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Living Carbocationic Copolymerization of Isobutylene with Styrene

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Received 27 September 2006; accepted 12 December 2006

DOI: 10.1002/pola.21945

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The carbocationic copolymerization of isobutylene (IB) and styrene (St), initiated by 2-chloro-2,4,4-trimethylpentane/TiCl₄ in 60/40 (v/v) methyl chloride/hexane at $-90\text{ }^{\circ}\text{C}$, was investigated. At a low total concentration (0.5 mol/L), slow initiation and rapid monomer conversion were observed. At a high total comonomer concentration (3 mol/L), living conditions (a linear semilogarithmic rate and M_n -conversion plots) were found, provided that the St concentration was above a critical value ($[\text{St}]_0 \sim 0.6\text{ mol/L}$). The breadth of the molecular weight distribution decreased with increasing IB concentration in the feed, reaching $M_w/M_n \sim 1.1$. St homopolymerization was also living at a high total concentration, yielding polystyrene with $M_n = 82,000\text{ g/mol}$, the highest molecular weight ever achieved in carbocationic St polymerization. An analysis of this system by both the traditional gravimetric-NMR copolymer composition method and FTIR demonstrated penultimate effects. IB enrichment was found in the copolymers at all feed compositions, with very little drift at a high total concentration and above the critical St concentration. © 2007 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 45: 1778–1787, 2007

Keywords: isobutylene; living carbocationic copolymerization; penultimate effects; reactivity ratios; real-time FTIR; styrene

INTRODUCTION

Polyisobutylene (PIB)-based polymers exhibit unique properties such as impermeability and high damping. The most important PIB-based polymer is commercially known as butyl rubber, a copolymer of isobutylene (IB) and 1–3 mol %

isoprene (IP), so the material can be vulcanized to obtain desired properties.^{1,2} Butyl rubber has been used in the tire industry as inner liners and tubes and in applications such as dampeners for vibrating equipment. A new type of butyl rubber, an IB-*para*-methylstyrene (PMS) copolymer called EXXPRO with improved resistance to heat aging, is marketed by ExxonMobil.³ Experimental terpolymers—brominated IB-IP-styrene (St) and IB-IP-PMS—have also been introduced.⁴ Some alternatives to vulcanized/crosslinkable butyl rubbers are thermoplastic elastomers (TPEs) based on PIB-polystyrene (PS) block

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 45, 1778–1787 (2007)
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copolymers. Kennedy and coworkers^{5,6} patented the first synthesis of linear PS-*b*-PIB-*b*-PS triblock copolymers with good physical strength without solvent extraction. Since then, other structures have been reported, the latest being TPEs with an arborescent PIB core.⁷ The route to the synthesis of these TPEs is via controlled carbocationic polymerization. Controlled/living carbocationic polymerization processes are currently being commercialized (e.g., SIBSTAR by Kaneka Co. and IBS Oppanol by BASF). Boston Scientific Co. markets its drug-eluting coronary stent using PS-*b*-PIB-*b*-PS under the trade name Translute as the drug carrier.⁸ Thus, the copolymerization of IB with St is of both academic and industrial interest. This article investigates the carbocationic copolymerization of these two monomers with real-time fiber-optic FTIR monitoring.

BACKGROUND

Carbocationic Homopolymerization of IB and St

The homopolymerization of IB initiated by 2-chloro-2,4,4-trimethylpentane (TMPCl)/titanium tetrachloride (TiCl₄) is the most investigated living carbocationic system, producing high-molecular-weight PIBs with narrow molecular weight distributions (MWDs).⁹ However, under conditions in which [TMPCl]₀ was greater than [TiCl₄]₀, initiation and monomer consumption proceeded simultaneously.¹⁰ Aliquots of the formed polymer were taken to measure the instantaneous fractional initiation efficiency, which was less than unity but rose toward unity at complete conversion. Despite this, the semilogarithmic monomer consumption plot was linear. A similar phenomenon had earlier been reported by Kamigaito et al.¹¹ in living vinyl ether polymerization. The reason for the apparent insensitivity of the monomer consumption rate to the changing polymer concentration is that the quasi-steady-state (QSS) approximation of $d[P^+]/dt \approx 0$ applied to both systems, yielding the following rate expression:

$$\ln \left(\frac{[M]_0}{[M]} \right) = k_p K_{eq} [I]_0 [LA]_0^n t \quad (1)$$

where M is the monomer, I is the initiator, LA is the Lewis acid, and K_{eq} is the equilibrium constant between active and dormant species. In both IB and St polymerizations initiated by 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene

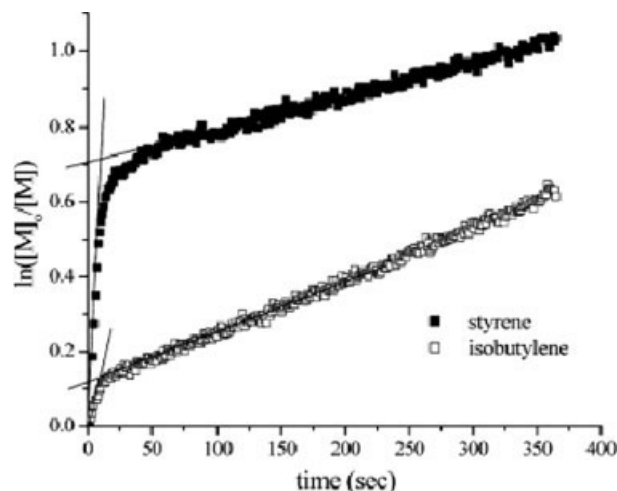


Figure 1. RMC reported for carbocationic IB and St polymerizations^{12,13} ([TiCl₄] = 0.0278 mol/L; [St]₀ = [IB]₀ = 0.5 mol/L; [bDCC]₀ = 0.0066 mol/L; [DtBP] = 0.004 mol/L; [*n*-Bu₄NCl] = 0.0005 mol/L; MCHex/MeCl = 60/40 v/v; temperature = -70 °C).

[blocked dicumyl chloride (bDCC)]/TiCl₄ (Fig. 1), a period of rapid monomer consumption (RMC) that coincides with the process of initiator consumption at the beginning of a living polymerization has been reported.^{12,13} The end of the RMC occurs when all initiators have undergone at least one successful ionization event and have thereby been converted into a dormant chain end characteristic of the monomer. The apparent rate constant for monomer consumption during RMC [$k_{app}(RMC)$] is typically larger than that observed after RMC. Later, De et al.¹⁴ also found RMC in St polymerization initiated by *p*-methyl-styryl-chloride/TiCl₄. Our interpretation of this phenomenon is that during RMC, $d[P^+]/dt$ is greater than 0, so QSS does not apply. When the carbocations forming from the initiator are more stable than the propagating active polymer, P^+ , temporary accumulation of $[I^+]$ may occur. This may lead to initial RMC until the steady state is reached. In Figure 1, $k_{app}(RMC)$ of St is about 10 times that of IB, and this scales with their k_p values measured by Mayr and Faust. Interestingly, Figure 1 shows that after RMC, IB polymerizes faster than St (the linear part of the plot).

Reports for St homopolymerization initiated by TMPCl/TiCl₄ are controversial; RMC has been reported under some conditions,¹⁰ but not under others.^{15–19} However, in all cases, slow initiation and broad MWDs have been consistently found. The TMPCl/TiCl₄ system is particularly important because it mimics blocking PS from living

PIB in PIB–PS block copolymer synthesis. It was shown that when St was added to living PIB at a high residual IB concentration, blocking was slow²⁰ because of slow copolymerization. Kim and Faust²¹ demonstrated penultimate effects in IB polymerization initiated by 3-chloro-1,1,3-trimethylbutylbenzene. When the first St unit reacted with TMP^+ in $\text{TMPCl}/\text{TiCl}_4$ -initiated St polymerization, the more stable TMP-St^+ cations could accumulate, leading to a transitory period in which QSS did not apply. Kinetic analysis led to the conclusion that in this system the rate of initiation depended on the absolute monomer concentration. Increasing $[\text{St}]_0$ from 0.5 to 2 mol/L accelerated the rate of initiation with respect to the rate of monomer consumption. At $[\text{St}]_0 = 2$ mol/L, no RMC was found, even though initiator and monomer consumption coincided until a relatively high monomer conversion.^{18,19} Evidently, under these conditions, QSS prevailed. The reported apparent rate constant of initiation, $k_{i,\text{app}} = 1.4 \text{ L}^2/\text{mol}^2 \text{ s}$, obtained from initiator consumption data,^{18,19} agreed well with $k_{i,\text{app}} = 1.3 \text{ L}^2/\text{mol}^2 \text{ s}$ obtained from RMC.¹³

Carbocationic Copolymerization of IB with St

The carbocationic copolymerization of IB with St has been studied extensively. Table 1 lists reactivity ratio data for carbocationic IB–St copolymerizations, which were compiled by Kennedy and Marechal.²² Most data indicate that IB is more reactive than St, but for a few systems, the reverse has been reported. The authors concluded that the data were inconsistent. Two sets (bolded in Table 1) were reevaluated with the Kelen–Tüdös (K–T) method,²³ yielding the reactivity ratios $r_{\text{IB}} = 1.5$ and 2.7 and $r_{\text{St}} = 0.17$ and 0.7 , respectively, and four systems (italicized in Table 1) indicated penultimate effects. Subsequently, Kaszas and coworkers produced ideal IB–St copolymers whose composition was identical to the feed over the entire monomer concentration range, using the $\text{TMPCl}/\text{TiCl}_4$ initiating system²⁴ and the concept of forced ideal copolymerization.²⁵ Recently, Hull and Kennedy²⁶ reported $r_{\text{IB}} = 3.41$ and $r_{\text{St}} = 1.40$ and azeotropic copolymerization at 21 mol % (11 wt %) IB, using the cumyl chloride (CumCl)/ $\text{TiCl}_4 \cdot \text{BCl}_3$ initiating system. The living copolymerization of IB with St has not been reported yet.

Although there is still disagreement concerning rate constants in carbocationic polymerizations,⁹ most data show $k_{p,\text{St}} > k_{p,\text{IB}}$. Mayr's linear

free energy relationship (LFER)²⁷ predicts $k_{\text{IB}} = 5.5 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ and $k_{\text{St}} = 5.8 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, and this is supported by experimental rate constants obtained from competition experiments.^{16,28} LFER also predicts high values for cross-propagation constants: we calculated $k_{12} = 7.35 \times 10^7$ and $k_{21} = 6.05 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ from Mayr's data, where 1 refers to IB and 2 refers to St. On the basis of the LFER-predicted kinetic rate constants, IB–St reactivity ratios of $r_1 = k_{11}/k_{12} = 7.5$ and $r_2 = k_{22}/k_{21} = 0.10$ would be expected. Although these predictions should be viewed with caution because of the very high rate constants, they have worked well in predicting reactivity ratios in IB–IP copolymerizations.²⁹

Against this background, we investigated the carbocationic copolymerization of IB with St, using both real-time FTIR and traditional gravimetric methods.

EXPERIMENTAL

Materials

Methyl chloride (MeCl ; 99.9%; Matheson) and IB (99%; Matheson) were dried by being passed through a packed bed consisting of CaCl_2/BaO . Methylcyclohexane (MeCHx ; 99%; Aldrich) was dried over molecular sieves, refluxed over sodium under dry nitrogen, and distilled before use. St (polymerization-grade; Aldrich) was vacuum-distilled before use. TMPCl was synthesized as reported²⁴ and was purified by vacuum distillation; its purity was checked by ^1H NMR. TiCl_4 , 2,6-di-tertiary-butylpyridine (DtBP), and N,N -dimethylacetamide (DMA ; Aldrich) were used as received.

Polymerization and Real-Time Data Collection

Polymerizations were conducted in an MBraun glovebox under a dry nitrogen atmosphere. The O_2 (~ 5 ppm) and moisture levels (< 5 ppm) were monitored during the reaction. The temperature of the bath was controlled at -90°C with liquid nitrogen and a PID (Proportional-Integral-Differential)/fuzzy logic controller. A typical experiment was conducted as follows. A three-necked, round-bottom flask was charged with a solvent mixture of MeCl and MeCHx (60/40 v/v), followed by monomers IB and St, initiator TMPCl , DtBP , and DMA . The reaction mixture was cooled to -90°C , and a chilled stock solution of TiCl_4 in

Table 1. Reactivity Ratios Compiled for Carbocationic IB–St Copolymerizations^a

Reaction Conditions and Temperature (°C)	Reactivity Ratio		Reference
	r_1	r_2	
SnCl₄/EtCl/0	1.60	0.17	Lyudvig et al. (1959)
<i>γ</i> -Ray/EtCl/–78	3.5	0.33	Abkin et al. (1961)
AlCl ₃ /MeCl/–92	9.02 ± 0.77	1.99 ± 0.24	Rehner et al. (1953)
AlCl ₃ /MeCl/–30	2.51 ± 0.05	1.21 ± 0.06	Rehner et al. (1953)
AlCl ₃ /MeCl/–30	2.36 ± 0.06	0.76 ± 0.13	Rehner et al. (1953)
<i>EtAlCl₂/MeCl₂/–100</i>	<i>2.8 ± 0.2</i>	<i>1.4 ± 0.2</i>	Kennedy and Chou (1975)
AlCl ₃ /MeCl/–90	1.66 ± 0.02	0.42 ± 0.02	Rehner et al. (1953)
AlCl ₃ /MeCl/–90	1.79 ± 0.02	0.24 ± 0.02	Rehner et al. (1953)
AlCl ₃ /MeCl/–103	3 ± 1	0.6 ± 0.3	Tegge (1953)
TiCl ₄ /Tol/–78	1.78 ± 0.10	1.20 ± 0.10	Okamura et al. (1961) and Imanishi et al. (1965)
<i>TiCl₄/Hx/–78</i>	<i>0.37 ± 0.07</i>	<i>2.41 ± 0.12</i>	Okamura et al. (1961) and Imanishi et al. (1965)
TiCl ₄ /Hx/–20	0.54 ± 0.24	1.20 ± 0.11	Imanishi et al. (1965)
TiCl ₄ /Hx/MeCl ₂ (75:25)/–20	2.63 ± 0.52	5.50 ± 0.55	Imanishi et al. (1965)
<i>TiCl₄/Hx/MeCl₂ (50:50)/–20</i>	<i>3.25 ± 0.25</i>	<i>2.75 ± 0.25</i>	Imanishi et al. (1965)
<i>TiCl₄/Hx/MeCl₂ (25:75)/–20</i>	<i>4.11 ± 0.19</i>	<i>1.70 ± 0.07</i>	Imanishi et al. (1965)
TiCl₄/MeCl₂/–20	4.48 ± 0.28	1.08 ± 0.07	Imanishi et al. (1965)
SnCl ₄ /Hx/MeCl ₂ (25:75)/–20	3.75 ± 0.45	1.92 ± 0.41	Imanishi et al. (1965)
TiCl ₄ /CS ₂ /–20	1.51 ± 0.15	2.44 ± 0.15	Okamura et al. (1961)
TiCl ₄ /decalin/–20	1.53 ± 0.03	2.61 ± 0.4	Okamura et al. (1961)
TiCl ₄ /MeCHx/–20	0.75 ± 0.15	1.30 ± 0.15	Okamura et al. (1961)
SnCl ₄ /SO ₂ /–78	3.1	1.1	Iino and Tokura (1964)
SnCl ₄ /SO ₂ –NOEt/–78	2.2	1.1	Iino and Tokura (1964)
SnCl ₄ /SO ₂ –EtCl ₂ /–78	1.5	1.0	Iino and Tokura (1964)
SnCl ₄ /SO ₂ –NOBz/–78	0.8	0.5	Iino and Tokura (1964)
SnCl ₄ /SO ₂ –Bz/–78	1.9	0.6	Iino and Tokura (1964)

^a The two bolded entries were reevaluated with the K–T method. The four italicized entries showed penultimate effects.

MeCHx (50–50 v/v) was then added to initiate the reaction. Tables 2 and 3 list the conditions for experiments with low (L) and high (H) overall monomer concentrations, respectively. The number represents the molar percentage of IB (L20 = 20 mol % IB).

The progress of the polymerization was monitored with attenuated total reflectance (ATR) probes for high monomer concentrations and with transmission (TR) probes for low monomer concentrations. Each probe was immersed in the polymerization medium and interfaced to a Bio-

Table 2. Copolymerization Data^a

Sample	[IB] ₀ (mol/L)	[St] ₀ (mol/L)	Initial k_{app} (1/s)		QSS k_{app} 1/s		
			IB	St	IB	St	Total
L100	0.50	0.00	—	—	0.0123	—	0.0123
L80	0.40	0.10	0.0044	—	0.0016	0.0001	0.0017
L66	0.33	0.17	0.0077	—	0.0014	0.0003	0.0017
L50	0.25	0.25	0.0062	—	0.0008	0.0002	0.0010
L34	0.17	0.33	0.0034	0.0034	0.00010	0.0002	0.0012
L20	0.10	0.40	0.0056	0.0020	0.0009	0.0004	0.0013
L0	0.00	0.50	—	0.0088	—	0.0027	0.0027

^a [IB]₀ + [St]₀ = 0.5 mol/L; [TiCl₄]₀ = 0.04 mol/L; [TMPCl]₀ = 0.004 mol/L; [DtBP] = 0.007 mol/L; DMA = 0.002 mol/L.

Table 3. Copolymerization Data^a

Sample	[IB] ₀ (mol/L)	[St] ₀ (mol/L)	<i>k_{app}</i> (1/s)
H100	3.00	0.00	0.0143
H95	2.85	0.15	0.0126
H80	2.40	0.60	0.0036
H66	2.00	1.00	0.0027
H50	1.50	1.50	0.0040
H34	1.00	2.00	0.0029
H20	0.60	2.40	0.0042
H5	0.15	2.85	0.0133
H0	0.00	3.00	0.0320

^a [IB]₀ + [St]₀ = 3 mol/L; [TiCl₄]₀ = 0.128 mol/L; [TMPCl]₀ = 0.004 mol/L; [DtBP] = 0.007 mol/L; [DMA] = 0.002 mol/L.

Rad FTS 175C FTIR unit by fiber-optic cables through a port in the dry box. A background spectrum (300 transients) was taken after the initiator and the solvents were added to establish a net zero baseline and minimize background noise. After initiation with TiCl₄, a spectrum (each consisting of 32 transients) was collected every 14–18 s. The spectra then were collated into one multifile (50–250 spectra). Data collection was accomplished online with Bio-Rad Win-IR software. In addition, in selected experiments, gravimetric samples were taken for NMR and size exclusion chromatography (SEC) analysis. The reactions were terminated by the addition of prechilled methanol, and the products were dried *in vacuo* at 40 °C. The FTIR data were evaluated with the GRAMS software with a Lorentzian curve fit. Calibration was used to establish proportionality between the IR peak areas and concentrations in the simultaneous presence of the comonomers.²⁹

NMR spectra were recorded on a Bruker Avance 500 instrument in deuterated chloroform with TMS as the internal reference.

The polymer molecular weights were determined by SEC with a Viscotek model 300 triple detector system equipped with a mixed-bed column (Viscogel GMHHRH) thermostated at 35 °C, a four-capillary differential viscometer, a right-angle laser light scattering detector, and an RI detector. THF was used as the mobile phase at a flow rate of 0.5 mL/min.

RESULTS AND DISCUSSION

The copolymerizations were carried out in a more polar solvent mixture (60/40 MeCl/MeCH_x) than

we normally use to achieve reasonable rates in both low- and high-concentration experiments.

Low-Monomer-Concentration Experiments

Figure 2 shows a typical waterfall plot for [IB]₀ + [St]₀ = 0.5 mol/L, monitoring the C=C stretch signals (1655 cm⁻¹ for IB and 1630 cm⁻¹ for St) by the TR probe.

On the basis of the linearity of the calibration plots, plots of $\ln(A_{0(\text{time zero})}/A_{t(\text{time } t)}) = \ln([M]_0/[M]_t)$ versus the time were constructed for each experiment. Figure 3 shows plots for St homopolymerization (L0) and the copolymerization in Figure 2 (L66).

Similarly to Figure 3(b), fast initial IB polymerization was observed in all five copolymerization experiments, reminiscent of the RMC reported by Storey and coworkers^{12,13} and Faust et al.¹⁶ with similar monomer and initiator concentrations. RMC was also observed in St homopolymerization [L0; Fig. 3(a)]. After the initial RMC burst, a steady consumption rate was displayed by both IB and St. The IB homopolymerization rate plot was linear (L100, not shown). The values of the apparent rate constant (*k_{app}*), calculated from both the initial and steady rates with eqs 2 and 3, are summarized in Table 2:

$$\ln \left(\frac{[\text{IB}]_0}{[\text{IB}]} \right) = k_{app}(\text{IB}) t \quad (2)$$

$$\ln \left(\frac{[\text{St}]_0}{[\text{St}]} \right) = k_{app}(\text{St}) t \quad (3)$$

IB homopropagation was faster than St homopropagation—*k_{p,app}* (1/s) = 0.0123 versus *k_{p,app}* (1/s) = 0.0088 (RMC) and *k_{p,app}* (1/s) = 0.0027 (steady rate)—in contrast to the measured *k_p* data. As mentioned before, Storey and Thomas¹³ also found faster propagation of IB than St following

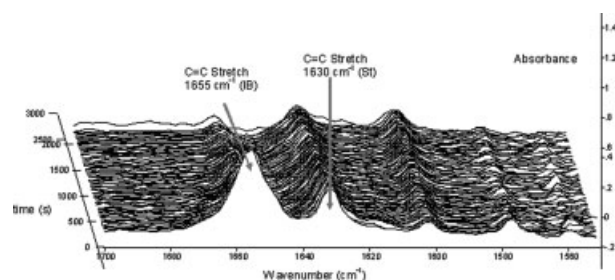


Figure 2. Waterfall plot of real-time FTIR monitoring of an IB–St copolymerization (L66, TR probe).

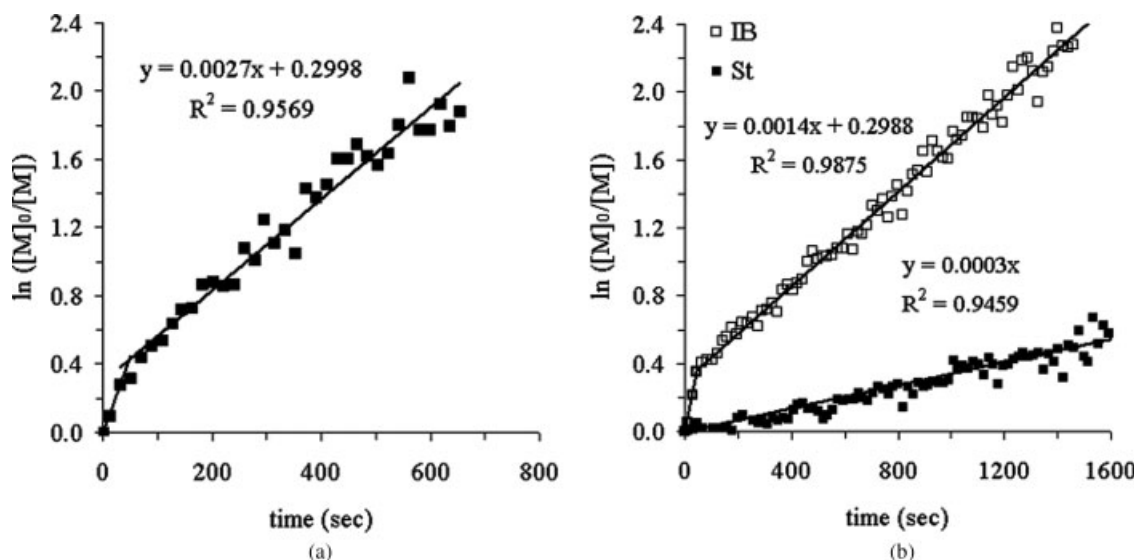


Figure 3. Plots of $\ln([M]_0/[M])$ versus the time for (a) St homopolymerization (L0) and (b) IB–St copolymerization from Figure 2 (L66): (■) St and (□) IB.

RMC (see Fig. 1). Both the IB and St consumption rates were suppressed in the presence of the other monomer, and IB polymerization proceeded faster than St polymerization at all monomer ratios. The steady rates of propagation of IB and St differed the most at $[IB]_0 = 80$ mol %, whereas $k_{app}(IB)$ changed very little in the 20–50 mol % $[IB]_0$ range.

As mentioned earlier, Puskas and coworkers showed that the rate of initiation in St polymerization was directly proportional to both $[TiCl_4]_0$ and $[St]_0$,¹⁸ and at $[St]_0 = 2$ mol/L, no RMC was seen even when the initiator and monomer consumption proceeded simultaneously.¹⁹ Thus, copolymerization experiments were carried out at high $TiCl_4$ and monomer concentrations (Table 3).

High-Monomer-Concentration Experiments

In the high-concentration experiments ($[M_1]_0 + [M_2]_0 = 3$ mol/L), rate plots were constructed from gravimetric conversion data, and the k_{app} values are listed in Table 3. The k_{app} values for H100 and H95 do not differ significantly from that for L100. It is likely that at a high IB concentration, a rate-determining reaction reached its diffusion limit. In contrast to the low-concentration measurements, no RMC was observed and St homopolymerized faster than IB, with $k_{p,app} = 0.032$ versus 0.014 L/mol s, in agreement with the measured k_p data. Similarly to the low-

concentration experiments, the copolymerization rates were very slow. The rate plot with $[St]_0 = 0.6$ mol/L (H80 in Table 3), shown in Figure 4, reveals RMC. However, in the experiments with $[St]_0 > 0.6$ mol/L, no RMC was found. A representative plot is shown in Figure 5. ATR–FTIR confirmed the absence of RMC; a representative plot is shown in Figure 6. Unfortunately, at a high monomer concentration, the FTIR data scatter was generally high. Figure 6 shows that at 34%

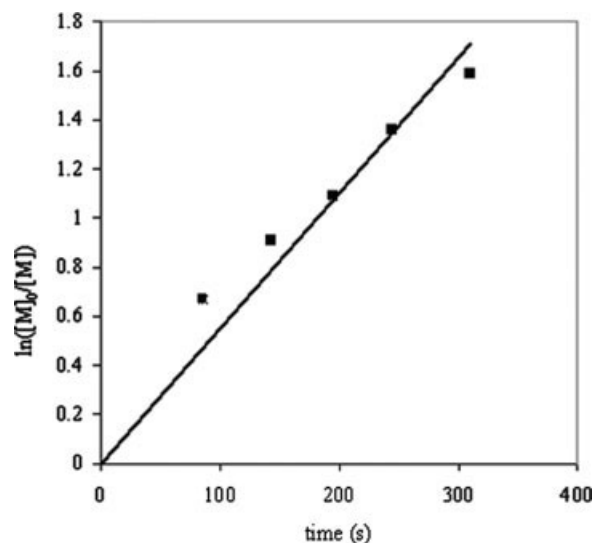


Figure 4. Plot of $\ln([M]_0/[M])$ versus the time for $[IB]_0 = 2.4$ mol/L and $[St]_0 = 0.6$ mol/L (Table 3, H80).

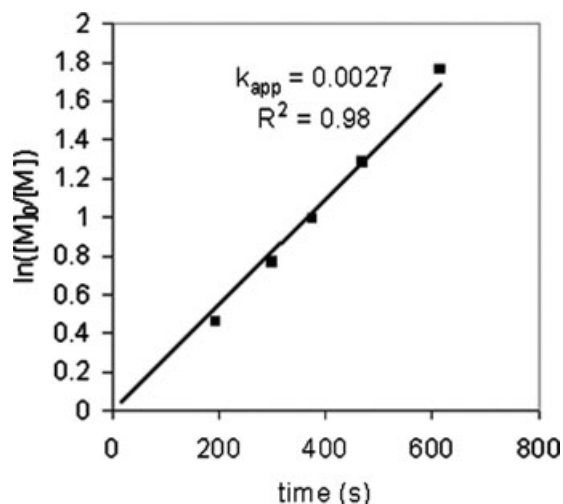


Figure 5. Plot of $\ln([M]_0/[M])$ versus the time for $[IB]_0 = 1.0$ mol/L and $[St]_0 = 2.0$ mol/L (Table 3, H34).

IB, this comonomer was consumed much faster than St ($k_{app,IB} = 0.0021$ s $^{-1}$ and $k_{app,St} = 0.0013$ s $^{-1}$). At 20% IB, however, the rates were much closer, with $k_{app,IB} = 0.0027$ s $^{-1}$ and $k_{app,St} = 0.0022$ s $^{-1}$ (not shown), with no RMC for either monomer.

At $[St]_0 > 0.6$ mol/L, living conditions were achieved; Figure 7 demonstrates a representative linear plot of M_n versus the conversion for H34. The measured final M_n values agreed within the experimental error with the theoretically expected M_n data, assuming 100% initiating effi-

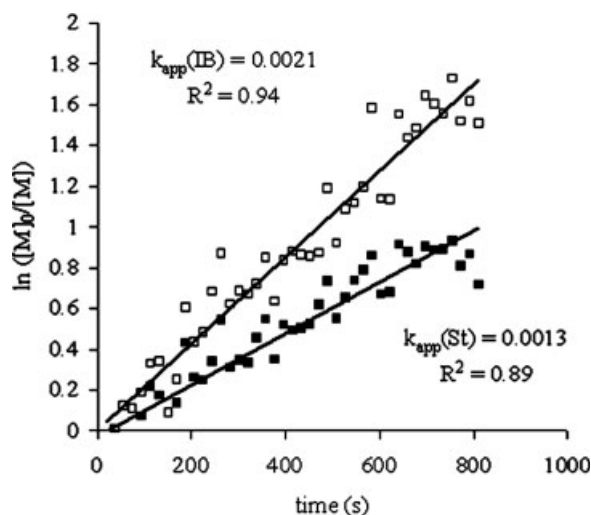


Figure 6. Plot of $\ln([M]_0/[M])$ versus the time for the C=C stretch of IB (1655 cm $^{-1}$) and St (1630 cm $^{-1}$) monitored with an ATR probe (H34, Table 3): (■) St and (□) IB.

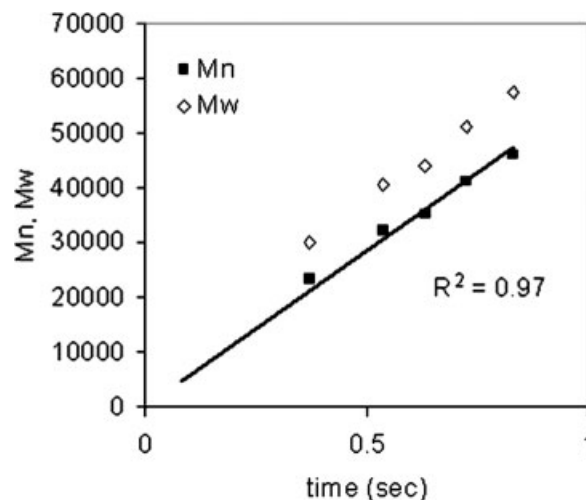


Figure 7. Plots of the molecular weight versus the conversion for $[IB]_0 = 1.0$ mol/L and $[St]_0 = 2.0$ mol/L (Table 3, H34).

ciency. Figure 8 shows that the breadth of the MWD decreased with increasing IB content in the feed, as expected in polymerizations governed by dormant–active equilibria. Beyond about 50 mol % IB in the feed, relatively narrow MWDs ($M_w/M_n \sim 1.2$ – 1.1) were achieved.

In summary, the results presented here demonstrate that both the relative and absolute $[St]_0$ values have a profound influence on the polymerizations rates, molecular weights, and MWDs. Living copolymerization was achieved at a high total comonomer concentration (3 mol/L). Below the critical concentration of $[St]_0 = 0.6$ mol/L, slow initiation was found, but at full conversion,

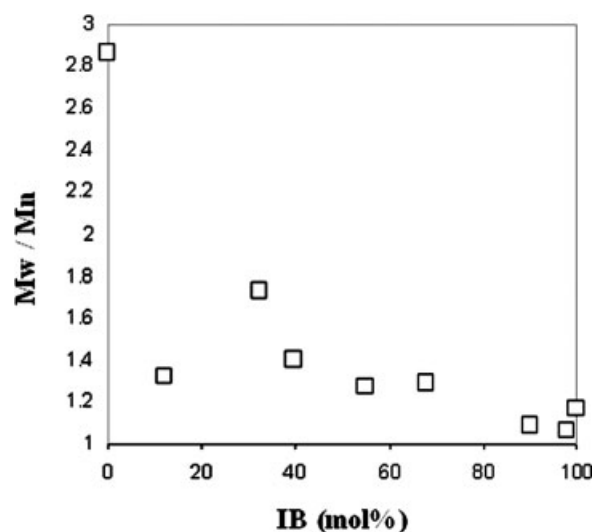


Figure 8. Plot of MWD versus the IB content for the high-concentration experiments (Table 3).

Table 4. Copolymer Compositions by ^1H NMR

Sample	Conversion (%)	Composition (mol % IB)
L34	27	44.1
	39	42.1
	57	36.9
	70	36.4
	89	32.4
L20	50	29.6
	63	25.5
	77	24.5
H95	58	99.0
	83	98.7
	95	98.4
H80	67	93.4
	90	92.7
H66	47	82.5
	71	79.4
	74	72.1
	85	73.2
H50	39.4	59.0
	45.0	54.9
	48.0	51.8
H34	37	42.7
	54	39.9
	63	42.7
	72	40.9
H20	83	40.4
	57	26.7
	77	24.9
H5	85	25.8
	52	12.3
	76	13.2
	81	12.1

copolymers with theoretical M_n values (within the experimental error) and $M_w/M_n \sim 1.1$ were produced. Above the critical St concentration, a linear semilogarithmic rate and M_n -conversion plots were achieved, indicating living conditions, but M_w/M_n increased with increasing St concentration. St homopolymerization yielded $M_n = 82,000$ g/mol, the highest ever produced by carbocationic polymerization.

Copolymer Composition

Table 4 shows copolymer composition data by ^1H NMR. We found IB enrichment in all copolymers. It can also be seen that below the critical St concentration, there is copolymer composition drift with increasing conversion in both the low- and high-concentration experiments. In contrast, above the critical value of $[\text{St}]_0 = 0.6$ mol/L, little or no drift was found (H34, H20, and H5). H20

showed nearly isotropic conditions, and this was similar to what was reported by Hull and Kennedy.²⁶

The K-T plot (extended to high conversions) constructed for the high-concentration experiments is displayed in Figure 9. The plot clearly shows penultimate effects in the IB-St copolymerization system. Reactivity ratios were estimated separately in the high and low IB concentration ranges (see the inset in Fig. 9). In the high $[\text{IB}]_0$ range, $r_{\text{IB}} = 7.24$ and $r_{\text{St}} = 1.96$ represent blocky behavior. In the low $[\text{IB}]_0$ (high St) range, with $r_{\text{IB}} = 1.02$ and $r_{\text{St}} = 0.37$, the system shifts to more random behavior. It is also interesting to note that r_{IB} at the high $[\text{IB}]_0$ range and r_{St} at the high $[\text{St}]_0$ range ($r_{\text{IB}} = 7.25$ and $r_{\text{St}} = 0.37$) are close to the values predicted by Mayr's LFER.

From the M-L (Mayo-Lewis) equation, we derived the following:³⁰

$$r_{\text{IB}} = \frac{k_{\text{app}}(\text{IB})}{k_{\text{app}}(\text{St})} = r_{\text{IB}(\text{inst})} \quad (4)$$

$$r_{\text{St}} = \frac{k_{\text{app}}(\text{St})}{k_{\text{app}}(\text{IB})} = r_{\text{St}(\text{inst})} \quad (5)$$

The instantaneous reactivity ratios obtained from FTIR data of low-monomer-concentration experiments with eqs 3 and 4 varied with the feed composition in a wide range ($r_{\text{IB}(\text{inst})} = 38.43$ to ~ 2.35 and $r_{\text{St}(\text{inst})} = 0.07$ – 0.81).³⁰ From FTIR data of high-concentration experiments (H34 and

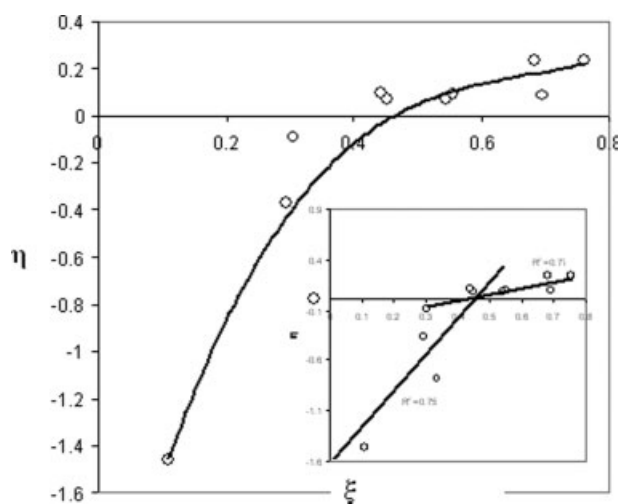


Figure 9. Extended K-T plot for the high-concentration data listed in Table 5.

Table 5. Reactivity Ratios of the IB–IP Copolymerization Systems

IB (mol %)	Probe	r_1		r_2	
		K–T	$k_{app(1)}/k_{app(2)}$	K–T	$k_{app(2)}/k_{app(1)}$
90.00	TR	1.15	1.05	0.87	0.95
79.75	ATR	1.05	1.03	0.92	0.98
62.50	TR	1.13	1.14	0.89	0.88
50.20	ATR	1.23	1.07	0.81	0.93
All data combined	ATR/TR	1.17	1.07	0.89	0.94

H2O, Table 3), $r_{IB} = 1.61$ and 1.23 and $r_{St} = 0.6$ and 0.81 were obtained. Thus, at a high total monomer concentration and above the critical value of $[St]_0 \sim 0.6$ mol/L, the IB–St copolymerization tends to be random.

For comparison, Table 5 lists the reactivity ratios reported for the copolymerization of IB with IP. In this system, the terminal model was found to be valid, and reactivity ratios were calculated from FTIR data, each polymerization experiment being treated as a series of low-conversion experiments.²⁹ These reactivity ratios were found to agree well with $r_{IB} = 1.32$ and $r_{IP} = 0.74$, which were calculated with Mayr's nucleophilicity scale. We calculated reactivity ratios from apparent rate constants measured by FTIR in these experiments and list these data in Table 5. The reactivity ratios from apparent rate constants are independent of the feed composition in the 90–50% IB range and agree well with the values obtained by the other reported FTIR techniques.²⁹

CONCLUSIONS

Real-time FTIR monitoring, together with traditional gravimetric sampling, has given unprecedented insight into IB–St copolymerization. At a high total comonomer concentration (3 mol/L), living conditions (a linear semilogarithmic rate and M_n –conversion plots) were found, provided that the St concentration was above a critical value ($[St]_0 \sim 0.6$ mol/L). The breadth of the MWD decreased with increasing IB concentration in the feed, reaching $M_w/M_n \sim 1.1$. St homopolymerization was also living at a high monomer concentration, yielding PS with $M_n = 82,000$ g/mol, the highest molecular weight ever achieved in carbocationic St polymerization. An analysis of this system by both the traditional gravimetric–NMR copolymer composition method

and FTIR demonstrated penultimate effects. We found IB enrichment in the copolymers at all feed compositions, with very little drift at a high total comonomer concentration and above the critical St concentration.

Financial support by LANXESS, Inc. (Canada), and the National Science Foundation (grant DMR-050968) is greatly appreciated.

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