Living Carbocationic Sequential Block Copolymerization of Isobutylene with α-Methylstyrene

Dawei Li and Rudolf Faust*

College of Arts and Sciences, University of Massachusetts, Lowell, One University Avenue, Lowell, Massachusetts 01854

Received August 2, 1994; Revised Manuscript Received November 7, 1994®

ABSTRACT: The polymerization of α-methylstyrene (αMeSt) was investigated using the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$/methyl chloride:hexane (40:60, v:v)/−80 °C system as a model to determine the efficiency of crossover from living polyisobutylene (PIB) to αMeSt. Low initiator efficiencies and broad molecular weight distributions were obtained. Living polymerization of αMeSt was achieved by first converting TMPCl to the corresponding diphenylalkylcarbenium ion by capping with 1,1-diphenylethylene (DPE), followed by the addition of titanium(IV) alkoxide to decrease the Lewis acidity. The initiator efficiencies, however, were lower than 100%. Living polymerization with ~100% initiator efficiency was achieved by $SnBr_4$ as coinitiator. First, TMPCl is transformed to the corresponding diphenylalkylcarbenium ion by capping with 1,1-diphenylethylene. Subsequently, titanium(IV) isopropoxide is introduced to deactivate $TiCl_4$, followed by the addition $SnBr_4$ and αMeSt. The success of the method was demonstrated by the synthesis of PIB–poly(α-methylstyrene) diblock copolymers without homopolymer contaminants.

Introduction

With the discovery of the living cationic polymerization of isobutylene[1] and styrenic monomers such as styrene,[2,3] *p*-chlorostyrene,[4] *p*-methylstyrene,[5,6] *p-tert*-butylstyrene,[7] and indene,[8] the synthesis of a new series of block copolymers with well-defined architecture, controlled molecular weights, and molecular weight distributions became possible. Triblock copolymers with rubbery middle segments and plastic outer segments have gained considerable interest as thermoplastic elastomers (TPEs).[3–5,8]

For the synthesis of pure block copolymers by living sequential block copolymerization, 100% crossover efficiency is required. 100% crossover efficiency may be obtained when the reactivities of the two monomers are similar; however, it is difficult to achieve when the crossover is from the less reactive to the more reactive monomer. Thus, polystyrene–polyisobutylene–polystyrene (PSt–PIB–PSt) with excellent mechanical properties was obtained using sequential monomer addition;[9] however, the crossover efficiency was found to be low from the PIB living end to *p*-methylstyrene (pMeSt)[5] and even lower to αMeSt[10] or isobutyl vinyl ether (IBVE).[11] Attempts to increase the crossover efficiency by adding Lewis bases or common ion salts have failed.[10,11]

We invented a novel strategy for the synthesis of block copolymers by sequential monomer addition when the second monomer is very reactive. The strategy was used for the synthesis of PIB–poly(*p*-methylstyrene) (PpMeSt) diblock or PpMeSt–PIB–PpMeSt triblock copolymers. The synthesis involved the living polymerization of isobutylene (IB) by the $TiCl_4$/methyl chloride:hexanes (40:60, v:v)/−80 °C system in the presence of the proton trap, di-*tert*-butylpyridine (DTBP). The living PIB chain end was converted to the corresponding diphenylalkyl end by capping with 1,1-diphenylethylene (DPE). Subsequently, titanium(IV) isopropoxide was added to decrease the Lewis acidity, and last pMeSt was introduced. The success of the method was demonstrated by pMeSt homopolymerization experiments with the TMPCl/$TiCl_4$/DPE/$Ti(OR)_4$ initiating system resulting in ~100% initiator efficiencies (I_{eff}s), ~100% crossover efficiencies in PIB–PpMeSt diblock copolymer synthesis,[12] and by the excellent mechanical properties of the PpMeSt–PIB–PpMeSt triblock copolymers synthesized according to our novel strategy.[13] The best triblocks exhibited ~22 MPa tensile strength, much higher than reported before[5] and close to what we have achieved with PSt–PIB–PSt TPE.[14]

A limitation of PSt- and PpMeSt-based TPEs is their low softening point. Since the T_g of PαMeSt is ~175 °C, PαMeSt-based TPEs are expected to have superior properties at elevated temperatures. Thus, we have embarked on the synthesis of PαMeSt–PIB–PαMeSt TPE. To determine the best synthetic method, we decided to study first the living homopolymerization of αMeSt using TMPCl as initiator and the sequential diblock copolymerization of IB with αMeSt.

Experimental Section

Materials. α-Methylstyrene (Aldrich) was purified according to the procedure described for St[14] and pMeSt.[12] Titanium ethoxide (Aldrich) was purified by vacuum distillation. Titanium tetrachloride (Aldrich) and tin tetrabromide (1 M in CH_2Cl_2; Aldrich) were used as received. All other materials have been described.[12]

Polymerization. αMeSt homopolymerization experiments were carried out in 75-mL test tubes. $TiCl_4$ solution (1:3, v:v) in hexanes (Hex) was added to a Hex/methyl chloride (MeCl) (60:40, v:v) mixture containing TMPCl initiator and DTBP precooled to −80 °C, followed by the addition of DPE. When capping was complete,[12] $Ti(OR)_4$ was added and reacted with $TiCl_4$ for 15 min to decrease the Lewis acidity. αMeSt in Hex/MeCl (60:40, v:v) was added last. At predetermined time intervals the polymerizations were terminated by adding prechilled methanol. The polymers were purified by dissolution–precipitation in dichloromethane/methanol and dried in vacuum prior to GPC measurements.

Diblock copolymerizations were carried out in 250-mL three-neck round-bottomed flasks equipped with an overhead stirrer. IB was polymerized by the TMPCl/$TiCl_4$/DTBP/Hex:MeCl (60:40, v:v)/−80 °C system. When the conversion of IB was ~100%, DPE was added. After completion of DPE capping, $Ti(OR)_4$ was introduced to deactivate $TiCl_4$ followed by the

* To whom correspondence should be addressed.

® Abstract published in *Advance ACS Abstracts,* February 1, 1995.

0024-9297/95/2228-1383$09.00/0

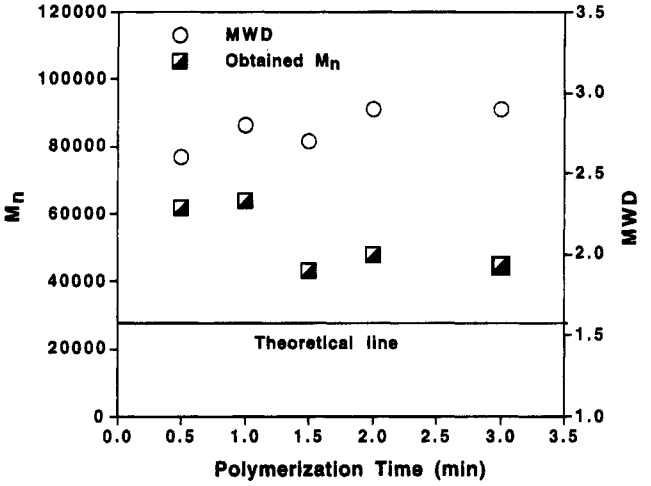


Figure 1. Molecular weights and molecular weight distributions vs polymerization time in the homopolymerization of αMeSt with the TMPCl/$TiCl_4$/DTBP system at −80 °C. $[M]_0$ = 0.35 M, [TMPCl] = 0.002 M, [DTBP] = 0.004 M, solvent, MeCl/Hex (40:60, v:v).

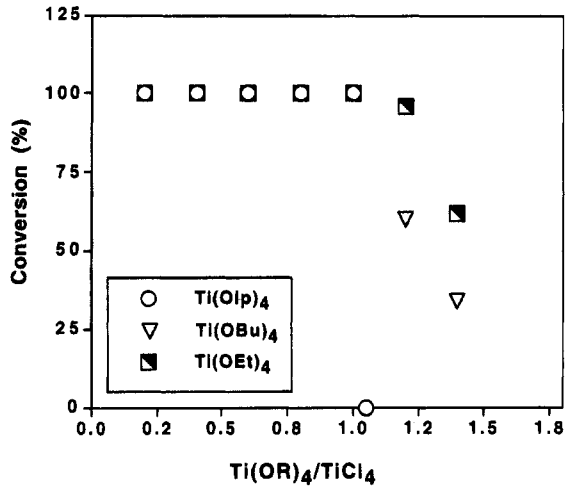


Figure 2. Conversion vs $Ti(OR)_4/TiCl_4$ in the homopolymerization of αMeSt with the TMPCl/$TiCl_4$/DPE/$Ti(OR)_4$ initiating system at −80 °C. Polymerization time = 30 min. $[M]_0$ = 0.35 M, [TMPCl] = 0.002 M, [DTBP] = 0.004 M, solvent, MeCl/Hex (40:60, v:v). (A circle in a box symbol indicates overlap of the three different symbols.)

addition of $SnBr_4$ and αMeSt. At predetermined polymerization times, samples were withdrawn by a prechilled pipet for molecular weight and conversion measurements.

In the copolymerization of DPE with αMeSt 0.3 g of DPE was added to the TMPCl/$TiCl_4$/Hex:MeCl (60:40, v:v)/−80 °C system. After 1 h, $Ti(OIp)_4$ was added to deactivate $TiCl_4$ ($Ti(OIp)_4/TiCl_4$ = 1.1). After an additional 15 min, $SnBr_4$ was added to regenerate the cations ([$SnBr_4$] = 0.09 M). Finally, 0.5 g of αMeSt was introduced. The solution mixture turned purple immediately after the addition of DPE. The solution became colorless after the addition of $Ti(OIp)_4$, and it turned orange after the addition of $SnBr_4$. The polymerization was quenched with MeOH after 3 h. According to ^1H NMR spectroscopy, the polymer (a white powder, M_n = 12 000, M_w/M_n = 1.05) contains the two monomers in close to equimolar amount (αMeSt/DPE = 1.1).

Extraction. Extraction studies were carried out using a Soxhlet extractor and methyl ethyl ketone (MEK) and *n*-pentane as solvents for 48 h each. The composition of the extracted products was determined by ^1H-NMR spectroscopy and GPC.

Characterization. Molecular weights were measured using a Waters HPLC system equipped with a Model 510 HPLC pump, Model 410 differential refractometer, Model 486 tunable UV/vis detector, on-line multiangle laser light scattering detector (MiniDawn, Wyatt Technology Inc.), Model 712 sample processor, and five Ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. The flow rate of THF was 1.0 mL/min. For data acquisition (RI and UV) and computing using a calibration curve obtained by well-characterized narrow MWD (<1.1) PIB (made by living polymerization) and PαMeSt samples (Polysciences Inc.), a Waters Baseline chromatography workstation was used. The detector signals (RI, UV, and LS) were simultaneously recorded on a MacIntosh computer for absolute molecular weight and molecular weight distribution determination by the laser light scattering detector using the ASTRette software. Refractive index increments (dn/dc) were measured by a laser interferometer (Optilab, Wyatt Technology Inc.).

NMR measurements were carried out by a Bruker 270-MHz instrument.

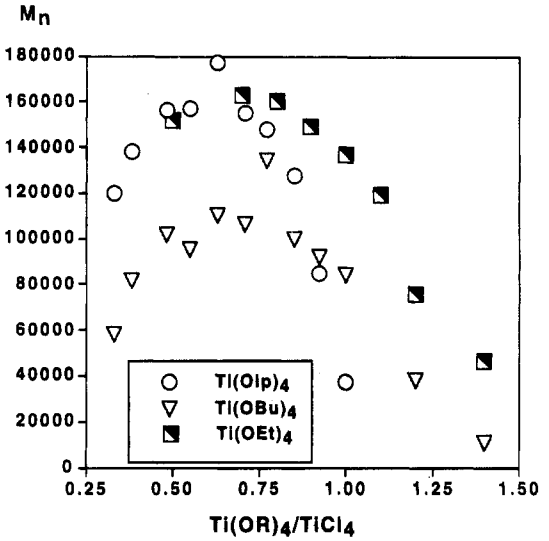


Figure 3. M_ns vs $Ti(OR)_4/TiCl_4$ in the hompolymerization of αMeSt with the TMPCl/$TiCl_4$/DPE/$Ti(OR)_4$ initiating system at −80 °C. Polymerization time = 30 min, $[M]_0$ = 0.35 M, [TMPCl] = 0.002 M, [DTBP] = 0.004 M, solvent, MeCl/Hex (40:60, v:v).

Results and Discussion

Homopolymerization of αMeSt. 1. TMPCl/$TiCl_4$ Initiating System. Recently the living polymerization of αMeSt was claimed with the TMPCl/$TiCl_4$/Et_3N/Hex:MeCl(60:40, v:v)/−80 °C system.[10] However, the initiator efficiencies (I_{eff}s) were found to be much lower (~40%) than 100%. Equally low crossover efficiencies (26−40%) were obtained in the PIB−PαMeSt diblock copolymer synthesis by sequential monomer addition. Low initiator efficiency (~40%) was also found in our research with the TMPCl/$TiCl_4$/DTBP/Hex:MeCl(60:40, v:v)/−80 °C system. High polymerization rates and much higher than theoretical M_ns were obtained (Figure 1). Similar to the findings of Tsunogae and Kennedy,[10] intramolecular alkylation was also observed.

2. TMPCl/$TiCl_4$/DPE/$Ti(OR)_4$ Initiating System. αMeSt homopolymerization experiments were carried out using DPE-capped TMPCl. Since the structure of TMPCl mimics the chain end of PIB, the initiator efficiency that can be easily measured was used to predict crossover efficiency. Experimentation started using the conditions found successful with pMeSt;[12] i.e., after capping the Lewis acidity was decreased by the addition of $Ti(OR)_4$ giving rise to $TiCl_n(OR)_{4-n}$ determined by the stoichiometry. Titanium tetraisoproxide ($Ti(OIp)_4$), titanium tetrabutoxide ($Ti(OBu)_4$), and titanium tetraethoxide ($Ti(OEt)_4$) were investigated.

At $Ti(OR)_4/TiCl_4$ < 1 100% conversions were obtained in 30 min with all three $Ti(OR)_4$ (Figure 2). There was

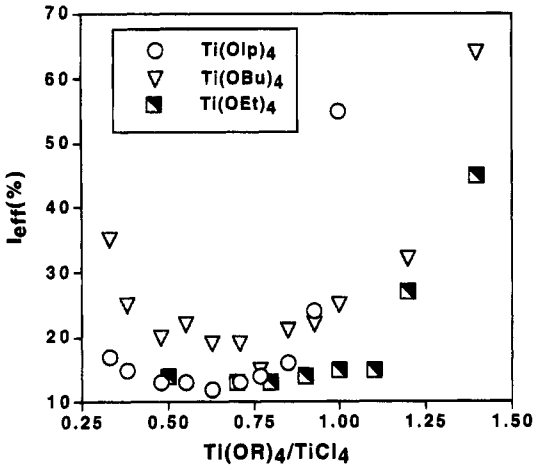


Figure 4. I_{eff} vs $Ti(OR)_4/TiCl_4$ ratio in the homopolymerization of αMeSt with the TMPCl/$TiCl_4$/DPE/$Ti(OR)_4$ initiating system at −80 °C. Polymerization time = 30 min, $[M]_0$ = 0.35 M, [TMPCl] = 0.002 M, [DTBP] = 0.004 M, solvent, MeCl/Hex (40:60, v:v).

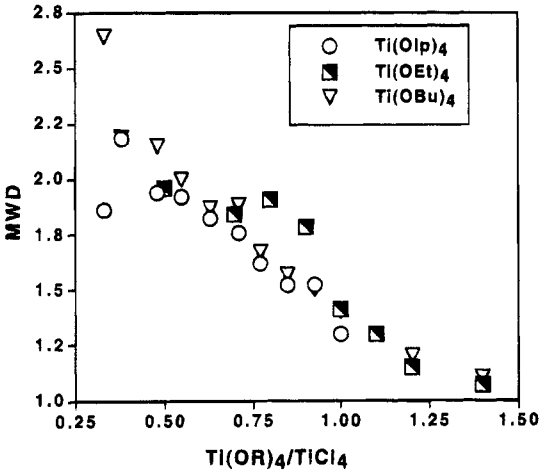


Figure 5. MWD vs $Ti(OR)_4/TiCl_4$ in the homopolymerization of αMeSt with the TMPCl/$TiCl_4$/DPE/$Ti(OR)_4$ initiating system at −80 °C. Polymerization time = 30 min, $[M]_0$ = 0.35 M, [TMPCl] = 0.002 M, [DTBP] = 0.004 M, solvent, MeCl/Hex (40:60, v:v).

a precipitous drop in conversion at $Ti(OR)_4/TiCl_4 > 1$. With the 1.1 $Ti(OR)_4/TiCl_4$ ratio ~90% and ~60% conversions were obtained in 30 min with R = Et and R = Bu, respectively. The polymerization was absent with $[Ti(OIp)_4]/[TiCl_4] = 1.1$. These results are in line with the expected Lewis acidity of the $TiCl_n(OR)_{4-n}$ compounds arising from the reaction of $TiCl_4$ and $Ti(OR)_4$ (based on the inductive effects of the alkoxide groups decreasing in the same order). The molecular weights and the initiator efficiencies are plotted against the $Ti(OR)_4/TiCl_4$ ratio in Figures 3 and 4. The M_ns vs $Ti(OR)_4/TiCl_4$ plot goes through a maximum. The maximum I_{eff} was 55% with $Ti(OIp)_4$ (at 100% conversion), 65% with $Ti(OBu)_4$ (at 35% conversion), and 45% with $Ti(OEt)_4$ (at 60% conversion) within the studied range of $Ti(OR)_4/TiCl_4$. The MWDs decreased continuously with increasing $Ti(OR)_4/TiCl_4$ ratio, and at $Ti(OR)_4/TiCl_4 = 1.3$ $M_w/M_n = 1.1$ was obtained (Figure 5).

Figure 4 suggests that higher I_{eff}s could be achieved with $Ti(OBu)_4$ or $Ti(OEt)_4$ by further increasing the $Ti(OR)_4/TiCl_4$ ratio. Therefore, additional experiments were carried out with $Ti(OBu)_4$ and $Ti(OEt)_4$. According to the conversion−polymerization time plot, at 1.4 and

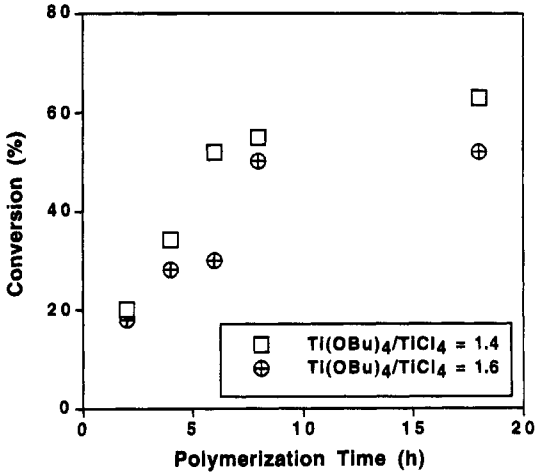


Figure 6. Conversion vs polymerization time in the homopolymerization of αMeSt with the TMPCl/$TiCl_4$/DPE/$Ti(OBu)_4$ initiating system at −80 °C. $[M]_0$ = 0.35 M, [TMPCl] = 0.002 M, [DTBP] = 0.004 M, solvent, MeCl/Hex (40:60, v:v).

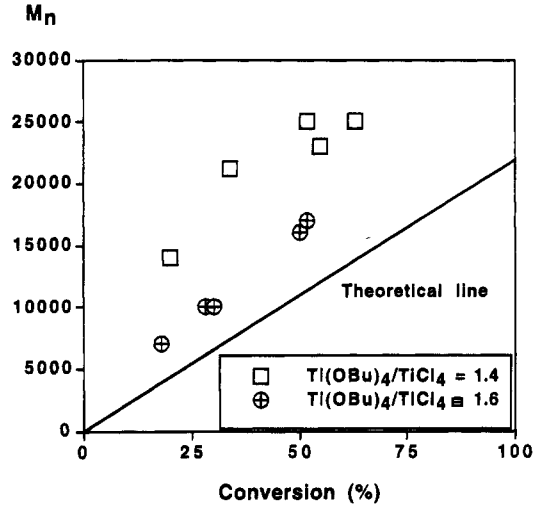


Figure 7. M_n vs conversion in the homopolymerization of αMeSt with the TMPCl/$TiCl_4$/DPE/$Ti(OBu)_4$ initiating system at −80 °C. $[M]_0$ = 0.35 M, [TMPCl] = 0.002 M, [DTBP] = 0.004 M, solvent, MeCl/Hex (40:60, v:v).

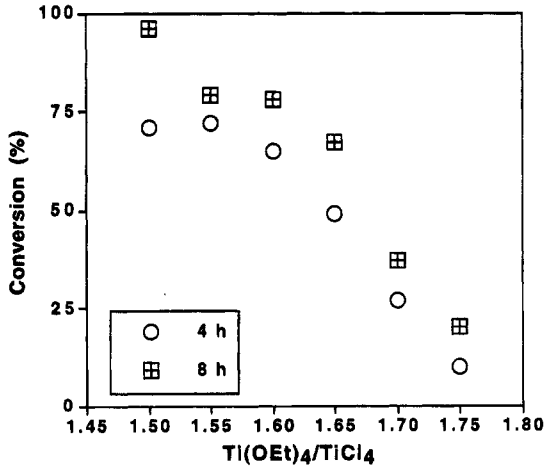


Figure 8. Conversion vs $Ti(OEt)_4/TiCl_4$ in the homopolymerization of αMeSt with the TMPCl/$TiCl_4$/DPE/$Ti(OEt)_4$ initiating system at −80 °C. $[M]_0$ = 0.35 M, [TMPCl] = 0.002 M, [DTBP] = 0.004 M, solvent, MeCl/Hex (40:60, v:v).

1.6 $Ti(OBu_4)/TiCl_4$ ratios (Figure 6) the polymerization is very slow and 50−60% conversion is reached in 18 h. At the $Ti(OBu)_4/TiCl_4 = 1.6$ ratio, the M_ns are closer to

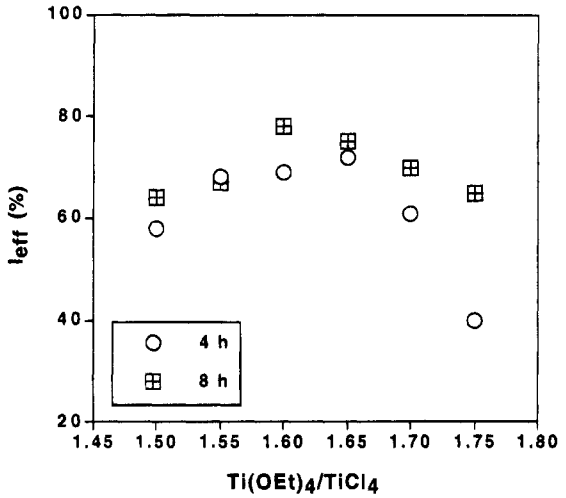


Figure 9. I_{eff} vs $Ti(OEt)_4/TiCl_4$ in the homopolymerization of αMeSt by the TMPCl/$TiCl_4$/DPE/$Ti(OEt)_4$ initiating system at −80 °C. $[M]_0$ = 0.35 M, [TMPCl] = 0.002 M, [DTBP] = 0.004 M, solvent, MeCl/Hex (40:60, v:v).

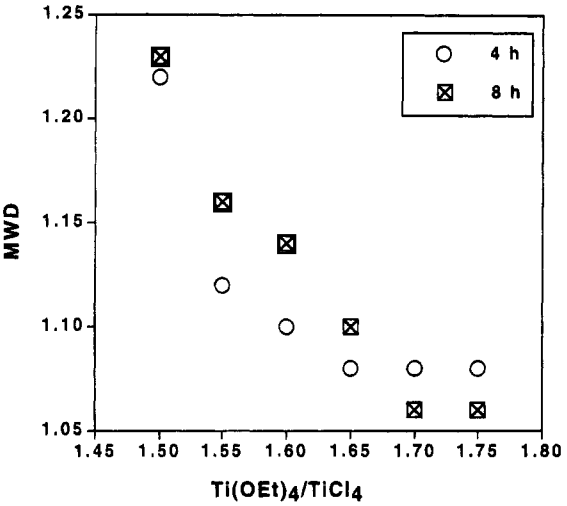


Figure 10. MWD vs $Ti(OEt)_4/TiCl_4$ in the homopolymerization of αMeSt by the TMPCl/$TiCl_4$/DPE/$Ti(OEt)_4$ initiating system at −80 °C. $[M]_0$ = 0.35 M, [TMPCl] = 0.002 M, [DTBP] = 0.004 M, solvent, MeCl/Hex (40:60, v:v).

the theoretical line (Figure 7) and reach ~60% I_{eff} at 50% conversion.

Figures 8−10 show the results obtained by the $Ti(OEt)_4/TiCl_4$ ratio from 1.5 to 1.75 at 4 and 8 h. The conversions decrease with increasing ratios (Figure 8). I_{eff} increases first and reaches 78% with $Ti(OEt)_4/TiCl_4$ = 1.6 at 75% conversion (Figure 9). Above this ratio the I_{eff} decreases due to decreasing conversions. (The extrapolated I_{eff}s to 75% conversions are ~90% for $Ti(OEt)_4/TiCl_4$ = 1.7 and ~100% for $Ti(OEt)_4/TiCl_4$ = 1.75.) The MWDs are narrow, decreasing from 1.23 at $Ti(OEt)_4/TiCl_4$ = 1.5 to 1.05 at $Ti(OEt)_4/TiCl_4$ = 1.75 (Figure 10). In conclusion the best I_{eff} (78%) was obtained using $Ti(OEt)_4$.

Figure 11 shows the ^1H NMR spectra (from 0 to 1.8 ppm) of PαMeSt samples prepared by the TMPCl/$TiCl_4$ and TMPCl/$TiCl_4$/DPE/$Ti(OIp)_4$ initiating systems. The peak at 1.35 ppm in spectrum A is due to intramolecular alkylation. This peak is absent in the product obtained using $Ti(OIp)_4$ (spectrum B). Comparison of the two spectra indicates that alkylation is eliminated by decreasing the Lewis acidity.

3. Polymerization of αMeSt Using $SnBr_4$. Living polymerization of αMeSt with 100% initiator efficiency

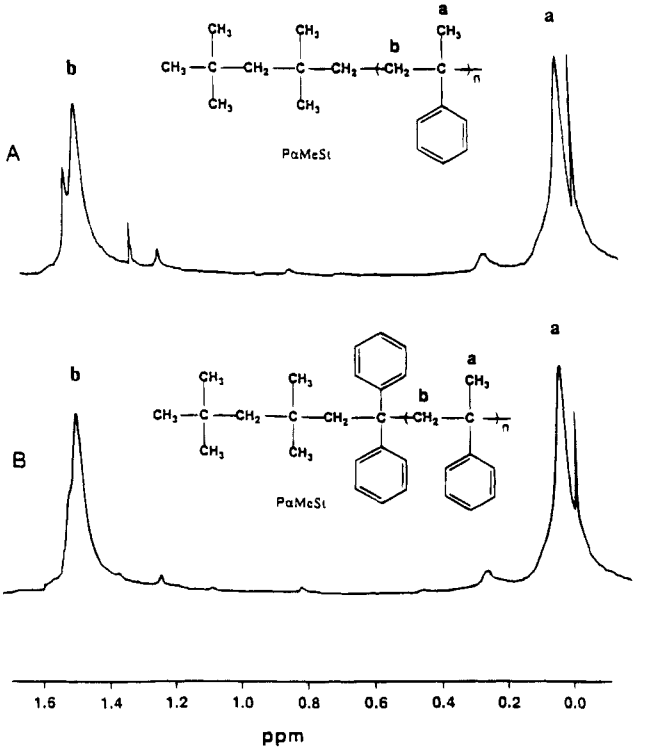


Figure 11. ^1H NMR spectra (0−1.8 ppm) of PαMeSt prepared as follows: (A) TMPCl/$TiCl_4$/solvent/−80 °C system (M_n = 90 000, MWD = 3.0). Detailed conditions in Figure 1. (B) TMPCl/$TiCl_4$/DPE/$Ti(OIp)_4$/solvent/−80 °C system (M_n = 38 000, MWD = 1.3). Detailed conditions in Figure 3.

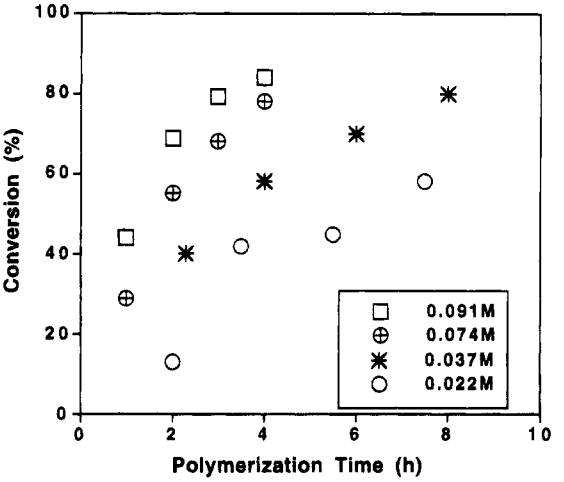


Figure 12. Conversion vs time in the polymerization of αMeSt initiated by the TMPCl/$TiCl_4$/DPE/$Ti(IpO)_4$/$SnBr_4$/MeCl:Hex (40:60, v:v)/−80 °C system at different concentrations of $SnBr_4$. [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.004 M, [DPE] = 1.5[TMPCl], [$Ti(IpO)_4$] = 1.15[$TiCl_4$], [αMeSt] = 0.35 M.

has recently been achieved by the $CH_3CH(OCH_2CH_2Cl)Cl/SnBr_4/CH_2Cl_2$/−78 °C initiating system.[15] Thus, we hypothesized that initiation would also be faster than propagation with the diphenylalkylcarbenium ion using $SnBr_4$ as Lewis acid. $TiCl_4$ is necessary for the polymerization of IB ($SnBr_4$ is ineffective) and for the DPE capping. However, $TiCl_4$ should be neutralized or eliminated from the polymerization system before the addition of αMeSt. Our strategy was to add a slight excess of $Ti(OIp)_4$ over $TiCl_4$ to prevent coinitiation by titanium compounds. Then $SnBr_4$ is introduced followed by the addition of αMeSt.

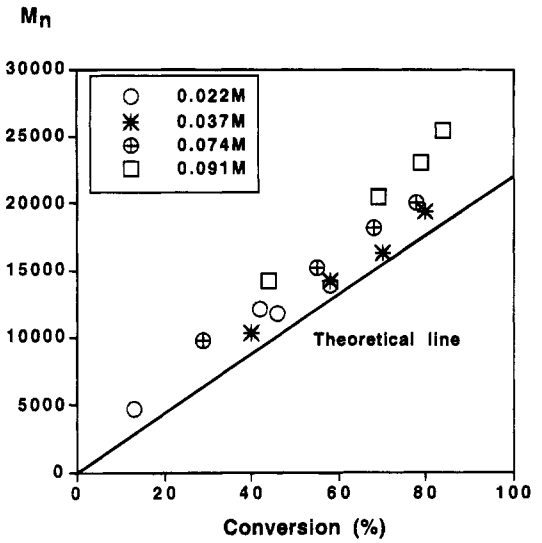


Figure 13. M_n vs conversion in the polymerization of αMeSi initiated by the TMPCl/$TiCl_4$/DPE/$Ti(IpO)_4$/$SnBr_4$/MeCl:Hex (40:60, v:v)/−80 °C system at different concentrations of $SnBr_4$. [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.004 M, [DPE] = 1.15[TMPCl], [$Ti(IpO)_4$] = 1.15[$TiCl_4$], [αMeSt] = 0.35 M.

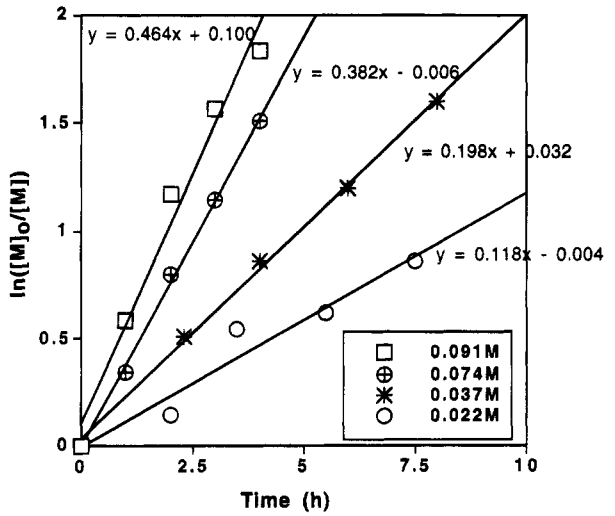


Figure 14. ln([M]$_0$/[M]) vs time in the block copolymerization of αMeSt by the PIB−DPE living ends (M_n = 10 000) using $SnBr_4$ at different concentrations. [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.004 M, [DPE] = 1.15[TMPCl], [$Ti(IpO)_4$] = 1.15[$TiCl_4$], [αMeSt] = 0.35 M.

Control experiments in the absence of initiator indicated the absence of direct initiation from $SnBr_4$. Next, a series of experiments were carried out with the TMPCl/DPE system using different concentrations of $SnBr_4$. At low $SnBr_4$ concentrations the polymerization is slow; 80% conversion was obtained in 8 h with [$SnBr_4$] = 0.037 M. The polymerization rate increased with increasing $SnBr_4$ concentration (Figure 12). According to the M_n−conversion plots (Figure 13), the molecular weights are close to the theoretical M_ns with [$SnBr_4$] = 0.022 and 0.037 M but somewhat higher with [$SnBr_4$] = 0.074 and 0.091 M. The MWDs were below 1.1. Thus, the living polymerization of αMeSt with $I_{eff} \sim$ 100% can be achieved using $SnBr_4$ as coinitiator.

The first-order plot for monomer with four different concentrations of $SnBr_4$ is shown on Figure 14. The linear plots obtained indicate the absence of termination. Furthermore, the polymerization rate constants at different concentrations of $SnBr_4$ show that the polymerization is first order in $SnBr_4$.

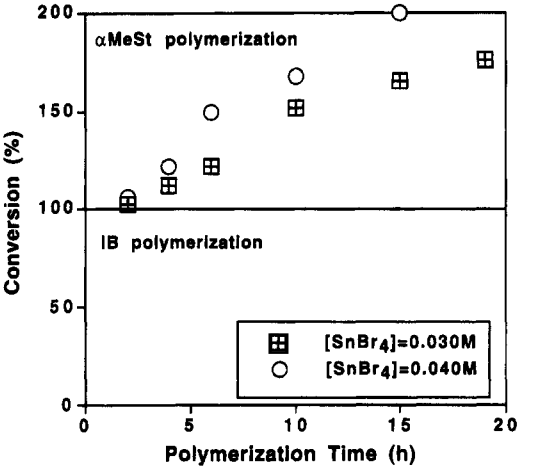


Figure 15. Conversion vs time in the block copolymerization of αMeSt by the PIB−DPE living ends (M_n = 10 000) using $SnBr_4$ at different concentrations. [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.004 M, [DPE] = 1.15[TMPCl], [$Ti(IpO)_4$] = 1.15[$TiCl_4$], [αMeSt] = 0.35 M.

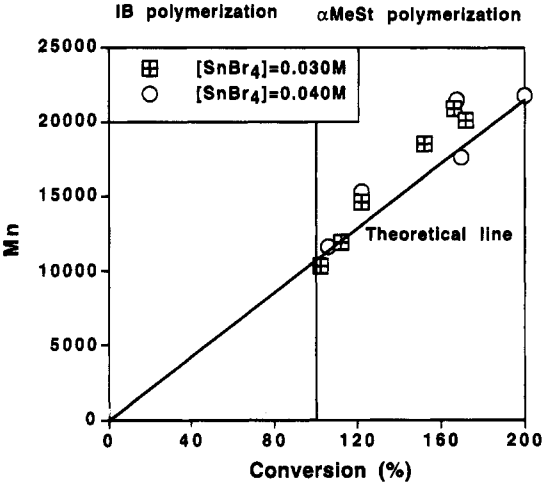


Figure 16. M_n vs conversion in the block copolymerization of αMeSt by the PIB−DPE living ends (M_n = 10 000) using $SnBr_4$ at different concentrations. [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.004 M, [DPE] = 1.15[TMPCl], [$Ti(IpO)_4$] = 1.15[$TiCl_4$], [αMeSt] = 0.35 M.

PIB−PαMeSt Diblock Copolymer Synthesis. The crossover efficiency (the initiator efficiency with a polymer initiator) is a measure of the efficiency of the block copolymerization. 100% crossover efficiency is mandatory in the triblock synthesis to avoid contamination by homopolymer or diblock copolymer, which significantly reduces the mechanical properties. The best method to determine the crossover efficiency is by diblock synthesis, since it is generally difficult to separate triblocks from diblocks in the triblock synthesis. Therefore, the above results were applied for the synthesis of PIB−PαMeSt diblock copolymer. Equal (10 000−10 000) block segments were planned to facilitate determination of the crossover efficiency. When the PIB segment is much longer than the second block, homoPIB contamination may not be readily visible by GPC and selective solvent extraction may not separate homopolymer from diblock copolymer.

Figure 15 shows the conversion versus polymerization time. The M_ns are plotted against the conversions on Figure 16. The observed M_ns are close to the theoretical ones. The MWDs were narrow; all M_w/M_n values were less than 1.1.

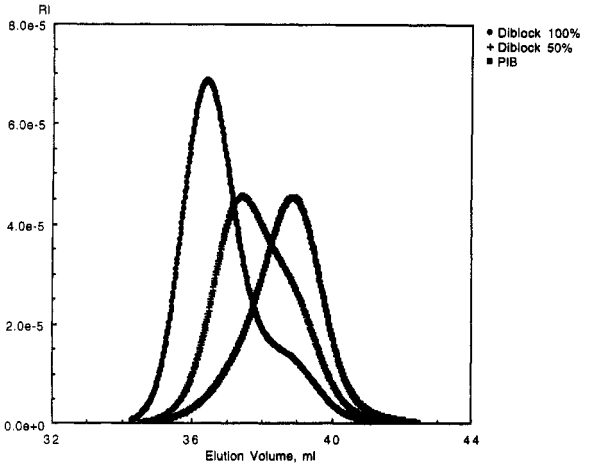


Figure 17. GPC RI traces of PIB and PIB–PαMeSt diblock copolymer at different αMeSt conversions obtained by the TMPCl/$TiCl_4$/DPE/$Ti(IpO)_4$/$SnBr_4$/MeCl:Hex (40:60, v:v)/−80 °C system. [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.004 M, [DPE] = 1.15[TMPCl], [$Ti(IpO)_4$] = 1.10[$TiCl_4$], [αMeSt] = 0.35 M.

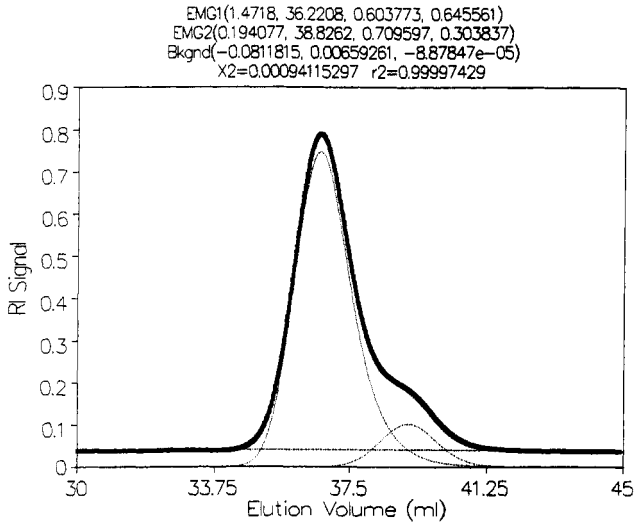
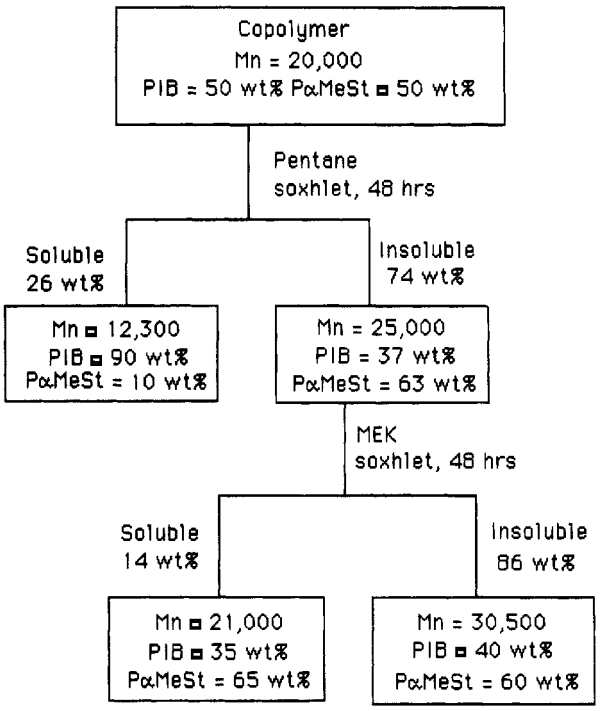


Figure 18. GPC RI traces of diblock copolymer (from Figure 17 with 100% conversion) and its separated peaks using an exponential Gaussian distribution.

Figure 17 shows the GPC traces of PIB and the diblock copolymer formed at different conversions. A small low molecular peak was found even after complete αMeSt conversion. The two peaks were separated by Peakfit (Jandel Scientific) using exponential Gaussian distribution. Figure 18 shows the original and the separated peaks. The position of the small peak is identical to that of the PIB segment. Based on the peak areas and d*n*/d*c* values, it is about 15 wt%. To determine if this low molecular weight fraction is due to unblocked homoPIB, selective solvent extraction was carried out. The diblock copolymer was extracted by pentane to remove homoPIB and subsequently by MEK to remove homoPαMeSt. As illustrated in Scheme 1, extraction with pentane for 48 h resulted in 26% soluble material, while 14% was soluble in MEK. ^{1}H NMR characterization of the pentane-soluble fraction indicated that it contains 10% of PαMeSt and 90% of PIB. Figure 19 shows the GPC traces of the pentane-soluble fraction and the diblock copolymer. If we assume that the pentane-soluble fraction is a diblock copolymer with a short αMeSt block segment, we must assume propagation by two separate species without appreciable

Scheme 1. Selective Solvent Extraction of a Representative Diblock copolymer



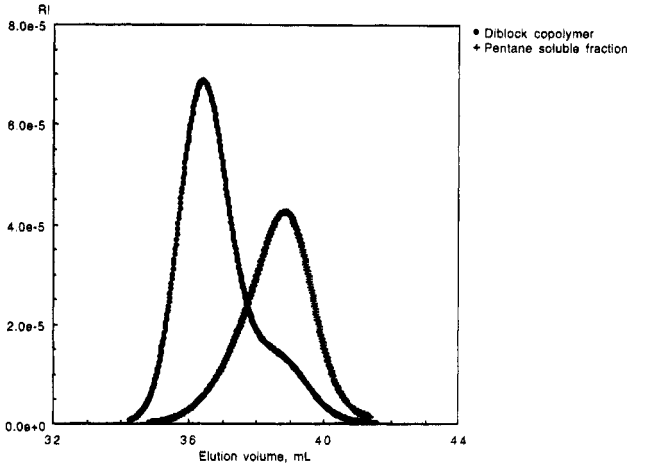


Figure 19. Comparison of GPC RI traces of the pentane-soluble fraction and the crude PIB–PαMeSt diblock copolymer (10 000–10 000) obtained by the TMPCl/$TiCl_4$/DPE/$Ti(IpO)_4$/$SnBr_4$/MeCl:Hex (40:60, v:v)/−80 °C system. [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.004 M, [DPE] = 1.15-[TMPCl], [$Ti(IpO)_4$] = 1.10[$TiCl_4$], [αMeSt] = 0.35 M.

exchange. Slow propagation may have been induced by still active titanium compounds; therefore, we have carried out diblock copolymerization with higher [Ti-$(OIp)_4$/[$TiCl_4$] = 1.4 and 1.6 ratios. The GPC traces of these diblocks are shown on Figures 20 and 21. The small low molecular weight peak has not been eliminated, indicating that the hypothesis is not correct.

Therefore, we must assume that the low molecular weight peak is due to homoPIB that, however, could not be completely separated from diblocks by selective solvent extraction. HomoPIB could have formed due to incomplete capping or by adding DPE before complete IB conversion.[14] If the polymerization system contains unreacted IB when the DPE is added, the DPE-capped PIB may react with IB, regenerating the PIB–Cl ends. $SnBr_4$, however, is too weak to ionize the PIB–Cl ends. A similar problem was encountered in the synthesis of

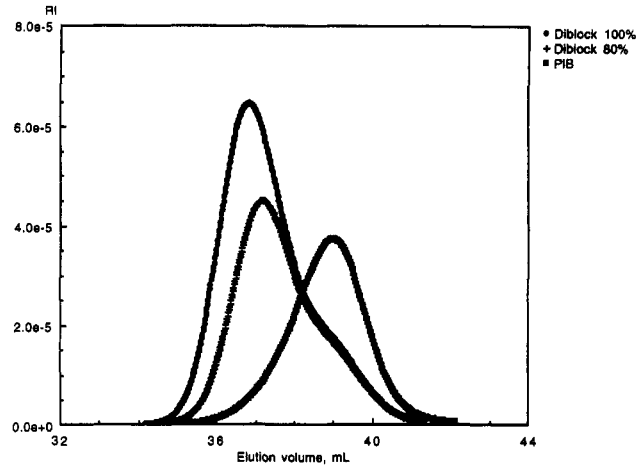


Figure 20. GPC RI traces of PIB and PIB–PαMeSt diblock copolymer at different αMeSt conversions obtained by the TMPCl/$TiCl_4$/DPE/$Ti(IpO)_4$/$SnBr_4$/MeCl:Hex (40:60, v:v)/−80 °C system. [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.004 M, [DPE] = 1.15[TMPCl], [$Ti(IpO)_4$ = 1.30[$TiCl_4$], [αMeSt] = 0.35 M.

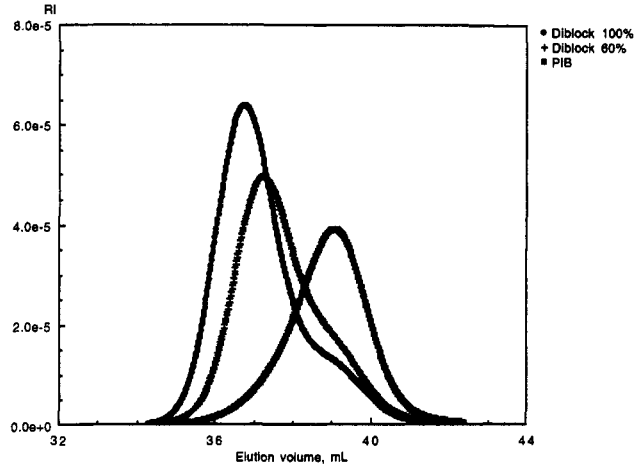


Figure 21. GPC RI traces of PIB and PIB–PαMeSt diblock copolymer at different αMeSt conversions obtained by the TMPCl/$TiCl_4$/DPE/$Ti(IpO)_4$/$SnBr_4$/MeCl:Hex (40:60, v:v)/−80 °C system. [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.004 M, [DPE] = 1.15[TMPCl], [$Ti(IpO)_4$] = 1.60[$TiCl_4$], [αMeSt] = 0.35 M.

PpMeSt–PIB–PpMeSt triblock copolymers. Instead of using impractically long polymerization times, it was successfully solved by increasing the amount of added DPE. With the higher DPE excess capping reaction times are lowered and more importantly PIBCl chain ends generated by the reaction between DPE-capped ends and IB may be converted back to diphenylalkylcarbenium ions by the addition of a second DPE. An experiment was carried out using this approach, with [DPE] = 2[TMPCl]. (According to a separate copolymerization experiment, the excess unreacted DPE copolymerize with αMeSt; see the Experimental Section). The low molecular weight peak is absent on the GPC plot of this product (Figure 22), indicating that pure diblock copolymer PIB–PαMeSt was obtained.

Conclusion

The first efficient synthesis of PIB–PαMeSt diblock copolymer was accomplished, giving rise to pure diblock

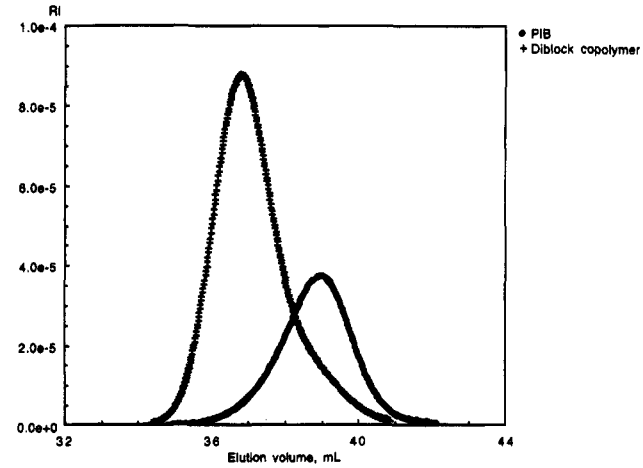


Figure 22. GPC RI traces of PIB (M_n = 9700, MWD = 1.10) and PIB–PαMeSt diblock copolymer (M_n = 21 000, MWD = 1.13) obtained by the TMPCl/$TiCl_4$/DPE/$Ti(IpO)_4$/$SnBr_4$/MeCl:Hex (40:60, v:v)/−80 °C system. [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.004 M, [DPE] = 2[TMPCl], [$Ti(IpO)_4$] = 1.60[$TiCl_4$], [αMeSt] = 0.35 M.

without homopolymer contaminants. A general synthetic scheme, developed for the synthesis of block copolymers by living carbocationic sequential block copolymerization when the second monomer is more reactive, was successfully employed. It involved DPE capping followed by tailoring the Lewis acidity to the reactivity of the second monomer. In a following publication we will report on the synthesis, characterization, and physical properties of PαMeSt–PIB–PαMeSt triblock copolymer thermoplastic elastomer.

Acknowledgment is made to the Center for Environmentally Appropriate Materials of the University of Massachusetts for support of this research.

References and Notes

(1) Faust, R.; Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1847–1869.
(2) Fodor, Zs.; Gyor, M.; Wang, H.-C.; Faust, R. *J. Macromol. Sci., Pure Appl. Chem.* **1993**, *A30* (5), 349–363.
(3) Kaszas, G.; Puskas, J. E.; Kennedy, J. P.; Hager, W. G. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 427.
(4) Kennedy, J. P.; Kurian, J. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 3725.
(5) Tsunogae, Y.; Kennedy, J. P. *Polym. Bull.* **1992**, *27*, 631.
(6) Kennedy, J. P.; Meguriya, N.; Keszler, B. *Macromolecules* **1992**, *24* (25), 6572.
(7) Kennedy, J. P.; Keszler, B.; Tsunogae, Y.; Midha, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (1), 310.
(8) Puskas, J. E.; Kennedy, J. P., Hager, W. G. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 41.
(9) Gyor, M.; Fodor, Zs.; Wang, H. C.; Faust, R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*, 562; *J. Macromol. Sci.* **1994**, *A31* (12), 2053.
(10) Tsunogae, Y.; Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 403–421.
(11) Lubnin, A. V.; Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, 77.
(12) Fodor, Zs.; Faust, R. *J. Macromol. Sci.* **1994**, *A31* (12), 1983.
(13) Fodor, Zs.; Faust, R. *J. Macromol. Sci.* **1995**, *A32* (3), 575.
(14) Gyor, M.; Wang, H. C.; Faust, R. *J. Macromol. Sci.* **1992**, *A29* (8), 639.
(15) Higashimura, T.; Kamigaito, M.; Kato, M.; Hasebe, T.; Sawamoto, M. *Macromolecules* **1993**, *26*, 2670–2673.

MA941176M