Melting behaviour and crystalline, intermediate and amorphous phase in poly(ethylene terephthalate) fibres

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It is well known that properties of oriented semicrystalline polymers depend on their morphological characteristics and that morphology of these systems can be varied considerably and controlled by thermal and mechanical treatments. Considerable work on understanding the morphological structure of PET fibres has involved some assumptions and simplifications. One is a two phase model consisting of crystalline and amorphous phases. However, there has been criticism of the two-phase model for PET fibres[1-2] and as an alternative the existence of three phases has been suggested by Prevorsek[3]. This model has an intermediate phase which consists of nearly extended molecular chains along the fibre axis. The amount of these three phases can be separated by Lindner's X-ray technique[4] and recent analysis[5] of drawn PET fibres by this technique has led to a semiquantitative relationship between phase indices and mechanical properties. The melting behaviour of melt crystallized PET has been extensively studied and attempts have been made to relate this with morphological structures. Different workers have assigned the double peak in thermograms of annealed PET in different ways although later work seems to support the idea of melting and recrystallization. However, the melting behaviour of PET fibrous systems is not clearly understood and a similar explanation as that for melt crystallized PET may not be correct.

The present paper deals with separation of crystalline, intermediate and amorphous phase indices of drawn PET fibres by Lindner's X-ray technique[4]. Further an attempt is made to relate these phase indices with melting peak area in thermograms obtained from differential thermal analysis (d.t.a.)

EXPERIMENTAL

The material selected was as-spun PET multifilament yarn (280/36/0) obtained from Shree Synthetics Ltd, Ujjain. Drawing of the PET multifilament was carried out at 140°C on a bench model machine. Draw ratios selected for this study were 1.0, 2.0, 3.0, 3.5, 4.0, 4.5, 5.0. Drawn fibres were dry heat-set at 120°C for 30 min. X-ray diffraction experiments were carried out using a Norelco X-ray generator and flat plate camera. The samples were exposed to Ni-filtered CuKα radiations. The fibre X-ray photographs obtained were scanned on a Joyce–Lobel microdensitometer for azimuthal (010) reflection intensities and for equitorial direction. A Stanton Redcroft 671-B differential thermal analyser was used for scanning the thermograms of the fibres. The heating rate was 20°C/min and experiments were carried out under nitrogen atmosphere.

Table 1 Crystalline, intermediate and amorphous phase indices as a function of draw ratio

Draw ratio	Crystalline phase index	Intermediate phase index	Amorphous phase index
1.0	0	0	1.0
2.0	0.15	0.07	0.78
3.0	0.32	0.21	0.47
3.5	0.34	0.22	0.44
4.0	0.36	0.27	0.37
4.5	0.40	0.30	0.30
5.0	0.42	0.34	0.24

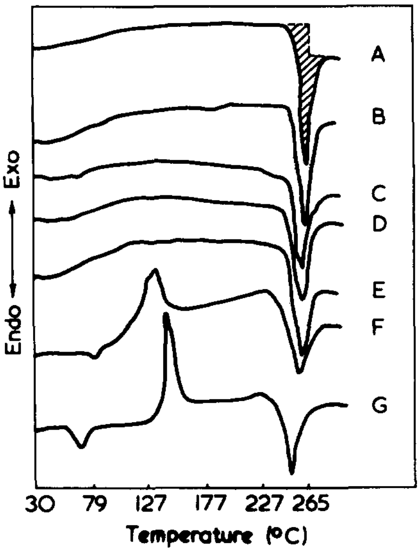

Figure 1 D.t.a. thermograms of PET samples of different draw ratios: A, 5.0; B, 4.5; C, 4.0; D, 3.5; E, 3.0; F, 2.0; G, 1.0

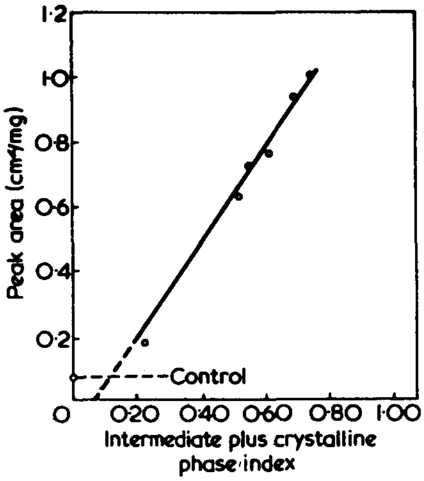

Figure 2 Melting peak area *versus* crystalline plus intermediate phase indices of PET samples of different draw ratios

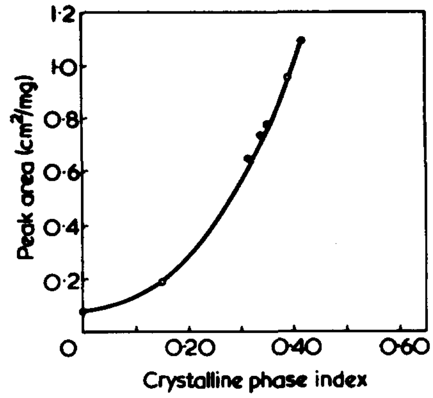

Figure 3 Melting peak area *versus* crystalline phase index of PET samples of different draw ratios

RESULTS AND DISCUSSION

Lindner's X-ray method was used to determine crystalline, intermediate and amorphous phase indices. These phase indices are given in *Table 1*. The intermediate phase index increases linearly with draw ratio. The continuous decrease of amorphous phase index with draw ratio shows that the increasing number of randomly oriented molecular chains are aligned along the fibre axis.

The d.t.a. scans of these fibres are shown in *Figure 1*. It is observed that the melting region becomes narrower with increasing draw ratio. For the undrawn sample and the sample of draw ratio up to 2.0, the glass transition is clearly seen at about 70°C. However, in addition to T_g there is another peak around 142°C for these samples, which is due to crystallization of the material. An attempt is made to relate the peak area under the melting curve with phase indices. The peak areas have been measured as shown in *Figure 1* for a sample of draw ratio 5.0. Appropriate correction factors have been used for melting peak areas due to crystallization before melting. This was carried out with the help of standard samples whose heat of fusions are known. The peak area thus measured is plotted as a function of crystalline plus intermediate and crystalline phase indices and are shown in *Figures 2* and *3* respectively. It is found that peak area is directly related to crystalline plus intermediate phase index. It is likely that the oriented amorphous regions of the samples attain a higher order of perfection with increasing temperature at a heating rate of 20°C/min here and finally melt, explaining the linear relationship. The relationship between peak area and crystalline phase index is found to give a continuous curve as shown in *Figure 3*. This can be used for the determination of crystalline phase index of an unknown sample. Thus the experimental relationships shown in *Figures 2* and *3* provide a procedure for the determination of crystalline, intermediate and amorphous phase indices of PET fibres from d.t.a. thermograms directly.

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^{13}C spin-lattice relaxation study of molecular motions of sidechains in α-helical polyglutamates

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A spin–lattice relaxation time T_1 from ^{13}C n.m.r. is useful for elucidating molecular motions of polypeptides containing the ring groups such as phenyl[1,2] and pyrrolidinyl[3]. A ^{13}C T_1 of a protonated carbon in macromolecules is governed mainly by dipole–dipole interactions with the directly attached protons[4]. It is demonstrated that the correlation times of carbons in a side chain attached to α-helical polyglutamates satisfy the extreme narrowing condition, and therefore one can simply interpret observed ^{13}C T_1s under this condition[2].

In a previous paper[5] it was shown that there is no internal rotation of the pendant carbazolyl (Cz) group in poly(*N*-vinylcarbazole) (PVCz) on the basis of the T_1 measurements. The hindrance of the side chain motion in PVCz arises presumably from the bulkiness of the Cz group[5,6]. It is interesting to find out how much the motion of a polyglutamate molecule is influenced when a bulky group such as Cz is introduced at the end of the side chain.

^{13}C n.m.r. spectra of the α-helical polyglutamates generally show no apparent peak corresponding to the α-carbon in the backbone. This is a result of line-broadening caused probably by polymer aggregation, if no solvent to prevent the aggregation (non-aggregate solvent) was added. In such non-aggregate solvents as dichloroacetic acid and trifluoroacetic acid (TFA), it is found that charge-transfer complexes form between the Cz group and the solvents*, and the molecular motions of the side chain are drastically disturbed by the complex formation. Thus, it is hard in such a case to distinguish the internal rotation of the side chain from the overall reorientations of the backbone. In order to overcome this difficulty, we prepared a modified poly(γ-methyl-D-glutamate) (PCDG) in which CH_3 groups are partly substituted by the Cz-ethyl groups so that we can compare T_1 values of the different terminal groups on the side chain attached to the identical backbone and obtain some information on the molecular motions of the side chains.

For comparison among the molecular motions of the different side chains in the α-helical polyglutamates ^{13}C T_1 of the terminal groups in the polymers, such as PCDG, poly(γ-methyl-D-glutamate) (PMDG) and poly(γ-benzyl-L-glutamate) (PBLG), dissolved in the neat helicogenic solvents were measured by the partly relaxed Fourier transform (*PRFT*) method. PMDG (degree of polymerization; $DP = 85$) and PBLG ($DP = 1320$) were supplied by Ajinomoto Co. PCDG ($DP = 85$), the partly ester-interchanged PMDG, which consists of 78.8% of β-*N*-carbazolylethyl-D-glutamate units and 21.2% of methyl-D-glutamate units was prepared from PMDG using a previously published method[7]. ^{13}C T_1 was measured by the PRFT method at 30°C employing either a Varian CFT-20 n.m.r. spectrometer (operating at 20 MHz) or a JEOL JNM-FX100 n.m.r. spectrometer (25.15 MHz). The sample solution was contained in a 10 mm o.d. n.m.r. tube, and no degassing was carried out as no appreciable effect of oxygen molecules to the ^{13}C relaxation in polymer solution has been reported[8]. Either $CDCl_3$ or $CDCl_2CDCl_2$ was used as the solvent, and TMS as the internal reference.

A set of PRFT spectra of PCDG in $CDCl_3$ is shown in *Figure 1*. The assignment of each peak was carried out by comparing the peaks with the ^{13}C spectra of poly(*N*-vinylcarbazole)[5] and of the other polyglutamates[1,2], and are given in *Figure 1*. The T_1 values of the resolved peak were determined by the semilog plot of the peak height against time[9], which lies fairly well on a straight line. In *Figure 2* the obtained T_1 values are shown as $N \cdot T_1$, where N is the number of the attached protons, for the several carbons in the side chains.

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* The solution changes from colourless to blue on addition of the non-aggregate solvents