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Anionic Polymerization of New Dual-Functionalized Styrene and α-Methylstyrene Derivatives Having Styrene or α-Methylstyrene Moieties

Akira Hirao,[*1] *Masahiro Kitamura,*[1] *Mayumi Hayashi,*[2] *Surapich Loykulnant,*[3] *Kenji Sugiyama*[1]

[1] Polymeric and Organic Materials Department, Graduate School of Science and Engineering, Tokyo Institute of Technology, H-127, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152-8552, Japan
Fax: (+81) 3 5734 2888; E-mail: ahirao@polymer.titech.ac.jp
[2] Petrochemicals Research Laboratory, Sumitomo Chemical Co., Ltd. 2-1, Kitasode, Sodegaura-city, Chiba 299-0295, Japan
[3] National Metal and Materials Technology Center, 73/1, Rama VI Road, Rajdhevee, Bangkok 10400, Thailand

Summary: Anionic polymerizations of four new dual-functionalized styrene and α-methylstyrene derivatives, 3-(4-(4-isopropenylphenoxy)butyl)styrene (**4**), 3-(4-(2-isopropenylphenoxy)butyl)-α-methylstyrene (**5**), 4-(4-(4-isopropenylphenoxy)butyl)-α-methylstyrene (**6**), and 4-(4-(2-vinylphenoxy)butyl)styrene (**7**), were carried out in THF at -78 °C with *sec*-BuLi as an initiator. Both **4** and **5** underwent anionic polymerization in a living manner to quantitatively afford functionalized polystyrenes and poly(α-methylstyrene)s having α-methylstyrene moiety in each monomer unit and precisely controlled chain lengths. On the other hand, insoluble polymers were obtained by the anionic polymerization of **6** and **7** under the same conditions. The positional effect of substituent on anionic polymerization was discussed.

Keywords: dual-functionalized styrene derivatives; living anionic polymerization; narrow molecular weight distribution; predictable molecular weight; selective living anionic polymerization

Introduction

It is well known that both styrene and α-methylstyrene undergo living anionic polymerization to produce the corresponding living anionic polymers under the identical conditions, for example, in THF at -78 °C. Although the polymerization rate of styrene is much faster than that of α-methylstyrene under such conditions, the resulting living polystyrene readily and quantitatively initiates the polymerization of α-methylstyrene and *vice-versa.*[1-6] This indicates that the living anionic polymer of styrene is similar in reactivity to that of α-methylstyrene and therefore α-methylstyrene is not able to survive as such with living anionic polymer of styrene.

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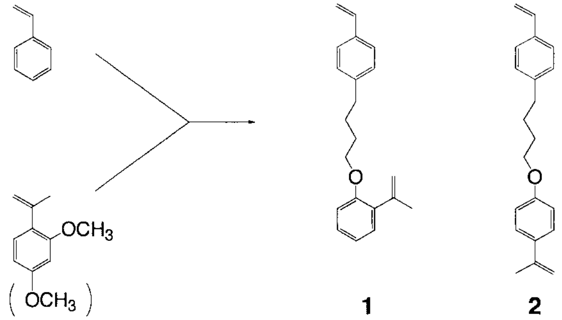
We have recently found that the anionic polymerization of either *o*- or *p*-methoxy-α-methylstyrene proceeds extremely sluggishly with *sec*-butyllithium (*sec*-BuLi) in THF at -78 °C and no polymeric material was obtained at all in either case after 6 h. Furthermore, neither the polymerization nor even the addition reaction of *o*-methoxy-α-methylstyrene with polystyryllithium occurred under the same conditions. Thus, the reactivity of α-methylstyrene toward anionic species was remarkably lowered by the introduction of methoxy group at either ortho or para position of the phenyl ring.[7-8]

On the basis of this finding, we considered that if styrene and either *o*- or *p*-methoxy-α-methylstyrene were linked to synthesize new dual-functionalized styrene derivatives having α-methylstyrene moiety and the resulting monomers were treated with an anionic initiator, the styrene parts would undergo living anionic polymerization with the α-methylstyrene moieties remaining as such. Actually, we have recently synthesized and anionically polymerized two new dual-functionalized styrene derivatives having α-methylstyrene moieties, 4-(4-(2-isopropenylphenoxy)butyl)styrene (**1**) and 4-(4-(4-isopropenylphenoxy)butyl)styrene (**2**) whose α-methylstyrene moieties are linked with the styrene parts by the butoxy ($OCH_2CH_2CH_2CH_2R$) group similar to methoxy one in structure and electronic effect, as illustrated in Scheme 1.[9]

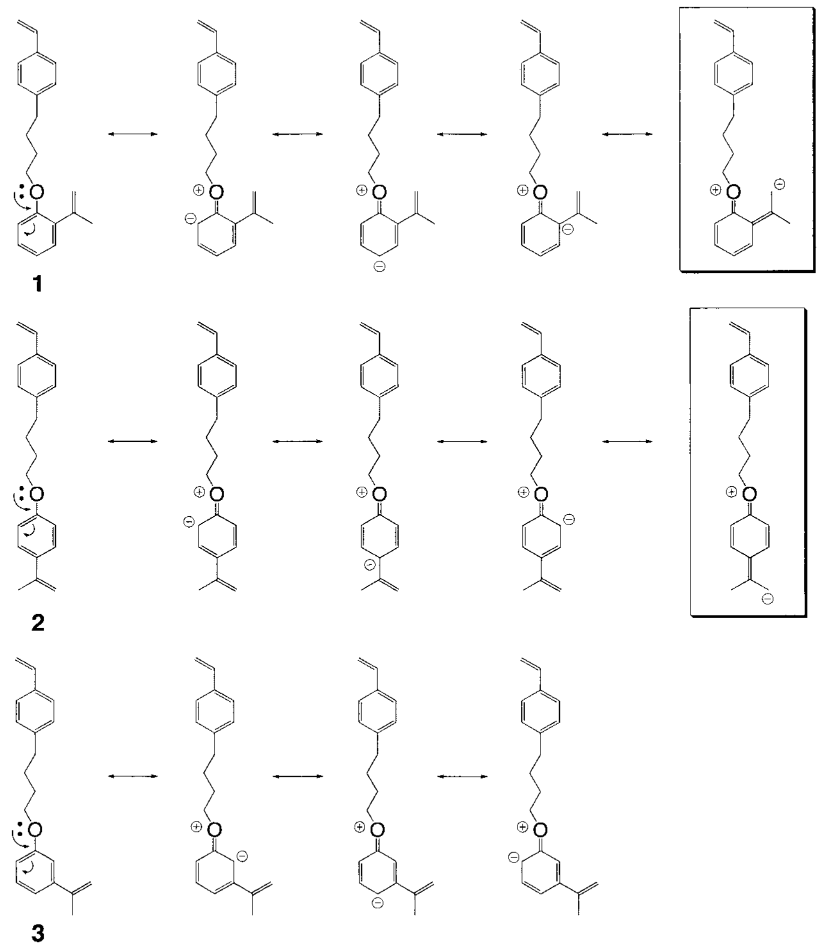


Scheme 1. Dual functionalized styrene derivatives having (-methylstyrene moiety.

As expected, the anionic polymerization of **1** with *sec*-BuLi in THF at -78 °C was quite successful in proceeding in a living manner to afford a stable living functionalized polystyrene having α-methylstyrene moiety in each monomer unit. Furthermore, both well-defined AB and BA diblock copolymers of **1** and styrene were successfully prepared. Similarly, the anionic polymerization of **2** also proceeded in a living manner. In this polymerization, however, the α-methylstyrene moiety was slowly attacked by the propagating chain-end styrene-derived anion mainly after the polymerization. Thus, the resulting living polymer was not so stable as would be expected from the reactivity of model monomer. Nevertheless, new functionalized polystyrenes having α-methylstyrene moiety in each monomer unit as well as precisely controlled chain lengths could be obtained by the careful termination of the living anionic polymer, although they usually included small amounts (2 ~ 5%) of high molecular weight shoulders removable by fractional precipitation.

It thus became possible to polymerize selectively only the styrene part in the presence of the α-methylstyrene moiety by linking both the groups *via* a butoxy group. The success of the selective living anionic polymerization of **1** and **2** can be explained by the resonance and steric hindering effects of their butoxy groups. As shown in Scheme 2, the electron density on β-carbon of α-methylstyryl CH_2=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 (*sec*-BuLi and the propagating chain-end anion) on the α-methylstyrene moiety of **1**. A similar resonance effect can be expected in the case of **2**. In this case, however, the anion attack gradually occurred after the polymerization. Therefore, the steric hindering effect of the *ortho*-substituent in **1** may also play an important role to suppress the anion attack. (The case of the *meta* isomer will be discussed in the proceeding section).

Herein, we report on the synthesis of additional four dual-functionalized styrene and α-methylstyrene derivatives structurally similar to **1** and **2** and their possibility of selective living anionic polymerization. More detailed studies on the anionic polymerization of this type of the dual-functionalized styrene derivatives are helpful to elucidate the successful reason for the success of this procedure and to discover more dual-functionalized monomers amenable to the selective living anionic polymerization.[10]



Scheme 2. Resonance effect for monomers **1** - **3**.

Experimental Section

Materials

All reagents were purchased from Aldrich, Japan unless otherwise stated. THF was distilled over $LiAlH_4$ under an atmosphere of nitrogen. It was then distilled from its sodium naphthalenide solution on the high vacuum line (10^{-6} torr). Benzene was washed with *conc*-H_2SO_4 and H_2O, and dried over $MgSO_4$. It was distilled over CaH_2 twice under nitrogen and finally distilled from its butyllithium solution containing a small amount of 1,1-diphenylethylene on the high vacuum line. Dual-functionalized styrene derivatives, 4-

(4-(2-isopropenylphenoxyl)butyl)styrene (**1**), 4-(4-(4-isopropenylphenoxyl)butyl)styrene (**2**), and 4-(4-(3-isopropenylphenoxyl)butyl)styrene (**3**) were synthesized according to the method previously reported.[9]

3-(4-Bromobutyl)styrene

To an ice-cooled THF solution (8 mL) containing 1,4-dibromobutane (90.7 g, 420 mmol) and Li_2CuCl_4 (0.80 mmol) were added dropwise the Grignard reagent prepared from 3-bromostyrene (10.2 g, 55.7 mmol) and magnesium (2.03 g, 83.6 mmol) in THF (40 mL) under nitrogen. The resulting mixture was stirred at 25 °C for 12 h. It was then acidified with 2N HCl, extracted with chloroform, and dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by flash column chromatography (hexanes) yielded the title styrene derivative (9.44 g, 39.5 mmol, 71 % yield) as colorless liquid. 300MHz ^1H NMR ($CDCl_3$): δ = 7.11-7.30 (m, 4H, Ar), 6.75 (dd, 1H, J = 11 Hz and 18 Hz, $CH_2{=}C\underline{H}$), 5.28 and 5.79 (2d, 2H, $C\underline{H}_2{=}CH$), 3.47 (t, 2H, CH_2Br), 2.68 (t, 2H, Ar-$C\underline{H}_2$), 1.78 1.99 (m, 4H, $C\underline{H}_2C\underline{H}_2$). 75MHz ^{13}C NMR ($CDCl_3$): δ =142.1, 137.7, 128.7, 128.0, 126.4, 123.9 (Ar), 137.0 ($CH_2{=}\underline{C}H$), 113.8 ($\underline{C}H_2{=}CH$), 35.0 ($\underline{C}H_2Br$), 33.7 (Ar-$\underline{C}H_2$), 32.3, 29.9 ($\underline{C}H_2\underline{C}H_2$).

3-(4-(4-Isopropenylphenoxyl)butyl)styrene (4)

Under nitrogen, NaH (0.634 g, 26.4 mmol) was added portionwise to a DMF (50 mL) solution of 4-isopropenylphenol (2.95 g, 22.0 mmol) and 3-(4-bromobutyl)styrene (5.00 g, 20.9 mmol) at 0 °C. The reaction mixture was allowed to gradually warm up to 25 °C and stir for further 12 h. It was neutralized with 2N HCl, extracted with chloroform, and dried over $MgSO_4$. After removal of solvents, flash column chromatography (hexanes/benzene = 4/1, v/v) gave **4** (5.07 g, 17.4 mmol, 83 % yield) as a white wax. 300MHz ^1H NMR ($CDCl_3$): δ = 6.91-7.46 (m, 8H, Ar), 6.77 (dd, 1H, J = 11 Hz and 18 Hz, $CH_2{=}C\underline{H}$), 5.29 and 5.81 (2d, 2H, $C\underline{H}_2{=}CH$), 5.05 and 5.35 (d, 2H, $C\underline{H}_2{=}CCH_3$), 4.04 (t, 2H, CH_2O), 2.75 (t, 2H, Ar-$C\underline{H}_2$), 2.19 (s, 3H, CH_3), 1.88 (m, 4H, $C\underline{H}_2C\underline{H}_2$). 75MHz ^{13}C NMR ($CDCl_3$): δ =158.6, 137.7, 137.0, 133.7, 128.6, 128.1 126.6, 126.4, 123.8, 114.2 (Ar), 142.6 ($CH_2{=}\underline{C}CH_3$), 142.5 ($CH_2{=}\underline{C}H$), 113.7 ($\underline{C}H_2{=}CH$), 110.6 ($\underline{C}H_2{=}CCH_3$), 67.8 (CH_2O), 35.6 (Ar-$\underline{C}H_2$), 27.9, 28.9 ($\underline{C}H_2\underline{C}H_2$), 22.0 ($CH_3$). Anal. Calcd for $C_{21}H_{24}O$: C, 86.26; H, 8.27; O, 5.47. Found: C, 85.54; H, 8.62; O, 5.84.

3-(4-Bromobutyl)-α-methylstyrene

The title α-methylstyrene derivative was obtained by the reaction of the Grignard reagent of 3-bromo-α-methylstyrene (10.5g, 53.3 mmol) with 1,4-dibromobutane (57.6 g, 267 mmol) by the method similar to that used in the case of 3-(4-bromobutyl)styrene. After usual work-up, column chromatography (hexanes) yielded the title compound (9.44 g, 37.3 mmol, 70% yield) as a colorless liquid. 300MHz ^{1}H NMR ($CDCl_3$): δ = 7.13-7.37 (m, 4H, Ar), 5.13 and 5.41 (2d, 2H, $C\underline{H}_2{=}CCH_3$), 3.47 (t, 2H, CH_2Br), 2.70 (t, 2H, Ar-$C\underline{H}_2$), 2.21 (s, 3H, CH_3), 1.79 2.00 (m, 4H, $C\underline{H}_2C\underline{H}_2$). 75MHz ^{13}C NMR ($CDCl_3$): δ = 143.4 ($CH_2{=}\underline{C}CH_3$), 141.7, 141.4, 128.3, 127.5, 125.6, 123.3 (Ar), 112.4 ($\underline{C}H_2{=}CCH_3$), 35.1 (CH_2Br), 33.7 (Ar-$\underline{C}H_2$), 32.3, 29.9 ($\underline{C}H_2\underline{C}H_2$).

3-(4-(2-Isopropenylphenoxyl)butyl)-α-methylstyrene (5)

The title α-methylstyrene derivative was synthesized by the Wittig reaction of methylene triphenylphosphorane with 2-(4-(3-isopropenylphenyl)butoxy)acetophenone prepared from the Williamson reaction of 3-(4-bromobutyl)-α-methylstyrene with 4-hydroxyacetophenone. Under nitrogen, NaH (0.634 g, 26.4 mmol) was added portionwise to a DMF (50 mL) solution of 4-hydroxyacetophenone (3.00 g, 22.1 mmol) and 3-(4-bromobutyl)-α-methylstyrene (5.08 g, 20.1 mmol) at 0 °C. The reaction mixture was allowed to gradually warm up to 25 °C and stir for further 12 h. It was neutralized with 2H HCl, extracted with chloroform, and dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by flash column chromatography (hexanes/ethyl acetate = 9/1, v/v) yielded 2-(4-(3-isopropenylphenyl)butoxy)acetophenone as colorless liquid. The thus obtained 2-(4-(3-isopropenylphenyl)butoxy)acetophenone (5.26 g, 17.1 mmol) dissolved in THF (20 mL) was added dropwise at 0 °C to a THF (30 mL) solution of methylene triphenylphosphorane prepared from methyltriphenylphosphonium bromide (7.32 g, 20.5 mmol) and potassium *tert*-butoxide (2.53 g, 22.6 mmol) under nitrogen. The reaction mixture was stirred at 25 °C for overnight and quenched with water. The organic layer was extracted with ether and dried over $MgSO_4$. It was concentrated and poured into hexane to remove triphenylphosphine oxide. After removal of solvents, flash column chromatography (hexanes/ethyl acetate = 15/1, v/v) gave **5** as a colorless liquid (4.44 g, 14.5 mmol, 85% yield). 300MHz ^{1}H NMR ($CDCl_3$): δ = 6.88-7.34 (m, 8H, Ar), 5.12 and 5.40 (d, 2H, $C\underline{H}_2{=}C(CH_3)C_6H_4O$), 5.12 and 5.16 (d, 2H, $C\underline{H}_2{=}C(CH_3)C_6H_4CH_2$), 4.04 (t, 2H, CH_2O), 2.74 (t, 2H, Ar-$C\underline{H}_2$), 2.20 (s, 3H, $CH_2{=}C(C\underline{H}_3)C_6H_4CH_2$), 2.18 (s, 3H, $CH_2{=}C(C\underline{H}_3)C_6H_4O$), 1.89 (m, 4H, $C\underline{H}_2C\underline{H}_2$). 75MHz ^{13}C NMR ($CDCl_3$): δ = 156.2, 142.2, 141.4, 132.9, 129.5, 128.3, 128.3, 127.6, 125.7, 123.1, 120.5, 111.8 (Ar), 144.4 ($CH_2{=}\underline{C}(CH_3)C_6H_4O$), 143.5 ($CH_2{=}\underline{C}(CH_3)C_6H_4CH_2$), 115.1 ($\underline{C}H_2{=}C(CH_3)C_6H_4O$), 112.4 ($\underline{C}H_2{=}C(CH_3)C_6H_4CH_2$), 68.0 ($CH_2O$), 35.7 (Ar-$\underline{C}H_2$), 29.0, 28.0 ($\underline{C}H_2\underline{C}H_2$), 23.3 ($CH_2{=}C(\underline{C}H_3)C_6H_4O$), 22.0 ($CH_2{=}C(\underline{C}H_3)C_6H_4CH_2$). Anal. Calcd for $C_{22}H_{26}O$: C, 86.23; H, 8.55; O, 5.22. Found: C, 86.12; H, 8.66; O, 5.22.

*4-(4-(4-Isopropenylphenoxyl)butyl)-α-methylstyrene (**6**)*

The title α-methylstyrene derivative was synthesized by the Williamson reaction of 4-(4-bromobutyl)-α-methylstyrene with 4-isopropenylphenol by the method similar to that used in the synthesis of **4**. After usual work-up, column chromatography (hexanes/benzene = 4/1, v/v) yielded **6** (5.21 g, 17.0 mmol, 82% yield) as white solid (mp = 47.6 °C). 300MHz ^{1}H NMR ($CDCl_3$): δ = 6.85-7.40 (m, 8H, Ar), 5.05 and 5.36 (d, 2H, $C\underline{H}_2=C(CH_3)C_6H_4CH_2$), 4.99 and 5.29 (d, 2H, $C\underline{H}_2=C(CH_3)C_6H_4O$), 3.98 (t, 2H, CH_2O), 2.69 (t, 2H, Ar-$C\underline{H}_2$), 2.15 (s, 3H, $CH_2=C(C\underline{H}_3)C_6H_4O$), 2.13 (s, 3H, $CH_2=C(C\underline{H}_3)C_6H_4CH_2$), 1.82 (m, 4H, $C\underline{H}_2C\underline{H}_2$). 75MHz ^{13}C NMR ($CDCl_3$): δ = 158.6, 143.1, 138.8, 133.7, 128.4, 126.6, 125.5, 114.2 (Ar), 142.6 ($CH_2=\underline{C}(CH_3)C_6H_4O$), 141.6 ($CH_2=\underline{C}(CH_3)C_6H_4CH_2$), 111.8 ($\underline{C}H_2=C(CH_3)C_6H_4CH_2$), 110.6 ($\underline{C}H_2=C(CH_3)C_6H_4O$), 67.8 ($CH_2O$), 35.5 (Ar-$\underline{C}H_2$), 28.9, 27.9 ($\underline{C}H_2\underline{C}H_2$), 22.0 ($CH_2=C(\underline{C}H_3)C_6H_4O$), 21.9 ($CH_2=C(\underline{C}H_3)C_6H_4CH_2$). Anal. Calcd for $C_{22}H_{26}O$: C, 86.23; H, 8.55; O, 5.22. Found: C, 85.66; H, 8.60; O, 5.74.

4-(4-(2-Vinylphenoxyl)butyl)styrene (7)

The title styrene derivative was synthesized by the Williamson reaction of 4-(4-bromobutyl)styrene with 2-vinylphenol by the method similar to that used in the synthesis of **4**. After usual work-up, column chromatography (hexanes/ethyl acetate = 30/1, v/v) yielded **7** (4.06 g, 14.6 mmol, 73% yield) as a colorless liquid. 300MHz ^{1}H NMR ($CDCl_3$): δ = 6.88-7.55 (m, 9H, Ar and $CH_2=C\underline{H}C_6H_4O$), 6.76 (dd, 1H, J = 11 Hz and 18 Hz, $CH_2=C\underline{H}C_6H_4CH_2$), 5.24-5.33 and 5.78-5.84 (2m, 4H, $C\underline{H}_2=CH$), 4.03 (t, 2H, CH_2O), 2.75 (t, 2H, Ar-$C\underline{H}_2$), 1.91 (m, 4H, $C\underline{H}_2C\underline{H}_2$). 75MHz ^{13}C NMR ($CDCl_3$): δ = 156.3, 142.0, 135.3, 128.8, 128.7, 126.9, 126.5, 126.3, 120.6 (Ar), 136.7 ($CH_2=\underline{C}HC_6H_4CH_2$), 131.8 ($CH_2=\underline{C}HC_6H_4O$), 114.3 ($\underline{C}H_2=CHC_6H_4O$), 113.0 ($\underline{C}H_2=CHC_6H_4CH_2$), 68.1 ($CH_2O$), 35.3 (Ar-$\underline{C}H_2$), 27.9, 28.9 ($\underline{C}H_2\underline{C}H_2$).). Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97; O, 5.75. Found: C, 86.07; H, 8.02; O, 5.91.

Anionic Polymerization

All operations were carried out under the high vacuum condition (10^{-6} torr) in the all glass apparatus equipped with break-seals. The polymerization was usually carried out in THF at -78 °C with vigorous shaking. The polymerization reaction was terminated with a small amount of degassed methanol. The polymer was precipitated by pouring the polymerization mixture into a large amount of methanol. The precipitated polymer was collected by filtration, purified by reprecipitation from THF solution to methanol two times, and freeze-dried from its benzene solution. A typical procedure is as follows: A THF solution (15.6 mL) of 3-(4-(4-isopropenylphenoxy)butyl)styrene (**4**) (0.774 g, 2.65 mmol) chilled to -78 °C was added at once to *sec*-BuLi (0.124 mmol in heptane, 2.54 mL) at -78 °C with vigorous shaking and the reaction mixture was allowed to react at -78 °C for 5 min. To terminate the reaction, a THF solution (3.05 mL) of degassed methanol (0.558 mmol) was added with shaking at -78 °C. The THF solution was poured into a 300 mL of methanol to precipitate the polymer. It was reprecipitated twice from its THF solution into methanol and was freeze-dried from its benzene solution for 24 h. Yield of the poly(**4**) was 0.759 g (98%) after purification.

Measurements

Both ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX300 in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to tetramethylsilane (δ 0) for ^{1}H NMR and relative to $CDCl_3$ (δ 77.1) for ^{13}C NMR. Size exclusion chromatography (SEC) was performed on a Tosoh HLC-8020 with ultraviolet (254 nm) or refractive index detection using THF as a carrier solvent at a flow rate of 1.0 mL/min at 40 °C. Calibration curves were made to determine number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) values with standard polystyrene samples. Vapor pressure osmometry (VPO) measurement for absolute M_n determination was made with Corona 117 in benzene solution at 40 °C. Static light scattering (SLS) measurement was performed on an Otsuka Electronics Photal SLS-600 equipped with a He-Ne laser source (633 nm) at 25 °C. The refractive index increment (dn/dc) was determined on an Otsuka Electronics DRM-1020.

Results and Discussion

*Anionic Polymerization of **1** and **2** with sec-BuLi in Benzene*

In our previous paper, the anionic polymerization behaviors of **1** and **2** with *sec*-BuLi were always examined under the conditions in THF at -78 °C.[9] The living anionic polymerization of styrene and its derivatives is also possible under the conditions in hydrocarbon solvents such as benzene and cyclohexane at 25 °C or higher temperatures. In addition, the polymerization at such higher temperatures is preferable to suppress the polymerization of the α-methylstyrene moiety, since the ceiling temperature of α-methylstyrene is much lower than 25 °C. For this reason, the anionic polymerization behaviors of **1** and **2** were examined with *sec*-BuLi in benzene at 25 °C.

An orange color characteristic to the styrene-derived anion was immediately developed by the addition of **1** to *sec*-BuLi, but gradually changed to red, indicating the generation of the α-methylstyrene-derived anion. The polymerization system became viscous and gelatinous with time. An insoluble polymer was obtained in 61 % yield after 1 h. A similar behavior was observed in the polymerization of **2** under the same conditions. Thus unfortunately, the selective living anionic polymerization of either **1** or **2** was not successful under the conditions in benzene at 25 °C.

Anionic Polymerization of 3-(4-(4-Isopropenylphenoxy)butyl)styrene (4)

The selective living anionic polymerizations of **1** and **2** were previously reported. The meta isomeric monomer, 4-(4-(3-isopropenylphenoxy)butyl)styrene (**3**), was also previously synthesized and anionically polymerized under the same conditions. In this polymerization, however, gelation occurred immediately on mixing *sec*-BuLi with **3**. In the case of meta isomer, as shown in Scheme 2, the electron donation to the α-methylstyryl CH_2=C group of **3** cannot be provided by the *meta*-substituted butoxy group *via* the resonance effect. Accordingly, the α-methylstyrene moiety of **3** may be similar in reactivity to that of α-methylstyrene and therefore attacked by the anionic species, resulting in the gelation by the cross-linking reaction. Thus, the influence of substituted position of the butoxy group linked to the α-methylstyrene moiety is of great significance on the anionic polymerization under the conditions in THF at -78 °C. On the other hand, the 4-(isopropenylphenoxy)butyl group is always substituted at the para position of the styrene part in each of the dual-functionalized monomers, **1** ~ **3**, so far synthesized. In order to study the positional effect of this substituent, 3-(4-(4-isopropenylphenoxy)butyl)styrene (**4**) having the 4-(isopropenylphenoxy)butyl group substituted at the meta position was newly synthesized and anionically polymerized.

The anionic polymerization of **4** was carried out with *sec*-BuLi in THF at -78 °C. An orange color characteristic to the styrene-derived anion was immediately developed by the addition of **4** to *sec*-BuLi. The polymerization was rapid and complete within 5 min. As shown in Figure 1, the polymer exhibited a sharp monomodal SEC distribution without any shoulder and tailing, the M_w/M_n value being 1.05. It was observed from the ^{1}H NMR spectrum of the resulting polymer that the signals at 6.77, 5.81, and 5.29 ppm corresponding to the styryl vinyl protons of **4** completely disappeared and, on the other hand, the signals at 5.35 and 5.06 ppm assigned to the α-methylstyryl vinylene protons remained as such. In addition, the relative signal intensity of these α-methylstyryl vinylene protons with both the methylene protons of -CH_2O- and the methyl protons of *sec*-Bu group agreed with those calculated. Thus evidently, only the styrene part was polymerized, while the α-methylstyrene moiety remained intact. Table 1 summarizes the M_n and M_w/M_n values of the resulting polymers. Although the M_n values estimated by SEC relative to polystyrene were somewhat smaller than those calculated from the $[\mathbf{4}]_0$ to $[sec\text{-BuLi}]_0$ ratios, the M_n values determined by VPO agreed well with those calculated. A relatively high molecular weight polymer (M_n = 19.0 kg/mol) with a narrow molecular weight distribution (M_w/M_n = 1.02) was also obtained. These results clearly indicate that the anionic polymerization of **4** proceeds in a living manner.

Table 1. Anionic polymerization of **4** in THF at -78 °C with *sec*-BuLi [a].

4	*sec*-BuLi	time	$M_n \times 10^{-3}$			M_w/M_n [b]
mmol	mmol	min	calcd [c]	SEC [b]	VPO [d]	
2.65	0.124	5	6.31	5.61	5.91	1.05
2.12	0.0326	5	19.1	15.9	19.0	1.02
2.15	0.0992	30	6.40	6.54	6.20	1.11 [e]

[a] Yields of polymers were quantitative in all cases.
[b] From SEC by using polystyrene standards.
[c] M_n (calcd) = [**4**] / [*sec*-BuLi] x (MW of monomer).
[d] Determined by VPO.
[e] 20% Shoulder.

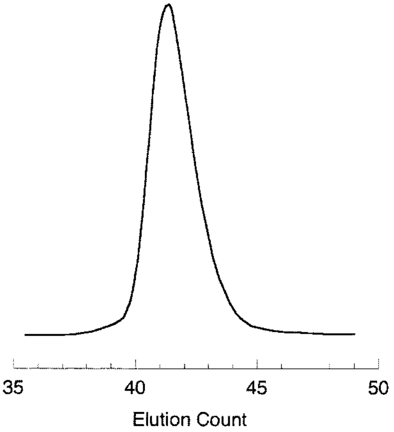
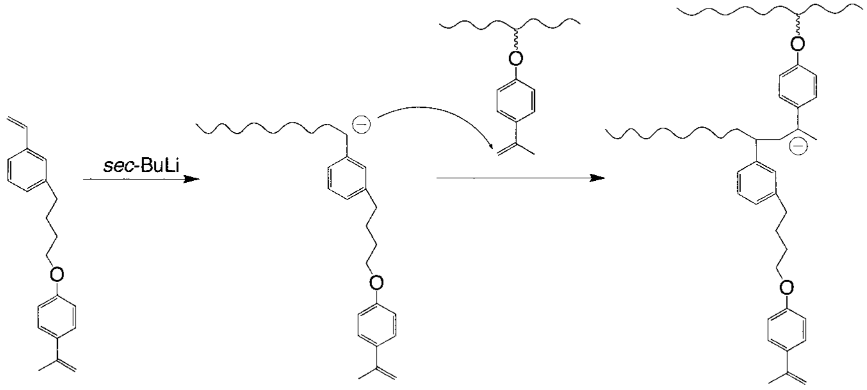


Figure 1. SEC curve of poly(**4**), M_n=5.91x10^3, M_w/M_n=1.05.

The polymer obtained after 30 min showed a sharp monomodal SEC peak along with a high molecular weight shoulder (~ 20 %), which appeared at an elution volume corresponding to double the M_n value of the main peak polymer. It is therefore likely that **4** undergoes the selective living anionic polymerization and after the conclusion of the polymerization, the resulting living chain-end anion attacks gradually with the α-methylstyrene moiety of another polymer chain, as illustrated in Scheme 3. Additional evidence for the anion attack was provided by the observation that the orange color changed with time to a dark red in color characteristic to the α-methylstyrene-derived anion generated by the attack. Thus, the overall anionic polymerization behavior of **4** is very similar to that of **1**. Accordingly, the anionic polymerization was not affected by the substituted position (*meta vs. para*) of the 4-(isopropenylphenoxy)butyl group.



Scheme 3. Overall anionic polymerization of **4** with *sec*-BuLi in THF at -78 °C.

*Anionic Polymerization of 3-(4-(2-Isopropenylphenoxy)butyl)-α-methylstyrene (**5**) and 4-(4-(4-Isopropenylphenoxy)butyl)-α-methylstyrene (**6**)*

As the next target dual-functionalized monomers, new α-methylstyrene derivatives, **5** and **6**, having α-methylstyrene moieties were synthesized. Each of these monomers possesses two α-methylstyrene functionalities in a molecule. If the two α-methylstyrene functionalities are differentiated by the presence of the butoxy group, these monomers will undergo a selective living anionic polymerization, similar to **1**, **2**, and **4**.

The anionic polymerization of **5** was carried out under the conditions in THF at -78 °C with *sec*-BuLi. A dark red color characteristic to the α-methylstyrene-derived anion was immediately developed on mixing **5** with *sec*-BuLi and appeared unchanged after 6 h under the same conditions. Like the anionic polymerization of α-methylstyrene, this polymerization was not rapid and was incomplete within 1 h. The polymer was obtained in 88% after 1 h and quantitatively after 6 h. The results are summarized in Table 2.

Table 2. Anionic polymerization of **5** - **7** in THF at -78 °C with *sec*-BuLi.

monomer	*sec*-BuLi	time	conversion	M_n x 10^{-3}			M_w/M_n [a]
mmol	mmol	min	%	calcd [b]	SEC [a]	NMR [c]	
5, 1.58	0.0922	120	88	4.64	4.69	4.25	1.11 [d]
5, 1.81	0.0752	360	100	8.31	8.19	9.11	1.07 [d]
6, 1.64	0.102	30	37 [e]	5.32	–	–	–
7, 2.11	0.199	5	100 [e]	4.92	–	–	–

[a] From SEC by using polystyrene standards.

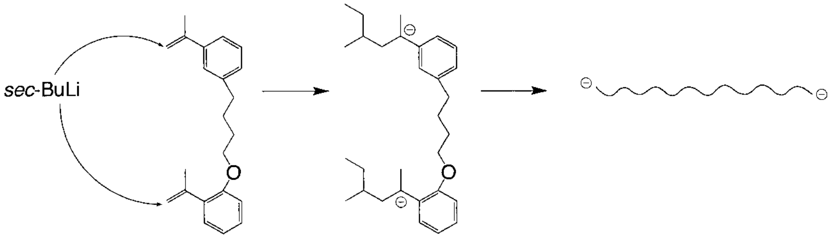
[b] M_n (calcd) = [monomer] / [*sec*-BuLi] x conversion x (MW of monomer).

[c] Determined by the ^{1}H NMR signal intensity ratio of the methylene protons of CH_2O to the methyl protons of *sec*-Bu group.

[d] 5% Shoulder.

[e] Cross-linked polymer.

The SEC profile of the polymer obtained after 1 h exhibited a sharp monomodal peak along with a small high molecular weight peak (~5%) whose molecular weight was doubly increased. A quite similar SEC distribution was observed in the polymer obtained after 6 h, thus showing that the high molecular weight shoulder was already present at the early stage of the polymerization and increased no more during and after the polymerization. Accordingly, there appears to be no attack of the propagating anion on the pendant α-methylstyrene moiety after the polymerization of **5**. It was observed from the ^{1}H NMR spectra of both polymers that the signals at 5.12 and 5.16 ppm corresponding to vinylene protons of the α-methylstyrene moiety attached to butyl group, $C\underline{H_2}{=}C(CH_3){-}C_6H_4{-}(CH_2)_4{-}$, completely disappeared and, on the other hand, the signals at 5.12 and 5.40 ppm assigned to those attached to butoxy group, $C\underline{H_2}{=}C(CH_3){-}C_6H_4{-}O(CH_2)_4{-}$, remained almost unchanged. The signal intensity of such α-methylstyryl vinylene protons were comparable to that of the CH_2O methylene protons within experimental error. Thus obviously, the α-methylstyrene moiety attached to butyl group participates the polymerization. Based on these results, we speculated that the polymerization behavior of **5** is as follows: The α-methylstyrene moiety attached to butyl group undergoes selectively living anionic polymerization of **5**. At the initiation stage, however, *sec*-BuLi may also react to a small extent (~5%) with the α-methylstyrene moiety attached to butoxy group to by-produce a difunctional anionic species as illustrated in Scheme 4. The polymer possessing double the molecular weight would be formed by the subsequent polymerization with the difunctional species. Therefore, the initiator of choice is important in the polymerization of **5** and a variety of initiators less reactive than *sec*-BuLi such as living oligomers of α-methylstyrene and cumylpotassium should be examined.



5

Scheme 4. Difunctional species by-produced at the initiation stage of **5**.

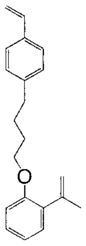
In contrast to the polymerization of **5**, the anionic polymerization of **6** was problematic. Under the same conditions, the polymerization system showed a dark red in color at first but became viscous and gelatinous with time. An insoluble polymer was obtained in 37% yield after 0.5 h. Obviously, the pendant α-methylstyrene moiety was attacked by the propagating chain-end α-methylstyrene-derived anion to cross-link. In this case, lowering the reactivity of the α-methylstyrene moiety by the *para*-substituted butoxy group *via* resonance effect was not enough to suppress the anion attack. Thus, it was found that the anionic polymerization of the dual-functionalized α-methylstyrene derivatives was significantly influenced by the substituted position (*ortho vs. para*) of the butoxy group.

Anionic Polymerization of 4-(4-(2-Vinylphenoxy)butyl)styrene (7)

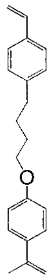
The possibility to differentiate two α-methylstyrene moieties in the same molecule was demonstrated in the anionic polymerization of **5**, although it was not perfect yet. Therefore, a new dual-functionalized monomer possessing two styrene functionalities, **7**, structurally similar to **1**, was synthesized and the anionic polymerization was attempted with *sec*-BuLi in THF at -78 °C. Unfortunately, however, the gelation occurred immediately on mixing *sec*-BuLi with **7** and an insoluble polymer was obtained quantitatively after only 5 min. Thus, the anionic polymerization of **7** failed. Unlike the cases of **1** and **5**, the introduction of one butoxy group at the ortho position was not enough to suppress the anion attack.

Conclusions

Four new dual-functionalized styrene and α-methylstyrene derivatives having styrene or α-methylstyrene moiety, **4** ~ **7**, were synthesized and their anionic polymerizations were examined under the conditions in THF at -78 °C with *sec*-BuLi as an initiator. The polymerization of **4** and **5** selectively proceeded in a living manner to afford functionalized polystyrene and poly(α-methylstyrene) having an α-methylstyrene moiety in each monomer unit. On the other hand, only insoluble polymers by cross-linking were obtained by the anionic polymerization of **6** and **7** under the same conditions. Table 3 summarizes the anionic polymerization behaviors of all the dual-functionalized monomers, **1** ~ **7**, so far synthesized under the conditions in THF at -78 °C with *sec*-BuLi.



1



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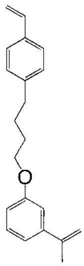

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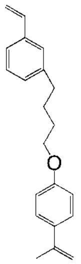

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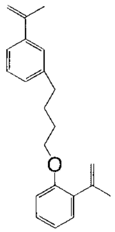

5

6

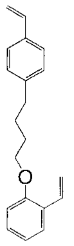

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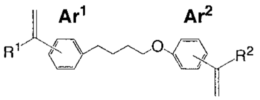
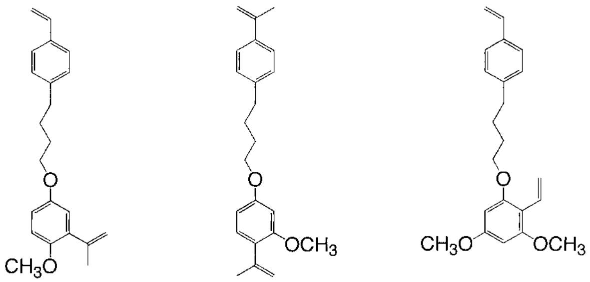
Table 3. Anionic polymerization of dual-functionalized monomers **1** - **7**.

	Ar^1	Ar^2	polymerization
1	St (*p*)	αMS (*o*)	+ +
2	St (*p*)	αMS (*p*)	+
3	St (*p*)	αMS (*m*)	–
4	St (*m*)	αMS (*p*)	+
5	αMS (*m*)	αMS (*o*)	+
6	αMS (*p*)	αMS (*p*)	–
7	St (*p*)	St (*o*)	–

These monomers are structurally similar styrene or α-methylstyrene derivatives having the styrene or the α-methylstyrene moiety linked by a butoxy group. Therefore, the influence of monomer structure on anionic polymerization can be directly compared. The symbol referred to as "++" indicates that the monomer undergoes selective living anionic polymerization to afford a stable living polymer. In the case where the monomer also undergoes living polymerization but after the polymerization, the resulting living polymer anion attacks slowly with the pendant α-methylstyrene moiety, the symbol "+" is employed. The "–" indicates the case where an insoluble polymer is obtained. Obviously, the significance of the introducing of butoxy group at an ortho or para position is demonstrated to achieve living anionic polymerization of this type of the dual-functionalized monomers. Recently, we have found that the reactivities of styrene and α-methylstyrene toward anionic species can be further lowered by the introduction of two or more methoxy groups into their phenyl rings. Therefore, by the introduction of methoxy groups into the dual-functionalized monomers listed in Table 3, for example, **3**, **6**, and **7**, the living anionic polymerization of such monomers shown in Scheme 5 will be expected. Their synthesis and anionic polymerization are now in progress.



Scheme 5. Dual functionalized monomers with methoxy groups.

Acknowledgement

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