Macromolecules 1993, *26*, 429–435

Polyisobutylene-Containing Block Polymers by Sequential Monomer Addition. 8. Synthesis, Characterization, and Physical Properties of Poly(indene-*b*-isobutylene-*b*-indene) Thermoplastic Elastomers[†]

Joseph P. Kennedy,[*] Sanjeev Midha,[‡] and Yasuo Tsunogae[§]

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909

Received November 19, 1991; Revised Manuscript Received September 17, 1992

ABSTRACT: Novel thermoplastic elastomers (TPEs) containing a central rubbery polyisobutylene (PIB) and glassy outer polyindene (PIn) segments have been prepared by living carbocationic polymerization by sequential monomer addition. The synthesis conditions for TPEs were developed with the help of model experiments using the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ initiating system and subsequent PIn-*b*-PIB-*b*-PIn triblock syntheses. Triblock copolymer compositions were determined by ^1H NMR and UV spectroscopy. The structural purity of the triblocks was determined by GPC, and the compositional purity was determined by selective solvent extraction. Characterization of triblocks by DSC, DMTA, and transmission electron microscopy (TEM) indicated a microphase-separated system. The thermal characterization of materials by TGA and melt viscosity versus shear rate indicated good thermal stability and ease of melt processability, respectively. The triblocks exhibited excellent thermoplastic elastomeric characteristics. Tensile strengths, 300% moduli, and hardness increased with increasing polyindene (PIn) content, while percent elongations decreased.

Introduction

TPEs are of great scientific and commercial importance.[1,2] These materials behave like vulcanized rubber at ambient temperature but can be solution cast or melt processed like thermoplastics.[3] An example is an ABA triblock copolymer, where A is a hard thermoplastic, for example, polystyrene, poly(methyl methacrylate), and B is an elastomer, for example, polyisoprene, polybutadiene, polyisobutylene, etc.[3]

Synthesis of TPEs with a saturated central rubbery block and high T_g outer thermoplastic blocks has long been desired because of the expected good oxidative and thermal stability of this material. The objective of this research was the synthesis of an inventory of PIn-*b*-PIB-*b*-PIn triblock copolymers and study of their select physical properties. Justification for this research are (1) the good oxidative, chemical, and thermal stability of PIB, (2) the reasonably high T_g (~200 °C) of the PIn outer segments, and (3) the possibility that molded goods made of this novel TPE may be sterilized at 100 °C without loss of shape.

This paper concerns the synthesis of an inventory of PIn-*b*-PIB-*b*-PIn triblocks, their molecular characterization, and a study of their select physical properties.

Experimental Section

Materials. High-purity isobutylene (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 and purification of 1,4-bis(2-methoxy-2-propyl)benzene (dicumyl ether, DCE) has been described.[4] $TiCl_4$ (Aldrich) was distilled from CaH_2 on the day of the experiment. Methylcyclohexane (MCHx; Aldrich) and toluene (Fisher Scientific Co.) were distilled from CaH_2. The purification of indene (In) has been described in the previous paper (purity 99.7%). Satisfactory results have also been obtained with In that was purified by silica gel column chromatography (column length 15 cm; product purity 95% by GC) followed by crystallization from pentane (purity >98% by GC); however, only the latter material was used. 2,6-Di-*tert*-butylpyridine (D*t*BP), *N*,*N*-dimethylacetamide (DMA), triethylamine (TEA), $CDCl_3$ (Aldrich), methanol, and THF (Fisher Scientific Co.) were used as received.

Synthesis of Triblock Polymers.[4] A typical synthesis procedure is as follows: To a 500-mL three-neck, round-bottomed flask equipped with a mechanical stirrer, were charged appropriate amounts of solvents, initiator, isobutylene, electron donor (ED), and proton trap (D*t*BP). The reaction mixture was stirred at −80 °C. After the mixture was thermostated, a solution of $TiCl_4$, precooled to −80 °C, was added rapidly (in less than 2 s).

After stirring for a designated time, a small sample was withdrawn using a precooled pipet and quenched into methanol. The purpose of this sample was to ascertain that all the IB has reacted and to determine the conversion, $\bar{M}_n$, and molecular weight distribution of the biliving $^+PIB^+$ segment.

To induce the blocking of In, a prechilled solution consisting of In, ED, and proton trap dissolved in the same solvent used for the initial charge was rapidly poured into the living $^+PIB^+$ dication charge at −80 °C. The solution was stirred for a designated time, and the living charge was quenched with a few milliliters of prechilled methanol. The quenched system was poured into methanol and stored overnight under a hood, and, after the solvents had evaporated, the precipitated product was dissolved in THF and reprecipitated into an excess of methanol. The product was dried until constant weight, and yields were determined gravimetrically.

Characterization Methods. Molecular weights and molecular weight distributions were determined by GPC (Waters high-pressure instrument, Model 6000A pump) using a series of μ-Styragel columns (100, 500, 10^3, 10^4, and 10^5 Å), a differential refractometer (Model 410), a UV detector (Model 440), and a Wisp (710B) automatic sampler. The temperature of the columns was 35 °C, and the flow rate was 1 mL of THF/min. The data were analyzed using Nelson-Analytical 3000 series chromatography software. The calibration curves were obtained with narrow molecular weight distribution polyisobutylene and polystyrene standards.

The number-average molecular weights of triblock copolymers were also determined by membrane osmometry (Mechrolab Inc., high-speed membrane osmometer, Model 503) at 37 °C using a porous RC-52 regenerated cellulose membrane.

^1H NMR spectra were obtained using a Varian Gemini 200-MHz spectrometer. The solutions were prepared either in $CDCl_3$

[*] Author to whom correspondence should be directed.

[†] Part 56 of "Living Carbocationic Polymerization".

[‡] Present address: The Procter and Gamble Co., 11511 Sharon Woods Technical Center, Cincinnati, OH 45241.

[§] Permanent address: Nippon Zeon Co., Research and Development Center, Kawasaki, Japan 210.

0024-9297/93/2226-0429$04.00/0

or in CD_2Cl_2. The weight percent In content in block and random copolymers was determined by the formula

$$\text{wt \% indene} = \frac{116.16A}{116.16A + 56.1\frac{(B-A)}{2}} \times 100$$

where A = integrated area from aromatic protons and B = integrated area from aliphatic protons.

The In content in triblock polymers was also calculated by UV spectroscopy[8] using a Perkin-Elmer 559 A UV/vis spectrophotometer. Identical 1-cm quartz cells were used for the measurements. Glass transition temperatures were determined using a Du Pont 910 DSC module with a Du Pont 9900 computer/thermal analyzer. A sample (10–30 mg) was heated rapidly to a temperature above its T_g and then brought down to the glassy state at a very slow cooling rate (2 °C/min) followed by rapid heating (10–20 °C/min) to obtain the thermogram. Because the heating rate had been faster than the cooling rate at which the glassy sample was prepared, the effect of structure relaxation that accumulated during the cooling was abruptly released at the T_g and well-defined transitions could be obtained in the thermograph.[9] TGA was conducted on a Du Pont 951 thermogravimetric analyzer. The heating rate was 10 °C/min. DMTA was conducted on a Polymer Laboratories automatic computer-controlled system. A heating rate of 2 °C/min and a frequency of 1 Hz were used. Triblock copolymer morphology was investigated by transmission electron microscopy. Very thin polymer films were cast from THF on copper grids and viewed under a JOEL 120 U TEM. Photographs were taken at different magnifications.

Physical Properties. For mechanical property studies, clear homogeneous films were cast from THF solution (20 wt %) and vacuum dried at 60 °C for at least 10 days. In some cases films were cast from toluene to study the effect of casting solvent on stress–strain properties. Stress–strain measurements were carried out on an Instron tensile tester at a cross-head speed of 50 cm/min (2.5-cm grip separation) at 23 °C. The averages of at least three readings are reported. The Shore A2 hardness of materials was determined according to ASTM D2240.

Processability Studies.[10] Melt viscosities of bulk triblock samples were measured using a Instron capillary rheometer (ASTM D3835-79), with a capillary length (*L*) of 1.8 in. and a diameter (*D*) of 0.06 in. (*L*/*D* ratio = 30). The data are reported as a plot of log apparent viscosity (in poise) versus log shear rate (in reciprocal seconds).

Results and Discussion

1. Synthesis of the Rubbery Midsegment. Preparation of the Macroinitiator $^+PIB^+$. For the synthesis of triblock copolymers by two-stage sequential polymerization, it is important to judge the time at which the synthesis of biliving $^+PIB^+$ is over because the introduction of In into the charge before complete polymerization of IB may cause formation of a triblock with copolymer outer segments, i.e., P(In-*co*-IB)-*b*-PIB-*b*-P(In-*co*-IB). The presence of IB in the outer segments may lead to decreased incompatibility of the glassy and rubbery phases and thus to poorer tensile properties.[3]

It has been demonstrated that in the absence of monomer the living $^+PIB^+$ centers irreversibly deteriorate.[5] Thus, the addition of fresh monomer (i.e., In) to a 100% polymerized aged living system may result in contamination by PIn and/or PIB-*b*-PIn diblocks. The presence of the diblock may cause decreased properties due to the PIn block being included in the glassy domain while the PIB block would be attached only at one end. So, the presence of even a few percent of diblock in the target triblock may exert a deleterious influence on the ultimate physical properties.[3]

Kinetic experiments were carried out to determine the time at which the IB polymerization was complete. Figure 1 shows the time versus conversion plot, along with the experimental conditions, for the synthesis of a representative $^+PIB^+$ macroinitiator. In other experiments, depending upon the experimental conditions, reaction times were adjusted to facilitate complete polymerization of IB.

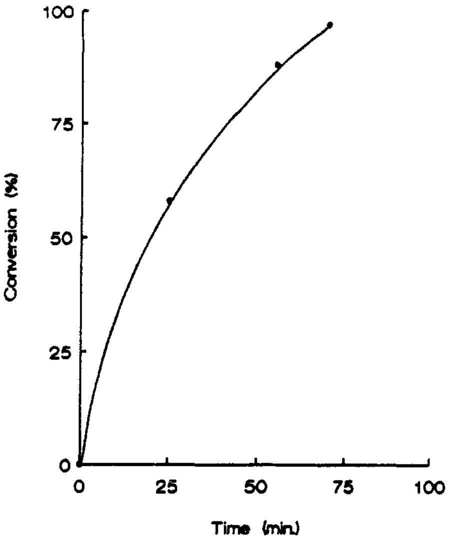
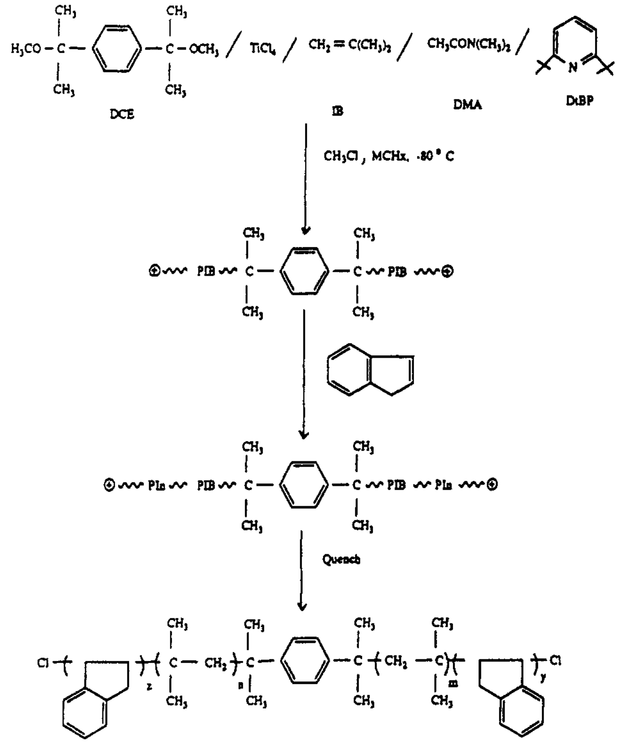


Figure 1. Time–conversion plot for the synthesis of a representative $^+PIB^+$ macroinitiator. Reaction conditions: [DCE] = [DMA] = [D*t*BP] = 1.6 M; [$TiCl_4$] = 0.0256; [IB] = 1.45 M; CH_3Cl/MCHx = 40/60 (v/v); V_0 = 150 mL; −80 °C.

Scheme I
General Strategy for the Synthesis of PIn-*b*-PIB-*b*-PIn Triblock Copolymers



2. Block Copolymerization of Indene from the Bifunctional Macroinitiator $^+PIB^+$. Aided by the information described in the preceding section, the stage was set for the blocking of In from $^+PIB^+$. Scheme I outlines the general strategy used for the synthesis of triblocks. Table I shows the experimental conditions and the results of a representative block copolymerization experiment. Figure 2 shows the GPC traces of the midsegment and of the final product. The shift in the peak position of the block polymer toward higher molecular weights (lower retention times) relative to the PIB midsegment indicates significant In incorporation. The symmetry and the narrowness of the peak associated with block polymer suggests good structural purity of the

Table I
Synthesis and Characterization of a Representative PIn-*b*-PIB-*b*-PIn Sample

Synthesis

Step 1. Midsegment synthesis: [DCE] = [DMA] = [D*t*BP] = 1.6 mM; [$TiCl_4$] = 0.0256 M; [IB] = 1.45 M; CH_3Cl/MCHx = 40/60 (v/v); 90 min; −80 °C
Step 2. End-segment synthesis: [DMA] = [D*t*BP] = 1.6 mM; [$TiCl_4$] = 0.0128 M; [In] = 0.37 M; 90 min

Characterization

PIB Midsegment

$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	I_{eff}[a] (%)
54 250	1.19	92

PIn-*b*-PIB-*b*-PIn Triblock

			wt % PIn	
$\bar{M}_n$[b]	$\bar{M}_n$[c]	A_w/A_n[d]	NMR	UV
93 400	93 600	1.39	40	41

[a] Initiation efficiency. [b] By ^{1}H NMR. [c] By membrane osmometry. [d] Apparent $\bar{M}_w/\bar{M}_n$ by GPC using PIB calibration.

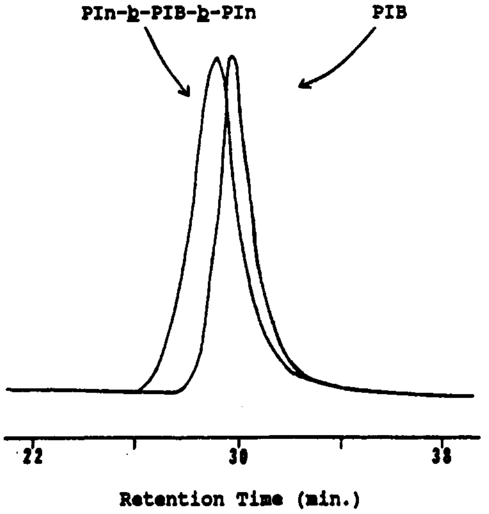


Figure 2. Gel permeation chromatograms of the PIB midsegment and the triblock copolymer.

triblock. The compositional purity of the product was determined by selective solvent extraction.

Scheme II shows the extraction strategy and the relative amounts and compositions of the individual fractions. The bulk of the sample was insoluble in hexanes, which is a good solvent for PIB and is a nonsolvent for PIn, indicating that the sample was predominantly the target triblock. Compositional analysis by ^{1}H NMR spectroscopy showed the presence of PIn in both soluble and insoluble fractions. PIn can be present in the soluble fraction only by being pulled into the solution by long PIB segments. GPC analysis of the fractions indicated that the molecular weight of the soluble fraction is lower than that of the insoluble fraction. Evidently fractionation occurred by molecular weights. The fractionation results coupled with compositional analysis suggest the absence of PIB homopolymer contamination and hence indicate high blocking efficiency.

High blocking efficiency (B_{eff}) was contrary to the low I_{eff}'s obtained in the model In blocking experiments carried out with the TMPCl initiator (see preceding paper). To understand the reason for the high B_{eff}, experiments were carried out to compare the rate of In polymerization in model blocking (TMP^+ initiator) and in actual blocking ($^+PIB^+$ initiator) experiments.

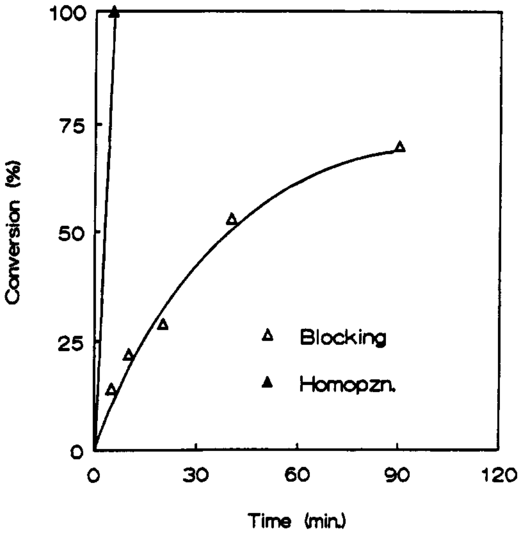
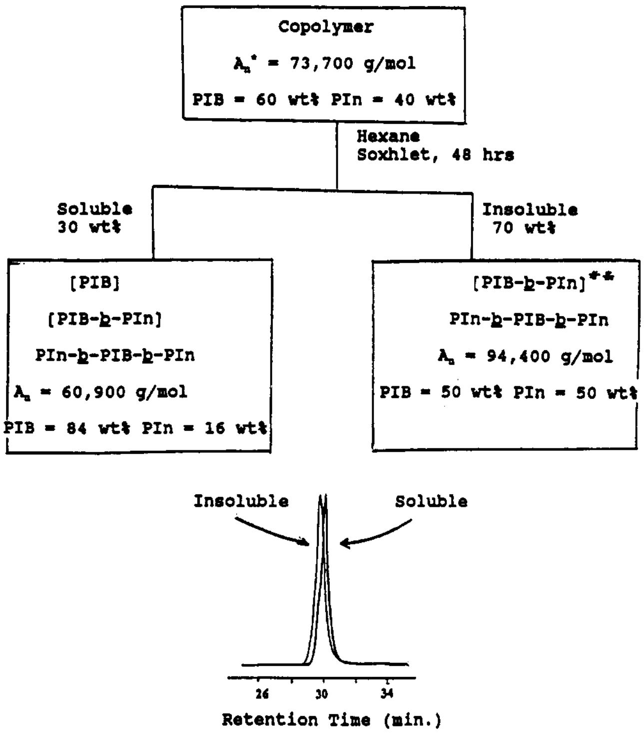


Figure 3. Rate of polymerization: indene homopolymerization and indene block polymerization. Homopolymerization: [TMPCl] = 3.22 mM; [$TiCl_4$] = 16.3 mM; [In] = 0.42 M; [DMA] = [TEA] (added in step 2) = 4.03 mM; CH_3Cl/Hex = 40/60 (v/v); −80 °C. Block copolymerization: same as above except initiator was [$^+PIB^+$] (for synthesis conditions see no. B4 in Table III).

Scheme II
Selective Solvent Extraction of a Representative Triblock Copolymer



*A_n (apparent molecular weight)[3]: by GPC using PIB calibration

** [ ] indicate presence of possible species

Figure 3 shows experimental conditions and results. Surprisingly, under identical conditions the rate of In polymerization in the blocking experiment was much slower than that observed in the model experiment. Since the viscosity of the system in the blocking experiment was much higher than that in the model experiment, it was theorized that the increased solution viscosity was affecting the rate of polymerization. Thus, a model blocking experiment (TMP^+ initiator) was carried out in which an amount of PIB (no. 4 in Table II) was added to the charge to render the solution viscosity comparable to that in the blocking experiment. As shown in Figure 4, the increased viscosity did not affect the rate of polymerization.

The next logical step was to investigate the effect of PIB^+ and $^+PIB^+$ molecular weights on the rate of In

Table II
Synthesis and Characterization of PIB$^+$ and $^+$PIB$^+$ Macroinitiators

no.^{a}	conv (%)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	I_{eff} (%)
1	100	1 400	1.15	71
2	100	16 200	1.17	93
3	100	27 200	1.19	110
4	100	44 700	1.18	112

^{a} [TMPCl] = 4.0 mM; [$TiCl_4$] = 20.0 mM; [IB] = 0.071 M; [TEA] = 5.0 mM; CH_3Cl/Hex = 40/60 (v/v); −80 °C; 180 min. 2: [DiCumCl] = 2.0 mM; [$TiCl_4$] = 20.0 mM; [IB] = 0.535 M; [DMA] = 5.0 mM; CH_3Cl/Hex = 40/60 (v/v); −80 °C; 180 min. 3: As in no. 1 except [IB] = 1.07 M. 4: As in no. 1 except [IB] = 1.78 M.

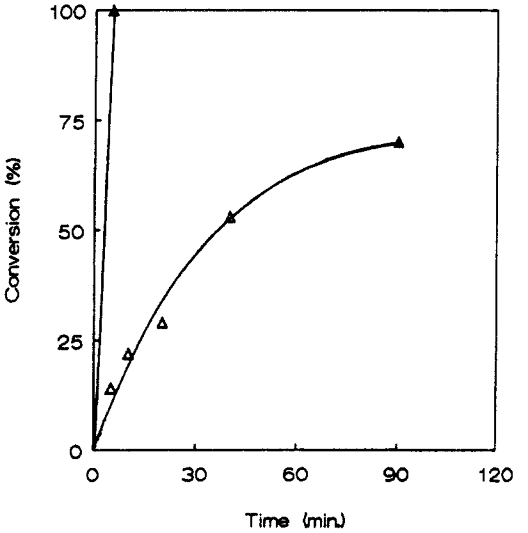


Figure 4. Conversion versus time of In polymerization in the presence of added PIB and by $^+$PIB$^+$. △: [TMPCl] = 3.22 mM; [PIB] = 2.14 mM; [$TiCl_4$] = 16.3 mM; [In] = 0.42 M; [DMA] = [TEA] (added in step 2) = 4.03 mM; CH_3Cl/Hex = 40/60 (v/v); −80 °C; $\bar{M}_n$ of PIB = 42 000. ▲: same as above except with $^+$PIB$^+$ initiator and absence of added PIB.

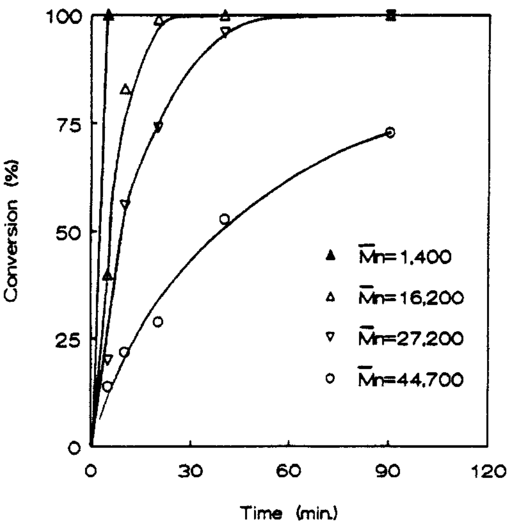


Figure 5. Effect of PIB$^+$ and $^+$PIB$^+$ molecular weights on the rate of indene polymerization. For reaction conditions of macroinitiator syntheses, see Table II. △: [PIB$^+$ (M_n = 1400)] = 2.3 mM; [$TiCl_4$] = 16.3 mM; [In] = 0.42 M; [DMA] = [TEA] (added in step 2) = 4.03 mM. ▲: [$^+$PIB$^+$ ($\bar{M}_n$ = 16 200)] = 1.5 mM. ▽: [$^+$PIB$^+$ ($\bar{M}_n$ = 27 200)] = 1.8 mM. ○: [$^+$PIB$^+$ ($\bar{M}_n$ = 44 700)] = 1.8 mM.

polymerization. Thus, a series of In polymerizations was induced by PIB$^+$ and $^+$PIB$^+$ macrocations of varying molecular weights. Table II and Figure 5 show the conditions of the experiments and the results. Evidently In propagation rate decreased with increasing $^+$PIB$^+$ molecular weight. Figure 6 shows the GPC traces of the PIB$^+$ and $^+$PIB$^+$ macrocations and of the various samples withdrawn at specific times during blocking reactions. As shown in Figure 5, when blocking of In was induced by PIB$^+$ ($\bar{M}_n$ = 1400), the rate of propagation was extremely high and the polymerization was complete in 5 min. The GPC trace (Figure 6) of the diblock polymer shows the presence of two peaks, one corresponding to the diblock and the other to the original PIB$^+$ macrocation. This indicates that blocking was not quantitative; i.e., In was consumed before all PIB$^+$ was converted quantitatively to PIB–In$^+$. Scheme III shows the results of selective solvent extraction of the diblock. The crude product was Soxhlet extracted with hexanes, a good solvent for homoPIB, and the soluble and insoluble fractions were analyzed by GPC and ^{1}H NMR. Most of the product (76 wt %) remained insoluble, and a monomodal GPC peak corresponding to diblock copolymer was obtained. The peaks corresponding to PIB in the ^{1}H NMR spectrum indicated that the product was a diblock. The GPC trace of the soluble fraction (24 wt %) showed bimodality. The low molecular weight peak corresponds to unblocked PIB chains. The second peak, toward high molecular weights, is probably due to diblocks with short polyindene segments. From these results it can be concluded that the crossover from PIB$^+$ + In → PIB–In$^+$ was incomplete.

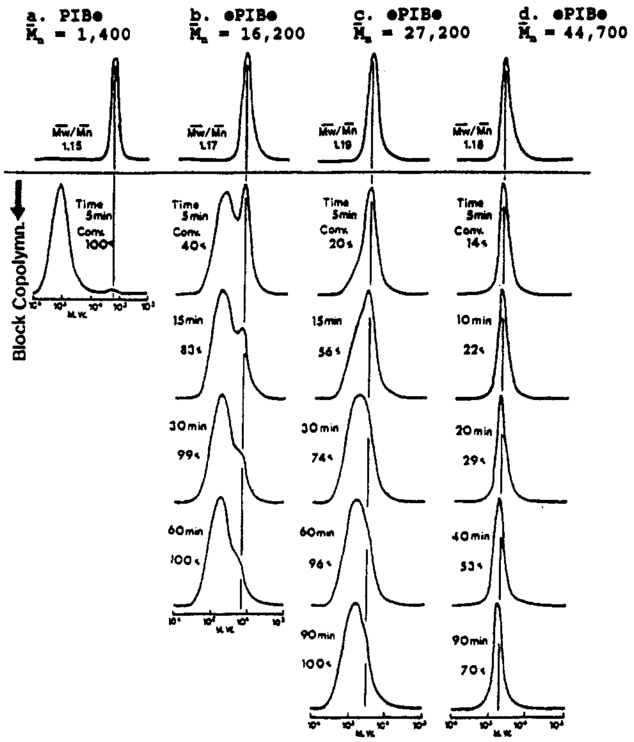
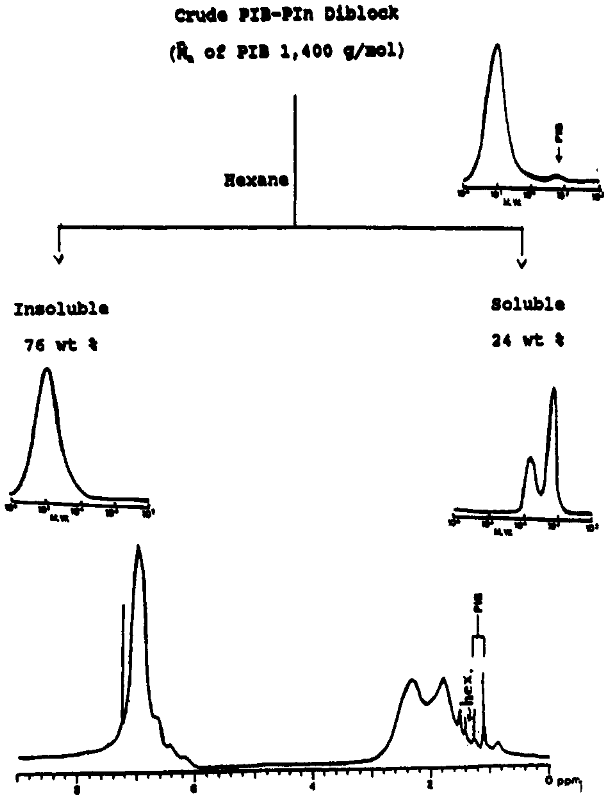


Figure 6. GPC traces (RI) of the PIB$^+$ and $^+$PIB$^+$ macrocations and of the various samples withdrawn at specific times during blocking reactions (reaction conditions in Figure 5).

When blocking was initiated from $^+$PIB$^+$ of $\bar{M}_n$ = 16 000, the first sample after In addition showed bimodality, but the low molecular weight peak decreased in size with increasing time due to the formation of new block polymer by new initiation (i.e., crossover). In propagation rate was relatively higher than that of crossover, and some PIB chains remained unblocked at the end of the reaction. However, the rate of the PIB$^+$ + In → PIB–In$^+$ crossover approached that of In propagation when the $\bar{M}_n$ of the macrocation was increased to 27 000, as indicated by the GPC traces (Figure 6). The GPC peaks remained monomodal and narrow when the blocking of In was induced by the $^+$PIB$^+$ macrocation of $\bar{M}_n$ = 44 700. According to this evidence, high blocking efficiency was obtained in this case. Apparently, the PIB$^+$ macrocation of sufficiently high molecular weight leads to a decreased In propagation

Scheme III
Selective Solvent Extraction of the Diblock Copolymer



rate relative to the rate of cationation ($k_c \geq k_p$) and results in high blocking efficiency.

An effort was made to understand the reason for this molecular weight effect. Since PIB is insoluble in CH_3Cl or in CH_2Cl_2, experiments were carried out to determine the intrinsic viscosity of a PIB sample of $\bar{M}_n$ = 43 000 in pure hexanes and in 40/60 (v/v) CH_2Cl_2/hexanes solvents. According to the results, $[\eta]_{PIB}$ in pure hexanes and in CH_2Cl_2/hexanes was 0.362 and 0.265 dL/g, respectively. Hence, it can be concluded that the PIB chains were not completely extended in 40/60 (v/v) CH_3Cl (or CH_2Cl_2)/hexanes (or MCHx) solvent. The same conclusion can be drawn for the triblock chains because PIn is insoluble in hexanes (or MCHx). Conceivably, during blocking of In from a high molecular weight PIB chain, In has to diffuse through the swollen PIB coil to reach the growing $^+PIB^+$ chain ends. Probably due to this diffusion process the rate of In polymerization (k_p) slows down and becomes comparable to (or less than) that of the rate of cationation (k_c) and results in high blocking efficiency. As a result of this analysis, other available systems were examined to see whether this molecular weight effect exists. Indeed in the blocking of styrene from the $^+PIB^+$ macrocation similar results were obtained.[6] A reviewer pointed out that the reduced rate of In propagation may also be due to chain end association and/or solvation. Indeed, extensive further experimentation would be needed to elucidate the details of these findings.

3. Synthesis of Poly(indene-*b*-isobutylene-*b*-indene) (PIn-*b*-PIB-*b*-PIn) Triblocks. The results of model and kinetic experiments were used to guide in the synthesis of an inventory of triblocks by sequential monomer addition (see Scheme I). Table III summarizes synthesis conditions and results. Minor variations were made in the individual experiments to study the effect of additives (see legend to Table III). Since In propagation rate was low in blocking experiments, additional $TiCl_4$ was added to the living charges in the second step (i.e., immediately after In addition) to increase the rate of polymerization. In case the second $TiCl_4$ addition was omitted, In conversions tended to be low, i.e., less than 100% (see B1, B3, and B5 in Table III).

Similar to an earlier observation with *p*-chlorostyrene,[7] the supplemental addition of an ED in the second step was found to be beneficial; that is, if ED was not added, triblocks with relatively broad molecular weight distributions (MWD) were obtained (e.g., B7 in Table III).

Experiment B8 was designed to demonstrate the effect of solvent polarity. In this experiment the solvent polarity was changed from the conventional 40/60 (v/v) CH_3Cl/MCHx ratio to 50/50 (v/v). As shown by the data (B8 in Table III), the MWD of the midsegment of the triblock synthesized in a more polar medium was broader. Moreover, greater than 100% I_{eff} was obtained, indicating initiation by adventitious moisture which could lead to contamination by diblock and/or homopolymer.

Characterization. The overall compositions of triblocks were determined by ¹H NMR and UV spectroscopies. Figure 7 shows the ¹H NMR spectrum of a

Table III
Synthesis and Characterization of Representative TPEs[a]

Synthesis

(A) Midsegment: [DCE] = [DMA] = [DtBP] = 1.6 mM; [$TiCl_4$] = 0.0256 M; [IB] = 1.45 M; CH_3Cl/MCHx = 40/60 (v/v); 90 min; −80 °C
(B) End segment: [DMA] = [D*t*BP] = 1.6 mM; [$TiCl_4$] = 0.0128 M; [In] = 0.37 M, 90 min

Characterization

	PIB midsegment				triblock					
					$\bar{M}_n$			end segment (wt %)		
no.[c]	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	I_{eff} (%)	In conv (%)	NMR	OSM	A_w/A_n[a]	NMR	UV	$\bar{M}_n$[b] of PIn
B1	74 600	1.10	89	40	93 850	93 000	1.20	20.5	23	9 200
B2	53 800	1.24	94	95	70 000		1.48	23.5	25	8 100
B3	45 000	1.18	103	70	60 800		1.30	26.0		7 900
B4	57 000	1.19	91	70	83 200	72 400	1.29	32.0	30	13 100
B5	45 350	1.16	107	73	72 000		1.31	37.0		13 325
B6	54 250	1.19	92	95	93 400	93 600	1.39	40.0	41	19 575
B7	47 350	1.33	99	98	83 000		1.86	43.0		17 800
B8	42 200	1.48	117	98	76 700	84 300	1.93	45.0		17 250

[a] By GPC. [b] By ¹H NMR. [c] B1. Midsegment: [IB] = 1.47 M; [DCE] = 1.25 mM; [D*t*BP] = 0.37 M; 60 min. End segment: [In] = 0.41 M; [DMA] = 1.25 mM; [D*t*BP] = 0.37 M; 35 min. B2. End segment: [In] = 0.22 M. B3. Midsegment: [IB] = 1.78 M; [DiCumCl] = 2 mM; [DMA] = 5 mM; [$TiCl_4$] = 2 mM; CH_3Cl/Hex = 40/60 (v/v); 150 min. End segment: [In] = 0.34 M; [triethylamine] = 4 mM; 100 min. B4. End segment: [In] = 0.32 mM. B5. As in no. 3 except [In] = 0.56 M. B7. End segment: [In] = 0.34 M; [$TiCl_4$] = 9.2 mM; No DMA. B8. Midsegment: [DMA] = [D*t*BP] = 0.8 mM; CH_3Cl/McHx = 50/50 (v/v). End segment: [In] = 0.44 M; [DMA] = 0.128 mM; [D*t*BP] = 0.064 mM; [$TiCl_4$] = 3.9 mM.

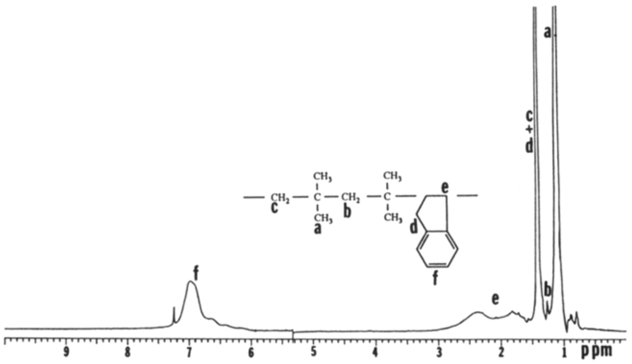


Figure 7. ^{1}H NMR spectrum of a representative triblock copolymer (sample B6 in Table III).

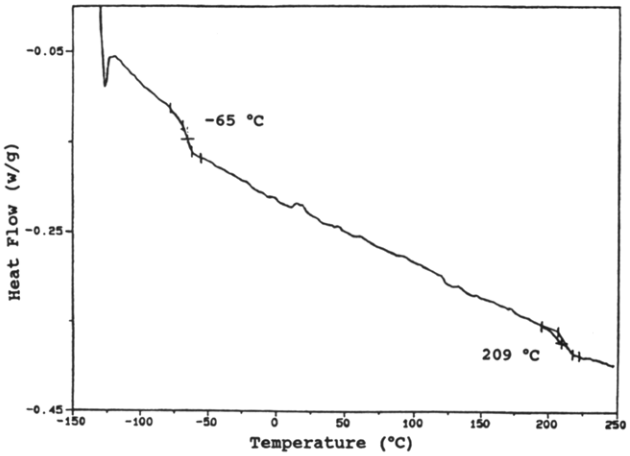


Figure 8. DSC scan of a representative triblock (sample B8 in Table III).

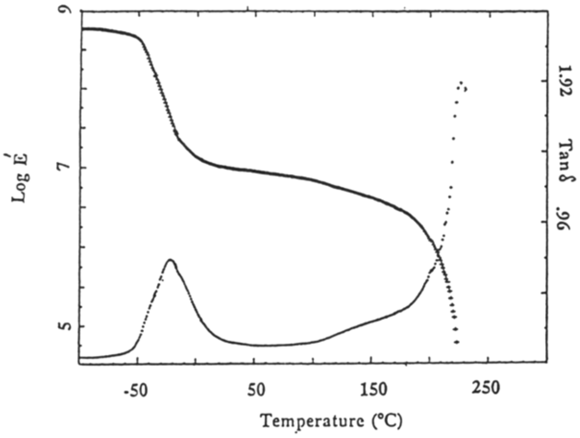


Figure 9. DMTA scan of a representative triblock (sample B6 in Table III).

Table IV
Physical Properties of Representative TPEs

sample	tensile strength (MPa)^a	tensile set 200%	elongation (%)	modulus 300% (MPa)	hardness Shore A2
B1	15.7		600	1.8	44
B3	15.5		500	6.0	50
B4	17.0	7	400	12	55
B6	20.5	15	400	17	60
B8	12.5		300		60

^{a} Cross-head speed: 50 cm/min. Grip separation: 2.5 cm. Temperature: 23 °C.

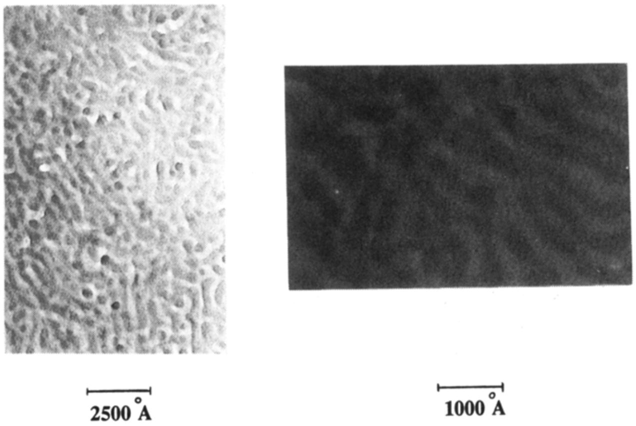


Figure 10. Electron micrographs of a representative triblock (sample 6 in Table III).

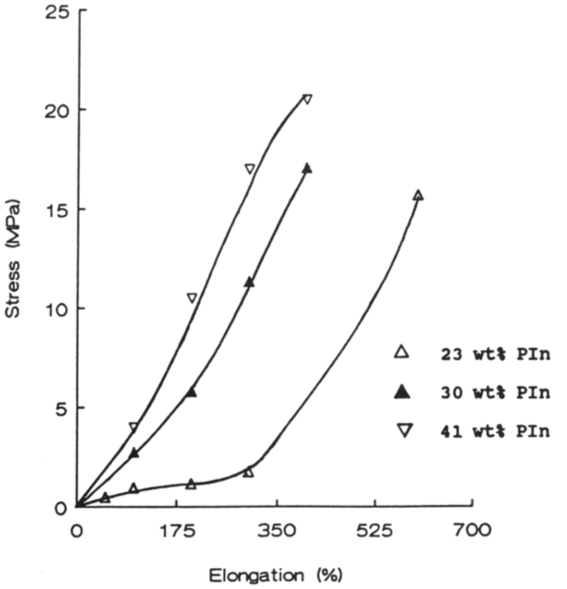


Figure 11. Effect of triblock composition on stress–strain values.

representative triblock (unextracted) (B6 in Table III) together with peak assignments. The composition of the triblock was calculated from the ratio of the peak area of aromatic protons to the peak area of the total number of protons (see the Experimental Section).

Block copolymer composition was also determined by UV spectroscopy.[7] The reliability of the results was satisfactory, as indicated by the excellent agreement of the compositions determined by two independent methods, i.e., ^{1}H NMR and UV (see Table III).

The $\bar{M}_n$'s of triblocks determined by membrane osmometry were in close agreement with the $\bar{M}_n$'s calculated on the basis of composition. According to this evidence, product homogeneity was satisfactory. A DSC scan (Figure 8; B8 in Table III) of a representative triblock shows two transitions (−63 and +209 °C) characteristic of segregated PIB and PIn domains. Evidence for two-phase morphology can be better seen from the modulus–temperature trace (Figure 9; B6 in Table III) obtained by dynamic mechanical measurements. The two tan δ peaks close to the T_g's of the homopolymers indicate a microphase-separated system.

Direct evidence for microphase separation was also obtained by TEM micrographs (Figure 10; sample B6 in Table III). The micrographs suggest PIn rods/cylinders (250–600 Å in length and 60–120 Å in diameter) dispersed in the PIB matrix.

Physical Properties. The block copolymers exhibit excellent TPE characteristics; select physical properties are summarized in Table IV.

Figure 11 shows the effect of triblock composition on stress–strain values. An examination of the results indicates that tensile strengths and 300% moduli increase

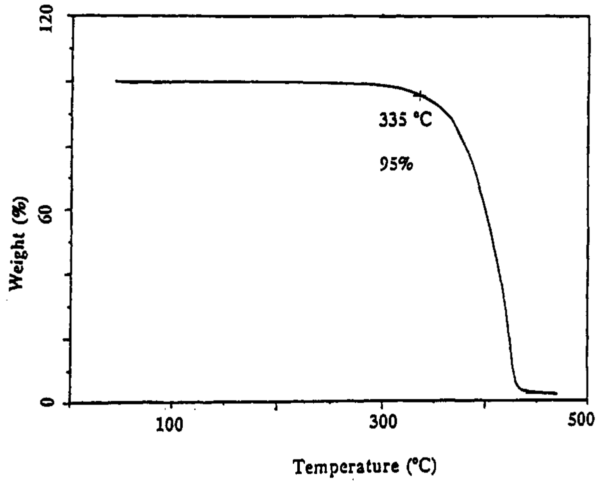


Figure 12. TGA scan of a representative triblock in air (sample 6 in Table III).

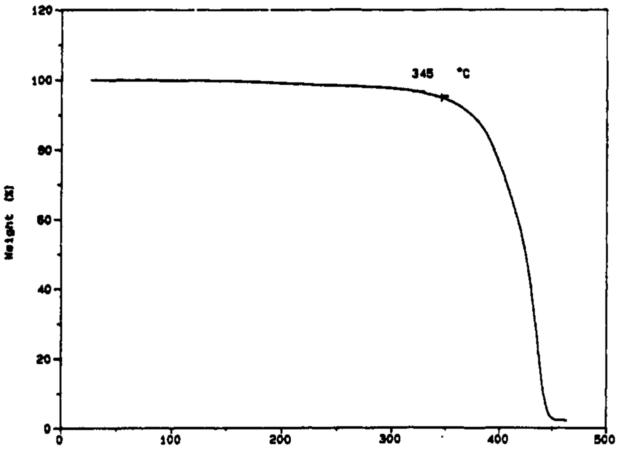


Figure 13. TGA scan of a representative triblock in nitrogen (sample 6 in Table III).

with increasing PIn content in the triblocks, while elongations decrease. As expected, the broadening of the molecular weight distribution causes a decrease in the tensile strength (sample B8 in Table III).

Materials exhibit good elastomeric characteristics as indicated by the low tensile set values (B4 and B6 in Table IV). The shore hardness of the materials is gratifyingly low (Table IV) compared to a commercial-available ABA, e.g., poly(styrene-*b*-butadiene-*b*-styrene) type TPEs.

Figures 12 and 13 show the TGA traces, obtained in air and in N_2 atmospheres, respectively, of a representative triblock (B6 in Table III). The material is thermally quite stable (up to 335 and 346 °C in air and N_2 atmospheres, respectively). Good thermostability is due to the saturated nature of the product.

Encouraged by the good thermal stability of the material, the melt processability of the triblocks was studied. Figure 14 shows the log–log plot of the apparent viscosity versus shear rate of a representative triblock (B5 in Table III). The material exhibited non-Newtonian behavior, as indicated by the rapid drop in melt viscosity with increasing shear rate. Visual degradation of the material was not observed during extrusion.

Conclusions

An inventory of PIn-*b*-PIB-*b*-PIn triblock copolymers was synthesized by sequential indene addition to biliving $^{+}$PIB^{+} segments. Before the synthesis of triblocks, systematic investigations were carried out to study the effect of $^{+}$PIB^{+} molecular weight on blocking efficiency. Results showed decreasing rates of propagation relative to that of cationation with increasing $^{+}$PIB^{+} molecular weight. Essentially quantitative blocking efficiencies were obtained when the In blocking was induced by PIB's of $\bar{M}_n \geq 44\,000$.

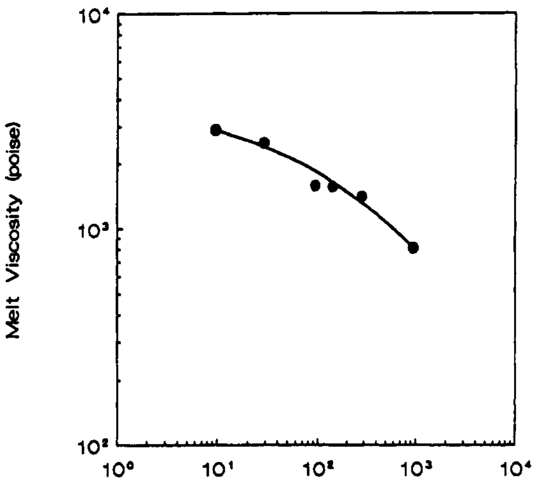
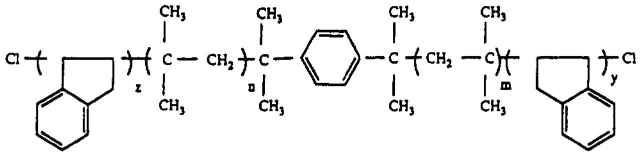


Figure 14. log–log plot of melt viscosity versus shear rate of a representative triblock (sample 5 in Table III) at 250 °C.

The results of kinetic experiments were used for the synthesis of an inventory of triblocks. High blocking efficiencies were obtained as shown by GPC, osmometry, and selective solvent extraction data.

Block copolymer compositions were determined by ^{1}H NMR and UV spectroscopies. The total structure of the triblock has been determined to be



DSC and DMTA analyses of representative triblocks indicated two-phase morphology. Transmission electron microscopy of a polymer containing 41 wt % PIn suggested PIn rods/cylinders (250–600 Å in length and 60–120 Å in diameter) dispersed in the PIB matrix. Triblocks exhibited excellent TPE characteristics. Cast TPE films were clear and gave tensile strengths of 12.4–20.5 MPa with elongations of 300–600%.

Acknowledgment. This material is based upon work supported by the National Science Foundation under Grant DMR 89-20826.

References and Notes

(1) Thorn, A. D. Thermoplastic Elastomers; *Rubber and Plastic Research Association of Great Britain*: Stawbury, England, 1980.
(2) Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G. *Encycl. Polym. Eng.* **1986**, *5*, 416.
(3) Fetters, L. J. *Block and Graft Copolymerization*; Ceresa, R. J., Ed.; John Wiley and Sons: New York, 1973; Vol. 1.
(4) Kennedy, J. P.; Keszler, B.; Tsunogae, Y.; Midha, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (1), 310.
(5) Kaszas, G.; Puskas, J. E.; Kennedy, J. P. *Macromol. Sym.* **1988**, 13/14, 473.
(6) Kennedy, J. P.; Tsuonogae, Y., unpublished results.
(7) Kennedy, J. P.; Kurian, J. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 3725.
(8) Ramelow, U.; Baysal, B. M. *J. Appl. Polym. Sci.* **1986**, *32* (7), 5865.
(9) Roe, R. J. *Encycl. Polym. Sci. Technol.* **1987**, *7*, 2nd ed., 531.
(10) Collins, E. A.; Bares, J.; Billmeyer, F. W., Jr. *Experiments in Polymer Science*; John Wiley and Sons: New York, 1973.