Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

New Transparent Flexible UV-Cured Films from Polyisobutylene-Polyisoprene Block Polymers

J. E. Puskas[ab]; G. Kaszas[ab]; J. P. Kennedy[a]
[a] Institute of Polymer Science The University of Akron, Akron, Ohio [b] POLYSAR RUBBER CO., Sarnia, Ontario, Canada

To cite this Article Puskas, J. E. , Kaszas, G. and Kennedy, J. P.(1991) 'New Transparent Flexible UV-Cured Films from Polyisobutylene-Polyisoprene Block Polymers', Journal of Macromolecular Science, Part A, 28: 1, 65 — 80
To link to this Article: DOI: 10.1080/00222339108052086
URL: http://dx.doi.org/10.1080/00222339108052086

J. MACROMOL. SCI.—CHEM., A28(1), pp. 65–80 (1991)

NEW TRANSPARENT FLEXIBLE UV-CURED FILMS FROM POLYISOBUTYLENE–POLYISOPRENE BLOCK POLYMERS

J. E. PUSKAS,† G. KASZAS,† and J. P. KENNEDY*

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

ABSTRACT

Novel polyisobutylene–polyisoprene (PIB–PIP) multiblock polymers have been synthesized and used for the preparation of UV-cured transparent flexible coatings. The block polymers were tailor-made by bidirectional living carbocationic polymerization of isobutylene (IB) followed by sequential isoprene (IP) addition. PIB–PIP multiblocks containing highly cyclized *tr*-1,4-PIP sequences were mixed with a bisazide and photocrosslinked. Epoxidized PIB–PIP blocks were blended with a cationic photoinitiator and UV-cured. Blocks having 23 mol% total PIP content and PIB segments of $\overline{M}_n$ = 16,600 and 18,800, respectively, gave transparent flexible coatings with 45 kg/cm^2 tensile strength and 450% elongation. The coatings exhibited good adhesion to aluminum and are expected to have excellent barrier properties due to the presence of PIB sequences.

A. INTRODUCTION

Advances in the understanding of the mechanism of living carbocationic polymerizations of IB [1–3] led to the synthesis of new block copolymers [4–6]. For example, linear tri- and branchy multiblocks consisting

---

†Present address: POLYSAR RUBBER CO., P.O. Box 3001, 1265 Vidal St., Sarnia, Ontario N7T 7M2, Canada.

of uniform (narrow molecular weight distribution) PIB rubbery segments and linear and/or cyclized *tr*-1,4-polyisoprene (PIP and/or PIP/cyPIP, where cyPIP stands for highly cyclized PIP) segments have recently been synthesized [4].

Rubbery UV-active coatings have been obtained from (meth)acrylate-capped telechelic PIBs [7]. It has occurred to us that PIB–(PIP/cyPIP) block polymers could be used as base polymers for UV-cured coatings. These coatings were expected to exhibit excellent flexibility; outstanding moisture and gas barrier properties; outstanding acid, alkali, and water resistance; combined with excellent adhesion to various surfaces. The new block polymers postcyclized to the maximum degree yield polymers containing rubbery PIB inner blocks and hard cyPIP outer segments [4] and, similarly to cyclized natural and synthetic PIPs that are important contemporary negative photoresists [8, 9], could also be photocrosslinked via the cyPIP segments [10]. Alternatively, residual double bonds in the PIP and PIP/cyPIP blocks could be epoxidized and the epoxy derivatives could be UV-cured by diaryliodonium salts (Crivello salts [11]).

This paper concerns the synthesis, characterization, and UV crosslinking of PIB–cyPIPs and epoxidized PIP–PIB–PIP and PIB–(PIP/cyPIP) block polymers, and a characterization of the networks obtained.

B. EXPERIMENTAL

B.1. Materials

The Synthesis of 1,4-Di(2-methoxy-2-propyl)benzene (DiCumOMe) has been described [12]; it was freshly purified by chromatography on neutral Al_2O_3 (activity III) using *n*-pentane eluent. Purity was ascertained by DSC analysis (mp = 49°C). Sources and purification of *methyl chloride, hexanes, titanium tetrachloride, IB, IP, and m-chloroperbenzoic acid* have been reported [4, 13, 14]. *Methylene chloride, chloroform, and carbon tetrachloride* were dried over molecular sieves (4 Å).

Sodium thiosulfate, potassium iodide, glacial acetic acid, starch, methanol, toluene, p-xylene, benzene, cyclohexane, tetrahydrofuran, trichloroacetic acid, boron trifluoride etherate, 2-methyl-5-isopropyl-1,4-benzoquinone (antioxidant, AO), 2,6-bis(azidobenzylidene)-4-methylcyclohexanone (DIAZ), and 2,2-dimethoxy-2-phenyl-acetophenone [Irgacure 651 (Aldrich)] were used as received. *Phenyl-(p-methoxy-*

phenyl)-iodonium-hexafluoro antimonate (Crivello salt) was generously provided by Dr. Crivello.

B.2. Procedures

B.2.1. Synthesis of PIP–PIB–PIP and PIB–(PIB/cyPIP) Block Copolymers

PIP-PIB-PIP triblocks and PIB-(PIP/cyPIP) multiblocks were synthesized by sequential monomer addition by the use of the DiCumOMe/$TiCl_4$ initiating system in CH_3Cl/*n*-hexane 40/60 v/v solvent mixture at −80°C, as described [4]. Bidirectional living polymerization of IB yielded $^+PIB^+$ macrodications whose $\overline{M}_n$ was controlled by the extent of IB consumption: $\overline{M}_{n,\mathrm{PIB}}$ = [IB]/[DiCumOMe]. The $^+PIB^+$s were then used in the same reactor for blocking IP from these macrodications. Blocking was allowed to proceed for 30 or 150 min, after which the charges were quenched with prechilled methanol. The solvents were evaporated, and the polymers were washed with methanol containing 1% AO and then with water to remove Ti-containing residues. After extraction, the products were dried in a vacuum oven at room temperature. Yields were determined gravimetrically.

B.2.2. Postcyclization of PIB–(PIP/cyPIP) Block Polymers

To a 500-mL round-bottom flask equipped with a condenser and magnetic stirrer and containing 10% block copolymer in cyclohexane solution, desired amounts of $TiCl_4$ and CCl_3COOH (5 parts $TiCl_4$ + 1.5 parts CCl_3COOH per 100 parts block copolymer) were added under dry nitrogen and refluxed for 24 h. The charge was cooled, the polymer was precipitated into excess methanol containing 1% AO, washed several times with methanol and then with water, and dried in a vacuum oven at room temperature.

B.2.3. Epoxidation of PIP–PIB–PIP Triblock and PIB–(PIP/cyPIP) Multiblock Polymers

To a 500-mL round-bottom flask equipped with a stirrer and a condenser, 15 g block copolymer was dissolved in 100 mL refluxing *p*-xylene. After cooling to room temperature, 100 mL chloroform was added. Then a suitable amount of *m*-chloroperbenzoic acid (20% excess based on the double bond content of the copolymer) dissolved in 100 mL chloroform was added and the epoxidation was allowed to proceed for 2 h at room temperature. The epoxidized product was precipitated in a large excess of methanol, redissolved in *n*-hexane, washed several times with aqueous sodium bicarbonate solution, and then with distilled water. The *n*-hexane solution was dried over $CaCl_2$, the solvent was removed (Rotavap), and the product was dried in a vacuum oven.

B.2.4. UV-Curing

The postcyclized PIB–cyPIP multiblocks were dissolved in hot *p*-xylene to give 10% solutions, and 5 wt% DIAZ (relative to the block copolymer) dissolved in 2 mL methylene chloride was added to the solutions. Epoxidized products were dissolved in carbon tetrachloride to give 10% solutions, and 5 wt% Crivello salt and 5 wt% Irgacure 651 (relative to the block copolymers) dissolved in methylene chloride were added.

The solutions were poured into Al-weighing dishes (circular, 3 in. diameter), the solvents were evaporated, and the films further dried in a vacuum oven at 55 °C for 4 h. The dry flexible films were illuminated with a Portacure F1500 UV-curing Unit (American Ultraviolet Co., 300 W/in.) for 60 s. The PIB–cyPIP/DIAZ systems were cured under a nitrogen blanket. The epoxy/Crivello salt systems required posttreatment in an oven at 55 °C for 24 h in order to ensure complete crosslinking [15]. The films became so strongly attached to the Al surface that they could not be removed without their destruction; thus the Al dishes were dissolved in concentrated aqueous NaOH, the crosslinked films were washed with distilled water to remove the surface debris, and dried in a vacuum oven at 55 °C for 24 h.

B.2.5. Characterization Methods

PIB molecular weights and molecular weight distributions were determined by GPC as described [13]. The molecular weights of the *tr*-1,4-PIP and cyPIP segments were estimated from GPC traces by the use of PIB and PSt calibrations, and independently from gravimetric data.

^{1}H-NMR spectra were obtained by a Varian T-60 and a Varian 300 MHz instrument using CCl_4 and $CDCl_3$ solvents, respectively.

The double bond content of the block polymers was determined by epoxide titration according to Ref. 14 and by ^{1}H-NMR spectroscopy from the ratio of intensities corresponding to the $=C\underline{H}-$ protons of the PIP sequences and the aromatic protons of the cumyl initiating fragment (5.12 and 7.2 ppm, respectively).

DSC measurements were taken on DuPont (1090 and 9900) Thermal Analyzers. The heating rate was 10°C/min. T_gs were determined by the midpoint method.

The cured films were extracted successively with toluene, methylene chloride, and *n*-pentane. Swelling experiments were carried out with *n*-pentane or benzene with samples (about 2 × 2 × 0.01 cm) cut from the films. The thickness of the films was determined by a thickness gauge, and their density was calculated from size and weight data. Equilibrium swelling was reached after a few days.

Stress-strain data were obtained on an Instron Universal Testing Instrument with a 500-g load cell and 10 cm/min crosshead speed at room temperature using microdumbbells.

C. RESULTS AND DISCUSSION

C.1. Synthesis of PIP-PIB-PIP and PIB-(PIP/cyPIP) Block Polymers

Figure 1 shows the synthesis route of the PIP-PIB-PIP and PIB-(PIP/cyPIP) precursors. Living polymerization of IB by the bifunctional DiCumOMe/$TiCl_4$ initiating system yields bidirectionally growing $^+PIB^+$ dications (I, Fig. 1) stabilized by the *in-situ* formed electron pair donor $TiCl_3OMe$ [1, 2]. The living $^+PIB^+$ dications were used to induce the blocking of short, essentially *tr*-1,4-PIP sequences, to yield linear $^+(PIP)\text{-}PIB\text{-}(PIP)^+$ dications [4]. This intermediate may either be isolated as a linear PIP-PIB-PIP triblock (II, Fig. 1) or may undergo simultaneous alkylation/cyclization to yield PIB-(PIP/cyPIP) multiblocks (III, Fig. 1). Figure 2 shows the mechanism proposed for the cyclization/alkylation [4]. Cyclization on the *tr*-1,4-PIP sequence may be induced by a growing polymer cation or a proton. The cyclization mechanism and possible structures of the tri- and multiblock copolymers have been discussed in detail [4].

Table 1 shows synthesis and characterizations data of the blocks prepared. The double bond contents determined by ^{1}H-NMR spectroscopy and epoxy titration were in excellent agreement. In the PIB-(PIP/cyPIP) multiblocks a fraction of the unsaturation was lost due to cyclization of *tr*-1,4-PIP sequences. While the blocking of IP from a relatively high molecular weight $^+PIB^+$ dication ($\overline{M}_{n(PIB)}$ = 51,300, Sample 1, Table 1) for 30 min yielded a linear PIP-PIB-PIP triblock, (mostly) pentablock

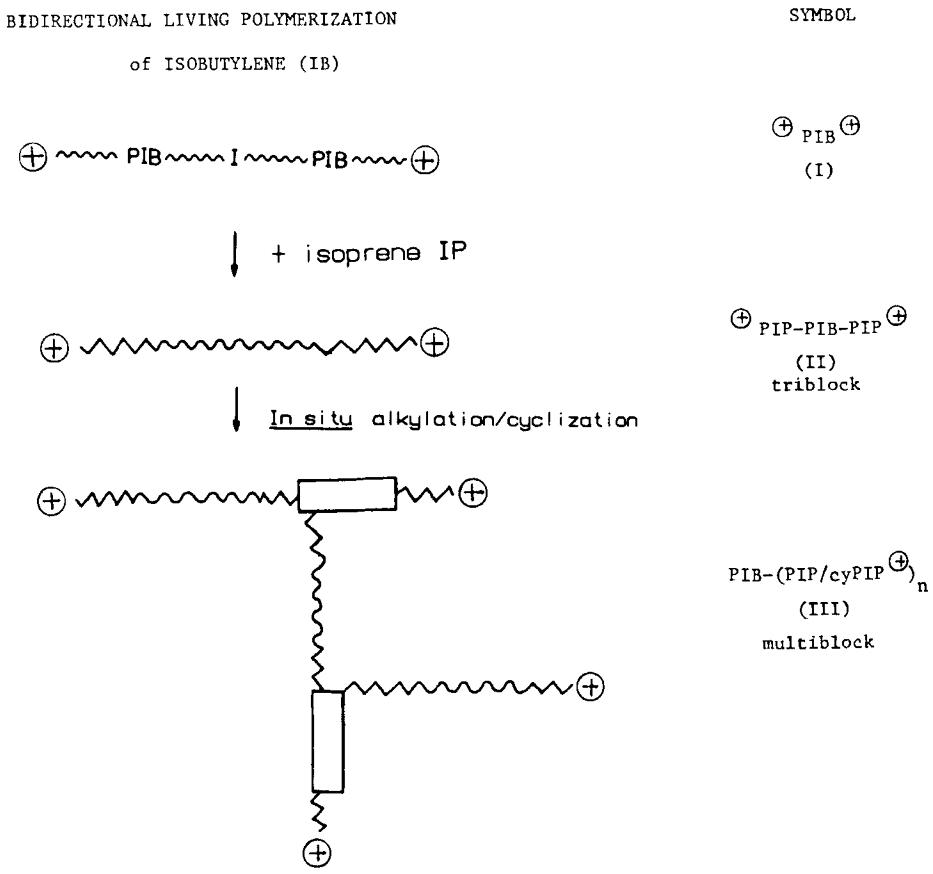


FIG. 1. Synthesis scheme of PIB-(PIP/cyPIP) block polymers [4].

was obtained by extending the reaction time to 150 min (Sample 2, Table 1). The latter product probably arose by a preformed $^{+}$PIP-PIB-PIP^{+} dication intermolecularly alkylating a PIP sequence of another dication. As alkylation/cyclization involves the reaction between two or more macromolecules, the rate of this reaction decreases by increasing the molecular weight and/or concentration of the $^{+}$PIP-PIB-PIP^{+} dication [4].

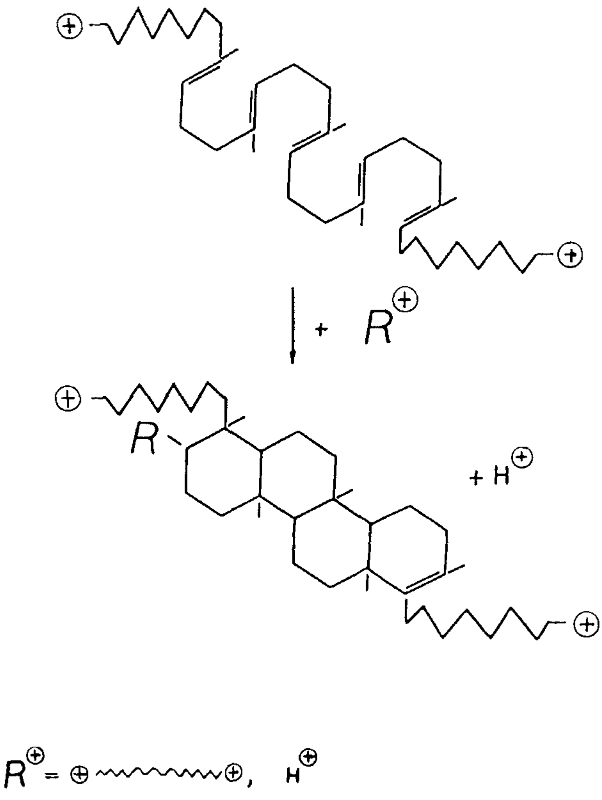


FIG. 2. Mechanism of alkylation/cyclization [4].

C.2. Formulation and UV Crosslinking of PIB–cyPIP/ Bisazide Compositions

Cyclized natural or synthetic polyisoprene rubbers cyPIPs in conjunction with bisazides are widely used as negative photoresists (Hunt NMR, Kodak KTFR, Merck Selectilux-N) by the contemporary electronic industry. The resists are exposed to UV light through a photomask, and networks are produced at the illuminated areas by the bisazide which photocleaves and thus produce nitrenes which crosslink the rubber [10]. The photocuring of random IB–IP copolymers containing 5–10 mol% IB units and cyPIP segments by a bisazide (DIAZ) has recently been

TABLE 1. Synthesis and Characterization of PIB-PIP Block Polymers[a]

	PIB segments		
Sample	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	Type
1	51,300	1.17	PIP-PIB-PIP
2	53,500	1.15	(PIP/cyPIP)-PIB-(PIP/cyPIP)$_2$-PIB-(PIP/cyPIP)[c]
3	16,600	1.29	Branchy multiblock with PIP/cyPIP outer blocks
4	18,800	1.15	Branchy multiblock with PIP/cyPIP outer blocks

[a]Synthesis. PIB step: [DiCumOMe] = [DMA] = 3.7–10.0 × 10^{-3} mol/L; $TiCl_4$/DiCumOMe = 16; [IB] = variable, see Experimental and Ref. 4; CH_3Cl/n-C_6H_{14} (40/60 v/v); −80°C. PIP-(PIP/cyPIP) step: IP = 48 mL; 30 and 150 min.

[b]By epoxy titration.

[c]Probably pentablock.

TABLE 2. UV-Cured Networks of PIB-cyPIP and Epoxidized PIB-PIP

Base polymers				
$\overline{M}_n$, PIB	Outer blocks	cyPIP, mol%	Epoxy,[a] mol%	Curing agent
18,800	cyPIP[c]	13.1	–	DIAZ
53,500	cyPIP[c]	6.8	–	DIAZ
16,600	Epoxy PIP/cyPIP	7.0	17.0	Crivello salt
			4.0	Crivello salt
51,300	Epoxy PIP	0		

[a]By epoxy titration, see Section B.2.2.

[b]All films were transparent.

[c]Postcyclized to the maximum degree, see Section B.2.3.

Block polymers				
Total IP, mol%	CyPIP content, %	Unsaturation (PIP units), mol%		Visual appearance
		^{1}H NMR	Epoxy[b]	
4.0	0	3.8	4.0	Colorless, sticky
16.2	1.2–1.8	14.4	15.0	Colorless, rubbery
24.0	7.0–7.2	16.8	17.0	Light yellow, rubbery
23.0	3–4.4	18.6	20.0	Light yellow, rubbery

Block Polymers

Networks					
Sol fraction, %	Tensile strength, kg/cm^2	Elongation, %	$\overline{M}_c$		Visual appearance[b]
			Benzene	*n*-Pentane	
8	45	450	9,600	7,600	Amber, tough, flexible
53	–	–	98,000	–	Amber, rubbery
6	45	450	9,300	9,600	Light brown, rubbery
60	–	–	51,100	–	Light brown, sticky

reported [16]. These random copolymers, however, yielded rigid coatings due to their low PIB contents. In contrast, PIB-(PIP/cyPIP) block polymers with more than 70 mol% PIB (see Table 1) were expected to yield flexible rubbery coatings.

Against this background, experiments have been carried out to demonstrate the preparation of flexible transparent nontacky coatings by photocrosslinking of novel PIB-cyPIP block copolymers. Table 2 summarizes the results. PIB-(PIP/cyPIP) blocks (Samples 2 and 4 in Table 1) were further cyclized by acid treatment to increase their cyPIP content. While the DSC scans of the PIB-(PIP/cyPIP) multiblocks were featureless due to the coexistence of linear *tr*-1,4-PIP and cyPIP sequences of various cyclicities, postcyclization yielded PIB-cyPIPs with somewhat more uniform, highly cyclized cyPIP sequences exhibiting glass transitions in the T_g = 95-190°C range [4]. After postcyclization,

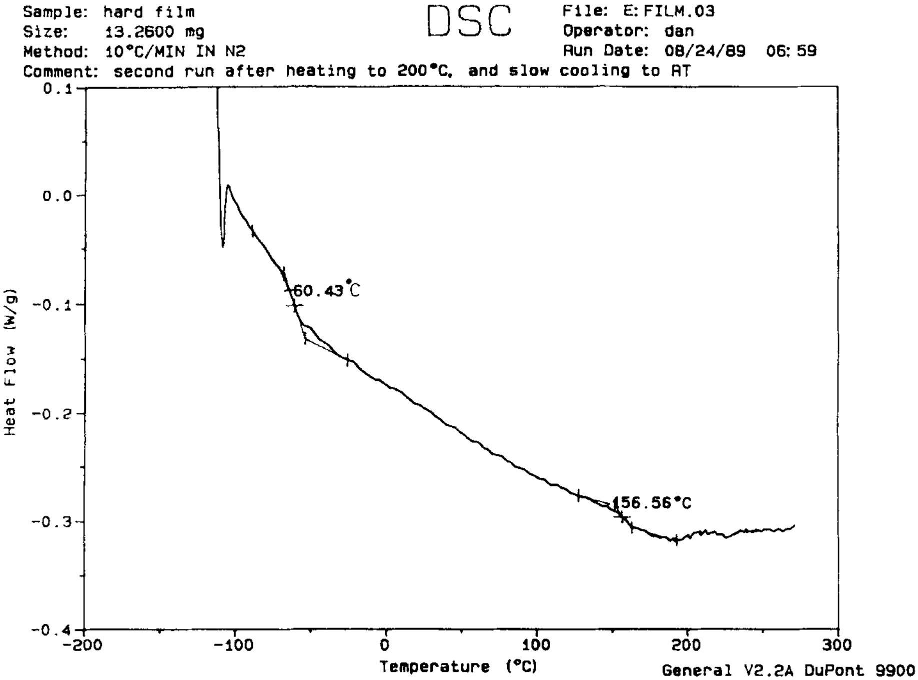


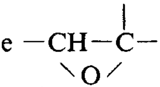
FIG. 3. DSC trace of a UV-cured film made of a postcyclized PIB-cyPIP block (Table 2, Line 1).

the remaining unsaturation in the blocks as determined by ^{1}H-NMR spectroscopy was 9.9 and 9.4 mol% (the total loss of unsaturation due to cyclization was 57 and 42%) so the cyPIP contents were 13.1 and 6.8 mol%, respectively. The block polymers turned darker yellow upon postcyclization. The postcyclized samples were subsequently blended with DIAZ and photocured (see Experimental).

The UV-cured films obtained from the multiblock with $\overline{M}_{n,\mathrm{PIB}}$ = 18,800 were transparent, deep amber, and nonsticky. Extraction with *n*-pentane and toluene for 24 h (8% sol fraction) indicated a very high degree of crosslinking. The extracted films exhibited 45 kg/cm^2 tensile strength and 450% elongation (Table 2, Line 1). The DSC scan of a cured film presented in Fig. 3 shows two distinctive T_gs at 60.4 and 156.6°C, respectively, indicating the presence of incompatible PIB and cyPIP phases.

The UV-cured film obtained from the PIB–cyPIP multiblock (pentablock) with $\overline{M}_{n,\mathrm{PIB}}$ = 53,500 was also deep amber, transparent, and nonsticky. However, extraction as above yielded 53% sol fraction, indicating incomplete crosslinking (Table 2, Line 2). Partial crosslinking was most probably due to the relatively lower overall PIP/cyPIP content and high PIB block molecular weight (i.e., the overall PIP/cyPIP content of the high MW block polymer was lower than that of the low MW product, 16.2 and 23 mol% PIP/cyPIP).

C.3. Synthesis and UV Crosslinking of Epoxidized PIP–PIB–PIP Block Copolymers

The photocrosslinking of epoxides in the presence of various Crivello salts yields high-quality coatings [11, 15]. The epoxidation of unsaturated polymers including unsaturated rubbers has been shown to be quantitative [14, 17]. In line with this background, PIB-(PIP/cyPIP) multiblocks and PIP–PIB–PIP triblock (see Samples 1 and 3, Table 1, respectively) were epoxidized. Figure 4 shows the ^{1}H-NMR spectra of the PIB–(PIP/cyPIP) multiblock (Sample 3, Table 1) before and after epoxidation. The signal at 5.12 ppm corresponding to the —CH= protons of the *tr*-1,4-PIP sequences has disappeared and a new peak at 2.8 ppm attributed to the  $\underset{\diagdown\,O\,\diagup}{-CH-\overset{|}{C}-}$ proton of the epoxidized PIP blocks has appeared [18]. The ^{1}H-NMR spectrum of the epoxidized PIP–PIB–PIP triblock also indicated complete epoxidation. The presence of epoxy

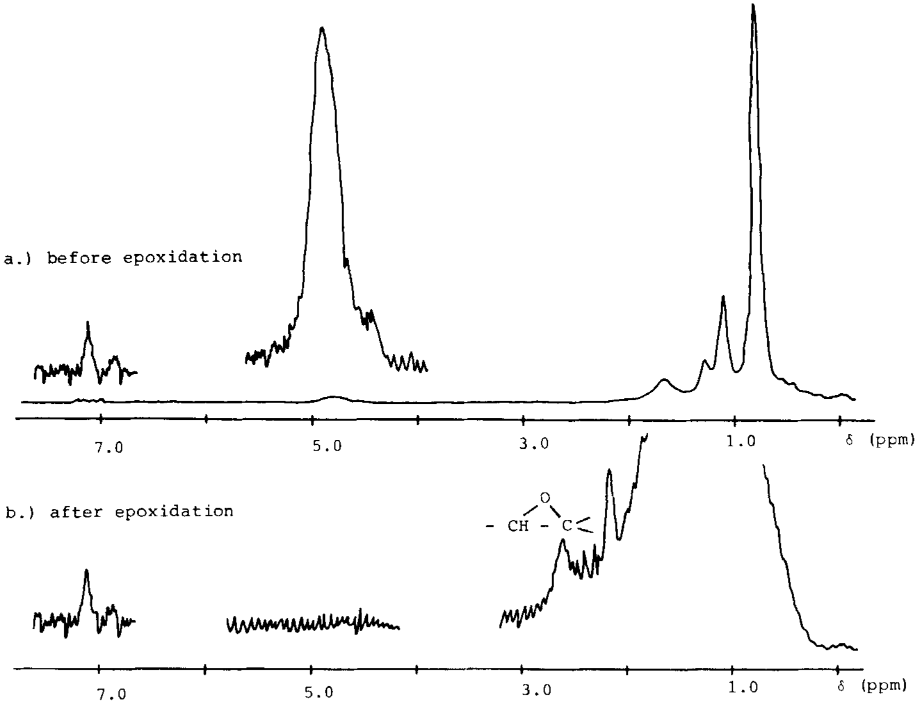


FIG. 4. ^{1}H-NMR spectra of a PIB-(PIP/cyPIP) multiblock (Table 1, Line 3) before and after epoxidation.

functions in both the multiblock and triblock was further substantiated by gelation tests. The addition of a few drops of BF_3OEt to epoxidized blocks in toluene solution caused rapid gelation.

Figure 5 shows the DSC trace of the epoxidized multiblock. The exotherm in the 120-240°C range indicates thermal crosslinking through the epoxy functions. Indeed, the network recovered from the DSC cell was insoluble in THF, toluene, and benzene.

The epoxidized blocks were blended with Crivello salt and Irgacure 651 photosensitizer, and photocrosslinked. In contrast to PIB-cyPIP/DIAZ systems, this cationic curing process does not require blanketing with an inert atmosphere. However, it does require posttreatment by heat [15].

Photocuring gave light brown, transparent, rubbery films (see Table 2). Extraction of the film obtained of the linear triblock (Table 2, Line

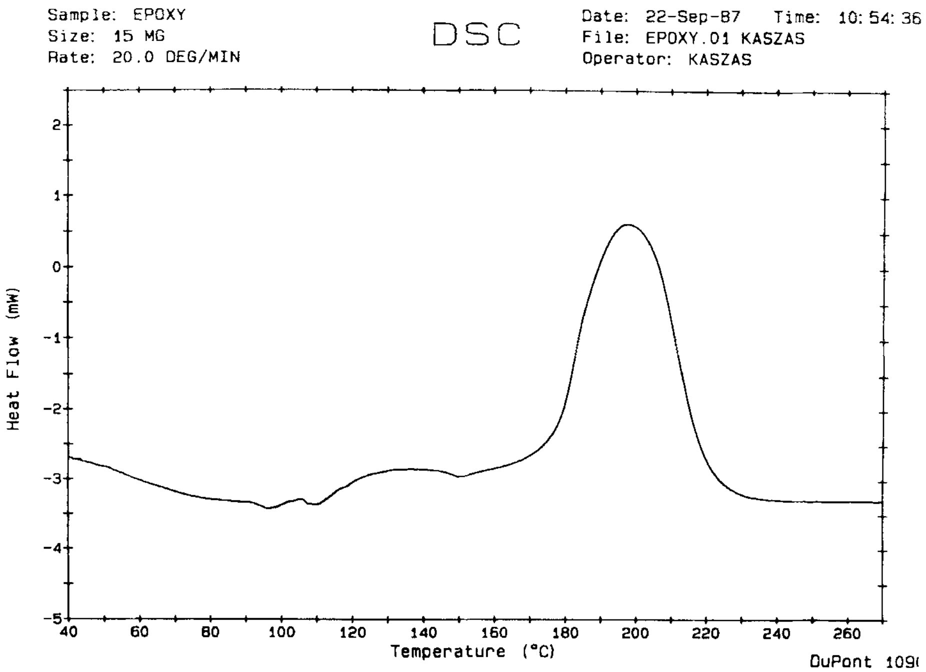


FIG. 5. DSC trace of an epoxidized PIB-(PIP/cyPIP) multiblock (Table 2, Line 3).

4) gave high sol (60%) with *n*-pentane and benzene, indicating only partial crosslinking, most probably due to the low epoxy content (4 mol%) and high molecular weight ($\bar{M}_{n(\mathrm{PIB})}$ = 51,300). In contrast, the film prepared of the epoxidized PIB-(PIP/cyPIP) multiblock yielded only 6% sol, indicating essentially complete crosslinking (Table 2, Line 3). The DSC trace of the cured multiblock presented in Fig. 6 shows only one T_g at −64°C, characteristic of PIB. The featureless higher temperature region is attributed to partially cyclized PIP-(PIP/cyPIP) (see Section C.2 and Ref. 4). The absence of an exotherm, as seen in the DSC of the epoxidized multiblock (see Fig. 5), also suggests virtually complete consumption by crosslinking of the epoxy functions.

The extracted film exhibited 45 kg/cm^2 tensile strength and 450% elongation. These values are essentially identical to those obtained with the DIAZ-photocured PIB-cyPIP films, which is not surprising in view

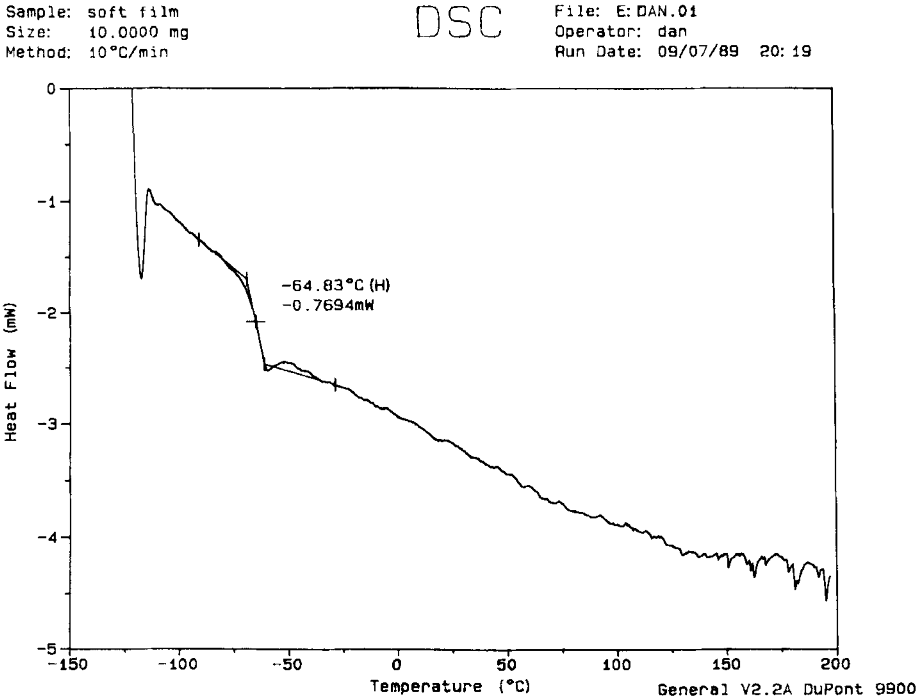


FIG. 6. DSC trace of a UV-cured film made of an epoxidized PIB-(PIP/cyPIP) multiblock (Table 2, Line 3).

of the similar compositions of the base multiblocks (see Samples 3 and 4, Table 1).

C.4. Swelling of PIB-PIP-Based Networks

The extracted UV-cured networks were swelled in benzene and/or *n*-pentane, and $\overline{M}_c$ values were calculated by the Flory-Rehner equation [19]. The density of the films, $d = 0.92\text{-}0.94$ g/cm^3 (determined from size and weight data), was found to be essentially equal to the density of PIB [20]. The crosslink functionality (the number of chains emanating from each crosslink) was assumed to be large due to the multifunctional nature of the base block copolymers. The values given for PIB/*n*-pentane and PIB/benzene ($K = 0.49$ and 0.5, respectively [20]) were used for the calculations. Table 2 shows M_c data.

Since the Flory-Rehner equation may not be valid for two component networks and the K values are unavailable for such systems, the M_c values are merely rough estimations. With this disclaimer in mind, it is of interest that the epoxidized triblock appears as an essentially perfect network ($\overline{M}_n = \overline{M}_c$). This network may, in fact, be regarded as a one-component cured rubber since the epoxidized *tr*-1,4-PIP sequences account for only 4 mol% of the triblock. The DIAZ-cured multiblock (mostly pentablock) yielded $\overline{M}_{n(\mathrm{PIB})} = \overline{M}_c$, which may be construed to indicate crosslinking at the end of the pentablocks. The networks obtained from the PIB-cyPIP/DIAZ and the epoxidized PIB-(PIP/cyPIP)/Crivello salt systems yielded low M_c values similar to those reported for (meth)acrylate-capped PIB-based networks [7].

These new PIB-cyPIP based networks are unique, because unlike "conventional" cured rubbers where crosslinking occurs randomly, in these rubbery cured films the distance between crosslinks is uniform due to the uniformity of the PIB segments. These networks are proposed to comprise a soft, continuous PIB matrix (~80 mol%) embedded into which are hard, highly cyclized cyPIP domains crosslinked by DIAZ or partially cyclized PIP/cyPIP domains crosslinked by epoxy chemistry. The dimensions of the hard domains must be below the wavelength of visible light since the films are transparent. These flexible films adhere very strongly to aluminum and are expected to have a desirable combination of properties associated with their components (PIB, PIP, and cyPIP).

ACKNOWLEDGMENTS

This material is based upon work supported by EPIC (Edison Polymer Innovation Corporation) and the Goodyear Tire and Rubber Company. The authors wish to thank D. Hederer for the DSC measurements.

REFERENCES

[1] G. Kaszas, J. E. Puskas, C. C. Chen, and J. P. Kennedy, *Polym. Bull., 20*, 413 (1988).

[2] G. Kaszas, J. E. Puskas, C. C. Chen, and J. P. Kennedy, *Macromolecules, 23*, 3909 (1990).

[3] G. Kaszas, J. E. Puskas, C. C. Chen, and J. P. Kennedy, *J. Macromol. Sci.—Chem., A26*(8), 1099 (1989).

[4] G. Kaszas, J. E. Puskas, and J. P. Kennedy, *J. Appl. Polym. Sci., 39*, 119 (1990).

[5] G. Kaszas, J. P. Kennedy, and J. E. Puskas, U.S. Patent 208,374 (1989).

[6] W. M. Hager, G. Kaszas, J. P. Kennedy, and J. E. Puskas, U.S. Patent Application 285,207 (1988).

[7] J. E. Puskas, G. Kaszas, C. C. Chen, and J. P. Kennedy, *Polym. Bull., 20*, 253 (1988).

[8] U.S. Patent 2,852,379 (1958), to Kodak; Japanese KTK 49-19162 (1974); 50-10752 (1975); 50-11258 (1975); 51-10521 (1976); 60, 208,749 (1985), to Japan Synthetic Rubber Co.; Ger. Offen. 3,014,261 (1980).

[9] Japanese KTK 80, 87-143 (1980).

[10] S. Clements, *Plastics for Electronics* (M. D. Goosey, ed.), Elsevier, New York, 1985.

[11] J. V. Crivello and J. H. W. Lam, *J. Polym. Sci., Polym. Symp., 56*, 1 (1976).

[12] M. K. Mishra and J. P. Kennedy, *Polym. Bull., 17*, 7 (1987).

[13] G. Kaszas, J. E. Puskas, and J. P. Kennedy, *Makromol. Chem., Macromol. Symp., 13/14*, 473 (1988).

[14] P. Dreyfuss and J. P. Kennedy, *Anal. Chem., 47*(4), 771 (1975).

[15] J. V. Crivello, *Annu. Rev. Mater. Sci., 13*, 173 (1983).

[16] J. E. Puskas, G. Kaszas, and J. P. Kennedy, *Polym. Mater. Sci. Eng., 57*, 77 (1987).

[17] E. Gipstein, F. Nichik, and J. A. Offenback, *Anal. Chem. Acta, 43*, 129 (1968).

[18] Aldrich NMR Library.

[19] P. J. Flory and J. Rehner, *J. Chem. Phys., 11*, 521 (1943).

[20] J. Brandrup and E. H. Immergut (eds.), *Polymer Handbook*, Wiley-Interscience, New York, 1975.

Received March 6, 1990
Revision received April 26, 1990