Macromolecules

Volume 32, Number 5 March 9, 1999

Synthesis of End-Functionalized Polymers by Means of Living Anionic Polymerization. 10. Reactions of Living Anionic Polymers with Halopropylstyrene Derivatives

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Received July 30, 1998; Revised Manuscript Received December 14, 1998

ABSTRACT: Three different ω−α-substituted styryl macromonomers with well-controlled structures were synthesized by directly terminating either polystyryllithium or polyisoprenyllithium with 4-(3-halopropyl)-α-methylstyrenes (**2**), α-(3-halopropyl)styrenes (**3**), and 1-[4-(3-halopropyl)phenyl]-1-phenylethylenes (**4**). With uses of their bromo and iodo derivatives as terminating agents, the reactions proceeded in a desired manner in THF at −78 °C to afford well-controlled ω-styryl polystyrene and polyisoprene macromonomers quantitatively. On the other hand, the synthetic utility of chloride derivatives as terminators was much dependent on both their polymerizable styryl groups and living polymers to be reacted. By comparison of these results with our previous results using 4-(3-halopropyl)styrenes (**1**), the scope and limitation of the methodology developed here were discussed from a viewpoint of quantitative synthesis of various ω-styryl macromonomers with well-controlled structures.

Introduction

End-functionalized polymers with styryl group (so-called ω-styryl macromonomers) are one of the most utilizable macromonomers, because of the polymerizability of the styryl group for a wide variety of initiators including radical, ionic initiators, and some transition-metal complexes.[1] Under specified conditions, styrene undergoes living polymerization with both anionic and cationic intiators.[2] Moreover, living radical polymerization of styrene has recently been realized.[3] Therefore, if such living polymerizations of ω-styryl macromonomers with controlled structures could be realized, well-defined graft, comb polymers as well as various branched polymers would be synthesized. Very unfortunately, to date these living polymerizations have not been well-established yet.

Several attempts to synthesize the ω-styryl macromonomers with controlled structures via anionic living polymerization were previously made.[4−8] In general, termination reactions of anionic living polymers with vinylbenzyl chlorides or the related derivatives were employed for this synthesis. The protocol as originally developed suffers one drawback when highly reactive anionic living polymers of styrene and isoprene were used. That is, it utilizes 4-vinylbenzyl chloride in the termination reaction and thus requires selective reaction of the chloride to living polymer anions. However, the living polymer anions are too reactive and often undergo competitively nucleophilic addition and/or polymerization with the styryl group, leading to the undesired products.

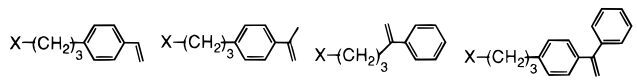
As one of the successful approaches to overcome this problem, Milkovich and co-workers proposed that the reactive polystyryl anion was transformed into a less reactive alcolate anion by end-capping with ethylene oxide before terminating.[4] In this case, the alcolate anion still reacts efficiently with the chloride, while it has no ability to react with the styryl group. Thus, well-controlled ω-styryl macromonomers could be successfully synthesized for the first time by reacting polystyryllithium with ethylene oxide, followed by treating with 4-vinylbenzyl chloride. Rempp and co-workers demonstrated that the end-capping with 1,1-diphenylethylene (DPE) was also effective to suppress the anion attack on the styryl groups in the reaction of living polystyrene with either 4-vinylbenzyl bromide or (4-isopropenyl)-benzyl bromide.[5] Recently, Deffieux and co-workers reported using DPE for end-capping polystyryllithium before the reaction with 4-vinylbenzyl chloride.[6]

10.1021/ma981189q CCC: $18.00
Published on Web 02/11/1999

This undesirable anion attack of living polystyrene can also be suppressed by using 4-vinylbenzyl chloride in a large excess (ca. a 10-fold or more excess) as reported by Asami and co-workers.[7] In this case, working at a low temperature of 0 °C in THF (or mixed solvents containing THF as a cosolvent) is also essential. However, they were not successful in suppressing completely the anion attack in the reaction of polyisoprenyllithium with 4-vinylbenzyl chloride even under identical conditions. For the successful synthesis of well-controlled ω-styryl polyisoprene macromonomers, the use of more reactive but relatively unstable 4-vinylbenzyl tosylate as a terminator was therefore required.[8]

We have recently found that the bromide moiety of 4-(3-bromopropyl)styrene (**1-Br**) reacts quite selectively with polystyryllithium in THF at −78 °C.[9] Moreover, **1-Br** could also react selectively with polyisoprenyllithium in a desired manner under the same conditions. More interestingly, even by using **1-Br** in only small excesses (a 1.5-fold excess), we did not find any clue to anion attack on the styryl group in these reactions. Well-controlled ω-styryl polystyrene and polyisoprene macromonomers were quantitatively synthesized by the reactions with **1-Br**. Thus, obviously **1-Br** is superior to the earlier reagents such as benzyl halides and tosylate in the synthesis of ω-styryl macromonomers. This complete bromide selectivity is very surprising, considering the fact that propyl bromide is less reactive than benzyl halides and tosylate in general S_N2 reactions.

On the basis of these successful results, it occurred to us that it should be possible to synthesize a variety of well-controlled substituted styryl macromonomers by carrying out the reactions of anionic living polymers with alkyl halide terminators containing substituted styryl groups. In this paper, we will report the scope and synthetic utility of the following series of propyl halides containing three α-substituted styryl groups (**2**−**4**) as terminating agents for the synthesis of well-controlled ω-styryl macromonomers:



1-Cl: X = Cl 1-Br: X = Br 1-I: X = I | 2-Cl: X = Cl 2-Br: X = Br 2-I: X = I | 3-Cl: X = Cl 3-Br: X = Br 3-I: X = I | 4-Cl: X = Cl 4-Br: X = Br 4-I: X = I

For our purposes, the halogen as well as the styryl group of **2**−**4** is systematically varied from Cl, Br, and I and less reactive α-methylstyryl, α-alkylstyryl, and more reactive α-phenylstyryl groups. The reaction patterns of anionic living polymers of styrene and isoprene with **2**−**4** will be examined in detail. The results obtained in this study will be compared with our results with 4-(3-halopropyl)styrene (**1**) previously reported.[9]

Experimental Section

Materials. Styrene and isoprene were purified according to the usual procedures. They were finally distilled over dibutylmagnesium and *n*-butyllithium, respectively, on the vacuum line into ampules with break-seals that were prewashed with 1,1-diphenylhexyllithium in heptane.

4-(3-Chloropropyl)-α-methylstyrene (2-Cl). 2-Cl was synthesized by the Li_2CuCl_4-mediated coupling reaction of the Grignard reagent of 4-(isopropenyl)phenyl chloride with 1-bromo-3-chloropropane. To an ice-cooled THF solution (50 mL) containing 1-bromo-3-chloropropane (22.7 g, 144 mmol) and Li_2CuCl_4 (1.0 mmol, 0.145 M, 6.9 mL), the Grignard reagent prepared from 4-(isopropenyl)phenyl chloride (11.0 g, 72 mmol) and magnesium (2.75 g, 108 mg atom) in THF (50 mL) was added dropwise over a period of 30 min. The resulting mixture was then stirred at 25 °C for 20 h. It was then acidified with 2 N HCl and extracted with hexane (50 mL × 3). The organic layer was washed with water and dried over $MgSO_4$. Removal of solvent under reduced pressure followed by fractional distillation yielded **2-Cl** (5.76 g, 29.7 mmol, 41%) as a colorless liquid: bp 74−75 °C (2−3 Torr); ^{1}H NMR ($CDCl_3$) δ 7.33 (m, 4H, HAr), 5.31, 5.11 (dd, 2H, J = 1.32 Hz, CH_2=), 3.53 (t, 2H, J = 6.48 Hz, $-CH_2Cl$), 2.69 (t, 2H, J = 7.36 Hz, $-CH_2CH_2CH_2Cl$), 1.89 (m, 2H, $-CH_2CH_2Cl$).

4-(3-Bromopropyl)-α-methylstyrene (2-Br). 2-Br was synthesized by a similar procedure as described in the case of **2-Cl.** 1,3-Dibromopropane was used instead of 1-bromo-3-chloropropane in the reaction. Usual workup followed by fractional distillation under reduced pressure gave **2-Br** (6.51 g, 2.72 mmol) in 38% yield as a pale yellow liquid: bp 141−142 °C (2 Torr); ^{1}H NMR ($CDCl_3$) δ 7.19 (m, 4H, HAr), 5.35, 5.05 (dd, 2H, J = 1.31 and 1.32 Hz, CH_2=), 3.59 (t, 2H, J = 6.5 Hz, $-CH_2Br$), 2.77 (t, 2H, J = 7.2 Hz, $-CH_2CH_2CH_2Br$), 2.14 (m, 2H, $-CH_2CH_2Br$); ^{13}C NMR ($CDCl_3$) δ 143.1, 139.9, 139.6, 128.4, 125.8, 111.9, 34.2, 33.8, 32.8, 21.8.

4-(3-Iodopropyl)-α-methylstyrene (2-I). 2-Cl (4.12 g, 23 mmol) and NaI (36.0 g, 240 mmol) were dissolved in dry acetone (200 mL), and the mixture was brought to reflux with stirring under a nitrogen atmosphere for 24 h. After cooling to room temperature, the mixture was diluted with hexane and washed with 10% $Na_2S_2O_3$ and water. The organic layer was dried over $MgSO_4$. Removal of solvent under reduced pressure followed by fractional distillation yielded **2-I** (2.95 g, 10.3 mmol, 45%) as a pale yellow liquid: bp 124−126 °C (1.0 Torr); ^{1}H NMR ($CDCl_3$) δ 7.33 (m, 4H, HAr), 5.34, 5.05 (dd, 2H, J = 1.43 and 0.55 Hz, CH_2=), 3.53 (t, 2H, J = 6.8 Hz, $-CH_2I$), 2.64 (t, 2H, J = 7.3 Hz, $-CH_2CH_2CH_2I$), 2.14 (m, 2H, $-CH_2CH_2I$); ^{13}C NMR ($CDCl_3$) δ 142.8, 139.6, 139.1, 128.4, 125.6, 112.0, 35.9, 34.8, 21.9, 6.4.

α-(3-Chloropropyl)styrene (3-Cl). 3-Cl was synthesized by a similar procedure as described in the synthesis of **2-Cl.** The Grignard reagent was prepared from α-bromostyrene (10.0 g, 54.6 mmol) and magnesium (2.00 g, 82.0 mg atom) in THF (50 mL) and reacted with 1-bromo-3-chloropropane (12.9 g, 81.9 mmol) in the presence of Li_2CuCl_4 (1.0 mmol, 0.145 M, 6.9 mL). The mixture was stirred for overnight. Usual workup and fractional distillation under reduced pressure gave **3-Cl** in 35% yield (3.49 g, 19.3 mmol) as a colorless liquid: bp 97−99 °C (1−2 Torr); ^{1}H NMR ($CDCl_3$) δ 7.36 (m, 5H, HAr), 5.31, 5.11 (dd, 2H, J = 1.32, CH_2=), 3.53 (t, 2H, J = 6.45 Hz, $-CH_2Cl$), 2.67 (t, 2H, J = 7.86 Hz, $-CH_2CH_2CH_2Cl$), 1.89 (m, 2H, $-CH_2CH_2CH_2Cl$); ^{13}C NMR ($CDCl_3$) δ 147.0, 140.7, 128.5, 127.7, 126.2, 113.4, 44.5, 32.5, 31.1.

α-(3-Bromopropyl)styrene (3-Br). 3-Br was synthesized by a similar procedure as described in the synthesis of **3-Cl.** 1,3-Dibromopropane was used instead of 1-bromo-3-chloropropane in the reaction. Usual workup followed by fractional distillation under reduced pressure gave **3-Br** in 35% yield (2.99 g, 13.3 mmol) as a colorless liquid: bp 76.0−80.0 °C (2 Torr); ^{1}H NMR ($CDCl_3$) δ 7.36 (m, 4H, HAr), 5.32, 5.12 (dd, 2H, J = 1.32, and 1.31 Hz, CH_2=), 3.40 (t, 2H, J = 6.49 Hz, $-CH_2Br$), 2.69 (t, 2H, J = 7.36 Hz, $-CH_2CH_2CH_2Br$), 1.97 (m, 2H, $-CH_2CH_2Br$); ^{13}C NMR ($CDCl_3$) δ 146.7, 128.4, 127.6, 126.1, 113.4, 48.5, 33.7, 33.3, 31.1.

α-(3-Iodopropyl)styrene (3-I). 3-Cl (2.49 g, 13.8 mmol) and NaI (20.7 g, 138 mmol) were dissolved in dry acetone (70 mL), and the mixture was brought to reflux with stirring under a nitrogen atmosphere for 24 h. After cooling to room temperature, the mixture was diluted with hexane and washed with 10% $Na_2S_2O_3$ and water. The organic layer was dried over $MgSO_4$. Removal of solvent under reduced pressure followed by fractional distillation yielded **3-I** (0.96 g, 3.53 mmol, 26%) as a pale yellow liquid: bp 82.0−85.0 °C (2−3 Torr); ^{1}H NMR ($CDCl_3$) δ 7.36 (m, 5H, HAr), 5.32, 5.12 (dd, 2H, J = 1.24 and 1.32 Hz, CH_2=), 3.40 (t, 2H, J = 6.81 Hz, $-CH_2I$), 2.69 (t, 2H, J = 7.14 Hz, $-CH_2CH_2CH_2I$), 1.99 (m, 2H, $-CH_3$, $-CH_2CH_2I$);

^{13}C NMR ($CDCl_3$) δ 146.9, 128.4, 127.6, 126.2, 113.3, 44.2, 36.1, 32.0, 6.0.

1-[4-(3-Chloropropyl)phenyl]-1-phenylethylene (4-Cl). 4-Cl was synthesized by the Li_2CuCl_4-mediated coupling reaction of the Grignard reagent of 1-(4-bromophenyl)-1-phenylethylene with 1-bromo-3-chloropropane. The Grignard reagent was prepared from 1-(4-bromophenyl)-1-phenylethylene (8.23 g, 32 mmol) and magnesium (2.10 g, 86 mmol) in THF (40 mL) and then reacted with 1-bromo-3-chloropropane (10.1 g, 64 mmol) in the presence of a catalytic amount of Li_2CuCl_4. After usual workup, fractional distillation under reduced pressure gave **4-Cl** (2.29 g, 8.9 mmol) in 29% yield as a colorless liquid: bp 132−134 °C (0.3 Torr); ^{1}H NMR ($CDCl_3$) δ 7.24 (m, 9H, HAr), 5.44 (dd, 2H, J = 1.3 Hz, CH_2=), 3.54 (t, 2H, J = 6.5 Hz, $-CH_2Cl$), 2.80 (t, 2H, J = 7.4 Hz, $-CH_2CH_2$-CH_2Cl), 2.10 (m, 2H, J = 4.8, $-CH_2CH_2Cl$); ^{13}C NMR ($CDCl_3$) δ 149.9, 141.6, 140.3, 139.4, 128.4, 128.3, 128.2, 128.0, 127.8, 114.0, 44.3, 34.0, 32.5.

1-[4-(3-Bromopropyl)phenyl]-1-phenylethylene (4-Br) and 1-[4-(3-Iodopropyl)phenyl]-1-phenylethylene (4-I). Both **4-Cl** and **4-I** were prepared by the Finkelstein halogen exchange reactions, similar to the cases of **2-I** and **3-I**. **4-Cl** (3.00 g, 12 mmol) and either LiBr (15.7 g, 180 mmol) or NaI (26.7 g, 178 mmol) were dissolved in dry acetone (100 mL), and the mixture was brought to reflux with stirring under a nitrogen atmosphere for 24 h. After cooling to room temperature, the mixture was diluted with hexane, washed with water, and dried over $MgSO_4$. Removal of solvent under reduced pressure followed by flash column chromatography (hexane as an eluent) yielded **4-Br** (2.42 g, 8.0 mmol, 67%) or **4-I** (3.68 g, 11 mmol, 92%) as a colorless liquid, respectively. **4-Br**: ^{1}H NMR ($CDCl_3$) δ 7.29 (m, 9H, HAr), 5.44 (dd, 2H, J = 1.3 Hz, CH_2=), 3.42 (t, 2H, J = 6.5 Hz, $-CH_2Br$), 2.79 (t, 2H, J = 7.4 Hz, $-CH_2CH_2CH_2Br$), 2.21 (m, 2H, J = 4.8, $-CH_2$-CH_2Br); ^{13}C NMR ($CDCl_3$) δ 149.8, 141.6, 140.2, 139.4, 128.4, 128.3, 128.2, 128.0, 127.7, 114.0, 34.1, 33.7, 33.1. **4-I**: ^{1}H NMR ($CDCl_3$) δ 7.29 (m, 9H, HAr), 5.44 (dd, 2H, J = 1.3 Hz, CH_2=), 3.19 (t, 2H, J = 6.5 Hz, $-CH_2I$), 2.72 (t, 2H, J = 7.4 Hz, $-CH_2$-CH_2CH_2I), 2.14 (m, 2H, J = 4.8, $-CH_2CH_2I$).

Polymerizations and Reactions of Anionic Living Polymers with 2−4. The polymerizations and the reactions were carried out under high-vacuum conditions in sealed glass reactors with break-seals. The reactors were always prewashed with the initiator solutions after being sealed off from a vacuum line and were used for the polymerizations followed by the reactions. The anionic polymerization of styrene was performed with *s*-BuLi in THF at −78 °C for 10 min. The polymerization of isoprene was carried out with *s*-BuLi in heptane at 40 °C for 2 h. In this case, an equal volume of THF was added to the heptane solution of polyisoprenyllithium at −78 °C prior to the termination reaction.

The living polymer solution was usually added dropwise into a THF solution of each terminating reagent at −78 °C over a period of 10 min, and the mixture was allowed to stand at −78 °C for an additional 20 min.

The polymers were precipitated in methanol and purified by the repeated reprecipitation from THF to methanol thrice to remove unreacted terminating agents. They were then freeze-dried and characterized. No difference was observed between macromonomers and nonfunctionalized polystyrenes (or polyisoprenes) in both apparent forms and solubilities.

End-Group Analysis of Macromonomers. To determine the degrees of end-functionalizations, the polymers were analyzed carefully by both ^{1}H NMR and UV spectroscopy.

The degrees of end-functionalizations of polystyrene macromonomers were determined by comparing the relative intensities of the ^{1}H NMR resonances at 4.9−5.4 ppm to the vinyl protons with those at 6.2−7.4 ppm to aromatic protons of the polystyrenes based on the M_n value measured by SEC. The resonance at 0.6 ppm to the methyl protons from the initiator residue of *s*-BuLi can be also utilized for this determination. Similarly, the degrees of end-functionalizations of polyisoprene macromonomers were determined. In these cases, the resonance at 5.2−5.4 ppm to the vinyl protons of *cis*-1,4-polyisoprene main chain was used. The resonance at 0.85 ppm to the methyl protons from the initiator residue was also used for this purpose. The errors are less than 5%. Chemical shifts of vinyl resonances for both terminators and macromonomers are summarized in Table 1. A typical ^{1}H NMR spectrum of the polystyrene end-functionalized with α-methylstyryl group is shown in Figure 1.

Table 1. Chemical Shifts (ppm) of the Vinyl Groups in $CDCl_3$

terminating agent		polystyrene macromonomer	polyisoprene macromonomer
2-Cl	5.11, 5.32		
2-Br	5.05, 5.35	5.02, 5.31	5.33[a]
2-I	5.05, 5.34		
3-Cl	5.11, 5.31		
3-Br	5.12, 5.32	4.93, 5.16	5.24[a]
3-I	5.12, 5.32		
4-Cl	5.44		
4-Br	5.44	5.37	5.41
4-I	5.44		

[a] Lower chemical shifts corresponding to vinyl protons were overlapped with those of polyisoprenes.

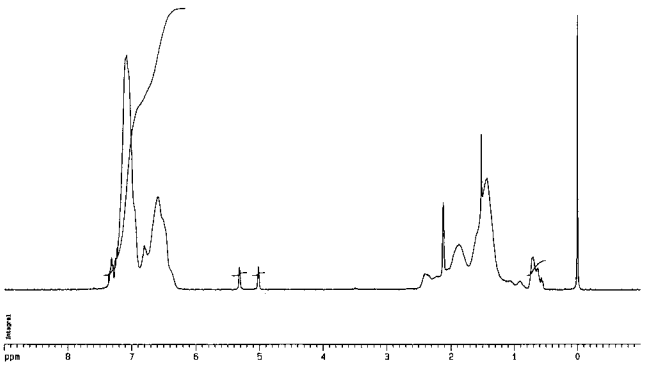


Figure 1. ^{1}H NMR spectrum of end-functionalized polystyrene with α-methylstyryl group.

The degrees of end-functionalizations could also be determined by using large values of the molar extinction coefficients of terminal styryl groups in the UV region in cyclohexane. 4-Propyl-α-methylstyrene (ϵ_{max} is 1.42 × 10^4 L/(mol cm) at 249.6 nm), α-propylstyrene (ϵ_{max} is 0.988 × 10^4 L/(mol cm) at 239.6 nm), and 1-(4-propyl)phenyl-1-phenylethylene (ϵ_{max} is 1.14 × 10^4 L/(mol cm) at 254.8 nm) were used as references. These ϵ_{max} are more than 10^2 times larger than those of polystyrene.

Furthermore, to examine the degrees of end-functionalizations, we have reacted the resulting macromonomers with polystyryllithium and determined the degrees of end-functionalizations of the macromonomers by analyzing the reaction products by SEC. This method was done by taking advantage of the reaction of the terminal styryl group of macromonomer with polystyrylanion. The macromonomers (M_n = ca. 2000) obtained were freeze-dried thrice from the absolute benzene solution and dissolved in THF. Polystyryllithium (M_n = 6000) separately prepared was allowed to react with the macromonomers in THF at −78 °C for several hours under the conditions where the anion was used in 3 times molar excess for the terminal styryl group estimated by ^{1}H NMR and UV. The mixture was poured into methanol to precipitate the polymers. The SEC chromatograms before and after the reaction were compared. Typical ones are shown in Figure 2. Peaks A, B, and C are those for the macromonomer, polystyrene used in the reaction, and the reaction product. As can be seen in the chromatogram after the reaction, the peak corresponding to the macromonomer disappears completely, while the peaks are observed for polystyrene (M_n = 6000) unreacted and the 1:1 addition product (M_n = 8000) of the macromonomer and polystyryllithium. The result clearly demonstrates that the end-functionalization degree of this macromonomer is quantitative. A direct evidence for the presence of the terminal

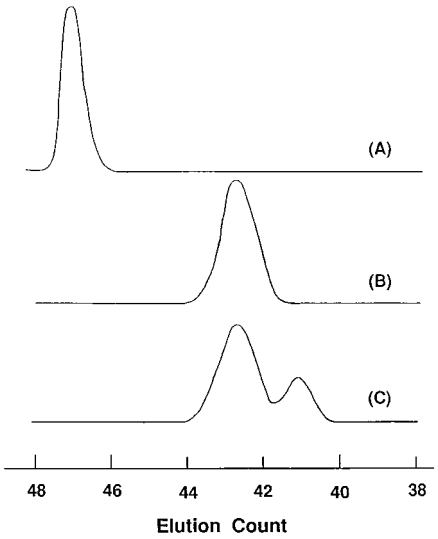


Figure 2. SEC curves of macromonomer (A), polystyrene (B), and reaction product (C).

styryl group of the macromonomer is also provided by this experiment. The accuracy of this method is governed by detector sensitivity of size-exclusion chromatography (SEC). Since 3 wt % polymer sample (for the original sample) added on purpose for comparison can be clearly detected by SEC, the errors are believed to be less than 3%.

Results and Discussion

We previously examined the utility of 4-(3-halopropyl)styrene derivatives (**1**) as terminating agents toward anionic living polymers of styrene and isoprene for the synthesis of ω-styryl macromonomers. As described in the Introduction, 4-(3-bromopropyl)styrene (**1-Br**) as a bromide derivative of **1** was a superior terminator to vinylbenzyl halides for such macromonomer synthesis. Satisfactory results were also obtained with 4-(3-iodopropyl)styrene (**1-I**) of the iodide.

It is however observed that undesired addition and/or polymerization of the styryl group with the living polymer anions significantly occurred in the reactions with the corresponding chloride (**1-Cl**). The situation was not improved by using **1-Cl** in a 13-fold excess.

Thus, the termination reactions of anionic living polymers with **1-Br** and **1-I** proceeded quite bromide and iodide selectively to afford quantitatively the well-controlled ω-styryl macromonomers, while **1-Cl** was not a suitable terminator with which synthesis of the macromonomer failed. This failure may possibly lie in the poor reactivity of chloride.

Termination Reactions with 4-(3-Halopropyl)-α-methylstyrenes. Our first attempts in this study focused on direct reactions of anionic living polymers of styrene and isoprene with 4-(3-halopropyl)-α-methylstyrenes (**2**). Because of electron-donating character and steric bulkiness of the methyl substituent, the α-methylstyryl moiety of **2** is considered to be less reactive (or less electrophilic) than the styryl one of **1** toward anionic species. The lower reactivity of the α-methylstyryl group is also estimated by comparison of the *e* value of styrene (−0.80) with that of α-methylstyrene (−1.27).

Owing to the established utilities of **1-Br** and **1-I** as terminators in macromonomer synthesis as mentioned above, we set the standard experiment according to the previous literature.[9] Both polystyryllithium and polyisoprenyllithium were employed as anionic living polymers to be reacted. The reactions were always carried out in THF or a THF−heptane mixture (ca. 1/1, v/v) at −78 °C by adding each living polymer slowly to each of the terminators. We used usually small excesses of terminators to living polymer anions (ca. 2.0-fold excess) in all reactions. The results are summarized in Table 2.

Table 2. Reactions of Anionic Living Polymers with 2[a]

terminating agent	living polymer[b]	functionality, %		
		^{1}H NMR	UV	SEC[c]
2-Cl	PS-Li	100		
2-Cl	PI-Li	100		
2-Br	PS-Li	100	100	100
2-Br	PI-Li	96	99	
2-I	PS-Li	100	100	100
2-I	PI-Li	100	100	

[a] Reactions were carried out at −78 °C for 20 min. About 2-fold excess of **2** was used. M_n values of macromonomers were in the range 2000−3000. M_w/M_n values were less than 1.10 in all polymer samples. [b] PS-Li and PI-Li indicate polystyryllithium and polyisoprenyllithium, respectively. [c] Functionality by end-group analysis using SEC of the products by the reaction of macromonomer with polystyryl anion (see Experimental Section).

Similar to the cases with **1-Br** and **1-I**, the reactions of the anionic living polymers with either the bromide (**2-Br**) or the iodide (**2-I**) were very fast and completed within a few seconds from the observation that the characteristic reddish orange or lemon-yellow colors disappeared instantaneously on mixing. The SEC curves of the resulting polymers showed that their peaks were unimodal and nearly monodispersed, the M_w/M_n values being around 1.05. There was a good agreement between M_n values calculated and observed. As can be seen in Table 2, the degrees of end-functionalization determined by ^{1}H NMR and UV measurements are quantitative in all cases. In addition to these measurements, we have directly estimated the degrees of end-functionalization by taking advantage of the reactions of the terminal substituted styryl groups with polystyryl anion. For example, the ω−α-methylstyryl macromonomer (M_n = 2000) obtained was purified and allowed to react with polystyrylanion (M_n = 6000) separately prepared. The reaction product was then analyzed by SEC. Typically, it is observed that the SEC peak corresponding to the macromonomer disappears completely, while the peaks for the addition products of the macromonomer with polystyrylanion newly appear, as can be seen in Figure 2 (see the Experimental Section). The result clearly indicates that the terminal α-methylstyryl group reacts completely with the polystyryl anion, and therefore the degree of end-functionalization for this macromonomer is quantitative. Furthermore, direct evidence for the presence of the ω−α-methylstyryl group is provided by this experiment.

On the basis of these analytical results, the reactions with either **2-Br** or **2-I** proceeded quite selectively in a desired manner to produce the well-controlled ω−α-methylstyryl macromonomers. Thus, the results with uses of **2-Br** and **2-I** were very satisfactory.

The reactions of the living polymers with the chloride (**2-Cl**) were observed to proceed not so rapidly. In these cases, the colors characteristic for living polymers faded gradually on mixing with **2-Cl** and remained for several minutes even after addition of all of **2-Cl**. Nevertheless, **2-Cl** underwent selective reaction with either anionic living polymer of styrene or isoprene. No attack of the anions on the α-methylstyryl moiety was observed. The

Table 3. Reactions of Anionic Living Polymers with 3[a]

terminating agent	living polymer[b]	functionality, %		
		^{1}H NMR	UV	SEC[c]
3-Cl	PS-Li	65	44	
3-Cl	PI-Li	100	100	
3-Br	PS-Li	88	95	100
3-Br	PI-Li	100	100	100
3-I	PS-Li	88	97	100
3-I	PI-Li	91	98	

[a] Reactions were carried out at −78 °C for 20 min. About 2-fold excess of **3** was used. M_n values of macromonomers were in the range 2000−3000. M_w/M_n values were less than 1.10 in all polymer samples. [b] PS-Li and PI-Li indicate polystyryllithium and polyisoprenyllithium, respectively. [c] Functionality by end-group analysis using SEC of the products by the reaction of macromonomer with polystyryl anion (see Experimental Section).

synthesis of well-controlled ω−α-methylstyryl macromonomers with use of **2-Cl** is thus successful.

The results with **2-Cl** are in marked contrast to those with **1-Cl** in which the desired macromonomers were not synthesized. Clearly, the α-methylstyryl moiety was much more robust than the styryl one and able to survive completely the treatment with anionic living polymers. Se and co-workers recently reported that 4-(2-chloroethyl)-α-methylstyrene, a structural analogue of **2-Cl**, also underwent selective reaction with poly(α-methylstyryl)lithium in THF at −78 °C.[10] They obtained quantitatively ω−α-methylstyryl poly(α-methylstyrene) macromonomers. The versatility of **2** including the chloride as terminators in the macromonomer synthesis is thus apparent.

Termination Reactions with α-(3-Halopropyl)-styrenes. Electrophilicities of the α-halopropylstyryl moieties of α-(3-halopropyl)styrenes (**3**) are estimated to be similar to that of α-methylstyrene. It was further surmised that the α-halopropyl substituents would provide steric hindrance around the styryl group more than the methyl substituent, thereby expecting to suppress anion attack on the styryl group of **3**.

Table 3 summarizes the results of the termination reactions of polystyryllithium and polyisoprenyllithium with **3** in THF at −78 °C. As one might expect, both the bromide (**3-Br**) and iodide (**3-I**) reacted very fast and quite selectively with both the living polymers. The resulting ω-2-phenylethenyl macromonomers possessed well-controllable molecular weights, narrow distributions, and nearly quantitative degrees of end-functionalization. The chloride (**3-Cl**) was also found to allow selective termination reaction of polyisoprenyllithium.

On the other hand, the reaction of polystyryllithium with **3-Cl** proved to be problematic, leading to the product with a low end-functionalization degree of 65%. The SEC trace however showed a symmetrical sharp unimodal peak in the absence of any shoulders and high molecular weight peaks. Furthermore, no resonance corresponding to the CH_2Cl protons was observed in the ^{1}H NMR of the product. Thus, we did not find any clue to polystyryl anion attack on the styryl moiety of **3-Cl**. For a possible reaction candidate to lower the functionalization, we tentatively consider that proton abstraction from **3-Cl** by the anion would occur competitively with the desired termination. More experiments should be needed for optimizing the functionalization reaction.

Termination Reaction of 1-[4-(3-Halopropyl)-phenyl]-1-phenylethylenes. 1,1-Diphenylethylene (DPE) is a special vinyl compound which is nonpolymerizable but undergoes monoaddition reaction quantitatively with strong anions such as organolithium compounds. Unfortunately, no reliable *e* value for DPE is available, since DPE is not normally copolymerized with other monomers because of the nonpolymerizable nature. From the previous results of anionic crossover reactions, however, the reactivity of DPE can be readily estimated to be much more electrophilic than those of styrene and α-methylstyrene. Taking the higher electrophilicity of DPE into consideration, it is of special interest to examine whether the reactions of anionic living polymers with 1-[4-(3-halopropyl)phenyl]-1-phenylethylenes (**4**) proceed selectively without anion attack on the diphenylethenyl moiety, permitting formation of the ω-1,1-diphenylethenyl macromonomers with well-controlled structures.

Table 4. Reactions of Anionic Living Polymers with 4[a]

terminating agent	living polymer[b]	functionality, %		
		^{1}H NMR	UV	SEC[c]
4-Cl	PS-Li	30[d]		
4-Cl	PI-Li	41[e]		
4-Br	PS-Li	95	100	
4-Br	PI-Li	100		100
4-I	PS-Li	98	98	100
4-I	PI-Li	91	95	

[a] Reactions were carried out in THF−heptane mixtures at −78 °C for 20 min. About 2-fold excess of **4** was used. M_n values of macromonomers were in the range 2000−3000. M_w/M_n values were less than 1.10 in all polymer samples. [b] PS-Li and PI-Li indicate polystyryllithium and polyisoprenyllithium, respectively. [c] Functionality by end-group analysis using SEC of the products by the reaction of macromonomer with polystyryl anion (see Experimental Section). [d] The degree of end-functionalization with CH_2Cl group was 77%. [e] The degree of end-functionalization with CH_2Cl group was 65%.

The synthesis of well-controlled macromonomers with terminal DPE functionalities was previously reported by two research groups. Quirk and co-workers first reported that such macromonomers were synthesized by addition of polystyryllithium with either 1,4-bis(1-phenylethenyl)benzene or the meta-substituted derivative.[11,12] Under careful conditions, living polystyrene reacted with only one of the diphenylethenyl moieties in each case, and no further addition by the diphenylalkyl anion generated was observed because of the nonpolymerizable nature of DPE. Abetz and co-workers have recently reported the successful synthesis by the termination reactions of polystyryllithium with 1-(4-bromomethylphenyl)-1-phenylethylene in THF at −60 °C.[13] In this synthesis, although the bromomethyl moiety was very reactive toward the anion, they end-capped polystyryllithium with DPE before terminating to prevent the addition of the polystyryl anion to the diphenylethenyl moiety of the terminator.

There have been however no reports on the synthesis of ω-1,1-diphenylethenyl macromonomer by means of the direct termination reaction of anionic living polymers of styrene and isoprene with the simple alkyl halides containing a DPE functionality like **4** which we will attempt in this section. The reactions of anionic living polymers of styrene and isoprene with **4** were carried out in THF at −78 °C. In each of all cases, the living polymer was added slowly to a 2-fold excess of **4**. The results are summarized in Table 4.

Similar to the reactions with the bromides and iodides used in this study, the characteristic colors of the living polymers disappeared instantaneously on mixing with the bromide (**4-Br**) and the iodide (**4-I**), indicating that these reactions were very fast and finished within a few

seconds. The SEC curves of the resulting polymers were shown to have symmetrically unimodal peaks. They also have predictable molecular weights and narrow molecular weight distributions as was seen in Table 4. Both ^{1}H NMR and UV analyses indicate that the DPE functionalization was almost quantitative in each of all cases. On the basis of these results, it was demonstrated that even direct reactions of the living polymers with either **4-Br** or **4-I** proceeded very bromide and iodide selectively. Thus, the well-defined ω-1,1-diphenylethenyl macromonomers could be quantitatively obtained by the direct termination reactions of anionic living polymers of styrene and isoprene with **4-Br** and **4-I**. Considering the high reactivity of the diphenylethenyl group, these results are surprising. It should be again emphasized here that the end-capping with DPE is not needed for our reaction systems.

By contrast, attack of living polymer anions on the diphenylethenyl moiety occurred significantly when the corresponding chloride (**4-Cl**) was used in the reaction. It was clearly observed that, on mixing of polystyryllithium with **4-Cl** in THF at −78 °C, the characteristic orange color immediately changed to a dark red, indicating that a 1,1-diphenylalkyl anion was generated. This color appeared to remain unchanged after adding all of **4-Cl** and even after several hours at −78 °C and disappeared by treating with a few drops of degassed methanol.

A unimodal sharp peak was observed by the SEC of the resulting polymer. In addition, this polymer also showed a small but detectable (ca. 5%) shoulder, which doubled the molecular weight of the parent polymer. The M_n value observed for the main peak agreed with that calculated, the M_w/M_n value being 1.09. The ^{1}H NMR of the polymer showed clearly the resonance at 3.47 ppm corresponding to the CH_2Cl protons. The resonance for the ethenyl protons appearing at 5.37 ppm was also observed, but the intensity was much smaller than that expected. The degrees of end-functionalizations with CH_2Cl and diphenylethenyl groups were determined from these resonances to be 0.77 and 0.30, respectively. Evidently, polystyrylanion reacts predominantly with the diphenylethenyl moiety instead of the chloropropyl group. It appears that the newly generated 1,1-diphenylalkyl anion is nearly inert to or reacted very sluggishly with the chloropropyl group in THF at −78 °C from the observation that the dark red color appeared to remain even after several hours. Moreover, there is a little possibility of further reaction between polymer chains leading to the dimeric product, as indicated by the SEC analysis.

The dark red color disappeared gradually with time by raising the reaction temperature to 0 °C after mixing at −78 °C. In this case, a small increase of diphenylethenyl functionalization was observed but was far from complete. The color disappearance may be the result of proton abstraction from THF and/or the ring-opening reaction of THF with the 1,1-diphenylalkyl anion, since the anion of this type is known to be unstable in THF at 0 °C.[14]

A similar result was obtained in the termination reaction of polyisoprenyllithium with **4-Cl**. The lemon-yellow color changed immediately to a dark red on mixing with **4-Cl** in a THF−heptane mixture (1/1, v/v) at −78 °C, and the resultant red color remained at −78 °C for several hours. The ^{1}H NMR spectrum showed that the polyisoprene obtained was end-functionalized with both CH_2Cl and diphenylethenyl groups in the yields of 65% and 41%, respectively. The SEC curve of the resulting polymer showed to be a symmetrical unimodal peak with a small high molecular weight shoulder (ca. 5%). The polymer had a narrow molecular weight distribution, the M_w/M_n value being 1.09. Obviously, the reaction of polyisoprenyllithium also reacts concurrently with the diphenylethenyl and chloropropyl groups of **4-Cl**, similar to the reaction between polystyryllithium and **4-Cl** as mentioned above.

Table 5. Reactions of Anionic Living Polymers with 1−4

terminating agent	PS-Li[a]	PI-Li[a]	terminating agent	PS-Li[a]	PI-Li[a]
1-Cl[b]	×	×	**3-Br**	○	○
2-Cl	○	○	**4-Br**	○	○
3-Cl	△	○	**1-I**[b]	○	○
4-Cl	△	△	**2-I**	○	○
1-Br[b]	○	○	**3-I**	○	○
2-Br	○	○	**4-I**	○	○

[a] PS-Li and PI-Li indicate polystyryllithium and polyisoprenyllithium, respectively. [b] Reference 9.

Thus, we failed to synthesize quantitatively well-controlled ω-1,1-diphenylethenyl macromonomers by the reaction of anionic living polymers with **4-Cl**. This failure can be, however, speculated to a certain extent from our previous results on the reactions of anionic living polymers with 4-(3-chloropropyl)styrene (**1-Cl**). In these reactions, anion attack on the styryl group significantly occurred, although the styryl group of **1-Cl** is less electrophilic than the 1,1-diphenylethenyl group of **4-Cl**.

From a viewpoint of macromonomer synthesis, all the results obtained here as well as our previous results with **1** are summarized in Table 5. In all cases, both polystyryllithium and polyisoprenyllithium were used directly without end-capping in the reactions. The symbol shown as ○ in the table indicates quantitative synthesis of well-controlled macromonomer, while the symbol △ indicates low (30−65%) yield of the desired macromonomers. The symbol × indicates no yield of macromonomer.

As can be seen, all the bromides and iodides employed here are excellent terminating agents toward both anionic living polymers of styrene and isoprene, regardless of their polymerizable groups in a wide range from the less reactive α-alkyl-substituted styryl group to the more reactive 1,1-diphenylethenyl group. On the other hand, the synthetic utility of the chlorides was much dependent on both their polymerizable groups and the living polymer to be reacted. It was found that both **2-Cl** and **3-Cl** react selectively with polyisoprenyllithium to afford the desired macromonomers. **2-Cl** was also an effective terminator for polystyryllithium. In the reaction of polystyryllithium with **3-Cl**, however, side reactions such as proton abstraction occurred to some extent to lower the end-functionalization degree of the resulting macromonomer. With use of **4-Cl** as well as **1-Cl** in the reactions, the attack of living polymer anions on the polymerizable groups always occurred significantly even in THF at −78 °C.

Conclusion

To synthesize three different ω−α-substituted styryl macromonomers with well-controlled structures, we have reacted each of **2**−**4** directly with anionic living polymers of styrene and isoprene in THF at −78 °C. If the bromides as well as the iodides of the terminators

are chosen, the desired macromonomers can be obtained quantitatively. Furthermore, even a chloride like **2-Cl** is also found to be an excellent terminator in the same reactions, while the syntheses of macromonomers were more or less unsuccessful with other chlorides of **1-Cl**, **3-Cl**, and **4-Cl**.

Acknowledgment. We are grateful to T. Himeno and H. Nagakari of our laboratory for carrying out a part of the experiments. Financial support of a Grand-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan is gratefully acknowledged. M.H. is also thankful for support from the Japan Society for the Promotion of Science Research Fellowships for Young Scientists.

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MA981189Q