Chapter 3

Synthesis of Cyclic Polybutadiene via Ring-Opening Metathesis Polymerization: The Importance of Removing Trace Linear Impurities

Abstract

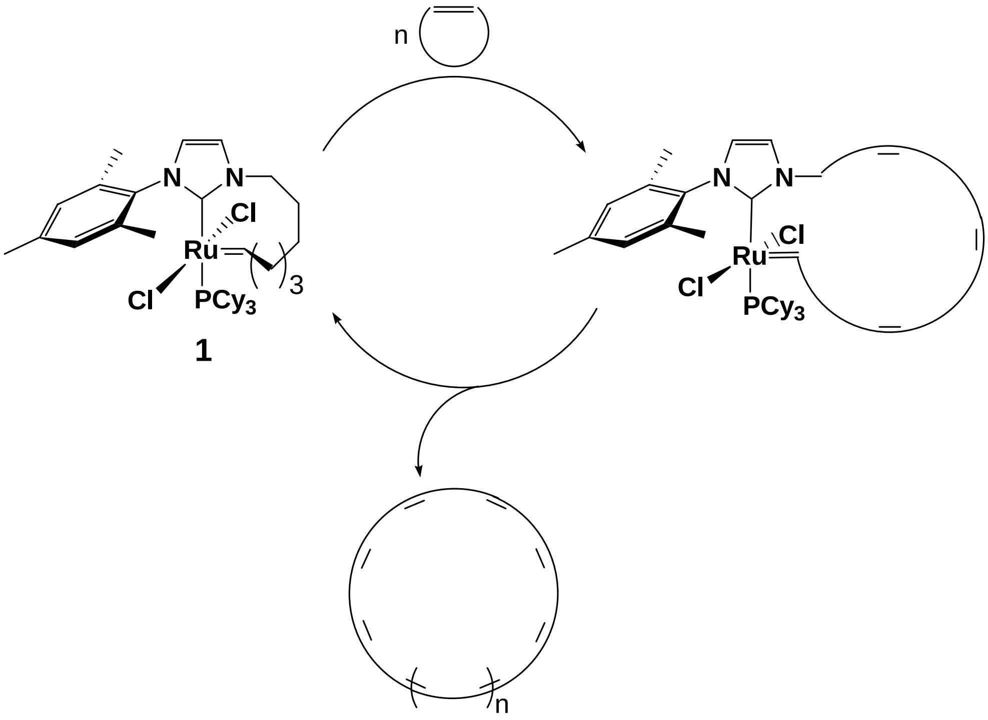
Cyclic polybutadiene was synthesized via the ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene (COD) using a cyclic Ru catalyst L(PCy$_3$)Cl$_2$Ru=CHR (L,R = chelating N-heterocyclic carbene). Molecular weights were tunable by varying the initial monomer/catalyst ratio and/or the initial monomer concentration. However, trace amounts (< 0.10%) of 4-vinylcyclohexene, a linear contaminant found in COD, were found to have deleterious effects on polymer purity. While low MW (< 10 kDa) samples were found to be almost entirely cyclic, only linear polymer was observed at higher MWs. These observations emphasize the need to use monomers that are rigorously pure of linear contaminants when preparing cyclic polymers using ROMP.

Portions of this chapter have been previously reported, see: Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 8424-8425.

Introduction

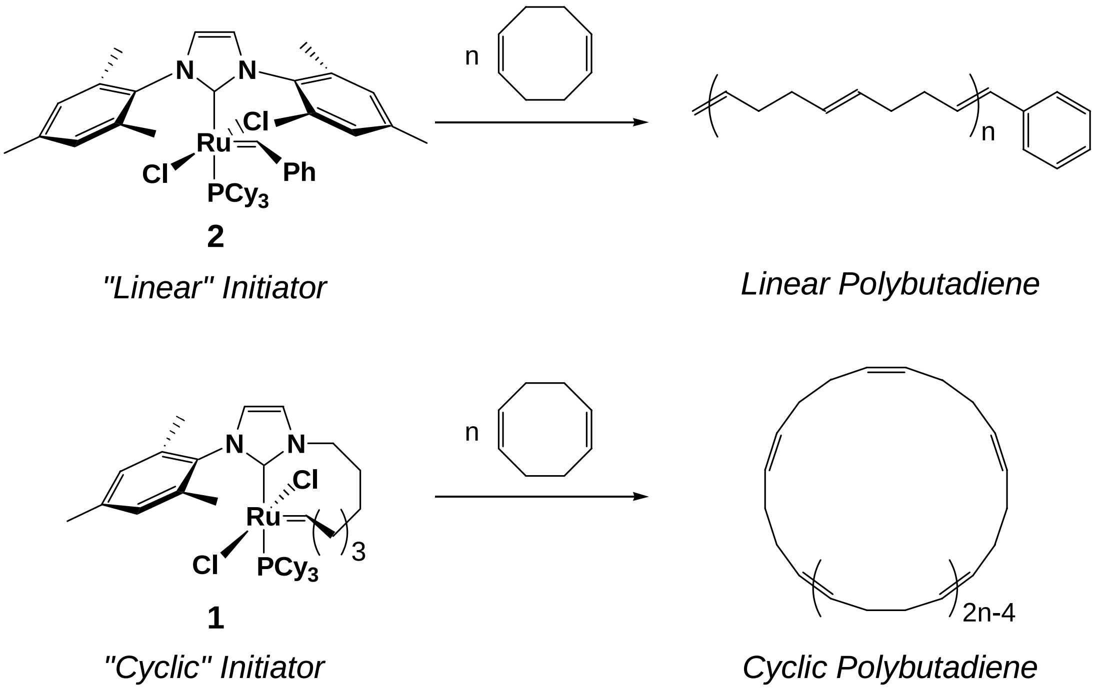
Polymers that lack end-groups are physically constrained to adopt a cyclic structure. This topological distinction from their linear analogs imparts a variety of interesting and unusual physical properties.[1] For example, cyclic polymers generally exhibit higher glass transition temperatures, are less viscous, and have smaller hydrodynamic volumes than their linear analogs. The synthesis of cyclic polymers generally involves first preparing linear "pre-polymers" that contain reactive end-groups followed by a subsequent coupling reaction with difunctional electrophiles under high dilution conditions. Alternatively, ring-chain equilibration methods have been successfully employed to prepare cyclic polymers with relatively low MWs. Both methods limit access to not only high molecular weights (MWs) but large quantities of material as well.

Recently, we reported an alternate approach to synthesizing cyclic polymers which involves no linear intermediates.[2] As shown in Scheme 1, upon the addition of a cyclic monomer to a "cyclic" analog[3] (**1**) of the olefin metathesis[4] catalyst $L(PCy_3)Cl_2Ru{=}CHPh$ (**2**) (L = 1,3-dimesitylimidazolyidene), both ends of the resultant polymer chain remain attached to the complex (**3**).[5] Subsequent intramolecular chain transfer affords the (kinetically favored) Ru complex **1** and cyclic polymer. The affinity of N-heterocyclic carbenes and alkylidene ligands for Ru prevents the cyclic integrity of the catalyst from being compromised during the course of the polymerization.[6]



Scheme 1. Cyclic polymers produced via ROMP.

Herein, we extend the approach to the synthesis of cyclic polybutadienes using 1,5-cyclooctadiene (COD) as the monomer (Scheme 2). Previous reported syntheses of cyclic polybutadiene involve the living anionic polymerization of 1,3-butadiene.[7] Unfortunately, linear contamination (from incomplete coupling, moisture, impurities, etc.) was always evident and thus complicated purification techniques (multiple fractional precipitations, chromatography, centrifugation, etc.) were often needed to obtain pure cyclic polymer. Furthermore, the inherent difficulty associated with anionic polymerization methods in controlling polymer microstructure (solvent, temperature, and additives are all strong contributors) makes tuning the material's thermal and mechanical properties challenging.[8] In contrast, our approach overcomes several of these obstacles since it does not require the rigorously exclusion of air, moisture or highly purified solvents. Elaborate equipment and experimental techniques are also not necessary. Furthermore, using COD as the monomer allows polybutadiene with a perfect 1,4-microstructure to be obtained. However, we found that high monomer purity was essential to obtain high MW cyclic polymer which was free of linear contamination.



Scheme 2. Linear and cyclic polybutadienes produced via ROMP.

Results and Discussion

The ROMP was initiated by adding Ru catalyst **1** to either bulk or (CH_2Cl_2) solutions of COD followed by heating the reaction vessel to 50 °C.[9] The polymerization was monitored using a combination of gas chromatography and gel permeation chromatography (GPC). As shown in Figure 1, monomer consumption was extremely fast ($\tau_{1/2} \sim 10$ min) with a concomitant rapid growth in polymer MW. However, the MW slowly attenuated over time due secondary chain transfer and finally reached equilibrium after about 12 h. The polymer was isolated by precipitation from acetone or methanol followed by collection by filtration. As shown in Table 1, the MW of the polymer was found to be affected by not only the initial monomer/catalyst ratio but the initial monomer concentration as well. In all examples, the polydispersity index (PDI) was found to be near 2.0.[10] Polymerization under extremely dilute conditions (< 0.1 M) resulted in the formation of only low MW cyclic oligomers and is probably related to the critical monomer concentration of COD.[11] Finally, ^{1}H and ^{13}C NMR spectroscopy indicated that the polybutadiene contained a perfect 1,4-microstructure with predominantly *trans* (65%) olefin geometry.

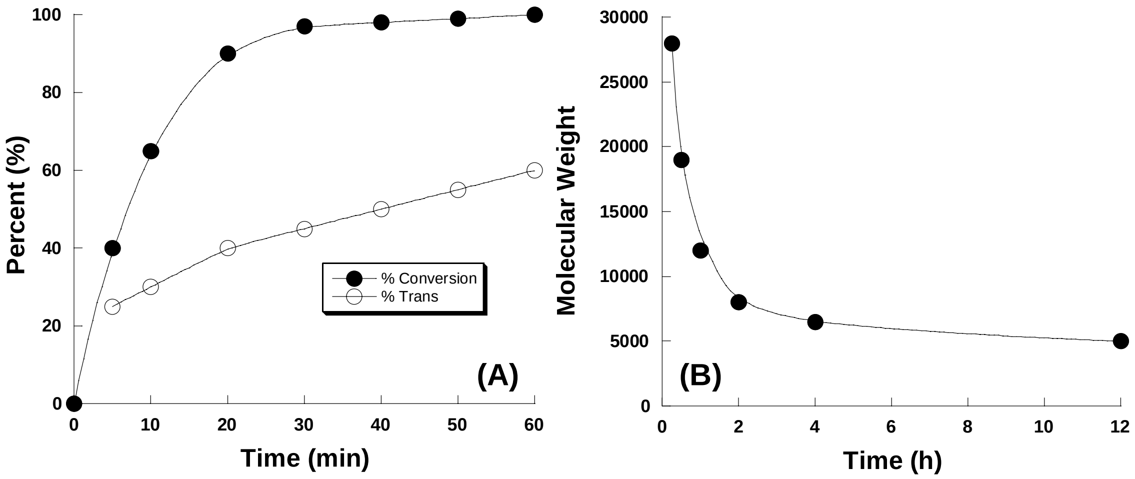


Figure 1. (A) Plot of monomer consumption and percent *trans* olefin in the polymer backbone *vs.* time. Conversions were monitored using gas chromatography. Olefin content was determined by ^{1}H NMR spectroscopy. (B) Plot of molecular weight (M_n) *vs.* time. The PDI at every point was between 1.7 and 2.0. The M_n and PDI values were determined by GPC and are reported relative to PS standards.

Table 1. Synthesis of polybutadiene with various molecular weights.[a]

M/C	Conc. (M)	% Yield[b]	M_n[c]	PDI[c]	% Cyclic[d]
25	1.0	84	2300	1.59	99
50	1.0	86	5000	1.7	98
100	1.0	88	8500	1.7	96
1150	1.0	87	86000	1.9	60
100	0.5	83	2200	1.7	99
100	0.1	0[e]	ND	ND	ND
100	4.0	90	26000	1.9	88
100	8.1[f]	95	145000	1.8	33

[a] Polymerizations were run in CH_2Cl_2 at 45 ºC for 12 h. Monomer (M) = 1,5-cyclooctadiene (COD). Catalyst (C) = **1**. [b] Isolated yields. [c] Determined by gel permeation chromatography in CH_2Cl_2. The values are reported relative to monodispersed polystyrene standards. [d] Theorertical purity of cyclic polymer based on the experimental MW and complete incorporation of a linear contaminant present in 0.05 mol %. [e] Only low MW (< 1.2 kDa) cyclic oligomers were observed. [f] Polymerization performed in bulk COD. ND = Not determined.

The circular nature of the polybutadienes was examined using a variety of techniques. As expected, end-groups were not observable on low MW (2.3 kDa) cyclic polymer samples using ^{1}H and ^{13}C NMR spectroscopy.[12,13] Mass peaks in the MALDI-MS spectrum were separated by 54.1 Da (C_4H_6) with a remainder equal to the matrix ion (Cu). Interestingly, this observation suggested that both olefinic moieties in the monomer were reactive and provided further evidence for chain transfer. However, because of the polydisperse nature of the samples, only low mass fragments (MW < 5 kDa) were observed even when high MW samples were analyzed. The physical constraints possessed by cyclic polymers results in solution conformations that are more compact than their linear analogs and therefore are generally less viscous and have smaller radii of gyration (R_g). The intrinsic viscosity ($[\eta]$) of the cyclic polymers over a range of MWs was measured using SEC coupled to a viscometer and compared to a linear analog (see Figure 2A).[14] In the low MW regime, the cyclic polymers were less viscous than their linear analogs, as expected.[15] However, the viscosity of the cyclic polymer gradually increased with MW and approached that of the linear analog. Nonlinear polymers may be characterized by the ratio of the root mean-square (RMS) R_g of the nonlinear polymer to a linear analog at the same MW: $g_M = \langle R_g^2\rangle_{\text{non-linear}}/\langle R_g^2\rangle_{\text{linear}}$. Zimm and Stockmayer have previously shown that when $g_M = 0.50$, the polymer has a ring-shaped structure.[16] Using SEC coupled to a multi-angle light scattering (MALS) detector, the RMS R_gs of the cyclic and linear polybutadienes prepared as described above were measured over a range of MWs.[17] As shown in Figure 2B, at lower MWs, g_M was near 0.50 and suggested that the sample was predominately cyclic. However, in accord with the intrinsic viscosity results, *g*M increased with MW indicating the sample was predominately linear in the high MW regime.

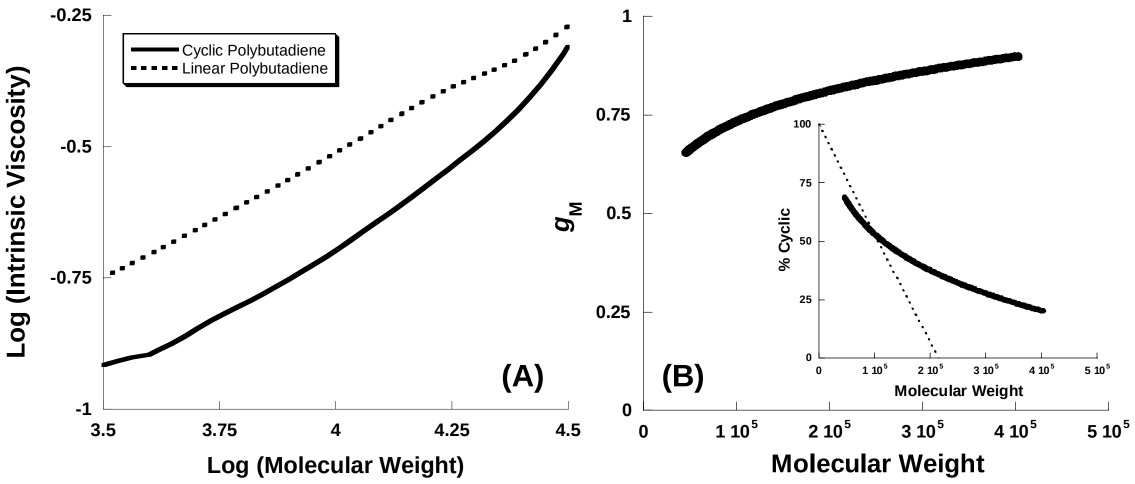


Figure 2. (A) Mark-Houwink Plot (Log IV vs. Log MW) of cyclic and linear polybutadienes. a (cyclic) = 0.71; a (linear) = 0.72. Conditions: Solvent = THF, Temp = 30 °C. (B) Plot of the ratio $g_M = <R_g^2>_{\text{non-linear}}/<R_g^2>_{\text{linear}}$ of polybutadiene prepared as described in the text as function of molecular weight. For reference, g_{M} (cyclic) = 0.50; g_{M} (linear) = 1.00. Inset graph shows the percent of the total polymer sample that is cyclic as a function of molecular weight. The dashed line represents the theoretical purity based on a 0.05 mol % linear contamination.

The source of the linear polymer contamination was traced to an impurity in COD: 4-vinylcyclohexene.[18] Close examination of relatively high MW (20 kDa) polybutadiene using ^{1}H NMR spectroscopy revealed signals at δ 5.1 ppm (vinyl) and δ 1.9 ppm (cyclohexyl), although the signals were not reliably quantifiable. To verify that their origin was from the impurity, a relatively low MW linear polymer (MW = 5 kDa) with a mixture of vinyl and cyclohexyl end-groups was prepared by adding 4-vinylcyclohexene during a Ru catalyzed ROMP of COD ($[\mathrm{COD}]_0/[\text{4-vinylcyclohexene}]_0 = 25$).[19] As expected, the chemical shifts of the end-groups were similar as the high MW polymer. The contaminant was found to range in concentrations from 0.05 to 0.09 mol % (as determined by GC) and depended on the source of COD. Based on quantitative incorporation of a linear contaminant present at 0.05 mol %, the theoretical purity of the polybutadiene (expressed as percent cyclic) was calculated as a function of polymer MW. As shown in Figure 2B (inset), reasonable correlation with the experimentally derived purity (obtained from the *g*M) was observed.[20]

While 1,5-cyclooctadiene completely free of the impurity could be obtained through multiple fractional distillations, this method proved to be too inefficient for practical use. Regardless, this may provide a means to synthesize high MW cyclic polybutadiene via ROMP. As previously reported, when monomers free of any linear contaminants (e.g., *cis*-cyclooctene) were used, highly pure cyclic polymers with MWs over 10^6 Da were obtained.[2]

Conclusion

The synthesis of cyclic polybutadiene using ring-opening metathesis polymerization (ROMP) has been described. Although the method was successful for preparing low MW samples with high (cyclic) purity, an acyclic contaminant in the monomer prevented the extension to higher MWs. These results underscore the need to use monomers that are free of linear contaminants when preparing cyclic polymers using ROMP.

References and Notes

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(2) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002**, *297*, 2041.

(3) The "cyclic" Ru complex $L(PCy_3)Cl_2Ru{=}CHR$ (**1**; L,R = chelating N-heterocyclic carbene) was prepared in a manner similar to a previously reported procedure, see: Furstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem. – Eur. J.* **2001**, *7*, 3236.

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(8) Odian, G. *Principles of Polymerization*, 3rd ed., New York: Wiley-Interscience, 1991.

(9) The polymerization was found to proceed very slowly ($t_{1/2}$ ~ hours) at ambient temperature.

(10) Extensive chain tranfer in olefin metathesis polymerizations approximate a step-growth polymerization where PDI's = 2.0 are expected at high conversion. See ref. 4 for further details.

(11) The critical monomer concentration of 1,5-cyclooctadiene has previously been determined to be approximately 0.25 M, see: (a) Suter, U. W.; Hocker, H. *Makromol. Chem.* **1988**, *189*, 1603. (b) Hocker, H.; Reif, L.; Reimann, W.; Riebel, K. *Recl. Trav. Chim. Pay. B* **1977**, *96*, M47. (c) Hocker, H.; Reimann, W.; Reif, L.; Ribel, K. *J. Mol. Catal.* **1980**, *8*, 191.

(12) Representative spectroscopic data for cyclic polybutadiene: ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.42 (C*H*, *trans*), 5.38 (C*H*, *cis*), 2.07 (CH_2, *cis*), 2.04 (CH_2, *trans*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.0, 129.9, 129.5, 129.3, 32.8, 32.8, 32.7, 27.5.

(13) For comparison, end-groups were clearly observable when COD was polymerized using acyclic Ru initiators or when symmetrical chain transfer agents, such as 1,4-diacetoxy-2-butene, were included (to form the corresponding end-functionalized telechelic polymers). For a review on telechelic polymers, see: Goethals, E. J. *Telechelic Polymers: Synthesis and Applications*, Boca Raton: CRC Press, 1989. For examples of forming telechelic polymers via ROMP, see: (a) Bielawski, C. W.; Morita, T.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 678. (b) Hillmyer, M. A.; Nguyen, S. T.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 718.

(14) Linear analogs were prepared by using linear Ru catalyst **2**. For examples of polymerization COD with Ru complexes coordinated with N-heterocyclic carbenes, see: (a) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2000**, *39*, 2903. (b) Frenzel, U.; Weskamp, T.; Kohl, F. J.; Schattenman, W. C.; Nuyken, O.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *606*, 8.

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(17) For an excellent description of how g_{M} was derived from SEC-MALS data, see: Podzimek, S.; Vlcek, T. *J. Appl. Polym. Sci.* **2001**, *82*, 454.

(18) The industrial synthesis of 1,5-cyclooctadiene involves a Ni catalyzed dimerization of 1,3-butadiene. Unfortunately, the formation of 4-vinylcyclohexane is an unavoidable side reaction. For further details, see: Gerhartz, W. *Ullmann's Encyclopedia of Industrial Chemistry*, VCH: Weinheim, Federal Republic of Germany, 1985.

(19) For similar examples of preparing telechelic polyalkenamers with end-groups containing differential functionality via ROMP, see: Bielawski, C. W.; Benitez, D.; Morita, T.; Grubbs, R. H. *Macromolecules* **2001**, *34*, 8610.

(20) Residual 4-vinylcyclohexene was still observable by GC after the ROMP has reached equilibrium. Thus, the deviation at higher molecular weights in Figure 2B (inset) probably stems from incomplete incorporation of the impurity into the polymer chains.