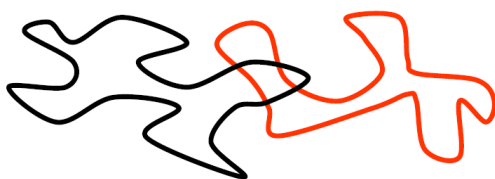


CHAPTER 5

The Importance of Molecular Weight Control for Cyclic Polymers Prepared via Ring Expansion Metathesis Polymerization

Abstract

This chapter describes the synthesis of cyclic and linear polyethylenes of various molecular weights, and the study of their physical properties. Molecular weight control of ring-opening and ring-insertion metathesis polymerizations is also discussed. In addition, two potentially more stable and active, new generation ruthenium catalysts, which might provide better molecular weight control of cyclic polymerization, are presented; and advances in their synthesis are reported.

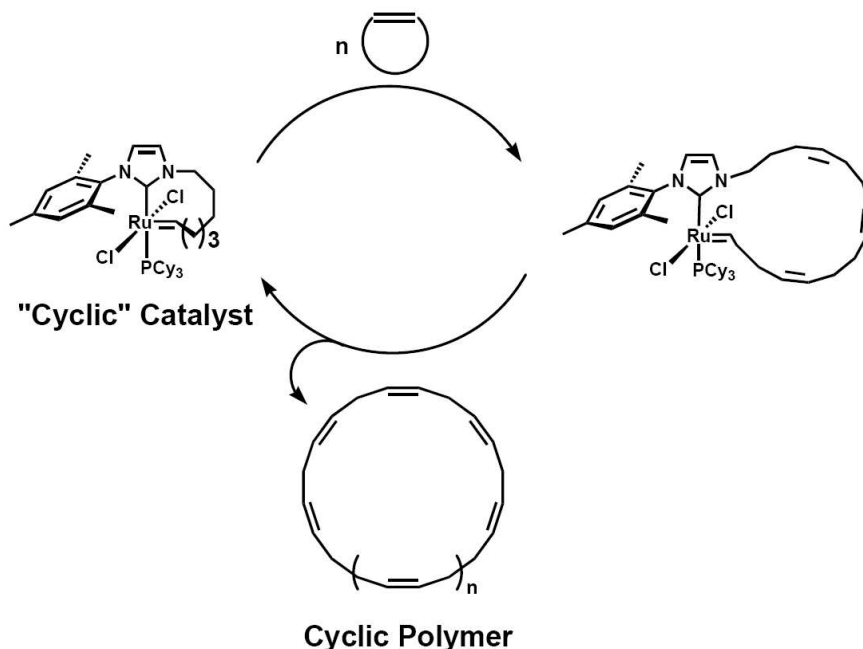


Introduction

Many of the important physical properties of a polymeric material, such as mechanical strength and viscosity, are the result of long-chain entanglements.¹ The end groups of a polymer chain are instrumental in this distinctively polymeric behavior, and, therefore, can have a considerable effect on the characteristics of the material. Consequently, a cyclic architecture, which lacks end groups entirely, may expand the scope of applications of well-established linear materials such as polyethylene or polyesters. Moreover, it has already been demonstrated that due to their different topology, ring polymers (of different chemical compositions) are less viscous, exhibit higher glass transition temperatures, and have smaller hydrodynamic volumes than their linear analogs.² However, this data is still too scarce for generalized predictions, due to 1) the limited availability of cyclic backbones,³⁻⁶ especially when compared to the current pool of linear polymers, and 2) the lack of efficient synthetic methods towards the clean (free of linear contaminants) production of cyclic polymers.⁷⁻¹⁰

A novel route to cyclic polymerization via ring-expansion olefin metathesis (REMP) with a “cyclic” catalyst (Scheme 5.1) has recently been developed by our group.¹¹ The method is similar to the ring-opening polymerization (ROMP) of strained cyclic alkenes, but it requires a specially designed, end-less, olefin metathesis catalyst. This direct polymerization route avoids the use of linear precursors, which are often employed in the construction of large rings,⁷⁻¹⁰ and, therefore, can provide access to multi-gram amounts of well-defined, pure cyclic polymers, whose physical properties can be extensively investigated.¹¹ In addition, the experimental data obtained from the study of a cyclic architecture, relative to a linear analogs, can facilitate a deeper understanding of macromolecular behavior and polymer properties in general.^{2,12} However, any exhaustive polymer structure-property relationship consideration necessitates access to a wide range of chain sizes with a low polydispersity index (PDI), which, in turn, requires good molecular weight control of the polymerization reaction of interest. However, molecular weight control of “end-less” REMP is an ongoing challenge. This chapter highlights two different rheological studies towards a better understanding of the physical properties of cyclic polymers. Furthermore, the challenges associated with the synthesis of very large and very small polymers via REMP are also discussed.

Scheme 5.1. Ring-expansion polymerization.¹¹



Results and Discussion

Part 1: Studies of shear-induced crystallization processes in polyethylene and the need for large cyclic polymers.

Properties of semicrystalline polymeric materials, such as polyethylene (PE) and polypropylene (PP), are strongly dependent on processing conditions.¹³ For example, the shearing stresses experienced by molten polymers during extrusion and molding affect the spatial arrangement and alignment of crystallites in the final product, defining its morphology and, consequently, its physical characteristics. Therefore, properties such as strength, permeability, and transparency can be tuned by altering the processing conditions.

The Kornfield group at Caltech has studied the effect of flow shearing stresses on the nucleation and crystallization in semicrystalline polymers. Furthermore, the group has designed and built an instrument that can impose high wall shear stresses for a controlled length of time at specified temperatures; the apparatus allows for shear-mediated crystallization studies to be performed with unusually small amounts of material (5g per loading/ $\sim$ 0.5g per experiment).¹⁴ This methodology was used to

demonstrate that incorporation of a small amount of long chains into a resin of much shorter chains of linear isotactic polypropylene (iPP) greatly enhances the orientation in the sample's outer layer/skin (where the effect of shear stresses is greatest during flow).¹⁵ Presumably, this morphology is the result of the shear stresses forcing the long chains to stretch into the threadlike precursors to crystallites, thereby orienting the short chains which cling to them (Figure 5.1b). Furthermore, this effect is not observed in systems where the molecular weight distribution is mono-modal. Moreover, the phenomena was shown to be cooperative, rather than single chain, and it has been attributed to the overlap of the long chains stretching under a shear force.¹⁵

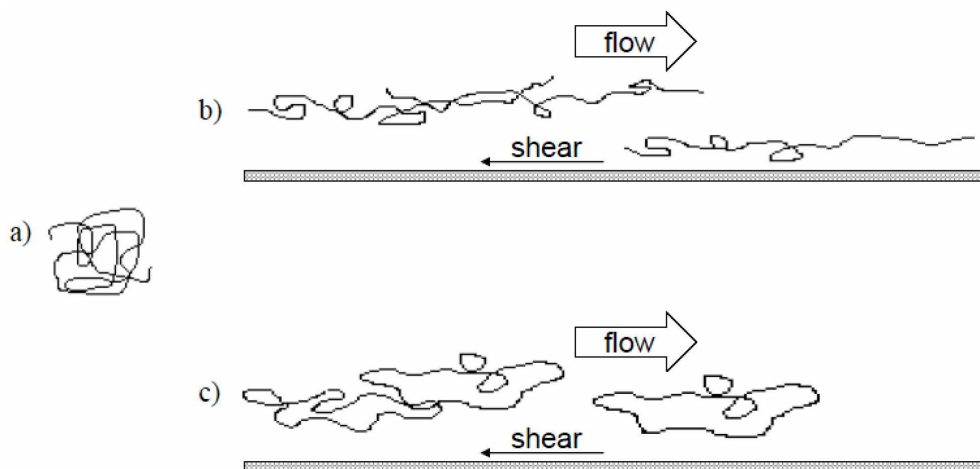


Figure 5.1. The effect of shear stress on polymer chain orientation. a) A relaxed polymer chain, b) linear chains under shear stress, c) cyclic chains under shear stress.

In light of these findings, it would be very instructive to examine the behavior of cyclic polymers under shear stress conditions. Of particular interest is the effect that large cyclic chains might have on the flow-induced crystallization of a host of short linear chains. As a result of its unique topology, each cyclic chain is expected to provide a shorter and thicker crystallization precursor, compared to a linear chain of the same size (Figure 5.1). Consequently, a large single ring might be able to act as two overlapped long linear chains, enhancing the crystallite growth and orientation in a sample to a greater extent than a linear chain.

In order to probe the effect of cyclic polymers on the flow induced morphology of PE, blends with varying fractions of large cyclic and long linear chains must be prepared

in a host of short linear polymers. Unlike industrial PE, which is traditionally prepared via Ziegler-Natta polymerization, polymers prepared via ROMP of plain, cyclic alkenes have absolutely no branches from the main chain and a much lower PDI. Consequently, since branching and polydispersity determine material's physical properties, the wealth of available information on the properties of industrial PE cannot be taken for granted in the investigation of PE architectures obtained via olefin metathesis. Therefore, all of the polyethylenes used for the studies—large, small, linear and cyclic—have to be prepared via olefin metathesis for a fair comparison of the two topologies.

The molecular weights required for flow-induced crystallization experiments were found to be 60–75 kDa for the short chain matrix and > 400 kDa for the long blend additives (as determined in a series of preliminary experiments with short linear PE chains of 21 kDa and 66 kDa). Molecular weight control of ROMP of strained cyclooctenes with ruthenium-based catalysts **1** and **2** (Figure 5.2) is well established, so the desired medium to large sized linear chains can be effortlessly obtained through the use of the appropriate catalyst loading. In fact, subjecting cyclooctene to **1** in 3630 monomer to catalyst ratio, successfully produced corresponding polyalkenamer with $M_w \sim 450$ kDa (slightly larger than the calculated 400 kDa) (Scheme 5.2A). However, the smaller polycyclooctenes (with $M_w < 100$ kDa) can be synthesized more efficiently with the aid of a chain transfer agent (CTA) and a more active catalyst **2**. Therefore, this method was used to make a short chain matrix material with $M_w \sim 58$ kDa (Scheme 5.2B). The molecular weights of all of the final polyethylene products (Scheme 5.2) were assumed to remain very close to those of the corresponding polyalkenamers; they could not be measured directly in our laboratory due to the low solubility of PE in common Size-Exclusion Chromatography (SEC) solvents at room temperature.

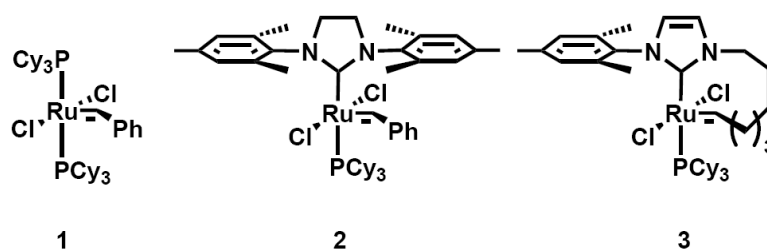
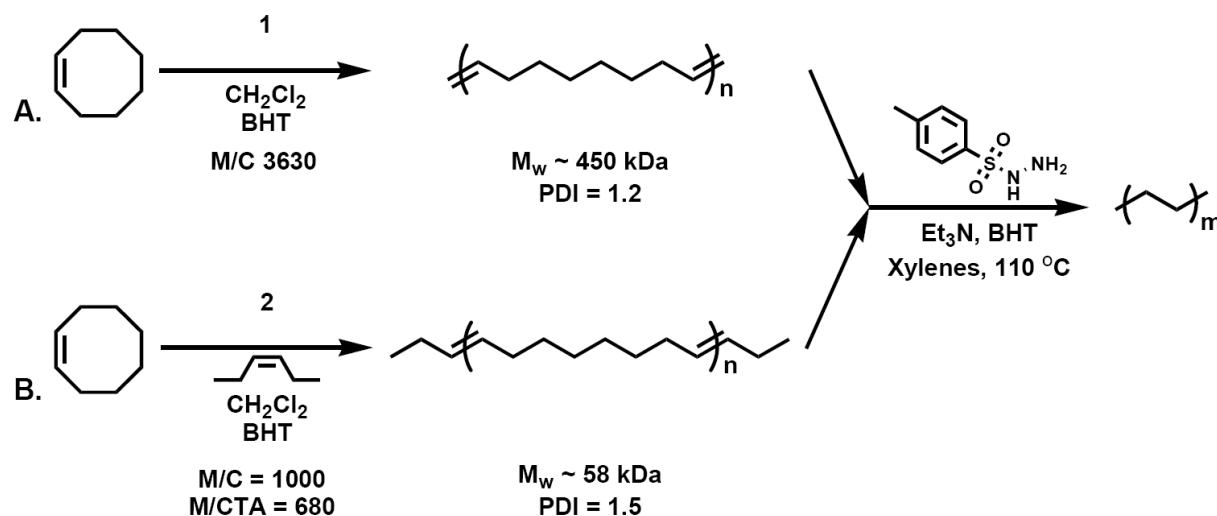


Figure 5.2. Catalysts required for the preparation of linear and cyclic polyalkenamers.

Scheme 5.2. Synthesis of long (A) and short (B) linear PE chains.

Molecular weight control of REMP with **3** is less straightforward than molecular weight control of ROMP with **1** and **2**. At the time of this study, the activity of the “cyclic” catalyst **3** was not yet well understood, and the synthesis of a polymer with the desired molecular weight of $\sim 400 \text{ kDa}$ required an additional polymerization conditions survey. Furthermore, since “cyclic” polymerization cannot rely on chain ends for size control, factors other than amount of the catalyst and use of CTA were considered; initial monomer concentration was one known factor.¹⁶ In addition, since our final synthetic goal was plain, fully reduced polyethylene, we chose to investigate the effect of the ring strain of various cyclic alkenes on the final molecular weight of the REMP products.

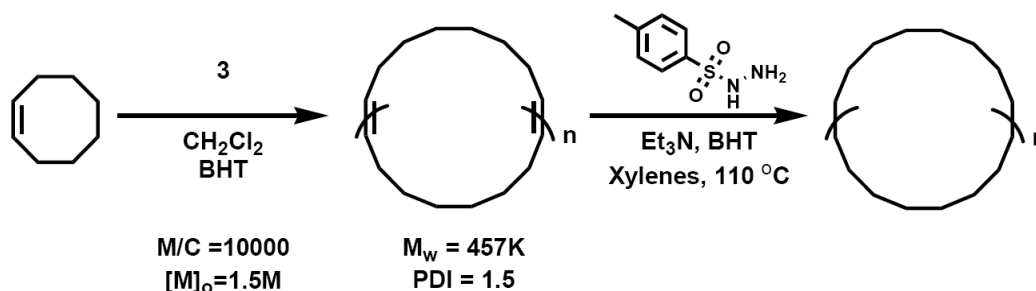
Table 5.1 summarizes the results of the study in which four cyclic alkenes with different ring strains were polymerized from a range of initial monomer concentrations and constant amount of **3**. It is immediately evident from this table that the more strained rings produce polymers of higher molecular weights in better yields. Furthermore, the data appears to confirm that the initial monomer concentration has a considerable effect on the molecular weight of the polymerization products. For example, polymerization does not occur in very dilute solutions ($[M]_0 = 0.1 \text{ M}$) of any of the considered monomers. On the other hand, the reaction of neat, strained cycloheptene and cyclooctene produces poorly soluble gels, which contain chains of very high molecular weight. Although the neat polymerization of the less strained cycloheptene gels to a

lesser extent than the neat polymerization of cyclooctene, and allows some material recovery, the obtained polymers have a smaller than expected size. The lower molecular weights of the products isolated from these gels are probably artifacts from inefficient stirring due to the high reaction viscosities of neat polymerizations. The exposure of cyclopentene to **3** produced only short oligomers in poor yields even at the highest monomer concentration, due to a lack of sufficient ring strain for ROMP ring strain. Based on this survey, the desired cyclic polymer with a molecular weight (M_w) of 457 kDa was successfully prepared from cyclooctene at a 1.5 M concentration (Scheme 5.3).

Table 5.1. Results (M_w / yield) for REMP of cyclic alkenes with **3**. Polymerization conditions: M/C = 2500 was used as a catalyst loading, and the reaction was conducted at 45 °C for 6 h. NP—no polymerization observed.

M/C = 2500		Monomer ring size (as # of carbons)		
		5	7	8
[M] ₀	Neat	2.2 kDa / 30 % (11.3 M)	Gel + 213 kDa (8.7 M)	Gel (7.7 M)
	5 M	1 kDa / 5 %	231 kDa / 60 %	Gel
	2.5 M	NP	90 kDa / 40 %	677 kDa / quant.
	1 M		NP	350 kDa / quant.
	0.5 M			75 kDa / 80 %
	0.1 M			NP

Scheme 5.3. Synthesis of large PE rings.



Initial investigation with all linear olefin metathesis-derived blend components (5% by weight of 450 kDa chains in a matrix of 58 kDa) confirmed the appropriateness of the selected molecular weights for the studies of PE samples. This study also provides

guidance for future experimental conditions (temperature, shear stress, time). As can be seen from Figure 5.3, polarized optical microscopy confirms that a higher shear pressure (Figure 5.3a vs. 5.3b) and longer shearing times (Figure 5.3c vs. Figure 5.3d) result in greater alignment in the PE sample's skin. Moreover, these micrographs appear to suggest that the long chains do enhance the skin's orientation even at the low doping of 5% concentration (Figure 5.3b vs. 5.3c). Experiments with higher concentrations of long chain and with cyclic polymers are currently underway.

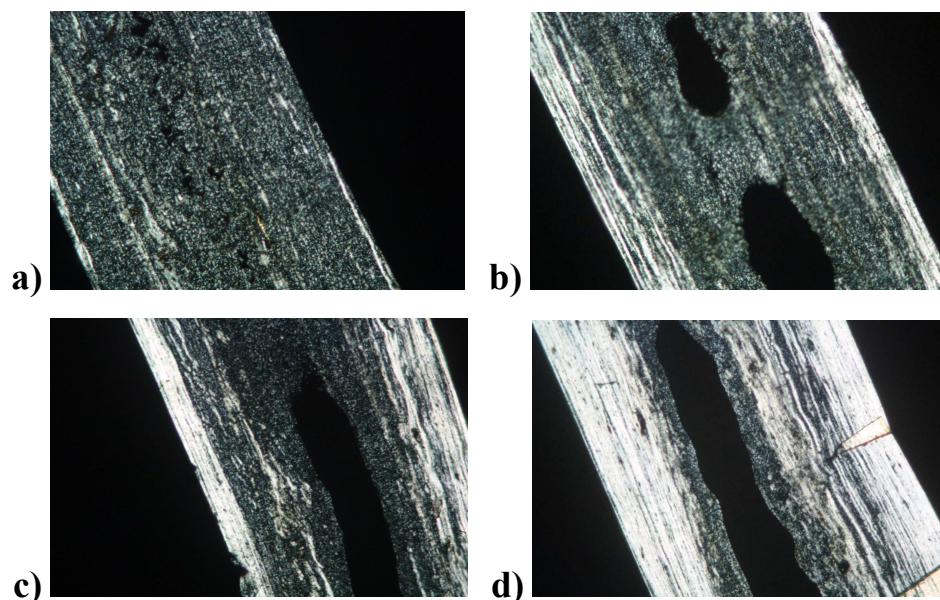


Figure 5.3. Polarized optical microscopy of selected samples. All blends are 5 % long ($M_w \sim 450$ kDa) linear chains in a matrix (~ 58 kDa) linear chains. Long white threads indicate chain alignment. a) Matrix only, 124 °C, 40 psi, 3 s; b) matrix only, 126 °C, 80 psi, 2 s; c) blend, 126 °C, 80 psi, 2 s; d) blend, 126 °C, 80 psi, 4s.

Part 2: Studies of the viscoelastic properties of cyclic polyethylene and the need for small cyclic polymers.

The reptation^{1,17} or tube¹² theory was first proposed by de Gennes in 1971 in an attempt to explain the effects of entanglement between long chains on the dynamical properties of polymer melts. This powerful model suggests that each chain in the high molecular weight polymer melt is confined to a topological tube, which is defined by the polymers around it. Moreover, since the chain in question is not allowed to cross any of

the boundaries of this three-dimensional, network-imposed constrain, it can only reptate along the tube in a snake-like movement, as one chain end follows another. The reptation model greatly simplifies melt rheology considerations, and offers a very good prediction for chain relaxation times and molecular size dependence of zero-shear viscosity ($\eta_0 \sim M^3$ vs. the experimentally derived $\eta_0 \sim M^{3.4}$) for polymeric materials consisting of chains capable of entanglement.

Rheological studies of cyclic polymers, which cannot reptate in the conventional sense, due to a lack of ends, should greatly improve the current understanding of the fundamentals of polymer chain dynamics. Although some experimental data on the melt behavior of macromolecular rings has been collected to date, it is limited to polymers 1) of very few chemical compositions such as poly(dimethylsiloxanes),^{2,18,19} polystyrene,^{20,21} and polybutadiene²², and 2) of limited sizes (usually on the smaller side), and 3) of, sometimes, questionable purity²³ (due to synthetic routes which involve linear precursors). Nevertheless, the existing data suggests that the cyclic polymers have lower zero-shear rate viscosities relative to corresponding linear analogs. However, the relevance of the η_0 - M_w relationship remains under debate, although the rings are believed to be less capable of entanglements due to the lack of chain ends.

The linear viscoelastic properties of cyclic polyethylene prepared by REMP with **3** were investigated in collaboration with the McKenna group at Texas Tech University (Figure 5.4a). Contrary to any previous reports on cyclic polymers, the cyclic PE in the molecular weight range from 85 to 380 kDa (which are all well above the critical PE chain entanglement sizes), appeared to be more viscous than the linear analogs (red dots in Figure 5.4a). To explain the observed phenomena, we hypothesized that, any possibility of linear contaminants aside, the rings tested were large enough to entangle much more than their linear analogs due to the “loop-loop interpenetration” effect implied by a lattice-tree model (Figure 5.4b).²⁴ Furthermore, smaller rings with sizes below some yet unknown critical molecular weight should have reduced “loop interpenetration” capabilities and entangle less than large cyclic polymer or corresponding linear chains, much like previously reported small cyclics. To test this theory (red line in Figure 5.4a), cyclic polymers covering range of molecular weights below 85 kDa need to be studied.

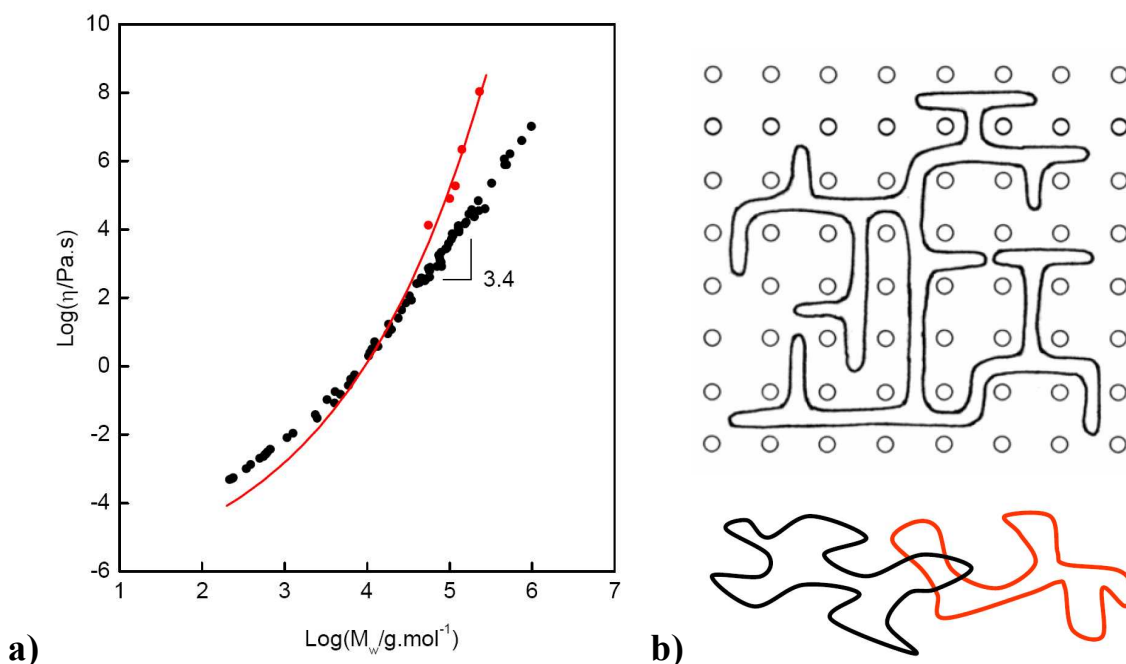


Figure 5.4. The results of the viscoelastic properties investigation of cyclic PE prepared by REMP. a) Plot of zero-shear-rate viscosity vs M_w (at 154 °C). Red dots represent experimental data for cyclic polymers, while red line represents the predicted $\eta_0 \sim M$ dependence; black dots represent the data for a metallocene polymerization derived linear PE reported elsewhere.²⁵ b) Lattice-tree animation theory.²⁴ Open circles represent the polymeric network/obstacles.

Although initial monomer concentration allows for reasonable control of REMP with **3** in the synthesis of large cyclic chains, this method of molecular weight control is very inefficient for the production of polymers smaller than 80-100 kDa. However, some of our studies of the polymerization behavior of **3** indicate initial rapid molecular weight build-up, followed by a slow decrease over the course of reaction (presumably due to the catalyst's re-insertion activity of the catalyst). Therefore, a second generation cyclic catalyst, which is more stable, long-living, and efficient than **3**, might be instrumental in the synthesis of smaller rings (among other advantages).²⁶ Catalysts **4** and **5** (Figure 5.5) might satisfy these criteria.

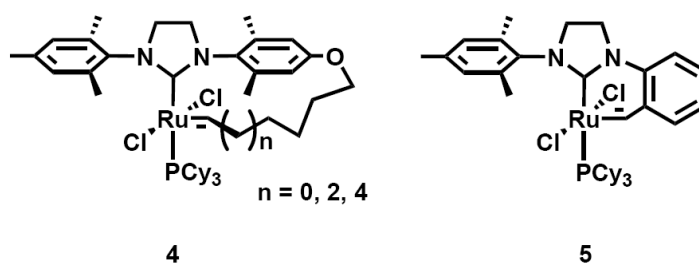
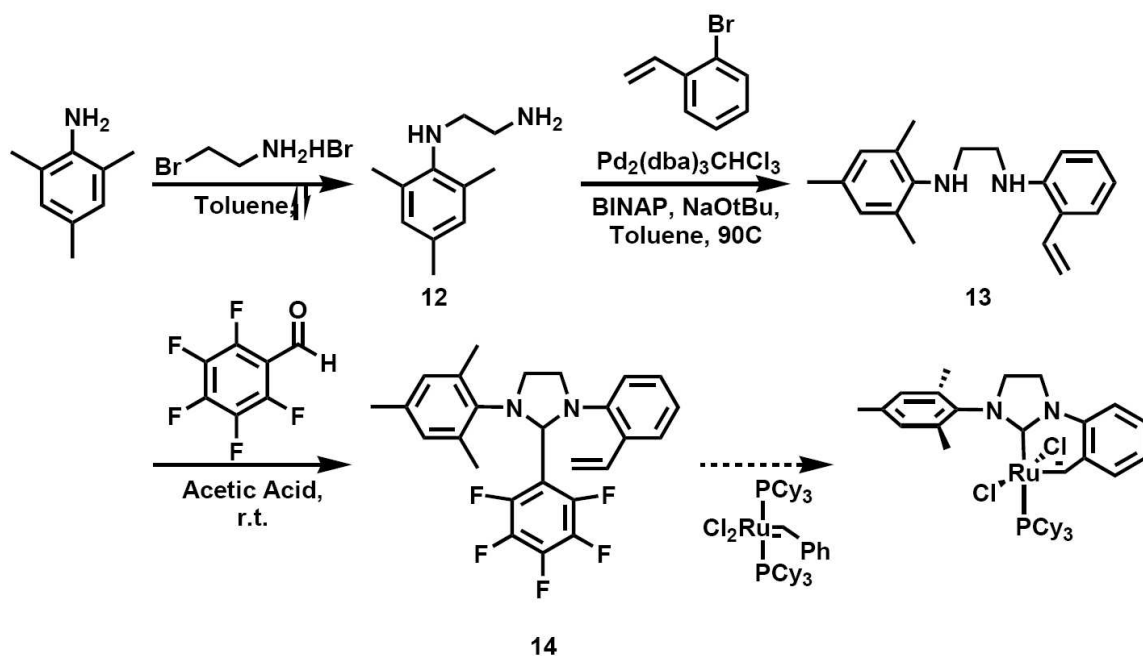


Figure 5.5. Proposed 2nd generation REMP catalysts.

Both catalysts **4** and **5** (Figure 5.5) boast a fully saturated imidazolyl ring and an aryl-fortified Ru-to-N tether. The saturation of the NHC-backbone should enhance the catalyst's activity,^{27,28} while the inserted dimethyl phenol should improve its stability, by preventing decomposition via C-H insertion by the ruthenium into the alkyl tether. In addition, **5** is a benzylidene, rather than an alkylidene-type catalyst, and, thus, might prove to be even more stable.²⁹ Although, there has been a report indicating that a phosphine-free, iso-propyloxy variant of **5**, is too stable to be metathesis active,³⁰ **5** might strike an appropriate balance between activity and stability.

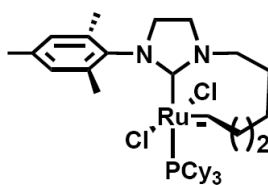
A synthetic route towards **4** is outlined in Scheme 5.4. Since the influence of the aryl moiety on the alkyl tether flexibility is unclear, three ligands with different linker lengths were prepared. Cyclic catalyst assembly usually proceeds via phosphine ligand exchange on **1**, followed by the intramolecular metathesis cyclization of the tether.^{26,31} However, despite evidence for a successful ligand exchange in some cases, no ring-closed species **4** could be obtained from any conditions or linker lengths tested.

Scheme 5.5. Synthetic route towards 2nd generation REMP catalyst **5**.

Conclusion

REMP of strained cyclic alkenes can provide multi-gram quantities of well-defined, cyclic polymers containing a wide variety of backbones. These can then be utilized to probe issues which are fundamental to polymer science. Furthermore, the rheological properties of cyclic polyethylene produced by this method are already being tested by a number of research groups and initial results indicate interesting behavior. Nevertheless, to fully realize the potential of this architecture for such investigations, polymer samples in a wide range of sizes and with a narrow PDIs are required. However, molecular weight control of REMP is difficult since there are no chain ends in the polymerization to rely upon. Although chains of larger sizes can be controllably produced by empirical variations in the reaction conditions, these methods fail to yield polymers much smaller than ~ 85 kDa. A number of 2nd generation REMP catalysts, which are expected to be more stable and active thereby affording small polymers, are currently being developed. Moreover, the recently reported complex **6** (Figure 5.6), which features a saturated NHC backbone and shortened tether, is promising and exhibits much improved stability and activity.²⁶ Taken together, these data and observations

underscore the potential of olefin metathesis for preparation of cyclic polymers with excellent molecular weight control.



6

Figure 5.6. First accomplished 2nd generation REMP catalyst.²⁶

Polymerization Experimental Procedures

Materials. All reagents, except for *cis*-3-hexene, were purchased from Aldrich at the highest available purity grade and used without further purification, unless otherwise noted. *Cis*-3-hexene was purchased from Fluka. CH_2Cl_2 was purified by passage through a solvent column and degassed with argon prior to use.

Instrumentation. NMR spectra were obtained using a Varian Mercury-300 spectrometer; samples were dissolved in CD_2Cl_2 .

Size exclusion chromatography (SEC) analysis was performed using a Viscotek triple detector system (model 270), equipped with a right angle laser light scattering (RALLS) detector, a differential viscosity detector, and a refractive index (RI) detector—all operating at 25°C. American Polymer Standards AM-GEL linear columns were used for SEC with CH_2Cl_2 as the eluent and a Shimadzu LC-10AD pump operating at 1 mL/minute.

Synthesis of High Molecular Weight Linear Polyoctenamer. A 100 mL disposable vial was charged with dry, degassed *cis*-cyclooctene (5.0 g, 45.5 mmol), dry, degassed CH_2Cl_2 (35 mL), 2,6-di-*tert*-butyl-4-methoxyphenol (BHT analog) (0.53 g, 2.27 mmol), and catalyst **1** (10.3 mg, 13.0 μmol , M/C = 3630). The mixture was heated to 45°C under argon atmosphere with stirring. The solution became very viscous within 15 min of heating, so 12 mL of CH_2Cl_2 was added to ensure efficient stirring and polymerization followed by an additional 12 mL of CH_2Cl_2 after another 30 min. After 12 h, the reaction solution was cooled to room temperature and poured over acetone. A white precipitate was collected on a Büchner funnel and washed with acetone. The product was redissolved in hot THF, precipitated from acetone, filtered, and dried under vacuum to produce 4.0 g (80% yield) of a white polymer. SEC: $M_w = 450 \text{ Kg/mol}$, PDI = 1.2.

Synthesis of Low Molecular Weight Linear Polyoctenamer—Chain Transfer Agent (CTA) Mediated Polymerization. *cis*-Cyclooctene (50.0 g, 0.45 mol) was degassed with argon and combined with dry CH_2Cl_2 (650 mL), 2,6-di-*tert*-butyl-4-methoxyphenol (5.3 g, 22.5 mmol), 3-*cis*-hexene (56 mg, 0.67 mmol, M/CTA = 680) and catalyst **2** (0.38 g, 0.45 mmol, M/C = 1000). The solution was purged with argon for an additional 0.5 h and heated to 45 °C. After 12 h of stirring under a positive argon

pressure, the mixture was cooled to room temperature and poured over acetone. The white precipitate was collected on a Büchner funnel and thoroughly washed with acetone. The product was then re-dissolved in CH₂Cl₂, precipitated from acetone, filtered, and dried under vacuum to give 39.0 g (75% yield) of a white polymer. SEC: M_w = 58 Kg/mol, PDI = 1.56.

Synthesis of Cyclic Polyoctenamer. Cyclic polyoctenamer was prepared and isolated according to the same procedure as described for the High Molecular Weight Linear Polyoctenamer from degassed *cis*-cyclooctene (5.0 g, 45.0 mmol), dry CH₂Cl₂ (25 mL + 10 mL added during the polymerization), 2,6-di-*tert*-butyl-4-methoxyphenol (0.53 g, 2.27 mmol), and catalyst **3** (3.3 mg, 4.5 μmol, M/C = 10000). SEC: M_w = 456 Kg/mol, PDI = 1.28.

Representative Hydrogenation Procedure (Matrix PE). Polyoctene (39.0 g, 0.35 mol of olefinic units), xylenes (1000 mL), and 2,6-di-*tert*-butyl-4-methoxyphenol (4.2 g, 17.7 mmol) were combined in a flask and purged with argon for 30 min, during which time the polymer partially dissolved. The solution was heated to 70 °C and vigorously stirred with argon purging for an additional 45 min, until all of the polymer completely dissolved. Tripropylamine (390 mL, 2.6 mol) and *p*-toluene-sulfonhydrazide (260 g, 1.4 mol) were added to the reaction mixture and the flask was heated to 110 °C. After 6 h more *p*-toluene-sulfonhydrazide (260 g, 1.4 mol) was added and the solution was stirred for more 12 h. The reaction vessel was cooled to room temperature, and the solution was poured over acetone. The resulting white precipitate was collected on a Büchner funnel, thoroughly washed with acetone, CH₂Cl₂, and isopropanol; and then dried *en vacuo* to produce an off-white powder in quantitative yield. ¹H NMR (300MHz, toluene-d₈, 100 °C, ppm): δ 1.33 (s).

References

- (1) Sperling, L. H. In *Introduction to Physical Polymer Science*; 2nd ed.; Wiley: New York, 1992, p 104-105.
- (2) *Cyclic Polymers*; 2nd ed.; Semlyen, J. A., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2000.
- (3) Kudo, H.; Sato, M.; Wakai, R.; Iwamoto, T.; Nishikubo, T. *Macromolecules* **2008**, *41*, 521-523.
- (4) Jeong, W.; Hedrick, J. L.; Waymouth, R. M. *J. Am. Chem. Soc.* **2007**, *129*, 8414-8415.
- (5) Kricheldorf, H. R.; Lee, S.-R.; Schittenhelm, N. *Macromol. Chem. Phys.* **1998**, *199*, 273-282.
- (6) Kricheldorf, H. R.; Eggerstedt, S. *Macromol. Chem. Phys.* **1998**, *199*, 283-290.
- (7) Tezuka, Y.; Komiya, R. *Macromolecules* **2002**, *35*, 8667-8669.
- (8) Oike, H.; Imaizumi, H.; Mouri, T.; Yoshioka, Y.; Uchibori, A.; Tezuka, Y. *J. Am. Chem. Soc.* **2000**, *122*, 9592-9599.
- (9) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16*, 843-849.
- (10) Geiser, D.; Höcker, H. *Macromolecules* **1980**, *13*, 653-656.
- (11) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002**, *297*, 2041-2044.
- (12) McLeish, T. C. B. *Adv. Phys.* **2002**, *51*, 1379-1527.
- (13) Kornfield, J. A.; Kumaraswamy, G.; Issaian, A. M. *Ind. Eng. Chem. Res.* **2002**, *41*, 6383-6392.
- (14) Kumaraswamy, G.; Verma, R. K.; Kornfield, J. A. *Rev. Sci. Instrum.* **1999**, *70*, 2097-2104.
- (15) Seki, M.; Thurman, D. W.; Oberhauser, J. P.; Kornfield, J. A. *Macromolecules* **2002**, *35*, 2583-2594.
- (16) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 8424-8425.
- (17) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572-579.
- (18) Orrah, D. J.; Semlyen, J. A.; Ross-Murphy, S. B. *Polymer* **1988**, *29*, 1452-1454.
- (19) Orrah, D. J.; Semlyen, J. A.; Ross-Murphy, S. B. *Polymer* **1988**, *29*, 1455-1458.

- (20) McKenna, G. B.; Hostetter, B. J.; Hadjichristidis, N.; Fetters, L. J.; Plazek, D. J. *Macromolecules* **1989**, *22*, 1834-1852.
- (21) Roovers, J. *Macromolecules* **1985**, *18*, 1359-1361.
- (22) Roovers, J. *Macromolecules* **1988**, *21*, 1517-1521.
- (23) Lee, H. C.; Lee, H.; Lee, W.; Chang, T.; Roovers, J. *Macromolecules* **2000**, *33*, 8119-8121.
- (24) Rubinstein, M. *Phys. Rev. Lett.* **1986**, *57*, 3023.
- (25) Aguilar, M.; Vega, J. F.; Sanz, E.; Martínez-Salazar, J. *Polymer* **2001**, *42*, 9713-9721.
- (26) Boydston, A. J.; Xia, Y.; Kornfield, J. A.; Gorodetskaya, I. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 12775-12782.
- (27) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543-6554.
- (28) Bielawski, C. W.; Grubbs, R. H. *Angewandte Chemie International Edition* **2000**, *39*, 2903-2906.
- (29) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100-110.
- (30) Vehlouw, K.; Gessler, S.; Blechert, S. *Angew. Chem. Int. Ed.* **2007**, *46*, 8082-8085.
- (31) Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem. Eur. J.* **2001**, *7*, 3236-3253.
- (32) Blum, A. P.; Ritter, T.; Grubbs, R. H. *Organometallics* **2007**, *26*, 2122-2124.
- (33) Nyce, G. W.; Csihony, S.; Waymouth, R. M.; Hedrick, J. L. *Chem. Eur. J.* **2004**, *10*, 4073-4079.