

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Polyisobutylene-Based Thermoplastic Elastomers. IV. Synthesis of Poly (Styrene-*block*-Isobutylene-*block*-Styrene) Triblock Copolymers Using *n*-Butyl Chloride as Solvent

Zsolt Fodor^{ab}; Rudolf Faust^a

^a College of Arts and Sciences University of Massachusetts Lowell, Lowell, MA ^b Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary

To cite this Article Fodor, Zsolt and Faust, Rudolf(1996) 'Polyisobutylene-Based Thermoplastic Elastomers. IV. Synthesis of Poly (Styrene-*block*-Isobutylene-*block*-Styrene) Triblock Copolymers Using *n*-Butyl Chloride as Solvent', Journal of Macromolecular Science, Part A, 33: 3, 305 – 324

To link to this Article: DOI: 10.1080/10601329608014322

URL: <http://dx.doi.org/10.1080/10601329608014322>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

POLYISOBUTYLENE-BASED THERMOPLASTIC ELASTOMERS. IV. SYNTHESIS OF POLY(STYRENE-*block*-ISOBUTYLENE-*block*-STYRENE) TRIBLOCK COPOLYMERS USING *n*-BUTYL CHLORIDE AS SOLVENT

ZSOLT FODOR† and RUDOLF FAUST*

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

ABSTRACT

The polymerization of isobutylene and styrene was studied using the 2-chloro-2,4,4-trimethylpentane/TiCl₄ initiating system in the presence of a proton trap in halogenated hydrocarbons as solvents at –80°C. The polymerization of isobutylene was found to be living, and both homopolymers were soluble in *n*-butyl chloride. However, side reactions, namely polymerization by direct initiation and intra- and intermolecular alkylation, are operational in the polymerization of St in *n*-butyl chloride. Polymerization by direct initiation can be minimized by increasing the initiator concentration, and intermolecular alkylation can be reduced by quenching the polymerization system when conversion reaches ~100%. A careful selection of the experimental conditions was necessary to minimize intramolecular alkylation and obtain complete styrene conversion. Polystyrene–polyisobutylene–polystyrene triblock copolymers prepared under these conditions by sequential monomer addition in *n*-butyl chloride exhibited ~24 MPa tensile strength, indicating the virtual absence of diblock contamination.

†Visiting scientist. Permanent address: Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary.

INTRODUCTION

In preceding papers of this series we reported the synthesis of polystyrene-polyisobutylene-polystyrene (PSt-PIB-PSt) [1], poly-*p*-methylstyrene-polyisobutylene-poly-*p*-methylstyrene (P*p*MeSt-PIB-P*p*MeSt) [2], and poly- α -methylstyrene-polyisobutylene-poly- α -methylstyrene (P α MeSt-PIB-P α MeSt) [3] triblock copolymers. The synthesis involved the living carbocationic sequential block copolymerization of the corresponding monomers using the hexanes (Hex):methylchloride (MeCl) or methylcyclohexane (MeChx):MeCl, 60:40 v:v solvent mixture. The mixed solvent system is necessary to dissolve both PIB and the styrenic end segments at -80°C . PIB is soluble in nonpolar solvents and insoluble in MeCl, but the styrenic polymers are soluble in MeCl and insoluble in nonpolar solvents. For the synthesis of P*p*MeSt-PIB-P*p*MeSt and P α MeSt-PIB-P α MeSt, the Hex:MeCl solvent mixture was used. However, for the synthesis of PSt-PIB-PSt, a more expensive MeChx:MeCl (60:40 v:v) solvent system was used due to the marginal solubility of the PSt segment in the Hex:MeCl, 60:40 v:v solvent mixture.

In our continuing studies in the synthesis and characterization of PIB-based thermoplastic elastomers (TPEs), we have started investigations to determine if the mixed solvent system could be replaced with a single solvent. Results of this investigation are reported in this paper.

EXPERIMENTAL

Sources and purification of isobutylene (IB), styrene (St), MeCl, Hex, and MeChx have been described [1, 2]. *n*-Propylchloride (*n*PrCl), *i*-propylchloride (*i*PrCl), *n*-butylchloride (*n*BuCl), and *s*-butylchloride (*s*BuCl), reagent grade (Ald-

TABLE 1. The Polymerization of IB in Halogenated Hydrocarbons at -80°C . Reaction Conditions: [TMPCl]₀ = 0.0020 M, [DTBP] = 0.0040 M, [TiCl₄] = 0.036 M, [IB]₀ = 1.7 M

Solvent	Reaction time, minutes	Conversion, %	M_n^a	M_w/M_n	$I_{\text{eff}}, \%$
<i>n</i> PrCl	8	82	46,000	1.3	85
	16	100	48,000	1.3	99
	32	97	49,000	1.3	94
<i>i</i> PrCl ^b	16	79	34,000	1.9	109
<i>n</i> BuCl	8	92	41,000	1.3	107
	16	100	44,000	1.3	109
	32	99	44,000	1.3	107
<i>s</i> BuCl	4	86	42,000	1.4	96
	8	97	48,000	1.3	96

^aCalculated with PIB calibration.

^b[DTBP] = 0.008 M.

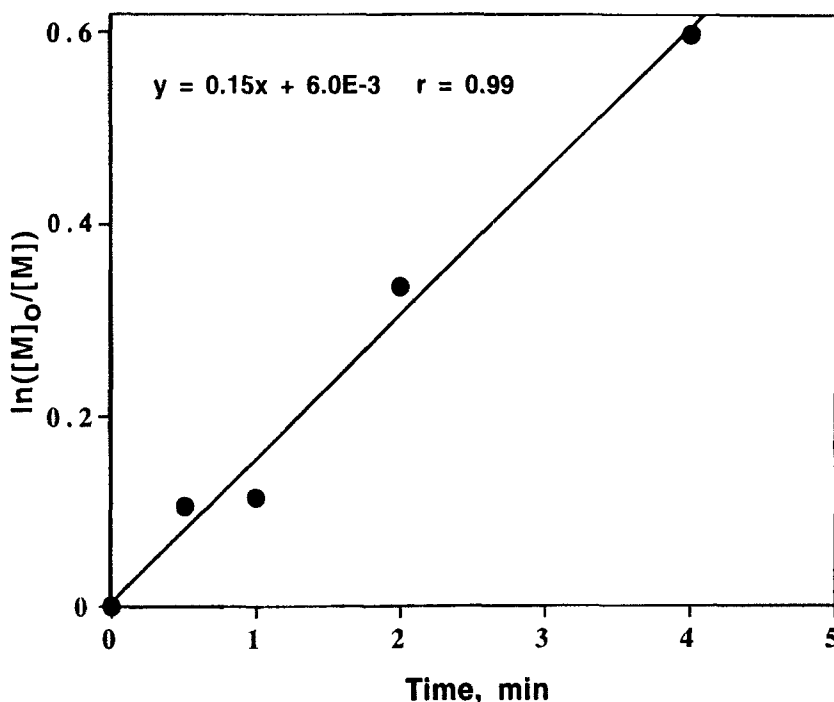


FIG. 1. The $\ln([M]_0/[M])$ vs time plot for the polymerization of IB using *n*BuCl at -80°C . $[\text{TMPCl}]_0 = 0.0020$ M, $[\text{TiCl}_4] = 0.036$ M, $[\text{DTBP}] = 0.0040$ M, $[M]_0 = [\text{IB}]_0 = 1.7$ M.

rich), were refluxed, shielded from light over CaH_2 under nitrogen for 24 hours and freshly distilled before use.

The proton trap 2,6-di-*tert*-butylpyridine (DTBP, Aldrich, 99.4% by GC) was used as received.

The synthesis of 2-chloro-2,4,4-trimethylpentane (2,4,4-trimethylpentylchloride, TMPCl), the initiator used in the homopolymerization experiments, and 5-*tert*-butyl-1,3-bis-(1-chloro-1-methylethyl)-benzene (hindered dicumyl chloride, *t*BuDiCumCl), the initiator in the triblock synthesis, have been described [4, 5].

Polymerizations were carried out in a MBraun stainless steel glove box under a dry nitrogen atmosphere [5]. Large (75 mL) test tubes were used in the homopolymerizations. The initiator, proton trap, and IB were added first, followed by the addition of TiCl_4 solution (TiCl_4 :solvent, 1:3 v:v). St polymerizations were started by the addition of St solution (20 v%) at -80°C .

The homopolymerization of IB using halogenated hydrocarbons was carried out under the conditions reported earlier [1, 5] using the Hex:MeCl 60:40 v:v or MeChx:MeCl 60:40 v:v solvent mixtures.

The triblock synthesis was carried out in a round bottom flask equipped with an overhead stirrer. IB was polymerized by adding three equal increments. When the polymerization of IB was complete, the solution of St in *n*BuCl (St:*n*BuCl 1:2 v:v) was added. The concentration DTBP was 0.0040 M. Additional TiCl_4 solution

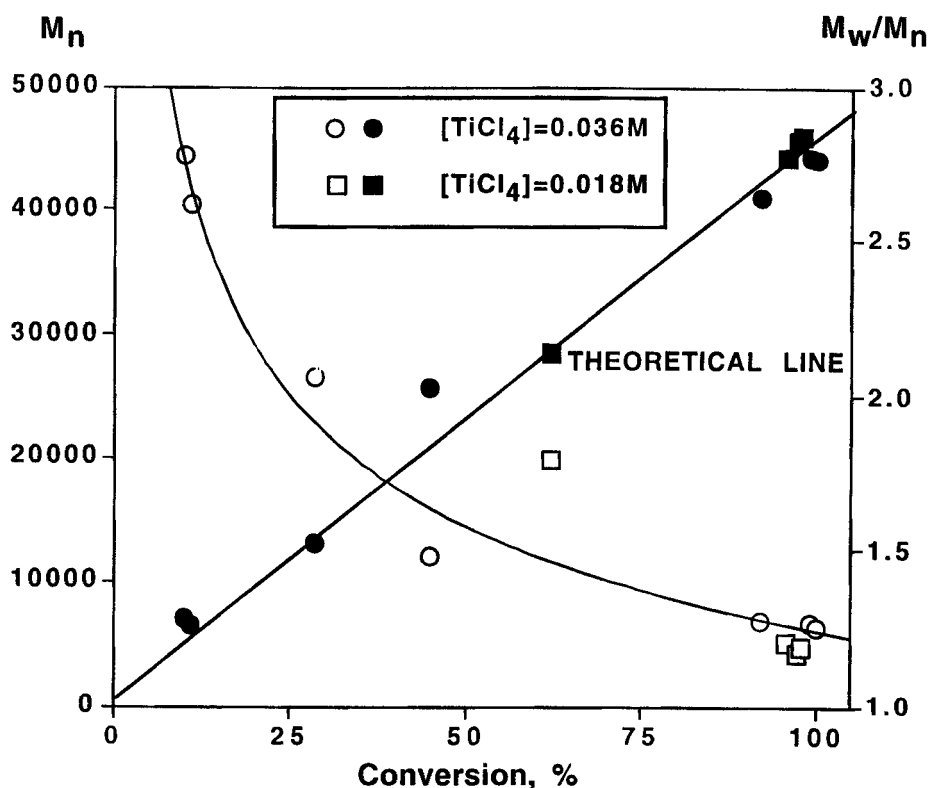


FIG. 2. The molecular weight and the polydispersity ratio (M_w/M_n) vs conversion plot for the polymerization of IB in *n*BuCl at -80°C . $[\text{DTBP}] = 0.0040\text{ M}$, $[\text{IB}]_0 = 1.7\text{ M}$, $[\text{TMPCl}]_0 = 0.0020\text{ M}$. Solid symbols, M_n ; open symbols, M_w/M_n .

was added before the St addition to compensate for dilution upon the addition of St solution. The corresponding section in previous parts of this series contain details.

The viscosity of the polymerization solutions was measured using a Cannon-Fenske type viscometer of size 450.

The reaction mixtures were quenched with prechilled methanol.

The purification of the polymers has been described [1, 2]. The molecular weights and the polydispersity ratios (M_w/M_n) were measured with a Waters GPC system equipped with RI, UV, and multiangle laser light-scattering (MALLS) detectors [2, 5]. The composition of the block copolymers was calculated by $^1\text{H-NMR}$ spectroscopy [5].

RESULTS AND DISCUSSION

Our goal was to find a single solvent with a polarity similar to the MeChx: MeCl (60:40 v:v) system. Since theoretical considerations based on dielectric constants and polarizability often fail for the selection of solvents relative to polymeri-

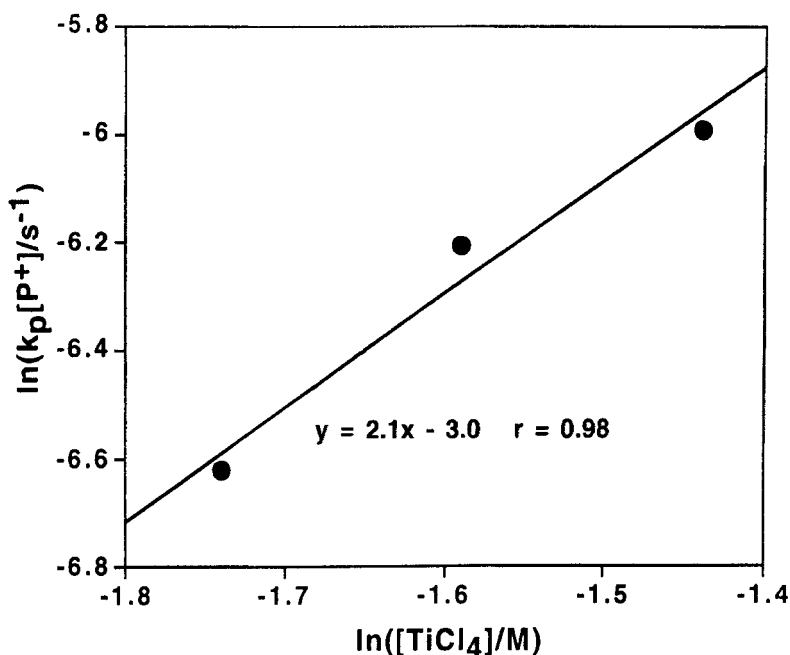


FIG. 3. The logarithms of the first-order rate constants (in terms of s^{-1}) plotted against the logarithms of the $TiCl_4$ concentrations (in terms of M). Experimental conditions: $[TMPCl]_0 = 0.0020$ M, $[IB]_0 = 1.7$ M, $[DTBP] = 0.0040$ M, $nBuCl$ solvent, $-80^\circ C$. $[P^+]$ stands for the concentration of the growing PIB^+ chain ends, and k_p is the propagation rate constant.

zation rates and behaviors, we decided to study the following series of halogenated hydrocarbons: $CH_3CH_2CH_2Cl$ ($nPrCl$), $CH_3CHClCH_3$ ($iPrCl$), $CH_3(CH_2)_3Cl$ ($nBuCl$), and $CH_3CH_2CHClCH_3$ ($sBuCl$). C_2H_5Cl was not included in this series because high molecular weight PIB is not soluble in this solvent at $-80^\circ C$. First, the homopolymerization of IB and St was studied.

Homopolymerization of IB

Results obtained in preliminary experiments with all four solvents are tabulated in Table 1. Close to theoretical molecular weights and narrow molecular weight distributions were obtained in all four solvents. Further experimentations with $nPrCl$ and $iPrCl$ were discontinued due to precipitation of PIB of $M_n \sim 50,000$. In addition, $iPrCl$, even after purification, contained a high concentration of protic impurities which necessitated the use of a high concentration (0.0080 M) proton trap. With a lower 0.0040 M proton trap concentration, 200% I_{eff} was obtained, most probably due to the presence of untrapped protic impurities.

As anticipated, PIB was soluble in $nBuCl$ and in $sBuCl$, and these solvents were studied in detail. Figure 1 shows the first-order plots obtained in $nBuCl$. The plot is linear, indicating the absence of irreversible termination. The M_n -conversion

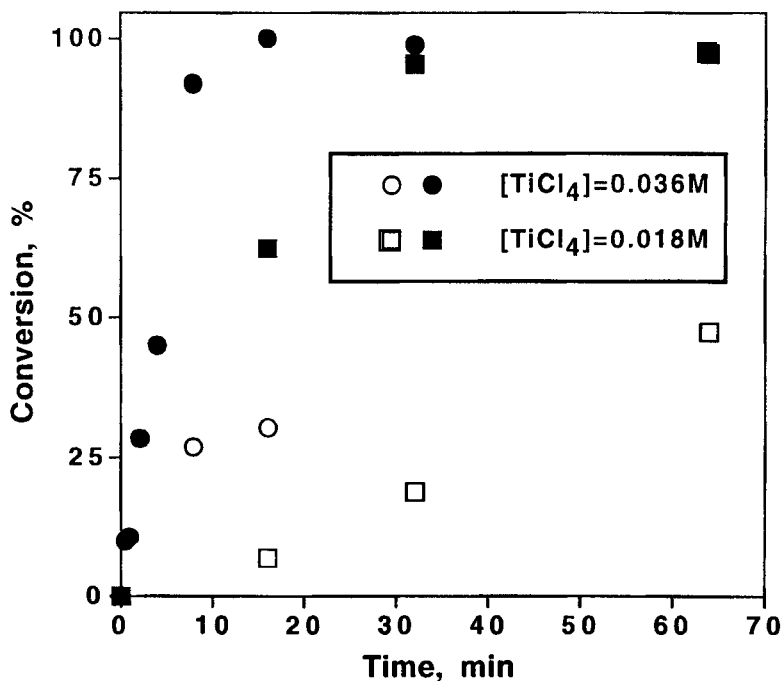


FIG. 4. The conversion vs time plot for the polymerization of IB using *n*BuCl at -80°C . $[\text{IB}]_0 = 1.7 \text{ M}$, $[\text{DTBP}] = 0.0040 \text{ M}$. Solid symbols, $[\text{TMPCl}]_0 = 0.0020 \text{ M}$; open symbols, $[\text{TMPCl}]_0 = 0$.

plot (Fig. 2) is also linear and proves the absence of chain transfer to monomer. The M_n s are close to the theoretical values. The M_w/M_n ratios decrease with increasing conversion, and reach 1.25 at $\sim 100\%$ conversion.

A change in TiCl_4 concentration only affected the rate of the polymerization and did not influence the M_n or M_w/M_n -conversion plots. The apparent propagation rate constants have been obtained from the $\ln([\text{M}]_0/[\text{M}])$ vs time plots. The logarithms of the apparent first-order rate constants are plotted against $\ln[\text{TiCl}_4]$ in Fig. 3. Figure 3 suggests that the polymerization is second order in TiCl_4 . A similar second-order dependency was also reported with the MeChx:MeCl or Hex:MeCl (60:40 v:v) solvent systems [1, 5], and was rationalized by the tendency of TiCl_4 to form dimers and dimeric gegenions (Ti_2Cl_7^-) [6].

Polymerizations carried out in the absence of TMPCl initiator were much slower. By comparing the conversion-time plots in the presence and absence of TMPCl, plotted in Fig. 4, we concluded that the rate of polymer formation by direct initiation is negligible compared to that initiated by TMPCl.

A linear first-order plot indicating the absence of irreversible termination was also obtained using *s*BuCl (Fig. 5). Results obtained in the absence of initiator are also shown. The concave plot is characteristic of living polymerization by direct initiation. Importantly, the rate of polymerization in the absence of TMPCl is much lower.

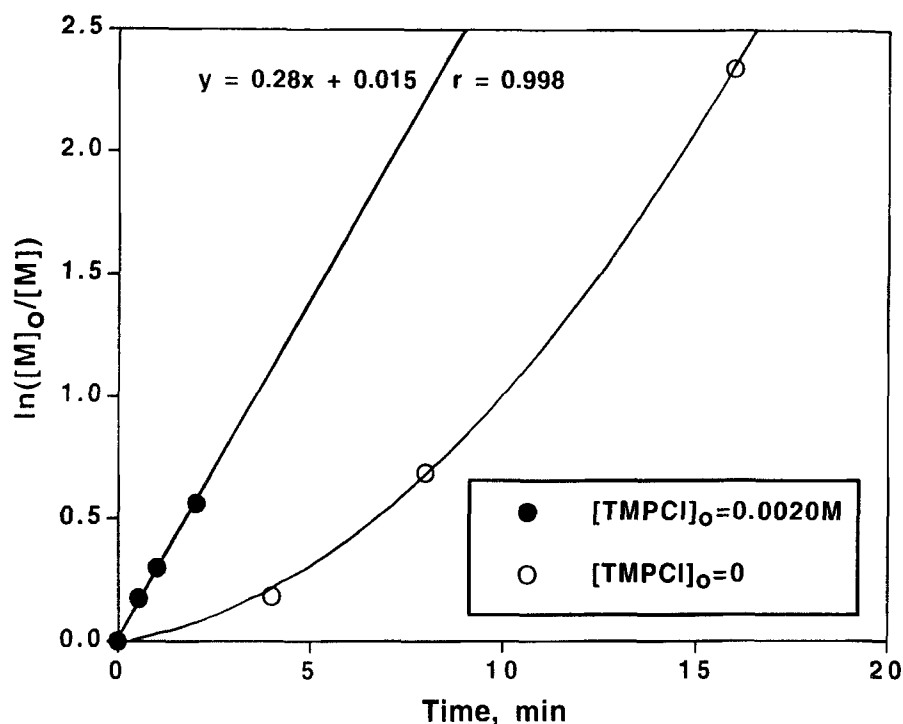


FIG. 5. The $\ln([M]_0/[M])$ vs time plot for the polymerization of IB in the presence and absence of initiator using *s*BuCl as solvent at -80°C . $[\text{TiCl}_4] = 0.036 \text{ M}$, $[M]_0 = [\text{IB}]_0 = 1.7 \text{ M}$.

The linear M_n vs conversion plot for TMPCl-initiated polymerizations, shown in Fig. 6, proves the absence of chain transfer, indicating that the polymerization is living. The curved M_n -conversion plot obtained in the absence of initiator is typical of direct initiation and has been observed before.

The apparent first-order rate constants (k_{app}), dielectric constants (ϵ), and dipole moments (μ) of the solvents used are collected in Table 2. Interestingly, a strong relation is found between k_{app} and ϵ , i.e., an increase in the dielectric constant brings about a proportional increase in the apparent propagation rate constant.

Homopolymerization of St

The homopolymerization of St was studied only in *n*BuCl. $\ln([M]_0/[M])$ is plotted against time at three different TiCl_4 concentrations in Fig. 7. The curved plots indicate that the active center concentration decreases during polymerization. This is most probably due to terminative chain transfer involving intramolecular alkylation. Following the formation of the indanyl ring, the eliminated proton is trapped by the proton trap (terminative chain transfer). The M_n vs conversion plot (Fig. 8) therefore follows the theoretical line, i.e., I_{eff} is close to 100% and chain

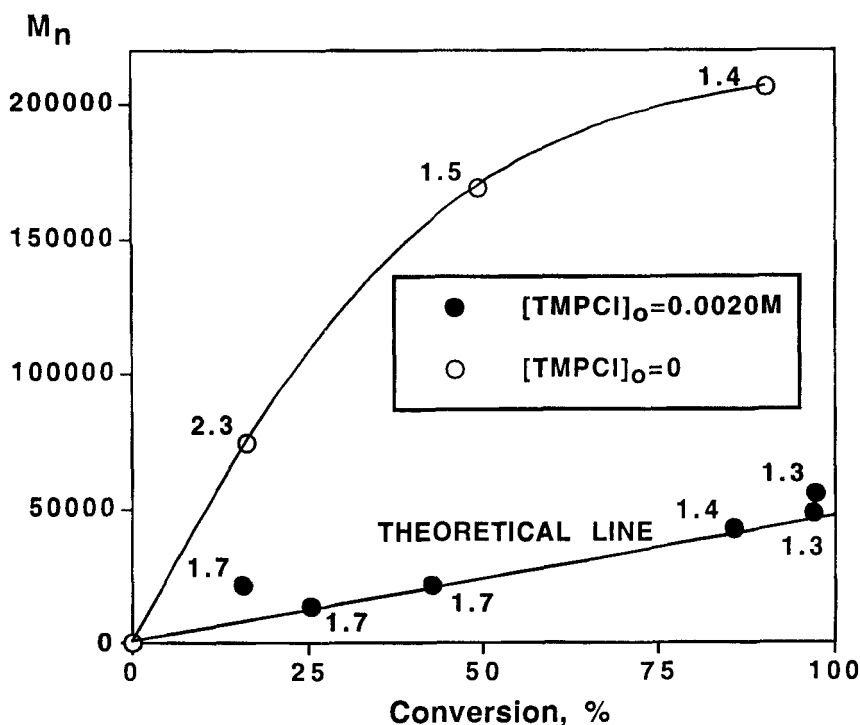


FIG. 6. The molecular weight vs conversion plot for the polymerization of IB in the presence and absence of initiator using *s*BuCl as solvent at -80°C . $[\text{TiCl}_4] = 0.036 \text{ M}$, $[\text{DTBP}] = 0.0040 \text{ M}$, $[\text{IB}]_0 = 1.7 \text{ M}$. The numbers are M_w/M_n values.

TABLE 2. The Relative Dielectric Constants (ϵ) and the Dipole Moments (μ) of Solvents Used and the Apparent Propagation Rate Constants ($k_{papp} = k_p[\text{P}^+ / [\text{TMPCl}]_0$) of IB Polymerization at -80°C . $[\text{TMPCl}]_0 = 0.0020 \text{ M}$, $[\text{TiCl}_4] = 0.036 \text{ M}$, $[\text{DTBP}] = 0.0040 \text{ M}$, and $[\text{IB}]_0 = 1.7 \text{ M}$

Solvent	ϵ	μ , debye	k_{papp} , $\text{M}^{-1} \cdot \text{s}^{-1}$
<i>n</i> PrCl	8.59	2.05	1.8 ^b
<i>i</i> PrCl ^a	9.82	2.17	0.80 ^b
<i>n</i> BuCl	7.28	2.05	1.3
<i>s</i> BuCl	8.56	2.04	2.3
MeCl:Hex 4:6 v:v	5.13 ^c		0.83
MeCl:MeChx 4:6 v:v	6.21 ^c		0.67

^a $[\text{DTBP}] = 0.0080 \text{ M}$.

^bEstimated.

^cCalculated assuming additivity in volume fraction.

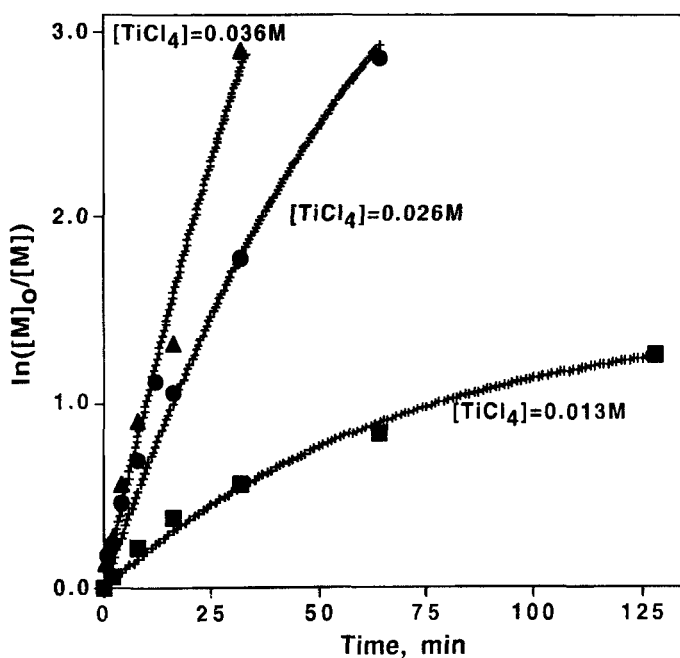


FIG. 7. The experimental and the calculated $\ln([M]_0/[M])$ vs time plots for the homopolymerization of St at -80°C using *n*BuCl as solvent. $[\text{TMPCl}]_0 = 0.0020 \text{ M}$, $[\text{DTBP}] = 0.0040 \text{ M}$, $[M]_0 = [\text{St}]_0 = 0.35 \text{ M}$.

transfer to monomer is absent. Intermolecular alkylation is clearly evident as the M_n s increase with time after 30 minutes when 100% conversion is reached (Fig. 9). From the rate of disappearance of polymer molecules (Fig. 9), alkylation proceeds at $\sim 0.4\%/ \text{min}$. Comparing this rate with rates obtained with the MeChx:MeCl 60:40 v:v and Hex:MeCl 60:40 v:v solvent systems [7], intermolecular alkylation is about two times faster in *n*BuCl. This is in line with the similarly higher polymerization rate, suggesting that *n*BuCl is more polar than MeChx:MeCl 60:40 v:v or Hex:MeCl 60:40 v:v.

The M_w/M_n values are plotted against the conversion in Fig. 10. The polydispersity decreases with an increase in the conversion. A change in the concentration of TiCl_4 does not affect the polydispersity at constant conversion.

Control experiments in the absence of initiator were also carried out to determine the effect of direct initiation. A comparison of the results corroborated that polymerization is significantly slower in the absence of initiator. Representative results of control experiments carried out in *n*BuCl and MeCl:MeChx 40:60 v:v solvents in the presence of 0.0040 M DTBP are shown in Table 3. According to Table 3, direct initiation is comparable in the two solvents.

The following kinetic scheme was devised to interpret the results of Figure 7.



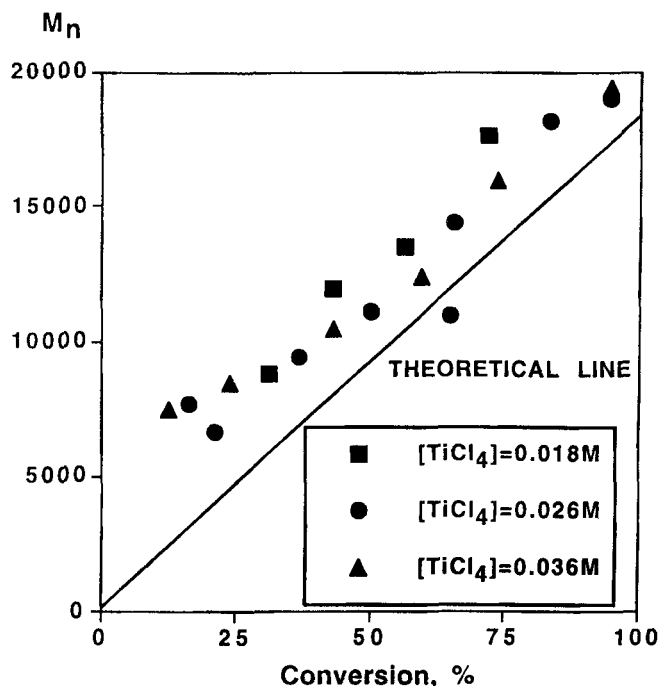


FIG. 8. The molecular weight vs conversion plot for the homopolymerization of St at -80°C using *n*BuCl as solvent in the presence of initiator. Other experimental conditions: $[\text{TMPCl}]_0 = 0.0020 \text{ M}$, $[\text{DTBP}] = 0.0040 \text{ M}$, $[\text{St}]_0 = 0.35 \text{ M}$.

where i is the degree of polymerization, P_i denotes the dead PSt chain end after proton elimination, and M denotes the monomer. Using $[\text{P}^+] = \sum [\text{P}_i^+]$ the corresponding differential equations can be obtained:

$$d[\text{P}^+]/dt = -k_t[\text{P}^+] \quad (1)$$

$$d[\text{M}]/dt = -k_p[\text{P}^+][\text{M}] \quad (2)$$

Integration of Eqs. (1) and (2) yields

$$[\text{P}^+] = [\text{P}^+]_0 \exp(-k_t t) \quad (3)$$

$$\ln([\text{M}]_0/[\text{M}]) = k_p[\text{P}^+]_0(1 - \exp(-k_t t))/k_t \quad (4)$$

where t is the time, $[\text{P}^+]_0$ is the cation concentrations at $t = 0$, and $[\text{M}]_0$ denotes the concentration of St at $t = 0$. $k_p[\text{P}^+]_0$ and k_t can be calculated from the experimental data using Eq. (4). The calculated $\ln([\text{M}]_0/[\text{M}])$ vs time curves, shown for all three TiCl_4 concentrations in Fig. 7, fit the experimental results well. $k_p[\text{P}^+]_0$ and k_t were calculated from the best fits.

From $k_p[\text{P}^+]_0/k_t$ the limiting conversion (C_{\max} at infinite time) that can be achieved under the given conditions can be calculated:

$$C_{\max} = \{([\text{M}]_0 - [\text{M}])/[\text{M}]_0\}_{\max} = 1 - \exp(-k_p[\text{P}^+]_0/k_t) \quad (5)$$

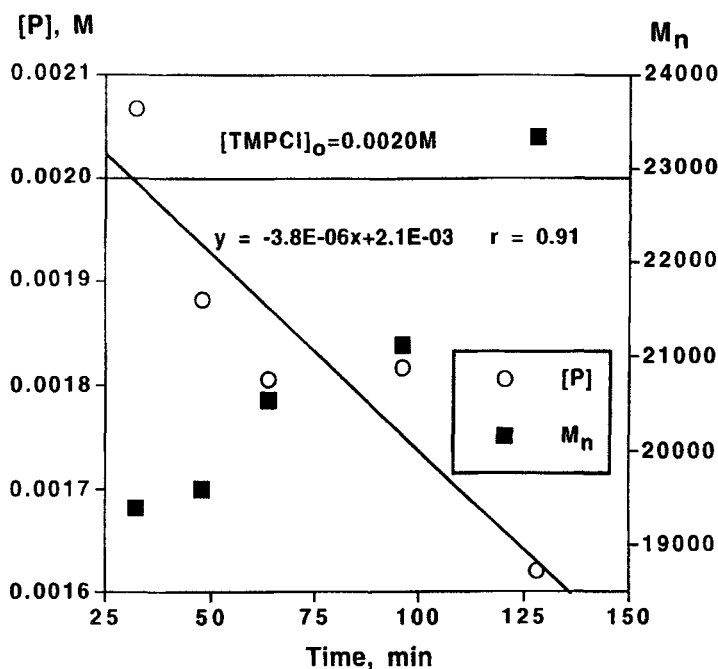


FIG. 9. The molecular weight and the concentration of polymer molecules ($[P]$) vs time plot for the homopolymerization of St at -80°C in $n\text{BuCl}$ after 100% conversion (30 minutes). $[\text{TMPCl}]_0 = 0.0020\text{ M}$, $[\text{TiCl}_4] = 0.036\text{ M}$, $[\text{DTBP}] = 0.0080\text{ M}$, $[\text{St}]_0 = 0.35\text{ M}$.

The maximum conversion and the obtained k_{papp} ($k_{papp} = k_p[P^+]_0/[\text{TMPCl}]_0$) values are listed in Table 4.

With the $k_p[P^+]_0$ values known, the order of polymerization can be calculated for TiCl_4 . The diagnostic plot is shown in Fig. 11. The $\ln(k_p[P^+]_0)$ vs $\ln[\text{TiCl}_4]$ plot is linear with a slope of nearly 2, indicating the presence of Ti_2Cl_7^- dimeric gegenions in $n\text{BuCl}$. Reassuringly, the same conclusion was reached based on results with IB.

According to Eq. (5), a higher C_{max} can be achieved at higher $[P^+]_0$. $[P^+]_0$ can be increased by increasing the TiCl_4 concentration and/or by using a higher initiator concentration. With a higher initiator concentration, a higher monomer concentration should be used to obtain the same molecular weight. By using a higher monomer concentration the rate of polymerization (first order in monomer) will increase while the rate of termination (zero order in monomer) remains constant, thus further minimizing terminative chain transfer. In conclusion, although the polymerization is not living, and can be described as slowly dying, termination can be minimized, especially for $M_n < 20,000$ end-segments.

Thus, in the following series of experiments a higher $[\text{TMPCl}] = 0.0030\text{ M}$ concentration was used while $[\text{TiCl}_4]$ was kept constant at 0.036 M . The monomer concentration was proportionally higher in order to obtain the same molecular weight. The transformed conversions are plotted against the polymerization time in Fig. 12 (Exp. D).

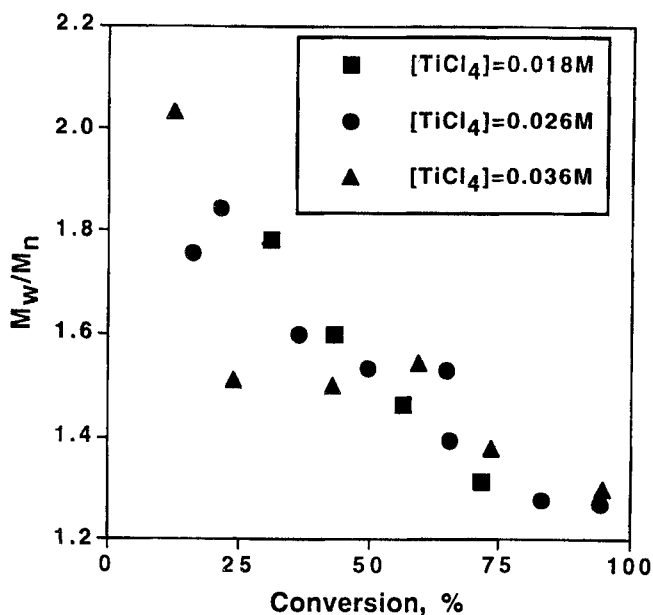


FIG. 10. The polydispersity ratio (M_w/M_n) vs conversion plot for the homopolymerization of St at -80°C using *n*BuCl as solvent in the presence of initiator. Other experimental conditions: $[\text{TMPCl}]_0 = 0.0020 \text{ M}$, $[\text{DTBP}] = 0.0040 \text{ M}$, $[\text{St}]_0 = 0.35 \text{ M}$.

A series of polymerization was also carried out in the Hex:*n*BuCl 15:85 v:v solvent mixture. Hex was used to adjust the polarity in place of PIB which is present during the triblock preparation. The corresponding transformed conversions are shown in Fig. 12 (Exp. E). For comparison, Fig. 12 includes the data of three parallel experiments using $[\text{TMPCl}]_0 = 0.0020 \text{ M}$.

According to Fig. 12, the rate of polymerization increased significantly with increases of $[\text{TMPCl}]_0$ and $[\text{St}]_0$. The $\ln([\text{M}]_0/[\text{M}])$ vs time curve is close to linear,

TABLE 3. The Polymerization of St at -80°C in the Absence of Initiator and in the Presence of Proton Trap ($[\text{DTBP}] = 0.0040 \text{ M}$). $[\text{St}]_0 = 0.35 \text{ M}^a$

Solvent	$[\text{TiCl}_4]$, M	Reaction time, minutes	Conversion, %
MeChx:MeCl 60:40 v:v	0.018	32	3.4
<i>n</i> BuCl	0.018	32	1.3
MeChx:MeCl 60:40 v:v	0.036	16	6.6
<i>n</i> BuCl	0.036	16	8.8

^aFor the MeChx:MeCl 60:40 v:v mixture interpolation, assuming first-order kinetics was used based on the data of Figs. 14 and 15 of Ref. 7.

TABLE 4. k_{papp} ($k_{papp} = k_p[P^+]_0/[TMPCl]_0$) and the Limiting Conversions in the Polymerization of St at -80°C in *n*BuCl. $[TMPCl]_0 = 0.0020\text{ M}$, $[St]_0 = 0.35\text{ M}$, $[DTBP] = 0.0040\text{ M}$. $k_t = 2.4 \times 10^{-1}$

$[TiCl_4], \text{M}$	$k_{papp}, \text{M}^{-1}\cdot\text{s}^{-1}$	Maximum conversion, %
0.018	0.18	77.7
0.026	0.58	99.3
0.036	0.91	~ 100

indicating that the rate of irreversible termination is negligible compared to the rate of polymerization.

Due to the decreased polarity of the solvent in the presence of 15 v% Hex, the rate of polymerization is lower and close to that observed in pure *n*BuCl with $[TMPCl] = 0.0020\text{ M}$.

The molecular weights approach the theoretical values, indicating that chain transfer to monomer and direct initiation are not significant (Fig. 13).

On the basis of the results, we conclude that St can be polymerized in a controlled if not truly living fashion using *n*BuCl as solvent at -80°C . Most importantly, the ~100% initiator efficiencies using TMPCl suggest ~100% crossover

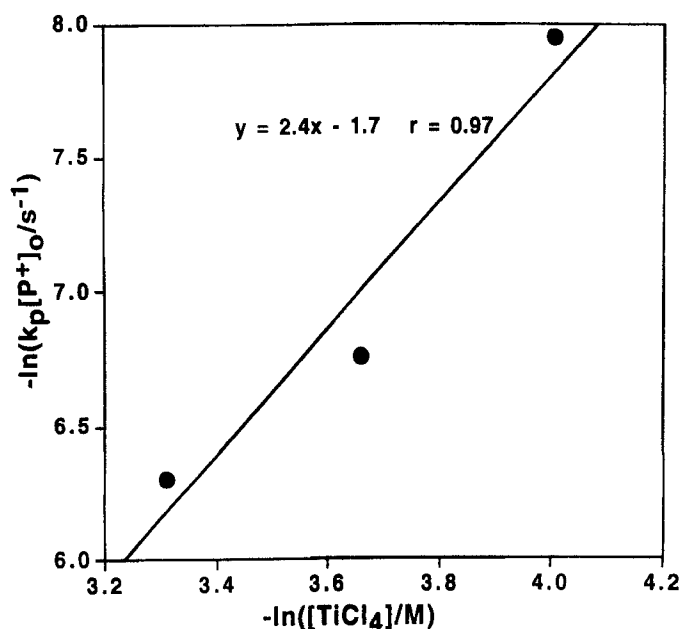


FIG. 11. The $\ln(k_p[P^+]_0)$ vs $\ln[TiCl_4]$ plot for the homopolymerization of St at -80°C using *n*BuCl as solvent in the presence of initiator. Other experimental conditions: $[TMPCl]_0 = 0.0020\text{ M}$, $[DTBP] = 0.0040\text{ M}$, $[St]_0 = 0.35\text{ M}$.

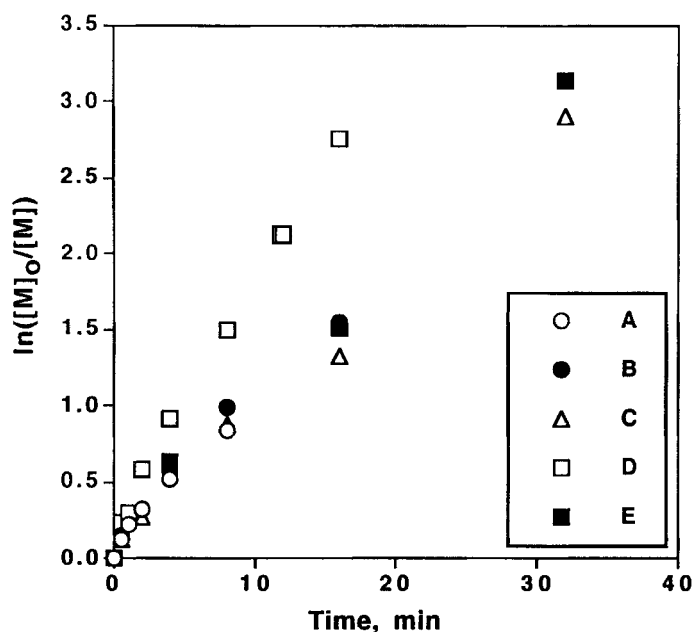


FIG. 12. The $\ln([M]_0/[M])$ vs time plot for the homopolymerization of St at -80°C . $[\text{TiCl}_4] = 0.036$ M, $[\text{DTBP}] = 0.0040$ M, other experimental conditions: A, B, and C $[\text{TMPCl}]_0 = 0.0020$ M, $[\text{St}]_0 = 0.35$ M, solvent *n*BuCl; D $[\text{TMPCl}]_0 = 0.0030$ M, $[\text{St}]_0 = 0.49$ M, solvent *n*BuCl; E $[\text{TMPCl}]_0 = 0.0030$ M, $[\text{St}]_0 = 0.49$ M, solvent Hex:*n*BuCl 15:85 v:v.

from PIB to St, the primary factor determining mechanical properties of the triblock copolymer thermoplastic elastomers.

PSt-PIB-PSt Preparation

After establishing the optimum conditions for the homopolymerization of IB and St using *n*BuCl as solvent, several PSt-PIB-PSt triblocks were prepared. The reaction conditions are listed in Table 5.

The conversions as well as the theoretical and observed M_n s are listed in Table 6.

During triblock synthesis, samples were taken for the determination of M_n and composition, which are listed in Table 7. The corresponding GPC RI traces are shown in Fig. 14.

The samples taken after St addition exhibit a low molecular weight tail, which most probably represents homoPSt formed via direct initiation. A shoulder on the high molecular weight side is also visible in the samples taken after 1 hour, i.e., after 100% conversion is reached, and indicates intermolecular alkylation.

The solution viscosity was measured during polymerization of Exp. 110294-1. The viscosity and conversion of IB and St are plotted against time in Fig. 15. The viscosity increased during the polymerization of IB due to the increase of the PIB molecular weight. After the addition of St, a continuous increase was observed in

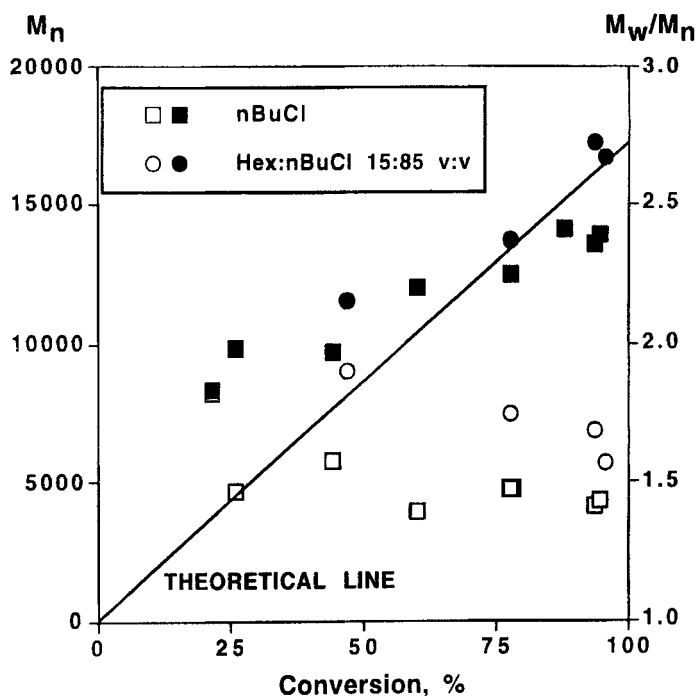


FIG. 13. The molecular weight and the polydispersity ratio (M_w/M_n) vs conversion plots for the homopolymerization of St in *n*BuCl and in Hex:*n*BuCl 15:85 v:v solvent mixture at -80°C . $[\text{TMPCl}]_0 = 0.0030 \text{ M}$, $[\text{TiCl}_4] = 0.036 \text{ M}$, $[\text{DTBP}] = 0.0040 \text{ M}$, $[\text{St}]_0 = 0.47 \text{ M}$. Solid symbols, M_n ; open symbols, M_w/M_n .

TABLE 5. The Conditions of the PSt-PIB-PSt Triblock Preparation Using *n*BuCl as Solvent at -80°C ^a

Experiment	$[\text{TiCl}_4]$, M	IB added, mL at -80°C	St: <i>n</i> BuCl 1:2 v:v, mL at 25°C	V , mL at -80°C	CH_3OH
072994-1	0.036	10.2 + 10.8 + 10.2 0, 5, 10	25 28	270	60
072994-2	0.036	10.5 + 11.0 + 9.9 0, 5, 10	33 28	280	60
072994-3	0.036	10.7 + 10.0 + 10.5 0, 5, 10	41 28	290	60
110294-1	0.036	11.6 + 11.6 + 11.6 0, 10, 20	31 65	330	157
110294-2 ^b	0.036	12.0 + 12.0 + 12.0 0, 10, 20	31 86	230	180

^aFirst line: The amount of the reagent added. Second line: The time coordinate of the addition in minutes. V : The volume of the reaction mixture just after St addition. $[\text{tBuDi-CumCl}]_0 = 0.0010 \text{ M}$.

^b $[\text{tBuDiCumCl}]_0 = 0.0015 \text{ M}$.

TABLE 6. Conversion of St and M_n Data of the PIB Middle Segments and the Triblocks. The Conversions of IB Are 100%

Experiment	M_n and M_w/M_n of the PIB middle segment			St conversion,		M_n and M_w/M_n of the triblock	
	M_n^a	M_w/M_n^a	M_n^b	M_w/M_n^b	%	M_n^b	M_w/M_n^a
072994-1	76,000	1.3	101,000	1.1	79	111,000	1.5
072994-2	79,000	1.3	109,000	1.1	77	123,000	1.5
072994-3	80,000	1.3	107,000	1.1	71	127,000	1.45
110294-1	81,000	1.2	92,000	1.1	100	121,000	1.45
110294-2	86,000	1.2	97,000	1.1	100	145,000	1.6

^aBased on calibration with PIB standards.

^bWith MALLS detector.

TABLE 7. The M_n s, the Polydispersity Ratios, and the St Contents of the Samples Taken during the Preparation of Triblocks 110294-1 and 110294-2. For Reaction Conditions, Refer to Table 5. The Reaction Time Is Calculated from the Addition of the Last Increment

Sample,	Time, minutes	M_n	M_w/M_n	St content, w%
PIB1	38	92,000	1.1	0
St added	45			
S11	48	106,000	1.1	19
S12	60	118,000	1.1	26
S13	73	114,000	1.2	29
S14	96	126,000	1.3	26
S15	112	120,000	1.3	33
Triblock1	137	121,000	1.4	28
PIB2	60	97,000	1.1	0
St added	66			
S21	69	110,000	1.1	15
S22	86	125,000	1.2	30
S23	98	124,000	1.3	31
S24	115	142,000	1.3	
S25	234	139,000	1.5	26
S26	147	124,000	1.7	
Triblock2	160	145,000	1.6	29

the viscosity with time, although St conversion was complete at ~ 73 minutes. The small extent of intermolecular alkylation cannot be responsible for the large increase in viscosity. Polymer chain overlap may explain the high viscosity, but this usually appears at higher concentrations ($\sim 25\%$) and would not explain the time dependence. We theorize that phase separation occurs and polymer aggregates are responsible for the increased viscosity.

The viscosity and the conversions are plotted against time in Fig. 16 for Exp. 110294-2. During the polymerization of IB, the viscosity increased and reached a limiting value at ~ 40 minutes. Apparently polymerization is complete after 40 minutes.

The viscosity increased sharply after the addition of St. The efflux times became extremely long (475, 1132, and 2316 seconds) and only three measurements were possible. Since the molecular weights of the polymers obtained in the last two experiments are similar, the very large viscosity difference is apparently due to the higher polymer concentration. The observed 20 times increase in the viscosity by increasing the polymer concentration by 50% suggests that the concentration is close to the boundary line in the phase diagram.

Due to the extremely high viscosity, the higher concentration may be impractical. It may be avoided by quenching the polymerization soon after 100% St conver-

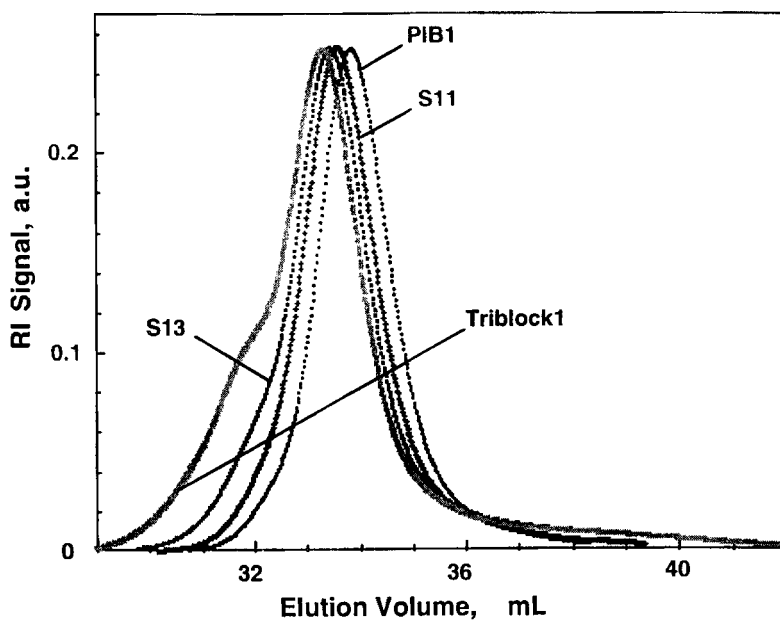


FIG. 14. The RI traces of the samples taken in different phases of the preparation of Triblock 110294-1 in Table 7.

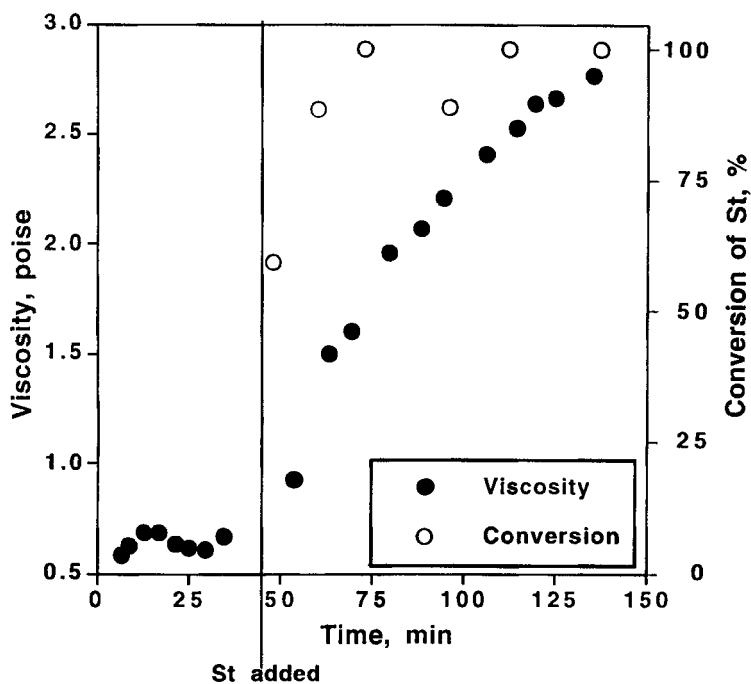


FIG. 15. The viscosity and the St conversion vs time functions in the synthesis of Triblock 110294-1. St added in the 45th minute.

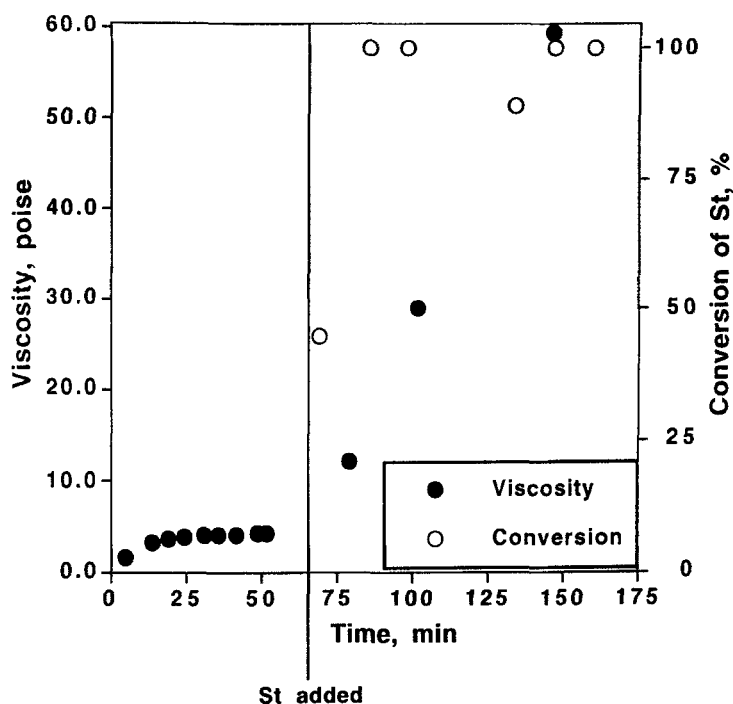


FIG. 16. The viscosity and the St conversion vs time functions in the synthesis of Triblock 110294-2. St added in the 66th minute.

sion, by discontinuing low shear stirring which promotes phase separation and aggregation, or by using high shear stirring to break up the aggregates.

The mechanical properties of the triblocks are summarized in Table 8.

It is known that even small amounts of diblock contamination cause a rather large drop in the tensile strength. It has been reported [8] for PSt-polybutadiene-PSt triblock copolymers that 5% diblock contamination decreases the tensile strength by ~30%. We have observed a similar decrease by mixing 5% PIB-poly(α -methylstyrene) diblock copolymer of identical segment lengths with poly(α -

TABLE 8. The St Content, the Tensile Strengths (σ), and the Elongations at Break (λ) of PSt-PIB-PSt Triblock Copolymers

No.	M_n of the PIB middle segment	St content, w%	σ , MPa	λ , %
072994-1	101,000	21	19	860
072994-2	109,000	25	20	720
072994-3	107,000	28	21	630
110294-1	92,000	28	24	830
110294-2	97,000	29	24	740

methylstyrene)-PIB-poly(α -methylstyrene) triblock copolymer [9]. Importantly, the excellent mechanical properties obtained in the present study equal those reported earlier [1], indicating close to 100% crossover from PIB⁺ to St and the virtual absence of diblock contamination.

ACKNOWLEDGMENTS

This material is based on research supported by Exxon Chemical Company. We wish to thank Dr. M. Bahadur of Exxon Chemical Co. for the stress-strain measurements.

REFERENCES

- [1] M. Györ, Zs. Fodor, H.-C. Wang, and R. Faust, *J. Macromol. Sci.—Pure Appl. Chem.*, **A31**, 2055 (1994).
- [2] Zs. Fodor and R. Faust, *Ibid.*, **A32**, 575 (1995).
- [3] D. Li and R. Faust, *Macromolecules*, **28**, 4893 (1995).
- [4] F. C. Whitmore, C. D. Wilson, J. V. Capinjola, C. O. Tonberg, G. H. Fleming, R. V. McGrew, and J. N. Cosby, *J. Am. Chem. Soc.*, **63**, 2035 (1941).
- [5] M. Györ, H.-C. Wang, and R. Faust, *J. Macromol. Sci.—Pure Appl. Chem.*, **A29**, 639 (1992).
- [6] C. S. Creaser and J. A. Creighton, *J. Chem. Soc., Dalton Trans.*, p. 1402 (1975).
- [7] Zs. Fodor, M. Györ, H.-C. Wang, and R. Faust, *J. Macromolecular Sci.—Pure Appl. Chem.*, **A30**, 349 (1994).
- [8] M. Morton, *Encyclopedia of Polymer Science and Technology*, Vol. 15, Wiley, New York, 1971, p. 528.
- [9] D. Li and R. Faust, Unpublished Results.

Received April 26, 1995

Revision received July 10, 1995