Macromolecules **1996,** *29,* 1789−1793 **1789**

Synthesis of ABA Triblock Copolymers of Norbornenes and 7-Oxanorbornenes via Living Ring-Opening Metathesis Polymerization Using Well-Defined, Bimetallic Ruthenium Catalysts

Marcus Weck, Peter Schwab, and Robert H. Grubbs*

Contribution No. 9135 from the Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

Received September 8, 1995; Revised Manuscript Received December 8, 1995[⊗]

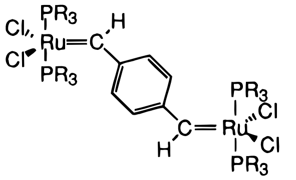
ABSTRACT: Norbornene and 7-oxanorbornene derivatives were polymerized by ring-opening metathesis polymerization (ROMP) in a living manner by employing three new well-defined, bimetallic ruthenium catalysts $(PR_3)_2Cl_2Ru({=}CH\text{-}p\text{-}C_6H_4C(H){=})RuCl_2(PR_3)_2$ [R = Ph, **1**; R = Cy (cyclohexyl), **2**; R = Cyp (cyclopentyl), **3**] as initiators to obtain ABA triblock copolymers with low polydispersities. **1**−**3** were synthesized via alkylidene transfer from 1,4-bis(α-diazomethyl)benzene to $RuCl_2(PPh_3)_3$ and subsequent phosphine exchange. Reactions of 7-oxanorbornenes **5** and **6** or a silicon-containing norbornene **7** with **3** resulted in polymers with low polydispersities ranging from 1.10 to 1.22, while polymerizations initiated by **2** displayed higher polydispersities ranging from 1.20 to 1.35. Polymerizations of **5**−**7** catalyzed by **2** and **3** fulfill the requirements for a living polymerization. However, catalyst **1** is not reactive enough to polymerize functionalized norbornenes or 7-oxanorbornenes. The living polymerizations were successfully used to prepare three ABA triblock copolymers of monomers **5**−**7**. In all cases, these ABA triblock copolymers have higher molecular weights than the homopolymers, and all polydispersities remained low.

Introduction

Triblock copolymers have unique physical properties. Many phase-separated block copolymers behave as thermoplastic elastomers or can be used as semipermeable membranes.[1] Living ring-opening metathesis polymerization (ROMP) has been the subject of numerous studies regarding the preparation of novel block copolymers with special properties and applications.[2,3] Recently, several ABA triblock copolymers synthesized by ROMP have been reported,[3b,g−i,4] which in most cases were obtained via a three-step polymerization. Up to now, only difunctional norbornene initiators were successfully used for the preparation of ABA triblock copolymers in a two-step polymerization.[4] We herein report a two-step ring-opening metathesis polymerization using two bimetallic, well-defined ruthenium catalysts which is living at both chain ends and thus results in the formation of ABA triblock copolymers.

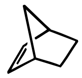
Recently, there has been considerable effort in our group to explore the metathesis activity of well-defined ruthenium complexes, which are generally more tolerant toward polar or functionalized groups than their early transition metal counterparts.[5,6] In the course of our continuing investigations, we developed a new class of ruthenium catalysts $RuCl_2({=}CHR')(PR_3)_2$ (R = Ph, Cy, or Cyp; R′ = (a) $CH{=}CPh_2$; (b) alkyl; (c) aryl) which are highly active for ROMP[6] and ring-closing metathesis (RCM).[7] For R = Cy, Cyp, these catalysts have been shown to induce living polymerization of 7-oxanorbornenes and functionalized norbornenes and have been used in the synthesis of block copolymers.[3f,8]

We now report the synthesis of a series of novel binuclear ruthenium bisalkylidenes $(PR_3)_2Cl_2Ru({=}CH\text{-}p\text{-}C_6H_4C(H){=})RuCl_2(PR_3)_2$ (R = Ph, **1**; R = Cy, **2**; R = Cyp, **3**), which were expected to initiate at both carbene moieties to yield a polymer that is living at both chain ends.

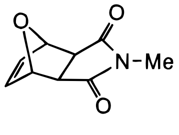


1: R=Ph
2: R=Cy
3: R=Cyp

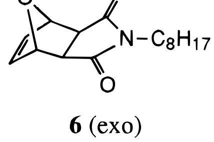
Employing catalysts **1**−**3**, we prepared a series of homopolymers of norbornene **4**, 7-oxanorbornenes **5** and **6**, and a silicon-containing norbornene derivative **7**. Monomer **7** was chosen due to the potential utility of silicon-containing polymers as semiconductors, photoconductors, photoresists, and nonlinear optical materials,[3f,9] while monomers **5** and **6** were chosen due to their hydrophilicity. The present work demonstrates that the above-mentioned alkylidenes are useful catalysts for the polymerization of norbornene, functionalized norbornenes, and functionalized 7-oxanorbornenes to obtain ABA triblock copolymers.



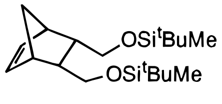
4



5 (exo)



6 (exo)



7 (endo)

Results and Discussion

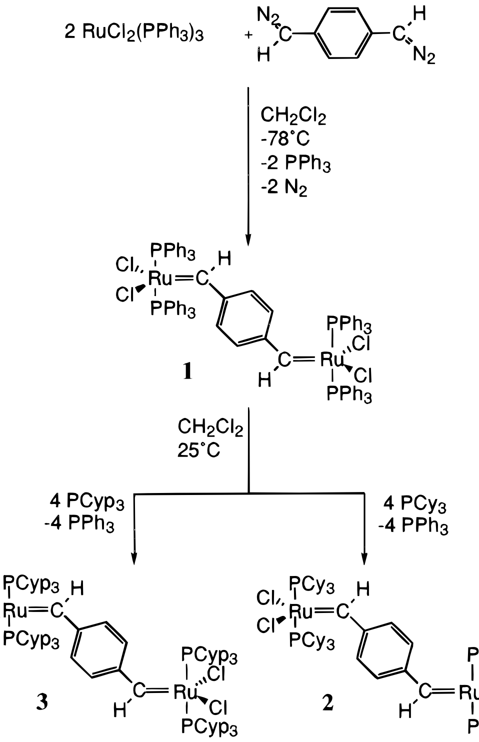
Catalyst Synthesis. Recently, well-defined ruthenium alkylidenes were synthesized, using diazoalkanes as a carbene source[6c,d] which can polymerize functionalized 7-oxanorbornenes and norbornenes in a living manner to generate block copolymers with narrow polydispersities.[8] These results prompted us to use 1,4-

---

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

0024-9297/96/2229-1789$12.00/0

Scheme 1. Preparation of Catalysts 1−3



bis(α-diazomethyl)benzene as a carbene source[10] to generate bisalkylidene ruthenium complexes. Each one consists of two carbene groups which initiate polymerization from both chain ends. The synthesis of $(PR_3)_2Cl_2Ru(=CH\text{-}p\text{-}C_6H_4C(H)=)RuCl_2(PR_3)_2$ (R = Ph, **1**; R = Cy, **2**; R = Cyp, **3**) is illustrated in Scheme 1.

$RuCl_2(PPh_3)_3$[12] was treated with 1,4-bis(α-diazomethyl)benzene at −78 °C in dichloromethane to form **1** as an air-stable green solid in 91% yield. Treatment of **1** with 4 equiv of tricyclohexylphosphine at room temperature resulted in the formation of **2**, which was isolated as an air-stable orange-brown solid in 93% yield. Previous results showed that the phosphine exchange of $RuCl_2(=CHPh)(PCy_3)_2$ (**8**) with $PCyp_3$ yielded an air-stable catalyst $RuCl_2(=CHPh)(PCyp_3)_2$ (**9**) which exhibited a higher solubility in organic solvents than **8** or $RuCl_2(=CHPh)(PPh_3)_2$ (**10**).[6c,d] Similarly, we found an increased solubility of **3**, which was obtained by phosphine exchange of **1** with tricyclopentylphosphine as a tan solid in 93% yield.

Homopolymerizations. Homopolymerizations were examined with each monomer (**4**−**7**) in dichloromethane at room temperature. All reactions were accompanied by a characteristic color change from brown to orange or red, which indicates complete initiation. The degree of initiation can also be judged by the appearance of a new propagating species in the NMR simultaneously with the disappearance of the initiating species. For example, in the polymerization of **5** catalyzed by **3**, the propagating species (18.82 ppm (t)) is clearly distinguished from the initiating species (20.64 ppm (s)). The polymerizations were terminated by adding ethyl vinyl ether. We found that catalyst **1** can quantitatively polymerize norbornene at room temperature in dichloromethane (PDI = 1.15, M_n (number-average molecular weight) = 65 000).[14] However, it is not sufficiently reactive to polymerize 7-oxanorbornenes and functionalized norbornenes, as already observed for its mononuclear analog **10**.[6c,d]

Table 1. ROMP of 7-Oxanorbornenes (5, 6) and Functionalized Norbornene (7) with $(PR_3)_2Cl_2Ru(=CH\text{-}p\text{-}C_6H_4\text{-}C(H)=)RuCl_2(PR_3)_2$ (R = Cy, 2; R = Cyp, 3) in CH_2Cl_2 at Room Temperature

catalyst	monomer	time (min)	yield (%)	[M]/[C]	$10^{-4}M_w$	$10^{-4}M_n$	PDI
2	**5**	25	>98	89	2.47	1.83	1.35
2	**7**	30	>98	130	4.86	4.05	1.20
3	**5**	25	>98	98	1.86	1.69	1.10
3	**7**	30	>98	96	5.55	4.65	1.19
3	**6**	30	>98	62	1.70	1.55	1.10

In contrast to **10**, ruthenium alkylidenes **8** and **9** were found to polymerize 7-oxanorbornenes and functionalized norbornenes in a living fashion, but, due to chain transfer and back-biting, the formation of monodisperse polymers with norbornene itself was not possible.[3f,6c,d,8] Encouraged by these results, we examined the ROMP of 7-oxanorbornenes and functionalized norbornenes using catalyst **2** or **3**. As expected, both catalysts polymerized monomers **5**−**7** in a living manner. As observed with the ROMP of norbornene with **8**, no monodisperse polymers are obtained by the polymerization of norbornene. Catalyst **2** polymerizes monomers **5** and **7** in quantitative yields with polydispersities between 1.20 and 1.35 (Table 1). This is comparatively high for the living polymerization of 7-oxanorbornenes, as in the case of monomer **5**, and can be explained as a change in the rates of initiation and propagation. Since polydispersity is to some extent controlled by the relative rates of initiation (k_i) and propagation (k_p), narrow PDIs are obtained if the initiation rate is in the range of the propagation rate or faster. We believe that the relatively high PDI of the product obtained by the polymerization of monomer **5** with catalyst **2** stems from a larger value for k_i/k_p than for the other systems. In the case of the polymerization of **5** catalyzed by **3**, full initiation observed by NMR was achieved after 1 min, while in the case of the polymerization of **5** with **2** the initiation slowed down and took up to 10 min. This results in a complex which starts to propagate on one chain end while the other carbene unit of the catalyst has not completed initiation, leading to a polymer with a higher PDI.

In contrast to complex **2**, catalyst **3** can quantitatively polymerize monomers **5**−**7** to produce polymers with lower PDIs (for example, 1.10 for the polymerization of **5** or **6**, or 1.19 for the polymerization of **7**). Table 1 summarizes the GPC results of the homopolymers obtained from the reactions with initiators **2** and **3**.

Controlled molecular weights, high efficiency of the catalyst, and absence of chain transfer and termination are characteristics of a living ring-opening metathesis polymerization system. Quirk and Lee proposed several experimental criteria for the characterization of living polymerizations.[11] One of the main criteria of living polymerization is that the molecular weight should be controlled by the stoichiometry of the reaction, which can be shown by the linear relationship between M_n and the corresponding monomer/catalyst ([M]/[C]) feed ratios. Figure 1 shows these linear relationships for various homopolymers prepared with complexes **2** and **3**.

Another fundamental criterion for living polymerization is that the polymerization to proceed until all monomer is consumed.[11] Further addition of monomer must result in continued polymerization to produce a homopolymer with a higher molecular weight, or a block copolymer when a different monomer is used; i.e., the

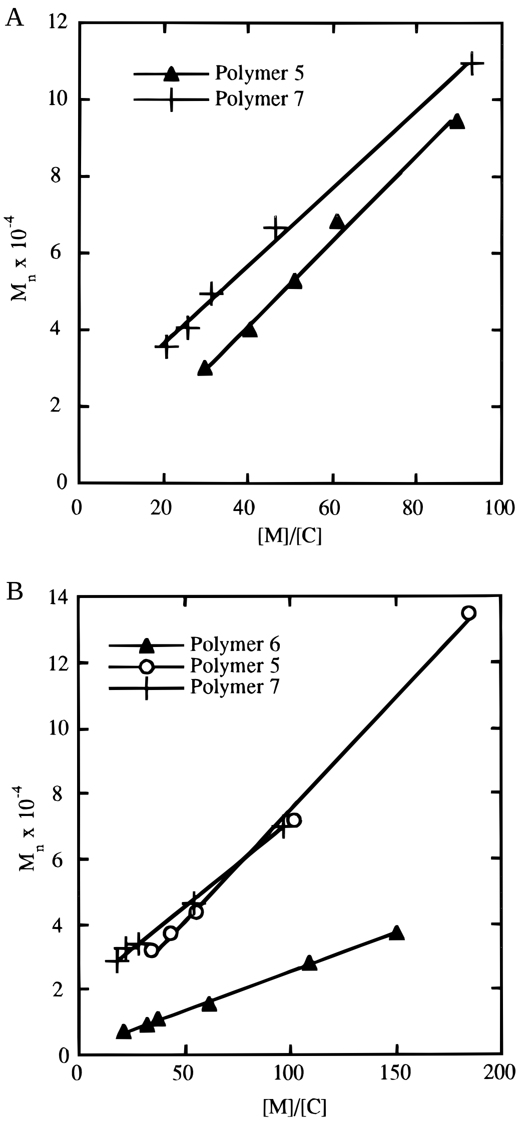


Figure 1. Plot of number-average molecular weight (M_n) versus monomer/catalyst ratio ([M]/[C]): (A) for polymers obtained from catalyst **2** at room temperature in CH_2Cl_2; (B) for polymers obtained from catalyst **3** at room temperature in CH_2Cl_2.

polymerization proceeds in the absence of chain termination and chain transfer. To demonstrate this criterion, a two-step polymerization using monomer **5** and catalyst **3** was carried out. Monomer **5** was polymerized until polymer growth stopped, the polymerization was allowed to sit for 4 h, and a second aliquot of **5** was added to the reaction. After 30 min, the polymerization was terminated with ethyl vinyl ether. The molecular weight increased dramatically for the final polymer relative to the first peak, and no residual base polymer was observed. Both chain termination and chain transfer would produce dead polymer, which will not increase in molecular weight upon addition of more monomer. The PDI increased moderately from 1.10 to 1.20 while the PDI for the first block, after sitting for 4 h, remained at 1.10. This clearly demonstrates the absence of chain transfer and chain termination, supporting the living character of the system. Figure 2 shows the GPC traces of the first and the second polymers.

Block Copolymerizations. The living polymerizations catalyzed by **2** or **3** were applied to ABA block copolymerizations of **5** with **6** or **7**. In all cases, **5** was polymerized to completion, followed by addition of either **6** or **7**. The polymerization was terminated by adding ethyl vinyl ether. Several polymerizations were monitored by GPC analysis of samples taken from the reaction mixture after the first monomer had been consumed. The ^{1}H NMR spectra of the triblock copolymers show the peaks corresponding to the homopolymers of the monomers.[15] Scheme 2 illustrates the ABA triblock copolymerization of monomers **5** and **7** with catalyst **2**.

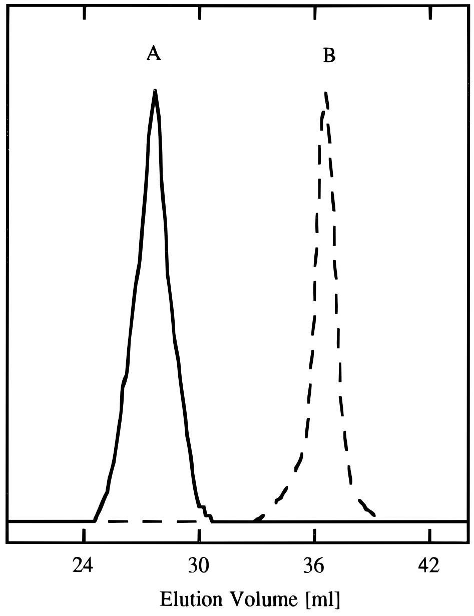


Figure 2. Gel permeation chromatograph traces for polymers obtained from **5** initiated by **3**. The peaks represent (B) polymer after complete incorporation of the monomer (PDI = 1.10) and (A) polymer after standing for 4 h and then continued polymerization of additional monomer (PDI = 1.20).

The polydispersity of the triblock copolymers ranged from 1.38 to 1.50 depending on the molecular weight, and the polydispersities decreased as the molecular weight of the polymers increased over the range from 100 000 to 250 000.[14] The lowest polydispersity was achieved for the block copolymerization of monomers **5** and **6** using catalyst **3**. For example, the molecular weight increased from 27 000 for the homopolymer of **5** to 43 000 for the copolymer,[14] while the polydispersity increased slightly from 1.10 to 1.11 (Figure 3).

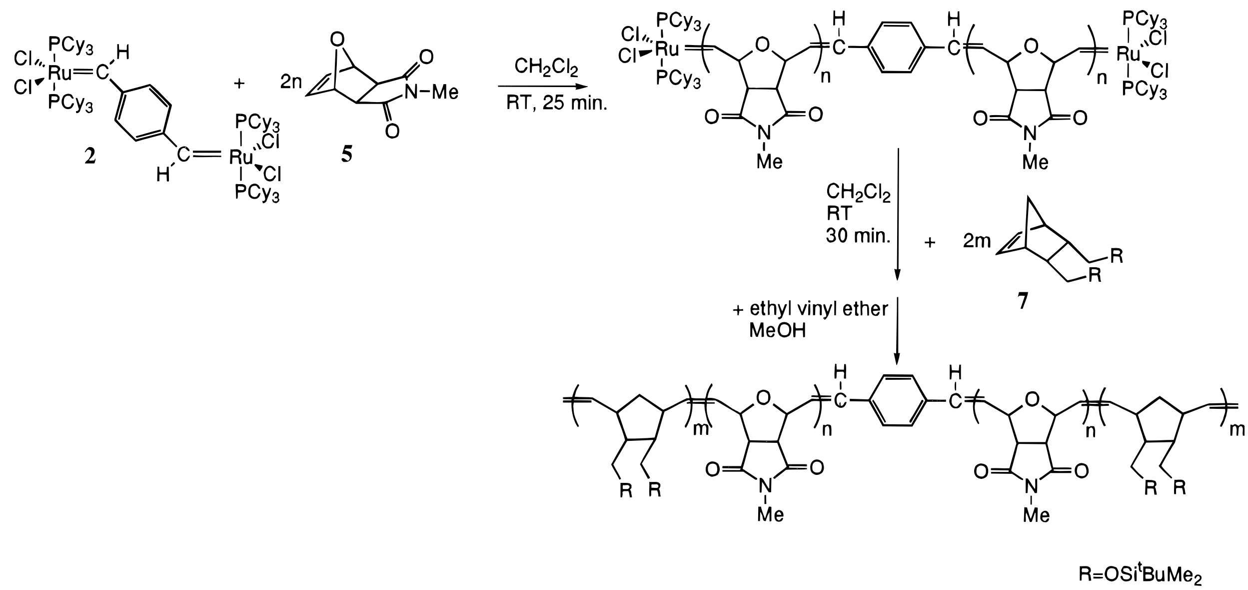
The synthesis of a triblock copolymer based on monomers **5** and **7** with initiator **3** was also examined. The resulting triblock copolymer had a higher molecular weight (M_n = 133 000) compared to the homopolymer of **5** (M_n = 100 000) and the polydispersities ranged from 1.26 to 1.28.[14] In all cases, the polymerizations were terminated prior to quantitative incorporation of the second monomer. Table 2 summarizes the GPC results of the triblock copolymers obtained.

In conclusion, we have demonstrated the living ring-opening metathesis polymerization of 7-oxanorbornenes (**5**, **6**) and functionalized norbornenes (**7**) with two bimetallic ruthenium catalysts. This living polymerization can be used for the preparation of ABA triblock copolymers. Examination of the physical properties and the morphologies of these ABA triblock copolymers is currently under investigation.

Experimental Section

General Procedures. All polymerizations and manipulations of air-sensitive compounds were carried out in an N_2-filled drybox or using standard Schlenk or vacuum line

Scheme 2. Preparation of the ABA Triblock Copolymer of Monomers 5 and 7 Initiated by 2



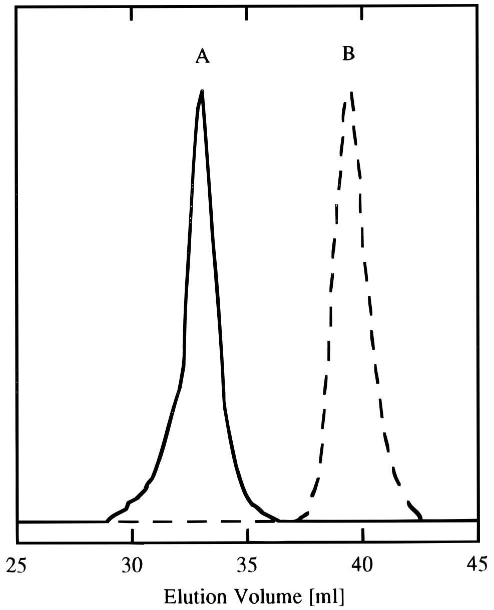


Figure 3. Molecular weight distribution curves of (A) the ABA triblock copolymer resulting from the successive polymerization of **5** and **6** with **3** and (B) precursor poly(7-oxanorbornene) obtained by the polymerization of **5** with **3**.

Table 2. ABA Triblock Copolymer of 7-Oxanorbornenes (5, 6) and Functionalized Norbornene (7) with $(PR_3)_2Cl_2Ru(=CH\text{-}p\text{-}C_6H_4C(H)=)RuCl_2(PR_3)_2$ (R = Cy, 2; R = Cyp, 3)

catalyst	first monomer	second monomer	$[M_1]/[M_2]/[C]$	$10^{-4}M_w$	$10^{-4}M_n$	PDI
2	**5**	**7**	189/137/1	18.25	10.87	1.38
3	**5**	**7**	200/112/1	13.35	10.62	1.26
3	**5**	**6**	216/116/1	10.27	9.35	1.11

techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å molecular sieves. ^1H NMR spectra were recorded on a JEOL GX-400 MHz (399.65 MHz ^1H), a QE Plus-300 MHz (299.7 MHz ^1H; 161.9 MHz ^{31}P) or a Bruker AM 500 (500.1 MHz ^1H; 125.8 MHz ^{13}C) spectrometer at 20 °C. Gel permeation chromatographs were obtained on a HPLC system utilizing an Altex Model 110A pump, a Rheodyne Model 7125 injector with a 100-μL injection loop, through an American Polymer Standards 10-μm mixed-bed column, and a Knauer differential refractometer. All GPC analyses were performed on a 0.5% w/v solution of polymer in dichloromethane. Calibration was based on polystyrene standards.

Materials. Monomers **5** and **7** were synthesized according to published procedures.[3f,13] Dichloromethane was distilled from calcium hydride and degassed by repeated freeze−pump−thaw cycles. Norbornene was dried over sodium, vacuum transferred, and stored under argon. All other solvents and compounds were used without further purification unless otherwise noted.

Synthesis of $(PPh_3)_2Cl_2Ru(=CH\text{-}p\text{-}C_6H_4C(H)=)RuCl_2(PPh_3)_2$ (1). A solution of $RuCl_2(PPh_3)_3$[12] (327 mg, 0.34 mmol) in dichloromethane (10 mL) was treated at −78 °C with a −50 °C solution of 1,4-bis(α-diazomethyl)benzene[10] (27 mg, 0.17 mmol, 0.5 equiv) in dichloromethane (3 mL). A spontaneous color change from orange-brown to brown-green and vigorous bubbling were observed. The solution was allowed to warm to −20 °C within 10 min, and then the solvent was removed. The residue was suspended in dichloromethane (10 mL), and pentane (20 mL) was added to precipitate a green solid. The mother liquid was separated via cannula filtration, and the residue was redissolved and reprecipitated. This procedure was repeated until the mother liquid was almost colorless. The remaining green microcrystalline solid was dried under vacuum for several hours. Yield = 232 mg (91%). ^1H NMR (CD_2Cl_2): δ 19.40 (t, J_{PH} = 10.8 Hz, Ru=CH), 7.85−7.64 and 7.10−6.80 (both m, C_6H_4 and $P(C_6H_5)_3$). ^{31}P NMR (CD_2Cl_2): δ 27.70 (s, PPh_3). Anal. Calcd for $C_{80}H_{66}Cl_4P_4Ru_2$: C, 64.26; H, 4.45. Found: C, 64.65; H, 4.43.

Synthesis of $(PCy_3)_2Cl_2Ru(=CH\text{-}p\text{-}C_6H_4C(H)=)RuCl_2(PCy_3)_2$ (2). A solution of **1** (213 mg, 0.14 mmol) in dichloromethane (20 mL) was treated with a solution of tricyclohexylphosphine (178 mg, 0.64 mmol, 4.4 equiv) in dichloromethane (5 mL) and stirred at room temperature for 1 h, during which a gradual color change from brown-green to red was observed. The solvent was removed under vacuum, and the residue was repeatedly washed with acetone and diethyl ether (10 mL portions) and dried *in vacuo*. An orange-brown microcrystalline solid was obtained. Yield 210 mg (93%). ^1H NMR (CD_2Cl_2): δ 20.36 (s, Ru=CH), 7.32−7.28 (m (br), C_6H_4), 2.66−2.58, 1.78−1.68, 1.48−1.39 and 1.22−1.15 (all m, $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 293.98 (t, J_{PC} = 9.5 Hz, Ru=CH), 150.41 (s, *ipso*-C of C_6H_4), 132.17 (s, C_6H_4), 32.56 (*pseudo*-t, J_{app} = 8.9 Hz, *ipso*-C of $P(C_6H_{11})_3$), 30.07 (s, *m*-C of $P(C_6H_{11})_3$), 28.15 (*pseudo*-t, J_{app} = 4.9 Hz, *o*-C of $P(C_6H_{11})_3$), 26.94 (s, *p*-C of $P(C_6H_{11})_3$). ^{31}P NMR (CD_2Cl_2): δ 35.80 (s, PCy_3). Anal. Calcd for $C_{80}H_{138}Cl_4P_4Ru_2$: C, 61.29; H, 8.87. Found: C, 60.73; H, 8.40.

Synthesis of $(PCyp_3)_2Cl_2Ru(=CH\text{-}p\text{-}C_6H_4C(H)=)RuCl_2(PCyp_3)_2$ (3). **3** is obtained in analogy to **2** as a tan microcrystalline solid, using **1** (726 mg, 0.49 mmol) and tricyclopentylphosphine (516 mg, 2.17 mmol, 4.4 equiv). Yield 638 mg (93%). ^{1}H NMR (CD_2Cl_2): δ 20.64 (s, Ru=CH), 8.45 (s, C_6H_4), 2.67−2.61, 1.81−1.76, 1.63−1.59 and 1.51−1.46 (all m, $P(C_5H_9)_3$). ^{13}C NMR (CD_2Cl_2): δ 299.55 (t, J_{PC} = 7.6 Hz, Ru=CH), 150.70 (s, *ipso*-C of C_6H_4), 132.27 (s, C_6H_4), 35.66 (*pseudo*-t, J_{app} = 10.9 Hz, *ipso*-C of $P(C_5H_9)_3$), 30.02 and 26.42 (both s, $P(C_5H_9)_3$). ^{31}P NMR (CD_2Cl_2): δ 29.54 (s, $PCyp_3$). Anal. Calcd for $C_{68}H_{114}Cl_4P_4Ru_2$: C, 58.36; H, 8.21. Found: C, 58.42; H, 7.79.

Synthesis of *exo*-*N*-Octyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (6). To a solution of *exo*-7-oxabicyclo-[2.2.1]hept-5-ene-2,3-dicarboximide (2 g, 0.012 mol) in dimethylformamide (50 mL), potassium carbonate (5 g, 0.036 mol) was added and the mixture was stirred at 90 °C for 30 min. Bromooctane (2.4 g, 0.012 mol) in dimethylformamide (30 mL) was added dropwise, and the mixture was then stirred at 90 °C for 1 h followed by 3 h at room temperature. The reaction mixture was filtered, and the solution was poured into water (200 mL) and then extracted three times with diethyl ether (200 mL). The organic phase was dried over $MgSO_4$ and evaporated to yield a dark red solution. Final purfication was achived by column chromatography (SiO_2/dichloromethane) to obtain a light red oil (68%). ^{1}H NMR (CD_2Cl_2): δ 6.47 (s,2H), 5.21 (s, 2H), 3.45 (t, 2H, $^3J_{HH}$ = 7.2 Hz), 2.79 (s, 2H), 1.53 (m, 2H), 1.21 (m, 10H), 0.86 (t, 3H, $^3J_{HH}$ = 6.4 Hz). Anal. Calcd for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05. Found: C, 68.71; H, 8.16; N, 4.96.

General Procedure for the Homopolymerizations. In a drybox, the catalyst and the monomer were weighed into vials and dissolved in 1 and 2 mL of dichloromethane, respectively. The reaction was initiated by adding the catalyst solution to the vigorously stirred monomer solution. The solution was stirred at room temperature for 20 min (in the case of monomers **5** and **6**) or for 30 min (in the case of monomer **7**). The polymerization was then quenched by addition of a small amount of ethyl vinyl ether. The reaction mixture was poured into 30−50 mL of methanol to precipitate the polymer. The resulting white polymer was purified by dissolving in dichloromethane and reprecipitating from methanol several times and dried *in vacuo*. The ^{1}H NMR spectra of the homopolymers of monomers **5** and **7** were identical with those previously reported.[3f,13] ^{1}H NMR polymer resulting from **6** (CD_2Cl_2): δ 6.06 (s, br, trans), 5.77 (s, br, cis), 5.00 (s, br, cis), 4.43 (s, br, trans), 3.43 (s, br), 3.28 (s, br), 1.53 (s, br), 1.24 (s, br), 0.85 (t, br). ^{13}C NMR ($CDCl_3$): δ 175.48, 131.88, 130.92, 81.02, 77.92, 53.45, 52.34, 38.94, 31.69, 29.03, 27.59, 26.71, 22.52, 13.95. Anal. Calcd for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05. Found: C, 68.95; H, 8.11; N, 5.11.

General Procedure for Triblock Copolymerization. Monomer **5** was polymerized according to the procedure outlined above. After 25 min, a monomer solution of **6** or **7** was added via a gas-tight syringe, and the solution was stirred vigoursly. After 20 min (in the case of monomer **6**) or 30 min (in the case of monomer **7**) the polymerization was terminated by addition of a small amount of ethyl vinyl ether, and the resulting polymers were purified as outlined above. All ABA triblock copolymers are white, flocculent solids, soluble in dichloromethane and chloroform and stable under air at room temperature. ^{1}H NMR polymer resulting from **5** and **6** (CD_2Cl_2): δ 6.04 (s, br, trans), 5.78 (s, br, cis), 5.00 (s, br, cis), 4.44 (s, br, trans), 3.43 (s, br), 3.28 (s, br), 1.53 (s, br), 1.24 (s, br), 0.85 (t, br). ^{13}C NMR ($CDCl_3$): δ 175.48, 131.88, 130.92, 81.02, 77.92, 53.45, 52.34, 38.94, 31.69, 29.03, 27.59, 26.71, 22.52, 13.95. Anal. Calcd for $C_{42.4}H_{66.7}N_2O_{8.3}Si_{2.3}$ (entry 2 in Table 2): C, 63.45; H, 8.33; N, 3.50. Found: C, 62.61; H, 8.05; N, 3.78. ^{1}H NMR polymer resulting from **5** and **7** (CD_2Cl_2): δ 6.06 (s, br, trans), 5.81 (s, br, cis), 5.48 (s, br, trans), 4.95 (s, br, cis), 4.49 (s, br, trans), 3.68 (s, br), 3.63 (s, br), 2.96 (s, br), 1.55 (s, br) , 0.90 (s, br), 0.11 (s, br). ^{13}C NMR ($CDCl_3$): δ 175.42, 131.67, 130.80, 77.23, 80.61, 53.25, 52.14, 38.72, 31.46, 28.77, 28.81, 27.38, 26.56, 24.79, 22.30, 13.74. Anal. Calcd for $C_{19}H_{23}N_{1.6}O_5$ (entry 3 in Table 2): C, 64.49; H, 6.52; N, 6.45. Found: C, 63.95; H, 6.49; N, 6.53.

Acknowledgment. This work was supported by the National Science Foundation. P.S. thanks the Alexander von Humboldt Foundation for a Feodor Lynen postdoctoral fellowship. We are especially grateful to David Lynn for helpful comments.

References and Notes

(1) Noshay, A.; McGrath, J. E. *Block Copolymers*; Academic Press: New York, 1977.

(2) For a survey of catalysts and monomers used in ring-opening methathesis polymerization, see: (a) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907. (b) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (c) Breslow, D. S. *Prog. Polym. Sci.* **1993**, *18*, 1141. (d) Leconte, M.; Basset, J. M.; Quignard, F.; Larroche, C. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; Vol 1, p 371 and references therein.

(3) (a) Grubbs, R. H.; Risse, W.; Novak, B. M. *Adv. Polym. Sci.* **1992**, *102*, 47. (b) Risse, W.; Grubbs, R. H. *J. Mol. Catal.* **1991**, *65*, 211. (c) Bazan, G. C.; Schrock, R. R.; Cho, H. N.; Gibson, V. C. *Macromolecules* **1991**, *24*, 4495. (d) Feast, W. J.; Gibson, V. C.; Ivin, K. J.; Khosravi, E.; Kenwright, A. M. *Makromol. Chem.* **1992**, *193*, 2103. (e) Wu, Z.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 3502. (f) Kanaoka, S.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 4707. (g) Craig, G. S. W.; Cohen, R. E.; Schrock, R. R.; Silbey, R. J.; Puccetti, G.; Ledoux, I.; Zyss, J. J. *J. Am. Chem. Soc.* **1993**, *115*, 860. (h) Craig, G. S. W.; Cohen, R. E.; Schrock, R. R.; Esser, A.; Schrof, W. *Macromolecules* **1995**, *28*, 2512. (i) Wu, Z.; Grubbs, R. H. *Macromolecules* **1994**, *27*, 6700.

(4) (a) Risse, W.; Grubbs, R. H. *Macromolecules* **1989**, *22*, 4462. (b) Risse, W.; Wheeler, D. R.; Canizzo, L. F.; Grubbs, R. H. *Macromolecules* **1989**, *22*, 3205.

(5) (a) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (b) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring Opening Polymerization of Cyclo-Olefins*, 2nd ed.; Wiley-Interscience: New York, 1985.

(6) (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974. (b) Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9858. (c) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039. (d) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.*, submitted for publication.

(7) (a) Kim, S.-H.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801. (b) Miller, S. J.; Kim, S.-H.; Chen, Z. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 2108. (c) Miller, S. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 5855. (d) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5426. (e) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 7324. (f) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 3800. (g) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856. (h) Fujimura, O.; Fu, G. C.; Grubbs, R. H. *J. Org. Chem.* **1994**, *59*, 4029. (i) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446.

(8) Weck, M.; Grubbs, R. H., unpublished results.

(9) (a) Zeigler, J. M.; Fearon, F. W. G., Eds. *Silicon-Based Polymer Science: A Comprehensive Resource*; American Chemical Society: Washington, DC, 1990. (b) Kornfield, J., unpublished results.

(10) Murray, R. W.; Trozzolo, A. M. *J. Org. Chem.* **1964**, *29*, 1268.

(11) (a) Quirk, R. P.; Lee, B. *Polym. Int.* **1992**, *27*, 359. (b) Webster, O. W. *Science* **1991**, *251*, 887 and references therein. (b) For living ROMP: Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.

(12) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945.

(13) Hillmyer, M. A.; Lepetit, C.; McGrath, D. V.; Novak, B. M.; Grubbs, R. H. *Macromolecules* **1992**, *25*, 3345.

(14) All molecular weights were calculated relative to polystyrene standards with no further corrections.

(15) The ^{1}H NMR spectra of the homopolymers of monomer **5** and **7** have been reported previously.[3f,10]

MA9513426