Synthesis and Properties of Poly(aryl ether ketone ketone)/Poly(aryl ether ether ketone ketone) Copolymers with Pendant Cyano Groups

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ABSTRACT: 2,6-Diphenoxybenzonitrile (DPOBN) was synthesized by reaction of phenol with 2,6-difluorobenzonitrile in *N*-methyl-2-pyrrolidone in the presence of KOH and K_2CO_3. Poly(aryl ether ketone ketone)/poly(aryl ether ketone ketone) copolymers with pendant cyano groups were prepared by the Friedel–Crafts electrophilic substitution reaction of terephthaloyl chloride with varying mole proportions of diphenyl ether and DPOBN using 1,2-dichloroethane as solvent and *N*-methyl-2-pyrrolidone as Lewis base in the presence of anhydrous $AlCl_3$. The resulting polymers were characterized by various analytical techniques, such as FT-IR, differential scanning calorimeter, thermal gravimetric analysis, and wide-angle X-ray diffraction. The crystallinity and melting temperature of the polymers were found to decrease with increase in concentration of the DPOBN units in the polymer. Thermogravimetric studies showed that all the polymers were stable up to 514°C in N_2 atmosphere. The glass transition temperature was found to increase with increase in concentration of the DPOBN units in the polymer when the molar ratios of DPOBN to DPE ranged from 10/90 to 30/70. The copolymers containing 30–40 mol % of the DPOBN units exhibit excellent thermostability at (350 ± 10)°C and have good resistance to acidity, alkali, and organic solvents. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3601–3606, 2007

Key words: poly(aryl ether ketone ketone) (PEKK); poly-(aryl ether ether ketone ketone) (PEEKK); 2,6-diphenoxy-benzonitrile; terephthaloyl chloride; polymerization

INTRODUCTION

Poly(aryl ether ketone)s (PAEK) are a type of high-performance polymers with excellent thermal, physical, and mechanical properties.[1] They are semicrystalline polymers having melting temperatures around 330–360°C and glass transition temperatures around 140–160°C. Among them poly(ether ether ketone) (PEEK) and poly(ether ketone ketone) (PEKK) have found many applications in aerospace, coating, and insulating materials.[2–5] In the synthesis of these polymers, two main strategies, nucleophilic polycondensation[6–9] and electrophilic polycondensation,[7,8,10] have been developed. However, because of their high crystalline property and high melting temperatures often restrict the use of these resins for some applications. Various structural changes have been introduced in the basic PEEK chain to obtain different properties and for different applications. Such structural changes have focused on the order and ratio of ether-ketone linkage,[11,12] on the ratio of *meta* and *para* phenyl substitution.[13] Groups with sp³-hybridized atoms, such as —CR_2— and —SO_2—, have also been introduced in the backbone of PEEK.[14,15] Introduction of pendant alkyl or phenyl groups on to the poly(aryl ether ether ketone) main chain is another important structural change.[16] Very recently, the thio-containing poly(ether ether ketone)s was also reported.[17]

The all-*para*-connected PEKK homopolymer, with a higher melting point, has made it difficult to process. The extremely poor flowing property and the too high processing temperature (over 430°C) for *p*-PEKK was even difficult for the processing capacity of the ZSK 30P 9P Lab extruding machine (from Germany). Because of this, its utility was limited and some modifications were made on *p*-PEKK.[18,19] The incorporation of low levels of 1,3-connected *meta*-phenylene linkages into the all-*para* backbone of PEKK has been shown to produce a substantial reduction in equilibrium melting temperature and a modest decrease in glass transition temperature,[20] this latter effect is attributed to an increase in overall chain flexibility with the introduction of the meta linkages. The electrophilic route has been the popular method to prepare various kinds of poly(aryl ether ketone)s because the monomers, which are used in the electrophilic route, have been more selective, cheaper, and easily available. Previously, we have synthesized simple linear poly(aryl ether ketone ketone) with high molecular weight by electrophilic polycondensation in solution at low temperature.[21] In this contribution, we synthesized the copolymers of poly(ether ketone

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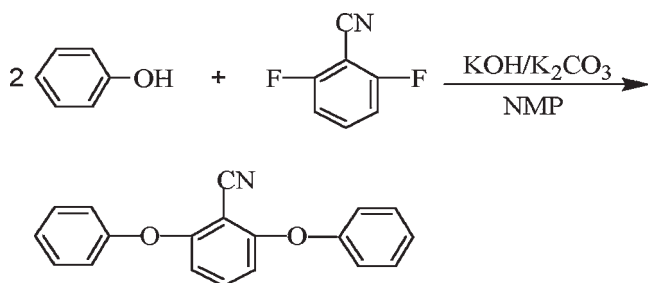
Scheme 1　Preparation of DPOBN.

ketone) (PEKK) and poly(ether ether ketone ketone) (PEEKK) containing pendant cyano groups. The crystallization behavior and the thermal properties were investigated by wide-angle X-ray diffraction (WAXD), differential scanning calorimeter (DSC), and thermal gravimetric (TG) analysis. The results indicated that the copolymers have a potentiality for industry.

EXPERIMENTAL

Materials

Phenol (Aldrich), 2,6-difluorobenzonitrile (Aldrich), anhydrous $AlCl_3$ (Aldrich) were used as received. 1,2-Dichloroethane (DCE, Aldrich) and diphenyl ether (DPE, Aldrich) were distilled prior to use. Terephthaloyl chloride (TPC, m.p. 82–83°C, Shuanglin Chemical, China) was distilled under reduced pressure before use. N-Methyl-2-pyrrolidone (NMP, Aldrich) was dried with molecular sieves (Type 4A) and distilled over CaH_2 under reduced pressure. The middle fractions were collected and stored over molecular sieves.

Synthesis

Preparation of DPOBN

2,6-Diphenoxybenzonitrile (DPOBN) was synthesized as shown in Scheme 1 by nucleophilic aromatic substitution reaction of 2,6-difluorobenzonitrile with phenol in the presence of KOH and K_2CO_3 in high boiling solvent NMP under N_2 atmosphere.

To a 100-mL, round-bottomed flask equipped with a mechanical stirrer, a thermometer, nitrogen inlet and outlet tubes, and a Dean-Stark trap, 72 mmol of phenol, 60 mmol of KOH, 12 mmol of K_2CO_3, 35 mL of NMP, and 25 mL of tolune were added. The reaction mixture was heated to 140°C until no further water was azeo-

tropically distilled from the reaction mixture, then the temperature was raised to 170°C to remove tolune. After being cooled to 40°C, 30 mmol of 2,6-difluorobenzonitrile was added and the reaction mixture was heated to 200°C and stirred at that temperature for 6 h. After cooling to room temperature, the product was precipitated from water. The solid product was washed with hot water, recrystallized three times from methanol to give 6.195 g of DPOBN. Yield 72%; m.p. 132–133°C; FT-IR (KBr) ν (cm^{-1}): 3063, 2231, 1578, 1494, 1251; ^{1}H-NMR (CDCl$_3$, δ): 6.47 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 7.6 Hz, 4H), 7.21–7.29 (m, 3H), 7.39–7.44 (m, 4H). ^{13}C-NMR (CDCl$_3$, δ): 161.4, 154.8, 134.2, 130.2, 125.3, 120.4, 113.2, 109.9, 95.3. Elemental Anal. Calcd for $C_{19}H_{13}NO_2$: C, 79.45; H, 4.53; N, 4.88. Found: C, 79.22; H, 4.35; N, 4.93.

Polymerization

PEKK/PEEKK copolymers with pendant cyano groups were prepared as shown in Scheme 2 by Friedel-Crafts reaction according to the method reported in the literature.[21] A typical preparative procedure for polymer II is described hereafter. Other polymers were also obtained in a similar manner.

To a 100-mL, round-bottomed flask equipped with a mechanical stirrer, a thermometer, nitrogen inlet and outlet tubes, 8.01 g (60 mmol) of anhydrous $AlCl_3$ and 20 mL of DCE were added. The flask was cooled to 0°C using an ice-water bath, then a solution of 2.3 mL of NMP in DCE (10 mL) was added dropwise with stirring over a period of 10 min, and the mixture was stirred for 30 min and then cooled to −15°C. Into the resulting suspension were added 0.287 g (1 mmol) of DPOBN, 1.530 g (9 mmol) of DPE, and 2.030 g (10 mmol) of TPC with stirring and the reaction mixture was warmed to 20°C over 2 h and the reaction was continued at this temperature for 6 h. The reaction mixture was quenched with methanol (50 mL) at 0°C, and the precipitate was crushed, washed with methanol, and extracted with boiling methanol for 24 h and allowed to dry in air. The air-dried product was heated at 100°C overnight under vacuum to give the polymer II.

Measurements

Differential scanning calorimeter

A Perkin–Elmer Pyris 1, interfaced with a computer via analogue to a digital converter, was used to
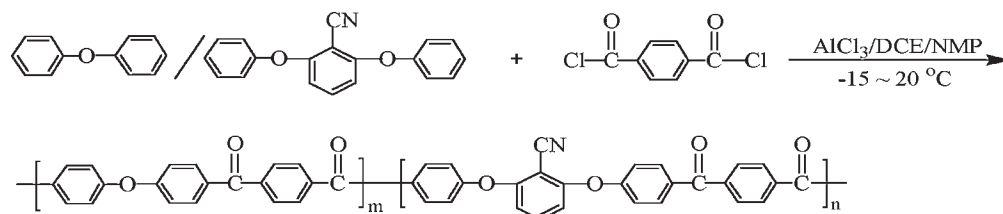
Scheme 2　Preparation of copolymers.

monitor the rate of heat flow from the sample during fusion. Each sample was placed in a DSC pan and heated at a rate of 20°C/min under an atmosphere of circulating dry nitrogen. To detect the glass transition temperature of the sample, this treatment was followed by cooling at a rate of 40°C/min from 400°C to room temperature and heating at a rate of 40°C/min.

Wide-angle X-ray diffraction

WAXD was measured with a Rigaku D/MAX-IIA X-ray diffractometer, using CuKα radiation, at 30 KV and 20 mA. The diffractograms were recorded at room temperature over the range of 10–40°. Samples were powder.

^{1}H-NMR and ^{13}C-NMR

^{1}H-NMR and ^{13}C-NMR spectra of the monomer were recorded with a Bruker PC-A400 (400 MHz) by using 5% (w/v) solution in CDCl$_3$. Chemical shifts were given in ppm using tetramethylsilane as an internal standard.

Infrared spectra

The FT-IR spectra of the polymers in KBr pellets (2%) were recorded using a Nicolet FT-IR (510P) spectrophotometer. For each spectrum two scans with 4 cm^{-1} resolution were coadded with air as the background.

Thermal gravimetric analysis

Thermogravimetric analysis (TG) was carried out on a Perkin–Elmer 7 Series thermal analysis system with an increasing rate of 10°C/min, N$_2$ atmosphere at the flow rate of 40 mL/min, scanning scope ranging from 75 to 750°C, and sample weight of 4.0–6.0 mg.

Ubbelodhe viscometer

Viscosities of the polymers were measured in 0.5 g/dL concentrated sulfuric acid solutions using an Ubbelodhe viscometer at 30°C. The inherent viscosity η$_{inh}$ was calculated by the One-Point Method and expressed in deciliters per gram:

$$\eta_{inh} = c^{-1} \ln t_1/t_0$$

Thermal stability testing

The thermal stability of the polymers was carried out on a hot plate at (350 ± 10)°C. The copolymer IV or V was each heated for 10, 20, 30, 60, 90, and 120 min.

The change of η$_{inh}$ values of the same polymer, which had been heated for different times were detected.

RESULTS AND DISCUSSION

Poly(ether ketone ketone) (PEKK)/poly(ether ether ketone ketone) (PEEKK) copolymers with pendant cyano groups were synthesized by Friedel-Crafts electrophilic displacement reaction of terephthaloyl chloride (TPC) with diphenyl ether (DPE) and 2,6-diphenoxybenzonitrile (DPOBN). The polymerization reaction is controlled by the addition of a controlling agent, which can suppress undesirable side reactions, particularly *ortho* substitution of activated aryloxy groups and alkylation of the polymer. Preferred controlling agents for the polymerization are organic Lewis bases such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP).[22] The Lewis acid (AlCl$_3$)/Lewis base complex appears to act as a solvent for the polymer-Lewis acid complex formed during the reaction, thereby maintaining the polymer in solution or in a reactive gel state. Further, the reaction mixture is more tractable, making work up of the polymer easier and ensuring effective removal of catalyst residues during purification. The solubilization property of the Lewis acid/Lewis base complex is particularly significant in the preparation of *para*-linked poly(arylene ether ketones). In the synthesis of the PEKK/PEEKK copolymers containing pendant cyano groups, different molar ratios of DPOBN to DPE were taken to obtain the copolymers. But the sum of moles of DPOBN and DPE should be equal to that of TPC, which would produce a high molecular weight according to the modified Carothers equation,[23] i.e., $X_n = (1 + r)/(1 - r)$, where X_n is the number–average degree of polymerization, and r is the sum of the molar ratio of both DPOBN and DPE to TPC. The molar ratios and inherent viscosities of the polymers are given in Table I. Inherent viscosity (η$_{inh}$) values reveal that high molecular weight polymers were obtained in DCE/NMP medium since the η$_{inh}$ values of the polymers were higher than the critical η$_{inh}$ value of the macromolecule. Thus, the polycondensation route is appropriate. The cyano pendant groups containing polymers possess slightly lower viscosity than the unsubstituted one which may be due to electron withdrawing effect (–I effect) of the cyano group, which reduces the nucleophilicity of the phenoxy group of DPOBN.

The elemental analysis values, i.e., C, H, and N content of polymers I–VI (Table I) are in close agreement with theoretical values confirming the proposed structure. The FT-IR spectra of all polymers show no absorption in the 1850–1720 cm^{-1} region indicating the absence of —COCl groups. All the spectra have a

TABLE I
Conditions and Viscosities of the Polymers

Polymer	DPE (mol %)	DPOBN (mol %)	Yield (%)	Elemental analysis (%)			η_{inh} (dL/g)
				C	H	N	
I	100	0	97.7	79.87 (80.00)	3.87 (4.00)		0.85
II	90	10	97.5	79.48 (79.69)	3.81 (3.95)	0.43 (0.45)	0.81
III	80	20	97.1	79.17 (79.41)	3.77 (3.90)	0.82 (0.87)	0.78
IV	70	30	96.5	78.95 (79.14)	3.69 (3.85)	1.16 (1.25)	0.75
V	60	40	96.2	78.64 (78.89)	3.70 (3.81)	1.49 (1.61)	0.72
VI	50	50	95.8	78.35 (78.66)	3.63 (3.77)	1.79 (1.95)	0.70

Values calculated are given in parentheses

1656 cm^{-1} stretching vibration for the C=O group, a 1587 cm^{-1} stretching vibration for the C=C bonds of the aryl ring, 1495 cm^{-1} for the C=C asymmetrical stretching vibration, 1243 cm^{-1} for the ether group asymmetrical vibration of —Ar—O—Ar—, and 2231 cm^{-1} stretching vibration for the C≡N group, except for polymer I where characteristic absorption for cyano group was absent.

The WAXD patterns of polymers I, III, IV, V, and VI are shown in Figure 1. Polymer I (p-PEKK) had five major diffraction peaks at 2θ that are 15.5° (020), 17.9° (110), 20.2° (111), 22.5° (200), and 27.8°(211). Copolymers III, IV, V, and VI kept nearly the same diffraction peaks as polymer I, but the diffraction peaks decreased in intensity with increasing D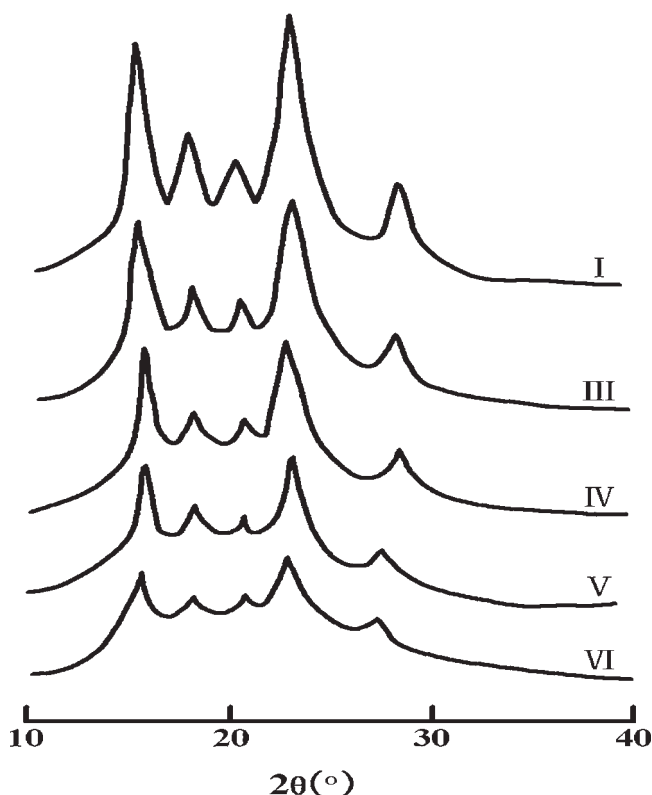POBN content. The degree of crystallinity of the copolymers was lower than that of the p-PEKK homopolymer and decreased with increasing DPOBN content because of the pendant cyano groups and 1,3-connected meta-phenylene linkages. The results above indicated that copolymers III, IV, V, and VI had the chain similar to that of the p-PEKK to form the crystal that was included in the orthorhombic system with the p-PEKK.[21]

The glass transition temperatures (T_gs), the melting points (T_ms), and the crystallization temperatures (T_cs) of the polymers were determined by DSC and the results are given in Table II. Although the polymer I (p-PEKK) had a higher T_g (169°C), its T_m (385°C) was too high, which made it difficult to process. The T_g values of the copolymers increased with increase in concentration of DPOBN in the copolymer when the molar ratio of DPOBN to DPE ranged from 10/90 to 30/70. This gradual increase in T_g may be due to the gradual increase in concentration of cyano pendant groups, which hinders the free rotation of aromatic ring. But the T_g of the copolymers containing 40–50 mol % DPOBN (V and VI) was lower than that of the copolymer IV containing 30 mol % DPOBN. As shown in Table II, the melting points (T_ms) of the polymers gradually decreased with increase in concentration of DPOBN in the polymer because of the pendant cyano groups and 1,3-connected meta-phenylene linkages. The crystallization temperatures (T_cs) of the polymers also decreased with increase in concentration of DPOBN in the polymer. The results agreed with the WAXD results. The T_m of the p-PEKK homopolymer (385°C) can be reduced to 336°C when

Figure 1 The WAXD patterns of the polymers.

TABLE II
Thermal Properties of the Polymers

Polymer	T_g (°C)	T_m (°C)	T_c (°C)	T_d (°C)[a]
I	169	385	319	544
II	159	371	297	528
III	170	354	262	525
IV	175	336	231	520
V	171	330	207	518
VI	167	312	192	514

[a] 5% weight loss temperature observed by TG.
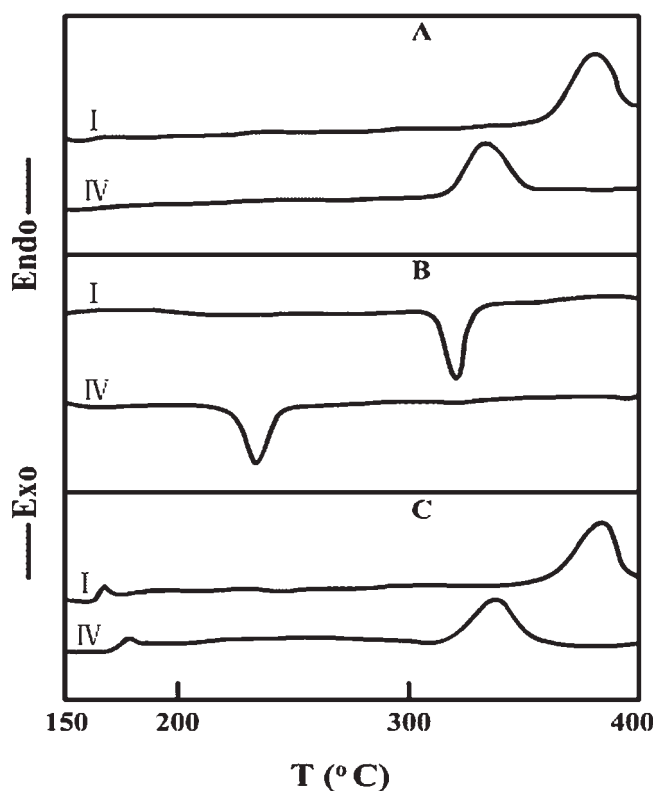
Figure 2 Typical DSC curves of the polymers I and IV. (A) 1st heating; (B) cooling; (C) 2nd heating.

Figure 3 Typical TG curves of the Polymers I and IV.

the molar ratio of DPOBN to DPE is 30/70. This might be attributed to two effects: the more flexible nature of the *meta*-phenylene units when compared with that of the *para*-phenylene units and the steric hindrance of cyano pendant groups, which cannot ''match'' the neat PEKK crystal structure and therefore reduces the crystallinity and its melting points. It can be concluded that the depression in the T_m of the polymers improves their processing properties. The typical DSC curves of the polymers I and IV are illustrated in Figure 2.

The thermal stabilities of the polymers were investigated by TG. The thermal decomposition temperatures (T_ds) of the polymers are also listed in Table II. All the polymers are thermally stable up to 514°C. The thermal stability of the materials is affected by the content of DPOBN in the polymer. Polymer I (*p*-PEKK), without cyano and *m*-phenylene groups, has the highest thermal decomposition temperature (544°C). The thermal decomposition temperatures (T_ds) of the copolymers with 10–50 mol % DPOBN are observed between 514 and 528°C. The small variations in the T_ds of the resultant copolymers make the copolymers II–VI acceptable for heat-resistance applications. The typical TG curves of the polymers I and IV are illustrated in Figure 3. The temperature difference between T_m and T_d of polymer IV or V was large, thus the fusion processing can be accomplished.
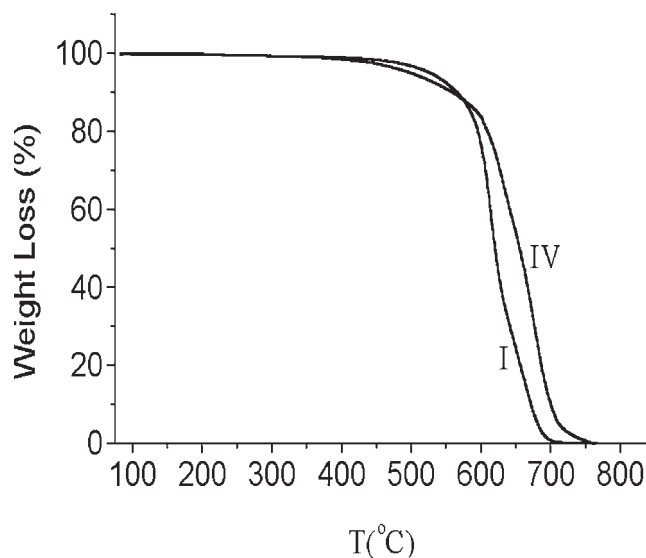
The solubility behavior of the polymers prepared in this study was determined for powdery samples in excess solvents at room temperature for 24 h and the results are listed in Table III. It is known that polymer I (*p*-PEKK) is insoluble in NMP, DMSO, and DMF. However, the copolymers with pendant cyano groups can be swelled in these solvents. But, all polymers prepared were insoluble in common solvents, such as THF, CHCl₃, EtOH, and so on. The copolymers were also insoluble in 30% aqueous NaOH or 30% aqueous HCl except for concentrated sulfuric acid. Thus, from the results above, we concluded that the copolymers with pendant cyano groups have good resistance to acidity, alkali, and common organic solvents.

The η_{inh} values of the copolymers IV and V when heated at (350 ± 10)°C for different times are shown in Table IV. We concluded that no significant change in the η_{inh} value took place compared with that of the original sample. Thus, no crosslinking took place when the copolymers of IV or V were heated for 2 h, respectively. The results showed that the copolymers IV and V appeared to have good thermal stability and also to have potential for fusion processing.

TABLE III
Solubility of the Polymers

Polymer	H₂SO₄	NMP	DMSO	DMF	THF	CHCl₃	EtOH
I	+	−	−	−	−	−	−
II	+	±	±	±	−	−	−
III	+	±	±	±	−	−	−
IV	+	±	±	±	−	−	−
V	+	±	±	±	−	−	−
VI	+	±	±	±	−	−	−

+, soluble; ±, swollen; −, insoluble.

Heating time (min)	η_{inh} (Polymer IV)	η_{inh} (Polymer V)
0	0.75	0.72
10	0.74	0.73
20	0.76	0.74
30	0.74	0.75
60	0.75	0.73
90	0.76	0.74

[a] Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30°C.

CONCLUSIONS

1. High molecular weight PEKK/PEEKK copolymers with pendant cyano groups can be synthesized by electrophilic displacement reaction of TPC with varying mole proportions of diphenyl ether (DPE) and 2,6-diphenoxybenzonitrile (DPOBN) in 1,2-dichloroethane-NMP medium under mild conditions.

2. The crystallinity and melting temperature of the copolymers were found to decrease with increase in concentration of the DPOBN units in the polymer.

3. The copolymers fundamentally bore the same number and site of diffraction peak of every crystal facecrystal plane in comparison with that of *p*-PEKK, because the copolymers had a chain similar to that of *p*-PEKK in forming the crystal, which was included to orthorhombic system.

4. The copolymers with 30–40 mol % DPOBN has a high T_g (171–175°C), a high T_d (518–520°C), and moderate T_m (330–336°C). The temperature difference between T_m and T_d of the copolymer

IV or V was large, and the copolymers of IV and V have good stability at (350 ± 10)°C. Thus, copolymers IV and V have good potential for fusion processing.

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