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RAMAN SCATTERING STUDIES OF CHAIN ORIENTATION IN HYDROSTATICALLY--ETC(U)

JUN 77 S K SATIJA, C H WANG, H KANETSUNA

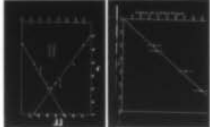
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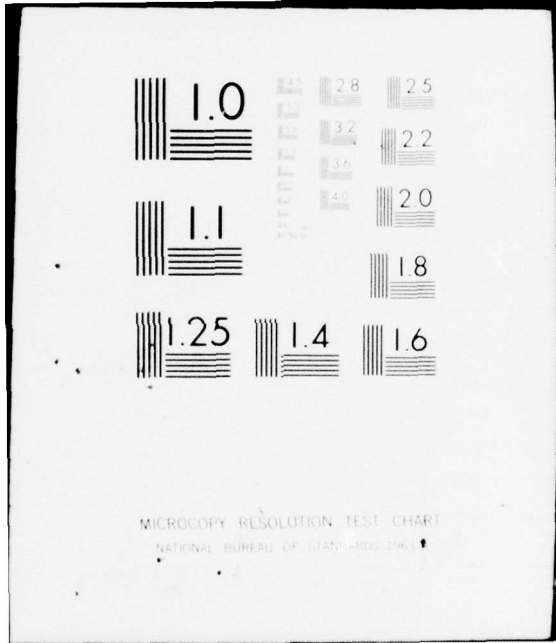
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to increase with the increase of the extrusion ratio. At the extrusion ratio equal to 6.3, about 90% of the polymer chains have been found to align along the direction of extrusion (the c-axis).

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RAMAN SCATTERING STUDIES OF CHAIN ORIENTATION
IN HYDROSTATICALLY EXTRUDED POLYPROPYLENE

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SYNOPSIS

Raman scattering is used in the study of hydrostatically extruded polypropylene as a function of the extrusion ratio. At a high extrusion ratio, polypropylene gives rise to Raman spectra with a well characterized polarization behavior. This result has been used to supplement the symmetry assignments of normal vibrations in polypropylene. The intensity ratios and depolarization ratios have also been measured as a function of the extrusion ratio. The c-axis alignment of the polymer chains has been found to increase with the increase of the extrusion ratio. At the extrusion ratio equal to 6.3, about 90% of the polymer chains have been found to align along the direction of extrusion (the c-axis).

INTRODUCTION

The study of molecular state in a solid polymer induced by drawing or external stresses is an important area of research in polymer science.

It is now established that imposition of hydrostatic pressure can cause substantial changes in the mechanical behavior of polymers.^{1,2} Hydrostatic extrusion has thus in recent years become a practical technique for altering the mechanical properties of polymers in a controllable manner. Hydrostatic extrusion gives rise to the plastic deformation of polymers and results in changes in molecular orientation as well as in the texture. At a high extrusion ratio (which is defined as the ratio of the cross sectional area of the virgin specimen to that of the extrudate through the die) the extruded sample are known to have highly-oriented fibre structure in which stacks of folded chain crystallites are present.^{3,4}

The extent of polymer-chain orientation is closely related to the mechanical and optical properties of a polymer and it is important to investigate the orientational state of the molecule as a function of the extrusion ratio. To date x-ray diffraction and birefringence have been used to determine the degree of orientation in extruded samples of polyethylene⁴. Williams has recently studied the tensile and torsional moduli of the hydrostatically extruded polypropylene³. It was found that the crystallinity of the extruded polypropylene increases with increasing the extrusion ratio. An increase of crystallinity is reflected by an increase in the degree of transparency⁴. Recently Yoon, Pae, and Sauer⁵ have also reported a study of the properties of extrudates of polypropylene. They have found that the c-axis orientation of chains occur upon extrusion and that the extent of the c-axis orientation is enhanced with increasing the extrusion ratio at a given temperature.⁵

The investigation of Raman spectra and depolarization ratios of various vibrational modes is another attractive method of obtaining information about the interrelationships between crystallinity and chain orientation in polymers. For this purpose, one needs to carry out studies of the polarized Raman intensities of various vibrational bands of oriented polymer samples in different scattering configurations. This paper reports this type of Raman study using hydrostatically extruded polypropylene samples. We have discussed the types of information for which the Raman scattering technique can offer. From the intensity measurements of vibration bands at several independent scattering configurations for polypropylene we have determined the degree of crystalline and amorphous orientation of the chain axis along the direction of extrusion as a function of the extrusion ratio.

EXPERIMENT AND RESULTS

The samples of extruded polypropylene were prepared according to a technique as described previously⁴. An unextruded sample and samples with the extrusion ratio, R_E , equal to 3.0, 3.4, 4.9, and 6.3 were used for the Raman scattering experiment. The extruded samples can be easily cleaved along the axis of extrusion. The cleaved samples were carefully polished on all sides to minimize surface imperfections which could give rise to the polarization scrambling of the Raman scattered light.

The Raman spectra were obtained by using a Spex 1401 double grating monochromator coupled to a photon counting system. An argon ion laser tuned to 4880 Å was used for excitation. The slit widths of the spectrometer were adjusted to yield a spectral resolution of the order of 2 cm^{-1} .

The orientations of extruded polypropylene samples used in the Raman experiment are given in Figure 1. The incident laser radiation directed along the space-fixed Y-axis with its electric field vector polarizing either along the Z- or the X-axis. The scattered light is observed along the X-axis, so it has an electric field component in either the Z or the Y direction. The Raman spectra of extruded polypropylene were taken in two sample orientations: one with its c-axis (the axis of extrusion) parallel to the space-fixed Z-axis (Orientation I) and the other with its c-axis perpendicular to the Z-axis (Orientation II).

RESULTS AND DISCUSSION

1) Raman Spectra:

The Raman spectra obtained at four different scattering geometries for the sample with the extrusion ratio $R_E=6.3$ are given in Figs. 2A and 2B. Here the standard notation Y(AB)X is used to differentiate the scattering configurations. The first and last letters outside the parenthesis indicate the directions of propagation of the incident and scattered radiation, respectively. The first and second letters inside the parenthesis indicate the polarization directions of the incident and scattered light respectively. One notes in Figs. 2A and 2B that the polarization selection for the $R_E=6.3$ sample is excellent. Each scattering geometry selects a rather unique spectrum, therefore indicating that the sample with $R_E=6.3$ is a highly orientated one. Except for a uniform intensity scaling throughout the whole spectral range the Y(CY)X, C(YC)X, and C(XC)X spectra are quite similar, thus suggesting that the extruded polypropylene has an approximate cylindrical optical symmetry.

The intensities of the polarized and depolarized components of each spectral line depend, to a large degree, on the extrusion ratio of the sample. The Raman spectra at two extrusion ratios in the three representative spectral regions are shown in Fig. 3.

According to the x-ray study, the crystalline isotactic polypropylene (IPP) contains three monomer units, $-\text{CH}_2-\text{CH}(\text{CH}_3)-$, in one turn in a helical conformation, with a fiber identity period of 6.50\AA .⁶ The skeletal chain is alternate sequences of trans and gauche conformations. The molecular vibrations of an infinitely extended helical IPP molecule can be analyzed under the factor group of the line group which is isomorphous to the point group C_3 . Analysis of this factor group indicates that the total of 77 vibrational modes are distributed among 25 totally symmetric A modes and 26 doubly degenerate E modes. Tadokoro, *et al.*⁷ and Snyder and Schachtschneider⁸ have calculated the normal modes of crystalline IPP. In the Raman spectra of molten IPP⁹, which is also believed to contain helical chains¹⁰, it was found that A modes are polarized and the E modes depolarized, in good agreement with the calculation. In the completely oriented IPP sample, A modes are present only in the Y(CC)X and C(Y)X configurations and E modes only in Y(CY)X, Y(XY)X and C(Y)X configurations, as shown by Snyder¹¹. In partially oriented IPP, A and E modes are present in all scattering configurations. The intensity ratios and the depolarization ratios of various bands at different scattering geometries reflect the information about chain ordering.¹²

As seen in Fig. 2, for the $R_E=6.3$ sample, the pure A modes at 398, 841, and 1254 cm^{-1} are nearly extinguished in the Y(CY)X spectrum, whereas

pure E modes at 528 and 1219 cm^{-1} almost disappear in the Y(CC)X spectrum. This result indicates that the sample with $R_E=6.3$ has a very high degree of the c-axis chain orientation.

The band at 50 cm^{-1} , which is present only in the C(Y)X spectrum, has not been reported previously. This band is not predicted by the normal mode calculation,⁷ and is probably a higher harmonics of the longitudinal acoustic mode or an intermolecular mode. The present work is insufficient to delineate the true nature of this peak. Assignments of Raman bands in the uniaxially oriented IPP have been given by Bailey, *et al.*¹³ While the results of the present study agree in general with their spectral assignments, from the intensity and polarization characteristics of the Raman spectra shown in Figs. 2A and 2B one notes that the peaks at 1333, 1362 and 1462 cm^{-1} are mostly of E symmetry and the peaks at 2843 and 2910 cm^{-1} are mostly of A symmetry. Previous work¹³ has suggested that these are of mixed A-E species.

2) Intensity Ratio and Orientational Alignment:

As mentioned above, the crystallinity of the polymer is affected by hydrostatic extrusion. The evidence for orientational alignment as well as for the change of crystallinity in IPP is clearly seen in the intensity behavior of the 809 and 841 cm^{-1} bands. The 841 cm^{-1} band corresponds to the CH_2 rocking mode, and is a pure A species; it displays a strong parallel dichroism⁷. The 809 cm^{-1} band is a CH_2 rocking mode coupled to the skeletal stretching, and belongs to a mixed A-E symmetry, with predominantly A. The intensity ratio of the 841 cm^{-1} peak to the 809 cm^{-1} peak displays a rather interesting orientational dependence. As shown in Fig. 4, in the

Y(CC)X spectrum, the intensity ratio decreases with increasing extrusion ratio, whereas in the C(Y Y)X spectrum, it increases with increasing extrusion ratio. The change in the intensity ratio is mainly due to the intensity variation of the 841 cm^{-1} band, and indicates that this pure CH_2 rocking band is very sensitive to the change in the degree of crystallinity due to extrusion. The fact that the intensity of the 841 cm^{-1} band in the C(Y Y)X spectrum is more intense than in the Y(CC)X spectrum is easy to understand because the CH_2 rocking motion is not expected to modulate as significantly as the c- component of the Raman polarizability (α^{cc}) as the transverse components (α^{aa} or α^{bb}) in an oriented polymer chain. A detailed study of the intensity behavior in different polarizations will doubtlessly yield information about the orientational state of the IPP molecule.

One can obtain some quantitative information about the degree of orientational alignment by measuring the depolarization ratios of A and E bands of IPP. Given in Table I are the depolarization ratios of the 398, 809, 970, 1172, and 1219 cm^{-1} bands. The first four bands are of A symmetry and the last is of E. The depolarization ratios for A-bands were obtained as the ratios of integrated intensities of the depolarized component to that of the polarized component, whereas the depolarization ratio for the E band was the reciprocal of this. The depolarization ratios of both orientations I and II were determined. Except for the samples of high extrusion ratio, the depolarization ratios are unavoidably subject to some experimental errors due to the polarization scrambling of the incident and scattered light as they propagate through the IPP sample. To minimize the amount of polarization scrambling, the intensity measurements were carried out with the laser radiation incident on the sample location as

close to the surface as possible. The values presented in Table I are the average values resulting from two to three measurements. The depolarization ratio values for all bands in the non-extruded sample were found to be close to unity for both orientation I and II. Random orientation of crystallites and opacity of the sample are responsible for the polarization scrambling. Thus, the intensity pattern of the Raman bands in the nonextruded sample serve as a baseline for obtaining the information about the degree of alignment in the extruded sample.

As one notices in Table I, the depolarization ratios (ρ) decrease as the extrusion ratio is increased, again indicating the increasing degree of orientational alignment along the c-axis due to extrusion.

For IPP, the Raman tensors for A and E modes are given respectively by

$$\underset{\sim}{\alpha}^{(A)} = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix}, \quad \underset{\sim}{\alpha}^{(E)} = \begin{pmatrix} a & b & c \\ b & -a & d \\ c & d & 0 \end{pmatrix}$$

The expression for depolarization ratio for vibrational modes can be expressed in terms of the above Raman tensor elements, and for molecules in the liquid and gaseous phases, in which molecular orientation is random, the expression for the depolarization ratio is well-known. However, in the partially oriented polymer chains, the depolarization ratio depends on the statistical orientational distribution of the constituent polymer segments. For samples of axial symmetry such as the crystalline IPP, the orientational distribution function describing the alignment of the polymer segments with respect to the symmetry axis (i.e. the axis of extrusion) of the polymer is given

by $f(\cos\theta)$, where θ is the angle between the microscopic axis (the C_3 -axis of IPP) and the symmetry axis. All previous experiments which characterize the degree of orientational alignment have amounted to measurements of the alignment parameter $\bar{P}_2 = \langle P_2(\cos\theta) \rangle = \int P_2(x)f(x)dx$, where $P_2(x)$ is the Legendre polynomial of order 2. Recent Raman studies of oriented nematic liquid crystals have shown that in addition to \bar{P}_2 , $\bar{P}_4 = \langle P_4(\cos\theta) \rangle$ can also be obtained.¹⁴

While the study of \bar{P}_2 and \bar{P}_4 in hydrostatically extruded polymers will be the subject of our future publication,¹² we consider here the extraction of semi-quantitative information about the degree of chain orientation in extruded IPP by assuming that hydrostatically extruded IPP is a two phase mixture containing amorphous and crystalline regions. This assumption was also used in the study of extruded polyethylene in which the degree of crystallinity has been shown to increase as the extrusion ratio is increased.⁴ For ideally oriented parts of both crystalline and amorphous regions of IPP, the Raman selection rule and depolarization ratio as obtained by Snyder¹¹ are applicable. On the other hand, the randomly oriented part in the amorphous phase is expected to result in a liquid like behavior. We assume that the values of the depolarization ratio for this part in the extruded IPP are the same as those for liquid IPP. This assumption is not unreasonable as it has been found that the depolarization ratio of Raman bands in the smectic form of IPP, in which disorder in the packing of the chain segments were found to exist, are similar to the ρ values obtained for liquid IPP.⁹

Consider for the moment an E band in Orientation I. In this case the ideally oriented parts of the polymer contributes only to the scattering intensity in the depolarized scattering spectra. The randomly oriented amorphous part contributes to the intensity of the polarized and depolarized

scattering spectra, with the depolarization ratio equal to that of the liquid or smectic value of the particular band under consideration. Another part of the intensity in both the polarized and depolarized spectra is due to random oriented crystallites, imperfections, etc. in the sample which scramble the polarization of the Raman scattered light. Therefore, the total scattered intensity in the depolarized spectrum of the E mode has contribution from three separate sources:

$$I_{\text{dep}}^{(E)} = I_1 + I_2 + I_3 \quad (2)$$

where I_1 represents the intensity from ideally oriented amorphous and crystalline parts of the polymer, I_2 represents the intensity from randomly oriented amorphous part, and I_3 is the intensity due to polarization scrambling by random oriented crystallites and imperfections in the polymer.

On the other hand, the total intensity in the polarized spectrum of the E mode has contribution from only two sources:

$$I_{\text{pol}}^{(E)} = I_4 + I_5 \quad (3)$$

where I_4 is the intensity from the randomly oriented amorphous part, and I_5 is due to the polarization scrambling in the polymer.

Clearly $I_3 = I_5$, and according to our earlier assumption, I_2/I_4 is equal to the ρ value for the liquid or smectic form of IPP. The precise intensity contribution due to polarization scrambling (I_3 or I_5) is somewhat difficult to ascertain. However, lacking something better, we assume that the scrambled part I_3 is related to the total scattering intensity I_{tot} by

$$I_3 = I_5 = K I_{\text{tot}} \quad (4)$$

where I_{tot} is the sum of polarized and depolarized scattering intensities. The K value can be estimated by extrapolating the scattered intensity at different sample locations to that at the surface. A K value of 0.1 would mean 10% of the total scattering intensity has been scrambled by the randomly oriented crystallites and imperfections in the polymer. Having obtained the value of I_5 , we can readily obtain the I_4 value from Eq. (3). From Eq. (2), we can then obtain the I_2 value. The fraction of polymer, F, which is ideally oriented can now be calculated by using the expression

$$F = \frac{I_1}{I_1 + I_2} \quad (5)$$

A similar procedure for analysis can also be carried out for the A modes in orientation I and II. The values of F obtained are plotted as a function of R_E in Fig. 5. The error bars represent the scatter of the F values obtained by analysis of different modes. The K values assumed for polymer samples at different extrusion ratios are given in Table II. Since the opacity increases for samples with a low extrusion ratio, in order to account for the polarization scrambling a somewhat larger K value has to be used for the extended IPP sample with a low R_E value.

For samples in orientation I, the A modes at 398, 1254 cm^{-1} and E mode at 1219 cm^{-1} are used for analysis. For samples in Orientation II, only the A modes at 398 and 841 cm^{-1} were analyzed. Analysis of E modes in Orientation II is complicated by the fact that even for the completely aligned sample both the polarized [C(Y)X] and depolarized [C(X)X or C(Y)X] components are non-vanishing, and the simple scheme used for analysis as described above is not applicable.

The fraction of ideally orientated polymer is closely related to the degree of chain orientation. As indicated in Fig. 5, the F value decreases with increasing R_E , indicating that the degree of chain orientation increases with the extrusion ratio. This is in agreement with the observation of Yoon, et al.⁵ using x-ray diffraction. They have observed that the extent of c-axis orientation in IPP is enhanced with increasing extrusion ratio at a given temperature. However, they did not calculate the degree of chain orientation from their x-ray data. In our analysis, at $R_E=6.3$, the F value is 0.9. This indicates that about 90% of the polymer chains have been aligned along the direction of extrusion.

SUMMARY AND CONCLUSION

We have studied the Raman spectra of hydrostatically extruded polypropylene in several scattering geometries. We have shown that some degree of uniaxial alignment has been achieved by hydrostatic extrusion. At a high extrusion ratio, the polypropylene displays Raman spectra with well defined polarization characteristics, and the classification of various Raman bands into appropriate symmetry classes is greatly facilitated. Using the present result we have supplemented the earlier assignments of normal vibrations in IPP.

We have also determined the intensity ratios as well as the depolarization ratios as a function of the extrusion ratio for several Raman bands with predominantly A or E symmetry. These ratios are related in the degree of the c-axis orientation of the amorphous and crystalline regions of the extruded IPP. At a high extrusion ratio, we have found that a large portion of polymer chains in polypropylene have been aligned along the direction of extrusion. We have demonstrated Raman scattering as a convenient technique to characterize the alignment of polymer chains.

Acknowledgment: We thank the Office of Naval Research for financial support.

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TABLE I

Depolarization ratios of various modes in IPP in two different orientations as a function of extrusion ratio.

Orientation I

A modes ($\frac{I_{cy}}{I_{cc}}$)

R_E cm^{-1}	398	809	841	974	1169	1254
6.3	.035	.08	.07	.05	.04	.025
4.9	.08	.16	.08	.17	.14	.10
3.4	.11	.23	.13	.34	.31	.16
3.0	.10	.23	.14	.35	.32	.17
1.0	1.0	1.0	1.0	1.0	1.0	1.0

Orientation I

E modes ($\frac{I_{cc}}{I_{cy}}$)

R_E cm^{-1}	1219	1336	1462
6.3	.1	.24	.34
4.9	.34	.54	.60
3.4	.78	.86	.90
3.0	.84	.92	.95
1.0	1.0	1.0	1.0

Orientation II

A modes ($\frac{I_{cy}}{I_{yy}}$)

R_E cm^{-1}	398	809	841
6.3	.05	.09	.05
4.9	.09	.18	.11
3.4	.13	.27	.15
3.0	.14	.29	.16
1.0	1.0	1.0	1.0

TABLE II

Assumed K values for IPP samples at different extrusion ratios.

Orientation I

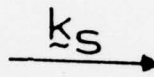
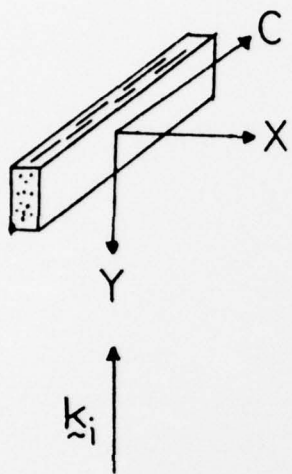
R_E	K
6.3	0.02
4.9	0.05
3.4	0.1
3.0	0.1

Orientation II

R_E	K
6.3	0.04
4.9	0.07
3.4	0.12
3.0	0.13

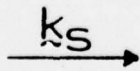
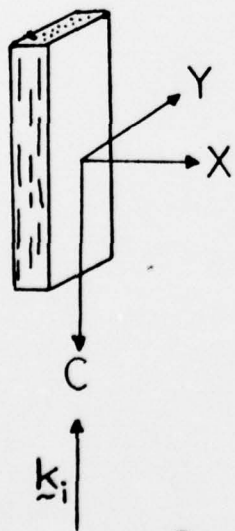
FIGURE CAPTIONS

- Figure 1. The orientations of extruded polypropylene samples used in the Raman experiment. The cylindrical axis is the axis of extrusion which is taken to be the c-axis.
- Figure 2. The Raman spectra obtained at different scattering geometries for the sample with the extrusion ratio equal to 6.3. Figure 2A covers the 0 - 1500 cm^{-1} region and Figure 2B ranges from 2700 to 3300 cm^{-1} .
- Figure 3. The Raman spectra at two extrusion ratios in the two representative spectra regions.
- Figure 4. The intensity ratios of the 841 and 809 cm^{-1} peaks obtained in Y(CC)X and C(Y)X. The 842 cm^{-1} peak belongs to A and 809 cm^{-1} belongs to mixed A and E symmetry.
- Figure 5. The fraction (F) of extruded IPP which is ideally oriented is shown as a function of extrusion ratio.



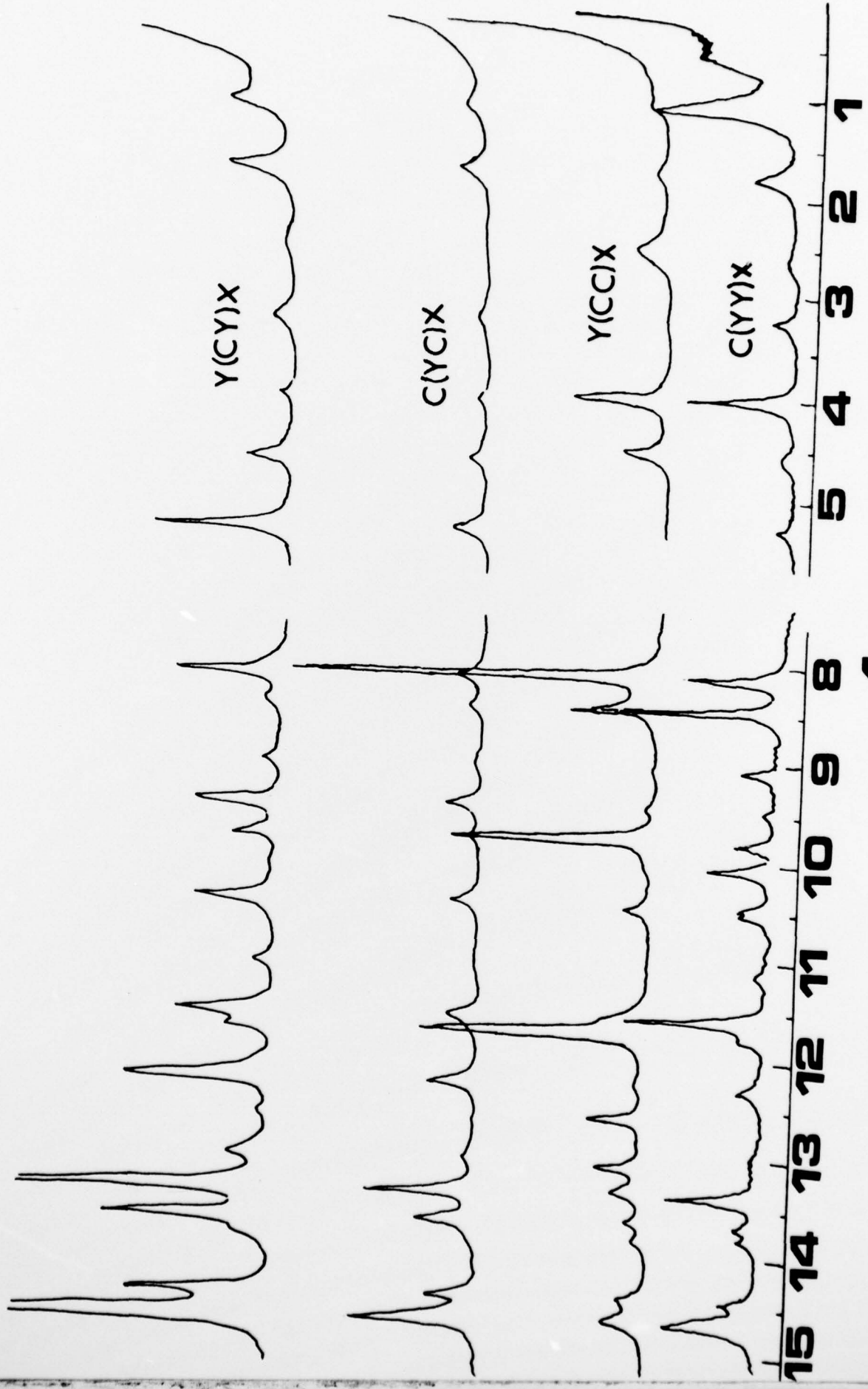
$$\hat{e}_i = \hat{c}, \hat{e}_s = \hat{c} \text{ or } \hat{y}$$

Orientation I



$$\hat{e}_i = \hat{y}, \hat{e}_s = \hat{y} \text{ or } \hat{c}$$

Orientation II



$\text{CM}^{-1} \times 100$

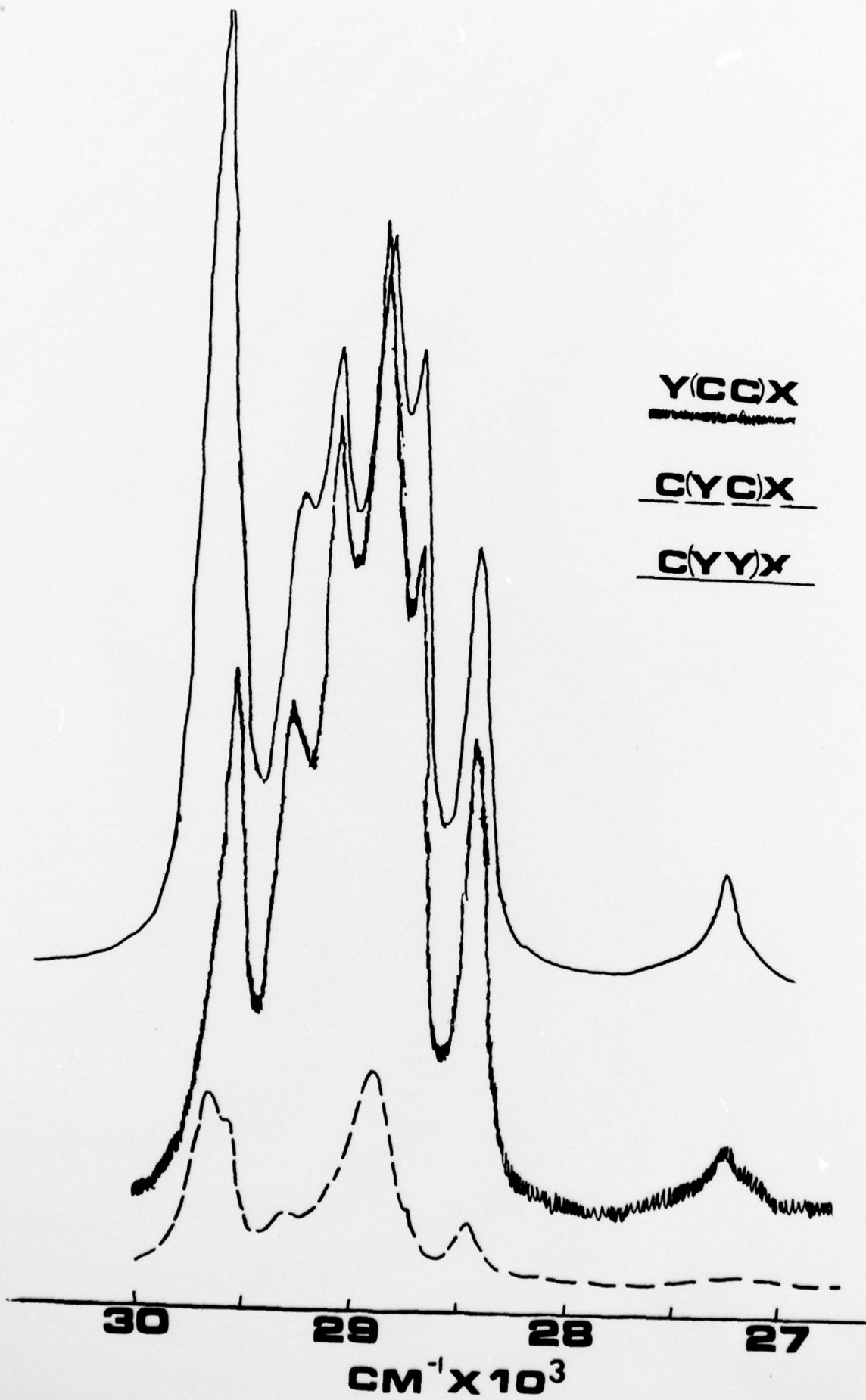


Fig. 2B

