Macromolecules **1995,** *28,* 4707−4713

Synthesis of Block Copolymers of Silicon-Containing Norbornene Derivatives via Living Ring-Opening Metathesis Polymerization Catalyzed by a Ruthenium Carbene Complex[†]

Shokyoku Kanaoka 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 January 31, 1995[®]

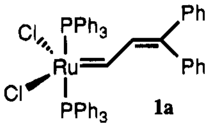
ABSTRACT: Block copolymers (**5**) of silicon-containing norbornene derivatives were prepared using living ring-opening metathesis polymerization (ROMP) with a well-defined ruthenium carbene complex [**1**, $(R_3P)_2Cl_2Ru{=}CHCH{=}CPh_2$: **1a**, R = phenyl; **1b**, R = cyclohexyl]. For example, the living polymerization of norbornene **2a** (NBE) by **1a** was carried out at room temperature in a mixture of methylene chloride and 1,2-dichloroethane. After 3 h, the polymer isolated had a narrow molecular weight distribution (MWD) ($\bar{M}_n = 58\,000$, $\bar{M}_w/\bar{M}_n = 1.20$). On addition of a silicon-containing norbornene derivative (**4**), polymerization immediately ensued at 50 °C from the living ends of **3** and afforded a block copolymer **5a**. The MWD curve of the resulting block polymer **5a** shifted toward the higher molecular weight region, and the polydispersity remained narrow ($\bar{M}_n = 129\,000$, $\bar{M}_w/\bar{M}_n = 1.25$). The segment ratio ($m{:}n = 1.86$) of **5a** determined by ^1H NMR was in good agreement with the calculated value ($m{:}n = 1.78$). Silicon-containing block copolymers with polar functional groups were also synthesized by ROMP with **1b**.

Introduction

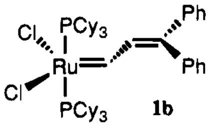
Silicon-containing polymers (homopolymers, block copolymers, and end-functionalized polymers) have interesting properties (gas permeability etc.) and also offer potential as semiconductor, photoconductor, and nonlinear optical materials.[1] An interesting possible application has been proposed most recently.[2] Phase separation of block copolymers on a surface (silicon, silicon oxide, etc.) gives a specific pattern where one layer includes a higher proportion of silicon atoms of the copolymer. The pattern can be changed in the nanometer range by varying the length of both segments. This material might be employed as a photoresist with high resolution after the oxidation of silicon in a polymer film.

Block copolymers have been synthesized by various types of living polymerization (anionic, cationic, etc.). In ring-opening metathesis polymerization (ROMP), block copolymers have been also prepared[3] since living polymerization was achieved by a titanium metallacyclobutane complex.[4] However, most of them consist of nonpolar segments,[3] because of the difficulty in preparing living polymers with polar functional groups by early transition metal catalysts. It was not until recently that block copolymers with pendant polar functional groups have been synthesized using a well-defined molybdenum-based catalyst.[5] In contrast to early transition metal complexes, group VIII metals can polymerize cyclic olefins with a variety of functional groups in protic solvents.[6] Our group has shown that ruthenium(II) complexes can polymerize functionalized 7-oxanorbornene derivatives in an aqueous environment.[7]

Recently, a well-defined ruthenium-based carbene complex (**1a**) has been synthesized in our group.[8] Although **1a** is active for the polymerization of NBE, it is not reactive enough to polymerize low-strained cyclic olefins and 7-oxanorbornene derivatives. Recently, a more active catalyst **1b** that has tricyclohexylphosphine ligands instead of triphenyl counterparts was developed in our group.[9] Complex **1b** can polymerize low-strained olefins (cyclooctadiene, substituted cyclooctene) and a 7-oxanorbornene derivative and is also a good catalyst for the metathesis of acyclic olefins.[10] An important feature of **1** is that they are exceptionally tolerant of polar functional groups and are stable in common organic solvents even in the presence of water or alcohol. These findings prompted us to synthesize silicon-containing block copolymers of norbornene and 7-oxanorbornene derivatives with polar functional groups.



1a



1b

The recent synthesis of catalysts **1a** and **1b** provides an excellent opportunity to study the ROMP of functionalized monomers. Catalyst **1b** is too reactive to give monodisperse polymers of norbornene derivatives because of chain transfer and back-biting reactions. In fact, polymerization of NBE was extremely fast and the product polymer had a broad molecular weight distribution (MWD).[9] In this study, the first objective was to study ROMP of functionalized monomers catalyzed by **1**; focusing on determining the optimum reaction conditions for the living ROMP of functionalized norbornene or 7-oxanorbornene derivatives by **1a** or **1b**. The second and major purpose was to examine the synthesis of silicon-containing block copolymers (**5**) by sequentially polymerizing a norbornene derivative (**2**) and a silicon-containing norbornene derivative (**4**) (Scheme 1). The similar synthesis of a block copolymer was also examined with a 7-oxanorbornene derivative (**6**) with an imide group.

Results and Discussion

1. Ring-Opening Metathesis Polymerization (ROMP) of Functionalized Monomers.

Homopolymerization of functionalized monomers was examined with the six norbornene and 7-oxanorbornene derivatives listed in Table 1; **2b**, **4**, **8**, and **9** are *endo* isomers, and **6** and **7** are *exo* isomers. ROMP of these monomers by **1** was carried out in dichloromethane (CH_2Cl_2) at

---

[†] Contribution No. 9050.

[®] Abstract published in *Advance ACS Abstracts,* May 15, 1995.

0024-9297/95/2228-4707$09.00/0

Scheme 1

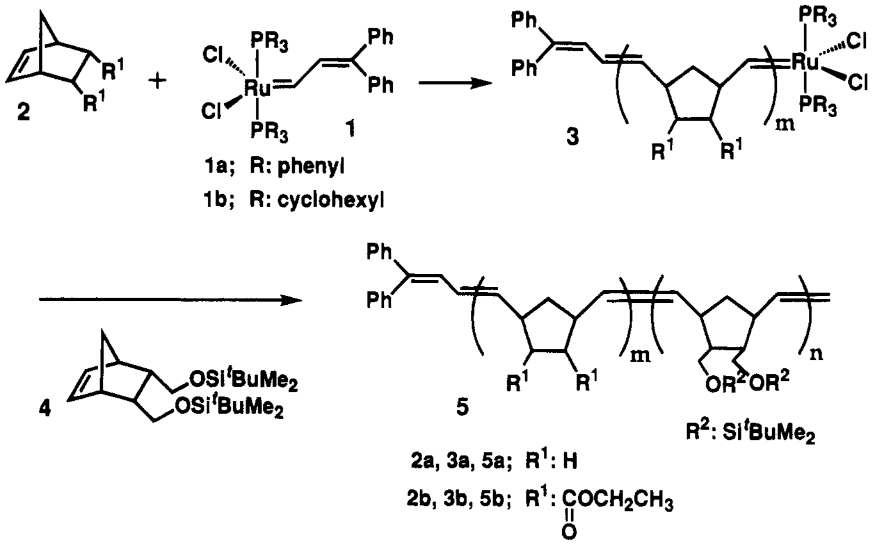
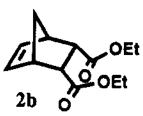
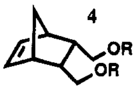
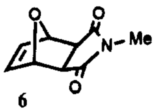
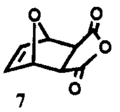
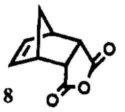
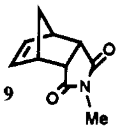


Table 1. Ring-Opening Metathesis Polymerization (ROMP) of Functionalized Norbornene and 7-Oxanorbornene Derivatives by 1

Monomer	Catalyst	Solvent	Temp., °C	[M]/[I][a]	Time, h	Yield, %
 2b	**1a**	$ClCH_2CH_2Cl$	50	149	15	no reaction
	1b	$ClCH_2CH_2Cl$	RT	162	4	26.8
	1b	$ClCH_2CH_2Cl$	50	150	4	95.1
 4 R: Si^{t}BuMe$_2$	**1a**	$ClCH_2CH_2Cl$	60	224[b]	11	87.0
	1b	$ClCH_2CH_2Cl$	RT	128	1	37.0
	1b	$ClCH_2CH_2Cl$	50	115	0.5	89.4
 6	**1a**	$ClCH_2CH_2Cl$	50	139	24	no reaction
	1b	$ClCH_2CH_2Cl$	RT	148	3	89.7
	1b	$ClCH_2CH_2Cl$	50	138	5 min	100
 7	**1a**	CH_2Cl_2	RT	209	8 days	no reaction
	1a	$ClCH_2CH_2Cl$	50	199	18	no reaction
	1b	CH_2Cl_2	RT	194	24	*e*
	1b	$ClCH_2CH_2Cl$	40	220	15	*e*
 8	**1a**	$ClCH_2CH_2Cl$	60	185	24	no reaction
	1b	$ClCH_2CH_2Cl$	50	173	18	*e*
	1b	$ClCH_2CH_2Cl$	50	177	9	*e*
 9	**1a**	CH_2Cl_2	RT	46[c]	48	no reaction
	1b	$ClCH_2CH_2Cl$	50	137[d]	9	36.0

[a] [M]: (**2b** and **6**) 0.26 M; (**4**) 0.20 M; (**7**) 0.38 M; (**8**) 0.32 M. [b] [M] = 0.37 M. [c] [M] = 0.093 M. [d] [M] = 0.25 M. [e] Insoluble products were obtained.

Table 2. ROMP of a Silicon-Containing Norbornene Derivative (4) by 1[a]

cat.	temp, °C	[M]/[I]	time, h	yield, %	$\bar{M}_n \times 10^{-4}$ [b]	$\bar{M}_w \times 10^{-4}$ [b]	PDI[b]
1a	RT	149	15	19.0	0.69	0.86	1.25
1a	60	224[c]	11	87.0	8.24	9.88	1.20
1b	RT	128	1	37.0	5.62	8.36	1.49
1b	40	118	0.5	78.7	3.13	4.15	1.33
1b	50	115	0.5	89.4	3.19	3.83	1.20

[a] Reaction conditions: in $ClCH_2CH_2Cl$ (in CH_2Cl_2 for the polymerization at room temperature by **1a**); [M] = 0.20 M. [b] By size-exclusion chromatography (SEC); polystyrene calibration. PDI = polydispersity index ($\bar{M}_w/\bar{M}_n$). [c] [M] = 0.37 M.

room temperature or in 1,2-dichloroethane ($ClCH_2CH_2Cl$) at higher temperatures (40–60 °C). Two types of ruthenium carbene complexes **1** were employed for polymerization: **1a** with triphenylphosphine and **1b** with tricyclohexylphosphine ligands. Catalyst **1a** polymerized a silicon-containing norbornene derivative (**4**) in $ClCH_2CH_2Cl$ at 60 °C to give a polymer with a narrow molecular weight distribution (MWD) ($\bar{M}_w/\bar{M}_n$ = 1.20, Table 2) in high yield. On the other hand, no reaction was observed with monomers (**2b**, **6**–**9**) containing polar functional groups under the conditions studied, and unreacted monomers were recovered after the reactions.[11]

The cyclohexyl-type catalyst **1b** also polymerized **4** to give a polymer in high yield (Tables 1 and 2). The polymerization of **4** by **1b** reached ca. 90% monomer conversion in 30 min at 50 °C, whereas that by **1a** reached almost the same conversion in 11 h at 60 °C (Table 2). The more electron-rich cyclohexylphosphine ligand apparently stabilizes the Ru(IV)–metallacyclobutane intermediate relative to the triaryl analog which increases the rate of ROMP.[9] In both cases, polymerization reactions are much slower than those of NBE. In contrast to NBE, **4** has large substituents in the *endo* position which hinder the polymerization reaction (see below).

As shown in Table 2, the polydispersity of the product polymer ($\bar{M}_w/\bar{M}_n$ = 1.49) obtained using **1b** at room temperature was broader than that obtained using **1a** ($\bar{M}_w/\bar{M}_n$ = 1.25). This broader MWD is due to a slow initiation relative to the propagation reaction. For example, the MWD of the product polymer became narrower at higher temperature ($\bar{M}_w/\bar{M}_n$ = 1.33 for 40 °C, Table 2), and at 50 °C, it became the same as that obtained by **1a** at 60 °C ($\bar{M}_w/\bar{M}_n$ = 1.20). These results indicate that the initiation reaction is enhanced at higher temperature more than the propagation reaction. The molecular weight of the polymer obtained at room temperature was larger than those at higher temperatures, even though the polymer yield was much lower (Table 2). The larger molecular weight of the polymer also suggests an inefficient initiation reaction at room

Table 3. ROMP of a Norbornene Derivative (2b) with Ester Groups by 1[a]

cat.	temp, °C	[M]/[I]	time, h	yield, %	$\bar{M}_n \times 10^{-4}$ [b]	$\bar{M}_w \times 10^{-4}$ [b]	PDI[b]
1a	50	149	15	no reactn			
1b	50	155	25.5	89.7	5.91	7.27	1.23[c]
1b	50	145	16.5	85.4	5.53	6.54	1.18[c]
1b	50	150	10	83.7	4.69	5.42	1.16[c]
1b	50	140	6	94.4	4.71	5.28	1.12
1b	50	150	4	95.1	5.64	6.24	1.11
1b	50	153	2	81.8	5.31	5.85	1.10
1b	RT	162	4	26.8	2.42	2.75	1.14

[a] Reaction conditions: in $ClCH_2CH_2Cl$; [M] = 0.26 M. [b] By SEC; polystyrene calibration. [c] The MWD curve shows an additional peak in the higher molecular weight region.

temperature. Apparently, the vinylcarbene ligand in **1** is less reactive than the alkyl-substituted carbene ligands of the propagating species.

In addition to **4**, catalyst **1b** polymerized other polar functionalized monomers (**6**–**9**) including 7-oxanorbornene derivatives (**6** and **7**) which **1a** cannot polymerize even if they have no polar functional groups. When anhydride-containing monomers **7** and **8** were polymerized with **1b** in $ClCH_2CH_2Cl$, however, a white product precipitated during the polymerization reaction which was insoluble in common organic solvents (Table 1).[12] The ester-containing norbornene **2b** was polymerized by **1b** in $ClCH_2CH_2Cl$ at room temperature or 50 °C. The polymerization of **2b** was completed in 4 h at 50 °C (Table 3), even though highly active catalyst **1b** was employed for the polymerization.

In general, an *endo* isomer is much less reactive than the corresponding *exo* isomer. Two explanations for the difference in reactivity between *exo*- and *endo*-substituted norbornene derivatives have been proposed.[6] One explanation is based on the differences in steric interactions of the substituents around the five-membered ring on going from monomer to polymer in the *endo* and *exo* isomers[6,13] and the other is due to catalyst inhibition by chelation of the propagating metal center by the *endo* functional group.[6] Although both **4** and **2b** are *endo*-substituted norbornene derivatives, **2b** is much less reactive than the bulkier **4** (see, Table 2). These results indicate that in this case the chelation of a metal center retards the ROMP of norbornene derivatives more than the steric factor. In the case of **2b**, the polymerization was quantitative, and the catalyst does not seem to be deactivated. Carbonyl groups in the *endo* position play a key role in retarding the polymerization. A carbonyl group of **2b** in the chain end possibly coordinates to the metal and slows down the polymerization. As an indication that it is an intramolecular effect, it was observed that polymerization of NBE by **1b** was almost completed in less than 1 min in the presence of ethyl acetate.

Figure 1 shows the MWD curves of the polymers of **2b** obtained with **1b** at varying times. The polymer obtained in 4 h has a very narrow MWD ($\bar{M}_w/\bar{M}_n$ = 1.11, Figure 1A). In contrast to the polymerization of **4**, a narrow polydispersity was achieved even at room temperature ($\bar{M}_w/\bar{M}_n$ = 1.14, Table 3). The ratio of the initiation and propagation rates was improved because of a slower propagation reaction. The polymer obtained after almost all monomers were consumed, however, includes a small amount of higher molecular weight polymers (Figure 1B), the amount of which increased with reaction time (Figure 1C). Inspection of Table 3 reveals that polymer yield decreased slightly with reaction time, whereas the MWD of the main peak remained narrow and the $-M_n$ and $\bar{M}_w$ are close to those of the polymer obtained in 4 h. The higher molecular weight polymer is probably formed by the polymer coupling reaction between two growing carbenes. The decrease in polymer yield at longer reaction times suggests that a slow back-biting reaction occurred after the polymerization to produce low molecular weight oligomers.

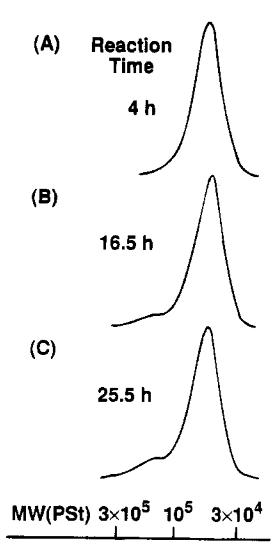


Figure 1. MWD curves of homopolymers of **2b** obtained with **1b** in $ClCH_2CH_2Cl$ at 50 °C: [M] = 0.26 M. Reaction time: (A) 4 h; (B) 16.5 h; (C) 25.5 h.

Table 4. ROMP of a Norbornene Derivative (9) with an Imide Group by 1[a]

cat.	temp, °C	[M]/[I]	time, h	yield, %	$\bar{M}_n \times 10^{-4}$ [b]	$\bar{M}_w \times 10^{-4}$ [b]	PDI[b]
1a	RT	46	48	no reactn			
1b	50	137	9	36.0	1.49	1.71	1.15
1b	50	133	48	81.9	2.49	2.96	1.19[c]

[a] Reaction conditions: in CH_2Cl_2 for **1a**, in $ClCH_2CH_2Cl$ for **1b**; [M]: 0.093 M for **1a**, 0.25 M for **1b**. [b] By SEC; polystyrene calibration. [c] The MWD curve shows an additional peak in the higher molecular weight region.

Polymerization of norbornene and 7-oxanorbornene derivatives possessing an imide group (**6** and **9**) was examined (Table 4). Polymerization of **9** catalyzed by **1b** was carried out in $ClCH_2CH_2Cl$ at 50 °C for 2 days and gave an 82% yield of polymer. At a lower conversion (36.0%, Table 4), the MWD of the polymer shows one sharp peak ($\bar{M}_w/\bar{M}_n$ = 1.15), whereas at a higher conversion (81.9%) higher molecular weight coupling byproducts were present in addition to the main sharp peak. ^1H NMR shows that the methanol-soluble fraction after purification of the polymer contained only monomer. In the polymerization of **9**, the polymer coupling reaction competed with the relatively slow propagating reaction.

In sharp contrast to **9**, polymerization of **6** was extremely fast, being completed in 5 min at 50 °C in $ClCH_2CH_2Cl$. The polymer, however, has a broader MWD ($\bar{M}_w/\bar{M}_n$ ≈ 1.8, Table 5). A fast propagation reaction relative to the initiation causes a broader MWD. The molecular weight of the polymer kept increasing with time even after the polymerization was completed, whereas polymer yield decreased clearly with reaction time because of the back-biting reaction. The increase of the molecular weight may be due to the polymer coupling reaction, but no evidence was observed

Table 5. ROMP of a 7-Oxanorbornene Derivative (6) with an Imide Group by 1b

solvent	temp, °C	[M]/[I][a]	time	yield, %	$\bar{M}_n \times 10^{-4\,b}$	$\bar{M}_w \times 10^{-4\,b}$	PDI[b]
$ClCH_2CH_2Cl$	RT	147	3 h	89.7	7.17	15.9	2.22
$ClCH_2CH_2Cl$	50	145	1 h	70.1	5.62	11.6	2.07
$ClCH_2CH_2Cl$	50	141	15 min	92.8	3.86	6.99	1.81
$ClCH_2CH_2Cl$	50	138	5 min	100	2.94	5.21	1.77
$ClCH_2CH_2Cl$	50	144	2 min	91.7	2.87	5.03	1.75
CH_2Cl_2	50	144	15 min	95.2	3.12	5.28	1.69
CH_2Cl_2	−78 50	158	24 h 15 min	100	5.15	9.44	1.83

[a] [M] = 0.26 M. [b] By SEC; polystyrene calibration.

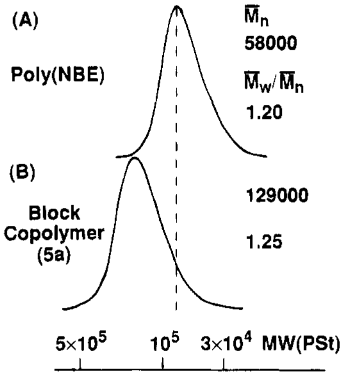


Figure 2. MWD curves of block copolymers **5a** and precursor poly(NBE) (**3a**) obtained by the sequential polymerization of NBE (**2a**) and **4** (Scheme 1) with **1a** in a mixture of CH_2Cl_2 and $ClCH_2CH_2Cl$ at 50 °C: (A) poly(NBE) (**3a**), $[NBE]_0 = 0.54$ M, $[NBE]_0/[\mathbf{1a}]_0 = 292$; (B) block copolymer **5a**, $[NBE]_0/[\mathbf{1a}]_0 = 292/228/1$. $CH_2Cl_2/ClCH_2CH_2Cl$: (A) 2:1 v/v; (B) 2:3 v/v.

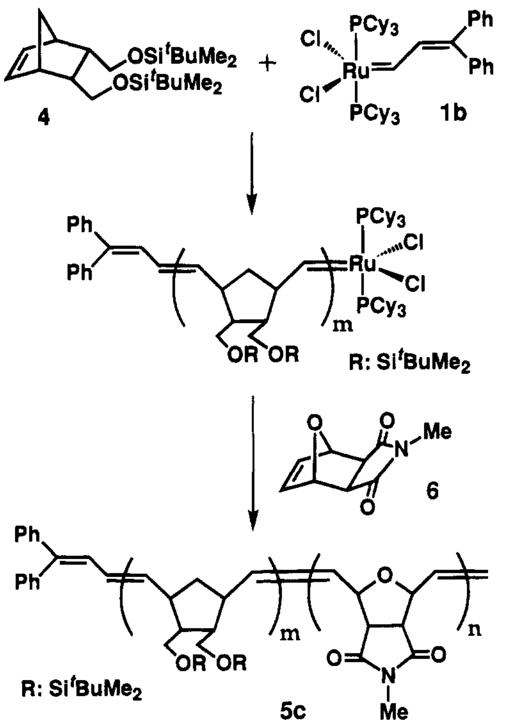
because the MWD of the product polymer is broad and unimodal.

The effects of reaction conditions were also examined with polymerization of **6**. At room temperature, a polymer was obtained in high yield in 3 h. The molecular weight of the polymer was clearly higher than those obtained at 50 °C. The larger molecular weight polymer probably results from an inefficient initiation. Polymerization in CH_2Cl_2 gave a similar result in the case of $ClCH_2CH_2Cl$. To depress the fast propagation reaction, the polymerization of **6** was carried out at low temperature. At first, the reaction was carried out at −78 °C for 24 h and then the temperature was raised to 50 °C. In 15 min, a polymer was obtained quantitatively, but the MWD of the polymer was as broad as those obtained under other reaction conditions. The reactivity of the original carbene should be improved to give a living polymer with a narrow MWD.

2. Synthesis of Silicon-Containing Block Copolymers 5. After accomplishing the living polymerization of **2b** and **4** by **1b**, we examined the block copolymerization of **4** and NBE (**2a**) or **2b**.

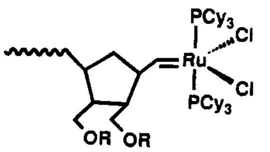
(a) Block Copolymerization of NBE and 4. NBE and **4** were sequentially polymerized by **1a** in a mixture of CH_2Cl_2 and $ClCH_2CH_2Cl$. Catalyst **1a** is mandatory because **1b** is too reactive to give monodisperse poly(NBE).[9] Homopolymerization of **4** was carried out in $ClCH_2CH_2Cl$, whereas block copolymerization of NBE and **4** was carried out in the mixture to keep poly(NBE) from precipitating during the first-stage polymerization. NBE was first polymerized with **1a** at room temperature. After 3 h, the polymer isolated had a narrow MWD ($\bar{M}_w/\bar{M}_n = 1.20$, Figure 2A). To a solution of a living polymer **3a** ($CH_2Cl_2/ClCH_2CH_2Cl$ = 2:1 v/v) was added a $ClCH_2CH_2Cl$ solution of **4** ($CH_2Cl_2/ClCH_2CH_2Cl$ = 2:3 v/v), and the polymerization temperature was raised to 50 °C. The second-stage polymerization ensued, being almost completed in 17 h. The MWD of the resulting block copolymer shifted toward the higher molecular weight region, and the polydispersity remained narrow ($\bar{M}_w/\bar{M}_n = 1.25$, Figure 2B).

Scheme 2

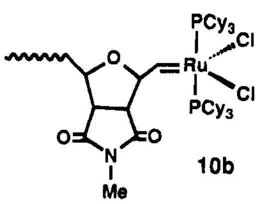


(b) Block Copolymers with Polar Functional Groups. Block copolymerization of **2b** and **4** was also examined. More reactive catalyst **1b** was employed for the polymerization because **1a** cannot polymerize the ester-containing monomer **2b**. In $ClCH_2CH_2Cl$ at 50 °C, **2b** and **4** were sequentially polymerized by **1b**. The resulting block copolymer has a higher molecular weight ($\bar{M}_n$ = 107 000) relative to that of the homopolymer of **2b** ($\bar{M}_n$ = 56 400).

Of the six monomers, **6** is most reactive, but the MWD of the polymer was broad. The initiation of the original carbene in the polymerization of **6** is not fast enough to give a polymer with a narrow MWD. If the polymerization is initiated by a carbene similar to the growing ends, a slow initiation might be accelerated. The growing ends (**10a**) of a living polymer of **4** may be similar in reactivity to those (**10b**)of polymers of **6**.



10a



10b

Thus, block copolymerization of **4** and **6** was carried out in $ClCH_2CH_2Cl$ at 50 °C (Scheme 2). Silicon-containing monomer **4** was first polymerized by **1b**, and then **6** was polymerized from the living growing ends. As shown in Figure 3, block copolymerization of **4** and **6** gave a polymer with a narrower MWD ($\bar{M}_w/\bar{M}_n = 1.26$, Figure 3B) compared to homopolymerization of **6** ($\bar{M}_w/\bar{M}_n$ = 1.75, Figure 3A). Initiation by the propagating carbene

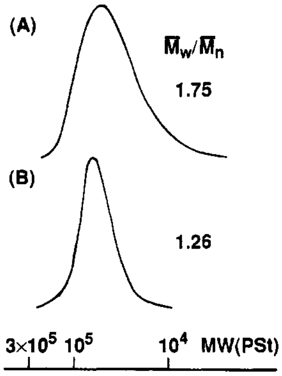


Figure 3. MWD curves of the homopolymer of **6** and block copolymer **5c**: (A) homopolymer of **6**, $[\mathbf{6}]_0 = 0.26$ M, $[\mathbf{4}]_0/[\mathbf{1a}]_0 = 144$; (B) block copolymer **5c**.

is likely to be faster than that by the original carbene complex ($k_{ib} > k_i$) and is fast enough ($k_{ib} > k_p$) to give a living polymer with a narrow MWD (Scheme 3).

The MWD of the product obtained 15 min ater the addition of **6**, however, showed an additional peak in the higher molecular weight region (Figure 4D), as was observed in the homopolymerization of **2b**. This high molecular byproduct decreased as the reaction time was shortened (Figure 4C) and was not present in the product obtained in 2 min (Figure 4B).[14] The molecular weight of the resulting block copolymer is clearly higher than that of the homopolymer of **4**, and the polydispersity remained narrow ($\bar{M}_w/\bar{M}_n = 1.25$, Figure 4B).

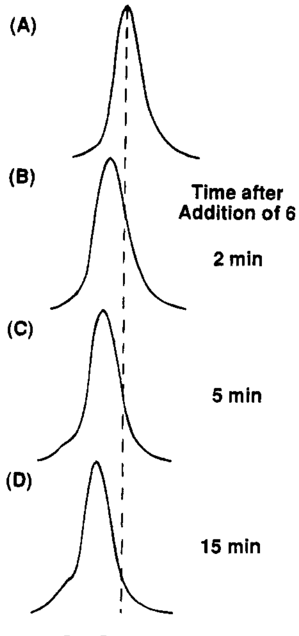
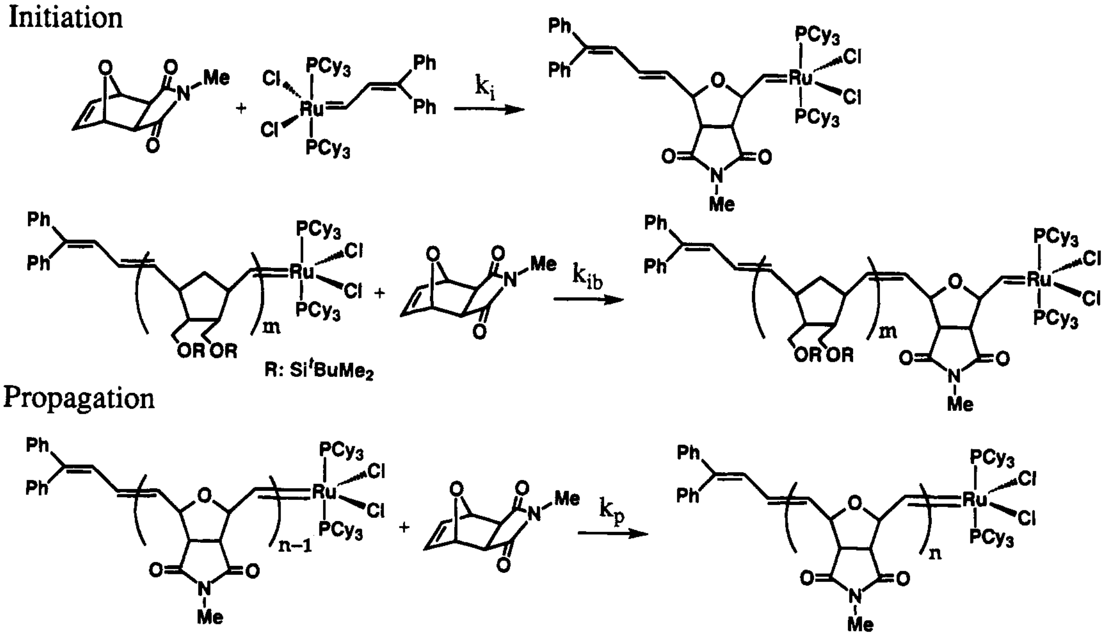


Figure 4. MWD curves of block copolymer **5c** and a precursor polymer of **4** obtained by the sequential polymerization of **4** and **6** (Scheme 2) with **1b** in $ClCH_2CH_2Cl$ at 50 °C: (A) homopolymer of **4**, $[\mathbf{4}]_0 = 0.20$ M, $[\mathbf{4}]_0/[\mathbf{1b}]_0 = 119$; (B–D) the products recovered after the second-stage polymerization of **6**, $[\mathbf{4}]_0/[\mathbf{6}]_0/[\mathbf{1b}]_0 = 119/113/1$. Reaction time after addition of **6**: (B) 2 min; (C) 5 min; (D) 15 min.

Figure 5 shows the ^{1}H NMR spectrum of the block copolymer of **4** and **6**. The spectrum of the block copolymer exhibits absorptions (c, d, and g) assigned to the units of **6**, in addition to those (a, b, e, and f) of the units of **4**. These results also support the formation of the block copolymers. The overall results of the block copolymerizations are summarized in Table 6. The segment composition of the polymer was determined from the ^{1}H NMR peak intensity ratio of some peaks of both units. For example, the composition of **5c** was calculated from the methine protons (peak d) adjacent to the carbonyl groups and the methyl protons (peak c) next to the nitrogen of **6** and the methylene protons (peak e) next to the oxygen of **4**. The calculated value was derived from the feed ratio and polymer yield. The observed ratios were in good agreement with the calculated values.

In conclusion, two norbornene derivatives (**2b** and **4**) can be polymerized in a living fashion catalyzed by **1b**. These are the first examples of polymers with a narrow MWD prepared by the cyclohexyl-type ruthenium catalyst **1b**. Silicon-containing block copolymers with polar functional groups were also synthesized via ROMP by **1**. A block copolymer of norbornene and 7-oxanorbornene derivatives was prepared for the first time.

Scheme 3



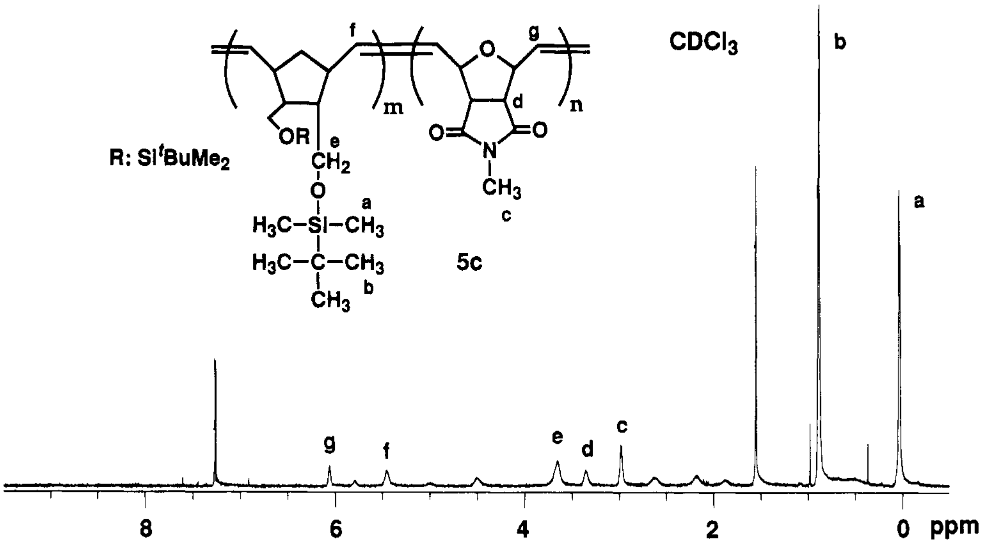


Figure 5. ^{1}H NMR spectrum of block copolymer **5c** in CDCl$_3$ at room temperature.

Table 6. Block Copolymers of Norbornene and 7-Oxanorbornene Derivatives

cat.	M$_1$	M$_2$	[M$_1$]/[M$_2$]/[I]^a	$\bar{M}_n \times 10^{-4}$ ^{b}	$\bar{M}_w \times 10^{-4}$ ^{b}	PDI^b	*m*:*n* calcd^c	*m*:*n* obsd^d
1a	**2a**	**4**	292/228/1	12.9	16.1	1.25	1.78	1.86
1b	**2b**	**4**	137/110/1	10.7	12.9	1.21	1.41	1.29
1b	**4**	**6**	116/113/1	5.08	6.41	1.26	1.20	1.19

^{a} The feed ratio of monomers and catalyst **1**. ^{b} By SEC; polystyrene calibration. ^{c} Calculated from the feed ratio and polymer yield; *m* = degree of polymerization of M$_1$, *n* = degree of polymerization of M_2. ^{d} Determined by ^{1}H NMR.

These results suggest that the ruthenium catalysts can be used to prepare a wide variety of homopolymers and block copolymers. To obtain narrower molecular weights, a more efficient initiator will be required. Such a complex is now being investigated.

Experimental Section

General Procedures. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). ^{1}H NMR spectra were recorded on a GE QE-300 (300 MHz) spectrometer at 25 °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, dichloromethane was used as the eluent at a flow rate of 1.0 mL/min. The $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_w/\bar{M}_n$ values of the polymers were calculated from the chromatographs on the basis of a polystyrene calibration.

Materials. Dichloromethane and 1,2-dichloroethane (polymerization solvent) were distilled from calcium hydride and degassed by repeated freeze–pump–thaw cycles. Ruthenium carbene complexes **1a**[8] and **1b**[9] were prepared as reported before. **2b** was prepared from the commercially available anhydride (**8**) and ethanol according to literature procedures.[15] **6** was prepared as reported before.[7c] **7** was prepared from the Diels–Alder reaction of furan and maleic anhydride in ether.[16] **8** was purchased from Aldrich Chemical Co. and used without further purification.

Preparation of *endo*-2,3-Bis((*tert*-butyldimethylsilyl)oxy)methyl)bicyclo[2.2.1]hept-5-ene (4). A solution of the commercially available anhydride (**8**) (14.2 g, 0.087 mol) was added dropwise to the LiAlH$_4$ (14.8 g, 0.39 mol) suspension. The reaction mixture was then allowed to stir for 2 h at room temperature. After workup, THF was removed and the residue was dried under vacuum to give white crystals (62% yield). This product was purified by recrystallization from hexane.

A CH$_2$Cl$_2$ solution of the diol (2.0 g, 0.013 mol) was added to a mixture of 9.7 g (0.037 mol) of *tert*-butyldimethylsilyl trifluoromethanesulfonate (Aldrich) and 6.0 mL of 2,6-lutidine (5.5 g, 0.052 mol) in 15 mL of CH$_2$Cl$_2$. This solution was stirred for 14 h at room temperature. The reaction mixture was poured into 80 mL of water, and then it was extracted with 100 mL of hexane three times. Hexane was removed and the crude product (yellow oil) was dried under dynamic vacuum overnight. This product was purified by a silica gel column to give a colorless oil (91% yield). ^{1}H NMR (CDCl$_3$): δ 0.02 (s, 12 H), 0.89 (s, 18 H), 1.27 (m, 1 H), 1.43 (m, 1 H), 2.34 (m, 2 H), 2.90 (m, 2 H), 3.17 (m, 2 H), 3.47 (m, 1 H), 6.11 (s, 2 H).

Preparation of *endo*-*N*-Methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylimide (9). The synthesis of the *endo* isomer of **9** was carried out in *o*-dichlorobenzene via Diels–Alder reaction of cyclopentadiene and *N*-methylmaleimide. To a solution of *N*-methylmaleimide (10.0 g, 0.090 mol) in *o*-dichlorobenzene (10 mL) at 173 °C was added dropwise *endo*-dicyclopentadiene (8.0 mL, 0.060 mol). This solution was then refluxed for 2 h. After cooling, the yellowish white product precipitated. This product was purified by a silica gel column. ^{1}H NMR (CDCl$_3$): δ 1.54 (m, 1 H), 1.75 (m, 1 H), 3.27 (m, 2 H), 3.39 (m, 2 H), 6.10 (s, 2 H).

Polymerization Procedure. In a nitrogen-filled drybox the monomer and ca. 5 mg of catalyst were weighed in a separate vial and dissolved in 2.0 and 1.0 mL of a solvent, respectively. The reaction was initiated by adding a monomer solution to the solution of the catalyst. For the polymerization at higher temperature, the vial was capped and brought out of the box, and then it was heated in an oil bath. The polymerization was terminated with a small amount (ca. 100 μL) of ethyl vinyl ether. The polymer was purified by precipitation twice from methanol. The polymer was then dried under dynamic vacuum overnight at room temperature.

Acknowledgment. This work was supported by the Caltech Consortium (DuPont, Kodak, and 3M) and the NSF. We would like to thank SonBinh T. Nguyen for providing the ruthenium carbene complexes.

References and Notes

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

(2) Kornfield, J. A., unpublished results.

(3) For a review, see: Novak, B. M.; Risse, W.; Grubbs, R. H. *Adv. Polym. Sci.* **1992**, *102*, 47.

(4) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.

(5) Bazan, G. C.; Schrock, R. R.; Cho, H.-N.; Gibson, V. C. *Macromolecules* **1991**, *24*, 4495.

(6) (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.

(7) (a) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960. (b) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542. (c) Hillmyer, M. A.; Lepetit, C.; McGrath, D. V.; Novak, B. M.; Grubbs, R. H. *Macromolecules* **1992**, *25*, 3345. (d) France, M. B.; Paciello, R. A.; Grubbs, R. H. *Macromolecules* **1993**, *26*, 4739. (e) France, M. B.; Grubbs, R. H.; McGrath, D. V.; Paciello, R. A. *Macromolecules* **1993**, *26*, 4742.

(8) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974.

(9) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858.

(10) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856.

(11) The product polymers were purified by precipitating them from methanol. ^{1}H NMR spectra of the methanol-soluble fractions after precipitation show only shifts due to monomers in all cases.

(12) No further attempts were made to clarify this phenomenon.

(13) Castner, K. F.; Calderon, N. *J. Mol. Catal.* **1982**, *15*, 47.

(14) Not all of **6** was consumed at this point (ca. 76% conversion).

(15) *Org. Synth. Collect. Vol.* **1963**, *4*, 304.

(16) Novak, B. M. Ph.D. Thesis, California Institute of Technology, 1989.

MA950117L