Vibrational spectrum of syndiotactic polypropylene. Raman tacticity bands and local structures of iso- and syndiotactic polypropylenes

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New Raman spectra of syndiotactic polypropylene (form I) are presented together with the infrared spectrum in the low energy region. Depolarization ratios of an optically transparent, solid block of polymer are also given. The vibrational assignments are re-discussed in combination with the results of normal coordinate calculations of other authors. The meaning and validity of the 'Syndiotacticity Index' proposed by other authors is discussed in terms of the concept of regularity bands. Raman bands characteristic of the stereoregularity of iso- and syndiotactic polypropylene are proposed. Their existence suggests the interesting fact that in the molten state stereo-regular diads or triads may exist which are locked into an average conformation which has to be the same as that taken up by the polymer chain upon crystallization.

INTRODUCTION

While the infrared spectrum of syndiotactic polypropylene (SPP) in both twofold helix (form I, SPP–I) and planar zig-zag (form II, SPP–II) conformations has been recorded and studied by several authors[1–7], the Raman spectrum has remained practically unknown until recently. The first Raman spectrum of SPP–I was reported by Zerbi and Hendra in 1969[8]. The experimental data collected by these authors were poor and their interpretation difficult. Since then no other Raman spectra were reported in the literature until 1977 when Chalmers published a Raman spectrum of SPP–I which represents, as the author pointed out, a substantial improvement over previous experiments[9].

The purpose of this paper is to try to carry the interpretation of the vibrational spectra of SPP–I a step forward which is by no means final. From a comparison of the experimental data derived on the spectra of isotactic and syndiotactic polypropylene some structural information of more general relevance is extracted.

Reported here are some additional experimental Raman data on two-fold helix crystalline SPP–I, discussed mainly on the basis of the previously reported normal coordinate calculations and infrared spectra. Even if our Raman spectrum is very similar to that by Chalmers[9], the advanced instrumentation available allows us to define and interpret finer details in the spectrum. The frequency shift region at wave numbers below 450 cm^{-1} is also analysed by comparison with infrared absorption data obtained in our laboratory.

In this paper we compare experimental data from polymer samples with a different content of 'ordered structure' which allow us to locate the spectral regions in the Raman effect which are most sensitive to 'structural disorder'. The sensitivity of the infrared spectrum of SPP–I to structural disorder was first discussed by Peraldo who proposed an empirical and semiquantitative method for the determination of 'structural disorder' in SPP–I. A Syndiotacticity Index (S.I.) has been proposed[3], and was first reported by Zambelli *et al.*[10]. Such a method has been widely applied in the study of the chemistry of syndiotactic polymerization for the characterization of the polymer[11,12]. A few comments on S.I. and its relation to structural disorder will be given later in this paper.

EXPERIMENTAL

A Jarrel–Ash mod. 25–300 double monochromator Raman spectrophotometer equipped with an ITT FW 130 photomultiplier and photon counting device was used to collect the Raman spectra. Excitation was performed by 4880 or 5145 Å lines from a Coherent Radiation CR3 Ar$^+$ laser. The scattering geometry at 90° was adopted everywhere.

The infrared spectra in the low energy region were collected with a Perkin Elmer mod. 180 (600–200 cm^{-1}) and a Hitachi–Perkin Elmer mod. FIS 3(400–50 cm^{-1}) spectrometer. Absorption measurements in the higher frequency region were made either on the mod. 180 or, for S.I. determinations where measurements above 4000 cm^{-1} are needed, on a Perkin Elmer mod. 125 spectrometer.

For a rough characterization of our samples we accepted the fact that the infrared spectrum of SPP is shown to be

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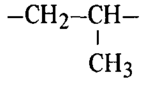
very sensitive to the degree of conformational order of a given sample; absorption measurements were then made in the 1500–700 cm^{-1} region.

The S.I. of each sample was also determined. For these measurements two specimens were prepared from each sample of the polymer: the first, in the form of thin film, for infrared absorption measurements, the second, as a pellet, for Raman scattering determinations. Before recording the spectra the two specimens were annealed together for 10 h at 110°C under vacuum. Under these conditions the annealing efficiency is likely to be the same for the two specimens. The infrared spectrum of the film should be a good probe for the content of ordered structure in the specimen used for the Raman scattering.

STRUCTURE AND SPECTRA

The ideally perfect molecular chain of SPP is an infinite repetition of



$$-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$$

monomer units linked in a head-to-tail sequence, with asymmetric carbon atoms forming ... dldl ... configurational sequence. The rototranslational repeat unit contains two monomer units (dl), independently of the configuration of the chain. It has been predicted[13,14] and experimentally shown[1–3,15] that SPP can take up two different low energy structures. Form I is described by a conformational sequence .. TGGTTG′G′T ..; form II contains all-*trans* C–C bonds thus forming a planar zig-zag chain. Form I is directly obtained from the polymerization process and appears to be the most stable structure; by quenching the melt and sudden stretching, from II is obtained. In this paper we consider only form I.

The crystalline structure of SPP–I determined by Corradini *et al.* from X-ray diffraction studies on stretched fibres, and doubly oriented films of the polymers, corresponds to an orthorhombic lattice, space group $C222_1$, with two helix segments per unit cell[16]. If we consider the single, infinite and isolated chain (one-dimensional model) the repeat distance of form I contains two rototranslational units (four monomer units) with the following symmetry elements: the identity and three mutually orthogonal twofold axes (the twofold axis lying along the chain axis is a screw axis which can be indicated as $R(\theta,1)$ where $\theta = 180°$ and $l = d/2$, d being the repeat distance). The factor group of the line group for the ideal one-dimensional crystal is isomorphous with the point group D_2. The rototranslational unit contains 18 atoms, and the dispersion curve $\nu(\phi)$ (where ν is the vibrational frequency in cm^{-1} and ϕ the phase shift between adjacent rototranslational units) is made up by 54 branches, of which two are acoustical and 52 optical. Spectroscopically active phonons correspond to the points on the dispersion curve with $\phi = 0$ and $\phi = \pi$. A and B_3 phonons correspond to $\phi = 0$, B_2 and B_1 phonons correspond to $\phi = \pi$*.

The 104 non-zero spectroscopically active phonons are distributed as follows: 26 A (Raman, p; i.r., i.a.), 26 B_1 (Raman, dp; ir, ⊥), 26 B_2 (Raman, dp; ir, ⊥) and 26 B_3 (Raman, dp; ir, //). Because of the large number of atoms in the repeat distance, dispersion curves would not be very useful and have not been calculated. Only spectroscopically active modes have been calculated using different vibrational potentials[4,6,15]. Calculations indicate that intrachain phase-dependent coupling is very weak for most of the vibrations and the splitting of each vibration of the monomeric unit into the four A, B_1, B_2 and B_3 chain modes, is very small.

Several authors have reported the infrared spectrum of form I of SPP unoriented[3–7], and one- or two-dimensionally oriented[3,4]. The number of bands observed in unoriented samples is far below that expected thus confirming the calculated predictions that many accidental degeneracies occur. Pairing between calculated and observed frequencies in the 1500–450 cm^{-1} range has been possible in the infrared by the excellent and unique work by Peraldo and Cambini[3] on the dichroic behaviour of a bidimensionally oriented specimen. This study has allowed to distinguish between B_1, B_2 and B_3 infrared active species.

The Raman spectrum of form I of SPP is expected to provide the same frequencies as the infrared spectrum for all B type modes, and in addition to show the totally symmetric A modes only active in the Raman. The experimental He–Ne laser Raman spectrum first reported by Zerbi and Hendra[8] showed a few lines emerging from an overwhelming background. On the basis of non-coincidence with infrared bands and normal coordinate calculations, these lines were assigned to A modes even if contributions from nearly accidentally degenerate B modes were also taken into account[8].

The Raman spectrum by Chalmers[9] is an excellent one as far as number of bands, signal-to-noise ratio and background level are concerned. Lack of fluorescence emission by the sample, which had been very strong in the spectrum of Zerbi and Hendra, allowed examination and interpretation of the whole frequency region from 180 to 1600 cm^{-1}. By comparison with our spectra, especially in the region near 800 cm^{-1}, we concluded that the sample examined by Chalmers was a highly regular one. From his new experimental data Chalmers could confirm all assignments previously made by Zerbi and Hendra to totally symmetric A modes. He was also able to suggest additional assignments for a few other A modes and several B modes.

RESULTS AND ASSIGNMENTS

Our interpretation of the Raman spectrum of SPP–I starts from the results of previous studies, namely normal coordinate calculations and infrared absorption measurements above 450 cm^{-1}, and is based on the new experimental data obtained in our laboratory.

These data include: (1) the Raman spectrum of several samples of polymer showing different values of the S.I. in the range from 0.8 to 2.3; (2) the Raman spectrum of the melt; (3) the polarized Raman spectrum of unoriented specimens; (4) the infrared spectrum in the low frequency region (450–50 cm^{-1}).

Figure 1 shows the Raman spectrum of a sample of helical SPP (form I). Examination of the infrared spectrum of the same sample led us to conclude that the spectrum of *Figure 1* is that of a highly regular polymer. More precisely, the relative weakness of the infrared features at 750, 963, 1130 and 1232 cm^{-1} strongly suggested a rather low content of structural disorder[3,12]. The S.I. of this sample was 2.3.

Table 1 shows the vibrational assignments of form I of SPP resulting from previous studies as well as from the pre-

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* The notation of axes and symbolism adopted in this work are those of reference 15

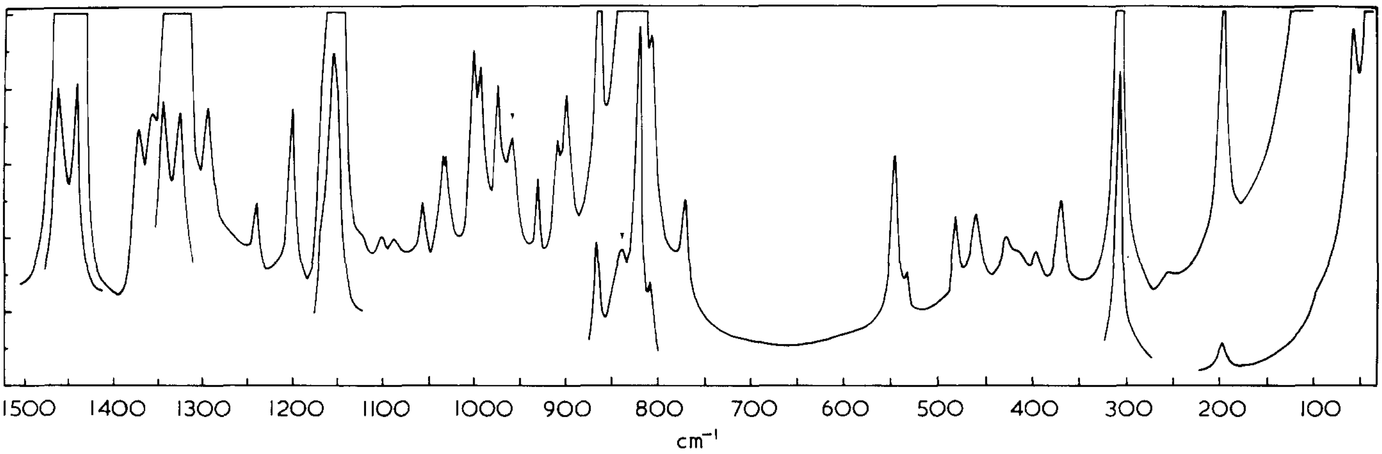

Figure 1 Raman spectrum from 50 to 1500 cm^{-1} of a highly regular sample of SPP–I (S.I. = 2.3). Exciting line, 4880 Å; power on the sample, 110 mW; spectral slit width, 3 cm^{-1}; sensitivity, 2 x 10^3 c.p.s.; time constant, 2 s.; scan speed, 10 cm^{-1}/min. The arrows indicate Raman features arising from the disordered phase

Table 1 Vibrational assignments of the single chain model of SPP—1

Calculated frequencies ν (cm^{-1})	Observed frequencies					Depolarization ratio ρ
	Infrared ν (cm^{-1})	Raman $\Delta\nu$ (cm^{-1})				
Ref 15	Ref 3	Ref 8	Ref 9	This work		This work
1465 B_1	1465					
1463 A				1465		0.76
		1463	1466			
1462 A						
1464 B_2	1463					
1464 B_3	1460					
1462 B_1	1460			(1463–1450)‡		
1455 B_2	1455					
1455 B_3	1455					
1454 B_2						
1454 A						
		1445	1445	1443		0.60
1452 A						
1453 B_1	1432			1432‡		
1380 B_1	1379					
1374 B_2	1378					
1378 B_3	1377				1376†	
				1376		
1373 B_3	1374		1374			
						0.80
1372 B_2	1373					
1372 A			1370		1375†	
1357 B_1						
1331 B_2	1360			1360		
1353 A		1346	1345			
				1345		0.72
1352 B_3	1346					
1352 B_1	1332					
1339 A		1331	1327	1325		0.50
1301 B_2	1311			1312		
1300 B_3	1293		1297	1296		
1275 B_1	1287			1287		
1265 B_3	1264			1263		
1259 A						
				1242		
1223 B_1	1242		1244			
1194 B_2	1202				1205†	
				1205		0.75
1191 A		1202	1204		1207	
1174 B_3	1167			1168		
1168 A		1158	1157	1158		
1159 B_2	1153					0.55
				1153		
1167 B_1	1152					
1115 B_2				1106		
1096 B_3				1094		
1113 B_1	1088, 1083			1088		

continues

Table 1 (cont.)

Calculated frequencies ν (cm^{-1})	Observed frequencies: Infrared ν (cm^{-1})	Observed frequencies: Raman $\Delta\nu$ (cm^{-1})				Depolarization ratio ρ
Ref 15	Ref 3	Ref 8	Ref 9	This work		This work
1068 B_3	1060		1061	1060		
1041 A		1040		1039		
			1034			0.65
1044 B_2	1035			1035		
980 B_1	1006			1005		
996 A		1000	1002	998	0.02	
974 B_3	977					
			978	978		
971 B_1	976					
931 B_2	935		933	935		
918 A			913	912	0.10	
903 B_1	906					
			903	901		
902 B_3	901					
878 B_2	870		872			
				871		
867 B_3	867					
829 B_3					823†	
				825		0.20
839 A		829	828		825†	
825 B_2	812			812		
786 B_1	776		776	776		
542 A			552	550		0.55
537 B_1	535			535		
476 B_2	483		486	484		
436 B_3	468		463			
433 B_2				462		
			424			
403 B_1						
	431*, 400*			429, 398		
410 B_3						
347 A			376	374		0.38
358 B_3	344*					
315 A		314	315	312		0.06
280 B_2						
	292*, 262*			292, 260		
264 B_1						
202 B_2						
200 B_3	240*, 206*					
			202			
196 B_1						
				200		0.45
199 A		204				
176 A		172				
171 B_2						
	166*, 147*					
170 B_1						
66 A				62		
74 B_3						
62 B_1						
	88*, 76*, 56* ?			102 ?		
60 B_3						
58 B_2						

* Infrared bands observed in this work

† Raman features resolved only in depolarization measurements

‡ Raman features resolved only at 0.6 cm^{-1} spectral slit width

sent work. In *Table 1* the frequencies calculated by Schachtschneider and Snyder (S–S)[15] are shown together with the experimental infrared data obtained by Peraldo and Cambini (limited to 450 cm^{-1})[3]. Takokoro *et al.*[4] and Miyazawa[6] have also reported normal coordinate calculations on helical SPP and their results do not differ much from those of S–S. For sake of uniformity with the arguments of reference 8 and 9 we list in *Table 1* the results of calculations of S–S. Only the infrared experimental frequencies by Peraldo and Cambini are reported in *Table 1* above 450 cm^{-1} since they are unique in presenting the results on doubly oriented specimens, such that a clear separation between B_1, B_2 and B_3 species is possible. The pairing between the two sets of data above 450 cm^{-1} of columns I and II of *Table 1* is taken from reference 15.

In the present study the proposed assignments of the Raman spectrum of SPP are the result of the application of several general guiding principles, already discussed and followed by Zerbi–Hendra and Chalmers in their works. These principles are briefly summarized in this section together with a few considerations which are specific to our experimental measurements.

(a) The examination of several samples of polymer allows us to distinguish Raman features originating from the regular double-helix chain from those due to defects, or disordered phase. Bands whose intensity appears to increase with decreasing S.I. of the sample are not taken into account in the present analysis.

(b) Even for perfectly crystalline samples, as in the case of form I of SPP, there is no hope of finding any evidence of crystalline structure from correlation field splittings. Indeed while X-ray crystallography defines an orthorhombic unit cell which accommodates two polymer chains[16], the primitive unit cell which determines the dynamical properties of the lattice is made up by only one polymer chain. Hence only the intramolecular spectrum of the single chain will appear. Only one vibrational lattice mode of species B_3 can in principle be Raman active, its frequency, however, has not yet been located. The interpretation of the spectrum is then made on the basis of the line-group symmetry of an isolated polymer chain.

(c) The specific assignments of the spectrum to phonons of the single chain starts from the good fitting of the experimental infrared data with the calculations, and the good general matching between infrared and Raman frequencies. To locate phonons of A species we choose first those Raman bands which have no counterpart in the infrared and for which calculations suggest frequencies in the same range. This simple and straightforward approach enables us immediately to locate A phonons at 1443, 1325, 1158, 998, 912, 825 and 550 cm^{-1}.

(d) Since B type phonons are active both in infrared and Raman, much care must be taken in analysing the Raman spectrum in frequency ranges where infrared features occur. Even weak features and shoulders observed in the Raman in coincidence with infrared bands are assigned to B type fundamental phonons. Because of instrumental reasons we consider infrared and Raman bands which occur within 3 cm^{-1} as 'coincident'. As examples we discuss here the assignments of the Raman bands at 1296 and 462 cm^{-1}.

The strong feature at 1296 cm^{-1} is soon assigned to the B_3 fundamental optical phonon calculated at 1300 cm^{-1} and observed in the infrared at 1293 cm^{-1}. There is no other possible choice since the shoulders observed in the Raman at 1312 and 1287 cm^{-1} find corresponding bands in the infrared at 1311 and 1287 cm^{-1}.

The band observed at 462 cm^{-1} in the Raman is assigned to the B_2 optical phonon which is calculated at 433 cm^{-1} and is not observed in the infrared. One could also assign the same Raman line at 462 cm^{-1} to the optical phonon of species B_3 observed in the infrared at 468 cm^{-1} and calculated at 436 cm^{-1}. Our experience on the whole frequency range suggests that a difference of 6 cm^{-1} between the Raman line (462 cm^{-1}) and the infrared band (468 cm^{-1}), is too large and does not allow us to consider them as coincident. We then take the Raman line at 462 cm^{-1} as a B_2 phonon and the infrared band at 468 cm^{-1} as a B_3 phonon. However, the Raman band appears to be rather broad and contribution on its high frequency side from the B_3 phonon cannot be excluded.

The substantial difference between calculated and observed frequencies is a common fact for all normal coordinate calculations in the low energy region of the spectrum. While the vibrations of hydrogen atoms are well accounted for in such calculations, the precise description of the skeletal modes still requires the collection of many more experimental data[17,18].

(e) Because of the weak intramolecular coupling among similar motions in different monomeric units many accidental degeneracies are predicted by calculations[15], and confirmed by experimental infrared work[3]. The observation of features a few wave numbers apart has been possible in the infrared by dichroic examination of doubly oriented specimens. These measurements also allow most of the B type optical phonons to be located in the infrared. A similar result is not to be expected in the Raman spectrum of *Figure 1* since measurements were done on an unoriented specimen.

On the basis of (d) above, and in the absence of any other experimental data, we suggest pairing of seemingly single Raman bands with infrared features which occur not more than 3 wave numbers apart. Such a value corresponds also to the spectral slit width of the spectrum of *Figure 1*. On this ground, for example, we correlate in *Table 1* the Raman band at 1376 cm^{-1} with five different B phonons observed in the infrared between 1379 and 1373 cm^{-1}. On the same ground A phonons are located in correspondence of Raman-infrared coincidences when calculations predict small shifts between A and B phonons (see the assignments of the Raman bands at 1465, 1345 and 1205 cm^{-1} in *Table 1*).

(f) In order to try a separation of closely spaced Raman signals a few bands have been scanned at higher resolution. In *Figure 1* two strong bands are observed between 1500 and 1400 cm^{-1}, centred at 1465 and 1443 cm^{-1}. S–S calculated twelve frequencies and assigned seven infrared bands to B type phonons in the same frequency range, leaving out the B_2 mode at 1454 cm^{-1}.

In *Figure 2* the Raman spectrum is reported of the same specimen as in *Figure 1*, at higher resolution. While the band at 1443 cm^{-1} is relatively narrow and symmetrical, that at 1465 cm^{-1} is broader and asymmetrical toward lower fre-

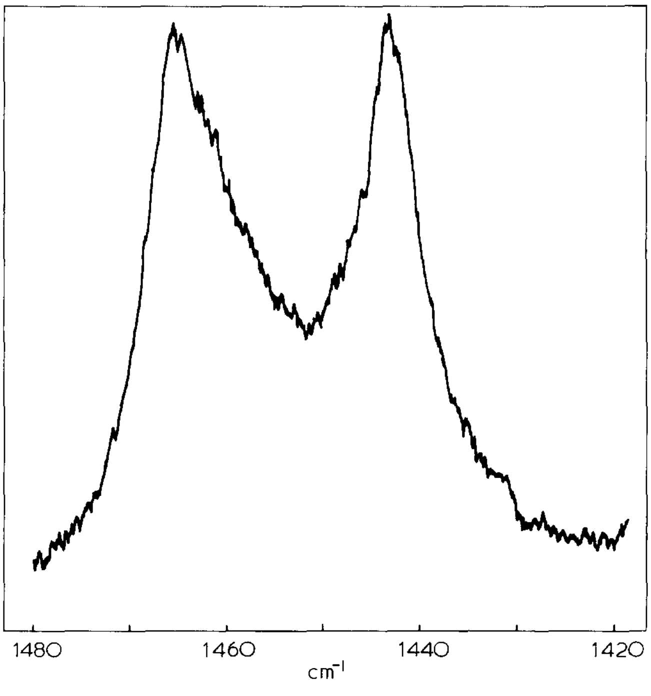

Figure 2 Raman spectrum from 1420 to 1480 cm^{-1} of the same sample as in *Figure 1*. Exciting line, 4880 Å; power on the sample, 110 mW; spectral slit width, 0.6 cm^{-1}; sensitivity, 5 x 10^2 c.p.s.; time constant, 10 s; scan speed 2 cm^{-1}/min

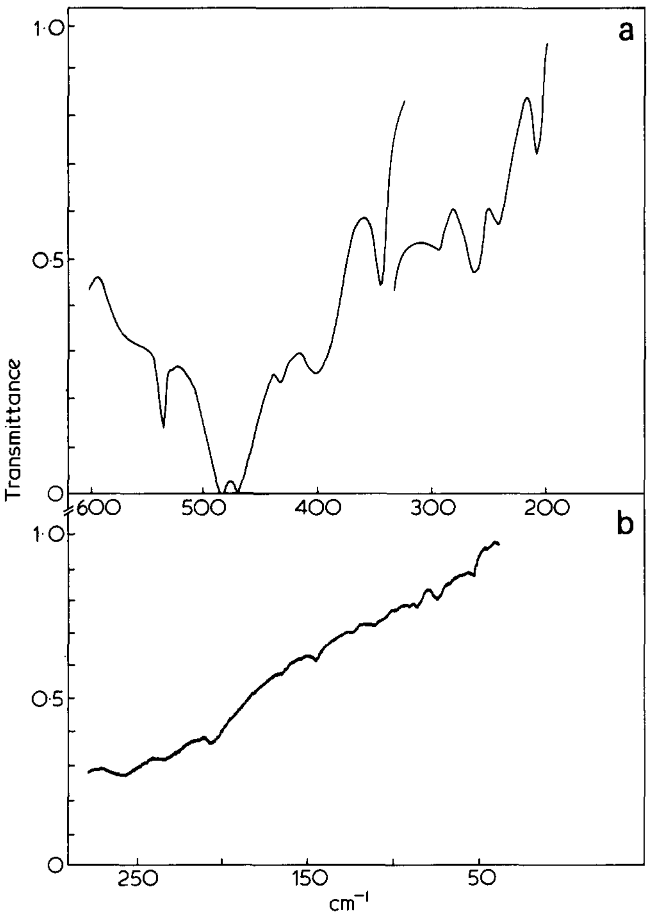

Figure 3 Infrared spectrum from 50 to 600 cm^{-1} of a highly regular sample of SPP–I (S.I. = 2.3). (a) Perkin–Elmer mod. 180 spectrophotometer; (b) Hitachi mod. FIS 3 spectrophotometer. The sample was 1.5 mm thick; scan speed, 2 cm^{-1}/min

quency shifts. Moreover shoulders are observed between 1463 and 1450 cm^{-1} which are interpreted as corresponding to the infrared features between 1463 and 1455 cm^{-1}. Another shoulder is found near 1432 cm^{-1} and is assigned in analogy with the infrared spectrum. These data, however, do not give additional information on the location of the B_2 phonon calculated at 1454 cm^{-1}.

(g) Specific assignments of the infrared spectrum of SPP below 450 cm^{-1} are not possible because of the lack of dichroic spectra. Infrared data down to 300 cm^{-1} have been reported by Koenig *et al.*[7]. From the i.r. spectrum at higher frequencies reported by these authors we feel that the polymer they studied was clearly less regular than those studied by us. This fact may explain the differences observed by us below 450 cm^{-1} with respect to that reported in reference 7.

In *Table 1* we report the infrared frequencies below 450 cm^{-1} obtained in our laboratory on an unoriented specimen of SPP–I. All these frequencies refer to clear and sharp infrared bands except those at 400 cm^{-1} (broad), and at 166, 88, 76 and 56 cm^{-1} (very weak, see *Figure 3*). Pairing between infrared and Raman spectra is not straightforward in this frequency range. The location of three out of five A bands expected in this region is simple on the basis of non-coincidence with the infrared features, and agrees with the assignments of Chalmers. The Raman band observed at 62 cm^{-1} with both 4880 and 5145 Å excitations had not been reported previously, and no indication was obtained to locate the A optical phonon calcualted at 176 cm^{-1}.

The assignment in *Table 1* of the Raman peak at 1242 cm^{-1} deserves further comment. A band at exactly the same frequency (1242 cm^{-1}) is observed in the infrared spectrum and has been assigned, on the basis of its dichroic behaviour, to the B_1 phonon calculated at 1223 cm^{-1} [15]. Because of the relatively large difference (19 cm^{-1}) between the calculated and experimental values compared with other pairs in the same frequency range, it has to be suspected that calculations are unreliable not only for the B_1 phonon above, but also for the A phonon which is calculated at 1259 cm^{-1}, and is described by substantially the same group coordinates (CH$_2$ twist + CH bend + C–C skeletal stretch). On the other hand, from an experimental point of view, the relative sharpness of the Raman peak at 1242 cm^{-1} seems to suggest its origin from a totally symmetric phonon and we tentatively assign it, by taking into account an accidental degeneracy, to both the B_1 and A phonons, calculated at 1223 and 125^{o} cm^{-1} respectively.

POLARIZATION MEASUREMENTS

Polarization measurements are useful in the Raman effect when homogeneous, optically clear materials are analysed. The technique generally allows polarized bands to be separated from depolarized ones, hence assignments to totally symmetric modes are possible on an experimental basis. In the case of semicrystalline, opaque polymeric materials, scrambling of both incident and scattered radiation, as well as re-scattering effects from the sample, generally prevent meaningful results being obtained from such experiments.

Vasko and Koenig reported the polarized Raman spectrum of smectic isotactic polypropylene (IPP)[19]. We report here results of similar measurements on SPP. The purpose was to ascertain to what extent such kinds of measurements can give information on the location of totally symmetric A phonons, and eventually to confirm the assignments previously made on the basis of unpolarized Raman spectra. In order to obtain meaningful results the sample was an optically transparent, solid block of polymer with rather low S.I. (0.95).

Figure 4 shows such a spectrum and *Table 1* gives the experimental depolarization ratios for bands assigned to A phonons. From these values of ρ it appears that the experimental determination of ρ is not conclusive in locating A phonons in such a sample, especially above 1000 cm^{-1}. Similar results were obtained by Vasko and Koenig on smectic IPP[19]. In the case of SPP this fact may be ascribed to: (i) mixing of A and B phonons in the same band, (ii) partial scrambling by the solid sample, (iii) presence of conformationally disordered phase in the polymer. Local symmetry effects must be also taken into account. As a general rule, we found that for the well-isolated A phonons occurring at low frequencies the depolarization ratios are substantially low, with values comparable to those reported for IPP. In the higher frequency range the B phonons appear to dominate over A phonons in determining the values of ρ when mixing occurs. This result is opposite to that found by Vasko and Koenig on IPP.

Since the disordered phase may well contribute to this situation we also tried to obtain polarization measurements on molten SPP (*Figure 5*). By comparing the data of *Figures 4* and *5* we found that the disordered phase, or local symmetry effects, strongly influence the ρ's in *Figure 4*. However, for suspected pure A bands, as those at 1443 and

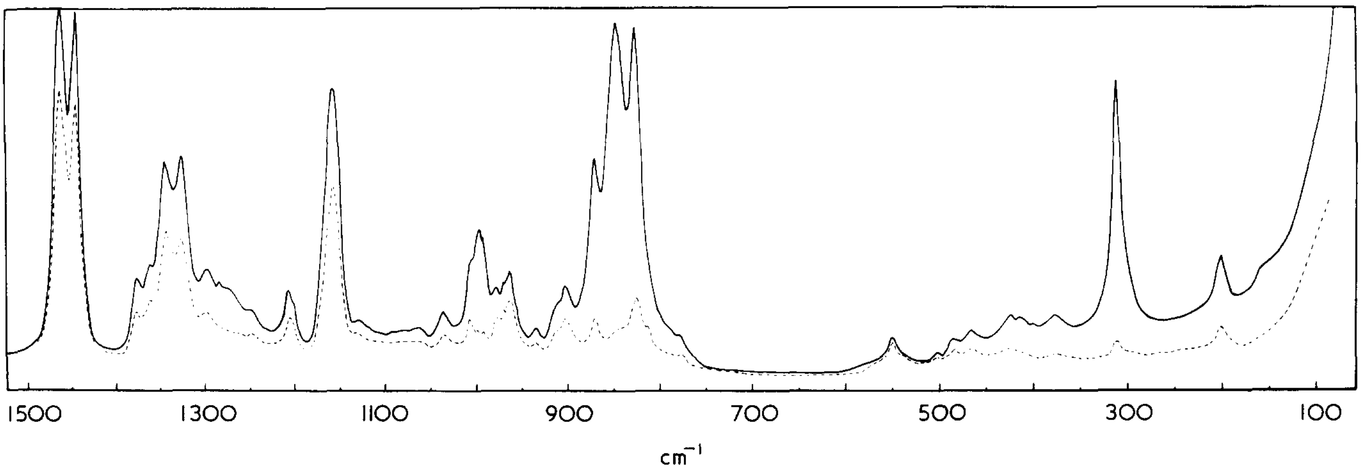

Figure 4 Polarized Raman spectra of a less regular sample of SPP–I (S.I. = 0.95). Full line, X(ZZ)Y spectrum; dashed line, X(ZX)Y spectrum. A scrambler was used in both spectra to depolarize the scattered light before entering the monochromator. Exciting line, 4880 Å; power on the sample, 70 mW; spectral slit width, 5 cm^{-1}; sensitivity, 2 x 10^3 c.p.s.; time constant, 2 s; scan speed, 20 cm^{-1}/min

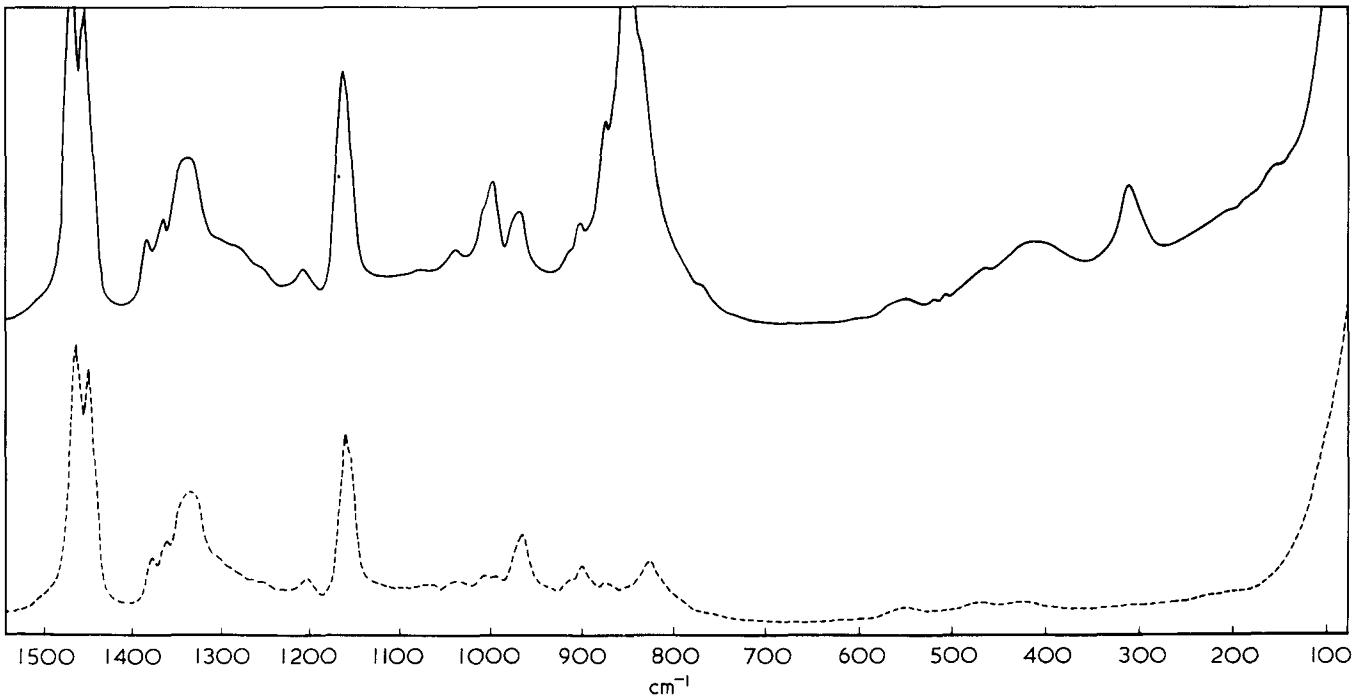

Figure 5 Polarized Raman spectra of molten SPP. Full line, X(ZZ)Y spectrum; dashed line, X(ZX)Y spectrum. A scrambler was used in both spectra to depolarize the scattered light before entering the monochromator. Exciting line, 4880 Å; power on the sample, 100 mW; spectral slit width, 3.5 cm^{-1}; sensitivity, 1 x 10^3 c.p.c.; time constant, 2 s; scan speed, 10 cm^{-1}/min

1325 cm^{-1}, a sensible decreasing of the depolarization ratio is observed in going from the melted to the solid polymer.

Polarization measurements have also allowed us to resolve closely spaced A–B components of apparently single Raman bands. The method is based on the observation of frequency changes in parallel and respectively perpendicular spectra. Examples are the doublets reported in *Table 1* at 1376–1375, 1207–1205 and 825–823 cm^{-1}. In any case, the reported values of ρ refer to the whole band.

RAMAN TACTICITY BANDS IN ISO- AND SYNDIOTACTIC POLYPROPYLENES

With the data presented in this paper and that of other authors for IPP, an attempt can be made to locate a few bands which are characteristic of the stereospecific structure of the polymer. The main requirement is that they do not disappear upon melting or in solution[20].

Many bands remain in the infrared[21] and Raman[19] spectrum of IPP in going from the crystalline to the melt which appear as weak 'souvenirs' of the helical structures which still remain in the molten state[22]. The same situation is observed in the infrared spectrum of SPP[3]. We discuss in this section only the case of clear and strong bands which do not change their appearance upon melting or in solution.

Vasko and Koenig[19] have reported the Raman spectrum of molten IPP while in *Figure 5* we report the Raman spectrum of molten SPP. In going from the solid (regular, i.e. with rototranslational symmetry) to the melt (generally irregular) most of the Raman bands due to $\phi = 0$ and $\phi = 2/3\ \pi$ phonons for IPP and $\phi = 0$ and $\phi = \pi$ for SPP–1 disappear because the chain periodicity is lost. A few bands

Table 2 Common features (cm^{-1}) in the Raman spectra of molten IPP and SPP

Molten IPP[19]	Molten SPP (this work)
1152	1156
1034	1035
900	902
841	842

Table 3 Non-coincident features (cm^{-1}) in the Raman spectra of molten IPP and SPP

Molten IPP[19]	Molten SPP (this work)
1002	993
973	966
398	310

unequivocally remain and can be taken as characteristic of the chemical and stereoregular structure.

In comparing the Raman spectra of molten IPP and SPP (in the spectral region below ~1200 cm^{-1} where large overcrowding of the bands is less likely) it is found that several bands coincide in frequency (*Table 2*) and do not allow any distinction between the two polymers. These bands must originate from normal modes highly localized in a specific group of atoms and uncoupled from the rest of the polymer chain. These modes are thus conformationally independent. They can be taken as 'group frequencies' as exacly defined by King and Crawford[23].

In *Table 3* we list some Raman bands whose frequencies do not coincide in the spectra of molten IPP and SPP and whose frequencies and overall intensities do not significantly change when the polymer chain coils up into a conformationally regular structure. Generally they only become sharper and more intense. The existence of bands as in *Table 3* shows that the intramolecular coupling for the corresponding modes must be such that one stereogroup knows the sterical structure of its neighbours (on one or both sides). This kind of coupling goes through at least two torsional angles on each side along the skeletal C–C bonds. The fact that these bands do not move upon melting, i.e. when the conformational sequence is generally disrupted, strongly suggests that a large percentage of sterical diads (or triads) are locked into a fixed local conformation which is approximately that later reached in the crystalline state. The process of crystallization should only organize these conformationally locked local units into a regular polymer chain.

We believe that the conformational microstructure of these stereoregular polymers, as revealed from the present analysis of the vibrational spectra, is an important structural property which deserves further experimental and theoretical explorations. For structural and analytical applications we suggest that of the three main tacticity bands for each polymer listed in *Table 3* the lowest frequency ones are more useful and important. It can be noticed that the frequency region at ~960 cm^{-1} is crowded by other overlapping medium bands which, from normal coordinate calculations, are variously described by different authors but substantially turn out to be a mixture of CH$_3$ rocking coupled with C–C skeletal stretching, C–CH$_3$ stretching and CH$_2$ or CH rockings. The bands at 398 and 310 cm^{-1} instead arise only from skeletal bending modes and it is reasonable to think they should depend upon the tacticity of the polymer.

RAMAN REGULARITY BANDS OF SPP–I

The 842–825 cm^{-1} bands

As mentioned above both infrared and Raman spectra of SPP–I are very sensitive to 'structural disorder'. This fact led Peraldo *et al.*[3,10] to propose the already discussed infrared Syndiotacticity Index. In the light of our present knowledge of dynamics and spectra of polymers[17,24–27] the experimental spectral observations from SPP–I must be accounted for in terms of precise structural aspects of this substance.

Figure 6 shows the Raman spectra between 800 and 900 cm^{-1} of three samples of SPP–I whose proposed S.I. values are 1.05, 1.3 and 2.2 (according to reference 12 structurally 'more ordered' polymers should have higher S.I. values). When S.I. values increase the Raman peak at 825 cm^{-1} steadily increases while the peak at 842 cm^{-1} decreases. For molten SPP (*Figures 5–6*) the 842 cm^{-1} peak strongly dominates over a shoulder at 825 cm^{-1}. Similar changes, though to a less extent, occur in the 960 cm^{-1} of the Raman spectrum of SPP–I. Parallel observations were made in the infrared mainly by Boor *et al.*[11,12] where the dominating band for large S.I. values

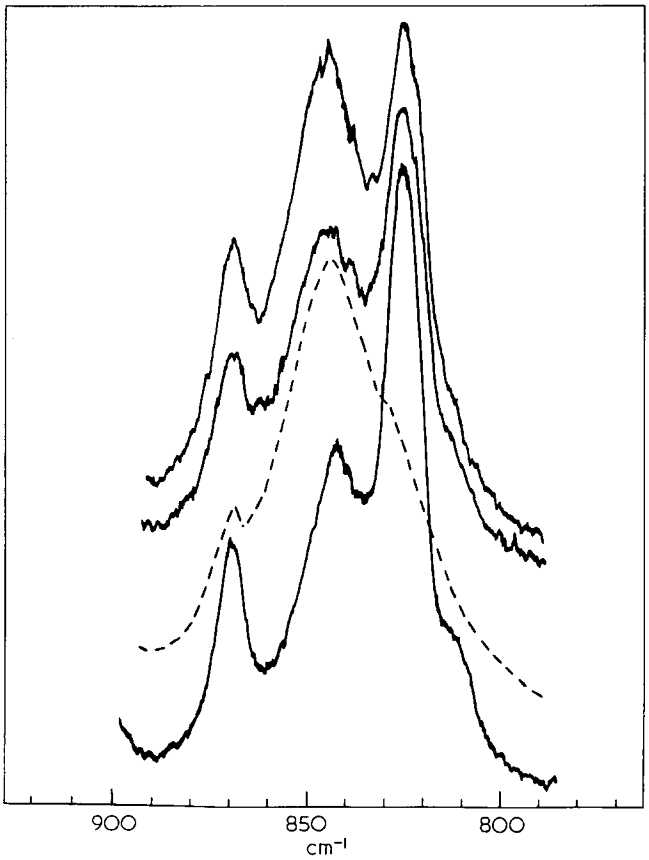

Figure 6 Raman spectra from 800 to 900 cm^{-1} of several samples of SPP–I showing different S.I. values. From the top to the bottom the S.I. is 1.05, 1.3, 2.2. The dashed line shows the spectrum of the melt. Exciting line, 4880 Å; power on the samples, 70 mW; spectral slit width, 4 cm^{-1}; sensitivity, 2 x 10^3 c.p.s.; scan speed, 20 cm^{-1}/min

occurs at 865 cm^{-1}. Boor and Youngman have also shown that the S.I. based on the 865 cm^{-1} band increases from zero to a limiting value by going from T = 140°C (melting point) to 20°C. The limiting value at 20°C changes with the percentage of crystallinity of the sample determined from density measurements.

All these experimental observations are consistent with the fact that the Raman peak at 825 cm^{-1} or the infrared peak at 865 cm^{-1} must be ascribed to a 'regularity band' or, in other words, to a spectroscopically active phonon only related to the existence of a long chain segment with rototranslational symmetry. From *Table 1* we see that the 825 cm^{-1} Raman peak corresponds to a phonon of species A calculated at 839 cm^{-1} and described in terms of Potential Energy Distribution as C–C skeletal stretch (38%), CH_3 rocking (24%), C–CH_3 stretch (17%) and C–C–C band (14%)[15]. The Raman peak at 842 cm^{-1} originates from a conformationally disordered structure where the . . . TGGTTG'G'T . . . sequence of torsional angles has been disrupted.

The considerations above show that the Raman spectrum of SPP indicates that in the molten state a certain amount of sections of helical segments still exist since the band at 825 cm^{-1} is still observed. A parallel observation was made by Zerbi *et al.* for IPP in the infrared[22]. For SPP there are yet no means to have an idea of the length of the helical segments present in the melt.

From the discussion in this section the meaning and validity of the S.I. become somewhat obscure. Chemists have used the S.I. as a measure of the amount of syndiotactic structure obtained in a given polymerization process. The behaviour of the infrared spectrum with temperature certainly cannot be accounted for in terms of changes of tacticity since none of these processes[11] are capable of changing the stereochemical structure of any stereoregular polymer.

In order to reconcile chemistry with spectroscopy, in this particular case only a vague correlation can be suggested, namely that samples with low S.I. contain more chemical or stereochemical defects thus making the polymer more conformationally disordered. This concept has been already clearly stated on the basis of the infrared spectrum by Boor and Youngman[11]. In the same work the authors compare the behaviour of an Index of Iso- and Syndiotacticity for IPP and SPP. The bands used for these determinations are clearly regularity bands.

CONCLUSIONS

In this paper we have added new experimental Raman and infrared data for a better interpretation of the vibrational spectrum of helical syndiotactic polypropylene (form I). We have located some additional spectroscopically active phonons of A and B type species.

We feel however that the main outcome of this work is the structural information derived from the analysis of the spectrum, namely:

(a) We have critically analysed and somewhat justified the spectral behaviour which led other authors to propose the Syndiotacticity Index. As discussed in the text, bands involved in the S.I. measurement are only regularity bands S.I. values must then be taken with caution.

(b) Evidence has been found that in the molten state a sample of SPP still contains some segments regularly coiled in a helical structure. Nothing can be said on the length of the segments.

(c) A few Raman bands are proposed as characteristic of iso- and syndiostereoregularity for polypropylene (tacticity bands). These bands should be useful to the chemist for structural and analytical studies.

(d) Attempts to understand the origin of the tacticity bands in terms of the vibrational motions suggest the possibility of the existence in the molten state of a large concentration of stereoregular diads or triads locked into a local conformation which is roughly the same as that taken up by the regular chain upon crystallization.

(e) We suggest that the spectral range 800–1000 cm^{-1} used by most of the authors is not very reliable in giving information on tacticity of polypropylenes or model compounds. A source of more reliable qualitative and quantitative data on tacticity is found in the Raman band at 398 cm^{-1} for IPP and at 310 cm^{-1} for SPP.

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