Title	Quantification of Stacking Faults in b-Form Single Crystals of Syndiotactic Polystyrene (STATES AND STRUCTURES-Polymer Condensed States)
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Quantification of Stacking Faults in β-Form Single Crystals of Syndiotactic Polystyrene

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The β-form single crystals of syndiotactic polystyrene, each of which inevitably contains the stacking faults, were grown isothermally from dilute solution at a crystallization temperature, *Tc*, ranging from 150 to 210°C. Theoretical treatment based on our structure model of the fault well explained the characteristic features of the electron diffraction patterns. Then the probability of presence of the fault was estimated for each *Tc* by measauring the mean half-breadth of the streaked reflections in the patterns. The probability thus estimated was in good agreement with that obtained from the number of the faults in a unit length: the number was counted directly in the high-resolution and/or the dark-field images taken by transmission electron microscopy.

Keywords: Syndiotactic polystyrene/ Single crystal/ Stacking fault/ Transmission electron microscopy/ TEM/ Electron diffraction/ Dark-field image/ High-resolution image/ Cryo-protection

In four polymorphs of syndiotactic polystyrene [s-PS] reported so far, the β-form (orthorhombic: *a*=2.87nm, *b*=0.88nm, *c*(chain axis)=0.51nm) always contains stacking faults. Existence of the stacking faults is readily deduced from the *hk*0 electron diffraction [ED] pattern of the β-form single crystal. The pattern is characterized by certain reflections (*h*+*k*=odd) streaked in the direction parallel to the a*-axis, while the other reflections (*h*+*k*=even) are spot-like. This feature is well explained by the following model (1). The regular structure of the β-form is composed of two kinds of motifs. Each motif is a bi-molecular layer, *i.e.*, it is composed of two mono-molecular layers extended parallel to the *bc*-plane (Fig.1). Thus the regular structure is defined as the alternating stack of two different motifs. A sequence of successive two motifs of the same type incorporated in the stack is regarded as the stacking fault. In this case, however, no change takes place in the *ac*- nor *bc*-projections. Therefore, *h*00 and 0*k*0 reflections are to remain spot-like. Theoretical formulation of the ED intensity distribution based on this model explains successfully the characteristic features observed in the real ED pattern. Accordingly, as the intensity distribution profile is directly related to the probability of presence of the stacking fault, *p*, then the faults can be quantified by measuring the ED intensity distribution (2). In this work, we propose a method to estimate *p* by analyzing the selected-area ED pattern from the s-PS single crystal. The *p* value thus estimated is compared with that obtained from the number of the faults in a unit length, which number was counted directly in the high-resolution images (1-3) and/or the dark-field [DF] images (2,3) taken by transmission electron microscopy [TEM]. The dependence of *p* on the

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Scope of research

Attempts have been made to elucidate the molecular arrangement and the mechanism of structural formation/change in crystalline polymer solids, polymer gels and elastomers, polymer liquid crystals, and polymer composites, mainly by electron microscopy and/or X-ray diffraction/scattering. The major subjects are: synthesis and structural analysis of polymer composite materials, preparation and characterization of polymer gels and elastomeric materials, structural analysis of crystalline polymer solids by direct observation at molecular level resolution and in situ *studies on structural formation/change in crystalline polymer solids.*

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crystallization temperature, *Tc*, will be then discussed on the basis of growth theory (4) of folded-chain polymer crystals.

The s-PS sample (Mw=7×10⁴) was supplied by Idemitsu Petrochemical Co., Ltd. A mixture of *n*-tetradecane /decahydronaphthalene (2:1 v/v) was used as the solvent. Single crystals of s-PS were isothermally grown on the newly cleaved NaCl surface from an 0.01wt% solution at a desired *Tc* ranging from 150 to 225°C. Some of the crystals grown at 165°C were annealed in air before removal of NaCl at a given temperature, *Ta*, ranging from 170 to 260°C (melting point: *ca*. 270°C). The specimens were morphologically investigated at room temperature by TEM with a JEOL JEM-200CS operated at 200kV. The intensity distribution in the ED pattern was measured by several methods (2). High-resolution TEM [HRTEM] was carried out with a cryogenic microscope (JEOL JEM-4000SFX operated at 400kV). In this case, specimens were cooled down to 4.2K to minimize their radiation damage. The moiré technique (3) was introduced to detect the position of the stacking fault in the HRTEM images, as a shift of (210) lattice fringes (see Fig.1).

Single crystals with a fairly large monolayered area were obtained below 210°C by isothermal crystallization for two hours. ED patterns were obtained from monolayered areas. In every ED pattern, the mean half-breadth of streaked reflections with $h+k$=odd was calculated, and then was corrected for "instrumental broadening" by using that of spot-like reflections with $h+k$=even as a reference. In this case, the structure factor of each motif is assumed to be constant in the range assigned to one reciprocal lattice point. The probability p was estimated with the following equation from this corrected mean half-breadth H of the streaked reflections:

$$p = [\cos\pi H - 1 + \{ (\cos\pi H - 2)^2 - 1 \}^{1/2}] /2$$

Figure 2 shows the weak dependence of p on *Tc*, and predicts that it is fairly difficult to grow a fault-free single crystal of the β-form. If p is determined only by the growth rates of the regular and the faulted structures, it might be expressed as (5):

$$p = G_F / (G_R + G_F)$$

Here G_R and G_F are the growth rates of the regular and the faulted structures, respectively. By introducing an energy difference ΔE between the regular and the faulted structures, p is expressed as a function of *Tc*. This calculation, however, showed much stronger dependence of p on *Tc* than that obtained experimentally, when ΔE was taken to be constant, namely independent of *Tc*. This discrepancy between the experimental and the theoretical *Tc*-dependence of p seems to come mainly from the *Tc*-dependence of ΔE. Assuming, therefore, that ΔE depends on *Tc*, we calculated $\xi(=\Delta E/\Delta h_f)$ by using the experimentally obtained *Tc*-dependence of p, where Δh_f is the heat of fusion for the regular structure.

The plot of ξ against *Tc* showed excellent linear relationship (5) for both of the growth regimes I and II (4), and this linearity well evidenced the validity of our treatment. It was, consequently, expected that the faulted structure becomes more stable (*i.e*., has lower free energy) than the regular one at temperatures higher than a certain critical temperature (*ca*. 223°C). This result thus means that in crystallization above the critical temperature, the faulted structure will become dominant (p>0.5). In addition, the above-mentioned theoretical formulation for the ED intensity distribution predicts that when p>0.5, the reflections with $h+k$=odd will disappear and each of the spot-like reflections with $h+k$=even is overlapped by a streak. This prediction suggests that a new crystal lattice will be formed when p>0.5 and is to correspond to the β'-form (6).

Isothermal annealing of the β-form single crystals prepared at *Tc*=165°C, which give the maximum value of p as seen in Fig.2, resulted in only a small decrease in the amount of the faults with an increase in *T*a up to 260°C (2). This result illustrates that once the faults are incorporated in the crystal, it might be very difficult to eliminate them only by annealing.

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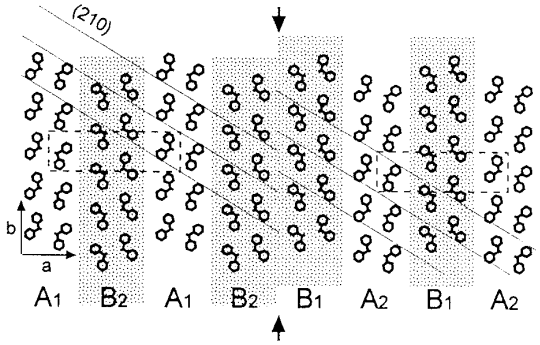

Figure 1. Definition of two types of motifs (1, 3).
A rectangle drawn with broken lines illustrates the unit cell of the regular structure. A pair of arrows indicate the position of the stacking fault. Oblique straight lines illustrate the (210) lattice planes in both sides of the fault.

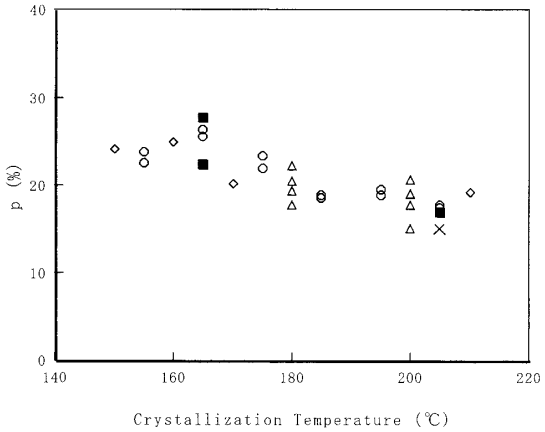

Figure 2. Dependence of p on the crystallization temperature, *T*c (2).
O, Δ and open square : ED, Closed square: DF, × : HRTEM.