Polyisobutylene-Based Thermoplastic Elastomers. 5. Poly(styrene-*b*-isobutylene-*b*-styrene) Triblock Copolymers by Coupling of Living Poly(styrene-*b*-isobutylene) Diblock Copolymers

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ABSTRACT: Poly(styrene-*b*-isobutylene-*b*-styrene) (PSt−PIB−PSt) triblock copolymers have been prepared for the first time via coupling of living PSt-PIB diblock copolymers in a one-pot procedure. The PSt−PIB diblock copolymer was synthesized by living sequential cationic polymerization in methylcyclohexane (MeChx)/methyl chloride (MeCl) or hexane (Hex)/MeCl solvent mixtures at −80 °C using $TiCl_4$ as co-initiator. It was found that, due to decomposition of the living PSt ends, the crossover efficiency (C_{eff}) from living PSt to IB decreases precipitously with time at close to 100% St conversion. To obtain high C_{eff}, IB must therefore be added at ≤95% St conversion. It was also found that in the presence of unreacted St the rate of IB block copolymerization decreases with time; this was attributed to the formation of relatively unreactive −St−IB−Cl ends. Due to the relatively high concentration of these ends, coupling of living PSt−PIB was slow and incomplete. The obtained PSt−PIB−PSt triblock copolymers exhibited reasonable but significantly lower tensile strength (16−20 MPa) than that (23−25 MPa) reported for model PSt−PIB−PSt triblock copolymers of similar composition.

Introduction

One of the most appealing features of living polymerizations is the ability to construct block copolymers by sequential block copolymerization. Since the discovery of the living cationic polymerization of isobutylene (IB),[1] the synthesis of ABA type triblock copolymer thermoplastic elastomers (TPEs) with a saturated and therefore highly stable polyisobutylene (PIB) middle block has been a desirable objective.

Following the successful synthesis of poly(styrene-*b*-isobutylene-*b*-styrene) (PSt−PIB−PSt) by living cationic sequential block copolymerization,[2] PIB-based TPEs where St was replaced with other styrenic monomers such as *p*-chlorostyrene,[3] *p*-*tert*-butylstyrene,[4] indene,[5] etc. have also emerged. The synthesis and properties of these TPEs have been reviewed recently.[6] The synthetic procedure invariably involved a bifunctional initiator in conjunction with $TiCl_4$ for the living polymerization of IB, followed by sequential addition of the styrenic monomer in a moderately polar solvent or solvent mixture at low temperatures (−80 to −90 °C). However, this technique failed to yield triblock copolymers with high structural integrity for *p*-methylstyrene and α-methylstyrene because of the unfavorable crossover rate relative to the polymerization rate of the styrenic monomer. This was circumvented by capping the living PIB end with 1,1-diphenylethylene (DPE) or 1,1-ditolylethylene (DTE) and then moderating the Lewis acidity before the addition of the second monomer.[7,8] Although this technique has been shown to be highly effective for the synthesis of a variety of di- or triblock copolymers,[9] we were intrigued by the general lack of effort to construct triblock copolymers by another method widely practiced in living anionic polymerization, namely the coupling of living diblock copolymers. The reason most probably is that while simple and efficient coupling agents are readily available in living anionic polymerization, effective coupling agents have not been reported for living cationic polymers until recently.

We have recently reported the extension of the synthetic utilization of non-(homo)polymerizable monomers such as bis-DPE and bis-furanyl compounds for the living coupling reaction of living PIB.[9,10] Using 2,2-bis[4-(1-phenylethenyl)phenyl]propane (BDPEP), 2,2-bis[4-(1-tolylethenyl)phenyl]propane (BDTEP), or certain bis-furanyl compounds as coupling agents, a rapid and quantitative coupling reaction of living PIB was achieved independently of the molecular weight of PIB. Kinetic studies indicated that 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.[10] 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 PSt−PIB−PSt block copolymers by coupling of living PSt−PIB diblock copolymers.

The synthesis of PSt−PIB diblock copolymers as intermediates for the synthesis of star block copolymers, using divinylbenzene as a linking agent, has been reported recently.[11,12] The two procedures were similar; first, St was polymerized with the cumyl chloride/$TiCl_4$ initiating system in the presence of pyridine or triethylamine in Hex (or MeChx)/MeCl 60/40 v/v or Hex/dichloromethane 50/50 v/v at −80 °C. At near quantitative St conversion the desired amount of IB was added and polymerized to obtain the PSt−PIB block copolymer arm. Although GPC traces of the products clearly indicated less than complete crossover from PSt^+ to IB,[12] the weight fraction of homoPSt was found to be negligible by selective solvent extraction.[11,12] This may not however indicate efficient blocking, since the PSt segment was generally much shorter than the PIB segment. The SEC UV trace, which would provide quantitative information on the efficiency of blocking, was not shown.

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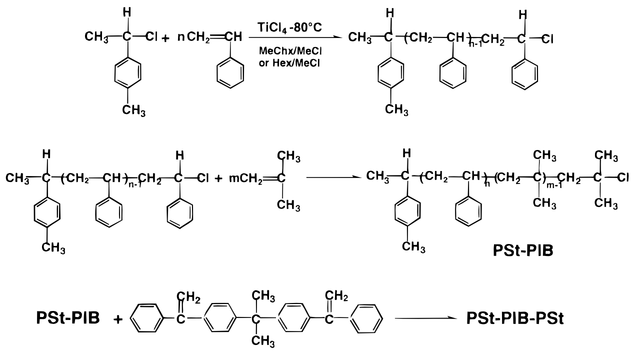
Scheme 1



In light of the lack of quantitative information, in this study we carried out a more detailed investigation on the synthesis of PSt−PIB diblock copolymer. Our goal was to identify optimum conditions for the coupling reaction to yield PSt−PIB−PSt triblock copolymer TPE (Scheme 1), which are reported herein.

Experimental Section

Materials. 1,3-Diphenyl-1-chlorobutane (DiSt·HCl) was synthesized by the hydrochlorination of olefinic St dimer, which was made by Rosen's method.[13] The St dimer was dissolved in olefin free dry Hex (1/7 v/v), and at −78 °C dry HCl was bubbled through the solution for 48 h. DiSt·HCl, a white precipitate, was was filtered on a glass filter at −78 °C and washed with prechilled, dry olefin-free hexane. The raw product was recrystallized from hexane at −78 °C (yield ∼ 25%). $M_p = 45{-}46.5$ °C. ^{1}H NMR: d = 1.34 (2H, $-CH_3$), 2.32 (16H, $-CH_2-$), 3.12 (6H, $-CH(C_6H_5)Cl$), 4.59 (4H, $CH_3CH(C_6H_5)$), 7.29 (10H, $-C_6H_5$). The ^{1}H NMR spectrum of the purified DiSt·HCl suggests that the product is one of the two diastereomers (one pair of enantiomers); apparently the other is soluble in Hex.

1-Chloro-1-(*p*-methylphenyl)ethane (pMeSt·HCl) was obtained from *p*-methylstyrene (DELTECH Corp.) by hydrochlorination in dichloromethane at −80 °C for 24 h. pMeSt·HCl was purified by vacuum distillation. 2,2-Bis[4-(1-phenylethenyl)phenyl]propane (BDPEP) was synthesized according to ref 10. All other chemicals and solvents were purified as described previously[14] or used as received.

Polymerization. All polymerizations were carried out under a dry nitrogen atmosphere in a Mbraun 150-M glovebox (Innovative Technology Inc., Newburyport, MA). Large (75 mL) culture tubes were used as polymerization reactors. The total volume of the reaction mixture was 25 mL. The initiator pMeSt·HCl was dissolved in Hex or methylcyclohexane (MeChx) at room temperature. The solution was then cooled to −80 °C, and MeCl, monomer, and proton trap 2,4-di-*tert*-butylpyridine (DTBP) were added. $TiCl_4$ dissolved in Hex or MeChx was added last.

The polymerization of St was carried out using the following concentrations: [pMeSt·HCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.0035 M, [St] = 0.288 M.

For the synthesis of PStCl with low (L) M_n (PSt_LCl) the pMeSt·HCl (0.02 M)/$SnCl_4$ (0.1 M) initiation system was used to polymerize St (0.2 M) in dichloromethane in the presence of nBu_4NCl (0.04 M) and DTBP (0.005 M) at −15 °C for 90 min.[15] The product was washed with 1 M aqueous HCl solution, precipitated by methanol, and dried in a vacuum oven.

For the synthesis of PSt−PIB diblock copolymer, St (0.288 M) was polymerized by pMeSt·HCl (0.002 M) and $TiCl_4$ (0.036 M) initiating system in MeChx/MeCl or Hex/MeCl at −80 °C in the presence of DTBP (0.0035 M) to reach ≥90% St conversion, and then IB (1.54 M) was added and polymerized for 120 min.

For the preparation of PSt−PIB−PSt triblock copolymer, BDPEP ([BDPEP]/[PSt−PIB] = 0.5) in MeChx/MeCl or Hex/MeCl at −80 °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. To accurately determine the coupling efficiency (CP_{eff}), the diblock copolymer as well as the products obtained after coupling was purified by dissolution/precipitation in dichloromethane/acetone to remove homoPSt.

Living PSt−PIB was also synthesized using 2.5-fold higher concentration of initiator and monomer: [pMeSt·HCl] = 0.005 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.0035 M, [St] = 0.72 M in MeChx/MeCl 60/40 v/v. St was polymerized first for 60 min at −80 °C, and then IB ([IB] = 3.0 M) was added and polymerized for 60 min ($C_{eff} \sim 85\%$). After dilution with MeChx/MeCl (to 50/50 v/v) and addition of $TiCl_4$ (to maintain [$TiCl_4$] = 0.036 M during coupling), BDPEP was added at [BDPEP]/[PSt−PIB] = 0.5.

The statistical copolymerization of IB (1.54 M) and St (0.0288 M) was carried out by DiSt·HCl (0.002 M) and TMPCl (0.002 M) in Hex/MeCl 50/50 v/v at −80 °C. The compositions of the copolymers were analyzed by using the GPC UV/RI peak area ratio to obtain relative St contents. The relative St contents were then correlated with ^{1}H NMR spectroscopic results (using 99.96% $CDCl_3$) of representative samples to obtain the absolute St content.

Stress−strain measurements were obtained according to ASTM D412. The test samples were compression molded for 15 min at 160 °C.

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-Styragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. THF was used 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_{eff}) was calculated using Peak fit software (Jandel Scientific, fitting function: Chromatography and EMG+GMG). Absolute molecular weights of representative samples were also measured using a Minidawn (Wyatt Technologies Inc.) GPC online multiangle laser light-scattering (MALLS) detector. The M_ns of the diblock copolymers and coupled products were calculated by assuming additivity of the d*n*/d*c* values. NMR spectroscopy was carried out on a Bruker 250 MHz instrument.

Results and Discussion

1. The Polymerization of St by pMeSt HCl/$TiCl_4$ in MeChx/MeCl and Hex/MeCl.

In a previous report,[14] we described the living polymerization of St with the TMPCl/$TiCl_4$/ MeChx:MeCl 60:40 v:v/−80 °C polymerization system in the presence of DTBP. Since initiation from TMPCl was found to be slow, on the basis of preliminary studies, pMeSt·HCl was selected as initiator for this investigation in conjunction with $TiCl_4$ in the presence of DTBP in MeChx/MeCl or Hex/MeCl solvent mixtures at −80 °C. Initiator and co-initiator concentrations identical to those used in the earlier report were chosen since direct initiation has been shown to be negligible at these concentrations. The theoretical molecular weight of PSt ($M_{n,theo}$ = 15 000) at complete monomer conversion was designed on the basis of our earlier finding that PSt−PIB−PSt triblock copolymers with PSt end segments of $M_n \geq 15\,000$ form well-defined microdomains without phase mixing and yield the best mechanical properties.

The M_n and M_w/M_n vs conversion plots are shown in Figure 1 for the MeChx/MeCl 60/40, 50/50, and 40/60 and the Hex/MeCl 50/50 v/v solvent systems. At all four solvent compositions the M_ns are close to the theoretical line. The polydispersities decrease with increasing

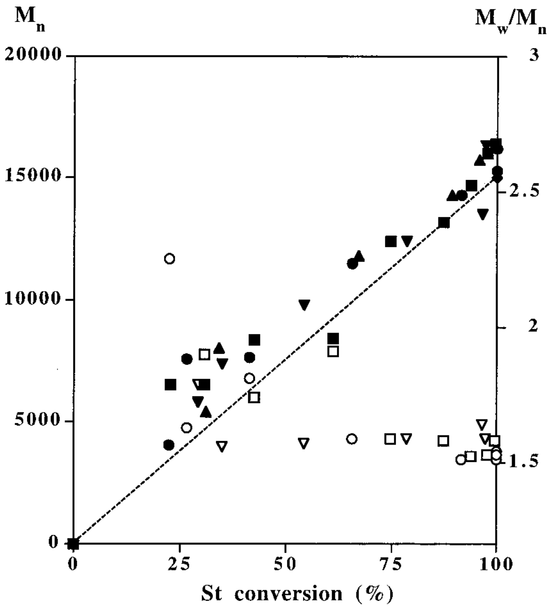


Figure 1. M_n (filled points) and M_w/M_n (open points) vs conversion plots for the polymerization of St at −80 °C: (■, □) MeChx/MeCl 60/40 v/v; (●, ○) MeChx/MeCl 50/50 v/v; (▲, △) MeChx/MeCl 40/60 v/v; (▼, ▽) Hex/MeCl 50/50 v/v.

Table 1. M_n and M_w/M_n for PSt Obtained at Extended Polymerization Time[a]

no.	solvent	pzn time (min)	M_n	M_w/M_n
1	MeChx/MeCl 50/50v/v	40	16 200	1.51
2	MeChx/MeCl 50/50v/v	60	16 900	1.53
3	MeChx/MeCl 50/50v/v	120	17 400	1.62
4	MeChx/MeCl 40/60v/v	30	17 900	1.53
5	MeChx/MeCl 40/60v/v	40	18 300	1.54
6	MeChx/MeCl 40/60v/v	60	17 600	1.66
7	Hex/MeCl 50/50v/v	40	15 400	1.84
8	Hex/MeCl 50/50v/v	60	15 200	2.0

[a] [pMeSt·HCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.0035 M, [St] = 0.288 M, at −80 °C. St conversions are complete.

Table 2. Apparent Propagation Rate Constants (k_{app}s, min^{-1}) of St Polymerizations[a]

solvent v/v	MeChx/MeCl 60/40	MeChx/MeCl 50/50	MeChx/MeCl 40/60	Hex/MeCl 50/50
k_{app}	0.049	0.106	0.160	0.127

[a] [pMeSt HCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.0035 M, [St] = 0.288 M, at −80 °C.

conversion, as often encountered in living cationic polymerizations (generally attributed to slow exchange between dormant and living centers) and reach ~1.5–1.6 above 50% conversion.

Intermolecular alkylation was found to be negligible at all solvent compositions up to ~10 half-lives of the monomer, as the M_ns remained constant with time after complete monomer consumption (Table 1). This is in accord with previous findings using similar low St concentrations.[12,14] The first-order plots (not shown) could be fitted with a linear up to $\ln([M]_0/[M]) \sim 3.0$ (~95% conversion); consequently, termination is undetectable in this region. The apparent rate constants ($k_{app} = k_p[P^+]$, where $[P^+]$ is the concentration of PSt^+ active centers) are listed in Table 2. In agreement with a commonly observed trend, k_{app} increases with increasing solvent polarity attributed to the corresponding increase in $[P^+]$. Similarly to earlier reports,[12,16] slightly higher k_{app} is observed when MeChx is replaced with Hex.

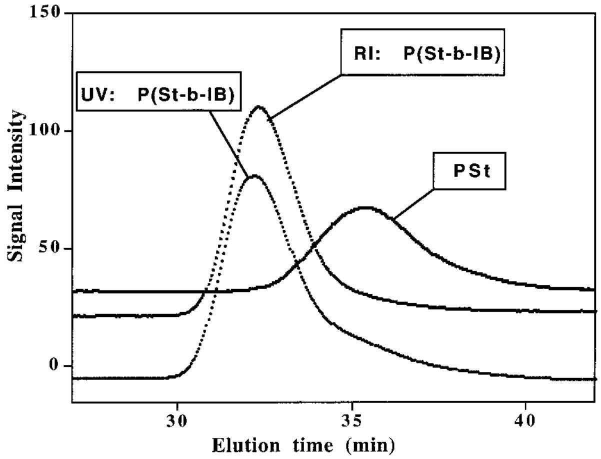


Figure 2. GPC traces of original PSt and PSt–PIB diblock copolymer obtained in MeChx/MeCl 50/50 v/v.

Experiments were also conducted with the Hex/MeCl 60/40 v/v ratio, but this solvent mixture was found to be a poor solvent for PSt as above 50% monomer conversion polymer precipitation was observed visually. Concurrently, the molecular weight distributions became bimodal (the peak at lower M_n corresponding to precipitated PSt remained unchanged with St conversion), and the first-order plot started to deviate from linearity. Further experimentation with the Hex/MeCl 60/40 v/v solvent mixture was therefore discontinued.

2. The Effect of St Conversion on the Crossover Efficiency (C_{eff}). We have recently reported[17] that in MeChx/MeCl 50/50 v/v at −80 °C at close to complete monomer conversion the PSt living centers undergo a slow decomposition. The decomposition rate was found to be independent of the M_n of PSt, indicating that the mechanism (which is still under investigation) is not intermolecular alkylation. The addition time of IB is therefore critical to the synthesis of PSt–PIB diblock copolymers with high crossover efficiency. This was investigated in the next series of experiments where St was polymerized for various times to reach different St conversions at ≥90%, and IB was then added and polymerized for 120 min. The products were analyzed by GPC with double detection (UV and RI). Representative GPC traces are shown in Figure 2.

Although the presence of homoPSt is hardly visible from the RI trace, it is conspicuous in the UV trace of the product after blocking, since PIB is UV transparent. The crossover efficency was calculated from the UV trace of the product obtained after the sequential block copolymerization of IB according to the equation

$$C_{eff}(\%) = A_{block} \times 100/(A_{block} + A_{PSt})$$

where A_{block} is the peak area corresponding to the PSt–PIB block copolymer and A_{PSt} is the peak area corresponding to homoPSt obtained by peak deconvolution. Representative samples were also analyzed by selective solvent extraction of homoPSt using acetone. The two methods yielded practically identical (±5%) crossover efficiencies. The C_{eff} and St conversion vs time plots for the MeChx/MeCl and Hex/MeCl 50/50 v/v solvent mixture are shown in Figure 3. (Similar plots with slightly higher polymerization rate were obtained for the MeChx/MeCl 40/60 v/v solvent mixture.) For comparison, we also plotted (without showing the actual data points) the percentage of remaining living PSt end that was

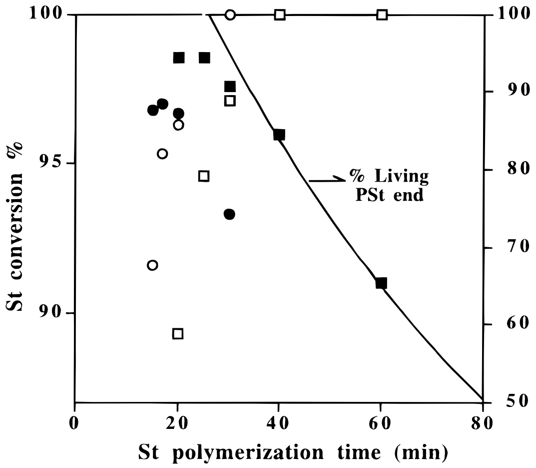


Figure 3. Conversion of St (open points) and C_{eff} (filled points) as a function of St polymerization time before addition of IB: (■, □) MeChx/MeCl 50/50 v/v; (●, ○) Hex/MeCl 50/50 v/v. The solid line (data points not shown) was obtained in MeChx/MeCl 50/50 v/v, by adding a second increment of St instead of IB.[17]

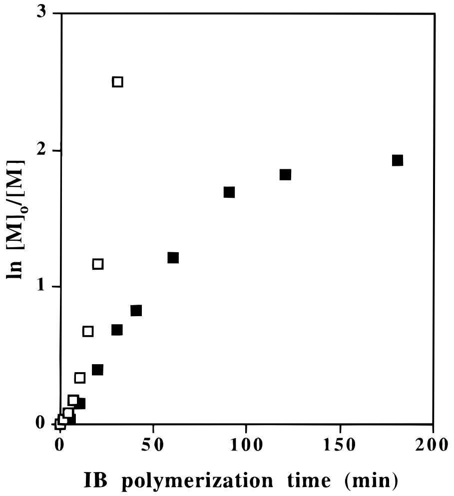


Figure 4. First-order plots for the polymerization of IB in Hex/MeCl 50/50 v/v at −80 °C: (□) IB polymerization by DiSt·HCl; (■) IB block copolymerization.

obtained in MeChx/MeCl 50/50 v/v under identical conditions, but instead of adding IB as the second monomer, a second increment of St was added.[17] The two curves for this solvent mixture are virtually identical, indicating that the decomposition of PSt living ends is the only reason for the decreased C_{eff}s with increasing time of IB addition. The polymerization rate is somewhat higher in the Hex/MeCl 50/50 v/v solvent mixture, as the conversion vs time plot is shifted to the left. However, the C_{eff} vs time plot is also shifted to the left; i.e., chain end decomposition is also faster. Therefore, it is necessary to add IB at <95% conversion to ensure high C_{eff}s independently of the solvent composition.

3. The Effect of Unreacted St on the Polymerization of IB. 3.1. Block Copolymerization of IB. During the study reported above, we found that the rate of IB block copolymerization is much lower than that of IB homopolymerization. In Figure 4, the semilogarithmic kinetic plots for the polymerization of IB initiated from DiSt·HCl and from living PSt are shown. The plot obtained with DiSt·HCl shows an upward curvature indicating slow initiation, which is confirmed by the curved M_n vs conversion plot (Figure 5). Slow initiation is also expected from living PSt but could not be confirmed. Due to a relatively broad molecular weight distribution of the starting PSt the GPC traces of the products which were monomodal after block copolymerization could not be separated into PSt-PIB and unreacted homoPSt. Physical separation also failed due to the similar solubility of homoPSt and PSt-PIB with a short PIB segment.

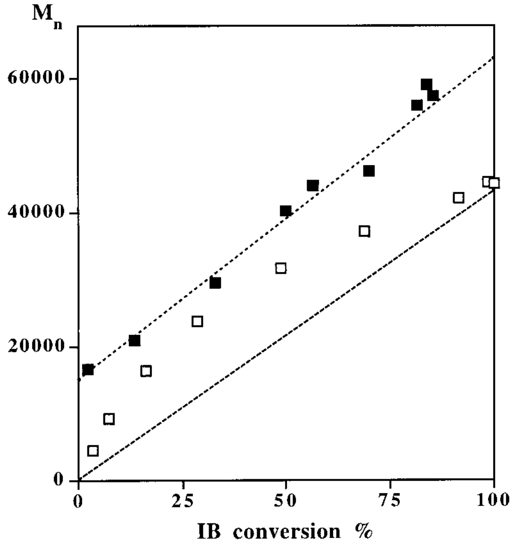


Figure 5. M_n vs IB conversion plot in IB polymerization and in block copolymerization. Other experiment conditions are shown in Figure 4.

On the basis of the kinetic plots in Figure 4, it appears that the homopolymerization of IB from DiSt·HCl is much faster compared to the copolymerization of IB and a small amount of unreacted residual St initiated by living PSt. The ln([M]$_0$/[M]) vs time plot for block copolymerization exhibits a similar initial slope but a downward curvature, which suggests either decreasing cation concentration and/or reactivity with time. A similar finding has been reported for the polymerization of indene initiated by TMPCl or living PIB by Kennedy et al.[5] and attributed to a decreased diffusion rate of indene through the PIB coil. As will be clear from the following, the explanation of our findings is quite different and analogous to that reported by Storey and Chisholm[18] for the block copolymerization of St from living PIB. Figure 6 shows the semilogarithmic kinetic plots (ln[M]$_0$/[M] vs time) for the polymerization of IB initiated by DiSt·HCl, living PSt, and two isolated chloro-terminated PSt, (PStCl) one with higher (H) and one with lower (L) M_n. $\mathrm{PSt_HCl}$ (M_n = 12 400, M_w/M_n = 1.57) was obtained by living polymerization of St using the pMeSt·HCl/$TiCl_4$ initiating system at −80 °C and quenching with methanol at ~90% conversion. It was made free of unreacted St by repeated precipitation into methanol. $\mathrm{PSt_LCl}$ (M_n = 1010, M_w/M_n = 1.08) was obtained using the $SnCl_4$ initiating system in CH_2Cl_2 at −15 °C.[15] It was isolated and purified. From Figure 6 it is apparent that the low rate of IB block copolymerization is due to the presence of unreacted St. When unreacted St is removed, the rate closely matches that observed with DiSt·HCl or $\mathrm{PSt_LCl}$. Importantly, slow initiation was confirmed by the curved M_n vs conversion plot obtained with $\mathrm{PSt_LCl}$, which was practically identical to that determined with DiSt·HCl, shown in Figure 5.

3.2. Statistical Copolymerization of St with IB. To clarify that the decreased polymerization rate is due

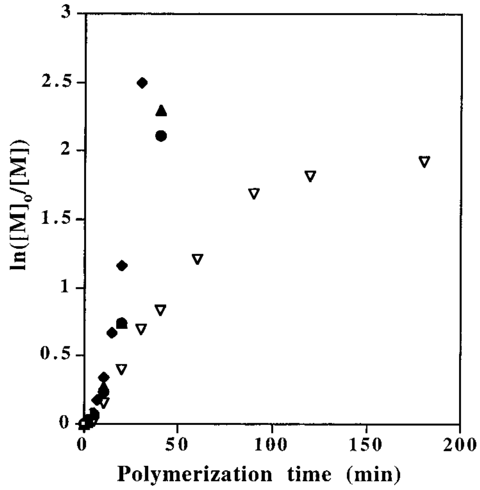


Figure 6. First-order plots for the polymerization of IB in Hex/MeCl 50/50 v/v at −80 °C. [DiSt·HCl] = [PSt_LCl] = [PSt_HCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.0035 M, [IB] = 1.54 M. (◆) IB polymerization initiated by DiSt·HCl, (●) PSt_LCl, (▲) PSt_HCl, (▽) PStCl synthesized in situ.

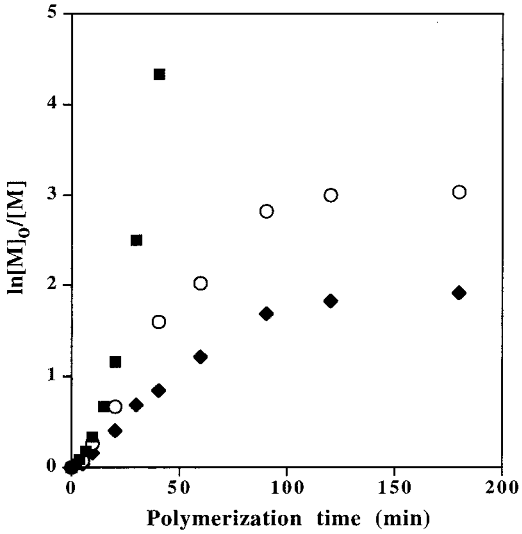


Figure 7. First-order plots for the homopolymerization and block copolymerization of IB and for the statistical copolymerization of IB with St, in Hex/MeCl 50/50 v/v at −80 °C: (■) IB homopolymerization by [DiSt·HCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.0035 M, [IB] = 1.54 M. (■) IB and St statistical copolymerization with [IB] = 1.54 M and [St] = 0.0288 M; (◆) IB block copolymerization.

to the presence of unreacted St, statistical copolymerization of IB and St was carried out using [IB] = 1.54 M and [St] = 0.0288 M (i.e., 3.4 wt %), with DiSt·HCl/$TiCl_4$ in Hex/MeCl (50/50 v/v) at −80 °C. This amount of St is approximately equivalent to the remaining unreacted St at the time of IB addition in the synthesis of PSt−PIB diblock copolymer.

The $\ln[M]_0/[M]$ vs time plot for the statistical copolymerization of IB/St is shown in Figure 7. The corresponding plots for the homopolymerization of IB using identical conditions and for the block copolymerization of IB from living PSt are also shown for comparison. It is evident that the statistical copolymerization of IB/St is much slower than the homopolymerization of IB, and the tendency is similar to that observed in the block copolymerization of IB. The slight difference between IB/St statistical copolymerization and IB block copolymerization from living PSt may be caused by a higher amount of unreacted St monomer in the later system. In conclusion, the main reason for the low rate of the IB block copolymerization is the presence of unreacted St monomer when IB is added.

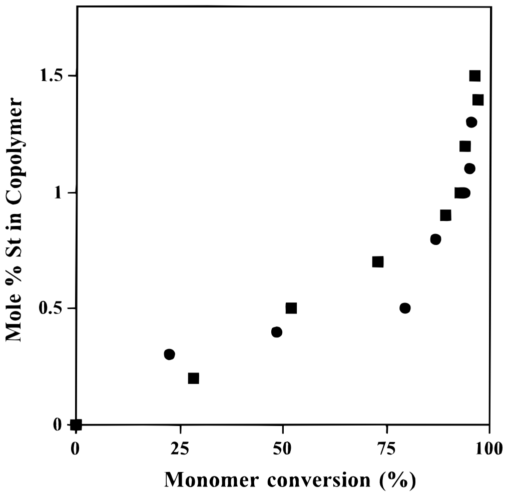


Figure 8. Mole percent St in the copolymer as a function of total monomer conversion for statistical copolymerization of IB and St in Hex/MeCl 50/50 v/v at −80 °C. [IB] = 1.54 M, [St] = 0.0288 M. (■) [TMPCl] = 0.002 M, (●) [DiSt·HCl] = 0.002 M; two St units due to initiator segment were deducted.

In Figure 8 the mole percent of St in the copolymer is plotted against the conversion. It is clear that very little St is copolymerized before 50% conversion. This explains why, at the early stage, the rate of IB/St statistical copolymerization is similar to that of IB homopolymerization. Figure 8 may be surprising, but it is in line with the reported reactivity ratios (*r*) according to the instantaneous copolymer composition equation. Using $TiCl_4$ in Hex/MeCl 60/40 v/v at −80 °C $r_{IB} = 5.9 \pm 1.8$ and $r_{St} = 5.7 \pm 1.9$ have been determined by us previously.[14] When $[St] \ll [IB]$, the instantaneous copolymer equation can be simplified (eq 1)

$$\frac{d[St]}{d[IB]} = \frac{[St]}{r_{IB}[IB]} \qquad (1)$$

Thus, according to eq 1, at low conversion the molar ratio of St/IB in the copolymer will be only about one-sixth of that in the feed. The St content will increase with the conversion, but IB and St will disappear at similar rates only when their concentration will be approximately equal (i.e., at the very end of the copolymerization). Equation 1 is based on the assumption that the reactivity of the chain end is not affected by the penultimate monomer unit. This assumption may or may not be valid, as will be discussed later.

4. The Effect of Unreacted St on the Coupling Reaction of Living PSt−PIB. In the foregoing sections we have discussed conditions under which PSt−PIB diblock copolymer with negligible homoPSt contamination can be produced by sequential block copolymerization. In situ coupling of the living PSt−PIB diblock copolymer is the last step to complete the triblock copolymer synthesis. Coupling experiments were carried out using BDPEP in MeChx/MeCl and Hex/MeCl 50/50 v/v at −80 °C. Samples were taken before and after addition of BDPEP to measure coupling efficiency (CP_{eff}) and coupling rate. GPC chromatograms of the coupled products remained monomodal and showed a clean shift to higher molecular weight with

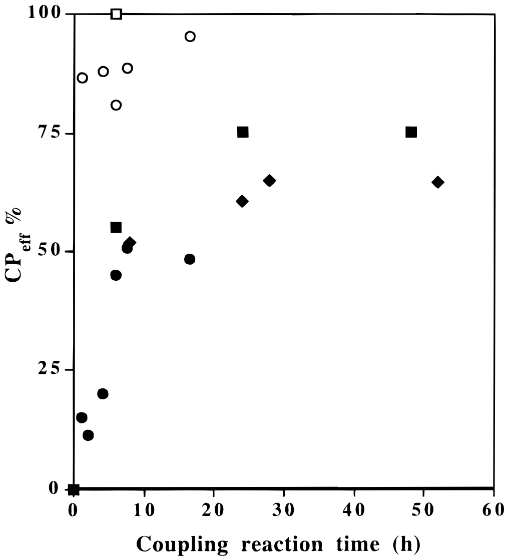


Figure 9. CP_{eff} vs coupling reaction time plot. [BDPEP]/[PIBCl] = 0.5. (■) PSt−PIB synthesized in Hex/MeCl 50/50 v/v; (◆) PSt−PIB synthesized in MeChx/MeCl 50/50 v/v; (●) IB/St statistical copolymer synthesized by [TMPCl] = 0.002 M, [IB] = 1.54 M, [St] = 0.0288 M in MeChx/MeCl 50/50 v/v; (□) PSt−PIB synthesized using [pMeSt·HCl] = 0.005 M, [St] = 0.72 M, [IB] = 3.0 M, and the reaction mixture was diluted to [PSt−PIB] = 0.002 M before coupling; (○) data from ref 10.

increasing coupling reaction time, indicating the progress of coupling. The coupling efficiency (CP_{eff}) was calculated from the total number-average molecular weight (M_{nt}) of the product according to the following equations:

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

where a is the mole fraction of uncoupled diblock, and $1 - a$ is the mole fraction of coupled diblock. M_{nt} can be obtained from the molecular weight of uncoupled PSt−PIB (M_{nu}) as

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

and therefore

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

The plot of CP_{eff} vs coupling reaction time is shown in Figure 9. For comparison, the results for coupling living homoPIB in Hex/MeCl 60/40 v/v[10] are also plotted. Similarly, rapid coupling was observed in MeChx/MeCl 60/40 v/v (CP_{eff} = 90% in 6 h). It is apparent that coupling of living PSt−PIB is very slow ($CP_{eff} \sim 80\%$ in 50 h in Hex/MeCl 50/50 v/v) compared to coupling of living homoPIB (~90% in 6 h).

Considering the low polymerization rate of IB in the presence of St monomer, the low coupling rate may also be attributed to the presence of unreacted St monomer. To verify this hypothesis, the coupling reaction of living IB/St statistical copolymer was carried out. IB and St were copolymerized by the TMPCl/$TiCl_4$ initiating system in MeChx/MeCl 50/50 v/v at −80 °C After 3 h copolymerization time, a sample was taken for M_n determination, and prechilled BDPEP ([BDPEP]/[TMPCl] = 0.5) in MeChx/MeCl 50/50 v/v was introduced to effect coupling. The CP_{eff} vs coupling reaction time plot (also shown in Figure 9) reveals that, as in the coupling of living PSt−PIB, the CP_{eff} increases slowly and remains low even after 15 h. These results confirm that the cation concentration and/or reactivity of the living IB/St statistical copolymer is different from that of living homoPIB; i.e, the chain end structure is different.

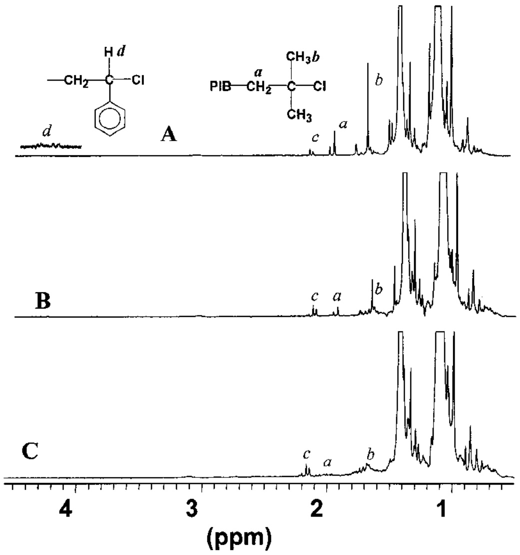


Figure 10. ^1H NMR spectra of IB/St statistical copolymers with low M_n. [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.0035 M, [IB] = 0.07 M, Hex/MeCl 50/50 v/v at −80 °C. (A) [St]/[IB] = 0.029 M, (B) [St]/[IB] = 0.060 M, (C) [St]/[IB] = 0.10 M.

It is apparent from the above discussion that to achieve high CP_{eff} and coupling rate, St should be completely polymerized before IB addition. However, this decreases the C_{eff} due to chain end decomposition. Since propagation is a bimolecular reaction and decomposition of living PSt end is assumed to be a unimolecular reaction, the ratio between the two can be increased by using high initiator and monomer concentration. Thus, for example, increasing the initiator and monomer concentration 2.5-fold increases the polymerization rate approximately 6-fold, but the rate of decomposition increases only 2.5-fold. Accordingly, higher conversion may be reached with lower extent of chain end decomposition. Coupling of a living PSt−PIB prepared using these concentrations (and diluted before coupling, see Experimental Section) was indeed much more rapid as shown in Figure 9.

5. The Structure of End Group. To facilitate the determination of the chain end structure, IB and St were copolymerized using low monomer concentrations ([IB] = 0.07 M) to obtain low M_n by the TMPCl/$TiCl_4$/Hex/MeCl (50/50 v/v)/−80 °C system. The ^1H NMR spectra of the products are shown in Figure 10. The ^1H NMR spectrum obtained using a low ratio of [St]/[IB] = 0.029 shows the characteristic resonance signals of the chloro-terminated PIB ($\sim CH_2C(CH_3)_2CH_2C(CH_3)_2Cl$), i.e., the methylene and methyl protons next to the chloro group at δ = 1.96 and 1.67 ppm. In addition, there is a new peak (c) at δ = 2.17 ppm, and with increasing [St]/[IB] ratio, the intensity of this peak increases while the intensity of the δ = 1.96 and 1.67 ppm peaks decreases and finally disappears at [St]/[IB] = 0.1. On the basis of the ^1H NMR spectrum of the model compound DiαMeSt−IBCl,[19] we identified this new peak (c) as corresponding to the methylene protons next to the chloro end in the $\sim CH_2CH(Ph)CH_2C(CH_3)_2Cl$ (−St−IB−Cl) end structure. It was recently shown by Mayr[20] that the rate of IB addition to a similar structure $(CH_3)_2C(Ph)CH_2C(CH_3)_2Cl$ (Cum−IB_1−Cl) is 20−35 times

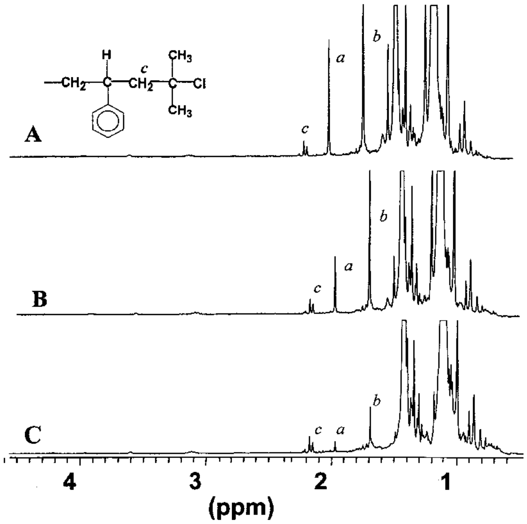


Figure 11. ^{1}H NMR spectra of IB/St statistical copolymers with low M_n. [TMPCl] = 0.002 M, [TiCl$_4$] = 0.036 M, [DTBP] = 0.0035 M, [IB] = 0.07 M [St] = 0.007 M, Hex/MeCl 50/50 v/v at −80 °C. Polymerization time: (A) 5 min, (B) 20 min, (C) 90 min.

lower than the rate of IB addition to Cum−IB$_2$−Cl, which changes little with further increase of *n* in Cum−IB$_n$−Cl. This was ascribed to intramolecular solvation of the cationic center and possibly also to the negative inductive effect of the phenyl ring.

To confirm that the increasing concentration of unreactive −St−IB−Cl ends is responsible for the decreasing homopropagation rate of IB as well as for the decreasing rate of coupling living PSt−PIB diblock copolymers, the copolymerization of IB/St was also carried out for different time using a [St]/[IB] = 1/10 ratio. The M_n of the copolymer followed the theoretical line in the whole conversion range (not shown). The copolymer composition vs conversion plot (not shown) was similar to the behavior shown in Figure 8. The ^{1}H NMR spectrum of the copolymer (Figure 11) shows that peak *c* increases, and resonances at 1.96 and 1.67 ppm, characteristic of chloro-terminated PIB end groups, decrease with polymerization time.

From the integration of resonances *c*, *a*, and *d* the mole fractions of −St−IB−Cl, −IB−IB−Cl, and −St−Cl end groups can be calculated. On the basis of the sum of the end groups, a M_n can be calculated that agrees well with M_ns determined by GPC.

The end group composition with polymerization time is shown in Figure 12. The percentage of −St−IB−Cl end group increases with time and reaches a plateau at ~60%, while −IB−IB−Cl decreases from 80% to ~25%, and the −St−Cl end group remains at low level throughout the polymerization. This explains the low IB polymerization and diblock coupling rate in the synthesis of triblock copolymers.

6. Mechanical Properties of PSt−PIB−PSt Triblock Copolymers. The stress−strain properties of two PSt−PIB−PSt triblock copolymers obtained by coupling living PSt−PIB diblock copolymers in MeChx/MeCl 60/40 and 50/50 v/v are shown in Table 3. The tensile strength is reasonably good although significantly lower than that reported for model PSt−PIB−PSt triblock copolymers of similar composition without diblock contamination.[21]

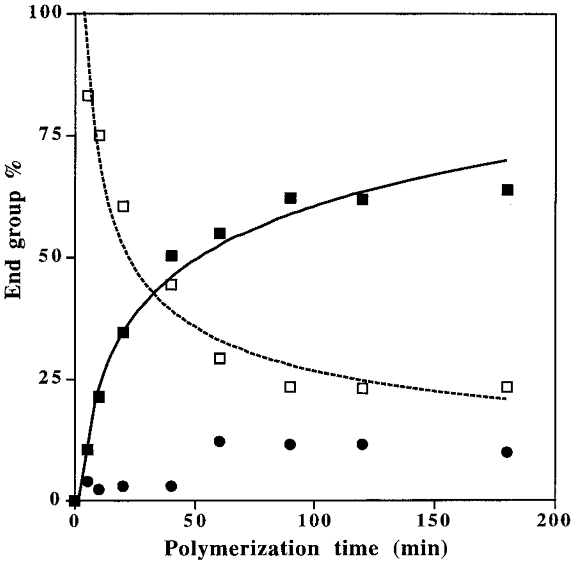


Figure 12. Composition of end group of IB/St statistical copolymer as a function of monomer conversion. Experimental condition are shown in Figure 11. (■) −St−IB−Cl, (□) −IB−IB−Cl, (●) −St−Cl.

Table 3. Stress−Strain Properties of PSt −PIB−PSt Triblock Copolymer[a]

no.	M_n PSt−PIB−PSt	coupling reaction time (h)	tensile stress (MPa)	strain (%)
1	15 000−96 000−15 000	50	15.9	915
2	15 000−96 000−15 000	72	19.8	1050

[a] [pMeSt·HCl] = 0.002 M, [TiCl$_4$] = 0.036 M, [St] = 0.288 M, in MeChx/MeCl 50/50 v/v at −80 °C, St polymerized for 23 min, then [IB] = 1.54 M was added and polymerized for 120 min, BDPEP ([BDPEP]/[PSt−PIB] = 0.5) was introduced last. No. 1: the coupling reaction was carried out in MeChx/MeCl 50/50 v/v; No. 2: the coupling reaction was carried out in MeChx/MeCl 60/40 v/v.

Conclusion

We have shown for the first time in living cationic polymerization that ABA type linear triblock copolymer thermoplastic elastomers can be prepared by coupling of living AB diblock copolymers. Due to decomposition of the living PSt (A block) 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. Our investigations are continuing to evaluate coupling for the synthesis of thermoplastic elastomers using different end blocks.

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