

Synthesis and Characterization of Poly(ether ketone ether ketone)/Poly(ether ether ketone ketone) Copolymers Containing Naphthalene and Pendant Cyano Groups

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ABSTRACT: 2,6-Bis(β -naphthoxy)benzotrile (BNOBN) was synthesized by reaction of β -naphthol with 2,6-difluorobenzotrile in *N*-methyl-2-pyrrolidone (NMP) in the presence of KOH and K_2CO_3 . Poly(ether ketone ether ketone ketone)(PEKEKK) /poly(ether ether ketone ketone) (PEEKK) copolymers containing naphthalene and pendant cyano groups were obtained by electrophilic Friedel-Crafts polycondensation of terephthaloyl chloride (TPC) with varying mole proportions of 4,4'-diphenoxybenzophenone (DPOBP) and 2,6-bis(β -naphthoxy)benzotrile (BNOBN) using 1,2-dichloroethane (DCE) as solvent and NMP as Lewis base in the presence of anhydrous $AlCl_3$. The resulting polymers were characterized by various analytical techniques, such as FTIR, DSC, TG, and WAXD. The results indicated that the crystallinity and melting temperature of the polymers

decreased with increase in concentration of the BNOBN units in the polymer, the glass transition temperature of the polymers increased with increase in concentration of the BNOBN units in the polymer. Thermogravimetric studies showed that all the polymers were stable up to 536°C in N_2 atmosphere. The copolymers have good resistance to acidity, alkali, and organic solvents. Because of the melting temperature (T_m) depression with increase in the BNOBN content in the reaction system, the processability of the resultant copolymers could be effectively improved. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3225–3231, 2009

Key words: poly(ether ketone ether ketone ketone); poly(ether ether ketone ketone); 2,6-bis(β -naphthoxy)benzotrile; terephthaloyl chloride; synthesis

INTRODUCTION

Poly(aryl ether ketone)s (PAEK) as high-performance engineering plastics have attracted much attention.^{1–4} In fact, their excellent mechanical properties, good resistance to acidity and alkali, high thermal and thermo-oxidative stability have made them very practical in our daily life and in industry. Among them poly(ether ether ketone) (PEEK), poly(ether ketone ketone) (PEKK) and poly(ether ketone ether ketone ketone) (PEKEKK) are the most widely used materials and have found many applications in aerospace, coating and insulating materials.^{5–7} There are two general synthetic pathways to producing PAEKs, namely, aromatic nucleophilic substitution reaction^{8–10} and aromatic electrophilic substitution (Friedel-Crafts acylation).^{9,11} However, their high crystalline property and high melting temperature often restrict the use of

these resins for some applications. A number of modifications have been adopted to reduce the processing temperature, such as softening the backbone and lowering the T_m of the PEEK.^{12–16} Introduction of pendant groups on to the poly(aryl ether ether ketone) main chain is another structural change.¹⁷ Recently, the thio-containing poly(ether ether ketone)s was also reported.¹⁸

The all-*para*-connected poly(ether ketone ketone) (*p*-PEKK) and poly(ether ketone ether ketone ketone) (*p*-PEKEKK) have made them difficult to process due to their higher melting points. The very poor flowing property and the too high processing temperature (over 430°C) for *p*-PEKK or *p*-PEKEKK was even difficult for the processing capacity of the ZSK 30P 9P Lab extruding machine (from Germany). To improve its glass transition temperature and processability, some modifications were made on *p*-PEKK.^{19,20} 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,²¹ this latter effect is attributed to an increase in overall chain flexibility with the introduction of the *meta* linkages.

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However, to the best of our knowledge, the modification on *p*-PEKEKK has received less attention.²² The synthesis and investigation of novel poly(aryl ether ketone)s would be very useful for a more rigorous structure-property correlation of this very interesting class of polymers. It is common knowledge that introduction of bulky groups in the main chain leads to an increase in the temperature of the glass transition. Also, the incorporation of pendant groups leads to an increase in T_g . However, in this case low crystallinity or amorphous polymers are obtained. Recently, we have synthesized a new monomer, 2,6-bis(β -naphthoxy)benzonitrile (BNOBN) from readily available 2,6-difluorobenzonitrile and β -naphthol. Considering the fact that the BNOBN contains rigid and bulky naphthalene, pendant cyano group, and 1,3-connected *meta*-phenylene linkage, we expected that the copolymers with high T_g s and moderate T_m s could be obtained by incorporation of lower content of BNOBN into the all-*para* backbone of *p*-PEKEKK. Previously, we have synthesized simple linear poly(aryl ether ketone) with high molecular weight from terephthaloyl chloride (TPC), isophthaloyl chloride (IPC) and diphenyl ether (DPE) by electrophilic Friedel-Crafts polycondensation in solution at low temperature.²³ In this paper, we synthesized the copolymers of poly(ether ketone ether ketone ketone) (PEKEKK) and poly(ether ether ketone ketone) (PEEKK) containing naphthalene and pendant cyano groups by electrophilic Friedel-Crafts solution copolycondensation of terephthaloyl chloride (TPC) with varying mole proportions of 4,4'-diphenoxybenzophenone (DPOBP) and 2,6-bis(β -naphthoxy)benzonitrile (BNOBN) using 1,2-dichloroethane (DCE) as solvent and NMP as Lewis base in the presence of anhydrous $AlCl_3$. The copolymers were characterized by FTIR, wide-angle X-ray diffraction (WAXD), differential scanning calorimeter (DSC), and thermal gravimetric analysis (TG). The results indicated that the copolymers have a potentiality for industry.

EXPERIMENTAL

Materials

β -Naphthol (Sigma-Aldrich Corp., St. Louis, MO), 2,6-difluorobenzonitrile (Aldrich), anhydrous $AlCl_3$ (Aldrich) were used as received. 1,2-Dichloroethane (DCE, Aldrich) was distilled prior to use. Terephthaloyl chloride (TPC, m.p. 82–83°C, Shuanglin Chemical, Nanchang, 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 (type 4A). 4,4'-Diphenoxybenzophenone

none was prepared according to the literature procedure (DPOBP, m.p. 146°C).²⁴

Synthesis

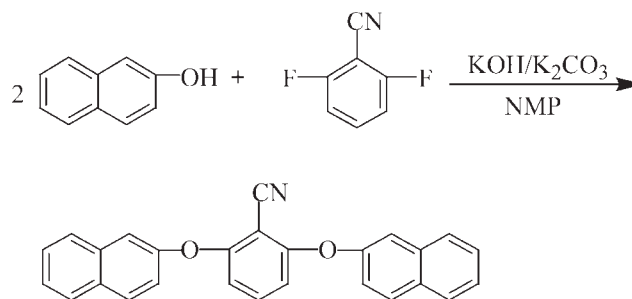
Preparation of BNOBN

2,6-Bis(β -naphthoxy)benzonitrile (BNOBN) was synthesized as shown in Scheme 1 by nucleophilic aromatic substitution reaction of 2,6-difluorobenzonitrile with β -naphthol in the presence of KOH and K_2CO_3 in high boiling solvent NMP under N_2 atmosphere.

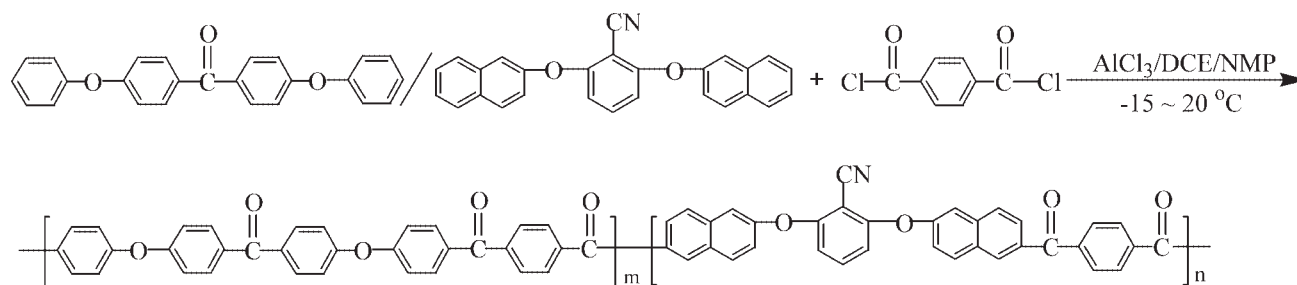
To a 100 mL, round-bottomed flask equipped with a mechanical stirrer, a thermometer, nitrogen inlet and outlet tubes, and a Dean-Stark trap, 72 mmol of β -naphthol, 60 mmol of KOH, 12 mmol of K_2CO_3 , 35 mL of *N*-methyl-2-pyrrolidone (NMP) and 25 mL of toluene were added. The reaction mixture was heated to 140°C until no further water was azeotropically distilled from the reaction mixture, then the temperature was raised to 170°C to remove toluene. 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 from DCE/EtOH ($V_{DCE}/V_{EtOH} = 1/4$) three times to give 8.011 g of 2,6-bis(β -naphthoxy)benzonitrile (BNOBN). Yield 69%; m.p. 149–151°C; FTIR (KBr): $\nu = 3065, 2227, 1576, 1497, 1254\text{ cm}^{-1}$; 1H -NMR ($CDCl_3$): $\delta = 7.93\text{--}7.86$ (m, 4H), 7.81–7.78 (m, 2H), 7.55–7.45 (m, 6H), 7.34–7.25 (m, 3H), 6.55 (d, $J = 8.4\text{ Hz}$, 2H); ^{13}C -NMR ($CDCl_3$): $\delta = 161.45, 152.45, 134.24, 134.14, 131.11, 130.39, 127.88, 127.45, 126.89, 125.68, 120.28, 116.81, 113.13, 110.29, 95.52$; MS: m/z (%) = 387 (M^+ , 100), 358 (24), 127 (71), 115 (37); Elemental analysis: calculated for $C_{27}H_{17}NO_2$: C, 83.71; H, 4.42; N, 3.61; Found: C, 83.52; H, 4.25; N, 3.75.

Polymerization

PEKEKK/PEEKK copolymers with naphthalene and pendant cyano groups were prepared as shown in



Scheme 1 Preparation of BNOBN.



Scheme 2 Preparation of copolymers.

Scheme 2 by Friedel-Crafts reaction. 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, 9.31 g (70 mmol) of anhydrous AlCl_3 and 25 mL of 1,2-dichloroethane (DCE) were added. The flask was cooled to 0°C using an ice-water bath, then a solution of 2.5 mL of *N*-methyl-2-pyrrolidone (NMP) in DCE (5 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 0.1935 g (0.5 mmol) of BNOBN, 3.477 g (9.5 mmol) of DPOBP and 2.030g (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

Inherent viscosities of the polymers were measured at 30°C by an Ubbelodhe-type viscometer in 0.5 g dL^{-1}

concentrated sulfuric acid solutions. The inherent viscosity η_{inh} was calculated by the One-Point Method and expressed in dL g^{-1} : $\eta_{\text{inh}} = c^{-1} \ln t_1/t_0$, where c is the concentration of polymer, t_1 and t_0 are for the flow of the polymer solution and the solvent, respectively.

The glass transition temperature (T_g) and melting temperature (T_m) were measured with a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC). Each sample was placed in a DSC pan and heated at a rate of $20^\circ\text{C min}^{-1}$ 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 $40^\circ\text{C min}^{-1}$ from 400°C to room temperature and heating at a rate of $40^\circ\text{C min}^{-1}$.

Thermogravimetric analysis (TG) was carried out on a Perkin-Elmer TGA-7 Series thermal analysis system with an increasing rate of $10^\circ\text{C min}^{-1}$, N_2 atmosphere at the flow rate of 40 mL min^{-1} , scanning scope ranging from 70 to 750°C , and sample weight of 4.0 – 6.0 mg .

Wide angle X-ray diffraction (WAXD) was measured with a Rigaku D/MAX-IIA X-ray diffractometer, using $\text{CuK}\alpha$ radiation, at 30 KV and 20 mA. The diffractograms were recorded at room temperature over the range of 10 – 40°C . Samples were powder.

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of the monomer were recorded with a Bruker PC-A400 (400 MHz) by using 5% (w/v) solution in CDCl_3 . Chemical shifts

TABLE I
Conditions and Viscosities of the Polymers

Polymer	DPOBP (mol %)	BNOBN (mol %)	Yield (%)	Elemental analysis(%)			η_{inh} (dL g^{-1})
				C	H	N	
I	100	0	97.9	79.41 (79.83)	3.93 (4.06)		0.80
II	95	5	97.7	79.51 (79.90)	3.89 (4.04)	0.11 (0.14)	0.78
III	90	10	97.7	79.46 (79.97)	3.90 (4.02)	0.23 (0.28)	0.76
IV	85	15	97.5	79.59 (80.04)	3.85 (4.00)	0.36 (0.42)	0.75
V	80	20	97.3	79.69 (80.12)	3.82 (3.98)	0.48 (0.56)	0.73
VI	75	25	97.0	79.73 (80.19)	3.85 (3.97)	0.62 (0.70)	0.71
VII	70	30	97.1	79.78 (80.26)	3.81 (3.95)	0.77 (0.84)	0.68
VIII	60	40	96.8	79.89 (80.40)	3.78 (3.91)	1.04 (1.11)	0.67

Values calculated are given in parentheses.

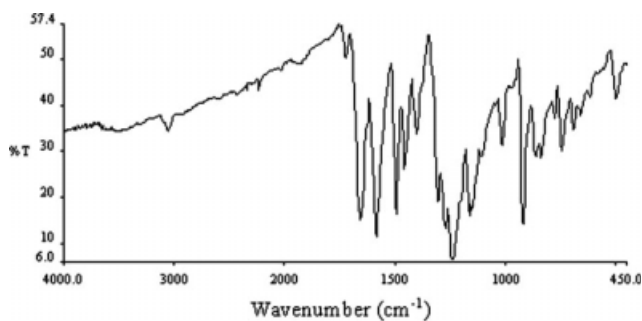


Figure 1 FTIR spectrum of polymer VI.

were given in ppm using tetramethylsilane (TMS) as an internal standard.

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

The thermal stability testing of the polymers was carried out on a hot plate at $(350 \pm 10)^\circ\text{C}$ in air. The copolymer VI or VII was each heated for 10, 20, 40, 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

2,6-Bis(β -naphthoxy)benzotrile (BNOBN) was conveniently prepared by reaction of β -naphthol with 2,6-difluorobenzotrile in *N*-methyl-2-pyrrolidone (NMP) in the presence of KOH and K_2CO_3 (Scheme 1). Poly(ether ketone ether ketone ketone) (PEKEKK)/poly(ether ether ketone ketone)(PEEKK) copolymers containing naphthalene and pendant cyano groups were synthesized by Friedel-Crafts electrophilic displacement reaction of terephthaloyl chloride (TPC) with 4,4'-diphenoxybenzophenone (DPOBP) and 2,6-bis(β -naphthoxy)benzotrile (BNOBN) (Scheme 2). The addition of a controlling agent is needed during the polymerization reaction to 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).²⁵ 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 (AlCl_3)/Lewis base complex is particularly significant in the preparation of *para*-linked poly(arylene ether ketones).

In the synthesis of the PEKEKK/PEEKK copolymers containing naphthalene and pendant cyano groups, different molar ratios of BNOBN to DPOBP were taken to obtain the copolymers. But the sum of moles of BNOBN and DPOBP should be equal to that of terephthaloyl chloride (TPC), which would produce a high molecular weight according to the modified Carothers equation,²⁶ 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 BNOBN and DPOBP 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

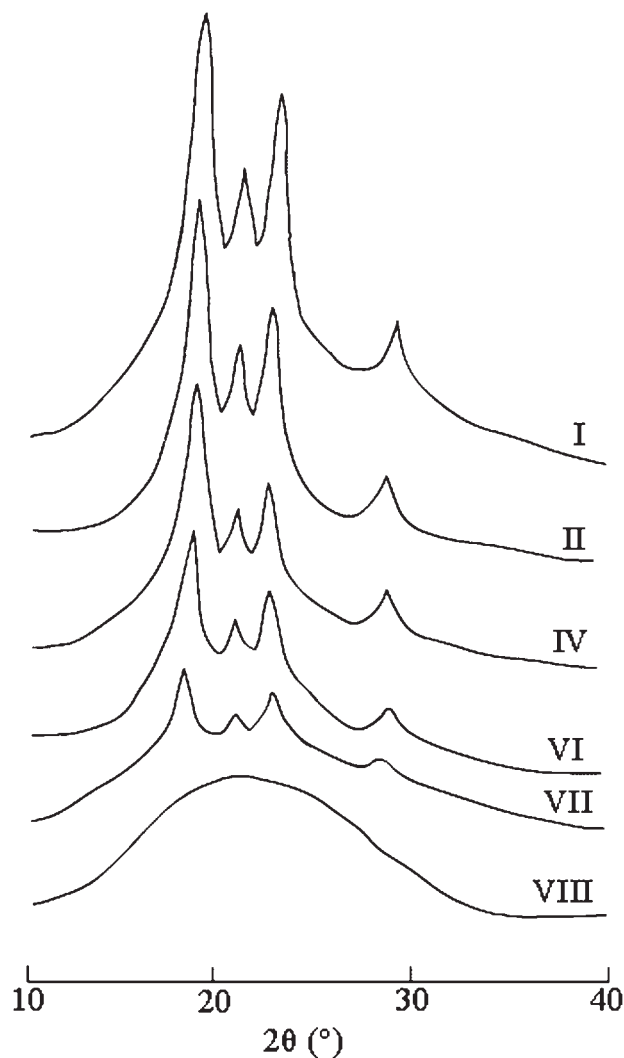


Figure 2 The WAXD patterns of the polymers.

TABLE II
Thermal Properties of the Polymers

Polymer	T_g (°C)	T_m (°C)	T_c (°C)	T_d (°C) ^a
I	164	378	265	548
II	167	371	258	544
III	169	363	249	542
IV	172	354	237	541
V	176	348	230	540
VI	181	336	218	539
VII	183	327	205	537
VIII	189			536

^a 5% weight loss temperature observed by TG.

macromolecule. Thus, the electrophilic polycondensation route is appropriate. The polymers containing cyano pendant groups 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 naphthoxy group of BNOBN.

The elemental analysis values, i.e., C, H, and N content of polymers I–VIII (Table I) are in close agreement with theoretical values confirming the proposed structure. The synthesized poly(ether ketone ether ketone)(PEKEKK)/poly(ether ether ketone ketone)(PEEKK) copolymers containing naphthalene and pendant cyano groups were characterized by FTIR spectroscopic analysis. The FTIR spectrum of the polymer VI is shown in Figure 1. The sample was quenched by immersion in the mixture of ice and water to make the material amorphous after heating to fusion. The characteristic absorptions for the polymer VI is situated at 2233, 1659, 1588, 1495, 1241, and 845 cm^{-1} . The first peak is attributed to stretching vibration for the $\text{C}\equiv\text{N}$ group. The next peak at 1659 cm^{-1} is attributed to stretching vibration for the $\text{C}=\text{O}$ group. The next two peaks at 1588, 1495 cm^{-1} are attributed to symmetrical stretching vibration and asymmetrical stretching vibration for the $\text{C}=\text{C}$ bonds of the aryl ring, respectively. The next peak at 1241 cm^{-1} is attributed to the ether group asymmetrical vibration of $-\text{Ar}-\text{O}-\text{Ar}-$. The last peak at 845 cm^{-1} is attributed to the 1,4-substitution of arone.

WAXD was used to analyze the crystal structures. The WAXD patterns of polymers I, II, IV, VI, and VIII are presented in Figure 2. Polymer I (*p*-PEKEKK) had four major diffraction peaks at 2θ that are 18.7° (110), 20.6° (111), 23.1° (200) and 28.9° (211). The WAXD patterns of copolymers II, IV, and VI fundamentally bore the same number and site of diffraction peak of every crystal face crystal plane in comparison with that of *p*-PEKEKK, but the diffraction peaks decreased in intensity with increasing BNOBN content. The degree of crystallinity of the copolymers was lower than that of the *p*-PEKEKK homopolymer and decreased with increasing BNOBN content due to the pendant cyano

groups, 1,3-connected *meta*-phenylene, and 2,6-connected naphthalene linkages. When the molar ratio of BNOBN to DPOBP was up to 40/60, the obtained copolymer VIII was amorphous and only showed a diffuse diffraction peak. The aforementioned results indicated that copolymers II, IV, and VI had the chain similar to that of the *p*-PEKEKK to form the crystal that was included in the orthorhombic system with the *p*-PEKEKK.²²

The glass transition temperatures (T_g s), the melting points (T_m s), and the crystallization temperatures (T_c s) of the polymers were determined by DSC and the results are given in Table II. Although the polymer I (*p*-PEKEKK) had a higher T_g (164°C), its T_m (378°C) was too high, which made it difficult to process. As shown in Table II, the T_g values of the copolymers gradually increased with increase in concentration of BNOBN in the copolymer and are higher than that of *p*-PEKEKK. This gradual increase in T_g may be due to the gradual increase in concentration of both bulky stiff naphthalene groups and cyano pendant groups, which hinders the free rotation of aromatic ring. However, the melting points (T_m s) of the polymers gradually decreased and then disappeared with an increase in concentration of BNOBN in the polymer due to the pendant cyano

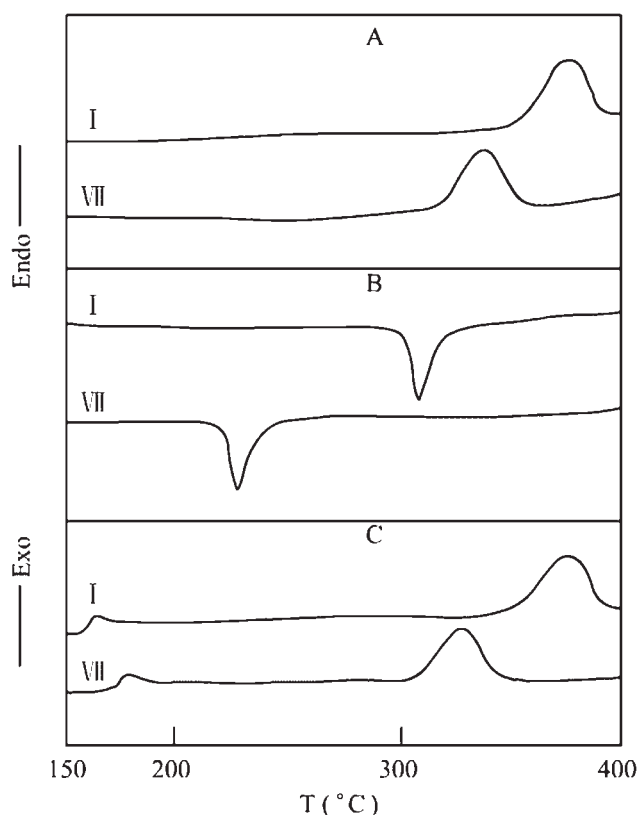


Figure 3 Typical DSC curves of the polymers I and VII. (A) First heating, (B) cooling, and (C) second heating.

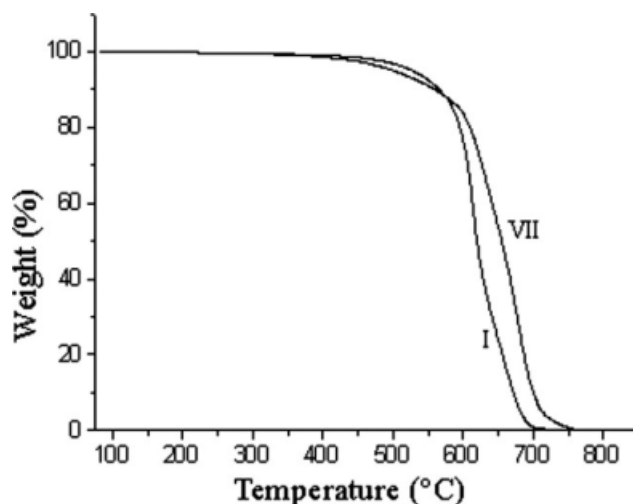


Figure 4 Typical TG curves of the polymers I and VII.

groups, 1,3-connected *meta*-phenylene, and 2,6-connected naphthalene linkages. When the molar ratio of BNOBN to DPOBP was up to 40/60, the obtained copolymer VIII was amorphous and no melting peak was observed in the DSC curve. The cold crystallization temperatures (T_c s) of the polymers also decreased gradually and then disappeared with an increase in concentration of BNOBN in the polymer. The results agreed with the WAXD results. The T_m of the *p*-PEKEKK homopolymer (378°C) can be reduced to 327°C when the molar ratio of BNOBN to DPOBP is 30/70, moreover the glass transition temperature of polymer VII can be up to 183°C, 19°C higher than that of *p*-PEKEKK. This might be attributed to two effects: the more flexible nature of the *meta*-phenylene units when compared to that of the *para*-phenylene units and the steric hindrance of cyano pendant groups and bulky stiff naphthalene groups, which cannot “match” the neat PEKEKK crystal structure and therefore reduces the crystallinity and its melting point. It can be concluded that the depression in the T_m of the polymers improves their processing properties and the increase in the T_g of the polymers improves their thermal properties.

The typical DSC curves of the polymers I and VII are illustrated in Figure 3.

Thermogravimetric analysis (TG) was used to examine the thermal stability of the materials under nitrogen. The thermal decomposition temperatures (T_d s) of the polymers are also summarized in Table II. All the polymers are thermally stable up to 536°C. The thermal stability of the materials is affected by the content of BNOBN in the polymer. Polymer I (*p*-PEKEKK), without cyano and naphthalene groups, has the highest thermal decomposition temperature (548°C). The thermal decomposition temperatures (T_d s) of the copolymers with 5–40 mol % BNOBN are observed between 536 and 544°C. The small variations in the T_d s of the resultant copolymers make the copolymers II–VIII acceptable for heat-resistance applications. The typical TG curves of the polymers I and VII is illustrated in Figure 4. The temperature difference between T_m and T_d of polymer VI or VII 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. The content of BNOBN in the copolymers affects the solubility of the polymer in organic solvents. It is known that polymer I (*p*-PEKEKK) is insoluble in NMP, DMSO, and DMF. However, the copolymers with naphthalene and pendant cyano groups can be swelled in these solvents. Polymer VIII, having 40 mol % BNOBN, can be dissolved in NMP. But, all polymers prepared were insoluble in common solvents such as THF, CHCl_3 , 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 naphthalene and pendant cyano groups have good resistance to acidity, alkali, and common organic solvents.

The η_{inh} values of the copolymers VI and VII when heated at $(350 \pm 10)^\circ\text{C}$ for different times are shown in Table IV. We concluded that no significant change in the η_{inh} value took place compared with

TABLE III
Solubility of the Polymers

Polymer	H_2SO_4	NMP	DMSO	DMF	THF	CHCl_3	EtOH
I	+	–	–	–	–	–	–
II	+	+/-	–	+/-	–	–	–
III	+	+/-	+/-	+/-	–	–	–
IV	+	+/-	+/-	+/-	–	–	–
V	+	+/-	+/-	+/-	–	–	–
VI	+	+/-	+/-	+/-	–	–	–
VII	+	+/-	+/-	+/-	–	–	–
VIII	+	+	+/-	+/-	–	–	–

+, soluble; +/-, swollen; –, insoluble.

TABLE IV
 η_{inh}^a Values of the Copolymers VI and VII at (350°C ± 10)°C

Heating time (min)	0	10	20	40	60	90	120
η_{inh} (Polymer VI)	0.71	0.72	0.73	0.72	0.74	0.73	0.73
η_{inh} (Polymer VII)	0.68	0.69	0.68	0.70	0.71	0.70	0.71

^a Measured at a concentration of 0.5 g dL⁻¹ in concentrated sulfuric acid at 30°C.

that of the original sample. Thus, no crosslinking took place when the copolymers of VI or VII were heated for 2 h, respectively. The results showed that the copolymers VI and VII appeared to have good thermal stability and also to have potential for fusion processing.

CONCLUSIONS

1. High molecular weight PEKEKK/PEEK copolymers with naphthalene and pendant cyano groups can be synthesized by electrophilic polycondensation of TPC with varying mole proportions of 2,6-bis(β -naphthoxy)benzotrile (BNOBN) and 4,4'-diphenoxybenzophenone (DPOBP) in 1,2-dichloroethane (DCE)-NMP medium at low temperature.
2. The crystallinity and melting temperature of the copolymers were found to decrease with increase in concentration of the 2,6-bis(β -naphthoxy)benzotrile (BNOBN) units in the polymer, the glass transition temperature of the copolymers increased with increase in concentration of BNOBN units in the polymer.
3. The copolymers II–VII fundamentally bore the same number and site of diffraction peak of every crystal face crystal plane in comparison with that of *p*-PEKEKK, because the copolymers had a chain similar to that of *p*-PEKEKK in forming the crystal, which was included to orthorhombic system.
4. The copolymers with 25–30 mol % BNOBN have a high T_g (181–183°C), a high T_d (537–539°C), and a moderate T_m (327–336°C). The temperature difference between T_m and T_d of the copolymer VI or VII was large, and the copolymers of VI and VII have good thermal stability at 350 ± 10°C. Thus, copolymers VI and VII have good potential for fusion processing.

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