

## Temperature and Microstructure Dependence of the Rheo-Optical Properties of Polybutadienes

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### Synopsis

The present investigation covers the isothermal stress-strain-birefringence behavior of various polybutadienes between  $-30^{\circ}\text{C}$  and  $110^{\circ}\text{C}$ . Birefringence measurements were also made under constant stress as a function of temperature in the low temperature region between  $-30^{\circ}\text{C}$  and  $-120^{\circ}\text{C}$ . The polybutadienes studied were two high *cis*-1,4 (prepared by different catalysts), a linear medium *cis*, and an emulsion polybutadiene. At temperatures at which the photoelasticity theory could be applied, the segmental polarizability anisotropy, its temperature dependence, and other parameters associated with an elastic polymeric network were determined. The influence of the degree of crosslinking was examined. At the low temperatures, microstructure was shown to have a pronounced effect on the photoelastic properties, the crystallization phenomena, and the glass-rubber transitions.

### INTRODUCTION

The optical properties of an elastic network were first calculated by Kuhn and Gr $\ddot{u}$ n<sup>1</sup> by an extension of the classical theory of rubber elasticity and the assumption of the additivity of bond polarizability.

The basic equation for a model of randomly jointed links relates the birefringence of the network,  $\Delta n = n_1 - n_2$ , with the applied stress  $t$  as follows:

$$\frac{\Delta n}{t} = \frac{2\pi}{45kT} \frac{(\bar{n}^2 + 2)^2}{\bar{n}} (\alpha_1 - \alpha_2) \quad (1)$$

where  $\bar{n}$  is the mean refractive index,  $k$  is the Boltzmann constant, and  $\alpha_1 - \alpha_2$  is the polarizability anisotropy of the optical link. The indices 1 and 2 indicate values along and perpendicular to the stretching direction.

In addition to such applications of the photoelastic properties as the study of crystallization phenomena,<sup>2,3</sup> rubber-glass transitions,<sup>4</sup> and relaxation processes,<sup>5</sup> knowledge of the monomer polarizability anisotropy  $b_1 - b_2$ , constituting the polymeric chain, indicates the relative flexibility of a series of polymers, because the larger the ratio in eq. (2), the stiffer the chain:

$$q = \frac{\alpha_1 - \alpha_2}{b_1 - b_2} \quad (2)$$

This quantity has been found<sup>2,6</sup> to correlate well with the degree of stiffness determined by geometric considerations. Recently,<sup>7-9</sup> experimental work on the temperature dependence of the optical link anisotropy allowed the testing of more realistic chain models whose conformational properties are taken into account.

It should be emphasized that the validity of the valence-optical scheme which underlies derivation of the above equations is still in need of a thorough test.<sup>10</sup> This is especially true of measurements carried out in the solid state.

For the randomly jointed link model the true stress is given by

$$t = N_c kT \left( \lambda^2 - \frac{1}{\lambda} \right) = \frac{dRT}{M_c} \left( \lambda^2 - \frac{1}{\lambda} \right) \quad (3)$$

where  $N_c$  is the number of effective chains between crosslinks per  $\text{cm}^3$ ,  $M_c$  is the mean molecular weight between crosslinks,  $\lambda$  is the extension ratio, and  $d$  is the density of the polymer.

A phenomenological equation to better fit the stress-strain data was introduced by Mooney and Rivlin<sup>11,12</sup>:

$$\frac{t}{\lambda^2 - (1/\lambda)} = 2(C_1 + C_2 \lambda^{-1}). \quad (4)$$

By analogy to eq. (4), the following equation proved useful<sup>13,14</sup> for the description of the strain dependence of birefringence:

$$\frac{\Delta n}{\lambda^2 - (1/\lambda)} = B_1 + B_2 \lambda^{-1} \quad (5)$$

Dividing by eq. (4), a strain-dependent stress-optical coefficient is obtained,

$$S = \frac{B_1 + B_2 \lambda^{-1}}{2(C_1 + C_2 \lambda^{-1})}, \quad (6)$$

in which the constants  $B_1$ ,  $B_2$ , and  $C_2$ , as of today, have not been associated quantitatively with any molecular parameters.

For copolymers, theoretical work has been presented recently<sup>15</sup> relating the stress-optical properties of the copolymer to those of the homopolymers. For a copolymer with two types of segments A and B of lengths  $l_A$  and  $l_B$  and optical link anisotropies  $(\alpha_1 - \alpha_2)_A$  and  $(\alpha_1 - \alpha_2)_B$ , respectively, it was proposed that

$$(\alpha_1 - \alpha_2)_{AB} = \frac{X_A(\alpha_1 - \alpha_2)_A l_A^2 + (1 - X_A)(\alpha_1 - \alpha_2)_B l_B^2}{X_A l_A^2 + (1 - X_A) l_B^2} \quad (7)$$

where  $(\alpha_1 - \alpha_2)_{AB}$  is the mean polarizability anisotropy of the copolymer segment and  $X_A$  is the mole fraction of component A.

An empirical approach that has been used<sup>6</sup> was to calculate an arithmetic mean for the polarizability of a "copolymer unit"  $(b_1 - b_2)_{AB}$ , using known

polarizability values of the monomers and the molar composition of the copolymer, as follows:

$$(b_1 - b_2)_{AB} = (b_1 - b_2)_A X_A + (b_1 - b_2)_B (1 - X_A). \quad (8)$$

Previous work<sup>16</sup> had shown a difference in the temperature dependence of the optical link anisotropy of the emulsion and high *cis*-polybutadienes. We decided to enlarge the study by including other types of polybutadienes of different microstructure and extend the measurements to low temperatures. It was expected that at these temperatures crystallization phenomena and glass transitions would influence the birefringence behavior in a manner dependent on the degree of disorder and/or tacticity of the geometric isomers along the main chain. It was also of interest to examine the effect of the degree of crosslinking and branching on the stress-optical properties.

Table I lists the polybutadienes covered in this study and their microstructures. In these polybutadienes, the degree of branching and polydispersity  $\bar{M}_w/\bar{M}_n$  increases in the following order: LPB < PB(A) < PB(B) < EPB. The degree of branching is not influenced by the microstructure.

The salient features of the micro- and macrostructural characteristics of the polybutadienes have been reviewed.<sup>17</sup>

While the results of the present work were being processed, two papers dealing with the stress-optical properties of the high *cis*-1,4-polybutadiene between 30° and 60°C<sup>8</sup> and of various rubbers<sup>6</sup> (including the polybutadienes) were published. A comparison with our work is made in the third section of this report. The effect of microstructure over a wide temperature range, the effect of the degree of crosslinking, and the low-temperature stress-optical behavior have not been covered before.

## EXPERIMENTAL

The apparatus and experimental procedure for isothermal stress-strain birefringence measurements have been described.<sup>16</sup>

Measurements could be extended to -20°C by circulating a 50% water solution of glycol thermostated by a combination of a Neslab thermostat and cooler. For the low temperature work, a cold chamber similar to that described by Hammack and Andrews<sup>4</sup> was used.

Measurements of the birefringence as a function of temperature at constant load were carried out either by lowering the temperature of a preloaded and relaxed sample or by warming polymer strips quenched in liquid nitrogen. In this case, some warping of the film took place which did not, however, introduce any significant distortional birefringence. Subsequently, the strip, attached on a suitable frame at one end, was quickly introduced into the precooled (to -180°C) chamber. The upper clamp of the strip was suspended from the arm of a balance sensitive to 0.1 g.

At these low temperatures and in stress-free condition, the films were in the glassy state, transparent with negligible birefringence. After reaching

TABLE I  
Types of Polybutadienes Studied

Polybutadiene	Geometric isomers, mole-%				Catalyst system	Source
	<i>cis</i> -1,4	<i>trans</i> -1,4	<i>vinyl</i> -1,2			
High <i>cis</i> -1,4-PB(A)	95.3	1.4	3.3		Ti <sup>+</sup> -based	Phillips
High <i>cis</i> -1,4-PB(B)	98	1	1		Co <sup>+</sup> -based	Polymer
Linear PB (LPB)	36	54	10		BuLi, anionic	Firestone
Emulsion PB (EPB)	5	74	21		Fe <sup>+</sup> peroxide, emulsion	Polymer

TABLE II  
Mean Refractive indices, Expansivities, and Densities of the Polybutadienes Investigated<sup>a</sup>

Polybutadiene	Refractive index $\bar{n}_D$						Expansivity $\frac{1}{l} \frac{dl}{dt} \times 10^4$ , deg <sup>-1</sup>	Density, <i>d</i> , g/cm <sup>3</sup>
	-10°C	10°C	30°C	50°C	70°C	110°C		
EPB	—	—	1.5122	1.5048	1.4975	1.4902	2.11	0.879
LPB	1.5310	1.5240	1.5170	1.5100	1.5025	1.4960	2.0	0.913
PB(A)	1.5342	1.5287	1.5215	1.5145	1.5072	1.5002	1.57	0.920
PB(B)	1.5342	1.5275	1.5207	1.5135	1.5063	1.4991	1.57	0.918
Atactic-1,2-PB	1.5300	1.5224	1.5050	1.4982	1.4912	1.4844	—	—
Syndiotactic-1,2-PB	—	1.5175	1.5120	1.5040	1.4960	1.4880	—	—

<sup>a</sup> Data for EPB and PB(B) above 30°C were taken from Kalfoglou and Williams.<sup>16</sup>

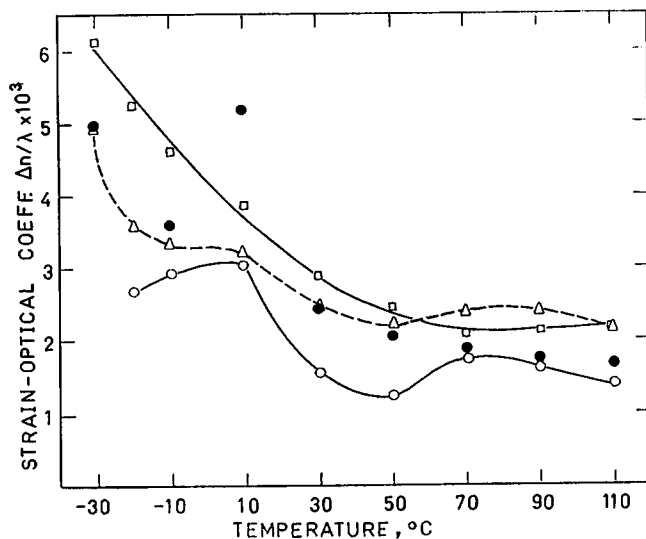


Fig. 1. Temperature dependence of strain-optical coefficient of polybutadienes: (●) EPB; (□) LPB; (△) PB(A); (○) PB(B).

temperature equilibrium, a load was applied to the sample, and the chamber was allowed to warm at a controlled rate.

Some experiments were also performed by quenching relaxed films stretched at 30°C.

The irradiation dose was varied between 4 and 16 Mrad. The effect of the degree of crosslinking was examined at 30°C. At all other temperatures, the irradiation dose was 8 Mrad. The mean refractive indices, densities, and linear expansivities used in the calculations are given in Table II.

## RESULTS AND DISCUSSION

### High Temperature

The stress-strain-birefringence results are given in Table III. For all the amorphous polybutadienes studied, the plots of birefringence versus true stress were linear. The stress-optical coefficient and optical link anisotropy,  $\alpha_1 - \alpha_2$ , could be determined. Whenever the dependence of  $\Delta n$  versus  $t$  was not linear because of crystallization, the data are presented in graphic form (see Figs. 2 and 3 below). No values for the quantity  $\alpha_1 - \alpha_2$  are given for temperatures below 30°C because of the possibility that the material has a small percentage of crystallinity. This is possibly true only for the EPB and LPB.

Plots of the birefringence versus  $\lambda$  were slightly concave toward the  $\lambda$  axis ( $x$  axis). The results are summarized in Table III and Figure 1 in terms of the strain-optical coefficient  $(\Delta n/\lambda)_{\lambda=1}$ .

TABLE III  
Temperature Dependence of the Rheo-optical Properties of the Polybutadienes\*

Polybutadiene	Temp., °C	$\frac{\Delta n}{t} \times 10^4$ , cm <sup>2</sup> /kg	$S \times 10^4$ , cm <sup>2</sup> /kg	$\left(\frac{\Delta n}{\lambda}\right)_{\lambda=1} \times 10^3$	$(\alpha_1 - \alpha_2) \times 10^{25}$ , cm
Emulsion PB (EPB)	-30	—	—	9.00	—
	-20	—	—	4.98	—
	-10	—	—	3.64	—
	10	4.12	—	5.20	—
	30	3.84	3.78	2.44	96.6
	50	3.40	3.38	2.04	91.6
	70	3.02	3.08	1.90	86.8
	90	2.72	2.82	1.74	83.3
	110	2.44	2.49	1.70	79.2
Linear PB (LPB)	-30	4.70	4.75	6.13	—
	-20	4.34	4.40	5.24	—
	-10	4.16	4.03	4.60	—
	10	3.70	—	3.92	—
	30	3.40	3.35	2.92	85.2
	50	2.98	3.02	2.48	80.0
	70	2.76	2.77	2.08	79.2
	90	2.64	2.65	2.14	80.5
	110	2.34	2.35	2.14	75.7
High <i>cis</i> -1,4-PB [PB(A)]	-30	—	—	4.96	—
	-20	3.80	—	3.60	—
	-10	3.74	—	3.36	—
	10	3.28	—	3.24	—
	30	3.08	3.08	2.50	76.9
	50	2.86	2.90	2.24	76.6
	70	2.76	2.76	2.40	82.7
	90	2.64	2.64	2.40	80.3
	110	2.46	2.43	2.12	79.3
High <i>cis</i> -1,4-PB [PB(B)]	-20	—	—	2.72	—
	-10	3.60	—	2.96	—
	10	3.44	—	3.08	—
	30	3.18	3.19	1.56	79.9
	50	2.88	2.94	1.24	77.1
	70	2.80	2.79	1.78	80.0
	90	2.70	2.68	1.60	82.1
	110	2.52	2.53	1.42	81.7
Atactic-1,2-PB	30	—	—	—	—
	to 110	0.33	—	—	7.5
Syndiotactic-1,2-PB	30	0.1	—	—	—
	50	0.0	—	—	—
	70	0.13	—	—	—
	90	0.12	—	—	—
	110	0.25	—	—	—

\* Stress-optical properties for EPB and PB(B) above 30°C were taken from Kalfoglou and Williams<sup>16</sup> for comparison purposes. Irradiation dose, 8 Mrad.

The temperature dependence of the strain-optical coefficient gives some evidence of structural changes in the polymeric network.<sup>16</sup> In Figure 1, we can identify primarily two temperature regions. Below 10°C there is a stress relaxation of the amorphous chains due to the onset of crystallization, and the modulus drops, leading to a smaller birefringence per unit elongation. At this temperature range the degree of crystallization is sufficiently low so that only the effect of the modulus decrease is apparent. The amount of crystallites and/or their degree of orientation is not sufficient to compensate the birefringence decrease of the amorphous region. When the degree of crystallization increases at lower temperatures, the crystallites reinforce the network and the ratio  $\Delta n/\lambda$  increases. The increase in birefringence may not be necessarily due to the higher refractive index of the crystalline phase. It may also be caused by the higher "true" elongation of the amorphous sections of the semicrystalline chains which takes place to compensate for the lack of extension of the solid phase.

The curve for PB(B) would also show the upward trend of the PB(A); however, light-scattering effects prevented accurate measurements below -20°C. This transition from rubbery to semicrystalline state is more regular for the LPB, for which the rate and the degree of crystallization is small compared to the other polybutadienes (see also under "Low Temperature"). This is presumably due to the high vinyl content of the polymer acting as a plasticizer and the fact that none of the geometric isomers is distinctly predominant. This leads to a more disordered main chain and low rate of crystallization (see also Figs. 3 and 4B). Therefore, as the temperature drops, the amorphous chains do not relax to a significant degree so that the birefringence contribution of the crystalline phase always predominates.

Above 10°C, there is a noticeable "hump" indicating a reinforcement (or a more "orientable" network) between 50° and 70°C for the high *cis*-polybutadienes.

At higher elongations,  $\lambda$  between 1.4 and 4.0, the true stress and birefringence could be fitted to eqs. (4) and (5). The constants  $C_1$ ,  $C_2$  and  $B_1$ ,  $B_2$  were determined graphically from the intercepts and slopes of the respective plots. The results are given in Tables IV and V.

Our  $C_1$ ,  $C_2$  values are smaller than those reported by Kraus<sup>18</sup> for the LPB, and the  $C_1$  values are lower than those reported by Ishikawa and Nagai<sup>8</sup> for the corresponding polybutadiene.

The constant  $C_1$  associated with the Gaussian behavior of the chain is increasing with the temperature. This term has been related<sup>19</sup> to molecular parameters as follows:

$$2C_1 = N_e k T \frac{\langle r^2 \rangle_t}{\langle r^2 \rangle_0} \quad (9)$$

where  $\langle r^2 \rangle_t$  is the mean square end-to-end distance of the network chains in the unstretched sample, and  $\langle r^2 \rangle_0$  is the corresponding value for the free chain.

TABLE IV  
Temperature Dependence of Stress-Strain and Birefringence-Strain  
Constants  $C$  and  $B$  of Polybutadienes<sup>a</sup>

Polybutadiene	Temp., °C	$B_1 \times 10^{-4}$	$B_2 \times 10^{-4}$	$2C_1$ , kg/cm <sup>2</sup>	$2C_2$ , kg/cm <sup>2</sup>
Emulsion PB (EPB)	30	2.95	7.70	0.70	2.20
	50	3.00	5.75	0.85	1.78
	70	3.05	4.70	0.90	1.70
	90	3.10	3.45	0.97	1.48
	110	3.35	3.15	1.35	1.25
Linear PB (LPB)	-30	5.5	18.5	1.10	4.00
	-20	5.2	18.2	1.25	4.00
	-10	4.0	17.0	1.15	3.65
	30	2.25	10.25	0.60	3.20
	50	2.25	8.50	0.85	2.60
	70	1.65	7.80	0.78	2.45
	90	2.20	7.00	0.80	2.70
High <i>cis</i> -1,4-PB [PB(A)]	110	2.55	6.40	1.15	2.60
	30	2.65	7.65	0.70	2.80
	50	2.50	7.20	0.80	2.60
	70	2.85	7.15	1.15	2.35
	90	3.20	6.55	1.30	2.30
High <i>cis</i> -1,4-PB [PB(B)]	110	2.95	5.75	1.35	2.10
	30	1.95	6.30	0.70	1.80
	50	2.10	5.80	0.80	1.80
	70	2.40	5.40	0.95	1.75
	90	2.73	4.85	1.15	1.55
	110	3.10	3.80	1.20	1.55

<sup>a</sup> Irradiation dose, 8 Mrad.

TABLE V  
Effect of Crosslinking on the Rheo-optical Properties of Polybutadienes at 30°C

Polybutadiene	Dose, Mrad	$M_c$ $\times 10^{-3a}$	$B_1$ $\times 10^{-4}$	$B_2$ $\times 10^{-4}$	$2C_1$ , kg/cm <sup>2</sup>	$2C_2$ , cm <sup>2</sup> /kg	$\frac{\Delta n}{t} \times 10^4$ , cm <sup>2</sup> /kg	
							$\lambda_{max}$	$\lambda_{max}$
Emulsion PB (EPB)	4	10.0	-0.60	14.50	0.45	1.85	3.84	4.35
	8	7.8	2.95	7.70	0.70	2.20	3.84	3.69
	16	4.6	—	—	1.60	3.30	3.84	1.44
Linear PB (LPB)	4	7.8	2.85	9.60	0.75	2.75	3.40	2.64
	8	6.8	2.25	10.25	0.60	3.20	3.40	3.94
	16	5.8	1.50	12.70	0.0	4.45	3.40	1.28
High <i>cis</i> -1,4-PB [PB(A)]	8	6.8	2.65	7.65	0.70	2.80	3.08	2.99
	16	5.3	5.05	8.20	1.40	3.10	3.08	2.53
High <i>cis</i> -1,4-PB [PB(B)]	4	13.5	1.10	4.60	0.36	1.39	3.18	5.49
	8	9.5	1.95	6.30	0.70	1.80	3.18	3.59
	16	6.1	5.70	7.40	2.00	1.85	3.18	2.36

<sup>a</sup>Using eq. (3)  $M_c = \frac{84.782 \times T \times d}{2(C_1 + C_2)}$ .



Use of our data to derive the temperature coefficient of the quantity  $\langle r^2 \rangle_0$  is not justified, however, because of the quasi-equilibrium nature of the experiments. The coefficient  $C_2$  associated with the non-Gaussian terms of the network, more specifically, the physical entanglements, decreases slightly with temperature. This indicates a weakening of the physical links with increasing temperature due to slippage or oxidative breakdown of the network.

At constant degree of crosslinking, since the entanglement restrictions measured by the term  $C_2$  decrease, one would expect an increase in the elongation-to-break ratio  $\lambda_{\max}$ . This is confirmed to a limited extent, up to 50°–70°C, for all of our samples. At higher temperatures, oxidative breakdown reduces the  $\lambda_{\max}$ .

The strain-dependent stress-optical coefficient  $S$ , eq. (6), was calculated for  $\lambda = 2.0$  and using the tabulated coefficients. The agreement with the quantity  $(\Delta n)/t$  is satisfactory in most cases (see Table III). The particular value of  $\lambda$  used was empirically chosen from the range of the curve fitting of eqs. (4) and (5),  $1.4 < \lambda < 4.0$ . Other values of  $\lambda$  within this range could also be used with less success. Outside this range (e.g.,  $\lambda = 1$  and especially  $\lambda = \infty$ ), eq. (6) failed to reproduce accurately the quantity  $\Delta n/t$ . This is to be expected since the range of validity of eqs. (4) and (5) is limited.

The effect of crosslinking on the stress-optical properties at 30°C is shown in Table IV. Though the stress-strain and birefringence-strain properties are dependent on it, the stress-optical properties are not affected as predicted by the theory. Except for the EPB, for which the results showed an increasingly positive curvature, plots of  $1/M_e$  versus dose (Mrad) gave straight lines. The intercepts at dose = 0 give an approximate measure of the maximum entanglement molecular weight  $M_e$  which was increasing in the expected order

$$M_e (\text{LPB}) < \text{PB(A)} < \text{PB(B)}.$$

Increasing the degree of crosslinking increases the coefficient  $C_2$ , indicating a higher degree of entanglement in the network. This would lead to a decreasing  $\lambda_{\max}$  with increasing dose at constant temperature, and our data (see Table V) confirm this prediction<sup>20</sup> for all polybutadienes except for the LPB. The coefficient  $C_1$  also increases, presumably the factor  $N_e$  in eq. (9) being predominant. Similar variation has been reported for amorphous polyethylene.<sup>21</sup>

Measurements were also carried out (see Table III) for the two stereoregular 1,2-polybutadienes, the atactic ( $T_g = -22^\circ\text{C}$ ) and the syndiotactic ( $T_g = -28^\circ\text{C}$ ) 1,2-polybutadienes. The elastic properties of the atactic-1,2 isomer were very poor due probably to considerable vinyl branching. The syndiotactic-1,2 isomer showed an anomalous birefringence dependence on temperature and at 50°C on the stress, changing sign to negative values at high loads. The anomalous behavior was possibly caused by the crys-

TABLE VI  
Optical-Link Anisotropy Values,  $(\alpha_1 - \alpha_2) \times 10^{26}$  cm<sup>3</sup>, of Polybutadienes.  
Comparison with Literature Data

Polybutadiene	Kruse and Timm <sup>34</sup>	Fisher and Henderson <sup>35</sup>	Ishikawa and Nagai <sup>8,9</sup>	Furukawa et al. <sup>6</sup>	This work	Streaming bire- fringence <sup>36</sup>
LPB		77		73	80	
High <i>cis</i> -1,4-PB			75-81 <sup>b</sup>	68	77, 80 <sup>c</sup>	63
EPB	73 <sup>a</sup>			53	88	
High <i>trans</i> -1,4- PB			86			71

<sup>a</sup> High-temperature emulsion PB; value at 20°C.

<sup>b</sup> Experimental data at 30°C on three samples, Ref. 8, Figure 5.

<sup>c</sup> Experimental data at 30°C of PB(A) and PB(B).

tallinity of the sample (12%). No analysis of the data was made on the basis of photoelasticity theory.

The polybutadienes studied are terpolymers in terms of microstructure, and it was expected that the stress-optical properties and their temperature dependence would indicate structural differences.

In general, the segmental anisotropy of the polybutadienes in the amorphous state is independent of temperature. This can be interpreted if one assumes that the conformational properties of the polybutadiene chain can be described by the rotational isomeric model.<sup>22</sup> The energy barriers between *trans* and *gauche* conformations have been determined<sup>8,9,23</sup> to be very small, 0.1-0.2 kcal/mole. For the polyethylene chain where the temperature dependence of the segmental anisotropy was significant,<sup>21,24</sup> using the same model much higher energy barriers between the rotational isomers were calculated.<sup>7</sup>

Application of eq. (8), using known monomer-polarizability anisotropy values<sup>6</sup> led to a stiffness factor  $q$ , see eq. (2), which decreased in the following order:

$$q(\text{EPB}) > \text{LPB} > \text{PB(A)} > \text{PB(B)}.$$

The series seems to correlate with the decreasing amount of the 1,2-vinyl isomer which, owing to the pendant 1,2-vinyl group, would hinder the rotations to a diminishing extent along the series. An additional contributing factor could be the decreasing content of the *trans*-1,4 isomer which has a slightly stiffer chain than the *cis*-1,4-polybutadiene. However, the method is not sensitive enough from the experimental point of view since serious disagreement exists between the  $\alpha_1 - \alpha_2$  values reported in the literature. The discrepancy cannot be accounted for solely by possible microstructure differences for the same type of polybutadiene. Table VI lists these values. Values obtained by the streaming birefringence technique are included for the sake of completeness. It is known that swollen samples give lower values.<sup>8,9,25</sup> It is apparent that swelling affects these networks in a manner

similar to that observed for polyethylene.<sup>21</sup> As Isihikawa and Nagai<sup>8,9</sup> point out, photoelastic measurements made on swollen samples (using an isotropic solvent) are more representative of isolated chains for which the available theory is strictly applicable. The value of the polarizability anisotropy, and hence of the stiffness parameter  $q$  obtained in the unswollen state, may possibly be modified by association with neighboring molecules.<sup>26</sup>

The degree of crosslinking as a source of the discrepancy between our results and those of Furukawa and co-workers<sup>6</sup> can be ruled out on the basis of our data in Table V. Some dependence was observed by the Japanese workers. The possible effect of the method of crosslinking for the high *cis*-polybutadiene is not supported by the findings of Ishikawa and Nagai<sup>8</sup> who used chemical and irradiation techniques.

It is possible that the degree of equilibrium attained during the measurements could have an effect. The close agreement of our values with those of Ishikawa and Nagai<sup>8</sup> for the high *cis*-1,4-polybutadiene indicates our conditions of measurement to be quite close to equilibrium. In Furukawa's work<sup>6</sup> the sample was continuously stretched at a rate which was 80 to 10 times higher than our average elongation rate. This higher rate with its attendant high rate of breaking of physical entanglements could conceivably "measure" a higher stress for the same degree of orientation (or  $\Delta n$ ), hence the ratio  $\Delta n/t$  would decrease.

Another cause for the discrepancy for the LPB and EPB could be introduced by the 1,2-vinyl component. The calculated monomer polarizability is given<sup>6</sup> as  $-6.0 \times 10^{-25} \text{ cm}^3$ .

For the segmental anisotropy, we determined a value of  $7.5 \times 10^{-25} \text{ cm}^3$ . The high reactivity of the pendant vinyl double bond may lead to a varying degree of saturation, depending on the crosslinking conditions, increasing the measured net polarizability. It should be noted in this respect that the  $\alpha_1 - \alpha_2$  value of the double bond is larger than that of the single bond approximately by a factor of two, according to Lefevre<sup>27</sup> and Clement and Bothorel.<sup>28</sup> According to Denbigh,<sup>29</sup> there is no difference for the same property.

### Low Temperature

The low-temperature isothermal measurements are summarized in Figures 2 and 3 and Table III. The linearity of the  $\Delta n$ -versus- $t$  relationship may persist even in the presence of a small percentage of crystallinity, as is the case for the LPB at  $-30^\circ\text{C}$ . For the high *cis*-1,4-polybutadienes, crystallization effects become significant below  $-20^\circ\text{C}$ . The PB(B) crystallizes more readily than the PB(A) because of the lower vinyl content and the "microblock" distribution of these units along the chain. It is reported<sup>30</sup> that for the PB(A) prepared with a  $\text{TiI}_4$ -alkylaluminum catalyst, the non-*cis* units are distributed more randomly.

Similar conclusions are drawn from Figure 4, where the birefringence (or Babinet reading) is measured at constant load while the temperature is lowered under equilibrium conditions. For the EPB, the higher content of

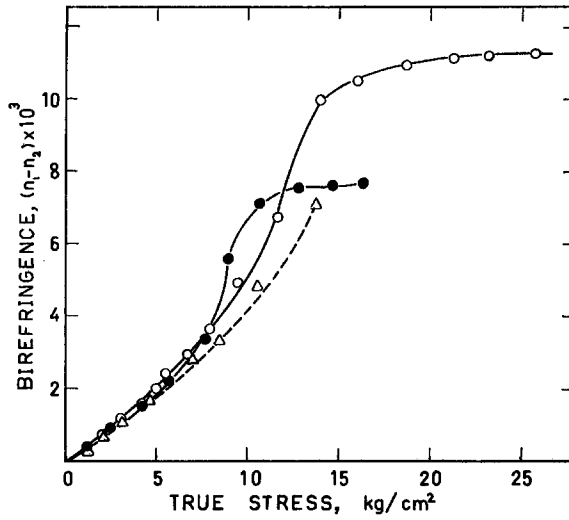


Fig. 2. Stress birefringence of polybutadienes at  $-20^{\circ}\text{C}$ : (O) EPB; (●) PB(B); ( $\Delta$ ) EPB (at  $-10^{\circ}\text{C}$ ).

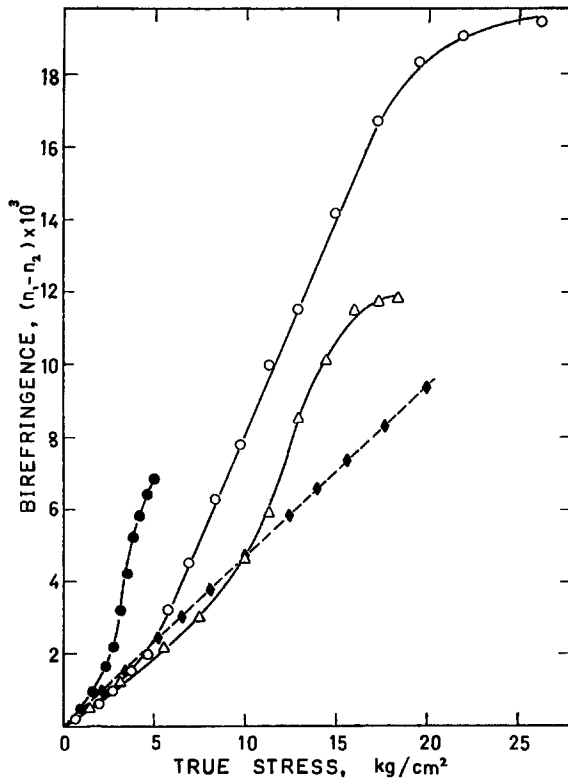


Fig. 3. Stress birefringence of polybutadienes at  $-30^{\circ}\text{C}$ : (O) EPB; ( $\blacklozenge$ ) LPB; (●) PB(A); ( $\Delta$ ) PB(A) (at  $-25^{\circ}\text{C}$ ).

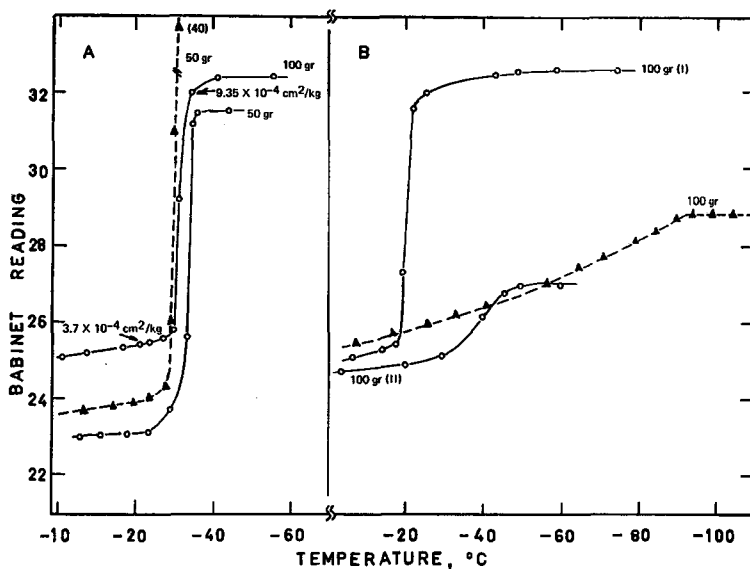


Fig. 4. Temperature dependence of birefringence under constant load. A: (O) PB(A); ( $\blacktriangle$ ) EPB. B: (O) PB(B), low (I) and high (II) cooling rate; ( $\blacktriangle$ ) LPB. Arrows indicate values of the stress-optical coefficient.

*trans* units leads to a higher crystallization temperature compared to PB(A) (Fig. 4A). Figure 4 also shows the effect of stress (or elongation) and of cooling rate on the degree of crystallization, indicated approximately by the amount of birefringence.

When crystallization sets in, the film viewed with white light has a milky appearance due to a Rayleigh scattering by the crystallites embedded in the amorphous phase. This is particularly true when the dimensions of the spherulites are comparable to the wavelength of the light inside the film. This scattering made difficult accurate measurements in the approximate range of  $-30^\circ\text{C}$  to  $-70^\circ\text{C}$ . In the case of the LPB, the short sequences of the geometric isomers along the chain combined with the significant amount of vinyl content did not allow the spherulites to grow; light scattering was slight, and accurate measurements could extend down to the glassy state (Fig. 4B).

More interesting information on microstructure effects was obtained by warming ( $0.5^\circ\text{C}/\text{min}$ ) quenched strips of polymer films as described in the experimental section. Figure 5 shows the results obtained by plotting the Babinet reading versus temperature for the various polybutadienes of comparable dimensions. The high *cis*-polybutadienes show a characteristic inflection point at approximately  $-115^\circ\text{C}$  leveling off at  $-100^\circ\text{C}$ , with another increase in birefringence starting around  $-85^\circ\text{C}$ . At this temperature, crystallization sets in as light-scattering phenomena indicate. This birefringence "step" is lower in the PB(A) and absent in the case of EPB and LPB, indicating that the high *cis*-1,4 structure is associated with

it. According to Boyer,<sup>31</sup> the  $T_g$  is due to a coordinated rotation involving a large number (30–40) of carbon atoms. If the resulting degree of orientation is sufficient, crystallization will also start, and this is the case for the LPB at  $-95^\circ\text{C}$ , EPB at  $-75^\circ\text{C}$ , and the high *cis*-PB(B) and high *cis*-PB(A) at approximately  $-85^\circ\text{C}$ . However, in the last two cases, because of the high microstructure purity in the *cis*-1,4 configuration, a “crankshaft rotation” of a more limited number of bonds is possible. Because of the limited orientation, crystallization is not induced at  $-115^\circ\text{C}$  but at higher temperature, where additional segmental motions make it possible. Thus

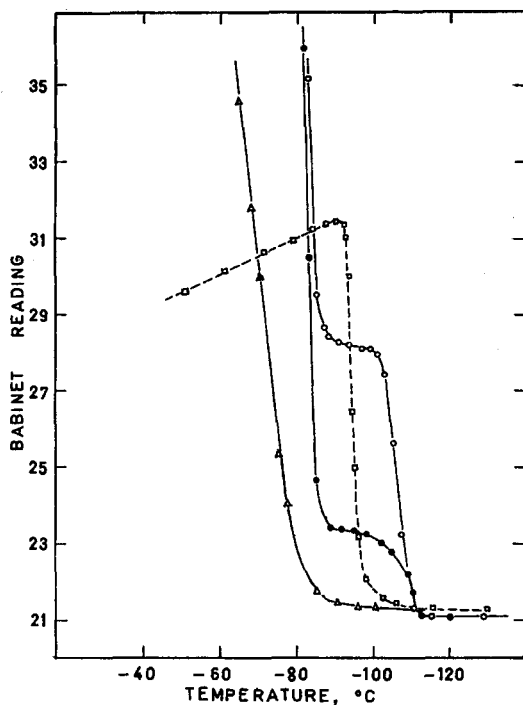


Fig. 5. Birefringence vs. temperature (increasing) of quenched polybutadienes: ( $\Delta$ ) EPB; ( $\square$ ) LPB; ( $\circ$ ) PB(B); ( $\bullet$ ) PB(A).

we get a distinct step in the retardation-versus-temperature plot. Initially, we attributed this to a genuine  $\gamma$  (or  $T_g^{\text{c31}}$ ) transition which is expected to be in this temperature region and just below the ordinary  $T_g$  for hydrocarbon chains. However, the experiment with the prestretched strip (see Fig. 6), giving the same birefringence, excluded this possibility.

It is our opinion that the two transitions merge, the  $\gamma$  transition triggering the longer segment movements. For a high *cis*-polybutadiene of unspecified purity, on the basis of NMR studies, Gupta<sup>32</sup> reported a transition at

$-98^{\circ}\text{C}$  which he attributed to the onset of segmental motion and melting of crystallites. For a *cis*-1,4-polybutadiene of approximately 98% purity, Dannis<sup>33</sup> reports a  $T_g$  value of  $-110^{\circ}\text{C}$ . For polybutadienes corresponding to our PB(A) and PB(B), van der Hoff and Buckler<sup>20</sup> reported a  $T_g$  value of  $-108^{\circ}\text{C}$  and  $-114^{\circ}\text{C}$ , respectively.

In the case of the LPB, the increase in birefringence (and of crystallization) does not proceed significantly compared to the other polymers. Under our experimental conditions, a maximum is attained at  $-90^{\circ}\text{C}$ . At higher temperature, the crystallites formed are melting thereby reducing the birefringence. This again reflects the microstructure disorder as mentioned before.

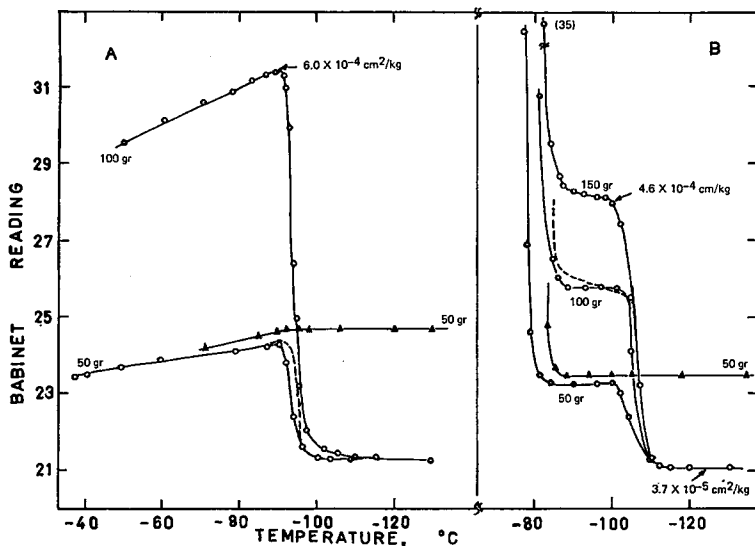


Fig. 6. Load and rate dependence of the "heating curves" of quenched polybutadienes A: (○) LPB; (▲) same after quenching in the stretched condition; (—) low heating rate. B: (○) PB(B); (▲) same after quenching in the stretched condition; (—) low heating rate.

As Figure 6 shows, the stress level does not alter perceptibly the  $T_g$ , except in cases where segment motion takes place and crystallization phenomena are observed. It was also observed for the PB(B) that increasing the degree of crosslinking does not affect the  $T_g$  at  $-115^{\circ}\text{C}$  but raises the transition at  $-85^{\circ}\text{C}$  (approx.  $+5^{\circ}\text{C}$  for the nominal irradiation dose difference of 8 Mrad). Lowering the heating rate by a factor of ten alters slightly the crystallization temperature (and the  $T_g$  if associated with it); but at these low temperatures where the rate of crystallization is slow, the effect is not significant.

## CONCLUSIONS

1. The stress-optical properties of the polybutadienes at moderate temperatures (30°–110°C) and elongations are described well by photoelasticity theory.

2. At these temperatures, the microstructural characteristics are not evident by the value of the segmental anisotropy and its temperature dependence, the latter because of the low conformational energy barrier between the *trans* and *gauche* rotational isomers.

3. At low temperatures, the tacticity and the degree of randomness of the geometric isomers along the chain influence the rheo-optical properties, the glass transition, and the crystallization phenomena in a characteristic way.

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