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# Articles

## Synthesis of ABA Triblock Copolymers of Styrene and *p*-Methylstyrene by Living Cationic Polymerization Using the Bifunctional Initiating System 1,4-Bis(1-chloroethyl)benzene/$SnCl_4$ in the Presence of 2,6-Di-*tert*-butylpyridine

**Jae-Min Oh, Su-Jin Kang, Oh-Sig Kwon, and Sam-Kwon Choi***

*Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1 Kusung-Dong, Yusung-Gu, Taejon, Korea*

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ABSTRACT: ABA triblock copolymers of styrene and *p*-methylstyrene were prepared by living cationic polymerization using a bifunctional initiating system in the presence of 2,6-di-*tert*-butylpyridine, which, as a proton-trapping agent, suppressed the initiation by adventitious impurities and thus enhanced the livingness of the styrene monomers. By using these characteristics, triblock copolymers of styrene and *p*-methylstyrene could be prepared easily. The polymers showed the same molecular weight as the theoretical value and narrow and unimodal molecular weight distributions (MWDs).

## Introduction

In the cationic polymerization of styrene monomers, the low stability of the propagating cations has prevented the formation of "living" polymers. However, several research groups reported the living cationic polymerization of styrene initiated by an aryl acetate/$BCl_3$[1,2] and (1-chloroethyl)benzene/tetra-*n*-butylammonium chloride/$SnCl_4$ initiating system[3] in $CH_2Cl_2$. Recently, we also reported the living polymerization of styrene by (1-chloroethyl)benzene/$SnCl_4$ in the relatively low polar solvent $CHCl_3$.[4] The stability of the propagating species was indicated by the linear increase of the polymer molecular weight with conversion and its further increase on addition of a new monomer feed when the first polymerization was completed.

In the course of our continuing investigations concerning the living cationic polymerization of styrene monomers, we have developed a new preparative method using a bifunctional initiating system including 2,6-di-*tert*-butylpyridine as a proton-trapping agent. Bifunctional initiators in the cationic polymerization aim at the preparation of telechelic polymers which are of use in the synthesis of ABA triblock copolymers and bifunctional prepolymers (telchelics) and in chain extension reactions. Our previous works[4] also suggested that the cationic polymerization of styrene by (1-chloroethyl)benzene/$SnCl_4$ did not always generate the living propagating species. Solvent polarity, concentration of Lewis acid, and polymerization temperature had great influences on the stability of the propagating species.

Therefore, this study first aims to clarify the optimum polymerization conditions of styrene using a bifunctional initiator. Secondly, we continue our study of the living polymerization of styrene derivatives in an effort to obtain a new living polymer of *p*-methylstyrene (pMSt), which greatly differs in reactivity from styrene because of the electron-donating effect of the alkyl group. The third purpose of this study is the synthesis of new block copolymers through living cationic polymerization. So far, several block copolymer syntheses by sequential cationic polymerization of vinyl monomers have been reported. Higashimura et al.[5] block copolymerized *p*-*tert*-butoxystyrene with *p*-methoxystyrene, *p*-methylstyrene, and isobutyl vinyl ether. These monomers are now known to undergo living cationic polymerizations in the presence of the $HI/ZnX_2$ initiating system. Recently, Higashimura et al. succeeded in the living cationic polymerization of styrene and *p*-methylstyrene by the [$CH_3CH(OR)Cl/SnCl_4/nBu_4NCl$] initiating system.[5f] Kennedy et al.[6] synthesized di- and triblock copolymers of styrene and isobutylene. They used tertiary halide or tertiary ether as an initiator in conjunction with $Et_2AlCl$ or $TiCl_4$. Based on our systematic study of the living polymerization of styrene and *p*-methylstyrene, we succeeded in the synthesis of a new block copolymer by applying these studies. This paper provides the methodology of the block copolymer synthesis such as the choice of an adequate initiator, the sequence of monomer addition, etc.

## Experimental Section

**Materials.** Styrene and *p*-methylstyrene were washed with 10% aqueous NaOH solution and then distilled water, dried over $CaH_2$, and distilled under vacuum. The gas chromatographic purity exceeded 99.8%. Chloroform (stabilizer free) was refluxed over $CaH_2$ for 1 day and distilled. $SnCl_4$ was purified by fresh distillation and was used as a 1 M solution in chloroform. 2,6-Di-*tert*-butylpyridine was used as received without further purification.

**Synthesis of 1,4-Bis(1-chloroethyl)benzene.** A standard Grignard procedure was used for the synthesis of methylmagnesium iodide in THF solution. To a flask charged with a THF (400 mL) solution of excess methylmagnesium iodide (121.8 g, 0.7 mol) was added terephthaldehyde (27 g, 0.2 mol) in THF (400 mL) at reflux temperature. After addition was completed, the mixture was refluxed overnight. After neutralization, the product was extracted in excess ether. Recrystallization was

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* To whom correspondence should be addressed.

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**Table 1. Cationic Polymerization of Styrene by Several Initiating Systems in $CHCl_3$ at −15 °C ($[M]_0$ = 0.82 M, No 2,6-DtBP Added)[a]**

| $[BCEB]_0$ (mM) | $[SnCl_4]_0$ (M) | $[H_2O]_0$ (mM) | conv (%) | time (h) | $\bar{M}_n$(calcd) | $\bar{M}_n$(obsd) | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|---|---|---|---|
| 12.5 | 0.375 | | 38 | 1.5 | 2798 | 2250 (2080) | 1.77 (1.32) (b) |
| 12.5 | 0.375 | | 100 | 8 | 7034 | 6480 (6320) | 1.44 (1.21) (b) |
| 12.5 | 0.1785 | | 33 | 1.5 | 2456 | 2180 | 1.14 (u) |
| 12.5 | 0.1785 | | 60 | 8 | 4301 | 3890 | 1.17 (u) |
| | 0.375 | | 15 | 4 | | 7730 | 1.87 (u) |
| | 0.375 | | 21 | 12 | | 8550 | 1.87 (u) |
| | 0.375 | 12.5 | 12 | 3 | 820 | 2690 (1870) | 4.30 (1.34) (b) |
| | 0.375 | 12.5 | 59 | 10 | 4030 | 3310 (2830) | 2.35 (1.42) (b) |

[a] b = bimodal MWD; u = unimodal MWD. Numbers in parentheses are the $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the low molecular weight fraction. $\bar{M}_n(\text{calcd}) = [M]_0/[I]_0 \times 104.15(M_{St}) \times \text{conv}(\%) + 202$ (for BCEB). $\bar{M}_n$(obsd) and $M_w/M_n$ were determined relative to standard polystyrene samples by GPC. GPC traces of high-MW polymer/low-MW polymer are shown in Figure 2.

promoted by the careful addition of hexane and cooling. After recrystallization, 4.3 g (10.0%) of impure product was obtained. Separation by column chromatography gave a pure product (mp 91−92 °C) as a white solid product. Chlorination was accomplished by excess thionyl chloride.

**Synthesis of 1,4-Bis(1-chloro-1-methylethyl)benzene.** Excess methylmagnesium iodide was prepared in ether solution; then terephthaloyl chloride in ether solution was added dropwise. After addition was completed, the mixture was reacted overnight under a nitrogen atmosphere.

After neutralization, $NH_4Cl$ solution was slowly added to a stirred reactor. The organic layer was separated and dried over anhydrous $MgSO_4$. The solvent was evaporated and the product was purified twice by recrystallization from ethyl acetate. Chlorination of the diol was carried out by treating with excess HCl solution below 5 °C. After stirring for 6 h, methylene chloride was added to the reaction mixture.

The organic layer was separated and then dried over anhydrous $MgSO_4$, and the solvent was evaporated at 0 °C.

**Procedures.** Polymerization was carried out under dry nitrogen in a baked round-bottom flask with a two-way stopcock for monomer addition and sampling.

The initiation system was also prepared under the same conditions. The reaction (for styrene polymerization) was initiated by adding via dry syringes prechilled 1,4-bis(1-chloroethyl)benzene (BCEB), $SnCl_4$ (1 M chloroform solution), 2,6-di-*tert*-butylpyridine, and styrene in this order into a solvent ($CHCl_3$) maintained at the polymerization temperature. For the polymerization of *p*-methylstyrene, the reaction was initiated by adding via a dry syringe prechilled 1,4-bis(1-chloro-1-methylethyl)benzene (BCMEB), 2,6-di-*tert*-butylpyridine, *p*-methylstyrene, and $SnCl_4$ (1 M chloroform solution) in this order into a solvent maintained at the polymerization temperature.

For the block copolymerization, after the polymerization of *p*-methylstyrene was completed, a predetermined amount of $SnCl_4$ and styrene in this order were added. The mixture was stirred vigorously. After suitable time intervals, samples were withdrawn by syringe through a septum cap and were injected into an excess of chilled methanol. Then they were shaken, filtered, and dried in a vacuum oven. Monomer conversion was determined from the residual monomer concentration measured by gas chromatography. Further experimental details are given in the tables and figures.

**Characterization.** The number-average molecular weight ($\bar{M}_n$) and MWD were obtained by a Waters high-pressure gel permeation chromatography (GPC) assembly (Model M590 pump, $\mu$-Styragel columns of $10^5$, $10^4$, $10^3$, 500, and 100 Å, refractive index detector). Elution counts were calibrated by well-defined polystyrene standards. THF solutions were used and the flow rate was 2 mL/min. GC analyses were carried out on a Perkin-Elmer instrument (Model 8410). $^1H$ NMR spectra were obtained on a Bruker AM-200 Fourier transform spectrometer.

## Results and Discussion

### 1. Living Cationic Polymerization of Styrene by Bifunctional Initiating System.

As part of a continuing study of the living cationic polymerization of styrene and its derivatives, we developed new synthetic methods using a bifunctional initiating system. In general, bifunctional initiators in cationic polymerization aim at the preparation telechelic polymers which are of use in the synthesis of ABA block copolymers and bifunctional prepolymers (telechelics) and in chain extension reactions.

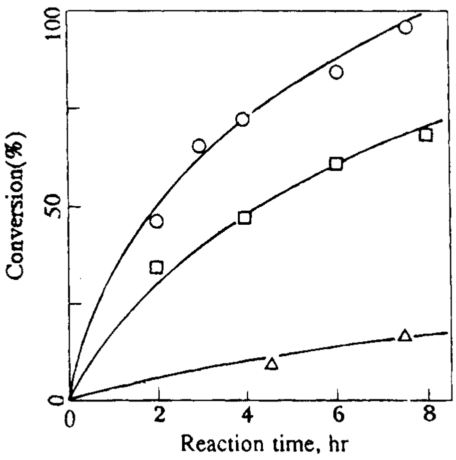

**Figure 1.** Time−conversion curves for the polymerization of styrene with BCEB/$SnCl_4$/$CHCl_3$ at −15 °C: $[M]_0$ = 0.82 M; [BCEB] = 12.5 mM. The different symbols indicate the $[SnCl_4]/[BCEB]$ ratio: (○) 30; (□) 15; (△) without BCEB, $SnCl_4$ = 0.51 M.

**Cationic Polymerization of Styrene.** Styrene was polymerized by the bifunctional initiating system BCEB/$SnCl_4$ in $CHCl_3$ solvent at −15 °C under the same polymerization conditions as those in our previous system of styrene.[4]

Figure 1 compares the time−conversion curves for the polymerization at −15 °C in $CHCl_3$ as a function of the amount of Lewis acid, $SnCl_4$. The conversion was 100% in 8 h at $[SnCl_4]/[BCEB]$ = 30 ($[SnCl_4]$ = 0.375 M), 60% in the same time at $[SnCl_4]/[BCEB]$ = 15 ($[SnCl_4]$ = 0.1875 M), and 18% without [BCEB] ($[SnCl_4]$ = 0.51 M). The polymerization without BCEB was thought to be initiated by adventitious water that could not be eliminated by conventional distillation. The polymerization proceeded smoothly up to quantitative conversion without an induction period, and the reaction mixture was homogeneous and colorless throughout the polymerization.

Table 1 and Figure 2 show the $\bar{M}_n$ and MWD of the polymers produced. The polymer for $[SnCl_4]/[BCEB]$ = 30 (Figure 2A) shows the broad MWD possessing the higher molecular weight fraction, which indicates a nonliving character. The polymers (Figure 2B) produced at $[SnCl_4]/[BCEB]$ = 15, however, exhibit a narrow MWD ($\bar{M}_w/\bar{M}_n$ < 1.2) without a higher molecular weight fraction and $\bar{M}_n$ values in good agreement with

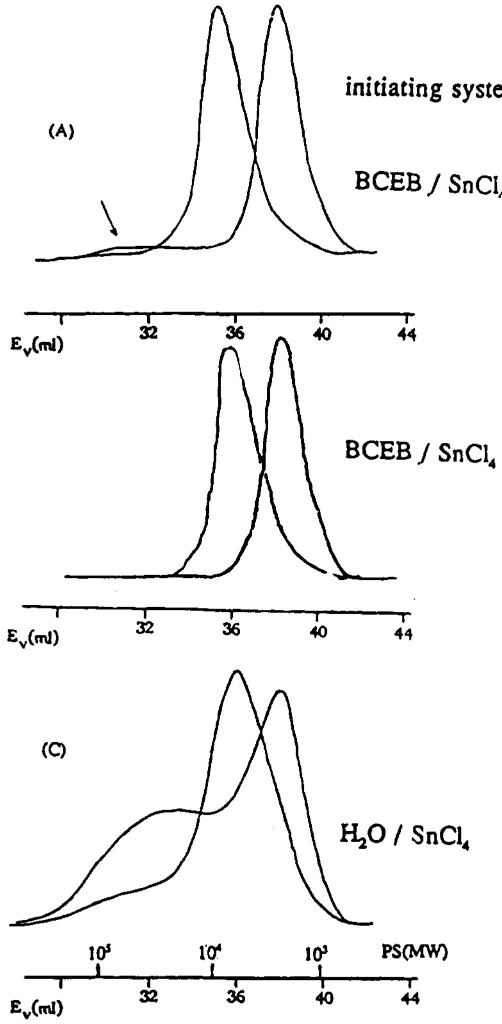

**Figure 2.** MWD curves of polystyrene obtained in the following polymerization conditions in $CHCl_3$ at −15 °C: (A) $[M]_0/[BCEB]_0/[SnCl_4]_0$ = 0.82 M/12.5 mM/0.37 M; (B) $[M]_0/[BCEB]/[SnCl_4]$ = 0.82 M/12.5 mM/0.187 M; (C) $[M]_0/[H_2O]/[SnCl_4]$ = 0.82 M/12.5 M/0.37 M.

the theoretical values. We thought that the deviation of $\bar{M}_n$ and the bimodal-like molecular weight distribution (MWD) appearing in the polymerization with a high concentration ratio of $[SnCl_4]$ ($[SnCl_4]/[BCEB]$ = 30) (Figure 2A) indicate the occurrence of coinitiation by adventitious water. To investigate these phenomena, we thus examined styrene polymerization with purposefully added water in conjunction with $SnCl_4$. In general, it has been well documented that water, as a protogen, is able to initiate the polymerization of styrene in the presence of $SnCl_4$. In addition, the initiation by water may occur parallel in the polymerization by the BCEB/$SnCl_4$ initiating system used in this study. Figure 2C illustrates the MWD of polymers produced by water as an initiator. The polymers turned out to be bimodal ($\bar{M}_w/\bar{M}_n$ = 7−5); the higher polymer fraction, the $\bar{M}_n$ of which does not change according to the conversion, showed a very broad MWD, and the lower polymer fraction, which shifted to high molecular weight according to conversion, showed a relatively narrow MWD. This higher molecular weight fraction is consistent with the portion of high molecular weight polymers that were obtained with use of a high concentration of $SnCl_4$ ($[SnCl_4]/[BCEB]$ = 30).

These results indicate that the polymerization proceeds via two kinds of propagating species initiated by $H_2O$, free protogen, and a BCEB-based system with $SnCl_4$, and the different polymer dispersities according to the amount of $SnCl_4$ indicate that the degree of initiation by water was greatly affected by the concentration of $SnCl_4$. As shown in Figure 2B, at a lower concentration of $SnCl_4$, a parallel initiation by water has little effect on the polymerization by BCEB/$SnCl_4$ in this polymerization time and therefore could be neglected.

To remove the effect by water completely, we examined styrene polymerization with 2,6-di-*tert*-butylpyridine (2,6-DtBP) as a proton-trapping agent,[6c] which was used to eliminate water impurities and to suppress the protogen to chain transfer to give living polystyrene.

**Living Cationic Polymerization of Styrene.** Styrene was polymerized by the BCEB/$SnCl_4$ initiating system in conjunction with 2,6-DtBP as a proton-trapping agent in chloroform at −15 °C ($[M]_0/[2,6\text{-DtBP}]/[BCEB]/[SnCl_4]$ = 0.825 M/24 mM/12.5 mM/0.357 M). A quantitative polymerization occurred without an induction phase, and the reaction rate was nearly the same as that for the polymerization without the proton-trapping agent as shown by the previous experiment (Figure 1). These facts indicate that 2,6-DtBP under these experimental conditions does not serve as an *electron donor to stabilize the carbocation;* the rate of the polymerization should be decreased when the carbocation stabilization by 2,6-DtBP occurred. The polymerization without the initiator, BCEB, was negligible in this polymerization time. This means that the parallel coinitiation by impurity water is suppressed by the proton-trapping agent, 2,6-DtBP.

Figure 3 shows a plot of the number-average molecular weights, ($\bar{M}_n$'s) and the molecular weight distribution (MWD) of the polymers obtained in the presence of 2,6-DtBP as a function of conversion. The $\bar{M}_n$ increased in direct proportion to the monomer conversion and was in good agreement with the calculated values assuming that one polymer chain forms per molecular of BCEB (the solid line in Figure 3). This means that there is no chain transfer to monomer because the molecular weight of the resulting polymer would have decreased if chain transfer to monomer occurred. The MWDs of the polymers were very narrow and nearly monodisperse ($\bar{M}_w/\bar{M}_n$ < 1.2). The livingness of the polymers was further confirmed by a monomer addition experiment (Figure 3). On addition of styrene feed, a second stage of polymerization immediately ensued at −15 °C. The $\bar{M}_n$ of the polymers continued to increase after the second monomer addition, again in direct proportion to conversion, and was very close to the calculated value for a living polymer (the solid line in Figure 3), while the polymer MWD stayed very narrow ($\bar{M}_w/\bar{M}_n$ < 1.2) and monodisperse throughout the reaction.

The above experiments show that the bifunctional initiating system BCEB/2,6-DtBP/$SnCl_4$ in $CHCl_3$ at −15 °C led to the living cationic polymerization of styrene.

**2. Living Cationic Polymerization of *p*-Methylstyrene by Bifunctional Initiating System. Polymerization Using BCEB.** This section discusses the possibility of living cationic polymerization of *p*-methylstyrene by the BCEB/$SnCl_4$ initiating system in a relatively nonpolar solvent ($CHCl_3$) as an extension of the corresponding process as above. With BCEB/$SnCl_4$, *p*-methylstyrene was polymerized much faster than styrene at −15 °C. Figure 4 shows the time−conversion curves for the polymerization of *p*-methylstyrene. The polymerization proceeded quantitatively without an

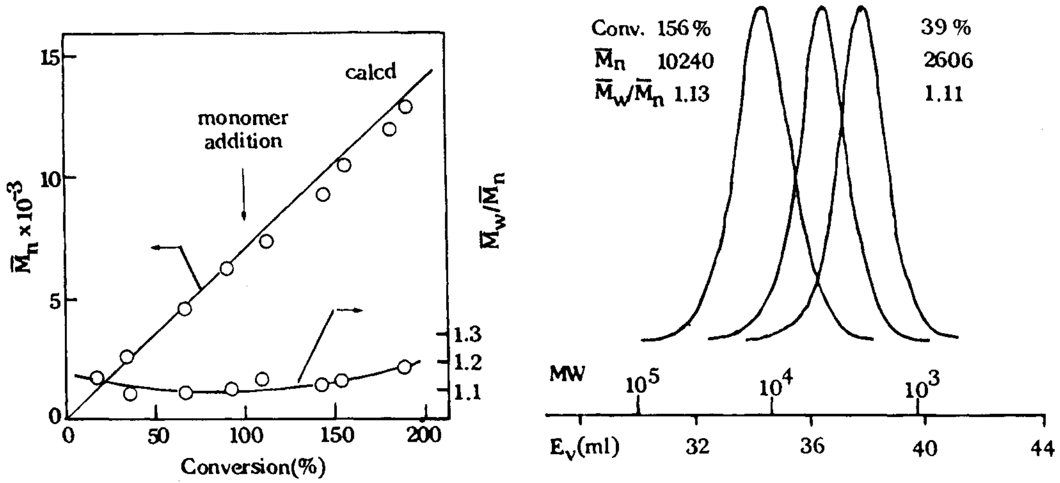

**Figure 3.** $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of polystyrene obtained with BCEB/SnCl$_4$/2,6-DtBP in monomer addition experiments in CHCl$_3$ at −15 °C. $[M]_0 = [M]_{add} = 0.82$ M, [BCEB] = 12.5 mM, [SnCl$_4$]/[BCEB] = 30, [2,6-DtBP] = 10 mM. The diagonal solid line $\bar{M}_n$−conversion profile indicates the calculated $\bar{M}_n$ values assuming one living chain per BCEB.

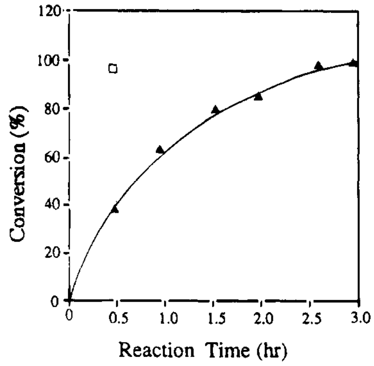

**Figure 4.** Time−conversion curve for the polymerization of *p*-methylstyrene with BCEB/2,6-DtBP/SnCl$_4$ in CHCl$_3$ at −15 °C. $[M]_0$/[BCEB]/[2,6-DtBP] = 0.95 M/17 mM/10 mM: (▲) [SnCl$_4$]/[BCEB] = 2; (□) [SnCl$_4$]/[BCEB] = 6.

**Table 2. Cationic Polymerization of *p*-Methylstyrene in CHCl$_3$ at −15 °C$^a$**

| initiator | [SnCl$_4$]-[init] | time (min) | conv (%) | $\bar{M}_n$-(theor) | $\bar{M}_n$-(obsd) | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|---|---|---|
| BCEB$^b$ | 30 | <10 | 100 | 6806 | 7850 | 1.34 |
| | 6 | 10 | 56 | 3811 | 5900 | 1.37 |
| | 6 | 30 | 100 | 6806 | 8282 | 1.39 |
| | 2 | 180 | 100 | 6806 | 9412 | 1.40 |
| BCMEB$^c$ | 2 | 90 | 100 | 6140 | 6289 | 1.10 |

[a] Total reaction volume: 25 mL. [b] [BCEB] = 17 mM, [2,6-DtBP] = 8 mM, $[M]_0 = 0.95$ M. [c] [BCMEB] = 16 mM, [2,6-DtBP] = 7.6 mM, $[M]_0 = 0.80$ M.

**Table 3. Block Copolymerization with *p*-Methylstyrene from Living Polystyrene in CHCl$_3$ at −15 °C$^a$**

| | conv (%) | | | | | |
|---|---|---|---|---|---|---|
| no. | St | pMSt | $\bar{M}_n$(theor) | $\bar{M}_n$(obsd) | $\bar{M}_w/\bar{M}_n$ | time (h) |
| 1 | 100 | | 6022 | 5456 | 1.11 | 9 |
| 2 | 100 | 30 | 8211 | 9064 | 1.29 | 9.5 |
| 3 | 100 | 65 | 10767 | 11130 | 1.31 | 10.5 |
| 4 | 100 | 100 | 13321 | 12736 | 1.34 | 12 |

[a] [St]/[BCEB]/[SnCl$_4$]/[2,6-DtBP]/[*p*MSt] = 0.95 M/17 mM/0.52 M/10 mM/1.05 M.

induction period. The polymerization mixtures were homogeneous and colorless throughout. Despite the relatively high reactivity of the monomer, SnCl$_4$ alone could not polymerize *p*-methylstyrene in this polymerization time. The polymerization rate increased according to the amount of Lewis acid, SnCl$_4$; the polymerization was completed in 3 h at [SnCl$_4$]/[BCEB] = 2 and in 0.5 h at [SnCl$_4$]/[BCEB] = 6. Table 2 illustrates the number-average molecular weight ($\bar{M}_n$) and MWD. The number-average molecular weights of the polymers were higher than the calculated values assuming that one polymer chain forms per unit BCEB and increased linearly with monomer conversion. All of the polymers exhibit broad molecular weight distributions (MWD), maintaining the $\bar{M}_w/\bar{M}_n$ ratio between 1.34 and 1.40 over the whole conversion range. We thought that the reason for these phenomena might be due to slow initiation between dormant and active species relative to propagation. Thus we synthesized 1,4-bis(1-chloro-1-methylethyl)benzene (BCMEB), which is a more reactive chloride than BCEB, and used it as initiator. This initiator would give a higher concentration of active species at the initiation step in the polymerization than BCEB. As shown in Table 2, the $\bar{M}_n$ of the polymer produced by using BCMEB as initiator was in good agreement with the calculated values assuming that one polymer chain forms per molecule of BCMEB, and the MWD was very narrow and nearly monodisperse below 1.15. From these results, we could conclude that the initiator which can produce more a stable cation compared with the propagating species produced from the reaction between the initiator and monomer gives fast initiation in the cationic polymerization. As a matter of course, the active species of an initiator which can produce a more unstable cation than the propagating center reacts with the monomer more quickly than the propagating center. However, the unstable initiator cation would have a shorter lifetime than the stable propagating center. The lifetime of a species is directly related to its concentration. Therefore it can be deduced that the effect of lifetime, i.e., concentration, of a stable initiator cation is more significant than that of the fast reaction between the unstable initiator cation and the monomer under the condition of constant concentration of catalyst that makes active species by the reaction with the initiator or the propagating center. In our initiating system, the cation produced from BCEB and one SnCl$_4$ is thought to be more reactive but less stable than the propagating center of poly(pMSt) because of the electron-withdrawing effect of the 1-chloroethyl group located *para* to the active site. BCEB did not give rise to the living polymerization of *p*-methylstyrene. In contrast to BCEB, BCMEB produces more a stable and less reactive cation than the propagating center of poly(pMSt). We could succeed in the living cationic polym-

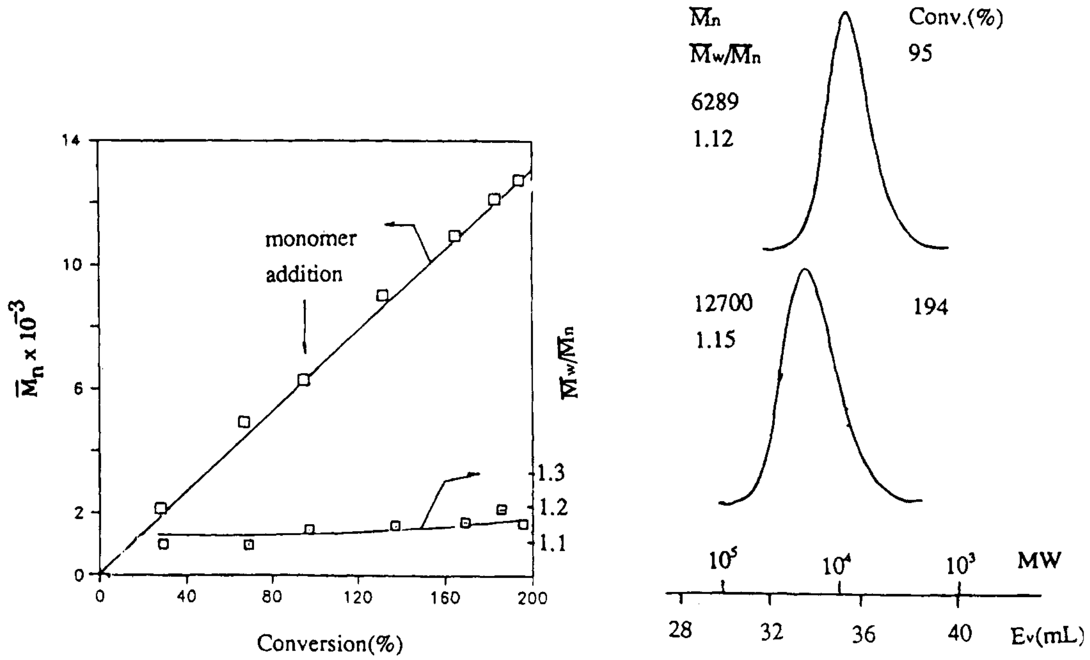

**Figure 5.** $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD of poly(*p*-methylstyrene) obtained with BCMEB/2,6-DtBP/SnCl$_4$ in monomer addition experiments in CHCl$_3$ at −15 °C. $[M]_0 = [M]_{add}$/[BCMEB]/[2,6-DtBP]/[SnCl$_4$] = 0.95 M/17 mM/10 mM/34 mM. The diagonal solid line indicates the calculated $\bar{M}_n$ values assuming one living chain per BCMEB.

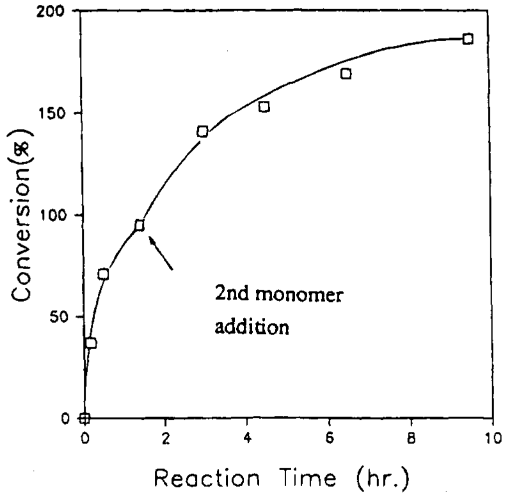

**Figure 6.** Time−conversion curves of St−pMSt−St block copolymerization obtained by blocking from living poly(pMSt) that was polymerized as follows: [pMSt]/[BCMEB]/[2,6-DtBP]/[SnCl$_4$] = 1.05 M/16 mM/10 mM/32 mM. After the addition of styrene (0.95 M), an additional dose of SnCl$_4$ (0.21 M) was carefully added to the reaction mixture.

erization of *p*-methylstyrene by using this initiator. Thus, we studied the living polymerization of *p*-methylstyrene by the BCMEB/SnCl$_4$/2,6-DtBP initiating system in CHCl3 at −15 °C.

**Living Cationic Polymerization of *p*-Methylstyrene by BCMEB.** With the BCMEB/SnCl$_4$/2,6-DtBP initiating system, *p*-methylstyrene was polymerized in CHCl$_3$ at −15 °C. The polymerization rate is faster than that for the BCEB/2,6-DtBP/SnCl$_4$ initiating system. The polymerization mixtures were all homogeneous and colorless throughout. Figure 5 plots the $\bar{M}_n$ of the polymers obtained in this initiating system as a function of conversion. The $\bar{M}_n$ increased in proportion to monomer conversion and was in good agreement with the calculated value assuming that one polymer chain forms per molecule of BCMEB (the solid line in Figure 5). The MWDs of the polymers were narrow and nearly

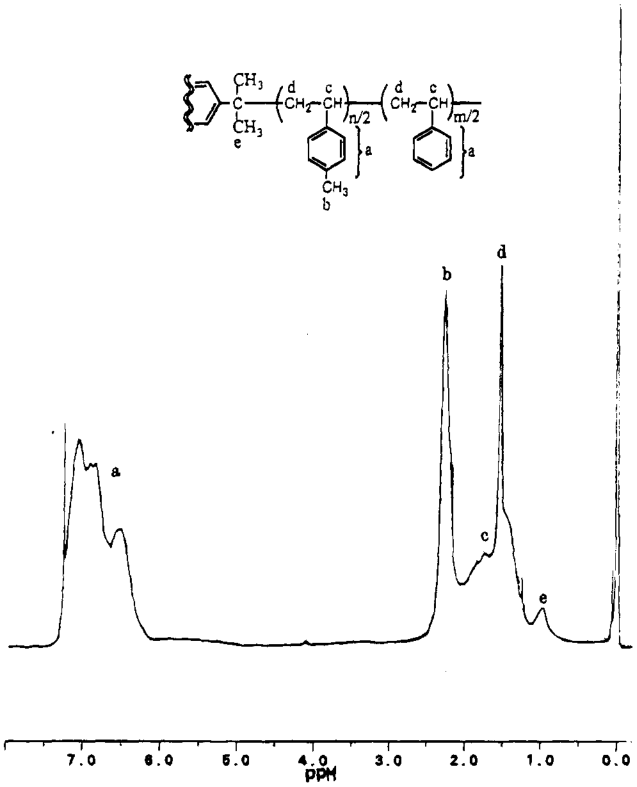

**Figure 7.** $^1$H NMR spectrum of the triblock copolymer of styrene and *p*-methylstyrene.

monodisperse below 1.15. The livingness of the polymers was further confirmed by so-called "monomer addition" experiments in which a fresh feed of *p*-methylstyrene was added to the completely polymerized reaction mixture. The added *p*-methylstyrene was smoothly polymerized to give polymers whose $\bar{M}_n$ maintained the linearly progressive increase with conversion commenced in the first-stage polymerization. The MWD of the polymers remained narrow ($\bar{M}_w/\bar{M}_n$ < 1.2) without tailing after the monomer addition though it was

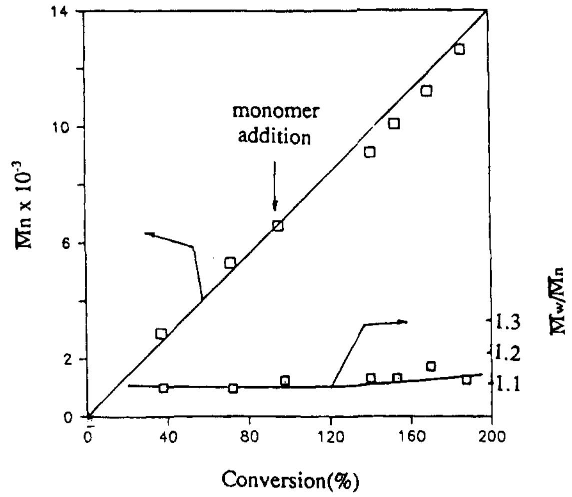

**Figure 8.** $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ curves of St−pMSt−St triblock copolymers obtained by blocking from living poly(pMSt) under the following conditions: [pMSt]/[BCMEB]/[2,6-DtBP]/[SnCl$_4$] = 1.05 M/16 mM/10 mM/32 mM in CHCl$_3$ at −15 °C. After the addition of styrene (0.95 M), an additional dose of SnCl$_4$ (0.21 M) was carefully added to the reaction mixture.

broader than that of the polymers from the first-stage polymerization.

The above results demonstrate that the BCMEB/2,6-DtBP/SnCl$_4$ initiating system in CHCl$_3$ at −15 °C leads to a living polymerization without chain transfer and termination, and initiation is quantitative and faster than propagation.

**3. Block Copolymerization of Styrene and *p*-Methylstyrene.** The living polymerization by BCMEB/SnCl$_4$/2,6-DtBP/CHCl$_3$ was applied to the block copolymerization between styrene and *p*-methylstyrene. These block copolymers appear interesting as block copolymers between monomers having different reactivity; *p*-methylstyrene is more reactive than styrene by the electron-donating effect of the *p*-methyl group. Block copolymers between a pair of monomers with similar reactivity have been synthesized by several groups, but there have been few reports on the synthesis of block copolymers between different reactive monomers.[5b,6]

In this study, the block copolymerization of styrene and *p*-methylstyrene was studied by blocking from living polystyrene to *p*-methylstyrene and vice versa.

**Block Copolymerization from Living Polystyrene.** Polystyrene was polymerized quantitatively by BCEB/SnCl$_4$/2,6-DtBP/CHCl$_3$ at −15 °C to yield monodisperse living polystyrene (Figure 3). When the styrene feed was depleted completely, prechilled *p*-methylstyrene in bulk was added to the reaction mixture. However, the MWDs of the product polymers (Table 3) were broad ($\bar{M}_w/\bar{M}_n \sim 1.3$) and were nearly constant according to the conversion.

Another block copolymerization from polystyrene was carried out where the addition and polymerization of *p*-methylstyrene were carried out at −40 °C; living polystyrene was prepared at −15 °C as described above. Although the second-stage polymerization of *p*-methylstyrene at −40 °C was much slower than at −15 °C and quantitative, the final products still showed somewhat broad MWDs that were similar to those obtained at −15 °C. The above results show that the living triblock copolymers were not obtained by the reaction of living polystyrene with the added *p*-methylstyrene and varying the temperature did not improve the deterioration of the living character in the second-stage polymerization of *p*-methylstyrene.

**Block Copolymerization from Living Poly(*p*-methylstyrene).** The reverse order of monomer addition, from *p*-methylstyrene to styrene, was also examined for the St−pMSt−St triblock copolymerization. Thus, *p*-methylstyrene was polymerized in CHCl$_3$ at −15 °C with the BCMEB/SnCl$_4$/2,6-DtBP initiating system, and when the *p*-methylstyrene feed was polymerized completely, bulk styrene was added to the reaction mixture. As shown above, styrene was hardly polymerized under the living polymerization condition

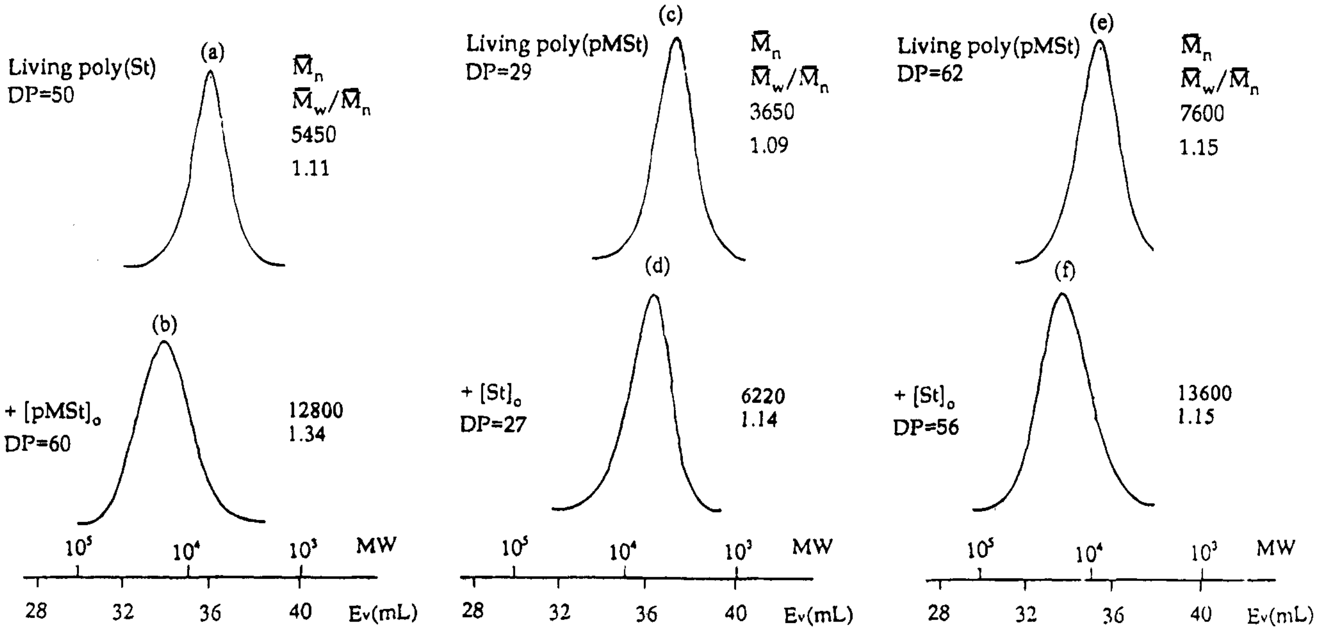

**Figure 9.** MWD of St−pMSt−St and pMSt−St−pMSt block copolymers obtained by blocking from living poly(pMSt) and poly(St): (a) starting polystyrene, [M]$_0$/[BCMEB]/[SnCl$_4$]/[2,6-DtBP] = 0.95 M/17 mM/0.52 M/10 mM; (b) triblock copolymers from polymer (a), pMSt/St = 1.2/1; (c) starting poly(pMSt), [M]$_0$/[BCMEB]/[SnCl$_4$]/[2,6-DtBP] = 1.05 M/34 mM/0.68 mM/10 mM; (d) triblock polymers from polymer (c), pMSt/St = 1.1/1; (e) starting poly(pMSt), [M]$_0$/[BCMEB]/[SnCl$_4$]/[2,6-DtBP] = 1.05 M/17 mM/0.34 mM/10 mM; (f) triblock polymers from polymer (e), pMSt/St = 1.1/1.

of *p*-methylstyrene because of the lower reactivity compared to that of *p*-methylstyrene. Thus, the additional $SnCl_4$ (solution in $CHCl_3$) was added in this polymerization mixture to lead to quantitative polymerization of added styrene feed. As shown in Figure 6, the polymerizations were completed in 9 h at −15 °C when an additional dose of $SnCl_4$ was added after the addition of the second monomer. The MWDs of the product polymers were narrow without tailing ($\bar{M}_w/\bar{M}_n < 1.18$) and shifted toward the higher molecular weight side than those of the starting poly(*p*-methylstyrene).

Figure 7 shows the $^1$H NMR spectrum of the resulting triblock copolymer of styrene and *p*-methylstyrene. All characteristic peaks of the triblock copolymer appear in the spectrum, and there is no peak at 1.98 ppm where methyl proton peak of BCMEB appears. The methyl proton peak of BCMEB appeared at 1.0 ppm when the chloride was substituted by an alkyl group. In Figure 7, the peak appeared at 1.0 ppm. This indicates that the initiation by BCMEB is successful in the first-stage polymerization of *p*-methylstyrene. The degree of polymerization ($DP_n$) for each monomer was calculated from the integrated peak intensity of peak a relative to that of peak e (Figure 7). The percentage of *p*-methylstyrene block in the integrated peak intensity of peak e can be determined by that of peak c. The observed $DP_n$ for each monomer was in good agreement with the calculated values based on the initial feed ratio of initiator to *p*-methylstyrene and styrene; e.g., $m/n$: calcd 59.2/38.5; obsd 60/36.2 ($\bar{M}_n = 11\,062$), where $m$ is the $DP_n$ for *p*-methylstyrene and $n$ is the $DP_n$ for styrene.

Figure 8 shows the $\bar{M}_n$ and MWD of the polymers obtained in this polymerization as a function of conversion. The $\bar{M}_n$ increased in proportion to the conversion of monomers and was in good agreement with the calculated value assuming that one polymer chain forms per molecule of BCMEB (the solid line in Figure 8).

Figure 9 shows the MWD curves of the polymers obtained in the above experiments. All MWD curves are unimodal without any shoulder.

These results indicate that well-defined triblock copolymers of styrene and *p*-methylstyrene were synthesized with the BCMEB/$SnCl_4$/2,6-DtBP initiating system in $CHCl_3$ at −15 °C. In conclusion, this study shows that the choice of initiator, monomer addition sequence, and the precise control of the polymerization conditions are very important in block copolymer synthesis by living cationic polymerization.

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