3728 *Macromolecules* **1997,** *30,* 3728−3731

Anionic Polymerization of Monomers Containing Functional Groups. 9. Anionic Polymerizations of 4-Vinylphenyl Methyl Sulfide, 4-Vinylbenzyl Methyl Sulfide, and 2-(4′-Vinylphenyl)ethyl Methyl Sulfide

Akira Hirao,* Hideki Shione, Takashi Ishizone, and Seiichi Nakahama

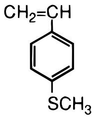
Department of Polymer Chemistry, Tokyo Institute of Technology,
2-12-1, Ohokayama, Meguro-ku, Tokyo 152, Japan

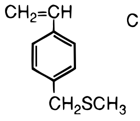
Received February 3, 1997; Revised Manuscript Received March 31, 1997⊗

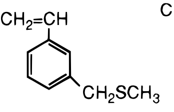
ABSTRACT: The anionic polymerization of 4-vinylphenyl methyl sulfide **(1)**, (4-vinylphenyl)methyl methyl sulfide **(2)**, and 2-(4′-vinylphenyl)ethyl methyl sulfide **(3)** were carried out in THF at −78 °C. Monomers **1** and **3** were found to undergo anionic living polymerization with typical initiators such as lithium and potassium naphthalenides, *sec*-butyllithium, and *sec*-butyllithium capped with α-methylstyrene. The resulting polymers possessed molecular weights predictable from [monomer] to [initiator] ratios and narrow molecular weight distributions, the values of M_w/M_n being less than 1.1. In contrast, attempts to polymerize **2**, which has a benzyl sulfide structure, failed. No appreciable polymerization occurred with **2** under the identical conditions used for the successful polymerizations of **1** and **3**. For this reason, we proposed the reaction mechanism based on a 1,6-elimination of anion, followed by the formation of the very reactive *p*-xylylene intermediate.

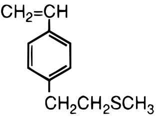
Introduction

Although sulfides, the so-called thioethers, are usually synthesized by the methods analogous to those used for synthesis of ethers, they are not similar to ethers in behavior and reactivity.[1] For example, sulfides are readily oxidized to convert sulfoxides and sulfones of tetra- and hexavalent sulfur compounds which do not exist in the oxygen analogues. A C−S bond is cleaved relatively easily with both nucleophiles and electrophiles. Furthermore, sulfides are transformed into α-sulfenyl carbanions, ylides, and sulfonium salts, which are very important intermediates in organic synthesis. Thus, sulfides are generally more reactive than ethers under normal reaction conditions. These high reactivities of sulfides provide the basis for many of the uses of sulfides as starting materials in the synthesis of organosulfur compounds. Accordingly, polymers containing sulfide functions are expected to have many advantages and potential applications as reactive functional polymers. 4-Vinylphenyl methyl ether (4-methoxystyrene) was previously reported to undergo anionic living polymerization to afford the polymers with well-controlled molecular weights and narrow molecular weight distributions.[2] On the other hand, no example of the anionic polymerization of 4-vinylphenyl methyl sulfide **(1)**, a sulfur analogue of 4-methoxystyrene, have so far been reported. Very recently, we have reported the first anionic living polymerization of 4-vinylphenyl *tert*-butyldimethylsilyl sulfide and 2-(4′-vinylphenyl)ethyl *tert*-butyldimethylsilyl sulfide, which are structurally similar to **1**.[3] This suggests the possibility to produce a living polymer from **1** by means of anionic polymerization. In this paper the anionic polymerizations of the following four monomers containing the methyl sulfide function will be developed with the expectation that they undergo living polymerization. The monomers employed here are **1** and its derivatives, (4-vinylphenyl)methyl methyl sulfide **(2a)**, (3-vinylphenyl)methyl methyl sulfide **(2b)**, and 2-(4′-vinylphenyl)ethyl methyl sulfide **(3)**.


(1)


(2a)


(2b)


(3)

Experimental Section

General polymerization techniques and measurements used are those previously reported.[4]

Materials. The monomers of **1**, **2a**, and **3** were synthesized by the reactions of the corresponding *Grignard* reagents with dimethyl disulfide in THF at 25 °C for 2−5 h. The following is a typical synthetic experiment.

4-Vinylphenyl Methyl Sulfide (1). A solution of dimethyl disulfide (13.5 g, 144 mmol) in dry ether (30 mL) was added dropwise at 0 °C to the *Grignard* reagent prepared from 4-chlorostyrene (15.1 g, 108 mmol) and Mg (3.46 g, 142 mmol) in dry THF (40 mL). The mixture was stirred at 25 °C for 3 h. After the usual workup, the remaining oil was fractionally distilled at 65−66 °C (0.30 mmHg) to give 12.4 g (77%) of **1** as a colorless liquid (lit.[5] 78−83 °C/0.85 mmHg): ^{1}H NMR ($CDCl_3$) δ 2.48 (3H, s, SCH_3), 5.21, 5.70 (2H, 2d, $J = 10.8, 17.6$ Hz, CH_2=), 6.68 (1H, dd, CH=), 7.14−7.40 (4H, m, Ar); ^{13}C NMR ($CDCl_3$) δ 15.7 (SCH_3), 113.1 (CH_2=), 126.6 (Ar, C2, C3), 134.5 (Ar, C1), 136.2 (CH=), 138.0 (Ar, C4); IR 1625, 1425, 991, 905 cm^{-1}. Anal. Calcd for $C_9H_{10}S$: C, 71.94; H, 6.72; S, 21.34. Found: C, 71.72; H, 6.84; S, 21.27.

(4-Vinylphenyl)methyl Methyl Sulfide (2a). 2a was synthesized by the reaction of 4-vinylbenzyl magnesium chloride with dimethyl disulfide. It was obtained at 69−70 °C (0.40 mmHg) in 72% yield as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 1.98 (3H, s, SCH_3), 3.65 (2H, s, S−CH_2−Ar), 5.22, 5.72 (2H, 2d, $J = 10.8, 17.6$ Hz, CH_2=), 6.70 (1H, dd, CH=), 7.19−7.42 (4H, m, Ar); ^{13}C NMR ($CDCl_3$) δ 14.8 (SCH_3), 38.0 (Ar−CH$_2$−S), 113.5 (CH_2=), 126.2 (Ar, C2), 129.0 (Ar, C3), 136.3 (Ar, C1), 136.4 (CH=), 137.9 (Ar, C4); IR 1629, 1436, 1425, 990, 907 cm^{-1}. Anal. Calcd for $C_{10}H_{12}S$: C, 73.10; H, 7.38; S, 19.52. Found: C, 72.74; H, 7.32; S, 19.42.

2-(4′-Vinylphenyl)ethyl Methyl Sulfide (3). 3 was synthesized by the reaction of 2-(4′-vinylphenyl)ethyl magnesium bromide with dimethyl disulfide. It was obtained at 72−73 °C (0.50 mmHg) in 71% yield as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 2.12 (3H, s, SCH_3), 2.66−3.01 (4H, m, S−CH_2−CH_2−Ar), 5.20, 5.70 (2H, 2d, $J = 10.8, 17.6$ Hz, CH_2=), 6.70 (1H, dd, CH=), 7.16, 7.36 (4H, 2d, $J = 8.3, 8.1$ Hz, Ar); ^{13}C NMR

⊗ Abstract published in *Advance ACS Abstracts,* May 15, 1997.

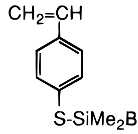
S0024-9297(97)00152-6 CCC: $14.00

($CDCl_3$) δ 16.7 (SCH_3), 35.7 (Ar−CH_2−CH_2−S), 35.8 (Ar−CH_2−CH_2−S), 113.2 (CH_2=), 126.3 (Ar, C2), 128.6 (Ar, C3), 135.8 (Ar, C1), 136.6 (CH=), 140.2 (Ar, C4); IR 1629, 1436, 1426, 990, 907 cm^{-1}. Anal. Calcd for $C_{11}H_{14}S$: C, 74.09; H, 7.93; S, 17.98. Found: C, 74.08; H, 8.09; S, 17.69.

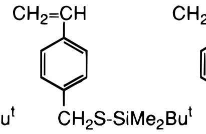
Measurements. ^1H and ^{13}C NMR spectra were recorded on JEOL FX-90Q (90 MHz) and JEOL GSX-500 (500 MHz) spectrometers in $CDCl_3$. Size exclusion chromatrography (SEC) was obtained at 40 °C with a TOSOH HLC 8020 instrument with UV (254 nm) or refractive index detection. THF was a carrier solvent at a flow rate of 1.0 mL/min. Three polystyrene−divinylbenzene gel columns (TSKgel G4000H_{XL}, G3000H_{XL}, and G2000H_{XL}) were used. Calibration curves were made to determine M_n and M_w/M_n values with standard polystyrene samples.

Results and Discussion

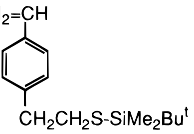
As mentioned in the Introduction, we have recently reported the first successful demonstration of the anionic living polymerization of the styrene derivatives containing *tert*-butyldimethylsilyl (TBDMS) sulfide function.[3] They were 4-vinylphenyl TBDMS sulfide **(4)** and 2-(4-vinylphenyl)ethyl TBDMS sulfide **(6)**, from which new stable living polymers were produced in THF at −78 °C. These results clearly show that a relatively weak S−Si bond is stable enough under the conditions of anionic living polymerization, and active protons next to TBDMS sulfide of **6** resist proton abstraction under the same conditions. The success provided the first possible access to the synthetic route to well-defined polystyrenes with thiol side groups by deprotecting the TBDMS group from the resulting polymers.



(4)



(5)



(6)

In marked contrast to the anionic polymerization behavior of **4** and **6**, no appreciable polymerization of (4-vinylphenyl)methyl TBDMS sulfide **(5)** occurred under exactly the same conditions. We first consider that the benzylic proton might be abstracted by the carbanion at the propagating chain end, since such proton abstractions are often observed to occur between benzyl sulfides and strong bases. However, the possibility of such a reaction can be ruled out from the experimental fact that an immediate gelation of the starting living polystyrene was observed when **5** was added to difunctional dipotassium polystyryl in THF at −78 °C. We therefore proposed an alternative and more likely mechanism for the inability of **5** to polymerize. The proposed mechanistic pathway is that the carbanion at the polymer chain end may induce a 1,6-elimination to generate the very reactive *p*-xylylene intermediate, which reacts readily by radical combination to form a cross-linked polymer network, as shown in Scheme 1.

Considering the structural analogy of **4**−**6**, we felt that the monomers of **1**−**3** employed here might be similar in the behavior of the anionic polymerization. However, more attention should be paid to the anionic polymerization of **1**−**3** due to the following inherent reactions of alkyl (aryl) sulfides with strong bases. For example, hydrogens of alkyls next to the S atom of alkyl sulfides are often abstracted with strong bases such as organolithium compounds used as typical anionic initiators.[6] Reductive cleavage of sulfides is known to be brought about in good yield, especially with benzylic sulfides.[7] Furthermore, many examples appear in reductive lithiation of the phenyl sulfide derivatives with lithium naphthalenide in which the C_6H_5S−C bonds can be cleaved relatively easily.[8,9] These reactions based on alkyl and aryl sulfides may also cause an inconvenience in controlling the anionic polymerizations of **1**−**3**.

Scheme 1

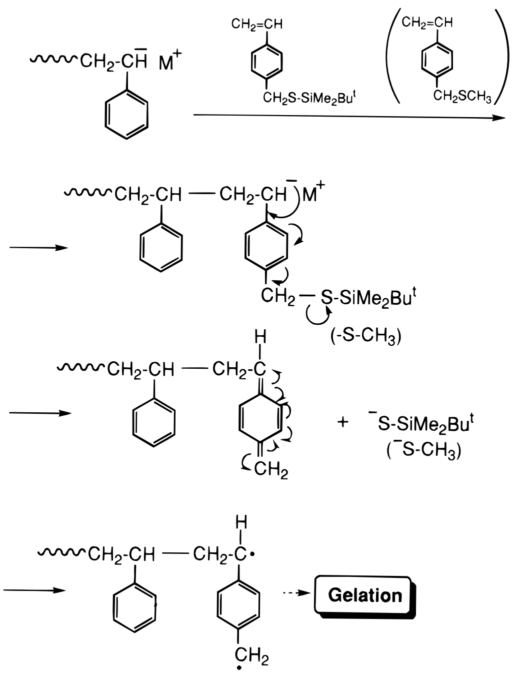


Table 1. Anionic Polymerization of 1 with *sec*-BuLi in Benzene

mmol of **1**	mmol of *sec*-BuLi	temp (°C)	yield (%)	M_n(calcd)	M_n(obsd)	M_w/M_n
5.44	0.0586	0	39	5500	9600	1.63
5.91	0.0568	20	63	9200	29500	3.93

Anionic Polymerization of 1. The polymerization of **1** was first attempted with *sec*-BuLi in benzene at either 0 or 20 °C. In each case, an orange color appeared immediately on mixing **1** into the initiator solution. The polymers were precipitated within 1 h even at 20 °C. Yields of polymers were very low for 1 h and far from complete even with a longer polymerization time up to 15 h. Polymers were obtained in 39% and 63% yield, respectively. The results are summarized in Table 1. The SEC traces showed that the resulting polymers at both 0 and 20 °C had relatively broad and multimodal distributions. Their M_n values were always higher than those calculated from [M]/[I] ratios. These results may be partly due to the inhomogeniety of the polymer in benzene. It was also suggested that some side reactions leading to chain termination reactions might occur during the course of the polymerization. Thus, it was possible that the anionic polymerization of **1** with *sec*-BuLi could take place in benzene but not far from the controlled polymerization. The polymerization of **1** was then carried out in THF at −78 °C. The initiators used were typical ones involving potassium naphthalenide, *sec*-BuLi, *sec*-BuLi capped with α-methylstyrene, and lithium naphthalenide capped with α-methylstyrene. In the case using potassium naphthalenide, an instantaneous color change to a dark red occurred upon addition of **1** into the initiator solution. The polymerization systems always showed an orange red color with each of the initiators having a lithium countercation. These

Table 2. Anionic Polymerization of 1 in THF at −78 °C[a]

mmol of **1**	initiator	amount (mmol)	M_n(calcd)	M_n(obsd)[b]	M_w/M_n
3.88	K−Nap[c]	0.0995	12 000	11 000	1.03
4.06	K−Nap	0.0626	20 000	20 000	1.03
4.43	K−Nap	0.0420	32 000	34 000	1.02
3.54	*sec*-BuLi	0.0562	13 000	11 000	1.02
4.49	*sec*-BuLi/α-MS[d]	0.0667	11 000	11 000	1.02
8.40	*sec*-BuLi/α-MS	0.0309	56 000	59 000	1.03
4.41	Li−Nap[e]	0.134	10 000	8 900	1.04

[a] Polymerizations were carried out for 30 min. Yields were 100% in all cases. [b] M_n(obsd) was obtained by VPO. [c] Potassium naphthalenide. [d] *sec*-BuLi capped with α-methylstyrene. [e] Lithium naphthalenide.

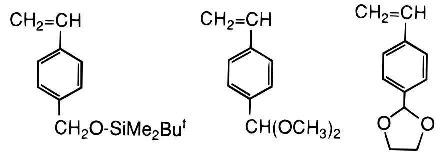
characteristic red colors strongly indicate the formation of styryl anions derived from **1** and appear to be stable in THF at −78 °C even after 24 h. Unlike the polymerization in benzene, no precipitation of polymer was observed in THF under these conditions. Yields of the polymers were quantitative in all cases after 0.5 h. The results are summarized in Table 2.

As can be seen, there is an excellent agreement between the M_n values determined by VPO and those calculated on the basis of [M]/[I] ratios. All the polymer samples had symmetrical molecular weight distributions composed of single peaks without any shoulders. Their molecular weight distributions were very narrow, the values of M_w/M_n always being less than 1.05. These results as well as the appearance of characteristic red colors in the polymerization systems clearly indicate the living character of the anionic polymerization of **1**. Obviously, any possible side reactions mentioned as before could be eliminated or suppressed under the conditions employed here. Both the methyl and phenyl sulfide functions of **1** are therefore completely stable toward the carbanions of both the initiators and the propagating chain ends in THF at −78 °C.

Anionic Polymerization of 2. The anionic polymerization of **2a** was carried out in THF at −78 °C for 0.5 h with potassium naphthalenide or potassium naphthalenide capped with α-methylstyrene. When the monomer **2a** was added to each initiator solution, the characteristic green or dark red color disappeared immediately. No polymeric material was obtained, and unreacted **2a** was recovered nearly quantitatively in each of both cases. Similarly, no appreciable polymerization took place with either *n*-BuLi or *sec*-BuLi as an initiator. Furthermore, it was observed that gelation was immediately caused at −78 °C by adding **2a** to a difunctional living polystyrene initiated with potassium naphthalenide. The IR spectrum showed that the gelatinous material consisted mostly of polystyrene, which was probably cross-linked, since it was insoluble in organic solvents. Most of the starting **2a** was also recovered from the reaction mixture in this case.

Such a polymerization behavior was exactly the same in the anionic polymerization of structurally similar **5** as mentioned in the preceding section.[3] Therefore, we propose herein the same mechanistic pathway as was seen in Scheme 1 to satisfy the polymerization behavior of **2a**. The polystyryl anion reacts with **2a** to produce a new anion which may induce a 1,6-elimination to generate the very reactive *p*-xylylene intermediate. It reacts readily by radical combination to form a cross-linked polymer network.

In our previous studies, the following styrenes of oxygen analogues were also observed to behave similarly in their anionic polymerizations under the identical conditions:[10,11]



Therefore, it is again ascertained here that this may be an inherent problem in the anionic polymerizations of the styrene derivatives bearing benzyl (silyl) ether and thio (silyl) ether linkages.

Obviously, the proposed mechanism can be effective for both para- and ortho-substituted styrenes. On the other hand, the meta-substituted isomer is not applicable to the mechanism. We therefore newly synthesized (3-vinylphenyl)methyl methyl sulfide **(2b)**, the meta isomer, and attempted to anionically polymerize it to support the mechanism proposed above.

The anionic polymerization of **2b** was carried out in THF at −78 °C for 0.5 h with either *sec*-BuLi capped with α-methylstyrene or potassium cumyl. Although the characteristic red colors of both the initiator solutions disappeared soon after mixing with **2b**, THF-soluble polymers were obtained in 58 and 56% yields, respectively. As listed in Table 3, the M_n values of the polymers were 13 000 and 5300, respectively, as estimated by SEC and were higher than those calculated from [M]/[I] ratios. Their SEC chromatograms showed multimodal distributions. Obviously, side reactions leading to transfer and/or termination occur competitively during the course of polymerization of **2b**. However, the fact that THF-soluble polymers were obtained in relatively good yields is different from the result obtained in the polymerization of **2a**, the para-substituted monomer. Therefore, an elimination of the methanethiolate anion followed by the generation of the xylylene intermediate proposed above may be ruled out in this case. Instead, benzylic proton abstraction may possibly take place concurrently with the polymerization.

Table 3. Anionic Polymerization of 2b in THF at −78 °C

mmol of **2b**	initiator	amount (mmol)	yield (%)	M_n(calcd)	M_n(obsd)[a]	M_w/M_n
2.04	*sec*-BuLi/ α-MS[d]	0.0639	58	5800	13000	2.08
2.20	cumyl−K[c]	0.0715	56	5000	6300	3.00

[a] M_n(obsd) was estimated by SEC. [b] *sec*-BuLi capped with α-methylstyrene. [c] Potassium cumyl.

Anionic Polymerization of 3. The anionic polymerization of **3** was carried out in THF at −78 °C with various initiators. When **3** in THF was added to each of the initiator solutions, the mixtures always exhibited an orange red and a dark red color with use of the initiators having Li^+ and K^+, respectively. The polymerizations were found to be complete within 5 min by GC analysis, and yields of polymers were quantitative in all cases. The results are summarized in Table 4.

As can be seen, there is a good agreement between the M_n values observed by VPO and predicted from the ratios of [M]/[I], ranging from 8200 to 26 000. The SEC curves showed narrow molecular weight distributions of the polymers obtained with the organolithium initiators (M_w/M_n < 1.09). Somewhat broad distributions were observed in the polymers obtained with potassium naphthalenide and the capped dianion with α-methyl-

Table 4. Anionic Polymerization of 3 in THF at −78 °C[a]

mmol of **3**	initiator	amount (mmol)	M_n(calcd)	M_n(obsd)[b]	M_w/M_n
3.17	*sec*-BuLi	0.0375	15 000	12 000	1.04
2.99	*sec*-BuLi/α-MS[c]	0.0614	9 300	8 200	1.06
3.03	*sec*-BuLi/α-MS	0.0309	19 000	17 000	1.04
5.12	*sec*-BuLi/α-MS	0.0337	28 000	26 000	1.05
3.58	Li−Nap[d]	0.0742	18 000	16 000	1.09
2.37	K−Nap[e]	0.0811	12 000	11 000	1.15
3.01	K−Nap/α-MS[f]	0.0758	15 000	14 000	1.13

[a] Polymerizations were carried out for 5 min. Yields were 100% in all cases. [b] M_n(obsd) was obtained by VPO. [c] *sec*-BuLi capped with α-methylstyrene. [d] Lithium naphthalenide. [e] Potassium naphthalenide. [f] Potassium naphthalenide capped with α-methylstyrene.

Table 5. Block Copolymerization of 1 with Styrene[a]

type	1st monomer (A)	2nd monomer (B)	M_n(calcd)	M_n(obsd)[b]	M_w/M_n
B−A−B	**1**	styrene	18 000 (9 000)[c]	17 000	1.03
A−B−A	styrene	**1**	30 000 (15 000)[c]	30 000	1.03
B−A−B	**3**	styrene	19 000 (9 000)[c]	19 000	1.09

[a] Polymerizations were carried out with potassium naphthalenide in THF at −78 °C. Yields of polymers were 100% in all cases. [b] M_n(obsd) was obtained by VPO. [c] M_n(calcd) of polymer produced at the first polymerization.

styrene, although their values of M_w/M_n were still less than 1.15.[12] These results clearly indicate that the anionic polymerization of **3** proceeds in a living manner, similar to that of **1**. The success of the living polymerization also demonstrates that the alkyl sulfide functions are stable and active protons in the CH_2SCH_3 moiety are resistant to the carbanion of the living polymer derived from **3**.

Anionic Block Copolymerization of either 1 or 3 with Styrene. New block copolymer syntheses of A−B−A and B−A−B types were attempted by the sequential addition of **1** or **3** (monomer A) and styrene (monomer B) with the use of potassium naphthalenide as an initiator and vice versa. Yields of polymers were quantitative in all cases. The results listed in Table 5 show that the resulting copolymers have predictable molecular weights and compositions as well as narrow distributions of molecular weight. Thus, well-defined triblock copolymers of A−B−A and B−A−B types were successfully synthesized. Furthermore, the success in preparing B−A−B block copolymers with the desired structures also provides very strong evidence that stable living polymers are formed from both **1** and **3**. These block copolymers could possibly become novel well-defined hydrophilic−hydrohobic block copolymers containing polycationic segments by transforming the CH_3S group into the corresponding sulfonium salt.

Conclusions

The results described here demonstrate that it is possible to realize the anionic living polymerization of 4-vinylphenyl methyl sulfide **(1)** and 2-(4′-vinylphenyl)ethyl methyl sulfide **(3)** in THF at −78 °C. Furthermore, the well-defined novel block copolymers poly(**1**-*b*-styrene-*b*-**1**), poly(styrene-*b*-**1**-*b*-styrene), and poly(styrene-*b*-**3**-*b*-styrene) were successfully prepared.

The finding that no polymerization occurs with **2a**, having benzyl sulfide structure, is of particular synthetic and mechanistic significance. This is an additional example of the monomers bearing benzyl ether and/or benzyl thioether structures that might undergo a 1,6-elimination reaction of the produced anionic species, followed by generation of the reactive *p*-xylylene intermediate under the condition of anionic polymerization.

References and Notes

(1) Johns, D. N. *Comprehensive Organic Chemistry, The Synthesis and Reactions of Organic Compounds. Vol. 3. Sulphur, Selenium, Silicon, Boron, Organometallic Compounds*; Pergamon Press: Oxford, England, 1979; p 33.

(2) In the anionic polymerization of 4-methoxystyrene in toluene at 20 °C, some side reactions were previously suggested to occur by Smets and his co-workers (Geerts, J.; Van Beylen, M.; Smets, G. *J. Polym. Sci., Part A-1* **1969**, *7*, 2859). On the contrary, we found that the polymerization with *sec*-BuLi proceeded quantitatively in THF at −78 °C to afford polymers of predictable molecular weights and narrow molecular weight distributions: M_n(calcd) = 10 000 and 18 000. M_n(obsd) = 10 000 and 20 000. M_w/M_n = 1.06 and 1.05. Furthermore, well-defined A−B−A and B−A−B block copolymers were successfully synthesized by the sequential addition of 4-methoxystyrene and styrene and vice versa. These results clearly show the living character of the anionic polymerization of 4-methoxystyrene.

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

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

(5) Tanimoto,S.; Horikawa, J.; Oda, R. *Kogyo Kagaku Zasshi* **1967**, *70*, 1269.

(6) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1966**, *31*, 4097.

(7) Biellmann, J. F.; Schmitt, J. L. *Tetrahedon Lett.* **1975**, 2643 and 3269.

(8) Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* **1978**, *43*, 1064.

(9) Cohen, T.; Bhupathy, M. *Acc. Chem. Res.* **1989**, *22*, 152.

(10) Ishizone, T.; Kato, R.; Ishino, Y.; Hirao, A.; Nakahama, S. *Macromolecules* **1991**, *24*, 1449.

(11) Hirao, A.; Kitamura, K.; Takenaka, K.; Nakahama, S. *Macromolecules* **1993**, *26*, 4995.

(12) It should be mentioned that small but detectable amounts (<3%) of high molecular weight shoulders often are observed in the polymer samples. The shoulders always have molecular weights equal to twice those of the main peaks and therefore probably arise from an elimination of metal hydride from the living end followed by a coupling reaction with another living polymer. It is reported by several research groups that this dimer formation by such a coupling reaction is often observed in the anionic living polymerization of styrene.

MA970152N