Macromolecules **2001,** *34,* 6147−6151

Solution-Grown Single Crystals of Perfectly Alternating Ethylene−Carbon Monoxide Copolymer

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Received April 2, 2001
Revised Manuscript Received May 22, 2001

Introduction

Recently, the catalytic polymerization method developed by Drent et al.[1,2] has enabled the synthesis of perfectly alternating ethylene−carbon monoxide copolymer (poly(3-oxotrimethylene)), which is a kind of poly(olefin ketone). (In this paper, the perfectly alternating copolymer in question is abbreviated as POK.) Lommerts et al.[3] have extensively characterized the new POK by ^{1}H nuclear magnetic resonance, thermal analysis, and X-ray diffraction. Compared with a conventional copolymer which is less perfect one, improvement of various physical properties has been reported; i.e., a higher melting temperature ($T_m \approx 257$ °C), a higher degree of crystallinity, better stability to UV irradiation (viz. photostability), and so on have been obtained.[2,3]

The perfect regularity of chemical structure, furthermore, leads to the change of crystal structure. X-ray structure analysis of POK by Lommerts et al.[3] revealed that there exists another new crystal structure (α-form; orthorhombic, *Pbnm*: $a = 0.691$ nm, $b = 0.512$ nm, c (chain axis) $= 0.760$ nm) in addition to the β-form which corresponds to the structure (orthorhombic, *Pnam*: $a = 0.797$ nm, $b = 0.476$ nm, c (chain axis) $=$ 0.757 nm) reported earlier by Chatani et al.[4] for a less perfect copolymer. That is to say, the new POK exhibits two polymorphic forms. The occurrence of the α- and/or β-form depends on the crystallization condition, applied stress, and so on.[5] Transmission electron microscopical studies on the POK crystals have been carried out so far.[6−8] Grayer et al. for the first time reported that this polymer can be crystallized epitaxially on the hydroquinone crystalline substrate, and the resulting crystals are folded-chain edge-on lamellae of the α-form.[6] Subsequently, we reported that epitaxial growth of the POK from its dilute solution can be successfully achieved using alkali halides as a substrate,[7,8] as in the case of polyethylene (PE) and polyoxymethylene (POM).[8−12]

In the present paper, it is shown that POK single crystals can be grown isothermally from solution. The single crystals are investigated by transmission electron microscopy (TEM). The fold-surface structure of the POK single crystals is examined by the method of surface decoration with vapor-deposited PE.[13] In addition, the lamellar thickness is measured by small-angle X-ray scattering (SAXS) of sedimented mats of single crystals.

Experimental Section

Preparation of Single Crystals. The POK sample used here 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).

Nitrobenzene was used as the solvent. The POK single crystals were isothermally grown at a desired crystallization temperature (T_c) for 24 h from a 0.01 wt % nitrobenzene solution (0.1 wt % for preparing the sedimented mat).

Transmission Electron Microscopy. Solution-grown single crystals were mounted on a carbon-film-coated Cu grid for TEM. The specimens were, under vacuum, shadowed, when needed, with Pt−Pd (the shadowing angle $= \tan^{-1}(1/4)$) for morphological observation, or coated with Au as a reference for calibration of the electron diffraction camera length in order to estimate lattice spacings of the POK crystals. To estimate regularity of the fold surface, PE (Sholex 6050) was evaporated and deposited onto the POK crystals under vacuum, before shadowing.[13]

TEM of the specimens thus prepared was performed at room temperature with a JEOL JEM-200CS (accelerating voltage = 200 kV). Bright-field images were recorded onto Fuji FG films to obtain higher contrast and selected-area electron diffraction (SAED) patterns onto more sensitive films (Mitsubishi MEM).[14] All the exposed films were developed with Mitsubishi Gekkol (full strength) at 20 °C for 5 min.[14]

Small-Angle X-ray Scattering. The lamellar thickness of the solution-grown single crystal was evaluated by SAXS of the sedimented single-crystal mats of POK. The X-ray beam was introduced into each mat in the direction parallel to its surface. A Rigaku RU-3H with a Cu target was used as an X-ray generator.

Results and Discussion

Morphology of Solution-Grown Single Crystal. Figure 1a shows an example of typical single crystals of POK isothermally grown at 139 °C from a 0.01 wt % nitrobenzene solution for 24 h. Similarly to other flexible linear polymers, the solution-grown POK single crystal is a faceted lamellar crystal with well-defined lateral growth faces. The lateral dimension of the crystals is in a range of micrometer scale, and the lamellar thickness is about 10 nm or less, estimated by the Pt−Pd shadowing. Taking account of the molecular weight, the solution-grown single crystal of POK is to be a folded-chain lamella. The lamellar crystal shown in this figure exhibits a truncated-lozenge lateral habit as well as that of PE obtained under a certain crystallization condition.[15−18]

Figure 1c is the SAED pattern corresponding to the crystal shown in Figure 1a. All the reflections could be well indexed on the basis of the α-form structure reported by Lommerts et al.[3] As schematically shown in Figure 1d, this pattern represents the *hk*0 net pattern of α-form The chain stems in the lamella are thus set perpendicular to its basal surface, namely the fold surface. It is well recognized that the lateral growth shapes of the single crystals reflect the symmetry of the α-form unit cell of POK. Such crystals are bound laterally by smooth low-index growth faces, as in the

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10.1021/ma010546l CCC: $20.00

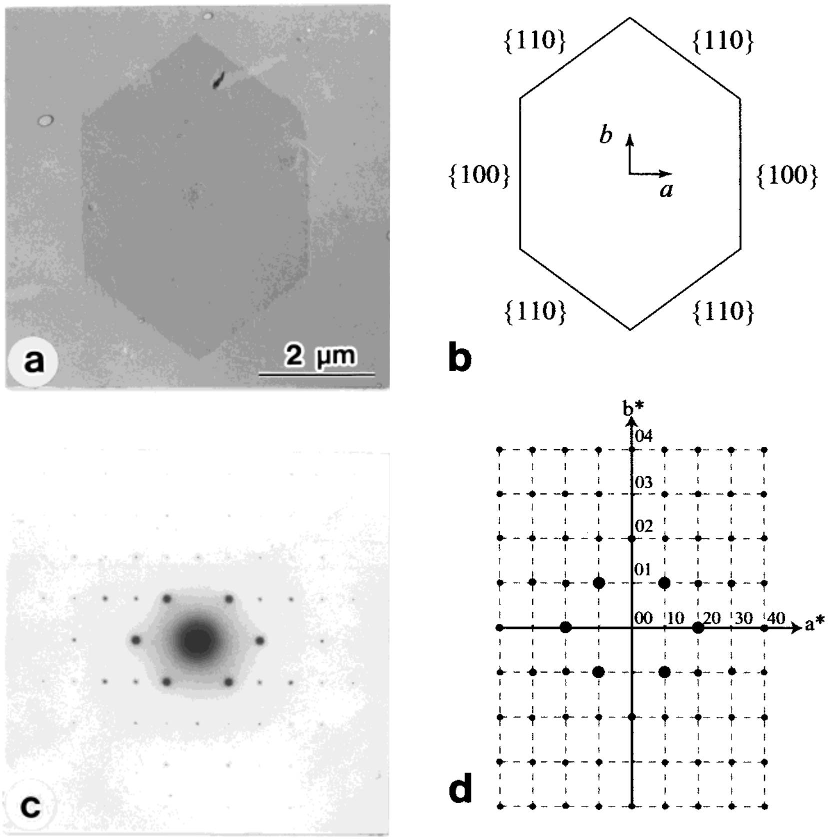

Figure 1. (a) A typical single crystal of POK grown isothermally from a 0.01 wt % nitrobenzene solution at 139 °C for 24 h. (b) Schematic representation of the crystal shown in (a) with lateral growth faces being indicated. (c) SAED pattern corresponding to (a). (d) Schematic drawing of the *hk*0 net pattern for the α-form (orthorhombic, *Pbnm*: $a = 0.691$ nm, $b = 0.512$ nm, c (chain axis) $= 0.760$ nm).[3]

case of other polymers. Taking account of the directional relationship between the morphology and the corresponding SAED pattern, the long diagonal of the crystal is in the direction parallel to the *b*-axis, and thus, truncated faces are identified as the $\{100\}_\alpha$ planes, and the other lateral faces as the $\{110\}_\alpha$ planes, as illustrated in Figure 1b. This feature in lateral habit of POK crystal is completely similar to that of PE and thus indicates that the folding manner of POK chain may be closely analogous to that of PE. A discussion in this connection will be given below.

Figure 2a shows another type of morphology of POK crystals grown under the same crystallization condition as that for Figure 1. This morphology was frequently observed together with truncated-lozenge-shaped crystals. Obviously, the overall shape differs from that of the truncated crystal (see Figure 1). Figure 2c is the corresponding SAED pattern, in which all the reflections could be well indexed on the basis of the α-form structure. Two *hk*0 net patterns are recognized, and a pair of 110_α reflections belonging to the one net superposes on those belonging to the other net, as shown schematically in Figure 2d. That is to say, the crystal shown in Figure 2a is the $(110)_\alpha$ twin crystal. Taking account of the directional relationship between the morphology and the corresponding SAED pattern, the lateral growth faces were identified as shown in Figure 2b.

As well as the twin crystals of other polymers reported so far,[19−21] the twin mode for the POK crystal shown in Figure 2a can be deduced. Figure 3 illustrates schematically the (110) twin mode of POK based on the geometry of the α-form unit cell. The less regularly hexagonal appearance indicated with bold lines is consistent with the external shape of the crystal shown in Figure 2a. Accordingly, it is suggested that the (110) twin boundary is located at the site illustrated with the broken line in Figure 2b.

The morphologies described above have not been observed when crystallized at higher T_c ($T_c = 150$ °C). In this case, the other types of crystals were often observed. Figure 4 shows an example of the POK single crystals isothermally grown at 150 °C from a 0.01 wt % nitrobenzene solution for 24 h. From the SAED experiments, it is elucidated that the crystals also exhibit the POK α-phase. Moreover, all six growth faces were identified as $\{110\}_\alpha$ planes. There should exist more than one $\{110\}_\alpha$ twin boundary in the crystal for making up such a lateral habit; i.e., this is a multiple-twin crystal.

The crystals examined in the present work do not reflect the structure of β-form modification but reflect only that of α-form one. It is deduced from this result that the POK single crystals grow directly in the α-form when they are sporadically grown. On the other hand, epitaxial crystallization of POK from solution onto alkali halides (for example, NaCl) gives both forms.[7,8] A certain but unknown effect due to substrates seems to stabilize the β-form to grow.

The thickness of these lamellar crystals was estimated by SAXS. In the present work, SAXS measurements for the sedimented single crystal mats of POK grown isothermally from nitrobenzene solutions at $T_c = 139$, 145, and 150 °C were carried out. The

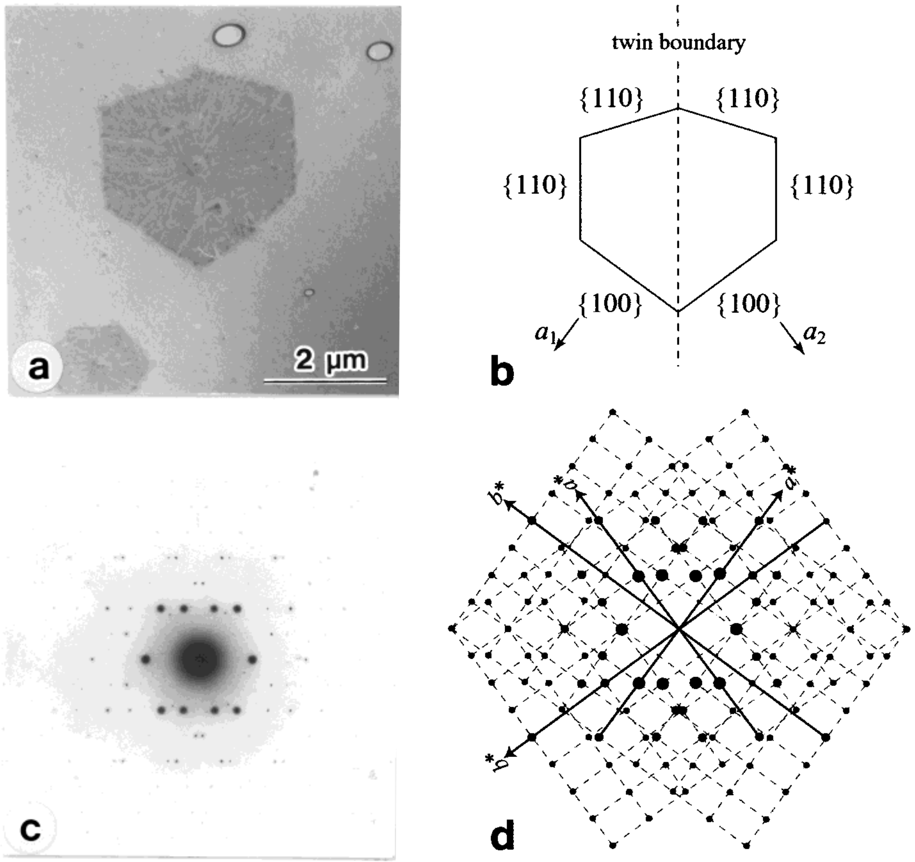

Figure 2. (a) A (110) twin crystal of POK grown isothermally from a 0.01 wt % nitrobenzene solution at 139 °C for 24 h. (b) Schematic representation of the crystal shown in (a) with lateral growth faces and the (110) twin boundary being indicated. (c) SAED pattern corresponding to (a). (d) Schematic drawing of the *hk*0 net patterns from the (110) twin crystal of α-form.

measured long periods, which are regarded as lamellar thicknesses, were as follows: 7.91 nm for $T_c = 139$ °C, 7.71 nm for 145 °C, and 8.04 nm for 150 °C. The experimental data did not exhibit a remarkable dependence on T_c. It is because the present system corresponds to a horizontal plateau in lamellar thickness when the thickness is plotted against T_c, viz., corresponds to a region of lower T_c. As will be presented in our forthcoming paper,[22] the feature of the lamellar thickness of POK single crystals is that the higher the T_c, the greater the thickness.

Surface Decoration with Vapor-Deposited Polyethylene (PE). The surface decoration of polymer single crystals with PE deposited from its vapor phase was for the first time carried out by Wittmann and Lotz[13] and is a useful method for estimating the structural regularity of fold surface. To investigate the fold-surface structure of POK single crystal, the decoration method was applied in the present work. Parts a and b of Figure 5 show examples of surface-decorated truncated and twin crystals, respectively, which were isothermally grown at 139 °C. As is the case with the single crystals of, for example, PE[10,13] and POM,[12,13] the vapor-deposited rodlike crystals of PE are oriented in some regular fashion in each sector of the POK crystals. This feature reveals the sectorization of the POK single crystals shown in Figure 5, each of which consists of six sectors. In each sector, the long axis of the rodlike crystals of PE is basically perpendicular to the lateral growth face of the POK crystal, though the (100) sectors appear to be more regular than the (110) ones in Figure 5. Accordingly, it is concluded that the preferential

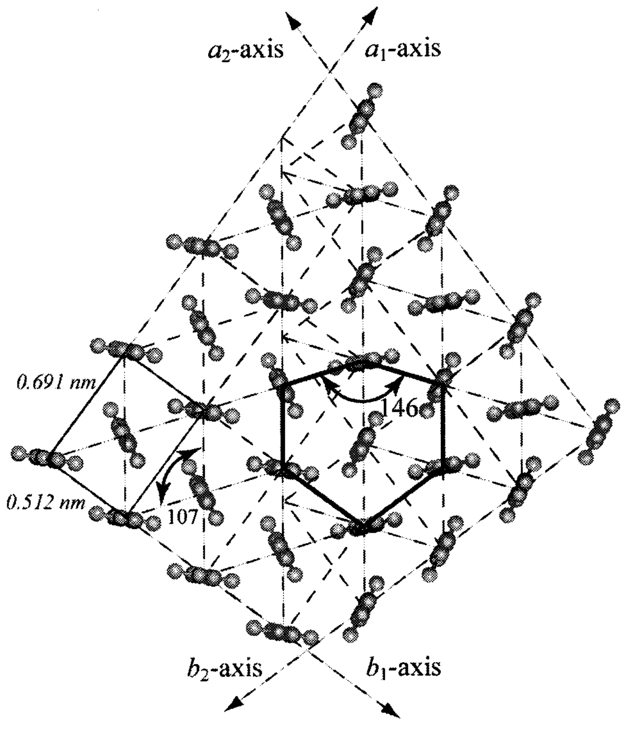

Figure 3. Schematic illustration of the (110) twin crystal of POK using the α-form unit cell viewed along the chain axis (*c*-axis). The numerical figures indicate angles. It is noted that the less regularly hexagonal appearance indicated with bold lines resembles well the shape of the crystal shown in Figure 2a,b.

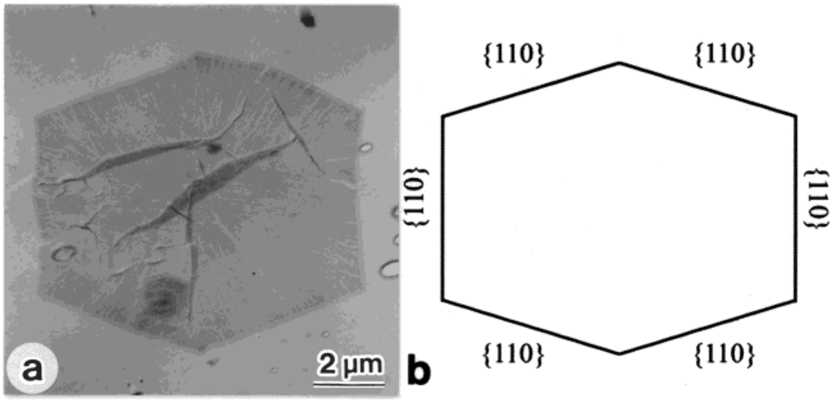

Figure 4. (a) A lamellar crystal of POK grown isothermally from a 0.01 wt % nitrobenzene solution at 150 °C for 24 h. (b) Schematic representation of the crystal shown in (a) with lateral growth faces being indicated.

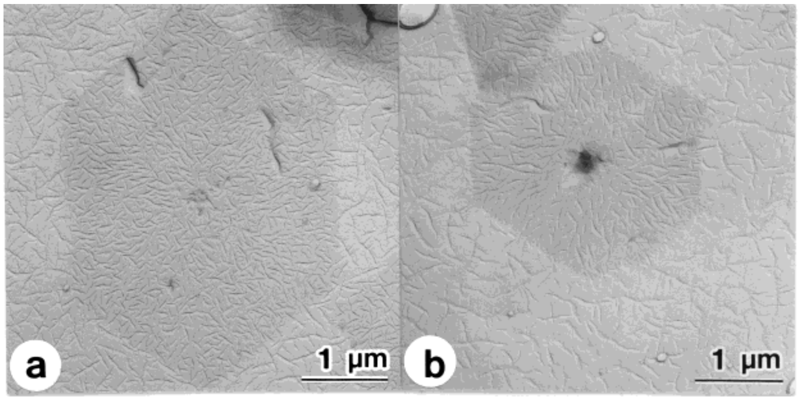

Figure 5. Surface-decorated single crystals of POK by vapor deposition of PE: (a) a truncated-lozenge-shaped crystal, (b) a (110) twin crystal, both of which were isothermally grown from a 0.01 wt % nitrobenzene solution at 139 °C for 24 h.

folding direction in the $\{110\}_\alpha$ sector is parallel to the $\{110\}_\alpha$ growth face and that in the $\{100\}_\alpha$ sector is parallel to the $\{100\}_\alpha$ growth face. This experimental result is in contradiction to the switchboard model for the structure of fold surface of polymer single crystals. That is to say, as for the POK single crystals, the switchboard model is excluded from among possible models of fold structure.

Concluding Remarks

In the present work, single crystals of POK have been successfully grown isothermally from its dilute solution in nitrobenzene. The features of the single crystals are analogous to those reported for other flexible linear polymers. The resulting faceted crystals are folded-chain lamellae with well-defined lateral growth faces. As determined by SAED experiments, the crystals exhibit only the α-phase. In addition to the truncated-lozenge-shaped crystals, the (110) twin crystals were frequently observed. The lamellar thickness of the single crystals is about 8 nm in our experimental range of T_c (139−150 °C).

The surface decoration of the POK single crystals by vapor deposition of PE proved that the rodlike crystals of PE preferentially orient at right angles to the lateral growth face in each sector of the POK crystals according to the folding direction of POK. Consequently, it is supposed that the fold surface of POK single crystal has some structural regularity, similarly to the case of PE and POM.

Acknowledgment. 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.

References and Notes

(1) Drent, E. European Patent 121,965 (Shell), 1984.
(2) Drent, E.; van 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.; van 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. *Polymer* **1995**, *36*, 1915.
(7) Fujita, M.; Tsuji, M.; Kohjiya, S.; Wittmann, J. C. *Macromolecules* **1999**, *32*, 4383.
(8) Fujita, M.; Ihn, K. J.; Tsuji, M.; Kohjiya, S. *Kobunshi Ronbunshu* **1999**, *56*, 786.
(9) Ihn, K. J.; Tsuji, M.; Kawaguchi, A.; Katayama, K. *Bull. Inst. Chem. Res., Kyoto Univ.* **1990**, *68*, 429.
(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) Wittmann, J. C.; Lotz, B. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 205.

(14) (a) Tsuji, M. In *Comprehensive Polymer Science*; Sir Allen, G., Bevington, J. C., Eds.; Pergamon: Oxford, 1989; Vol. 1 (Booth, C., Price, C., Vol. Eds.), Chapter 34, pp 785−840. (b) Tsuji, M.; Kohjiya, S. *Prog. Polym. Sci.* **1995**, *20*, 259. (c) Toasaka, M.; Yamakawa, M.; Tsuji, M.; Kohjiya, S.; Ogawa, T.; Isoda, S.; Kobayashi, T. *Microsc. Res. Tech.* **1999**, *46*, 325.

(15) Bassett, D. C.; Frank, F. C.; Keller, A. *Nature* **1959**, *184*, 810.

(16) Bassett, D. C.; Keller, A. *Philos. Mag.* **1961**, *6*, 345.

(17) Bassett, D. C.; Frank, F. C.; Keller, A. *Philos. Mag.* **1963**, *8*, 1753.

(18) Kawai, T.; Keller, A. *Philos. Mag.* **1965**, *11*, 1165.

(19) Blundell, D. J.; Keller, A. *J. Macromol. Sci., Phys.* **1968**, *B2*, 301.

(20) Kovacs, A. J.; Lotz, B.; Keller, A. *J. Macromol. Sci., Phys.* **1969**, *B3*, 385.

(21) Wittmann, J. C.; Kovacs, A. J. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 901.

(22) Fujita, M.; Tsuji, M.; Kohjiya, S. Submitted to *Macromolecules*.

MA010546L