

# Living Cationic Polymerization of *p*-Chloro- $\alpha$ -methylstyrene and Its Sequential Block Copolymerization with Isobutylene

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**ABSTRACT:** The homopolymerization of *p*-chloro- $\alpha$ -methylstyrene (pCl $\alpha$ MeSt) and its sequential block copolymerization with isobutylene (IB) initiated by 1,3-dimethyl-1,3-diphenyl-1-chlorobutane (Di $\alpha$ MeSt-HCl) in conjunction with BCl<sub>3</sub> was investigated in methylcyclohexane/methyl chloride (60/40, v/v) at –80 °C. The homopolymers exhibited close to theoretical  $M_n$ 's, and the diagnostic  $M_n$ –conversion and first-order (ln[M]<sub>0</sub>/[M]–time) plots were linear; thus, chain transfer and termination were not detected. The propagating chain end of poly(pCl $\alpha$ MeSt) was exceptionally stable; no decomposition could be detected even after 5 h under monomer-starved conditions. According to the <sup>1</sup>H NMR spectrum of homopoly-(pCl $\alpha$ MeSt), the polymer is 94% syndiotactic; however, the precipitated polymer exhibited only a glass transition at 198 °C. Recrystallization from methylcyclohexane–methyl ethyl ketone solvent mixture yielded a semicrystalline polymer with  $T_m$  = 229 °C. Sequential block copolymerization of pCl $\alpha$ MeSt with IB was also carried out by the addition of IB to the solution of living poly(pCl $\alpha$ MeSt), followed by the addition of TiCl<sub>4</sub>. By gel permeation chromatography, the crossover efficiency was ~100%, and no homopolymer contamination was detected.

## Introduction

One of the most important aspects of living polymerization is the ability to prepare block copolymers by sequential monomer addition. This ability has been utilized in living carbocationic polymerization to synthesize a wide variety of linear and star-branched block copolymers, mainly with polyisobutylene (PIB) as the rubbery block segment and plastic segments based on styrene,<sup>1,2</sup>  $\alpha$ -methylstyrene,<sup>3,4</sup> indene,<sup>5</sup> and *p*-methyl-,<sup>6</sup> *p*-*tert*-butyl-,<sup>7</sup> *p*-chloro-, and *p*-fluorostyrene.<sup>8</sup> Triblock copolymers having a PIB central block segment and the above plastic end segments are useful thermoplastic elastomers. A comprehensive review on the subject is available.<sup>9</sup> The syntheses of PIB block copolymers with a crystalline (mainly polyester) block segment so far involved a much more difficult, multistep, site transformation process. Sequential monomer addition has not been reported for this type of block copolymer due to limitations in the availability of monomers that undergo living cationic polymerization and give rise to crystalline polymers. Polymer crystallinity is usually the consequence of a (stereo)regular macromolecular structure, which is conducive to packing in the crystalline lattice. Most of the above styrenic monomers, however, give rise to atactic polymers. Cationic polymerization of  $\alpha$ -methylstyrene ( $\alpha$ MeSt) yields a mostly syndiotactic polymer, which, however, does not crystallize even when the syndiotactic content is higher than 90%.<sup>3</sup> Polymers of *p*-methyl- and *p*-chloro-substituted  $\alpha$ MeSt (pCl $\alpha$ MeSt) have been reported to be crystalline with high  $T_g$  (~140–175 °C) and  $T_m$  (~210–220 °C).<sup>10</sup> Due to our interest in PIB based block copolymers, we were attracted to pCl $\alpha$ MeSt, whose reactivity should be closer to IB than *p*-methyl-substituted  $\alpha$ MeSt.

Lenz has reported on the polymerization of para-substituted  $\alpha$ MeSt monomers at –78 °C using various Friedel–Crafts acids (in conjunction with adventitious protons) and solvents.<sup>11</sup> Poly(pCl $\alpha$ MeSt) synthesized with TiCl<sub>4</sub> in methylene chloride at –78 °C exhibited

$M_n$  =  $1.71 \times 10^5$  and PDI = 2.4. The solvent polarity strongly influenced the tacticity; polar solvent favored the formation of highly syndiotactic polymers (up to 96%). The influence of Friedel–Crafts acid was less important in polar solvent but was quite substantial in hexane. The polymerization of pCl $\alpha$ MeSt by the 2-chloro-2,4,4-trimethylpentane/TiCl<sub>4</sub> initiating system in CH<sub>2</sub>Cl (MeCl)/methylcyclohexane (MeChx) (40/60, v/v) at –80 °C has also been reported by Chakraborty et al.<sup>12</sup> The syndiotactic diad fraction of the polymer ( $M_n$  =  $2.0 \times 10^4$  and PDI = 3.4) was 0.8. Information on the crystallinity was not reported.<sup>12</sup> More recently the electropolymerization of pCl $\alpha$ MeSt was investigated.<sup>13</sup> The polymers were reportedly crystalline, but details were not provided.

This publication reports on the living cationic polymerization of pCl $\alpha$ MeSt and on the synthesis of poly-(pCl $\alpha$ MeSt-*b*-IB) block copolymer by living cationic sequential block copolymerization.

## Experimental Section

**Materials.** 1,3-Dimethyl-1,3-diphenyl-1-chlorobutane (Di $\alpha$ MeSt-HCl) was synthesized by the hydrochlorination of 2,4-diphenyl-4-methyl-1-pentene ( $\alpha$ MeSt dimer, Aldrich, 99%) as described before.<sup>14</sup> *p*-Chloro- $\alpha$ -methylstyrene (pCl $\alpha$ MeSt, Aldrich, 98%) was mixed with a small amount of dibutylmagnesium (1.0 M heptane solution) and distilled under vacuum before use. Methyl chloride (MeCl) and IB were dried in the gaseous state by passing them through in-line gas-purifier columns packed with BaO/Drierite. They were condensed in the cold bath of a glovebox prior to polymerization. Methylcyclohexane (MeChx, Aldrich, 99%) was refluxed for 24 h with concentrated sulfuric acid, washed with 5% NaOH solution then neutral with distilled water, dried on Na<sub>2</sub>SO<sub>4</sub>, and distilled from CaH<sub>2</sub> under nitrogen before use. Titanium tetrachloride (Aldrich, 99.9%), 2,6-di-*tert*-butylpyridine (DTBP, Aldrich, 97%), and boron trichloride (Aldrich, 99.9%) were used as received.

**Polymerization.** All polymerizations were carried out under a dry nitrogen atmosphere in an Mbraun 150-M glovebox (Innovative Technology Inc., Newburyport, MA). Large (75 mL) culture tubes were used as polymerization reactors. The total volume of the reaction mixture was 25 mL.

The polymerization of pCl $\alpha$ MeSt was carried out using the following concentrations: [Di $\alpha$ MeSt·HCl] = 0.002 M, [BCl<sub>3</sub>] = 0.006 M, [pCl $\alpha$ MeSt] = 0.282 M, [DTBP] = 0.0035 M, unless noted otherwise. The order of addition was MeChx, MeCl, proton trap, di $\alpha$ MeSt·HCl, BCl<sub>3</sub>, and the monomer. The polymerization mixture was quenched with prechilled methanol, and then the polymer was precipitated into 50 mL of methanol containing 100 ppm of 2,6-di-*tert*-butyl-4-methylphenol as an antioxidant. After decanting the solvent, the polymer was washed again with methanol and dried.

The polymer was crystallized in a MeChx–methyl ethyl ketone solvent mixture. Polymer (1.2 g) was suspended in 200 mL of MeChx, and then methyl ethyl ketone was added until the entire polymer dissolved (~20 mL). The solution was left in an uncovered beaker for 3 days. The remaining material was dried in a vacuum at 130 °C for 1 day.

**Synthesis of PpCl $\alpha$ MeSt–PIB Diblock Copolymer.** To synthesize PpCl $\alpha$ MeSt, 10.4 mL of MeChx, 6.6 mL of MeCl, 1.0 mL of DTBP solution in MeChx (0.15 M), 1.075 g (7 mmol) of pCl $\alpha$ MeSt, 1.0 mL of Di $\alpha$ MeSt·HCl solution in MeCl (0.05 M), and 1.0 mL of BCl<sub>3</sub> in a MeChx/MeCl 60/40 (v/v) mixture were added at –80 °C in this order. The polymerization was carried out for 20 min. An aliquot was then taken and quenched with prechilled methanol to determine  $M_n = 2.1 \times 10^4$  and  $M_w/M_n = 1.30$  for the first block segment. To the rest of the solution were added 3.0 mL (38.5 mmol) of IB and 1.0 mL of TiCl<sub>4</sub> solution (0.90 M). After 120 min the polymerization mixture was quenched with prechilled methanol, and then the polymer was precipitated into 50 mL of methanol. The overall monomer conversion was 99.5%. The block copolymer exhibited  $M_n = 6.2 \times 10^4$  and  $M_w/M_n = 1.21$ .

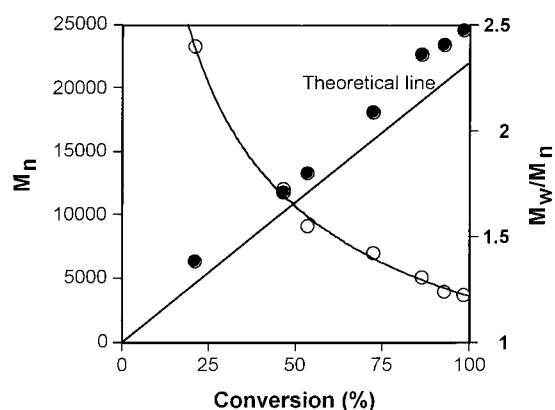
**Characterization.** Molecular weights were measured using a Waters HPLC system equipped with a model 510 HPLC pump, a model 250 dual refractometer/viscometer detector (Viscotek), a model 486 UV/vis detector, a model 712 sample processor, and five ultra-Styrigel GPC columns connected in the following series: 500, 10<sup>3</sup>, 10<sup>4</sup>, 10<sup>5</sup>, and 100 Å. THF was used as eluent at a flow rate of 1.0 mL/min. The measurements were carried out at room temperature. The molecular weights and polydispersities were determined using the universal calibration curve and Viscotek TriSEC GPC software. The  $dn/dc$  values and therefore the  $M_n$ 's of poly(pCl $\alpha$ MeSt) and poly-(pCl $\alpha$ MeSt-*b*-IB) diblock copolymers were calculated by assuming 100% recovery of the injected mass. <sup>1</sup>H NMR spectroscopy was carried out on a Bruker 250 MHz instrument.

## Results and Discussion

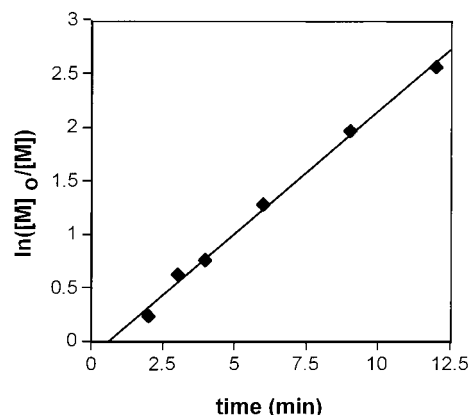
**Living Polymerization of pCl $\alpha$ MeSt.** We reported earlier<sup>14</sup> on the living cationic polymerization of  $\alpha$ MeSt initiated by the hydrochlorinated olefinic  $\alpha$ MeSt dimer (Di $\alpha$ MeSt·HCl)/BCl<sub>3</sub> initiating system in MeCl/hexanes (Hex) or MeCl/MeChx (40/60, v/v) mixtures at –60 to –80 °C. The polymerization of pCl $\alpha$ MeSt was first investigated under identical conditions. In MeChx/MeCl 60/40 (v/v) at –80 °C the polymerization is slower than that of  $\alpha$ MeSt, but still relatively rapid, and 100% conversion is reached in about 16 min. The  $M_n$ –conversion plot, shown in Figure 1, is linear and close to the theoretical line, indicating the absence of chain transfer to monomer. The  $M_w/M_n$  values decrease with increasing conversion and reach about 1.2 at complete monomer conversion. The  $M_w/M_n$ –conversion function is typical of slow exchange between active and dormant centers relative to the rate of propagation. Fitting of the  $M_w/M_n$ –conversion plot with eq 1,<sup>15</sup>

$$M_w/M_n \approx 1 + \frac{1}{\beta} \left( \frac{2}{x} - 1 \right) \quad (1)$$

where  $x$  is the fractional conversion and  $\beta = (k_{-i})/(k_p[I]_0)$  ( $k_{-i}$  and  $k_p$  are the rate constants of deactivation and propagation, respectively, and  $[I]_0$  is initiator



**Figure 1.** A  $M_n$ –conversion plot for the polymerization of pCl $\alpha$ MeSt: filled symbols,  $M_n$ ; open symbols,  $M_w/M_n$ . Reaction conditions: [Di $\alpha$ MeSt·HCl] = 0.002 M, [DTBP] = 0.0035 M, [BCl<sub>3</sub>] = 0.006 M, [pCl $\alpha$ MeSt] = 0.282 M, MeChx/MeCl 60/40 (v/v); temperature = –80 °C.



**Figure 2.** A  $\ln([M]_0/[M])$ –time plot for the polymerization of pCl $\alpha$ MeSt. Reaction conditions: [Di $\alpha$ MeSt·HCl] = 0.002 M, [DTBP] = 0.006 M, [BCl<sub>3</sub>] = 0.006 M, [pCl $\alpha$ MeSt] = 0.282 M, MeChx/MeCl 60/40 (v/v); temperature = –80 °C.

concentration) yielded a  $\beta$  value of 5.7. Thus, propagation is ~88 times faster than deactivation, which results in broad molecular weight distributions, especially at low conversion. Interestingly, propagation is only 23 times faster than deactivation in the polymerization of  $\alpha$ MeSt ( $\beta = 21.5$  was calculated from the data of ref 14 for polymerizations carried out under the same conditions). Since  $k_{-i}$  is not expected to be lower for pCl $\alpha$ MeSt (PpCl $\alpha$ MeSt<sup>+</sup> should be less stable than P $\alpha$ MeSt<sup>+</sup>),  $k_p$ (pCl $\alpha$ MeSt) must be higher than  $k_p$ ( $\alpha$ MeSt). Therefore, it seems that the effect of *p*-chloro substituent on cation reactivity is larger than its effect on monomer reactivity.

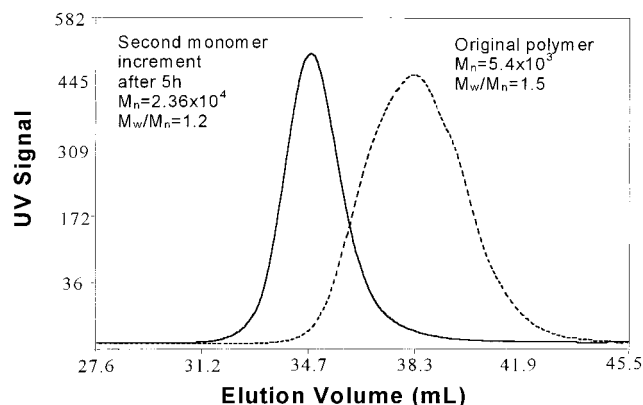
The first-order ( $\ln([M]_0/[M])$ –time) plot, shown in Figure 2, is also linear starting at close to the origin, and thus termination is not detected. Therefore, we conclude that the polymerization of pCl $\alpha$ MeSt in conjunction with BCl<sub>3</sub> in MeChx/MeCl (60/40 v/v) at –80 °C is living.

The lifetime of the propagating chain end of poly-(pCl $\alpha$ MeSt) was measured in a separate experiment. First, a low molecular weight polymer ( $M_n = 5.4 \times 10^3$ ) was prepared, and the polymerization mixture was left under monomer-starved conditions for different times. After a given time, a second monomer increment was added (0.334 M,  $M_{n\text{total}}(\text{theoretical}) = 2.55 \times 10^4$ ) and polymerized for 30 min. Table 1 lists the total conversions and the  $M_n$  and  $M_w/M_n$  values.

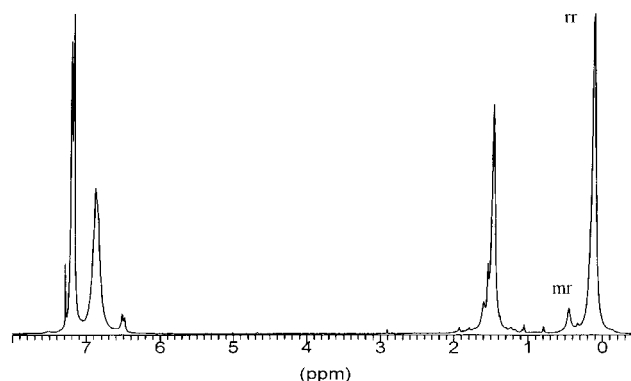
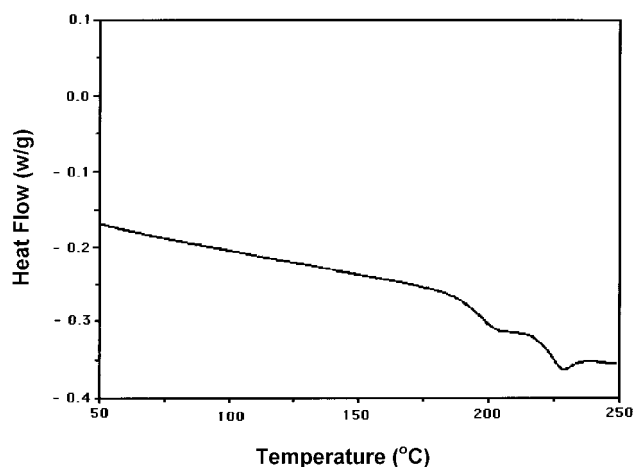
**Table 1.** Characteristics of Poly(pCl $\alpha$ MeSt) after a Second Monomer Addition<sup>a</sup>

time of addition of second monomer increment (min)	conv (%)	$M_n \times 10^{-3}$	$M_w/M_n$
original	87.4	5.4	1.51
90	90.8	24.2	1.19
180	84.4	22.2	1.22
240	82.4	21.2	1.26
300	89.8	23.6	1.21

<sup>a</sup> Reaction conditions: [Di $\alpha$ MeSt $\cdot$ HCl]<sub>0</sub> = 0.002 M, [DTBP] = 0.006 M, [BCl<sub>3</sub>] = 0.006 M, [pCl $\alpha$ MeSt]<sub>1</sub> = 0.0521 M, [pCl $\alpha$ MeSt]<sub>2</sub> = 0.334 M;  $M_n$ (100% conversion) =  $2.55 \times 10^4$ . Polymerization time for original sample: 30 min.

**Figure 3.** GPC chromatograms (UV traces) of the starting polymer and the final polymer obtained by adding the second portion of pCl $\alpha$ MeSt after 5 h monomer starvation. Reaction conditions are given in Table 1.

Upon addition of the second monomer increment a smooth polymerization takes place, apparently with the same rate as the first increment. The molecular weight distributions of the products remain constant ( $M_w/M_n = 1.2$ ), independent of the time of the second monomer addition. Interestingly, the polymer obtained by adding the second monomer increment even after 5 h exhibited a monomodal GPC chromatogram without any trace of dead polymer (see Figure 3). Thus, the chain end is very stable and much more stable than living P $\alpha$ MeSt, which starts to decompose after  $\sim 30$ – $40$  min under monomer-starved conditions; living P $\alpha$ MeSt has a half-life of  $\sim 3$  h under identical conditions.<sup>16</sup> Since intramolecular backbiting (indanyl ring formation) is the most important side reaction in the polymerization of  $\alpha$ MeSt, the exceptional stability of the PpCl $\alpha$ MeSt living end suggests a very low rate of intramolecular alkylation. In the absence of steric hindrance the reactivity (stability) of the polymer cation and the reactivity of the aromatic ring determine the rate of intramolecular alkylation. Cumyl chloride hydrolyzes 5 times faster than *p*-chloro-substituted cumyl chloride,<sup>17</sup> which indicates the lower stability of the *p*-chloro-substituted cumyl cation. The higher reactivity of the PpCl $\alpha$ MeSt<sup>+</sup> chain end, however, is most likely compensated by the lower equilibrium constant of ionization. This is suggested by a comparison of the overall polymerization rates (the polymerization  $\alpha$ MeSt is about 3 times faster than that of pCl $\alpha$ MeSt under identical conditions) and monomer reactivities (the reactivity of  $\alpha$ MeSt is estimated<sup>18</sup> to be about 3 times higher than that of pCl $\alpha$ MeSt). In other words, the lower rate of pCl $\alpha$ MeSt polymerization can be accounted for mainly by the lower monomer reactivity due to the *p*-chloro substituent. This leads us to conclude that the stability of the living PpCl $\alpha$ MeSt is

**Figure 4.** <sup>1</sup>H NMR spectrum of poly(pCl $\alpha$ MeSt) ( $M_n = 2.55 \times 10^4$ ,  $M_w/M_n = 1.23$ ).**Figure 5.** DSC thermogram of poly(pCl $\alpha$ MeSt) ( $M_n = 2.4 \times 10^4$ ). The scanning rate is 10 °C/min.

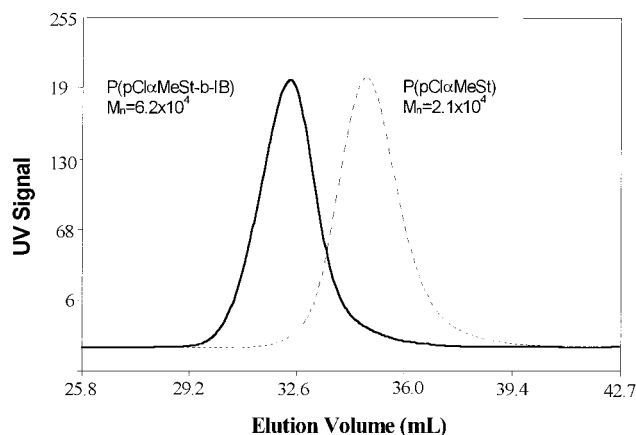
due to the much lower reactivity of the aromatic ring in intramolecular alkylation because of the *p*-chloro substituent. It is known that halogens deactivate the aromatic ring in Friedel–Crafts alkylation, but since they are ortho–para orienting, the deactivation of the meta position is much larger. For instance, the partial rate factors for nitration of chlorobenzene are 0.28 (para), 0.028 (ortho), and 0.001 (meta).<sup>19</sup> A large 65-fold difference in the alkylation rate of toluene and *p*-chloro-substituted toluene with allyldichlorosilane in the presence of AlCl<sub>3</sub> as catalyst<sup>20</sup> is also in line with our conclusion.

#### Tacticity and Thermal Behavior of PpCl $\alpha$ MeSt.

According to the <sup>1</sup>H NMR spectrum of homopoly-(pCl $\alpha$ MeSt) (Figure 4), the polymer is 94% syndiotactic. Despite this high syndiotacticity, the DSC thermogram of the precipitated polymer does not show any melting point; i.e., the polymer is completely amorphous. After crystallization from methylcyclohexane–methyl ethyl ketone solvent mixture a distinct melting point shows up at 229 °C ( $T_g = 198$  °C at 10 °C/min scanning rate) (Figure 5). Thermal gravimetric analysis revealed that above the melting point the polymer begins to decompose; therefore, the baseline drift after  $T_m$  in Figure 5 is attributed to this decomposition.

**Sequential Block Copolymerization of pCl $\alpha$ MeSt with IB.** To determine the crossover efficiency from living PpCl $\alpha$ MeSt to IB, poly(pCl $\alpha$ MeSt-*b*-IB) diblock copolymer was prepared by sequential monomer addition (see Experimental Section). Since BCl<sub>3</sub> is unable to ionize the poly(pCl $\alpha$ MeSt)-IB<sub>*n*</sub>-Cl ends (where *n* is





**Figure 6.** GPC chromatograms (UV traces) of the copolymer and the starting poly(pCl $\alpha$ MeSt). Reaction conditions: [Di $\alpha$ MeSt-HCl]<sub>0</sub> = 0.002 M, [DTBP] = 0.006 M, [BCl<sub>3</sub>] = 0.006 M, [pCl $\alpha$ MeSt]<sub>0</sub> = 0.282 M, [TiCl<sub>4</sub>] = 0.036 M, [IB]<sub>0</sub> = 1.54 M;  $M_n$ (poly(pCl $\alpha$ MeSt)) =  $2.1 \times 10^4$ ,  $M_n$ (poly{pCl $\alpha$ MeSt-*b*-IB} diblock copolymer) =  $6.2 \times 10^4$ .

presumably 1)<sup>16</sup> that form upon addition of IB to the solution of living poly(pCl $\alpha$ MeSt), addition of TiCl<sub>4</sub> is necessary to polymerize IB. Figure 6 shows the UV traces of the GPC chromatograms of the starting poly(pCl $\alpha$ MeSt) and the resulting poly(pCl $\alpha$ MeSt-*b*-IB) diblock copolymer. The UV trace of the diblock copolymer smoothly moved to lower elution volumes (higher molecular weights) without any tailing, and the experimental  $M_n$  ( $= 6.2 \times 10^4$ ) is close to the theoretical  $M_n$  ( $= 6.4 \times 10^4$ ). On the basis of these observations, we conclude that the blocking efficiency is close to 100% and that there is no detectable homopolymer contamination. This is a major improvement over the ~60% blocking efficiency obtained in the synthesis of poly( $\alpha$ MeSt-*b*-IB) diblock copolymer under essentially identical conditions.<sup>16</sup> Since the low blocking efficiency was explained by intramolecular alkylation involving the poly( $\alpha$ MeSt)-IB<sub>1</sub><sup>+</sup> cation,<sup>16</sup> we attribute the essentially quantitative blocking observed in this work with poly(pCl $\alpha$ MeSt-*b*-IB) to the reduced tendency to form indanyl ring due to deactivation of the aromatic ring.

## Conclusion

The living polymerization of pCl $\alpha$ MeSt can be achieved using the 1,3-dimethyl-1,3-diphenyl-1-chlorobutane (Di $\alpha$ MeSt-HCl)/BCl<sub>3</sub> initiating system in methylcyclohexane/methyl chloride (60/40, v/v) at -80 °C. The highly stereoregular (94% syndiotactic) polymer is semicrystalline, exhibiting a  $T_g$  at 198 °C and  $T_m$  at 229 °C. Although the extent of crystallinity is presently unknown, it is most likely low considering the small enthalpy of fusion (~2 J/g). Therefore, the synthesis of

PIB block copolymers with a highly crystalline block segment involving a simple sequential monomer addition remains a challenge. The propagating chain end of poly(pCl $\alpha$ MeSt) is exceptionally stable and in conjunction with TiCl<sub>4</sub> can efficiently initiate the sequential block copolymerization of IB. These attributes may be utilized for the efficient synthesis of triblock copolymers by coupling living diblock copolymers. This concept has recently been applied for the synthesis of a P( $\alpha$ MeSt-*b*-oligo(pCl $\alpha$ MeSt)-*b*-IB-*b*-oligo(pCl $\alpha$ MeSt)-*b*- $\alpha$ MeSt) thermoplastic elastomer reported elsewhere.<sup>21</sup>

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