Laser Raman spectrum of isotactic polybutene-1 fibres

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Detailed polarized laser Raman spectra of isotactic hexagonal polybutene-1 fibres are presented. The use of different scattering geometries enables us to determine unambiguously the symmetry of Raman bonds from 300 to 3000 cm^{-1}. The comparison between calculated and observed intensities enables us to test the individuality of CH_2 and CH_3 group vibrations and shows that some bands, more particularly those located between 800 and 1200 cm^{-1}, can only be explained by the coupling of skeleton vibrations with side group vibrations.

INTRODUCTION

Isotactic polybutene-1 (IPB) exhibits three crystalline modifications: a stable hexagonal form, an unstable tetragonal form and a stable orthorhombic form[1-4]. These forms are designed respectively as modifications I, II and III and exhibit significantly different infra-red[5-8] and Raman[9] spectra.

Ukita[10], however, measured the polarized infra-red spectra of oriented films of IPB in the 700–3200 cm^{-1} region and he calculated the normal vibrations of this polymer by the use of the G.F. matrix method with a modified Urey–Bradley force field. No Raman spectra data relative to oriented samples of IPB are available to date. In this paper we present the laser Raman spectra, with analysis of the scattering light, of IPB fibres in its hexagonal form, in different scattering geometries. The experimental results enable a complete determination of the symmetry of Raman active normal modes from 300 to 3200 cm^{-1}. Also, the comparison between the observed and calculated intensities enables us to test the individuality of the vibrations of CH_2 and CH_3 groups and shows that several Raman bands can only be explained by the coupling of vibrations of groups directly linked to the skeleton of the chain, therefore being characteristic of the helicoidal structure of this polymer.

EXPERIMENTAL

Raman spectra were recorded on a double grating spectrometer built in our laboratory[11] using a Spectra Physics argon ion laser at 5145 Å wavelength (500 mW power) as excitation source. The polarization of the incident light was carried out using a half wave plate centred on 5145 Å, that of the scattering light using two other half wave plates centred on 5380 and 6080 Å respectively (850 and 2990 cm^{-1} from the excitation line). Wavelength accuracy was about ± 2 cm^{-1}.

Two scattering geometries were used (*Figure 1*), the stretching axis of the fibres being either perpendicular to the scattering plane (case A) or parallel to the laser incident direction (case B). The different possibilities of polarization enabled us to obtain the spectra relative to all the Raman tensor elements.

	$I_\perp$	$i_\perp$	$I_\parallel$	$i_\parallel$
case A:	ε^2_{zz}	ε^2_{xz}	ε^2_{zy}	ε^2_{xy}
case B:	ε^2_{yy}	ε^2_{zy}	ε^2_{yx}	ε^2_{zx}

x,y,z being axis linked to the sample (z parallel to the stretching axis, x any normal direction to the stretching axis, y normal to x and z). Also, the presence of spectra relative to the same elements of the Raman tensor in the two scattering geometries enabled us to compare the spectra all together.

The samples used were CdF chimie commercial IPB fibres, obtained by stretching of polybutene-1 characteristics of which are: $M_w = 394000$, $M_n = 80700$, isotacticity 99%. An X-ray diagram had shown the disorientation of chains with regard to the fibres axis is not more than 5 degrees. To avoid their deterioration by the laser beam, particularly in A geometry, they were placed in water and held stretched and parallel with one another by an appropriate device.

The Raman spectra obtained in the different polarization cases are represented on *Figures 2* (300–1500 cm^{-1} region) and *3* (2700–3000 cm^{-1} region). The importance of stray light in the A scattering geometry prevented the observation of all signals under 500 cm^{-1}. The nomenclature used to indicate the geometry of the Raman experiments in the *Figures 2* and *3* is due to Porto[12].

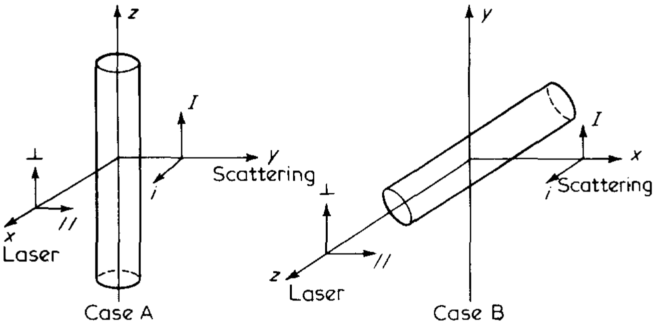

Figure 1 The different scattering geometries used

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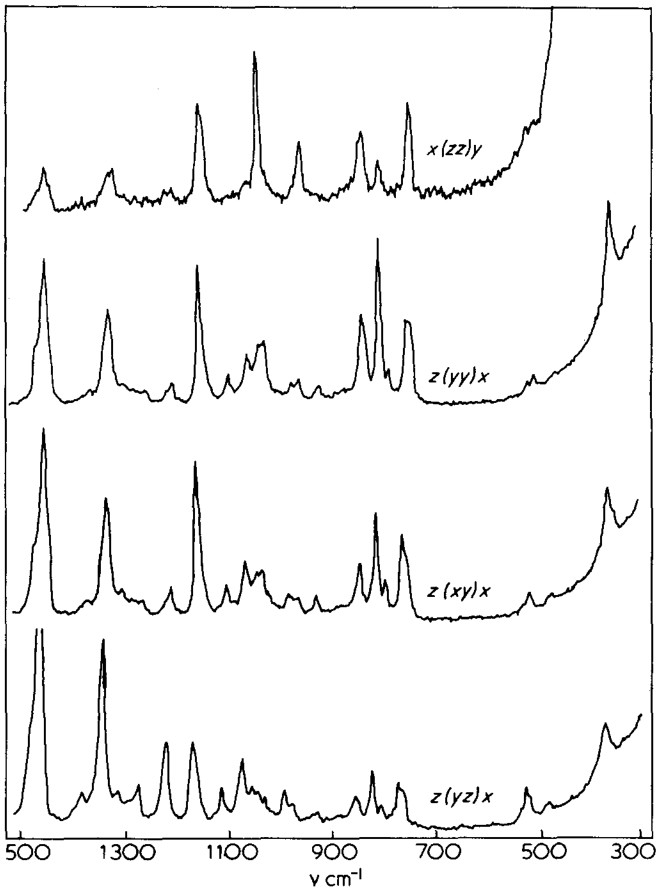

Figure 2 Raman spectra of polybutene-1 fibres in the region 300–1500 cm^{-1}. The relative intensity of the *x*(*zz*)*y* spectrum is multiplicated by 2

DISCUSSION

Symmetry of Raman modes

Modification I of isotactic polybutene-1 belongs to the R_{3c} or $R_{\bar{3}c}$ space group with six 3_1 helices in a hexagonal unit cell[2]; theoretically, the polymer normal modes would be classified into the symmetry species characteristic of the factor groups isomorphous with the above space groups. However, interchain interactions are weaker than intrachain interactions in polymers, expecially in polybutene-1 in which the unit cell contains chains in a statistical arrangement, the number of which is greater than in other polymers such as polyethylene or polypropylene. A good approximation exists, therefore, to take into account the symmetry of the isolated chain.

In hexagonal IPB repeating units, the polymer chain contains three structural units related to each other by a three fold helix axis. Thus, the normal vibrations of the polymer can be treated under the factor group of the line group, $C(2\pi/3)$ which is isomorphous with the point group C_3. Consequently in the assumption there is no crystalline interactions, the molecular vibrations of hexagonal IPB are classified into 34 modes belonging to A species and 35 degenerate modes belonging to E species, each of these modes being Raman active.

The sample used is formed by a group of parallel fibres in which the main axis of the chains is parallel to the stretching direction, the two other axes having no particular orientation in a plane perpendicular to the main axis; then, the Raman tensors relative to the A and E vibrations of the polymeric chain have, in the *xyz* axis as formerly described, the following respective forms:

$$\begin{vmatrix} A & & \\ & A & \\ & & B \end{vmatrix} \quad \text{and} \quad \begin{vmatrix} C & C & D \\ C & C & D \\ D & D & O \end{vmatrix}$$

The study of the spectra relative to the ε_{zz} element on the one hand, ε_{xy}, ε_{xz} or ε_{yz} elements on the other hand enables us to distinguish, theoretically at least, the A species vibrations from those of E species whereas the spectra relative to the ε_{xx} or ε_{yy} element contains the two species of vibrations at once. It must be taken into account that the orientation of the fibres cannot be perfect and that, the material being transluscent, there could be polarization scrambling particularly in the case of observation B. Weak bands in the spectra relative to a given polarization may come from strong bands of a different polarization. *Table 1* gives the frequency and the symmetry of the different Raman modes observed as well as data obtained by Ukita by infra-red techniques on orientated films[10] and by Cornell[9] on non-oriented samples.

The Raman spectra of the fibres is richer than the infrared spectra of orientated films but there is no major contradiction between the two series of results; only a few bands which had a well determined symmetry in infra-red spectra present a mixed character in Raman (818, 1152, 1298, 2851, 2879, 2958 cm^{-1}). Generally the frequency of A and E bands coming from a same mode coincide; however we do ascertain some important splitting, as for example, those which concern the bands 1097–1040 cm^{-1}

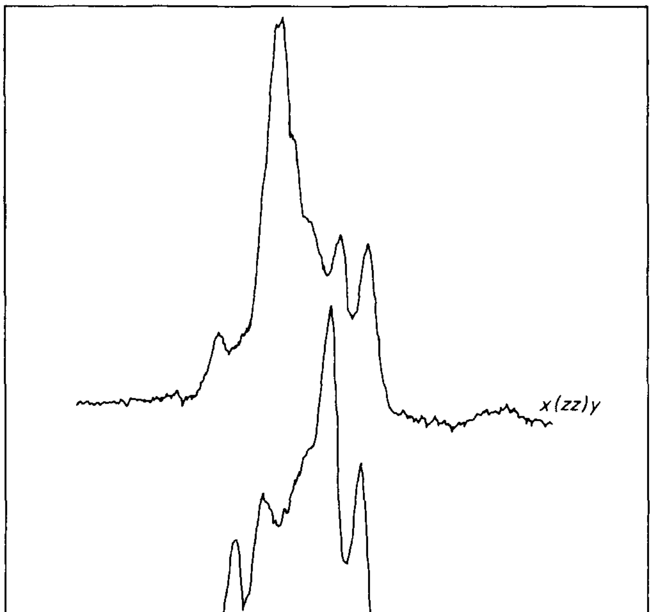

Figure 3 Raman spectra of polybutene-1 fibres in the region 2700–3100 cm^{-1}

Table 1 Frequencies (cm^{-1}) of: Polybutene-1 vibrations

I.r. (Ukita) ref 10	Raman (Cornell) ref 9	Raman (this study)
		2974 A m
		2974 E w
2961 A vs	2960 mw	2956 A w
2958 E vs		2956 E m
		2934 E m
	2932 m	2934 A vs
	2908 m	2917 A sh
2914 E vs		2917 E sh
		2897 A sh
	2879 s	2879 A vs
2874 E s		2879 E s
		2873 A s
2851 E s		2851 E s
	2854 m	2851 A s
		2728 A vw
	2730 w	2728 E vw
1463 E s		1456 E sh
1458 A s	1461 m	1456 A sh
1441 A s	1447 s	1447 A m
1439 E s		1447 E s
1380 E s	1376 w	1382 E vw
		1378 A vw
1366 E s	1363 w	1366 E w
1342 A m	1341 m	1336 A vw
1331 E m	1327 s	1328 E s
1321 A w		1323 A w
1302 E w		1298 E vw
	1299 w	1298 A vw
1263 E w	1260 w	1258 E w
1222 A m		1219 A vw
1207 E w	1206 m	1207 E w
1150 E w		1152 E m
	1150 ms	1152 A s
1096 E w	1094 mw	1097 E w
	1058 m	1059 E w
	1038 ms	1040 A s
1028 A w		1028 E w
1015 E w	1001 w	1015 E vw
977 E w	973 mw	976 E w
	962 w	961 A w
924 E s	923 w	921 E vw
848 A w	846 ms	848 A m
816 A m	817 ms	818 A m
		818 E w
798 E w	798 mw	
764 E w		767 E m
758 A s	757 ms	757 A m
		537 A vw
		525 E w
		485 E vw
		376 E m
		376 A m

vs: very strong, s: strong, m: medium, w: weak, vw: very weak, sh: shoulder

and 921–848 cm^{-1}: which explains the disappearance of the bands 1097 and 848 cm^{-1} when the helicoidal structure disappears, in the modification II or in the amorphous state.

Individuality of the vibrations

To test the individuality of the vibrations of CH_2 and CH_3 groups in the polymer, we compared the Raman intensities observed in the different polarization cases with the intensities calculated in the assumption where there is no interaction between vibrations of a different nature. In this hypothesis, the Raman active vibrations of the polymer chain come from a coupling of the homologous vibrations of the three chain structural units contained in the unit cell. This coupling is described by the symmetrical coordinates of the chain:

$$S(\mathrm{A}) = (3)^{-1/2}(q_1 + q_2 + q_3)$$
$$S(\mathrm{E}) = (2/3)^{1/2}(q_1 - \tfrac{1}{2}q_2 - \tfrac{1}{2}q_3)$$
$$S(\mathrm{E}') = (2)^{-1/2}(-q_2 + q_3)$$

Where q_1, q_2 and q_3 are the normal coordinates relative to the vibration into consideration in each of the three structural units. The Raman tensors (T(A), T(E) and T(E′)) of a chain vibration are now linear functions of the $T_{x'y'z'}$ tensors relative to this vibration in the three structural units, these latter tensors being expressed in the x' y' z' chain axis (z' parallel to the main axis of the chain, x' given direction perpendicular to z', y' both perpendicular to x' and z').

Also:

$$T_{x'y'z'} = M\,T_{uvw}\,M^{-1}$$

where T_{uvw} is the Raman tensor of the vibration in the $u\,v\,w$ axis of the CH_2 of CH_3 group under study and M the transformation matrix relating $x'y'z'$ and uvw axis, which characterize the position of the group in relation to the chain.

Finally, the sample having a uniaxial symmetry, the intensity scattered by all the chains, for a given vibration, is obtained by averaging the squares of the T(A), T(E) and T(E′) tensor elements over all the equiprobable orientations of the x' and y' chain axis in relation to the x and y sample axis, z' being parallel to z.

A vibration of a structural group characterized in the $x'y'z'$ axis, by a Raman tensor $T_{x'y'z'}$ such as:

$$\begin{vmatrix} a' & d' & e' \\ d' & b' & f' \\ e' & f' & c' \end{vmatrix}$$

gives rise to A and E vibrations of all the chains, the intensities of which are characterized by the following expressions:

—for the A species vibrations:

$$\varepsilon_{xx}^2 = \varepsilon_{yy}^2 = \tfrac{3}{4}(a' + b')^2 = A^2$$
$$\varepsilon_{zz}^2 = 3\,c'^2 = B^2$$
$$\varepsilon_{xy}^2 = \varepsilon_{xz}^2 = \varepsilon_{yz}^2 = 0$$

—for the E species vibrations:

$$\varepsilon_{xx}^2 = \varepsilon_{yy}^2 = \varepsilon_{xy}^2 = \tfrac{3}{16}(a' - b')^2 + \tfrac{3}{4}d'^2 = C^2$$
$$\varepsilon_{zz}^2 = 0$$
$$\varepsilon_{xz}^2 = \varepsilon_{yz}^2 = \tfrac{3}{4}(e'^2 + f'^2) = D^2$$

Table 2 gives for each vibration coming from CH_2 or CH_3 groups the theoretical intensities calculated in the hypothesis above in terms of the T_{uvw} tensor elements. The M matrices relative to the different groups under study have been calculated from structural data of the polybutene-1[3]. Furthermore we have noted in *Table 3* the Raman band intensities measured with an arbitrary unit (the intensity of the definite band having a frequency of 1152 cm^{-1}, in the polarization relative to ε_{zz} being taken equal to 10). When two or several bands overlapped, we assumed that each one of them had a lorentz shape on decomposition. An accurate agreement between observed and calculated frequencies missing, the comparison of

Table 2 Theoretical Raman intensities relative to CH_2 and CH_3 vibrations in polybutene-1 fibres

		Calculated intensities[c]	
Mode[a]	Raman tensor[b]	A species: $\begin{array}{ccc} A^2 & & \\ & A^2 & \\ & & B^2 \end{array}$	E species: $\begin{array}{ccc} C^2 & C^2 & D^2 \\ C^2 & C^2 & D^2 \\ D^2 & D^2 & 0 \end{array}$
$\nu_s(CH_3)$ $\delta_s(CH_3)$	$\begin{array}{ccc} a & \cdot & \cdot \\ \cdot & a & \cdot \\ \cdot & \cdot & b \end{array}$	$A^2 = 0.9\,a^2 + 0.6\,b^2 + 1.5\,ab$ $B^2 = 2.3\,a^2 + 0.03\,b^2 + 0.5\,ab$	$C^2 = 0.3\,(a - b)^2$ $D^2 = 0.15\,(a - b)^2$
$\nu_a(CH_3)$ $\delta_a(CH_3)$ $\rho_a(CH_3)$	$\begin{array}{ccc} c & \cdot & d \\ \cdot & -c & \cdot \\ d & \cdot & \cdot \end{array}$	$A^2 = 0.8\,c^2 + 0.3\,d^2 + cd$ $B^2 = 2.3\,c^2 + d^2 + 3.2\,cd \simeq 3\,A^2$	$C^2 = 0.4\,c^2 + 0.14\,d^2 + 0.26\,cd$ $D^2 = 0.13\,c^2 + 0.92\,d^2 + 0.7\,cd$
$\nu'_a(CH_3)$ $\delta'_a(CH_3)$ $\rho'_a(CH_3)$	$\begin{array}{ccc} \cdot & -c & \cdot \\ -c & \cdot & d \\ \cdot & d & \cdot \end{array}$	$A^2 \simeq 0$ $B^2 = 0$	$C^2 = 0.26\,c^2 + 1.32\,d^2 - 0.19\,cd$ $D^2 = 1.3\,c^2 + 0.15\,d^2 + 0.87\,cd$
$\nu_s(CH_2)_m$ $\delta(CH_2)_m$	$\begin{array}{ccc} a & \cdot & \cdot \\ \cdot & b & \cdot \\ \cdot & \cdot & c \end{array}$	$A^2 = 0.76\,a^2 + 0.60\,b^2 + 1.44\,ac$ $B^2 = 2.9\,b^2 + 0.23\,bc$	$C^2 = 0.35\,(c - a)^2$ $D^2 = 0.05\,(c - b)^2$
$\nu_s(CH_2)_s$ $\delta(CH_2)_s$	$\begin{array}{ccc} a & \cdot & \cdot \\ \cdot & b & \cdot \\ \cdot & \cdot & c \end{array}$	$A^2 = 0.08\,a^2 + 0.75\,b^2 + 0.37\,c^2 + 0.48\,ab + 0.34\,ac + bc$ $B^2 = 1.35\,a^2 + 0.27\,c^2 + 1.20\,ac$	$C^2 = 0.04\,a^2 + 0.38\,b^2 + 0.18\,c^2 - 0.24\,ab + 0.17\,ac - 0.52\,bc$ $D^2 = 0.33\,a^2 + 0.33\,c^2 - 0.66\,ac$
$\nu_a(CH_2)_m$ $\rho(CH_2)_m$	$\begin{array}{ccc} \cdot & \cdot & e \\ \cdot & \cdot & \cdot \\ e & \cdot & \cdot \end{array}$	$A^2 \simeq 0$ $B^2 = 0$	$C^2 = 1.45\,e^2$ $D^2 = 0.06\,e^2$
$\nu_a(CH_2)_s$ $\rho(CH_2)_s$	$\begin{array}{ccc} \cdot & \cdot & e \\ \cdot & \cdot & \cdot \\ e & \cdot & \cdot \end{array}$	$A^2 = 0.68\,e^2$ $B^2 = 2.43\,e^2$	$C^2 = 0.34\,e^2$ $D^2 = 0.21\,e^2$
$tw(CH_2)_m$	$\begin{array}{ccc} \cdot & d & \cdot \\ d & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{array}$	$A^2 \simeq 0$ $B^2 = 0$	$C^2 = 0.05\,d^2$ $D^2 = 1.44\,d^2$
$tw(CH_2)_s$	$\begin{array}{ccc} \cdot & d & \cdot \\ d & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{array}$	$A^2 \simeq 0$ $B^2 = 0$	$C^2 = 0.49\,d^2$ $D^2 = d^2$
$w(CH_2)_m$	$\begin{array}{ccc} \cdot & \cdot & \cdot \\ \cdot & \cdot & f \\ \cdot & f & \cdot \end{array}$	$A^2 = 0.11\,f^2$ $B^2 = 0.41\,f^2$	$C^2 = 0.05\,f^2$ $D^2 = 1.26\,f^2$
$w(CH_2)_s$	$\begin{array}{ccc} \cdot & \cdot & \cdot \\ \cdot & \cdot & f \\ \cdot & f & \cdot \end{array}$	$A^2 \simeq 0$ $B^2 = 0$	$C^2 = 1.05\,f^2$ $D^2 = 0.45\,f^2$

[a] ν ν_s: symmetric stretching; ν_a ν'_a: antisymmetric stretching; δ δ_s: symmetric bending; δ_a δ'_a: antisymmetric bending; *tw*: twisting; ρ ρ_a ρ'_a: rocking; ω: wagging; $(CH_2)_m$: CH_2 group of the main chain; $(CH_2)_s$: CH_2 group of the side chain

[b] in *u v w* axis of CH_2 or CH_3 groups

[c] in *x y z* axis of the sample

observed and calculated intensities has been made taking into account the frequency regions characteristic of CH_2 or CH_3 group vibrations.

The presence of several unknown parameters in the Raman tensors of the stretching and deformation symmetric vibrations of CH_2 groups makes this comparison difficult. However, if one supposes that for the stretching vibration $a<b$ and $a<c$, there is no contradiction between the experimental intensities for the 2851 and 2873 cm^{-1} bands and the theoretical intensities of $\nu_s(CH_2)_s$ and $\nu_s(CH_2)_m$ vibrations; particularly the predominance of the intensities relative to ε_{zz} spectrum for the 2873 cm^{-1} band and to ε_{xx} spectrum for the 2851 cm^{-1} band is in agreement with the theory. Alternatively, for a bending vibration $b>a$ and $b>c$; in these conditions the importance of the intensity relative to the ε_{xz} or ε_{yz} spectrum for the 1447 cm^{-1} band leads to a complete discordance with theoretical intensities of $\delta(CH_2)_m$ and $\delta(CH_2)_s$ vibrations. This can be explained by the coupling of bending vibrations of CH_2 groups of the main chain and those of the side chain. Also, the 2897 and 2917 cm^{-1} bands relative to CH_2 asymmetrical stretching vibrations being located in shoulder of important bands (2879 and 2934 cm^{-1} respectively), their intensity measuring was imprecise and allows no comparison at all.

For the wagging, twisting and rocking modes of CH_2 groups there is a splitting of A and E vibrations. There is good agreement between the theoretical and measured intensities for the following bands:

1328 cm^{-1}: $\omega(CH_2)_m + \omega(CH_2)_s$	(E species)
1323 cm^{-1}: $\omega(CH_2)_m$	(A species)
1207 cm^{-1}: $tw(CH_2)_m + tw(CH_2)_s$	(E species
767 cm^{-1}: $\rho(CH_2)_m + \rho(CH_2)_s$	(E species)
757 cm^{-1}: $\rho(CH_2)_s$	(A species)

In addition, it should be observed that the very weak

Table 3 Observed intensities of polybutene-1 fibre Raman bands

	Observed intensities[a]					
ν (cm^{-1})	ϵ^2_{yy}	ϵ^2_{zz}	ϵ^2_{xy}	$\epsilon^2_{xz} = \epsilon^2_{yz}$	Species	Assignment[b]
2974	–	6.7	–	1.5	A + E	$\nu_a(CH_3)$[d]
2956	8.9	–	7.4	2.9	A + E	$\nu'_a(CH_3)$
2934	16.3	50.3	7.4	4.4	A + E	
2917	23.7	25.2	10.4	5.9	A + E	$\nu_a(CH_2)$
2897					A	$\nu_a(CH_2)$
2879	44.4	–	16.3	7.4	A + E	$\nu_s(CH_3)$
2873	–	15.5	–	–	A	$\nu_s(CH_2)_m$
2851	26.6	10.2	8.9	2.9	A + E	$\nu_s(CH_2)_s$
2728	w[c]	w	w	w	A + E	
1456	1.5	w	1.5	1.8	A + E	$\delta_a(CH_3)$
1447	7.4	6.6	7.4	11.1	A + E	$\delta(CH_2)_m$, $\delta(CH_2)_s$
1382	w	–	w	w	E	$\delta_s(CH_3)$
1378	–	w	–	–	A	
1366	w	–	w	1.1	E	
1328	7.4	–	7.4	11.1	E	$w(CH_2)_m + w(CH_2)_s$
1323	w	3	–	–	A	
1298	w	w	w	w	A + E	
1258	w	–	w	1	E	
1219	w	w	–	–	A	$tw(CH_2)_m + tw(CH_2)_s$
1207	0.7	–	0.7	4.4	E	
1152	5.9	10	5.2	3	A + E	
1097	1.9	–	1.9	1.5	E	
1059	3.3	w	3.3	3.7	E	
1040	2.2	9.6	–	w	A	
1028	2.6	–	2.6	w	E	
1016	w	–	w	w	E	
976	1.1	–	1.1	1.5	E	
961	1.1	3.7	w	w	A	
921	1.1	–	1.1	w	E	
848	6.7	8.1	–	–	A	
818	7.8	3	3.7	2.2	A + E	
767	3.7	–	3.7	1.4	E	$\rho(CH_2)_m + \rho(CH_2)_s$
757	1.9	6.7	w	w	A	

[a] In arbitrary units (see text) [b] Only for the CH_2 and CH_3 group modes [c] *w*: band intensity less than 0.5 [d] see *Table 2*

band located at 1219 cm^{-1} could represent the twisting vibrations of A species and that the $\omega(CH_2)_s$ and $\rho(CH_2)_m$ vibrations of A species have zero theoretical intensities.

As far as the CH_3 group vibrations are concerned, there is good agreement between the 2879 cm^{-1} band intensities and the $\nu_s(CH_3)$vibration theoretical intensities, if one assumes that in a stretching vibration b > a, there is no incompatibility between the intensities of the 2974 and 2956 cm^{-1} bands and $\nu_a(CH_3)$ and $\nu'_a(CH_3)$ vibration theoritical intensities; the weakness of the 1382 cm^{-1} band intensities relative to $\delta_s(CH_3)$ and those of the 1456 cm^{-1} band in a shouldering position and relative to $\delta_a(CH_3)$ does not give a conclusion. However, between 1150 and 800 cm^{-1}, there is no band where the intensity is in agreement with the theoretical intensities of CH_3 rocking vibrations.

An analogous intensity calculation has shown that none of these bands could be assigned to an individual vibration relative to the chain skeleton or the C–H vibrator.

CONCLUSION

The study, in Raman spectroscopy, or polybutene-1 fibres has enabled us to determine the symmetry of normal modes of the polymer chain.

The comparison between the theoretical and observed intensities shows that CH_2 group vibrations, not including bending vibrations, and CH_3 group stretching vibrations possess a certain individuality. We can assign several bands of the polybutene-1 spectra to well defined and individual vibrations. However, the intensities of the bands situated between 1200 and 800 cm^{-1} are not comparable to any of the theoretical intensities. These bands come from the coupling of several vibrations, particularly the skeleton stretching vibrations and the CH_3 rocking vibrations and can then be considered as characteristic of this polymer chain.

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