Synthesis of Functionalized Polyethers by Ring-Opening Metathesis Polymerization of Unsaturated Crown Ethers

Heather D. Maynard 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

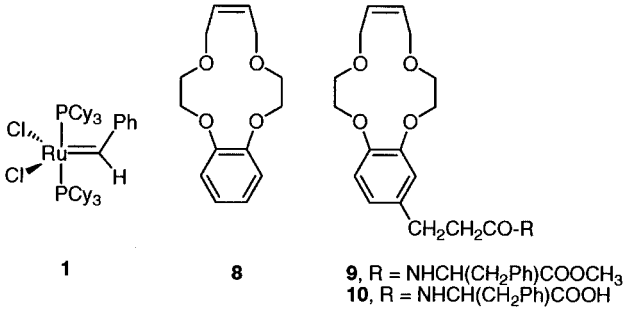
Received May 13, 1999; Revised Manuscript Received August 17, 1999

ABSTRACT: A variety of polyethers were synthesized by a tandem approach incorporating ring-closing metathesis (RCM) followed by ring-opening metathesis polymerization (ROMP) using $RuCl_2(=CHPh)(PCy_3)_2$ (**1**) as an initiator. Unsaturated crown ether monomers, including a 12-crown-4 analogue (**3**), a benzocrown ether (**8**), and a benzocrown ether with a pendent phenylalanine methyl ester (**9**), were synthesized in good yields using a lithium ion as a template and **1** as a catalyst for RCM. Saponification of **9** afforded the benzocrown phenylalanine carboxylic acid monomer **10**. The ROMP of **3**, **8**, and **9** with **1** as an initiator yielded the homopolymers **11**, **12e**, and **13e**, respectively. The relative concentrations of **3** to **1** were varied to produce **11** with a wide range of molecular weights (M_n from 10 900 to 206 300). Hydrogenation of **11** proceeded quantitatively to yield a saturated polyether. Monomers **8** and **9** were copolymerized with **3** to generate polymers **12a**−**d** and **13a**−**d**, respectively. The copolymer composition corresponded to the feed ratio of the monomers. Crown ether **10** was copolymerized with **3** at a low feed ratio to form the corresponding polyether with pendent amino acids.

Introduction

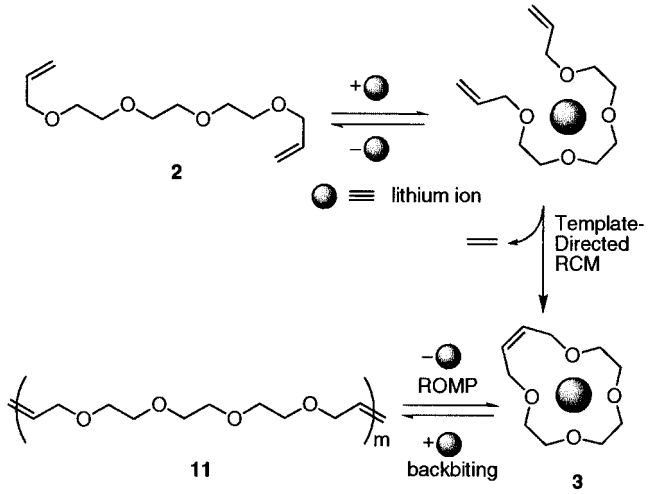
Polyethers are of commercial importance in areas such as polyurethane synthesis, lubricants, cosmetics, and elastomers.[1] A notable example is poly(ethylene glycol) (PEG) which has been widely used in the biotechnical and biomedical communities due to its water solubility, low toxicity, and protein-resistant properties.[2] PEG has been attached to surfaces and to molecules such as proteins, enzymes, and small-molecule pharmaceuticals to impart stability and biocompatibility to these materials.[2,3] Typically, modification is at one or both ends of the polymer, limiting the attachment sites for a linear polymer to two. However, there are a number of applications including drug delivery where having many molecules per polymer chain is desirable. [4]

Poly(oxyalkylene)s such as poly(epichlorohydrin) have been synthesized and subsequently modified with a number of functional groups.[5] However, since reactions on a polymer chain can prove difficult and may not result in quantitative conversions, it is advantageous to polymerize functionalized monomers. In this contribution, we describe the synthesis of polyethers similar to PEG having amino acid side groups by ring-opening metathesis polymerization (ROMP) of phenylalanine-containing crown ethers **9** and **10** using ruthenium complex **1**.[6] In these cases, the polymer compositions were readily controlled by the choice and initial concentration of the monomers, and polymers with varying amounts of phenylalanines per chain were synthesized.



1 **8** **9**, R = NHCH(CH$_2$Ph)COOCH$_3$
10, R = NHCH(CH$_2$Ph)COOH

Scheme 1

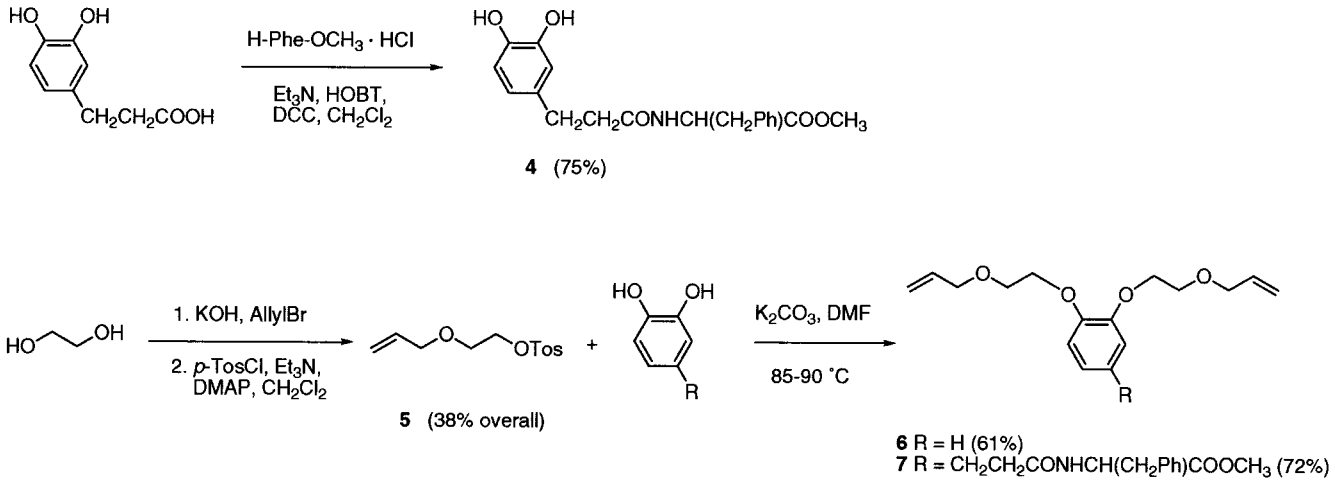


Few examples of the synthesis of polyethers by metathesis polymerization have been published. Wagener et al. reported the synthesis of polyethers having the structure $[-CH_2{=}CH-(CH_2)_n-O-(CH_2)_n-]$ by acyclic diene metathesis polymerization (ADMET) using a tungsten or molybdenum catalyst.[7] The polymerization of α,ω-dienes, di-4-pentenyl ether ($n = 3$) and di-5-hexenyl ether ($n = 4$), resulted in high yields of polymers with moderate molecular weights. However, these polyethers do not contain PEG units (which are necessary to impart water solubility to the polymers). The ADMET of ethylene glycol diallyl ether was described, but this gave only oligomers. They also reported the ROMP of 2,5-dihydrofuran to give a polymer with high molecular weight; however, the yields were low (~33%).[7b]

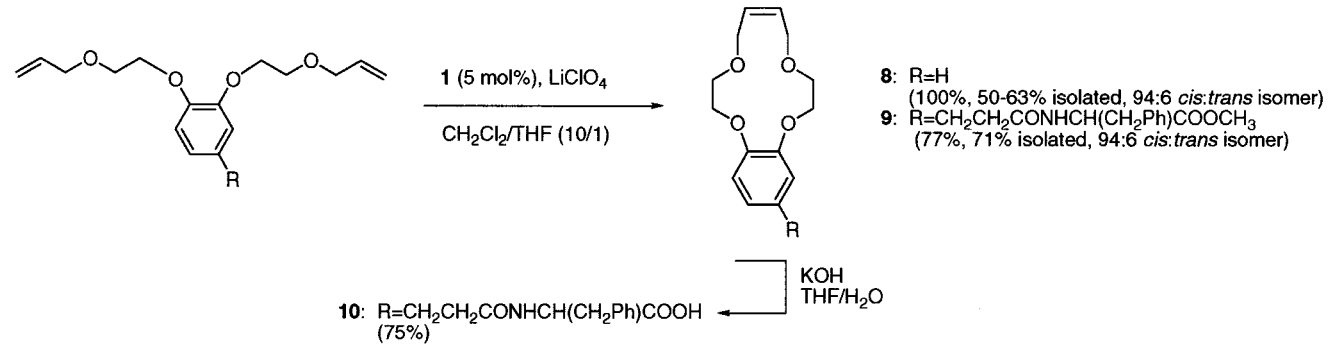
We recently reported the synthesis of high molecular weight, water-soluble polyethers similar in structure to PEG (Scheme 1).[8] For example, crown ether **3** was

10.1021/ma990749y CCC: $18.00
Published on Web 09/29/1999

Scheme 2



Scheme 3



synthesized by ring-closing metathesis (RCM) using ruthenium complex **1** as a catalyst and a lithium ion as a template. Subsequent ROMP of **3** afforded high yields of polyether **11** with high molecular weights. The ADMET of the α,ω-diene **2** to yield **11** was attempted but resulted in low yields of **11** with low molecular weights; therefore, the chain growth polymerization route, ROMP, is preferred over the step growth polymerization route, ADMET. This template-directed RCM followed by ROMP methodology is readily adapted to synthesize other polyether backbones such as the polymer of **8** and functionalized polyethers from ROMP of monomers **9** and **10**.

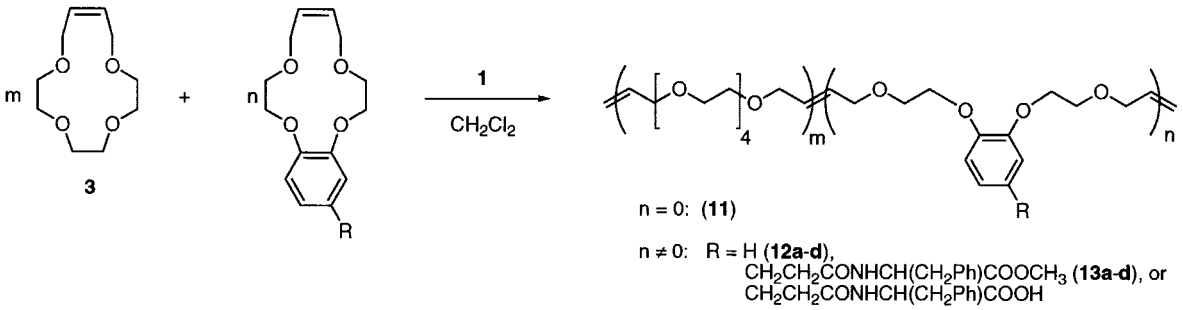
Ruthenium alkylidene **1**[6] is stable in the presence of many functional groups and is active in many solvents including water.[9] Due to the development of this catalyst and others, the ROMP of monomers with biologically relevant units has been recently undertaken. For example, polymers with pendent sugars have been synthesized[10] and used to explore protein−saccharide interactions.[10c,d] Additionally, polymers substituted with nucleotide bases,[11] antibiotics,[12] and amino acid esters[13] have been synthesized using ruthenium and molybdenum complexes. Although these examples have been based on poly(norbornene) and poly(7-oxonorbornene) backbones, they demonstrate the feasibility of producing polyethers with biorelevant side groups. This paper describes the synthesis of monomers **3**, **8**, **9**, and **10** by template-directed RCM. The polymerization of these monomers to form various polyether backbones with pendent amino acids is described.

Results and Discussion

Monomer Synthesis. α,ω-Diene precursors for RCM were readily prepared (Schemes 1 and 2). Synthesis of triethylene glycol diallyl ether (**2**) from triethylene glycol, sodium hydride, and allyl bromide proceeded in 70% yield. The syntheses of 1,2-bis(2-allyloxyethyoxy)-benzene (**6**) and 1,2-bis(2-allyloxyethyoxy)benzene substituted with a pendent phenylalanine methyl ester (**7**) were undertaken as shown in Scheme 2. Phenylalanine methyl ester hydrochloride salt was coupled to 3,4-dihydroxyhydrocinnamic acid using standard peptide coupling procedures employing HOBT and DCC in CH_2Cl_2 to give **4** in 75% yield. Ethylene glycol was treated with allyl bromide and base to form the ethylene glycol monoallyl ether, and the alcohol was subsequently converted to a tosyl group to give **5** (38% overall yield). Reaction of **5** with catechol or **4** in the presence of potassium carbonate in DMF gave **6** (61% yield) and **7** (72% yield), respectively.

Template-directed RCM using a lithium ion ($LiClO_4$) as a template and complex **1** as a catalyst was undertaken to form the unsaturated crown ethers (Schemes 1 and 3). Synthesis of crown ether **3** from **2** was previously described, and it was demonstrated that the lithium ion preorganized the diene for RCM, giving high yields and selectivity for the cis isomer (100:1 cis:trans).[8] In a similar manner, **6** was converted to **8** in quantitative yield as determined by ^1H NMR spectroscopy; however, the isolated yields were much lower (50−63%). Template-directed RCM of **7** afforded **9** in 71% isolated yield. In both cases, the cis isomer was formed preferentially (94:6 cis:trans).

Scheme 4



We previously determined that the synthesis of **3** in the absence of a lithium ion (all other conditions the same) favored the trans isomer (38:62 cis:trans), and the yield obtained was much lower (39% yield).[8] The effect of the lithium ion in this reaction was further confirmed when the synthesis of **8** and **9** was performed without a lithium ion and monitored by ^{1}H NMR spectroscopy. The overall yields of the crude mixtures obtained from the ^{1}H NMR spectrum were lower than RCM with a lithium ion (73% for **8** and 60% for **9**). In both cases, the trans isomers formed predominately with a cis:trans ratio of 35:65 for **8** and 56:64 for **9**.

In RCM, an equilibrium exists between the ring-closed and the ring-opened species.[8,14] The template effect, coupled with running the reaction under conditions of high dilution, favors the ring-closed product over the ring-opened product in these examples. This was demonstrated in both the syntheses of **3** and **8** where only the ring-closed product was observed at the end of the reaction. However, in the synthesis of **9**, a linear oligomer was detected in the crude reaction product by ^{1}H NMR spectroscopy. Even upon rigorous purification of the substrate, this oligomer persisted as 1−5% of the final product.

To obtain the crown ether with a pendent phenylalanine carboxylic acid, the saponification of **9** was carried out (Scheme 3). Reaction of **9** with hydroxide base gave **10**. The linear oligomers in the starting material were removed during product isolation to afford **10** in 75% yield.

Polymer Synthesis and Characterization. In a typical polymerization, complex **1** in CH_2Cl_2 was added to a vial containing monomer or a mixture of monomers (Scheme 4). The solutions were stirred for 4−5 h, and ethyl vinyl ether was added to terminate the reactions. The polymers were isolated by precipitation into ether chilled to 0 °C. Many of the polymers were slightly soluble in ether, and thus the isolated yields were decreased by this purification process.[15] The polymers generally were viscous oils or sticky solids at room temperature.

The ROMP of **3** gave polymer **11** in quantitative yield, as determined by ^{1}H NMR spectroscopy of the crude reaction mixture (78% isolated yield). The number-average polymer molecular weight (M_n) was determined by gel permeation chromatography to be 65 900 and the polydispersity index (PDI) to be 1.96. The glass transition temperature (T_g) of this polymer at −59 °C was obtained by differential scanning calorimetry (DSC). Hydrogenation of **11** using Crabtree's catalyst[16] quantitatively gave the saturated polyether with a T_g at −65 °C.

A wide range of polymer molecular weights was accessible by this methodology. This may be useful, as structurally similar polymers such as poly(ethylene glycol) are not commercially available between molecular weights of 20 000 and 200 000.[17] The molecular weight of polymers produced by living ROMP of strained monomers can be readily controlled by the initial monomer-to-catalyst ratio ([M]/[C]). Although the monomers described here do not polymerize in a living fashion, since the initiator remains active throughout the reaction, the molar mass should be proportional to the [M]/[C] ratio.

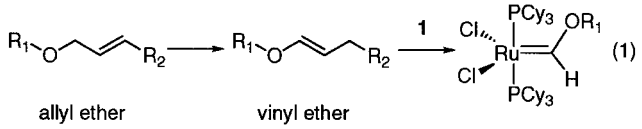
Table 1. Results for Polymerization of 3 with Various [M]/[C][a]

[M]/[C]	yield,[b] %	$M_n \times 10^{-4}$ [c]	PDI[c]	trans/cis[b]
25	>95	1.09	1.50	5.4
100	>95	6.59	1.96	4.1
1000	83	9.12	2.29	3.1
3000	78	15.5	1.83	2.6
4000	71	20.6	1.73	2.4

[a] [**3**] = 1.2 M in CH_2Cl_2, 25 °C, 4 h. [b] Determined from ^{1}H NMR spectra. [c] Determined by GPC, polystyrene calibration.

To test this, the polymerization of **3** with [M]/[C] between 25/1 and 4000/1 was performed, and the results are shown in Table 1. The molecular weights did increase as [M]/[C] increased to yield polymers with M_n between 10 900 and 206 000. PDI values were all between 1.7 and 2.3. As the catalyst loading was decreased, the polymer yields (determined by ^{1}H NMR spectroscopy) decreased from >95% ([M]/[C] = 25/1) to 71% ([M]/[C] = 4000/1).

At a low loading of **1**, the polymerization of **3** can result in very low to zero yields. Inspection of the crude reaction mixtures in these cases revealed the presence of a small amount (<5%) of a vinyl ether species, suggesting that isomerization of an allyl ether (from monomer and/or polymer) to a vinyl ether had occurred. It is known that the reaction of **1** with a vinyl ether forms the metathesis-inactive $RuCl_2(=CHOR)(PCy_3)_2$ complex.[6b] In fact, ethyl vinyl ether is frequently used to terminate metathesis reactions catalyzed by **1**. The isomerization and subsequent termination of **1** could therefore compete with polymerization, resulting in low yields (eq 1). Occurrence of this on a small scale would be more problematic when using low concentrations of catalyst.



(1)

To study this possibility, **3** was polymerized in CD_2Cl_2, and the propagating alkylidene of **1** was monitored by ^{1}H NMR spectroscopy. In the cases where low yields were obtained, a peak at 14.45 ppm was observed in

Table 2. Results for Homopolymerization of 8 and Copolymerization of 3 and 8[a]

polymer	mol % **8** feed	mol % **8** polymer[b]	yield,[b,c] %	$M_n \times 10^{-4}$ [d]	PDI[d]	trans/cis[b]	T_g (T_m), °C[e]
12a	11	11	>95 (68)	2.75	1.84	3.0	−56.9
12b	25	24	83 (52)	2.53	1.63	2.7	−49.8
12c	50	49	69 (55)	1.97	1.75	2.6	−36.5
12d	75	80	60 (48)	1.76	1.67	2.6	−20.7 (6.6)
12e[f]	100	100	58 (54)	1.63	1.57	2.9	−7.9 (8.0)

[a] [M]/[C] = 100, [M] = 1.2 M in CH_2Cl_2, 25 °C, 5 h. [b] Determined from ^1H NMR spectra. [c] Isolated yields in parentheses. [d] Determined by GPC, polystyrene calibration. [e] Determined by DSC, second heat, scan rate 20 °C/min. [f] [M] = 0.7 M in CH_2Cl_2.

Table 3. Results for Homopolymerization of 9 and Copolymerization of 3 and 9[a]

polymer	mol % **9** feed	mol % **9** polymer[b]	yield,[b,c] %	$\bar{M}_n \times 10^{-3}$ [d]	PDI[d]	$\bar{M}_n \times 10^{-3}$ [d,e]	PDI[d,e]	trans/cis[b,e]	T_g (°C)[f]
13a	10	13	91 (76)	32.0	2.95	15.8	1.74	3.8 (7.6)	−49.1
13b	25	23	95 (91)	31.4	4.10	13.6	2.18	3.6 (10.0)	−34.3
13c	50	51	94 (82)	9.18	3.73	4.95	2.25	3.5 (7.8)	−6.0
13d	74	69	84 (76)	4.58	2.58	2.76	2.07	4.2 (13.9)	9.8
13e[g]	100	100	95 (79)	3.46	2.00	2.49	1.73	5.2 (16.7)	24.9

[a] Initial [M]/[C] = 100, [M] = 1.2 M in CH_2Cl_2, 25 °C, 5 h. [b] Determined from ^1H NMR spectra. [c] Isolated yields in parentheses. [d] Determined by GPC, polystyrene calibration. [e] Polymers resubjected to **1**, [repeat unit]/[C] = 25, [repeat unit] = 2.4 M in CH_2Cl_2, 25 °C, 1 week. [f] Determined by DSC, second heat, scan rate 20 °C/min. [g] Initial [M]/[C] = 50.

the ^1H NMR spectrum in addition to the desired α-H alkylidene resonance at 19.19 ppm. The propagating carbene resonance decreased in intensity as the peak at 14.45 ppm increased in intensity until no propagating carbene was observed.[18] The peak at 14.45 ppm compares very closely to the α-H peak of $RuCl_2(=CHOCH_2CH_3)(PCy_3)_2$ at 14.51 ppm obtained by the reaction of **1** with ethyl vinyl ether in CD_2Cl_2. This indicates that isomerization to a vinyl ether and subsequent termination of **1** was occurring in these cases. The reason for this isomerization is not yet understood, although it is probably related to ruthenium hydride impurities in the catalyst.[19] However, this detrimental reaction was not problematic unless very low concentrations of **1** (high [M]/[C]) and impure catalyst were used.

The hompolymerization of **8** and copolymerization of **8** and **3** were undertaken (Scheme 4), and the results are shown in Table 2. Homopolymerization of **8** gave a 54% isolated yield of polymer **12e** with a M_n of 16 300 and PDI of 1.57. Thermal analysis indicated that polymer **12e** possessed both a glass transition (T_g = −7.9 °C) and a melting point (T_m = 8.0 °C). Copolymers **12a**−**d** were synthesized in moderate yields between 48% and 68%. The T_g of copolymers **12a**−**d** varied between those of the two homopolymers (**11,** −59.0 °C; **12e**, −7.9 °C). However, the crystallization of the copolymers was inhibited by the incorporation of **3**, and only copolymer **12d** exhibited a melting point (T_m = 6.6 °C). The PDIs and trans-to-cis ratios were all similar and ranged from 1.57 to 1.84 and 2.6 to 3.0, respectively.

An important component of a copolymerization reaction is the final concentration of the monomers in the polymer (copolymer composition) relative to the initial concentrations of the monomers (feed composition).[1b] A desirable characteristic for the copolymers in this research was that the incorporation into the copolymer of the two monomers be dependent on the feed composition. In this way, the copolymer composition (and pendent groups) could be changed by simply altering the initial monomer concentrations. This was the case as demonstrated by the results for **12a**−**d** in Table 2; for each copolymer the mole percent **8** incorporated was the same as the feed.

The polymer yields decreased with increasing amounts of **8** (Table 2). The ^1H NMR spectra of the crude reaction mixtures quenched after 5 h indicated the presence of both polymer and unreacted **3** and **8**. (Residual monomers were in the same ratio as initially.) When the homopolymerization of **8** was carried out for 23 h, the ^1H NMR spectrum of the crude reaction mixture indicated a >95% yield of **12e** (versus 58% yield after 5 h). This result indicates that higher yields may be obtained by using longer polymerization times.

The homo- and copolymerizations of **9** and **3** were conducted (Scheme 4), and the results are shown in Table 3. The homopolymerization of **9** using a [M]/[C] of 50 gave **13e** in 79% isolated yield with a molecular weight of 3460 and PDI of 2.00. The GPC trace contained a slight low-molecular-weight shoulder. The copolymerizations with various mole percent of **9** in the feed gave polymers **13a**−**d** in good yields. Analogous to **12a**−**d**, the mole percent of **9** incorporated into the polymers was similar to the mole percent of **9** in the feed.

Similar to polymer **13e,** the molecular weight distributions for the copolymers were all broad, and the GPC traces of **13b**−**d** exhibited either a high- or low-molecular-weight shoulder. Copolymer **13b** had the broadest molecular weight distribution and largest shoulder as shown by the GPC trace in Figure 1a. As discussed earlier, **9** contained a small amount of a linear oligomer which could have caused chain transfer reactions during ROMP.[20] After only 5 h of reaction time the polymerizations would not have reached equilibrium, leaving some long chains and some short chains.[20,21] Typically, ROMP chain transfer reactions proceed for hours to days before reaching equilibrium.[21,22]

With the addition of fresh catalyst to the polymers and longer reaction times, the chains could equilibrate to narrower molecular weight distributions due to backbiting along the polymer chain.[20,21a] To investigate this, catalyst **1** ([repeat unit]/[C] = 25)[23] and isolated polymers **13a**−**e** were reacted for 1 week. The compositions of the polymers did not change. However, the results given in Table 3 demonstrate that the molecular weights lowered and, most significantly, the PDIs narrowed, and molecular weight distributions were monomodal. This change was most marked for polymer **13b** where the PDI went from 4.10 with a high-molecular-weight shoulder to 2.18 and monomodal

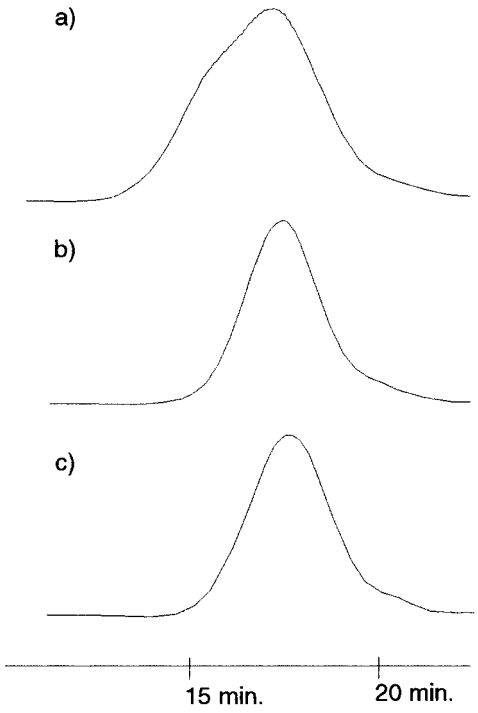


Figure 1. GPC traces for polymers **13b** and **13f**: (a) monomers polymerized for 5 h with [M]/[C] = 100 (**13b**); (b) polymer (**13b**) subjected to [repeat unit]/[C] = 25 for 1 week; (c) monomers polymerized for 1 week with [M]/[C] = 25 (**13f**).

(Figure 1a,b). Additionally, the trans-to-cis ratios of each of the polymers increased (Table 3). This demonstrates that the trans product is thermodynamically more stable than the cis product. There was no discernible change in the trans-to-cis ratios for the polymers stirred in solution in the absence of catalyst.

In principle, the same narrowing affect should occur for the polymerization of **3** and **9** at long reaction times. To test this, **9** (25% in feed) and **3** were subjected to complex **1** ([M]/[C] = 25) for 1 week. The resulting polymer (**13f**) contained 24 mol % of **9.** Also, the polymer had a monomodal GPC trace with a molecular weight of 12 300 and a PDI of 2.32. The GPC trace compared very closely to that obtained for **13b** after stirring with **1** for 1 week (Figure 1b,c). These results indicate that long polymerization times are necessary for the copolymerization of **3** and **9** to obtain polymers with monomodal molecular weight distributions.

The homopolymerization of **10** was attempted but yielded an intractable mixture due to the low solubility of the material formed. The copolymerizations of **10** and **3** were performed employing **1** with a [M]/[C] of 50 (Scheme 4). The polymerization of **10** (8 mol % in feed) with **3** yielded a polymer with ~5% of **10** incorporated into the polymer, a M_n of 6990, and PDI of 2.04 in 95% yield. Attempts at incorporating larger amounts of **10** resulted in oligomers and polymers of limited solubility. However, the copolymer made had a monomodal molecular weight distribution, which is consistent with the fact that no linear oligomers were present in this monomer.

Conclusions

We have demonstrated that polyethers can be synthesized using a tandem approach involving template-directed RCM followed by ROMP. An analogue of 12-crown-4, a benzocrown ether, and a benzocrown ether with a pendent phenylalanine methyl ester were synthesized in high yields with selectivity for the cis isomer using a lithium ion as a template for ring-closing metathesis. Polymers containing PEG and butenediol units were synthesized in a wide range of molecular weights by ROMP of the 12-crown-4 analogue using different catalyst loadings. Various polyether backbones were synthesized from the benzocrown ether and the 12-crown-4 analogue. Excellent correlation between the initial monomer compositions and final polymer compositions was observed. In a similar manner, polymers with pendent phenylalanine methyl esters and phenylalanine carboxylic acids were made. In the case of the phenylalanine methyl ester polymers, long polymerization times were necessary to obtain polymers with monomodal molecular weight distributions.

In addition to synthesizing polyethers with new backbone structures, the synthesis of these polymers with pendent amino acids demonstrates the feasibility of producing biorelevant polyethers via ROMP. An advantage of synthesizing materials in this way is the ability to produce polymers with many bioactive groups per polymer chain where the number of groups can be readily controlled by the initial concentrations of the monomers. Such polymers have potential uses in tissue engineering, drug delivery, and other biomedical applications. Studies of the toxicity and biocompatibility of these polymers as well as those with other biologically relevant molecules are underway.

Experimental Section

Materials. Allyl bromide, sodium hydride, 4-(dimethylamino)pyridine (DMAP), *p*-toluenesulfonyl chloride, triethylamine (Et_3N), catechol, lithium perchlorate ($LiClO_4$), ethyl vinyl ether, and 1,3-dicyclohexylcarbodiimide (DCC) were purchased from Aldrich and used as received. Triethylene glycol and ethylene glycol were purchased from Aldrich and dried over 4 Å molecular sieves (Linde). 3,4-Dihydroxyhydrocinnamic acid was purchased from Aldrich and dried under 30 mTorr vacuum for 24 h. L-Phenylalanine methyl ester hydrochloride and 1-hydroxybenzotriazole (HOBT) were purchased from Sigma and used as received. Anhydrous potassium carbonate (K_2CO_3) and potassium hydroxide were purchased from Mallinckrodt and used as received. Tris(hydroxymethyl)-phosphine and Crabtree's catalyst were purchased from Strem Chemicals and used as received. Dry tetrahydrofuran (THF) and methylene chloride (CH_2Cl_2) were rigorously degassed and passed through purification columns.[24] *N*,*N*-Dimethylformamide (DMF) was distilled from $MgSO_4$ and stored over 4 Å molecular sieves (Linde). All other solvents were purchased from EM Science and used as received.

Techniques. Unless otherwise noted, all operations were carried out under a dry nitrogen or argon atmosphere. Drybox operations were performed in a nitrogen-filled Vacuum Atmospheres drybox. Column chromatography was performed using silica gel 60 (230−400 mesh) from EM Science. ^{1}H NMR (300.1 MHz) and ^{13}C NMR (75.49 MHz) spectra were recorded on a General Electric QE-300 spectrometer. ^{1}H NMR (399.65 MHz) spectra to monitor polymerizations were taken on a JEOL GX-400 spectrometer. Chemical shifts are reported downfield from tetramethylsilane (TMS). Polymer ^{1}H NMR spectra were obtained using a pulse delay of 60 s. Infrared spectroscopy was performed on a Perkin-Elmer Paragon 1000 FT-IR spectrometer using a thin film of sample cast on a NaCl plate unless otherwise indicated. High-resolution mass spectra were provided by the Southern California Mass Spectrometry Facility (University of California, Riverside). Gel permeation chromatographs were obtained with CH_2Cl_2 as the eluent (flow rate of 1 mL/min) using an HPLC system equipped with 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. The molecular weights and polydispersities were reported versus monodispersed polystyrene standards. Differential scanning calorimetry was measured on a Perkin-Elmer DSC-7. The results are given for the second heating using a scan rate of 20 °C/min for all cases.

Monomer Synthesis. (a) Synthesis of Triethylene Glycol Diallyl Ether (2). To a room temperature, stirred solution of allyl bromide (4 mL, 46.2 mmol) and sodium hydride (1.35 g, 56.3 mmol) in dry THF (125 mL) was added, over a period of an hour, a solution of triethylene glycol (3.0 mL, 22.5 mmol) in THF (25 mL). The reaction was allowed to stir at room temperature for a total of 12 h. THF was removed in vacuo, and the crude product was taken up in ether and extracted with water three times. The ether layer was separated and dried over $MgSO_4$, and the solvent was removed in vacuo. The crude product was purified by column chromatography (ether eluent) to afford 3.52 g (70%) of **2** as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 5.82−5.95 (m, 2H), 5.13−5.28 (m, 4H), 3.98−4.01 (m, 4H), 3.56−3.66 (m, 12 H). ^{13}C NMR ($CDCl_3$): δ 134.65, 116.99, 72.12, 70.52, 69.30. IR: 3072, 2864, 1462, 1420, 1348, 1291, 1249, 1109, 995, 917. HRMS (CI): calcd for $(MH)^+$ 231.1596; found 231.1596.

(b) Synthesis of 1,4,7,10-Tetraoxacyclotetradec-12-ene (3). The following is a modified synthesis and purification from that previously reported for crown ether **3**.[8] THF (59 mL) was added to **2** (3 g, 13.0 mmol) and $LiClO_4$ (6.91 g, 65.2 mmol), and the solution was stirred for 30 min or until all solids had dissolved. *[Precaution should be used when handling perchlorate salts due to the explosive nature of these compounds; a blast shield should be used at all times.]* Dry CH_2Cl_2 (580 mL) was added to the flask followed by a solution of catalyst **1** (537 mg, 0.652 mmol) in CH_2Cl_2 (10 mL). The mixture was heated to 40 °C for 90 min before cooling to room temperature, adding ∼1 mL of ethyl vinyl ether and stirring for 30 min. The solution was extracted with a minimal amount of water to remove the lithium, the organic layer was dried over $MgSO_4$, and the solvent removed in vacuo. The residue was subjected to chromatography (ether eluent) to yield **3** as a brown liquid in 74−99% yield. A further purification to remove residual ruthenium could be undertaken utilizing tris(hydroxymethyl)-phosphine during an aqueous wash according to literature procedure.[25] ^{1}H NMR ($CDCl_3$): δ 5.75−5.78 (m, 2), 4.29−4.30 (m, 4H), 3.64−3.72 (m, 12 H).

(c) Synthesis of Ethylene Glycol Monoallyl Ether. The compound was synthesized according to literature procedure[26] with potassium hydroxide (16.8 g, 0.3 mmol), ethylene glycol (16.7 mL, 0.3 mmol), and allyl bromide (26.1 mL, 0.3 mmol) to afford 12.9 g (42%) of the product as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 5.81−5.94 (m, 1H), 5.13−5.28 (m, 2H), 3.97−4.00 (m, 2H), 3.68−3.71 (m, 2H), 3.50−3.53 (m, 2H), 2.52 (bs, 1H).

(d) Synthesis of Ethylene Glycol Allyl Ether *p*-Tosylate (5). Ethylene glycol monoallyl ether (1.71 g, 16.8 mmol) and *p*-toluenesulfonyl chloride (3.20 g, 16.8 mmol) were dissolved in CH_2Cl_2 (50 mL), and triethylamine (3.5 mL, 25.2 mmol) and DMAP (catalytic amount) were added. The solution was stirred for 12 h before water was added, and the solution was acidified with 10% citric acid to a pH of 7. The organic layer was extracted with water (2×) followed by brine (1×), dried over $MgSO_4$, and concentrated in vacuo to give a colorless, viscous oil of **5** (3.90 g, 91% yield). ^{1}H NMR ($CDCl_3$): δ 7.81−7.84 (m, 2H), 7.35−7.37 (m, 2H), 5.79−5.88 (m, 1H), 5.16−5.32 (m, 2H), 4.17−4.20 (m, 2H), 3.95−3.98 (m, 2H), 3.63−3.66 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (CD_2Cl_2): δ 145.65, 134.89, 133.20, 130.41, 128.39, 117.40, 72.47, 70.06, 67.94, 21.88. IR: 2868, 1598, 1452, 1357, 1190, 1177, 1097, 1019, 920, 817, 777, 665 cm^{-1}. HRMS (CI): calcd for $(M + NH_4)^+$ 274.1113; found 274.1108.

(e) Synthesis of 1,2-Bis(2-allyloxyethoxy)benzene (6). Compound **5** (838 mg, 3.27 mmol), catechol (180 mg, 1.64 mmol), and anhydrous K_2CO_3 (905 mg, 6.55 mmol) were dissolved in dry DMF (8 mL), and the mixture was heated to 85−90 °C for 24 h. Ether was added, the solution was washed with 10% NaOH (2×), water (3×), and brine (1×) and dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was subjected to column chromatography (25% ethyl acetate, 75% hexanes eluent) to yield 277 mg (61%) of **6** as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 6.89−6.96 (m, 4H), 5.88−6.01 (m, 2H), 5.17−5.35 (m, 4H), 4.16−4.20 (m, 4H), 4.10−4.12 (m, 4H), 3.81−3.84 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 148.90, 134.58, 121.47, 116.90, 114.72, 72.12, 68.74, 68.46. IR: 3072, 2916, 2864, 1592, 1503, 1451, 1254, 1218, 1114, 1042, 927, 798, 798, 741 cm^{-1}. HRMS (EI): calcd for $(M)^+$ 278.1518; found 278.1518.

(f) Synthesis of 6,7,9,12,14,15-Hexahydro-5,8,13,16-tetraoxabenzocyclotetradecene (8). Using the same procedure as for the synthesis of **3**, treatment of **6** (238 mg, 0.856 mmol) and $LiClO_4$ (454 mg, 4.28 mmol) in dry THF (3.9 mL) and CH_2Cl_2 (37 mL) with catalyst **1** (35.2 mg, 0.0428 mmol) in CH_2Cl_2 (1.9 mL) formed **8** in quantitative yield by ^{1}H NMR spectroscopy. Subjecting the crude product to column chromatography (1−2 times, ether eluent) gave 50−63% (94% cis isomer) isolated yields of **8** as a white, crystalline solid. ^{1}H NMR ($CDCl_3$): δ 6.89−6.94 (m, 4H), 5.75−5.78 (m, 2H), 4.41−4.42 (m, 4H), 4.15−4.18 (m, 4H), 3.86−3.88 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 148.99, 129.81, 121.58, 114.48, 70.80, 67.82, 67.34. IR: 2922, 2859, 1592, 1501, 1451, 1252, 1220, 1121, 1053, 971, 917, 745 cm^{-1}. HRMS (EI): calcd for $(M)^+$ 250.1205; found 250.1205.

(g) Synthesis of 2-[3-(3,4-Dihydroxyphenyl)propionylamino]-3-phenylpropionic Acid Methyl Ester (4). To a solution of L-phenylalanine methyl ester hydrochloride (1.33 g, 6.17 mmol) in CH_2Cl_2 (30 mL) was added triethylamine (1.3 mL, 9.34 mmol), and the mixture was stirred for 15 min. Then 3,4-dihydroxyhydrocinnamic acid (1.12 g, 6.17 mmol) and HOBT (1.08 g, 8.00 mmol) were added, and the solution was stirred until all solids had dissolved. DCC (1.27 g, 6.17 mmol) was added, and the solution was stirred for 12 h. The organic layer was filtered, washed with 10% citric acid (1×), water (2×), and brine (1×), and dried with $MgSO_4$, and the solvent was removed in vacuo. The residue was subjected to column chromatography (ethyl acetate eluent) to yield 1.58 g (75%) of **4** as a white, extremely hydroscopic solid. ^{1}H NMR (CD_2Cl_2): δ 7.18−7.29 (m, 3H), 6.93−6.96 (m, 2H), 6.74 (d, J = 8.1 Hz, 1H), 6.69 (d, J = 2.1 Hz, 1H), 6.55 (dd, J = 2.1 Hz, J = 8.1 Hz, 1H), 6.04 (bd, J = 7.5 Hz, 1H), 4.77−4.83 (m, 1H), 3.66 (s, 3H), 3.00−3.03 (m, 2H), 2.76 (t, J = 7.5 Hz, 2H), 2.40−2.46 (m, 2H). ^{13}C NMR (CD_2Cl_2): δ 173.83, 172.45, 144.77, 143.38, 136.35, 133.22, 129.76, 129.08, 127.61, 120.70, 115.94, 115.84, 54.02, 52.91, 38.68, 38.23, 31.34. IR: 3342, 2947, 1732, 1649, 1602, 1519, 1441, 1363, 1275, 1218, 1109, 808, 746, 699 cm^{-1}. HRMS (CI): calcd for $(MH)^+$ 344.1498; found 344.1497.

(h) Synthesis of 2-{3-[3,4-Bis(2-allyloxyethoxy)phenyl]-propionylamino}-3-phenylpropionic Acid Methyl Ester (7). Using the same procedure as for **6** except with **4** (1.20 g, 3.50 mmol), **5** (1.79 g, 7.00 mmol), and K_2CO_3 (1.93 g, 14.0 mmol) in DMF (17.5 mL) gave the crude product which after subjecting to column chromatography (70% ethyl acetate, 30% hexanes eluent) gave 1.29 g (72%) of **7** as a white, waxy solid. ^{1}H NMR ($CDCl_3$): δ 7.21−7.26 (m, 3H), 6.92−6.97 (m, 2H), 6.68−6.84 (m, 3H), 5.84−5.96 (m, 3H), 5.15−5.32 (m, 4H), 4.85−4.89 (m, 1H), 4.06−4.14 (m, 8H), 3.75−3.80 (m, 4H), 3.69 (s, 3H), 3.05 (d, J = 5.4, 2H), 2.81−2.86 (m, 2H), 2.40−2.47 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 172.48, 172.11, 149.61, 148.03, 136.26, 135.29, 134.69, 129.78, 129.10, 127.67, 121.69, 117.63, 115.65, 72.84, 69.67, 69.48, 69.20, 53.55, 52.88, 38.89, 38.41, 31.52. IR: 3294, 2931, 2868, 1741, 1651, 1510, 1451, 1433, 1261, 1216, 1139, 1116, 1035, 994, 926, 808, 745, 670 cm^{-1}. HRMS (FAB): calcd for $(M)^+$ 511.2570; found 511.2570.

(i) Synthesis of 2-[(3-(6,7,9,12,14,15-Hexahydro-5,8,13,16-tetraoxabenzocyclotetradecen-2-yl-propionylamino)]-3-phenylpropionic Acid Methyl Ester (9). Using the same procedure as for **3** except with **7** (1.56 g, 3.05 mmol), $LiClO_4$ (1.62 g, 15.3 mmol) in dry THF (13.9 mL), and dry CH_2Cl_2 (137 mL) with catalyst **1** (126 mg, 0.153 mmol) in CH_2Cl_2 (2 mL) gave the crude product in 77% yield by ^{1}H NMR spectroscopy. The product was subjected to column chromatography (70% ethyl acetate, 30% hexanes eluent) and resubjected (ethyl acetate eluent) to yield 1.04 g (71% yield, 94% cis isomer, 1−5% linear diene) of **9**. ^{1}H NMR (CD_2Cl_2): δ 7.20−

7.28 (m, 3H), 6.95−6.98 (m, 2H), 6.70−6.82 (m, 3H), 5.95 (bd, J = 7.5, 1H), 5.65−5.76 (m, 2H), 4.77−4.83 (m, 1H), 4.34−4.35 (m, 4H), 4.07−4.11 (m, 4H), 3.77−3.81 (m, 4H), 3.67 (s, 3H), 3.02−3.05 (m, 2H), 2.80−2.85 (m, 2H), 2.39−2.45 (m, 2H). ^{13}C NMR (CD_2Cl_2): δ 172.43, 171.83, 149.65, 148.03, 136.72, 134.98, 130.39, 130.25, 129.80, 128.98, 127.50, 121.56, 115.23, 115.18, 71.53, 71.26, 68.60, 68.49, 67.94, 53.64, 52.70, 38.64, 38.31, 31.43. IR: 3298, 3028, 2922, 2865, 1744, 1653, 1509, 1451, 1432, 1364, 1263, 1215, 1162, 1133, 1051, 1027, 979, 695 cm^{-1}. HRMS (CI): calcd for $(MH)^+$ 484.2335; found 484.2334.

(j) Synthesis of 2-[(3-(6,7,9,12,14,15-Hexahydro-5,8,13,16-tetraoxabenzocyclo tetradecen-2-yl-propionylamino)]-3-phenylpropionic acid (10). KOH (400 mg, 7.14 mmol) was added to a solution of **9** (950 mg, 1.97 mmol) in THF (14.8 mL) and deionized water (4.9 mL), and the reaction was stirred for 13 h. Water was added and the solution extracted with CH_2Cl_2 (1×). The aqueous layer was acidified with 10% citric acid to a pH 3 and, with the addition of NaCl, extracted with ether (5×). The ether layers were combined and dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was subjected to column chromatography (97% ethyl acetate, 3% acetic acid eluent), taken up in water, and reextracted (adding NaCl) with ether (5×). The ether layers were consolidated and dried over $MgSO_4$, and the solvent was removed in vacuo to yield **10** as a white solid in 75% yield (694 mg). ^{1}H NMR (CD_3OD): δ 7.06−7.21 (m, 5H), 6.80−6.85 (m, 2H), 6.68−6.71 (m, 1H), 5.70−5.72 (m, 2H), 4.55−4.62 (m, 1H), 4.37−4.39 (m, 4H), 4.07−4.10 (m, 4H), 3.78−3.82 (m, 4H), 3.08−3.15 (m, 1H), 2.89−2.93 (m, 1H), 2.70−2.74 (m, 2H), 2.38−2.44 (m, 2H). ^{13}C NMR (CD_3OD): δ 175.73, 174.01, 149.53, 147.88, 137.88, 135.17, 130.10, 130.00, 129.50, 128.53, 126.83, 121.60, 115.30, 115.18, 71.25, 70.97, 68.34, 68.21, 67.61, 54.90 37.98, 37.79, 31.43. IR (KBr pellet): 3310, 3030, 2926, 2864, 2584, 1732, 1649, 1514, 1451, 1426, 1265, 1228, 1161, 1135, 1047, 974, 912, 808, 741, 699 cm^{-1}. HRMS (FAB): calcd for $(MNa)^+$ 492.1998; found 492.2020.

Polymer Synthesis. (a) General Procedure for the Polymerization of Crown Ethers. Polymers were synthesized according to literature procedure[8] where in a nitrogen-filled drybox a solution of complex **1** in CH_2Cl_2 (to give a final monomer concentration of 1.2 M) was added to the monomer (homopolymers) or a mixture of monomers (copolymers), and the reaction mixture was stirred at room temperature for 5 h. The initial [M]/[C] was 100. The polymerizations were terminated by ethyl vinyl ether, and the solutions were stirred for an additional 15−30 min. The polymers were precipitated into cold ether, stirred for 15 min, centrifuged, washed with cold ether (3×), and dried under vacuum. Deviations from this literature procedure are noted in specific cases below. Data not reported within the text are also reported below.

(b) Polymerization of 3 with Various [M]/[C] (11). The typical procedure given above was followed, except a polymerization time of 4 h was used and [M]/[C] was varied between 25 and 4000. ^{1}H NMR ($CDCl_3$): δ 5.78−5.81 and 5.70−5.73 (trans and cis, both m, 2H), 4.08−4.09 and 4.00−4.02 (trans and cis, both m, 4H), 3.56−3.66 (m, 12H). IR: 3570, 2864, 1457, 1353, 1296, 1249, 1114, 979, 881, 855 cm^{-1}.

(c) Hydrogenation of 11. The hydrogenation of **11** was undertaken using Crabtree's catalyst (2.5 mol %) according to literature procedure.[27] ^{1}H NMR ($CDCl_3$): δ 3.54−3.63 (m, 12H), 3.43−3.46 (m, 4H), 1.59−1.63 (m, 4H). IR: 3926, 2866, 1479, 1449, 1351, 1297, 1247, 1115, 844 cm^{-1}.

(d) Homopolymerization of 8 (12e). The typical procedure given above was followed, except that the initial monomer concentration was 0.7 M. ^{1}H NMR ($CDCl_3$): δ 6.90−6.91 (bm, 4H), 5.82−5.84 and 5.73−5.76 (trans and cis, both bm, 2H), 4.13−4.17 (bm, 4H), 4.08−4.09 (bm, 4H), 3.77−3.81 (bm, 4H). IR: 3419, 2922, 2865, 2350, 2331, 1589, 1500, 1440, 1251, 1218, 1124, 1054, 1033, 744 cm^{-1}.

(e) Copolymerizations of 3 and 8 (12a−d). The typical procedure given above was followed. For the following data, shifts are the same for all copolymers, but peak resonances vary in intensity according to percent incorporation of the comonomers. ^{1}H NMR (CD_2Cl_2): δ 6.90 (bs), 5.79−5.84 and 5.69−5.73 (trans and cis, both bm), 4.13−4.14 (bm), 4.05−4.07 (bm), 3.98−3.99 (bm), 3.76−3.79 (bm), 3.56−3.58 (bm). IR: 3474, 2921, 2864, 1591, 1501, 1452, 1354, 1253, 1217, 1115, 1030, 977, 930 cm^{-1}.

(f) Homopolymerization of 9 (13e). The typical procedure given above was followed, except that [M]/[C] = 50 was used. ^{1}H NMR (CD_2Cl_2): δ 7.20−7.22 (bm, 3H), 6.95−6.97 (bm, 2H), 6.66−6.79 (bm, 3H), 6.02 (bs, 1H), 5.77−5.83 and 5.68−5.73 (trans and cis, both bm, 2H), 4.74−4.80 (bm, 1H), 3.98−4.13 (bm, 8H), 3.70−3.73 (bm, 4H), 3.64 (bs, 3H), 2.99−3.02 (bm, 2H), 2.76−2.81 (bm, 2H), 2.36−2.42 (bm, 2H). IR: 3294, 2922, 2859, 1741, 1651, 1510, 1451, 1429, 1356, 1261, 1216, 1134, 1116, 1030, 980, 745, 700 cm^{-1}.

(g) Copolymerizations of 3 and 9 (13a−d, f). The typical procedure given above was followed, except that for **13f**, [M]/[C] = 25, the initial monomer concentration was 0.8 M, and the polymerization proceeded for 1 week. For the following data, shifts are the same for all copolymers, but peak resonances vary in intensity according to percent incorporation of the comonomers. ^{1}H NMR (CD_2Cl_2): δ 7.23−7.25 (bm), 6.97−6.99 (bm), 6.69−6.82 (bm), 5.95 (bs), 5.77−5.84 and 5.67−5.74 (trans and cis, both bm), 4.76−4.82 (bm), 4.06−4.12 (bm), 3.98−3.99 (bm), 3.75−3.76 (bm), 3.67 (bs), 3.54−3.58 (bm), 3.03−3.05 (bm), 2.79−2.83 (bm), 2.39−2.44 (bm). IR: 3538, 3303, 2922, 2868, 1741, 1664, 1510, 1451, 1352, 1261, 1220, 1116, 1026, 980, 750, 700 cm^{-1}.

(h) Polymers 13a−e Subjected to Catalyst 1. The typical procedure given above was followed except that **1** was reacted with polymer ([repeat unit]/[C] = 25), the initial polymer concentration was 2.4 M (per repeat unit), and the reaction time was 1 week. The characterization was identical to that given for polymers **13a**−**e** above.

(i) Copolymerization of 3 and 10. The typical procedure given above was followed except that a [M]/[C] = 50 was used. The copolymerization containing a feed of 8 mol % **10** was conducted at 35 °C. ^{1}H NMR (CD_2Cl_2): δ 7.20−7.25 (bm), 7.02−7.07 (bm), 6.68−6.83 (bm), 5.77−5.80 and 5.68−5.70 (trans and cis, both bm), 4.68−4.78 (bm), 4.05−4.06 (bm), 3.98−3.99 (bm), 3.75−3.77 (bm), 3.56−3.58 (bm), 3.04−3.07 (bm), 2.79−2.83 (bm), 2.39−2.44 (bm). IR: 3321, 2864, 1732, 1654, 1514, 1451, 1353, 1259, 1114, 1031, 974, 875, 850, 744, 706 cm^{-1}.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant CHE-9809856) and the National Institute of Health (Grant GM 3133213) for funding of this research. Dr. Michael J. Marsella is thanked for his contributions to the initial parts of this work. Dr. Delwin L. Elder and Dr. David M. Lynn are thanked for their critical reading of this manuscript.

References and Notes

(1) (a) Clinton, N.; Matlock, P. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. C., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1986; Vol. 6, pp 225−273. (b) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley-Interscience: New York, 1991.

(2) Harris, J. M., Ed. *Poly(ethylene glycol) Chemistry, Biotechnical and Biomedical Applications*; Plenum Press: New York, 1992.

(3) Harris, J. M., Zalipsky, S., Eds. *Poly(ethylene glycol) Chemistry and Biological Applications*; American Chemical Society: Washington, DC, 1997.

(4) For a review of polymeric drug delivery, see: Langer, R. *Nature* **1998**, *392*, 5−10.

(5) For examples see: Body, R. W.; Kyllingstad, V. L. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. C., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1986; Vol. 6, pp 307−322 and references therein.

(6) (a) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039−2041. (b) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110.

(7) (a) Wagener, K. B.; Brzezinska, K. *Macromolecules* **1991**, *24*, 5273−5277. (b) Wagener, K. B.; Brzezinska, K.; Bauch, C. G. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 74−81.
(8) Marsella, M. J.; Maynard, H. D.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1101−1103.
(9) Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 784−790.
(10) (a) Fraser, C.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 7248−7255. (b) Nomura, K.; Schrock, R. R. *Macromolecules* **1996**, *29*, 540−545. (c) Manning, D. D.; Hu, X.; Beck, P.; Kiessling, L. L. *J. Am. Chem. Soc.* **1997**, *119*, 3161−3162. (d) Kanai, M.; Mortell, K. H.; Kiessling, L. L. *J. Am. Chem. Soc.* **1997**, *119*, 9931−9932.
(11) Gibson, V. C.; Marshall, E. L.; North, M.; Robson, D. A.; Williams, P. *Chem. Commun.* **1997**, 1095−1096.
(12) Biagini, S. C. G.; Gibson, V. C.; Giles, M. R.; Marshall, E. L.; North, M. *Chem. Commun.* **1997**, 1097−1098.
(13) (a) Coles, M. P.; Gibson, V. C.; Mazzariol, L.; North, M.; Teasdale, W. G.; Williams, C. M.; Zamuner, D. *J. Chem. Soc., Chem. Commun.* **1994**, 2505−2506. (b) Biagini, S. C. G.; Coles, M. P.; Gibson, V. C.; Giles, M. R. Marshall, E. L.; North, M. *Polymer* **1998**, *39*, 1007−1014. (c) Biagini, S. C. G.; Davies, R. G.; Gibson, V. C.; Giles, M. R.; Marshall, E. L.; North, M.; Robson, D. A. *Chem. Commun.* **1999**, 235−236.
(14) Miller, S. J.; Kim, S.-H.; Chen, Z. −R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 2108−2109.
(15) Ether was more effective than hexanes for the precipitation removal of residual catalyst and monomer.
(16) For a review of Crabtree's catalyst see: Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331−339.
(17) Typically, poly(ethylene glycol) refers to polymers with molecular weights below 20 000 and poly(ethylene oxide) refers to higher molecular weights above 100 000. The upper molecular weight limit for poly(ethylene glycol)s is due to side reactions during the industrial scale base-catalyzed polymerization of ethylene oxide; see ref 1.
(18) Propagating akylidene degradation could be slowed by the use of some additives such as α,α-dichlorotoluene. The reasons for this are under investigation. Maynard, H. D.; Grubbs, R. H., unpublished results.
(19) McGrath, D. V.; Grubbs, R. H. *Organometallics* **1994**, *13*, 224−235.
(20) Acyclic olefins act as chain transfer agents in ROMP. See: Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, 1997.
(21) (a) Hillmyer, M. A.; Nguyen, S. T.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 718−721. (b) Maughon, B. R.; Morita, T.; Grubbs, R. H. *Macromolecules*, accepted. (c) Bielawski, C. W.; Grubbs, R. H. *Macromolecules*, accepted.
(22) Another explanation for the non-Gaussian molecular weight distributions is that the monomers were forming homopolymers rather than copolymers. However, this is less likely because the T_g scale proportionally between those of the two homopolymers (−59.0 °C for **11** and 24.5 °C for **13e**) as one would expect for the copolymers.
(23) In this case [M]/[C] is the ratio of repeat unit to catalyst concentration.
(24) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.
(25) Maynard, H. D.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 4137−4140.
(26) Mitchell, T. N.; Heesche-Wagner, K. *J. Organomet. Chem.* **1992**, *436*, 43−53.
(27) Stork, G.; Kahne, D. E. *J. Am. Chem. Soc.* **1983**, *105*, 1072−1073.

MA990749Y