Synthesis of Poly(macromonomer)s by Repeating Ring-Opening Metathesis Polymerization (ROMP) with $Mo(CHCMe_2Ph)(NAr)(OR)_2$ Initiators

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ABSTRACT: Various poly(macromonomer)s of ring-opened poly(norbornene) backbone containing ring-opened poly(norbornene) derivatives in the side chain have been prepared efficiently by repeating the ring-opening metathesis polymerizations (ROMP) using well-defined molybdenum initiator of the type, $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}^iPr_2C_6H_3)(OR)_2$ [OR = $OCMe_3$, $OCMe(CF_3)_2$]. The key steps for synthesis of the macromonomer are both exclusive end-capping and quantitative esterification of hydroxy group at the polymer chain end with norbornene carboxylic acid chloride, and the use of $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}^iPr_2C_6H_3)[OCMe(CF_3)_2]_2$ was found to be an effective initiator in order for this polymerization to proceed to the complete conversion. The present synthetic approach should be useful for preparing various poly(macromonomer)s containing functional groups, especially amphiphilic poly(macromonomer) architectures precisely.

Introduction

Considerable attention has been devoted to the synthesis and properties of highly branched polymers, and poly(macromonomer)s thus represent important class of branched polymers whose main characteristic is axisymmetric distribution of branching points along the central backbone contour.[1,2] A macromonomer is usually defined as a polymeric or oligomeric monomer with a polymerizable or copolymerizable functional group at one end, and upon polymerization of macromonomers, polymers of extremely high branch density and uniform branch length can be obtained, which would not be the case using other synthetic strategies such as star−polymer syntheses. In fact, comb-shaped poly(macromonomer) (**a** in Chart 1) which may be prepared by the homopolymerization may actually be forced to take a conformation that looks like a brush or star (**b** or **c** in Chart 1, respectively), depending on the relative length of the macromonomer branch vs poly(macromonomer) backbone. Interest in poly(macromonomer)s arises from their unique properties in solution and in bulk;[3] however, little attention has been paid to the efficient synthesis of these multibranched systems in contrast to the case of star polymers. One major limitation associated with the homopolymerization of macromonomers is the difficulty of obtaining complete conversion and precise size control of the branched structure formed.

Molybdenum alkylidene complexes of the type $Mo(CHCMe_2Ph)(NAr)(OR)_2$ (Ar = $2,6\text{-}^iPr_2C_6H_3$, $2,6\text{-}Me_2C_6H_3$; OR = O^tBu, $OCMe(CF_3)_2$ etc., Chart 2) are useful initiators for the living ring-opening metathesis polymerization (ROMP) of cyclic olefins, especially norbornenes and substituted norbornadienes, as demonstrated especially by Schrock.[4−9] The absence of chain-transfer and termination reactions in such polymerizations allows the production of homopolymers and block copolymers of narrow molecular weight distributions and allows the control of terminal group in the initiation site and in the termination site. The fact that a wide variety of nonprotic functionalities are also tolerated by this catalyst allows architectural and functional possibilities for ROMP polymers.[10]

It has already been reported by Gnanou et al. and Feast et al. that macromonomers can be polymerized without chain-transfer and termination reactions via ring-opening metathesis mechanism using the molybdenum−alkylidene initiator.[11−19] These reports indicate that the ROMP is one of the most efficient methods to prepare poly(macromonomer) with complete conversion as well as with a uniform molecular weight distribution. However, the results presented there were only the cases coupled with living anionic polymerization, and several limitations still exist in preparing various poly(macromonomer)s with precise size control.

We recently reported as a preliminary communication that efficient polymerization of norbornene-based macromonomer bearing a ring-opened poly(norbornene) can be accomplished by repeating the ROMP using the Schrock-type molybdenum initiator, $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}^iPr_2C_6H_3)[OCMe(CF_3)_2]_2$.[20] The key steps for the macromonomer synthesis are (i) exclusive end capping of ring-opened poly(norbornene) with *p*-$Me_3SiOC_6H_4$-CHO, (ii) hydrolysis of the $SiMe_3$ group, and (iii) exclusive esterification of OH group at the polymer chain end with norbornene carboxylic acid chloride (Scheme 1). Since we expected from these results that it would be possible not only to prepare block copolymers with different macromonomers but also to prepare poly(macromonomer)s bearing ring-opened poly(norbornene) containing a block copolymer in the side chain by utilizing this synthetic approach and also since these poly(macromonomer)s should be especially interesting and should have unique properties due to their precisely ordered structures, we thus explored this chemistry in detail. In this paper, we thus wish to present synthesis

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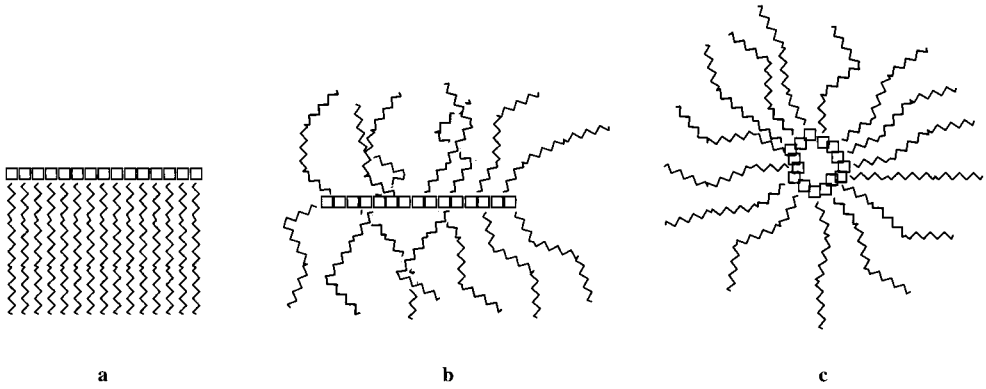
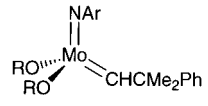
Chart 1



a **b** **c**

Chart 2



OR = O^{t}Bu (**A**), OCMe(CF$_3$)$_2$ (**B**)
NAr =2,6-^{i}Pr$_2$C$_6$H$_3$

of various poly(macromonomer)s by repetitive ROMP chemistry.

Results and Discussion

1. Synthesis and Polymerization of Norbornene Macromonomer, Poly(3), Containing Ring-Opened Poly(norbornene) in the Side Chain.[21] Norbornene was polymerized in toluene at room temperature by using Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ (catalyst **A**) as the initiator. The polymerization was carried out in toluene by adding norbornene, 25−100 equiv, to the initiator, and the resultant polymers were cleaved from the initiator fragment metal in a Wittig-like reaction with *p*-Me$_3$SiOC$_6$H$_4$CHO. This is an established method of cleaving the ROMP polymer−metal bond as demonstrated in particular by Schrock, and the polymer yields exceeded 90% (Table 1).

The ^{1}H NMR spectrum of the resultant polymer, poly(**1**), showed relatively broad resonances at 5.2 and 5.3 ppm due to the olefinic protons and showed broad resonances between 0.9 and 2.0 ppm and between 2.4 and 2.8 ppm characteristic of the ring-opened polymers of norbornene. In addition, a peak characteristic of SiMe$_3$ group was observed at 0.3 ppm and a number of resonances characteristic of vinyl protons at the polymer chain end group were also observed.[22] The resultant polymer was a mixture of cis- and trans-isomers (64% trans-form, run 3).

The M_n value (determined by GPC vs polystyrene standard in THF) increased linearly upon the increase in initial norbornene/molybdenum molar ratio, and the molecular weight distributions of poly(**1**) were relatively narrow (M_w/M_n = 1.09−1.16). Although the M_n values determined by GPC were relatively higher than those calculated based on the initial monomer/initiator molar ratio,[21] the M_n values calculated based on ^{1}H NMR spectra (integration ratio with SiMe$_3$ group at the polymer chain end) were in good agreement with the calculated values. These results would indicate that this polymerization is a living polymerization with a quantitative initiation efficiency as established previously.[4−6,8−10]

Hydrolysis of SiMe$_3$ group in poly(**1**) was performed in a mixed solution consisting of 5 N NaOH aqueous solution and methanol (1/4, v/v) at room temperature (Scheme 1). The ^{1}H NMR spectrum for the resultant polymer, poly(**2**), showed that the peak ascribed to SiMe$_3$ (0.3 ppm) disappeared without any changes in the other resonances, strongly suggesting the formation of poly(**2**). The yields were quantitative in all cases (Table 2), and the M_n values by GPC did not change significantly from those of poly(**1**).

The macromonomer, poly(**3**), could be prepared by the reaction of poly(**2**) with norbornene carboxylic acid chloride in THF containing NEt$_3$. A slightly excess amount of the chloride [1.5 equiv to poly(**2**)] was added to attain the complete conversion of poly(**2**), and the chloride remained in the solution was removed by pouring the reaction mixture into MeOH in which the product, the methyl ester, is soluble.

As shown in Table 2, the M_n as well as M_w/M_n values did not change during these procedures [from poly(**1**) through poly(**3**)]. In addition, the M_n values determined by MALDI−TOF mass spectrometry were almost the same as those calculated based on initial monomer/initiator molar ratio. These results demonstrate that norbornene macromonomer containing ring-opened poly(norbornene) in the side chain with precise monomer unit could be prepared exclusively by using this synthetic procedure.[23]

Polymerization of Macromonomer. Two types of catalysts [Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ (catalyst **A**), and Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$ (catalyst **B**)] were chosen for polymerization of poly(**3**), and the reactions were performed in toluene and were terminated by adding PhCHO in excess (Scheme 2). The results are summarized in Table 3.

The ^{1}H NMR spectrum for the resultant polymer, poly(**4**), did not show resonances (6.02−6.19 ppm) corresponding to the olefinic proton of the norbornene skeleton, indicating that the polymerization took place in the ring-opening fashion under these conditions. The disappearance of olefinic carbon of norbornene was also observed in the ^{13}C NMR spectrum.[24] In addition, GPC traces for the resultant polymers, poly(**4**), prepared by catalyst **B**, showed unimodal molecular weight distributions, and the values for the degree of polymerization based on both the GPC data and the mass spectrum were in good agreement with the calculated values. Moreover, the M_n values by the mass spectra were almost the same as those calculated based on initial monomer/initiator molar ratios and Schemes 1 and 2.

Scheme 1

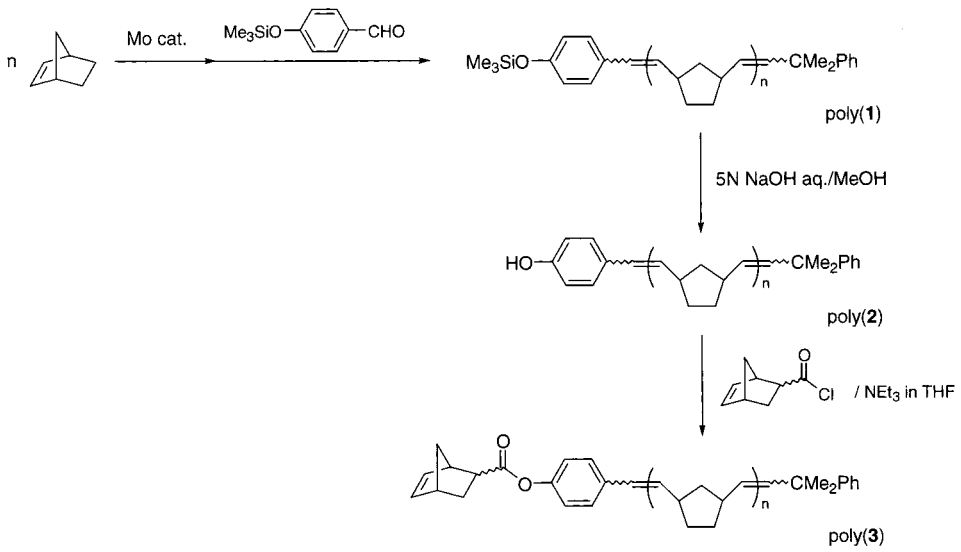


Table 1. Ring-Opening Metathesis Polymerization of Norbornene with Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ Initiator[a]

run no.	norbornene/Mo molar ratio	M_n(GPC)[b] $\times 10^{-4}$	M_w/M_n[b]	M_n(calcd)[c] $\times 10^{-4}$	M_n(NMR)[d] $\times 10^{-4}$	yield,[e] %
1	25	0.68	1.14	0.27	0.29	90
2	25	0.68	1.16	0.27		98
3	50	1.05	1.09	0.50	0.66	90
4	100	1.70	1.12	0.97	1.13	98

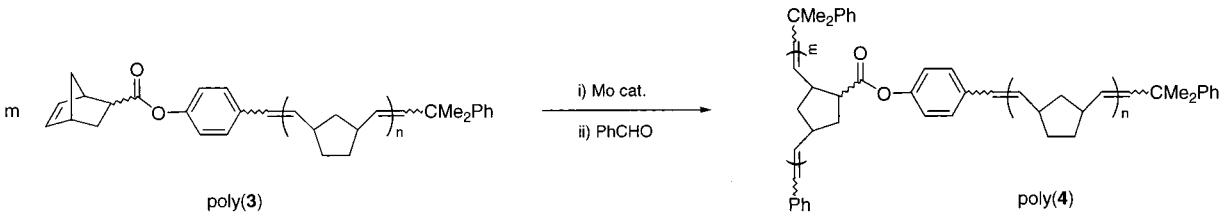
[a] Conditions: toluene (5.0 g) at 25 °C, 20−60 min. [b] GPC data in THF vs polystyrene standard. [c] Calculated by norbornene/Mo initial molar ratio. [d] Calculated by ^{1}H NMR spectra (using integration ratio vs SiMe$_3$ group). [e] Isolated yield.

Table 2. Preparation of Norbornene Macromonomer, Poly(3).[a]

		poly(**1**)		poly(**2**)			poly(**3**)				
run[b] no.	norbornene/Mo molar ratio	M_n(GPC)[c] $\times 10^{-4}$	M_w/M_n[c]	M_n(GPC)[c] $\times 10^{-4}$	M_w/M_n[c]	yield,[d] %	M_n(GPC)[c] $\times 10^{-4}$	M_w/M_n[c]	M_n(calcd)[e] $\times 10^{-4}$	M_n(MS)[f] $\times 10^{-4}$	yield,[d] %
1	25	0.68	1.14	0.66	1.14	95	0.64	1.16	0.27	0.27	90
2	25	0.68	1.16	0.77	1.12	98	0.70	1.21	0.27		95
3	50	1.05	1.09	1.04	1.11	95	1.18	1.11	0.51	0.50	90

[a] For the experimental details, see the Experimental Section. [b] Sample number for poly(**1**) shown in Table 1. [c] GPC data in THF vs polystyrene standard. [d] Isolated yield. [e] Calculated value based on initial norbornene/Mo initial molar ratio and Scheme 1. [f] Determined value by MALDI−TOF mass spectrum.

Scheme 2



Since the polymer prepared by the catalyst **A** showed broad, bimodal molecular weight distributions consisting of poly(**3**) and poly(**4**) by GPC under the same conditions, it is thus clear that catalyst **B** should be more suited than catalyst **A** as the initiator for this polymerization. The observed difference would be due to the different propagation rates and different reactivities toward olefinic double bonds in norbornene derivatives, poly(**3**), among these two molybdenum−alkylidene species.

2. Synthesis and Polymerization of Norbornene Macromonomers Derived from Substituted Norbornene. *cis*-2,3-*endo*-Bis[(*tert*-butyldimethylsiloxy)methyl]norborn-5-ene was prepared from *cis*-2,3-*endo*-bis(hydroxymethyl)norborn-5-ene according to the analogous method as used for *trans*-2,3-bis[(trimethylsiloxy)methyl]norborn-5-ene[25] in this study. Polymerization of the monomer was performed in toluene, and the yields were almost quantitative (96−98%) in all cases (Table 4). In addition, M_n values by GPC increased linearly upon the increase in the initial monomer/initiator molar ratio, and the molecular weight distributions were narrow and unimodal (M_w/M_n = 1.11−1.15).

Hydrolysis of poly(**5**) was performed in a mixed solution of 5 N NaOH aqueous solution and MeOH under the same conditions for preparing poly(**2**) (Scheme 3). The ^{13}C NMR spectrum for the resultant polymers, poly(**6**), showed the disappearance of the resonance ascribed to the SiMe$_3$ group at 0.2 ppm, although no significant changes were observed in the ^{1}H NMR

Table 3. Ring-Opening Metathesis Polymerization of Poly(3)[a]

		poly(**3**)					poly(**4**)					
run no.[b]	n[c]	M_n(GPC)[d] $\times 10^{-4}$	M_w/M_n	M_n(MS)[e] $\times 10^{-4}$	catalyst[f]	poly(**3**)/Mo molar ratio	M_n(GPC)[d] $\times 10^{-4}$	M_w/M_n[d]	M_n(calcd)[g] $\times 10^{-4}$	M_n(MS)[e] $\times 10^{-4}$	DP_n,[h] m	yield,[i] %
1	25	0.64	1.16	0.27	**A**	10	6.20	1.41[j]	2.73			85
1	25	0.64	1.16	0.27	**B**	10	7.14	1.20	2.73	2.80	10.4	94
3	50	1.18	1.11	0.50	**B**	10	12.7	1.14	5.09	5.18	10.4	92
3	50	1.18	1.11	0.50	**B**	13	15.6	1.19	5.09			95

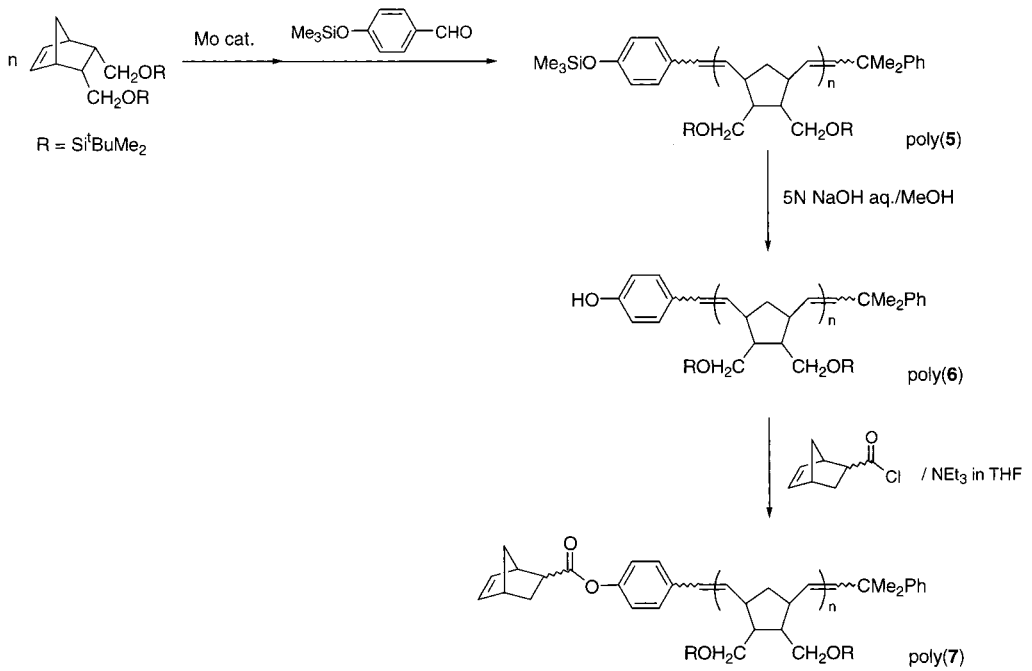
[a] Conditions: toluene (5 mL), 25 °C, 30−60 min. [b] Sample number for poly(**1**) in Table 1. [c] Initial norbornene/Mo molar ratio for poly(**1**). [d] GPC data in THF vs polystyrene standard. [e] Determined value by MALDI−TOF mass spectrum. [f] Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ (**A**) and Mo(CHCMe$_2$Ph)(2,6-^{i}Pr$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$ (**B**). [g] Calculated value based on initial norbornene/Mo molar ratio and Scheme 2. [h] Degree of polymerization calculated based on M_n(MS). [i] Isolated yield. [j] Bimodal molecular weight distribution consisted of poly(**3**) and poly(**4**).

Table 4. Preparation of Poly(5) by ROMP with Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ Initiator and Preparation of Poly(7)[a]

		poly(**5**)			poly(**6**)			poly(**7**)				
run no.	monomer/Mo[b] molar ratio/n	M_n(GPC)[b] $\times 10^{-4}$	M_w/M_n[c]	yield,[d] %	M_n(GPC)[c] $\times 10^{-4}$	M_w/M_n[c]	yield,[d] %	M_n(GPC)[c] $\times 10^{-4}$	M_w/M_n[c]	M_n(calcd)[e] $\times 10^{-4}$	M_n(MS)[f] $\times 10^{-4}$	yield,[d] %
5	20	0.77	1.15	98	0.78	1.17	96	0.72	1.16	0.80	0.85	98
6	25	1.08	1.11	96	1.22	1.15	98	1.02	1.17	0.99	0.97	94
7	30	1.32	1.11	96	1.40	1.17	95	1.50	1.05	1.18	1.26	93
8	50	1.90	1.11	96	1.86	1.13	96	1.98	1.05	1.95	1.99	94

[a] For the experimental details, see the Scheme 3 and the Experimental Section. [b] Initial molar ratio of *cis*-2,3-*endo*-bis[(*tert*-butyldimethylsiloxy)methyl]norborn-5-ene/molybdenum. [c] GPC data in THF vs polystyrene standard. [d] Isolated yield. [e] Calculated value based on initial monomer/Mo molar ratio and Scheme 3. [f] Determined value by MALDI−TOF mass spectrum.

Scheme 3



spectrum during the hydrolysis procedures. In addition, the M_n and M_w/M_n values by GPC did not change during the reaction. These results thus suggest that $SiMe_3$ group in poly(**5**) could be removed exclusively without eliminating Si^tBuMe_2 group under these hydrolysis conditions.

Preparation of the macromonomer, poly(**7**), was performed under the same conditions for poly(**3**), and the yields were quantitative in all cases (Table 4). The resultant polymer, poly(**7**), could be identified by ^{1}H and ^{13}C NMR spectra. Both M_n and M_w/M_n value by GPC did not change during these preparation procedures from poly(**5**) through poly(**7**) (Scheme 3), and the M_n values determined by MALDI−TOF mass spectrometry were almost identical with the calculated values (Table 4). These results indicate that the present synthetic approach should be very useful for preparing norbornene-based macromonomer containing substituted poly(norbornene) in the side chain.

Table 5 summarizes the results for polymerization of poly(**7**) in toluene by using catalyst **B** as the initiator (Scheme 4). It turned out that these polymerizations proceeded efficiently in ring-opening fashions, affording poly(macromonomer)s, poly(**8**), in high yields.

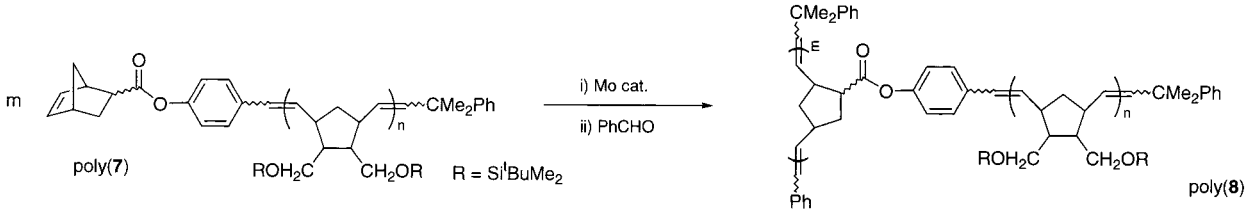
^{1}H and ^{13}C NMR spectra for the resultant polymer showed no resonance corresponding to olefinic proton or carbon characteristic of norbornene derivatives. On the other hand, it might be interesting to note that resonance attributed to olefinic proton of the ring-opened polymer showed relatively broad singlet (or

Table 5. Ring-Opening Metathesis Polymerization of Poly(7) by Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$ Initiator[a]

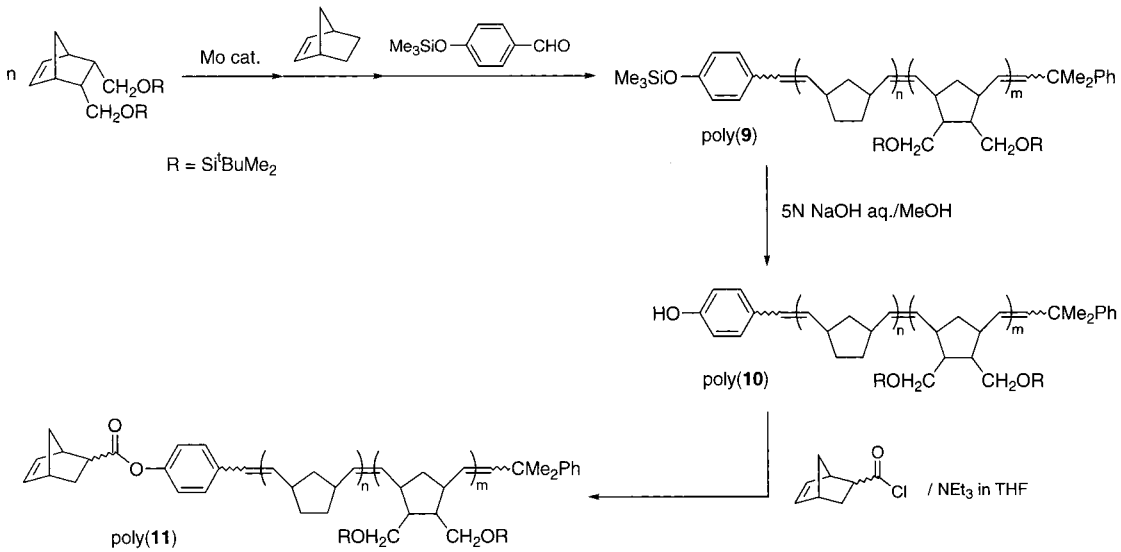
		poly(**7**)			poly(**8**)					
run no.[b]	n[c]	M_n(GPC)[d] $\times 10^{-4}$	M_w/M_n[d]	M_n(MS)[e] $\times 10^{-4}$	M_n(GPC)[d] $\times 10^{-4}$	M_w/M_n[d]	M_n(calcd)[f] $\times 10^{-4}$	M_n(MS)[e] $\times 10^{-4}$	DP$_n$,[g] m	yield,[h] %
5	20	0.72	1.16	0.85	4.68	1.17	4.03	3.97	6.5	75
6	25	1.25	1.11	0.97	6.41	1.06	4.99	4.95	5.1	85
7	30	1.50	1.05	1.26	7.15	1.07	5.94	5.43	4.8	90
8	50	1.98	1.05	1.99	10.1	1.08	9.77	9.78	5.1	85

[a] Conditions: in toluene 25 °C, 20 min, poly(**7**)/Mo = 5 (molar ratio). [b] Sample number for poly(**7**) shown in Table 4. [c] Initial monomer/Mo molar ratio for poly(**5**) (Scheme 3). [d] GPC data in THF vs polystyrene standard. [e] Determined value by MALDI−TOF mass spectrum. [f] Calculated value based on poly(**7**)/Mo molar ratio. [g] Calculated based on GPC data. [h] Isolated yield.

Scheme 4



Scheme 5



mixture of multiplet) at 5.44 ppm during these polymerization procedures [from poly(**5**) through poly(**8**), Schemes 3 and 4] if *cis*-2,3-*endo*-bis[(*tert*-butyldimethylsiloxy)methyl]norborn-5-ene were used as the starting monomer. This would suggest that the stereospecific (probably cis) polymerization takes place under these conditions.

GPC traces for the resultant polymers showed narrow, unimodal molecular weight distributions (M_w/M_n = 1.06−1.17, Table 5), and the degrees of polymerizations based on GPC data are in good agreement with the calculated values. In addition, the M_n values determined by the mass spectrometry were almost the same as those calculated based on initial monomer/initiator molar ratios and as shown in Schemes 3 and 4.[26]

Taking into account the above results, it is thus clear that the present synthetic strategy should be very useful for preparing poly(macromonomer)s containing ring-opened poly(norbornene)s with various functional group in the side chain.

3. Synthesis of Block Copolymer. Since the present well-defined initiator is effective for preparing block copolymers by adding monomers sequentially so that the polymerization proceeds in a living manner, we thus explored the possibility of preparing various amphiphilic block copolymers.

Poly(**9**) could be prepared by the addition of *cis*-2,3-*endo*-bis[(*tert*-butyldimethylsiloxy)methyl]norborn-5-ene and norbornene according to Scheme 5, and norbornene was added after the consumption of the former monomer. The polymerization results are summarized in Table 6, the yields were quantitative (93 and 96%) in all cases, and the resultant polymer, poly(**9**), possessed unimodal, narrow molecular weight distribution.

Hydrolysis of poly(**9**) affording poly(**10**) and preparation of the macromonomer, poly(**11**), were performed under the same conditions as that for poly(**2**) and poly(**6**) and for poly(**3**) and poly(**7**), respectively, and the yields were almost quantitative in all cases (Table 6). The M_n and M_w/M_n values did not change during these preparation procedures [from poly(**9**) through poly(**11**)], and the M_n values for poly(**11**) by mass spectrometry were the same as those calculated based on the initial monomer/initiator molar ratios and Scheme 5. The resultant polymers could also be identified by ^{1}H and ^{13}C NMR spectra.

Table 6. Preparation of Poly(9) by the ROMP with Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ Initiator, and Preparation of Poly(11)[a]

		poly(**9**)			poly(**10**)			poly(**11**)				
run no.	monomer/Mo molar ratio[b] n/m	M_n(GPC)[c] $\times 10^{-4}$	M_w/M_n[c]	yield,[d] %	M_n(GPC)[c] $\times 10^{-4}$	M_w/M_n[c]	yield,[d] %	M_n(GPC)[c] $\times 10^{-4}$	M_w/M_n[c]	M_n(calcd)[e] $\times 10^{-4}$	M_n(MS)[f] $\times 10^{-4}$	yield,[d] %
9	25/25	1.99	1.12	98	1.99	1.12	98	1.96	1.12	1.23	1.14	95
10	50/25	2.99	1.07	98	3.00	1.07	96	3.01	1.06	1.46	1.45	89

[a] For the experimental details, see Scheme 5 and the Experimental section. [b] See Scheme 5. [c] GPC data in THF vs polystyrene standard. [d] Isolated yield. [e] Calculated value based on initial monomer/Mo molar ratio and Scheme 5. [f] Determined value by MALDI−TOF mass spectrum.

Table 7. Ring-Opening Metathesis Polymerization of Poly(11) by Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$ Initiator[a]

	poly(**11**)			poly(**12**)				
run no.	n/m[c]	M_n(GPC)[d] $\times 10^{-4}$	M_w/M_n[d]	M_n(GPC)[d] $\times 10^{-4}$	M_w/M_n[d]	M_n(calcd)[e] $\times 10^{-4}$	M_n(MS)[f] $\times 10^{-4}$	yield,[g] %
9	25/25	1.96	1.12	7.98	1.12	6.16	6.65	92
10	50/25	3.01	1.06	14.2	1.09	7.34	8.05	96

[a] Conditions: in toluene, 25 °C, 30 min, poly(**11**)/Mo = 5 (molar ratio); for more details, see the Experimental Section. [b] Sample number for poly(**11**) shown in Table 6. [c] See Schemes 5 and 6. [d] GPC data in THF vs polystyrene standard. [e] Calculated M_n value [for poly(**11**)] based on initial monomer/Mo molar ratio and Schemes 5 and 6. [f] Determined value by MALDI−TOF mass spectrum. [g] Isolated yield.

Scheme 6

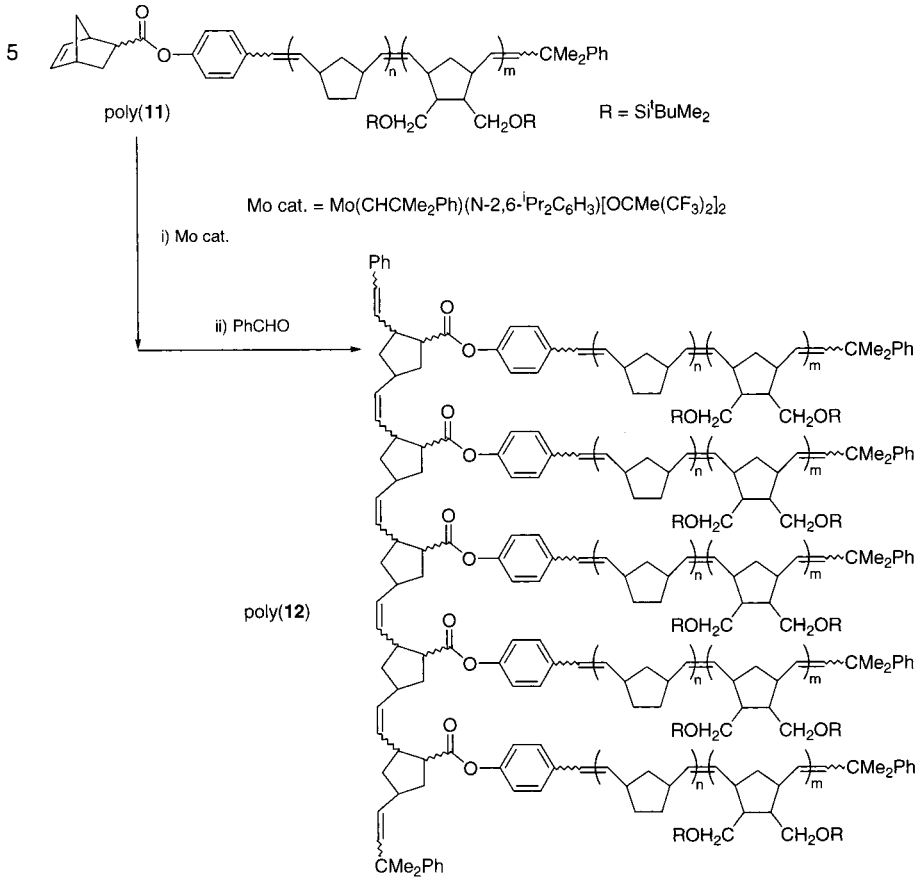


Table 7 summarizes the results for polymerization of poly(**11**) in toluene by using catalyst **B** as the initiator. As expected from the above results in polymerization of both poly(**3**) and poly(**7**), the resultant polymer, poly(**12**), possessed narrow, unimodal molecular weight distribution, and the polymer could also be identified by ^{1}H and ^{13}C NMR spectra and mass spectrometry (Scheme 6). Since a wide variety of nonprotic functionalities are tolerated by this polymerization method, it is thus evident that the present method should be useful for preparing poly(macromonomer)s containing ROMP block copolymers in the side chain. In addition, since the ^{t}BuMe$_2$Si group in the poly(**12**) could be easily removed by hydrolysis using CF_3CO_2H/H_2O solution, as described below, the present synthetic approach should also be useful for preparing poly(macromonomer)s containing amphiphilic block copolymers in a precisely controlled manner.

According to Scheme 7, *cis*-2,3-*endo*-bis[(*tert*-butyldimethylsiloxy)methyl]norborn-5-ene and poly(**3**) were added sequentially in toluene at room temperature in the presence of catalyst **B** as the initiator, affording a block copolymer, poly(**13**), consisting of ring-opened poly(norbornene) containing substituent and poly(mac-

Scheme 7

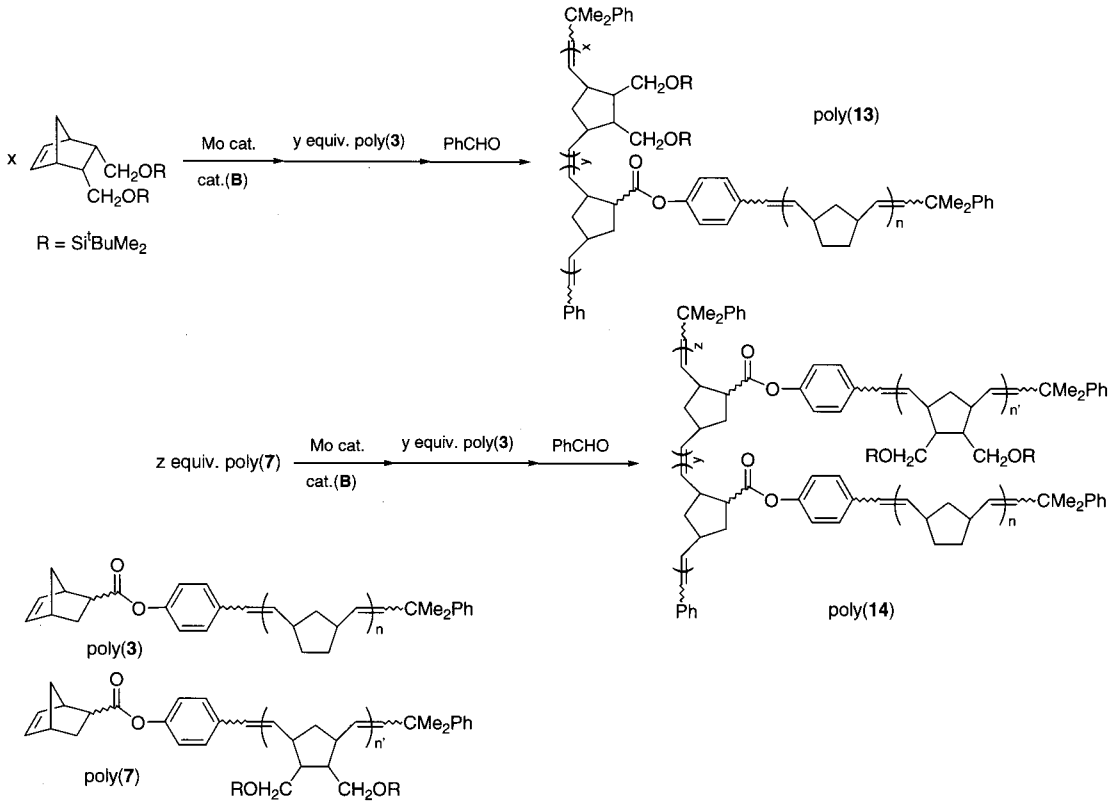


Table 8. Preparation of Poly(13)[a]

		poly(**3**)				poly(**13**)				
run no.	x[b]	M_n(GPC)[c] $\times 10^{-4}$	M_w/M_n[c]	M_n(MS)[d] $\times 10^{-4}$	poly(**3**)/Mo molar ratio/y[b]	M_n(GPC)[c] $\times 10^{-4}$	M_w/M_n[c]	M_n(calcd)[e] $\times 10^{-4}$	M_n(MS)[d] $\times 10^{-4}$	yield,[f] %
11	25	0.64	1.14	0.27	10	4.5	1.27	3.69	4.09	90

[a] For details, see the Experimental Section and Scheme 7, Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$, in toluene, 25 °C. [b] See Scheme 7. [c] GPC data in THF vs polystyrene standard. [d] Determined by MALDI−TOF mass spectrum. [e] Calculated M_n value based on initial monomer/Mo molar ratio. [f] Isolated yield.

Table 9. Preparation of Poly(14)[a]

	poly(**3**)			poly(**7**)		poly(**14**)				
run no.	M_n(GPC)[b] $\times 10^{-4}$	M_w/M_n[b]	M_n(MS)[c] $\times 10^{-4}$	M_n(GPC)[b] $\times 10^{-4}$	M_w/M_n[b]	M_n(GPC)[b] $\times 10^{-4}$	M_w/M_n[b]	M_n(calcd)[d] $\times 10^{-4}$	M_n(MS)[c] $\times 10^{-4}$	yield,[e] %
12	1.18	1.11	0.50	1.98	1.05	11.8	1.16	12.3	11.5	95

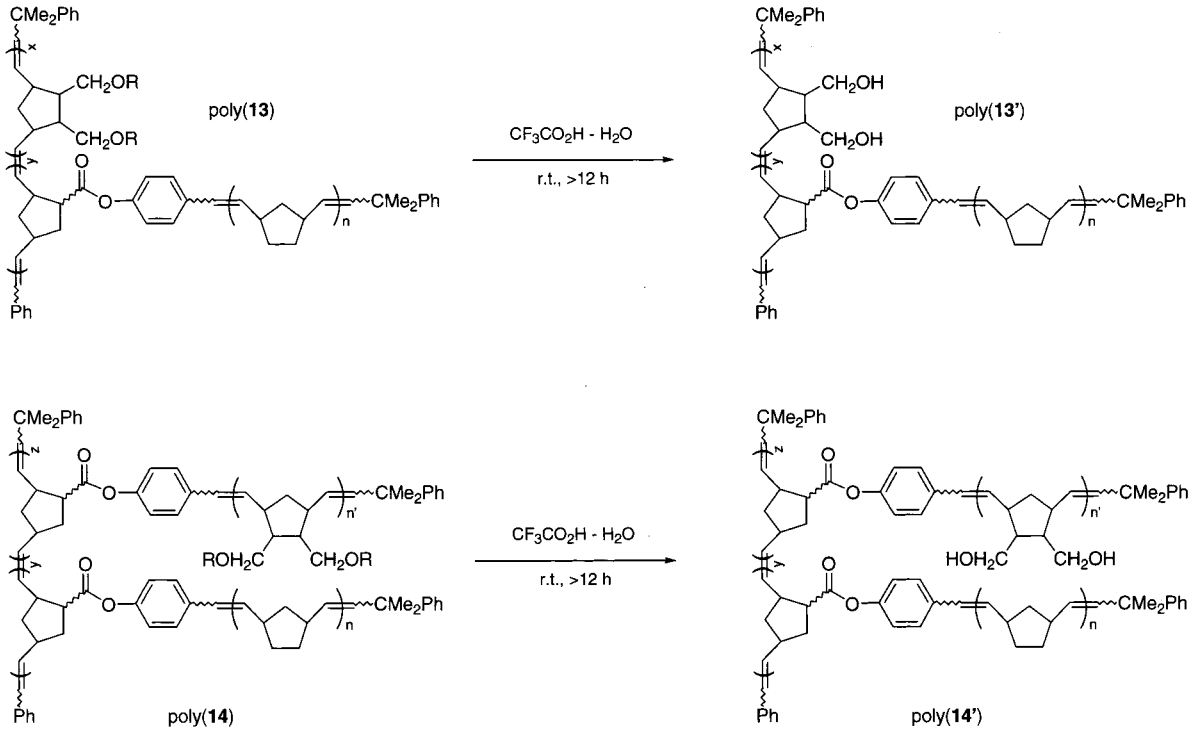
[a] For details, see the Experimental Section and Scheme 7, in toluene, 25 °C. [b] GPC data in THF vs polystyrene standard. [c] Determined value by MALDI−TOF mass spectrum. [d] Calculated M_n value based on initial monomer/Mo molar ratio and Scheme 7. [e] Isolated yield.

romonomer) containing ring-opened poly(norbornene) in relatively high yield (90%, Table 8). The resultant polymer could be identified by ^{1}H NMR, GPC, and mass spectrometry. Poly(**14**), a block poly(macromonomer) consisting of two different norbornene-based macromonomers, poly(**3**) and poly(**7**), was also characterized in the same manner (Scheme 7, Table 9). The resultant polymer could also be identified by the same manner (GPC, MALDI−TOF mass spectrometry, ^{1}H and ^{13}C NMR spectra).

We have shown that various poly(macromonomer)s can be prepared by using the present synthetic procedure. The key steps for the macromonomer synthesis are (i) selective end capping of ring-opened poly(norbornene) with *p*-Me$_3$SiOC$_6$H$_4$CHO, (ii) exclusive hydrolysis of the SiMe$_3$ group, and (iii) quantitative preparation of macromonomer by esterification of OH group at the polymer chain end with norbornene carboxylic acid chloride. In addition, the use of catalyst **B** should be very useful to polymerize macromonomer with complete conversion. We believe that our synthetic strategy shown here should be the powerful tool for preparing poly(macromonomer)s with various functions, not only because the present synthetic approach, repeating the living ROMP technique using molybdenum−alkylidene type initiator, is very simple, but also because the number of monomer unit can be controlled precisely only by varying the monomer/initiator molar ratio due to that the polymerization takes place with both quantitative initiation efficiency and complete conversion.

4. Hydrolysis of Poly(macromonomer)s. A mixed solution consisting of trifluoroacetic acid and water was chosen to remove the ^{t}BuMe$_2$Si group by hydrolysis, not only because the reaction can be usually performed under mild conditions but also because many functional groups are not attacked. For example, poly(**13**) was added into a mixed solution of CF$_3$CO$_2$H/H$_2$O (9/1, v/v) at room temperature, and the resultant polymer was

Scheme 8



Scheme 9

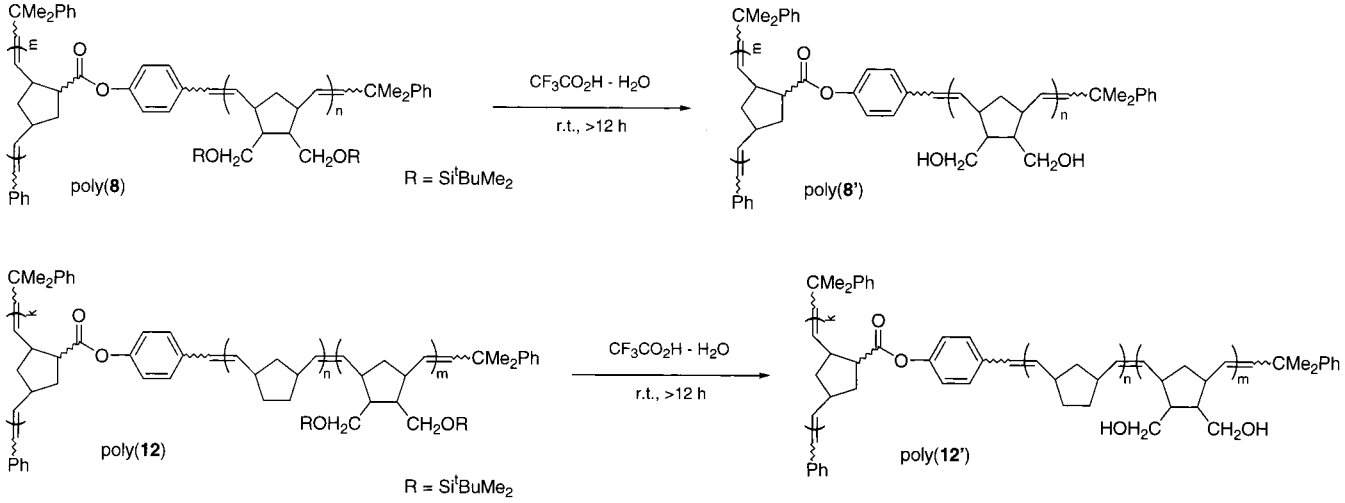


Table 10. Deprotection of Si^{t}BuMe$_2$ Group of Poly(12), Poly(13) and Poly(14)[a]

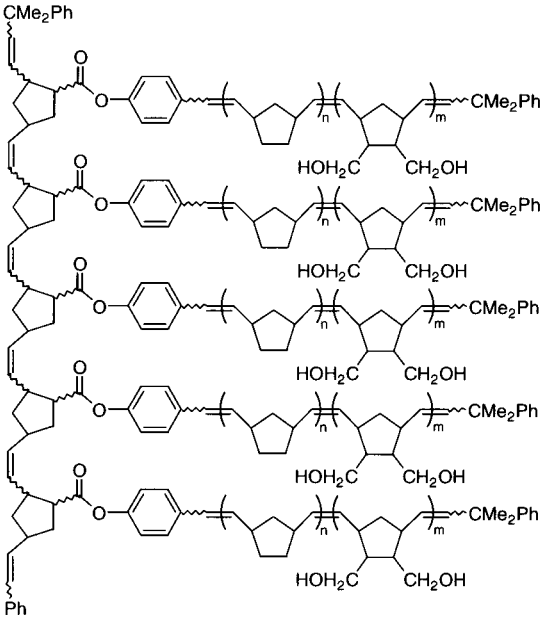
	poly(**12**), poly(**13**), or poly(**14**)					poly(**12′**), poly(**13′**) or poly(**14′**)			
run no.[b]	substrate	M_n(GPC)[c] × 10^{-4}	M_w/M_n[c]	M_n(calcd)[d] × 10^{-4}	M_n(MS)[e] × 10^{-4}	product	M_n(calcd)[d] × 10^{-4}	M_n(MS)[e] × 10^{-4}	yield,[f] %
9	poly(**12**)	7.98	1.12	6.16	6.65	poly(**12′**)	3.31	3.37	93
10	poly(**12**)	14.2	1.09	7.34	8.05	poly(**12′**)	4.48	4.51	95
11	poly(**13**)	4.51	1.27	3.69	4.09	poly(**13′**)	3.12	3.27	92
12	poly(**14**)	11.8	1.16	12.3	11.5	poly(**14′**)	6.60	6.74	93

[a] Conditions: see Experimental Section. [b] Sample number in Tables 8 and 9. [c] GPC data in THF vs polystyrene standard. [d] Calculated value. [e] Determined value by MALDI−TOF mass spectrometry. [f] Isolated yield.

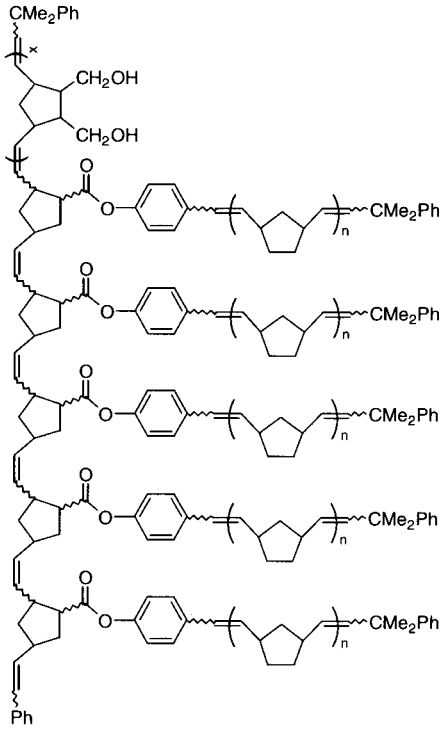
isolated by pouring the reaction mixture into water as a white precipitate of poly(**13′**) (Scheme 8). The ^{1}H NMR spectrum for the resultant polymer showed no resonances attributed to the ^{t}BuMe$_2$Si group, and all other characteristic resonances for the polymer backbone corresponding to poly(**13′**) were present. In addition, typical strong absorption band corresponding to the carbonyl group (1781 cm^{-1}) did not change during this hydrolysis procedure, and the M_n value determined by the MALDI−TOF mass spectrum was the almost same as the calculated value (Table 10). These results strongly suggest that the ^{t}BuMe$_2$Si group could be eliminated exclusively by this hydrolysis procedure.

The ^{t}BuMe$_2$Si group in poly(**14**) could also be removed by the same manner (Table 10), and the resultant polymer could be identified as poly(**14′**) by ^{1}H NMR,

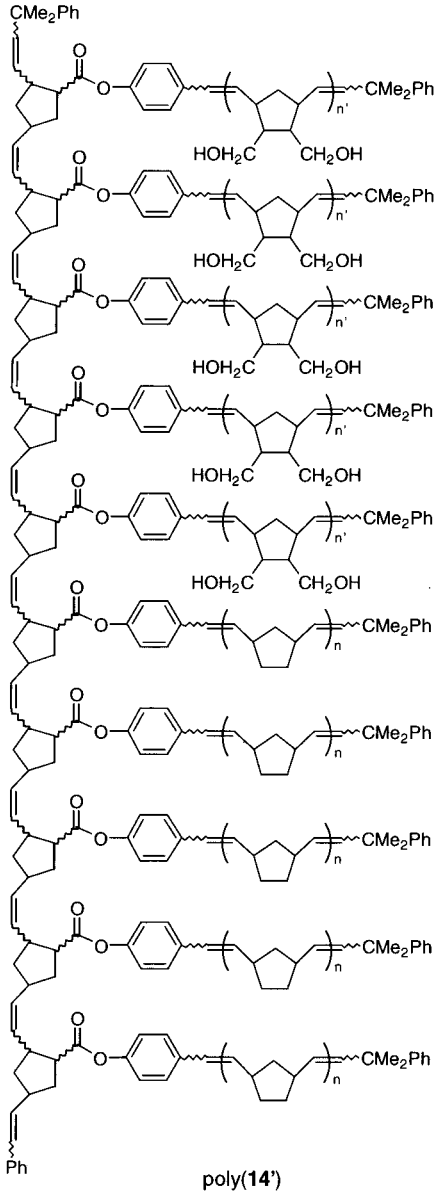
Chart 3



poly(**12'**)



poly(**13'**)



poly(**14'**)

mass spectrometry, and FT-IR (carbonyl absorption band at 1781 cm^{-1}). On the other hand, the reaction product from poly(**8**) and poly(**12**) could only be identified by mass spectrometry (Tables 10 and 11), because the resultant polymer was insoluble in common solvents such as THF, $CHCl_3$, CH_2Cl_2, toluene, and DMF and even in water. Poly(**13′**) and poly(**14′**) were slightly soluble in $CHCl_3$ and THF, and these polymers could be thus analyzed by ^1H NMR, but attempts to obtain ^{13}C NMR spectra were unsuccessful due to the low solubilities.

Summary

We have shown that various series of poly(macromonomer)s bearing various ROMP polymers in the side chains have been prepared by repetitive ROMP technique using well-defined molybdenum initiator. Since the polymerization proceeds in a living manner with quantitative initiation efficiency in most cases, it is possible to prepare various poly(macromonomer)s containing ring-opened poly(norbornene) with functional group. Since the number of monomer units in the side chain as well as number of main chains can be con-

Table 11. Deprotection of Si^{t}BuMe$_2$ Group of Poly(8)[a]

	poly(**8**)					poly(**8′**)		
run no.[b]	n[c]	M_n(GPC)[d] $\times 10^{-4}$	M_w/M_n[d]	M_n(calcd)[e] $\times 10^{-4}$	M_n(MS)[f] $\times 10^{-4}$	M_n(calcd)[c] $\times 10^{-4}$	M_n(MS)[f] $\times 10^{-4}$	yield,[g] %
5	20	4.68	1.17	4.01	3.97	1.74	1.82	85
6	25	6.41	1.06	4.98	4.95	2.13	2.04	93
7	30	7.15	1.07	5.94	5.43	2.51	2.39	95
8	50	10.1	1.08	9.77	9.78	4.06	4.09	95

[a] Conditions: see the Experimental Section. [b] Sample number for preparing poly(**8**) from poly(**5**). [c] Initial molar ratio of monomer/Mo for poly(**5**). [d] GPC data in THF vs polystyrene standard. [e] Calculated value. [f] Determined value by MALDI−TOF mass spectrometry. [g] Isolated yield.

trolled precisely by this method, the present synthetic strategy should have a variety of applications for preparing poly(macromonomer)s containing functional groups. Various novel amphiphilic block copolymers have been prepared by this technique, and we are now studying the properties of these copolymers in the solution and/or in bulk. These will be reported in the near future.

Experimental Section

General Procedure. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Polymerization grade toluene was distilled from sodium and benzophenone, stored over sodium/potassium alloy, and passed through alumina prior to use. Tetrahydrofuran for monomer synthesis was distilled from sodium and benzophenone under nitrogen atmosphere. All chemicals used were of reagent grades and purified by the standard procedures. *p*-Me$_3$SiOC$_6$H$_4$CHO was prepared by the reaction of *p*-hydroxybenzaldehyde with Me$_3$SiCl in THF containing NEt$_3$. *p*-Me$_3$SiOC$_6$H$_4$CHO was then distilled in the presence of molecular sieves under nitrogen atmosphere, and was stored in the drybox at −30 °C. Synthesis of Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_4$)(OR)$_2$ [OR = O^{t}Bu (catalyst **A**), and OCMe(CF$_3$)$_2$ (catalyst **B**)] was according to the literature.[27−29] 5-Norbornene carboxylic acid chloride was prepared according to the literature,[30] and *cis*-2,3-*endo*-bis-[(*tert*-butyldimethylsiloxy)methyl]norborn-5-ene was also prepared by the analogous method for preparing *trans*-2,3-bis[(trimethylsiloxy)methyl]norborn-5-ene[25] from *cis*-2,3-*endo*-bis(hydroxymethyl)norborn-5-ene and ^{t}BuMe$_2$SiCl in the presence of NEt$_3$ in THF.

All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^{1}H; 100.40 MHz, ^{13}C), and all chemical shifts are given in ppm and are referenced to tetramethylsilane. Obvious multiplicities and routine coupling constants are usually not listed, and all spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. HPLC grade THF was used for GPC and was degassed prior to use. GPC analyses were performed at 40 °C on a Shimazu SCL-10A using a RID-10A detector (Shimazu Co. Ltd.) in THF (containing 0.03 wt % 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mmϕ) were calibrated vs polystyrene standard samples. MALDI−TOF mass spectra were taken by using Voyager-DE STR MALDI−TOF mass spectrometer (Perseptive Biosystem Co.) with a 3-indoleacetic acid matrix. FT-IR spectra for the poly(macromonomer)s were measured by using a HORIBA FT-730 spectrometer.

Synthesis of Homopolymers, Poly(1). A toluene solution of Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ (catalyst **A**, 80 μmol in toluene 1.0 g) was added in one portion to a rapidly stirred toluene solution (4.0 g) containing prescribed amount of norbornene at room temperature, and the reaction mixture was stirred for 30 min. The polymerization was quenched by adding *p*-Me$_3$SiOC$_6$H$_4$CHO in excess amount after the consumption of monomers, stirred for 1 h for completion. The resultant solution was poured dropwise to stirred cold methanol (∼200 mL), affording a white−pale yellow precipitate. The polymer was collected by filtration and was then dried in vacuo. Yield: 90−98%. ^{1}H NMR (CDCl$_3$): δ 5.22 and 5.35 (br.m, 2H olefinic), 2.80 and 2.37 (br.s, 2H), 1.85 and 1.08 (m, 2H), 1.81 and 1.36 (m, 4H), and 0.26 (s, Si(CH$_3$)$_3$). Peaks corresponding to the polymer chain end could also be observed: δ 6.26 (d, PhCH=CH−), 6.04 (dd, PhCH=CH−), 5.56 (d, PhMe$_2$CCH=CH−), and 5.39 (m, PhMe$_2$CCH=CH−). Other resonances corresponding to phenyl group were also observed. ^{13}C NMR (CDCl$_3$): δ 134.0, 133.9, 133.8, 133.7, and 133.1, 133.0, and 132.8 (olefinic), 128.0, 126.9, 126.1, 125.5, and 120.1 (aromatic carbon), 68.0, 50.8, 43.4, 43.2, 42.7, 42.1, 41.3, 38.6, 38.4, 33.1, 32.9, 32.3, 32.2, 25.6, 21.3, and 0.2 [Si(CH$_3$)$_3$].

Hydrolysis of Poly(1). Poly(**1**) (368 mg) prepared by the above procedure was dissolved in a minimum amount of THF, and the solution was then poured into a mixed solution consisting of methanol (20 mL) and 5 N NaOH aqueous solution (5 mL) at room temperature. The reaction mixture was stirred overnight, and the resultant precipitate was collected by filtration, washed with water, and then dried in vacuo. The resultant precipitate was dissolved in a minimum amount of THF and then poured into cold methanol. ^{1}H NMR (CDCl$_3$): δ 5.32 and 5.19 (br m, 2H olefinic), 2.77 and 2.41 (br s, 2H), 1.85 and 1.05 (m, 2H), 1.75 and 1.33 (m, 4H). Peaks corresponding to the polymer chain end could also be observed.

Preparation of Macromonomer, Poly(3). The deprotected polymer, poly(**2**), and NEt$_3$ (ca. 1.1 equiv to the polymer based on M_n value calculated by the initial monomer/initiator molar ratio) were dissolved in THF, and norbornene carboxylic acid chloride (1.5 equiv) was then added dropwise. The reaction mixture was stirred for 2 h at room temperature and was then refluxed for 5 h. The mixture was then poured dropwise into a cold methanol solution. The resultant precipitate collected by filtration was then dried in vacuo. The prepared macromonomer was further purified by passing through an alumina column (as the toluene solution) in the drybox. ^{1}H NMR (CDCl$_3$): δ 6.32 and 6.07 (m, olefinic, norbornene), 5.37 and 5.18 (br m, olefinic), 3.36−2.96 (m, norbornene nonolefinic), 2.78 and 2.41 (br s), 1.85 and 1.03 (m), 1.77 and 1.34 (m). Other peaks corresponding to norbornene nonolefinic protons were covered with the polymer resonances, and peaks corresponding to the polymer chain end could also be observed. ^{13}C NMR (CDCl$_3$): δ 173.3 (C=O), 149.7 (phenoxy), 138.5, 138.3, 138.1, 135.7, 135.6 (norbornene olefinic), 133.9−134.1, 133.5, 133.3, 132.8−133.1, 131.2, 129.6, 128.1, 126.7−127.1, 126.3, 125.7, 121.6, 121.3 (olefinic and aromatic), 49.9, 46.9, 46.1, 43.5, 43.3, 42.9, 42.2, 41.5, 41.3, 40.2, 38.8, 38.5, 33.2, 33.1, 32.5, 32.3, 32.2, 29.1−29.5 (nonolefinic).

Poly(4). The typical procedure is as follows. The poly(**3**) (80 mg, 10 equiv to the catalyst **B**) was dissolved in toluene (2.0 g), and the catalyst solution (toluene 0.5 g) was added in one portion at room temperature. The mixture was stirred for 30 min, and the polymerization was terminated by the addition of benzaldehyde in excess amount. The solution was stirred for 1 h for completion, and the solution was poured into cold methanol to isolate the polymer as a white precipitate. Yield: 96%. ^{1}H NMR (CDCl$_3$): δ 5.27 and 5.14 (br m, 2H olefinic), 2.70 and 2.37 (br s, 2H), 1.78 and 0.97 (m, 2H), 1.48 and 1.30 (m, 4H). ^{13}C NMR (CDCl$_3$): δ 167.3, 149.4, 144.0, 137.9, 133.5−133.8, 132.8−133.0, 131.4, 131.0, 130.0, 127.9, 126.0, 125.5,

42.8−43.4, 42.0−42.1, 41.4, 40.2, 38.7, 38.5, 38.4, 33.2, 33.0, 32.4, 32.3, 30.1, 29.1.

Poly(5). The basic procedure for preparing poly(**5**) was the same as that in poly(**1**) except that *cis*-2,3-*endo*-bis[(*tert*-butyldimethylsiloxy)methyl]norborn-5-ene was used in place of norbornene. Basic conditions: toluene 5.0 g, catalyst **A** in toluene 1.0 g, monomer 500 mg, room temperature, 1 h. Yield: 96−98%. ^{1}H NMR ($CDCl_3$): δ 5.44 (br s, 2H, olefinic), 3.63 (br s, 4H), 2.60 (br s, 2H), 2.16 (br s, 2H), 1.48 and 1.86 (br s, 2H), 0.87 (s, 18H), 0.02 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 132.2−133.3, 129.0, 128.2, 120.2, 61.6, 50.9, 48.0, 44.2−44.5, 39.5−39.6, 25.8, 18.0, 0.2, −5.6.

Poly(6). The basic procedure for preparing poly(**6**) was the same as that in poly(**2**). Yield: 95−98%. ^{1}H NMR ($CDCl_3$): δ 5.44 (br s, 2H olefinic), 3.63 (br s, 4H), 2.60 (br s, 2H), 2.16 (br s, 2H), 1.85 and 1.50 (br s, 2H), 0.87 (s, 18H), 0.02 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 132.3, 127.9, 61.3, 50.9, 47.9, 44.2−44.5, 39.5, 26.0, 18.2, −5.3.

Poly(7). The basic procedure for preparing poly(**7**) was the same as that in poly(**3**). Yield: 93−98%. ^{1}H NMR ($CDCl_3$): δ 6.26 and 6.1 (m, olefinic norbornene), 5.44 (br s), 3.63, 3.45, 3.23, 2.98, 2.60 (br s), 2.16 (br s), 1.86, 1.47, 0.87 (s), 0.02 (s). ^{13}C NMR ($CDCl_3$): δ 175.2, 140.8−141.0, 132.2−4, 131.5−8, 129.0, 128.0, 126.7, 61.3, 53.1−2, 52.1, 47.7−8, 47.2−3, 45.8, 44.4−6, 43.4, 43.1, 39.6−7, 36.7−8, 25.9, 18.2, −5.4.

Poly(8). The basic procedure for preparing poly(**8**) was the same as that in poly(**4**) except that poly(**7**) was used in place of poly(**3**). Yield: 85−90%. ^{1}H NMR ($CDCl_3$): δ 5.44 (br s), 3.63 (br s), 2.60 (br s), 2.16 (br s), 1.86 (br s), 1.54 (br s), 0.87 (s), 0.02 (s).

Poly(9). The basic procedure for preparing poly(**9**) was the same as that in poly(**1**) except that *cis*-2,3-*endo*-bis[(*tert*-butyldimehtylsilyloxy)methyl]norborn-5-ene and norbornene were added sequentially. Yield: 93−96%. ^{1}H NMR ($CDCl_3$): δ 5.43, 5.31, 5.18 (olefinic), 3.63 (br s), 2.76 (br s), 2.58 (br s), 2.38 (br s), 2.16 (br s), 1.83 (m), 1.75 (m), 1.52 (br s), 1.33 (m), 1.02 (m), 0.87 (s), 0.02 (s).

Preparation of Poly(10) and Poly(11). The basic procedures were the same as those in poly(**2**) and poly(**3**). Yield: 89−96%. ^{1}H NMR spectrum of poly(**10**) ($CDCl_3$): δ 5.43, 5.31, 5.18 (olefinic), 3.63 (br s), 2.76 (br s), 2.58 (br s), 2.38 (br s), 2.16 (br s), 1.83 (m), 1.75 (m), 1.52 (br s), 1.33 (m), 1.02 (m), 0.87 (s), 0.02 (s). ^{1}H NMR spectrum of poly(**11**) ($CDCl_3$): δ 6.32 (m), 6.07 (m), 5.43, 5.32, 5.18, 3.63 (br s), 3.42, 3.20, 2.95−3.10 (m), 2.76 (br s), 2.59 (br s), 2.40 (br s), 2.15 (br s), 1.83, 1.76, 1.53, 1.33, 1.02, 0.87, 0.01. ^{13}C NMR spectrum of poly(**11**) ($CDCl_3$): δ 168.3, 133.0, 132.2−4, 129.5, 127.5, 61.4, 49.7, 47.9, 45.7, 44.4, 44.2, 43.1, 41.4, 38.4, 35.6, 32.5, 32.4, 32.2, 26.0, 21.0, 18.2, −5.3.

Poly(12). The basic procedure was the same as that in poly(**4**) except that poly(**11**) was used in place of poly(**3**). Yield: 92−96%. ^{1}H NMR ($CDCl_3$): δ 5.35, 3.64, 2.58, 2.40, 2.10, 1.88, 1.67, 1.53, 1.24, 1.11, 0.86 (s), 0.01 (s).

Poly(13). The basic procedure for preparing poly(**13**) was the same as that in poly(**12**) except that *cis*-2,3-*endo*-bis[(*tert*-butyldimethylsiloxy)methyl]norborn-5-ene and poly(**3**) were added sequentially. Yield: 90%. ^{1}H NMR ($CDCl_3$): δ 5.43, 5.32, 5.18, 3.63, 2.77, 2.59, 2.41, 2.15, 1.84 (m), 1.76 (m), 1.33, 1.02, 0.87 (s), 0.02 (s).

Poly(14). The basic preparation procedure was the same as that in poly(**13**) except that poly(**7**) and poly(**3**) were added sequentially. ^{1}H NMR ($CDCl_3$): δ 5.52, 5.32, 5.18, 3.63 (br s), 2.77 (br s), 2.60 (br s), 2.41 (br s), 2.15 (br s), 1.86 (m), 1.77 (m), 1.54, 1.32, 1.02 (m), 0.87 (s), 0.02 (s). ^{13}C NMR ($CDCl_3$): δ 173.1, 133.9, 132.9, 132.3, 61.3, 48.0, 44.6, 44.4, 44.3, 43.4, 43.1, 38.7, 38.4, 33.1, 32.9, 32.2, 26.0, 18.2, −5.3.

Hydrolysis Procedure (Deprotection of *tert*-Butyldimethylsilyl Group). Poly(**8**) (or poly(**12**), poly(**13**), or poly(**14**), ca. 20 mg) was added dropwise to a stirred solution consisting of CF_3CO_2H/H_2O (9/1, v/v, 3.0 g), and the reaction mixture was stirred overnight at room temperature. The solution was then poured dropwise into a vigorously stirred water (50 mL) to collect poly(**8′**) as the white precipitate (yield 90−98%).

The ^{1}H NMR ($CDCl_3$) spectrum of poly(**8′**) was almost the same as that in poly(**8**) except that resonances corresponding to ^{t}BuMe$_2$Si group (δ 0.87 and 0.02 ppm) was disappeared. These deprotected polymers [poly(**8′**), poly(**12′**), poly(**13′**), poly(**14′**)] were identified by ^{1}H NMR, FT-IR, and MALDI−TOF mass spectrometry. ^{1}H NMR (in $CDCl_3$) of poly(**13′**): δ 5.33, 5.19, 3.63, 2.77 (br s), 2.41 (br s), 2.11, 1.84, 1.75 (m), 1.68, 1.34, 1.02 (m). ^{1}H NMR (in $CDCl_3$) of poly(**14′**): δ 5.46, 5.42, 5.33, 4.36, 4.26, 2.84, 2.59, 2.42, 2.13, 1.83, 1.77, 1.35, 1.02.

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not explain the fact that why the M_n values by GPC for the resultant polymer, especially poly(**1**), were somewhat higher than those calculated based on the initial norbornene/molybdenum molar ratio, although the ROMP chemistry should be accomplished as the quantitative initiation efficiency. In this paper, we traced these experiments in some parts and characterized the resultant polymer by GPC, ^{1}H NMR, and MALDI−TOF mass spectrometry, in particular for measurement of molecular weight of the resultant polymers.

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(24) One point that is not clear at this moment is whether the regularity of the resultant poly(macromonomer), poly(**4**), might be a mixture of head-to-tail, head-to-head, and tail-to-tail arrangement of the repeated unit or not. Due to the steric bulk of ester function in the macromonomer, it is assumed that the resultant poly(macromonomer) might have a regioregularity in the head-to-tail repeating unit.

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