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Synthesis of End-Functionalized Polymer by Means of Anionic Living Polymerization. 6. Synthesis of Well-Defined Polystyrenes and Polyisoprenes with 4-Vinylphenyl End Group

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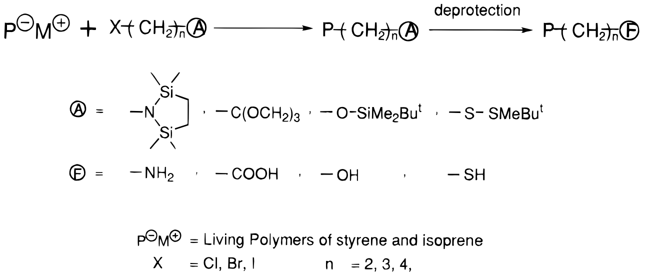
ABSTRACT: In order to synthesize end-functionalized polymers with 4-vinylphenyl group (so-called ω-styryl macromonomers), anionic living polymers of styrene and isoprene were allowed to react with five 4-(ω-haloalkyl)styrene derivatives in THF at −78 °C. 4-Vinylphenyl-terminated polymers of well-controlled molecular weights and narrow molecular weight distributions ($M_w/M_n < 1.05$) as well as with nearly quantitative end functionalities were obtained in 100% yields by the reactions with 4-(2-bromoethyl)styrene, 4-(3-bromopropyl)styrene, 4-(3-iodopropyl)styrene, and 4-(4-bromobutyl)styrene. On the other hand, the reactions of anionic living polymers with 4-(3-chloropropyl)styrene were complicated by competitive side reactions of anion attack on the vinyl groups of terminating agent and the macromonomer produced.

Introduction

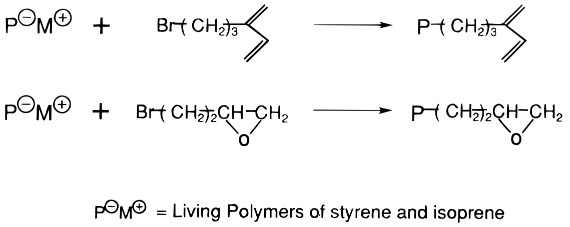
We have recently been developing a new methodology for synthesizing well-defined end-functionalized polymers that have controllable chain lengths with nearly uniform distributions as well as high degrees of functionalization.[1−3] The methodology utilizes the termination reactions of anionic living polymer of styrene or isoprene with the following specially designed haloalkanes containing protected functionalities in a manner of nucleophilic substitution. Although it is known that nucleophilic substitution reactions of carbanions with alkyl halides usually proceed competitively with some side reactions such as α-metalation, β-elimination, and undesirable coupling reaction via metal−halogen interchange and/or single-electron transfer pathway, the reactions of anionic living polymers with the haloalkanes have been observed to proceed efficiently and nearly quantitatively without any such side reactions. The polymers with amino,[1] carboxy,[2] hydroxy,[3] and mercapto end groups[3] were actually obtained with very high degrees of end functionalization (>95%). The polymers thus obtained possessed well-controlled molecular weights and narrow molecular weight distributions as expected.

Throughout the experimental observations in these termination reactions, it was found that the reactions proceeded very fast, especially with the bromo- and iodoalkanes, and finished within seconds. This is evident from the fact that the characteristic colors of anionic living polymers disappeared virtually instantaneously on mixing with the haloalkanes. Taking into consideration such rapid reaction rates as well as the quantitative nature of the reactions, we next attempted the reactions of anionic living polymers with the bromoalkanes containing anion-sensitive 1,3-butadienyl and 1,2-epoxy groups with a hope that the reactions would proceed as outlined in Scheme 2.

Scheme 1



Scheme 2



In these reactions, it is anticipated that nucleophilic additions and/or polymerizations of the butadienyl and epoxy groups by the anions may possibly compete with the expected reactions. The sucsess of the reactions using anionic living polymers may be attributed to the employment of the reaction conditions in a polar solvent at a low temperature (in THF at −78 °C) which are different from those of analogous works previously reported. In much of the earlier work, the reactions were carried out in hydrocarbon solvents at or above room temperature. Indeed, both the groups are known to be very sensitive toward carbanions[4] and reported to react readily with anionic living polymers of styrene and isoprene.[5] Very fortunately, however, the reactions predominantly occurred only with the bromoalkyl parts of the bromoalkanes, and both 1,3-butadienyl and 1,2-epoxy groups remained intact during the course of the reactions. The polymers with 1,3-butadienyl and 1,2-epoxy end groups were thus obtained, and their degrees of end functionalizations in both cases were nearly quantitative.[6,7] The ease of the desired termination reactions with the functional haloalkanes is undoubtedly a consequence that the reactions with the bromoalkyl parts are much more rapid than the addition with 1,3-butadienyl and 1,2-epoxy groups. Thus, we have demonstrated the possible use of the functional haloalkanes containing such anion-sensitive groups without protection under the conditions needed to proceed according to Scheme 2.

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These successful results encourage us to investigate similar termination reactions with haloalkanes containing other anion-sensitive functional groups, so as to determine the real scope and the limitation of this useful method for synthesizing well-defined end-functionalized polymers. Herein, we will focus on the 4-vinylphenyl group as an anion-sensitive group and report the reactions of anionic living polymers with five 4-(ω-haloalkyl)styrenes for synthesizing well-defined polymers end-functionalized with 4-vinylphenyl group (so-called ω-styryl macromonomers).

Experimental Section

Materials. Styrene and isoprene were purified according to the usual procedure. They were washed with 5% NaOH and dried over $MgSO_4$. They were filtered and distilled over CaH_2 under an atmosphere of nitrogen. They were finally distilled over phenylmagnesium chloride and *n*-butyllithium, respectively, on the vacuum line into ampules with break seals that were prewashed with (1,1-diphenylhexyl)lithium in heptane. *sec*-Butyllithium (*s*-BuLi) was purchased from Kanto Chemical Co., Ltd., and used without purification. Potassium naphthalenide was prepared by the reaction of potassium metal with a 1.2-fold excess of naphthalene in THF at 25 °C for 12 h.

Synthesis of Terminating Agents 1−5. 4-(2-Bromoethyl)styrene (1). **1** was synthesized by the bromination of 4-(2-hydroxyethyl)styrene as follows: To a mixture of 4-(2-hydroxyethyl)styrene (4.93 g, 33.3 mmol) and CBr_4 (14.3 g, 66.6 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added Ph_3P (9.75 g, 37.2 mmol) dropwise with stirring. The mixture was stirred at 0 °C for 3.5 h. Standard workup followed by flash column chromatography using hexane as an eluant gave **1** in 90% yield as a colorless liquid which was further purified by distillation over CaH_2 under reduced pressure: bp 90−95 °C (2.5 Torr); 90 MHz ^{1}H NMR ($CDCl_3$) δ 7.26 (m, 4H, HAr), 6.70 (dd, 1H, J = 17.5, 10.8 Hz, -CH=), 5.75, 5.22 (dd, 2H, J = 17.5, 10.8 Hz, CH$_2$=), 3.52 (t, 2H, J = 7.0 Hz, -CH$_2$Br), 3.13 (t, 2H, J = 6.9 Hz, -CH_2CH$_2$Br); 23 MHz ^{13}C NMR ($CDCl_3$) δ 138.6 (-CH=), 136.7 (Ar, C1), 128.8 (Ar, C3), 126.6 (Ar, C2), 113.7 (=CH$_2$), 39.3 (CH$_2$CH$_2$Br), 32.5 (CH$_2$Br).

4-(3-Chloropropyl)styrene (2). **2** was synthesized by the reaction of (4-vinylphenyl)magnesium chloride with 1-bromo-3-chloropropane in the presence of Li_2CuCl_4 according to the procedure reported by Tamura and Kochi.[8] To an ice-cooled THF solution (50 mL) containing 1-bromo-3-chloropropane (22.67 g, 144 mmol) and Li_2CuCl_4 (221 mg, 1.0 mmol) was added (4-vinylphenyl)magnesium chloride, prepared from 4-vinylphenyl chloride (8.66 mL, 72 mmol) and magnesium (2.75 g, 108 mg-atom), in THF (60 mL) dropwise over a period of 30 min. The resulting mixture was 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** (6.32 g, 49%) as a colorless liquid: bp 65−75 °C (1−2 Torr); 90 MHz ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 4H, HAr), 6.70 (dd, 1H, J = 17.6, 10.8 Hz, -CH=), 5.71, 5.21 (dd, 2H, J = 17.6, 10.8 Hz, CH$_2$=), 3.52 (t, 2H, J = 7.3 Hz, -CH$_2$Cl), 2.78 (t, 2H, J = 6.3 Hz, -CH_2CH$_2$CH$_2$Cl), 2.08 (m, 2H, -CH_2CH$_2$Cl); 23 MHz ^{13}C NMR ($CDCl_3$) δ 140.4 (Ar, C4), 136.7 (-CH=), 135.9 (Ar, C1), 128.7 (Ar, C3), 126.4 (Ar, C2), 113.1 (=CH$_2$), 44.0 (-CH$_2$Cl), 34.0 (ArCH$_2$), 32.6 (-CH$_2$CH$_2$Cl).

4-(3-Bromopropyl)styrene (3). **2** (2.71 g, 15 mmol) and dry LiBr (20.5 g, 195 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 fractional distillation yielded **3** (2.92 g, 87%) as a colorless liquid: bp 72.5−73.0 °C (0.5 Torr); 90 MHz ^{1}H NMR ($CDCl_3$) δ 7.24 (m, 4H, HAr), 6.70 (dd, 1H, J = 18.0, 11.0 Hz, -CH=), 5.70, 5.20 (dd, 2H, J = 19.0, 12.0 Hz, CH$_2$=), 3.38 (t, 2H, J = 6.5 Hz, -CH$_2$Br), 2.78 (t, 2H, J = 7.2 Hz, -CH_2CH$_2$CH$_2$Br), 2.15 (m, 2H, -CH_2CH$_2$Br); 23 MHz ^{13}C NMR ($CDCl_3$) δ 140.1 (Ar, C4), 136.6 (-CH=), 135.8 (Ar, C1), 128.6 (Ar, C3), 126.3 (Ar, C2), 113.1 (=CH$_2$), 34.0 (ArCH$_2$), 33.7 (-CH$_2$Br), 32.7 (-CH$_2$CH$_2$Br).

4-(3-Iodopropyl)styrene (4). **2** (5.23 g, 29 mmol) and dry NaI (65.2 g, 435 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 **4** (5.17 g, 66%) as a pale yellow liquid: bp 83.5−84.0 °C (0.5 Torr); 90 MHz ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 4H, HAr), 6.70 (dd, 1H, J = 17.6, 10.9 Hz, -CH=), 5.70, 5.20 (dd, 2H, J = 17.6, 10.9 Hz, CH$_2$=), 3.15 (t, 2H, J = 6.7 Hz, -CH$_2$I), 2.71 (t, 2H, J = 7.1 Hz, -CH_2CH$_2$CH$_2$I), 2.17 (m, 2H, -CH_2CH$_2$I); 23 MHz ^{13}C NMR ($CDCl_3$) δ 140.1 (Ar, C4), 136.8 (-CH=), 135.9 (Ar, C1), 128.7 (Ar, C3), 126.5 (Ar, C2), 113.3 (=CH$_2$), 36.1 (CH$_2$CH$_2$I), 34.9 (ArCH$_2$), 5.7 (-CH$_2$I).

4-(4-Bromobutyl)styrene (5). This was synthesized by the same procedure as described for **2**. 1,4-Dibromobutane was used instead of 1-bromo-3-chloropropane in this case. Fractional distillation under reduced pressure gave **5** in 60% yield as a colorless liquid: bp 92−93 °C (1.0 Torr); 90 MHz ^{1}H NMR ($CDCl_3$) δ 7.22 (m, 4H, HAr), 6.70 (dd, 1H, J = 17.7, 10.9 Hz, -CH=), 5.70, 5.19 (dd, 2H, J = 17.7, 10.9 Hz, CH$_2$=), 3.40 (t, 2H, J = 6.4 Hz, -CH$_2$Br), 2.62 (t, 2H, J = 6.7, -CH_2CH$_2$CH$_2$CH$_2$Br), 1.81 (m, 4H, -CH_2CH_2CH$_2$Br); 23 MHz ^{13}C NMR ($CDCl_3$) δ 141.6 (Ar, C4), 136.7 (-CH=), 135.5 (Ar, C1), 128.6 (Ar, C3), 126.3 (Ar, C2), 113.1 (=CH$_2$), 34.7 (ArCH$_2$), 33.6 (CH$_2$Br), 32.3 (ArCH$_2$$CH_2$), 29.8 ($CH_2CH_2$Br).

To the terminating agents **1**−**5** was added phenylmagnesium chloride (ca. 5 mol %), and the mixtures were degassed and stirred for 1 h. They were then distilled on a vacuum line into ampules with break seals that were prewashed with sodium naphthalenide in THF.

Polymerizations and Reactions of Anionic Living Polymers with 1−5. 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 used for the polymerization followed by the reactions. The anionic polymerization of styrene was performed with either *s*-BuLi or potassium naphthalenide in THF at −78 °C for 10 min. The polymerization of isoprene was carried out with *s*-BuLi in heptane at 40 °C for 4 h. In this case, an equal volume of THF was added to the heptane solution of poly(isoprenyllithium) at −78 °C prior to the termination reaction.

The living polymer solution was usually added dropwise into a THF solution of each terminating agent at −78 °C over a period of 10 min, and the mixture was allowed to stand at −78 °C for an additional 10 min (method A). In this method A, the amount of terminating agent is always larger than that of the anion of living polymer. A reverse addition method in which the terminating agent was added to living polymer at once was also attempted in some cases (method B). This method seems to be disfavorable for the expected termination reaction, since the terminating agent and the macromonomer produced were exposed with an excess anion of living polymer.

The polymers were precipitated in methanol and purified by the repeated reprecipitation from THF to methanol thrice to remove unreacted terminating agent. They were then freeze-dried and characterized by various analyses.

End-Group Analysis of Macromonomers. (1) ^{1}H NMR Method. The degrees of end functionalization of ω-styryl polystyrene macromonomers were determined by comparison between the relative values of the ^{1}H NMR peak intensities at 5.1−5.8 ppm to the CH$_2$ protons of vinyl group and 6.2−7.4 ppm to the aromatic protons of polystyrene based on M_n value measured by SEC. The peak at 0.6 ppm to methyl protons from the initiator residue of *s*-BuLi is also useful for this determination. On the end-functionalization degrees of ω-styryl polyisoprene macromonomers, the peak intensities at 5.6−6.9 ppm to the CH$_2$= protons of vinyl group and 5.1 ppm to the CH= proton of *cis*-1,4-polyisoprene main chain were used.

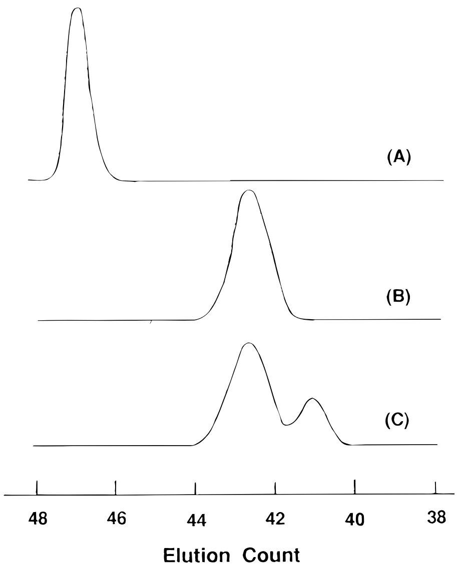


Figure 1. SEC curves of macromonomer (A), polystyrene (B), and reaction product (C).

The peak at 0.85 ppm to methyl protons derived from initiator residue was also used in the polymer sample obtained by the polymerization initiated with *s*-BuLi. The errors in this method of end-group analysis are <5%.

(2) UV Spectroscopy Method. The degrees of end functionalization could be determined by using a large value of the molar extinction coefficient of terminal styryl group in UV region. 4-Propylstyrene, a model compound, was used as a reference. Its ϵ_{max} is 1.77×10^4 L/mol·cm at 254.4 nm which is more than 10^2 times larger than those of polystyrene and polyisoprene at 254.4 nm. The experimental errors in this method are <3%.

(3) SEC Method via Polymer Reaction. This method was done by taking advantage of the reaction of the terminal styryl group of macromonomer with polystyryl anion. The macromonomer (M_n = ca. 2100) obtained by the reaction of poly(styryllithium) with **5** was freeze-dried thrice from the absolute benzene solution and dissolved in THF. Poly(styryllithium) ($M_n = 6000$), separately prepared, was allowed to react with the macromonomer in THF at −78 °C for several hours under the condition 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 1. The peaks A−C are those for the macromonomer, the 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 peaks are observed for polystyrene ($M_n = 6000$) unreacted and the 1:1 addition product ($M_n = 8100$) of the macromonomer and poly(styryllithium). The result clearly demonstrates that the end-functionalization degree of this macromonomer is quantitative. A direct evidence for the presence of terminal styryl group of the macromonomer is also provided by this experiment. The accurancy 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 <3%.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer (89.6 MHz ^{1}H NMR and 22.53 MHz ^{13}C NMR) in $CDCl_3$. UV spectra were recorded on a JASCO 660 UV/vis spectrophotometer. SEC was obtained at 40 °C 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. Three polystyrene gel columns (TSK$_{gel}$ G4000H$_{XL}$, G3000H$_{XL}$, and G2000H$_{XL}$) were used. Calibration curves were made to determine M_n and M_w/M_n values with standard polystyrene and polyisoprene samples.

Results and Discussion

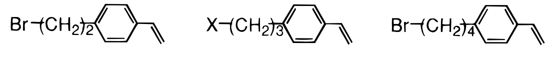
The synthesis of ω-styryl macromonomers via anionic approach was previously reported by Milkovich et al.,[9] Rempp et al.,[10] and Deffieux et al.[11] This was accomplished by treating polystyryl anion with either ethylene oxide or 1,1-diphenylethylene followed by reacting with 4-vinylbenzyl chloride. Later, Asami and his co-workers successfully synthesized such macromonomers by a direct reaction of living polystyrene with large excesses of 4-vinylbenzyl chloride.[12]

In the first two methods, polystyryl anion was end-capped to reduce its reactivity to avoid the side reactions of nucleophilic addition and/or polymerization of vinyl group with anionic living polystyrene. The use of highly reactive 4-vinylbenzyl chloride is essential for forcing the reactions with the end-capped anions of relatively low reactivities. In the reaction where polystyryl anion was directly used, 4-vinylbenzyl chloride seems to also be preferable for promoting the expected reaction to suppress the reaction toward the vinyl bond. It was however observed that even with the use of a large excess 4-vinylbenzyl chloride, the addition reaction of the vinyl group with polyisoprenyl anion occurred concurrently, and therefore more reactive 4-vinylbenzyl tosylate was required to complete the reaction leading to ω-styryl polyisoprene macromonomer.[13]

As mentioned in the Introduction, we have demonstrated that the less reactive bromopropyl group of 2-(3-bromopropyl)-1,3-butadiene reacts efficiently with polystyryl anion and even polyisoprenyl anion to afford well-defined ω-butadienyl polystyrene and polyisoprene macromonomers quantitatively.[6] No attack of the butadienyl group by their anions was observed at all during the reactions. This suggests that use of highly reactive alkyl halides such as 4-vinylbenzyl chloride and tosylate is not always necessary in these kinds of reactions with anionic living polymers. Therefore, we have investigated the possible use of 4-(ω-haloalkyl)styrene derivatives with less reactive alkyl halide moieties in the reactions with anionic living polymers for synthesis of well-defined ω-styryl macromonomers.

4-(ω-Haloalkyl)styrene Derivatives. As terminating agents for anionic living polymers of styrene and isoprene, we have chosen five 4-(ω-haloalkyl)styrenes: 4-(2-bromoethyl)styrene (**1**), 4-(3-chloropropyl)styrene (**2**), 4-(3-bromopropyl)styrene (**3**), 4-(3-iodopropyl)styrene (**4**), and 4-(4-bromobutyl)styrene (**5**). The variation of halogen and methylene chain length was examined in order to explore suitable terminating agents instead of 4-vinylbenzyl chloride and tosylate for synthesizing well-defined ω-styryl macromonomers. For this purpose, it is required that the reactions of anionic living polymers with the haloalkyl parts are much more rapid than those with the vinyl groups of **1**−**5**.

Terminating agents



(**1**)

(**2**) X = Cl
(**3**) X = Br
(**4**) X = I

(**5**)

Before attempting the reactions with **1**−**5**, we would like to estimate the reactivities of their alkyl halides and compare them with those of 4-vinylbenzyl chloride and tosylate. The termination reaction is considered to

Table 1. Results of Termination Reactions of Polystyryl Anions with 1−5[a]

terminating agent	method	SEC of reaction products[b]		ω-styryl polystyrene macromonomer[c] functionality, %		
		P, %	$(P)_n$, %	^{1}H NMR	UV	SEC[d]
1	A	52	48			
2	A	0	100			
2[e]	A	30	70			
3	A	100	0	∼100	98	
3	B	82	18	81	80	
3[f]	A	100	0		93	100
4	A	100	0	95		100
4	B	95	5	92	91	
5	A	100	0	100	93	

[a] Reactions were carried out in THF−heptane mixtures at −78 °C for 20 min. About 2-fold excess of **1**−**5** was used. [b] P indicates the yield of macromonomer based on the SEC peak areas. $(P)_n$ indicates the yields of dimeric, oligomeric, and polymeric materials. [c] M_n values of macromonomers were in the range of 2000−5000. M_w/M_n values were <1.10 in all polymer samples. [d] Functionality by end-group analysis using SEC of the products by the reaction of macromonomer with polystyrylanion (see the Experimental Section). [e] A 13-fold excess of **2** to polystyrylanion was used. [f] Polystyryl dipotassium was used as a difunctional polystyrylanion.

proceed by an S_N2 pathway. The rate of the reaction depends not only on the structure of the alkyl halide but also on the nature of the halogen. According to the previous literatures related to similar reactions, the reactivity order of **1**−**5** can be roughly estimated to be in the order of $\mathbf{4} > \mathbf{1} > \mathbf{3} \geq \mathbf{5} \gg \mathbf{2}$,[14] although the trend is sensitive to reaction temperature, solvent effects, and steric conditions around the nucleophile and the center of substitution. The reactivity of 4-vinylbenzyl chloride may be slightly higher than that of **4**. 4-Vinylbenzyl tosylate is undoubtedly the most reactive terminating agent among those used in the reaction.

Reactions of Polystyryl Anion with 1−5. The reactions of polystyryl anion with **1**−**5** were first attempted to synthesize ω-styryl macromonomers. The reactions were generally carried out in THF at −78 °C by adding polystyryl anion dropwise to each of the terminating agents (method A). About 2-fold excess of the terminating agent for anion was usually used. Accordingly, the amount of the terminating agent is always larger than that of polystyryl anion during the reaction. In the reactions with (bromoalkyl)styrenes **1**, **3**, and **5** and the iodo derivative **4**, the characteristic red color of polystyryl anion disappeared instantaneously on mixing with the terminating agent, although it faded to colorless for seconds near the end of addition. Thus, the reactions appear to proceed very rapidly in these cases. On the other hand, the reaction with the chloro analogue **2** was not so rapid from the observation that the color faded gradually on mixing with **2** and remained for several minutes even after addition of all of **2**. The results are summarized in Table 1.

As can be seen, the results of the reactions with **3**−**5** are very satisfactory. The SEC of all the resulting polymers showed that their distribution peaks were unimodal without any tailings and shoulders and nearly monodispersed. Typically, the M_w/M_n value was about 1.05. The good agreement between M_n values predicted and observed was also demonstrated in the range of 2000−5000 for all polymer samples.

The degrees of end functionalization of these samples were determined using various analytical methods such as SEC, ^{1}H NMR, and UV spectroscopy. In addition to these methods, we have directly estimated the degree of end functionalization by taking advantage of the reaction of the terminal styryl group with polystyryl anion. For example, the ω-styryl macromonomer (M_n = 2100) obtained was purified and allowed to react with polystyryl anion (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 polystyryl anion newly appear, as can be seen in Figure 1 (see the Experimental Section). The result clearly indicates that all the terminal styryl groups react completely with polystyryl anion, and therefore the degree of end functionalization for this macromonomer is quantitative. Furthermore, a direct evidence for the presence as well as reactivity of ω-styryl group is provided by this experiment.

Again as can be seen in Table 1, each of these methods demonstrates that the degrees of end functionalization for the polymer samples obtained are virtually quantitative. Similarly, a well-defined α,ω-distyryl-functionalized polystyrene could be synthesized by the reaction with **3** with difunctional living polystyrene initiated with potassium naphthalenide. From these results, the reactions of polystyryl anion with the bromoalkyl and iodopropyl groups of **3**−**5** are much more rapid than those with their vinyl groups and the vinyl groups of the macromonomers produced. The reactions of polystyryl anion with **3**−**5** proceed very efficiently in a desired way to afford well-defined ω-styryl polystyrene macromonomers.

What was unexpected was that reverse addition (method B), that is, addition of the terminating agent **3** or **4** to polystyryl anion, gave the corresponding macromonomers in excellent yields of 82% and 95%, respectively. The low reactivities of the vinyl groups of **3** and **4** and their macromonomers produced toward the excess of polystyryl anion present during the course of the reaction are thus surprising. It is also supported by this result that the reaction between polystyryl anion and the bromoalkyl part of **3** or **4** is rapid enough to permit the synthesis of macromonomers.

On the contrary, the attempts for quantitative synthesis of the macromonomers failed in both the reactions of poly(styryllithium) with **1** and **2**. The reaction with **1** was observed to rapidly proceed similarly to the reactions with the bromo derivatives. The product was however a mixture of the macromonomer (52%) with an M_n of 2000 and a polymeric material that has a M_n value of ca. 10^5 with a broad molecular weight distribution. Since neither dimeric nor oligomeric products were formed in the product, polymerization of the macromonomer was indicated to occur near the final stage of the reaction.

As was mentioned, the reaction with **2** appeared to proceed slowly. The SEC trace of the product showed only a relatively sharp peak with a M_n of 13 000 but not a peak for the corresponding macromonomer (M_n = 2000). The ^{1}H NMR showed that only a small signal for vinyl group was detected in the product. In addition, the resonance signal corresponding to CH_2Cl protons was observed. Accordingly, polymerization of the macromonomer and/or the polymerization of **2** followed by reacting with the remaining poly(styryllithium) was likely to occur. Undoubtedly, this is attributed to the slow reaction of polystyryl anion with the chloropropyl group. In an attempt to improve the yield of macromonomer, the reaction of poly(styryllithium) with a

Table 2. Results of Termination Reactions of Poly(isoprenyllithium) with 1−5[a]

		SEC of reaction products[b]		ω-styryl polystyrene macromonomer[c] functionality, %		
terminating agent	method	P, %	$(P)_n$, %	^{1}H NMR	UV	SEC[d]
1	A	100	0		97	100
2	A	55	45			
3	A	100	0	96		100
4	A	100	0	∼100	98	
4	B	100	0	∼100	∼100	100
5	A	97	3	92		100

[a] Reactions were carried out in THF−heptane mixtures at -78 °C for 20 min. About 2-fold excess of **1**−**5** was used. [b] P indicates the yield of macromonomer, based on the SEC peak areas. $(P)_n$ indicates the yields of dimeric, oligomeric, and polymeric materials. [c] M_n values of macromonomers were in the range of 2230−2890. M_w/M_n values were <1.08 in all polymer samples. [d] Functionality by end-group analysis using SEC of the products by the reaction of macromonomer with polystyrylanion (see the Experimental Section).

13-fold excess of **2** was performed. Even under this condition, the reaction gave a mixture of the corresponding macromonomer (ca. 30%) and dimeric and higher molecular weight products. Unfortunately, the reaction of polystyryl anion with the chloropropyl group of **2** was not rapid enough, and accordingly the reactions of polystyryl anion with the vinyl groups of **2** and the macromonomer produced could not be completely suppressed under the condition using a large excess of **2**.

Reactions of Polyisoprenyl Anion with 1−5. The termination reactions of poly(isoprenyllithium) with **1**−**5** were carried out at -78 °C in a mixture of THF and heptane in a similar manner to the case of poly(styryllithium). The lemon-yellow color of polyisoprenyl anion disappeared instantaneously on mixing with the bromo and iodo derivatives, while it faded gradually in the reaction with the chloro derivative of **2**. The results are summarized in Table 2.

As can be seen, the good agreement of M_n values between predicted and measured as well as the narrow distributions of molecular weight is observed in the polymers obtained by the reactions of poly(isoprenyllithium) with all the terminating agents except for **2**. Their degrees of end functionalization are found to be almost quantitative by the different analytical methods. Accordingly, the termination reactions with **1** and **3**−**5** proceed efficiently without any side reactions to afford well-defined ω-styryl polyisoprene macromonomers. It was relatively surprising that the reaction with **1** underwent with success, while a significant amount of polymeric material was produced in the reaction of poly(styryllithium) with **1**, as mentioned before. Surprisingly, the desired macromonomer could be obtained in 100% yield by the reaction with **4**, even using method B which seems to be disfavorable for the termination reaction. The result of the reaction with the iodo derivative of **4** can be somewhat accepted, although a trace amount of the dimeric product (ca. 3%) was detected by SEC, and therefore further optimization should be needed.

Thus, the termination reactions with the use of α-(ω-haloalkyl)styrenes such as **1** and **3**−**5** also provide a convenient route to well-defined ω-styryl polyisoprene macromonomers. This is a sharp contrast to the previous reported result that the attack of the vinyl bond of 4-vinylbenzyl chloride by poly(isoprenyllithium) was not completely suppressed to produce the dimeric side product.[13] Furthermore, it should be emphasized that slight excesses (usually ca. 2-fold excess and even 1.4-fold excess in the case of **5**) of the terminating agents were enough to use for proceeding with the expected reactions, whereas 4-vinylbenzyl chloride was employed in a large excess amount (11.5-fold excess). Thus, advantages of **1** and **3**−**5** over 4-vinylbenzyl chloride as terminating agents are obvious, especially in the reaction of polyisoprenyl anion.

Table 3. Results of Termination Reactions of Anionic Living Polymers with 1−5, 4-Vinylbenzyl Chloride, and 4-Vinylbenzyl Tosylate[a]

terminating agent	polystyryl anion	polyisoprenyl anion
1	52	100
2	0	55
3	100	100
4	100	100
5	100	97
4-vinylbenzyl chloride[b]	100	78
4-vinylbenzyl tosylate[c]		100

[a] Living polymers were added dropwise into each of the terminating agents (method A). Figures in the table indicate the yields of macromonomers. [b] Cited from ref 12. [c] Cited from ref 13.

The reaction with **2** was not successful with respect to the yield of macromonomer. The macromonomer was obtained in 55% yield together with 45% of dimeric, trimeric, and polymeric materials. Obviously, in the reaction of **2**, undesirable side reactions such as the addition and/or the polymerization of macromonomer with polyisoprenyl anion occurred competitively with the expected termination reaction. The cause for this can be explained by the low reactivity of chloropropyl group toward polyisoprenyl anion, similar to the case using poly(styryllithium).

All the results of the reactions attempted here are summarized in Table 3. The results with 4-vinylbenzyl chloride and tosylate previously reported are also added for comparison in this table. As can be seen, well-defined ω-styryl polystyrene as well as ω-styryl polyisoprene macromonomers are synthesized quantitatively by the termination reactions of their anionic living polymers with 4-(ω-haloalkyl)styrenes such as **1** and **3**−**5**. On the other hand, dimeric, oligomeric, and polymeric materials were more or less produced as side products in the reactions of poly(isoprenyllithium) with **2**. Dimeric side product was also produced in the reaction of poly(isoprenyllithium) with 4-vinylbenzyl chloride.

It seems likely to consider that the use of activated alkyl halides such as benzyl halides and tosylate is desirable for facilitating the expected termination reaction. However, the results of the reactions are not always consistent with the reactivity orders of haloalkyl parts of the terminating agents, as estimated in the preceding section: 4-vinylbenzyl tosylate ≫ 4-vinylbenzyl chloride ≥ **4** > **1** > **3** ≥ **5** ≫ **2**. Since most probable side reactions are nucleophilic addition and/or polymerization of both the vinyl group of terminating agent and the macromonomer with anionic living polymer, it is therefore necessary to elucidate the vinyl reactivities of the terminating agent as well as the macromonomer toward anionic species. The values of ^{13}C NMR chemical shifts of the β-carbons of vinyl groups may be conveniently used for this purpose, since they reflect closely the electron density on the β-carbon.[15] Usually, vinyl groups showing higher chemical shifts have higher electron densities and therefore lower reactivities toward anionic species. The values of the β-carbons of **1**−**5** and 4-vinylbenzyl chloride were 113.7, 113.2, 113.1, 113.1, 113.1, and 114.5 ppm in $CDCl_3$. As a reference, the value of styrene was also measured to be 113.8 ppm. The values of the resulting macromonomers all obtained here are possibly estimated to be similar to that of 4-methylstyrene (112.8 ppm).

Surprisingly, the value of 4-vinylbenzyl chloride (114.5 ppm) is similar to those of the following 4-substituted styrenes with electron-withdrawing groups: 4-chlorostyrene (114.4 ppm), 4-bromostyrene (114.6 ppm), 4-(*N*,*N*-diethylamido)styrene (114.8 ppm), and 4-(*N*-*tert*-butylimino)styrene (114.9 ppm).[16] Accordingly, the vinyl group of 4-vinylbenzyl chloride should be more reactive than those of styrene and **1** and much more reactive than those of **2**−**5**. It can be reasonably explained from this higher vinyl reactivity of 4-vinylbenzyl chloride that the addition reaction of polyisoprenyl anion with the vinyl group occurs competitively with the expected reaction to form dimeric side product, although the benzyl chloride is highly reactive.

As mentioned before, the reaction of poly(styryllithium) with **1** produced a significant amount of polymeric material in addition to the corresponding macromonomer. It is therefore advisable that use of a terminating agent whose vinyl reactivity is similar to that of styrene is not preferable in the termination reaction. In this case, a more reactive haloalkyl part than 2-bromoethyl substituent would be required.

The vinyl reactivities of **2**−**5** show almost the same because the halogens are separated by more than three methylene chains from 4-vinylphenyl group and therefore have little effect on the reactivity. Furthermore, their reactivities may be similar to those of the resulting macromonomers obtained as estimated above. In comparison with the value of styrene, their vinyl groups are much less reactive toward anion than that of styrene. Evidently, each of these haloalkyl substituents exhibits an electron-donating character. Their electronic effects are just opposite from that of chloromethyl group of electron-withdrawing character. With the use of **3**−**5**, because of the low reactivities of the vinyl groups, the expected termination reactions may precede the reactions of the vinyl groups with anion to produce the macromonomers in quantitative yields. Thus, we consider that the low vinyl reactivities of **3**−**5** as well as the macromonomers may strongly contribute to the success. In the case of **2**, however, the reactions of living polymers with the chloropropyl group of **2** are not rapid so as to suppress completely the reactions of the vinyl group with their anions, even if the vinyl reactivity of **2** is low. As expected, the reactivity balance between the vinyl- and haloalkyl groups of (ω-haloalkyl)styrene is thus important to realize the expected termination reaction. The information available in this study should be extremely useful for considering the molecular design of (haloalkyl)styrene as a terminating agent.

In conclusion, we have successfully synthesized well-defined ω-styryl polystyrene and polyisoprene macromonomers by the termination reactions of their anionic living polymers with some 4-(ω-haloalkyl)styrene derivatives such as **1** and **3**−**5**. Therefore, this method based on the termination reaction should be very useful for the synthesis of ω-styryl macromonomers. Furthermore, the results obtained here indicate strongly that as the haloalkyl part of terminating agent an activated alkyl halide like benzyl halide is not necessary in this kind of termination reaction.

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