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Crystal Morphology and Phase Identifications in Poly(aryl ether ketone)s and Their Copolymers. 1. Polymorphism in PEKK

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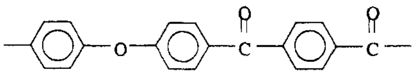
ABSTRACT: Poly(ether ketone ketone) (PEKK) with all-*para* linkages in phenylene groups is one member of the poly(aryl ether ketone) family. This polymer has been reported to exhibit two polymorphisms (forms I and II) based on wide-angle X-ray diffraction (WAXD) experiments. The form I crystal structure has been determined to have two-chain orthorhombic packing with $a = 0.767$ nm, $b = 0.606$, and $c = 1.008$ nm. For form II, however, two different structures have been proposed: both are orthorhombic, but with different size and symmetry.[1,2] Through our morphological observations, two different crystal forms have been isolated. Using electron diffraction (ED) experiments combined with WAXD, we have found that form II of PEKK should have a two-chain orthorhombic lattice. This unit cell dimension is consistent with the form II cell reported by Blundell *et al.*,[1] namely, $a = 0.417$ nm, $b = 1.134$ nm, and $c = 1.008$ nm. Two maps of the formation of these forms with crystallization conditions are also discussed.

Introduction

Poly(aryl ether ketone)s and their copolymers are the most common members of a new class of high-temperature, high-performance engineering thermoplastics with potential applications as matrix resins in composites. Their useful properties include high melting and glass transition temperatures, a wide range of attainable crystallinities, high chemical resistance, low flammability, and ease of processability into various forms such as molded parts, composites, films, fibers, and coatings.[3-5] Among the poly(aryl ether ketone)s, poly(ether ether ketone) (PEEK) has received the most attention in scientific studies and industrial applications during the past 15 years.

The PEEK crystal structure is very similar to the crystal structure of poly(p-phenylene oxide).[6] Chains in the crystals adopt an extended conformation with the phenylene rings alternating an angle of *ca.* ±37° to the plane of the zigzag backbone. It has also been shown that the ether linkage and ketone groups are crystallographically equivalent, and the unit cell consists of two-chain orthorhombic packing with the $Pbcn$-D_{2h}^{14} space group, in which one chain is at the center of the ab projection in the unit cell and 4 × 1/4 chains are at the corners.[7-9] This crystal form is commonly observed in all members of the poly(aryl ether ketone) family with minor dimension variations. For poly(ether ketone ketone) (PEKK) with all-*para* linkages in phenylene groups,



wide-angle X-ray diffraction experiments reveal that this crystal form possesses an orthorhombic lattice with $a = 0.769$ nm, $b = 0.606$ nm, and $c = 1.008$ nm (form I) as shown in Figure 1a.[1] The effect of sequence and proportion of the ether linkages and ketone groups in the crystal structures of this form in the poly(aryl ether ketone) family has been investigated by Blundell *et al.*[1] They reported a new crystal form (form II) with a two-chain orthorhombic unit cell with $a = 0.417$ nm, $b = 1.134$ nm, and $c = 1.008$ nm as shown in Figure 1b based on WAXD fiber patterns in their study. With similar WAXD results, Gardner *et al.* also reported a form II structure of a one-chain orthorhombic unit cell with dimensions of $a = 0.393$ nm, $b = 0.575$ nm, and $c = 1.016$ nm (Figure 1c).[2] Recently, polymorphism in other poly(aryl ether ketone)s has also been reported.[10] With increasing chain stiffness and decreasing chain mobility, the ability to form the second form (form II) has been found to be significantly enhanced.

In principle, a WAXD fiber pattern alone for a uniaxially oriented polycrystalline sample may not unambiguously define ($hk0$) planes since in this sample only the c-axis is generally aligned along the chain direction and both the a- and b-axes are randomly distributed. An example is the case here for PEKK of which two different lattices and symmetries have been reported for the form II structure.[1,2] Electron diffraction (ED) experiments on polymer single lamellar crystals are necessary to determine the ($hk0$) reciprocal lattice. On the basis of these crystal lattices and symmetries, we expect that they should possess different ($hk0$) ED patterns, as shown in Figure 2. Nevertheless, growing sizable single lamellar crystals in semicrystalline polymers becomes increasingly difficult with increasing chain stiffness. Furthermore, ED experiments must accompany morphological observations of the polymer crystals via transmission electron microscopy (TEM).

A morphological study of PEEK crystallized from the melt was reported by Lovinger *et al.* for thin-film samples[11,12] and Bassett *et al.* for replicas via permanganic etching.[13] PEEK spherulites consist of narrow lamellae and have the b-axis of the unit cell radial. At high temperatures in the ultrathin films, the spherulites attain an extraordinary cylindrical symmetry as a result of growth of the lamellae on edge, with the c-axis parallel to the film surface and the a-axis corresponding to the cylinder axis. At lower temperatures, a more or less random lamellar disposition is seen in the film spherulites, although edge-

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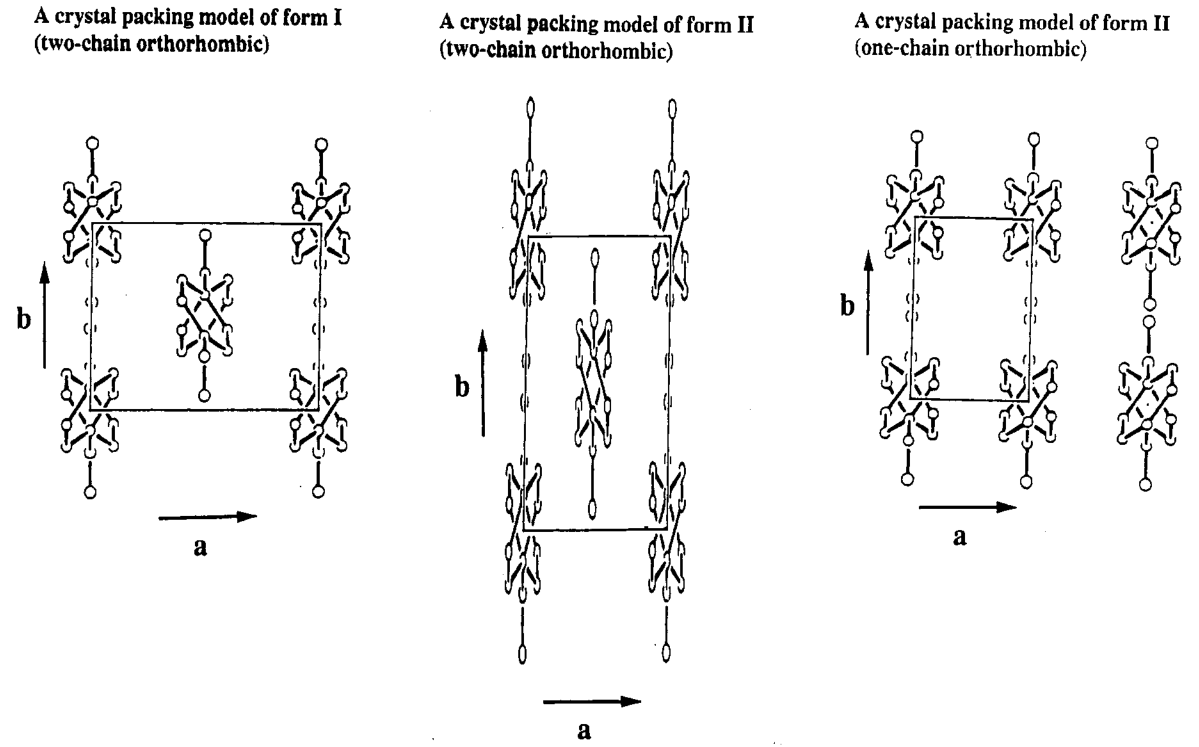
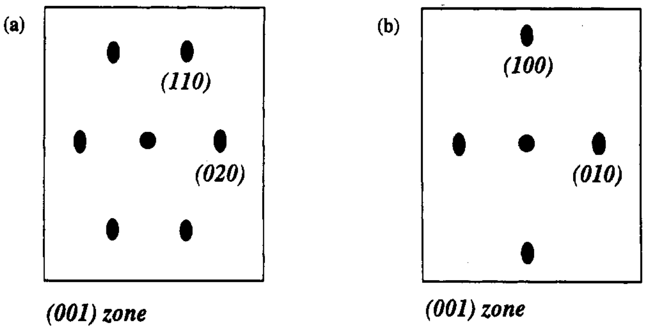

A crystal packing model of form I (two-chain orthorhombic)

A crystal packing model of form II (two-chain orthorhombic)

A crystal packing model of form II (one-chain orthorhombic)

Figure 1. A crystal packing model of form I (two-chain orthorhombic) (a, left), form II (two-chain orthorhombic)[1] (b, middle), and form II (one-chain orthorhombic)[2] (c, right).



(001) zone *(001) zone*

Figure 2. Predicted form II ED patterns based on both crystal lattices and symmetries proposed by Blundell *et al.*[1] (a) Gardner *et al.*[2] (b).

on lamellae still predominate. Cold crystallization from the amorphous glassy state in the films forms random lamellar aggregates and small spherulites without any consistent morphological features down to a level of resolution of 1.0 nm.[11] Recently, a second morphological form of PEEK in thin films has been found at high crystallization temperatures. This consists of large (micron sized), faceted single crystals. Lamellar crystals of this kind have the same unit cell and *b*-axis preferred-growth direction as the usual PEEK lamellae. The molecular chains are inclined to the lamellar normal by 38.1° about the *b*-axis, leading to a {102}-type fold surface.[12] For the crystal morphology of PEKK, TEM images of the replica have also been briefly reported by Gardner *et al.*[2]

In this paper, we report our attempt to study the polymorphism of PEKK via both WAXD and ED experiments. Through growing lamellar crystals in PEKK under different conditions, polymorphic structural formation maps are obtained. After form I and form II single lamellar crystals are isolated, both crystalline lattices are determined.

Experimental Section

Materials and Samples. Developmental grade PEKK was provided by DuPont Co. The polymer was prepared from diphenyl ether and terephthalic acid in a two-step process. The number-average molecular weight of the samples is 10 000, and the polydispersity is 3.

For the WAXD study, PEKK films were cast onto glass slides using a 2% PEKK–pentafluorophenol (PFP) (w/w) solution at *ca.* 80 °C to obtain thicknesses ranging from 0.05 to 0.1 mm. The solvent was then evaporated in a vacuum oven. The samples were heated to *ca.* 20 °C above their equilibrium melting temperature (410 °C[2]) for several minutes in a dry nitrogen atmosphere and then either quenched in liquid nitrogen to generate the amorphous glassy films for later cold crystallization or rapidly cooled to a preset temperature for melt crystallization. For solvent-induced crystallization, amorphous glassy films were exposed to methylene chloride at room temperature for 1 week. After solvent-induced crystallization, the solvent was evaporated in a vacuum oven at 50 °C under reduced pressure for 2 days.

Ultrathin PEKK films with thicknesses ranging between 0.01 and 0.1 μm were prepared for TEM observations by casting a 0.1% (w/w) PEKK–PFP solution onto glass slides which were coated with carbon. After different crystallization conditions were applied, the films were stripped and floated onto the water surface and then picked up using copper grids.

Instrumentation and Experiments. PEKK crystal morphology and ED patterns were observed via a JEOL (1200 EX II) TEM using a 120-kV accelerating voltage. The PEKK films were shadowed by Pt and coated with carbon for TEM morphological observations. A tilting stage in the ED experiments was also used to determine the three-dimensional lattice. Calibration of the electron diffraction spacings was carried out using Au and TlCl (*d*-spacing < 0.384 nm, the largest spacing for TlCl). Spacing values larger than 0.384 nm were calibrated by doubling the *d*-spacings of those reflections based on the spacing of their first-order reflections.

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. The crystallization conditions of the PEKK films were the same as those in the TEM and ED experiments.

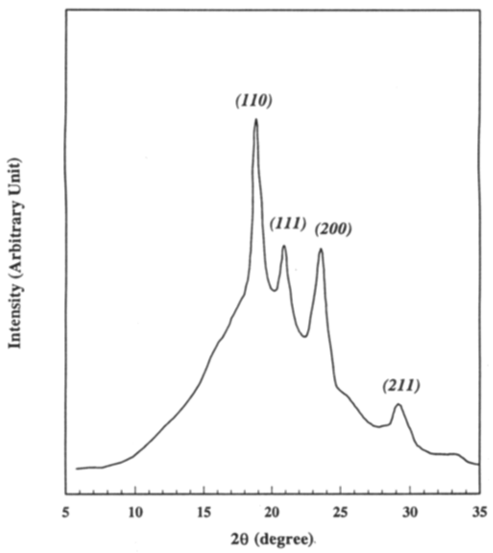


Figure 3. WAXD pattern for PEKK crystallized at 340 °C for 60 min from the isotropic melt.

Results and Discussion

Identification of Polymorphs. Form I can always be isolated when PEKK film is crystallized from the isotropic melt. The WAXD pattern of PEKK crystallized at 340 °C for 60 min from the melt is shown in Figure 3. With the *c*-axis dimension determined by Blundell,[1] the diffraction peaks can be indexed via a two-chain orthorhombic unit cell as shown in Figure 1a. The cell dimensions are calculated to be $a = 0.767$ nm, $b = 0.606$ nm, and $c = 1.008$ nm, and this structure is designated as form I. The reflection peak positions are the (110) reflection ($2\theta = 18.69°$), the (111) reflection ($2\theta = 20.61°$), the (200) reflection ($2\theta = 23.21°$), and the (211) reflection ($2\theta = 28.92°$), respectively. The diffraction pattern is very similar to that of all-*para* members in poly(aryl ether ketone)s such as PEEK. The corresponding crystal morphology of form I in PEKK ultrathin films is shown in Figure 4 under the same crystallization conditions. It is surprisingly that large single lamellar crystals can be found with the highly faceted shape. The ED pattern of these single lamellar crystals is also included in Figure 4. The electron beam is parallel to the $[1\bar{1}\bar{1}]$ zone since the (110) and (211) reflections are observed. This indicates that the *c*-axis of the lamellar crystals is not perpendicular to the substrate surface (also the lamellar surface). An angle of 25.7° inclination of the molecular chains to the lamellar normal has been found, and the inclined molecular chains lead to {114}-type fold surfaces. A similar observation of such tilting of the molecular chains to the lamellar normal has recently been reported by Lovinger *et al.* in PEEK.[12] The ED patterns of the PEKK single lamellar crystals with the [001] and $[1\bar{1}0]$ zones can also be obtained via the tilting stage as shown in Figure 5.

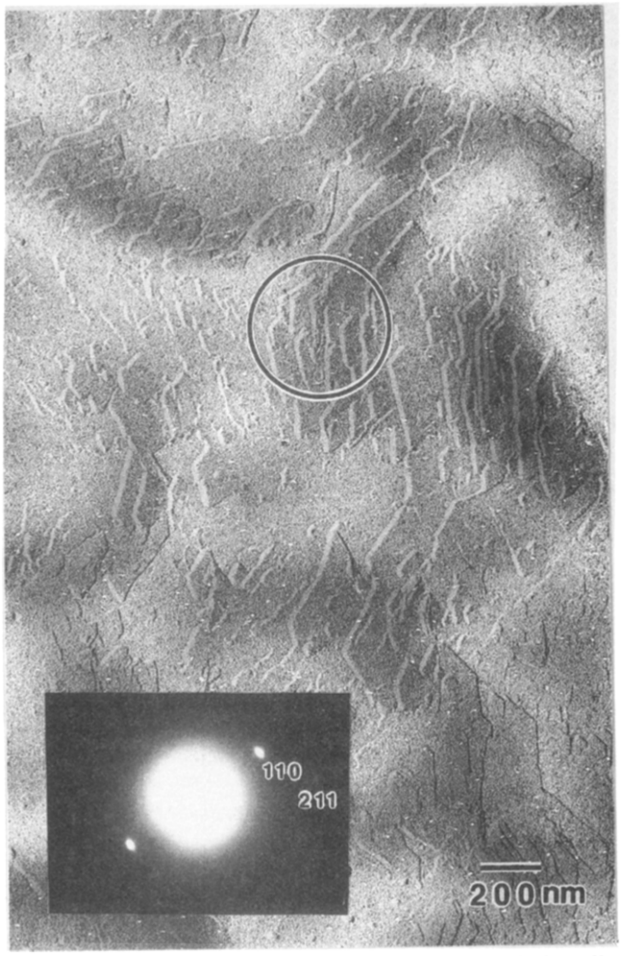


Figure 4. TEM observation of PEKK form I single lamellar morphology crystallized at 340 °C for 60 min from the melt. The ED pattern is originated from the circled area of the micrograph and shown in correct orientation.

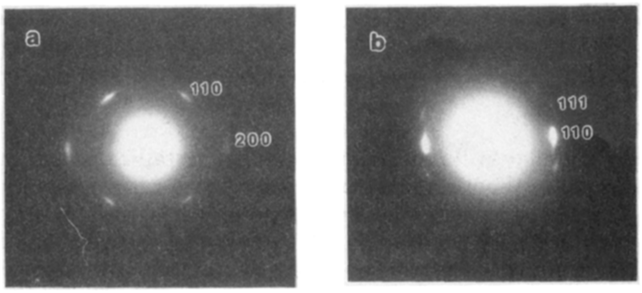


Figure 5. ED patterns for PEKK form I obtained from the single lamellar crystals: (a) along the [001] zone; (b) along the $[1\bar{1}0]$ zone.

Pure form II can be obtained by two different crystallization processes: solvent-induced crystallization[2] and/or cold crystallization from the glassy state. WAXD patterns for PEKK obtained from both crystallization processes are shown in Figure 6. It is evident that these reflections results are entirely different from those obtained from form I in PEKK crystallized from the melt (Figure 3). For indexing the reflection peaks, one has to decide on using the form II crystal structure proposed by Blundell *et al.*[1] or that of Gardner *et al.*[2] In Figure 6, the indices are those of Blundell *et al.* (see below for reasons). TEM of the crystalline morphology via solvent-induced crystallization shows very small crystallites with a typical size of <50 nm in three dimensions (Figure 7). These crystallites are too small to be individually detected via ED experiments to determine the crystal lattice. Only a powder-like ED pattern is found (Figure 7). When form II crystals are grown from cold crystallization, single lamellar crystals can also be obtained. Figure 8 shows the morphological observation of the PEKK crystals formed at 340 °C for 60 min from the glassy state. Apparently, flat-on, faceted single lamellar crystals can be found and are in the sub-micron size range. An ED pattern of the single crystals only shows *b*-axis reflections of (020) and (040), indicating that the *c*-axis of the single crystals is not perpendicular to the lamellar surface. However, a precise angle of inclination may not be obtained based on this ED pattern due to the lack of other reflections. Through the tilting stage, ED patterns of the crystals are taken (Figure 9) along the [001], [100], and $[20\bar{1}]$ zones. A roughly

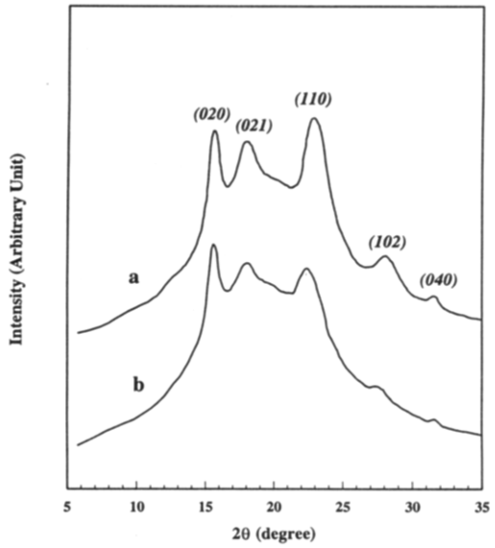


Figure 6. WAXD patterns for both (a) solvent-induced crystals and (b) crystals grown from the glassy state at 180 °C. The indices follow the unit cell proposed by Blundell *et al.*[1]

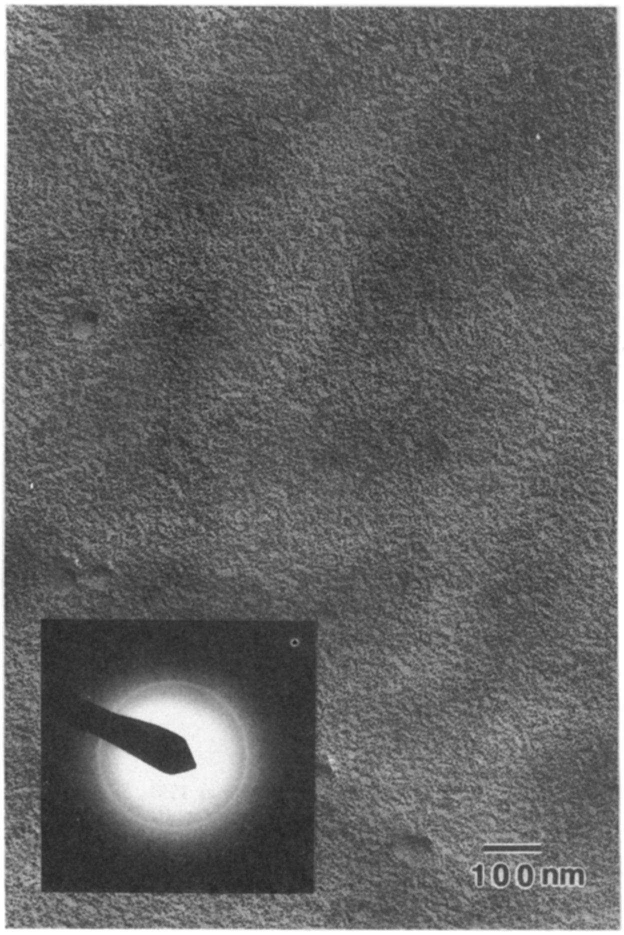


Figure 7. TEM observations of PEKK crystals obtained via solvent-induced crystallization. The ED pattern is also included.

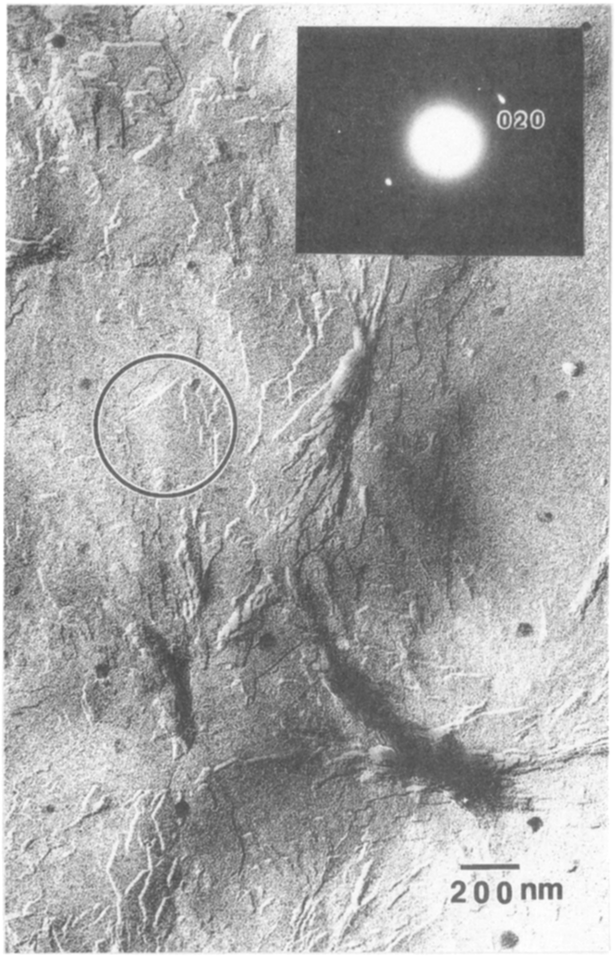


Figure 8. TEM observations of PEKK crystals grown from the glassy state at 340 °C for 60 min. The ED pattern is originated from the circled area of the micrograph and shown in correct orientation.

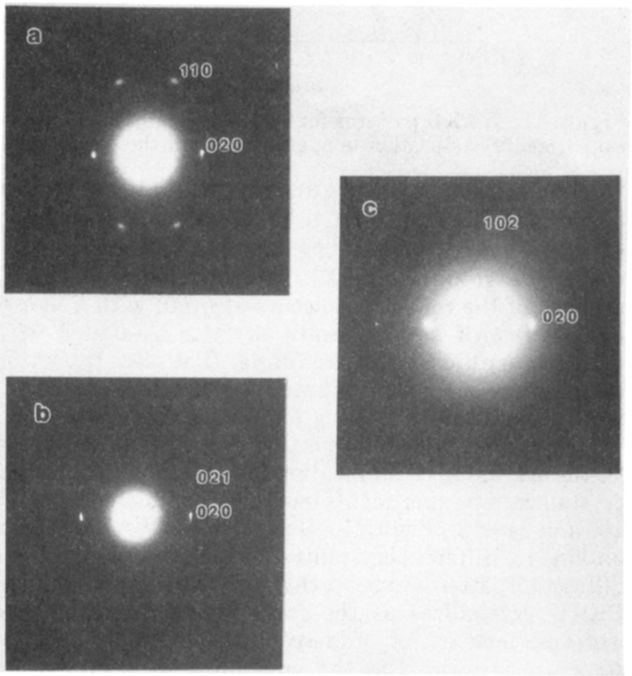


Figure 9. ED patterns for PEKK form II obtained from the single lamellar crystals (a) along the [001] zone, (b) along the [100] zone, and along the [20$\bar{1}$] zone.

estimated 40 ± 5° of molecular inclination to the lamellar normal can be found. The [001] zone ED pattern obtained shows exactly the same form II lattice and symmetry as that predicted in Figure 2 as proposed by Blundell *et al.*; a two-chain orthorhombic unit cell can be determined with dimensions of $a = 0.42$ nm and $b = 1.13$ nm, and, therefore, the (020), (040), and (110) reflections can be observed (Figure 9a). The ED pattern of the [100] zone (Figure 9b) exhibits the (020), (040), and (021) reflections, in which the c-axis dimension of 1.01 nm is determined. From the ED pattern of the [20$\bar{1}$] zone (Figure 9c), the (020), (040), and (102) reflections have been found. The (102) reflection corresponds to the reflection peak at $2\theta = 27.77°$ in the

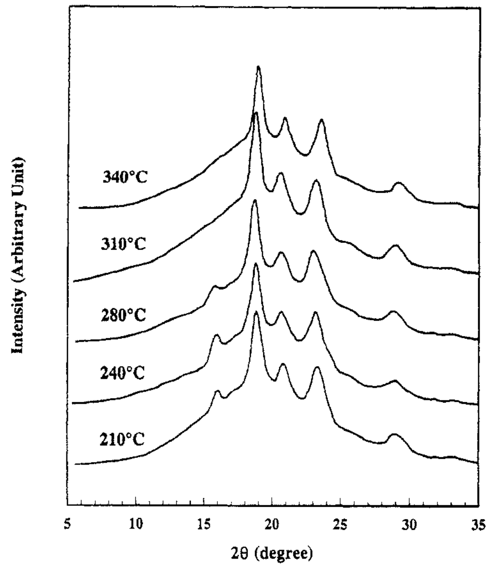


Figure 10. WAXD patterns for PEKK crystallized at various isothermal crystallization temperatures from the isotropic melt.

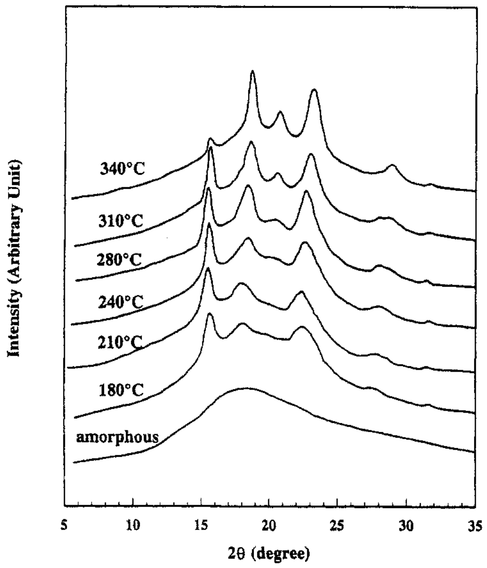


Figure 11. WAXD patterns for PEKK crystallized at various isothermal crystallization temperatures from the glassy state.

WAXD diffraction (Figure 6). No (013) reflection (2θ = 27.69°) and (120) reflection (2θ = 26.53°) have been found in the ED experiments. These results are consistent with the space group $Pbcn\text{-}D_{2h}^{14}$, in which the systematic absence of the reflections occurs at ($hk0$) with $h + k$ = odd, ($0kl$) with k = odd, and ($h0l$) with l = odd.[14]

Polymorphic Structure Maps. The glass transition temperature of PEKK has been reported to be *ca.* 165 °C, and its equilibrium melting temperature is *ca.* 410 °C.[2] The crystallization window is thus over 200 °C, and at 265 °C the maximum crystallization rate is found. Isothermal crystallization experiments have been conducted between 180 and 340 °C. Figure 10 illustrates the WAXD results obtained at different crystallization temperatures. All the diffraction patterns indicate that in this temperature range, PEKK crystallizes as the form I structure from the isotropic melt at low undercoolings. A minor form II structure is formed as the crystallization temperature approaches (or passes through) the maximum crystallization rate temperature (265 °C). On the other hand, when isothermal crystallization experiments are carried out from the glassy state, as shown in Figure 11 for WAXD results, reflection peaks are somewhat different at various temperatures. At low temperatures (high undercoolings), WAXD patterns reveal that the pure form II crystal structure is formed as in the case of crystallization temperature at 180 °C. As the cold crystallization is conducted at higher temperatures, the reflection peaks of the form I structure start appearing in the WAXD patterns. A mixed form I and form II reflection is seen. A typical example is the cold crystallization at 310 °C (see Figure 11). With increasing crystallization temperature for cold crystallization, the ability to grow the form I structure is significantly enhanced. This is possibly due to the effect of chain mobility on the nucleation type obtained. Since form I is thermodynamically more stable than form II, it is conceivable that when the chain molecules possess more mobility and form primary nuclei slowly, the more stable form I nuclei can be formed. Otherwise, the less stable form II nuclei are dominant in a crystallization process where primary nuclei form very quickly with limited molecular mobility. These results are consistent with the polymorphism study in poly(aryl ether ketone)s reported by Gardner *et al.*[10]

Conclusion

We have confirmed that PEKK exhibits polymorphism. Pure form I can be found when PEKK is crystallized from the isotropic melt at low undercoolings. Based on WAXD reflection and ED patterns, a two-chain orthorhombic unit cell with a = 0.767 nm, b = 0.606 nm, and c = 1.008 nm is determined as the form I structure. Form II can be isolated by two different crystallization processes: solvent-induced crystallization and cold crystallization from the glassy state. A two-chain orthorhombic unit cell with a = 0.42 nm, b = 1.13 nm, and c = 1.01 nm can be determined from the ED patterns of isolated single lamellar crystals. This form II unit cell is consistent with the structure proposed by Blundell *et al.*[1] The formation of the thermodynamically more stable form I nuclei is critically associated with crystallization conditions. Only enough molecular mobility and a slow primary nucleation rate can permit form I crystal growth.

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