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Orientation and crystallisation mechanisms during fast drawing of poly(ethylene terephthalate)

D. J. Blundell[1], R. J. Oldman[1], W. Fuller[2], A. Mahendrasingam[2], C. Martin[2], D. H. MacKerron[3], J. L. Harvie[3], C. Riekel[4]

[1] ICI Technology, P.O. Box 90, Wilton, Middlesbrough TS90 8JE, UK
[2] Department of Physics, University of Keele, Staffordshire ST5 5BG, UK
[3] DuPont(UK) Ltd., P.O. Box 2002, Wilton, Middlesbrough TS90 8JF, UK
[4] ESRF, Grenoble, France

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Summary

Synchrotron radiation has been used to record the diffraction patterns from Poly(ethylene terephthalate) for a range of draw rates (0.1 to 10sec^{-1}) and temperatures (90 to 120°C). The patterns were analysed to derive the development of the $<P_2(\cos\theta)>$ order parameter and the rates of crystallisation. The effects of temperature and draw rate can be unified with a WLF time-temperature shift factor. Comparison with estimates of chain relaxation processes show that, when the draw rate is faster than the chain retraction process, the onset of crystallisation is delayed until the end of drawing. Crystallisation is very sensitive to both temperature and orientation and has an approximate 4th power dependence on $<P_2(\cos\theta)>$.

Introduction

Poly(ethylene terephthalate) (PET) is used extensively in the manufacture of fibres, bottles and films. All of these applications make use of PET based polymers in the oriented crystalline state. Although there is an extensive literature on the crystallisation of PET from the unoriented state, there has been relatively little information on the faster crystallisation process that occurs in an oriented polymer. However recent studies using synchrotron radiation have now for the first time enabled real-time observation of oriented crystallisation during drawing at fast rates comparable with industrial processing conditions (1,2). These experiments revealed behaviour which differed from that deduced from laboratory experiments carried out at slower draw rates or those in which samples were quenched to room temperature before characterising the crystallinity. The paper will present intitial results from more recent experiments that give new insight into the kinetics of the oriented crystallisation process in PET and its relationship to the orientation and relaxation processes of the entangled molecular network. A full account of the details and implications of these experiments will be published later.

With the fast drawing conditions used in our previous observations (~10sec^{-1}), we have shown that within the time resolution of the experiments, the onset of crystallisation does not occur until the end of the extension process, irrespective of the final draw ratio(1,2). The kinetics of the oriented crystallisation were also found to follow approximately a first order transformation process from which a characteristic crystallisation rate could be deduced. These deductions differed from reported experiments carried out at slower draw rates and those in which samples were quenched to room temperature before characterising the crystallinity(5,6), where crystallisation was claimed to start at a particular stage of the extension process. Some recent real-time experiments of Middleton (7) using both lab and synchrotron X-ray sources have now provided definitive evidence of crystallisation occurring before the end of draw when drawing at slower rates (<0.1sec^{-1}). Our previous results have also indicated that, unlike conventional isotropic crystallisation, the crystallisation rate appeared to be insensitive to temperature. Amongst other suggestions it was speculated that this surprising insensitivity may be the result of two opposing effects. The more recent experiments that are reported here have attempted to address these issues by examining a wider range of drawing conditions including the effects of draw rate.

Experimental

The wide angle X-ray diffraction data was recorded on beamline ID13 at the ESRF in Grenoble using an X-ray camera that had been purpose designed and constructed in the Keele Physics Department workshops(3). Diffraction patterns were recorded using a Photonics Science CCD detector with a sensitive area 92 x 69mm and with exposure times of 40msec. The pattern was integrated within the detector before being digitised by a Synoptic i860 framegrabber within an 8-bit word to enable 124 frames to be detected "end-to-end" with essentially no dead-time between frames. The variations in size and shape of the specimen during deformation were recorded simultaneously with a video camera.

Specimens of PET strips 10mm wide were cut from a sheet of cast amorphous film 840µm thick and were mounted in the jaws of the camera with a 10mm gauge length and then heated to the deformation temperature (90 to 130°C) to equilibrate for 2minutes. They were then drawn to various final draw ratios (between 2 and 4) by stopping the motors after various numbers of predefined steps using a range of drawing rates (~0.1 to 10sec^{-1}). Because of necking effects it is difficult to draw to an exact predetermined draw ratio. Independent estimates of the progress of the draw were derived from the total detector count by assuming that this was related to the thickness of the specimen at the precise region from which the diffraction was recorded.

These experiments generate very large amounts of data whose analyses are only feasible on an acceptable time scale by semi-automatic techniques. A suite of programmes has therefore been developed which allow frame manipulation and objective quantitative analysis of the diffraction patterns to give a quantitative measure of the development of crystallinity, orientation and the local draw ratio at the position of the beam. Estimates of crystallinity were obtained from radial scans along the equator by fitting a Pearson VII function to the *{010}* crystal reflection. The development of orientation was followed by analysing azimuthal circular scans of successive frames at a reciprocal space vector of 0.28Å^{-1} to obtain the orientation order parameter $<P_2(\cos\theta)>$ (4).

Results and Discussion

Effects on Chain Orientation: An important aspect of this analysis is the development of chain segment orientation during the deformation prior to the onset of crystallisation. Figure 1 shows the development of $<P_2(\cos\theta)>$ for selected experiments covering a range of draw rates and draw temperatures. As may be anticipated from the competition between the imposed extension and chain relaxation, the molecular orientation achieved for a given draw ratio is reduced with increasing temperature and with reducing draw rate. For simplicity, the effectiveness of the drawing process can be characterised from the slope of the $<P_2(\cos\theta)>$ versus Draw Ratio data in Figure 1. This is shown plotted against draw rate in Figure 2. It is a well established practice in polymer relaxation studies to employ time-temperature superposition methods to unify the effects of temperature and deformation rate. For amorphous polymer in the temperature region above the glass transition it is appropriate to use a WLF relationship for the superposition. Studies by Le Bourvellec have established the following WLF relationship for PET(8):

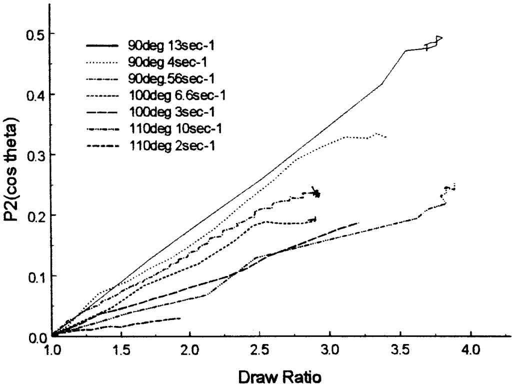

Figure 1: Dependence of Orientation on Draw Ratio

$$\log_{10}a = \log_{10}\frac{\tau_T}{\tau_{84.2}} = -\frac{8.4(T-84.2)}{42.4+T-84.2}$$

Figure 3 shows a modified plot of the data in which this WLF shift factor has been used to shift the data to a 90°C reference temperature. The close clustering of the data points delineate the underlying master curve which demonstrates how temperature and draw rate can be appropriately interchanged to achieve the same overall effects in terms of the response of the chains to deformation. The reduction of the $<P_2(\cos\theta)>$ dope in figure 2 at lower draw rates is a consequence of the relaxation of the deformed, entangled chains.

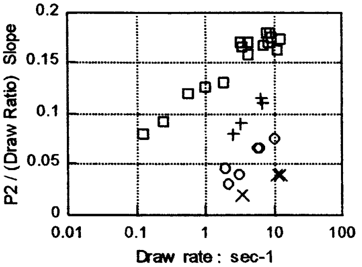

Figure 2: Development of Orientation with Draw Rate □=90°C; + = 100°C; o = 110°C; × = 120°C.

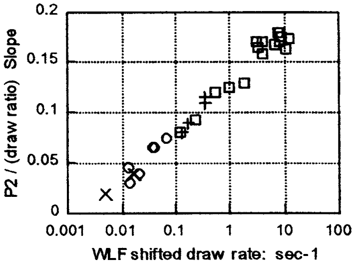

Figure 3: Development of Orientation with WLF shift to 90°C Reference Temperature.

Current understanding of relaxation of deformed chains is derived from the theoretical framework of Doi and Edwards(9) of an enclosing tube and the concept of reptation introduced by de Gennes(10). The basic model involves three interlinked mechanisms occurring over different timescale regimes. As a result of macroscopic deformation, the tubes whose topography is defined by entanglements are appropriately deformed. The fastest relaxation motion, characterised by a relaxation time τ_A, involves the Rouse modes between two entanglements. These motions operate on a time scale in which the entanglements can be considered as fixed and enable the chain strands between the "fixed" entanglements to move to equilibrium configurations. The second relaxation, characterised by τ_B, is enabled by the Rouse motions and involves a retraction of chains within the deformed tube in order to recover their equilibrium curvilinear lengths. This process results in an increase in the length of chain strands between some entanglements. The third stage, characterised by τ_C, involves the reptation of the chains out of their original deformed tubes to form fresh undeformed tubes and results in the chains attaining isotropic configurations.

The fastest motions are related to the molecular weight between entanglements, M_e:

$$\tau_A \sim \frac{\zeta}{T} b^2 M_e^2$$

The slower relaxations are related to τ_A:

$$\tau_B \cong 2\tau_A \left(\frac{M}{M_e}\right)^2 \qquad \tau_C \cong \tau_A \left(\frac{M}{M_e}\right)^3$$

Lapersonne(11) has estimated the values of τ_A for PET to be around 10-2 sec at 85°C and 10-4 secs at 97°C. The temperature dependence of the Rouse modes is mainly due to the molecular friction coefficient ζ which is expected to be governed by the WLF type of relationship. Table 1 shows estimates of the three relaxation times based on Lapersonne's data and extrapolated to other temperatures with the WLF relationship. Also shown in Table 1 are the reciprocals of the relaxation times in order to illustrate the rates of the fundamental mechanisms. It will be noted in comparison with Figure 1, that when $1/\tau_B$

becomes comparable to the deformation rate that the slope of the plots is significantly lower.

Temperature °C	τ_B sec	τ_C sec	$1/\tau_B$ sec^{-1}	$1/\tau_C$ sec^{-1}
80	190	6,400	0.005	1.6 x 10-4
90	2.2	74	0.45	0.014
100	0.12	4	8.3	0.25
110	0.015	0.5	66	2
120	0.003	0.11	310	9.2
130	0.001	0.03	1,000	30

Table 1: **Magnitude of chain relaxation times based on data of Le Bourvellec (8), using** M=40,000; M_e=1200; τ_A at 90°C = 0.001sec

Onset of Oriented Crystallisation Process: Table 2 compares the onset of crystallisation with the end point of the extension process for experiments carried out at 90 °C with different draw rates. These observations are based on analyses of individual diffraction frames. For faster draw rates the crystallisation onset is consistent with our previous observations and coincides closely with the end of draw. However for draw rates slower than 1sec-1, there is evidence of increasing levels crystallisation occurring while the drawing is still in progress and is therefore consistent with the recent observations of Middleton (7). It will be noted from Table 1 that this change in behaviour occurs at a draw rate which is close to the rate of the chain retraction process. This important observation appears to imply that as long as the deformation rate is fast compared with chain retraction processes, the chains do not have the freedom and mobility to organise into crystals while deformation is still in progress. This emphasises the need for the

Draw Rate sec^{-1}	End of Draw frame number	Start of Crystallisation frame number	%Crystallinity at end of draw
12.8	6	6	0
11.1	6	6	0
6.9	8	8	0
4.2	14	14	0
1.8	26	25	5
1	52	48	25
0.56	90	50	30
0.24	210	180	70
0.12	425	350	85

Table 2: **Point of onset of crystallisation and extent of crystallisation at end of draw.**

chains to have an independence of movement to enable crystallisation to proceed. Examination of experiments at higher temperatures show that a similar change in the onset behaviour occurs but at a faster critical draw rate. At higher temperatures it can also be observed that when the draw rate is slower than the reptation rate, oriented crystallisation ceases to occur.

Oriented Crystallisation Rate: It is well established that the rate of crystallisation is very sensitive to the degree of molecular orientation. However there has so far been little information on the nature of this relationship. Figure 4 shows our observed crystallisation rates plotted against the value of the <P $_2$(cosθ)> order parameter at the onset point of crystallisation. This figure clearly demonstrates the high sensitivity of the crystallisation rate to both molecular orientation and temperature. The plot indicates that the apparent insensitivity to temperature from our more limited previous experiments (1,2) was in fact a fortuitous deduction resulting from opposing factors. The plot shows a systematic clustering with respect to draw temperature with each cluster exhibiting a similar underlying trend with respect to orientation but with a vertical shift of the data. It is to be expected that the crystallisation process must involve the transport of chain segments into crystallographic register and that therefore the difference in temperature will be largely governed by chain mobility. Therefore in order to extract the underlying relationship between crystallisation rate and molecular orientation it is appropriate to attempt to eliminate the effect of chain mobility by using the above WLF shift factor.

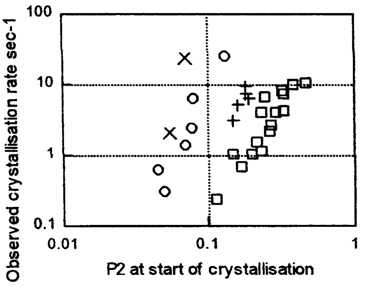

Figure 4: **Dependence of Crystallisation Rate on Orientation.** □=90°C; + = 100°C; o = 110°C; x = 120°C.

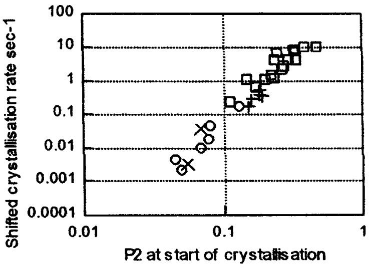

Figure 5: **Crystallisation Rate shifted with WLF to 90°C Reference Temperature.** □=90°C; + = 100°C; o = 110°C; x = 120°C.

Figure 5 shows the result of vertically shifting the observed crystallisation rates to a reference temperature of 90°C. Although there is still a degree of scatter in these shifted data, they do appear to reveal an underlying relationship. From the slope of this log-log plot, the oriented crystallisation rate would appear to be approximately proportional to the 4th power of <P$_2$(cosθ)> of the oriented network at the onset of crystallisation.

Conclusions

1. The effects of draw temperature and draw rate on molecular orientation, $<P_2(\cos\theta)>$, can be inter-related by a WLF shift factor to reveal the influence of the underlying chain relaxation processes.
2. For the fast draw regime where draw rate is faster than the rate of the chain retraction process, the onset of crystallisation is delayed until the end of the drawing process.
3. For the regime when the draw rate becomes comparable to the rate of retraction (but faster than the chain reptation rate), crystallisation is able to start during the draw process.
4. After rescaling with a WLF factor, there appears to be an underlying relationship in which crystallisation rate is approximately proportional to the 4th power of $<P_2(\cos\theta)>$.

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