NOTES

Variation in Unit Cell Parameters with Crystallization Temperature in Poly(ether diphenyl ether ketone)

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Poly(ether ether ketone) (PEEK), a semicrystalline thermoplastic, is usually a temperature-resistant high performance resin and reinforced matrix. It undergoes the widest conceivable range of processing to produce engineering components and it can be applied in various areas of engineering including aerospace, automobile, and electricity.¹ Many authors have studied its crystal structure.^{2–17} Each cell has two molecular chains, one crosses through the center, and another occupies four corners and is shared with three other molecular chains. The *c*-axis direction parallels molecular chains which align with zigzag. Two opinions are proposed on the length of *c*-axis, *i.e.*, it occupied a 2/3 repeat unit with about 10 Å,^{2–7} Wakelyn⁸ reported a *c*-axis owning two repeat units with 30 Å. A schematic description is shown in Figure 1a. The average length of three parts (1, 2, 3) is about 10 Å and the sum is 30 Å.

EXPERIMENTAL

Poly(ether diphenyl ether ketone) (PEDEK) was synthesized with 4,4'-diphenol and 4,4'-difluorobenzophenone, diphenylsulfone as solvent and alkali metal carbonate as catalyst through a nucleophilic substitution route. The glass transition temperature (T_g) of 171°C and melting temperature (T_m) of 409°C were measured by differential scanning calorimeter (DSC). The powered resin, with inherent viscosity $\eta_{iv} = 1.30 \text{ dl g}^{-1}$ measured in 98% concentrated H_2SO_4 at 25°C, was molded at 440°C and a sheet was quenched as quickly as possible into ice/water mixture, this piece of sheet is demonstrated to be amorphous by wide angle X-ray diffraction (WAXD) pattern.

WAXD was measured using a PW1700 diffractometer (Philips Co., Holland) with a nickel-filter and $\text{Cu-K}\alpha$ radiation at a scanning rate of $0.3^\circ \text{ min}^{-1}$ in a range $5^\circ \leq 2\theta \leq 60^\circ$.

The film was used in the note.

RESULTS AND DISCUSSION

Figure 1b shows two ether diphenyl ether ketone (EDEK) repeat units. Parts 1 and 2 are longer than part 3, accept Wakelyn's idea, *i.e.*, the length of *c*-axis includes two repeat units. Figure 2 exhibits the WAXD pattern, for the sample with a greater crystallinity because it was annealed for a long time on a hot press machine. The four main diffraction peaks were located at 18.73° , 19.89° , 22.97° , and 28.20° corresponding to the reflection of 110, 113, 200, and 213. The cell parameter by least square method, was $a = 7.74 \pm 0.03 \text{ Å}$, $b = 5.98 \pm 0.02 \text{ Å}$, $c = 37.8 \pm 0.4 \text{ Å}$, cell volume is $1750 \pm 13 \text{ Å}^3$, and crystalline density 1.382 g cm^{-3} . The above data are thus

Figure 1. Two repeat units of PEEK (a) and PEDEK (b).

Figure 2. WAXD pattern of PEDEK cooled slowly from the melt to the ambient temperature.

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in agreement with the results reported by Blundell,⁹ *i.e.*, $a = 7.72 \text{ \AA}$, $b = 5.94 \text{ \AA}$, $c = 37.5 \text{ \AA}$.

Wakelyn investigated PEEK lattice parameters with annealing temperature from 189°C to 323°C . The dimensions of a - and b -axes decreased with annealing tem-

perature and the length of c -axis show no regularity. Hay¹⁰ reported the decrease in a -, b -, and c -axes with crystallization temperature except at 250°C possibly due to the maximum crystallization rate appearing at this temperature, and some re-arrangement of atoms within the cell must occur.

The samples^{8,9} were annealed at a temperature for a given time, and measured by X-ray diffractometer at room temperature. Blundell¹¹ selected uniaxially drawn sample, which was examined in the transmission mode using copper K_α with a Philips vertical goniometer to which was attached a thermostatically controlled hot stage, X-ray can scan at a given temperature. The thermal expansion rate in a -axis is about three times greater than in the b -axis. The overall cell volume increased linearly with temperature up to 300°C . Blundell's test belongs to

Figure 3. WAXD patterns of PEDEK crystallized at a given temperature for 30 min. a, amorphous; b, 200°C ; c, 230°C ; d, 280°C ; e, 350°C ; f, 390°C .

Table I. The main diffraction peak positions at different crystallization temperatures

$T_c/^\circ\text{C}$	$2\theta/\text{degree}$			
	(110)	(113)	(200)	(213)
200	18.35	19.55	22.44	28.35
230	18.35	19.56	22.50	28.40
280	18.39	19.64	22.50	28.53
350	18.58	19.78	22.70	28.71
390	18.58	19.78	22.92	28.98

Figure 4. Variation of cell parameters with crystallization temperature. a, a -axis; b, b -axis; c, c -axis; d, volume of a cell.

a dynamic process.

PEDEK films were crystallized at a temperature for 30 min. The WAXD patterns are shown in Figure 3. Diffraction peak positions are listed in Table I. The following equation was used to calculate the cell parameters by least square to fit experimental data.

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Variation of cell parameters with crystallization temperature is illustrated in Figure 4. As shown in Figure 4, the length of a -axis decreased rapidly, and b - and c -axes become small and the overall cell volume shrank with crystallization temperature. This conclusion has been obtained from other poly(aryl ether ketone).^{7,10} The shrinkage rate in a -axis is larger than the b - and c -axes. On increasing crystallization temperature, of the torsional angle of benzyl ring becomes larger, and this gives rise to change in lateral packing of the molecular chain and the torsional angle of phenylene ring and the bridge bond angle of diaryl carbonyl and ether. Steric effects of the adjacent *ortho*-hydrogen decrease and the bridge bond angles in C–CO–C and C–O–C decrease. Thus the c -axis shortens with close packing in a - and b -direction. However, the c -axis is extraordinarily small at 280°C perhaps due to rapid crystallization rate at this temperature. The temperature for the maximum crystallization rate (theoretical value) is about 300°C. The linear regression analysis gives shrinkage for a , b , and c -axes and volume of cell.

$$a(T) = 8.33(1 - 1.01 \times 10^{-4}T) \pm 0.03 \text{ \AA}$$

$$b(T) = 6.28(1 - 5.74 \times 10^{-5}T) \pm 0.02 \text{ \AA}$$

$$c(T) = 38.32(1 - 2.51 \times 10^{-5}T) \pm 0.4 \text{ \AA}$$

$$Vc(T) = 1999(1 - 1.73 \times 10^{-4}T) \pm 13 \text{ \AA}^3$$

T is Kelvin temperature.

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