DOI: 10.1002/masy.200650803

Real-Time FTIR Monitoring of the Carbocationic Copolymerization of Isobutylene with Styrene

Judit E. Puskas,[1] Polly Chan,[1,2] Kimberley B. McAuley,[2]*
Gabor Kaszas,[3] Sohel Shaikh[4]

Summary: The carbocationic copolymerization of isobutylene (IB) and styrene (St) was investigated using *real time* FTIR monitoring. Depending on the concentration of the individual monomers, and their ratio in the feed, initial rapid monomer consumption was observed. Instantaneous reactivity ratios ($r_{IB(inst)}$ and $r_{St(inst)}$) obtained from apparent rate constants of monomer consumption strongly depended on concentration.

Keywords: carbocationic copolymerization; isobutylene; reactivity ratios; styrene

Introduction

Polyisobutylene (PIB)-based copolymers are commercially important materials and exhibit unique properties such as impermeability and high damping. The most important PIB-based copolymer is commercially known as butyl rubber, with 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 liner and tube, and in applications such as dampeners for vibrating equipment. A new type of butyl rubber, IB-*para*methylstyrene (PMS) copolymer called Exxpro is marketed by ExxonMobil.[3] Recent studies have shown that brominated IB-IP-styrene and IB-IP-PMS terpolymers (experimental new bromobulyl) showed improved resistance to hot air aging when compared to brominated IB-PMS[4]. An alternative to vulcanized/crosslinkable rubbers are thermoplastic elastomers (TPEs) based on PIB-polystyrene (PS) block copolymers[5]. Kennedy *et al.* patented the first synthesis of linear PS-PIB-PS triblock copolymers with good physical strength without solvent extraction[6]. Since then, other structures have been reported, the latest being TPEs with arborescent PIB core[7]. The route to the synthesis of these TPEs is via controlled carbocationic polymerizations. 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 medicated coronary stent using PS-PIB-PS under the trade name of Translute® as the drug carrier. Thus the copolymerization of IB with St is of both academic and industrial interest.

In 1982 Kennedy and Marechal compiled data for carbocationic IB-St copolymerizations[8]. Most data showed IB more reactive than St, but in a few systems the reverse was reported. The data were inconsistent, and only two sets could be reevaluated by the Kelen-Tüdös (K-T) method[9], yielding $r_{IB} = 1.5$ and 2.7, and $r_{IP} = 0.17$ and 0.7, respectively. Four other systems indicated penultimate effects. Kaszas et al.[10] produced ideal IB-St copolymers (whose composition was identical to the feed over the entire monomer concentration range) using the "Forced Ideal Copolymerization" concept[11]. Recently,

---

[1] Department of Polymer Science, the University of Akron, Akron, OH 44325-3909
Fax: 001-330-972-5290
E-mail: jpuskas@uakron.edu

[2] Department of Chemical Engineering, Queen's University. Kingston, Ontario, Canada K7L 3N6

[3] Lanxess Inc. 1265 Vidal St. South, Sarnia, Ontario, Canada N7T 7M2

[4] Department of Chemical Engineering, the University of Western Ontario, London, ON Canada N6A 5B9

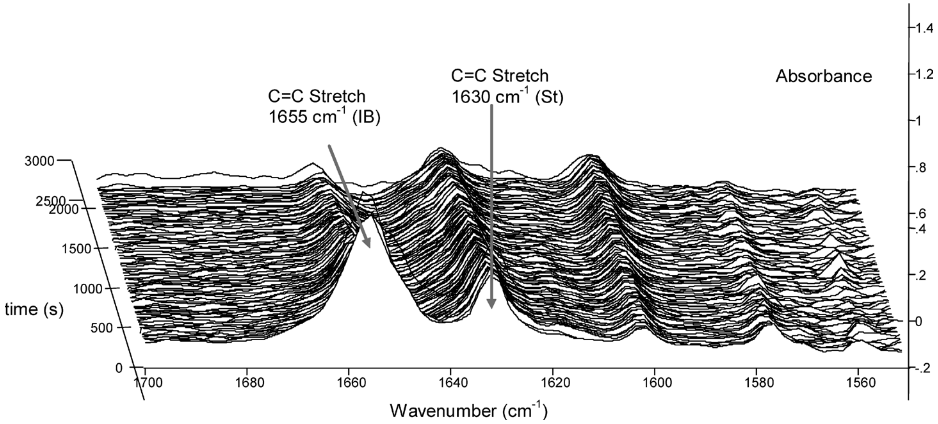

Figure 1.
Waterfall Plot of *real-time* FTIR monitoring of an IB-St copolymerization (Transmission TR probe): $[IB]_0 = 0.33$ mol/L, $[St]_0 = 0.17$ mol/L, $[TMPCl]_0 = 0.004$ mol/L, $[TiCl_4]_0 = 0.04$ mol/L, [D*t*BP] = 0.007 mol/L, [DMA] = 0.002 mol/L MeCHx/MeCl 60/40 v/v, T = −80 °C.

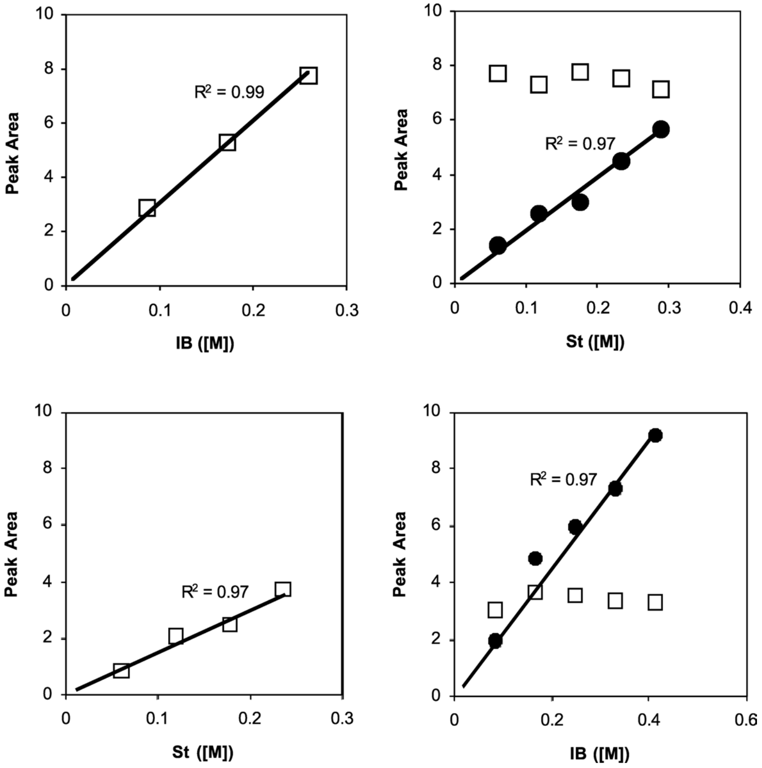

Figure 2.
Calibration of the TR probe. a) IB □; b) St ● in the presence of IB □; c) St ●; d) IB □ in the presence of St ●.

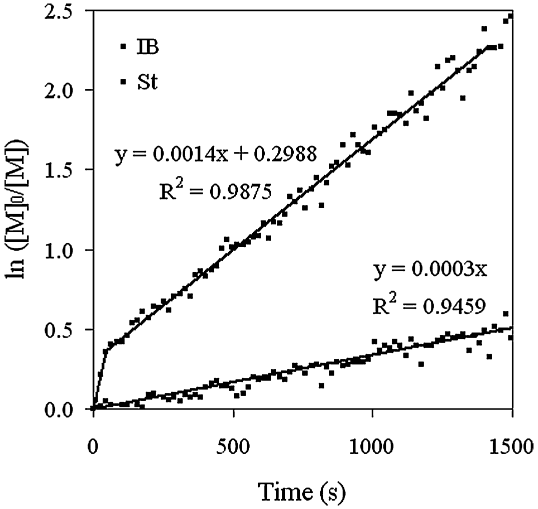

Figure 3.
ln([M]$_o$/[M]) vs time plots of an IB-St copolymerization (conditions in Figure 1).

Hull and Kennedy reported $r_{IB} = 3.41$ and $r_{St} = 1.40$, and azeotrop copolymerization at 21 mol% IB content[12].

Against this background, IB-St copolymerization experiments were carried out and monitored with *real-time* fiber-optic FTIR[13] and this paper will report the first results.

FTIR Monitoring

In copolymerization experiments traditional gravimetry yields cumulative monomer consumption data, while *in situ* FTIR techniques allow monitoring the consumption of each monomer individually. Fiber-optic *real-time* FTIR was used to develop a high-throughput method to measure reactivity ratios, and the validity of the approach was demonstrated in the copolymerization of IB with isoprene (IP)[13]. In the current work, five copolymerization experiments were carried out with 80, 66, 50, 34 and 20 mol% IB. A three-necked round bottom flask was charged with a solvent mixture of methylcyclohexane and methyl chloride (MeCHx/MeCl = 40/60, v / v), followed by monomers (IB & St), initiator (2-chloro-2,4,4-trimethyl-pentane TMPCl), proton trap (2,6-di-*tertiary*-butylpyridine D*t*BP) and electron pair donor dimethylacetamide (DMA. The reaction mixture was cooled to −80 °C, and a chilled stock of $TiCl_4$ in MeCHx (50–50 v/v) was then added to initiate the reaction. During polymerization the C=C stretch signals

Table 1.
$k_{p,app}$ values in IB-St copolymerizations monitored with *real-time* FTIR.

[IB]$_o$ mol/L	Initial Rate		Steady Rate	
	$k_{p,app}$ (IB) 1/s	$k_{p,app}$ (St) 1/s	$k_{p,app}$ (IB) 1/s	$k_{p,app}$ (St) 1/s
0	—	0.0088	—	0.0027
80	0.0044	—	0.0016	0.0001
66	0.0077	—	0.0014	0.0003
50	0.0062	—	0.0008	0.0002
33	0.0034	0.0034	0.0010	0.0002
20	0.0056	0.0020	0.0009	0.0004
100	0.0123	—	0.0123	—

Table 2.
Instantaneous reactivity ratios of IB-St copolymerization.

$[IB]_0$ mol/L	Initial Rate				Steady Rate			
	$r_{IB(inst)}$	CI	$r_{St(inst)}$	CI	$r_{IB(inst)}$	CI	$r_{St(inst)}$	CI
80	38.43	7.23	—	—	13.53	2.06	0.07	0.01
66	23.92	0.04	—	—	4.34	0.20	0.23	0.01
50	25.92	2.01	—	—	3.44	0.37	0.29	0.02
33	1.24	0.93	0.81	0.78	4.36	0.39	0.23	0.02
20	2.92	0.41	0.34	0.02	2.35	0.15	0.43	0.01

CI = 95% confidence interval.

(1655 cm^{-1} for IB and 1630 cm^{-1} for St) were monitored by FTIR. A background spectrum (300 transients) was taken after the initiator and the solvents were added, to establish a net zero baseline and minimized background noise. After initiation with $TiCl_4$, a spectrum (each consisting of 32 transients) was collected every 14~18 seconds. Figure 1 shows a typical waterfall plot. Proportionality between peak areas (A) and monomer concentrations ([M] was established by calibration in the simultaneous presence of both monomers; Figure 2 displays the calibration plots. Based on the linearity of the calibration plots, $\ln(A_0/A_t) = \ln([M]_0/[M]_t)$ vs. time plots were constructed for each experiment. Figure 3 shows a representative plot.

Similarly to that in Figure 3, a fast initial IB polymerization was observed in all five copolymerization experiments, reminiscent of the "Rapid Monomer Consumption" phenomenon (RMC) reported by Storey et al.[14] RMC was also observed in the St plot of the experiments with low IB concentration (20 and 34 mol%). After the initial RMC burst, a steady rate of both IB and St consumption was evident from the graphs. St homopolymerization also displayed RCM, while the IB homopolymerization rate plot was linear.

Reactivity Ratio Calculation

Instantaneous reactivity ratios ($r_{IB(inst)}$ and $r_{St(inst)}$) were calculated from the Mayo-Lewis (M-L) differential equation using apparent rate constants of monomer consumption (the detailed derivation will be published elsewhere).

From the M-L equation we derived that:

$$r_{IB} = \frac{k_{p,app}(IB)}{k_{p,app}(St)} = r_{IB}(\text{inst}) \tag{1}$$

$$r_{St} = \frac{k_{p,app}(St)}{k_{p,app}(IB)} = r_{St(\text{inst})} \tag{2}$$

where $k_{p,app}$, the apparent rate constant of propagation is defined for each monomer

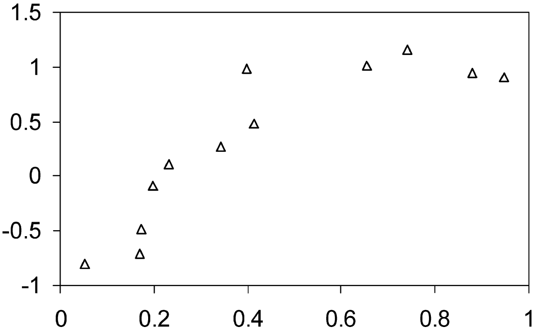

Figure 4.
K-T plot constructed from ref. [10] (Series I).

as:

$$\ln\left(\frac{(IB)_0}{(IB)}\right) = k_{\text{app}}(IB)\ t \tag{3}$$

$$\ln\left(\frac{(St)_0}{(St)}\right) = k_{\text{app}}(St)\ t \tag{4}$$

The $k_{\text{p,app}}$ values calculated from both initial and steady monomer consumption rates are summarized in Table 1. Comparison of the apparent rate constants showed that both the IB and St rate were suppressed in the presence of the other monomer, and IB polymerization proceeded faster than St at all monomer ratios. The steady rates of propagation of IB and St differ the most at $[\text{IB}]_0 = 80$ mol%. In the range of 20 to 50 mol% $[\text{IB}]_0$, the $k_{\text{p,app}}(\text{IB})$ changes very little (0.0002 s^{-1}). The statistical uncertainty in the calculated values of $r_{\text{IB(inst)}}$ and $r_{\text{St(inst)}}$ is related to the uncertainty in the slopes $k_{\text{p,app}}(\text{St})$ and $k_{\text{p,app}}(\text{IB})$, which were determined by linear regression. The half-widths ($\text{w}_{\text{kp,app(IB)}}$ and $\text{w}_{\text{kp,app(IB)}}$) of the 95% confidence intervals for $r_{\text{IB(inst)}}$ and $r_{\text{St(ins)}}$ are propagated from those of $k_{\text{p,app}}$ (IB) and $k_{\text{p,app}}$ (St). Table 2 summarizes the calculated reactivity ratios together with their 95% confidence intervals.

It can be seen that monomer consumption rates (and with that, instantaneous reactivity ratios) are highly concentration-dependent. At high [IB]/[St] ratio, IB is consumed much faster than St. In the $[\text{IB}]_0 = 66 - 33$ mol% range, similar $\text{r}_{\text{IB(inst)}}$ and $\text{r}_{\text{St(inst)}}$ values were obtained for the steady rate period. In contrast, at low [IB]/[St] relatively low $\text{r}_{\text{IB(inst)}}$ and relatively high $\text{r}_{\text{St(inst)}}$ value was found. Thus at high IB/St ratio this system tends to have long PIB blocks, while at low ratios randomization occurs. We explain the peculiar behaviour of the IB-St copolymerization system with penultimate effects. Reevaluation of the Hull-Kennedy data using the K-T method clearly demonstrated deviation from the terminal model; the plot is shown in Figure 4. This also explains the inconsistency in reactivity ratios reported for this system[8].

Conclusion

Fiber-optic *in-situ* FTIR monitoring gave unprecedented insight into the copolymerization of IB with St, allowing simultaneous monitoring of individual monomer consumption. The instantaneous reactivity ratios determined from apparent rate constants of propagation showed strong concentration dependence.

[J.E. Puskas, G. Wilson, J. Duffy, in: "*Ullman's Encyclopedia of Industrial Chemistry*", 7th ed.John Wiley & Sons, Inc., 2004, Section 3.3.

[2] J.E. Puskas, G. Kaszas, in: "*Encyclopedia of Polymer Science and Technology*", John Wiley & Sons, Inc., 2003, Vol. 5, p. 382.

[3] H.C. Wang, K.W. Powers, Paper #80, ACS Rubber Division Meeeting, Toronto, Canada, 1991.

[4] G. Kaszas, B. Tran, *Rubber Chem Techn.* **2002**, *75*, 155.

[5] 4,946,899 (1990), The University of Akron, invs.: J.P. Kennedy, J. E. Puskas, G. Kaszas, W. G. Hager.

[6] J.P. Kennedy, J.E. Puskas, in: "*Thermoplastic Elastomers*", 3rd Ed,G. Holden, H.R. Kricheldorf, R. Quirk (Eds.), Hanser Publishers, Munich, 2004, p. 285.

[7] J.E. Puskas, Y. Kwon, P. Antony, A.K. Bhowmick, *J. Polym. Sci. A*, **2005**, *43*(9), 1811; Cover Page.

[8] J.P. Kennedy, E. Marechal, "*Carbocationic Polymerization*", John Wiley & Sons, Inc., 1982, p 263.

[9] T. Kelen, F. Tüdös, *J. Macromol. Sci.-Chem.*, **1975**, *A9*(1), 1.

[10] D.L. Hull, J. P. Kennedy, *J. Polym. Sci., Part A, Polym. Chem.*, **2001**, *39*, 1515.

[11] G. Kaszas, M. Györ, J. P. Kennedy, *J. Macromol. Sci.-Chem.*, **1982–83**, *A18*(9), 1367.

[12] J.E. Puskas, G. Kaszas, J. P. Kennedy, T. Kelen, F. Tüdös, *J. Macromol. Sci., Chem.*, **1982–83**, *A*(18), 1315.

[13] S. Shaikh, J. E. Puskas, G. Kaszas, *J. of Polym. Sci. Part A: Polym. Chem.*, **2004**, *42*(16), 4084.

[14] R. F. Storey, S. J. Jeskey, *A. M. S. Poly. Preprint*, **2000**, 41(2), 1895.