involves “trading” bonding partners between two olefins:



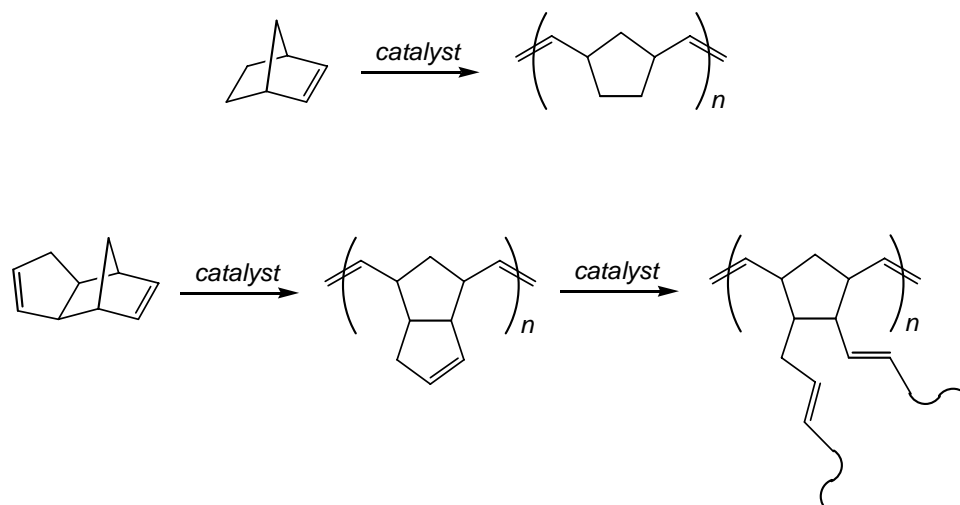
Ring-opening metathesis polymerization, similarly, converts cyclo-olefins into linear polyalkenes:



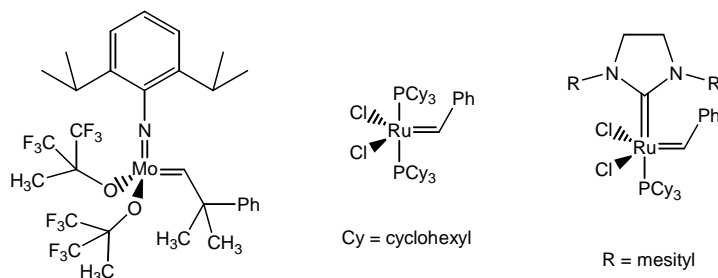
Ring-opening metathesis polymerization has been used for quite some time to make polyalkenes; for example, poly(norbornene) and poly(dicyclopentadiene) are synthesized via ROMP and are commercially available. Because dicyclopentadiene has two olefins that are metathesis-active, poly(dicyclopentadiene) is formed as a thermoset at room temperature.

¹ Grubbs, R. H.; Tumas, W. *Science* **1989**, 243, 907-915.

² Mol, J. C.; Ivin, K. J. *Olefin Metathesis and Metathesis Polymerization* (Academic Press: San Diego, 1997), chapter 11.



Initially (in the 1970s and 80s), ROMP polymerizations were not well controlled and gave broad molecular weight distributions. More recently, however, a number of research groups have improved the ROMP process by tailoring the activity and stability of ROMP catalysts. In particular, both Robert Grubbs' (Caltech) and Richard Schrock's (MIT) research groups have recently reported organometallic complexes which catalyze olefin metathesis in a "living" manner.³⁻⁷



In this lab, you will be using the third of these catalysts to polymerize cyclooctene to poly(cyclooctene).

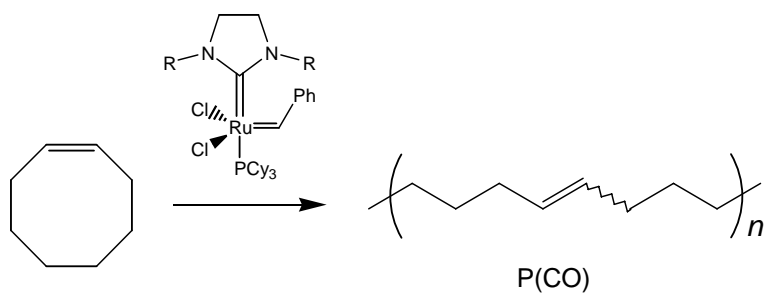
³ Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; Dimare, M.; O'Regan, M. J. *J. Am. Chem. Soc.* **1990**, *112*, 3875-3886.

⁴ Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100-110.

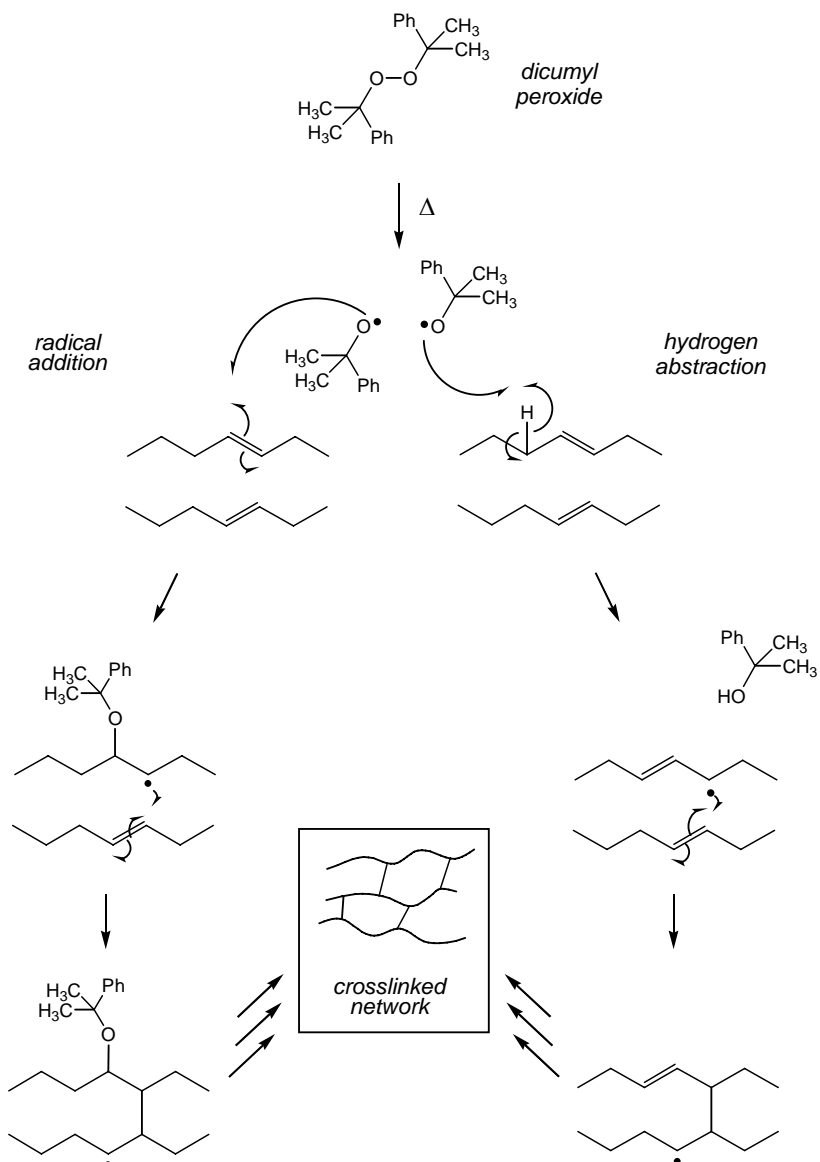
⁵ Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18-29.

⁶ Bielawski, C. W.; Grubbs, R. H. *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 2903-2905.

⁷ Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546-2558.

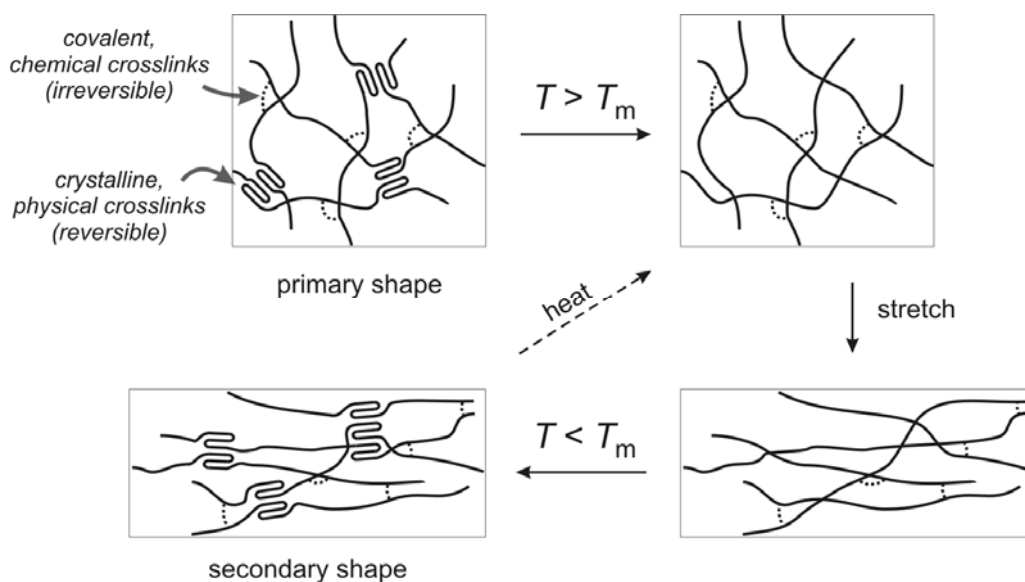


Metathesis of cyclooctene leads to a mixture of *cis*- and *trans*-olefins, and the relative fraction of *cis*- and *trans*-olefin in the P(CO) product depends on reaction conditions. P(CO) is a crystalline thermoplastic, and is readily and reversibly molded above its T_m of about 60 °C. (The material



also shows a T_g of about $-60\text{ }^\circ\text{C}$.) However, if the P(CO) material is combined with a crosslinking agent that can interconnect the polymer chains during heating, the combination is a *thermoset* that forms an irreversibly networked material as it is molded.⁸ You will be crosslinking your P(CO) with dicumyl peroxide, which both dissociates into cumyloxy radicals and crosslinks available olefins above $120\text{ }^\circ\text{C}$.⁹ In this lab, you will be thermosetting your polymer/peroxide mixture as a film in the same hot press you used in Lab 4.

The covalent crosslinks in the polymer network serve to interrupt the regular crystallinity found in the uncrosslinked material. As a result, at high crosslink densities, the material loses its T_m at $60\text{ }^\circ\text{C}$. However, at low crosslink densities, the material still retains some crystallinity. Lightly crosslinked P(CO) can be both elastomeric and crystalline, and shows two regimes of mechanical behavior with different elastic moduli.⁶ Below T_m , the P(CO) elastomer is fairly stiff, but above T_m it behaves more like a typical soft rubber. An interesting consequence of this is that crosslinked P(CO) polymer is a “shape-memory” material; i.e., while the material is crosslinked into one permanent elastomeric shape, it can be deformed and reversibly locked into a second elastomeric shape. This is possible because the crystalline domains that are formed below T_c can act as physical crosslinks in the material, just as the peroxide-induced C-C bonds are chemical crosslinks.



The secondary shape is itself elastomeric, and will regain its (secondary) shape if deformed below the crystalline melting temperature. However, if the crystalline domains in the secondary shape are melted, the material will be “deprogrammed” and return to its primary shape. Shape-memory behavior has been known for some time in metals (and served as the inspiration for the liquidy villain in *Terminator 2*), but recent research has explored its use in polymeric materials. A number of technological uses have been suggested for shape-memory polymers, but a particularly promising one is biodegradable, self-closing suture fiber for closing wounds. Prof. Robert Langer, an engineer at MIT, and his coworker Andreas Lendlein have written a number of recent

⁸ Liu, C.; Chun, S. B.; Mather, P. T.; Zheng, L.; Haley, E. H.; Coughlin, E. B. *Macromolecules* **2002**, *35*, 9868-9874.

⁹ Sultan, B.-A., “Crosslinking of Polyolefins,” in *Polymeric Materials Encyclopedia* (CRC Press: Boca Raton, 1996), pp.1552-1565.

articles on this subject^{10,11}—including pictures of test surgeries on animals in which shape-memory fiber was shown to be more effective at repairing incisions than normal suture wire. (The explanation of why it works better is pretty interesting—so if you don't mind looking at post-operative pictures of rabbits, you might want to check out the *Science* article in particular.) “Smart materials” such as these are also being investigated for many other applications, including “artificial muscles”, catheters and remote surgical devices, and responsive aerospace flight surfaces.

A characteristic feature of crosslinked elastomers (regardless of whether they exhibit shape memory or not) is that, when exposed to a solvent that is good for the polymer, they swell rather than dissolving. Crosslinked polymers that are immersed in a good solvent can swell to be many times larger than the original polymer sample. (Crosslinked hydrogel bath toys that swell in water are a good example of this phenomenon.) In this lab we will correlate swelling in our polymer samples with the amount of crosslinker added. In principle, the degree of swelling is determined by the Flory-Rehner equation,

$$-\left[\ln(1-v_2) + v_2 + \chi_1 v_2^2\right] = V_1 n \left[v_2^{1/3} - \frac{v_2}{2} \right]$$

where v_2 is the volume fraction of polymer in the swollen material, V_1 is the molar volume of the solvent, n is the number of chain segments (which is inversely related to the number of crosslinks), and χ_1 is the Flory-Huggins solubility parameter between the (uncrosslinked) polymer and solvent. (In other words, for the purpose of understanding how well a crosslinked polymer swells, it is treated like an uncrosslinked polymer that is physically prevented from dissolving.) The general gist of this equation is that swelling increases with increasing solvent quality and with decreasing crosslink density. You'll test this idea in this lab.

Experimental

Poly(cyclooctene) via ROMP (April 20/21)

The goal of this experiment is to prepare a polyolefin and blend it with a peroxide crosslinker for thermosetting.

- From the stockroom or the back of lab, check out a heat/stirplate and a large stirbar that will fit in a 500 mL beaker. Try to make sure that the stirplate is not one of the square, “Magne stir” variety—we find that these give off a lot of heat (even when you don't want them to), and this may negatively impact the final properties of your polymer.
- In the 500 mL beaker, combine 7.8 mL (6.6 g) of *cis*-cyclooctene, your stir bar, and 50 mL of CH₂Cl₂. Allow this to stir.
- Pick up a glass vial containing 5.1 mg ruthenium catalyst from the TA. Add 2-3 mL CH₂Cl₂ to the vial to dissolve the catalyst. Pipette this solution into the beaker, and allow to stir for 30 minutes. The polymerization should turn viscous after a while; you may add 10 mL aliquots of CH₂Cl₂ solvent to help keep the beaker contents stirring.

¹⁰ Lendlein, A.; Langer, R. “Biodegradable, elastic shape-memory polymers for potential biomedical applications”, *Science* **2002**, 296, 1673.

¹¹ Lendlein, A.; Kelch, S. “Shape-memory polymers”, *Angew. Chem., Int. Ed. Engl.* **2002**, 41, 2034.

- Dissolve three drops of ethyl vinyl ether in 20 mL CH_2Cl_2 . After the 30 minutes are up, add this solution to the beaker to terminate the polymerization. Stir for 2 minutes.
- Precipitate the polymer by adding 200 mL MeOH, and stir with a spatula to mix completely. Decant the overlying solvent away from the resulting polymer glob, and use a spatula or paper towels to squeeze the remaining solvent out of the polymer as much as possible. Then dry the polymer in the vacuum oven (set at room temperature) for 10 minutes. Measure a crude yield of your material.
- Set aside 2 g of your dried polymer sample in an aluminum pan. Weigh the remainder of your polymer. Cut up the remainder into small bits, and in a 250 mL beaker, dissolve this material in 100 mL CHCl_3 with stirring. You may want to cover the beaker with foil to minimize evaporation. After the mixture has stirred for 15 minutes, add the assigned amount of dicumyl peroxide (1, 2, 3, 4, 5 wt%). Allow this mixture to stir in the hood overnight. The following day, the TA's will remove your foil cover so that solvent evaporates from your mixture to leave dry polymer. Again, make sure that your stirplate doesn't get hot while it stirs, and try to put your sample in a cool, dark part of the hood. Label the beaker so that, if we need to move your material, you can recover it.
- Place the rest of your solid, set-aside material back in the vacuum oven and allow it to dry overnight.

Molding and crosslinking poly(cyclooctene) in a hot press (April 27/28)

The goal of this experiment is press a film in preparation for mechanical testing and swelling.

- Before pressing, set up a hot-water bath in a large beaker at your bench, at the temperature assigned by the TA. Put a thermometer in the beaker so that the temperature can be verified.
- Recover your crosslinked material from the hood and weigh it. If the combined mass of polymer and crosslinker are less than what you started with, recalculate your wt% crosslinker.
- You will press your samples in Amundsen 324, in the Polymer Processing Lab. Be sure to bring both your pure P(CO) as well as your P(CO)/peroxide blends with you to the hot press. Things the group will also need to bring:
 - Two press plates. (TA should have these.)
 - Teflon film.
 - A micrometer.
 - Scissors.
- You will need to do two sample pressings: the first to press the air out of all of your material, and the second to permanently crosslink these forms for the samples containing peroxide. Sandwich your material between two pieces of Teflon film, and load it between the press plates. Pile your material high rather than spreading it too thin across the Teflon, so that it is all pressed effectively. Load your sandwiched sample in the press.
- The TA will set the press to 80 °C; press your polymer into a film about ½ mm thick. (This may require ~ 2000 lbs.)
- The TA will open the press. Remove the plate sandwich from the press, and remove your polymer from between the press plates; the film should be mostly clear plastic. Cut away any opaque white parts (which still contain air). Measure the thickness of the film with the

micrometer, and reload this film between the press plates and back in the press. If the film was too thick, press again at 80 °C at higher pressure before the next step. If the film was the right thickness, great—put it in the press anyway for the next step.

- The TA will set the press pressure back to the highest pressure previously experienced for your sample, and the temperature at 140 °C. Allow to press for 30 min. After this time, remove your film. You will use this crosslinked material for mechanical and swelling measurements.

Solvent swelling of crosslinked poly(cyclooctene) (April 27/28)

The goal of this experiment is to test the swelling of crosslinked polymer with compatible solvents.

- Cut three 1 cm × 1 cm pieces of uncrosslinked and crosslinked material from each of your pressed films. Put each piece into its own tared, small vial. Weigh each of the pieces before exposure to solvent.
- Next, add enough solvent—methanol, acetone, and chloroform—into each vial to cover the elastomer piece. Allow the material to soak for a few minutes. If the material soaks up all the solvent, add more.
- Next, pipette out any residual solvent, and re-weigh the vial to determine the weight of solvent added. If you can, also remove the polymer piece from the vial with tweezers and measure it with a ruler.
- What *volume* of solvent swelled each polymer sample you investigated?

Shape-memory behavior in poly(cyclooctene) (April 27/28)

The goal of this experiment is to observe the impact of crystallinity on shape memory in a crosslinked polymer.

- First, cut a 1-cm wide strip of the material you've made. Is it plastic? Is it elastic? If elastic, what is the timescale at which the material returns to its original (primary) shape? Crystalline materials are often translucent or opaque because crystalline domains scatter light; is your material transparent or not?
- Using your test-tube holder or a clip, dip your sample into a water bath heated to 80 °C for a minute. Take it back out—how has the material changed? How has its appearance changed? Has its elasticity changed? As the sample cools on the benchtop, does it return to its original appearance and elasticity? How long does it take to do this?
- Try these tests in the other water baths. What temperature is required for your material to undergo phase transition? Other groups will have samples with other degrees of crosslinking—do their samples exhibit the same transition temperatures as yours?
- Prepare an ice water bath that is big enough to accommodate your sample. Heat the sample in the 80 °C water bath again, take the sample out, and bend the material into a shape. (You might wrap your strip into a coil around a glass rod, for example.) Fasten or hold onto the material so that the sample retains the shape you've chosen. Then, dip your sample into an ice bath for a minute. Remove it from the bath and the clip—does the material keep its new (secondary) shape? If you try to straighten the object back to its original shape, does it resist?

- Drop the sample back in the heat bath. What shape does the sample assume in the heat bath—the primary shape (flat) or secondary shape?

There is no Lab Report due for this Lab. Instead, you will analyze your results in Assignments.