Ring-Opening Metathesis Polymerization Using Alkenyl Sulfides as Chain-Transfer Agents: Efficient Routes to Unsymmetrical Poly(norbornene)-Based Macroinitiators Bearing a Terminal Hydroxy Group

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Received May 18, 2003; Revised Manuscript Received July 16, 2003

ABSTRACT: Convenient routes to hydroxy-terminated poly(norbornene)s (PNBEs) have been developed. Hydroboration of PNBEs bearing a terminal vinyl group with 9-BBN followed by oxidation with H_2O_2/NaOH forms hydroxy-terminated PNBEs in high yields. The parent PNBEs are prepared by ring-opening metathesis polymerization (ROMP) of norbornene using vinylic sulfides as chain-transfer agents (CTAs). On the other hand, ROMP of norbornene using (*Z*)-1-phenylthio-1-propen-3-ol as a CTA causes one-step synthesis of *ω*-hydroxy-terminated PNBE, where the molecular weight of polymer depends linearly on the initial feed ratio of CTA to monomer. Similarly, ROMP reactions using (*Z*)-1-phenylthio-1-propen-3-ols having bromo, amino, and 4-(chloromethyl)benzamido substituents at the para position of the phenyl group as CTAs afford the corresponding α,*ω*-heterodifunctionalized (heterotelechelic) PNBEs. The resulting PNBEs serve as macroinitiators for anionic ring-opening polymerization (AROP) of *ϵ*-caprolactone and atom-transfer radical polymerization (ATRP) of styrene, giving AB- and ABC-type block copolymers.

Introduction

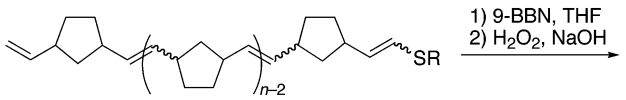
Ring-opening metathesis polymerization (ROMP) has attracted growing interest because of its capability of producing the polymers that are unable to be prepared by other polymerization methods.[1] In this context, considerable efforts have been made in recent years for ROMP approach to end-functionalized polymers,[2−4] which are useful intermediates for constructing block copolymers and polymeric networks. One of the most efficient ways of incorporating end-functionalities in ROMP is the use of acyclic olefins bearing functional groups as chain-transfer agents (CTAs), where two types of polymers are formed according to the structures of CTAs. When symmetrically substituted olefins are employed as CTAs, the resulting polymers have the same substituents at both chain ends. On the other hand, the reactions using unsymmetrical CTAs afford the polymers bearing different substituents at α- and *ω*-ends, respectively. Most of the ROMP/CT reactions reported so far fall into the former class.[2,3] This is probably because the use of symmetrical olefins circumvents the regiochemical issue associated with the CT process, which still remains a principal subject in olefin metathesis.

We recently reported that ROMP/CT reactions in the latter class are selectively operative using vinyl chalcogenides as CTAs.[4] For example, polymerization of norbornene (NBE) in the presence of CH_2═CHER (E = O, S, Se) and a catalytic amount of $RuCl_2$(═C═CHBu^t)-(PCy_3)$_2$ or $RuCl_2$(═CHEPh)(PCy_3)$_2$ (E = S, Se) affords poly(norbornene) (PNBE) bearing −CH_2═CHER and CH_2═CH− groups at α- and *ω*-ends, respectively (Scheme 1). Thus, it became feasible to incorporate various functionalities into the α-end of PNBE by the choice of R group in vinyl chalcogenides.[4b]

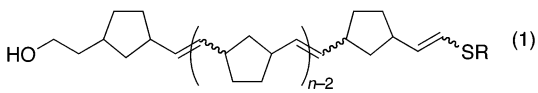
On the other hand, we found in this study that the other chain end of PNBE (*ω*-end) is selectively functionalized for hydroxy group by hydroboration of *ω*-vinyl group or by ROMP using (*Z*)-1-arylthio-1-propen-3-ols as CTAs. These reactions are applicable to the synthesis of heterotelechelic polymers bearing two different functional groups at each chain-end, and the resulting PNBEs serve as macroinitiators for constructing AB- and ABC-type block copolymers.

Results and Discussion

Hydroxylation of Vinyl-Terminated Poly(norbornene)s. Two kinds of PNBEs bearing a vinyl group at the *ω*-end (PNBE-**1** and -**2** in eq 1) were prepared



PNBE-**1**: R = Ph, $M_{n,NMR}$ = 1300, M_w/M_n = 1.56
PNBE-**2**: R = $C_6H_4CH_2Cl$-*p*, $M_{n,NMR}$ = 1700, M_w/M_n = 1.70



(1)

PNBE-**3**: R = Ph, $M_{n,NMR}$ = 1300, M_w/M_n = 1.58
PNBE-**4**: R = $C_6H_4CH_2Cl$-*p*, $M_{n,NMR}$ = 1800, M_w/M_n = 1.78

for the starting materials by ruthenium-catalyzed ROMP of norbornene using CH_2═CHSPh and CH_2═CHSC_6H_4-CH_2Cl-*p* as CTAs, respectively. Hydroboration of PNBE-**1** with a 3 mol quantity (based on the *ω*-vinyl group) of 9-BBN in THF followed by oxidation using

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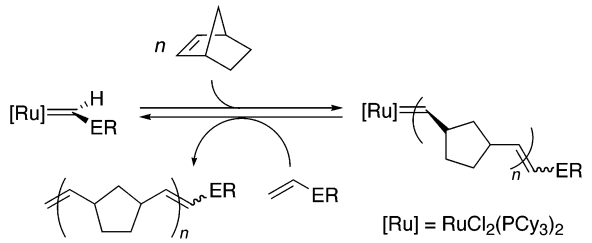
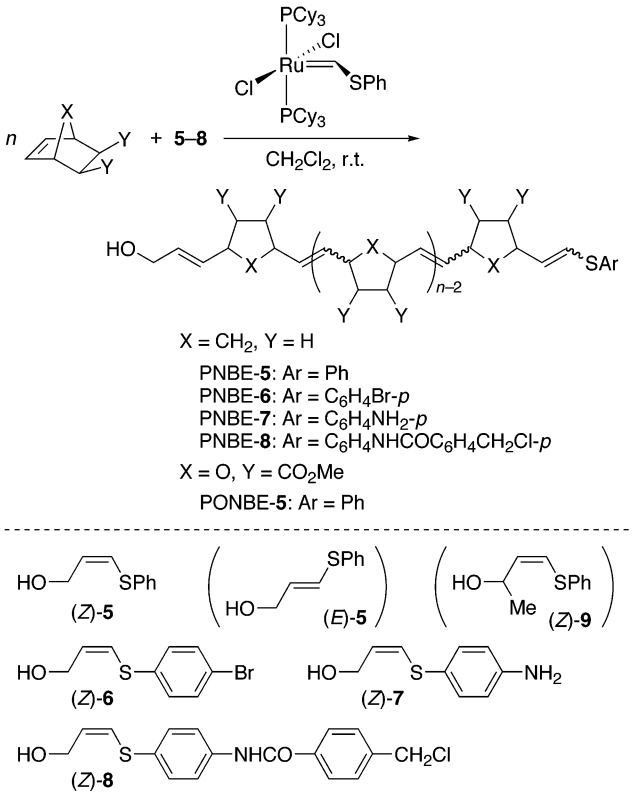
10.1021/ma034653m CCC: $25.00
Published on Web 08/16/2003

Scheme 1. ROMP Using Vinyl Chalcogenides as CTAs



Scheme 2. ROMP Using (*Z*)-1-Arylthio-1-propen-3-ols as CTAs



H_2O_2/NaOH afforded an ω-hydroxy-terminated polymer (PNBE-**3**) in 82% yield. The ^{1}H NMR spectrum exhibited characteristic signals of $HOCH^aCH^b_2$ group at δ 3.65 (dt, J = 6.8, 5.5 Hz, H^a) and 1.61 (dt, J = 6.8, 6.4 Hz, H^b) along with the main signals of polymer backbone, while the signals due to the original ω-vinyl group disappeared completely. The molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of PNBE-**3** were almost identical with those of PNBE-**1** as confirmed by ^{1}H NMR and GPC analysis.[5] Hence the selective hydroxylation of terminal vinyl group was evidenced. PNBE-**2** was hydroxylated under the same reaction conditions to afford an 89% yield of PNBE (**4**) bearing 4-(chloromethyl)phenyl and hydroxy groups at α- and ω-ends, respectively.

ROMP Using (*Z*)-1-Arylthio-1-propen-3-ols as CTAs. The hydroxylation method described above was successful also with the vinyl-terminated PNBE-**1** with M_n = 2800. On the other hand, hydroboration of PNBE-**1** with higher molecular weights (M_n = 5800, 6500) was incomplete with 3 mol quantities of 9-BBN, and the reaction using a large excess amount of 9-BBN (>10 mol quantity) gave a complex mixture of products. Therefore, we sought other synthetic means of hydoxy-terminated PNBEs, and as a result, we found that the use of (*Z*)-1-arylthio-1-propen-3-ols as CTAs enables one-step synthesis of hydroxy-terminated PNBEs with a wide molecular weight range (Scheme 2).

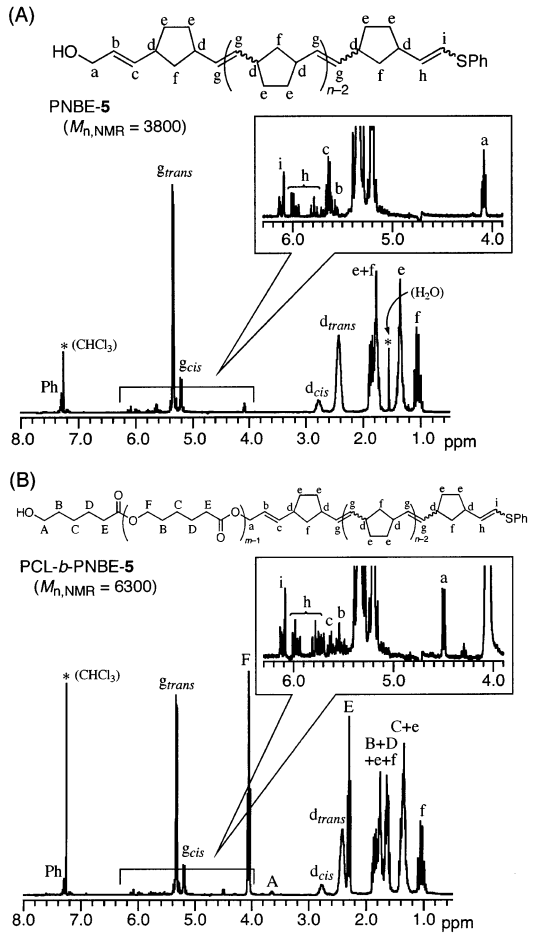


Figure 1. ^{1}H NMR spectra of (A) PNBE-**5** (entry 2 in Table 1) and (B) PCL-*b*-PNBE-**5** (entry 3 in Table 2).

Treatment of NBE with a 0.2 mol quantity of (*Z*)-rich 1-phenylthio-1-propen-3-ol ((*Z*)-**5**; *E*/*Z* = 8/92) in CH_2Cl_2 in the presence of 1 mol % of $RuCl_2$(=CHSPh)-$(PCy_3)_2$[4a,6] gave a white solid of polymer (PNBE-**5**) in 93% yield. This reaction was completed in 2 h at room temperature. The ^{1}H NMR spectrum (Figure 1A) clearly shows incorporation of a 1:1 ratio of $HOCH_2CH$=CH− and −CH=CHSPh groups into the PNBE chain. The $HOCH_2CH$=CH− group exclusively adopted (*E*)-configuration (*E*/*Z* > 99/1), whereas the −CH=CHSPh group was a mixture of (*E*)- and (*Z*)-isomers (*E*/*Z* = 57/43). The molecular weight estimated from peak integration ($M_{n,NMR}$ = 3800) was in good agreement with the VPO data ($M_{n,VPO}$ = 3900). These observations are consistent with the PNBE structure bearing $HOCH_2CH$=CH− and −CH=CHSPh groups at α- and ω-ends, respectively.[7]

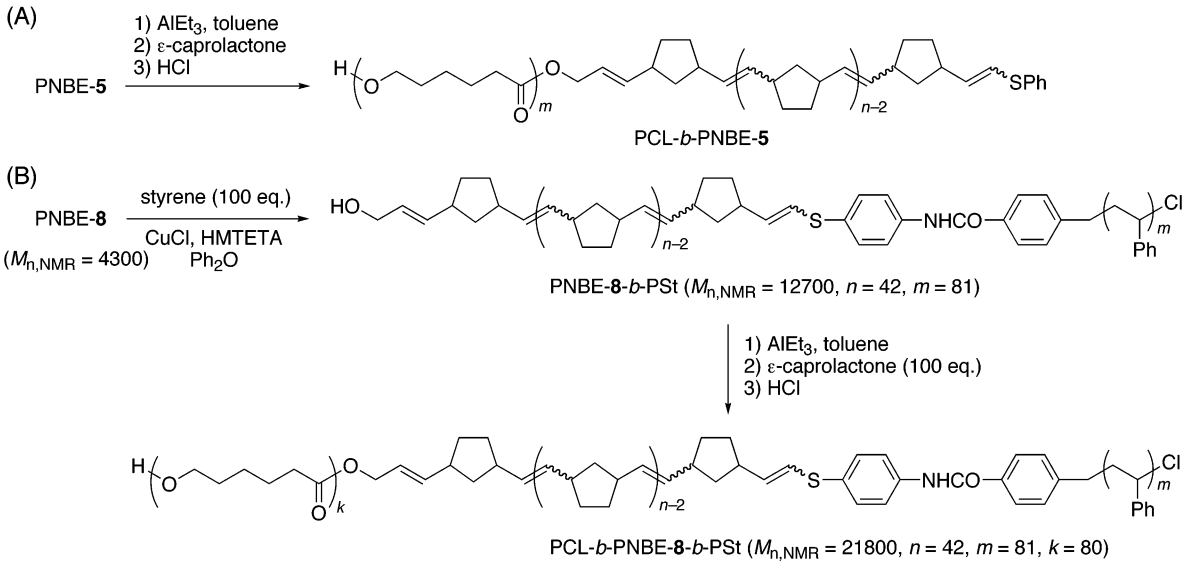
Table 1 lists the results of ROMP/CT of NBE and *exo*,*exo*-5,6-bis(methoxycarbonyl)-7-oxa-2-norbornene (ONBE) using five kinds of CTAs (**5**−**9**). Molecular weight of PNBE-**5** linearly increased as the initial ratio of (*Z*)-**5** to NBE decreased, and thus suggested high efficiency of (Z)-**5** as a CTA (entries 1−4, Figure 2). Similarly, (*Z*)-rich 1-phenylthio-1-propen-3-ols having bromo, amino, and 4-(chloromethyl)benzamido substituents at the para position of phenyl group (**6**−**8**) served as good CTAs to afford heterotelechelic PNBEs (PNBE-**6**−**8**) with well-controlled molecular weights (entries 5−7). Hydroxy-terminated PONBE was also successfully synthesized (entry 8). On the other hand, (*E*)-**5** and

Table 1. ROMP of Norbornene (NBE) and *exo,exo*-5,6-Bis(methoxycarbonyl)-7-oxa-2-norbornene (ONBE) in the Presence of Chain-Transfer Agents 5−9[a]

entry	M[b]	CTA (*E*/*Z*)[c]	$[M]_0/[CTA]_0$	yield/%[d]	$M_{n,NMR}$	$M_{n,VPO}$[e]	M_w/M_n[f]
1	NBE	(*Z*)-**5** (8/92)	100/50	82	2500	2800	2.18
2	NBE	(*Z*)-**5** (8/92)	100/20	93	3800	3900	2.37
3	NBE	(*Z*)-**5** (8/92)	100/12	94	6000	6000	3.06
4	NBE	(*Z*)-**5** (8/92)	100/10	90	7100	7000	2.70
5	NBE	(*Z*)-**6** (28/72)	100/10	86	9500	11 000	2.92
6	NBE	(*Z*)-**7** (<1/99)	100/10	78	5500	5100	2.50
7	NBE	(*Z*)-**8** (29/71)	100/20	66	4300	4800	2.49
8	ONBE	(*Z*)-**5** (8/92)	100/5	72	6100	6300	1.59
9	NBE	(*E*)-**5** (>99/1)	100/10	93		(139000)[f]	1.89
10	NBE	(*Z*)-**9** (8/92)	100/10	98		(106900)[f]	2.08

[a] All reactions were run at room temperature for 2 h: $[M]_0 = 0.10$ M, $[RuCl_2(=CHSPh)(PCy_3)_2]_0 = 1.0$ mM. Solvent: CH_2Cl_2 (entries 1−5 and 8−10); THF (entries 6 and 7). [b] Monomer. [c] Determined by ^{1}H NMR. [d] Isolated yield based on the total amount of monomer employed and CTA converted. [e] Measured in $CHCl_3$ at 40 °C. [f] Determined by GPC based on polystyrene standards.

Scheme 3. Synthesis of AB- (A) and ABC-type (B) Block Copolymers



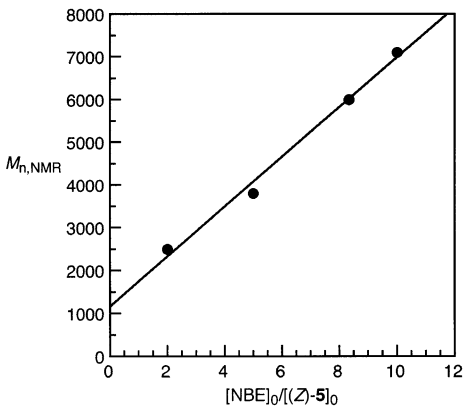


Figure 2. Plot of the $M_{n,NMR}$ values of poly(norbornene) (PNBE-**5**) vs the ratio of norbornene to (*Z*)-1-phenylthio-1-propen-3-ol ((*Z*)-**5**) (entries 1−4 in Table 1).

(*Z*)-**9** having a methyl group at the allylic position exhibited apparently no CTA activity, giving PNBEs with high molecular weights (entries 9 and 10).

Synthesis of Block Copolymers. The end-functionalized PNBEs thus prepared were tested as macroinitiators. At first, monofunctionalized PNBE-**5** was subjected to anionic ring-opening polymerization (AROP) of ϵ-caprolactone (CL) to give an AB-type diblock copolymer (Scheme 3A). The results for the synthesis of PCL-*b*-PNBE-**5** with a variety of unit ratios are summarized in Table 2. For example, treatment of PNBE-**5** ($M_{n,NMR} = 3800$, $M_w/M_n = 2.37$) with $AlEt_3$ (1 equiv) in toluene at room temperature for 2 h, followed by with CL (25 equiv) for 24 h afforded PCL-*b*-PNBE-**5** in 77% yield (entry 3). The ^{1}H NMR spectrum is given in Figure 1B. In addition to the signals arising from the PNBE-**5** part (a−i), the signals assignable to PCL (A−F) are clearly observed. The ratio of CL to NBE unit in the block copolymer was estimated to be 0.36. This value corresponds to the molecular weight ($M_{n,NMR}$) of 6300 and is fairly consistent with the reaction stoichiometry ($M_{n,theor} = 6700$). The GPC analysis of the copolymer isolated from the reaction system of entry 4 revealed a clean shift of the monomodal peak profile of PNBE-**5** to a high-molecular-weight region (Figure 3). Further evidence for the formation of block copolymer was obtained by TEM analysis. As seen from Figure 4A, PCL-*b*-PNBE-**5** exhibited a microphase-separated structure, characteristic of copolymers having polar and nonpolar blocks. On the other hand, the development of PCL spherulites (white region) in PNBE (gray region) was clearly noted in the polymer blend of PCL and PNBE (Figure 4B).

The synthesis of an ABC triblock copolymer was also successful (Scheme 3B). Thus, heating a mixture of styrene, PNBE-**8** ($M_{n,NMR} = 4300$, $M_w/M_n = 2.49$), CuCl, and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) in a 100:1:2:6 ratio in diphenyl ether at 130 °C for 22 h led to atom-transfer radical polymerization (ATRP) of styrene at the α-end of PNBE-**8** to

Table 2. AROP of ϵ-Caprolactone (CL) Using Hydroxy-Terminated Poly(norbornene)s (PNBE-5) as Macroinitiators[a]

entry	PNBE-**5** $M_{n,NMR}$ (M_w/M_n)	$[CL]_0/[PNBE\text{-}5]_0$	yield/%[b]	$M_{n,theor}$[c]	$M_{n,NMR}$	M_w/M_n[d]	PCL/PNBE[e] (unit ratio)
1	7500 (3.18)	15	92	9200	9000	2.66	14/86
2	5200 (2.87)	25	86	8100	7700	2.40	29/71
3	3800 (2.37)	25	77	6700	6300	1.73	36/64
4	3800 (2.37)	100	88	15 200	13 600	2.04	69/31
5	2800 (2.27)	100	88	16 500	16 100	1.40	81/19

[a] All reactions were run in toluene at room temperature. [b] Isolated yield based on total mass of PNBE-**5** and CL. [c] $M_{n,theor} = M_{n,NMR}$(PNBE-**5**) + MW(CL) × (molar ratio). [d] Determined by GPC based on polystyrene standards. [e] Determined by ^{1}H NMR.

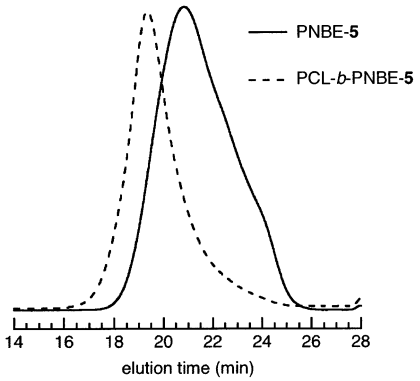


Figure 3. GPC curves for PNBE-**5** (entry 2 in Table 1) and PCL-*b*-PNBE-**5** (entry 4 in Table 2).

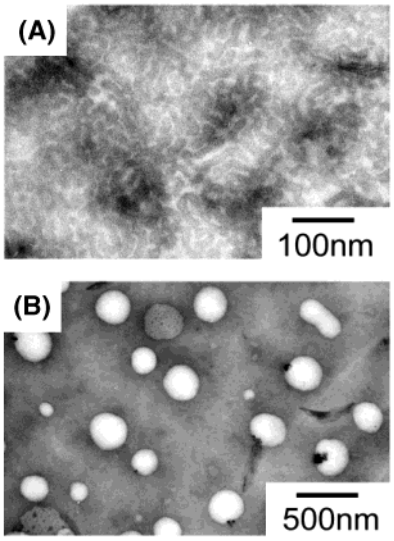


Figure 4. TEM profiles of (A) PCL-*b*-PNBE-**5** ($M_{n,NMR}$ = 6300) and (B) polymer blend of PCL ($M_{n,NMR}$ = 3900) and PNBE ($M_{n,NMR}$ = 3800) in a 35:65 ratio. The sample films were cast from toluene solutions and dyed with OsO_4. The white and gray regions represent PCL and PNBE, respectively.

give PNBE-**8**-*b*-PSt in 76% yield ($M_{n,NMR}$ = 12 700, M_w/M_n = 2.70). The resulting polymer reacted with a 100 M quantity of CL under AROP conditions similar to those in the reaction in Scheme 3A, affording PCL-*b*-PNBE-**8**-*b*-PSt in 81% yield ($M_{n,NMR}$ = 21 800, M_w/M_n = 2.63). Similarly, heterotelechelic PNBE-**4** served as a bifunctional macroinitiator for constructing ABC-type block copolymer. To our knowledge, this is the first example of the synthesis of an ABC triblock copolymer by the combination of olefin metathesis, radical, and anionic polymerization processes.

Conclusion

We have described a new efficient route to PNBEs bearing a terminal hydroxy group. Although ROMP/CT approach to hydroxy-terminated polymers have been studied to a considerable extent owing to the significant utility of product polymers, all of them are related to the reactions using symmetrically substituted acyclic olefins $X(CH_2)_nCH{=}CH(CH_2)_nX$ (X = AcO, TBDMSO, 9-BBN, etc.) as CTAs.[2] Accordingly, the resulting polymers inevitably have hydroxy groups at both chain ends. Furthermore, since the CTAs so far employed have "masked" hydroxy groups such as OAc and 9-BBN in most cases,[8] deprotection or chemical transformation of terminal groups into hydroxy groups has been needed to obtain desirable hydroxy-terminated polymers. On the other hand, in the present ROMP/CT reactions using (*Z*)-1-arylthio-1-propen-3-ols as CTAs, it is unnecessary to protect the hydroxy group prior to polymerization. Moreover, since the resulting polymers have hydroxy group only at one chain end, the other chain end may be applied to other functionalities. Clearly, the present ROMP/CT system is a hitherto unknown type, and its applicability has been demonstrated in the synthesis of AB and ABC block copolymers (Scheme 3).

Experimental Section

General Experimental Procedures and Materials. All manipulations were performed under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was purified by passing successively through the columns of an activated copper catalyst (BASF, R3-11) and P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a Varian Mercury 300 (^{1}H NMR, 300.11 MHz; ^{13}C NMR, 75.46 MHz) spectrometer. Chemical shifts are reported in δ (ppm), referenced to the ^{1}H (of residual protons) and ^{13}C signals of deuterated solvents. Mass spectra were measured with a Shimadzu QP-5000 GC-mass spectrometer (EI, 70 eV). GLC analysis was performed on a Shimadzu GC-14B instrument equipped with an FID detector and a capillary column (CBP-1, 25 m × 0.25 mm). Flash column chromatography was performed using Merck silica gel 60 (230−400 mesh). Gel permeation chromatography (GPC) was carried out on a JASCO GPC assembly consisting of a model PU-980 pump, a model RI-1530 refractive index detector, and three GPC gel columns (Shodex KF-801, KF-803L, KF-805L). Polystyrene standards were used for calibration, and THF was used as the mobile phase with a flow rate of 1.0 mL/min. Vapor pressure osmometry (VPO) was carried out on a Knauer K-7000 osmometer in chloroform at 40 °C using sucrose octaacetate for calibration. Transmission electron microscopy (TEM) observations were performed with Hitachi 7100TE, operating at 100 kV.

Dichloromethane and THF were dried over CaH_2 and sodium benzophenone ketyl, respectively. These solvents were distilled and stored over activated molecular sieves (MS4A) under a nitrogen atmosphere. Norbornene was distilled from sodium prior to use. ϵ-Caprolactone and styrene were distilled from CaH_2 prior to use. Thiocarbene complex $RuCl_2$(=CHSPh)-$(PCy_3)_2$ was prepared from $[RuCl_2(p\text{-cymene})]_2$, PCy_3, and Cl_2-CHSPh according to the literature.[4a] *exo,exo*-5,6-Bis(methoxycarbonyl)-7-oxa-2-norbornene,[9] phenyl vinyl sulfide,[10] *p*-bromophenyl disulfide,[11] (*Z*)-1-phenylthio-1-propen-3-ol ((*Z*)-**5**),[12] (*E*)-1-phenylthio-1-propen-3-ol ((*E*)-**5**),[13] and (*Z*)-1-phenylthio-1-buten-3-ol ((*Z*)-**9**)[14] were synthesized according to the

literature. All other chemicals were obtained from commercial suppliers and used without further purification.

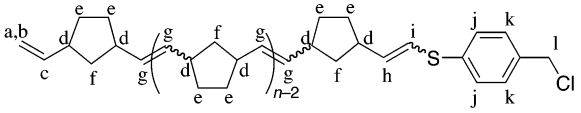
Preparation of *p*-Bromophenyl Vinyl Sulfide. Ethylene gas was gently bubbled into a solution of *p*-bromophenyl disulfide (11.61 g, 30.87 mmol) in CH_2Cl_2 (44 mL). A solution of bromine (5.7 g, 36 mmol) in CH_2Cl_2 (10 mL) was slowly added over 40 min at room temperature. Ethylene gas was added continuously until the color of the bromine disappeared. DBU (10 g, 66 mmol) was added at room temperature, and the reaction mixture was refluxed for 48 h. The reaction mixture was cooled to room temperature and then quenched with 1.0 M aqueous ammonia (10 mL). The organic layer was separated, washed with water, and dried over anhydrous $MgSO_4$. After the drying agent was filtered off, the solution was concentrated to dryness to give an orange oil. The crude product was purified by flash column chromatography with hexane as eluent to give the title compound as a pale yellow oil (9.55 g, 72% yield). ^{1}H NMR ($CDCl_3$): δ 7.47−7.42 (m, 2H, C_6H_4), 7.26−7.21 (m, 2H, C_6H_4), 6.54 (dd, J = 16.7, 9.5 Hz, 1H, C*H*=CH_2), 5.40 (d, J = 9.5 Hz, 1H, CH=C*H*$_2$), 5.37 (d, J = 16.7 Hz, 1H, CH=C*H*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 133.5, 132.2, 131.8 (each s, C_6H_4), 131.0 (s, *C*H=CH_2), 121.1 (s, C_6H_4), 116.5 (s, CH=*C*H$_2$). MS, *m*/*z* (rel intensity, %): 216 (M^++1, 39), 214 (M^+−1, 38), 169 (11), 136 (11), 135 (100), 134 (39), 109 (20), 108 (30), 91 (58), 82 (10), 76 (10), 69 (20), 67 (33). Anal. Calcd for C_8H_7BrS: C, 44.67; H, 3.28. Found: C, 44.52; H, 3.19.

Preparation of *p*-(Hydroxymethyl)phenyl Vinyl Sulfide. A mixture of *p*-bromophenyl vinyl sulfide (4.93 g, 22.9 mmol), magnesium (0.55 g, 23 mmol), 1,2-dibromoethane (20 μL), and THF (15 mL) was stirred at 40 °C for 1 h. To the resulting yellow solution was added paraformaldehyde (0.69 g, 23 mmol) at room temperature. The reaction mixture was stirred at 50 °C for 3 h and then quenched with saturated aqueous NH_4Cl (15 mL). The organic layer was separated, and the aqueous layer was extracted with ether (100 mL × 2). The combined organic layer was washed with water and dried over anhydrous $MgSO_4$. After the drying agent was filtered off, the solution was evaporated to give a yellow liquid. The crude product was purified by flash column chromatography with hexane:AcOEt (4:1) as eluent to give the title compound as a colorless oil (1.34 g, 35% yield). ^{1}H NMR ($CDCl_3$): δ 7.40−7.30 (m, 4H, C_6H_4), 6.52 (dd, J = 16.7, 9.7 Hz, 1H, C*H*=CH_2), 5.36 (d, J = 9.7 Hz, 1H, CH=C*H*$_2$), 5.34 (d, J = 16.7 Hz, 1H, CH=C*H*$_2$), 4.67 (d, J = 5.5 Hz, 2H, C*H*$_2$OH), 1.92 (t, J = 5.5 Hz, 1H, CH_2O*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): 139.9, 133.4 (each s, C_6H_4), 131.7 (s, *C*H=CH_2), 130.7, 127.7 (each s, C_6H_4), 115.5 (s, CH=*C*H$_2$), 64.7 (s, CH_2OH). MS, *m*/*z* (rel intensity, %): 166 (M+, 64), 147 (12), 135 (100), 109 (13), 105 (15), 91 (26), 79 (35), 77 (46), 69 (11), 65 (14), 59 (41), 51 (30). Anal. Calcd for $C_9H_{10}OS$: C, 65.02; H, 6.06. Found; C, 64.88; H, 5.96.

Preparation of *p*-(Chloromethyl)phenyl Vinyl Sulfide. A colorless solution of *p*-(hydroxymethyl)phenyl vinyl sulfide (0.94 g, 5.7 mmol) and PPh_3 (1.92 g, 7.32 mmol) in CCl_4 (5.6 mL) was stirred at 60 °C for 1 h. The resulting white suspension was evaporated, and the residue was purified by flash column chromatography with hexane as eluent to give the title compound as a colorless oil (0.31 g, 29% yield). ^{1}H NMR ($CDCl_3$): 7.39−7.33 (m, 4H, C_6H_4), 6.54 (dd, J = 16.7, 9.5 Hz, 1H, C*H*=CH_2), 5.41 (d, J = 16.7 Hz, 1H, CH=C*H*$_2$), 5.41 (d, J = 9.5 Hz, 1H, CH=C*H*$_2$), 4.57 (s, 2H, CH_2Cl). ^{13}C-{^{1}H} NMR ($CDCl_3$): 136.2, 135.0 (each s, C_6H_4), 131.1 (s, *C*H=CH_2), 130.2, 129.3 (each s, C_6H_4), 116.6 (s, CH=*C*H$_2$), 45.7 (s, CH_2Cl). MS, *m*/*z* (rel intensity, %): 186 (M^++2, 14), 184 (M^+, 37), 149 (100), 134 (20), 121 (13), 105 (33), 89 (11), 77 (14), 74 (15), 63 (13). Anal. Calcd for C_9H_9ClS: C, 58.53; H, 4.91. Found: C, 58.38; H, 4.93.

ROMP of Norbornene Using Vinylic Sulfides as CTAs. Synthesis of PNBE-1 and -2. PNBE-**1** was synthesized from norbornene (720 mg, 7.64 mmol), phenyl vinyl sulfide (84 mg, 0.62 mmol), and $RuCl_2$(=CHSPh)(PCy_3)$_2$ (128 mg, 150 μmol) according to the reported procedure.[4a] Similarly, PNBE-**2** was synthesized using *p*-(chloromethyl)phenyl vinyl sulfide in place of phenyl vinyl sulfide. These compounds were characterized by ^{1}H NMR and GPC analysis (PNBE-**1**, $M_{n,NMR}$ = 1300, M_w/M_n = 1.56; PNBE-**2**, $M_{n,NMR}$ = 1700, M_w/M_n = 1.70). The ^{1}H NMR data of PNBE-**1** were identical with those previously reported.[4c]

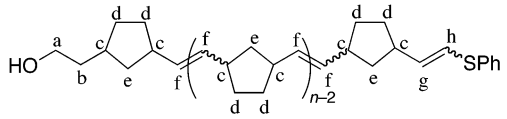
PNBE-**2**:



^{1}H NMR ($CDCl_3$): δ 7.32−7.25 (m, H^{j,k}), 6.10 (d, J = 15.0 Hz, (*E*)-H^i), 6.09 (dd, J = 9.0, 0.7 Hz, (*Z*)-H^i), 6.01 (dd, J = 15.0, 7.1 Hz, (*E*)-H^h), 5.85 (apparent t, J = 9.0 Hz, (*Z*)-H^h), 5.80 (ddd, J = 17.6, 10.0, 7.3 Hz, (*E*)-H^c), 5.39−5.28 (m, H^g of *trans*-polymer), 5.24−5.16 (m, H^g of *cis*-polymer), 4.96 (ddd, J = 17.6, 2.0, 1.3 Hz, H^a), 4.86 (ddd, J = 10.0, 2.0, 1.1 Hz, H^b), 4.56 (s, H^l), 2.85−2.69 (m, H^d of *cis*-polymer), 2.56−2.36 (m, H^d of *trans*-polymer), 2.05−1.70 (m, H^{e,f}), 1.45−1.26 (m, H^e), 1.12−0.97 (m, H^f).

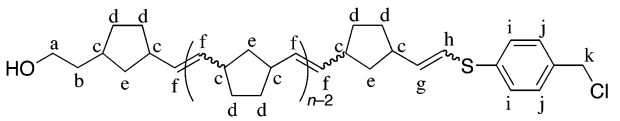
Hydroxylation of PNBE-1 and -2. A typical procedure is as follows. To a solution of PNBE-**1** (513 mg, 0.395 mmol) in THF (3.3 mL) was added a 0.5 M solution of 9-BBN (2.3 mL, 1.1 mmol). The mixture was stirred at room temperature for 2 h. To the resulting solution were successively added 6 M aqueous NaOH (1.0 mL, 6.0 mmol) and 30% aqueous H_2O_2 (0.92 mL, 8.1 mmol). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (20 mL × 4). The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated. The oily residue was redissolved in CH_2Cl_2, and the solution was poured into a vigorously stirred MeOH to give a white precipitate of PNBE-**3** which was collected by filtration, washed with methanol, and dried under vacuum (410 mg, 82% yield). The ^{1}H NMR and GPC analysis of PNBE-**3** revealed its molecular weight and molecular weight distribution to be 1300 and 1.58, respectively. PNBE-**2** was similarly hydroxylated to afford PNBE-**4** ($M_{n,NMR}$ = 1800, M_w/M_n = 1.78) in 89% yield.

PNBE-**3**:



^{1}H NMR ($CDCl_3$): δ 7.35−7.27, 7.22−7.15 (each m, Ph), 6.11 (dd, J = 15.0, 0.7 Hz, (*E*)-H^h), 6.11 (dd, J = 9.2, 0.9 Hz, (*Z*)-H^h), 5.98 (dd, J = 15.0, 7.7 Hz, (*E*)-H^g), 5.79 (apparent triplet, J = 9.2 Hz, (*Z*)-H^g), 5.39−5.29 (m, H^f of *trans*-polymer), 5.22−5.19 (m, H^f of *cis*-polymer), 3.65 (dt, J = 6.8, 5.5 Hz, H^a), 2.86−2.71 (m, H^c of *cis*-polymer), 2.52−2.32 (m, H^c of *trans*-polymer), 1.99−1.70 (m, H^{d,e}), 1.61 (dt, J = 6.8, 6.4 Hz, H^b), 1.44−1.23 (m, H^d), 1.11−0.97 (m, H^e).

PNBE-**4**:



^{1}H NMR ($CDCl_3$): δ 7.32−7.25 (m, H^{i,j}), 6.10 (d, J = 15.0 Hz, (*E*)-H^h), 6.09 (dd, J = 9.0, 0.7 Hz, (*Z*)-H^h), 6.01 (dd, J = 15.0, 7.1 Hz, (*E*)-H^g), 5.85 (apparent t, J = 9.0 Hz, (*Z*)-H^g), 5.39−5.28 (m, H^f of *trans*-polymer), 5.24−5.16 (m, H^f of *cis*-polymer), 4.56 (s, H^k), 3.65 (dt, J = 6.5, 4.0 Hz, H^a), 2.85−2.69 (m, H^c of *cis*-polymer), 2.56−2.36 (m, H^c of *trans*-polymer), 2.05−1.70 (m, H^{d,e}), 1.61 (dt, J = 6.8, 6.5 Hz, H^b), 1.45−1.26 (m, H^d), 1.12−0.97 (m, H^e).

Preparation of 1-(*p*-Bromophenylthio)-1-propen-3-ol (6). The following procedure was based on the synthesis of (*Z*)-1-phenylthio-1-propen-3-ol ((*Z*)-**5**) reported by Owen et al.[12] To a mixture of propargyl alcohol (7.11 g, 127 mmol) and powdered KOH (238 mg, 4.24 mmol) was slowly added *p*-bromothiophenol (20.1 g, 106 mmol) at 125 °C. The resulting

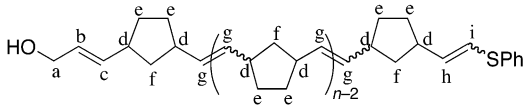
dark brown solution was stirred at 125 °C for 3 h. The solution was diluted with ethyl acetate, washed with aqueous NaOH and water, and dried over magnesium sulfate. After the drying agent was filtered off, the filtrate was evaporated. The residual brown liquid was purified by distillation under reduced pressure (115−120 °C at 0.14 mmHg) and then by flash column chromatography over silica gel eluted with hexane/ether (2/1). Evaporation of the eluate afforded **6** as a white solid (9.81 g, 38% yield). ^{1}H NMR ($CDCl_3$): δ 7.46−7.41, 7.25−7.18 (each m, 4H, C_6H_4), 6.41 (dt, J = 15.0, 1.5 Hz, 0.28H, (*E*)−CH═C*H*S), 6.30 (dt, J = 9.5, 1.3 Hz, 0.72H, (*Z*)−CH═C*H*S), 6.00 (dt, J = 9.5, 6.2 Hz, 0.72H, (*Z*)-C*H*═CHS), 5.99 (dt, J = 15.0, 5.7 Hz, 0.28H, (*E*)-C*H*═CHS), 4.36 (dd, J = 6.2, 1.3 Hz, 1.44H, (*Z*)−CH_2), 4.22 (dd, J = 5.7, 1.5 Hz, 0.56H, (*E*)−CH_2), 1.60 (br, 1H, OH). MS, *m*/*z* (rel intensity, %): 246 (M^+, 20), 244 (20), 207 (25), 190 (79), 188 (74), 109 (91), 108 (42), 69 (26), 65 (20), 57 (56), 55 (23), 51 (20), 50 (37), 44 (100). Anal. Calcd for C_9H_9BrOS: C, 44.10; H, 3.70. Found: C, 44.23; H 3.61.

Preparation of 1-(*p*-Aminophenylthio)-1-propen-3-ol (7). This compound was synthesized by a procedure similar to that described for **6** using propargyl alcohol (2.68 g, 47.8 mmol), KOH (107 mg, 1.91 mmol), and *p*-aminothiophenol (5.00 g, 39.9 mmol), to give a yellow oil (770 mg, 16% yield). ^{1}H NMR (THF-d_8): δ 7.09−7.05, 6.55−6.50 (each m, 4H, C_6H_4), 6.05 (dt, J = 9.7, 1.5 Hz, 1H, (*Z*)−CH═C*H*S), 5.63 (dt, J = 9.7, 5.9 Hz, 1H, (*Z*)-C*H*═CHS), 4.68 (br, 2H, NH_2), 4.14 (ddd, J = 6.2, 5.9, 1.5 Hz, 2H, CH_2), 3.76 (t, J = 6.2 Hz, 1H, OH). MS, *m*/*z* (rel intensity, %): 181 (M^+, 77), 150 (7), 125 (65), 93 (100), 80 (38), 65 (22). Anal. Calcd for $C_9H_{11}NOS$: C, 59.64; H, 6.12; N 7.73. Found: C, 60.01; H, 6.17; N, 7.31.

Preparation of 4-Chloromethyl-*N*-[4-(3-hydroxypropenylthio)phenyl]benzamide (8). A solution of 4-chloromethylbenzoyl chloride (2.60 g, 14.0 mmol) in CH_2Cl_2 (16 mL) was added dropwise at 0 °C to a solution of **7** (*E*/*Z* = <1/99; 2.54 g, 14.0 mmol) and pyridine (4.1 g, 52 mmol) in CH_2Cl_2 (18 mL). The mixture was stirred at room temperature for 2 h. The resulting yellow suspension was diluted with ethyl acetate, washed with water and brine, and dried over magnesium sulfate. After the drying agent was filtered off, the filtrate was evaporated to give a yellow solid, which was purified by flash column chromatography over silica gel eluted with hexane/THF (1/2). Evaporation of the eluate afforded **8** as a white solid (2.63 g, 57% yield). ^{1}H NMR (THF-d_8): δ 9.46 (br, 1H, NHCO), 7.93, 7.78, 7.52, 7.32 (each d, J = 6.6 Hz, 8H, C_6H_4), 6.41 (dt, J = 14.8, 1.6 Hz, 0.29H, (*E*)−CH═C*H*S), 6.25 (dt, J = 9.5, 1.5 Hz, 0.71H, (*Z*)−CH═C*H*S), 5.88 (dt, J = 14.8, 5.0 Hz, 0.29H, (*E*)-C*H*═CHS), 5.87 (dt, J = 9.5, 6.0 Hz, 0.71H, (*Z*)-C*H*═CHS), 4.70 (s, 2H, CH_2Cl), 4.21 (d, J = 6.0 Hz, 1.42H, (*Z*)-C*H*$_2$OH), 4.06 (d, J = 5.0 Hz, 0.58H, (*E*)-C*H*$_2$OH), 3.92 (br, 1H, OH). Anal. Calcd for $C_{17}H_{16}ClNO_2S$: C, 61.16; H, 4.83; N, 4.20. Found: C, 60.89; H, 4.87; N, 4.11.

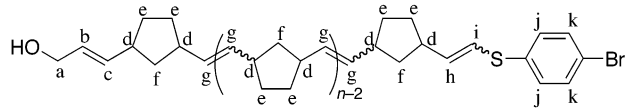
A Typical Procedure for ROMP Using (*Z*)-1-Arylthio-1-propen-3-ols as CTAs (Entry 2 in Table 1). To a solution of norbornene (123 mg, 1.30 mmol), (*Z*)-**5** (*E*/*Z* = 8/92; 44 mg, 0.26 mmol), and decane (19 mg; internal standard for GLC analysis) in CH_2Cl_2 (13 mL) was added solid $RuCl_2$(═CHSPh)-$(PCy_3)_2$ (11 mg, 13 mmol) at room temperature. The mixture was stirred for 2 h. The GLC analysis of the resulting solution revealed a complete consumption of norbornene and 10% conversion of (*Z*)-**5**. The solution was concentrated to ca. 2 mL and then slowly added to a vigorously stirred MeOH (ca. 30 mL). A white solid of poly(norbornene) (PNBE-**5**) thus precipitated was collected by suction filtration, washed with MeOH repeatedly, and dried under vacuum (119 mg, 93% yield). All the reactions listed in Table 1 were similarly carried out.

PNBE-**5**:



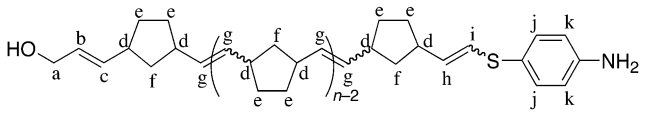
^{1}H NMR ($CDCl_3$): δ 7.35−7.29, 7.22−7.15 (each m, Ph), 6.10 (d, J = 15.0 Hz, (*E*)-H^i), 6.09 (dd, J = 9.0, 0.7 Hz, (*Z*)-H^i), 5.98 (dd, J = 15.0, 7.5 Hz, (*E*)-H^h), 5.79 (apparent t, J = 9.2 Hz, (*Z*)-H^h), 5.68 (dd, J = 15.4, 6.4 Hz, H^c), 5.60 (dt, J = 15.4, 5.3 Hz, H^b), 5.40−5.29 (m, H^g of *trans*-polymer), 5.24−5.16 (m, H^g of *cis*-polymer), 4.09 (apparent t, J = 5.3 Hz, H^a), 2.85−2.69 (m, H^d of *cis*-polymer), 2.56−2.36 (m, H^d of *trans*-polymer), 1.94−1.70 (m, H^{e,f}), 1.45−1.26 (m, H^e), 1.12−0.97 (m, H^f).

PNBE-**6**:



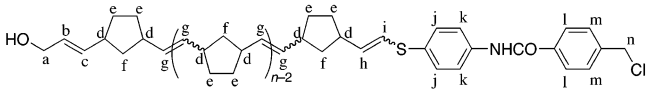
^{1}H NMR ($CDCl_3$): δ 7.42−7.40, 7.20−7.17 (each m, H^{j,k}), 6.06 (d, J = 15.8 Hz, (*E*)-H^i), 6.04 (d, J = 8.6 Hz, (*Z*)-H^i), 5.99 (dd, J = 15.8, 7.2 Hz, (*E*)-H^h), 5.83 (apparent t, J = 8.6 Hz, (*Z*)-H^h), 5.68 (dd, J = 15.6, 6.8 Hz, H^c), 5.60 (dt, J = 15.6, 5.0 Hz, H^b), 5.39−5.28 (m, H^g of *trans*-polymer), 5.24−5.16 (m, H^g of *cis*-polymer), 4.09 (d, J = 5.0 Hz, H^a), 2.85−2.70 (m, H^d of *cis*-polymer), 2.54−2.34 (m, H^d of *trans*-polymer), 1.90−1.72 (m, H^{e,f}), 1.45−1.26 (m, H^e), 1.11−0.97 (m, H^f).

PNBE-**7**:



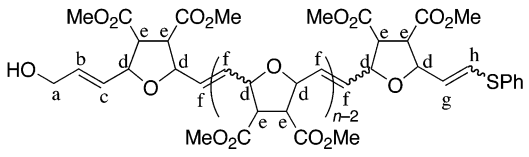
^{1}H NMR (THF-d_8): δ 7.07−7.04, 6.54−6.51 (each m, H^{j,k}), 6.00 (d, J = 15.2 Hz, (*E*)-H^i), 5.95 (d, J = 9.3 Hz, (*Z*)-H^i), 5.61 (dd, J = 15.2, 6.8 Hz, (*E*)-H^h), 5.57−5.46 (m, (*Z*)-H^h and H^{b,c}), 5.41−5.30 (m, H^g of *trans*-polymer), 5.22−5.15 (m, H^g of *cis*-polymer), 4.65 (br, NH_2), 3.91 (dd, J = 5.3, 4.4 Hz, H^a), 3.82 (br, OH), 2.90−2.74 (m, H^d of *cis*-polymer), 2.54−2.34 (m, H^d of *trans*-polymer), 1.88−1.68 (m, H^{e,f}), 1.46−1.28 (m, H^e), 1.12−0.97 (m, H^f).

PNBE-**8**:



^{1}H NMR ($CDCl_3$): δ 7.87 (d, J = 8.1 Hz, H^l), 7.59 (d, J = 8.4 Hz, H^k), 7.52 (d, J = 8.1 Hz, H^m), 7.33 (d, J = 8.4 Hz, H^j), 6.09 (d, J = 14.8 Hz, (*E*)-H^i), 6.08 (d, J = 9.0 Hz, (*Z*)-H^i), 5.93 (dd, J = 14.8, 7.7 Hz, (*E*)-H^h), 5.77 (apparent t, J = 9.0 Hz, (*Z*)-H^h), 5.68 (dd, J = 15.4, 6.8 Hz, H^c), 5.60 (dt, J = 15.4, 5.1 Hz, H^b), 5.39−5.28 (m, H^g of *trans*-polymer), 5.24−5.16 (m, H^g of *cis*-polymer), 4.64 (s, H^n), 4.09 (d, J = 5.1 Hz, H^a), 2.85−2.70 (m, H^d of *cis*-polymer), 2.56−2.34 (m, H^d of *trans*-polymer), 1.90−1.71 (m, H^{e,f}), 1.45−1.26 (m, H^e), 1.11−0.97 (m, H^f). The amido proton signal was obscure due to broadening.

PONBE-**5**:

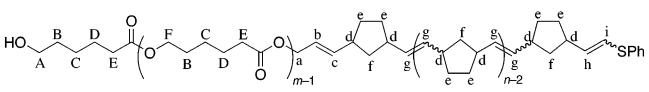


^{1}H NMR ($CDCl_3$): δ 7.37−7.22 (m, Ph), 6.57 (dd, J = 14.7, 3.8 Hz, (*E*)-H^h), 6.46 (dd, J = 9.5, 3.8 Hz, (*Z*)-H^h), 5.88 (br s, H^f of *trans*-polymer), 5.76 (dd, J = 14.7, 7.0 Hz, (*E*)-H^g), 5.66−5.52 (m, H^f of *cis*-polymer), 5.06 (br s, H^d of *cis*-polymer), 4.69 (br s, H^d of *trans*-polymer), 4.15 (br s, H^a), 3.68 (s, CO_2Me), 3.08 (s, H^e). The signals of H^{b,c} were obscure.

A Typical Procedure for Anionic Ring-Opening Polymerization of ϵ-Caprolactone (CL) Using PNBE-5 as a Macroinitiator (Entry 3 in Table 2). To a solution of PNBE-**5** (100 mg, 26.3 mmol) in toluene (2.0 mL) was added a 0.93 M solution of $AlEt_3$ in toluene (30 mL, 28 mmol) at room temperature. The mixture was stirred for 2 h, during which evolution of ethane gas was observed. Then, a stock solution

of CL in toluene (1.9 M, 0.35 mL, 0.67 mmol) and decane (10 mg; internal standard for GLC analysis) were added, and the mixture was stirred at room temperature for 24 h. GLC analysis of the resulting solution revealed a complete consumption of CL. The viscous mixture thus obtained was quenched by adding aqueous HCl (0.1 M, 0.8 mL), and then poured into cold MeOH (ca. 50 mL) with stirring. A white solid of block copolymer PCL-*b*-PNBE-**5** thus precipitated was collected by suction filtration, washed with MeOH, and dried under vacuum (136 mg, 77% yield). All the reactions listed in Table 2 were similarly carried out.

PCL-*b*-PNBE-**5**:

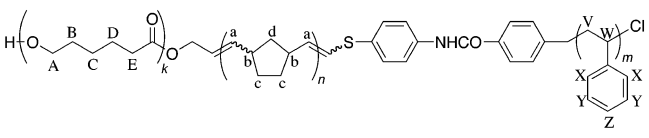


^{1}H NMR ($CDCl_3$): δ 7.32−7.28, 7.21−7.15 (each m, Ph), 6.11 (dd, J = 15.0, 0.7 Hz, (*E*)-H^i), 6.10 (dd, J = 8.7, 0.9 Hz, (*Z*)-H^i), 5.97 (dd, J = 15.0, 7.7 Hz, (*E*)-H^h), 5.78 (apparent t, J = 8.7 Hz, (*Z*)-H^n), 5.74 (dd, J = 15.0, 7.7 Hz, H^c), 5.51 (dt, J = 15.0, 6.7 Hz, H^b), 5.39−5.28 (m, H^g of *trans*-polymer), 5.24−5.16 (m, H^g of *cis*-polymer), 4.50 (d, J = 6.7 Hz, H^a), 4.06 (t, J = 6.6 Hz, H^F), 3.65 (dt, J = 6.2, 5.1 Hz, H^A), 2.85−2.70 (m, H^d of *cis*-polymer), 2.54−2.34 (m, H^d of *trans*-polymer), 2.31 (t, J = 7.3 Hz, H^E), 1.90−1.56 (m, H^{B,D,e,f}), 1.45−1.26 (m, H^{C,e}), 1.10−0.97 (m, H^f).

Synthesis of ABC-Type Triblock Copolymer PCL-*b*-PNBE-8-*b*-PSt. (i) Atom-Transfer Radical Polymerization of Styrene (St) Using PNBE-8 as a Macroinitiator. A mixture of PNBE-**8** (184 mg, 42.8 mmol), styrene (444 mg, 4.26 mmol), CuCl (8.4 mg, 85 mmol), 1,1,4,7,10,10-hexamethyltriethylenetetramine (59 mg, 0.26 mmol), and diphenyl ether (0.85 mL) was degassed by three freeze−pump−thaw cycles, and then heated at 130 °C for 22 h. The resulting viscous mixture was slowly added to vigorously stirred MeOH (ca. 30 mL) to give a white precipitate of diblock copolymer PNBE-**8**-*b*-PSt, which was collected by suction filtration, washed with MeOH, and dried under vacuum (477 mg, 76% yield). GLC analysis of the filtrate indicated ca. 20% recovery of styrene. The molecular weight of PNBE-**8**-*b*-PSt estimated by ^{1}H NMR was in good agreement with the theoretical value ($M_{n,NMR}$ = 12 700, $M_{n,theor}$ = 12 600). The GPC measurement showed a monomodal peak profile ($M_{n,GPC}$ = 20 700, M_w/M_n = 2.70).

(ii) Anionic Ring-Opening Polymerization of CL Using PNBE-8-*b*-PSt as a Macroinitiator. According to the procedure for the synthesis of PCL-*b*-PNBE-**5**, PNBE-**8**-*b*-PSt (102 mg, 8.0 mmol) was reacted with $AlEt_3$ (24 mmol) and CL (92 mg, 0.80 mmol) in toluene at room temperature. After the reaction was stirred for 22 h, a complete conversion of CL was confirmed by GLC analysis of the reaction solution. Quenching with aqueous HCl followed by reprecipitation from MeOH afforded a white solid of triblock copolymer PCL-*b*-PNBE-**8**-*b*-PSt (157 mg, 81% yield). The molecular weight was estimated by ^{1}H NMR to be 21 800; the value was fairly consistent with the theoretical value ($M_{n,theor}$ = 24 100). The GPC data are as follows: $M_{n,GPC}$ = 30 700, PDI = 2.63. The GPC analysis of the copolymer revealed a clean shift of the monomodal peak profile of PNBE-**8**-*b*-PSt to a high-molecular-weight region, indicating a clean formation of the triblock copolymers.

PCL-*b*-PNBE-**8**-*b*-PSt:



^{1}H NMR ($CDCl_3$): δ 7.30−6.88, 6.75−6.30 (each m, H^{X-Z}), 5.39−5.28 (m, H^a of *trans*-polymer), 5.24−5.16 (m, H^a of *cis*-polymer), 4.06 (t, J = 6.6 Hz, H^A), 2.85−2.70 (m, H^b of *cis*-polymer), 2.54−2.28 (m, H^b of *trans*-polymer), 2.31 (t, J = 7.3 Hz, H^E), 2.10−1.61 (m, H^{B,D,d,c,V}), 1.60−1.25 (m, H^{C,c,W}), 1.10−0.97 (m, H^d). The signals due to terminal and linking groups were obscure.

Acknowledgment. This work was supported by a Grand-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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(5) The $M_{n,NMR}$ values and the [monomer]/[CTA] ratios incorporated into hydroxy-terminated PNBEs (**3**−**7**) were determined by peak integration of the ^{1}H NMR spectra. The signals of the hydroxy-bonded methylene protons (δ 3.65 or 3.91−4.15) and the vinylene group protons of the main chain (ca. δ 5.3 for trans, 5.2 for cis) are well-separated from the other signals, providing a principal basis of estimating the values. It has been also confirmed that signal intensities of the other signals are consistent with the compositions.

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(7) The regioselective formation of α,ω-heterotelechelic PNBE-**5** was consistent with the following stoichiometric observation. Thus, the treatment of (*Z*)-**5** with $RuCl_2$(=CHPh)(PCy_3)$_2$ as a model of propagating alkylidene complex at room temperature caused the cross-metathesis, giving quantitative yields of thiocarbene complex $RuCl_2$(=CHSPh)(PCy_3)$_2$ and cinnamyl alcohol in perfect regioselectivity. Therefore, it is convincing that the highly selective ROMP/CT process similarly to Scheme 1 is operative for the reaction system with (*Z*)-**5** as well.

(8) Grubbs and co-workers reported that unprotected *cis*-2-butene-1,4-diol serves as a CTA for ROMP of cyclooctadiene catalyzed by benzylideneruthenium bearing a diaminocarbene ligand.[2a]

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