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Observation of a transient structure prior to strain-induced crystallization in poly(ethylene terephthalate)

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Abstract

Using time-resolved X-ray diffraction at the European Synchrotron Radiation Facility we have observed a highly oriented weak transient diffraction peak which persists for about 0.2 s prior to strain-induced crystallization during the uniaxial drawing of poly(ethylene terephthalate) (PET) under industrial processing conditions. This structure may be identified with the mesophase structure proposed by a number of workers to occur during drawing of PET, poly(ethylene naphthalate) (PEN) and random copolymers of PET and PEN. In our studies, the transient structure was not observed at draw temperatures greater than 90°C nor when the draw conditions resulted in a degree of polymer orientation below a critical level. The possibility that this transient structure is a precursor of strain-induced crystallization is suggested by our observation of a correlation between the decay of the diffraction associated with it and an increase in the intensity of diffraction peaks associated with the development of crystallistion. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Mesophase; PET; Crystallization

1. Introduction

The exploitation of PET as a polymer material for bottles typically involves mechanical deformation at elevated temperatures close to its glass transition temperature (T_g). Such processing can have major effects on the degree of polymer orientation and crystallinity and hence on the physical properties of the material. X-ray diffraction provides one of the most powerful techniques for characterizing polymer orientation and crystallinity and hence for exploring the relationship between the industrial processing conditions and the properties of the finished artefact. The increasing availability of synchrotron radiation sources during the last decade, with a brilliance in the X-ray region many orders of magnitude greater than conventional laboratory rotating anode sources, has dramatically extended the power of diffraction techniques for investigating polymer conformation and organization and, in particular, for following the development and decay of transient structures on very short time-scales. The information obtainable from these techniques has been of fundamental importance for developing an understanding of strain-induced crystallization processes which occur when polymers such as PET are oriented close to their T_g [1]. In this communication we report the observation of a highly oriented weak transient diffraction peak which occurs immediately prior to strain-induced crystallization in PET when sheets of the polymer are drawn close to T_g. This peak may be identified with the mesophase proposed by Bonart [2–4], Asano and Seto [5], Nicholson et al. [6] and Carr et al. [7] following the drawing of PET and PEN. This oriented transient diffraction has recently been reported and briefly analysed as a mesophase by Welsh et al. [8] for a series of random copolymers of PET and PEN units, as well as for the two parent homopolymers. In their study the transient structure was stabilized by quenching during or immediately after drawing.

2. Experimental

Wide angle X-ray diffraction data were recorded on beamline ID13 at the European Synchrotron Radiation

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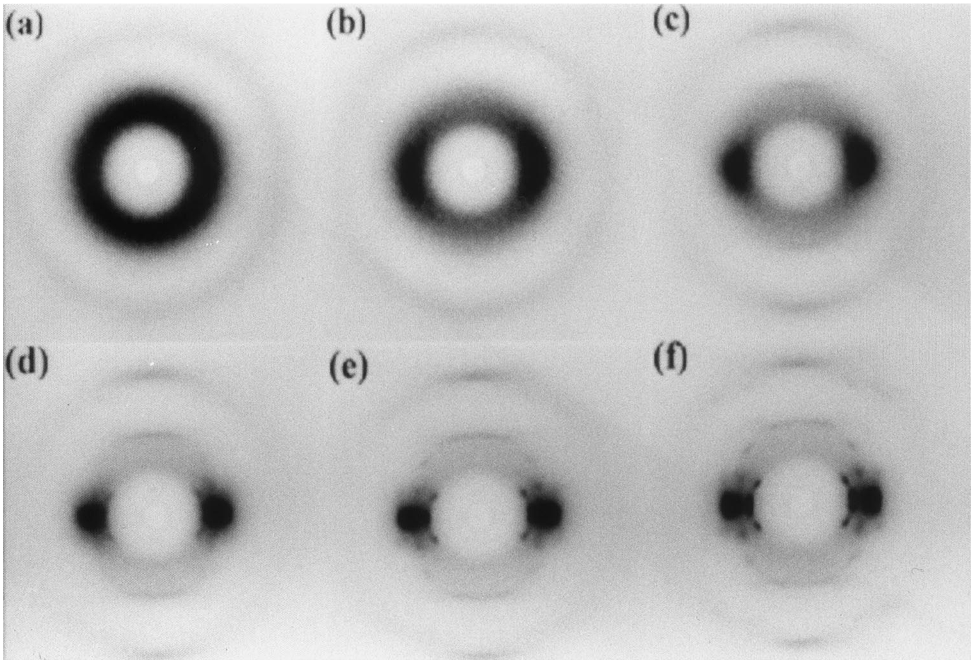

Fig. 1. Selected X-ray diffraction patterns of a PET sample drawn at 90°C with an overall draw rate of 72 000%/min and an overall draw ratio of 3.7:1. (a)–(f) shows Frames 1, 4, 5, 7, 12 and 124, respectively, from a series of 124 frames. Each frame was recorded in 40 ms with no "dead-time" between frames.

Facility (ESRF), Grenoble using purpose designed X-ray diffraction instrumentation constructed in the Keele Physics Department [1,9,10]. The temperature of the oven could be controlled to within 1°C and the maximum temperature available was ∽350°C. The sample of PET was clamped between two jaws attached to stepper motors which allowed uniaxial bidirectional drawing at an overall rate of ∽13 s^{-1}.

Diffraction patterns were recorded using a Photonics Science CCD detector with a sensitive area $92 \times 69\ mm^2$ and an effective pixel area of $120 \times 120\ \mu m^2$. The specimen to detector distance was 6 cm with d spacings from ~15 to ~1.5 Å recorded with exposure times of 40 ms. Up to 124 frames could be recorded "end-to-end" with essentially no dead-time between frames. The variation in the overall size and shape of the specimen during drawing was also recorded and sychronized with X-ray diffraction.

Specimens ~10 mm wide were cut from a sheet of ~500 μm thick cast film of amorphous disoriented PET. An ink calibration scale was drawn with a line separation of 1 mm on the specimen at right angles to the draw direction to enable the degree of extension at the point in the specimen from where the diffraction data was recorded to be calculated from the video camera image. Independent estimates of draw ratio were obtained by assuming that the total detector count in each frame was proportional to the amount of polymer material scattering when the frame was recorded and hence was proportional to the thickness of the specimen at the precise region of the specimen from which the diffraction was recorded. There is a high degree of correspondence between the two methods for periods of the draw prior to crystallization. The method based on total detector count had the advantage that it could be applied automatically without additional measurement of the variation in the separation of the reference stripes drawn on the specimen. This method also gives a more precise determination of the end of local draw at the point monitored by the X-ray beam.

The specimen was mounted in the jaws of the camera with a 10 mm gauge length. The specimens were heated in the camera to a pre-determined temperature in the range 85–120°C for 2 min before the sample was deformed. They were then drawn to various final draw ratios by stopping the motors after a pre-determined number of steps. Intensity distributions were corrected for the background effects by pixel-by-pixel subtraction of "blanks" recorded in the absence of the specimen immediately after each draw.

3. Results

A selection from a series of 124 time-resolved wide-angle X-ray scattering (WAXS) patterns is shown in Fig. 1. Each diffraction pattern was recorded as a separate frame with an exposure time of 40 ms during drawing of a sample of PET at 72 000%/min (corresponding to a draw rate of 13 s^{-1}) at 90°C to a draw ratio of 3.7:1 In this figure the single essentially unoriented diffraction ring in Frame 1 indicates essentially no polymer orientation or crystallinity in the specimen. The development in Frame 4 of equatorial orientation within this ring indicates an increasing degree of polymer orientation within the specimen in response to mechanical deformation but with no indication of discrete reflections associated with crystallinity. Frame 5 was

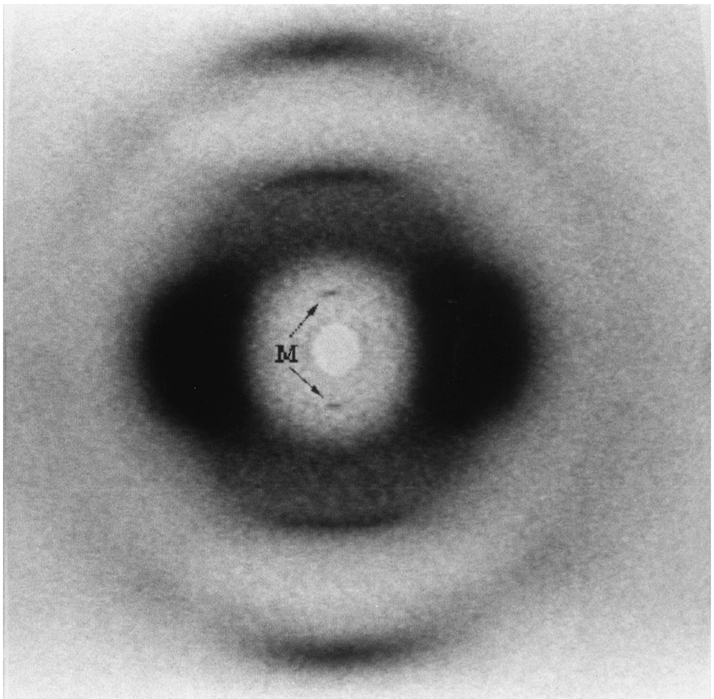

Fig. 2. Frame 7 in Fig. 1 enlarged with contrast in increased to highlight the meridional reflection identified with the mesophase. This reflection is marked as "M" in the diffraction pattern.

recorded close to the end of the draw and shows, in addition to a high degree of equatorial orientation in the ring (although still no indications of discrete reflections associated with crystallinity), a highly oriented, although weak meridional diffraction peak with a spacing of 0.098 Å^{-1}. Through Frames 5 and 7 there is a marked increase in the intensity of the meridional diffraction peak at 0.098 Å^{-1} although it still remains weak compared to the rest of the diffraction pattern. Frame 7 shows the first indications of crystallinity within the equatorial diffraction. From Frame 7 to Frame 12 there is a gradual decrease in the intensity of the meridional diffraction peak at 0.098 Å^{-1} and a continuing

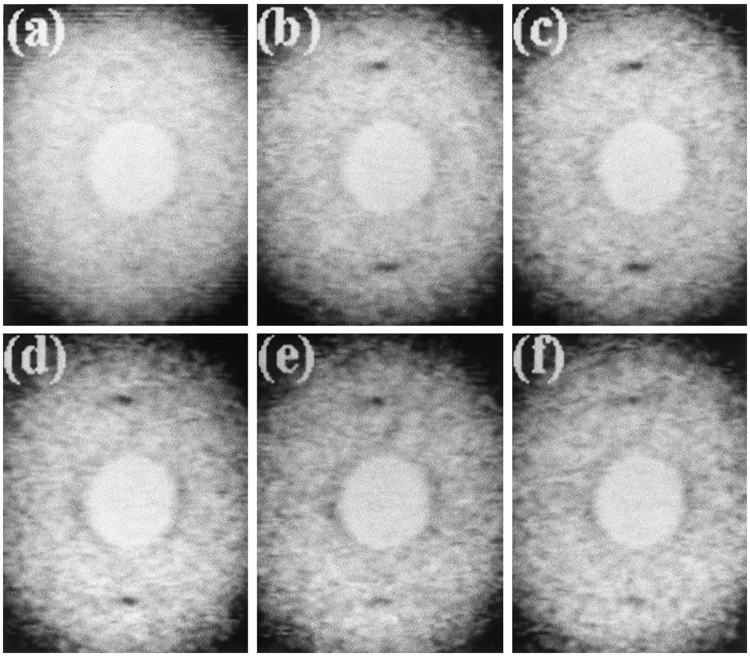

Fig. 3. (a)–(f) shows selected area of Frames 5–10 from the sequence of X-ray diffraction patterns from which the patterns in Fig. 1 were selected, to highlight the variation in the intensity of the meridional reflection identified with the mesophase.

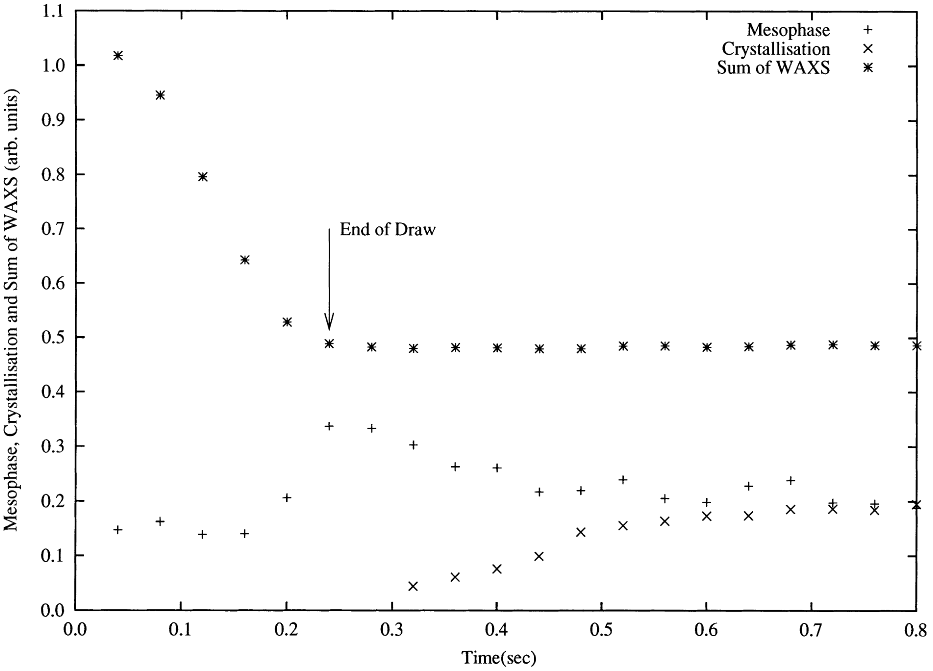

Fig. 4. Plot of the variation in thinning of the sample (⁎) crystallinity (×) and the integrated intensity of the meridional reflection identified with the mesophase (+), calculated for the sequence of X-ray diffraction patterns from which the patterns in Fig. 1 were selected. The arrow indicates the first frame with detectable crystallinity. This frame coincides with the end of draw.

increase in crystallinity within the equatorial diffraction. Comparison of Frame 124 with Frame 12 shows that there was essentially no change in the diffraction pattern during the subsequent 4 s of the experiment.

The observation of a transient highly oriented weak meridional diffraction peak with a spacing of 0.098 $Å^{-1}$ which can be associated with the occurrence of a mesophase is the novel feature of these studies. The meridional reflection corresponding to the mesophase in a typical WAXS pattern from PET drawn under industrial processing conditions is highlighted in Fig. 2. The increase and subsequent decay in intensity of this meridional diffraction over Frames 5–10 (i.e. a period of ∽0.2 s) during the final stages of the draw and immediately prior to achievement of maximum crystallization can be seen in Fig. 3. In this figure the middle part of each diffraction pattern has been extracted from the corresponding frame to highlight the intensity variation of this reflection. The initial appearance of the meridional diffraction at 0.098 $Å^{-1}$ can be seen in Frame 5 with the intensity of this diffraction increasing to a maximum through Frames 6 and 7 followed by a decrease in intensity through Frames 8–10 while the intensity of the equatorial reflections associated with the development of strain-induced crystallization increases.

The variation of the integrated intensity of the meridional diffraction at 0.098 $Å^{-1}$ during this experiment is shown in Fig. 4. The development of strain-induced crystallinity during this same period was followed by fitting radial traces of the variation in intensity across the equator of successive frames by a family of Pearson VII [11] functions to represent overlapping crystalline reflections and oriented and non-oriented diffuse diffraction. The full details of this method is described elsewhere [12]. Fig. 4 clearly illustrates the correlation between the increase in the intensity associated with crystallinity and that associated with the decrease in intensity of that associated with the mesophase. The development of orientation during the draw was followed by analysing azimuthal scans of successive frames at a reciprocal space distance of 0.28 $Å^{-1}$. This corresponds to the position of the maximum in the equatorial scan of the diffuse diffraction at the onset of crystallization. For simplicity the curves were characterized by calculating the orientation order parameter $\langle P_2(\cos\theta)\rangle$ of the Pearson VII component of the fit using the expression derived by Lovell and Mitchell [13]. This is a convenient way of following the development of non-crystalline orientation during the mechanical drawing process. The variation in draw ratio derived from the integrated WAXS intensity is plotted in Fig. 4. The arrow on the plot indicates the end of draw derived from this integrated intensity. It is interesting to note that the orientation parameter reaches a value around 0.30 before any sign of the reflection associated with the mesophase is observed.

The increase and decrease in intensity of the oriented meridional peak at 0.098 $Å^{-1}$ is similarly observed in other experiments in which PET is drawn at 85 or 90°C where the draw rate and draw ratio are both sufficiently high for the orientation parameter $\langle P_2(\cos\theta)\rangle$ to reach a value of at least 0.30. We have not so far observed this oriented peak for draw temperatures greater than 90°C.

4. Conclusions and further work

Although the oriented meridional diffraction peak at 0.098 Å^{-1} is weak there is no doubt that it represents a genuine structural feature occurring during strain induced crystallization of PET. This peak is difficult to observe in time-resolved studies because of its weakness and the relatively short time (~0.2 s) during which it persists. However its observation is highly reproducible The detailed observations summarized in Fig. 4 are also convincing because of the fact that the peak was only observed when the orientation parameter of the oriented amorphous material in the sample reached 0.30 and began to disappear at the onset of crystallization. The strength of these correlations provides convincing evidence that the structural feature corresponding to this peak plays a key role in the strain induced crystallization process.

There is an increasing body of evidence that polymer crystallization in general may be assisted by the formation on an intermediate metastable state. In studies of disoriented PET, Imai et al. [14] have detected a SAXS component during the induction period before crystallization and have ascribed it to the spinodal evolution of density fluctuations causing a segregation of rod-like configuration from more random chain configurations. Associated phenomenon have been observed by Terril et al. [15] in both oriented and disoriented polypropylene. Olmsted et al. [16] have recently formalized a mechanism for this spinodal assisted crystallization via a metastable liquid–liquid phase. Strobl [17] has proposed that oriented PET crystallizes via a spinodal process but has no direct observation of an intermediate state.

The present synchrotron experiments on oriented PET show definitive evidence of the function of the formation of oriented, non-crystalline order before crystallization that would be consistent with the proposed segregated rod-like configurations. However a degree of caution is needed in generalizing this observation since the transient diffraction feature has so far only been detected at temperatures 90°C where high network extension occurs due to restricted chain relaxation.

Work is in progress to identify the extent to which polymer orientation within a mesophase is related to final levels of crystallinity and also to establish the parameter window-defined in terms of draw rate, ratio and temperature and polymer molecular weight and composition during which mesophase formation occurs.

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References

[1] Blundell DJ, MacKerron DH, Fuller W, Mahendrasingam A, Martin C, Oldman RJ, Rule RJ, Riekel C. Polymer 1996;37:3303.

[2] Bonart R. Kolloid-Z 1966;213:1.

[3] Bonart R. Kolloid-Z 1966;210:16.

[4] Bonart R. Kolloid-Z 1968;231:438.

[5] Asano T, Seto T. Polym J 1973;5:72.

[6] Nicholson TM, Davies GR, Ward IM. Polymer 1994;35:3861.

[7] Carr PL, Nicholson TM, Ward IM. Polym Adv Technol 1997;8:592.

[8] Welsh L, Blundell DJ, Windle AH. Macromolecules 1998;31(21): 7562.

[9] Mahendrasingam A, Fuller W, Forsyth VT, Oldman RJ, MacKerron DH, Blundell DJJ. Rev Sci Instrum 1992;63:1087.

[10] Hughes DJ, Mahendrasingam A, Martin C, Oateway WB, Heeley EL, Bingham, Fuller W. Rev Sci Instrum 1999; in press.

[11] Hall MM, Veeraraghavan VG, Rubin H, Winchell PG. J Appl Cryst 1977;10:66.

[12] Mahendrasingam A, Martin C, Fuller W, Blundell DJ, Oldman RJ, Harvie JL, MacKerron DH, Riekel C, Engstrom P. Polymer 1999;40(20):5553.

[13] Lovell R, Mitchell GR. Acta Cryst A 1981;37:135.

[14] Imai M, Kaji K, Kanaya T. Macromolecules 1994;27:7103.

[15] Terril NJ, Fairclough PA, Towns-Andrews E, Komanschek BU, Young RJ, Ryan AJ. Polymer 1998;39:2381.

[16] Olmsted PD, Poon WCK, McLeish TCB, Terril NJ, Ryan AJ. Phys Rev Lett 1998;81:373.

[17] Strobl G. The physics of polymers, 2nd ed. Berlin: Springer, 1997. p. 173.