*Macromolecules* **1999,** *32,* 4383−4389

# Perfectly Alternating Ethylene−Carbon Monoxide Copolymer Crystallized Epitaxially on Alkali Halides. 1. Morphological Observation by TEM

**Masahiro Fujita,[†,§] Masaki Tsuji,[*,†] Shinzo Kohjiya,[†] and Jean Claude Wittmann[‡]**

*Laboratory of Polymer Condensed States, Division of States and Structures III, Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611-0011, Japan, and Institut Charles Sadron, CNRS, 6 rue Boussingault, 67083 Strasbourg, France*

*Received March 2, 1999; Revised Manuscript Received April 22, 1999*

ABSTRACT: Epitaxial crystallization on the (001) substrate face of NaCl and KI of a perfectly alternating ethylene−carbon monoxide copolymer (poly(3-oxotrimethylene); POK) from its nitrobenzene solution has been successfully achieved. Transmission electron microscopy observations reveal that (a) the resulting crystal modification and orientation depend on the substrate and (b) POK chain stems in the rodlike crystals are parallel to the substrate surface and perpendicular to the long axis of the rod (namely, the edge-on folded-chain lamella). For the edge-on lamellae grown on KI, lattice images were successfully obtained in which (110) lattice fringes could be clearly identified. The length of the lattice fringes, viz., the stem length or crystalline core thickness, is estimated at about 60% of the total thickness of one epitaxially grown POK lamella.

## Introduction

The polymerization method developed by Drent and co-workers.[1,2] allows for the synthesis of perfectly alternating ethylene−carbon monoxide copolymers (poly(3-oxotrimethylene), abbreviated as POK). Compared with less perfect copolymers, a perfectly alternating one exhibits a higher melting temperature and a higher degree of crystallinity[2,3] and is more stable to UV light.[3]

Lommerts et al.[3] reported that such a strictly alternating polymer exhibits two polymorphic forms: the $\alpha$-form (orthorhombic, *Pbnm*: $a = 0.691$ nm, $b = 0.512$ nm, $c$ (chain axis) $= 0.760$ nm) and the $\beta$-form (orthorhombic, *Pnam*: $a = 0.797$ nm, $b = 0.476$ nm, $c$ (chain axis) $= 0.757$ nm),[4] the latter corresponding to the structure reported by Chatani et al.,[4] for a radiation-polymerized, viz., a less perfect, polymer. The chain conformation is planar-zigzag for both crystalline forms, in which they thus have nearly the same $c$-axis. In contrast, the chain packing is quite different. Extensive studies on POK including the above-mentioned work by Lommerts et al. revealed that the occurrence of the $\alpha$- and/or $\beta$-form depends, along with the regularity of chemical structure of the polymer chain, on the crystallization temperature ($T_c$), applied stress, etc.[5]

In addition, Grayer et al.[6] reported recently that epitaxial growth of this polymer can successfully be achieved on the hydroquinone crystalline substrate by using the hypoeutectic growth procedure.[7−9] Transmission electron microscopy (TEM) revealed that the epitaxially grown POK crystals are “edge-on” lamellae of the $\alpha$-form, oriented in a single direction. The polymer chain axis lies parallel to the surface of the hydroquinone substrate, and the contact plane with the substrate is the $(100)_\alpha$ plane of POK.

In the present work it is shown that POK crystals can be grown epitaxially on alkali halide substrates from solution. The resulting morphologies of the POK crystals are investigated by TEM, and the orientation and crystal form of the POK crystals grown on the alkali halides are discussed. Since Grayer et al.[6] reported that this polymer might be less sensitive to electron irradiation damage than other flexible linear polymers, high-resolution TEM (HRTEM) observations of the epitaxially grown POK lamellar crystals were also performed.

## Experimental Section

**Sample Preparation.** The POK sample used is the same as the one studied by Grayer et al.;[6] its limiting viscosity number is 1.3 dL g$^{-1}$ (*m*-cresol, 25 °C).

Epitaxial crystallization of this polymer was achieved using the methods described in previous works.[10−12] Freshly cleaved (001) faces of NaCl or KI were used as substrates. The epitaxial crystallization of a 0.01 wt % nitrobenzene solution of POK was performed isothermally at 150 °C $\leq T_c \leq$ 180 °C under a nitrogen atmosphere for up to 5 min (mostly, 180 °C for 5 min). The precision of temperature regulation was at worst within ±1 deg for a given $T_c$.

Two test tubes were prepared, one for pure solvent (nitrobenzene) and the other for a nitrobenzene solution of POK. NaCl or KI was cleaved in air and heated in the test tube containing the pure solvent thermostated at a desired $T_c$. To make a 0.01 wt % solution, POK was dissolved in nitrobenzene at its boiling point under a nitrogen atomosphere. After complete dissolution, the test tube containing the solution was transferred into the oil bath held at the $T_c$, and then immediately the preheated substrate (NaCl or KI) was immersed in the solution. After the desired crystallization time ($t_c$) had elapsed, the substrate was taken out, dipped in the pure solvent ($T_c$) to rinse it, and dried. The polymer samples deposited on the alkali halide substrates were subsequently shadowed with Pt−Pd and then coated with vapor-deposited carbon under vacuum. The shadowing angle was tan$^{-1}$(1/4), and the shadowing direction was parallel to the [100] direction of the substrate. The substrates were dissolved in water, and the polymer samples floating at the water surface were picked

---

[*] To whom correspondence should be addressed. E-mail: tsujimas@scl.kyoto-u.ac.jp.

[†] Kyoto University.

[‡] Institut Charles Sadron.

[§] Research Fellow of the Japan Society for the Promotion of Science.

10.1021/ma990321z CCC: $18.00

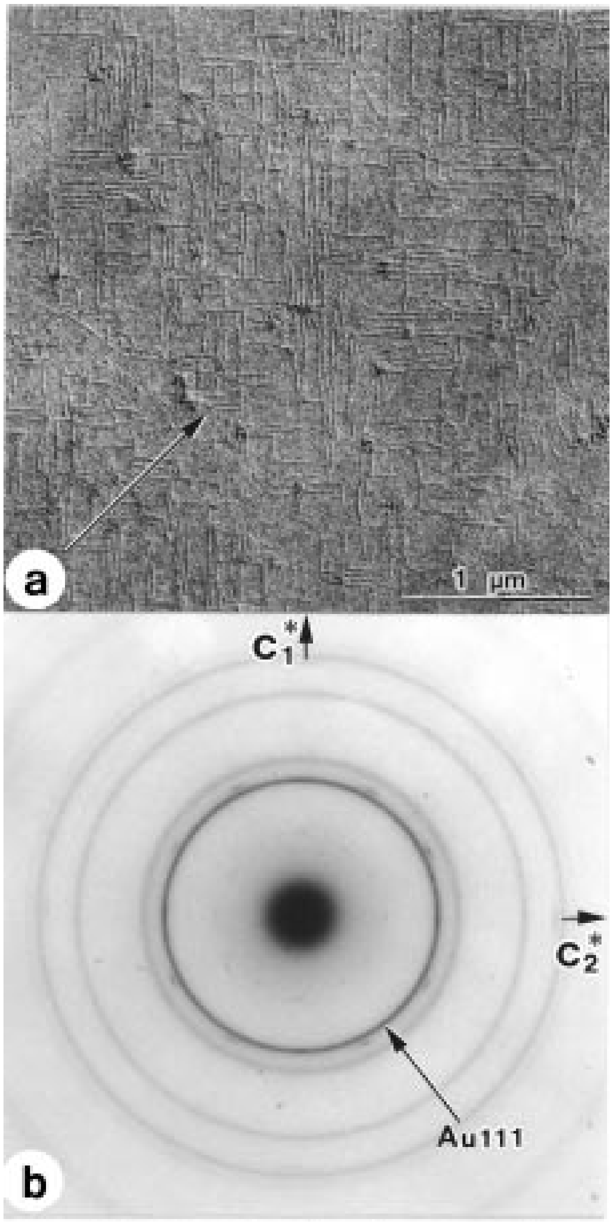

**Figure 1.** (a) Bright-field electron micrograph of POK crystals grown epitaxially on an (001) NaCl cleavage face at 180 °C from a 0.01 wt % nitrobenzene solution. The arrow indicates the Pt−Pd shadowing direction which is parallel to the [100] substrate direction. (b) Corresponding SAED pattern. The Debye−Scherrer rings arise from Au and are used for calibration of the camera length. All the reflections in the figure can be indexed with the unit cell constants of both α- and β-forms (see Figure 2). Two perpendicular directions of the $c^*$-axis with subscripts 1 and 2, corresponding to the perpendicular orientations of the epitaxial crystals, are shown.

up onto TEM copper grids. To calibrate the selected-area electron diffraction (SAED) patterns, some of the samples were shadowed with Au instead of Pt−Pd.

**Transmission Electron Microscopy.** The TEM observations were made at room temperature with a JEOL JEM-200CS microscope for morphology and SAED or a JEM-2010 for high-resolution imaging (both were operated at 200 kV). For the SAED experiments, a rotation-tilt specimen holder (JEOL EM-SRH10) for JEM-200CS was used. Bright-field images were recorded onto Fuji FG films to obtain higher contrast and SAED patterns and HRTEM images onto more sensitive films (Mitsubishi MEM).[13] The exposed films were developed with Mitsubishi Gekkol (full strength) at 20 °C for 5 min (10 min for HRTEM).

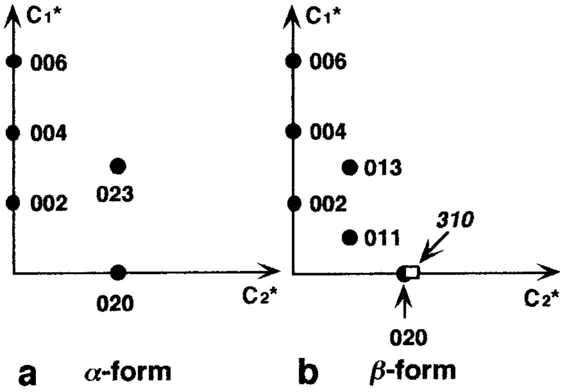

**Figure 2.** Indexing of the α- (a) and β-phase (b) reflections observed in Figure 1b. All the indexed reflections in (a) and (b) belong to a single orientation with the $c_1^*$-axis lying along the meridional direction.

**Table 1. Expected Strong Reflections on the Equator in the SAED Pattern by Specimen Tilting around the Meridian (One of the Two $c^*$-Axes) for Several Assumed Contact Planes of POK**

| assumed contact plane | tilting angle (deg) | expected reflection |
|---|---|---|
| $(100)_\alpha$ | 37 | $110_\alpha$ |
| $(110)_\alpha$ | 17 | $110_\alpha$ |
| | 37 | $200_\alpha$ |
| $(100)_\beta$ | 31 | $110_\beta$ |
| $(110)_\beta$ | 28 | $110_\beta$ |
| | 31 | $200_\beta$ |

## Results and Discussion

**Epitaxial Growth of POK Crystals on NaCl.** Figure 1a shows the typical rodlike morphology of POK crytallized epitaxially on the (001) face of NaCl from a nitrobenzene solution ($T_c = 180$ °C, $t_c = 5$ min). This morphology is closely similar to those observed for polyethylene (PE) and polyoxymethylene (POM) crystals grown on various alkali halides.[10−12,14−25] The two orthogonal sets of POK rodlike crystals are oriented at 45° to the shadowing direction (the arrow in Figure 1a), i.e., parallel to the [110] and [$\bar{1}$10] directions of the substrate. The width of the rodlike crystals grown under these conditions is 13−15 nm.

Figure 1b shows the corresponding SAED pattern. Indexing of this pattern clearly reveals that it is a composite pattern resulting from the presence of the α and β polymorphic forms of POK. It is in fact composed of two $0kl$ ($k$ = even) net patterns of the α-form superimposed on two $0kl$ ($k + l$ = even) net patterns of the β-form, together with two pairs of $310_\beta$ reflections. Single $0kl$ net patterns of both types, with almost identical $00l$ reflections ($c_\alpha = 0.760$ nm, $c_\beta = 0.757$ nm; $l$ = even), are schematically illustrated in Figure 2a,b.

From these TEM observations, it can be deduced that the rodlike crystals shown in Figure 1 represent in fact six different sets of edge-on POK lamellae: (i) two sets of α-form lamellae, oriented at right angles to each other and with their $(100)_\alpha$ crystallographic plane in contact with the (001) NaCl substrate face, (ii) two orthogonal sets of β-form edge-on lamellae with a $(100)_\beta$ contact plane, and finally (iii) two similar sets of β-form lamellae but with $(110)_\beta$ acting as contact plane.

Furthermore, for all these edge-on lamellae, the polymer chain axis is oriented in either the [$\bar{1}$10] or the [110] direction of the substrate; i.e., as usually observed for epitaxially grown polymer crystals, the chain axis lies parallel to the substrate surface.

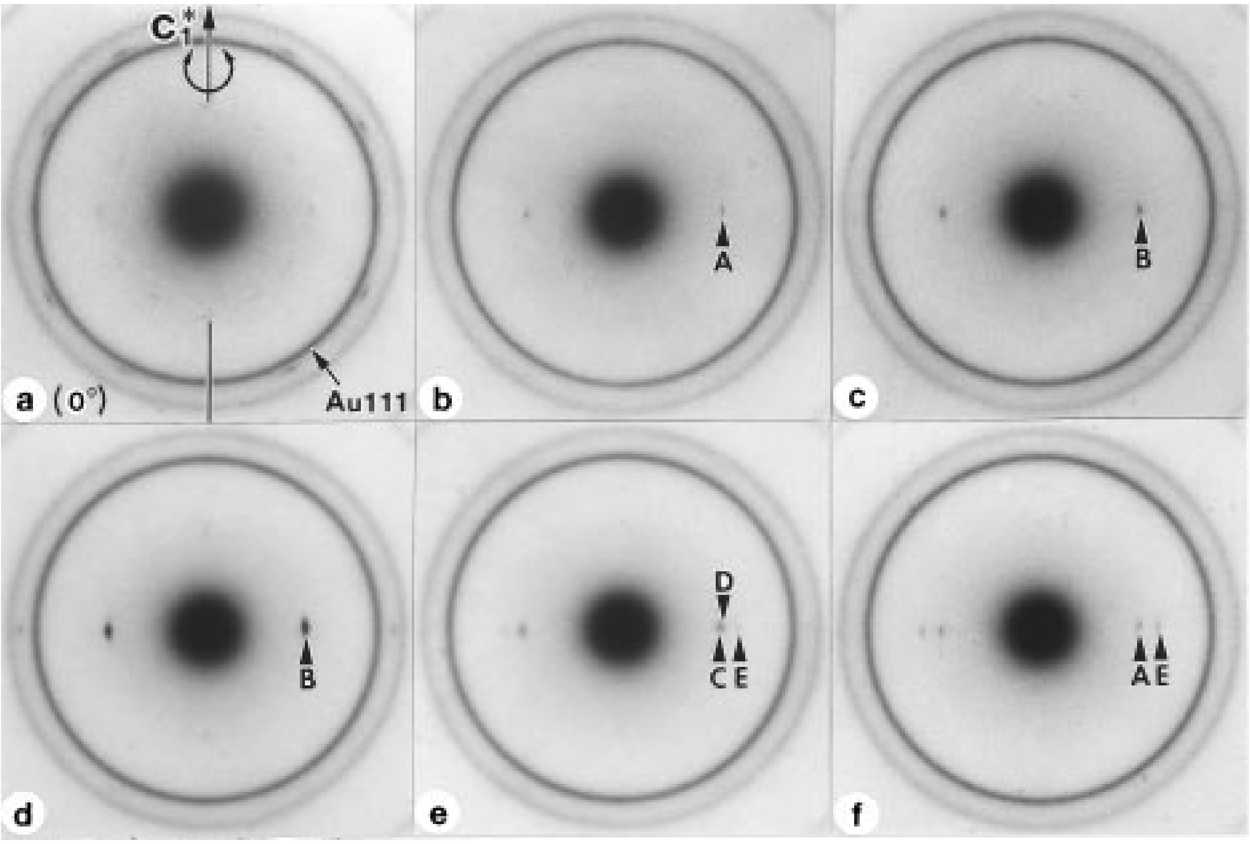

**Figure 3.** A series of SAED patterns of oriented POK crystals as shown in Figure 1a and tilted at different angles around the $c_1^*$-axis (meridian): (a) 0°, (b) 17°, (c) 28°, (d) 31°, (e) 34°, and (f) 37°. The arrowheads and letters A to E indicate the representative strong 110 and 200 reflections of the α- and $\beta$-forms observed on the equator (A, $110_\alpha$; B, $110_\beta$; C, $110_\alpha$ or $110_\beta$; D, $200_\beta$; E, $200_\alpha$).

To sustain these conclusions, a series of SAED rotation-tilt experiments have been performed using the $c_1^*$-axis (meridional axis in Figure 1b) of POK as tilt axis. The various tilting angles used together with the reflections expected to appear for the different types of oriented POK lamellae described previously are listed in Table 1.

Figure 3 shows the series of SAED patterns obtained for oriented POK crystals untilted (Figure 3a) and tilted by 17°, 28°, 31°, 34°, and 37° around the $c_1^*$-axis (Figure 3b−f). First, the appearance of equatorial $110_\alpha$ and $200_\alpha$ reflections at tilting angles of 17° (Figure 3b) and 37° (Figure 3f), respectively, indicates that, in addition to the $(100)_\alpha$ contact plane mentioned previously, epitaxial growth of α-form POK lamellae with a $(110)_\alpha$ contact plane also occurs under the growth conditions used throughout this work. Second, as expected (cf. Table 1) for $(110)_\beta$ and $(100)_\beta$ contact planes, the $110_\beta$ reflection is observed for tilting angles of 28° and 31°, respectively. Similarly, $110_\alpha$ and $200_\alpha$ reflections are observed at a 37° tilt angle, thus confirming the existence of both the $(100)_\alpha$ and $(110)_\alpha$ contact planes. However, the fact that these various reflections are also observed at a 34° tilt angle points to the existence of an orientation distribution of the crystallites around the chain axis (*c*-axis). All these results are tabulated in Table 2.

In summary, the present SAED experiments demonstrate that the epitaxial growth of POK on the (001) face of NaCl is rather nonspecific since it leads to edge-on lamellae of both polymorphic forms with, for each of them, two different orientations and therefore two different contact planes.

**Table 2. Result of the Tilting Experiment Shown in Figure 3**[a]

| | tilting angle (deg) | | | | | |
|---|---|---|---|---|---|---|
| reflection | 0 | 17 | 28 | 31 | 34 | 37 |
| $110_\alpha$ | − | + | − | − | × | + |
| $200_\alpha$ | − | − | − | − | + | + |
| $110_\beta$ | − | − | + | + | × | − |
| $200_\beta$ | − | − | − | − | + | − |

[a] + = observed; − = not observed; × = not determined whether the observed reflection is from the α- or $\beta$-phase.

**POK Crystals Grown on KI.** As shown in Figure 4a, POK lamellae grown epitaxially on the (001) face of KI from a nitrobenzene solution ($T_c$ = 180 °C, $t_c$ = 5 min) differ from those grown on NaCl (Figure 1a) mainly by their greater aspect ratio and the fact that they are oriented parallel and perpendicular to the shadowing direction (arrow in Figure 4a), i.e., that they are aligned along the [100] and [010] directions of the substrate. Furthermore, in contrast to the "cross-hatched" morphologies usually observed on NaCl (cf. Figure 1a in this paper and Figure 1 in ref 12), which resemble an aerial photograph of the road network in the countryside, the rodlike crystals of POK grown on KI form rather large domains with a single orientation.

Figure 4b shows the SAED pattern corresponding to Figure 4a. Indexing of this pattern leads to the conclusion that only the POK α-phase is formed in the presence of a KI substrate.The reflections present in Figure 4b are of two types: (i) 0*kl* reflections (*k* = even) forming two orthogonal net patterns of the α-form; (ii) two pairs of $210_\alpha$ and $310_\alpha$ reflections (A and B, respectively) lying on the equator and also on the meridian.

From the relative orientation of the polymer and substrate crystal [the SAED pattern from a domain in

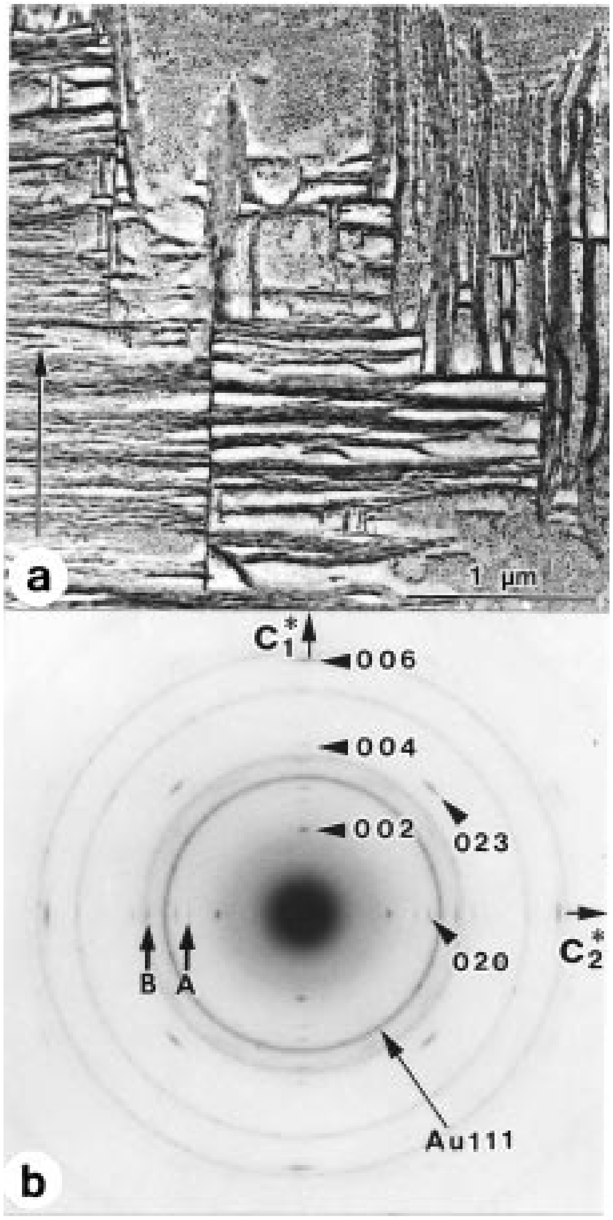

**Figure 4.** (a) POK crystals grown epitaxially on an (001) KI cleavage face at 180 °C from a 0.01 wt % nitrobenzene solution (rodlike crystals aligned parallel and perpendicular to the shadowing direction (arrow) which is parallel to the [100] substrate direction). (b) Corresponding SAED pattern. All the reflections in this figure are attributed to the α-phase (A, $210_\alpha$; B, $310_\alpha$).

which the rodlike crystals of POK (lying parallel to either the [100] or the [010] substrate direction) are horizontal is characterized by an $00l$ reflection line lying on the meridian], it can be deduced that the first type of reflections obviously arise from rodlike crystals, viz., edge-on lamellae with the *b*-axis and the *c*-axis (chain axis) oriented parallel to the substrate (001) face and [100] or [010] directions. As for POK on hydroquinone,[6] the contact plane of the polymer with the (001) KI cleavage face is therefore the crystallographically dense $(100)_\alpha$ plane.

However, as revealed by the presence of the two pairs of $210_\alpha$ and $310_\alpha$ reflections, the growth of edge-on lamellar POK crystals with a (110) contact plane also occurs under the present preparation conditions.

The diffraction evidence gained from SAED of POK crystals tilted around one of the chain axes ($c_1$* in Figure 5a) is consistent with the above observations. Indeed, the $110_\alpha$ and $200_\alpha$ reflections expected to appear for crystals with a (100) or a (110) contact plane tilted at 17° and 37° (cf. Table 1) are clearly recognized in Figure 5b,c. However, as was the case for POK on NaCl, these reflections are present on the equator at any given tilt angle between 17° and 37°, their intensities increasing with the tilting angle. This observation may again be explained by a crystal orientation distribution around the chain axis.

It is worth noting that, in addition to the morphology shown in Figure 4, another POK morphology and crystal orientation could often be observed in the same samples. As can be seen in Figure 6a, the long dimension of these crystals is shorter than that in Figure 4, but the width is similar (13−15 nm). The corresponding SAED pattern (Figure 6b) differs strongly from that shown in Figure 4b but is closely similar to the one obtained for crystals with either a (100) or a (110) contact plane, tilted at 37° (cf. Figure 5c). In Figure 6b, the reflection marked B corresponding to a lattice spacing of 0.35 nm is indexed as $200_\alpha$. The other reflections in this figure, including the reflection marked A, are *hhl* reflections. Unfortunately, it cannot determined whether these crystals are in the α- and/or *β*-form, because there is only a very small difference in lattice spacing for *hhl* reflections of both phases. Furthermore, the orientation, which according to the diffraction pattern shown in Figure 6b involves a (210) or a (310) contact plane of either the α- or the *β*-form, is quite unusual and rather difficult to explain in terms of epitaxy. Nevertheless, these edge-on lamellae are the most appropriate for

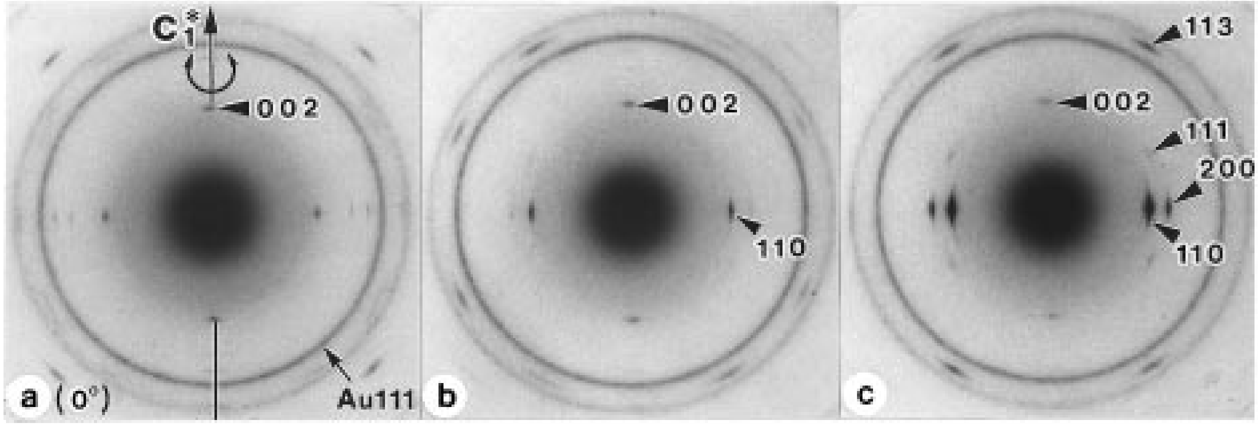

**Figure 5.** A series of SAED patterns of oriented POK crystals grown epitaxially on an (001) KI face: (a) untilted (as in Figure 4b); (b, c) tilted around the $c_1$*-axis by 17° and 37°, respectively.

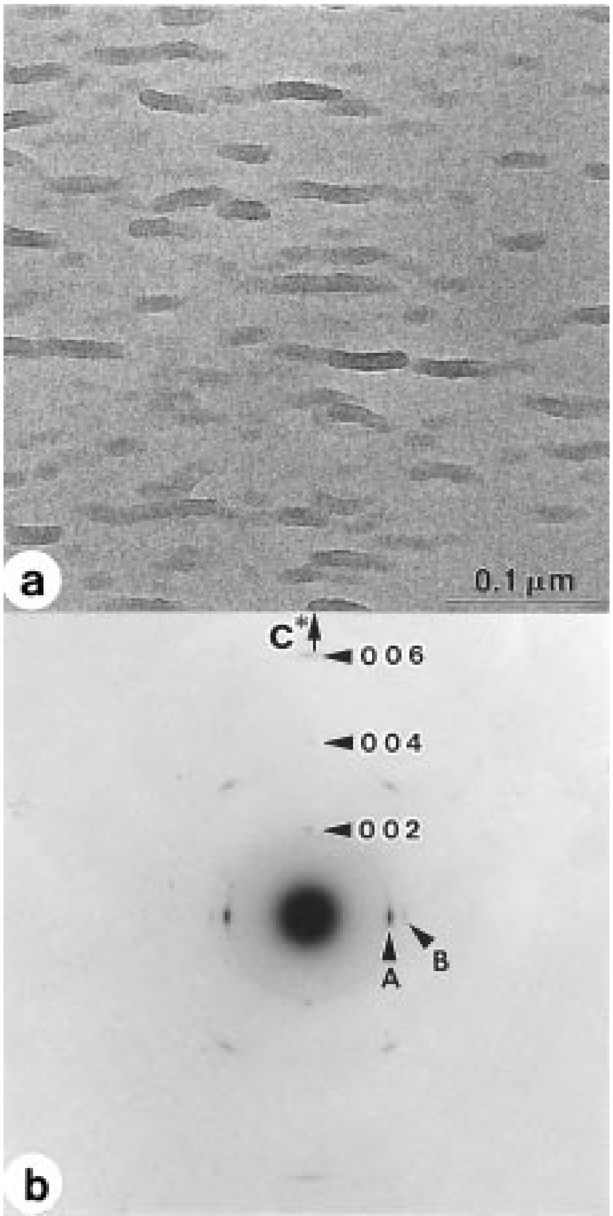

**Figure 6.** POK crystals of a different type grown epitaxially on an (001) KI face and often observed in areas different from those shown in Figure 4: (a) morphology (not shadowed); (b) corresponding SAED pattern with the reflection marked A ($110_\alpha$ or $110_\beta$) and the one marked B ($200_\alpha$). See text.

HRTEM observations because of the presence of the very strong 110 reflection (marked A; its lattice spacing = 0.41 nm) in the SAED pattern of the untilted sample.

**High-Resolution Transmission Electron Microscopy.** Due to rather high sensitivity to electron irradiation, it is usually very difficult to take an HRTEM image of polymer crystals.[13] Our attempts to take HRTEM images of edge-on lamellae of PE or POM[10,12] have so far been unsuccessful due to both electron irradiation damage and inadequate crystal orientation. According to preliminary experiments,[26] the POK crystal are as sensitive to electron irradiation as PE and POM crystals. Indeed the total end-point dose, which is the electron dose needed for the total loss of crystallinity of the POK sample, was estimated to be about 900 electrons/nm$^2$ for 200 kV electrons at room temperature, viz., only slightly larger than for PE and POM crystals. Nevertheless, as exemplified in Figure 7, fairly well-defined HRTEM images of the POK lamellae could be obtained. Dark domains indicated with arrowheads in Figure 7a are Au particles with which the edge-on lamellae were shadowed in order to identify their outline more distinctly. Two fairly large particles are certainly attached to the lower basal surface of the lamella which is discriminated in contrast, as illustrated in Figure 7d. The Au small particles recognized at the top of Figure 7a are attached onto the lower basal surface of another lamella which is certainly observed in the original negative. A single edge-on lamella of a slightly darker gray shade than its surrounding as well as (110) lattice fringes of 0.41 nm can be distinguished. The estimated overall lamellar thickness is about 15 nm and very close to the value derived from the bright field TEM micrographs (Figure 6a). Figure 7b is a highly enlarged photograph from the rectangular area drawn in Figure 7a, and Figure 7c is the optical diffraction pattern obtained from such an area by using the original negative. The length of the lattice fringes, viz., the stem length or the crystalline core thickness, is about 7−8 nm. Thus, it is concluded that, as schematically illustrated in Figure 7d, the surface layer thickness of the POK lamella, on each side of the crystalline core, is about 3 nm, namely 20−25% of the total lamellar thickness. These values are in good agreement with those derived previously for PE and POM by dark-field TEM imaging.[10,12] Note that the fact that no lattice fringes are observed in these surface layers does not necessarily mean that they are totally disordered or amorphous so that the degree of crystallinity of the epitaxially grown POK lamellae may well be greater than the ratio of the crystalline core thickness to the overall lamellar thickness derived from the HRTEM images.

A more detailed investigation by dark-field TEM and HRTEM of epitaxially grown polymer crystals has been undertaken in order to study the variation of the lamellar structure and its crystalline core thickness with the crystallization conditions used, as was already carried out for POM.[12]

## Concluding Remarks

In the present work, rodlike crystals of perfectly alternating ethylene−carbon monoxide copolymer (POK) have been successfully oriented on the (001) cleavage faces of the NaCl and KI single crystals by isothermal crystallization from a 0.01 wt % solution in nitrobenzene. The morphology, with a perpendicular orientation of the deposited rodlike crystals, bears close resemblance to that observed for PE and POM crystals grown on various alkali halides; that is to say, the rodlike crystals of PE and of POM are oriented in the ⟨110⟩ directions of the substrates.[10−12,14−25] Though the orthorhombic PE grows favorably on KBr, the monoclinic form grows transiently just on NaCl, and the growth transition to the orthorhombic one occurs within a few nanometers from the NaCl surface.[9,20] As for POM, for example, the hexagonal form grows on KCl and NaCl, but the orthorhombic form is mingled with the hexagonal one on KI and KBr.[21] The present TEM study on POK reveals the following: (i) Epitaxial interactions of POK with the NaCl (001) face are rather nonspecific in terms of crystalline phase as well as of contact plane. Indeed, both the POK α- and β-modifications are formed with, for each of them, two different contact planes (the crystallographically dense (100) and (110) planes) and therefore two different orientations. In all cases, the

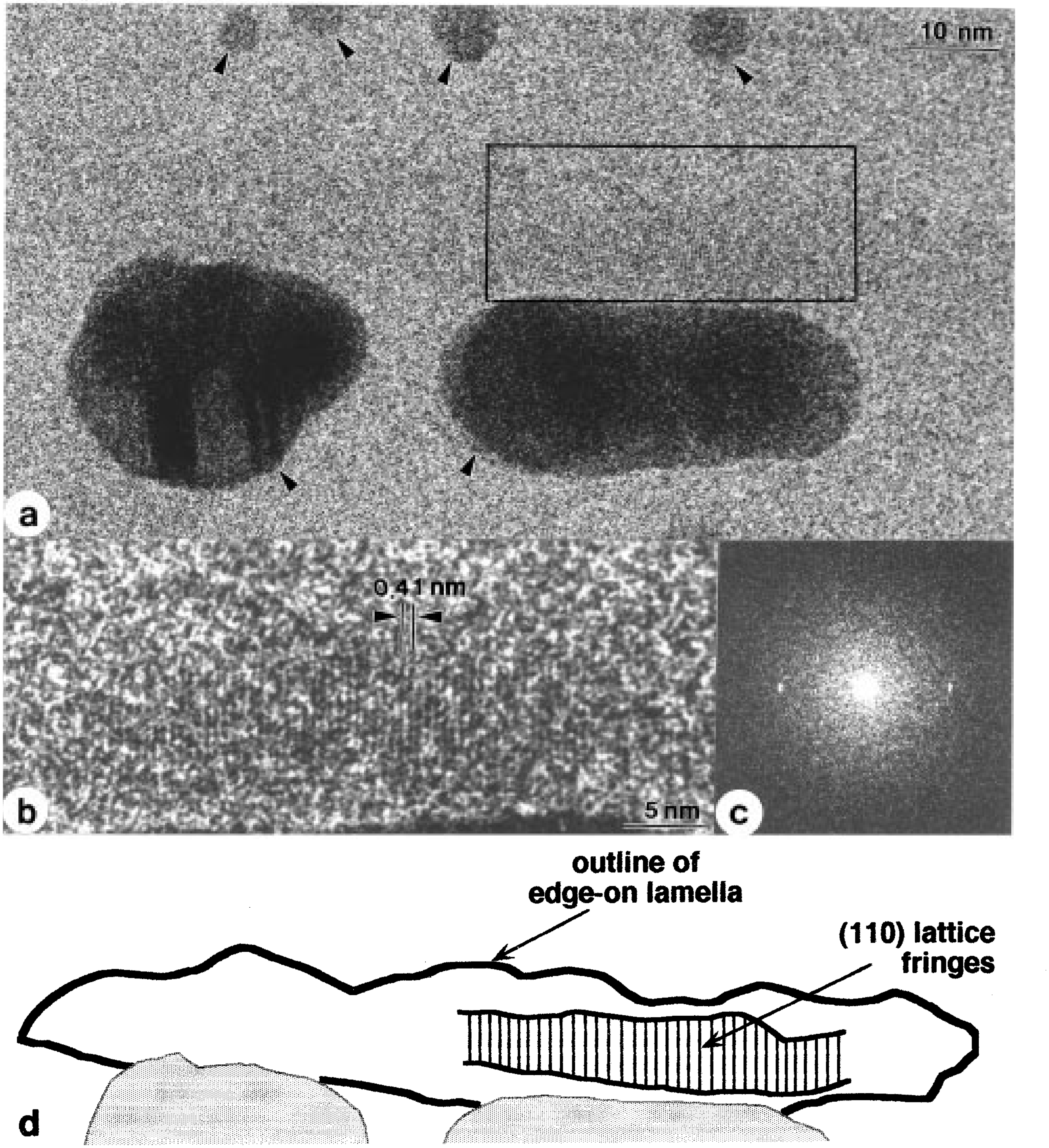

**Figure 7.** (a) HRTEM image of an edge-on lamella of POK grown epitaxially on an (001) KI face. The dark domains (arrowheads) are Au particles *decorating* one edge (viz., one basal surface of each POK edge-on lamella). (b) Highly enlarged photograph of the rectangular area shown in (a) and containing the (110) lattice fringes. (c) Optical diffractogram of the original negative. (d) Schematic drawing of the edge-on lamella showing the crystalline core with the 0.41 nm spaced (110) lattice fringes and the outline (or external shape) of the lamella distinguishable in (a).

chain axes are oriented parallel to the ⟨110⟩ substrate directions. (ii) Epitaxial growth of POK on KI generates only the α-phase. The crystallographic $(100)_\alpha$ and $(110)_\alpha$ planes act again as contact planes, but the chain axes are oriented in the ⟨100⟩ instead of the ⟨110⟩ subtrate directions.

Finally, another minor population of edge-on lamellae is often observed in samples isothermally crystallized on a KI substrate. Although the exact crystallographic relationship between the polymer and the substrate could not be derived from the SAED patterns obtained so far, and despite the relative weak electron beam resistance of POK, successful HRTEM imaging could be achieved. The HRTEM images disclose well-defined (110) lattice fringes and provide us with a direct view of an “isolated” folded-chain edge-on lamella and of its internal “disordered”−crystalline−“disordered” structure[12] in the chain axis direction. This “edge-on view” of the POK lamellar crystal supports the structural model proposed in our recent work on dark-field TEM imaging of edge-on lamellae of PE and POM.[10,12]

**Acknowledgment.** This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan (M. Fujita). M. Fujita expresses his thanks to the Research Fellowships of the Japan Society for the Promotion of Science (JSPS) for appointing him as a JSPS Research Fellow.

## References and Notes

(1) Drent, E. European Patent 121,965 (Shell), 1984.
(2) Drent, E.; v. Broekhoven, J. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235.
(3) Lommerts, B. J.; Klop, E. A.; Aerts, J. *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31*, 1319.
(4) Chatani, Y.; Takizawa, T.; Murahashi, S.; Sakata, Y.; Nishimura, Y. *J. Polym. Sci.* **1961**, *55*, 811.
(5) Klop, E. A.; Lommerts, B. J.; Veurink, J.; Aerts, J.; v. Puijenbroek, R. R. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 315.
(6) Grayer, V.; Lommerts, B. J.; Smith, P.; Lotz, B.; Wittmann, J. C. *Polym. Commun.* **1995**, *36*, 1915.
(7) Wittmann, J. C.; Manley, R. St. J. *J. Polym. Sci., Polym. Phys.* **1978**, *16*, 1891.
(8) Hodge, A. M.; Kiss, G.; Lotz, B.; Wittmann, J. C. *Polymer* **1982**, *23*, 985.
(9) Wittmann, J. C.; Lotz, B. *Prog. Polym. Sci.* **1990**, *15*, 909.
(10) Tsuji, M.; Ihn, K. J. *Bull. Inst. Chem. Res., Kyoto Univ.* **1995**, *72*, 429.
(11) Fujita, M.; Hamada, N.; Tosaka, M.; Tsuji, M.; Kohjiya, S. *J. Macromol. Sci., Phys.* **1997**, *B36*, 681.
(12) Fujita, M.; Tsuji, M.; Kohjiya, S. *Polymer* **1999**, *40*, 2829.
(13) Tsuji, M.; Kohjiya, S. *Prog. Polym. Sci.* **1995**, *20*, 259.
(14) Willems, J.; Willems, I. *Experientia* **1957**, *13*, 465.
(15) Fisher, E. W. *Kolloid-Z.* **1958**, *159*, 108.
(16) Koutsky, J. A.; Walton, A. G.; Baer, E. *J. Polym. Sci., Part A-2* **1966**, *4*, 611.
(17) Koutsky, J. A.; Walton, A. G.; Baer, E. *Polym. Lett.* **1967**, *5*, 177.
(18) Kiss, K.; Carr, S. H.; Walton, A. G.; Baer, E. *Polym. Lett.* **1967**, *5*, 1087.
(19) Carr, S. H.; Keller, A.; Baer, E. *J. Polym. Sci., Part A-2* **1970**, *8*, 1467.
(20) Wellinghoff, S.; Rybnikar, F.; Baer, E. *J. Macromol. Sci., Phys.* **1974**, *B10*, 1.
(21) Rickert, S. E.; Baer, E. *J. Appl. Phys.* **1976**, *47*, 4304.
(22) Mauritz, K. A.; Baer, E.; Hopfinger, A. J. *J. Polym. Sci., Macromol. Rev.* **1978**, *13*, 1.
(23) Balik, C. M.; Tripathy, S. K.; Hopfinger, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2003.
(24) Ghavamikia, H.; Rickert, S. E. *J. Mater. Sci. Lett.* **1983**, *2*, 103.
(25) Sato, Y. *J. Polym. Sci.* **1990**, *28*, 1163.
(26) Tsuji, M.; Fujita, M.; Kohjiya, S. *Nihon Reoroji Gakkaishi* **1997**, *25*, 235.

MA990321Z