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Anionic Polymerization of Monomers Containing Functional Groups. 4.[1] Anionic Living Polymerization of *N*,*N*-Dialkyl-4-vinylbenzenesulfonamides

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ABSTRACT: Anionic polymerizations of *N*,*N*-dimethyl-4-vinylbenzenesulfonamide (**6a**), *N*,*N*-diethyl-4-vinylbenzenesulfonamide (**6b**), and *N*-methyl-*N'*-[(4-vinylphenyl)sulfonyl]piperazine (**6c**) were carried out at −78 °C in tetrahydrofuran. The initiators included potassium naphthalenide, oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium, (1,1,4,4-tetraphenylbutanediyl)dilithium and -dipotassium, [1,1-bis-[(4'-(trimethylsilyl)phenyl]hexyl]lithium, and [1,1,4,4-tetrakis[4'-(trimethylsilyl)phenyl]butanediyl]dipotassium. These polymerizations gave poly(**6**)s in quantitative yields. In all cases, the obtained polymers had narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.15$) and molecular weights predicted from the molar ratio of monomer to initiator, indicating that the anionic polymerizations of these monomers gave stable living polymers. Novel block copolymers, poly(**6b**-*b*-styrene-*b*-**6b**), poly(**6b**-*b*-isoprene-*b*-**6b**), poly(**6b**-*b*-2-vinylpyridine-*b*-**6b**), poly(2-vinylpyridine-*b*-**6b**-*b*-2-vinylpyridine), poly(methyl methacrylate-*b*-**6b**-*b*-methyl methacrylate), poly(*tert*-butyl methacrylate-*b*-**6b**-*b*-*tert*-butyl methacrylate), and poly(**6c**-*b*-styrene-*b*-**6c**) were synthesized using these living systems.

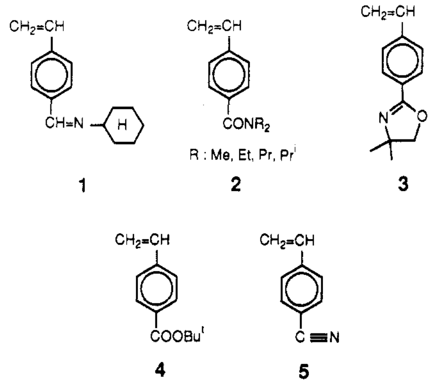
Introduction

The anionic living polymerization of styrene is undoubtedly the best established method to prepare polymers with strictly controlled chain structures.[2] Actually, the molecular weights of polystyrene can be precisely controlled in a wide range (10^3–10^6) by this method. These samples possess very narrow molecular weight distributions (MWDs). In addition, well-defined block copolymers and end-functionalized polystyrenes are readily synthesized by the use of living polystyrene. Unfortunately, only a very limited number of styrene derivatives were amenable to this living polymerization method until the beginning of the 1980s. The reliable examples were alkyl-[3] and aryl-substituted[4] styrenes and styrene derivatives having alkoxy[5] and *N*,*N*-dimethylamino groups.[6] The styrenes para-substituted with SiR_3,[7] GeR_3,[8] and $SnPh_3$[9] were also reported to undergo anionic living polymerization. Under specific conditions, the living polymer of 4-bromostyrene was possibly prepared in 1983.[10] However, styrenes with potentially useful functional groups are believed not to yield living polymers by anionic methods. This is because these groups are normally incompatible with both highly reactive anionic initiators and propagating chain ends in the anionic living polymerization of styrene.

In order to overcome this difficulty, we have introduced a protective method into the anionic polymerization of functional styrene derivatives. The method involves the suitable protection of functional groups and anionic living polymerization of the protected styrene monomers, followed by complete deprotection. According to our strategy, several successful examples have been demonstrated in the last 10 years.[11]

More recently, we have found a very interesting fact that a family of styrene derivatives para-substituted with electron-withdrawing groups undergo anionic living polymerization without difficulty. These monomers include *N*-cyclohexylimine,[12] *N*,*N*-dialkylamide,[13] oxazoline,[14] *tert*-butyl ester,[15] and nitrile.[16] (Chart I). Thus, we successfully synthesized new types of polystyrenes with these functional groups in each monomer unit. The polystyrenes possess nearly monodispersed distributions of molecular weight and controllable molecular weights. However, the success of living polymerization of **1**–**5** is very surprising, since their functional groups are known to readily react with nucleophiles such as organolithium compounds, whose reactivities are similar to those of the anionic initiators and active propagating chain ends formed in the anionic polymerization of styrene. The reason for this success may be due to the stabilization of propagating polystyryl carbanions by the electron-withdrawing effects of these substituents. Moreover, the extension of the π-conjugation system of benzylic carbanion (polystyryl carbanion at the propagating chain end) may also play an important role in the stabilization to produce living polymers from the monomers of this class.

Chart I



As an extension of a series of studies on the anionic polymerization of monomers containing electron-withdrawing groups, we report here the anionic polymerization of styrene derivatives para-substituted with tertiary sulfonamide groups. The monomers employed are *N*,*N*-dimethyl-4-vinylbenzenesulfonamide (**6a**), *N*,*N*-diethyl-4-vinylbenzenesulfonamide (**6b**), and *N*-methyl-*N'*-[(4-vinylphenyl)sulfonyl]piperazine (**6c**) as shown in Chart II.

Results and Discussion

The tertiary sulfonamide group is a well-known electron-withdrawing group. In fact, the Hammett σ-value of the *N*,*N*-dimethylsulfonamide group is reported to be 0.9.[17]

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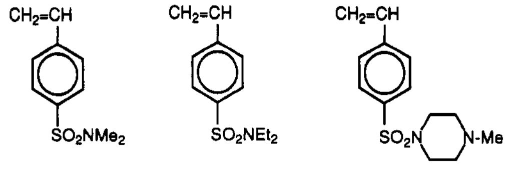
Chart II



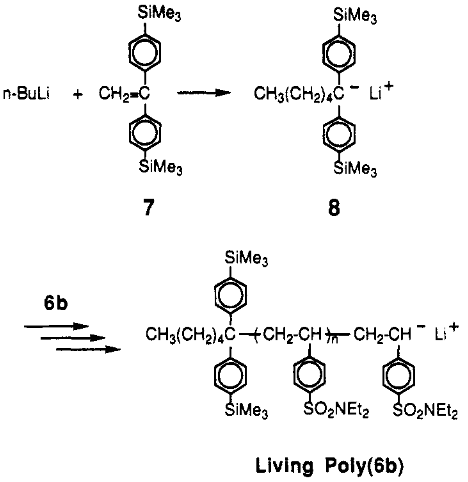
6a **6b** **6c**

This value means that the sulfonamide can compete in terms of electron-withdrawing character with cyano and nitro groups, whose values are 0.69 and 0.80,[17] respectively. Reynolds et al.[18] reported that the evaluations of substituent effects were realized from the chemical shifts of the β-carbon of the vinyl group in ^{13}C NMR spectra of 4-substituted styrenes. By using the chemical shifts of β-carbons of **6a–c**, the Hammett σ-values of the *N,N*-dialkylsulfonamide groups of these monomers could be estimated to be between 0.60 and 0.70, which are again comparable to those of cyano and nitro groups.

N,N-Dialkylsulfonamides are reported to be relatively stable to very strong nucleophiles like organolithium compounds. For example, some tertiary sulfonamides are observed to be compatible with organolithium compounds.[19] In fact, methyllithium has a half-life of 14 h even at room temperature in *N,N*-diethyltrimethylmethanesulfonamide. Hauser and co-workers[20] characterized proton-lithium exchange reaction between *N,N*-dimethylbenzenesulfonamide and *n*-butyllithium (*n*-BuLi) at 0 °C in THF–hexane. The important point of this reaction is that no sulfonyl attack by *n*-BuLi occurs but the ortho-lithiated compounds yield efficiently in the reaction. Furthermore, the resulting ortho-lithiated compounds with tertiary sulfonamide groups are quite stable and widely used in various organic syntheses.[21-30] These observations strongly indicate that the sulfonamide moiety can coexist with the carbanionic species, which can be regarded as models for the living polymers. Therefore, in great expectation of success, we could perform the anionic polymerizations of a series of styrene monomers containing electron-withdrawing tertiary sulfonamide functionalities, **6**.

Anionic Polymerization of *N,N*-Diethyl-4-vinylbenzenesulfonamide (6b). First of all, we attempted the anionic polymerization of **6b** (*N,N*-diethyl-substituted derivative). The polymerization was carried out at −78 °C with the use of [1,1-bis[4′-(trimethylsilyl)phenyl]hexyl]lithium (**8**, Scheme I), and [1,1,4,4-tetrakis[4′-(trimethylsilyl)phenyl]butanediyl]dipotassium (**9**) as initiators. They were prepared by reactions of 1,1-bis[4′-(trimethylsilyl)phenyl]ethylene (**7**) with *n*-BuLi in THF/pentane, and **7** with potassium naphthalenide in THF, respectively. Upon adding **6b** to rose red initiator solutions, the color changed rapidly to orange red (Li^+ counterion) or dark red (K^+ counterion). The resulting characteristic color remained unchanged at −78 °C, even after 4 h. It disappeared immediately upon adding a few drops of methanol for termination, indicating the presence of styryl carbanionic species derived from **6b**. The polymer was obtained quantitatively by precipitation into a large excess of water. The resulting polymer was purified by two reprecipitations with a THF(soluble)–hexane(precipitate) system.

Scheme I



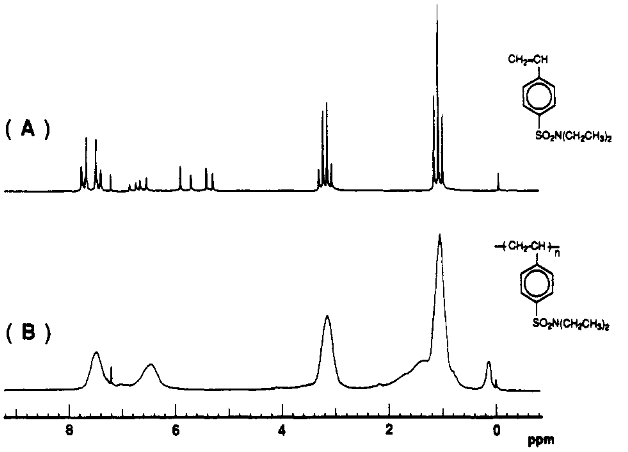


Figure 1. ^{1}H NMR spectra of **6b** (A) and poly(**6b**) obtained with **9** as an initiator (B) in $CDCl_3$. The trimethylsilyl protons of the initiator residues (at 0.15 ppm) appear to have their expected intensities in the spectrum of the polymer (Table I, run 2).

Figure 1 presents the ^{1}H NMR spectra of **6b**(A) and the resulting polymer(B) initiated with **9**. In comparison of the spectrum of A with that of B, the signals (5.3–6.8 ppm) of the vinyl group of the monomer completely disappeared and the broad signals corresponding to CH_2CH of the polymer main chain (0.8–2.1 ppm) appeared. The trimethylsilyl protons of the initiator residues (0.15 ppm) were also observed in the spectrum of the polymer. Similarly, in the ^{13}C NMR spectrum of the polymer, signals due to the secondary and tertiary carbons of the polymer main chain were observed and signals for vinyl carbons (117.0 and 135.4 ppm) were absent. In the infrared spectrum of the polymer, the absorptions corresponding to the vinyl group of the monomer at both 990 and 850 cm^{-1} thoroughly disappeared. In addition, the strong absorptions of the $-SO_2-$ linkage at 1333 and 1155 cm^{-1} were observed, slightly shifted toward higher wavenumber from those of the monomer. From these results, it is obvious that anionic polymerization of **6b** proceeds exclusively in the vinyl polymerization mode to afford the expected poly(*N,N*-diethyl-4-vinylbenzenesulfonamide).

Table I summarizes the polymerization results of **6b**. In all cases, the yield of poly(**6b**) was quantitative. The GPC chromatogram of each polymer exhibited unimodal distribution of molecular weight both in DMF and THF as eluents. The polydispersity indices, $\bar{M}_w/\bar{M}_n$ values, of the resulting polymers are determined to be in the range 1.03–1.15, indicating narrow MWDs of all poly(**6b**)s. It is observed that the number-average molecular weights calculated from the molar ratios of monomer to initiator in the feed are in proportion to those estimated by the GPC calibration using standard polystyrenes. However, the $\bar{M}_n$ values thus obtained by GPC both in THF and

Table I
Anionic Polymerization of 6b in THF at −78 °C for 0.5–4 h[a]

run	**6b**, mmol	initiator, mmol	$10^{-3}\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$) calcd[c]	NMR	GPC(THF)[d]	GPC(DMF)[e]	$10^{-3}\bar{M}_w$(LS)[b]	$\bar{M}_w$(LS)/$\bar{M}_n$(NMR)
1	3.56	K-Naph,[f] 0.234/7, 0.444	7.9	6.8	5.2 (1.15)	13 (1.14)	6.9	1.01
2	4.19	K-Naph, 0.146/7, 0.216	14	14	9.1 (1.12)	20 (1.13)	18	1.29
3	5.67	K-Naph, 0.107/7, 0.174	26	27	16 (1.11)	35 (1.12)	35	1.30
4	7.43	*n*-BuLi, 0.0622/7, 0.148	27	28	16 (1.05)	35 (1.08)		
5	6.89	*n*-BuLi, 0.0493/7, 0.134	33	38	22 (1.06)	44 (1.09)	50	1.32
6	6.04	*n*-BuLi, 0.0322/7, 0.0450	45	59	48 (1.03)	91 (1.08)	70	1.19

[a] Yields of polymers were almost quantitative in each case. [b] $\bar{M}_w$(LS) was obtained by light scattering in THF at 25 °C. [c] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × f/[initiator] + MW of initiator; f = 1 or 2, corresponding to the functionality of the initiators. [d] $\bar{M}_n$(GPC(THF)) was obtained by GPC calibration using standard polystyrenes in THF solution. [e] $\bar{M}_n$(GPC(DMF)) was obtained by GPC calibration using standard polystyrenes in DMF solution. [f] Potassium naphthalenide.

Table II
Anionic Polymerization of 6a, 6b, and 6c in THF[a]

run	monomer, mmol	temp (°C), time	initiator, mmol	$10^{-3}\bar{M}_n$ calcd[b]	obsd[c]	$\bar{M}_w/\bar{M}_n$[d]
7	**6a**, 1.37	−78, 20 h	K-Naph,[e] 0.0499/7, 0.181	12	10[f]	1.10
1	**6b**, 3.56	−78, 30 min	K-Naph, 0.234/7, 0.444	7.9	6.8[f]	1.14
2	**6b**, 4.19	−78, 30 min	K-Naph, 0.146/7, 0.216	14	14[f]	1.13
3	**6b**, 5.67	−78, 30 min	K-Naph, 0.107/7, 0.174	26	27[f]	1.12
4	**6b**, 7.43	−78, 80 min	*n*-BuLi, 0.0622/7, 0.148	27	28[f]	1.08
5	**6b**, 6.89	−78, 4 h	*n*-BuLi, 0.0493/7, 0.134	33	38[f]	1.09
6	**6b**, 6.04	−78, 60 min	*n*-BuLi, 0.0322/7, 0.0450	45	59[f]	1.08
8	**6b**, 2.48	0, 30 min	K-Naph, 0.100/α-MeSt[g] 0.269	13	14	1.23
9	**6b**, 4.95	0, 60 min	K-Naph, 0.124/α-MeSt, 0.263	20	22	1.23
10	**6b**, 2.88	−78, 30 min	K-Naph, 0.0941	15	17	1.11
11	**6b**, 2.43	−78, 30 min	Li-Naph,[h] 0.0851/α-MeSt, 0.273	14	16	1.10
12	**6b**, 2.43	−78, 30 min	Na-Naph,[i] 0.102/α-MeSt, 0.394	12	12	1.12
13	**6b**, 2.66	−78, 30 min	K-Naph, 0.0871/α-MeSt, 0.277	15	19	1.12
14	**6b**, 2.70	−78, 30 min	Li-Naph, 0.101/DPE,[j] 0.177	13	16	1.12
15	**6b**, 2.75	−78, 30 min	K-Naph, 0.0977/DPE, 0.180	13	16	1.11
16	**6c**, 3.14	−78, 20 h	*n*-BuLi, 0.103/7, 0.186	8.5	10[f]	1.08
17	**6c**, 4.35	−78, 20 h	*n*-BuLi, 0.0598/7, 0.171	20	26[f]	1.10
18	**6c**, 4.16	−78, 20 h	cumyl-K,[k] 0.0744/DPE, 0.0968	15	15	1.09

[a] Yields of polymers were almost quantitative in each case. [b] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × f/[initiator] + MW of initiator; f = 1 or 2, corresponding to the functionality of the initiators. [c] $\bar{M}_n$(obsd) was determined by eq 2 using the GPC calibration of poly(**6b**)s in DMF solution. [d] $\bar{M}_w/\bar{M}_n$ was obtained by GPC in DMF solution. [e] Potassium naphthalenide. [f] $\bar{M}_n$(obsd) was obtained by ^{1}H NMR spectroscopy. [g] α-Methylstyrene. [h] Lithium naphthalenide. [i] Sodium naphthalenide. [j] 1,1-Diphenylethylene. [k] Cumylpotassium.

DMF deviated from the calculated ones (Table I). In THF, the molecular weights by GPC were approximately two-thirds of the calculated values. In contrast, the relationship was opposite in DMF and the $\bar{M}_n$ values were about 1.4 times the theoretical ones.

Therefore, we have utilized an alternative method to determine the absolute molecular weights of the polymers. It is a trimethylsilyl end group analysis developed in our preceding paper.[16] The polymers initiated with either **8** or **9** had trimethylsilyl protons of the initiator residues at their chain ends or in the middle of their polymer chains,[31] as can be seen in Figure 1B. By using the relative NMR intensities of trimethylsilyl to aromatic protons in the polymer samples, the $\bar{M}_n$(NMR)s of poly(**6b**) were determined. Actually, this method was previously found to be very effective to determine the $\bar{M}_n$ values of poly(4-cyanostyrene)[16] and poly(methyl methacrylate).[32] As can be seen in Table I, good agreement between the $\bar{M}_n$(NMR)s thus obtained and molecular weights calculated from the molar ratios of monomer to initiator are observed in the cases both of mono- and difunctional initiators.

The weight-average molecular weights of some samples were also determined by light scattering measurements. They are comparable to the weight-average molecular weights calculated from the $\bar{M}_n$(NMR)s and the MWDs by GPC. These predicted molecular weights and values of $\bar{M}_w/\bar{M}_n$ (1.08–1.14) of the poly(**6b**)s strongly suggest that the anionic polymerization of **6b** is free from termination and chain transfer reactions, characteristic of the living nature of the polymerization system. In addition, the closeness between $\bar{M}_w$(LS)s and $\bar{M}_n$(NMR)s, considering the narrow MWDs, supports the reliability of the molecular weights determined by the end group analysis. From comparison of the predicted $\bar{M}_n$(NMR) values with $\bar{M}_n$(GPC)s in THF and DMF, they were correlated by the following equations, which are practically useful to estimate the molecular weights of poly(**6b**) samples:

$$\bar{M}_n(\text{obsd}) = 1.18 \times \bar{M}_n(\text{GPC(THF)}) + 5970 \quad (1)$$

$$\bar{M}_n(\text{obsd}) = 0.653 \times \bar{M}_n(\text{GPC(DMF)}) + 2880 \quad (2)$$

Next, to examine the scope of the initiators, **6b** was anionically polymerized with various initiators, such as potassium naphthalenide, 1,4-dilithio- and 1,4-dipotassio-1,1,4,4-tetraphenylbutanes, and oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium in THF at −78 to 0 °C for 30 min. A nearly quantitative yield of polymer was obtained in each case. The molecular weights of the polymer samples were determined using the above-mentioned GPC calibration for poly(**6b**) in DMF (equation (2)). The polymers of **6b** prepared at −78 °C possess the predicted molecular weights and narrow MWDs in all cases with different initiator countercations and functionalities, as shown in Table II. The polymer obtained at 0 °C had also the predicted molecular weight, and the polydispersity index was slightly broad ($\bar{M}_w/\bar{M}_n$ = 1.23).

Since it is also of great importance to estimate the stability of the active chain end for the proof of livingness

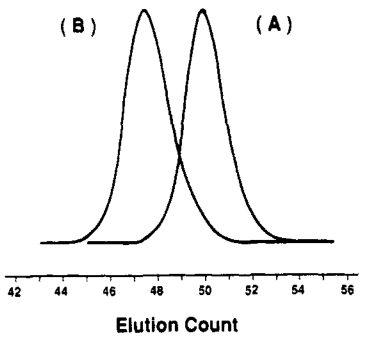


Figure 2. GPC curves (DMF) of poly(**6b**)s obtained at -78 °C: first polymerization (A), $\bar{M}_n$(obsd) = 12 000, $\bar{M}_w/\bar{M}_n$ = 1.05; second polymerization (B), $\bar{M}_n$(obsd) = 19 000, $\bar{M}_w/\bar{M}_n$ = 1.08 (the second monomer was added 30 min after the first addition).

of polymerization, postpolymerization was carried out (see Experimental Section for details). After the first polymerization of **6b** with oligo(α-methylstyryl)dipotassium at -78 °C for 30 min, the second feed of **6b** was added to the reaction mixture and then reacted for 30 min to complete the further polymerization. The postpolymer was quantitatively obtained after quenching as well as the prepolymer. From the GPC chromatogram of the postpolymer shown in Figure 2, it was observed that the peak of the prepolymer disappeared and that the peak of postpolymer shifted to the higher molecular weight side. Furthermore, the resulting postpolymer possessed the desirable molecular weight and a narrow MWD. Consequently, it is clearly evident that the propagating carbanion of living poly(**6b**) is stable at -78 °C at least for 30 min and initiates further polymerization. This complete survival of the terminal carbanion is a satisfactory result to synthesize the tailor-made block copolymers of **6b**.

Anionic Polymerization of *N,N*-Dimethyl-4-vinylbenzenesulfonamide (6a) and *N*-Methyl-*N'*-[(4-vinylphenyl)sulfonyl]piperazine (6c). The anionic polymerization of two additional related monomers, **6a** and **6c**, was attempted to evaluate the effect of the *N*-alkyl substituent on the polymerization. The polymerization of these monomers was similarly carried out at -78 °C for 20 h in THF. The polymers were produced in quantitative yields in all cases. It should be mentioned that the polymerization of **6a** always suffered from the precipitation of polymer during the polymerization under the experimental conditions.[33] Occurrence of the vinyl polymerization of **6a** and **6c** was ascertained by ^{1}H NMR, ^{13}C NMR, and IR spectroscopic measurements. The resulting polymers from both **6a** and **6c** possess molecular weights close to the calculated values as shown in Table II. The GPC traces of polymers in DMF were unimodal and represented the narrow MWD; the values of $\bar{M}_w/\bar{M}_n$ were around 1.10. These results indicate the living character of the anionic polymerizations of **6a** and **6c** as well as of **6b**.

Thus, the achievement of anionic living polymerization of **6a–c** provides for a valuable extension of monomers capable of living anionic polymerization. The high stability of living poly(**6a–c**) might be explained by the resistivity of tertiary sulfonamide toward nucleophilic attack[19-30] and by the stabilization of active chain ends with the strongly electron-withdrawing sulfonamide groups as discussed in the next section.

Table III summarizes the solubilities of poly(**6a–c**) obtained in this study. It is generally observed that poly(**6a–c**) are insoluble in common organic solvents such as benzene, carbon tetrachloride, diethyl ether, and ethyl acetate. The range of useful solvents of poly(**6a–c**) is more limited than that of polystyrene. The high polarity of tertiary sulfonamide moieties of the polymers may promote the solubilities of poly(**6a–c**) in polar solvents. Among the resulting poly(**6a–c**), the poly(**6a**) particularly shows limited solubility in the various solvents. It is soluble only in polar *N,N*-dimethylformamide and only swells even in dimethyl sulfoxide. Poly(**6c**) is of interest, because it contains a tertiary amino moiety on the piperazine ring in each monomer unit in addition to the polar sulfonamide moiety. This polymer may be converted into tailor-made polyelectrolytes through the quaternization of the tertiary amino group. In fact, the poly(**6c**) swells in 6 *N* HCl, probably due to the protonation of tertiary amino function on the piperazine ring.

Table III
Solubilities of Poly(6)s and Polystyrene[a]

solvent	poly(6a)	poly(6b)	poly(6c)	polystyrene
hexane	I	I	I	I
benzene	I	I	I	S
carbon tetrachloride	I	I	I	S
diethyl ether	I	I	I	S
ethyl acetate	I	I	I	S
chloroform	I	S	S	S
acetone	I	S	S	S
1,4-dioxane	I	S	I	S
tetrahydrofuran	I	S	S	S
N,N-dimethylformamide	S	S	S	S
dimethyl sulfoxide	Sw	S	S	I
ethanol	I	I	I	I
methanol	I	I	I	I
water	I	I	I	I
6 N HCl	I	I	Sw	I

[a] I, insoluble; S, soluble; Sw, swelling.

The glass transition temperatures (T_gs) of all polymer samples were determined by differential scanning calorimetry. The T_gs of poly(**6a**), poly(**6b**), and poly(**6c**) were 187, 140, and 171 °C, respectively. As expected, these values were higher than that of polystyrene (T_g = 93 °C) with comparable molecular weight.

Block Copolymerization of 6s with Styrene, Isoprene, 2-Vinylpyridine, Methyl Methacrylate, and *tert*-Butyl Methacrylate. The success of living polymerization of **6a–c** opens the way for synthesis of block copolymers with strictly controlled chain structures, which are of interest as new heterophase materials containing polar poly(**6**) segments.

At first, the synthesis of an ABA type triblock copolymer, poly(**6b**-*b*-styrene-*b*-**6b**), was carried out by the sequential polymerization of styrene and **6b** with potassium naphthalenide at -78 °C in THF. Both polymerizations proceeded to attain 100% conversions of styrene and **6b**, respectively. The ^{1}H NMR analysis showed good agreement between the molar ratio of monomer units of both polymer segments and the initial molar ratio of the monomers. The GPC curve of the copolymer shifted toward higher molecular weight region from that of the styrene homopolymer (Figure 3). As shown in Table IV, the resulting polymer was found to have the predicted molecular weight and a relatively narrow MWD. Consequently, the polymer is the expected ABA triblock copolymer with well-defined block lengths. Similarly, a tailor-made poly(**6c**-*b*-styrene-*b*-**6c**) could be synthesized quantitatively by addition of **6c** to the difunctional living polystyrene.

To examine the feasibility of synthesis of other block copolymers, two additional polymerizations were performed by using difunctional living polymers of isoprene and 2-vinylpyridine (2VP) as polymeric initiators of **6b**. Both triblock copolymers, i.e., poly(**6b**-*b*-isoprene-*b*-**6b**)

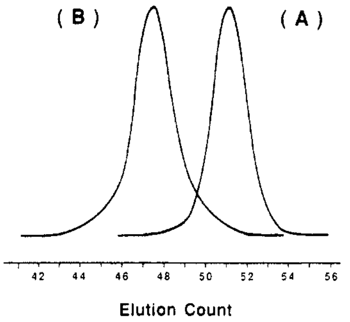


Figure 3. GPC curves (DMF) of polystyrene (A) at the first polymerization and poly(**6b**-*b*-styrene-*b*-**6b**) (B): peak A, $\bar{M}_n$(obsd) = 12 000, $\bar{M}_w/\bar{M}_n$ = 1.08; peak B, $\bar{M}_n$(obsd) = 19 000, $\bar{M}_w/\bar{M}_n$ = 1.12 (the second monomer was added 10 min after the first addition).

and poly(**6b**-*b*-2VP-*b*-**6b**), were synthesized in quantitative yield. It was found that they had the predictable segment compositions as well as the regulated chain lengths. The results are also listed in Table IV (runs 20 and 21).

Next, we attempted to synthesize the triblock copolymer with reversed sequence of a BAB type, where A was poly(**6b**) and B was an other polymer segment. We prepared a difunctional living polymer of **6b** as described in the preceding section and added either isoprene or styrene to the living polymer. Virtually, no further polymerization occurred in either case, even after several hours in THF at −78 °C. Homopolymers of **6b** and the unreacted monomers were quantitatively recovered from the polymerization systems. Thus, the living poly(**6b**) could not initiate the polymerizations of either isoprene or styrene. On the other hand, more anionically reactive monomers, such as 2VP, methyl methacrylate (MMA), and *tert*-butyl methacrylate (tBuMA), were quantitatively polymerized with difunctional living poly(**6b**). The GPC and NMR analyses of the resulting polymers indicate that they are block copolymers with desirable segment lengths.

The crossover reaction of **6b** to and from the living polymers of various monomers not only makes available the controlled synthesis of block copolymers containing poly(**6b**) segments but also elucidates the relative reactivities of the monomers and the carbanions of living polymers. The living poly(**6b**) is able to initiate the polymerization of 2VP and alkyl methacrylates but is ineffective toward the initiation of styrene and isoprene. In contrast, both living polymers of styrene and isoprene have abilities to initiate the polymerization of **6b**. Accordingly, the living poly(**6b**) has a lower reactivity than living polystyrene and polyisoprene.

These results clearly demonstrated that the electron-withdrawing sulfonamide group significantly affects the reactivity of the living carbanion derived from **6b**. The electron density of the terminal carbanion is decreased by the electron-withdrawing effect of sulfonamide, resulting in the lower nucleophilicity of living poly(**6b**) than that of living polystyrene. In addition to this, it have been proposed that the SO_2 moiety adjacent to the aromatic ring tends to accept negative charge and stabilize the carbanion adjacent to the ring through π-electron resonance analogous to carbonyl, cyano, and nitro moieties.[34] According to the proposal, the extension of the π-conjugated system of the benzylic carbanion may also stabilize the propagating carbanion due to the resonance effect of the para-substituted sulfonamide group (Scheme II). Such a stabilized carbanion may react with various monomers having electron-withdrawing groups to produce anionic polymerization in a living manner. In fact, the anionic living polymerizations of styrene derivatives bearing electron-withdrawing groups are possible. The monomers are *N*-alkylimine, *N*,*N*-dialkylamide, oxazoline, ester, and nitrile as mentioned in the Introduction.[12-16] More accurate evaluation of the reactivities of new carbanions derived from these monomers will be the subject of forthcoming papers.

In conclusion, we have demonstrated that three *N*,*N*-dialkyl-4-vinylbenzenesulfonamides, **6a–c**, were anionically polymerized to afford new types of living polymers. This is the first example of anionic living polymerizations of the styrene derivatives containing of *N*,*N*-dialkylsulfonamide groups. (*N*,*N*-Dialkylamino)sulfonyl functional groups in the monomers and the polymers tolerate the initiation and the repeated propagation reactions during the course of anionic living polymerization. By means of the living polymerization of **6a–c**, homopolymers and the block copolymers with controlled molecular weights and narrow MWDs ($\bar{M}_w/\bar{M}_n$ = 1.03–1.17) are quantitatively synthesized.

Experimental Section

Materials. Sodium *p*-styrenesulfonate purchased from Tokyo Kasei Co. Ltd. was used without further purification. *N*,*N*-Dimethylformamide (DMF) was dried and distilled from calcium hydride under vacuum. Dimethylamine was distilled under nitrogen from a 40 wt % aqueous solution through a column packed with potassium hydroxide and trapped over calcium with a dry ice–acetone bath. Diethylamine and *N*-methylpiperazine were dried and distilled over calcium hydride under nitrogen. Methyl methacrylate, *tert*-butyl methacrylate, α-methylstyrene, styrene, and isoprene were dried over calcium hydride and distilled on the vacuum line. 2-Vinylpyridine was dried with potassium hydroxide and then distilled from calcium hydride under vacuum. 1,1-Diphenylethylene (DPE), prepared by a literature method,[35] was purified by fractional distillation and finally distilled from *n*-BuLi/pentane under vacuum. Tetrahydrofuran (THF) used as a polymerization solvent was refluxed over sodium wire for 5 h and distilled from lithium aluminum hydride and finally through the vacuum line from sodium naphthalenide solution. Trimethylsilyl chloride, 1,4-dichlorobenzene, and ethyl acetate was purified by standard techniques.[36]

Initiators. Commercially available *n*-BuLi was used without purification and it was diluted by *n*-heptane. Metal naphthalenides were prepared by the reactions of a small excess amount of naphthalene with the corresponding alkali metal in THF. Cumylpotassium was prepared by the reaction of cumyl methyl ether with sodium–potassium alloy in THF at room temperature. Oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium were freshly prepared just prior to polymerizations from the corresponding metal naphthalenides and a 2–4 molar excess of α-methylstyrene at 20 °C for 1 min and then at −78 °C for 10 min. These initiators were stored in ampules equipped with breakseals. The concentrations of initiators were determined by colorimetric titration with standardized 1-octanol in a sealed reactor under vacuum.[37]

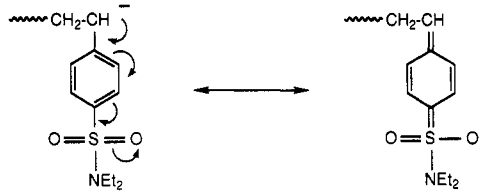
4-(Trimethylsilyl)chlorobenzene. To a suspension of dry, clean magnesium turnings (10.50 g, 432 mmol) in dry THF (30 mL) at reflux temperature under nitrogen, 1,4-dichlorobenzene (30.04 g, 204 mmol) in dry THF (100 mL) was added dropwise over 30 min. After a further 8 h at reflux, the reaction mixture was cooled to 0 °C. To the reaction mixture, trimethylsilyl chloride (26.0 mL, 205 mmol) was added dropwise over 30 min with cooling in an ice bath and then stirred overnight at room temperature. The reaction mixture was quenched with saturated ammonium chloride solution, and the layers were separated. The aqueous layer was extracted three times with diethyl ether. The organic phase was combined and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was distilled under vacuum to give a colorless liquid of 4-(trimethylsilyl)chlorobenzene (14.9 g, 80.7 mmol, 40%, bp 52–53 °C/1.2 mmHg). 90-MHz ^1H NMR ($CDCl_3$) δ 0.00 (s, 9 H, $SiCH_3$), 7.10–7.26 (m, 4 H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ −1.1 ($SiCH_3$), 128.1 (Ar, C2), 134.8 (Ar, C3), 135.2 (Ar, C1), 138.8 (Ar, C4); IR

Table IV
Block Copolymerization of 6b and 6c with Styrene, Isoprene, 2-Vinylpyridine, Methyl Methacrylate, and *tert*-Butyl Methacrylate at −78 °C in THF[a]

run	counter-cation	block	A monomer	B monomer	block copolymer (homopolymer[b])		
					$10^{-3}\bar{M}_n$(calcd)[c]	$10^{-3}\bar{M}_n$(obsd)[d]	$\bar{M}_w/\bar{M}_n$
19	K^+	A–B–A	**6b**	styrene	22 (13)	19 (12)	1.12 (1.08)
20	K^+	A–B–A	**6b**	isoprene	21 (11)	23 (13)	1.16 (1.09)
21	Li^+	A–B–A	**6b**	2VP	21 (9.5)	20 (9.5)	1.16 (1.09)
22[e]	Li^+	B–A–B	**6b**	MMA	17	16	1.16
23	K^+	B–A–B	**6b**	tBuMA	26 (12)	23 (12)	1.10 (1.08)
24	Li^+	B–A–B	**6b**	2VP	21 (12)	21 (13)	1.17 (1.15)
25	K^+	A–B–A	**6c**	styrene	21 (12)	22 (11)	1.05 (1.05)

[a] Yields of polymers were nearly quantitative in each case. Difunctional initiators were used in all block polymerizations. [b] Homopolymers were obtained at the first-stage polymerization. [c] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × 2/[initiator] + MW of initiator. [d] The molecular weights of the block copolymers were determined by using the molecular weights of the homopolymers and the molar ratios of monomer units in the block copolymer analyzed by ^{1}H NMR. [e] Homopolymer of **6b** was not isolated in this case.

Scheme II



(KBr, cm^{-1}) 2958, 1577, 1484, 1381, 1251, 1085, 1016, 841, 810, 756, 736. Anal. Calcd for $C_9H_{13}SiCl$: C, 58.51; H, 7.09; Cl, 19.19. Found: C, 58.36; H, 7.06; Cl, 19.35.

1,1-Bis[4-(trimethylsilyl)phenyl]ethylene (7). To a suspension of dry, clean magnesium turnings (3.19 g, 131 mmol) in dry THF (10 mL) at reflux temperature under nitrogen, 4-(trimethylsilyl)chlorobenzene (16.2 g, 87.6 mmol) in dry THF (50 mL) was added dropwise over 30 min. After a further 8 h at reflux, the reaction mixture was cooled to 0 °C. To the reaction mixture, dry ethyl acetate (3.48 g, 39.5 mmol) was added dropwise with cooling in an ice bath and then stirred for 1 h at room temperature. The reaction mixture was quenched with saturated ammonium chloride solution, and the layers were separated. The aqueous layer was extracted three times with diethyl ether. The organic phase was combined and concentrated under reduced pressure.

To the residue, 20% H_2SO_4 (26 mL) was added and then the resulting mixture was heated at reflux for 2 h. The reaction mixture was cooled to room temperature to give a yellow solid. The solid was taken up in ether (100 mL), and the solution was washed twice with water, five times with saturated $NaHCO_3$ solution, and twice with water. The organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure to give slightly yellow solids (9.42 g, 74%). The solids were recrystallized from methanol three times to yield pure white crystals of 7 (3.77 g, 11.6 mmol, 29%): mp 112.0–113.0 °C; 90-MHz ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 18 H, $SiCH_3$), 5.48 (s, 2 H, CH_2=), 7.37–7.55 (m, 8 H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ −1.0 ($SiCH_3$), 114.0 (CH_2=), 127.7 (Ar, C2), 133.3 (Ar, C3), 139.9 (Ar, C1), 141.9 (Ar, C4), 150.2 (–C=); IR (KBr, cm^{-1}) 2955, 1247, 1118, 1085, 914, 857, 831, 753, 727. Anal. Calcd for $C_{20}H_{28}Si_2$: C, 74.00; H, 8.69. Found: C, 73.82; H, 8.90.

After careful recrystallization, 7 was finally distilled from *n*-BuLi/pentane in an apparatus equipped with a breakseal under vacuum and then diluted with dry THF. The resulting THF solution (0.05 M) of 7 was used in the anionic polymerization.

4-Vinylbenzenesulfonyl Chloride. To thionyl chloride (65 mL) under nitrogen in an ice bath was added sodium *p*-styrenesulfonate (26.3 g, 128 mmol) in small portions with stirring below 10 °C for 10 min. To the resulting suspension, dry DMF (35 mL) was added dropwise under cooling. The reaction system became homogeneous, and it was stirred for 6 h at room temperature. The reaction mixture was stand in a refrigerator overnight and poured into ice water to quench unreacted thionyl chloride. The aqueous solution was extracted three times with diethyl ether, and the combined organic layer was washed three times with water and then dried over $MgSO_4$. Concentration of the organic solution under reduced pressure gave a solution of 4-vinylbenzenesulfonyl chloride (23.6 g, 116 mmol, 91%) in ether.[38] The resulting solution was used without further purification in the following reaction with dialkylamine, because the sulfonyl chloride tended to spontaneously polymerize in high concentration. 90-MHz ^{1}H NMR ($CDCl_3$) δ 5.55 and 5.96 (2 d, 2 H, *J* = 11 and 18 Hz, CH_2=), 6.80 (dd, 1 H, –CH=), 7.56–8.04 (m, 4 H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ 119.4 (vinyl, CH_2=), 127.2 (Ar, C2 and C3), 134.8 (vinyl, –CH=), 143.0 (Ar, C1), 144.5 (Ar, C4); IR (KBr, cm^{-1}) 1593, 1374, 1190, 1173, 1082, 988, 927, 844, 651.

***N,N*-Dimethyl-4-vinylbenzenesulfonamide (6a).**[39-41] To a mechanically stirred solution of dimethylamine (18.2 g, 404 mmol) in dry ether (80 mL) under nitrogen, 4-vinylbenzenesulfonyl chloride (26.10 g, 129 mmol) in dry ether (30 mL) was added dropwise with cooling in an ice bath and then stirred overnight at room temperature. The precipitated ammonium salt was filtered off, and the filtrate was washed twice with 2 N HCl, twice with saturated $NaHCO_3$ solution, and twice with water and then dried over $MgSO_4$. Concentration of the organic solution under reduced pressure gave yellow colored crystals of **6a** (20.7 g, 98.1 mmol, 76%). Five recrystallization from methanol gave 1.6 g (7.7 mmol, 6%) of **6a** as pure white crystals: mp 64.0–64.5 °C (lit.[37] mp 63–63.5 °C); 90-MHz ^{1}H NMR ($CDCl_3$) δ 2.71 (s, 3 H, NCH_3), 5.44 and 5.89 (2 d, 2 H, *J* = 11 and 18 Hz, CH_2=), 6.78 (dd, 1 H, –CH=), 7.50–7.80 (m, 4 H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ 37.9 (NCH_3), 117.4 (vinyl, CH_2=), 126.6 (Ar, C3), 128.0 (Ar, C2), 134.5 (Ar, C4), 135.3 (vinyl, –CH=), 141.8 (Ar, C1); IR (KBr, cm^{-1}) 1596, 1453, 1397, 1337, 1189, 1162, 1092, 992, 953, 935, 851, 710. Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63; S, 15.17. Found: C, 56.52; H, 6.32; N, 6.51; S, 14.47.

***N,N*-Diethyl-4-vinylbenzenesulfonamide (6b). Method A.** The same procedure was followed as described for **6a** using (4-vinylbenzenesulfonyl chloride (9.03 g, 37.8 mmol) and diethylamine (6.90 g, 94.5 mmol) in place of dimethylamine, and recrystallization from petroleum ether gave 7.37 g (30.8 mmol, 81%) of **6b**.

Method B. To a mechanically stirred solution of diethylamine (9.60 g, 132 mmol) and 5% NaOH solution (200 mL), (4-vinylbenzenesulfonyl chloride (26.30 g, 130 mmol) in ether (100 mL) was added dropwise with cooling in an ice bath over 30 min and then stirred vigorously overnight at room temperature. The aqueous layer was extracted three times with diethyl ether. The combined ether layer was washed twice with 2 *N* HCl, twice with saturated $NaHCO_3$ solution, and twice with water and then dried over $MgSO_4$. After evaporation of ether, the residue was recrystallized from petroleum ether and gave **6b** (25.60 g, 107 mmol, 84%) as white crystals: mp 74.5–75.0 °C; 90-MHz ^{1}H MMR ($CDCl_3$) δ 1.13 (t, 6 H, *J* = 7 Hz, CH_3), 3.24 (q, 4 H, NCH_2), 5.41 and 5.85 (2 d, 2 H, *J* = 11 and 18 Hz, CH_2=), 6.75 (dd, 1 H, –CH=), 7.45–7.81 (m, 4 H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ 14.2 (CH_3), 42.0 (NCH_2), 117.0 (vinyl, CH_2=), 126.6 (Ar, C3), 127.3 (Ar, C2), 135.4 (vinyl, –CH=), 139.3 (Ar, C4), 141.4 (Ar, C1); IR (KBr, cm^{-1}) 1596, 1469, 1331, 1200, 1152, 1089, 1019, 990, 933, 850, 700. Anal. Calcd for $C_{12}H_{17}NO_2S$: C, 60.22; H, 7.16; N, 5.85; S, 13.40. Found: C, 60.17; H, 7.44; N, 5.78; S, 13.07.

***N*-Methyl-*N*′-[(4-vinylphenyl)sulfonyl]piperazine (6c).** To a mechanically stirred solution of *N*-methylpiperazine (13.40

g, 134 mmol) and 5% NaOH solution (200 mL), 4-vinylbenzenesulfonyl chloride (27.14 g, 134 mmol) in ether (100 mL) was added dropwise with cooling in an ice bath over 30 min, and then mixture was stirred vigorously overnight at room temperature. The aqueous layer was extracted three times with diethyl ether. The combined ether layer was washed three times with water and then dried over $MgSO_4$. Concentration of the organic solution under reduced pressure gave slightly yellow crystals of **6c** (30.2 g, 114 mmol, 89%). Recrystallization from ethanol ten times gave **6c** (4.30 g, 16.2 mmol, 12%) as pure white crystals: mp 115.5–116.5 °C; 90-MHz ^1H NMR ($CDCl_3$) δ 2.28 (s, 3 H, NCH_3), 2.50 (t, 4 H, J = 5 Hz, CH_2NCH_3), 3.06 (t, 4 H, J = 5 Hz, SO_2NCH_2), 5.44 and 5.87 (2 d, 2 H, J = 11 and 18 Hz, $CH_2{=}$), 6.76 (dd, 1 H, $-CH{=}$), 7.48–7.76 (m, 4 H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ 45.5 (NCH_3), 45.7 (CH_2NCH_3), 53.9 (SO_2NCH_2), 117.3 (vinyl, $CH_2{=}$), 126.5 (Ar, C3), 128.0 (Ar, C2), 134.2 (Ar, C4), 135.2 (vinyl, $-CH{=}$), 142.0 (Ar, C1); IR (KBr, cm^{-1}) 2851, 1596, 1453, 1350, 1331, 1286, 1168, 1152, 1095, 942, 848, 733. Anal. Calcd for $C_{13}H_{18}N_2O_2S$: C, 58.62; H, 6.81; N, 10.52; S, 12.04. Found: C, 58.50; H, 6.57; N, 10.43; S, 11.34.

Monomer Purification. After careful recrystallization, the purified monomer was dried over P_2O_5 for 48 h at ambient temperature in an apparatus equipped with a breakseal under vacuum (10^{-6} mmHg) and then diluted with dry THF. The resulting monomer solutions (0.3–0.5 M in THF) were stored at −30 °C until ready to use for the anionic polymerization.

Polymerization Procedures. All polymerizations were carried out at low temperature with shaking under high-vacuum conditions in the all-glass apparatus equipped with breakseals as previously reported.[37] The polymerization was quenched with methanol. The reaction mixture was concentrated, redissolved in THF, and then poured into a large excess of water to precipitate the polymers. Polymers collected by filtration were purified by reprecipitation twice with a petroleum ether–THF system. Poly(**6**)s thus obtained were characterized by ^1H and ^{13}C NMR, IR, and elemental analysis. The following is the full list.

Poly(6a): 90-MHz ^1H NMR (DMF-d_7) δ 1.2–2.2 (m, 3 H, CH_2CH), 2.6 (br, 6 H, NCH_3), 6.5–7.8 (m, 4 H, aromatic); 23-MHz ^{13}C NMR (DMF-d_7) δ 38 (NCH_3), 41–46 (CH_2CH), 128–130 (Ar, C2 and C3), 133.6 (Ar, C1), 150.4 (Ar, C4); IR (KBr, cm^{-1}) 2926, 1598, 1459, 1413, 1340, 1163, 1092, 952, 777. Anal. Calcd for poly(**6a**), $(C_{10}H_{13}NO_2S)_n$: C, 56.85; H, 6.20; N, 6.63; S, 15.17. Found: C, 57.39; H, 6.19; N, 6.34; S, 13.44. T_g = 187 °C.

Poly(6b): 90-MHz ^1H NMR ($CDCl_3$) δ 0.8–2.1 (overlapping m, 3 H, CH_2CH), 1.1 (br, 6 H, CH_3), 3.2 (br, 4 H, NCH_2), 6.3–7.8 (m, 4 H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ 14.1 (CH_3), 41–43 (CH_2CH), 42.1 (NCH_2), 127.1 and 127.8 (Ar, C2 and C3), 138.9 (Ar, C1), 148.9 (Ar, C4); IR (KBr, cm^{-1}) 2978, 2936, 1598, 1333, 1202, 1155, 1092, 1019, 935, 785, 700. Anal. Calcd for poly(**6b**), $(C_{12}H_{17}NO_2S)_n$: C, 60.22; H, 7.16; N, 5.85; S, 13.40. Found: C, 59.84; H, 7.22; N, 5.47; S, 12.90. T_g = 140 °C.

Poly(6c): 90-MHz ^1H NMR ($CDCl_3$) δ 1.1–3.4 (overlapping m, 3 H, CH_2CH), 2.24 (s, 3 H, NCH_3), 2.49 (br, 4 H, CH_2NCH_3), 2.98 (br, 4 H, SO_2NCH_2), 6.5–7.8 (m, 4 H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ 41–46 (CH_2CH), 45.8 (NCH_3 and CH_2NCH_3), 54.1 (SO_2NCH_2), 127–129 (Ar, C2 and C3), 134.1 (Ar, C1), 149.6 (Ar, C1); IR (KBr, cm^{-1}) 2886, 2798, 1598, 1455, 1380, 1288, 1168, 1152, 1087, 948, 787, 726. Anal. Calcd for poly(**6c**), $(C_{13}H_{18}N_2O_2S)_n$: C, 58.62; H, 6.81; N, 10.52; S, 12.04. Found: C, 58.29; H, 6.74; N, 9.72; S, 11.34. T_g = 171 °C.

Postpolymerization. In the all-glass apparatus in vacuo, by the reaction of oligo(α-methylstyryl)dipotassium and **6b** in THF at −78 °C for 30 min the prepoly(**6b**) was quantitatively prepared and somewhat sampled to determine the characteristics. To the residual reaction mixture at −78 °C, the second feed of **6b** in THF solution was again added and reacted for 30 min to complete the further polymerization. After quenching with methanol, both pre- and postpolymer were obtained in quantitative yield. In both cases of postpolymerization at 0 °C and that carried out with lithium countercation at −78 °C, similar results were obtained. Block copolymerizations of **6**s were performed in a similar manner.

Measurements. Infrared spectra (KBr disk) were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz ^1H, 22.53 MHz ^{13}C) in $CDCl_3$ or DMF-d_7. Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0.00) for ^1H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standard. Chemical shifts of poly(**6a**) were reported in ppm downfield relative to DMF-d_7 (δ 8.05) for ^1H NMR and (δ 162.5) for ^{13}C NMR as standard. Gel permeation chromatograms (GPC) for MWD determinations of poly(**6**)s were obtained at 40 °C with a Toyo Soda HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H$_{XL}$, G4000H$_{XL}$, and G3000H$_{XL}$) with ultraviolet (254 nm) or refractive index detection. THF or DMF was the carrier solvent at a flow rate of 0.8 mL min^{-1}. Laser light scattering measurements for weight-average molecular weight determination were performed at 25 °C with an Ootsuka Electronics SLS-600R instrument in THF solution. The glass transition temperature was measured by differential scanning calorimetry using a Perkin Elmer DSC7 apparatus and analyzed by a Perkin Elmer PC data station. The samples were first heated to 200 °C, cooled rapidly to room temperature, and then scanned again at a rate of 20 °C min^{-1}.

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(31) The 18 (initiator **8**) or 36 (initiator **9**) trimethylsilyl protons of these initiator residues in the polymers provide valuable probes for determining number-average molecular weights by ^{1}H NMR analysis. The propagating carbanion of poly(**6b**) caused no crossover reaction with **7** due to the low nucleophilicity, which indicated that the polymer contained no 1,1-bis[4'-(trimethylsilyl)phenyl]ethylene unit other than the initiator residue.

(32) Using **8** as an initiator, poly(methyl methacrylate) with a narrow MWD ($\bar{M}_w/\bar{M}_n$ = 1.02) and predicted molecular weight ($\bar{M}_n$(obsd) = 12 000 and $\bar{M}_n$(calcd) = 12 000) was quantitatively produced in THF at −78 °C. From this experiment, it is clear that **8** is a good initiator for living polymerization of methyl methacrylate.

(33) It should be mentioned that **6a** in a bulk and in a solution show the high polymerization tendency in a wide range of concentrations and temperature.[39] It is therefore necessary for purification of the monomer to take care of recrystallization.

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Registry No. **6a** (homopolymer), 60472-41-5; **6b** (homopolymer), 126428-08-8; **6b**/styrene (block copolymer), 142723-51-1; **6b**/isoprene (block copolymer), 142723-52-2; **6b**/2VP (block copolymer), 142723-53-3; **6b**/MMA (block copolymer), 126428-09-9; **6b**/*t*BuMA (block copolymer), 142723-54-4; **6c** (homopolymer), 142723-56-6; **6c**/styrene (block copolymer), 142723-57-7; **8**, 130985-32-9; **9**, 130985-33-0; DPE, 530-48-3; K-Naph, 4216-48-2; Li-Naph, 7308-67-0; Na-Naph, 3481-12-7; Cumyl-K, 3003-91-6; α-MeSt, 98-83-9; *n*-BuLi, 109-72-8.