Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Fodor, Zsolt and Faust, Rdolf(1994) 'Living Carbocationic Polymerization of *p*-Methylstyrene and Sequential Block Copolymerization of Isobutylene with *p*-Methylstyrene', Journal of Macromolecular Science, Part A, 31: 12, 1985 — 2000

To link to this Article: DOI: 10.1080/10601329409350113

URL: http://dx.doi.org/10.1080/10601329409350113

J.M.S.—PURE APPL. CHEM., A31(12), pp. 1985–2000 (1994)

LIVING CARBOCATIONIC POLYMERIZATION OF *p*-METHYLSTYRENE AND SEQUENTIAL BLOCK COPOLYMERIZATION OF ISOBUTYLENE WITH *p*-METHYLSTYRENE

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ABSTRACT

A novel scheme was developed for the synthesis of pure polyisobutylene–poly(*p*-methylstyrene) block copolymers by sequential monomer addition. The synthesis involves the living polymerization of isobutylene by the $TiCl_4$/methyl chloride:methylcyclohexane or hexanes 40:60 v:v/ −80°C system in the presence of di-*tert*-butylpyridine. When the polymerization of isobutylene is complete, the living polyisobutylene chain end is transformed to the corresponding diphenyl alkyl end by capping with 1,1-diphenylethylene. Subsequently, titanium(IV) isopropoxide or titanium(IV) butoxide is added to decrease the Lewis acidity followed by the addition of *p*-methylstyrene. The success of the method was demonstrated by *p*-methylstyrene homopolymerization experiments initiated by 2-chloro-2,4,4-trimethylpentane that resulted in ~100% initiator efficiencies when the $TiCl_4$/titanium(IV) isopropoxide or -butoxide ratio was less than 25/7, as well as by the clean synthesis of polyisobutylene–poly(*p*-methylstyrene) diblock copolymers.

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INTRODUCTION

Recently the living polymerization of *p*-methylstyrene (pMeSt) was reported [1] in the presence of Et_3N as "electron donor." Homopolymerization experiments using 2-chloro-2,4,4-trimethylpentane (TMPCl) indicated low initiator efficiencies (I_{eff} ~ 50%). Interestingly, high initiator efficiencies were claimed in the synthesis of PpMeSt-PIB-PpMeSt triblock copolymers by sequential monomer addition based on the reportedly high blocking efficiencies. The efficiency of the initiation from the $^{+}PIB^{+}$ ends, however, cannot be evaluated based on pMeSt blocking efficiencies. High blocking efficiencies only indicate the absence of chain transfer to monomer. The mechanical properties of these triblock copolymer thermoplastic elastomers were rather poor, suggesting contamination by homopolymers and/or diblocks. A synthetic scheme essentially similar to that of Tsunogae et al. [1] was used by Everland and coworkers [2] for the synthesis of PpMeSt-PIB-PpMeSt triblock copolymers. The mechanical properties, however, were not reported.

In a series of recent publications we reported the living polymerization of isobutylene (IB) and styrene (St) in the presence of the 2,6-di-*tert*-butylpyridine (DTBP) in concentrations comparable to the concentration of protic impurities in the system [3-5]. We have confirmed that the living nature of the polymerization is not due to carbocation stabilization, and suggested that the polymerizations are living due to the absence of chain transfer and reversible termination. The purpose of DTBP is to trap protic impurities in the polymerization system. The results were applied for the synthesis of PSt-PIB-PSt triblock copolymers by sequential monomer addition [6]. Tensile strength as high as 25 MPa (3700 psi) indicated that PIB-based perfect triblock copolymer thermoplastic elastomers (TPEs) exhibit mechanical properties similar to those of styrenic TPEs obtained by anionic polymerization.

We extended our studies to other styrenic monomers, and in the present publication the results obtained with pMeSt are reported.

EXPERIMENTAL

Materials

TMPCl was obtained from 2,4,4-trimethyl-1-pentene (Aldrich) by hydrochlorination. pMeSt (DELTECH Corporation) was purified by washing it with 10% aqueous sodium hydroxide solution, followed by distilled water until neutral. Traces of water remaining after drying on $MgSO_4$ were removed by treatment with dibutylmagnesium (DBM, Lithco, 14 wt% in heptane), followed by vacuum distillation. Methyl chloride (MeCl, Linde) was dried by passing the gas through in-line gas-purifier columns packed with BaO/Drierite, and condensed in the cold bath of the glove box prior to polymerization. Methylcyclohexane (MeChx, Aldrich) was refluxed for two days with concentrated sulfuric acid. It was washed with distilled water until neutral, dried over molecular sieves, refluxed, and distilled from CaH_2 under nitrogen atmosphere. Hexanes (Hex, Aldrich) were purified similarly. Titanium tetrachloride (Aldrich), the proton trap DTBP (99.4% by GC, Aldrich) or 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, 99.5% by GC, Aldrich), 1,1-diphenylethylene (DPE, Aldrich), titanium(IV) isopropoxide ($Ti(IpO)_4$, Aldrich, 97%), and titanium(IV) butoxide ($Ti(BuO)_4$, 99%, Aldrich) were used as received.

Procedures

All polymerizations were carried out under a dry nitrogen atmosphere in a MBraun 150-M glove box (Innovative Technology Inc., Newburyport, Massachusetts). The moisture level inside the glove box was kept under 1.0 ppm by continuous circulation of the internal nitrogen atmosphere through the MB 150-M gas purification system before the experiments. Large (75 mL) test tubes were used as polymerization reactors for kinetic experiments. The total volume of the reaction mixture was 25 mL. The initiator, coinitiator, and proton trap were dissolved in MeChx or Hex at room temperature. The solution was then cooled to −80°C and MeCl was added. $TiCl_4$ solution (1/3 v/v) in MeChx or Hex was added next, followed by the addition of monomer solution in MeCl/MeChx or MeCl/Hex 60/40 v/v. The reaction mixture was stirred vigorously by a Vortex stirrer, then placed back into the temperature-controlled heptane bath.

For the preparation of diblock copolymer, IB was polymerized as described above. When the polymerization of IB was complete (~30 minutes), DPE solution was added, and after ~30 minutes it was followed by the addition of $Ti(IpO)_4$ or $Ti(BuO)_4$ solution. Finally, 10 minutes later the pMeSt solution was introduced. All of the solutions were prepared using MeCl/MeChx or MeCl/Hex solvent. The initiator and coinitiator concentrations were chosen to be similar to concentrations that would be used in the triblock copolymer synthesis. The molecular weights therefore were adjusted by adjusting the monomer concentrations.

The polymerizations were terminated by adding prechilled methanol. The polymers were purified by dissolution-precipitation in dichloromethane/methanol, and dried in vacuo prior to GPC measurements.

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 μ-Styragel 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. A calibration curve obtained by PSt standards (Polysciences Inc.) was used. For data acquisition and computing, a Waters Baseline chromatography workstation was used. Absolute molecular weights of representative samples were also measured using a miniDawn (Wyatt Technologies Inc.) GPC on-line multiangle laser light-scattering (MALLS) detector. NMR measurements were carried out by a Bruker 270 MHz instrument.

RESULTS AND DISCUSSION

Preliminary pMeSt homopolymerization experiments were carried out under conditions found necessary for the living polymerization of IB and St, i.e., $TiCl_4$/MeCl:MeChx 40:60 v:v/−80°C. Experimentation started with control experiments, i.e., polymerizations in the absence of initiator and in the absence or presence of DTBP. In the absence of DTBP the polymerizations were very fast; conversions reached 93% after 1 minute. In the presence of 0.004 M DTBP, due to effective

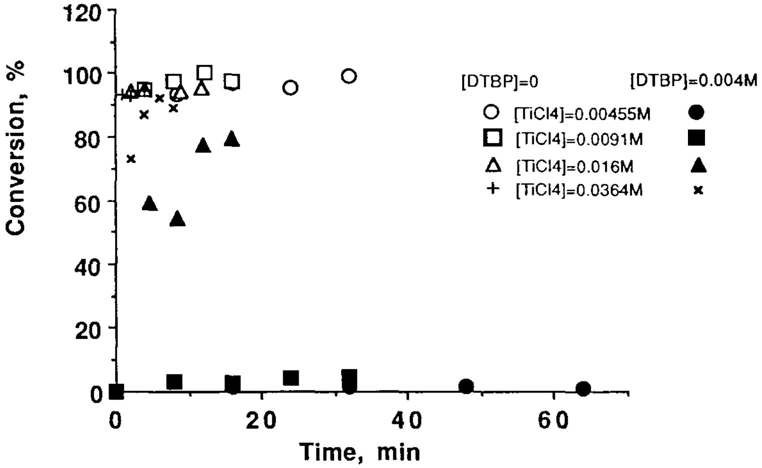


FIG. 1. Conversion vs time plot for the polymerization of pMeSt in the absence of initiator and in the absence and presence of a proton trap using a MeCl/MeChx 40/60 v/v solvent mixture at −80°C. $[\mathrm{pMeSt}]_0 = 0.35$ M.

trapping of protic impurities, the rates are substantially reduced, and with a negligible amount of polymer formed in 1 hour $[\mathrm{TiCl_4}] \leq 9.1 \times 10^{-3}$M. The results are plotted in Fig. 1.

The molecular weight versus conversion plot is shown in Fig. 2. The molecular weights are somewhat scattered around 40,000 daltons. The M_W/M_n ratios were between 4.2 and 5.6. In the absence of DTBP, the MWD is broader due to the two different types of initiation (direct and protic). The molecular weight-conversion

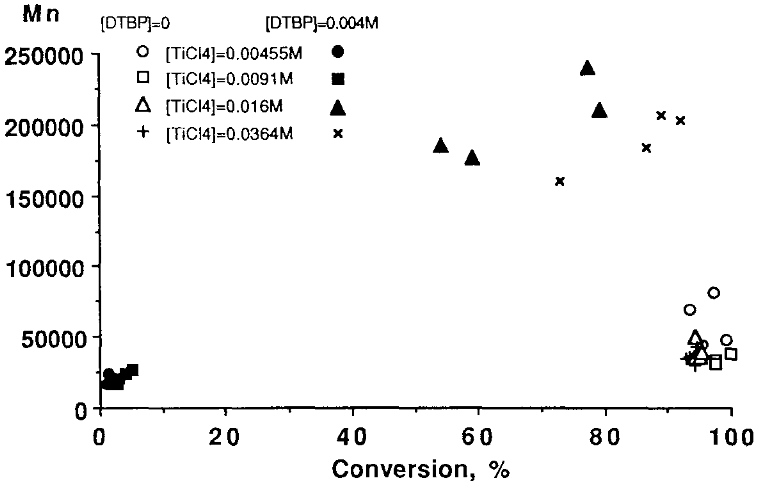


FIG. 2. Molecular weight vs conversion plot for the polymerization of pMeSt in the absence of initiator and in the absence and presence of a proton trap using the MeCl/MeCH 40/60 v/v solvent mixture at −80°C. $[\mathrm{pMeSt}]_0 = 0.35$ M.

plot in the presence of DTBP (Fig. 2) appears to follow a straight line. The M_W/M_n ratios were in the range of 1.9 to 5.0 in the high conversion region. In the presence of DTBP, protic initiation is prevented and the MWD is narrower. Polymer formation, presumably by direct initiation, is much slower although still faster than that of St [5].

Polymerization experiments using TMPCl as initiator were also carried out to determine if controlled initiation of pMeSt can be achieved. TMPCl was chosen as a model of the PIB living end. The experiments were carried out at two different DTBP concentrations and at the three lower $TiCl_4$ concentrations as the polymerization rate, even in the absence of initiator, was too high with $[TiCl_4] = 0.0364$ M. The first-order plots are shown in Fig. 3. The polymerization rates are similar at the different DTBP concentrations. Comparison of the rates in the presence and absence of TMPCl reveals that at [TMPCl = 0.002 M polymer formation is essentially from the initiator, and direct initiation is negligible.

The molecular weight-conversion plots (Fig. 4), however, are not linear and do not follow the theoretical line. The initiator efficiencies increase with conversion but they do not exceed 27% even at close to complete monomer conversion. Evidently initiation is very slow compared to propagation.

In the polymerization of St, intermolecular alkylation, most probably involving the para position, was encountered at close to 100% conversion. We hypothesized that with pMeSt, alkylation is absent or negligible. To determine that the higher than theoretical molecular weights are not the result of intermolecular alkylation polymerization, experiments were carried out with longer polymerization times. Experimental conditions were similar to those used in Reference 5, i.e., much higher initiator, coinitiator, and monomer concentrations were used than usual. The results are in Table 1 which shows that alkylation is indeed slow even at these high concentrations. From the results of Table 1 we calculated that intermolecular

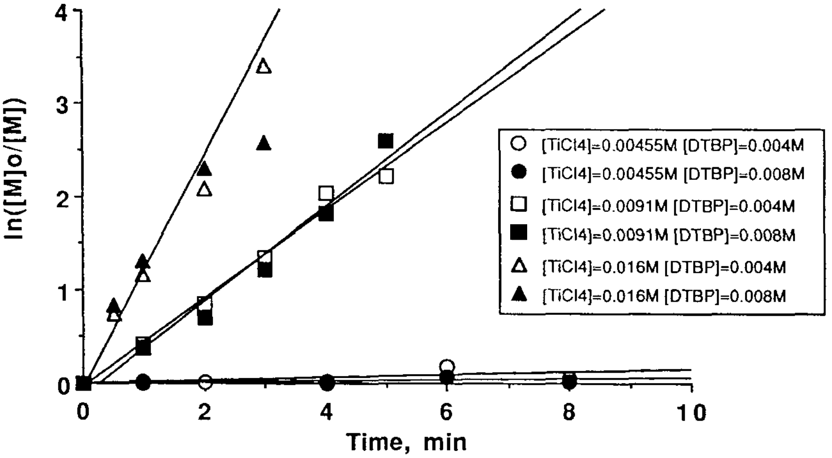


FIG. 3. $\ln([M]_0/[M])$ vs time plots for the polymerization of pMeSt using the MeCl/MeChx 40/60 v/v solvent mixture at −80°C. $[M]_0 = [pMeSt]_0 = 0.35$ M, [TMPCl] = 0.002 M.

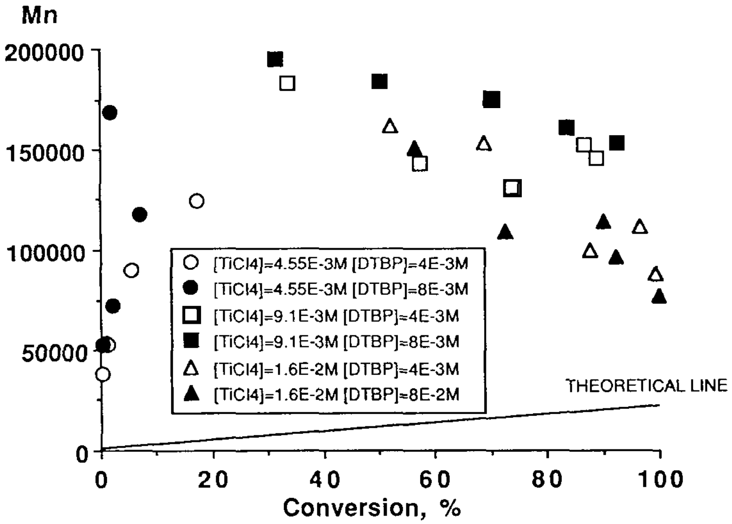


FIG. 4. Molecular weight vs conversion plot for the polymerization of pMeSt at various $TiCl_4$ and DTBP concentrations using MeCl/MeChx 40/60 v/v solvent mixtures at −80°C. $[\text{pMeSt}]_0$ = 0.35 M, [TMPCl] = 0.002 M. The $\bar{M}_w/\bar{M}_n$ values are in the 2.0 to 3.9 range.

alkylation proceeds at a constant rate, N decreases by 0.6%/min. Even though propagation is much faster with pMeSt, this is only about one-third of the rate that we found with styrene [5]. The corresponding rate for the customary initiator (0.002 M), coinitiator (0.036 M), and monomer (0.35 M) concentrations is ~0.006%/min; that is, alkylation can be considered negligible during the polymerization.

Experiments were also carried out using Hex instead of MeChx. Similar polymerization rates and molecular weight-conversion plots were obtained, indicating slow initiation. The results of incremental monomer addition were similar to that reported in References 1 and 7, i.e., the initiator efficiencies were well below 50%.

To gain more insight, IB-pMeSt copolymerization experiments were carried

TABLE 1. Conversions, Molecular Weights, and Polydispersities Determined by GPC MALLS, and Polymer Concentration (N) in the Polymerization of pMeSt Using MeCl/MeChx 40/60 v/v Solvent Mixture at −80°C. $[\text{pMeSt}]_0$ = 1.73 M, [TMPCl] = 0.00445 M, [DTBP] = 0.0089 M, $[TiCl_4]$ = 0.0828 M

Time, min	Conversion, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	N, mol/L
4	96	51,200	2.08	0.0038
20	100	59,900	2.02	0.0034
63	100	87,700	2.18	0.0023

out. Conversions were kept under 5%. The reactivity ratios were calculated by the Kelen-Tüdös method [8] (Fig. 5). The reactivity ratios ($r_{IB} = 0.35 \pm 0.01$, $r_{pMeSt} = 2.6 \pm 1.17$) indicate close to ideal copolymerization ($r_1 r_2 \sim 1$), and both chain ends prefer to add pMeSt. Since the apparent propagation rate constant of pMeSt is about 100 times higher that of IB, $k_{IB\text{-}pMeSt}/k_{pMeSt\text{-}pMeSt}$ is about 0.03, i.e., initiation is very slow relative to propagation.

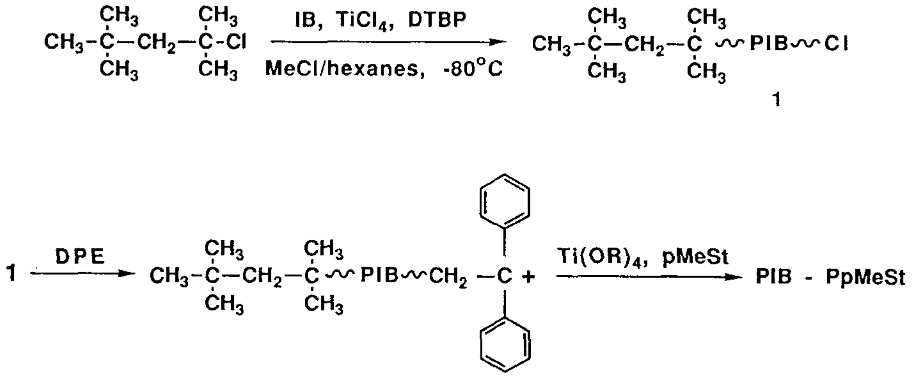
From the homopolymerization and copolymerization experiments we concluded that the conditions used to achieve the living polymerization of IB and St, the polymerization of pMeSt by TMPCl, and consequently by the living PIB$^+$ end, cannot be initiated efficiently.

We invented a novel strategy for the synthesis of PIB–PpMeSt diblock or PpMeSt–PIB–PpMeSt triblock copolymers by capping PIB with DPE that does not homopolymerize due to steric hindrance. Scheme 1 shows the PIB–PpMeSt diblock copolymer synthesis.

Since the diphenyl alkyl cation is more stable than the *p*-methylstyryl cation, the Lewis acidity can be decreased to a desired level by adding titaniumalkoxide to decrease the rate of homopolymerization and still maintain satisfactory crossover rates.

We have recently discovered that DPE adds to the living PIB chain end quantitatively [9]. Under the studied conditions ($TiCl_4$, MeCl/Hex, or MeCl/MeChx, 40/60 v/v, −80°C) only monoaddition occurred even when a large excess of DPE was used compared to the living PIB ends. The methanol quenched polymer of the DPE-capped PIB carried exclusively $-OCH_3$ functionality, suggesting that all diphenyl alkyl chain-ends are in a cationic form which was confirmed by conductivity studies [9]. This is in accordance with the results we reported for the living polymerization of St [10], pMeSt [11], and 2,4,6-triMeSt [12] using BCl_3.

After establishing conditions for the quantitative capping of PIB or TMPCl with DPE [9], the blocking step was modeled using DPE-capped TMPCl. The initiator efficiency that can be easily measured was used to predict crossover efficiency. The polymerizations were fast using MeCl/MeChx as well as using MeCl/Hex, but somewhat faster when MeCl/Hex was used. The conversions are shown as the function of polymerization time in Fig. 6. Using MeCl/Hex, the molecular



SCHEME 1

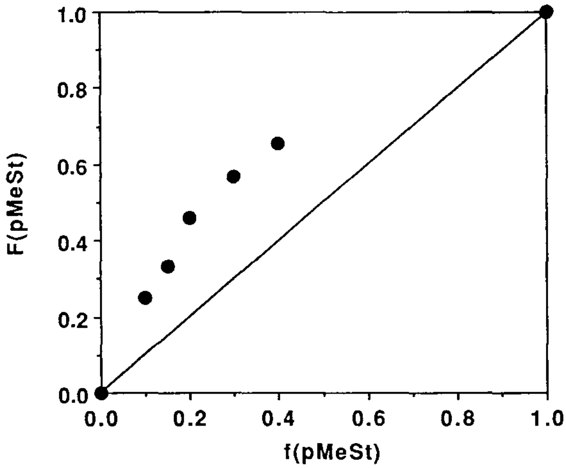


FIG. 5. Dependence of copolymer composition (F_{pMeSt}) on the comonomer feed composition (f_{pMeSt}) in the copolymerization of IB with pMeSt by the TMPCl/$TiCl_4$/MeCl:Hex, 40:60 v:v/ −80°C system in the presence of a proton trap.

weights were much higher than the theoretical values (Fig. 7), but lower than without DPE (cf. Fig. 4). Evidently the rate of initiation is still lower than that of propagation. Using MeCl/MeChx, I_{eff} approaches 100% at ~80% conversion. At lower than 80% conversions, however, the I_{eff}s are substantially lower. Therefore, decreasing the Lewis acid concentration or acidity is necessary to obtain controlled polymerization and theoretical molecular weights.

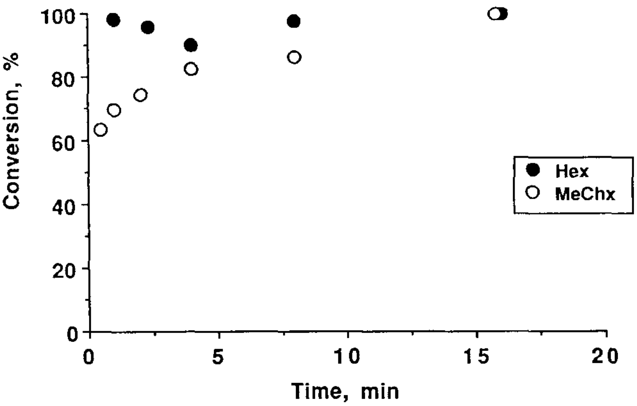


FIG. 6. Conversion vs time plot for the polymerization of pMeSt with DPE-capped TMPCl using the MeCl/Hex or MeChx 40/60 v/v solvent mixture at −80°C. $[\text{pMeSt}]_0$ = 0.35 M, [TMPCl] = 0.002 M, [DPE] = 0.00206 M, [DTBP] = 0.004 M.

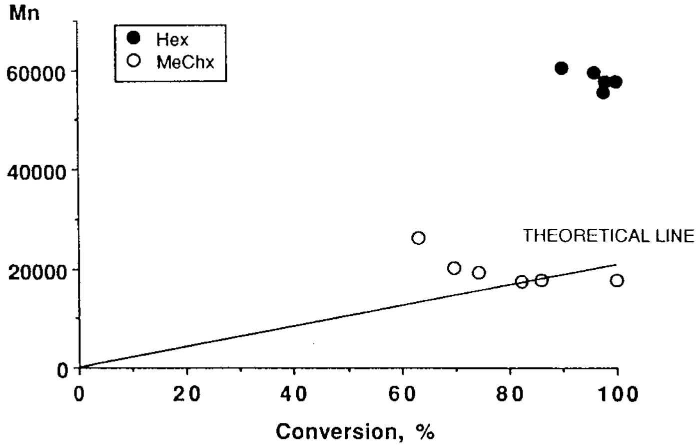


FIG. 7. Molecular weight vs conversion plot for the polymerization of pMeSt with the DPE-capped TMPCl/$TiCl_4$ system in the absence of tetraalkoxy titanium compounds using the MeCl/Hex or MeCl/MeChx 40/60 v/v solvent mixture at −80°C. $[pMeSt]_0 = 0.35$ M, [TMPCl] = 0.002 M, $[TiCl_4] = 0.0364$ M, [DPE] = 0.00206 M, [DTBP] = 0.004 M.

Experiments with Methylcyclohexane

In the following experiments, varying amounts of $Ti(IpO)_4$ or $Ti(BuO)_4$ were added 30 minutes after the addition of DPE to decrease the Lewis acidity. The monomer pMeSt was added last.

On addition of the tetraalkoxy titanium compounds, the orange color of the solution started fading. After a few minutes no further color change could be observed. In three separate experiments, pMeSt was introduced 5, 10, and 15 minutes after the $Ti(IpO)_4$ addition using $TiCl_4/Ti(IpO)_4 = 7$. Polymerization rates and molecular weights were practically the same, indicating that the equilibrium is reached in less than 5 minutes.

Experiments were designed to study the influence of the $TiCl_4/Ti(IpO)_4$ ratio on the polymerization of pMeSt at a constant $[TiCl_4] = 0.0364$ M concentration. The $\ln([M]_0/[M])$ vs time plots are shown in Figs. 8 and 9. The rate of the polymerization using the 7/1 $TiCl_4/Ti(IpO)_4$ ratio was similar to rates obtained with $TiCl_4$ alone. The increased overall Lewis acid concentration apparently compensated for the decreased acidity. Decreasing the $TiCl_4/Ti(IpO)_4$ ratio to 13/3, 3/1, 5/3, and 3/2 resulted in a corresponding decrease in the polymerization rate.

Experiments were also carried out with $Ti(BuO)_4$ using the $TiCl_4/Ti(BuO)_4$ 13/3 ratio (Fig. 8). The polymerization rate is somewhat higher using $Ti(BuO)_4$, i.e., it is a stronger Lewis acid compared to $Ti(IpO)_4$.

Although the polymerization is expected to be first order in monomer, the $\ln([M]_0/[M])$ vs time plots are not linear. Similar behavior was observed in all other experiments when the initiator DPE-capped TMPCl. This phenomenon has been observed before [10]. It indicates that a high ionicity of the initiating diphenyl heptyl carbenium ions will not instantaneously decrease to a lower ionicity corresponding to the growing PpMeSt chain end structure.

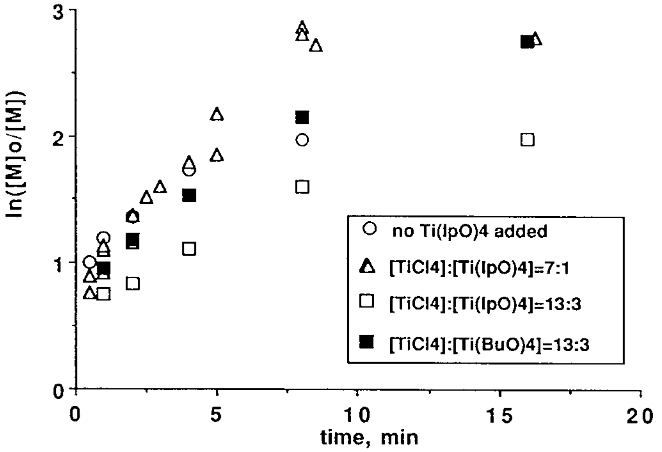


FIG. 8. Ln($[M]_0/[M]$) vs time plots for the polymerization of pMeSt with the DPE-capped TMPCl/$TiCl_4$:$Ti(IpO)_4$ or $Ti(BuO)_4$ system using the MeCl/MeChx 40/60 v/v solvent mixture at −80°C. [$TiCl_4$] = 0.0364 M, [DTBP] = 0.004 M, [TMPCl] = 0.002 M, [DPE] = 0.00206 M (reaction time, 30 minutes), $[M]_0$ = $[pMeSt]_0$ = 0.35 M.

The molecular weights vs conversion plots are shown in Figs. 10 and 11. The M_ns approach the theoretical line. It is difficult to obtain lower than 50% conversion using $TiCl_4/Ti(BuO)_4$ or $TiCl_4/Ti(IpO)_4$ ratios higher than 13/3 since the polymerization is very fast.

At lower $TiCl_4/Ti(IpO)_4$ ratios, close to theoretical molecular weights were obtained. In conclusion, lower Lewis acidity is necessary for the living polymerization of pMeSt with controlled M_n.

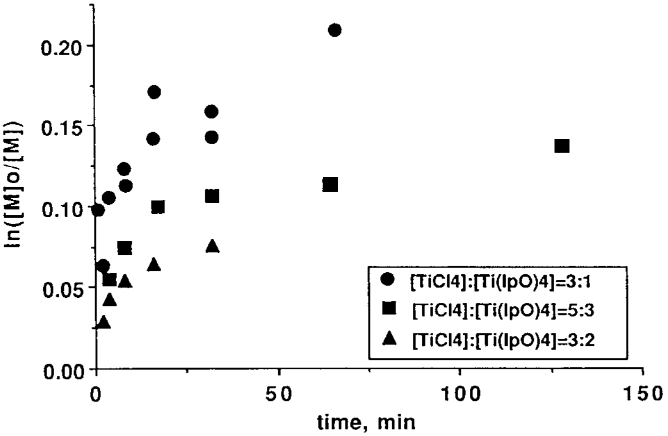


FIG. 9. Ln($[M]_0/[M]$) vs time plots for the polymerization of pMeSt with the DPE-capped TMPCl/$TiCl_4$:$Ti(IpO)_4$ system using the MeCl/MeChx 40/60 v/v solvent mixture at −80°C. $[M]_0$ = $[pMeSt]_0$. Other experimental conditions as in Fig. 8.

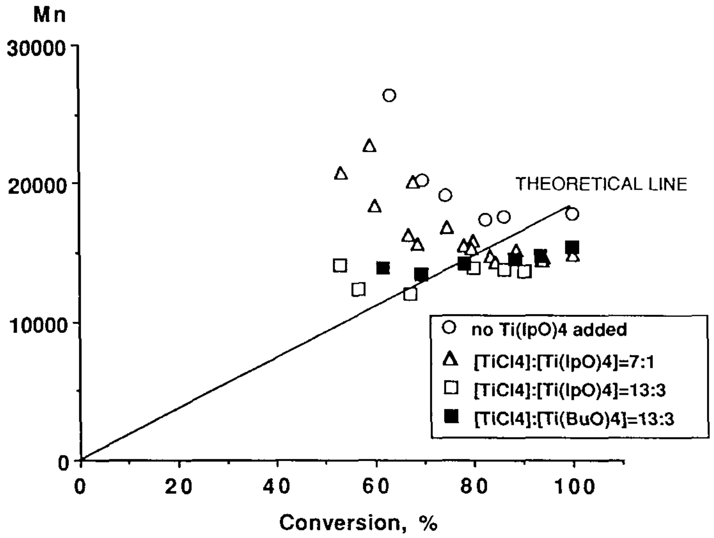


FIG. 10. Molecular weight vs conversion plot for the polymerization of pMeSt with the DPE-capped TMPCl/$TiCl_4$:$Ti(IpO)_4$ or $Ti(BuO)_4$/MeCl:MeChx 40:60 v:v/ −80°C system. For the other experimental conditions, see the legend of Fig. 8.

Experiments with Hexanes

Similar to results obtained with MeCl/MeChx, control experiments carried out in the absence of initiator using MeCl/Hex revealed that direct initiation is much slower than controlled initiation.

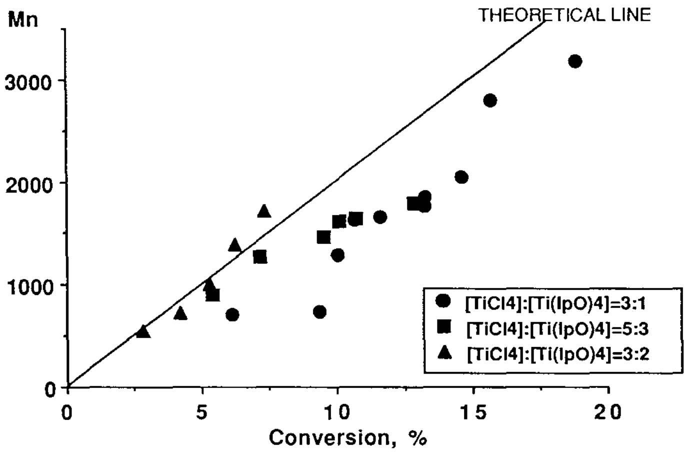


FIG. 11. Molecular weight vs conversion plot and the theoretical line for the polymerization of pMeSt with the DPE-capped TMPCl/$TiCl_4$:$Ti(IpO)_4$ system using MeCl/MeChx 40/60 v/v solvent at −80°C. For the other experimental conditions, see the legend of Fig. 8.

The polymerization rate with the DPE-capped TMPCl/$TiCl_4$:$Ti(IpO)_4$ 1:7/ MeCl/Hex system was higher compared to the MeCl/MeChx solvent system. The molecular weights were, however, substantially higher than the theoretical values (I_{eff} ~ 50%).

Since polymerization is faster using the MeCl/Hex solvent mixture compared to MeCl/MeChx under the same conditions, we further decreased the $TiCl_4$/$Ti(IpO)_4$ ratio to 25/7 and 3/1, and set the $Ti(BuO)_4$ ratio to 3/1. Since the polymerization rate with the $TiCl_4/Ti(IpO)_4 = 3$ ratio was too slow at $[TiCl_4] = 0.0364$ M, experiments with excess DPE were carried out with increased $TiCl_4$ concentration. The conversions are plotted against time in Fig. 12. According to the M_n-conversion plot in Fig. 13, there is good agreement between the observed molecular weights and the theoretical ones, i.e., I_{eff} ~ 100%.

To confirm that the 100% I_{eff} using TMPCl as initiator symbolizes complete crossover from PIBCl to pMeSt, PIB–PpMeSt diblock copolymers were prepared by sequential monomer addition using the MeCl/MeChx or MeCl/Hex solvent mixture and the 25/7 $TiCl_4$/$Ti(IpO)_4$ ratio. Control block copolymerization experiments by conventional sequential monomer addition were also carried out. The GPC traces of the products obtained in these control experiments are bimodal and indicate much lower than 100% blocking efficiency. The GPC traces for the MeCl/Hex solvent system are shown in Fig. 14. Similar bimodal distribution was obtained with the MeCl/MeChx system. The GPC traces of the products obtained according to our novel synthetic strategy using MeCl/MeChx are shown in Fig. 15. Similarly, the GPC traces were monomodal and shifted to higher molecular weights with increasing pMeSt conversion when the MeCl/Hex mixture was used. In Fig. 16 the RI and UV traces of the starting PIB homopolymer and the final diblock copolymer are shown. The UV response of the homo-PIB is due to the DPE end since PIB

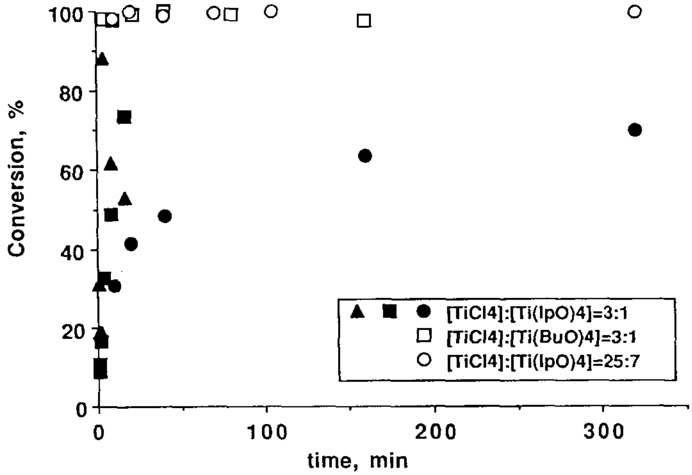


FIG. 12. Conversion vs time plots for the polymerization of pMeSt with the DPE-capped TMPCl/$TiCl_4$:$Ti(IpO)_4$ system using the MeCl/Hex 40/60 v/v solvent mixture at −80°C. $[Ti(IpO)_4] = [TiCl_4]/3$, (▲, ■ $[TiCl_4] = 0.056$ M). For the other experimental conditions, see the legend of Fig. 8.

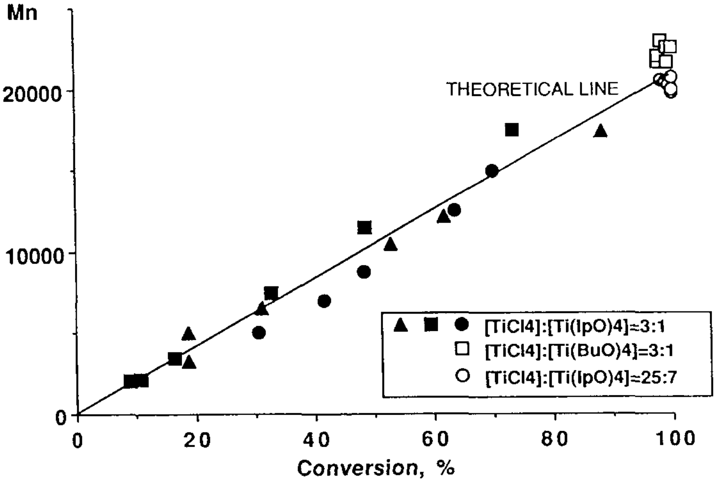


FIG. 13. Molecular weight vs conversion plots for the polymerization of pMeSt with the DPE-capped TMPCl/$TiCl_4$:$Ti(IpO)_4$ or $Ti(BuO)_4$ system using the MeCl/Hex 40/60 v/v solvent mixture at −80°C. [$Ti(IpO)_4$] = [$TiCl_4$]/3, (▲, ■ [$TiCl_4$] = 0.056 M), (▲ [DPE] = 0.004 M, ■ [DPE] = 0.006 M). For the other experimental conditions, see the legend of Fig. 8.

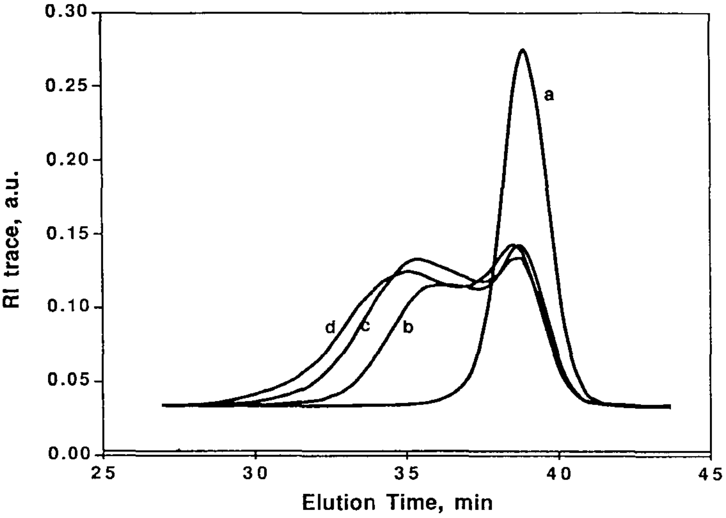


FIG. 14. MWD curves of PIB and PIB-PpMeSt diblocks obtained by the TMPCl/$TiCl_4$ initiating system using the MeCl/Hex 40/60 v/v solvent mixture at −80°C. (a) PIB, M_n = 12,000, M_w/M_n = 1.14. (b) PIB-PpMeSt, 1 minute, 53.6% pMeSt conversion. (c) PIB-PpMeSt, 2 minutes, 88.7% pMeSt conversion. (d) PIB-PpMeSt, 3 minutes, 98.3% pMeSt conversion. Other experimental conditions: [$TiCl_4$] = 0.0364 M, [DTBP] = 0.004 M, [TMPCl] = 0.002 M, $[pMeSt]_0$ = 0.35 M.

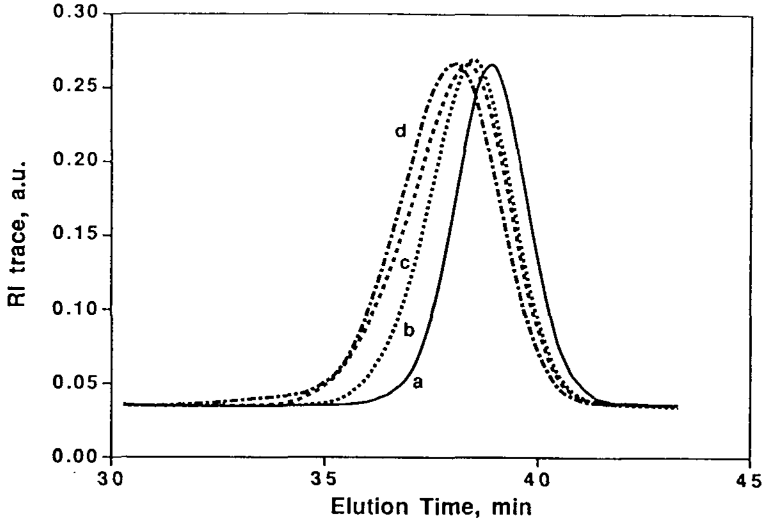


FIG. 15. MWD curves of the starting PIB and the PIB–PpMeSt diblocks at different polymerization times and pMeSt conversions prepared according to Scheme 1 using the MeCl/MeChx 40/60 v/v solvent mixture at −80°C. $[TiCl_4]/[Ti(IpO)_4]$ = 25/7. (a) PIB, M_n = 11,600, M_w/M_n = 1.16. (b) PIB–PpMeSt, 2 minutes, 22.3% pMeSt conversion. (c) PIB–PpMeSt, 8 minutes, 38.1% pMeSt conversion. (d) PIB–PpMeSt, 32 minutes, 47.0% pMeSt conversion. Other experimental conditions: $[TiCl_4]$ = 0.0364 M, [DTBP] = 0.004 M, [TMPCl] = 0.002 M, [DPE] = 0.00206 M, $[pMeSt]_0$ = 0.35 M.

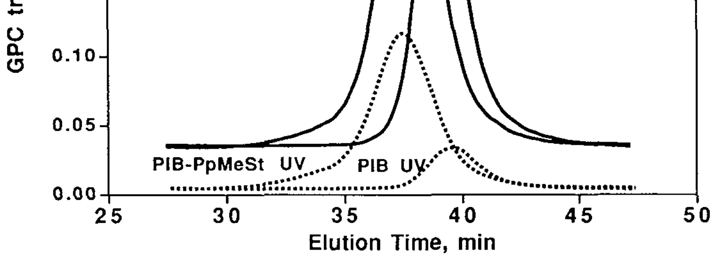


FIG. 16. RI and UV traces of the starting DPE-capped PIB and those of the PIB–PpMeSt diblock prepared according to Scheme 1 using TMPCl and the MeCl/Hex 40/60 v/v solvent mixture. For the other experimental conditions, see the legend of Fig. 15. PIB: M_n = 11,100, M_w/M_n = 1.16. PIB–PpMeSt: M_n = 18,800, M_w/M_n = 1.34.

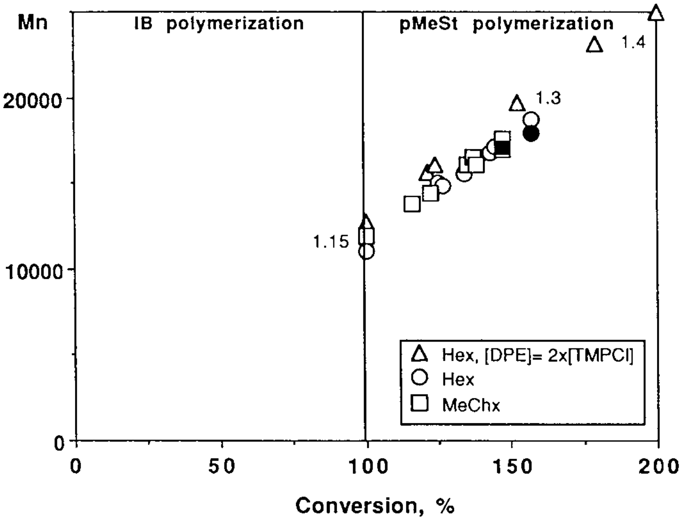


FIG. 17. M_n-conversion plot for the sequential block copolymerization of IB with pMeSt according to Scheme 1 using the MeCl/HX or MeChx 40/60 solvent mixture at −80°C. The filled symbols represent data obtained by a GPC on-line MALLS detector. The numbers are MWDs. IB polymerization: [TMPCl] = 0.002 M, [DTBP] = 0.00494 M, $[TiCl_4]$ = 0.0364 M, $[IB]_0$ = 0.354 M, V = 25 mL, polymerization time = 30 minutes, [DPE] = 1.03 × [TMPCl], V_{final} = 30.7 mL. Final concentrations: $[pMeSt]_0$ = 0.138 M, $[TiCl_4]$ = 0.0296 M, $[TiCl_4]/[Ti(IpO)_4]$ = 25/7, [DTBP] = 0.004 M.

initiated with TMPCl is UV transparent. After blocking, the RI trace as well as the UV trace is shifted toward higher molecular weights, and simultaneously the UV intensity is increased.

The molecular weight-conversion relationship is shown in Fig. 17. Both the PIB and PpMeSt segment lengths were planned to be 10,000 daltons. Although the I_{eff} for the IB polymerization is somewhat lower than 100% (~85%), the M_n-conversion plot after pMeSt addition is linear and can be extrapolated back to zero, indicating that the polymer concentration remains constant. The M_ns were identical within 3% based on PIB as well as on PSt calibration. Representative diblock samples were also measured using a GPC on-line MALLS detector (filled symbols in Fig. 17); the M_ns obtained from laser light scattering were about 6% lower.

In the next paper we will report on the preparation of PpMeSt-PIB-PpMeSt triblock copolymers using our novel synthetic strategy [13] and on the characterization of these thermoplastic elastomers.

ACKNOWLEDGMENTS

This material is based on research supported by the Exxon Chemical Company. Acknowledgment is also made to the Center for Environmentally Appropriate Materials of the University of Massachusetts for partial support.

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Received November 20, 1993
Revision received February 18, 1994