Crystal Structure of Poly(ϵ-caprolactone)

Hengliang Hu and Douglas L. Dorset*

Electron Diffraction Department, Medical Foundation of Buffalo, Inc., 73 High Street, Buffalo, New York 14203

Received January 30, 1990; Revised Manuscript Received April 18, 1990

ABSTRACT: Electron diffraction intensities of two zones, (0*kl*) and (*hhl*), obtained from poly(ϵ-caprolactone) epitaxially crystallized on benzoic acid, were used for a quantitative crystal structure determination. Combining the data from epitaxially oriented samples with those obtained from solution-grown crystals permitted a nearly complete three-dimensional structure analysis to be carried out. The structural analysis demonstrates that the chains pack in the nonplanar structure in space group $P2_12_12_1$ proposed by Chatani et al. rather than an alternative planar chain conformation. The *R*-factor is 0.199.

Introduction

X-ray diffraction data from crystalline fibers are often utilized for structure determination of many linear polymers. Such determinations, however, are limited by the small number of diffraction intensities, which are also difficult to separate if several reflections have nearly the same reciprocal spacing. Furthermore, the overlapping of reflections in these patterns hampers the determination of accurate unit cell dimensions and space group symmetry. Because single microcrystalline preparations from most polymers can be grown, even along the direction normal to the chain length, electron diffraction techniques have proven to be a valuable alternative for determination of linear chain structures.[1-3] This is because of the large scattering cross section of matter for electrons, which permits collection of single-crystal diffraction data from individual microcrystals.

Two X-ray fiber diffraction studies on poly(ϵ-caprolactone) have been reported,[4,5] both in space groups $P2_12_12_1$ with essentially identical unit cell parameters but with appreciably different derived chain conformations and packings. However, the appearance of the X-ray fiber patterns from both studies does not seem to account for the two different structure models shown in Figure 1, since they are very similar to one another. Model I (Figure 1a) is based on a nonplanar zigzag conformation[4] and model II (Figure 1b) on a planar chain.[5] Electron diffraction from solution-grown microcrystals of poly(ϵ-caprolactone) was expected to distinguish between those two proposed models,[6] but because (*hk*0) diffraction patterns only provide a projection along the chain axes, the observed difference in calculated data is not very large, since many atoms are eclipsed. It was therefore difficult to conclude that one structure is to be preferred over the other.[6] Although data from epitaxially oriented samples[7] were latter collected to resolve the ambiguity by providing a projection onto the chain axes, the diffraction patterns from untilted samples indicated that the crystals were rather disordered so that intensities were found from more than one zone.[8] Further work on epitaxial crystallization on a trioxane substrate did not succeed in improving the quality of the diffraction patterns.

To solve a structure problem with electron diffraction data,[2,3] it is quite important to obtain good single crystals so that the ambiguities characteristic of fiber diffraction techniques are overcome. To achieve this for poly(ϵ-caprolactone), we tried several possible substrates for epitaxial growth and utilized controlled annealing to increase the crystalline perfection. After improvement of the crystallization technique, we obtained data yielding structural results showing that the nonplanar model[4] is more reasonable than the other,[5] as will be described below.

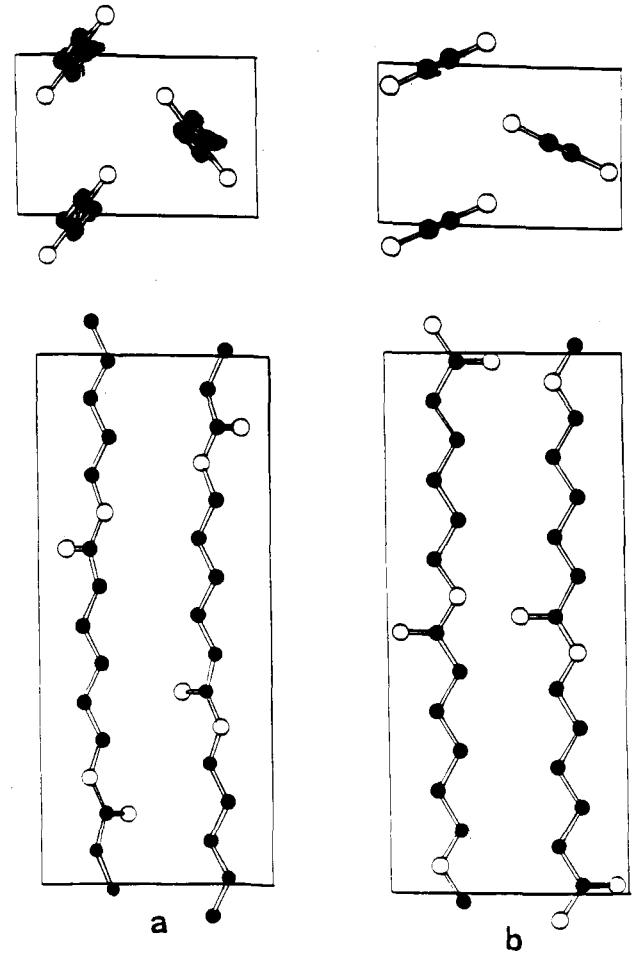


Figure 1. Two alternative models for the crystal structure of poly(ϵ-caprolactone) suggested by previous fiber X-ray studies: (a) the nonplanar conformation, model I;[4] (b) the planar conformation, model II.[5] The atomic coordinates from the previous publications were used for our structure analysis.

Materials and Methods

Commercially available poly(ϵ-caprolactone)s from Scientific Polymer Products, Inc. (Sp^2, Ontario, NY), and Aldrich Chemical Co., Inc. (Milwaukee, WI), were made up as dilute chloroform solutions. The weight-average molecular weight, M_w, of the Sp^2 product is about 14 600; the corresponding number-average molecular weight, M_n, is 9300.

Microcrystals that were grown from a drop of solution dried on the carbon-coated grid produced (*hk*0) electron diffraction

0024-9297/90/2223-4604$02.50/0

patterns. Other zones were obtained from epitaxially oriented specimens produced in the following way: After a few drops of the chloroform solution was evaporated on the mica sheets and a substrate, e.g., benzoic acid, trioxane, or naphthalene, was added, the epitaxial crystals were obtained by comelting the two components and cooling, following the methodology described before.[9] The only procedural change for poly(ϵ-caprolactone) is that, before removing the grids from the substrate, epitaxially crystallized polymer was annealed at 50 °C in the presence of the nucleating sustrate for 30 min on a Mettler FP82 hot stage, a condition found also to improve the crystallinity of epitaxially oriented polyethylene.[3]

Selected area electron diffraction patterns obtained at 100 kV with a JEOL JEM-100CXII electron microscope were recorded on Kodak DEF-5 X-ray film. As usual, precautions were taken to minimize radiation damage to the specimens.[10] The camera length is calibrated with a gold Debye–Scherrer diagram. Measurements of interpeak spacings on electron diffraction patterns were made with a film-reading device manufactured by Charles Supper, Inc.

Because of the arciform density distribution of recorded diffraction peaks, it is necessary to measure the integrated intensities. For this purpose, we employed different slit heights on a Joyce-Loebl MK III C microdensitometer and twice scanned each reflection spot in mutually perpendicular directions. The product of two peak-height intensities from different scans of a single reflection was used as the integrated intensity. There is no Lorentz correction.

Kinematical structure factors, F_{hkl}, were computed in the usual way; i.e.

$$F_{hkl} = \sum_j f'_j(\mathbf{s}_{hkl}) \exp(i2\pi \mathbf{r}_j \cdot \mathbf{s}_{hkl}) \quad (1)$$

where f'_j is the Doyle–Turner electron form factor[11] for atom j corrected for isotropic thermal motion, $\mathbf{r}_j$ is the atomic position in the unit cell, and $\mathbf{s}_{hkl}$ is the reciprocal vector for reflection hkl. Isotropic thermal parameters used as $B_C = 6.0$ Å, $B_O = 6.0$ Å^2, and $B_H = 8.0$ Å^2.

Because of the multilayer crystal morphology in epitaxial and solution-growth crystallization of polymers,[2,3] incoherent multiple scattering can be a major perturbation of reflection intensity. Correction for this scattering phenomenon was carried out as described previously.[3,12]

Thus, several sets of intensity data, from different zones and approximation of kinematical scattering conditions, were obtained. Since some reflections with the same indices might appear in several zones, a least-squares optimization could be used for obtaining a set of three-dimensional data, also following a procedure described earlier.[3]

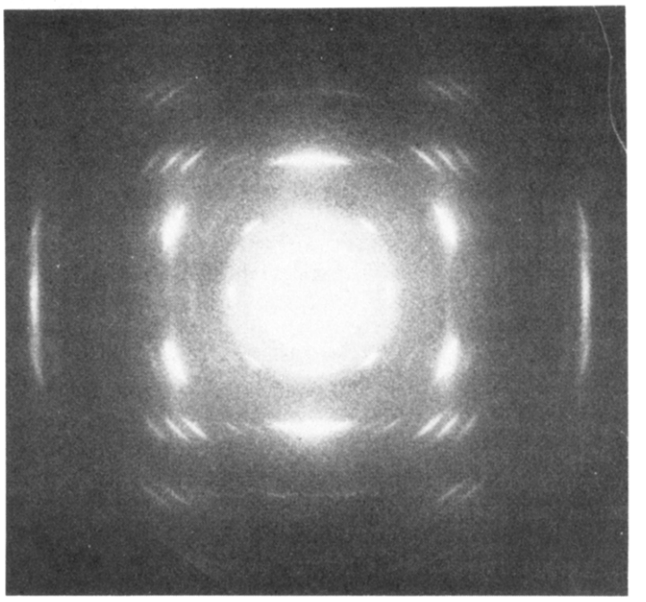
The usual crystallographic R-factor

$$R = \{\sum ||F_o| - k|F_c||\} / \sum |F_o| \quad (2)$$

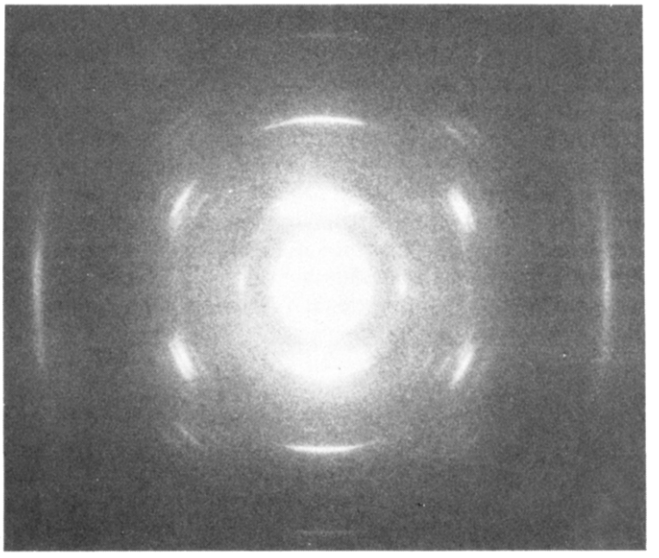
was used to estimate the fitting of the structure model to observed data, where k is a scaled factor such that $k\sum|F_c| = \sum|F_o|$.

Results

In our attempts to use different organic substrates for epitaxial growth of crystals, only samples oriented on benzoic acid (BA) were adequately ordered to diffract as spot patterns with sufficient resolution, and thus the results discussed here imply the use of this substrate. With employment of the Aldrich product, several kinds of diffraction patterns were obtained from untilted specimens of epitaxially grown polymer crystals, and referral to the Sp^2 product, which apparently is a purer material, allows us to identify the pattern that corresponds to the poly(ϵ-caprolactone) examined earlier.[8,9] (This is because the diffraction pattern from the impurity violates the extinction conditions for $P2_12_12_1$.) The diffraction pattern in Figure 2a, therefore, is the $0kl$ net for the polymer, and films of this type from samples prepared from either source could be measured for collection of intensity data.



(a)



(b)

Figure 2. (a) ($0kl$) zone diffraction pattern from poly(ϵ-caprolactone) crystal epitaxially oriented on benzoic acid, obtained from an untilted sample. (b) (hhl) zone diffraction pattern. The specimens are tilted at 30–35°. (Note that "hhl" means an hkl zone where the Miller indices have the relationship $h \equiv k$.)

At a specimen tilt angle of 30–35°, an (hhl) single-zone pattern from poly(ϵ-caprolactone) could be obtained (Figure 2b). (Again signs of a polymeric impurity are observed in the Aldrich sample. The Sp^2 material can be used to obtain useful diffraction data.) Measured unit cell parameters determined from electron diffraction patterns are quite consistent with the orthorhombic unit cell of poly(ϵ-caprolactone) determined from X-ray data;[4] i.e.

$$a = 7.48 \pm 0.02 \text{ Å}$$
$$b = 4.98 \pm 0.02 \text{ Å}$$
$$c = 17.26 \pm 0.03 \text{ Å}$$

For crystal structure analysis based on the observed data, we utilized the average intensity of several reflections, which are symmetry equivalent. Correction of the zonal data for n-beam dynamical scattering did not produce any significant improvement in the residual R, after using

various crystal thicknesses in the model calculation. Because of the small projected cell length for epitaxial crystals, elastic bend distortions should not have a major influence on the intensity values.[8,13,14]

For the incoherent multiple-scattering correction, we were required to choose the respective conformational models in Figure 1 as starting structures. When we started with the (0*kl*) zone, the calculated electron diffraction data based on the nonplanar conformation model I closely matched the observed data without consideration of *n*-beam dynamical scattering and crystal-bending corrections. The *R*-factor is 0.263. The incoherent multiple scattering for the (0*kl*) zone also has a small influence on the observed intensities,[2] since, after the correction, the *R*-factor is 0.250. From the planar molecular model II, the *R*-factor before the incoherent scatter correction is 0.673 and is unchanged after correction for incoherent scattering. Similarly, the respective *R*-factors before and after incoherent scatter correction for the (*hhl*) zone for both models also were not very different. The results obviously demonstrate that model I is more reasonable than model II.

After the intensity data from (0*kl*) and (*hhl*) zones were combined to produce the three-dimensional set, the best agreement of that data set to calculated data from model I again proved that the epitaxial poly(ϵ-caprolactone) crystals preferentially pack in the nonplanar chain structure. The *R*-factor for the nonplanar chain, model I, is 0.213, compared to the $R = 0.458$ for model II. To continue the three-dimensional structure determination, we combined these data from (0*kl*) and (*hhl*) with the observed (*hk*0) intensities[6] (again using the scaling procedure in ref 3 to obtain a normalized set, assuming that the kinematical model is correct). From this set of 47 reflection intensities, the *R*-factors for models I and II are 0.199 and 0.387, respectively (Table I).

Discussion

From the above results, comparison of *R*-factors from the three data sets (Table II) showed that a major difference in the two structural models is expressed by the (0*kl*) intensity data and there is only a small difference found with the (*hk*0) data, consistent with previous analyses. However, we tried to find the reasons that would have caused two different crystal structures to be determined from essentially the same fiber X-ray diffraction pattern. Using Table I to locate the reflections that showed the biggest discrepancies between $|F_o|$ and $|F_c(II)|$, we find that most (designated in Table I with an asterisk) were not included in the study by Bittiger et al.[5] Other observed reflections used in their fiber study (marked by Δ) still were significantly different from the calculated values.[5] The study of Chatani et al.,[4] on the other hand, included more than half of the reflections marked by an asterisk in Table I, leading to the correct result, the nonplanar conformation model I. Although, in many cases, it may be difficult to obtain complete three-dimensional intensity data by electron diffraction—perhaps for different reasons than those experienced in fiber X-ray studies—one should, nevertheless, make sure that the diffraction data have included most of structure-sensitive reflections, to avoid a spurious structure determination. The study outlined here has included two orthogonal projections of the crystal structure to provide views along and onto the polymer chain axes. In terms of the orthorhombic methylene subcell, all of the intense reflections were recorded in our diffraction experiment, enabling the determination to be complete.

Table I
Comparison of Combined (0*kl*), (*hhl*), and (*hk*0) Observed Structure Factor Data to Calculated Kinematical Data $|F_c(I)|$ from Model I and $|F_c(II)|$ from Model II[a]

hkl	$\|F_o\|$	$\|F_c(I)\|$	$\|F_c(II)\|$
004	22.74	18.89	9.46*
006	5.74	2.27	12.77*
008	10.28	9.76	11.61
0,0,10	7.68	7.53	9.33
0,0,12	4.00	1.64	7.98*
0,0,14	23.91	18.96	7.13*
011	2.00	6.87	22.70Δ
013	17.49	22.42	18.51
017	44.54	68.02	27.86*
018	9.27	7.40	5.33
0,1,13	6.32	5.32	0.94*
0,1,14	15.40	17.49	25.58*
020	58.35	53.17	99.18Δ
021	33.27	18.51	3.37*
023	4.47	8.71	7.82
024	7.07	11.38	0.57*
026	16.37	15.45	1.72*
027	17.87	22.20	22.80
028	11.70	6.90	2.55*
029	0.10	0.25	7.95*
0,2,10	5.00	5.78	1.08*
0,2,11	0.50	0.79	5.17*
0,2,13	0.10	0.33	3.35*
0,2,14	5.90	3.01	3.36
031	9.20	11.52	3.82*
037	14.20	18.10	11.25
038	10.02	11.70	4.06*
110	182.16	177.55	201.45
111	45.64	39.90	16.12*
117	42.17	38.10	40.32
1,1,14	14.63	10.65	6.35*
220	50.65	34.62	61.85
221	14.20	11.87	2.49*
227	21.71	15.83	19.98
200	151.90	175.37	140.34
210	44.50	46.12	35.38
120	27.40	22.88	16.64
310	76.20	58.36	43.24
400	52.90	40.60	26.20
320	22.80	23.17	18.09
410	11.40	9.61	19.97
130	36.10	17.17	41.30
230	11.40	8.42	11.02
420	16.80	17.27	12.45
510	21.70	16.43	8.07
330	11.40	4.45	23.81
520	10.00	11.59	14.40
R-factor		0.199	0.387

[a] Asterisks indicate values whose reflections had the biggest discrepancies between $|F_o|$ and $|F_c|$. Superscript deltas indicate other observed reflections used in Bittiger et al.'s study that were significantly different from the calculated values.

Table II
Comparison of *R*-Factors for Three Data Sets with Different Numbers of Zones[a]

R-factor	set 1	set 2	set 3
model I	0.250	0.213	0.199
model II	0.673	0.458	0.387
R(II)/*R*(I)	2.69	2.15	1.94

[a] Set 1, (0*kl*); set 2, (0*kl*) + (*hhl*); set 3; (0*kl*) + (*hhl*) + (*hk*0).

The structure favored in this determination should not be surprising since linear chain esters are anticipated to have a nonplanar geometry in the region of the linkage atoms. One can refer to the crystal structures of *n*-propyl stearate[15] or ethylene bis(11-bromoundecanoate),[16] for example, for which the chain twisting is more localized than in the nonplanar model used for this polyester. In fact,

in the cited diester crystal structure, the twisting is extreme enough to form a gauche–trans–gauche^{-1} linkage of the chain atoms in the region of the ethylene moiety. Another advantage of the model constructed by Chatani et al.[4] over the planar chain packing[5] (Figure 1) is that the carboxyl groups do not lie at the same levels along the molecular axes for neighboring chains. As shown by Aleby et al.,[17] symmetric long-chain wax esters generally pack in layers with inclined molecular axes to avoid steric crowding of adjacent ester linkages. Only asymmetric esters can pack in rectangular layers of that type adopted also by this polymer. For the polyester, however, for which no layer end-plane constraints are imposed (due to the anticipated folds at a lamellar surface), an antiparallel packing with a mutual shift of adjacent chains will effectively lower the internal energy of the stem region.

Acknowledgment. Research described in this paper was funded by a grant from the National Science Foundation (DMR8610783), which we gratefully acknowledge. We thank Dr. J. C. Wittmann for suggesting the annealing of the samples to improve crystalline perfection.

References and Notes

(1) Moss, B.; Dorset, D. L. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1919.
(2) Hu, H.; Dorset, D. L.; Moss, B. *Ultramicroscopy* **1989**, *27*, 161.
(3) Hu, H.; Dorset, D. L. *Acta Crystallogr.* **1989**, *B45*, 283.
(4) Chatani, Y.; Okita, Y.; Tadokoro, H.; Yamashita, Y. *Polym. J.* **1970**, *1*, 555.
(5) Bittiger, H.; Marchessault, R. H.; Niegisch, W. D. *Acta Crystallogr.* **1970**, *B26*, 1923.
(6) Brisse, F.; Marchessault, R. H. *Fiber Diffraction Methods*; French, A. D., Gardner, K. H., Eds.; ACS Symposium Series 141; American Chemical Society: Washington, DC, 1980; p 267.
(7) Wittmann, J. C.; Manley, R. St. J. *J. Polym. Sci., Polym. Phys.* **1977**, *15*, 1089.
(8) Moss, B.; Dorset, D. L.; Wittmann, J. C.; Lotz, B. *J. Macromol. Sci., Phys.* **1985–1986**, *B24*, 99.
(9) Wittmann, J. C.; Hodge, A. M.; Lotz, B. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 2495.
(10) Dorset, D. L. *J. Electron Microsc. Tech.* **1985**, *2*, 89.
(11) Doyle, P. A.; Turner, P. S. *Acta Crystallogr.* **1968**, *A24*, 390.
(12) Cowley, J. M.; Rees, A. L. G.; Spink, J. A. *Proc. Phys. Soc.* **1951**, *A64*, 609.
(13) Cowley, J. M. *Acta Crystallogr.* **1961**, *14*, 920.
(14) Dorset, D. L. *Acta Crystallogr.* **1980**, *A36*, 592.
(15) Aleby, S. *Acta Chem. Scand.* **1968**, *22*, 3146.
(16) Dorset, D. L.; Hybl, A. *Science* **1972**, *176*, 806.
(17) Aleby, S.; Fischmeister, I.; Iyengar, B. T. R. *Lipids* **1971**, *6*, 421.