

Novel thermoplastic elastomers via selective modification of conjugated diene block copolymers

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A new class of amorphous thermoplastic elastomers, potentially important commercially and scientifically, was synthesized from conjugated dienes only by first synthesizing polyisoprene–polybutadiene–polyisoprene (IBI) block copolymers with 1,4-structures with alkyl lithium anionic initiators and subsequently selectively cyclizing polyisoprene blocks with different cationic catalysts. The resulting, essentially gel-free products, consisting of poly(cyclized isoprene-*b*-butadiene-cyclized isoprene) IcBIc, exhibited heterophase domains of Ic in the polybutadiene matrix. They exhibited stress–strain properties typical of polystyrene–polybutadiene–polystyrene, SBS, thermoplastic elastomers, for instance, Shell Oil Company's Kraton D-1101, but with improved tear strength and superior tensile strength *versus* temperature profile. This is because the Ic block has higher T_g by about 15°C than displayed by the polystyrene block. The best thermoplastic elastomers were obtained from IBIs containing 35–45 polyisoprene. © 1998 Elsevier Science Ltd. All rights reserved.

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Introduction

A most exciting development was ushered in over three decades ago by the inventions and developments of several new types of rubbers called thermoplastic elastomers. Amorphous poly(styrene-*b*-conjugated diene-*b*-styrene) ABA-type thermoplastic elastomers, which became commercially available in 1965, exhibit unique properties of high tensile strength and high elongation without curing or reinforcement by fillers owing to their heterophase morphology^{1–4}. The incompatibility of the polystyrene A blocks—a minority component—and the polydiene B blocks produces a dispersion of very small polystyrene domains within the polydiene matrix. These polystyrene domains, which are glassy at room temperature, function as both fillers and thermally reversible crosslinks for the rubbery polydiene matrix, and thus account for the thermoplastic elastomer (TPE) properties of these amorphous triblock copolymers. The methods of synthesizing a wide variety of thermoplastic elastomers and their characteristics have been described in the patent literature, scientific journals and books^{4–21}.

The uncertainties in the availability of styrene²² in the mid-1970s prompted us to synthesize styrene-free, novel amorphous thermoplastic elastomers from conjugated dienes only^{23,24}. Our approach, in its simplest form, was to replace the polystyrene blocks in poly(styrene-*b*-butadiene-*b*-styrene) (SBS) with cyclized polyisoprene blocks. We accomplished this by resorting to both anionic and cationic reaction techniques—first synthesizing poly(isoprene-*b*-butadiene-*b*-isoprene) (IBI) block copolymers with 1,4-polyisoprene configuration via classical 'living' polymerization methods, and subsequently selectively cyclizing the terminal polyisoprene blocks with a suitable Lewis acid to form poly(cyclized isoprene-*b*-butadiene-*b*-cyclized isoprene) (IcBIc).

Experimental, results and discussion

Selectively cyclized thermoplastic block copolymers. In a series of experiments, symmetrical IBI block copolymers containing 20, 30 and 50 wt% isoprene were prepared in bottles with a dilithium anionic initiator, DiLi-3²⁵, by the sequential addition of butadiene and isoprene in heptane solvent. The polymerizations were terminated with a small quantity of methanol. The molecular weights of the block copolymers were measured by the osmotic pressure method (Macrolab 501 Osmometer) and they ranged from 56 000 to 94 000. The block copolymers were essentially gel-free. Cyclization was carried out on 6 wt% solution of the triblocks in benzene with the cationic SnCl₄/CCl₃COOH system (molar ratio, 2.5:1, 80°C; 5 h). Stress–strain properties of benzene-cast films of the cyclized products at 25°C are shown in *Table 1*. In another series of experiments, symmetrical IBI block copolymers containing 35, 45 and 65 wt% isoprene were prepared with *sec*-BuLi initiator by the sequential addition of isoprene, butadiene and isoprene. Cyclization was carried out with SnCl₄/CCl₃COOH, TiCl₄/CCl₃COOH, or BF₃·Et₂O cationic catalysts. Cyclizations were stopped by cooling the polymer solution to ambient temperature and adding a stabilizer solution of di-*tert*-butyl-*p*-cresol in methanol. The cyclized polymers were recovered by precipitation into excess methanol and dried at 40°C in a vacuum oven. The physical properties of films cast from benzene solution, filtered through a fine nylon mesh cloth to remove gel, if any, are shown at 25°C in *Table 2*. These results show that semi-solid IBIs can be converted to gel-free thermoplastic materials. The best thermoplastic elastomers were obtained from IBIs containing about 35–45 wt% polyisoprene, whereas cyclized products suitable for coatings or films were obtained from an IBI containing about 65% isoprene. Only polyisoprene block underwent cyclization as determined by infrared and ¹H-NMR (300 MHz) spectroscopy.

Like the SBS block copolymers, the cyclized isoprene–butadiene–isoprene block copolymers show a strong dependence of stress–strain behaviour on the molecular

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Table 1 Stress-strain properties^a of benzene-cast films of cyclized^b IBIs^c

Isoprene content (wt%)	No. av. mol. wt ^d ×103	Inherent viscosity (dl g ⁻¹)	Gel (%)	Tensile strength (MPa ^e)	Elongation at break (%)	100% modulus (MPa ^e)
20	56	1.1	0.5	4.375	980	1.07
30	94	2.4	1.0	16.92	600	3.20
50	72	0.7	0	21.02	365	12.75

^aASTMD D 412 method at 25°C. Dumbell specimens (0.25 mm thick and 2.54 mm wide) were pulled at a grip separation speed of 12.7 cm min⁻¹

^bIBI block copolymers prepared with a dilithium initiator, DiLi-3, in benzene solvent. Cyclization carried out with SnCl₄/CCl₃COOH (molar ratio 2.5:1; 80°C; 5 h, except 4 h for IBI with 50 wt% isoprene). See Lal²³, Tables 1 and 2

^cSee Lal²³, Tables 1 and 2

^dMeasured prior to cyclization

^eMegapascals. To convert to psi (pounds per square inch) multiply MPa by 145

Table 2 Physical properties (25°C) of benzene-cast films of cyclized IBIs^a

Isoprene content (wt%)	Inherent viscosity ^b (dl g ⁻¹)	Tensile strength (MPa)	Elongation at break (%)	100% modulus (MPa)	Crescent tear (kN m ⁻¹)
35	1.0	19.98 ^c	700	2.27	—
35	1.0	17.57 ^c	580	2.65	36.8
35	1.0	26.18 ^d	755	2.4	—
35	1.0	20.67 ^c	730	2.07	—
45	1.5	34.45 ^c	650	6.75	80.5
44	1.0	22.7 ^c	680	770/5.30	63
65	0.9	11.9 ^d	5	—	—

^aSee Lal²³, Tables 3, 5 and 6 for additional details of synthesis, and cyclization conditions

^bMeasured before cyclization

^cCyclized with SnCl₄/CCl₃COOH

^dCyclized with TiCl₄/CCl₃COOH

^eCyclized with BF₃.Et₂O

weights of the end blocks and the whole block copolymer as well as copolymer composition. In our work, the molecular weights of polyisoprene blocks were kept above 10 000 and those of the block copolymers were about 80 000–100 000.

The molecular weights and molecular weight distribution of the IBI and IcBIc containing 40 wt% isoprene were measured in THF solution using a Waters and Associates GPC model 200 with styrogel packings of 10⁶, 10⁵, 10⁴ and 10³ Å packings. The molecular weight estimates were based on polystyrene standards since 'k' and 'a' values of these block copolymers are not known. The size exclusion chromatogram for the cyclized block polymer shows two peaks and a considerable proportion of high molecular weight tail (*Figure 1*). The shape of the GPC curve of the cyclized block copolymer and broadening of its molecular weight distribution appear to be indicative of both scission and branching/crosslinking reactions taking place during the cyclization process.

A transmission electron micrograph (TEM) of a cyclized IBI block copolymer containing 45% isoprene showed clearly heterophase morphology (*Figure 2*), as in SBS. Staining was done with osmium tetroxide. The sample was moulded in a press and allowed to cool to ambient temperature while in the press. The sample was not annealed after that. The light regions represent domains (500–680 Å) resulting from the aggregation of cyclized polyisoprene blocks in the matrix of polybutadiene. Unlike SBS (33% styrene; domain size 350–500 Å), the cyclized polyisoprene domains are somewhat irregular in shape.

An unusual feature of IcBIc is that stress-strain properties of films are not sensitive to the nature of the solvent examined in casting films^{23,24}. This observation may be related to the possibility that Ic and B have solubility parameters that are closer to one another than is the case with polystyrene and polybutadiene blocks in SBS. Another feature of IcBIc is its superior tensile strength *versus*

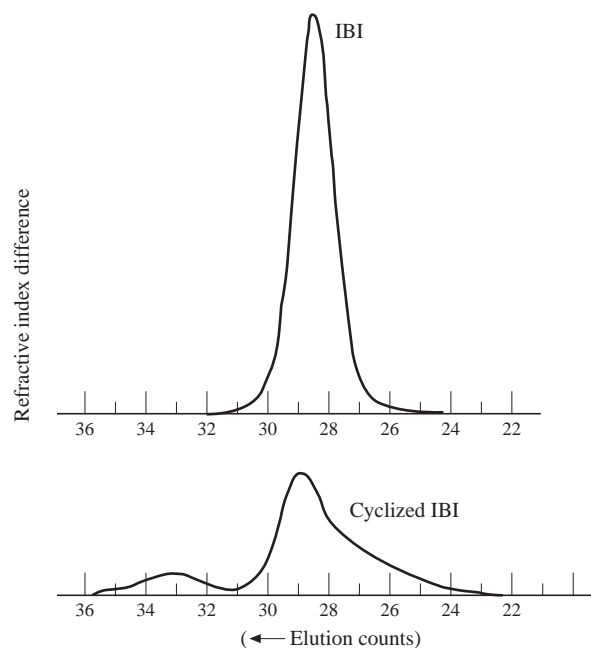
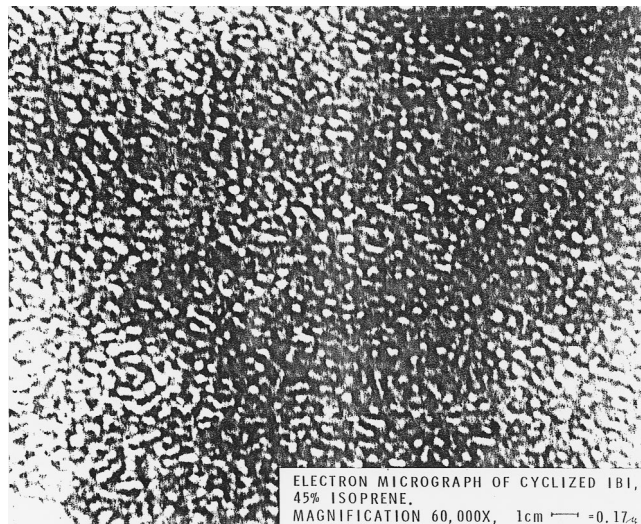


Figure 1 Size exclusion chromatograms of poly (isoprene-*b*-butadiene-*b*-isoprene) (IBI) (40 wt. % isoprene) and the corresponding cyclized poly (isoprene-*b*-butadiene-*b*-isoprene) (IcBIc) in tetrahydrofuran solution

temperature profile compared with commercial Kraton D-1101 (Shell Oil Company's SBS thermoplastic elastomer, 33% styrene). A comparison of stress-strain properties of benzene-cast films of cyclized IBI (35 wt% isoprene) and the commercial SBS is shown in *Table 3*. The results show that cyclized IBI retained fair strength up to 71°C, whereas the SBS showed a significantly lower value than this even at 60°C. Other data showed that cyclized IBI is superior to the

Table 3 Selectively cyclized thermoplastic block copolymers: T.S. *versus* temperature profile. Effect of temperature on strength properties^a of cyclized ibi and Kraton D-1101: tensile strength, MPa/100% modulus, MPa/elongation at break, %

Polymer	25°C	49°C	60°C	71°C
Cyclized IBI ^b	20.67/4.58/480	14.0/3.76/580	9.2/2.7/535	7.23/2.41/620
Kraton D-1101	24.12/1.93/610	7.27/1.96/640	4.7/1.52/510	—

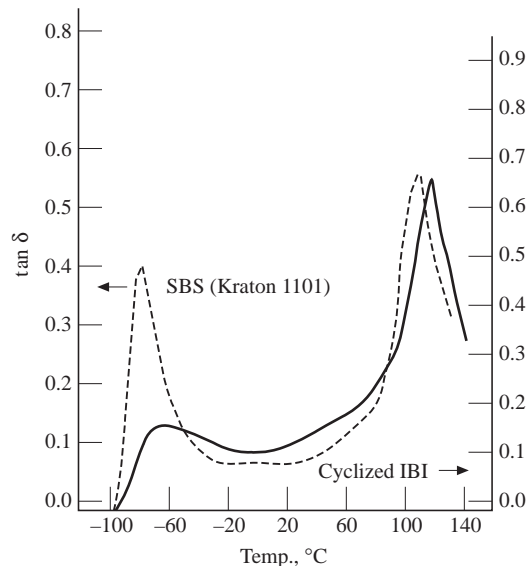
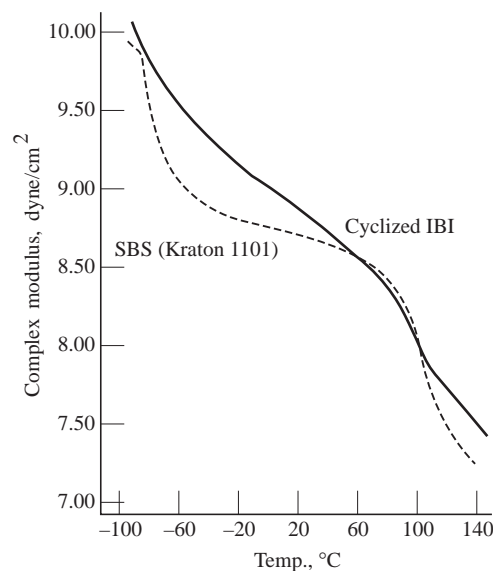
^aCompression-moulded samples^b45 wt% isoprene cyclized with SnCl₄**Figure 2** Transmission electron micrograph of IcBIc (45 wt. % isoprene). The white regions represent the cyclized polyisoprene and the black, the high 1,4-polybutadiene. Staining was done with osmium tetroxide

commercial SBS in 100%, 300%, 500% moduli, tensile strength and Elmendorf tear strength (ASTM D 1922).

It should be noted that the properties of selectively cyclized block copolymers are dependent on the degree of cyclization of polyisoprene blocks (i.e. per cent loss of unsaturation) and the distribution of various fused ring structures (see Patterson *et al.*²⁶ and References 1–6, 13–17 therein). In contrast, SBS has terminal blocks of atactic polystyrene, i.e. phenyl groups on alternating carbon atoms of a polymethylene chain.

We have made detailed studies²⁶ of the microstructure of cyclized polyisoprenes, namely, lithium polyisoprenes, guayule rubber and hevea rubber as model polymers, using ¹H and ¹³C NMR spectroscopic methods in tandem. Total alkene level by ¹³C NMR and the extent of cyclization by ¹H NMR (at 200 or 300 MHz) to compute average cyclicity (average number of rings per cyclized polyisoprene molecule) were thus determined. Most of the data are for lithium polyisoprene cyclized with TiCl₄/Cl₃CCOOH at 80°C in cyclohexane. Here, the average cyclicity, defined above, of extensively cyclized (more than 70% loss of unsaturation) ranges from about three to about five. Thus, we may visualize cyclized polyisoprene as a segmented polymer comprised of fairly short fused rings, in conformity with the view (see References 1–6, 13–16 in Patterson *et al.*²⁶) that cyclized polyisoprene is, or can be, modestly polycyclic.

The dynamic mechanical behaviour of IcBIc (40% isoprene) was compared with that of the commercial SBS on Rheovibron at 110 Hz on compression-moulded samples which had been exposed to 30 Mrad of Co-60 γ -radiation to minimize cold flow at higher temperatures. A plot of mechanical loss factor, $\tan \delta$, *versus* temperature (Figure 3)

**Figure 3** A comparison of viscoelastic behaviour of IcBIc (40 wt% isoprene) with that of Kraton D-1101 as a function of temperature on Rheovibron at 110 Hz, using compression moulded samples which had been partially crosslinked with 30 Mrad of Co-60 γ -radiation to minimize cold flow at higher temperatures**Figure 4** A comparison of complex modulus of IcBIc (40 wt% isoprene) with that of Kraton D-1101 as a function of temperature on Rheovibron at 110 Hz, using same samples as in Figure 3

shows two peaks for both SBS and IcBIc. $\tan \delta$, also termed 'loss tangent' or damping is a measure of energy loss per cycle. The lower temperature peak is for the polybutadiene block. The higher temperature peak for cyclized polyisoprene in cyclized IBI is about 15°C higher than that observed for polystyrene in SBS, indicating a higher T_g.

The complex modulus *versus* temperature behaviour for both these samples is shown in *Figure 4*. Poly(styrene-*b*-butadiene-*b*-styrene) shows a well-defined plateau, also reported by previous investigators. However, IcBIc does not exhibit a well-defined plateau, but instead shows a steady decline in complex modulus values as the temperature is raised. It is noteworthy that the complex modulus of IcBIc is greater than that of the SBS in the temperature ranges of -90°C to 60°C and 100°C to 140°C .

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