Quantitative Ring-Closing Metathesis of Polyolefins

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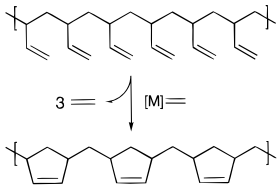
An important topic in polymer chemistry is the controlled variation of polymer properties through postpolymerization modifications. Unfortunately, this strategy often yields heterogeneous polymers due to incomplete chemical conversion and a lack of selectivity. Despite these potential limitations, successes have been realized;[1] of particular relevance to this paper is the area of polyolefin cyclizations.[2,3] In this paper, we report the highly selective and quantitative cyclization of neighboring vinyl substituents in 1,2-polydienes using metathesis catalysts (Scheme 1).

Scheme 1



Ring-closing metathesis of simple α,ω-dienes to generate cycloolefins has been extensively explored.[4] Given the high yields typically observed in reactions involving the formation of five- and six-membered rings, we initiated investigations on polymeric substrates containing suitably-spaced olefins. We first studied the reaction of the ruthenium alkylidene complex $Cl_2(PCy_3)_2Ru{=}CH_2$ (**1**, Cy = cyclohexyl)[5] with atactic 1,2-polybutadiene (**2**, 1,2-PBD).[6] Shown in Figure 1 are the ^{1}H NMR spectra of the olefin regions of the substrate and the isolated product. These spectra clearly demonstrate that greater than 97% of the olefins of **2** have undergone cyclization.[7] Hydrogenation of **3** yields a polymer with NMR spectra identical to those of atactic poly(methylene-1,3-cyclopentane),[8] which confirms the structure drawn for **3** in Figure 1.

Gel-permeation chromatographic (GPC) analysis reveals that **3** is of lower molecular weight and of broader polydispersity than **2**. In order to determine the origin of degradation in the ring-closing process, two samples of **2** were synthesized which

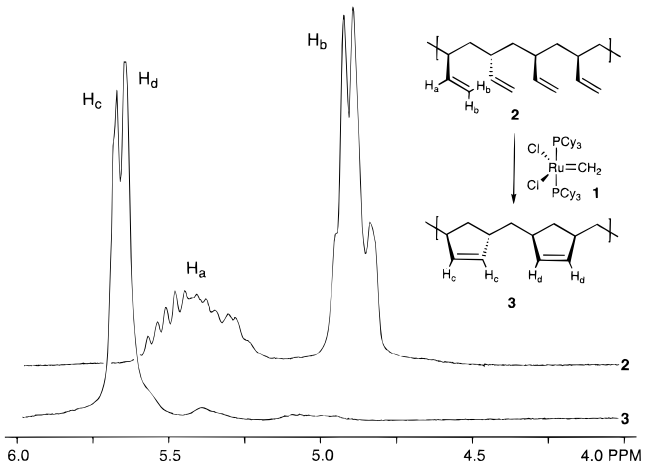


Figure 1. Olefin regions of ^{1}H NMR spectra of **2** and **3**.

were identical in microstructure (97% 1,2-units),[9] but different in molecular weight (Table 1, entries 1, 2). Treatment with **1** yields polymers of nearly identical molecular weight. This result suggests that metathetical cleavage of the infrequent 1,4-units of the polymer backbone occurs during the ring-closing process. Previous metathetical degradation studies of 1,4-polybutadienes suggest that the degradation of **2** yields polymers with cyclopentene and vinylcyclohexene end groups (Figure 2).[10] These results suggest that reaction of 1,2-PBDs with metathesis catalysts constitutes a highly sensitive technique to determine the regiochemistry (1,2- versus 1,4-enchainment) of high 1,2-content polybutadienes, where the molecular weight of the cyclized product is related to the 1,2-content of the polymer.[11]

Our next objective was to use ring-closing metathesis to synthesize highly stereoregular cyclopolymers from tactic polyolefin precursors. Reaction of the molybdenum alkylidene complex $(R_FO)_2(NAr)Mo{=}CHCMe_2Ph$ (**4**, R_F = $CMe(CF_3)_2$, Ar = 2,6-(^{i}Pr)$_2$C$_6$H$_3$)[12] with syndiotactic 1,2-poly((*Z*)-pentadiene) (**5**, 1,2-PZP)[13,14] yields the trans-diisotactic cyclopolymer **6** (Table 1, entry 3). The ^{1}H NMR spectrum of **6** is exceptionally clean (Figure 3), with no detectable traces of the initial polyolefin resonances.

One of the remarkable attributes of this ring-closing process is that the pendant olefins of the polyolefin precursor are quantitatively paired off, with no isolated and unreacted olefins remaining in the product. This observation immediately suggests two intriguing mechanisms: (1) the alkylidene catalyst travels from one end of the polymer to the other, cyclizing adjacent olefins sequentially as it "cascades" down the chain; and (2) the catalyst randomly closes adjacent olefins until only isolated olefins remain; then the catalyst migrates up and down the chain until all olefins are cyclized. For mechanism 1, olefin cyclization should proceed at a constant rate for the entire reaction. However, in mechanism 2 it might be predicted that the reaction would proceed rapidly until most of the olefins are paired and then proceed slowly until all of the isolated olefins

(1) For reviews covering the functionalization of unsaturated polymers, see: (a) McGrath, M. P.; Sall, E. D.; Tremont, S. J. *Chem. Rev.* **1995**, *95*, 381−398. (b) Schulz, D. N.; Turner, S. R.; Golub, M. A. *Rubber Chem. Technol.* **1982**, *55*, 809−859 and references therein.

(2) For a review, see: Bartlett, P. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: Orlando, 1983; Vol. 3, pp 341−409.

(3) For transition-metal-catalyzed polyolefin cyclizations, see: (a) Tietze, L. F.; Beifuss, U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 131−163. (b) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1993**, *115*, 9421−9438.

(4) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446−452 and references therein.

(5) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039−2041.

(6) These polymers contain 97% 1,2-units. Halasa, A. F.; Lohr, D. F.; Hall, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1357−1360.

(7) The resonances in Figure 1 at 5.0 and 5.4 ppm are likely due to end groups (*vide infra*).

(8) (a) Cheng, H. N.; Khasat, N. P. *J. Appl. Polym. Sci.* **1988**, *35*, 825−829. (b) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953−4954. (c) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91−98.

(9) The polymer samples were prepared according to ref 6 (25 °C, 1,2-dipiperidinoethane:butyllithium ratio of 5.0).

(10) (a) Hummel, K. *Pure Appl. Chem.* **1982**, *54*, 351−364. (b) Hummel, K. In *Olefin Metathesis and Polymerization Catalysts*; Imamoglu, Y., Zümreoglu-Karan, B., Amass, A. J., Eds.; Kluwer Academic Publishers: Dordrecht, 1990; pp 209−232. (c) Thorn-Csányi, E. *Rubber Chem. Technol.* **1994**, *67*, 786−796 and references therein.

(11) The maximum degree of polymerization of the cyclized polymer should be inversely proportional to the fraction of 1,4-units.

(12) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185−198 and references therein.

(13) 1,2-PZP was chosen over 1,2-PBD due to its greater solubility in benzene, and catalyst **4** was employed due to its high reactivity with disubstituted olefins.

(14) Ricci, G.; Italia, S.; Porri, L. *Macromolecules* **1994**, *27*, 868−869.

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Table 1. Cyclization of Polyolefins **2** and **5**

	substrate polymer					cyclized polymer			
entry	polymer	% 1,2[a]	M_n[b]	PDI[b]	reactn conditns[a]	yield (%)	% cyc[d]	M_n[b]	PDI[b]
1	**2**	97	12900	1.04	A	100	>97	3240	3.14
2	**2**	97	25000	1.04	A	100	>97	3150	3.21
3	**5**	>98	5180	2.12	B	100	>99	4690	1.52

[a] Determined by ^{13}C NMR, $CDCl_3$. [b] Determined by GPC (CH_2Cl_2) versus polystyrene standards. [c] All reactions were conducted in evacuated flasks with volumes which were four times greater than the solution volume. A: CH_2Cl_2, catalyst **1**, 35 °C, 21 h, $[olefin]_i$ = 0.12 M, $[olefin]_i$:[Ru] = 50:1. B: benzene, catalyst **4**, 40 °C, 16 h, $[olefin]_i$ = 0.15 M, $[olefin]_i$:[Mo] = 20:1. [d] Determined by ^1H NMR, $CDCl_3$.

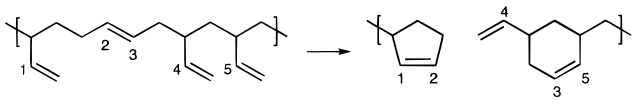


Figure 2. Proposed mechanism of degradation of **2**.

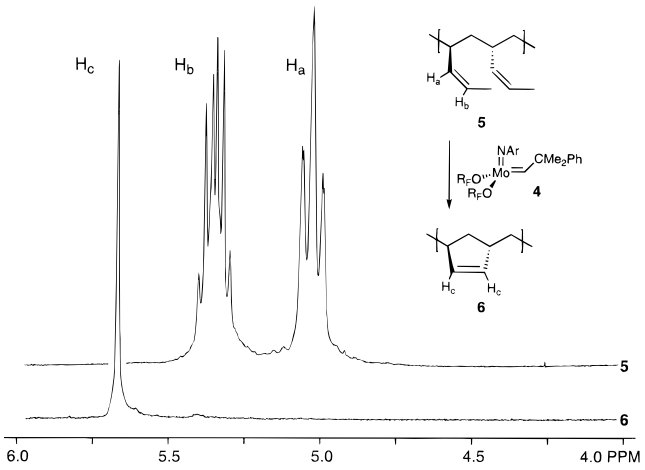


Figure 3. Olefin regions of ^1H NMR spectra of **5** and **6**.

are reacted. In 1939 Flory derived mathematical expressions to model irreversible reactions between adjacent substituents in vinyl polymers.[15] Specifically, he determined that, in nonequilibrium reactions, the fraction of unreacted substituents that become isolated between cyclized units in the polymer is $1/e^2$ (13.5%). Therefore if mechanism 2 is to operate, a break in the percent cyclization versus time plot at 86.5% conversion might occur.

In order to differentiate between these two mechanisms, we monitored the reaction of ruthenium catalyst **1** with atactic 1,2-PBD (**2**) by ^1H NMR. The result is displayed in Figure 4. The reaction proceeds rapidly to approximately 90% conversion and then slowly climbs to >98% conversion. Also, the ^1H NMR resonances of the unreacted $=CH_2$ protons shift downfield during the reaction, presumably due to a change in environment of the olefin. These observations are consistent with mechanism 2, as displayed in Scheme 2.

In summary, we report the quantitative ring-closing metathesis of 1,2-polydienes. The process is highly sensitive to the microstructure of the polymers, where the amount of degradation is proportional to the amount of 1,4-units. In addition, cyclization of tactic polymers provides a novel route to stereoregular cyclopolymers. The mechanism of the reaction appears to have two manifolds, an initial random pairing of olefins, followed by migration of the catalyst along the polymer chain to scavenge

(15) (a) Flory, P. J. *J. Am. Chem. Soc.* **1939**, *61*, 1518−1521. (b) Platé, N. A.; Noah, O. V. *Adv. Polym. Sci.* **1979**, *31*, 133−173.

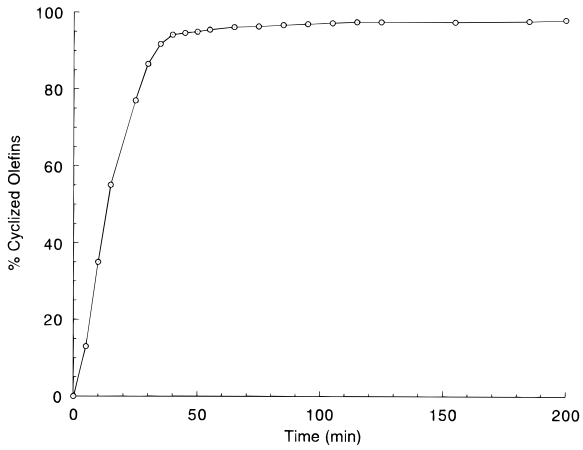
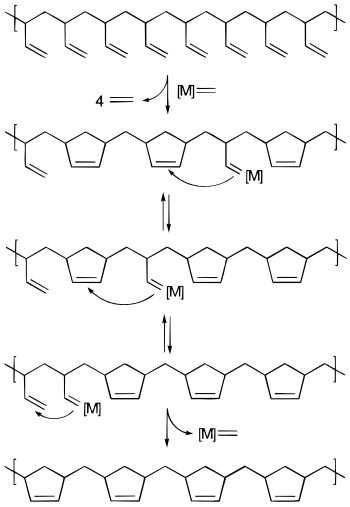


Figure 4. Kinetic profile for olefin cyclization of **2** with **1**.

Scheme 2



isolated olefins. Future studies include the development of this ring-closing process as a powerful technique for the microstructural analysis of 1,2-PBDs (i.e., amount and distribution of 1,4-units as well as tacticity) and the ring closing of appropriately designed olefin-containing block copolymers and functionalized polymers.

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