Letter

A DRDF study of liquid crystalline poly(ethylene terephthalate) and *p*-hydroxybenzoic acid copolyester

A series of nematic liquid crystalline copolyesters were prepared recently by the acidolysis reaction of poly(ethylene terephthalate) (PET) with appropriate dicarboxylic acids and acetylated dicarboxylic acids and acetylated difunctional phenols[1,2]. Similar to non-polymeric liquid crystalline materials[3,4], these copolyesters also show thermotropic liquid crystalline characteristics of turbid melts, shear-sensitive melt viscosities, and readily induced anisotropic solid properties. It is the purpose of this communication to report a differential radial distribution function (DRDF) analysis of wide-angle X-ray scattering (WAXS) from one such high molecular weight liquid crystalline material. The analysis also falls within our overall objective of achieving a better understanding of macromolecular chain packing in the 'amorphous' molten or glassy states of polymers.

The particular polymer chosen for this study was a copolyester of PET modified with 60 mol %*p*-hydroxybenzoic acid (PHB), 40PET/60PHB, (provided by Dr W. J. Jackson, Jr of the Tennessee Eastman Company. The polymer, with an inherent viscosity of 0.63, was compression moulded at 295°C in the liquid crystalline mesophase and rapidly quenched into ice water. The sample was non-crystalline, i.e. devoid of any three dimensional crystalline order, according to its WAXS pattern. The thickness of the rectangular specimen was 0.564 mm, and the bulk density was 1.389 g/cm^3. The procedures used for WAXS data collection, data correction and reduction, including the DRDF analysis are the same as those given in our previous studies of PET[5] and natural rubber (NR)[6].

Scattering data were collected on a Philips Norelco diffractometer employing a monochromatized CuKα radiation. Measurements were performed by step scanning in the range of 2θ scattering angle of 6° to 145°. The intensities were then corrected for background air scattering, absorption in the specimen, polarization, and multiple scattering by standard methods. Afterwards, the corrected WAXS data were normalized using the conservation of energy method, and the incoherent Compton scattering was then subtracted. Since the material used in this study is a random copolymer[1,2], a hypothetical structural unit of $(C_{10}H_8O_4)_{0.4}(C_7H_4O_2)_{0.6}$ or $(C_{8.2}H_{5.6}O_{2.8})$, based on the starting composition of the copolyester, was assumed in the analysis.

The corrected and normalized coherent WAXS intensity is shown in *Figure 1* as a function of 2θ. Three peaks are present at 2θ = 20.2°, 43°, and 83°. The inset shows the diffraction pattern of glassy PET taken from ref 5. It is noted that the intermolecular peak of the liquid crystalline 40PET/60PHB has a higher intensity than that of the glassy PET by approximately 50%. Although not directly comparable, the intensity of the principal scattering maximum for some non-polymeric materials was also found to be 5 to 15% greater for the nematic mesophase than its corresponding isotropic liquid[4]. Also, the 2θ position of the intermolecular peak is shifted from 21.2° for the glassy PET to 20.2° for the copolyester.

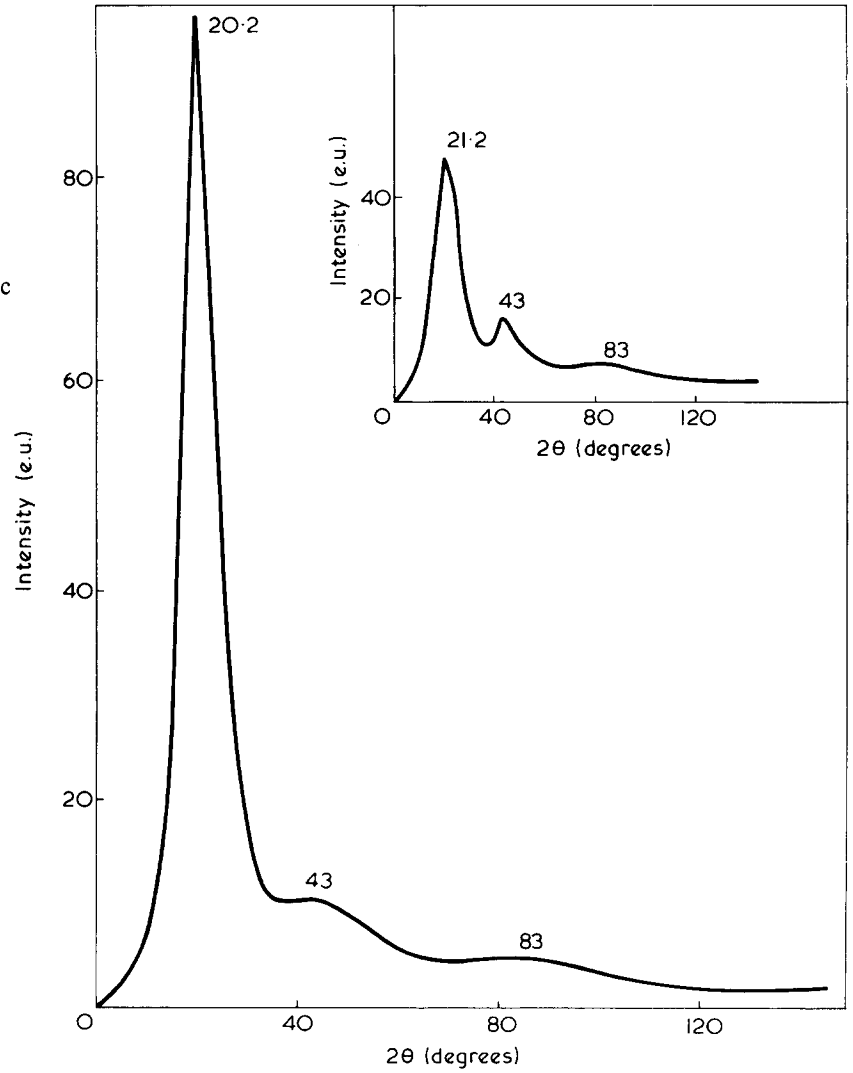

Figure 1 Corrected and normalized WAXS intensity *versus* scattering angle, 2θ, for 40PET/60PHB copolyester. The inset shows a similar curve for glassy PET taken from ref 5

The resultant DRDF was calculated from:

$$4\pi r^2\rho_0 H(r) = \frac{2r}{\pi}\int_0^\infty sI(s)\sin(sr)\mathrm{d}s$$

where ρ_0 is the average density of atoms in the system, $s = (4\pi/\lambda)\sin\theta$, and $I(s)$ is the interference function as defined previously[5]. The DRDF given in *Figure 2* was smoothed, starting from $r = 2.6$ Å, by multiplication of the corresponding $I(s)$ with a damping factor, $\exp(-0.030s^2)$. As seen from the curve (*Figure 2*), nine prominent peaks, located at 1.55, 2.40, 5.0, 9.9, 14.2, 18.9, 23.2, 27.5, and 31.7 Å, are present. The first two relatively sharper peaks in the DRDF are due to the average first and the average second nearest intramolecular atomic distances. The remaining peaks, as in the case of PET and NR, are predominantly intermolecular in origin, as judged by the presence of a nearly constant periodicity of about 4.5 Å in the DRDF. The periodicity is attributed to the nematic ordering of neighbouring chain segments. Thus, in the 40PET/60PHB copolyester a liquid crystalline order with a lateral extent of about 60 Å is deduced from the current study.

It is of interest to compare the present finding, namely the presence of a ~60 Å lateral order in the liquid crystalline 40PET/60PHB, with the 20–40 Å lateral order found in glassy PET[5,7] and the 80–100 Å lateral order in partially crystalline PET[5]. It appears that lateral ordering in amorphous polymers can be substantially impr̀oved by modification of the chemical configuration of macromolecules. In the copolyester, the improvement is brought about by incorporating more of the planar *para*-substituted PHB moieties.

Our study also suggests that DRDF analyses, when properly applied, can reveal the presence and the extent of local order in non-crystalline polymeric materials. The analysis is now being used to study other PET and PHB copolyesters and Kapton, a commercially available liquid crystalline polymer.

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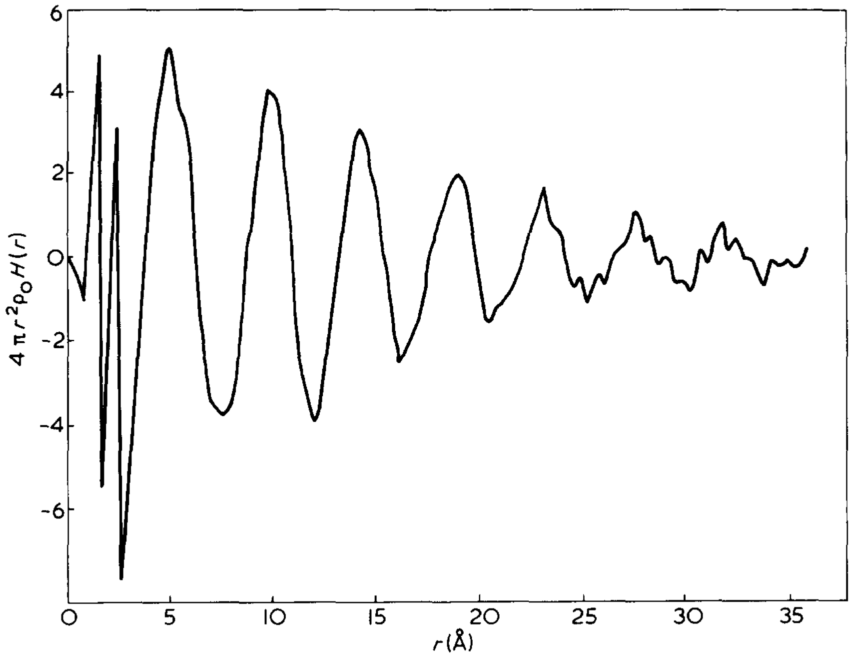

Figure 2 DRDF for the liquid crystalline 40PET/60PHB copolyester

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