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Crystallization of random copolymers of poly(ethylene terephthalate) and poly(ethylene naphthalene-2,6-dicarboxylate)

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The crystalline structures of a range of specially synthesized random copolyesters of poly(ethylene terephthalate) (PET) and poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) have been studied. It is shown that this system has a crystallization and melting behaviour typical of random copolymers. Significant crystallinity can be induced in the copolymers of all compositions by hot drawing, even if the composition is in the 50/50 region. The results from wide angle X-ray scattering experiments indicate that in two different composition ranges these copolymers show distinctly different crystal structures. The lattice parameters of each of these structures change smoothly with the composition, while the repeat along the chain direction within the crystal is aperiodic. These experimental facts will be discussed in relation to the possibility of co-crystallization of the two types of units.

(Keywords: crystallization; random copolymer; X-ray diffraction)

INTRODUCTION

In the study of the crystalline and mesogenic structures of polymers, some traditional views are frequently challenged by unexpected experimental facts. In a random copolymer chain, two or more different types of chemical units are joined together at random, so that it is unlikely that such chains can be packed into a three-dimensional, long-range ordered lattice to form an ideal crystalline structure. However, numerous experiments have verified that crystallites can form in random copolymers under some circumstances.

The first hypothesis to explain crystallization in random copolymers was due to Flory in 1947[1]. It was suggested that random copolymers that exhibit crystallinity consist of units of type A which are capable of crystallizing and units of type B which do not crystallize under given conditions. Homopolymer sequences of crystallizable component A, occurring by chance in random copolymer chains, are able to segregate and crystallize. Wunderlich[2] introduced kinetic constraints into the Flory model. Based on his 'cold crystallization' model, only nearest neighbours are capable of crystallizing without redistribution of sequences of like units, while the other types of units incorporated in the crystal are treated as defects. In contrast to the models of homopolymer sequence matching, Windle *et al.*[3] suggested that, on the basis of diffraction and microscopic evidence, the crystallinity in some random copolymers may result from the segregation and lateral matching of similar yet random sequences of the neighbouring molecules. The crystals themselves thus contain mixtures of the different monomer units and lack periodicity in the chain direction. They are called non-period-layer (NPL) crystallites and hitherto have been observed in thermotropic copolyesters. Parallel with the NPL model, the 'plane start register model' has been proposed by Gutierrez *et al.*[4] to account for crystallinity in the same type of copolymer. In this model, the three-dimensional order is seen to arise from the parallel arrangement of a number of random but non-identical sequences with just one monomer in register at the centre of each sequence. While the contention between the Cambridge and Case Western groups has spurred much detailed investigation[3–14], the issue seems to have focused on the thickness of the segregated region in the chain direction, and whether this thickness is sufficient to be considered sequence matching.

A very recent result[15] indicates that the sequence segregation occurs in the liquid crystalline phase, crystallization representing the subsequent development of lateral order within the pre-segregation regions.

While much of the recent work in this field has concentrated on liquid crystalline aromatic random copolymers in which there is limited conformational freedom, (especially random copolymers of *p*-hydroxybenzoic acid (HBA) and hydroxy-2,6-naphthoic acid (HNA)), studies of crystallinity in the atactic olefins poly(vinyl chloride) and polyacrylonitrile[16,17] have opened up the role that can be played by conformational adjustments, which can minimize the disruptive effect of mixed units on crystal formation.

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However, the fact that the sequence matching ideas have emerged from studies of liquid crystalline random copolymers, opens the question as to whether they might have a wider relevance to conventional random copolymers. For this reason, a study has been made of the closely related random copolyester system of poly(ethylene terephthalate) (PET) and poly(ethylene naphthalene-2,6-dicarboxylate) (PEN). The presence of the ethylene glycol units means that the flexibility of the chain is too great to permit liquid crystallinity at any composition[18]. On the other hand, the system has been shown to exhibit crystallinity, at least for compositions comparatively rich in either PET or PEN[19].

EXPERIMENTAL

Materials

Synthesis. A series of PET/PEN random copolymers was synthesized from dimethyl terephthalate (*I*), dimethyl 2,6-naphthalenedicarboxylate (*II*) and ethylene glycol (*III*) using 0.015 mol% of titanium tetraisopropoxide (*IV*) as catalyst. All monomers were purified before the reaction. *I* and *II* were recrystallized under nitrogen from anhydrous methanol and anhydrous toluene, respectively. *III* was dried, firstly by magnesium sulfate then by refluxing with sodium under nitrogen, and was finally distilled in vacuum. The catalyst *IV* was used as received. After the reaction finished, the polymer was dissolved in the mixture of phenol and 1,1,2,2-tetrachloroethane (62.5:37.5 wt%), and subsequently precipitated in cold acetone. It was then washed with acetone several times and dried in vacuum at 40°C for 4 h.

Composition and sequence distribution measurements. ^{1}H n.m.r. spectra were measured on the synthesized PET/PEN copolymer series to determine the real composition and sequence distribution. The analysis result was kindly provided by ICI and is shown in *Table 1*. The result shows that the sequence distribution of this copolymer series is random, although a very small degree of blockiness can be detected by comparing the fraction of dyads of the measured values to the calculated values for a completely random system (*Table 1*). The only measured composition which deviates from the nominal values by more than 5% is that of the 80 mol% PET (nominal) sample. There is thus a suggestion that the dimethyl naphthalene-2,6-dicarboxylate may be slightly more reactive than dimethyl terephthalate.

Molecular weight measurements. The inherent viscosities of the PET/PEN random copolymers in the mixture of phenol and 1,1,2,2-tetrachloroethane (62.5:37.5 wt%), as far as they are soluble, were measured on a VB2 LAUDA automatic Ubbelohde viscometer at the concentration of 0.25 g per 100 ml and temperature of 25°C. The apparent number average molecular weights of these copolymers were calculated from measured inherent viscosities by using the equation calibrated based on PET: $\bar{M}_n = 3.92 \times 10^4 (\eta_{inh})^{1.47}$ (ref. 20). For those copolymers which are soluble in chloroform, molecular weights and polydispersities were also measured by g.p.c. for which

Table 1 The properties of synthesized PET/PEN random copolymers

Feed composition (PET/PEN mol%)	Composition measured by n.m.r.	Fraction of dyads (%)		$\bar{M}_n$ (polydispersity)		Solubility[a]
		Measured by n.m.r.	Random	Measured by g.p.c.	Measured by η_{inh}	
100.0/0.0					24 300	–
90.0/10.0					13 200[b]	+
80.0/20.0	74.3/25.7	TET[c] 55.2	55.2		26 100[b]	+
		TEN[c] 38.3	38.2			
		NEN[c] 6.5	6.6			
70.0/30.0				17 700 (1.77)	12 300[b]	+ +
59.8/40.2	58.5/41.5	TET 35.2	34.2	42 300 (1.82)	27 800[b]	+ + +
		TEN 46.9	48.6			
		NEN 17.9	17.2			
50.0/50.0	48.9/51.1	TET 24.8	23.9	31 200 (1.75)	35 200[b]	+ + +
		TEN 48.3	50.0			
		NEN 26.9	26.1			
40.0/60.0	39.0/61.0	TET 16.3	15.2	50 500 (2.02)	26 700[b]	+ +
		TEN 45.5	47.6			
		NEN 38.2	37.2			
20.0/80.0	19.6/80.4	TET 4.5	3.8		8 700[b]	+
		TEN 30.3	31.5			
		NEN 65.2	64.6			
0.0/100.0						– –

[a] + + +, Soluble in chloroform; + +, soluble in chloroform when heated; +, not soluble in chloroform but soluble in the mixed solvent used (phenol/1,1,2,2-tetrachloroethane 62.5/37.5 wt%); –, soluble in the mixed solvent used only when heated; – –, not soluble in any solvent mentioned above

[b] Apparent number average molecular weight

[c] TET, PET–PET dyad; TEN, PET–PEN dyad; NEN, PEN–PEN dyad

polystyrene was used as standard. Molecular weights and solubilities of the PET/PEN random copolymer series produced are given in *Table 1*. The degree of polymerization corresponding to these measured molecular weights is within the range of commercial products, i.e. about 50–150.

Sample preparation

Amorphous sample. The polymer was heated to 300°C and held for 2 min to ensure complete melting. It was then quenched in the mixture of acetone and dry ice.

Annealed sample. An amorphous sample was reheated to the temperature half way between its glass transition temperature (T_g) and melting temperature (T_m). It was held at that temperature for 15 h prior to cooling at approximately 10°C min^{-1}.

Dynamic crystallized sample. Treatment was similar to that of the amorphous sample except that the polymer was cooled at 10°C min^{-1} to 40°C.

Fibre sample. Fibres were drawn out from the melt on a hot plate. They were then stretched further in a silicon oil bath at about 10°C above the T_g, held for 30 s at this temperature, then cooled to room temperature rapidly.

Annealed fibre sample. Fibre samples were reheated in a silicon oil bath to the temperature half way between the T_g and T_m, and held at constant length for 4 h before cooling to room temperature.

Thermal analysis

The d.s.c. measurements were performed on a Perkin–Elmer DSC 7. All samples were heated at a rate of 10°C min^{-1} from 40 to 300°C in a nitrogen atmosphere.

Wide angle X-ray scattering

Unoriented specimens. For unoriented amorphous and annealed samples the wide angle X-ray scattering experiments were carried out on a Siemens diffractometer D500TT, using Ni-filtered CuKα radiation, at 25°C. Scan speed was 1° min^{-1}.

Uniaxially oriented fibre specimens. Equatorial scans on parallel assemblies of fibres were carried out under the same condition described above, except that the scan speed was 0.5° min^{-1}. To determine the positions of equatorial peaks, the crystalline peaks and the amorphous peak were separated using standard curve fitting routing (by assuming all peaks to have a normal distribution). Wide angle X-ray photographs were taken using a transmission camera with Ni-filtered CuKα radiation at room temperature, and subsequently digitized. The peak positions obtained from equatorial diffractometer scans were used to calibrate the distance between the sample and the film.

Estimation of crystallinity

The crystallinities of the unoriented samples were estimated by fitting the X-ray diffraction profiles of amorphous samples to those of partially crystalline samples according to the Hermans–Weidinger method[21].

RESULTS AND DISCUSSION

Crystallization and melting behaviour

Dependence of melting point on composition. The melting points of PET/PEN random copolymer series obtained from d.s.c. measurements are shown in *Figure 1*. The points corresponding to different crystallization conditions fall quite close together on the same curve, the form of which is similar to that for liquid crystalline random copolyesters based on *p*-hydroxybenzoic and hydroxy-2,6-naphthoic units[22]. The lower melting points in the middle composition region were attributed in this case to the statistic limitation of crystallite size inherent in the sequence matching models[5].

Effects of annealing and drawing. Figure 2 shows that the melting enthalpy (ΔH_m) of the PET/PEN random copolymers is increased by annealing and hot drawing treatments. This effect seems to be linked with an increase in crystallinity, as suggested by the similar form of the curves showing the dependence of melting enthalpy and the crystallinity on the composition for the annealed samples (*Figures 2* and *3*). However, it is difficult to explain the comparatively high melting enthalpy in the 50/50 composition region of the annealed fibre samples solely in terms of increased crystallinities, as its level would suggest crystallinities clearly in excess of those apparent from the X-ray fibre diagrams. It is possible that the existence of a 'rigid-amorphous' fraction[23] must be taken into account. Nevertheless, annealing does increase both crystallinity and crystal order, as shown by the significantly improved sharpness of X-ray diffraction peaks.

For all crystallization conditions the melting enthalpy reaches its lowest value at compositions of around 50 mol% PET. This fact implies that at this composition the crystallinity achievable is the smallest or the

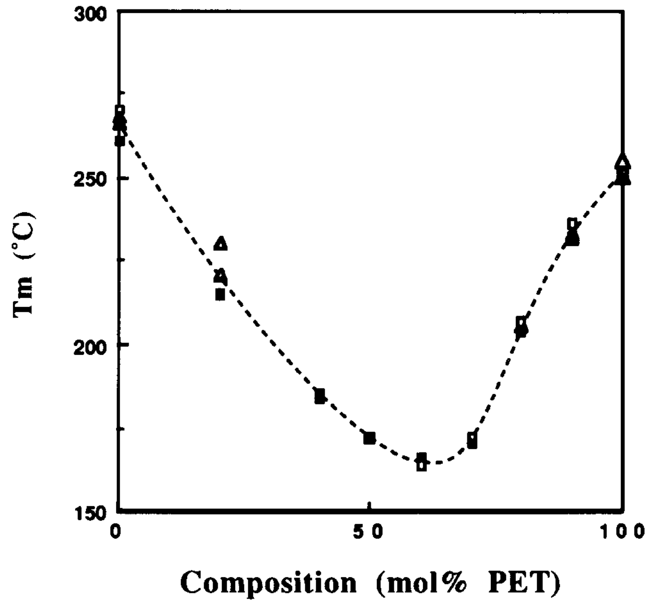

Figure 1 Dependence of the melting points (T_m) of PET/PEN random copolymers on composition: △, dynamic crystallized sample; ▲, annealed sample; □, fibre sample; ■, annealed fibre sample. Conditions for sample preparation and d.s.c. measurement are described in the Experimental section

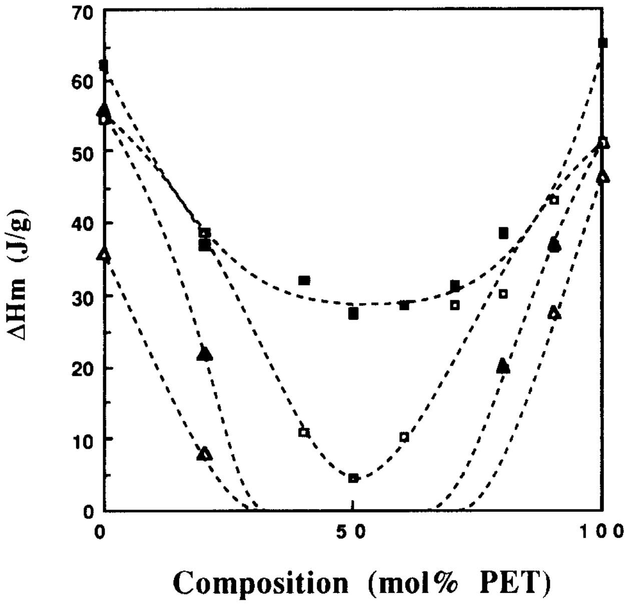

Figure 2 The effects of annealing and drawing on the melting enthalpies (ΔH_m) of PET/PEN random copolymers: △, dynamic crystallized sample; ▲, annealed sample; □, fibre sample; ■, annealed fibre sample. Sample preparation and d.s.c. measurement conditions are described in the Experimental section

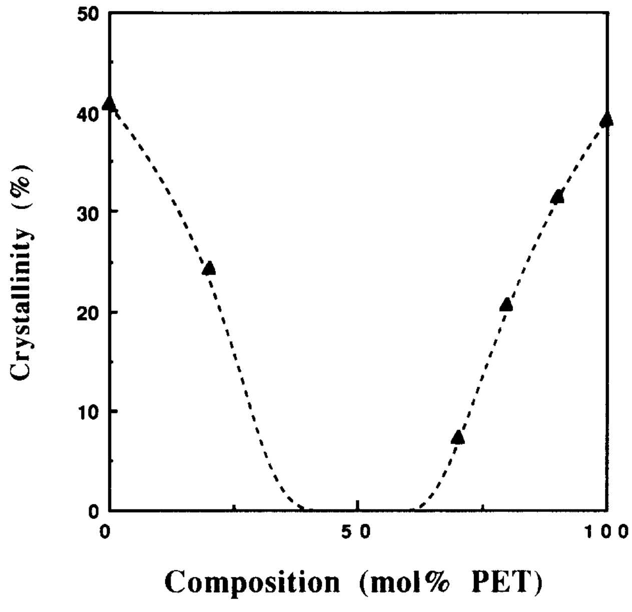

Figure 3 The estimated crystallinities of annealed unoriented samples of PET/PEN random copolymers, measured by X-ray method

crystalline structure formed is the least perfect, which would be compatible with the sequence matching models. Also, at this composition the melting enthalpy is most sensitive to changes of crystallization conditions, which suggests that the influence of kinetic constraints is increased at compositions furthest from the pure homopolymer.

The fact that the heat treatment and drawing have a large effect on the melting enthalpy and crystallinity, but not on the melting point, indicates that it is the increasing crystallinity rather than crystal size or perfection which is the major factor.

X-ray fibre diffraction patterns

Figures 4a–f show a series of typical fibre X-ray diffraction patterns of the PET/PEN random copolymer series in the annealed condition. The main feature of the patterns is the strong evidence for crystallinity across the full range of random copolymer composition. The strongest crystal peaks are on the equator. Compared with the pattern from liquid crystalline random copolymers, where the equatorial diffraction has both a sharp and a diffuse component, the sharp peaks here are accompanied not by diffuse but by highly oriented non-Bragg scattering. Even in the copolymers in the centre of the range, there are a number of sharp peaks located in the off-equator regions, which definitely indicates the presence of some three-dimensional order. Precise analysis of these features will give significant further information.

From the positions of the reflections, it is easy to divide the diffraction patterns into two classes. In the composition range of 0–60 mol% PET (*Figures 4a–c*), the patterns are quite similar to that for the PEN homopolymer (*Figure 4a*) where well defined layer lines are observed, although as the amount of PET units increases the reflections on the second and third layer lines become increasingly weak. The resemblance between these patterns suggests that the shapes of the unit cells in this composition range are closely related to each other, in what we call the 'N' unit cell type. Correspondingly, the patterns for the copolymers with 80–100 mol% of PET units (*Figures 4e* and *f*) were generally similar to each other, but distinct from those in the 0–60 mol% PET range. The unit cell for this composition range is defined as 'T' type. A conspicuous common feature of these PET-rich patterns is that the reflections are not well aligned on the layer lines, i.e. they are displaced above or below their mean layer-line positions, which can be seen most clearly in the pattern from the copolymer containing 80 mol% of PET units (*Figure 4e*). At the composition of 70 mol% PET (*Figure 4d*), both 'N' and 'T' type unit cell patterns appear to be superimposed.

Analysis of the displacement of reflections from layer lines

The displacement of reflections from layer lines has been reported for PET[24] and some other triclinic systems[25]. It is believed that the displacement of reflections is due to the tilting of the c axis of the unit cell from the fibre axis by a few degrees by rotation about an axis lying in a particular direction in the a^*b^* plane, which is caused by relaxation during the annealing. The effect of tilting on a fibre pattern is explained schematically in *Figure 5*, where an assumed reflection point on the equator is split into two points slightly off the equator.

In principle, an equivalent pattern could be given by a single crystal rotated around a direction inclined at a few degrees to its c axis, therefore tilted patterns can be analysed by the method that has been developed for such patterns[26]. On the basis of the PET indexing, the tilt angles and the positions of tilt axes were determined by the optimum fitting of calculated reflection positions to observed ones for PET/PEN random copolymers. These are shown in *Table 2*. In the composition range of 0–60 mol% PET, i.e. for the 'N' type of crystal, the tilt angle is set to zero because any displacements of the reflections from layer lines are too small to be seen. At

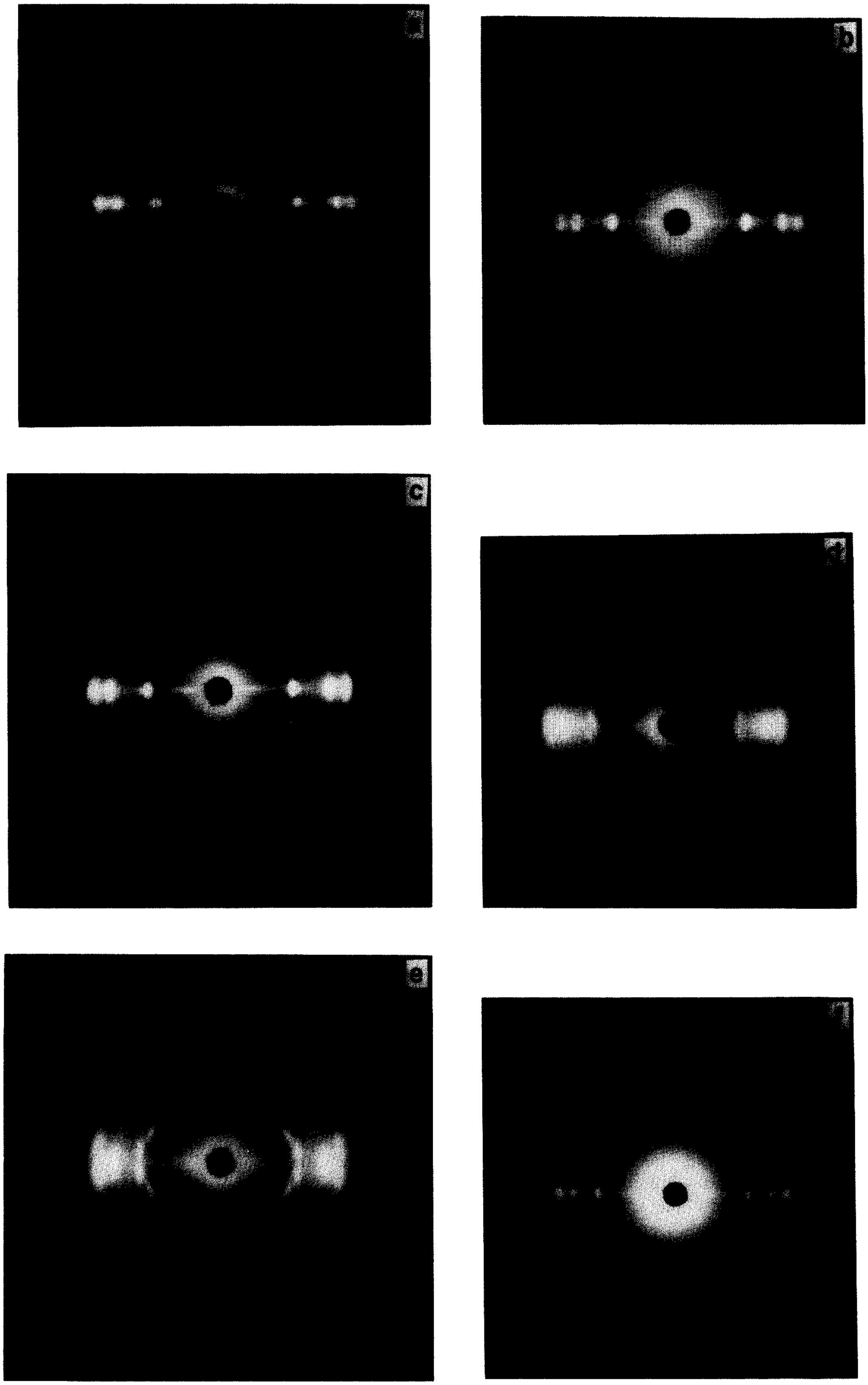

Figure 4 Fibre X-ray diffraction patterns: (a) PEN (annealed fibre sample); (b) PET/PEN copolymer containing 20 mol% of PET units (annealed fibre sample); (c) PET/PEN copolymer containing 50 mol% of PET units (annealed fibre sample); (d) PET/PEN copolymer containing 70 mol% of PET units (annealed fibre sample); (e) PET/PEN copolymer containing 80 mol% of PET units (annealed fibre sample); (f) PET (annealed fibre sample)

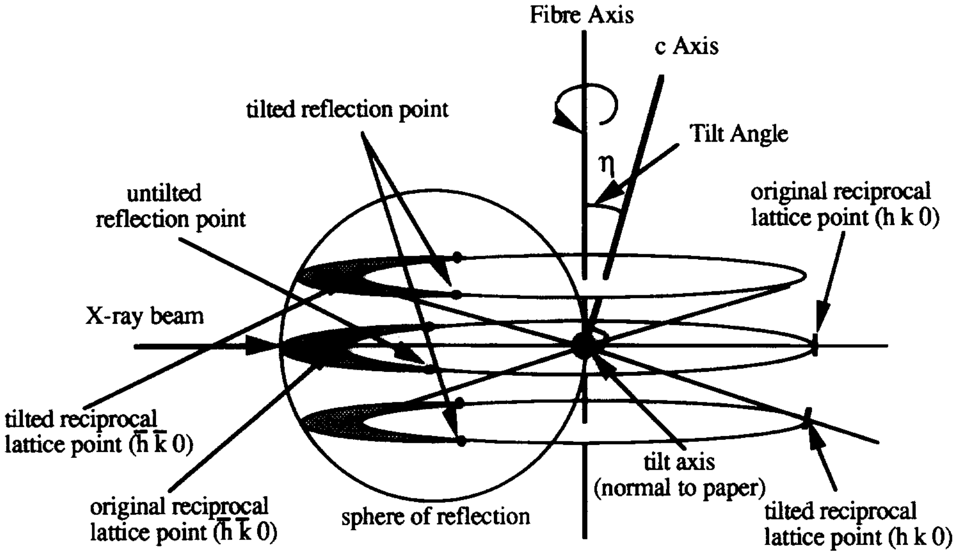

Figure 5 Schematic illustration of the tilting effect on a fibre pattern where the *c* axis is not parallel to the fibre axis. The tilt axis is drawn as perpendicular to the paper and there is a reciprocal lattice point ($hk0$) on the line perpendicular to this axis. Note that a reflection lying on the tilt axis would not be displaced

Table 2 The tilt angles and the positions of tilt axes of PET/PEN random copolymers

Feed composition (mol% PET)	Tilt angle, η^a (deg.)	Tilt azimuth, μ^b (deg.)
100	−4	−6
90	−6	−15
80	−8	−16
70	difficult to quantify	
0–60	0	–

[a] The tilt angle η is the angle between the fibre and the *c* axes and it is positive if rotation from the fibre to the *c* axes is clockwise viewed from the a^* positive region of the lattice

[b] The tilt azimuth μ is defined as the angle measured from the tilt axis to the projection of the *a* axis onto the a^*b^* plane and it is positive if made in a clockwise direction looking from the positive *c*

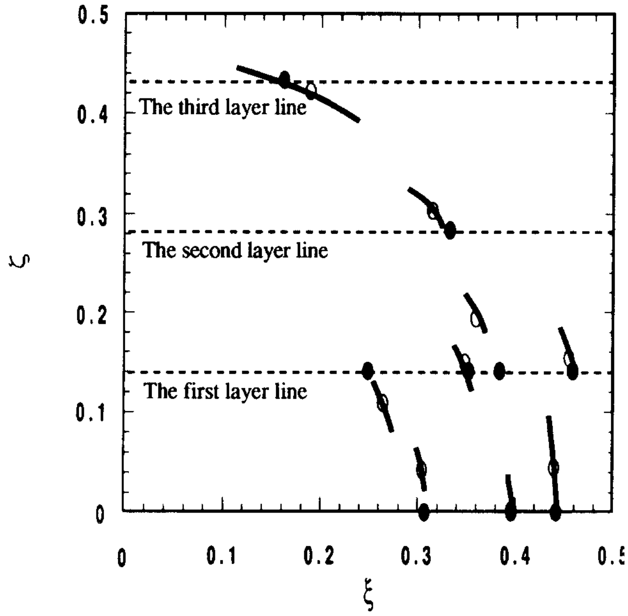

Figure 6 General example of X-ray diffraction pattern tilted so that fibre and *c* axes are not coincident. The schematics are based on the pattern of PET/PEN random copolymer (80 mol% PET): ——, observed reflection positions (see *Figure 4e*); ○, reflection positions determined with tilt and azimuth angles, on the basis of PET indexing, set to the optimum fit to observed data; ●, calculated reflection positions after correction for tilt

the composition of 70 mol% PET, although significant tilting could be recognized simply from the pattern (*Figure 4d*), it is difficult to separate the contribution of the 'N' type of unit cells from the mixed pattern to obtain a secure result. For the 'T' type of crystal, the tilt angle increases as the percentage of PET units decreases. There is thus a suggestion of an intrinsic relationship between the tilting behaviour and the shape of the unit cell. *Figure 6* is a schematic diagram of a tilted pattern for the 80 mol% PET example. The calculated reflection positions in both tilted and untilted situations are compared with observed ones. The agreement is most satisfactory.

Dependence of lattice parameters on composition

It is known that both PET and PEN crystallize in the triclinic form and it is apparent from the observed patterns that the whole series of PET/PEN random copolymers also crystallizes in the similar form. After correcting the tilting effect, the lattice parameters could be calculated for the PET/PEN random copolymers in the whole composition range. As the first step of the work, since a proper indexing has not been assigned for all the reflections of patterns, the lattice was resolved into two parts—in the chain direction and perpendicular to the chain direction.

Perpendicular to the chain direction. From the positions of equatorial reflections, a two-dimensional network, i.e. the projection of the unit cell onto the plane normal to the *c* axis of the unit cell, was determined. Here, the indexing for PEN and PET homopolymer was used for the 'N' type of unit cells and the 'T' type of unit cells, respectively. At the composition of 70 mol% PET, only

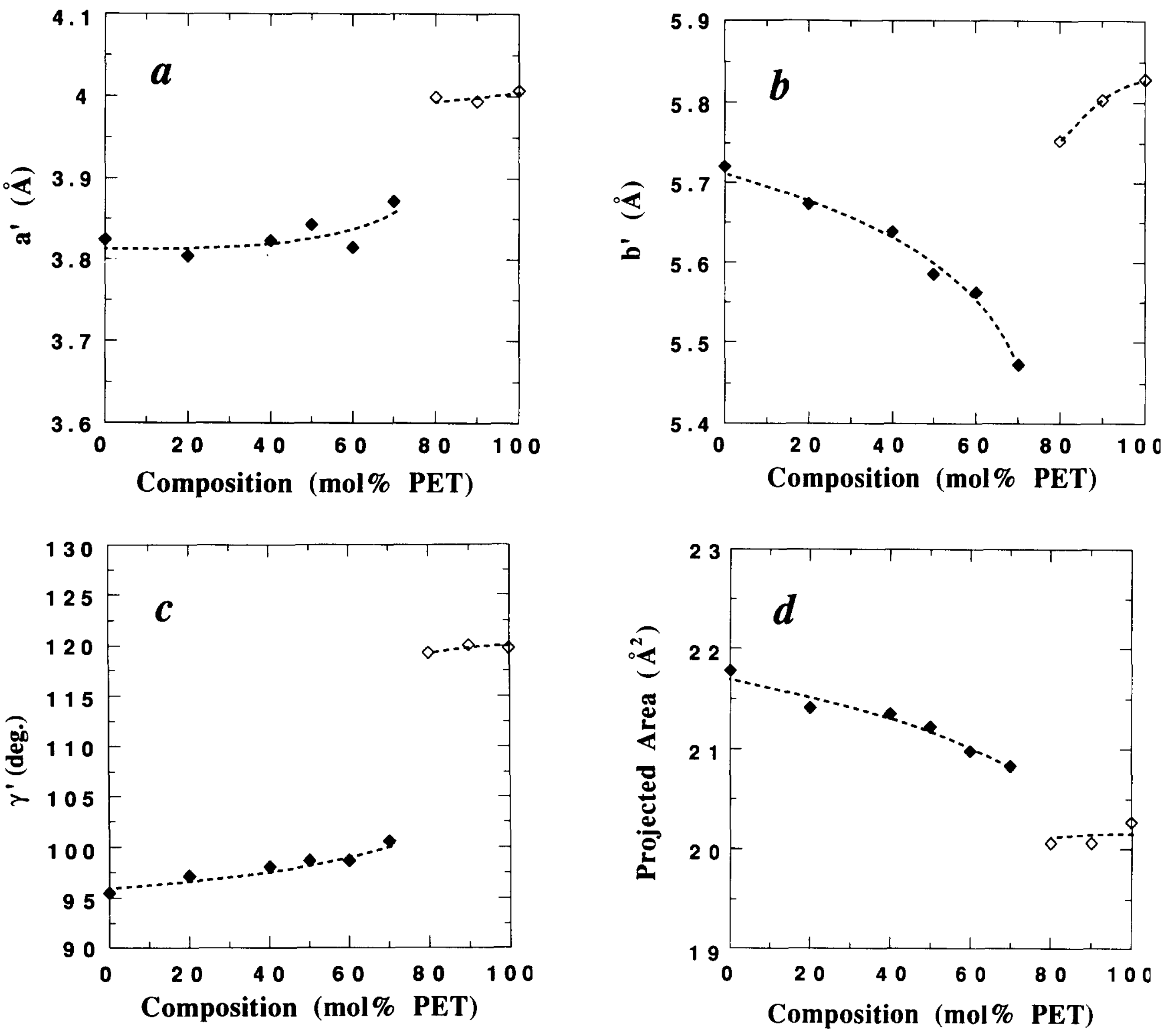

Figure 7 (a) a'. The projection of the 'a' unit cell parameter onto the plane normal to the chain axis, as a function of composition. (b) b'. The projection of the 'b' unit cell parameter as above, as a function of composition. (c) The angle γ' between a' and b' as a function of composition. (d) The area of the projected a–b plane of the unit cell as defined by a', b' and γ'. In each case, ◆ corresponds to the 'N' type of unit cells and ◇ to the 'T' type. At the composition of 70 mol% PET the parameters are determined only for the 'N' type cell

the parameters for the 'N' type of unit cell could be reliably measured. The parameters for these projected unit cells are shown in *Figures 7a–c*. For each type of unit cell, the projected a axis (a' in *Figure 7a*), b axis (b' in *Figure 7b*) and the angle between a' and b' (γ' in *Figure 7c*) change smoothly as the composition changes, but between these two types there is a sudden change of lattice parameters. The same trend was found for the projected area of unit cells (*Figure 7d*). The fact that the lattice parameters which describe the packing of the chains of both the 'N' and 'T' phases change uniformly with composition strongly suggests that the composition of the crystals follows that of the random copolymer as a whole, and that the crystals are based on mixtures of both types of chemical unit.

In the chain direction. *Figure 8* shows the c 'repeat' of the structure determined by the spacing between the zero and the first layer lines. As the amount of PET unit increases, this length changes continuously from the c parameter of PEN to the c parameter of PET. This observation further confirms that both PET and PEN units are included in the crystallites, and that the proportion of these two units is closely linked with the overall compositions of the random copolymers. What is more, the c distance is not affected by the change in packing (N → T transition) at 70 mol% PET. The similarities with the HBA/HNA liquid crystalline system are strong. Again, there is strong evidence that the crystals are mixed, although in this case the relationship is 'skewed' rather than linear, and in this respect it is in better agreement with the prediction of statistical models of HBA/HNA than with the experimental data from that system itself.

One of the most striking consequences of crystals consisting of matched aperiodic sequences is the presence of aperiodic layer lines[4]. X-ray diffraction data from a series of HNA/HBA random copolymers gives a d spacing of the first meridional peak which changes smoothly

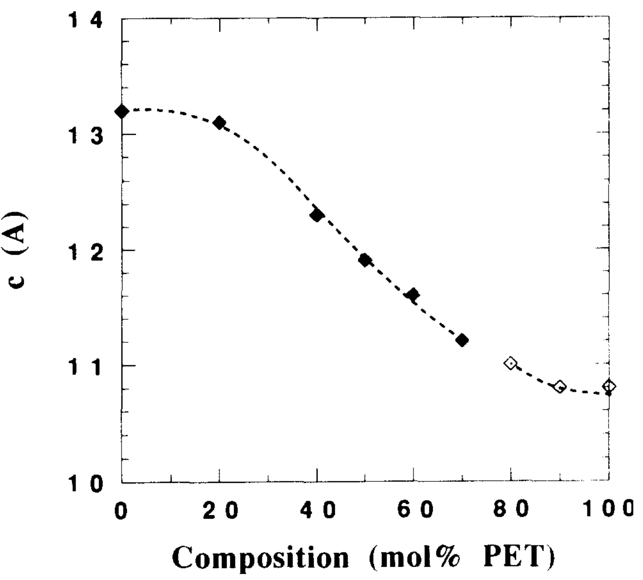

Figure 8 The c axis of the unit cell as determined by the spacing of the first layer line: ◆, the 'N' type of unit cells; ◇, the 'T' type of unit cells. At the composition of 70 mol% PET the c parameter for the 'T' type of unit cells has not been calculated owing to uncertainty over the tilting correction

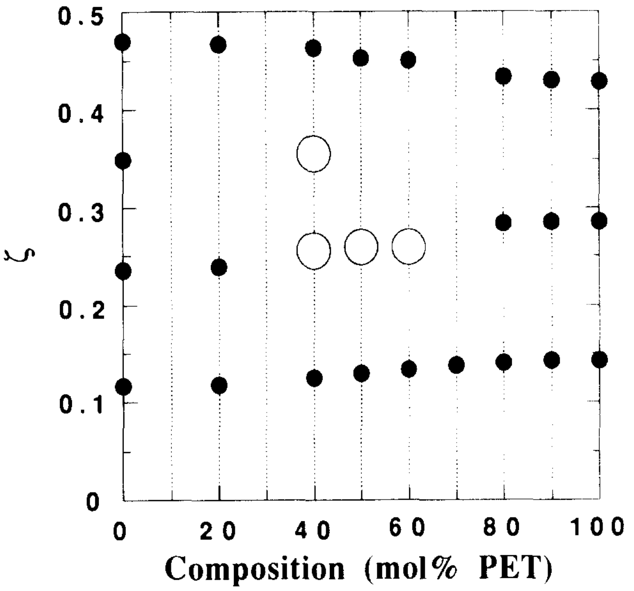

Figure 9 The reciprocal lattice coordinates of layer lines in the chain direction ($\zeta = 2\sin\theta$): ●, layer lines defined by several hkl reflections; ○, layer lines along which the hkl reflections are too indistinct to permit measurement. In the latter case the layer-line positions are defined by the lateral (unsampled) streaks which would correspond to the transform of an isolated molecule in the crystalline conformation. For the 70 mol% PET sample the measured layer-line spacing corresponds to the 'N' type phase only

between limits corresponding to the lengths of HNA and HBA units. It is significant that this behaviour is now apparent in another random copolymer system, but one which is 'conventional' rather than liquid crystalline.

The positions of the first four layer lines in the diffraction patterns, which were sufficiently intense to be measured precisely, are shown in *Figure 9*. The distances between the layers of the reciprocal 'lattice' are not equal to each other; this is easy to see from the position dots of the first layer line, which incline in an opposite way to those of the fourth layer line. As with the thermotropic HBA/HNA series, it is clear that the crystals are mixed, in that they contain both PET and PEN units.

SUMMARY AND CONCLUSIONS

There is evidence that significant crystallinity is present in fibres of random copolymers of PET/PEN of all compositions. The lattice parameters vary with composition to indicate that the crystals are composed of both types of units. In particular, the c axis repeat determined from the position of the first layer line changes smoothly with composition, and the positions of the layer lines of crystalline peaks are aperiodic. These data indicate that the crystals contain matched random sequences giving NPL crystallites, as has been previously observed in the thermotropic random copolyester based on HBA/HNA. Indeed, the similarities with this liquid crystalline system are compelling. We thus conclude that the many detailed reports of crystal structure in HBA/HNA random copolymers and closely related systems, are not in any way specific to liquid crystallinity, but expose principles relevant to random copolymers in general.

While the similarity in crystal organization between the conventional and liquid crystalline random copolymer systems is the main conclusion of this study, there are differences in detail which are revealing in themselves:

(a) The enthalpy of melting (ΔH_m) of the mid-range compositions was considerably higher in the drawn samples, although the crystal melting points appear to lie on the same curve, independent of sample preparation.
(b) The possible explanation of the high value of ΔH_m in the fibre samples may be the presence of oriented non-crystalline material (the rigid-amorphous portion of Cheng and Wunderlich[23]) associated in some way with the crystals. The presence of this material may be the cause of the continuous layer-line streaks seen in some of the fibre patterns.
(c) The PET/PEN series showed a crystal structure transition at 70 mol% PET.
(d) The continuous variation in the c 'repeat', as determined from the first layer line, with composition, was not as linear as in the case of the HBA/HNA system. In fact its sigmoidal form is closer to that previously predicted[5] by statistical models of sequence matching, and would suggest that the composition of the crystals was skewed towards the component of the polymer present in the greater concentration.

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