

New Thermoplastic Elastomers of Rubbery Polyisobutylene and Glassy Cyclopolyisoprene Segments

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Synopsis

New thermoplastic elastomers (TPEs) consisting of a central rubbery polyisobutylene (PIB) and glassy outer cyclopolyisoprene (cy-PIP) segments have been prepared by living carbocationic polymerization by sequential monomer addition. First the homopolymerization of isobutylene (IB) and isoprene (IP) have been investigated. The living polymerization of isobutylene initiated by the *p*-dicumyl methoxy (*p*-DiCumOMe)/TiCl₄ system in CH₂Cl/*n*-C₆H₁₄ mixtures at -80°C gave living \oplus PIB \oplus dications of desired molecular weights. The polymerization of IP induced by cumyl acetate (CumOAc)/TiCl₄ or cumyl methyl ether (CumOMe)/TiCl₄ systems in the same solvent at -40°C readily yielded gel-free off-white powders comprising *trans*-1,4-PIP units and cy-PIP sequences. The polymerization most likely proceeds by *trans*-1,4-PIP \oplus cations that undergo inter/intramolecular alkylation and cyclization leading to branched multiblocks. Block copolymers were synthesized by the addition of IP to charges containing \oplus PIB \oplus dications of different molecular weights. Under select conditions pure (*tr*-1,4-PIP)-*b*-PIB-*b*-(*tr*-1,4-PIP) triblocks with relatively short *tr*-1,4-PIP sequences have been obtained. Extended reaction times result in multiblocks; most likely \oplus (*tr*-1,4-PIP)-*b*-PIB-*b*-(*tr*-1,4-PIP) \oplus dications induce alkylation and cyclization of PIP sequences. The extent of alkylation can be regulated by the viscosity of the medium (molecular weight and/or concentration of the PIB midblock). The rate of IP incorporation decelerates after an initial fast polymerization; however, it can be accelerated by adding fresh Lewis acid to the system. Although *tr*-1,4-PIP endblocks of linear triblocks can be completely cyclized by acid treatment to saturated products, multiblocks cannot, probably because of their branched structure. Transmission electron microscopy of multiblocks shows phase separation with PIB (95–70 mol %) the continuous phase ($T_g = -73^\circ\text{C}$) and cy-PIP blocks (5–30 mol %) the discrete phase. The T_g of the cy-PIP domain is in the range 95–190°C and it is affected by the extent of cyclization and/or the length of the cy-PIP sequence. The new multiblock TPEs are soluble in organic solvents and can be melt-processed above ~140°C. A multiblock TPE film containing 15 mol % glassy cy-PIP block and 85 mol % rubbery PIB block of $\bar{M}_n = 55,500$ cast from CCl₄ exhibited to MPa tensile strength [120 MPa engineering strength (sigma true)] and 1200% elongation. The completely cyclized linear triblock shows higher T_g ($\approx 180^\circ\text{C}$) but, due to its low cy-PIP content, exhibits unsatisfactory tensile properties.

INTRODUCTION

Increased insight into the mechanism of carbocationic polymerizations prompted us to undertake the synthesis of a new triblock copolymer consisting of a saturated rubbery PIB central block flanked by *tr*-1,4-PIP outer blocks. The possibility of cyclization of the *tr*-1,4-PIP segments promised to increase the T_g of the outer blocks to 170°C or higher and at the same time to reduce their level of unsaturation. In this manner we have envisioned the synthesis of a new family of TPEs.

The preparation of TPEs with PIB midblocks ($T_g = -73^\circ\text{C}$) is a most desirable objective because of the unique combination of properties of this rubber, i.e., outstanding moisture and gas barrier properties, excellent oxidative and thermal stability, and high chemical resistance.

This paper describes the synthesis, characterization and some physical properties of (*tr*-1,4-PIP)-*b*-PIB-*b*-(*tr*-1,4-PIP) and (*cy*-PIP)-*b*-PIB-*b*-(*cy*-PIP) triblock copolymers and other PIP/PIB multiblocks containing these structural elements.

EXPERIMENTAL

Materials

The synthesis of *2-phenyl-2-acetyl-propane* (cumyl acetate, CumOAc) has been reported.¹ Purity of the product was checked by $^1\text{H-NMR}$ spectroscopy. *2-Methoxy-2-propyl-benzene* (cumyl methyl ether, CumOMe) was synthesized as reported.² The extent of etherification was analyzed by $^1\text{H-NMR}$ spectroscopy and purity was checked by GC analysis. *1,4-Di(2-methoxy-2-propyl)benzene* (*p*-dicumyl methoxy, DiCumOMe) was synthesized as described³ and was freshly purified by chromatography on neutral Al_2O_3 (activity III). Upon elution with *n*-pentane pure DiCumOMe was obtained. Purity was ascertained by DSC analysis (mp = 49°C). Sources and purification of *methyl chloride*, *hexanes*, *titanium tetrachloride*, and *IB* have been reported.⁴ *IP* (Aldrich) was extracted with 10% aqueous NaOH, washed neutral with water, dried over molecular sieves (4 Å), and distilled over CaH_2 on the day of the experiment. *m-Chloro-perbenzoic acid* was purified as described.⁵ *Methylene chloride* and *carbon tetrachloride* were dried over molecular sieves (4 Å). *Sodium thiosulfate*, *potassium iodide*, *glacial acetic acid*, *starch*, *methanol*, *toluene*, *p-xylene*, *cyclohexane*, *trichloro acetic acid*, *boron trifluoride etherate*, *2-methyl-5-isopropyl-1,4-benzoquinone*, and *tetrahydrofuran* were used as received.

Procedures

Polymerizations were carried out in a dry box under dry nitrogen. A 250-mL round-bottom flask equipped with a stirrer was charged with the initiator and 150 mL methyl chloride/*n*-hexane (40/60 v/v) mixture and the charge was cooled to the desired temperature.

Homopolymerizations

For IP homopolymerization first 7.5×10^{-4} mol initiator (CumOAc or CumOMe) and then 1.2×10^{-2} mol TiCl_4 were added to the charge and after 1 min of mixing polymerization was started by the addition of 24 mL (0.24 mol) prechilled IP. Polymerization was continued for 60 min and stopped by prechilled methanol.

For the preparation of telechelic living $\oplus\text{PIB}\oplus$ dication *p*-DiCumOMe and 6 mL (0.077 mol) prechilled IB were added to the solvent mixture followed by the addition of TiCl_4 . Concentration etc. data are given in the text, and table or figure captions. IB addition was repeated (6 mL/15 min)

until the desired molecular weight \oplus PIB \oplus macrodication was obtained. \overline{M}_n was controlled by monomer consumption (the living carbocationic polymerization of IB obeys $\overline{DP}_n = [M]/[I]$, where $[M]$ and $[I]$ are the amount of monomer and initiator molecules consumed, respectively). Samples were withdrawn from the charge from time to time to check the \overline{M}_n of the PIB by GPC. The time interval between IB additions (15 min) was dictated by the polymerization rate: Monomer concentrations should be below 0.5 mol/L in order to avoid undesirable solvent effects caused by high monomer concentrations.⁴ $[I]$ was usually in the 10^{-3} to 10^{-2} mol/L range to ensure 100% IB conversion at the given feeding rate.

Block Copolymerizations

After the IB was consumed, 48 mL (0.48 mol) prechilled IP was added. Although during IB polymerization the charges were light yellow, the introduction of IP turned them deep red, indicating the onset of IP polymerization. Polymerizations were allowed to proceed for specified times and the reactions were quenched with prechilled methanol. The solvents were evaporated, and the polymers were washed with methanol and water to remove Ti-containing residues. After extraction the products were dried in a vacuum oven at room temperature. Yields were determined gravimetrically.

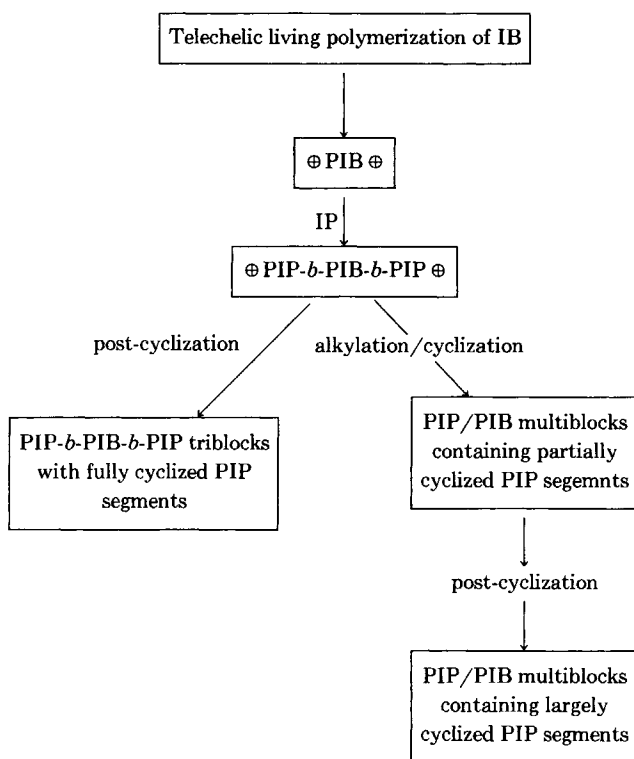
Cyclization of Block Copolymers

To a 500-mL round-bottom flask equipped with a condenser and a magnetic stirrer containing 10% block copolymer in cyclohexane solution, an acid system was added under dry nitrogen and refluxed for a given time period (concentration etc. data are given in the text and figure or table captions). The charge was cooled; the polymer was precipitated into excess methanol, washed several times with methanol and water, and dried in a vacuum oven at room temperature.

PIB molecular weights were determined by GPC as described.⁴ The molecular weights of the *tr*-1,4-PIP and cy-PIP segments were estimated from the GPC traces by the use of PIB and PSt calibrations, and from gravimetric data. The double bond content of the block copolymers was determined quantitatively by epoxide titration according to Ref. 5.

¹H-NMR spectra were obtained by the use of a Varian T-60 and a Varian 300 MHz instrument in CCl₄ and CDCl₃ solvents, respectively. IR spectra were recorded on a Beckman FT 2100 FTIR instrument on thin films cast on NaCl plates from chloroform solution. DSC and TG measurements were taken on a DuPont 1090 thermal analyzer. The heating rates were 20 and 10°C/min, respectively. T_g 's were determined by the midpoint method.

Test specimens (microdumbbells) for stress-strain measurements were prepared by dissolving samples in toluene or carbon tetrachloride (10% solution), pouring the solutions in a Teflon mold (10 × 10 cm), and slowly evaporating the solvents by first storing in a hood for 24 h, then drying in a convection oven under nitrogen at 55°C for 24 h, and finally in a vacuum oven at room temperature for 24 h. The thickness of the films was determined by a thickness gauge.



Scheme 1. Roadmap of transformations investigated.

Stress-strain measurements were obtained by an Instron universal testing instrument with a 500 g load cell at 50 cm/min crosshead speed at room temperature. Hysteresis was recorded by stretching the samples to 50% of their ultimate elongation at 10 cm/min crosshead speed.

TEM was performed by a JEOL 120 U instrument. Samples were prepared by casting thin films from 1 wt % THF solution on grids and staining with OsO_4 .

RESULTS AND DISCUSSION

Scheme 1 outlines the systems and types of reactions investigated. Briefly, this research concerned the synthesis of linear telechelic polyisobutylene dications $\oplus \text{PIB} \oplus$ by living IB polymerizations and their subsequent use for the block of short, essentially *trans*-1,4-PIP sequences [$\oplus (tr\text{-}1,4\text{-PIP})\text{-}b\text{-PIB}\text{-}b\text{-}(tr\text{-}1,4\text{-PIP}) \oplus$]. This important intermediate may be cyclized by acids to yield TPE triblocks with fully cyclized short PIP segments (left side of Scheme I). Alternatively, the $\oplus (tr\text{-}1,4\text{-PIP})\text{-}b\text{-PIB}\text{-}b\text{-}(tr\text{-}1,4\text{-PIP}) \oplus$ may undergo simultaneous intermolecular alkylation/intramolecular cyclization processes to yield PIP/PIB multiblocks with relatively longer partially cyclized PIP segments which can be further post-cyclized by acids to give multiblocks

with maximum-cyclized PIP segments. The latters exhibit interesting TPE and flexible film properties (right side of Scheme I).

The Synthesis of the Central Rubbery Block: The Preparation of \oplus PIB \oplus Macroinitiators

The living carbocationic polymerization using monofunctional⁴ and bifunctional⁶ initiators to one-living-ended or telechelic two-living-ended PIBs, respectively, has been described. The present research focuses on the convenient synthesis of telechelic PIB macrodications \oplus PIB \oplus capable of initiating the polymerization of IP. After some orienting experimentation, this objective was reached and telechelic living \oplus PIB \oplus dications have been prepared by the DiCumOMe/TiCl₄ initiating system at -80°C to avoid the formation of indanyl structures.⁶ In the course of this project, various molecular weight ($\bar{M}_n = 10,500, 16,600, 18,800, 51,300, 68,500, \text{ and } 70,000$) \oplus PIB \oplus s have been prepared to serve as middle blocks.

The characterization of PIB middle blocks is now summarized: A low \bar{M}_n sample was analyzed by high resolution (300 MHz) ¹H-NMR spectroscopy to facilitate the detection of undesirable (indanyl) structures. Figure 1 shows pertinent data. The resonances between 7.20 and 7.30 ppm are characteristic of aromatic protons of the DiCumOMe fragment and their exact position is determined by the number of IB units (one or more) on each arm.⁷ Resonances characteristic of indanyl structures should appear in the 6.80–7.40 ppm range.⁸ Although the spectrum shows traces of indanyl (6.96–7.18 ppm) and diindanyl protons (6.82 ppm), the amounts are near the limit of detectability, i.e., undesirable indanyl structures are essentially absent. The expected structure was further corroborated by ¹H-NMR spectroscopy of some quantitatively derivatized $-\text{CH}_2\text{CH}(\text{CH}_3)=\text{CH}_2$ terminated PIBs. The methodology of this routine analysis has repeatedly been discussed.^{9,10}

The telechelic nature (i.e., bidirectional growth) of the living \oplus PIB \oplus has been substantiated by kinetic experiments. In these studies the living polymerization of IB was initiated with an equimolar mixture of a bifunctional DiCumOMe plus a monofunctional CumOMe initiator, in conjunction with TiCl₄. Figure 2 shows the GPC results. The polymerization with the bifunctional initiator is twice as fast as that with the monofunctional one and gives double molecular weight product. Both species obey $\overline{\text{DP}}_n = [\text{M}]/[\text{I}]$ and exhibit $\bar{M}_w/\bar{M}_n = 1.1$ (determined by peak deconvolution).

On the basis of these experiments and past experience with such systems,⁴ we have concluded that the DiCumOMe/TiCl₄ system indeed yields the expected telechelic living \oplus PIB \oplus dication.

The Blocking of Isoprene from \oplus PIB \oplus Dications

Neither the mechanism nor the structure of cationically prepared PIPs have been satisfactorily established. As a result of our examination of kinetic and structural information^{11–22} and orienting experimentation, it became apparent that in order to reach our objective we had to reexamine the cationic polymerization of IP in general, and initiation with cumyl acetate and cumyl ether initiators in particular. Thus we undertook an examination of the

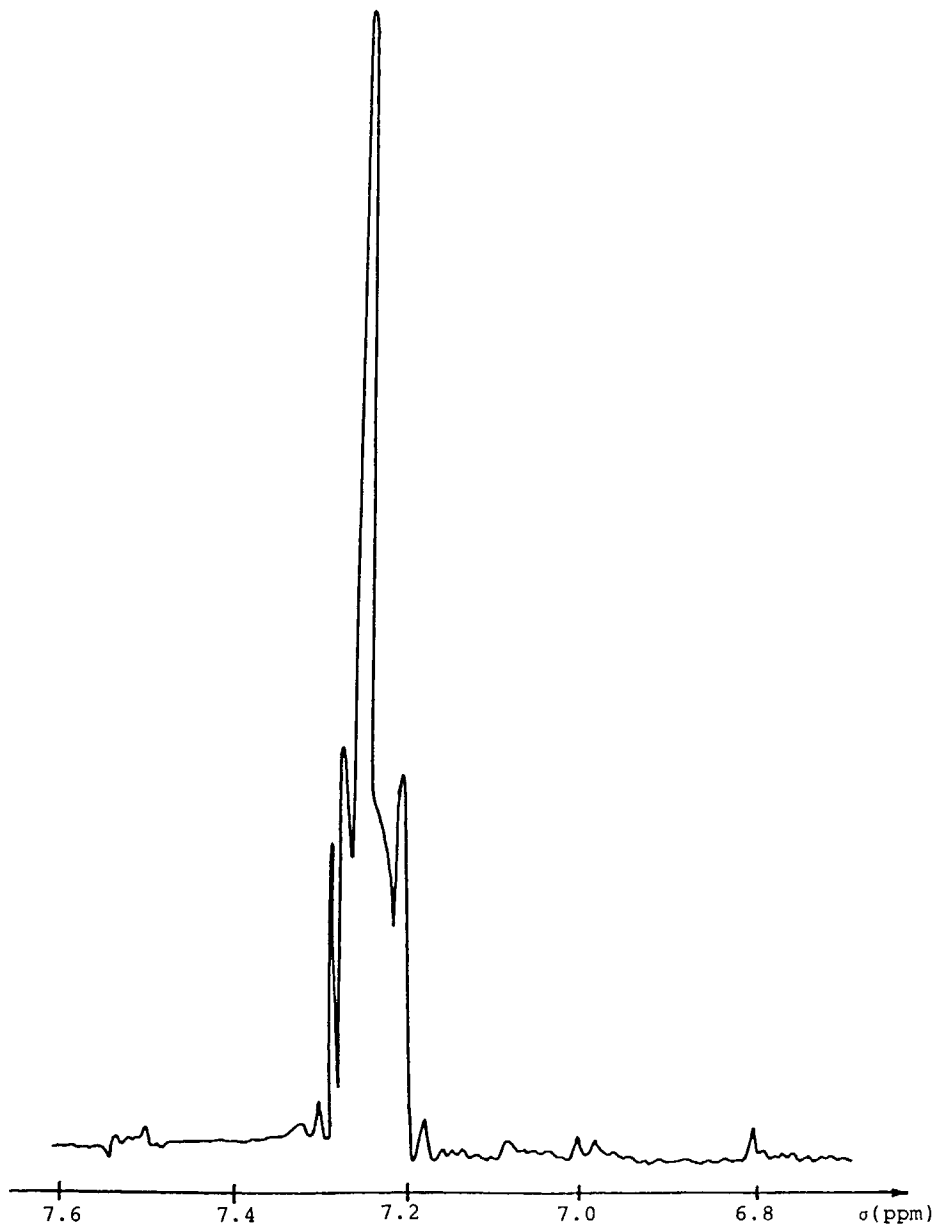


Fig. 1. The aromatic region of the 300 MHz $^1\text{H-NMR}$ spectrum of a telechelic PIB sample $\bar{M}_n = 900$; $\bar{M}_w/\bar{M}_n = 1.25$. Experimental conditions: $[\text{DiCumOMe}]_0 = 6.4 \times 10^{-3}$ mol/L; $[\text{TiCl}_4]_0/[\text{DiCumOMe}]_0 = 2$; IB = 35 mL; $V_0 = 1270$ mL $\text{CH}_3\text{Cl}/n\text{-C}_6\text{H}_{14}$ 40/60; -80°C .

polymerization behavior of IP by $\text{CumOAc}/\text{TiCl}_4$ and $\text{CumOMe}/\text{TiCl}_4$ initiating systems.

Homopolymerization of IP by $\text{CumOAc}/\text{TiCl}_4$ and $\text{CumOMe}/\text{TiCl}_4$ Initiating Systems

There is general agreement that cationically prepared PIP contains largely $\sim 75\%$ *tr*-1,4 enchainment and that massive amount of cyclization also occur

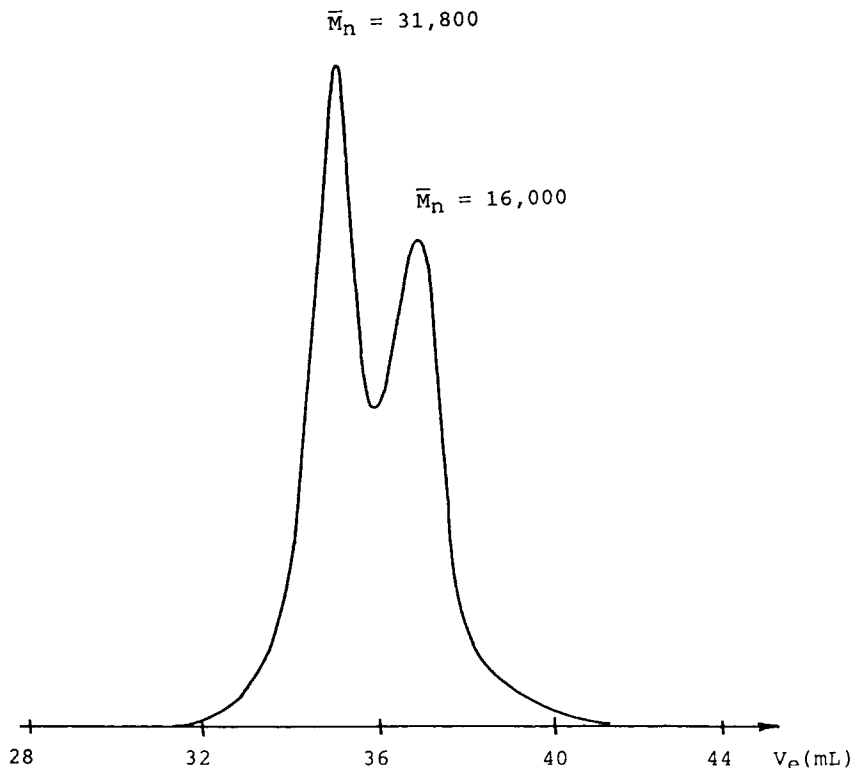


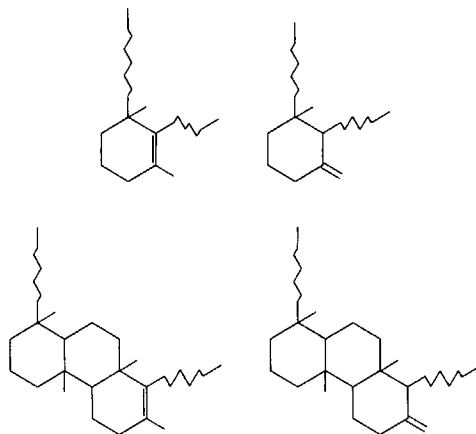
Fig. 2. GPC trace of a PIB prepared by equimolar amounts of mono- and bifunctional initiators. Experimental conditions: $[\text{CumOMe}]_0 = [\text{DiCumOMe}]_0 = 2.8 \times 10^{-3}$ mol/L; $[\text{TiCl}_4]_0 = 7.3 \times 10^{-2}$ mol/L; $[\text{IB}] = 2$ mL; $V_0 = 25$ mL $\text{CH}_3\text{Cl}/n\text{-C}_6\text{H}_{14}$, 40/60 v/v; -80°C .

during the polymerization.¹¹⁻²² The extent of cyclization is usually expressed by the extent of the loss of unsaturation.

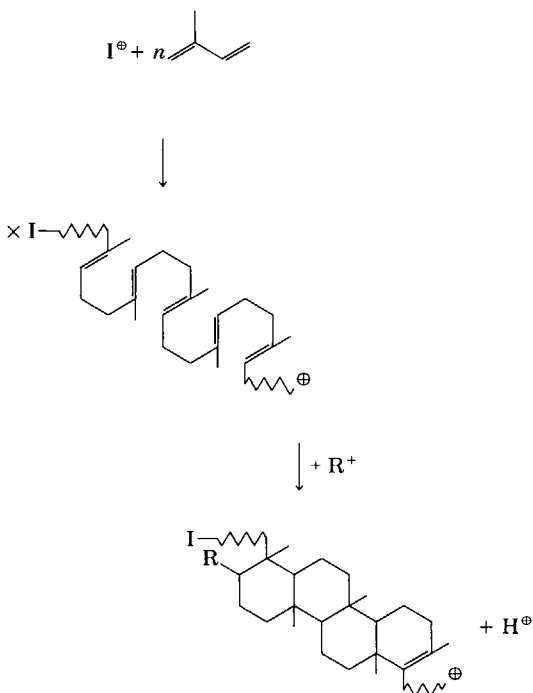
Homogeneous polymerizations by the use of $\text{CumOAc}/\text{TiCl}_4$ or $\text{CumOMe}/\text{TiCl}_4$ complexes in $\text{CH}_3\text{Cl}/n\text{-C}_6\text{H}_{14}$ (see Experimental) at -40°C for 60 min gave 30% conversions. Extending the reaction times beyond 60 min may result in gelation. The products were off-white powders readily soluble in CCl_4 or toluene. Figure 3 shows $^1\text{H-NMR}$ and IR spectra of a representative sample. The sharp resonance at 7.18 ppm is characteristic of the aromatic protons of the cumyl initiator fragment in the polymer while resonances at 5.12, 1.93, and 1.60 ppm correspond to the $=\text{CH}-$, $-\text{CH}_2-$, and CH_3- protons of *trans*-1,4-PIP units, respectively. The strong resonance at 0.93 ppm is characteristic of CH_3- protons of cy-PIP units. The CH_3- protons of a 1,2-PIP unit would also exhibit a resonance at around 0.9 ppm; however, this enchainment cannot be present since the IR spectrum does not show the out-of-plane vibration at 908 cm^{-1} of this unit.¹⁷ The formation of cyclic structures is suggested by the substantial loss of unsaturation (70%) calculated from $^1\text{H-NMR}$ spectra, by the 10 cm^{-1} upshift of the absorption maximum of the asymmetric deformation vibration of the CH_3- group, and the deformation vibration of the $-\text{CH}_2-$ group.¹⁷ The resonance at 4.68 ppm corresponds to the $\text{CH}_2=$ protons of external double bonds while the shoulder at around 6 ppm indicates $-\text{CH}_2-$ protons of internal double bonds (5.24

ppm) of cyclic structures identified in cy-PIPs obtained by acid treatment of natural or synthetic linear *trans*- or *cis*-1,4-PIPs,²³⁻³³

Thus our PIPs most likely comprise linear *tr*-1,4-PIP segments together with the following isolated or fused cyclic units:



where $\sim\sim = tr$ -1,4-PIP. The formation of these structural elements can be readily accounted for by invoking conventional carbocationic processes;³⁴ for example,



where $I^{\oplus} = C_6H_5\overset{\oplus}{C}(CH_3)_2$, H^{\oplus} or $\oplus PIB \oplus$,

$\text{---}\sim\sim\text{---} = tr$ -1,4-PIP, $R^{\oplus} = H^{\oplus}$ or tr -1,4-PIP \oplus .

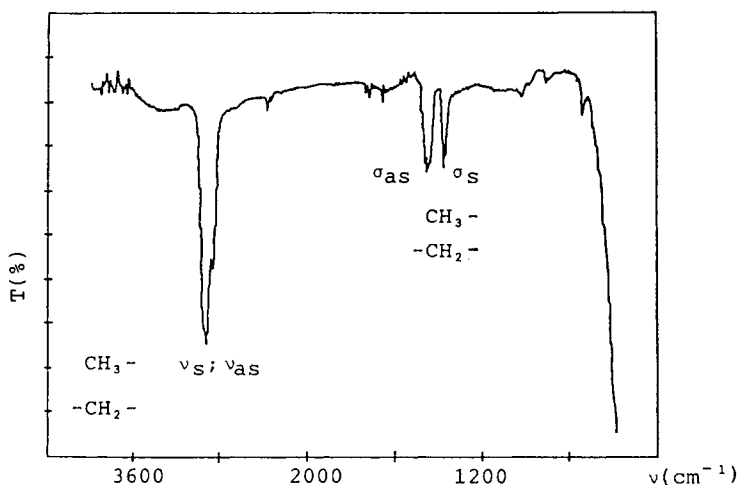
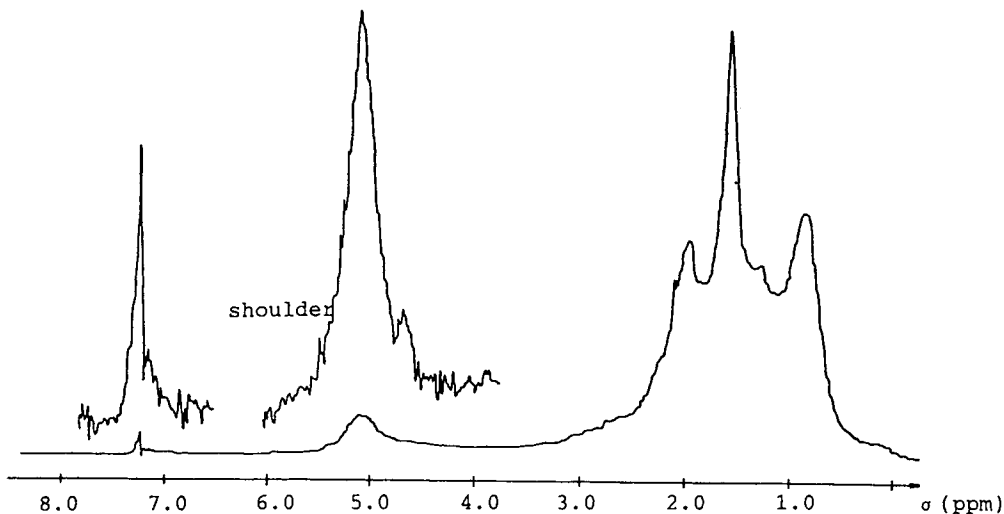


Fig. 3. $^1\text{H-NMR}$ and IR spectra of a cy-PIP. Experimental conditions: $[\text{CumOAc}]_0 = 5 \times 10^{-2}$ mol/L; $[\text{TiCl}_4]_0/[\text{CumOAc}]_0 = 16$; IP = 24 mL; $V_0 = 150$ mL; $\text{CH}_3\text{Cl}/n\text{-C}_6\text{H}_{14}$ 40/60 v/v; -40°C .

Cyclization may be induced by attack of adventitious protons or by growing cations at any point along a sufficiently long *tr*-1,4-PIP block: However, the direction of cyclization may progress only along the same path 1,4-propagation has occurred. The formation of isolated rings reduces the original level of unsaturation by 50% (one ring for every two IP units), whereas the formation of fused rings reduces it by 66% or higher, depending on the number (i.e., 2, 3, etc.) of condensed rings.³⁰ The substantial loss of unsaturation (> 70%) detected in our products points to the presence of multifused rings. Cyclization terminates by proton loss and the liberated proton may start a new chain or start further cyclization.

The coexistence of various cyclic structures is implied by featureless DSC scans (cf. Fig. 4). Figure 4 also shows a representative TG trace according to which cyclized PIPs are thermally quite stable (up to 350°C) suggesting highly fused rings. Alkylation of a *tr*-1,4-PIP unit by a growing chain will result in branching and a sudden increase in molecular weights. This is reflected by the

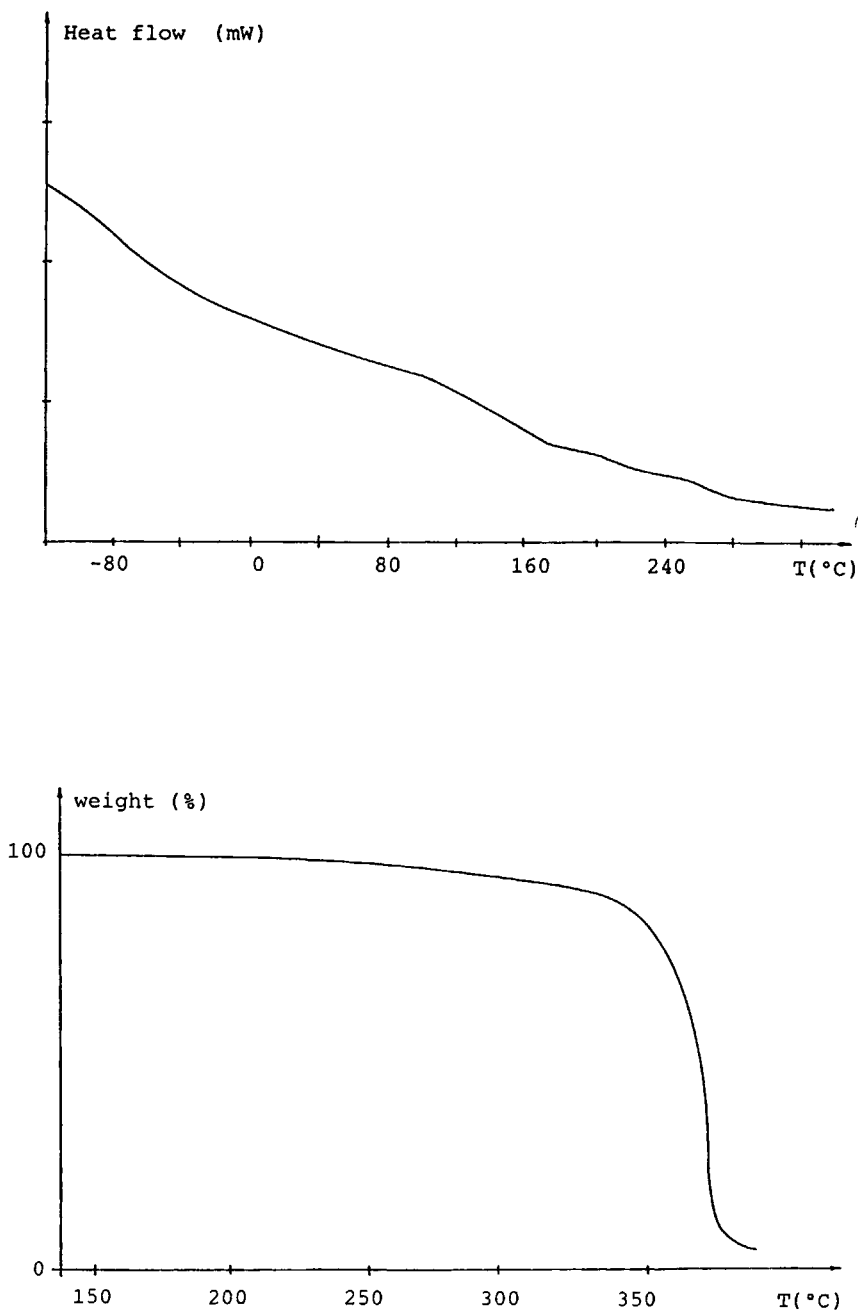
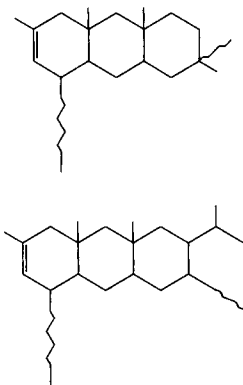


Fig. 4. DSC and TG traces of a cy-PIP. Experimental data as in Figure 3.

very high molecular weight tail in the GPC trace (cf. Fig. 5). Extended reactions result in gelation.

Interestingly, our cy-PIPs exhibit a rather strong UV absorption (cf. Fig. 5), a phenomenon first observed by Gaylord.¹⁵ Thus the products must also contain conjugated unsaturation whose concentration is evident only by sensitive UV spectroscopy.

In contrast to our results, the most frequently quoted propositions^{19,22} claim that cationic cyclopolymerization of IP leads to the following ladder structures:



These fused rings may form from 3,4-PIP units but the formation of significant amounts of 3,4-units has never been observed under cationic conditions. The absence of 3,4-PIP units in our cy-PIPs was indicated by spectroscopic analysis and independently by copolymerization studies. The objective of these copolymerization studies was to elucidate the microstructure of cationically prepared PIP units by intermingling them with IB units and thus preventing the formation of long PIP sequences capable of cyclization. According to ¹H-NMR spectroscopy, the copolymers exhibited exclusively *tr*-1,4-PIP enchainment, i.e., the absence of 3,4- or cy-PIP units. The unsaturation levels were in good agreement with the theoretical IP contents calculated by using r_{IP} and r_{IB} values of conventional IP/IB copolymers.³⁵ The GPC traces of these products ($\bar{M}_w/\bar{M}_n = 2.0$) did not show the high molecular weight tail characteristic of cy-PIPs. These results and considerations support the proposition that cationically synthesized PIP mainly consists of *tr*-1,4-PIP and cy-PIP units arising from linear *tr*-1,4-PIP sequences; the distribution and lengths of these sequences are obscure at this time. The relative proportion of these structural elements will affect the ultimate properties of the PIP, i.e., *tr*-1,4-units will impart flexibility and oxidative vulnerability while the saturated cyclic units will convey rigidity and oxidative stability.

Block Copolymerization of IP from \oplus PIB \oplus

The Synthesis of Triblocks and Multiblocks. Aided by the information described in the preceding subsections the stage was set for the blocking of IP from \oplus PIB \oplus . Orienting experiments indicated that the major obstacle toward well-defined (*tr*-1,4-PIP)-*b*-PIB-*b*-(*tr*-1,4-PIP) triblocks was intermolecular alkylation, giving rise to branchy polymers and cy-PIP segments.

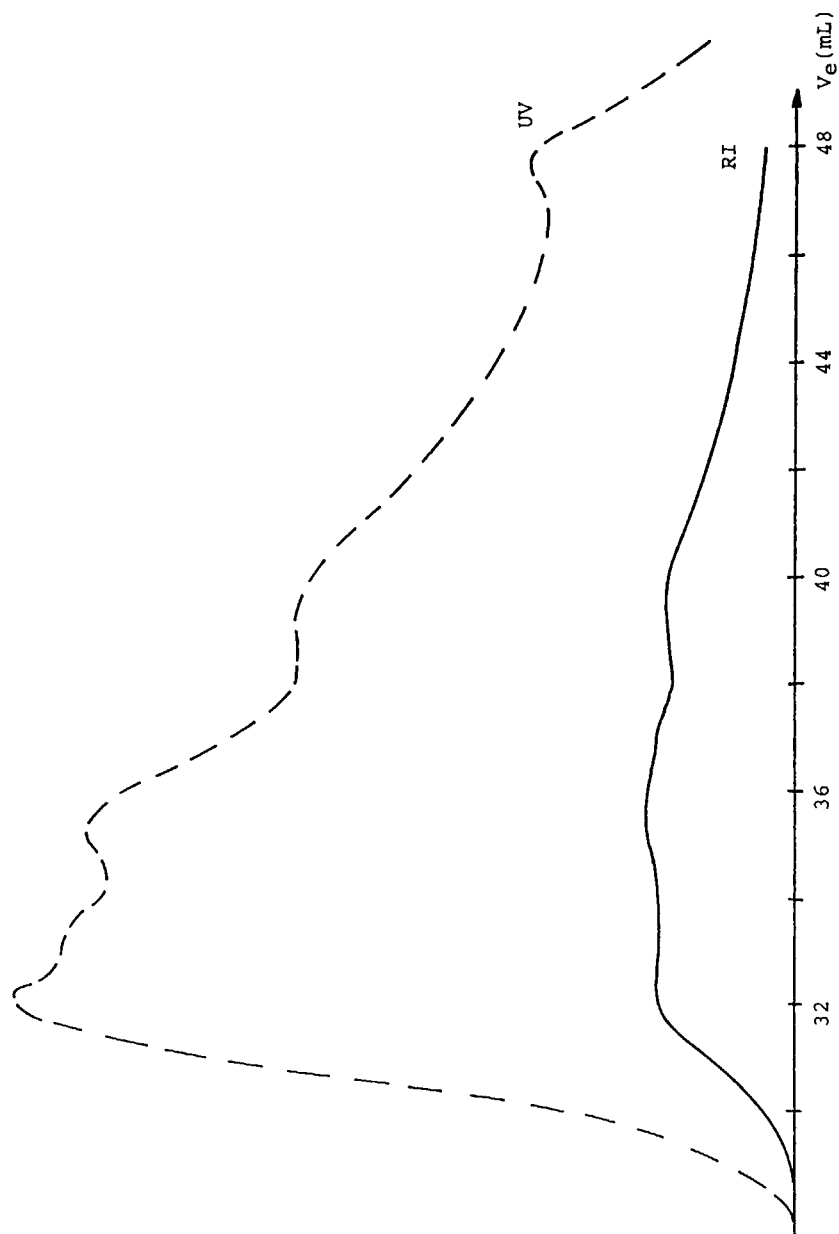


Fig. 5. GPC traces of a cy-PIP. Experimental data as in Figure 3.

TABLE I
Effect of \bar{M}_n and Concentration of the \oplus PIB \oplus Macro-dication on
the Loss of Unsaturation in the cy-PIP Segments of PIB/PIP
Block Copolymers^a

\oplus PIB \oplus concn (g/L)	PIB \bar{M}_n	PIB \bar{M}_w/\bar{M}_n	Loss of unsat. (%)	Product
117.0	70,000	1.17	< 5	Linear
115.0	68,500	1.13	< 5	triblocks
144.0	51,300	1.17	< 5	
28.7	10,500	1.40	50	Branchy,
54.0	16,600	1.29	30	cyclic
72.0	18,800	1.15	19	multiblocks

^a[DiCumOMe] = 1.5–6.4 mmol/L; [TiCl₄]/[DiCumOMe] = 16; -80°C, CH₃Cl/*n*-C₆H₁₄ 40/60 v/v, 30 min.

Since these reactions involve the interaction between two chains, it was theorized that they would be suppressed in a viscous medium, just as termination by radical combination (the well-known Tromsdorff effect) is strongly reduced by the viscosity of the medium in free-radical polymerizations. Thus a series of IP polymerizations were induced by \oplus PIB \oplus macrodications by changing the viscosity of the medium, i.e., by varying the concentrations and/or molecular weights used. Table I shows representative results. The viscosity of the medium was controlled by the use of low (10,000–19,000) or high (50,000–70,000) \bar{M}_n and/or low (0–72 g/L) or high (115–144 g/L) \oplus PIB \oplus concentration; the extent of branching/cyclization was quantitated by determining the loss of unsaturation by ¹H-NMR. Gratifyingly, cyclization was essentially absent under high-viscosity conditions and spectroscopic analysis showed (see below) the products to be (*tr*-1,4-PIP)-*b*-PIB-*b*-(*tr*-1,4-PIP) triblocks. In contrast, products obtained in relatively low viscosity media exhibited loss of unsaturation (i.e., substantial cyclization) and therefore were most likely branched as well.

The products have been characterized by GPC and ¹H-NMR spectroscopy: The GPC trace of the (*tr*-1,4-PIP)-*b*-PIB-*b*-(*tr*-1,4-PIP) (not shown) was monomodal and very narrow ($\bar{M}_w/\bar{M}_n = 1.17$). IP incorporation was indicated by a shift of the RI trace toward lower elution volumes (higher MW) relative to that of the initiating \oplus PIB \oplus macrodication, and by the increase of UV absorption due to the PIP blocks (the small UV absorption of the initiating \oplus PIB \oplus dication is due to the aromatic initiator fragment). The ¹H-NMR spectrum of a representative triblock, shown in Figure 6, exhibits the expected $\underline{\text{CH}}_3$ — and — $\underline{\text{CH}}_2$ — resonances of the PIB middle block at 1.11 and 1.43 ppm, respectively, and the aromatic proton resonances of the initiating moiety at 7.2 ppm. The new resonances at 1.60, 1.93, and 5.12 ppm, respectively, indicate the presence of $\underline{\text{CH}}_3$ —, — $\underline{\text{CH}}_2$ —, and — $\underline{\text{CH}}=$ protons of the *tr*-1,4-PIP blocks. According to the relative ratio of aromatic initiator fragment (four aromatic protons per chain) and — $\underline{\text{CH}}=$ PIP protons, the triblock contains 35 IP units per molecule. Epoxy titration of the PIP double bonds and yield data assuming no loss of unsaturation gave 36 IP units per molecule. The excellent agreement between these analytical data also indi-

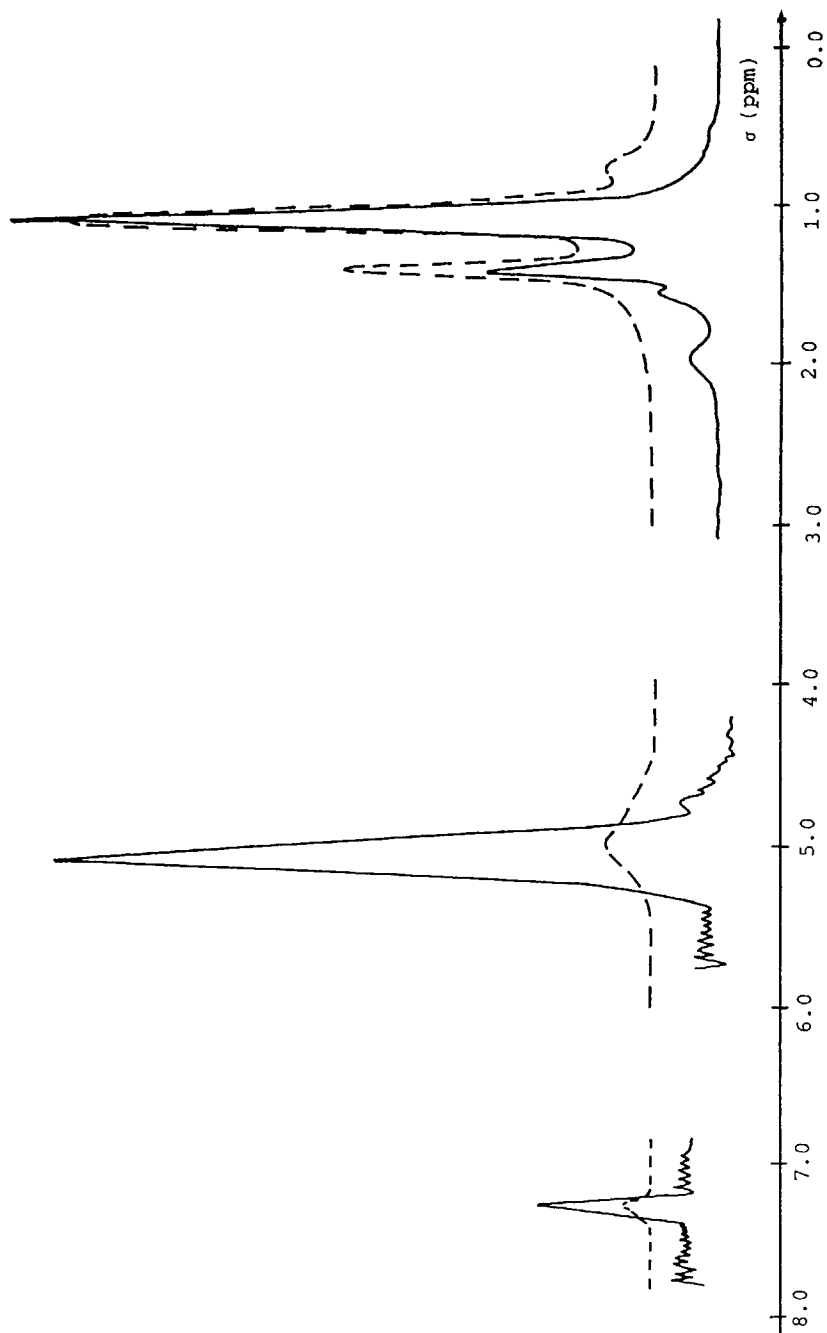


Fig. 6. $^1\text{H-NMR}$ spectra of a (*tr*-1,4-PIP)₃-*b*-PIB-*b*-(*tr*-1,4-PIP) triblock ($\bar{M}_{n(\text{PIB})} = 51,300$, —) and a *cy*-PIP/PIB multiblock ($\bar{M}_{n(\text{PIB})} = 10,500$, ···). Experimental details in Table I.

cates the absence of double bond loss (cyclization) in these well-defined new (*tr*-1,4-PIP)-*b*-PIB-*b*-(*tr*-1,4-PIP) triblocks.

In contrast, GPC and ¹H-NMR analysis of products obtained in relatively low viscosity media indicated substantial branching/cyclization, i.e., multiblock formation. A representative GPC (RI and UV) trace of a product obtained with a \oplus PIB \oplus of $\bar{M}_n = 16,600$, shown in Figure 7, exhibits a series of peaks in the 35–25 mL V_e range whose positions (i.e., molecular weights) indicate the formation of branched multiblocks (the molecular weights of the species in the product mix were $1\times$, $2\times$, $3\times$, $4\times$, etc. multiples of the molecular weight of the initial triblock). Moreover, the sudden increase in the UV/RI plot constructed from the UV and RI GPC traces suggests the sudden appearance of strong UV-absorbing cyclic structures at higher molecular weights. The broad UV absorption at very low molecular weights (> 38 mL V_e) is most likely due to *cy*-PIP formed by chain transfer to IP. ¹H-NMR spectroscopy (cf. Fig. 6) of this product shows the presence of PIB and *tr*-1,4-PIP segments; however, it also reveals a resonance at 0.93 ppm characteristic of CH_3- groups in *cy*-PIP units. In line with this observation the spectrum suggests a $\sim 30\%$ loss of unsaturation due to cyclization.

The appearance of featureless DSC scans (similar to that shown in Fig. 4) are in agreement with the mixed (multiblock, branched, cyclized) nature of the PIP segments.

Attempts To Increase the PIP Sequence Length in IP/IB Block Copolymers. Since the synthesis of high strength TPEs requires the presence of at least 20 wt % glassy blocks in the copolymers, our aim was to increase the PIP sequence lengths in the triblocks and multiblocks. Efforts to increase the *tr*-1,4-PIP content of linear well-defined triblocks by increasing the IP polymerization time in relatively viscous media were unsuccessful and also yielded branched/cyclized multiblocks, and the rate of IP incorporation into the linear triblock fractions had to be determined indirectly.

First a calibration curve was constructed by plotting the UV/RI ratio obtained from GPC traces of the linear triblock fractions of various PIP/PIB block copolymers as a function of their PIP content. These PIP/PIB block copolymers (mixtures of linear triblocks and branched multiblocks whose overall composition is determined by the length of the polymerization time) were prepared by initiating a series of IP polymerizations by \oplus PIB \oplus dications ($\bar{M}_n \approx 50,000$) and letting the reactions proceed for various times. It was assumed that the PIP content of the linear triblock fractions is directly proportional to the overall PIP content (determined gravimetrically) of the above PIP/PIB block copolymers. Figure 8 shows the calibration curve, and the linearity of the correlation demonstrates the validity of the assumption.

Next, in two series of experiments IP polymerization was initiated by \oplus PIB \oplus s ($\bar{M}_n = 52,500$ and $55,500$, $\bar{M}_w/\bar{M}_n = 1.17$ and 1.16 , [\oplus PIB \oplus] = 138 and 140 g/L, respectively) and samples for IP polymerization rate studies were withdrawn from the charge in 5–30 min time intervals for a total of 210 and 330 min, respectively. Final IP conversions were 27 and 40%, respectively. GPC traces showed a gradual shift toward higher molecular weights with time, i.e., growing triblocks, and the appearance of multimodal distributions with molecular weight multiplets similar to the trace shown in Figure 7. The unsaturation levels determined by ¹H-NMR spectroscopy and epoxy titration,

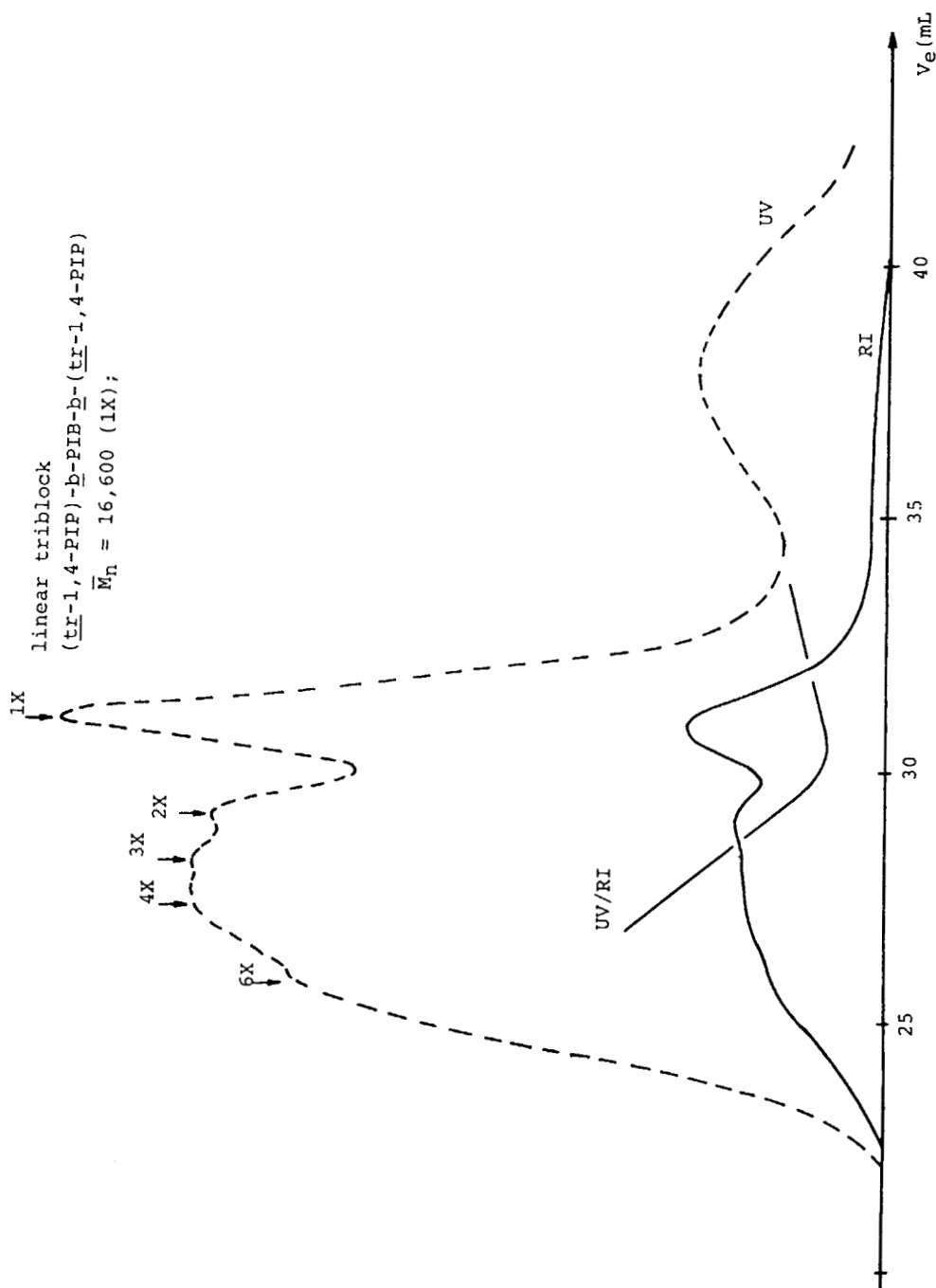


Fig. 7. GPC traces of a cy,PIP/PIB multiblock ($\bar{M}_{n(\text{PIB})} = 16,600$). Experimental details in Table I.

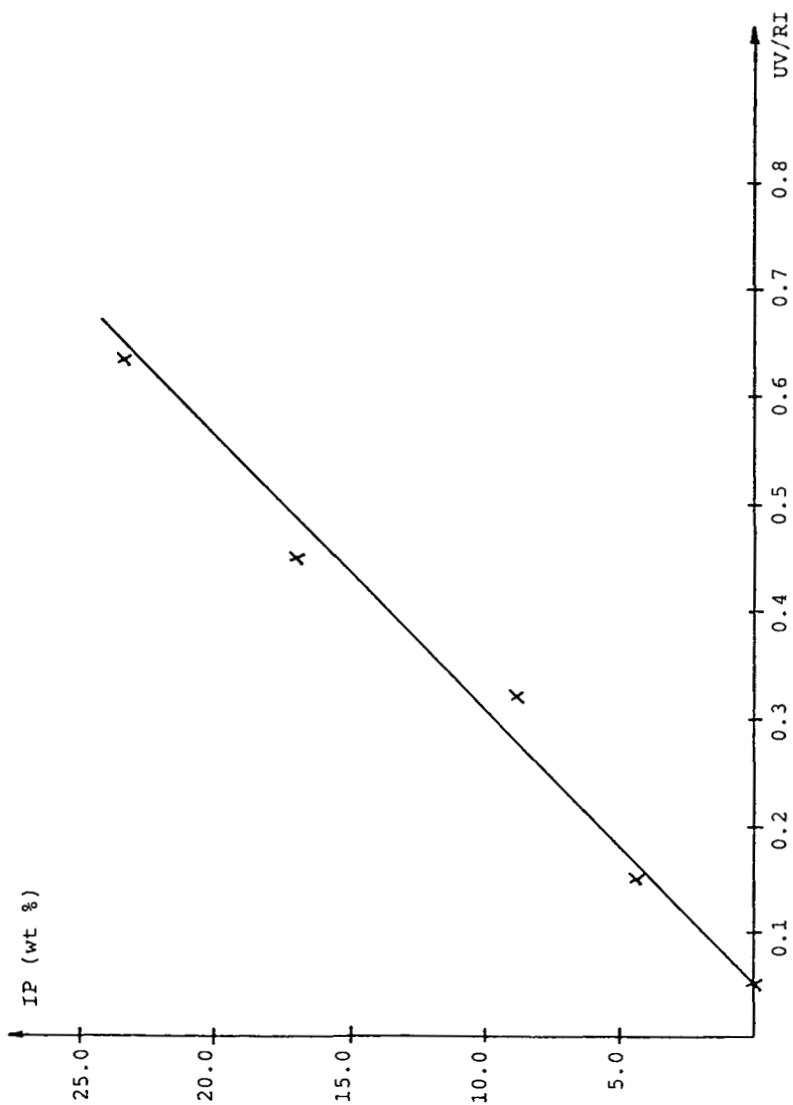


Fig. 8. Correlation between IP contents and UV/RI ratios of (*tr*-1,4-PIP)-*b*-(*tr*-1,4-PIP) fractions of *cy*-PIP/PIB block copolymers with $\bar{M}_{n(\text{PIB})} \approx 50,000$. Experimental conditions; $[\text{PIB}\Phi]_0 = 2.7 \times 10^{-3}$ mol/L; $[\text{TiCl}_4]_0/[\text{PIB}\Phi] = 16$; IP = 48 mL; $V_0 = 150$ mL $\text{CH}_2\text{Cl}/n\text{-C}_6\text{H}_{14}$ 40/60 v/v; -80°C .

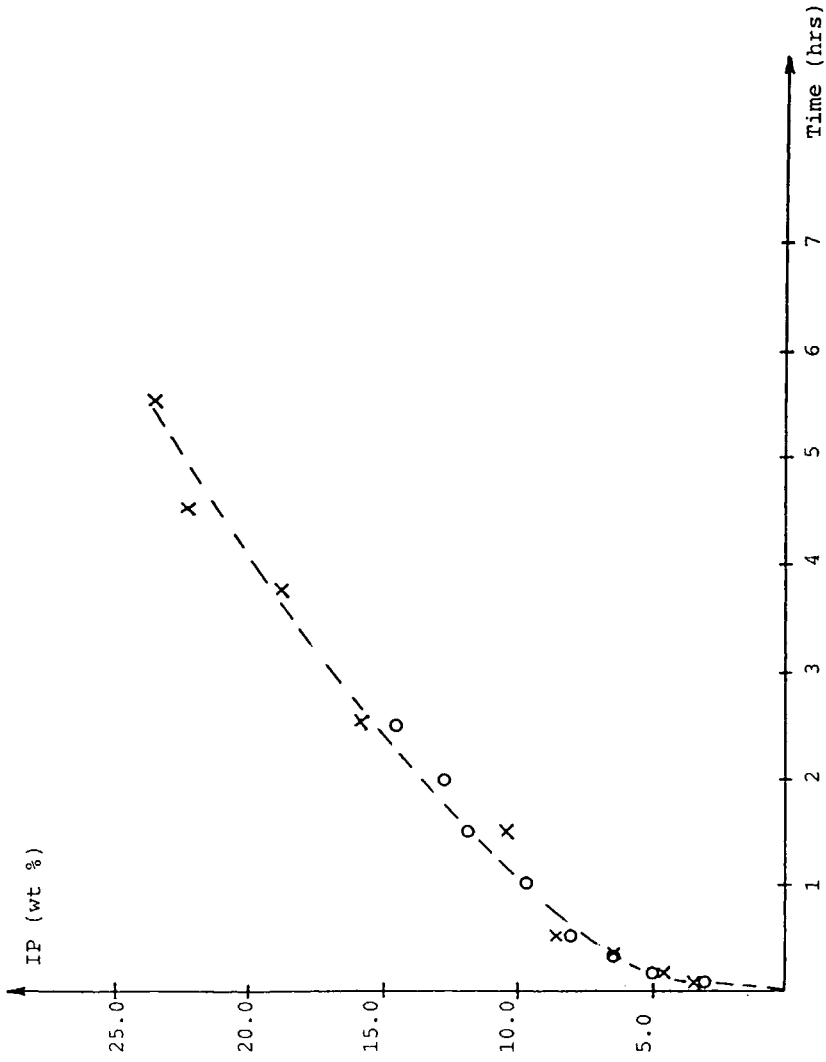


Fig. 9. IP incorporation as a function of time: (X) $\bar{M}_{n(\text{PIB})} = 55,500$; (O) $\bar{M}_{n(\text{PIB})} = 52,500$. Experimental data as in Figure 8.

indicated massive cyclization, i.e., 36 and 56% loss of unsaturation. The IP content of the end products (17 and 23.4 wt %) was determined gravimetrically. The IP contents of the linear (*tr*-1,4-PIP)-*b*-PIB-*b*-(*tr*-1,4-PIP) fractions were obtained from the calibration curve in Figure 8 using the UV/RI ratios calculated from the corresponding GPC traces, and the data were plotted against the reaction time. According to this plot shown in Figure 9, about 30 min of relatively rapid IP consumption is followed by an extended much slower polymerization. Deceleration of IP incorporation cannot be due to a decrease in IP concentration since IP conversion is only 5% after 30 min. The addition of fresh monomer and/or TiCl₄ accelerates the rate and this process can be repeated several times until the system reaches the gel point. A similar phenomenon has been described by Gaylord et al.,^{15,18} who attributed deceleration to the formation of IP/TiCl₄ complexes in equilibrium with monomer. The existence of rather weak IP/TiCl₄ complexes has been confirmed by Murachev et al.³¹ It is difficult to explain these findings by IP/TiCl₄ complexes, because one is forced to postulate that the rate of complex formation is low and that faster polymerization may proceed for ~ 30 min.

In sum, increasing the length of linear PIP blocks in (*tr*-1,4-PIP)-*b*-PIB-*b*-(*tr*-1,4-PIP) triblocks is hampered by alkylation/cyclization of the *tr*-1,4-PIP sequences. The resulting multiblocks may contain 10–25 wt % *cy*-PIP, depending on reaction conditions.

Cyclization of *tr*-1,4 PIP Sequences of Block Copolymers

As discussed above *cis*- or *trans*-1,4-PIP can be cyclized to rigid, glassy materials. Lal³² prepared TPEs from linear triblocks containing *tr*-1,4-PIP endblocks and a *cis*-1,4-polybutadiene midblock by treating them with acids. Under select conditions the PIP endblocks can be selectively cyclized and thus TPEs be obtained.

Cyclization of a linear (*tr*-1,4-PIP)-*b*-PIB-*b*-(*tr*-1,4-PIP) triblock ($\bar{M}_n = 80,800$, $\bar{M}_w/\bar{M}_n = 1.26$; \bar{M}_n (PIB) = 68,500 with $\bar{M}_w/\bar{M}_n = 1.13$, PIP content = 5.6 ± 0.2 m % by gravimetry and ¹H-NMR spectroscopy) was effected by BF₃OEt₂ or TiCl₄ in refluxing cyclohexane for 4 h under dry nitrogen. According to ¹H-NMR spectroscopy treatment with BF₃OEt₂ and TiCl₄ lead to 60 and 100% loss of unsaturation, respectively. Figure 10 shows the DSC traces. The (*cy*-PIP)-*b*-PIB-*b*-(*cy*-PIP) cyclized by BF₃OEt₂ shows two T_g 's at 104 and 183°C, suggesting at least cyclic structures. The higher T_g is assigned to relatively long cyclic segments. Treatment with TiCl₄ yielded an essentially saturated product (loss of unsaturation 100%). The DSC trace shows a distinct T_g at 183°C. According to TG analysis (Fig. 11) decomposition starts at 412°C. The TPE is completely soluble in organic solvents and is processible above 170°C. A sheet prepared by heating chunks of block copolymer to 170°C in a Teflon mold was sticky but during storage at room temperature lost its stickiness and became stronger. Due to the low PIP content (5.6 m %), however, the sheet remained too weak for meaningful tensile studies.

Multiblocks were similarly post-cyclized by acid treatment. Table II demonstrates the results. Multiblocks containing partially cyclized PIP segments cannot be converted into saturated products, probably because the branches prevent complete cyclization. Extended reaction times (to 48 h) did

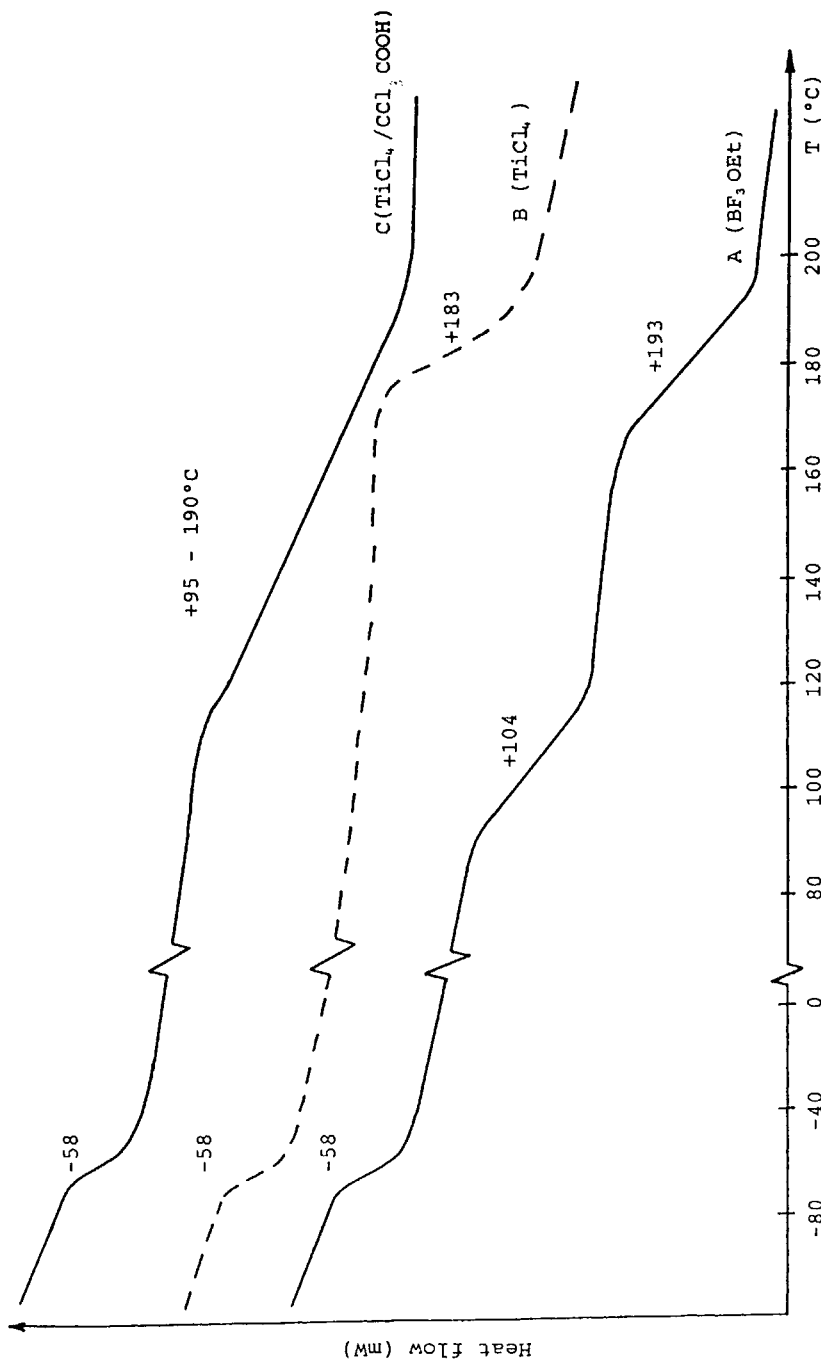


Fig. 10. (A and B) DSC traces of (cy-PIP)-*b*-PIB-*b*-(cy-PIP)s obtained by acid treatment of (*tr*-1,4-PIP)-*b*-PIB-*b*-(*tr*-1,4-PIP); $\bar{M}_n = 80,000$; $\bar{M}_w/\bar{M}_n = 1.26$; $\bar{M}_{n(\text{PIB})} = 68,5000$; $\bar{M}_w/\bar{M}_n = 1.13$. (c) DSC trace of an acid-treated cy-PIP/PIB multiblock $\bar{M}_{n(\text{PIB})} = 55,500$. Further data in Table II.

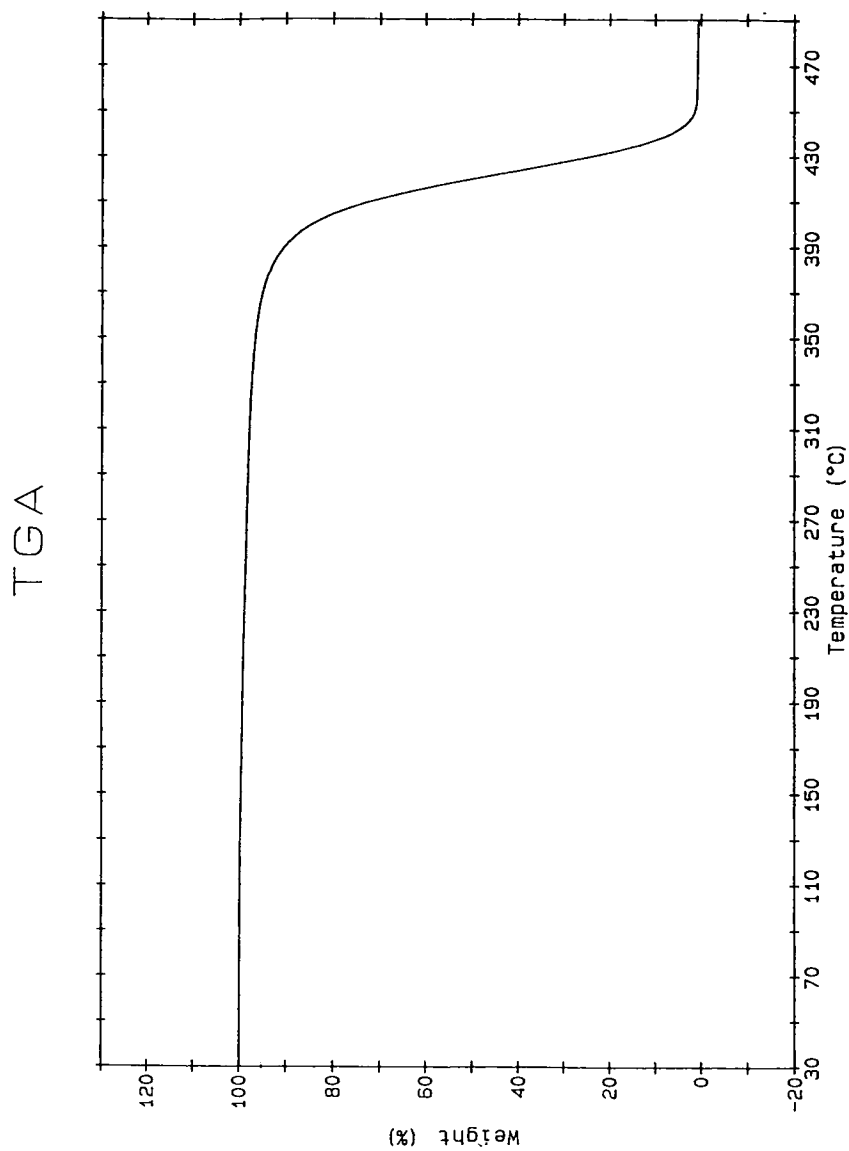


Fig. 11. TG trace of a (*cy*-PIP)-*b*-PIB-*b*-(*cy*-PIP) triblock obtained upon TiCl_4 treatment of a (*tr*-1,4-PIP)-*b*-PIB-*b*-PIB-*b*-(*tr*-1,4-PIP) triblock. Experimental data as in Figure 10.

TABLE II
Post-Cyclization of PIP/PIB Multiblocks by Acid Treatment^a

PIB soft segment		PIP content of block copolymers ^b (%)	Loss of unsaturation (%)	
\bar{M}_n	\bar{M}_w/\bar{M}_n		Before	After acid treatment
18,800	1.15	23	19	54 (57°)
18,800	1.15	23	19	Degradation ^d
55,500	1.16	20	52	68
55,500	1.16	14.4	35	80

^a Five parts TiCl_4 + 1.5 parts CCl_3COOH per 100 parts copolymers, 24 h in refluxing cyclohexane.

^b By yield data.

^c 48-h reflux.

^d Ten parts TiCl_4 + two parts $\text{CCl}_3\text{COOH}/100$ parts copolymer, 24 h in refluxing toluene.

not significantly increase the loss of unsaturation. In comparison, linear triblocks can be converted into essentially saturated product in 4 h. Acid treatment at higher temperatures degrade multiblocks. Oxidative damage demonstrated by IR spectroscopy (i.e., the presence of carbonyl and hydroxyl groups; see Fig. 12) can be prevented by antioxidants (e.g., 2-methyl-5-isopropyl-1,4-benzoquinone).

The DSC trace of a post-cyclized branched multiblock is presented in Figure 10. The transition corresponding to cy-PIP blocks covers a wide temperature range (95–190°C). Evidently the branched structures prevent the

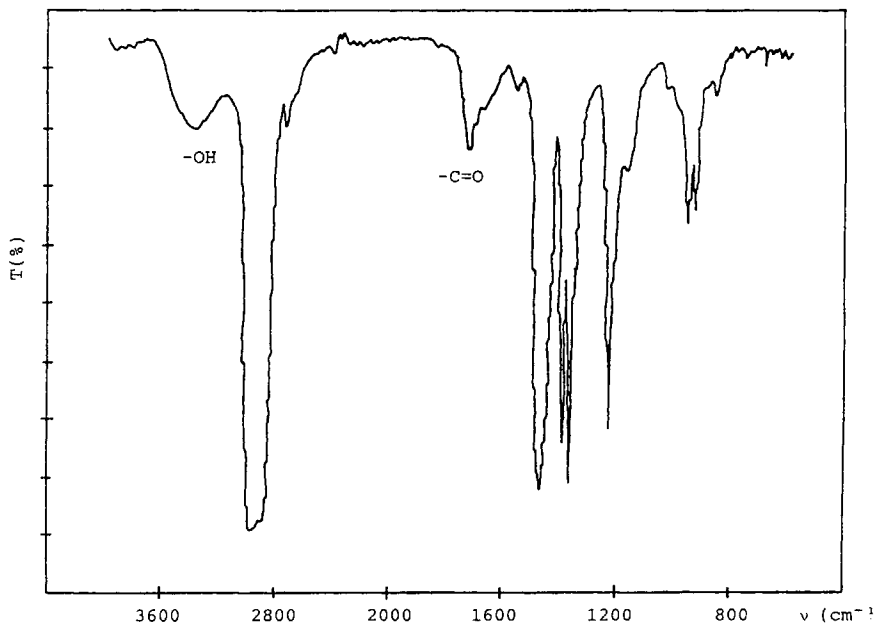


Fig. 12. IR spectrum of a cy-PIP/PIB multiblock after 150°C 2 h treatment in the absence of antioxidant. $\bar{M}_{n(\text{PIB})} = 55,500$. Experimental details in Table II.

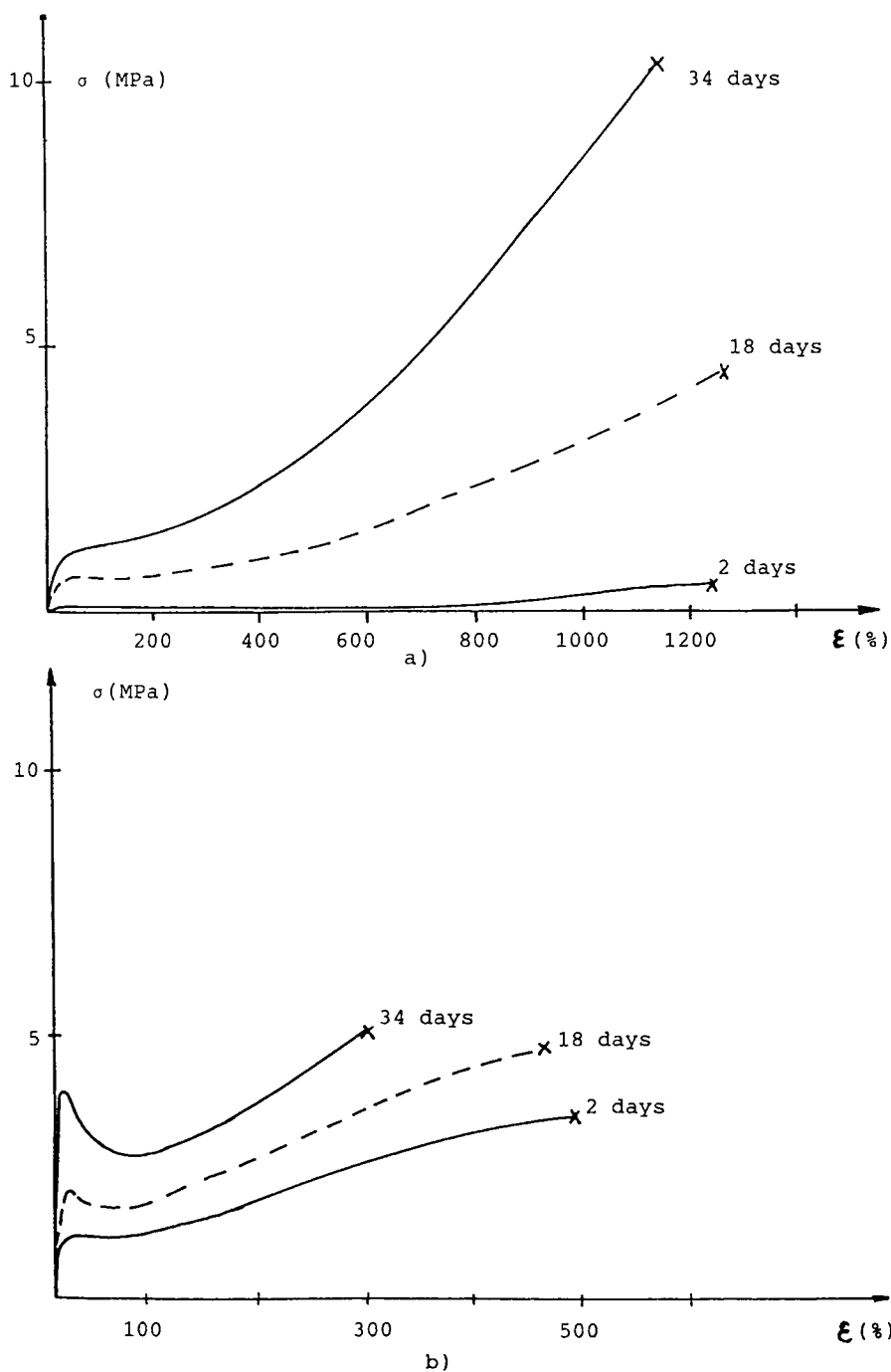


Fig. 13. Stress-strain plots of two cy-PIP/PIB multiblocks: (a) $\bar{M}_{n(\text{PIB})} = 55,500$; cy-PIP content = 14.4 mol %; (b) $\bar{M}_{n(\text{PIB})} = 18,800$; cy-PIP content = 23.0 mol %. Further data in Table II.

TABLE III
Solubility Parameters of cy-PIP, PIB, Polybutadiene and Polystyrene

	(36)	(37)
PIB	7.78	7.51
cy-PIP	7.66	7.49
Polybutadiene	8.67	8.99
Polystyrene	9.21	9.27

formation of well-defined cyclic structures. The cy-PIP content of post-cyclized multiblocks is higher than those of linear (cy-PIP)-*b*-PIB-*b*-(cy-PIP) triblocks and exhibit thermoplastic elastomeric behavior.

Physical Characterization of Multiblock Copolymers

cy-PIP/PIB multiblock copolymers are expected to exhibit TPE behavior particularly after post-cyclization. Transmission electron microscopy of a branched (cy-PIP)/PIB multiblock containing 28 m % cy-PIP (with $\approx 50\%$ unsaturation loss) and 72 m % rubbery PIB blocks (\bar{M}_n (PIB) = 10,500, $\bar{M}_w/\bar{M}_n = 1.32$) indicated phase separation with PIB the continuous phase. Compression molding (20 tons, 150°C, 20 min) yielded a toluene-insoluble discolored gel showing macrophase separation. A film cast from CCl₄ showed 3.5 MPa tensile strength and 250% elongation. The film was also soluble in boiling toluene. The DSC trace of this multiblock showed an exotherm in the 120–200°C range, indicating some degradation in the presence of air.

Post-cyclization improves the physical properties of multiblocks. As shown by the data in Figure 13, films cast from CCl₄ of post-cyclized samples (Table II, samples 4 and 1) showed increasing tensile strength with time. Slow strengthening might be due to slow phase separation of the PIB and cy-PIP domains. Indeed the solubility parameters of the cy-PIP and PIB are quite similar. Table III shows some representative solubility parameters (ν) calculated from group parameters given by Small³⁶ and Hoy³⁷ for several polymer pairs. The ν values for cy-PIP were calculated considering the proposed fused cyclic structure (two or four attached cyclic structures gave very similar values). The solubility parameter difference is the largest between cy-PIP and polybutadiene while is the smallest between cy-PIP and PIB. This may explain the slow increase in tensile properties. The strengthened samples became insoluble in CCl₄ while they remained readily soluble in hot toluene and flowed above 140°C. Interestingly, samples cast from toluene exhibited 3–4 MPa and did not show tensile strength increase with time. Figure 14 demonstrates hysteresis behavior of the above two representative samples.

In sum, new thermoplastic elastomers comprising soft PIB and glassy cy-PIP segments have been prepared. The linear (cy-PIP)-*b*-PIB-*b*-(cy-PIP) triblocks are essentially saturated, however, they exhibit unsatisfactory tensile properties on account of their low cy-PIP content. Post-cyclized multiblocks contain residual unsaturation, are self-reinforcing with time, and remain reprocessable. These new thermoplastic elastomers exhibit a desirable combination of properties and should find use as moisture and gas-barriers, hot-melt coatings, UV-crosslinkable coatings, etc.

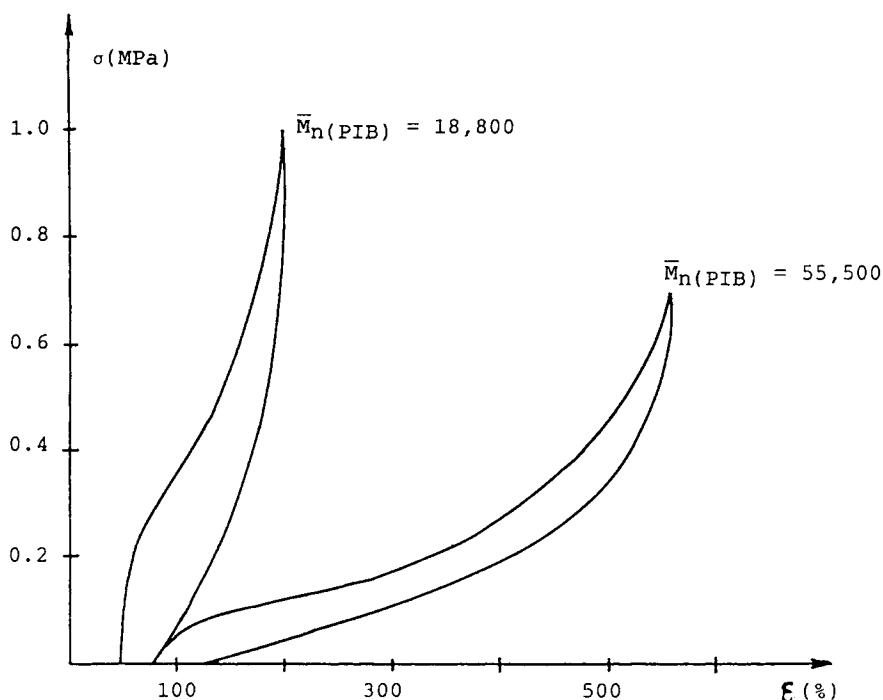


Fig. 14. Hysteresis of two cy-PIP/PIB multiblocks. Experimental data as in Figure 13.

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