

리빙/조절 양이온중합에 의한 알파메틸스티렌 호모중합 및 이소부틸렌과의 블록공중합에 대한 반응속도론 연구

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Kinetic Studies on Homopolymerization of α -Methylstyrene and Sequential Block Copolymerization of Isobutylene with α -Methylstyrene by Living/Controlled Cationic Polymerization

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Abstract : The controlled/living cationic polymerization of α -methylstyrene (α MeSt) and sequential block copolymerization of isobutylene (IB) with α MeSt were achieved using 2-chloro-2,4,4-trimethyl-pentane (TMPCl)/titanium tetrachloride (TiCl_4)/titanium isopropoxide ($\text{Ti}(\text{OiPr})_4$)/2,6-ditert-butylpyridine (DtBP) initiating system in CH_3Cl /hexane (50/50 v/v) solvent mixture at -80°C . The polymerization rate decreased with increasing $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]$ ratio in the homopolymerization of α MeSt. The effects of $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]$ ratios and PIB^+ molecular weight on the polymerization rate and blocking efficiency were also investigated. Well-defined poly(isobutylene-*b*- α -methylstyrene)s were demonstrated by ^1H -NMR and triple detection SEC; refractive index (RI), multiangle laser light scattering (MALLS) and ultraviolet (UV) detectors. Blocking efficiencies for the poly(isobutylene-*b*- α -methylstyrene)s of almost 100% were obtained when α MeSt was induced by PIB^+ s of $M_n \geq 41000$ at $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=1$. Differential scanning calorimetry (DSC) of the block copolymers showed two glass transition temperatures, thereby demonstrating microphase separation.

Keywords : controlled/living carbocationic polymerization, poly(α -methylstyrene), kinetics, poly(isobutylene-*b*- α -methylstyrene).

Introduction

Controlled/living cationic polymerization is a most valuable technique in polymer synthesis. To control uniform size of polymer, living cationic polymerization provides the simplest and most convenient method for the preparation of block copolymers by sequential monomer addition. The key to living polymerization is the high stability of growing

end where the nucleophilic counter anion strongly interacts with the cationic active site. To effect living polymerization of the highly reactive α -methylstyrene (α MeSt), weak Lewis acids, such as BCl_3 ^{1–3} are required as co-initiators, while that of isobutylene necessitates strong Lewis acids such as titanium (IV) chloride.^{4–7} The living poly α MeSt cannot initiate the polymerization of IB, and the introduction of α MeSt to living PIB reaction mixtures leads to low crossover efficiency, due to an unfavorable ratio of crossover rate over propagation rate (R_c/R_p).⁸

A new strategy for the synthesis of block copolymers

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with 100% crossover efficiency by living cationic sequential block copolymerization was reported when the second monomer was more reactive than the first one. It involves capping of PIB chain ends with 1,1-diphenylethylene (DPE) or 1,1-ditolylethylene (DTE), followed by lowering the Lewis acidity to match the reactivity of the second monomer. This has been carried out using three different methods: (a) by the substitution of a strong Lewis acid with a weaker one, employed in the block copolymerization of IB with 4-*tert*-butoxystyrene,⁹ (b) by the addition of *n*Bu₄NCl in the block copolymerization of IB with isobutyl vinyl ether (IBVE),¹⁰ (c) by the addition of titanium (IV) alkoxide in the block copolymerization of IB with *p*MeSt,^{11,12} *p*-(*tert*-butyldimethylsiloxy)styrene,¹³ and cyclohexyl vinyl ether (MVE).¹⁴ When titanium (IV) alkoxide is introduced in polymerization system, weaker Lewis acid Ti₂Cl_{8-n}(OR)_n (R=Et, *n*Bu, *i*Pr) is formed rapidly.¹⁴ Lewis acidity of Ti₂Cl_{8-n}(OR)_n determined by stoichiometry directly effects polymerization rate. To the best of our knowledge, the effect of titanium (IV) alkoxide concentration and molecular weight of PIB⁺ on propagation rate (*R_p*) relative to the crossover rate (*R_c*) in block polymerization has been rarely investigated. This article reports the results for kinetics studies on homopolymerization of α MeSt and sequential block copolymerization of isobutylene with α -methylstyrene.

Experimental

Materials. 1,1-Diphenylethylene (DPE) (Alfa, 98%), titanium tetrachloride (TiCl₄) (Beijing Chemical Co., 99.9%), 2,6-di-*tert*-butylpyridine (DtBP) (Alfa, 97%) were used as received. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was synthesized by reacting 2,4,4-trimethyl-1-pentene with gaseous HCl. Titanium isopropoxide (Ti(OiPr)₄) (Alfa, 97%) was purified by vacuum distillation. Methyl chloride (MeCl) and IB were dried in the gaseous state by passing them through in-line gas-purifier columns packed with CaSO₄/Drierite, and they were condensed in the cold bath of a glovebox prior to polymerization. Hexane (Hex) (Beijing Chemical Co., 99%) was refluxed for 24 h with concentrated sulfuric acid, washed with 5% NaOH solution then neutralized with distilled water, dried on MgSO₄, and distilled from CaH₂ under nitrogen before use.

Polymerization. All polymerizations were carried out under a dry nitrogen atmosphere in a stainless steel glovebox using CH₃Cl/Hex (50/50 v/v) solvent mixtures. The homopolymerization of α MeSt was initiated by the TMPCl/TiCl₄/DtBP/DPE/-80 °C, followed by the addition of Ti(OiPr)₄. After 10 min the monomer α MeSt was added. In the diblock pre-

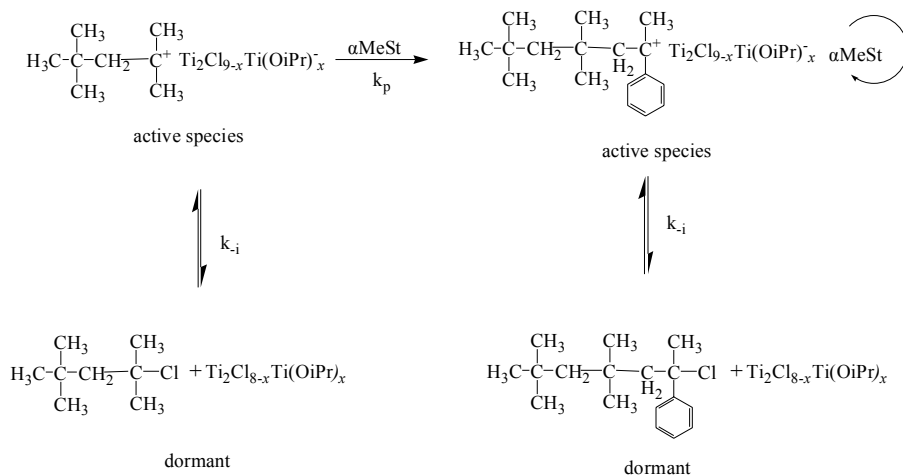
paration, IB was also first polymerized by the TMPCl/TiCl₄/DtBP/-80 °C system. When the conversion of IB was ~100%, DPE was added. After completion of DPE capping, Ti(OiPr)₄ was introduced to decrease Lewis acidity of TiCl₄, followed by α MeSt. The polymerizations were terminated at a specific time by prechilled methanol. After the evaporation of volatiles, the polymer was washed with isopropyl alcohol and then dried in a vacuum oven at 40 °C to a constant weight. The monomer conversion was determined gravimetrically.

Characterization. Molecular weights were measured with a size-exclusion chromatography system equipped with a Model 510 HPLC pump, differential refractometer (Wyatt Technology, Optilab REX), a model 2478 tunable UV detector (Water), on-line multiangle laser light scattering detector (Mini Dawn, Wyatt Technology Inc.) with the light wavelength at 690 nm, and four Ultra-styragel gel permeation chromatography (GPC) columns connected in the following series: 10³, 10⁴, 10⁵ and 100 Å. THF was used as a carrier solvent with a flow rate of 1 mL/min. ¹H-NMR spectroscopy for structural analysis was carried out on a Bruker 400 MHz spectrometer using CDCl₃ as a solvent. The glass-transition temperatures of the copolymer were determined by a TA Instruments Q2000 differential scanning calorimeter using a heating rate of 10 °C/min.

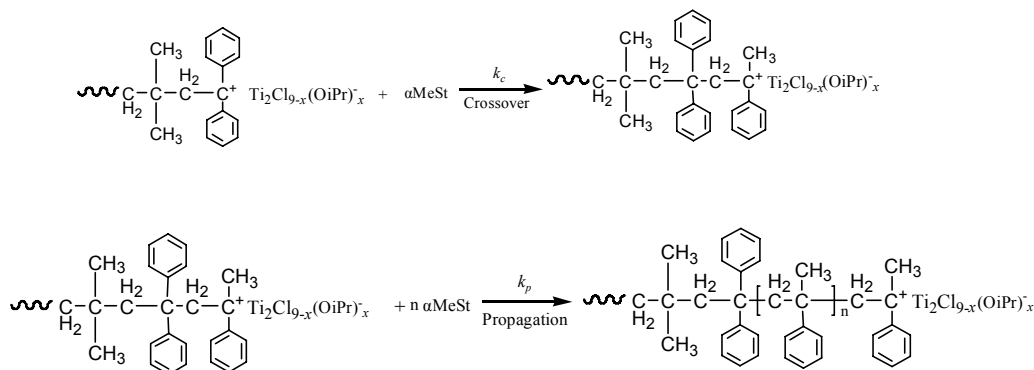
Results and Discussion

Homopolymerization of α MeSt. As shown in Schemes 1 and 2, carbocationic polymerizations of α MeSt initiated by the TMPCl / TiCl₄ / DtBP / DPE were carried out in CH₃Cl/Hex in the absence of and in the presence of Ti(OiPr)₄ at -80 °C. The conversion-time curves are given in Figure 1. From the experimental observations and experimental results in Figure 1, it can be seen that homopolymerization of α MeSt initiated by DPE-capped TMPCl / TiCl₄ system without Ti(OiPr)₄ was an uncontrolled process with an extremely rapid reaction rate and gave complete monomer conversion within 20 s. The monomer conversion gradually increases with increasing polymerization time by the introduction of small amounts of Ti(OiPr)₄. Upon addition of Ti(OiPr)₄, the orange color of diphenyl carbenium ion turned into the yellow-green color. This indicates that highly reactive species convert into less reactive species. The conversion decreases with increasing the [Ti(OiPr)₄]/[TiCl₄] ratio. Interestingly, there is a precipitous drop in conversion at [Ti(OiPr)₄]/[TiCl₄] ratio > 1. With the 1.1 of [Ti(OiPr)₄]/[TiCl₄] ratio, ~6% conversion was obtained in 1 h. It seems that Lewis acidity of Ti₂Cl_{8-n}(OiPr)_n remarkably decreases when *n* > 4.

The *M_n*-conversion plots, shown in Figure 2, are linear



Scheme 1. The procedure for the synthesis of poly(α MeSt).



Scheme 2. The crossover and propagation reaction in blocking of α MeSt from a PIB chain.

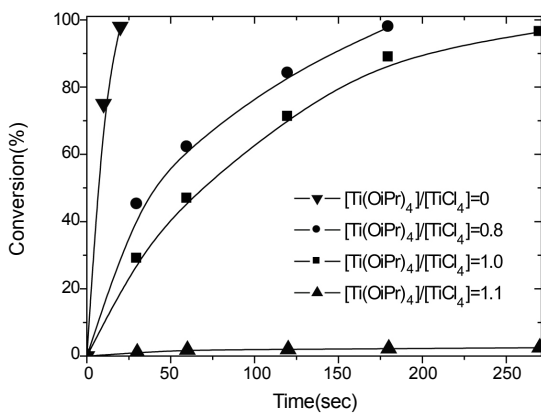


Figure 1. Time-conversion plots of α MeSt polymerization at different $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]$ ratios. Condition: $[\text{TiCl}_4] = 0.036 \text{ M}$, $[\text{DTBP}] = 0.002 \text{ M}$, $[\text{TMPCl}] = 0.002 \text{ M}$, $[\alpha\text{MeSt}] = 1.0 \text{ M}$, Hex/MeCl = 50/50 v/v; $T = -80^\circ \text{C}$.

indicating the absence of chain transfer to monomer. The M_n s are somewhat higher than the theoretical values and the initiator efficiencies (I_{eff} s) were found to be lower than 100%. The representative SEC traces of the poly(α MeSt)s

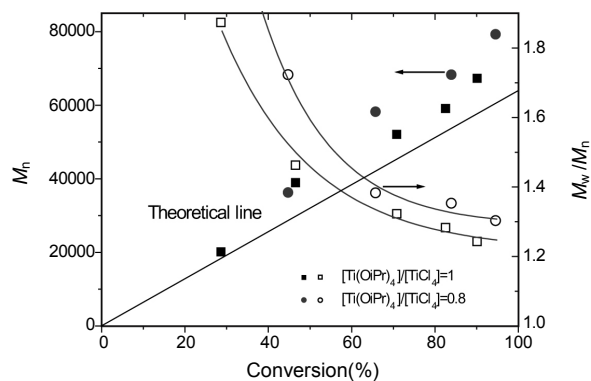


Figure 2. The M_n and M_w/M_n versus conversion plots for the polymerization α MeSt.

are shown in Figure 3. The M_w/M_n values decreased with increasing conversion and $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]$ ratio, and $M_w/M_n = 1.24$ is obtained at $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]$ ratio = 1.0 when monomer conversion reaches to $\sim 100\%$. The M_w/M_n -conversion function is typical of exchange between active and dormant centers relative to the rate of propagation. Fitting of the M_w/M_n -conversion plot with equation (1),^{15,16}

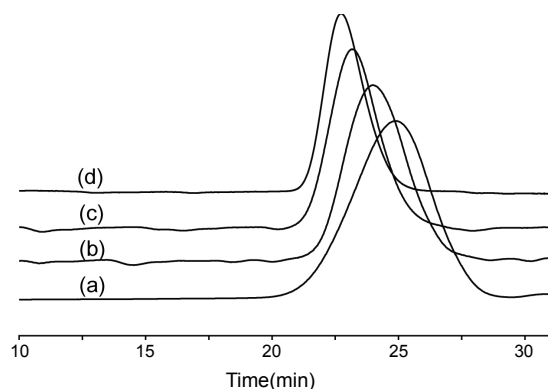


Figure 3. SEC(RI) traces of P α MeSt at different monomer conversion. SEC(RI) traces of P α MeSt at different monomer conversion, (a) Conv.=45%, $M_n=36000$, $M_w/M_n=1.72$; (b) Conv.=66%, $M_n=57900$, $M_w/M_n=1.38$; (c) Conv.=66%, $M_n=68000$, $M_w/M_n=1.35$; (d) Conv.=94.8%, $M_n=79000$, $M_w/M_n=1.32$.

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

Where x is the fractional conversion and $\beta = (k_{-i}) / (k_p [I]_{\text{eff}})$ (k_{-i} and k_p are the rate constants of deactivation and propagation, respectively, and $[I]_{\text{eff}}$ is efficiency initiator concentration). β value calculated from the data of Figure 2 decreases from 6.5 at $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=1$ to 4.5 at $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=0.8$. Thus, propagation is 154 times faster than deactivation in the polymerization of α MeSt at $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=0.8$. However, propagation is only 90 times faster than deactivation at $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=1$. Since k_{-i} is not expected to be lower at $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=0.8$ (P α MeSt $^+$ at $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=0.8$ should be less stable than at $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=1$), k_p must be higher at $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=0.8$. Therefore, it seems that the decrease of k_p by increasing $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]$ ratio directly led to the decrease of polymerization rate and the M_w/M_n values.

The kinetics of the cationic polymerization of α MeSt in the presence of $\text{Ti}(\text{OiPr})_4$ were determined by the gravimetric monitoring of the polymer yield as a function of the reaction time. The data is expressed in terms of the kinetic rate law for cationic polymerization:

$$R_p = -d[M]/dt = K[\text{TMPCl}]^a [\text{TiCl}_4]^\beta [\text{Ti}(\text{OiPr})_4]^\gamma [M] = K_p^A [M] \quad (2)$$

Where R_p is the rate of polymerization; $[M]$ is the concentration of the monomer; and K_p^A is the apparent first-order rate constant for propagation, which depends on the concentrations of the initiator, coinitiator, and $\text{Ti}(\text{OiPr})_4$. According to the integrated form of equation (2), plots of

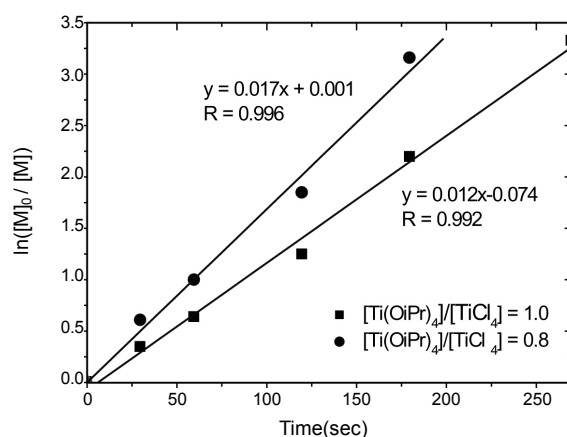


Figure 4. First-order plots for the polymerization of α MeSt.

$\ln([M]_0/[M])$ versus time are used to determine the value of K_p^A for each particular set of $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]$ ratios. It can be seen that linear plots of $\ln([M]_0/[M])$ versus time pass through the origin. The linearity of those first-order kinetic plots in Figure 4 demonstrates the expected first-order dependence on the monomer concentration, which proves that the concentration of growing centers remains constant. This result combined with linear of M_n -conversion plots confirms that the polymerization is living. The K_p^A values obtained from the slope of the corresponding linear plot show that the rate of the polymerization decreases with increasing $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]$ ratios. This also suggests that the Lewis acidity of $\text{Ti}_2\text{Cl}_{8-n}(\text{OiPr})_n$ decreases with increasing with $[\text{Ti}(\text{OiPr})_4]$ to $[\text{TiCl}_4]$ ratio.

Block Copolymerization of IB with α MeSt. After the successful homopolymerization of α MeSt, a block copolymerization was carried out by sequential monomer addition. As shown in Figure 5, the rate of α MeSt polymerization in the blocking experiment is much slower than observed in the homopolymerization of α MeSt under identical conditions. Figure 6(a) shows the SEC(RI) traces of the PIB-DPE $^+$ segments and of the diblock copolymer formed at different conversions. The SEC traces of the diblock polymer obtained at $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=0.8$ ratio show bimodal molecular weight distribution, and the peak of low molecular weights moves toward high molecular weights. To determine if this low molecular weight fraction was due to unblocked homoPIB, the crude product was extracted with pentane, a good solvent for homoPIB. While ^1H -NMR characterization of the pentane-soluble fraction indicated, it contained the P α MeSt segments. If we assume that the pentane-soluble fraction is a diblock copolymer with a short α MeSt block segment, we must assume propagation by two separate species without appreciable exchange. A slow propagation can be induced by still active titanium compounds. Therefore, we have carried

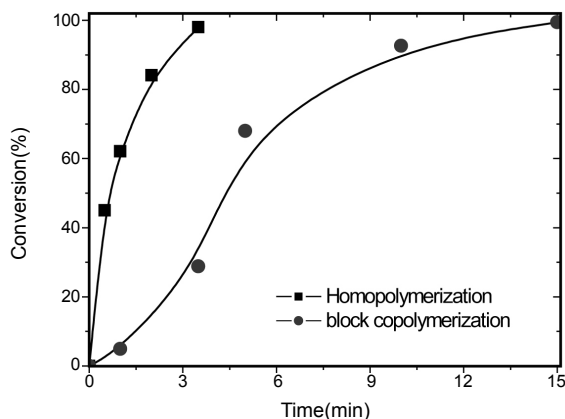


Figure 5. Plots of the monomer conversion versus the polymerization time in α MeSt homopolymerization and α MeSt block copolymerization. Homopolymerization: [TMPCl]=0.002 M; [DtBP]=0.002 M; $[\text{TiCl}_4]=0.036$ M; $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=0.8$; $[\alpha\text{MeSt}]=1.0$ M, $\text{C}_6\text{H}_{12}/\text{MeCl}=50/50$ v/v; $T=-80$ °C. Block copolymerization: same as above except initiator was $[\text{PIB}^+]$.

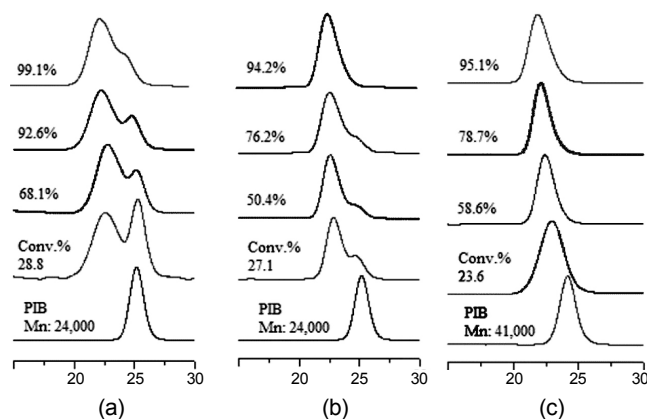


Figure 6. SEC(RI) traces in the block copolymerization of IB with α MeSt with $\text{TMPCl}/\text{TiCl}_4/\text{Ti}(\text{OiPr})_4/\text{DTBP}$ initiating system at -80 °C. (a) $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=0.8$, $M_n(\text{PIB})=24000$ g/mol; (b) $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=1.0$, $M_n(\text{PIB})=24000$ g/mol; (c) $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=1.0$, $M_n(\text{PIB})=41000$ g/mol.

out diblock copolymerization with higher $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=1$ ratio. The SEC traces of these copolymers are shown on Figure 6(b). The low molecular weight peak decreased evidently in size with increasing conversion and eliminated at high conversion, indicating that the hypothesis was correct. So the S-shaped time-conversion curve in Figure 5 and bimodality in Figure 6(a) indicate that α MeSt propagation rate is relatively higher than that of crossover at $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=0.8$ ratio (Scheme 2). α MeSt was consumed before all PIB-DPE^+ was converted quantitatively to $\text{PIB-DPE-}\alpha\text{MeSt}^+$ and some PIB-DPE^+ chains remained unblocked at the end of the reaction. However, the rate of α MeSt propagation approached that of crossover when

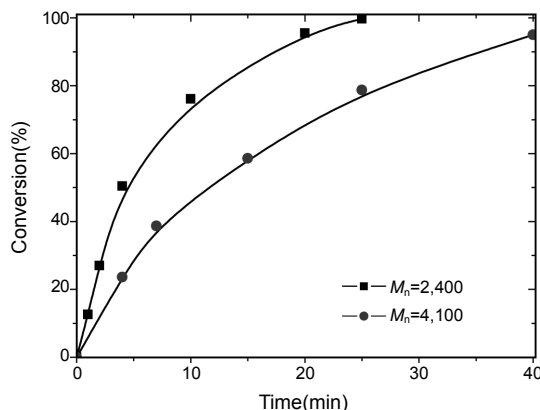


Figure 7. Plots of the monomer conversion versus the polymerization time in blocking of α MeSt from different molecular weight of PIB^+ .

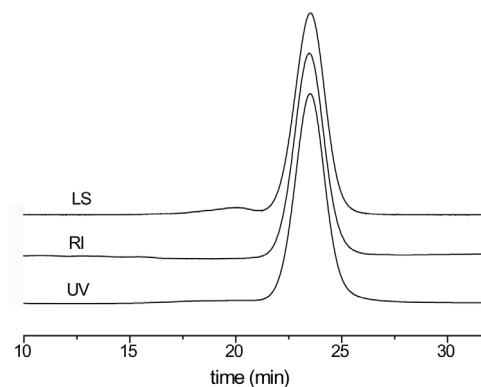


Figure 8. SEC(RI/LS/UV) traces of poly(isobutylene-*b*- α -methylstyrene) copolymer.

$[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]$ ratio increased to 1.

This result prompted us to further slow the propagation by increasing the M_n of PIB-DPE^+ macrocation. Thus, a series of diblock copolymerization was induced by higher molecular weight of PIB-DPE^+ macrocation. Figure 7 shows the conversion versus polymerization time at different molecular weight of PIB-DPE^+ macrocation. Evidently α MeSt propagation rate decreases with increasing PIB-DPE^+ macrocations. The SEC(RI) (Figure 6(c)) traces of the resulting block copolymer remain monomodal and narrow when the M_n of PIB-DPE^+ macrocation was increased to 41000. The LS, RI and UV traces of SEC have the same eluting time without any tailing (in Figure 8). Figure 9 shows the $^1\text{H-NMR}$ spectrum of a resulting block copolymer together with peak assignments. Complete disappearance of the peaks at 2.5 ppm (which assigned to chloro-DPE end functions) and appearance of new peaks due to the presence of the $\text{P}\alpha\text{MeSt}$ block at 0.15 and 1.5~1.6 ppm indicate that the crossover was $\sim 100\%$. During blocking of α MeSt from a high molecular weight PIB

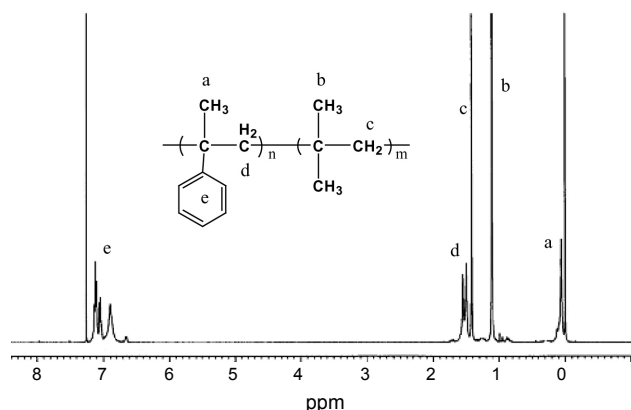


Figure 9. ^1H -NMR spectra of poly(isobutylene-*b*- α -methylstyrene) copolymer in CDCl_3 .

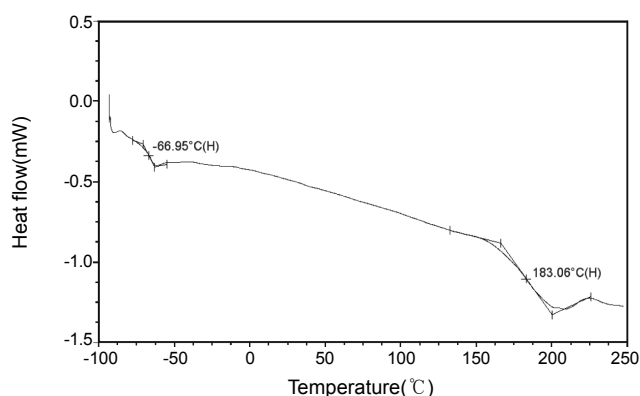


Figure 10. DSC scans of a representative poly(isobutylene-*b*- α -methylstyrene) copolymer.

chain, α MeSt had to diffuse through the swollen PIB coil to reach the growing PIB^+ chain end. Probably due to this diffusion process, the rate of α MeSt polymerization (k_p) slowed down and became comparable to (or less than) that of the rate of crossover (k_c) and results in high blocking efficiency. A DSC scan of the block copolymer showing two glass transitions (-67 and 183°C) indicates the presence of two microphases (Figure 10).

Conclusions

The living polymerization of α MeSt has been accomplished in $\text{TMPCl} / \text{TiCl}_4 / \text{Ti}(\text{OiPr})_4 / \text{DTBP}$ initiating system. The amount of added $\text{Ti}(\text{OiPr})_4$ relative to that of TiCl_4 is critical, rate of α MeSt polymerization decreases with increasing $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]$ ratio which suggests that the Lewis acidity of $\text{Ti}_2\text{Cl}_{8-n}(\text{OiPr})_n$ decreases with $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]$ ratio. The polymerization rate is first-order dependence on monomer concentration combined with linear of M_n -con-

version plots confirm that the polymerization of α MeSt is living. Systematic investigations were also carried out to study the effect of $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]$ ratio and PIB^+ molecular weight on blocking efficiency in block copolymerization of IB with α MeSt. α MeSt propagation rate is relatively higher than that of crossover at $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]=0.8$ ratio which leads to low blocking efficiencies. Rate propagation decreases with increasing $[\text{Ti}(\text{OiPr})_4]/[\text{TiCl}_4]$ ratio or increasing PIB^+ molecular weight. Close to 100% blocking efficiencies of block copolymers are obtained when α MeSt is induced by PIB's of $M_n \geq 41000$ at $[\text{Ti}(\text{OIP})_4]/[\text{TiCl}_4]=1$. DSC analyses of representative block copolymer indicate two-phase morphology.

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References

1. Y. Kwon and R. Faust, *J. Macromol. Sci., Pure Appl. Chem.*, **A42**, 385 (2005).
2. Z. Fodor and R. Faust, *J. Macromol. Sci., Pure Appl. Chem.*, **A35**, 375 (1998).
3. Y. Kwon, X. Y. Cao, and R. Faust, *Macromolecules*, **32**, 6963 (1999).
4. X. Xu, Y. X. Wu, Y. X. Qiu, C. L. Dong, and G.Y. Wu, *Eur. Polym. J.*, **42**, 2791 (2006).
5. J. E. Puskas, S. Sohel, Z. Y. Kevin, B. Kim, and K. Gabor, *Eur. Polym. J.*, **41**, 1 (2005).
6. Y. Kwon and J. E. Puskas, *Eur. Polym. J.*, **40**, 119 (2004).
7. J. E. Puskas, Y. Chen, and M. Tomkins, *Eur. Polym. J.*, **39**, 2147 (2003).
8. Y. H. Zhou, R. Faust, S. J. Chen, and P. G. Samuel, *Macromolecules*, **37**, 6716 (2004).
9. B. Hassen, S. Abhijit, S. Laszlo, and R. Faust, *J. Macromol. Sci., Pure Appl. Chem.*, **A44**, 359 (2007).
10. S. Hadjikyriacou and R. Faust, *Macromolecules*, **28**, 7893 (1995).
11. Z. Fodor and R. Faust, *J. Macromol. Sci.; Pure Appl. Chem.*, **A32**, 575 (1995).
12. L. Sipos, A. Som, and R. Faust, *Biomacromolecules*, **6**, 2570 (2005).
13. Y. Zhou and R. Faust, *Macromolecules*, **38**, 8183 (2005).
14. D. W. Li and R. Faust, *Macromolecules*, **28**, 1383 (1995).
15. L. Sipos, X. Y. Cao, and R. Faust, *Macromolecules*, **34**, 456 (2001).
16. P. De, L. Sipos, R. Faust, M. Moreau, B. Charleux, and J. P. Vairon, *Macromolecules*, **38**, 41 (2005).