apart and gave the ϵ-coisotacticity = 0.230. Retention or inversion at the reaction site does not give such a value.

Copolymer Properties. The ethylene–methyl methacrylate alternating copolymer obtained above (run 7, with 2% lactone unit) had a number-averaged molecular weight of 32 000 and a weight-averaged molecular weight of 48 000 as determined by GPC with reference to polystyrene standards. Another sample of copolymer **3** with a number-averaged molecular weight of 24 000 (a degree of polymerization of 116) gave a copolymer **2** with a number-averaged molecular weight of 14 000 (a degree of polymerization of 109) after the reduction. Thus no significant degradation occurred during the tin hydride reduction. The copolymer **2** formed a transparent soft and rubbery film. It was soluble in chloroform, benzene, acetone, THF, and *N*,*N*-dimethylformamide. A cooling DSC experiment showed no crystallization peak but showed a glass transition temperature at 19 °C. Ethylene–ethylene–methyl methacrylate periodic copolymer (1) in the previous paper[1] was partially crystalline and had a glass transition temperature of 45 °C.

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Synthesis of Polymers with Amino End Groups. 3. Reactions of Anionic Living Polymers with α-Halo-ω-aminoalkanes with a Protected Amino Functionality

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ABSTRACT: Well-defined polymers amino functionalized at their chain ends were synthesized by the reactions of either anionic living polystyrenes or polyisoprenes with α-halo-ω-aminoalkanes with a protected amino functionality. The reactions generally proceeded well in THF at −78–25 °C to afford the aminated polymers in good yields. Careful analyses of the resulting polymers by a combination of acid–base titration ($HClO_4$), size-exclusion chromatography (SEC), and thin-layer chromatography (TLC) indicated that these polymers had high degrees of amination (>95%) at their end groups as well as predictable molecular weights and narrow molecular weight distributions. The usefulness of applying the TLC/flame ionization detection technique to quantitative analysis of the resulting polymers was discussed.

Introduction

The synthesis of chain end functionalized polymers (or the so-called telechelic polymers) is still of great interest because they have practically and potentially numerous applications. Anionic living polymerization is the preferred method for preparing such polymers because it leads to predictable polymer molecular weights and narrow molecular weight distributions. Many possible end functionalizations of anionic living polymers have been reported and well reviewed.[1-7] Widely studied and successful examples are hydroxyl and carboxyl end functionalized polymers that can be synthesized by the reaction of an anionic living polymer with either ethylene oxide[8-11] or carbon dioxide.[12-15] The resulting polymers have well-defined structures (e.g. molecular weight and molecular weight distribution as well as degree of end functionalization).

On the other hand, a general method for introducing primary amino groups to the terminals of living polymer has not been well established yet, although a couple of new methods have been reported so far. For example, Schulz and Halasa prepared the polyisoprenes and poly(1,3-butadienes) with amino groups at their polymer chain ends by using the initiator *p*-lithio-*N*,*N*-bis(trimethylsilyl)aniline which had a primary amine protected group.[16] The method appeared to be excellent for preparation of mono aminated polymers. However, it is relatively difficult to prepare aminated polymers at both chain ends by this system because they are prepared only by the coupling reaction which requires a very high precision in the stoichiometry of the living polymer and coupling agent, e.g. dimethylsilane dichloride.

We have recently developed a new aminating reagent, *N*-(phenylmethylene)trimethylsilanamine, which reacts efficiently with a variety of organolithium compounds to

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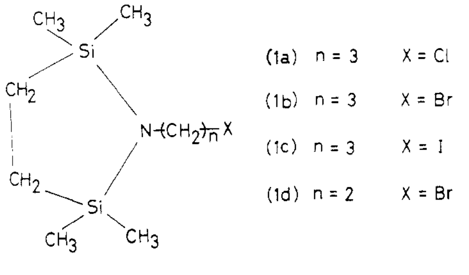
afford the corresponding primary amines.[17,18] This method could successfully be applied to the amination reactions of living polystyrene and polyisoprene.[19,20] The reactions proceeded well to give the aminated polystyrenes and polyisoprenes at one or two ends. The degrees of amination were excellent (90–100%) with the use of polystyryl- and polyisopropenyllithiums. However, the reactions of this reagent with sodium and potassium salts of living polystyrenes resulted in disappointedly low yields (17–48%) of end functionalization.

Very recently, Quirk and Cheng have reported that polystyryllithium has been aminated with 92% efficiency by using the reagent generated from methoxyamine and methyllithium at −78 °C.[21] The reactions of polystyrylsodium and -potassium with the reagent were not described.

We wish to report here the general and effective method for the synthesis of polymers with amino end groups by the reaction of anionic living polymers with the following reagents with a protected amino functionality (**1a–c** and **2**).

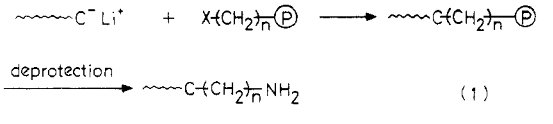


(1) - (2)

Results and Discussion

Preparation of Polymers with Amino End Groups. It is well-known that carbanions like organolithium compounds (RLi) react efficiently with primary alkyl halides (R′X) to yield addition products (R–R′) via new C–C bond formation. The reactions of anionic living polymers with R′X were reported to proceed similarly to afford the functionalized polymers with R′ groups at the ends generally in good yields.[22,23] Recent study by Richards, Service, and Stewart has shown that tertiary amino groups are efficiently introduced into the polymer chain ends by the reactions of poly(1,3-butadienyl)lithium with *N*-(3-chloropropyl)dialkylamines.[24] The yields were excellent, up to more than 95% in one case.

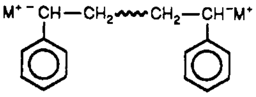
If α-halo-ω-aminoalkanes, where the amino protons were substituted with suitable protecting groups, were used in place of *N*-(3-chloropropyl)dialkylamines in the above reactions, the reaction followed by deprotection would allow a convenient route for synthesizing polymers with amino end groups as shown in eq 1. The key point of this reaction is finding a suitable protecting group for the amino function that is stable toward a highly reactive anionic living polymer and can be removed selectively and completely under the conditions that do not cleave and decompose the polymer structure. One of the most excellent candidates that can satisfy the above criteria is trialkylsilyl-protected amine functionality. Currently, there have been several reports that demonstrate the stability of the N–Si bonds toward alkyl- and aryllithium compounds and the easy cleavage of these bonds under very mild conditions.[16,25–28] For the protection of amino groups of α-halo-ω-aminoalkanes, it is sufficient to treat the corresponding amine hydrohalide with 1,1,4,4-tetramethyl-1,4-dichloro-1,4-disilabutane in the presence of triethylamine.[29] The amine-protected α-halo-ω-aminoalkanes (**1a–c** and **2**) were prepared in good yields. However, isolated yields of the reagents with high purity (>99.9%) were 50–60% for **1** and only 22% for **2** after repeated fractional distillations.



(1)

Ⓟ : Protecting group

Table I
Reactions of Living Polystyrenes with 1a–c and 2[a]

	degree of amination,[b] %			
	1a[c]	**1b**[c]	**1c**[d]	**2**[c]
M = Li	99	94	99	93
M = Na	93	91	99	91
M = K	96	98	99	94

[a] Isolated yields of the aminated polymers were 90–95%. $\bar{M}_n$ values of the parent polystyrenes or the benzoylated polymers were in the range of 10 000 to 50 000. Their $\bar{M}_w/\bar{M}_n$ values were around 1.1. [b] Degrees of amination were determined by a combination of amine content by titration and $\bar{M}_n$ values by SEC and VPO (titration-$\bar{M}_n$ method). [c] The reactions were carried out in THF at −78 °C for 1 min and at 25 °C for 1 h. [d] The reactions were carried out in THF at −78 °C for 1 h.

The reaction of living polystyrene with either of the reagents, **1a–c** or **2**, was carried out in THF or THF–pentane mixtures. A slight excess of the reagent added to the carbanion was enough to complete the reaction. The efficiency of the reaction was evaluated by a combination of acid–base titration of the amine with $HClO_4$ and $\bar{M}_n$ determined by size-exclusion chromatography (SEC). It should be noted that $\bar{M}_n$ was that of the base polymer obtained by methanol quenching of an aliquot of living polystyrene prior to the reaction, since the aminated polymer was difficult to characterize directly by SEC as described later.

The reaction rates are seen to be strongly dependent on the reagents used and are qualitatively estimated by the time required for the disappearance of the characteristic red color of the living polystyrene in the system. For example, the reaction of polystyrylpotassium with the iodide derivative **1c** was very fast and was completed within a few seconds even at −78 °C. Under the same conditions, the bromide **1b** required 1 h for a complete reaction. The reaction with the chloride derivative **1a** was sluggish as evident from the fact that the red color still remained at −78 °C after 12 h. On the other hand, the reactions with **1a** and **1b** proceeded at faster rates at 25 °C and were completed within 5 min for **1b** and 20 min for **1a**. The reactivity of **2** was found to be almost the same as that of **1b**. Similar reactivities of **1** and **2** were observed in the reactions of polystyryllithium and -sodium. Accordingly, the reactivities of the reagents **1a–c** and **2** toward living polystyrene are in the order **1c** > **1b** ≈ **2** > **1a** regardless of countercation.

The general reaction conditions were being allowed to stand for 1 h at 25 °C with **1a**, **1b**, and **2** and for 1 h at −78 °C with **1c** after the living polymers and **1a–c** and **2** were mixed at −78 °C. The data obtained from typical reactions of living polystyrenes with either of the reagents, **1a–c** or **2**, are listed in Table I. As can be seen, the reactions in any combination proceed well to introduce efficiently amino groups at the polymer chain ends. With

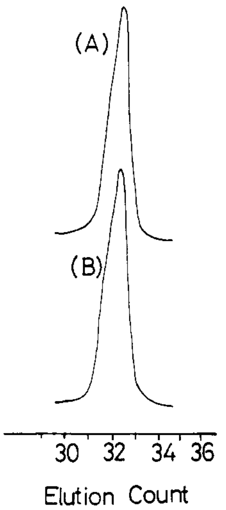


Figure 1. SEC curves of base polystyrene (A) and benzoylated sample of aminated polystyrene (B): peak A, $\bar{M}_n$(obsd) = 14 200, $\bar{M}_w/\bar{M}_n$ = 1.10; peak B, $\bar{M}_n$(obsd) = 14 200, $\bar{M}_w/\bar{M}_n$ = 1.09.

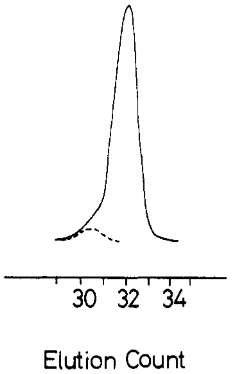


Figure 2. SEC curve of aminated polystyrene obtained by the reaction of polystyryldipotassium with **1c**.

Table II
Reactions of Mono- and Difunctional Living Polystyrenes with 1b[a]

	living polymer		aminated polymer		
polymer	counter-ion	function-ality	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	degree of amination,[b] %
polystyrene	K	2[c]	2 480	1.12	98
polystyrene	K	2[c]	5 350	1.11	97
polystyrene	K	2	16 900	1.15	95
polystyrene	K	2	31 300	1.19	95
polystyrene	K	2	76 000	1.13	94
polystyrene	Li	1[d]	2 720	1.06	98
polystyrene	Li	1[d]	5 200	1.09	98
polystyrene	Li	1	14 200	1.10	97
polystyrene	K	1	28 600	1.12	95
polystyrene	K	1	89 300	1.09	97
polyisoprene	K	2	12 400[d]	1.07	100
polyisoprene	Li	1[d]	9 100[e]	1.03	94

[a] Reactions were carried out in THF at −78 °C for 1 min and at 25 °C for 1 h. Yields of polymers were 90–95% in all cases. [b] Degrees of amination were determined by the titration–$\bar{M}_n$ method. [c] Polymerizations were carried out in pentane, and reactions were carried out in THF–pentane mixtures (ca. 1/1, v/v). [d] Polymerizations were carried out in benzene, and reactions were carried out in THF–benzene mixtures (ca. 1/5, v/v). [e] Microstructure: trans 1,4, 8%; 1,2, 38%, 3,4, 54%. [f] Microstructure: cis 1,4, 70%; trans 1,4, 25%; 3,4, 5%.

the use of **1a**, **1b**, and **2**, the lack of undesired side reactions such as the coupling reaction between living polymers in this system is clearly demonstrated by the very close agreement between $\bar{M}_n$s before and after the reaction, followed by benzoylation of the resulting polymer, as well as their $\bar{M}_w/\bar{M}_n$ ratios observed in their SEC chromatograms. Actually, the shapes of both chromatograms were found to be almost identical in every case as shown in Figure 1. On the other hand, the chromatograms of the polymers obtained with **1c** always showed single peaks with the presence of small shoulders at higher molecular weight regions as shown in Figure 2. Since the susceptibility of organic halides toward Wurtz-type reactions is known to be in the order RI > RBr > RCl, the higher molecular weight shoulders observed may probably result from Wurtz-type coupling reaction between living polystyrenes. Accordingly, **1a**, **1b**, and **2** are recommended for efficient introduction of amino functions to the polymer terminal. The reactions of living polystyrenes with **2** were also found to be excellent.[30] This is somewhat surprising since vicinal disubstituted reagents like **2** are believed to follow a β-proton elimination reaction.

Additional results on the aminated polymers with one and two end groups having a wide variety of $\bar{M}_n$s are summarized in Table II. They were synthesized from the reactions of **1b** and living polystyrenes obtained with either mono- or difunctional initiators. Furthermore, the treatment of living polyisoprenes with **1b** resulted in the successful formation of aminated polyisoprenes at one and two end groups.

The data in Tables I and II demonstrate once again that amino end functionalized polystyrenes and polyisoprenes can be made with high degrees of amination as well as narrow molecular weight distributions and predictable molecular weights, simply by the reactions of living polymers with either of the reagents **1a**, **1b**, or **2** that are readily prepared by one step from commercially available compounds.

As mentioned before, the $\bar{M}_n$s of amino-functionalized polymers could not be determined by SEC analysis. Their chromatograms always showed apparently broad molecular weight distributions with low-molecular-weight tails. These phenomena were especially significant in polymers with $\bar{M}_n$s less than 10^4. This problem could be overcome by the treatment of the aminated polymer with an excess of benzoic acid anhydride. The chromatograms of benzoyl derivatives thus obtained were very narrow, symmetrical, and nearly identical with those of the corresponding base polymers. Accordingly, the observed values of $\bar{M}_n$ shown in the aminated polymers (Tables I and II) were either those of base polymers or the benzoylated derivatives of the aminated polymers. Quirk and Cheng have reported similar trouble in the analysis of their aminated polystyrenes by the SEC measurement.[21] Unusual physical absorption of these polymers during the size-exclusion process may be responsible for this difficulty, as suggested by these authors.

Characterization of Aminated Polymer by Thin-Layer Chromatography (TLC) and TLC/Flame Ionization Detection (FID). Quirk and Cheng[21] have reported that the aminated polystyrene can be successfully separated by TLC and column chromatography using silica gel (SiO_2). Our samples were also found to be separated by the same techniques in preliminary experiments.

Since we have synthesized a variety of mono- and diaminated polystyrenes at their end groups having different molecular weights, we have studied the detailed behavior of the polymers on TLC aimed at finding the conditions for separating each of these polymers. For this purpose, we have selected 15 polymers summarized in Table

Table III
List of Samples of Polystyrenes and Aminated Polystyrenes for TLC and TLC-FID Measurements

PSt[a]		PSt-NH$_2$[b]		H$_2$N-PSt-NH$_2$[c]	
no.	$\bar{M}_n$	no.	$\bar{M}_n$	no.	$\bar{M}_n$
S-1	3 200	M-1	2 720	D-1	2 480
S-2	5 100	M-2	5 200	D-2	5 350
S-3	12 000	M-3	14 200	D-3	16 900
S-4	42 700	M-4	28 600	D-4	31 300
S-5	107 000	M-5	89 300	D-5	76 000

[a] Polystyrenes. [b] Aminated polystyrenes at one and group. [c] Aminated polystyrenes at two end groups. $\bar{M}_w/\bar{M}_n$ values of these polymer samples were in the range of 1.01–1.19.

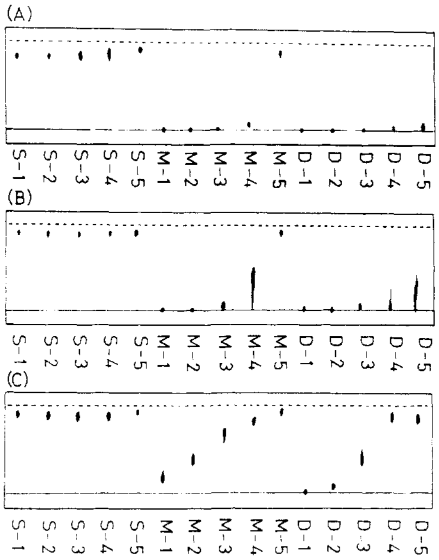


Figure 3. SiO$_2$-based thin-layer chromatograms of polystyrenes (S), aminated polystyrenes (M), and diaminated polystyrenes (D): (A) toluene; (B) chloroform; (C) chloroform–methanol (9/1, v/v).

III, in which symbols S, M, and D indicate polystyrene and mono- and diaminated polystyrenes at their end groups, respectively.

When the proper solvent system was chosen, well-separated spots were observed in the chromatograms. Some representative chromatograms are shown in Figure 3. For example, when toluene was used as the eluent, the polystyrenes all were well mobile and showed single spots of significantly high R_f values (0.80–0.90), whereas less or slow-moving spots (R_f < 0.10) were observed with the aminated samples except for M-5. This result clearly indicates that the aminated samples except for M-5 are separable from the polystyrenes by TLC or column chromatography with toluene. Furthermore, it is interesting that the difference in R_f values of M-5 and D-5 indicates the possibility of separation between mono- and diaminated samples with nearly the same $\bar{M}_n$ of about 8×10^4. Thus, the amino group on polymer seems to be strongly interacted with SiO$_2$, and therefore the aminated polystyrene can be separated from the unfunctionalized polystyrene. In some cases, the polymers can possibly be separated by the difference in amine content in the polymer as in the case of M-5 and D-5. Similar chromatograms were observed with the use of chloroform as the eluent, although there appeared spots with significant tailing for some aminated samples.

The behavior of aminated polystyrenes on TLC with chloroform/methanol (9/1, v/v) is also of interest because a molecular weight dependency on the R_f value is observed in the series of monoaminated polystyrene samples (M series). As can be seen, the R_f value increased with $\bar{M}_n$ in these samples. Accordingly, the aminated polymer has a possibility to be separated by the difference in $\bar{M}_n$. Careful observation suggests that the isolations between M-1 and D-1 as well as between M-2 and D-2 may be performed with this eluting solvent system, since their spots are well-separated from each other. Similar tendencies were observed on alumina (Al$_2$O$_3$) TLC, their chromatograms being shown in Figure 4. Thus, several practical chromatographic separations among the amino-functionalized and -unfunctionalized polystyrenes may possibly be realized by suitably selecting the eluent system and the chromatographic material.

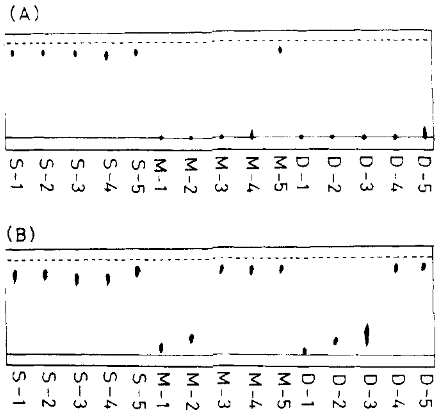


Figure 4. Al$_2$O$_3$-based thin-layer chromatograms of polystyrenes (S), monoaminated polystyrenes (M), and diaminated polystyrenes (D): (A) toluene; (B) chloroform–methanol (9/1, v/v).

The advantages of TLC have thus been recognized, but the method using TLC plates seems not to be suitable for quantitative analysis with high accuracy. For this purpose, the TLC/FID technique, developed by Padley,[31] appears to be one of the most practical methods. This method used a thin quartz rod instead of a plate on which the chromatographic separation was made under the nearly identical conditions employed in the separation by TLC. When the rod was scanned with sufficient heating to ionize, each component of the samples separated on the rod was quantitatively analyzed by FID. The results reported so far suggest that the sensitivity and reproducibility are enough for quantification of polymers.[32-35] In addition, the use of a scanning apparatus equipped with FID eliminates the isolation step which is laborious and time consuming and causes some errors.

In order to investigate the feasibility of applying TLC/FID for the quantification of aminated polymers, we prepared seven mixed samples each with a known composition. The polystyrene ($\bar{M}_n$ = 12 000, $\bar{M}_w/\bar{M}_n$ = 1.03) and the monoaminated polystyrene ($\bar{M}_n$ = 14 200, $\bar{M}_w/\bar{M}_n$ = 1.10) were used as polymer samples, respectively. The degree of amination in this aminated sample was 97% as determined by both HClO$_4$ titration and $\bar{M}_n$ by SEC analysis. Seven rods were spotted with toluene solutions containing seven mixed samples. On the remaining two rods, the polystyrene and the aminated sample were spotted as references. The typical chromatograms are presented in Figure 5. As can be seen, both peaks corresponding to the polystyrene and the aminated polystyrene are clearly separated and the ratio of both peak areas observed in good in agreement with that calculated on the basis of the composition. Similarly, agreement in other samples was observed as summarized in Table IV. Duplicates usually agreed to less than 3% for each peak area in all runs. Furthermore, the chromato-

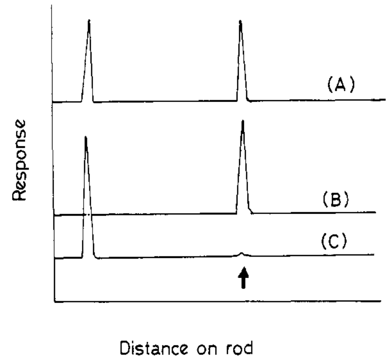


Figure 5. Chromatograms (Iatroscan) of polystyrene, aminated polystyrene, and the mixed sample: (A) a mixture of polystyrene and aminated polystyrene (58/42, w/w); (B) polystyrene; (C) aminated polystyrene (degree of amination = 97%).

Table IV
TLC-FID Measurement of Mixed Samples of Polystyrenes and Aminated Polystyrenes at One End Group

PSt-NH_2 content, %			
in mixed samples	measd by the TLC-FID method	in mixed samples	measd by the TLC-FID method
97	97	39	38
87	90	29	24
78	74	0	0
58	58		

Table V
Comparison of the Degree of Amination Determined by the Titration-$\bar{M}_n$ Method and by the TLC-FID Method

aminated polystyrene functionality	$\bar{M}_n$	degree of amination, %	
		titration-$\bar{M}_n$	TLC-FID
1	2 720	98	97
1	5 200	98	99
1	28 600	95	95
2	2 480	98	99
2	5 350	97	97
2	31 300	95	95

[a] $\bar{M}_w/\bar{M}_n$ of these polymer samples were in the range of 1.06–1.19.

grams obtained from the aminated polystyrene showed the presence of a small peak corresponding to the unfunctionalized polystyrene in addition to the main peak for the aminated polystyrene. The ratio of small peak to main one is calculated to be 3/97 which is exactly equal to that determined by both acid-base titration and $\bar{M}_n$ by SEC analysis. These results unequivocally indicate that the TLC/FID technique is applicable to quantitative analysis of our polymer samples.

Attempts to analyze the amine content in the polymer by the TLC/FID method were indeed successful. The representative results are summarized in Table V. As can be seen, the observed values are in fair agreement with the values evaluated on the basis of titration and $\bar{M}_n$, again indicating obviously the validity of this method.

Generally, microgram orders of the sample are enough for analysis with the TLC/FID method, whereas the titration of amine with $HClO_4$ essentially requires gram orders especially with the samples having molecular weights higher than 5×10^4. Furthermore, the ratio of mono- and diaminated polystyrenes with the same $\bar{M}_n$s can possibly be determined in some cases by the TLC/FID method as mentioned above. This is very useful for the determination of the functionality of diaminated samples which has so far been difficult by any other method.

Chain Extension Reaction. The chain extension reactions of end-functionalized polymers are of great importance from the viewpoint of block copolymer formation and the preparation of uniform model networks obtained by the reaction of the polymer with a trifunctionalized or a more functionalized coupling reagent. Furthermore, the molecular weight increase brought about by the chain extension reaction provides good evidence for the high degree of functionalization at the polymer chain ends.

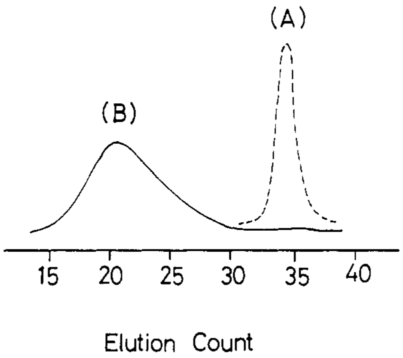


Figure 6. SEC chromatograms of aminated polystyrene (A) and chain-extended polymer (B).

The reaction of diaminated polystyrene ($\bar{M}_n$ = 5350) with 2,4-tolyl diisocyanate is a typical case of chain extension reactions. Figure 6 shows the chromatograms of both polymer samples before and after the chain extension reaction. As can be seen, the molecular weight of chain-extended polyurea reaches a $\bar{M}_n$ of 230 000. The peak corresponding to the starting polymer has completely disappeared. The polymer yield was quantitative. The nearly 43-fold increase in $\bar{M}_n$ points to at least a 98% degree of amination of this sample. The value agreed well with those obtained by both titration and TLC-FID methods. In addition, the result also indicated high reactivities of amino groups at the polymer chain ends.

Experimental Section

Materials. Styrene, α-methylstyrene, and isoprene were purified according to standard procedures. They were distilled twice over calcium hydride under a nitrogen atmosphere. For removal of impurities in the monomers, phenylmagnesium chloride (1.0 mL, 0.5 M THF solution) was added to each of these monomers (10 g) at 0 °C and the mixtures were stirred for 1 h and degassed. THF and each of these monomers were then distilled on a vacuum line into ampules fitted with break seals that were prewashed with sodium naphthalenide in THF solution before distillation. Purified monomers in THF thus obtained were stored at -30 °C until used. When a pentane solution of isoprene was required, butyllithium (1.0 mL, 0.5 M pentane solution) was added at -78 °C to isoprene (10 g) obtained by distillation over calcium hydride and the mixture was stirred for 3 h at -30 °C and degassed. Pentane and isoprene were then distilled on a vacuum line into ampules fitted with break seals that were prewashed with butyllithium in pentane before distillation. THF was refluxed over sodium wire for 5 h and distilled from its sodium naphthalenide solution. Pentane 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 its butyllithium solution. Naphthalene was purified by sublimation. Lithium, sodium, or potassium naphthalenide was prepared by the reaction of naphthalene with an excess of the corresponding metal in THF. Cumylpotassium was prepared by the reaction of cumyl methyl ether with potassium-sodium alloy in THF at 25 °C for 10 h.[36] Metal naphthalenides and cumylpotassium were colorimetrically in situ titrated by using standardized 1-octanol to a colorless end point in sealed reactors via break seals. The oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium were freshly prepared just prior to polymerization from the corresponding metal naphthalenides and a 2–4 M quantity of α-methylstyrene at 30 °C for 1 min and then at −78 °C for 30 min. Commercially available butyllithium and *sec*-butyllithium were used without purification as received.

2,2,5,5-Tetramethyl-1-(3-chloropropyl)-1-aza-2,5-disilacyclopentane (1a). **1a** was prepared according to the method previously reported.[29,37] A solution of 1,1,4,4-tetramethyl-1,4-dichloro-1,4-disilabutane (8.6 g, 40 mmol) in 20 mL of dry dichloromethane was added to a mixture of 3-chloropropylamine hydrochloride (5.2 g, 40 mmol) and dry triethylamine (17 mL, 120 mmol) in 20 mL of dry dichloromethane at 25 °C under a nitrogen atmosphere. The mixture was stirred for 2 h at 25 °C. The solvent was evaporated in vacuo, and the residue was triturated with hexane, filtered, washed with 5% NaOH, and evaporated. The crude product was purified by repeated fractional distillations at 66–67 °C (3 mmHg). Finally, 4.8 g (21 mmol, 52%) of **1a** was obtained as a colorless liquid. The purity was checked by gas chromatography and found to be more than 99.9%: 90-MHz ^{1}H NMR ($CDCl_3$) δ 3.52 (2 H, t, J = 6.5 Hz, $ClCH_2$), 2.94 (2 H, t, J = 7.0 Hz, NCH_2), 1.88 (2 H, m, CH_2), 0.73 (4 H, s, $SiCH_2$), 0.09 (12 H, s, $SiCH_3$); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ 42.8 ($ClCH_2$), 39.8 (NCH_2), 36.9 (CH_2), 8.3 ($SiCH_2$), 0.0 ($SiCH_3$). In order to remove impurities in **1a**, phenylmagnesium chloride (5 mL, 0.5 M solution of THF) was added to **1a** (4.8 g, 21 mmol) at 0 °C under a nitrogen atmosphere and the mixture was stirred for 30 min at 0 °C. It was then degassed and distilled on a vacuum line into the ampules fitted with break seals that were prewashed with sodium naphthalenide in THF solution. The **1a** thus obtained was stored at −30 °C.

2,2,5,5-Tetramethyl-1-(3-bromopropyl)-1-aza-2,5-disilacyclopentane (1b). This was prepared similarly by the reaction of 1,1,4,4-tetramethyl-1,4-dichloro-1,4-disilabutane, 3-bromopropylamine hydrobromide, and triethylamine in dry dichloromethane. Pure **1b** was obtained in 51% yield by repeated fractional distillations at 49–50 °C (1 mmHg) (lit.[29] 85–90 °C (1–2 mmHg)): 90-MHz ^{1}H NMR ($CDCl_3$) δ 3.44 (2 H, t, J = 6.6 Hz, $BrCH_2$), 2.97 (2 H, t, J = 7.0 Hz, NCH_2), 1.96 (2 H, m, CH_2), 0.73 (4 H, s, $SiCH_2$), 0.09 (12 H, s, $SiCH_3$); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ 40.7 (NCH_2), 37.0 (CH_2), 31.3 ($BrCH_2$), 8.3 ($SiCH_2$), 0.0 ($SiCH_3$).

2,2,5,5-Tetramethyl-1-(3-iodopropyl)-1-aza-2,5-disilacyclopentane (1c). This was prepared similarly by the reaction using 3-iodopropylamine hydroiodide. However, in order to prevent the self-quaternarization of 3-iodopropylamine, the addition of the reagents was changed as follows. A solution of triethylamine (9.0 mL, 60 mmol) in 20 mL of dry dichloromethane cooled at 0 °C was added dropwise to a mixture of 3-iodopropylamine hydroiodide (6.3 g, 20 mmol) and 1,1,4,4-tetramethyl-1,4-dichloro-1,4-disilabutane (4.3 g, 20 mmol) in 20 mL of dry dichloromethane at 0 °C for 30 min. The mixture was then stirred for 2 h at 25 °C. The solvent was evaporated in vacuo and the residue triturated with hexane, filtered, washed with 5% $NaHCO_3$, and evaporated. The crude product was purified by repeated fractional distillations. Pure **1c** (3.8 g, 12 mmol) was obtained in 58% yield at 77–78 °C (0.5 mmHg): 90-MHz ^{1}H NMR ($CDCl_3$) δ 3.12 (2 H, t, J = 7.0 Hz, ICH_2), 2.84 (2 H, t, J = 8.3 Hz, NCH_2), 1.88 (2 H, m, CH_2), 0.73 (4 H, s, $SiCH_2$), 0.09 (12 H, s, $SiCH_3$); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ 42.9 (NCH_2), 37.9 (CH_2), 8.3 ($SiCH_2$), 4.0 (ICH_2), 0.0 ($SiCH_3$).

2,2,5,5-Tetramethyl-1-(2-bromoethyl)-1-aza-2,5-disilacyclopentane (2). The synthesis of **2** requires some special care. Similarly in the case of **1c**, the addition order was that triethylamine was added to a mixture of 2-bromoethylamine hydrobromide and 1,1,4,4-tetramethyl-1,4-dichloro-1,4-disilabutane in dichloromethane. The reaction was always accompanied by the formation of undesired side products in considerable amounts that were rather difficult to remove from **2**. The use of excess silyl chloride added to the amine decreased the formation of these byproducts to a fair extent. 2-Bromoethylamine hydrobromide (4.1 g, 20 mmol), 1,1,4,4-tetramethyl-1,4-dichloro-1,4-disilabutane (5.6 g, 26 mmol), and triethylamine (9 mL, 60 mmol) were used, respectively. The reaction was carried out at 0 °C. The crude product after the workup was purified by repeated fractional distillations. Pure **2** (1.2 g, 4.5 mmol) was obtained in 22% yield at 64–65 °C (3 mmHg): 90-MHz ^{1}H NMR ($CDCl_3$) δ 3.14 (4 H, s, $BrCH_2$ and NCH_2), 0.73 (4 H, s, $SiCH_2$), 0.09 (12 H, s, $SiCH_3$); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ 44.9 (NCH_2), 34.0 ($BrCH_2$), 7.9 ($SiCH_2$), 0.0 ($SiCH_3$).

Polymerizations and Reactions of Living Polymers with 1a–c and 2. Polymerizations and reactions were carried out under high vacuum conditions (10^{-6} mmHg) in sealed glass reactors with break seals. Precautions were taken to avoid the presence of adventitious impurities that might react with the initiator or inhibit polymerization. The reactors were always prewashed with the initiator solution after being sealed off from a vacuum line and were used for polymerizations followed by reactions. Anionic polymerization of styrene, initiated either by metal naphthalenides, oligo(α-methylstyryl)alkali metals, or cumylpotassium, was carried in THF at −78 °C for 0.5 h. Anionic polymerization of isoprene was performed either with *sec*-butyllithium in pentane at 35 °C for 1 h or with oligo(α-methylstyryl)dipotassium in THF at −78 °C for 3 h. The polymer solution was then divided into two portions, one of which was terminated with methanol to act as a standard for the $\bar{M}_n$ determination. An excess (1.5–2.0 equiv to initiator) of a dried and purified reagent in THF solution (0.2–0.4 M) was added to the remaining solution of the living polymer at −78 °C, and the reaction mixture was allowed to stand for 1 h at 25 °C in the cases of **1a**, **1b**, and **2** and for 1 h at −78 °C in the case of **1c**. The polymer was then precipitated by the addition of an excess of methanol. It was purified by repeated reprecipitations using the benzene–methanol system at least five times. The silyl protecting groups at the polymer ends were completely deprotected during the reprecipitation steps. The complete deprotection was confirmed by the IR and ^{1}H and ^{13}C NMR spectra of the resulting purified polymer. The polymer was characterized by SEC, VPO, TLC, and TLC–FID measurements.

Benzoylation of Aminated Polymer. The amino-functionalized polymers at their end groups were benzoylated with an excess of benzoic acid anhydride in dry pyridine at 25 °C for 5 h. The polymers were purified by reprecipitation three times. The complete benzoylation of the polymers was checked by TLC analysis. The molecular weights and their distributions were estimated by SEC measurement. The observed values of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were found to be almost the same as those of the base polymers when the $\bar{M}_n$s of the polymers were more than 5×10^3.

Chain Extension Reaction. The reaction was carried out with an exact equivalence of the diaminated polystyrene ($\bar{M}_n$ = 5350) and 2,4-tolyl diisocyanate in dry benzene at 50 °C for 96 h under a nitrogen atmosphere. A catalytic amount of dibutyltin dilauriate was used, and the concentration of polymer was 3% (w/w). The reaction was terminated with a small amount of hexamethylenediamine, and the mixture was then added to methanol to precipitate the chain-extended polymer. The polymer was purified by reprecipitation and dried in vacuo. It was soluble in DMF but insoluble in chloroform, benzene, dioxane, and THF. The molecular weight and the distribution were estimated by the SEC measurement with DMF as the eluent.

Measurements. IR spectra were run with a JEOL AQS-20M spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q and JEOL FX-200 spectrophotometers in $CDCl_3$. Chemical shifts were reported in parts per million downfield relative to tetramethylsilane (δ 0) for ^{1}H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as a standard. Number-average molecular weights ($\bar{M}_n$) were determined by using a vapor pressure osmometer (VPO) which was made with Corona 117 instrument using a benzene solution. Size-exclusion chromatograms (SEC) were obtained with Toyo Soda HLC 802 instrument with UV (254 nm) or refractive index detection. THF was the carrier solvent at a flow rate of 1.4 mL min^{-1} and a temperature of 40 °C. The molecular weights and their distributions were determined from the chromatograms by using calibration with standard polystyrene samples. Each of the samples was measured by SEC at least three times, and the averaged value was listed in the table. The experimental error was generally within 3%. Thin-layer chromatography (TLC) was carried out on SiO_2 plates (Merck Art 5554) or Al_2O_3 plates (Merck Art 5550) with a fluorescent indicator. The instrument for the TLC/flame ionization detection (FID) method was an Iatoron thinchrograph, Model TH-10 (Iatron Co., Ltd., Tokyo, Japan). Specially designed quartz rods (150 × 2.0 mm) were employed on which silica gel or alumina particles were sintered in advance. They were commercially available SII and SIII for SiO_2 rods and A for Al_2O_3, respectively. Air flow (200 mL min^{-1}) and hydrogen pressure (0.85 kg cm^{-2}) were set for the analysis. The principles and equipment for this method as well as a schematic diagram of the instrument were described in detail in the literatures.[31,32,34,35,38,39]

Characterization of Aminated Polymer. The concentration of amine at the polymer chain ends was determined by acid-base titration as follows: The polymer sample was dissolved in a 1/1 (v/v) mixture of benzene and glacial acetic acid, and the solution was titrated with standard $HClO_4$ in glacial acetic acid by using crystal violet as the indicator.[40] The degree or the efficiency of amination was evaluated by a combination of the amine content by the titration and the $\bar{M}_n$ determined by SEC or VPO analysis. The degree of amination was also determined by the TLC/FID method. The results by both methods were compared and found to be identical within errors in measurements.

References and Notes

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Registry No. **1a**, 124286-59-5; **1b**, 95091-93-3; **1c**, 124286-60-8; **2**, 124286-61-9.