Macromolecules **1994,** *27,* 5877-5881 **5877**

Structural Study on X-ray Diffraction Curves Using the Crystallite Structure Factor for Polymers

Hiroshi Kusanagi* and Masaru Kashima

Unitika Research Laboratories Inc., Kozakura, Uji, Kyoto 611, Japan

Received August 18, 1993; Revised Manuscript Received March 7, 1994[*]

ABSTRACT: For the X-ray structure analyses of polymers, a concept of the crystallite structure factor was defined, in which the structure factors are not only calculated on a unit cell but also summarized over the whole of a crystal. Accordingly, it has been found that X-ray diffraction intensities are varied with the shape and size of small crystallites as well as with the atomic coordinates. This method gave the new structural information on the crystalline region of synthetic fibers such as nylon and polyester.

Introduction

In the X-ray analyses of polymers the diffraction spots are broad and diminish rapidly with increasing diffraction angle.[1,2] This experimental feature originates from the fact that polymer crystalline regions coexist with the amorphous ones: the size of the crystallites is small and yet contains a considerable number of irregularities. Therefore, the X-ray diffraction theory based on single crystals of low-molecular-weight substances is not applicable in the explicit treatment of polymer samples. There are a few studies in this direction.[3-6] In 1948, Wallner found that the peak position of an X-ray photograph shifts from the predicted position when the crystallite size is small and proposed a method on the basis of the fundamental theory of X-ray diffraction.[3,4] Kaji successfully used this method to determine the crystallite size along the fiber axis of Nylon 6.[6] Nowadays, a computer program is available for the simulated predictions of the X-ray powder and fiber patterns of the crystals.[7] In this study, we will report an approach to this problem, i.e., an appropriate theory for polymer crystals, by taking not only the crystallite size but also the crystallite shape as the parameters to be determined. In addition, our method was successfully applied to the structure analyses of some synthetic fibers and monofilaments with small crystals.

Experimental Section

Poly(ethylene terephthalate) (PET) monofilaments, commercially available, were annealed at 135 °C for 9 days in steam. Thereafter, the mechanical strength was measured using a Tensilon tester. The breaking strength (340 MPa) of the original monofilament reduced to 84 MPa after annealing treatment. Moreover, the intrinsic viscosity $[\eta]$ of PET was measured in phenol/tetrachloroethane (=5/5) solution at 25 °C. According to Conix's equation,[8] the number-averaged molecular weight M_n was calculated from $[\eta]$. As a result, M_n of monofilaments was found to reduce from 20 500 to 11 200 during the steam annealing. For the structural consideration on the change of their mechanical properties, X-ray diffraction curves of these uniaxially-oriented samples were measured by an X-ray diffractometer (Ni-filtered Cu Kα radiation).

On high-crystalline Nylon 66 multifilaments, which were produced by the high-speed spinning process, the crystallite structure was also analyzed. Nylon 66 chips of Monsanto Co., M_n = 12 000, were used. The fibers were spun at 270 °C with the nozzle plate of four spinneret orifices and were directly taken upon the goddet roller. A takeup velocity of 10 km/min gave an X-ray diffraction curve sharp enough to analyze the fiber structure.

Theoretical Section

According to the dimension of crystallites, X-ray diffraction formulas are sorted to two kinds, (A) and (B), as follows.

(A) X-ray Diffraction Intensity by an Infinitely Large Crystal. A crystal of infinite size diffracts only in discrete diffraction corresponming to discrete points in reciprocal space. Diffraction intensity I of a point with the hkl Bragg reflection indices is given by

$$I(hkl) = KmPLA|F(hkl)|^2 \tag{1}$$

where K, m, P, L, and A are the scale factor, multiplicity, polarization factor, Lorentz factor, and absorption factor, respectively. And the unit cell structure factor F is also given by

$$F(hkl) = \sum f_j \exp[2\pi i(hx_j + ky_j + lz_j)] \tag{2}$$

where x_j, y_j, and z_j are the fractional coordinates of the jth atom in the unit cell and f_j is the atom scattering factor.

(B) X-ray Diffraction Intensity by a Finitely Large Crystal. When the crystal has the finite crystal size, the diffraction takes place in extended regions surrounding the Bragg diffraction points. The broadening of diffraction points can be represented by two different kinds of equations.

(i) Wallner's Method.[3,4] Diffraction intensity function I corresponding to any point (ξ,η,ζ) in the reciprocal space is given by

$$I(\xi,\eta,\zeta) = KmPLA|F(\xi,\eta,\zeta)|^2|G(N_a,N_b,N_c)|^2 \tag{3}$$

where F is the unit cell structure factor and G is the Laue function which includes the crystal size factors and can denote the broadening of the reflection.

$$F(\xi,\eta,\zeta) = \sum f_j \exp[2\pi i(\xi x_j + \eta y_j + \zeta z_j)] \tag{4}$$

$$G(N_a,N_b,N_c) = \prod [\sin(\pi\xi N_a)/\pi\xi, \sin(\pi\eta N_b)/\pi\eta, \sin(\pi\zeta N_c)/\pi\zeta] \tag{5}$$

In eq 5, the crystal size is given by three numbers N_a, N_b, and N_c of the unit cells stacked along the a, b, and c crystal axes.

Basically, Wallner's method can treat only the small single crystals. On the other hand, polymer samples such as synthetic fibers are usually uniaxially-oriented and give X-ray fiber diagrams that correspond to the rotation photographs of single crystals. Therefore, the application

---

[*] Abstract published in *Advance ACS Abstracts,* August 15, 1994.

0024-9297/94/2227-5877$04.50/0

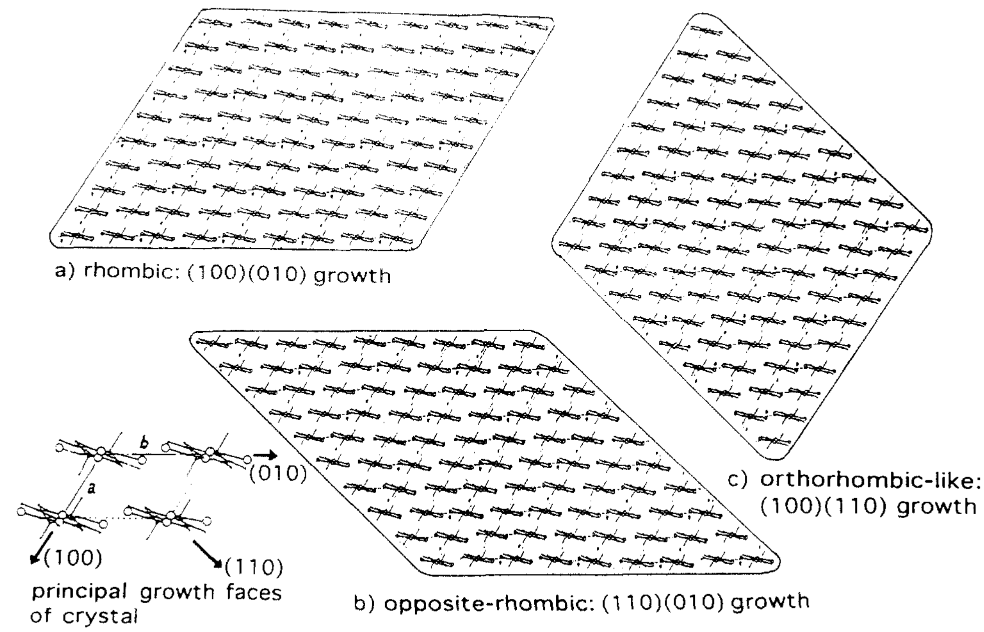

Figure 1. Schematic drawings of PET crystals with different shapes (*c*-axis projection): (a) rhombic shape with (100) and (010) growth faces; (b) opposite-rhombic shape with (110) and (010) growth faces; (c) orthorhombic shape with (100) and (110) growth faces.

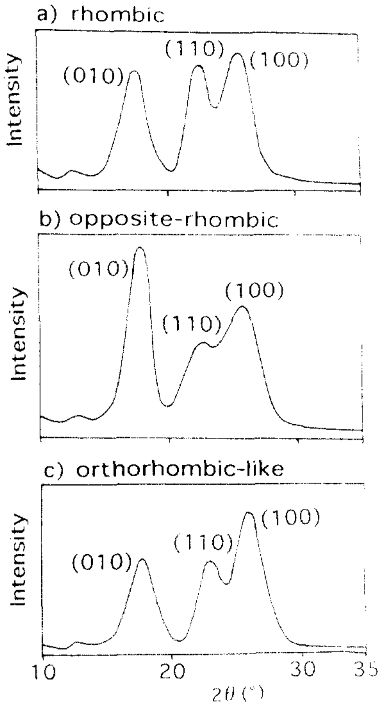

Figure 2. Calculated equatorial X-ray diffraction curves for PET crystal with different shapes: (a) rhombic; (b) opposite-rhombic; (c) orthorhombic.

of Wallner's method is restricted to only the meridian diffraction curve of fiber samples such as Nylon 6.[3-5]

(ii) Present Method.[9] Our purpose is to derive the method applicable to the X-ray diffraction curve along the layer lines of such X-ray fiber diagrams, of course, including the meridian diffraction curve. Here, we adopted two ideas: (i) the Laue function is incorporated into the structure factor's term, and (ii) the Ψ-averaged molecular structure factor reported by Tadokoro[10] is developed to the stage of the crystal. Consequently, a concept of the crystallite structure factor for fibrous polymers is defined, in which the structure factors are not only calculated on a unit cell but also summarized over the whole of a crystal.

Thereby, for the uniaxially-oriented samples (fibrous polymers), the X-ray diffraction intensity $I(2\theta,l/c)$ along the lth layer line is calculated as a function of the reciprocal space cylindrical coordinates $(R,\Psi,l/c)$ as

$$I(2\theta,l/c) = KPLA\langle|F(R,\Psi,l/c)|^2\rangle_\Psi \tag{6}$$

and

$$\langle|F(R,\Psi,l/c)|^2\rangle_\Psi = \sum f_j f_{j'} J_0(2Rr_{jj'}) \exp[2\pi i l(z_j - z_{j'})/c] \tag{7}$$

$$r_{jj'}^{\,2} = (x_j - x_{j'})^2 + (y_j - y_{j'})^2 \tag{8}$$

$$R = \sqrt{(2(\sin\theta)/\lambda)^2 - (l/c)^2} \tag{9}$$

where $\langle|F(R,\Psi,l/c)|^2\rangle_\Psi$ is defined as the Ψ-averaged structure factor of a crystallite, i.e., the crystallite structure factor, instead of the above molecular structure factor. Multiplicity m is dropped from eq 6, because of the Ψ averaging. In eqs 7–9, l and c are the number of layer lines and the fiber period in the X-ray fiber diagram, x_j, y_j, and z_j are the Cartesian coordinates of the jth atom in the crystallite, N is the number of total atoms contained in the crystallite, and J_0 is the 0th order Bessel function. Equation 9 is derived by substituting the Bragg's condition $2d \sin\theta = \lambda$ into the equation $(1/d_{(\xi,\eta,\zeta)})^2 = R^2 + (l/c)^2$ representing a reciprocal lattice point on the lth layer line.

By means of these equations, (6)–(9), the calculated intensity of the lth layer line could be directly compared with the observed diffraction curves along the diffraction angle 2θ. A software program is derived for the computer workstation, which can perform the above calculation on the crystal composed of the maximum 50 000 atoms. For example, it makes it possible to calculate a crystallite of polyethylene with three dimensions 103 Å × 97 Å × 101 Å composed of about 43 700 carbon atoms.

Application and Discussion

PET Fibers. First, we examined the relation between the calculated diffraction curves and the crystallite shape of PET using the present method. The crystal structure of PET has a triclinic unit cell with a = 4.56 Å, b = 5.94 Å, c (fiber axis) = 10.75 Å, α = 98.5°, β = 118°, and γ = 112°.[11] With respect to crystal growth for the directions

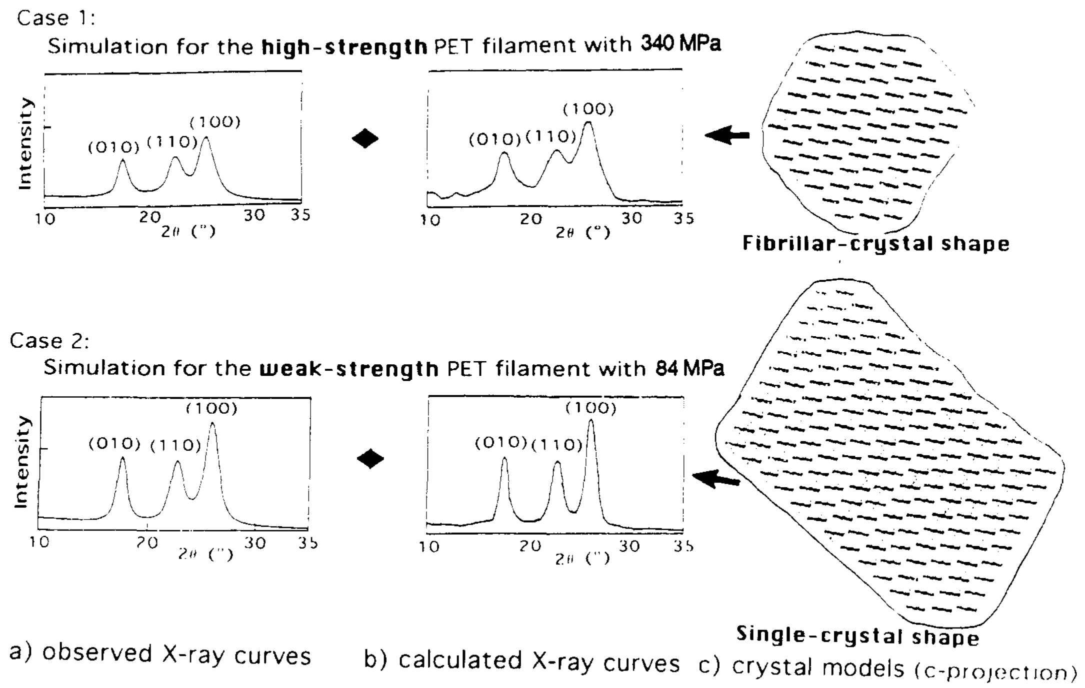

Figure 3. Effect of the crystal size and shape of PET on equatorial X-ray diffraction curves: (a) observed X-ray curves; (b) calculated X-ray curves; (c) assumed crystal models. Case 1 and case 2 denote the original and annealed PET monofilaments, respectively.

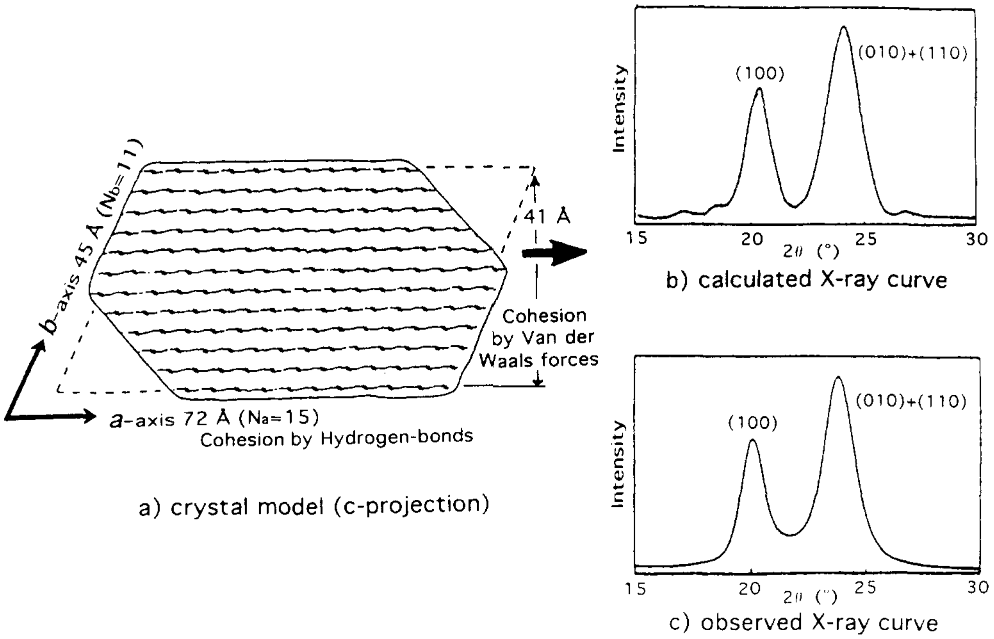

Figure 4. (a) Scheme of the Nylon 66 crystal existing in the fiber produced by means of the spinning speed 10 km/min. (b) Its calculated X-ray curve. (c) Observed X-ray curve.

normal to the fiber axis, principal shapes of PET crystal are grouped to three types, as shown in Figure 1. Crystals with (100) and (010) growth faces may be called rhombic crystallite; the remaining two are the opposite-rhombic crystallite with the (110) and (010) growth faces and the orthorhombic-like crystallite with the (100) and (110) growth faces. For these three crystallite models with the nearly same size composed of 90 molecular chains in the a–b sectional plane, X-ray diffraction curves on the 0th (equatorial) layer were calculated at 2θ = 10–35° using eqs 6–9. In the structure factor calculations, (i) unit cell dimensions and atomic coordinates by Bunn[11] were used, (ii) the isotropic temperature factor was assumed to be $B = 8$ Å^2, and (iii) hydrogen atoms were neglected. Each curve of this 2θ range shows two peaks which correspond to the intermolecular distances. There are large differences in the calculated diffraction intensities among these three curves, as shown in Figure 2. It may be seen for the first case of polymers, due to the diffraction theory, that the X-ray diffraction intensity is affected by the crystallite shape. But, it should be emphasized that the effect of crystallite shape is large when the crystallite size is small and becomes small with the increase of crystallite size. This phenomenon is directly attributed to the small numbers $N_{(hk0)}$ of stacking diffraction planes normal to the X-ray diffraction direction. Here, effective $N_{(hk0)}$ is calculated from the relation $N_{(hk0)}d_{(hk0)} = D_{(hk0)}$ and Bragg's equation $2d \sin\theta = \lambda$, where N is the stacking number of diffraction planes, d is the distance among the diffraction planes, and D is the virtual crystallite dimension in the ($hk0$) direction. Therefore, the diffraction intensity of a large Bragg angle, 2θ = ~90°, is not too affected even if the crystallite size is small, because of large numbers of diffraction planes $N_{(hk0)}$ in proportion to $1/d_{(hk0)}$. The morphology of real crystals existing in PET fibers may be different from these three principal shapes. This situation will be examined next.

Next, we analyzed simultaneously effects of both shape and size of a crystallite actually existing in PET monofilaments. Figure 3a (upper and bottom) shows the observed diffraction curves on the equator of both monofilaments before and after annealing treatments, respectively. For both observed curves, we searched the crystallite models of PET, whose calculated diffraction curves give good agreements with the observed ones. Taking into account the basic relation between the crystal shape and diffraction curve profile as shown in Figures 1 and 2, the shapes and sizes of crystallite models were varied, in trial-and-error procedure, so that the calculated intensities (Figure 3b) agreed with the observed ones. As a result, reasonable crystal models were obtained, as shown in Figure 3c. At the present stage of this work, the distribution of crystal size and shapes was not considered for the clarity of the size and shape effects on the diffraction curves. Their distributions will be expected to cause further broadening of the diffraction peaks. The crystallites of the unannealed PET are of small size and shape near a circular section; i.e., the original monofilament of high strength has the fibrillar-like crystallite. On the other hand, the crystallite of the annealed PET monofilament has further grown for the (100) and (010) principal faces, and thereby has changed to the foldlike crystallite.[12] These recrystallizations from the extended chain structure to the chain-fold crystal must be accelerated during the steam annealing at 135 °C. From the view point of the chemical (the reduction of M_n) and physical (the fold-chain crystal) structures, the present study has clarified the reason that the breaking strength of monofilaments dropped from 340 to 84 MPa during the annealing treatment.

Nylon 66 Fibers. An equatorial X-ray diffraction curve of Nylon 66 fibers, which were produced by a high-speed melt-spinning procedure and have a high crystalline structure, was simulated by using the present method. Here, the unit cell structure of Nylon 66 is also fixed to that of Bunn[13] (a = 4.9 Å, b = 5.4 Å, c (fiber axis) = 17.2 Å, α = 48.5°, β = 77°, and γ = 63.5°) and the shape and size of the crystallite were varied in the trial-and-error procedure. A crystal model as shown in Figure 4a gives the calculated diffraction curve of Figure 4b, which is in agreement with the observed one of figure 4c. The first and second peaks corresponding to (100) and (010) + (110) reflections contain the structural information along the hydrogen bond and van der Waals molecular arrangements, respectively. In the spinning speed of 10 km/min, the dimensions of the crystals existing in the fibers are 72 and 41 Å for both the direction of the hydrogen bond and the van der Waals stacking, respectively. This large anisotropy for both directions is understandable from the consideration that the difference of cohesive energies (~5 and ~0.5 kcal/mol) along both directions reflects on the driving force of crystal growth, since no external driving force acts on the yarn during the crystallization process of high-speed melt spinning.

The second peak composed of (010) and (110) reflections has an approximately symmetrical profile in the observed and calculated curves of Figure 4. This fact directly relates to Bragg spacings $d_{(hkl)}$ due to the unit cell constants decided by Bunn, d_{010} = 3.69 Å and d_{110} = 3.64 Å. The change of peak profile due to the (010) and (110) reflections was examined when the unit cell constants were varied[14] but the crystal shape remained the same; d_{010} = 3.75 Å and d_{110} = 3.50 Å. Figure 5a shows that the (010) and (110) reflections have the double peaks when the difference Δd between d_{010} and d_{110} is rather large, ~0.25 Å. On the other hand, when these two reflections have rather small Δd, ~0.05 Å, such as Bunn's unit cell, they may form an approximately symmetrical single profile, as shown in Figure 5b. Moreover, this situation clearly relates to the rather large half-widths (from a small crystal) and the similar peak heights (from a strange coincidence), which are suggested from Figure 5a.

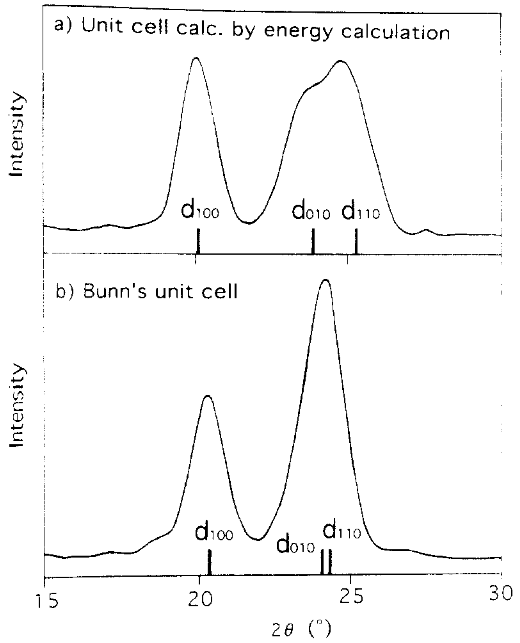

Figure 5. Relation between the X-ray diffraction curves and the unit cell constants: (a) unit cell calculated with energy calculation;[14] (b) unit cell decided with X-ray analysis.[13] The size and shape of crystals are the same in both. 2θ values corresponding to Bragg $d_{(hkl)}$ spacings are indicated.

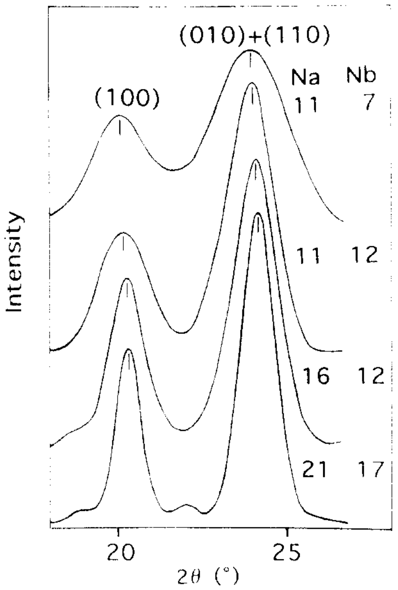

Figure 6. Calculated X-ray diffraction curves of Nylon 66 crystals with different crystallite sizes.

Figure 6 shows the variation of calculated X-ray diffraction curves when the crystallite sizes D_p of the a and b axes are varied. With the decrease of crystallite sizes D_p, not only does the width of the diffraction peaks become broad but also the peak positions shift to a lower diffraction angle. This phenomenon reveals that the d spacings are overestimated when the broad peaks are used for their calculations (Figure 7). The crystallite sizes D_s

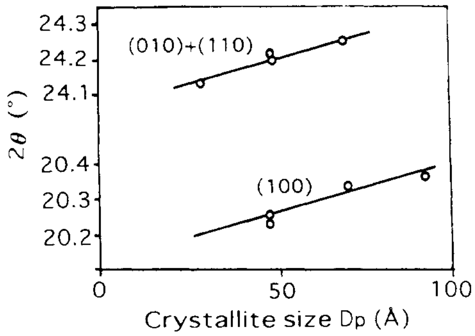

Figure 7. Diffraction peak positions versus crystallite size.

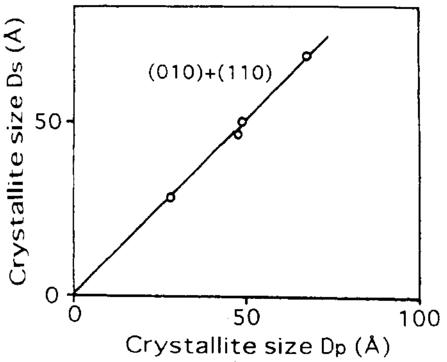

Figure 8. Correlation of crystallite sizes estimated by Scherrer and present methods.

were also estimated from the width of calculated X-ray diffraction peaks using the Scherrer method.[15,16] Figure 8 shows the relation between crystallite sizes D_p (the present method) and D_s (Scherrer method). A good agreement is obtained among them.

Finally, it was found that the real crystals existing in nylon or polyester fibers are insufficiently small to ignore the effect of crystallite shape and size.

Conclusion

The proposed method makes it possible to analyze the crystal structure of real crystallites which actually exist in synthetic fibers and plastics, and thereby the structure–property relation of polymer materials will be considered in more detail. Accordingly, we renew the importance of the concept of the crystallite structure factor in the X-ray analyses of polymers.

After completion of this paper, we noticed that a similar theoretical X-ray treatment of the crystal with the finite size had been studied independently by Iannelli and Immirzi.[17] Their method aims at the crystal structure determination and refinement of polymers, while our method is concerned with a different purpose, as studied in this work, and cannot be applicable to the crystal structure refinement. Our concept of the crystallite structure factor was first reported at the Annual Meeting of the Polymer Society of Japan in September 1987, under the title "A method for the calculation of X-ray diffraction intensity on polymers with small crystallite size" (*Polym. Prepr. Jpn* **1987**, *36*, 2327). A developed method was also reported at the Annual Meeting of the Polymer Society of Japan in December 1991.[9]

References and Notes

(1) Tadokoro, H. *Structure of Crystalline Polymers*; Wiley-Interscience: New York, 1979; p 37.
(2) Kusanagi, H.; Tadokoro, H.; Chatani, Y. *Macromolecules* **1976**, *9*, 531.
(3) Wallner, L. G. *Monatsh. Chem.* **1948**, *79*, 86.
(4) Wallner, L. G. *Monatsh. Chem.* **1948**, *79*, 279.
(5) Vainshtein, B. K. *Diffraction of X-rays by Chain Molecules*; Elsevier: Amsterdam, 1966; p 257.
(6) Kaji, K.; Sakurada, I. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1491.
(7) Blundell, D. J. *Polymer* **1992**, *33*, 3773.
(8) Conix, A. *Makromol. Chem.* **1958**, *26*, 226.
(9) Kusanagi, H.; Kashima, M.; Ishimoto, A. *Polym. Prepr. Jpn.* **1991**, *40*, 3904.
(10) Tadokoro, H. *Structure of Crystalline Polymers*; Wiley-Interscience: New York, 1979; p 431.
(11) Daubeny, R. de P.; Bunn, C. W.; Brown, C. J. *Proc. R. Soc., London* **1954**, *A226*, 531.
(12) Yamashita, Y. *J. Polym. Sci., Part A* **1965**, *3*, 81.
(13) Bunn, C. W.; Garner, E. V. *Proc. R. Soc., London* **1947**, *89*, 39.
(14) A crystal structure model of Nylon 66 was calculated with the energy calculation. Its unit cell constants with $a = 4.85$ Å, $b = 5.22$ Å, c (fiber axis) $= 17.2$ Å, $\alpha = 49.4°$, $\beta = 75.56°$, and $\gamma = 65.26°$ give a fairly good agreement with those by Bunn. This work is to be published.
(15) Scherrer, P. *Gottinger Nacrichten* **1918**, *2*, 98.
(16) Klug, H. P.; Alexander, L. E. *X-ray Diffraction Procedures*; John Wiley & Sons, Inc.: New York, 1954; p 491.
(17) Iannelli, P.; Immirzi, A. *Macromolecules* **1990**, *23*, 1375.