

SYNTHESIS AND CRYSTALLIZATION BEHAVIOR OF POLY(ETHER ETHER
KETONE ETHER KETONE) (PEEKEK)*

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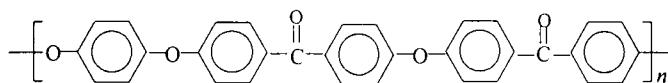
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Abstract In this paper, the synthesis and crystallization behavior of poly(ether ether ketone ether ketone) (PEEKEK) are reported. PEEKEK was prepared from 4,4'-bis(*p*-fluorobenzoyl) diphenyl ether (4,4'-FBDE) and hydroquinone along the nucleophilic substitution route. The thermal properties were investigated by using DSC and TGA. The crystallization behavior of PEEKEK under several conditions, i.e., crystallization from the molten state (melt crystallization), crystallization from a quenched sample (cold crystallization) and crystallization induced by exposing glassy sample to methylene chloride (solvent-induced crystallization) has also been investigated. The results show that crystallization of PEEKEK could be induced by the above methods, and no polymorphism was found. The differences in the crystallization of PEEKEK induced by the above methods are seen in their degree of crystallinity.

Keywords Poly(aryl ether ketone)s, Synthesis, Crystallization

INTRODUCTION

Aromatic poly(aryl ether ketone)s (PAEKs), as a type of high-performance engineering thermoplastics, have received special attention in the last decade^[1]. Although poly(aryl ether ether ketone) (PEEK) is the most typical member among the aryl ether ketone family, many other variants have been developed in order to meet various practical requirements^[2-5]. At the same time, the structural and morphological studies of PAEKs are a favorable and interesting object of study because of their high thermal stability and semicrystalline nature. However, it should be noted that these investigations were mainly focused on PEEK, and to a lesser extent on other commercially available variants^[6]. As a member of this aryl ether ketone family, poly(ether ether ketone ether ketone) (PEEKEK) has not received much attention, and only a few papers have dealt with it^[7,8]. In this paper, a PEEKEK sample was prepared along the nucleophilic substitution route and was characterized by IR, DSC and TGA. The crystallization behavior of PEEKEK under several conditions has been investigated. PEEKEK has the following composition:



EXPERIMENTAL

The ¹³C-NMR spectrum was obtained on a Varian-Unity 400 instrument and IR spectra were recorded on a Nicolet-5DX spectrometer. WAXD pattern was recorded over the angular range 5° to 60° on a Rigaku D/max IIB powder X-ray diffractometer. The glass transition temperature, taken as the midpoint of the baseline, was

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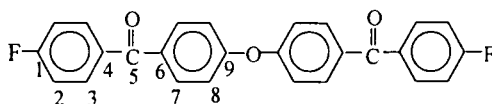
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measured with a Perkin-Elmer DSC-7 instrument at a heating rate of 10 K/min. Melting point, taken as the peak maximum, was also measured using the same instrument. Thermogravimetric analysis was performed on a Perkin-Elmer TG-7 instrument at a heating rate of 20 K/min in nitrogen.

*Synthesis of 4,4'-Bis(*p*-fluorobenzoyl) Diphenyl Ether (4,4'-FBDE) Monomer*

A solution of diphenyl ether (21.27 g, 0.125 mol) and 4-fluorobenzoyl chloride (39.64 g, 0.25 mol) in methylene chloride (50 mL) was added to a stirred slurry of anhydrous powdered aluminium chloride (41.69 g, 0.315 mol) in methylene chloride (100 mL) maintained at 10–15°C. The resulting solution was allowed to slowly warm to room temperature, and stirred for about 18 h, and then poured into a cold aqueous hydrochloric acid to produce a gummy solid. The residual methylene chloride was removed by evaporation and the resulting white solid was washed with dilute aqueous sodium bicarbonate and dried. The monomer 4,4'-bis(*p*-fluorobenzoyl) diphenyl ether (4,4'-FBDE) was recrystallized from toluene to give a white crystalline solid. The yield was 63% (m.p. 213–215°C), IR (KBr): 1646 cm⁻¹ (C=O), ¹³C-NMR (CDCl₃): 165.9, 163.4 (F coupling, C₁), 115.0, 114.8 (F coupling, C₂), 131.9 (C₃), 133.4 (C₄), 193.0 (C₅), 132.6 (C₆), 131.1 (C₇), 118.2 (C₈) and 159.3 (C₉).



Synthesis of PEEKEK

PEEKEK was prepared from 4,4'-bis(*p*-fluorobenzoyl) diphenyl ether (4,4'-FBDE) and hydroquinone along the nucleophilic substitution route. To a 100 mL four-necked round bottom flask fitted with a magnetic stirrer, a thermometer, a nitrogen inlet and a nitrogen outlet, 4,4'-FBDE (5.000 g, 0.0121 mol), hydroquinone (1.355 g, 0.0121 mol) and diphenylsulphone (20 g) were added. The flask was heated in a liquid metal bath to 180°C, at that temperature the contents were liquid. An excess amount of potassium carbonate (2.5 g) was added. The reaction temperature was raised to 320°C over 90 min and held at that temperature for 3 h, before the addition of a further quantity of 4,4'-FBDE (0.05 g, 0.121 mmol) to control the molecular weight. After a further 5 min, the product, a viscous polymer solution, was poured onto an aluminum sheet, and cooled down to room temperature. The solid reaction product was powdered and extracted successively with acetone and water to remove diphenyl sulphone and inorganic salts. The yield of the polymer was nearly 90%. The polymer was dried at 90°C under vacuum and was found to have an inherent viscosity of 0.68 (measured at 25°C on a 0.1% W/V solution of the polymer in 98% sulfuric acid). Samples for X-ray diffraction experiments were compression molded at 400°C and were then either quenched in water/ice to the glassy state or melt crystallized at 200°C for 3 h. The quenched samples were either solvent-induced crystallized (by exposure to methylene chloride at room temperature for one week and then dried in vacuum to drive off the residual solvent), or cold crystallized at 200°C for 3 h.

RESULTS AND DISCUSSION

The chemical structure of the resulting polymer PEEKEK was characterized by its IR spectrum which was similar to that of PEEK. The IR spectrum of PEEKEK has a characteristic strong absorption for carbonyl —CO— at around 1652 cm⁻¹ and for —C—O— at 1160 cm⁻¹. Absorption peaks appearing at 1594 and 1493 cm⁻¹, are assigned to Ph—O—Ph stretching and those at 1309 and 928 cm⁻¹ to Ph—CO—Ph. Other peaks at 1231 cm⁻¹ (asymmetric Ph—O—Ph stretching), 3028 and 764 cm⁻¹ (Ar—H stretching) further confirm the chemical structure of PEEKEK.

The thermal properties of PEEKEK were investigated by DSC. From a DSC trace for a quenched sample of PEEKEK at a heating rate of 10 K min⁻¹, the glass transition temperature (*T_g*) and melting point (*T_m*) could be determined. The *T_g* and *T_m* were found to be 146°C and 343°C, respectively. When heating the sample from the glassy state, an exothermic peak *T_{c,h}* at 176°C associated with crystallization was found, while on cooling the sample from the melt a crystallization exotherm *T_{c,c}* at 303°C was found. The heating and cooling rates were fixed at 10 K min⁻¹. From the results obtained above, it could be found that the thermal resistance of PEEKEK is about 10 K higher as compared with PEEK.

The thermal stability of PEEKEK was affirmed by thermogravimetric analysis. PEEKEK has excellent thermal stability with a decomposition temperature beyond 520°C, at which the polymer loses 5% of its weight. This indicates that PEEKEK has the same good thermal stability as other PAEK variants.

With reference to the correlation of structure and physical property, it is known that the thermal properties (melting and glass transition temperature) of *para*-linked aromatic poly(aryl ether ketone)s are strongly dependent on the ether/ketone ratio which influences the lattice parameters of the orthorhombic unit cell. The chain packing of PEEKEK is similar to that found for poly(*p*-phenylene oxide) (PPO) and for PEEK^[9–11]. For poly(aryl ether ketone)s with a carbonyl content larger than 50% such as poly(aryl ether ketone ether ketone ketone) (PEKEKK) and poly(ether ketone ketone) (PEKK), Blundell and Newton observed additional reflections in the X-ray pattern of oriented samples which were indexed in terms of a new orthorhombic crystallographic form (Form II)^[8]. Compared with Form I, the value of the *a*-axis becomes shorter; however, the value of the *b*-axis becomes longer in Form II. Gardner *et al.* reported new results on the polymorphism of aromatic poly(aryl ether ketone)s with different ether/ketone ratios crystallized under different conditions, and more recently on poly(aryl ether ketone)s containing isophthalic units^[12–14]. In the case of poly(aryl ether ketone)s crystallized from the melt the first orthorhombic packing model (Form I) is always observed for all poly(aryl ether ketone)s irrespectively of their carbonyl content. However, samples prepared by cold crystallization and solvent crystallization, with a carbonyl content larger than 50% (PEKEKK and PEKK), showed exclusively the second crystallographic form (Form II). In our previous work, polymorphism induced by uniaxial drawing of poly(aryl ether ether ketone ketone) (PEEKK) and poly(aryl ether diphenyl ether ketone ketone containing *meta*-phenyl links) (PEDEKmK) have been studied^[15,16]. In this paper, the crystallization behavior of PEEKEK under different conditions was studied.

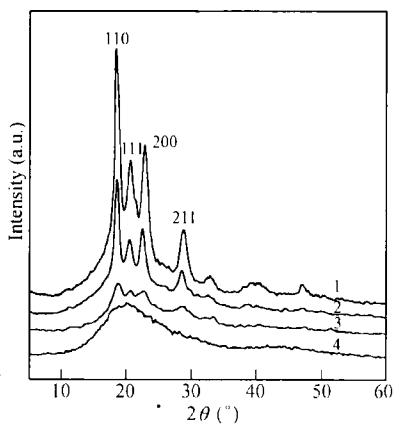


Fig. 1 WAXD patterns for PEEKEK crystallized under different conditions

1) melt-crystallized (at 200°C), 2) cold-crystallized (200°C), 3) solvent-induced and 4) amorphous PEEKEK

Figure 1 shows the X-ray diffraction patterns of 1) melt-crystallized (at 200°C), 2) cold-crystallized (200°C), 3) solvent-induced and 4) amorphous PEEKEK. The melt-crystallized PEEKEK exhibited four distinct diffraction peaks at $2\theta = 18.58^\circ$, 20.58° , 22.78° and 28.76° , respectively, for the (110), (111), (200) and (211) planes in terms of the orthorhombic unit cell with the lattice dimensions $a = 0.780$ nm, $b = 0.603$ nm and $c = 1.008$ nm. At the other extreme, the amorphous PEEKEK showed only an amorphous halo. Furthermore, the X-ray diffraction pattern of PEEKEK obtained via solvent-induced crystallization showed all the distinct peaks of the melt crystallized ones, and no other peaks appeared which could not be indexed according to the orthorhombic unit cell mentioned above. However, the crystallinity and the intensity of the diffraction peaks of the sample crystallized via the solvent-induced method are lower than those of the melt-crystallized ones. The X-ray diffraction pattern of the cold-crystallized PEEKEK also showed all the four diffraction peaks similar to the

melt-crystallized and solvent-crystallized PEEKEK. Moreover, the intensity of the diffraction peaks of the cold-crystallized PEEKEK is lower than that of the melt-crystallized ones and stronger than that of the solvent-crystallized sample, indicating the crystallinity in the cold-crystallized PEEKEK is higher than in the solvent-crystallized sample and lower than in the melt-crystallized ones.

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