polymer papers

Fourier-transform infra-red dichroism study of molecular orientation in high *cis*-1,4-polybutadiene

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Molecular orientation in uniaxially stretched networks of polybutadienes has been investigated by Fourier-transform infra-red dichroism. Evidence of a strain-induced crystallization as well as a conformational change has been seen for the high *cis*-1,4 polymer. The second moment of the orientation function has been deduced by taking into account the conformational energy calculations performed by Abe and Flory, and Fraser's limits.

(Keywords: *cis*-1,4-polybutadiene; orientation; infra-red dichroism; Fourier-transform infra-red spectroscopy)

INTRODUCTION

Chain segments in polymeric networks orientate under a macroscopically applied deformation. Spectroscopic techniques provide valuable information on the molecular orientation, particularly important in determining physical properties, especially mechanical properties of macromolecular systems. Infra-red dichroism, which does not require any chain labelling, is a suitable method for a quantitative measurement of this orientation. The degree of orientation of the segments may conveniently be described by the second Legendre polynomial, defined as:

$$\langle P_2(\cos\theta)\rangle = (3\cos^2\theta - 1)/2$$

where θ is the angle between the chain axis and the stretching direction. The present work is devoted to an analysis of molecular orientations in uniaxially deformed polybutadienes with a high *cis*-1,4 configuration (96.5%) as well as with a 37% *cis*-1,4 content.

EXPERIMENTAL

Preparation of samples

The polymer used is a polybutadiene with a high *cis*-1,4 content (BR 1220, 96.5% *cis*). The results are compared with those for another polybutadiene of different microstructure (Diene 45 NF, 37% *cis*, 51% *trans*, 12% 1,2).

The sample preparation and stretching conditions have been described previously[1]. The crosslinking agent was dicumyl peroxide (dicup) with 0.05 wt% in bulk.

Infra-red measurements

The polarized spectra were recorded on 35 μm thick samples using a Nicolet 7199 Fourier-transform infra-red spectrometer under experimental conditions reported elsewhere[1].

Absorptions parallel $A_\parallel$ and perpendicular $A_\perp$ to the stretching direction were measured as a function of the extension ratio λ ($\lambda = l/l_0$, where l_0 and l are respectively the undeformed and deformed lengths).

Light-scattering experiments

The light-scattering patterns were obtained with a helium–neon laser. The incident beam was polarized parallel to the stretching direction (i.e. vertical) and an analyser—also vertical—was placed in the scattered beam (V_V pattern).

RESULTS

A convenient parameter characteristic of the effect of anisotropy on a given absorption band is the dichroic ratio R, defined as $R = A_\parallel/A_\perp$ ($A_\parallel$ and $A_\perp$ being the absorbances measured with radiation polarized parallel and perpendicular to the stretching direction, respectively). The orientation function $\langle P_2(\cos\theta)\rangle$ is related to the dichroic ratio R by the expression:

$$\langle P_2(\cos\theta)\rangle = (R-1)(R_0+2)/(R+2)(R_0-1) \qquad (1)$$

Here $R_0 = 2\cot^2\alpha$ where α is the angle between the transition moment vector of the vibrational mode considered and the local chain axis of the polymer. Equation (1) can be rewritten:

$$\langle P_2(\cos\theta)\rangle = F \times 2/(3\cos^2\alpha - 1) \qquad (2)$$

where $F = (R-1)/(R+2)$ is the dichroic function.

High cis-*1,4-polybutadiene BR 1220*

The infra-red dichroic behaviour of the bands located at 1405, 1267 and 1240 cm^{-1} has been analysed. These bands are respectively ascribed to the C–H in-plane asymmetrical bending mode (δ_a(CH)), the C–H in-plane

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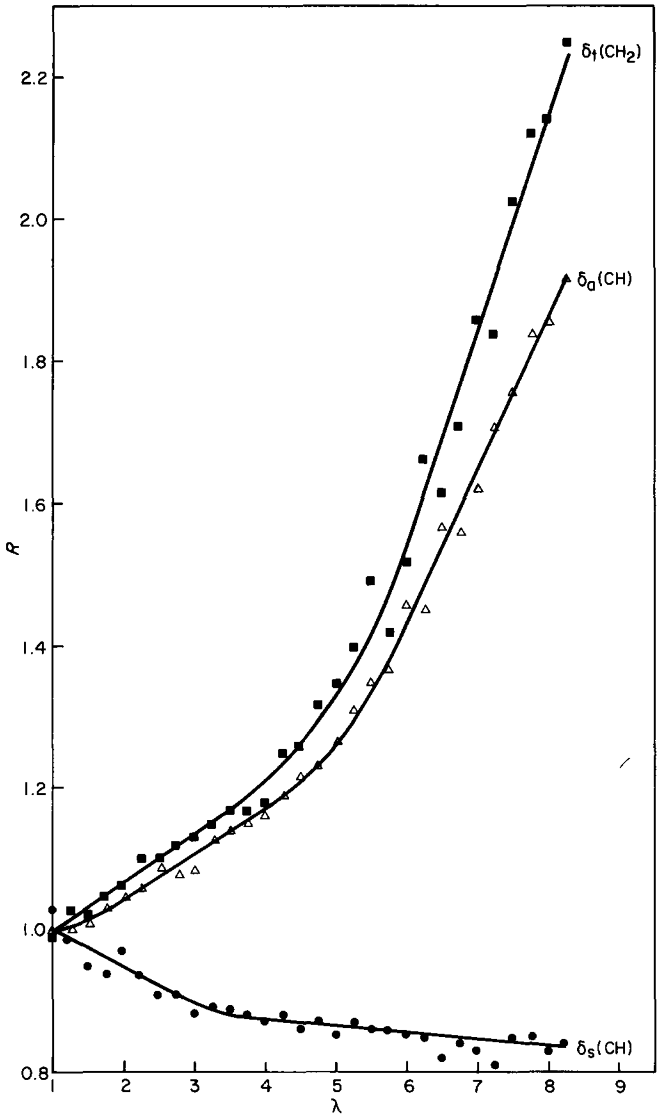

Figure 1 Dichroic ratios *versus* draw ratio for the 1240 cm^{-1} (■), 1405 cm^{-1} (△) and 1267 cm^{-1} (●) absorption bands of BR 1220

symmetrical bending mode (δ_s(CH)) and the CH$_2$ twisting vibration (δ_t(CH$_2$)) of the *cis* units. The transition moment directions associated with the δ_a(CH) and δ_s(CH) modes are respectively parallel and perpendicular to the C=C chemical bond, while that associated with δ_t(CH$_2$) is perpendicular to the plane of the methylene group.

Other bands could have been examined, for instance those related to the out-of-plane bending mode (γ(CH)) located at 740 cm^{-1} and to the C=C stretching vibration at about 1655 cm^{-1}. Unfortunately, the complex spectral pattern as well as the high absorbance of the 740 cm^{-1} band preclude any measurement. On the other hand, the 1655 cm^{-1} band exhibits a perpendicular dichroism while a parallel one is expected. The same result can also be deduced from Binder's spectra[2]. This behaviour may be explained by the fact that the 1655 cm^{-1} band contains, in addition to the ν(C=C) absorption, other components whose transition moments differ from that of the double bond stretching mode.

The dichroic ratios of the δ_a(CH), δ_s(CH) and δ_t(CH$_2$) bands have been plotted against the extension ratio λ in *Figure 1*. As expected, the 1405 and 1240 cm^{-1} bands exhibit a parallel dichroism while the 1267 cm^{-1} band has a perpendicular one. The 1200–1360 cm^{-1} region was analysed by curve resolving on account of an overlap of the absorption bands (*Figure 2*).

In the following treatment, α_a, α_s and α_t are the angles between the local chain axis and the transition moment directions respectively related to δ_a(CH), δ_s(CH), δ_t(CH$_2$), and F_a, F_s and F_t are the associated dichroic functions.

Diene 45 NF

The wavenumbers of the δ_a(CH), δ_s(CH) and δ_t (CH$_2$) bands of the *cis* residues do not differ from those of the same vibrational modes in BR 1220. The respective dichroic ratios have been plotted *versus* the extension ratio in *Figure 3*. Unfortunately, Diene 45 NF breaks much sooner ($\lambda_{max} \simeq 3$) than BR 1220, which limits the range of experiments.

Strain-induced crystallization in BR 1220

Strain-induced crystallization of polybutadienes with high *cis*-1,4 contents, already reported[3], may be

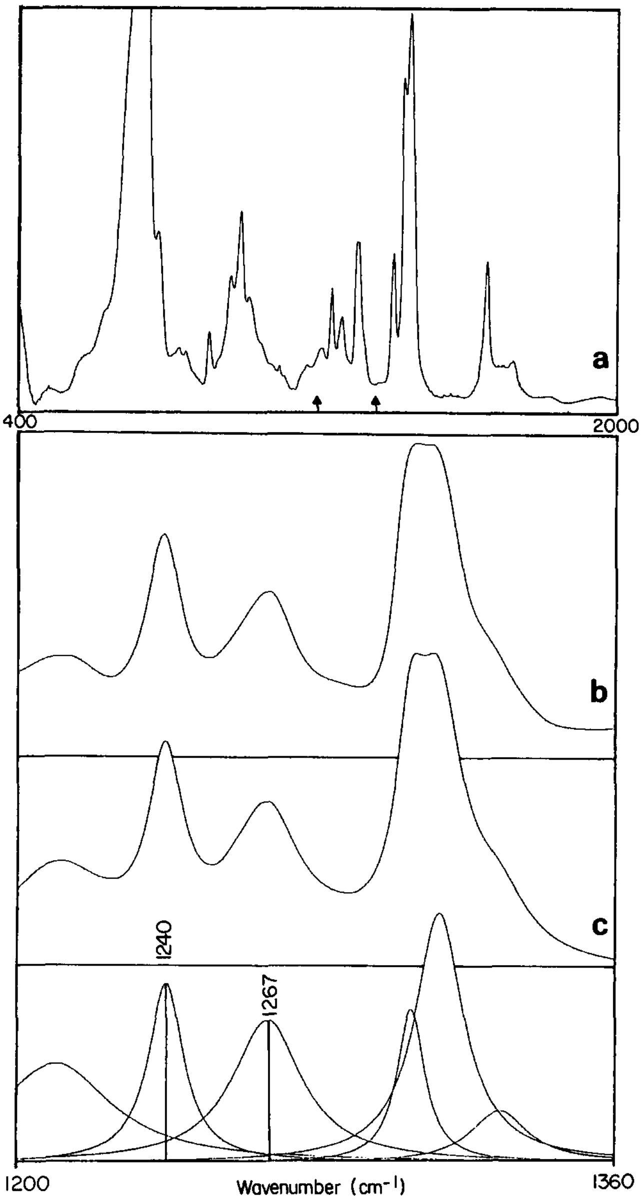

Figure 2 Infra-red spectrum analysis of BR 1220. (a) Experimental spectrum in the 400–2000 cm^{-1} range. The analysed region is between the arrows. (b) Experimental spectrum analysed by curve resolving. (c) Best fit with elementary bands. This example is taken before elongation ($\lambda = 1$)

considered as a consequence of the high steric regularity of the polymer. Experimental evidence of this phenomenon is obtained by the light-scattering method, previously used by Yau and Stein[4]. V_V light-scattering patterns reported in *Figure 4* show the appearance at $\lambda = 3$ of a horizontal streak indicating a crystallization process with a rod-like structure parallel to the stretching direction[5].

Furthermore, an important parameter that may reflect crystallization is the absorbance A_0 of a band, exclusive of contributions due to orientation, which is called structural absorbance and defined for a uniaxial orientation by:

$$A_0 = (A_{\parallel} + 2A_{\perp})/3 \quad (3)$$

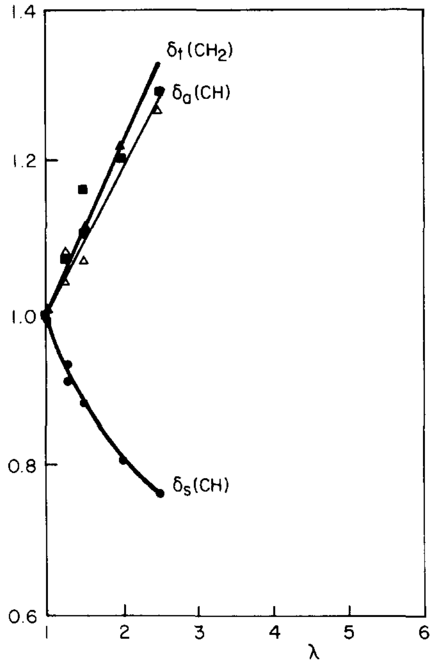

Figure 3 Dichroic ratios *versus* draw ratio for the 1240 cm^{-1} (■), 1405 cm^{-1} (△) and 1267 cm^{-1} (●) absorption bands of Diene 45 NF

For a non-crystalline band, A_0 decreases owing to a reduction of sample thickness during elongation. So, in order to compensate for this variation of the sample thickness, the ratios $A_0(1267)/A_0(1240)$ and $A_0(1405)/A_0(1240)$ have been plotted as a function of strain.

On account of its low steric regularity the Diene 45 NF does not crystallize under strain (*Figure 5*). On the other hand, in the case of BR 1220, the significant decrease of the above ratios for $\lambda > 4$ (*Figure 6*), consecutive to a change in absorptivities, should be attributed to strain-induced crystallization.

DISCUSSION

In a previous paper[1] dealing with orientation in high *cis*-1,4-polyisoprene and natural rubber, we have shown that, when the local chain axis is unknown, access to the second-order moment of the orientation function $\langle P_2(\cos\theta)\rangle$ can be obtained by treating simultaneously the dichroic ratio measurements of three bands whose transition moments form a set of three linearly independent vectors. Owing to the high monomeric symmetry of *cis*-1,4-polybutadiene, the same metho-

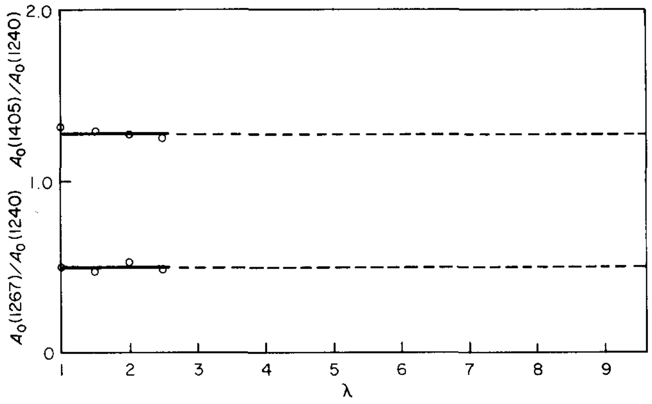

Figure 5 Structural absorbance ratios $A_0(1405\ \text{cm}^{-1})/A_0(1240\ \text{cm}^{-1})$ and $A_0(1267\ \text{cm}^{-1})/A_0(1240\ \text{cm}^{-1})$ *versus* draw ratio for Diene 45 NF

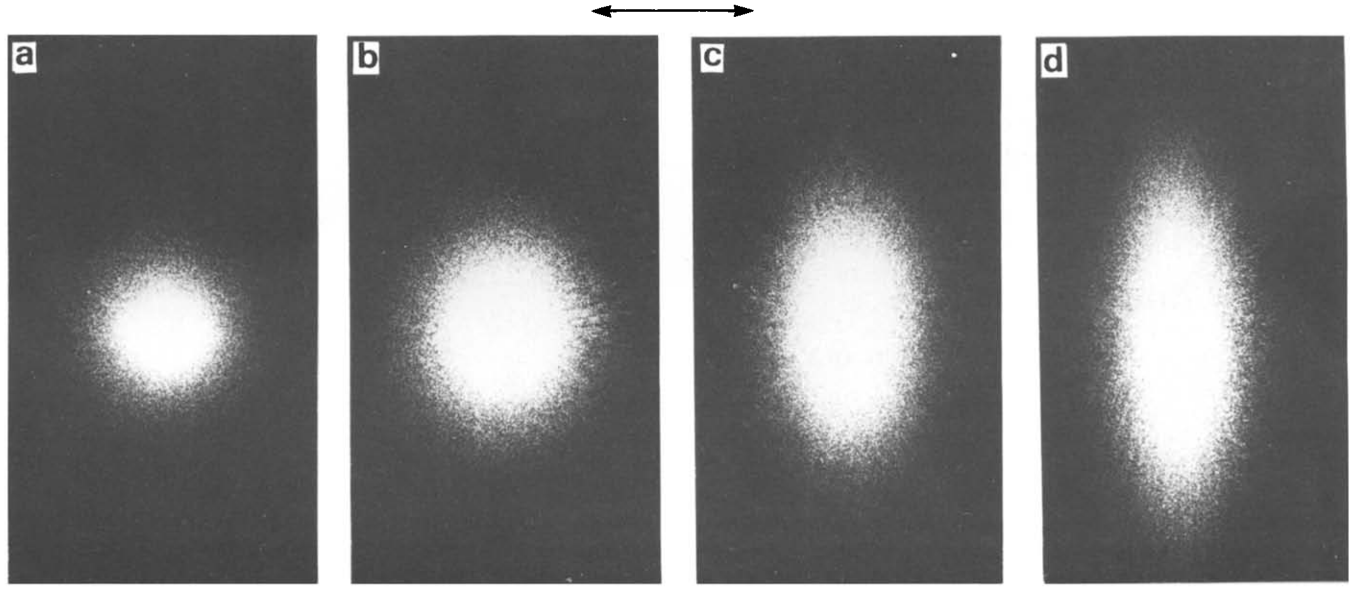

Figure 4 V_V light-scattering patterns obtained for BR 1220 for extension ratios of 1 (a), 2 (b), 3 (c) and 5 (d). Stretching direction is vertical and represented by the arrows

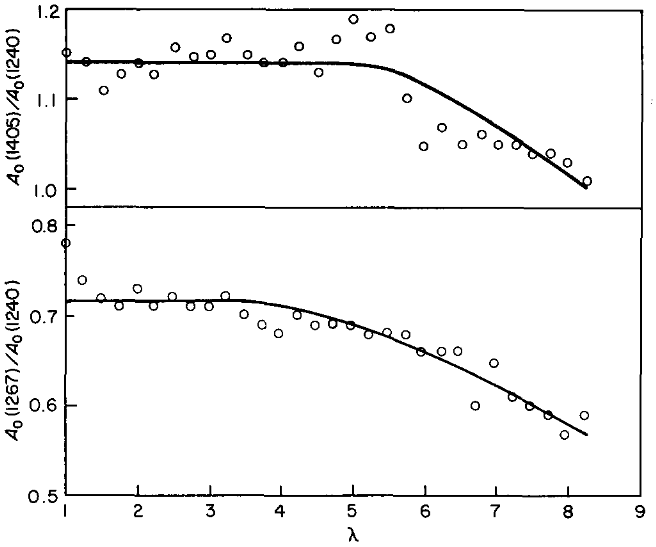

Figure 6 Structural absorbance ratios $A_0(1405\,\mathrm{cm}^{-1})/A_0(1240\,\mathrm{cm}^{-1})$ and $A_0(1267\,\mathrm{cm}^{-1})/A_0(1240\,\mathrm{cm}^{-1})$ *versus* draw ratio for BR 1220

dology cannot be applied here. Effectively, contrary to the case of polyisoprene, the transition moments associated with the bands analysed in this study form a set of three mutually perpendicular vectors related by the following relation:

$$\cos^2\alpha_1+\cos^2\alpha_2+\cos^2\alpha_3=1 \qquad (4)$$

where α_i is the angle between the local chain axis and the transition moment vector M_i.

Assuming that $\langle P_2(\cos\theta)\rangle$ at a given extension ratio is the same for all the vibrational bands, equations (2) and (4) lead to:

$$F_1+F_2+F_3=0 \qquad (5)$$

F_i being the dichroic function associated with M_i. Consequently, on account of this relation linking the dichroic functions, the determination of $\langle P_2(\cos\theta)\rangle$ has to be performed in a way differing from that used in the polyisoprene study.

Conformational change occurring upon crystallization

The dichroic functions F_a, F_s and F_t have been plotted against the extension ratio λ in *Figure 7*. Contrary to F_a and F_t, exhibits for $\lambda>4$ a slower variation than that obtained in the first part of the curve. Such behaviour suggests a decrease of α_s and its occurrence at $\lambda\simeq4$ may reveal a conformational change upon crystallization.

Under the assumption that $\langle P_2(\cos\theta)\rangle$, at a given λ, is the same for two absorption bands, the ratios of two dichroic functions:

$$F_a/F_s=(3\cos^2\alpha_s-1)/(3\cos^2\alpha_a-1) \qquad (6)$$

$$F_t/F_s=(3\cos^2\alpha_s-1)/(3\cos^2\alpha_t-1) \qquad (7)$$

lead to a relation between the respective transition moment angles.

As seen in *Figures 8* and *9*, the above ratios remain constant before crystallization within experimental accuracy. Besides the highly improbable hypothesis that there is a simultaneous variation upon drawing of α_a, α_t and α_s in such a way that the ratios remain constant, one simple explanation that comes to mind is to assume for each angle a constant value before crystallization.

Fraser's study[6] enables an estimation of the angles α from the experimental dichroic ratios. The same procedure yields the following limits: before crystallization ($\lambda<4$), for example at $\lambda=3.75$:

$$32°\leqslant\alpha_a\leqslant53°$$

$$90°\geqslant\alpha_s\geqslant56°$$

$$29°\leqslant\alpha_t\leqslant53°$$

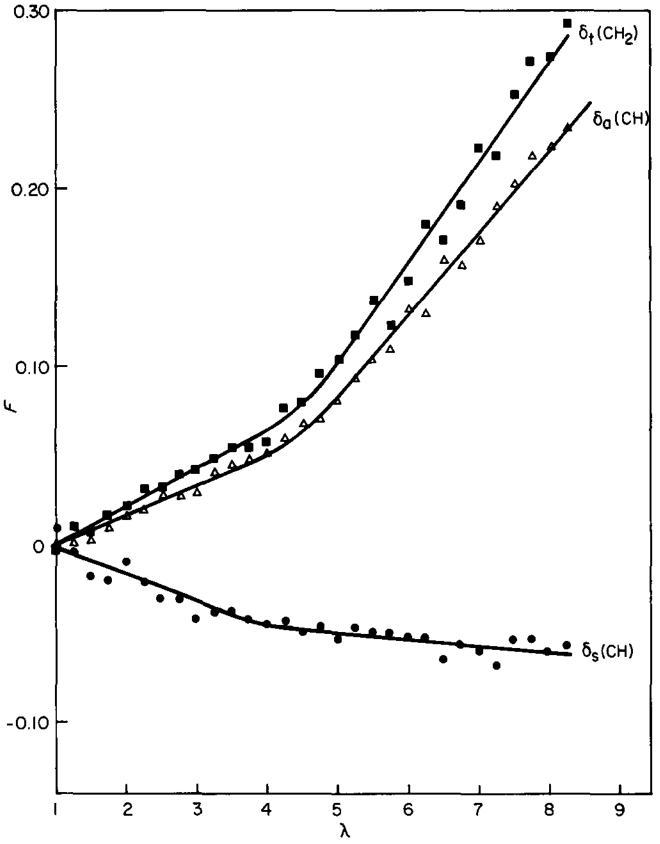

Figure 7 Dichroic functions *versus* draw ratio for the 1240 cm^{-1} (■), 1405 cm^{-1} (△) and 1267 cm^{-1} (●) absorption bands of BR 1220

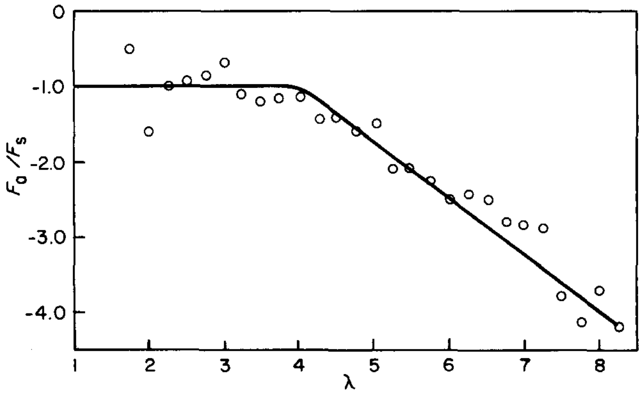

Figure 8 Dichroic function ratio F_a/F_s *versus* draw ratio for BR 1220

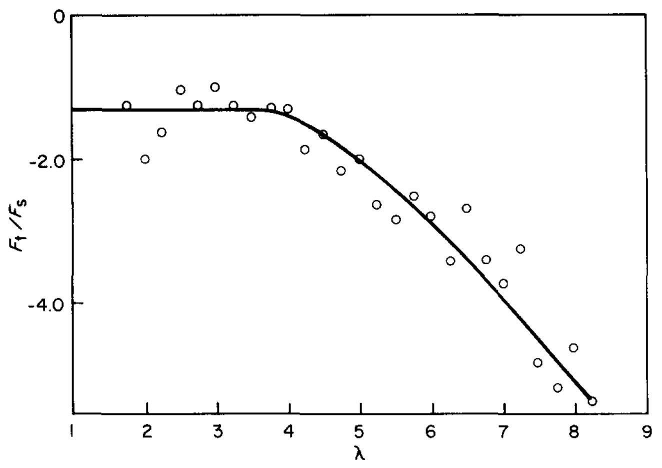

Figure 9 Dichroic function ratio F_t/F_s *versus* draw ratio for BR 1220

Table 1 Conformational probabilities $P_{\eta;\lambda}$ for a CH_2–CH_2–CH=CH– *cis* unit at 20°C for a draw ratio of 3.75

	Rotational conformation	$P_{\eta;3.75}$
1	ts^+cs^+	0.081
2	ts^-cs^-	0.081
3	$g^+s^+cs^+$	0.079
4	$g^-s^-cs^-$	0.079
5	$g^-s^+cs^+$	0.079
6	$g^+s^-cs^-$	0.079
7	ts^+cs^-	0.067
8	ts^-cs^+	0.067
9	$g^+s^+cs^-$	0.066
10	$g^-s^-cs^+$	0.066
11	$g^+s^-cs^+$	0.066
12	$g^-s^+cs^-$	0.066

and after crystallization ($\lambda > 4$), for example at $\lambda = 8.25$:

$$21° \leqslant \alpha_a \leqslant 46°$$
$$63° \geqslant \alpha_s \geqslant 57°$$
$$0° \leqslant \alpha_t \leqslant 43°$$

Conformational aspects

The spectroscopic data have outlined the conformational changes that take place during stretching. So, in order to gain further understanding of these aspects, we have started our investigation of the local conformations present from the results of Abe and Flory[7] relative to the configurational statistics of 1,4-polybutadiene treated in terms of conformationally independent units CH–CH_2–CH_2–CH=. The set of rotational states appropriate for the C–C bond adjoining the *cis* C=C bond is *skew* plus (s^+) and *skew* minus (s^-) while that of the CH_2–CH_2 bond is *trans* (t), *gauche* plus (g^+) and *gauche* minus (g^-).

The mean *a priori* probability, $P_{\eta;\lambda}$, that a unit selected at random in a chain occurs in a conformational state specified by η is given by the following expression[1]:

$$P_{\eta;\lambda} = P_\eta\{1 + \delta_{\eta;2}[(\lambda^2 + 2/\lambda)/3 - 1]\}$$

P_η corresponds to the same probability for the undeformed polymer and $\delta_{\eta;2}$ are coefficients indicative of the intrinsic susceptibility to isomerization by extension of the chain. Their values, calculated by Abe and Flory[7], show that rotational isomerization by stretching favours the $s^{+\,-}cs^{+\,-}$ conformations.

Using the statistical-weight matrices and the temperature dependence of the statistical-weight parameters, we have determined the probabilities of the 12 most probable conformations at 20°C and for $\lambda = 3.75$ (just before crystallization). The results are listed in *Table 1*. Assuming that a sequence of three butadiene units is sufficient to reflect the average conformational state of the polymer chain, we have calculated the different probabilities knowing that:

$$P_{\eta\eta';\lambda} = P_{\eta;\lambda} \times P_{\eta';\lambda} \quad \text{for two butadiene units}$$

$$P_{\eta\eta'\eta'';\lambda} = P_{\eta\eta';\lambda} \times P_{\eta'';\lambda} \quad \text{for three butadiene units}$$

Six conformations are the most probable for a sequence of three butadiene units, each with a statistical weight of 5.3×10^{-4} at 20°C and for $\lambda = 3.75$. If the chain axis is represented by the end-to-end vector of the three butadiene units, the transition moment angles α_a and α_s associated respectively with δ_a(CH) and δ_s(CH) can be estimated (*Table 2*).

Orientation of the amorphous BR 1220 before crystallization ($\lambda < 4$)

The calculation of the second moment of the orientation distribution $\langle P_2(\cos\theta)\rangle$ has been performed (*Figure 10*) by using the dichroic function F_s associated with δ_s(CH) and $\alpha_s = 80°$, this latter value being nearly constant within the six most probable conformations (*Table 2*).

In an attempt to determine the conformations present before crystallization, we have derived from equation (6) an average value of 37° for α_a. The α_s and α_a values, in accordance with Fraser's limits, may indicate the simultaneous presence of [1,2,1] (or [2,1,2]) and [1,1,2] (or [2,2,1]) conformations.

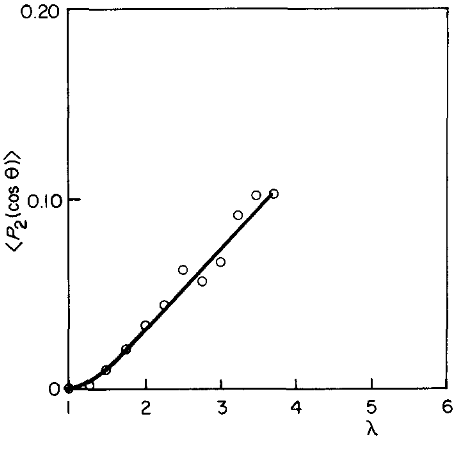

Figure 10 Second moment of the orientation distribution *versus* draw ratio for BR 1220 before crystallization

Table 2 Conformation angles α for *cis*-1,4-polybutadiene

Conformation	α_a (deg)	α_s (deg)
1,1,1	60	85
2,2,2	60	85
1,1,2	45	80
2,2,1	45	80
1,2,1 } alternated	20	80
2,1,2 } conformation	20	80

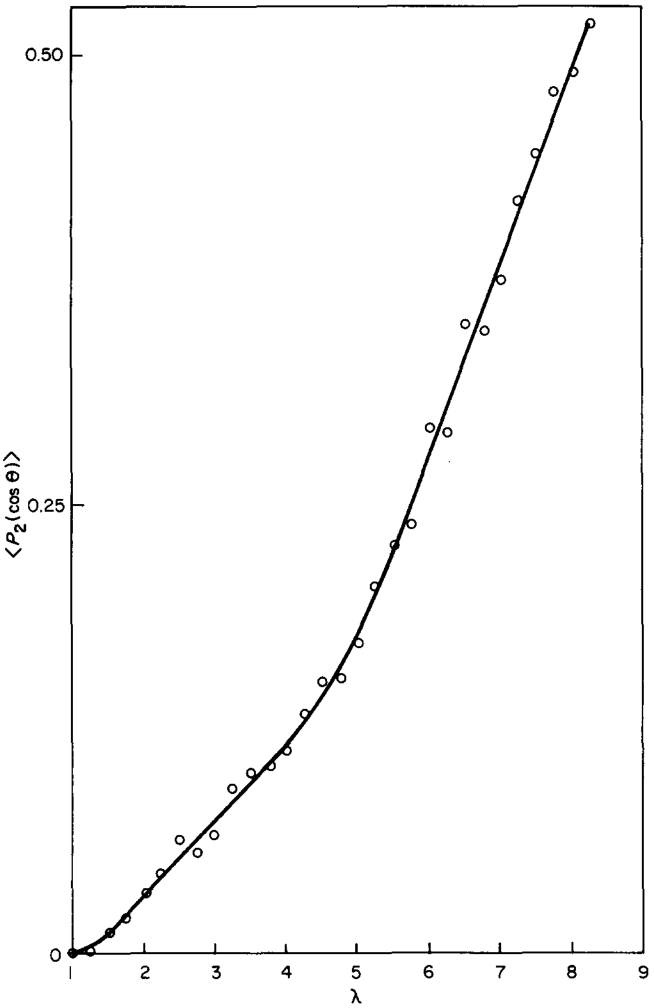

Figure 11 Second moment of the orientation distribution *versus* draw ratio for BR 1220

Orientation of strain-induced semicrystalline BR 1220

As shown above, our experimental results as well as Fraser's limits ($57° \leqslant \alpha_s \leqslant 63°$) have shown a decrease of α_s consecutive to a conformational change. But the conformation deduced from the work of Abe and Flory as well as that generated during thermally induced crystallization[8] $[ts^+cs^+, ts^-cs^-]_n$ cannot account for a decrease of α_s.

The morphology of polymeric networks crystallized under strain may be different from that obtained by cooling[9]. Cesari *et al.*[10,11] have investigated the crystallization of *cis*-1,4-polybutadiene by X-ray diffraction techniques. Their results are consistent with the formation of two types of crystals: one depending mainly on stretching, the other on temperature.

The $[s^-s^+cs^+, s^+s^-cs^-]_n$ conformation, differing from the temperature-induced crystalline one by a rotation of the CH_2–CH_2 single bonds from t to s^+ or s^- ($\pm 60°$), can occur during crystallization under stretching. The value of α_s has been found to decrease to 65° while the value of 30° for α_a does not differ very much from that obtained in the amorphous state (37°). This last value averaged over amorphous and crystalline conformations has been taken to calculate $\langle P_2(\cos\theta)\rangle$ for $\lambda > 4$ (*Figure 11*).

Influence of microstructure

Abe and Flory's results[7] show that the $s^{+-}cs^{+-}$ conformations of the *cis* residues are also favoured by stretching in a non-completely *cis*-polybutadiene like Diene 45 NF. So it seems reasonable to assume that the angles between the transition moment direction of the vibrational modes considered and the local chain axis are not significantly different from those of BR 1220. The dichroic ratios of the two investigated polymers can thus be compared (*Figures 1* and *3*). It appears that the *cis* units in the Diene 45 NF orientate to a much higher extent than in BR 1220. This fact is probably related to the presence of 51% *trans* units in Diene 45 NF.

CONCLUSIONS

Crystallization under strain and the conformational change accompanying this crystallization have been seen in the investigated high *cis*-1,4-polybutadiene. Consideration of the conformational calculations performed by Abe and Flory allows a determination of the second moment of the orientation function.

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