Fourier-transform infra-red dichroism study of molecular orientation in synthetic high *cis*-1,4-polyisoprene and in natural rubber

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Infra-red dichroism was used to investigate the molecular orientation of uniaxially stretched networks of natural rubber (pale crepe) and of a synthetic polyisoprene with 92% *cis*-1,4 content. Separate orientation functions were derived for the crystalline and amorphous phases of the natural rubber. The extension ratio dependence of the orientation of the transition moments of the considered vibrational modes relative to the polymer chains highlighted the occurrence of conformational changes. The results are in agreement with conformational energy calculations performed by Abe and Flory.

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

INTRODUCTION

Molecular orientation studies of polymeric systems are of particular interest since they provide valuable information on the mechanisms involved in polymer deformation. Infra-red dichroism is one of the most useful tools for a quantitative measurement of this orientation. One of the advantages of this technique is the separation of the crystalline and amorphous contributions to molecular orientation in semi-crystalline polymers. The distribution of chain orientation is characterized in an uniaxially oriented polymer by the second moment of the orientation function $<P_2(\cos\theta)>$ where θ is the angle between the chain axis and the stretching direction.

This paper presents the results of the application of Fourier transform infra-red (*FT*i.r.) spectroscopy to the determination of the molecular orientation parameters in crosslinked synthetic polyisoprene and natural rubber.

EXPERIMENTAL

Materials

Samples were generously provided by Manufacture Française des Pneumatiques Michelin (Clermont-Ferrand, France). The measurements were made with a commercially available synthetic polyisoprene (IR) of high *cis*-1,4 configuration (Shell, IR 307 : 92% *cis* and 5% *trans*, T_g(d.s.c.) = −60°C) and with natural rubber (NR) (pale crepe). The polymers were mixed with varying amounts of dicumyl peroxide (0.5, 1.0, and 1.5 wt% in bulk) and cured between Mylar sheets in a hot press for 30 min at 170°C. Curing time and temperature were chosen to ensure full decomposition of peroxide. Sample designation, thickness, number-average molecular weight, M_n, of polymer precursor after mixing with dicup and number-average molecular weight between crosslinks, M_c, are reported in *Table 1* for IR 307 and pale crepe. M_c values have been determined from stress–strain curves using the Flory–Erman treatment[1,2]. Complete stress–strain data and corresponding analyses will be reported in a forthcoming paper.

Sample stretching

The specimens (15 mm × 30 mm strips) were stretched with a manual stretching machine that allows symmetrical, uniaxial deformation. The extension ratio ($\lambda = l/l_0$, where l_0 and l are the undeformed and deformed lengths, respectively) was accurately measured on the stretching maching with a calliper-square.

Infra-red measurements

The infra-red spectra were recorded with a Fourier-Transform Infra-red Nicolet 7199 Spectrometer. A resolution of 2 cm^{-1} and an accumulation of 32 scans were chosen. The infra-red beam was polarized by a

Table 1 Characterization of synthetic polyisoprene and natural rubber samples

Sample	Thickness (10^{-6}m)	$10^{-5} \times M_n$ (g mol^{-1})	Dicup[a]	$10^{-3} \times M_c$ (g mol^{-1})
IR 2	41	3.0	1.0	5.55
IR 3	33	3.2	0.5	6.86
NR 1	29	1.6	1.5	4.33
NR 2	62	1.6	1.0	5.56
NR 3	32	1.7	0.5	7.19

[a] Wt% in bulk

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Perkin-Elmer gold wire grid polarizer which was set between the sample and the detector. Sample position was carefully adjusted at the convergence point of the incident beam.

One of the most important practical problems in infrared dichroism measurements arises from the requirement of band absorbances to be sufficiently low to permit use of the Beer–Lambert law and therefore very thin films had to be used. The second moment of the orientation function $<P_2\ (\cos\theta)>$ is obtained from measurements of the dichroic ratios of well assigned bands, using the following expression:

$$\langle P_2(\cos\theta)\rangle = \tfrac{1}{2}(3\langle\cos^2\theta\rangle - 1) = \frac{R-1}{R+2}\frac{R_0+2}{R_0-1} \qquad (1)$$

where θ is the angle between the chain axis and the stretching direction, $R = A_\parallel / A_\perp$ the dichroic ratio ($A_\parallel$ and $A_\perp$ being the absorbances measured with radiation polarized parallel and perpendicular to the stretching direction, respectively) and $R_0 = 2\cot^2\alpha$ where α is the angle between the transition moment vector of the considered vibrational mode and the local chain axis of the polymer.

RESULTS AND DISCUSSION

As noted above, the determination of the orientation function by infra-red spectroscopy requires well defined vibrational bands.

In the present study, we have examined the dichroic behaviour of the bands located at 837, 1376 and 1663 cm^{-1} ascribed to the C–H out-of-plane bending mode, the CH_3 symmetrical deformation and the C=C stretching vibration, respectively.

On account of the small mass of the hydrogen atom and of the large force constant of the double bond, the transition moment directions corresponding to the bands at 1376 cm^{-1} and 1663 cm^{-1} are respectively localized along the CH_3–C and the C=C chemical bonds. Furthermore the transition moment direction of the C–H out-of-plane bending mode is perpendicular to the plane of the double bond.

The dichroic functions $(R-1)/(R+2)$ of these three bands have been previously reported by Gotoh[3] for natural rubber but this author did not have access to the orientation function, the respective transition moment angles (α) being unknown. In a recent review, Siesler[4] showed that rheo-optical *FT*i.r. spectroscopy is particularly useful in studying the phenomenon of strain-induced crystallization on-line to the deformation process of the natural rubber. This technique can also yield some information concerning the orientation of the polymer chains in the average polymer relative to those in the crystallized domains. Under the assumption that the transition moment angle α of the 1126 cm^{-1} band (rocking mode of the methyl group) is zero, the author derived an angle of approximately 40° for the transition moment direction of the ν (C=C) absorption band at 1662 cm^{-1} and the polymer chain axis. From the orientation and dichroic functions of the 1126 cm^{-1} and 1662 cm^{-1} bands, the average inclination angles, θ, of the polymer chain relative to the stretching direction have been roughly estimated. At an extension ratio of 6.30, for the polymer chain ensemble, a value of about 44° was determined, whereas for the polymer chains involved in the crystal phase this angle is around 35°, indicating a higher orientation of the crystalline regions.

Our purpose in this work is to determine the second-order moment of the orientation function without any assumption concerning the local chain axis and thus the angles α. The methodology is to treat simultaneously the dichroic ratio measurements of the three bands whose transition moments form a set of three linearly independent vectors. These vectors allow the definition of an orthonormal set of basis vectors bound to the monomer unit in which the calculation of the orientation fucntion will be performed. This calculation is based on the fact that the same value of the orientation function must be obtained from the three absorption bands. The program has been performed on an Apple IIe microcomputer using BASIC software. Substitution of orientation and dichroic functions into equation (1) yields directly the values R_0 and hence angle α between the transition moment of each absorption band and the local chain axis.

Crosslinked synthetic high cis-*1,4-polyisoprene IR 307*

In *Figure 1*, the dichroic functions for the three absorption bands are plotted against the extension ratio for the IR 3 sample. As expected, the 837 and the 1376 cm^{-1} bands exhibit a perpendicular dichroism while the 1663 cm^{-1}, a parallel one. Curve A in *Figure 2* represents, for this sample, a plot of the coefficient $\langle P_2\rangle$ of the orientation distribution function at room temperature as a function of the extension ratio.

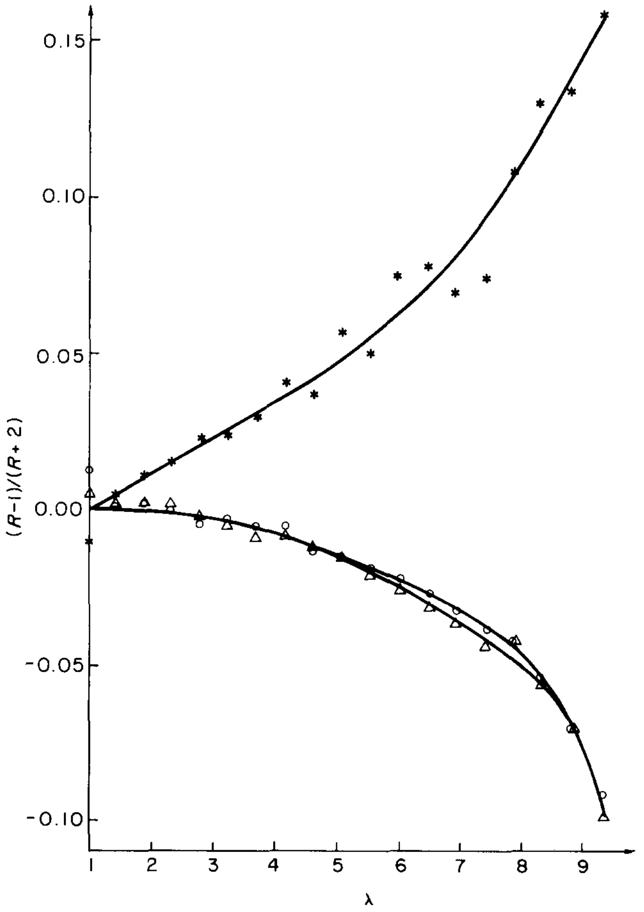


Figure 1 Dichroic functions *versus* draw ratio for the 837 cm^{-1} (△), the 1376 cm^{-1} (○) and the 1663 cm^{-1} (*) absorption bands of a synthetic polyisoprene sample (IR 3)

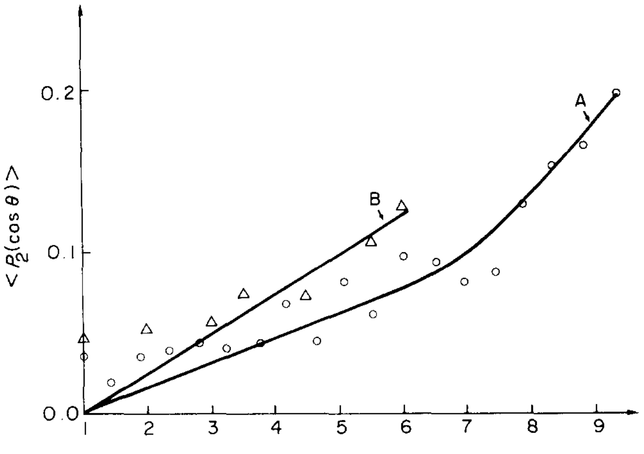


Figure 2 Influence of the crosslinking density on the orientation function for synthetic polyisoprene samples. (A) (○), IR 3; (B) (△), IR 2

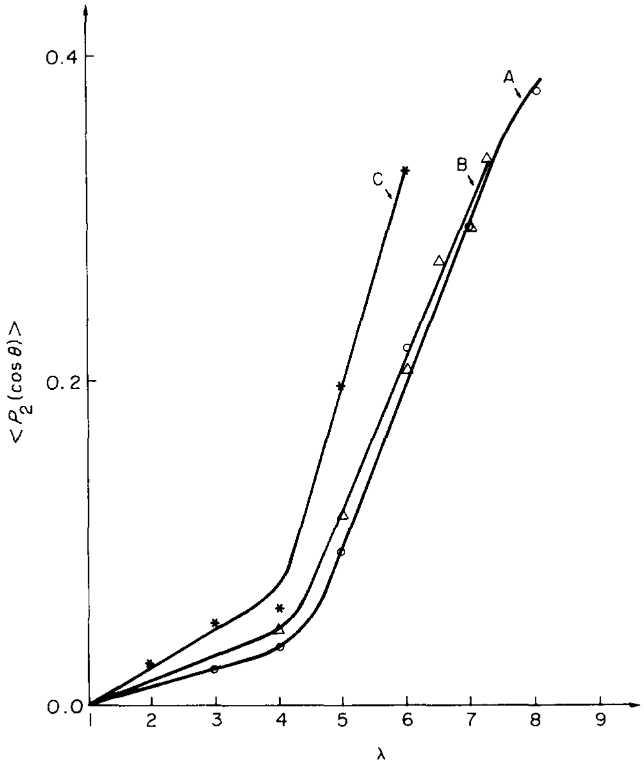


Figure 3 Influence of the crosslinking density on the orientation function for natural rubber samples. (A) (○), NR 3; (B) (△), NR 2; (C) (*), NR 1

The results obtained with the IR2 specimen and reported in curve B in *Figure 2* show that the orientation increases with the crosslinking density.

Natural rubber

It is well known that natural rubber crystallizes upon application of stress at room temperature or by cooling at temperatures between 20°C and −50°C with a maximum rate of crystallization at −25°C[5-7]. As previously shown[3,4] the characteristic feature observed in the infrared spectrum upon polymer crystallization is the shift of the C–H out-of-plane frequency from 837 cm^{-1} to 844 cm^{-1}. This 844 cm^{-1} absorption band can be considered to be specific for the crystalline regions. The average orientation function $\langle P_2 \rangle_{av}$, derived from the dichroic ratios of the three absorption bands, is represented in *Figure 3*. There is an approximately linear relationship between $\langle P_2 \rangle$ and λ from $\lambda = 1$ to *ca.* $\lambda = 4$ followed by a significant enhancement with strain. The steeper slope obtained for *ca.* $\lambda > 4$ is a consequence of strain-induced crystallization and proves the high chain alignment with the extension axis in the crystal phase. The linear part obtained in the small deformation range is quite similar in magnitude to that observed in the case of the synthetic polymer.

In order to isolate the individual contributions (crystalline and amorphous components) from the total orientation function, we characterized separately the absorbance components of the crystalline and amorphous phases in the absorption band associated with the C–H out-of-plane bending mode.

A sample of natural rubber which was kept at −35°C for one day was rapidly transferred to the sample compartment of the *FT*i.r. spectrometer. The absorbance subtraction technique performed on the absorbance spectra of the semi-crystalline and amorphous polymer allowed a determination of the shape of the 844 cm^{-1} band. The same result can be obtained by subtraction of the structural absorbance spectra of the unstretched and stretched material.

By using a Dupont Curve Resolver (Model 310) and the Curve Analysis Program available on the Nicolet FTIR, it was possible to separate the crystalline and amorphous contributions to the C–H out-of-plane absorption band for each draw ratio and each polarized spectrum (*Figure 4*).

The transition moment angle associated with the 844 cm^{-1} band has been derived from crystallographic data[8] and that associated with the 837 cm^{-1} band deduced from the $\langle P_2 \rangle$ values of the synthetic polyisoprene. This latter assumption seems reasonable since the two polymers exhibit, in the low extension ratio range, the same orientational behaviour. It was thus easy from the respective dichroic ratios to determine the $\langle P_2 \rangle$

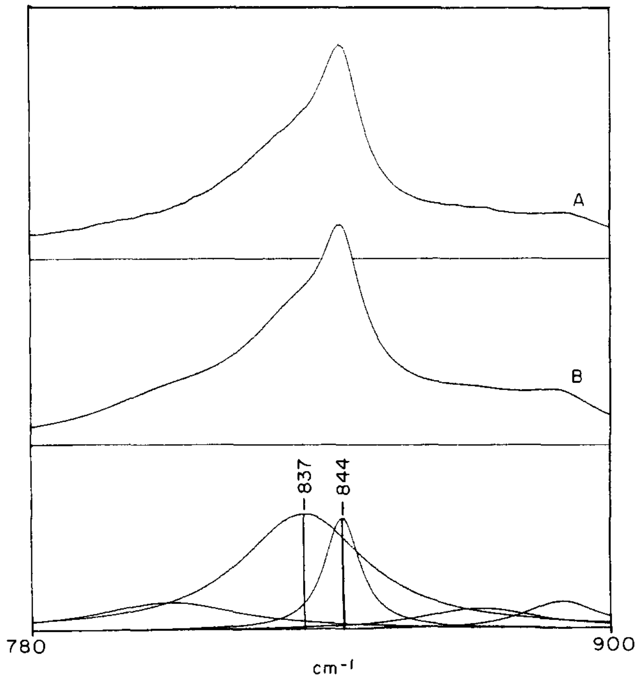


Figure 4 Spectrum analysis of natural rubber (NR 3) in the 780–900 cm^{-1} range: (A) experimental spectrum; (B) best fit with elementary bands. This example is taken at an extension ratio of 7 (perpendicular spectrum)

values related to the crystalline $\langle P_2 \rangle_{cr}$ and the amorphous $\langle P_2 \rangle_{am}$ phases (*Figure 5*). Our results show for the amorphous component an approximately linear relationship between $\langle P_2 \rangle_{am}$ and λ from $\lambda = 1$ to 3 followed, for $\lambda > 3.5$, by an upturn increasingly steeper with increasing λ. Such an upturn can be explained by the presence of crystallites acting as crosslinks and yielding an enhancement of the orientation. In the λ range where the stress-induced crystallization starts ($3 < \lambda < 3.5$) a slight decrease in the orientation function of the amorphous parts is observed, which reflects the slight disorientation of the polymer segments in the amorphous phase consecutive to the occurrence, at a fixed extension ratio, of higher oriented crystal domains.

Furthermore, as for the synthetic polyisoprene, the orientation in natural rubber increases with the crosslinking density, as shown in *Figure 3*.

Conformational aspects

During the stretching of an elastomeric network, not only the macromolecular chains orientate but conformational changes may also occur. Therefore, some knowledge of the local conformations present is of particular importance in understanding the molecular behaviour.

The configurational statistics of 1,4-polyisoprene have been treated by Abe and Flory[9] in terms of conformationally independent units $CH–CH_2–CH_2–C(CH_3)=$. The conformational energy calculations confirm their choice, in the case of the *cis*-1,4-polyisoprene, of s^{+-} (skew) rotational states for the first and third single bonds of the structural unit, the second single bond being assigned the usual t (*trans*) and g^{+-} (*gauche*) states.

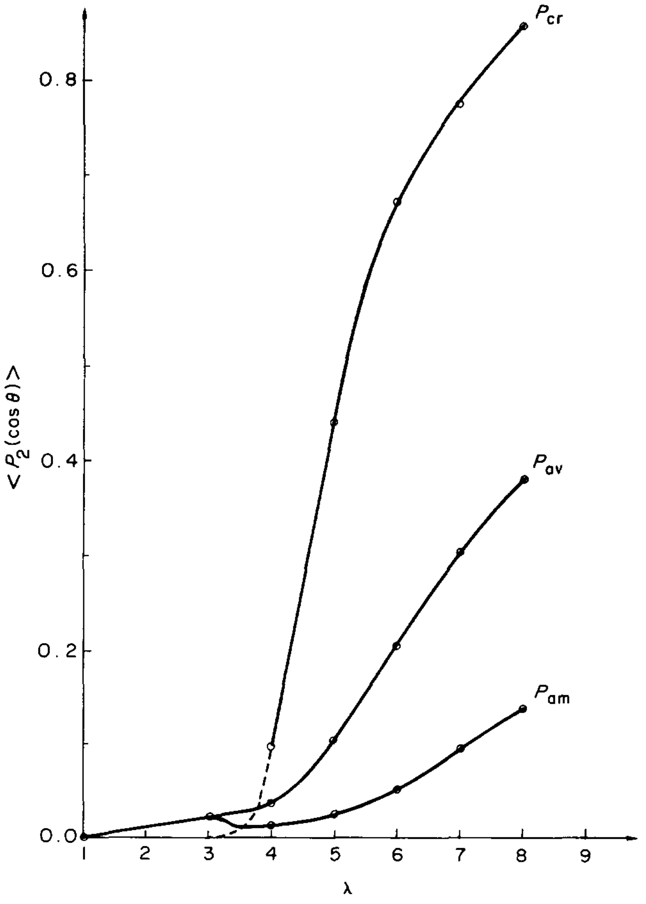


Figure 5 Decomposition of the average orientation function P_{av} in amorphous P_{am} and crystalline P_{cr} contributions in natural rubber (NR 3)

Table 2 Conformational probabilities $P_{\eta:\lambda}$ for a $CH_2–CH_2–C(CH_3)=CH–$ unit at 20°C for a draw ratio of 7

Rotational conformation	$P_{\eta:7}$
1: $t\ s^+ c\ s^+$	0.144
2: $t\ s^- c\ s^-$	0.144
3: $g^+ s^+ c\ s^+$	0.072
4: $g^- s^- c\ s^-$	0.072
5: $g^- s^+ c\ s^+$	0.072
6: $g^+ s^- c\ s^-$	0.072
7: $t\ s^+ c\ s^-$	0.094
8: $t\ s^- c\ s^+$	0.094
9: $g^+ s^+ c\ s^-$	0.047
10: $g^- s^- c\ s^+$	0.047
11: $g^+ s^- c\ s^+$	0.047
12: $g^- s^+ c\ s^-$	0.047

The twelve most probable conformations are given in the first column of *Table 2*.

The mean *a priori* probability, $P_{\eta;r}$, that a unit selected at random in a chain with end-to-end distance r, occurs in a conformational state specified by η, is given by the following expression[9]:

$$P_{\eta;r} = P_\eta\{1 + \delta_{\eta;2}[(r^2/\langle r^2 \rangle_0) - 1] + O(x^{-2})\} \qquad (2)$$

where P_η corresponds to the same probability for the unperturbed polymer chain characterized by the mean-square end-to-end distance $\langle r^2 \rangle_0$, r^2 is the square of the end-to-end distance for a specified state of the chain, x is the initial number of monomer units and $\delta_{\eta;2}$ is dependent on the chain structure.

In the case of a deformation of a network of long chains, r^2 may be identified with its average value $\langle r^2 \rangle$ taken over all chains. For simple elongation, under the assumption (simplest theory) of affine transformation of the distribution of chain vectors, the following expression has been established[10]:

$$\langle r^2 \rangle / \langle r^2 \rangle_0 = (V/V_0)^{2/3}(\lambda^2 + 2/\lambda)/3$$

where V is the volume of the deformed network and λ is the extension ratio measured relative to the length of the undistorted (isotropic) specimen at the same volume V, and V_0 is the volume in the isotropic reference state wherein $\langle r^2 \rangle = \langle r^2 \rangle_0$, the value for the unperturbed chain.

It is known that the volume and the density of a piece of rubber remain nearly constant under tension, the body changing its shape far more readily than its volume under stress[11]. Therefore equation (2) can be written as:

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

The $\delta_{\eta;2}$ coefficients which are indicative of the intrinsic susceptibility to isomerization by extension of the chain have been calculated by Abe and Flory[9]. Their results show firstly that the rotational isomerization by stretching takes place predominantly in $C–C(CH_3)=CH–C$ bond sequences; secondly, that under stress the number of $s^{+-}cs^{+-}$ conformations increases while that of $s^{+-}cs^{-+}$ decreases. Rotational isomerization favouring the former is consistent with the fact that they are more extended conformations than the latter. Changes in the *trans* and *gauche* populations of $CH_2–CH_2$ bonds are very small.

Using the statistical-weight matrices and the temperature dependence of the statistical-weight parameters, we have determined the probabilities $P_{\eta;\lambda}$ at 20°C of state η for each draw ratio λ; those obtained for $\lambda = 7$ are reported as a typical example in the second column of *Table 2*.

For two isoprene-units: $P_{\eta\eta';\lambda} = P_{\eta;\lambda} \times P_{\eta';\lambda}$ and for three isoprene-units: $P_{\eta\eta'\eta'';\lambda} = P_{\eta\eta';\lambda} \times P_{\eta'';\lambda}$. For a three isoprene-unit sequence, five conformations are the most probable, each with a statistical-weight of 0.0030: 1,1,1; 2,2,2; 1,1,2; 2,2,1; 1,2,1.

Estimation of the orientation of the transition moments relative to the polymer chain

One important feature in network orientation is the behaviour of the end-to-end vector of a polymer chain.

Table 3 Amorphous and crystalline conformation angles, α (degrees)

Amorphous conformations	α_1^a	α_2^a	α_3^a
1,1,1	80	65	40
2,2,2	80	65	40
1,1,2	65	45	45
2,2,1	65	45	45
1,2,1	65	20	80
Crystalline conformation	α_1^c	α_2^c	α_3^c
$(1,2)_n$	65	20	80

α^a angles for the amorphous state are defined with respect to the end-to-end vector of the sequence

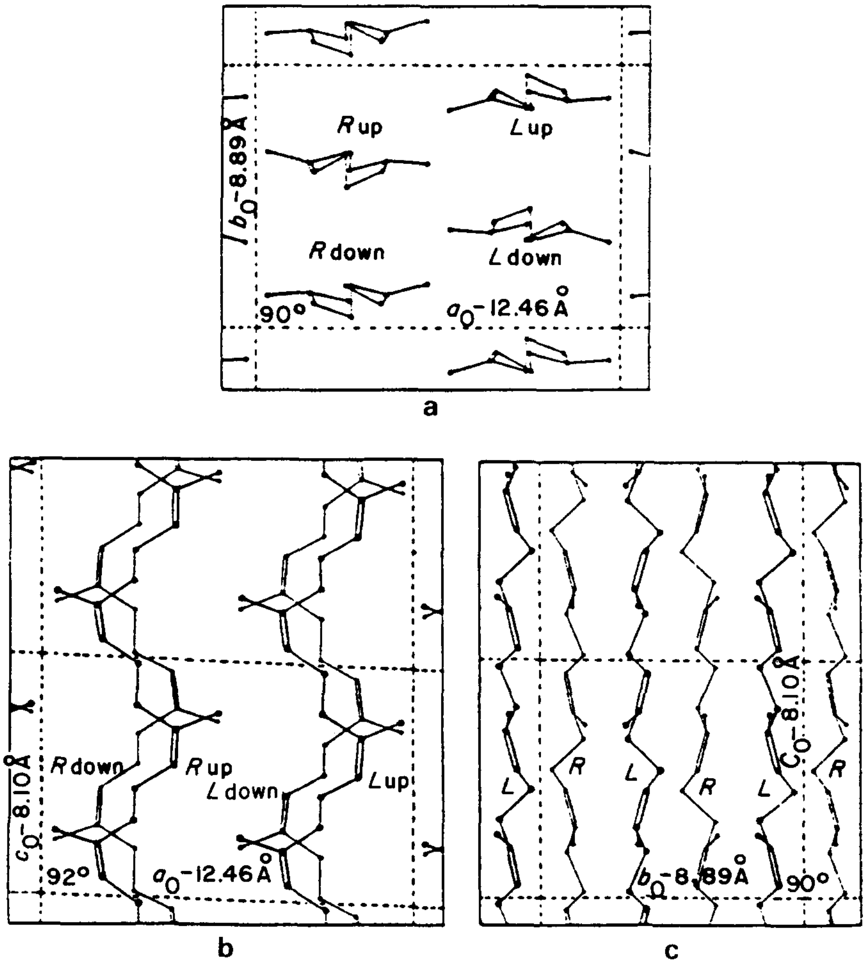
α^c angles for the crystalline state are defined with respect to the crystallographic *c*-axis

From a knowledge of the most probably conformations of the *cis*-1,4-polyisoprene sequences, we have tentatively estimated the orientation of the transition moments of the above considered vibrational modes with regard to the end-to-end vector of the polymer sequence. In order to achieve representative results, we have considered a sequence of three isoprene units. Such a sequence roughly corresponds to two Kuhn statistical segments and should be sufficient to reflect the average conformational state of the polymer chain. It should be noted that consideration of longer sequences demands a considerably more complex treatment.

Thus, the five most probably conformations have been built by using molecular models, the chain axis being estimated by the end-to-end vector of the three isoprene units. The transition moment angles α_1, α_2, α_3 associated respectively with the CH_3 symmetrical deformation $\delta_s(CH_3)$, the $\nu(C{=}C)$ stretching vibration and the C–H out-of-plane bending mode have been estimated for each conformation. The values have been reported in *Table 3*.

Furthermore, the α_1, α_2, α_3 angles have been determined for the conformation in the crystalline state $[ts^+cs^+, ts^-cs^-]$ of a sequence which contains two isoprene-units. This determination has been realized from the projections of Bunn[8] (*Figure 6*), the molecular chain axis being taken along the crystallographic *c*-axis.

In the case of IR 307, sample IR 3, for each λ value, we have deduced from the dichroic functions $(R-1)/(R+2)$ and the obtained orientation function $\langle P_2(\cos\theta)\rangle$, the angles α of the transition moments of the considered



a

b

c

Figure 6 Crystal structure of natural rubber (from Bunn, ref. 8). (a) Seen along *c* axis. (b) Seen along *b* axis. (c) Seen along *a* axis

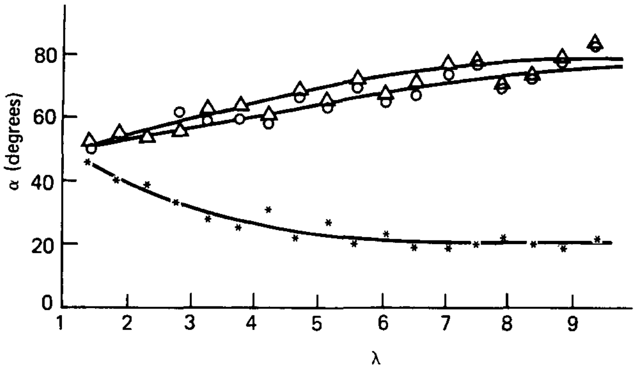


Figure 7 Evolutions of the angles α_1, α_2, α_3 between transition moments directions and the local chain axis as a function of draw ratio for a synthetic polyisoprene sample (IR 3). (○): α_1 (1376 cm^{-1}), $\delta_s(CH_3)$. (*): α_2 (1663 cm^{-1}), $\nu(C{=}C)$. (△): α_3 (837 cm^{-1}), $\gamma(CH)$

vibrational modes. The corresponding results are plotted *versus* the extension ratio in *Figure 7*.

One striking feature of these results is the fact that at low extension ratios, the angle values corresponding to the different vibrational modes are close to each other. At high elongation, each angle tends to level to a value characteristic of the vibrational mode, specifically 65° for 1376 cm^{-1}, 20° for 1663 cm^{-1} and 75° for 837 cm^{-1}. It is worth noting that the same limiting values are obtained for IR 2, which corresponds to a higher crosslinking density; however the levelling occurs at a lower extension ratio.

The observed change in α values with λ indicates that conformational changes occur with stretching. The fact that the limiting values are in rather good agreement with the estimated values for a conformation sequence 1,2,1 would confirm that the $ts^{+-}cs^{+-}$ conformations are predominantly attained by stretching. This result agrees with the predictions of Abe and Flory based on rotational isomeric state calculations[9]. It is important to notice that this 1,2,1 conformation is the same as the crystal-phase conformation in natural rubber.

In the case of natural rubber, the orientation functions before crystallization ($\lambda < 4$) are similar to those obtained for the synthetic polyisoprene. The α_1, α_2, α_3 angles are also of similar magnitude in the two samples, and this fact leads us to conclude that the strain-induced conformational change is the same in natural rubber before crystallization as in the synthetic polymer.

The assumption made by Siesler[4] on the 0° angle for the 1126 cm^{-1} absorption band led him to an angle of 40° for the transition moment of the 1662 cm^{-1} band. This value is quite different from the one that we have obtained without making any *a priori* assumption.

CONCLUSION

It has been shown that for polyisoprene chains, using the three vibrational modes at 837, 1376 and 1663 cm^{-1}, it is possible to determine the orientation function of the network without any *a priori* choice of the local chain axis.

In the case of natural rubber, the different orientational behaviours of the amorphous and crystalline parts have been observed in addition to the slight decrease in orientation of the amorphous phase associated with the beginning of the strain-induced crystallization.

The use of the rotational isomeric state calculations performed by Abe and Flory, has led us to the conclusion that, by stretching, conformational changes occur which increase the number of $s^{+-}cs^{+-}$ conformations.

REFERENCES

1 Flory, P. J. and Erman, B. *Macromolecules* 1982, **15**, 800
2 Queslel, J. P. and Mark, J. E. *J. Chem. Phys.* 1985, **82**, 3449
3 Gotoh, R., Takenaka, T. and Hayama, N. *Kolloid Z. Z. Polym.* 1965, **205**(1), 18
4 Siesler, H. W. *Adv. Polym. Sci.* 1984, **65**, 1
5 Wood, L. A. and Bekkedall, N. *J. Appl. Phys.* 1946, **17**, 362
6 Tobolsky, A. V. and Brown, G. M. *J. Polym. Sci.* 1955, **17**, 547
7 Gent, A. N. *Trans. Faraday Soc.* 1954, **50**, 521
8 Bunn, C. W. *Proc. Roy. Soc. London* 1942, **A 180**, 40
9 Abe, Y. and Flory, P. J. *Macromolecules* 1971, **4**, 219
10 Abe, Y. and Flory, P. J. *J. Chem. Phys.* 1970, **52**, 2814
11 Matsuoka, S. and Kwei, T. K., in 'Macromolecules, An Introduction to Polymer Science', (Ed. F. A. Bovey and F. H. Winslow), Academic Press, New York, 1979, ch. 6, p. 342