

**Assignment 21****Due:** *In Lab*, Thursday, April 20/Friday, April 21

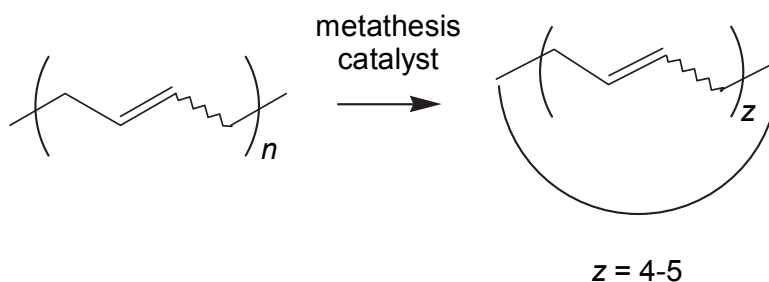
1. One thing that distinguishes ring-opening metathesis polymerization (ROMP) from other polymerization techniques is how mild the polymerization conditions are; for many monomers, ROMP is spontaneous at or just above room temperature. This means that molds or forms can be filled with a mixture of monomer and catalyst, and that polymer will be cast within minutes from the mixture. This has been particularly effective for poly(dicyclopentadiene), which is now used in sporting goods and hardness coatings. Read more at Materia, a company that commercializes ROMP technology:  
[http://www.materia-inc.com/app\\_meta\\_materials.html](http://www.materia-inc.com/app_meta_materials.html). Two *Chemical and Engineering News* articles are also good reading on the background and mechanism of ROMP: “Olefin Metathesis: Big-Deal Reaction” (2002, vol. 80, pp. 29-33; <http://pubs.acs.org/cen/coverstory/8051/8051olefin.html>); and “Olefin Metathesis: The Early Days” (2002, vol. 80, pp. 34-38; <http://pubs.acs.org/cen/coverstory/8051/8051olefin2.html>).

Poly(dicyclopentadiene) is a resin rather than a thermoplastic, because the two metathesis reactions per monomer yield a crosslinked polymer product. One of the two double bonds in DCPD is much more reactive than the other, and as result the monomer sequentially polymerizes into a linear polymer and then crosslinks. Which double bond is more reactive? Why?



dicyclopentadiene (DCPD)

2. One potential problem in living polymerizations (such as ROMP) is depolymerization, in which the polymer spontaneously breaks down into component monomers or oligomers. Depolymerization is a particular problem for systems in which the thermodynamic driving force towards polymer formation is not strong. In ROMP, depolymerization can cause re-formation of monomer when ring strain in the monomer is only barely sufficient to promote polymerization, or can convert a single polymer chain to many cyclic oligomers when the concentration of living polymer is too low. For example, poly(1,4-butadiene) can spontaneously form oligomers in the presence of a ROMP catalyst.<sup>1</sup>



In terms of principles of thermodynamics, why might this happen? Why would a polymer spontaneously dissociate into smaller fragments?

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<sup>1</sup> Marmo, J. C.; Wagener, K. B. *Macromolecules* **1995**, *28*, 2602.

After polymerization, your ROMP polymer will be mixed with dicumyl peroxide and heated (next week) to crosslink the chain olefins. Use the following weight percent of dicumyl peroxide (with respect to your final polymer product):

wt% peroxide	Group #
1%	1,8
2%	2,9
3%	3,10
4%	4,11
5%	5,6
6%	7