Laser-Raman spectrum of helical syndiotactic polypropylene

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A more intense and more detailed laser-Raman spectrum than previously reported for the two-fold helix conformation of syndiotactic polypropylene is presented. Good agreement is found between the observed Raman shifts and those predicted by other authors; hence assignment to symmetry species of much of the experimental data is possible.

INTRODUCTION

In their review Youngman and Boor[1] emphasize the need for a complete characterization study of polypropylene, in order to understand and interrelate polymer structure property relationships. Since all steric arrangements can be prepared, from syndiotactic through atactic to isotactic, the study of polypropylene has special relevance to an elucidation of Ziegler-type catalysis and polymer behaviour[1].

The vibrational spectrum of isotactic polypropylene has been the subject of many papers. These include normal coordinate calculations and their comparison with experimental infra-red data[2–8], infra-red spectra[8–11] and Raman data [12–15]. Vibrational frequencies for both crystalline forms of the syndiotactic polymer (SPP) have been determined from force-field calculations derived from a series of saturated hydrocarbons[5] by Schachtsneider and Snyder[16] and transferred from isotactic polypropylene[3] by Miyazawa[17] and Miyazawa and Ideguchi[18]. These calculated frequencies have been compared with the experimental infra-red data of Peraldo and Cambini[19] and Tadokoro *et al.*[20]. Koenig *et al.*[21] have also compared the infra-red spectra of the helical forms of both isotactic and syndiotactic polypropylene with that of the atactic material.

Previous reports of experimental Raman data for helical SPP are limited to those of Zerbi and Hendra[22] for a highly crystalline powder sample and a brief reference by Zerbi[23] to a 'regularity band' in the skeletal vibration region near 850 Δcm^{-1}. Unfortunately the observation of Raman signals by Zerbi and Hendra[22] was severely hampered by fluorescence, and consequently only the most intense Raman bands, ascribed to A modes, were evident in their spectrum. In addition their recorded spectrum exhibited a strong emission for which no reasonable explanation was offered other than that fluorescence was responsible. In this paper we present a Raman spectrum (*Figure 1*) of syndiotactic polypropylene in the two-fold helix conformation which is a substantial improvement over that previously published, being more intense and also free of fluorescence background. The data recorded allow a more complete observation of Raman signals in the region 180–4000 Δcm^{-1} and a better comparison with the predicted vibrational frequencies[16,17]. The good agreement found between observed and predicted frequencies permits assignment to symmetry species of much of the experimental data.

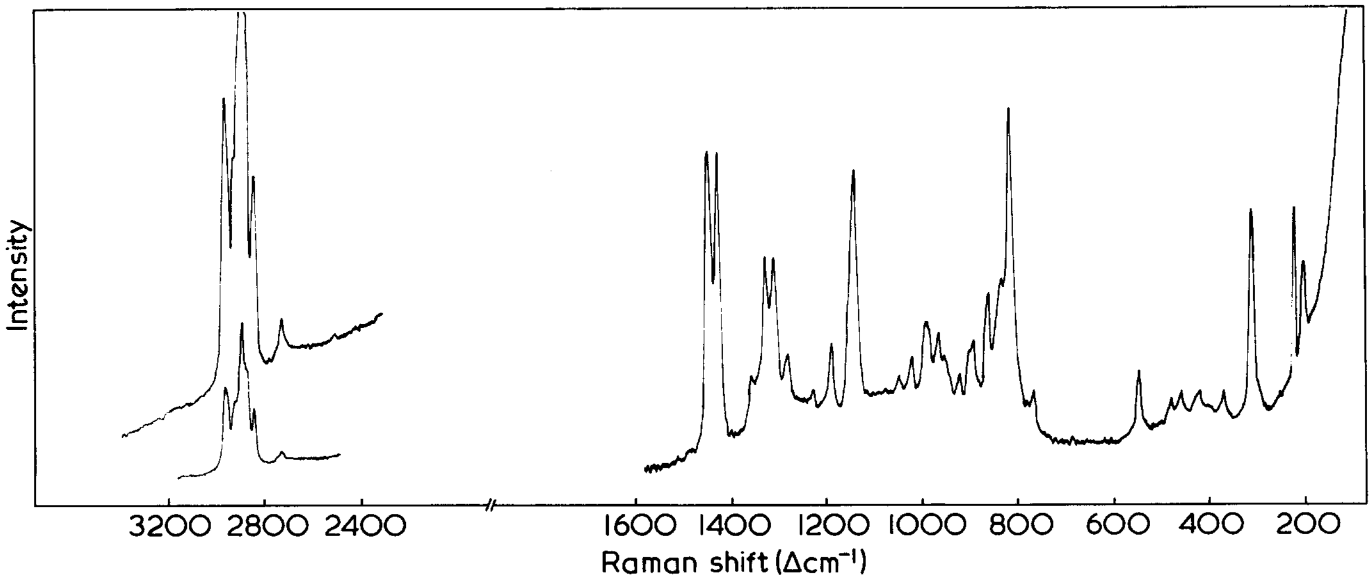

Figure 1 Laser-Raman spectrum for a crystalline powder sample of helical syndiotactic polypropylene

EXPERIMENTAL

The spectrum shown in *Figure 1* was recorded from a crystalline powder sample using 488.0 nm excitation from an argon ion Lexel model 75 laser (~80 mW power at the sample) on a Cary 83 laser-Raman spectrometer. The slit width was set at 5 cm^{-1}, the pen period at 10 sec and the scan speed at 0.2 Δcm^{-1}/sec. All the bands excepting that at ~220 Δcm^{-1} (plasma emission) arose from Raman emission by the sample. The poor stray-light discrimination properties of the small 'bench-top' Cary 83 Raman spectrometer prevented the observation of any signals at frequencies below 180 Δcm^{-1}.

The polymer was characterized by ^{13}C n.m.r. and X-ray spectroscopic techniques. The triad sequences of ^{13}C n.m.r. spectra of polypropylene are well characterized[24] and for this sample only rr- and mr-centred[25] units were detected from the spectrum. The former triads represented about 90% of the observed resonances. Since there was no evidence for mm-centred units the latter triads must be present as rmr sequences. It may therefore be considered to be an SPP sample of high purity. The X-ray powder photograph was characteristic[26] of the two-fold helix conformation of SPP[27].

DISCUSSION

Syndiotactic polypropylene can be prepared in two crystalline modifications[28]: the more stable helical conformation, and a planar zig-zag form. The helical conformation, the subject of this paper, has a polymer chain with four monomeric units per translational repeat distance and three mutually perpendicular two-fold axes, the helix axis and two-fold axes passing through the CH$_2$ groups, and has a conformation described[16] as *TGGTTG'G'T*. The line group of this model is isomorphous with the point group D_2 and there are 26 spectroscopically active vibrations[16,17] for each of the species A, B$_1$, B$_2$ and B$_3$. The A modes are Raman active only. Schachtsneider and Snyder[16] define the B$_1$, B$_2$ and B$_3$ species as those modes with transition moments parallel to the two-fold axis passing through the external CH$_2$, the two-fold axis passing through the internal CH$_2$ and the chain axis respectively. Where quoted, the species as defined by Miyazawa[17] have been transformed to agree with this notation. Although there is reasonable agreement between the calculated frequencies of Schachtsneider and Snyder[16] and Miyazawa[17], the values quoted by the former authors are used to compare to the Raman shifts observed in this study. The more complete assignment and good agreement obtained in the infra-red by a comparison of their predictions with the studies of Peraldo and Cambini[19] on bi-dimensionally oriented specimens leads us to favour their assignments.

VIBRATIONAL ASSIGNMENTS

In the absence of any other data (anisotropic scattering, temperature dependence)[12], and because of the many accidental degeneracies arising from the weak intramolecular coupling[22], it is not possible to assign unambiguously the observed Raman bands to vibrations of A, B$_1$, B$_2$ and B$_3$ species. However, the good agreement found by Schachtsneider and Snyder[16] between observation and prediction for the infra-red spectrum, and the frequency coincidence or near coincidence of many of the Raman bands seen in this study with the infra-red absorption bands deter-

Table 1 Observed and calculated frequencies for the D_2 form of SPP

ν_{Calc} (cm^{-1})			ν_{Obs} (cm^{-1})		
				Raman	
Ref 17	Ref 16		Infra-red Ref 16*	This study	Ref 22
1463	1463	A		1466 s	1463 w
1458	1462	A			
1438	1454	A		1445 s	1445 m–w
1435	1452	A			
1462	1465	B$_1$	1465		
1458	1462	B$_1$	1460		
1437	1453	B$_1$	1432		
1462	1464	B$_2$	1463		
1461	1461	B$_2$	1455		
1437	1454	B$_2$			
1461	1464	B$_3$	1460		
1458	1462	B$_3$	1455		
1387	1380	B$_1$	1379		
1384	1374	B$_2$	1378?		
1384	1378	B$_3$	1377	1374 w	
1355	1373	B$_3$	1374		
1363	1372	B$_2$	1373		
1387	1372	A		1370 sh,w?	
1366	1357	B$_1$			
1368	1353	A		1345 m	1346 vs
1329	1352	B$_1$	1332		
1349	1352	B$_3$	1346		
1338	1339	A		1327 m	1331 vs
1345	1331	B$_2$	1360		
1287	1301	B$_2$	1311		
1300	1300	B$_3$	1293	1297 w	
1289	1275	B$_1$	1287		
1263	1265	B$_3$	1264		
1211	1259	A			
1190	1223	B$_1$	1242	1244 vw	
1195	1194	B$_2$	1202		
1190	1191	A		1204 w–m	1202 vw
1147	1174	B$_3$	1167		
1139	1168	A		1157 s	1158 m
1147	1167	B$_1$	1152		
1148	1159	B$_2$	1153		
1115	1115	B$_2$			
1113	1113	B$_1$	1088, 1083		
1062	1096	B$_3$			
1057	1068	B$_3$	1060	1061 vw	
1033	1044	B$_2$	1035	1034 w	
1112	1041	A			1040 vw
1007	996	A		1002 m	1000 vw
979	980	B$_1$	1006		
948	974	B$_3$	977	978 w–m	
939	971	B$_1$	976? a		
			963 a†	966 w	
929	931	B$_2$	935	933 vw	
926	918	A		913 sh,w	
901	903	B$_1$	906	903 w	
904	902	B$_3$	901		
883	878	B$_2$	~870	872 m	
873	867	B$_3$	867		
			845 †	844 sh,w	
857	839	A		828 s	829 m–s
820	829	B$_3$			
826	825	B$_2$	812		
824	786	B$_1$	776	776 w	
529	542	A		552 w–m	
545	537	B$_1$	535		
484	476	B$_2$	483	486 w	
469	436	B$_3$	468	463	

v = very; w = weak; m = medium; s = strong; sh = shoulder; a = amorphous.

* The frequencies listed in this column are those given by Schachtsneider and Snyder[16] from data supplied by Natta, Peraldo and Cambini prior to their own publication[19]. Slight discrepancies, nominally not more than ±1 Δcm^{-1}, exist between these two sets of figures. The most notable differences are for two B$_2$ bands quoted as 1153 and 1035 cm^{-1} in reference 16 and as 1160 and 1032 cm^{-1} respectively in reference 19. Potential energy distributions and descriptions of the vibrations are thoroughly covered in reference 16.

† Data from reference 19

Table 2 Observed and calculated frequencies for the D_2 form of SPP, annotations as for *Table 1*

ν_{Calc} (cm^{-1})			ν_{Obs} (cm^{-1})		
				Raman	
Ref 17	Ref 16		Infra-red Ref 16*	This study	Ref 22
2963,2962	2962,2962	A		2962 s	2960 w
2963,2962	2962,2962	B_1	2960–2950		
2963,2962	2962,2962	B_2			
2963,2962	2962,2962	B_3	2959,2948		
2903	2929	B_1	2927	2922 sh,w	
2904	2929	B_2	2923		
2906	2930	B_3	~2925		
2902	2928	B_3			
2926	2906	A		2887 vs	2904 m
2927–2926	2904,2904	B_1,B_2	2915,2915		
	2903	B_3	2912		
2873	2882	A		2873 sh, w–m	2892–2872 m
2872–2873	2882	B_1	2882,2866		
	2882	B_2	2982,2967		
	2882	B_3	2882,2867		
2849	2856	A		2840 m	2848 w–m
2844	2855	A			
2847	2855	B_1	2843		
2847	2855	B_2	2837		
				2725 w	

mined by Peraldo and Cambini[19], suggest origins for much of the Raman data. (Schachtsneider and Snyder[16] were able to assign nearly all of the observed absorption bands[19] and with the exclusion of the C–H stretching frequencies and the calculated frequency of the symmetric <CCC bending, which was obviously out of line[16], their average error between the two sets of data was 0.85%.) We have also adhered to the criterion of Zerbi and Hendra[22] that the totally symmetric A modes are most likely to give rise to the most intense Raman bands. Bands observed only in the Raman spectrum are also likely to be A modes. This makes possible assignments of the majority of the observed Raman bands.

THE REGION 1500–450 Δcm^{-1}

Origins or major contributors to the intensity of the Raman bands observed for the region 1500–450Δcm^{-1} are given in *Table 1*. At the high frequency end of this range, distinct splitting of each vibration into four easily separable species is poor; however, as expected[22], most of the observed Raman emission intensity between 1100 and 1500Δcm^{-1} seems to be attributable to A modes. Near-neighbour B species may well contribute to the asymmetry seen on the high frequency side of the 1157Δcm^{-1} band and implied in the complex emission centred at about 1335Δcm^{-1}. It is difficult, however, to reconcile any of the observations with origination from the A mode prediction at 1259 cm^{-1}, the nearest (very weak) observation at 1244Δcm^{-1} seeming to favour assignment to the species B_1. The weak feature at 966Δcm^{-1} does not appear to correspond to a normal mode of vibration for helical SPP. It is best assigned as arising from zig-zag regions of the SPP chain in the amorphous state[19]. A similar weak feature was observed in the infra-red spectrum[19] and strong bands near 963Δcm^{-1} were seen in the infra-red spectra of the zig-zag conformation of SPP and for SPP in solution and in the molten state. The weak shoulder at 844Δcm^{-1} corresponds with the weak infra-red absorption at 845 cm^{-1} and is associated with non-helical conformations[19,23].

THE REGION 450–180 Δcm^{-1}

Below 450Δcm^{-1} four bands were observed: 424 (weak), 376 (weak), 315 (strong) and 202 (medium). The intense band at 315Δcm^{-1} must be assigned to the A mode described as a mixture of <C–C–C bend and C–C skeletal stretch[16,22], the predicted frequency of which is coincident with the observation. The medium intensity band at 202 Δcm^{-1}, which originates from CH_3 torsion, is best attributed to the A mode (199 cm^{-1}); the corresponding B_1 (196), B_2 (202) and B_3 (200) species possibly contribute to its intensity. Schachtsneider and Snyder[16] found that their calculated frequency of the symmetric <CCC bending of the $C(C_3)$ group was obviously out of line and the B_3 mode predicted at 436 cm^{-1} was found in the infra-red at 468 cm^{-1}. (Miyazawa[17] calculated this mode to occur at 469 cm^{-1}.) The contribution of this symmetric bend to the potential energy distribution[16] was 46%; similar errors might then be expected for the B_2 mode (37%) predicted at 433 cm^{-1}, the B_1 mode (40%) at 403 cm^{-1} and the A mode (27%) at 347 cm^{-1}. Both the above B species might therefore be considered as candidates for the weak feature at 424 Δcm^{-1} with the A mode possibly giving rise to the observation at 376Δcm^{-1}. (The only other predictions in this region were B_3 modes at 410 cm^{-1} and 358 cm^{-1}.) Amorphous or intermediate conformations cannot be precluded as alternative origins for these two bands. Zerbi and Hendra[22] also observed low frequency bands near 315 Δcm^{-1} and 200Δcm^{-1}, at 314Δcm^{-1} (medium strong) and 204Δcm^{-1} (weak) respectively and an additional weak feature at 172 Δcm^{-1} (A-mode predicted[16] at 176 cm^{-1}).

THE REGION 3000–2700 Δcm^{-1}

The data for this region are given in *Table 2*. The CH-stretching region appears again to be dominated by A modes with the 2922Δcm^{-1} observed Raman shift originating from one or several coincident B species. The 2725 Δcm^{-1}

observation probably arises as an overtone or combination of the intense bands observed in both the infra-red and Raman spectra near 1450 cm^{-1} and 1350 Δcm^{-1}.

CONCLUSION

The laser Raman spectrum for the two-fold helix conformation of syndiotactic polypropylene recorded shows many more vibrational bands than previously reported. The good correlation found between observation and prediction verifies further the force field of Schachtsneider and Snyder[16] and proposed polymer structure.

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REFERENCES

1 Youngman, E. A. and Boor, J. *Macromol. Rev.* 1967, **2**, 33

2 Miyazawa, T. and Ideguchi, Y. *Bull. Chem. Soc. Jpn* 1963, **36** 1125

3 Miyazawa, T. *J. Polym. Sci. (C)* 1964, **7**, 59

4 Schachtsneider, J. H. and Snyder, R. G. *Spectrochim. Acta* 1964, **20**, 853

5 Schachtsneider, J. H. and Snyder, R. G. *J. Polym. Sci. (C)*, 1964, **7**, 99

6 Tadokoro, H., Kobayashi, M., Ukita, M., Yasufuku, K., Murahashi, S. and Torii, T. *J. Chem. Phys.* 1965, **42**, 1432

7 Zerbi, G. and Piseri, L. *J. Chem. Phys.* 1968, **49**, 3840

8 Miyazawa, T., Ideguchi, Y. and Fukishima, K. *J. Chem. Phys.* 1963, **38**, 2709

9 Peraldo, M. and Farina, M. *Chim. Ind. Milan* 1960, **42**, 1349

10 Chantry, G. W., Fleming, J. W., Pardoe, G. W. F., Reddish, W. and Willis, H. A. *Infrared Phys.* 1971, **11**, 109

11 McDonald, M. P. and Ward, I. M. *Polymer* 1961, **2**, 341

12 Fraser, G. V., Hendra, P. J., Watson, D. S., Gall, M. J., Willis, H. A. and Cudby, M. E. A. *Spectrochim Acta (A)* 1973, **29**, 1525

13 Bailey, R. T., Hyde, A. J. and Kim, J. J. *Spectrochim. Acta (A)* 1974, **30**, 91

14 Vasko, P. D. and Koenig, J. L. *Macromolecules* 1970, **3**, 597

15 Schaufele, R. F. *J. Opt. Soc. Am.* 1967, **57**, 105

16 Schachtsneider, J. H. and Snyder, R. G. *Spectrochim. Acta* 1965, **21**, 1527

17 Miyazawa, T. *J. Chem. Phys.*, 1965, **43**, 4030

18 Miyazawa, T. and Ideguchi, Y. *Rep. Prog. Polym. Phys, Jpn* 1965, **8**, 49

19 Peraldo, M. and Cambini, M. *Spectrochim. Acta* 1965, **21**, 1509

20 Tadokoro, H., Kobayashi, M., Kobayashi, S., Mori, K., Murahashi, S., Nozakura, S. and Yasufuku, Y. *Symp. High Polym., Tokyo* 1964

21 Koenig, J. L., Wolfram, L. E. and Graselli, J. D. *Spectrochim. Acta* 1966, **22**, 1233

22 Zerbi, G. and Hendra, P. J. *J. Mol. Spectrosc.* 1969, **30**, 159

23 Zerbi, G. *Proc. Fifth Int. Conf. Raman Spectrosc.* 1976, p 485

24 Zambelli, A., Dorman, D. E., Brewster, A. I. R. and Bovey, F. A. *Macromolecules* 1973, **6**, 925

25 Frisch, H. L., Mallows, C. L. and Bovey, F. A. *J. Chem. Phys.* 1966, **45**, 1565

26 Personal communication

27 Natta, G., Pasquon, I., Corradini, P., Peraldo, M., Pegoraro, M. and Zambelli, A. *Rend. Accad. Naz. Lincei* 1960, **28**, 539

28 Natta, G., Peraldo, M. and Allegra, G. *Makromol. Chem.* 1964, **75**, 215