

## Polyisobutylene based thermoplastic elastomers: VI. Poly( $\alpha$ -methylstyrene-*b*-isobutylene-*b*- $\alpha$ -methylstyrene) triblock copolymers by coupling of living poly ( $\alpha$ -methylstyrene-*b*-isobutylene) diblock copolymers

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### Summary

Poly( $\alpha$ -methylstyrene-*b*-isobutylene-*b*- $\alpha$ -methylstyrene) (P $\alpha$ MeSt-PIB-P $\alpha$ MePSt) triblock copolymers have been prepared via coupling of living diblock copolymers in a one pot procedure. The P $\alpha$ MeSt-PIB diblock copolymers were synthesized by living sequential cationic polymerization in methylcyclohexane (MeChx)/methylchloride (MeCl) solvent mixtures at -80 °C using BCl<sub>3</sub> for  $\alpha$ MeSt polymerization and TiCl<sub>4</sub> for IB polymerization as coiniciators. The crossover efficiency, however, was only ~57 %, due to intermolecular alkylation (indanyl ring formation) after the addition of TiCl<sub>4</sub>. By modifying the P $\alpha$ MeSt end with a short segment of *p*-chloro- $\alpha$ -methylstyrene before IB addition the crossover efficiency was increased to 90 %. Coupling of the living block copolymers with 2,2-bis[4-(1-phenylethenyl)phenyl]propane (BDPEP) was rapid and gave ~90 % efficiency.

### Introduction

Polyisobutylene (PIB) based thermoplastic elastomers (TPEs) are normally ABA type linear or star-block copolymers where the middle segment (B) is rubbery PIB flanked by hard plastic end segments (A). Since PIB possesses excellent oxidative, chemical and thermal stability due to its saturated chain structure, synthesis of PIB based TPEs has long been desired. (1) Following the discovery of living cationic polymerization of isobutylene (IB), (2) PIB based TPEs with various plastic end-segments, such as styrene, (3,4)  $\alpha$ -methylstyrene ( $\alpha$ MeSt), (5,6) *p*-methylstyrene (*p*MeSt), (7) *p*-chlorostyrene, (8) *p*-*tert*-butylstyrene, (9) indene (10) were successfully synthesized by living cationic sequential block copolymerization. The crossover from the living PIB ends to *p*MeSt or  $\alpha$ MeSt is slow relative to propagation of the styrenic monomer, however, and products (a mixture of triblock and diblock copolymer) obtained by a simple sequential block copolymerization exhibited low tensile strength. The slow crossover was circumvented by an intermediate capping of the living PIB with 1,1-diphenylethylene (DPE) followed by moderating the Lewis acidity before the addition

of  $\alpha$ MeSt for the synthesis of PpMeSt-PIB-PpMeSt (7) and P $\alpha$ MeSt-PIB-P $\alpha$ MeSt (6)

ABA type triblock copolymers can also be prepared by coupling of living diblock copolymers. This is a general method in living anionic polymerization and equally applicable in cationic polymerization. We have recently developed bis-DPE and bis-furanyl compounds that are efficient coupling agents for the living coupling reaction of living PIB (12,13). The coupling reactions are rapid and quantitative independently of the molecular weight of PIB. The coupling reaction of living PIB by bis-DPE compounds is a consecutive reaction where the second addition is much faster than the first one. As a result, high coupling efficiency was also observed when excess BDPEP was used. This coupling agent is therefore the best suited for the synthesis of triblock copolymers by coupling of living diblock copolymers. We recently reported the synthesis of PSt-PIB-PSt triblock copolymers by coupling of living PSt-PIB diblock copolymers with BDPEP. Due to decomposition of the living PSt ends at close to complete St conversion, IB must be added at ~95% St conversion to obtain living PSt-PIB diblocks with negligible homoPSt contamination. The residual unreacted St, however, gives rise to a relatively high concentration of unreactive -St-IB-Cl chain ends, which causes coupling to be slow and incomplete. Due to diblock contaminants in the product the mechanical properties were satisfactory but inferior to the best triblocks made by difunctional initiation and two-step sequential monomer addition. Consequently, the latter technique is more suitable for the synthesis of PSt-PIB-PSt. However coupling should be the method of choice for the preparation of P $\alpha$ MeSt-PIB-P $\alpha$ MeSt triblock copolymer, since crossover from living PIB to  $\alpha$ MeSt is unfavorable. In this publication we report on the synthesis of P $\alpha$ MeSt-PIB-P $\alpha$ MeSt by coupling of living P $\alpha$ MeSt-PIB.

## Experimental

### *Materials*

1,3-Dimethyl-1,3-diphenyl-1-chloro-butane (Di $\alpha$ MeSt-HCl) was synthesized by the hydrochlorination of 2,4-diphenyl-4-methyl-1-pentene (olefinic  $\alpha$ MeSt dimer, Aldrich, 99 %) as described before. (11) BDPEP was synthesized according to Reference. (13) P-Chloro- $\alpha$ -methylstyrene (pCl $\alpha$ MeSt) and  $\alpha$ -MeSt were mixed with a small amount of dibutylmagnesium (1.0 M heptane solution) and distilled in vacuum before use. All other chemicals and solvents were purified as described previously (4) or used as received.

### *Polymerization*

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

For the synthesis of P $\alpha$ MeSt-PIB diblock copolymer,  $\alpha$ MeSt (0.35 M) was polymerized by Di $\alpha$ MeSt-HCl (0.002 M) and BCl<sub>3</sub> (0.006 M) system in the presence of DTBP (0.0035 M) in MeChx/MeCl at -80 °C for 4 min, then [IB] = 1.85 or 1.54 M

was added to react with  $P\alpha\text{MeSt}$  cation for 20 min, then  $\text{TiCl}_4$  (0.036 M) was added last to polymerize IB for 120 min.

For the preparation of  $P\alpha\text{MeSt-PIB-P}\alpha\text{MeSt}$  triblock copolymer, BDPEP ( $[\text{BDPEP}]/[P\alpha\text{MeSt-PIB}] = 0.5$ ) in MeChx/MeCl at  $-80\text{ }^\circ\text{C}$  was added to the solution of the living diblock copolymer. Samples were taken before and during coupling to measure coupling efficiency. The polymerizations were terminated by adding prechilled methanol. In order to accurately determine coupling efficiency ( $CP_{\text{eff}}$ ), the diblock copolymer as well as the products obtained after coupling were purified by dissolution/precipitation in dichloromethane/acetone to remove homo $P\alpha\text{MeSt}$ .

For the synthesis of  $P\alpha\text{MeSt-oligo}(p\text{Cl}\alpha\text{MeSt})\text{-PIB}$ ,  $\alpha\text{MeSt}$  was polymerized first and after 4 min polymerization different amounts of  $p\text{Cl}\alpha\text{MeSt}$  were added, and polymerized for 15 minutes. Then IB was introduced, and after 5 minutes  $\text{TiCl}_4$  was added.

### *Characterization*

Molecular weights were measured using a Waters HPLC system equipped with Model 510 HPLC pump, Model 410 differential refractometer, Model 486 UV/Vis detector, Model 712 sample processor, and five ultra-Styrigel GPC columns connected in the following series: 500,  $10^3$ ,  $10^4$ ,  $10^5$ , and  $100^\circ\text{A}$ . THF was used at room temperature as eluent at a flow rate of 1.0 mL/min. Determination of the molecular weights and polydispersities was carried out by the universal calibration curve and Viscotek TriSEC GPC software. The crossover efficiency ( $C_{\text{eff}}$ ) was calculated from the area of UV traces determined by PeakFit software (Jandel Scientific, fitting function: Chromatography/EVAL4 Area Tailed). Absolute molecular weights of representative samples were also measured using a Minidawn (Wyatt Technologies Inc.) GPC on-line multiangle laser light-scattering (MALLS) detector.

$^1\text{H}$  NMR spectroscopy was carried out on a Bruker 250 MHz instrument.

## **Results and Discussion**

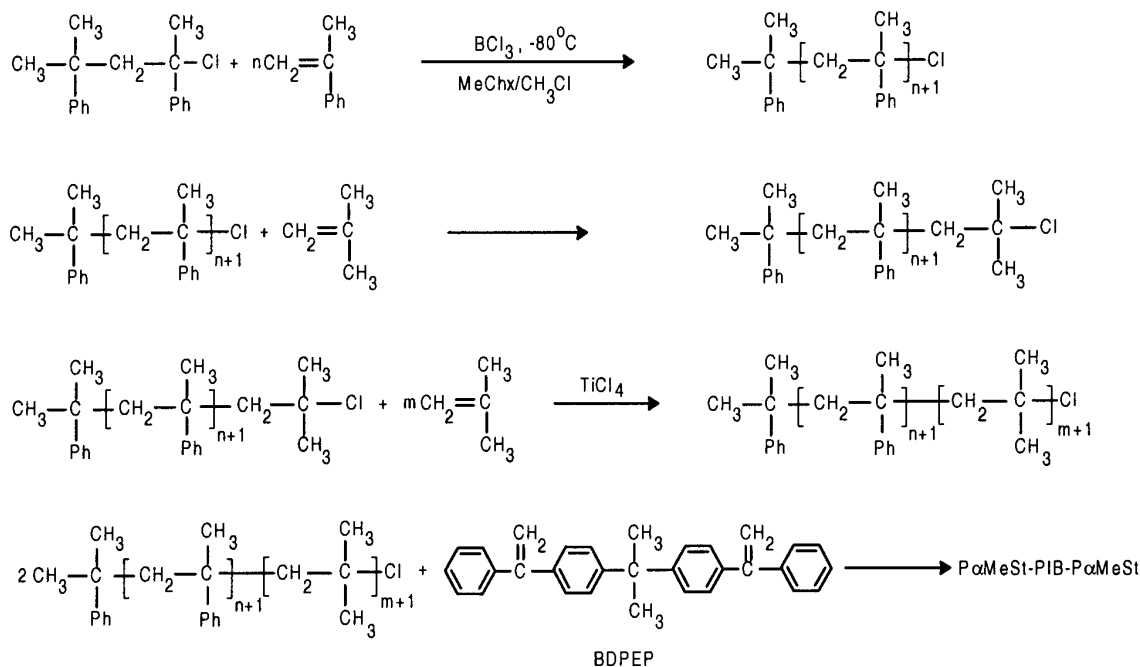
### *Crossover efficiency from living $P\alpha\text{MeSt}$ to IB*

We recently reported the synthesis of  $P\alpha\text{MeSt-PIB}$  diblock copolymers via sequential monomer addition, using  $\text{Di}\alpha\text{MeSt-HCl}$  as initiator in the presence of 2,6-di-*tert*-butylpyridine (DTBP) in MeChx/MeCl (60/40 v/v) at  $-80\text{ }^\circ\text{C}$ . In the first step of the synthesis employing  $\text{BCl}_3$  as coinitiator, well-defined  $P\alpha\text{MeSt}$  with controlled molecular weight and narrow molecular weight distribution ( $M_w/M_n \sim 1.1$ ) was obtained. Chain end decomposition was not detected for up to 30 min. under monomer starved condition. Model reactions with  $\text{Di}\alpha\text{MeSt-HCl}$  indicated that upon addition of IB, quantitative crossover takes place followed by immediate termination and the selective formation of  $P\alpha\text{MeSt-IB}_1\text{-Cl}$ . Therefore the addition of  $\text{TiCl}_4$  was necessary to polymerize IB. In this study the same synthetic scheme was used to prepare living  $P\alpha\text{MeSt-PIB}$  followed by coupling to obtain  $P\alpha\text{MeSt-PIB-P}\alpha\text{MeSt}$  (Scheme 1). The  $M_n$  of PIB block was planned to be  $\sim 50,000$ , and that of  $P\alpha\text{MeSt}$  block was chosen to be  $\sim 20,000$  to obtain well-defined micro-domains. (6) The GPC

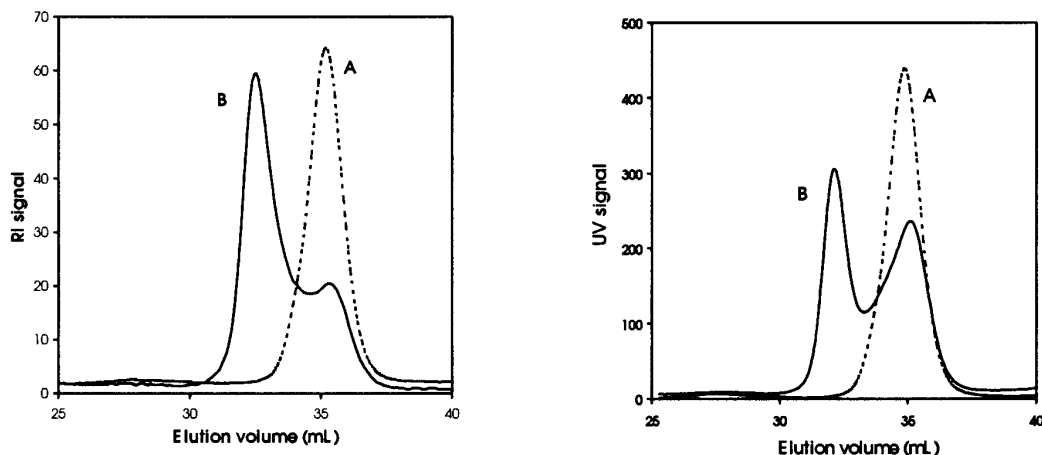
RI and UV traces of the precursor homo-P $\alpha$ MeSt (A) and the P $\alpha$ MeSt-PIB diblock product (B) are shown in Figure 1. Both RI and UV traces are bimodal. The peak at higher elution volume is identified as homo-P $\alpha$ MeSt because its position is identical to trace "A". In order to determine the crossover efficiency ( $C_{\text{eff}}$ ), the GPC UV traces were used. Since PIB is transparent in the UV region, the crossover efficiency can be calculated according to equation 1.

$$C_{\text{eff}} \% = A_{\text{P}\alpha\text{MeSt-PIB}} / (A_{\text{P}\alpha\text{MeSt-PIB}} + A_{\text{P}\alpha\text{MeSt}}) \quad (1)$$

In Eq. 1  $A_{\text{P}\alpha\text{MeSt-PIB}}$  is the area of the UV trace of P $\alpha$ MeSt-PIB diblock copolymer and  $A_{\text{P}\alpha\text{MeSt}}$  is the area of the UV trace of homo-P $\alpha$ MeSt.



**Scheme 1** Synthesis of P $\alpha$ MeSt-PIB-P $\alpha$ MeSt triblock copolymer



**Figure 1.** GPC RI and UV traces of original P $\alpha$ MeSt (A) and P $\alpha$ MeSt-PIB diblock copolymer (B) obtained in MeChx/MeCl 60/40 v/v at -80 °C. [Di $\alpha$ MeSt·HCl] = 0.002 M, [ $\alpha$ MeSt] = 0.35 M, [BCl<sub>3</sub>] = 0.006 M, [DTBP] = 0.0035 M, [TiCl<sub>4</sub>] = 0.036 M, [IB] = 1.85 M.

From the UV trace in Figure 1  $C_{\text{eff}}$  was calculated to be ~57 %. This low  $C_{\text{eff}}$  is attributed to intermolecular alkylation (indanyl ring formation) after the addition of TiCl<sub>4</sub>. (14) It was shown earlier (14) that  $C_{\text{eff}}$  is linearly dependent of [IB], and thus  $C_{\text{eff}} = 70\%$  was achieved by increasing the concentration of IB to [IB] = 2.85M. Increasing IB concentration, however, is not preferred in the triblock synthesis due to the very high viscosity during coupling.

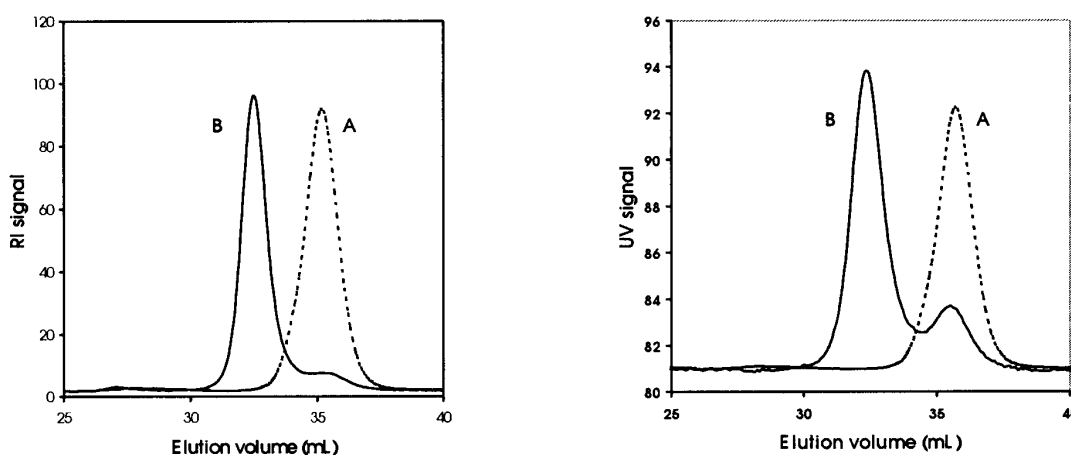
#### *Synthesis of P $\alpha$ MeSt - oligo(pCl $\alpha$ MeSt) - PIB*

Very recently we reported the living homopolymerization and sequential block copolymerization of pCl $\alpha$ MeSt with IB under conditions identical to that used for the synthesis of P $\alpha$ MeSt-PIB above. (15) Importantly we found that the living PpCl $\alpha$ MeSt chain end has very high stability, much higher than that of living P $\alpha$ MeSt, which starts to decompose after ~30-40 min under monomer starved conditions and has a half-life of ~3h under identical conditions. This was attributed to the lower tendency of intramolecular back-biting and hydride transfer due to the p-chloro substituent. It was also reported that sequential block copolymerization with IB yields PpCl $\alpha$ MeSt-PIB free of homopolymer contamination. Thus it occurred to us that homo-P $\alpha$ MeSt contamination might be avoided if the block copolymerization was carried out by adding pCl $\alpha$ MeSt to living P $\alpha$ MeSt before the addition of IB. Thus, in the next series of experiments after 4 min polymerization of  $\alpha$ MeSt, different amounts of pCl $\alpha$ MeSt were added and polymerized for 15 minutes. Then IB was introduced and after 5 minutes TiCl<sub>4</sub> was added. The crossover efficiencies for experiments where the concentration of pCl $\alpha$ MeSt was varied from 0.004M to 0.02M ([pCl $\alpha$ MeSt]/[chain end] = 2-10) are listed in Table 1. By increasing the concentration of pCl $\alpha$ MeSt the crossover efficiency increases from 57 % to 88 %. At [pCl $\alpha$ MeSt]/[chain end] = 2 the distribution of pCl $\alpha$ MeSt among P $\alpha$ MeSt chain ends is apparently not uniform, i.e., there are P $\alpha$ MeSt chains without any pCl $\alpha$ MeSt (and consequently some contain more than 2 pCl $\alpha$ MeSt molecules per chain), and the crossover efficiency is only ~70%. By increasing the [pCl $\alpha$ MeSt]/[chain end] ratio to 7-10, most polymers must contain at least one molecule of pCl $\alpha$ MeSt at the chain end since the crossover efficiency increased to ~90% (Figure 2)

Table 1. Effect of pCl $\alpha$ MeSt concentration on the crossover efficiency

[pCl $\alpha$ MeSt], (M)	$C_{\text{eff}}$ (%)
-	57
0.004	70
0.008	82
0.014	88
0.020	88

Reaction conditions: [Di $\alpha$ MeSt-HCl]<sub>0</sub> = 0.002 M, [DTBP] = 0.006 M, [BCl<sub>3</sub>] = 0.006 M, [ $\alpha$ MeSt]<sub>0</sub> = 0.35 M, [TiCl<sub>4</sub>] = 0.036 M, [IB]<sub>0</sub> = 1.54 M



**Figure 2.** GPC RI and UV traces of original P $\alpha$ MeSt (A) and P $\alpha$ MeSt-oligo(pCl $\alpha$ MeSt)-PIB copolymer (B) obtained in MeChx/MeCl 60/40 v/v at  $-80$  °C. [Di $\alpha$ MeSt-HCl] = 0.002 M, [ $\alpha$ MeSt] = 0.35 M, [BCl<sub>3</sub>] = 0.006 M, [DTBP] = 0.0035 M, [pCl $\alpha$ MeSt] = 0.014 M, [TiCl<sub>4</sub>] = 0.036 M, [IB] = 1.85 M.

*The coupling reaction of living P $\alpha$ MeSt-PIB and P $\alpha$ MeSt - oligo(pCl $\alpha$ MeSt) - PIB copolymers*

Figure 3 shows the GPC RI traces of starting P $\alpha$ MeSt (A), the P $\alpha$ MeSt-PIB diblock copolymer (B) and the coupled product (C). The trace of the diblock copolymer is bimodal indicating that the crossover efficiency is less than 100%. Upon coupling the position and relative area of the lower molecular weight peak corresponding to dead P $\alpha$ MeSt is unchanged. From the purified, homoP $\alpha$ MeSt free samples, the  $M_n$ s of the products were measured and the coupling efficiency ( $CP_{\text{eff}}$ ) was calculated from the total number average molecular weight ( $M_{\text{nt}}$ ) of the product according to the equations shown below.

$$CP_{\text{eff}} = 100(1-a) \quad (2)$$

In Eq. (2)  $a$  is the mole fraction of uncoupled diblock, and  $1-a$  is the mole fraction of coupled diblock.  $M_{\text{nt}}$  can be obtained from the molecular weight of uncoupled PSt-PIB ( $M_{\text{nt}}$ ) from Eq. (3) and  $CP_{\text{eff}}$  can be calculated from Eq.(4).

$$M_{nt} = 2M_{nu}/(1 + a) \quad (3)$$

$$CP_{eff} = 2(M_{nt} - M_{nu}) \times 100 / M_{nt} \quad (4)$$

As expected, coupling is rapid as ~90%  $CP_{eff}$  is reached in 3h (Table 2). Thus the coupling reaction of living P $\alpha$ MeSt-PIB is as fast as that of homoPIB.

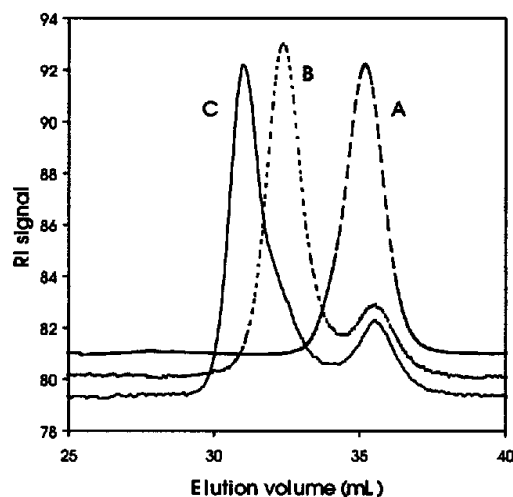
Figure 3 and 4 shows the GPC RI traces of the original P $\alpha$ MeSt, P $\alpha$ MeSt-PIB (Fig. 3) and P $\alpha$ MeSt-oligo(*p*Cl $\alpha$ MeSt)-PIB block copolymer (Fig. 4) and the coupled products. As shown by Figure 4, by using *p*Cl $\alpha$ MeSt to modify the P $\alpha$ MeSt end  $C_{eff}$  ~ 90% is achieved, and coupling is nearly quantitative.

Table 2. The effect of coupling reaction time on  $CP_{eff}$

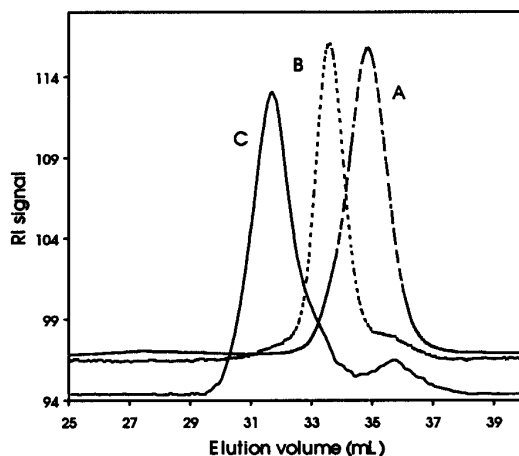
MeChx/MeCl v/v *	Coupling reaction time (hr)	$M_n$ diblock	$M_n$ coupled	$CP_{eff}$ (%)
56/44	1	70,900	110,800	72.0
56/44	2	70,900	115,800	77.5
56/44	3	70,900	115,000	76.7
56/44	4	64,200	115,000	80.9
40/60	3	68,400	120,000	86.0
40/60	6	68,400	112,000	77.9
40/60	18	68,400	108,000	73.3

[Di $\alpha$ MeSt:HCl] = 0.004 M, [BCl<sub>3</sub>] = 0.006 M, [DTBP] = 0.007 M, [ $\alpha$ MeSt] = 0.70 M MeChx/MeCl

60/40 v/v 10 mL.  $\alpha$ MeSt was polymerized for 2 min in MeChx/MeCl 60/40 v/v at -80°C, then IB (3.0 M) was added to react with P $\alpha$ MeSt active center for 20 min, and then TiCl<sub>4</sub> ([TiCl<sub>4</sub>] = 0.036 M) was added to polymerize IB for different time. The reaction system was diluted with MeChx/MeCl (total volume of reaction system: 20 mL) before the addition of coupling agent ([BDPEP]/[P( $\alpha$ MeSt-*b*-IB)] = 0.525). \* solvent composition during coupling reaction.



**Figure 3.** GPC RI traces of original P $\alpha$ MeSt (A) P $\alpha$ MeSt–PIB block copolymer (B) and the coupled product (C). The experimental conditions for the synthesis of P $\alpha$ MeSt–PIB diblock copolymer are shown in Table 2. [BDPEP]/[Di $\alpha$ MeSt·HCl] = 0.5/1



**Figure 4.** GPC traces of original P $\alpha$ MeSt (A) P $\alpha$ MeSt–oligo(pCl $\alpha$ MeSt)-PIB block copolymer (B) and the coupled product (C). [BDPEP]/[Di $\alpha$ MeSt·HCl] = 0.5/1.

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