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Synthesis of Polystyrene Having an Aminoxy Terminal by the Reactions of Living Polystyrene with an Oxoaminium Salt and with the Corresponding Nitroxyl Radical

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ABSTRACT: In order to introduce the C–O–N linkage at the polymer chain end, the reactions of poly(styryllithium) with 1-oxo-4-methoxy-2,2,6,6-tetramethylpiperidinium salt (OAS) and with the corresponding nitroxyl radical (MTEMPO) were investigated in THF at −78 °C. The aminoxy terminal was found to be introduced in quantitative efficiency by the reactions of the living polymer with OAS in the presence of MTEMPO. It is considered that the reactions proceed *via* one-electron transfer from the polystyryl anion to OAS, resulting in the polymer radical, which is coupled with MTEMPO to yield the polystyrene with an aminoxy terminal. Similarly, the electron-transfer reaction proceeded between the poly(styryllithium) and MTEMPO to yield the aminoxy-terminated polystyrene quantitatively. The resulting polystyrene could initiate the radical polymerizations of methyl, ethyl, and butyl acrylates to afford the corresponding block copolymers.

Introduction

Great interest has been devoted to end-functional polymers as prepolymers for the syntheses of block and graft copolymers, polymer networks, and chain-extended high polymers.[1] A number of publications have been reported on functionalization of terminal groups of vinyl polymers by free-radical and anionic polymerizations. Although the free-radical method suffers broad molecular weight distribution and side reactions resulting in a nonfunctionalized terminal, anionic living polymerization is an excellent method for the syntheses of polymers with predictable molecular weights, very narrow molecular weight distributions, and quantitatively functionalized terminals. Conventional routes to carboxy- and hydroxy-terminated polystyrenes and polyisoprenes were established in the 1960s by the reaction of anionic living polymers with carbon dioxide[2] and ethylene oxide,[3] respectively, and have still been investigated for the precise syntheses of the telechelics.[4,5] Recently, we have developed a new procedure for the preparation of polystyrene and polyisoprene having primary amino moieties at the chain ends by the reaction of respective living polymers and α-halo-ω-aminoalkanes with a protected amino functionality.[6] Carboxy-terminated polystyrene has also been synthesized in a similar manner.[7]

In recent years, much attention is being paid to the polymer having a C–O–N linkage at the chain end since homolytic cleavage of the C–O bond of the terminal is caused by heating to generate the polymer radical. Rizzardo *et al.* reported that radical polymerization of methyl acrylate initiated with highly hindered alkoxyamine produced the poly(methyl acrylate) with an aminoxy terminal.[8] Similarly, Georges mentioned that the radical polymerization of styrene with BPO in the presence of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) gave the polystyrene terminated with aminoxy group.[9] Such polymers with aminoxy terminals are capable of initiating radical polymerization to afford block copolymers. Although cationic polymerization of isobutyl vinyl ether was initiated with oxoaminium salts to yield the poly(isobutyl vinyl ether) with an aminoxy moiety at the head group, the resulting polymer was unable to initiate the radical polymerization probably due to the primary carbon attached to the O–N< residue.[10]

A sterically hindered oxoaminium salt, 1-oxo-2,2,6,6-tetramethylpiperidinium salt (OAS), arises by the revers-

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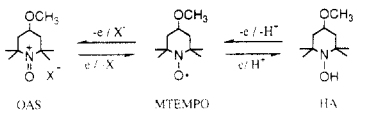
Scheme 1



ible redox system including 4-methoxy-2,2,6,6-tetramethylpiperidin-1-oxyl (MTEMPO) and hydroxylamine as shown in Scheme 1. OAS and MTEMPO (or TEMPO) were reported to cause an electron-transfer reaction with several carbanions and carbocations to form the corresponding radicals, which may be coupled with MTEMPO to form the C–O–N linkage. Benzylmagnesium bromide reacted with OAS to give the benzoyloxyamine *via* a coupling reaction between the resulting benzyl radical and MTEMPO.[11] Similarly, the reaction of *n*-butyllithium with TEMPO proceeded *via* electron transfer from the butyl anion to TEMPO to result in the butoxyamine.[12] Futhermore, the electron transfer from TEMPO to triphenylmethyl perchlorate occurred to afford a triphenylmethyl radical, which was not coupled with TEMPO on account of the steric hindrance.[13]

In this study, it is found that OAS and MTEMPO can be used as end-capping agents of anionic living polystyrene through the electron-transfer and radical coupling reactions, to afford the corresponding polymers containing C–O–N linkages at the chain end groups. The polymers with the C–O–N terminal are expected to give polymeric radicals upon heating, which would lead to block copolymers by radical polymerization.

Experimental Section

Measurement. The infrared spectra were recorded with a JEOL AQS-20M spectrophotometer. ^{1}H NMR spectra were obtained with a JEOL FX-90Q NMR spectrometer. Gel permeation chromatography (GPC) was performed with a Tosoh HLC 8020 instrument (eluent, THF, 40 °C, 1.0 mL/min; columns, polystyrene gels ($G4000H_{XL}$, $G3000H_{XL}$, and $G2000H_{XL}$); calibration, polystyrene standards). The instrument for the thin layer chromatography (TLC)/flame ionization detection (FID) method was an Iatron thinchrograph, Model TH-10 (Iatron Co., Ltd., Tokyo, Japan).[6]

Materials. Styrene was distilled twice over calcium hydride under reduced pressure and was distilled from the THF solution of benzylmagnesium chloride on a vacuum line into ampules fitted with break-seals. Purified styrene in THF was stored at −30 °C until used. Commercially available *sec*-butyllithium was used without purification as received. THF was refluxed over sodium for several hours and distilled from the sodium naphthalenide solution. Heptane was washed with concentrated H_2SO_4, 1 M NaOH, and water successively and dried over $CaCl_2$. It was refluxed over calcium hydride for 10 h and distilled from a 1,1-diphenylhexyllithium solution. 1-Oxo-4-methoxy-2,2,6,6-tetramethylpiperidinium hexafluoroantimonate (OAS, X = SbF_6)[10] and 4-methoxy-2,2,6,6-tetramethylpiperidin-1-oxyl (MTEMPO)[14] were prepared using previously reported methods. MTEMPO was distilled over calcium hydride on a vacuum line into ampules fitted with break-seals. OAS was placed in an ampule fitted with break-seals and dried on a vacuum line for several hours.

Reactions of Living Polystyrene with OAS (X = SbF_6) and with MTEMPO. The reactions were carried out under high-vacuum conditions (10^{-6} mmHg) in sealed glass reactors with break-seals. Prior to reaction, reactors were always prewashed with the 1,1-diphenylhexyllithium solution after being sealed off from the vacuum line. Anionic polymerization of styrene (19.6 mmol, 0.919 M THF solution) initiated with *sec*-butyllithium (0.791 mmol, 0.162 M heptane solution) was carried out in THF at −78 °C for 5 min. Aliquots of the reaction mixture were withdrawn and quenched for the characterization of the prepolymer. The remaining poly(styryllithium) in THF was added to a suspension of OAS (313 mg, 0.741 mmol) in THF (6 mL) at −78 °C. The mixture was kept at −78 °C for 15 h and then quenched with methanol. The product was purified by repeated precipitations from THF to methanol and lyophilized with benzene. The other reactions of poly(styryllithium) with OAS in the presence of MTEMPO, with MTEMPO in the presence of LiCl, *etc*, were carried out in similar manners.

Transmetalation of the propagating end was performed by addition of magnesium dibromide (1.40 mmol, 0.248 M THF solution) to the poly(styryllithium) solution (obtained from *sec*-BuLi, 0.236 mmol, and styrene, 8.48 mmol) at −78 °C for 10 min. The resulting solution was added to a suspension of OAS (179 mg, 0.424 mmol) in THF (6.0 mL) at −78 °C. The mixture was kept at −78 °C for 15 h. Isolation and purification of the product were achieved similarly to the case of the reaction product from poly(styryllithium).

Radical Polymerization Initiated by the Polystyrene with an Aminoxy Terminal. A mixture of ethyl acrylate (2.77 g, 27.6 mmol) and the polystyrene with an aminoxy terminal (100 mg, 0.0316 mmol; M_n = 3200) in benzene (3 mL) was placed in an ampule. After degassing the contents, the ampule was sealed *in vacuo*. The mixture was heated at 120 °C for 6 h and cooled with dry ice/methanol to terminate the polymerization. The mixture was evaporated under reduced pressure to remove the residual monomer and benzene. The residue was lyophilized with benzene to obtain the product (1.93 g).

Results and Discussion

Reaction of Living Poly(styryllithium) with OAS. Anionic living polystyrene was prepared with *sec*-butyllithium in THF at −78 °C. When the THF solution of the living polystyrene was added to a yellow suspension of OAS (1.0 equiv; X = SbF_6) in THF at −78 °C (Scheme 2), the color of the living polystyrene disappeared. After complete addition, a red color was slightly observed probably due to MTEMPO formed by the one-electron transfer from the living end to OAS. This phenomenon is described later (Scheme 3, path a). Aliquots of the living polystyrene were withdrawn prior to the reaction with OAS and were quenched separately. The molecular weights of the resulting prepolymers were determined by GPC using a calibration with standard polystyrenes. The values of the molecular weights were close to the calculated ones from the ratio of monomer to initiator in the feed, and the molecular weight distributions were very narrow. In the ^{1}H NMR spectrum of the polymer, the broad signal at 0.4–0.8 ppm was assigned to methyl protons of the *sec*-butyl group of the initiator fragment at the chain end and peaks at 1.2–2.5 and 6.2–7.3 ppm were due to methylene and methine protons of the main chain and aromatic protons, respectively. Based on the molecular weight of the polymer and the intensity ratio of methyl (*sec*-butyl group) and aromatic proton signals, it is confirmed that the initiator fragment is quantitatively attached to the polymer chain end.

After the reaction mixture had been kept at −78 °C for 15 h, it was quenched with methanol. The polymer was isolated and purified by repeated precipitation from the THF solution to methanol to obtain a white powder in quantitative yield (96%; Table 1, expt no. 1). The ^{1}H NMR spectrum of the polystyrene obtained is shown in Figure 1. Besides the proton signals of the polymer main chain and those of the initiator fragment (a), two singlet signals at 0.95 and 1.05 ppm (b) and a signal at 3.25 ppm (c) were observed. These are assigned to methyl (b) and methoxy (c) protons of the OAS moiety attached to the other polymer chain end from comparison with the ^{1}H NMR spectrum of the authentic compound.[11] Therefore, the degree of introduction of the aminoxy group could be estimated from the intensity ratio of the methoxy protons at the chain end (c) to the methyl protons of the *sec*-butyl chain head group (a) to be 57% (Table 1, expt no. 1).

Table 1. Reactions of Living Poly(styryllithium) with OAS (X = SbF_6) and MTEMPO

	prepolymer[a]			substrate, equiv			DI,[b] %		product[a]	
expt no.	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	additive (equiv)	OAS	MTEMPO	isolated yield, %	^{1}H NMR	TLC/FID	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
1	2900	1.11		1.0		96	57	72	3500	1.19
2	2700	1.11	LiCl (1.5)	1.3		83	57	76	3000	1.14
3	2400	1.13		1.5	9.3	80	86	94	2800	1.13
4	3300	1.08	LiCl (1.9)	1.2	9.0	98	100	98	3500	1.07
5	2800	1.09			1.1	100	47	49	3100	1.13
6	3200	1.09			17.0	72	101	99	3600	1.11
7	3000	1.21	$MgBr_2$ (3.4)	1.4		88	94	95	3400	1.21
8	2900	1.10	$MgBr_2$ (3.2)		7.4	88	100	100	3200	1.10

[a] Estimated by GPC based on PSt standards. [b] Degree of introduction of the aminoxy moiety in the polymer end.

Scheme 2

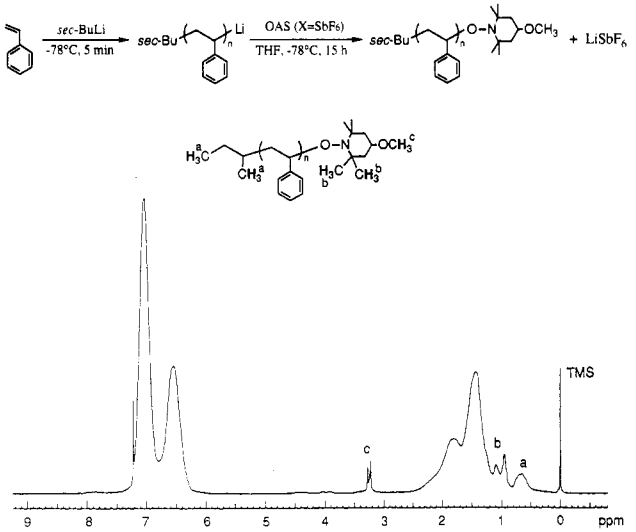


Figure 1. ^{1}H NMR spectrum of the product obtained by the reaction of poly(styryllithium) with OAS. The conditions and results are shown in Table 1, expt no. 1.

As shown in parts a and b of Figure 2, the polystyrene isolated from the reaction mixture showed a bimodal GPC in contrast to a sharp uniomdal curve of the prepolymer. The main peak of the bimodal GPC was almost identical to that of the prepolymer ($\bar{M}_n$ = 2900), while a shoulder was discerned at the higher molecular weight side. The molecular weight of the polymer in the shoulder was estimated to be 5600, corresponding to almost twice that of the main peak. This suggests that a coupling product between polystyryl radicals (PSt–PSt) is generated *via* an electron-transfer mechanism as follows (Scheme 3, path a).

The same polymer product was subjected to a silica gel based thin layer chromatogram (TLC) developed with a benzene/cyclohexane (2/1, v/v) mixture to show the two apparent spots at R_f values 0.20 (A) and 0.63 (B) (Figure 3). These two portions could be preparatively separated by flash column chromatography. Polymer A corresponding to the lower spot on the TLC showed a unimodal GPC curve ($\bar{M}_n$ = 3100, $\bar{M}_w/\bar{M}_n$ = 1.11), which is almost the same as that of the prepolymer (Figure 2a,c). From the ^{1}H NMR spectrum, the aminoxy moiety was found to be quantiatively present in polymer A, designated as PSt–ON<. The elemental analysis data of polymer A also agreed well with those calculated by assuming quantitative introduction of the aminoxy group to the chain end (Table 2).

The other polystyrene (B) of the upper spot (R_f = 0.63) isolated by flash column chromatography was found to contain no nitrogen at all by the elemental analysis, and the NMR signals at 0.95, 1.05, and 3.25 ppm attributable to the OAS moiety were not observed in the ^{1}H NMR

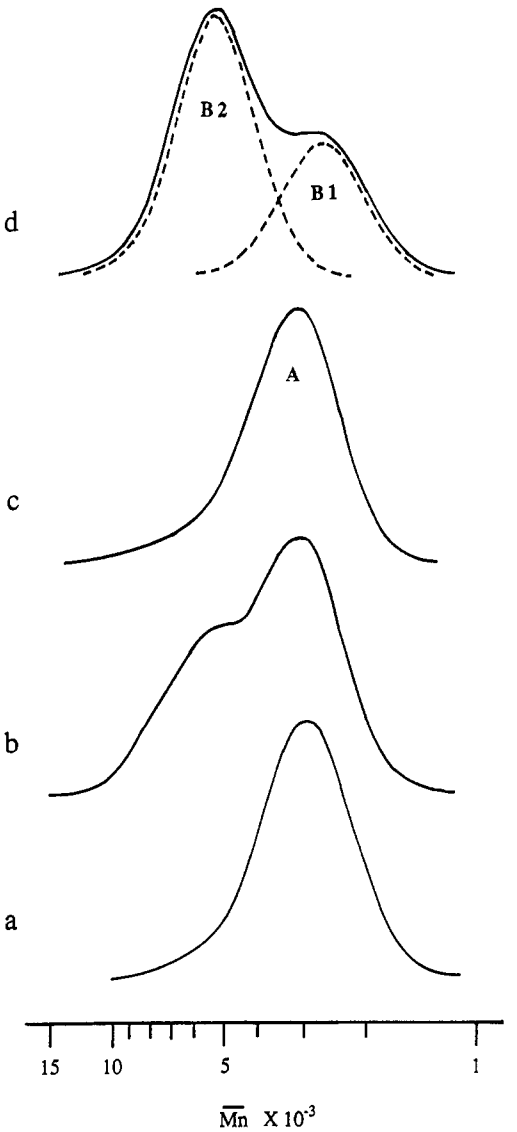


Figure 2. GPC profiles of the polystyrenes obtained before (a) and after (b) the reaction and the separated polystyrenes with an aminoxy terminal (c) and without an aminoxy group (d). The conditions and results are shown in Table 1, expt no. 1., and in Figure 3.

spectrum. Futhermore, the R_f value (0.63) of the polymer B was the same as that of the prepolymer. These results indicate that polymer B is a homopolymer of styrene without an aminoxy group. The GPC profile of polymer B is shown in Figure 2d. As can be seen, the GPC consists of two peaks, the lower molecular weight one (B1) is almost the same as that of polymer A and the higher one (B2) corresponds to doubling of the molecular weight ($\bar{M}_n$ = 5600). It is suggested that polystyrene B2 is produced by a coupling reaction of polymer radicals formed *via* one-electron transfer from the propagating carbanion to OAS

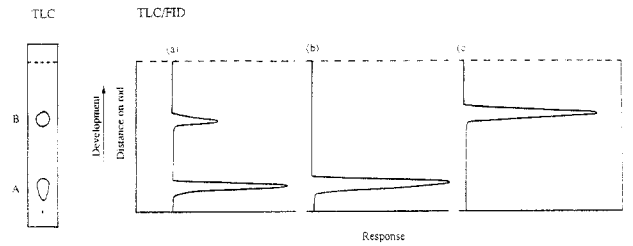


Figure 3. Thin layer chromatogram (TLC; benzene/cyclohexane, 2/1) of the reaction product (expt no. 1), TLC/FID (benzene/cyclohexane, 2/1) of the reaction product (expt no. 1) (a), and the separated polystyrenes with an aminoxy terminal (b; R_f = 0.20) and without an aminoxy terminal (c; R_f = 0.63).

Scheme 3

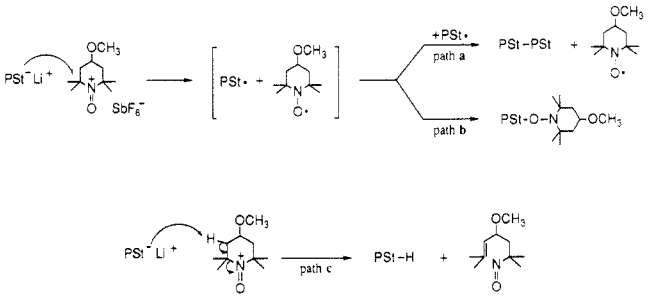


Table 2. Elemental Analysis (%) of the Separated Polystyrenes

	polymer A		polymer B	
	calcd	found	calcd	found
H	8.08	7.98	7.91	7.88
C	90.41	90.23	92.09	91.80
N	0.46	0.42	0.00	0.00

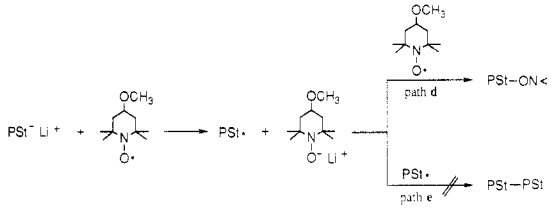
as mentioned above (Scheme 3, path a). The polystyrene B1 may be generated by β-elimination on OAS[15] (Scheme 3, path c) but not by disproportionation of polystyryl radicals, because polystyryl radicals were confirmed to undergo exclusively recombination in the termination reaction of radical polymerization using a ^{14}C-labeled initiator.[16,17] The ratio of the coupled polystyrene (B2) to the proton-terminated polystyrene (B1) (PSt–H) could be estimated to be 65:35 from the weight ratio of the respective peak areas of the GPC.

The polymer product isolated from the reaction mixture was again subjected to TLC-FID, which was capable of quantitative analysis with high accuracy by flame ionization detector.[6] From the peak area in the TLC/FID shown in Figure 3a, the degree of introduction of the aminoxy moiety into the polymer was estimated to be 72%. This value is more reliable than that estimated by ^{1}H NMR. Based on this value and on the ratio of the two types of homopolymers described above, the relative molar amounts of the three polystyrenes were calculated to be PSt–ON<: PSt–PSt:PSt–H = 72:18:10 (weight ratio).

Teyssie *et al.* reported that poly(styryllithium) modified with LiCl could initiate anionic polymerization of *tert*-butyl acrylate to result in a block copolymer with a narrow molecular weight distribution.[18] Accordingly, it was anticipated that the reactivity of poly(styryllithium) might be modified with LiCl to enhance the efficiency of reaction with aminoxy groups. No improvement, however, was achieved in the experiment in the presence of LiCl (Table 1, expt no. 2).

When the living polymer is allowed to react with OAS in the presence of MTEMPO, the coupling reaction of a polystyryl radical with MTEMPO (Scheme 3, path b) can be promoted and that of the polystyryl radicals with each other (path a) may be correlatively suppressed. As expected, reaction in the presence of MTEMPO led to almost quantitative introduction of an aminoxy moiety to the polymer terminal, which was confirmed by both ^{1}H NMR and TLC/FID measurements (Table 1, expt no. 3). Furthermore, the most satisfactory result was obtained by reaction in the presence of MTEMPO and LiCl (Table 1, expt no. 4).

Scheme 4



Reaction of Poly(styryllithium) with MTEMPO. Previously, Whitesides reported that *n*-butyllithium reacted with nitroxyl radical to afford the corresponding butoxyamine with some byproducts.[12] The reaction was considered to proceed *via* a one-electron transfer from butyllithium to the nitroxyl radical, resulting in the butyl radical, which coupled with another nitroxyl to produce the butoxyamine. Similarly, poly(styryllithium) was allowed to react with 1 equiv of MTEMPO. The characteristic color of the living polymer remained even after completion of the reaction, suggesting that not all the living polymer had been involved in the electron-transfer reaction with MTEMPO. Analyses of the reaction products by GPC, ^{1}H NMR, and TLC/FID measurements revealed that about 50% of the polystyrene had the aminoxy end group (Table 1, expt no. 5). The other polystyrene without the aminoxy terminal possessed the same molecular weight and molecular weight distribution as those of the prepolymer. In addition, no coupling product, PSt–PSt, with double molecular weight was detected by GPC (Scheme 4, path e). This indicates that the polystyryl radical generated preferably reacted with MTEMPO before MTEMPO was consumed by the electron-transfer reaction (Scheme 4, path d). When the reaction of poly(styryllithium) was performed with a large excess of MTEMPO, the polystyrene with an aminoxy terminal was obtained in quantitative yield (Table 1, expt no. 6). These results can be explained from the oxidation and reduction potentials of MTEMPO.[19] The values of the oxidation–reduction potential between MTEMPO and HA and those of OAS and MTEMPO are −1.28 and 0.57 V vs SCE, respectively, suggesting that electron transfer from the polystyryl anion to MTEMPO is slower than that to OAS. In the former case, the concentration of the polystyryl radical should be extremely low during the reaction because the rate constant of the electron transfer is much smaller than that of the coupling reaction of the polystyryl radical with MTEMPO. As a result, the amount of the coupled product, PSt–PSt, became negligible. On the contrary, the rate constant of electron transfer from the polystyryl anion to OAS is relatively large (as compared to that to MTEMPO) because of the higher redox potential, as mentioned above. Hence, the concentration of the polystyryl radicals produced may be high, especially in the reaction of poly(styryllithium) with OAS without addition of MTEMPO (expt no. 1). Thus, the coupling according to path a took place competitively, to give polystyrene, PSt–PSt, with twice the molecular weight of the prepolymer.

Reactions of Poly(styrylmagnesium bromide) with OAS and with MTEMPO. The reactions of OAS with

$(PhCH_2)_2Hg$,[20] $PhCH_2SnMe_3$,[20] and $PhCH_2MgBr$[11,21] have also been proposed as efficient routes to benzyloxyamines. In all cases, it is considered that these reactions proceed *via* radical intermediates, by electron transfer, similarly to the reaction of butyllithium with OAS. To examine an alternate way for the effective synthesis of polystyrene with an aminoxy terminal, poly(styryllithium) was transformed into poly(styrylmagnesium bromide), which was allowed to react with OAS. It was found that the aminoxy moiety was very effectively introduced to the polymer chain end, even with a small excess amount of OAS (Table 2, expt no. 7). Transmetalation at the propagating end may have lowered the basicity to suppress the side reaction of β-elimination (Scheme 3, path c). In addition, the formation of the coupling product, PSt–PSt (path a), was also depressed, although the exact reason for this is not clear yet. Finally, the reaction of poly(styrylmagnesium bromide) with a large excess of MTEMPO was performed, in order to obtain the quantitative introduction of the aminoxy moiety to the polystyrene chain end (Table 1, expt no. 8).

Aminoxy-terminated polymers were also obtained by cationic polymerization of vinyl ethers with OAS[10] and by radical polymerization of styrene in the presence of MTEMPO.[9] Although the poly(isobutyl vinyl ether) obtained with OAS was confirmed to have an aminoxy moiety at the chain head group, no block copolymer was produced upon heating the polymer with methyl methacrylate. This may be due to thermal stability of the C–O bond of the aminoxy residue attached to a primary carbon at the head group of poly(isobutyl vinyl ether), as compared to that linked to a secondary or tertiary carbon, such as benzyloxyamine. On the other hand, the aminoxy group was quantitatively introduced to the polymer chain end by the reactions of OAS or MTEMPO with poly(styryllithium) having a predictable molecular weight and a very narrow molecular weight distribution. The aminoxy terminal of the polystyrene possibly causes the homolytic scission at the C–O bond of the aminoxy moiety upon heating, due to the relatively stable benzyl radicals produced.

Radical Polymerization Initiated by the Polystyrene Having an Aminoxy Moiety at the End Group. Several investigations on the transformation of living anionic to free-radical polymerization have been performed by modification of the anionic propagating end. Richards reported that reaction of the anionic living polystyrene with triethyllead chloride[22] or with bromine[23] led to the free-radical species. More recently, Hazer and his coworkers[24] described that the peroxide-capped polystyrene was prepared by the reaction of anionic living polystyrene with 4,4′-bis(bromomethyl)benzoyl peroxide. In this study the poly(styryllithium) was transformed into an alkoxyamino-terminated polystyrene, which could be used as an iniferter in living free-radical polymerization.[8] To confirm this possibility, radical polymerizations of methyl acrylate (MA), ethyl acrylate (EA), and *n*-butyl acrylate (BA) were carried out with PSt–ON< (expt no. 8) as an initiator in benzene at 120 °C for 6 h. The conversions of these acrylate monomers to polymer were 15% (MA), 67% (EA), and 20% (BA). The results are shown in Table 3. The GPC curves of the obtained polymers detected by UV absorption at 254 nm were similar to those detected from refractive index detection, suggesting that the products were mostly block copolymers of styrene and the acrylates and contained only small amounts, if any, of homopolymers of the acrylates generated by chain-transfer and thermal polymerization. Figure 4 illustrates the typical GPC profile of the product obtained upon polymerization of

Table 3. Radical Polymerization of Acrylates Initiated by the Polystyrene with an Aminoxy Terminal[a]

monomer	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	initiation efficiency,[c] %
MA	14 000	1.75	93
EA	55 000	1.33	96
BA	15 000	1.96	92

[a] Polystyrene used as an initiator (Table 1, expt no. 8, $\bar{M}_n$ = 3200, $\bar{M}_w/\bar{M}_n$ = 1.10), in benzene at 120 °C for 6 h. [b] Estimated by GPC based on PSt standards. [c] Estimated from respective area % of aminoxy-terminated polystyrenes and their block copolymers in GPC.

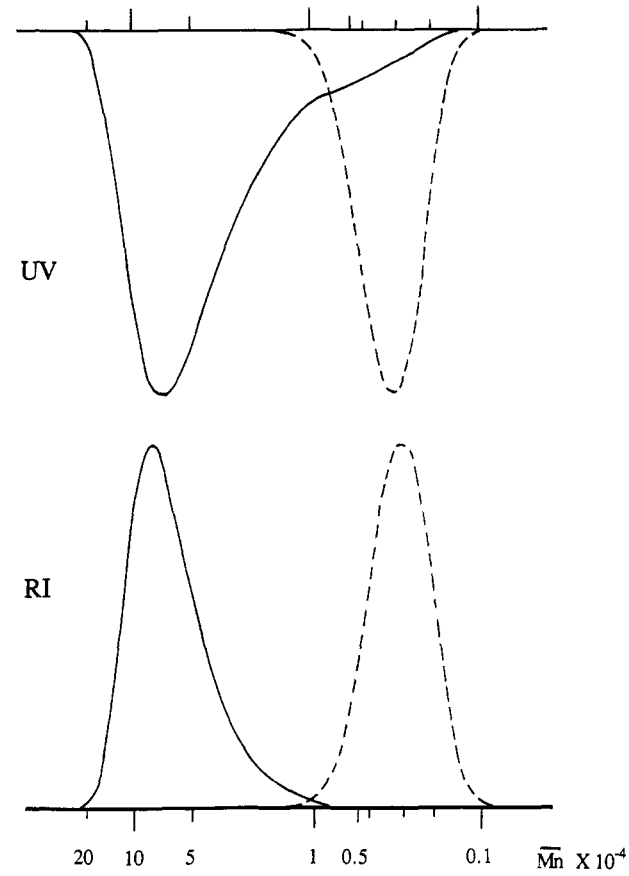
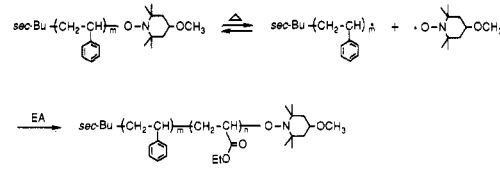


Figure 4. GPC profiles of poly(St-*b*-EA) (Table 3, EA; solid line) and PSt–ON< as an initiator (broken line).

Scheme 5



EA. Only a small part of unreacted PSt–ON< appears as a shoulder in the UV–GPC curve at the same molecular weight region of the prepolymer. The initiation efficiency was estimated from the area ratio of the UV–GPC to be 96%. In addition, polymerization of EA initiated by the polystyrene without aminoxy terminals was carried out under similar conditions. No peak was observed except for that of the starting polystyrene in UV–GPC of the product, although some amount of ethyl acrylate homopolymer formed by thermal polymerization was detected in the RI–GPC. It can be assumed that the thermal homolytic scission of the C–O bond of the aminoxy moiety caused the radical polymerization to afford poly(styrene-*b*-EA). This scission was suggested to be reversible, owing to the fact that the radical polymerization of EA initiated by PSt–ON< did not proceed in the presence of 3 equiv of MTEMPO (Scheme 5).

It is found that OAS and MTEMPO can be regarded as site-transforming agents from living anionic to living free-radical polymerization, and the aminoxy-terminated polystyrene functions as a polymeric initiator of radical polymerization.

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