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Synthesis and Hydrogenation of 1,2-1,4-1,2-Stereotriblock Polybutadienes and the Study of Their Properties

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ABSTRACT

The effects of various polar modifiers, their concentration, and the polymerization temperature on the microstructure of polybutadiene obtained during anionic polymerization using lithium α-methyl naphthalene as the bifunctional initiator were studied. 1,2-1,4-1,2-Stereotriblock polybutadiene was synthesized by polymerization in cyclohexane to a certain conversion and polymerization was completed in the presence of diethylene glycol dimethyl ether. The microstructure of the stereotriblock copolymer was characterized by IR and ^{1}H-NMR. GPC showed that the stereoblock polybutadiene has a narrow MWD. Two T_g's of the copolymer with higher molecular weight exist, as shown by dynamic mechanical test. The stereotriblock copolymer was hydrogenated using cobalt 2-ethyl hexanoate and triisobutyl aluminum as the catalyst. The hydrogenated product was shown to be a (butene-1-ethylene-butene-1) triblock copolymer which consists of more than 30% crystallinity and exhibits the behavior of a thermoplastic elastomer. The relationship between stress-strain properties and the contents of the blocks was also studied.

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Stereoblock copolymer is a special type of block copolymer. Early in 1958 Fox and co-workers synthesized an isotactic-syndiotactic block polymethyl methacrylate [1]. Then in 1963 Kern made a tactic-atactic stereoblock polystyrene [2]. About 10 years ago, Falk [3], Duck [4], and Asai [5] found separately the stereoblock polymerization of butadiene using butyllithium initiator through adding polar modifier in the course of polymerization, resulting in a 1,4-1,2-stereodiblock polybutadiene. In 1980 Cohen et al. [6], using dipiperidene ethane as polar modifier, synthesized 1,4-1,2-stereoblock polybutadiene. However, most of these works were concerned with diblock copolymer. Only Falk [3] coupled the diblock copolymer with ethylene bromide, forming 1,4-1,2-1,4-triblock polybutadiene.

This paper deals with the synthesis of 1,2-1,4-1,2-stereotriblock polybutadiene, using lithium α-methyl naphthalene as a bifunctional initiator and cyclohexane as the solvent, and changing the 1,4-polymerization into 1,2-polymerization by means of adding polar modifier in the course of polymerization. The copolymers thus obtained were characterized by IR, NMR, GPC, and the torsional pendulum test. The 1,2-1,4-1,2-stereotriblock polybutadienes were hydrogenated into (butene-1-ethylene-butene-1)triblock copolymers, which behave like a thermoplastic elastomer.

EXPERIMENTAL

1. Materials

Butadiene was purified by passing it through a 4A molecular sieve. Cyclohexane, n-butyl chloride, and α-methyl naphthalene were purified by having them stand over a 4A molecular sieve overnight. Tetrahydrofuran, N, N'-tetramethyl ethylene diamine, and diethylene glycol dimethyl ether were treated both with a 4A molecular sieve and lithium ribbon. n-Butyllithium, lithium α-methyl naphthalene [7], and cobalt 2-ethyl hexanoate [8] were self-made according to the literature.

2. Polymerization

The preparation of catalyst solution and the polymerization were carried out in baked glass bottles under a purified nitrogen atmosphere. n-Butyllithium was used as a scavenger for removing impurities in the polymerization system. After the addition of lithium α-methyl naphthalene as initiator, polymerization was carried out in a thermostat at 30°C. After a certain conversion, the polymerization bottle was cooled to 0°C. Then a certain amount of polar modifier was added and the polymerization was continued in a 0°C thermostat. At the end of polymerization, ethyl alcohol containing 0.5% antioxidant 264 was added to stop the reaction. The product was vacuum dried at 50°C.

3. Hydrogenation

The stereotriblock polybutadiene was dissolved in cyclohexane and put in an autoclave. After purging with purified nitrogen, a catalyst composed of cobalt 2-ethyl hexanoate and triisobutyl aluminum at a molar ratio of Al/Co = 3.2 was added. The content was stirred and heated to 50°C. Then hydrogen was bubbled in for 30 min at 2.5-2.8 kg/cm^2. The hydrogenated product was washed with 6% hydrochloric acid, several times with water till neutral, precipitated with isopropyl alcohol containing 0.5% antioxidant 264, and vacuum dried at 50°C.

4. Characterization

The IR was measured by a Perkin-Elmer 580B spectrophotometer using a KBr crystal coated with the specimen. Absorptions at 738, 911 and 967 cm^{-1} are characteristic of cis-1,4, 1,2, and trans-1,4 microstructures, respectively. Proton NMR spectra were obtained with a 100-MHz spectrometer using CCl_4 as solvent and TMS as the internal standard. The peak at 5.12δ is due to =CH– protons of 1,4 and 1,2 microstructure; 4.76, 2.00, 1.19, and 1.81δ are for the $=CH_2$, $-\overset{|}{C}H-$, and $-CH_2-$ of the 1,2 microstructure and $-CH_2-$ of the 1,4 microstructure respectively, [9]. The molar content of 1,4 and 1,2 units can be calculated from $2M_{1,4} + 0.5M_{1,2} = A$ and $2.5M_{1,2} = B$, where A and B represent the relative integral heights of the peaks at 5.12 and 4.76δ, respectively. GPC was carried out in a SN-01 type apparatus, using THF as the eluant. The glass transition temperature was determined by a torsional pendulum apparatus made by Fudan University. Crystallinity was measured by a Rigaku 3015 x-ray diffraction apparatus.

RESULTS AND DISCUSSION

1. The Effect of Polymerization Temperature and Polar Modifier on the Microstructure of Polybutadiene

Figure 1 shows how the polymerization temperature affects the microstructure of polybutadiene. Without the addition of polar modifier, the 1,2 contents of the polybutadienes were almost constant at polymerization temperatures above 30°C, whereas below 30°C the 1,2 content increases with a decrease of polymerization temperature. In the presence of polar modifier, the 1,2 content decreases with an increase of temperature in the range from -20 to 50°C.

Different kinds of polar modifiers have different influences on the

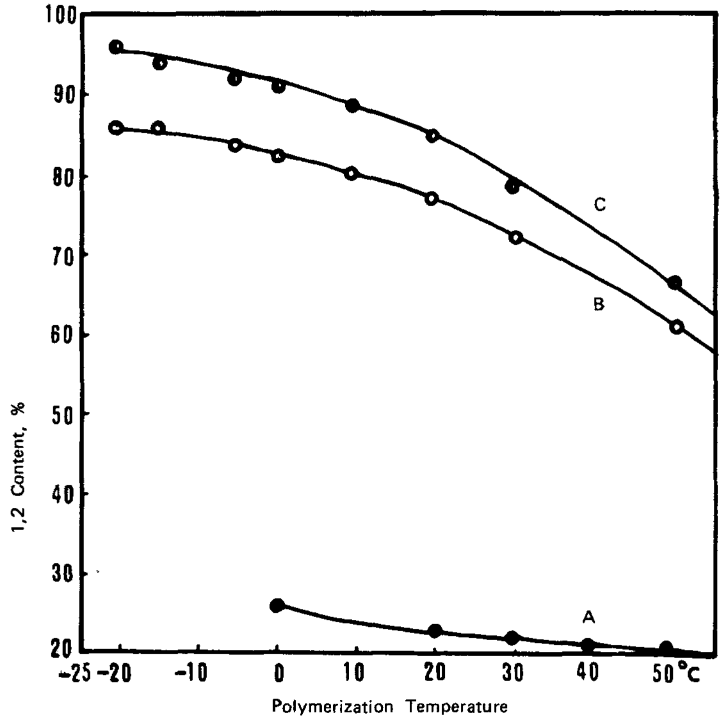

FIG. 1. Dependence of 1,2 content of polybutadiene on polymerization temperature. (A) Without polar modifier. (B) TMEDA/Li = 3/1. (C) DGM/Li = 3/1.

microstructure of polybutadiene, as shown in Table 1 and Fig. 2. Diethylene glycol dimethyl ether showed the most evident effect of the polar modifiers studied, and when its molar ratio to initiator is 3, the 1,2 content can reach to 90%.

2. Control of Blocks Ratio

Preliminary experiments indicated that when the butadiene concentration was 100 g/L and the solvent was cyclohexane, polymerization of butadiene using lithium α-methyl naphthalene as the initiator was better when carried out at 30°C. Not only was the 1,4 content higher, but there was little temperature rise and the polymerization was easier to control. Figure 3 represents the conversion-time curve and linear relationship between conversion and molecular weight. This condition is convenient for the addition of polar modifier in the course of polymerization in order to control the blocks ratio. Since the 1,2

TABLE 1. Effect of Different Polar Modifiers on the 1,2-Content of Polybutadiene

	Polar modifier/initiator, molar ratio			
Polar modifiers	1:1	4:1	40:1	80:1
Tetrahydrofuran	37.1	49.9	-	80.2
Dioxane	-	-	61.8	76.1
Anisole	-	-	40.3	63.4
Ethylene glycol dimethyl ether	-	66.2	78.2	-
Diethylene glycol diethyl ether	79.2	88.6	-	-
Diethylene glycol dimethyl ether (DGM)	90.5	91.5	-	-
Tetramethyl ethylene diamine (TMEDA)	82.2	82.5	-	-

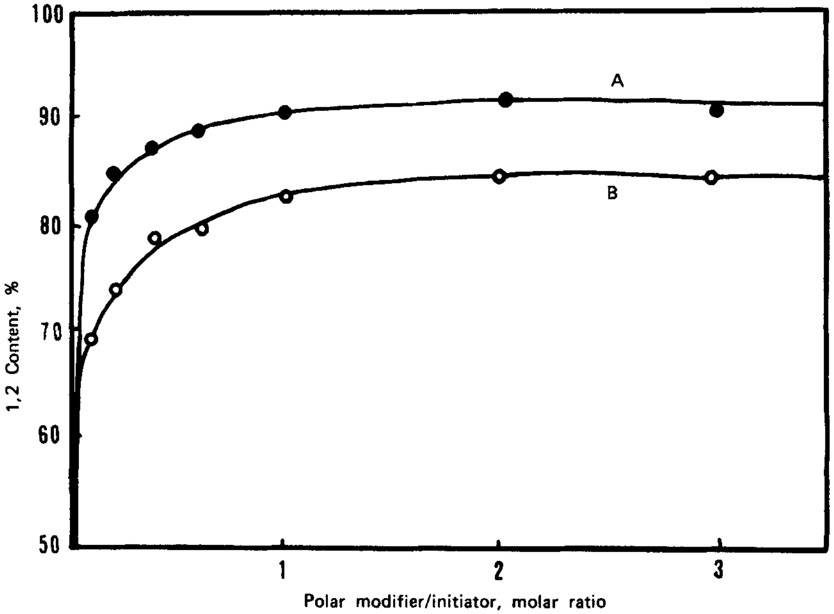

FIG. 2. Dependence of 1,2 content on concentration of polar modifiers. (A) DGM. (B) TMEDA.

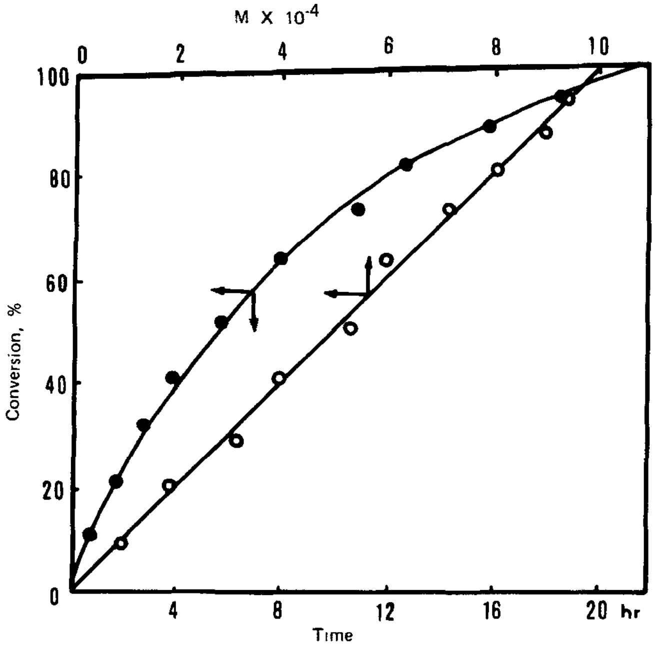

FIG. 3. Relation between time-conversion and conversion-molecular weight.

content of polybutadiene increases with a decrease of polymerization temperature in the presence of a polar modifier, the formation of 1,2 block was better when carried out at 0°C. Table 2 compares the predicted molecular weight and the 1,2/1,4/1,2 blocks ratio of the stereoblock polybutadiene with experimental ones. The experimental blocks ratios were calculated by

$$C = 0.21B + 0.90\,(1 - B) \quad \text{and} \quad A = (1 - B)/2$$

where C represents the 1,2 content of polybutadiene measured by IR or ^{1}H-NMR spectrometry, and B and A are the percentages of 1,4 block (79% 1,4) and 1,2 block (90% 1,2), respectively.

Both IR spectra (Fig. 4) and ^{1}H-NMR spectra (Fig. 5) show the presence of cis-1,4, trans-1,4, and 1,2 microstructures in stereotriblock polybutadiene. Their contents, calculated by both methods, were within a relative error of 5%.

It can be seen from Table 2 that the blocks ratio of stereotriblock polybutadiene can be well controlled during synthesis.

TABLE 2. Relation between Predicted and Experimental Molecular Weights and Blocks Ratios

Polymerization time before adding modifier, h	Predicted $M_n \times 10^{-4}$	Experimental $[\eta]$	Experimental $M \times 10^{-4}$	Predicted 1,2/1,4/1,2[a]	Experimental 1,2/1,4/1,2
-	10	1.60	11	0/100/0	0/100/0
-	10	1.42	12	50/0/50	50/0/50
2	10	1.40	-	40/20/40	37/26/37
4	10	1.44	11.4	30/40/30	29/42/29
7.3	10	1.42	-	20/60/20	18/64/18
10.5	10	1.59	-	12.5/75/12.5	11/78/11

[a] 1,2/1,4/1,2 represents 1,2-polybutadiene block/1,4-polybutadiene block/1,2-polybutadiene block.

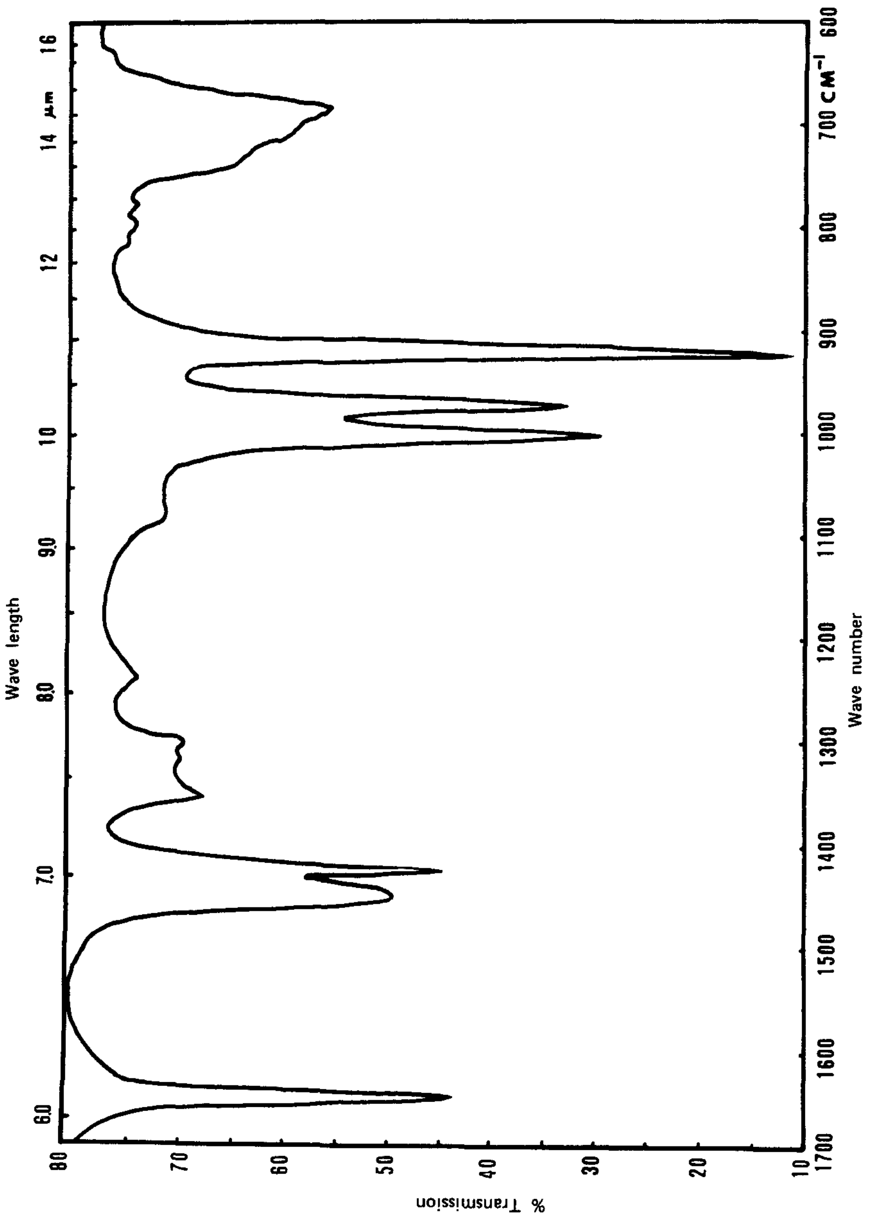

FIG. 4. IR spectrum of a stereotriblock polybutadiene.

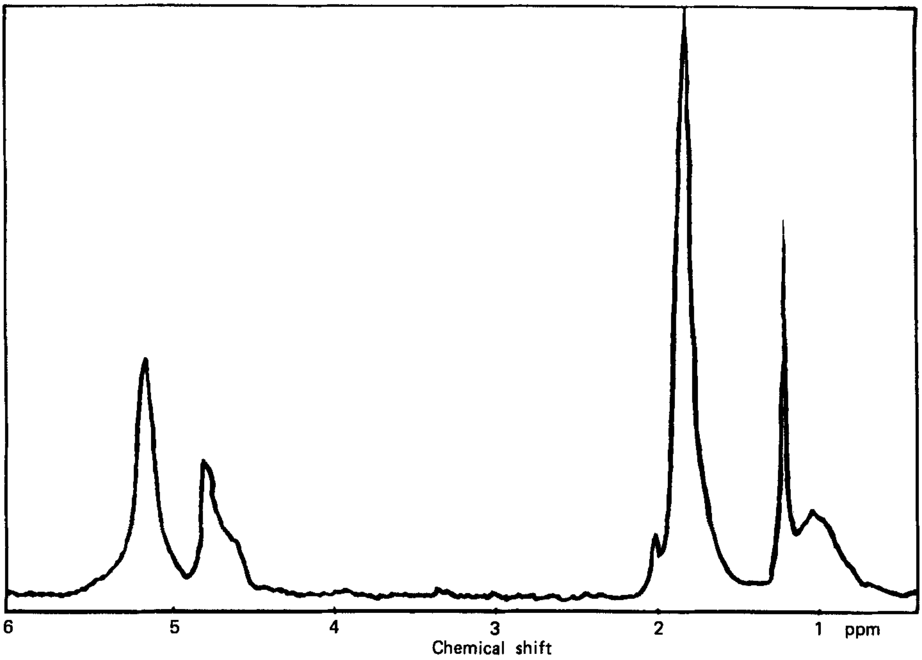

FIG. 5. ^{1}H-NMR spectrum of a stereotriblock polybutadiene.

3. Molecular Weight Distribution of Stereotriblock Polybutadiene

Both homopolybutadiene and the stereotriblock polybutadiene have a quite narrow molecular weight distribution ($M_w/M_n = 1.1$) when synthesized using lithium α-methyl naphthalene initiator. Figure 6 shows the GPC curve of the stereotriblock polybutadiene. This indicates that the addition of polar modifier in the course of polymerization did not induce chain termination of the transfer process and that the synthesized polybutadiene was not a blend.

4. Dynamic Mechanical Behavior of the Stereotriblock Polybutadiene

Figure 7 is a plot of the dynamic mechanical properties of one of the stereotriblock polybutadienes with $M_n = 2.4 \times 10^5$ and a blend of 1,4 and 1,2 homopolybutadienes with close molecular weights. Both of them are shown to be heterogeneous, having two transition tempera-

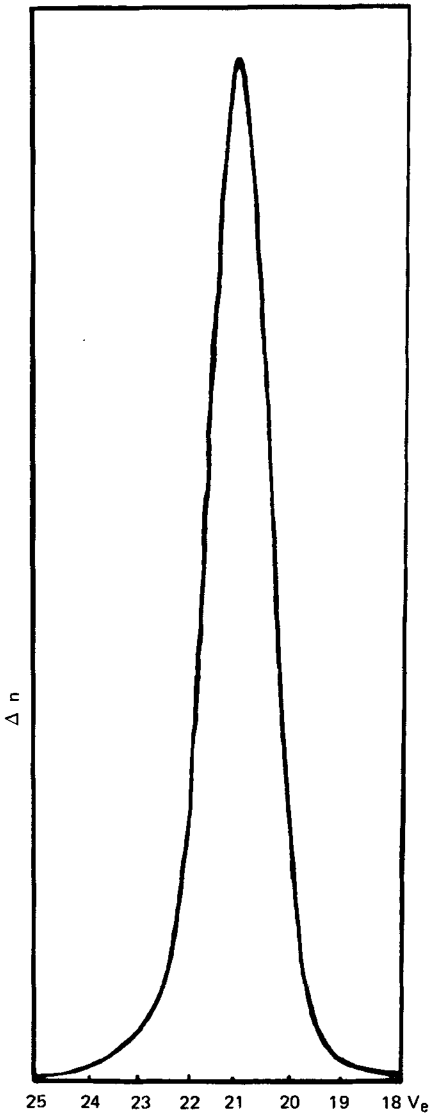

FIG. 6. GPC curve of a stereotriblock polybutadiene.

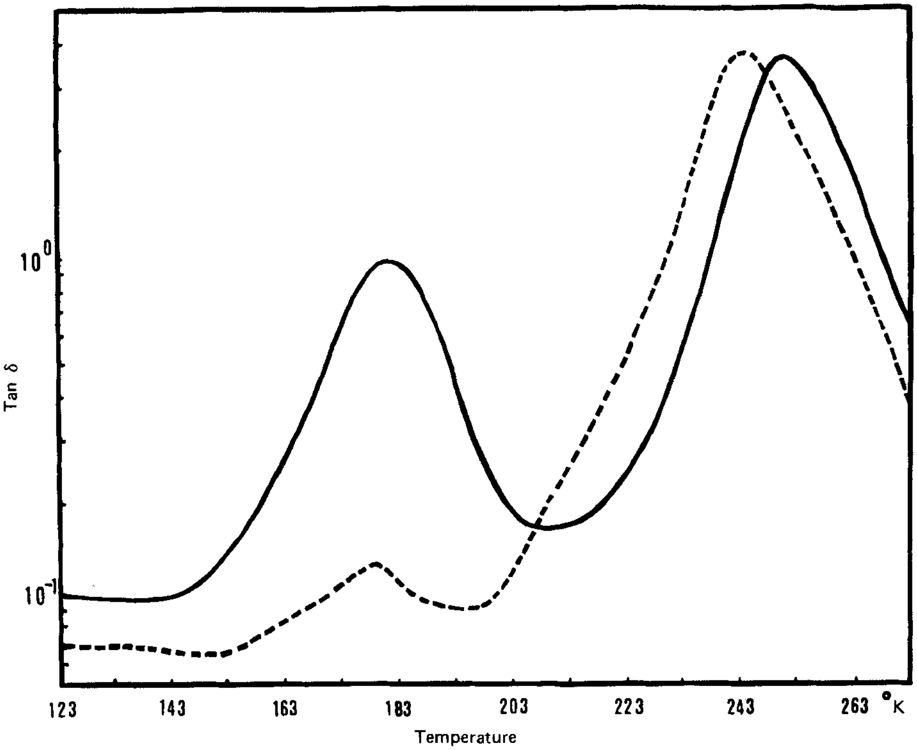

FIG. 7. Dynamic mechanical property of stereotriblock polybutadiene (dashed curve) and blend of 1,4 and 1,2 homopolybutadiene.

tures close to those of the homopolybutadienes. This implies that the polybutadiene we synthesized is not a random copolymer.

5. Microstructure of the Hydrogenated Stereotriblock Polybutadiene

The IR spectrum of the hydrogenated product in Fig. 8 shows the presence of the characteristic absorption of $-CH_2-CH_2-$ at 720 cm^{-1}, that of $CH_2-CH(C_2H_5)-$ at 775 and 1379 cm^{-1}, and almost the total disappearance of double bond absorption at 738, 911, and 967 cm^{-1}.

The hydrogenated stereotriblock polybutadiene was treated in two ways. (1) It was dissolved in tetralin, which is usually a solvent for polyethylene, and precipitated with phenyl ethyl alcohol. (2) It was dissolved in o-dichlorobenzene, a good solvent for polybutene-1, and

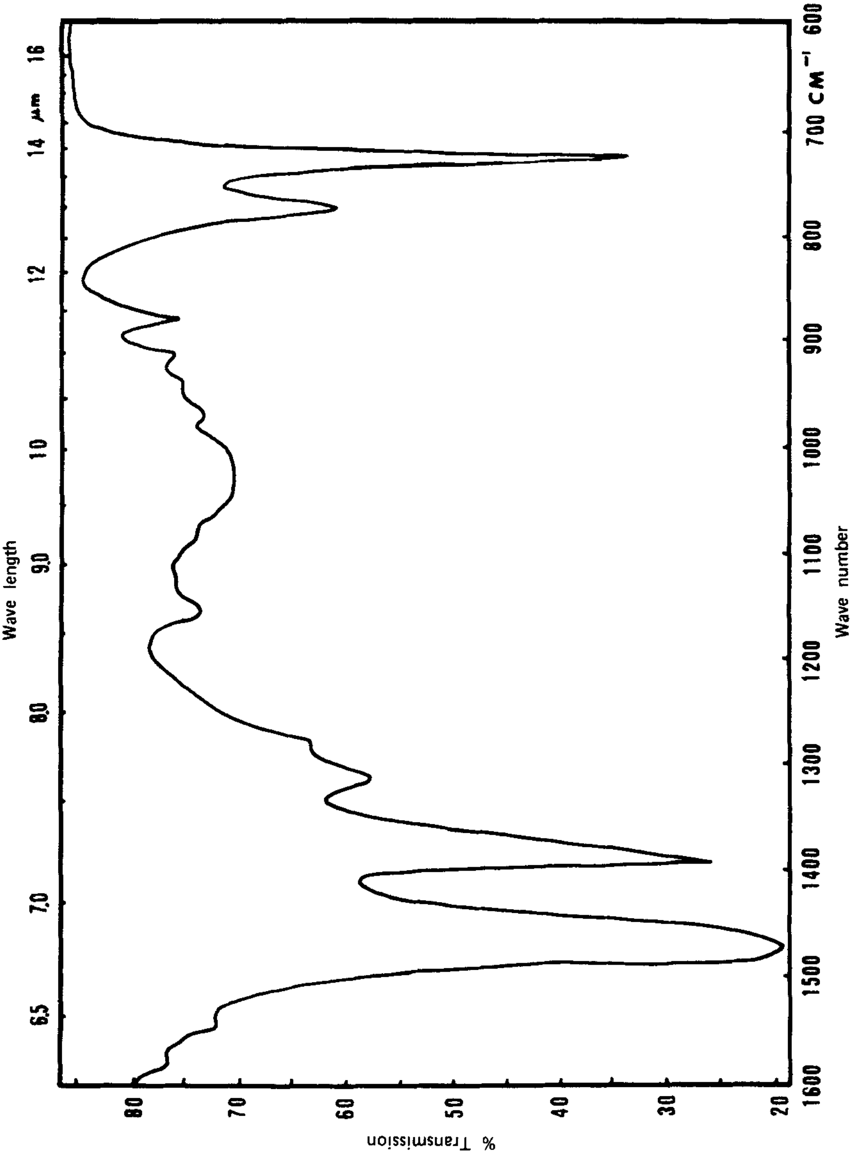

FIG. 8. IR spectrum of a hydrogenated stereoblock polybutadiene.

TABLE 3. Mechanical Properties of the Hydrogenated Stereotriblock Polybutadienes

[η]	PBE B/PE B/PBE B[a]	Tensile strength, kg/cm^2	Elongation, %	Permanent set, %
2.39	11/78/11	52.4	510	8
2.18	16/68/16	47.9	540	10
2.26	29/42/29	46.7	680	12
2.10	37/26/37	14.1	880	18
1.60	0/100/0	38.0	170	8
1.59	11/78/11	27.5	200	4
1.42	18/64/18	15.3	360	6
1.44	50/0/50	9.2	560	22
1.59	11/78/11	27.5	200	4
2.08	12/76/12	48.9	480	8
2.39	11/78/11	52.4	510	8
1.42	18/64/18	15.3	360	6
2.18	16/68/16	47.9	540	10
2.40	17/66/17	47.7	600	10

[a] PBE B/PE B/PBE B represents polybutene block/polyethylene block/polybutene block.

then precipitated with dimethylformamide. These two precipitates had the same content of ethylene and butene units as measured by IR. This means that the hydrogenated product is indeed a (butene-1-ethylene-butene-1) triblock copolymer. X-ray diffraction analysis showed that it contained over 30% crystallinity.

6. Mechanical Properties of the Stereotriblock Polybutadienes and Their Hydrogenated Products

The steroetriblock polybutadiene can be hot-pressed into film. Its tensile strength was ~10 kg/cm^2 and the elongation was ~500% without vulcanization. The hydrogenated product behaves like a thermoplastic elastomer. Its tensile strength, elongation, and permanent set varied from 20 to 50 kg/cm^2, 400 to 800%, and 4 to 22%, respectively. Table 3 shows that elongation of the hydrogenated block copolymer increases with an increase of the polybutene-1 block length, whereas the tensile strength increases with an increase of the polyethylene block length. When the microstructure of the copolymers are almost the same, tensile strength and elongation increase with increasing molecular weight. In general, the mechanical properties are better when $M_n > 2.0 \times 10^5$ and the polybutene-1 content varies from 20 to 60%.

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