Synthesis of Functionalized Polymers by Means of Anionic Living Polymerization. 1. Synthesis of Functionalized Polymers with α-Methylstyryl Groups by Anionic Reactions with Use of 1-{4-[3-(4-Isopropenylphenyl)propyl]phenyl}-1-phenylethylene

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ABSTRACT: Well-defined end-functionalized poly(methyl methacrylate), poly(*tert*-butyl methacrylate), poly[(2-perfluorobutyl)ethyl methacrylate), and poly(2-hydroxyethyl methacrylate) with α-methylstyryl groups were synthesized by the anionic living polymerization of the corresponding methacrylate monomers (or the trimethylsilyl-protected monomer in the case of poly(2-hydroxyethyl methacrylate)) with the adduct prepared from *s*-BuLi and 1-{4-[3-(4-isopropenylphenyl)propyl]phenyl}-1-phenylethylene (**1**). Well-defined end-functionalized polystyrene and polyisoprene with α-methylstyryl groups were also synthesized by directly reacting their anionic living polymers with **1** in THF at −78 °C. Furthermore, the polystyrene end-functionalized with two α-methylstyryl groups, the poly(styrene-*b*-MMA) functionalized with the α-methylstyryl group between the block segments, and the polystyrene functionalized with the α-methylstyryl group within the polymer chain were successfully synthesized by the anionic reactions of polystyryllithium with **1** followed by treating with 4-(3-bromopropyl)-α-methylstyrene, MMA, or the polystyrene with the terminal bromobutyl functionality.

Introduction

The method of anionic living polymerization coupled with the functionalized 1,1-diphenylethylene (DPE) derivatives is one of the most excellent systems for development of a general functionalization reaction of the polymer chain end.[1] A key point in this methodology is to utilize the characteristic nature of DPE that is nonpolymerizable but undergoes monoaddition reaction quantitatively with anionic species. For example, the functionalized DPEs readily react with organolithium compounds to quantitatively produce 1:1 adducts. These adducts can be used as functional initiators in the anionic living polymerization of several monomers. The functional groups of the DPEs are thus introduced at the initiating ends of the resulting polymer chains. The functionalized DPEs also react similarly in a monoaddition manner with highly reactive living polymer anions derived from styrene and 1,3-dienic monomers to afford the functionalized polymers at the terminating chain ends. Thus, to date a variety of end-functionalized polymers have been synthesized by means of initiation and termination reactions of anionic living polymerization with use of the functionalized DPE derivatives.[2−7] As expected, the resulting polymers usually possessed nearly quantitative degrees of end functionalizations as well as well-controllable molecular weights and narrow molecular weight distributions.

Unlike most electrophilic functionalization reactions, anionic reactions with the functionalized DPEs are not simple termination reactions. New 1,1-diphenylalkyl anions are always generated from the original anions in addition to the desired functionalizations. These anions are still reactive and can be used as initiators in subsequent polymerizations of additional monomers. This procedure is named as a “living functionalization reaction” by Quirk[1] and has been developed by his research group for synthesis of the novel block copolymer functionalized at the interface between blocks.[8] For example, polystyryllithium was first reacted with 1-[4-(dimethylamino)phenyl]-1-phenylethylene, followed by the anionic living polymerization of 1,3-butadiene with the 1,1-diphenylalkyl anion newly generated from the starting living polystyryl anion. The resulting diblock copolymer of poly(styrene-*b*-1,3-butadiene) thus obtained has a *N*,*N*-dimethylanilino group between the block segments. Similarly, heteroarmed star branched polymers have been synthesized by reacting polystyryllithium with 1,3-bis(1-phenylethenyl)benzene, followed by the anionic living polymerization of 1,3-butadiene.[9,10]

Unfortunately, most of the functional groups of interest such as hydroxy, amino, and carbonyl groups cannot be used directly in the functionalization reactions with DPEs because of their incompatibility with carbanions. Therefore, the functional groups of the DPEs are usually protected during the reactions. One exception for this is a 1,1-diphenylethenyl group which is stable and undergoes no further reaction with diphenylalkyl anions because of the nonpolymerizable nature of DPE. In fact, polystyrene macromonomers with terminal DPE functionality were successfully synthesized by the reaction of living polystyrene with functionalized DPEs with a 1,1-diphenylethenyl group like 1,3-bis(1-phenylethenyl)benzene.[10,11]

In this paper, we would like to describe new functionalized reactions of anionic living polymers with α-methylstyryl groups by using 1-{4-[3-(4-isopropenylphenyl)propyl]phenyl}-1-phenylethylene (**1**), which is a DPE derivative substituted with the α-methylstyryl group. Throughout our study developed here, we will show that the α-methylstyryl group of **1** is a stable and utilizable functional group without protection in the functionalization reactions.

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Experimental Section

Materials. Monomers were purified according to the usual procedures. 2-(Trimethylsiloxy)ethyl methacrylate was synthesized according to the procedure previously reported.[12] Methacrylate monomers were distilled over CaH_2 and then over $(C_8H_{17})_3Al$ on the vacuum line into ampules with breakseals that were prewashed with (1,1-diphenylhexyl)lithium in heptane. Styrene and isoprene were distilled over $(C_4H_9)_2Mg$ and *n*-BuLi, respectively, on the vacuum line.

1-(4-Bromophenyl)-1-phenylethylene. To a mixture of methyltriphenylphosphine bromide (37.7 g, 106 mmol) and *t*-BuOK (15.4 g, 137 mmol) in THF (100 mL) at 0 °C was added 4-bromobenzophenone (25.1 g, 95.9 mmol) in THF (55 mL) dropwise over a period of 30 min. The mixture was allowed to stand at 0 °C for 1 h and then at 25 °C for an additional 1.5 h. Usual work-up followed by flash column chromatography on silica gel eluting with hexanes gave a pure title compound (22.6 g, 91%) as a colorless liquid which was further purified by distillation over CaH_2 at 145−146 °C (0.45 Torr): 300 MHz ^1H NMR ($CDCl_3$) δ 7.45 (d, 2H, $J = 8.52$ Hz, Ar), 7.32 (m, 5H, Ar), 7.20 (d, 2H, $J = 8.41$ Hz, Ar), 5.46 (s, 1H, $CH_2{=}$), 5.44 (s, 1H, $CH_2{=}$); 75 MHz ^{13}C NMR ($CDCl_3$) δ 149.1, 141.0, 140.5, 131.4, 130.0, 128.4, 128.3, 128.0, 121.9, 114.8.

1-{4-[3-(4-Isopropenylphenyl)propyl]phenyl}-1-phenylethylene (1). To a mixture of 4-(3-bromopropyl)-α-methylstyrene[13] (14.8 g, 61.9 mmol) and Li_2CuCl_4 (0.674 g, 3.08 mmol) in THF (13 mL) at 0 °C was added the Grignard reagent prepared from 1-(4-bromophenyl)-1-phenylethylene (12.3 g, 47.6 mmol) and Mg (1.97 g, 81.0 mmol) in THF (47 mL) dropwise over a period of 30 min. The mixture was stirred at 25 °C for an additional 3 h. The gray suspension was then poured into 1 N HCl (100 mL), and the product was extracted with ether (30 mL × 3). The combined organic layer was washed with water and dried over $MgSO_4$. Removal of solvent under reduced pressure followed by flash column chromatography on silica gel eluting with hexanes gave **1** (3.54 g, 20%) as a colorless liquid: 300 MHz ^1H NMR ($CDCl_3$) δ 7.45−7.14 (m, 13H, Ar), 5.45 (s, 1H, $CH_2{=}$), 5.41 (s, 1H, $CH_2{=}$), 5.35 (s, 1H, $CH_2{=}$), 5.04 (s, 1H, $CH_2{=}$), 2.67 (m, 4H, $CH_2CH_2CH_2$), 2.14 (s, 3H, CH_3); 75 MHz ^{13}C NMR ($CDCl_3$) δ 150.0, 143.1, 142.0, 141.8, 141.6, 139.0, 138.8, 128.4, 128.3, 128.3, 128.2, 127.7, 125.5, 113.8, 111.8, 76.7, 35.2, 35.1, 32.9, 21.9.

Synthesis of End-Functionalized Poly(methyl methacrylate)s with α-Methylstyryl Group. The adduct was prepared by reacting *s*-BuLi with a slight excess (ca. 1.5-fold excess) of **1** in THF at −78 °C for 0.5 h and used as an initiator for the anionic polymerization of MMA. The polymerization was usually carried out in the presence of 2−3 equiv of LiCl in THF −78 °C for 20 min. Similarly, *tert*-butyl methacrylate, 2-(perfluorobutyl)ethyl methacrylate, and 2-(trimethylsiloxy)ethyl methacrylate were anionically polymerized with the adduct in the presence of LiCl in THF at −78 °C for 20 min, except for the case of *tert*-butyl methacrylate where 2 h was required for the polymerization. Concentrations of monomers and initiators in the polymerizations were in the ranges 0.2−0.5 and (0.75−1.5) × 10^{-2} M, respectively.

The end-functionalized polymers of methyl methacrylate and 2-(perfluorobutyl)ethyl methacrylate were precipitated by pouring the polymerization mixtures, after evaporation, into a large excess of hexane and purified by reprecipitation two times from THF to hexane. They were then freeze-dried from their benzene solutions. The polymer of *tert*-butyl methacrylate was first precipitated in water and corrected to dryness. It was purified by SiO_2-based column chromatography using a mixted elution solvent (hexanes: ethyl acetate, 10/1, v/v) and freeze-dried from the benzene solution. The polymer of 2-(trimethylsiloxy)ethyl methacrylate was precipitated in methanol containing a few drops of 2 N HCl. The polymer was completely hydrolyzed at this stage to transform into poly(2-hydroxymethyl methacrylate) [poly(HEMA)]. The degree of end functionalization was determined by ^1H NMR in CD_3OD. The polymer was then esterified with 10 equiv of benzoic anhydride in pyridine at 25 °C overnight. The benzoylated polymer was precipitated in methanol and purified by reprecipitation from THF solution into methanol. The M_n and M_w/M_n values were measured by SEC using the calibration curve of the poly(2-benzoyloxyethyl methacrylate)s with known M_n values and narrow molecular weight distributions ($M_w/M_n < 1.1$) prepared by our group.

Synthesis of End-Functionalized Polystyrene and Polyisoprene with α-Methylstyryl Group. The anionic polymerizations of styrene and isoprene were carried out with *s*-BuLi in THF at −78 °C for 20 min and in heptane at 40 °C for 2 h, respectively. Concentrations of monomers and initiators were in the ranges 0.5−0.7 and (1.4−1.7) × 10^{-2} M, respectively. With use of polyisoprenyllithium, the polymerization mixture was cooled to −78 °C, and an equal volume of THF was added before the reaction. The reaction of polyisoprenyllithium with **1** was therefore carried out in a mixture of heptane and THF (1/1, v/v) at −78 °C for 30 min. In the reactions conducted in benzene, polystyryllithium was prepared by the polymerization of styrene with *s*-BuLi in benzene at 30 °C for 1 h. The living polymer solution was usually added dropwise to **1** (ca. 1.5-fold excess) in THF at −78 °C or in benzene at 30 °C over a period of 5 min, and the mixtures were allowed to stand for an additional 30 min in all cases. The end-functionalized polymers were precipitated in methanol and purified by reprecipitation from THF to methanol three times and freeze-dried from their benzene solutions.

Synthesis of End-Functionalized Polystyrene with Two α-Methylstyryl Groups. The title polystyrene was obtained by first reacting polystyryllithium with **1** in THF at −78 °C for 30 min and then with 4-(3-bromopropyl)-α-methylstyrene in THF at −78 °C for an additional 1.5 h. The end-functionalized polymer was precipitated in methanol and purified by reprecipitation from THF to methanol three times and freeze-dried from the benzene solution.

Synthesis of Functionalized Poly(styrene-*b*-MMA) with α-Methylstyryl Group between the Block Segments. The title block copolymer was obtained by first reacting polystyryllithium with **1** in THF at −78 °C for 30 min and then adding MMA to be polymerized in the presence of LiCl in THF at −78 °C for 20 min. The functionalized block copolymer was precipitated in methanol and purified by reprecipitation from THF to methanol three times and freeze-dried from the benzene solution. The M_n was determined from both the M_n value of the polystyrene obtained at the first stage of the polymerization by SEC and the composition of each segment of the resulting block copolymer by ^1H NMR.

Synthesis of Functionalized Polystyrene with α-methylstyryl Group within the Polymer Chain. The title polymer was prepared by reacting the living end-functionalized polystyrene with the α-methylstyryl group with a 1.2-fold excess of the polystyrene end-functionalized with the bromobutyl group[14] in THF at −78 °C for 90 h. The functionalized polystyrene within the polymer chain was isolated by the fraction of the resulting polymer mixture with SEC. The functionalized polymer was precipitated in methanol and purified by reprecipitation from THF to methanol three times and freeze-dried from the benzene solution.

Measurements. ^1H and ^{13}C NMR spectra were recorded on a BRUKER DPX spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C in $CDCl_3$. The spectrum of poly(HEMA) was measured in CD_3OD. Size-exclusion chromatography (SEC) was performed on a TOSOH HLC 8020 instrument with UV (254 nm) and refractive index detection. THF was used as a carrier solvent at a flow rate of 1.0 mL/min. Three polystyrene gel columns (TSKgelG4000H_{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 poly(methyl methacrylate) samples. The polymers of isoprene and *tert*-butyl methacrylate with known M_n's determined by vapor pressure osmometry and narrow molecular weight distributions ($M_w/M_n < 1.05$) were prepared by anionic living polymerizations of the corresponding monomers and used to make their calibration curves for determinimg the M_n and M_w/M_n values. For the poly(HEMA), the calibration curve using our samples prepared was used as mentioned before. Values of M_n and M_w/M_n of the end-functionalized poly[2-(perfluorobutyl)ethyl meth-

Table 1. Anionic Polymerization of Methacrylates with *s*-BuLi/1/LiCl in THF at −78 °C for 20−120 min

			monomer		$M_n \times 10^{-3}$			
s-BuLi (mmol)	**1** (mmol)	LiCl (mmol)	type	mmol	calcd	obsd[a]	M_w/M_n[a]	functionality[b]
0.302	0.415	1.21	MMA	13.2	4.8	5.1	1.03	1.00
0.151	0.425	1.01	tBMA	4.26	4.4	4.2	1.02	0.99
0.268	0.393	1.10	F_4-MA[c]	3.23	4.4	4.1[d]	1.08	1.00[e]
0.252	0.520	1.12	HEMA-TMS[f]	7.03	4.0	3.4	1.07	1.00

[a] Determined by SEC using calibration curves of poly(methyl methacrylate), poly(*tert*-butyl methacrylate), and poly[2-(benzoyloxy)ethyl methacrylate]. [b] Determined by ^{1}H NMR (see text). [c] 2-(Perfluorobutyl)ethyl methacrylate. [d] Estimated by ^{1}H NMR (peak for polymer side chains vs peak for initiator fragment). [e] Determined by ^{1}H NMR (peak for vinyl protons of the α-methylstyryl groups vs peak for $COOCH_2$ protons of the polymer side chain). [f] 2-(Trimethylsiloxy)ethyl methacrylate.

acrylate] were estimated by SEC using calibration curve of poly(methyl methacrylate). The absolute M_n was determined by comparing the peak areas for polymer side chain and initiator fragment in the ^{1}H NMR spectrum.

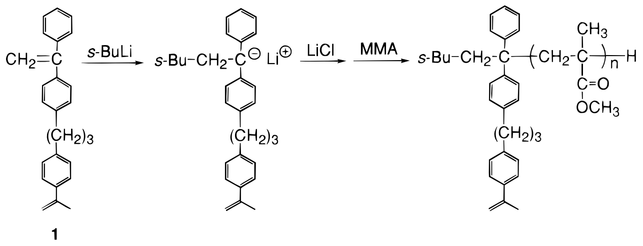
Results and Discussion

To realize the functionalization reactions of anionic living polymers with 1-{4-[3-(4-isopropenylphenyl)-propyl]phenyl}-1-phenylethylene (**1**), two criteria must be satisfied. At first, the anionic species must react predominantly only with the 1,1-diphenylethenyl group of **1**, but not with the α-methylstyryl substituent at all. Second, the α-methylstyryl group introduced in the polymer chain must be stable and inert toward the 1,1-diphenylalkyl anion generated after the reaction. It is generally believed that 1,1-diphenylalkyl anions might be too stable to be effective initiators for styrene.[1] Based on the previous results as well as our experience, however, it is observed that 1,1-diphenylhexyllithium from DPE and *n*-butyllithium (*n*-BuLi) initiates the polymerization of styrene even in THF at −78 °C. Quirk and co-workers have demonstrated that the related diphenylalkyl anions derived from some functionalized DPEs quantitatively initiate the anionic living polymerization of styrene to afford polymers with narrow molecular weight distributions when the polymerization is carried out in benzene at room temperature.[2,8,15] Accordingly, it is certain that styrene can react more or less with 1,1-diphenylalkyl anions.[16]

α-Methylstyrene is estimated to be less reactive than that of styrene toward anionic species, because of electron-donating ability and steric bulkiness of the methyl substituent. This lower reactivity is also indicated by comparing the *e* value of α-methylstyrene (−1.27) with that of styrene (−0.80).

Before examining the utility of **1** as a functionalized agent as we desired, we have further checked by a model reaction in order to answer the question whether α-methylstyrene is anionically polymerized or not with 1,1-diphenylalkyl anions. For this purpose, we capped polystyryllithium with 1,1-diphenylethylene in THF at −78 °C and used it as an initiator for the polymerization of α-methylstyrene. The mixture was allowed to stand at −78 °C for 1 h. After treating the mixture with degassed methanol, polystyrene homopolymer and unreacted α-methylstyrene were nearly recovered. The α-methylstyrene unit was observed not to be incorporated at all in the polystyrene recovered by careful analysis of ^{1}H NMR. Clearly, the 1,1-diphenylalkyl anion has no ability to react and/or polymerize α-methylstyrene under the conditions in THF at −78 °C for 1 h. Thus, **1** would be expected to be used as a functionalized agent for the introduction of α-methylstyrene functionality from the result of the model reaction in addition to taking the estimated lower reactivity of α-methylstyrene than styrene into consideration.

Scheme 1



Polymerization of Methacrylate Monomers with the Adduct Prepared from 1 and *s*-Butyllithium. We have first examined the synthetic utility of **1** as a functionalized agent by the reaction of **1** with *s*-butyllithium (*s*-BuLi), followed by the polymerization of MMA. The reaction was carried out in THF at −78 °C by using **1** in a 1.4-fold excess to *s*-BuLi. A characteristic dark red color appeared instantaneously as soon as **1** was added to *s*-BuLi, strongly indicating the generation of a 1,1-diphenylalkyl anion derived from **1**. This color appeared to remain unchanged at least for 30 min and for an additional 15 min after addition of LiCl in THF at −78 °C. As expected, the color disappeared immediately by adding MMA to the mixture for the polymerization. The polymerization was further conducted for an additional 20 min in THF at −78 °C and quenched with degassed methanol. A polymer yield was quantitative. The results are summarized in Table 1.

The SEC trace of the resulting polymer showed a unimodal sharp peak without any shoulders and tailings. There is a good agreement between the M_n values observed and calculated. The molecular weight distribution was quite narrow, the M_w/M_n value being 1.03. ^{1}H NMR of the polymer revealed clearly resonance peaks at 5.35 and 5.04 ppm corresponding to vinyl protons of the α-methylstyryl group. No resonance assigned to the diphenylethenyl group was observed in this spectrum. The degree of α-methylstyryl functionality was determined from peak area ratio of the peaks at 5.35 and 5.04 ppm with the peak of methyl protons of the polymer side chain at 3.60 ppm, since the M_n was measured by SEC. It was found to be quantitative within analytical errors. Thus, clearly *s*-BuLi reacted quite selectively with the diphenylethenyl group of **1**, while no attack of *s*-BuLi on the α-methylstyryl moiety occurred during the reaction as illustrated in Scheme 1. Furthermore, the results also indicate that the α-methylstyryl moiety is quite robust and able to survive in the presence of the diphenylalkyl anion in THF at −78 °C.

The polymerization of *tert*-butyl methacrylate with the adduct from **1** and *s*-BuLi also proceeded quantitatively in THF at −78 °C to afford the poly(*tert*-butyl methacrylate) with a predictable molecular weight and a narrow distribution ($M_w/M_n = 1.02$) as seen in Table 1. The end-functionalization degree of the α-methyl-

Table 2. Reaction of Anionic Living Polymers with 1 in THF at −78 °C for 30 min

	monomer				$M_n \times 10^{-3}$			
s-BuLi (mmol)	type	mmol	**1** (mmol)	method[a]	calcd	obsd[b]	M_w/M_n[b]	functionality[c]
0.291	styrene	9.16	0.448	A	3.7	3.4	1.05	0.99
0.306	styrene	10.2	0.470	B	3.9	3.9	1.05	1.00
0.361	isoprene[d]	15.4	0.405	B	3.3	3.0	1.05	1.00

[a] See text. [b] Determined by SEC using standard polystyrene and polyisoprene calibration curves. [c] Determined by ^{1}H NMR. [d] Polymerization of isoprene was carried out in heptane at 40 °C for 2 h.

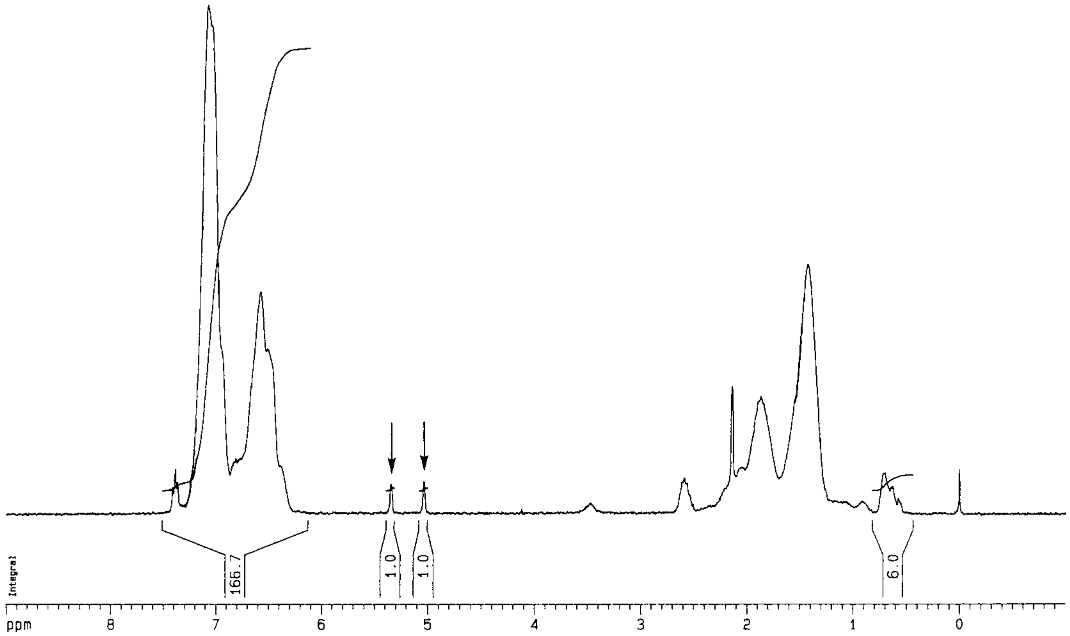


Figure 1. ^{1}H NMR spectrum of polystyrene end-functionalized with α-methylstyryl group.

styryl group was quantitative by the ^{1}H NMR analysis (peaks at 5.34, 5.04 ppm vs peak at 1.4 ppm for methyl protons of the polymer side chain). Again, no resonance for 1,1-diphenylethenyl group was observed in this spectrum.

Similarly, the adduct proved to be an effective functional initiator for the anionic living polymerization of either (2-perfluorobutyl)ethyl methacrylate or (2-trimethylsiloxy)ethyl methacrylate[12] in THF at −78 °C. The degrees of end functionalization with α-methylstyryl groups were determined by their ^{1}H NMR spectra to be almost quantitative in both cases. In these cases, the peaks at 5.35 and 5.04 ppm for vinyl protons of the α-methylstyryl group and either peak at 3.81 ppm or that at 4.07 ppm for $COOCH_2$ protons of each polymer side chain were compared. Thus, well-controlled poly[(2-perfluorobutyl)ethyl methacrylate] and poly(2-hydroxyethyl methacrylate) end-functionalized with α-methylstyryl groups were successfully synthesized. The latter polymer was obtained quantitatively by acid hydrolysis of the resulting poly[(2-trimethylsiloxy)ethyl methacrylate]. These polymers are of special interest because of the characteristic natures of their polymer chains.

Thus, **1** coupled with *s*-BuLi becomes a useful functional initiator in THF at −78 °C for various methacrylate monomers and functionalizes their polymers with a α-methylstyryl group at the initiating chain ends. As indicated from all of the analytical evidence, an essentially quantitative functionalization is achieved in each case. This adduct will also potentially be a functional initiator for *tert*-butyl acrylate and some heterocyclic monomers such as ethylene oxide, propylene sulfide, and lactones.

Reactions of Polystyryllithium and Polyisoprenyllithium with 1. In this section, we will examine the possible utility of **1** as a functional terminator for highly reactive anionic living polymers of styrene and isoprene.

The reaction of **1** with polystyryllithium was carried out in THF at −78 °C by adding polystyryllithium slowly to **1** (method A). On adding living polystyrene to **1**, the orange color characteristic of polystyryllithium changed instantaneously to a dark red color, similar to the reaction between **1** and *s*-BuLi, indicating rapid transformation from polystyryl anion into the diphenylalkyl anion. The color appeared to remain unchanged at −78 °C for 30 min and disappeared immediately by treating with degassed methanol. The resulting polymer was characterized by SEC and ^{1}H NMR analyses, and the results are summarized in Table 2.

The SEC showed that the polymer had a symmetrical SEC distribution composed of a single peak and was narrow in molecular weight distribution ($M_w/M_n = 1.05$). There was a good agreement between Mn values calculated and observed by the SEC. As can be seen in Figure 1, the ^{1}H NMR spectrum of the polymer exhibits characteristic resonances at 5.35 and 5.04 ppm for vinyl protons of the α-methylstyryl group and, on the other hand, no resonance for diphenylethenyl protons. The degree of the end functionalization with the α-methylstyryl group was almost quantitative ($f = 0.99$) from peak area ratio of two singlets at 5.35 and 5.04 ppm with a multiplet at 0.70 ppm for two methyl protons of the initiator fragment. These results clearly show that polystyryllithium reacts only with the diphenylethenyl moiety of **1**, and the resulting α-methylstyryl group introduced at the chain end remains intact in the

Table 3. Reaction of Polystyryllithium with 1 in Benzene at 30 °C for 1 h

				$M_n \times 10^{-3}$			
s-BuLi (mmol)	styrene (mmol)	**1** (mmol)	TMEDA[a] (mmol)	calcd	obsd[b]	M_w/M_n[b]	functionality[c]
0.313	8.54	0.573		3.2	3.2	1.13	0.66
0.106	8.21	2.18		8.4	9.1	1.05	0.67
0.265	7.46	0.482	0.289	3.3	3.2	1.07	0.33

[a] *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine. [b] Determined by SEC using standard polystyrene calibration curves. [c] Determined by ^{1}H NMR.

presence of the 1,1-diphenylalkyl anion generated after the reaction.

A satisfactory result was also obtained by reversely adding **1** to polystyryllithium (method B). Surprisingly, the α-methylstyryl group introduced in the polymer chain was found to remain intact, although the α-methylstyryl group was in contact with polystyryllithium for some periods (maybe for a few seconds) in this additional way. Similarly, polyisoprenyllithium was quantitatively and selectively functionalized with the α-methylstyryl group at the chain end by the reaction with **1** in a THF−heptane mixture (ca. 1/1, v/v) at −78 °C. Thus, **1** works well as an excellent terminator with which α-methylstyrene can be introduced at the terminating chain ends of living polymers of styrene and isoprene.

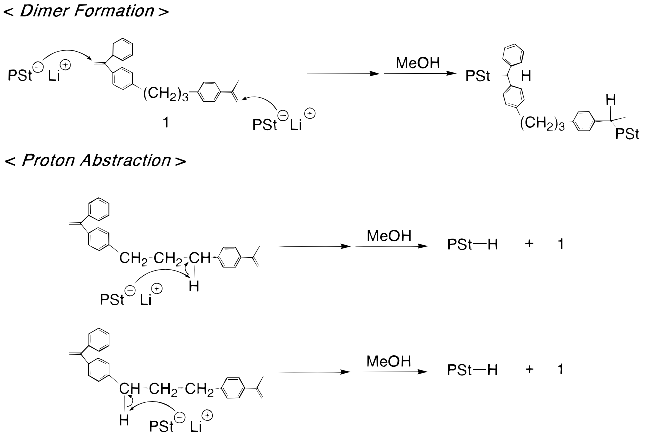
In contrast to the successful results obtained in THF at −78 °C, undesirable side reactions were observed to take place when the reaction of **1** with polystyryllithium was conducted in benzene. In the reaction in benzene at 30 °C for 1 h, for example, an appreciable amount (16%) of the dimer of the parent polystyrene was formed. The ^{1}H NMR spectrum exhibited the resonances assigned to vinyl protons of the α-methylstyryl group, with no resonance for the 1,1-diphenylethenyl group at all. The degree of functionalization with the α-methystyryl group was 66% (see Table 3). This value of 66% makes it reasonable to assume that the dimer is formed by the intermolecular reaction of the α-methylstyryl group at the chain end with another living polystyrene. In this assumption, the degree of functionalization can be calculated to be 68% (100% − (16 × 2)% = 68%).

The dimer formation was almost suppressed (<2%) by using **1** in a 21-fold excess. Nevertheless, in this case the α-methylstyryl group was introduced only in the degree of 67%. Thus, the degree of end functionalization was not improved. The dimer formation was also decreased considerably from 16% to less than 5% by use of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) as an additive. Disappointingly, the degree of end functionalization was further dropped to 33%. Accordingly, the cause of lower functionalization degrees was not due to the dimer formation in both cases. It is well-known that proton abstraction from benzylic protons by carbanionic species often occurs in similar reactions. Accordingly, we believe that the most likely candidate for side reaction is such a benzylic proton abstraction of **1** to deactivate the starting living polystyrenes as illustrated in Scheme 2.

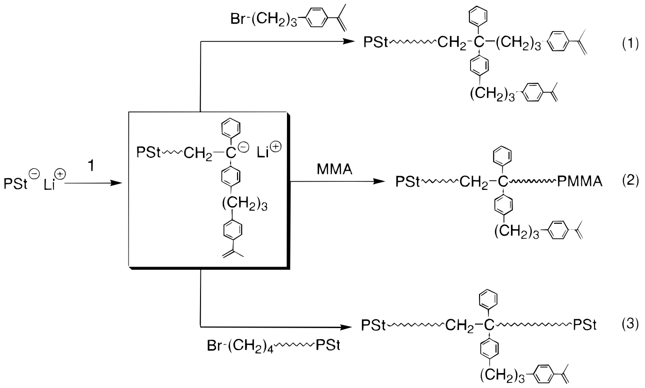
Unfortunately, the excess use of **1** as well as the addition of TMEDA may promote this proton abstraction, although the evidence is not available at the present time. Thus, quantitative synthesis of the macromonomer was not successful in benzene at 30 °C at the present time.

Synthesis of End-Functionalized Polystyrene with Two α-Methylstyryl Groups. As described above, the reaction of living polystyrene with **1** in THF at −78 °C gave the desirable end-functionalized polymer with the α-methylstyryl group. In this reaction, the polystyryl anion was not terminated but transformed quantitatively into the 1,1-diphenylalkyl anion. Therefore, further functionalization reactions are possibly performed by utilizing this anion which is somewhat less reactive than the parent polystyryl anion but still nucleophilic enough to react with a wide variety of electrophiles. Here we have attempted to synthesize a polymer end-functionalized with two α-methylstyryl groups.

Scheme 2



Scheme 3



The reaction of polystyryllithium with **1** was carried out in THF at −78 °C for 0.5 h, followed by treating with 4-(3-bromopropyl)-α-methylstyrene under the same conditions. The characteristic dark red color changed to a bright blue in a moment and then a pale yellow soon after mixing with 4-(3-bromopropyl)-α-methylstyrene. These reactions are illustrated in Scheme 3 (1), and the results are listed in Table 4.

The resulting polymer was observed by SEC to have a symmetrical unimodal peak with a narrow distribution. The M_n value obtained by SEC agreed with that calculated, and the M_w/M_n value was 1.05. Very interestingly, two distinguished resonance pairs are observ-

Table 4. Synthesis of Various Macromonomers with α-Methylstyryl Groups in THF at −78 °C

s-BuLi (mmol)	styrene (mmol)	**1** (mmol)	electrophile		time (min)	$M_n \times 10^{-3}$		M_w/M_n[a]	functionality[b]
			type	mmol		calcd	obsd[b]		
0.247	8.07	0.462	$Br-(CH_2)_3-\alpha MS$[c]	0.338	30	4.0	3.8	1.05	1.00,[d] 0.99[e]
0.313	10.0	0.383	MMA	12.4	20	7.7	7.0[f]	1.05	1.00
0.124	5.27	0.188	$Br-(CH_2)_4-PSt$[g]	0.146	90 h	9.1	9.7	1.06	1.00

[a] Determined by SEC using standard polystyrene calibration curves. [b] Determined by ^1H NMR (see text). [c] 4-(3-Bromopropyl)-α-methylstyrene. [d] α-Methylstyryl group firstly introduced. [e] α-Methylstyryl group secondly introduced. [f] Determined from the M_n values of polystyrene by SEC and the composition by ^1H NMR. [g] ω-(4-Bromobutyl)polystyrene.

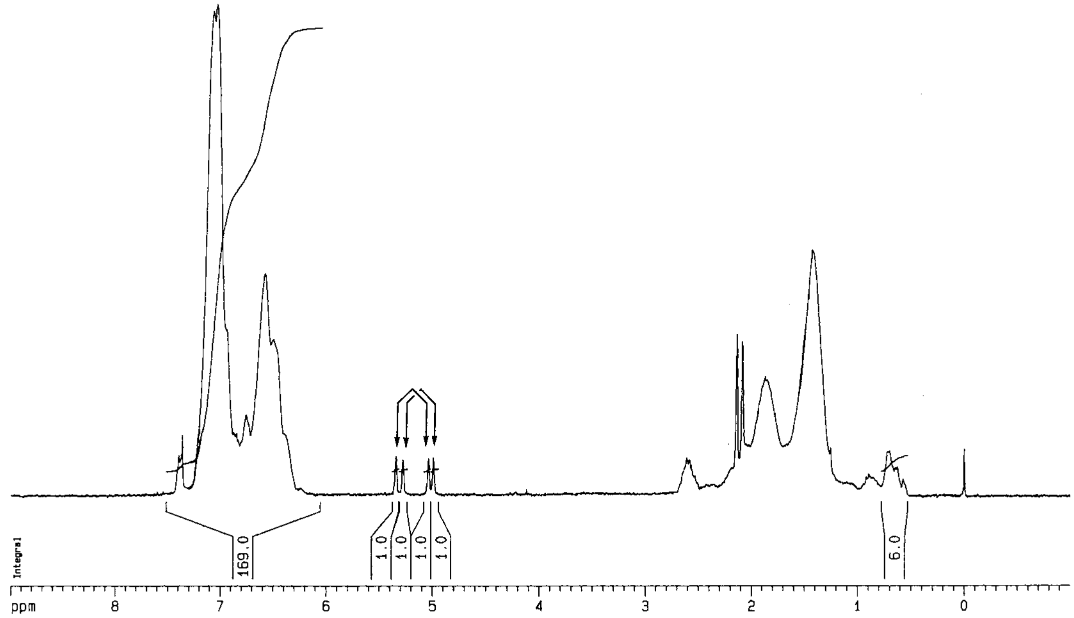


Figure 2. ^1H NMR spectrum of polystyrene end-functionalized with two α-methylstyryl groups.

able at 5.04, 5.35 and 4.99, 5.28 ppm in the ^1H NMR spectrum, as can be seen in Figure 2. They are readily assigned to vinyl protons of the α-methylstyryl groups firstly and secondly introduced, respectively. The degrees of functionalization determined by these resonance intensities were 1.00 and 0.99, respectively (peaks for vinyl protons of the α-methylstyryl groups vs peak at 0.70 ppm for methyl protons of the initiator fragment). Obviously, two reactions illustrated in Scheme 3 (1) proceeded efficiently to afford a well-controlled polystyrene with two α-methylstyryl end groups.

Synthesis of Poly(styrene-*b*-MMA) Functionalized with α-Methylstyryl Group at the Interface between the Blocks. The synthetic possibility of block copolymer functionalized at the interface between the block segments via means of living functionalization reaction was first proposed by Quirk.[1] As mentioned in Introduction, his research group synthesized successfully the block copolymer of poly(styrene-*b*-1,3-butadiene) functionalized with the *N,N*-dimethylanilino group between the blocks by first end-functionalizing polystyryllithium with 1-[4-(dimethylamino)phenyl]-1-phenylethylene, followed by the anionic living polymerization of 1,3-butadiene.[15]

In this section, we will synthesize a well-defined poly(styrene-*b*-MMA) functionalized with a α-methylstyryl group between the blocks as illustrated in Scheme 3 (2).

The living, end-functionalized polystyrene with the α-methylstyryl group was used as an anionic macroinitiator of MMA in THF at −78 °C. Prior to the polymerization of MMA, LiCl was added to narrow the molecular weight distribution. The results are also summarized in Table 4.

As was seen, the resulting block copolymer possessed a predictable molecular weight and a narrow molecular weight distribution. The composition of both segments predicted agreed well with that determined by ^1H NMR. The degree of functionalization with the α-methylstyryl group was quantitative. The peaks for vinyl protons of the α-methylstyryl group and those at 7.2−6.4 ppm (aromatic protons of the polystyrene side chain) and at 3.60 ppm (methyl protons of the poly(methyl methacrylate) side chain) were compared, since the M_n values of both segments were measured by SEC and ^1H NMR. Thus, all of the data clearly show the successful synthesis of poly(styrene-*b*-MMA) functionalized with α-methylstyrene between the blocks. This polymer is a new type macromonomer with a variety of potential applications.

Synthesis of Polystyrene Functionalized with α-Methylstyryl Group within the Polymer Chain. Unlike the case previously described in the preceding section, the living, end-functionalized polymer with the α-methylstyryl group may not be used as a macroinitiator for the polymerization of styrene and 1,3-dienes. Because of high reactivities of their anionic living polymers, the α-methylstyryl group introduced in the polymer chain must be attacked by the living polymer anions. Instead of the initiation method used above, we employed the termination method for synthesis of the polystyrene functionalized with the α-methylstyryl group within the polymer chain.

For this purpose, we first synthesized an end-functionalized polystyrene with the bromobutyl group by reacting polystyryllithium end-capped with DPE followed by treating with 1,4-dibromobutane as previously

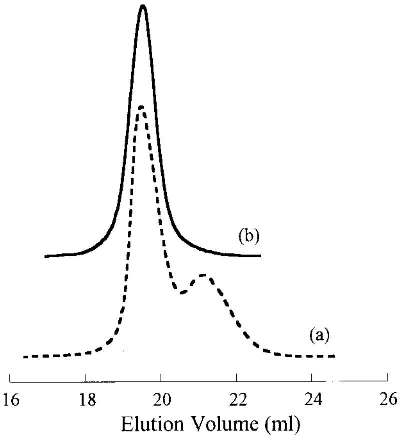


Figure 3. SEC curves of polystyrene functionalized with α-methylstyryl group within the polymer chain before (a) and after (b) fractionations with SEC.

reported.[14] Then, the living, end-functionalized polystyrene with the α-methylstyryl group was reacted with a slight excess of this polystyrene with the terminal bromobutyl functionality in THF at −78 °C in Scheme 3 (3) as illustrated before.

The reaction was observed to proceed efficiently as can be seen in Figure 3. The desired polymer was isolated directly by the fractionation with SEC and characterized by both SEC and ^{1}H NMR measurements (see also Table 4). The SEC showed that the polymer possessed a unimodal sharp peak ($M_w/M_n = 1.06$) as expected. The M_n value observed reasonably agreed with that calculated from both parent polymers. The functionality of α-methylstyrene by ^{1}H NMR was quantitative ($f = 1.00$). The polystyrene functionalized with α-methylstyrene almost at the cental position of the polymer chain was thus obtained. Accordingly, we can place the α-methylstyryl group at essentially any position in a polystyrene chain by changing the molecular weights of the parent living polystyrene and the polystyrene with a terminal bromobutyl functionality. Furthermore, if different kinds of living polymers and the brominated polymers are used, a variety of block copolymers functionalized with the α-methylstyryl group between the blocks could also be synthesized by this termination method.

In conclusion, we have demonstrated that *s*-BuLi, polystyryllithium, and polyisoprenyllithium react quite selectively only with the 1,1-diphenylethenyl group of **1** and, on the other hand, the α-methylstyryl moiety of **1** remains intact completely during the reactions and in the presence of the 1,1-diphenylalkyl anion generated after the reactions. By utilizing such characteristic reactivities of **1** toward such anionic species, we have successfully designed and synthesized various polymers functionalized with α-methylstyryl groups at the initiating as well as terminating chain ends and within the block segments and the polymer chain.

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(16) We examined separately the reaction of *s*-BuLi with 1-{4-[3-(4-vinylphenyl)propyl]phenyl}-1-phenylethylene, a DPE derivative substituted with a styryl group, in THF at −78 °C for 30 min. Unlike the reaction of *s*-BuLi with **1**, insoluble polymeric material and a small amount of soluble polymer with a very broad molecular distribution were obtained in the reaction. This clearly indicates that undesirable side reactions such as polymerization and/or addition reactions of both the styryl and 1,1-diphenylethenyl groups occur simultaneously. Accordingly, the anionic functionalization reaction using the DPE substituted with a styryl group was unsuccessful under the conditions employed here.

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