Macromolecules **2002,** *35,* 1133−1136 **1133**

Notes

Ring-Opening Metathesis Polymerization of Norbornene Using Vinylic Ethers as Chain-Transfer Agents: Highly Selective Synthesis of Monofunctional Macroinitiators for Atom Transfer Radical Polymerization

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Received June 14, 2001
Revised Manuscript Received October 23, 2001

Introduction

Synthesis of the polymers with well-defined structures is among the central subjects in polymer chemistry.[1] The use of macroinitiators is an attractive way to block copolymers from this viewpoint.[2] Thus, the polymers bearing an end-functionality, which is capable of initiating polymerization, allow the combination of mechanistically compatible or incompatible polymerization processes, leading to a variety of block copolymers with well-defined structures.[3−5]

Recently, two groups reported ROMP (ring-opening metathesis polymerization) approach to macroinitiators which are reactive toward atom transfer radical polymerization (ATRP). Matyjaszewski et al. prepared poly(norbornene) and poly(dicyclopentadiene) bearing an α-bromobenzyl unit by Mo-promoted living polymerization followed by Wittig-like end-capping with *p*-(bromomethyl)benzaldehyde.[4] Grubbs et al. synthesized bifunctional macroinitiators using Ru-catalyzed ROMP of 1,5-cyclooctadiene in the presence of 1,4-disubstituted 2-butenes as chain-transfer agents (CTA).[5] On the other hand, we found in this study that monofunctional macroinitiators can be selectively synthesized by ROMP of norbornene in the presence of vinylic ethers **1**−**3** as CTAs and vinylideneruthenium complex **4** as a catalyst precursor (Scheme 1).

Results and Discussion

The present catalytic system is based on our recent findings.[6,7] Although vinylic ethers are generally utilized as a terminator of ROMP, we noticed that they serve as good CTAs for the vinylidene complex-catalyzed systems. Thus, the molecular weight of polymer can be efficiently controlled by the monomer to CTA ratio, not by the monomer-to-catalyst ratio. In addition, the resulting polymer precisely possesses a CTA unit at one of the termini of polymer chain. Therefore, we examined this catalysis using vinylic ethers **1**−**3** having the functionalities capable of initiating ATRP.[8]

The CTAs **1**−**3** were readily prepared by esterification of ethylene glycol monovinyl ether with the corresponding carboxylic acid halides in the presence of pyridine (see Experimental Section). ROMP of norbornene using CTAs **1**−**3** was conducted in dichloromethane at room temperature. Table 1 summarizes the results. All reactions afforded end-functionalized poly(norbornene)s (PNBE-**1**−**3**) in high yields. The resulting polymers were characterized by ^{1}H NMR, VPO, and GPC analysis. Figure 1A shows the ^{1}H NMR spectrum of PNBE-**1** isolated from the reaction system of entry 3 in Table 1. Besides the major peaks arising from the polymer backbone (d−g), eight sets of signals assignable to terminal vinyl (a−c) and (*Z*)-CH=CHO(CH$_2$)$_2$OCOCHCl$_2$

Scheme 1

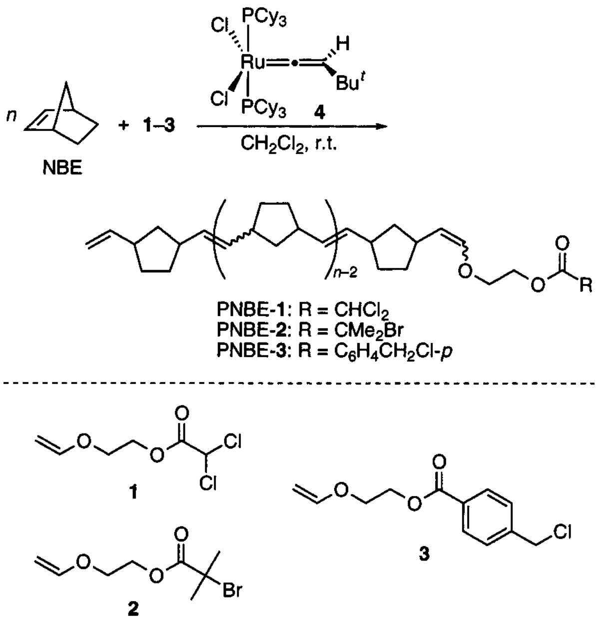

Table 1. ROMP of Norbornene (NBE) in the Presence of Chain-Transfer Agents 1−3[a]

entry	CTA	NBE/CTA/**4** (molar ratio)	yield/%[b]	$M_{n,NMR}$	$M_{n,VPO}$[c]	PDI[d]
1	**1**	100/1/0.5	95	6300	6000	2.27
2	**1**	100/2/0.5	91	4500	4400	3.20
3	**1**	100/10/0.5	92	3300	2900	2.17
4	**2**	100/1/0.5	98	9300	8600	2.57
5	**2**	100/2/0.5	97	5600	5500	1.99
6	**2**	100/5/0.5	98	3800	3500	2.96
7	**2**	100/10/0.5	94	3000	2700	2.49
8	**2**	100/2/0.1	94	5600	5700	2.97
9	**2**	100/2/0.01	89	5600	*e*	3.62
10	**3**	100/1/0.5	98	10600	9200	2.63
11	**3**	100/2/0.5	$>$99	5600	5600	2.73
12	**3**	100/10/0.5	96	4000	4000	2.53

[a] All reactions were carried out in dichloromethane at room temperature for 20−52 h. [b] Isolated yield based on the total amount of NBE employed and CTA converted. [c] VPO measurements were carried out in toluene at 40 °C, except for entry 8 (CHCl$_3$, 40 °C). [d] Determined by GPC based on polystyrene standards. [e] Not determined.

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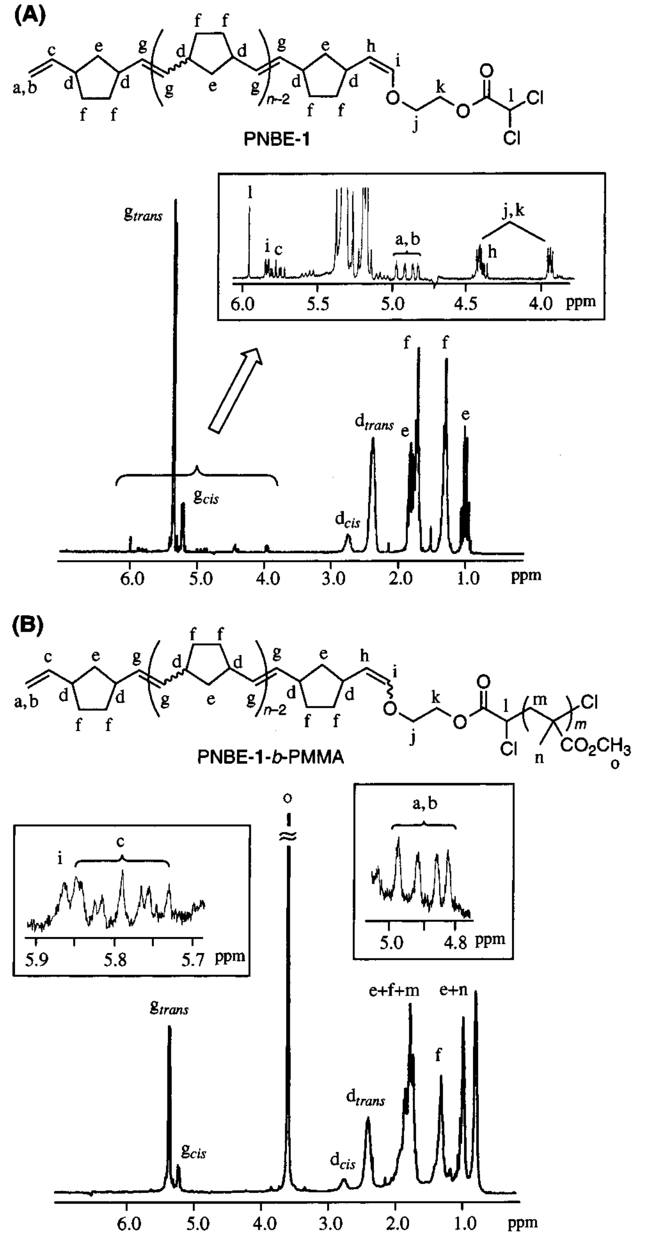


Figure 1. ^{1}H NMR spectra of PNBE-**1** (A) and PNBE-**1**-*b*-PMMA (B).

group (h–l) are observed. The molecular weight calculated from peak integration was in good agreement with the VPO data ($M_{n,NMR}$ = 3300; $M_{n,VPO}$ = 2900).[9] Thus the selective formation of the polymer bearing H_2C=CH– and –CH=$CHO(CH_2)_2OCOCHCl_2$ groups at each chain-end was evidenced.

As seen from Table 1, the molecular weight was clearly dependent upon the initial concentration of CTAs; plots of the M_n values obtained from NMR measurements ($M_{n,NMR}$) against the $[NBE]_0/[CTA]_0$ ratios exhibited good linear correlations (Figure 2). On the other hand, the amount of catalyst precursor **4** little affected the polymerization rate and the molecular weight (entries 5, 8, 9). It is noteworthy that the molecular weight control could be successfully performed with only 0.01 mol % of **4** (entry 9).

The PNBEs thus prepared were tested as macroinitiators for ATRP of methyl methacrylate (MMA) and styrene (St) (Table 2). It was found that vinylideneruthenium complex **4** in combination with $Al(OPr^i)_3$ serves

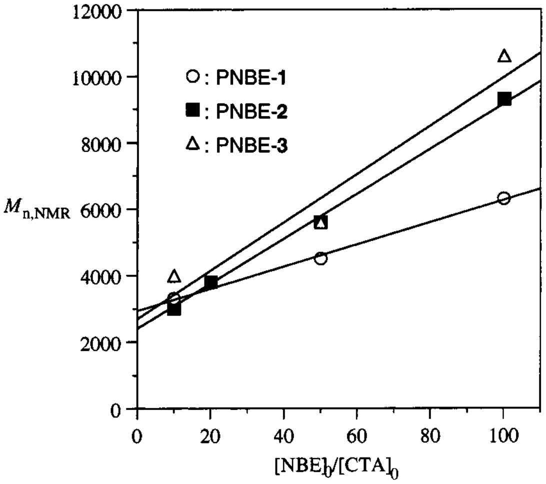


Figure 2. Plot of $M_{n,NMR}$ values vs initial ratios of NBE to CTAs (**1**–**3**).

Table 2. ATRP of Methyl Methacrylate (MMA) and Styrene (St) Using Macroinitiators PNBE-1–3[a]

macroinitiator ($M_{n,NMR}$, PDI)	monomer (molar ratio)	yield/%[b]	$M_{n,NMR}$	$M_{n,theor}$[c]	PDI[d]
PNBE-**1** (3300, 2.17)	MMA (57)	90	9000	9000	1.74
PNBE-**1** (3300, 2.17)	MMA (200)	92	23000	23300	1.62
PNBE-**2** (3000, 2.49)	MMA (50)	84	7300	7900	1.26
PNBE-**3** (4000, 2.53)	St (111)	79	13300	15500	1.80

[a] Reaction conditions are as follows. For ATRP of MMA: at 80 °C for 74 h in toluene; ATRP promoter = **4** + $4Al(OPr^i)_3$ ($[promoter]_0/[macroinitiator]_0$ = 0.43). For ATRP of St: at 90 °C for 26 h in toluene; ATRP promoter = CuBr + 2bipy ($[promoter]_0/[macroinitiator]_0$ = 1.0). [b] Isolated yield based on total mass of macroinitiator and monomer. [c] $M_{n,theor}$ = $M_{n,NMR}$(macroinitiator) + MW(monomer) × (molar ratio). [d] Determined by GPC based on polystyrene standards.

as a good ATRP promoter for MMA, comparable to $RuCl_2(PPh_3)_3$[10] and $RuCl_2$(*p*-cymene)(PR_3)[11] so far reported. Thus, heating a toluene solution of MMA, PNBE-**1**, **4**, and $Al(OPr^i)_3$ in a 57/1/0.43/1.7 ratio at 80 °C for 74 h gave the desired AB block copolymer (PNBE-**1**-*b*-PMMA) in 90% yield. The GPC analysis revealed a clean shift of the molecular weight from the parent PNBE-**1**, with keeping a monomodal peak profile.

Figure 1B shows the ^{1}H NMR spectrum. In addition to the signals arising from the PNBE-**1** part (a–l), the signals assignable to PMMA (m–o) are clearly observed. Although the signals of terminal groups are somewhat obscure due to broadening, the vinylic proton signals (a–c) are still observed. On the basis of relative peak integration between the olefinic protons of PNBE main chain (g) and the CO_2CH_3 protons of PMMA (o), the ratio of norbornene to methyl methacrylate unit in the block copolymer was estimated to be 0.58, which corresponds to the $M_{n,NMR}$ value of 9000. These values are fully consistent with the reaction stoichiometry: $[MMA]_0/[PNBE\text{-}\mathbf{1}]_0$ = 57, $M_{n,theor}$ = 9000.

As seen from Table 2, PNBE-**1** afforded the block copolymer having almost the ideal molecular weight even in the reaction with 200 molar ratio of MMA, showing the extremely high efficiency as macroinitiator. PNBE-**2** also exhibited a good performance for the ATRP of MMA. The ATRP of styrene was successfully conducted with PNBE-**3** as a macroinitiator and CuBr·2bipy as a promoter.[12]

In conclusion, we demonstrated that the ROMP reactions using vinylic ethers as CTAs and vinylideneruthenium as a catalyst precursor can be utilized as a highly selective route to monofunctional macroinitiators having a poly(norbornene) chain. Since the vinylic ethers of the present type can be easily prepared from ethylene glycol monovinyl ether which is commercially available, the present method will be applicable to the synthesis of a variety of macroinitiators for a range of polymerization processes. Further work along this line is in progress.

Experimental Section

General Experimental Procedure 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 a FID detector and a capillary column CBP-1 (25 m × 0.25 mm). Vapor pressure osmometry (VPO) was carried out on a Knauer model No. 11.00 in toluene or chloroform at 40 °C using dibenzyl for calibration. Gel permeation chromatography (GPC) was carried out on a Chromato Science CS-300H system equipped with three 5 μm TSK gel columns (G5000H$_{XL}$, G4000H$_{XL}$, G2500H$_{XL}$). Polystyrene standards were used for calibration, and THF was used as the mobile phase with a flow rate of 1.0 mL/min.

Dichloromethane and pyridine were dried over CaH_2. Toluene was dried over sodium benzophenone ketyl. These solvents were distilled and stored over activated molecular sieves (MS4A) under a nitrogen atmosphere. Norbornene was distilled from sodium prior to use. Methyl methacrylate and styrene were distilled prior to use. $RuCl_2(=C=CHBu^t)(PCy_3)_2$ (**4**) was synthesized according to the literature.[13] All other chemicals were obtained from commercial sources and used without further purification.

Preparation of Chain-Transfer Agents 1—3. A typical procedure for synthesizing **1** is as follows. Ethylene glycol monovinyl ether (5.50 g, 62.4 mmol) was dissolved in dichloromethane (120 mL) and pyridine (60 mL). To this solution was added dropwise a solution of dichloroacetyl chloride (9.19 g, 62.4 mmol) in dichloromethane (30 mL) at room temperature. The mixture was stirred at room temperature for 3 h and then quenched with water (50 mL). The organic layer was separated, and the aqueous layer was extracted with ether (50 mL × 2). All of the organic layers were combined and dried over anhydrous $MgSO_4$. After the drying agent was filtered off, the solution was concentrated to dryness to give a brown liquid. The crude product was purified by distillation under reduced pressure (0.2 mmHg, 55−57 °C) to afford colorless liquid of **1** (6.37 g, 51%). Compounds **2** and **3** were similarly prepared using the corresponding carboxylic acid halides.

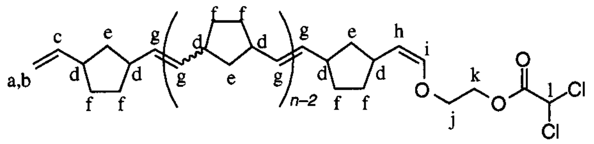
2-Vinyloxyethyl Dichloroacetate (1). ^{1}H NMR ($CDCl_3$): δ 6.47 (dd, $J = 14.3$, 6.8 Hz, 1H, CH=CH$_2$), 5.98 (s, 1H, CHCl$_2$), 4.51−4.48, 3.96−3.93 (each m, 4H, OCH$_2$), 4.21 (dd, $J = 14.3$, 2.4 Hz, 1H, CH=CH_2), 4.07 (dd, $J = 6.8$, 2.4 Hz, 1H, CH=CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.5 (s, C=O), 151.1 (s, CH=CH$_2$), 87.4 (s, CH=CH$_2$), 65.4, 65.0 (each s, OCH$_2$), 64.0 (s, CHCl$_2$). MS, m/z (rel intensity, %): 198 ($M^+ - H$, 1), 157 (31), 155 (48), 87 (11), 85 (64), 83 (100), 76 (21), 57 (13). Anal.Calcd for $C_6H_8Cl_2O_3$: C, 36.21; H, 4.05. Found: C, 36.46; H, 4.13.

2-Vinyloxyethyl 2-Bromoisobutyrate (2). Colorless liquid (63% yield). The NMR data were identical with those reported.[14]

2-Vinyloxyethyl 4-Chloromethylbenzoate (3). Colorless solid (53% yield). ^{1}H NMR ($CDCl_3$): δ 8.07−8.04, 7.48−7.45 (each m, 4H, C$_6$H$_4$), 6.52 (dd, $J = 14.5$, 6.8 Hz, 1H, CH=CH$_2$), 4.62 (s, 2H, CH$_2$Cl), 4.58−4.55 (m, 2H, OCH$_2$), 4.24 (dd, $J = 14.5$, 2.4 Hz, 1H, CH=CH_2), 4.07 (dd, $J = 6.8$, 2.4 Hz, 1H, CH=CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.9 (s, C=O), 151.5 (s, CH=CH$_2$), 142.4 (s, C^4 of C$_6$H$_4$), 130.2 (s, C^{2,3,5,6} of C$_6$H$_4$), 129.8 (s, C^1 of C$_6$H$_4$), 128.5 (s, C^{2,3,5,6} of C$_6$H$_4$), 87.1 (s, CH=CH$_2$), 65.8, 63.3 (each s, OCH$_2$), 45.3 (s, CH$_2$Cl). Anal. Calcd for $C_{12}H_{13}ClO_3$: C, 59.88; H, 5.44. Found: C, 59.61; H, 5.47.

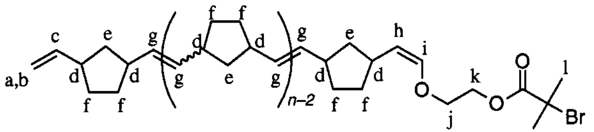
ROMP of Norbornene in the Presence of Chain-Transfer Agents 1—3. A typical procedure (Table 1, entry 3) is as follows. A solution of norbornene (471 mg, 5.00 mmol), **1** (99 mg, 0.50 mmol), and **4** (21 mg, 0.025 mmol) in dichloromethane (50 mL) was stirred at room temperature for 52 h. GLC analysis using anisole as an internal standard revealed 32% conversion of **1**. The reaction mixture was poured into vigorously stirred MeOH (150 mL). A white fluffy solid thus precipitated was collected by suction filtration, washed with methanol repeatedly, and dried under vacuum at room temperature to give spectroscopically pure PNBE-**1** (463 mg, 92%). All the polymerizations listed in Table 1 were similarly carried out.

PNBE-**1**:



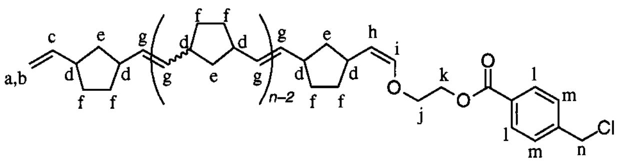
^{1}H NMR ($CDCl_3$): δ 5.98 (s, H^l), 5.86 (d, $J = 6.2$ Hz, H^i), 5.80 (ddd, $J = 17.2$, 9.9, 7.3 Hz, H^c), 5.40−5.29 (m, H^g of *trans*-polymer), 5.24−5.16 (m, H^g of *cis*-polymer), 4.96 (ddd, $J = 17.2$, 1.3, 1.3 Hz, H^b), 4.87 (ddd, $J = 9.9$, 1.3, 1.3 Hz, H^a), 4.45−4.42 (m, H^{j,k}), 4.41 (dd, $J = 9.0$, 6.2 Hz, H^h), 3.98−3.95 (m, H^{j,k}), 2.82−2.72, 2.50−2.35, 1.92−1.69, 1.43−1.25, 1.12−0.96 (each m, H^{d-f}).

PNBE-**2**:



^{1}H NMR ($CDCl_3$): δ 5.88 (dd, $J = 6.2$, 1.1 Hz, H^i), 5.80 (ddd, $J = 17.4$, 10.3, 7.5 Hz, H^c), 5.39−5.28 (m, H^g of *trans*-polymer), 5.22−5.19 (m, H^g of *cis*-polymer), 4.96 (ddd, $J = 17.4$, 2.0, 1.1 Hz, H^b), 4.86 (ddd, $J = 10.3$, 2.0, 0.9 Hz, H^a), 4.38 (dd, $J = 9.0$, 6.2 Hz, H^h), 4.36−4.32, 3.96−3.93 (each m, H^{j,k}), 2.84−2.71, 2.50−2.35, 1.90−1.71, 1.45−1.28, 1.12−0.97 (m, H^{d-f}), 1.94 (s, H^l).

PNBE-**3**:

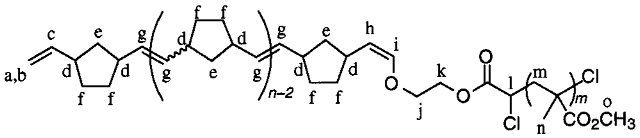


^{1}H NMR ($CDCl_3$): δ 8.06, 7.47 (each d, $J = 1.8$ Hz, H^{l,m}), 5.92 (dd, $J = 6.2$, 0.9 Hz, H^i), 5.80 (ddd, $J = 17.4$, 10.3, 7.5 Hz, H^c), 5.39−5.28 (m, H^g of *trans*-polymer), 5.22−5.19 (m, H^g of *cis*-polymer), 4.96 (ddd, $J = 17.4$, 2.0, 1.1 Hz, H^b), 4.87 (ddd, $J = 10.3$, 2.0, 0.9 Hz, H^a), 4.62 (s, H^n), 4.51−4.47 (m, H^{j,k}), 4.39 (dd, $J = 9.0$, 6.2 Hz, H^h), 4.05−4.02 (m, H^{j,k}), 2.84−2.71, 2.50−2.34, 1.90−1.68, 1.45−1.26, 1.13−0.97 (each m, H^{d-f}).

ATRP of Methyl Methacrylate Using PNBE-1 and PNBE-2 as Macroinitiators. A typical procedure is as follows. To a solution of methyl methacrylate (198 mg, 1.98

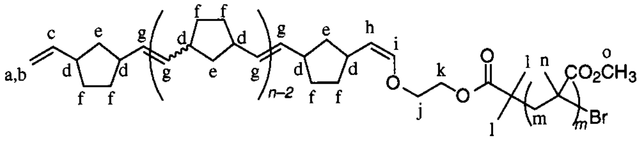
mmol) and PNBE-**1** (101 mg, 0.0348 mmol) in toluene (1.5 mL) were added **4** (13 mg, 0.015 mmol) and Al(OPr^i)$_3$ (13 mg, 0.060 mmol). The mixture was degassed by three freeze−pump−thaw cycles and stirred at 80 °C for 74 h under a nitrogen atmosphere. The viscous mixture thus obtained was poured into vigorously stirred MeOH (100 mL) to give a white precipitate, which was collected by suction filtration, washed with MeOH, and dried under vacuum at room temperature to afford block copolymer PNBE-**1**-*b*-PMMA (270 mg, 90%).

PNBE-**1**-*b*-PMMA:



^{1}H NMR (CDCl$_3$): δ 5.85 (br d, J = 6.0 Hz, H^i), 5.79 (ddd, J = 17.2, 9.9, 7.0 Hz, H^c), 5.40−5.28 (m, H^g of *trans*-polymer), 5.24−5.16 (m, H^g of *cis*-polymer), 4.97 (br d, J = 17.2 Hz, H^b), 4.84 (br d, J = 9.9 Hz, H^a), 4.42−4.20 (br, $H^{h,j-l}$), 3.60 (s, H°), 2.85−2.71, 2.50−2.35 (each br, H^d), 2.08−1.70 (m, $H^{e,f,m}$), 1.50−1.20 (m, H^f), 1.03 (br, H^e), 0.85 (br, H^n).

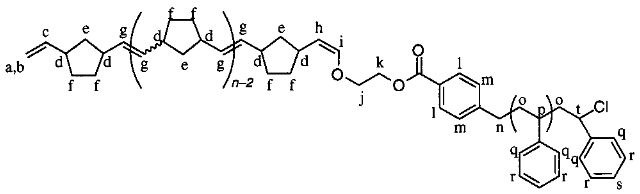
PNBE-**2**-*b*-PMMA:



^{1}H NMR (CDCl$_3$): δ 5.86 (br d, J = 6.0 Hz, H^i), 5.79 (ddd, J = 17.7, 10.4, 7.2 Hz, H^c), 5.38−5.28 (m, H^g of *trans*-polymer), 5.24−5.15 (m, H^g of *cis*-polymer), 4.96 (br d, J = 17.7 Hz, H^b), 4.86 (br d, J = 10.4 Hz, H^a), 4.40−4.32, 4.25−4.18 (each br m, $H^{h,j,k}$), 3.58 (s, H°), 2.84−2.71, 2.50−2.35 (each br, H^d), 2.08−1.70 (m, $H^{e,f,m}$), 1.45−1.19 (m, H^f), 1.02 (br, H^e), 0.84 (br, H^n).

ATRP of Styrene Using PNBE-3 as a Macroinitiator. To a mixture of styrene (289 mg, 2.78 mmol), PNBE-**3** (101 mg, 0.025 mmol), and toluene (0.1 mL) were added CuBr (3.6 mg, 0.025 mmol) and 2,2′-bipyridine (7.9 mg, 0.051 mmol). The mixture was degassed by three freeze−pump−thaw cycles and stirred at 90 °C for 26 h under a nitrogen atmosphere. The viscous mixture thus obtained was diluted in THF (2 mL) and poured into vigorously stirred MeOH (100 mL) to give a white precipitate, which was collected by suction filtration, washed with MeOH, and dried under vacuum at room temperature to afford block copolymer PNBE-**3**-*b*-PSt (308 mg, 79%).

PNBE-**3**-*b*-PSt:



^{1}H NMR (CDCl$_3$): δ 8.06, 7.48 (each d, J = 7.5 Hz, $H^{l,m}$), 7.30−6.88, 6.88−6.30 (each br m, H^{q-s}), 5.93 (br d, J = 6.3 Hz, H^i), 5.81 (ddd, J = 17.4, 10.1, 7.1 Hz, H^c), 5.40−5.30 (m, H^g of *trans*-polymer), 5.26−5.17 (m, H^g of *cis*-polymer), 4.98 (br d, J = 17.4 Hz, H^b), 4.88 (br d, J = 10.1 Hz, H^a), 4.63 (s, H^t), 4.52−4.38, 4.06−3.90 (each br m, $H^{h,j,k}$), 2.85−2.70, 2.54−2.34 (each br, H^d), 2.15−1.67 (m, $H^{e,f,n,o}$), 1.65−1.20 (br m, $H^{f,n,o,p}$), 1.14−0.98 (m, H^e).

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan. We thank Prof. Dr. T. Takata, Dr. N. Kihara, and Dr. S. Matsumura at Osaka Prefecture University for their assistance in GPC measurements.

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MA0110249