Carbocationic Copolymerization of Isobutylene and Indene: Copolymer Characterization and Reactivity Ratios

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CARBOCATIONIC COPOLYMERIZATION OF ISOBUTYLENE AND INDENE: COPOLYMER CHARACTERIZATION AND REACTIVITY RATIOS

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ABSTRACT

The copolymerization of the isobutylene (IB)–indene (In) mono-mer pair has been investigated by using the 2-chloro-2,4,4-trimethylpen-tane/$TiCl_4$ initiating system and methyl chloride–methylcyclohexane (40/60 v/v) solvent mixture $-80°C$. According to the Kelen–Tüdös method, the reactivity ratios are $r_{IB} = 1.56 \pm 0.72$ and $r_{In} = 3.48 \pm 0.89$. The formation of copolymers was confirmed by ^{1}H-NMR spectros-copy, selective solvent extraction, and glass transition temperature (T_g) measurements. Copolymerization experiments in the presence of N,N-dimethylacetamide indicate that this electron donor does not affect the reactivity ratios.

INTRODUCTION

The synthesis by living carbocationic polymerization of novel thermoplastic elastomers (TPEs) containing a central rubbery polyisobutylene (PIB) flanked by two glassy outer polyindene (PIn) segments (PIn-b-PIB-b-PIn) has recently been reported [1, 2]. The PIn-b-PIB-b-PIn triblocks are expected to exhibit the good oxidative, chemical, and thermal stability of PIB combined with the relatively high

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FIG. 1. Kelen–Tödös plot. Experimental conditions: TMPCl $= 1.25 \times 10^{-4}$ mol; TiCl$_4$ $= 2.0 \times 10^{-3}$ mol; M$_1$(IB) + M$_2$(In) $= 2$ mL; $V_0 = 25$ mL; CH$_3$Cl/MCHx $= 40/60$ (v/v); $-80°$C; $\mu = 2.0706$, $\alpha = 1.63$.
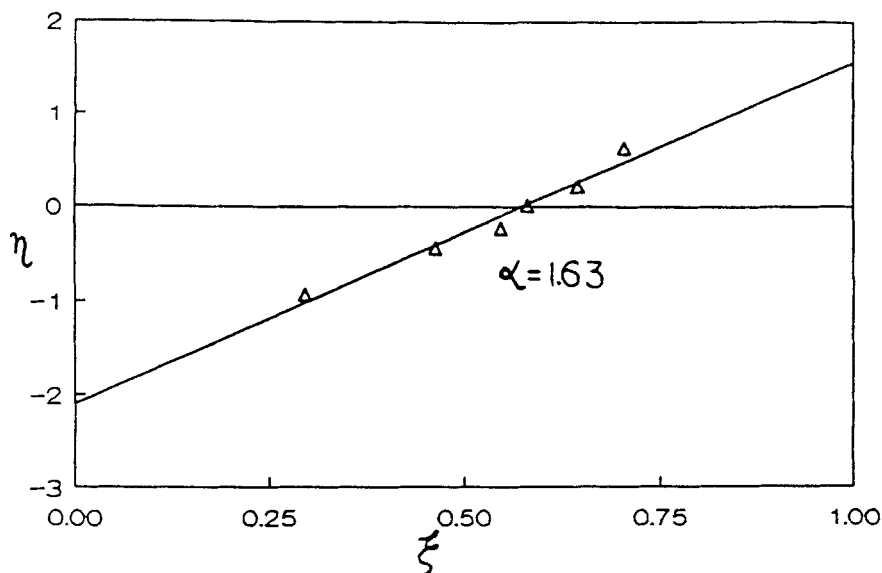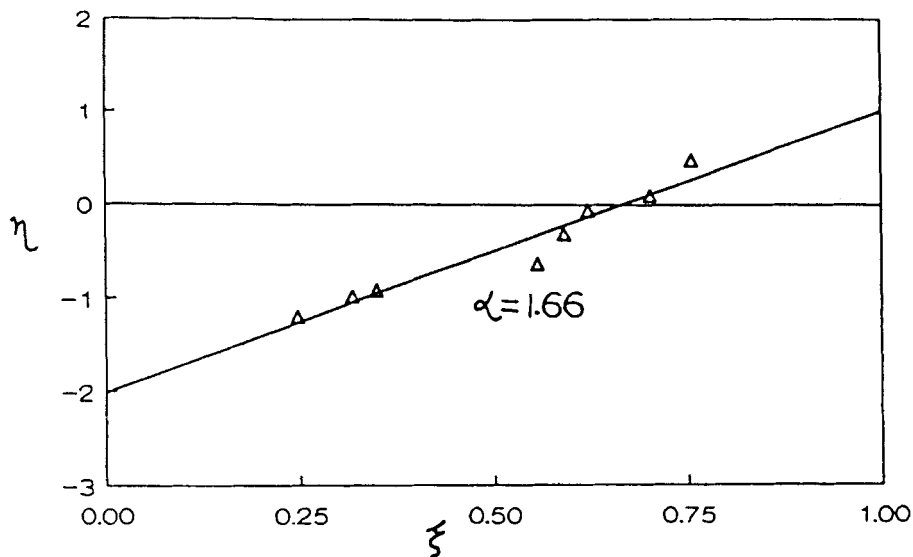

FIG. 2. Kelen–Tüdös plot. Experimental conditions: TMPCl $= 1.25 \times 10^{-4}$ mol; TiCl$_4$ $= 2.0 \times 10^{-3}$ mol; M$_1$(IB) + M$_2$(In) $= 2$ mL; $V_0 = 25$ mL; CH$_3$Cl/MCHx $= 40/60$ (v/v); DMA $= 2.5 \times 10^{-4}$ mol; DtBP $= 1.25 \times 10^{-4}$ mol; $-80°$C; $\mu = 2.0706$, $\alpha = 1.66$.
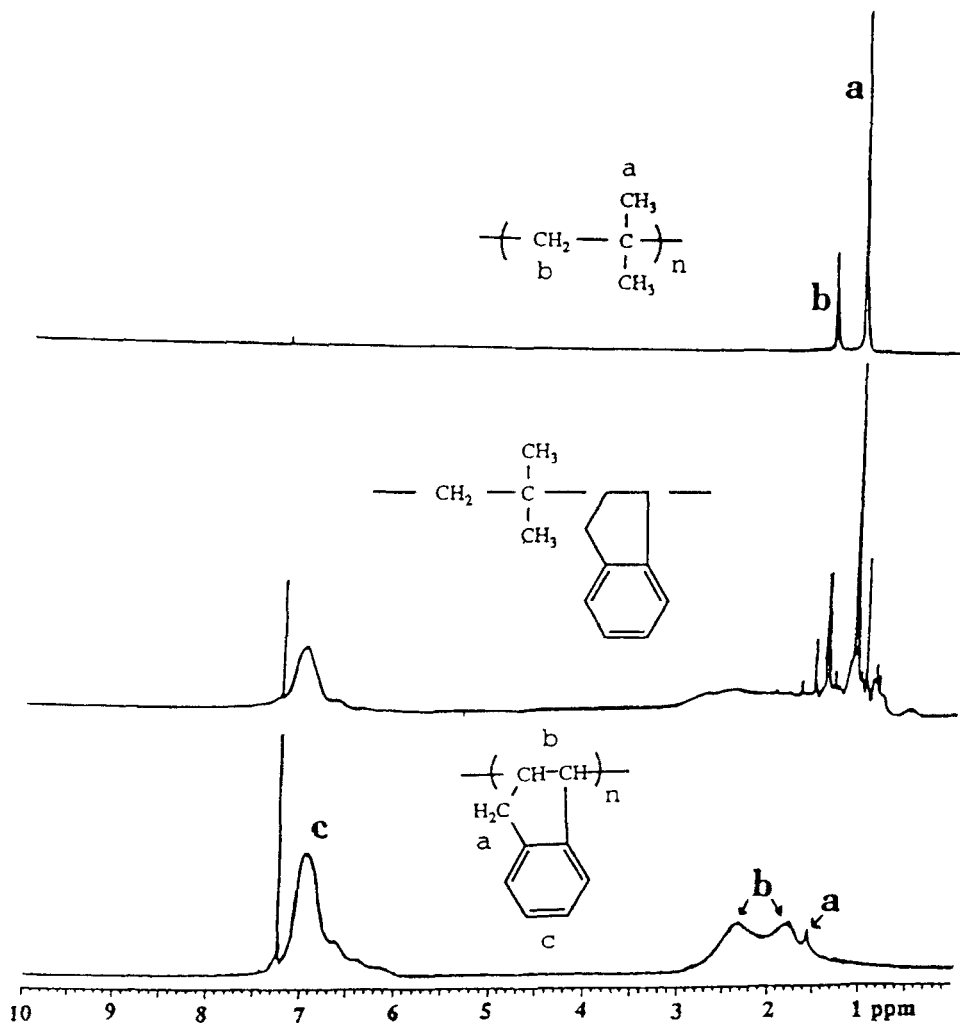
FIG. 3. ^{1}H-NMR spectrum of a representative copolymer (containing 49 mol% In units) together with the representative homopolymers.

T_g ($\sim 209°C$) of the PIn outer segments [3]. Success in regard to the synthesis of PIn-*b*-PIB-*b*-PIn triblocks prompted an investigation into the possibility of copolymerization of the In/IB system.

According to the results presented in this paper, the IB/In monomer pair readily yields copolymers. The monomer reactivity ratios have been determined, and the effect of copolymer composition on T_g has been investigated.

EXPERIMENTAL SECTION

Materials

IB and methyl chloride (Linde) were dried by passing the gases through columns packed with BaO and condensing under a dry N_2 atmosphere. The synthesis

In(mol%)

16

49

74

89

1.2   1.0   0.8   0.6   0.4   0.2 PPM 0.0
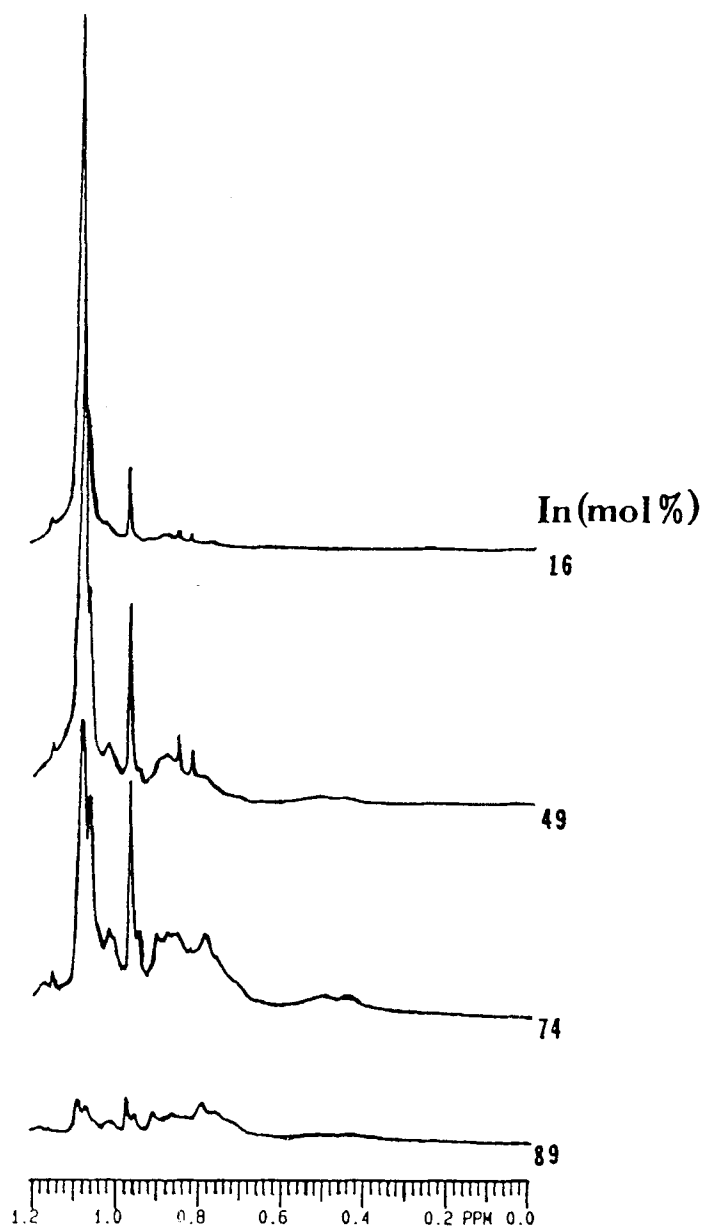
FIG. 4. ^{1}H-NMR spectra of a series of IB-*co*-In copolymers.

and purification of 2-chloro-2,4,4-trimethylpentane (TMPCl) has been described
[4]. TiCl$_4$ (Aldrich) was distilled from CaH$_2$ on the day of the experiment. Methyl-
cyclohexane (MCHx) (Aldrich) was distilled from CaH$_2$. The purification of In
(Aldrich) has been described [5], and its purity (~99.7%) was determined by GC
(Perkin-Elmer instrument, Model 8419, fused silica columns, helium carrier gas).
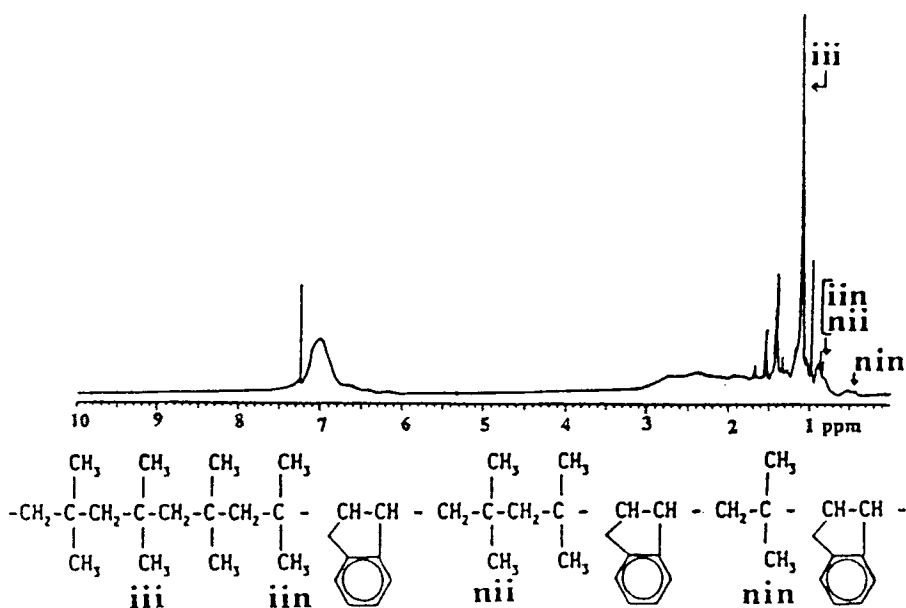
FIG. 5.   ¹H-NMR analysis of a representative IB-*co*-In copolymer.

2,6-Di-*tert*-butylpyridine (D*t*BP), *N,N*-dimethylacetamide (DMA), CDCl₃ (Aldrich), methanol, and THF (Fisher) were used as received.

Procedures

Copolymerizations were carried out in large culture tubes (~75 mL) in a drybox [6]. Experiments were carried out by the conventional "all monomer in (AMI)" technique [6]. The reactions were quenched with cold methanol immediately after initiation. The solvents were evaporated, the precipitated polymers were dissolved in THF, filtered, and reprecipitated into methanol to remove titanium-containing residues (TiO₂, etc.). The products were dried in vacuo at 60°C, and the yields were determined gravimetrically.

Copolymers were Soxhlet extracted for 48 hours with *n*-pentane, a good solvent for PIB. The *n*-pentane was evaporated using a rotovap, and the extracted products were dried in vacuo at 60°C for 7 days. Percent extractable were determined gravimetrically. The overall compositions of extracted and unextracted products were determined by ¹H-NMR spectroscopy.

Characterization

GPC eluograms were obtained by a Waters high-pressure instrument (Model 6000A pump), a series of *μ*-Styragel columns (100, 500, 10³, 10⁴, 10⁵ Å), a differential refractometer (Model 410), and a UV detector (Model 410), using polystyrene (PSt) calibration. ¹H-NMR spectra of copolymer solutions in CDCl₃ were

```
                    ┌─────────────────────────┐
                    │        Copolymer        │
                    │  IB/In:62/38 (mol/mol)  │
                    │   Ā_n** = 8,560 g/mol   │
                    └─────────────────────────┘
                                 │
                Soxhlet              Pentane
                Extraction           2 Days
                    ┌────────────────────┴────────────────────┐
        ┌───────────────────────────┐        ┌───────────────────────────┐
        │   Soluble = 40 wt %       │        │   Insoluble = 60 wt %     │
        │  IB/In:65/35 (mol/mol)    │        │  IB/In:58/42 (mol/mol)    │
        │   Ā_n = 6,000 g/mol       │        │   Ā_n = 9,000 g/mol       │
        └───────────────────────────┘        └───────────────────────────┘
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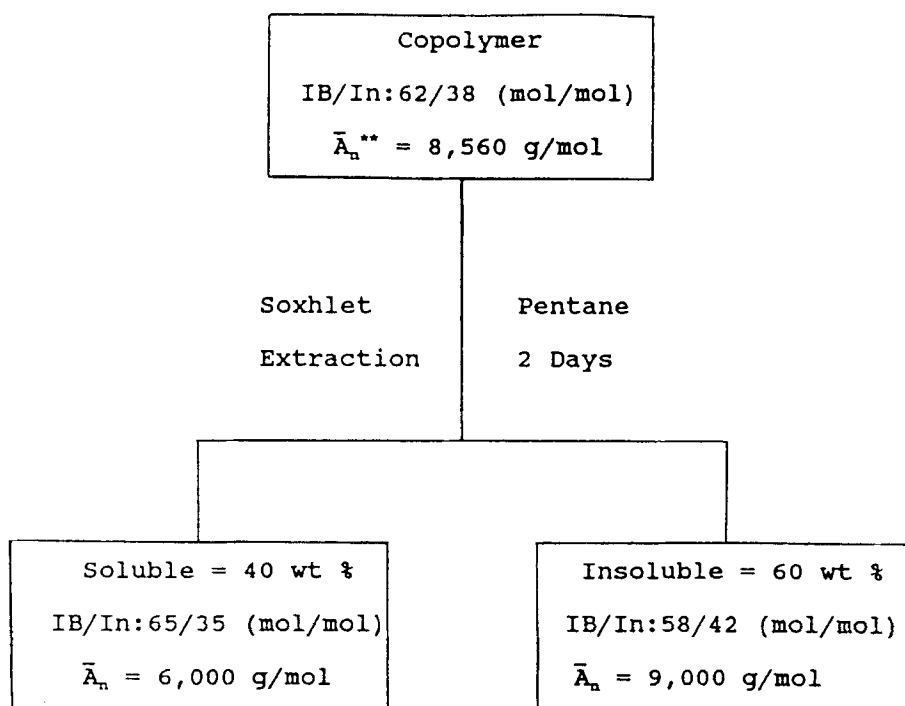
SCHEME 1.   Selective solvent extraction of a representative copolymer prepared by the TMPCl/TiCl$_4$/CH$_3$Cl:MCHx (40/60, v/v)/DMA/DtBP/ $-80\,°$C system.

obtained using a Varian Gemini 200 MHz spectrometer. Glass transition temperatures were determined by using a Du Pont 910 DSC module with a Du Pont 9900 computer/thermal analyzer. Thermograms were obtained by heating samples (10–30 mg) above their T_gs, slowly cooling (2°C/min) to the glassy state, followed by rapid reheating (10–20°C/min).

RESULTS AND DISCUSSION

Determination of Reactivity Ratios

The reactivity ratios, r_{IB} and r_{In}, were determined by the Kelen–Tüdös method which can be used up to rather high conversions ($\leq 40\%$) [7, 8]. Confidence intervals for the reactivity ratios were also determined [9]. Figure 1 shows the Kelen–Tüdös (η versus ξ) plot together with the experimental conditions. Conversions were kept within the limits ($\leq 40\%$) required by the Kelen–Tüdös method [8, 9]. Copolymer composition was determined by ^{1}H-NMR spectroscopy. The linearity of the plot is indicative of the validity of the method [7]. The r_{IB} and r_{In} were determined from the intercept and slope, respectively. Thus, r_{IB} = 1.56 ± 0.72 and r_{In} = 3.48 ± 0.89, which indicates that In is relatively more reactive than IB.

The effect of an electron donor, DMA, on the copolymerization was also investigated. Figure 2 shows the η versus ξ plot together with the experimental
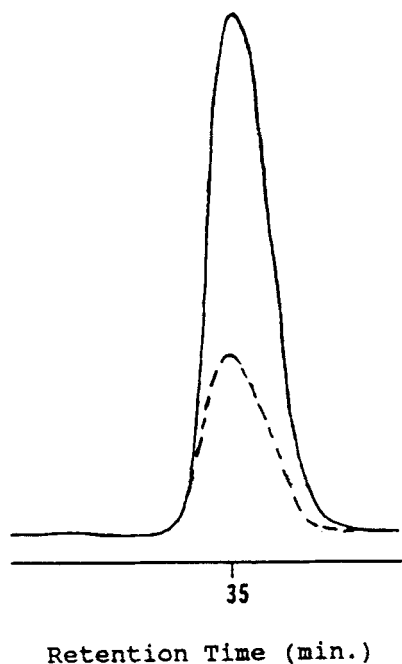
Retention Time (min.)

FIG. 6.   GPC traces of a representative IB-*co*-In copolymer (containing 36 mol% In units): (——) RI, (- - -) UV.

conditions. The slope and intercept give, respectively, r_{IB} = 1.02 ± 0.47 and r_{In} = 3.37 ± 0.84. The reactivity ratios obtained in the presence of DMA are within the confidence interval of those obtained in the absence of DMA. These results indicate that while DMA reduces the reactivity of individual propagating ends, it does not affect the monomer reactivity ratios. The fact that the product of the reactivity ratios is larger than 1 indicates that the copolymerization of IB and In produces somewhat blocky products.

Characterization

Evidence for copolymer formation was obtained by ^{1}H-NMR spectroscopy. Figure 3 shows the ^{1}H-NMR spectrum of a representative copolymer containing 49 mol% In units, together with the respective homopolymers. A comparison of the spectra of the copolymer with those of the respective homopolymers reveals new peaks in the aliphatic region. Figure 4 shows the expanded aliphatic region of the ^{1}H-NMR spectra of the copolymers containing various amounts of In units. The proton resonance due to the *gem*-dimethyl groups in the copolymer appears as several partially resolved resonances (Fig. 5). By using the terminology of Kennedy and Chou [10], the singlet at 1.1 ppm has been assigned to "fully-crowded" *gem*-dimethyls (i.e., *gem*-dimethyl groups flanked on both sides by other *gem*-dimethyl groups, iii triad), the singlet at 1 ppm to the *gem*-dimethyl groups on the fifth
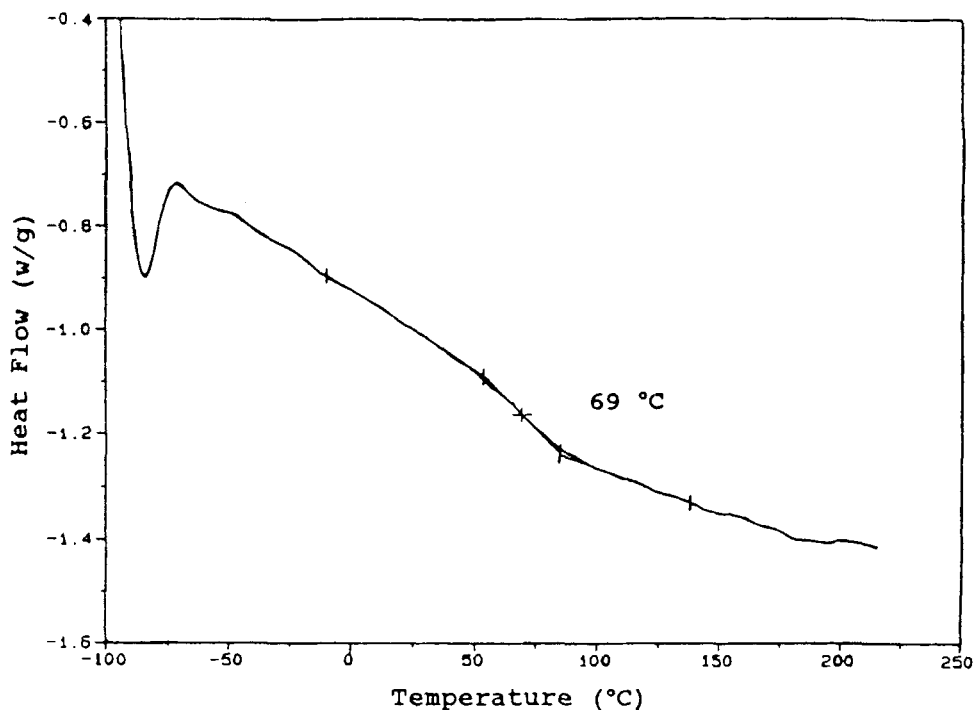
FIG. 7.   DSC scan of a representative copolymer (containing 62 wt% In).

carbon from the aromatic ring [11], the resonances in the $\delta = 0.7-0.9$ range to "half-crowded" gem-dimethyl groups (i.e., a gem-dimethyl group flanked by only one gem-dimethyl group, nii or iin traids), and the resonances in the $\delta = 0.4-0.6$ ppm range to "uncrowded" gem-dimethyls (i.e., gem-dimethyl groups flanked on both sides by two indene units (nin triads)) [10]. The latter two ranges show complex unresolved peaks, indicating pentads or other effects. The peak at $\delta = 1.5$ ppm remains unidentified.

TABLE 1.   Effect of IB-co-In Copolymer Composition on T_g [a]

	$\overline{M}_n$, g/mol	In, mol%	In, wt%	T_g, °C
1	10,000	0	0	-65
2	10,000	38	57	70
3	10,700	42	62	103
4	11,600	58	74	112
5	10,900	68	82	131
6	10,000	100	100	200

[a]Copolymers prepared by TMPCl/TiCl$_4$/CH$_3$Cl/MCHx (40/60, v/v)/DMA/DtBP/ -80°C system
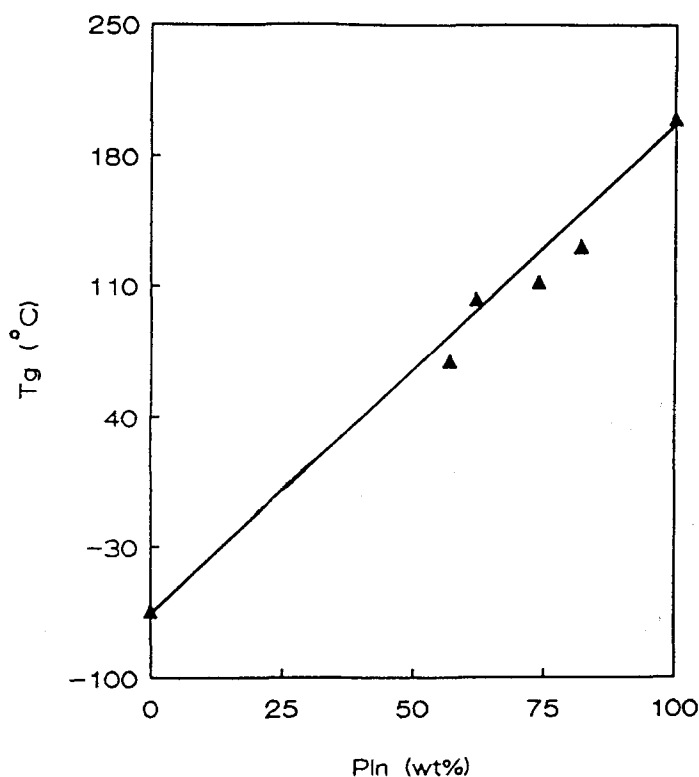
FIG. 8.   Effect of IB-*co*-In copolymer composition on T_g.

Evidence for copolymer formation has also been obtained by selective solvent extraction. Thus, a representative copolymer sample was extracted with *n*-pentane (a good solvent for homo-PIB), and the resulting fractions were analyzed by ^{1}H-NMR and GPC. Scheme 1 shows the extraction procedure and results. The composition of both fractions were essentially identical, as shown by ^{1}H-NMR spectroscopy. GPC analysis of the fractions indicated that the molecular weight of the soluble fraction was lower than that of the insoluble fraction. Evidently fractionation occurred by molecular weights. According to the results, the product was not a mixture of homopolymers.

Figure 6 depicts GPC traces (obtained by RI and UV detectors) of a representative copolymer. The UV and RI course of the traces are virtually identical, indicating a uniform distribution of In units across the molecular weight distribution in the copolymer. The absence of skewing or shoulders suggests the absence of significant amounts of homopolymers.

Figure 7 shows the DSC scan of a representative copolymer containing 62 wt% In units. The presence of a single transition ($T_g = 69°C$) is indicative of true copolymer. The T_gs of a series of copolymers of essentially the same molecular weight but of varying compositions were determined by a rigorous procedure (see Experimental Section). Table 1 shows the results and Fig. 8 the T_g versus copolymer

composition plot. Evidently the T_gs increase with increasing In content, reflecting the influence of the "hard" In repeat unit in the copolymer. The close to linear T_g versus In content plot suggests the existence of essentially random IB/In copolymers. According to these results, the T_g of the outer hard blocks in PIn-*b*-PIB-*b*-PIn triblocks may be controlled by copolymerization of IB and In.

CONCLUSIONS

The copolymerization of IB with In was investigated. According to the reactivity ratio data, In is relatively more reactive than IB, and copolymerization results in a block copolymer. The reactivity ratios obtained in the presence of an electron donor, DMA, were within the confidence intervals of the reactivity ratios obtained in the absence of DMA, indicating that the electron donor affects only the reactivity of the active chain-end but does not affect its preference for adding one or the other monomer. Characterization by ^{1}H-NMR, DSC, selective solvent extraction, and GPC showed the formation of copolymers.

Experiments were carried out to study the possibility of the control of outer-block T_g by copolymerization of In with IB. DSC data of the copolymers showed increased copolymer T_g with increasing PIn content. From these results it was concluded that outer block T_g of PIn-*b*-PIB-*b*-PIn triblocks can be controlled by copolymerization.

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