Living Anionic Polymerization of

4-(4-(2-Isopropenylphenoxy)butyl)styrene: A New Dual-Functionalized Styrene Derivative Having α -Methylstyrene Functionality

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ABSTRACT: The anionic polymerization of a substituted styrene with α -methylstyryl moiety, 4-(4-(2isopropenylphenoxy)butyl)styrene (1), was carried out in THF at -78 °C with sec-BuLi as an initiator. In the anionic polymerization, only the styryl group of 1 can be selectively polymerized, and on the other hand, the α -methylstyryl moiety remains intact to afford a stable living polymer carrying α -methylstyryl functionality in each monomer unit. The resulting polymers possessed precisely controlled molecular weights and narrow molecular weight distributions. Furthermore, well-defined AB and BA diblock copolymers, poly(1)-block-polystyrene and polystyrene-block-poly(1), could also be synthesized by a twostep sequential monomer addition, namely, 1 followed by styrene, or vice versa. The anionic polymerization of the para-isomeric monomer, 4-(4-(4-isopropenylphenoxy)butyl)styrene (2), proceeded quantitatively within 5 min under similar conditions in THF at -78 °C. The resulting polymers were observed to possess precisely controlled molecular weights and narrow molecular weight distributions, but with small amounts (2-15%) of high molecular weight shoulders, which were presumably arose from the attack of the anionic species on the pendant α -methylstyrene functionality after the conclusion of the polymerization. With use of the meta-isomeric monomer 4-(4-(3-isopropenylphenoxy)butyl)styrene (3) in the polymerization with sec-BuLi, gelation occurred immediately. An insoluble polymer was obtained in 100% yield after 5 min. All attempts to obtain soluble polymers failed in the anionic polymerization of 3. We discussed such different polymerization behaviors of 1-3 in terms of electron-donation to the α -methylstyryl vinyl group via the resonance effect and steric hindrance.

Introduction

It is known that both styrene and α -methylstyrene undergo living anionic polymerization under the identical conditions to produce stable living polymers.^{1,2} The living anionic polymer of styrene thus produced readily and quantitatively initiates the polymerization of α methylstyrene and vice versa to afford well-defined AB diblock copolymers of polystyrene-*block*-poly(α -methylstyrene) as well as poly(α -methylstyrene)-*block*-polystyrene.³⁻⁶ Accordingly, the chain-end anion of living polystyrene appears similar in reactivity to that of α -methylstyrene. This indicates that α -methylstyrene cannot coexist as such with living anionic polymer of styrene.

During our studies on the living anionic polymerization of a series of functionalized styrene derivatives,^{7–10} we have recently found that the anionic polymerization of a new dual-functionalized styrene derivative with α -methylstyryl moiety, 4-(4-(2-isopropenylphenoxy)butyl)styrene, (**1**), proceeds in a living manner in THF at -78 °C with *sec*-BuLi. Indeed, the styryl group of **1** could be selectively polymerized, while the α -methylstyrene functionality remained completely intact in the polymerization. This finding may present an exciting opportunity for the synthesis of polymers of precisely controlled chain lengths as well as α -methylstyrene functionality.

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Herein, we report on the selective living anionic polymerization of **1** and the related substituted styrene derivatives with α -methylstyryl moiety. The objective of this study is to explore the possibility and limitation of living anionic polymerization of such dual-functionalized styrene derivatives with α -methylstyryl moiety as a part of our program to investigate the anionic polymerization of a series of functionalized styrene derivatives.¹¹

Experimental Section

Materials. The reagents were purchased from Aldrich Japan, unless otherwise stated. Styrene (98%), α -methylstyrene (98%), tetrahydrofuran (99%, THF), and benzene (98%) were purified using standard high-vacuum anionic polymerization techniques reported by Hadjichristidis and co-workers.¹² *sec*-BuLi (1.3 M, in cyclohexane) was used as received. Potassium naphthalenide was prepared according to the procedure previously described.¹¹

Measurements. Both ¹H (300 MHz) and ¹³C (75 MHz) NMR spectra were measured in CDCl₃ using a Bruker DPX300 spectrometer. Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0.00) for ¹H NMR and to CDCl₃ (δ 77.1) for ¹³C NMR. Size-exclusion chromatograms (SEC) were performed with a TOSOH HLC-8020 instrument with UV (254 nm) or refractive index detection. THF was used as a carrier solvent at a flow rate of 1.0 mL/min at 40 °C. Three polystyrene gel columns of bead size 5 μ m and pore size of 200, 75, and 20 Å or bead size 9 μ m and pore size of 650, 200, and 75 Å were used. These sets of the column covered the molecular weight ranges 10³-4 × 10⁵ g/mol and 10⁴-4 × 10⁶ g/mol, respectively. A calibration curve was made to determine

 $M_{\rm n}$ and $M_{\rm w}/M_{\rm n}$ values with standard polystyrenes. Static light scattering (SLS) equipped with a He–Ne laser ($\lambda = 632.8$ nm) was performed with Ohotsuka Electronics DSL-600R instrument in benzene at 25 °C. The refractive index increment (dn/ dc) in benzene at 25 °C was determined with an Ohotsuka Electronics DRM-1020 refractometer operating 632.8 nm. Vapor pressure osmometry (VPO) measurements were made with a Corona 117 instrument in benzene at 40 °C with a highly sensitive thermoelectric couple (TM-32K: sensitivity 35 000 μ V \pm 10%/1 M) and with equipment of very exact temperature control. Therefore, molecular weight can be measured up to 100 kg/mol with an error of about 5%. The apparatus constant was obtained by measuring standard polystyrene samples ($M_{\rm n} = 5.05, 10.2, 20.5, \text{ and } 45.0 \text{ kg/mol}$) and calibrating their values against M_n values. FT-IR spectra were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer.

4-(4-Bromobutyl)styrene. The title styrene derivative was synthesized by the Li_2CuCl_4 -mediated coupling reaction of 4-vinylphenylmagnesium chloride with 1,4-dibromobutane according to the similar procedure previously reported.¹³

4-(4-(2-Isopropenylphenoxy)butyl)styrene (1). The title styrene derivative was synthesized by the reaction of 4-(4bromobutyl)styrene with the sodium salt of 2-hydroxyacetophenone, followed by treatment with CH₃Ph₃PBr and potassium tert-butoxide. Under nitrogen. NaH (0.576 g. 24 mmol) was added dropwise to a dry DMF solution (50 mL) containing 4-(4-bromobutyl)styrene (5.00 g, 21 mmol) and 2-hydroxyacetophenone (3.26 g, 24 mmol) at 0 °C. The reaction mixture was stirred at 25 °C for 12 h. It was acidified with 1 N HCl, extracted with ether, and dried over MgSO₄. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using a mixture of hexane and ethyl acetate (8/2, v/v). The eluted portions showing one spot were collected, and the solvent was evaporated to afford 2-(4-(4-vinylphenyl)butoxy)acetophenone as a colorless oil (5.20 g, 18 mmol, 85%). ¹H NMR (CDCl₃) δ : 7.76–6.90 (m, 8H, HAr), 6.71 (dd, 1H, $CH_2=CH-$, J = 10.9, 17.6 Hz), 5.72 (d, 1H, CH₂=CH-, J = 17.6 Hz), 5.21 (d, 1H, CH₂=CH-, J = 10.9 Hz), 4.07 (t, 2H, -CH₂-CH₂-O-, J = 5.67 Hz), 2.70 (t, 2H, $-Ph-CH_2-CH_2-$, J = 6.87 Hz), 2.62 (s, 3H, -Ph-C(O)-CH₃), 1.85 (m, 4H, -CH₂-C).

Under nitrogen, a suspension of CH₃Ph₃PBr (2.86 g, 22 mmol) and potassium tert-butoxide (7.85 g, 26 mmol) in THF (30 mL) were stirred for 30 min; 2-(4-(4-Vinylphenyl)butoxy)acetophenone (5.20 g, 18 mmol) dissolved in dry THF (20 mL) was added dropwise to this suspension at 0 °C, and the reaction mixture was stirred at 25 °C for 12 h. Water was added to the reaction mixture, and the organic layer was extracted with ether and dried over MgSO₄. After the solvent was removed under reduced pressure, hexane was added to precipitate triphenylphoshine oxide. After filtration, hexane was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using a mixture of hexane and ethyl acetate (30/1, v/v). The eluted portions showing one spot were collected, and the solvent was evaporated to afford 1 as a colorless oil (3.73 g, 13 mmol, 72%). ¹H NMR (CDCl₃) δ: 7.34-6.87 (m, 8H, HAr), 6.69 (dd, 1H, CH₂=CH-, J = 10.9, 17.6 Hz), 5.70 (d, 1H, CH₂=CH-, J = 17.6 Hz), 5.19 (d, 1H, CH₂=CH-, J = 10.9 Hz), 5.11 (s, 1H, $-CH_2=C-CH_3$), 5.06 (s, 1H, $-CH_2=C-CH_3$), 3.98 (t, 2H, $-CH_2-CH_2-O-$, J = 5.67 Hz), 2.66 (t, 2H, $-Ph-CH_2-CH_2-$, J = 6.81 Hz), 2.12 (s, 3H, $-CH_2 = C - CH_3$), 1.80 (m, 4H, $-CH_2 - CH_3$) CH2-CH2-CH2-). ¹³C NMR (CDCl3): 156.2, 144.4, 142.0, 136.8 (CH₂=CH), 135.3, 133.0, 129.5, 128.7, 128.3, 126.3, 120.5, 115.1, 113.0 (CH2=CH), 111.9 (CH2=C(CH3)), 68.0, 35.3, 28.9, 27.9, 23.3. Anal. Calcd for C21H24O: C, 86.26; H, 8.27; O; 5.47. Found: C, 86.19; H; 8.32; O; 5.49.

4-(4-(4-Isopropenylphenoxy)butyl)styrene (2). The title styrene derivative was synthesized by the reaction of 4-(4-bromobutyl)styrene with the sodium salt of 4-hydroxyac-etophenone, followed by treatment with CH_3Ph_3PBr and potassium *tert*-butoxide, similar to the synthetic procedure employed for **1**. The styrene, **2**, was obtained in 75% yield as

Table 1. Anionic Polymerization of 1 with sec-BuLi in THF at $-78~^\circ\text{C}$ for 0.5 h^a

[1] ₀ /[<i>sec</i> -BuLi] ₀	calcd	SEC	$^{1}\text{H NMR}^{b}$	$SLS^{c}(VPO)^{d}$	$M_{\rm w}/M_{\rm n}^e$
18.2	5.38	4.76	5.40	(5.74)	1.04
47.7	14.0	12.8	13.7	(13.9)	1.02
106	31.1	24.0	31.8	32.5	1.03
215	63.0	49.2	66.7	64.5	1.03

^{*a*} Yields of polymers were quantitative in all cases. ^{*b*} M_n (¹H NMR) values were calculated from the area ratio of ¹H NMR signals corresponding to aromatic side chains (7.3–6.3 ppm) and initiator fragment (0.7–0.5 ppm). ^{*c*} M_n (SLS) values were calculated from M_w values measured by SLS (dn/dc = 0.0874, in benzene) and M_w/M_n estimated by SEC. ^{*d*} M_n (VPO) values were determined by VPO in benzene. ^{*e*} M_w/M_n values were estimated by SEC using standard polystyrene calibration curve.

a white crystal; mp 51.2–51.3 °C. ¹H NMR (CDCl₃) δ : 7.42 (d, 2H, CH₂=C(CH₃)–*H*Ar, J = 8.73 Hz), 7.36 (d, 2H, CH₂= CH–*H*Ar, J = 8.01 Hz), 7.18 (d, 2H, CH₂=CH–*H*Ar, J = 8.01 Hz), 6.87 (d, 2H, CH₂=C(CH₃)–*H*Ar, J = 8.73 Hz), 6.72 (dd, 1H, CH₂=CH–, J = 10.9, 17.6 Hz), 5.73 (d, 1H, CH₂=CH–, J = 17.6 Hz), 5.31 (s, 1H, $-CH_2$ =C–CH₃), 5.22 (d, 1H, CH₂=CH–, J = 17.6 Hz), 5.31 (s, 1H, $-CH_2$ =C–CH₃), 5.22 (d, 1H, CH₂=CH–, J = 6.87 Hz), 2.501 (s, 1H, $-CH_2$ =C–CH₃), 4.01 (t, 2H, $-CH_2$ -CH₂–O, J = 5.67 Hz), 2.70 (t, 2H, $-Ph-CH_2$ -CH₂–, J = 6.87 Hz), 2.15 (s, 3H, $-CH_2$ =C–CH₃), 1.84 (m, 4H, $-CH_2$ -CH₂–CH₂–CH₂–C, J = 6.87 Hz), 136.7, 135.4, 133.7, 128.7, 126.6, 126.3, 114.2, 113.0 (CH₂=CH), 110.6 (CH₂=C(CH₃)), 67.8, 35.4, 28.9, 27.8. Anal. Calcd for C₂₁H₂₄O: C, 86.26; H, 8.27; O; 5.47. Found: C, 86.54; H; 8.62; O; 5.84.

4-(4-(3-Isopropenylphenoxy)butyl)styrene (3). The title styrene derivative was synthesized by the reaction of 4-(4bromobutyl)styrene with the sodium salt of 3-hydroxyacetophenone, followed by treatment with CH₃Ph₃PBr and potassium tert-butoxide, similar to the synthetic procedure employed for 1. The styrene, 3, was obtained in 66% yield as a colorless oil. ¹H NMR (CDCl₃) δ : 7.41–6.84 (m, 8H, HAr), 6.76 (dd, 1H, CH₂=CH-, J=10.9, 17.6 Hz), 5.86 (d, 1H, CH₂= CH-, J = 17.6 Hz), 5.42 (s, 1H, $-CH_2 = C - CH_3$), 5.26 (d, 1H, $CH_2 = CH_{-}, J = 10.9 \text{ Hz}$, 5.14 (s, 1H, $-CH_2 = C_{-}CH_3$), 4.04 (t, 2H, $-CH_2-CH_2-O-$, J = 5.46 Hz), 2.74 (t, 2H, $-Ph-CH_2 CH_2-$, J = 6.42 Hz), 2.20 (s, 3H, $-CH_2=C-CH_3$), 1.90 (m, 4H, -CH₂-CH₂-CH₂-CH₂-). ¹³C NMR (CDCl₃): 159.1, 143.3, 142.8, 142.0, 136.7 (CH₂=CH), 135.3, 129.2, 128.7, 126.3, 118.0, 113.2, 113.0 (*C*H₂=CH), 112.7 (*C*H₂=C(CH₃)), 112.2, 67.7, 35.4, 29.0, 27.9, 21.9. Anal. Calcd for C₂₁H₂₄O: C, 86.26; H, 8.27; O; 5.47. Found: C, 86.60; H; 8.50; O; 5.90.

Anionic Polymerization of 1–3. The anionic polymerization was carried out under a high-vacuum condition (10^{-6} Torr) in sealed glass reactors with break-seals. The reactors were always prewashed with the initiator solutions after being sealed off from the vacuum line. A typical polymerization experiment was as follows: A THF (12.6 mL) solution of 1 (3.21 mmol) kept at -78 °C was added to a heptane (1.44 mL) solution of *sec*-BuLi (0.0331 mmol) through the break-seal with vigorous stirring at -78 °C. The reaction mixture was allowed to stand for additional 0.5 h at -78 °C and quenched with degassed methanol. The polymer was precipitated in methanol, reprecipitated twice from THF to methanol, and freeze-dried from its absolute benzene solution for 24 h. A polymer yield was 100%. The polymer was characterized by ¹H and ¹³C NMR, SEC, and SLS, and the results are summarized in Table 1.

Similarly, the anionic polymerizations of 1-3 were carried out in THF at -78 or -95 °C and in benzene at 25 °C.

Block Copolymerization. An AB diblock copolymer of **1** and styrene was synthesized by the sequential addition of **1** followed by styrene in a manner similar to the homopolymerization. The first stage polymerization was carried out in THF at -78 °C by mixing a THF (14.2 mL) solution of **1** (3.41 mmol) with *sec*-BuLi (0.0714 mmol) in heptane (2.11 mL). The reaction mixture was allowed to stir for an additional 0.5 h, and then a small portion was sampled to determine the

Table 2. Block Copolymerization of 1 and Styrene with
sec-BuLi in THF at -78 °Ca

first	second	$[M_1]_0/$	$[M_2]_0/$	$M_{ m n}$ ×	$M_{\rm w}$	
monomer	monomer	[I] ₀	[I] ₀	calcd	obsd ^b	$M_{\rm n}$
1	styrene	47.7	138	14.0-14.4	13.7-15.0	1.02
styrene	1	154	60.9	16.1 - 17.9	17.0 - 18.3	1.04

 a Yields of polymers were quantitative in all cases. b Molecular weights of block copolymers were determined from $M_{\rm n}$ values of the first polymers by VPO and compositions of block copolymers determined by $^1{\rm H}$ NMR.



Figure 1. SEC profiles of poly(**1**).



Figure 2. ¹H NMR spectra of 1 (A) and poly(1) (B).

molecular weight and molecular weight distribution. The second block was prepared by adding a THF (7.90 mL) solution of styrene (6.56 mmol) to the living polymer solution (0.0476 mmol) obtained at the first stage polymerization. After 0.5 h, the reaction mixture was quenched with degassed methanol, and the polymer was precipitated in methanol. A yield of polymer was quantitative. The polymer was purified by reprecipitation twice from THF to methanol and freeze-dried. The polymers obtained at the first and second stages of the polymerization were characterized by ¹H and ¹³C NMR, SEC, and SLS, and the results are summarized in Table 2.

Results and Discussion

During our studies on the anionic polymerization of the protected vinylphenol derivatives, ¹⁴ we found that the anionic polymerization of either 2-methoxy- α -methylstyrene proceeded unexpectedly sluggishly with *sec*-BuLi in THF at -78

°C. The polymeric products were not obtained in both cases after 0.5 h. Therefore, *sec*-BuLi was reacted with each of the monomers at around 1:3 molar ratios under the same conditions, and after treatment of the reaction mixtures with $(CH_3)_3$ SiCl, the reaction products were examined. Very surprisingly, both monomers were recovered nearly quantitatively, and the addition products were obtained in <5% yields. It was further confirmed by careful analyses of the reaction products that neither ortho-lithiation nor oligomerization occurred. Thus, it was found that the reactivity of the C=C bond of α -methylstyrene toward *sec*-BuLi was significantly lowered by introducing a methoxy group at either ortho or para position of the phenyl ring.

On the basis of this unexpected finding, we speculate that if the α -methylstyrene molecule was introduced into styrene skeleton via methoxy linkage and the resulting styrene monomer was treated with an anionic initiator, the selective anionic polymerization of the C=C bond of the styrene part would occur, and on the other hand, the α -methylstyrene part thus introduced would remain as such. We therefore designed a substituted styrene derivative with a α -methylstyryl moiety in such a way that the α -methylstyryl molecule was introduced into styrene skeleton by OCH₂CH₂CH₂CH₂CH₂ linkage similar to methoxy group in structure and electronic effect. The following three substituted styrene derivatives with α -methylstyryl moiety, **1**, 4-(4-(4-isopropenylphenoxy)butyl)styrene (2), and 4-(4-(3-isopropenylphenoxy)butyl)styrene (3) have been newly synthesized and polymerized under the conditions of usual anionic polymerization.



Anionic Polymerization of 4-(4-(2-Isopropenylphenoxy)butyl)styrene (1). The anionic polymerization of 1 was first carried out in THF at -78 °C for 0.5 h with *sec*-BuLi as an initiator ([1]₀/[*sec*-BuLi]₀ = 18.2). The addition of the first aliquot of 1 to *sec*-BuLi instantaneously turns to an orange color, indicating the generation of styrene-derived anion from 1. This color remains unchanged and disappeared immediately by quenching with degassed methanol. The polymer was quantitatively obtained. It was purified by reprecipitation twice from THF to methanol and freeze-dried from its absolute benzene solution.

As shown in Figure 1, SEC profile of the polymer exhibits a sharp symmetrical monomodal distribution, the M_w/M_n value being 1.04. Neither shoulder nor tailing was observed. Figure 2 shows ¹H NMR spectra of **1** and the resulting polymer. The signals at 6.69, 5.70, and 5.19 ppm corresponding to the styryl CH₂=CH protons of **1** completely disappeared, and on the other hand, the signals at 5.11 and 5.06 ppm assigned to the α -methylstyryl CH₂=C protons remained in expected



Figure 3. SEC profiles of poly(1) (A) and poly(1)-*block*-polystyrene (B).

intensities. As expected in spectrum B, all peaks appeared broader after the polymerization. New signals corresponding to the CH₂CH protons appeared at 1.1–2.0 ppm. The broad signals that newly appeared at 0.5–0.7 ppm were those of methyl protons of the initiator fragment. Furthermore, ortho-aromatic protons toward the former vinyl bond were shifted due to the polymerization. The ¹³C NMR spectra also showed that the styryl CH₂=CH carbons had completely reacted, while the resonance at 111.9 ppm assignable to the β -carbon of CH₂=C of the α -methylstyryl moiety was present as such. Thus, evidently, only the styryl group was selectively polymerized, and on the other hand, the α -methylstyryl moiety completely remained intact.

Three more sets of the polymerization were carried out at higher monomer-to-initiator ratios under the same conditions.¹⁵ The characterization results of these polymers are summarized in Table 1. Although the estimated M_n values by SEC relative to polystyrene were always somewhat smaller than those calculated from [1]₀ to [*sec*-BuLi]₀ ratios, all of the observed values of molecular weight by VPO and SLS agreed quite well with those calculated. Their molecular weight distributions were extremely narrow, and M_w/M_n values were less than 1.04. These results clearly indicate that the selective anionic polymerization of **1** proceeds in a living manner to afford polymers with precisely controlled chain lengths and α -methylstyrene functionality in each of all repeating unit.

The orange color of the styrene-derived anion remained unchanged even after 3 h. Furthermore, no change was observed in shape and molecular weight distribution at all in SEC profiles of the polymers terminated after 0.5 and 3 h. Thus, the styrene-derived anion was sufficiently stable and α -methylstyrene functionality remained as such for at least 3 h under the conditions in THF at -78 °C.

To further elucidate the living character of the polymerization of **1**, the block copolymerization of **1** and styrene was carried out with *sec*-BuLi in THF at -78 °C by a two-step sequential monomer addition, **1** followed by styrene. The first and second polymerization times were 0.5 and 0.5 h, respectively. Yields of polymers were quantitative. The results are summarized in Table 2.

Figure 3 shows SEC profiles of the polymers obtained at the first and second stages of the polymerization. The SEC peak of poly(1) obtained at the first stage of the polymerization moves toward higher molecular weight after the addition of styrene, whereas the peak of poly-(1) completely disappears. All analytical results on

Table 3. Anionic Polymerization of 2 in THF at -78 °C for 5 min^a

		$M_{ m n} imes 10^{-3}$				
$[2]_0/[I]_0$	initiator	calcd	SEC	¹ H NMR	VPO	$M_{\rm w}/M_{\rm n}$
18.6 58.2 55.3 ^d 53.3 19.1	sec-BuLi sec-BuLi sec-BuLi (α-MS) _n Li ^f K-Naph ^h	5.50 17.4 16.2 16.0 11.2	4.94 15.1 13.9 13.9 14.6	5.66 16.5 15.1 16.0	5.90 17.0 16.7 16.0 17.7	1.06^b 1.06^c 1.09^e 1.08^g 1.12^i

^{*a*} Yields of polymers were quantitative in all cases. ^{*b*} 2% Shoulder. ^{*c*} 5% Shoulder. ^{*d*} -95 °C. ^{*e*} 9% shoulder. ^{*f*} Oligo(α -methylstyryl)lithium. *n* = av 2. ^{*g*} 10% shoulder. ^{*h*} Potassium naphthalenide. ^{*i*} 15% shoulder.

molecular weights, molecular weight distributions, and composition by SEC, VPO, and ¹H NMR listed in Table 2 indicate that the block copolymerization proceeds as desired to afford the expected AB diblock copolymer of poly(1)-*block*-polystyrene. The success of this block copolymerization further confirms the living character of the polymerization of **1**. A well-defined BA diblock copolymer, polystyrene-*block*-poly(1), was also successfully synthesized by reversing the sequence of monomer addition, namely, styrene followed by **1** (see also Table 2). These results clearly indicate that the electrophilicities of **1** and styrene as well as the nucleophilicities of their living anionic polymers are very similar in reactivity.

The anionic polymerization of **1** with *sec*-BuLi was also attempted under the conditions in benzene at 25 °C. A characteristic orange color was immediately developed by the addition of **1** to *sec*-BuLi. After a few minutes, however, the color changed to a dark red in color, indicating the generation of α -methylstyrene-derived anion presumably by attack of the chain-end styrene-derived anion on the pendant α -methylstyrene functionality. The subsequent addition of the anion thus formed to the α -methylstyrene functionality among polymer chains occurred to cross-link. An insoluble polymer was obtained in 80% yield after 1 h. Thus, the selective anionic polymerization of 1 failed under the conditions in benzene at 25 °C.

Anionic Polymerization of 4-(4-(4-Isopropenylphenoxy)butyl)styrene (2). The anionic polymerization of 2 was carried out under the identical conditions in THF at -78 °C with *sec*-BuLi. In each polymerization, an orange color characteristic of the styrene-derived anion was immediately developed by the addition of 2 to *sec*-BuLi. The polymerizations were rapid and complete within 5 min. The results are summarized in Table 3.

The polymers always exhibited sharp monomodal SEC peaks along with small high molecular weight shoulders whose M_n values were doubly increased. Undoubtedly, the formation of high molecular weight shoulder was attributable to the addition reaction of the chain-end anion to the α -methylstyrene functionality among polymer chains. The high molecular weight shoulder becomes more significant with a longer reaction time to 30 min as expected (5 min; 5%; 30 min, 20%). The formation could not be completely suppressed by lowering the polymerization temperature to -95 °C, changing the initiator to $oligo(\alpha$ -methylstyryllithium) or potassium naphthalenide, and the addition of LiCl or $(C_4H_9)_2Mg$. The extents were usually in the range of 2-15% relative to the main peak area. The $M_{\rm n}$ values of the polymers determined by ¹H NMR and VPO were very close to those calculated from the ratios of $[2]_0/[sec-$ Scheme 1. Resonance Effect of Monomers 1-3



BuLi]₀. It is therefore likely that **2** undergoes the selective anionic polymerization in a living manner similar to the polymerization of **1**, and after the conclusion of the polymerization, the resulting chain-end anion attacks gradually with the pendant α -methylstyrene functionality of another polymer chain. Additional evidence for the anion attack on the α -methylstyrene functionality was provided by the observation that the orange color changed with time to a dark red in color possibly for the α -methylstyrene-derived anion.

The anionic polymerization of the meta-isomeric monomer, **3**, was more problematic. On mixing **3** with *sec*-BuLi in THF at -78 °C, gelation immediately occurred, and an insoluble polymer was obtained virtually quantitatively after 5 min. Several attempts to obtain soluble polymers from **3** by using various initiators (*sec*-BuLi/ α -methylstyrene, Li and K naphthalenides) and additives (LiCl and KO'Bu) were not successful. Thus, the influence of substituted position of the isopropenyl group is of significance on the anionic polymerization behavior.

We tentatively consider the reason for success of the selective living anionic polymerization of 1 as follows: As shown in Scheme 1, the electron density on the β -carbon of α -methylstyryl CH₂=C group becomes higher by the electron-donating character of the ortho-substituted butoxy group via the resonance effect, thereby suppressing the attack of anionic species on the α -methylstyrene functionality of 1. A similar effect can be expected in the case of 2. However, the anion attack occurred after the conclusion of the polymerization of 2, although it was found to be slow in this case. Therefore, the steric hindering effect of the ortho substituent in 1 may also play an important role to suppress the anion attack. In the case of 3 as shown in Scheme 1, the electron donation to the α -methylstyryl $CH_2=C$ group of **3** cannot be expected by the metasubstituted butoxy group. Accordingly, the α -methylstyryl CH₂=C group of **3** may be similar in reactivity to that of α -methylstyrene and therefore readily attacked by anionic species, resulting in the occurring of the cross-linking reaction.

More detailed studies on the anionic polymerization of a series of similar styrene derivatives substituted with styrene and α -methylstyrene functionalities, socalled dual-functionality monomers, are now under investigation in order to elucidate the reason for the successful polymerization of $\mathbf{1}$ and to find extra examples amenable to the selective living anionic polymerization.

Conclusions

We have successfully demonstrated the selective living anionic polymerization of 1 in THF at -78 °C with sec-BuLi in which only the styryl group can be selectively polymerized in a living manner with the remaining α -methylstyrene functionality as such. The resulting living anionic polymers of 1 were sufficiently stable to afford quite new functionalized polystyrenes with precisely controlled chain lengths and α -methylstyrene functionality in each monomer unit. Well-defined AB as well as BA functionalized diblock copolymers, poly-(1)-*block*-polystyrene and polystyrene-*block*-poly(1), were successfully synthesized by a two-step sequential monomer addition. The para-isomeric monomer, 2, also underwent the selective anionic polymerization, but the undesirable anion attack on the α -methylstyrene functionality could not be completely suppressed under the identical conditions. Gelation occurred immediately on mixing the meta-isomeric monomer. 3. with sec-BuLi. Soluble polymers were not obtained in the anionic polymerization of **3** under various conditions.

Needless to say, the synthetic significance of the present polymerization of **1** lies in the fact that a stable living anionic polystyrene carrying α -methylstyrene functionality can be obtained for the first time.¹⁶ New aspects on precise polymer syntheses will be expected by molecular design based on the living anionic polymerization of **1**, followed by further modification of the highly reactive α -methylstyrene functionality.

References and Notes

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- (14) Recently, we have successfully demonstrated that the protected vinylphenol derivatives such as 2-, 3-, and 4-methoxy-styrenes, 3- and 4-methoxymethoxystyrenes, and 4-tetrahydropyranyloxystyrene undergo living anionic polymerization with *sec*-BuLi in THF at -78 °C. On the other hand, polymerization of neither 2- nor 4-methoxy- α -methylstyrene occurred at all under the identical conditions as mentioned in this section.
- (15) The addition of Bu₂Mg was needed to kill the impurities in **1** in the polymerization where the target molecular weight was 30 kg/mol or higher molecular weight. Otherwise, polymers with higher molecular weights than those predicted were always obtained. For example, a polymer of a M_n value of 55 kg/mol ($M_w/M_n = 1.04$) was quantitatively obtained in

the polymerization of 1 with *sec*-BuLi in THF at -78 °C for 0.5 h without Bu₂Mg. (The target M_n value was 30 kg/mol in this polymerization.) Taking into consideration on the amount of impurities estimated from the results of the above polymerization, ca. 2 mol % of Bu₂Mg to 1 was added and allowed to stand for 1 h prior to the polymerization of 1. A similar additive effect of Bu₂Mg on the anionic polymerization was observed in our previous paper (see: Loykulnant, S.; Hirao, A. *Macromolecules* **2000**, *33*, 4757).

(16) The anionic polymerizations of distyryl monomers such as p-divinylbenzene and m- and p-diisopropenylbenzenes were previously reported. As expected, gelation occurred immediately in the anionic polymerization of p-divinylbenzene (see: Eschwey, H.; Burchard, W. Polymer 1975, 16, 180; J. Polym. Sci., Polym. Symp. 1975, 53, 1 and Worsfold, D. J.; Zilliox, J. G.; Rempp, R. Can. J. Chem. 1969, 47, 3379). On the other hand, soluble polymers with relatively narrow molecular weight distributions were obtained at relatively low conversion (~50%) in the anionic polymerization of diisopropenylbenzenes, but branching and cross-linking occurred at higher conversions (see: Lutz, P.; Beinert, G.; Rempp, P. Makromol. Chem. 1982, 183, 2787; Okamoto, A.; Mita, I. J. Polym. Sci., Polym. Chem. Ed. 1978, 16, 1187).

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