Macromolecules **2000,** *33,* 4765−4771

Anionic Synthesis of Well-Defined Poly(*m*-halomethylstyrene)s and Branched Polymers via Graft-onto Methodology

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Received October 25, 1999

ABSTRACT: The anionic polymerization of *m*-(*tert*-butyldimethylsilyl)oxymethylstyrene (**1**) was carried out with *s*-BuLi in THF at −78 °C. Under these conditions, the polymerization proceeds in a living manner to afford polymers with predictable molecular weights and narrow molecular weight distributions. Well-defined block copolymers of **1** with styrene were successfully synthesized. Poly(**1**)s were transformed quantitatively into poly(*m*-halomethylstyrene)s (halogen: Cl, Br, I) by treating with BCl_3, $(CH_3)_3SiCl$−LiBr, and $(CH_3)_3SiCl$−NaI, respectively. The resulting polymers with highly reactive benzyl halides in all monomer units retained the well-controlled structures of their parent polymers. The well-defined poly(*m*-halomethylstyrene)s were then coupled with living anionic polymers of styrene in THF. Well-defined comblike branched polystyrenes having almost one branch per monomer unit were prepared by coupling poly(*m*-chloromethylstyrene) both with polystyryllithium in THF at −78 °C for 72 h and with polystyryllithium end-capped with 1,1-diphenylethylene (DPE) in THF at −40 °C for 168 h. They were also prepared by the coupling reactions of poly(*m*-bromomethylstyrene)s with the DPE end-capped polystyryl anions in THF at −78 °C for 72 h and at −40 °C for 168 h. Their backbone and branch chains had well-controlled molecular weights and narrow molecular weight distributions.

Introduction

The coupling reaction of living anionic polymers with chloromethylated polystyrenes or the related polymers is one of the most widely utilized reaction methods for the preparation of branched polymers and graft copolymers.[1−16] An advantage of this method is that backbone and branches (or grafted chains) with well-controlled molecular weights and nearly monodisperse distributions can be used. Therefore, the resulting branched polymers are controlled with respect to their backbone and branches (or grafted chains). Another advantage is that a variety of living anionic polymers can be utilized as branches. They are, for example, living anionic polymers of styrene,[1−10] isoprene,[11,12] vinylpyridines,[13] methyl methacrylate,[14] *tert*-butyl methacrylate,[14,15] and ethylene oxide.[16]

Chloromethylated polystyrenes with controlled molecular weights and narrow molecular weight distributions are prepared by living anionic polymerization of styrene and subsequent chloromethylation. The degrees of chloromethylation are typically in the range of 10−50% per phenyl ring. Polymer functionalization with less than 5% can be obtained by varying the reaction conditions. On the other hand, highly chloromethylated polystyrenes (> 90%) are very difficult to prepare without cross-linking the main chains.[17] Therefore, the preparation of well-defined branched polymers having one branch per monomer unit or even with highly dense branches cannot be prepared by this coupling reaction with chloromethylated polystyrenes.

Well-defined branched polymers having one branch per monomer unit have been recently prepared by the living polymerization of well-defined macromonomers. Typical examples are those obtained by the living anionic polymerization of ω-methacryloyl polystyrene[18] and α-benzyl-ω-vinylbenzyl polystyrene macromonomers[19] and by the living ring-opening methathesis polymerization of norbornene-based polystyrene,[20] poly(ethylene oxide), poly(styrene-*b*-ethylene oxide), and poly(1,3-butadiene) macromonomers.[21] Unfortunately, high molecular weight polymers have not been prepared so far by these living polymerizations, while radical-initiated polymerization of macromonomers gives extremely high molecular weight poly(macromonomer)s (up to 10^7).[22−24]

Very recently, Schappacher and Deffieux successfully prepared well-defined graft copolymers with similar branched structures by coupling polystyryllithium with poly(chloroethyl vinyl ether)s having controlled molecular weights and narrow molecular weight distributions obtained by living cationic polymerization.[25,26] The coupling reaction proceeded quantitatively to afford well-defined comblike poly(chloroethyl vinyl ether-*g*-styrene)s having one grafted chain per monomer unit. This is the first successful preparation of such well-defined comblike graft copolymers by the "grafting onto" method using a coupling reaction.

Despite the successful preparation of well-defined densely grafted copolymers reported by Schappacher and Deffieux, the generality and versatility of this method using coupling reactions to prepare well-defined comblike branched polymers has not been established yet.

We recently synthesized a series of well-defined poly(*m*-halomethylstyrene)s with well-controlled chain lengths by a new methodology that involves the living anionic polymerization of *m*-(*tert*-butyldimethylsilyl)oxymethylstyrene (**1**)[27] and subsequent transformation from *tert*-butyldimethylsilyloxy into halogens. This paper reports the detailed synthesis of well-defined poly(*m*-halomethylstyrene)s, and the preparation of branched polystyrenes having one branch per monomer unit by the coupling reaction of well-defined poly(*m*-halomethylstyrene)s with living anionic polymers of styrene.

10.1021/ma991793g CCC: $19.00

Table 1. Anionic Polymerization of *m*-(*tert*-Butyldimethylsilyl)oxymethylstyrene (1) at −78 °C

entry	[**1**]	[**1**]$_0$/[*s*-BuLi]$_0$	[St]$_0$/[*s*-BuLi]$_0$	time, min	$10^{-3}M_n$ calcd	$10^{-3}M_n$ obsd^a	M_w/M_n^{a}	yield, %
1	0.35	25.5		10	6.3	6.7	1.05	~100
2	0.36	37.4		10	9.0	8.0	1.04	~100
3	0.43	79.7		20	20.0	22.0	1.02	~100
4^b	0.40	30.7	54.2	20	13.3	13.3	1.02	~100
5^b	0.42	79.0	78.5	40	28.0	31.0	1.02	~100

[a] Determined by SEC relative to polystyrene. [b] Poly[(**1**)-*b*-styrene] obtained from sequential addition of **1** and styrene. Composition (DP): entry 4, $[(31)-(53)]_{\mathrm{NMR}}$; entry 5, $[(80)-(81.5)]_{\mathrm{NMR}}$. Weight ratio (%): entry 4, $[(58)-(42)]_{\mathrm{NMR}}$; entry 5, $[(70)-(30)]_{\mathrm{NMR}}$.

Experimental Section

Materials. Solvents were distilled from CaH_2. Styrene was washed with 10% aqueous NaOH and distilled twice from CaH_2 under reduced pressure. BCl_3 (1.0 M, in CH_2Cl_2, Aldrich) and *tert*-butyldimethylchlorosilane (99.5%, Shinnetsu Chemical Co., Ltd.) were used without purification. *m*-(*tert*-Butyldimethylsilyl)oxymethylstyrene (**1**) was prepared as described previously[27] and purified twice by fractional distillation from CaH_2 under reduced pressure. Finally **1** was distilled from benzylmagnesium chloride under high vacuum (10^{-6} Torr).

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX (300 MHz for ^{1}H and 75 MHz for ^{13}C) in $CDCl_3$. Size-exclusion chromatography (SEC) was performed at 40 °C with a TOSOH HLC 8020 instrument with UV (254 nm) or refractive index detection. THF was used as the eluent at a flow rate of 1.0 mL/min. Three polystyrene gel columns (measurable molecular weight range: 1×10^4 to 4×10^6) were used. Calibration curves were made to determine M_n and M_w/M_n values with standard polystyrene. Fractionation by HPLC was performed at 40 °C using a TOSOH HLC 8020 Type fully automatic instrument equipped with a TSK-G4000H$_{\mathrm{HR}}$ column (300 mm in length and 7.8 mm in diameter), and THF as an eluent. The concentration of the polymer solution for fractionation was adjusted to 10−20 w/v %, depending on the molecular weight of the sample. Static light scattering (SLS) measurements were performed with an Ootsuka Electronics DSL-600R instrument (633 nm) in benzene.

Anionic Polymerization of 1. Monomer **1** was polymerized using *s*-BuLi in THF at −78 °C for 10−30 min with stirring under high vacuum employing break-seal technique. In a typical polymerization procedure, a THF (12.5 mL) solution of monomer **1**, 1.24 g (5.00 mmol), chilled to −78 °C was added at once to *s*-BuLi (0.248 mmol in heptane, 2.25 mL) at −78 °C with stirring and the reaction mixture was stirred at −78 °C for an additional 10 min. After terminating with degassed methanol, the mixture was poured into a large amount of methanol to precipitate the polymer. It was reprecipitated twice from THF into methanol and freeze-dried from benzene for 24 h to yield 1.22 g (98%) of poly(**1**). No monomer was detected in the reaction mixture by gas chromatography. $M_n = 5 \times 10^3$, $M_w/M_n = 1.05$. ^{1}H NMR: δ 7.2−6.4 (m, 4H, C_6H_4), 4.60 (s, 2H, CH_2O), 2.1−1.1 (m, 3H, CH_2CH), 0.99 (s, 9H, $Si-C-CH_3$), 0.10 (s, 6H, $Si-CH_3$). Similarly, the block copolymerization was carried out with *s*-BuLi in THF at −78 °C by the sequential addition of **1** and styrene. $M_n = 13.3 \times 10^3$, $M_w/M_n = 1.02$. The amounts of monomers and *s*-BuLi are listed in Table 1.

Transformation Reactions. The transformation reactions were performed similarly to those in our previous paper.[28] The reaction of poly(**1**) with a 1.5-fold excess of BCl_3 was carried out in CH_2Cl_2 at −30 °C for 0.5 h under an atmosphere of nitrogen. A solution of BCl_3 (3.8 mmol) in CH_2Cl_2 (3.8 mL) was added dropwise at −30 °C to a CH_2Cl_2 (15 mL) solution of poly(**1**) (0.62 g, 2.5 equiv per *tert*-butyldimethylsilyloxymethyl group) under a nitrogen atmosphere and the mixture was stirred for an additional 0.5 h. The polymer was then precipitated in methanol and purified by repeated precipitation from CH_2Cl_2 into methanol. It was finally freeze-dried three times from benzene for the next coupling reaction. The reaction of poly(**1**) with either $(CH_3)_3SiCl-LiBr$ or $(CH_3)_3SiCl-NaI$ was carried out in a mixture of acetonitrile and chloroform (3/4, v/v) at 40 °C for 48 h under an atmosphere of nitrogen.

A typical reaction procedure is as follows. Poly(**1**) (0.40 g, 1.6 equiv per *tert*-butyldimethylsilyloxymethyl groups) dissolved in dry $CHCl_3$ (40 mL) was added dropwise to a CH_3CN (30 mL) solution of $(CH_3)_3SiCl$ (4.8 mmol) and LiBr (5.0 mmol) during 0.5 h at 25 °C and the mixture was allowed to stir at 40 °C for an additional 48 h under a nitrogen atmosphere. The mixture was then poured into water and extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$, concentrated to ca. 1 mL, and poured into hexanes to precipitate the polymer. The polymer was reprecipitated twice from THF into methanol and freeze-dried three times from benzene. Similarly, the reaction of poly(**1**) with $(CH_3)_3SiCl-NaI$ was performed under the same conditions. $M_n = 5.5 \times 10^3$, $M_w/M_n = 1.04$. ^{1}H NMR: δ 7.2−6.4 (m, 4H, C_6H_4), 4.37 (s, 2H, CH_2Cl) (or 4.30 (s, 2H, CH_2Br), 4.29 (s, 2H, CH_2I)), 2.1−1.1 (m, 3H, CH_2CH).

Coupling Reactions. Branched polystyrenes were prepared in THF by coupling the well-defined poly(*m*-halomethylstyrene)s with living anionic polymers of styrene. The coupling reaction of polystyryllithium with either poly(*m*-chloromethylstyrene) or poly(*m*-bromomethylstyrene) was carried out in THF at −78 °C for 72 h, while the reactions with polystyryllithiums end-capped with 1,1-diphenylethylene (DPE) were performed in THF at −40 °C for 168 h. The polystyryl anions were used in ca. 1.5−2.0-fold excesses relative to the halomethyl groups. The poly(*m*-halomethylstyrene) was added at once to the polystyryl anion in the reaction. After 72−168 h, the reactions were quenched with degassed methanol and poured into methanol to precipitate the polymers. They were reprecipitated two times and freeze-dried. The resulting polymers were then fractionated by HPLC to remove homopolymers used in excess and byproducts formed by side reactions.

A typical reaction procedure of poly(*m*-bromomethylstyrene) with the DPE end-capped polystyryl anion is as follows. Polystyryllithium was prepared by the polymerization of styrene (1.04 g, 10.0 mmol) in THF (12 mL) with *s*-BuLi (0.221 mmol) in heptane (2.05 mL) at −78 °C for 20 min and end-capped with DPE (0.0720 g, 0.400 mmol) in THF (4.55 mL) for 30 min. Poly(*m*-bromomethylstyrene) (0.0291 g, 0.147 equiv per bromomethylphenyl unit) in THF (2.91 mL) was added to the end-capped polystyryl anion at once at −78 °C. The reaction mixture was then allowed to stand at −40 °C for 168 h. After quenching with degassed methanol, the polymer was precipitated by pouring the reaction mixture into a large excess of methanol to yield 0.75 g (99%) of comblike polymer. M_n (SEC) $= 55.4 \times 10^3$, $M_w/M_n = 1.02$, M_w (SLS) $= 163 \times 10^3$. ^{1}H NMR: δ 7.3−6.4 (aromatic, H), 2.3−0.8 (CH_2CH), 0.7−0.6 (*s*-butyl, CH_3).

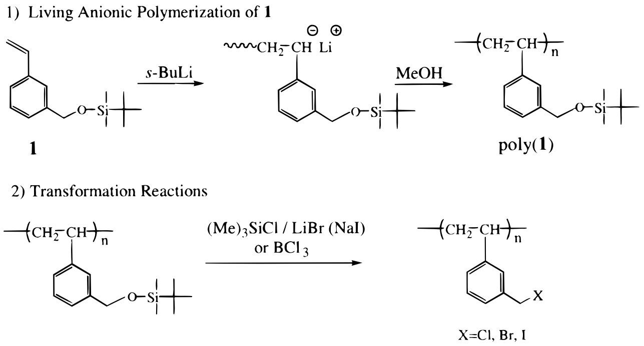
Results and Discussion

Anionic Synthesis of Well-Defined Poly(*m*-halomethylstyrene)s. (1) Living Anionic Polymerization of *m*-(*tert*-Butyldimethylsilyl)oxymethylstyrene (1). Soluble poly(*p*-chloromethylstyrene)s can be obtained by free-radical polymerization of *p*-chloromethylstyrene, although free-radical polymerization undergoes chain transfer and termination.[17] Recently, polymers with somewhat controlled molecular weights and molecular weight distributions ($M_w/M_n \sim 1.2$) were prepared using the nitroxide-mediated radical polymerization of *p*-(chloromethyl)styrene.[29,30]

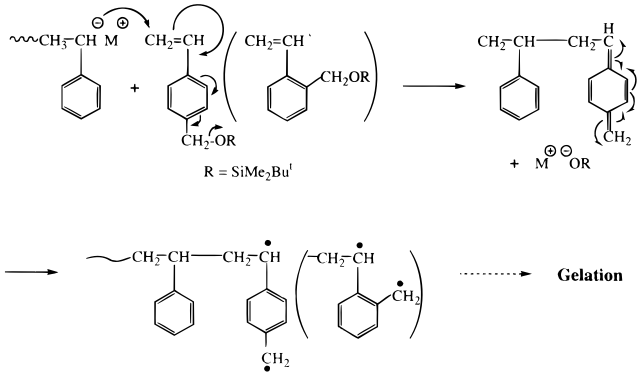
We have developed an alternative methodology that provides poly(*m*-halomethylstyrene)s with more precisely controlled chain lengths. The methodology involves the living anionic polymerization of **1**[27] and subsequent transformation of the *tert*-butyldimethylsilyloxy into halogens as illustrated in Scheme 1.

In this methodology, the *tert*-butyldimethylsilyloxy group acts as both a protecting group for hydroxy during

Scheme 1

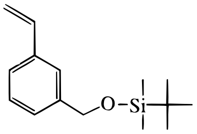


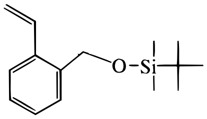
Scheme 2

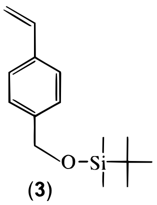


the living anionic polymerization and as a precursor of chloro, bromo, or iodo groups.

In our previous paper,[27] we demonstrated that *m*-(*tert*-butyldimethylsilyl)oxymethystyrene (**1**) undergoes living anionic polymerization in THF at −78 °C. Polymers with predictable molecular weights and narrow molecular weight distributions ($M_w/M_n = 1.08-1.19$) were quantitatively obtained. In contrast, both the ortho and para isomers, *o*-(*tert*-butyldimethylsilyl)oxymethystyrene (**2**) and *p*-(*tert*-butyldimethylsilyl)oxymethylstyrene (**3**), failed under identical conditions. To reasonably explain this, we proposed a reaction pathway involving a predominant 1,4- or 1,6-elimination reaction of its chain-end carbanion, thereby preventing polymerization (Scheme 2).


(**1**)


(**2**)


(**3**)

The living anionic polymerization of **1** was previously reported to proceed in THF at −78 °C with various initiators such as lithium naphthalenide, *n*-butyllithium (BuLi), potassium naphthalenide, and cumylpotassium.[27] However, we have recently found that the initiators with potassium countercation are not suitable for preparing high molecular weight polymers with narrow molecular weight distributions. Higher shoulders or tailings and even multimodal distributions were observed in SEC traces of the polymers obtained with such initiators.

In contrast, *sec*-BuLi in THF at −78 °C is the most suitable initiator system for obtaining polymers with very narrow molecular weight distributions ($M_w/M_n < 1.05$). Table 1 summarizes the results of the homopolymerization and block copolymerization of **1** with styrene using this initiator system. Their molecular weights were well-controlled up to 20K and molecular weight distributions were extremely narrow. All features of the anionic polymerization of **1** with *s*-BuLi in THF at −78 °C indicates a living process. However, higher molecular weight shoulders formed when the polymerizations proceeded for longer reaction times (e.g., 5−10% after 1 h and 25% after 2 h). This may be due to dimerization by coupling between polymer chains after the polymerization, although we do not understand this at this time. On the other hand, such shoulders are not observed in polymers isolated within 10 min.

A well-defined AB-diblock copolymer, poly(**1**-*b*-styrene), was synthesized in THF at −78 °C by the sequential addition of **1** and styrene. The M_n and composition estimated by SEC and ^{1}H NMR agreed with the calculated values. The molecular weight and composition of the block copolymers were varied by changing the amounts of **1** and styrene (see entry 5 in Table 1). The success of these block copolymerizations also supports the living character of the polymerization of **1** under these conditions. Since the ^{13}C NMR chemical shift (113.8 ppm) of the β-carbon of **1** is quite similar to that of styrene, the reactivities may be very similar in anionic polymerizations. A BA-type diblock copolymer of styrene and **1** might also be synthesized, although we did not attempt to synthesize it. These polymers were used in the subsequent transformation reactions.

(2) Transformation Reactions. Several transformation reactions of alkyl trimethylsilyl ethers into alkyl halides have been reported,[31−36] while those using alkyl *tert*-butyldimethylsilyl ethers are less known.[37] However, we recently succeeded in transforming the *p*-(*tert*-butyldimethylsilyloxy)methylphenyl group at the polystyrene chain end into the *p*-chloromethylphenyl functionality by treatment with BCl_3.[28] The chain ends were also quantitatively transformed into *p*-bromo and *p*-iodomethylphenyl groups using $(CH_3)_3SiCl-LiBr$ and $(CH_3)_3SiCl-NaI$, respectively. We have now applied these successful reactions to poly(**1**) for the synthesis of well-defined poly(*m*-halomethylstyrene)s.

At first, we attempted to transform poly(**1**) into poly(*m*-chloromethylstyrene) by treatment with BCl_3 in CH_2Cl_2 at −30 °C for 0.5 h. The ^{1}H NMR spectra in Figure 1 shows a new resonance at 4.37 ppm with a reasonable integral ratio for the chloromethyl protons simultaneously with the disappearance of the two peaks at 0.99 and 0.10 ppm due to the *tert*-butyldimethylsilyl protons. This demonstrates that poly(**1**) is quantitatively transformed into poly(*m*-chloromethylstyrene). The SEC diagrams of the polymers before and after the reaction exhibit narrow molecular weight distributions as shown in Figure 2. The SEC-determined M_n value (5.5 K) of the transformed polymer agreed with the calculated value (5.0 K). A more reliable M_n value (4.9 K) was calculated by both ^{1}H NMR peak areas of the chloromethyl and methyl protons from the initiator (*s*-BuLi) fragment and agreed well with the theoretical value. There was, however, a very small amount (~3%) of a high molecular weight shoulder in the resulting poly(*m*-chloromethylstyrene) as seen in Figure 2B.[38] This shoulder may be produced by Friedel−Crafts alkylation between polymer chains. Small high molecular weight

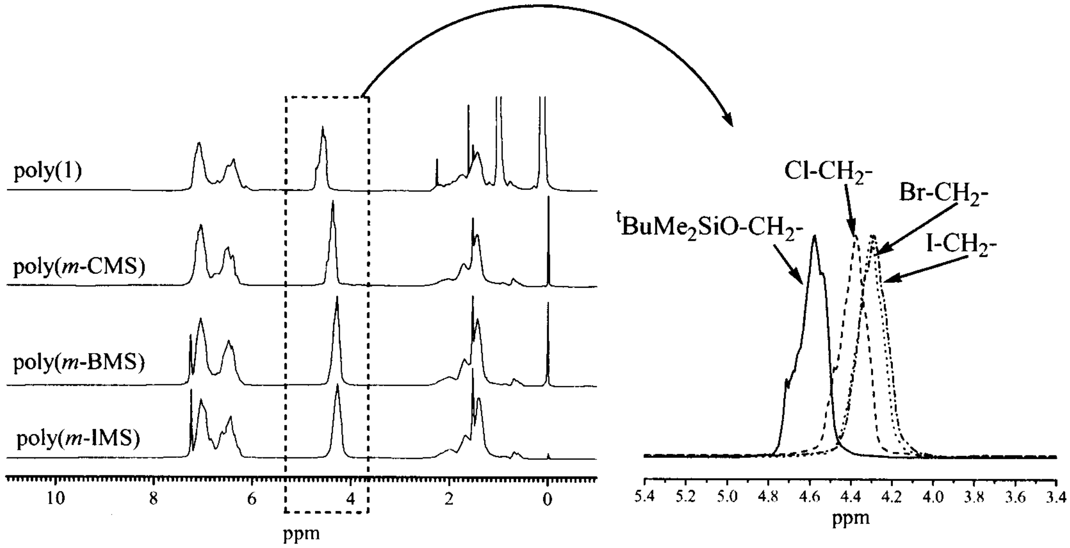


Figure 1. ^{1}H NMR spectra before and after transformation reactions. Poly(*m*-CMS): poly(*m*-chloromethylstyrene). Poly(*m*-BMS): poly(*m*-bromomethylstyrene). Poly(*m*-IMS): poly(*m*-iodomethylstyrene).

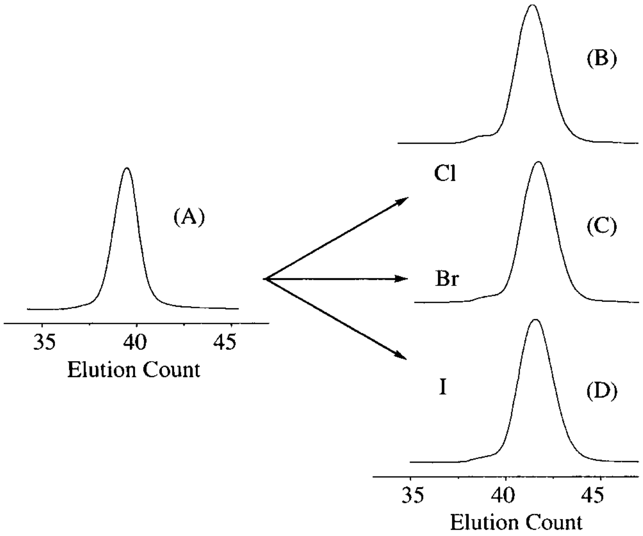


Figure 2. SEC curves of poly(*m*-halomethylstyrene)s obtained by transformation reaction of poly(**1**): (A) parent poly(**1**); (B) poly(*m*-chloromethylstyrene); (C) poly(*m*-bromomethylstyrene); (D) poly(*m*-iodomethylstyrene). See entry numbers 2Cl, 2Br, and 2I, respectively, in Table 2.

products were often observed in similar polymer reactions with BCl_3.[28,39]

The transformation reaction of poly(**1**) with either $(CH_3)_3SiCl-LiBr$ or $(CH_3)_3SiCl-NaI$ was carried out in a mixture of acetonitrile and chloroform (3/4, v/v) at 40 °C for 48 h. ^{1}H NMR spectra of the resulting polymers showed the appearance of new resonances at 4.30 and 4.29 ppm, corresponding to bromomethyl and iodomethyl protons, respectively. Integral ratios of both resonances and those for aromatic protons were reasonable for a quantitative reaction. The complete transformation into either bromomethyl or iodomethyl groups was also confirmed by the disappearance of two resonances at 0.99 and 0.10 ppm due to *tert*-butyldimethylsilyl protons. The SEC diagrams show that both polymers after the reactions possess symmetrical unimodal peaks with narrow molecular weight distributions (Figure 2, parts C and D) and retain the same peak shapes.[38] Thus, these reactions appeared to proceed cleanly and quantitatively. Their theoretical M_n values (6.4K and 7.4K) deviated somewhat from those observed by SEC (5.5K and 5.6K) based on polystyrene calibration, but agreed quite well with those determined from ^{1}H NMR peak areas of the halomethyl and methyl protons (6.5K and 7.3K).

Similarly, a poly(**1**) ($M_n = 20K$, $M_w/M_n = 1.02$) was quantitatively transformed into poly(*m*-bromomethylstyrene) ($M_n = 17K$, $M_w/M_n = 1.02$) without problem. The transformation of poly[(**1**)-*b*-styrene] of an AB type diblock copolymer with $(CH_3)_3SiCl-LiBr$ also proceeded satisfactorily under the same conditions. These results are summarized in Table 2. Thus, the combination of living anionic polymerization of **1** with subsequent transformation provides an excellent methodology for the synthesis of well-defined poly(*m*-halomethylstyrene)s.

Coupling Reactions of Either Poly(*m*-chloromethylstyrene)s or Poly(*m*-bromomethylstyrene)s with Living Anionic Polymers of Styrene To Prepare Branched Polystyrenes With One Branch per Monomer Unit. As mentioned in the Introduction, several researchers have attempted to prepare branched polystyrenes by coupling living anionic polymers of styrene with chloromethylated polystyrenes and related polymers.[1−10] The coupling reactions were usually carried out in THF and benzene. The reaction temperatures ranged from −78 to +23 °C. The grafting efficiencies in these coupling reactions were influenced significantly by solvent, temperature, concentration, and the countercation of the polystyryl anions. Although the reactions apparently proceed with good to excellent efficiencies, side reactions occur, including metal−halogen exchange, α-proton abstraction, single-electron-transfer reactions, and even carbene generation.[40] These reactions, except for proton abstraction, were often accompanied by dimerization of the polystyryl anions. The steric bulk of the branch segments also limit the grafting efficiency.[8] Accordingly, the preparation of highly branched polymers seems difficult by this method.

However, Gauthier and Möller reported that the side reactions are markedly reduced and the efficiency of the coupling reaction is significantly improved by end-capping polystyryllithium with DPE.[10] With this modified polystyryl anion, the coupling reaction with a 30 mol % chloromethylated polystyrene is 96% efficient at −30 °C. Thus, they were successful in preparing highly

Table 2. Transformation Reactions into Benzyl Halides[a]

entry	reagents	$[\text{reagent}]_0/[\text{ArCH}_2\text{OSiR}_3]_0$	time, h	temp, °C	$10^{-3}M_n$ calcd	SEC[b]	NMR	M_w/M_n[b]	functions[c] halogen	%
2Cl	BCl_3	1.5	0.5	−30	5.0	5.5	4.9	1.04	Cl	100
2Br	$(CH_3)_3SiCl/LiBr$	3.0	48	40	6.4	5.5	6.5	1.04	Br	100
2I	$(CH_3)_3SiCl/NaI$	3.0	48	40	7.4	5.6	7.3	1.04	I	100
3Br	$(CH_3)_3SiCl/LiBr$	3.0	48	40	17.2	14.7	17.5	1.02	Br	100
4Br[d]	$(CH_3)_3SiCl/LiBr$	3.0	48	42	11.7	10.3	12.0	1.02	Br	100

[a] M_n and M_w/M_n of starting polymers were listed in Table 1: 2Cl, 2Br, 2I; entry 2, 3Br; entry 3; 4Br, entry 4, respectively. Yields of polymer were ~100% in all cases. [b] Determined relative to polystyrene. [c] Functionality of each polymer was calculated by ^{1}H NMR analysis. [d] Poly[(**1**)-*b*-styrene]; see entry 4 in Table 1. Composition (DP): $[(31)-(53)]_{NMR}$. Weight ratio (%): $[(53)-(47)]_{NMR}$.

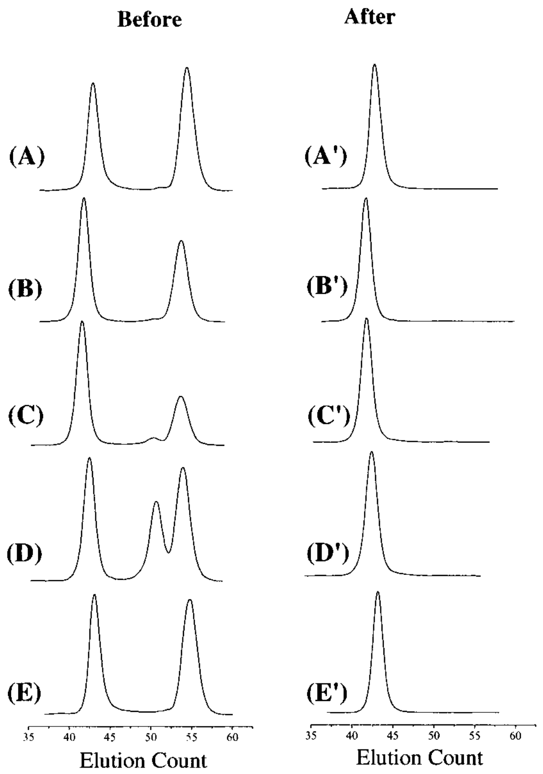


Figure 3. SEC curves of highly branched polystyrene before and after fractionation: (A) 2Cl-1, (B) 2Cl-2, (C) 2Cl-3, (D) 2Br-1, and (E) 2Br-2, in Table 3, respectively.

branched polystyrenes with an arborescent structure by successive chloromethylation and coupling reactions with the DPE end-capped polystyryl anion.[10]

On the basis of their successful result, we have coupled well-defined poly(*m*-halomethylstyrene)s with the DPE end-capped polystyryl anions in order to prepare branched polystyrenes having one branch per monomer unit. We previously observed that a similar coupling reaction of either polystyryllithium having two chloromethylphenyl termini failed in benzene at 30 °C in both the absence and presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.[39] Therefore, we avoided using hydrocarbon solvents at room or higher temperatures.

The coupling reaction of a poly(*m*-chloromethylstyrene) ($M_n = 4.9$ K, $M_w/M_n = 1.04$) with the DPE end-capped polystyryl anion was first carried out in THF at −78 °C. After 72 h, the reaction was terminated with degassed methanol. The SEC trace of the reaction mixture is shown in Figure 3A. They have two sharp single peaks at high and low molecular weight corresponding to the coupling product and excess unreacted DPE end-capped polystyrene. No peak corresponding to dimeric product was observed, indicating that the coupling reaction proceeded without this side reaction.

The high molecular weight coupling product was isolated by HPLC fractionation and characterized by SEC to estimate roughly their linear polystyrene equivalent M_n and M_w/M_n values. The single sharp SEC peak shown in Figure 3A′ implies that the isolated polymer is pure and completely free of its precursor polymers. The apparent molecular weight distribution was very narrow ($M_w/M_n = 1.02$), while the M_n value estimated by SEC was much lower than the calculated expected value. The absolute M_w value were therefore determined by static light scattering (SLS) measurement. As a rough approximation, the absolute M_n was estimated based on the M_w from LS and the apparent M_w/M_n from SEC, although it is not exactly correct. The results are summarized in Table 3. The M_w of this polymer determined by SLS was 152K. The M_n estimated by the M_w from SLS and M_w/M_n from SEC was 149K and slightly lower than that calculated value (162K). From these values, the coupling efficiency is 91%. The same coupling reaction was then carried out at −40 °C for up to 168 h to complete the reaction. Parts B and B′ of Figure 3 are the SEC diagrams of the reaction mixture and the branched polystyrene isolated by HPLC fractionation. Again, there are only two sharp single SEC peaks for the branched polymer and its excess precursor polystyrene at high and low molecular weight. No dimer peak was observed. The M_n value estimated by the M_w from SLS and the M_w/M_n from SEC was 218K and agreed well with that calculated (215K). On the basis of these M_n values, the coupling efficiency was quantitative. Furthermore, no resonance for the chloromethyl protons was observed by ^{1}H NMR. These results indicate that the coupling reaction of poly(*m*-chloromethylstyrene) with the DPE end-capped polystyryl anion at −40 °C for 168 h is quantitative. Thus, the use of DPE as an end-capping agent markedly reduced or suppressed the side reactions reported previously by Gauthier and Möller.[10] Moreover, the branches apparently do not sterically hinder this coupling reaction. The resulting branched polystyrene should therefore have almost one branch per monomer unit and both the backbone and branch chains have essentially well-defined molecular weights and narrow molecular weight distributions.

We also coupled the same poly(*m*-chloromethylstyrene) with polystyryllithium that was not end-capped with DPE in THF at −78 °C for 72 h. Parts C and C′ of Figure 3 show the SEC diagrams of this reaction mixture and the coupling product isolated by HPLC. There are two peaks at high and low molecular weights in Figure 3C. In addition to the low molecular weight peak, it has <5% of a higher molecular weight shoulder. However, this shoulder may not result from side reactions in the coupling reaction, because this shoulder also forms when polystyryllithium itself stands in THF at −78 °C for 72 h before terminating with methanol.[41,42−44]

Table 3. Coupling Reaction of Poly(*m*-halomethylstyrene)s with Living Polystyryl Anion[a]

				branched polymer					
				$10^{-3}M_n$		SLS			
entry	living PSt[b] M_n[c]	time, h	temp, °C	calcd	SEC[c]	$10^{-3}M_w$	$10^{-3}M_n$[d]	M_w/M_n[c]	CE,[e]%
2Cl-1	4900[g]	72	−78	162	60	152	149	1.02	91
2Cl-2	6600[g]	168	−40	215	83	222	218	1.02	100
2Cl-3	6400	72	−78	209	85	231	226	1.02	~100
2Br-1	5900	72	−78	193	69	177	174	1.02	88
2Br-2	4700[g]	72	−78	157	64	165	161	1.02	~100
2Br-3	6700[g]	168	−40	220	84	251	246	1.02	~100
2Br-4	24700[g]	168	−40	795	272	877	860	1.02	~100
4Br-1[f]	3400[g]	72	−50	112	46	122	118	1.02	~100

[a] Yields of polymer were ~100% in all the cases. [b] *s*-BuLi was used as an initiator. [c] Determined relative to polystyrene. [d] M_n was recalculated by using M_w/M_nvalue of SEC. [e] Coupling efficiency (CE) based on the molecular weight determined by SLS and SEC. [f] Poly[(**1**)-*b*-styrene]. [g] Living polystyryl anion was end-capped with DPE.

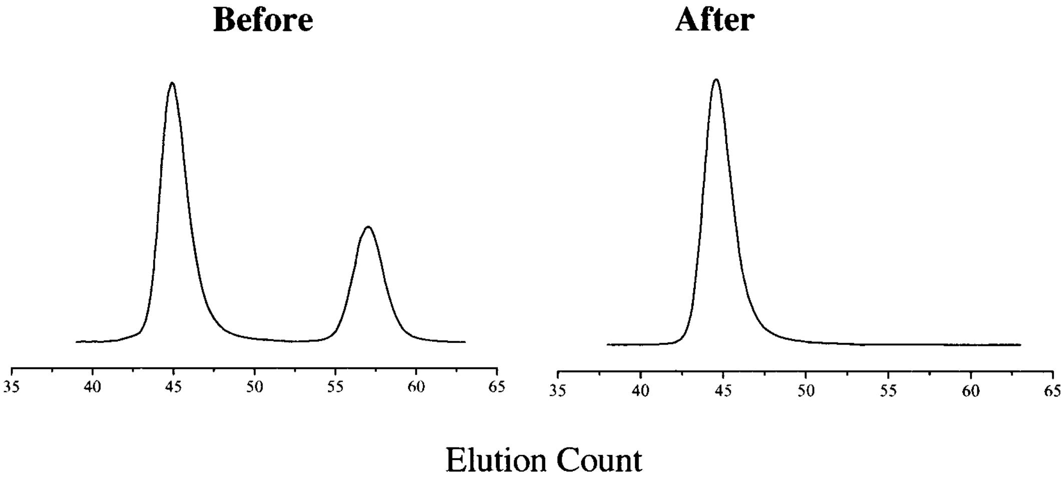


Figure 4. SEC curves of highly branched polystyrene before and after fractionation of 4Br-1 in Table 3.

The agreement between the M_n (226K) estimated by SLS and SEC and that calculated (209K) was within the usual analytical limit (see 2Cl-3 in Table 3). Accordingly, coupling directly with polystyryllithium is also quantitative in THF at −78 °C, despite the previously reported side reactions and reduced efficiencies caused by steric hindrance of the branches.

In contrast, side reactions apparently occur in the coupling reaction of a poly(*m*-bromomethylstyrene) (M_n = 6.5 K, M_w/M_n = 1.04) with polystyryllithium in THF at −78 °C for 72 h (see 2Br-1 in Table 3). Figure 3D shows a significant amount of dimer. The dimer may form by Li−Br exchange and/or single-electron-transfer reactions, followed by coupling with their intermediates (PS−Br + PS−Li and PS radicals). These side reactions are reasonable, since metal−halogen exchange reactions and single-electron-transfer pathway are more preponderant with bromides than the corresponding chlorides.[45]

The resulting branched polymer was isolated by HPLC fractionation. Its calculated and estimated M_n values were 193K and 174K, respectively, and the coupling efficiency was 88%. The resulting branched polystyrene retained a narrow molecular weight distribution (M_w/M_n = 1.02).

The DPE end-capped polystyryl anion was then coupled with poly(*m*-bromomethylstyrene) under the same conditions. The SEC curve in Figure 3E shows only two single sharp SEC peaks for the coupling product and its precursor polystyrene at high and low molecular weight; the peak corresponding to dimeric product was not observed. The M_n (161K) of the isolated polymer estimated by SLS and SEC agreed well with the theoretical value (157K). Thus, end-capping of polystyryllithium with DPE suppressed the side reactions in the coupling reaction with poly(*m*-bromomethylstyrene). The same coupling reaction proceeded quantitatively in THF at −40 °C for 168 h (see 2Br-3 in Table 3).

To examine the effect of the molecular weight of branch segment on the coupling efficiency, a higher molecular weight polystyryllithium (M_n = 24.7K) end-capped with DPE was coupled with the same poly(*m*-bromomethylstyrene) (M_n = 6.5K) in THF at −40 °C for 168 h. The coupling reaction also proceeded quantitatively and generated the expected high molecular weight (M_w = 877K) branched polystyrene with a narrow molecular weight distribution (M_w/M_n = 1.02) (see 2Br-4 in Table 3). Since the degree of polymerization of the branch (DP = 237) was much higher than that of the main chain (DP = 32), it should form an almost spherical starlike structure.

Finally, polystyryllithium end-capped with DPE was coupled with a poly(*m*-bromomethylstyrene-*b*-styrene) at −50 °C for 72 h as a model reaction for the preparation of well-defined block-graft copolymers. The coupling reaction proceeded without formation of dimeric side-product as shown in Figure 4. The branched polymer isolated by HPLC has a sharp unimodal SEC peak. The molecular weight (118K) estimated by SLS and SEC agrees fairly well with that calculated (112K). Thus, the reaction also proceeded with quantitative coupling efficiency.

These coupling reactions will be extended to prepare graft copolymers with similar branched architectures. However, the influence of the molecular weights of backbone and branched chains, in addition to reaction variables such as reaction temperature, solvent, and concentration, on the coupling product should be further investigated and optimized. These results will be published in the near future.

Conclusions

Well-defined poly(*m*-halomethylstyrene)s (halogen: Cl, Br, and I) were successfully synthesized by the living anionic polymerization of **1** in THF at −78 °C with *s*-BuLi and subsequent transformations with BCl_3, $(CH_3)_3SiCl-LiBr$, and $(CH_3)_3SiCl-LiBr$, respectively. These poly(*m*-halomethylstyrene)s were coupled with living anionic polymers of styrene to prepare well-defined comblike branched polystyrenes. The coupling reaction of poly(*m*-chloromethylstyrene) with either polystyryllithium or the DPE end-capped polystyryl anion proceeded quantitatively in THF at −78 °C for 72 h or at −40 °C for 168 h. The reaction of poly(*m*-bromomethylstyrene) with the DPE end-capped polystyryl anion was also quantitative under these conditions. The grafted or branch segments apparently did not sterically hinder either coupling reactions, although more systematic experiments using backbone and branch polymers having different molecular weights are required.[46] The resulting polymers were well-defined comblike branched polystyrenes having almost one branch per monomer unit and well-controlled backbone and branch chains. These successful results suggest that the "graft onto" coupling reactions is also highly useful for preparing comblike branched polymers having branch (or grafted) chain per monomer unit.

References and Notes

(1) Altares, T., Jr.; Wyman, D. P.; Allen, V. R.; Meyerson, K. J. *J. Polym. Sci., Part A* **1965**, *3*, 4131.
(2) Fujimoto, T.; Narukawa, H.; Nagasawa, M. *Macromolecules* **1970**, *3*, 57.
(3) Noda, I.; Horikawa, T.; Kato, T.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1970**, *3*, 795.
(4) (a) Pannell, J. *Polymer* **1971**, *12*, 558. (b) Pannell, J. *Polymer* **1972**, *13*, 2.
(5) Candau, F.; Franta, E. *Makromol. Chem.* **1971**, *149*, 41.
(6) Price, C.; Wood, D. *Polymer* **1973**, *14*, 82.
(7) Ishizu, K.; Fukutomi, T.; Kakurai, T. *Polym. J.* **1975**, *7*, 228.
(8) (a) Takaki, M.; Asami, R.; Ichikawa, M. *Macromolecules* **1977**, *10*, 850. (b) Takaki, M.; Asami, R.; Kuwata, Y. *Macromolecules* **1979**, *12*, 378. (c) Takaki, M.; Asami, R.; Inukai, H.; Inenaga, T. *Macromolecules* **1979**, *12*, 383. (d) Takaki, M.; Asami, R.; Kuwata, Y. *Polym. J.* **1979**, *11*, 425.
(9) Roovers, J. *Polymer* **1979**, *20*, 843.
(10) (a) Gauthier, M.; Möller, M. *Macromolecules* **1991**, *24*, 4548. (b) Gauthier, M.; Möller, M. Burchard, W. *Macromol. Symp.* **1994**, *77*, 43.
(11) Rahlwes, D.; Roovers, J. E. L.; Bywater, S. *Macromolecules* **1977**, *10*, 604.
(12) Barrie, J. A.; Rezanian, I. *Polymer* **1987**, *28*, 1217.
(13) Selb, J.; Gallot, Y. *Polymer* **1979**, *20*, 1259, 1275.
(14) Pitsikalis, M.; Sloula, S.; Pispas, S.; Hadjichristidis, N.; Cook, D. C.; Li, J.; Mays, J. W. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4337.
(15) Pitsikalis, M.; Woodward, J.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **1997**, *30*, 5384.
(16) Candau, F.; Afchar-Taromi, F.; Rempp, P. *Polymer* **1977**, *18*, 1253.
(17) Montheard, J.-P.; Chatzopoulos, M.; Camps, M. *Desk Reference of Functional Polymers. Synthesis and Applications*; Arshady, R., Ed.; American Chemical Society: Washington, DC, 1996; pp 3−18.
(18) Rempp, P.; Lutz, P.; Masson, P.; Chaumount, P.; Franta, E. *Makromol. Chem. Suppl.* **1985**, *13*, 47.
(19) Tsukahara, Y.; Inoue, J.; Ohta, Y.; Kohjiya, S.; Okamoto, Y. *Polym. J.* **1994**, *26*, 1013.
(20) Feast, W. J.; Gibson, V. C.; Johnson, A. F.; Khosravi, E.; Mohsin, M. A. *Polymer* **1994**, *35*, 3542.
(21) (a) Breunig, S.; Heroguez, V.; Gnanou, Y.; Fontanille, M. *Macromol. Symp.* **1995**, *95*, 151. (b) Heroguez, V.; Gnanou, Y.; Fontanille, M. *Macromol. Rapid Commun.* **1996**, *17*, 137. (c) Heroguez, V.; Breunig, S.; Gnanou, Y.; Fontanille, M. *Macromolecules* **1996**, *29*, 4459. (d) Heroguez, V.; Gnanou, Y.; Fontanille, M. *Macromolecules* **1997**, *30*, 4791.
(22) Tsukahara, Y.; Tsutsumi, K.; Yamashita, Y.; Shimada, S. *Macromolecules* **1990**, *23*, 5201.
(23) Tsukahara, Y.; Ohta, Y.; Senoo, K. *Polymer* **1995**, *36*, 3413.
(24) Dziezok, P.; Sheiko, S. S.; Fisher, K.; Schmidt, M.; Möller, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2812.
(25) Schappacher, M.; Deffieux, A. *Macromol. Chem. Phys.* **1997**, *198*, 3953.
(26) Schappacher, M.; Billaud, C.; Paulo, C.; Deffieux, A. *Macromol. Chem. Phys.* **1999**, *200*, 2377.
(27) Hirao, A.; Kitamura, K.; Takenaka, K.; Nakahama, S. *Macromolecules* **1993**, *26*, 4995.
(28) Hirao, A.; Hayashi, M. *Macromolecules* **1999**, *32*, 6450.
(29) Kazmaier, P. M.; Daimon, K.; Georges, M. K.; Hamer, G. K.; Veregin, R. P. *Macromolecules* **1997**, *30*, 2228.
(30) Wendler, U.; Bohrisch, J.; Jaeger, W.; Rother, G.; Dautzenberg, H. *Macromol. Rapid Commun.* **1998**, *19*, 185.
(31) Airpurua, J. M.; Cossio, F. P.; Palomo, C. J. *J. Org. Chem.* **1986**, *51*, 4941.
(32) Mattes, H.; Benezra, C. *Tetrahedron Lett.* **1987**, *28*, 1697.
(33) Jung, M. E.; Ornstein, P. L. *Tetrahedron Lett.* **1977**, 2659.
(34) Lauwers, M.; Regnier, B.; Van Eenoo, M.; Dennis, J. N.; Krief, A. *Tetrahedron Lett.* **1979**, 1801.
(35) Friedrich, E. C.; DeLucca, G. *J. Org. Chem.* **1983**, *48*, 1678.
(36) Olah, G. A.; Narrang, S. C. *Tetrahedron* **1982**, *38*, 2225 and references therein.
(37) Kim, S.; Park, J. H. *J. Org. Chem.* **1988**, *53*, 3111.
(38) A very small shoulder (<1%) was already present in the starting polymer before the transformation reactions.
(39) Hayashi, M.; Kojima, K.; Hirao, A. *Macromolecules* **1999**, *32*, 2, 2425.
(40) Hsieh, H. L.; Quirk. R. P. *Anionic Polymerization. Principle and Practical Applications*; Marcel Dekker: New York, Basel, Hong Kong, 1996, pp 379−380.
(41) We guess to form the dimer as follows: The CH═CH(Ph) group may possibly be generated by the elimination of lithium hydride from the chain end of polystyryllithium[42−44] and reacted with another polystyryllithium to produce the dimer.
(42) Burley, J. W.; Young, R. N. *J. Chem. Soc. B* **1971**, 1018.
(43) Glasse, M. D. *Prog. Polym. Sci.* **1983**, *9*, 133.
(44) Hsieh, H. L.; Quirk. R. P. *Anionic Polymerization. Principle and Practical Applications*; Marcel Dekker: New York, Basel, Hong Kong, 1996; pp 173−196.
(45) Ashby, E. C.; Sun, X.; Duff, J. L. *J. Org. Chem.* **1984**, *58*, 1270.
(46) The grafting efficiency was observed to decrease with increasing the molecular weight of poly(chloroethyl vinyl ether) used as the backbone polymer. However, it was still high and over 90% in the coupling reaction of poly(chloroethyl vinyl ether)s ($DP_n = 764$) with polystyryllithium ($DP_n = 29$).

MA991793G