

# Time resolved WAXS study of the role of mesophase in oriented crystallisation of poly(ethylene terephthalate-*co*-isophthalate) copolymers

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Received 18 November 2004; received in revised form 28 April 2005; accepted 28 April 2005

Available online 14 June 2005

## Abstract

Poly(ethylene terephthalate-*co*-isophthalate) copolymers containing up to 18 mol% isophthalate have been drawn at 90 °C at a deformation rate of  $\sim 15 \text{ s}^{-1}$  while recording two dimensional wide angle X-ray scattering patterns. All polymers, including homopolymer controls, show the development of an oriented smectic mesophase during the last stages of deformation. After the end of deformation, the mesophase decays and is replaced by oriented triclinic crystals which increase according to first order transformation kinetics. The characteristic meridional spacing of the smectic mesophase reduces systematically with increasing isophthalate comonomer and indicates that the comonomer participates in the smectic structure. Unlike isotropic crystallisation from the melt, the crystallinity and crystallisation rate show little variation with comonomer content. This is attributed to the fact that both monomers participate in the intermediate smectic mesophase. © 2005 Elsevier Ltd. All rights reserved.

*Keywords:* PET; WAXS; Smectic mesophase

## 1. Introduction

This paper describes real time observations using a synchrotron X-ray source on the crystallisation of poly(ethylene terephthalate-*co*-isophthalate) copolymers during rapid deformation from the amorphous state. It is concerned with the effects of ethylene isophthalate (EI) comonomers on the crystallisation rate of oriented poly(ethylene terephthalate) (PET) and on the role of a transient intermediate mesophase.

An important aspect of these experiments is the use of high deformation rates that are comparable with the draw rates experienced in industrial production of polyester films and bottles. Our previous studies of PET homopolymer have

shown that when the deformation rate is faster than the chain retraction relaxation mechanism, the onset of crystallisation is delayed until the end of the deformation [1]. This contrasts with the use of slower draw rates often used in laboratory experiments where crystallisation commences while deformation is still in progress. Our previous experiments also showed evidence of the formation of a transient smectic mesophase during the last stages of deformation followed by a decay that was linked with the growth of the triclinic crystalline phase [2]. This paper now addresses how the introduction of random isophthalate comonomer influences these effects previously seen in the homopolymer.

Comonomers are often employed to modify the behaviour and properties of homopolymers and usually result in a reduction of melting point, crystallisation rate and degree of crystallinity. For example, Hachiboshi et al showed that the melting point is reduced by about 20 °C after incorporation of 15 mol % of isophthalate comonomer [3]. Wu et al. [4] and Karayannidis et al. [5] report that the rate of crystallisation from the melt is significantly reduced and Yu et al. [6] found that copolymers with more than 20% EI remained amorphous. The conclusion of Lee et al. [7] from their time resolved studies is that the EI units are

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excluded from the crystals and is in line with many other copolymer systems during crystallisation from the isotropic melt. In contrast, the current experiments now provide information on crystallisation from the highly oriented state where our previous experience with PET has indicated a different mechanism involving an oriented mesophase [1,2].

There has been much interest in the nature of the PET mesophase from the early recognition by Bonart [8,9] to the more recent studies by Auriemma [10], Asano and coworkers [11,12], Nicholson et al. [13] and Windle and coworkers [14,15]. These studies have been mainly carried out on cold drawn and annealed samples which enable the mesophase to be stabilised and studied at leisure. Bonart [8] recognised both nematic and smectic states and suggested that these mesophase states characterize stages in the oriented crystallisation process. The nematic state is characterised by diffuse equatorial diffraction associated with the parallel alignment of chain segments that are packed laterally in a liquid like manner. The smectic mesophase is characterised by an additional sharp meridional reflection of narrow lateral width and an absence of sharp equatorial and off-axis reflections. The observed spacing of the smectic meridional reflection (1.03 nm) is slightly less than the *c*-axis repeat of the triclinic crystal cell (1.075 nm) and indicates well aligned chains with conformations that are more relaxed than in the crystal [8–15]. The absence of other sharp reflections indicates the monomer segments are not packed in a three dimensional lattice. However the relatively narrow lateral width of the meridional reflection shows there is a degree of register between adjacent chains consistent with a smectic arrangement of monomer units. Recent SAXS studies of the oriented mesophase have revealed equatorial scatter with maxima that suggest the mesophase is linked to a fibrillar morphology [16]. Similar SAXS equatorial maxima have also been observed by Hsiao et al, who suggest the fibrillar morphology is also present in the precursor nematic state [17].

The current experiments have been carried out on several polymers covering the range zero to 18 mol% of the EI comonomer. The experiments follow the procedures used in previous studies of PET homopolymer [1,2] and involve 40 ms time resolved observations of two dimensional WAXS patterns while drawing samples at 90 °C at a draw rate around 15 s<sup>-1</sup>.

## 2. Experimental

The experimental data were collected on beamline ID2A at the ESRF in Grenoble using X-rays of wavelength  $\lambda=0.0995$  nm. The experiments were carried out in situ with the samples mounted in the jaws of a stretching X-ray camera that had been purpose designed and constructed in the Keele Physics Department workshops [18,19]. The

temperature of the oven could be controlled to within 1 °C. The jaws of the camera were attached to stepper motors that allowed uniaxial, bi-directional drawing.

The polymer materials were provided by ICI plc in the form of amorphous sheets about 0.25 mm thick. They consisted of a range of higher molecular weight polymers incorporating 0, 5 and 10 mol % ethylene isophthalate with intrinsic viscosities close to 0.8 dl/g and two lower molecular weight polymers containing 0 and 18 mol% ethylene isophthalate with an intrinsic viscosity of around 0.65 dl/g. Specimens 10 mm wide were cut from the sheets and ink reference stripes were drawn with a separation of 1 mm on the specimen at right angles to the draw direction to enable the degree of extension to be deduced from a video camera image. The specimen was mounted in the jaws of the camera with a 10 mm gauge length.

Full WAXS pattern was recorded with a Photonics Science CCD detector with a specimen-detector distance of 60 mm. Each diffraction pattern was recorded with an exposure time of 40 ms. Over this period the pattern was integrated within the detector, before being digitised by a Synoptic i860 frame grabber. The specimens were heated in the camera to the drawing temperature of 90 °C and allowed to equilibrate for 2 min before being drawn. They were then drawn to a nominal final draw ratio of around 3.5:1 at a draw rate of around 15 s<sup>-1</sup>, during which 124 frames were recorded sequentially, with essentially no dead time between frames. As indicated in Table 1, there were slight differences in the final draw ratio due to differences in the draw characteristics of the samples.

The development of crystallinity was obtained by following the change in intensity of a reflection in the fibre diffraction pattern using the methods developed previously [1,2]. Estimates of the overall crystallinity were obtained empirically from the total WAXS data by separating crystalline reflections and amorphous diffraction. A randomised intensity  $I(s)$  was obtained by summing the contributions of radial slices  $i(s,\phi)$  taking account of axial symmetry:

$$I(s) = \sum_{\phi} i(s,\phi)\sin(\phi) \quad (1)$$

where  $\phi$  is the azimuthal angle relative to the draw direction and  $s=2 \sin \theta/\lambda$ . The diffraction profile for the initial unoriented sample was taken as a model for the amorphous

Table 1  
Summary of samples and experimental data

% EI	Intrinsic viscosity dl/g	Max Draw ratio	Crystallisation rate sec <sup>-1</sup>	Fractional crystallinity index
0	0.8	3.65	5.5	.32
5	0.8	3.8	6.7	.32
10	0.8	4.0	4.0	.32
0	0.65	3.9	6.3	.29
18	0.65	4.7	5.5	.28

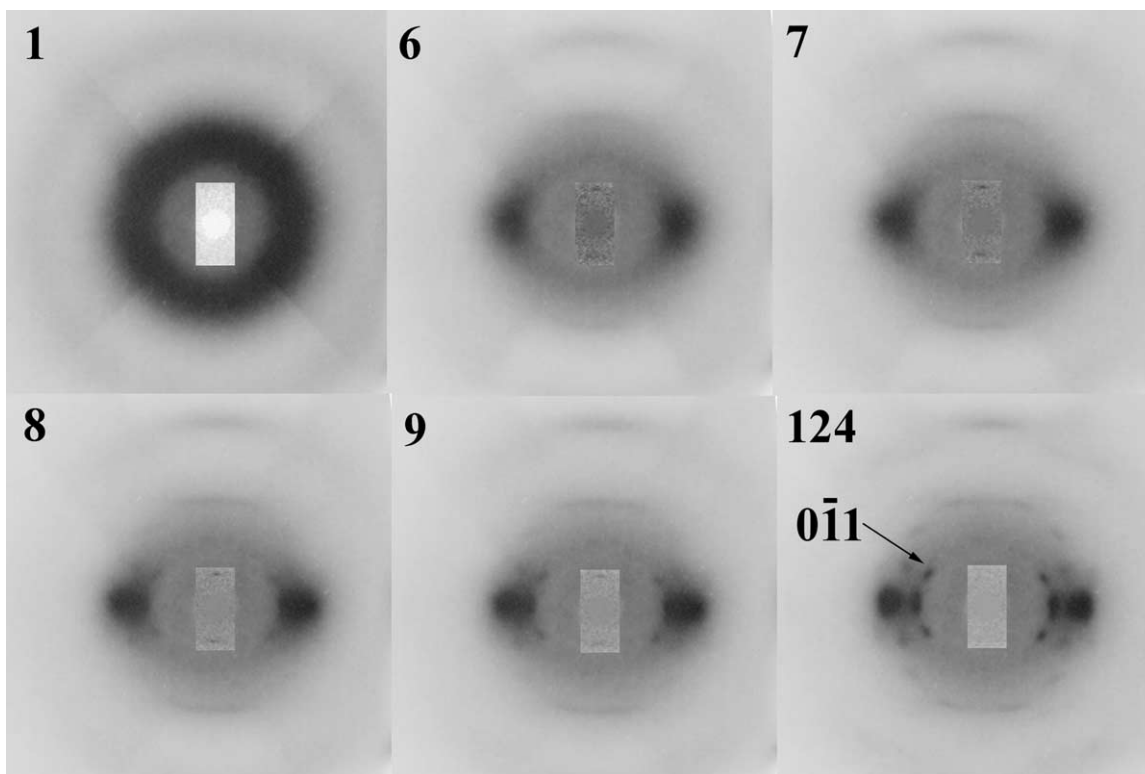


Fig. 1. WAXS patterns for frames 1, 6, 7, 8, 9 and 124 for the experiment with the 10% EI copolymer. The central region along the meridian is highlighted to aid the resolution of the smectic reflection. The arrow in frame 124 indicates the reflection used for monitoring the triclinic crystal phase.

component. A crystallinity index for the total crystalline content was calculated from the ratio of the crystalline component relative to the total scatter.

### 3. Results

The general features of the developing diffraction patterns are similar for the whole range of copolymer compositions and are broadly consistent with our previous studies of PET homopolymer. An example is illustrated in Fig. 1 which shows selected WAXS frames from the experiment with the 10 mol% copolymer. The central parts of the patterns have been highlighted in order to aid the identification of the meridional reflections. The variation of draw ratio with frame number in this experiment is shown in Fig. 2. The initial pattern of the undrawn sample in frame 1 shows a diffuse isotropic halo. As drawing proceeds there is a gradual intensification of the halo on the equator leading to diffuse equatorial spots in frame 7, characteristic of a highly oriented non-crystalline structure. Frame 7 corresponds to the time when the main tensile deformation has finished. A sharp meridional reflection becomes detectable at frame 6 and beyond. This is the characteristic reflection of the smectic mesophase and shows that there are extended regions where there is a degree of registration of segments in adjacent oriented chains. Beyond frame 7, sharp diffraction

spots develop which are characteristic of the oriented triclinic crystalline structure of PET.

The variation in intensity from the smectic mesophase was obtained by scanning across the meridional reflection. The variation of the intensity from the triclinic crystalline phase was obtained from a radial scan through the  $(0\bar{1}1)$  isolated crystalline reflection denoted by the arrow in frame 124 in Fig. 1. Examples of the change in intensity of the smectic and crystalline reflections are shown plotted along with draw ratio in Figs. 2 and 3, respectively for the 10% IPA higher molecular weight copolymer and the 18% IPA lower molecular weight polymers. These data show that the

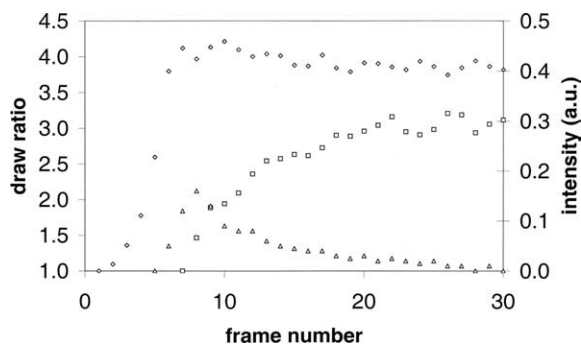


Fig. 2. Plot showing the development of draw ratio, ◇ and the intensities of the smectic reflection, △ and triclinic  $(0\bar{1}1)$  reflection, □, for the 0.8 IV, 10% EI sample. Each frame corresponds to a time interval of 40 ms.

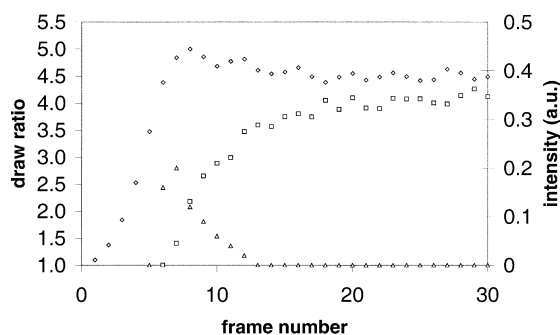


Fig. 3. Plot showing the development of draw ratio,  $\diamond$ , and the intensities of the smectic,  $\Delta$ , and triclinic reflection ( $0\bar{1}1$ ),  $\square$ , for the 0.65 IV, 18% EI sample. Each frame corresponds to a time interval of 40msec.

smectic mesophase grows in the last stages of deformation and then, after attaining maximum draw ratio, decays simultaneously with the growth of the triclinic crystalline phase. The mesophase is more prominent in the higher molecular weight samples. The onset of crystallisation is close to the point where the deformation has ceased. This is consistent with our previous studies PET homopolymer when drawn at these rates, where the onset was also found to be delayed until the end of deformation.

Following our previous studies [20,21], the increase in crystallinity of the triclinic phase was analysed in terms of the crystallisation kinetics of a first order transformation process fitted to the equation:

$$(\phi_{\infty} - \phi)/\phi_{\infty} = e^{-kt} \quad (2)$$

where  $\phi_{\infty}$  represents the final attained crystallinity,  $\phi$  is the crystallinity after time  $t$  and  $k$  is a rate parameter. Table 1 lists the crystallisation rate parameters along with the maximum draw ratio and final crystallinity index.

The scans through the smectic meridional reflection show that there are small but measurable variations in the diffraction angle of the reflection. Fig. 4 is a plot of the corresponding periodic spacing. The plot shows a small but significant reduction in the spacing with increasing comonomer content.

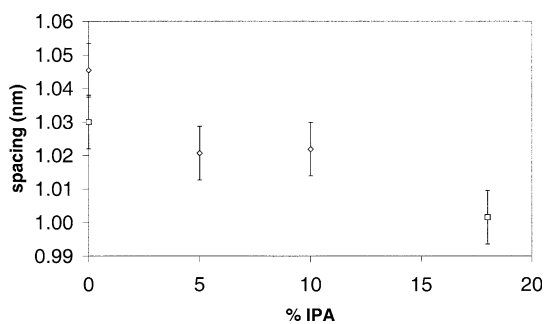


Fig. 4. Plot showing variation of the spacing of the meridional reflection for the 0.8 IV,  $\diamond$ , and 0.65 IV samples,  $\square$ .

#### 4. Discussion

The results demonstrate that the smectic mesophase occurs as a transient intermediate phase for the whole composition range 5 to 18 mol% IPA and thus follows the behaviour observed in our previously reported experiments on homopolymer PET [2]. However, with increasing IPA content there is a small but important reduction in the spacing of the meridional reflection. This spacing is a defining characteristic of the smectic mesophase. The systematic reduction is therefore strong evidence that the EI units are participating in the smectic structure.

This meridional spacing is expected to be related to the average length of the conformations of successive monomer units along the oriented chains within the mesophase. The study of the smectic mesophase by Auriemma et al. [10] and a similar study by Nicholson et al. [13] show that the spacing of  $\sim 1.03$  nm in homopolymer PET is consistent with a random sequence of different, minimum energy conformations. The extended conformations of IPA monomer units will be different from the PET monomers. The limited information in the literature indicates that the EI units might be slightly less extended than in PET. According to Kobayashi and Hachiboschi [22], the chain repeat in the crystalline form of homopolymer poly(ethylene isophthalate) is 1.06 nm and is shorter than the repeat in the triclinic form of PET at 1.075 nm. The comparative study by Aharoni [23] of the unperturbed chain dimensions indicates that the ratio,  $r_0/M^{1/2}$  (the ratio of the unperturbed root mean square end-to-end distance to the square root of molecular weight), for PEI is about 10% less than for PET. This indicates that chain configurations in PEI are less straight than in PET. These observations provide circumstantial evidence that the meridional spacing of a mixed PET-PEI mesophase would be expected to be less than in homopolymer PET and is in line with the trend in Fig. 4.

The data in Table 1 show small variations in the crystallisation rate although there is no consistent trend. However our previous studies of the oriented crystallisation process in homopolymer PET [1,21] have shown that the rate is closely related to the degree of chain orientation, which is influenced by both final draw ratio and strain rate. In the present samples there is the additional effects of comonomer content and molecular weight, both of which influence the molecular dynamics. The observed variations can therefore be partly attributed to the complex interaction of all these effects.

Even taking account of these effects, a remarkable aspect of the results is the relative insensitivity of the comonomer content on the oriented crystallisation rate compared with crystallisation from the isotropic state. The studies by previous workers of crystallisation from the isotropic melt have demonstrated that the isophthalate units have a very deleterious effect on the crystallisation process [3–7]. For instance Wu et al. [4] found that 12% isophthalate units increased the crystallisation half time by a factor of  $\sim 7.5$ .

Our DSC observations on the present 18% comonomer sample found that the crystallisation rate is too slow to measure accurately by standard isothermal crystallisation methods and indicated that the rate is of the order of 50 times slower than the corresponding homopolymer.

This contrast in behaviour can be attributed to the different mechanisms involved in the crystallisation processes. In the drawing experiments, the high chain orientation provides the conditions that favour the formation of a smectic mesophase that is able to contain EI as well as ET units. The formation of the oriented mesophase therefore does not suffer from the deleterious effects of comonomer exclusion that appears to occur in crystallisation from the isotropic melt [7]. As was also observed in our previous fast drawing investigations, the kinetics of the subsequent transformation from the smectic mesophase to the triclinic crystal phase appears to follow a first order transformation process. This form of kinetics is consistent with a sporadic nucleation of crystals within the framework of the smectic mesophase. The insensitivity of this process to the presence of EI units suggests there is sufficient mobility in the smectic mesophase to enable neighbouring chains to attain a registration appropriate for the triclinic phase.

Thus the participation of the isophthalate units in the important intermediate smectic state enables the oriented crystallisation process to proceed with little impediment. The situation is analogous to the findings of Windle and coworkers in random PET/PEN copolymers where oriented crystallisation can occur over the whole composition range [24,25] and where a smectic mesophase occurs as a transient intermediate containing both ET and EN units [15]. Significantly they found that the subsequent crystals were also a random mixture of comonomers. They concluded that the mixed crystals were most likely in the form of non-periodic layer (npl) crystals where neighbouring chains in the crystals have lateral matching of monomer sequences [24,25]. In principle the same npl crystals could be occurring in the PET/PEI copolymers. The triclinic crystal structure of PEI homopolymer determined by Kobayashi and Hachiboschi [22] has a strong planarity of phenyl rings and a projection along the chain axis which are both similar to those in the triclinic crystal structure of PET. It would thus be feasible for the layered sequences of neighbouring EI units to be incorporated in an npl structure without much disruption to the packing of ET sequences. In fact it is interesting to note that in a study of melt crystallised copolymers, Wu et al have proposed that an additional melting process could be associated with a possible mixed monomer crystal [4]. However in the analogous case of PET/PEN copolymers there is a large difference in the *c*-axis repeat length of the two monomers making the effect of co-crystallisation more obvious. In the current case of PET/PEI the repeat length of PEI (1.06 nm) is very close to the repeat in PET (1.075 nm) and it is more difficult to verify that co-crystallisation is occurring.

## 5. Conclusions

An oriented transient mesophase is observed to occur over the whole compositions range 0 to 18 mol% isophthalate. The systematic reduction in the meridional spacing associated with the mesophase indicates that both isophthalate as well as terephthalate moieties participate in the smectic domains.

The rate of the oriented crystallisation process is relatively insensitive to the presence of isophthalate comonomer compared with the very marked reduction in crystallisation rate when crystallised from the unoriented melt state. This can be attributed to the key role played by the oriented smectic mesophase that is able to accommodate both TA and IA units. It is a possibility that IA units may also be incorporated in the final triclinic crystals, possibly in the form of non-periodic layer crystals.

## Acknowledgements

We thank Dr D H MacKerron and Dr S Jenkins for providing the samples. This work was supported by the allocation of beam time at the ESRF. We are grateful to MG Davies, EJT Greasley, and MP Wallace for technical support.

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