Crystal Structure and Drawing-Induced Polymorphism in Poly(aryl ether ether ketone). IV

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ABSTRACT: A new crystal modification induced by strain and denoted as form II exists alongside the dominant form I structure in the uniaxially oriented poly(ether ether ketone) (PEEK) and the related polymers. The crystal structure of form II for PEEK is also found to possess a two-chain orthorhombic packing with unit cell parameters of a equal to 0.475 nm, b equal to 1.060 nm, and c equal to 1.086 nm. More extended and flattened chain conformation of form II relative to that of form I is expected to account for an 8% increase in c-axis dimension, which is attributed to the extensional deformation fixed *in situ* through strain-induced crystallization during uniaxial drawing. Annealing experiments suggest that form II is thermodynamically metastable and can be transformed into more stable form I by chain relaxation and reorganization at elevated temperature without external tension. This strain-induced polymorphism exists universally in the poly(aryl ether ketone) family. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 237–243, 1999

Key words: poly(ether ether ketone); crystal structure; drawing-induced polymorphism

INTRODUCTION

As semicrystalline high-performance thermoplastic engineering materials, poly(aryl ether ketone)s (PAEKs) have received extensive attention in theoretical research and practical industrial applications in the past 20 years. Among PAEK family, poly(ether ether ketone) (PEEK) is the most typical and widely used member due to its excellent physical and mechanical properties. A number of structural studies were performed on PEEK and found that its crystal structure was very similar to that of PPO.¹ Polymer chains in the crystals adopt an extended conformation with the phenylene rings alternating an angle of approximately $\pm 37^{\circ}$ to the plane of the zigzag backbone and ether-ketone bridge bond angle of approximately 126°. The unit cell consists of twochain orthorhombic packing with the $Pbcn - D_{2h}^{14}$ space group, in which one chain is at the center of ab projection in the unit cell and the other $4 \times \frac{1}{4}$ chains are at the corners.²⁻³ This crystal form (form I) is commonly observed in all members of PAEK family with minor dimension variation.

Recently, the polymorphism in poly(ether ketone ketone)s (PEKKs) with a high ketone-toether ratio (2.0) and different incorporations (para- or meta-linkage) was induced by exposure to solvents or by cold crystallization.⁴⁻¹¹ The related results previously reported were summarized in Table I. Form II of PEKK(T), which was prepared from diphenyl ether and terephthalic acid, was isolated by two different crystallization processes: solvent-induced crystallization and cold crystallization from the glassy state. And, a

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	Form I			Form II			Form III			
PEKKs	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	<i>a</i> (nm)	b (nm)	<i>c</i> (nm)	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	Reference Source
PEKK(T)		_		0.417	1.134	1.008				6
	0.769	0.606	1.016	0.393	0.575	1.016				7
	0.767	0.606	1.008	0.42	1.13	1.01				8
PEKK(I)	0.766	0.611	1.576							9
PEKK(T/I)	0.778	0.610	3.113	0.417	1.108	3.113	0.641	0.610	3.504	10

 Table I
 Polymorphism in Poly(aryl ether ketone ketone)s (PEKKs)

two-chain orthorhombic lattice was determined from the ED patterns of isolated single lamellar crystals. The *c*-axis of form II is almost identical to that of form I.⁸ Polymorphism induced by solvent crystallization in other PAEKs has also been reported.¹² With increasing chain stiffness and decreasing chain mobility, the ability to form form II has been found to be significantly enhanced.

In our previous work, the crystal structure and drawing-induced polymorphism in PEDEKmK and PEEKK have been reported.^{12–14} Up to now, despite many investigations carried out on the crystal structure of PEEK, no work has been done on its polymorphism probably due to its low ketone-to-ether ratio (0.5). In this article, the existence of a new crystal form was shown in the drawn samples of PEEK and the related polymers.

EXPERIMENTAL

Materials and Preparation

PEEK (Victrex 450G, ICI) was obtained in pellet form. The amorphous film, 0.3 mm thick, was made by compression-molding at 400°C for 10 min and then quenched in ice water. The dumbbell specimens with a size of 0.3 imes 4.2 imes 40.0 mm³, which were marked by lines across the width of the bars at 5-mm intervals in order to find the subsequent draw ratio (DR), were cut from the amorphous film and then drawn into stripes with DR the equal to 3 at 165°C with use of an Instron Mode-1121 tensile tester with a gauge length of 20 mm and a strain rate of 50 mm min. The as-drawn samples were subsequently postannealed under uniaxial restraint at 280°C in an air-circulating oven. Other drawn samples of PAEKs (whose synthesis and characterization had been reported previously^{8,12-13}) were prepared and treated with the same procedure. Their chemical repeating units and notations are listed in Scheme 1.

X-ray Measurements

To obtain a wide-angle X-ray diffraction (WAXD) fiber pattern, the highly oriented PEEK fiber was prepared. First, PEEK was melt-spun to a monofilament with a screw extruder; and then, it was drawn into fiber at above the glass transition temperature, typically with diameter of 0.5 mm; last, the as-received fiber was annealed isothermally in a fixed length above the cold-crystallization temperature (ca. 180°C) to induce crystallization. WAXD was performed at room temperature by use of a Rigaku D/max II B powder X-ray diffractometer and $CuK_{\alpha 1}$ (curved graphite crystal monochromator) radiation ($\lambda = 0.15406$ nm). The oriented samples were mounted on a rotating stage equipped with the diffractometer in order to eliminate the anisotropic effect, so a suitable average of the diffracted intensity in reciprocal space can be obtained. The fiber axis (here, *c*-axis) is perpendicular to an incident monochromatic X-ray beam. The angular scale of recorder was calibrated to an accuracy of $\pm 0.01^{\circ}$ with polycrystalline silicon. Data were collected in a fixed time mode with a step-scanning interval of 0.1° from 5 to 45°. An X-ray fiber pattern was taken with a cylindrical camera (diameter of 57.3 mm) attached to a Rigaku X-ray generator (CuK_a radiation, $\lambda = 0.15418$ nm). Then, the the fiber identity period could be calculated from the X-ray cylindrical film fiber pattern.

RESULTS AND DISCUSSION

Figure 1(a) showed the X-ray fiber photograph for the annealed PEEK fiber. The main reflections,



Scheme 1 Chemical repeat units of poly(aryl ether ketone)s.

(110), (200), (111), and (211) for form I crystal with corresponding d-spacings of 0.468, 0.390, 0.423, and 0.309 nm, respectively, could be clearly identified. The unit cell dimensions of form I, based on two-chain orthorhombic lattice, were thus determined to be a equal to 0.780 nm, bequal to 0.592 nm, and c equal to 1.005 nm, and these values were in good agreement with those reported by Hay et al.³ However, some additional diffraction spots (denoted as II(hkl)) with relatively strong streaks indicated by arrows could be seen together with those of the form I crystal, and they could not be indexed based on the conventional reciprocal lattice of the form I crystal, the most noticeable one of which was the inner equatorial spot at $2\theta = 16.5^{\circ} (\xi = \lambda/d_{hkl} = 0.288,$ where ξ is the reciprocal lattice coordinate) [Fig. 1(b)]. This observation suggested that a new crystal modification (form II) distinctly existed in the drawn PEEK fiber. In order to index these additional reflections, the two-chain orthorhombic lattice for form II crystal for PEKK proposed by Ho et al. was referred to.⁸ In fact, these reflections of PEEK showed a similar disposition to the predicted fiber pattern of form II. Therefore, it was indicated that this strain-induced crystal modification also possessed a two-chain orthorhombic packing, and the unit cell parameters were estimated as a equal to 0.475 nm, b equal to 1.060 nm, and *c* equal to 1.086 nm, based on the refinements on the additional reflections. The results of strain-induced polymorphism for several PAEKs were collected in Table II.

It was evident that the *c*-axis of form II was substantially larger than that of form I, which could be attributed to the extensional deformation during uniaxial drawing and formed in situ through strain-induced crystallization.¹²⁻¹⁴ Based on the dimension of the *c*-axis and the standard bond lengths and angles, the ether-ketone bridge bond angle was calculated to be 126°, which was consistent with the value previously reported (125°).³ In the form II structure, it was anticipated that the polymer chains took a more extended conformation; the 8% increased in *c*-axis repeat unit for form II relative to that for form I should be mainly attributed to the opening of ether-ketone bond angle (θ) [see Fig. 8 in Wang et al.¹³], though some minor changes in bond lengths and aromatic ring geometries might lead to the increase in the *c*-axis distance. Owing to chain extension, the steric repulsion between adjacent rings was to be weakened, and, accordingly, the torsion angle ϕ of aromatic rings relative to the zigzag backbone plane may be a little smaller than that found for form I $(37^{\circ})^{15}$; that is, chains in form II adopted a slightly more flattened conformation than those in form I. Thus, the increased interchain interaction might give an energy penalty to the enough-extended chain conformation.



Figure 1 WAXD cylindrical-film fiber pattern for the highly oriented PEEK after annealing at 280°C for 3 h under tension: the main reflections of form I, denoted as I(hkl), and several reflections of Form II, II(hkl), were indicated by arrows (a); and (b) its equatorial plane of the reciprocal lattice of PEEK form I crystal, $\lambda a^* = 0.197$, $\lambda b^* = 0.260$. Notice that the equatorial reflection spots with streaks indicated by question marks cannot be fit into the reciprocal lattice of form I.

PAEKs		Form I					
	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	a (nm)	<i>b</i> (nm)	<i>c</i> (nm)	Reference Source
PEDEKmK	0.784	0.600	4.745	0.470	1.504	5.064	13
PEEKK	0.772	0.600	1.004	0.461	1.074	1.080	14
PEEK	0.780	0.592	1.005	0.475	1.060	1.086	а

Table II Drawing-Induced Polymorphism of Poly(aryl ether ketone)s (PAEKs)

^a The results of this article.

However, it should be pointed out that form II was thermodynamically metastable and was able to be transformed into more stable form I structure as observed for the solvent-induced form II crystal.¹⁰ It was found that the reflection at $2\theta = 16.5^{\circ}$ (020 reflection for form II) was gradually weakened with annealing at elevated temperature without external tension, whereas the main reflections for form I were substantially enhanced (Fig. 2). The enough-extended chains in form II were prone to relaxation and reorganization so as to form more stable crystal structure at elevated temperature under no restriction of external tension.¹²⁻¹⁴

It was worth pointing out that the strain-induced form II crystals were also observed on other members of PAEKs, such as PEEKK,^{13–14} PEKK, PEDEKmK,¹² and PEEKmK (Fig. 3). The extra crystalline peaks indicated that the strain-induced crystallization took place below the coldcrystallization temperature during uniaxial drawing. It was found that the ease of inducing form II crystals was intrinsically related to the chain rigidity of PAEKs. As ether linkages have a relatively shallow rotational conformation energy barrier and, thus, are more flexible than a ketone linkage,¹⁵ the ability to form a form II structure is significantly enhanced by increasing the ketone content or the chain stiffness [Fig. 3(a)]. On the other hand, the incorporation of isophthaloyl moieties was observed to increase the chain flexibility⁷; therefore, introducing meta-linkage into polymer chains should make it difficult to form the second crystalline phase; but the case is opposite when introducing more rigid biphenyl groups into the polymer chains [Fig. 3(b)]. It has also found that the formation of form II of PAEKs depended quantitatively on the drawing conditions, such as draw rate and temperature.¹²⁻¹⁴ Moreover, mechanical properties of crystalline polymers, in general, depend strongly on their crystal structures and crystallinity, as well as

orientation. Strain-induced crystal modifications of polymers should have an effect on the properties of the products during applications. Studies on this issue will be reported in a succeeding article.

CONCLUSIONS

A new crystal modification (denoted as form II) is produced by using the uniaxial drawing experiments, which coexists with the conventional form



Figure 2 WAXD patterns for the isotropic PEEK sample annealed at 280°C for 1 h (a), the uniaxially oriented PEEK sample (DR = 3) annealed at 280°C for 15 min under external tension (b), and the same sample as (b) annealed at 280°C for 15 min without external tension (c).



Figure 3 A set of WAXD patterns for various as-drawn PAEKs (DR = 3). The films are drawn at 15°C below corresponding cold-crystallization temperatures.

I structure in the uniaxially oriented PEEK and the related polymers. The crystal structure of form II for PEEK can be identified through the X-ray cylindrical film fiber photograph and wideangle X-ray diffraction, which is similar to that of form I (a = 0.780 nm, b = 0.592 nm, and c= 1.005 nm), and also possesses a two-chain orthorhombic packing with unit cell parameters of a equal to 0.475 nm, b equal to 1.060 nm, and c equal to 1.086 nm. More extended and flattened chain conformation of form II relative to that of form I might be expected to account for an 8% increase in the dimension of the *c*-axis, which is attributed to the extensional deformation fixed in situ through drawing-induced crystallization during the uniaxial drawing process.

Annealing experiments suggest that the form II structure belongs to a metastable state, which is thermodynamically unstable and can be transformed into the more stable form I structure by chain relaxation and reorganization at elevated temperature without external tension.

It has been seen that this strain-induced polymorphism universally exists in the poly(aryl ether ketone) family. And, it has been found that the ease of inducing the form II crystal is intrinsically related to the chain rigidity of PAEKs. The ability to form the form II structure is significantly enhanced by increasing the contents of ketone or biphenyl groups, which will elevate the chain stiffness. Moreover, the introduction of meta-linkage into polymer chains can make it difficult to form the second crystalline phase.

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