Crystallization of Syndiotactic Polystyrene in β-Form. 3. Energetic Analysis of the Incorporation Mechanism of Stacking Faults into the Crystal

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ABSTRACT: Crystallization-temperature (T_c) dependence of the probability of the presence of stacking faults, p, in the solution-grown β-form single crystal of syndiotactic polystyrene (s-PS) was analyzed on the basis of the growth theory of the polymer crystal. By comparing the experimentally obtained T_c dependence of p with the theoretical one, it is deduced that the relative energy difference, $\Delta E/\Delta h_f$, between the regular and the faulted structures of s-PS decreases linearly with increasing T_c: Here, $(\Delta h_f - \Delta E)$ and Δh_f mean the heat of fusion for the faulted structures and that for the regular one, respectively. This result leads to an expectation that the faulted structure will be dominant when T_c is above a certain critical temperature. Such a fault-rich crystal is to give the $hk0$-diffraction pattern, in which the reflections with $h + k =$ odd are absent. This feature has been really found in the X-ray diffraction pattern from the β'-form crystal by De Rosa *et al.* (*Polymer* **1993**, *33*, 1423).

Introduction

Syndiotactic polystyrene (s-PS) is known to show complicated polymorphism, as is summarized schematically by Kellar *et al.*[1] The polymorphism in melt-crystallized samples was studied by Guerra *et al.*,[2] and the crystal structures were classified into four forms. According to their nomenclature, the β-form is characterized by the planar-zigzag conformation of the backbone chain and the orthorhombic unit cell. The crystal structure of the β-form was analyzed by Chatani *et al.*[3] and De Rosa *et al.*[4] Both of them, and we,[5] suggested that the β-form crystals always involve a kind of disorder. In our model, the disorder is due to stacking faults that take place in stacking alternately two types of "motif", that is, of bimolecular layer. According to De Rosa *et al.*, the "disordered modification" is the β'-form which is obtained by melt-crystallization, while the "ordered modification" is named the β''-form, which corresponds to the perfectly regular β-form (space group: $P2_12_12_1$).[4] In the X-ray diffraction patterns from the β'-form, $hk0$ reflections with $h + k =$ odd are absent.[2,4]

We could obtain the β-form single crystals from a dilute solution in n-tetradecane/decahydronaphthalene at crystallization temperatures ranging from 150 to 210 °C.[5−7] The molecular chains are set perpendicular to the basal surface of the single crystal platelet, and accordingly, we could observe clearly defined $hk0$ reflections in the electron diffraction (ED) pattern. Because of the presence of stacking faults, reflections with $h + k =$ odd are inevitably streaked along the a^*-direction in the ED pattern from every single crystal. (The assignment of a- and b-axes in this paper is different from that by other researchers, as indicated also in our previous publications.[5−8]) The interfacial energy at the fault is slightly greater than that for the regular structures, by computing each energy for the equilibrium state.[5,8,9] The stacking faults occur statistically in the alternate stack of two types of motif extending parallel to the bc-plane of the single crystal. The faulted plane is virtually a kind of vertical section of the single crystal, which is deduced from the dark-field (DF) images of the s-PS single crystals observed by transmission electron microscopy (TEM).[6] We, therefore, defined the probability of the presence of the stacking faults as the ratio of the number of faulted planes to that of total planes.[7] The intensity distribution of the streak in the ED pattern has been formulated theoretically as a function of the probability value, p, in our work.[5] By analysis of DF images, high-resolution (HREM) ones, and ED patterns, p was estimated experimentally, and the dependence of p on crystallization and annealing temperatures has been reported in our previous work.[7]

In this report, we further analyze the relationship between p and the packing energy difference between the faulted and regular structures on the basis of the growth theory of polymer crystals,[10] for the single crystals grown isothermally at given temperatures from dilute solution. The equilibrium dissolution temperature of β-form single crystals of s-PS in the mixed solvent is also estimated, and its value is then used for the subsequent calculation.

Theoretical Basis

On the basis of the secondary nucleation theory, we assume that the stacking fault is involved at a certain probability when a new growth surface is formed onto the (200) face of the s-PS crystal as a substrate. On the growth surfaces not parallel to the (200) plane, stacking faults will not be newly involved but the location of stacking faults in a new surface will be the same as that in the previous surface.[6] The planes of the fault, consequently, will be parallel to the bc-plane. The interconversion between the regular and the faulted structures is very difficult and may be negligible.[7] The thickness of a lamella is regarded to be uniform throughout it, because we could not find any significant fluctuation in thickness of a lamella when its fold surface was investigated topographically with atomic force microscopy.[6] Accordingly, we regard the statistical incorporation of stacking faults into the crystal as the growth competition between the regular and the faulted struc-

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tures that are newly formed onto the (200) face of the substrate.

In the macroscopic viewpoint, the competition will be described in terms of the crystal growth rate. The difference in growth rate between the regular and the faulted structures comes from the different packing energies.[8−9] Before discussing the growth rates, we have to define the dissolution temperature of the faulted structure. As for the crystal of regular structure, the change in Gibbs free energy, ΔG, at its equilibrium dissolution temperature, $T_d{}^0$, is written as

$$\Delta G = \Delta h_f - T_d{}^0 \Delta S = 0 \tag{1}$$

Here Δh_f is the heat of fusion and ΔS is the entropy change. Of course, it is reasonably assumed that the faulted structure is less stable than the regular one, and hence it is expected that the equilibrium dissolution temperature of the faulted structure, $T_d{}^0{}_F$, may be lower than that ($T_d{}^0$) of the regular one. The number of states allowed for a chain molecule in the faulted structure is reasonably assumed to be equal to that in the regular one, because the chain-stem conformation is the same in both the structures. In solution, there is no distinction in conformation for the chain molecules in spite of the fact that they are from/to the regular or the faulted structure. We assume, therefore, that ΔS for the regular structure and that for the faulted one are equal and, additionally, that the temperature dependence of ΔS is very small. Then the following relation is derived from eq 1

$$\Delta h_f / T_d{}^0 = (\Delta h_f - \Delta E)/T_d{}^0{}_F$$

$$\therefore T_d{}^0{}_F = T_d{}^0 (\Delta h_f - \Delta E)/\Delta h_f = T_d{}^0 (1 - \xi) \tag{2}$$

Here $(\Delta h_f - \Delta E)$ means the heat of fusion for the faulted structure and ΔE is the packing energy difference between the faulted and the regular structures. In eq 2, ξ is defined as $\xi = \Delta E/\Delta h_f$, and therefore, ξ means the relative energy difference between the regular and the faulted structures.

If p, namely the probability of the presence of stacking faults, is determined only by the growth rates of the regular and the faulted structures, it may be expressed as

$$p = G_F/(G_R + G_F) \tag{3}$$

Here G_R and G_F are the growth rates of the regular and the faulted structures, respectively. The stacking fault newly occurs only when a couple of chain stems are apposed onto the growth surface parallel to the *bc*-plane.[3−9] G_R and G_F are, therefore, the advancing speeds of the (200) growth face. When the growth faces are not parallel to the *bc*-plane, stacking faults will not be newly involved, as mentioned above. On the basis of the growth theory of polymer crystals, the growth rate of the lateral face is expressed as a function of supercooling.[10]

$$G_R = C \exp[-K T_d{}^0 / T_c (\Delta T)(\Delta h_f)]$$

$$G_F = C \exp[-K T_d{}^0{}_F / T_c (\Delta T_F)(\Delta h_f - \Delta E)] \tag{4}$$

Here T_c is the crystallization temperature and C is the parameter that contains several factors, for example, the activation energy of diffusion in solution, and so on. The detail of this type of equation is described in ref 10. Assuming that the crystals in question will grow in regime II, then $K = 2b\sigma\sigma_e/k$. Here b is the thickness of the surface nucleus in the growing direction, k is the Boltzmann constant, and σ and σ_e are surface free energies of lateral and fold surfaces, respectively. It is not clear whether we should assume regime II or regime I. Judging from the curved outline of the single crystals,[6] regime II may be appropriate in this case.[11] (In Regime I, of course, $K = 4\mathrm{b}\sigma\sigma_e/k$.) ΔT and ΔT_F are the supercoolings for the regular and the faulted structures, respectively. Combining eqs 2−4, yields the probability p as follows:

$$p = 1/\{1 + \exp[K(T_d{}^0)^2 \xi / T_c (\Delta h_f)(\Delta T)(\Delta T - \xi T_d{}^0)]\} \tag{5}$$

Even if ξ depends on T_c, it can be determined from the experimentally estimated p value for every T_c,

$$\xi = T_c (\Delta T)^2 \ln[(1-p)/p] / \{(K/\Delta h_f)(T_d{}^0)^2 + T_c (\Delta T)(T_d{}^0) \ln[(1-p)/p]\} \tag{6}$$

Experimental Section

The s-PS sample ($M_w = 7 \times 10^4$) was kindly supplied by Idemitsu Petrochemical Co., Ltd., and was used without further purification. Single crystals of the β-form were prepared on the NaCl (001) face from a 0.01 wt % solution in the mixed solvent (*n*-tetradecane/decahydronaphthalene, 2:1 v/v) by isothermal crystallization. The experiment was made at T_c ranging from 150 to 225 °C. Some single crystals were shadowed with Pt−Pd at a prefixed shadowing angle θ ($=\tan^{-1}(1/4)$) before removal of NaCl. Then the NaCl with s-PS crystals that were reinforced with vapor-deposited carbon was put into water, and the s-PS specimen was floated away from NaCl and picked up onto a copper grid for TEM. The detailed procedure in preparing the specimens for TEM is written in refs 5−7.

The specimens thus prepared were investigated with a transmission electron microscope (JEOL JEM-200CS) operated at 200 kV, and ED patterns, bright-field images, and DF ones were recorded at room temperature. HREM images were taken with a cryogenic transmission electron microscope (JEOL JEM-4000SFX) operated at 400 kV. In this case, specimens were cooled to the liquid helium temperature (4.2 K) to suppress their radiation damage. The probability p was estimated as described in ref 7. Lamellar thickness was estimated from the length of the metal shadow in the magnified electron micrograph.

Results and Discussion

Single crystals of β-form s-PS could be successfully grown isothermally at crystallization temperatures (T_c) ranging from 150 to 210 °C. Their morphologies and ED patterns are shown in our previous publications.[5−7] Figure 1 shows the dependence of the lamellar thickness on T_c. As is also recognized for the crystals of other polymers, the lamellar thickness of s-PS single crystals increases with increasing T_c. According to the growth theory of polymer crystals, the T_c dependence of the lamellar thickness is formulated as[10]

$$lg^* = [2\sigma_e T_d{}^0 / \Delta h_f (\Delta T)] + \delta l \tag{7}$$

Here lg^* is the lamellar thickness and δl is a quantity that is a weak function of undercooling near the dissolution temperature. The β-form crystal of s-PS may follow this equation. By seeking a $T_d{}^0$ that will result in a better linear relationship between the lamellar

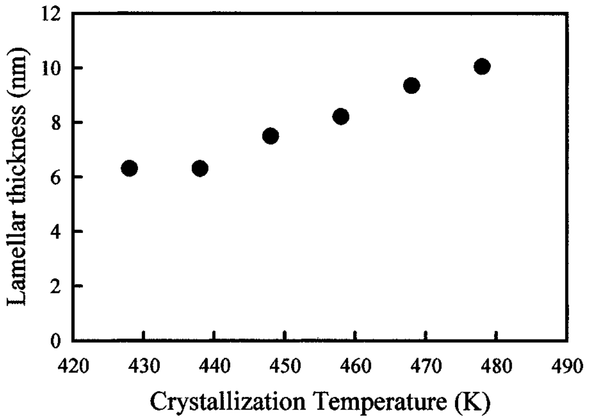

Figure 1. Dependence of the lamellar thickness of solution-grown single crystals on crystallization temperature.

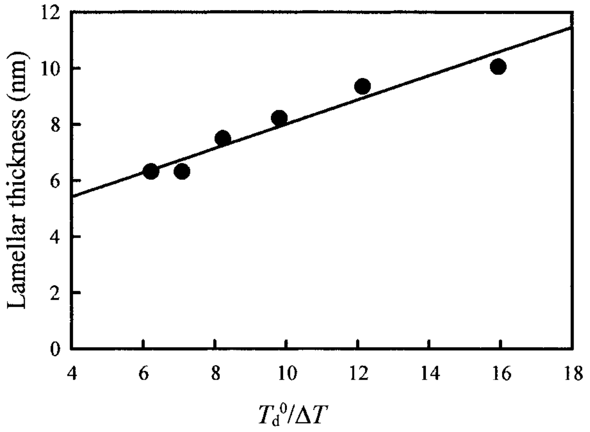

Figure 2. Lamellar thickness of the solution-grown single crystals as a function of $T_d^0/\Delta T$, by assuming $T_d^0 = 510$K. The slope of the line gives $2\sigma_e/\Delta h_f$.

thickness and $T_d^0/\Delta T$ when $2\sigma_e/\Delta h_f$ is assumed to be constant, we estimated T_d^0 at about 510 K. This value seems to be reasonable because it is a little higher than the real dissolution temperature of the s-PS sample observed in our experiment. The mixed solvent used here boils at 233 °C (506 K), and no precipitation was observed at this temperature. Of course, T_d^0 is an imaginary temperature for an infinitely thick crystal. We adopted, therefore, this estimated value of 510K as T_d^0 for the regular structure of β-form s-PS. Figure 2 shows the plot of the lamellar thickness against $T_d^0/\Delta T$ under an assumption of $T_d^0 = 510$ K. From the slope of the line drawn in Figure 2, we could also estimate $\sigma_e/\Delta h_f$ approximately at 0.2 nm. The value of T_d^0 thus estimated may not be so accurate but must not be too far from its correct value.

We examined, at first, the case that ξ is independent of T_c. Figure 3 shows the temperature dependence of p on T_c: p was calculated theoretically for various constant values of ξ using eq 5. Here we assumed $b = 1.4 \times 10^{-7}$cm, $\sigma = 4.1$ erg/cm^2, $\sigma_e = 31$ erg/cm^2, and $\Delta h_f = 9.4 \times 10^8$ erg/cm^3 according to refs 12 and 13. Half the size of the a-dimension was employed as the b value because the stacking fault occurs between the bimolecular layers with a thickness of $a/2$.[5-8] That is to say, a set of two coupled chain stems, namely a pair of stems in the bimolecular layer, is regarded as a constituent unit of a surface nucleus. Figure 3 shows a much stronger dependence of p on T_c than that obtained experimentally. Even when we changed the values of T_d^0, σ, σ_e, and Δh_f in their respective reasonable ranges, the feature in this figure was essentially unchanged. Only when T_d^0 was assumed to be an unlikely high temperature could p show a weak temperature dependence.

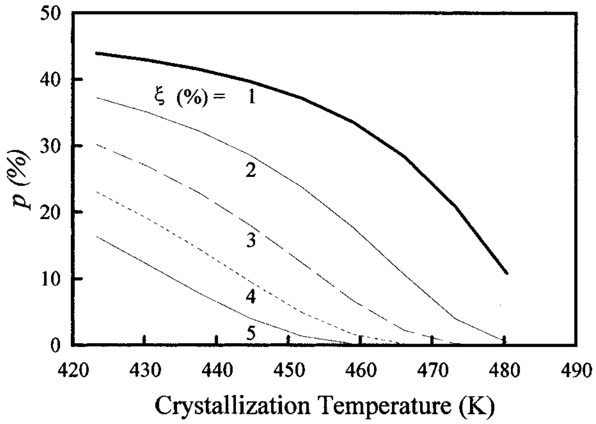

Figure 3. Theoretical estimation of the probability p for various constant values of ξ as a function of crystallization temperature. The p values were calculated according to eq 5, by assuming that ξ is independent of crystallization temperature.

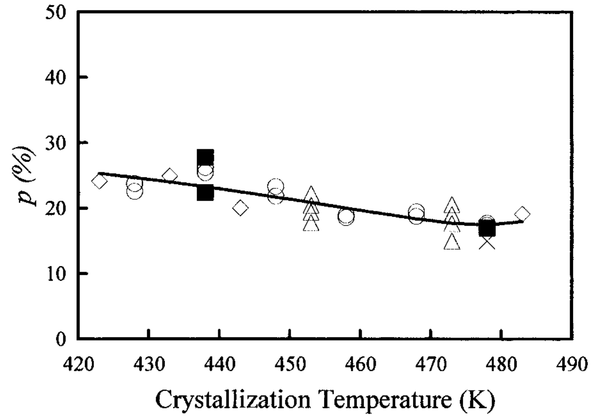

Figure 4. Experimentally obtained p values as a function of crystallization temperature. Samples were crystallized isothermally from dilute solution in the mixed solvent for 2 h. Each symbol indicates the method[7] to estimate the p value; (circle, open diamond, and triangle) ED; (closed square) DF; (cross (x)) HREM. The curve shows the calculated T_c dependence of p according to eq 5, by assuming the T_c dependence of ξ obtained from the straight line in Figure 5.

Figure 4 shows the experimentally obtained dependence of p on T_c.[7] As a result, we could not fit the theoretical curve eq (5) to the experimental data when ξ was assumed to be independent of T_c. As discussed above, the energetic disadvantage at the faulted structure will result in a lower $T_d{}^0{}_F$. The supercooling for the faulted structure is smaller than that for the regular structure at a given T_c, and the difference in supercooling has the greater effect on the growth rate as T_c approaches $T_d{}^0{}_F$. The ratio G_F/G_R, will become smaller and smaller with increasing T_c. Furthermore, if T_c is higher than $T_d{}^0{}_F$, the faulted structure will not be able to grow and the stacking fault will not be formed, as it was postulated in eq 4 that $G_F = 0$ at $T_c \geq T_d{}^0{}_F$. As a result, the abrupt decrease of p near T_d^0 was inevitable in this theoretical estimation. We concluded, thus, that this discrepancy between the experimental and theoretical T_c dependence of p comes mainly from our previous assumption that ξ is independent of T_c. We evaluate, next, the dependence of ξ on T_c with p values obtained experimentally.

Figure 5 is the plot of ξ against T_c, calculated from p using eq 6. Here the value (0.2 nm) estimated from

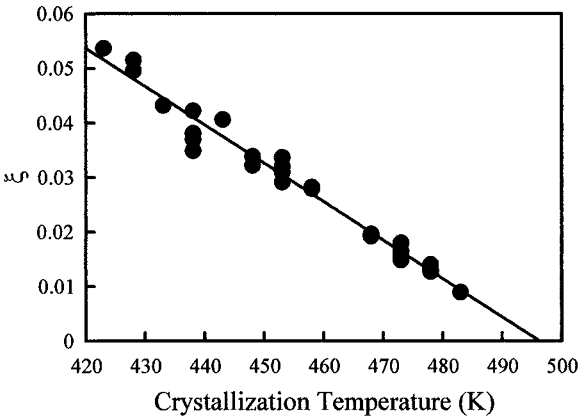

Figure 5. Dependence of ξ on crystallization temperature (T_c). The values of ξ were calculated with eq 6, by assuming the crystal growth of regime II. The straight line was determined with the method of least squares. By extrapolating the line down to $\xi = 0$, the critical temperature was estimated at about 496 K (= 223 °C). When regime I was assumed, the plot of ξ against T_c also gave a straight line with a less-steep slope and predicted almost the same critical temperature.

Figure 2 was used for $\sigma_e/\Delta h_f$. An excellent linear relationship can be seen in this figure. Although the linearity of the plot does not directly mean the propriety of our theoretical treatment, this result suggests to us intuitively that the treatment is not so wrong. The propriety will be shown later by presenting the existence of another crystal structure deduced from Figure 5. This figure suggests that as T_c increases, the relative energetic difference, ξ, between the regular and the faulted structures decreases. The straight line in this figure was drawn on the basis of the result by the least-squares method. By using this linear T_c dependence of ξ, the curve was drawn in Figure 4 and illustrates the T_c dependence of p calculated according to eq 5. This curve well reproduces the observed T_c dependence of p, showing that the estimated linear T_c dependence of ξ is fairly reasonable.

The faulted structure will become more stable ($\xi < 0$) than the regular one at temperatures higher than a certain critical temperature (about 496 K) that is estimated by extrapolating the line down to $\xi = 0$ in Figure 5. The case for $\xi < 0$ was not realized in solution crystallization. How about the melt crystallization? The faulted structure (a sequence of the same motifs) itself is not an inherently irregular structure but a part of another ordered structure incorporated in the so-called regular crystal structure (the sequence of alternating stack of two types of motif). In other words, a consecutive sequence of repeated faulted structures will result in another regular lattice. The packing energies of both (the regular and the faulted) structures, principally that of the faulted structure, may vary with temperature, and hence, ξ may vary with temperature. It is probable that the "faulted" structure will become more stable than the originally "regular" structure, and hence the relative energetic difference, ξ, will have a negative value. Accordingly, the growth rate of the faulted structure, G_F, will exceed that of the regular structure, G_R, above the critical temperature. The result shown in Figure 5 thus means that in crystallization above the critical temperature, the faulted structure will become dominant ($p > 0.5$). That is, this result suggests that a different crystal lattice in which the "faulted" structure takes the place of the originally "regular" structure will be formed. The question is raised whether this situation will really occur or not. As mentioned above, we could not grow the single crystal from dilute solution above this critical temperature, which is very close to the dissolution temperature of the sample. However, we can crystallize s-PS from the melt above the critical temperature. The discussion about ξ may be valid also for the melt-crystallized β-form, because ξ is related mainly to the crystal structure but independent of the crystallization method. In conclusion, the β′-form crystallized at a higher temperature from the melt corresponds to the different crystal lattice in which the faulted structure is dominant.

Our theoretical formulation for the ED intensity distribution[5,7] predicts that when $p = 0.5$, the streaked reflections with $h + k =$ odd will fuse into a continuous (without strong peaks) long streak modulated only by the structure factor on each layer line (with a fixed k ($\neq 0$)). It also predicts that when $p > 0.5$, the streaked reflections with $h + k =$ odd will disappear and each of the spotlike reflections with $h + k =$ even is overlapped with a short streak. Extinction of the reflection peaks at the positions with $h + k =$ odd in the ED pattern corresponds with that recognized in the powder X-ray diffraction pattern from the β′-form,[4] if we suppose that any streaks were not recognized apparently in the powder X-ray pattern. In the ED patterns from the melt-grown single crystals, which must be attributed to the β′-form, we could surely observe the streaks overlapping the spotlike reflections, with no intensity maxima at reciprocal lattice points of $h + k =$ odd. The detailed description of this feature of the ED patterns will be presented in our future publication.[14] The structural model for the β′-form proposed by De Rosa *et al.* is, according to our understanding, almost the same as the case for $p = 0.5$ in this report. However, the proper structure model of the β′-form may correspond to the case for $p > 0.5$, when the β′-form denotes the crystal structure grown at a higher temperature from the melt and presents a diffraction pattern in which $hk0$ reflections with $h + k =$ odd are absent. The case for $p > 0.5$ is consistent not only with the current theory but also with the arrangement of molecular stems in the *ab*-projection of the crystal structure, which arrangement is visualized in the HREM images of the melt-grown single crystals.[15] In either case, $p = 0.5$ or $p > 0.5$, the β′-form is related to the structure that is expected from the temperature dependence of ξ shown in Figure 5. The existence of the β′-form strongly supports our theoretical treatment presented here. More detailed analysis of the crystal structure of the β′-form is in progress.[14]

Conclusion

On the basis of the growth theory of polymer crystal, the T_c dependence of p was discussed. From the experimentally obtained T_c dependence of p, it was postulated that the relative energy difference, ξ (= $\Delta E/\Delta h_f$), namely the energy difference ΔE if Δh_f is constant, between the regular and the faulted structures of s-PS decreases linearly with increasing T_c. This result suggested that the faulted structure will become dominant when T_c is above a certain critical temperature. The feature expected in the diffraction pattern from the fault-rich crystal has really been recognized in the X-ray and electron diffraction pattern from the β′-form crystallized at a higher temperature from the melt. The existence of the β′-form strongly supports our theoretical treatment.

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