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Synthesis of Cross-Linkable Telechelic Poly(butenylene)s Derived from Ring-Opening Metathesis Polymerization

Bob R. Maughon, Takeharu Morita, Christopher W. Bielawski, and Robert H. Grubbs*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

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ABSTRACT: The synthesis of ring-opening metathesis polymerization (ROMP) chain transfer agents (CTA)s bearing methacrylate or epoxide end functionality was accomplished. In the presence of these CTAs, the ROMP of cyclooctadiene (COD) initiated with $(PCy_3)_2Cl_2Ru{=}CHPh$ afforded the respective telechelic poly(butenylene)s with either methacrylate or epoxide end groups. Control over the polymer molecular weight was demonstrated by varying the COD/CTA ratio. Successful cross-linking by thermal or photochemical initiation of the bis(methacrylate)-functionalized telechelic poly(butenylene)s or through acid catalysis of the bis(epoxide)-functionalized telechelic poly(butenylene)s was accomplished. While cross-linking was found to reduce solubility of the polymers, it greatly enhanced their thermal stability.

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. The development of telechelic polymers with cross-linkable end groups such as methacrylate or epoxide groups has led to the preparation of interpenetrating polymer networks, AB cross-linked polymeric materials, more thermally and chemical resistant materials, and materials for the immobilization of enzymes.[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. 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 prepared in this manner.[5,8−11] A synthetic route that could generate cross-linkable telechelic polymers in one step would be of considerable utility.

Since the early 1980s, olefin metathesis has been found to be an extremely effective method for the generation of telechelic polymers.[12−27] Although metathesis-mediated degradation of poly(butenylene) backbones in the presence of functionalized acyclic olefins[16−18,20−22] and nonmetathesis-mediated degradation of copolymers synthesized by ring-opening metathesis polymerization (ROMP)[24] have been explored, the most studied and widely utilized is ROMP in the presence of functionalized chain transfer agents (CTAs).[12−15,17−19,23,25,26] In the latter method, where termination is kept to a minimum and low initiator loadings are employed, number-averaged degree of functionality (F_n) values approaching two are typically achieved. 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 acidic nature of this system, often unwanted byproducts and initiator deactivation were observed when reactive functional groups were incorporated in the CTAs.[12−15] However, the polymerization of cyclooctene, cyclooctadiene (COD), norbornene, and cyclopentene in the presence of bis(ester)-functionalized CTAs using WCl_6/Me_4Sn resulted in the high yielding syntheses of bis(diester)-functionalized telechelic polymers.[12−15,26] Chung et al. applied borane methodology for the preparation of hydroxytelechelic poly(butenylene) (HTPBD) and bis(iodo)-functionalized telechelic poly(butenylene) through polymerization of COD with WCl_6/Me_4Sn in the presence of a bis(9-borabicyclononane)-functionalized CTA followed by post-polymerization chemical transformations.[17,18]

In an effort to hopefully expand the functional group tolerance in these systems, recent studies were accomplished that utilized well-defined Lewis acid free metathesis initiators for the preparation of HTPBD. The polymerization of COD in the presence of bis(silyl ether)-functionalized CTAs with 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] resulted in bis(silyl ether)-functionalized telechelic poly(butenylene) which could be deprotected to synthesize HTPBD.[19,23] Using the more functional group tolerant initiator $(PCy_3)_2Cl_2Ru{=}CHCH{=}CPh_2$ (**1**),[28] polymerization of COD with the commercially available *cis*-2-butene-1,4-diol diacetate

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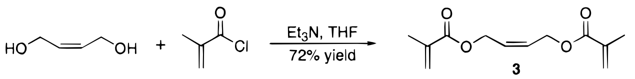
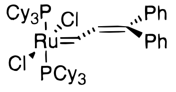
Scheme 1



provided bis(acetoxy)-functionalized telechelic poly(butenylene)s which again could be deprotected to provide a high yielding synthesis of HTPBD.[25]

The development of the functional group tolerant ruthenium-based metathesis initiators $(PCy_3)_2Cl_2Ru{=}CHR'$ (**1**: $R' = (CH{=}CPh_2)$; **2**: $R' = Ph$)[28,30] has enabled



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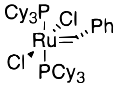

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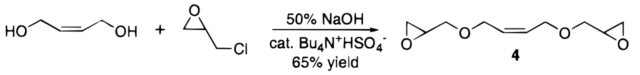
the application of ROMP to monomers with a vast array of functional groups including ethers, esters, carboxylic acids, amides, ketones, and amines.[31-33] In a recent example, initiator **1** was successfully applied to the preparation of cross-linkable polymers through the ring-opening metathesis copolymerization of COD and 5-methacrylate-1-cyclooctene, thus demonstrating the stability of the ruthenium carbene species toward the methacrylate group.[32] As a result of the known functional group tolerance of these ruthenium-based metathesis initiators, the synthesis of telechelic poly(butenylene)s bearing highly reactive methacrylate and epoxide end groups in one step was investigated through the polymerization of COD with **2** in the presence of bis(methacrylate)- and bis(epoxide)-functionalized CTAs. The high functional group tolerance of **2** 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 investigated. Controlled cross-linking of these telechelic polymers both thermally and photochemically in the case of the bis(methacrylate)-functionalized telechelic poly(butenylene) or with H_2SO_4 for the bis(epoxide)-functionalized telechelic poly(butenylene) was accomplished providing for the facile preparation of cross-linked poly(butenylene) networks.

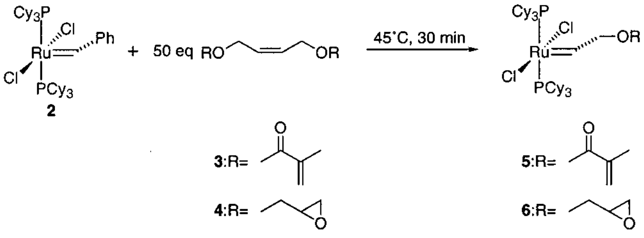
Results and Discussion

Synthesis of the CTA *cis*-2-Butene-1,4-diol Dimethacrylate (3). Synthesis of the bis(methacrylate)-functionalized CTA, *cis*-2-butene-1,4-diol dimethacrylate (**3**), was accomplished as shown in Scheme 1. Simple esterification of the commercially available *cis*-2-butene-1,4-diol using methacryloyl chloride resulted in compound **3** in 72% yield. However, compound **3** 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 %). To prevent this polymerization side reaction, higher loadings of *p*-methoxyphenol (20 wt %) were required which suppressed any observable polymerization of **3** over 6 months. Although this was a reasonably high inhibitor concentration, it was previously shown that ruthenium vinylcarbene initiator **1** was tolerant of this inhibitor.[32] Thus, we expected that removal of the inhibitor prior to using CTA **3** in ROMP would not be necessary (see below).

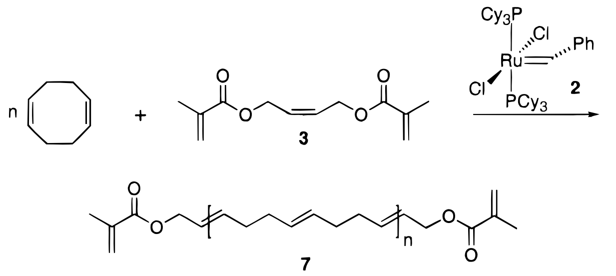
Scheme 2



Scheme 3



Scheme 4



Synthesis of the CTA *cis*-2-Butene-1,4-diol Diglycidyl Ether (4). The synthesis of the bis(epoxide)-functionalized CTA, *cis*-2-butene-1,4-diol diglycidyl ether (**4**), was also accomplished in one step as illustrated in Scheme 2. This procedure was modified from Okahara's preparation of ethylene glycol diglycidyl ether.[34] 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 **4** in 65% yield. Samples of compound **4** stored at room temperature exhibited no decomposition over 6 months.

Reaction of CTAs 3 and 4 with the Ruthenium Benzylidene Initiator 2. The reaction of either the ruthenium benzylidene initiator **2** or a propagating ruthenium alkylidene with the functionalized CTAs **3** or **4** to generate a methacrylate- or epoxide-functionalized ruthenium alkylidene species is a key step in the mechanism forming telechelic polymers via ROMP.[19,27] However, previous studies in other ROMP systems using ruthenium-based metathesis initiators **1** and **2** and functionalized CTAs demonstrated the susceptibility of 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.[33] Therefore, the reaction of the ruthenium benzylidene **2** with both **3** and **4** was investigated. Treatment of **2** with 50 equiv of CTA's **3** or **4** at 45 °C for 30 min resulted in the formation of the corresponding methacrylate- or epoxide-functionalized ruthenium alkylidenes **5** or **6** (Scheme 3). Relevant ^1H and ^{31}P NMR data of these complexes are summarized in Table 1 and strongly support the bis(phosphine)ruthenium alkylidene species as illustrated in Scheme 3.[33] In addition, the alkylidenes showed no decomposition over 24 h at room temperature.

ROMP of COD Initiated with 2 in the Presence of CTA 3. In the presence of the CTA **3**, the ruthenium-catalyzed ROMP of COD resulted in the bis(methacrylate)-functionalized telechelic poly(butenylene) **7** as

Table 1. Selected NMR Data for Complexes 5 and 6[a]

complex	^{1}H (ppm)[b]	J_{HH} (Hz)[c]	^{31}P (ppm)[d]
5	19.48	4.4	37.42
6	19.79	3.6	36.91

[a] Spectra were acquired in $CDCl_3$ and were referenced to the residual protiated solvent peak or to an external 85% H_3PO_4 standard. [b] Refers to the α-H carbene resonance. [c] Carbene signal appeared as a triplet. [d] No free phosphine was observed.

Table 2. Optimization Studies for the ROMP of COD in the Presence of Bis(methacrylate) CTA 3[a]

[COD]/[**3**]	[COD]/[**2**]	rxn time (h)	% yield[b]	M_n (NMR)[c]
15	2000	24	80	3500
15[d]	2000	24	81	3300
15	4000	24	75	5500
10	2000	24	85	2500
10	2000	48	87	2300

[a] Polymerizations were run neat at 25 °C and were initiated with ruthenium catalyst **2**. *p*-Methoxyphenol (20 wt %) was included with **3** to prevent radical polymerization. [b] Isolated yields after purification. [c] Determined by ^{1}H NMR spectroscopy assuming $F_n = 2.0$. [d] *p*-Methoxyphenol was removed from **3** prior to polymerization.

Table 3. Synthesis of Bis(methacrylate)-Functionalized Telechelic Poly(butenylene)s 7[a]

[COD]/[**3**]	% yield[b]	% *cis*-olefin (backbone)[c]	% *cis*-olefin (end group)[c]	M_n (NMR)[d]	M_n (GPC)[e]	PDI[e]
15	88	50	25	3700	5 400	1.74
40	89	55	20	8000	10 100	1.86
60[f]	90	60	25	14500	11 900	2.02
80[g]	90	55	25	17700	15 300	1.99

[a] Polymerizations were run neat at 25 °C for 48 h with [COD]/[**2**] = 2000. [b] Isolated yields after purification. [c] Determined by ^{1}H NMR spectroscopy. [d] Determined by ^{1}H NMR spectroscopy assuming $F_n = 2.0$. [e] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards. [f] To ensure better mixing, [COD] = 12.4 M in benzene was utilized. [g] [COD] = 9.3 M in benzene was utilized.

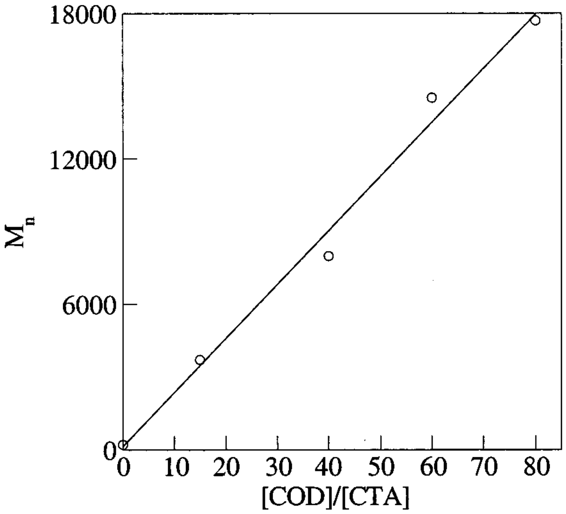


Figure 1. Dependence of the observed M_n values for the bis(methacrylate)-functionalized telechelic poly(butenylene)s **7** on the [COD]/[CTA] ratio. The M_n was determined by ^{1}H NMR spectroscopy assuming $F_n = 2.0$.

Table 4. Optimization Studies for the ROMP of COD in the Presence of Bis(epoxide) CTA 4[a]

[COD]/[**2**]	rxn time (h)	temp (°C)	% yield[b]	M_n (NMR)[c]
2000	48	25	60	3700
4000	48	25	61	3600
2000	24	45	67	3400
2000	48	45	67	3400
4000	24	45	63	3500
4000	48	45	61	3700

[a] Polymerizations were run neat with [COD]/[**4**] = 15 and were initiated with ruthenium catalyst **2**. [b] Isolated yields after purification. [c] Determined by ^{1}H NMR spectroscopy assuming $F_n = 2.0$.

shown in Scheme 4. The polymerizations were initiated with **2** and were run neat according to the different sets of experimental conditions described in Table 2. Control experiments confirmed that the presence of the free radical inhibitor *p*-methoxyphenol (which was added to **3** to prevent radical polymerization) had little or no effect on the polymerization. However, when polymerizations were run at 45 °C, low yields and insoluble polymeric materials were formed which were attributed to thermally induced polymerization of the methacrylate groups (even in the presence of 20 wt % *p*-methoxyphenol). Based on these initial studies, all of the polymerizations of COD with **3** were run with a [COD]/[**2**] ratio of 2000:1 for 48 h at 25 °C. In addition, the polymerizations were run in the dark to prevent photoinduced 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(butenylene)s were synthesized with [COD]/[**3**] ratios ranging from 15:1 to 80:1 in an attempt to control the molecular weights of these telechelic poly(butenylene)s. The results are presented in Table 3. In general, the polymerizatons were run as concentrated as possible so as to prevent the solution from becoming too viscous, yet allowing the highest possible conversions of monomer. This approach is common in ROMP, as all cyclic monomers have a critical equilibrium concentration whereby further conversion of the monomer (or cyclic oligomer) to polymer ceases once this concentration is reached.[35] Using this strategy, yields between 88 and 90% were obtained, and the molecular weights were controlled resulting in bis(methacrylate)-functionalized telechelic poly(butenylene)s with M_n (NMR) values ranging between 3700 and 17 700. Excellent molecular weight control based on the [COD]/[**3**] ratio was observed as illustrated in the linear plot of M_n (NMR) versus the [COD]/[**3**] ratio in Figure 1. The telechelic poly(butenylene)s contained between 50 and 60% *cis*-olefin in the backbone and between 20 and 25% *cis*-olefin at the polymer end groups. Monomodal peaks were observed in the GPC chromatograms with polydispersities (PDIs) of 1.74−2.02. Both ^{1}H and ^{13}C NMR spectroscopy supported a F_n near two for these polymers, as no non-methacrylate end groups were detected.[36] Furthermore, agreement between the molecular weights obtained through NMR spectroscopy and GPC provide additional evidence for the difunctionality ($F_n \approx 2.0$) of these polymers. This is in accord with other results obtained by using symmetrically disubstituted internal olefin CTAs for the preparation of telechelic polymers by ROMP.[12−15,17−19,23,25,26]

ROMP of COD Initiated with 2 in the Presence of CTA 4. The ROMP of COD was carried in the presence of CTA **4** under a variety of conditions summarized in Table 4 (see also Scheme 5). Unlike the polymerization of COD in the presence of **3** where elevated temperatures must be avoided, polymerizations in the presence of **4** at 45 °C resulted in slightly higher

Scheme 5

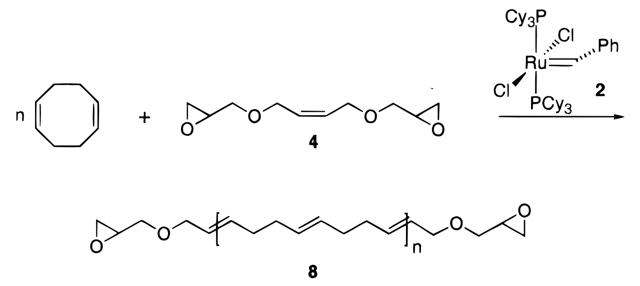


Table 5. Synthesis of Bis(epoxide)-Functionalized Telechelic Poly(butenylene)s 8[a]

[COD]/[**4**]	% yield[b]	% *cis*-olefin (backbone)[c]	% *cis*-olefin (end group)[c]	M_n (NMR)[d]	M_n (GPC)[e]	PDI[e]
15	71	60	30	3000	4000	1.55
40	80	65	25	7800	6900	1.89
60[f]	87	50	30	11000	10500	1.87
80[g]	84	55	25	16800	16100	1.94

[a] Polymerizations were run neat at 45 °C for 48 h with [COD]/[**2**] = 2000. [b] Isolated yields after purification. [c] Determined by ^{1}H NMR spectroscopy. [d] Determined by ^{1}H NMR spectroscopy assuming $F_n = 2.0$. [e] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards. [f] To ensure better mixing, [COD] = 12.4 M in benzene was utilized. [g] [COD] = 9.3 M in benzene was utilized.

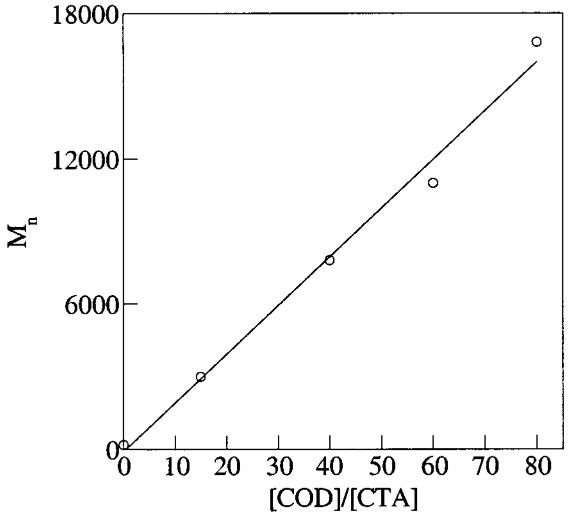


Figure 2. Dependence of the observed M_n values for the bis(epoxide)-functionalized telechelic poly(butenylene)s **8** on the [COD]/[CTA] ratio. The M_n was determined by ^{1}H NMR spectroscopy assuming $F_n = 2.0$.

yields. Based on these studies, all subsequent polymerizations with COD and CTA **4** were carried out at 45 °C with a [COD]/[**2**] ratio of 4000:1 for 24 h.

By varying the [COD]/[**4**] ratio from 15:1 to 80:1, M_n values ranging from 3000 to 16 800 were obtained with yields between 71 and 87% (Table 5). A linear relationship between the molecular weight and the [COD]/[**4**] ratio was observed (Figure 2) and indicated excellent molecular weight control was achieved. The bis(epoxide)-functionalized telechelic poly(butenylene)s contained a *cis*-olefin content in their backbone (50−65%) and end groups (25−30%) that was similar to that observed for the poly(butenylene)s **7** described above. Again, both ^{1}H and ^{13}C NMR spectroscopy supported a F_n near 2 for these materials,[36] and good agreement between the M_n's obtained by NMR spectroscopy (using $F_n = 2.0$) and GPC was observed.

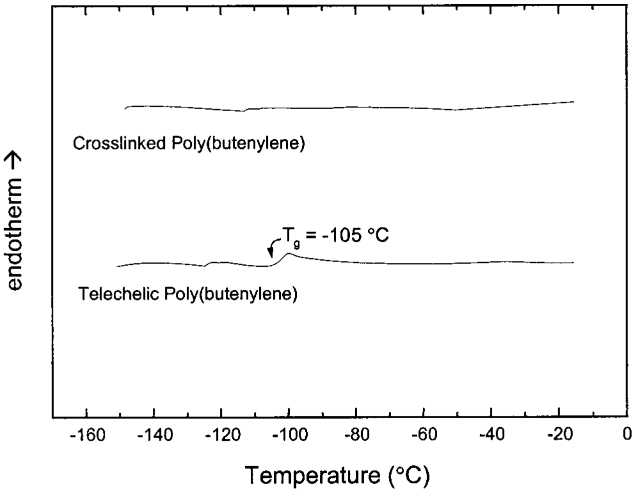


Figure 3. Typical thermograms of telechelic poly(butenylene)s **7** or **8** and their cross-linked derivatives. Data for **7** (M_n = 14 500) are shown. Data were obtained via DSC at a scan rate of 10 °C/min under an atmosphere of helium.

Cross-Linking of the Telechelic Poly(butenylene)s 7 and 8. With the successful development of the syntheses of the telechelic poly(butenylene)s **7** and **8** described above, preliminary studies on the cross-linking of these materials were examined. The cross-linking of the bis(methacrylate)-functionalized telechelic poly(butenylene) **7** was accomplished both thermally and photochemically. For thermal cross-linking, concentrated solutions of polymer **7** (100 mg of polymer **7** in 200 μL toluene) 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 common organic solvents such as CH_2Cl_2, $CHCl_3$, benzene, toluene, diethyl ether, ethyl acetate, and DMSO. The functionalized telechelic polymer **7** was also cross-linked photochemically by combining either benzoyl peroxide or 2,2-dimethoxy-2-phenylacetophenone (2 wt %) with the concentrated polymer solution and photolyzing for 15 min using a Hanovia 450 W medium-pressure mercury arc lamp. As in the thermally induced cross-linking reactions, a tacky insoluble material was formed within 5 min, and after 15 min a highly cross-linked rubbery material was obtained. In addition, the band between 800 and 815 cm^{-1} (characteristic of the methacrylate group) found in the infrared (IR) spectrum of **7** was not observed in its cross-linked derivative.[37] This provided direct evidence for the cross-linking reaction.

The cross-linking of the bis(epoxide)-functionalized telechelic poly(butenylene) **8** was accomplished by treatment with acid. Solutions of polymer **8** (100 mg of polymer **8** in 500 μL of toluene) were treated with catalytic amounts of H_2SO_4 which caused the immediate formation of an insoluble, rubbery, polymeric solid. Treatment with other acids such as HCl (1 M in Et_2O), *p*-toluenesulfonic acid, and $BF_3{\cdot}Et_2O$ were found to be inefficient and required up to several days to reach completion. In accordance with the cross-linked derivatives of **7**, these materials were found to be insoluble in common organic solvents.

Further evidence for the cross-linking reaction was provided through thermal analysis using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). As shown in Figure 3, the glass tran-

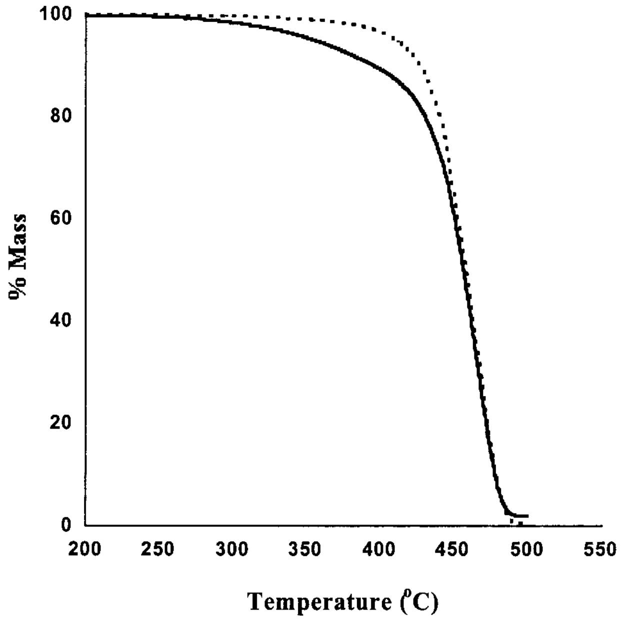


Figure 4. Comparison of thermal stability between telechelic poly(butenylene) **7** (M_n = 14 500) (solid line) and the cross-linked derivative (dotted line). Data was obtained via TGA at a scan rate of 10 °C/min under an atmosphere of nitrogen. See text for cross-linking procedures. See also Table 6.

Table 6. Comparison of Thermal Decomposition Data between Telechelic Poly(butenylene)s 7 and 8 and Their Cross-Linked Derivatives[a]

polymer	T_d (°C)[b]	polymer	T_d (°C)[b]
7	396	**8**	398
7[c]	423	**8**[c]	426

[a] All values were obtained using TGA, under an atmosphere of nitrogen at a scan rate of 10 °C/min. See also Figure 4. [b] T_d is the decomposition temperature and is defined as the temperature at which 10% weight loss occurs. [c] Polymer was cross-linked as described in the text.

sistion temperature (T_g) of the telechelic poly(butenylene)s **7** and **8** were found to occur around −105 °C. However, upon cross-linking, this T_g disappeared, and no other distinctive phase transitions were observed. Since cross-linking generally enhances thermal stability, this should be reflected in the decompostion temperature (T_d), the temperature at which 10% weight loss occurs, as determined by TGA. As shown in Figure 4, the T_d of the cross-linked poly(butenylene)s increased by an average of 27.5 °C (see Table 6) relative to poly(butenylene)s **7** or **8**.

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(butenylene)s bearing either methacrylate or epoxide end groups. The molecular weight of these telechelic poly(butenylene)s could be controlled by varying the initial [COD]/[CTA] ratio. Thermal, photochemical, and acid-catalyzed cross-linking of the bis-functionalized telechelic poly(butenylene) were demonstrated. In contrast to the previously published approach for the preparation of cross-linkable polymers by ring-opening metathesis copolymerization of COD and 5-methacrylate-1-cyclooctene,[32] 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 will focus on the cross-linking densities and swelling properties of these poly(butenylene) networks and the preparation of interpenetrating polymer networks from these materials.

Experimental Section

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 ^{1}H; 75.49 MHz ^{13}C) spectrometer or 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. Chemical shifts were recorded in parts per million (δ) and referenced to residual protio solvent. Coupling constants, J, are reported in hertz (Hz). 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 μm 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 Hanovia 450 W medium-pressure mercury arc lamp. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Pyris-7 DSC using a scan rate of 10 °C/min under an atmostphere of helium. Thermogravimetric analysis was performed on a Perkin-Elmer TGA-7, using a scan rate of 10 °C/min under an atmosphere of nitrogen.

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, $BF_3{\cdot}Et_2O$, and H_2SO_4 were purchased from the Aldrich Chemical Co. and used without further purification. COD was purchased from the Aldrich Chemical Co. and degassed by stirring in vacuo for 2 h before use in polymerizations.

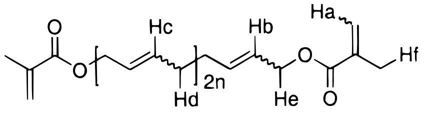
Preparation of *cis*-2-Butene-1,4-diol Dimethacrylate (3). *cis*-2-Butene-1,4-diol (14.04 g, 0.16 mol, 1.0 equiv) was mixed with THF (500 mL) and triethylamine (40.34 g, 0.48 mol, 3.0 equiv) in a 1 L round-bottom flask under argon. To the reaction flask was added 90% methacryloyl chloride (53.9 g, 0.46 mol, 2.9 equiv) 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 × 200 mL), aqueous NaOH (15% w/w, 4 × 200 mL), and deionized water (3 × 200 mL). The organics were dried over anhydrous $MgSO_4$ 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 drybox. In general, the inhibitor was not removed prior to using CTA **3** in the polymerizations described in the text. ^{1}H 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.

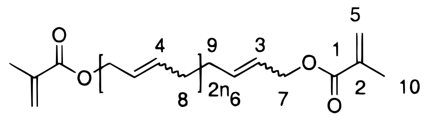
Preparation of *cis*-2-Butene-1,4-diol Diglycidyl Ether (4). In a 1 L Erlenmeyer flask, epichlorohydrin (270 g, 3.00 mol, 10 equiv), aqueous NaOH (50% w/w) (240 g, 3.00 mol, 10 equiv), and $Bu_4N^+HSO_4^-$ (5.0 g) were combined at room temperature with magnetic stirring. A thermometer was placed in the flask to monitor the temperature during the reaction. To this flask was added *cis*-2-butene-1,4-diol (26.5 g, 0.30 mol, 1 equiv) dropwise slowly over 30 min. The reaction was extremely exothermic, and so the temperature was maintained between 30 and 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 × 200 mL), dried over anhydous $MgSO_4$, and concentrated in vacuo to obtain a yellow oil. This was distilled at 0.2 mmHg/105−110 °C to give a clear, colorless 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, $J_1 = 3.0$ Hz, $J_2 = 11.4$ Hz, 2H), 3.30 (dd, $J_1 = 5.7$ Hz, $J_2 = 11.4$ Hz, 2H), 3.11−3.06 (m, 2H), 2.73 (dd, $J_1 = 4.2$ Hz, $J_2 = 4.8$ Hz, 2H), 2.54 (dd, $J_1 = 2.7$ Hz, $J_2 = 4.8$ Hz, 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 3 or 4 with the Ruthenium Benzylidene 2. All manipulations were carried out in a nitrogen-filled drybox. In a 10 mL vial, ruthenium benzylidene **2** (6.0 mg, 7.3 μmol, 1.0 equiv), CTA (either **3** or **4**) (370 μmol, 50 equiv), and C_6D_6 (0.70 mL) were combined to form a homogeneous solution. This solution was transferred to a NMR tube that was capped with a rubber septa and removed from the drybox. 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 ^1H and ^{31}P NMR spectroscopy.

General Polymerization Procedure. All manipulations were carried out in a nitrogen-filled drybox. In a 10 mL vial, the correct amounts of either **3** or **4** and COD were weighed out. A separate vial was charged with the initiator and a stir bar and then combined with the COD/CTA mixture. The vial was then capped, removed from the drybox, and left to stir for the desired time. For reactions involving the methacrylate CTA **3**, aluminum foil was wrapped around the reaction vessel to prevent photoinduced cross-linking. At the end of the desired reaction time, ethyl vinyl ether (600 equiv relative to initiator) was pipetted into the vial along with an equal volume of toluene. After 1 h, the reaction mixture was poured into MeOH, causing polymer to precipitate. 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(butenylene)s were concentrated in vacuo and then characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopy, GPC, DSC, and TGA.

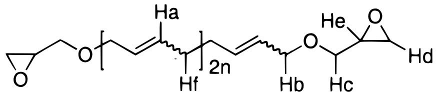
Bis(methacrylate)-Functionalized Telechelic Poly(butenylene) (7). Spectral data for the polymer derived from a 15:1 [COD]/[**3**] ratio (M_n (NMR) = 3700, DP = 32). The ^1H and ^{13}C NMR spectra of **7** were assigned as follows:

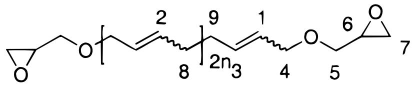




^1H NMR ($CDCl_3$): δ 6.13 (bs, Ha), 5.86−5.54 (bm, Hb cis and trans), 4.68 (bd, $J = 6.0$ Hz, Hc trans), 4.57 (bd, $J = 6.6$ Hz, Hc cis), 2.43−1.72 (bm, Hd cis and trans, He, and Hf). ^{13}C NMR ($CDCl_3$): δ 167.22 (C1, t), 167.14 (C1, c), 136.37 (C2), 135.49 (C3, tc), 135.41 (C3, tt), 134.50 (C3, cc and ct), 130.66 (C4, tc), 129.94 (C4, tt), 129.55 (C4, cc), 129.38 (C4, ct), 128.67 (C5), 125.34 (C6, tc), 124.23 (C6, tt), 124.14 (C6, cc), 123.84 (C6, ct), 60.60 (C7, t), 60.53 (C7, c), 32.93 (C8, tt), 32.65 (C8, tc), 27.66 (C8, cc), 27.36 (C8, ct), 27.01 (C9, t), 26.67 (C9, c), 18.34 (C10). 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(butenylene) (8). Spectral data for the polymer derived from a 15:1 [COD]/[**4**] ratio (M_n (NMR) = 3000, DP = 26). The ^1H and ^{13}C NMR spectra of **8** were assigned as follows:





^1H NMR ($CDCl_3$): δ 5.77−5.17 (bm, Ha cis and trans), 4.09−3.91 (bm, Hb), 3.72−3.61 (bm, Hc), 3.41−3.30 (bm, Hd), 3.17−3.08 (bm, Hd), 2.81−2.72 (bm, He), 2.62−2.53 (bm, Hf cis), 2.35−1.64 (bm, Hf trans). ^{13}C NMR ($CDCl_3$): δ 134.49 (C1, tc), 134.43 (C1, tt), 133.19 (C1, cc and ct), 130.03 (C2, tc), 129.93 (C2, tt), 129.52 (C2, cc), 129.35 (C2, ct), 126.19 (C3, tc), 126.06 (C3, tt), 125.90 (C3, cc and ct), 70.65 (C4, t), 70.46 (C4, c), 66.81 (C5), 50.72 (C6), 44.33 (C7, t), 44.26 (C7, c), 32.91 (C8, tt), 32.63 (C8, tc), 27.63 (C8, cc), 27.37 (C8, ct), 27.10 (C9, t), 26.76 (C9, c). 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(butenylene)s (7). In a 2 mL glass vial, polymer **7** (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 W 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 that was completely insoluble in common organic solvents such CH_2Cl_2, $CHCl_3$, benzene, toluene, diethyl ether, ethyl acetate, and DMSO. The resulting material was characterized by IR spectroscopy, DSC, and TGA.

Cross-Linking of Bis(epoxide)-Functionalized Telechelic Poly(butenylene)s (8). In a 2 mL vial, polymer **8** (100 mg) was dissolved in toluene (500 μL), and a stir bar was added. This solution was then stirred at room temperature, and a catalytic amount of H_2SO_4 was added. Immediate formation of an insoluble rubbery solid was observed for each of the different molecular weight polymers synthesized. These materials were insoluble in common organic solvents (see above). In addition, the resulting material was characterized by DSC and TGA.

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