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A Fourier-transform Raman study of the strain-induced crystallization and cold crystallization of natural rubber

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The Fourier-transform Raman spectrum of natural rubber is presented as a function of time of cold soaking at −25°C and of strain with respect to laser polarization. Under both sets of conditions, changes occur in the spectra that can be attributed to crystallization. Difference spectra showing only those bands due to crystallization (i.e. spectra of crystalline natural rubber) are presented, which allows the crystallization process to be discussed with respect to the conditions under which crystallites are formed. A combination of Fourier-transform Raman and Fourier-transform infra-red depolarization spectra has been used to deduce preliminary assignments for some of the vibrational bands of natural rubber. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Natural rubber, *cis*-1,4-polyisoprene, is an important, well studied elastomer. As is typical of an elastomer, its mechanical and physical properties are dependent upon the degree and nature of crosslinking and may be significantly influenced by the surrounding physical environment. Of particular interest is the ability of natural rubber to crystallize under two very different sets of conditions: cold crystallization occurs when the material is cold soaked for a period of time (between −40°C and 0°C[1], optimized at −25°C[2]), and strain-induced crystallization takes place whilst the material is stretched. Crystallization affects properties such as tear strength[3], maximum extensibility[3] and modulus[3,4] as well as having a practical effect on processing[5]. Strain-induced crystallization is an elastomeric property often exploited in applications, whereas thermal crystallization of rubber is an unwanted phenomenon.

It has been suggested that the two crystallization processes occur by different methods. Stretching is thought to form *micelle-type* crystals almost instantaneously. In contrast, cooling unstretched rubber is thought to form *lamellar-type* crystals slowly[6]. X-ray diffraction studies[7] conclude that the crystal structure is the same in both cases, exhibiting a monoclinic unit cell of four chains per unit cell and with dimensions $a = 12.5$ Å, $b = 8.9$ Å and $c = 8.1$ Å and $\beta = 92°$ (ref. 8).

Stretching produces crystals with a preferred orientation in the direction of the applied stress, whereas thermal crystals have a random orientation. The degree of crystallinity is dependent on elongation, temperature and crosslink density; at room temperature crosslinked natural rubber possesses ~30% crystallinity when maintained in a highly stretched state[9]. This is comparable with cold crystallization, which results in a maximum of ~30% crystalline material for the latex[10]. Crosslinking reduces the degree of thermal crystallization, particularly when sulfur is used.

The infra-red spectrum of natural rubber has been recorded and comprehensively assigned[11,12], although a number of the weaker bands still remain unexplained. To complement this, a good-quality conventional visible-laser Raman spectrum of synthetic *cis*-polyisoprene has been reported[13]. However, until recently, sample fluorescence due to impurities has prevented the acquisition of a useful Raman spectrum of natural rubber[14]. Fluorescence is a particular problem in crosslinked materials. The use of a near-i.r. excitation laser source in conjunction with Fourier-transform (*FT*) laser Raman spectroscopy has reduced the problem, allowing good-quality spectra of natural rubbers to be obtained[15,16].

The orientation of stretched natural rubber has been extensively studied by *FT* i.r.[17–19]. Stevenson[20] applied *FT*-Raman spectroscopy to the study of stretched dicumyl peroxide-cured natural rubber. Although the technique was proven, the spectra covered a restricted frequency range and were of relatively low quality. More recently, further *FT*-Raman work has been completed on stretched crosslinked natural rubber[21] but the results are inconclusive. In addition, there has been a comprehensive *FT*-Raman study of crosslinked natural rubber upon cold crystallization[22,23].

This paper reports the changes that occur in the *FT*-

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Raman spectrum of natural rubber (using both uncured rubber and rubber crosslinked with dicumyl peroxide) when cold crystallized and under strain-induced crystallization. In particular, the spectral differences are analysed.

MATERIALS

Two natural rubber samples of grade SMRL were provided by the Malaysian Rubber Producers Research Association. In the stretching experiments rubber crosslinked with 1% dicumyl peroxide was used, while an uncured and hence non-crosslinked sample was examined in the thermal crystallization experiments. For the infra-red experiments, described later, *Mates natural* (natural rubber) condoms were used as they provide a relatively transparent source of natural rubber. They were cleaned prior to examination with acetone.

EXPERIMENTAL

Raman spectra of the cold crystallized samples were recorded using a standard Perkin-Elmer system 2000 *FT*-Raman spectrometer. A near-infra-red c.w. excitation source was provided by a Spectron Laser Systems Nd^{3+} : YAG laser. Typically, spectra were accumulated for Raman shifts in the range 200 to 4000 cm^{-1} by co-adding 100 scans at 4 cm^{-1} resolution and using a laser power of 600 mW. Raman spectra of stretched samples were recorded using a similar laser set-up and a Perkin-Elmer system 1760 *FT*-Raman spectrometer, as it allowed experiments to be carried out using a polarization analyser in the optical train. In these experiments spectra were accumulated in the range 200 to 4000 cm^{-1} at 4 cm^{-1} resolution as above, but an average of 200 scans was used and a slightly lower laser power of 500 mW. Preliminary experiments by Arruebarrena de Báez[21] had shown that sample heating by the laser could easily *melt* any crystals formed. Therefore, in the work reported here, samples were crystallized by cold soaking or stretching and then cooled before study. Two specially designed cells were used. Small unstretched specimens were examined in a cold cell of the transfer gas type, to be described in detail elsewhere; *Figure 1a* shows this transfer gas cold cell, which operates at liquid-nitrogen temperatures (77 K, −196°C) (LN cell) and was used for all cold-crystallized samples. Extension followed by cooling was carried out in a specially constructed glass Dewar; *Figure 1b* shows this cell, which is cooled by liquid nitrogen boil-off to maintain a temperature of ~223 K (−60°C) (LNBO cell). The cell has a glass vacuum jacket (b) with ends closed by two Delrin discs. In one end there is a glass inlet tube (a) for the liquid nitrogen boil-off. A gas outlet hole and thermocouple (c) are situated in the other end. The Delrin discs are separated by two metal legs (g). The strip of sample (e) is passed over a stirrup (f) and the two ends are clamped in (d), which is fixed to the Delrin disc at the gas outlet end. To stretch the sample, the rod attached to the stirrup (f) is pulled until the desired strain (extension) is achieved and is then locked in place. The entire cell, held horizontally or vertically, is mounted in the spectrometer and the sample viewed through the walls of the glass Dewar (b). This cell can also be used to heat the sample by flowing through hot gas.

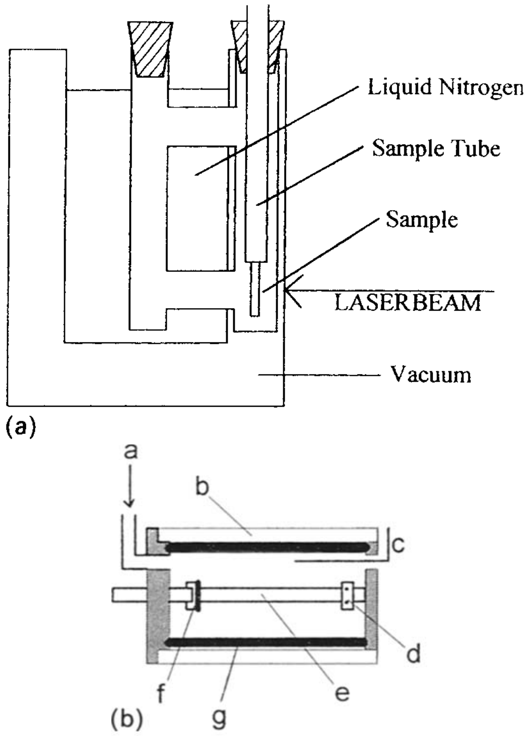


Figure 1 (a) Transfer gas cold cell cooled with liquid nitrogen and used for all the cold-crystallization studies. (b) Liquid nitrogen boil-off cell used for all the stress-induced crystallization studies: (a) gas inlet tube, (b) glass vacuum jacket, (c) thermocouple, (d) clamp for securing sample, (e) strip of sample, (f) stirrup over which sample is passed and (g) metal support/separation legs

To investigate thermal crystallization the samples were cold soaked in a refrigerator (+4°C) or domestic freezer (−25°C) for various lengths of time from 1 day to 2 months (see 'Results'). To avoid irreversible changes in structure, each sample was directly transferred to the LN cell before spectroscopic study without being allowed to warm above +4°C or −25°C, respectively.

The study of strain-induced crystallization required orientation considerations as the spectrometer is sensitive to sample alignment with respect to the laser polarization. In the laboratory frame, it is defined that the laser polarization direction is Z, the laser propagation direction is X and then Y is the third mutually perpendicular axis. Experiments were performed in which the sample was stretched in the Z direction, referred to as parallel orientation, and in which the sample was stretched in the Y direction, referred to as perpendicular orientation. By convention, orientations are usually defined with respect to the molecular axes using Porto nomenclature[39]. In this case, z is along the chain backbone, which is assumed to be parallel to the direction of stretching. Therefore, the experiments with no analysing polarizer are defined:

$$\text{(i) parallel} \quad \begin{array}{c} x \\ y \end{array}\begin{pmatrix} zz \\ zx \\ zy \end{pmatrix}\begin{array}{c} x \\ y \end{array}$$

$$\text{(ii) perpendicular} \quad x\begin{pmatrix} yy \\ yx \\ yz \end{pmatrix}x + y\begin{pmatrix} xx \\ xy \\ xz \end{pmatrix}y$$

Similarly, the experiments with an analysing polarizer are defined:

(i) parallel experiment 1 $\begin{matrix}x\\y\end{matrix}(zz)\begin{matrix}x\\y\end{matrix}$

experiment 2 $\begin{matrix}x\\y\end{matrix}\begin{pmatrix}zx\\zy\end{pmatrix}\begin{matrix}x\\y\end{matrix}$

(ii) perpendicular experiment 3 $x\begin{pmatrix}yy\\yx\end{pmatrix}x+y\begin{pmatrix}xx\\xy\end{pmatrix}y$

experiment 4 $x(yz)x + y(xz)y$

where the x and y axes are indistinguishable. The laser polarization and propagation directions must be orthogonal, limiting the possible experimental descriptions in the perpendicular case, as shown.

Spectra were recorded using the LNBO cell at −60°C and then at +60°C (by passing heated nitrogen gas through the cell) to separate spectral changes due to crystallization and orientation effects, respectively; above T_m there can be no crystallization, so any changes in the spectrum must be due to orientation alone. For natural rubber, $T_g \approx -73°C$ (200 K) and $T_m \approx +28°C$ (301 K)[24]. In addition to this, experiments were carried out using a polarization analyser placed between the sample and the detector. The polarization results obtained will be used as the basis for further work.

RESULTS AND DISCUSSION

Two rubber samples (cured and uncured) were used in the studies reported. It was established that the room-temperature spectra in both cases were identical. An example spectrum is shown in *Figure 2* and the line frequencies with known assignments are listed in *Table 1*. The results reported below are directly attributable to changes arising from the physical treatment of the samples and can therefore be compared.

Cold crystallization

Cold-crystallization studies on natural rubber were carried out at +4 and −25°C for a duration of 2 months. The samples stored at 4°C showed no changes in the *FT*-Raman spectrum in this time period and will not be discussed any further. In contrast, the samples stored at −25°C exhibited a number of apparent changes from the control sample. The differences observed are given in *Table 2* and the difference spectrum (spectrum of untreated natural rubber subtracted from spectrum of natural rubber cold soaked for 2 months) is presented in *Figure 3*. These band changes must be due to crystallization; the broad background is a fluorescence feature associated with the LN cell. It should be noted that all the reported changes can be seen after 1 day, although they are very weak. As the duration of cold soaking extends, the features become more pronounced. This observation is consistent with the results from X-ray diffraction studies and volumetric analysis[25], which report that crystallization at −25°C is virtually complete after 8 h. However, these cold soaking *FT*-Raman studies would suggest that, although there is a significant amount of crystallization after 24 h, the process continues and changes are still occurring up to 2 months later.

Table 1 *FT*i.r. and *FT*-Raman vibrational mode assignments for the spectrum of natural rubber. For the infra-red results the band intensities are also shown

Infra-red frequency[a] (cm^{-1})	Raman frequency (cm^{-1})	Assignment[b]
3292 broad w		
3114 sh. w		
3036 m	3038	ν(=CH) in (C(CH$_3$)=CH)
2996–2855 vs	2962	ν(CH$_3$)
	2931	ν_1(CH$_2$)
	2912	ν_s(CH$_3$)
	2885	
	2854	ν_s(CH$_2$)
2726 m	2727	
1663 m/s	1666	ν(C=C)
1637 sh. m		
1548 w		
1452 broad s	1452	ν_a(CH$_3$)
1432 broad s	1440	δ_a(CH$_3$)
1376 s	1375	
1362 sh. m	1363	δ(CH$_2$)
1324 sh. w	1325	δ(=CH) in-plane
1309 m	1311	CH$_2$ twist[c]
1287 w	1287	δ(CH) bending[c]
1259 m		
1244 sh. m	1243	CH$_2$ twist
	1208	
	1143	
1128 m	1131	ν(C–C) *cis* or CH$_2$ wag[c]
1091 broad m		
1038 m	1040	γ_r(CH$_3$)
1015 m		C–CH$_2$ stretch[c]
	1000	
985 sh. w		C–CH$_3$ stretch[c]
971 sh. w		
930 w		
889 m		CH$_3$ wag[c]
		CH of CH$_2$=C(CH$_3$)[d]
837 s		CH$_2$–CH$_2$ stretch[c]
		C–H out-of plane of *cis*-C(CH$_3$)=CH[d]
	820	CH wag[c]
799 sh. m		
764 w		CH$_2$ rock[c]
		C(CH$_3$)=CH[d]
741 w		CH$_2$ rock[c]
		C(CH$_3$)=CH[d]
	724	
598 sh. w		
573 m	572	
506 broad m		
488 broad m	492	γ_r(=CC$_2$), γ_s(=CC$_2$)
	428	γ_r(CC$_2$)
	367	γ_s(–CC$_2$)
	205	

[a] Band intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak and sh. = shoulder
[b] According to Cornell and Koenig[13] except where noted
[c] Saunders and Smith[11]
[d] Binder[12]

The results are in broad agreement with those reported previously[21,22] except for some changes in intensity in the C–H stretching region, which seem much more pronounced in earlier work[22]. This latter observation could be attributed to the nature of the sample, in particular its inhomogeneity. As there is an exact correspondence between the bands that change in all reported cold-crystallization experiments but not in their intensities, the observed spectral changes are thought to be due to crystallization and not impurities.

Fairly large differences resulting from cold soaking are observed in the region between 3200 and 2700 cm^{-1},

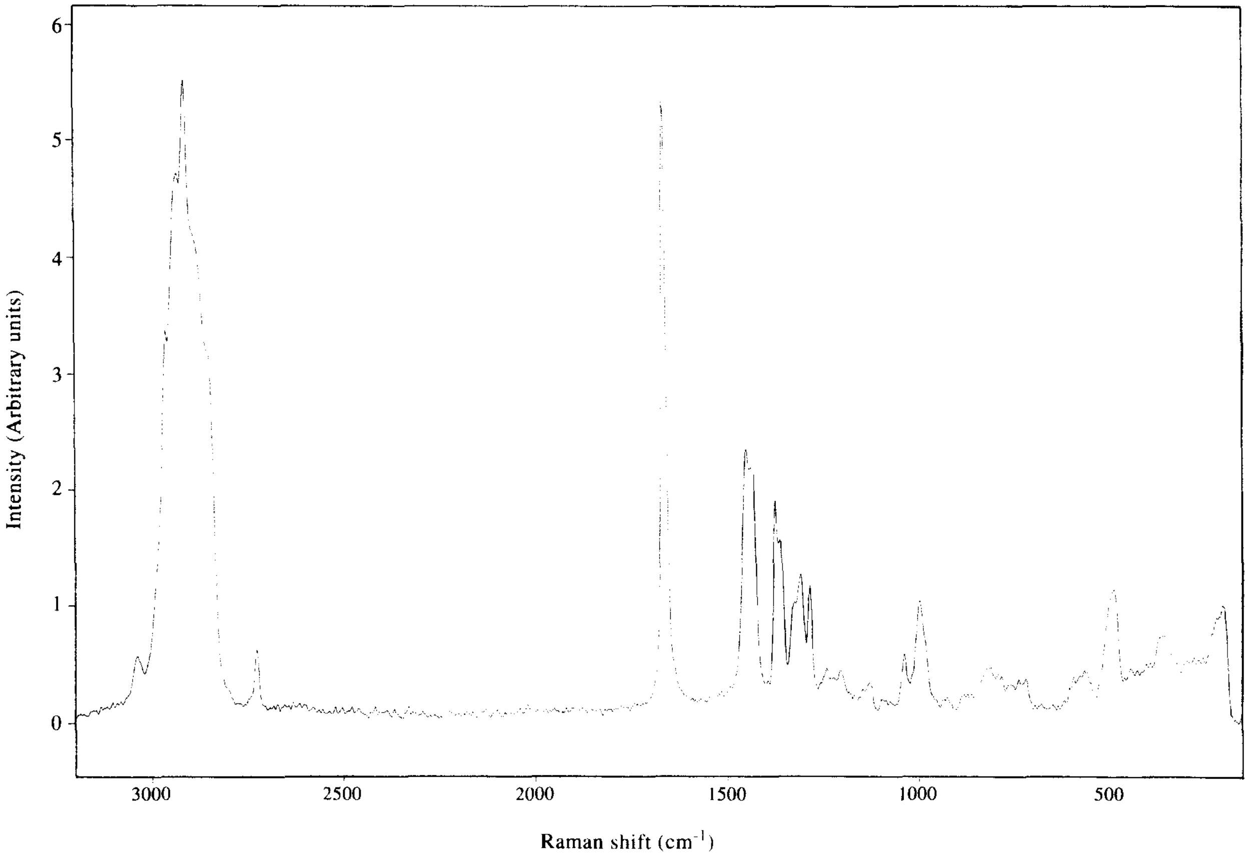


Figure 2 *FT*-Raman spectrum of natural rubber recorded at room temperature

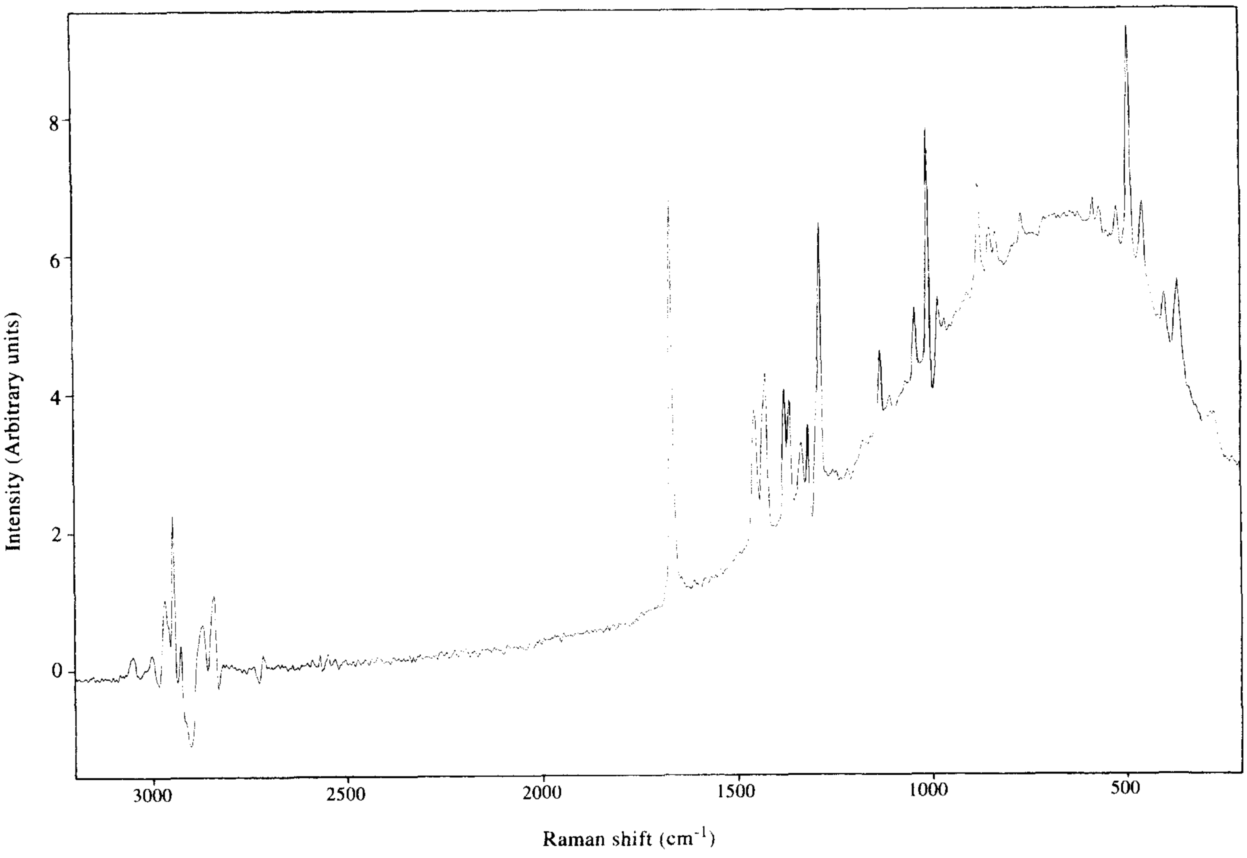


Figure 3 Difference spectrum (control spectrum subtracted from cold-soaked spectrum) showing the vibrational modes of natural rubber due to crystallization after cold soaking at −25°C for 2 months

Table 2 Frequencies of changes observed in the vibrational spectrum of natural rubber due to crystallization

Cold crystallization	Strain-induced crystallization (laser and sample parallel)	Strain-induced crystallization (laser and sample perpendicular)
2969	2965	2965
2948		2945
2929	2930	2932
2904	2901	2906
2873	2873	2874
2843	2839	2841
1668	1671	1672
1453	1454	1454
1425	1429	1427
1377	1374	1374
1363	1360	
1333	1332	
1316		1317
1284	1286	1286
1130	1129	1128
1040	1042	1042
1007	1004	1004
981		981
876		876
848		849
833		
765		763
584		
568		
524		521
490	492	490
456		460
398		
365		

which have been assigned to C–H stretching modes (see *Table 1*). The most significant change is the appearance of a new band at 2948 cm^{-1}. A second feature near 3046 cm^{-1} masks an existing one at 3042 cm^{-1}. In addition the bands at 2843, 2873, 2929 and 2969 cm^{-1} are observed to increase in intensity. At present it is not possible to give a detailed explanation of these changes because of the complexity of this part of the spectrum, except to say that they are obviously indicative of the alteration in the structure of natural rubber on crystallization. The isolated band at 1668 cm^{-1} is assigned as a C=C stretch, which undergoes a marked increase in intensity on cold soaking.

The fingerprint region exhibits a large number of spectral differences, which are perhaps of more interest in terms of the structural changes occurring. Consider first the region 1500 to 1000 cm^{-1}. Of particular note here are the new fairly strong bands at 1316, 1130 and 1007 cm^{-1}; although previously unassigned, it is proposed that the band at 1007 cm^{-1} may be assigned as a C–C stretch. It is not yet possible to assign the other two features. Furthermore, there are many increases in band intensity, the most notable of which is the apparent relative tripling in intensity of the band near 1284 cm^{-1}, which has been assigned as C–H bending mode[11]. The feature at 1040 cm $^{-1}$ also increases in intensity and is assigned as a CH_3 rocking motion. Finally in this region, there is extra resolution of features near 1440, 1370 and 1320 cm^{-1}. These have previously been explained as effects of sample cooling[23], but as the control here was recorded under identical cold conditions, they must, in fact, arise from the cold soaking and be dependent on the crystallinity of the sample.

Cold soaking results in a rise in the number of bands below 1000 cm^{-1}; hence it appears that the majority of bands in this region are *new*. Of the bands below 1000 cm^{-1} corresponding to bands in the spectrum of untreated natural rubber, most show some observable difference after sample treatment. The major changes are the new bands at 876 and 456 cm^{-1} and an increase in features near 490 and 365 cm^{-1}. Moreover, further new weak peaks are seen at 848, 833, 765, 584, 524 and 398 cm^{-1} and there is a small increase in the peak at 568 cm^{-1}.

Strain-induced crystallization

In all studies, the samples were stretched to ~500% elongation. As previously mentioned, it is necessary to consider strain-induced crystallization as a function of direction of sample stretch with respect to the laser polarization. The results show that the bands which may be attributed to crystallization are orientation-dependent, and this will be discussed. It should be noted that *FT*-Raman spectra recorded in a parallel direction show significantly stronger bands (although they could not be described as intense) than those recorded in a perpendicular direction.

In a strain-crystallized material, three distinct regions exist: (i) disordered amorphous, (ii) ordered amorphous (orientation effects on stretching) and (iii) ordered crystalline. The spectra were recorded (i) unstretched and heated, (ii) stretched and heated so any crystals would have melted, and (iii) stretched and cooled to study crystallization effects. The spectrum of unstretched natural rubber was found to be temperature-invariant with the exception of the C=C stretch in the region of 1666 cm^{-1}, which will be discussed later. By comparing the stretched and heated samples with the unstretched heated (control) ones, the changes in the *FT*-Raman spectrum of natural rubber due to some orientational ordering of the amorphous material can be isolated. Similarly, by comparing spectral changes between the stretched and cooled samples and stretched and heated ones, features due solely to crystallization can be identified.

To confirm that the spectral features observed are due to crystallization, an X-ray diffraction experiment was performed. A stretched sample showed a broad peak consistent with a low proportion of crystallization and small crystallites. An unstretched sample gave no apparent diffractogram.

Stretch direction parallel to laser polarization. There were a number of weak spectral differences arising from the presence of ordered amorphous material. These are given in *Table 3*. All the changes are increases in intensity of existing bands; as would be expected, no new features are observed. The most significant change is to the C=C stretch at 1661 cm^{-1}. Significantly, the ordered amorphous spectrum only demonstrates features above 950 cm^{-1}.

The *FT*-Raman spectra of a strip of stretched natural rubber held parallel to the laser polarization direction when heated (+60°C) and cooled (−60°C) show a number of dissimilarities. The spectral differences arising from sample crystallization are listed in *Table 2* and the spectrum thought to be associated with crystalline rubber (stretched/heated subtracted from stretched/cooled) is displayed in

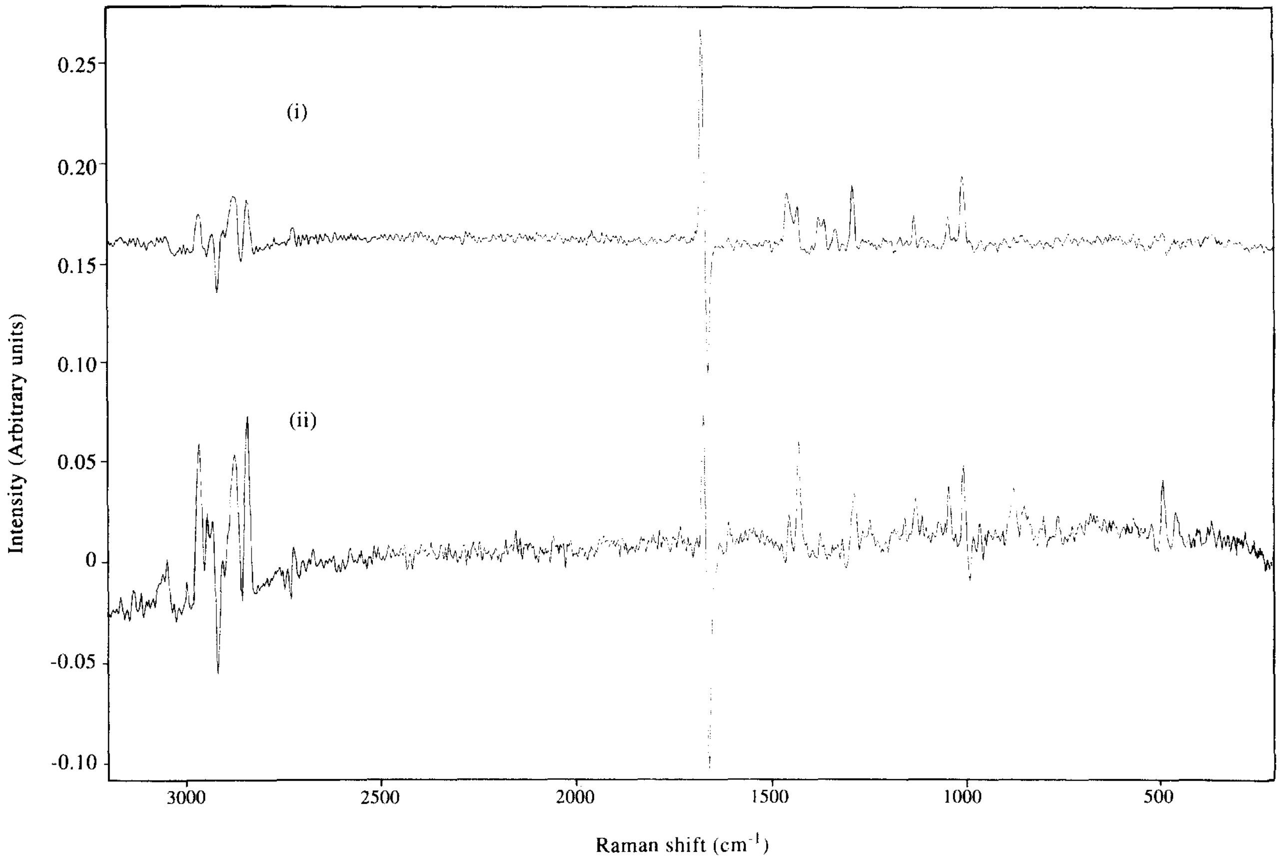


Figure 4 Difference spectra (control spectrum subtracted from stretched spectrum) showing the vibrational modes of natural rubber due to crystallization on stretching to very high extensions: (i) stretch orientation parallel to the laser polarization and (ii) stretch orientation perpendicular to the laser polarization

Table 3 Frequencies of changes observed in the vibrational spectrum of natural rubber due to orientation effects when stretching the sample to very high extensions. All bands due to orientation effects on stretching are very weak

Orientation bands due to stretching—parallel	Orientation bands due to stretching—perpendicular
2937	
2917	
2985	
2860	
1661	1659
1464	1458
1451	1446
1437	
1371	1379
1363	1312
1286	
996	

Figure 4(i). The majority of the bands occurring in this orientation are at frequencies above 1000 cm^{-1}.

As rubber crystallizes, a number of specific changes can be identified, which are discussed below in detail. In the C–H stretching region, bands at 2965, 2930, 2901, 2873 and 2839 cm^{-1} are seen to increase in intensity. The complexity of the spectrum prevents any further comment. There is a small increase in the peak intensity of the C=C stretch at 1671 cm^{-1}. Comparison with the spectrum of amorphous natural rubber shows that this peak has undergone a 6 cm^{-1} shift from 1665 cm^{-1}, which accounts for the pseudo-first-derivative lineshape observed in *Figure 4(i)*. The peak position appears to be temperature-dependent, although it is known to be generally insensitive to the isomerism about the C=C group[13,15]. Therefore, this was a completely unexpected observation, for which there is, as yet, no explanation.

The mid-frequency region (1500 to 1000 cm^{-1}) displays the most significant changes. New bands are seen at 1129 and 1004 cm^{-1}. Also, the bands at 1286 and 1042 cm^{-1} show a relatively large increase in intensity. These are assigned as a δ(C–H) bend and a CH_3 rocking motion, respectively. For this discussion, consider the bands at (i) 1374 and 1360 cm^{-1} and (ii) 1454 and 1429 cm^{-1} as *doublets*. In each case, both components have increased intensity and, furthermore, as a consequence, there is apparent enhancement in the band resolution. For doublet (ii), the higher-frequency band shows a slightly larger intensity increase than the lower-frequency band whereas the change is comparable for both bands in doublet (i). In contrast, only the high-frequency component of the third pseudo-doublet at 1332 cm^{-1} exhibits any change. Below 1000 cm^{-1}, only one band at 492 cm^{-1} shows any difference, and this is very weak.

Stretch direction perpendicular to laser polarization. The changes in the spectrum of natural rubber due to ordered amorphous material were negligible in this case. The differences observed were all very weak increases in intensity of existing bands and are shown in *Table 3*. All the bands affected fall in the mid-frequency region, 1700 to 1300 cm^{-1}, of the spectrum.

The *FT*-Raman spectra of a strip of stretched natural rubber held perpendicular to the laser polarization direction when heated (+60°C) and cooled (−60°C) show a number of dissimilarities. The spectral differences arising from sample crystallization are listed in *Table 2* and the spectrum of crystalline rubber (stretched/heated subtracted from stretched/cooled) is displayed in *Figure 4(ii)*. Apart from being much weaker than the equivalent parallel spectrum, there are a number of other significant differences between them; in particular, there are a large number of changes below 1000 cm^{-1} that are not observed for the parallel orientation.

The changes in the C–H stretching region are almost exactly analogous to the parallel case. Peak increases are seen at 2965, 2932, 2906, 2874 and 2841 cm^{-1}. The exception is the peak at 2945 cm^{-1}, which only appears in the spectrum for the perpendicular orientation. Again, the ambiguous behaviour of the C=C stretch is observed; the peak increases in intensity on crystallization and is shifted to 1672 cm^{-1}, hence giving rise to the lineshape in *Figure 4(ii)*.

Between 1500 and 1000 cm^{-1} the observations are broadly similar to the parallel case. There is a new band at 1004 cm^{-1}, and others at 1042, 1128 and 1286 cm^{-1} are again seen to be of increased intensity, but to a relatively much lesser extent than observed for the parallel orientation. Both components of the doublet at 1454 and 1427 cm^{-1} increase in intensity, although the 1427 cm^{-1} peak shows a much larger change. This is the converse of the parallel situation and, moreover, the effect is more pronounced. From the assignment of Koenig[13], this band is a CH_3 deformation, which would be expected to have the polarization tensor elements off-axis and therefore be more prominent in the perpendicular spectrum. Again the band resolution is apparently greater. The band at 1374 cm^{-1} increases in intensity whereas that at 1360 cm^{-1} does not, which contrasts with the parallel spectrum, in which both bands show similar spectral changes. A further difference is the appearance of a new band at 1317 cm^{-1}.

The largest differences between the sample having parallel and perpendicular orientation occur in the fingerprint region. The only coincidence between the two spectra is the increase in intensity of the band at 490 cm^{-1}. In addition in the perpendicular case, there are new bands observed at 981, 876, 849, 763, 521 and 460 cm^{-1}. These are all weak features, although those at 876, 490 and 460 cm^{-1} are the more notable changes.

COMPARISON OF SPECTRA FROM STRAIN-INDUCED AND THERMAL CRYSTALLIZATION IN NATURAL RUBBER

A general observation is that the spectral characteristics of crystalline natural rubber are much weaker in stretched samples than in cold-soaked ones. The most significant result is that the observed band frequencies are identical for strain-induced and thermal crystallization except for the anomaly of the shifting C=C stretch band at ~1665 cm^{-1} in the stretched cases. In the thermal case there can be no orientation of the crystallites and hence all possible spectral changes are observed in a single spectrum. Stretching the rubber forces the crystallites to have some order, resulting in the total spectrum being partially resolved into perpendicular and parallel components. It would be intuitively expected that the stretching vibrations would be predominantly seen in the parallel spectrum and the wags and bends in the perpendicular one. Twists would be expected in both. This would appear to be very generally the case as the main features in the parallel spectrum are in the mid-frequency range whereas those in the perpendicular spectrum are in the low-frequency range. Ideally, it would be desirable to compare the sum of the perpendicular and parallel spectra with the cold-crystallization spectrum, but the scale differences make this impracticable using our current computer software.

The discussion of the individual bands falls in the preceding subsections. The spectral differences due to crystallization have been subdivided into two categories: those which have changed existing bands and those where new bands are generated. It is of interest that the parallel spectrum shows only changes to the existing bands with the exception of the appearance of a feature at 1004 cm^{-1}. In comparison, the perpendicular spectrum shows many of the changes to existing bands, although often to a lesser extent, but also contains all of the new bands.

Cold soaking slowly forms *lamellar-type* crystals[6], which are stable. Stretching natural rubber produces unstable crystallites, which are thought to be *bundle-like* in nature. From this work, the similarity of the vibrational bands due to crystallization suggests that the packing is the same in both cases. It has been reported that cold crystallization of natural rubber can result in a maximum of 48% crystallization[26] but is generally much lower than this[26,27]; the typically accepted value is currently ~30% crystallization. In comparison, reports suggest that stretching natural rubber results in a degree of crystallinity dependent upon the sample extension, the strain rate[28], the exact composition of the natural rubber and the nature of the crosslinking, in particular the composition of vulcanizates[26,27,29]. Crystallinity for an average natural rubber sample may be as low as 5% at 400% extension and >30% at 800% extension. At 500% extension, as used for the experiments described, there will be between 15 and 30% crystallinity. Therefore, the spectral changes due to crystallization of natural rubber would, in the most favourable case, be expected to be of a similar order of magnitude whether formed by prolonged cooling or stretching to large extensions, as the degree of crystallinity would be approximately the same. In the least favourable case corresponding to minimum crystallinity on stretching, the crystalline spectrum of highly extended rubber would be expected to be significantly weaker than that for the cold-crystallized sample. In fact, as mentioned earlier, the spectral changes for a highly extended sample are significantly weaker than those resulting from prolonged cooling, suggesting less crystallization of the sample on stretching than from cold soaking. In addition to the explanation given above, it is possible that this apparent discrepancy could also be partially explained by the anisotropic nature of the stretched sample or due to the differences in the Raman scattering cross-section between the two morphologies.

RAMAN POLARIZATION EXPERIMENTS FOR STRAIN-INDUCED CRYSTALLIZATION

The results described are completely consistent with the well known concept that strain-induced crystallization

Table 4 Polarization analysis for the crystallization bands from the *FT*-Raman spectrum of natural rubber: sample stretched in *parallel* orientation with respect to the laser polarization direction

Frequency (cm^{-1})	Analyser parallel	Analyser perpendicular	Assignment
2965		x	$\nu(CH_3)$
2930		x	$\nu_1(CH_2)$
2901		x	
2873		x	
2839		x	
1671	x	x	$\nu(C{=}C)$
1454	x	x	$\nu_a(CH_3)$
1429		x	
1374	x		
1360	x		$\delta(CH_2)$
1332	x		
1286	x	x	δ(CH) bending
1129	x		ν(C–C) *cis* or CH_2 wag
1042	x	x	γ_r (CH_3)
1004	x	x	
492		x	$\gamma_r(=CC_2)$, $\gamma_s(=CC_2)$

Table 5 Polarization analysis for the crystallization bands from the *FT*-Raman spectrum of natural rubber: sample stretched in *perpendicular* orientation with respect to the laser polarization direction

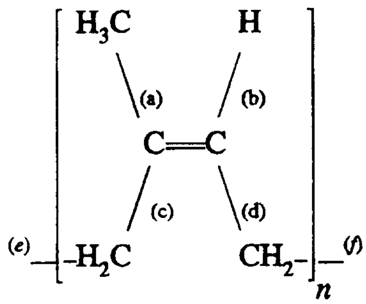
Frequency (cm^{-1})	Analyser parallel	Analyser perpendicular	Assignment
3046		x	$\nu(=CH)$ in ($C(CH_3)=CH$)
2965	x		$\nu(CH_3)$
2945	x	(x), vw	
2932	x		$\nu_1(CH_2)$
2906	x		
2874	x	(x), vw	
2841	x	(x), vw	
1672	x	x	$\nu(C{=}C)$
1454	x		$\nu_a(CH_3)$
1427	x	x	
1374	x		
1317	x		
1286		x	δ(CH) bending
1128	x		ν(C–C) *cis* or CH_2 wag
1042		x	$\gamma_r(CH_3)$
1004	x	x	
981		x	
876	x	x	
849		x	
763		x	
521		x	
490		x	$\gamma_r(=CC_2)$, $\gamma_s(=CC_2)$
460	x		

results in oriented crystallites. Therefore it should be possible to investigate the molecular structure within these units by elucidating information on the Raman tensor components. Experiments to allow further analysis of the parallel and perpendicular spectra were performed by placing a polarizing filter in the *analyser region* (between the sample and detector) and orienting it parallel with and perpendicular to the laser polarization. *Tables 4* and *5* present the polarizing filter results for the crystallization bands of natural rubber in which the sample is oriented parallel and perpendicular, respectively. Where they are known, the assignments are also given. As many of the band assignments are currently unknown, the following discussion will, of necessity, be restricted. Although it appears that many of the bands are exclusively seen with one experimental arrangement, it should be borne in mind that the changes due to crystallization are weak (since there is only a relatively small proportion of crystalline material) and may not be observable in others due to experimental limitations.

For parallel orientation of the sample, most of the CH stretching bands in the region 3000 to 2800 cm^{-1} were observed with the analyser in a perpendicular orientation, whilst the mid-frequency range bands were predominantly observed with the analyser parallel. At lower frequencies the bands were again detected in the spectrum for the analyser perpendicular. It is intuitively convincing that those bands observed with the analyser parallel are undergoing highly symmetric vibrations.

Similar generalizations can be made for perpendicular orientation of the sample. Most of the bands with frequencies higher than 1000 cm^{-1} were observed when the analyser was oriented parallel, whereas, almost exclusively, bands with lower frequencies were only detected when the analyser was perpendicular.

It is difficult to present a meaningful discussion beyond the handwaving description given without making assumptions about the symmetry class of crystalline natural rubber. The repeat unit in rubber (*cis*-polyisoprene) is:



The isoprene unit is a planar entity[30] in which there is no rotation about the double bond, but free rotation is allowed about bonds (e) and (f), which can assume *trans* (*t*) and *gauche* ($g^{\pm}$) conformations. Skew conformational states ($s^{\pm}$) can be adopted by the C–CH_2 bonds ((c), (d) and the equivalent to (d) in the preceding unit) attached to the double bond[31,32]. In amorphous rubber, the flexibility suggests that it is reasonable to choose a single isoprene unit as the repeat period. Therefore, natural rubber will probably have a very low line-group symmetry, possibly Cs, which is applicable when analysing the depolarization ratios of the amorphous natural rubber spectrum. In this symmetry group, the diagonal polarization tensor components and α_{xy} have A′ symmetry, whilst the α_{xz} and α_{yz} components have A″ symmetry. It is more usual, particularly for crystal considerations, to define two isoprene units as the repeat period along the fibre length; neighbouring isoprene units have the double-bond substituents on opposite sides of the polymer backbone (the backbone acts as a mirror plane). If planar, this unit has Cs symmetry, otherwise it only possesses $C_2^s(z)$ and E symmetry elements (see later discussion); it is not considered applicable to the analysis of the amorphous rubber spectrum.

The crystal symmetry and hence the space-group symmetry have not been unambiguously determined. There is some argument as to whether strain-induced

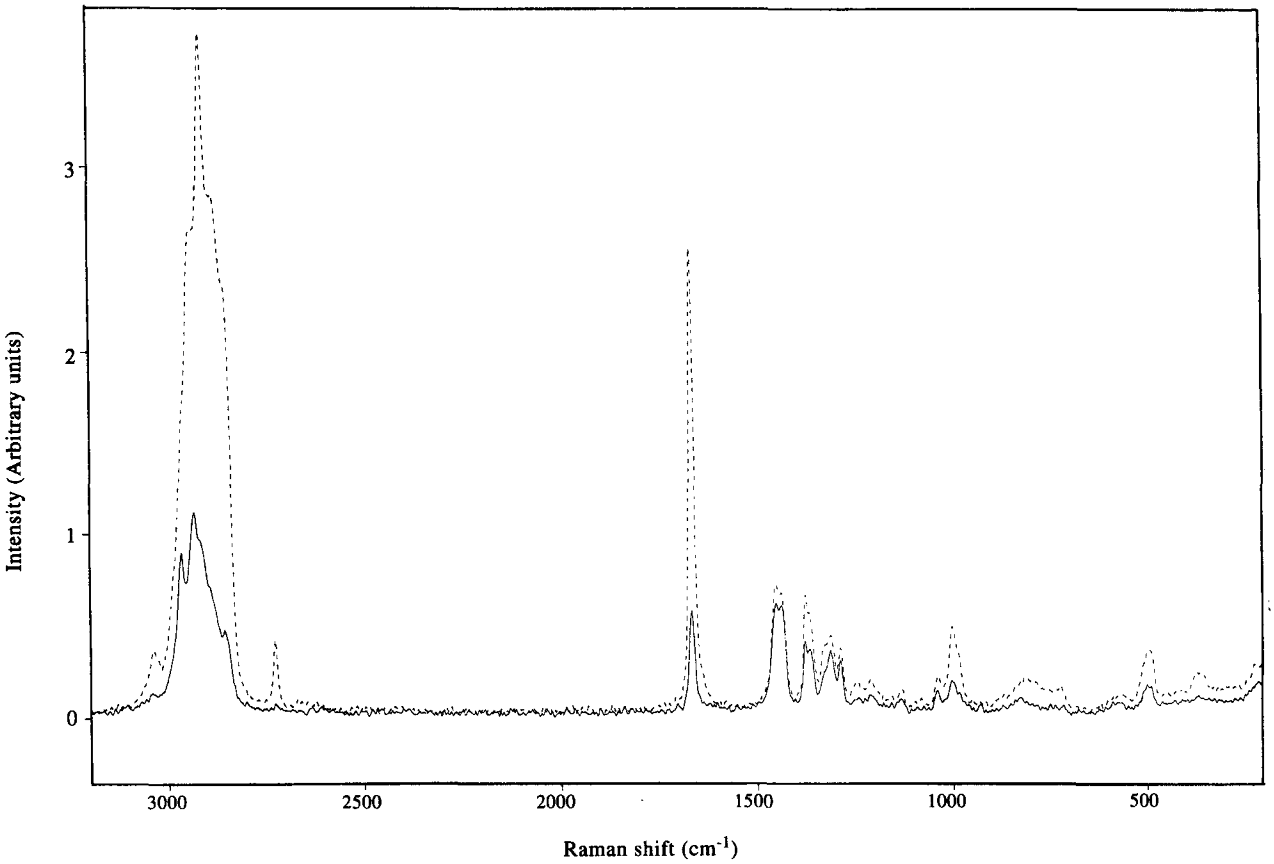


Figure 5 *FT*-Raman spectra of amorphous natural rubber with a polarizing filter in the analyser region (i) parallel (dashed) and (ii) perpendicular (solid) with respect to the laser polarization

crystals of natural rubber have a monoclinic or an orthorhombic unit cell[8,29,30,33–35], although the monoclinic cell arrangement appears to be the one more generally accepted[8,30,35]. The only difference between the two proposed structures is in the angle β: the monoclinic cells have $\beta = 92°$, whereas for the orthorhombic cells β is 90° (ref. 36). As previously mentioned, the other cell dimensions are $a = 12.5$ Å, $b = 8.9$ Å and $c = 8.1$ Å (ref. 8). Both unit cells contain four long chains parallel to the c axis; the c repeat unit of each molecule contains two isoprene units. It is thought, however, that the measured values of the lattice parameters, a and b, change as a function of applied strain (i.e. stress to which the crystals are subjected)[36]. Additionally, these parameters are considered to be a function of the resulting lattice defect concentration in the crystals. This change, for which there is no simple explanation, is small for extensions of up to 400%; as this work focuses on larger extensions, it should perhaps be borne in mind that the cell dimensions could, in fact, be slightly different from those given.

The most comprehensive study commonly referenced is that presented by Bunn[8]. These X-ray studies on both thermal and strain-induced crystals of natural rubber have shown the crystal structures to be identical. The four component molecules of the monoclinic unit cell are asymmetric; two have left-handed screws and two have right-handed screws, with one molecule up and one molecule down in each case. The space group is $P2_1/a$, which corresponds to the C_{2h} symmetry group[37]. More recent studies[30,35] showed general agreement with Bunn[8] except for the proposed regular crystal ordering. Nyburg[30] concluded that, in the individual molecules, the isoprene groups are planar and are connected by slightly *short bonds* having normal tetrahedral angles between them, giving the molecular conformation *cis*-STS–*cis*-STS[37]. A statistically disordered crystal was proposed in which two mirror image forms of the molecular chain exist with equal proportion. They were unable to determine the angle β accurately, but it was thought to be close to or possibly equal to 90°. In comparison, Natta and Corradini[35] concluded that statistical disorder only occurs along the a axis.

Therefore, the following analysis is given assuming a monoclinic unit cell with C_{2h} symmetry. From the C_{2h} character table, it can be seen that the diagonal polarization tensor components and α_{xy} have A_g symmetry, whilst the α_{xz} and α_{yz} components belong to the B_g class. This scheme can easily be translated to correspond to an orthorhombic cell with D_{2h} symmetry[38]. The appropriate correlation elements are shown in *Table 6*. Hence, the symmetries of the tensor components are A_g for α_{xx}, α_{yy} and α_{zz}, B_{1g} for α_{xy}, B_{2g} for α_{xz} and B_{3g} for α_{yz}.

As a precursor to analysing the crystalline bands, the depolarization spectra of natural rubber were studied. Natural rubber in its standard state is a completely random amorphous material. Therefore recording the spectra with an analysing polarization filter with Z and Y orientation (in the laboratory axes defined earlier), respectively, should allow depolarization ratios to be calculated and hence indicate some band assignments.

Figure 5 shows the comparative depolarization spectra with the analysing filter (i) parallel (dashed) and (ii)

Table 6 Correlation table between C_{2h} symmetry, which applies to the monoclinic unit cell, and D_{2h} symmetry, which applies to the orthorhombic unit cell

C_{2h}	→	D_{2h}
A_g	→	$A_g + B_{1g}$
B_g	→	$B_{2g} + B_{3g}$
A_u	→	$A_u + B_{1u}$
B_u	→	$B_{2u} + B_{3u}$

perpendicular (solid) to the laser polarization. The weak nature of many of the bands in the spectrum and imperfect instrument characteristics necessarily mean there is a relatively large experimental error in the depolarization ratios, ρ. It is known that the instrument used in these experiments gives poor polarization results irrespective of the sample. Despite strenuous efforts to identify and eradicate the problem, it is only possible to claim that a value of $\rho = 0.1$ is the best that can be expected in a spherically symmetric situation. As a consequence, the familiar range 0 to 0.75 becomes 0.1 to 0.85. Therefore, assuming Cs symmetry, it would be expected that A′ modes would have ρ close to 0.1 and A″ modes would have $\rho \approx 0.85$. In spite of these limitations, it is however possible to deduce that the bands at 1452, 1440, 1311, 1287 and 1131 cm^{-1} are of A″ symmetry, and those at 3038, 2727, 1666 and 1002 cm^{-1} are A′ symmetry. Referring to *Table 1*, this would indicate that the A″ assignments are $\nu_a(CH_3)$, $\delta_a(CH_3)$, CH_2 twist, CH bending and CH_2 wag, respectively. Similarly, the A′ assignments are ν(=CH) in $(C(CH_3)=CH)$, unassigned, ν(C=C) and unassigned, respectively.

As the crystals formed under strain are oriented, it is not possible to calculate meaningful depolarization ratios. It is however possible to deduce some symmetry assignments of the crystalline bands according to the analysis for C_{2h} symmetry in *Table 7*. It can be seen that the information derived from Raman scattering tensor components is identical for C_{2h} and D_{2h} crystal symmetries[40]. Therefore it is straightforward to switch between the two possible structural cases. Experimental assignments are difficult and tenuous because of very weak signals and overlapping bands. It is thought that, on the evidence available, the bands at 1454, 1374, 1360, 1332, 1317 and 1129 cm^{-1} have A_g symmetry, whilst those at 3046, 1429, 1042 and 492 cm^{-1} are more likely to be of the B_g class.

Experiment 1, as defined in *Table 7*, gives unique information on the α_{zz} polarization tensor component, which must lie along the axis of the molecule. Therefore, the bands at 1374, 1360, 1332 and 1129 cm^{-1} have a dominant α_{zz} value in their tensor matrices in order to observe significant Raman scattering in the aforementioned experiment. In particular, the band at 1360 cm^{-1} is only significantly observed in experiment 1, whereas the other bands are also observed in experiment 3, which gives information predominantly on the α_{xx} and α_{yy} tensor components, lying perpendicular to the axis of the molecule. Furthermore, the lines at 1454, 1317 and 460 cm^{-1} are only present in experiment 3, suggesting that their dominant polarization tensor components are α_{xx} and α_{yy}. It should be noted that experiments 2 and 4 are predicted to be identical. This was found to be the case within experimental error. Hence, the bands at 3046, 1429, 1042 and 492 cm^{-1} have significant α_{xz} and α_{yz} tensor components.

INFRARED POLARIZATION EXPERIMENTS FOR STRAIN-INDUCED CRYSTALLIZATION

Owing to the nature of the Raman scattering experiment, there is always some ambiguity in polarization analysis. The situation is often much clearer if an infra-red experiment can be performed.

Experimental

Infra-red transmission spectra were recorded using a standard Perkin-Elmer system 2000 *FT*i.r. spectrometer with a mid-i.r. source and TGS (triglycine sulfate) detector. The polarization analyser was of the gold wire type and was kept fixed throughout the experiments. Spectra were accumulated in the range 450 to 4000 cm^{-1} by averaging 10 scans at 4 cm^{-1} resolution. The sample was a section from a condom that had been cleaned in acetone; the *FT*-Raman spectrum is identical to that described earlier. These products are invariably made of natural rubber and are, of course, conveniently thin in section. Unstretched sample spectra were mounted on a standard holder. For stretched samples the apparatus shown in *Figure 1b* and described earlier was used but without the glass jacket; the nature of the sample requires >700% extension to give appropriate results.

Spectra were recorded with the sample stretched and unstretched. In each case there were three experiments: (i) no analysing infra-red polarizer, (ii) the analysing polarizer set parallel to the sample stretch direction, and (iii) the analysing polarizer set perpendicular to the sample stretch direction.

Results and discussion

A typical *FT*i.r. spectrum of natural rubber is shown in *Figure 6a* and the absorption frequencies are listed in *Table 1*. An equivalent *FT*i.r. spectrum for a stretched

Table 7 Summary of Raman polarization tensor analysis from analysing polarizer experiments as applicable to natural rubber; it should be noted that z refers to the orientation of the sample (stretch direction) and that x and y are indistinguishable (see discussion in text)

			Assignment	
Experiment	Porto nomenclature[39]	Tensor information[40]	(C_{2h})	(D_{2h})
1	$x(zz)x + y(zz)y$	$(\alpha_{zz})^2$	A_g	A_g
2	$x(zy)x + y(zx)y$	$\frac{1}{2}[(\alpha_{yz})^2 + (\alpha_{zx})^2]$	B_g	$B_{2g} + B_{3g}$
3	$x(yy)x + y(xx)y + x(yx)x + y(xy)y$	$\frac{1}{8}[2(\alpha_{xx} + \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{yy})^2 + 4(\alpha_{xy})^2]$	A_g	B_{2u}
4	$x(yz)x + y(xz)y$	$\frac{1}{2}[(\alpha_{yz})^2 + (\alpha_{zx})^2]$	B_g	$B_{2u} + B_{3u}$

Table 8 Polarization analysis for the crystallization bands from the infra-red spectrum of natural rubber; band intensities are denoted according to the key in *Table 1*. The polarizer orientation is given relative to the direction of sample stretch

*FT*i.r. strain-induced crystallization bands (cm^{-1})	Analyser parallel	Analyser perpendicular
3043 w		x (B_u)
2965–2865 broad m	x	x
1684 w	x	
1667 w	x (A_u)	
1662 w	x (A_u)	
1653 w	x	x
1643 w	x	x
1635 w	x	x
1615 w	x	
1558 w	x	x
1540 w	x	x
1521 w	x	x
1506 w	x	x
1463 sh. m		x (B_u)
1456 m	x	x
1448 m	x	x
1436 m	x	x
1376 m	x	x
1362 m	x (A_u)	
1338 sh. w		x
1289 w		x
1271 w	x (A_u)	
1263 w	x	x
1251 vw	x	x
1231 w	x A_u)	
1209 w		x (B_u)
1175 w	x	x
1124 m	x (A_u)	
1103 m	x (A_u)	
1058 vw	x (A_u)	
1039 w	x	x
1019 vw	x	x
979 w	x (A_u)	
963 w	x (A_u)	
908 w	x	x
873 w	x	x
845 m	x	x
801 w	x	x
763 w	x	x
681 m	x (A_u)	
668 s	x (A_u)	
655 m	x (A_u)	
618 w	x	x
565 m	x (A_u)	
546 w		x (B_u)
489 w		x (B_u)

sample of natural rubber is given in *Figure 6b*. Comparison between the spectra of stretched and unstretched samples clearly shows that there are a number of significant differences which can be directly attributed to crystallization and which are discussed below in detail. A sample extension of ~700% was chosen to give the optimum crystalline natural rubber spectrum; it is well known that crystallization-sensitive bands vary with the degree of crystallinity[37]. By subtracting the unstretched sample spectra from that of the equivalent stretched sample spectra, it is possible to isolate the changes in the infra-red spectrum due to both crystalline and ordered amorphous material. It has been mentioned previously that the spectral changes in the Raman scattering due to ordered amorphous material are much weaker than the crystalline effects and cannot account for any new bands. Hence, the analysis is essentially that for the crystalline material. *Figure 7* shows the *FT*i.r. difference spectrum corresponding to the spectrum of crystalline natural rubber: (a) 3500 to 2500 cm^{-1} and (b) 1700 to 450 cm^{-1}. The crystallization bands, with assignments where they are unambiguous, are listed in *Table 8*.

Most changes observed in the spectrum of the stretched natural rubber sample are weak. In general, these changes, which are thought to be due to crystallization, are more pronounced in the fingerprint region. However, there are differences observed in the region between 3500 and 2500 cm^{-1} where bands are assigned to C–H stretching modes. Unfortunately, owing to the complex nature of the spectrum in this region, characterized by the similar intensities of the many overlapping bands, it is not possible to deduce anything further.

In the region 1700 to 450 cm^{-1} there are a large number of spectral changes. It is well known that the C–H bending vibration at 837 cm^{-1} in amorphous rubber shifts to 844 cm^{-1} on crystallization[6]. This has been observed; the band at 837 cm^{-1} in the unstretched spectrum of natural rubber does not appear in the corresponding stretched spectrum and a new fairly broad band appears at 843 cm^{-1}, which confirms that the stretched sample contains regions of crystallinity. Furthermore, a number of new bands are observed at 1653 (m), 1646 (w), 1635 (w), 1576 (w), 1569 (w), 1558 (w), 1540 (w), 1522 (w), 1506 (w), 1233 (sh. m), 1210 (sh. w), 980 (w) 684 (w), 668 (m) and 655 cm^{-1} (w). These would also suggest that the sample is partially crystalline. Moreover, they exhibit several noteworthy features. In particular, the band at 668 cm^{-1} is extremely sharp and fairly strong compared to all other resolved features. Similarly, the bands at 1653, 1646, 1635, 1576, 1569, 1558, 1540, 1522 and 1506 cm^{-1} are also sharp but of weak intensity. There are changes in intensity of the bands at 1456 (s), 1448 (s), 1436 (s), 1376 (s), 1362 (sh. m), 1038 (m), 1015 (sh. m), 503 (sh. w) and 490 cm^{-1} (m). Some of these can be assigned. The features at 1456 and 1015 cm^{-1} are described as CH_3 and C–CH_2 stretching modes, respectively, whilst that at 1362 cm^{-1} is assigned as a CH_2 bending motion. Both bands at 1038 and 490 cm^{-1} are rocking modes for CH_3 and $=CC_2$ groups, respectively.

By placing an infra-red polarizer between the unstretched sample and infra-red detector, it is possible to assign symmetries to a number of the vibrational bands in crystalline natural rubber assuming C_{2h} space-group symmetry. In this case, the T_z component (along the axis of the molecule) has A_u symmetry and the $T_{x,y}$ components (perpendicular to the axis of the molecule) are of the B_u classification. The alternative D_{2h} space-group symmetry results in the T_x, T_y and T_z components having B_{3u}, B_{2u} and B_{1u} symmetry, respectively. As the x and y axes are indistinguishable, only B_{1u} symmetry can be isolated; a simple correlation therefore exists between the two symmetries (see *Table 6*). *Figure 8* presents the *FT*i.r. difference spectra (unstretched sample spectrum subtracted from stretched sample spectrum) with (i) polarizer parallel to sample stretch (dashed) and (ii) polarizer perpendicular to sample stretch (solid). Only the fingerprint region is displayed, as this is where the crystalline spectrum can potentially be analysed. The results are given in *Table 8*. It has been deduced that the bands at 3043, 1463, 1209, 546 and

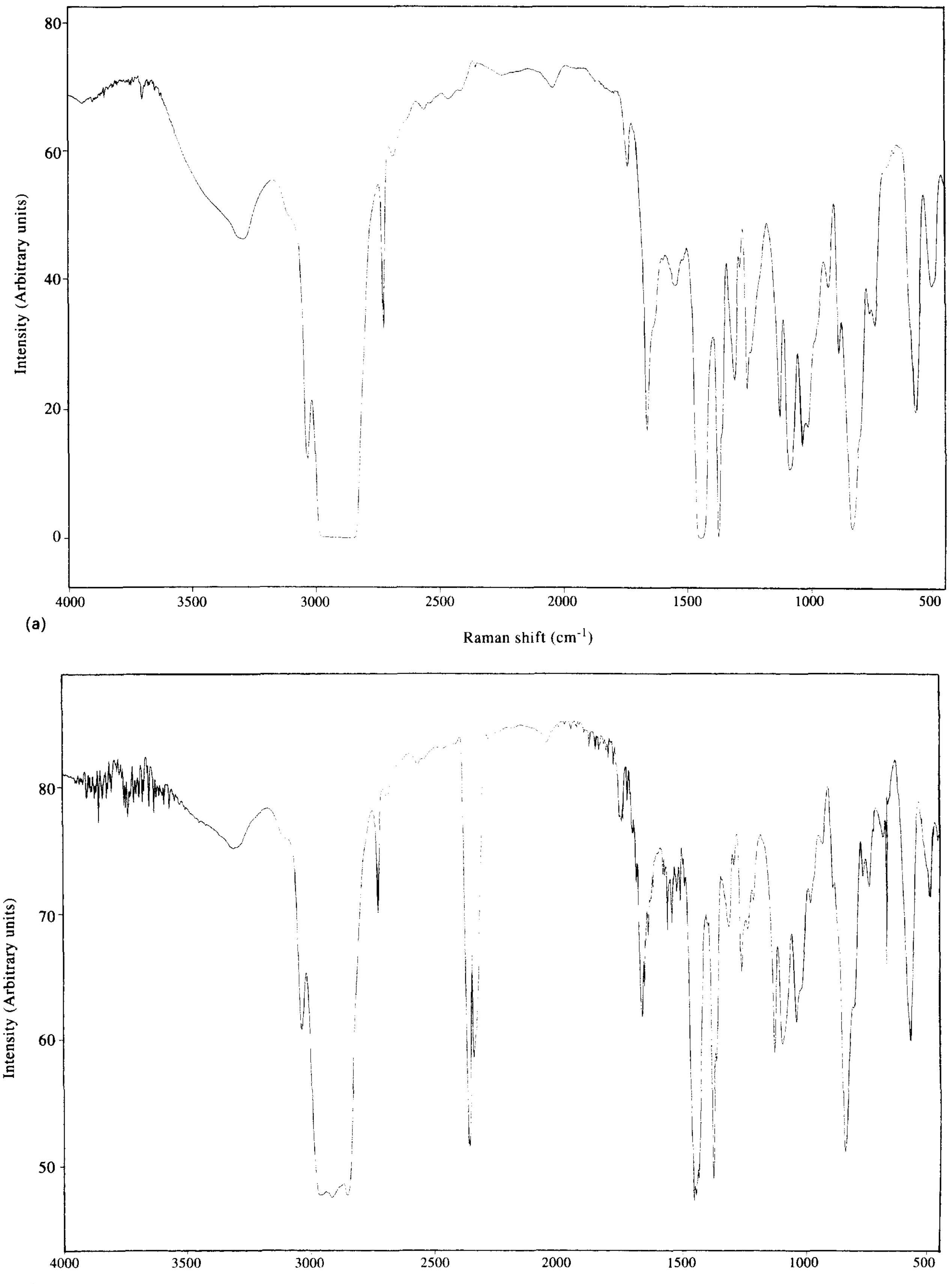


Figure 6 *FT*i.r. spectrum of natural rubber recorded at room temperature: (a) amorphous (unstretched) and (b) stretched to ~700%. The strong peak near to 2400 cm^{-1} is a background effect and of no relevance to the discussion

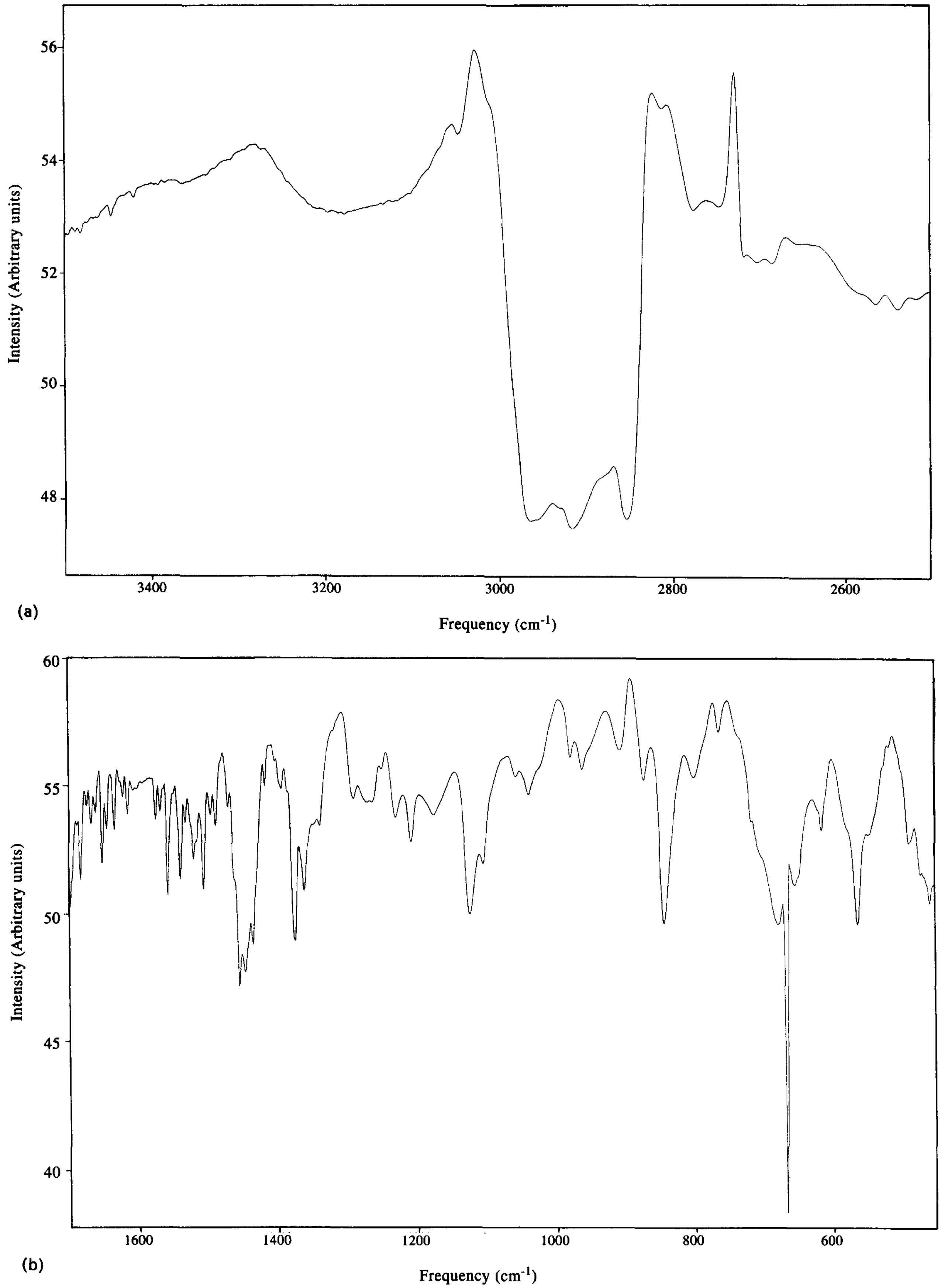


Figure 7 *FT*i.r. difference spectrum (spectrum for unstretched sample subtracted from that for stretched sample) showing the vibrational modes of natural rubber due to crystallization on stretching to very high extensions: (a) 3500 to 2500 cm^{-1} and (b) 1700 to 450 cm^{-1}

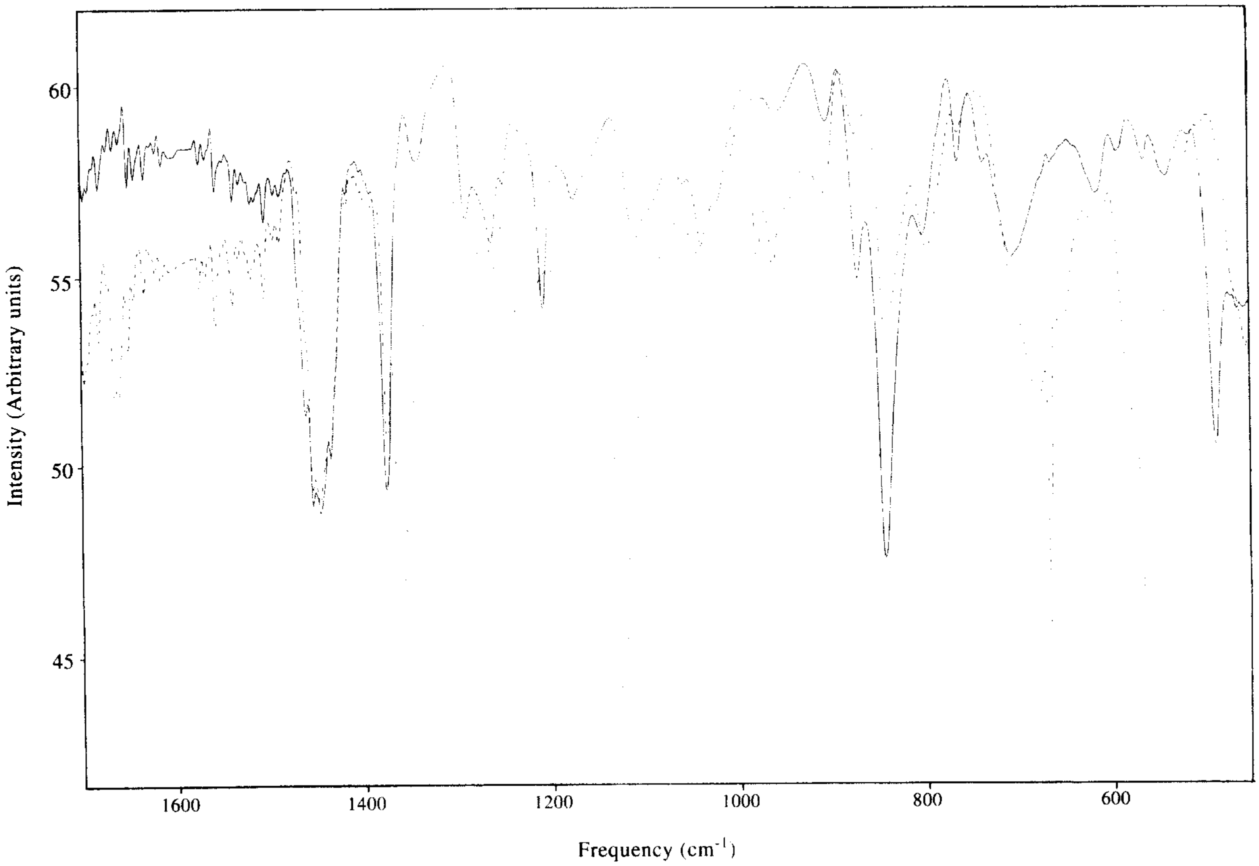


Figure 8 *FT*i.r. difference spectra (spectrum for unstretched sample subtracted from that for stretched sample) showing the vibrational modes of natural rubber due to crystallization on stretching to very high extensions: (i) analysing polarizer parallel to (dashed) and (ii) analysing polarizer perpendicular to (solid) the sample stretch direction

489 cm^{-1} are of B_u symmetry, whilst those at 1667, 1662, 1362, 1271, 1231, 1124, 1104, 1058, 979, 963, 681, 668, 655 and 565 cm^{-1} are of A_u symmetry.

SUMMARY OF RESULTS FROM POLARIZATION EXPERIMENTS

It has been possible to propose symmetry assignments for a number of the crystalline bands in natural rubber using both *FT*i.r. and *FT*-Raman techniques. In addition, a number of proposed assignments have been made for the vibrational bands in amorphous natural rubber using depolarization ratios calculated from *FT*-Raman scattering experiments. These assignments are summarized in *Table 9*.

The correlation between Cs and C_{2h} symmetries is:

$$A' \rightarrow A_g + B_u \qquad \text{and} \qquad A'' \rightarrow A_u + B_g$$

In the Raman scattering experiment, only the A_g and B_g modes are active, whereas in the infra-red experiment, the A_u and B_u modes may appear as absorptions. The crystalline results are consistent with this statement of mutual exclusion, giving confidence in the correctness of the analysis. As would be expected, vibrational bands are often not found in both the amorphous and crystalline spectra of natural rubber. Furthermore, it has only been possible to assign a small proportion of the reported bands in each case. Of the assigned bands, only those at 1452, 1131 and 1666 cm^{-1} are observed for both amorphous and crystalline natural rubber. Using the above correlation, it seems surprising that the bands at

Table 9 Summary of vibrational band symmetry assignments for natural rubber using a Cs line group for the amorphous material and C_{2h} space group for the crystalline material

Cs symmetry assignment	A′	A″
Amorphous natural rubber, Raman (cm^{-1})	3038	1452
	2727	1440
	1666	1311
	1002	1287
		1131
C_{2h} symmetry assignment	A_g	B_g
Crystalline natural rubber, Raman (cm^{-1})	1454	3046
	1374	1429
	1360	1042
	1332	492
	1317	
	1129	
C_{2h} symmetry assignment	A_u	B_u
Crystalline natural rubber, *FT*i.r. (cm^{-1})	1667	3043
	1662	1463
	1362	1209
	1271	546
	1231	489
	1124	
	1104	
	1058	
	979	
	963	
	681	
	668	
	655	
	565	

1452 and 1131 cm^{-1} assigned as A$''$ in amorphous natural rubber have been assigned as A_g in the Raman spectrum of crystalline natural rubber. Similarly, the C=C stretch at 1666 cm^{-1}, which is known to lie along the main axis of the molecule, has A$'$ symmetry in amorphous rubber whereas it has A_u symmetry in crystalline rubber. These contrary results could only be explained if the molecules in the crystal were oriented perpendicular to the direction of stretch, which conflicts with existing data[8]. In general, X-ray diffraction results conclude that the natural rubber molecules have their chain axes parallel to the direction of elongation[6]. However, in contrast, Siesler[17] analyses his infra-red results on a 650% drawn sample of sulfur-crosslinked natural rubber to suggest that the average polymer molecules and the polymer chains in the crystal phase are oriented at 40° and 30°, respectively, with respect to the direction of stretch. At this stage, it is necessary to do further experiments and analysis before anything more conclusive can be deduced. Any analysis is hampered by the generally weak crystalline spectra, particularly from Raman scattering experiments, and by the limited spectral assignment.

CONCLUSION

FT-Raman spectroscopy has been shown to be a useful tool in the study of crystallization processes in polymers. A large number of changes have been observed in the spectrum of natural rubber in which there is some crystallization. When natural rubber was cold soaked at −25°C, results were obtained in good agreement with previous studies[23]. All spectral changes can be attributed to crystallization, as the sample is otherwise completely amorphous. Stretching natural rubber produced spectral changes which have not been presented elsewhere. Stevenson[20] made some attempt to record the data but the studies proved inconclusive. It has been possible to extract information on amorphous ordered material and crystallization effects. Ordered amorphous material does exhibit detectable spectral changes, which had not been fully appreciated in previous studies. These are weak compared to the crystallization features. The crystallites are oriented and this is reflected in the differences between the parallel and perpendicular spectra. Furthermore, the main changes in the parallel spectrum are in the mid-frequency range, whereas in the perpendicular spectrum there are a significant number of changes in the low-frequency region, consistent with stretches and deformations, respectively. Overall, the bands from cold crystallization and stress-induced crystallization are identical. New bands tend to appear in the perpendicular spectrum and band changes show more pronounced effects in the parallel spectrum. These spectral similarities would confirm that the crystals formed thermally and under extreme stress are of the same type.

FT i.r. spectroscopy has also proven useful for crystallization studies. In general, the observed spectral differences arising from crystallization are stronger in an infra-red experiment than in an equivalent Raman one; this is consistent with the inherent signal strengths expected for the two techniques. Additionally, the infra-red experiment necessarily results in a complete strain-induced crystallization spectrum, irrespective of the direction of sample stretch. As for Raman scattering, the infra-red spectrum of stretched natural rubber shows some band changes and the appearance of many new features. The new bands tend to be fairly sharp relative to the other spectral features, which is indicative of crystal vibrations. Polarization experiments confirm that the crystals are, in fact, oriented.

Furthermore, both *FT*-Raman and *FT* i.r. experiments in which a polarizer is placed between the sample and detector have proven useful in preliminary symmetry assignments for bands in the crystalline vibrational spectra of natural rubber. In particular, the stronger infra-red spectrum yields an unambiguous analysis. At present, the Raman spectra are too weak to give conclusive results. All the results are consistent with the C_{2h} space-group symmetry for the crystal with a monoclinic unit cell. Further assignments require better depolarization spectra (which is a function of both sample and instrument characteristics) and improved vibrational band assignments.

In summary, there are a number of important results arising from this work:

1. The first Raman and infra-red spectra of crystalline natural rubber are presented.
2. The cold-crystallization spectrum is identical to the strain-induced crystallization spectrum, confirming that the crystallites must be the same in both cases.
3. Anisotropic scattering data have been recorded for strain-induced crystals, demonstrating that, as expected, the crystallites must be oriented.
4. There is some evidence that the amorphous spectrum of natural rubber is different from that of the amorphous material in extended rubber. This could be due to a different rotational isomeric temperature in the two cases. The entropy reduction on stretching would of course suggest that the oriented amorphous material would have a lower rotational temperature than the relaxed material.
5. Unexpectedly, the C=C stretching frequency is temperature-dependent and yet it is identical in both the *cis* and *trans* isomers of polyisoprene.
6. Preliminary symmetry assignments for some vibrational bands are deduced in accordance with the generally accepted C_{2h} space-group symmetry[8].

The disappointing polarization measuring capability of the instrument available makes it unattractive to consider any attempt at the urgently needed rigorous assignment of the vibrational spectrum of crystalline natural rubber. This problem will be addressed in a further publication.

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