Macromolecules **1994,** *27,* 5787–5793

Crystal Morphology and Phase Identifications in Poly(aryl ether ketone)s and Their Copolymers. 2. Poly(oxy-1,4-phenylenecarbonyl-1,3-phenylenecarbonyl-1,4-phenylene)

Rong-Ming Ho, Stephen Z. D. Cheng,* Howard P. Fisher, and Ronald K. Eby

Maurice Morton Institute and Department of Polymer Science, The University of Akron, Akron, Ohio 44325-3909

Benjamin S. Hsiao and Kenncorwin H. Gardner

Central Research and Development Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19880-0302

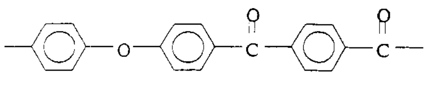
Received April 25, 1994; Revised Manuscript Received July 5, 1994⊛

ABSTRACT: The crystal structure and morphology of poly(oxy-1,4-phenylenecarbonyl-1,3-phenylenecarbonyl-1,4-phenylene) [PEKK(I)] containing one *meta* linkage in the three phenylene repeat units have been studied. Only one crystal form was found based on wide-angle X-ray diffraction (WAXD) and electron diffraction (ED) experiments. The crystal unit cell possesses a two-chain orthorhombic lattice 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. Through our morphological observations, lamellar crystals are edge-on in most thin films. The crystal growth direction is along the b-axis, and the a-axis is perpendicular to the film surface. The flat-on lamellae can only be observed in the "eye" of the spherulites. The crystal unit cell dimensions change with the isothermal crystallization temperatures. In particular, the c-axis shrinks drastically with increasing temperature. This can be attributed to the conformation changes in *meta*-linked phenylene groups, which is evident by comparing the data for PEKK(I), PEKK with all-*para*-linked phenylene groups, and poly(ether ether ketone) (PEEK).

Introduction

Since the development of the poly(aryl ether ketone) family about 15 years ago, poly(ether ether ketone) (PEEK) has received the most attention in both scientific and industrial studies. A large number of works on the crystal structure, morphology, thermal and mechanical properties, and blends can be found in the literature. It is shown that the PEEK crystal structure is similar to the structure of poly(p-phenylene oxide) (PPO).[1] Chains in the PEEK crystals adopt an extended conformation with the phenylene rings alternating at angles of ca. ±37° 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 $Pbcn\text{-}D_{2h}^{14}$. In this case, one chain is located in the center of the ab projection, and four 1/4 chains are located at the corners.[2-4] This crystal form is commonly observed in all members of the poly(aryl ether ketone) family with only minor dimension variations.

Recently, a series of poly(ether ketone ketone)s prepared from diphenyl ether (DPE), terephthalic acid (T), and isophthalic acid (I) have been investigated.[5-7] As prepared, these polymers can be thought of as consisting of "phthalate diads" containing linkages such as $-(\mathrm{DPE{-}T})_n-$ or $-(\mathrm{DPE{-}I})_n-$. For poly(ether ketone ketone) with all-*para* linkages in the phenylene groups, [PEKK(T), $-(\mathrm{DPE{-}T})_n-$], its chemical structure is



Two polymorphs have been observed via wide-angle X-ray diffraction (WAXD)[5-8] and single-crystal electron diffraction (ED) experiments[7] in PEKK(T): a two-chain orthorhombic lattice with dimensions of a = 0.769 nm, b = 6.06 nm, and c = 1.008 nm (form I) and a two-chain orthorhombic lattic with a = 0.417 nm, b = 1.134 nm, and c = 1.008 nm (form II). Polymorphism in other poly(aryl ether ketone)s has also been reported.[8] With increasing chain stiffness and decreasing chain mobility, the ability to form the second form (form II) has been found to be significantly enhanced. The effects of sequence and proportion of ether and ketone linkages in the crystal lattices of the all-1,4-linked poly(aryl ether ketone) family have also been investigated by Blundell *et al.*[5]

Morphological studies of PEEK crystallized from the melt were reported by Lovinger *et al.* for thin-film samples[9,10] and Bassett *et al.* for replicas via permanganic etching.[11] PEEK spherulites consist of narrow lamellae and have the b-axis of the unit cell oriented radially. At high temperatures in the ultrathin films, the spherulites attain an extraordinarily cylindrical symmetry as a result of the "edge-on" lamellar growth. Its c-axis is parallel to the film surface, and the a-axis corresponds to the cylinder axis. At lower temperatures, a more or less random lamellar disposition is seen in the spherulites, although the edge-on lamellae are still predominant. Recently, a second morphological form of PEEK in the thin films has been found at high crystallization temperatures, which showed large (micron sized), faceted single crystals. Lamellar crystals of this kind have the same unit cell as found in 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.[10] Similar observations have been found in PEKK(T) in which the c-axis of the lamellar crystals is not perpendicular to the substrate surface (thus lamellar fold surface). In the case of the form I structure in PEKK(T), an angle of 25.7° inclination of the chains to the lamellar normal has been found, which results in a {114}-type fold surface. For the form II structure, an estimate of 40 ± 5° molecular inclination to the lamellar normal has been observed.[7]

---

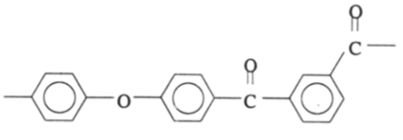
* To whom correspondence should be addressed.

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

0024-9297/94/2227-5787$04.50/0

The variation of unit cell parameters in PEEK via crystallization temperature has been reported by Wakelyn *et al.*[12] and Hay *et al.*[13] They observed that the unit cell dimensions along the three directions, *a*, *b*, and *c*, decrease with increasing crystallization temperature. Although crystal defects such as mismatch of adjacent chains might be expected to occur at low crystallization temperature, such an argument does not account for the observed dimensional changes due to temperature. Instead, variation in chain packing and conformation such as the bond angles between the plane of adjacent phenylenes are speculated to be responsible.[13]

In this paper, we report our attempt to study the effect of the partially *meta*-linked phenylene groups, PEKK(I), in the crystal structure and morphology via both WAXD and ED experiments. The chemical structure of PEKK(I) [–(DPE–I)$_n$–] is



Variations of the unit cell dimensions with crystallization temperature in the poly(aryl ether ketone) faimly are also discussed.

Experimental Section

Materials and Samples. Developmental grade PEKKs were provided by DuPont Co. Both polymers, PEKK(T) and PEKK(I), were prepared from diphenyl ether (DPE) and terephthalic acid (T) or isophthalic acid (I) in a two-step process. The number-average molecular weight of the samples are around 10000 and 7000, respectively, and the polydispersity is about 3 for both samples.

For the WAXD study, PEKK(T and I) films were cast onto glass slides using a 2% PEKK–pentafluorophenol (PFP) (w/w) solution at ca. 80 °C to obtain thicknesses ranging from 0.1 to 0.2 mm. The solvent was then evaporated under vacuum. The samples were heated to ca. 20 °C above their equilibrium melting temperatures (410 °C for PEKK(T) and 310 °C for PEKK(I)[6]) for several minutes 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. Monofilaments of the PEKK(I) fibers were spun from the melt and drawn at temperatures above the glass transition temperature to obtain molecular orientation (draw ratio is ca. 6). This monofilament was then annealed at fixed lengths isothermally above the glass transition temperature to induce crystallization.

Ultrathin PEKK(I) films with thicknesses ranging from 0.01 to 0.1 μm were prepared for transmission electron microscopy (TEM) observations by casting a 0.1% (w/w) PEKK(I)–PFP solution onto carbon-coated glass slides. After crystallization at different temperatures and times, the films were stripped and floated onto the water surface and then 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 chosen 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.

PEKK(I) crystal morphology and ED patterns were observed via a JEOL (1200 EX II) TEM using an accelerating voltage of 120 kV. The PEKK(I) films were shadowed by Pt and coated with carbon for TEM observations. A tilting stage was also used in the ED experiments to determine the three-dimensional crystalline 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 their first-order reflections. The crystallization conditions of the PEKK(I) films were the same as those in the WAXD experiments.

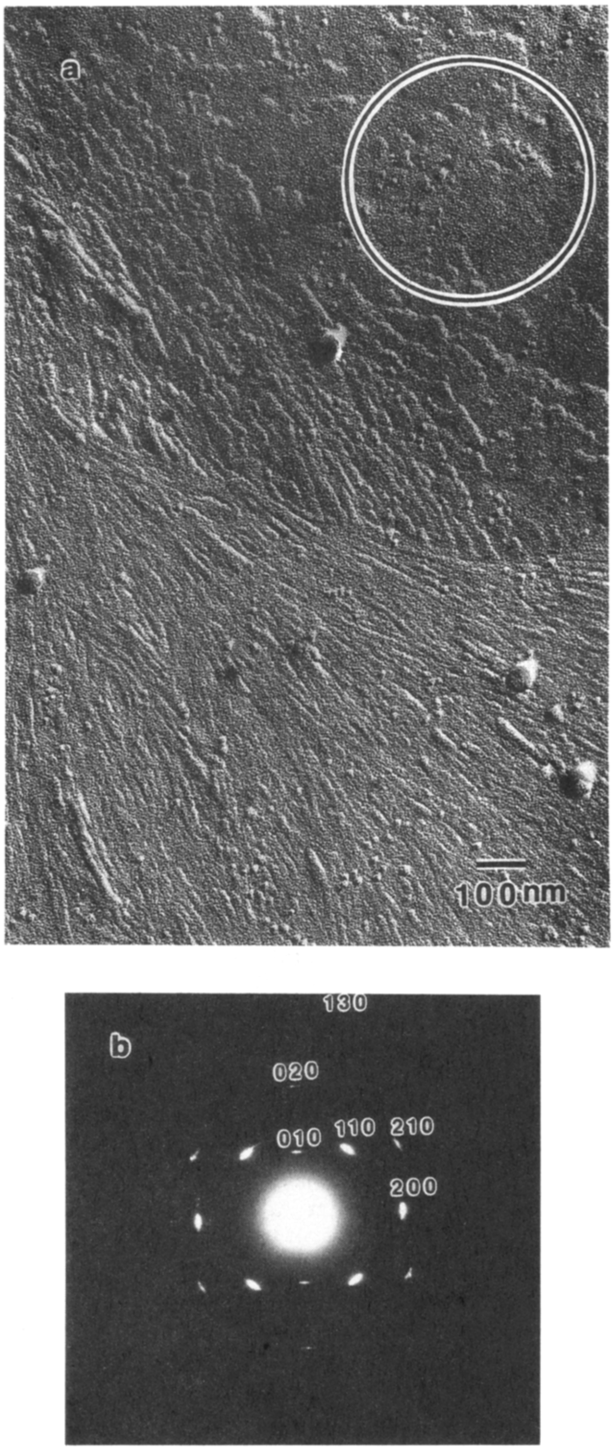


Figure 1. TEM observation of PEKK(I) crystallized at 260 °C for 60 min from the melt: (a) an "eye"-like morphology with the flat-on orientation in the eye; (b) ED pattern. The ED pattern originates from the circled area of the micrograph and is shown in correct orientation.

Molecular mechanics calculations were carried out on a Silicon Graphics 4D/35 workstation using Sybyl molecular modeling software version 6.0 (Tripos Associates Inc., St. Louis, MO).

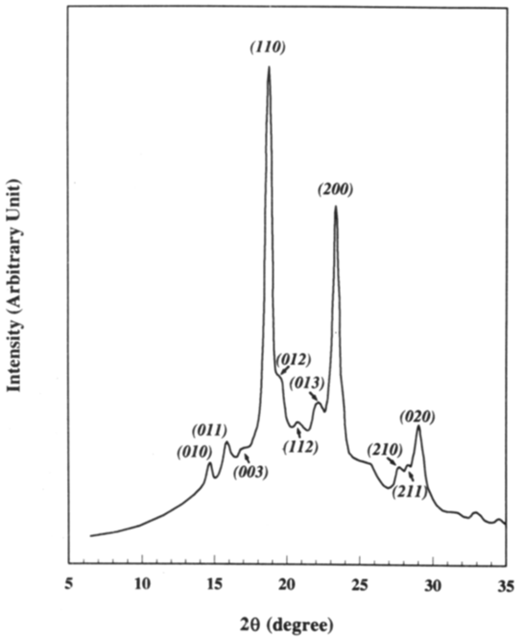


Figure 2. WAXD powder pattern for PEKK(I) crystallized at 260 °C for 60 min from the isotropic melt.

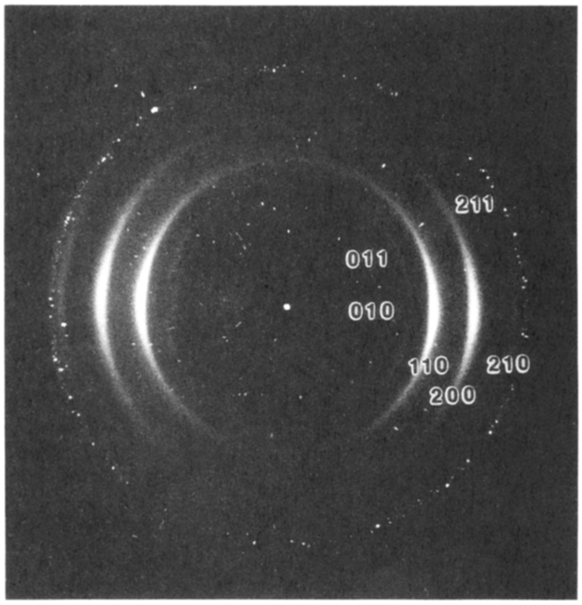


Figure 3. WAXD fiber pattern for PEKK(I) after annealing at 160 °C for 12 h.

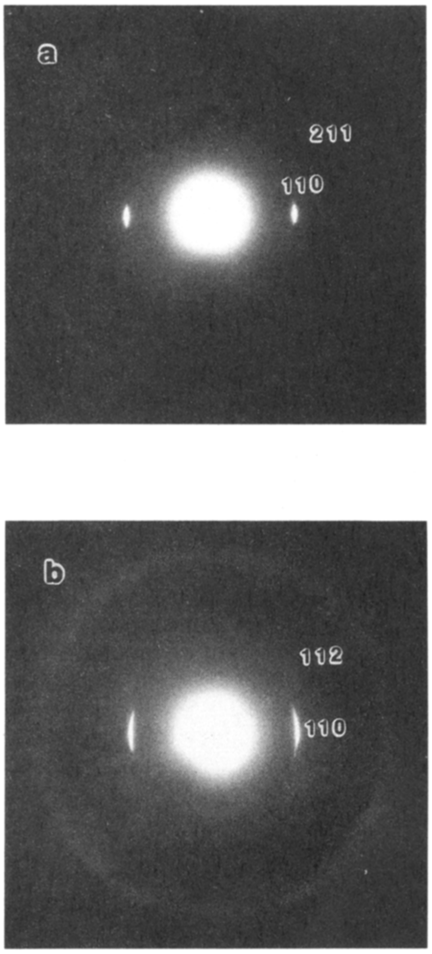


Figure 4. Tilted ED patterns for PEKK(I) obtained from the crystals grown at 260 °C for 60 min from the melt (a) along the [$1\bar{1}\bar{1}$] zone and (b) along the [$1\bar{1}0$] zone.

Results and Discussion

Identification of the Crystal Structure of PEKK(I). Figure 1a shows the PEKK(I) crystal morphology after isothermal crystallization from the melt at 260 °C for 60 min. A spherulitic texture is evident. Most of the spherulites show an "eye"-like morphology near the spherulitic centers during crystallization, where the lamellae are grown in a flat-on fashion. This is evident by the decent ED patterns showing the [00*l*] zone (Figure 1b); only the (*hk*0) diffractions are observed. These morphological observations are similar to those reported in PEEK by Lovinger *et al.*[9] Based on the major diffractions of the (200), (010), (020), (110), and (210) in this pattern, a two-chain orthorhombic lattice can be determined with dimensions of a = 0.79 nm and b = 0.63 nm after refinements. Figure 2 shows the WAXD powder pattern of PEKK(I) crystallized isothermally at 260 °C for 60 min from the melt. Based on the ED results, we recorded five independent (*hk*0) reflections: the (010) reflections at 2θ = 14.5(1)°, the (110) reflection at 2θ = 18.5(8)°, the (200) reflection at 2θ = 23.2(1)°, the (210) reflection at 2θ = 27.5(4)°, and the (020) reflection at 2θ = 28.8(8)°. All of them can be satisfactorily indexed via the use of an orthorhombic unit cell with the cell dimensions of a = 0.766 nm and b = 0.611 nm after refinements.

Two possible c-axis dimensions of the unit cell exist: one with three-phenylene groups and the other with six-phenylene groups in the crystallographic unit. In Figure 2, we use the three-phenylene c-axis to index the reflections. In addition to the WAXD powder pattern, a WAXD fiber pattern was obtained as shown in Figure 3. Based on the two-chain orthorhombic unit cell, the (010), (110), (200), and (210) reflections along the equator can be clearly identified. However, the meridional reflections and (020) are absent due to the limitation of the low-temperature annealing. Attempts to anneal at high temperatures failed due to a surprisingly large shrinkage along the c-axis (see below for detailed discussion). Therefore, assignments of the reflections in the quadrants remain unsolved. For example, the (011) and the (211) reflections are assigned in the fiber pattern based on the three-phenylene c-axis in one crystallographic repeat unit, and they may be assigned as the (012) and the (212) reflections when the six-phenylene c-axis is considered.

To determine the dimension of the c-axis, a tilted ED pattern of PEKK(I) lamellar crystals with [$1\bar{1}\bar{1}$] zone were carried out as shown in Figure 4a. In this pattern, the strong (110) reflection and a weak reflection can be

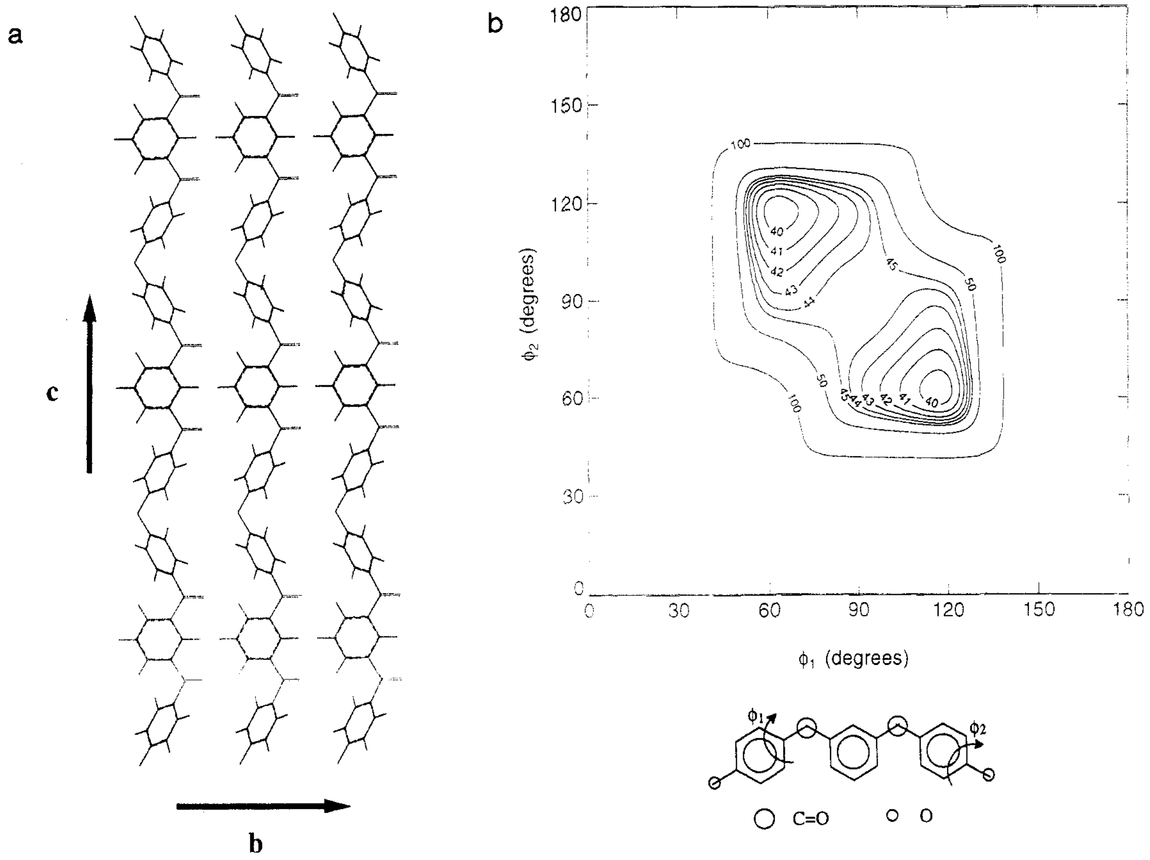


Figure 5. (a) PEKK(I) chains with three repeat units each in the crystal lattice. (b) An energy diagram calculated based on the Sybyl Tripos force field (see text).

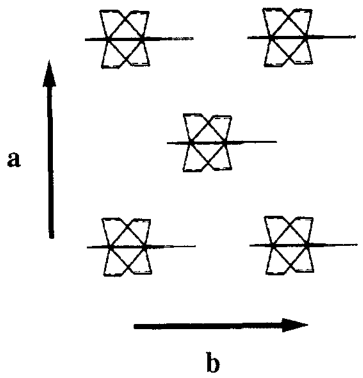


Figure 6. Crystal packing model of the two-chain orthorhombic structure for PEKK(I) in projections perpendicular to the chain direction.

observed. Combined with the WAXD results, this weak reflection may be indexed as either the (211) reflection for a three-phenylene *c*-axis in one repeat unit or the (212) reflection for a six-phenylene *c*-axis in one repeat unit. Based on the principle of diffraction, the (212) and (110) reflections cannot coexist in the same [1$\bar{1}\bar{1}$] diffraction zone. Therefore, a three-phenylene *c*-axis in one repeat unit for the crystal lattice is identified. An ED pattern of the PEKK lamellar crystals along the [1$\bar{1}$0] zone has also been obtained via a tilting stage as shown in Figure 4b in which the (110) and (112) reflections are found based on the three-phenylene *c*-axis.

In Figure 2, a weak (003) reflection can also be observed when the crystallization temperature is high. However, the *c*-axis repeat unit determined by the (011) reflection (c = 1.456 nm) is about 7.6% lower than the value deduced from the position of the (003) reflection (c = 1.576 nm). The cause of such a discrepancy is not clear at this time. The discrepancy of the *c*-axis dimension has also been reported for PEEK by Nakamae *et al.*[14] and Blundell *et al.*[5] Nakamae *et al.* also noted a discrepancy in the apparent crystal modulus and concluded that using the higher indexing reflection to determine the *c*-axis dimension was more reliable, which leads to a larger dimension of the *c*-axis. Therefore, the *c*-axis dimension of 1.576 nm has been deduced from the (003) reflection. It is known that for all members of the 1,4-linked poly(aryl ether ketone)s, the ether and ketone groups are crystallographically equivalent. Obviously, the *meta* linkages are not crystallographically equivalent as compared to the *para* linkages.

The three-phenylene *c*-axis can also be supported *via* the molecular mechanics calculation. These calculations were carried out by the molecular mechanics modeling using the Sybyl Tripos force field. In the chosen reference state, all the phenylenes were in the same plane and the ether and ketone bridge bond angles were set to 120°. The position of the *meta* linked phenylenes in each repeat unit was fixed while the adjacent *para*-linked phenylenes were rotated in a 1° increment over a range of 180° in the grid searching calculation mode. Holding the *meta*-phenylenes fixed enabled the entire chain to retain a linear zigzag conformation (Figure 5a). The resulting energy values are illustrated in the contour plot shown in Figure 5b. Based on the minimum energy conformation, we suggest that the chain conformation and packing in a crystal is a planar zigzag backbone as shown in Figure 6. The *para*-linked phenylenes are torsionally rotated in opposite directions on either side of the ether or ketone linkages. Also, they are related to the plane of the zigzag backbone at angles around ±60°. However, the *meta*-linked phenylene is aligned in the plane of the zigzag backbone. Molecular dynamics was also used as a means of examining additional conformational possibilities. While the major-

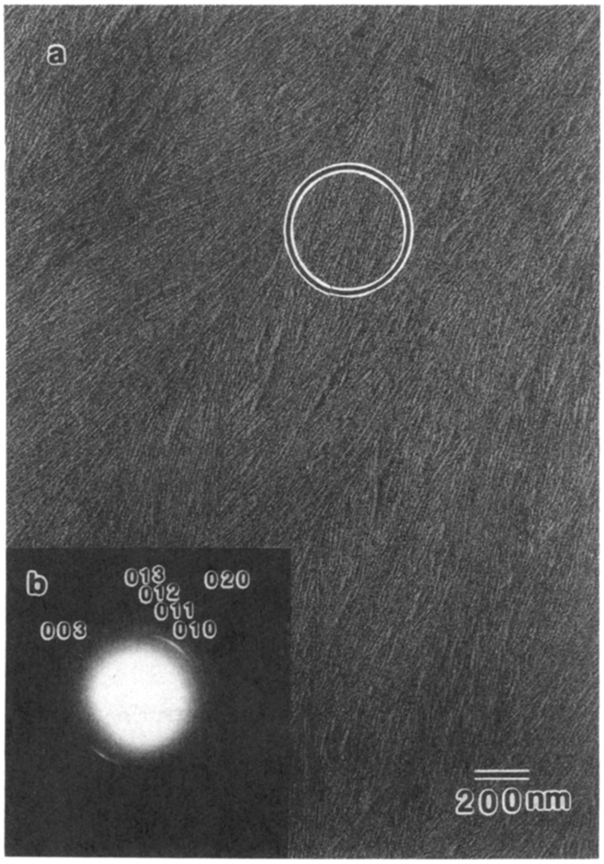


Figure 7. TEM observation of PEKK(I) crystallized at 260 °C for 60 min from the melt: (a) edge-on morphology; (b) ED pattern. The ED pattern originates from the circled area of the micrograph and is shown in correct orientation.

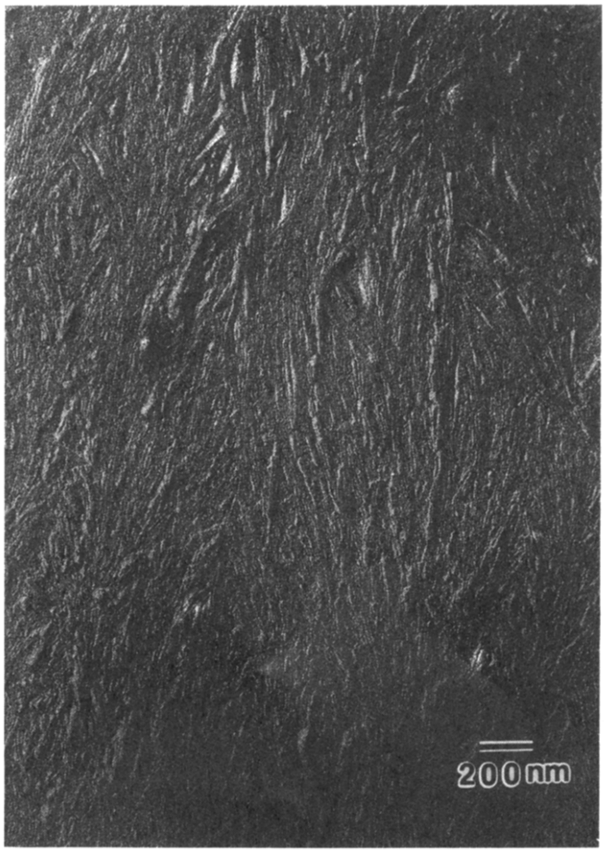


Figure 8. TEM observation of lamellar morphology of PEKK-(I) crystallized at 180 °C for 60 min from the melt.

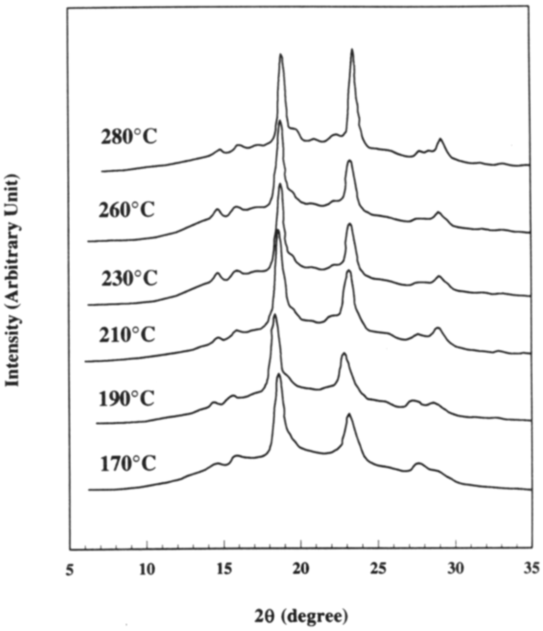


Figure 9. SET of WAXD patterns of PEKK(I) crystallized at various crystallization temperatures from the glassy state.

ity of these structures had a lower single repeat energy in vacuum, intermolecular interactions occurring upon packing would be prohibitively large.

Crystal Morphology in PEKK(I). It is interesting to find that, in contrast to both PEEK[10] and PEKK(T),[7] isolated PEKK(I) single lamellar crystals of micron-size are not formed. Despite our extensive efforts on isothermal crystallizations at different temperatures and various sample preparation procedures, such large single crystals have not been observed. This seems to indicate that the growth of isolated micro-sized single lamellar crystals is largely dependent upon the symmetry of the chain molecules in this family. The *meta*-linked phenylenes certainly introduce structural asymmetry, leading to relatively difficult chain packing in the crystals, which therefore result in smaller lamellar crystal sizes. A sector of typical spherulite grown at 260 °C for 60 min from the melt is shown in Figure 7a. Note that this temperature is only 25 °C below the observed melting temperature. The spherulite consists of fibrillar lamellae with no unusual features. The ED pattern is taken from these lamellar crystals (Figure 7b). It consists of the (010), (020), (011), and (013) reflections and the weak (003) and (012) reflections. This suggests that the thin-film specimens crystallized on carbon-coated glass slides exhibit a unique orientation in which the *b*-axis is radial, the molecular *c*-axis is tangential in the plane of the film, and the *a*-axis is tangential normal to the spherulitic plane (indicating that an edge-on growth is preferred). This morphological observation seems to be a common feature in all the members of this poly(aryl ether ketone) family. When the crystallization temperature is decreased, a more random lamellar arrangement is seen in these spherulites as shown in Figure 8. The size of the spherulites also becomes smaller due to the increasing number of nucleation sites. This is similar to the morphological observations reported in PEEK by Lovinger *et al.*[9]

Temperature Dependence of the Unit Cell Dimensions. Isothermal crystallization experiments have been conducted between the glass transition temperature and the melting temperature. Figure 9 illustrates a set of WAXD patterns obtained at different crystallization temperatures. It indicates that, in the chosen temperature range, PEKK(I) crystals possess a two-chain orthorhombic lattice as crystallized from the glassy state. A progressive change of the diffraction angular positions of the major reflections toward higher 2θ angles with crystallization temperature is observed. At low crystallization temperatures, the (020) reflection disappears. This result is consistent with the WAXD fiber pattern in which the (020) reflection is missing due to the low annealing temperature. In addition, the quadrant (*hkl*) reflections gradually appear with increasing crystallization temperatures. The same results have also been found as PEKK(I) was crystallized from the melt in this temperature range. To study the crystallization temperature dependence of the unit cell dimensions, the sizes of the *a*- and *b*-axes were determined by five major reflections: (010), (110), (200), (210), and/or (020) reflections after refinements. The *c*-axis dimension was determined by the (011) reflection because of the weak (003) reflection when the crystals were grown at low temperatures. The temperature dependence for all three dimensions, the *a*-, *b*-, and *c*-axes, can be seen from Figure 10a–c. In Figure 10a–c, the temperature dependencies of the PEEK and PEKK(T) unit cell are also included for comparison. The PEEK data are quoted from the work of Hay *et al.*,[13] while the unit cell dimensions of PEKK(T) crystallized at various crystallization temperatures are from our laboratory,[15] which were determined based on the (110), (111), and (200) reflections for WAXD. Note that in Figure 10c the *c*-dimension for PEKK(I) is normalized (the *c*-dimension times 2/3) and compared to the *c*-dimensions of both PEEK and PEKK(T) since the latter two contain only two-phenylene groups along the *c*-axis in one repeat unit. It is interesting to see that there is no significant dimension change with crystallization temperatures along the *b*-axis for all three polymers, but a different temperature dependency can be found along the *a*-axis. The slope of the *a*-dimension change for PEEK is about double that in PEKK(T), and that of PEKK(I) is about 2 times higher than that of PEKK(T). The former may be due to the decrease of the ketone content,[2-4] and the latter may be due to the introduction of the *meta*-linked phenylenes (PEKK(T) and PEKK(I) have equal ketone contents).

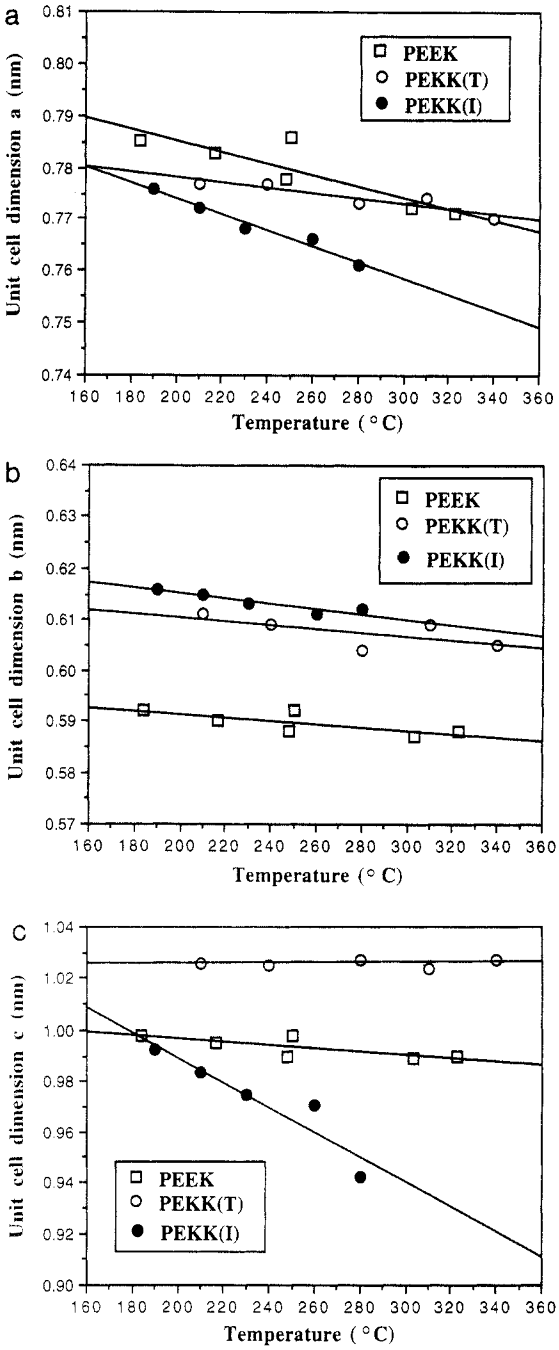


Figure 10. Unit cell dimensions: (a) *a*-dimensional, (b) *b*-dimensional, and (c) *c*-dimensional changes with the isothermal crystallization temperature for PEEK, PEKK(T), and PEKK(I).

However, it is surprising to find that a dramatic dimensional decrease among the *c*-axis occurs with increasing crystallization temperature in PEKK(I) (Figure 10c). The slope of this change is about 1 order of magnitude higher than that of PEKK(T) and PEEK. We suggest that this dramatic change along the *c*-dimension is due to the *meta*-linked phenylenes. Several possibilities have been proposed to explain the unit cell dimensional changes with crystallization temperatures. This includes the effect of lamellar thickness. It is known that the chain packing on the crystal surfaces must perturb the perfection of the crystal lattice because of chain folding, long loops, and cilia. As a result, a lattice strain may be introduced,[16] and the average unit cell dimensions, in particular, the *a*- and/or *b*-axes, may increase as the lamellar thickness decreases. However, this effect would most affect the lateral dimension, but produce insignificant change along the *c*-axis. The second possibility is due to the defects incorporated in the crystals at the lower crystallization temperature. This is sometimes portrayed as the irregular packing of adjacent chains with the ketone and ether linkages, which results in packing disorder in the crystal lattice. However, the mismatch of these two groups (ether and ketone linkages) in PEKK(I) should be more difficult compared to the *para*-linked PEKK(T) since the *meta*-linked phenylene group is asymmetric with respect to its neighboring *para*-linked phenylene (Figure 5a). Furthermore, this kind of defect should not have much effect on the size of the *c*-axis. Another possibility lies in the variations of the bridging bonds and the torsional angles, specifically in the *meta*-linked phenylenes. We speculate that with decreasing crystallization temperature, the torsional angle of the *meta*-linked phenylenes continuously deviates from the zigzag plane of the backbone chain and increases the bridging bond distortion. This leads to a subsequent lengthening of the *c*-axis and loosening of the packing along the *a*- and *b*-axes. This speculation has also been supported via the molecular mechanics calculation. When the *meta*-linked phenylenes slightly rotate away from the plane of the zigzag backbone, the length of the repeat unit increases. Such a deviation caused by the rotation of *meta*-linked phenylenes also leads to a disordering of the PEKK-

(I) crystals. This is also suggested by the absence of weak quadrant (*hkl*) reflections at low crystallization temperatures. The disappearance of the (020) and (003) reflections at low temperatures may also be evidence of this disordering. A detailed computer simulation is in progress and will be published elsewhere.[17]

Conclusion

The crystal unit cell of PEKK(I) has been determined via both WAXD and ED experiments. It possesses a two-chain orthorhombic lattice with a = 0.766 nm, b = 0.611 nm, and c = 1.576 nm. In particular, the *c*-axis only contains three phenylenes in the crystallographic repeat unit. This is also supported by the molecular mechanics calculation. The crystal morphology shows an edge-on growth in the thin-film samples. The *c*-axis is parallel to the film surface and the *b*-axis is the growing direction. In contrast to PEEK and PEKK(T), no isolated micron-sized single lamellar crystals can be found. At low crystallization temperatures, the edge-on lamellar crystals exhibit an increasing disorder in the cylindrical arrangement of the spherulites. A very strong temperature dependence of the *c*-dimension has been found, and it is explained by the changes of the torsional and bridging angles in the *meta*-linked phenylene groups.

Acknowledgment. This work was supported by S.Z.D.C.'s Presidential Young Investigator Award from the National Science Foundation (Grant DMR-91-75538).

References and Notes

(1) Boon, J.; Magre, E. P. *Makromol. Chem.* **1969**, *126*, 130.

(2) Dawson, P. C.; Blundell, D. J. *Polymer* **1980**, *21*, 577.

(3) Hay, J. N.; Kemmish, D. J.; Langford, J. I.; Rae, A. I. M. *Polym. Commun.* **1984**, *25*, 175.

(4) Fratini, A. V.; Cross, E. M.; Whitaker, R. B.; Adams, W. W. *Polymer* **1986**, *27*, 861.

(5) Blundell, D. J.; Newton, A. B. *Polymer* **1991**, *32*, 308.

(6) Gardner, K. H.; Hsiao, B. S.; Matheson, R. R.; Wood, B. A. *Polymer* **1992**, *33*, 2484.

(7) Ho, R. M.; Cheng, S. Z. D.; Hsiao, B. S.; Gardner, K. H. *Macromolecules* **1994**, *27*, 2136.

(8) Gardner, K. H.; Hsiao, B. S.; Faron, K. L. *Polymer*, in press.

(9) Lovinger, A. J.; Davis, D. D. *J. Appl. Phys.* **1985**, *58*, 2843.

(10) Lovinger, A. J.; Hudson, S. D.; Davis, D. D. *Macromolecules* **1992**, *25*, 1752.

(11) Olley, R. H.; Bassett, D. C.; Blundell, D. J. *Polymer* **1986**, *27*, 344.

(12) Wakelyn, N. T. *J. Polym. Sci., Polym. Lett. Ed.* **1987**, *25*, 25.

(13) Hay, J. N.; Langford, J. L.; Lloyd, J. R. *Polymer* **1989**, *30*, 489.

(14) Nakamae, K.; Nishino, T.; Shimizu, Y.; Matsumoto, T. *Polym. J.* **1987**, *19*, 451.

(15) Ho, R. M. Ph.D. Dissertation, Department of Polymer Science, The University of Akron, Akron, Ohio, in preparation.

(16) Hoffman, J. D.; Miller, R. L.; Marand, H.; Rotiman, D. B. *Macromolecules* **1992**, *25*, 2221.

(17) Fisher, H. P.; Eby, R. K., in preparation.