# Chapter 2

# An “Endless” Route to Cyclic Polymers

## Abstract

A new synthetic route to cyclic polymers has been developed in which the ends of growing polymer chains remain attached to a metal complex throughout the entire polymerization process. The approach eliminates the need for linear polymeric precursors and high dilution, drawbacks of traditional macrocyclization strategies, and effectively removes the barrier to producing large quantities of pure cyclic material. Ultimately, the strategy offers facile access to a unique macromolecular scaffold which may be used in meeting the increasing demand of new applications for commercial polymers. As a demonstration of its potential utility, cyclic polyethylenes were prepared and found to exhibit a variety of physical properties that were distinguishable from their linear analogs.

Portions of this chapter have been previously reported, see: Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002**, *297*, 2041.

## Introduction

At a yearly production rate of over 40 million tons, polyethylene remains one of the most valuable synthetic polymers in the world. It has found application in products ranging from grocery bags and milk containers to high performance fibers and medical devices. Its versatility stems from our ability to tune the material's crystallinity, mechanical strength, and thermal stability by altering the architecture of the individual polymer chains[1]. However, the rising number of applications for polyethylene demands its material properties to be broadened even further. While most efforts have been focused on synthesizing polyethylene with increasing structural complexity, we were interested in exploring whether unique properties could be obtained through the simplest of topological modifications. For example, tying the ends of a linear precursor together to form a cyclic polymer conceptually represents only a minimal variation in structure. However, the additional physical constraints imposed on such a cyclic polymer would not only restrict conformational freedom but also reduce its overall dimensions and therefore may lead to unusual or unexpected properties.

Although cyclic polymers have been previously synthesized, access to high molecular weight material (MW > 100 kDa), which is often required for many polymers to show their characteristic physical properties, is exceedingly challenging.[2] The typical synthetic route involves intramolecular macrocyclization of linear precursors at extremely low concentrations. Alternatively, the balance between linear and cyclic products that occurs for many polymerizations (e.g., polycondensations, metathesis polymerizations, etc.) may be shifted to maximize formation of cyclic product (which again generally involves using low concentrations). Incomplete cyclizations or undesired side reactions are common for both approaches and therefore elaborate purification procedures are often required to remove the acyclic contaminants.[3] Furthermore, many monomers, including ethylene, are not amenable to these types of polymerizations. As a result, there are very few reported examples of cyclic polyethylenes, especially in the high molecular weight (MW > $10^4$ Da) regime, and thus the physical properties and potential applications of this material remain largely unexplored.[4,5]

The drawbacks of the cyclization techniques listed above could be circumvented by eliminating the linear intermediates. This would require an "endless" polymerization process where cyclic monomers are linked together in such a fashion so that the overall circularity of the system is not compromised during polymer growth.[6] Finally, it is preferable that the resulting cyclic polymer is easily isolable, stable, and possesses no evidence of the polymerization process (i.e., no incorporation of undesired functional groups). Herein, we demonstrate these requirements can be met using ring-opening metathesis polymerization (ROMP)[7] in conjunction with cyclic Ru based catalysts.[8]

## Results and Discussion

The cyclic Ru complex $L(PCy_3)Cl_2Ru{=}CHR$ (noted here as **A**) was prepared in a manner similar to a previously reported procedure.[9] As shown in Figure 1, addition of **A** to *cis*-cyclooctene (monomer) in the bulk or in solution at 40 °C initiated the polymerization. After a pre-determined amount of monomer is polymerized, the resulting macrocyclic complex (**B**) undergoes intramolecular chain transfer to yield cyclic polymer and **A**.[10] After the polymerization reached completion (ca. 12 h), the addition of excess acetone or methanol caused polymer to precipitate which was then simply isolated by filtration. No additional purification steps were necessary.[11] A variety of polymers with number-averaged molecular weights ($M_n$'s) up to 300 kDa were prepared by varying the initial monomer/catalyst ratio and/or the initial monomer concentration.[12] However, low yields of polymer were obtained when the intial monomer concentration was near or lower than the critical monomer concentration (0.25 for COE in toluene, 25 °C). In all cases, the polydispersity indices (PDIs) of the resulting polymers were around 2.0.[13]

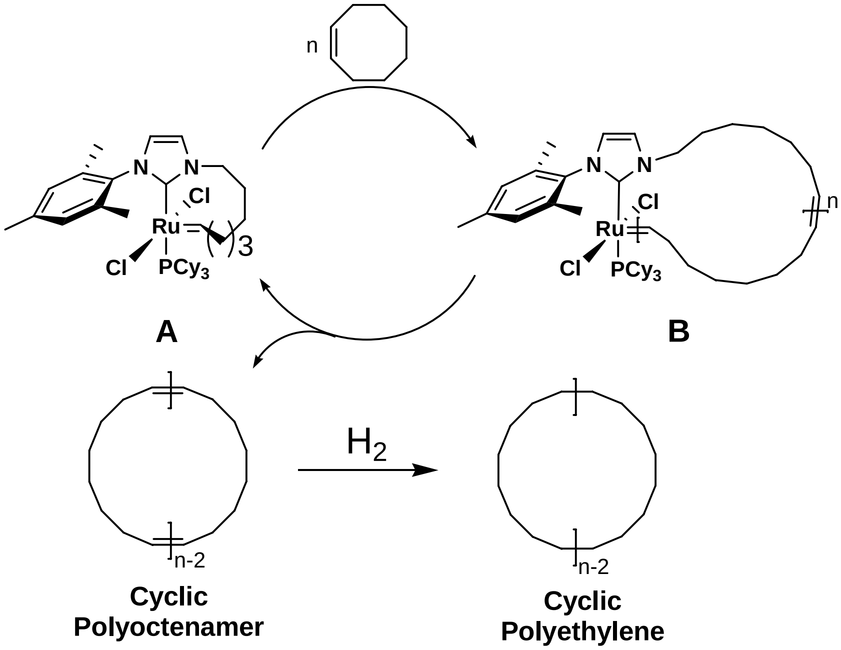
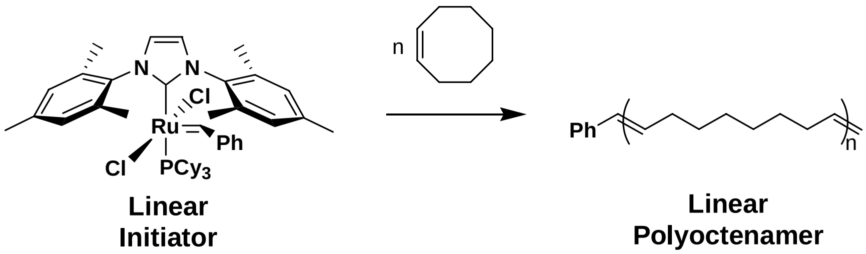


**Figure 1.** Synthesis of cyclic polymers using ring-opening metathesis polymerization. Addition of *cis*-cyclooctene (monomer) to cyclic complex **A** resulted in the transient formation of macrocyclic complex **B**. Subsequent intramolecular chain transfer provided cyclic polyoctenamer and regenerated **A**. Hydrogenation of the cyclic polyoctenamer afforded cyclic polyethylene.



(1)

The circular structure of the polyoctenamers prepared above was confirmed using a variety of characterization techniques. For comparison, a series of linear polyoctenamers with similar molecular weights and PDIs were synthesized using previously reported procedures (see Eq. 1). As shown in Figure 2A and Figure 2B, respectively, size-exclusion chromatography (SEC) indicated that the physically more compact cyclic polymers possessed smaller hydrodynamic volumes (i.e., they eluted later than their linear analogs) and had lower intrinsic viscosities than their linear analogs ($[\eta]_{cyclic}/[\eta]_{linear} = 0.4$).[14] Furthermore, Mark-Houwink plots (log $\eta$ vs. log $M_w$, Figure 2B) ruled out the possibility that these effects were related to conformational differences, as both polymers appeared to behave as random coils in solution (the Mark-Houwink parameter was 0.7 in both cases). The root mean square (RMS) radius ($<R_g^2>^{0.5}$) of the cyclic and linear polymers was measured using SEC coupled to a multi-angle light scattering detector. As shown in Figure 2C, the corresponding ratio $<R_g^2>_{cyclic}/<R_g^2>_{linear}$ was found to be approximately 0.5 over a wide range of molecular weights, as predicted by theory.[15] Finally, end-groups were not observable in the NMR spectra in any of the isolated cyclic polymers[16] and signals in the mass spectrum (obtained using a MALDI-TOF mass spectrometer) were multiples of 110.2 ($C_8H_{12}$) with a remainder equal only to the matrix ion.

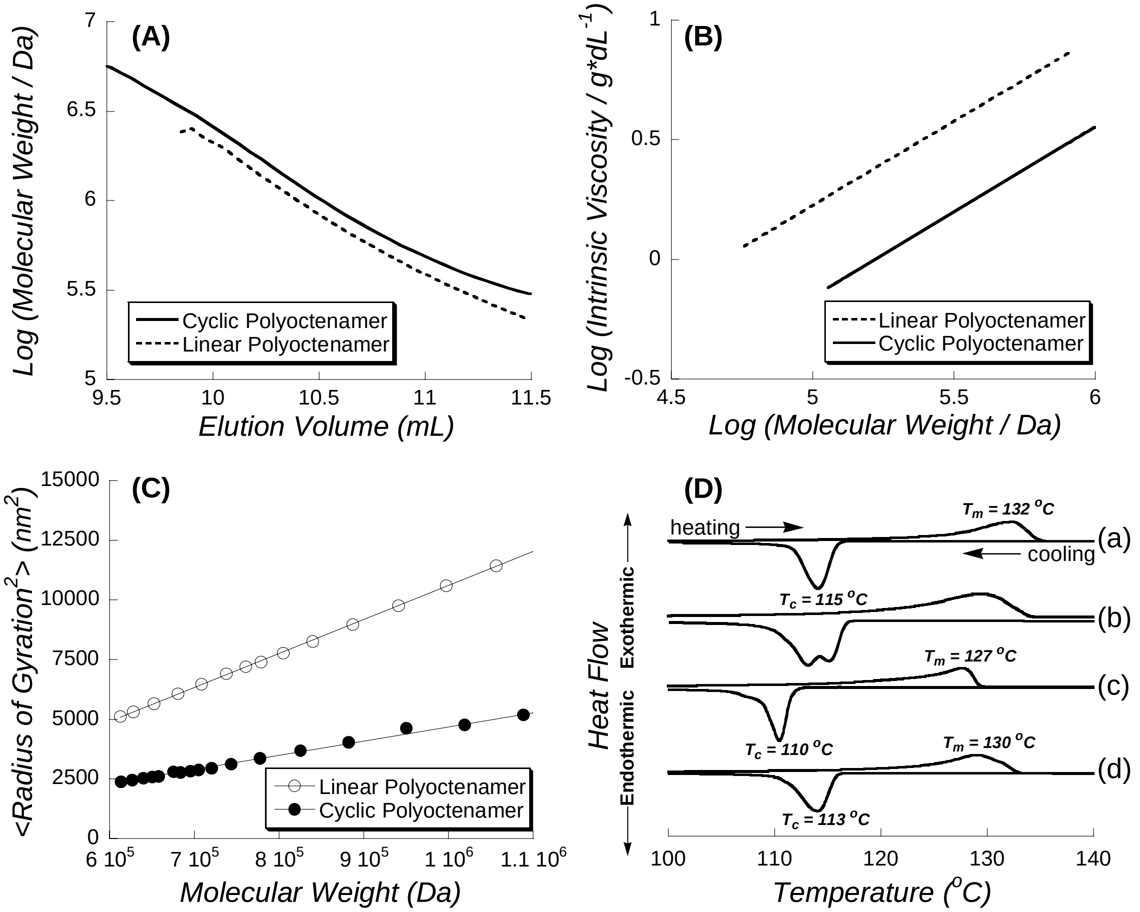


**Figure 2.** Comparison of the physical properties of the cyclic and linear polymers prepared in this work. (A) Plot of elution volume vs. molecular weight (eluent = THF; the reported molecular weights were determined by light scattering methods and are therefore considered absolute). (B) Plot of log η vs. log $M_w$ (Mark-Houwink plot). (C) Plot of the mean square radius ($<R_g^2>$) vs. molecular weight. (D) Differential scanning calorimetry thermograms: (a) Cyclic polyethylene, $M_n \approx 200$ kDa; (b) An equal mixture of cyclic and linear polyethylene after they were melted (200 °C), cooled to 25 °C, and then annealed for 36 h; (c) An equal mixture of cyclic and linear polyethylene, previously dissolved in xylenes, after solvent was removed; (d) Linear polyethylene, $M_n \approx 200$ kDa. In all cases, the heating/cooling rates were 10 °C/min and the analyses were performed under an atmosphere of nitrogen.

Although the characterization techniques described above provided strong physical evidence for circularity of the polymers synthesized, additional proof was obtained from chemical methods as well. Substrates containing 1,2-diols are known to undergo carbon-carbon bond cleavage to produce the corresponding bis-carboxylic acid species upon addition of excess Jones' Reagent ($CrO_3/H_2SO_4$).[17] Linear (MW = 35 kDa, PDI = 1.8) and cyclic (MW = 9 kDa, PDI = 1.9) polyoctenamers containing on average only one 1,2-diol group per polymer chain were obtained by adding a small amount of 1,2-diol-5-cyclooctene during the ROMP of *cis*-cyclooctene.[18] After the cyclic and linear polyoctenamers were independently reacted with Jones' Reagent, the resultant polymers were precipitated from excess acetone and collected. As shown in Figure 3, cleaving the 1,2-diol containing cyclic polyoctenamer afforded a polymer with a similar polydispersity but a larger apparent molecular weight (14 kDa vs. 9 kDa). The increased molecular weight was expected as linear polymers have larger hydrodynamic volumes than their cyclic analogs. In contrast, the polymer obtained by cleaving the linear polyoctenamer showed not only an apparent molecular weight that was nearly cut in half (MW = 19 kDa, PDI = 2.3) but was more polydisperse as well.[19]

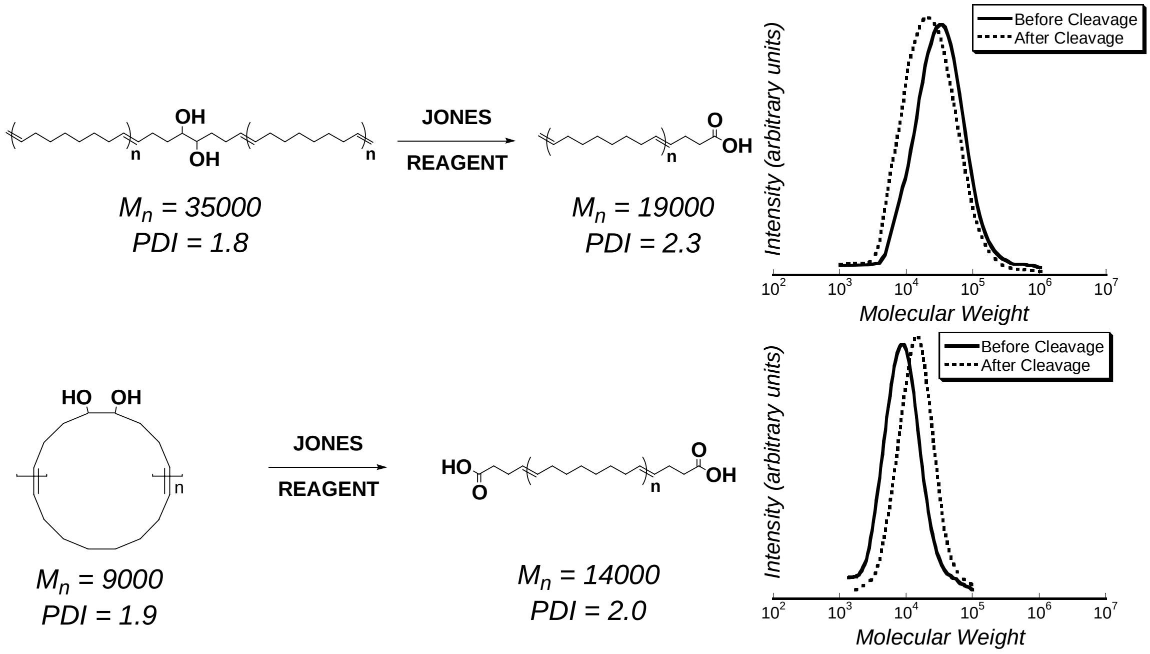


**Figure 3.** Cleavage experiments that aided in distinguishing between cyclic and linear polymers. Linear (top) and cyclic (bottom) polyoctenamers containing, on average, only one 1,2-diol unit per polymer chain were synthesized. Each polymer was separately reacted with Jones' Reagent ($CrO_3/H_2SO_4$) which selectively cleaved the 1,2-diol into the corresponding bis-carboxylic acids. The molecular weight and PDI information listed above was obtained from the SEC chromatographs shown directly to the right of each example.

Hydrogenation of the isolated cyclic polyoctenamers afforded the corresponding cyclic polyethylenes.[20] As shown in Figure 2D, differential scanning calorimetry (DSC) was used to compare the thermal properties of high molecular weight (MW ≈ 200 kDa) cyclic polyethylene with a linear analog of similar molecular weight. The cyclic polymer had slightly higher melting ($T_m$ = 132 ºC) and crystallization points ($T_c$ = 115 ºC) when compared to its linear analog ($T_m$ = 130 ºC, $T_c$ = 113 ºC). Since the enthalpy of fusion was found to be identical for both samples ($\Delta H_f \approx$ 100 J/mol K), the difference appears be related to the increased disorder (entropy) of the linear polymer. Interestingly, when equal amounts of linear and cyclic polyethylenes were mixed and melted together (200 ºC) then slowly cooled (1 ºC/min to 25 ºC) and annealed (150 ºC, 36 h), their characteristic $T_m$ and $T_c$ points were again observed upon subsequent thermal cycling. However, when equal amounts of the two samples were dissolved in hot xylenes followed by rapid solvent evaporation, depressed melting and crystallization points ($T_m$ = 127 ºC, $T_c$ = 110 ºC) were observed. We believe that the low mobility of the high molecular weight chains caused by polymer entanglement and/or threading prevented phase separation even under prolonged annealing. These two observations suggest that the cyclic and linear polyethylenes are not phase compatible and in the latter experiment, they were effectively behaving as contaminants for each other. For comparison, phase separation is known to occur in mixtures of linear and highly branched (> 8 branches/100 backbone carbons) polyethylene.[21]

We postulated that the lack of end-groups could also influence surface topology. Thin films of low molecular weight cyclic and linear polyethylenes (MW ≈ 10 kDa) were cast from xylenes and their interfacial contact angle with water was measured following literature methods.[22] The film composed of the cyclic polymer showed a larger contact angle ($\theta = 105 \pm 2°$) than its linear analog ($\theta = 96 \pm 2°$) which indicated that the interface with water was smaller on the cyclic polymer's surface. Migration of the linear polymer's end-groups to the surface would be expected to form a different interfacial topology than the cyclic polymer and thus may lead to contact angle hysteresis.[23]

## Conclusion

In summary, a new strategy for the synthesis of cyclic polymers that circumvents the need for linear precursors and low concentrations which have been limiting factors in traditional approaches has been developed. A metal complex was designed to effectively hold the ends of growing polymer chains together while catalyzing the continued addition of monomer. The foundation of the technique is based on Ru mediated ring-opening metathesis polymerization which is intrinsically mild, robust, and permits easy access to large quantities of polymers with tunable molecular weights. As a demonstration of the versatility and potential utility of this strategy, cyclic polyethylenes, which have remained elusive despite polyethylene’s ubiquity, were synthesized and found to display physical properties in solution, in bulk, and at the interface that were distinctive from chemically identical linear analogs.

## References and Notes

(1) Peacock, A. J. *Handbook of Polyethylene: Structure, Properties, and Applications*, Marcel Dekker: New York, 2000.

(2) Semlyen, J. A. *Cyclic Polymers, 2$^{nd}$ Ed.,* Kluwer Academic: Dordrecht, The Netherlands, 2000.

(3) Lee, W.; Lee, H.; Lee, H. C.; Cho, D.; Chang, T.; Gorbunov, A. A.; Roovers, J.; *Macromolecules* **2002**, *35*, 529.

(4) Höcker, H.; Riebel, K. *Makromol. Chem.* **1977**, *178*, 3101.

(5) Lee, K. S.; Wegner, G. *Makromol. Chem. -Rapid* **1985**, *6*, 203.

(6) Shea and co-workers reported a similar approach to functionalized cyclic polyethylenes using "polyhomologation." However, their strategy employs acyclic monomers and only low molecular weight boron containing polymers were reported, see: Shea, K. J.; Lee, S. Y.; Busch, B. B. *J. Org. Chem.* **1998**, *63*, 5746.

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(8) For a review of the development of Ru based olefin metathesis catalysts, see: Trnka, T.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.

(9) Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem. -Eur. J.* **2001**, *7*, 3236.

(10) Over 80% of complex **A** can be recovered from the polymerization by column chromatography (neutral silica gel, pentane/diethyl ether as eluent).

(11) The presence of even small amounts of acyclic olefins leads to linear polymer contamination. For example, linear polymer was observed when attempts were made at synthesizing cyclic polybutadiene from 1,5-cyclooctadiene which contains approximately 0.1% of 4-vinylcyclohexene as an impurity.

(12) When initial monomer concentrations of less than 0.2 M were employed, only low molecular cyclic oligomers (MW < 2 kDa) were obtained. The result is probably related to the critical monomer concentration of *cis*-cyclooctene (~ 0.25 M in toluene).

(13) Olefin metathesis polymerization with extensive chain transfer approximates a step-growth polymerization where polymers with PDIs = 2.0 are expected. Chain transfer is known to occur during metathesis polymerizations when catalyzed by Ru complexes ligated with N-heterocyclic carbenes, see: Bielawski, C. W.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2000**, *39*, 2903.

(14) Viscosity measurements were performed in tetrahydrofuran at 30 ºC using a SEC-viscometer apparatus. The observed ratio of 0.4 is in accord with theory for cyclic and linear polymers in good solvents, see: W. Burchard, in *Cyclic Polymers,* Elsevier Applied Science: London, 1986, pp. 43-84.

(15) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17,* 1301.

(16) The geometry of the olefins in polymer backbone was determined to be predominately *trans* (~ 66%).

(17) Wiberg, K. B. *Oxidation in Organic Chemistry*, Academic Press: New York, 1965.

(18) [1,2-Diol-5-cyclooctene]$_0$/[*cis*-Cyclooctene]$_0$ = 25; [Total Monomer]$_0$ = 0.5 M in $CH_2Cl_2$.

(19) By assuming a continuous and random distribution of cleavable groups into infinitely long chains, the PDI was calculated to increase by a factor of 4/3 after cleavage.

(20) The cyclic polyoctenamers were hydrogenated using either standard $H_2$/Pd/C procedures or tosylhydrazine decomposition, see: S. F. Hahn, *J. Polym. Sci., Part A: Polym. Chem.* **30**, 397 (1992). Either procedure resulted in hydrogenation of more than 99% of the olefins in the polyoctenamer's backbone, as determined by $^1$H and $^{13}$C NMR spectroscopy.

(21) Wignall, G. D.; Alamo, R. G.; Londono, J. D.; Mandelkern, L.; Kim, M. H.; Lin, J. S.; Brown, G. M.; *Macromolecules* **2000**, *33*, 551.

(22) Kwok, D. Y.; Neumann, A. W. *Adv. Colloid Interface Sci.* **1999**, *81*, 167.

(23) No differences in θ were observed between high molecular weight (~ 200 kDa) cyclic and linear polyoctenamers. This supports our belief that surface topology is affected by the presence (or absence) of end-groups.