Effect of composition on molecular alignment in polyethylene terephthalate copolymers

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In this study molecular alignment in copolymers of polyethylene terephthalate (PET) and p-hydroxybenzoic acid (PHB) was examined by means of differential radial distribution function (*DRDF*) analysis of wide angle X-ray scattering data. The study was carried out using two representative copolymers with the PHB content of 30 and 60 mol%. The *DRDF* curves for the amorphous and the partially crystalline samples of these copolymers showed periodic intermolecular peaks up to various radial distances. The appearance of these peaks at ~ 5 Å periodicity suggested the existence of more-or-less parallel chain segments in the copolymers. The extent of the lateral molecular organization was ~ 15 and 30 Å for the amorphous copolymers containing 30 and 60 mol% PHB, respectively. A substantial structural difference was therefore shown for the copolymers in this composition range. The *DRDF* curve for the amorphous copolymer with 30 mol% PHB was found to be very similar to that for the previously reported glassy PET with 0 mol% PHB, indicating that the two materials had almost the same intermolecular structure. The structural information revealed by these *DRDF* results was in agreement with the various property changes caused by varying PHB contents of the copolymers.

Keywords Polymers; liquid crystalline; differential radial distribution function; wide angle X-ray scattering; molecular alignment; polyethylene terephthalate; copolymers

INTRODUCTION

Recently Jackson and Kuhfuss[1] prepared a series of random copolymers with interesting properties. The copolymers were obtained by incorporating various amounts of p-hydroxybenzoic acid (PHB) into the backbone of polyethylene terephthalate (PET). The preparation involved acidolysis of the polyester with p-acetoxybenzoic acid and polycondensation through the acetate and carboxyl groups. It was found that the copolymers with PHB contents over 30 to 80 mol% gave turbid melts, low melt viscosities, and readily shear-induced anisotropic solids. The unusual properties were attributed to the nematic liquid crystalline nature of the polymer melts by McFarlane, Nicely, and Davis[2]. The mesophase was a result of the possible improvement in alignment of polymer chains due to the presence of planar PHB moieties in the copolymers.

In this study the alignment of chain segments in the new copolymers was examined by means of differential radial distribution function (*DRDF*) analysis of wide angle X-ray scattering (WAXS) intensities. The study provides information leading towards a better understanding of polymer properties in molecular terms. It is part of our work to ascertain the nature of the molecular organization in 'amorphous' molten and glassy polymers.

The *DRDF* analysis was applied to the amorphous and the partially crystalline copolymers containing 30 mol% PHB (70 PET/30 PHB) and 60 mol% PHB (40 PET/60

PHB). The two compositions are representative since the interesting properties of the copolymer series started to appear when the PHB content was just over 30 mol% and became most pronounced at 60 mol%. The *DRDF* results of the copolymers were compared with that of the base polyester, i.e., polyethylene terephthalate containing 0 mol% PHB (100 PET/0 PHB) to reveal the structural change caused by varying the composition. The structure of the glassy and the partially crystallized 100 PET/0 PHB has been studied previously using the *DRDF* analysis by Longman, Sheldon, and Wignall[3] and Gupta and Yeh[4].

Some *DRDF* results of the amorphous 40 PET/60 PHB have been reported in a preliminary communication[5].

EXPERIMENT AND ANALYSIS

The 70 PET/30 PHB and 40 PET/60 PHB copolymers used in this study were provided by Dr W. J. Jackson, Jr., of Tennessee Eastman Company. For each copolymer both amorphous and partially crystalline samples of approximately 0.6 mm thick were prepared. The amorphous samples were compression moulded at 295°C and rapidly quenched in ice water[2]. The partially crystallized samples were prepared by subsequent annealing of the amorphous sheets in a vacuum oven. Pertinent information on the preparation and properties of the four copolymer samples is given in *Table 1*.

The procedures employed for WAXS data collection and analysis have been described in detail elsewhere[4-6]. The X-ray scattering measurements were made on a Philips Norelco diffractometer using monochromatized Cu Kα radiation (wavelength $\lambda = a.542$ Å). The WAXS

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Table 1 Description of the preparation and properties of the copolymer samples

Sample	1	2	3	4
Composition	70 PET/ 30 PHB	40 PET/ 60 PHB	70 PET/ 30 PHB	40 PET/ 60 PHB
Thermal history	quenched	quenched	annealed 190°C, 0.5 h	annealed 230°C, 8.0 h
Density (g cm⁻³)	1.341	1.389	1.357	1.401

intensities for each sample were recorded by a step scanning procedure in the range of $6° < 2\theta < 145°$. Intensities for the lower scattering angles, i.e., $2\theta < 6°$, were obtained by extrapolating the experimental curve smoothly to zero at zero scattering angle.

Afterwards, the raw intensity data were corrected for experimental factors, including background air scattering, absorption, polarization, and multiple scattering, according to standard methods[7-10]. The corrected intensity data, I_{expt}, were then normalized using the equation:

$$\int \sum_i (x_i f_i^2 + x_i I_i) ds = \partial \int I_{expt} ds \quad (1)$$

where x_i is the atomic fraction, f_i the scattering factor, and I_i the Compton scattering of the i-type atom, $s = (4\pi/\lambda)\sin\theta$, and ∂ is the normalization constant. Since the polymers used were random copolymers, hypothetical chemical units of $(C_{9.1}H_{6.8}O_{3.4})$ for 70 PET/30 PHB and $(C_{8.2}H_{5.6}O_{2.8})$ for 40 PET/60 PHB were assumed in the analysis based on the starting compositions of the copolymers.

The Fourier analysis of scattering intensities for a system containing several different types of atoms, in this case C, H, and O, has been given by Waser and Schomaker[11], discussed by Pings and Waser[12], and applied by Longman and coworkers[3,13] and Gupta and Yeh[4]. Following this analysis, the DRDF, $4\pi r^2 \bar{\rho} H(r)$, for each copolymer sample was derived according to the equations:

$$4\pi r^2 \bar{\rho} H(r) = \frac{2r}{\pi} \int_0^{s_{max}} s i(s) \sin sr \, ds \quad (2)$$

$$i(s) = (I_{coh} - \sum_i x_i f_i^2) / (\sum_i x_i f_i)^2 \quad (3)$$

where $\bar{\rho}$ is the average atomic density, $s_{max} = 16 \text{ Å}^{-1}$, and I_{coh} is the coherent intensity obtained by subtracting Compton scattering from the normalized intensity data. The term $\sum_i x_i f_i^2$ is not strongly dependent on the way of

defining the hypothetical chemical units since differences in $\sum_i x_i f_i^2$ values between PET and PHB segments are

always small (within ~1–4%). The obtained DRDF was further smoothed beyond its second peak by multiplying a damping factor, $\exp(-0.03 s^2)$, by $i(s)$. Possible errors in the scattering factors were also removed by adjusting the DRDF curve below ~1 Å to a straight line having the theoretically expected slope of $-4\pi\bar{\rho}$ (refs. 9 and 10).

Further discussions on proper construction of reliable DRDF have been given previously by examining all the available literature information[4,6].

RESULTS AND DISCUSSION

The corrected and normalized WAXS intensities for the quenched 70 PET/30 PHB and 40 PET/60 PHB copolymers are shown in *Figure 1*. Similar to most of the amorphous polymers, three peaks are present at 21.0°, 43°, and 83° 2θ for the 70 PET/30 PHB and at 20.2°, 43°, and 83° for the 40 PET/60 PHB. The WAXS patterns comprise no Bragg reflections, indicating the structure of the copolymer samples is noncrystalline. A comparison of the WAXS data of 70 PET/30 PHB and glassy 100 PET/0 PHB shows that the two polymers have very similar patterns in both peak intensity and position[4]. For 40 PET/60 PHB the intensity of the principal peak at 20.2° is higher than that of the glassy 100 PET/0 PHB by approximately 50%. Also, the peak position is shifted from 20.2° to 21.2° when the PHB content is varied from 60 to 0 mol% in the polymers. The other two maxima at 43° and 83° are virtually not affected by the composition.

The WAXS data for annealed copolymer samples are shown in *Figure 2*. It is seen that annealing of the amorphous 70 PET/30 PHB copolymer results in splitting of the 21.0° peak into three sharp reflections at 18.0° (Bragg spacing $d = 4.93$ Å), 22.2° ($d = 4.00$ Å), and 25.3° ($d = 3.52$ Å). Similarly, three reflections at 19.7° ($d = 4.51$ Å), 20.7° ($d = 4.29$ Å), and 22.4° ($d = 3.97$ Å) are observed in the WAXS pattern for partially crystallized 40 PET/60 PHB. The peaks at 43° and 83° are unaffected by the thermal treatment for both copolymers.

The resultant DRDF curves for quenched and annealed copolymers are shown in *Figures 3* and *4*, respectively. For amorphous 70 PET/30 PHB prominent peaks at 1.4, 2.5, and 4.7 Å and very weak peaks at 6.4, 8.6, 10.7, 12.9, and 14.9 Å are observed. The DRDF for amorphous 40 PET/60 PHB copolymer shows nine well-shaped peaks at
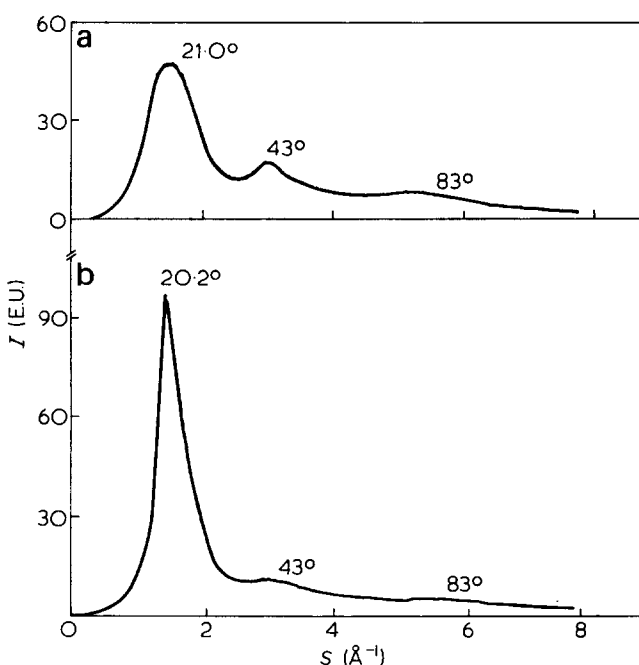

Figure 1 Corrected and normalized experimental WAXS data for quenched (a) 70 PET/30 PHB and (b) 40 PET/60 PHB

1.5, 2.5, 5.1, 9.8, 14.2, 18.9, 23.2, 27.5, and 31.7 Å. The results of annealing are shown by the presence of additional and prominent $DRDF$ peaks up to 40–50 Å for the two partially crystalline samples. According to previous calculations of the intramolecular distances and their contributions to the local density fluctuation in polymers, the $DRDF$ curve for glassy 100 PET/0 PHB consists of intramolecular peaks at ~1.5 and 2.5 Å and intermolecular peaks beyond the radial distance of ~4.5
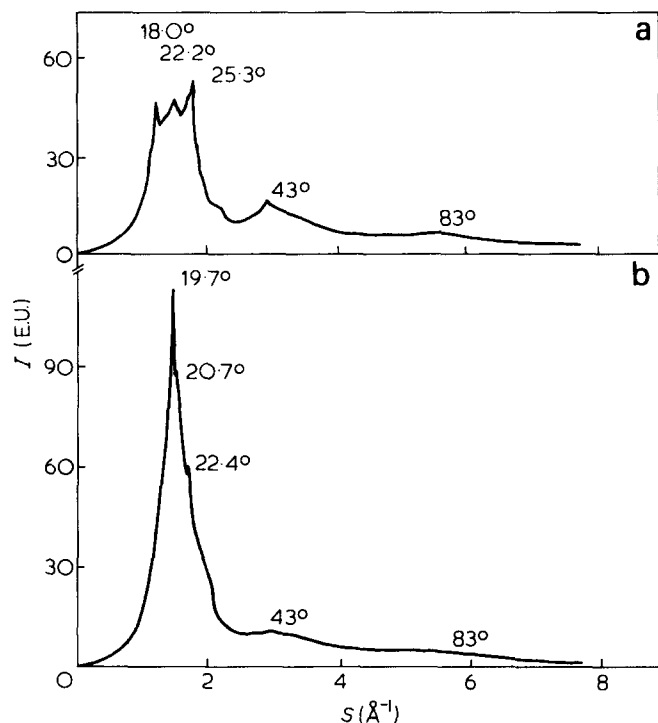

Figure 2 Corrected and normalized experimental WAXS data for annealed (a) 70 PET/30 PHB and (b) 40 PET/60 PHB
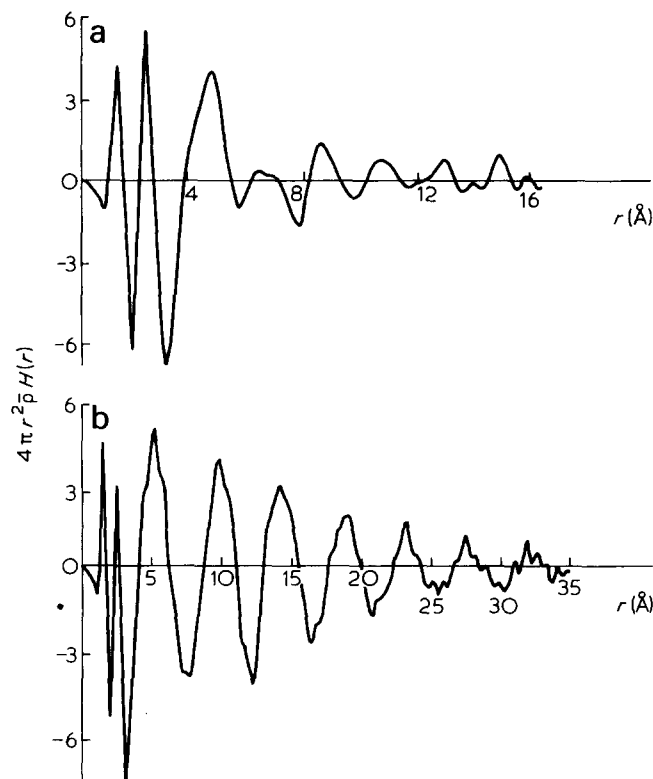

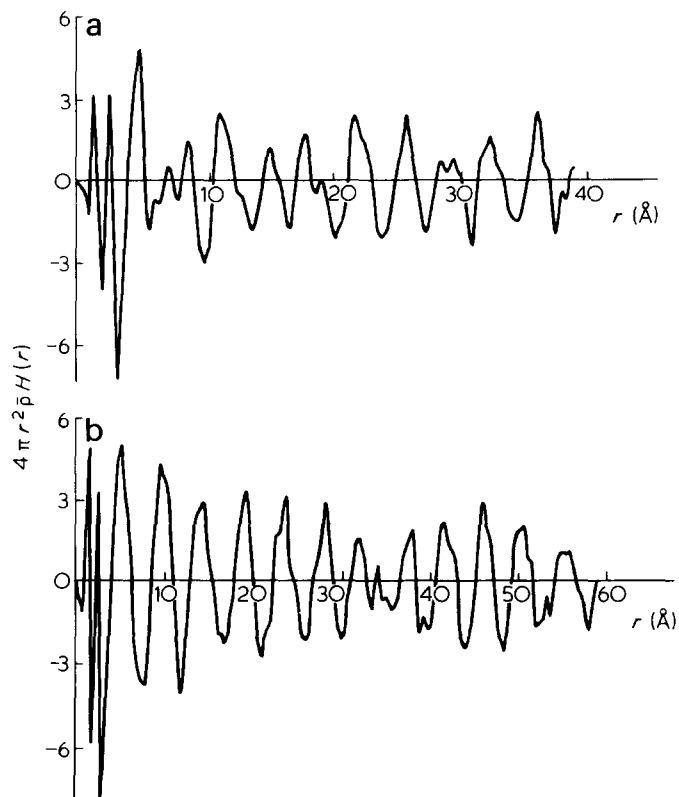Figure 3 DRDF curves for quenched (a) 70 PET/30 PHB and (b) 40 PET/60 PHB

Figure 4 DRDF curves for annealed (a) 70 PET/30 PHB and (b) 40 PET/60 PHB

Å[3,4]. In order to ascertain the intermolecular structural changes caused by incorporating PHB moieties into the PET backbone, the present study is focused on examining the $DRDF$ curves beyond 4.5 Å. The positions and heights of these intermolecular $DRDF$ peaks are given in *Table 2* for amorphous and partially crystallized 100 PET/0 PHB[4], 70 PET/30 PHB, and 40 PET/60 PHB.

The $DRDF$ results of glassy and partially crystalline 100 PET/0 PHB obtained by Gupta and Yeh[4] have led to the suggestion of a highly distorted nematic lateral ordering in the amorphous polymer. The presence of local molecular organization was also suggested previously by Yeh and Geil[14] based on dark field electron microscopy studies on thin polyester films. In this study the $DRDF$ curve for amorphous 70 PET/30 PHB is found to be very similar to that for the glassy 100 PET/0 PHB as shown in *Table 2*. The result indicates that a similar local structure is present in the amorphous 70 PET/30 PHB copolymer. Additionally, the existence of local alignment of chain segments is suggested by the significant enhancement of the intermolecular $DRDF$ peaks at 4.7, 10.7, and 14.9 Å when the copolymer is annealed. The periodicity of ~5 Å observed from these peaks represents the average distance between the more-or-less parallel neighbouring chains. The $DRDF$ results therefore suggest the presence of a short range molecular organization of ~15 Å in the quenched 70 PET/30 PHB copolymer. The molecular alignment is markedly improved by annealing of the copolymer as shown by the appearance of prominent and additional periodic intermolecular peaks up to a much higher radial distance in the $DRDF$ for annealed 70 PET/30 PHB sample.

For amorphous 40 PET/60 PHB a periodicity of ~4.5 Å is observed from the seven well-shaped intermolecular $DRDF$ peaks given in *Table 2*, suggesting the existence of

Table 2 Description of the intermolecular DRDF peaks

100 PET/0 PHB* (quenched)		100 PET/0 PHB* (190°C, 0.25 h)		70 PET/30 PHB (quenched)		70 PET/30 PHB (190°C, 0.5 h)		40 PET/60 PHB (quenched)		40 PET/60 PHB (230°C, 8.0 h)	
P	H†	P	H	P	H	P	H	P	H	P	H
4.8	4.1	4.8	5.3	4.7	4.0	4.7	4.9	5.1	5.1	5.0	5.0
6.8	0.6	7.3	2.2	6.4	0.3	7.1	0.6	–	–	–	–
8.5	1.5	8.3	1.7	8.6	1.2	8.5	1.5	9.8	4.1	9.7	4.2
11.1	0.6	11.3	3.7	10.7	0.6	11.0	2.5				
12.5	0.5	–	–	12.9	0.6	–	–	–	–	–	–
15.4	0.2	14.5	0.5	14.9	0.8	14.8	1.4	14.2	3.1	14.4	2.8
17.4	0.6	17.7	4.5	–	–	17.4	1.8	18.9	2.0	19.1	3.3
–	–	21.7	2.2	–	–	21.5	2.5	23.2	1.7	23.5	3.1
–	–	24.3	1.3	–	–	25.6	2.5				
–	–	28.2	2.4	–	–	28.3	0.9	27.5	1.2	27.8	3.0
–	–	31.6	1.2	–	–	32.2	1.7	31.7	0.9	32.0	1.5
–	–	–	–	–	–	35.9	2.5	–	–	37.9	1.9
–	–	–	–	–	–	–	–	–	–	41.6	2.2
–	–	–	–	–	–	–	–	–	–	45.9	2.8
–	–	–	–	–	–	–	–	–	–	50.5	2.0

* Data taken from ref. 4 and recalculated by applying the damping factor $\exp(-0.03\,s^2)$
† Peak position P and peak height H

lateral ordering of ~ 30 Å in the copolymer. The periodic peaks are explained by the higher concentration of those interatomic distances resulting from more-or-less parallel neighbouring chains. Similar to amorphous 100 PET/0 PHB[4] and 70 PET/30 PHB, the lateral alignment of chain segments is improved by annealing as shown by increases in number of intermolecular peaks and in intensities of the higher distance DRDF peaks. As indicated by McFarlane and coworkers[2], the 40 PET/60 PHB copolymer can be classified as a liquid crystalline material. The finding of lateral molecular alignment in this copolymer from the present DRDF results is consistent with the basic idea of the low molecular weight liquid crystals. The liquid crystalline polymers have been recognized as a special type of polymeric system occupying a position intermediate between amorphous and crystalline polymers[15]. Although this paper is not intended for exploring the liquid crystalline characteristics of the new copolymer, it is of interest to note that the extent of lateral ordering of 40 PET/60 PHB falls between those of the typical amorphous and crystalline polymers as revealed by the DRDF analysis.

Further, the study has shown that DRDF curves for amorphous 100 PET/0 PHB and 70 PET/30 PHB are very similar. This result indicates that the PHB content up to 30 mol% is insufficient to cause any major change in molecular alignment of the polymers. The structural similarity is in agreement with the very small property difference observed previously for the copolymers in this composition range[1,2]. By increasing the PHB content from 30 to 60 mol%, a substantial improvement in the lateral chain alignment in the copolymers is shown by the increase in the extent of ordering from 15 to 30 Å. The improvement can be attributed to the modification of the chemical configuration of macromolecules due to the incorporation of more planar para-substituted PHB moieties into the polyester. The structural change explains the reported profound differences in melt viscosity and density between 70 PET/30 PHB and 40 PET/60 PHB[1,2].

CONCLUSION

The presence of locally aligned chain segments in the copolymers containing 30 and 60 mol% PHB is suggested based on the DRDF study of quenched and annealed copolymer samples. The extent of the lateral molecular alignment is ~ 15 Å for amorphous 70 PET/30 PHB and ~ 30 Å for 40 PET/60 PHB. The structural modification revealed by the DRDF results is consistent with the property changes caused by varying the PHB content of the copolymers.

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