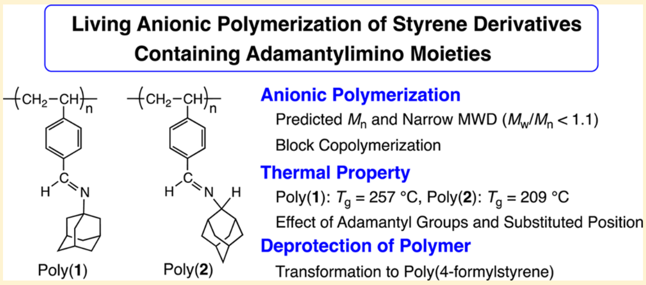
Macromolecules

Living Anionic Polymerization of *N*-(1-Adamantyl)-*N*-4-vinylbenzylideneamine and *N*-(2-Adamantyl)-*N*-4-vinylbenzylideneamine: Effects of Adamantyl Groups on Polymerization Behaviors and Thermal Properties

Beom-Goo Kang,[†] Hideo Shoji,[‡] Hiroshi Kataoka,[‡] Reo Kurashima,[‡] Jae-Suk Lee,[§]
and Takashi Ishizone*[,‡]

[†]Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States
[‡]Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1-S1-13, Ohokayama, Meguro-ku, Tokyo 152-8552, Japan
[§]School of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), 123 Cheomdangwagi-ro, Buk-gu, Gwangju 500-712, Korea

S *Supporting Information*



ABSTRACT: The anionic polymerization of *N*-(1-adamantyl)-*N*-4-vinylbenzylideneamine (**1**) and *N*-(2-adamantyl)-*N*-4-vinylbenzylideneamine (**2**) was performed using various initiators, such as oligo(α-methylstyryl)dipotassium, potassium naphthalenide, diphenylmethylpotassium, and diphenylmethyllithium, in THF at −78 °C for 1 h to investigate the effects of adamantyl groups on the polymerization behaviors and thermal properties of the resulting polymers. The well-defined poly(**1**) and poly(**2**) with predictable molecular weights and narrow molecular weight distributions were successfully obtained, indicating that the bulky adamantyl groups effectively protected the carbon−nitrogen double bond (C═N) from the nucleophilic attack of the initiators and the propagating chain ends. The stability of the propagating chain end of poly(**1**) was confirmed by the quantitative efficiencies in the postpolymerization and the sequential copolymerization with *tert*-butyl methacrylate. A poly(4-formylstyrene) was quantitatively formed by the acidic hydrolysis reaction of the *N*-adamantylimino groups of the poly(**1**). The resulting poly(**1**) and poly(**2**) showed significantly high glass transition temperatures (T_g) at 257 and 209 °C, respectively, due to the bulky and stiff adamantyl substituents. It was also found that the substituted position of adamantane unit and the linkage between polystyrene backbone and adamantyl groups played very important roles to determine the T_g values of the substituted polystyrenes.

INTRODUCTION

Among many living polymerization methods, anionic polymerization is still the best synthetic system to prepare well-defined polymers with controlled chain lengths.[1−6] The hydrocarbon-based monomers, such as styrene, α-methylstyrene, isoprene, and 1,3-butadiene, can be anionically polymerized without any side reactions. However, the most functional monomers are incompatible with anionic species, such as anionic initiators and propagating chain-end carbanions, causing nucleophilic attack on the functional groups or abstraction of the acidic hydrogens prior to the polymerization. In order to overcome such synthetic problems in the anionic system, the protected monomers have been used for the anionic polymerization.[4−6] For example, the living anionic polymerization of styrene derivatives with hydroxyl,[7,8] thiol,[9] and acetyl groups[10] has been successfully performed by introducing the *tert*-butyldimethylsilyl protecting group, and the original functional groups of the polymers have been recovered by the following deprotection reaction.

The imine functions (CH═N−R) have been believed to be incompatible to the conditions of living anionic polymerization due to its high reactivity with anionic species. In our previous investigations, we succeeded in the living anionic polymerization of styrene derivatives *para*-substituted with *N*-alkyl-[11] and *N*-arylimino groups[12] (Figure 1). It was found that the bulkiness of *N*-alkyl and *N*-aryl substituents was a very important factor to achieve the anionic polymerization of styrene derivatives containing imino groups. In fact, the bulky *N*-substituents, including ethyl, isopropyl, cyclohexyl, *tert*-butyl, and 2,6-dialkylphenyl groups, effectively prevented the side reactions of the CH═N bond with the nucleophilic carbanions, although the living anionic polymerizations of 4-(*N*-methylimino)styrene and 4-(*N*-phenylimino)styrene were not successful possibly due to

Received: September 20, 2015
Revised: October 31, 2015

ACS Publications © XXXX American Chemical Society

DOI: 10.1021/acs.macromol.5b02075

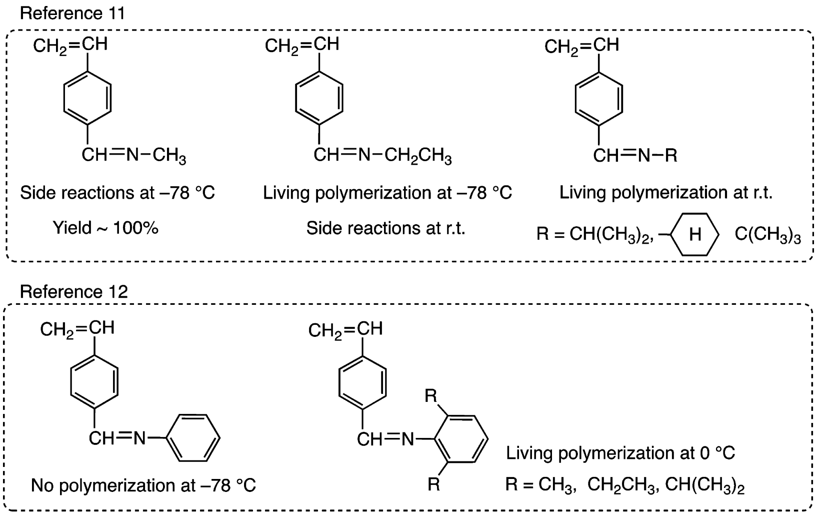


Figure 1. Summary of anionic polymerization of styrene derivatives *para*-substituted with *N*-alkyl- and *N*-arylimino groups.

the undesirable side reactions of the anionic species with the −CH═N−R groups. Additionally, the resulting polystyrenes carrying *N*-alkylimino and *N*-arylimino groups could be transformed into a well-defined poly(4-formylstyrene) by the acidic hydrolysis. Of course, the poly(4-formylstyrene) is an attractive reactive polymer due to the high electrophilicity of the formyl group.[4−6,11,12] From the synthetic point of view, this versatility of the polymers containing imino groups can provide chances to form well-defined polymers with various functionalities.

It has been known that adamantane (tricyclo[3.3.1.1^{3,7}]-decane), which is a tricyclic hydrocarbon with a highly symmetrical structure, shows thermal stability, resistance to oxidation, hydrophobicity, low surface energy, and high density.[13−15] In particular, this bulky and rigid molecule plays a very important role to improve thermal properties of the polymers. The introduction of adamantane unit as a pendent group into the vinyl polymers certainly allowed the parent polymers to show the high glass transition temperature (T_g) and the excellent thermal stabilities.[16−22] In recent years, we have carried out the living anionic polymerization of methacrylate, styrene, and butadiene derivatives containing pendent adamantyl groups in order to investigate the effect of bulky adamantyl group on the thermal properties of the polymers.[18−20] As shown in Figure 2, the T_g values of the resulting polymers were drastically enhanced by incorporating the adamantyl skeletons. Based on the effect of adamantyl skeleton on T_g enhancement, new thermoplastic elastomers showing high service temperature could be synthesized by the sequential anionic copolymerization of 4-(1-adamantyl)styrene and isoprene.[22]

In this study, we designed and anionically polymerized new styrene derivatives containing *N*-adamantylimino groups, *N*-(1-adamantyl)-*N*-4-vinylbenzylideneamine (**1**), and *N*-(2-adamantyl)-*N*-4-vinylbenzylideneamine (**2**) (Scheme 1). The monomers **1** and **2** are corresponding to the structural isomers and undergo the living anionic polymerization to form the well-defined polymers quantitatively. The influences of bulky adamantyl groups on the anionic polymerization behaviors and the thermal properties of the polymers are discussed. The synthesis of block copolymer by the sequential copolymerization and the synthesis of a tailored poly(4-formylstyrene) by the hydrolysis of the *N*-adamantylimino groups are also attempted.

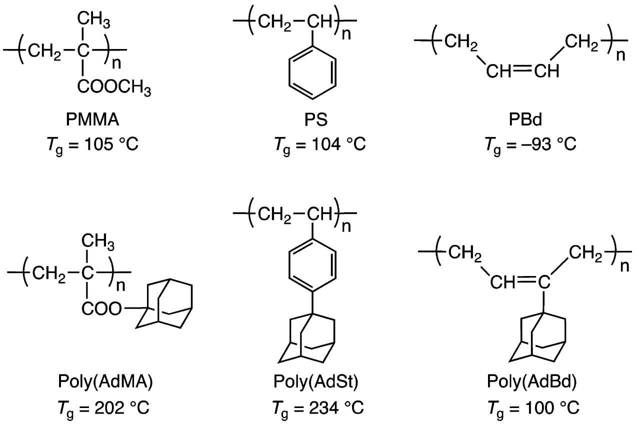
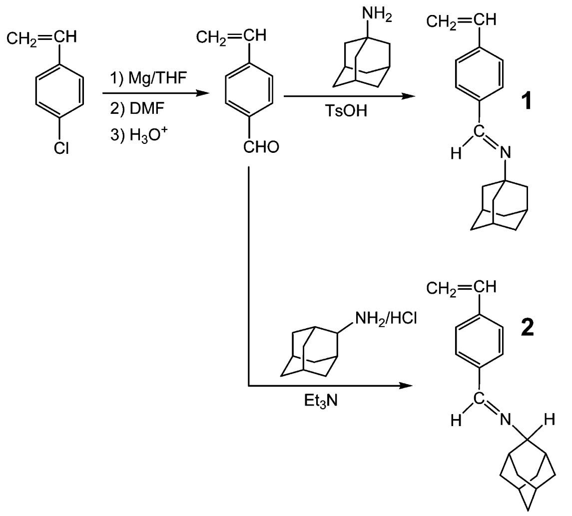


Figure 2. Effect of adamantyl group on T_g of the polymers.

Scheme 1. Synthesis of 1 and 2



■ EXPERIMENTAL SECTION

Materials. All reagents were purchased from Tokyo Chemical Industry Co., Ltd., unless otherwise stated. 4-Formylstyrene was prepared from 4-chlorostyrene as previously reported.[23] 1-Adamantylamine (Aldrich, 97%) and 2-adamantylamine hydrochloride (Aldrich, 99%) were used without further purification. Triethylamine was distilled over CaH_2. *tert*-Butyl methacrylate (*t*BMA) was distilled over CaH_2 *in vacuo* and subsequently distilled from trioctylaluminum (2 mol %) on a vacuum line.[24] THF utilized in the polymerization procedure was refluxed over sodium wire for 5 h and then distilled from lithium aluminum hydride and eventually distilled from its sodium naphthalenide (Na-Naph) solution on the vacuum line. Lithium naphthalenide (Li-Naph) and potassium naphthalenide (K-Naph) were prepared by the reactions of a small excess amount of naphthalene with the corresponding alkali metal in dry THF at room temperature. Diphenylmethylpotassium (Ph_2CHK) and diphenylmethyllithium (Ph_2CHLi) were synthesized by the reactions of 1.5 molar excess of diphenylmethane with the corresponding alkali metal naphthalenide (K-Naph and Li-Naph) in dry THF at room temperature for 3 days. Oligo(α-methylstyryl)dipotassium was prepared prior to the polymerizations from K-Naph and 2–4-fold α-methylstyrene (α-MeSt) in THF at −78 °C for 10 min. The initiators and *t*BMA were stored at −30 °C in ampules equipped with break-seals.

Measurements. ^1H and ^{13}C NMR spectra were measured on a Bruker DPX300 in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to $CHCl_3$ (δ 7.26) and $CDCl_3$ (δ 77.1) for ^1H and ^{13}C NMR as standard, respectively. IR spectra (KBr disk) were recorded on a JASCO FT/IR-4100 instrument. Size exclusion chromatogram (SEC) curves for determination of M_w/M_n were obtained in THF at 40 °C at flow rate of 1.0 mL min^{-1} with a Viscotek TDA302 equipped with three polystyrene gel columns (TSKgelG5000H_{HR} + G4000H_{HR} + G3000H_{HR}). The combination of viscometer, right angle laser light scattering detection (RALLS), and refractive index (RI) detection was applied for the online SEC system in order to determine the absolute molecular weights of polymer. A Seiko Instrument TG/DTA6200 was used for TGA analysis at 30–600 °C under nitrogen flow with heating rate of 20 °C min^{-1}. The T_g of the polymer was measured by DSC using a Seiko instrument DSC6220 apparatus under nitrogen flow. The polymer sample was first heated to 100 °C, cooled to 30 °C, and then scanned at a rate of 20 °C min^{-1} under nitrogen.

***N*-(1-Adamantyl)-*N*-4-vinylbenzylideneamine (1).** A benzene (50 mL) solution of 4-formylstyrene (8.74 g, 66.2 mmol), 1-adamantylamine (11.0 g, 72.8 mmol), and catalytic amount of *p*-toluenesulfonic acid was refluxed for 24 h with azeotropic separation of water by means of a Dean–Stark water trap (Scheme 1). The reaction was quenched with $NaHCO_3$ solution, and the layer was separated. The aqueous layer was extracted three times with diethyl ether. The organic phase was combined and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was purified by the recrystallization from hexane to afford a white solid (12.30 g, 46.4 mmol, 70%, mp = 82–83 °C). ^1H and ^{13}C NMR spectra of **1** are shown in Figure S1. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.67–1.78 (m, 6H, $C(2)H_2$), 1.82 (s, 6H, $C(4)H_2$), 2.17 (s, 3H, C(3)H), 5.27–5.83 (2d, 2H, CH_2═, *J* = 10.9 and 17.6 Hz), 6.69–6.78 (dd, 1H, −CH═, *J* = 10.9 and 17.6 Hz), 7.42–7.72 (m, 4H, aromatic), 8.26 (s, 1H, CH═N). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.7 (C3), 36.7 (C4), 43.2 (C2), 57.7 (C1), 114.8 (Cβ), 126.4 (Cb), 128.2 (*Cc*), 136.5 (Cd), 136.8 (Cα), 139.4 (Ca), 154.7 (Ca′). IR (KBr, cm^{-1}): 3002, 2902, 2848, 1642 (CH═N), 1606, 1563, 1509, 1450, 1407, 1342, 1301, 1089, 986, 925, 904, 868, 837. Anal. Calcd for $C_{19}H_{23}N$: C, 85.99; H, 8.74; N, 5.28. Found: C, 86.17; H, 8.60; N, 5.22.

***N*-(2-Adamantyl)-*N*-4-vinylbenzylideneamine (2).** A benzene (100 mL) solution of 4-formylstyrene (8.12 g, 61.1 mmol), 2-adamantylamine hydrochloride (11.88 g, 63.4 mmol), and triethylamine (100 mL) was refluxed for 4.5 h with azeotropic separation of water by means of a Dean–Stark water trap (Scheme 1). The reaction mixture was quenched with $NaHCO_3$ solution, and the layer was separated. The aqueous phase was extracted three times with diethyl ether. The combined organic phase was dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was purified by the recrystallization from hexane to afford a white needle crystal (10.03 g, 37.8 mmol, 62%, mp = 123–124 °C). ^1H and ^{13}C NMR spectra of **2** are shown in Figure S2. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.52–1.55 (m, 2H, C(7)H, C(8)H), 1.80–1.93 (m, 10H, $C(3)H_2$, $C(4)H_2$, $C(5)H_2$, $C(6)H_2$, $C(9)H_2$), 2.40–2.43 (m, 2H, C(2)H), 3.45 (s, 1H, C(1)H), 5.28–5.83 (2d, 2H, CH_2═, *J* = 10.9 and 17.6 Hz), 6.69–6.79 (dd, 1H, −CH═, *J* = 10.9 and 17.6 Hz), 7.42–7.75 (m, 4H, aromatic), 8.32 (s, 1H, CH═N). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.8–28.7 (C7, C8), 32.4 (C4, C6), 35.9 (C2), 37.8 (C3, C5), 38.5 (C9), 74.9(C1), 115.1 (Cβ), 126.7 (Cb), 128.7 (*Cc*), 136.9 (Cd), 137.0 (Cα), 139.7 (Ca), 157.7 (Ca′). IR (KBr, cm^{-1}): 2932, 2893, 2849, 1640 (CH═N), 1604, 1560, 1448, 1387, 1352, 1300, 1105, 1056, 1018, 966, 909, 849, 838. Anal. Calcd for $C_{19}H_{23}N$ (265.39): C, 85.99; H, 8.74; N, 5.28. Found: C, 86.17; H, 9.15; N, 5.12.

Anionic Polymerization of 1 and 2. All polymerizations were carried out under high-vacuum conditions in the sealed all-glass reactors equipped with break-seals.[8] The reactors were prewashed with initiator solutions after sealing off from the vacuum line. The polymerizations were usually performed by pouring a THF solution of monomer to the initiator solutions in THF at −78 °C (dry ice−acetone bath) for 1 h. The polymerizations were terminated with degassed methanol, and the reaction solutions were poured into methanol to precipitate polymers. The polymers were further purified by reprecipitation in THF/MeOH. The resulting polymers were then dissolved in benzene and freeze-dried under vacuum condition for characterization. The resulting poly(**1**) and poly(**2**) were characterized by ^1H and ^{13}C NMR, IR, and elemental analysis. ^1H and ^{13}C NMR spectra of poly(**1**) are shown in Figure 3b and Figure S3a, respectively. ^1H and ^{13}C NMR spectra of poly(**2**) are shown in Figure S4. IR spectra of poly(**1**) and poly(**2**) are shown in Figure S3b and Figure S5, respectively. The followings are the IR and EA data of poly(**1**) and poly(**2**).

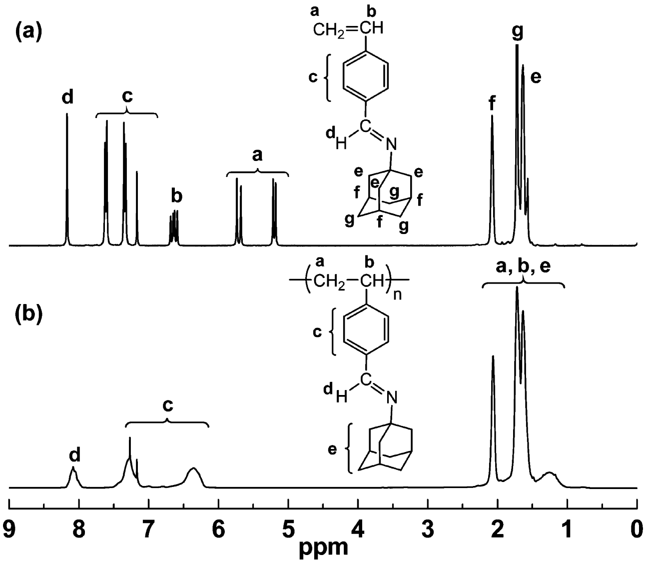


Figure 3. ^1H NMR spectra of **1** and poly(**1**) obtained with Ph_2CHK in THF.

Poly(**1**). IR (KBr, cm^{-1}): 3020, 2904, 2848, 1703, 1640 (CH═N), 1607, 1571, 1508, 1451, 1419, 1307, 1173, 1089, 1016, 984, 925, 865, 826. Anal. Calcd for $(C_{19}H_{23}N)_n$: C, 85.99; H, 8.74; N, 5.28. Found: C, 85.72; H, 9.89; N, 5.13.

Poly(**2**). IR (KBr, cm^{-1}): 2900, 2848, 1645 (CH═N), 1607, 1572, 1509, 1448, 1299, 1215, 1174, 1102, 1053, 1018, 962, 828. Anal. Calcd for $(C_{19}H_{23}N)_n$: C, 85.99; H, 8.74; N, 5.28. Found: C, 85.88; H, 8.72; N, 5.16.

Block Copolymerization of 1. The first-stage polymerization of **1** was performed with Ph_2CHK in THF at −78 °C for 1 h in an all-glass apparatus equipped with break-seals under high vacuum. After a small portion of the poly(**1**) solution was sampled, *t*BMA in THF was added to the residual living poly(**1**) in THF at −78 °C. The second-stage polymerization of *t*BMA was continued for an additional 1 h to achieve the complete conversion. The reaction solutions were terminated with methanol and poured into methanol to afford a poly(**1**) and a poly(**1**)-*b*-

Table 1. Anionic Polymerization of 1 and 2 in THF at −78 °C for 1 h

run	monomer, mmol	initiator, mmol	yield (%)	M_n (kg/mol) calcd[a]	M_n (kg/mol) obsd[b]	M_w/M_n[b]	T_{10}[c] (°C)	T_g[d] (°C)
1	**1**, 2.31	K-Naph, 0.107/α-MeSt, 0.301	100	12	12	1.05	378	238
2	**1**, 2.81	K-Naph, 0.107/α-MeSt, 0.310	100	15	15	1.09	378	246
3	**1**, 5.79	K-Naph, 0.109/α-MeSt, 0.310	100	29	25	1.03	380	251
4	**1**, 2.46	K-Naph, 0.0750	95	17	18	1.05	401	251
5	**1**, 2.34	Ph_2CHK, 0.0969	100	6.6	6.4	1.04	389	230
6	**1**, 2.37	Ph_2CHK, 0.0320	100	20	23	1.02	391	251
7[e]	**1**, 6.62	Ph_2CHK, 0.0700	100	25	51	1.02	396	254
8	**1**, 6.59	Ph_2CHK, 0.0420	100	42	100	1.04	395	257
9	**2**, 1.95	Ph_2CHK, 0.0977	100	6.6	8.4	1.08	384	203
10	**2**, 2.90	Ph_2CHK, 0.0982	100	8.0	9.1	1.04	396	201
11	**2**, 4.05	Ph_2CHK, 0.0574	100	19	18	1.03	402	209
12	**2**, 4.33	Ph_2CHK, 0.0373	100	31	31	1.03	412	208
13[f]	**2**, 2.86	Ph_2CHK, 0.0740	100	10	10	1.04	383	202
14	**2**, 3.15	Ph_2CHLi, 0.0788	100	11	12	1.04	383	204

[a] M_n(calcd) = (molecular weight of monomer) × [monomer] × f/[initiator]; f = 1 or 2, corresponding to the functionality of the initiators. [b] M_n(obsd) and M_w/M_n were obtained by RALLS-SEC using THF as an eluent. [c] 10% weight loss temperature by TGA measurement. [d] Glass transition temperature determined by the second scan of DSC measurement. [e] Polymerized for 80 min. [f] Polymerized at 0 °C.

poly(*t*BMA). The resulting block copolymer was characterized by SEC and ^{1}H NMR (Figure 7 and Figure S6).

Deprotection. A mixture of poly(**1**) (0.24 g), THF (15 mL), and 12 N HCl (1 mL) was stirred at 80 °C for 4 h. The reaction mixture was quenched with an excess amount of 5% NaOH aqueous solution. Then, the organic and aqueous layers were separated using a separating funnel. The organic layer was concentrated by evaporation and poured into hexane to precipitate the polymer. After filtration, the polymer was purified by reprecipitation with a THF/hexane and freeze-dried from its THF/benzene solution for the characterization. The resulting poly(4-formylstyrene) was characterized by means of ^{1}H NMR and IR (Figure 8).

■ RESULTS AND DISCUSSION

Anionic Polymerization of 1 and 2. The anionic polymerization of **1** was carried out using oligo(α-methylstyryl)dipotassium or Ph_2CHK as an initiator in THF at −78 °C for 1 h. First, the polymerization was performed with oligo(α-methylstyryl)dipotassium prepared by the reaction of K-Naph and 2−4-fold α-MeSt. When **1** was added into the initiator solution, the color of the initiator immediately changed from red to dark red. This solution color was retained until the termination with methanol, indicating the presence of the active chain end.

As shown in Figure 3, the ^{1}H NMR spectra of **1** and poly(**1**) reveal that the vinyl polymerization proceeded exclusively. The signals of vinyl group of **1** completely disappear after the polymerization, while the broad characteristic signals of the CH═N, phenyl, and adamantyl groups are observed. In addition to the ^{1}H NMR analysis, the characteristic signal and absorption corresponding to the CH═N moiety were observed at 155.1 ppm and 1640 cm^{-1} in the ^{13}C NMR and IR spectra of the poly(**1**), respectively (Figure S3). The polymerization results summarized in Table 1 (runs 1−3) show that the well-defined poly(**1**) with controlled M_n (12 000−25 000 g/mol) and narrow molecular weight distribution (MWD) (M_w/M_n = 1.03−1.09) was successfully synthesized by the oligo(α-methylstyryl)dipotassium initiator system. The observed M_n values were in well accordance with the calculated ones based on monomer-to-initiator ratios, and all SEC curves of the polymers were narrow and unimodal. Similarly, potassium naphthalenide (K-Naph), a typical radical anion, gave a tailored poly(**1**) almost quantitatively via the single electron transfer and the subsequent coupling reaction followed by the propagation (Table 1, run 4). The SEC curve of poly(**1**) produced with K-Naph shows a narrow shape (M_w/M_n = 1.05), as can be seen in Figure 4a.

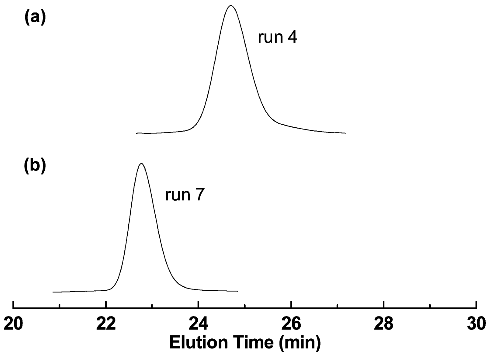


Figure 4. SEC curves of (a) poly(**1**) prepared with K-Naph (Table 1, run 4) and (b) poly(**1**) prepared with Ph_2CHK (Table 1, run 7).

The anionic polymerization of **1** similarly proceeded even with Ph_2CHK showing a low nucleophilicity, which is usually used to initiate the reactive polar monomers, such as methacrylates and 2-vinylpyridine, in THF at −78 °C. When **1** was added into the orange-colored Ph_2CHK solution, the color of the solution immediately changed to dark red, which is the same color as that observed during polymerization initiated with oligo(α-methylstyryl)dipotassium. As listed in Table 1 (runs 5 and 6), the well-controlled poly(**1**) with tailored M_n and narrow MWD was precisely prepared. However, a deviation between the calculated M_n and the observed one occurred in the poly(**1**) samples with higher molecular weights (runs 7 and 8), while their MWDs were very narrow (M_w/M_n = 1.02−1.04). For instance, Figure 4b shows that the SEC trace of poly(**1**) obtained with Ph_2CHK (Table 1, run 7) presents a unimodal and very narrow distribution (M_w/M_n = 1.02), while the observed molecular weight (M_n = 51 000 g/mol) is much higher than the calculated value (M_n = 25 000 g/mol). We now consider that this is probably due to the effect of trace amount of impurity in the monomer. Partial deactivation of the initiator with the impurity might occur at the initial stage of the polymerization, and the polymerization proceeded with the residual initiator.

The results of the polymerization using Ph_2CHK indicate that the anionic polymerizability of **1** is higher than that of styrene, since the initiation efficiency of styrene with Ph_2CHK is lower than 50%. The observed high anionic polymerizability of **1** is derived from its reduced π-electron density of the vinyl group by the electron-withdrawing effect of the *N*-alkylimino group.[11] It is well-known that the anionic polymerizability of styrene derivatives can be predicted by the ^{13}C NMR chemical shift of the vinyl β-carbon of monomer, since it strongly reflects the π-electron density of the monomer.[25] In fact, the ^{13}C NMR chemical shift of vinyl β-carbon of **1** observed at 114.8 ppm supports that the electron density of vinyl group of **1** is significantly lowered compared with that of the parent styrene (113.8 ppm), indicating the higher anionic polymerizability of **1**.

Based on the polymerization results of **1**, the anionic polymerization of the corresponding isomer, **2**, was performed with Ph_2CHK or Ph_2CHLi in THF. The polymerization system of **2** also showed a dark red color during the course of the polymerization. The ^1H and ^{13}C NMR spectra of poly(**2**) show that the vinyl polymerization exclusively proceeded similar to the polymerization of **1** (Figure S4). The resulting poly(**2**)s produced at −78 °C had predictable M_ns (8400−31 000 g/mol) and narrow MWDs (M_w/M_n = 1.03−1.08), as shown in Table 1 (runs 9−12). Interestingly, a well-defined poly(**2**) was also obtained with Ph_2CHK in THF even at 0 °C (run 13). The SEC curve of the poly(**2**) obtained at 0 °C shows a narrow and unimodal MWD, indicating the side reactions are completely suppressed by the bulky adamantyl substituent even at 0 °C (Figure 5a), as previously observed in the anionic polymerizations of *N*-isopropyl-, *N*-cyclohexyl-, and *N*-*tert*-butyliminostyrenes.[11] Furthermore, the polymerization with Ph_2CHLi carrying a lithium countercation also succeeded in creating a well-controlled poly(**2**) (run 14). The observed M_n (12 000 g/mol) matched well with the predicted one (11 000 g/mol), and the SEC curve showed a very narrow shape (M_w/M_n = 1.04), as shown in Figure 5b.

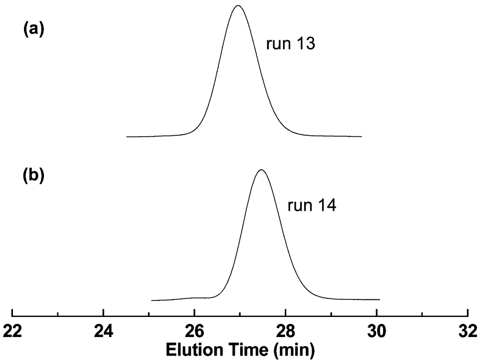


Figure 5. SEC curves of (a) poly(**2**) prepared with Ph_2CHK at 0 °C (Table 1, run 13) and (b) poly(**2**) prepared with Ph_2CHLi (Table 1, run 14).

Thus, the polymerization results clearly demonstrate that both **1** and **2** are quantitatively polymerized without occurrence of any side reactions under the polymerization conditions employed in this study. The bulky adamantyl group can protect CH═N linkage sterically from the nucleophilic attack of either the anionic initiators or the propagating chain-end anions regardless of the substituted position of the CH═N group on the adamantane ring.

Postpolymerization of 1. We carried out the postpolymerization of **1** using Ph_2CHK in THF at −78 °C in order to verify the living nature of the polymerization. The first-stage polymerization of **1** was performed for 1 h in an all-glass apparatus equipped with break-seals under high vacuum. After sampling of a small portion of prepolymer of **1**, the second feed of **1** was then added into the residual polymerization system. The reaction system was maintained for an additional 1 h to complete the second-stage polymerization. The terminated polymerization solutions were poured into a large amount of methanol to obtain pre- and postpolymer. Table 2 indicates that the polymers were precisely synthesized under the reaction conditions employed here (run 15). The observed M_n values of pre- and postpolymer were 5900 and 13 000 g/mol, respectively, which agreed well with the calculated ones, 6000 and 13 000 g/mol. In addition, the SEC curve of the postpolymer was narrow (M_w/M_n = 1.02) and symmetrical and shifted from the prepolymer toward the higher M_n region, as shown in Figure 6. These results demonstrate that the propagating carbanion of poly(**1**) stably exists at −78 °C for at least 1 h without undesirable side reactions.

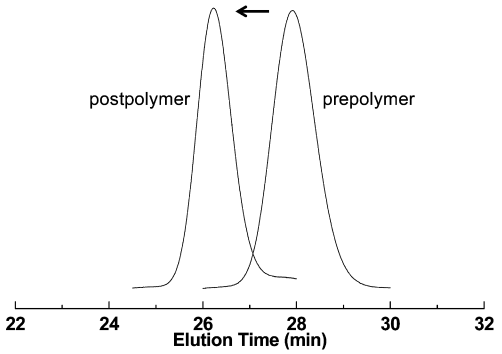


Figure 6. SEC curves of poly(**1**) at the first-stage polymerization (prepolymer) and at the second-stage polymerization (postpolymer) (Table 2, run 15).

Block Copolymerization of 1. On the basis of the postpolymerization, we attempted the sequential copolymeriza-

Table 2. Postpolymerization and Block Copolymerization of 1 with Ph_2CHK in THF at −78 °C[a]

				polymer of second stage (prepolymer)		
		monomer		M_n (kg/mol)		
run	Ph_2CHKmmol	first, mmol	second, mmol	calcd[b]	obsd[c]	M_w/M_n[c]
15	0.103	**1**, 2.26	**1**, 2.13	13 (6.0)	13 (5.9)	1.02 (1.04)
16	0.126	**1**, 2.50	*t*BMA, 5.77	13 (5.4)	11 (4.7)	1.02 (1.03)

[a] Yields of polymers were quantitative. [b] M_n(calcd) = (molecular weight of monomer) × [monomer]/[initiator]. [c] M_n(obsd) and M_w/M_n were obtained by RALLS-SEC using THF as an eluent.

tion of **1** with *tert*-butyl methacrylate (*t*BMA)[12,26−28] to synthesize the well-defined block copolymers containing a poly(**1**) segment. The block copolymerization was conducted by the sequential addition of **1** as the first monomer and *t*BMA as the second monomer using Ph_2CHK in THF at −78 °C (Table 2, run 16). When *t*BMA was added into the living poly(**1**) anion, the color of the polymerization system immediately changed from dark red to colorless, indicating the occurrence of the rapid crossover reaction from the active chain end of poly(**1**) to *t*BMA. After termination, a copolymer of **1** and *t*BMA was obtained in a quantitative yield. The ^1H NMR spectrum of the resulting copolymer showed the broad peaks of the adamantyl and phenyl groups of poly(**1**) segment and the characteristic signals of CH=N moiety (8.2 ppm) derived from the poly(**1**) block and *tert*-butyl group (1.4 ppm) of poly(*t*BMA) segment (Figure S6). Along with the ^1H NMR characterization, Table 2 supports that the well-defined poly(**1**)-*b*-poly(*t*BMA) with predictable M_n (11 000 g/mol) and narrow MWD (M_w/M_n = 1.02) was quantitatively synthesized. The observed M_n and the composition of the resulting block copolymer were in well accordance with the calculated ones. Moreover, a SEC curve of poly(**1**)-*b*-poly(*t*BMA) clearly shifts from the elution volume of the poly(**1**) toward the higher M_n side, as shown in Figure 7. It is thus demonstrated that *t*BMA can be smoothly polymerized by the living poly(**1**) anion, suggesting that propagating chain end derived from **1** is sufficiently nucleophilic to synthesize the well-defined poly(**1**)-*b*-poly(*t*BMA).

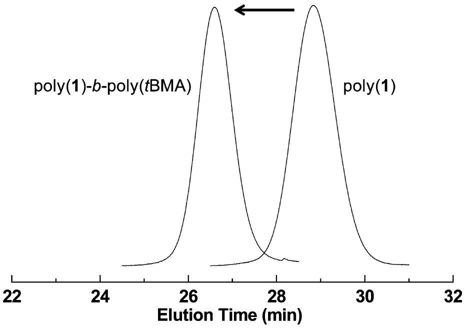
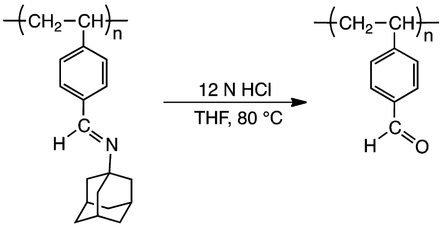


Figure 7. SEC curves of poly(**1**) and poly(**1**)-*b*-poly(*t*BMA) (Table 2, run 16).

Deprotection. Next, we examined the hydrolysis of the CH=N linkage of the anionically obtained poly(**1**). The deprotection of the *N*-adamantylimino group from the poly(**1**) was performed with 12 N HCl in THF at 80 °C for 4 h to obtain a poly(4-formylstyrene), as shown in Scheme 2. After washing with NaOH aqueous solution, the polymer solution in THF was poured into hexane to precipitate a polymer. The yield of the deprotected polymer was nearly quantitative. It was verified from the ^1H NMR spectra before and after deprotection that the hydrolysis reaction proceeded well. As can be seen in Figure 8a, the characteristic ^1H NMR signal of formyl group is newly observed at 9.9 ppm, and the signals corresponding to the CH=N (8.2 ppm) and adamantyl groups completely disappear after the deprotection. The completion of the deprotection was also found in the IR spectra, as shown in Figure 8b. The absorption at 1640 cm^{-1} corresponding to the CH=N linkage disappears, and a strong characteristic absorption due to the CHO group appears at 1701 cm^{-1} after the hydrolysis reaction. The ^1H NMR and IR data of the resulting polymer after the deprotection were in accordance with the reported ones of poly(4-formylstyrene).[11,12] These results strongly indicate that the acidic hydrolysis of the bulky *N*-adamantylimino group of poly(**1**) quantitatively proceeded, and the poly(**1**) was transformed into the highly electrophilic poly(4-formylstyrene) under the reaction conditions employed here.

Scheme 2. Acidic Hydrolysis of Poly(1)



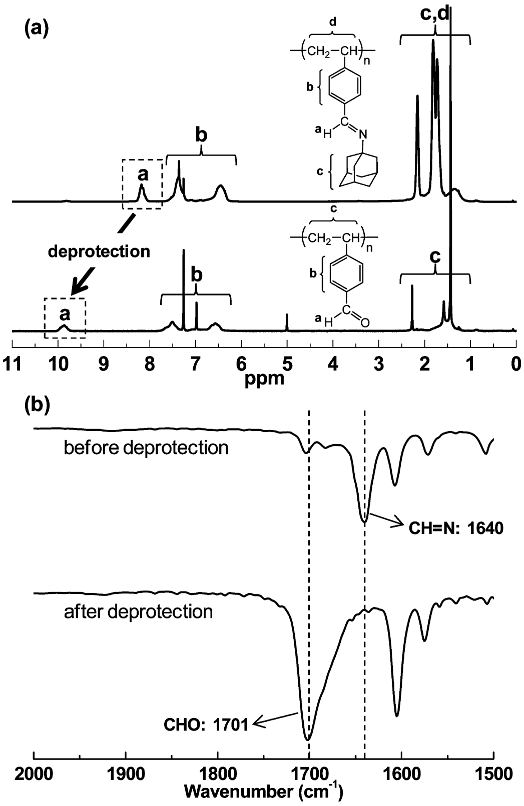


Figure 8. (a) ^1H NMR and (b) IR spectra of poly(**1**) before and after deprotection.

Solubility and Thermal Properties. The solubilies of poly(**1**) and poly(**2**) were tested by using a series of common organic solvents at room temperature. Both polymers showed the same solubilities and were soluble in benzene, carbon tetrachloride, chloroform, and THF but were insoluble in *n*-hexane, acetone, ethyl acetate, diethyl ether, *N*,*N*-dimethylformamide, methanol, and water. The solubility was considerably changed after the deprotection, as expected. The resulting poly(4-formylstyrene) was soluble in chloroform, acetone, THF, and *N*,*N*-dimethylformamide and was insoluble in *n*-hexane, benzene, carbon tetrachloride, ethyl acetate, diethyl ether, methanol, and water.[11,12]

Thermal stabilities of poly(**1**) and poly(**2**) were investigated by thermogravimetric analysis (TGA) under nitrogen. The TGA thermograms of poly(**1**) (Table 1, run 4, M_n = 18 000 g/mol) and poly(**2**) (Table 1, run 12, M_n = 31 000 g/mol) show single degradation patterns, as shown in Figure 9. Both polymers started to decompose around 380 °C, and the 10% weight loss temperatures (T_{10}) were observed at 401 and 412 °C, respectively. As listed in Table 1, all the poly(**1**) and poly(**2**) synthesized in this study exhibited high T_{10} values (378−412 °C), indicating their excellent thermal stability.

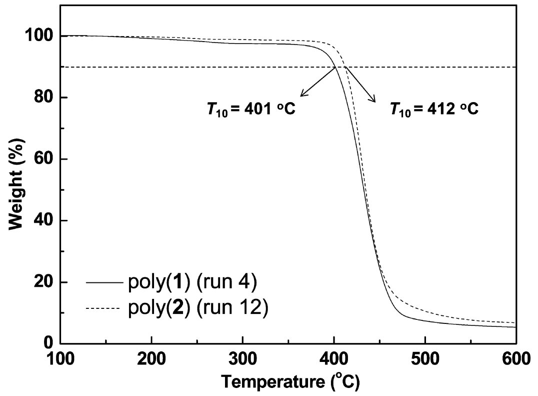


Figure 9. TGA thermograms of poly(**1**) (Table 1, run 4) and poly(**2**) (Table 1, run 12).

The T_g values of poly(**1**) and poly(**2**) were then examined by differential scanning calorimetry (DSC). Figure 10 shows that the T_g values of both polymers are apparently dependent on the M_ns of the polymers as well as the poly(4-(1-adamantyl)-styrene).[19] In each case, the T_g increased with increasing the M_n and became constant at the high molecular weight region. The T_g value of poly(**1**) and poly(**2**) reached 257 and 209 °C, respectively, in the case of high molecular weight sample. Interestingly, the poly(**1**) carrying 1-adamantyl group apparently showed higher T_g values than the isomeric poly(**2**) carrying the 2-adamantyl group, although both polymers possessed the same CH═N linkage between the polystyrene main chain and the adamantyl substituents. This is probably due to the effect of the substituted position on the adamantane ring. A similar tendency was reported in the T_g values of poly(vinyl ether)s carrying 1-adamantyl and 2-adamantyl groups.[29] In fact, the T_g values of poly(1-adamantyl vinyl ether) and poly(2-adamantyl vinyl ether) were reported to be 205 and 178 °C, respectively.

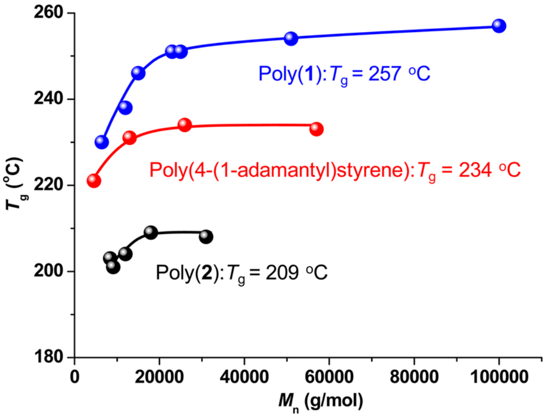


Figure 10. Relationship between M_ns and T_g values of poly(**1**), poly(**2**), and poly(4-(1-adamantyl)styrene).

Moreover, the T_g values of poly(4-(*N*-alkylimino)styrene)s including *N*-ethyl-, *N*-isopropyl-, *N*-cyclohexyl-, and *N*-*tert*-butyl groups were reported to be 98, 105, 144, and 112 °C, respectively.[11] The T_g of poly(**1**) at 257 °C is significantly higher than those T_g values. Such a remarkable difference in T_g indicates that the incorporation of bulky *N*-adamantyl group decreases the mobility of the polymer main chain and thus leads to the significant T_g enhancement.[16,17] Even the T_g of poly(**1**) is almost 20 °C higher than that of poly(4-(1-adamantyl)-styrene).[19] To our best knowledge, the observed T_g of poly(**1**) (257 °C) is the highest value for adamantyl-substituted polystyrene derivatives reported to date. These investigations on thermal properties of adamantyl-substituted polystyrene derivatives suggest that the substituted position and the linkage between the polystyrene backbone and the adamantyl skeleton are important factors to determine the T_g values of the polymers.

■ CONCLUSIONS

We have succeeded in the living anionic polymerization of styrene derivatives containing *N*-adamantylimino groups, **1** and **2**, to form the polymers with well-defined architectures. The bulky 1-adamantyl and 2-adamantyl groups can effectively protect the electrophilic CH═N linkage from the undesirable side reactions. The living nature of the propagating carbanion of poly(**1**) enables the synthesis of the well-defined block copolymer, poly(**1**)-*b*-poly(*t*BMA). The acid hydrolysis of poly(**1**) results in a formation of functional poly(4-formylstyrene) with controlled chain structures. The T_g values of the resulting poly(**1**) and poly(**2**) are significantly increased by the incorporation of bulky and stiff adamantyl groups. Furthermore, thermal properties of adamantyl-substituted polystyrene derivatives depend on the substituted position and the linkage between the polystyrene backbone and the adamantyl substituents. The high T_g values of polymers and the living nature of the polymerization systems will allow the synthesis of new thermoplastic elastomers showing high service temperatures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b02075.

> ^{1}H and ^{13}C NMR spectra of **1**; ^{1}H and ^{13}C NMR spectra of **2**; ^{13}C NMR and IR spectra of poly(**1**); ^{1}H and ^{13}C NMR and IR spectra of poly(**2**); ^{1}H NMR spectrum of poly(**1**)-*b*-poly(*t*BMA) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tishizon@polymer.titech.ac.jp (T.I.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Grant-in Aid (No. 18550105) from the Ministry of Education, Science, Sports, and Culture, Japan. T.I. appreciates the financial support from the Yazaki foundation and JX Corporation. 4-Chlorostyrene was kindly supplied from Hokko Chemical Industry Co., Ltd.

■ REFERENCES

(1) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel Dekker Inc.: New York, 1996.

(2) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211.

(3) Uhrig, D.; Mays, J. W. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6179.

(4) Hirao, A.; Loykulnant, S.; Ishizone, T. *Prog. Polym. Sci.* **2002**, *27*, 1399.

(5) Ishizone, T.; Sugiyama, K.; Hirao, A. *Polymer Science: A Comprehensive Reference*; Elsevier BV: Amsterdam, 2012; Vol. *3*, pp 591−621.

(6) Hirao, A.; Goseki, R.; Ishizone, T. *Macromolecules* **2014**, *47*, 1883.

(7) Hirao, A.; Yamaguchi, K.; Takenaka, K.; Suzuki, K.; Nakahama, S.; Yamazaki, N. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 941.

(8) Hirao, A.; Takenaka, K.; Packirisamy, S.; Yamaguchi, K.; Nakahama, S. *Makromol. Chem.* **1985**, *186*, 1157.

(9) Hirao, A.; Shione, H.; Wakabayashi, S.; Nakahama, S. *Macromolecules* **1994**, *27*, 1835.

(10) Hirao, A.; Kato, K.; Nakahama, S. *Macromolecules* **1992**, *25*, 535.

(11) Ishizone, T.; Sueyasu, N.; Sugiyama, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1993**, *26*, 6976. We previously reported the anionic polymerization of 4-(*N*-methylimino)styrene (**3**), a methyl counterpart of **1** and **2**. A polymer of **3** was quantitatively obtained with oligo(α-methylstyryl)dipotassium in THF at −78 °C within 10 min. However, the resulting poly(**3**) already possessed a bimodal molecular weight distribution with a high molecular weight shoulder, although the main GPC curve was sharp (M_w/M_n = 1.19). Furthermore, the GPC curve of the resulting poly(**3**) became multimodal after 30 min, indicating that the serious intermolecular reaction took place between the propagating carbanion and the pendant $CH{=}N{-}CH_3$ groups even at −78 °C. Actually, the insoluble gel was formed at −78 °C after 90 min or at room temperature after 10 min from the polymerization system.

(12) Ishizone, T.; Utaka, T.; Ishino, Y.; Hirao, A.; Nakahama, S. *Macromolecules* **1997**, *30*, 6458.

(13) Fort, R. C.; Schleyer, P. V. R. *Chem. Rev.* **1964**, *64*, 277.

(14) Schwertfeger, H.; Fokin, A. A.; Schreiner, P. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 1022.

(15) Matsumoto, A.; Tanaka, S.; Otsu, T. *Macromolecules* **1991**, *24*, 4017.

(16) Cypcar, C.; Camelio, P.; Lazzeri, V.; Mathias, L. J. *Macromolecules* **1996**, *29*, 8954.

(17) Acar, H. Y.; Jensen, J. J.; Thigpen, K.; McGowen, J. A.; Mathias, L. J. *Macromolecules* **2000**, *33*, 3855.

(18) Ishizone, T.; Tajima, H.; Torimae, H.; Nakahama, S. *Macromol. Chem. Phys.* **2002**, *202*, 2375.

(19) Kobayashi, S.; Matsuzawa, T.; Matsuoka, S.; Tajima, H.; Ishizone, T. *Macromolecules* **2006**, *39*, 5979.

(20) Kobayashi, S.; Kataoka, H.; Ishizone, T. *Macromolecules* **2009**, *42*, 5017.

(21) Kobayashi, S.; Kataoka, H.; Ishizone, T. *J. Phys.: Conf. Ser.* **2009**, *184*, 012017.

(22) Kobayashi, S.; Kataoka, H.; Ishizone, T.; Kato, T.; Ono, T.; Kobukata, S.; Ogi, H. *Macromolecules* **2008**, *41*, 5502.

(23) Ishizone, T.; Sugiyama, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1993**, *26*, 3009.

(24) Allen, R. D.; Long, T. E.; McGrath, J. E. *Polym. Bull.* **1986**, *15*, 127.

(25) Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1993**, *26*, 6964.

(26) Giebeler, E.; Stadler, R. *Macromol. Chem. Phys.* **1997**, *198*, 3815.

(27) Ludwig, S.; Böker, A.; Voronov, A.; Rehse, N.; Magerle, R.; Krausch, G. *Nat. Mater.* **2003**, *2*, 744.

(28) Schacher, F.; Walther, A.; Ruppel, M.; Drechsler, M.; Müller, A. H. E. *Macromolecules* **2009**, *42*, 3540.

(29) Hashimoto, T.; Makino, Y.; Urushisaki, M.; Sakaguchi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1629.

DOI: 10.1021/acs.macromol.5b02075
Macromolecules XXXX, XXX, XXX−XXX