Anionic Polymerization of Secondary Aminostyrene and Characterization of the Polymer

KAZUNORI SE,[1] SHINICHI KUDOH[2]

[1]Department of Materials Science and Engineering, Faculty of Engineering, Fukui University, Bunkyo 3-9-1, Fukui 910-8507, Japan

[2]Department of Chemistry, Faculty of Engineering, Nagaoka University of Technology, Kamitomioka 1603-1, Nagaoka, Niigata 940-21, Japan

ABSTRACT: Preparation by anionic living technique and characterization of poly(secondary aminostyrene) having narrow molecular weight distribution were investigated. *N*-isopropyl-*N*-trimethylsilyl-4-vinylbenzylamine (SBA) was purified by use of *sec*-butylmagnesium bromide as a purging reagent under high vacuum. SBA was anionically polymerized with *n*-butyllithium or cumylpotassium in tetrahydrofuran at $-78°C$ under high vacuum to yield the corresponding polymer (PSBA) in 100% yield. Subsequent deprotection of the trimethylsilyl group from PSBA produced poly(*N*-isopropyl-4-vinylbenzylamine) (PBA) of the desired molecular weights (M_n: 1.3×10^4–17×10^4, determined by membrane osmometry) with narrow molecular weight distribution (M_w/M_n: 1.07–1.03, determined by gel permeation chromatography). The living lithium carbanion of PSBA can initiate styrene (St) to yield PSBA-*b*-PSt block copolymer ($M_n = 4.0 \times 10^4$, $M_w/M_n = 1.05$), and the polystyryllithium can initiate SBA to yield PSt-*b*-PSBA ($M_n = 3.7 \times 10^4$, $M_w/M_n = 1.25$). The deprotection of the trimethylsilyl group from the two block copolymers produced new block copolymers containing poly(secondary aminostyrene) block. Anionic reactivity of SBA and basic properties of PSBA are discussed in terms of the ^{13}C chemical shift of β-carbon in the vinyl group of SBA and steric effect. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2039–2048, 1999

Key words: anionic polymerization; secondary aminostyrene; poly(*N*-isopropyl-*N*-trimethylsilyl-4-vinylbenzylamine); poly(*n*-isopropyl-4-vinylbenzylamine); deprotection

INTRODUCTION

As shown in Figure 1, poly(aminostyrene)s have amino groups classified as primary, secondary, and tertiary amino groups. Each of these three amino groups is also classified as phenyl-, benzyl-, or phenethylamine. These poly(aminostyrene)s[1,2] provide an interesting example of a stable inter-mediate of final polymers[3] and a high-performance polymer.[4] For these purposes, the polymers should be prepared by anionic living mechanisms so as to have desired molecular weights and narrow molecular weight distribution (MWD).

Anionic polymerization of three tertiary aminostyrenes—*N*,*N*-dimethyl-4-vinylphenylamine, *N*,*N*-dimethyl-4-vinylbenzylamine, and *N*,*N*-dimethyl-4-vinylphenethylamine with cumylpotassium or cumylcesium in tetrahydrofuran (THF) at $-78°C$ under high vacuum—was investigated by the present authors.[5] From the Men-

Figure 1 Molecular structure of poly(aminostyrene)s, which have amino groups classified as primary (R_1 = H, R_2 = H), secondary (R_1 = H, R_2 = an alkyl group), and tertiary (R_1 = an alkyl group, R_2 = an alkyl group) groups. Each of these three amino groups is also classified as phenylamine (m = 0), benzylamine (m = 1), and phenethylamine (m = 2).

schutkin reactivity[6] of these three poly(tertiary aminostyrene)s, the electron density on the nitrogen atom was found to decrease in the sequence: phenethyl-, benzyl-, and phenylamine.[7] These poly(tertiary aminostyrene)s were used as prepolymer of crosslinked polymers,[8] charge-mosaic membranes,[9] and photochemical recording material.[8]

On the other hand, primary and secondary aminostyrenes could not be polymerized by anionic living mechanisms due to deactivation of the initiators by the labile proton of the amino groups. Thus, to regenerate the original amino groups, the amino groups should be protected during a process of anionic polymerization, and the protective group can be readily and completely removed after the polymerization. For preparing a poly(primary and phenyl aminostyrene), anionic polymerization of *p-N,N-bis*(trimethylsilyl)aminostyrene with lithium naphthalide in THF was conducted at −78°C by Nakahama and colleagues.[10,11] After complete deprotection of the silyl protecting groups, poly(phenylamine) having narrow MWD was prepared. This polymer seems unsuitable for backbone chains of graft copolymers and for introducing other functions,[12] because the polymer has two labile protons on the same nitrogen atoms of the primary aminostyrene and lower basic property of phenylamine,

compared with benzylamine and phenethylamine.

These results enabled the preparation of poly-(secondary aminostyrene) with benzylamine, for employment as a stable intermediate of final polymers, such as backbone chains of graft copolymers.[3,13,14] First, *N*-isopropyl-*N*-trimethylsilyl-4-vinylbenzylamine (SBA), shown in Figure 2 was synthesized. Anionic polymerization of SBA was conducted in detail to yield the corresponding polymer (PSBA). Subsequent deprotection of the trimethylsilyl group from PSBA produces poly-(*N*-isopropyl-4-vinylbenzylamine) (PBA) having desired molecular weight and narrow MWD. To elucidate anionic reactivity of SBA and prepare well-defined diblock copolymers having a PBA block in the present study, diblock copolymerization of SBA and styrene was conducted.

EXPERIMENTAL

Secondary Aminostyrenes

Secondary aminostyrenes are classified as phenylamine, benzylamine, or phenetylamine. To synthesize secondary phenylamines, two synthetic approaches were proposed and tested. The first approach is as follows: ethylbromide was added to 4-vinylphenylamine to produce *N*-ethyl-4-vinylphenylamine. The resultant products contained three aminostyrenes of primary (reactant), secondary (product), and tertiary aminostyrenes (byproduct). *N*-ethyl-4-vinylphenylamine was produced in <5% yield. The second approach is as

Figure 2 Molecular structure of SBA.

follows: 4-vinylphenylamine was reacted for 2 h with trimethylsilyl chloride under a presence of excess hexamethyldisilazane at a reflux temperature. N-trimethylsilyl-4-vinylpenylamine was produced in 85% yield. Two equivalents of ethylmagnesium bromide were added to the monosilylated 4-vinylphenylamine in THF at room temperature and allowed to react for 2 h. Then, 4 equivalents of ethylbromide were added to the solution at room temperature and allowed to react overnight to produce N-ethyl-N-trimethylsilyl-4-vinylphenylamine. However, the final product could not be synthesized in >2% yield.

An attempt was made to synthesize secondary phenethylamine: isopropylamine was added to 4-vinyl-phenethyl chloride to produce N-isopropyl-4-vinylphenethylamine. However, the final product could not be synthesized in >2% yield. These three synthetic approaches were found to be unusable for preparation of the secondary aminostyrene. Therefore, in the present experiment, SBA was synthesized.

SBA Monomer

SBA was synthesized as follows: p-chlorostyrene (200 g) was reacted with magnesium turning (35 g) in THF (700 mL) to yield a Grignard reagent. N,N-Dimethylformamide (105 g) was added to the Grignard reagent at room temperature and allowed to react for 10 h. Following hydrolysis of the product, p-formylstyrene was prepared in 70% (130 g) yield; b.p., 60°C/1 mm Hg. p-Formylstyrene (130 g) was reacted with isopropylamine (59 g) to yield N-isopropyl-4-vinylbenzylimine in 75% (112 g) yield; b.p., 68°C/1 mm Hg. The product (112 g) was reduced by $NaBH_3CN$ (43 g) in methanol (600 mL) to produce N-isopropyl-4-vinylbenzylamine (BA) in 65% (75 g) yield; b.p., 78°C/1 mm Hg. After THF (200 mL) solution of ethymagnesium bromide (113 g) was added to the THF (75 mL) solution of BA (75 g) and allowed to react for 2 h, the THF (200 mL) solution of trimethylsilylchloride (135 g) was carefully added to the resultant solution. The organic layer was separated from crystalline $MgBr_2$ with cyclohexane. After cyclohexane was evaporated from the solution, SBA was obtained by fractional distillation under reduced pressure in 48% (50 g) yield; b.p., 95°C/1 mm Hg. The molecular structure of SBA was confirmed by means of nuclear magnetic resonance (NMR): 270 MHz ^{1}H-NMR ($CDCl_3$) δ 0.17 [9H, s, $(CH_3)_3Si$], 1.10–1.11 [6H, d, $C(CH_3)_2$], 3.13–3.46

(1H, m, N—CH), 3.73–4.21 (2H, t, CH_2—N), 5.12–5.83 (2H, m, CH_2=C), 6.50–7.00 (1H, m, C=CH), 7.11–7.54 (4H, m, C_6H_4).

Because the nitrogen—silicon bond of SBA was efficiently cleaved by water vapor under atmosphere or heating >250°C, purification of SBA was carefully conducted in vacuum. After drying SBA over calcium hydride, SBA was purified by two purging reagents of octylbenzophenone sodium $(C_8BP\text{-}Na)$[3,5,15] and sec-butylmagnesium bromide (BuMgBr). Styrene (St) was purchased and purified by the same procedure used in previous studies.[3,15,16]

Reagents

n-Butyllithium (n-BuLi) was purchased (Nakarai Chemicals Ltd., Kyoto, Japan) and diluted with purified n-heptane. Cumylpotassium (Cumyl K) was synthesized by reaction of cumylmethyl ether with sodium-potassium alloy in THF.[3,15,16] Concentrations of the initiators were determined by titration with standard hydrochloric acid. THF used for the polymerization was dried with sodium wire and distilled in vacuum with anthracene sodium anion. Finally, it was distilled over α-methylstyrene tetramer-sodium dianions.

Polymerization and Deprotection of the Trimethylsilyl Group

Polymerization was conducted in a sealed glass apparatus at −78°C at 10^{-5} torr. Diblock copolymerization of SBA and St was performed by sequential addition of two monomers. Anionic polymerization techniques are almost the same as those used in previous studies.[3,15,16]

Deprotection of the trimethylsilyl group from PSBA was conducted by standing the polymer in methanol at 40°C for 12 h. Then, the solution was poured into an excess of water. The polymer was recovered by filtration and washed with water.

Molecular Characterization

All polymer samples were tested on gel permeation chromatography (GPC; Model HLC-803, Tosoh Co., Tokyo, Japan) with two high-resolution columns of GMH6 and G4000H8 (7.8 mm i.d. × 60 cm; Tosoh Co.) using standard polystyrenes (TSK polystyrenes, Tosoh Co.) to estimate molecular weight heterogeneities (M_w/M_n values). To suppress adsorption of poly(aminostyrene)s having polar amino group onto the surface of the GPC

Table I   Effect of Purging Reagents on Anionic Polymerization of SBA

Purging Reagent	Monomer (mmol)	Initiator n-BuLi (mmol)	Solvent THF (mL)	Polymerization Time (h)	Yield (%)	$10^{-4} M_k$[a]	$10^{-4} M_n$[b]
C$_8$BP-Na[c]	14	0.10	110	24	0	3.5	
BuMgBr	6.0	0.11	70	24	0	1.3	
BuMgBr/THF/once[d]	11	0.22	150	1	Trace	1.2	4.0
BuMgBr/THF/twice[d]	6.2	0.18	110	3	17	0.85	3.8
BuMgBr/THF/thrice[d]	17	0.066	70	24	100	6.4	6.0

[a] Molecular weights calculated from the amounts of monomer and initiator.
[b] Number-average molecular weights determined from the GPC measurements.
[c] Octylbenzophenone sodium.
[d] THF solution of SBA was dried over BuMgBr once, twice, or thrice.

gels, a mixture of THF and N-methylpyrrolidine (2 v/v %)[5,7] was used as carrier solvent. Number-average molecular weights (M_n) of the samples were determined by osmometry in toluene at 30°C using a Hewlett-Packard Type-502 high-speed membrane osmometer. ^{1}H-NMR spectra were measured in CDCl$_3$ at room temperature using with JNM-GX270, Fourier transform-NMR spectrometer (JEOL Ltd., Cranford, NJ). Infrared spectrum was recorded on a JASCO IRA-102 spectrophotometer (Japan Spectroscopic Co., Ltd., Tokyo, Japan).

RESULTS

Purification of SBA

SBA monomer was distilled twice at 95°C/1 mm Hg. Subsequent purification of SBA was conducted at 10^{-5} torr in an all-glass apparatus equipped with breakseals. After being dried with calcium hydride at room temperature for 15 h, SBA was distilled into ampoules fitted with breakseals. To remove further impurities in SBA monomer, octylbenzophenone sodium (C$_8$BP-Na)[3,5,15] as a purging reagent was added to SBA at 0°C. The mixture was stirred for 15 min and then distilled into an ampoule. After being dried over C$_8$BP-Na twice, SBA was diluted with carefully purified THF. When the THF solution of SBA was added to THF solution of n-BuLi at −78°C, the solution momentarily showed a characteristic yellow color, then immediately became colorless. No polymer could be obtained.

After this purification, SBA was dried over BuMgBr as a purging reagent. Thus, purified SBA could not be polymerized by n-BuLi. Gas

chromatograms of SBA distilled over C$_8$BP-Na and BuMgBr show a tiny peak at the lower boiling point side of the main peak. On comparison of these chromatograms with a gas chromatogram of BA, the tiny peak was identified as BA having no trimethylsilyl protective group. These results suggest that the anionic initiator was deactivated by BA, which was a preproduct of SBA.

BuMgBr was not sufficiently soluble in SBA. Hence, the THF solution of SBA was dried over BuMgBr at room temperature for 15 min. After the removal of THF, SBA was distilled from the mixture of SBA and BuMgBr. As determined by gas chromatography, the amount of the impurity decreased gradually with the number of purifications. When SBA dried once over BuMgBr in THF was added to the initiator solution, the solution showed a yellow color, corresponding to a characteristic color of the living carbanion. The color disappeared immediately. The SBA dried twice over BuMgBr in THF showed a yellow color, remaining unchanged for 3 h. When methanol was added to the yellow solution, the solution suddenly became colorless. As shown in Table I, the resultant poly(N-isopropyl-N-trimethylsilyl-4-vinylbenzylamine), PSBA was prepared in 17% yield. The SBA dried thrice was polymerized for 24 h to yield PSBA in 100% yield. Figure 3 shows the three corresponding GPC chromatograms of PSBA polymers prepared from SBA monomers purified by means of different purging methods. The employment of several purifications was found to be preferred as a method for preparing PSBA with narrow MWD. Therefore, in the present study, SBA monomer was thrice dried over BuMgBr in THF, and then subsequent an-

Figure 3 GPC chromatograms of PSBA prepared from SBA (a) once, (b) twice, and (c) thrice dried over BuMgBr in THF. Experimental conditions are as follows: a carrier solvent of THF containing N-methylpyrrolidine (2 v/v %), a flow rate of 1.0 mL min^{-1}, an RI detector, a polymer concentration is 0.05 w/v %, and two GMH6 + G4000H8 columns.

ionic polymerization of the thus-purified SBA was conducted.

Anionic Polymerization of SBA

Table II shows the results of anionic polymerization of SBA at $-78°$C. When n-BuLi was used as initiator, the polymerization solution showed a yellow color. When methanol was added to the solution, the solution became colorless. A degree of polymer conversion was 100%. As shown in Figure 4, a GPC chromatogram of PSBA shows a sharp peak. The molecular heterogeneities, M_w/M_n values, decreased from 1.17 to 1.03 with increasing molecular weight of PSBA. Well-de-

fined PSBA of M_n between 1.3×10^4 and 17×10^4 and $M_w/M_n < 1.10$ were successfully prepared.

When Cumyl K was used as the initiator, the polymerization solution remained red overnight at $-78°$C. The solution became colorless on addition of methanol. A degree of polymer conversion was 100%. The M_w/M_n value of 1.04 was less than that of the polymer having the same molecular weight prepared by n-BuLi.

GPC measurements were conducted by injecting the polymerization solution to the instrument without further purification. In contrast, when membrane osmometry was performed, PSBA was precipitated in methanol from the polymerization solution, dried in vacuum, dissolved in benzene, freeze-dried, and dissolved in toluene at certain concentrations. During these processes, a slight trimethylsilyl protective group was removed from PSBA by atmosphere and methanol containing carbon dioxide. Thus, the resultant toluene solution was a mixture of PSBA and deprotected PSBA, namely PBA. In contrast, PBA could be easily prepared from PSBA in 100% yield. Apparently, PBA is preferable to PSBA for conducting precise osmometry. Therefore, number-average molecular weight of PBA ($M_{n\text{OSM}}^{\text{PBA}}$) was measured by means of membrane osmometry. Then, number-average molecular weight of PSBA ($M_{n\text{OSM}}^{\text{PSBA}}$) with the silyl protective group could be calculated by multiplying $M_{n\text{OSM}}^{\text{PBA}}$ by the molecular weight ratio of the two monomers.

The results are also shown in Table II. The $M_{n\text{OSM}}^{\text{PSBA}}$ values agree with kinetic molecular weights (M_k) expected from the amounts of monomer and initiator. Number-average molecular weights determined by GPC measurements

Table II   Anionic Polymerization of SBA in THF at $-78°$C

Monomer (mmol)	Initiator Name	Initiator mmol	Solvent THF (mL)	Polymerization Time (h)	Yield (%)	$10^{-4} M_k$[a]	$10^{-4} M_n$ $M_{n\text{GPC}}^{\text{PSBAb}}$	$10^{-4} M_n$ $M_{n\text{OSM}}^{\text{PSBAc}}$	M_w/M_n[b]	f[d]
10	n-BuLi	0.39	30	12	100	0.63	0.60		1.17	
15	n-BuLi	0.22	50	24	100	1.7	1.3		1.07	
17	n-BuLi	0.066	70	24	100	6.4	6.0	7.1	1.05	0.90
21	n-BuLi	0.035	100	24	100	15	16	17	1.03	0.89
15	Cumyl K	0.11	55	24	100	3.4	2.5	3.8	1.04	0.89

[a] Molecular weights calculated from the amounts of monomer and initiator.
[b] Number-average molecular weights determined from GPC measurements.
[c] Number-average molecular weights determined from membrane osmometry.
[d] Initiation efficiency of the initiator.

$(M_{n\text{GPC}}^{\text{PSBA}})$ using standard polystyrene were smaller than those of the $M_{n\text{OSM}}^{\text{PSBA}}$ values. This result is reasonable, because compared with polystyrene, PSBA has a large pendant group at the side chain. Initiation efficiency of the initiator (f) was calculated as follows;

$$f = M_k/M_{nOSM}^{PSBA}$$

As shown in Table II, the f values were not 1.0, but $\sim$ 0.9; namely, the values did not decrease with increasing M_k. This result suggests that the deactivation of the initiator should occur not in a process of polymerization, but during storage in a refrigerator. From a NMR spectrum of the product (top of Fig. 5), anionic polymerization was found to proceed without removal of the trimethylsilyl group from PSBA.

Block Copolymerization of SBA and St

After SBA was polymerized by n-BuLi in THF at $-78°C$, St was added to the polymerization so-

Figure 4 GPC chromatograms of (a) PSBA (—), M_n = 1.7 × 10⁵, and the resultant PBA (------), M_n = 1.2 × 10⁵ after removal of the trimethylsilyl protective group.

Figure 5 ¹H-NMR spectra of PSBA (top) and the resultant PBA (bottom) after removal of the trimethylsilyl protective group. A sharp NMR signal of PSBA at 0 ppm was due to the trimethylsilyl group and was completely disappeared in PBA, whereas a sharp NMR signal of PBA at 1.0 ppm was newly observed and assigned to the amino group.

lution to yield poly(N-isopropyl-N-trimethylsilyl-4-vinylbenzylamine)-*block*-polystyrene (PSBA-*b*-PSt). When the St monomer was added to the polymerization solution, the solution immediately changed from yellow to orange, corresponding to a characteristic color of polystyryllithium carbanion in THF at $-78°C$. In contrast, after St was polymerized by n-BuLi in THF at $-78°C$, SBA was added to the polymerization solution to yield

Table III Preparation of the Two Block Copolymers Containing PSBA and PSt Blocks Using *n*-BuLi as an Initiator in THF at −78°C

First Monomer			Second Monomer			Initiator *n*-BuLi (mmol)	Solvent THF (mL)	Yield (%)	PSBA Content[a] (%)	$10^{-4} M_k$[b]	$10^{-4} M_n$[c]	M_w/M_n[c]
Name	mmol	Time (h)	Name	mmol	Time (h)							
SBA	10	20	St	30	4	0.15	140	100	44	3.7	4.0	1.05
St	29	4	SBA	11	20	0.16	145	100	47	3.6	3.7	1.25

[a] Determined from ^{1}H-NMR spectrum.
[b] Molecular weight calculated from the amounts of monomer and initiator.
[c] Number-average molecular weight determined from GPC measurement.

PSt-*b*-PSBA. Thus, two block copolymers of PSBA and PSt were prepared. The polymerization results are shown in Table III; a degree of polymer conversion was ∼ 100%, and the M_n values were close to the M_k values. The compositions of the block copolymers as determined by ^{1}H-NMR spectrum were found to be nearly equal to those calculated from both monomers fed in the polymerization solution. Regardless of the sequence of addition of the two monomers, both block copolymers seemed to be prepared precisely.

However, as shown in Figure 6, PSBA-*b*-PSt shows a sharp GPC peak ($M_w/M_n = 1.05$) and PSt-*b*-PSBA shows a broad peak ($M_w/M_n = 1.25$). The sequence of addition of the two monomers is thought to be important for preparing well-defined block copolymer[17,18] of PSt and PSBA. The reason will be described in the "discussion" section.

Removal of the Trimethylsilyl Protective Group

Figure 5 shows NMR spectra of PSBA and the deprotected product (PBA) left standing in methanol at 40°C for 12 h. As compared with the spectrum of PSBA, the spectrum of the deprotected product shows no signal of the trimethylsilyl protective group at 0 ppm, but does show an additional signal assigned to the amino group at 1 ppm.[19,20] Other signals of both the polymers are coincident with each other. As shown in Figure 7, an infrared spectrum of the deprotected product shows no strong band at 1000 cm^{-1} or 1220 cm^{-1} for the trimethylsilyl group (Si—CH$_3$ stretching vibration), but does show a strong band at 1180 cm^{-1} for secondary amine (C—N stretching vibration) and a broadband at 3200–3600 cm^{-1} for secondary amine (N—H stretching vibration).[19,20] This result indicates that the removal of the trimethylsilyl group from PSBA proceeded completely in methanol at 40°C during a period of 12 h.

Figure 4 also shows the GPC chromatogram of PSBA and the resultant PBA. The chromatogram of PBA shifted to a lower molecular weight side of the corresponding PSBA. The peak shift probably corresponds to a decrease in the molecular weight attributable to the removal of the trimethylsilyl protective group. Molecular heterogeneities of both the polymers were approximately the same; namely, the deprotection did not cause any degradation or crosslinkage of the polymer chains of PSBA and PBA. PBA of well-defined structure, desired M_n, and narrow MWD was successfully prepared.

Removal of the trimethylsilyl protective group from PSBA-*b*-PSt and PSt-*b*-PSBA block copolymers was also conducted under the same condition as that for PSBA homopolymer. On compar-

(a) PSBA - *b* - PSt   **(b) PSt - *b* - PSBA**

Elution Volume / ml

Figure 6 GPC chromatograms of (a) PSBA-*b*-PSt and (b) PSt-*b*-PSBA. The sequence of addition of the two monomers was inverted.

Figure 7 An infrared spectrum of PBA. A strong band at 1180 cm^{-1} (C—N stretching vibration) and a broad band at 3200–3600 cm^{-1} (N—H stretching vibration) for the secondary amine were newly observed.

ison of NMR spectra and GPC chromatograms of the deprotected products with those of the corresponding original polymers, the deprotection of the block copolymers was found to have proceeded in 100% yield to produce new diblock copolymers having a poly(secondary aminostyrene) as a block.

DISCUSSION

Special attention should be directed to the anionic reactivity of SBA monomer and basic properties

of PSBA polymer. Table IV summarizes SBA and four other aminostyrene derivatives discussed in this section. When a tertiary aminostyrene of N,N-dimethyl-4-vinylphenylamine (DBA) was anionically polymerized by n-BuLi or Cumyl-K in THF at −78°C, the resultant PDBA polymer had respective M_w/M_n values of 1.38 and 1.09.[5] These results were explained by solvation of Li ion with the amino group. That is to say, during propagation, the tertiary amino group at the growing polymer end may participate in the solvation of Li ion because of high affinity of the amino group for Li ion.[5,7] Structural heterogeneity of the living end with Li ion induced broadening of MWD of the final polymer. In contrast, a weak anionic initiator of Cumyl K may play no role of solvation with the amino group; hence, the initiator may produce the final polymer with narrow MWD. In case of SBA studied in the present paper, the amino group has a bulky isopropyl group and trimethyl group on the nitrogen atom. According to this steric hindrance, the amino group at the growing polymer end may not participate in the solvation of Li ion. The structural homogeneity of the living end with Li or K ion should produce PSBA of narrow MWD.

Substituent effect of the amino groups on anionic reactivity of the vinyl group should be attributed to not only steric effect, but also electronic effect. The electronic effect of the vinyl group can be estimated from the ^{13}C chemical shift of a β-carbon in the vinyl group.[21–23] As shown in Table IV, the ^{13}C chemical shifts of the

Table IV Aminostyrene Derivatives Discussed in This Article

Monomer	Polymer	R^{a}	β-carbon[b]/ppm
DPA[c]	PDPA	—N—CH$_3$ └—CH$_3$	108
DBA[d]	PDBA	—CH$_2$—N—CH$_3$ └—CH$_3$	110
SBA	PSBA	—CH$_2$—N—CH(CH$_3$)$_2$ └—Si(CH$_3$)	110
SPA[e]	PSPA	—N—Si(CH$_3$)$_3$ └—Si(CH$_3$)$_3$	110
St	PSt	—H	112

[a] p-Substituent group of the aminostyrene derivatives.
[b] A carbon of CH$_2$ in CH$_2$ = CH—Phenyl—R, where R is an amino substituent group.
[c] N,N-dimethyl-4-vinylphenylamine.[5,7]
[d] N,N-dimethyl-4-vinylbenzylamine.[5,7]
[e] N,N-bis(trimethylsilyl)phenylamine.[10,11]

β-carbon in the aminostyrenes decreased from that of St monomer due to electron-releasing ability of the amino groups. Thus, the decrease in the ^{13}C chemical shift corresponds to the increasing electron density on the β-carbon in the vinyl group, further corresponding to lower anionic reactivity of aminostyrene monomers, relative to that of St. This prediction was confirmed by the relationship between the slower anionic polymerization rate and ^{13}C chemical shift values in the sequence of St, DBA, and N,N-dimethyl-4-vinyl-phenylamine for tertiary aminostyrenes. From the same viewpoint of ^{13}C chemical shift, the anionic reactivity of SBA is expected to be lower than that of St. Hence, the living carbanion of PSBA can easily initiate St, whereas the living carbanion of PSt can initiate SBA with difficulty. Thus, the PSBA-b-PSt block copolymer has a M_w/M_n value of 1.05, whereas the PSt-b-PSBA block copolymer has a M_w/M_n value of 1.25.

As pointed out by Nakahama and colleagues,[10] PSt-b-PSPA-b-PSt block copolymer (M_n = 1.8 $\times$ 10^4) prepared by the aminostyryl dianion of poly(N,N-bis(trimethylsilyl)phenylamine) (PSPA) shows a sharp GPC chromatogram. To investigate the anionic reactivity of SPA monomer in detail in the present study, diblock copolymerizations of SPA and St were also conducted. The resultant PSPA-b-PSt block copolymer (M_n = 10 $\times$ 10^4) has a M_w/M_n value of 1.09, whereas the PSt-b-PSPA block copolymer (M_n = 4.7 $\times$ 10^4) has a M_w/M_n value of 1.26. These results are well explained by the same electronic effect as described, namely the value of ^{13}C chemical shift of a β-carbon in the vinyl group of SPA is smaller than that of St (as shown in Table IV).

The removal of the trimethylsilyl protective group from PSBA proceeded completely in methanol at 30°C during a period of 12 h, whereas the removal of the trimethylsilyl group from PSPA proceeded in the THF-methanol (9 : 1, v/v) solution at reflux temperature during a period of 3 h. The nitrogen—silicon bond of PSBA seems to be unstable, compared with that of PSPA. The difference in deprotection of the trimethylsilyl protective group can be explained by the difference in basicity, namely electron density on the nitrogen of the amino group and steric hindrance in the vicinity of the nitrogen atom. This result corresponds to the fact that the dissociation constant, K_b, of benzylamine is 10^9 as large as that of aniline. This result was also confirmed by quaternization reactivity of the amino groups of the

two poly(tertiary aminostyrene)s with n-butyl bromide[7]; namely the quaternization reactivity decreased in the sequence of PDBA (benzyl group) and PDPA (phenyl group). Therefore, PSBA having high electron density on the nitrogen atom and small ethylene group as steric hindrance in the vicinity of the nitrogen atom has high basicity, and hence forms the nitrogen—silicon bond which, in comparison with that of PSPA, is unstable against an acid.

In conclusion, the amino group at the growing polymer end of PSBA might not participate in the solvation of Li ion by steric hindrance. Thus, SBA was anionically polymerized by n-BuLi in THF at −78°C to yield PSBA and PSBA-b-PSt block copolymer with narrow MWDs. According to the increasing electron density on the nitrogen of the amino group and depressing steric hindrance in the vicinity of the nitrogen atom of PSBA relative to PSPA, the trimethylsilyl protective group can be completely removed from PSBA without difficulty to yield the corresponding PBA and PBA-b-PSt block copolymer with narrow MWDs. PBA seems suitable for backbone chains of graft copolymers and for introducing other functions. This research is in progress.

REFERENCES

1. Pepper, K. W.; Paisley, H. M.; Young, M. A. J Org Chem 1953, 18, 4097.
2. Higo, Y.; Chosi, H.; Fujimoto, T.; Nagasawa, M. Polym J 1980, 12, 729.
3. Se, K.; Yamazaki, H.; Shibamoto, T.; Takano, A.; Fujimoto, T. Macromolecules 1997, 30, 1570.
4. Okamura, M. in Specialty Polymers; Ise, N.; Tabushi, I., Eds.; Cambrige University Press: New York, 1980.
5. Se, K.; Kijima, M.; Fujimoto, T. Polymer J 1988, 20, 791.
6. Menschutkin, N. Z Physik Chem 1890, 5, 589.
7. Se, K.; Kijima, M.; Ohtomo, R.; Fujimoto, T. J Polym Sci, Part A: Polym Chem 1997, 35, 1219.
8. Se, K.; Kijima, M.; Fujimoto, T. Polymer 1992, 33, 2401, Polymer 1997, 38, 5755.
9. Miyaki, Y.; Nagamatsu, H.; Iwata, M.; Ohkoshi, K.; Se, K.; Fujimoto, T. Macromolecules 1984, 17, 2231.
10. Yamaguchi, K.; Hirano, A.; Suzuki, K.; Takenaka, K.; Nakahama, S.; Yamazaki, N. J Polym Sci, Polym Lett Ed 1983, 21, 395.
11. Hirao, A.; Yamamoto, A.; Takenaka, K.; Yamaguchi, K.; Nakahama, S. Polymer 1987, 28, 303.
12. Smith, J. W. In The Chemistry of the Amino Group; Patai, S., Ed.; Interscience Publ.: New York, 1968, p. 161.

13. Se, K.; Watanabe, O.; Isono, Y.; Fujimoto, T. Makromol Chem, Macromol Symp 1989, 25, 249.

14. Se, K.; Miyawaki, K.; Hirahara, K.; Takano, A.; Fujimoto, T. J Polym Sci, Part A: Polym Chem 1998, 37, to appear.

15. Se, K.; Matsumura, K.; Kazama, T.; Fujimoto, T. Polym J 1997, 29, 434.

16. Fujimoto, T.; Nagasawa, M. Polym J 1975, 7, 398.

17. Szwarc, M. Carbanions, Living Polymers and Electron Transfer Processes; Interscience Publ.: John Wiley & Sons, New York, 1968.

18. Norhay, A.; McGrath, J. E. Block Copolymers; Academic Press: New York, 1977.

19. Matsuba, A.; Baba A. In Kiki Bunnseki no Tebiki, Vol. 4, 2nd ed.; Izumi, N.; Ogawa, K.; Katou, S.; Shiokawa, J.; Shiba, T., Eds.; Kagakudojin: Tokyo, 1996, p. 16.

20. Bovey, F. A. In Structural Studies of Macromolecules by Spectroscopic Methods; Ivin, K. J., Ed.; John Wiley & Sons: London, 1976.

21. Higashimura, T. Cationic Polymerization; Kagaku Dohjin: Tokyo, 1971.

22. Yuki, H.; Hatada, K.; Nagata, K.; Emura, T. Polym J 1970, 1, 269.

23. Dorman, D. E.; Angyal, S. J.; Roberts, D. J Am Chem Soc 1970, 92, 1351.