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Crystal Morphology and Phase Identification in Poly(aryl ether ketone)s and Their Copolymers. 3. Polymorphism in a Polymer Containing Alternated Terephthalic Acid and Isophthalic Acid Isomers

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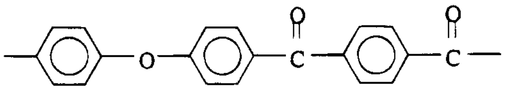
ABSTRACT: Crystal structures and morphology of a polymer containing alternated terephthalic acid (T) and isophthalic acid (I) linked phenylene units in poly(ether ketone ketone) [PEKK(T/I)] have been investigated *via* transmission electron microscopy (TEM), electron diffraction (ED), wide angle X-ray diffraction (WAXD), and differential scanning calorimetry (DSC) experiments. When the polymer is crystallized at high temperatures (at and above 310 °C), only one orthorhombic crystal unit cell (form I) is found, and the crystal dimensions are $a = 0.778$ nm, $b = 0.610$ nm, and $c = 3.113$ nm. At the crystallization temperature below 200 °C, another orthorhombic crystal unit cell (form II) forms, having the dimensions of $a = 0.417$ nm, $b = 1.108$ nm, and $c = 3.113$ nm. Even at this low-temperature range, form II always coexists with form I except in the case of solvent-induced crystallization. A possibility of the existence of a new form (form III) is identified in a temperature range between 200 and 300 °C, and usually coexists with form I. This form also possesses an orthorhombic unit cell with dimensions of $a = 0.641$ nm, $b = 0.610$ nm, and $c = 3.504$ nm. Transformations from form II to both forms I and III require melting and recrystallization. Relatively regular-shaped lamellar crystals in PEKK(T/I) can be observed.

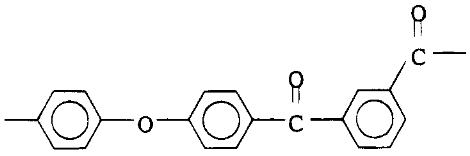
Introduction

A series of poly(ether ketone ketone)s (PEKKs) prepared from diphenyl ether (DPE) and terephthalic acid (T) or isophthalic acid (I) have been investigated. As polymerized, these polymers can be thought of as consisting of "phthalate diads" containing linkages such as −DPE−T−DPE−T− or −DPE−I−DPE−I−. For poly(ether ketone ketone) with all-*para* linkages in phenylene groups [PEKK(T)], its chemical structure is



Polymorphism for the crystal structures of PEKK(T) has been observed *via* wide angle X-ray diffraction (WAXD)[1−5] and single crystal electron diffraction (ED) experiments.[4] A two-chain orthorhombic unit cell with dimensions of $a = 0.769$ nm, $b = 6.06$ nm, and $c = 1.008$ nm (form I) and a two-chain orthorhombic unit cell with $a = 0.417$ nm, $b = 1.134$ nm, and $c = 1.008$ nm (form II) have been identified. Chains in the crystals adopt an extended conformation with the phenylene groups alternating at fixed angles to the plane of the zigzag backbone. It has also been shown that the ether and ketone groups are crystallographically equivalent and the unit cell consists of two-chain orthorhombic packing with a space group of *Pbcn*-D_{2h}^{14}, in which one chain is in the center of the *ab* projection for the unit cell, and 4 × $^{1}/_{4}$ chains at the corners.[6−8] Polymorphism is not only observed in PEKK(T), but also in other members of this poly(aryl ether ketone) family.[5] In general, the ability to develop the second form (form II) has been found to be significantly enhanced with increasing chain stiffness and linearity.

Crystal structure and morphology of a poly(ether ketone ketone) with one *meta*-linked phenylene in the backbone [PEKK(I)],



has also been studied. Only one crystal form has been found on the basis of WAXD and ED experiments. The unit cell possesses a two-chain orthorhombic unit cell with $a = 0.766$ nm, $b = 0.611$ nm, and $c = 1.576$ nm. It is particularly interesting that the *c*-axis contains three phenylene groups in which the chain conformation in a crystal is planar zigzag. The *para*-linked phenylenes are torsionally rotated in opposite directions at approximately ±60° to the plane of the zagzag backbone on either side of ether or ketone linkages, and the *meta*-linked phenylene groups are aligned to the plane of the zagzag backbone. Furthermore, the crystal unit cell dimensions have been found to change with isothermal crystallization temperatures. Specifically, the *c*-axis shrinks drastically with increasing temperature. This has been attributed to the increasing alignment of the *meta*-linked phenylenes into the zigzag plane of the backbone at high temperatures.[9]

Spherulitic morphology is evident for PEKK(T) and PEKK(I) crystals grown at different crystallization conditions. Most of the spherulites show "eye" structure during their development, and the lamellae in the "eyes" are basically grown in a flat-one arrangement.[10] Re-

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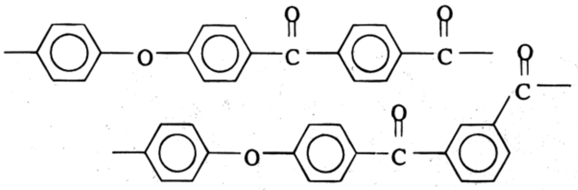
cently, a second morphological form of PEKK(T) in the thin films has been found at high crystallization temperatures, which consists of large (micrometer-size), faceted single crystals. The molecular chains along the *c*-axis of the crystals are inclined to the lamellar normal. In the case of form I, molecular chains are inclined to the lamellar fold surface. Form II also exhibits a molecular inclination to the lamellar normal.[4] These observations are similar to those reported by Lovinger *et al.* in poly(ether ether ketone) (PEEK).[11] In PEKK(I), however, isolated micrometer-size single lamellar crystals are not formed. This suggests that the growth of isolated single lamellar crystals is largely dependent upon the symmetry of the chain molecules in this family. The *meta*-linked phenylenes certainly introduce a structural asymmetry and lead to relatively difficult chain packing in the crystals and therefore, result in smaller lamellar crystal sizes.[9]

In this paper, we report our attempt to study the crystal structure and morphology of a polymer [PEKK(T/I)] containing alternating T and I. The chemical compositions of both T and I are 50%. The chemical structure is



Experimental Section

Materials and Samples. Developmental grade PEKKs were provided by DuPont Co. PEKK(T/I) was prepared from diphenyl ether (DPE) and terephthalic acid (T) or isophthalic acid (I) in a two-step process. From the chemical synthesis route, it is clear that this polymer possesses a perfect alternating sequence of T and I. The number-average molecular weight of the samples is around 10 000, and the polydispersity is approximately 3.

For the WAXD study, PEKK(T/I) films were cast onto glass slides using 2% PEKK–pentafluorophenol (PFP) (w/w) solution at *ca.* 80 °C. The solvent was evaporated in a vacuum oven and films ranged in thickness from 0.1 to 0.2 mm. The samples were heated to *ca.* 20 °C above the equilibrium melting temperature (350 °C for PEKK(T/I)[3]) for several minutes and, then, either quenched in liquid nitrogen to generate amorphous glassy films for cold crystallization or rapidly cooled to a preset temperature for melt-crystallization experiments. For solvent-induced crystallization, the amorphous glassy films were exposed at room temperature in methylene chloride for 1 week. Uniaxially oriented PEKK(T/I) samples were obtained by drawing the thin films at temperatures above T_g (typically, a draw ratio of 4 can be achieved). They were then annealed at a fixed length at different temperatures above the T_g.

Ultrathin PEKK(T/I) films with a thickness ranging from 0.05 to 0.1 μm were prepared for TEM observations by casting a 0.1% (w/w) PEKK(I)–PFP solution onto carbon-coated glass slides. After isothermal crystallization at different temperatures and times, the films were quenched to room temperature, stripped, floated onto the water surface, and recovered using nickel grids.

Instrumentation and Experiments. Reflection WAXD experiments were conducted with a Rigaku 12 kW rotating-anode generator (Cu Kα) and diffractometer. The X-ray beam was monochromatized using a graphite crystal. The 2θ angle region ranges between 5 and 35° with a scanning rate of 0.2°/min. The diffraction peak positions and widths observed from WAXD experiments were carefully calibrated with silicon crystals with known crystal sizes. Fiber WAXD patterns were obtained using a flat-plate vacuum camera attached to a Rigaku tube X-ray generator.

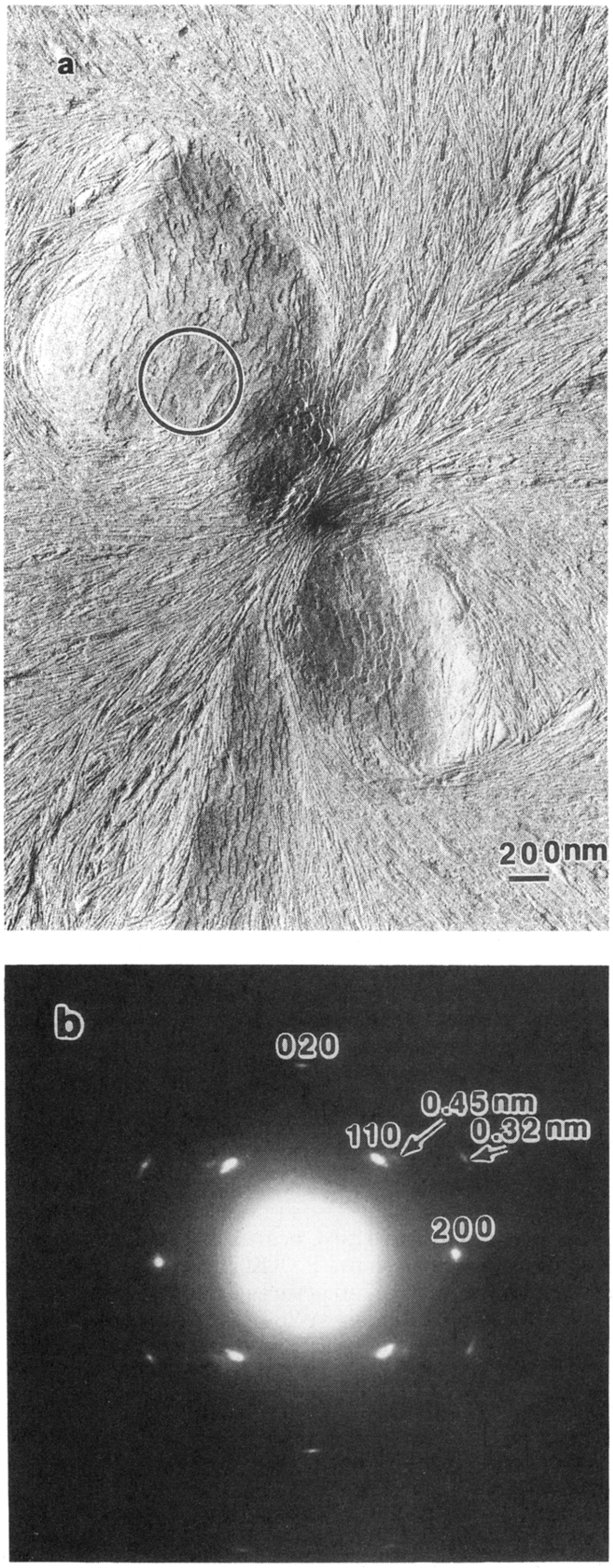


Figure 1. TEM observations of PEKK(T/I): (a) "eye" structure morphology with the flat-on orientation in the eyes; (b) an ED pattern crystallized at 260 °C for 60 min from the melt. The ED pattern is originated from the circled area of the micrograph and shown in correct orientation.

PEKK(T/I) crystal morphology and ED patterns were observed *via* a JEOL (1200 EX II) TEM using an accelerating voltage of 120 kV. The ultrathin PEKK(T/I) films were shadowed by Pt and coated with carbon for TEM observations.

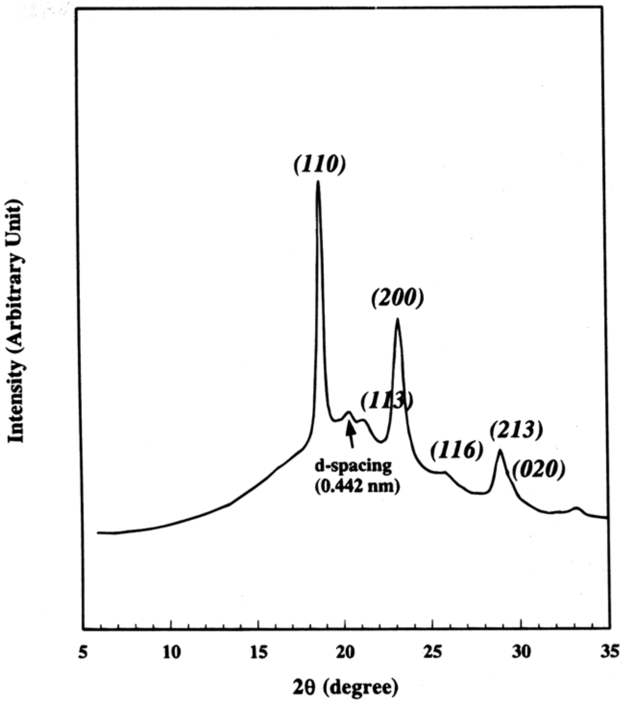


Figure 2. WAXD powder pattern for PEKK(T/I) crystallized at 260 °C for 60 min from the melt.

Figure 3. Tilted ED pattern along the $[03\bar{1}]$ zone for PEKK-(T/I) crystallized at 260 °C for 60 min from the melt.

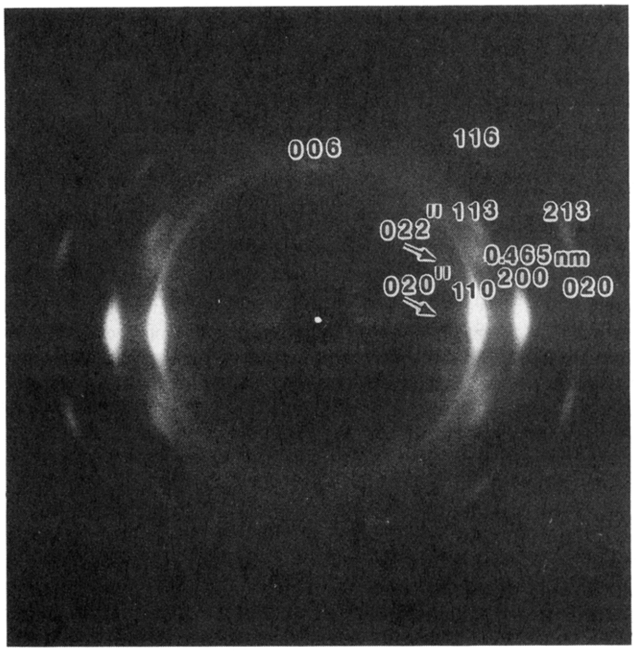


Figure 4. WAXD fiber pattern for PEKK(T/I) after annealing at 280 °C for 15 h.

A tilting stage was also used in ED experiments to determine three-dimensional crystalline unit cells. Calibration of the electron diffraction spacings were carried out using Au and TlCl in a d-spacing range smaller than 0.384 nm, which is the largest spacing for TlCl. Spacing values larger than 0.384 nm were calibrated by doubling the d spacings of those reflections on the basis of their first-order reflections. The crystallization conditions of the PEKK(T/I) films were the same as those in WAXD experiments.

Thermal measurements were performed on a DuPont DSC910. The temperatures and heat flow scales were carefully calibrated using standard materials over a wide temperature range at a heating rate of 10 °C/min. The sample weight was typically 2–3 mg. Samples were encapsulated in hermetically sealed aluminum pans.

Results and Discussion

Identification of the Crystal Structures of PEKK(T/I). Figure 1a shows PEKK(T/I) crystal spherulitic morphology with "eye" structures after isothermal crystallization from the melt at 260 °C for 60 min. Decent ED patterns with the $[00l]$ zone can be obtained from the lamellae in the "eye" of the spherulites, as shown in Figure 1b. These morphological observations are similar to those reported in PEKK(T),[12] PEKK(I),[9] and PEEK.[10] Based on three major reflections of the (110), (200), and (020) in this pattern, a two-chain orthorhombic unit cell with dimensions of $a = 0.80$ nm and $b = 0.62$ nm (form I) can be determined after refinements. However, two reflections in this ED pattern, at d spacings of 0.45 and 0.31 nm, cannot be indexed on the basis of the form I unit cell with the $[00l]$ zone. Figure 2 shows the WAXD powder pattern of PEKK(T/I) crystallized under the same conditions, as in the case of Figure 1. Two ($hk0$) reflections, the (110) reflection at $2\theta = 18.4(9)°$ and the (200) reflection at $2\theta = 22.8(9)°$, can be assigned and fit into an orthorhombic unit cell with dimensions of $a = 0.778$ nm and $b = 0.610$ nm (other reflections will be discussed below). A tilted ED pattern of PEKK(T/I) lamellar crystals with a $[03\bar{1}]$ zone, as shown in Figure 3, consists of the (113), (213), and (200) reflections. The reflection having a d spacing of 0.31 nm in the ED pattern with the $[00l]$ zone (Figure 1b) possesses the same d spacing as the (213) reflection found in this tilted ED pattern. Nevertheless, the coexistence of the (213) and ($hk0$) reflections in Figure 1b needs further explanation under an assumption that the ED pattern in Figure 1b is a combination of two individual ED patterns having $[00l]$ and $[hkl]$ zones. For the $[hkl]$ zone ED pattern, one of the possibilities is that the (213) and (020) reflections coexist when the electron beam remains parallel to the $[30\bar{2}]$ zone (the reason for this choice will be seen below). This coexistence of the (213) reflection in the ED pattern with the $[00l]$ zone might be attributed to a possible lamellar thickness effect. The (hkl) reflections with higher order l may show up in the ED pattern with the $[00l]$ zone when the lamellae are very thin and easily banded. However,

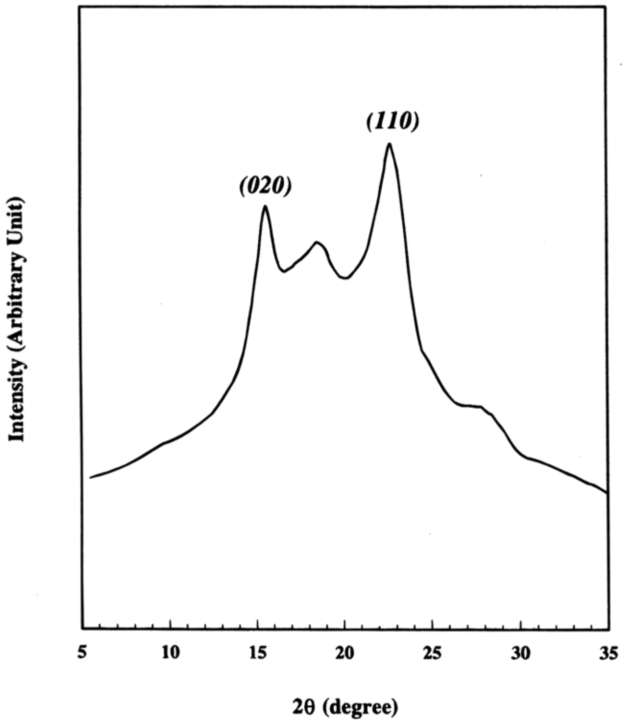


Figure 5. WAXD powder pattern for PEKK(T/I) crystallized *via* solvent-induced crystallization.

to observe reflections with both [00*l*] and [30$\bar{2}$] zones, the lamellae have to be banded at an angle of about 80°, which is too large to occur. Another possibility is that the ED pattern taken from the crystals may involve two lamellar orientations. One is flat-on with the [00*l*] zone and another is almost edge-on with the [30$\bar{2}$] zone. Furthermore, these two orientation arrangements seem to have certain specific crystallographic relationships since only the coexistence of their reflections along both [00*l*] and [30$\bar{2}$] zones is found (over one hundred ED patterns were taken) and no other zone combinations have been observed. This relationship may be either due to a microscopic epitaxy growth of two kinds of lamellar crystals or attributed to the macroscopic orientation of the edge-on lamellae in which the growing direction is along the *b*-axis. Thus, the flat-on lamellae may only grow parallel to this direction (see below). Further study is necessary to obtain a definite conclusion.

A WAXD fiber pattern for PEKK(T/I) crystallized at relatively high annealing temperature (280 °C) has been obtained (Figure 4). On the basis of the two-chain orthorhombic unit cell with the dimensions of $a = 0.778$ nm and $b = 0.610$ nm, the (110), (020), and (200) reflections along the equator can be clearly identified. The (006) reflection in the meridian and the (113) and (213) reflections in the quadrant can also been found. On the basis of (006) reflection, a six-phenylene *c*-axis in one repeat unit is determined, and its dimension is $c = 3.113$ nm. These reflections have also been recorded in WAXD powder patterns [the (113) reflection at $2\theta = 20.8(7)°$ and the (213) reflection at $2\theta = 28.6(6)°$, respectively, as shown in Figure 2]. As a result, the form I crystal structure can be determined as a two-chain orthorhombic unit cell with $a = 0.778$ nm, $b = 0.610$ nm, and $c = 3.113$ nm. Furthermore, two weak reflections appeared in the fiber pattern, and they cannot be fit into the form I unit cell. In fact, they are the residual reflections of form II (see below). If the fiber is annealed at higher temperature (say 300 °C), these two reflections disappear.

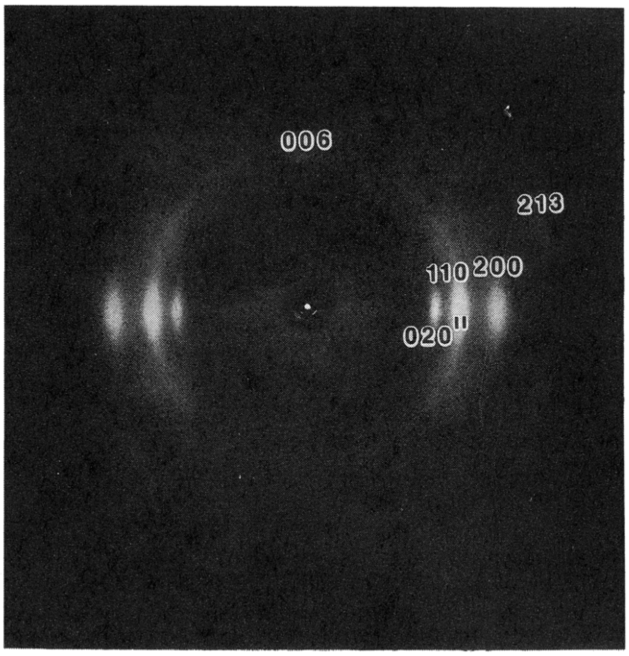


Figure 6. WAXD fiber pattern for PEKK(T/I) after annealing at 180 °C for 15 h.

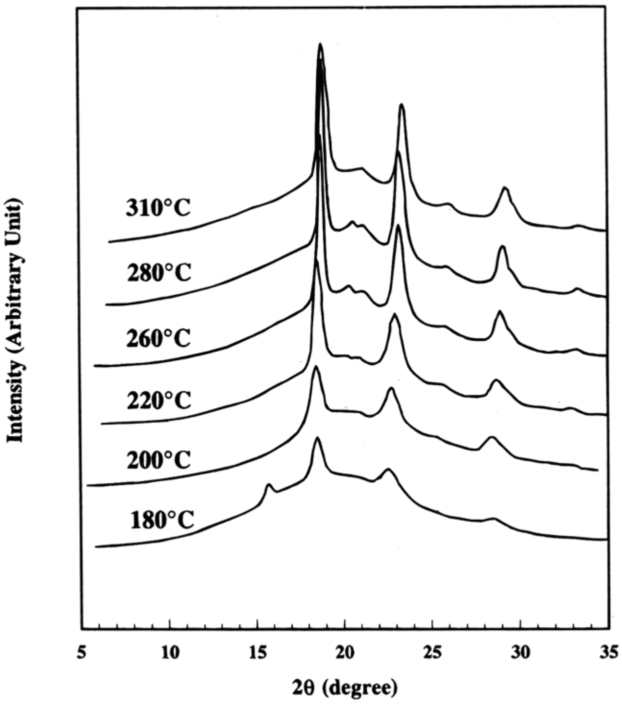


Figure 7. Set of WAXD patterns for PEKK(T/I) crystallized at various crystallization temperatures from the melt.

A new crystal structure (form II) can be obtained *via* solvent-induced crystallization. The WAXD powder pattern of PEKK(T/I) obtained from this crystallization process is shown in Figure 5. The (020) and (110) reflections are found at $2\theta = 16.0(0)$ and $22.8(3)°$, respectively. These reflections suggest a two-chain orthorhombic unit cell with dimensions of $a = 0.417$ nm and $b = 1.108$ nm. A WAXD fiber pattern of PEKK(T/I) crystallized at low annealing temperature (180 °C) has also been obtained, as shown in Figure 6. Reflections suggest a mixture of crystal forms I and II. Only one reflection is found along the meridian, and it is the same as that shown in Figure 4. We suggest that both

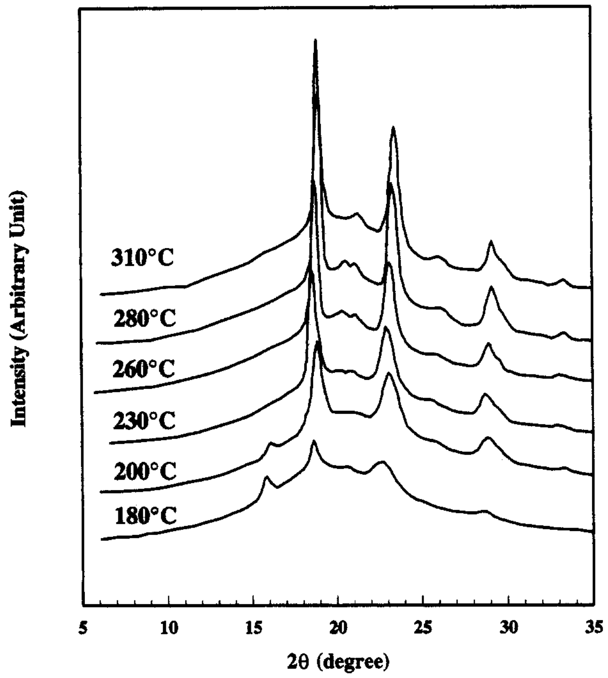


Figure 8. Set of WAXD patterns for PEKK(T/I) crystallized at various crystallization temperatures from the glassy state.

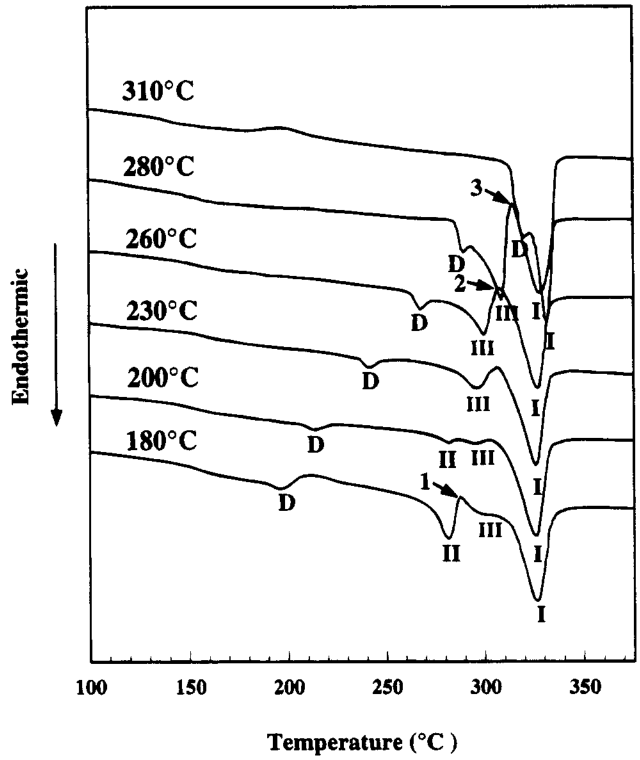


Figure 9. Melting endotherms of PEKK(T/I) crystallized at various crystallization temperatures from the melt. All scans are at 10 °C/min.

forms possess the same c-axis dimension. Therefore, the reflection can be indexed as the (006) reflection, and form II is determined to be a two-chain orthorhombic unit cell with dimensions of $a = 0.417$ nm, $b = 1.108$ nm, and $c = 3.113$ nm.

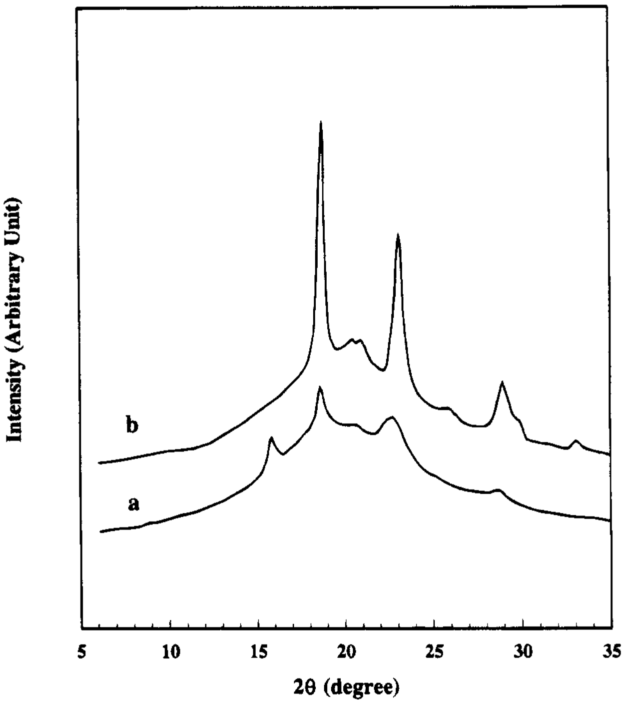


Figure 10. WAXD patterns for PEKK(T/I) crystallized at 180 °C for 15 h from the glassy state (a) before annealing and (b) after annealing at 290 °C for 30 min.

However, the remaining reflection at $2\theta = 20.0(9)^\circ$ (d spacing of 0.442 nm) in Figure 2 cannot be indexed on the basis of the proposed form I and form II orthorhombic unit cells. However, it corresponds to the reflection at a d spacing of 0.45 nm observed in the ED pattern with the [00l] zone (Figure 1b). Furthermore, one of the reflections in the quadrants of the WAXD fiber pattern (Figure 4) exhibits a d spacing of 0.465 nm. This reflection represents different c-axis dimensions as compared with the c-axis dimension of both forms. Combined observations from WAXD and ED patterns suggest a possible formation of an intermediate form (form III). From the ED pattern (Figure 1b), the reflection (the d spacing of 0.45 nm) possesses the same b-axis dimension ($b = 0.62$ nm) but different a-axis dimensions when compared to the form I unit cell. If this reflection is assigned to be (110) of form III, the a-axis dimension is thus 0.65 nm. Note that this reflection can also be found in the WAXD powder pattern at $2\theta = 20.0(8)^\circ$ (d spacing of 0.442 nm) in Figure 2. This suggests that an orthorhombic unit cell with $a = 0.641$ nm and $b = 0.610$ nm may exist. In the WAXD fiber pattern (Figure 4), the (110) reflection is in the equatorial direction and merged with the strong reflection of the (110) reflection of form I. However, the quadrant reflection at a d spacing of 0.465 nm can be assigned as (113) on the basis of the form III dimensions. This reflection can also be found in the tilted ED pattern with the $[03\bar{1}]$ zone, as shown in Figure 3. The c-axis dimension for this form can thus be determined to be 3.504 nm. As a result, form III should possess an orthorhombic unit cell having dimensions of $a = 0.641$ nm, $b = 0.610$ nm, and $c = 3.504$ nm. Computer modeling work is carried out to study possible chain conformation changes in these two different c-axis dimensions.

Identification of Multiple Melting Endotherms. Isothermal crystallization experiments have been conducted between the glass transition and the melting temperatures. Figure 7 illustrates a set of WAXD patterns obtained at different crystallization temperatures from the melt. At high crystallization temperatures, the diffraction patterns indicate that PEKK(T/I) is crystallized in the form I structure. When temperature decreases to close to T_g (for example, 180 °C), a minor amount of the form II crystals also coexists with

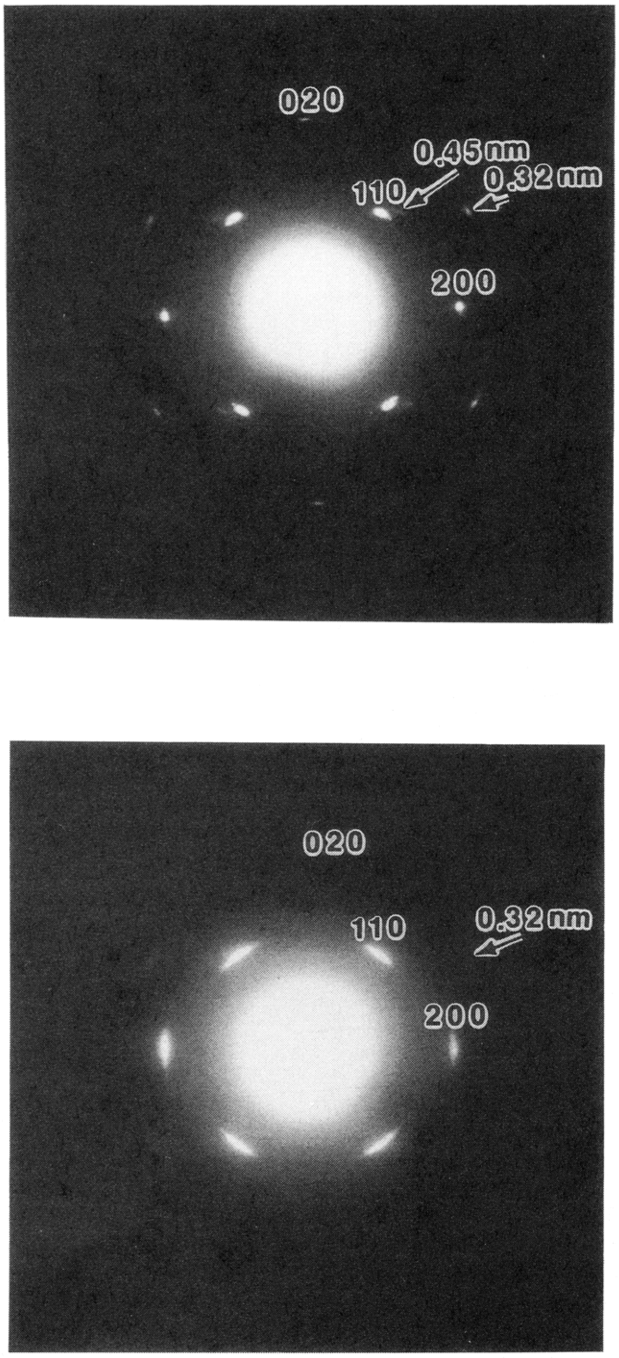


Figure 11. ED patterns along the [00*l*] zone for PEKK(T/I) crystallized at 260 °C for 60 min from the melt (a) before annealing and (b) after annealing at 310 °C for 10 min.

form I. Similar observations can also be found as crystallization is carried out from the glassy state (Figure 8). Corresponding DSC heating diagrams have also been obtained, as shown in Figure 9. Multiple melting endotherms are found and identified by Roman numerials. Melting endotherms D are known as double melting peak behavior,[13] of which a melting endotherm at *ca.* 10–20 °C above the isothermal crystallization temperatures is always observed.

Annealing experiments have been designed in order to identify the structure origin of the multiple melting endotherms. PEKK(T/I) crystallized at 180 °C from the melt is annealed at temperature 1 (above the melting temperature of endotherm II; see Figure 9) for 30 min. After this annealing process, the WAXD reflections of form II crystals in the powder pattern disappear (Figure 10), indicating that the melting endotherm II is attributed to the form II crystal melting. On the other hand, PEKK(T/I) crystallized at 260 °C from the melt is annealed at temperature 2 (above the melting temperature of endotherm III; see Figure 9) for 10 min, and the reflection at a *d* spacing of 0.45 nm in the [00*l*] zone ED pattern disappears as shown in Figure 11. The reflection at $2\theta = 20.0(8)°$ (*d* spacing of 0.442 nm) in the WAXD powder pattern also vanishes (Figure 12). Similar observations have also been found for PEKK(T/I) crystallized at 280 °C from the melt and annealed at temperature 3 for 10 min. Therefore, one may conclude that the endothermic peak III corresponds to the form III crystal melting.

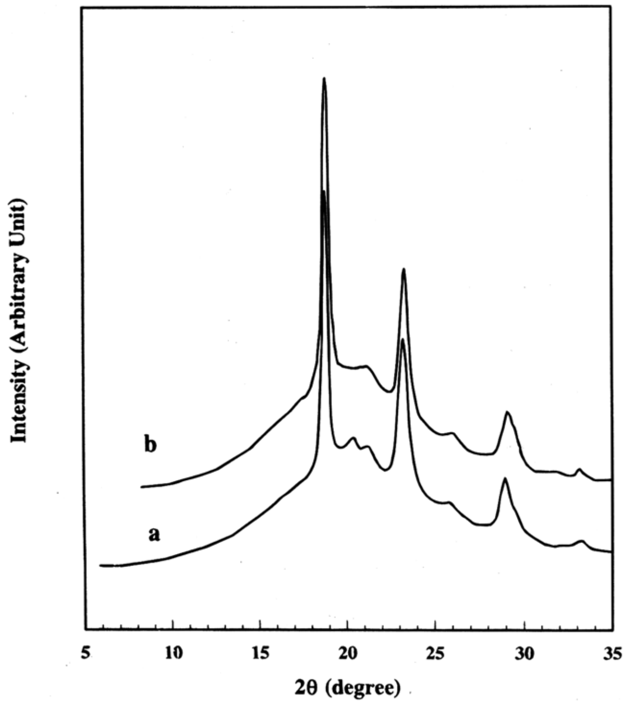


Figure 12. WAXD patterns for PEKK(T/I) crystallized at 260 °C for 60 min from the melt (a) before annealing and (b) after annealing at 310 °C for 10 min.

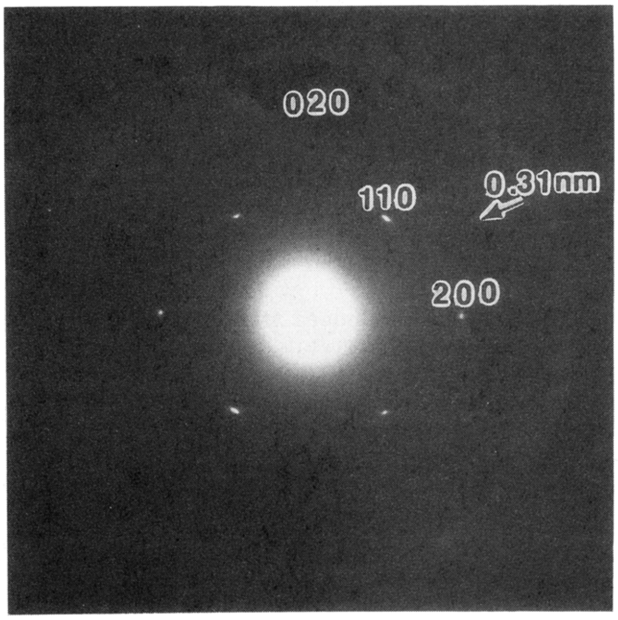


Figure 13. ED pattern along the [00*l*] zone for PEKK(T/I) crystallized at 310 °C for 15 h from the melt.

When the melt crystallization occurs at and above 310 °C, only pure form I can be found, as shown in Figure

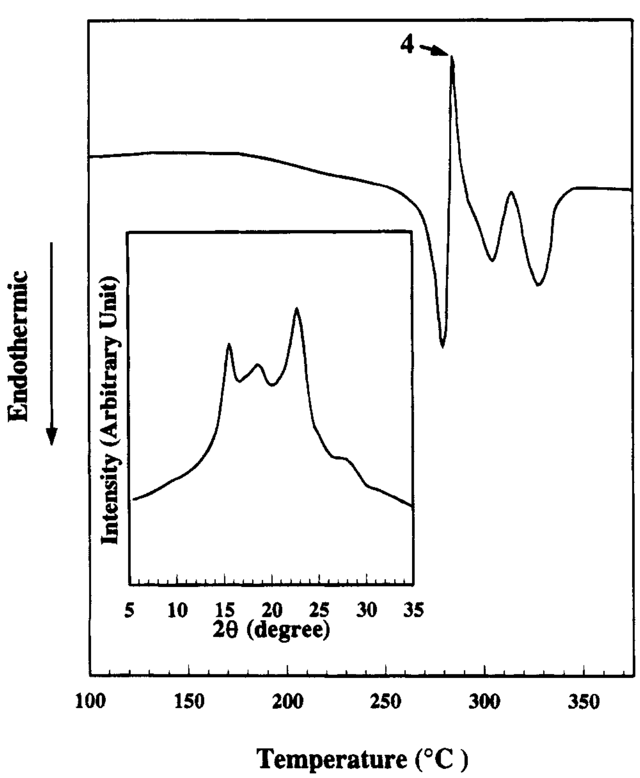


Figure 14. WAXD pattern and a DSC heating diagram (10 °C/min) for PEKK(T/I) crystallized *via* solvent-induced crystallization.

13 (an ED pattern at $T_c = 310$ °C) and Figure 7 (one of the WAXD powder patterns). This manifests that endotherm I is attributed to the form I crystal melting. Interestingly, the intensities of the (213) and the (020) reflections in the ED pattern are also drastically reduced. This may be an indication that the population of the flat-on lamellar crystals increase at high crystallization temperatures. Furthermore, the reduced intensity of (020) compared to that in Figure 1b reveals that this reflection is indeed attributed to both reflections of the lamellar crystals having [00*l*] and [30$\bar{2}$] zones.

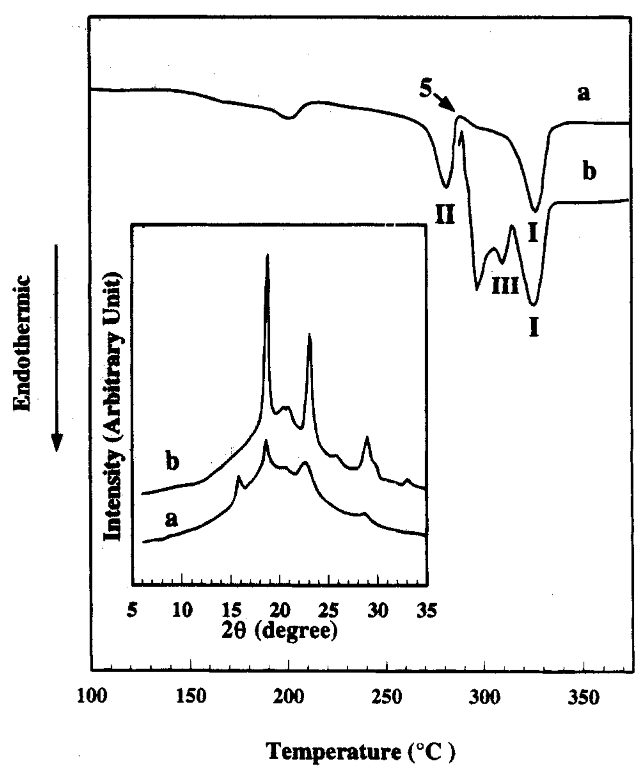


Figure 15. WAXD pattern and a DSC heating diagram (10 °C/min) for PEKK(T/I) crystallized at 180 °C for 15 h from the glassy state (a) before annealing and (b) after annealing at 290 °C for 30 min.

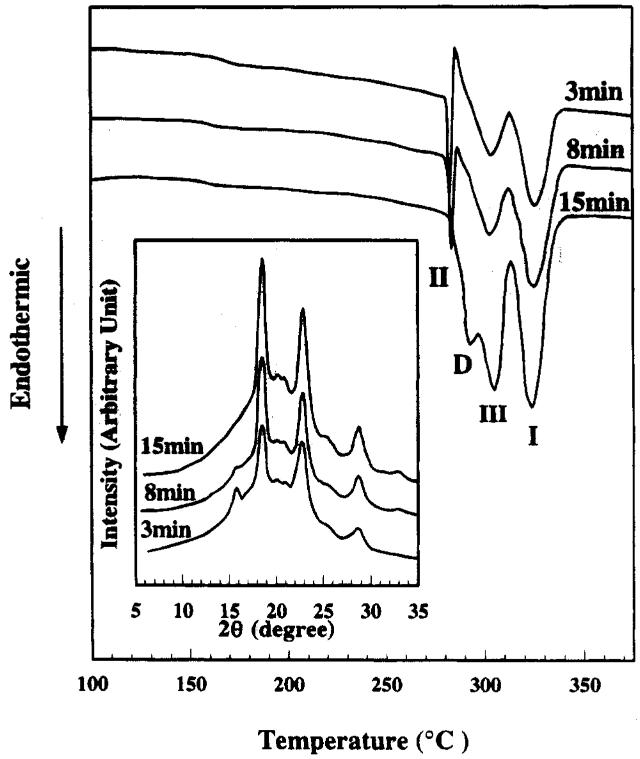


Figure 16. WAXD patterns and DSC heating diagrams (10 °C/min) for PEKK(T/I) crystallized *via* solvent-induced crystallization after annealing at 280 °C for different times.

Phase Transformations in PEKK(T/I). A recrystallization process between the melting endotherms III and I has been found during heating (Figure 9), indicating the type of phase transformation between these two forms. A recrystallization process between endotherms II and III can also be identified from DSC heating experiments on PEKK(T/I) crystallized *via* solvent-induced crystallization, as shown in Figure 14. Annealing experiments were also designed to investigate the phase transformation between these polymorphisms. After PEKK(T/I) was crystallized at 180 °C from the glassy state, the sample was annealed at a temperature slightly above the melting temperature of endotherm II (temperature 5 at around 290 °C in Figure 15) for 30 min. The WAXD powder reflections of form II crystals completely disappeared. Instead, the mixed reflections of forms I and III crystals are present, as shown in Figure 15. A corresponding DSC heating diagram is also included in this figure. It is evident that two endotherms are associated with forms I and III. Furthermore, when PEKK(T/I) was crystallized *via* solvent-induced crystallization and annealed at a temperature 4 (around 280 °C, see Figure 14) for different annealing times, similar results can be observed, as shown in Figure 16. It can thus be concluded that form II crystals are able to be transformed into both form I and III crystals after the crystal melting and recrystallization. It is logical that the melting/recrystallization process occurs due to the difference of crystal unit cells of these three forms. It is interesting that the enthalpy change of form III shown in the DSC heating diagrams is quite substantial and occupies up to about 30% of the overall

Figure 17. TEM observation of PEKK(T/I) crystallized at 310 °C for 15 h from the melt.

enthalpy change. The WAXD and ED experiments show that, however, only minor reflections are associated with this form. Further structural investigation and computer simulation are necessary to find the answer of this issue.

Crystal Morphology in PEKK(T/I). Different from the case for PEEK and PEKK(T), isolated micrometer-size single lamellar crystals in PEKK(T/I) are not formed despite extensive efforts to induce them through isothermal crystallization at different temperatures, times and various sample preparation procedures. Similar observations have also been found in PEKK(I).[9] However, relatively regular-shaped, more or less flat-on single lamellar crystals crystallized at high temperatures can be obtained in PEKK(T/I) (Figure 17). We speculate that the growth of isolated micrometer-size single lamellar crystals must be largely dependent upon the symmetry of the chain molecules. For PEKK(T/I) crystals, there is 50% less content of *meta*-linked phenylenes and, therefore, less structural asymmetry compared to PEKK(I). As a result, submicrometer regular-shaped crystals can still be found. The ED experiments indicate that the growing direction of the lamellar crystals is along the *b*-axis. However, even in Figure 17 some population of the edge-on lamellar crystals can also be seen. It is interesting that the direction of these edge-on lamellar also grows along the *b*-axis as in the case of the flat-on type of lamellae. This observed morphology further supports the observation and explanation of the coexistence of (*hk*0) and (213) reflections in one ED pattern (Figure 1b).

Conclusion

Polymorphism has been found in PEKK(T/I) *via* TEM, ED, WAXD, and DSC experiments. When the polymer is crystallized at high temperatures (at and above 310 °C), only one orthorhombic crystal unit cell (form I) can grow. The crystal unit cell dimensions are $a = 0.778$ nm, $b = 0.610$ nm, and $c = 3.113$ nm. At the crystallization temperature below 200 °C, the form II crystal is also observed. The pure form II unit cell possesses dimensions of $a = 0.417$ nm, $b = 1.108$ nm, and $c = 3.113$ nm and can be obtained *via* solvent-induced crystallization. A new, intermediate orthorhombic unit cell (form III) having dimensions of $a = 0.641$ nm, $b = 0.610$ nm, and $c = 3.504$ nm also possibly exists in a temperature range between 200 and 300 °C, and it usually coexists with form I. The thermodynamic stability of this form is between those of forms I and II. Crystal melting and recrystallization have been observed for the phase transformations between these forms. Relatively regular-shaped single crystals can be observed at high crystallization temperatures. This may be closely associated with the symmetry of the chain molecules.

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