Perfectly Alternating Ethylene−Carbon Monoxide Copolymer Crystallized Epitaxially on Alkali Halides. 3. Lamellar and Crystalline Core Thicknesses

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Received April 2, 2001; Revised Manuscript Received July 27, 2001

ABSTRACT: Edge-on lamellar crystals of perfectly alternating ethylene−carbon monoxide copolymer (poly(3-oxotrimethylene); POK) were isothermally grown from a dilute solution in nitrobenzene epitaxially on the (001) surface of KI at various crystallization temperatures (T_c = 150−190 °C). The resulting crystals were observed by transmission electron microscopy (TEM) in bright- and dark-field imaging modes and also by high-resolution TEM (HRTEM), to measure the lamellar and the crystalline core thicknesses of the POK edge-on lamellae. The dark-field images obtained by conventional TEM and the (110) lattice images obtained by HRTEM showed that the crystalline core thickness of each lamella is inevitably smaller than the corresponding lamellar thickness. For the crystals grown at any T_c, the crystalline core thickness is, roughly speaking, 50−60% of the corresponding lamellar thickness. The crystalline core thickness increases with increasing T_c and, of course, with increasing lamellar thickness. Thus, the POK lamella has a surface layer (20−25% of the lamellar thickness) containing folds on each basal side of the lamella.

Introduction

It has been found that poly(3-oxotrimethylene) (POK) can be crystallized from its nitrobenzene solution.[1] Transmission electron microscopy (TEM) revealed that the features of the resulting crystals are analogous to those reported for other flexible linear polymers:[2−4] The appearance of the crystals is characteristically platelike with well-defined lateral growth faces; that is to say, the crystals are thin and well-facetted lamellae. Taking account of the lamellar thickness and the molecular weight of POK, these POK platelike crystals grown isothermally from a dilute solution in nitrobenzene are, therefore, folded-chain single crystals.[1] Surface decoration of the POK single crystal with vapor-deposited polyethylene (PE) indicated that the structure of fold surface has some regularity in each growth sector.[1] In addition, selected-area electron diffraction (SAED) showed that these single crystals exclusively exhibit the α-form[5] (orthorhombic, *Pbnm*: a = 0.691 nm, b = 0.512 nm, c (chain axis) = 0.760 nm).[1]

On the other hand, epitaxial crystallization of the POK from its nitrobenzene solution on alkali halides has also been successfully achieved.[6] TEM revealed that the resulting rodlike crystals are edge-on lamellae in which the chain stems are set parallel to the substrate surface and perpendicularly to the long axis of rodlike crystal and that the crystal modification and orientation depend on the kinds of substrate (NaCl or KI): The orientation of the chain-stem axis (*c*-axis) of POK crystals was found in the ⟨110⟩ directions on NaCl and in the ⟨100⟩ ones on KI,[6] and these orientational relationships on NaCl and KI were both confirmed well by calculations of interfacial energy.[7] Furthermore, lattice images of the edge-on lamellae grown on KI were successfully obtained by high-resolution TEM (HRTEM), in which the lattice fringes of 0.41 nm spacing could be clearly identified.[6] (An example of such lattice images will be shown below in Figure 3 of this report.)

It is, hence, advantageous to utilize the edge-on lamellar crystal of POK in order to obtain, at molecular level resolution, the detailed information on the structures of crystalline core and of fold surface (viz., on the edge-on view structure) in the polymer single crystal, because the HRTEM images can be taken for POK, though for polyoxymethylene (POM)[8] and PE[9] structural investigation has been restricted only to morphological observations by bright- and dark-field TEM and to SAED experiments. Indeed, the HRTEM image of the isolated edge-on lamella of POK provided us with a direct view of its internal "disordered"−crystalline−"disordered" structure in the chain direction,[6] and this edge-on view structure well supports the structure model of polymer single crystal proposed in our previous papers.[8−10]

In the present work, more detailed investigation by both dark-field TEM and HRTEM of the POK edge-on lamellae are undertaken to study the variation of the lamellar structure, especially of its crystalline core thickness, with the crystallization conditions, as was carried out before for POM.[8] For this purpose, the edge-on lamellar crystals of POK are isothermally grown from solution epitaxially on the freshly cleaved (001) surface of KI at various crystallization temperatures (T_c = 150−190 °C). The resulting crystals are observed by conventional TEM in bright- and dark-field imaging modes and also by HRTEM to measure the lamellar thickness and the crystalline core thickness of POK edge-on lamellae.

Experimental Section

Sample Preparation. The POK sample used in this study is the same as the one studied by Grayer et al.;[11] its limiting viscosity number is 1.3 dL g^{-1} (*m*-cresol, 25 °C). The procedure

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10.1021/ma0105486 CCC: $20.00

of epitaxial crystallization of POK to prepare specimens for TEM was almost the same as that in our previous paper.[6] The substrate used here was, however, only KI, the (001) surfaces of which were freshly cleaved just before epitaxial crystallization, because the edge-on lamellae of POK are often to grow on KI in a fashion which is adequate to take the HRTEM images.[6] Solvent used here was nitrobenzene. At a desired T_c (=150−190 °C), the epitaxial crystallization was performed isothermally in a 0.01 wt % nitrobenzene solution of POK under a nitrogen atmosphere for up to 5 min. (The crystallization time at each T_c was designated so as not to cause the resulting crystals to lean or to collapse.) The precision of temperature regulation was within ±1 deg for a given T_c.

The specimen on KI was shadowed under vacuum with Pt−Pd for morphological observation and thereafter coated with vapor-deposited carbon (C) under vacuum. The shadowing angle was $\tan^{-1}(1/4)$, and the shadowing direction was parallel to the [100] direction of the substrate (KI). For dark-field TEM and HRTEM, however, the specimen on the substrate was coated and reinforced only with vapor-deposited C. Substrates with the specimens were then floated on the water surface with the specimen side facing up, and after dissolution of the substrates the floating specimens were picked up on Cu grids for TEM or on microgrids for HRTEM.

Transmission Electron Microscopy. The TEM observations were performed at room temperature with a JEOL JEM-200CS for morphological and SAED investigation or with a JEM-2010 (spherical aberration coefficient = 0.5 mm) for HRTEM, both of which were operated at 200 kV. For SAED and dark-field imaging, a specimen-rotating/tilting holder (JEOL EM-SRH10) was utilized. Bright-field images were recorded on Fuji FG films to obtain higher contrast. SAED patterns, HRTEM images, and dark-field images were recorded on Mitsubishi MEM films which are more sensitive than FG ones.[12] All the exposed films were developed with Mitsubishi Gekkol (full strength) at 20 °C for 5 min (SAED and morphological observations) or for 10 min (HRTEM).

Results and Discussion

As reported in our previous paper,[6] the rodlike crystals (namely, the edge-on lamellar crystals) of POK orient on the (001) surface of KI with their long axis being in the ⟨100⟩ directions of the substrate: That is to say, the chain stems of POK on KI orient in the ⟨100⟩ directions of the substrate, and this orientation was confirmed by energy calculation.[7]

Dark-Field Imaging. The procedure of the dark-field TEM observation was, in detail, already described in the previous papers for POM.[8,13] It has been found that the POK edge-on lamellae of two types can be grown epitaxially on the (001) surface of KI, as shown in Figures 4 (type I) and 6 (type II) of ref 6, but the chain-stem axis (*c*-axis) in both types is parallel to the ⟨100⟩ directions of KI (by SAED, type I was identified as the α-form, but unfortunately at the present stage it is unknown whether type II is the α-form or not although type II is assumed to be the α-form in this study).[6,10] There is difference only in the appearance and contact plane between both types.[6,10] Hence, the dark-field TEM observations were carried out for both types. By using the 110 reflection of POK, attempts were made to take the dark-field images because the 110 reflection is strong enough to yield easily the dark-field images. As for the type I, when the specimen is tilted by 17° or 37° around a meridian (viz. around the chain axis), the 110 reflection appears on the corresponding equator (see Figure 5 of ref 6). In this work, the 110 dark-field images of type I were taken from the specimen tilted by 37°. On the other hand, as for the type II, its 110 dark-field images were obtained from the untilted specimen in this work, because the 110 reflection can be recognized without specimen tilting (see Figure 6 of ref 6).

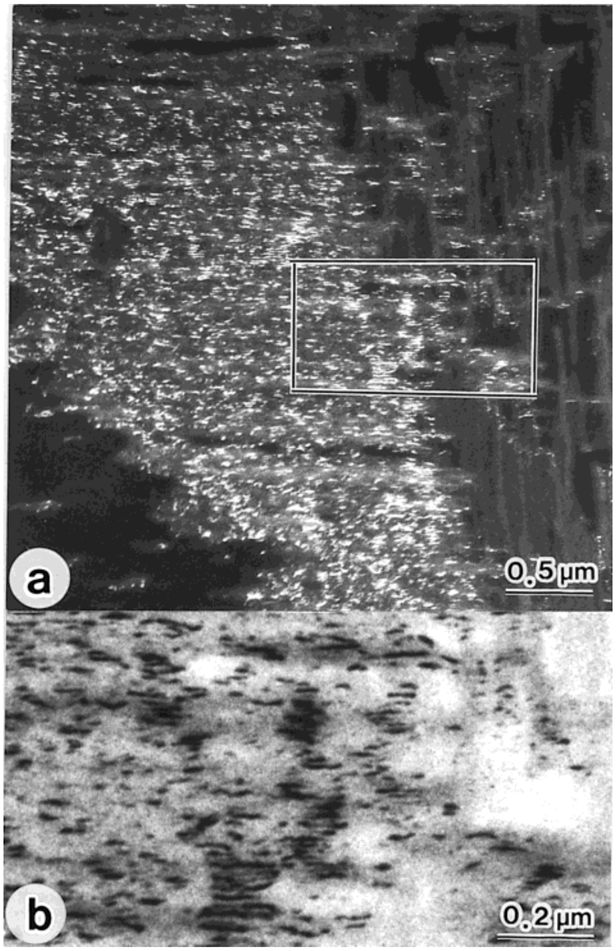

Figure 1. (a) Dark-field image of POK edge-on lamellar crystals (type I) grown epitaxially on the (001) surface of KI at 170 °C in a 0.01 wt % nitrobenzene solution. This image was taken by using the 110 reflection from the specimen tilted by 37° around the vertical axis. (b) Highly enlarged photograph from the rectangular area in (a), but with reversed contrast.

Figure 1a shows an example of the 110 dark-field images of POK edge-on lamellae grown epitaxially on the (001) surface of KI at T_c = 170 °C in a 0.01 wt % nitrobenzene solution, which images were taken from type I, according to the above-mentioned procedure of specimen tilting. (Figure 1b was highly enlarged from the rectangular area in Figure 1a, but the contrast in Figure 1b was reversed.) In Figure 1a, bright striations oriented in the horizontal direction can be clearly recognized. Each bright striation in this dark-field image (of course, each “dark” one in Figure 1b) corresponds to the crystalline core of an edge-on lamella, which contributes to the 110 reflection in the SAED pattern. From the dark-field images, we can directly estimate the crystalline core thickness, viz., the stem length in an edge-on lamella, by measuring the width of the bright striations in Figure 1a (or that of the dark ones in Figure 1b). It was confirmed that there is no difference, within experimental error, between the crystalline core thickness of type I and that of type II. For the specimens prepared under this crystallization condition, the average crystalline core thickness was estimated at 7.3 nm.

In contrast to the case of POM,[8] the 00*l* reflections of POK can be definitely observed in the SAED patterns

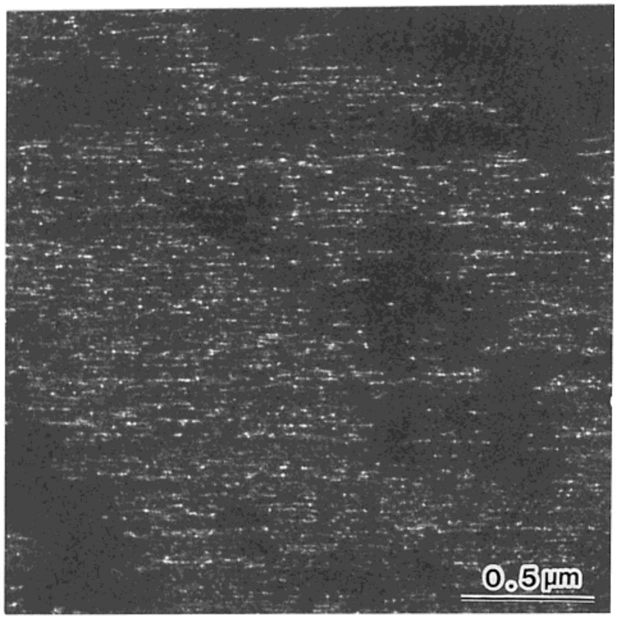

Figure 2. Dark-field image (untilted) of POK edge-on lamellar crystals (type I) grown epitaxially on the (001) surface of KI at 170 °C in a 0.01 wt % nitrobenzene solution. This image was taken by using the 006 reflection.

for both type I and type II.[6] It was found that the 006 dark-field images with sufficient contrast can be obtained without specimen tilting, although the intensity of the 006 reflection is smaller than that of the 110 reflection. Figure 2 shows one of the 006 dark-field images of the POK edge-on lamellae (type I) grown epitaxially on the (001) surface of KI at 170 °C in nitrobenzene. (This crystallization condition is the same as that for Figure 1.) The edge-on lamellae oriented in the horizontal direction can be clearly recognized in Figure 2. Each bright striation in this dark-field image corresponds to the crystalline core of an edge-on lamella, which contributes to the 006 reflection in the SAED pattern. The average crystalline core thickness estimated from the 006 dark-field images was 7.3 nm and is in accord with that measured from the 110 dark-field images (for example, Figure 1). This fact means that the surface layer of POK single crystal is a more or less "disordered" region which does not contribute to the 110 or 006 reflections because the corresponding lamellar thickness, which will be given below, is fairly greater than the obtained crystalline core thickness (7.3 nm).

For POK edge-on lamellae of type II, the lattice images consisting of the fringes of 0.41 nm spacing can be taken, as presented in our previous paper.[6] The crystalline core thickness or the stem length in the lamella can be estimated from the length of lattice fringes more precisely and reliably than that obtained by dark-field TEM, because 0.41 nm lattice fringes are used as an internal standard for magnification calibration. Though, as mentioned above, type II is assumed to be the α-form in the present study, this spacing, 0.41 nm, can be assigned to the lattice spacing of the (110) plane of α-form or to that of the (110) one of β-form[14] (orthorhombic, *Pnam*: $a = 0.797$ nm, $b = 0.476$ nm, c (chain axis) $= 0.757$ nm) because these two spacings for both forms are almost identical with each other. The 0.41 nm fringes are, therefore, termed simply the (110) lattice fringes, as in ref 6. In this study, thus, HRTEM observations of the edge-on lamellae (type II) prepared under the same condition as those for the dark-field TEM observations were also carried out, and the crystalline core thickness was estimated from the length of (110) lattice fringes. Figure 3 is one of the examples of (110) lattice images of type II lamellae, which were epitaxially grown at 180 °C on the (001) surface of KI in a 0.01 wt % nitrobenzene solution. The length of the lattice fringes is not constant within the lamella; i.e., there exists a distribution of the length, as recognized also in Figure 7 of ref 6. In Figure 3, the length of the lattice fringes is measured to be 5−7 nm. It is noted that, so long as the identical diffracted wave (the 110 diffracted wave) is utilized in both image formations of dark-field TEM and HRTEM, information on crystallite size (in this case, crystalline core thickness) should be in principle consistent with each other, as illustrated in Figure 4. Indeed, the crystalline core thickness estimated from the (110) lattice images has agreed very closely with that obtained by 110 dark-field imaging within the experimental error (see Figure 6).

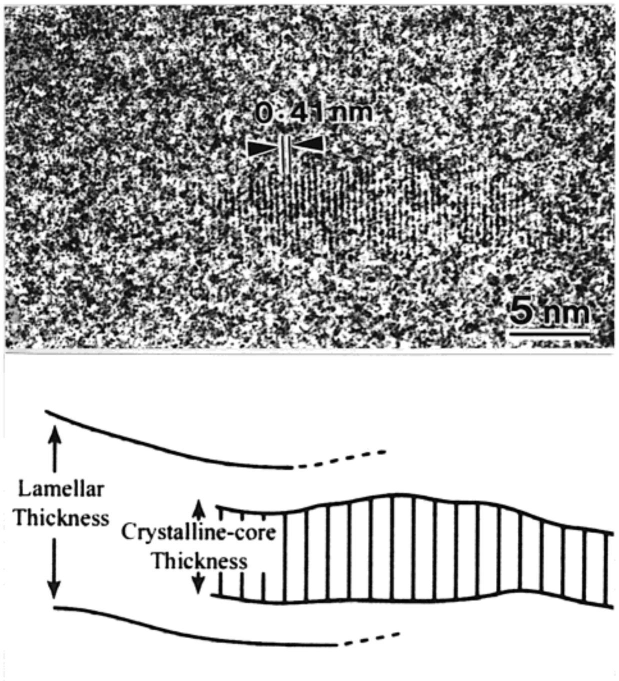

Figure 3. HRTEM image of a POK edge-on lamellar crystal (type II) grown epitaxially on the (001) surface of KI at 180 °C in a 0.01 wt % nitrobenzene solution. This image shows the (110) lattice fringes of 0.41 nm spacing within an edge-on lamella of POK. At the bottom of the figure, the edge-on lamella is schematically illustrated in order to indicate the relationship between the crystalline core defined by the fringes and the outline (or external width) of the lamella: the outline was certainly observed in the original negative of this HRTEM image.

Internal Structure of Solution-Grown POK Lamellae and Its Dependence on Crystallization Temperature (T_c). As presented in our previous paper for POM,[8] the lamellar thickness must be known in order to discuss the internal structure of POK single crystal. In ref 8, instead of the width of the POM edge-on lamellae, data of the long period measured by small-angle X-ray scattering (SAXS) of the POM single crystal mats were cited from the literature as lamellar thickness. In the present study, however, the average values of the width of the POK edge-on lamellae directly measured from the bright-field TEM images were mainly utilized, in addition to the SAXS data (namely,

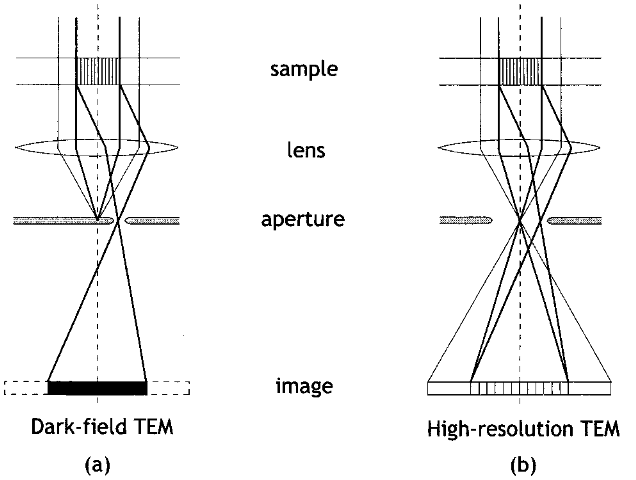

Figure 4. Schematic representations of dark-field imaging with diffraction contrast (a) and of lattice imaging due to interference between two beams (b) in TEM. The scattering angle of the diffracted electron beam is the same for both (a) and (b). In this figure, "sample" = specimen in the object plane, "lens" = objective lens, "aperture" = objective lens aperture, and "image" = image made by the objective lens in its image plane.

the long period)[1] obtained from the sedimented mats of lamellae which were grown sporadically from a 0.1 wt % solution in nitrobenzene isothermally at T_c = 139−150 °C. According to ref 9, one rodlike crystal of PE grown epitaxially on NaCl consisted of one or more lamellae (stacked-lamellar structure), and accordingly, the width of seemingly one rodlike crystal was an integral multiple of the true lamellar thickness of crystals grown from solution at the same T_c. (In this connection, it should be mentioned that the true lamellar thickness of PE grown on NaCl was the same as that of lamellar single crystals grown sporadically from solution at a given T_c.[9]) For POK, however, such rodlike crystals consisting of stacked lamellae, namely of lamellae in close contact with each other, have never been recognized so far.

Figure 5a shows an example of the bright-field TEM images of the POK edge-on lamellae grown epitaxially on the (001) surface of KI at 170 °C in a 0.01 wt % nitrobenzene solution, and Figure 5b is highly enlarged from Figure 5a. The arrow in each figure indicates the shadowing direction of Pt−Pd, viz., the [100] direction of the substrate. Figure 5, therefore, indicates clearly that the rodlike crystals (namely, the edge-on lamellar crystals) of POK are oriented on KI in the ⟨100⟩ directions of the substrate, as reported before.[6,10] Due to the Pt−Pd shadowing, each isolated edge-on lamella can be clearly recognized with sufficient contrast to measure the lamellar thickness. In this case, the average lamellar thickness was estimated at 10.6 nm. For the POK lamellar crystals grown at 170 °C, thus, the crystalline core thickness (7.3 nm obtained by dark-field TEM) is undoubtedly smaller than the corresponding lamellar thickness (10.6 nm), and consequently, the surface-layer thickness on each basal side of the lamellar crystal could be estimated at about 2 nm.

Similarly, the crystalline core thickness and the corresponding lamellar thickness of POK crystals grown at various T_c's were measured. Figure 6 shows the T_c dependence of the crystalline core thickness, which was obtained by dark-field TEM and HRTEM, and also that of the lamellar thickness, which was obtained by the bright-field TEM observation of the edge-on lamellae and by SAXS of the sedimented mats. As is apparent, inevitably the crystalline core thickness is smaller than the corresponding lamellar thickness at any T_c. That is to say, the crystalline core thickness is, roughly speaking, 50−60% of the lamellar thickness at any T_c. Furthermore, the crystalline core thickness increases with increasing lamellar thickness and with increasing T_c. As in the case of POM,[8] Figure 6 demonstrates that the surface-layer thickness has no tendency to decrease at higher T_c. The surface layer thickness appears to be

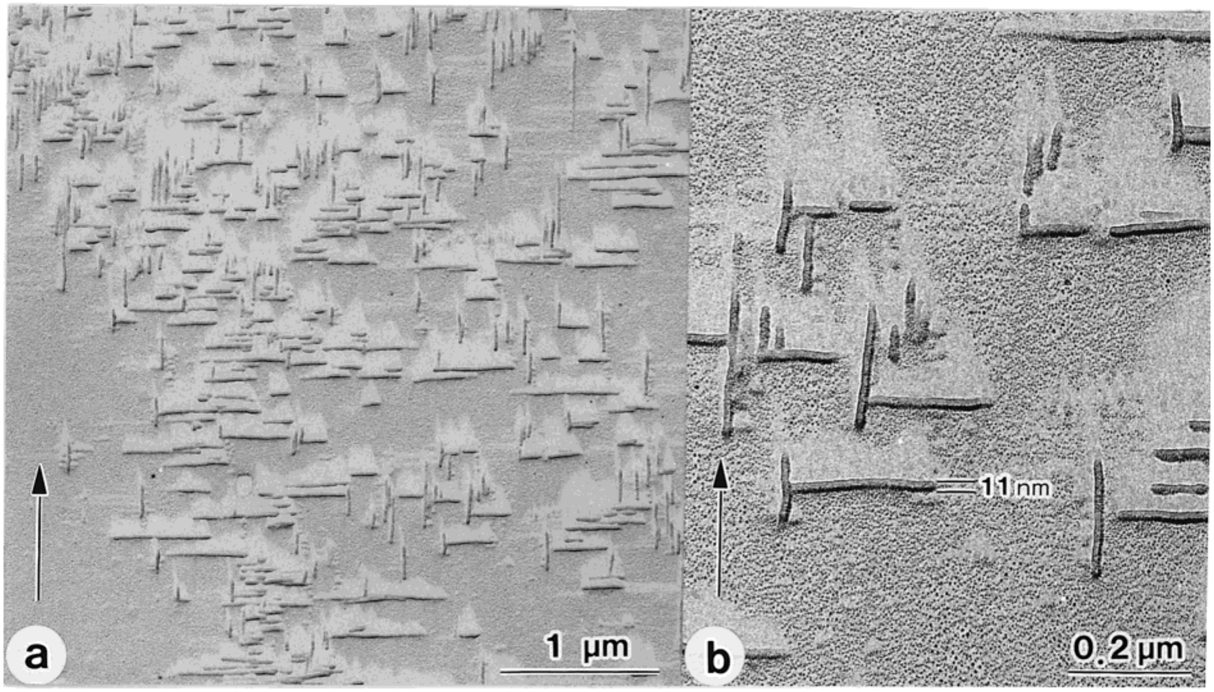

Figure 5. (a) Bright-field image (untilted) of POK edge-on lamellar crystals grown epitaxially on the (001) surface of KI at 170 °C in a 0.01 wt % nitrobenzene solution: (b) Highly enlarged from (a). The arrow in each figure indicates the [100] direction of the substrate, and the specimen was shadowed with Pt−Pd in this direction at a shadowing angle of $\tan^{-1}(1/4)$.

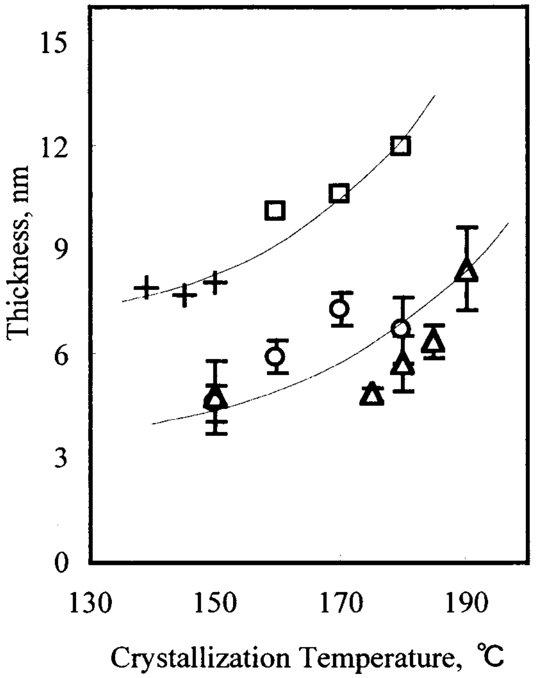

Figure 6. Crystalline core thickness (○, Δ) and lamellar thickness (+, □) plotted against the crystallization temperature (T_c): ○, measured by dark-field TEM; Δ, by HRTEM; +, by SAXS;[1] □, by bright-field TEM. The vertical bars represent standard deviations. Each curve indicates a rising tendency in lamellar thickness or in crystalline core thickness with increasing T_c.

constant independently of T_c in the present temperature range, although it is difficult to determine whether the surface-layer thickness is really constant or increases/decreases with T_c. The constant thickness of surface layer leads to an interpretation that the folding manner of polymer chains during crystallization (or the resulting chain-folded structure) might be nearly identical, independent of T_c. That is to say, it is postulated that the regularity of fold structure in the single crystals grown even at higher T_c does not improve.

Concluding Remarks

In this paper, the edge-on lamellae of POK were isothermally grown from a dilute solution in nitrobenzene epitaxially on the (001) face of KI at various T_c's. The dark-field images (by TEM) and the (110) lattice images (by HRTEM) of the resulting edge-on lamellae showed that inevitably the crystalline core thickness of a lamella is smaller than the corresponding lamellar thickness that was measured by bright-field TEM of the edge-on lamellae and/or by SAXS[1] of the single-crystal mats. This fact is similar to the cases of PE[9] and POM.[8] For the crystals grown at any T_c, the crystalline core thickness is, roughly speaking, 50−60% of the corresponding lamellar thickness. As schematically illustrated at the bottom of Figure 3, the outline (or external width) of the lamella was sometimes recognized together with the lattice fringes in the original negative. Figure 3, therefore, demonstrates directly that in an edge-on lamella of POK the crystalline core is sandwiched by surface layers. In this figure, which is one of the examples of HRTEM images taken from type II edge-on lamellae of POK, the length of the lattice fringes is much smaller than the external width of the lamella and is only about 50% of the corresponding lamellar thickness.

The crystalline core thickness increases with increasing T_c, and, of course, with an increase in lamellar thickness. Thus, the edge-on lamella of POK has a surface layer (20−25% of the lamellar thickness) containing folds on each basal side of the lamella. The crystalline core gives the 110 reflection and/or the 006 one in the SAED pattern, but the surface layer containing folds makes a small or no contribution to both of these reflections due to, possibly, its "disorder". The HRTEM images such as Figure 3 in this report and Figure 7 in ref 6 give a direct view of an isolated folded-chain edge-on lamella and of its internal "disordered"−crystalline−"disordered" structure in the chain direction, which structure has been proposed in our previous reports on the basis of dark-field TEM observations of edge-on lamellae of PE[9] and POM.[8] The surface layer in question is, of course, not supposed to be fully disordered as that of the switchboard model,[15] by taking into account the results of surface decoration to the POK single crystals.[1] It is, accordingly, considered that the layer is composed, basically, of adjacent-reentrant folds, which have some fluctuation in contour length and resultant fluctuation in conformation, as in the case of PE single crystal.[9] Such fluctuation might come from the fluctuation of the fold period during crystallization.[10,16,17] As mentioned above for Figure 3, the length of the (110) lattice fringes in Figure 3 of this report (and also in Figure 7 of ref 6) is not constant within the edge-on lamella under consideration. This result might be a direct evidence of some fluctuation of the stem length due to the fluctuation of the fold period within the resulting lamellar crystal of POK. For example, recent Monte Carlo simulations of crystallization in dilute solution for a model polymer of monodisperse flexible long chains were reported to reveal, under certain simulation conditions, that the basal crystal surfaces are rough and there are many loops on the surfaces but that occasionally very short stems became incorporated into a crystal though large loops almost never occurred.[18] These simulations, therefore, seem to indicate that, to say the least, there exist, for instance, shorter chain stems, namely stems with shorter fold length, than their surrounding ones in a folded-chain polymer crystal grown from solution, though the authors of ref 18 would expect some degree of chain sliding and evening out of monomers between adjacent stems in a real crystal.

Acknowledgment. The authors express their deep gratitude to Dr. Jean Claude Wittmann, Institut Charles Sadron, CNRS, Strasbourg, France, for offering the samples of poly(3-oxotrimethylene) and for his useful comments. M. Fujita expresses his thanks to the Research Fellowships of the Japan Society for the Promotion of Science (JSPS). This work was supported partly by a Grant-in-Aid for JSPS Fellows (No. 9796; to M. Fujita) and also partly by a Grant-in-Aid for Scientific Research on Priority Areas, "Mechanism of Polymer Crystallization" (No. 12127207; to M. Tsuji), both of which were from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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MA0105486