JOURNAL OF MATERIALS SCIENCE 20 (1985) 1370–1374

Morphological instability of poly(ethylene terephthalate) cyclic oligomer crystals

ALEKSANDRA PEROVIC*
Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario L5K 2L1, Canada

The mechanism of formation of depressions and cavities in the middle of the basal faces of hexagonal plates of poly(ethylene terephthalate) oligomer single crystals upon growth during heat treatment is investigated. It is proposed that this effect is caused by two simultaneously occurring processes: supersaturation inhomogeneity in the centre of the plates and formation of the kinematic (shock) waves at the edges of the plates.

1. Introduction

The migration of the cyclic trimers (the predominant cyclic species) from the interior of poly (ethylene terephthalate) (PET) fibres to the surface has been known and reported in a number of papers [1–5]. Most of the studies were stimulated by problems caused during the dyeing of PET fibres. The other interest was connected with the use of the equilibrium cyclic oligomer content.

It has been demonstrated [3, 5] that at temperatures between 130 and 230° C the cyclic oligomeric trimers migrate to the surface and crystallize with maximum rate of growth at around 190° C. The morphology of PET oligomer crystals has been presented by optical and scanning electron micrographs [2, 3, 5] demonstrating different crystalline forms and a variety of morphological features. There has been no attempt, however, to elucidate the mechanism of growth and consequently the causes of morphological instabilities characteristic of the growth of these crystals.

In this paper, we will investigate the mechanism of formation and development of the depressions and cavities present in the centre of basal hexagonal planes of the oligomer crystals.

2. Experimental procedure

The samples of PET (Mylar 400 D, 100 μm thick) were obtained from DuPont. The samples were heat treated in an air oven at different temperatures ranging from 130 to 230° C, for different lengths of time. The heat-treated samples, coated with a 20 nm thick gold/palladium film were examined in a Philips-505 scanning electron microscope.

3. Results and discussion

Figs. 1a and b show the characteristic growth features of surface oligomer crystals heat-treated at 200° C. The crystals are the nearly perfect hexagonal plates with basal and prism faces very well developed. The basal faces of the crystals are smooth without any visible instability of growth (Fig. 1a). After prolonged heat treatment, at about 10 μm of linear crystal dimension, the formation of depressions and cavities in the middle of hexagonal crystal faces is observed (Fig. 1b). The growth features of oligomer crystals shown in Fig. 1 are common to all PET samples heat treated in the temperature range 130 to 230° C.

Fig. 2 shows the average crystal size (linear dimension) as a function of annealing temperature. All data have been taken after 20 min of annealing. The curve shows a maximum at 190° C and its shape is characteristic of the temperature-dependent particle growth mechanism, involving nucleation and growth processes as described by the Turnbull–Fisher equation [6] for polymers.

---

*Present address: Ontario Hydro Research Division, Metallurgical Department, M8Z 5S4, Toronto, Ontario, Canada.

0022–2461/85 $03.00 + .12

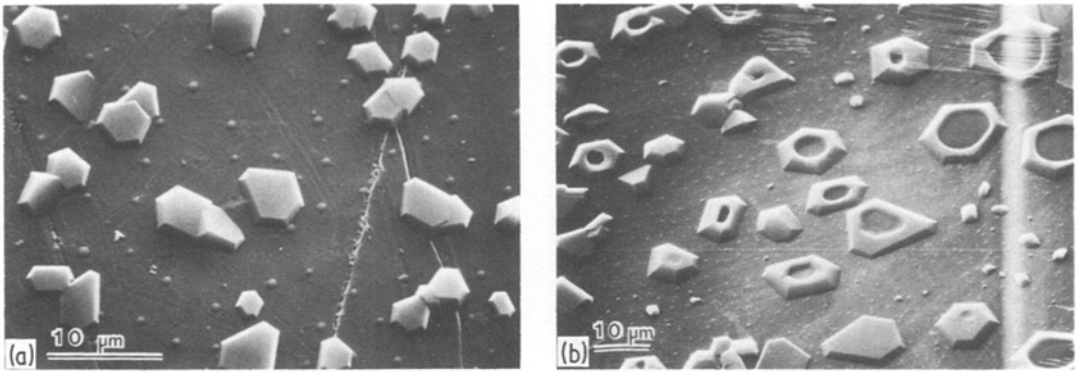

Figure 1 Scanning electron micrographs of PET heat treated at 200° C: (a) 30 min, (b) 2 h.

The rate of diffusion increases with temperature whereas the rate of nucleation decreases with increasing temperature; hence the overall rate of transformation passes through a maximum where the two factors are comparable. The rapid decrease of crystal size towards the higher temperature and its gradual decrease at lower temperature are also in agreement with the above theory.

In this study we were interested mostly with the conditions that had caused morphological transformation of a smooth face of hexagonal plates to a face developing a depression or a cavity in its middle.

Figs. 3a to d are the results obtained by heat treatment at 130° C. In the early stage of growth, the crystals are perfect hexagonal plates, with smooth basal faces. The linear dimension of the crystals reaches 5 to 6 μm (Fig. 3a). Fig. 3b shows a slight depression formed in the middle of the basal face of the crystal of ~7 to 8 μm in size. With further growth, the depression becomes bigger and deeper (Fig. 3c) and finally after a longer time, when the crystal size reaches ~10 to 12 μm, a big, broad cavity is developed, leaving the crystal as of "picture frame" morphology. The same growth pattern is obtained at all temperatures in the range from 130 to 200° C.

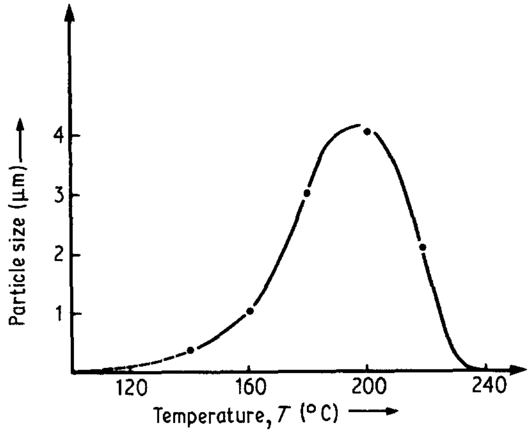

Figure 2 Average crystal linear dimension as a function of annealing temperature, at 20 min of annealing.

According to theoretical considerations the face instability of faceted crystals with anisotropic interface kinetics is related to the difference in supersaturation over different points of a crystal face as a result of diffusion [7–11].

The supersaturation inhomogeneity (the supersaturation being minimum at the centre of the face and maximum at the corners and edges) is proportional to $\beta L/D$ (where β is the kinetic coefficient of the crystal face, L is a linear crystal dimension and D is the bulk diffusion coefficient) and increases as the crystal enlarges. The reduced supersaturation in the middle of the crystal face produces face distortions in the form of a slight curvature, which in turn leads to a still further drop in concentration at the face centre and to a still greater depression and so forth. The process is finally completed by the formation of a cavity, that is, an orientation appears on the surface, in the middle of the crystal face that deviates sharply from the orientation of the singular face.

A critical size L_c, exists at which the instability develops and the cavity appears given by the inequality

$$L_c < \frac{D}{\beta}\,\frac{\beta(\Psi_c)-\beta(\Psi_1)}{\beta(\Psi_c)} \tag{1}$$

where β, $\beta(\Psi_c)$ and $\beta(\Psi_1)$ are the values of the kinetic coefficients of the main habit plane, vicinal planes forming the walls of the cavity and the close-packed face, respectively. Unfortunately, we could not verify Equation 1 due to the lack of

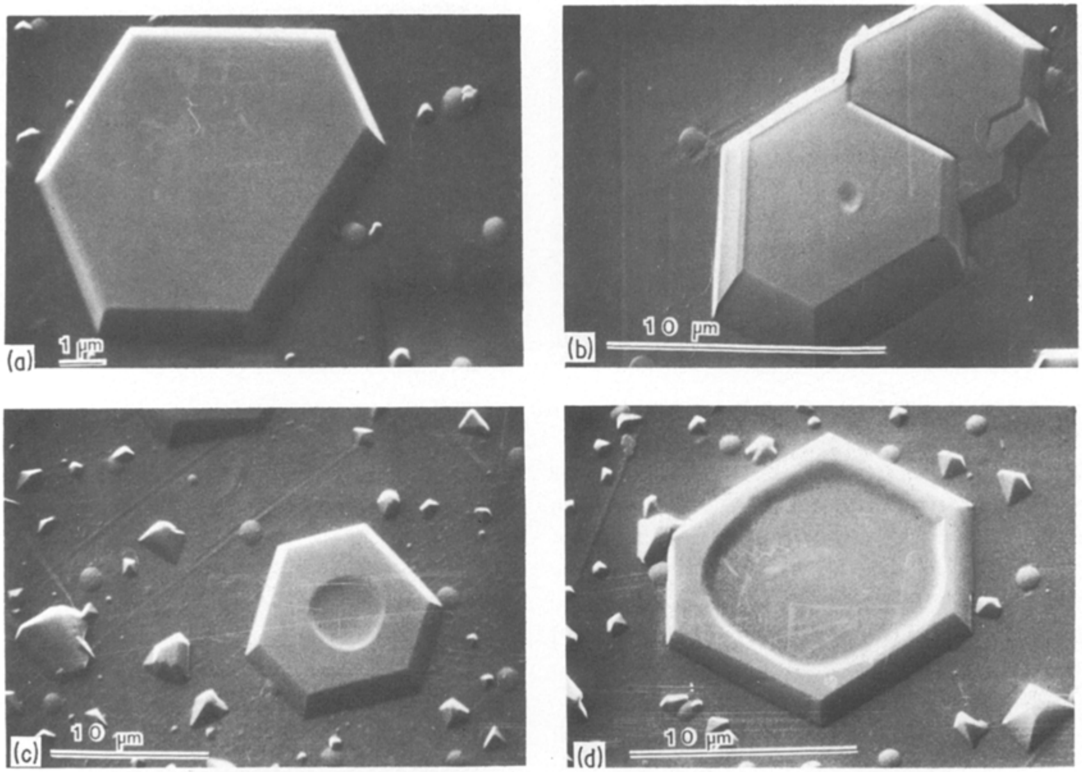

Figure 3 Scanning electron micrograph of PET heat treated at 130° C: (a) 1 h, (b) 3 h, (c) 7 h, (d) 17 h.

knowledge of parameters entering it. However, the experimental finding that the basal face is smooth in small crystals while a cavity appears in larger ones under the same experimental conditions agrees qualitatively with the conclusion of the theory.

The situation in growth of oligomer crystals is not fully covered by arguments presented in the above theory, which relates to a crystal embedded in a continuous matrix and growth governed by bulk diffusion. Instead the oligomer crystals formed on the film surface are growing by the supply of cyclic molecules coming only from the film bulk, by surface diffusion, the initial feeding of a crystal starting therefore at the sides of the crystals. A recent work by Bermond and Venables [12] deals with the vapour growth of a three-dimensional crystal exhibiting facets bounded by sharp edges and corners and comprehends such a growth shape as a result of supply processes (volume and surface diffusion) and capillarity. The thin, flat crystals are described as formed by trapping all the arriving adatoms by surface diffusion on side faces due to a high kink density on these faces as compared to flat, basal faces, at low temperatures.

The growth of thin oligomer crystal plates can similarly be envisaged as forming by molecules diffusing up the sides of the crystal faces only where they become incorporated, thus favouring the growth of the top face. The further thickening proceeds by two-dimensional nucleation and spreading the layers from the edges of the plate towards its centre. Two-dimensional nucleation is easier at the corners and the edges than at any other point on the flat surface due to a lack of kinks on the flat surface needed for adatom incorporation.

The growth instability of the basal face develops with further crystal growth when the linear crystal dimension reaches the critical size L_c (7 to 8 μm). The supersaturation becomes smaller in the centre of the face than at the edges as a result of diffusion and a depression forms. The growth instability which is only due to the presence of a supersaturation inhomogeneity would be expected to have gradually developed depresssions leading to a saucer-type crystal form.

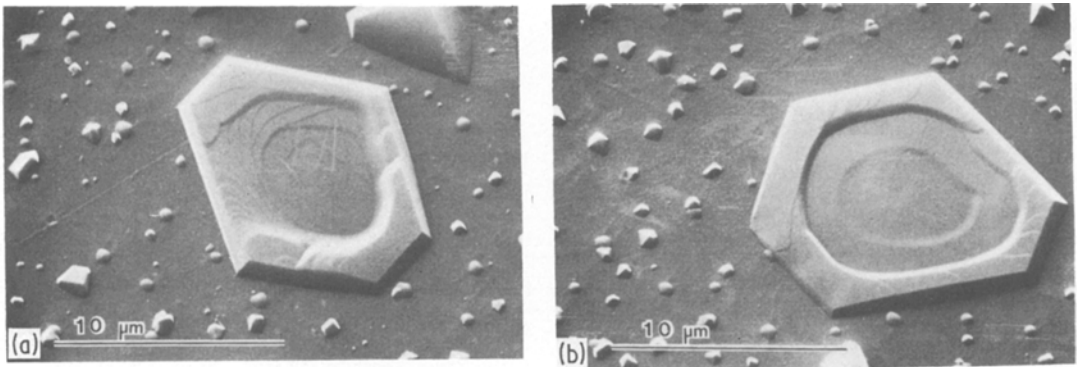

Figure 4 (a, b) Scanning electron micrographs of PET heat treated at 170° C for 2 h.

In most of our experimental evidence, cavities with very pronounced sharp walls are formed (Fig. 3d). Such a cavity form can be explained by further growth, additionally complicated by formation of kinetic (shock) waves. Indeed, it is quite easy to comprehend the formation of kinematic waves at the edges of hexagonal plates under given experimental growth conditions.

It is to be expected that as the crystal grows, the diffusion distance becomes too large for the molecules to move readily away from the edge, and the molecules happen to crowd at the edges leading to a nucleation of many close-spaced steps whose diffusion fields may overlap and mutually interfere. If two consecutive steps are formed close together before one step can travel away from the edge towards the centre, it gets caught by the second step, and a macrostep is formed. In this way, visible steps of micron-size height may appear from the growing edge.

We have been able to observe the bunching of the steps at the edges of the crystals as illustrated in Figs. 4a, b. One should note that the transient stage of nucleating the macrosteps and their spreading along the edges is a fast (shock) process, and is not readily observed experimentally.

The gradient of supersaturation along the crystal face, together with the formation of large macrosteps (kinematic waves) at the edge of the hexagonal plates cause preferential thickening at the periphery, accentuating starvation of the face centre and developing a "hopper" or "picture-frame" morphology of the crystal.

Fig. 5 is a schematic representation of the steps in the growth mechanism involved during the formation of oligomer crystals.

Fig. 6 is the scanning electron micrograph of PET film heat treated at 190° C for 46 h. A very complicated morphology is developed. Many layers have formed on top of each other, forming overhanging layers and transforming the crystal into a skeletal form.

4. Summary

Experimental evidence for the instability of planar growth interfaces with anisotropic surface kinetics is presented. The experimental observation of cavity formation on the basal faces of hexagonal plate-like oligomer crystals in PET film agrees qualitatively with the theoretical consideration given by Chernov [7–10]. The supersaturation inhomogeneity along with anisotropic surface kinetics contributes to the growth instability. The particular shape of cavities developed in oligomer crystals in the later stage of growth is explained by further growth of the kinematic (shock) waves formed at the crystal edges.

Acknowledgement

The author would like to thank Dr P. R. Sundar-

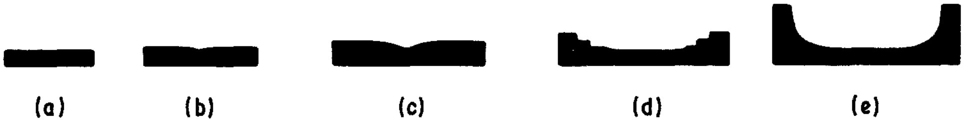

Figure 5 Schematic representation of the mechanism of cavity formation in oligomer crystals.

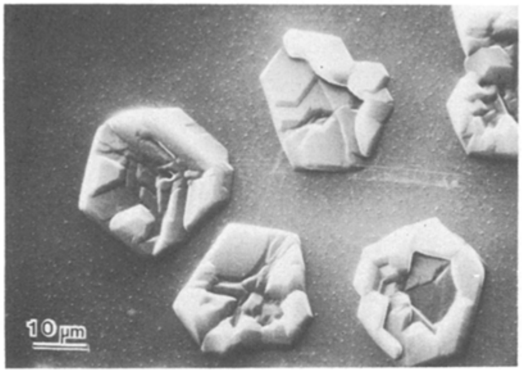

Figure 6 Scanning electron micrograph of PET heat treated at 190° C for 46 h.

arajan for the initiation of this project and his helpful suggestions and discussions.

References

1. G. L. BINNS, J. S. FROST, F. S. SMITH and E. C. YEADON, *Polymer* 7 (1966) 583.
2. E. ITO and S. OKAJIMA, *Polym. Lett.* 7 (1969) 483.
3. J. DERIMONT, R. HAGEGE and J. JACQUEMART, *Bull. Sci. ITF* 5 (1976) 355.
4. H. L. NEEDLES, R. S. BERNS, W. C. LU and K. ALGER, *J. Appl. Polym. Sci.* **25** (1980) 1737.
5. A. PEROVIC and P. R. SUNDARARAJAN, *Polym. Bull.* 6 (1982) 277.
6. D. TURNBULL and J. C. FISHER, *J. Chem. Phys.* 17 (1949) 71.
7. A. A. CHERNOV, *Kristallografiya* 8 (1) (1963) 87.
8. *Idem, ibid.* 8 (4) (1963) 492.
9. *Idem, J. Cryst. Growth* **24/25** (1974) 11.
10. *Idem, Sov. Phys. Crystall.* **16** (4) (1972) 734.
11. A. SEEGER, *Phil. Mag.* **44** (1953) 1.
12. J. M. BERMOND and J. A. VENABLES, *J. Cryst. Growth* 64 (1983) 239.

Received 30 December 1983
and accepted 21 June 1984