Structural Analysis of Polyoxymethylene Whisker Single Crystal by the Electron Diffraction Method

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ABSTRACT: The whisker of polyoxymethylene produced in the cationic polymerization process of trioxane is a single crystal of extended chain crystal morphology. Since it has a quite small size of several microns in radius and several tens of microns in length, the crystal structure analysis of POM whisker had been tried by using an electron diffraction technique, but it was easily damaged by an electron beam. We have succeeded in taking the electron diffraction patterns of the POM whisker from the different directions by reducing the electron beam intensity as much as possible and by using a highly sensitive imaging plate detector. Application of the direct method, which is useful for solving the so-called phase problem in structure analysis, allowed us to obtain the helical conformation of POM chain packed in the trigonal unit cell. However, the refinement of the thus-obtained initial structure was difficult since the electron diffraction intensities were modified seriously from the original values by the multiple reflection effect in the single crystal. Rather, the refinement was made successfully by combining the initial structure obtained by the electron diffraction data with the X-ray diffraction data taken for the γ-ray-polymerized POM multiple crystalline sample, suggesting a usefulness of an organized combination of electron and X-ray diffraction techniques in the structure analysis of polymer crystals.

Introduction

Polyoxymethylene (POM) crystallizes into a thin single crystal of folded chain morphology when the dilute solution is slowly cooled to room temperature, as shown in Figure 1a. On the other hand, as shown in Figure 1b, POM crystallizes into a whisker or a single crystal of fully extended chain crystal morphology when the ring-opening polymerization reaction of trioxane is made with cationic catalyst.[1] This POM whisker is important both industrially and scientifically because it may be assumed as an ideal state of polymer crystal although the size is quite small, several tens of microns in length and several microns in radius. Of course, we know already the existence of fully extended chain crystal of POM which is polymerized from trioxane single crystal under an irradiation of γ-rays, but this POM crystal is not a single crystal but a multiple crystal consisting of many single-crystal-like domains.[2,3] POM whisker is a real single crystal, making us expect that the many and sharp reflections should be collected which is useful for the precise structure analysis of the whisker. But we have not yet obtained any detailed information about the crystal structure of the whisker because of its small size of electron microscopic scale. The X-ray diffraction pattern was taken only for the powdered whisker sample to check that the POM chains are packed in a trigonal unit cell with regular (9/5) helical conformation.[4−7] It may be more powerful to utilize a single crystal or a needle of whisker in order to obtain the structural information more directly.

Many trials were made to take an electron diffraction pattern of POM whisker without any success because the sample was damaged quite easily by an irradiation of electron beam. We have succeeded for the first time to take the electron diffraction patterns from the various directions by reducing an incident electron beam as much as possible and by using a highly sensitive 2-dimensional imaging plate detector. The integrated intensities were evaluated for the observed reflections and the application of the direct method, which is useful for solving the phase problem in the crystal structure analysis,[8] allowed us to obtain the crystal structure, as will be reported here.

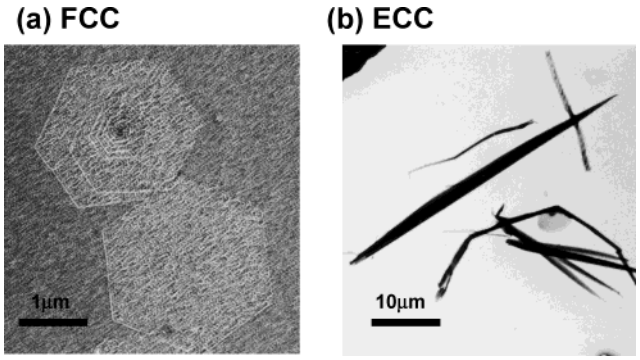

Figure 1. Electron microscopic images of (a) folded chain crystal and (b) whisker or extended chain crystal of polyoxymethylene.

Experimental Section

POM whisker shown in Figure 1b was used, which was kindly supplied by Drs. M. Iguchi and M. Shimomura of the Research Institute for Polymers and Textiles, Japan. The electron beam intensity was reduced as much as possible because the sample was quite easily damaged by the electron irradiation as shown in Figure 2, where many parallel stripes are seen on the crystal. They are the parts damaged due to the chain scission by the electron beam.

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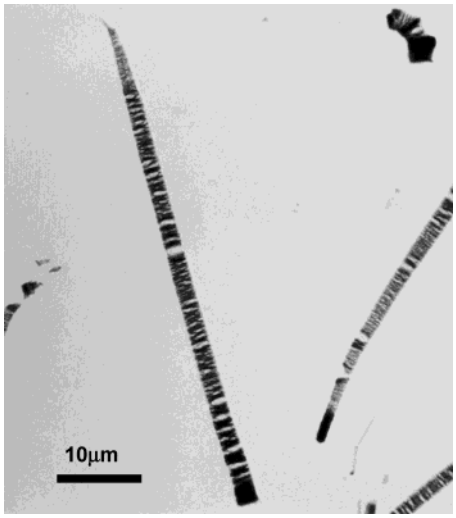

Figure 2. Electron microscopic image of polyoxymethylene whisker damaged by electron beam.

The electron diffraction was measured with a JEOL JEM1010 transmission electron microscope equipped with an imaging plate as a 2-dimensional detector. The acceleration voltage was set to 100 kV, and the wavelength of incident electron beam was 0.0037 Å. The diffraction patterns on the imaging plates were read out by using a DL2000 IP reader (JEOL), and the digitized data were stored in a workstation. The reflection indexing, the determination of the lattice parameters, and the integration of the reflection intensity were performed with a software developed by ourselves.[5] The structure analysis was made on the basis of kinetic theory with a commercial software Crystan GM (MAC Science, Co. Ltd., Japan). The direct method was applied to find out the initial models, where the software SIR92 developed by Altmare et al. was used.[9] Least-squares refinement was made on the basis of the full matrix method by using the quantity $\sum w(|F_o|^2 - |F_c|^2)^2$ as a minimized function with the weight $w = \exp[FA \sin^2 \theta/\lambda^2]/[\sigma^2(F_o) + FB F_o^2]$, where $\sigma^2(F_o)$ was the square standard deviation of the observed structure factor F_o and the coefficients FA and FB were initially set to the values 0.0 and 0.03, respectively. The finally obtained reliability factors R and R_w were defined by the following equations: $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(||F_o| - |F_c||)^2/\sum w|F_o|^2\}^{1/2}$. Further refinement of the thus-obtained structure was made on the basis of X-ray diffraction data taken for the POM sample prepared by γ-ray solid-state polymerization reaction of trioxane needle crystal, where the details of X-ray data collection were described in the previous paper.[5]

Results and Discussion

In Figure 3 are shown the two types of electron diffraction patterns, which were taken by irradiating the electron beam along the two different directions perpendicular to the long axis of the whisker (see Figure 4). These diffraction patterns were found to be reasonably indexed on the basis of a trigonal unit cell. The diffraction pattern (a) in Figure 3 was obtained when the electron beam was incident along the direction perpendicular to the a^* axis as shown in Figure 4 (1), while the pattern (b) in Figure 3 was taken along the direction normal to the (110) axis (case 2 in Figure 4). As schematically indicated in the right half side of Figure 3, only the ($h0l$) reflections were observed in the case (a), while only the (hhl) reflections were observed in the case (b). The 48 reflections were observed in total: 37 ($h0l$) reflections and 11 (hhl) reflections. The unit cell parameters estimated in this indexing process are as follows: the trigonal system $P3_1$ with $a = b = 4.46$ Å, c(fiber axis) = 17.51 Å, and $\gamma = 120.0°$. They are in good accordance with the values obtained by the X-ray structural analysis,[5−7] $a = b = 4.464$ Å, c(chain axis) = 17.389 Å, and $\gamma = 120°$. The c-axial length was longer by ca. 0.7% in the electron diffraction case, but it should be due to an experimental error, although there might be any positive reason for tensioning the chains in the whisker sample.

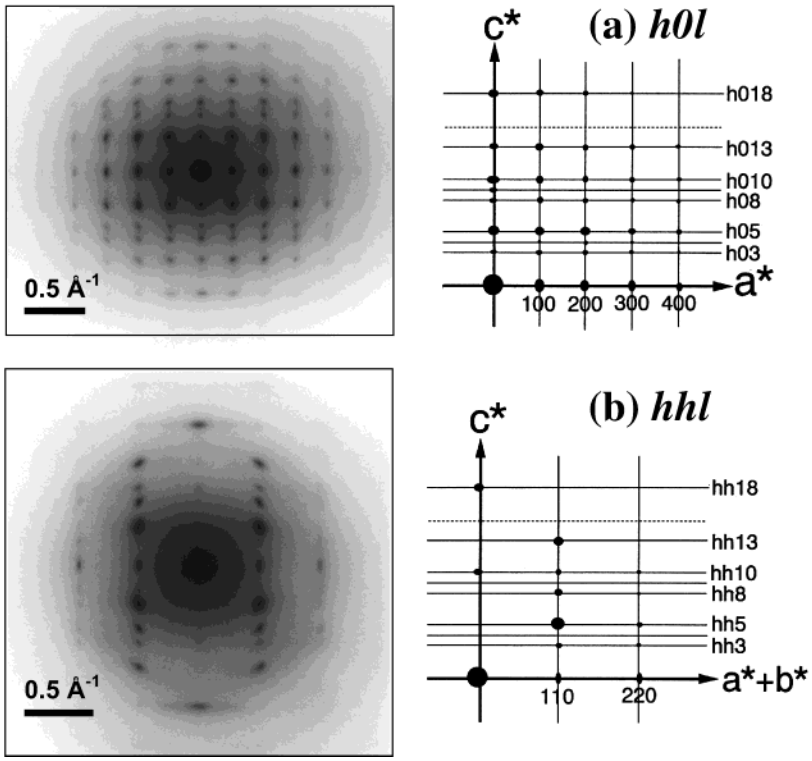

Figure 3. Electron diffraction patterns taken for polyoxymethylene whisker with the electron beam incident along the two different directions: (a) observation of $h0l$ reflections and (b) hhl reflections (refer to Figure 4).

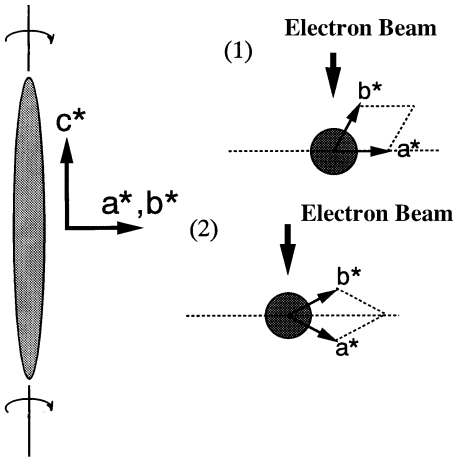

Figure 4. Reciprocal lattice axes of polyoxymethylene whisker and the two types of electron diffraction measurement geometry.

The integrated intensities were estimated for these observed reflections. Different from the case of X-ray analysis, the absolute values of the observed structure factors $|F_{obs}|$ were calculated directly from the observed intensities (I_{obs}) using an equation $I_{obs} = Km|F_{obs}|^2$, where m was a multiplicity and K was a scale factor.[10] To extract an initial structural model which is needed for the structural refinement, the direct method was applied to know the phase relation between the observed reflections.[9] The structural refinement was made so that the calculated reflection intensities were as close to the observed values as possible. The thus-obtained structure of POM molecular chain is shown in Figure 5a. The final R factor was 37.5% and the R_w factor was 38.2%, too high to judge the structure as a reasonable one. In fact, the averaged structural parameters were quite unreasonable: the bond length CO = 1.22 Å, the bond angles OCO = 123.8° and COC = 124.8°, and the torsional angle COCO = −92.5°. This abnormal result is considered to come from the modification of reflection intensities due to the multiple reflection phenomenon in the single crystal.[10] Here we have a limitation of electron diffraction method even for the single crystal sample, although we can collect many sharp reflections useful for the application of the direct method to obtain the initial structure models. The situation is in quite contrast to the case of X-ray diffraction measurement of semicrystalline sample, in which the small number of board reflections is obtained in general, making the application of direct method difficult. But, as for the diffraction intensity, the X-ray diffraction data are better than the electron diffraction data because the kinetic theory can be applied reasonably in the structure analysis.

Then we had an idea to combine these two diffraction techniques together. The initial structure obtained by the electron diffraction method was refined by using the X-ray diffraction data which were collected for a POM sample obtained by γ-ray solid-state polymerization reaction of the trioxane single crystal. The X-ray data were transferred from ref 5. The final R factor was 4.7% for the 72 observed reflections. The thus-obtained molecular chain structure is shown in Figure 5b. The molecular chain takes a regular helical structure, and the averaged structural parameters are as follows: bond length CO = 1.42 Å, bond angles OCO = 109.0° and COC = 114.8°, and torsional angle COCO = −77.8°, quite reasonable when compared with the standard

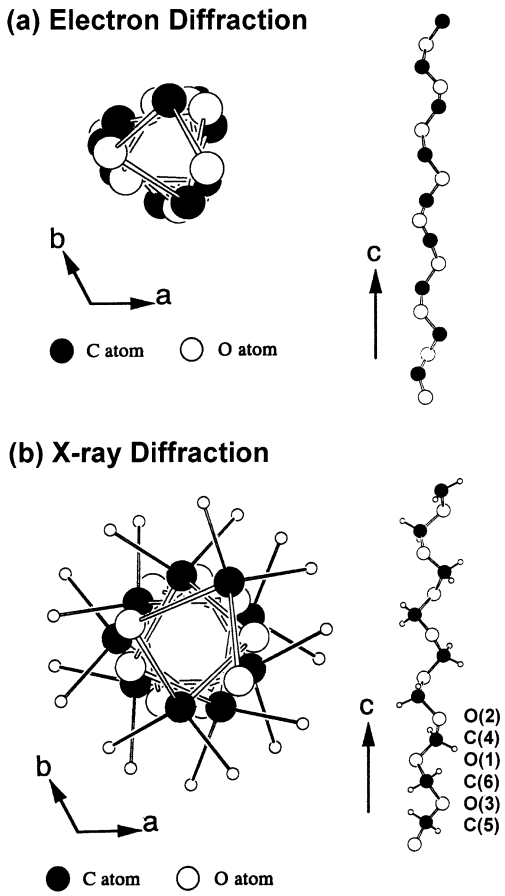

Figure 5. Molecular structure of polyoxymethylene obtained (a) by applying the direct method to the electron diffraction data of the whisker and (b) by the refinement of structure (a) by combining with the X-ray diffraction data taken for γ-ray polymerized sample.

values.[5−7] (For example, the energetically minimized crystal structure of POM has the following parameters: CO = 1.42 Å, bond angles OCO = 109.0° and COC = 114.2°, and torsional angle COCO = −78.0° in average, where a software Cerius[2] (Accerlys Inc.) was used for the calculation with the force field parameters set COMPASS.[11]) The fractional coordinates and the anisotropic thermal parameters of the atoms in a basic structural unit are shown in Table 1. The comparison between the observed and calculated structure factors is made in Table 2a for electron diffraction and in Table 2b for X-ray diffraction. (The structure factors listed in Table 3 are slightly different from those reported in the previous paper.[5] This might come from the usage of slightly different atomic coordinates obtained after more or less different convergence in the least-squares refinement of the initial structural model extracted from the ED data.)

Conclusions

As reported in the present paper, we succeeded in taking the electron diffraction patterns of POM whisker for the first time and obtained the crystal structure consisting of helical chains as shown in Figure 5a. But the electron diffraction data could not give us a stereochemically reasonable structure because of the multiple reflection effect. Then, by combining this structure model with the X-ray diffraction data, the reasonable crystal structure was obtained as shown in Figure 5b.

Table 1. Atomic Fractional Coordinates and Anisotropic Thermal Parameters of Polyoxymethylene after Refinement[a]

atoms	*x/a*	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(6)	0.157(10)b	0.559(18)	0.137(6)	0.04(2)	0.03(3)	0.02(2)	0.02(2)	0.0	0.0
C(5)	0.504(11)	0.734(27)	0.247(7)	0.05(3)	0.06(3)	0.01(3)	0.02(4)	0.0	0.0
C(4)	0.173(11)	0.677(25)	0.361(6)	0.06(4)	0.03(2)	0.03(3)	0.01(3)	0.0	0.0
O(3)	0.318(16)	0.808(10)	0.197(2)	0.07(2)	0.02(2)	0.03(2)	0.01(2)	0.0	0.0
O(2)	0.290(20)	0.510(10)	0.310(2)	0.08(3)	0.03(2)	0.02(2)	0.02(3)	0.0	0.0
O(1)	0.435(15)	0.833(6)	0.415(3)	0.05(3)	0.05(2)	0.02(2)	0.01(2)	0.0	0.0
H(6A)	−0.006	0.604	0.111	0.10	0.10	0.10	0.0	0.0	0.0
H(6B)	0.036	0.333	0.160	0.10	0.10	0.10	0.0	0.0	0.0
H(5A)	0.612	0.625	0.220	0.10	0.10	0.10	0.0	0.0	0.0
H(5B)	0.681	0.944	0.270	0.10	0.10	0.10	0.0	0.0	0.0
H(4A)	−0.038	0.510	0.386	0.10	0.10	0.10	0.0	0.0	0.0
H(4B)	0.136	0.847	0.336	0.10	0.10	0.10	0.0	0.0	0.0

[a] Numbering of atoms is referred to in Figure 5. The temperature factor T is given as $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] The number in parentheses is a standard error. For example, 0.157(10) is 0.157 ± 0.010.

Table 2. Comparison between Observed and Calculated Structure Factors of Polyoxymethylene Trigonal Crystal

hkl	$\lvert F_{obs}\rvert$	$\lvert F_{calc}\rvert$	*hkl*	$\lvert F_{obs}\rvert$	$\lvert F_{calc}\rvert$	*hkl*	$\lvert F_{obs}\rvert$	$\lvert F_{calc}\rvert$
				(a) Electron Diffraction				
0 0 3	11.41	6.29	0 0 9	8.73	11.97	0 0 18	9.33	10.90
1 0 0	68.09	81.78	1 0 3	6.30	4.95	1 0 4	16.83	5.31
1 0 5	38.02	28.47	1 0 8	12.35	5.01	1 0 9	8.07	8.62
1 0 10	12.74	2.09	1 0 13	12.51	7.53	1 0 18	7.44	8.39
1 1 0	26.11	36.57	1 1 3	3.80	3.80	1 1 5	46.98	26.53
1 1 8	13.43	3.86	1 1 10	6.85	6.19	1 1 13	15.46	10.07
2 0 0	37.22	24.34	2 0 3	6.78	5.39	2 0 4	11.76	4.72
2 0 5	27.87	28.52	2 0 8	10.99	7.81	2 0 9	7.35	2.72
2 0 10	11.72	2.53	2 0 13	10.49	7.97	2 0 18	3.17	3.27
2 2 0	8.85	5.39	2 2 3	3.66	2.85	2 2 5	1.70	7.12
2 2 8	4.74	5.28	2 2 10	3.18	4.20	3 0 0	20.00	0.98
3 0 3	5.18	5.18	3 0 4	7.40	1.47	3 0 5	15.21	15.84
3 0 8	8.41	6.08	3 0 9	3.43	0.51	3 0 10	8.22	4.42
3 0 13	4.11	4.14	3 0 18	1.15	0.43	4 0 0	8.67	3.68
4 0 5	6.54	5.85						
				(b) X-ray Diffraction				
1 0 0	70.38	70.04	1 0 3	3.08	3.04	1 0 4	3.47	3.49
1 0 5	37.51	37.18	1 0 6	1.84	1.32	1 0 8	10.00	9.63
1 0 9	9.91	9.86	1 0 10	4.20	5.21	1 1 0	14.82	14.90
1 1 1	3.85	4.08	1 1 3	6.36	7.21	1 1 4	8.93	9.09
1 1 5	30.74	30.69	1 1 6	1.93	1.62	1 1 8	13.71	13.66
1 1 9	3.54	3.15	1 1 10	9.04	10.23	1 1 13	14.99	15.78
1 1 14	3.19	3.19	1 1 15	1.26	2.17	2 0 0	4.10	4.29
2 0 1	3.45	3.26	2 0 3	7.57	7.57	2 0 4	8.69	9.18
2 0 5	24.52	24.85	2 0 6	3.01	2.67	2 0 8	14.50	14.43
2 0 9	1.79	1.64	2 0 10	11.58	11.95	2 0 13	13.43	13.30
2 0 14	1.43	1.76	2 0 15	1.90	2.72	2 1 0	7.55	7.92
2 1 1	4.22	4.73	2 1 2	2.39	2.06	2 1 3	8.40	7.58
2 1 4	4.76	4.73	2 1 5	11.85	11.85	2 1 6	1.15	1.24
2 1 8	11.78	11.93	2 1 10	11.44	10.55	2 1 13	6.98	6.63
2 1 15	4.45	4.33	2 2 0	7.81	8.34	2 2 1	2.31	1.86
2 2 2	2.90	3.33	2 2 3	5.95	6.41	2 2 8	5.74	6.31
2 2 10	5.21	5.64	3 0 0	8.80	9.20	3 0 1	3.38	2.50
3 0 2	2.10	1.79	3 0 3	7.61	7.28	3 0 4	2.88	2.85
3 0 5	5.53	5.31	3 0 6	1.94	2.50	3 0 8	10.19	9.84
3 0 10	9.32	9.12	3 0 13	3.49	3.29	3 0 15	6.57	5.16
3 1 0	8.41	7.41	3 1 1	2.28	2.22	3 1 2	3.73	4.02
3 1 3	6.92	6.86	3 1 8	5.90	5.42	3 1 10	5.29	5.00
3 2 0	3.31	2.97	3 2 2	4.22	3.74	3 2 3	4.32	4.22
4 0 0	3.77	4.86	4 0 2	2.37	2.40	4 0 3	4.17	4.34

This seems to be one good example showing a usefulness of combining the electron and X-ray diffraction methods in the structural analysis of crystalline polymer. Generally speaking, the extraction of initial structure model is one of the most difficult and most important stages of structure analysis of semicrystalline polymer. As mentioned above, the X-ray diffraction pattern of semicrystalline polymer sample consists of limited number of broad and diffuse reflections, making the application of direct method practically impossible in the process of speculating the initial structure model, though we experienced some lucky cases as exceptions.[5] On the other hand, the electron diffraction may give us many number of sharp reflections if the single crystal can be obtained for the corresponding polymer, allowing us to apply the direct method. Unfortunately, however, the thus-obtained initial structure model is not reasonable, even after refinement, because of the seriously large modification of electron diffraction intensities due to the multiple scattering effect. One idea is (i) to measure the electron diffraction pattern of the single crystal grown from the solution, for example, (ii) to get the initial structure model on the basis of the intensity data collected for many number of sharp reflections, (iii) to transfer this initial structure model to the X-ray structure analysis process, and (iv) to refine the struc-

ture by using the X-ray intensity data collected for the semicrystalline polymer sample. Of course, this combination must be made by assuming that the crystal structure is essentially the same in both the single crystal and the semicrystalline solid state.

Another ideal method for the structural analysis of POM whisker may be to measure the X-ray diffraction patterns by setting a tiny whisker needle on an X-ray goniometer head and by irradiating a synchrotron-sourced microfocused X-ray beam under vacuum to obtain the data of high signal-to-noise ratio with low background due to air scattering. We are now performing this type of experiment by using the synchrotron system Spring-8, Japan. A quite opposite approach to the structural analysis of POM whisker may be a utilization of the Rietveld method useful for the powdered sample.[12] But we are afraid of grinding the brittle POM whisker to obtain the homogeneously powdered sample because the sample might change to a highly fibrilled and/or non-single-crystalline state. As to the ED data themselves, a development of highly improved electron microscopic apparatus may allow us to collect more number of ED spots than that detected in the present paper. Anyway, we have still various possibilities of techniques for the analysis of crystal structure of POM whisker. We hope this paper will be a trigger to develop a technique to analyze the structure of any kind of polymer whisker.

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References and Notes

(1) Iguchi, M. *Polymer* **1983**, *24*, 915.
(2) Hayashi, K.; Okamura, S. *Makromol. Chem.* **1961**, *47*, 230.
(3) Chatani, Y.; Uchida, T.; Tadokoro, H. *J. Macromol. Sci., Phys.* **1968**, *B2*, 567.
(4) Kobayashi, M.; Itoh, Y.; Tadokoro, H.; Shimomura, M.; Iguchi, M. *Polym. Commun.* **1983**, *24*, 38.
(5) Tashiro, K.; Asanaga, H.; Ishino, I.; Tazaki, R.; Kobayashi, M. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 1667.
(6) Uchida, T.; Tadokoro, H. *J. Polym. Sci., Part A2* **1967**, *5*, 63.
(7) Takahashi, Y.; Tadokoro, H. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 123.
(8) For example: *Theory and Practice of Direct Methods in Crystallography*; Ladd, M. F. C., Palmer, R. A., Eds.; Plenum Press: New York, 1980.
(9) Altmare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.
(10) Dorset, D. L. *Structural Electron Crystallography*; Plenum Press: New York, 1995.
(11) Sun, H. *J. Phys. Chem. B* **1998**, *102*, 7338.
(12) For example: *The Rietveld Method*; Young, R. A., Ed.; Oxford University Press: New York, 1995.

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