Tailoring Polymer Synthesis with Designer Ruthenium Catalysts

Thesis by
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Acknowledgments

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My entire family lives at least 2000 miles away (Chicago and beyond) which, to them, is about as far away as the moon. (They also think California is filled with "fruits and nuts"…but that's another story.) So, their visits were, at best, infrequent. I really appreciate Bob's family (Helen, Katy, Brendan, and Barney) taking the initiative and helping out to fill that void in my life. It was so nice to often see their warm smiles and hear their words of encouragement at group parties, weekend excursions, dinners, and late night pub crawls.

My undergraduate advisor, Professor Jeff Moore, has also played a huge part in my professional and personal life. Not many people know this (including Jeff or myself

at the time), but we basically grew up less than one mile from each other. While I think this gave us a sense of camaraderie, it was his intensity as a teacher and a scientist that really turned me on to chemistry. It was the first time I ever met someone with such deep passion for their work. He challenged me to join his group and pushed me very hard while I was there. However, he also spent a lot of time with me, teaching me how to be good researcher and how to perform top-notch science. If I end up with half the success that Jeff has enjoyed, I will consider myself very lucky.

Dr. Janis Louie deserves special recognition for being a great co-worker over the years. She is an amazing experimentalist with great chemical intuition and the hands to match. I am convinced that if Mother Nature permits it, she can do it! Without her, I don't think many of our projects would have been completed. I wish her the best of luck in her own independent career at the University of Utah.

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Diego Benitez is without a doubt one of the smartest and most well-rounded individuals I have ever met. His knowledge of science and worldly things is unsurpassed. Even with all this, Diego somehow manages to stay modest. He has been a particularly good friend of mine and I am indebted to him for helping to pull me through some tough periods in my personal life. I also want to thank him for putting up with my somewhat "aggressive" behavior over the years and not getting upset over it.

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cyclic polymers). ("Chuck" is a theoretical mechanical engineer - I still have no idea what that means!) I wish him and his new wife Stacey the best of luck in the future.

I am grateful to Professor Walter Stockmayer, the founder of Macromolecules (!) and (still) on faculty at Dartmouth College, for helping us interpret data on our cyclic polymer project. Dr. Michelle Chen and Dr. Stepan Podzimek, who are both with Wyatt Corporation, were instrumental in helping to obtain and interpret light scattering data on our cyclic polymers as well. Special thanks also go to Dr. Angelo DiBilio for helping me with the EPR instrument and Dr. Chi Ma for the SEM instrument.

I would also like to thank the entire Grubbs' group (past and present) for a memorable five years. (For fear of leaving someone out, I'm not going to list everyone.) But, suffice to say, that the Grubbs' group is a very dynamic and interactive environment filled with many different personalities and views on life. I've learned that this is actually an enormous advantage and I found that it creates energy for driving research forward. Many thanks to everyone for their challenges and for making lab an interesting, yet exciting, place in which to work.

I am grateful for the support of my committee members: Prof. Tirrell, Prof. Goddard, and Prof. Gray. Special thanks go to Prof. Tirrell for accepting me as a post-doc. (I am looking forward to walking across campus to my new home and learning a little more about proteins other than just how to eat them.) I would also like to give special thanks to Prof. Gray for dealing with all my last-minute scheduling. Although not on my committee, I am grateful to Prof. Brian Stolz and his wife Erna for being great listeners and for their invaluable advice.

Abstract

The research presented in this thesis focuses on applying ring-opening metathesis polymerization (ROMP) toward the synthesis of advanced macromolecular architectures. Chapter 1 provides an overview of the olefin metathesis reaction and evaluates the various synthetic tools currently employed for preparing complex polymeric structures.

Chapters 2 and 3 summarize the performance of various Ru-based catalysts in ROMP. Chapter 2 focuses on complexes coordinated with various N-heterocyclic carbene ligands while Chapter 3 focuses on their phosphine ligated analogs and methods to improve their initiation efficiency. The scope and utility of these catalysts in various ROMP reactions are discussed.

Chapters 4 and 5 describe the synthesis of acetoxy, hydroxy, and vinyl end-functionalized polybutadienes (PBDs) and polynorbornenes. By including allyl acetate, 1,4-bis(acetoxy)-2-butene, or 2-butene-1,4-diol as chain transfer agents (CTAs) during a Ru mediated ROMP of cyclooctadiene (COD) or norbornene (NBE), the respective end-functionalized polymers with molecular weights controllable up to 30 kDa could be obtained in high yield.

Chapter 6 describes a one-pot synthesis of triblock copolymers composed of mechanistically incompatible segments. Bis(allyl chloride) and bis(2-bromopropionate) end-functionalized telechelic PBDs were synthesized by the ROMP of COD in the presence of the corresponding difunctional CTAs. These telechelic PBDs were subsequently used as difunctional macroinitiators for the atom transfer radical

polymerization (ATRP) of styrene or methyl methacrylate (MMA) to form the respective block copolymers.

Chapter 7 describes the synthesis of a multifunctional Ru complex which was found to be capable of mediated both the ROMP of COD and the ATRP of MMA to form diblock copolymers. Depending on the reaction conditions, the complex was found to catalyze both polymerizations either in tandem or simultaneously. Introduction of hydrogen at the conclusion of the polymerizations resulted in quantitative saturation of the polymer backbone.

Chapters 8 and 9 describe a new synthetic route to cyclic polymers. In this approach, the ends of growing polymer chains remain attached to a cyclic Ru catalyst throughout the entire polymerization process. This effectively excludes all types of linear intermediates, which were a major drawback of previous approaches to cyclic polymers. Techniques for characterizing and determining the purity of cyclic polymers are also discussed.

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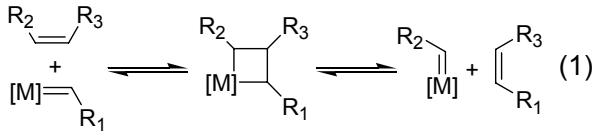
Chapter 1

General Introduction to Olefin Metathesis and the Art of Precision Polymer Synthesis

Olefin Metathesis

General Aspects. Olefin metathesis, a unique process of carbon-carbon double bond rearrangement, has developed into an indispensable tool for the synthetic chemist.[1] The mechanism, originally proposed by Chauvin in 1971, is generally accepted to involve the formation and subsequent cleavage of a metallacyclobutane intermediate (Scheme 1).[2] The cleavage can either occur in a productive fashion to afford a new olefin and a new metal carbene complex or a non-productive fashion to afford starting material. Generally, each step is reversible and the reaction is under thermodynamic control.



Scheme 1. Mechanism of olefin metathesis according to the Chauvin model.

A large number of transition metals are known to catalyze olefin metathesis. First generation catalysts were ill-defined, multicomponent mixtures that only were capable of polymerizing strained cyclic olefins.[1] However, within the last 15 years, a series of well-defined complexes has been developed which has greatly enhanced the utility of olefin metathesis.[3,4,5] The titanocyclobutane complex **1** was the first example of well-defined system that could be isolated.[3,4] While it was capable of polymerizing norbornene in a living fashion, the catalyst was not very functional group tolerant. Esters, ketones, and aldehydes (as well as protic species) reacted with **1** preferentially over olefins. Single-component Ta and Re catalysts were developed shortly after and found to display similar activites in mediating olefin metathesis as **1**.

A variety of Mo and W catalysts were developed by Schrock and co-workers in the late 1980's and early 1990's.[3] With appropriate ligand substitution, these catalysts were highly active in polymerizing a wide range of cyclic olefins. However, their viability is limitied by a low thermal stability and high sensitivity to oxygen, water, and functional groups such as such as alcohols and aldehydes. In addition, rigorously purified solvents and starting materials must be used to avoid premature catalyst decomposition.

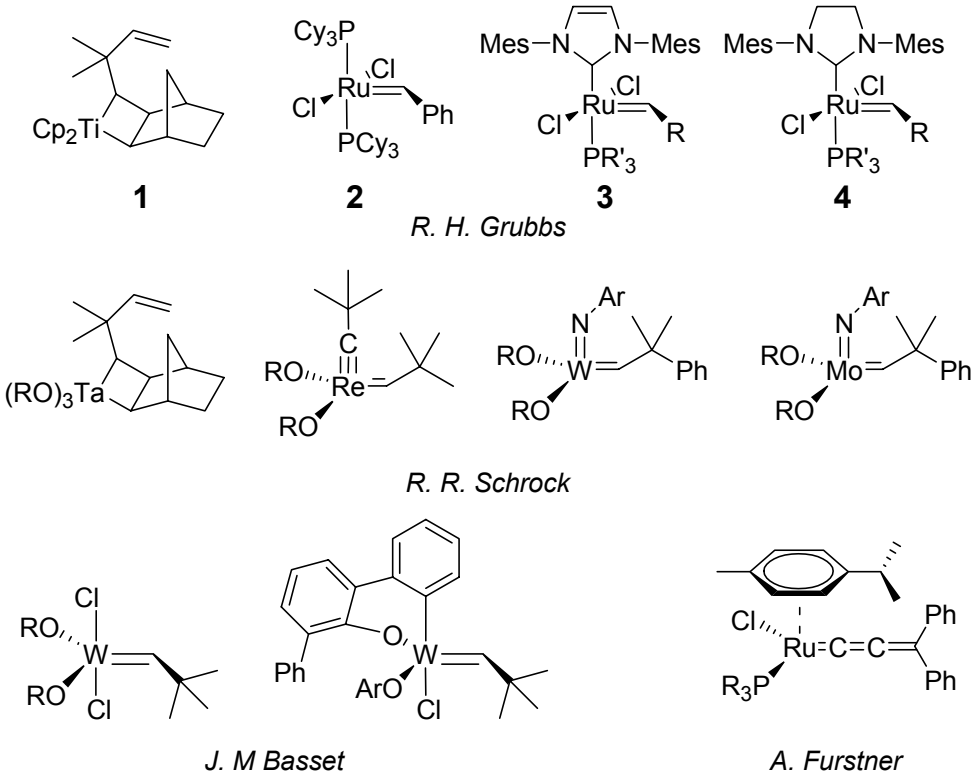
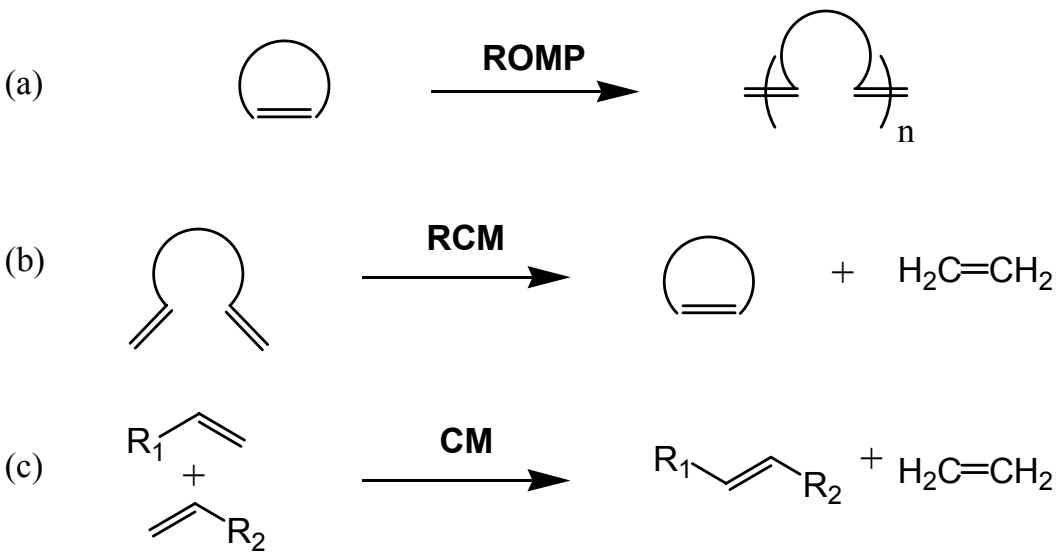


Figure 1. Representative examples of single-component transitional metal complexes used for catalyzing olefin metathesis.

A new class of olefin metathesis catalysts based on Ru was reported by Grubbs in 1992.[5] These catalysts were found to be stable to a wide range of functional group

including alcohols, aldehydes, acids, air, and protic solvents.[6] Subsequent efforts focused on facilitating their synthesis, tuning their initiation characteristics through carbene ligand modifications, and the development of chiral analogs.[7] Although Ru catalysts are typically more functional group tolerant than their Mo counterparts, their activity is typically much lower. However, in 1999, another breakthrough occurred and another new class of Ru based catalysts was developed.[8] Replacement of one of the phosphine ligands in complex **2** with an N-heterocyclic carbene ligand such as 1,3-dimesityl-imidazol-2-ylidene or its saturated analog, resulted in catalysts **3** and **4**, respectively. These catalysts not only display activities that rival the Mo based systems, but surpass the functional group tolerance level of previous Ru catalysts. In addition, catalysts **3** and **4** also display improved thermal stabilities, are relatively inert towards oxygen, and permit the use of extremely low catalyst loadings.

As shown in Scheme 2, olefin metathesis has successfully been employed to prepare polymeric materials through ring-opening metathesis polymerization (ROMP) and small molecules, both cyclic and acyclic, through ring-closing metathesis (RCM) and cross-metathesis (CM), respectively.



Scheme 2. Various types of metathetical reactions: (a) ring-opening metathesis polymerization (ROMP); (b) ring-closing metathesis; (c) cross-metathesis.

Ring-Opening Metathesis Polymerization (ROMP). ROMP is the conversion of cyclic olefins to unsaturared polyalkenamers.[1] It is enthalpically driven by the release of ring-strain associated with the monomer. Thus, strained cycloalkenes such as norbornenes,[9] cyclobutenes,[10] and barrelenes[11] have been successfully polymerized using a variety of metal alkylidenes. In contrast, monomers that possess a relatively low strain energy, such as cyclopentenes, are more difficult to polymerize and far fewer catalysts are known to be capable of polymerizing such monomers.[12] Since ROMP is also under thermodynamic control and thus is an equilibrium controlled process, depolymerizations can occur where growing chains "back-bite" or chain transfer to form cyclic olefins and shorter polymeric chains.[13]

Figure 2. Representative examples of cyclic olefins used in ROMP.

A major advantage of ROMP is that its characteristics can be tuned which allows unsurpassed control over of the polymer's size, shape, and functionality. Through careful catalyst selection, ROMP can be used as a living polymerization where chain transfer is absent and polymers with predictable molecular weights and low polydispersity can be synthesized.[14] Block copolymers *via* the sequential addition of different monomers have been prepared using ROMP.[15] Through appropriate functionalization, ROMP has also been used to prepare highly cross-linked,[12] conducting,[16] liquid-crystalline,[17] water soluble,[6] biologically active,[18] and surface-bound polymers.[19]

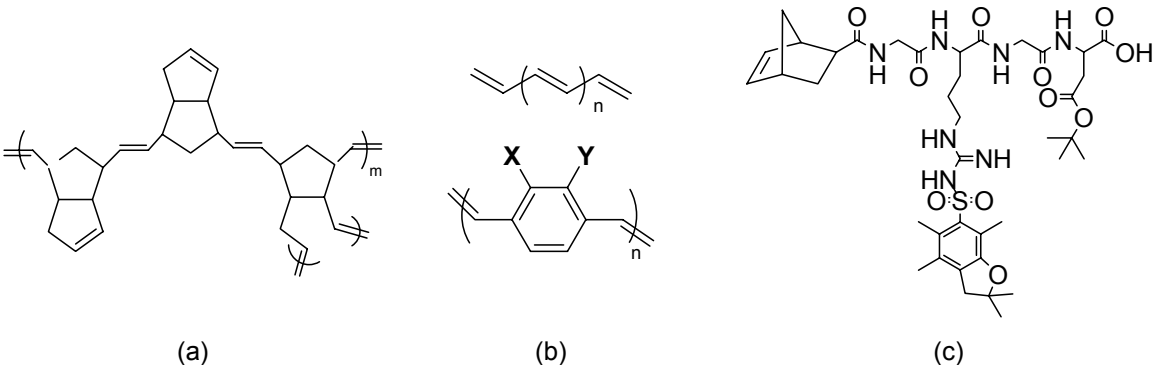
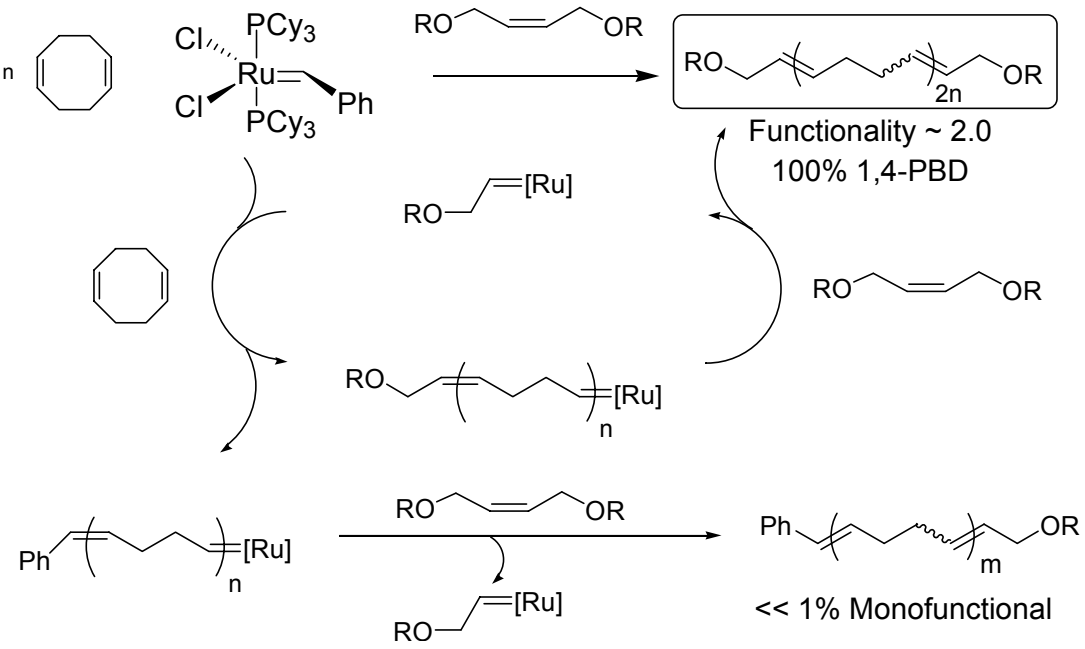


Figure 3. Represenative examples of polymers prepared using ROMP: (a) polyDCPD, which possesses high mechanical stability due to its cross-linked structure; (b) polyacetylene and polyphenylene, which are conducting organic polymers; (c) polynorbornene with a pendant bioactive peptide.

ROMP can also be used to prepare end-functionalized (telechelic) polymers, which have been traditionally difficult to prepare using other polymerization methods.[20] Such polymers have application in chain extension processes, cross-linked polymeric networks, and reaction injection molding.[21] One versatile approach involves the ROMP of a cyclic olefin monomer in the presence of an acyclic functionalized alkene that behaves as a chain transfer agent (CTA). The general mechanism for this process is outlined in Scheme 3. Propagating polymer chains react with a CTA such that the functional group is effectively transferred to the active growing species. This results in a polymeric chain and a new metal carbene each containing a functional group from the CTA. The new metal carbene can then react with either monomer (producing a new polymer chain) or a preformed polymer chain (transferring the active species). The only polymer endgroups that do not contain functional groups originating from the CTA are those from the initiating metal carbene and the terminating agent, which in principle, can be chosen to match those of the CTA. In absence of any termination reactions, the number of active centers is preserved, and can lead to telechelic polymers with a number averaged degree of functionality (F_n) that approaches 2.0.



Scheme 3. General scheme for the synthesis of telechelic polymers *via* ROMP.

Ring-Closing Metathesis (RCM). RCM of α,ω-dienes is used to form cyclic olefins.[22,23] In contrast to ROMP, RCM is enthalpically disfavored. The reaction is entropically driven by the release of volatile small molecules (e.g., ethylene). However, ring formation is limited by the relative ring strain of the product; highly strained olefins such as norbornene cannot be synthesized using RCM.

Since initial reports in 1992 and 1993, the cyclization of a variety of medium-sized rings (6, 7, 8 membered) and larger ring systems have been reported.[18] Tri- and tetra-substituted cyclic olefins,[24] bicyclic aza compounds,[25] and β-lactams[26] have also been prepared using RCM. Tandem cyclizations where sequential RCM reactions have been used in the formation of multicyclic ring systems.[27] A number of natural products including epothilone A, coronafacic acid, and frontalin have been synthesized using RCM as the key step.[28]

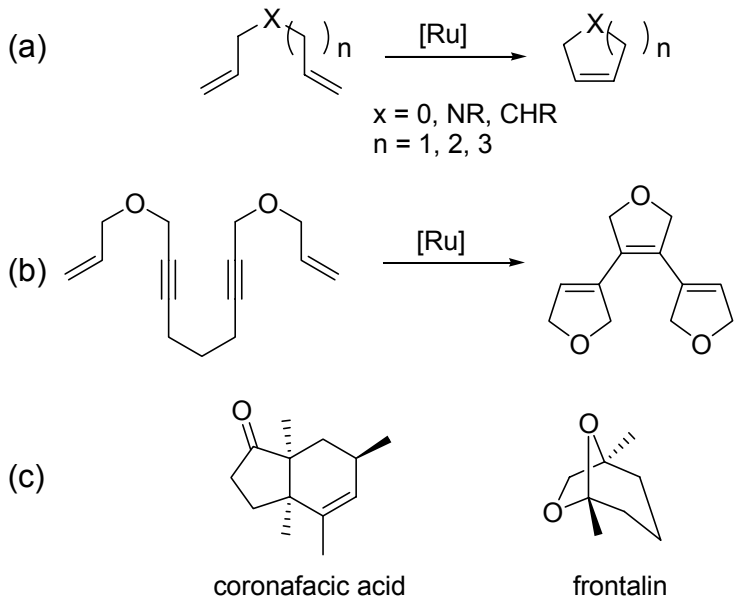
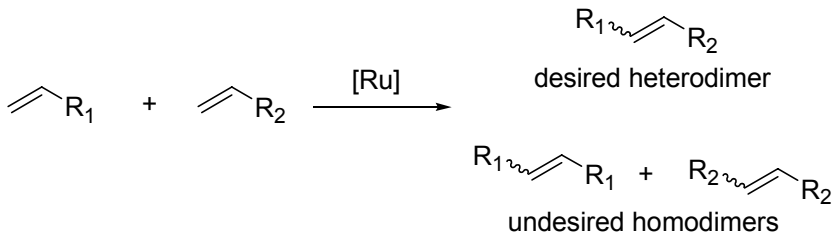


Figure 4. Representative examples of ring-closing metathesis: (a) RCM of α,ω-dienes to form 5, 6, and 7 membered rings; (b) tandem RCM to form a multi-cyclic substrate; (c) examples of natural products prepared using RCM.

Cross-Metathesis (CM). CM between acyclic olefins is thermodynamically analogous to RCM: the reaction is entropically driven by the loss of small molecules.[29] However, the reaction differs from RCM in two ways: 1.) there is no energy associated with ring strain and 2.) since homodimerization is possible, and often competitive with heterodimerization, mixtures of products are typically obtained. Cis and trans isomers are also possible, which complicates the product mixture even further. Nevertheless, the reaction has achieved extraordinary success in solving synthetic problems in organic chemistry.[29,30]



Scheme 4. General scheme for cross-metathesis.

Recent Advances in RCM and CM. Dramatic improvement in the utility of RCM and CM activity is observed with catalysts **3** and **4**. While Ru complex **2** has been extensively employed in small molecule synthesis (through RCM and CM) because of its high functional group tolerance, it was found that the catalyst was relatively inert towards sterically hindered olefins.[31] This is an enormous disadvantage as substituted olefins are a recurring motif in many natural products.[1b-d] As shown in Figure 5, 5-8 membered cyclic compounds with tri- and tetrasubstituted olefins were obtained from the RCM of sterically hindered olefins using catalysts **3** and **4**.[5b,5e,32] Reactions with these substrates were previously restricted to the highly active Mo systems. The yields obtained (63-95%) in these Ru catalyzed RCM reactions rival those obtained using the early transition metal based catalysts. In addition, the synthesis of trisubstituted acyclic alkenes with predominately *trans* olefin geometries using CM is now possible using complex **4**.[33]

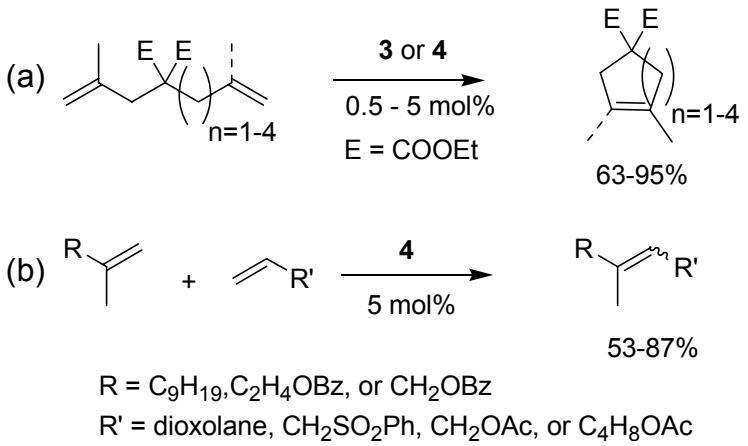
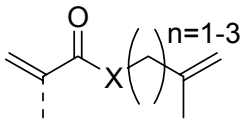
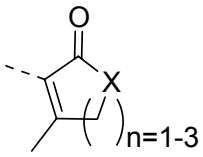
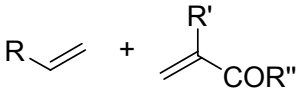
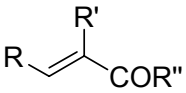
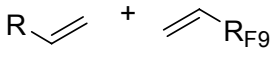
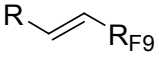
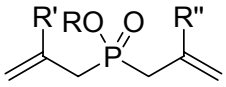
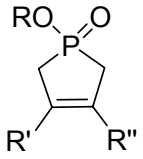
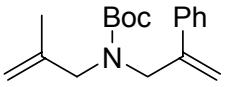
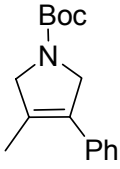
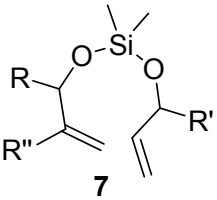
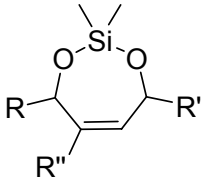


Figure 5. Representative examples of (a) RCM and (b) CM using Ru catalysts coordinated with N-heterocyclic carbene ligands.

Electron deficient and α-functionalized olefins are relatively unreactive towards Ru complex **2**.[34] However, as shown in Table 1, catalysts **3** and **4** were found to be extremely efficient in the RCM and CM of acrylates, methacrylates, α,β-unsaturated ketones and aldehydes, and olefins with fluorinated side chains.[10,35] As discussed above, the N-heterocyclic carbene places more electron density at the Ru metal center which may promote coordination to electron deficient olefins.

The improved functional group tolerance of catalysts **3** and **4** over Ru complex **2** was demonstrated by Nolan *et al.* in the synthesis of heterocycles using RCM.[36] Phosphinic acids (**5**) were successfully cyclized with catalyst **3** in excellent yields (88-100%). Sterically demanding amino templates (**6**) and silaketals (**7**) were also successfully cyclized with **3**. The ability to prepare the latter compounds is especially notable as they were found to be useful precursors to allylic diols. The parent Ru complex **2** is not reactive towards any of these substrates and the early transition based catalysts require extensive functional group protection to prevent catalyst decomposition.

Table 1. RCM of highly functionalized acyclic olefins.

Substrate	Catalyst (mol%)	Product	Yield
 X=O, NH	**3** or **4** (5 mol%)		42-97%
 R=C_8H_{16}OTBS, R'=CH_3, R''=OCH_3 R=C_8H_{16}OBz, R'=H, R''=OCH_3 R=C_8H_{16}OAc, R'=CH_3, R''=H R=C_8H_{16}OAc, R'=H, R''=CH_3	**3** or **4** (5 mol%)		62-99%
 R=C_8H_{16}OBz, R_{F9}=C_4F_9	**4** (5 mol%)		34%
 **5** R=R'=R''=H R=Bn, R'=R''=CH_3 R=Bn, R'=H, R''=Ph	**3** (5 mol%)		88-100%
 **6**	**3** (14 mol%)		83%
 **7** R=R'=C_3H_7, R''=H R=C_3H_7, R'=H, R''=Ph	**3** (5 mol%)		100%

Increasing attention has been directed towards the synthesis of medium and large rings using RCM.[1b-d] As shown in Scheme 3, the **4** catalyzed RCM of unsaturated ester **8** afforded 14-member lactone **9** with high *trans* stereoselectivity (E/Z~12).[37] The high selectivity is not related to ligand arrangement around the Ru metal center but actually stems from secondary metathetical reactions (continual *cis*-*trans* isomerization of the alkene bond) to form the more thermally stable *trans* isomer. Less active complex **2** was significantly less effective at catalyzing secondary metathesis isomerization as the same RCM reaction afforded product with a noticeably reduced *trans* selectivity (E/Z~4).

In a recent report from Mioskowski *et al.* on the attempted synthesis of 13-membered lactone **10**, RCM of the acyclic unsaturated ester **11** afforded 26-membered bis-lactone dimer **12** in an overwhelming 77% yield.[15] If the same reaction is performed using Ru complex **2**, only the acyclic dimer is observed.[38] No explanation has been given for these "unexpected" results. However, semi-empirical calculations[39] suggest that formation of the 26-membered bis-lactone (**12**) is energetically favored over the "expected" 13-membered lactone (**10**) and any of their isomeric forms. Thus, it appears that complexes **3** and **4** can achieve thermodynamic equilibrium much more efficiently than complex **2**. If this equilibrium can be determined *a priori*, it may be now possible to accurately predict the product distribution.

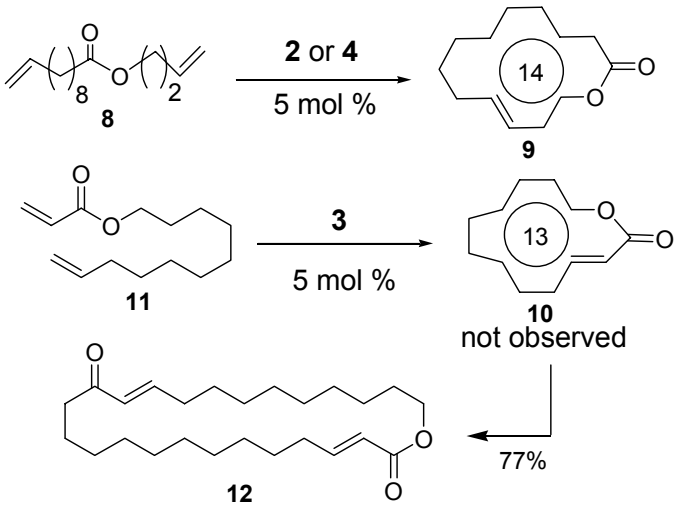


Figure 6. Synthesis of large unsaturated rings using RCM.

While catalysts **3** and **4** are relatively new, their high activity coupled with their remarkable functional group tolerance leaves little doubt that they will become essential to the synthetic organic chemist. Schreiber[40] and Smith[41] have already reported the preparation of structurally complex substrates for diversity-orientated synthesis and (-)-cylindrocyclophanes A and F, respectively, using catalyst **4** in key reaction steps (Figure 7). It is expected that synthetic routes to other natural products and complex organic compounds will increasingly access metathetical pathways made possible through these catalysts.

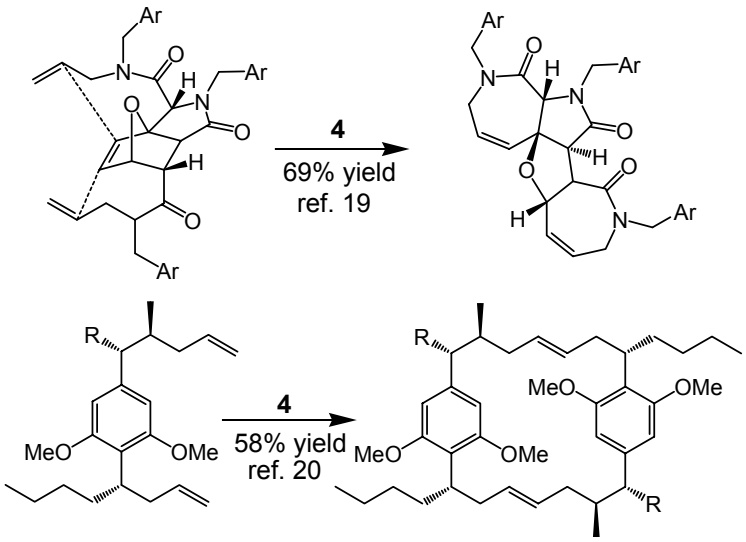


Figure 7. Examples of preparing of structurally complex and functionally divserse substrates using olefin metathesis.

Precision Polymer Synthesis

General Aspects. Synthetic tools that provide a high degree of control over polymer chain architecture can be used to prepare materials with tunable physical properties.[42] Shown in Scheme 1 are some examples of major macromolecular architectures.[43] The synthesis of these polymers has been accomplished through various polymerization techniques which are considered "living." The term "living polymerization" was first coined by Szwarc because propagating chain ends remain active until termination.[44] Furthermore, as first noted by Flory, all the chain ends grow at the same rate and thus the degree of polymerization (DP) and thus the molecular weight (MW) can generally be predicted by the relative amounts of monomer (M) and initiator (I) ($DP = M_0/I_0$).[45]

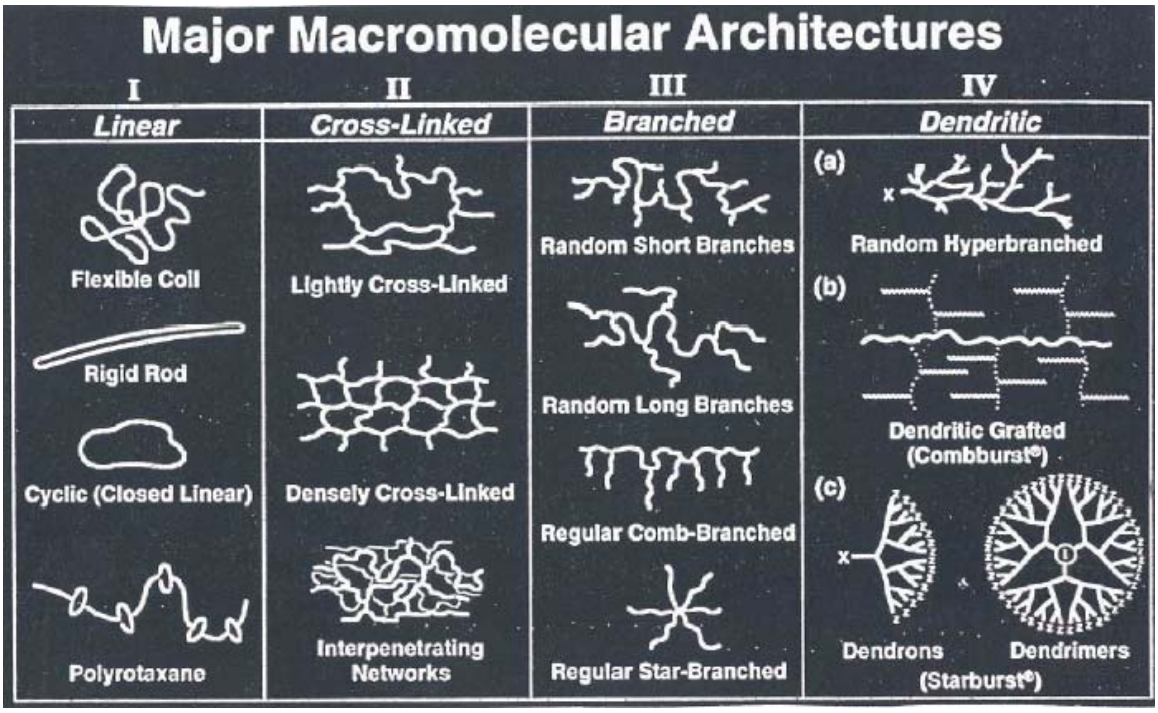


Figure 8. Major macromolecular architectures. Adapated from ref. 43.

Living polymerizations also afford polymers which generally have very narrow molecular weight distributions.[3] The polydispersity index (PDI) follows: PDI = M_w/M_n = 1 + 1/DP, where M_w is the weight-averaged molecular weight, M_n is the number-averaged molecular weight, and DP is the degree of polymerization (i.e., the average number of monomer units per polymer chain). Living polymerizations can be distinguished from condensation or kinetically controlled (i.e., free radical) polymerizations by analyzing the evolution of the polymer's molecular weight as a function of monomer conversion. In condensation polymerization, high molecular polymer is only formed at very high conversions while in kinetically controlled polymerizations, high molecular polymer is formed at relatively early stages. In living polymerizations, since all chain ends are growing at the same rate, molecular weight is directly proportional to monomer conversion. However, it is imperative to use systems in

which the initiation step is faster or the same rate as chain propagation in order to obtain control over the molecular weight.

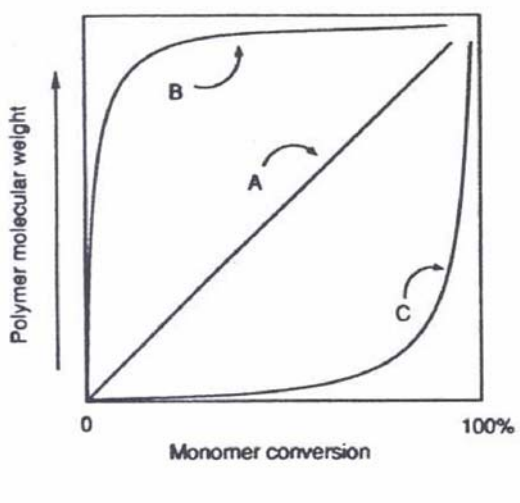


Figure 9. Molecular weight evolution as a function of monomer conversion for various types of polymerization methods: (a) living polymerization; (b) free-radical polymerization; (c) condensation polymerization. Adapted from ref. 42.

Most living polymerizations are based on anionic or cationic based methods.[42] The inability for charges of the same sign to couple keeps the chain ends active until the polymerization is intentionally terminated. The major monomer classes used in anionic living polymerizations are styrenes, butadienes, methacrylates, acrylates, ethylene oxide, and lactones. In contrast, cationic methods are used mostly to polymerize cyclic and unsaturated ethers and isobutene. Combined, the scope of both polymerizations is quite large, however, they both suffer from a very low functional group tolerance. In general, scrupulously clean monomers and solvents must be used to prevent premature termination. Because of this drawback, attention has greatly shifted to using free radical based methods, which are inherently much more robust.

Atom-Transfer Radical Polymerization (ATRP). One of the most successful strategies for controlled free radical polymerization is ATRP, first reported independently by Sawamato[46] and Matyjaszewski.[47] The mechanism[48] of ATRP is outlined in Figure 10 and is based on a reversible, metal-mediated halide exchange process. Control is achieved because the relative rates of activation and deactivation (i.e., the equilibrium constant) are on the order of 10^{-7}. Thus, the concentration of growing radicals is sufficiently low (*ca*. 10^{-8} M) to effectively eliminate bimolecular termination. PS[49] and PMMA[50] with pre-determined MWs and low (1.05 to 1.50) polydispersity indices (PDIs) have been obtained using ATRP. Copper chloride and 2,2′-bipyridine (bipy) are often employed as the organometallic catalyst in these polymerizations.[51]

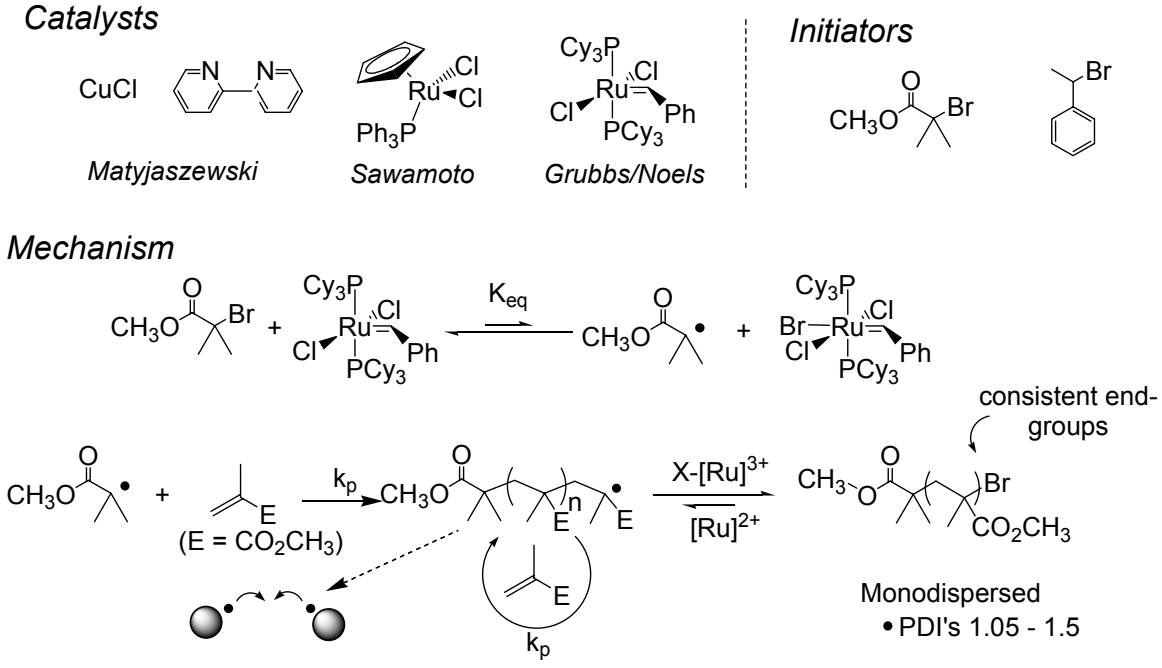


Figure 10. Overview of atom-transfer radical polymerization (ATRP).

Ring-Opening Metathesis Polymerization (ROMP). As discussed above, living ROMP is another commonly used technique for polymer synthesis. Like the

anionic and free radical based methods described above, ROMP uses unsaturated monomers. However, in ROMP, the unsaturation is conserved in the polymer which presents a distinct advantage since the unsaturated groups provide extra sites for further functionalization and can aid in reducing the polymer's glass transition temperature.[52]

Mechanistically Incompatible Polymers. Block copolymers often exhibit the properties of each of their individual homopolymers.[14] Furthermore, they are used to provide an additional level of control over morphology (through differential phase separation behavior) as well. The most common approach to preparing block copolymers is the sequential addition of two different monomers (Figure 11a).[14,53] However, when two (or more) monomers that cannot be polymerized by the same mechanism are used, multiple steps are required. For example, poly(styrene)-*b*-poly(norbornene) and poly(methyl acrylate)-*b*-poly(norbornene) diblock copolymers have been prepared by combing ATRP with ROMP.[54] Norborene was polymerized using ROMP and capped with an agent that was subsequently used as an initiator for the ATRP of styene or methyl acrylate (Figure 11b). In addition to linear block copolymers, the combination of various living polymerization techniques has been used to prepare others types of polymer architectures with mechanistically incompatible monomer segments including triblock copolymers,[55] comb or graft-type polymers,[56] and star-shaped polymers.[57]

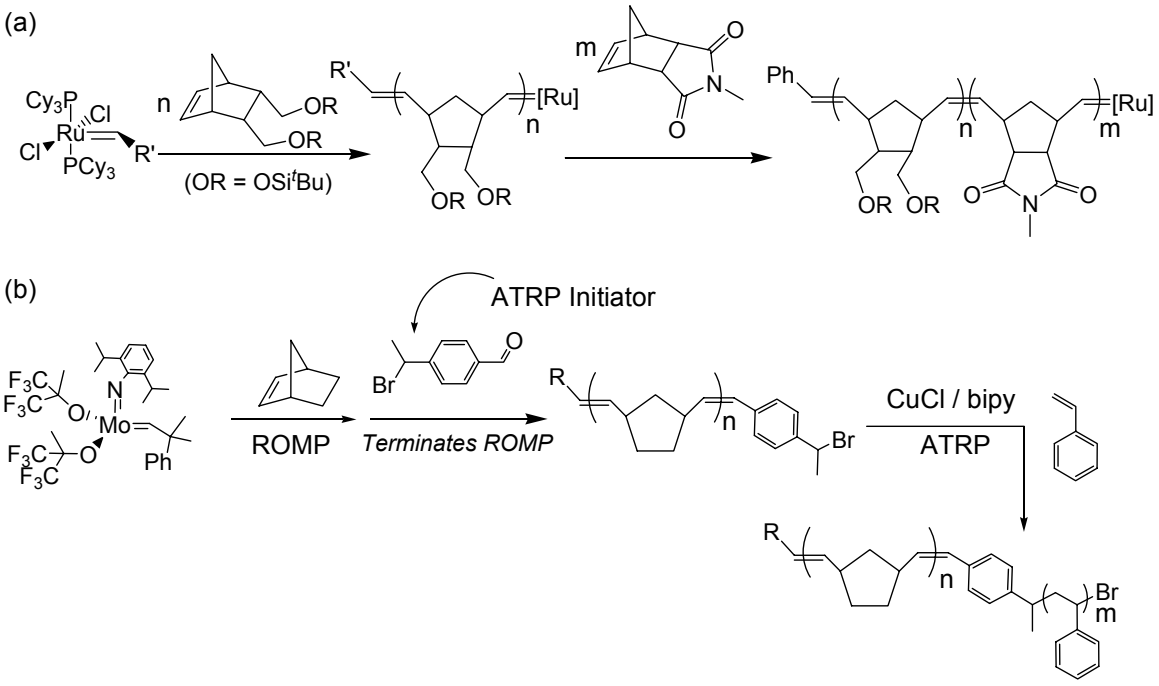


Figure 11. Examples of preparing block copolymers using (a) sequential addition and (b) macroinitiation. In the second approach, the intermediate polynorbornene contains a functional end-group which allows it to be used as a macroinitator for the next polymerization (ATRP).

Integration of Living Polymerization Methods with Traditional Synthetic Techniques. While extremely useful in controlling a wide range of polymeric architectures, living polymerization methods have their limits. For example, dendrimetric polymers, which require an iterative, step-wise procedure for their synthesis, cannot be prepared by living polymerization.[58] Another example is the closely related hyperbranched polymers, where differential rates of chain growth are required.[59] However, the combination of living polymerizations with traditional synthetic techniques used by organic and inorganic chemistry is quickly being recognized as a means of achieving the ultimate control over polymer architecture. Polymeric precursors[60] to polyrotaxanes,[61] cyclic polymers,[62] cross-linked polymers,[63] interpenetrating polymeric

networks[64] and other relatively exotic architectures[65] have all been prepared using one (or more) of the listed living polymerization techniques. After the precursor is obtained, subsequent reactions are performed to obtain the desired architecture.

Thesis Research

The research presented herein describes recent contributions to the art of precisely controlling polymer structure. Chapters 2 and 3 focus on the development and evaluation of catalysts that will be used as synthetic tools throughout the rest of the thesis. Specifically, Chapter 2 evaluates the activity and scope of the newest generation of Ru based complexes, coordinated with N-heterocyclic carbene ligands, in various ROMP reactions. Chapter 3 provides a simple method for improving the initiation characteristics and performance of the early generation bisphosphine Ru catalysts. Chapters 4 and 5 describe the synthesis of telechelic polybutadienes and polynorbornes, respectively, using the catalysts developed in the first two chapters. Chapter 6 describes the synthesis of telechelic polymers whose end-groups can be used to initiate the ATRP of various vinyl monomers. This approach provides a new synthetic route to triblock copolymers composed of mechanistically incompatible polymer segements. Chapter 7 describes the synthesis of a new Ru based catalyst that can simultaneously mediate both ROMP and ATRP. The catalyst was designed as a "two-headed" initiator to grow two different polymers in opposite directions. This approach provides a highly efficient route to mechanistically incompatible block polymers. Chapter 8 describes the design of cyclic Ru catalysts and their application to the synthesis of cyclic polymers. Chapter 9 is an extension of Chapter 8 and focuses on the importance of excluding linear

contaminants during the polymerization, which were found lead to the formation of linear polymer during the ROMP.

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Chapter 2

Highly Efficient Ring-Opening Metathesis Polymerization Using Ruthenium Catalysts Containing N-Heterocyclic Carbene Ligands[†]

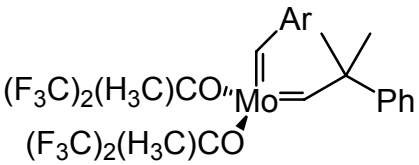
Abstract

A series of Ru-based ring-opening metathesis polymerization (ROMP) initiators containing various N-heterocyclic carbene ligands were synthesized and their performance in a variety of ROMPs was evaluated. They were found to polymerize cyclic olefins with a low strain energy, such as cyclooctadiene and cyclooctene, at rates higher than most other Ru and Mo based systems. The catalysts also display a high degree of functional group tolerance as functionalized cyclic olefins with pendant alcohol and ester groups were polymerized. Furthermore, several sterically hindered monomers, including 1,5-dimethyl-1,5-cyclooctadiene which was previously unreactive in ROMP, were polymerized using these new initiators. Finally, their high activity enabled the use of extremely low catalyst loadings (initial monomer/catalyst ratios as high as 100,000 were used) which makes the complexes highly efficient and an ideal choice when selecting catalysts for ROMP reactions.

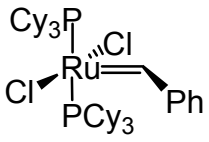
Introduction

Ring-opening metathesis polymerization (ROMP) has become an effective tool for the preparation of a wide variety of macromolecular architectures.[1] To date, the most widely used catalysts for ROMP and other metathesis reactions are the well-defined complexes based on molybdenum[2] (**1**) and ruthenium[3] (**2**). The former complex displays much higher activity than the latter, thus permitting polymerization of many sterically hindered or electronically deactivated cyclic olefins.[1a,2] However, the latter catalyst is stable under ambient conditions and tolerates a much larger range of protic and polar functional groups including alcohols, acids, and aldehydes.[1a,4]

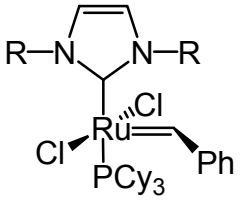
Replacement of one of the phosphine ligands with a more electron donating N-heterocyclic carbene ligand produced ruthenium complexes **3a-b** which displayed dramatically improved metathesis activity, thermal stability and inertness towards oxygen and moisture when compared to **2**.[5] Recently, complexes[6,7] **4a-c** have been prepared which utilize N-heterocyclic carbene ligands with saturated backbones. These complexes display catalytic activity in ring-closing metathesis[6-8] (RCM) and cross-metathesis[7,9] (CM) that not only in many cases exceed **3a-b** but also begin to rival molybdenum complex **1** *while maintaining the functional group compatibility of 2*. Herein, we report that complexes **3a-b** and **4a-c** are *more active* than **1** in ROMP and demonstrate their utility in the synthesis of a variety of polymeric structures.



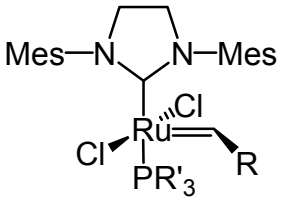
1: Ar=C_6H_3-2,6-(*i*Pr)



2



3a: R=*i*Pr or Cy
3b: R=mesityl (Mes)



4a: R=Ph, R'=Cy
4b: R=CHC$(CH_3)_2$, R'=Cy
4c: R=CHC$(CH_3)_2$, R'=Cp

Scheme 1. Various initiators used in ring-opening metathesis polymerization.

Results and Discussion

An effective method for comparing relative activities between various catalysts is through monitoring the ROMP of a low-strain cyclic olefin such as *cis*,*cis*-cycloocta-1,5-diene (COD).[5c-d,10,11] The ROMP of COD was initiated with **1**, **3b**, and **4a-c** and the percent monomer converted to polymer was followed over time using ^{1}H NMR spectroscopy (Figure 1).[12] The polymerization rate of COD when initiated with **4a** was found to be significantly higher than when initated with the molybdenum complex **1** at 20 ºC. In addition to activity trends observed in RCM and CM,[6-9] complex **4a** which contains a saturated N-heterocyclic carbene ligand also displayed increased activity in ROMP relative to its unsaturated analog (**3b**). When elevated temperatures (55 ºC) were employed, complexes **3b**, **4b**, and **4c** also exhibited activities greater than **1** (Figure 2). Interestingly, the activity of the various ruthenium complexes appears related to both the

phosphine ligands and alkylidene moiety substitution. For example, the discrepancy in polymerization rates between **4a** and **4b** may be related to the initiation rate,[13] since the propagating species resulting from both catalysts are identical. Thus, the bulkier benzylidene ligand may facilitate phosphine dissociation to a greater extent than the dimethylvinyl carbene ligand, thereby enhancing initiation. In addition, the bulkier tricyclohexyl phosphine (PCy_3) in **4b** may dissociate to a higher degree than the tricyclopentyl phosphine (PCp_3) in **4c**,[14] thereby providing a relatively higher concentration of the highly active (phosphine dissociated) species.

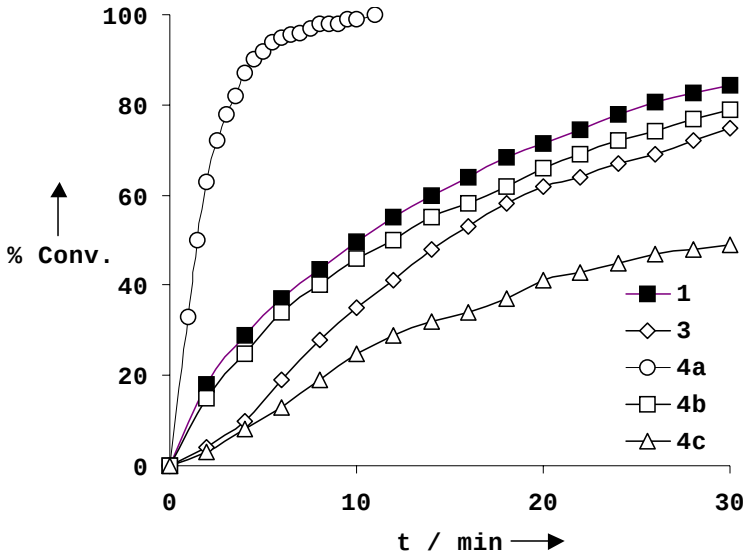


Figure 1. ROMP of COD using catalysts shown in Scheme 1. Conditions: 20 ºC, monomer/catalyst=300, [catalyst]=0.5 mM, CD_2Cl_2 as solvent. Conversion determined by ^1H NMR spectroscopy.

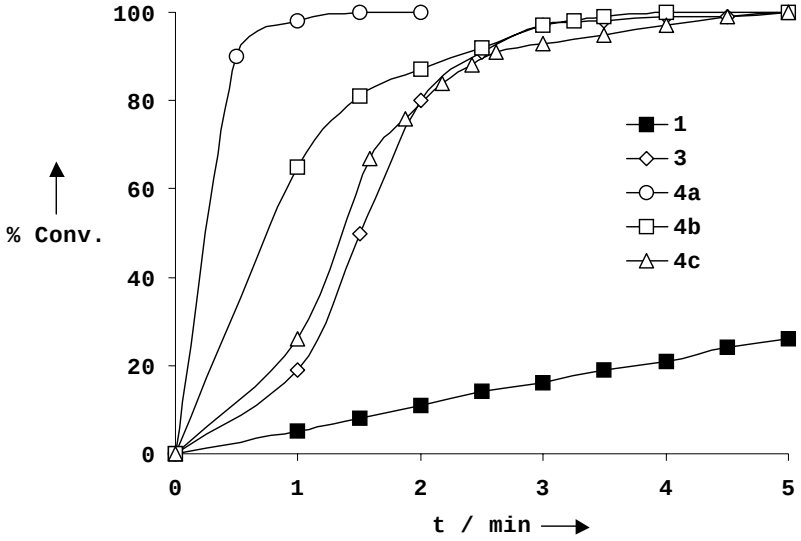
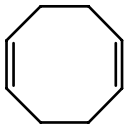
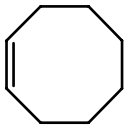
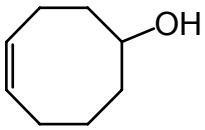
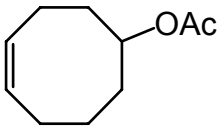
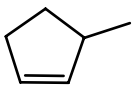


Figure 2. ROMP of COD using catalysts shown in Scheme 1. Conditions: 55 ºC, monomer/catalyst=300, [catalyst]=0.5 mM, CD_2Cl_2 as solvent. Conversion determined by ^{1}H NMR spectroscopy.

As shown in Table 1, catalysts **4a-c** polymerized a variety of low strain cyclic olefins with extremely low catalyst loadings (up to monomer/catalyst=100000).[15] In agreement with the results obtained above, elevated temperatures (55 ºC) generally increased the yields of polymer while reducing reaction times. Monomers such as 5-hydroxy- or 5-acetoxycyclooctene were also effeciently polymerized, providing access to polymers with a high degree of backbone functionality.[16,17] In general, ^{1}H NMR spectroscopy indicated a predominately (75-95%) *trans*-olefin microstructure in these polymers. As expected for an equilibrium controlled polymerization where chain transfer occurs, longer polymerization times result in higher *trans*-olefin values.[1a]

Table 1. ROMP of various low strain cyclic olefins.[a]

Monomer	M/C[b]	T (ºC)	t (h)	% Y	M_n[c]	PDI[c]	% Trans[d]
	100000	55	0.5	85	112400	2.3	70
	10000	25	24	85	92900	2.5	85
	25000[e]	55	24	89	10700	2.1	90
	100000	55	<0.1	[g]	[g]	[g]	[h]
	10000	25	0.5	[g]	[g]	[g]	[h]
	25000[f]	55	24	75	2200	1.6	85
	100000	55	<0.1	[g]	[g]	[g]	[h]
	10000	25	0.5	[g]	[g]	[g]	[h]
	25000[f]	55	24	85	2600	2.3	85
	10000	55	<0.1	50	103900	2.8	85
	1000	25	1	60	79300	3.2	90
	1000	25	24	50	23000	2.5	50
	1000	25	24 h	52	9000	2.5	90

[a] Bulk polymerizations using catalyst **4c**. Catalyst **4a** gives similar results. [b] Initial monomer/catalyst ratio. [c] Determined by CH_2Cl_2 or THF GPC and results are reported relative to polystyrene standards. [d] Percent *trans* olefin in the polymer backbone, as

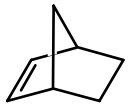
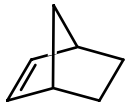
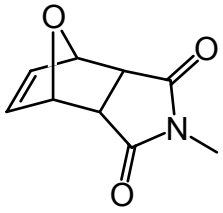
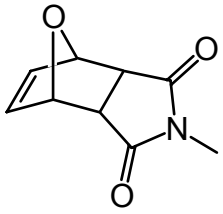
determined by ^{1}H and ^{13}C NMR analysis. [e] 1,4-diacetoxy-cis-2-butene was included as CTA. Monomer/CTA = 80. [f] Monomer/CTA = 10. $[Monomer]_0$ = 4.5 M in $C_2H_4Cl_2$. [g] Polymer was insoluble. [h] Not determined.

Close examination of Table 1 reveals that these highly active ruthenium systems do not form well-defined polymeric structures.[1a] The PDIs of the resulting polymers are relatively high and strongly suggest that significant chain transfer occurred during the polymerization. The percent *trans* olefin in the polymer backbone gradually increased with time which suggests that secondary metathesis isomerizations are also occurring. In addition, monitoring the ROMP of COD (50 equivalents) using catalyst **4a** *via* ^{1}H NMR spectroscopy (CD_2Cl_2, 25 ºC) indicated that less than 5% of the catalyst initiated before the ROMP was complete (<1 min). After 15 min at 55 ºC, complete conversion of unreacted initiator to propagating species through chain transfer was observed. The slow initiation rate explains the relatively high experimental molecular weights when compared to their theoretical values (based on initial monomer/catalyst ratios).

However, as shown in Table 1, the molecular weights were easily regulated through the inclusion of acyclic olefins which effectively act as chain transfer agents (CTAs).[1] This technique is extremely useful when poorly soluble polymers are obtained by polymerizing monomers such as cyclooctene in bulk. Including functionalized CTAs during the ROMP of cyclic olefins has been shown to afford end-functionalized (telechelic) polymers[18] which are useful as intermediates in the syntheses of triblock copolymers and in the formation of polymeric networks.[19] Due to its high functional group tolerance, complex **2** has been the catalyst of choice when preparing telechelic polymers using this approach; however, only low strain monomers have been used.[1a,18]

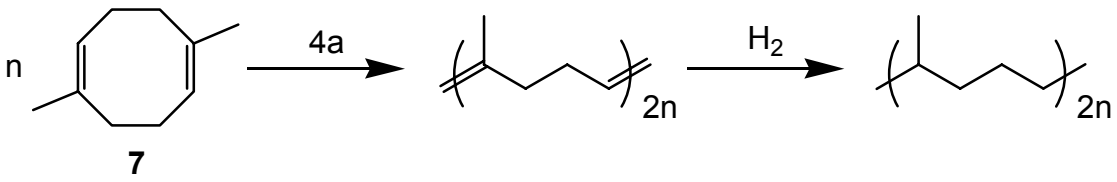
As summarized in Table 2, when 1,4-diacetoxy-2-butene was included as a CTA during the **4a** catalyzed ROMP of highly strained monomers such as norbornene **5** and N-methyl-7-oxanorbornenedicarbimide[20] **6**, acetoxy end-functionalized polymer was obtained. Excellent agreement between theoretical and experimental molecular weights (based on the initial monomer/CTA ratio) were observed when norbornene was employed as the monomer and led to the formation of bis(acetoxy) end-functionalized polymer. However, in the case of the oxanorbornene derivative **6**, the CTA did not completely incorporate and produced polymer with a higher-than-expected molecular weight. The monomer is a cyclic ether that may coordinate to the catalyst and sufficiently attenuate its ability to transfer polymer chains. Nevertheless, the molecular weight could still be regulated and an acetoxy end-group was observed on the polymer chains. These results are particularly notable since end-functionalized polymers composed of highly strained monomers are relatively difficult to obtain using other methods. For example, a metathesis degradation approach using tungsten-based metathesis catalysts has been used to prepare telechelic polyoxanorbornenes and polynorbornenes.[21] However, the catalyst's tolerable range of functional groups limits the choice of CTAs. The "pulsed addition" approach has also been employed using catalysts **1** and **2**, but requires carefully timed additions of monomer and/or CTA, thereby reducing the ease of performing these polymerizations.[22]

Table 2. Synthesis of acetoxy end-functionalized polymers composed of highly strained monomers.[a]

Monomer	M/CTA[b]	% Yield	X_n (NMR)[c]	M_n (GPC)[d]	PDI[d]
 **5**	5	95	6	800	2.0
 **5**	20	97	20	2100	2.0
 **6**	1	90	[e]	4200	2.0
 **6**	10	98	[e]	12500	1.9

[a] General polymerization conditions: T = 55 ºC; 12 h; $C_2H_4Cl_2$ as solvent; [**4a**]$_0$ = 10-30 mM; [monomer] = 3-5 M; nitrogen atmosphere. CTA = 1,4-bis(acetoxy)-*cis*-2-butene [b] Initial monomer/CTA ratio. [c] Average number of monomer units per polymer chain. Determined by end-group analysis using ^{1}H NMR spectroscopy and assumes the number of functional groups per polymer chain is exactly two. [d] Determined by CH_2Cl_2 GPC and results are reported relative to polystyrene standards. [e] Not determined.

As shown in Scheme 2, **4a** initiated the ROMP of 1,5-dimethyl-1,5-cyclooctadiene (**7**),[23] a sterically hindered, tri-substituted cyclic olefin, affording poly(isoprene) (M_n=10000, PDI=2.3) in 90% yield (monomer/catalyst=1000, 55 ºC, 24 h). Subsequent hydrogenation using *p*-toluenesulfonhydrazide as the hydrogen source afforded an ethylene-propylene copolymer (as determined by NMR analysis) in quantitative yield.[24] Previously, a six step synthesis was necessary to obtain a similar copolymer *via* a metathetical route.[25] To the best of our knowledge, this is the first example of the ROMP of this trisubstituted monomer.



Scheme 2. Synthesis of an ethylene-propylene copolymer via ROMP of ,5-dimethyl-1,5-cyclooctadiene (**7**) followed by hydrogenation.

Conclusion

We have demonstrated that complexes **4a-c** are high-performance ROMP catalysts that can be used to synthesize a variety of polymeric materials including functionalized, telechelic, and trisubstituted polymers. It is important to note that these catalysts are late transition metal complexes and demonstrating high functional group tolerance. Through careful tuning of the ligand environment and reaction conditions, these catalysts display metathetical activity that exceeds both previous ruthenium based catalysts and early transition metal catalysts such as the Mo complex **1**.

References and Notes

† Portions of this chapter have been previously reported, see: Bielawski, C. W.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2000**, *39,* 2903-2906.

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(13) A similar observation is obtained when comparing the ROMP activity of **2** (~300 equiv COD/hr) and its dimethylvinyl carbene derivative (~200 equiv COD/hr, catalyst structure not shown).

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(23) The 1,5-dimethyl-1,5-cyclooctadiene (**6**) employed in this study contained 1,6-dimethyl-1,5-cyclooctadiene (20%) as an inseparable mixture.

(24) The ethylene-propylene copolymer obtained was not "perfectly" alternating because of the impurity in 1,5-dimethyl-1,5-cyclooctadiene (**6**).[25] We believe that if pure **6** was polymerized, the poly(isoprene) obtained would have perfectly alternating head to tail microstructure since trisubstituted alkylidenes have not been observed to form. Thus, a perfectly alternating ethylene-propylene would be obtained after hydrogenation.

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Chapter 3

Increasing the Initiation Efficiency of Ruthenium-Based Ring-Opening Metathesis (ROMP) Initiators: The Effect of Excess Phosphine[†]

Abstract

Recent mechanistic studies of Ru based olefin metathesis catalysts (i.e., catalysts of the type $(PCy_3)_2Cl_2Ru=CHPh$) indicate that the phosphine ligands are not only labile but that they exhange rates that are higher than olefin metathesis. Thus, the addition of excess phosphine during an olefin metathesis reaction should slow the catalyst activity down due to competitive ligand coordination and aid in promoting catalyst initiation characteristics. Inclusion of relatively labile phosphines (e.g., PPh_3) in $(PCy_3)_2Cl_2Ru=CHPh$ initiated ring-opening metathesis polymerizations were found to not only increase the initiation efficiency of the complexes but also reduced polymer polydispersity. A variety of polymers with very narrow polydispersity indices (as low as 1.04) were synthesized using this method.

Introduction

Ring-opening metathesis polymerization (ROMP) has evolved into a valuable tool for the polymer chemist. The polymerization is generally mild, well controlled, and a large pool of readily available cyclic olefins (monomers) can be polymerized to nearly any size or shape.[1] Employing the Ru based initiator[2] **1** (or its more active derivative[3] **2**) permits incorporation of high degrees of functionality and affords polymers with novel mechanical, electronic, and more recently biological properties.[4] However, the polydispersities of the polymers obtained from initiator **1** are generally broad (polydispersity indices between 1.3 and 1.5). The reason stems from an unfavorable rate of initiation (k_i) relative to propagation (k_p) as well as considerable secondary metathesis (intra- and intermolecular chain-transfer). This creates difficulties when attempting to accurately predict polymer molecular weight *a priori* or when preparing well-defined block copolymers (where complete initiation is necessary).

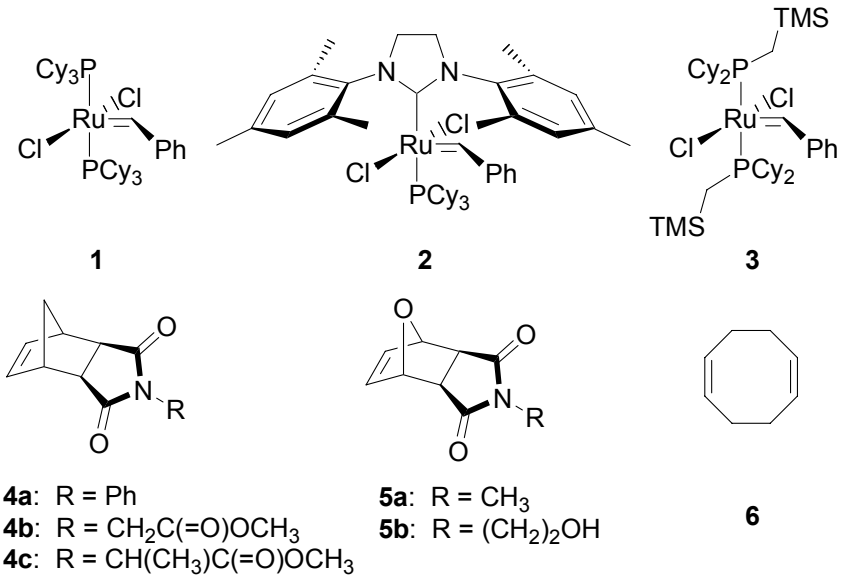


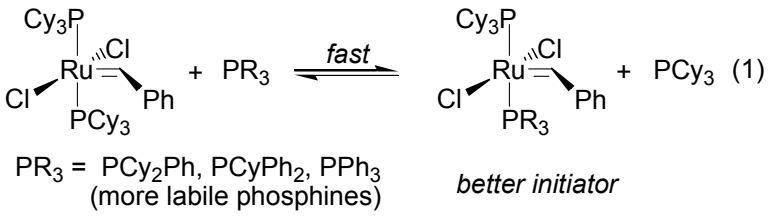
Figure 1. Various Ru based ROMP initiators and monomers.

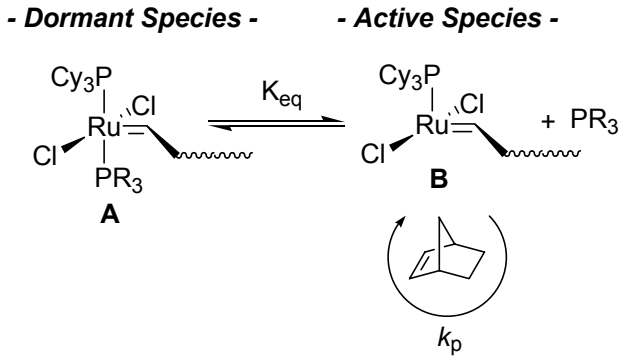
A recent disclosure from Gibson and co-workers revealed that the initiation efficiency of **1** was enhanced when the PCy_3 ligands were substituted with $Cy_2PCH_2Si(CH_3)_3$.[5] When the resulting complex (**3**) was used to initiate the ROMP of norbornene derivatives (similar to **4**), the k_i/k_p was found to be 4.35 (up from 0.06 when initiated with **1**) and the resulting polymers were nearly monodispersed (PDIs ~ 1.1). The enhanced initiation was attributed to a combination of the lower basicity and smaller size of $Cy_2PCH_2Si(CH_3)_3$ (relative to PCy_3) which respectively helped facilitate phosphine dissociation (a key step in Ru based ROMP, see below) [6] and increase monomer accessibility.

Results and Discussion

Herein, we claim that similar results can be obtained without synthesizing new complexes or phosphines. Recent studies in our group have determined that the rate of phosphine exchange is much faster (~10^4) than the rate of reaction with olefin in $X_2(PR_3)_2Ru{=}CHR'$ type catalysts.[6] We have also previously noted that complexes with more labile phosphines (e.g., PPh_3) exhibit high rates of initiation.[2] These concepts were combined to enhance the initiation efficiency of complex **1** by simply including additional phosphine (specifically phosphines more labile than PCy_3) during the polymerization. Since phosphine exchange is relatively fast, formation of a Ru complex with a relatively labile phosphine precedes initiation (Eq. 1), and thus exhibits better initiation characteristics (higher k_i). In addition, as shown in Scheme 1, the added phosphine effectively competes with monomer for the Ru center and thus helps attenuate the polymerization rate (lower k_p). This concept is similar to controlled free radical

polymerizations where various transition metals (e.g., Cu or Ru) or nitroxides (e.g., TEMPO) are added to minimize the concentration of propagating radicals.[7]





Scheme 1. The role of phosphine exchange in Ru mediated ROMP.

The rates of initiation (k_i) and propagation (k_p) were measured in CD_2Cl_2 at 20 ºC using ^{1}H NMR spectroscopy.[8] The polymerizations were initiated with Ru complex **1** and the *exo*-norbornene phenylimide **4a** was chosen as the monomer. To ascertain the inherent initiation efficiency of Ru complex **1** under these conditions, k_i and k_p were initially measured in the absence of any additional phosphine. The k_i/k_p ratio was found to be 0.73, which is significantly higher than the value (0.06) reported by Gibson for the related monomer **4b**.[5] Although **4b** contains a polar ester functional group that may coordinate (inter- or intramolecularly) to the Ru center, such effects were negligible as a

similar k_i/k_p ratio (0.96) was found for this monomer. Thus, solvent ($CDCl_3$ *vs.* CD_2Cl_2) appears to be the source of the discrepant k_i/k_p ratios since both studies were performed under otherwise similar conditions (M_0/I_0, temperature, etc).[9]

As shown in Table 1, inclusion of free phosphines with varying steric and electronic properties (PCy_3, PCy_2Ph, $PCyPh_2$, and PPh_3) during the ROMP had remarkable effects on the k_i/k_p ratio. In general, the k_i/k_p improved as the size and basicity of the phosphine decreased. Additional enhancement was observed by increasing the quantity of added phosphine. However, the best results were obtained with PPh_3 where as little as one equivalent (relative to initiator) afforded a k_i/k_p of 2.43 (which subsequently increased to 10.2 when five equivalents were added).

The enhancement appears to stem from a combination of steric and electronic effects. The propagating species contains a bulky polymer chain that may sterically hinder phosphine coordination and thus result in relatively high concentrations of the "active" (phosphine-dissociated) species (**B**) (Scheme 1). (Incidentally, this provides an explanation for the relatively high propagation rates commonly observed with **1**.) Thus, the use of relatively small phosphines may facilate coordination to this bulky species and subsequently shift the equilibrium towards the "dormant" (phosphine-associated) species (**A**). In addition, ^1H NMR spectroscopy confirmed that the lower limit of phosphine exchange ($\sim 10^2$ min^{-1} for all phosphines studied) was several orders of magnitude greater than the rate of propagation (see Table 1). Thus, when PCy_2Ph, $PCyPh_2$, or PPh_3 were employed, equilibrium between initiator **1** and an initiator containing a mixed ligand set, i.e., $(PR_3)(PCy_3)Cl_2Ru{=}CHPh$, was established prior to initiation. Therefore, the enhanced initiation may also be related to the greater ability of PCy_3 to labilize the

relatively less basic PCy_2Ph, $PCyPh_2$, or PPh_3, affording relatively increased rates of phosphine dissociation.

Table 1. The effect of added phosphine on k_i/k_p.[a]

Entry	PR_3	Eq[b]	k_i[c] ($x10^{-3}$ min^{-1})	k_p[d] ($x10^{-3}$ min^{-1})	k_i/k_p
1	(none)	--	204	278	0.73
2	PCy_3	1	27.6	27.1	1.02
3	PCy_3	5	8.37	8.24	1.02
4	PCy_2Ph	1	47.7	36.9	1.29
5	PCy_2Ph	5	17.3	8.83	1.96
6	$PCyPh_2$	1	22.2	11.0	2.02
7	$PCyPh_2$	5	7.10	1.41	5.04
8	PPh_3	1	44.3	18.2	2.43
9	PPh_3	5	20.5	2.02	10.2

[a] Polymerizations were performed in CD_2Cl_2 at 20 °C and monitored using ^1H NMR spectroscopy. $[\mathbf{1}]_0$ = 10 mM. $[\mathbf{4a}]_0/[\mathbf{1}]_0$ = 25. [b] Molar equivalents of added phosphine to initiator. [c] Initiation rate constant. [d] Propagation rate constant.

The exchange and initiation processes were observed using ^1H NMR spectroscopy. As shown in Figure 2, in the presence of five equivalents of PPh_3, the mixed ligand initiator, $(PCy_3)(PPh_3)Cl_2Ru{=}CHPh$, was observed (20.2 ppm) at low monomer conversion (< 5%) and rapidly converted to growing polymer chains. In addition, signals attributed to the propagating species $(PCy_3)Cl_2Ru{=}CHR$ (18.8 ppm) and

$(PPh_3)Cl_2Ru$=CHR (17.8 ppm) (R = polymer) maintained a relatively equal intensity throughout the polymerization (which we believe is a consequence of the rapid phosphine exchange process). As expected, only small amounts (< 10%) of the propagating species $(PCy_3)_2Cl_2Ru$=CHR (19.5 ppm) was observed.

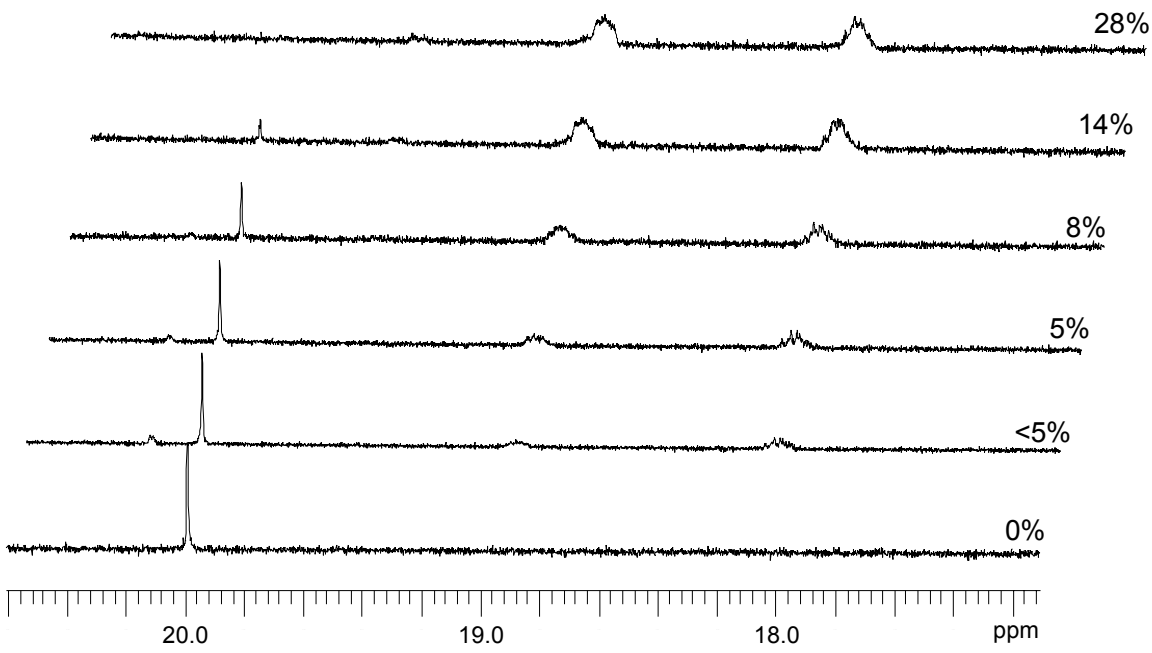


Figure 2. Stacked ^{1}H NMR spectra of the [Ru]=CHR region showing the initiation process of **1** in the presence of PPh_3. See Table 1, Entry 9 for conditions. Monomer conversion is indicated on the right.

As shown in Table 2, the inclusion of phosphine during ROMP had remarkable effects on the molecular weights and polydispersities of the resulting polymers.[8] In accord with increased initiation rates, the resulting polymers were in better agreement with their predicted values and became nearly monodispersed (PDIs as low as 1.04) as increased quantities of smaller phosphines were used. This was observed over various M/C loadings and concentrations. The presence of excess phosphine did not compromise

the functional group integrity of **1** as the polymers from highly functionalized monomers, such as the amino esters **4b** and **4c** and a monomer containing a free alcohol (**5b**), exhibited very low polydispersity. Similar results were obtained when a monomer with relatively low ring strain, 1,5-cyclooctadiene (COD) (**6**), was employed.

Table 2. ROMP of monomers **4-6** in the presence of various phosphines.[a]

Mon.	M_0/I_0	PR_3	Eq[b]	% Y[c]	$M_{n,\ calcd}$[d]	$M_{n,\ gpc}$[e]	PDI[e]
4a	50	(none)	--	95	12000	16000	1.25
4a	50	PCy_3	1	90	12000	14900	1.14
4a	50	PCy_2Ph	1	90	12000	14600	1.13
4a	50	$PCyPh_2$	1	92	12000	12900	1.10
4a	50	PPh_3	5	85	12000	11600	1.07
4a	25	PPh_3	1	95	6000	5400	1.08
4a	100	PPh_3	1	90	24000	22300	1.06
4a	250	PPh_3	1	85	59800	70200	1.04
4c	100	PPh_3	2	96	29500	32000	1.18
5a	100	PPh_3	2	97	28000	31200	1.13
5b	100	PPh_3	2	75	27300	26000	1.10
6	100	PPh_3	2	91	10800	8000	1.19

[a] Polymerizations were performed in CH_2Cl_2 at 23 °C and were initiated with Ru complex **1**. $[\mathbf{1}]_0 = 10$ mM. [b] Molar equivalents of added phosphine to initiator. [c] Isolated yields after quenching the ROMP with excess ethyl vinyl ether and precipitation from methanol. [d] Calculated from the M_0/I_0. [e] M_n and PDI were determined by GPC and are reported relative to monodispersed polystyrene standards.

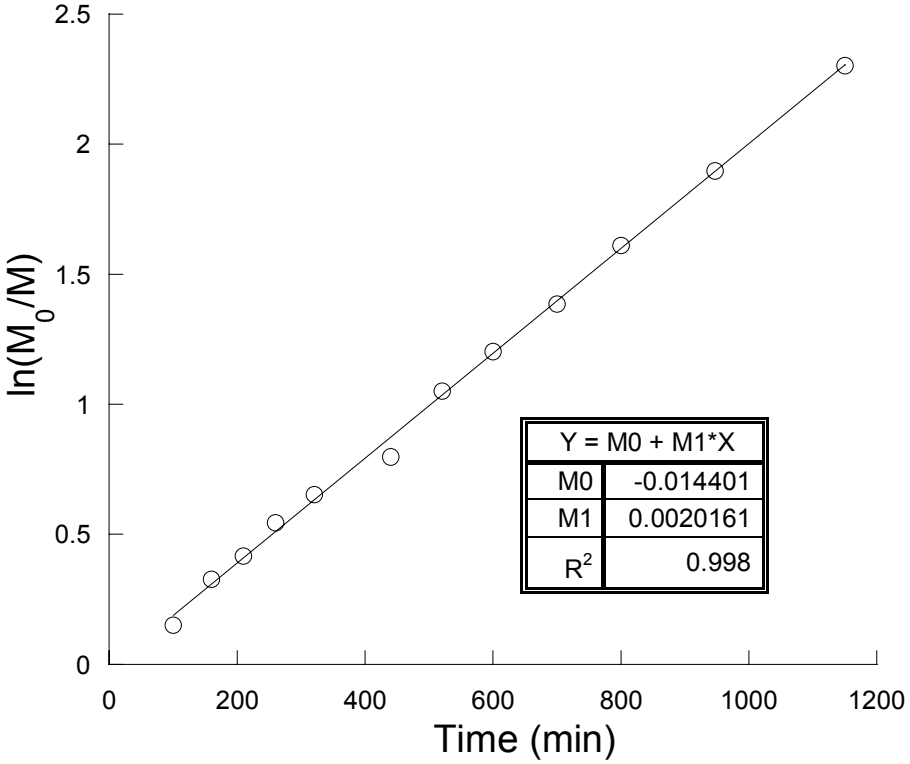
Conclusion

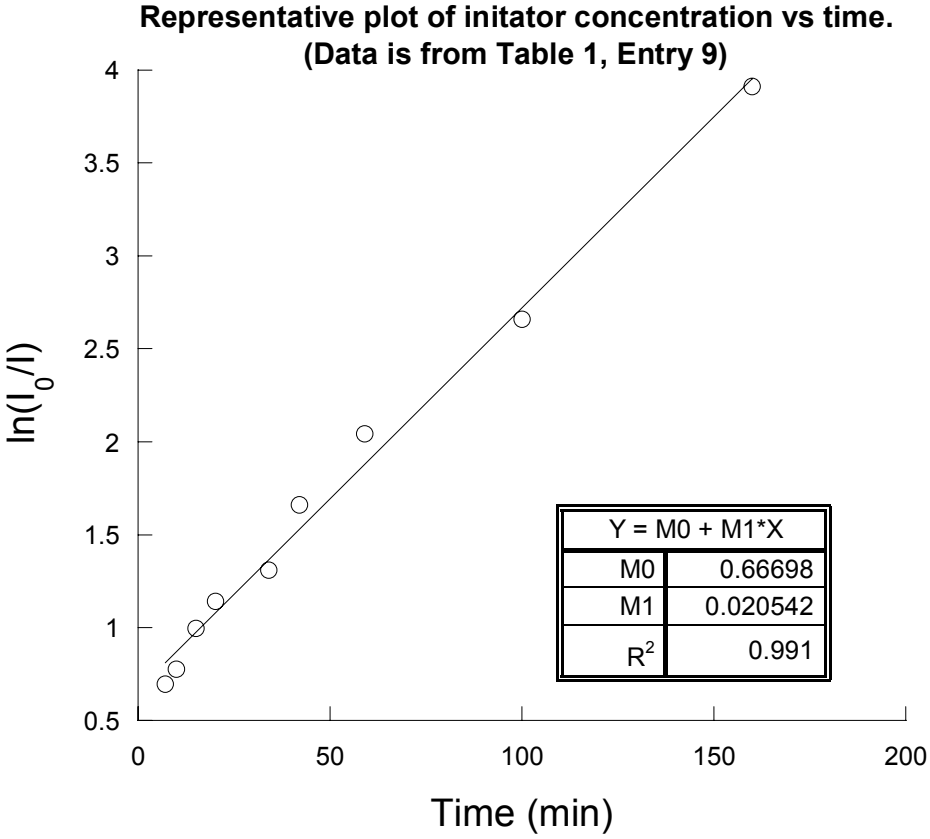
In summary, polymers with narrow polydispersities can be obtained from ROMP initiator **1** when commercially available phosphines are included. Similar to controlled radical polymerizations, we believe the enhanced control is related to a fast, dynamic equilibrium that exists between dormant and active species and is mediated by the type and quantity of phosphine employed.

Experimental Section

Determination of Initiation and Propagation Rates. In a nitrogen filled drybox, monomer **4a** (150 μmol, 25 equiv), an appropriate amount (6 μmol or 30 μmol) of desired phosphine (PCy_3, PCy_2Ph, or PPh_3), and ferrocene (3 mg, internal standard) were weighed into a NMR tube and dissolved in CD_2Cl_2 (0.5 mL). The resulting mixture was then treated with a CD_2Cl_2 solution of Ru initiator **1** (0.2 mL, 6 μmol, 1 equiv) and a ^1H NMR routine immediately commenced. The initiation rate constants (k_i) were determined by integrating the Ru=CH resonances of the initiating and propagating species. The propagating rate constants (k_p) were determining by monitoring the conversion of monomer to polymer vs. the internal standard. Representative plots are shown below. Additional results are given in Table 1.

Representative plot of monomer concentration vs time.
(Data is from Table 1, Entry 9)





General Procedure for Preparative Scale Polymerizations. All polymerizations were setup in a nitrogen filled drybox. An appropriate amount of monomer (25 to 250 equivalents) and phosphine (1 to 5 equivalents) were added to a small vial and dissolved in ca. 2 mL of CH_2Cl_2. A CH_2Cl_2 solution of the initiator (0.1 mL, ca. 7 mg, 1 equiv) was then added directly to the rapidly stirring monomer solution. After an adequate amount of time (5 to 24 hours), excess ethyl vinyl ether was added to quench the polymerization. After stirring for an additional 1 h, the reaction mixture was added dropwise to an excess of rapidly stirring methanol (30 mL) which caused a white

powder to precipitate. The powder was collected by filtration and dried under dynamic high vacuum.

References and Notes

† Portions of this chapter have been previously reported, see: Bielawski, C. W.; Grubbs, R. H. *Macromolecules* **2001**, *34*, 8838.

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(8) See experimental section for further details.

(9) Depressed k_i/k_p ratios were observed in acid-contaminated $CDCl_3$.

Chapter 4

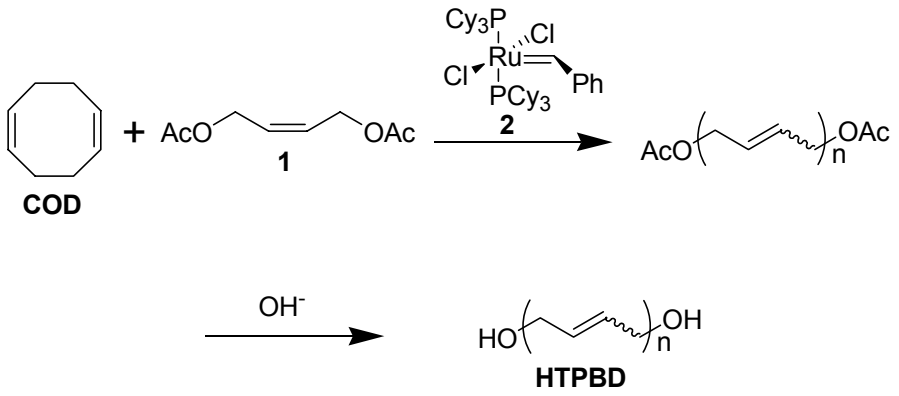
Highly Efficient Syntheses of Acetoxy and Hydroxy End-Functionalized Telechelic Polybutadienes Using Ruthenium Catalysts Coordinated with N-Heterocyclic Carbene Ligands[†]

Abstract

Bis(acetoxy) terminated telechelic polybutadienes (PBDs) with molecular weights controllable up to $3.0x10^4$ have been prepared *via* the ring-opening metathesis polymerization (ROMP) of cyclooctadiene (COD) when 1,4-bis(acetoxy)-2-butene was included as a chain transfer agent (CTA). The polymerizations were catalyzed by a highly active ruthenium catalyst 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene)(PCp_3)(Cl_2Ru=$CHCHC(CH_3)_2$ (Cp=cyclopentyl) (**6**) with monomer/catalyst ratios as high as $9.8x10^4$. Removal of the acetoxy groups with sodium hydroxide afforded hydroxy end-functionalized telechelic PBD (HTPBD). Examination of the telechelic PBDs revealed an exclusive 1,4-PBD microstructure with a predominately trans geometry (up to 90%). The high activity and stability of **6** permitted a one-step synthesis of HTPBD using the unprotected free alcohol, 2-butene-1,4-diol, as the CTA.

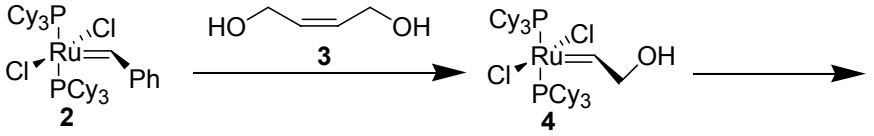
Introduction

Telechelic polymers, which contain two reactive functional groups situated at both termini of the polymeric chains, have been employed as key components in the synthesis of block copolymers and polymeric networks, in reaction injection molding applications, and as cross-linking agents to enhance thermal and mechanical properties of other materials.[1-3] Hydroxy terminated telechelic polybutadiene (HTPBD) is a particularly useful telechelic polymer and is of great importance in the polyurethane industry.[4] We previously reported the synthesis of HTPBD *via* the ring-opening metathesis polymerization (ROMP) of cyclooctadiene (COD) in the presence of *cis*-1,4-bis(acetoxy)-2-butene (**1**), catalyzed by ruthenium catalyst **2** (Scheme 1).[5,6] The acyclic olefin acts as a chain transfer agent (CTA) that not only aids in regulating molecular weight but also effectively transfers functionality (in this case the acetoxy groups) to the ends of the polymer chains.[7] Using this method, the average number of functional groups per polymer chain (F_n) is close to two, the molecular weights are controllable up to 10 kDa, and *only* 1,4-linkages are observed in the PBD backbone. In addition, this approach has been recently extended to the synthesis of amino- and carboxyl- terminated PBDs.[8] Other metathetical routes to HTPBDs have also been reported.[7-14] While radical or anionic polymerization methods are often employed, demanding conditions are usually necessary and varying amounts of 1,2-linkages are introduced into the polymer backbone.[3.4.15-17] This not only leads to F_n values that deviate greatly from two, but also limits the material's elastomeric potential.[3]



Scheme 1. Synthesis of hydroxy-end terminated telechelic polybutadienes via ROMP.

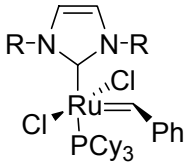
One drawback of our previously reported route to HTPBD is that it necessitates a post-polymerization deprotection step.[5] When the free alcohol, *cis*-2-butene-1,4-diol (**3**), was used directly, it was found that telechelic PBD obtained contained significant amounts of aldehyde end-groups.[5,18,19] We believe that either Ru species **4**, which forms from the cross-metathesis of catalyst **2** with **3**, decomposes over the timescale of the polymerization (Equation 1), or **2** simply decomposes in the presence of **3**. In either case, the decomposition product, which has been previously suggested to be a ruthenium hydride species, then catalyzes the isomerization of the allyl alcohol end-group to an aldehyde.[5,19,20]



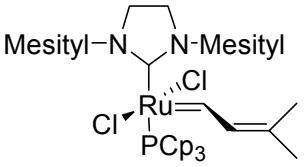
(1)

Recently, several new highly active ruthenium catalysts (**5** and **6**), which utilize N-heterocyclic carbene ligands, have been reported.[21-26] In particular, catalyst **6,** displays an unsurpassed level of activity and functional group tolerance in ring-closing metathesis

(RCM), cross-metathesis (CM), and ring-opening metathesis polymerization (ROMP) when compared to other ruthenium catalysts.[21-31] Herein, we report that the high activities of catalyst **6** have allowed for the preparation of acetoxy terminated PBDs, using **1** as the CTA, with extremely low catalyst loadings (up to a monomer/catalyst = 98000). In addition, as described below, these catalysts are stable in the presence of the free alcohol **3**. Thus, we report a *one-step* synthesis of HTPBD *via* the ROMP of COD using catalyst **6**, *in the presence of the free alcohol **3***.



5: R = iPr, cyclohexyl (Cy), or mesityl (2,4,6-trimethylphenyl)



6: Mesityl = 2,4,6-trimethylphenyl, Cp = cyclopentyl

Results and Discussion

Preparation of bis(acetoxy) terminated telechelic polybutadienes. Previously, while exploring the preparation of telechelic PBDs via the ROMP of COD in the presence of CTA **1** and catalyst **2**, we reported the maximum monomer/catalyst ratio that could be employed was 10000.[5,19] At lower catalyst loadings, **2** began to lose activity over the timescale of the polymerization and led to reduced yields of polymer and CTA incorporation. However, as shown in Table 1, when catalyst **6** was employed bis(acetoxy) terminated telechelic PBDs were prepared with monomer/catalyst ratios up to 9.8×10^4. We attribute the ability to use lower catalyst loadings to the increased stability and higher activity of catalyst **6** over **2**. Isolated yields of telechelic polymer ranged between 62 and 75%, and the microstructure of the PBD backbone was found to

contain predominately trans geometry. In all cases, ^{1}H NMR and ^{13}C NMR analysis supported an F_n near two. Molecular weights obtained by ^{1}H NMR analysis were in excellent agreement with their theoretical values (based on yield). Molecular weights obtained by GPC were higher than predicted and may be explained by the differences in hydrodynamic volume of PBD and the polystyrene standards used for calibration. In all cases the acetoxy groups were easily cleaved using a methanolic solution of sodium hydroxide to afford the corresponding HTPBDs.[5]

Such low monomer/catalyst loadings permitted the synthesis of much higher molecular weight telechelic PBDs. It is important to remember that non-functional end-groups (which cause deviations in F_n from two) come predominately from the catalyst (e.g., the dimethylvinyl carbene group on **6** or the benzylidene group on **2**).[7,19] Thus, to prepare a telechelic PBD with an F_n>1.99, a CTA/catalyst ratio of >200 must be employed.[19] Since MW~COD/CTA, the maximum MW is ~5500 for a catalyst with maximum COD/catalyst = $1.0x10^4$. As shown in Table 2, by varying the COD/CTA ratio and adjusting the COD/catalyst ratio, telechelic PBD with MWs controllable up to 30000 have been prepared when using **6**. A linear relationship between the COD/CTA and the MW of the isolated telechelic polymer was observed (Figure 1). Molecular weights determined by end-group analysis using ^{1}H NMR spectroscopy and gel permeation chromatography were in good agreement with their theoretical values.

Table 1. Synthesis of bis(acetoxy) telechelic PBD under a variety of conditions.[a]

Entry	M/C[b]	Temp (ºC)	Time (h)	Yield[c] (%)	MW[d], nmr	M_n[e], gpc	PDI[e]	Trans[f] (%)
1	10300	25	12	75	1300	2100	1.6	65
2	10300	25	24	72	1200	2000	1.5	70
3	10300	25	12	72	1300	1900	1.5	75
4	10300	25	24	72	1250	1600	1.5	85
5	10300	55	12	70	950	1500	1.4	90
6	10300	55	24	69	1050	1700	1.4	90
7	10300	55	12	71	950	1500	1.4	90
8	10300	55	24	68	1100	1700	1.4	90
9	26100	25	12	62	1650	2600	1.6	80
10	26100	25	24	69	1550	2400	1.6	75
11	26100	25	12	69	1600	2400	1.7	80
12	26100	25	24	69	1450	2100	1.6	60
13	26100	55	12	73	1050	1600	1.5	70
14	26100	55	24	68	1150	1800	1.4	70
15	26100	55	12	74	1150	1700	1.5	50
16	26100	55	24	68	1250	1900	1.4	50
17	49200	55	24	66	1100	1900	1.4	90
18	98300	55	24	74	1250	2000	1.4	70

[a] Bulk polymerization of COD using catalyst **6**. 1,4-bis(acetoxy)-2-butene was included as a CTA. COD/CTA=5 in all cases. Theoretical MW = 700 (at 100% conversion). [b]

Monomer (COD) to catalyst **6** ratio. [c] Isolated yield of polymer. [d] Molecular weight determined using end-group analysis (^{1}H NMR), assuming F_n=2.0. [e] Determined using GPC with THF as the eluent. Values reported relative to polystyrene standards. [f] Percent trans olefin in polymer backbone determined using ^{1}H NMR spectroscopy.

Table 2. Synthesis of telechelic PBDs with a variety of molecular weights.[a]

Entry	M/C[b]	COD/CTA[c]	MW[d], theo	MW[e], nmr	M_n[f], gpc	PDI[f]	Yield[g] (%)	Trans[h] (%)
1	26100	5	500	1150	1800	1.4	68	70
2	19800	10	1200	2150	2600	1.7	88	90
3	23000	15	1750	2650	3100	1.8	89	90
4	19600	20	2300	3250	3800	2.0	92	90
5	24500	60	6600	7900	7200	2.5	91	90
6	24500	80	8800	9300	10700	2.1	95	90
7	24500	100	10900	10200	15200	2.2	89	90
8	49000	200	21750	24500	30000	2.0	98	90

[a] Bulk polymerization of COD using catalyst **6**. 1,4-bis(acetoxy)-2-butene was included as a CTA. Reaction time=24 hours. Reaction temperature=55 ºC. [b] Monomer (COD) to catalyst **6** ratio. [d] Theoretical molecular weight = (% Yield)x(COD/CTA)x(MW of COD)+(MW of CTA). [e] Molecular weight determined using end-group analysis (^{1}H NMR), assuming F_n=2.0. [f] Determined using GPC with THF as the eluent. Values reported relative to polystyrene standards. [g] Isolated yield of polymer. [h] Percent trans olefin in polymer backbone determined using ^{1}H NMR spectroscopy.

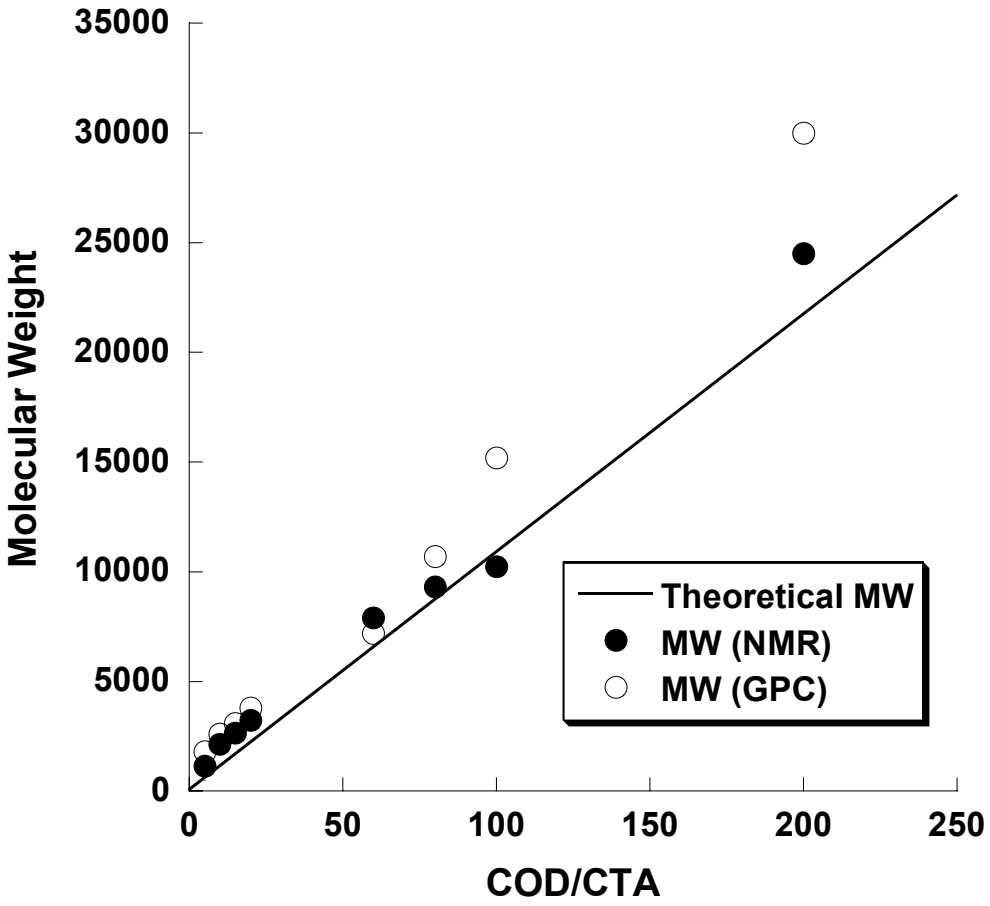
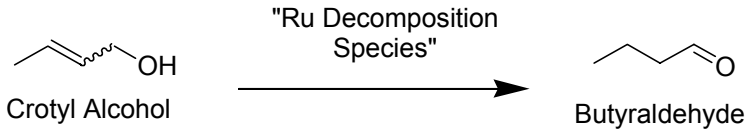


Figure 1. Dependence of PBD molecular weight on COD/CTA.

^{1}H NMR analysis of 2 and 6 in the presence of allylic alcohols. As previously mentioned, when HTPBD was prepared from the ROMP of COD in the presence of CTA **3**, aldehyde end-groups were observed indicating that the allylic functionality isomerized over the timescale of the polymerization. To help gain a better understanding of this drawback, the stability and metathetical activity of catalysts **2** and **6** in the presence of the

free diol **3** (~500 equivalents, 95+% cis) were examined by ^{1}H NMR spectroscopy in CD_2Cl_2 (25 ºC). Over 15 minutes, catalyst **2** isomerized the predominately cis olefin (95+%) to its trans isomer (70%), while **6** afforded 95% trans olefin over the same timescale. In addition, formation of [Ru]=$CHCH_2OH$ from cross-metathesis of the starting catalyst ([Ru]=CHPh **2** or [Ru]=$CHCHC(CH_3)_2$ **6**) with **3** was observed**.** No catalyst decomposition or aldehyde formation was observed in either case (**2** or **6**).

The lack of ruthenium hydride species or aldehyde substrates does not rule out the possibility that olefin migration (followed by tautomerization) occurs *after* the CTA has been incorporated into the polymer chains. Using crotyl alcohol as a model compound for the termini of the HTPBD, the isomerization of crotyl alcohol to butyraldehyde (Equation 2) in the presence of **2** and **6** was examined in a variety of solvents. In benzene-d_6 or CD_2Cl_2, alcohol isomerization was observed within minutes, regardless of which catalyst (**2** or **6**) was used (Equation 2). It has been previously proposed that the decomposition products contain ruthenium hydride species that can isomerize allylic alcohols to aldehydes.[5,20] While complete decomposition was observed for both catalysts (complete loss of carbene proton signals) within a few hours, no ruthenium hydride species were observed.



(2)

Surprisingly different results were obtained in THF-d_8. In the presence of ~250 equivalents of crotyl alcohol, extremely small amounts (<<1%) of butyraldehyde were observed after 24 hours, when either catalyst was employed. However, decomposition of **2** occurred rapidly (<2 hours) while **6** was more robust and appeared active for over 6 hours. Complete decomposition of **6** was observed after 21 hours. Representative ^{1}H NMR spectra summarizing these results are shown in Figure 2. In addition, no ruthenium hydride species (for either catalyst) were observed.

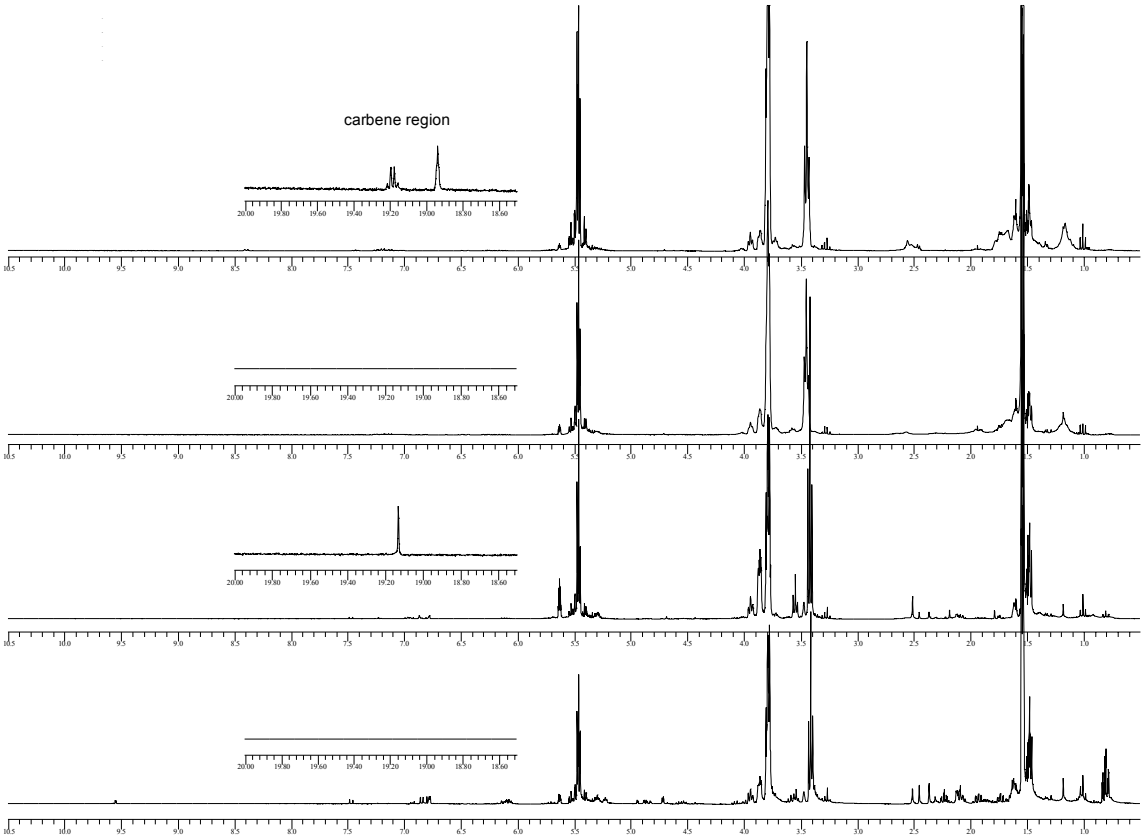
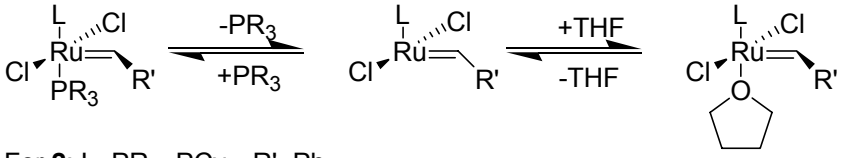


Figure 2. ^{1}H NMR spectra of crotyl alcohol in the presence of ruthenium catalysts **2** and **6**, solvent=THF-d_8. (a) Catalyst **2**, 20 minutes. (b) Catalyst **2**, 7 hours. (c) Catalyst **6**, 20 minutes. (d) Catalyst **6**, 21 hours.

It has been previously observed that well-defined ruthenium catalysts exhibit lower metathesis activity in THF relative to solvents such as benzene or CH_2Cl_2.[32,33] While THF may reduce activity, catalyst lifetimes seem to be extended. The mechanism of olefin metathesis using well-defined ruthenium catalysts appears to be predominately dissociative in nature.[34] In addition, catalyst decomposition also appears to be bimolecular and dependent on phosphine concentration (higher phosphine concentrations give longer catalyst lifetimes).[35] As shown in Equation 3, THF may coordinate to the ruthenium center after phosphine dissociation suppressing metathetical activity and attenuating bimolecular decomposition pathways.



(3)

For **2**: L=PR_3=PCy_3, R'=Ph
For **6**: L=N-heterocyclic carbene, PR_3=PCp_3, R'=$CHC(CH_3)_2$

Synthesis of hydroxy end-functionalized polybutadiene (HTPBD). In order to prepare HTPBD with F_n values that approach two using the free diol **3**, any alcohol isomerization to aldehyde functionality must be minimized. The stability of **6** in the presence of the free diol **3** and crotyl alcohol poised us to prepare HTPBD *via* the ROMP of COD using the unprotected diol **3** as the CTA. As shown in Table 3, when THF was used as solvent, HTPBD was obtained in a modest yield of 29%. THF solutions of low molecular weight PBD are difficult to precipitate in methanol, which may account for the low yield. However, ^1H and ^{13}C NMR supported an F_n near two and no aldehyde resonances were observed. In accordance with the model study of crotyl alcohol, when

non-coordinating solvents such as 1,2-dichloroethane or benzene were employed, isomerization of the allylic alcohol end-groups occurred as aldehyde end-groups were observed in the isolated polymer. Interestingly, when a mixture of benzene/THF (9/1 v/v) was employed, an increased yield (45%) of telechelic polymer was obtained without compromising any structural integrity of the allyl alcohol end-group. Attempts at preparing HTPBD under similar conditions using catalyst **2** afforded no polymer, which was in accord with the results obtained above that indicate **2** decomposes rapidly in the presence of the free diol **3**.

Table 3. One-step synthesis of HTPBD.[a]

Entry	Solvent System[b]	COD/ CTA[c]	Yield (%)[d]	MW, nmr[e]	M_n, gpc[f]	PDI[f]	Trans (%)[g]
1	A	15	29	2250	3900	1.7	40
2	B	10	36	1280[h]	2380	2.8	25
3	C	5	26	390[h]	1340	1.7	25
4	D	20	45	2400	3600	1.5	45

[a] ROMP of COD using catalyst **6**. Monomer/catalyst = 5000 in all entries. *Cis*-2-butene-1,4-diol (**3**) was included as a CTA. [b] A: THF. B: Benzene. C: CH_2Cl_2. D: Benzene/THF (9/1 v/v). [c] Monomer (COD) to CTA **3** ratio. [d] Isolated yield of polymer. [e] Molecular weight determined using end-group analysis (^{1}H NMR), assuming F_n=2.0. [f] Determined using GPC with THF as the eluent. Values reported relative to polystyrene standards. [g] Percent trans olefin in polymer backbone determined using ^{1}H NMR spectroscopy. [h] Aldehyde resonances were observed in the ^{1}H and ^{13}C NMR spectra.

Close examination of the HTPBD prepared *via* this one-step method revealed that relatively high amounts (~60%) of cis olefin were present in the PBD backbone. This was an unexpected result as generally high trans PBD is observed in the ROMP of COD with **1** and **6** (Tables 1 and 2) and stems from secondary metathesis reactions that form the more thermally stable olefin isomer.[7] In the absence of secondary metathesis reactions, the ROMP of COD should yield at least 50% cis olefin in the resulting PBD backbone. Figure 3 suggests that **6** may kinetically favor the formation of the cis isomer as at up to an 80% conversion of COD to PBD, a very high cis content (>75%) is observed in the polymer. Thus, our results (high amounts of cis olefin, low yields, and F_n values near two) may be explained by a relatively high rate of CTA incorporation countered with catalyst decomposition occurring over the timescale of the polymerization, limiting secondary metathesis reactions.

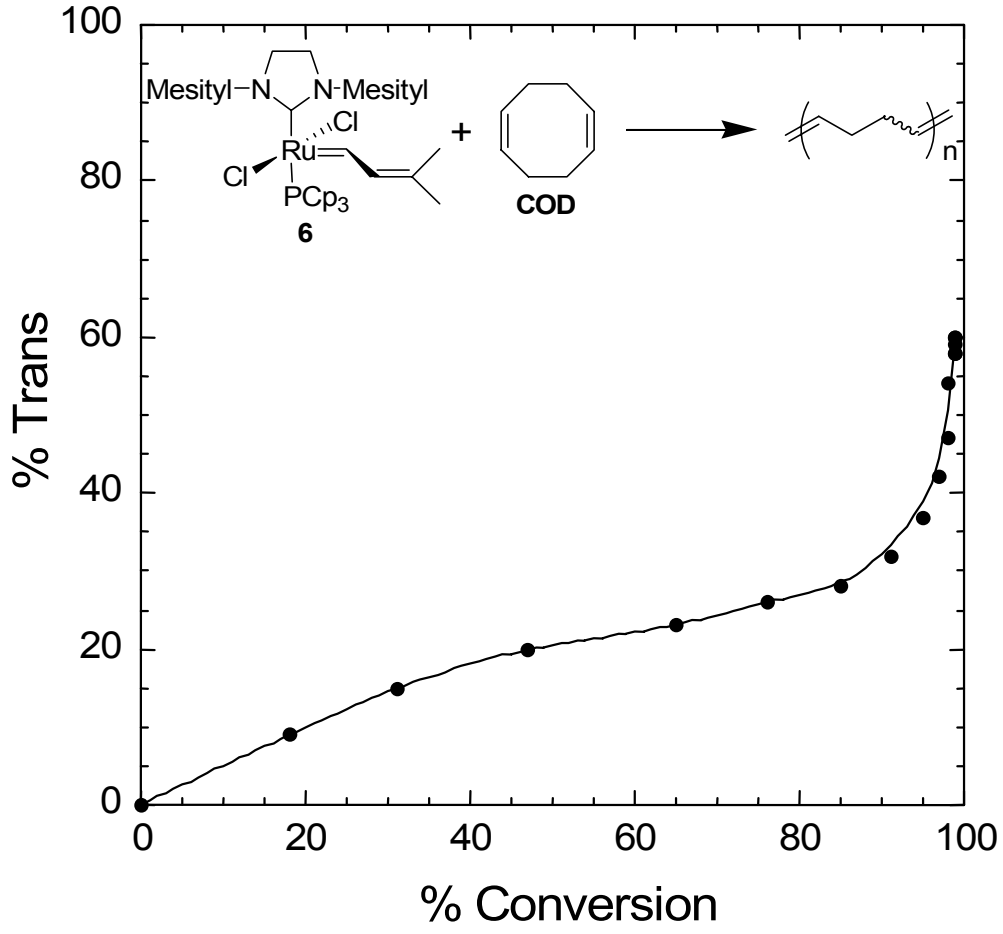


Figure 3. % Trans olefin in PBD backbone vs. % conversion of COD to polymer using catalyst **6**. Polymerization monitored using ^{1}H NMR spectroscopy. Solvent = CD_2Cl_2. Temp = 25 ºC. $[\mathbf{6}]_0$ = 0.5 mM. COD/**6** = 300.

Conclusion

Highly active ruthenium catalyst **6** has allowed the preparation of bis(acetoxy) terminated telechelic PBDs with molecular weights controllable up to 30000. The polymers were obtained *via* the ROMP of COD in the presence of an acetoxy

functionalized chain transfer agent (CTA) using monomer/catalyst ratios as high as 98000. The acetoxy groups were easily cleaved with methanolic solutions of sodium hydroxide to afford high yields of HTPBD. ^{1}H NMR spectroscopy studies in CD_2Cl_2 or benzene-d_6 using crotyl alcohol as a model for the HTPBD termini suggest that 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene)(PCp_3)(Cl_2Ru=CHCHC$(CH_3)_2$ (Cp=cyclopentyl) (**6**) and $(PCy_3)_2RuCl_2$(CHPh) (**2**) decompose in the presence of allylic alcohols and their decomposition products isomerize allylic alcohols to aldehydes. While no isomerization was observed in THF-d_8, the stability of **2** still appeared limited. In contrast, the stability and activity of **6** did not diminish and led to the successful one-step preparation of HTPBD using the unprotected 2-butene-1,4-diol (**3**) as the CTA.

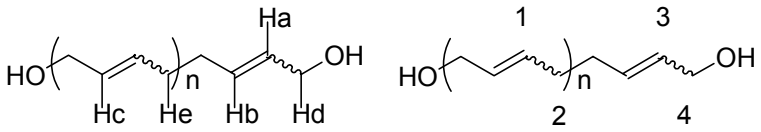
Experimental Section

Materials and characterization methods. Cyclooctadiene (redistilled, 99+%) and cis-2-butene-1,4-diol were purchased from Aldrich. Cis-1,4-bis(acetoxy)-2-butene was purchased from TCI America and distilled from CaH_2 prior to use. The cis-2-butene-1,4-diol was distilled prior to use. All monomers, chain transfer agents, and solvents were purged with argon prior to use. Catalysts **2** and **6** were prepared as previously reported.[6,25,26]

Gel permeation chromatography (GPC) measurements were carried out using an Alltech 510 liquid chromatography pump equipped with a Viscotek refractometer using HPLC grade THF as the eluent. The GPC columns (10 micron linear mixed bed, American Polymer Standards Corp.) were calibrated against monodispersed polystyrene standards (Shodex). All ^{1}H and ^{13}C NMR spectra were recorded on a GE NMR

spectrometer (300 MHz, ^{1}H; 75 MHz, ^{13}C), and all chemical shifts are given in ppm and were referenced to residual protio solvent. All spectra were obtained in the solvent indicated at 25 ºC unless otherwise noted.

Polymerization of cyclooctadiene using catalyst 6 with 3 as the chain-transfer agent. All polymerizations were setup using standard Schlenk techniques. A small flask equipped with a magnetic stirring bar was de-gassed, backfilled with argon, and then sealed with a rubber septum. A typical example is given as follows. Cyclooctadiene (4.7 g, 44 mmol), CTA **3** (190 mg, 2.2 mmol), THF (0.3 mL), and benzene (2.8 mL) were transferred into the flask *via* syringe. Inside a dry box under nitrogen atmosphere, a small vial was charged ruthenium catalyst **6** (6.9 mg, 8.8 μmol) and dissolved in a minimal amount of benzene. The catalyst solution was removed from the dry box, transferred into a syringe, and injected into the above reaction mixture, which was preheated to 55 ºC in an oil bath. After 24 hours, the reaction mixture was opened to air and poured into rapidly stirring acidic methanol (~0.1 M HCl). Non-solvent was decanted away from the precipitated polymer and the polymer was washed with fresh methanol several times. The polymer was then dried under dynamic high vacuum and characterized by ^{1}H NMR, ^{13}C NMR, and GPC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.6-5.7 (m, H_a, H_b, cis and trans), 5.42 (bs, H_c, trans), 5.38 (bs, H_c, cis), 4.18 (d, H_d, cis), 4.09 (d, H_d, trans), 2.09 (bs, H_c, cis), 2.04 (bs, H_c, trans). ^{13}C NMR (75 MHz, $CDCl_3$): 132.70 (C_3, tc), 130.30 (C_3, tt), 130.09 (C_1, tc), 129.99 (C_1, tt), 129.60 (C_1, cc), 129.42 (C_1, ct), 63.77 (C_4, t), 58.60 (C_4, c), 32.68 (C_2, t), 27.39 (C_2, c). GPC (THF, relative to polystyrene standards): M_n=3600, PDI=1.5.



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† Portions of this chapter have been previously reported, see: Bielawski, C. W.; Scherman, O. A.; Grubbs, R. H. *Polymer* **2001**, *42*, 4939.

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Chapter 5

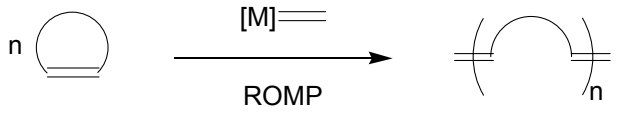
Synthesis of End-Functionalized Polynorbornenes *via* Ring-Opening Metathesis Polymerization (ROMP)[†]

Abstract

The synthesis of a variety of polynorbornenes (PNB)s bearing acetoxy, hydroxy, and vinyl end-groups was accomplished. PNBs with an acetoxy group at one terminus and a vinyl group at the other were prepared using norbornene, ruthenium-based olefin metathesis catalyst $(PCy_3)_2Cl_2Ru{=}CHPh$, and allyl acetate as a chain transfer agent (CTA). Employing a more active catalyst, (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)$(PCy_3)Cl_2Ru{=}CHPh$, and 1,4-diacetoxy-2-butene as the CTA afforded telechelic PNBs bearing acetoxy groups at both ends of the polymer chains. Molecular weights were controlled by varying the initial monomer/CTA ratio and were in agreement with their theoretical values. Using a similar procedure, acetoxy end-functionalized PNBs were also obtained by degradation of high molecular weight PNB. Removal of the acetoxy groups afforded the corresponding hydroxy terminated polymers with number averaged functionalities close to two. Mechanisms are proposed for the formation of the end-functionalized polymers. Correction factors for characterizing PNBs by gel-permeation chromatography (GPC) are also suggested.

Introduction

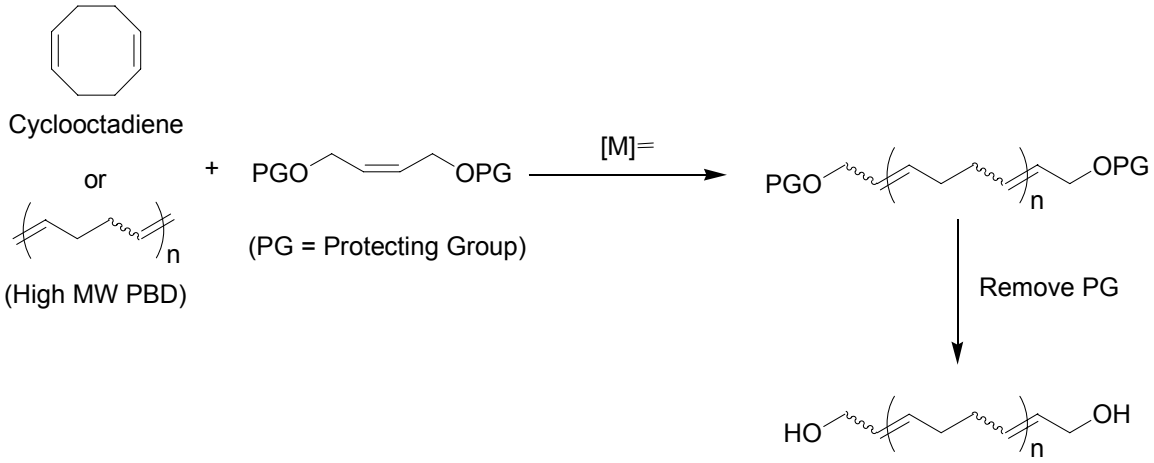
Telechelic polymers, or polymers with functional groups selectively positioned at the termini of any given chain, have been extensively employed in a variety of applications including intermediates in the synthesis of block copolymers, use as cross-linking agents, and in the formation of polymeric networks.[1-4] Since these applications are often dependent on structural, mechanical, and thermal properties of the telechelic polymer, expanding the range of selectable monomers remains a synthetic goal in polymer chemistry. While most telechelic polymers are prepared using either free radical or ionic polymerization, there exists several classes of polymers that cannot be synthesized using either of these methods.[1] Ring-opening metathesis polymerization[5] (ROMP) is an attractive alternative which provides polyalkenamers capable of functioning as elastomers with low glass transition temperatures (T_g) (Eq. 1).



(1)

Previously, several metathetical approaches towards hydroxy-terminated telechelic polybutadienes (HTPBD) have been reported.[6-12] HTPBD has been extensively used in the polyurethane industry as a cross-linking agent for products ranging from rocket propellant binders to sealants and adhesives.[13] The approach generally involves using an olefin metathesis catalyst, an appropriate chain transfer agent (CTA) such as 2-butene-1,4-diacetate, and 1,5-cyclooctadiene (COD) or high molecular weight

polybutadiene (PBD) as the butadiene equivalent (Scheme 1). The CTA not only provides the hydroxy functional group (which is usually protected to attenuate premature catalyst decomposition and therefore must be deprotected in a post-polymerization step) but also aids in regulating the molecular weight.[1,3,5] This approach has a distinct advantage over the free radical polymerization methods generally employed to prepare HTPBD as it provides polymers with an average of two functional groups per chain (F_n), as desired. Recently, we reported that the high functional group tolerance of $Cl_2(PCy_3)_2Ru$=CHPh (Cy = cyclohexyl) (**1**)[14] allowed the approach to be extended to the synthesis of amino and carboxyl terminated telechelic PBDs.[15]



Scheme 1. General approach employed to prepare hydroxy end-functionalized telechelic polybutadienes *via* olefin metathesis.

Few reports exist on synthesis of telechelic polymers using highly strained cyclic olefins such as norbornene (bicyclo[2.2.1]hept-2-ene).[16-20] Polynorbornene (PNB) contains an expanded structure that can absorb large amounts of aromatic petroleum liquids or oils. This provides a convenient handle to tune the polymer's mechanical and

thermal properties through plasticization. The material has successfully been used in sound barriers, oil spill recovery, and after cross-linking, in sealants and mechanical damping applications.[21] These properties make the material highly desirable for use in block copolymers and polymeric networks.[1] In addition, a wide variety of derivatives of norbornenes are available through simple Diels-Alder reactions. Unfortunately, placing functional groups at the end (or both ends) of the polymer chains remains challenging.

Fontanille and co-workers prepared ester-terminated telechelic PNBs using $WCl_6/Sn(CH_3)_4$ as the metathesis catalyst, unsaturated diesters as the CTAs, and norbornene as the monomer.[17] High catalyst loadings were necessary and ultimately lead to a depressed average of functional groups per polymer chain (1.7 to 1.9). In addition, poor agreement between the theoretical and experimental molecular weights was observed. Nevertheless, the ester functionality was successfully reduced to obtain hydroxy terminated telechelic PNBs. More recently, Gibson *et al.* extended this approach using Ru catalyst **1** to prepare hydroxy terminated telechelic *tert*-butyl ester functionalized PNBs.[19] While excellent control over molecular weight and end-functionality was achieved, carefully timed reagent additions were necessary and each polymer chain required an appropriately functionalized catalyst (as the initiator). Thus, there is a demand to increase the synthetic feasibility of preparing telechelic PNBs and reduce the catalyst loading.

The procedure described below for the synthesis of ester, hydroxy, and vinyl terminated telechelic and semi-telechelic (polymers possessing only one functional group per chain) PNBs is analogous to the approaches previously employed by our group to prepare telechelic PBDs from COD and an appropriate chain transfer agent.[11,12,15] The

method uses low catalyst loadings, provides excellent end-group control, and permits the preparation of polymers with tunable molecular weights.

Results and Discussion

The ROMP of norbornene using Ru catalyst **1** has been previously shown to be extremely rapid and generally affords only high molecular weight material.[22] This result is observed even when high catalyst loadings are employed which would theoretically increase the number of polymer chains and therefore reduce molecular weight. This has been attributed to a slow rate of initiation (k_i) relative to propagation (k_p).[14] As discussed above, a well-known method for controlling molecular weight in ROMP is through the inclusion of acyclic olefins which effectively act as CTAs.[1,3,5] In addition, it has been previously shown that telechelic polymers can be obtained under certain conditions when symmetrically functionalized CTAs are employed.[6-12] When CTA 1,4-bis(acetoxy)-*cis*-2-butene (**2**) was included in the ROMP of norbornene (initiated by complex **1**), only high molecular weight polymer was obtained. Similar results were observed even when relatively high CTA loadings (CTA/monomer = 10) were employed. Congruent with an analogous system using COD as the monomer to form telechelic PBDs,[12] high molecular weight polymer was observed to form first. However, since the solvent extensively swelled the PNB, the reaction mixture became extremely viscous and further reaction between the growing polymer chains and the CTA was severely suppressed. In addition, the double bonds in PNB are less reactive in ROMP due to the steric hindrance of the adjacent centers.

Since Ru carbenes are known[23] to exhibit high rates of reactivity towards terminal olefins, efforts were shifted towards using allyl acetate as the CTA. When the polymerizations were performed in toluene ($[monomer]_0$ = 2.6 M, CTA/monomer = 5) using a monomer/catalyst loading = 4000 at 25 ºC, no polymer precipitation or swelling was observed. After 24 hours, the solvent was evaporated, and the resultant mixture of polymers was separated using column chromatography (silica gel, CH_2Cl_2 as eluent). Predominately (~72 %) PNB **3**, capped with allyl acetate on one terminus of the polymer chain and a vinyl group on the other, was obtained (Eq. 2) in addition to small amounts of bis-vinyl (**4**) (~14 %) and bis-acetoxy (**5**) (~14 %) end-functionalized PNBs. End-group analysis of PNB **3** using ^{1}H NMR spectroscopy indicated a perfect 1:1 stoichiometry between the acetate and vinyl end-groups with a number average molecular weight of 1800 g/mol. This result was in agreement with the theoretical value of 1500 g/mol (based on monomer and CTA consumption as determined by gas chromatography). Gel permeation chromatography (GPC) revealed the polymer distribution was monomodal (PDI = 1.8) with a molecular weight of 1700 g/mol (relative to polystyrene standards in THF). The PNB backbone contained *ca*. 85% *trans* olefin geometry, as expected for polymerizations of norbornene with **1**.[24] Similarly, end-group geometries were determined to be approximately 70% *trans*. The polymerizations were repeated in a similar fashion as described above using a variety of monomer/CTA ratios (Table 1) and afforded good yields (70 - 80%) of semi-telechelic polymer **3** over a wide range of molecular weights.

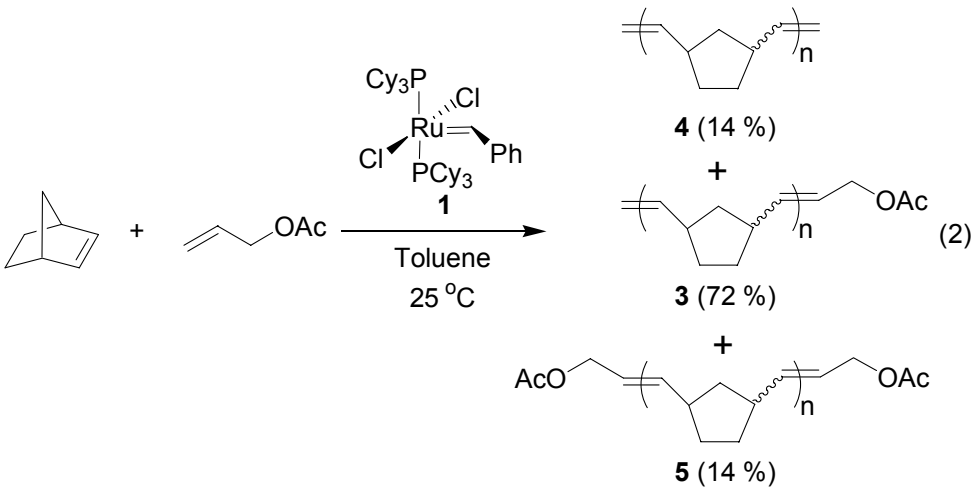
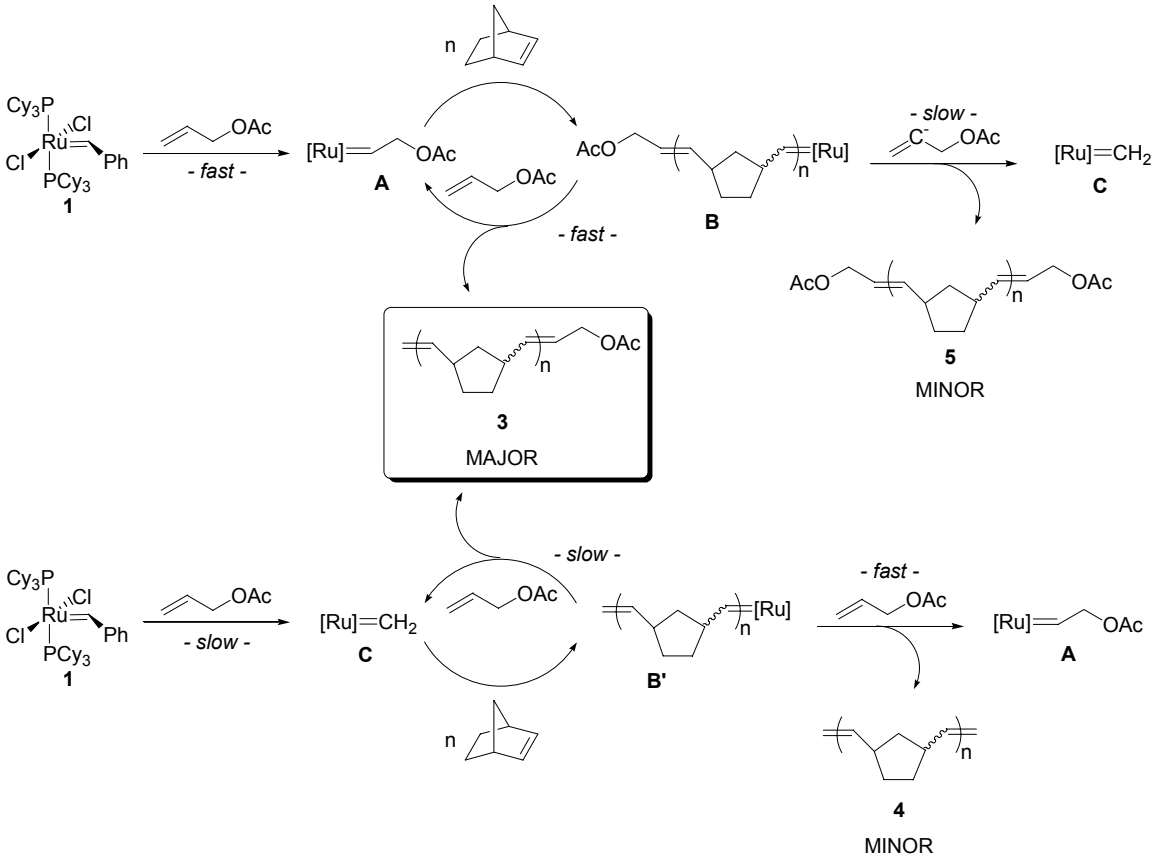


Table 1. Synthesis of a variety of acetoxy end-functionalized semi-telechelic poly-(norbornene)s **3**.[a]

M/CTA[b]	Yield[c] (%)	MW[d] (theo)	MW[e] (NMR)	M_n[f] (GPC)	PDI[f]	F_n[g]	Trans[h] (%)
5	72	1500	1800	1700	1.8	1.0	85
10	82	3400	3000	3600	1.7	1.0	82
25	75	8600	9400	8800	2.1	1.1	80

[a] Polymerizations conditions: Toluene as solvent, $[Norbornene]_0$ = 2.6 M, Temp = 23 ºC, Time = 12 h, Ar atmosphere, monomer/catalyst (**1**) = 4000, CTA = allyl acetate (**2**). [b] $[Monomer]_0/[CTA]_0$. [c] Isolated yield. [d] Theoretical MW based on residual monomer and CTA as determined by GC. [e] MW determined ^{1}H NMR end-group analysis. An average of one functional group per polymer chain was assumed. [f] Determined by gel permeation chromatography using THF as the eluent. The values are reported relative to monodispersed polystyrene standards. [g] Averaged ratio of ester groups to terminal olefins per polymer chain. [h] Percent *trans* olefin in the polymer backbone, as determined by ^{1}H and ^{13}C NMR spectroscopies.

To gain a mechanistic understanding of how the end-functionalized polymers were formed, the polymerization (monomer/CTA = 5) was monitored over time using a combination of ^{1}H and ^{31}P NMR spectroscopies and the results are summarized in Scheme 2. Following rapid disappearance of initiator **1** from reaction with allyl acetate or monomer, three distinct carbene species were observed throughout the polymerization: acetate functionalized complex **A**, propagating species **B** (and **B´** which was indistinguishable from **B**), and to a lesser extent methylidene complex **C**.[25] Species **A** and **C** resulted from the cross-metathesis of **1** (or **B**) with allyl acetate, while **B** formed after the polymerization was initiated. Only a small amount of methylidene **C** was observed (signal intensity of **C** was <10% of **A**+**B**). The pathway in Scheme 2 leading to the formation of mono-functionalized PNBs **3** was that anticipated from the relative reactivities found in model systems.[26] In addition, the ratio of propagating species **B** to complex **A** was approximately 15:1 which was in agreement with the number of monomer units found in the resulting polymer chains ($X_n \approx 17$ by ^{1}H NMR spectroscopy, $X_n \approx 16$ by GPC). Thus, the molecular weight of the PNB appears to have been kinetically determined by the relative rates of reaction of the propagating species with CTA or monomer.[27,28] A similar mechanism has been recently proposed by Ozawa *et al.* in the ROMP of norbornene in the presence of heteroatom substituted vinyl substrates (using structurally similar Ru vinylidene initiators).[29]

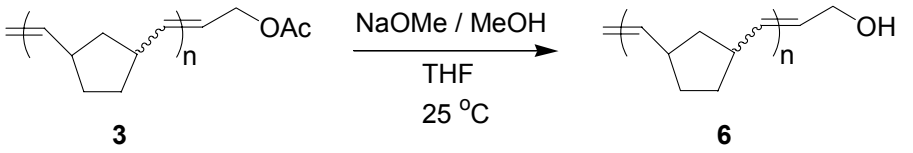


Scheme 2. Proposed mechanistic pathways leading to the formation of end-functionalized polynorbornenes.[23,26]

The kinetically controlled polymerization may stem from the lower reactivity of the propagating species towards olefins in the PNB backbone. For example, attempts to produce monofunctional PBD by the ROMP of COD in the presence of allyl acetate (using similar conditions as above) afforded a statistical mixture (1:2:1) of non, mono, and bis end-(acetoxy) functionalized polymers. In this case, the reactivities of the propagating species with monomer and olefins in the PBD backbone was similar and thus the reaction reached equilibrium. Furthermore, the reactivity of the propagating species appeared to depend on temperature as well. Performing the polymerizations described

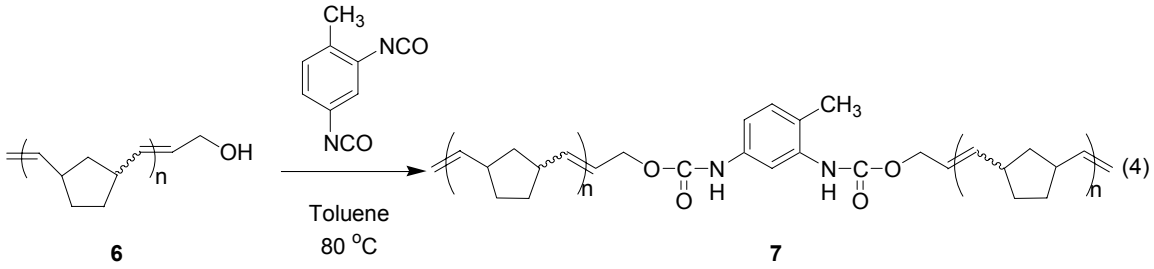
above (i.e., norbornene and CTA) at elevated temperatures (50 °C) also afforded statistical mixtures of end-functionalized PNBs.

Deprotection of the acetate group on PNB **3** using a mixture of sodium methoxide in methanol/THF gave hydroxy terminated PNB **6** in 86% isolated yield (Eq. 3). As expected, the molecular weight of **6** was slightly lower than **3** (M_n = 1500 g/mol by GPC) with no significant change in the polydispersity (PDI = 1.9) or polymer microstructure (85% *trans* olefin).

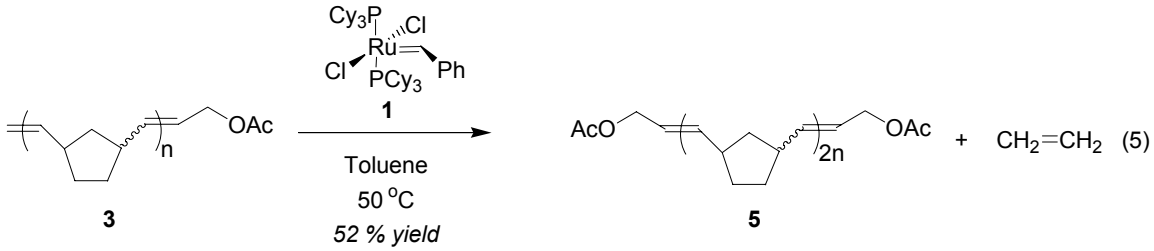


3 **6** (3)

Reaction of two equivalents of PNB **6** with tolylene 2,4-diisocyanate in toluene at 80 ºC quantitatively afforded PNB **7** (Eq. 4). The presence of terminal vinyl groups and absence of hydroxy end-groups in the ^{1}H and ^{13}C NMR spectra indicated that the dimerization was complete. In addition, the ratio of the vinyl end-groups to the aromatic group on the diisocyanate was found to be 2:1. Accordingly, the molecular weight of the resulting polymer was nearly twice the starting material **6** by ^{1}H NMR spectroscopy (MW = 3100 g/mol) and GPC (M_n = 2900 g/mol, PDI = 2.5). Again, no change in the polymer backbone microstructure (85% *trans*) was observed during the deprotection or coupling reactions.



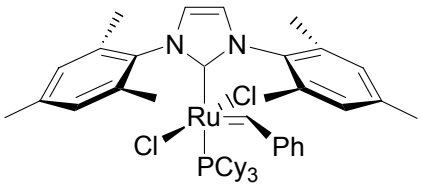
While the above procedure proved successful for preparing hydroxy mono-terminated (semi-telechelic) PNBs, the preparation of telechelic PNBs with hydroxy groups on *both* ends remained elusive and other synthetic protocols were explored. Cross-metathesis between two terminal olefins has become a powerful method for preparing complex organic substrates.[30] As shown in Eq. 5, dimerization of PNB **3** *via* cross-metathesis afforded a statistical mixture of PNBs **4**, **3**, and **5** (1:2:1). Elevated temperatures (50 ºC) were necessary to achieve acceptable reaction rates, which as described above, may have resulted in extensive chain transfer which allowed the reaction to reach equilibrium.



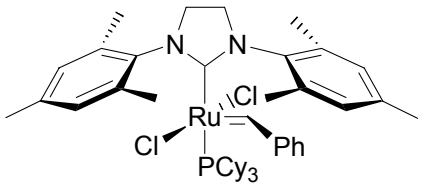
Metathesis degradation of high molecular weight PBD (in the bulk or in solution) using Ru catalyst **1** and a CTA has been shown to be an alternative but powerful synthetic route to end-functionalized PBDs.[31] For example, bis(trimethylsilyl) end-functionalized telechelic PBD has been prepared through the metathetical degradation of high molecular weight PBD in the presence of an appropriately functionalized acyclic olefin.[8] The

mechanism of degradation appears to proceed through (a catalyst mediated) chain transfer process between high molecular weight polymer chains and the CTA. This not only increases the number of chains (and concomitantly causes a reduction in the molecular weight) but also successfully transfers a functional group from the CTA to the end of the polymer chain.[5] Unfortunately, attempts at extending this methodology to PNB (in the bulk or solution) were unsuccessful. A possible explanation for the differential reactivity between PNB and PBD with **1** may be an increased steric hindrance around the olefins in the former polymer. Alternatively, in the case of bulk degradation, the difference may derive from the glass transition temperature (T_g) of the polymers. The T_g of 1,4-PBD is below -60 ºC, while the T_g of PNB is near 45 ºC (*vida infra*) which reflects depolymerizing a viscous liquid versus a solid polymer. [32] Performing the reaction at elevated temperatures (~60 ºC) resulted in only marginal degradation, which may be attributed to reduced catalyst lifetimes at higher temperatures.[33]

These barriers were overcome by employing catalysts with higher activity and thermal stability. Ruthenium complexes[34,35] **9** and **10,** which bear highly electron donating N-heterocyclic carbene ligands, have been shown to exhibit dramatically improved metathesis activity in ring-closing metathesis (RCM), cross-metathesis (CM), and ROMP when compared to the parent complex **1**.[34-38] In addition, these catalysts are thermally robust and are relatively inert towards oxygen and moisture.[34d]

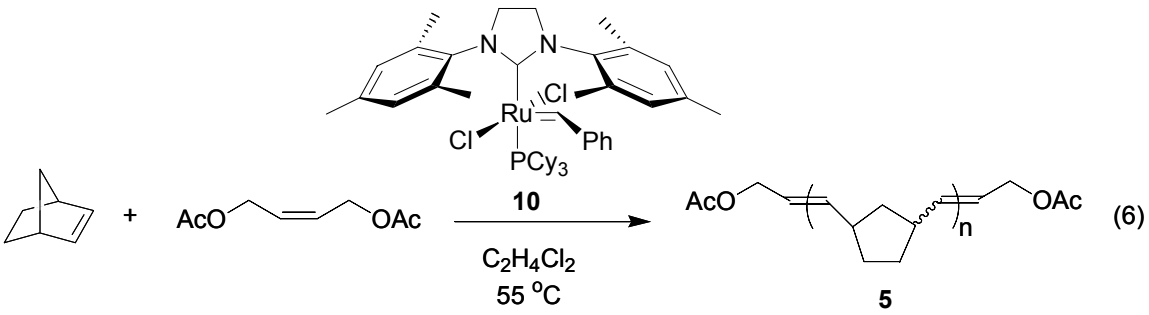


9



10

When the ROMP of norbornene was initiated by **10** (monomer/catalyst = 2000) and 1,4-bis(acetoxy)-*cis*-2-butene (**2**) was included as a CTA (monomer/CTA = 20), telechelic PNB **5** was obtained in 95% yield (Eq. 6). The polymerizations were performed in 1,2-dichloroethane at 55 ºC using $[monomer]_0$ = 1.25 M. After 12 h, the reaction mixture was poured into excess methanol and the precipitated polymer was collected by filtration. The molecular weight of the resulting PNB was determined by ^{1}H NMR spectroscopy to be 2000 g/mol by assuming an average of two functional groups per chain. This is in excellent agreement to the value expected (2100 g/mol) based on complete monomer and CTA incorporation. GPC indicated that the polymer had a polydispersity close to 2.0 and a molecular weight of 2100 g/mol (relative to polystyrene standards in THF). The T_g of the polymer was 45 ˚C as determined by differential scanning calorimetry (DSC). The *trans* olefin content in the polymer backbone was found to be between 60% and 65% by ^{1}H and ^{13}C NMR spectroscopy, which is lower than the *trans* content obtained when norbornene was polymerized with **1** and may reflect inherent *cis/trans* selectivities of the catalyst for norbornene. In addition, the stereochemistry of the polymer end-groups was determined to be approximately 65% *trans* olefin geometry. No vinyl end-groups olefins were observed.



(6)

The polymerizations were performed in a similar fashion as described above using a variety of monomer/CTA ratios (Table 2). The procedure afforded excellent yields (~90%) of telechelic polymer over a wide range of molecular weights. While most of the polymers prepared in Table 2 were isolated by simple precipitation (from methanol) and filtration procedures, the low molecular weight PNBs (MW < 1500 g/mol) remained soluble in the methanol/1,2-dichloroethane mixture. In these cases, solvent was simply evaporated after the polymerization was complete and residual catalyst was removed using silica gel chromatography. As shown in Figure 1, excellent agreement between the theoretical and experimental molecular weights was observed which reflects the high fidelity of this reaction. In addition, it is important to note that the PDI of each polymer described in Table 1 was near 2.0. Metathesis polymerizations with extensive chain transfer approximate a step-growth polymerization which yields polydispersity indices near two at high monomer conversion.[5]

Physical observations made throughout the polymerization provided strong mechanistic implications. High molecular weight PNB separated almost immediately when a 1,2-dichloroethane solution of norbornene (2.5 M) was added to a pre-heated (55 °C) solution of the catalyst **10** (1.3 mM) and CTA. This observation was analogous to when **1** was employed as the catalyst (*vide supra*). However, as the propagating Ru species (and any residual initiator) underwent chain transfer with the CTA, the molecular weight of the polymer decreased and therefore slowly dissolved over time. These observations are summarized in the mechanism proposed in Scheme 3. Monitoring the polymerization using GPC provided further evidence for this mechanism. As shown in

Figure 2, the molecular weight of the (soluble) polymer in the liquid phase of the reaction mixture was found to decrease over time.

Table 2. Synthesis of a variety of bis(acetoxy) end-functionalized telechelic polynorbornenes **5**.[a]

M/CTA[b]	Yield[c] (%)	MW[d] (theo)	MW[e] (NMR)	M_n[f] (GPC)	PDI[f]	F_n[g]	Trans[h] (%)
5	89	649	650	640	2.8	1.89	62
10	86	1120	1200	1100	2.3	1.90	62
20	86	2061	2100	2000	2.2	1.90	63
50	87	4886	4900	4800	2.0	1.93	65
100	91	9594	11000	11200	2.0	1.95	67
200	93	19010	20000	19500	2.0	1.95	67

[a] Polymerizations conditions: 1,2-dichloroethane as solvent, $[Norbornene]_0$ = 1.0 M, Temp = 55 ºC, Time = 12 h, Ar atmosphere, monomer/catalyst (**10**) = 2000, CTA = 1,4-diacetoxy-2-butene (**2**). [b] $[Monomer]_0/[CTA]_0$. [c] Isolated yield. [d] Theoretical MW based on complete monomer conversion and CTA incorporation. [e] MW determined by ^1H NMR end-group analysis. An average of two functional groups per polymer chain was assumed. [f] Determined by gel permeation chromatography using THF as the eluent. The values are reported relative to monodispersed polystyrene standards. [g] Average number of functional groups per polymer chain as determined by removal of the acetoxy groups followed by back-titration of the liberated acetate anion (see text for more details). [h] Percent *trans* olefin in the polymer backbone, as determined by ^1H and ^{13}C NMR spectroscopies.

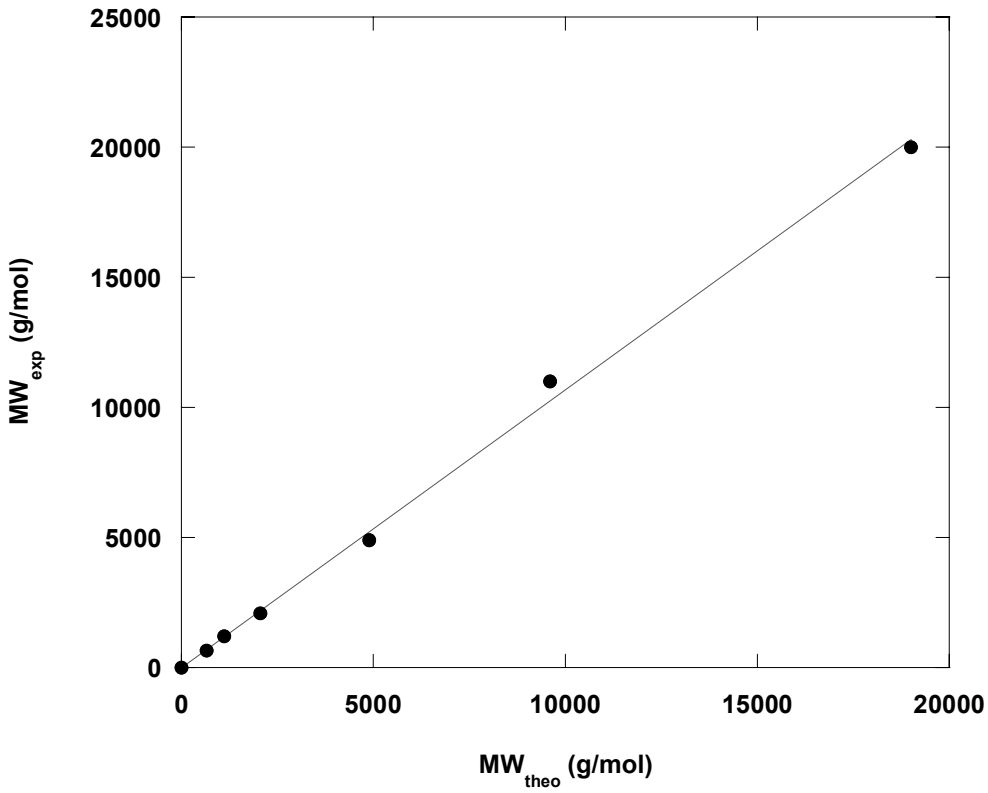


Figure 1. Comparison of theoretical molecular weights (based on complete monomer conversion and CTA incorporation) and their corresponding experimentally determined values (using ^{1}H NMR spectroscopy and assuming an average of two functional groups per polymer chain) for the synthesis of a variety of bis(acetoxy) end-functionalized telechelic polynorbornenes **5**. The values were taken from Table 2.

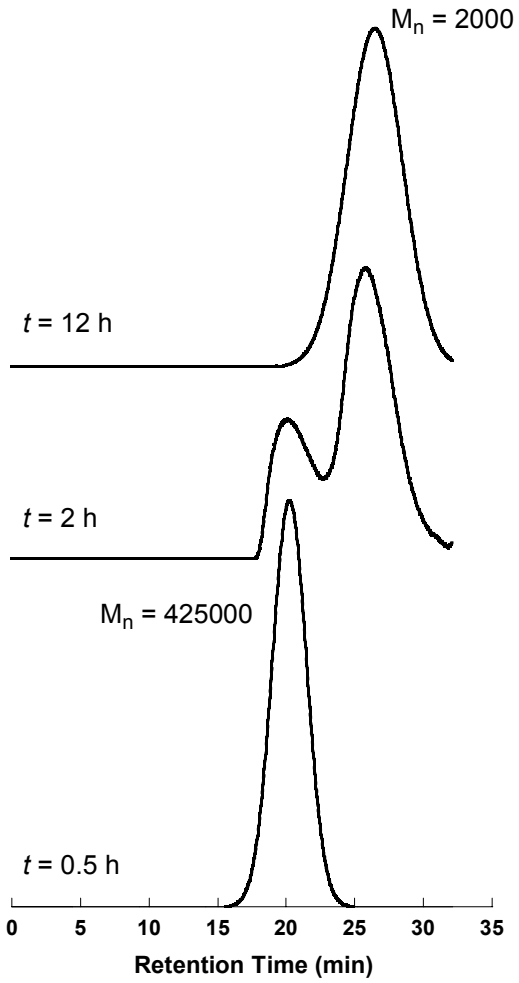
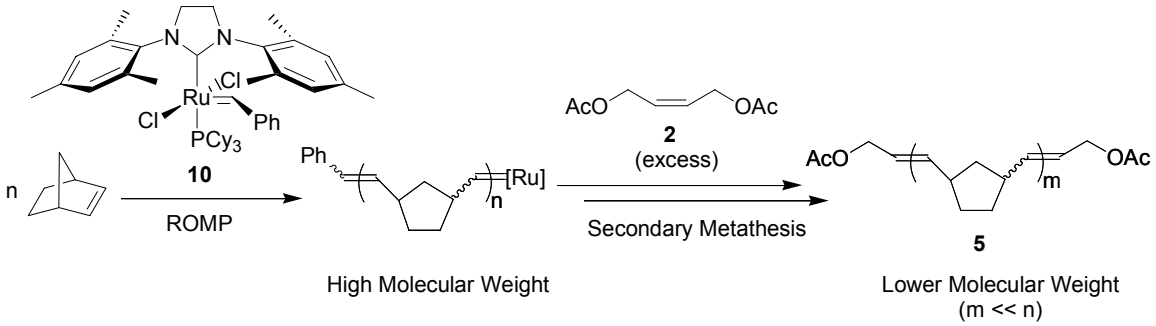


Figure 2. Molecular weight evolution of polynorbornene as a function of time. M_n was determined by GPC using THF as the eluent. The values are reported relative to monodispersed polystyrene standards. Conditions: 1,2-dichloroethane as solvent, Temp = 55 ºC, Ar atmosphere, $[Norbornene]_0$ = 1.0 M, monomer/catalyst (**10**) = 2000, CTA = 1,4-diacetoxy-2-butene (**2**), $[Monomer]_0/[CTA]_0$ = 20.



Scheme 3. Proposed mechanism leading to the formation of bis(acetoxy) end-functionalized telechelic polynorbornenes **5**.

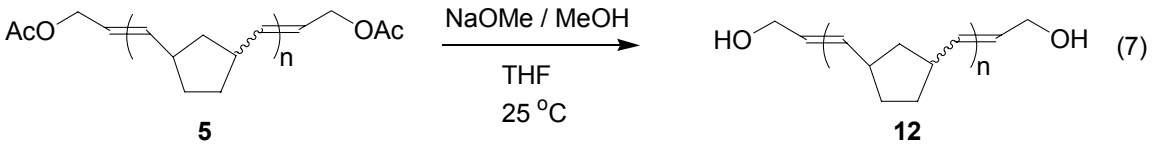
As described above, an alternative approach to telechelic polymers prepared *via* olefin metathesis has been through the degradation of high molecular polymer in the presence of a symmetrically substituted CTA.[5] We attempted to extend this approach to the preparation of telechelic PNBs using the highly active Ru catalyst **10**. A benzene mixture of commercially available[39] high molecular weight PNB (MW 3,000 – 4,000 kg/mol), CTA **2** (monomer/CTA = 20), and catalyst **10** (monomer/catalyst = 2000) was heated to 55 ºC for 24 h. While a significant portion of the polymer dissolved, an unidentified contaminant in the commercial polymer separated from the liquid phase of the reaction mixture. The contaminant did not dissolve in boiling toluene and was probably cross-linked PNB. The dissolved polymer was precipitated into rapidly stirring methanol and examined by ^{1}H and ^{13}C NMR spectroscopies and GPC. While molecular weight reduction was observed (M_n = 3200 g/mol by GPC), the distribution of polymer chains was multi-modal. In addition, several unidentifiable resonances in both the aliphatic and olefin regions of the ^{1}H and ^{13}C NMR spectra were observed. These resonances may stem from a lightly (non-metathetical) cross-linked PNB network.

Nevertheless, allyl acetate end-groups were observed, suggesting that the reaction was successful to some extent.

To prove that a desired degree of degradation could be obtained in the absence of contaminants, high molecular PNB was prepared *via* the ROMP of norbornene using $(PPh_3)_2Cl_2Ru=CHPh$ (**11**), a catalyst capable of mediating the living polymerization of norbornene.[14] Combination of norbornene and **11** (monomer/catalyst = 10000) in toluene ($[monomer]_0$ = 0.5 M) at 25 ºC afforded PNB (M_n = 130 kg/mol by GPC, PDI = 1.3) in 90% yield. This PNB was subjected to the same degradation conditions as the commercial PNB described above. Complete dissolution was observed within 4 hours, and characterization of the resulting polymer indicated that the desired degree of degradation was achieved. GPC analysis revealed that the M_n was 1900 g/mol as expected, with a polydispersity of 2.1. Only allyl acetate end-groups were observed by ^1H and ^{13}C NMR spectroscopy and the polymer's molecular weight was calculated to be 2050 g/mol. In addition, the amount of *trans* olefin in the PNB backbone decreased from 80% (found in the starting PNB) to 65%. Thus, it appears in the absence of (possibly cross-linked) contaminants, telechelic PNBs can be obtained *via* the degradation of high molecular PNB.

Deprotection of the bis(acetoxy) end-functionalized telechelic PNBs **5** (i.e., removal of the acetate groups) was accomplished using a methanolic/THF solution of sodium methoxide followed by an acidic workup (Eq. 7). This afforded the corresponding hydroxy end-functionalized PNB **12** in quantitative yield. Potentiometric titration of the liberated acetate (generated using a slight modified deprotection procedure, see the experimental section for further details) on a range of PNB samples

indicated an average of 1.9 ± 0.1 hydroxy groups per polymer chain (Table 2).[40] These numbers not only illustrated the success of the reaction but also justified the assumption (of using two functional groups per polymer chain) taken to determine MW by NMR spectroscopy. No change in the *cis*/*trans* ratio of the polymer backbone was observed.



5 **12** (7)

Since PNB standards are not commercially available to calibrate GPC instrumentation, it is common to report the molecular weight of the polymer relative to monodispersed polystyrene samples. The hydrodynamic volumes of these two polymers are not identical and therefore a correction factor has been generally applied to achieve agreement between experimental and theoretical molecular weights. Unfortunately, several inconsistencies in the factors are found throughout the literature, especially in the low molecular weight regime.[41] Since our titration experiments fully supported the assumptions taken to determine molecular weight by NMR end-group analysis (an independent method of determining molecular weight), we compared these values to those obtained *via* GPC (calibrated with polystyrene standards) in two different solvents. As shown in Figure 3, when THF was used at the GPC eluent, excellent agreement between the NMR spectroscopic and GPC determined molecular weights was observed. However, using CH_2Cl_2 as the GPC eluent, the molecular weights of the PNBs were approximately twice those obtained by NMR spectroscopy. Apparently, the hydrodynamic volume of a PNB chain in CH_2Cl_2 is approximately one-half of a comparable molecular weight poly(sytrene) chain, while in THF the hydrodynamic

volumes of the two polymers are similar. Thus, when characterizing low molecular weight PNBs (MW < 25 kg/mol) by GPC against polystyrene standards, we suggest that no correction factor be applied when THF is used as eluent and 0.5 x M_n be applied when using CH_2Cl_2.

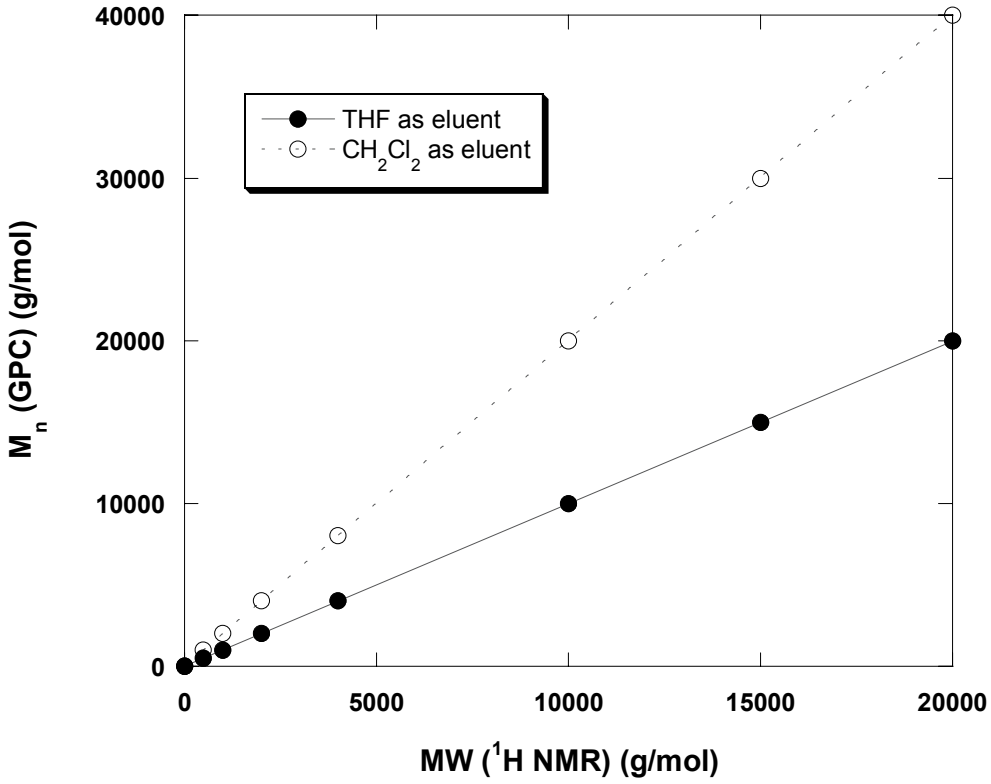


Figure 3. Comparison of molecular weights of a variety of bis(acetoxy) end-functionalized telechelic PNBs **5** determined by ^{1}H NMR spectroscopy and GPC. Standard end-group analysis procedures were employed for the ^{1}H NMR spectroscopic measurements. Either THF or CH_2Cl_2 was used the eluent in the GPC measurements and the values are reported relative to monodispersed polystyrene standards.

Conclusion

The synthesis of a variety of polynorbornenes bearing acetoxy, hydroxy, and vinyl end-groups was accomplished using ring-opening metathesis polymerization (ROMP). PNBs with an acetoxy group at one terminus and a vinyl group at the other were prepared using norbornene, $(PCy_3)_2Cl_2Ru$=CHPh (**1**), and allyl acetate as a chain transfer agent (CTA). Molecular weight appears to be kinetically determined by the relative rates of reaction between the propagating species and monomer or CTA. Removal of the acetoxy groups was accomplished with sodium methoxide and afforded the corresponding hydroxy terminated polymers. Bis(vinyl) end-functionalized telechelic PNB was obtained by coupling the hydroxy end-functionalized to tolylene 2,4-diisocyanate. Attempts at preparing the bis(acetoxy) end-functionalized PNBs through dimerization of mono acetoxy end-functionalized semi-telechelic PNB afforded a statistical mixture of end-functionalized polymers.

An alternative and successful route to bis(acetoxy) end-functionalized PNBs was the result of using a more active olefin metathesis ruthenium based catalyst bearing an imidazolylidene ligand (**10**). Reaction of norbornene, 1,4-diacetoxy-2-butene as the CTA, and the highly active catalyst led to the formation of the desired bis(acetoxy) end-functionalized PNB. The mechanism appears to initially proceed through the formation of high MW PNB followed by polymer depolymerization from chain transfer reactions with the CTA. The experimentally determined molecular weights of the resulting telechelic polymers were in excellent agreement with their theoretical values and were easily controlled by simply varying the initial monomer/CTA ratio. Acetoxy end-functionalized PNBs were also obtained by degradation of high molecular weight PNB.

As with the mono end-functionalized polymers, the acetoxy groups were removed to obtained hydroxy terminated telechelic PNBs with number average functionalities close to 2.0.

Prior to this study, few routes to end-functionalized (especially telechelic) PNBs existed. In addition, these prior methods required high catalyst loadings and in some cases were unsuccessful in controlling molecular weight. The procedures outlined above provide several synthetically feasible, cost-effective routes to end-functionalized PNBs. Past experience has suggested that functionalized norbornenes will undergo similar reactions and will provide a wide range of telechelic functional materials. These polymers are expected to complement or substitute other telechelic polyalkenamers commonly employed in industry.

Experimental Section

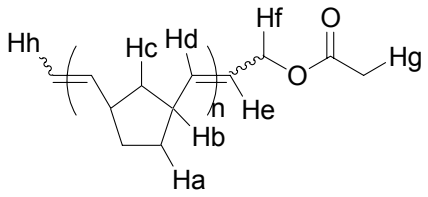
General. Argon was purified by passage through columns of BASF R-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde).[42] NMR spectra were recorded in a GE QE-300 Plus (300.10 MHz ^{1}H ; 75.49 MHz ^{13}C) spectrometer or a JEOL GX-400 (399.65 MHz ^{1}H; 100.00 MHz ^{13}C; 161.85 MHz ^{31}P) spectrometer. Chemical shifts were recorded in parts per million (δ) and referenced to residual protio solvent. Coupling constants, *J*, are reported in hertz (Hz). Gel permeation chromatographs were obtained on either a HPLC system using an Altex model 110A pump, a Rheodyne model 7125 injector with a 100 μL loop, two American Polymer Standards, Inc. 10 μm mixed bed columns, and a Knauer differential refractometer using CH_2Cl_2 as eluent or on an analogous system using THF as the eluent. In either system, the flow rate was set to 1.0

mL/min and molecular weights and polydispersities were reported relative to monodispersed polystyrene standards (obtained from American Polymer Standards, Inc.). Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Pyris-7 calorimeter using a scan rate of 10 ˚C/min under an atmosphere of nitrogen.

Materials. Catalysts **1**, **10**, and **11** were prepared as previously described.[14,35] Norbornene (Aldrich) was distilled from sodium metal. 1,4-Diacetoxy-2-butene and allyl acetate were purchased from TCI America, Inc. and distilled prior to use. 1,2-Dichloroethane was purged with Ar for 30 minutes. Toluene was purified by passage through a solvent column.[42] Tolylene 2,4-diisocyanate (Aldrich) was used as received. All other solvents were reagent grade and used without further purification.

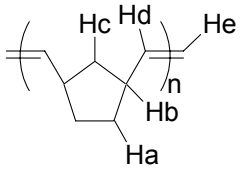
Representative Procedure for Preparing Acetoxy End-functionalized Semi-Telechelic Polynorbornene 3. Inside a N_2 filled drybox, a small vial was charged with 10.9 mg (13.2 μmol) of catalyst **1** and a stir bar. A separate vial was charged with 5.00 g (53.1 mmol) of norbornene, 1.06 g (10.6 mmol) of allyl acetate, and 20 mL of toluene. Both vials were sealed and cooled to –30 ºC. The toluene solution was then transferred to the vial containing the catalyst via syringe and allowed to warm to room temperature under vigorous stirring. After 24 h at 25 °C, 0.6 mL (6.3 mmol, 500 equiv. relative to catalyst) of ethyl vinyl ether was added to quench the polymerization. The reaction mixture was then poured into excess stirring methanol (100 mL) causing precipitation of a white solid. The methanol was decanted away and the resulting solid was washed with fresh methanol (25 mL) three times. The material was collected and purified by silica gel

chromatography to afford 3.9 g of semi-telechelic PNB **3** (72% yield, based on complete monomer conversion and 40% allyl acetate consumption as determined by GC analysis). GPC: M_n = 1700, M_w = 3000, PDI = 1.8. The ^{1}H NMR spectrum was assigned as follows:



^{1}H NMR ($CDCl_3$): δ 5.84-5.65 (bm, Hd + He), 5.28 (bd, Hd *trans*), 5.20 (bd, Hd *cis*), 5.01-4.82 (m, Hh), 4.62 (d, Hf, *cis*), 4.50 (d, Hf, *trans*), 2.74-2.65 (bs, Hb *cis*), 2.60-2.31 (bs, Hb, *trans*), 2.04 (s, Hg), 1.93 (bm, Hc), 1.77 (bm, Ha), 1.51-1.26 (bs, Ha), 1.18-0.97 (bm, Hc), MW = 1800 (end-group analysis).

Also recovered (0.81 g, 14%) from the reaction mixture was telechelic polynorbornene **4**. GPC: M_n = 1500, M_w = 2400, PDI = 1.6. The ^{1}H NMR spectrum was assigned as follows:

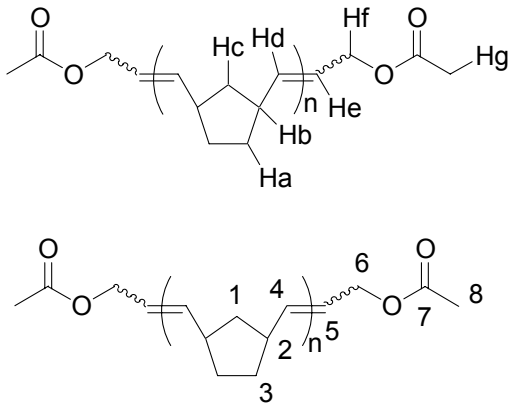


^{1}H NMR ($CDCl_3$): δ 5.86-5.74 (m, Hd), 5.40-5.33 (bm, Hd *trans*), 5.21 (bd, Hd *cis*), 5.00-4.85 (m, He), 2.79 (bs, Hb *cis*), 2.43 (bs, Hb, *trans*), 1.95-1.68 (bm, Hc), 1.47-1.29 (bm, Ha), 1.17-1.04 (bm, Hc), MW = 1400 (end-group analysis).

Acetoxy end-termined telechelic polynorbornene **5** (0.81 g, 14%) was also recovered from the reaction mixture. GPC: M_n = 2100, M_w = 3800, PDI = 1.8.

Assignment of its ^{1}H NMR spectrum can be found below; MW = 1900 (end-group analysis).

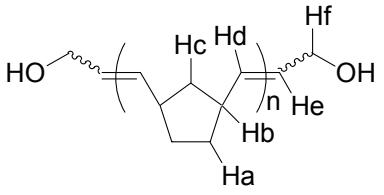
General Polymerization Procedure for Preparing Acetoxy End-functionalized Telechelic Polynorbornenes 5. Inside a N_2 filled drybox, a 5 dram vial was charged with catalyst **10** (5 mg, 6 μmol), 5 mL of 1,2-dichloromethane, and a stir bar. The vial was then capped with a rubber septum and removed from the drybox. After adding 1,4-diacetoxy-2-butene (0.1 mL, 0.6 mmol) *via* syringe, the vial was immersed in an oil bath thermostatted at 55 ºC. Under vigorous stirring, 5.12 mL (12.8 mmol) of norbornene (as a 2.5 M solution in 1,2-dichloroethane) was added via syringe. Separation of high molecular weight polynorbornene occurred almost immediately. The polymer then gradually dissolved over the next 2 hours. After 12 hours at 55 °C, the reaction was poured into excess stirring methanol (100 mL) causing precipitation of a white solid. The material was collected by filtration affording 1.2 g of telechelic PNB **5** (95 % yield). (In cases where low MW polymer was prepared, the reactions were passed through a short column of silica gel followed by evaporation of solvent under reduced pressure.) GPC: M_n = 2000, M_w = 4400, PDI = 2.2. DSC: T_g = 45 ºC. The ^{1}H and ^{13}C NMR spectra were assigned as follows:

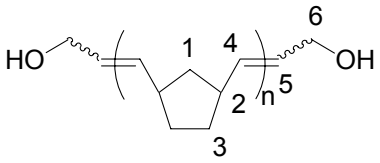


^{1}H NMR ($CDCl_3$): δ 5.81-5.94 (bm, Hd + He), 5.27 (bs, Hd *trans*), 5.13 (bd, Hd *cis*), 4.12 (bd, Hf, *cis*), 3.98 (bd, Hf, *trans*), 2.72 (bs, Hb, *cis*), 2.36 (bs, Hb, *trans*), 2.05 (bs, Hg), 1.78 (bm, Hc), 1.69 (bs, Ha), 1.28 (bs, Ha), 0.96 (bm, Hc). ^{13}C NMR ($CDCl_3$): δ 171.10 (C7), 141.08 (C5, t), 140.93 (C5, c), (134.46 (C4, tcc), 134.41 (C4, tct), 134.33 (C4, ccc), 134.28 (C4, ctc), 133.70 (C4, cct), 133.58 (C4, ttc), 133.58 (C4, ttt), 133.47 (C4, ctt), 65.67 (C6), 44.07 (C2, tc), 43.79 (C2, tt), 43.32 (C1, cc), 42.66 (C1, ct and tc), 41.93 (C1, tt), 38.73 (C2, cc), 39.22 (C2, ct), 33.62 (C3, cc), 33.45 (C3, ct), 32.91 (C3, tc), 32.76 (C3, tt), 21.37 (C8); MW = 2100 (end-group analysis).

General Procedure for Removing the Acetoxy Groups from the End-functionalized Polynorbornenes. A 25 mL Erlenmeyer flask was charged with 500 mg (0.25 mmol) of acetate protected PNB **5** (MW = 2000) and 0.16 g (3 mmol) of $NaOCH_3$ (12 equiv. per polymer chain), 15 mL of THF, and 5 mL of CH_3OH. This mixture was stirred for 48 h at 45°C (higher temperatures appeared to result in cis/trans isomerization). Afterwards, residual base was quenched with a 1:3 methanol-water

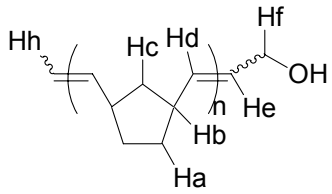
solution saturated with NH_4Cl and the resulting polymer was extracted (2 x 20 mL) into THF. The THF polymer solution was washed with water and evaporated under reduced pressure to afford 405 mg (88% yield) of hydroxy-terminated telechelic PNB **12** (as a highly viscous gel). GPC: M_n = 1900, M_w = 3900, PDI = 2.1. DSC: T_g = 43 ºC. The ^1H and ^{13}C NMR spectra were assigned as follows:





^1H NMR ($CDCl_3$): δ 5.82-5.91 (bm, Hd + He), 5.31 (bs, Hd *trans*), 5.17 (bd, Hd *cis*), 4.15 (bs, Hf, *cis*), 4.04 (bs, Hf, *trans*), 2.70 (bs, Hb, *cis*), 2.34 (bs, Hb, *trans*), 1.77 (bm, Hc), 1.73 (bs, Ha), 1.26 (bs, Ha), 0.95 (bm, Hc). ^{13}C NMR ($CDCl_3$): δ 140.83 (C5, t), 140.69 (C5, c), 134.04 (C4, tcc), 133.98 (C4, tct), 133.92 (C4, ccc), 133.87 (C4, ctc), 133.83 (C4, cct), 133.21 (C4, ttc), 133.09 (C4, ttt), 132.94 (C4, ctt), 60.98 (C6), 43.51 (C2, tc), 43.22 (C2, tt), 42.81 (C1, cc), 42.18 (C1, ct and tc), 41.45 (C1, tt), 38.73 (C2, cc), 38.48 (C2, ct), 33.15 (C3, cc), 32.98 (C3, ct), 32.42 (C3, tc), 32.27 (C3, tt); MW = 2000 (end-group analysis).

An similar procedure was employed to prepare acetoxy end-functionalized semi-telechelic PNB **6** (86% yield) via deprotection of PNB **3** (M_n = 1700, PDI = 1.8). GPC: M_n = 1500, M_w = 2850, PDI = 1.9. The ^1H NMR spectrum was assigned as follows:



^{1}H NMR (toluene-d_8): δ 5.80-5.63 (bm, Hd + He), 5.42 (bd, Hd *trans*), 5.28 (bd, Hd *cis*), 5.02-4.83 (m, Hh), 3.97 (bs, Hf, *cis*), 3.82 (bs, Hf, *trans*), 2.85-2.68 (bs, Hb *cis*), 2.59-2.25 (bs, Hb, *trans*), 2.02-1.83 (bm, Hc), 1.83-1.62 (bm, Ha), 1.58-1.25 (bs, Ha), 1.14-1.03 (bm, Hc); MW = 1600 (end-group analysis).

Titration Experiments. A 25 mL flask was charged with 500 mg (0.25 mmol) of bis(acetoxy)-functionalized telechelic PNB **5**, 100 mg (2.5 mmol) of crushed NaOH, and 15 mL of acetonitrile and then heated to reflux (under Ar) for 6 h. After cooling the solution to 0 ˚C (ice-bath), a 1.0 M solution (1.6 mL) of perchloric acid was slowly added to neutralize the excess base. The liberated acetate anion was then potentiometrically backtitrated with a freshly prepared pre-standarized[43] 0.1083 M perchloric acid solution in ethanol. The end point (and thus F_n) was determined using the Gran plot method.[44]

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† Portions of this chapter have been previously reported, see: Bielawski, C. W.; Benitez, D.; Morita, T.; Grubbs, R. H. *Macromolecules* **2001**, *34*, 8610.

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(27) If the polymerization was thermodynamically controlled, a statistical formation (1:2:1) of non, mono, and bis (acetoxy) end-functionalized PNBs would be expected.

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Chapter 6

Synthesis of ABA Triblock Copolymers *via* a Tandem Ring-Opening Metathesis Polymerization (ROMP) – Atom Transfer Radical Polymerization (ATRP) Approach[†]

Abstract

The synthesis of poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene) (SBS) and poly(methyl methacrylate)-*b*-poly(butadiene)-*b*-poly(methyl methacrylate) (MBM) triblock copolymers with poly(butadiene) (PBD) segments containing 100% 1,4-microstructure is described. Bis(allyl chloride) and bis(2-bromopropionate) terminated telechelic PBD's were synthesized by the ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene in the presence of the corresponding difunctional chain transfer agents. These telechelic PBDs were subsequently used as difunctional macroinitiators for the heterogeneous atom transfer radical polymerization (ATRP) of styrene and methyl methacrylate to form SBS and MBM triblock copolymers. Triblock structure was confirmed by selective PBD degradation. In addition, the tandem ROMP-ATRP approach was successfully extended to a "one-pot" synthesis.

Introduction

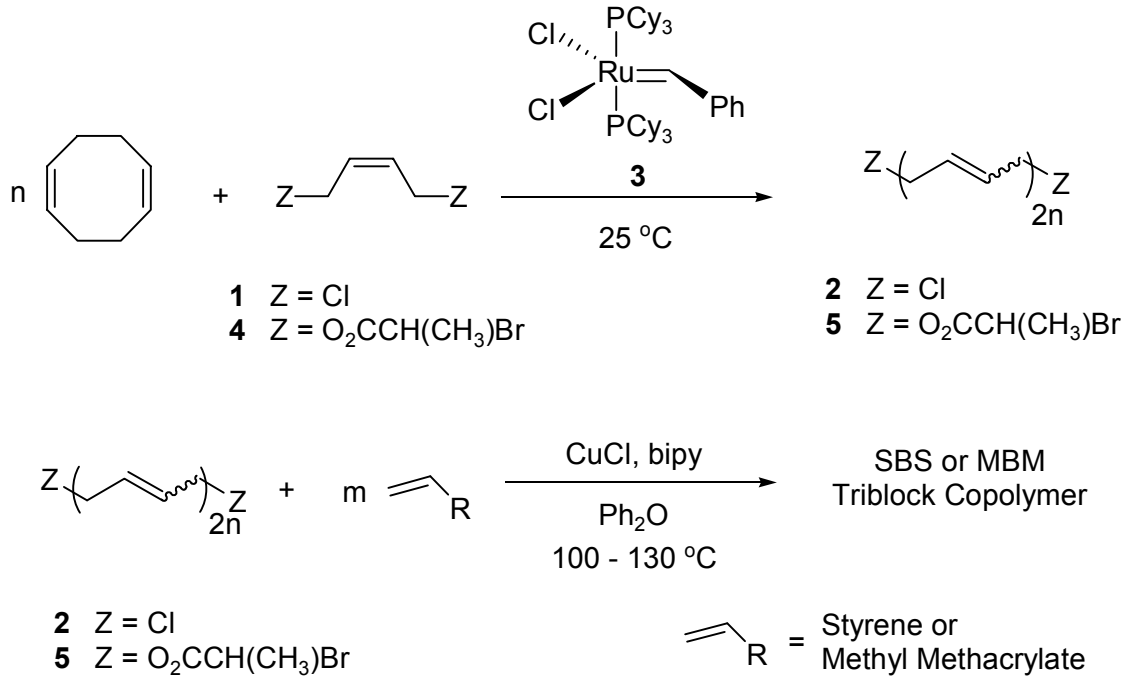
Recently, great attention has been directed toward the synthesis of ABA triblock copolymers that function as thermoplastic elastomers.[1-4] Thermoplastic elastomers such as poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene) (SBS) triblock copolymers have been known for over three decades and have found many commercial applications.[2] However, since the useful service temperature of these polymers is limited by the glass transition temperature (T_g) of the poly(styrene) segments, there has been an increasing demand for thermoplastic elastomers that retain their function at higher temperatures.[3] Poly(methyl methacrylate)-*b*-poly(butadiene)-*b*-poly(methyl methacrylate) (MBM) triblock co-polymers have been considered alternatives, as the PMMA blocks should have a higher T_g than their analogous PS counterparts. Although well-defined MBM triblock copolymers have been synthesized[4] by Jérôme *et al. via* anionic polymerization methods, the elastomeric properties of these copolymers are limited by a relatively high 1,2-PBD content (> 40%) formed during the polymerization.

Ring-opening metathesis polymerization (ROMP) is a well-known technique for the preparation of telechelic PBDs with 100% 1,4 microstructures.[5] For example, the ROMP of 1,5-cyclooctadiene (COD) in the presence of an appropriate chain transfer agent (CTA) has provided routes to telechelic PBDs end-capped with amino, hydroxy, methacrylate, and carboxy functional groups.[6]

The integration of ROMP with other polymerization methods such as atom transfer radical polymerization (ATRP),[7] a controlled radical polymerization process, has permitted the preparation of novel block copolymers. For example, this approach has successfully been used to synthesize poly(styrene)-*b*-poly(norbornene) and poly(methyl

acrylate)-*b*-poly(norbornene) diblock copolymers.[8] In these cases, the ROMP of norbornene was terminated with an agent that could also function as an ATRP initiator. While this was found to be an effective route for preparing diblock copolymers, the synthesis of triblock copolymers requires a telechelic polymer[9] with initiating groups on *both* ends.

This report describes the synthesis and characterization of two new telechelic PBDs prepared by ROMP. The polymers were endcapped with allyl chloride[10] or 2-bromo propionyl ester[11] groups, known ATRP initiators. The utility of these macroinitiators in the ATRP of styrene and methyl methacrylate to prepare SBS and MBM triblock copolymers with 100% 1,4-PBD microstructures was investigated (Scheme 1).



Scheme 1. Synthesis of ABA triblock copolymers using ROMP and ATRP.

Results and Discussion

The ROMP of COD in the presence of the commercially available CTA 1,4-dichloro-*cis*-2-butene **1** (COD/CTA = 5/1) resulted in bis(allyl chloride) functionalized telechelic PBD **2**. Polymerization was performed in neat monomer at ambient temperature and initiated by ruthenium catalyst[5b] **3** ($[M]_0/[I]_0$ = 2000/1). After 24 hours, the solutions were poured into an excess of methanol to afford telechelic PBD **2** (M_n=2400, PDI=1.59) in 75% isolated yield. ^{1}H and ^{13}C NMR spectroscopies indicate that the polymer backbone contains a "perfect" 1,4-PBD microstructure.[12] 1,4-Linkages are highly ideal as they display elastomeric properties superior to 1,2-linkages.[1-4] Both ^{1}H and ^{13}C NMR spectroscopy supported an end-group functionality ratio (F_n) near 2.0, in accordance with previous results obtained by ROMP using symmetrically disubstituted olefin CTAs.[6a]

Telechelic PBD **2** was used to initiate the heterogeneous ATRP of styrene in the presence of CuCl/2,2'-bipyridine (bipy) (1/3 molar ratio) at 130 °C.[10] After 7 hours, the reaction mixture was diluted with tetrahydrofuran and poured into an excess of methanol to afford SBS triblock copolymer. Table 1 summarizes the polymerization results for a variety of styrene/macroinitiator ratios. Gel permeation chromatography (GPC) indicated the $M_{n,gpc}$ values of the SBS triblock copolymers agree with the theoretical molecular weights ($M_{n,theo}$) which were calculated based on monomer conversion and the assumption that each macroinitiator chain contained two allyl chloride end groups. In addition, the MW distributions were unimodal, with no detectable signal attributable to the starting macroinitiators (Figure 1). Lower PDIs could be obtained (1.25 *vs.* 1.45) by employing a more soluble bipy derivative (e.g., 4,4′-diheptyl-2,2'-bipyridine). The SBS

triblock copolymers were also characterized by ^{1}H and ^{13}C NMR spectroscopy which indicated that the 1,4-PBD microstructure of the macroinitiator was conserved.[13]

Table 1. Synthesis of SBS and MBM triblock copolymers *via* ATRP of styrene and methyl methacrylate using telechelic PBDs **2** and **5** as ATRP macroinitiators.[a]

Polymer	$[M]_0/[I]_0$[b]	$M_{n,theo}$[c]	$M_{n,gpc}$[d]	$M_{n,nmr}$[e]	PDI	% Conv[f]	Yield[g]
SBS	20	4200	4800	4300	1.48	88	75
SBS	40	6500	7300	6900	1.45	99	99
SBS	80	10200	10100	12300	1.45	93	93
SBS	120[h]	14900	13800	15900	1.52	97	89
SBS[i]	80[j]	8100	8000	8500	1.63	73	70
SBS[k]	80	10100	10000	10400	1.25	92	90
MBM	20	4400	9400	4700	1.58	86	77
MBM	80	10600	18100	11500	1.54	99	90
MBM	180	20600	28300	23900	1.59	99	88
MBM	360[h]	38700	39600	41700	1.68	99	99

[a] General reaction conditions: Initiator/CuCl/bipy = 1/2/6, Ph_2O as solvent, N_2 atmosphere. For SBS synthesis: 130 °C, 7 h, telechelic PBD **2** MW (NMR)=2400, PDI=1.59. For MBM synthesis: 100 °C, 2.5 h, telechelic PBD **5** MW (NMR)=2700, PDI=1.57. [b] Initial monomer/macroinitiator ratio. $[I]_0$ = 50 mM for SBS, 25 mM for MBM. [c] Calculated based on monomer conversion and assumes F_n=2.0. [d] Relative to PS (SBS) or PMMA (MBM) standards in THF. [e] Determined by ^{1}H NMR spectroscopy using end-group analysis. [f] Determined by GC. [g] Isolated yield. [h] Reaction performed in bulk monomer. [i] "One-pot" synthesis. PBD **2** MW was assumed to be 2400. Air atmosphere. Styrene contained BHT. [j] Ratio is approximated. [k] 4,4′-diheptylbipyridine was used in lieu of bipy.

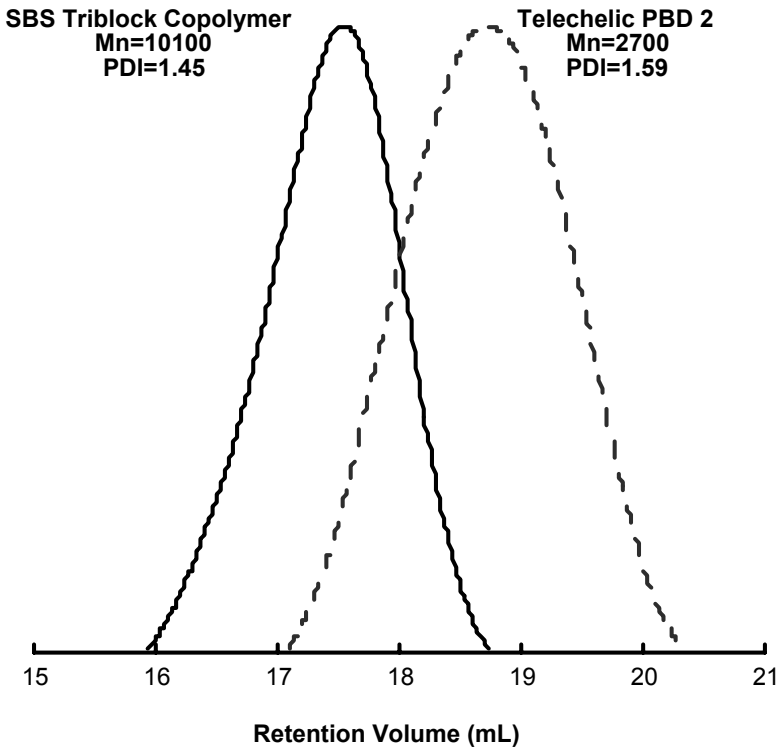


Figure 1. Representative GPC traces of PBD **2** (dotted line) and SBS (solid line) synthesized by ATRP of styrene initiated with **2** (catalyzed with CuCl/bipy). Molecular weights are reported relative to PS standards.

Since GPC and ^{1}H NMR spectroscopy do not allow discrimination between diblock and triblock copolymers of identical MW, a characterization method based on the cleavage of the PBD segment was used to determine block arrangement.[14] Selective PBD degradation of a SBS polymer (M_n=12300) with OsO_4/H_2O_2 gave PS (T_g = 91 ˚C) with $M_{n,\ gpc}$=4900 (PDI=1.23), as expected for a triblock structure. No PBD was observed in

the ^{1}H NMR spectra of these degraded samples, indicating that the degradation was complete.

Radical polymerizations must generally be carried out under inert atmospheres to prevent reaction of oxygen with free radicals and catalyst. However, Matyjaszewski *et al.* have recently shown[15] that ATRP can be carried out in a closed system under an atmosphere of air and in the presence of radical scavengers when Cu^{0} (combined with small amounts of CuX_2) is used in lieu of Cu^{I} halide salts. The application of this technique toward our system permitted the synthesis of SBS triblock copolymers *via* a "one-pot" procedure. Telechelic PBD **2** was prepared as above with an assumed MW of 2400 and yield of 75% based on prior results. After terminating the ROMP of COD by the addition of ethyl vinyl ether,[5b] the flask was charged with appropriate amounts of phenyl ether, styrene, bipy, copper powder, and $CuBr_2$ under air, capped, and then heated to 130 °C for 7 hours. As shown in Table 1, monomer conversion was lower than the analogous two-step synthesis described above, presumably due to relatively more dilute conditions. However, good agreement between the theoretical and the experimental MW was observed.

Attempts at preparing MBM triblock copolymers using PBD **2** as the macroinitiator for the ATRP of MMA resulted in bimodal distributions in the GPC traces. In these cases, the low MW peaks were in the MW range of unreacted macroinitiator, suggesting that the high MW peak corresponded to a mixture of triblock and diblock copolymers. The bimodality was presumably due the initiation rate being slower than propagation. This was supported by a decrease in the low MW peak area with monomer

conversion, and the observation of residual allyl chloride resonances in the ^{1}H NMR spectra of the isolated polymers.

The problem of inefficient initiation was overcome by the incorporation of 2-bromopropionate, a known[11] MMA initiator, into the CTA used during the ROMP of COD. The ROMP of COD in the presence of CTA **4** was performed in a similar manner as above and resulted in bis(2-bromopropionate) functionalized telechelic PBD **5** (M_n=5500, PDI=1.57) in 80% yield. ^{1}H and ^{13}C NMR spectroscopy indicated the presence of only 1,4-PBD linkages in the polymer backbone[12] and supported a F_n near 2.0. Telechelic PBD **5** was used as a macroinitiator for the heterogeneous ATRP of MMA to produce MBM triblock copolymers. The polymerizations were run under similar conditions as for the synthesis of SBS (CuCl/bipy catalyst system) using a variety of MMA/macroinitiator ratios (Table 1). The ^{1}H NMR spectra of the MBM triblocks revealed no change in the PBD microstructure relative to the PBD **5** macroinitiator.[13] GPC data (Figure 2) indicated that the MBM triblock copolymer MW distributions were unimodal and low (*ca.* 1.6). Selective PBD degradation[14] suggested a triblock structure[16] and provides evidence that discrepancies between the $M_{n,gpc}$ of the MBM triblock copolymers and the theoretical $M_{n,theo}$ were due to differences in the hydrodynamic volumes of MBM and the PMMA standards used for GPC calibration. To the best of our knowledge, this is the first report of a well-defined MBM triblock copolymer containing a 100% 1,4-PBD microstructure.

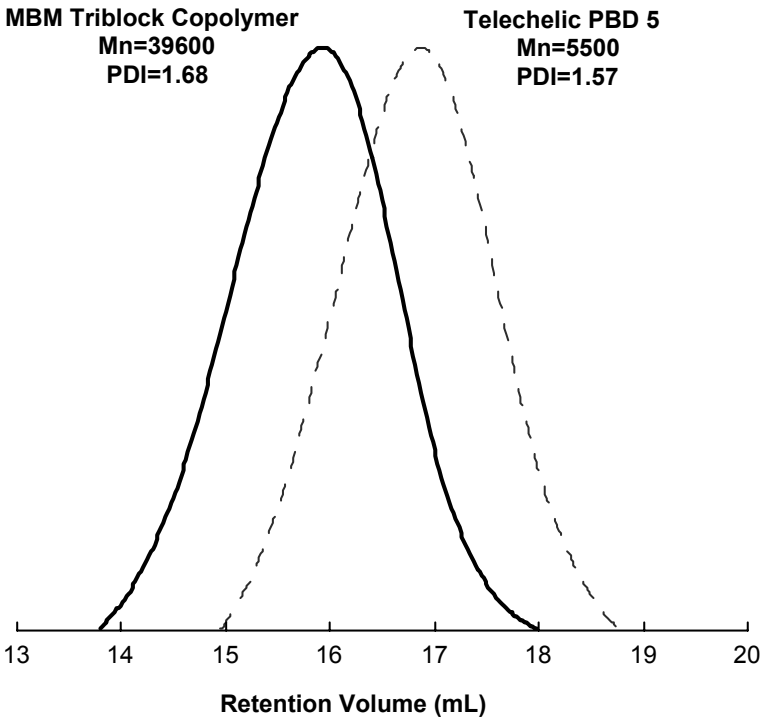


Figure 2. Representative GPC traces of PBD **5** (dotted line) and MBM (solid line) synthesized by ATRP of MMA initiated with **5** (catalyzed with CuCl/bipy). Molecular weights are reported relative to PMMA standards.

The thermal properties of the SBS and MBM triblock copolymers synthesized in this work were analyzed using differential scanning calorimetry (DSC). The T_g of the PBD segments appeared at –108 ˚C, indicating a high 1,4-microstructure. Unfortunately, the phase transition of the PS or PMMA segments occurred over a very broad temperature range preventing an accurate determination of the T_g.[17] This behavior has

been previously observed with other low molecular weight SBS triblock copolymers and may result from high compatibility between the PBD and PS microphases.[18]

Conclusion

The synthesis of telechelic PBDs with allyl chloride or 2-bromopropionate end-groups by the ROMP of COD in the presence of an appropriate CTA has been described. These polymers serve as bifunctional macroinitiators for the ATRP of styrene or MMA to form well-defined SBS and MBM triblock copolymers with 100% 1,4-PBD microstructures.

References and Notes

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(12) The PBD macroinitiator contained approximately 64% cis-olefin by ^{1}H NMR spectroscopy.

(13) No change in the cis/trans ratio of the PBD segment in the triblock copolymers relative to the PBD macroinitiators was found by ^{1}H NMR spectroscopy.

(14) Yu, Y. S.; Jérôme, R.; Fayt, R.; Teyssie, Ph. *Macromolecules* **1994,** *27,* 5957.

(15) Matyjaszewski, K.; Coca, S.; Gaynor, S. G.; Wei, W.; Woodworth, B. E. *Macromolecules* **1998,** *31,* 5967.

(16) For example, degradation of an MBM sample (M_n = 23900) gave PMMA with a M_n=12200, PDI = 1.51 (T_g = 92 ˚C).

(17) The MBM triblock copolymers showed distinctive T_g's between 115-125 ˚C on the first heating cycle, which broadened upon additional thermal cycling. Thermal analysis of these polymers using other methods are currently in progress.

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Chapter 7

Expedient Routes to Mechanistically Incompatible Block Copolymers Using Single Component Ruthenium Complexes[†]

Abstract

The synthesis of a multi-functional Ru based complex that was found to be effective in mediating both the ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene and the atom-transfer radical polymerization (ATRP) of methyl methacrylate is described. Using this complex, both polymerizations could be performed in "one pot" to form poly(butadiene)-*b*-poly(methyl methacrylate) block copolymers with tunable molecular weights and low polydispersities (1.5-1.6). In the presence of excess PCy_3, the polymerizations occurred simultaneously and appeared to be mediated by a single species. Introduction of hydrogen at the conclusion of the polymerizations transformed the complex into a species capable of hydrogenating a high degree (75-95%) of the unsaturation in the polymer backbone.

Introduction

Organometallic catalysts are traditionally designed and optimized to mediate a single reaction.[1] As the number of applications that require combinatorial and other high-speed synthetic protocols increases,[2] it will become desirable for catalysts to mediate multiple, mechanistically distinct transformations directly or upon simple modification. As an example of such a system, we demonstrate the ability of single component pre-catalysts to mediate up to three different reactions to form well-defined block copolymers.

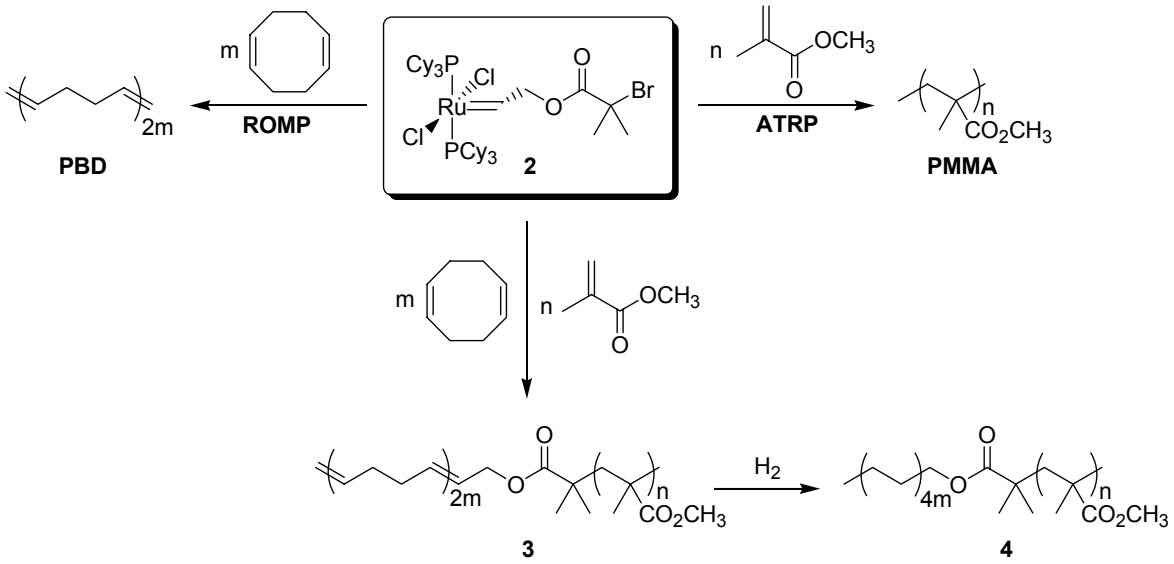
The preparation of block copolymers composed of segments that cannot be prepared by the same polymerization mechanism remains a challenge in synthetic polymer chemistry.[3] Thus, many new strategies have emerged which are based on using substrates that are capable of initiating more than one type polymerization. In general, various "controlled"/living radical polymerization methods[4] have been combined with ionic or ring-opening polymerization.[5] However, while a few of these protocols permit the combination of all the desired monomers at the beginning of the polymerization, the majority require timed additions (i.e., one polymerization must finish before another can begin).[6] Furthermore, in addition to the initiator, a number of organometallic complexes and co-catalysts must be included to control the polymerizations. Ultimately, it would be desirable to have the necessary catalyst(s) and initiator(s) in a single component system; therefore requiring only the addition of desired monomers (preferably at the same time) to form block copolymers.[7]

Results and Discussion

The ruthenium-based catalyst, $Cl_2(PCy_3)_2Ru=CHPh$ (**1**), is effective for initiating the ring-opening metathesis polymerization (ROMP) of a variety of cyclic olefins.[8] Recently, Noels and co-workers demonstrated that **1** is also an effective catalyst for the atom-transfer radical polymerization (ATRP) of methyl methacrylate.[9] We proposed that a difunctional complex that incorporates both a ROMP and an ATRP initiator could mediate both polymerizations simultaneously.[10] A variety of such complexes that met these requirements (**2**) were conveniently prepared from readily available allyl propionate and butyrates esters 2-bromo-2-methylpropionate[11] and **1** in 75% isolated yield using previously reported methods.[8a] Furthermore, at the conclusion of the aforementioned polymerizations, we reasoned that the residual ruthenium species could be transformed into a catalyst capable of hydrogenating the unsaturation in the polymer backbone (formed during the ROMP of the cyclic olefin).[12]

As shown in Scheme 1, initial investigations confirmed that the complexes could initiated ROMP and ATRP independently. For example, the ROMP of 1,5-cyclooctadiene (COD) in solution or bulk afforded poly(cyclooctadiene), equivalent to poly(butadiene) (PBD), in yields ranging from 85 to 95% and with polydispersity indices (PDIs) near two (Table 1). As expected, these results were similar to those obtained when $Cl_2(PCy_3)_2Ru=CHPh$ (**1**) was used as the ROMP initiator.[8] Similarly, addition of MMA to a solution of **2** in toluene afforded poly(methyl methacrylate) (PMMA) after 18 hours at 65 ºC (75% yield, Table 1). In addition, a linear relationship between monomer conversion and polymer molecular weight was observed which suggested **2** effectively controlled the polymerization. However, as observed in other ruthenium-based ATRP

systems, the molecular weights were higher than expected which may be related to the initiation efficiency.[9,12] Nevertheless, nearly monodispersed polymers (PDI<1.2) were obtained. To the best of our knowledge, **2** is the first example of a complete ATRP system containing both the transition metal mediator and the radical initiator, all in a single complex.



Scheme 1. A single-component pre-catalyst can be used to mediate up to three reactions. Ru complex 2 is effective in mediating ring-opening metathesis polymerization (ROMP) and atom transfer radical polymerization (ATRP), either independently or simultaneously. At the conclusion of these polymerizations, H_2 can be added to form a Ru hydride complex *in situ*.

Table 1. Synthesis of homopolymers and block copolymers.[a]

Polymer	t[b]	F_{MMA}[c]	% Yield[d]	$M_{n,th}$[e]	$M_{n,gpc}$[f]	PDI
PMMA	18	100 (100)	75	9100	12600	1.2
PBD	18	0 (0)	91	5000	6200[g]	2.1
3a	18	43 (42)	65	9400	9700	1.5
3b	24	42 (42)	71	7500	8500	1.6
3c[h]	30	37 (38)	58	6300	7700	1.6
3d	18	73 (77)	68	15440	14500	1.5
3e	18	16 (18)	82	20480	17300	1.6

[a] General polymerization conditions: 65 ºC, nitrogen atmosphere, toluene as solvent, $[\mathbf{2}]_0$=20-40mM, $[MMA]_0$=0.9-3.9 M, $[COD]_0$=1.0-3.8 M. [b] Reaction time (hours). [c] Molar percent of MMA in the total monomer feed. The value in parenthesis is the molar percent of MMA found in the polymer as determined by ^{1}H NMR spectroscopy. [d] Isolated yield (%). [e] Theoretical molecular weight based on percent conversion as determined using gas chromatography. [f] Molecular weight relative to monodispersed PMMA standards in CH_2Cl_2. [g] Molecular weight relative to monodispersed PBD standards in CH_2Cl_2. [h] THF was used as solvent.

As summarized in Table 1, **2** was employed in the "one pot" copolymerization of COD and MMA under a variety of conditions. After 18-30 h, the reaction mixtures were poured into excess methanol to afford polymer in yields of 58-82%. Analysis of the resulting polymers by ^{1}H NMR spectroscopy indicated the presence of both PBD and PMMA in the expected ratios based on percent conversion. Gel permeation chromatography (GPC) suggested that PBD-PMMA diblock copolymers (**3**) were formed

as monomodal polymer distributions were observed (PDI 1.5-1.6) with apparent molecular weights in qualitative agreement with their theoretical values.[13] To verify that the copolymers were structurally diblock, isolated copolymer **3d** (Table 1) was treated with OsO_4/H_2O_2 to completely degrade the PBD segment.[14] The molecular weight of the remaining PMMA (M_n=15800, PDI=1.2) was found to be in agreement with the value expected[15] (M_n=16100) based on the amount of monomer consumed during the polymerization.[16]

The ability of a single metal complex to mediate two different types of polymerizations was further explored. The large differential rate between the ROMP of COD ($k_{obs}=3.5x10^{-3}$ s^{-1}) and the ATRP of MMA ($k_{obs}=1.2x10^{-5}$ s^{-1}) indicated that the polymerizations occurred in tandem.[17] However, the rates were nearly identical (ROMP: $k_{obs}=3.6x10^{-5}$ s^{-1} vs. ATRP: $k_{obs}=3.7x10^{-5}$ s^{-1}) when excess PCy_3 (10 equivalents) was added to the reaction mixture (Figure 1).[18] Furthermore, these copolymerization rates were comparable to the individual homopolymerization rates performed separately in presence of PCy_3.[19] This suggested that a single ruthenium alkylidene complex successfully mediated two mechanistically distinct polymerizations, *simultaneously*.[20]

At the conclusion of a COD/MMA copolymerization using **2**, the reaction vessel was exposed to a constant hydrogen pressure (150 psi, 65 ºC) for 8 h. We propose that under an atmosphere of hydrogen the residual ruthenium species were transformed[21] into $Ru(H_2)(H)Cl(PCy_3)_2$, a known[22] hydrogenation catalyst.[11] The extent of the hydrogenation was determined to be approximately 75% by ^1H NMR spectroscopy. The degree of hydrogenation increased to greater than 95% when THF was included, which may help attenuate bimolecular decomposition pathways through coordination.[23] This

provides an extremely efficient route to copolymers composed of poly(ethylene) and PMMA (**4**).[24]

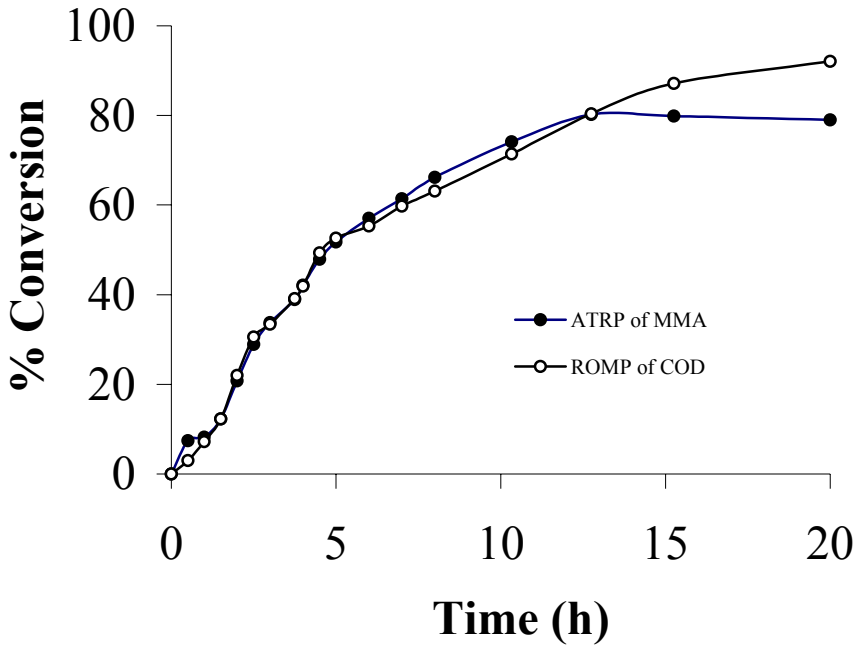


Figure 1. ROMP of COD and ATRP of MMA monitored using ^{1}H NMR spectroscopy. Conditions: $[\mathbf{2}]_0$=0.03 M, $[PCy_3]$=0.30 M, $[COD]_0=[MMA]_0$=0.75 M, in toluene-d_8, 65 ºC.

Conclusion

In summary, the ability of a single multifunctional complex, i.e., $Cl_2(PCy_3)_2Ru{=}CHCHCH_2OC(=O)C(CH_3)_2Br$ (**2**), to mediate three mechanistically distinct reactions was demonstrated. The complex was effective in initiating and mediating both the ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene and the atom-transfer radical polymerization (ATRP) of methyl methacrylate. Under appropriate conditions, the polymerizations were simultaneously by

a single catalyst. This provided a highly efficient route poly(butadiene)-*b*-poly(methyl methacrylate) block copolymers with tunable molecular weights and low polydispersities (1.5-1.6). Furthermore, at the conclusion of the polymerizations, the complex can be transformed into a species capable of hydrogenating a high degree of the unsaturation in the polymer backbone.

Experimental Section

General information. All manipulations were performed in a N_2 filled drybox or using standard Schlenk techniques. Benzene, allyl 2-bromo-2-methylpropionate, and methanol were obtained from Aldrich and degassed by purging with Ar prior to use. $Cl_2(PCy_3)_2Ru{=}CHPh$ (**1**) was prepared as previously reported.[8] ^1H and ^{13}C NMR spectra were recorded on a GE-300 NMR spectrometer and are internally referenced to residual protio solvent. ^{31}P NMR spectra were recorded on a JEOL GX-400 NMR spectrometer and referenced to H_3PO_4 (external standard). IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Elemental analyses were performed at Midwest Microlab LLC., Indianapolis, IN.

Synthesis of $Cl_2(PCy_3)_2Ru{=}CHCH_2OC(=O)C(CH_3)_2Br$ (2). A solution of $Cl_2(PCy_3)_2Ru{=}CHPh$ (**1**) (550 mg, 0.67 mmol) in 15 mL benzene was treated with allyl 2-bromo-2-methylpropionate (740 mg, 3.5 mmol) at room temperature. A color change from purple to maroon was observed after 1 hour. The solvent was removed under vacuum, and the residue was repeatedly washed with ice-cold methanol (15 mL portions) until the filtrate was colorless and then dried under vacuum. A maroon microcrystalline

solid was obtained. Yield = 470 mg (75%). ^{1}H NMR (300 MHz, C_6D_6): δ 19.53 (t, *J*=3.7 Hz, 1H), 5.41 (d, *J*=4.4 Hz, 2H), 2.73 (bm, 6H), 2.03-2.00 (bm, 14H), 1.80 (s, 6H), 1.80-1.24 (bm, 46H). ^{13}C NMR (75 MHz, C_6D_6): δ 303.55 (s), 84.83 (s), 56.19 (s), 32.79 (t, *J*=9.2 Hz, *J*=9.7 Hz), 30.40 (s), 28.47 (t, *J*=5.1 Hz), 27.23 (s). ^{31}P NMR (122 MHz, C_6D_6): δ 37.3 (s). IR (KBr) 2929 (vs), 2852 (s), 1731 (vs, C=O), 1496 (w), 1445 (s), 1386 (w), 1346 (w), 1329 (w), 1265 (s), 1198 (w), 1152 (s), 1130 (w), 1109 (m), 1005 (m), 959 (w), 917 (w), 898 (w), 846 (m), 817 (w), 736 (m), 696 (w), 642 (w), 519 (w), 508 (w), 487 (w), 466 (w). Anal. Calcd for $RuCl_2P_2C_{42}H_{75}BrO_2$: C, 54.48; H, 8.16. Found: C, 54.40; H, 7.98. The crystal structure for this compound has been determined and its solid state structure is shown in Figure 2. Representative bond distances and bond angles are reported in Table 1.

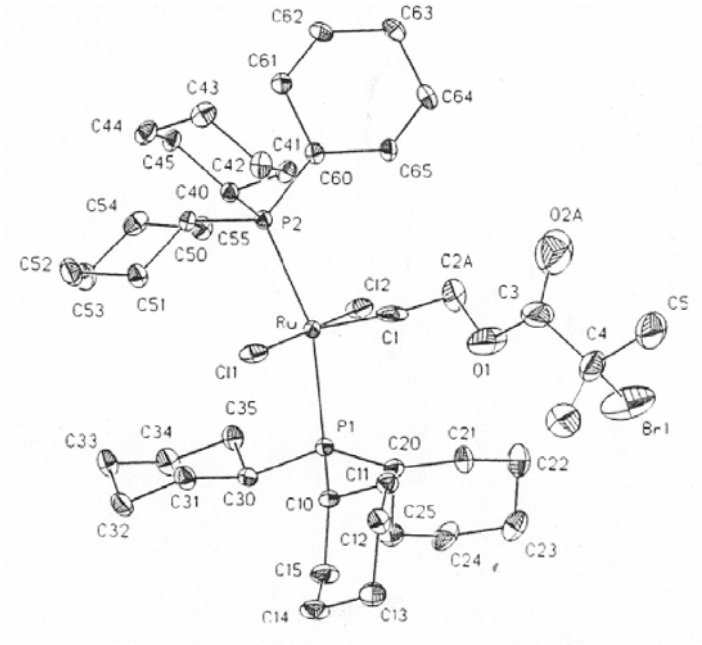


Figure 2. Labeled view of complex **2** with 50% probability ellopsoids.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for complex **2**.

	Bond Lengths (Å)		
Ru-C(1)	1.797(5)	Ru-P(1)	2.4071(12)
Ru-Cl(2)	2.3931(12)	Ru-P(2)	2.4134(12)
Ru-Cl(1)	2.3970(12)	Br(1)-C(4)	1.924(6)
C(1)-Ru-Cl(2)	90.9(3)	Cl(1)-Ru-P(1)	87.80(4)
	Bond Angles (deg)		
C(1)-Ru-Cl(1)	95.2(3)	C(1)-Ru-P(2)	102.18(16)
Cl(2)-Ru-Cl(1)	173.89(5)	Cl(2)-Ru-P(2)	87.20(4)
C(1)-Ru-P(1)	98.08(6)	Cl(1)-Ru-P(2)	91.61(4)
Cl(2)-Ru-P(1)	91.23(4)	P(1)-Ru-P(2)	159.70(4)

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(16) While secondary metathesis reactions could theoretically lead to the formation of PBD homopolymer and PMMA-PBD-PMMA triblock copolymers, we found no evidence for their existence by GPC or chromatographic analysis.

(17) The polymerization rates were determined using ^{1}H NMR spectroscopy; conditions: $[\mathbf{2}]_0$=0.03 M, $[COD]_0=[MMA]_0$=0.75 M, in toluene-d_8, 65 ºC.

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(20) No catalyst decomposition was observed over the course of the polymerizations.

(21) The addition of H_2 to complex **1** (or **2**) afforded $Ru(H)_2Cl_2(PCy_3)_2$ or $Ru(H_2)(H)Cl(PCy_3)_2$ depending on reaction conditions. Both complexes are effective hydrogenation precatalysts.[22] See also: Montserrat, O.; Caulton, K. G. *Inorg. Chem.* **1999**, *38*, 566.

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(23) Similar conclusions have been drawn using **1** immobilized on a silica support for the heterogeneous hydrogenation of olefins.[11b]

(24) Optically clear films were obtained by casting toluene solutions of the isolated PMMA-PE copolymers. This provides further support for efficient diblock formation.

Chapter 8

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.

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]

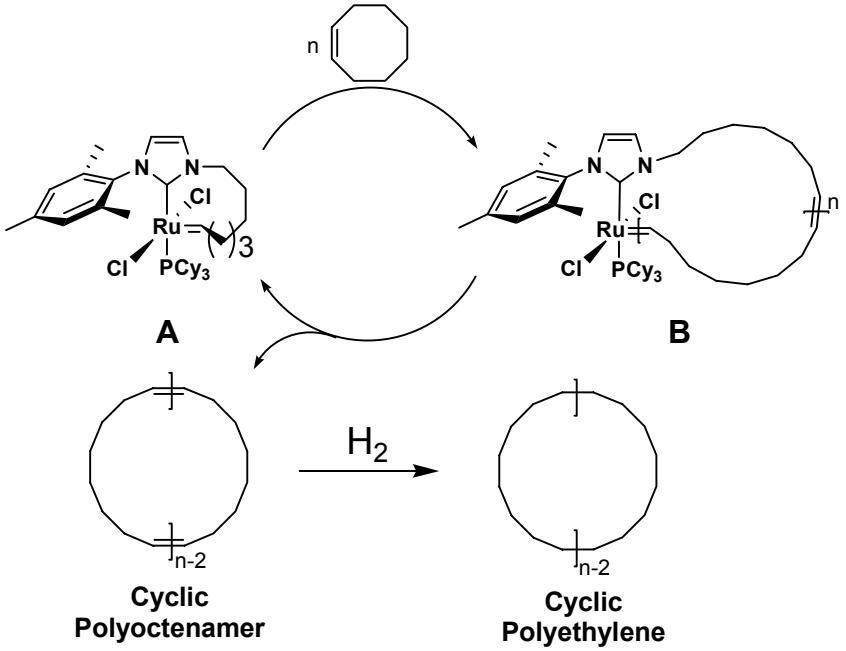
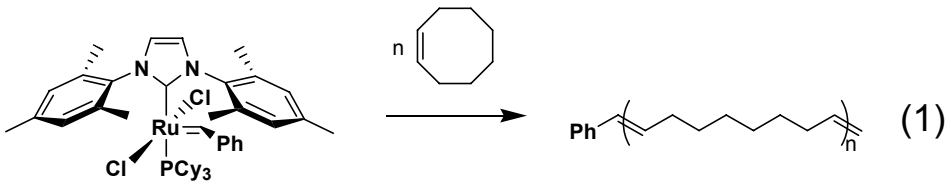


Figure 1. Synthesis of cyclic polymers using ring-opening metathesis polymerization. Addition of *cis*-cyclooctene (monomer) to cyclic complex **A** resulted in the transient formation of macrocyclic complex **B**. Subsequent intramolecular chain transfer provided cyclic polyoctenamer and regenerated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



Linear Initiator **Linear Polyoctenamer**

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 η 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.

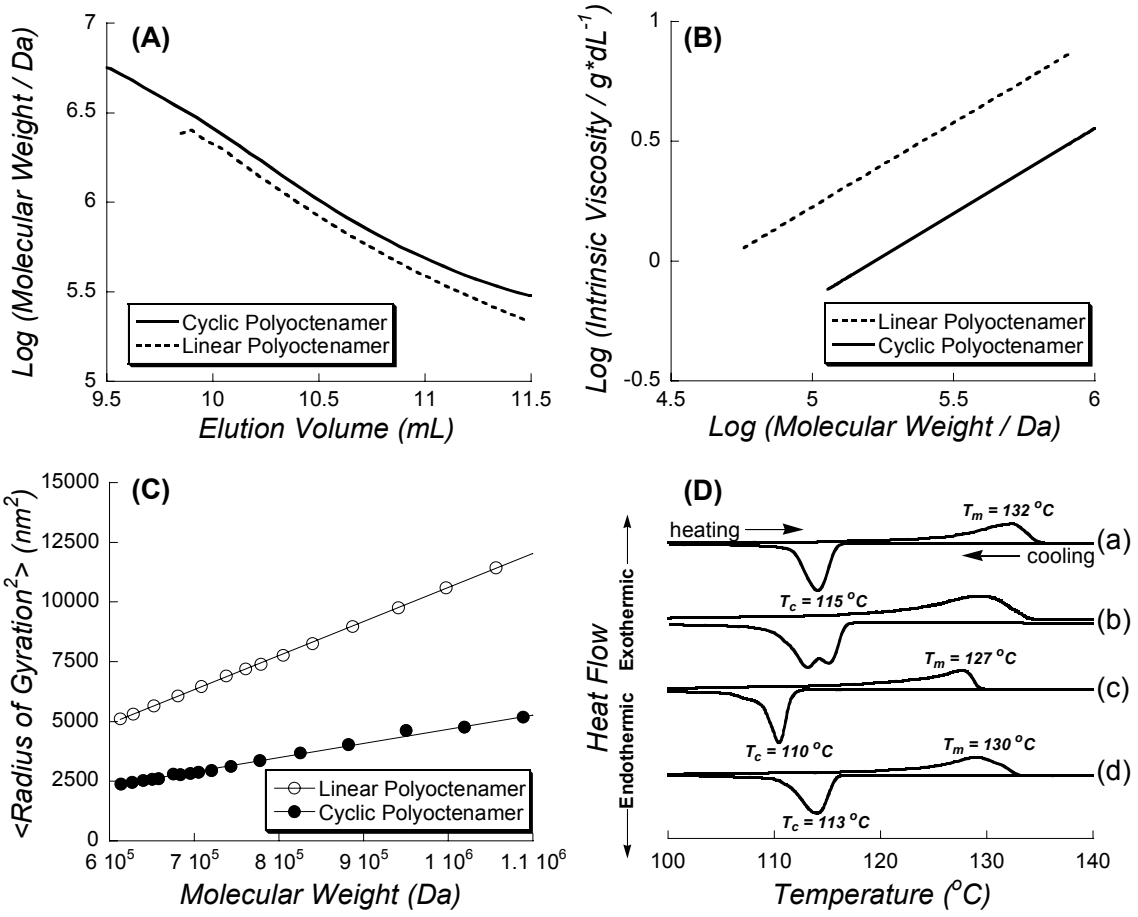


Figure 2. Comparison of the physical properties of the cyclic and linear polymers prepared in this work. (A) Plot of elution volume vs. molecular weight (eluent = THF; the reported molecular weights were determined by light scattering methods and are therefore considered absolute). (B) Plot of log η 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]

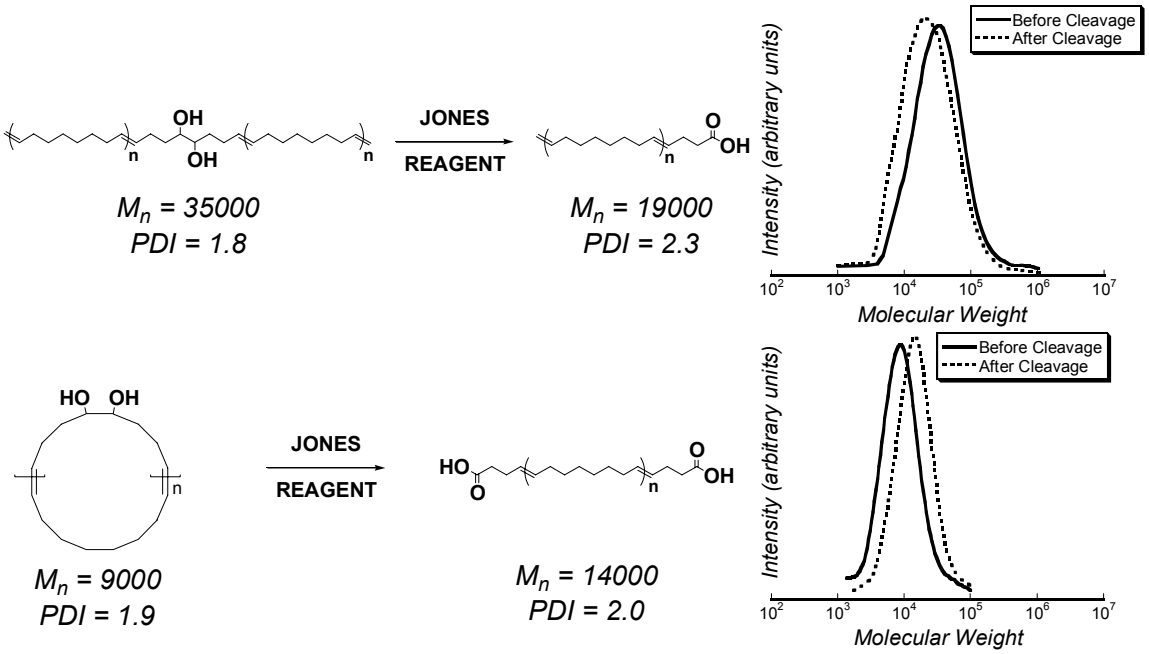


Figure 3. Cleavage experiments that aided in distinguishing between cyclic and linear polymers. Linear (top) and cyclic (bottom) polyoctenamers containing, on average, only one 1,2-diol unit per polymer chain were synthesized. Each polymer was separately reacted with Jones' Reagent (CrO_3/H_2SO_4) which 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.

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(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.

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

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(18) $[1,2\text{-Diol-5-cyclooctene}]_0/[cis\text{-Cyclooctene}]_0 = 25$; $[\text{Total Monomer}]_0 = 0.5$ 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.

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(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.

Chapter 9

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

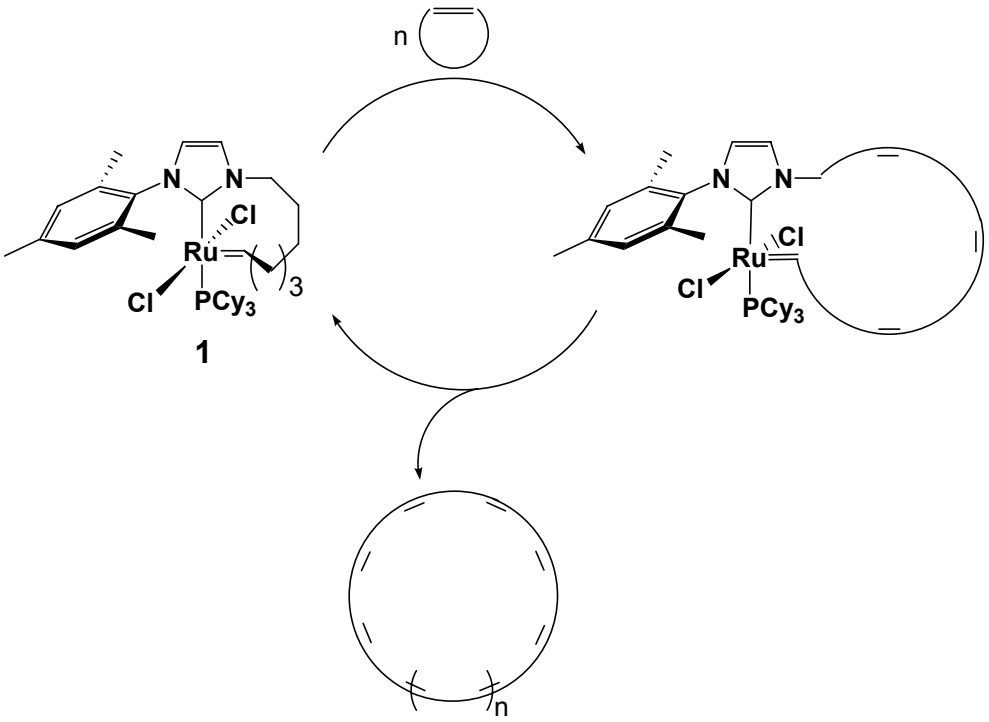
Abstract

Cyclic polybutadiene was synthesized via the ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene (COD) using a cyclic Ru catalyst $L(PCy_3)Cl_2Ru{=}CHR$ (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.

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.

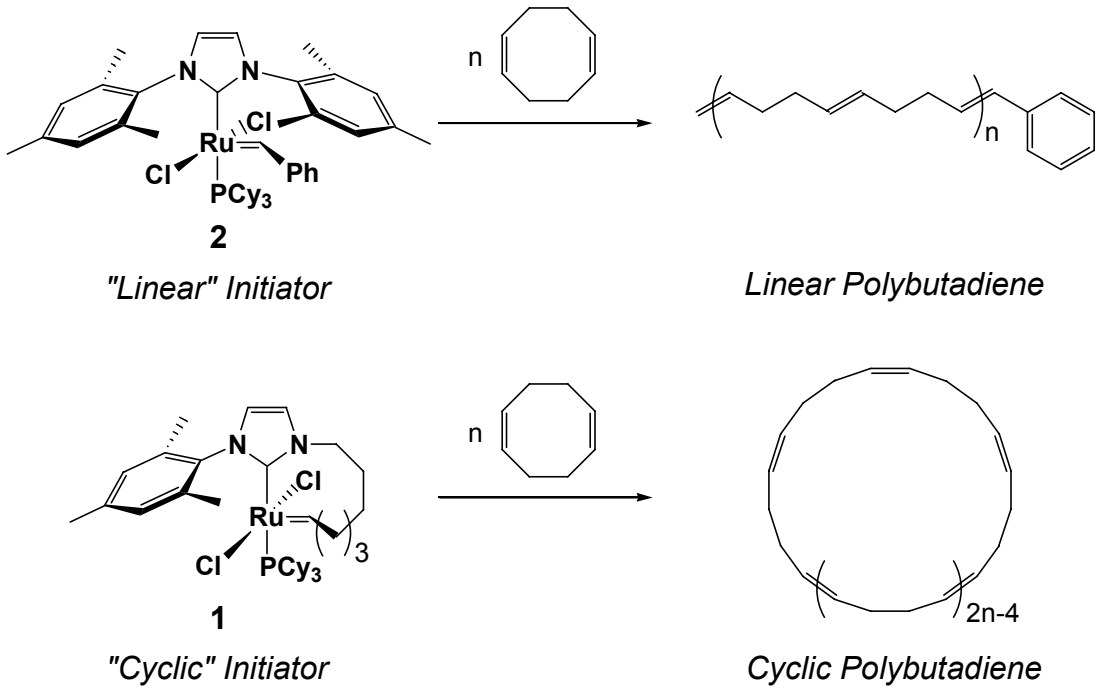
Recently, we reported an alternate approach to synthesizing cyclic polymers which involves no linear intermediates.[2] As shown in Scheme 1, upon the addition of a cyclic monomer to a "cyclic" analog[3] (**1**) of the olefin metathesis[4] catalyst $L(PCy_3)Cl_2Ru{=}CHPh$ (**2**) (L = 1,3-dimesitylimidazolyidene), 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 ($\tau_{1/2}$ ~ 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.

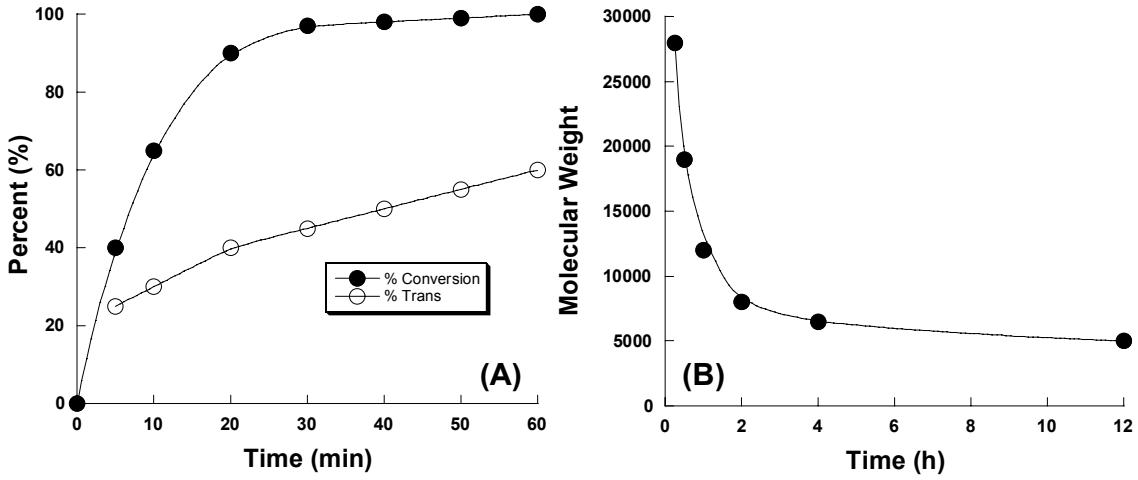


Figure 1. (A) Plot of monomer consumption and percent *trans* olefin in the polymer backbone *vs.* time. Conversions were monitored using gas chromatography. Olefin content was determined by ^{1}H NMR spectroscopy. (B) Plot of molecular weight (M_n) *vs.* time. The PDI at every point was between 1.7 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 ^1H 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 ([η]) 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: $g_M = \langle R_g^2 \rangle_{non\text{-}linear} / \langle R_g^2 \rangle_{linear}$. 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.

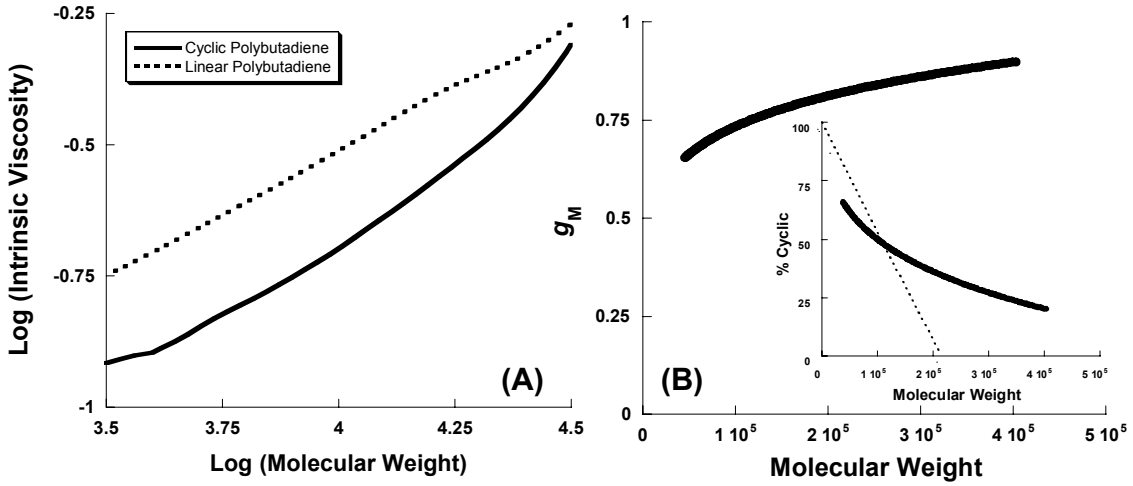


Figure 2. (A) Mark-Houwink Plot (Log IV vs. Log MW) of cyclic and linear polybutadienes. a (cyclic) = 0.71; a (linear) = 0.72. Conditions: Solvent = THF, Temp = 30 °C. (B) Plot of the ratio $g_M = \langle R_g^2 \rangle_{non\text{-}linear} / \langle R_g^2 \rangle_{linear}$ of polybutadiene prepared as 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 ($[COD]_0/[4\text{-vinylcyclohexene}]_0 = 25$).[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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(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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(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.