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Polymer 46 (2005) 4987–4990

polymer

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Polymer Communication

Morphological study by TEM on uniaxially oriented thin films of PBT

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Received 19 January 2005; received in revised form 6 April 2005; accepted 21 April 2005

Abstract

We prepared uniaxially oriented thin films of poly(butylene terephthalate) (PBT) by applying shear strain to the melt and studied their resulting morphology by transmission electron microscopy (TEM), and could show visually that stacked-lamellar structures are formed in aromatic polyesters. On the basis of crystallographic consideration, we assigned each of the recognized stacked-lamellar structures to a shish-kebab structure or a part of it. In addition, we successfully demonstrated that in one shish-kebab structure all or almost all kebabs (namely, lamellae) have a same crystallographic orientation.

Keywords: Polyester; TEM; Shish-kebab structure

1. Introduction

Crystallization of synthetic polymers from melt or solution that have undergone extensional flow has been an attractive subject for a long time. In 1965, Pennings et al. [1] discovered a characteristic morphology referred to as the shish-kebab structure in the crystallization of polyethylene (PE) from flowing solutions. According to Pennings [2], the shish-kebab structure consists of a central filament or backbone which is covered with platelets at rather regular intervals. After the discovery of this structure by Pennings et al. many researches have been reported on the shish-kebab structure of polymers, which have a relatively simple primary structure such as PE, isotacatic polystyrene (iPS) and isotactic polypropylene (iPP), when the polymers are crystallized from solution [3,4] and also from melt [5,6].

Poly(butylene terephthalate) (PBT) is an aromatic polyester well known as an engineering thermoplastic. Two reversible modifications of triclinic crystal system, the α- and β-modifications, were reported for relaxed and stressed PBT, respectively, [7–10]. Several morphological studies on PBT crystallized under a static condition have been reported so far [11–13]. On the other hand, there have been few reports on the morphology of PBT crystallized under an extensional flow field. The molecular weight of aromatic polyesters is smaller by one order or more than that of polymers (e.g. PE, iPS, iPP) used in the reports in which the shish-kebab structure was clearly recognized. Furthermore, the molecular weight of aromatic polyesters falls off easily in the molten state, mostly due to the transesterification reaction [14]. Thus, the formation of shish crystal (namely, extended-chain crystal) has been considered to be fairly difficult, and even the formation of kebab crystal (namely, folded-chain crystal) seems to be difficult [14]. Therefore, the stacked-lamellar structure model or the shish-kebab structure model, both of which have been regarded as a model structure for many synthetic fibers, has not been accepted so far for the fiber structure of aromatic polyesters including PBT. However, Li and de Jeu [15], recently, investigated the shear-induced crystallization behavior of PBT by in-situ small-angle X-ray scattering, and proposed, on the bases of Avrami exponent, a microshish model or a point-precursor model at higher crystallization temperatures.

In this communication, uniaxially oriented thin films of PBT were prepared by applying shear strain to the melt and

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doi:10.1016/j.polymer.2005.04.046

the resulting morphology was studied by transmission electron microscopy (TEM).

2. Experimental section

The 0.5 wt% solution of PBT in 1,1,1,3,3,3-hexafluoro-2-propanol was dropped and spread on a glass slide and then covered with another glass slide (both glass slides were pre-heated at 260 °C). Just after evaporation of the solvent, a thin molten polymer film was sheared/crystallized by displacing one of the two glass slides at the relative displacing speed of the glass slides of 12 m/min and then quenched to room temperature [16]. The film thickness is assumed to be about 50 nm which value was judged empirically from the transmittance for 200 kV electrons [16].

Crystallized thin films on the glass slides were coated with vapor-deposited carbon under vacuum for reinforcement. Then, with the aid of the aqueous solution (ca. 25%) of polyacrylic acid (PAA) [17], the appropriate portion of the specimen film was transferred to and mounted on a copper grid for TEM.

Morphological observation by TEM of resulting specimens was performed at room temperature with a JEOL JEM-200CS operated at an accelerating voltage of 200 kV. All the images were recorded on photographic films (Mitsubishi MEM) which were then developed with Mitsubishi Gekkol (full strength) at 20 °C for 5 min. The details of specimen preparation and TEM will be described in the next paper [18].

3. Results and discussion

Fig. 1 is a conventional bright-field image of the uniaxially oriented thin film. This image was taken at nearly in focus (namely, at the Gaussian focus). In this figure, dark striations oriented in the horizontal or nearly horizontal direction correspond each to a crystalline lamella. Such striations appear to be stacked each other in the shearing direction (vertical direction), i.e. the stacked-lamella-like structure is recognized very clearly. It seems that the stacked-lamella-like structure is formed densely over a rather large specimen area (region) in the specimen film. The long period is estimated from this image to be about 18 nm. It should be emphasized that there is no report which demonstrates visually the formation of stacked-lamellar structure in aromatic polyesters, except for our previous report concerning poly(ethylene 2,6-naphthalene dicarboxylate) (PEN) [16].

Fig. 2 is a set of dark-field images obtained from the same specimen region. These images were taken mainly by using a 100_α equatorial reflection: here, the subscript, α, means the α-modification of PBT. We have confirmed, by selected-area electron diffraction (SAED), that only the

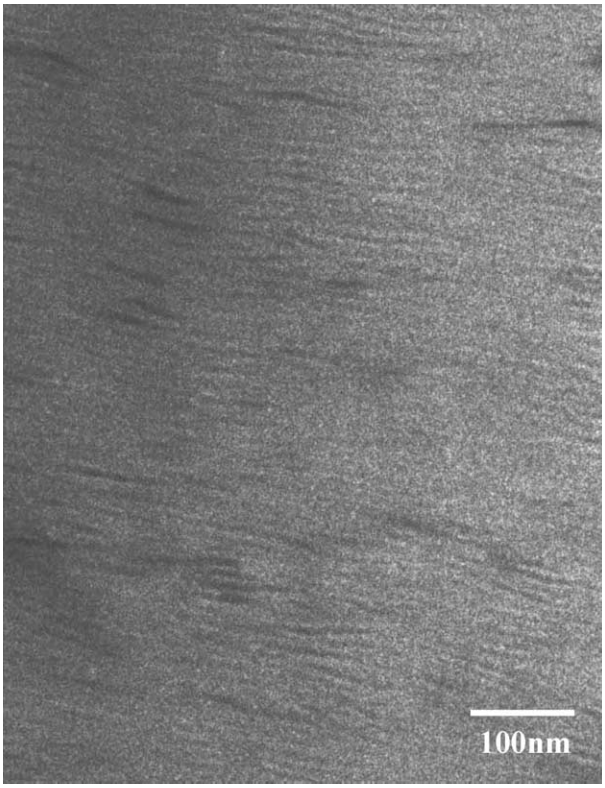

Fig. 1. Bright-field image of the uniaxially oriented thin film. The shearing direction is vertical.

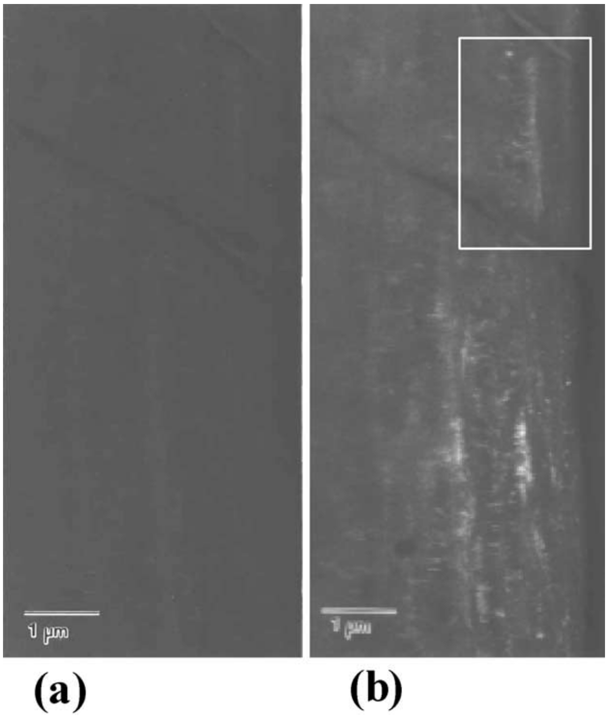

Fig. 2. Dark-field images taken from the same specimen area: (a) un-tilted and (b) tilted by 15° around the vertical axis (shearing direction). Both images were taken mainly by using a 100_α reflection. The rectangular area in (b) is enlarged into Fig. 3. The shearing direction is vertical.

crystal structure of α-modification is formed in the specimen film. Fig. 2(a) is the dark-field image taken from the untilted specimen film, and Fig. 2(b) is the one taken from the film tilted by 15° around the shearing direction (vertical direction of the figure). In Fig. 2(a), any remarkable morphology is not found. In Fig. 2(b), however, some stacked-lamellar structures over 1 μm in length along the shearing direction are recognized here and there clearly as bright entities. This change in appearance of the stacked-lamellar structures, depending on the direction of the incident electron beam to the same specimen region, suggests that all of the lamellae in one observed group as a stacked-lamellar structure have a same crystallographic orientation against the direction of incident electron beam. That is to say, each group of the stacked-lamellar structure has a preferential orientation of a specific lattice plane. The long period was measured to be about 20 nm which consists of a crystalline region about 7 nm thick and an amorphous one about 13 nm thick. Thus the long period estimated from Fig. 2(b) agrees approximately with that measured in Fig. 1.

An enlarged photograph of the rectangular area in Fig. 2(b) which was taken from the specimen tilted by 15° is shown in Fig. 3. In Fig. 3, we can clearly recognize a crystalline entity showing a well-defined stacked-lamellar structure which reminds us of the shish-kebab structure. In this figure, the average length of the lamellae was roughly estimated at 100–200 nm and the overall length of this shish-kebab-like structure is beyond 2 μm in the shearing direction. As in most of the studies on the shish-kebab structure, the backbone entity which is to correspond to a ‘shish’ is not recognized even in this figure (Fig. 3). On the basis of the following two points, however, we propose strongly that this stacked-lamellar structure is a shish-kebab structure or a part of it: (1) all of the lamellae, which are constituents of this stacked-lamellar structure, appeared together by tilting the specimen, that is, it seems that the lamellae grow epitaxially from the backbone entity with a same crystallographic orientation between the entity and the lamellae (2) in some regions, the location (namely, the height from the bottom of this figure) of a lamella growing in the right-hand direction from the backbone entity does not coincide with that of the corresponding lamella growing in the left-hand direction.

Fig. 3. Dark-field image enlarged from the rectangular portion in Fig. 2(b). The shearing direction is vertical.

In the point (1), it is essential that the backbone entity is to be coherent over a certain length. The existence of a tie-crystallite connecting adjacent crystalline lamellae, which probably corresponds to a part of a shish entity, has been demonstrated by high-resolution TEM in oriented thin films of poly(aryl-ether-ether-ketone) [19] by Kawamura et al. and of PE and poly(4-methyl-1-pentene) [20] by Tsuji et al. Particularly, in the oriented thin film of iPS, the isolated coherent region in which (110) lattice fringes running parallel to the fiber axis were observed attains to 200 nm in length, and this region corresponds to one shish entity or a part of it [21]. So we believe the existence of the backbone crystalline entity which has a coherent region with a certain length even in the uniaxially oriented thin film of PBT. Thus it is speculated that a shish-kebab structure is composed of the lamellae which have a same crystallographic orientation over a certain large length, although the shish entity seems to be too thin to directly observe.

4. Conclusion

We prepared uniaxially oriented thin films of PBT by applying shear strain to the melt and studied their resulting morphology by TEM. In each film, stacked-lamellar structures were undoubtedly recognized. Consequently, we could show visually that the stacked-lamellar structure is formed in aromatic polyesters. This stacked-lamellar structure is to correspond to a shish-kebab structure or a part of it. In addition, we successfully demonstrated that in a shish-kebab structure all or almost all kebabs (namely, lamellae) have a same crystallographic orientation. The detailed results and discussion will be reported in the near future [18].

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific

Research (C) (2), No. 14550847 (and partly, No.16550174), from Japan society for the promotion of science (JSPS), to which M.T. and Y.K. wish to express their gratitude.

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