

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

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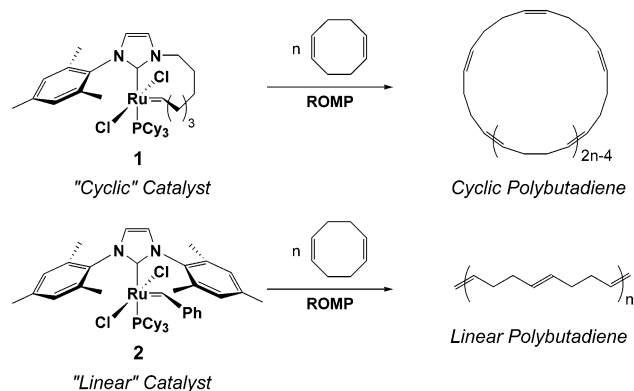
The topological restrictions imposed upon cyclic polymers result in a variety of physical properties that distinguishes them from their linear counterparts. For example, cyclic polymers are less viscous, exhibit higher glass transition temperatures, and have smaller hydrodynamic volumes and radii (R_g) than their respective linear analogues.¹ Their synthesis generally involves the preparation of linear polymeric precursors which contain reactive end-groups followed by intramolecular coupling under highly dilute conditions. Alternatively, polymerizations governed by a ring–linear chain equilibrium may be optimized to maximize formation of the cyclic polymer. Unfortunately, either approach offers only limited access to high-molecular weight (MW) polymer or large quantities of material.

Recently, we disclosed an alternative procedure for synthesizing cyclic polymers that circumvents the need for linear polymeric precursors.² The approach employs a “cyclic” analogue (**1**) of the olefin metathesis catalyst $L(PCy_3)Cl_2Ru=CHPh$ (**2**) ($L = 1,3$ -dimesitylimidazolylidene) in conjunction with the ring-opening metathesis polymerization (ROMP) of strained cyclic olefins (as monomer).^{3–5} Polymer formation is believed to proceed through the formation of a transient macrocyclic complex in which both ends of the growing polymer chain remain attached to the Ru center. Subsequent intramolecular chain transfer later releases cyclic polymer from the intermediate complex. The high affinity of N-heterocyclic carbenes for Ru prevents the overall circular nature of the system from being compromised during the course of the polymerization.⁶ In our previous report, we described the synthesis of cyclic polyoctenamers and cyclic polyethylenes using *cis*-cyclooctene as the monomer.

Herein, we extend the approach to the synthesis of cyclic polybutadienes using 1,5-cyclooctadiene (COD) as the monomer (see Scheme 1). Previously reported syntheses of cyclic polybutadienes involve the living anionic polymerization of 1,3-butadiene followed by a subsequent intramolecular cyclization reaction.⁷ Unfortunately, the inherent sensitivity associated with anionic polymerizations leads to samples contaminated with linear polymer. Furthermore, since polybutadiene’s microstructure (1,2- vs 1,4-regioisomers) remains highly dependent on reaction conditions (e.g., solvent, temperature, additives, etc.), its control remains challenging. In contrast, our approach overcomes these obstacles since it does not require the rigorous exclusion of air, moisture, or highly purified solvents. Elaborate purification techniques are also not necessary.⁸ Finally, the ROMP of COD is well-known to afford polybutadiene with an exclusive 1,4-regioisomeric backbone.

The ROMP of COD was initiated by adding the cyclic Ru complex **1** to a CH_2Cl_2 solution of the monomer at 45 °C.⁹ After 12 h, the polymer was isolated by precipitation from cold acetone or methanol followed by filtration. Polymers with a range of molecular weights were prepared by varying the initial monomer/catalyst (**1**) ratio or the initial monomer concentration (see Sup-

Scheme 1



porting Information). In all cases, the polydispersity indices (PDIs) of the polymeric products were found to be near 2.0.¹⁰ Polymerizations under dilute conditions (<0.1 M) resulted in the formation of only low-MW oligomers which was believed to be related to the critical monomer concentration of COD.¹¹

The circular nature of the polymers was examined using a variety of techniques and compared with linear analogues of similar MW.¹² As expected, end-groups were not observable by ¹H- or ¹³C NMR spectroscopy on low-MW (~2.3 kDa) samples prepared using complex **1**.¹³ Mass peaks in the MALDI-MS spectrum were separated by 54.1 Da (C₄H₆) with a remainder equal to the matrix ion. The intrinsic viscosities ($[\eta]$) of the cyclic and linear polymers were measured over a range of MWs using a size-exclusion chromatograph coupled to a differential viscometer (see Figure 1A). In the low-MW regime, the cyclic polymers were less viscous than their linear analogues, as expected.¹⁴ However, as the MW increased, the viscosities of the two polymers approached and eventually converged with each other. This suggested that the cyclic polymer was contaminated with its linear analogue.

The source of the linear polymer contamination is believed to stem from an acyclic impurity in COD: 4-vinylcyclohexene (4VC).¹⁵ The contaminant was found to range in concentrations from 0.05 to 0.10 mol % (as determined by gas chromatography), depending on the source. Although attempts were made to remove the impurity from COD through fractional distillation, trace amounts were always evident. Attention was then shifted toward using 1,5,9-*trans-cis-trans*-cyclododecatriene (CDT) as the monomer since it is commercially available, free of 4VC, and also provides 1,4-polybutadiene via ROMP.^{15,16} As shown in Figure 1B, when CDT was used as the monomer¹⁷ the $[\eta]$ of the cyclic polymer was lower than its linear analogue over the entire range of MWs measured. Furthermore, the cyclic polymers were also found to elute later than their linear analogues in the size-exclusion chromatogram (see Figure 2) which provided additional evidence that the polymer formed was cyclic.

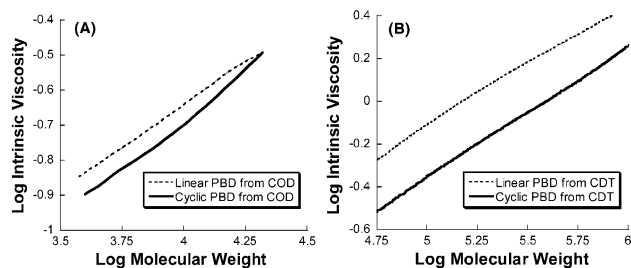


Figure 1. Mark-Houwink plots ($\log [\eta]$ vs \log MW) of cyclic and linear polybutadienes prepared via ROMP using either COD (A) or CDT (B) as the monomer. Conditions: THF, 30 °C.

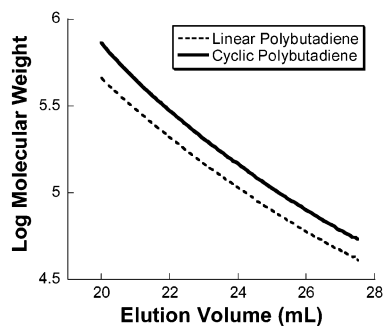


Figure 2. Plot of \log MW vs elution volume for linear and cyclic polybutadienes prepared via ROMP. The values were determined using a triple detecting (light scattering/differential viscometer/differential refractometer) apparatus coupled to a size-exclusion chromatograph (CH_2Cl_2 as eluent).

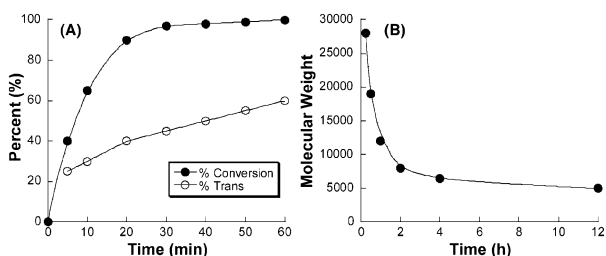


Figure 3. (A) Plot of monomer consumption and percent trans olefin in the polymer backbone vs time. Monomer conversion was monitored using gas chromatography. The average olefin geometry was determined by ^1H NMR spectroscopy. (B) Plot of molecular weight (M_n) vs time. The PDI at each point was between 1.7 and 2.0. The M_n and PDI values were determined by SEC (CH_2Cl_2 as eluent) and are reported relative to polybutadiene standards.

As with the ROMP of COD described above, the MW of the polybutadienes prepared from CDT could be tuned by varying the initial monomer/catalyst ratio or the initial monomer concentration (see Supporting Information). To help gain a mechanistic insight into the polymerization process, the dynamics of the ROMP of CDT were monitored using a combination of gas chromatography, size-exclusion chromatography, and ^1H NMR spectroscopy. As shown in Figure 3, monomer consumption was extremely fast ($\tau_{1/2} \approx 10$ min) with a concomitant rapid growth in polymer MW. However, depolymerization was evident as the average MW subsequently decreased slowly over time and finally plateaued after about 12 h. In addition, the average olefin geometry in the polymer backbone slowly increased over time to represent about 65% of the *trans* isomer. Furthermore, the PDIs of the resultant polymers were near 2.0 which are typical of equilibrium-controlled polymerizations.

In conclusion, we report the synthesis of cyclic polybutadienes using ring-opening metathesis polymerization (ROMP). The method uses a cyclic Ru catalyst in conjunction with either 1,5-cyclooctadiene (COD) or 1,5,9-*trans-cis-trans*-cyclododecatriene (CDT). The presence of an acyclic impurity, 4-vinylcyclohexene, found in the COD led to linear polymer contaminants. In contrast, CDT, which was free of the impurity, afforded cyclic polymer with little to no contamination over a wide range of molecular weights. Collectively, these results demonstrated how samples of pure cyclic polymer can be discerned from samples which contain linear analogues. More importantly, they underscore the need to use monomers that are free of acyclic impurities when preparing cyclic polymers using ROMP.

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Supporting Information Available: Tables summarizing the various polymerization conditions and physical attributes of polybutadienes prepared in this study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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