Synthesis of Functionalized Polymers by Ring-Opening Metathesis Polymerization (ROMP)

Thesis by

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To My Parents, Dianne, and Lady

Acknowledgments

I consider myself fortunate to have worked under the direction of Professor Bob Grubbs over the past four years. Bob has provided me not only with valuable guidance during my graduate studies, but also more importantly he has given me the freedom to learn independently through my own successes and failures. This freedom has shaped the chemist that I have become, and for that I am truly thankful. The lessons and experiences that I take with me from this group will be ones that I will never forget.

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During my thesis research, a number of other people have contributed significantly to my work. In the study on cross-linkable telechelic poly(butadiene)s in Chapter 2, I collaborated with Takeharu Morita. In addition to the respect that I have for him as a

chemist, I consider him a close friend as well. Dr. Eric Dias aided in the study of the functional group chelation described in Chapter 3. Collaborations with Marcus Weck and Dr. Bernhard Mohr led to the research in Chapter 4 on side-chain liquid crystalline polymers. Their considerable knowledge in this area and their interest in this project were the primary reasons for its success. Marcus has provided advice and insight into many of my other projects as well, for which I am grateful. Many other group members including Rob (Chump Change) Li, Martin Wagner, Bill Zuercher, Dave Lynn, Helen Blackwell, and Tom Kirkland deserve acknowledgment as well for many helpful discussions during the course of my work.

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Most importantly, I thank my parents and my wife, Dianne, for their love and support. Everything that I have achieved I owe to them.

Abstract

In Chapter 1, the ROMP of 5-methacrylate-1-cyclooctene and the copolymerization of this monomer with cyclooctadiene using the initiator $(PCy_3)_2Cl_2Ru{=}CHCH{=}CPh_2$ were investigated to produce polymers with cross-linkable side-chains. The impact of concentration, monomer to initiator ratio, and the amount of inhibitor in the polymerization was examined. These polymers were cross-linked through the methacrylate side-chains with either thermal or photochemical initiation, and the incorporation of these polymers into poly(methyl methacrylate) (PMMA) to produce AB cross-linked materials was accomplished. A comparison of the physical properties of PMMA and these new materials demonstrated that these materials had higher thermal stability and solvent resistance than pure PMMA.

As an extension of the work presented in Chapter 1, Chapter 2 illustrated an alternative approach for the preparation of cross-linkable polymers by ROMP. The synthesis of ring-opening metathesis polymerization chain transfer agents bearing methacrylate and epoxide end-functionality was accomplished. In the presence of these chain transfer agents, cyclooctadiene was polymerized via a ruthenium benzylidene initiator, $(PCy_3)_2Cl_2Ru{=}CHPh$, to produce telechelic poly(butadiene)s with either methacrylate or epoxide end groups. The impact of initiator concentration, reaction time, and temperature on the polymer yield and chain transfer agent incorporation was examined. Control over the polymer molecular weight through the cyclooctadiene/chain transfer agent ratio was demonstrated providing for a range of telechelic poly(butadiene) molecular weights. Successful cross-linking of these polymers by thermal or photochemical initiation in the case of the bis(methacrylate)-functionalized telechelic poly(butadiene)s or through acid catalysis in the case of the bis(epoxide)-functionalized telechelic poly(butadiene)s was accomplished.

In an effort to further explore the functional group tolerance of the ruthenium-based

metathesis initiators developed in our group, the investigation presented in Chapter 3 encompassed the synthesis and living ring-opening metathesis polymerization (ROMP) of substituted cyclobutenes with the functional group tolerant polymerization initiators $(PCy_3)_2Cl_2Ru{=}CHCH{=}CPh_2$ and $(PCy_3)_2Cl_2Ru{=}CHPh$. Synthetic methodology was developed for the synthesis of a wide variety of 3-functionalized cyclobutenes containing ether, ester, alcohol, amine, amide, and carboxylic acid substituents. Coordination of these functional groups to the propagating carbene was observed resulting in the formation of a chelated propagating species with concomitant loss of one phosphine ligand from the metal center. Studies aimed at understanding this chelation and its effect on the polymerization were undertaken. Based on these results, the synthesis of a series of functionalized cyclobutenes was accomplished which minimized this chelation and allowed for living polymerizations. A new class of functionalized poly(butadiene) homopolymers and diblock copolymers was synthesized and the thermal properties analyzed by thermogravimetric analysis and differential scanning calorimetry.

In Chapter 4, the effect of backbone flexibility on the mesomorphic behavior of side-chain liquid crystalline polymers synthesized by ring-opening metathesis polymerization was investigated. The synthesis of norbornene and cyclobutene monomers containing a *p*-nitrostilbene moiety as the mesogenic group and polymerization of these monomers with the metathesis initiator $(PCy_3)_2Cl_2Ru{=}CHPh$ to produce side-chain liquid crystalline polymers with low polydispersities and defined molecular weights was accomplished. The relatively rigid poly(norbornene)s displayed enantiotropic nematic mesomorphism with glass transitions from 44-64°C and isotropization temperatures between 108-121°C, whereas the more flexible poly(butadiene)s showed enantiotropic smectic A mesomorphism with glass transition temperatures from 14-31°C and isotropization temperatures between 74-111°C. A diblock copolymer containing a 1:1 mixture of the poly(norbornene) and poly(butadiene) backbones also exhibited a smectic A mesophase. The dependence of the degree of polymerization and flexible spacer length on

the phase transitions of these systems was determined demonstrating stabilization of the mesophase by both increasing molecular weight and flexible spacer length.

A short chapter on the development of methodology for an improved synthesis of 3-methyl-3-phenylcyclopropene was included in Appendix 1. This research was investigated in hopes of developing a more facile and inexpensive procedure for the preparation of this compound than has been previously reported. Phase transfer catalyzed dichlorocarbene addition to α-methylstyrene followed by a selective catalytic Bu_3SnH reduction resulted in the 1-chloro-2-methyl-2-phenylcyclopropane intermediate in excellent yield. Base-induced elimination of this compound resulted in the desired 3-methyl-3-phenylcyclopropene. This approach allowed for the preparation of this cyclopropene on large scale utilizing inexpensive reagents.

Table of Contents

List of Tables, Schemes, and Figures

Chapter 1

Chapter 2

Chapter 3

Tables

Schemes

Chapter 1:
Synthesis and Controlled Cross-Linking of Polymers Derived from the Ring-Opening Metathesis Polymerization (ROMP) of 5-Methacrylate-1-cyclooctene

Abstract

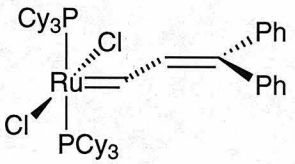
The ROMP of 5-methacrylate-1-cyclooctene and the copolymerization of this monomer with cyclooctadiene were investigated to produce polymers with cross-linkable side-chains. The impact of concentration, monomer to initiator ratio, and the amount of inhibitor in the polymerization was examined. These polymers were cross-linked through the methacrylate side-chains with either thermal or photochemical initiation, and the incorporation of these polymers into poly(methyl methacrylate) (PMMA) to produce AB cross-linked materials was accomplished. A comparison of the physical properties of PMMA and these new materials demonstrated that these materials had higher thermal stability and solvent resistance than pure PMMA.

Introduction

In recent years, cross-linkable polymers have found a wide demand in the areas of interpenetrating polymer networks,[1] non-linear optical materials,[2] macro- and microlithography,[3] and in the formation of more thermally and chemically resistant materials.[4] Polymers with siloxane,[5] vinyl,[6] acrylate,[7] and phosphazene[8,9] backbones are but a few examples of materials that have been synthesized with reactive cross-linkable side-chains.

One of the most widely employed cross-linkable side-chains is the cinnamate group which undergoes controlled photo-induced [2+2] dimerization, as demonstrated in the above examples. However, a more versatile cross-linkable side-chain is the methacrylate group, which polymerizes both thermally and photochemically in the presence of free radical initiators and photo-sensitizers, respectively. The methacrylate group has found many applications in the UV curing of photoresists,[10] coatings, and printing inks.[11-13] Due to the sensitivity of many metathesis initiators to functional groups, the use of ROMP in the formation of these cross-linkable polymers has been limited. However, the development of the new functional group tolerant initiators $(PCy_3)_2Cl_2Ru{=}CHR$ [14-16] has allowed for the ROMP of a series of functionalized cyclooctenes.[16,17] The high functional group tolerance of these initiators has prompted an investigation of the use of ROMP in the formation of cross-linkable polymers.

In this study, 5-methacrylate-1-cyclooctene was synthesized and polymerized by initiator **1** resulting in an alternating terpolymer of poly(butadiene), poly(ethylene), and poly(vinyl methacrylate) with cross-linkable side-chains spaced on average every eight



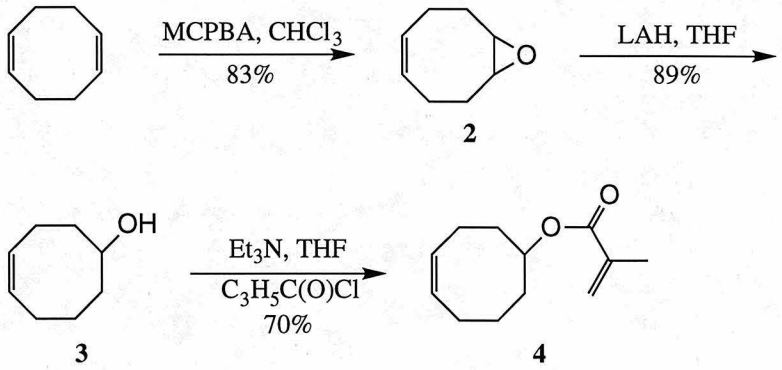
1

carbons. In addition, this monomer was copolymerized with cyclooctadiene (COD), the homopolymer of which is poly(butadiene), at varying feed ratios to systematically vary the number of methacrylate groups per chain. Rapid cross-linking of these polymers was accomplished both thermally and photochemically. Reaction of this multifunctionalized methacrylate polymer with methyl methacrylate under free radical polymerization conditions led to the formation of new AB cross-linked systems of poly(methyl methacrylate) (PMMA).

Results and Discussion

Synthesis of 5-methacrylate-1-cyclooctene. Synthesis of 5-methacrylate-1-cyclooctene (**4**) was accomplished in three steps from commercially available COD (Scheme 1). Epoxidation with *m*-chloroperbenzoic acid (MCPBA) in chloroform afforded compound **2** in 83% yield. Reduction of **2** to the alcohol **3** using lithium aluminum

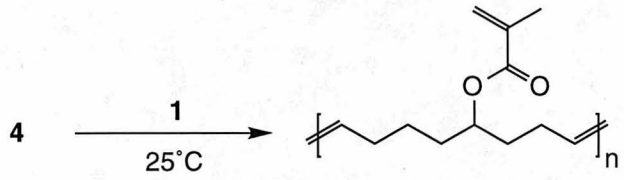
Scheme 1



hydride (LAH) proceeded in 89% yield. Subsequent esterification of **3** using methacryloyl chloride and triethylamine provided 5-methacrylate-1-cyclooctene (**4**) in 70% yield. With an overall yield of 52% in only three steps, this synthesis allowed for the large scale preparation of **4**.

Initial polymerization studies. Initial polymerizations were carried out as shown in Scheme 2. Gel formation was observed during the polymerization when THF,

Scheme 2



benzene, toluene, or methylene chloride was used as solvent. The polymer isolated from this gel was insoluble in all common organic solvents and was presumed to be highly cross-linked. Free radical cross-linking of this side-chain was one plausible explanation for the observed gelation. Another possible mechanism of cross-linking was the metathesis-mediated dimerization of the pendant methacrylate groups. Polymerizations under dilute concentration (0.75 M) afforded a 40% yield of polymer. This polymer had a broad, multimodal molecular weight distribution with a $\overline{M}_n$ of 16,500 and a PDI of 14.9, much broader than the PDI of ~2.0 expected for this polymerization. A PDI of ~2.0 should result for this type of polymerization in which the polymer chains are in equilibrium through chain transfer and backbiting reactions.[4] This polymer cross-linked on standing overnight at room temperature to yield an insoluble solid regardless of whether stored neat or in solution, even when shielded from light in an inert atmosphere.

***p*-Methoxyphenol (MEHQ) as a free radical inhibitor.** To establish the free radical nature of the cross-linking process, the polymerizations were studied in the presence of a free radical inhibitor. The effect of the inhibitor MEHQ on the polymerization was thus examined (Table 1).[18] When 18 mol% MEHQ was used, polymers with monomodal molecular weight distributions were formed in moderate yields.[19] Use of less than 18 mol% MEHQ in the polymerization again resulted in broad, multimodal molecular weight distributions. These results supported the free radical mechanism of cross-linking.

The effect of the monomer to initiator ([M]/[I]) ratio on the polymerization was studied (Table 2). Only in the case of high [M]/[I] ratios were monomodal polymers

Table 1. Effect of mol% MEHQ on the polymerization

[M]	[M]/[I]	Rxn. Time (h)	Mol% MEHQ	% Yield[a]	$\overline{M}_n$[b]	PDI
0.75 M	1383	12	18	44	21200	3.15[c]
0.75 M	1329	12	9	47	14000	13.9[d]
0.76 M	1344	12	0	42	16500	14.9[d]

[a] Isolated yields after purification. [b] Determined by Gel Permeation Chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards. [c] Monomodal molecular weight distribution. [d] Multimodal molecular weight distribution.

obtained which were stable to cross-linking. An explanation for this observed dependence of the polymer properties on the [M]/[I] ratio will be discussed in the next section.

Table 2. Effect of [M]/[I] ratio on the polymerization

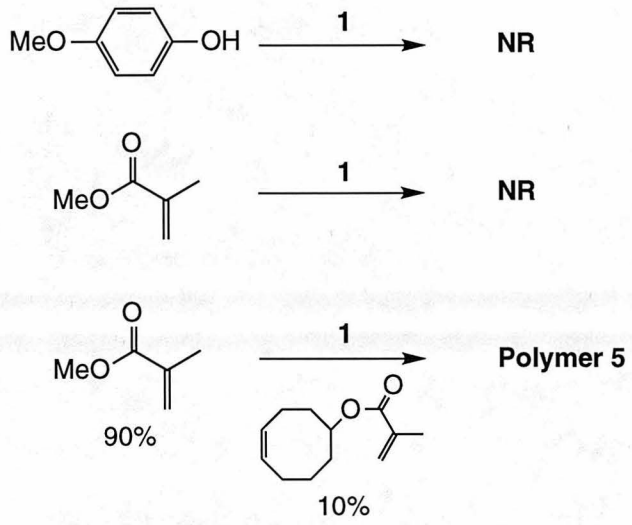
[M]	[M]/[I]	Rxn. Time (h)	Mol% MEHQ	% Yield[a]	$\overline{M}_n$[b]	PDI[b]
0.75 M	850	12	18	52	13800	13.9[c]
0.75 M	1383	12	18	44	21200	3.15[d]
0.75 M	1574	12	18	30	15700	4.02[d]

[a] Isolated yields after purification. [b] Determined by Gel Permeation Chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards. [c] Multimodal molecular weight distribution. [d] Monomodal molecular weight distribution.

Exclusion of the metathesis-based mechanism of cross-linking. To conclusively exclude the mechanism of cross-linking through metathesis-mediated dimerization of the pendant methacrylate groups, several control experiments were run. A mixture of the initiator and methyl methacrylate (MMA) (**6**) in toluene showed no reaction over 12 h at room temperature. The possibility that the propagating carbene species, not the starting vinyl carbene, was reacting with the methacrylate side-chain was ruled out by the addition of 10% of **4** to the MMA and initiator reaction mixture. Over 12 h, the polymerization of **4** was observed while no reaction of the MMA occurred. The reaction of

the initiator with MEHQ was also examined to ensure that no side reaction occurred between the initiator and inhibitor. Again, no reaction was observed over 12 h.

Scheme 3



Finally, the reaction of monomodal homopolymer **5** with initiator under four conditions was studied. The homopolymer $\overline{M}_n$=14,200 and a PDI=3.15 was dissolved in toluene and combined with initiator (condition 1), with initiator and MEHQ (condition 2), with MEHQ only (condition 3), and with no additives (condition 4) for 12 h. As shown in Table 3, no significant change in the polymer was observed for conditions 3 and 4 where no initiator was employed, while a significant reduction in the molecular weight was

Table 3. Effect of initiator on a monomodal sample of homopolymer **5**

Condition #	$\overline{M}_n$[a]	PDI[a]
1	900	9.39
2	1100	12.7
3	13300	3.10
4	12700	3.13

[a] Determined by Gel Permeation Chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards.

observed for conditions 1 and 2, presumably due to depolymerization and backbiting. If the metal carbene was reacting with the methacrylate side-chains, this would have resulted in chain coupling, and higher molecular weights would have been observed. These results showed that the proposed side reaction of the metal carbene with the methacrylate group to give chain coupling and cross-linked products was not significant. The dominant side reaction of the metal carbene was with the polymer backbone olefins resulting in depolymerization and backbiting.

The free radical mechanism of cross-linking was most consistent with these results. This conclusion also explained the results from Table 2 which showed the effect of [M]/[I] ratio on the polymerization. These results showed that low [M]/[I] ratios resulted in multimodal molecular weight distributions. It has been observed that the yields of polymer increased with the amount of initiator used. So, as lower [M]/[I] ratios were used, the reaction mixture became more viscous due to higher conversion to polymer, and this more viscous solution formed lowered the efficiency of MEHQ in solution. The effect of reaction concentration on the polymerizations paralleled these results. The higher the concentration, the more gelation and multimodal molecular weight distributions were observed.

Copolymerization of 4 with COD. To systematically control the concentration of cross-linkable groups on the polymer backbone, **4** was copolymerized with COD in several feed ratios. Homopolymerization of **4** and its copolymerization with cyclooctadiene yielded polymers **5**-**10** in Table 4. Two significant differences between the homopolymerization and copolymerizations were immediately recognized. First, it was possible to run the copolymerizations at higher concentrations resulting in higher yields than in the case of the hompolymerization. As the amount of **4** in the feed ratio was decreased, the more the concentration of the polymerization could be increased. Second, the amount of MEHQ needed in the reaction was drastically reduced for the copolymerizations without the formation of any cross-linked side products.

Table 4. Polymerization results for the homopolymerization of **4** and its copolymerization with COD

#	[M] total	%COD in Feed	[M]/[I]	Mol% MEHQ	%COD in Prod.[a]	% Yield[b]	$\overline{M}_n$[c]	PDI[c,d]
5	0.8 M	0	1383	18	0	44	21200	3.15
6	1.2 M	30.4	1490	4	37	60	30300	2.37
7	2.9 M	50.6	1660	4	56	72	36500	2.89
8	5.8 M	79.7	1673	4	84	86	34600	2.56
9	6.0M	89.4	1865	4	92	84	37100	2.39
10	5.7 M	94.8	1777	4	95	87	32900	2.14

[a] Determined by ^{1}H NMR integration. [b] Isolated yields after purification. [c] Determined by Gel Permeation Chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards. [d] Monomodal molecular weight distribution.

These copolymers (**6**-**10**) could have consisted of either a random, alternating, or blocky-type composition. Attempts to determine the composition through analysis of the ^{1}H and ^{13}C NMR spectra of the homopolymer and copolymers were inconclusive. Analysis of the alkyl region between 20-40 ppm in the ^{13}C NMR was used to exclude a perfect diblock structure; however, this analysis was unable to rule out tapered or multiple block materials. A highly blocky composition was unlikely due to the relative stability of these copolymers to cross-linking compared to the homopolymer. Such blocky copolymers should have exhibited similar difficulties with cross-linking as in the case of the homopolymer. One experiment to probe this question of copolymer composition was the polymerization of a 1:1 ratio of **4**/COD in toluene-d_8 monitored by ^{1}H NMR. At 10% conversion, the ratio of **4**/COD in the polymer was 39:61, determined by NMR integration. These percentages were within experimental error of the 44:56 ratio observed for the isolated 1:1 copolymer (Table 3) demonstrating that the polymer composition was relatively invariant during the reaction. Although this did not conclusively rule out a blocky composition, these results were in agreement with a more alternating or random

composition. The polymer composition could only have been determined conclusively through an extensive study of the reactivity ratios for the copolymerization.[20]

Controlled thermal and photochemical cross-linking of polymers 5-10. The controlled cross-linking of monomodal samples of the homopolymer **5** and copolymers **6-10** was achieved in all cases. Both thermal initiation with benzoyl peroxide or AIBN at 80°C as well as photochemical initiation using 2,2-dimethoxy-2-phenylacetophenone resulted in cross-linked polymers in less than 5 min. However, solutions of these polymers in toluene containing 5% (w/w) MEHQ were stable to cross-linking conditions. MEHQ is an excellent free radical inhibitor for this system. Removal of the solvent *in vacuo* resulted in a rubbery, clear solid which was insoluble in all common organic solvents. IR spectra exhibited a sharp decrease in the C=C stretch at approximately 1640 cm^{-1} as compared to the starting polymers due to the cross-linking of the pendant methacrylate groups.

Synthesis of AB cross-linked systems of polymer 9 and PMMA. The success that was observed in these experiments led to an investigation of the formation of AB cross-linked systems with PMMA. Despite the many current industrial applications of PMMA, there are problems with impact resistance, thermal stability, and chemical resistance.[21,22] The incorporation of a rubbery polymer through chemical cross-links in PMMA could improve many of these limitations. By polymerizing MMA in the presence of one of the methacrylate polymers **5-10**, cross-links should form with the methacrylate side-chains of these polymers, thus yielding AB cross-linked materials.

Two different materials were made in this study. Copolymer **9** was dissolved in MMA as a 5% (w/w) and as a 10% (w/w) solution. Benzoyl peroxide, 1% (w/w), was added to both solutions as a free radical initiator. When heated above 80°C, MMA polymerized and cross-links were formed simultaneously with **9**. The result was a hard, clear solid which molded to the shape of the container. While PMMA was soluble in benzene, toluene, chloroform, or methylene chloride, the new materials were insoluble in

these organic solvents and exhibited only minor swelling in chloroform and methylene chloride. The thermal properties were also compared with pure PMMA using the T_d, temperature at 10% weight loss, determined by thermogravimetric analysis (TGA).

Table 5. Comparison of thermal decomposition of the new materials with PMMA

Wt% of Copolymer **9** Used in Polymerization	T_d (°C)[a]
0% (100% PMMA)	229.9
5% (95% PMMA)	271.4
10% (90% PMMA)	328.6

[a] All values are obtained under an atmosphere of argon at a scan rate of 10°C/min.

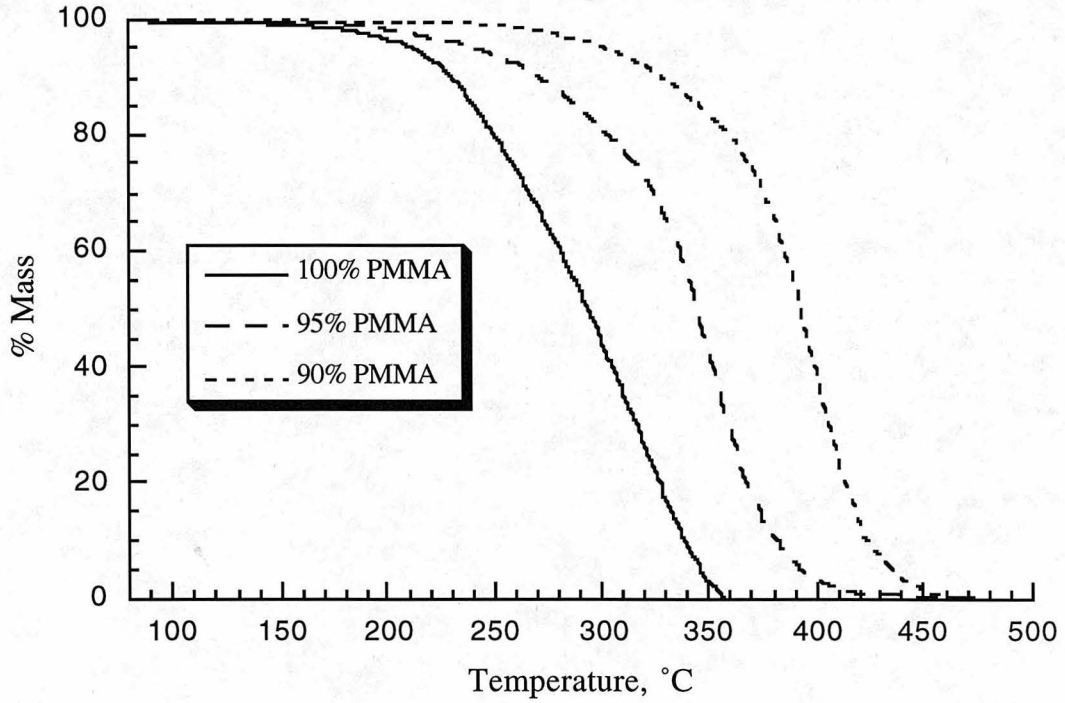


Figure 1. Comparison of thermal stability between PMMA and the new AB cross-linked materials by TGA in an argon atmosphere with a scan rate of 10°C/min.

Increases in thermal stability of 41.5°C (95% PMMA) and 108.7°C (90% PMMA) were

observed for these new materials relative to pure PMMA (Table 5). As shown in Figure 1, the TGA results clearly demonstrated the difference in thermal stability between these materials.

Conclusions

An efficient synthesis of 5-methacrylate-1-cyclooctene was accomplished, and the controlled ROMP of this monomer to create a linear polymer with methacrylate side-chains was demonstrated. The copolymerization of this monomer with cyclooctadiene allowed for the incorporation of a varying number of methacrylate side-chains on the polymer backbone. The effect of reaction concentration, solvent, amount of inhibitor, and [M]/[I] ratio on the polymerization was elucidated. In addition, both thermal and photochemical initiated cross-linking of these materials were accomplished, as well as the determination of an efficient inhibitor for these cross-linking processes. These successful cross-linking reactions led to a study of AB cross-linked systems of these polymers with PMMA resulting in new PMMA materials that had higher thermal stability and solvent resistance than pure PMMA.

Experimental

General. Argon was purified by passage through columns of BASF R-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). NMR spectra were recorded on GE QE-300 Plus (300.1 MHz; 75.49 MHz ^{13}C) spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. Gel permeation chromatographs were obtained on a HPLC system using an Altex model 110A pump, a Rheodyne model 7125 injector with a 100 μL injection loop, two American Polymer Standards 10 micron mixed bed columns, and a Knauer differential-refractometer using CH_2Cl_2 as eluent at a 1.0 mL/min flow rate. Molecular weights and polydispersities were reported versus monodispersed polystyrene

standards. Thermogravimetric analysis was carried out on a Perkin-Elmer TGA-2. Photolysis was accomplished with a 450 watt medium pressure mercury Hanovia lamp.

Materials. The toluene used in polymerizations was distilled from CaH_2 under vacuum. Dry THF was obtained by distillation under atmospheric pressure from CaH_2. All other solvents were reagent grade and used without purification. *m*-Chloroperbenzoic acid, methacryloyl chloride, *p*-methoxyphenol, lithium aluminum hydride, triethylamine, and 2,2-dimethoxy-2-phenylacetophenone were purchased from the Aldrich Chemical Company and used without further purification. COD was purchased from the Aldrich Chemical Company and degassed by stirring *in vacuo* for 2 hours before use in polymerizations.

Preparation of cyclooctadiene monoepoxide (2) and 5-hydroxy-1-cyclooctene (3). The preparation of these compounds was carried out using a recent modification[17] of a literature procedure.[23]

Preparation of 5-methacrylate-1-cyclooctene (4). Compound **3** (16.2 g, 129 mmol, 1 eq) was mixed with THF (100 mL) and triethylamine (14.3 g, 142 mmol, 1.1 eq) in a 500 mL round bottom flask under argon. To the reaction flask 90% methacryloyl chloride (17.9 g, 154 mmol, 1.2 eq) was added by syringe over 45 min at 0°C. The ice bath was then removed and the reaction was left to stir for 3 h at room temperature. The solid was removed by filtration and washed with diethyl ether (300 mL). The organics were then washed with 15% NaOH (3 x 200 mL), deionized water (200 mL), and brine (200 mL). The organics were then dried over $MgSO_4$ and concentrated *in vacuo*. The product was then distilled at 1 mm Hg/78°C to give 17.5 g (70%) of pure product. ^{1}H NMR ($CDCl_3$) δ 6.04 (dt, J_1=1.5Hz, J_2=0.9Hz, 1H), 5.67 (m, 2H), 5.50 (q, J=1.5Hz, 1H), 4.88 (m, 1H), 2.40-2.04 (m, 4H), 1.90 (dd, J_1=0.9Hz, J_2=1.5Hz, 3H), 1.89-1.54 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 166.8, 136.9, 129.8, 129.7, 124.8, 75.7, 33.7, 33.3, 25.5, 24.8, 22.2, 18.3; IR (thin film on a NaCl plate) 3017, 2933, 2859, 1710, 1638,

1467, 1450, 1402, 1381, 1328, 1318, 1294, 1174, 1038, 972.6, 932, 885, 815, 727 cm^{-1}; HRMS (FAB) calcd for $C_{12}H_{18}O_2$ $(M)^+$ 194.1307, found 194.1311.

General polymerization procedures. All manipulations were carried out in a dry box. In a 10 mL vial, the correct amount of **4** and cyclooctadiene was weighed out. In a separate vial, the initiator was weighed out and dissolved in the appropriate amount of toluene with MEHQ. The initiator solution was then pipetted into the first vial and a small Teflon coated stirbar was added. The vial was then capped, removed from the dry box, wrapped with aluminum foil, and left to stir for the desired time. Ethyl vinyl ether (600 eq) was pipetted into the vial along with an equal volume of toluene. This was left to stir for 1 h followed by precipitation into MeOH to isolate the polymer. Polymers **5-10** were synthesized by this method and characterized by standard methods including ^1H NMR, ^{13}C NMR, IR, and GPC.

Polymer 5. ^1H NMR ($CDCl_3$) δ 6.06-6.00 (bm, 1H), 5.51-5.45 (bm, 1H), 5.38-5.22 (bm, 2H), 4.98-4.82 (bm, 1H), 2.00-1.90 (bm, 4H), 1.91 (s, 3H), 1.60-1.42 (bm, 4H), 1.39-1.20 (bm, 2H); ^{13}C NMR ($CDCl_3$) δ 167.10, 136.67, 130.36, 130.20, 129.92, 129.78, 129.72, 129.62, 129.33, 129.10, 124.99, 74.0, 34.06, 33.98, 33.89, 33.75, 33.69, 33.61, 32.42, 28.44, 27.02, 26.98, 25.29, 25.26, 25.18, 25.13, 23.19, 23.13, 23.11, 18.41; IR (thin film on a NaCl plate) 3002, 2931, 2837, 1719, 1631, 1443, 1402, 1372, 1314, 1290, 1167, 1067, 1008, 967, 932, 814, 719 cm^{-1}.

Polymer 6. ^1H NMR ($CDCl_3$) δ 6.06-6.00 (bm, 1H), 5.51-5.45 (bm, 1H), 5.38-5.22 (bm, 4H), 4.98-4.82 (bm, 1H), 2.00-1.90 (bm, 8H), 1.91 (s, 3H), 1.60-1.42 (bm, 4H), 1.39-1.20 (bm, 2H); ^{13}C NMR ($CDCl_3$) δ 167.10, 136.67, 130.34-128.85 (m, *C* olefin), 124.96, 74.00, 34.05-23.12 (m, *C* alkyl), 18.40; IR (thin film on a NaCl plate) 3006, 2932, 2858, 1716, 1637, 1464, 1401, 1379, 1318, 1295, 1166, 967, 937, 725 cm^{-1}.

Polymer 7. ^1H NMR ($CDCl_3$) δ 6.06-6.00 (bm, 1H), 5.51-5.45 (bm, 1H), 5.38-5.22 (bm, 7H), 4.98-4.82 (bm, 1H), 2.00-1.90 (bm, 14H), 1.91 (s, 3H), 1.60-1.42

(bm, 4H), 1.39-1.20 (bm, 2H); ^{13}C NMR ($CDCl_3$) δ 167.10, 136.68, 130.33-128.83 (m, *C* olefin), 124.94, 74.01, 34.04-23.18 (m, *C* alkyl), 18.39; IR (thin film on a NaCl plate) 3006, 2925, 2847, 1715, 1636, 1454, 1403, 1379, 1316, 1295, 1164, 966, 729 cm^{-1}.

Polymer 8. ^1H NMR ($CDCl_3$) δ 6.06-6.00 (bm, 1H), 5.51-5.45 (bm, 1H), 5.38-5.22 (bm, 23H), 4.98-4.82 (bm, 1H), 2.00-1.90 (bm, 46H), 1.91 (s, 3H), 1.60-1.42 (bm, 4H), 1.39-1.20 (bm, 2H); ^{13}C NMR ($CDCl_3$) δ 167.11, 136.70, 130.37-128.84 (m, *C* olefin), 124.95, 74.03, 34.04-23.19 (m, *C* alkyl), 18.41; IR (thin film on a NaCl plate) 3005, 2921, 2845, 1717, 1638, 1449, 1401, 1316, 1295, 1165, 966, 729 cm^{-1}.

Polymer 9. ^1H NMR ($CDCl_3$) δ 6.06-6.00 (bm, 1H), 5.51-5.45 (bm, 1H), 5.38-5.22 (bm, 46H), 4.98-4.82 (bm, 1H), 2.00-1.90 (bm, 92H), 1.91 (s, 3H), 1.60-1.42 (bm, 4H), 1.39-1.20 (bm, 2H); ^{13}C NMR ($CDCl_3$) δ 167.10, 136.71, 130.47-128.2 (m, *C* olefin), 124.94, 74.07, 74.01, 34.06-23.20 (m, *C* alkyl), 18.40; IR (thin film on a NaCl plate) 3006, 2919, 2844, 1717, 1638, 1448, 1402, 1316, 1295, 1165, 966, 727 cm^{-1}.

Polymer 10. ^1H NMR ($CDCl_3$) δ 6.06-6.00 (bm, 1H), 5.51-5.45 (bm, 1H), 5.38-5.22 (bm, 84H), 4.98-4.82 (bm, 1H), 2.00-1.90 (bm, 168H), 1.91 (s, 3H), 1.60-1.42 (bm, 4H), 1.39-1.20 (bm, 2H); ^{13}C NMR ($CDCl_3$) δ 167.10, 136.68, 131.39-127.99 (m, *C* olefin), 125.01, 73.70, 73.64, 33.42-24.97 (m, *C* alkyl), 18.35; IR (thin film on a NaCl plate) 3006, 2918, 2844, 1717, 1654, 1448, 1403, 1372, 1316, 1165, 965, 728 cm^{-1}.

Determination of polymer composition at 10% conversion. In a dry box, **1** (1.3 mg, 1.4 μmol, 1 eq), **4** (225 mg, 1.16 mmol, 825 eq), COD (122 mg, 1.13 mmol, 804 eq), and MEHQ (12 mg, 96.8 μmol) were combined in toluene-d_8 (0.8 mL), and this polymerization was monitored by ^1H NMR. When the polymerization was at 10%

conversion, the reaction mixture was precipitated in MeOH and the polymer composition analyzed by ^{1}H NMR integration.

Reaction of MMA and 1. In a dry box, **1** (7.4 mg, 8 μmol, 1 eq), MMA (**6**) (48 mg, 479 mmol, 59.9 eq), and the internal standard, mesitylene, were combined and dissolved in toluene-d_8 (0.5 mL), and the solution was then transferred to an NMR tube and removed from the dry box. The reaction was then monitored by ^{1}H NMR for 12 h for the disappearance of catalyst or MMA. No reaction was observed during this time.

Reaction of MMA, 4, and 1. In a dry box, **1** (7.4 mg, 8 μmol, 1 eq), MMA (**6**) (43 mg, 347 μmol, 53.8 eq), compound **4** (9.3 mg, 47.9 μmol, 6.0 eq), and mesitylene were combined and dissolved in toluene-d_8 (0.5 mL), and the solution was then transferred to an NMR tube and removed from the dry box. Monitoring by ^{1}H NMR showed no reaction over 12 h except for the polymerization of **4**.

Reaction of 1 and MEHQ. In a dry box, **1** (7.4 mg, 8 μmol, 1 eq), MEHQ (53 mg, 427 μmol, 59.1 eq), and mesitylene were combined in toluene-d_8 (0.5 mL) and the solution was transferred to an NMR tube and removed from the box. The reaction was monitored by ^{1}H NMR, but no reaction was observed over 12 h.

Reaction of 1 with homopolymer 5. In a dry box, homopolymer **5** (50 mg, 258 μmol, 99 eq) was dissolved in toluene (0.75 mL) in each of four vials. In vial 1, **1** (2.4 mg, 2.6 μmol, 1.0 eq) was added; in vial 2, the same amount of initiator and MEHQ (10 mg) were added; in vial 3, only MEHQ (10 mg) was added; and in vial 4, nothing else was added. The four vials were removed from the box and allowed to react at room temperature for 12 h. The polymer was then precipitated in MeOH and analyzed by GPC.

General procedure for PMMA AB cross-linked systems. The desired ratio of MMA and copolymer **9** was combined with benzoyl peroxide and agitated until a solution resulted. This was then heated open to air with stirring at 90°C. After 15 min, the solution became viscous, and the vial was removed from the 90°C bath. The stirbar was removed, the vial capped, and then the vial was placed in a 40°C bath and left for 10 h.

After this time, the vial was removed from the bath, and the resulting polymer was isolated by breaking away the glass to obtain a hard, clear solid. Reaction at 90°C for longer than 15 min led to foamy, brittle materials due to trapping of unreacted monomer in the polymeric solid.

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Chapter 2:

Synthesis and Controlled Cross-Linking of Telechelic Poly(butadiene)s Derived from Ring-Opening Metathesis Polymerization (ROMP)

Abstract

The synthesis of ring-opening metathesis polymerization chain transfer agents bearing methacrylate and epoxide end-functionality was accomplished. In the presence of these chain transfer agents, cyclooctadiene was polymerized via a ruthenium benzylidene initiator, $(PCy_3)_2Cl_2Ru{=}CHPh$, to produce telechelic poly(butadiene)s with either methacrylate or epoxide end groups. The impact of initiator concentration, reaction time, and temperature on the polymer yield and chain transfer agent incorporation was examined. Control over the polymer molecular weight through the cyclooctadiene/chain transfer agent ratio was demonstrated providing for a range of telechelic poly(butadiene) molecular weights. Successful cross-linking of these polymers by thermal or photochemical initiation in the case of the bis(methacrylate)-functionalized telechelic poly(butadiene)s or through acid catalysis in the case of the bis(epoxide)-functionalized telechelic poly(butadiene)s was accomplished.

Introduction

Telechelic polymers can be simply defined as polymers that bear reactive functional groups at their chain ends.[1-4] The interest in these polymeric materials is derived from the fact that through these reactive end groups, a vast number of macromolecular materials can be prepared. Telechelic polymers have found application in the synthesis of block copolymers, star polymers, cross-linked polymer networks, and ionic polymer networks. Low molecular weight liquid telechelic polymers have been successfully used in reaction injection molding, and the formation of ABA triblock and multiblock copolymers via telechelic polymers has dramatically impacted the development of thermoplastic elastomers.[1-4] Based on these numerous valuable applications, considerable research efforts have been devoted to improving the synthesis of telechelic polymers.[1-4]

The development of telechelic polymers with cross-linkable end groups such as methacrylate or epoxide groups is of interest for the preparation of interpenetrating polymer networks, AB cross-linked polymeric materials, more thermally and chemical resistant materials, and for the immobilization of biomaterials.[1,2,5-7] However, these reactive end groups have been typically incorporated through a post-polymerization transformation due to the instability of these functional groups to many polymerization reaction conditions.[5,8-11] Bis(methacrylate)- and bis(epoxide)-functionalized telechelic poly(ethylene glycol)s, poly(propylene glycol)s, poly(divinylbenzene)s, and poly(isobutylene)s are just a few of the cross-linkable telechelic materials that have been previously studied.[5,8-11] A synthetic route which could generate cross-linkable telechelic polymers in one step would be of considerable interest.

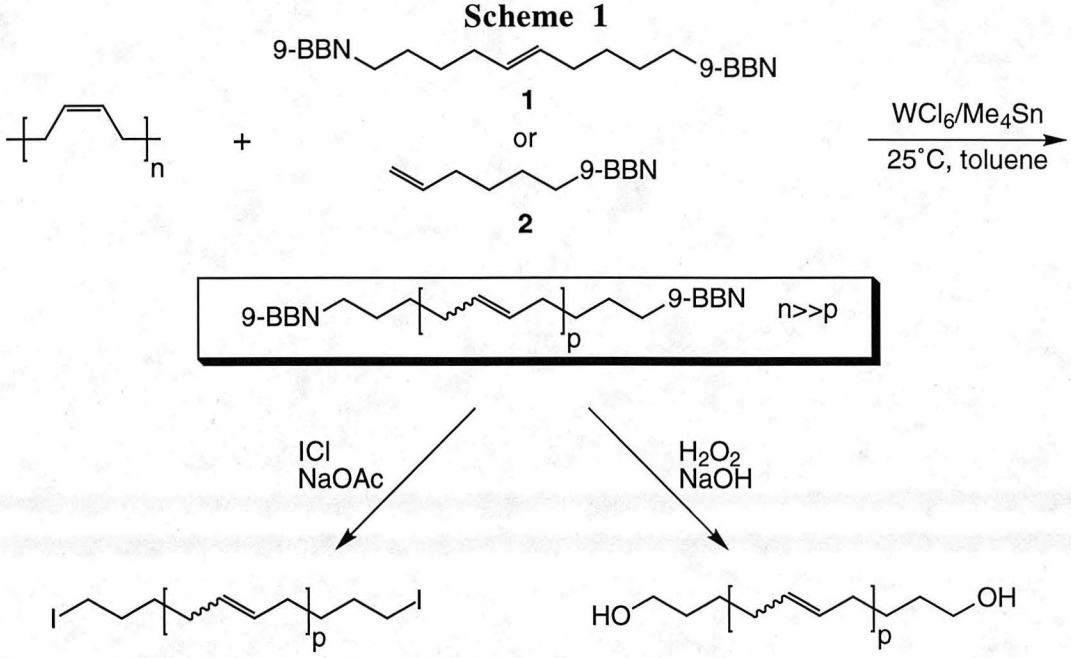
Five major approaches have been employed successfully for the preparation of telechelic polymers. Incorporation of end group functionality has been accomplished through 1) the use of functionalized chain transfer agents (CTAs); 2) the use of either functionalized initiators or terminators (or both), most successfully in living polymerizations; 3) the controlled degradation of polymer backbones; 4) the addition of

monofunctional compounds into step polymerizations; and 5) stochiometry control in step polymerizations.[1-4,12] All five of these methods have been widely utilized with varying degrees of success for many different polymerization methods including radical, anionic, cationic, ring-opening, group transfer, and step growth polymerizations.[1-4,12]

Since the early 1980's, olefin metathesis was found to be an extremely effective method for the generation of telechelic polymers.[13-28] Three distinct approaches were utilized including 1) metathesis-mediated degradation of poly(butadiene) polymer backbones in the presence of functionalized acyclic olefins;[17-19,21-23] 2) non-metathesis-mediated degradation of copolymers synthesized by ring-opening metathesis polymerization (ROMP);[25] and 3) ROMP in the presence of functionalized acyclic olefin CTAs.[13-16,18-20,24,26,27]

The degradation of polymers bearing olefinic groups in the polymer backbone using acyclic olefins and metathesis initiators has been well documented.[28,29] By incorporating functional groups into these acyclic olefins, telechelic polymers were prepared. The method utilized by Chung relied on the use of borane-functionalized acyclic olefins including symmetrically disubstituted olefins such as 1,10-bis(9-BBN)-5-decene (**1**) and α-olefins such as 6-(9-BBN)-1-hexene (**2**).[17-19] In the presence of WCl_6/Me_4Sn (5:1) and either **1** or **2**, *cis*-1,4-poly(butadiene) ($\overline{M}_n$=172000) was degraded over 30 min into low molecular weight telechelic oligomers of poly(butadiene) which contained 9-BBN end groups (Scheme 1). The molecular weights of these polymers were low ($\overline{M}_n$<2000); however, little control over these molecular weights by varying the acyclic olefin concentration was observed, and often inconsistent results were obtained from run to run. The advantage to this route was that the borane end group could be further functionalized into either alcohol or iodide end groups through subsequent chemical transformations. In addition, this method employed commercially available *cis*-1,4-poly(butadiene) making it appealing from a cost standpoint. However, as previously stated, little control over the

Scheme 1

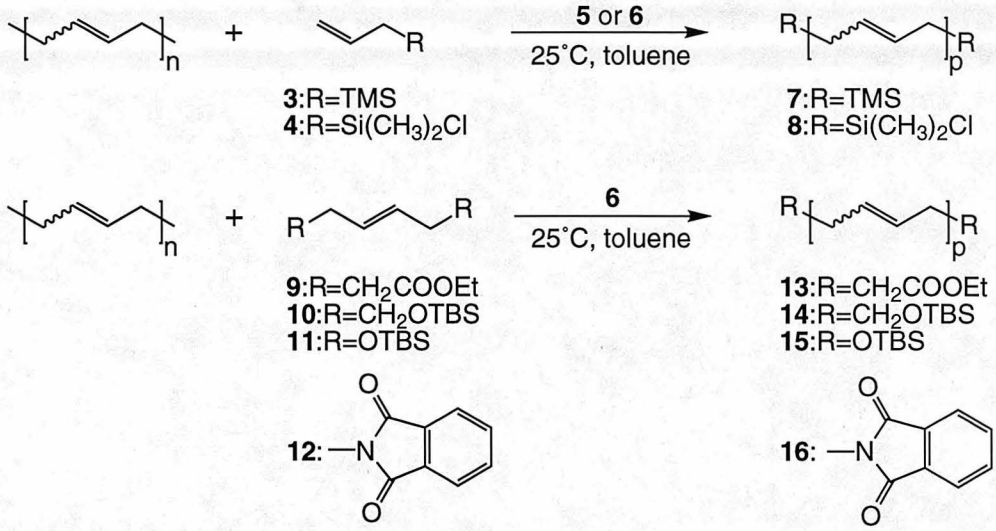


telechelic polymer molecular weight was realized.[17-19] In the case of **2** as the acyclic olefin CTA, only 56% of the polymeric products had a number average functionality ($\overline{F}_n$) of 2 (both ends functionalized), whereas 18% had no borane incorporation and 26% had only a $\overline{F}_n$=1 (one end functionalized).[17,19] A $\overline{F}_n$ near 2 was obtained with the use of the symmetrically disubstituted **1** as the acyclic olefin.[18,19] This method was successfully applied to poly(isobutylene-*co*-butadiene) as well in order to prepare bis(alcohol)- and bis(iodo)-functionalized telechelic poly(isobutylene)s.[23]

Using a similar approach to Chung, Wagener employed functionalized acyclic olefins for the preparation of telechelic poly(butadiene)s via a metathesis-mediated degradation of 1,4-poly(butadiene). Treatment of 1,4-poly(butadiene) ($\overline{M}_n$=87000) with 10 eq of either allyltrimethylsilane, **3**, or allylchlorodimethylsilane, **4**, in the presence of M(CHC(CH$_3$)$_2$Ph)(NAr)(OC(CH$_3$)(CF$_3$)$_2$)$_2$ [Ar=2,6-diisopropylphenyl; **5**: M=W or **6**: M=Mo] as an initiator over 48 h led to a quantitative conversion to bis(trimethylsilyl)- (**7**) or bis(chlorodimethylsilyl)-functionalized (**8**) telechelic poly(butadiene) oligomers with a degree of polymerization between 2-4 and a $\overline{F}_n$=2 (Scheme 2).[21] Using the more

functional group tolerant initiator (**6**), symmetrically disubstituted olefins including diethyl 4-octene-1,8-dioate (**9**), bis(*tert*-butyldimethylsilyl)-3-hexene-1,6-diol diether (**10**), bis(*tert*-butyldimethylsilyl)-*cis*-2-butene-1,4-diol diether (**11**), and *cis*-2-butene-1,4-diylbis(pthalimide) (**12**) were employed as well resulting in high yielding syntheses of bis(ester)-, bis(silyl ether)-, and bis(imide)-functionalized telechelic poly(butadiene) oligomers (**13**-**16**) with DPs between 1-2 and $\overline{F}_n$ values near 2 (Scheme 2).[22]

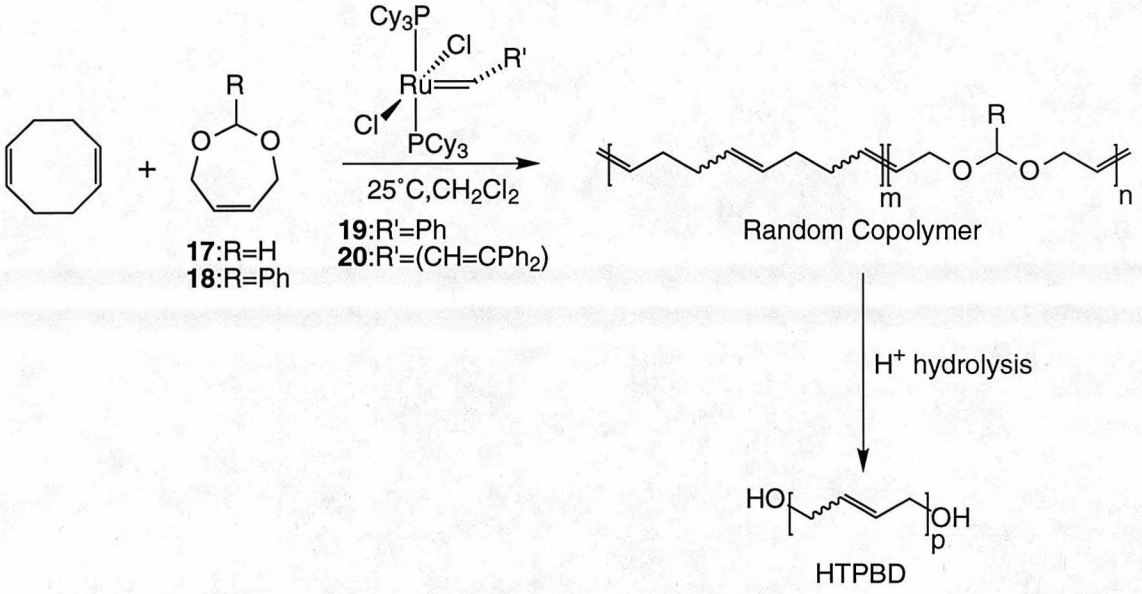
Scheme 2



Recently, a non-metathesis-mediated polymer degradation approach was applied to polymers derived from ROMP. Copolymerization of cyclooctadiene (COD) with either *cis*-4,7-dihydro-1,3-dioxepan (**17**) or *cis*-4,7-dihydro-2-phenyl-1,3-dioxepan (**18**) using well-defined ruthenium-based metathesis initiators $(PCy_3)_2Cl_2Ru{=}CHR'$ [**19**: R'=Ph or **20**: R'=$(CH{=}CPh_2)$][30-32] resulted in a polymer bearing both poly(butadiene) and acetal units along the backbone.[25] Subsequent acid hydrolysis of these acetal units resulted in the desired hydroxytelechelic poly(butadiene) (HTPBD) oligomers in moderate yields (Scheme 3). Control over the molecular weight of these telechelic oligomers was achieved by varying the ratio of [COD]/[**17** or **18**] in the copolymerization step resulting in $\overline{M}_n$ values between 400-3100 and a $\overline{F}_n$=2.[25] Although a successful approach for the synthesis of

HTPBD, this method was not applicable for the preparation of other end groups on the telechelic polymers.

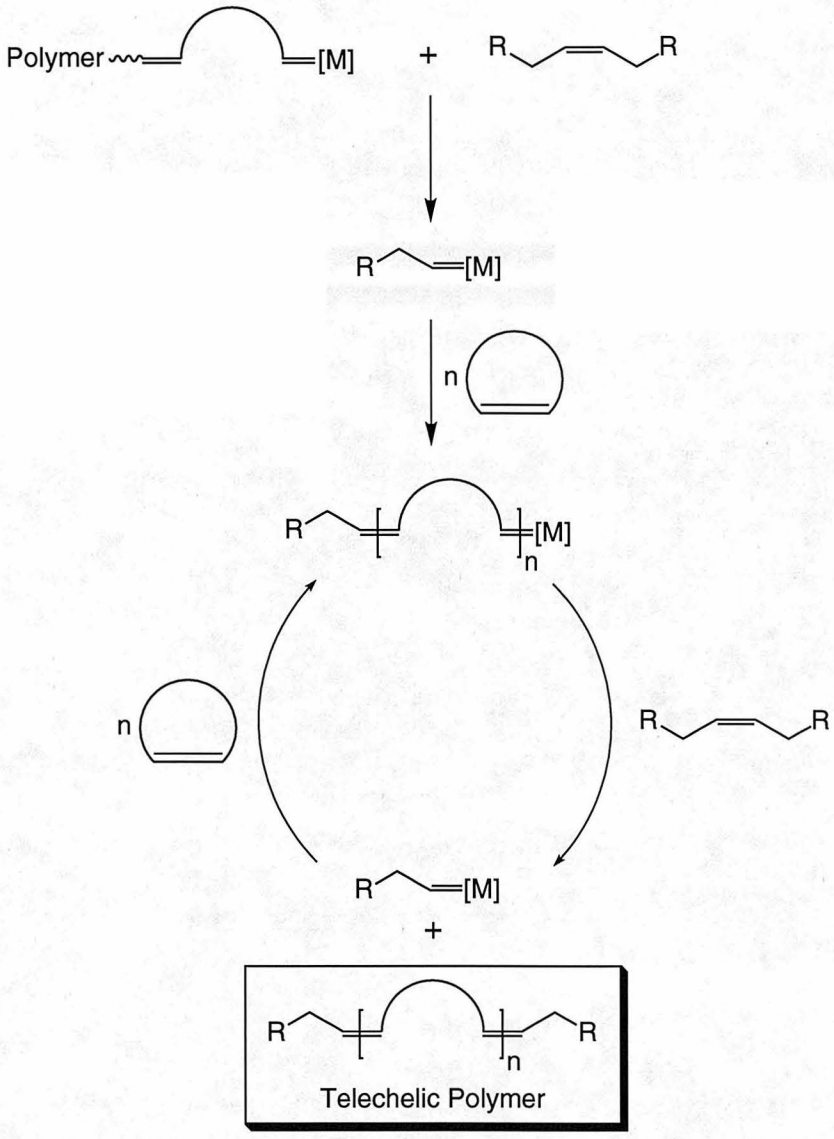
Scheme 3



Despite the successes encountered in these above approaches, the use of functionalized acyclic olefin CTAs in the ROMP of cyclic olefins has been by far the most intensely investigated method for the generation of telechelic polymers by olefin metathesis.[13-16,18-20,24,26,27] In this approach, polymerization of a cyclic olefin (cyclopentene, COD, norbornene, etc...) is initiated with a standard metathesis initiator to generate a polymer with a metal carbene propagating species. Reaction of this propagating species with the CTA results in functional group incorporation at the polymer end group and the formation of a functionalized metal alkylidene. This alkylidene can then initiate a new polymer chain, and this process can be repeated thus incorporating functionality at both ends of the polymer chains (Scheme 4). In addition to this method of incorporation, metathesis-mediated polymer backbone degradation as described above can also contribute to functional group incorporation and molecular weight reduction. In systems where

termination is kept to a minimum and low initiator loadings are employed, $\overline{F}_n$ values approaching 2 are typically achieved.[13-16,18-20,24,26,27]

Scheme 4



Initial studies on telechelic polymer synthesis using this approach were accomplished with the ill-defined Lewis acidic WCl_6/Me_4Sn initiator system. Due to the Lewis acidic nature of this system, often unwanted byproducts and initiator deactivation were observed when reactive functional groups were utilized in the CTAs. In addition,

often irreproducible initiator activities and polymerization results were observed limiting the application of this method.[13-16] However, the polymerization of cyclooctene, COD, norbornene, and cyclopentene in the presence of either dimethyl or diethyl 3-hexene-1,6-dioate using WCl_6/Me_4Sn resulted in the high yielding syntheses of bis(diester)-functionalized telechelic polymers.[13-16] Chung applied his borane methodology for the preparation of HTPBD and bis(iodo)-functionalized telechelic poly(butadiene) through polymerization of COD with WCl_6/Me_4Sn in the presence of **1** followed by post-polymerization chemical transformations.[18,19] An economical two step procedure was recently developed by Amoco in which methyl undecylenate was self-metathesized using WCl_6/Me_4Sn to generate dimethyl 10-eicosene-1,20-dioate (65-70% *cis*). Upon isolation of the self-metathesis product and treatment with either COD or 1,5,9-cyclododecatriene and WCl_6/Me_4Sn, the bis(diester)-functionalized telechelic polymers were isolated in excellent yield.[27]

In an effort to hopefully expand the functional group tolerance in these systems, recent studies were accomplished which utilized well-defined Lewis acid free metathesis initiators for the preparation of HTPBD. The polymerization of COD in the presence of bis(*tert*-butyldimethylsilyl)-*cis*-3-hexene-1,6-diol diether or bis(*tert*-butyldimethylsilyl)-*cis*-2-butene-1,4-diol diether using the well-defined initiators $W(CHAr)(NPh)(OC(CH_3)(CF_3)_2)_2(THF)$ [Ar=*o*-methoxyphenyl] or $Mo(CHC(CH_3)_2Ph)(NAr)(OC(CH_3)(CF_3)_2)_2$ [Ar=2,6-diisopropylphenyl] (**6**) resulted in bis(silyl ether)-functionalized telechelic poly(butadiene)s.[20,24] Higher yields were obtained with bis(*tert*-butyldimethylsilyl)-*cis*-3-hexene-1,6-diol diether as the CTA due to the greater separation between the olefin and the silyl ether moiety and with **6** as the initiator due to the better functional group tolerance of this molybdenum-based initiator.[24] These telechelic polymers were easily deprotected using TBAF to synthesize HTPBD.[20,24] Using the more functional group tolerant initiator $(PCy_3)_2Cl_2Ru{=}CHCH{=}CPh_2$ (**20**),[30] polymerization of COD with the readily available *cis*-2-butene-1,4-diol diacetate provided bis(acetoxy)-

functionalized telechelic poly(butadiene)s.[26] Separation of the olefin and the functional group by two methylene units was not necessary in this case to achieve high yields because of the higher functional group tolerance of the ruthenium initiator. This material was readily deprotected with NaOMe/MeOH to give a high yielding synthesis of HTPBD.[26] The utilization of ROMP with functionalized CTAs as in the above examples has proven to be a more general method of telechelic polymer synthesis providing for high yields, incorporation of a range of functional groups, control over polymer molecular weights through the [monomer]/[CTA] ratio, and $\overline{F}_n$ values approaching 2.

The development of the functional group tolerant ruthenium-based metathesis initiators $(PCy_3)_2Cl_2Ru{=}CHR'$ (**19** and **20**)[30-32] has enabled the application of olefin metathesis to compounds with a vast array of functionality. As discussed in Chapter 1 and in a recent publication, initiator **20** was successfully applied to the preparation of cross-linkable polymers through the ROMP copolymerization of COD and 5-methacrylate-1-cyclooctene thus demonstrating the stability of this ruthenium carbene species in the presence of a methacrylate group.[33] In addition, ring-closing metathesis of acyclic dienes[34,35] and the ROMP of cyclic olefins [33,36,37] has been achieved with **19** and **20** in the presence of numerous other polar functionalities including alcohols, carboxylic acids, esters, amides, ketones, amines, and many others. As a result of this functional group tolerance, the synthesis of telechelic poly(butadiene)s bearing highly reactive methacrylate and epoxide end groups in one step was investigated through the polymerization of COD with $(PCy_3)_2Cl_2Ru{=}CHPh$ (**19**) in the presence of bis(methacrylate)- and bis(epoxide)-functionalized CTAs. The high functional group tolerance of **19** allowed the polymerization to occur resulting in the incorporation of the methacrylate and epoxide end groups at the polymer chain ends. The impact of initiator concentration, reaction time, and temperature on the polymer yield and CTA incorporation was determined. Controlled cross-linking of these telechelic polymers both thermally or photochemically in the case of the bis(methacrylate)-functionalized telechelic poly(butadiene)s or with H_2SO_4 for the

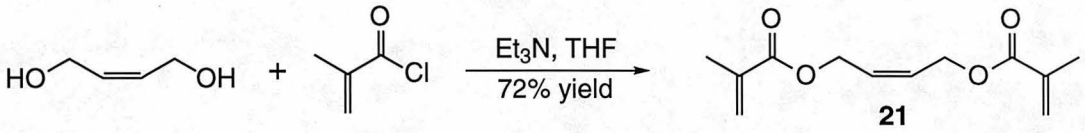
bis(epoxide)-functionalized telechelic poly(butadiene)s was accomplished providing for the facile preparation of cross-linked poly(butadiene) networks. This research was accomplished in collaboration with Takeharu Morita.

Results and Discussion

Synthesis of the CTA *cis*-2-butene-1,4-diol dimethacrylate (21).

Synthesis of the bis(methacrylate)-functionalized CTA *cis*-2-butene-1,4-diol dimethacrylate (**21**) was accomplished as shown in Scheme 5. Simple esterification of the commercially available *cis*-2-butene-1,4-diol using methacryloyl chloride resulted in compound **21** in

Scheme 5



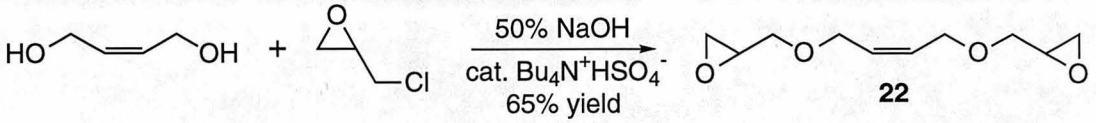
72% yield. However, compound **21** was extremely unstable and polymerized to form an insoluble solid in less than 1 week, even when stored at -30°C in the presence of the free radical inhibitor *p*-methoxyphenol (5 wt%). In order to prevent this polymerization side reaction, compound **21** was stored at -30°C with a higher concentration of *p*-methoxyphenol (20 wt%). This higher inhibitor loading was quite effective resulting in no observed polymerization of **21** over 6 months. Although this was a reasonably high inhibitor concentration, it was previously shown that ruthenium vinylcarbene initiator **20** was tolerant of this inhibitor,[33] and one would expect similar results using the ruthenium benzylidene initiator **19**. Therefore, the polymerization of COD with initiator **19** in the presence of CTA **21** should be possible without the need for removal of this inhibitor prior to polymerization.

Synthesis of the CTA *cis*-2-butene-1,4-diol diglycidyl ether (22).

The synthesis of the bis(epoxide)-functionalized CTA *cis*-2-butene-1,4-diol diglycidyl ether

(**22**) was accomplished in one step as illustrated in Scheme 6. This procedure was a modification of that of Okahara used for the preparation of ethylene glycol diglycidyl ether.[38] Treatment of *cis*-2-butene-1,4-diol with excess epichlorohydrin in the presence of aqueous NaOH (50% w/w) and the phase transfer catalyst $Bu_4N^+HSO_4^-$ resulted in CTA **22** in 65% yield. Unlike the unstable CTA **21**, compound **22** was extremely stable and was purified by distillation at 105-110°C *in vacuo*. Samples of compound **22** stored at room temperature exhibited no decomposition over 6 months.

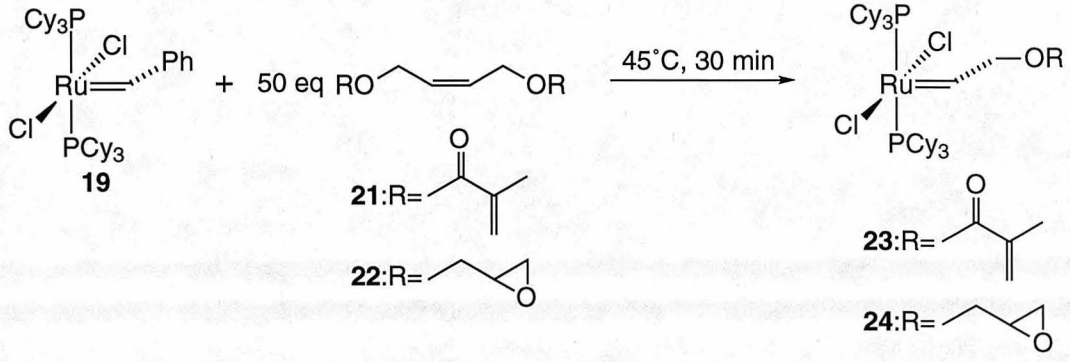
Scheme 6



Reaction of CTAs 21 and 22 with the ruthenium benzylidene initiator 19. The reaction of either the ruthenium benzylidene initiator **19** or the propagating ruthenium alkylidene with the functionalized CTAs **21** and **22** to generate a methacrylate- or epoxide-functionalized ruthenium alkylidene species is a key step in the synthesis of telechelic polymers by ROMP, as shown in Scheme 4. However, previous studies in other ROMP systems using ruthenium-based metathesis initiators **19** and **20** demonstrated the susceptibility of substituted ruthenium carbenes to functional group chelation to the metal center with the loss of a phosphine ligand. These chelated carbene species were less reactive and often decomposed on the time scale of the polymerization.[37] Therefore, the reaction of the ruthenium benzylidene **19** with both **21** and **22** was investigated. Treatment of **19** with 50 eq of the bis(methacrylate)-functionalized CTA **21** at 45°C for 30 min resulted in the formation of a methacrylate-functionalized ruthenium alkylidene **23**. This alkylidene exhibited an α-H carbene resonance at 19.48 ppm (t, J_{HH}=4.4Hz) in the ^1H NMR and a ^{31}P resonance at 37.42 ppm with no observed free phosphine, and this alkylidene showed no decomposition over 24 h at room temperature. The lack of observed

free phosphine and the ^{1}H and ^{31}P resonances were indicative of a bis(phosphine) ruthenium alkylidene species as illustrated in Scheme 7.[37]

Scheme 7



Treatment of **19** with 50 eq of the bis(epoxide)-functionalized CTA **22** at 45°C for 30 min resulted in the formation of an epoxide-functionalized ruthenium alkylidene **24**. This alkylidene exhibited an α-H carbene resonance at 19.79 ppm (t, J_{HH}=3.6Hz) in the ^{1}H NMR and a ^{31}P resonance at 36.91 ppm with no observed free phosphine, and again no decomposition of this alkylidene was observed over 24 h at room temperature. As before, the lack of observed free phosphine and the ^{1}H and ^{31}P resonances were indicative of a bis(phosphine) ruthenium alkylidene species as illustrated in Scheme 7.[37] These results were promising in that the methacrylate and epoxide functional groups appeared not to significantly interact with the metal center of the ruthenium carbenes.

Polymerization of COD in the presence of 21. In the presence of the CTA **21**, polymerization of COD resulted in the bis(methacrylate)-functionalized telechelic poly(butadiene) **25** as shown in Scheme 8. In an initial study, the impact of the [COD]/[**19**] ([COD]/[I]) ratio, reaction time, and temperature on the polymer yield and CTA incorporation was investigated. The polymerizations were run neat according to the different sets of conditions described in Table 1. In the first two entries, reaction time and

Scheme 8

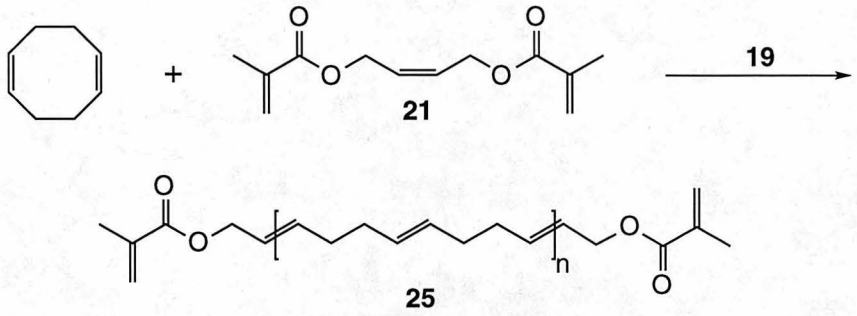


Table 1. Optimization studies for the polymerization of COD with **21**

[COD]/[**21**]	[COD]/[I]	Rxn. Time (h)	Temp. (°C)	% Yield[a]	$\overline{M}_n$ (Theoretical)[b]	$\overline{M}_n$ (NMR)[c]
15	2000	24	25	80	1844	3500
15	4000	24	25	75	1844	5500
10	2000	24	25	85	1304	2500
10	2000	48	25	87	1304	2300

[a] Isolated yields after purification. [b] Determined by ([COD]/[**21**])(MW of COD)+(MW of **21**). [c] Determined by ^{1}H NMR integration assuming a number average functionality of 2.

temperature were held constant at 24 h and 25°C while the [COD]/[I] ratio was increased from 2000:1 to 4000:1. Although only a slight decrease in the yield of 5% was observed, the $\overline{M}_n$ increased from 3500 to 5500 presumably due to a reduced incorporation of the CTA **21** during the polymerization. The impact of reaction time was investigated by comparing the results for [COD]/[**21**]=10, [COD]/[I]=2000, and a temperature of 25°C for reaction times of 24 and 48 h. As seen in the third and fourth entries, increasing the reaction time resulted in a slight increase in yield and a lower molecular weight due to an improved incorporation of **21**. The impact of temperature was unable to be investigated because of the instability of **21**. When polymerizations were run at 45°C, low yields and insoluble polymeric materials were formed most likely as a result of a thermally-induced

polymerization of the methacrylate groups. Based on these initial studies, all of the polymerizations of COD with **21** were run with a [COD]/[I] ratio of 2000:1 for 48 h at 25°C. In addition, the polymerizations were covered in aluminum foil to prevent photo-induced polymerization of the methacrylate groups.

One of the advantages of using ROMP with functionalized CTAs for the preparation of telechelic polymers is the ability to control the polymer molecular weights through the [monomer]/[CTA] ratio. A series of bis(methacrylate)-functionalized telechelic poly(butadiene)s were synthesized with [COD]/[**21**] ratios of 15, 40, 60, and 80:1 in an attempt to control the molecular weights of these telechelic poly(butadiene)s, and the results are presented in Table 2. Yields between 88-90% were obtained, and the molecular weight

Table 2. Synthesis of bis(methacrylate)-functionalized telechelic poly(butadiene)s **25**

[COD] / [**21**]	% Yield[d]	% *Cis*-Olefin (Backbone)[e]	% *Cis*-Olefin (End Group)[e]	$\overline{M}_n$ (Theoretical)[f]	$\overline{M}_n$ (NMR)[g]	$\overline{M}_n$ (GPC)[h]	PDI[h]
15[a]	88	50	25	1844	3700	5400	1.74
40[a]	89	55	20	4544	8000	10100	1.86
60[b]	90	60	25	6704	14500	11900	2.02
80[c]	90	55	25	8864	17700	15300	1.99

[a] Polymerizations were run neat at 25°C for 48 h with [COD]/[I]=2000. [b] To ensure better mixing and higher yields, [COD]= 12.4 M in benzene was utilized. [c] To ensure better mixing and higher yields, [COD]= 9.3 M in benzene was utilized. [d] Isolated yields after purification. [e] Determined by ^{1}H NMR integration. [f] Determined by ([COD]/[**21**])(MW of COD)+(MW of **21**). [g] Determined by ^{1}H NMR integration assuming a number average functionality of 2. [h] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards.

was indeed controlled resulting in bis(methacrylate)-functionalized telechelic poly(butadiene)s with $\overline{M}_n$ values between 3700 to 17700. Although these molecular weights were significantly higher than the theoretical molecular weights, excellent

molecular weight control based on the [COD]/[**21**] ratio was observed as illustrated in the plot of $\overline{M}_n$ versus the [COD]/[**21**] ratio in Figure 1. The higher molecular weight values found experimentally compared to the theoretical values were presumably due to

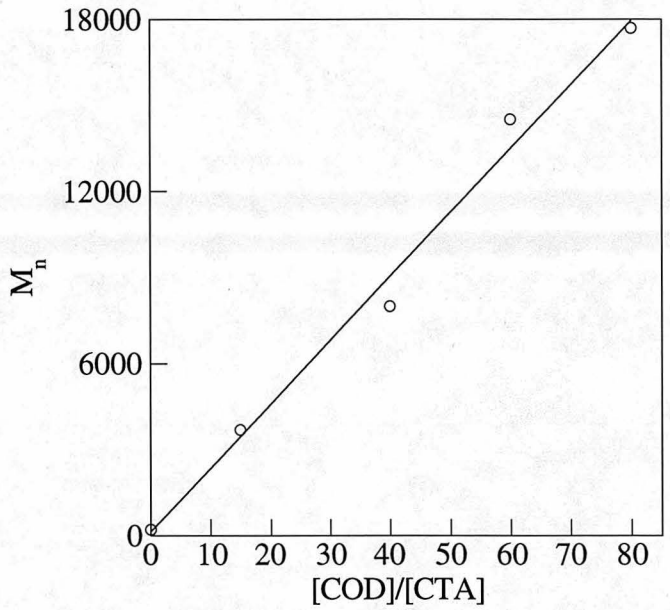


Figure 1. Dependence of the observed $\overline{M}_n$ values for the bis(methacrylate)-functionalized telechelic poly(butadiene)s **25** on the [COD]/[CTA] ratio. The $\overline{M}_n$ was determined by ^{1}H NMR integration assuming a number average functionality of 2.0.

incomplete incorporation of the CTA **21** during the polymerization as has been previously observed in a similar system using the ruthenium vinylcarbene initiator **20**.[26] However, increased reaction times and initiator loadings were unable to improve the incorporation of the CTA **21**. The telechelic poly(butadiene)s contained between 50-60% *cis*-olefin in the backbone and between 20-25% *cis*-olefin at the polymer end groups, and polydispersities (PDIs) of 1.74-2.02 were obtained. Both ^{1}H and ^{13}C NMR supported a $\overline{F}_n$ near 2 for these materials as one would expect based on the previous results obtained for the use of symmetrically disubstituted internal olefin CTAs for the preparation of telechelic polymers by ROMP.[13-16,18-20,24,26,27]

Polymerization of COD in the presence of 22. In the presence of the CTA **22**, polymerization of COD resulted in the bis(epoxide)-functionalized telechelic poly(butadiene) **26** as shown in Scheme 9. As accomplished above for the polymerization of COD in the presence of **21**, the impact of the [COD]/[I] ratio, reaction time, and

Scheme 9

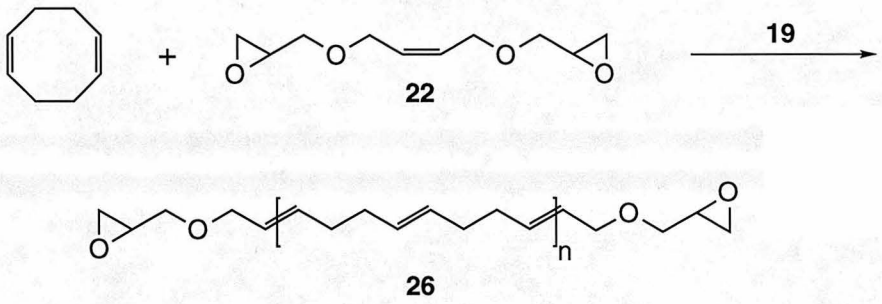


Table 3. Optimization studies for the polymerization of COD with **22**

[COD]/[**22**]	[COD]/[I]	Rxn. Time (h)	Temp. (°C)	% Yield[a]	$\overline{M}_n$ (Theoretical)[b]	$\overline{M}_n$ (NMR)[c]
15	2000	48	25	60	1820	3700
15	4000	48	25	51	1820	3600
15	2000	24	45	67	1820	3400
15	2000	48	45	67	1820	3400
15	4000	24	45	63	1820	3500
15	4000	48	45	61	1820	3700

[a] Isolated yields after purification. [b] Determined by ([COD]/[**22**])(MW of COD)+(MW of **22**). [c] Determined by ^{1}H NMR integration assuming a number average functionality of 2.

temperature on the polymer yield and CTA **22** incorporation was examined. All of these polymerizations were run neat according to the conditions described in Table 3. In the first two entries in Table 3, the impact of the [COD]/[I] ratio on the polymerization was examined at 25°C for 48 h. Although similar molecular weight values were observed, a

significantly lower yield (51% compared to 60%) was observed at the lower initiator loading. So, for this polymerization to be run at 25°C, a 2000:1 [COD]/[I] ratio was necessary to optimize the yield. However, unlike the polymerization of COD with **21** in which elevated temperatures were unable to be employed, polymerizations using **22** were successful at 45°C. Comparing entries 3-6 in Table 3 which were run at 45°C, similar yields and molecular weights were observed regardless of changes in the reaction time or the [COD]/[I] ratio. Therefore, based on these results, all polymerizations with COD and CTA **22** were carried out at 45°C with a [COD]/[I] ratio of 4000:1 for 24 h.

As for the polymerization of COD with **21**, the polymerization of COD with **22** was accomplished at [COD]/[**22**] ratios of 15, 40, 60, and 80:1 in order to investigate the control of molecular weight in the synthesis of bis(epoxide)-functionalized telechelic poly(butadiene)s **26**. By varying the [COD]/[**22**] ratio from 15 to 80:1, $\overline{M}_n$ values between 3000-16800 were achieved with yields between 71-87% (Table 4). Again,

Table 4. Synthesis of bis(epoxide)-functionalized telechelic poly(butadiene)s **26**

[COD] / [**22**]	% Yield[d]	% *Cis*-Olefin (Backbone)[e]	% *Cis*-Olefin (End Group)[e]	$\overline{M}_n$ (Theoretical)[f]	$\overline{M}_n$ (NMR)[g]	$\overline{M}_n$ (GPC)[h]	PDI[h]
15[a]	71	60	30	1820	3000	4000	1.55
40[a]	80	65	25	4520	7800	6900	1.89
60[b]	87	50	30	6680	11000	10500	1.87
80[c]	84	55	25	8840	16800	11600	1.94

[a] Polymerizations were run neat at 45°C for 24 h with [COD]/[I]=4000. [b] To ensure better mixing and higher yields, [COD]= 12.4 M in benzene was utilized. [c] To ensure better mixing and higher yields, [COD]= 9.3 M in benzene was utilized. [d] Isolated yields after purification. [e] Determined by ^{1}H NMR integration. [f] Determined by ([COD]/[**22**])(MW of COD)+(MW of **22**). [g] Determined by ^{1}H NMR integration assuming a number average functionality of 2. [h] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards.

excellent molecular weight control was observed as illustrated in the plot of the $\overline{M}_n$ versus the [COD]/[**22**] ratio seen in Figure 2. As in the polymerization of COD with **21**, the experimental molecular weights were significantly higher than the theoretical values presumably due to incomplete incorporation of **22** during the polymerization.[26] The bis(epoxide)-functionalized telechelic poly(butadiene)s **26** contained between 50-65% *cis*-olefins in the backbone and between 25-30% *cis*-olefins in the end groups, similar to the results obtained for the bis(methacrylate)-functionalized telechelic poly(butadiene)s **25**, and PDIs of 1.55-1.94 were observed. Again, both ^{1}H and ^{13}C NMR supported a $\overline{F}_n$ near 2 for these materials.

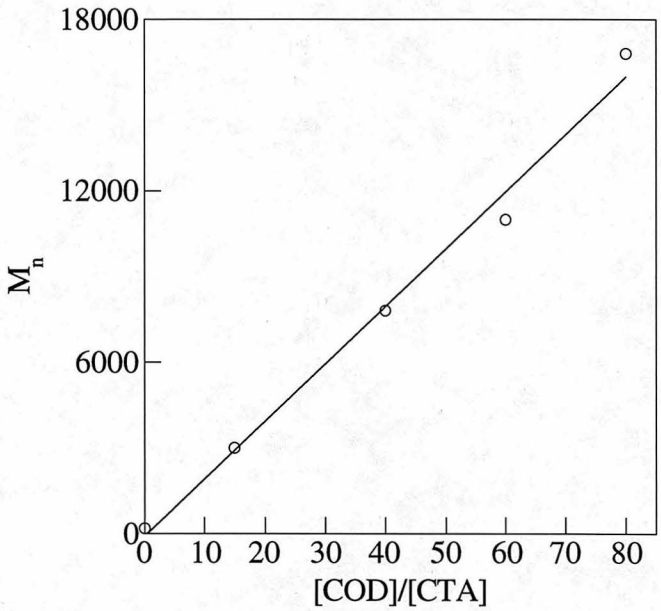


Figure 2. Dependence of the observed $\overline{M}_n$ values for the bis(epoxide)-functionalized telechelic poly(butadiene)s **26** on the [COD]/[CTA] ratio. The $\overline{M}_n$ was determined by ^{1}H NMR integration assuming a number average functionality of 2.0.

Cross-linking of the telechelic poly(butadiene)s 25 and 26. With the successful development of the syntheses of the telechelic poly(butadiene)s **25** and **26**

described above, preliminary studies on the cross-linking of these materials were examined. The cross-linking of the bis(methacrylate)-functionalized telechelic poly(butadiene)s **25** was accomplished both thermally and photochemically. For thermal cross-linking, concentrated solutions of polymer **25** (100 mg of polymer **25** in 200 μL toluene) ($\overline{M}_n$ values between 3700 to 17700) were combined with benzoyl peroxide (2 wt%) and heated to 90°C. Within 5 min, a tacky insoluble material was observed, and within 15 min, a rubbery polymeric solid was formed which was completely insoluble in all common organic solvents including CH_2Cl_2, $CHCl_3$, benzene, toluene, Et_2O, ethyl acetate, and DMSO. These materials were also cross-linked photochemically by combining either benzoyl peroxide or 2,2-dimethoxy-2-phenylacetophenone (2 wt%) with the concentrated polymer solutions and photolyzing the solutions for 15 min using a 450 watt medium pressure mercury Hanovia lamp. As in the thermally-induced cross-linking reactions, a tacky insoluble material was formed within 5 min, but only after 15 min was a highly cross-linked rubbery material obtained.

The cross-linking of the bis(epoxide)-functionalized telechelic poly(butadiene)s **26** was accomplished by acid treatment. Solutions of polymer **26** (100 mg of polymer **26** in 500 μL toluene) ($\overline{M}_n$ values between 3000 to 16800) were stirred with a magnetic stirrer and treated with H_2SO_4 (cat.). Upon addition of the acid, immediate formation of a rubbery polymeric solid was observed which was insoluble in all common organic solvents including CH_2Cl_2, $CHCl_3$, benzene, toluene, Et_2O, ethyl acetate, and DMSO. Treatment with other acids such as HCl (1 M in Et_2O) and *p*-toluenesulfonic acid resulted in no significant cross-linking even at elevated temperatures. Treatment of the polymer solutions with BF_3-Et_2O (cat.) resulted in cross-linking; however, the cross-linking required 2-3 h at room temperature and often gave inconsistent results. Treatment with H_2SO_4 (cat.) was by far the simplest and most rapid method for the cross-linking of the bis(epoxide)-functionalized telechelic poly(butadiene)s **26**.

Conclusions

The syntheses of bis(methacrylate)- and bis(epoxide)-functionalized CTAs were presented. These CTAs were successfully employed in the ROMP of COD for the preparation of cross-linkable telechelic poly(butadiene)s bearing either methacrylate or epoxide end groups. The influence of the initiator concentration, reaction time, and temperature on the polymer yield and chain transfer agent incorporation were examined for these polymerizations, and control over the molecular weight of these telechelic poly(butadiene)s through the [COD]/[CTA] ratio was demonstrated. The controlled thermal, photochemical, and acid catalyzed cross-linking of these materials was accomplished providing for numerous methods for the preparation of cross-linked poly(butadiene) networks. In contrast to the previous approach for cross-linkable polymers by ROMP discussed in Chapter 1, this methodology provides for the control of the polymer molecular weight between cross-links and should be more applicable to the preparation of cross-linkable polymers with varied backbone structures. Future studies on the cross-linking densities and swelling properties of these poly(butadiene) networks and the preparation of interpenetrating polymer networks from these materials should be investigated.

Experimental

General. Argon was purified by passage through columns of BASF R-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). NMR spectra were recorded on GE QE-300 Plus (300.1 MHz; 75.49 MHz ^{13}C) spectrometer and a JEOL GX-400 (399.65 MHz ^{1}H; 100 MHz ^{13}C; 161.85 MHz ^{31}P) spectrometer. ^{31}P NMR spectra were referenced to an external 85% H_3PO_4 standard. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. Gel permeation chromatographs were obtained on a HPLC system using an Altex model 110A pump, a Rheodyne model 7125 injector with a 100 μL injection loop, two American Polymer Standards 10 micron mixed bed columns, and a Knauer

differential-refractometer using CH_2Cl_2 as eluent at a 1.0 mL/min flow rate. Molecular weights and polydispersities were reported versus monodispersed polystyrene standards. Photolysis was accomplished with a 450 watt medium pressure mercury Hanovia lamp.

Materials. The benzene used in polymerizations was distilled from CaH_2 under vacuum. Dry THF was obtained by distillation under atmospheric pressure from CaH_2. All other solvents were reagent grade and used without purification. *cis*-2-Butene-1,4-diol, methacryloyl chloride, triethylamine, NaOH, $Bu_4N^+HSO_4^-$, epichlorohydrin, *p*-methoxyphenol, MeOH, benzoyl peroxide, 2,2-dimethoxy-2-phenylacetophenone, BF_3-Et_2O, and H_2SO_4 were purchased from the Aldrich Chemical Company and used without further purification. COD was purchased from the Aldrich Chemical Company and degassed by stirring *in vacuo* for 2 hours before use in polymerizations.

Preparation of *cis*-2-butene-1,4-diol dimethacrylate (21). *cis*-2-Butene-1,4-diol (14.04 g, 0.16 mol, 1.0 eq) was mixed with THF (500 mL) and triethylamine (40.34 g, 0.48 mol, 3.0 eq) in a 1 L round bottom flask under argon. To the reaction flask 90% methacryloyl chloride (53.9 g, 0.46 mol, 2.9 eq) was added via an addition funnel over 1 h at 0°C during which time a white precipitate was observed. The ice bath was then removed, and the reaction was left to stir overnight at room temperature. Deionized water (150 mL) was then added to dissolve the precipitated salts, and the reaction mixture was poured into a 2 L separatory funnel containing petroleum ether (750 mL). The organics were then washed with deionized water (3 x 200 mL), aqueous NaOH (15% w/w, 4 x 200 mL), and deionized water (3 x 200 mL). The organics were dried over $MgSO_4$ and concentrated *in vacuo*. The product was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes, R_f=0.45) to give 26.5 g (74%) of pure product as a viscous oil. To prevent cross-linking, this material was stored with *p*-methoxyphenol (20 wt%) at -30°C in a dry box. ^1H NMR ($CDCl_3$) δ 6.08-6.06 (m, 2H), 5.81-5.71 (m, 2H), 5.54-5.52 (m, 2H), 4.78-4.69 (m, 4H), 1.90-1.89 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 166.95, 136.03, 128.01, 125.67, 60.26, 18.19; IR (thin film on a NaCl plate) 3105, 3036, 2981,

2959, 2929, 2894, 1719, 1637, 1512, 1452, 1403, 1378, 1348, 1318, 1293, 1152, 1012, 975, 942, 815, 734, 651 cm^{-1}; HRMS (CI) calcd for $C_{12}H_{16}O_4$ $(M+H)^+$ 225.1127, found 225.1129.

Preparation of *cis*-2-butene-1,4-diol diglycidyl ether (22). In a 1L Erlenmeyer flask, epichlorohydrin (270 g, 3.00 mol, 10 eq), aqueous NaOH (50% w/w) (240 g, 3.00 mol, 10 eq), and $Bu_4N^+HSO_4^-$ (5.0 g, cat.) were combined at room temperature with magnetic stirring. A thermometer was placed in the flask to monitor the temperature during the reaction. To this flask, *cis*-2-butene-1,4-diol (26.5 g, 0.30 mol, 1 eq) was added dropwise slowly over 30 min. The reaction was extremely exothermic, and so the temperature was maintained between 30-40°C by controlling the addition rate as well as by intermittent cooling in an ice bath. At the end of the addition, the reaction temperature remained near 40°C for approximately 1 h, and when it began to cool, the reaction flask was heated at 40°C in an oil bath for an additional 1 h. The flask was allowed to cool, and then deionized water was added (200 mL). This mixture was then extracted with Et_2O (3 x 200 mL), dried over $MgSO_4$, and concentrated *in vacuo* to obtain a yellow oil. This was distilled at 0.2 mm Hg/105-110°C to give a clear oil (38.0 g, 65% yield). ^1H NMR ($CDCl_3$) δ 5.8-5.61 (m, 2H), 4.11-4.00 (m, 4H), 3.67 (dd, J_1=3.0Hz, J_2=11.4Hz, 2H), 3.30 (dd, J_1=5.7Hz, J_2=11.4Hz, 2H), 3.11-3.06 (m, 2H), 2.73 (dd, J_1=4.2Hz, J_2=4.8Hz, 2H), 2.54 (dd, J_1=2.7Hz, J_2=4.8Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 129.13, 70.76, 66.74, 50.61, 44.03; IR (thin film on a NaCl plate) 3055, 2999, 2922, 2867, 1511, 1472, 1439, 1411, 1327, 1253, 1162, 1094, 1016, 968, 947, 901, 855, 762 cm^{-1}; HRMS (CI) calcd for $C_{12}H_{18}O_2$ $(M+H)^+$ 201.1127, found 201.1128.

Reaction of CTAs 21 and 22 with the ruthenium benzylidene 19. All manipulations were carried out in a dry box. In a 10 mL vial, ruthenium benzylidene **19** (6.0 mg, 7.3e-6 mol, 1.0 eq), CTA (either **21** or **22**) (3.7e-4 mol, 50 eq), and C_6D_6 (0.70 mL) were combined to form a homogeneous solution. This solution was transferred to an NMR tube which was capped with a rubber septa and removed from the dry box. The

NMR tube was placed in an oil bath at 45°C for 30 min. After this time, the NMR tube was removed from the oil bath, and the reaction was analyzed by both ^{1}H and ^{31}P NMR.

General polymerization procedure. All manipulations were carried out in a dry box. In a 10 mL vial, the correct amount of either **21** or **22** and COD were weighed out. In a separate vial, the initiator was weighed out and a stirbar added, and this was combined with the COD/CTA mixture. The vial was then capped, removed from the dry box, and left to stir for the desired time. For reactions involving the methacrylate CTA **21**, aluminum foil was wrapped around the reaction vial to prevent photo-induced cross-linking. At the end of the desired reaction time, ethyl vinyl ether (600 eq relative to initiator) was pipetted into the vial along with an equal volume of toluene. This was left to stir for 1 h followed by precipitation into MeOH to isolate the polymer. The MeOH was decanted away, and the polymer was washed with excess fresh MeOH to remove any remaining COD or CTA. The resulting telechelic poly(butadiene)s were concentrated *in vacuo* and then characterized by standard methods including ^{1}H NMR, ^{13}C NMR, IR, and GPC.

Bis(methacrylate)-functionalized telechelic poly(butadiene) (25). Spectral data for the polymer derived from a 15:1 [COD]/[**21**] ratio ($\overline{M}_n$ (NMR)=3700, DP=32). ^{1}H NMR ($CDCl_3$) δ 6.13 (bs), 5.86-5.54 (bm), 4.68 (bd, *J*=6.0Hz), 4.57 (bd, *J*=6.6Hz), 2.43-1.72 (bm); ^{13}C NMR ($CDCl_3$) δ 167.224, 167.14, 136.37, 135.49, 135.41, 134.50, 130.66, 130.42, 130.06, 129.94, 129.55, 129.38, 128.95, 128.76, 128.67, 125.34, 124.23, 124.14, 123.84, 123.67, 65.29, 60.60, 60.53, 32.93, 32.65, 32.28, 31.89, 27.66, 27.36, 27.01, 26.67, 18.34; IR (thin film on a NaCl plate) 3005, 2937, 2844, 1721, 1655, 1639, 1446, 1403, 1318, 1294, 1239, 1159, 1079, 1010, 966, 814, 733 cm^{-1}.

Bis(epoxide)-functionalized telechelic poly(butadiene) (26). Spectral data for the polymer derived from a 15:1 [COD]/[**22**] ratio ($\overline{M}_n$ (NMR)=3000, DP=26). ^{1}H NMR ($CDCl_3$) δ 5.77-5.17 (bm), 4.09-3.91 (bm), 3.72-3.61 (bm), 3.41-3.30 (bm),

3.17-3.08 (bm), 2.81-2.72 (bm), 2.62-2.53 (bm), 2.35-1.64 (bm); ^{13}C NMR ($CDCl_3$) δ 134.49, 134.43, 133.19, 130.26, 130.03, 129.93, 129.73, 129.52, 129.35, 126.19, 126.06, 125.90. 71.95, 70.65, 70.46, 66.81, 50.72, 44.33, 44.26, 32.91, 32.63, 32.29, 32.04, 27.97, 27.63, 27.35, 27.10, 26.76; IR (thin film on a NaCl plate) 3006, 2918, 2846, 1654, 1437, 1403, 1348, 1312, 1240, 1158, 1101, 966, 845, 732 cm^{-1}.

Cross-linking of bis(methacrylate)-functionalized telechelic poly(butadiene)s (25). In a 2 mL glass vial, polymer **25** (100 mg) was dissolved in toluene (200 μL) with either benzoyl peroxide or 2,2-dimethoxy-2-phenylacetophenone (2 mg, 2 wt%). This solution was then either subjected to heat in an oil bath at 90°C (benzoyl peroxide-initiated) or light using a 450 watt medium pressure mercury Hanovia lamp (benzoyl peroxide- or 2,2-dimethoxy-2-phenylacetophenone-initiated) in a photolysis chamber. Although an insoluble material was formed within 5 min under these conditions for each of the different molecular weight polymers synthesized, heating or photolysis for 15 min resulted in a more highly cross-linked rubbery material which was completely insoluble in all common organic solvents including CH_2Cl_2, $CHCl_3$, benzene, toluene, Et_2O, ethyl acetate, and DMSO.

Cross-linking of bis(epoxide)-functionalized telechelic poly(butadiene)s (26). In a 2 mL vial, polymer **26** (100 mg) was dissolved in toluene (500 μL) and a stir bar was added. This solution was then stirred at room temperature and H_2SO_4 (cat.) was added. Immediate formation of an insoluble rubbery solid was observed for each of the different molecular weight polymers synthesized. These materials were completely insoluble in all common organic solvents including CH_2Cl_2, $CHCl_3$, benzene, toluene, Et_2O, ethyl acetate, and DMSO.

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Chapter 3:

Ruthenium Alkylidene-Initiated Living Ring-Opening Metathesis Polymerization (ROMP) of 3-Substituted Cyclobutenes

Abstract

The synthesis and living ring-opening metathesis polymerization (ROMP) of substituted cyclobutenes were investigated with the functional group tolerant initiators $(PCy_3)_2Cl_2Ru=CHCH=CPh_2$ (**1**) and $(PCy_3)_2Cl_2Ru=CHPh$ (**2**). Synthetic methodology was developed for the synthesis of a wide variety of 3-functionalized cyclobutenes containing ether, ester, alcohol, amine, amide, and carboxylic acid substituents. Coordination of these functional groups to the propagating carbene was observed resulting in the formation of a chelated propagating species with concomitant loss of one phosphine ligand from the metal center. Studies aimed at understanding this chelation and its effect on the polymerization were undertaken. Based on these results, the synthesis of a series of functionalized cyclobutenes was accomplished which minimized this chelation and allowed for living polymerizations. A new class of functionalized poly(butadiene) homopolymers and diblock copolymers was synthesized and the thermal properties analyzed by thermogravimetric analysis and differential scanning calorimetry.

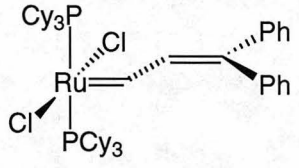
Introduction

Ring-opening metathesis polymerization (ROMP) of strained cyclic olefins has allowed for the synthesis of a wide range of functionalized polymers with control over polymer molecular weight and structure.[1-3] In particular, the ROMP of cyclobutenes to form poly(cyclobutene)s (equivalent to poly(butadiene)s) has been well documented, and this polymerization is driven by the high strain energy of the cyclobutene ring (29.8 kcal/mol).[4] Dall'Asta first observed the ROMP of cyclobutene in 1962 using $TiCl_4/Et_3Al$ resulting in high *cis*-poly(butadiene).[5] Two component initiator systems such as $TiCl_4/(\pi\text{-}C_4H_7)_4Mo$,[6] $V(acac)_3/Et_3Al$,[7] $VCl_4/BuLi$,[8] $Cr(acac)_3/Et_3Al$,[7] $MoCl_3/Et_3Al$,[7] $MoCl_5/(\pi\text{-}C_4H_7)_4W$,[9] $MoCl_5/(\pi\text{-}C_4H_7)_2Mo$,[9] and $WCl_6/(\pi\text{-}C_4H_7)_4W$[9] were among the many later initiator systems used for the polymerization of cyclobutene and its derivatives. In addition, one component catalysts such as $Ph(MeO)C{=}W(CO)_5$,[10] $Ph_2C{=}W(CO)_5$,[11] and $RuCl_3$[12] were successful as well. Titanocene methylidenes were active for the polymerization of 3,4-diisopropylidenecyclobutene leading to a cross-conjugated polymer that was a precursor to conducting polymers.[13]

In none of these cases was a living polymerization of the cyclobutenes observed.[14,15] In the past few years, though, a few examples of the living polymerization of cyclobutenes were published. The alteration of the rates of initiation and propagation using PMe_3 for W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ [Ar=2,6-diisopropylphenyl] in the polymerization of cyclobutene led to the first living polymerization and the synthesis of block copolymers.[16,17] In a similar fashion, 3-methylcyclobutene and 3,3-dimethylcyclobutene were polymerized in a living manner using $Mo(CHC(CH_3)_2Ph)(NAr)(OC(CH_3)_2CF_3)_2$ [Ar=2,6-diisopropylphenyl] and $PPhMe_2$.[18,19] The living polymerization of bicyclo[3.2.0]heptene using $(PPh_3)_2Cl_2Ru{=}CHCH{=}CPh_2$ was also observed.[20] Recently, the synthesis of poly(butadiene)s bearing acid and alcohol functionality was accomplished through the living ROMP of 3,4-disubstituted cyclobutenes bearing benzyl ether and benzyl ester

protecting groups.[21,22] Unfortunately, the introduction of the alcohol and carboxylic acid groups was accomplished only after a post-polymerization deprotection step due to the intolerance of the initiator toward these functionalities.

The ultimate goal would be the development of methodology to allow for the living ROMP of highly functionalized cyclobutenes without the need for protection of functional groups, providing for the one-step synthesis of a wide range of functionalized poly(butadiene)s. This would allow for a more complete study of the properties of functionalized poly(butadiene)s that would be difficult to synthesize through other methods, and the synthesis of block copolymers with a number of functional groups would be possible resulting in the formation of a wide range of new materials and a detailed study of the properties of block copolymers.[23] With the development of the highly functional group tolerant metathesis initiators $(PCy_3)_2Cl_2Ru{=}CHCH{=}CPh_2$ (**1**)[24,25] and $(PCy_3)_2Cl_2Ru{=}CHPh$ (**2**),[26,27] such a goal seemed attainable. These and related complexes have been applied to the polymerization of cyclooctenes bearing a a variety of polar functional groups.[28,29] However, these polymerizations were not living due to the



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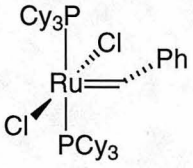


2

facile backbiting and chain transfer reactions that occurred during the polymerization. A system which could produce high initiation with no backbiting, chain transfer, or chain termination side reactions would result in a living polymerization producing polymers with low polydispersity.[14,15] This report presents the synthesis and polymerization of a series of 3-functionalized cyclobutenes. The development of a living polymerization of these cyclobutenes was achieved only after a complete understanding was obtained of the effect

of the functional groups on the polymerization mechanism. Thermal analysis of the resulting functionalized poly(butadiene) homopolymers and diblock copolymers was accomplished by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Results and Discussion

Initial investigations. Before an intensive investigation of the synthesis and ROMP of 3-substituted cyclobutenes was undertaken, the factors affecting the stability of these compounds needed to be addressed. The conrotatory electrocyclic ring-opening of cyclobutenes to butadienes posed a complication for their use in polymerizations.[30] The presence of butadiene impurities in the monomer would lead to chain transfer through a side reaction of the propagating carbene with the butadiene olefins, thus broadening the polymer polydispersity (PDI) and preventing a living polymerization. The activation barriers for this ring-opening were determined for a series of 3-substituted cyclobutenes as presented in Table 1.[31-35] The presence of polar functionality in the 3-position lowered

Table 1. Activation energies for the conrototatory electrocyclic ring-opening of selected cyclobutenes

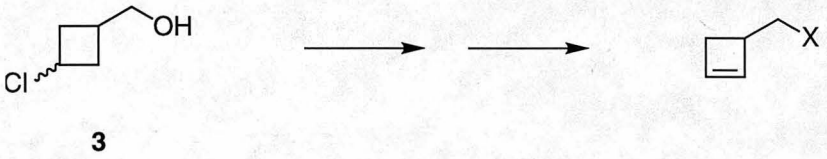
Compound	E_a (kcal/mol)
cyclobutene	32.5
3-methylcyclobutene	31.6
3-chlorocyclobutene	29.4
3-acetoxycyclobutene	27.8
3-formylcyclobutene	27.0
3-ethoxycyclobutene	23.5

this activation barrier significantly.[33-35] In fact, 3-formylcyclobutene undergoes this ring-

opening at 25°C with a half-life of 50 h.[35] Due to these observations, placement of the functional group at least one carbon removed from the ring at the 3-position was proposed in order to provide more stable monomers in which this electrocyclic ring-opening reaction was minimized.

Utilization of a common intermediate which could be readily transformed into a series of functionalized cyclobutenes would simplify the synthetic approach. *Cis, trans*-1-(3-chlorocyclobutane)methanol (**3**) appeared to be an attractive intermediate for this strategy. This compound provided not only a route for the incorporation of various functionalities through the elaboration of the alcohol substituent but also a route to the cyclobutene olefin by chloride elimination (Scheme 1). Compound **3** had been previously synthesized as illustrated in Scheme 2.[36,37] However, the low overall yield (15%)

Scheme 1



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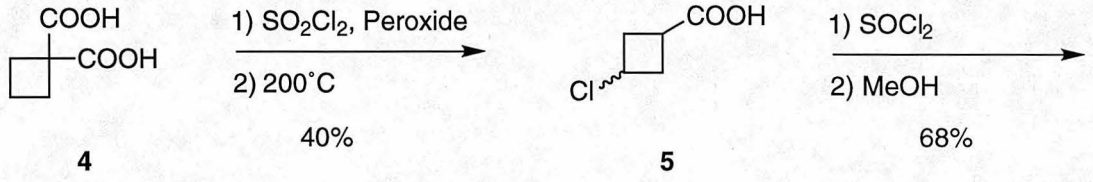
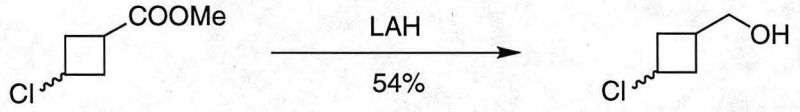
Scheme 2



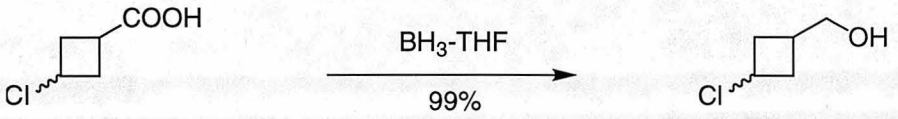
4 **5**



6 **3**

prompted an investigation into a more efficient synthesis of this compound. By simple reduction of the carboxylic acid **5** with BH_3-THF,[38] compound **3** was formed in quantitative yield as illustrated in Scheme 3. After optimization of the first step coupled with the high yielding reduction step, a higher overall yield (50%) than the literature value was achieved with the elimination of one step in the procedure.

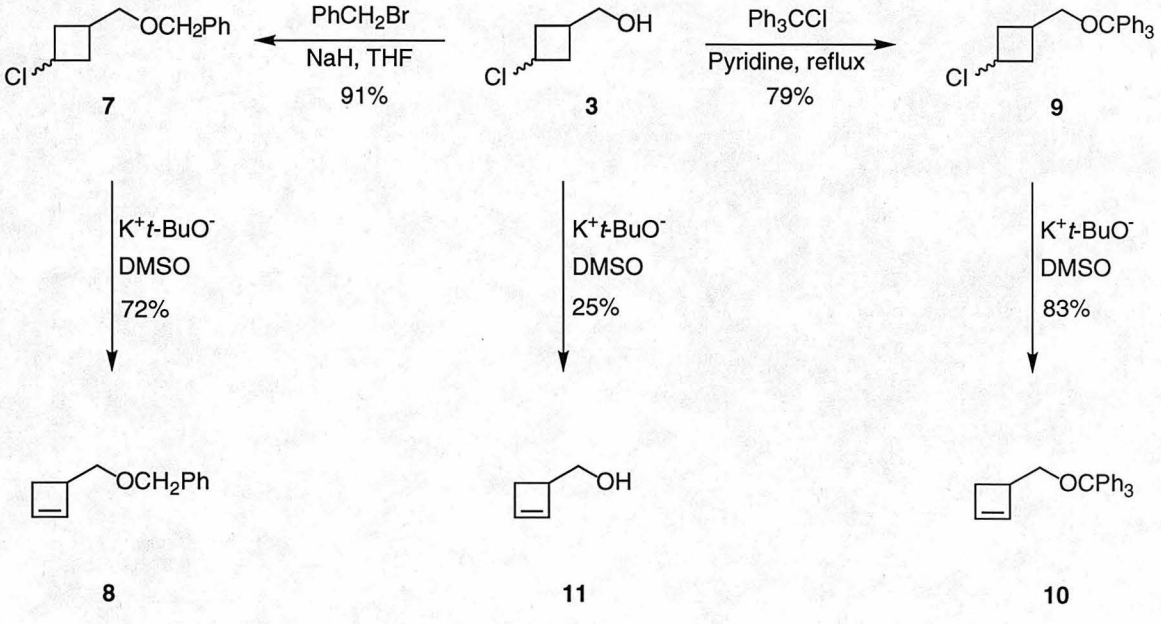
Scheme 3



5 **3**

With an efficient synthesis of **3**, cyclobutenes bearing benzyl ether, trityl ether, and alcohol functionality were synthesized as shown in Scheme 4. Alkylation of **3** with either benzyl bromide or trityl chloride and subsequent elimination of the resulting ethers **7** and **9**

Scheme 4

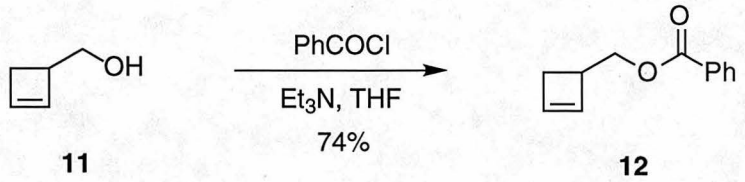


7 **3** **9**

8 **11** **10**

with K^+t-BuO^- in DMSO resulted in good yields of benzyl [1-(2-cyclobutenyl)methyl] ether (**8**) and [1-(2-cyclobutenyl)methyl] trityl ether (**10**), respectively. Attempted elimination with other bases including $NaNH_2$ (THF), LDA (THF), K^+t-BuO^- (THF), DBU (benzene), and KH (THF) resulted in no reaction which was consistent with results observed in similar systems.[36,37] Elimination of **3** resulted in (2-cyclobutenyl)methanol (**11**) in 25% yield using a literature procedure.[36,37] Esterification of **11** with benzoyl chloride resulted in 1-(2-cyclobutenyl)methyl benzoate (**12**) in 74% yield as in Scheme 5. As expected, all the cyclobutenes were thermally stable resulting in the lack of butadiene formation even after heating to >90°C.

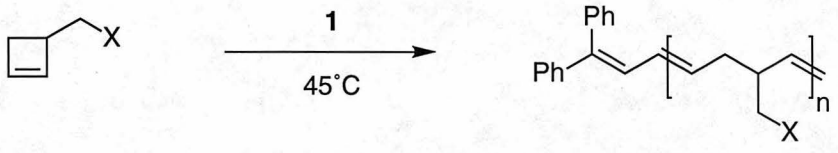
Scheme 5



11 **12**

Initial polymerization of monomers **8**, **10**, **11**, and **12** was accomplished with initiator **1** as in Scheme 6. The polymerization of these monomers allowed for the investigation of the influence of functional groups of differing electronic and steric

Scheme 6



environments on the polymerization. Unfortunately, polymerization of (2-cyclobutenyl)methanol (**11**) resulted in a polymer that was insoluble in all the solvents compatible with initiator **1** including CH_2Cl_2, $CHCl_3$, toluene, benzene, and THF. The fact that polymer formation was observed was promising in that **1** appeared to be active for

the polymerization of these cyclobutenes, in contrast to the results observed by Perrott and Novak for 3,4-disubstituted cyclobutenes with **1**.[21,22] Polymerization of **8**, **10**, and **12** presented no such complication. Optimal polymerization conditions employed for these monomers were at 45°C in toluene with a monomer concentration ([M]) of 0.57 M (Table 2). Polymerization of these compounds at varying [monomer]/[initiator] ([M]/[I]) ratios

Table 2. Initial polymerization results for compounds **8**, **10**, and **12**[a]

Entry	Monomer	[M]/[I]	Rxn. Time (h)	$\overline{M}_n$[b]	PDI[b]
1	**8**	25.7	1.0-1.5	4900	1.18
2	**8**	53.1	1.0-1.5	8000	1.17
3	**8**	71.1	1.0-1.5	10700	1.17
4	**8**	96.7	1.0-1.5	15900	1.15
5	**8**	152	1.0-1.5	21300	1.16
6	**10**	8.70	<0.5	6500	1.60
7	**10**	51.6	<0.5	12600	1.44
8	**10**	94.6	<0.5	25900	1.31
9	**10**	189	<0.5	34900	1.30
10	**12**	26.0	<0.5	4200	1.70
11	**12**	47.1	<0.5	5600	1.65
12	**12**	70.6	<0.5	9000	1.60
13	**12**	131	<0.5	11100	1.57
14	**12**	218	<0.5	15300	1.71

[a] Polymerizations were run in toluene at 45°C with [M]=0.57 M. [b] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards.

was accomplished, allowing for the control over the polymer molecular weight for all three

monomers. A linear correlation between the $\overline{M}_n$ and the [M]/[I] ratio was observed, providing initial support for a living polymerization (Figure 1). However, comparison of

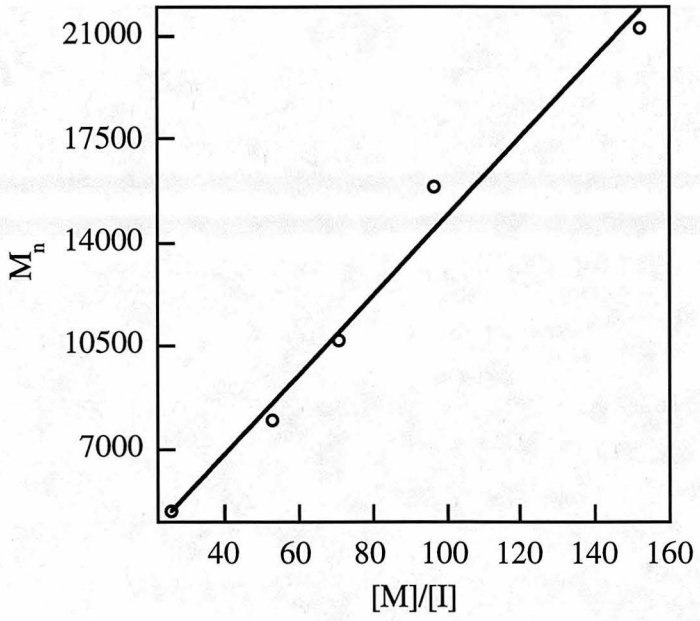


Figure 1. Molecular weight dependence of the polymerization of **8** on the [M]/[I].

the PDIs of the polymers obtained showed that despite the fact that these monomers differed only in steric or electronic features reasonably far removed from the olefinic moiety, dramatic changes in the PDIs were observed. For benzyl [1-(2-cyclobutenyl)methyl] ether (**8**), the polymerization reached completion after 1-1.5 h and low PDIs between 1.15 and 1.18 were obtained (entries 1-5), while for [1-(2-cyclobutenyl)methyl] trityl ether (**10**), which differed from **8** predominantly in its steric environment surrounding the ether oxygen, the polymerization reached completion after <0.5 h and PDIs between 1.30-1.60 were obtained. 1-(2-Cyclobutenyl)methyl benzoate (**12**), which differed from **8** in the electronic character of the oxygen atom but was

sterically similar, polymerized to completion in <0.5 h and resulted in even broader PDIs of 1.57-1.71 (entries 10-14).

In order to gain more insight into the causes for these PDI differences, the propagating carbenes were investigated by ^{1}H and ^{31}P NMR. The monomers were polymerized under the standard conditions at 45°C in toluene-d_8 ([M]=0.57 M) for 1 h, and then they were analyzed by ^{1}H and ^{31}P NMR. For the benzyl ether (**8**), two distinct regions were observed at 19.84 and 17.73 ppm for the α-H of the carbene in the ^{1}H NMR in a ratio of 1.00:8.91 (Table 3). By ^{31}P NMR, a major species at 57.76 ppm and a minor

Table 3. ^{1}H NMR analysis of the polymerization propagating species

X	% Initiation with 5 eq. [M][a]	^{1}H NMR Carbene Resonance of A[b]	^{1}H NMR Carbene Resonance of B[b]	Ratio B/A[b]	$(10^3K_{eq})^b$
OCH_2Ph	>99 %	19.84	17.73	8.91	81
$OC(Ph)_3$	25 %	19.86	18.41	1.43	8.5
OC(O)Ph	15 %	19.83	17.79	0.567	2.0
OH	>99 %	-----	17.70	>99.0	>990
$N(i\text{-}Pr)_2$	>99 %	-----	17.97	>99.0	>990
OCH_2COOH	>99 %	-----	17.74	>99.0	>990
OCH_2COOMe	>99 %	19.80	17.91	12.5	120
OCH_2CONMe_2	>99 %	-----	17.84	>99.0	>990
$OCH_2CON(i\text{-}Pr)_2$	>99 %	-----	17.76	>99.0	>990

[a] Polymerizations were run in toluene-d_8 at 45°C for 1 h at [M]=0.11 M and [I]=0.022 M and analyzed by ^{1}H NMR using a JEOL GX-400 spectrometer. [b] Polymerizations were run in toluene-d_8 at 45°C for 1 h at [M]=0.57 M and [I]=0.010 M and analyzed by ^{1}H NMR using a JEOL GX-400 spectrometer.

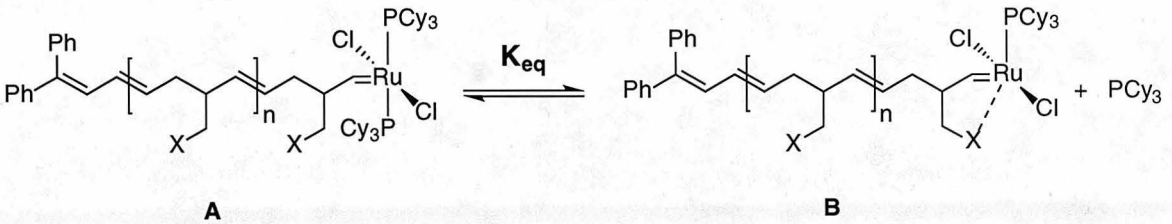
species at 37.35 ppm were observed in addition to free PCy_3 at 10.82 ppm which integrated to 1.02 relative to the species at 57.76 ppm. For the trityl ether (**10**), again two

distinct regions were observed in the ^{1}H NMR at 19.86 and 18.41 ppm in a 1.00:1.43 ratio (Table 3). ^{31}P NMR showed a multiplet at 38.90 and a multiplet at 36.60-35.21 ppm with free PCy_3 at 10.80 ppm integrating to 1.05 relative to the peak at 38.90 ppm. Finally, the benzoate ester (**12**) had multiplets at 19.83 and 17.79 ppm in a 1.80:1.00 ratio in the ^{1}H NMR (Table 3), and the ^{31}P NMR showed peaks at 40.28 ppm and a broad multiplet from 37.01-35.00 ppm with free PCy_3 integrating to 1.01 relative to the peak at 40.28 ppm. These results were compared with the species observed for the polymerization of cyclooctadiene (COD) which resulted in a broad triplet at 19.67 ppm in the ^{1}H NMR and 36.42 ppm in the ^{31}P NMR with no observed free PCy_3.

Based on these combined results, it was proposed that the upfield resonance in the ^{1}H NMR corresponded to a monophosphine propagating species (B) and the downfield resonance corresponded to the normal bisphosphine species (A). The results were based primarily on the fact that the polymerization of COD which showed the presence of no free PCy_3 resulted in a ^{1}H NMR carbene resonance at 19.67 ppm, similar to the values at 19.84, 19.86, and 19.83 ppm for compounds **8**, **10**, and **12**. In addition, the more upfield resonances in the ^{1}H NMR between 17.73-18.41 appeared to correspond with the more downfield shifts in the ^{31}P NMR based on integration measurements, and these downfield resonances in the ^{31}P NMR integrated with equal intensity to the free PCy_3. Considering that the propagating species for the polymerization of COD is identical to that for cyclobutene, the observation of free PCy_3 in the polymerization of these substituted cyclobutenes must be the result, in part, of the functional groups on the cyclobutene ring. The most probable explanation for the role of the functional group was coordination of this group to the metal center resulting in stabilization of the monophosphine species. This was consistent with the observed ratios of mono- and bisphosphine species observed. The more Lewis basic benzyl ether (**8**) resulted in the highest preference of monophoshine species followed by the more bulky trityl ether (**10**), and lastly the more electron poor benzoate ester (**12**).

The monophosphine (B) and bisphosphine species (A) were proposed to be in equilibrium as presented in Scheme 7. In order to help support this hypothesis, free PCy_3 (10.6 eq) was added to the benzyl ether polymerization described above. If there were an

Scheme 7



A **B**

equilibrium between monophoshine (B) and bisphosphine species (A) as presented in Scheme 7, then the ratio of the two species in the ^1H NMR should shift upon the addition of PCy_3. As discussed above, the ratio of the resonances at 19.84 and 17.73 ppm was 1.00:8.91 initially; however, after the addition of phosphine, this ratio shifted to 1.46:1.00. The calculated equilibrium constant[39] should have been identical in both cases, and it was calculated for both resulting in $K_{eq}=8.1x10^{-2}$ before the addition of phosphine and $K_{eq}=7.3x10^{-2}$ after the addition. These values were within the experimental error expected based on the use of NMR integration for these measurements. Another experiment used to support the equilibrium proposed in Scheme 7 was to study the ratio of the two propagating species at variable temperatures. Polymerization of the benzyl ether (**8**) was accomplished as above, and the equilibrium constants were determined through NMR integration of the ^1H NMR resonances of the propagating species A and B. By cooling the reaction mixture, entropically-driven processes should be more disfavored relative to enthalpically-driven ones, thus resulting presumably in the increase of species A at lower temperatures. This was the observed trend which is represented in a van't Hoff plot (Figure 2). From the van't Hoff plot, the standard enthalpy and entropy of the equilibrium were determined as 7.3 ± 0.7 kcal/mol and 20 ± 2 cal/mol·K, respectively. These values were consistent with the expected large and positive entropy term due to the loss of free PCy_3 and chelation of

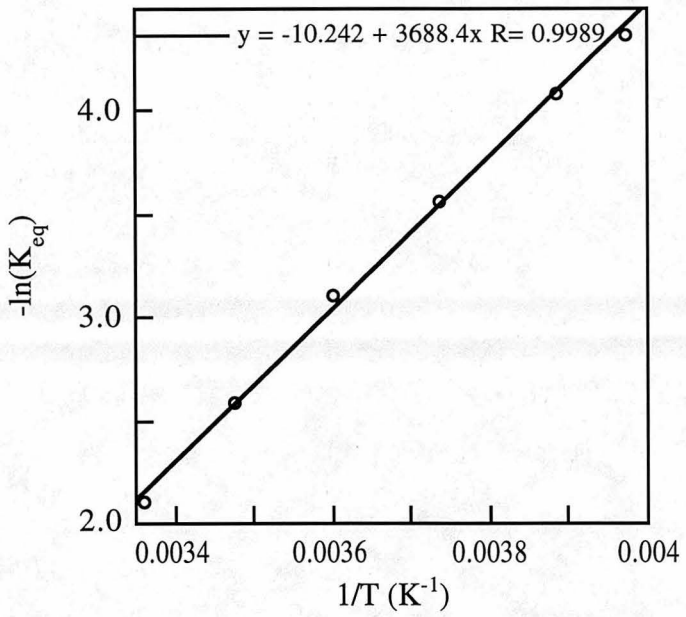


Figure 2. Van't Hoff plot of the benzyl [1-(2-cyclobutenyl)methyl] ether (**8**) polymerization propagating species.

the ether functionality and the positive enthalpy term resulting from loss of the ruthenium-phosphine bond in exchange for the weaker ruthenium-ether bond.

In addition to the nearest neighbor chelation illustrated in Scheme 7, several alternate hypotheses for the nature of this coordination were envisioned. First, the monophosphine complex could have been the result of simple coordination of the monomer to the propagating species, resulting in loss of phosphine. However, this hypothesis was ruled out by two experiments. One, polymerization of COD as described above in THF-d_8 instead of toluene-d_8 resulted in no free phoshine or significant shift in either the ^{1}H carbene resonance (19.43 ppm) or the ^{31}P NMR resonance (36.14 ppm). If coordination of the ether functionality of the monomer to the metal center was occurring resulting in loss of phosphine, free phosphine should have been observed when the polymerization of COD

was run in THF. Second, the percentage of mono- and bisphosphine species were found to be invariant during the polymerization, even after all the monomer had been consumed. Another mechanistic consideration was intermolecular coordination of a functional group from another polymer chain instead of the proposed intramolecular coordination. This proposal was excluded for the same reasons as the monomer coordination proposal. The fact that THF resulted in no free phosphine even when used in large excess as solvent contradicted an intermolecular coordination proposal. The large, positive entropy term determined above also tended to exclude this intermolecular coordination. One final possibility was that the coordination was intramolecular as proposed, but that the coordination was not limited to the nearest neighbor functional group and could have occurred through other side-chains on the polymer further removed from the propagating species. Intuitively chelation through the 5 or 6-membered ring that results from nearest neighbor coordination seemed more reasonable than chelation resulting in larger, more kinetically and thermodynamically disfavored ring sizes, but this proposal cannot be completely excluded.

The question still remained as to what effect, if any, the relative amounts of mono- and bisphosphine propagating species had on the observed PDIs for the polymerization of **8**, **10**, and **12**. In an effort to understand the differing PDIs displayed in Table 2, the relative k_p/k_i values were examined for these polymerizations. 5 eq of monomers **8**, **10**, **12** ([M]=0.11 M) were treated with initiator **1**, and the percent initiation was measured by ^{1}H NMR integration of the propagating carbene α-protons (Table 3). The percent initiation observed was used as a measure of the relative k_p/k_i values for the different polymerizations. For monomer **8** complete initiation was observed, while for the trityl ether (**10**) 25% initiation was observed, and for the benzoate ester (**12**), 15% initiation was observed. Complete initiation of **1** with the trityl ether (**10**) was accomplished only after the addition of another 20 eq of **10**, and the initiation of **1** with the benzoate ester (**12**) resulted only after the addition of ~30 eq of **12**. Therefore, as the degree of chelation

increased, a reduction in the relative k_p/k_i was observed. A reduction in the k_p/k_i should have resulted in more narrowly dispersed polymers, and this was the observed trend.[23]

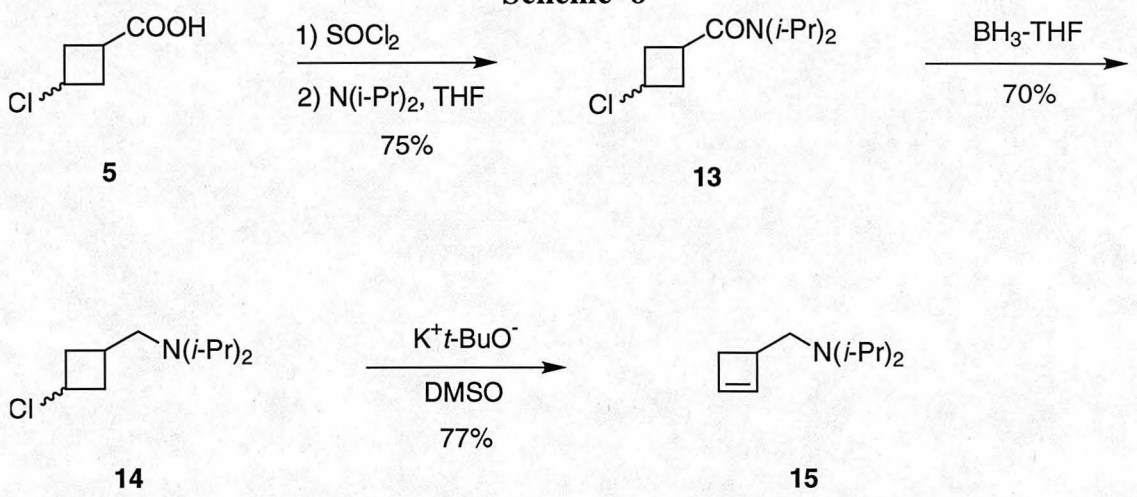
The alteration of k_p/k_i in metathesis polymerizations through the addition of Lewis basic compounds has precedent in the literature. As described in the introduction, the addition of phophines to certain W and Mo alkylidenes slowed k_p relative to k_i through preferential binding of the base to the propagating carbene.[16-19] The addition of quinuclidine to the polymerization of acetylene with W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ [Ar=2,6-diisopropylphenyl] led to lower values of k_p/k_i which was again explained by preferable binding of the quinuclidine to the propagating species over the starting complex.[40] THF was also observed to slow propagation when used as a solvent in the polymerization of cyclooctatetraene with W(CHC(CH$_3$)$_3$)(NAr)(OC(CF$_3$)$_2$CH$_3$)$_2$ [Ar=2,6-diisopropylphenyl].[41] Evidence for binding of functionality on the polymer backone itself in affecting rates of propagation has been observed as well. In the polymerization of 5-alkylthiocyclooctenes with a metallacyclic aryloxo(chloro)neopentylidenetungsten complex, the rate of polymerization was determined to be dependent on the steric parameters of alkyl group present on the sulfur. With bulkier alkyl groups, more rapid polymerization was achieved presumably due to blocking of sulfur coordination to the metal center.[42] In the living polymerization of bicyclo[3.2.0]heptene with (PPh$_3$)$_2$Cl$_2$Ru=CHCH=CPh$_2$, weak coordination of olefins in the backbone to the propagating species was proposed as well resulting in a lowering of k_p/k_i.[20]

Polymerization of monomers bearing even more Lewis basic functional groups than the benzyl ether should have resulted in an even higher ratio of mono- to bisphosphine propagating species (B/A). Despite the fact that the polymerization of (2-cyclobutenyl)methanol (**11**) resulted in an insoluble material, polymerization of 5 eq of **11** ([**11**]=0.11 M) was possible without polymer precipitation. Complete initiation was observed with only one propagating species at 17.70 ppm in the ^{1}H NMR (Table 3) and 56.79 ppm in the ^{31}P NMR with 1.05 equivalents of free PCy$_3$; no bisphosphine species

was present. The insolubility of poly(**11**) prevented a more intensive study of this polymerization, so the polymerization of a cyclobutene bearing an amine side-chain was studied. This too was expected to result in complete chelation with no bisphosphine species due to the Lewis basicity of the amine, yet initiator **1** was known to have decreased activity and/or to decompose in the presence of amines.[43] Therefore, the sterically hindered diisopropyl(1-(2-cyclobutene)methyl)amine (**15**) was chosen as a target.

The synthesis of **15** was achieved through several relatively straightforward, high yielding steps as shown in Scheme 8. Formation of the acid chloride of **5** with thionyl

Scheme 8



5 **13** **14** **15**

chloride followed by treatment with diisopropylamine resulted in amide (**13**) in 75% yield. BH_3-THF reduction of the amide[38,44] followed by elimination using the standard conditions resulted in diisopropyl(1-(2-cyclobutene)methyl)amine (**15**) in good yield. Treatment of **1** with 5 eq of **15** ([**15**]=0.11 M) resulted in complete initiation of **1**. Polymerization under the standard conditions of [**15**]=0.57 M, 45°C, in toluene-d_8 resulted in complete formation of a new propagating carbene at 17.97 ppm in the ^{1}H NMR. In the ^{31}P NMR, a multiplet at 43.68 ppm was observed in a 1.00:1.11 ratio with free phosphine at 10.79 ppm. So, as expected, a higher degree of coordination was observed for the more Lewis basic amine resulting in a $K_{eq} \geq 9.9 \times 10^{-1}$ compared to the value of 8.1×10^{-2} for the

benzyl ether (**8**) (Table 3). Complete conversion of **15** to polymer required 4.5 h at 45°C with no polymer precipitation compared to **11**, and a linear correlation between the $\overline{M}_n$ and the [M]/[I] ratio was observed. Low PDIs between 1.13-1.25 were obtained as expected due to the complete formation of the chelated monophosphine propagating species (Table 4). This chelation was consistent with the longer reaction time necessary for complete

Table 4. Polymerization results for amine **15**[a]

[M]/[I]	$\overline{M}_n$[b]	PDI[b]
25.4	5900	1.13
44.1	8000	1.16
73.6	12500	1.18
100	14800	1.22
147	18400	1.25

[a] Polymerizations were run in toluene at 45°C with [**15**]=0.57 M for 4.5 h. [b] Determined by gel permeation chromatography in THF relative to monodispersed polystyrene standards.

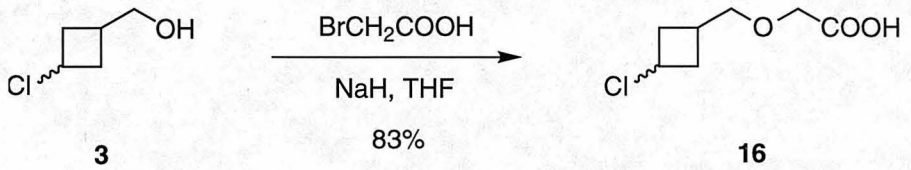
polymerization due to a significant reduction in k_p. However, decomposition of the propagating carbene was evident in both the ^{31}P NMR and in the GPC. As the polymerization neared completion, the formation of a new species at 23.47 ppm in the ^{31}P NMR was observed presumably the result of some decomposition pathway. In addition, at higher [M]/[I] ratios, broadening in the PDI was observed in the GPC due to a low molecular weight tail which was also consistent with decomposition of the propagating species.

Attempted manipulation of the chelation effect. From the initial investigations, the importance of the presence of a Lewis basic functionality in the monomer was evident. With more Lewis basic functional groups, monophosphine chelated propagating species were favored over the bisphosphine species resulting in a

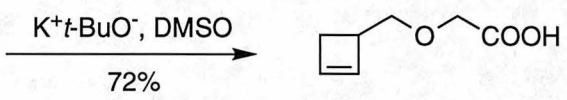
reduction in the relative k_p/k_i and therefore producing more narrowly dispersed polymers. One problem, though, was that all of these monomers resulted in differing amounts of the two propagating species and different reaction rates. If a major goal is the application of these polymerizations in the synthesis of block copolymers, difficulties may arise due to this variance in the properties of the propagating species. Ideally, monomers used in block copolymer synthesis should appear similar in their reaction with the propagating species, therefore producing more narrowly dispersed blocks.

As a result, a new series of monomers were synthesized bearing both an ether linkage and a secondary functional group. The ether linkage was incorporated in order to aid in the synthesis of more narrowly dispersed polymers based on the earlier research in the lowering of k_p/k_i. In addition, the hope was that the monomers would have similar polymerization rates since they all contain the Lewis basic ether group, and therefore they would be applicable for the synthesis of narrowly dispersed block copolymers. Alkylation of **3** with bromoacetic acid followed by elimination using the standard conditions resulted in [3-oxa-4-(2-cyclobutenyl)]butyric acid (**17**) as in Scheme 9. Compound **17** contained both the ether linkage as well as the carboxylic acid group which allowed for the installation of a series of other functional groups (Scheme 10). Synthesis of methyl [3-oxa-4-(2-

Scheme 9

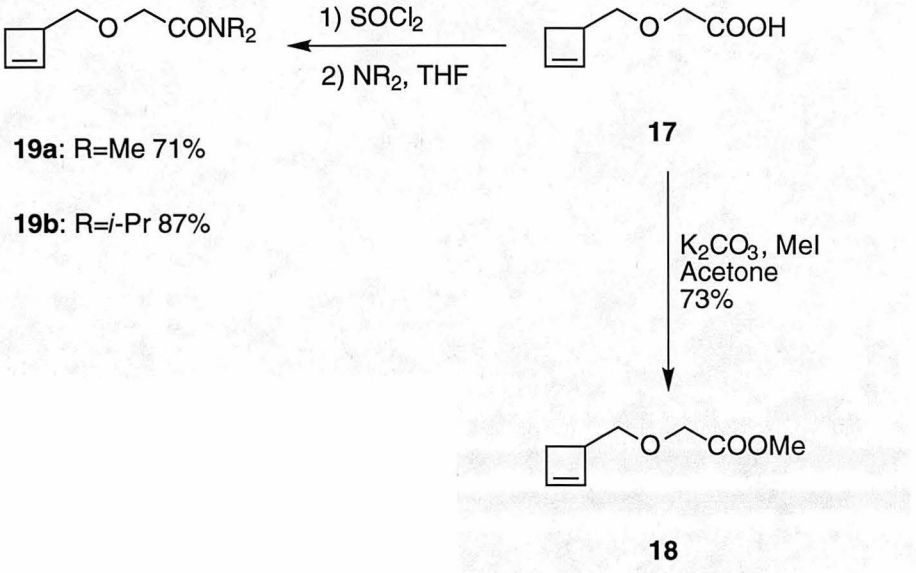


3 **16**



17

Scheme 10



cyclobutenyl)]butyric acid (**18**) with K_2CO_3 and MeI was accomplished in 73% yield. Treatment of **17** with thionyl chloride followed by the addition of the resulting acid chloride to either dimethyl amine in H_2O or diisopropyl amine in THF resulted in *N,N*-dimethyl-[3-oxa-4-(2-cyclobutenyl)]butyramide (**19a**) and *N,N*-diisopropyl-[3-oxa-4-(2-cyclobutenyl)]butyramide (**19b**) in yields of 71 and 87%, respectively.

Polymerizations were attempted at 45°C in toluene with [M]=0.57 M for monomer **18** and **19a,b**, while THF was required for compound **17** for solubility reasons. As predicted due to the presence of the ether functionality, complete initiation was observed with 5 eq of **17**, **18**, and **19a,b** under the standard conditions (Table 3). Polymerization of **18** resulted in the formation of two propagating species in the ^1H NMR at 19.80 and 17.91 ppm in a ratio of 1.00:12.54 (Table 3) which was slightly higher than the ratio observed for the benzyl ether (**8**). In the ^{31}P NMR, multiplets at 57.94 and 36.91 ppm were present with free PCy_3 integrating to 1.01 relative to the species at 57.94 ppm. The polymerization was complete after 2 h, and the dependence of the $\overline{M}_n$ on the [M]/[I] was linear (Table 5). As for the amine **15**, significant broadening of the PDI was observed at higher [M]/[I] ratios which was the result of a low molecular weight tail in the GPC

Table 5. Polymerization results for **18**[a]

[M]/[I]	$\overline{M}_n$[b]	PDI[b]
25.1	8600	1.16
75.5	17900	1.26
104	29600	1.30
153	41900	1.44

[a] Polymerizations were run in toluene at 45°C with [M]=0.57 M for 2.0 h. [b] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards.

consistent with decomposition of the propagating carbene. In addition, during the polymerization, the appearance of a new peak at 48.01 ppm was observed in the ^{31}P NMR also favoring some decomposition reaction of the propagating species.

Polymerization of **17** resulted in the formation of one propagating species in the ^{1}H NMR at 17.74 ppm representative of the chelated monophosphine species. However, in the ^{31}P NMR, in addition to the multiplet at 56.84, a multitude of other species were present and only a minor amount of free PCy_3 was observed. Monitoring of the polymerization by ^{1}H NMR revealed that conversion reached a maximum at ~70% even though the propagating carbene was still evident at 17.74 ppm. In order to understand why only minimal free PCy_3 was observed even though the propagating carbene was a monophosphine species, PCy_3 was reacted with compound **17** under identical conditions used in the polymerization. After 1 h, a new peak at 53.57 ppm was observed in a 1:2.13 ratio with free PCy_3, presumably through protonation of the phosphine. It was unclear why the multitude of decomposition products were observed during the polymerization, but a pathway resulting in the removal of free PCy_3 from the solution was evident. Such a side reaction would have locked the propagating carbene in the chelated form and therefore could have slowed if not prevented further polymerization.

Polymerization of **19a** and **19b** resulted in interesting results as well. Both of these compounds fully initiated **1** with the addition of 5 eq monomer as described above. However, once **1** was initiated, no further polymerization was observed, and in fact ~80% monomer remained after the initiation in the above experiment. ^{1}H NMR of the attempted polymerizations of these compounds revealed one carbene resonance at 17.84 and 17.86 ppm respectively. ^{31}P NMR revealed multiplets at 56.94 and 56.70 ppm respectively with 1.00 eq of free PCy_3. Presumably, coordination of the amide to the metal center in addition to the ether group resulted in stronger chelation, thus preventing further propagation. Due to the similar results obtained for the dimethylamide **19a** and the more bulky diisopropylamide **19b**, it was unlikely that this coordination was occurring through the nitrogen. Instead, this secondary coordination appeared to be occurring through the amide carbonyl which would have been less sensitive to steric environment around the nitrogen, thus explaining the similar results obtained for **19a** and **19b**.

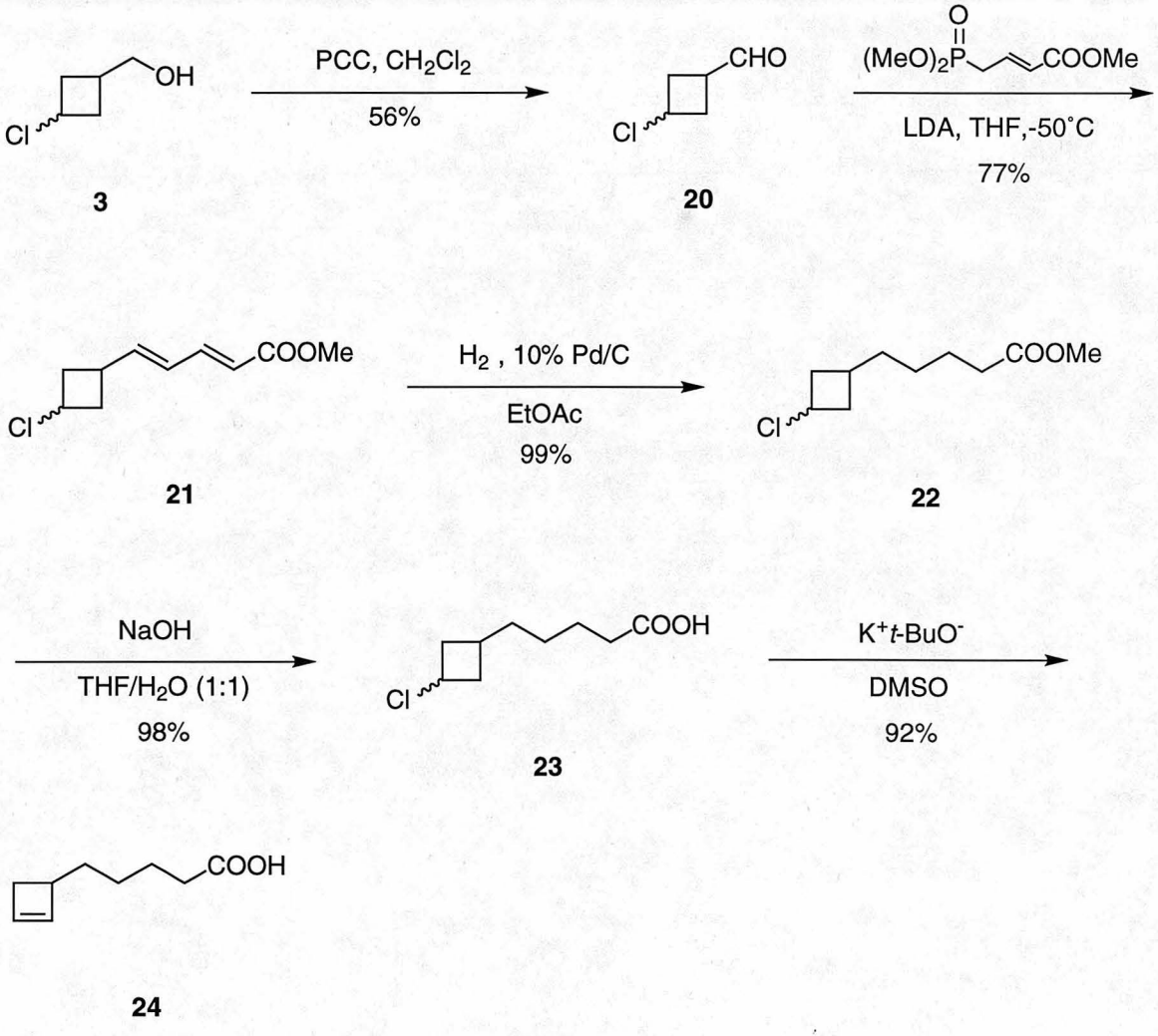
The incorporation of the ether functionality was successful in lowering the k_p/k_i as observed with the complete initiation of **1** with only 5 eq of **17**, **18**, and **19a**,**b**. However, the chelation was detrimental in that propagation rates were reduced significantly, even resulting in the absence of propagation for compounds **19a** and **19b**. In addition, with slower propagation rates, decomposition pathways which might have otherwise been suppressed became important. While these monomers have found application in the synthesis of side-chain liquid crystalline polymers,[45] the goal of achieving a living polymerization was never reached.

Living polymerization results. The development of initiator **2** provided a solution to the above difficulties. Although both complexes **1** and **2** resulted in the same propagating species, compound **2** had been shown to have much higher rates of initiation than compound **1**.[26,27] To test the initiation for this system, **2** was used to polymerize the benzoate ester (**12**) with a [**12**]/[**2**] ratio of 220:1. The resulting polymer had a $\overline{M}_n$ =29,500 and a PDI=1.22 compared with the results using **1** which gave a $\overline{M}_n$=15,300 and

a PDI=1.71. The PDI was significantly reduced due to higher initiation of this complex compared to **1**. Treatment of **2** with 5.0 eq of **12** using the standard procedure resulted in complete initiation compared to the 15% initiation observed with **1**.

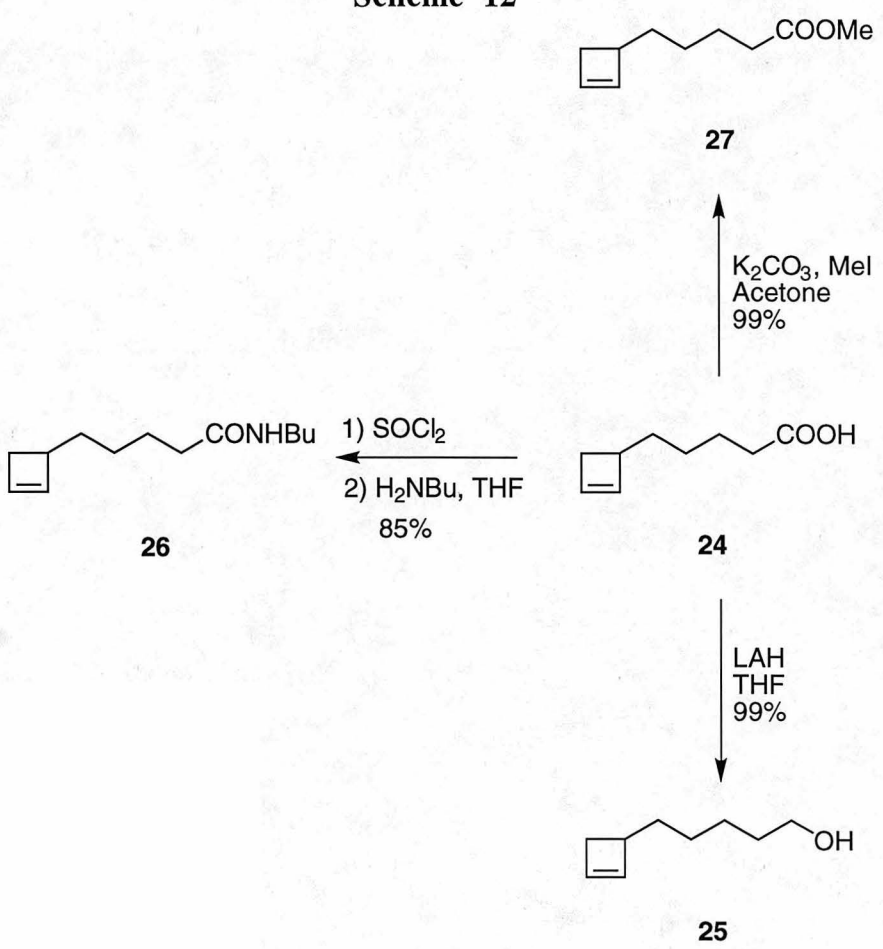
Using complex **2**, polymerization appeared possible to produce low polydisperse polymers without the need for the chelated monophosphines propagating species. Therefore, a series of compounds was synthesized which did not contain the ether linkage in the side-chain (Scheme 11). The removal of the ether group should have reduced the

Scheme 11



amount of chelated monophosphine propagating species present during the polymerization, thus increasing the propagation rates and hopefully minimizing any decomposition side reactions. Oxidation of **3** with PCC[46] resulted in moderate yield of *cis,trans*-3-chlorocyclobutanecarboxaldehyde (**20**). This was subjected to a Horner-Emmons reaction[47,48] with trimethyl 4-phosphonocrotonate using the method of Roush[49] to generate **21**. Hydrogenation of the diene with Pd/C and subsequent saponification of the ester produced nearly quantitative yield of **23**. Elimination using the standard conditions resulted in 5-(2-cyclobutenyl)pentanoic acid (**24**) in 92% yield. Conversion of **24** into a series of functionalized cyclobutenes was then attempted (Scheme 12). Reduction of **24**

Scheme 12



with LAH produced 5-(2-cyclobutenyl)pentanol (**25**) in quantitative yield. Treatment of **24** with thionyl chloride followed by reaction with *n*-butylamine resulted in *N*-butyl-[5-(2-cyclobutenyl)]pentanamide (**26**) in 85% yield. Finally, alkylation of the carboxylic acid **24** with K_2CO_3 and MeI gave a quantitative yield of the methyl [5-(2-cyclobutenyl)]pentanoate (**27**). These four monomers **24-27** contained a variety of functional groups; however, with the functional group well removed from the ring system, it was predicted that the amount of chelation would be similar and the monomers would react at similar rates.

Optimal polymerization conditions were at room temperature for 1.5 h with a [M]=0.17 M using initiator **2**. A slight reduction in the PDIs was observed at lower [M] resulting in the optimum concentration at 0.17 M. THF was chosen as a solvent because the polymers of the acid and alcohol monomers **24** and **25** were insoluble in all other solvents compatible with **2**. As seen in Table 4, complete initiation was observed employing 5 eq of monomers **24-27** with **2**. Analysis of the carbene propagating species by ^1H and ^{31}P NMR was then undertaken. The ^1H NMR for the polymerization of **24-27** were similar in the four cases, so only the results for **24** will be discussed in detail (Table 6). Two species at 19.49 and 17.90 ppm were observed in a ratio of 1.00:0.41. ^{31}P NMR

Table 6. ^1H NMR analysis of polymerization propagating species

X	% Initiation with 5 eq. [M][a]	^1H NMR Carbene Resonance of A[b]	^1H NMR Carbene Resonance of B[b]	Ratio B/A[b]	$(10^3K_{eq})^b$
$(CH_2)_3COOH$	>99 %	19.49	17.90	0.41	1.2
$(CH_2)_4OH$	>99 %	19.49	17.79	0.57	2.1
$(CH_2)_3C(O)NHBu$	>99 %	19.47	17.89	0.35	0.89
$(CH_2)_3COOMe$	>99 %	19.49	17.89	0.51	1.7

[a] Polymerizations were run in THF-d_8 at room temperature for 1 h at [M]=0.11 M and [I]=0.022 M and analyzed by ^1H NMR using a JEOL GX-400 spectrometer. [b] Polymerizations were run in THF-d_8 at room temperature for 1 h at [M]=0.17 M and [I]=0.0099 M and analyzed by ^1H NMR using a JEOL GX-400 spectrometer.

displayed nearly identical spectra for the four cases and the results for **24** were representative with a multiplet at 38.58 ppm for the chelated species and a series of peaks from 37.11-34.19 ppm for the bisphosphine species. Free PCy_3 was found at 10.80 ppm integrating 1.00:1.02 with the multiplet at 38.58. So, as expected, the bisphosphine species was favored over the chelated monophosphine species and the observed ratios were similar for all four compounds (Table 6). In contrast to the polymerization of **17**, free phosphine was present in the polymerization of **24**, and no decomposition products were observed. To further examine this, PCy_3 was reacted for 1 h with **24** under the conditions used in the polymerization at room temperature in THF with a [**24**]=0.17 M and a $[PCy_3]$=0.01 M. Unlike for **17**, no reaction was observed. To better compare the two cases, the reaction was repeated using the same conditions as for **17** at 45°C with a [**24**]=0.57 M and a $[PCy_3]$=0.01 M. In this case, only a minor species was observed at 52.82 integrating to 8.9% compared with free PCy_3. The marked difference in reactivity of **17** and **24** with free PCy_3 was proposed to be the result simply of the difference in acidity expected for these carboxylic acids. Using pentanoic acid and methoxyacetic acid as models for **24** and **17**, the pK_a values are 4.80 and 3.57[50] providing a plausible reason for reduced protonation of PCy_3 by **24**. The lack of reactivity of **24** with PCy_3 was one explanation for the successful polymerization of **24** compared to the decomposition found in the polymerization of **17**. Further study of these polymerization is necessary to conclusively determine the cause of these contrasting polymerization results.

In order to fully investigate these polymerizations, the dependence of the $\overline{M}_n$ on the [M]/[I] ratio was studied. The dependence was linear for all four monomers providing for control over the polymer molecular weight, and the polymers produced were of low polydispersity between 1.11-1.20 in all cases (Table 7). Figure 3 illustrates the dependence for the polymerization of the carboxylic acid **24**. The linear dependence observed was supportive of a living polymerization,[14,15] but further proof was necessary.

In addition to the molecular weight study, evidence for the lack of chain transfer and chain termination reactions must be demonstrated to prove that a polymerization is living. A

Table 7. Polymerization results for monomers **24**-**27**[a]

Entry	Monomer	[M]/[I]	$\overline{M}_n$[b]	PDI[b]
1	**24**	25.0	5000	1.15
2	**24**	50.0	9200	1.16
3	**24**	75.0	12400	1.16
4	**24**	104	15700	1.16
5	**24**	150	20300	1.19
6	**25**	25.0	4200	1.15
7	**25**	50.4	7400	1.15
8	**25**	75.6	10100	1.17
9	**25**	101	13800	1.15
10	**25**	161	23300	1.20
11	**26**	25.2	4800	1.11
12	**26**	50.4	8800	1.11
13	**26**	73.3	11400	1.11
14	**26**	105	16400	1.12
15	**26**	151	20800	1.12
16	**27**	25.3	4600	1.14
17	**27**	50.5	8000	1.14
18	**27**	73.5	11800	1.13
19	**27**	106	16100	1.15
20	**27**	143	23100	1.16

[a] Polymerizations were run in THF at rt with [M]=0.17 M. [b] Determined by gel permeation chromatography in THF relative to monodispersed polystyrene standards.

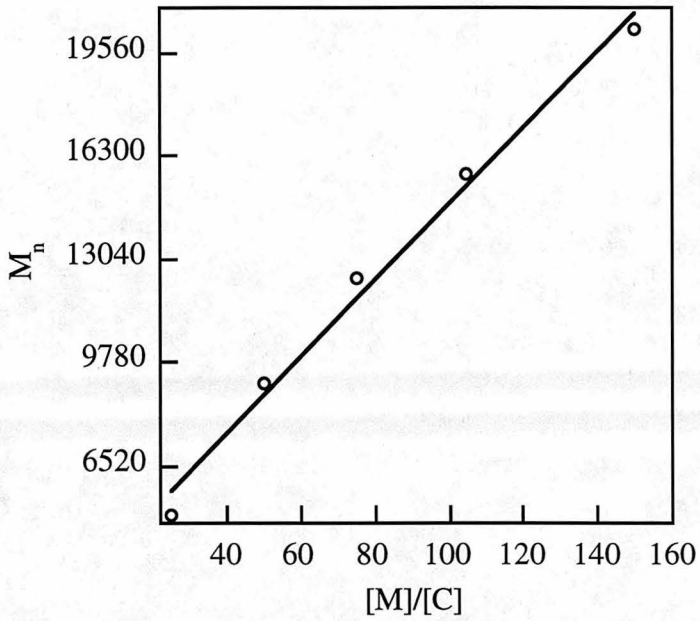


Figure 3. Molecular weight dependence of the polymerization of **24** on the [M]/[I].

sequential monomer addition experiment was proposed to address the living nature of these polymerizations.[14] This experiment was run for all four monomers, but the results for the polymerization of carboxylic acid **24** were representative. Using initiator **2**, 25 eq of **24** were polymerized for 2 h under the standard conditions. The solution was then divided into three portions. Portion A was removed and analyzed by GPC. Portion B was left stirring for an additional 4 h. To portion C, an additional 350 eq of monomer were added, and this was left to react for 4 h. Portions B and C were then analyzed by GPC. As seen in Figure 4, no significant change was observed from the 2 h reaction (A) and the 6 h reaction (B). After 2 h, the $\overline{M}_n$=4400 and PDI=1.14, and after 6 h, the $\overline{M}_n$=4400 and PDI=1.14. If any significant chain transfer processes had been operative during this time, broadening of the PDI would have been observed. Portion C in which 350 additional eq of **24** had been polymerized resulted in a $\overline{M}_n$ =53400 and a PDI=1.34. Despite the fact that the PDI broadened, a clean shift in the GPC peaks was accomplished, proving that no

chain termination processes were occurring. Chain termination would have resulted in inactive chain ends after the polymerization of the first 25 eq monomer which would have produced a bimodal GPC trace after additional polymerization. The absence of both chain transfer and chain termination reactions was indicative of a living polymerization of the monomers **24**-**27**.

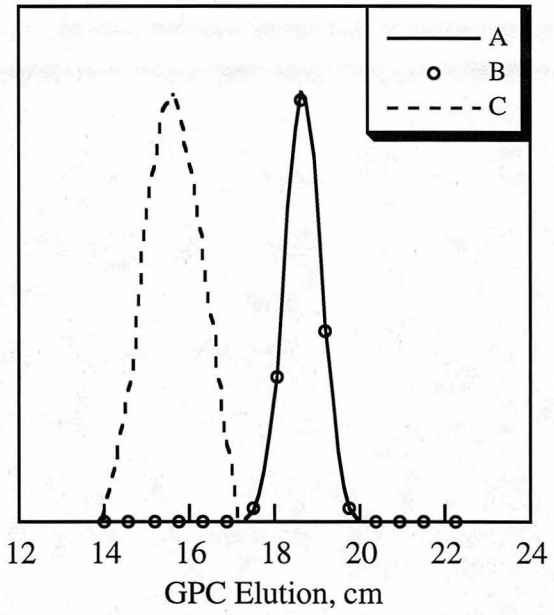


Figure 4. Sequential monomer addition experiment with A) 25 eq of **24** after 2 h, B) 25 eq of **24** after 6 h, and C) condition A after 350 additional eq of **24**.

Polymer characterization. Through polymerization of these substituted cyclobutenes, a new group of poly(butadiene)s bearing a wide range of functional groups were prepared (Table 8). Even though the polymerization yields were quantitative by ^{1}H NMR, isolated yields were lower due to loss in the purification step. No significant bias in the olefin configuration was evident for these polymerizations with between 40 to 50% *cis*-olefin present in the polymer backbone. These results were consistent with that seen

previously for initiators **1** and **2**.[28] An accurate determination was impossible for poly(**10**) and poly(**15**) due to the lack of resolution of the olefinic resonances in the ^{1}H NMR

Table 8. Polymerization results

Polymer	X	% Yield[a]	% *Cis*-Olefin[b]
Poly(**8**)	OCH_2Ph	87	40
Poly(**10**)	$OC(Ph)_3$	91	nd[c]
Poly(**12**)	OC(O)Ph	95	50
Poly(**15**)	$N(i\text{-}Pr)_2$	79	nd[c]
Poly(**18**)	OCH_2COOMe	84	40
Poly(**24**)	$(CH_2)_3COOH$	93	50
Poly(**25**)	$(CH_2)_4OH$	95	50
Poly(**26**)	$(CH_2)_3CONHBu$	92	50
Poly(**27**)	$(CH_2)_3COOMe$	96	50

[a] Isolated yields after purification. [b] Determined by ^{1}H NMR integration of the olefinic resonances. [c] Not determined; the olefinic resonances were not resolved well enough to determine this value accurately.

spectrum. Based on analysis of the olefin region of the ^{13}C NMR spectrum of the polymers, a lack of regioselectivity for monomer insertion in the polymerizations was determined,[51] again consistent with previous observations with these initiators in similar systems.[28] If chelation occurs during the initial monomer coordination step, one might expect some regioselectivity due to energetic differences in the two possible chelate ring sizes. The lack of regioselectivity observed in these polymerizations is thus supportive of the proposal that chelation occurs after the ring-opening metathesis step and therefore plays no role in affecting the regioselectivity of monomer insertion.

Analysis of the thermal properties of these polymers was undertaken as well using both differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table 9). The T_g values for these polymers ranged from -46.6 to 69.4°C demonstrating the

Table 9. Polymer thermal behavior

Polymer	X	T_g (1)(°C)[a]	T_d (Argon) (°C)[b]	T_d (Air) (°C)[b]
Poly(**8**)	OCH_2Ph	-22.6	306	254
Poly(**10**)	$OC(Ph)_3$	69.4	308	240
Poly(**12**)	OC(O)Ph	24.0	349	341
Poly(**15**)	$N(i\text{-}Pr)_2$	-15.8	294	249
Poly(**18**)	OCH_2COOMe	-42.9	334	311
Poly(**24**)	$(CH_2)_3COOH$	1.3	352	359
Poly(**25**)	$(CH_2)_4OH$	-37.1	220	265
Poly(**26**)	$(CH_2)_3CONHBu$	0.1	283	259
Poly(**27**)	$(CH_2)_3COOMe$	-46.6	345	286

[a] Analysis by differential scanning calorimetry with a scan rate of 10°C/min. [b] Analysis by thermal gravimetric analysis with a scan rate of 10°C/min.

striking influence of the side-chains on the phase transitions of these poly(butadiene)s; however, no melting transitions were observed for any of the materials. TGA results were compared using the T_d, the temperature at 10% decomposition. T_d values between 220 and 349°C were observed in an inert atmosphere, but no consistent trend was evident.

Diblock copolymerization experiments. The ability to prepare well-defined block copolymers has been realized through the development of living polymerization methods.[15] Such polymeric materials have found application for many types of materials including compatiblizers for polymer blends, thermoplastic elastomers, surface-active agents, and semipermeable membranes.[15,52,53] The attainment of living polymerizations

of monomers **24-27** using initiator **2** prompted an investigation of the synthesis of diblock copolymers using these monomers. Highly functionalized diblock copolymers with acid, ester, amide, and alcohol functionalities were envisioned through these diblock copolymerization experiments.

In these diblock copolymerization experiments, initiator **2** was treated with 50 eq of the first monomer for 1.5 h. At the end of this reaction time, 50 eq of the second monomer was then added, and the reaction was allowed to proceed at room temperature for an additional 2 h (Scheme 13). The polymerization was then quenched with ethyl vinyl ether and purified as always to result in the diblock copolymer. Five different diblock copolymers were prepared using this methodology in order to generate diblock copolymers with a wide range of functional groups. Ester-alcohol, ester-acid, amide-ester, amide-acid, and alcohol-acid diblock copolymers were synthesized. As seen in Table 10, the yields were excellent between 92-98%, and by ^{1}H NMR integration, a 1:1 ratio of the two polymer blocks was achieved in all cases. As previously observed in the homopolymerizations of monomers **24-27**, approximately 50% *cis*-olefin was obtained in all of the diblock copolymers. Although the polydispersities were slightly broader than in the homopolymerizations, low polydispersities between 1.17-1.24 were achieved demonstrating the high degree of control in the living polymerizations of these functionalized cyclobutenes.

Scheme 13

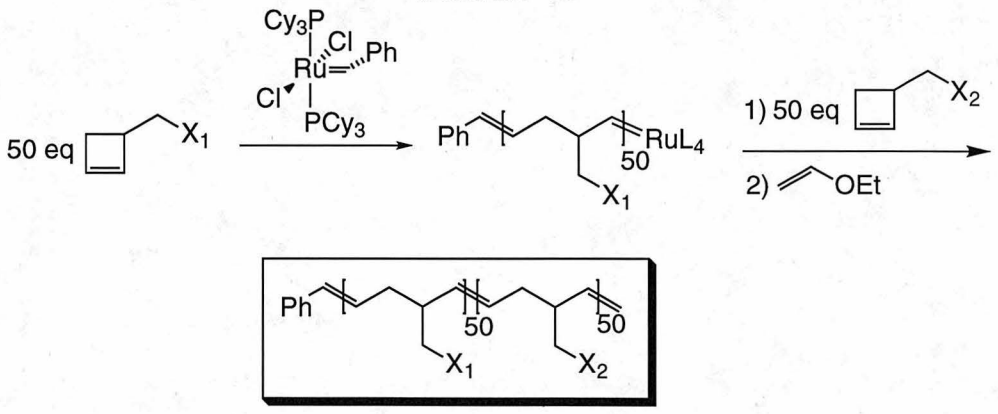


Table 10. Diblock copolymerization results

X_1	X_2	% Yield[a]	% *Cis*-Olefin[b]	$\overline{M}_n$[c]	PDI[c]
$(CH_2)_3COOMe$	$(CH_2)_4OH$	95	50	13300	1.24
$(CH_2)_3COOMe$	$(CH_2)_3COOH$	92	50	13700	1.22
$(CH_2)_3C(O)NHBu$	$(CH_2)_3COOMe$	98	50	12300	1.19
$(CH_2)_3C(O)NHBu$	$(CH_2)_3COOH$	97	50	12300	1.17
$(CH_2)_4OH$	$(CH_2)_3COOH$	96	50	13600	1.20

[a] Isolated yields after purification. [b] Determined by ^1H NMR integration of the olefinic resonances.
[c] Determined by gel permeation chromatography in THF relative to monodispersed polystyrene standards.

With the preparation of these five diblock copolymers, initial investigations of their thermal properties were undertaken. As before, TGA was used to study the thermal stability of these polymeric materials by comparing their T_d in both argon and air atmospheres. As shown in Table 11, these materials exhibited similar thermal stabilities with T_d values between 302-383°C without any significant trend in the data.

Table 11. Diblock copolymer thermal behavior

X_1	X_2	T_g (1) (°C)[a]	T_g (2) (°C)[a]	T_d (Argon) (°C)[b]	T_d (Air) (°C)[b]
$(CH_2)_3COOMe$	$(CH_2)_4OH$	-45.3	-18.0	371	383
$(CH_2)_3COOMe$	$(CH_2)_3COOH$	-44.6	0.2	373	369
$(CH_2)_3C(O)NHBu$	$(CH_2)_3COOMe$	-1.9	-45.9	368	302
$(CH_2)_3C(O)NHBu$	$(CH_2)_3COOH$	2.2	-----	349	352
$(CH_2)_4OH$	$(CH_2)_3COOH$	-7.5	-----	322	325

[a] Analysis by differential scanning calorimetry with a scan rate of 10°C/min. [b] Analysis by thermal gravimetric analysis with a scan rate of 10°C/min.

The DSC analysis, however, provided more interesting results. For the ester-alcohol, ester-acid, and amide-ester diblock copolymers, two T_gs were obtained. This result was not surprising in that most diblock copolymers phase separate resulting in the observation of T_gs for each of the polymer segments in the diblock copolymer. Typically, these T_gs are identical to the T_gs of the corresponding homopolymers, although some deviation can often be observed.[52,53] With the exception of the alcohol T_g in the ester-alcohol diblock copolymer which was shifted to higher temperature compared to the homopolymer, this was exactly what was observed. However, in the amide-acid and alcohol-acid diblock copolymers, only one T_g was observed which was between the T_gs of the two corresponding homopolymers, and this was indicative of mixing of the two phases in these diblock copolymers.[52,53] In comparing the different diblock copolymers, it was observed that in the first three cases in Table 11, a poor hydrogen bond donor-acceptor (COOMe) was paired with reasonably good hydrogen bond donors-acceptors (OH, COOH, C(O)NHBu), possibly explaining why phase separation occurred in these cases. In the last two cases, however, two good hydrogen bond donors-acceptors (C(O)NHBu, COOH, OH) were paired in each case. By pairing these good hydrogen bond donor-acceptor groups, perhaps mixing of the phases was more favorable thereby explaining the one T_g that was observed in these cases. Further research into the analysis of these diblock copolymers as well as the preparation of new block copolymers should be investigated in order to fully understand the properties of the highly functionalized materials.

Conclusions

The synthesis of 3-substituted cyclobutenes bearing a wide range of functionalities was demonstrated. The polymerization of these compounds with initiators **1** and **2** was accomplished resulting in a series of new functionalized poly(butadiene)s. In probing the polymerization mechanism, coordination of Lewis basic functional groups on the polymer side-chains to the metal center was observed. This coordination produced a new, chelated monophosphine propagating species in addition to the expected bisphosphine species

which resulted in the lowering of the k_p/k_i for these polymerizations. While this coordination led to lowered PDIs using initiator **1**, propagation rates were significantly reduced in these polymerizations and often decomposition of the propagating species was competitive with propagation. The combination of higher initiation employing complex **2** and the removal of the functional group further from the ring system resulted in the living polymerization of functionalized cyclobutenes bearing carboxylic acid, alcohol, amide, and ester functionalities, and diblock copolymers with a wide range of functionalities were prepared in high yields with low polydispersities. This research illustrates the importance of understanding initiator-monomer functionality interactions in developing a living polymerization process. Hopefully, the analysis of these interactions presented in this study will enable further advances in the application of ROMP for the living polymerization of other functionalized monomer systems.

Experimental

General. Argon was purified by passage through columns of BASF R-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). NMR spectra were recorded on both a GE QE-300 Plus (300.1 MHz ^1H; 75.49 MHz ^{13}C) spectrometer and a JEOL GX-400 (399.65 MHz ^1H; 100 MHz ^{13}C; 161.85 MHz ^{31}P) spectrometer. Unless otherwise noted, the majority of the spectra were recorded on the GE QE-300 Plus. ^{31}P NMR spectra were referenced to an external 85% H_3PO_4 standard. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. CH_2Cl_2 gel permeation chromatographs were obtained on a HPLC system using an Altex model 110A pump, a Rheodyne model 7125 injector with a 100 μL injection loop, two American Polymer Standards 10 micron mixed bed columns, and a Knauer differential-refractometer using a 1.0 mL/min flow rate. THF gel permeation chromatographs were obtained on a HPLC system using an Altex model 426 pump, a Rheodyne model 7125 injector with a 100 μL injection loop, two American Polymer Standards 10 micron mixed bed columns, and a Viscotek model 200 differential

refractometer/viscometer using a 1.0 mL/min flow rate. Molecular weights and polydispersities were reported versus monodispersed polystyrene standards. Differential scanning calorimetry was measured on a Perkin-Elmer DSC-7, and thermogravimetric analysis was carried out on a Perkin-Elmer TGA-2.

Materials. When dry solvents were used, they were distilled from CaH_2. All other solvents were reagent grade and used without purification. 1,1-Cyclobutanedicarboxylic acid, sulfuryl chloride, BH_3-THF, benzyl bromide, trityl chloride, NaH, K^+t-BuO^-, dimethylamine, MeI, pyridinium chlorochromate, lithium diisopropylamide, palladium on activated carbon, and ethyl vinyl ether were purchased from the Aldrich Chemical Company and used without further purification. 2,2'-Azobis(2-methylpropionitrile) was purchased from Eastman Laboratory Chemicals and used without further purification. Technical grade trimethyl 4-phosphonocrotonate was purchased from Lancaster Synthesis.

Synthesis of *cis,trans*-3-chlorocyclobutanecarboxylic acid (5). The synthesis of **5** was accomplished from compound **4** in two steps according to a modified procedure of that of Nevill, Frank, and Trepka.[54,55] The use of dry benzene, and the use of 2,2'-azobis(2-methylpropionitrile) instead of benzoyl peroxide as a free radical initiator were the only changes made to this procedure. This allowed for the formation of purer material due to the elimination of any benzoic acid impurities. **5** was obtained in 50% yield as a mixture of isomers. ^{1}H NMR ($CDCl_3$) δ 12.10-11.80 (bs, 1H), 4.52-4.21 (m, 1H), 3.43-3.16 (m, 1H), 2.98-2.45 (m, 4H).

Synthesis of *cis,trans*-1-(3-chlorocyclobutyl)methanol (3). Compound **5** (41.5 g, 309 mmol, 1.0 eq) was dissolved in dry THF (100 mL) and placed under argon with a magnetic stirrer. An addition funnel was connected to the reaction flask and BH_3-THF (1.0 M, 464 mL, 464 mmol, 1.5 eq) was added via a cannula. The system was kept under argon, and the reaction flask was cooled to 0°C. Addition was then carried out dropwise over 1 h. The flask was allowed to warm to room temperature and stirring was

continued for 1.5 h. Deionized water (150 mL) was added slowly to quench the reaction, and the reaction was saturated with K_2CO_3. The organic layer was removed, and the aqueous layer was extracted with diethyl ether (3 x 75mL). The combined organics were then dried over $MgSO_4$ and concentrated *in vacuo* to give a clear liquid. This was distilled at 0.2 mm Hg/52-60°C to give **3** (36.8 g, 99% yield) as a mixture of two isomers. ^1H NMR ($CDCl_3$) δ 4.52-4.21 (m, 1H), 3.63-3.60 (m, 2H), 2.68-2.00 (m, 5H).

Synthesis of benzyl [*cis,trans*-1-(3-chlorocyclobutyl)methyl] ether (7). Compound **3** (5.00 g, 42.0 mmol, 1.0 eq) and dry THF (40 mL) were combined and cooled to 0°C. NaH (2.50 g, 104 mmol, 2.5 eq) was then added in portions over 5 min. Benzyl bromide (7.1 g, 42.0 mmol, 1.0 eq) was then added dropwise via a syringe to the reaction over 15 min. The ice bath was removed, and the reaction was allowed to stir at room temperature for 2.5 h. Diethyl ether (100 mL) was added, and the organics were washed with deionized water (3 x 150 mL), dried over $MgSO_4$, and concentrated *in vacuo* to give a yellow liquid. This was purified by distillation at 0.2 mm Hg/80-82°C to give **7** (8.1 g, 91% yield) as a mixture of isomers. ^1H NMR ($CDCl_3$) δ 7.41-7.20 (m, 5H), 4.52-4.19 (m, 3H), 3.43-3.37 (m, 2H), 2.80-1.99 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 138.36, 128.39, 127.56, 74.04, 73.12, 73.03, 72.70, 52.09, 49.17, 38.05, 36.70, 30.48, 29.93; IR (thin film on a NaCl plate) 3087, 3064, 3030, 2941, 2856, 2793, 1604, 1586, 1496, 1454, 1365, 1279, 1205, 1123, 1098, 1028, 986, 841, 737, 698 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{15}ClO$ $(M)^+$ 210.0811, found 210.0820.

General procedure for the base elimination of 3-chlorocyclobutanes. The elimination of benzyl [*cis,trans*-1-(3-chlorocyclobutyl)methyl] ether (**7**) will be used as an example, but the same general procedure was used in all cases. K^+*t*-BuO^- (7.4 g, 66 mmol, 3.5 eq) was dissolved in dry DMSO (100 mL) and placed in a flask connected to an addition funnel under argon. To the addition funnel, a solution of **7** (3.7 g, 19 mmol, 1.0 eq) in dry DMSO (25 mL) was transferred, and dropwise addition over 20 min was accomplished. The reaction was then left to stir at room temperature overnight. During

this time, the solution turned from faint yellow to a dark brown. The reaction mixture was then poured into ice water (150 ml) and extracted with diethyl ether (3 x 100 mL). The organics were then washed with deionized water (3 x 100 mL), dried over $MgSO_4$, and concentrated *in vacuo* to give a yellow oil. This material was purified by distillation at 0.2 mm Hg/49-51°C to give pure **8** (2.50 g, 83% yield). ^1H NMR ($CDCl_3$) δ 7.34-7.24 (m, 5H), 6.12-6.06 (m, 2H), 4.54 (s, 2H), 3.53-3.51 (m, 2H), 3.13-3.11 (m, 1H), 2.65 (dd, J_1=3.3 Hz, J_2=10.2 Hz, 1H), 2.19 (d, J=10.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 138.53, 138.31, 136.85, 128.29, 127.58, 127.45, 73.77, 73.02, 43.45, 34.43; IR (thin film on a NaCl plate) 3064, 2987, 2941, 2856, 1496, 1454, 1365, 1279, 1098, 1028, 737, 698 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{14}O$ $(M)^+$ 174.1000, found 174.1001

Synthesis of [*cis,trans*-1-(3-chlorocyclobutyl)methyl]trityl ether (9). Compound **3** (5.00 g, 41.5 mmol, 1.0 eq), trityl chloride (12.73 g, 45.7 mmol, 1.1 eq), and dry pyridine (60 mL) were combined and connected to a reflux condenser under argon. This reaction mixture was heated to reflux for 1 h and then allowed to cool. A short path was then connected to the reaction flask, and the pyridine was removed by distillation at reduced pressure. The solid residue was dissolved in CH_2Cl_2 (300 mL) and washed with deionized water (5 x 150 mL) and brine (1 x 150 mL). The organics were then dried over $MgSO_4$ and concentrated *in vacuo* to give an orange oil. The material was then purified by flash column chromatography (silica gel, 15% ethyl acetate/hexanes, R_f=0.60) to give **9** (11.9 g, 79% yield) as a mixture of isomers. ^1H NMR ($CDCl_3$) δ 7.61-7.22 (m, 15H), 4.53-4.27 (m, 1H), 3.20-3.08 (m, 2H), 3.05-2.08 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 144.09, 143.88, 128.61, 128.57, 127.79, 127.74, 127.01, 126.91, 86.28, 86.07, 66.83, 65.57, 52.31, 49.27, 38.00, 36.72, 30.69, 30.08; IR (thin film on a NaCl plate) 3085, 3057, 3031, 2942, 2862, 1596, 1490, 1448, 1389, 1317, 1280, 1220, 1182, 1153, 1116, 1087, 1071, 1032, 1002, 979, 942, 928, 899, 842, 775, 763, 746, 705, 646, 632 cm^{-1}; HRMS (FAB) calcd for $C_{24}H_{23}ClO$ $(M)^+$ 362.1437, found 362.1423.

[1-(2-cyclobutenyl)methyl] trityl ether (10). The standard elimination procedure as above was used for compound **9**, but purification was accomplished by recrystallization from hot ethanol to obtain **10** (9.2 g, 72% yield) as white crystalline solid. ^{1}H NMR (CD_2Cl_2) δ 7.53-7.22 (m, 15H), 6.14 (d, *J*=2.7 Hz, 1H), 6.08 (d, *J*=2.7 Hz, 1H), 3.14-3.12 (m, 3H), 2.65 (dd, J_1=1.2 Hz, J_2=13.5 Hz, 1H), 2.15 (d, *J*=13.5 Hz, 1H); ^{13}C NMR (CD_2Cl_2) δ 144.85, 139.02, 137.03, 129.03, 128.06, 127.22, 86.44, 67.39, 44.10, 34.60; IR (thin film on a NaCl plate) 3055, 2917, 2860, 1596, 1490, 1448, 1218, 1068, 1032, 898, 762, 745, 703, 632 cm^{-1}; HRMS (FAB) calcd for $C_{24}H_{22}O$ $(M)^+$ 326.1671, found 326.1669.

Synthesis of 1-(2-cyclobutenyl)methanol (11). Compound **11** was synthesized from **3** according to a literature procedure.[36,37] Isolated yield was 25% of pure material. ^{1}H NMR ($CDCl_3$) δ 6.15 (d, *J*=2.4 Hz, 1H), 6.04 (d, *J*=2.4 Hz, 1H), 3.68 (d, *J*=6.0 Hz, 2H), 3.11-3.02 (m, 1H), 2.60 (dd, J_1=3.6 Hz, J_2= 13.5 Hz, 1H), 2.22 (d, *J*=13.5 Hz, 1H).

Synthesis of 1-(2-cyclobutenyl)methyl benzoate (12). Compound **11** (1.93 g, 23.0 mmol, 1.0 eq) was dissolved in dry THF (30 mL) along with triethylamine (2.63 g, 26.0 mmol, 1.1 eq) and cooled to 0°C under argon. The benzoyl chloride (7.36 g, 52.0 mmol, 2.2 eq) was then added dropwise via syringe over 15 min. The ice bath was then removed, and the reaction was left to sir at room temperature for 6 h. Deionized water was added (75 mL), and the aqueous phase was extracted with diethyl ether (3 x 150 mL). The organics were then washed with 1 M HCl (2 x 150 mL) and deionized water (1 x 150 mL), dried over $MgSO_4$, and concentrated *in vacuo* to give a clear viscous liquid. This was then distilled at 0.3 mm Hg/92-95°C to give **12** (3.2 g, 74% yield). ^{1}H NMR ($CDCl_3$) δ 8.08-8.04 (m, 2H), 7.59-7.54 (m, 1H), 7.48-7.42 (m, 2H), 6.16 (d, *J*=2.1 Hz, 1H), 6.10 (d, *J*=2.1 Hz, 1H), 4.45-4.34 (m, 2H), 3.30-3.24 (m, 1H), 2.73 (dd, J_1=4.2 Hz, J_2= 13.5 Hz, 1H), 2.22 (d, *J*=13.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 166.60, 137.40, 137.28, 132.78, 130.49, 129.56, 128.29, 67.62, 42.40, 34.08; IR (thin film on a

NaCl plate) 3126, 3051, 2948, 2921, 2845, 1720, 1602, 1584, 1492, 1451, 1379, 1315, 1274, 1176, 1111, 1070, 1026, 957, 789, 711 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{12}O_2$ $(M)^+$ 188.0837, found 188.0831.

Synthesis of *N,N*-diisopropyl[*cis,trans*-1-(3-chlorocyclobutyl)methyl]amide (13). Thionyl chloride (39.8 g, 335 mmol, 3.0 eq) was added dropwise over a period of 30 min to compound **5** (15.0 g, 112 mmol, 1.0 eq). The mixture was then brought to reflux and monitored for the formation of gases. After 1.5 h, the evolution of gases had ceased, and the reaction flask was cooled. Then, the excess thionyl chloride was removed *in vacuo*. The remaining liquid (14.2 g, 93.0 mmol, 79% crude yield) was added dropwise over 10 min to a flask containing dry THF (300 mL) and diisopropylamine (28.2 g, 278 mmol, 3.0 eq). Immediate formation of a white precipitate was observed, and this was left to stir overnight at room temperature. Deionized water (250 mL) was then added, and the aqueous layer was extracted with diethyl ether (3 x 250 mL). The organics were then washed with deionized water (3 x 300 mL), dried over $MgSO_4$, and concentrated *in vacuo* to give a clear yellow oil. This was purified by distillation at 0.3 mm Hg/95-100°C to give **13** (18.2 g, 75% yield) as a mixture of isomers. ^1H NMR ($CDCl_3$) δ 4.52-4.19 (m, 1H), 3.80-3.63 (m, 2H), 3.47-3.29 (m, 1H), 3.23-2.33 (m, 4H), 1.38-1.28 (m, 6H), 1.16-1.00 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 172.53, 170.62, 51.52, 49.16, 48.12, 48.08, 45.80, 45.61, 37.46, 36.61, 34.42, 33.39, 20.87, 20.47; IR (thin film on a NaCl plate) 2999, 2967, 2937, 1637, 1474, 1441, 1371, 1349, 1290, 1215, 1157, 1135, 1041, 845, 814, 732 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{20}ClNO$ $(M)^+$ 217.1233, found 217.1231.

Synthesis of diisopropyl[*cis,trans*-1-(3-chlorocyclobutyl)methyl]amine (14). BH_3-THF (1.0 M, 156 mL, 156 mmol) was placed in a flask at 0°C connected to an addition funnel under argon. Compound **13** (17.0 g, 78 mmol, 1.0 eq) in dry THF (75 mL) was added dropwise over a period of 20 min to the reaction flask. The addition funnel was then replaced with a reflux condenser, and the

flask was heated to reflux for 1.5 h. During the reflux, a white precipitate formed which increased during the reaction. The flask was then cooled to 0°C, and 6 M HCl (50 mL) was added slowly resulting in the disappearance of the white precipitate. The THF was then removed by distillation at atmospheric pressure, and the remaining liquid was made basic with aqueous NaOH (50% w/w). This was extracted with diethyl ether (3 x 75 mL), dried over $MgSO_4$, and concentrated *in vacuo* to give a yellow liquid. Distillation at 0.2 mm Hg/65-70°C results in **14** (11.0 g, 70% yield) as a mixture of isomers. ^{1}H NMR ($CDCl_3$) δ 4.52-4.19 (m, 1H), 2.98-2.81 (m, 4H), 2.65-1.80 (m, 5H), 0.93 (d, *J*=6.6 Hz, 12H); ^{13}C NMR ($CDCl_3$) δ 52.80, 51.16, 49.41, 49.02, 48.01, 47.59, 40.03, 37.58, 30.78, 30.09, 20.83; IR (thin film on a NaCl plate) 2965, 2870, 2801, 1464, 1390, 1362, 1275, 1208, 1158, 1117, 1000, 840, 740 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{22}ClN$ $(M)^+$ 203.1441, found 203.1436.

Diisopropyl[1-(2-cyclobutenyl)methyl]amine (15). The standard elimination procedure was used for **14**, but purification was accomplished by distillation at 0.3 mm Hg/28°C to yield **15** (77% yield) as a clear liquid. ^{1}H NMR ($CDCl_3$) δ 6.13 (d, *J*=2.7 Hz, 1H), 6.03 (d, *J*=2.7 Hz, 1H), 2.97 (septet, *J*=6.6 Hz, 2H), 2.89-2.83 (m, 1H), 2.60-2.40 (m, 3H), 2.03 (d, *J*=13.8 Hz, 1H), 0.96 (d, *J*=6.6 Hz, 12H); ^{13}C NMR ($CDCl_3$) δ 140.84, 135.36, 49.44, 48.21, 44.7, 35.27, 20.87; IR (thin film on a NaCl plate) 3120, 3044, 2964, 2870, 2841, 2797, 1586, 1561, 1465, 1382, 1361, 1321, 1276, 1207, 1160, 1119, 1058, 1042, 965, 882, 795, 723, 702, 686 cm^{-1}; HRMS (EI) calcd for $C_{34}H_{43}NO_5$ $(M)^+$ 167.1674, found 167.1676.

Synthesis of [*cis,trans*-3-oxa-4-(3-chlorocyclobutyl)]butyric acid (16). NaH (13.55 g, 565 mmol, 4.0 eq) was added slowly in portions to a cooled solution (0°C) of **3** (17.0 g, 141 mmol, 1.0 eq) in THF (400 mL). This was stirred under argon for 15 min, then a solution of bromoacetic acid (18.63 g, 134 mmol, 0.95 eq) in THF (100 mL) was added to the reaction over 1 h. The reaction flask was then heated to reflux over 2 h during which time a large amount of a white precipitate formed. This was

allowed to cool to room temperature, and it was quenched with 2 M HCl until pH<2. The organic layer was removed, and the aqueous layer was extracted with diethyl ether (3 x 100 mL). The combined organics were then dried over $MgSO_4$ and concentrated *in vacuo* to give a yellow oil. This was distilled at 0.2 mm Hg/105-110°C to give **16** (20.9 g, 83% yield) as a mixture of isomers. ^{1}H NMR ($CDCl_3$) δ 10.20–9.75 (bs, 1H), 4.51-4.11 (m, 3H), 3.63-3.53 (m, 2H), 3.07-2.02 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 176.01, 175.86, 75.50, 74.22, 67.76, 67.67, 51.76, 48.88, 37.71, 36.32, 30.11, 29.44; IR (thin film on a NaCl plate) 3736-2360 (b), 1732, 1472, 1431, 1352, 1244, 1135, 1046, 935, 841, 747, 674 cm^{-1}; HRMS (EI) calcd for $C_7H_{11}ClO_3$ $(M)^+$ 178.0397, found 178.0397.

Synthesis of [3-oxa-4-(2-cyclobutenyl)]butyric acid (17). The standard elimination procedure was used for compound **16** with a few modifications. Instead of simply pouring the reaction mixture into ice water to quench the reaction, the reaction mixture was acidified with 2 M HCl until the pH<2. Purification was accomplished by flash column chromatography (silica gel, 30% ethyl acetate/68% hexanes/2% acetic acid, R_f=0.45) to give **17** as a clear oil (74% yield). ^{1}H NMR ($CDCl_3$) δ 10.22–9.60 (bs, 1H), 6.10 (d, *J*=1.8 Hz, 1H), 6.05 (d, *J*=1.8 Hz, 1H), 4.12 (s, 2H), 3.67-3.57 (m, 2H), 3.14-3.08 (m, 1H), 2.69 (dd, J_1=3.3 Hz, J_2=14.7 Hz, 1H), 2.21 (d, *J*=14.7 Hz, 12H); ^{13}C NMR ($CDCl_3$) δ 175.14, 137.56, 137.32, 75.29, 67.85, 42.94, 34.22; IR (thin film on a NaCl plate) 3712-2345 (b), 1734, 1560, 1437, 1351, 1204, 1156, 1026, 954, 921, 705 cm^{-1}; HRMS (EI) calcd for $C_7H_{10}O_3$ $(M)^+$ 142.0630, found 142.0623.

Synthesis of methyl [3-oxa-4-(2-cyclobutenynl)]butyrate (18). [3-oxa-4-(2-cyclobutenyl)]butyric acid (**17**) (5.0 g, 35.2 mmol, 1.0 eq) was combined with K_2CO_3 (24.3 g, 176 mmol, 5 eq) and MeI (100 g, 705 mmol, 20.0 eq) in acetone (200 mL). This was allowed to stir overnight at room temperature. The acetone was removed *in vacuo*, and the reaction mixture was dissolved in deionized water (100 mL). This was extracted with diethyl ether (3 x 100 mL), and the organics were dried over $MgSO_4$ and concentrated *in vacuo* to give a yellow oil. This was distilled at 0.2 mm Hg/42°C to give

18 as a clear liquid (4.02 g, 73% yield). ^{1}H NMR ($CDCl_3$) δ 6.06(d, *J*=2.7 Hz, 1H), 6.03 (d, *J*=2.7 Hz, 1H), 4.06 (s, 2H), 3.70 (s, 3H), 3.60-3.53 (m, 2H), 3.11-3.06 (m, 1H), 2.65 (dd, J_1=4.2Hz, J_2=12.9 Hz, 1H), 2.19 (d, *J*=12.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 170.87, 137.81, 137.06, 75.21, 68.29, 51.68, 43.07, 34.26; IR (thin film on a NaCl plate) 3124, 3046, 2951, 2920, 2848, 1757, 1738, 1462, 1454, 1436, 1288, 1209, 1132, 1027, 990, 954, 921, 902, 885, 844, 700 cm^{-1}; HRMS (EI) calcd for $C_8H_{12}O_3$ $(M)^+$ 156.0786, found 156.0781.

Synthesis of *N,N*-dimethyl-[3-oxa-4-(2-cyclobutenyl)]butyramide (19a). **17** (2.9 g, 20.4 mmol, 1.0 eq) was mixed with thionyl chloride (7.29 g, 61.3 mmol, 3.0 eq), and this was heated to reflux under argon until all evolution of gases had ceased (1.5 h). The excess thionyl chloride was removed *in vacuo* to result in an orange oil. This oil was then added to an ice cold solution of dimethylamine (40 wt% in water, 20 mL, 177 mmol, 8.7 eq). This was left to stir for 1 h at room temperature, and then it was extracted with diethyl ether (3 x 30 mL). The organics were then dried over $MgSO_4$ and concentrated *in vacuo* to give a orange oil. This material was purified by distillation at 0.2 mm Hg/83-85°C to give **19a** as a clear oil (2.45 g, 71% yield). ^{1}H NMR ($CDCl_3$) δ 6.12(d, *J*=2.4 Hz, 1H), 6.08 (d, *J*=2.4 Hz, 1H), 4.15 (s, 2H), 3.60-3.57 (m, 2H), 3.17-3.11 (m, 1H), 3.04 (s, 3H), 2.97 (s, 3H), 2.66 (dd, J_1=4.2Hz, J_2=13.8 Hz, 1H), 2.22 (d, *J*=13.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 169.26, 137.98, 139.96, 74.79, 70.54, 43.21, 36.37, 35.38, 34.31; IR (thin film on a NaCl plate) 3123, 3044, 2920, 2849, 1646, 1504, 1470, 1446, 1400, 1344, 1289, 1265, 1202, 1178, 1108, 1040, 1022, 961, 921, 903, 803, 781, 703, 603 cm^{-1}; HRMS (EI) calcd for $C_9H_{15}NO_2$ $(M)^+$ 169.1103, found 169.1100.

Synthesis of *N,N*-diisopropyl-[3-oxa-4-(2-cyclobutenyl)]butyramide (19b). **17** (4.5 g, 31.7 mmol, 1.0 eq) was mixed with thionyl chloride (13.2 g, 111 mmol, 3.5 eq), and this was heated to reflux under argon until all evolution of gases had ceased (1.5 h). The excess thionyl chloride was removed *in vacuo* to result in an orange

oil. This oil was then added to an ice cold solution of diisopropylamine (32.1 g, 317 mmol, 10.0 eq) in THF (150 mL). This was left to stir overnight at room temperature, and then it was quenched by the addition of deionized water (50 mL). The organic layer was removed, and the aqueous layer was extracted with diethyl ether (3 x 40 mL). The combined organics were then dried over $MgSO_4$ and concentrated *in vacuo* to give a orange oil. This was purified by flash column chromatography (silica gel, 15% ethyl acetate/hexanes, R_f=0.21) to give **19b** as a clear liquid (6.21 g, 87% yield). ^{1}H NMR ($CDCl_3$) δ 6.07-6.04 (m, 2H), 4.08-3.95 (m, 4H), 3.54 (d, *J*=6.9 Hz, 2H), 3.52-3.32 (m, 1H), 2.66 (dd, J_1=4.2Hz, J_2=13.8 Hz, 1H), 2.20 (d, *J*=13.8 Hz, 1H), 1.37 (d, *J*=6.6 Hz, 6H), 1.15 (d, *J*=6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 168.08, 138.10, 136.93, 74.74, 72.33, 48.18, 45.77, 43.24, 34.34, 20.80, 20.41; IR (thin film on a NaCl plate) 3124, 3046, 2999, 2966, 2924, 2873, 1645, 1474, 1446, 1368, 1336, 1308, 1290, 1214, 1138, 1099, 1043, 1022, 958, 919, 902, 884, 862, 807, 738, 706, 604 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{23}NO_2$ $(M)^+$ 225.1729, found 225.1730.

Synthesis of methyl [5-*cis,trans*-(3-chlorocyclobutyl)]-*trans,trans*-pentadienoate (21). **3** (30.0 g, 249 mmol, 1.0 eq) was dissolved in CH_2Cl_2 (600 mL) and pyridinium chlorochromate (107 g, 498 mmol, 2.0 eq) was added in portion over 30 min. The reaction was left stirring for 2.5 h at room temperature. Diethyl ether (500 mL) was added to the reaction flask, and the mixture was poured through 2 inches of silica gel. The black precipitate was washed with diethyl ether (4 x 300 mL), and these washings were passed through the silica plug as well resulting in a yellow solution. This was concentrated *in vacuo* (5°C, ~20 mm Hg) resulting in approximately 30 mL of crude *cis,trans*-3-chlorocyclobutanecarboxaldehyde (**20**) dissolved in a minimal amount of solvent. This product was observed to be extremely sensitive and any attempts at further purification resulted in extremely low isolated yields.

Lithium diisopropylamide (LDA) (21.8 g, 203 mmol, 1.5 eq) was dissolved in dry THF (400 mL) and cooled to -78°C under argon. To this, trimethyl 4-phosphonocrotonate

(45.3 g, 217 mmol, 1.6 eq) in dry THF (100 mL) was added dropwise over 30 min. This was left for an additional 30 min at -78°C, and then the flask was warmed to -50°C. The crude aldehyde synthesized above was then dissolved in THF (50 mL) and added dropwise over 15 min to the reaction mixture. The flask was then allowed to warm to room temperature over 1 h. The reaction was quenched with 1 M HCl until the pH<2, and the reaction mixture was then poured into a separatory funnel containing petroleum ether/deionized water (800 mL, 1:1). The organic layer was washed with deionized water (3 x 200 mL), dried over $MgSO_4$, and concentrated *in vacuo* to obtain the product **21** as a mixture of isomers (20.9 g, 77% yield) with <10% *cis*-olefin formed. The spectral data for the major two isomers of methyl [5-*cis,trans*-(3-chlorocyclobutyl)]-*trans,trans*-pentadienoate were as follows: ^{1}H NMR ($CDCl_3$) δ 7.54–7.16 (m, 1H), 6.27-6.07 (m, 2H), 5.80 (d, *J*=15 Hz, 1H), 4.49-4.22 (m, 1H), 3.72 (s, 3H), 3.44-2.08 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 167.29, 145.27, 145.03, 144.29, 144.22, 127.53, 127.48, 120.24, 120.06, 52.35, 51.41, 51.38, 48.27, 40.87, 39.41, 33.67, 32.57; IR (thin film on a NaCl plate) 3023, 2990, 2948, 2842, 1716, 1644, 1617, 1434, 1366, 1332, 1307, 1269, 1244, 1157, 1137, 1065, 1038, 1000, 915, 873, 847, 827, 759, 725, 716, 652, 624 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{13}ClO_2$ $(M)^+$ 200.0604, found 200.0613.

Synthesis of methyl [5-*cis,trans*-(3-chlorocyclobutyl)]pentanoate (22). Methyl [5-*cis,trans*-(3-chlorocyclobutyl)]pentadienoate (**21**) (26.7g, 133 mmol, 1.0 eq) was dissolved in ethyl acetate (400 mL) and combined with 10% Pd/C (7.08 g, 6.7 mmol, 0.05 eq) under an atmosphere of hydrogen. This was left for 6 h at room temperature under hydrogen at which time the reaction mixture was poured through 1 inch of silica gel. The plug was washed with diethyl ether (3 x 100 mL), and the combined organics were concentrated *in vacuo* to obtain **22** as a clear oil as a mixture of isomers (27.2 g, 99% yield). ^{1}H NMR ($CDCl_3$) δ 4.47–4.15 (m, 1H), 3.64 (s, 3H), 3.05-1.12 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 173.90, 52.69, 52.58, 51.33, 48.87, 41.12, 39.23, 36.55, 35.37, 34.96, 33.94, 30.68, 30.03, 26.97, 26.68, 24.74, 24.69; IR (thin film on a

NaCl plate) 2977, 2935, 2855, 1740, 1456, 1435, 1370, 1308, 1278, 1242, 1195, 1172, 1103, 1013, 988, 883, 838, 731, 702, 644, 619 cm^{-1}; HRMS (CI) calcd for $C_{10}H_{17}ClO_2$ $(M+H)^+$ 205.0995, found 205.0993.

Synthesis of 5-*cis,trans*-(3-chlorocyclobutyl)pentanoic acid (23). Methyl [5-*cis,trans*-(3-chlorocyclobutyl)]pentanoate (**22**) (26.7 g, 131 mmol, 1.0 eq) was dissolved in 1:1 THF/deionized water (600 mL), and NaOH pellets (15.6 g, 393 mmol, 3.0 eq) were added. Initially two phases were observed, but after 1 h, a clear solution was formed. After 2 h, the reaction was acidified with 3 M HCl until pH< 2, and the organic layer was removed. The aqueous layer was saturated with NaCl and extracted with diethyl ether (3 x 200 mL). The combined organics were then dried over $MgSO_4$ and concentrated *in vacuo* to obtain the product **23** as a mixture of isomers (24.3 g, 98% yield). ^1H NMR ($CDCl_3$) δ 4.48-4.16 (m, 1H), 3.08-1.14 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 180.21, 52.63, 48.91, 41.07, 39.13, 36.53, 35.31, 34.89, 33.94, 30.56, 29.96, 26.87, 26.57, 24.43, 24.37; IR (thin film on a NaCl plate) 3630-2348 (b), 1712, 1459, 1413, 1279, 1241, 1210, 1132, 1103, 1006, 939, 889, 838, 815, 731, 696, 642, 622 cm^{-1}; HRMS (EI) calcd for $C_9H_{14}ClO$ $(M-OH)^+$ 173.0733, found 173.0733; HRMS (EI) calcd for $C_9H_{15}O_2$ $(M-Cl)^+$ 155.1072, found 155.1074. No parent mass was observed.

Synthesis of 5-(2-cyclobutenyl)pentanoic acid (24). Synthesis of 5-(2-cyclobutenyl)pentanoic acid (**24**) (24.3 g, 127 mmol) was accomplished as in analogy to [3-oxa-4-(2-cyclobutenyl)]butyric acid (**17**) (18.0 g, 92% yield). ^1H NMR ($CDCl_3$) δ 6.08 (d, J=3.0 Hz, 1H), 6.02 (d, J=3.0 Hz, 1H), 2.80-2.73 (m, 1H), 2.65 (dd, J_1=3.9 Hz, J_2=13.2 Hz, 1H), 2.34 (t, J=7.2 Hz, 2H), 2.15 (d, J=13.2 Hz, 1H), 1.68-1.29 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 180.60, 140.73, 135.28, 43.84, 36.79, 34.13, 34.10, 27.44, 24.71; IR (thin film on a NaCl plate) 3629-2140 (b), 1709, 1603, 1562, 1458, 1413, 1288, 1236, 1207, 1111, 1057, 1004, 934, 818, 787, 732, 699 cm^{-1}; HRMS (EI) calcd for $C_9H_{14}O_2$ $(M)^+$ 154.0994, found 154.0995.

Synthesis of 5-(2-cyclobutenyl)pentanol (25). 5-(2-cyclobutenyl)pentanoic acid (**24**) (4.5 g, 29.2 mmol, 1.0 eq) in dry THF (25 mL) was added to a mixture of LAH (2.21 g, 58.4 mmol, 2.0 eq) in dry THF (75 mL) at 0°C over 30 min. The reaction was then warmed to room temperature and allowed to stir for 3 h. The reaction was quenched by the careful sequential addition of deionized water (5 mL), aqueous NaOH (15% w/w, 5 mL), and deionized water (5 mL). The white precipitate was removed by filtration, and this was washed with diethyl ether (3 x 150 mL). The combined organics were then dried over $MgSO_4$ and concentrated *in vacuo* to obtain the product **25** (4.0 g, 99% yield). ^{1}H NMR ($CDCl_3$) δ 6.09 (d, *J*=3.0 Hz, 1H), 6.02 (d, *J*=3.0 Hz, 1H), 3.63 (t, *J*=6.6 Hz, 2H), 2.79-2.72 (m, 1H), 2.64 (dd, J_1=4.2 Hz, J_2=13.5 Hz, 1H), 2.15 (d, *J*=13.5 Hz, 1H), 1.62-1.27 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 140.94, 135.16, 62.93, 44.06, 36.83, 34.54, 32.74, 27.80, 25.82; IR (thin film on a NaCl plate) 3642-3124 (b), 3045, 2920, 2853, 1589, 1562, 1462, 1434, 1377, 1322, 1289, 1199, 1120, 1055, 1004, 938, 913, 899, 804, 726, 697 cm^{-1}; HRMS (EI) calcd for $C_9H_{16}O$ $(M)^+$ 140.1201, found 140.1193.

Synthesis of *N*-butyl-[5-(2-cyclobutenyl)]pentanamide (26). Using the same procedure as for *N,N*-dimethyl-[3-oxa-4-(2-cyclobutenyl)]butyramide (**19a**), treatment of 5-(2-cyclobutenyl)pentanoic acid (**24**) (3.9 g, 25.3 mmol, 1.0 eq) with thionyl chloride (9.0 g, 76 mmol, 3.0 eq) resulted in the formation of the acid chloride. Addition of the acid chloride to a solution of *n*-butyl amine (18.5 g, 253 mmol, 10.0 eq) in THF (150 mL) resulted in the product **26** (4.5 g, 85%). ^{1}H NMR ($CDCl_3$) δ 6.07 (d, *J*=2.7 Hz, 1H), 6.02 (d, *J*=2.7 Hz, 1H), 5.35 (bs, 1H), 3.25 (q, *J*=6.6 Hz, 2H), 2.80-2.72 (m, 1H), 2.63 (dd, J_1=4.2 Hz, J_2=13.5 Hz, 1H), 2.14 (t, *J*=6.6 Hz, 2H), 2.02 (d, *J*=13.5 Hz, 1H), 1.99-1.25 (m, 10H), 0.90 (t, *J*=7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 172.97, 140.77, 135.21, 43.90, 39.15, 36.83, 36.79, 34.26, 31.71, 27.66, 25.90, 20.03, 13.71; IR (thin film on a NaCl plate) 3289, 3123, 3084, 3046, 2927, 2860, 1646, 1558, 1463,

1438, 1378, 1288, 1240, 1201, 1153, 1113, 1058, 982, 964, 944, 918, 901, 854, 731, 698 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{23}NO$ $(M)^+$ 209.1780, found 209.1786.

Synthesis of methyl [5-(2-cyclobutenyl)]pentanoate (27). Using the same procedure as for the synthesis of methyl [3-oxa-4-(2-cyclobutenynl)]butyrate (**18**), treatment of 5-(2-cyclobutenyl)pentanoic acid (**24**) (3.9 g, 25.3 mmol, 1.0 eq) with K_2CO_3 (17.5 g, 127 mmol, 5.0 eq) and MeI (71.9 g, 510 mmol, 20.0 eq) in acetone (200 mL) resulted in the desired product **27** (4.2 g, 99% yield). ^1H NMR ($CDCl_3$) δ 6.08 (d, J=3.0 Hz, 1H), 6.02 (d, J=3.0 Hz, 1H), 3.65 (s, 3H), 2.80-2.71 (m, 1H), 2.64 (dd, J_1=4.5 Hz, J_2=16.8 Hz, 1H), 2.30 (t, J=7.5 Hz, 2H), 2.15 (d, J=16.8 Hz, 1H), 1.67-1.25 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 174.18, 140.76, 135.21, 51.40, 43.87, 36.77, 34.15, 34.04, 27.52, 25.00; IR (thin film on a NaCl plate) 3124, 3040, 2938, 2852, 1742, 1604, 1587, 1562, 1456, 1436, 1364, 1201, 1174, 1110, 983, 918, 881, 834, 818, 770, 732, 700 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{16}O_2$ $(M)^+$ 168.1150, found 168.1148.

Determination of the % initiation of complexes 1 and 2 with the cyclobutenes. In a dry box, an aliquot (0.60 mL) of a stock solution of initiator **1** or **2** dissolved in toluene-d_8 or THF-d_8 (0.022 M) was removed. In a separate vial, the desired cyclobutene (5.0 eq relative to **1** or **2**) was weighed out. The initiator solution was then transferred to the cyclobutene vial and agitated until a solution resulted. This was then transferred to an NMR tube and capped with a septa. The NMR tube was then removed from the dry box and placed in an oil bath at either room temperature or 45°C for 1 h. At this time, an ^1H NMR was taken and the % initiation was determined by integration of the H_α carbene resonances present.

Temperature dependence of the coordination equilibrium constant in the polymerization of benzyl [1-(2-cyclobutenyl)methyl] ether (8). In a dry box, a stock solution of initiator **1** in toluene-d_8 (28.0 mg, 3.00 mL) was prepared and a 0.60 mL aliquot was removed. Benzyl [1-(2-cyclobutenyl)methyl] ether (**8**) (60.0 mg, 57.0 eq) was weighed out and combined with the initiator solution in an NMR tube. The

tube was capped with a septa and removed from the box. The tube was heated to 45°C for 1 h, and then it was allowed to cool to room temperature. The ratio of chelated and non-chelated propagating species was determined by integration of the respective carbene resonances at 17.73 and 19.84 ppm at temperatures from -21.5 to 24.6°C. NMR spectra were recorded using a JEOL GX-400 spectrometer. At each temperature, multiple spectra were recorded until a constant value was acheived to ensure that the equilibrium had been reestablished.

Large scale preparation of poly(8, 10, 12, 15, and 18). In a dry box, the desired amount of initiator **1** was weighed into a large vial. The cyclobutene was added to a separate vial and dissolved in toluene or THF (0.57 M). This solution was then transferred to the initiator vial, and a stir bar was added. The vial was capped and removed from the box. This vial was then heated to 45°C until the reaction was complete. Removal of the solvent was accomplished *in vacuo*, and the resulting tacky solid was stirred with acidic methanol (5 mL of 1 M HCl/200 mL MeOH) for 1 h. This was then followed by washing with methanol (2 x 50 mL), and finally diethyl ether (2 x 50 mL). Simple removal of the residual solvent *in vacuo* yielded pure polymer.

Large scale preparation of poly(24-27). In a dry box, the desired amount of initiator **2** was weighed into a large vial. The cyclobutene was added to a separate vial and dissolved in THF (0.17 M). This solution was then transferred to the initiator vial, and a stir bar was added. The vial was then capped, removed from the box, and then left to sir at room temperature for 1.5 h. Ethyl vinyl ether (600 eq) was then added, and this was left for 30 min to quench the reaction. Removal of the solvent was accomplished *in vacuo*, and the resulting tacky solid was washed with diethyl ether (4 x 20 mL). Simple removal of the residual solvent *in vacuo* yielded pure polymer.

Poly(8), X=OCH_2Ph. The yield of polymer was 87%. ^1H NMR (CD_2Cl_2) δ 7.38-7.17 (bm, 5H), 5.42-5.18 (bm, 2H), 4.43-4.36 (bm, 2H), 3.38-3.20 (bm, 2H), 2.76-2.59 (bm, 1H), 2.40-1.83 (bm, 2H); ^{13}C NMR ($CDCl_3$) δ 138.82, 133.11-127.55

(m, Backbone C-Olefin), 128.25, 127.42, 127.34, 73.61, 73.53, 72.94, 42.99-29.68 (m, Backbone C-Alkyl); IR (thin film on a NaCl plate) 3062, 3028, 3005, 2851, 2786, 1496, 1453, 1361, 1205, 1102, 1028, 968, 735, 697 cm^{-1}.

Poly(10), X=OC(Ph)$_3$. The yield of polymer was 91%. ^1H NMR (CD_2Cl_2) δ 7.60-6.95 (bm, 15H), 5.20-4.93 (bm, 2H), 3.02-2.88 (bm, 2H), 2.62-1.77 (bm, 3H); ^{13}C NMR (CD_2Cl_2) δ 144.37, 133.25-128.47 (m, Backbone C-Olefin), 128.74, 127.64, 126.79, 86.35, 86.23, 66.84, 66.81, 66.78, 43.74-29.62 (m, Backbone C-Alkyl); IR (thin film on a NaCl plate) 3057, 3021, 2916, 2862, 1596, 1490, 1448, 1219, 1153, 1068, 1032, 898, 763, 745, 705, 632 cm^{-1}.

Poly(12), X=OC(O)Ph. The yield of polymer was 95%. ^1H NMR ($CDCl_3$) δ 8.21-7.83 (bm, 2H), 7.58-7.18 (bm, 3H), 5.56-4.98 (bm, 2H), 4.37-3.96 (bm, 2H), 2.88-2.65 (bm, 1H), 2.51-1.83 (bm, 2H); ^{13}C NMR ($CDCl_3$) δ 166.25, 132.82, 132.31-128.92 (m, Backbone C-Olefin), 130.27, 129.48, 128.30, 67.19, 66.98, 42.17-29.36 (m, Backbone C-Alkyl); IR (thin film on a NaCl plate) 3063, 3009, 2947, 2850, 1716, 1602, 1584, 1451, 1378, 1314, 1272, 1176, 1113, 1070, 1026, 970, 911, 709, 687 cm^{-1}.

Poly(15), X=N(*i*-Pr)$_2$. The yield of polymer was 79%. ^1H NMR ($CDCl_3$) δ 5.41-4.99 (bm, 2H), 3.02-2.88 (bm, 2H), 2.56-1.61 (bm, 5H), 0.84 (bs, 12H); ^{13}C NMR ($CDCl_3$) δ 134.74-128.51 (m, Backbone C-Olefin), 50.23, 50.05, 49.98, 49.73, 49.43, 49.29, 47.63, 47.55, 42.92-30.60 (m, Backbone C-Alkyl), 21.68, 19.81; IR (thin film on a NaCl plate) 2963, 2933, 2870, 1654, 1468, 1382, 1361, 1207, 1170, 1115, 1065, 965, 883, 758, 718 cm^{-1}.

Poly(18), X=OCH$_2$OCOOMe. The yield of polymer was 84%. ^1H NMR ($CDCl_3$) δ 5.50-5.07 (bm, 2H), 3.95(bs, 2H), 3.61 (bs, 3H), 3.45-3.19 (bm, 2H), 2.80-1.79 (bm, 3H); ^{13}C NMR ($CDCl_3$) δ 170.61, 132.47-128.09 (m, Backbone C-Olefin), 74.50, 68.08, 51.41, 42.54-29.06 (m, Backbone C-Alkyl); IR (thin film on a NaCl plate) 3005, 2952, 2908, 2858, 1757, 1740, 1437, 1352, 1282, 1209, 1140, 974, 884, 765, 706 cm^{-1}.

Poly(24), X=$(CH_2)_3$COOH. The yield of polymer was 95%. ^{1}H NMR (acetone-d_6) δ 11.24-9.62 (bs, 1H), 5.56-5.00 (bm, 2H), 2.55-1.06 (bm, 11H); ^{13}C NMR (acetone-d_6) δ 175.81, 136.88-128.96 (m, Backbone C-Olefin), 44.20-25.75 (m, C-Alkyl); IR (thin film on a NaCl plate) 3570-2257 (b), 1709, 1458, 1412, 1286, 1232, 1093, 968, 939, 810, 766, 668 cm^{-1}.

Poly(25), X=$(CH_2)_4$OH. The yield of polymer was 96%. ^{1}H NMR (THF-d_8) δ 5.54-5.04 (bm, 2H), 3.74-3.37 (bm, 3H), 2.78-1.00 (bm, 11H); ^{13}C NMR (THF-d_8) δ 137.34-125.86 (m, Backbone C-Olefin), 62.70, 44.59-30.80 (m, Backbone C-Alkyl), 34.08, 28.32, 27.21, 27.08; IR (thin film on a NaCl plate) 3656-3072 (b), 2999, 2927, 2851, 1473, 1432, 1406, 1356, 1330, 1271, 1151, 1071, 1055, 968, 882, 752, 729 cm^{-1}.

Poly(26), X=$(CH_2)_3$C(O)NHBu. The yield of polymer was 92%. ^{1}H NMR ($CDCl_3$) δ 7.37-6.68 (bs, 1H), 5.43-4.91 (bm, 2H), 3.31-3.05 (bm, 2H), 2.42-1.01 (bm, 15H), 0.86 (bt, *J*=7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 173.46, 135.89-125.41 (m, Backbone C-Olefin), 43.19-24.97 (m, C-Alkyl), 39.15, 31.64, 20.08, 13.77; IR (thin film on a NaCl plate) 3294, 3083, 2956, 2860, 1655, 1560, 1459, 1438, 1376, 1331, 1261, 1228, 1153, 1116, 1075, 1023, 969, 921, 891, 734, 644 cm^{-1}.

Poly(27), X=$(CH_2)_3$COOMe. The yield of polymer was 96%. ^{1}H NMR ($CDCl_3$) δ 5.41-4.98 (bm, 2H), 3.63 (s, 3H), 2.28-1.03 (bm, 11H); ^{13}C NMR ($CDCl_3$) δ 173.83, 136.23-127.72 (m, Backbone C-Olefin), 51.16, 43.14-33.62 (m, Backbone C-Alkyl), 34.17, 29.70, 27.18, 27.10, 27.01, 26.86, 25.45, 25.33, 25.02; IR (thin film on a NaCl plate) 3009, 2999, 2918, 2850, 1740, 1456, 1436, 1362, 1318, 1250, 1197, 1172, 1107, 1017, 970, 883, 847, 766 cm^{-1}.

Diblock Copolymerizations using monomers 24-27. In a dry box, the desired amount of initiator **2** was weighed into a large vial. The cyclobutene (50 eq) was added to a separate vial and dissolved in THF (0.17 M). This solution was then transferred to the initiator vial, and a stir bar was added. The vial was then capped and left to sir at

room temperature for 1.5 h. At this time, the second monomer (50 eq) was weighed out and dissolved in THF (0.85 M). This monomer solution was then transferred to the reaction vial, and the mixture ([M]=0.14 M) was left to stir for an additional 2 h. Ethyl vinyl ether (600 eq) was then added, and this was left for 30 min to quench the reaction. Removal of the solvent was accomplished *in vacuo*, and the resulting tacky solid was washed with diethyl ether (4 x 20 mL). Simple removal of the residual solvent *in vacuo* yielded pure polymer.

Poly[poly(27)-*block*-poly(25)], $X_1=(CH_2)_3COOMe$ and $X_2=(CH_2)_4OH$. The yield of polymer was 95%. ^1H NMR ($CDCl_3$) δ 5.50-5.02 (bm, 4H), 3.73-3.47 (bm, 6H), 2.74-0.99 (bm, 22H); ^{13}C NMR ($CDCl_3$) δ 173.65, 137.87-128.38 (m, Backbone C-Olefin), 62.69, 51.27, 44.69-25.77 (m, C-Alkyl); IR (thin film on a NaCl plate) 3690-3011 (b), 2999, 2929, 2855, 1740, 1458, 1436, 1363, 1323, 1251, 1198, 1172, 1055, 969, 882, 758 cm^{-1}.

Poly[poly(27)-*block*-poly(24)], $X_1=(CH_2)_3COOMe$ and $X_2=(CH_2)_3COOH$. The yield of polymer was 92%. ^1H NMR (THF-d_8) δ 5.51-5.02 (bm, 4H), 3.57 (s, 3H), 2.49-1.04 (bm, 22H); ^{13}C NMR (THF-d_8) δ 174.88, 173.64, 137.26-128.41 (m, Backbone C-Olefin), 51.23, 44.76-25.86 (m, C-Alkyl); IR (thin film on a NaCl plate) 3670-2100 (b), 1740, 1707, 1458, 1436, 1414, 1363, 1248, 1229, 1200, 1173, 1106, 969, 943, 886, 766 cm^{-1}.

Poly[poly(26)-*block*-poly(27)], $X_1=(CH_2)_3C(O)NHBu$ and $X_2=(CH_2)_3COOMe$. The yield of polymer was 98%. ^1H NMR ($CDCl_3$) δ 7.31-6.74 (bs, 1H), 5.41-4.85 (bm, 4H), 3.58 (s, 3H), 3.22-3.04 (bm, 2H), 2.34-0.98 (bm, 26H), 0.90 (bt, J=7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 173.84, 173.27, 136.25-126.61 (m, Backbone C-Olefin), 51.15, 43.40-24.80 (m, C-Alkyl), 20.05, 13.64; IR (thin film on a NaCl plate) 3448, 3298, 3084, 2917, 2899, 1739, 1642, 1551, 1459, 1437, 1363, 1251, 1227, 1171, 1019, 969, 738 cm^{-1}.

Poly[poly(26)-*block*-poly(24)], $X_1=(CH_2)_3C(O)NHBu$ and $X_2=(CH_2)_3COOH$. The yield of polymer was 97%. ^1H NMR (THF-d_8) δ 7.97-7.58 (bs, 1H), 5.52-5.00 (bm, 4H), 3.29-3.06 (bm, 2H), 2.49-1.09 (bm, 26H), 0.85 (bt, J=7.5 Hz, 3H); ^{13}C NMR (THF-d_8) δ 174.85, 173.44, 138.21-125.87 (m, C-Olefin), 44.75-27.06 (m, C-Alkyl), 21.06, 14.33; IR (thin film on a NaCl plate) 3715-2237 (b), 1709, 1648, 1560, 1459, 1439, 1367, 1257, 1228, 1156, 1098, 1048, 969, 891, 835, 742 cm^{-1}.

Poly[poly(25)-*block*-poly(24)], $X_1=(CH_2)_4OH$ and $X_2=(CH_2)_3COOH$. The yield of polymer was 96%. ^1H NMR (THF-d_8) δ 5.57-4.99 (bm, 4H), 3.54-3.30 (bm, 2H), 2.52-1.05 (bm, 22H); ^{13}C NMR (THF-d_8) δ 174.83, 136.49-128.03 (m, Backbone C-Olefin), 62.35, 44.54-24.05 (m, C-Alkyl); IR (thin film on a NaCl plate) 3733-2241 (b), 1709, 1456, 1440, 1410, 1361, 1268, 1230, 1097, 1071, 1050, 969, 891, 834, 751 cm^{-1}.

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Chapter 4:

Influence of Backbone Rigidity on the Thermotropic Behavior of Side-Chain Liquid Crystalline Polymers (SCLCPs) Synthesized by Ring-Opening Metathesis Polymerization (ROMP)

Abstract

The effect of backbone flexibility on the mesomorphic behavior of side-chain liquid crystalline polymers synthesized by ring-opening metathesis polymerization was investigated. The synthesis of norbornene and cyclobutene monomers containing a *p*-nitrostilbene moiety as the mesogenic group and polymerization of these monomers to produce side-chain liquid crystalline polymers with low polydispersities and defined molecular weights was accomplished. The relatively rigid poly(norbornene)s displayed enantiotropic nematic mesomorphism with glass transitions from 44-64˚C and isotropization temperatures between 108-121˚C, whereas the more flexible poly(butadiene)s showed enantiotropic smectic A mesomorphism with glass transition temperatures from 14-31˚C and isotropization temperatures between 74-111˚C. A diblock copolymer containing a 1:1 mixture of the poly(norbornene) and poly(butadiene) backbones also exhibited a smectic A mesophase. The dependence of the degree of polymerization and flexible spacer length on the phase transitions of these systems was determined demonstrating stabilization of the mesophase by both increasing molecular weight and flexible spacer length.

Introduction

Since their initial discovery in 1888 by Reinitzer,[1] liquid crystalline materials have been investigated intensely for their scientific and technological potentials. The ability of these anisotropic molecules to form supramolecular structures through self-organization prompted research to determine the criteria for the formation of liquid crystalline mesophases.[2,3] As information about these materials was accumulated, it was observed that increasing liquid crystalline order was found in many systems on passing from low molecular weight monomeric compounds to the corresponding polymeric materials.[4,5] Liquid crystalline polymers were divided into two major classes: 1) polymers containing the mesogenic group in the backbone (main-chain liquid crystalline polymers, MCLCPs), and 2) polymers with the mesogenic group on the side-chains of the polymers (side-chain liquid crystalline polymers, SCLCPs) which were the focus of this study.[4,5]

Finkelmann and Ringsdorf's[6,7] discovery that the addition of a flexible spacer between the rigid mesogen and the polymer backbone greatly enhanced the observed liquid crystallinity in SCLCPs allowed for the systematic preparation of a wide variety of these materials. The flexible spacer enabled a partial decoupling of the motions of the polymer backbone and the mesogens, thus providing the mesogens with the ability to stack in organized domains.[6,7] Based on these initial results, SCLCPs have been synthesized utilizing various polymer backbones including poly(acrylate)s,[8-12] poly(methacrylate)s,[13,14] poly(siloxane)s,[15-18] and poly(phosphazene)s.[19-21] However, the methods of polymerization utilized for these systems, including free radical polymerization, hydrosilation, and ring-opening polymerization, were limited by the lack of control over polymer molecular weight and polydispersity (PDI). In order to control these properties, the application of living polymerization methods to these systems was necessary.[22] Recently, living cationic [23-25] and group transfer[24,26] polymerizations have

been utilized for the production of SCLCPs with control over molecular weight and polydispersity.

Developments in ring-opening metathesis polymerization (ROMP)[27,28] have led to the ability to generate living polymerizations of strained cyclic olefins. The living ROMP of functionalized norbornenes bearing rigid biphenyl mesogens led to a series of new poly(norbornene) SCLCPs demonstrating enantiotropic nematic and smectic mesophases.[29-38] The effect of mesogen, degree of polymerization (DP), polydispersity, and flexible spacer length were investigated which has given insight on the effect of these factors on the liquid crystallinity of the poly(norbornene)s.

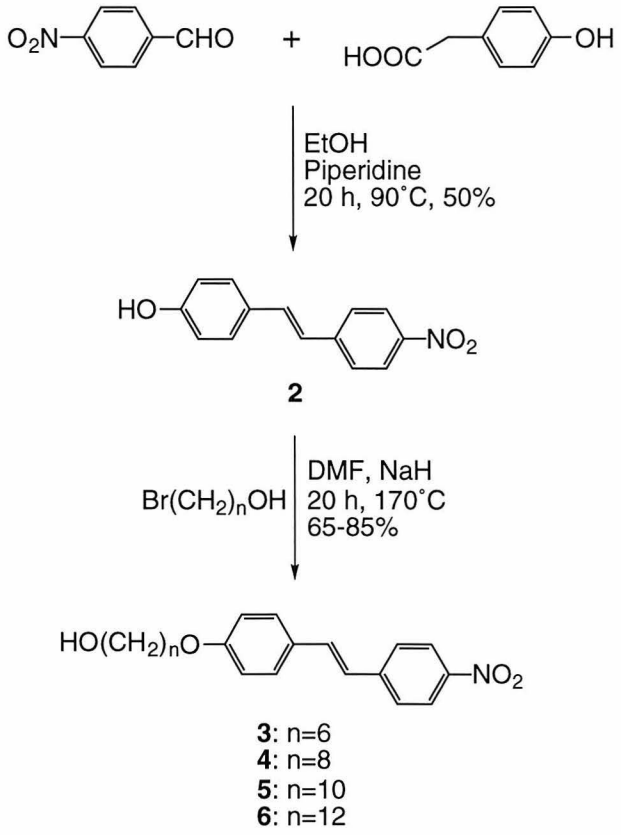
The influence of backbone rigidity on SCLCP behavior was another feature of these polymeric systems of interest. To examine the role of the backbone rigidity on the liquid crystallinity of SCLCPs, a comparison of the fairly rigid poly(norbornene) backbone with a more flexible poly(butadiene) backbone was undertaken. The synthesis of substituted norbornenes and cyclobutenes bearing a *p*-nitrostilbene moiety as the mesogenic unit was accomplished. ROMP of these monomers with the highly functional group tolerant initiator $(PCy_3)_2Cl_2Ru{=}CHPh$ (**1**)[39,40] produced SCLCPs with poly(norbornene) and poly(cyclobutene) (equivalent to poly(butadiene)) backbones, respectively. The role of the backbone rigidity in effecting the liquid crystalline transitions and mesophase behavior of the resulting poly(norbornene)s and poly(butadiene)s was examined by differential scanning calorimetry (DSC) and polarizing optical microscopy. The effect of the degree of polymerization and the flexible spacer length on the liquid crystallinity was determined as well resulting in further insight on the effect of these properties in SCLCPs derived from ROMP. This work was completed in collaboration with Marcus Weck and Dr. Bernhard Mohr. Marcus Weck completed the synthesis, polymerization, and analysis of the norbornene monomers, and Dr. Bernhard Mohr carried out the polarizing optical microscopy studies for both the poly(norbornene)s and poly(butadiene)s. However, all of the results will be

presented together in this chapter in order for a better comparison of the experimental results.

Results and Discussion

Functionalized mesogen synthesis. 4-Hydroxy-4'-nitrostilbene **2** was synthesized in 50% yield by the Knoevenagel condensation[41] of *p*-nitrobenzaldehyde and *p*-hydroxyphenylacetic acid.[42] Alkylation of **2** with a series of bromoalcohols under basic conditions led to the desired hydroxy-functionalized mesogens **3**-**6** in 65-85% yields (Scheme 1).

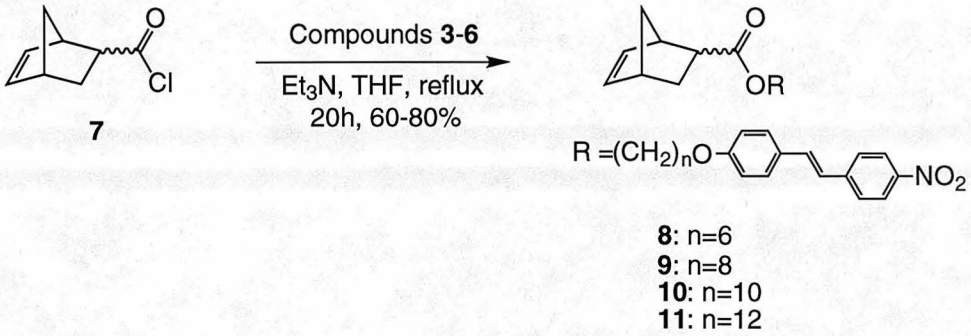
Scheme 1



Monomer synthesis. Nobornene monomers **8**-**11** were synthesized in one step from the esterification of norborn-2-ene-5-carbonyl chloride (**7**)[43] with hydroxy-

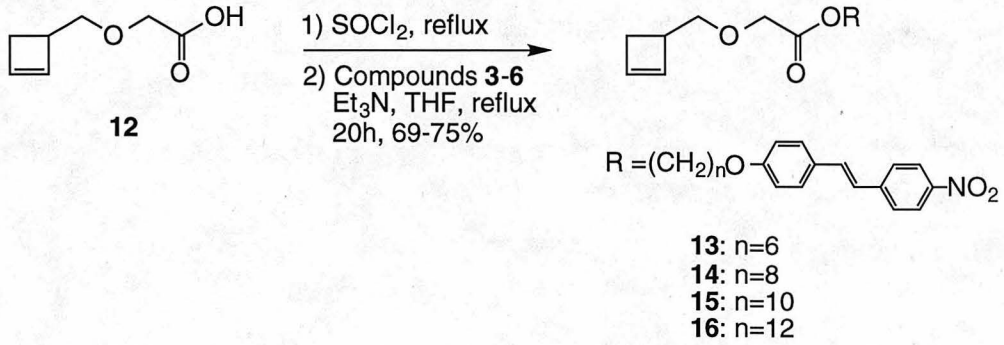
functionalized mesogens **3-6**. The reaction was carried out in THF in the presence of triethylamine resulting in monomers **8-11** in 60-80% yield after flash column chromatography (Scheme 2). Monomers **8-11** were crystalline solids exhibiting a single phase transition to the isotropic state.

Scheme 2



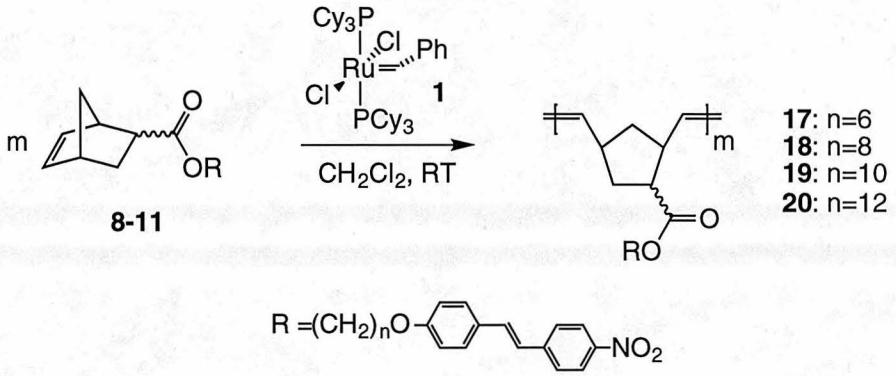
Cyclobutene monomers **13-16** were synthesized in a two step procedure by the initial conversion of [3-oxa-4-(2-cyclobutene)]butyric acid **12**[44] to the corresponding acid chloride with thionyl chloride ($SOCl_2$) and subsequent esterification with compounds **3-6** (Scheme 3). Monomers **13-16** were isolated in 69-75% yields after flash column chromatography resulting in crystalline solids exhibiting only a single phase transition to the isotropic state.

Scheme 3



Synthesis of poly(norbornene) SCLCPs. Polymerization of the norbornene monomers **8-11** with initiator **1** was accomplished over 1 h at room temperature in CH_2Cl_2 as shown in Scheme 4. Polymerizations were quenched by treatment with an

Scheme 4



excess of ethyl vinyl ether to cleave the propagating carbene from the polymer chain. Precipitation of the reaction mixture in methanol resulted in poly(norbornene)s **17-20** as fluffy, yellow solids in 90-99% isolated yields. The impact of the flexible spacer length (n) using monomers **8-11** and the degree of polymerization using monomer **9** at varying monomer to initiator ([M]/[I]) ratios on the liquid crystallinity of the polymers were examined as shown in Table 1. The polymerizations resulted in materials with narrow PDI(s) between 1.08-1.11 and controlled molecular weights. Tests performed by Marcus Weck demonstrated the living nature of these poly(norbornene) polymerizations with no observable chain transfer or chain termination occurring on the time scale of the polymerizations.[45]

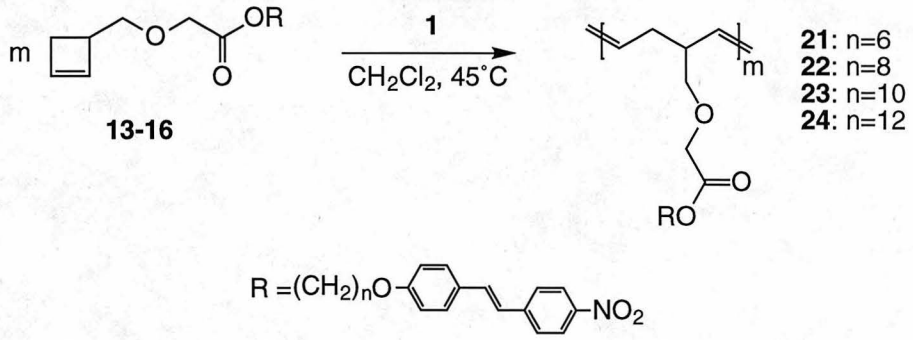
Synthesis of poly(butadiene) SCLCPs. Polymerization of the cyclobutene monomers **13-16** was accomplished as shown in Scheme 5. These reactions were performed with initiator **1** in CH_2Cl_2 at 45°C in a sealed vial for 24 h. Precipitation of the reaction mixture in acidic methanol (5% v/v of 1M HCl/methanol) resulted in cleavage of the propagating carbene from the polymer chain yielding polymers **21-24** as tacky yellow

Table 1. Polymerization results for norbornenes **8-11**

				Phase Transition[b] (°C)	
Monomer	[M]/[I]	$\overline{M}_n$[a]	PDI[a]	heating	cooling
8	25	13400	1.08	g64n121i	i117n60g
9	25	13000	1.08	g52n117i	i114n48g
10	25	22000	1.11	g50n108i	i104n46g
11	25	20800	1.10	g44n108i	i106n40g
9	5	7300	1.11	g46n108i	i107n43g
9	10	9800	1.09	g50n114i	i111n46g
9	25	13000	1.08	g52n117i	i114n48g
9	50	18000	1.07	g51n118i	i116n50g
9	100	23200	1.08	g49n121i	i118n44g

[a] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards. [b] Analysis by differential scanning calorimetry with a scan rate of 10°C/min.

Scheme 5



solids in 82-97% isolated yields. Cleavage with HCl was necessary because the propagating carbene in this system was unreactive with ethyl vinyl ether. Coordination of the ether-ester functionality to the propagating carbene produced a more inactive carbene which propagated at a much slower rate than in the norbornene polymerizations and was stable to excess ethyl vinyl ether. This resulted in the much longer reaction

times required for this polymerization.[44] As presented in Table 2, polymerization of monomers **13-16** with differing flexible spacer lengths as well as the polymerization of **14** at varying [M]/[I] ratios were accomplished. Control of the polymer molecular weight and low polydispersities of 1.11-1.38 were observed for these polymerizations. Despite

Table 2. Polymerization results for cyclobutene monomers **13-16**

				Phase Transition[b] (°C)	
Monomer	[M]/[I]	$\overline{M}_n$[a]	PDI[a]	heating	cooling
13	25	33300	1.16	g31s104i	i91s18g
14	25	35400	1.15	g25s104i	i95s13g
15	25	31900	1.16	g23s111i	i97s10g
16	25	38500	1.14	g21s108i	i99s11g
14	5	15000	1.13	g23s74i	i61s10g
14	10	21600	1.11	g21s86i	i78s9g
14	25	35400	1.15	g25s104i	i95s13g
14	50	57000	1.27	g15s105i	i96s5g
14	100	89100	1.38	g14s107i	i98s5g

[a] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards. [b] Analysis by differential scanning calorimetry with a scan rate of 10°C/min.

the effective control over the polymer molecular weight, this polymerization was not living, which was especially evident in the broadening of the PDI as the [M]/[I] ratio was increased. This broadening was the result of a lower molecular weight tail in the GPC, consistent with chain termination processes during the polymerization. However, at low [M]/[I] ratios, apparently the polymerization was able to reach completion before significant decomposition occurred, thus resulting in the lower PDI(s). This propagating carbene decomposition was presumed to result from the extended reaction times and

higher temperatures employed as compared to the conditions used in the norbornene polymerizations.[44]

Diblock copolymer synthesis. Based on the living polymerization of monomer **9**, though, the synthesis of a block copolymer was accomplished by sequential polymerization of monomer **9** followed by monomer **14** using initiator **1**. Polymerization of **9** was run for 1 h with a [M]/[I] ratio of 27:1 at RT, followed by the addition of **14** ([M]/[I] ratio of 28:1) and continued polymerization for 24 h (Scheme 6). Precipitation in acidic methanol resulted in polymer **25** as a fluffy yellow solid in 96% isolated yield. The PDI of this polymer was 1.12 (Table 3), and ^{1}H and ^{13}C NMR results were consistent with a 1:1 mixture of a poly(butadiene) and a poly(norbornene) backbone.

Scheme 6

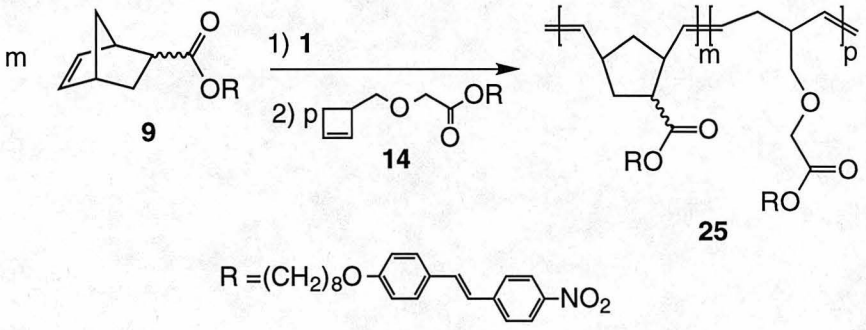


Table 3. DSC analysis of the block copolymer **25**

					Phase Transition[b] (°C)	
M_1	M_2	$[M_1]/[M_2]/[I]$	$\overline{M}_n$[a]	PDI[a]	heating	cooling
9	**22**	27:28:1	12800	1.12	g27s104i	i103s26g

[a] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards. [b] Analysis by differential scanning calorimetry with a scan rate of 10°C/min.

Thermal characterization of poly(norbornene) SCLCPs. Analysis of the phase behavior of these polymers was accomplished using DSC and polarizing optical

microscopy. All heating and cooling scans were completely reversible for each of the polymers. The second heating and first cooling scans were reported in all cases. Figure 1 shows the effect of the flexible spacer length on the phase transition temperatures. A decrease in the isotropization temperature from 121°C to 108°C was observed on

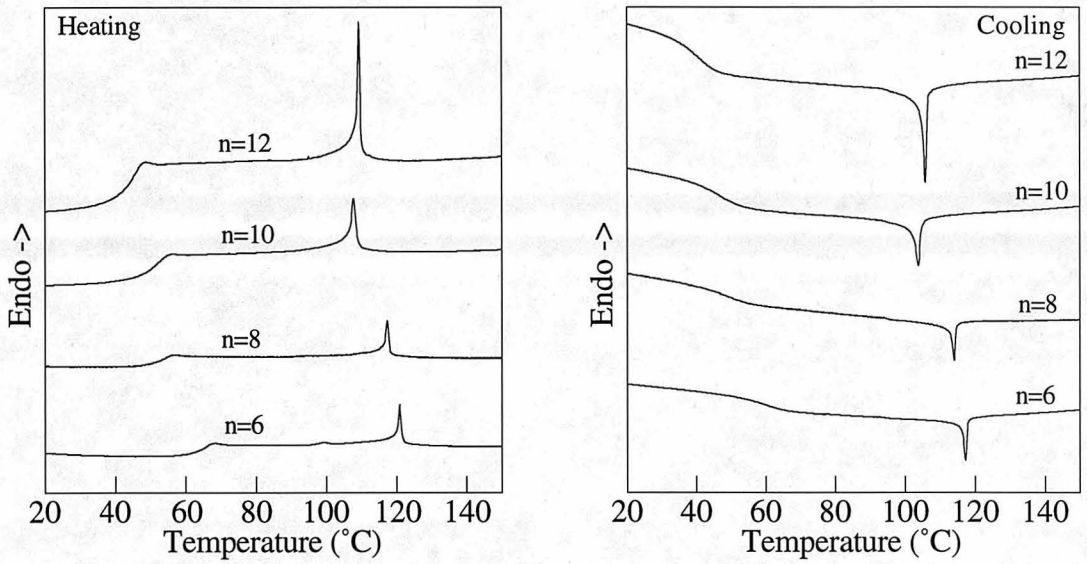


Figure 1. Normalized differential scanning calorimetry thermograms for the poly(norbornenes)s **17**-**20** of different flexible spacer lengths (n) with a scan rate of 10°C/min.

increasing the flexible spacer length, while the T_g lowered from 64°C to 44°C. The net result was an overall stabilization of the mesophase by 7°C by increasing the spacer length. Typically, upon increasing the flexible spacer length, the packing density of the chains is reduced, thus lowering the T_g. For most reported systems, the isotropization temperature is observed to be unaffected by an increase in the spacer length or to decrease only slightly compared to the significant decrease observed in the T_g, resulting in a stabilization of the mesophase.[29,36,46]

The effect of the DP on the phase transitions was also investigated for the polymerization of **9** (Figure 2). The isotropization temperature increased from 108°C for the 5mer to 121°C for the 100mer, yet the temperature was relatively invariant for a DP

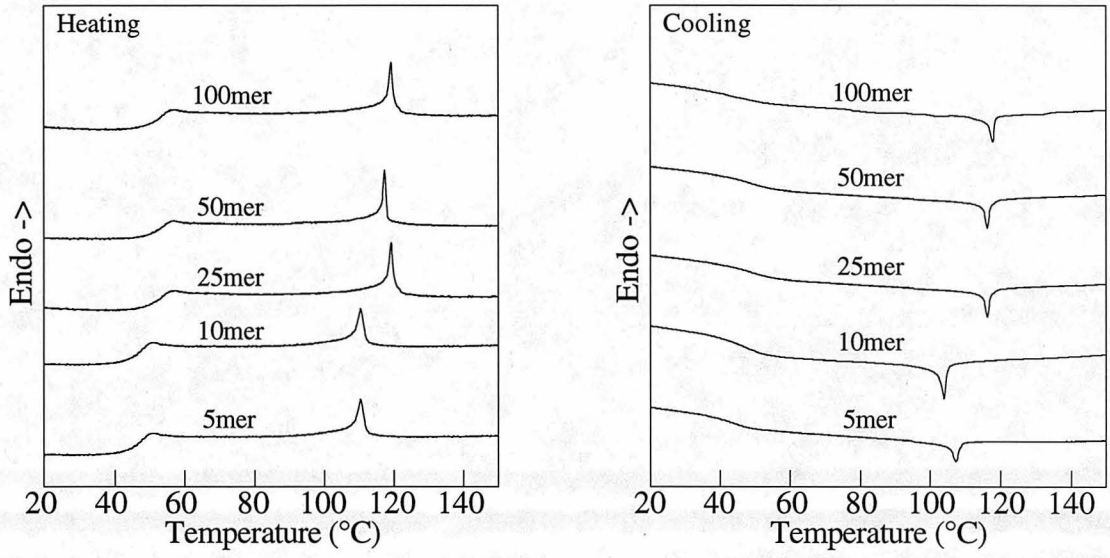


Figure 2. Normalized differential scanning calorimetry thermograms for the poly(norbornene) **18** (n=8) at different [M]/[I] ratios obtained at a scan rate of 10°C/min. The degree of polymerization shown is based solely on the initial [M]/[I] ratio employed.

greater than 10-25. Similar independence of the isotropization temperature on the DP past a certain threshold has been found for other systems including poly(siloxane)s (DP~12),[15] poly(vinyl ether)s (DP~10-20),[24,25] poly(acrylate)s (DP~12-40),[8,9] poly(methacrylate)s (DP~12),[26] and poly(norbornene)s (DP~30-50).[29-31,33,35] The change in the T_g appeared to be independent of the DP resulting in a range from 46-57°C with no apparent trend. The result of increasing DP, therefore, was a stabilization of the mesophase by 10°C.

Polarizing optical microscopy was used to identify the mesophases associated with the observed liquid crystalline transitions of the poly(norbornene)s **17-20**. For each polymer, a schlieren texture was observed upon cooling from the isotropic state, representative of a nematic mesophase.[47] These nematic mesophases were consistent with the results of previously studied SCLCP poly(norbornene)s,[29-36,38] and corresponded to the lowest order of alignment of the mesogenic units. The schlieren texture presented in Figure 3 was obtained at 100.0°C with a magnification of 50X.

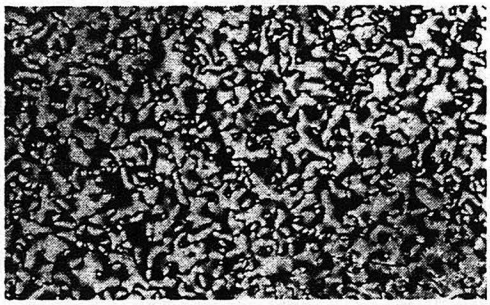


Figure 3. Polarizing optical micrograph (magnification 50X) of the nematic schlieren texture observed for poly(norbornene) **18** (n=8, 10mer) on cooling from the isotropic state at 100.0°C.

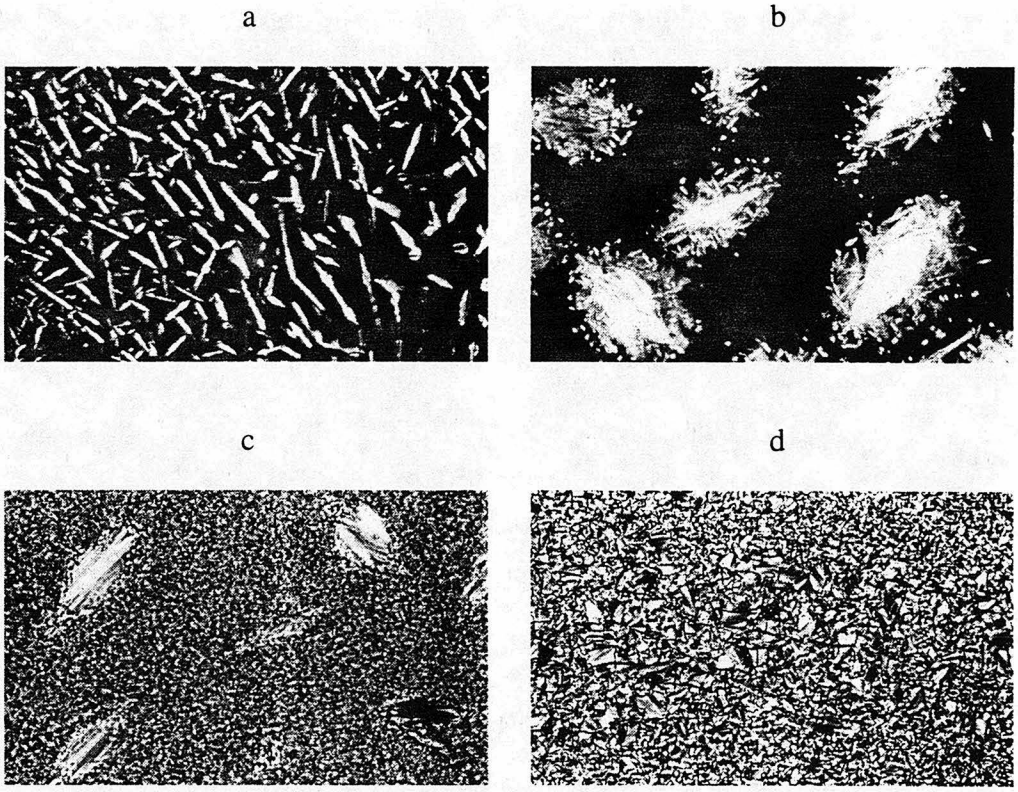


Figure 6. Polarizing optical micrographs (magnification 50X) of the smectic A textures observed for poly(butadiene) **24** (n=12, 25mer) on cooling from the isotropic state at a) 118.8°C, fine bâtonnets observed b) 113.8°C, bâtonnets of larger domains c) 105.9°C, bâtonnets transforming into new texture and d) 100.0°C, final texture typical for a smectic A mesophase (magnification 20X).

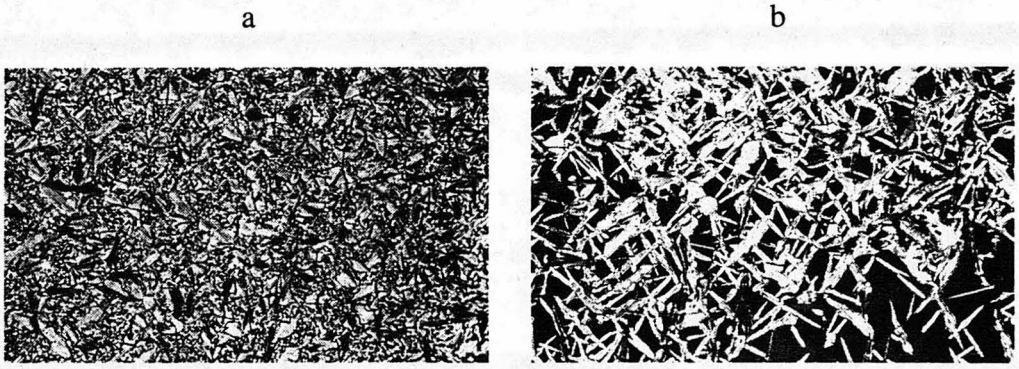


Figure 7. Polarizing optical micrographs (magnification 50X) of the smectic A textures observed for the diblock copolymer **25** on cooling from the isotropic state at a) 110.3°C, final texture typical for smectic A mesophase and b) 111.0°C, bâtonnet texture.

Thermal characterization of poly(butadiene) SCLCPs. The phase transition temperatures for the poly(butadiene)s displayed many similarities to the poly(norbornene)s. The effect of flexible spacer length was investigated, and as observed in the poly(norbornene) systems, stabilization of the mesophase was observed by increasing the spacer length (Figure 4). As the spacer length was increased, the isotropization temperature increased slightly from 104°C to 108°C while the T_g decreased from 31°C to 21°C resulting in a 14°C stabilization of the mesophase.

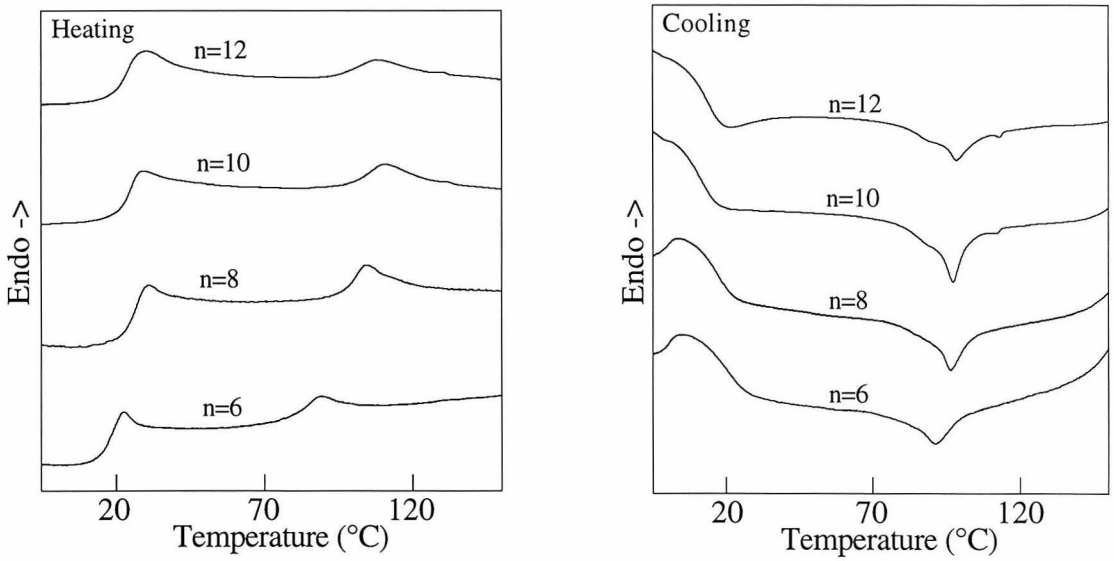


Figure 4. Normalized differential scanning calorimetry thermograms for the poly(butadiene)s **21-24** of different flexible spacer lengths (n) with a scan rate of 10°C/min.

The dependence of the phase transitions on the DP of the polymerization of **14** was studied as shown in Figure 5. A significant increase in the isotropization temperature from 74°C to 107°C was observed, but this temperature became relatively invariant at a DP greater than 10-25. The T_g varied between 23 and 14°C with no consistent trend. The net stabilization of 33°C of the mesophase for poly(butadiene)s was much larger than that observed for the poly(norbornene)s; however, the trend in stabilization of the

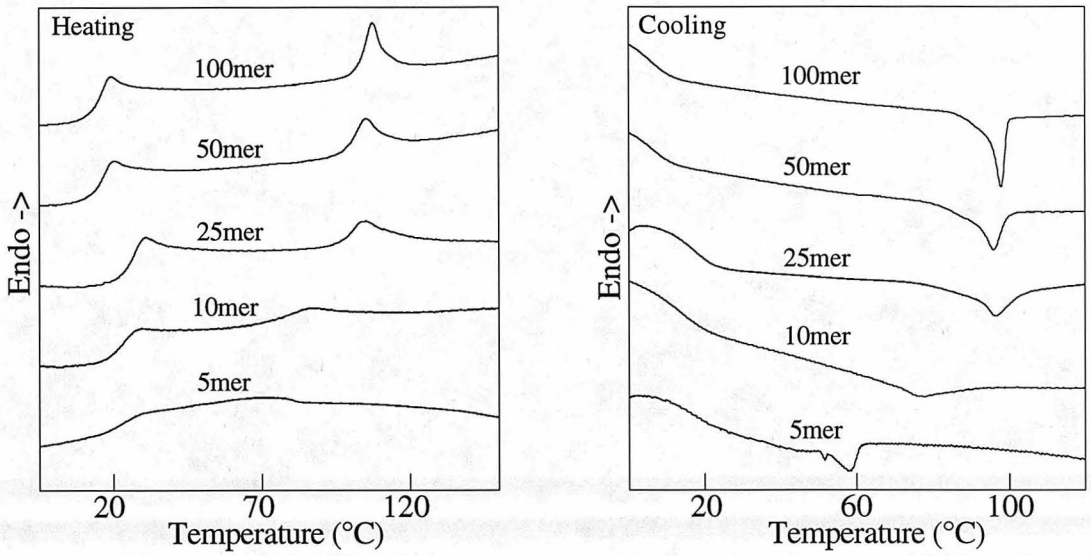


Figure 5. Normalized differential scanning calorimetry thermograms for the poly(butadiene) **22** (n=8) at different [M]/[I] ratios obtained at a scan rate of 10°C/min. The degree of polymerization shown is based solely on the initial [M]/[I] ratio employed.

mesophase by increasing the DP was consistent for both polymer backbones. Interestingly, the peak widths significantly increased for poly(butadiene) **22** as the DP decreased. This broadening has been observed in other systems and presumably results from the higher sensitivity of low molecular weight polymers to the isotropization temperature compared to higher molecular weight polymers. If individual chains are assumed to act independently, broadening of the isotropization temperature at lower molecular weights would be expected.[29,48]

The most remarkable contrast in comparing the poly(butadiene) and poly(norbornene) backbones was revealed in the polarizing optical microscopy. In contrast to the schlieren textures observed for the poly(norbornene)s, a bâtonnet texture was observed upon cooling just below the isotropic state. The bâtonnet texture has been well documented as evidence for a smectic A mesophase which corresponds to a higher degree of alignment of the mesogenic units.[47,49] This texture has been typically observed as a kinetic effect on cooling just below the isotropic state, and upon further cooling more pronounced textures representative of smectic A have been achieved.[47,49] This was also

observed for the poly(butadiene)s. As shown in Figure 6, the growth of the final texture in Figure 6d from the initial bâtonnets in Figure 6a was observed on slow cooling from the isotropic state. These observations were obtained for all the poly(butadiene)s **21**-**24**.

Thermal characterization of the diblock SCLCP. To elucidate which backbone would dominate the polymer phase behavior, a 1:1 diblock copolymer was synthesized containing both the poly(butadiene) and poly(norbornene) backbones. The DSC results for this diblock copolymer are presented in Table 3. As seen in Figure 7a, a texture typical of smectic A mesophase was observed, and, as for the poly(butadiene)s, a bâtonnet texture was observed just below the isotropic state (Figure 7b). The poly(butadiene) backbone dominated the mesophase behavior of the diblock copolymer **25** resulting in a smectic A mesophase instead of a nematic mesophase as observed for the poly(norbornene)s. Although diblock copolymers have been investigated containing an amorphous and a liquid crystalline block,[32,50,51] diblock copolymers containing two liquid crystalline blocks of differing phase behavior have not been investigated to our knowledge. An understanding of the factors that determine which phase will dominate the overall phase behavior of such block copolymers can only be acheived through further research in this area.

Conclusions

The synthesis and characterization of SCLCPs with both poly(norbornene) and poly(butadiene) backbones of controlled molecular weights and low polydispersities were achieved. Examination of the effect of the degree of polymerization and the length of the flexible spacer on the phase transitions was accomplished. Stabilization of the mesophase was observed with both increasing degrees of polymerization and flexible spacer lengths. Despite similar isotropization temperatures for the poly(norbornene) and poly(butadiene) polymers, these polymers differed substantially in their mesophase behavior. The SCLCPs with the poly(norbornene) backbone exhibited textures typical of

nematic mesophases whereas the poly(butadiene) based materials displayed textures representative of smectic A mesophases. This remarkable contrast appeared to result from the differing backbone rigidity for these two systems; the more flexible poly(butadiene) backbone allowed a higher order of alignment of the mesogenic units resulting in a more ordered liquid crystalline phase. A 1:1 diblock copolymer of the poly(norbornene) and poly(butadiene) materials also exhibited a smectic A mesophase demonstrating the influence of the poly(butadiene) backbone in dictating the diblock copolymer mesophase behavior. This research has prompted further studies on the ROMP of mesogenic cyclooctenes and cyclobutenes to further delineate the effect of these more flexible backbones on SCLCP mesomorphism. [52,53]

Experimental

General. Argon was purified by passage through columns of BASF R-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). NMR spectra were recorded on GE QE-300 Plus (300.1 MHz; 75.49 MHz ^{13}C) spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. Gel permeation chromatographs were obtained on a HPLC system using an Altex model 110A pump, a Rheodyne model 7125 injector with a 100 μL injection loop, two American Polymer Standards 10 micron mixed bed columns, and a Knauer differential-refractometer using CH_2Cl_2 as eluent at a 1.0 mL/min flow rate. Molecular weights and polydispersities were reported versus monodispersed polystyrene standards. Differential scanning calorimetry was carried out on a Perkin-Elmer DSC-7 with a scan rate of 10°C/min. Polarizing optical microscopic observations of the textures were made using a Zeiss Axiophot polarizing microscope equipped with a Linkam THM 600 hot stage and a TMS 90 thermal control unit. All polarizing micrographs were taken with a 50-fold magnification unless noted otherwise.

Materials. CH_2Cl_2 was distilled from calcium hydride and degassed by repeated freeze-pump-thaw cycles. All other solvents were used without further purification

unless otherwise noted. Sodium hydride, piperidine, *p*-hydroxybenzaldehyde, *p*-nitrophenylacetic acid, potassium carbonate, thionyl chloride, triethylamine, ethyl vinyl ether, and the series of bromoalcohols were purchased from the Aldrich Chemical Company and used without further purification. Initiator **1** was graciously provided by Dr. Peter Schwab.

Preparation of 4-hydroxy-4'-nitrostilbene 2. Following the procedure by McCulloch,[42] piperidine (47.4 g, 0.56 mol) was added dropwise to a hot solution of *p*-nitrophenylacetic acid (100 g, 0.55 mol) and *p*-hydroxybenzaldehyde (68.8 g, 0.55 mol) in ethanol. The reaction mixture was stirred under reflux for 20 h. After 30 min, the color changed from yellow to dark red. The reaction was neutralized with 1M HCl. The resulting precipitate was collected and recrystallized from ethanol/water (1.5 L) (18:1) to yield 61.9 g (46.7%) of an orange colored powder. ^{1}H NMR (acetone-d_6) δ 8.72 (s, 1H), 8.20 (d, *J*=8.9 Hz, 2H), 7.78 (d, *J*=8.9 Hz, 2H), 7.53 (d, *J*=8.4 Hz, 2H), 7.44 (d, *J*=16.4 Hz, 1H), 7.19 (d, *J*=16.4 Hz, 1H), 6.88 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (acetone-d_6) δ 158, 146, 144.6, 133.1, 128.4, 128.0, 126.4, 123.6, 123, 115.5; IR (thin film on a NaCl plate) 3422, 1631, 1587, 1500, 1438, 1339, 1318, 1266, 1213, 1193, 1109, 974, 955, 872, 844, 818, 750, 688, 535 cm^{-1}.

Preparation of 6-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-1-hexanol 3. A solution of **2** (11.5 g, 0.048 mol) and sodium hydride (1.6 g, 0.065 mol) in dry dimethylformamide (200 mL) was treated with a solution of 6-bromo-1-hexanol (10 g, 0.055 mol) in dry dimethylformamide (20 mL) and stirred at 90°C for 3 h. During this time, a color change from deep purple to yellow was observed. The product precipitated as a yellow solid after 3 days at 0°C. The solid was purified by flash column chromatography (silica/CH_2Cl_2) to yield 10.7 g (65%). ^{1}H NMR ($CDCl_3$) δ 8.18 (d, *J*=8.7 Hz, 2H), 7.57 (d, *J*=8.7 Hz, 2H), 7.46 (d, *J*=8.7 Hz, 2H), 7.20 (d, *J*=16.3 Hz, 1H), 6.98 (d, *J*=16.3 Hz, 1H), 6.90 (d, *J*=8.7 Hz, 2H), 4.00 (t, *J*=7.6 Hz, 2H), 3.50 (t, *J*=5.9 Hz, 2H), 1.76 (q, *J*=7.0 Hz, 2H), 1.53-1.40 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 159.6, 146.2,

144.1, 135.5, 132.7, 128.5, 128.2, 126.2, 123.9, 123.7, 114.7, 67.7, 62.3, 32.4, 29.5, 28.9, 28.8, 25.6, 25.3; IR (thin film on a NaCl plate) 3424, 2932, 2859, 1639, 1508, 1344, 1254, 1178, 1110, 1021, 959, 842, 745, 533 cm^{-1}; Anal. Calcd for $C_{20}H_{23}NO_4$: C, 70.17; H, 7.07; N, 4.09. Found: C, 69.59; H, 7.17; N, 3.98.

Preparation of 8-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-1-octanol 4. **4** was synthesized according to the procedure described above using **2** (14 g, 0.058 mol) and 1-bromo-10-octanol (13 g, 0.062 mol) to yield 13 g (60%). ^1H NMR ($CDCl_3$) δ 8.18 (d, *J*=8.7 Hz, 2H), 7.57 (d, *J*=8.7 Hz, 2H), 7.46 (d, *J*=8.4 Hz, 2H), 7.20 (d, *J*=16.2 Hz, 1H), 6.98 (d, *J*=16.2 Hz, 1H), 6.90 (d, *J*=8.4 Hz, 2H), 3.70 (t, *J*=6.4 Hz, 2H), 3.63 (t, *J*=6.4 Hz, 2H), 1.82 (m, 2H), 1.60 (q, *J*=6.7 Hz, 2H), 1.39 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 159.6, 146.1, 144.1, 132.7, 128.5, 128.2, 126.2, 123.9, 123.7, 114.6, 67.9, 62.7, 32.5, 29.1, 29.0, 25.7, 25.4; IR (thin film on a NaCl plate) 3542, 2931, 2855, 1606, 1587, 1572, 1511, 1474, 1424, 1344, 1306, 1272, 1254, 1175, 1111, 1037, 970, 962, 874, 842, 809, 750, 717, 688, 583, 533 cm^{-1}; Anal. Calcd for $C_{22}H_{27}NO_4$: C, 71.52; H, 7.37; N, 3.79. Found: C, 70.98; H, 7.39;N, 3.66.

Preparation of 10-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-1-decanol 5. **5** was synthesized according to the procedure described above using **2** (9.66 g, 0.04 mol) and 1-bromo-10-decanol (10 g, 0.042 mol) to give 14.1 g (89%). ^1H NMR ($CDCl_3$) δ 8.19 (d, *J*=8.7 Hz, 2H), 7.58 (d, *J*=8.7 Hz, 2H), 7.47 (d, *J*=8.4 Hz, 2H), 7.21 (d, *J*=16.1 Hz, 1H), 6.98 (d, *J*=16.1 Hz, 1H), 6.90 (d, *J*=8.4 Hz, 2H), 3.98 (t, *J*=6.4Hz, 2H), 3.64 (t, *J*=6.7 Hz, 2H), 1.79 (q, *J*=7.0 Hz, 2H), 1.56-1.31 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 159.6, 146.1, 144.1, 132.8, 128.4, 128.2, 126.2, 123.9, 123.7, 114.7, 67.9, 62.8, 32.5, 29.2, 29.2, 29.1, 29.0, 25.8, 25.5; IR (thin film on a NaCl plate) 3544, 2924, 2850, 1586, 1572, 1509, 1473, 1341, 1256, 1180, 1110, 1053, 1021, 960, 841, 688, 533 cm^{-1}; Anal. Calcd for $C_{24}H_{31}NO_4$: C, 72.61; H, 7.86; N, 3.52. Found: C, 71.98; H, 8.01; N, 3.59.

Preparation of 12-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-1-dodecanol 6. **6** was synthesized according to the procedure described above using **2** (4.5 g, 0.019 mol) and 1-

bromo-12-dodecanol (5 g, 0.02 mol) to give 5.5 g (69%). ^{1}H NMR ($CDCl_3$) δ 8.19 (d, *J*=8.7 Hz, 2H), 7.58 (d, *J*=8.7 Hz, 2H), 7.47 (d, *J*=8.4 Hz, 2H), 7.21 (d, *J*=16.3 Hz, 1H), 6.98 (d, *J*=16.3 Hz, 1H), 6.90 (d, *J*=8.4 Hz, 2H), 3.98 (t, *J*=6.6 Hz, 2H), 3.63 (t, *J*=6.7 Hz, 2H), 1.79 (q, *J*=7.8 Hz, 2H), 1.56-1.28 (m, 18H); ^{13}C NMR ($CDCl_3$) δ 159.6, 146.1, 144.1, 132.8, 128.5, 128.2, 126.2, 123.9, 123.7, 114.6, 67.9, 62.8, 32.6, 29.3, 29.2, 29.1, 29.0, 25.8, 25.5; IR (thin film on a NaCl plate) 3542, 2921, 2850, 1606, 1586, 1572, 1509, 1474, 1424, 1341, 1321, 1270, 1255, 1195, 1181, 1111, 1056, 1039, 960, 871, 748, 718, 687, 584, 533 cm^{-1}; Anal. Calcd for $C_{26}H_{35}NO_4$: C, 73.54; H, 8.24; N, 3.27. Found: C, 73.72; H, 8.31; N, 3.24.

Preparation of [6-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-hexyl]-[3-oxa-4-(2-cyclobutene)]butyrate 13. [3-oxa-4-(2-cyclobutene)]butyric acid **12**[44] (2.4 g, 0.017mol) was combined with thionyl chloride (6.0 g, 0.050 mol) in a 25 ml round bottom flask. This mixture was then heated to reflux for 1.5 h at which point gas evolution had ceased. The flask was then concentrated *in vacuo*. The resulting orange oil was then added over 5 min to a solution of **3** (4.0 g, 0.012 mol) and triethylamine (1.88 g, 0.019 mol) in THF (200 mL). The reaction was then heated to reflux under argon overnight. A solution of saturated K_2CO_3 (75 mL) was added, and the organic layer was separated and dried over $MgSO_4$. Following concentration *in vacuo*, the yellow solid was purified by flash column chromatography (silica/15% ethyl acetate/hexanes) to give 4.26 g (75%). ^{1}H NMR ($CDCl_3$) δ 8.18 (d, *J*=9.0 Hz, 2H), 7.57 (d, *J*=9.0 Hz, 2H), 7.46 (d, *J*=9.0 Hz, 2H), 7.18 (d, *J*= 16.2 Hz, 1H), 6.93 (d, *J*=16.2 Hz, 1H), 6.89 (d, *J*=9.0 Hz, 2H), 6.07 (dd, J_1=3.0 Hz, J_2=10.5 Hz, 2H), 4.16 (t, *J*=6.6 Hz, 2H), 4.08 (s, 2H), 3.97 (t, *J*=6.6 Hz, 2H), 3.60 (d, *J*=6.9 Hz, 2H), 3.11 (m, 1H), 2.6 (dd, J_1=4.2 Hz, J_2=13.8 Hz, 1H), 2.2 (d, *J*=13.8 Hz, 1H), 1.90-1.33 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 170.6, 159.8, 146.5, 144.3, 137.9, 137.1, 133.0, 128.9, 128.4, 126.4, 124.1, 124.0, 114.9, 75.3, 68.5, 67.9, 64.6, 43.3, 34.3, 29.1, 28.5, 25.6; IR (thin film on a NaCl plate) 3055, 2943, 2866, 1742, 1605, 1588,

1570, 1512, 1474, 1339, 1272, 1252, 1205, 1176, 1135, 1110, 1011, 969, 956, 844, 750, 718, 670 cm^{-1}; HRMS (FAB) calcd for $C_{34}H_{43}NO_5$ $(M)^+$ 465.2151, found 465.2130.

Preparation of [8-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-octyl]-[3-oxa-4-(2-cyclobutene)]butyrate 14. Compound **14** was synthesized from **12** (1.98 g, 0.014 mol) and **4** (3.5 g, 0.0095 mol) as above to yield 3.42 g (73% yield). ^1H NMR ($CDCl_3$) δ 8.18 (d, *J*=9.0 Hz, 2H), 7.54 (d, *J*=9.0 Hz, 2H), 7.44 (d, *J*=9.0 Hz, 2H), 7.19 (d, *J*=16.2 Hz, 1H), 6.95 (d, *J*=16.2 Hz, 1H), 6.87 (d, *J*=9.0 Hz, 2H), 6.07 (dd, J_1=2.7 Hz, J_2=9.3 Hz, 2H), 4.13 (t, *J*=6.6 Hz, 2H), 4.07 (s, 2H), 3.95 (t, *J*=6.6 Hz, 2H), 3.58 (d, *J*=6.9 Hz, 2H), 3.12 (m, 1H), 2.65 (dd, J_1=4.8 Hz, J_2 =13.8 Hz, 1H), 2.22 (d, *J*=13.8 Hz, 1H), 1.81-1.33 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 170.6, 159.8, 146.4, 144.3, 137.9, 137.0, 133.0, 128.8, 128.4, 126.4, 124.1, 123.9, 114.9, 75.2, 68.5, 68.0, 64.8, 43.3, 34.3, 29.2, 29.1, 28.5, 25.9, 25.8; IR (thin film on a NaCl plate) 3028, 2921, 2854, 1743, 1587, 1573, 1513, 1470, 1423, 1339, 1270, 1245, 1208, 1176, 1135, 1115, 1024, 968, 954, 841, 748, 665, cm^{-1}; HRMS (FAB) calcd for $C_{34}H_{43}NO_5$ $(M)^+$ 493.2464, found 493.2449.

Preparation of [10-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-decyl]-[3-oxa-4-(2-cyclobutene)]butyrate 15. Compound **15** was synthesized from **12** (0.79 g, 0.006 mol) and **5** (1.5 g, 0.004 mol) as above to yield 1.40 g (71% yield). ^1H NMR ($CDCl_3$) δ 8.18 (d, *J*=9.0 Hz, 2H), 7.57 (d, *J*=9.0 Hz, 2H), 7.45 (d, *J*=9.0 Hz, 2H), 7.20 (d, *J*=16.2 Hz, 1H), 6.93 (d, *J*=16.2 Hz, 1H), 6.89 (d, *J*=9.0 Hz, 2H), 6.07 (dd, J_1=3.0 Hz, J_2=10.5 Hz, 2H), 4.13 (t, *J*=6.6 Hz, 2H), 4.07 (s, 2H), 3.97 (t, *J*=6.6 Hz, 2H), 3.60 (d, *J*=7.2 Hz, 2H), 3.12 (m, 1H), 2.67 (dd, J_1=4.2 Hz, J_2=13.5 Hz, 1H), 2.22 (d, *J*=13.5 Hz, 1H), 1.85-1.05 (m, 16H); ^{13}C NMR ($CDCl_3$) δ 170.6, 159.9, 146.5, 144.3, 137.9, 137.0, 133.0, 128.8, 128.4, 126.4, 124.1, 123.9, 114.9, 75.3, 68.6, 68.2, 64.9, 43.3, 34.3, 29.4, 29.3, 29.2, 29.1, 28.6, 26.0, 25.8; IR (thin film on a NaCl plate) 3056, 2923, 2852, 1747, 1589, 1572, 1513, 1477, 1467, 1438, 1340, 1270, 1245, 1214, 1176, 1135, 1111, 1041, 1020, 979, 954, 842, 748, 716, 687, 702, 671 cm^{-1}; HRMS (FAB) calcd for $C_{34}H_{43}NO_5$ $(M)^+$ 521.2777, found 521.2768.

Preparation of [12-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-dodecyl]-[3-oxa-4-(2-cyclobutene)]butyrate 16. Compound **16** was synthesized from **12** (0.84 g, 0.006 mol) and **6** (1.7 g, 0.004 mol) as above to yield 1.52 g (69% yield). ^{1}H NMR ($CDCl_3$) δ 8.18 (d, *J*=9.0 Hz, 2H), 7.57 (d, *J*=9.0 Hz, 2H), 7.46 (d, *J*=9.0 Hz, 2H), 7.19 (d, *J*=16.2 Hz, 1H), 6.93 (d, *J*=16.2 Hz, 1H), 6.89 (d, *J*=9.0 Hz, 2H), 6.07 (dd, J_1=3.0 Hz, J_2=9.9 Hz, 2H), 4.13 (t, *J*=6.6 Hz, 2H), 4.07 (s, 2H), 3.97 (t, *J*=6.6 Hz, 2H), 3.58 (d, *J*=6.6 Hz, 2H), 3.13 (m, 1H), 2.6 (dd, J_1=4.5 Hz, J_2=14.1 Hz, 1H), 2.2 (d, *J*=14.1 Hz, 1H), 1.90-1.33 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 170.6, 159.9, 146.5, 144.4, 138.0, 137.0, 133.0, 128.8, 128.4, 126.4, 124.1, 124.0, 115.0, 75.3, 68.5, 68.2, 64.9, 43.3, 34.4, 29.5, 29.3, 29.3, 29.2, 28.6, 26.0, 25.8; IR (thin film on a NaCl plate) 3043, 2921, 2851, 1750, 1606, 1589, 1573, 1514, 1469, 1424, 1340, 1271, 1250, 1206, 1179, 1134, 1110, 1032, 972, 953, 839, 824, 749, 699, 686 cm^{-1}; HRMS (FAB) calcd for $C_{34}H_{43}NO_5$ $(M)^+$ 550.3169, found 550.3194.

General polymerization procedure for the cyclobutene monomers (13-16). Under an inert atmosphere, the initiator and the monomer were weighed into vials and dissolved in CH_2Cl_2 such that the overall [M] was 0.3 M. The reaction was initiated by adding the initiator solution to the vigorously stirred monomer solution. The reaction mixture was allowed to stir under argon for 24 h at 45°C. The reaction mixture was poured into methanol (~150 mL) containing 1M HCl (5% v/v) to precipitate the polymer, and this was left to stir for 30 min. The polymer was then redissolved in CH_2Cl_2 and reprecipitated into methanol (~150 mL). The polymer was then isolated by filtration and dried *in vacuo*. Isolated yields ranged from 82 to 98% (100% by ^{1}H NMR).

Polymer 21. ^{1}H NMR ($CDCl_3$) δ 8.12 (bs, 2H), 7.51 (bs, 2H), 7.41 (bs, 2H), 7.38-6.75 (bm, 4H), 5.51-5.13 (bm, 2H), 4.21-3.80 (bm, 6H), 3.51 (bs, 2H), 2.70 (bs, 1H), 2.44-1.26 (bm, 10H); ^{13}C NMR ($CDCl_3$) δ 170.4, 159.8, 146.9, 144.2, 132.9, 132.6-131.1 (Backbone C-*Olefin*) 128.9, 128.4, 126.4, 124.1, 114.9, 74.8, 68.5, 67.9, 64.5, 42.8-35.2 (Backbone C-*Alkyl*) 29.1, 28.6, 25.7; IR (thin film on a NaCl plate) 2933, 2856,

1751, 1628, 1589, 1512, 1473, 1341, 1254, 1197, 1175, 1139, 1110, 1022, 967, 842, 749, cm^{-1}.

Polymer 22. ^{1}H NMR ($CDCl_3$) δ 8.15 (bd, 2H), 7.56 (bd, 2H), 7.43 (bd, 2H), 7.39-6.75 (bm, 4H), 5.51-5.12 (bm, 2H), 4.19-3.82 (bm, 6H), 3.51 (bs, 2H), 2.73 (bs, 1H), 2.43-1.07 (bm, 14H); ^{13}C NMR ($CDCl_3$) δ 170.4, 159.8, 146.5, 144.3, 132.9, 132.5-131.3 (Backbone C-*Olefin*) 128.9, 128.4, 126.4, 124.0, 114.9, 74.8, 68.5, 68.1, 64.7, 42.8-35.1 (Backbone C-*Alkyl*) 29.7, 29.2, 29.1, 28.6, 26.0, 25.8; IR (thin film on a NaCl plate) 2928, 2854, 1751, 1589, 1511, 1474, 1341, 1253, 1196, 1175, 1139, 1110, 1026, 967, 841, 749, 717 cm^{-1}.

Polymer 23. ^{1}H NMR ($CDCl_3$) δ 8.19 (bd, 2H), 7.57 (bd, 2H), 7.45 (bd, 2H), 7.38-6.78 (bm, 4H), 5.59-5.17 (bm, 2H), 4.24-3.87 (bm, 6H), 3.56 (bs, 2H), 2.73 (bs, 1H), 2.45-1.13 (bm, 18H); ^{13}C NMR ($CDCl_3$) δ 170.4, 159.9, 146.6, 144.3, 133.0, 132.5-131.6 (Backbone C-*Olefin*) 128.9, 128.4, 126.4, 124.1, 115.0, 74.9, 68.6, 68.2, 64.7, 42.9-35.2 (Backbone C-*Alkyl*) 29.5, 29.4, 29.3, 29.3, 29.2, 28.7, 26.0, 25.9; IR (thin film on a NaCl plate) 2927, 2854, 1753, 1630, 1589, 1513, 1468, 1394, 1342, 1254, 1196, 1175, 1140, 1110, 1031, 967, 842, 749, 718, 688 cm^{-1}.

Polymer 24. ^{1}H NMR ($CDCl_3$) δ 8.15 (bd, 2H), 7.54 (bd, 2H), 7.44 (bd, 2H), 7.35-6.78 (bm, 4H), 5.54-5.14 (bm, 2H), 4.19-3.84 (bm, 6H), 3.53 (bs, 2H), 2.85 (bs, 1H), 2.42-1.01 (bm, 22H); ^{13}C NMR ($CDCl_3$) δ 170.4, 159.9, 146.6, 144.3, 133.0, 132.4-131.5 (Backbone C-*Olefin*) 128.9, 128.4, 126.4, 124.0, 115.0, 74.8, 68.5, 68.2, 64.7, 42.8-35.2 (Backbone C-*Alkyl*) 29.5, 29.4, 29.3, 28.7, 26.0, 25.9; IR (thin film on a NaCl plate) 2924, 2852, 1752, 1589, 1512, 1467, 1341, 1303, 1254, 1196, 1175, 1140, 1109, 1025, 966, 872, 841, 749, 718, 687 cm^{-1}.

Preparation of the block copolymer 25. **9** (150 mg, 3.07e-4 mol) was polymerized with initiator **1** (9.3 mg, 1.13e-5 mol) in analogy to the procedure outlined above for the norbornene monomers. After 1 h, **14** (150 mg, 3.22e-4 mol) in CH_2Cl_2 (1 mL) was added via a gas tight syringe. The vial was sealed and the mixture was stirred

for 24 h at 45°C. The solution was then poured into methanol (100 ml) containing 5% 1M HCl (v/v). The yellow precipitate was filtered and reprecipitated several times to yield **25** in 96% (288 mg) yield. ^{1}H NMR ($CDCl_3$) δ 8.13 (bs), 7.52 (bs), 7.42 (bs), 7.15 (bd), 6.93 (bd), 6.85 (bs), 5.36 (bs), 4.08 (bs), 4.01 (bs), 3.92 (bs), 3.38 (bs), 3.16 (bs), 2.84 (bs), 2.71 (bs), 2.34 (bs), 1.94 (bs), 1.73 (bs), 1.54 (bs), 1.40 (bs), 1.30 (bs); ^{13}C NMR ($CDCl_3$) δ 174.2, 174.2, 159.6, 146.2, 144.0, 132.7, 134.3-129.4 (Backbone C-*Olefin*) 128.6, 128.1, 126.2, 123.8, 114.7, 74.5, 68.3, 67.9, 64.4, 63.9, 49.5-34.9 (Backbone C-*Alkyl*) 29.0, 28.9, 28.5, 28.4, 25.7, 25.5.

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Appendix 1:

Synthesis of 3-Methyl-3-phenylcyclopropene

Abstract

The synthesis of 3-methyl-3-phenylcyclopropene was investigated in hopes of developing a more facile and inexpensive procedure for the preparation of this compound than has been previously reported. Phase transfer catalyzed dichlorocarbene addition to α-methylstyrene followed by a selective catalytic Bu_3SnH reduction resulted in the 1-chloro-2-methyl-2-phenylcyclopropane intermediate in excellent yield. Base-induced elimination of this compound resulted in the desired 3-methyl-3-phenylcyclopropene. This approach allowed for the preparation of this cyclopropene on large scale utilizing inexpensive reagents.

Introduction

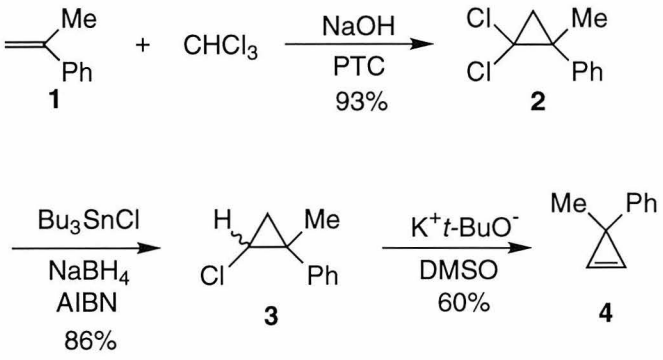
In recent years, 3,3-disubstituted cyclopropenes have emerged as new and promising carbene sources. They have been used both as reagents in the synthesis of metal vinylcarbene complexes[1-8] and as synthons in the catalytic generation of vinylcyclopropanes and vinylcyclopropenes.[2,8-10] The metal vinylcarbene complexes are active olefin metathesis catalysts and have found numerous applications in both polymer chemistry[1,3-7,11] and organic synthesis.[12-15] In addition, vinylcyclopropanes and vinylcyclopropenes are considered to be important intermediates in organic synthesis. These developments have stressed a need for easily accessible routes to 3,3-disubstituted cyclopropenes.

3,3-Diphenylcyclopropene was first isolated in 1969 from the photolysis of 3,3-diphenyl pyrazolenin.[16] Subsequently, the complete syntheses for both 3,3-diphenylcyclopropene and 3-methyl-3-phenylcyclopropene from the *gem*-disubstitued olefins were reported by Bovin and coworkers.[17] These workers employed the expensive and toxic Bu_3SnH as a stoichiometric reducing agent to convert dihalocyclopropanes to the monohalocyclopropane intermediates. The synthesis presented here of 3-methyl-3-phenylcyclopropene followed essentially the same sequence prescribed by Bovin[17]: (1) Dihalocarbene addition to an olefin to generate a *gem*-dihalocyclopropane. (2) Selective reduction of the *gem*-dihalocyclopropane to a monohalocyclopropane. (3) Base-induced elimination of the monohalocyclopropane to the final cyclopropene. This procedure, however, differed from that of Bovin in that it employed inexpensive reagents and could be scaled up easily through simple, high yielding reactions. Such a facile synthetic approach should allow for further investigations into the utility of cyclopropenes as synthons in both organic and organometallic chemistry.

Results and Discussion

Synthesis of 3-methyl-3-phenylcyclopropene (**4**) was accomplished as in Scheme 1. The first step was a modification of that described by Makosza[18] where the

Scheme 1



dichlorocarbene was prepared through phase transfer catalysis with cetyltrimethylammonium bromide employing NaOH and $CHCl_3$ in water. The dichlorocarbene addition proceeded in 93% yield without need for purification of the crude *gem*-dichlorocyclopropane **2**. These conditions can be compared with those of Bovin[17] which utilized K^+t-BuO^- and $CHBr_3$ in rigorously dry solvent to generate the *gem*-dibromocyclopropane. The Bu_3SnH reduction of the *gem*-dibromocyclopropanes to monobromocyclopropanes reported by Bovin gave only moderate yields and required the use of stoichiometric amounts of the expensive and toxic Sn reagent.[17] In the modified procedure presented here, catalytic Bu_3SnCl in the presence of $NaBH_4$ was used in the preparation of 1-chloro-2-methyl-2-phenylcyclopropane (**3**) in greater than 86% yield. $NaBH_4$ was used to form Bu_3SnH from Bu_3SnCl, and therefore only a catalytic amount of Bu_3SnCl was needed if excess $NaBH_4$ was used.[19] This allowed for a reduction in costs as well as limiting the amount of toxic Sn materials used in the procedure. The elimination step with K^+t-BuO^- in DMSO proceeded in only 60% yield due to the inefficient elimination of HCl from the *r*-1-chloro-*trans*-2-methyl-2-phenylcyclopropane isomer which remained essentially unchanged under the reported reaction conditions. Longer reaction

times or higher temperature only led to low yields from the decomposition of the product. It was interesting that the two isomers of 1-chloro-2-methyl-2-phenylcyclopropane had such differing reactivities toward elimination by base. Perhaps the *trans*-phenyl group played a role in assisting the elimination of chloride. This observation fit well into the trend in which 1-chloro-2,2-diphenylcyclopropane eliminated easily at room temperature[20] and 1-chloro-2,2-dimethylcyclopropane eliminated at 90°C over several hours.[21]

Conclusions

A synthesis involving inexpensive reagents resulting in a high yield of 3-methyl-3-phenylcyclopropene was presented. The reactions were carried out in air without the need for drying solvents and reagents, and they proceeded in short reaction times with relatively simple work-up procedures. As a result, large scale preparation of 3-methyl-3-phenylcyclopropene was possible at relatively low cost, thereby allowing for a more intensive study of its utility in organic and organometallic chemistry.

Experimental

General. NMR spectra were recorded on GE QE-300 Plus (300.1 MHz; 75.49 MHz ^{13}C) spectrometer.

Materials. α-methylstyrene, cetyltrimethylammonium bromide, Bu_3SnCl, $NaBH_4$, *n*-propanol, and K^+*t*-BuO^- were purchased from the Aldrich Chemical Company. 2,2'-Azobis(2-methylpropionitrile) was purchased from Eastman Laboratory Chemicals, and NaOH, $CHCl_3$, diethyl ether, petroleum ether, and DMSO were purchased from EM Science. All of the above reagents were used without further purification.

The preparation of 1,1-dichloro-2-methyl-2-phenylcyclopropane. In a 500 mL Erlenmeyer flask equipped with a 1-inch Teflon-coated magnetic stirbar, α-methylstyrene (30 g, 254 mmol, 1 eq), $CHCl_3$ (60.7 g, 40.7 mL, 508 mmol, 2 eq), 50% aqueous NaOH solution (102 mL, 1.27 mol, 5 eq), and cetyltrimethylammonium bromide

(3 g, 8.2 mmol, 0.03 eq) were combined and stirred vigorously for 2 h. During this time, the reaction turned from a cloudy white mixture to a brown one and an exotherm was apparent. After the 2 h, the flask began to cool, and diethyl ether (200 mL) was added to the mixture and stirred slowly for 2 min. The contents of the flask were then poured into a 1000 mL separatory funnel, and the organic layer was separated. The remaining aqueous layer was further extracted with diethyl ether (2 x 200 mL) according to the above procedure. The combined organics were successively washed with 0.5 M aqueous HCl (150 mL), deionized water (150 mL), and saturated aqueous NaCl (150 mL); dried over anhydrous $MgSO_4$; and filtered through a coarse fritted funnel. The filtrate was then concentrated *in vacuo* at 55˚C to give a brown liquid product. Yield=47.5 g (93%). Despite the color impurities, this material was sufficiently pure to be used in the next step. ^1H NMR ($CDCl_3$) δ 7.3 (m, 5H), 1.94 (d, 1H), 1.66 (s, 3H), 1.57 (d, 1H).

The preparation of 1-chloro-2-methyl-2-phenylcyclopropane. In a 2000 mL round bottom flask equipped with a 1-inch Teflon-coated magnetic stir bar, 1,1-dichloro-2-methyl-2-phenylcyclopropane (30 g, 149 mmol, 1.0 eq), Bu_3SnCl (7.29 g, 22.4 mmol, 0.15 eq), 2,2'-azobis(2-methylpropionitrile) (2 g, 12.2 mmol, 0.08 eq), and *n*-propanol (600 mL) were combined and stirred vigorously. Next, $NaBH_4$ (8.47 g, 224 mmol, 1.5 eq) was added in portions to the reaction mixture over 5 min. Once the addition was complete, the flask was capped with a water-cooled reflux condenser and placed in a 110˚C oil bath. The reaction was kept at reflux for 1 h during which time NaCl could be seen precipitating from the solution. At this point, the flask was removed from the oil bath and oxalic acid (3.0 g, 33.3 mmol, 0.22 eq) was added in portions over 5 min. The reflux condenser was then replaced with a distillation head, and the flask was lowered back into the oil bath. The *n*-propanol was then distilled away from the reaction mixture. The flask was again removed from the oil bath and allowed to cool to room temperature. Petroleum ether (300 mL) was added and the mixture was transferred to a 1000 mL separatory funnel where the organic layer was washed with deionized water (3 x 200 mL). The organic layer

was then dried over $MgSO_4$, filtered over a coarse fritted funnel, and concentrated *in vacuo* at 50˚C to give a yellow liquid. This crude material was then further purified by vacuum distillation (49-50˚C/ 2.5 mmHg) to give a clear liquid product. The yield=21.4 g (86.2%), and this material was pure enough to use in the next step. The product isomeric distribution is ca 2:1 *cis*-Cl-*cis*-methyl / *cis*-Cl-*cis*-phenyl . ^{1}H NMR ($CDCl_3$) *cis*-Cl-*cis*-methyl isomer: δ 7.3 (m, 5H), 3.27 (dd, 1H), 1.58 (s, 3H), 1.52 (dd, 1H), 0.98 (dd, 1H). *cis*-Cl-*cis*-phenyl isomer: d 7.3 (m, 5H), 3.14 (dd, 1H), 1.4 (s, 3H), 1.27 (m, 2H).

The preparation of 3-methyl-3-phenylcyclopropene. In a 500 mL round bottom flask equipped with a 1-inch Teflon-coated magnetic stirbar, 1-chloro-2-methyl-2-phenylcyclopropane (20 g, 120 mmol, 1.0 eq) was combined with DMSO (150 mL), and this flask was connected to a 250 mL addition funnel. In a separate 250 mL round bottom flask, K^+*t*-BuO^- (27 g, 241 mmol, 2.0 eq) was dissolved in DMSO (150 mL) (with heating as necessary). This basic solution was then quickly poured into the addition funnel over the first flask. The reaction flask was then cooled to ca 15-20˚C, and the K^+*t*-BuO^- solution was added dropwise over 2 h. During the addition, the color changed to orange, then red, then green, then finally brown. The reaction was left stirring for another 2.5 h at the same temperature. The reaction mixture was then poured into a 2000 mL separatory funnel containing ice (300 mL) to give a cloudy yellow mixture. The aqueous layer was extracted with diethyl ether (3 x 500 mL). The combined organics were then washed successively with saturated aqueous NaCl solution (400 mL) and distilled water (2 x 400 mL), dried over anhydrous Na_2SO_4, and filtered over a coarse fritted funnel. This solution was then concentrated to a minimum *in vacuo*. The resulting yellow liquid was then further purified by flash column chromatography (silica gel, petroleum ether, R_f = 0.65). This was isolated to give a clear liquid. Yield=9.4 g (60%). ^{1}H NMR (C_6D_6) δ 7.22-7.16 (m, 5H), 6.79 (s, 2H), 1.57 (s, 3H).

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