Fourier transform infra-red study of polypropylene

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Infra-red bands characteristic of isotactic polypropylene in the preferred 3_1 helical conformation and in the irregular conformations of the amorphous phase have been isolated from the spectrum of the semicrystalline polymer using the absorbance subtraction technique. The spectrum of the ordered component makes available new information concerning band assignments. The spectrum of the amorphous phase has been compared to the spectrum of the melt. Certain features of the former can be attributed to a degree of ordered conformation in the amorphous phase of a melt–quenched sample.

INTRODUCTION

Considerable progress in the analysis of the infra-red spectra of semicrystalline polymers has resulted from the application of the digital subtraction capability of computerized instruments[1–4]. Providing that samples of different degrees of order can be prepared, the spectra of the crystalline and amorphous phases can be separately generated. Subtle spectral changes, such as the shift in frequency of the crystalline bands of polychloroprene as a function of the incorporation of defects into the lattice[1,2], have been revealed by these techniques. More recently, an analysis of the infra-red spectrum of poly(ethylene terephthalate) by D'Esposito and Koenig[4] produced evidence for local regions of order in the amorphous component of the annealed polymer. In order to determine if this morphology is unique to PET or polymers with similar chemical structures we have applied these techniques to a study of isotactic polypropylene. Furthermore, the separation of the spectral components of the crystalline and amorphous phases permits an accurate determination of the frequencies of the vibrational modes of the polymer chain in the preferred conformation, clarifying the assignment of bands to ordered or amorphous components.

EXPERIMENTAL

Isotactic polypropylene, (sample number 6570 F) was obtained from the Hercules Chemical Company. Thin films were prepared by placing small amounts of sample between sheets of aluminium foil in a press maintained at 200°C. Immediately upon release of pressure the films were plunged into appropriate baths of ice water or dry ice–acetone. Films were annealed in a vacuum oven at 130°C.

Spectra were recorded on a Digilab FTS-14 Fourier Transform Infrared spectrophotometer. The frequency scale is calibrated internally by a helium–neon laser and is accurate to 0.2 cm^{-1}. Two hundred scans at a resolution of 1 cm^{-1} with double precision hardware were used to record spectra.

RESULTS AND DISCUSSION

The procedure for obtaining difference spectra characteristic of the ordered or amorphous phases of a semicrystalline polymer has been described in detail previously[3] and will only be briefly outlined here. Thin films of IPP with different degrees of crystallinity were prepared by first quenching from the melt into ice–water or dry ice–acetone and then annealing to increase the proportion of chains in the preferred conformation. The spectra of such a quenched (ice–water) and subsequently annealed sample are compared in *Figure 1*. Melt pressed samples are too thick to allow the observation of the very strong C–H stretching absorptions, so that this discussion is confined to the region of the spectrum between 2000 and 450 cm^{-1}.

The amorphous component of the spectrum of the annealed sample is removed by subtracting a proportion of the spectrum of the quenched material. The appropriate fraction is determined on a trial-and-error basis. The procedure is more complicated for polypropylene than previously studied polymers since bands assigned solely to an amorphous component have not been identified. However, it became apparent that the methyl deformation mode at 1376 cm^{-1} has a slightly different frequency in the amorphous phase, so that a negative (below the baseline) dip in the different spectrum was apparent at 1378 cm^{-1} if too large a proportion of the quenched film was subtracted. The difference spectrum obtained by bringing this negative component to the baseline is also shown in *Figure 1*. Similar results were obtained upon quenching films into dry ice–acetone and annealing.

This difference spectrum corresponds to how we would intuitively expect the spectrum of a completely ordered material to appear. The bands are sharp and extremely well resolved, so that shoulders in the annealed spectrum now appear as separate bands. It may not be completely accurate to term this the crystalline spectrum, since no effects due to intermolecular interactions are apparent. It is more precisely described as being characteristic of long lengths of the poly-

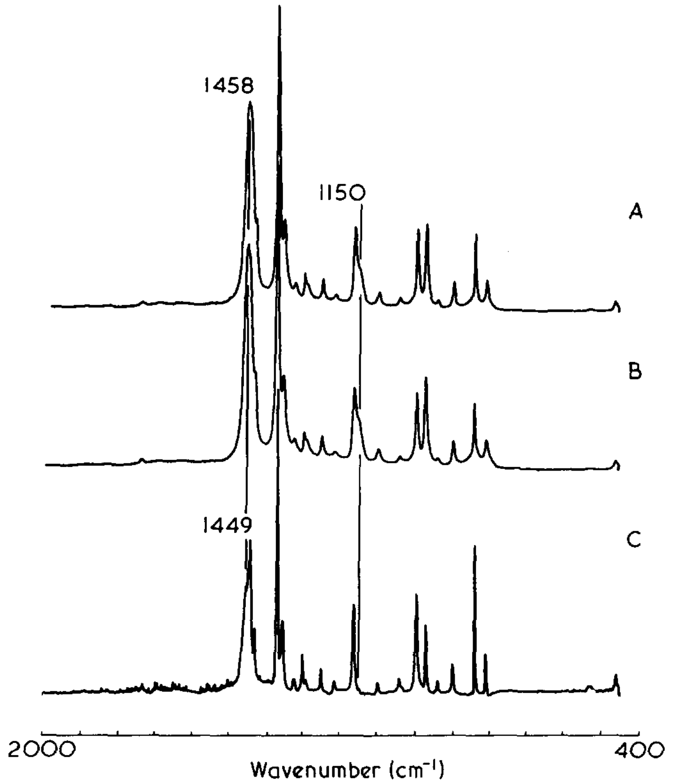

Figure 1 A, Infra-red spectrum (plotted in absorbance) of an annealed sample of isotactic polypropylene; B, spectrum of quenched sample; C, difference spectrum obtained by subtracting the spectrum of the quenched sample from that of the annealed

Table 1 Observed frequencies of IPP (cm^{-1})

		Difference spectra		
Quenched (ice–water)	Annealed (20 min, 130°C)	Annealed–quenched	Quenched–annealed	Melt
1458	1458	1458(sh) 1449	1458	1459
1436	1436	1435	1437	
1376	1376	1376	1378	1378
1359	1359	1359	1358 sh	1358(sh)
1330	1330	1330(sh) 1325		
1304	1304	1305	1302	
1296	1296	1296		
1255	1255	1255	1257	1256
1219	1219	1219		
1168	1168	1168		
1154 sh	1154 sh		1160	1152
1103	1103	1103		
1044	1044	1044		
998	998	998	995	
974	973	972	975	972
842	841	840	(843)	
809	809	809	806	
459	459	459		

mer chain in the preferred conformation. However, in most polymers such ordered chains are incorporated into a crystal lattice. Under certain conditions polypropylene is apparently an exception to this rule. Quenching into ice–water can produce a smectic phase in which ordered polymer chains are arranged parallel but with little or no lateral register[5,6]. Annealing such quenched samples produced the monoclinic form. We could detect no spectral effect due to differences in chain packing. Difference spectra were obtained in a number of ways, for example by subtracting the spectrum of a film quenched into dry ice–acetone or liquid nitrogen from that of a film quenched into ice–water. All difference spectra characteristic of the ordered phase corresponded closely to that shown in *Figure 1*. The observed frequencies of the quenched, annealed the difference spectra are presented in *Table 1*.

Two components of the asymmetric methyl deformation mode, which are superimposed to give a single band at 1458 cm^{-1} in the spectra of the quenched and annealed samples, have been observed in dichroism studies[6]. These components are resolved separately in the difference spectrum characteristic of the ordered chain. The 1449 cm^{-1} A mode is now revealed to be more intense than the E mode at 1458 cm^{-1}, corresponding to the intensity relationship predicted for these two bands[6]. In previous work the 1458 cm^{-1} band appeared to be more intense, so that the assumed transition moment directions were seriously questioned[6]. This anomaly can now be seen to be due to the strong absorption of the amorphous component at 1458 cm^{-1}.

The symmetric methyl deformation mode at 1376 cm^{-1} is extremely sharp and relatively more intense in the difference spectrum than in the unsubtracted spectra. The results we will present below will also demonstrate the surprising sensitivity of both the frequency and intensity of this band to conformation. This vibration is usually considered to be localized in the methyl group to the extent that it has been used to measure the composition of ethylene–propylene copolymers. However, the calculations of Schachtschneider and Snyder[8] indicated that CH and CH_2 deformations also contribute to this mode, presumably due to a degree of mixing of vibrational energy levels with the 1359 cm^{-1} mode. Conversely, the vibrational analysis of Tadokoro *et al.*[8] and Miyazawa, *et al.*[9] suggested that this mode is predominantly localized. The results presented here indicate that the calculations of Schachtschneider and Snyder are a more accurate reflection of the potential energy distribution.

The shoulder observed near 1154 cm^{-1} in the spectra of the annealed and quenched samples is completely removed in the difference spectrum of *Figure 1*. This band has been variously assigned as a fundamental mode or predominantly associated with the amorphous component[8,10]. The strong Raman line at 1151 cm^{-1} can now be considered to be the fundamental of the ordered chain, while this mode only has appreciable intensity in the infra-red spectrum when the polymer chain has an irregular conformation.

By subtracting the spectrum of the annealed sample from that of the quenched it should be possible to obtain a difference spectrum characteristic of the amorphous regions of the sample. This procedure is relatively straight forward with polymers such as PET which have large monomer repeat units and little intramolecular coupling[4]. However, a number of modes of polypropylene consist of highly coupled vibrations. The different distribution of sequence lengths of polymer chain in the preferred 3_1 helical conformation of the quenched sample relative to the annealed could lead to frequency shifts in the bands assigned to the ordered conformation. These bands would then not subtract correctly. This effect occurs to a major extent in only one band of polypropylene. The difference spectrum characteristic of the amorphous phase is compared to that of the ordered conformation in *Figure 2*. The 841 cm^{-1} CH_2 rocking mode has both a positive and negative component due to the factors discussed above. Even though the difference in

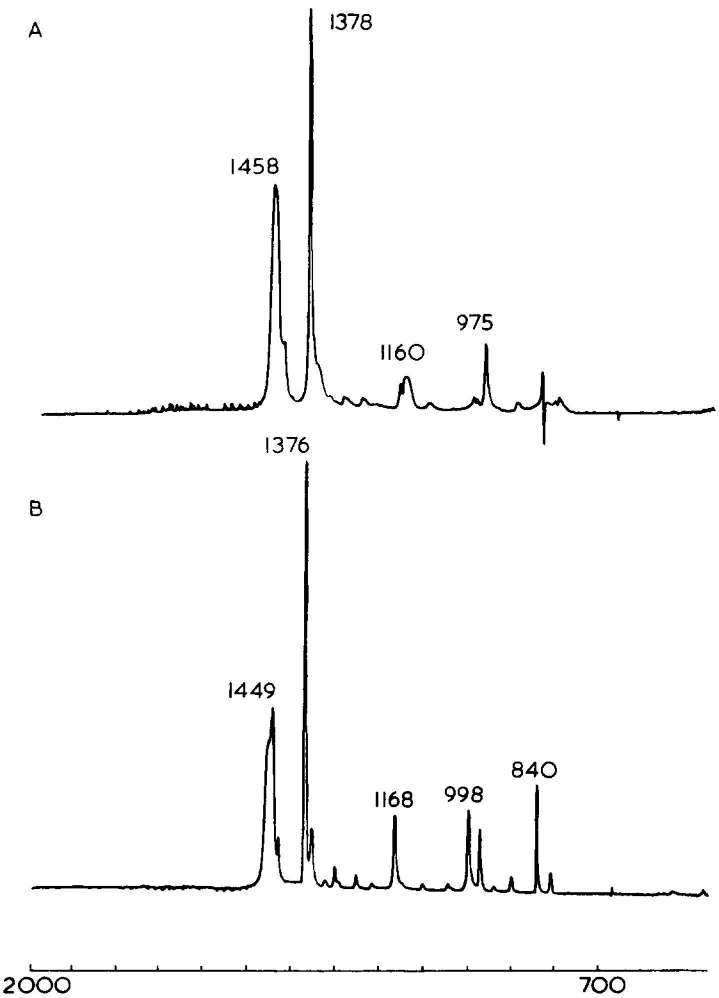

Figure 2 A, Difference spectrum characteristic of the amorphous phase of the quenched sample; B, difference spectrum characteristic of the ordered phase of the annealed sample

ordered sequence length has only a slight effect on the frequency of this band in the quenched and annealed samples, the absorbance subtraction method magnifies the difference.

Compared to the spectrum of the helical polymer chain, the bands characteristic of irregular conformation sequences are broader and a few are considerably weaker in intensity. The asymmetric methyl deformation mode now has its strongest component centred at 1458 cm^{-1}. The symmetric deformation mode is less intense and shifted to 1378 cm^{-1}. The sharp band at 1168 cm^{-1} is now much broader and shifted to 1160 cm^{-1}. The 998 cm^{-1} band is reduced considerably in intensity in the spectrum of the amorphous component but is still present. A weak band at this frequency in the spectrum of the melt was interpreted by Zerbi *et al.*[11] as being due to segments of at least five monomer units maintaining their helical conformation. The spectrum of the amorphous component of a semicrystalline sample is compared to the spectrum of the melt in *Figure 3*. Although this latter spectrum displays evidence of slight oxidation it corresponds closely to previously reported spectra[5]. The observed frequencies are listed in *Table 1*. As might be expected, the bands of the molten sample are broader. The asymmetric methyl deformation mode has a frequency of 1459 cm^{-1} while the peak height of the symmetric mode is considerably weaker. The band at 1168 cm^{-1} in the spectrum of the helix and 1160 cm^{-1} in the amorphous component is shifted to 1152 cm^{-1} in the melt. The band at 975 cm^{-1} shifts to 972 cm^{-1} upon melting.

Broadly speaking, the spectrum of the irregular regions of the semicrystalline polymer resembles the spectrum of the melt closely. However, in terms of the frequencies of many of the bands the amorphous spectrum is intermediate between the spectrum of the melt and the helical chains. Such band shifts and broadening could be due to temperature effects alone. Even though such shifts in the spectra of polymers are usually only of the order of 1 or 2 cm^{-1} in this temperature range, we have no way of knowing the size of the anharmonic terms for specific normal modes. Nevertheless, the features in the spectrum of the melt that led Zerbi *et al.*[11] to conclude that there are ordered helical chain segments in the melt are more pronounced in the spectrum of the amorphous phase. Consequently, these results strongly indicate that there is a portion of helical polymer chain segments in the amorphous phase. It should be kept in mind that the difference spectrum is that of the amorphous phase in the quenched polymer, where a number of defects have been introduced by rapid cooling from the melt. At this time we have no evidence concerning the conformation of the polymer chain lengths excluded from the crystal in a sample where the maximum degree of crystallinity has been attained.

Gezovich and Geil[12] observed grains in electron micrographs of the glassy state and suggested that these consist of clusters of ordered polymer chain segments. The infra-red evidence presented in this communication adds some sup-

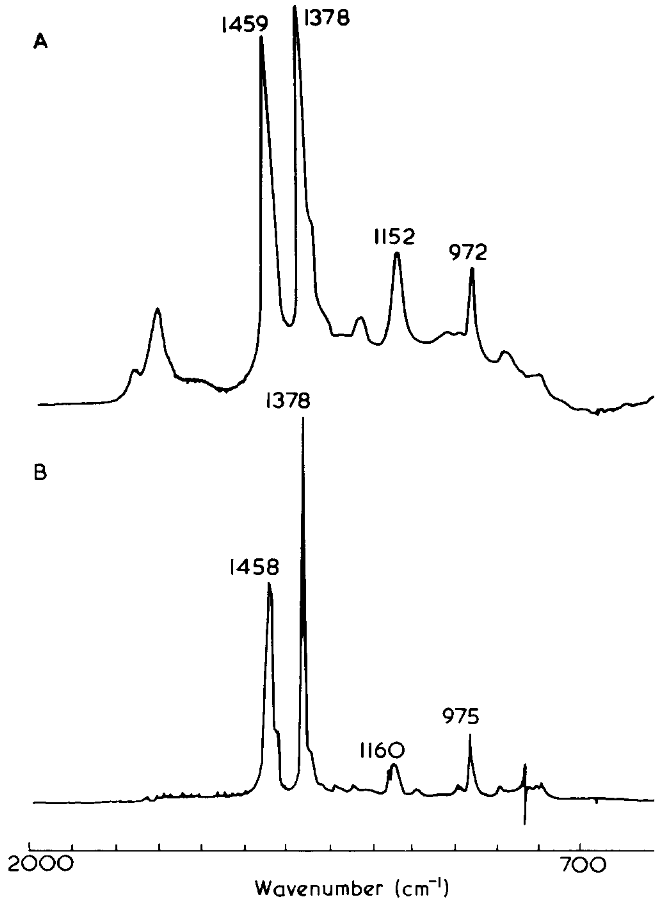

Figure 3 A, Infra-red spectrum of polypropylene in the melt; B, difference spectrum characteristic of the amorphous phase

port to this proposal. Taken in conjunction with the results of the study of PET[4] there is increasing evidence that the development of short lengths of ordered conformation is a prerequisite for three-dimensional lattice crystallization from the glass.

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