PII: S0032-3861(97)10249-X

Polymer Vol. 39 No. 21, pp. 5273–5275, 1998
0032-3861/98/$ – see front matter

High-resolution TEM of the melt-crystallized modification of syndiotactic polystyrene

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(Received 1 September 1997; revised 16 October 1997; accepted 22 October 1997)

The melt-crystallized orthorhombic modification of syndiotactic polystyrene (s-PS) was investigated by transmission electron microscopy. Single crystals of the β' modification were prepared from a thin film by melt crystallization at 240°C. Their high-resolution images viewed along the molecular stem axis were successfully obtained, from which images the lateral arrangement of the individual molecular stems in the modification can be read out. The ''faulted'' structure defined in our previous papers seems to hold a majority in the β' modification, to make a different ''ordered'' structure. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: syndiotactic polystyrene; high-resolution TEM; image processing)

Introduction

The complexity of the polymorphic behavior of syndiotactic polystyrene (s-PS) has been reported previously[1–4]. In addition to four main crystalline forms which are named α, β, γ and δ, each of the α and β forms has two modifications (α', α'', β' and β'')[1,2]. These modifications were discussed in terms of ''disordered'' and ''ordered''. In the case of the β form which is characterized by the planar zigzag conformation of molecular stems and by the orthorhombic unit cell with $a = 2.87$ nm, $b = 0.88$ nm and c (chain axis) $= 0.51$ nm[2,5,6], the β' and the β'' modifications were attributed to the ''disordered'' and the ''ordered'' ones, respectively[1,2]. (Our assignment of the *a*- and *b*-axes in this report is different from that by other researchers, in order to follow our previous works[6–9].) In this case, the word ''ordered'' denotes the low frequency of occurrence of the stacking faults[2,5,6]. The energy calculation at the equilibrium state for these two modifications indicated that the β'' modification is more stable than the other[6,10]. However, the β' to β'' transformation does not occur even if the sample of the β' modification is annealed up to the melting region; nevertheless the sample shows a double-peak melting endotherm in the DSC trace, which is due to the recrystallization phenomenon below the melting point[1,2]. The growth itself of the β' modification is incompatible with the expectation that the polymeric crystal will grow in a more stable form with few faults as the supercooling becomes smaller and smaller. For example, in Refs 1 and 2, the β' sample was prepared from the melt by cooling at a comparatively slow cooling rate, and the growth of the β'' modification has not been reported in such a process. We need, thus, more information to answer the following question: What is the driving force in the growth of the β' modification?

In our previous work[9], we evidenced the temperature dependence of relative interfacial energy between the regular and the faulted structures, which predicts different symmetries of the resulting crystal structures at below and above a certain ''critical temperature'': the crystal grown above the critical temperature, which should be attributed to the β' modification, is expected to have another symmetry different from that reported for the β form. We reexamined, therefore, the crystal structure of the β' modification by transmission electron microscopy (TEM). As a preliminary result, the high-resolution (HREM) image of the melt-crystallized β' modification of s-PS is presented here.

Experimental

The s-PS sample (Mw $= 1.6 \times 10^5$) was kindly supplied by Idemitsu Petrochemical Co., Ltd., and was used without further purification. Single crystals of the β' modification were grown isothermally from a thin film by melt crystallization at 240°C, which film had been made by casting an s-PS solution in cyclohexanone onto the surface of water. The crystal platelets were reinforced with vapor-deposited carbon and transferred onto a microgrid for TEM. A detailed description of the sample preparation will be reported elsewhere[11]. HREM images were taken with a cryogenic transmission electron microscope (JEOL JEM-4000SFX) operated at 400 kV with a built-in minimum dose system (MDS) at a direct magnification of 1×10^5. In this case, the specimen mounted on a microgrid was cooled down to the liquid helium temperature (4.2 K) to suppress radiation damage. The electron dose on the specimen for taking one micrograph was set at 7×10^3 electrons nm^{-2} for Mitsubishi MEM films, which were developed for 10 min in the full-strength Mitsubishi GEKKOL developer.

The HREM images thus obtained were processed with a computer for identification of the domains in which certain lattice fringes appear. For this purpose, one of the HREM images was enlarged by printing off onto photographic paper and then the photograph magnified totally up to $\times 10^6$ was scanned with an image scanner (SHARP JX-330M) at a resolution of 120 pixels inch^{-1} (0.21 nm pixel^{-1}). The digitized image data were transferred into a personal computer and a square region of 768 × 768 pixels clipped from the data was processed with a Fourier-filtering

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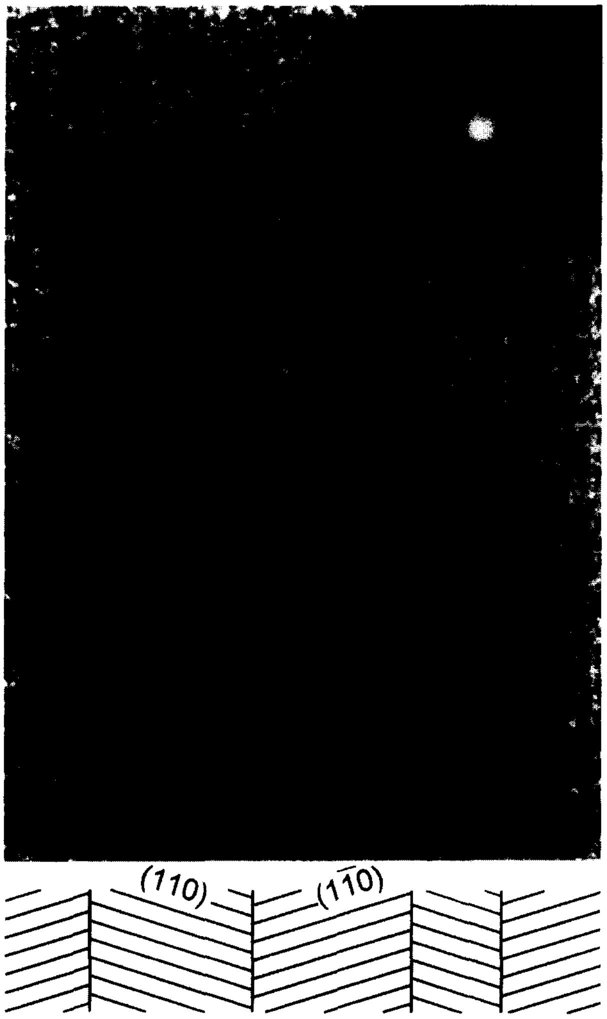

Figure 1 Example of the HREM images of the s-PS single crystal grown isothermally from the melt. The inset is the optical diffractogram of the original negative. The schematic drawing at the bottom of the figure shows the domain structure which was determined from *Figure 2*. In each domain partitioned with vertical lines, stronger fringes between (110) and ($\bar{1}10$) ones are indicated

technique available in a commercial software package (Synoptics Semper6 for Windows). Two different images were created from one original square image: 110 and $\bar{1}\bar{1}0$ reflections were selected for one processed image, and $\bar{1}10$ and $1\bar{1}0$ reflections were selected for the other (for both cases, the origin, 000, was not included in processing). Each resulting image was further processed by calculating the "local standard deviation" of 5 × 5 pixels surrounding and including every given pixel, which is a kind of smooth-edge detector and returns a larger value leading to an increase in brightness over a certain domain with inherent lattice fringes. The Fourier-filtering is likely to incorporate artifacts (artificial lattice fringes) in the processed image. Such artifacts are expected to have lower contrast, namely smaller variation in brightness, than inherent lattice fringes, and therefore "the standard deviation" around the artifact will be smaller than that in the regions with inherent fringes. By the latter image processing, only the regions with inherent lattice fringes, namely strong fringes recorded in a high contrast, ought to be detected.

Results and discussions

Figure 1 shows a typical example of the HREM images, taken at 4.2 K, of a single crystal of s-PS in the β' modification. The inset is the optical diffractogram of the original negative. The streaked feature in the diffractogram shows that the information concerning the arrangement of molecular stems was sufficiently recorded in this HREM image. In *Figure 1*, each dark dot seems to correspond to the projected molecular stem viewed along its axis. The arrangement of dark dots in the HREM image seems to be slightly different from the one expected from the model structure of the β' modification proposed by De Rosa *et al.*[2]. In most of the figure, the arrangement of the dots may correspond to the "faulted" structure which was defined in our previous reports[6–9]. It seems that "faulted" structures are in the majority, as if the crystal has a different "ordered" structure. We can recognize some domains (or layers) which are elongated along the b-axis direction and show either strong (110) or ($\bar{1}10$) lattice fringes in a large area of the original HREM image which includes the area in *Figure 1*. In such a large area, a domain with strong ($\bar{1}\bar{1}0$)

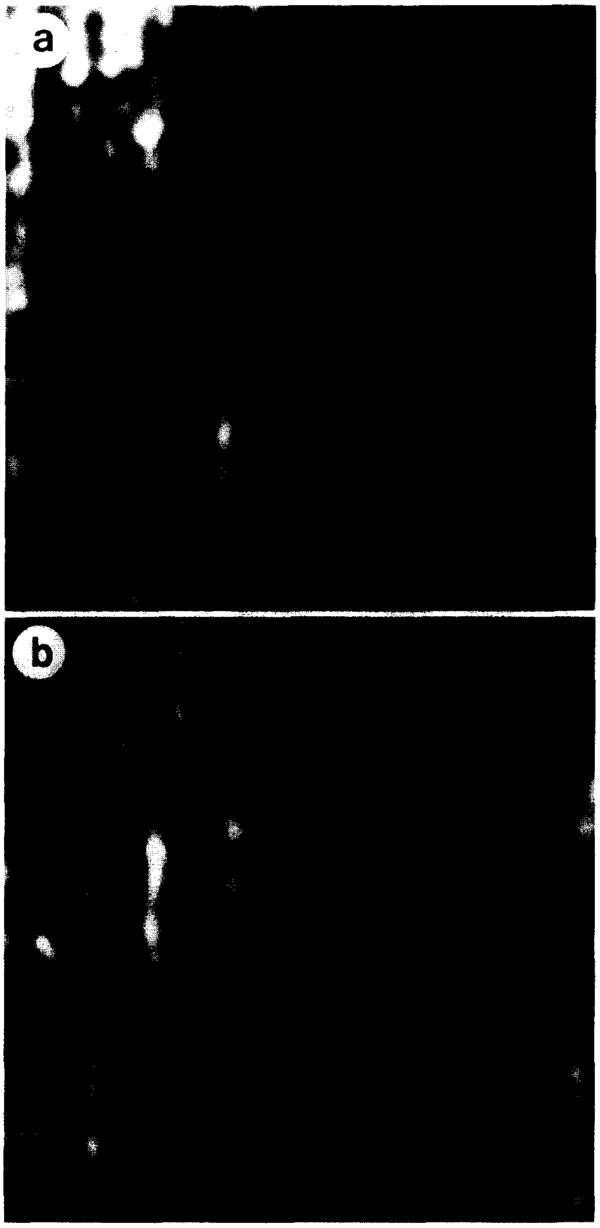

Figure 2 Processed images from the HREM image including the area shown in *Figure 1*. The degree of brightness of the domains elongated in the vertical direction represents the strength of lattice fringes in the original image: (110) fringes in (a) and ($\bar{1}10$) ones in (b). The rectangle in each figure indicates the position and size of the area shown in *Figure 1*.

fringes and one with $(\bar{1}10)$ fringes seems to be stacking alternately in the a-axis direction, as illustrated at the bottom of *Figure 1*. By processing the HREM image with a computer, we can visualize the arrangement of individual elongated domains more clearly.

Figure 2 shows a pair of processed images from a much larger area including the area shown in *Figure 1*. In *Figure 2(a)*, the elongated domains with strong (110) lattice fringes are indicated in a bright contrast, and those with $(\bar{1}10)$ fringes are indicated in this way in *Figure 2(b)*. It is well evidenced that both kinds of domains are elongated along the b-axis direction and are also stacking alternately. Elongated domains attributed to each type of fringes are almost separately visualized in this figure. The lateral width of the bright domains in *Figure 2* has a distribution from 3 to 7 nm, approximately. Of course, the width corresponds to the dimension of the domains in the a-axis direction. This dimension is $1\sim2.5$ times the unit cell parameter along the a-axis direction ($a = 2.87$ nm).

The HREM image presented here, which demonstrates well the succession of the "faulted" structures, strongly supports our theory which predicts that the "faulted" structure is preferable to the "regular" one in the β' modification[9]. Additional experiments for the crystals grown at different crystallization temperatures are in progress. The results obtained so far indicate essentially similar domain structures to that in this report. A more detailed study on the crystal structure of the β' modification, which is related to the nature of the stacking fault identified in the solution-grown single crystals of s-PS, is now in progress[11].

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