Investigations of the Practical Routes, Structure, and Properties for Poly(aryl ether ketone ketone) Polymers

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ABSTRACT: Different routes for preparing poly(aryl ether ketone)s (PEKKs) are presented and compared. The properties of PEKKs are related to the content of metaphenyl links in the molecular main chains, the molecular chain branching degree, the gelation content by molecular crosslinks, and, especially, the relative content of crystal form II to crystal form I of the PEKK polymorphism. When the molecular T/I ratio of 50/50 in the polymer chains is reached, the obtained PEKK has a lower melting point and gelation content (2% or so). The PEKKs prepared from the electronical substitution route (E route) often have a 0–30% content of crystal form II (relative to the mixed form I and form II), which is much more than that in PEKKs from the nucleophilic substitution route (N route, form II accounts for 0–20%). The relatively unstable crystal form II resulted in the unstable and difficultly predicted thermal properties of PEKKs. PEKKs from different routes provide samples with melting points from 360 to 397°C (T_m) and glassy transition temperatures (T_g) from 167 to 176°C and the equilibrium melting point of 411°C for *para*-PEKK, while the tensile strength of the homopolymer PEKK and copolymers of PEEKK (poly(aryl ether ether ketone ketone)–PEKK can reach 100 MPa prepared by the N route. The high T_g makes PEKK polymers practically useful while too high T_m and a very small difference between T_m and T_d (degradation temperature) produce obstacles to its wide application. The reaction mechanisms of both electrophilic and nucleophilic routes are investigated and discussed in detail. Results show that the molecular chain branched by solvents and monomers with many activated points may be partly reduced to some extent by the oligomer and extruding route. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 659–677, 1998

Key words: poly(ary ether ketone ketone)s (PEKKs); electrophilic substitution reaction; nucleophilic substitution reaction; thermal properties; polymorphism; molecular structure

INTRODUCTION

Since the 1980s, it has been very well known that poly(aryl ether ether ketone)s (PEEKs) are high-performance thermoplastics resistant to heat,

acidity, and alkali and they have already been commercialized (named APC-2 by the ICI.[1–3]). Corresponding to PEEK, poly(aryl ether ketone ketone)s (PEKKs) have also been the subject of much research. The literature has adopted two routes to prepare the PEEKs' family. One of them is to adopt a nucleophilic substitution route[1–3]; the other is to follow the electrophilic substitution methods.[4–8] The former route is generally more

successful than the latter one. Research on the synthesis of poly(aryl ether ketone)s by the latter routes are still frequently reported,[8-13] especially for PEKK. Since Bonner et al. reported preparing PEKK via Friedel–Crafts condensation of diphenyl ether (DPE) and terephthaloyl (TPC) in a solvent of $PhNO_2$,[4] many attempts to prepare high molecular weight of PEKK have been reported.[14-21] All these practical reports show that satisfied results have been obtained, but the unsteady properties of the obtained polymers need to be further improved.

In previous studies, PEEK and PEEKK (poly(aryl ether ether ketone ketone)) have been produced to some scale by extruding the former at 390°C and the latter at 410°C.[30,31] Contrary to PEEK and PEEKK, PEKK obtained by different methods has quite unstable and different properties which have produced obstacles to practical applications for quite a long time. Even so, attempts to improve PEKK properties have been reported by many researchers.[7,10,13] Their attempts result from the interest in producing PEKK in the "cheapest" or of the "lowest" budget.

In this article, the synthesis of PEKK by different routes mentioned above was compared. This work focused on the relationship of a polymer's properties with its preparation route, molecular structure, polymorphism, and heating treatment. Especially, the reaction mechanism including choosing the proper solvents is presented and discussed. According to these comparison results, we suggest practical routes based on calculations of the ratio of the performance to the cost of the polymers obtained by different routes.

## EXPERIMENT AND CHARACTERIZATION

Materials

Terephthaloyl chloride (TPC) (mp 85°C) was prepared in our laboratory by reacting terephthalic acid with sulfinyl dichloride with $AlCl_3$ as the catalyst. Isophthaloyl chloride (IPC) (mp 37–43°C) was from the Jiangxi Agriculture Medicine Factory, China. Diphenyl ether (DPE) (mp 26–30°C) and nitromethane (CH_3NO_2, 99%) were from the Shanghai Reagent Factory. 4,4′-Di(paraflorobenzoyl)benzene (mp 218°C) was prepared in our laboratory and by the literature[22] methods. Phenol (mp 40°C), dimethylacetamide (DMAc, bp 165°C), and potassium carbonate (an-

hydrous, 99.7%) were obtained from the Tianjin Chemical Reagent Factory. Sodium carbonate (anhydrous, 99.8%) and dimethylformamide (DMF, 99%) were from the Shengyang Reagent Factory. Diphenyl sulfone (mp 128–129°C) was prepared by reacting pure benzene with concentrated H_2SO_4.

Preparation Routes

E_1 Route

In this route, PEKK is prepared through the electrophilic substitution method by using the monomers of DPE (N_A) and TPC (N_B). In this route, different ratios of N_A to N_B ($r = N_A/N_B$) are taken to observe the changing principles of the polymers, which can be controlled more effectively by the ratio of r. But, usually, this route provides PEKK with lower molecular weights. The major reason for this is that the oligomers formed in the preparation are crystallized in the solvent of, e.g., dichloroethane, which will interfere with further polymerization, while oligomers with a polymerization degree of 10 are often adopted to obtain polymers in the extruding machine according to the following route:

PEKK POLYMER (1)
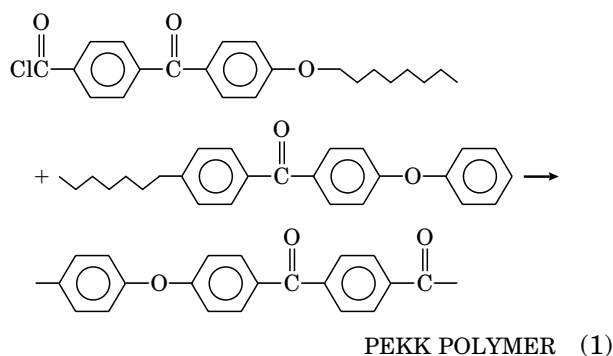
In route (1), the oligomers with both end group of ClC=O and that of ArO— are prepared at first by the electrophilic substitution reaction (see E_2 route). These oligomers usually have good rheology and processing properties; thus, they are quite suitable for processing by the extrusion method. The byproduct of HCl in the reaction controls the product's molecular weight, which will be eliminated by adding some absorbents to the original oligomers. Although the obtained PEKK polymers do not have high molecular weights, their properties are easily improved by mixing them with other fillers, e.g., carbon fibers and/

or glass fibers. Thus, this route is thought to be practical not only in cost (cheaper monomers) but in processing as well.

E_2 Route

This route is mainly for the copolymerization or modification of all *para*-PEKK by the electrophilic substitution reaction. In this route, different ratios of TPC to IPC (T/I) are adopted with the molar sum of T and I the same as that of DPE. In this route, the byproduct HCl is got rid of in a NaOH solution (5% wt). The catalyst of $AlCl_3$ is stoichiometrically excessive to that of the monomers of TPC and/or IPC, which will improve the solubility of the formed oligomers. The solvents adopted have a direct effect on the molecular weight of the PEKK polymer products, which is discussed in the latter part of this article.

NE_3 Route

This route is the two-step method referred to as a nucleophilic substitution reaction combined with an electrophilic substitution method such as in the following:
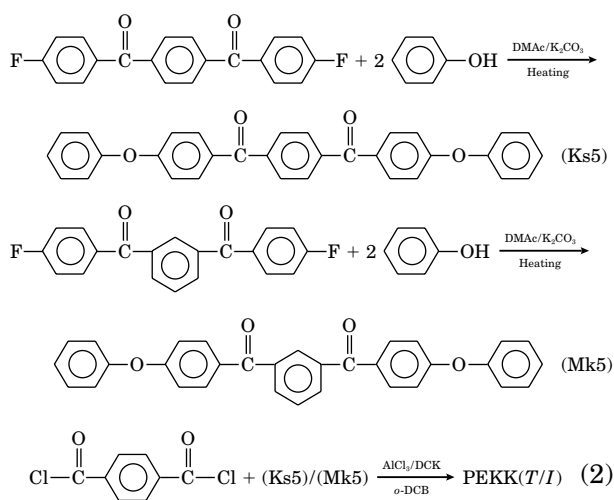
In this NE_3 route, when KS_5 and TPC are taken, the obtained polymers are defined as all *para*-PEKK, while MK_5 and IPC, as *meta*-PEKK (or PEKmK), and KS_5 with IPC resulted in the copolymer PEKK (or PEKK T/I). In the reaction, complex solvents of both 1,2-dichloroethane (DPE) and *o*-dichlorobenzene (*o*-DCB) are taken to improve the solubility of the formed oligomers in the reaction.

N Route

This route depends greatly on the monomer called 4,4′-di(*para*-hydrobenzoyl)benzene (orDP-HBB), the preparation of which is shown in the following [see eq. (3) where A is 4,4-di(*para*-florine benzoyl)benzene or DPFBB]

CHARACTERIZATION

IR, DSC, TGA, Viscosity, and NMR

An infrared spectrum (IR) was run on a Mateson FTIR equipment, scanning from 4000 to 400 cm^{-1} with transmittance from 20 to 100% and a resolution of 4 cm^{-1} or so. Samples were compressed with KBr powder with a film thickness from 1 to 2 mm.

Differential scanning calorimetry (DSC) was run on both DuPont-910 equipment under the TA-2000 system and the Perkin-Elmer Delta Series DSC-7 system. Scanning ranges were from 50 to 460°C with a N_2 gas flow. Sample weight was 6.8–10.0 mg obtained in the optical balance (exactly 0.0001 g).

Thermogravimetry analysis (TGA) was made on a PE TGA-7 system with a scanning rate of 10°C/min from 50 to 600°C under a N_2 gas flow and a sample weight from 5.0 mg to 10.0 mg. All the samples' viscosity was measured at 25°C on Ulman viscosity meter with a sample concentration of 0.1 g per 100 mL concentrated H_2SO_4 (96%).

Nuclear magnetic resonance (NMR) was run on both a Varian Unity-400 and FT-80A. The sample's ^{13}C-NMR spectra on the Unity-400 NMR equipment were obtained with an acquisition time (AT) from 0.3 to 0.5 s, pulse delay (PD) from 0.3 to 2.0 s, amount of transient time (NT) from 500 to 25,000, and pulse angle (PA) of 45°, while in the measurement by FT-80A, AT was from 0.5 to 1.0 s, PD from 0.3 to 2.0 s, and NT from 1500 to 70,000 and PA was 45°. Samples were solved in DMSO-d_6, CDCl$_3$ mixed with DMSO-d_6, or H_2SO_4 (96%). When the samples were solved in H_2SO_4 (96%), 1,4-dioxyhexalring ($C_4H_8O_2$) was added as an internal reference to the chemical shifts. The samples all have concentrations of 5.0% or so.

Quantum mechanical calculation (QMC)

Ab initio calculation of the molecular structure and Mulliken charges of diphenyl sulfone (DPS)

(3)
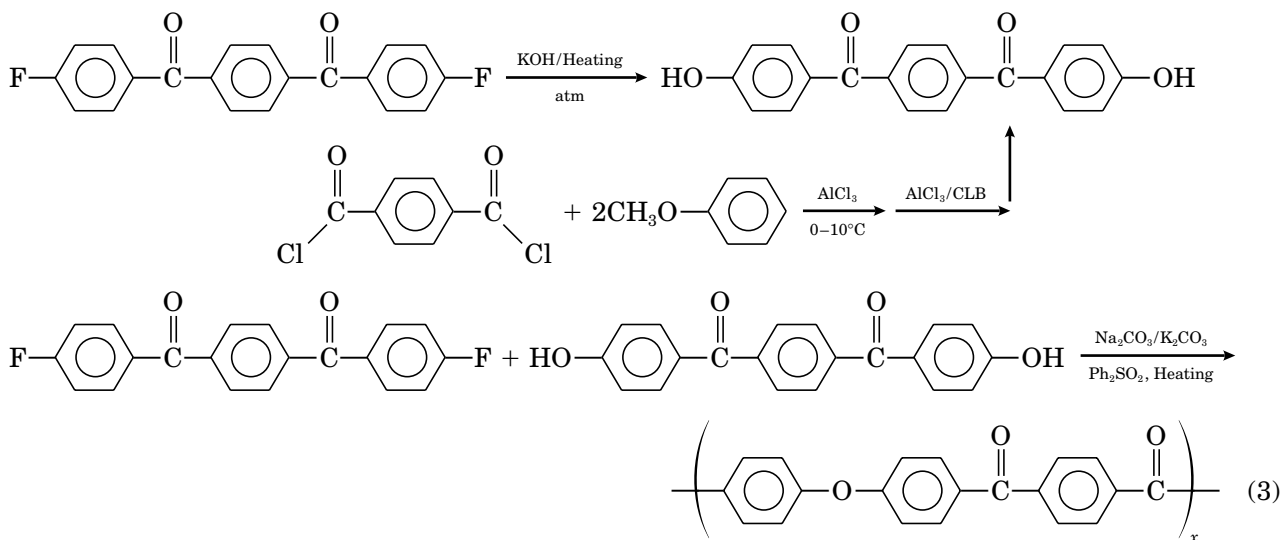
and CH_3NO_2 were made on the Cray S-MP II computer. The program adopted was the ab initio 3-21 G basis set in GAUSSIAN 94.[21] The convergency standard of energy for these molecules is 10^{-7} (for DPS) to 10^{-8} (for CH_3NO_2).

Mechanical Properties

The tensile strength for PEKK samples was measured on a DL-1000 electronic tensile strength machine with a tensile rate from 5 to 50 mm/min, following the national standard of China (GB 1039-70 and GB 1040-70), which is similar to the international ASTM standard.

Element Analysis

Analysis of the elements of C, H, and F was run on the PE-240 with a N_2 gas flow at 1000°C or so.

RESULTS AND DISCUSSION

Electrophilic Substitution Reaction

The molecular structure of monomers and polymers is shown in Figure 1. The physical properties of the polymers and oligomers prepared from route E1 are shown in Figure 2(a) and (b).

Figure 2(a) shows that polymers of PEKK from E1 have a heat of fusion (ΔH) ranging from 40 to 60 J g^{-1} [see the experimental points for $X_n > 30$ in Fig. 2(b)]. It is shown that the oligomers have a much higher ΔH than that of

the polymers. The sharper change of ΔH occurs when the polymerization degree (X_n) reaches 10 ($X_n = 10$). The obtained oligomers have a greater dispersion degree than that of the polymers, which is shown in Figure 2(b), in which-
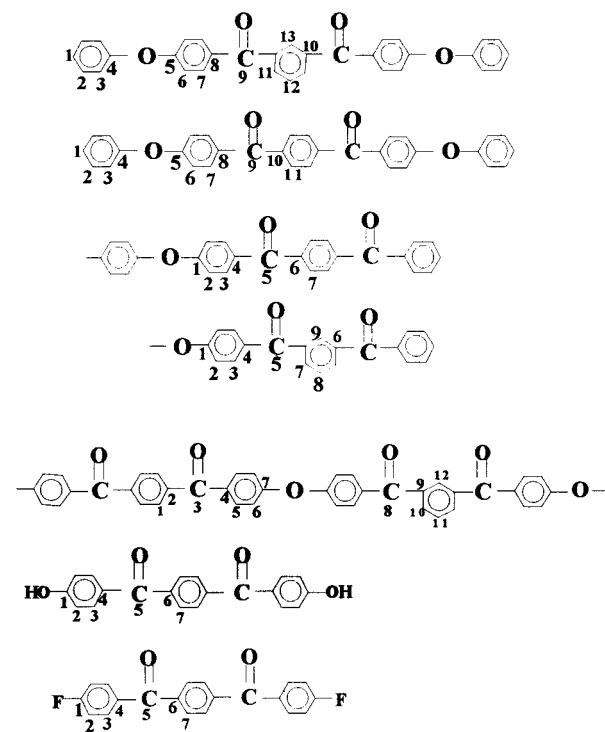

Figure 1 Molecular structure for the PEKKs' polymer system and their monomers.
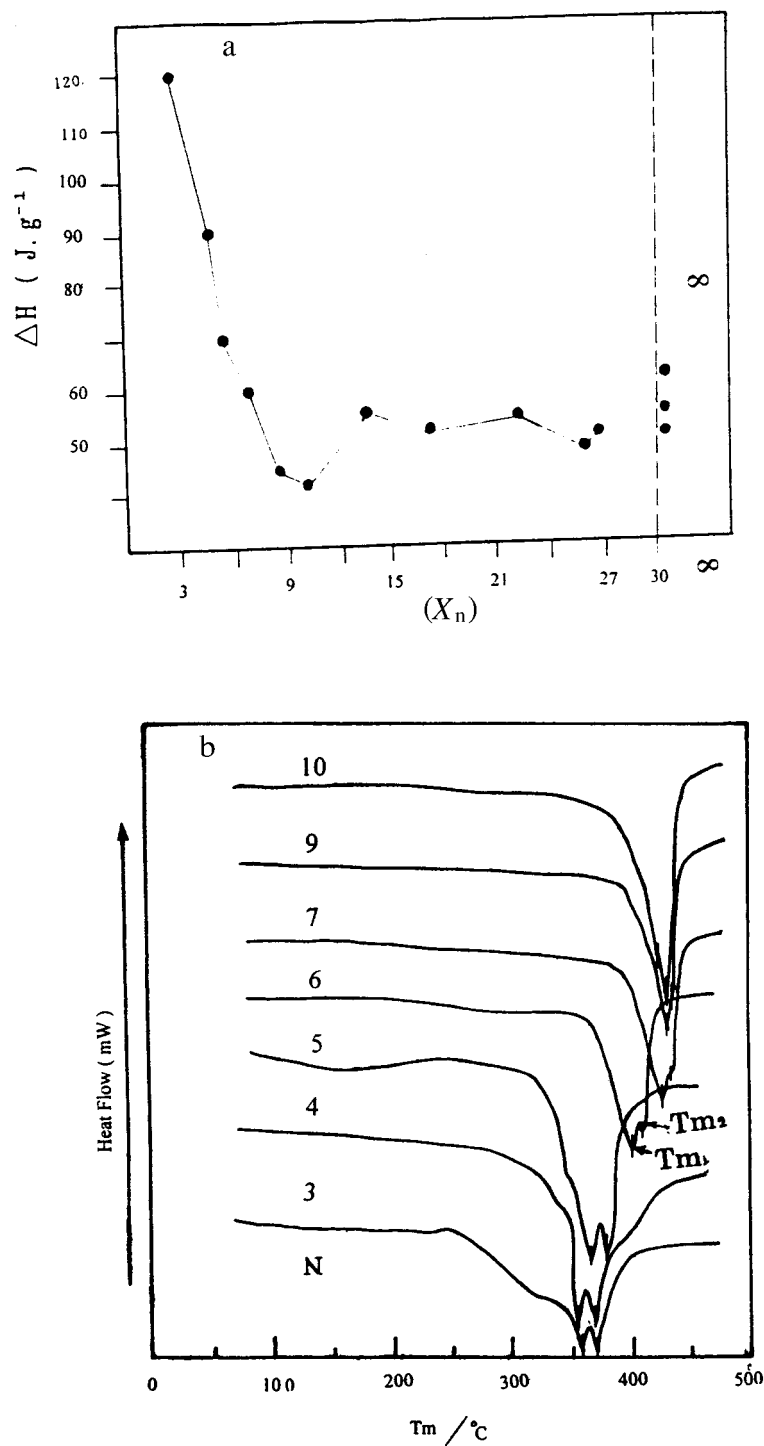
Figure 2 (a) Relationship between polymerization degree (X_n) and the heat of fusion for PEKK oligomers and polymers; (b) DSC scanning results of as-polymerized PEKK oligomers with different polymerization degrees (X_n).

two melting points (T_{m_1} and T_{m_2}) are characterized by the mixed melting behavior of the dispersion crystals including polymorphism. When the polymerization degree of X_n reaches 10, the multiple melt peaks begin to merge into one, while the oligomer's heat of fusion shows a slight

change. Thus, the oligomer with an X_n of 10 is thought to be a prepolymer and was chosen to prepare the polymers by the extrusion methods (see route E1). According to the statistical law of $X_n = (1 + r)/(1 - r)$ (X_n is the number-average polymerization degree; and r, the molar ratio of N_A to N_B in the reaction of A—A + B—B. The number-average molecular weight of the polymers are $M_n = X_n (M_r)/2$, and M_r, the molecular weight of the repeat unit for PEKK (M_r = 300.1 for PEKK). Based on the previous work, the concentrated H_2SO_4 (96–98%) was often taken to serve as the solvent for measuring the inherent viscosity of the PEKK family. The empirical formulas of $\eta = C (M_w)^n$ is adopted to describe the relationship between the average molecular weight and the viscosity. η is the inherent viscosity for samples in H_2SO_4, and the constants of C and n are decided by experiments with a C of 6.481×10^{-5} and n of 0.94 obtained from the extrapolation method.[22] Then, the polymerization dispersion degree of α is decided by the ratio of M_w/M_n, where M_n is the number-average molecular weight, and M_w, the weight-average molecular weight.

In the E1 and/or E2 reactions, the ratio of r is an important factor in controlling the molecular weight. Only when r reaches 1 can the maximum inherent viscosity of the samples be reached, e.g., η up to 0.97 with $r = 1$, but η does not surpass 1.20 for PEKKs in practice. Despite the above limitation, the reaction route E_1 has great advantages, such as easy control, high productivity (over 90%), and high melting point ($T_m > 390°C$). This high melting point of PEKK partly results from the introduction of more ketone groups into its molecular main chains. However, another reason is that the polymers obtained with different end groups may be crosslinked (see later discussions). The high melting point of PEKK from E_1 also has made its processing temperature very high (over 430°C). The gelation content (from crosslinking) in the reaction E_1 was usually one of the major factors controlling the polymer's melting points. When the gelation content is over 4%, the polymer PEKK will have quite a different melting point. This disadvantage can partly be overcome by using an additive of CH_3NO_2 with DCE. The CH_3NO_2 can improve the obtained oligomers' solubility and slow down the reaction rate. Based on the ab initio calculation of CH_3NO_2 (see its structure and charges in Table II), the

mechanism for CH_3NO_2 to improve the PEKK preparation reaction is shown below:
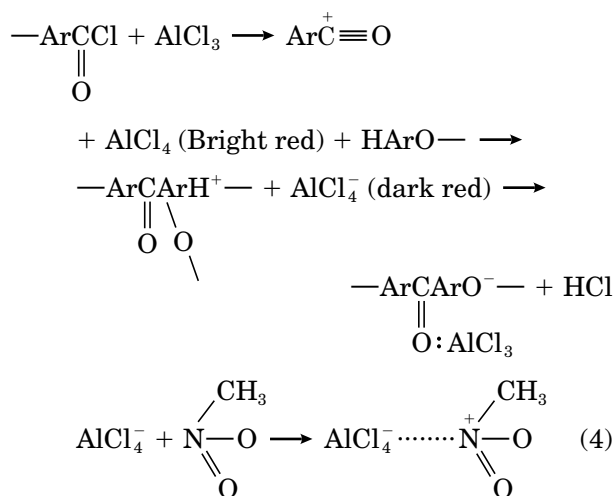
From formula (4), the formation of the complex compound of CH_3NO_2 with $AlCl_4^-$ improves the molecular weight and performance of polymers formed and also slows down the reaction rate of DPE with TPC. For a similar reaction mechanism for CH_3NO_2, DMF is also used to control the reaction rate. The selection of CH_3NO_2 and $HCO(CH_3)_2$ as additive solvents is quite successful and practical.

The relationship of T_m with X_n for the obtained PEKK polymers shows that the T_m of PEKK increases to 407°C when X_n is greater than 6 and less than 10. Thus, it is believed that in this range for $6 < X_n < 10$ polymers are obtained of lower molecular weight with an end group of —COCl (1721 cm^{-1} in the vibration peak of the IR). When X_n is greater than 10, the obtained polymers with an end group of —COCl have properties close to the polymers with high tensile strength. When the above polymers were treated with methanol, water, and alkali, the end groups became —COOH [3344 and 1721 cm^{-1} shown in the IR spectra of Fig. 3(a)]. This end group transition probably causes the different melting points of PEKK.

To gain high molecular weight PEKK, the molar ratio of $ALCl_3$ to the ketone group, the solid content, and even the purity of monomers also have obvious influence on the polymer molecular weight, which will be discussed later.

Seen in Table I, the *meta*-phenyl links are introduced into all *para*-phenyl PEKK by isophthaloyl chloride (IPC). It is seen that through the copolymerization of TPC/IPC monomers PEKK
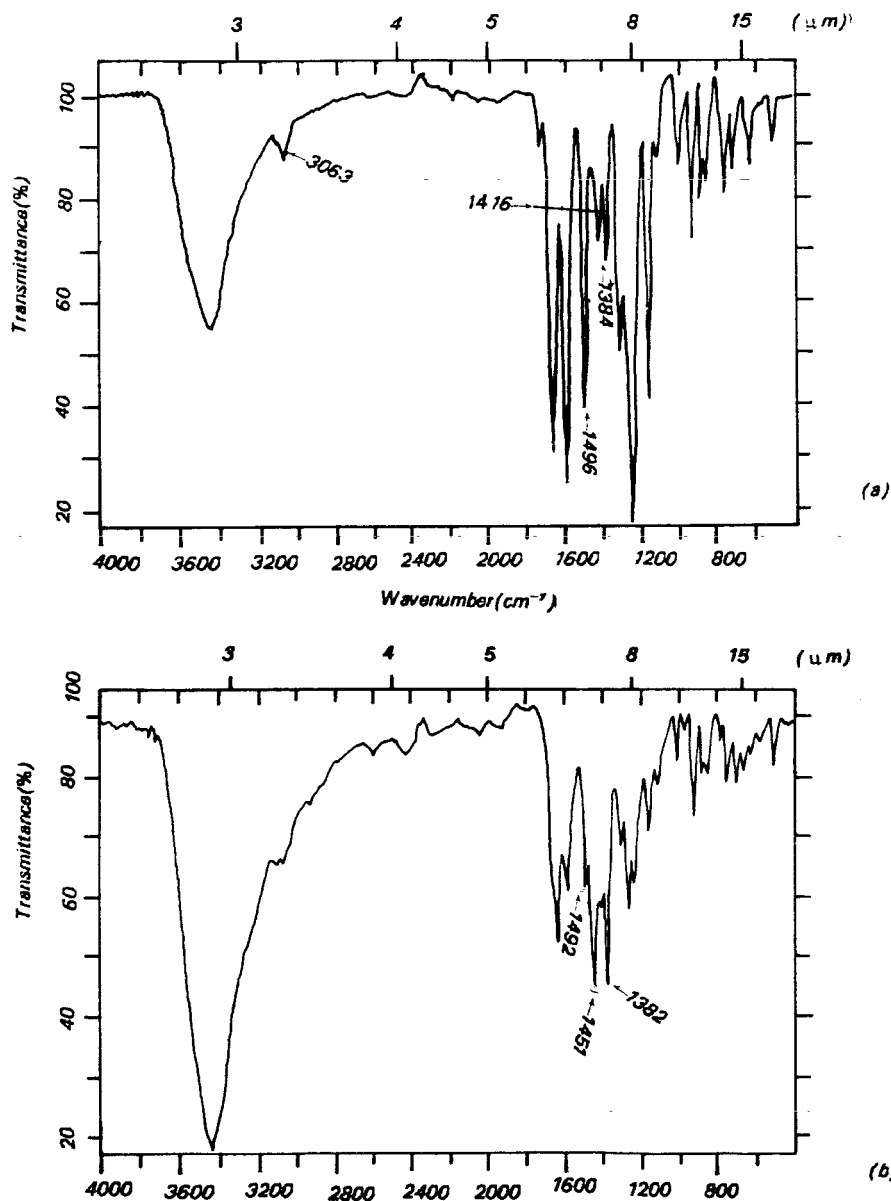
Figure 3 (a) IR spectra of PEKK (T/I = 30/70) from route E following the treatment with hydration and (b) PEKK from route N without hydration.

composite properties, especially their processing properties, can be enhanced. The melting point of PEKK decreased with the introduction of the IPC segment, which has made it easier to process (processing temperature from 350 to 400°C), meanwhile keeping the higher degradation temperature (>520°C at a weight loss of 5%). Table I shows that the obtained polymers usually have higher solubility in DMF. However, the very important phenomenon is that the above copolymer system appears to have the lowest melting point

(T/I = 30/70), which is clearly shown in Table I. It is shown that the lowest melting point is 252°C at a T/I of 30/70, while the glassy transition of the T_g has a straight-line relation with $T/(T + I)$. This kind of phenomenon is also observed in other copolymer systems. In the copolymer system of PEEKK–PEBEKK (where B is the biphenyl group), the lowest mp is 313°C,[24] compared with an mp of 363°C for the homopolymer of PEEKK and 419°C for PEBEKK. Also, the lowest melting point is 289°C for the copolymer system of PEEK–

Table I Physical Properties of PEKK with Different Compositions of TPC/IPC by E1 and/or E2 Routes

T/I	T_m (°C)	T_{d1} (°C)	T_{d2} (°C)	DMF/KT	T (h)	η_{iv} (mL/g)	Yield (%)
100/0	385	415	511	2–4	24	0.82	99
80/20	366	466	525	2–4	24	0.79	94
75/25	356	415	490	2–4	28	0.80	92
64/36	326	445	505	2–4	28	—	90
50/50	330	—	—	2–4	24	0.91	91
30/70	252	419	487	2–4	28	—	90
0/100	285	459	487	2–4	28	0.69	98

T_{d1} and T_{d2}, temperatures at sample weight loss of 2.5 and 5.0%, respectively. DMF/KT, molar ratio of DMF to ketone group. η_{iv}, the viscosity measured in H_2SO_4 (96%) at 25°C.[4]

PEBEK,[23] compared with the mp of 334°C of PEEK and 409°C of PEBEK.[23] The reason for this is that the *meta*-phenyl links have introduced asymmetrical factors and produced incomplete crystallites in the polymer crystals. Thus, the entropy of the copolymers is increased with the relative content of *I* segments while the enthalpy of the copolymers is decreased with *I* segments in the PEKK (*T/I*) systems, which leads to the reduction of the melting point of these copolymer systems. Based on the above results, it is thought that the copolymers obtained have a more at- tracting processing temperature while keeping the required glassy transition. Thus, how to con- trol the *T/I* ratio in the copolymer system is surely important. The IR spectra of PEKK (*T/I*) copoly- mers in Table I are similar; the 1645–1658 cm^{-1} for the vibration of the —CO group, the vibrations at both 1409–1417 cm^{-1}, and the 1485–1492 cm^{-1} are for the characterization of the relevant content of *para*-links to *meta*-links in the molecu- lar main chains. The transmittance at these two peaks (belts) are expressed by the function of (1/ *I* 1492)/(1/*I* 1417) with *T*/(*T* + *I*) × 100% to show

Table II Mulliken Charges on Atoms of Both (DPS) and CH$_3$NO$_2$ by Ab Initio 3-21G

DPS				CH$_3$NO$_2$	
Atoms	Charges	Atoms	Charges	Atoms	Charges
C1	−0.559306	C11	−0.114970	O1	−0.349361
C2	−0.182246	C12	−0.235222	N2	0.223705
C3	−0.235545	C13	−0.264186	O3	−0.358909
C4	−0.229650	C14	−0.197394	C4	−0.342014
C5	−0.236792	C15	−0.225259		
C6	−0.162298	O8	−0.846555		
S7	1.429746	O9	−0.619194		
C10	0.203722				

The optimized structure parameters of DPS are (C—C)avg = 0.1395 nm, (C—S) = 0.1784 nm, (C—H)avg = 0.1075 nm, (O═S) = 0.1443 nm, ∠(CCS) = 118.3°, ∠CSC = 102.7°, ∠OSO = 118.5° ∠(CCC)avg = 120.0°, (HCC)avg = 120.0°, and E(HF) = −1001.19616096 (au) on the C1 symmetry by ab initio 3-21G, and of CH$_3$NO$_2$, (C—N) = 0.1376 nm, (O—M) = 0.125 nm, (H—C) = 0.11 nm, ∠ONO = 120°, ∠HCN = 111.5°, and E(HF) = −242.1643942 (au), and the optimized structure symmetry is C1 by ab initio 3-21G.
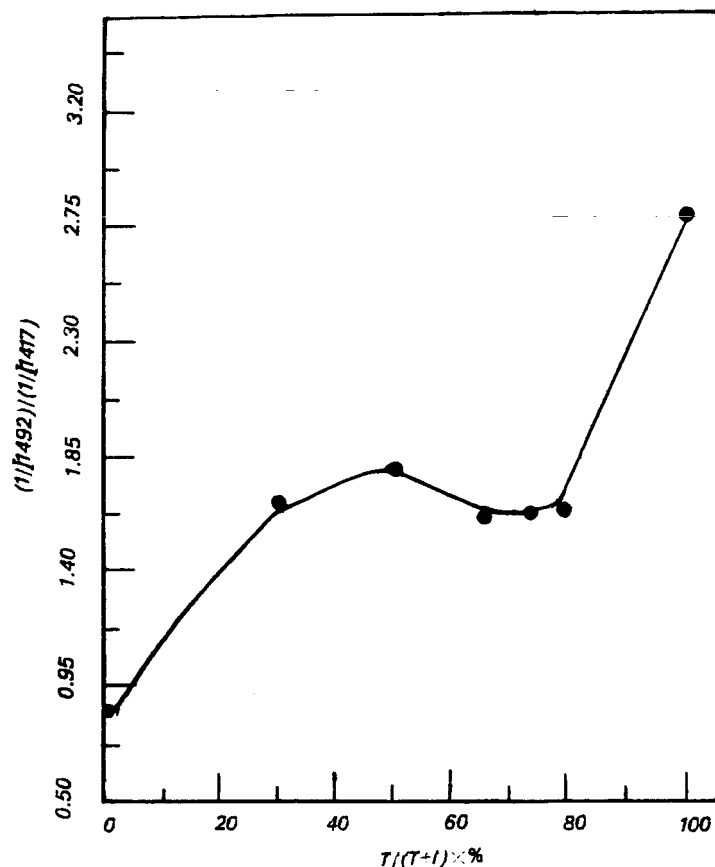
Figure 4 Plot from IR spectra to show the quantity relationship between the characteristic peaks' (I1492 and I1417) intensity with *para*-substituted (*T*) and/or *meta*-substituted (*I*) links in the molecular main chain.

the relative content of *para*- or *meta*-links. This function is plotted in Figure 4, which strongly shows that the relative intensity at the 1492 cm^{-1} peak is increased with the *T* content, while a higher content of IPC (*I*) will produce the complicated spectra and the spectra's splitting of PEKKs.

The linearity relationship for the PEKK system will be reduced when the IPC segment is introduced into the molecular chain. The complicated peak patterns appear in the characteristic zone (1416–1496 cm^{-1}). The peak at 1400 cm^{-1} has been split into two peaks (1384 and 1416 cm^{-1}) due to the introduction of the IPC segment. It is also seen that partially alkylated products have probably formed because of the solvents of DCE reacting on the polymer (see peak at 3063 cm^{-1} for the —CH$_2$— group). This side reaction can also be partially controlled by using the complex solvents of DMF/DCE. This results from the fact that the formed AlCl4$^-$ ions have produced a com-

plex which will reduce the activation of the catalyst; its mechanism was discussed above. Although the obtained polymers with *T*/*I* segments have produced more side reactions, the polymers have satisfactory and practical properties.

Molecular Structure

The ^{13}C-NMR results of the obtained PEKK polymers are listed in Table III. The monomers of KS$_5$ and MK$_5$ are synthesized in the route of NE$_3$. Their NMR chemical shifts are also listed in Table III. The spectra of MK$_5$ and KS$_5$ are shown in Figure 5(a) and (b). Table III shows that the samples in concentrated H$_2$SO$_4$ have chemical shifts much greater than those in DMSO-d_6 or DMSO-d_6 with CDCl$_3$. Especially, for the ketone group (e.g., C$_5$ in DPFBB or C$_9$ in MK$_5$), they have their chemical shifts 6–14 ppm in H$_2$SO$_4$ greater than those in DMSO-d_6 or CDCl$_3$ plus DMSO-d_6, while the carbons connected with the ketone

Table III ^{13}C-NMR Chemical Shift of Monomers and Polymers of PEKK in Solvents of DMSO-d_6, CDCL$_3$ + DMSO-d_6, and H$_2$SO$_4$

Molecules	Atoms	Chemical Shift (ppm)	Atoms	Chemical Shift (ppm)	Atoms	Chemical Shift (ppm)
DPFBB	C1	164.6 (173.9)	C4	113.0 (126.8)	C6	139.5 (138.0)
	C2	114.4 (119.6)	C5	192.8 (206.9)	C7	128.2 (134.1)
	C3	131.5 (142.0)				
KS5	C1	125.1 (133.0)	C5	162.9 (170.9)	C9	195.5 (201.4)
	C2	129.8 (129.8)	C6	117.7 (119.6)	C10	141.6 (136.5)
	C3	120.5 (121.7)	C7	132.9 (141.8)	C11	130.5 (132.7)
	C4	156.4 (157.6)	C8	132.1 (123.4)		
MK5	C1	124.9 (134.3)	C6	117.1 (119.7)	C10	137.4 (141.4)
	C2	130.4 (129.9)	C7	132.5 (141.1)	C11	131.0 (132.1)
	C3	120.1 (122.0)	C8	132.9 (124.3)	C12	129.3 (130.8)
	C4	154.9 (157.9)	C9	193.7 (201.9)	C13	130.3 (136.9)
	C5	161.3 (170.3)				
PEKK	C1	167.7	C4	126.3	C6	137.6
	C2	121.6	C5	205.0	C7	141.3
	C3	133.4				
PEKK	C1	140.6	C5	138.2	C9	140.9
	C2	121.7	C6	127.1	C10	133.8
T/I = 50/50	C3	204.9	C7	167.4	C11	133.5
	C4	140.9	C8	204.7	C12	138.2

Values in parentheses were measured in H$_2$SO$_4$. The spectra of PEKK and PEKK (*T/I* 50/50) were measured in H$_2$SO$_4$, while the spectra of KS$_5$ and MK$_5$, were measured in both H$_2$SO$_4$ and DMSO-d_6 and/or DMSO-d_6 plus CDCL$_3$.

group (e.g., C$_4$ in DPFBB or C$_8$ in MK$_5$) have their chemical shifts 6–9 ppm in H$_2$SO$_4$ smaller than those in DMSO-d_6 or CDCl$_3$ plus DMSO-d_6 (see values in Table III). These variations can be used to explain the high chemical shifts of 204–205 ppm of the polymer PEKKs shown in Figure 5(a) and (b). The reasons for this above phenomenon was explained in Ref. 30 as the molecular polarization by a polarized solvent (e.g., H$_2$SO$_4$). The molecular chain polarization of PEKKs is shown in Figure 6 by the UV spectra. The wavenumber shifts from 304 nm in Figure 6(a) for the samples

in CDCl$_3$ to 419 nm in Figure 6(b) for samples in H$_2$SO$_4$ are obvious. The NMR spectra of all *meta* (*I*)-links PEKK or PEKmK are indexed according to the polarization mechanism as above, which is shown in Figure 7, where the characteristic carbons of C6, C7, C8, and C9 are also shown.

In the synthesis of PEKK through the route of NE$_3$, the complex solvents of both DCE and *o*-dichlorobenzene are used with a solid concentration the same as in E$_1$ and/or E$_2$. However, in route NE$_3$, the molar ratio of AlCl$_3$ to the ketone group of the monomers is quite different from
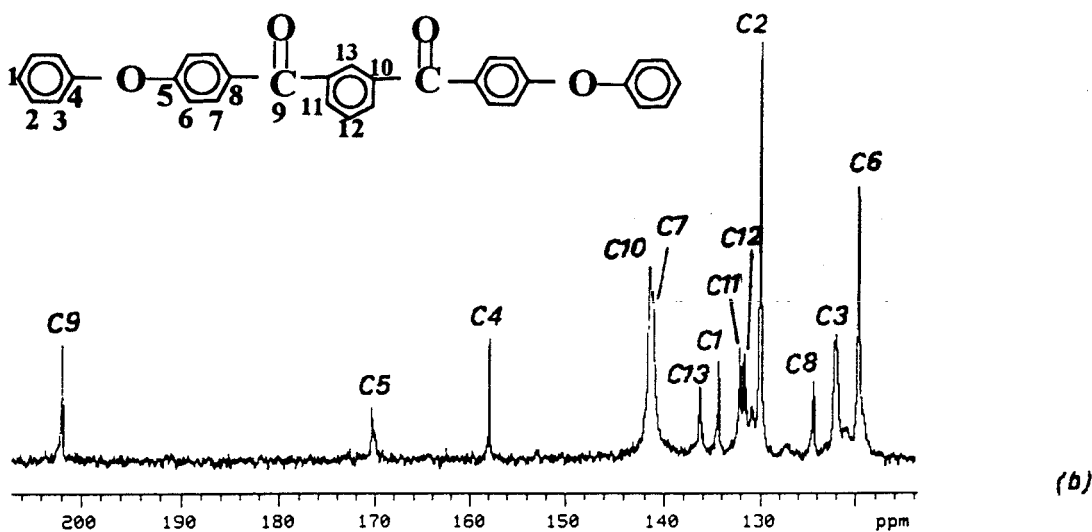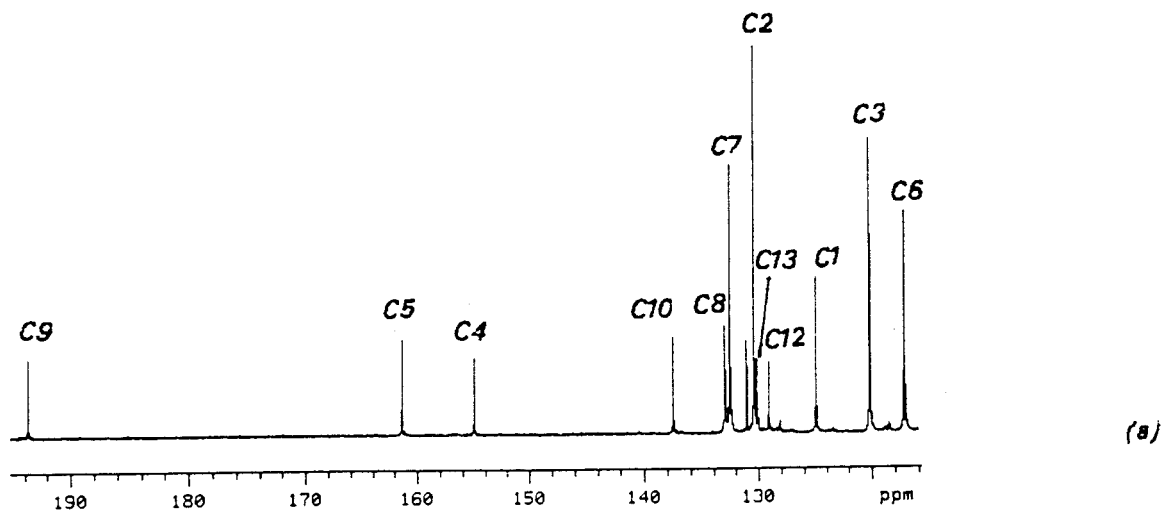
Figure 5 The ^{13}C-NMR spectra of MK$_5$ in solvents of (a) DMSO-d_6 and (b) H$_2$SO$_4$ by a Varian-400NMR to show the polarization of molecular chains.

those in routes E$_1$ and E$_2$. This mainly resulted from the fact that the monomers of MK$_5$ and KS$_5$ themselves have ketone groups, which will react with AlCl$_3$ and consume it. Thus, the molar content of AlCl$_3$ should be very overestimated. In route NE$_3$, the molar ratio of AlCl$_3$ to ketone is 5/1 or so. Here, so much AlCl$_3$ used will affect the posttreatment process, and also the polymer's properties. Even so, this route has presented high-

quality samples of PEKK with a gel content less than 2%. Also, the linearity of the obtained PEKK samples is quite good.

The Nucleophilic Substitution Reaction

The practices above strongly show that the reactions for preparing PEKK samples by the E route are easy to run or control. The productivity of
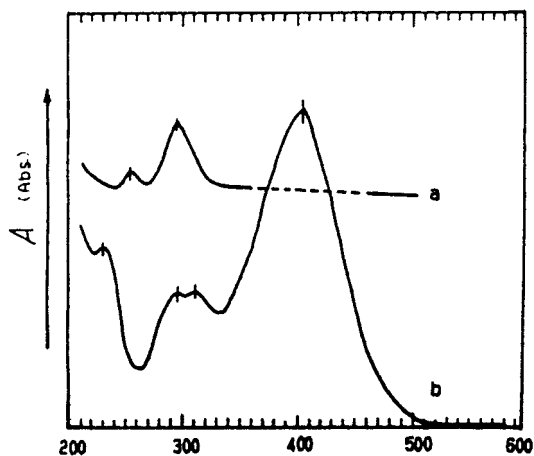
Figure 6 UV spectra for oligomer MK$_5$ in solvent of (a) CHCl$_3$ and (b) in H$_2$SO$_4$ to show the wavenumber red shift and molecular polarization.

these reactions is usually very high (>90%). However, the usual polymers of very high molecular weight are required to obtain practical mechanical properties, which will require further improvement of the synthesis practices as mentioned above. The proper choice is the nucleophilic substitution route which has adopted nearly the same process as that in PEEK and PEEKK.[1–14] In our attempts to try route N, very successful results have been shown in the later part. In route N, the monomer B (DPHBB) is the key factor; DPHBB can be obtained from DPFBB in route NE$_3$ by the hydration process or directly from TPC (see route N in the article). However, the catalysts of K$_2$CO$_3$ and Na$_2$CO$_3$ have different effects

on the polymers' properties of PEKK. When only K$_2$CO$_3$ is adopted, the polymers obtained do not have satisfactory mechanical properties (tensile strength and elongation rate). When the catalyst system of 50% K$_2$CO$_3$ + 50% Na$_2$CO$_3$ is used, the polymer mechanical properties are somewhat enhanced. But when the catalyst system becomes 10% K$_2$CO$_3$ + 90% Na$_2$CO$_3$, the complex properties of the obtained polymers are enhanced significantly ($\eta \geq 1.10$, $\sigma_B \geq 100$ MPa). Route N strongly shows that the nucleophilic substitution route may be one of the most practical ways to prepare the PEKK polymer system. The IR spectra of the homopolymer PEKK from route N is shown in Figure 3(b), which also shows that some branching side reaction occurs [see the wavenumbers from 1409 to 1500 cm^{-1} in Fig. 3(b)].

Via route N, the copolymers of PEKK–PEEKK can be properly obtained by the polycondensation of DPFBB with different ratios of hydroquinone to DPHBB, together with the solvent of Ph$_2$SO$_2$ (DPS). This copolymerization obviously improves the polymers' complex properties, especially the lowered processing temperature, the reason of which is supposed to be the reduction of the endotherm and the increase of the exotherm for the copolymer molecular chains, which lead to the lower melting point of the obtained copolymer systems. The obtained PEKK–PEEKK copolymers and their properties are shown in Table IV.

It is thought that DPS plays a role not only in the solvent, but also in the catalyst as well in the mixed catalyst system of Na$_2$CO$_3$ with K$_2$CO$_3$. The mechanism for this will be discussed here based
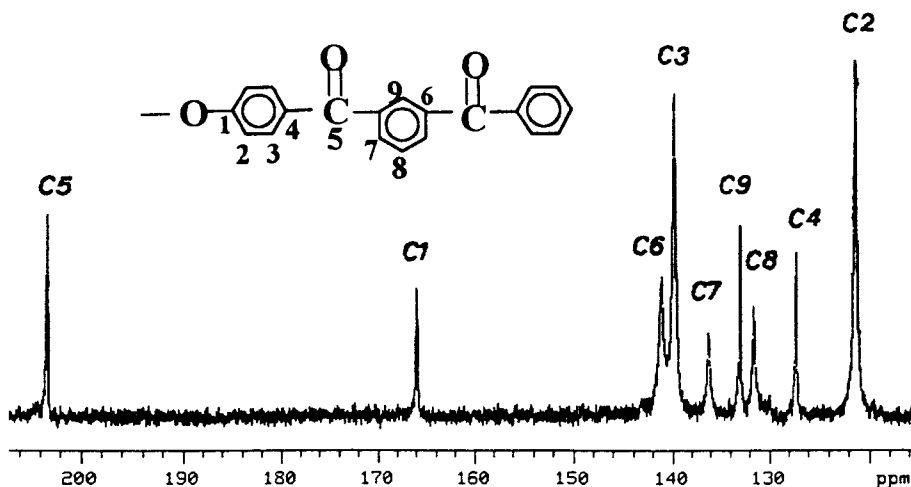

Figure 7 ^{13}C-NMR spectra for polymer PEKmK in H$_2$SO$_4$-d_2.

Table IV   Physical Properties of PEKK–PEEKK Copolymers

Sample	DPFBB (mol)	DPHBB (mol)	Hq (mol)	η_{iv} (mL/g)	T_m (°C)	T_g (°C)	σ_t (MPa)
EKK20	0.10	0.02	0.08	1.14	340	154	103.4
EKK30	0.10	0.03	0.07	0.79	354	157	76.0
EKK40	0.10	0.04	0.06	0.69	350	—	56.0
EKK50	0.10	0.05	0.05	0.66	368	—	Brittle

η_{iv} was measured in H_2SO_4 (96%) at 25°C.

on the structure and Mulliken charges of DPS (see Table III). The mechanism for the catalyze of DPS on the PEKK polymerization reaction is shown below:

(5)
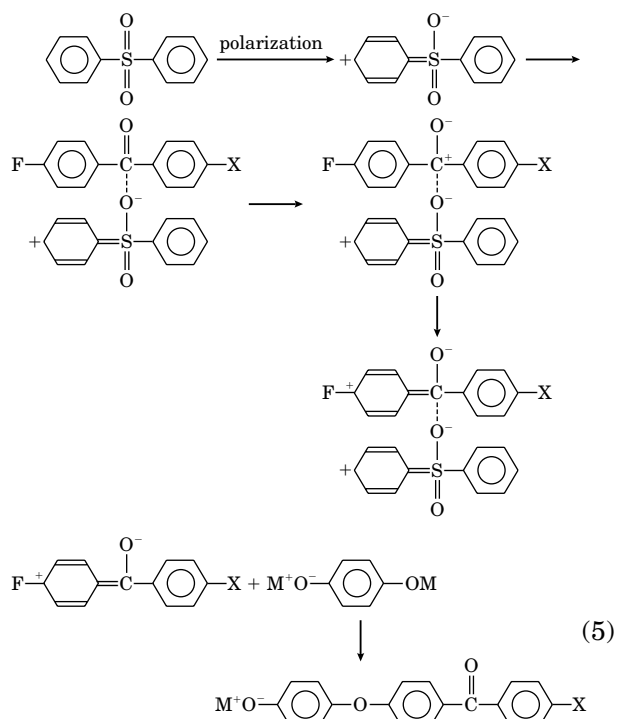
In the monomer molecules with the floro-ended group, the electronic charges turn to accumulate on their carbonyl groups. Due to the charge movement on the atoms of DPS, it is clearly shown that the positive charges strongly accumulate on the atoms of sulfur in DPS, while the negative charges, on the oxygens in DPS. It is very easy to realize the following polarization:
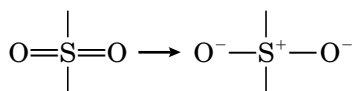
From the mechanism in formulas (5), it is believed that the floro-ended monomers are first activated by the activated DPS; then, the salt of hydroquinone reacts with these activated monomers in the prepolymerization stage. These mechanisms demonstrate that the temperature controlling the polymerization step is vital. Generally, the temperature in the prepolymerization step is controlled at lower than 300°C for PEKK, which will let the formation of salts of hydroquinone be complete. The side reaction product of water is preferred to be got rid of, but if the gas flow of nitrogen is controlled properly, the water can be let off as much as possible. Then, the polymer of high molecular weight is usually obtained. PEKK prepared from the N route usually has a very high molecular weight or inherent viscosity. Thus, their overall properties including both thermal and mechanical aspects are enhanced significantly compared with PEKK from other routes. Figure 8 shows the WAXD patterns of PEKK(N) amorphous samples treated at 180°C
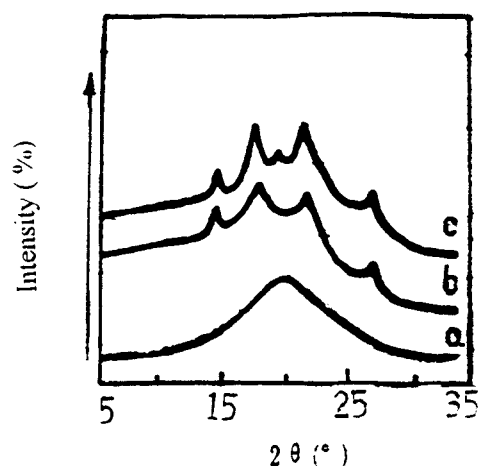

Figure 8 WAXD patterns of PEKK(N) crystallized at 180°C for different times from the glassy state: (a) 180°C, 5 min; (b) 180°C, 15 min; (c) 180°C, 160 min.
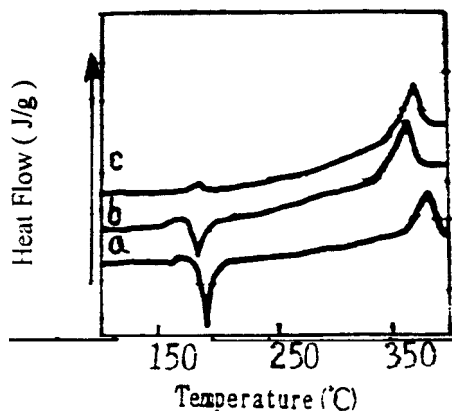
Figure 9 DSC scanning results of PEKK(N) crystallized from the glassy state (a) at 180°C for 5 min, (b) at 180°C for 15 min, and (c) at 180°C for 160 min.

for 5, 15, and 160 min, the DSC results of which are shown in Figure 9. Due to very high molecular weight of PEKK(N), the molecular chain movement has difficulty in responding to the heat impact, e.g., at 5 min, the samples seem to be still amorphous. When the annealing time is longer, e.g., 15 or 160 min, the WAXD patterns have peaks appearing at 15° of the 2θ position, which has been defined as crystal form II in the literature.[26,27,29] This literature reports form II by using samples from the electrophilic route (E_1 or E_2), while PEKK from the nucleophilic route (N) has appeared with different results (see Figs. 8 and 9).

Figure 10 shows that PEKK(N) crystallized at a lower temperature from the melt appears a bit as form II. When the temperature increases, form II changed gradually into form I, which dominates at temperatures above 250°C. When PEKK(N) was crystallized from the glassy state, form II accounts for a great part of the overall crystallites (see Fig. 11). When the temperature increases, form II dominates at temperatures above 250°C until above 350°C, while the form I ($2\theta = 20.7°$) peak increases gradually. Evaluated from PEKK(N) samples crystallized from both the melt and glassy state, it is calculated that form II accounts for 0–20%. DSC patterns of PEKK from the N route shows that the polymorphism and/or the content of form II has an effect on the stable properties of the polymers.

The Relative Content of Crystal Form I and Form II

The crystal form II is less stable than is form I for the PEKK system which is shown in Figures

10 and 11 and also shown in the literature.[8,26,29] It is thought that the appearance of form II depends on the experiment and sample-treating conditions. PEKK as-polymerized samples from the E1 and E2 routes always produce form II crystals, the relative content of which is 5–30% expressed by the WAXD method. Form II often appears when the PEKK samples were crystallized from the glassy state, which is shown in Figure 12. Calculated from the WAXD patterns, form II accounts for 0–30% of the overall crystals of the PEKKs. It is seen from Figure 12 that the relative content of the T/I ratio in the molecular main chain decides the relative content of form II, e.g., when $T/I = 30/70$, form II disappears and its relative content is 0%. Taking all *para*-PEKK as an example (its WAXD patterns are shown in Fig. 13), the relative content of form II accounts for 10–30% when samples are crystallized from the glassy state. Judging from the DSC patterns of all *para*-PEKK, form II accounts for 10–30% under the designated treating conditions which are shown in Figure 14. The all-*para* PEKK has its
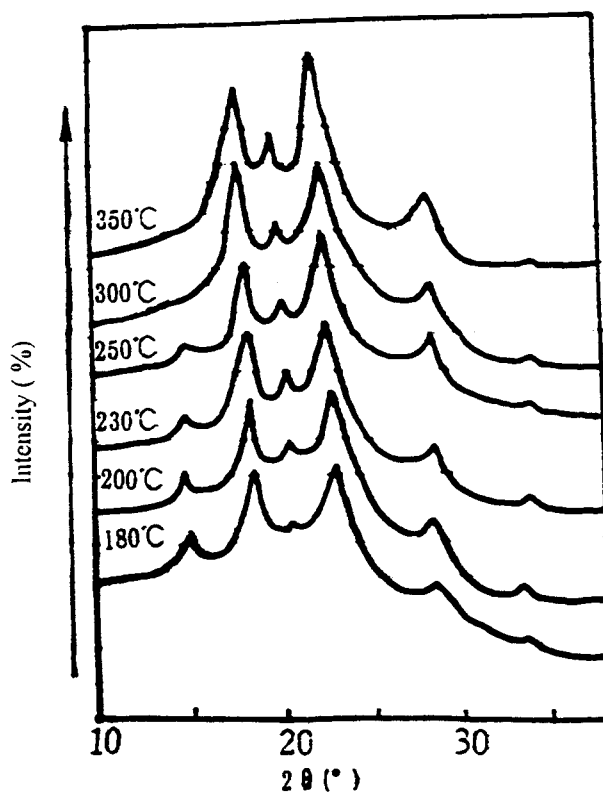

Figure 10 WAXD patterns of PEKK(N) crystallized at different temperatures for 30 min from the melt state.
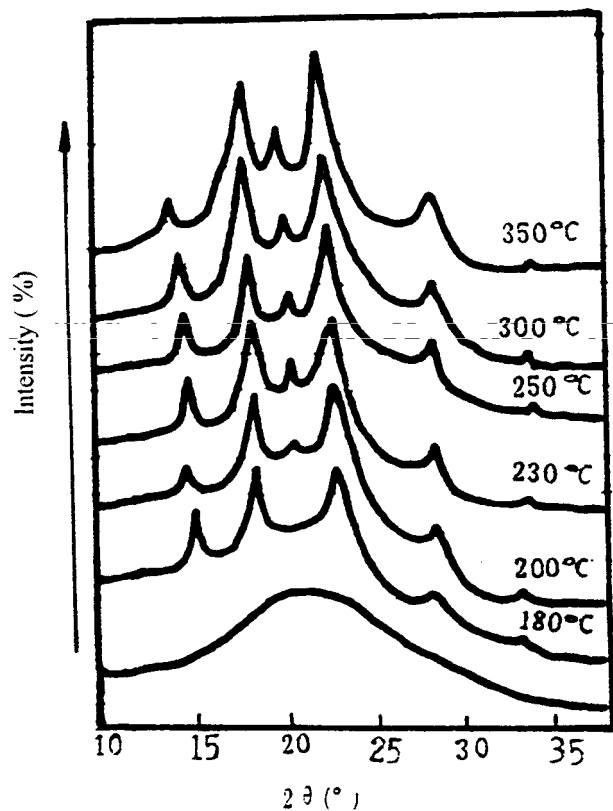
Figure 11 WAXD patterns of PEKK(N) crystallized at different temperatures for different times from the glassy state.

equilibrium melting point at 411°C, shown in Figure 15. When crystallized from the melt, the crystal form II does not appear until the crystallization at 180°C (see Fig. 13).

All the practices mentioned above have been compared; the polymers from different routes have their T_m and T_g decided by DSC via the extrapolation method. The values of thermal properties for PEKKs from both E and N routes together with the NE route are obtained in the range from 360 to 397°C (T_m) and from 167 to 176°C (T_g). The optimization reaction system for the preparation of PEKK polymers is listed in Table V.

These above results show that PEKK from different routes has different melting points and glassy transition temperatures. Also, these PEKKs have different degradation temperatures (say, at the weight loss of 5%), the result of which is shown in Figure 16. From the comparisons in Figure 16, it is seen that PEKK from route N has the highest degradation temperature with the highest molecular weight in PEKKs from the other preparation routes.

CONCLUSIONS

For different reasons of utilities, different routes for synthesizing PEKK are presented as above. It is concluded that the optimization reaction systems for PEKK are as such in Table V for both the nucleophilic (N) and electrophilic (E) substitution routes. The best solvent is $C_2H_4Cl_2$ and/or o-DCB for the E route, and the reaction time depends on the additives used (e.g., CH_3NO_2 or DMF), while DPS is the best solvent for PEKK preparation from the N route, and the best catalyst system is mixed Na_2CO_3 with K_2CO_3. The results obtained show that the N route is especially good for obtaining the homopolymer or copolymers of PEKK with very high molecular weight. Some of these samples have diffraction patterns similar to the literature reports,[26–29]
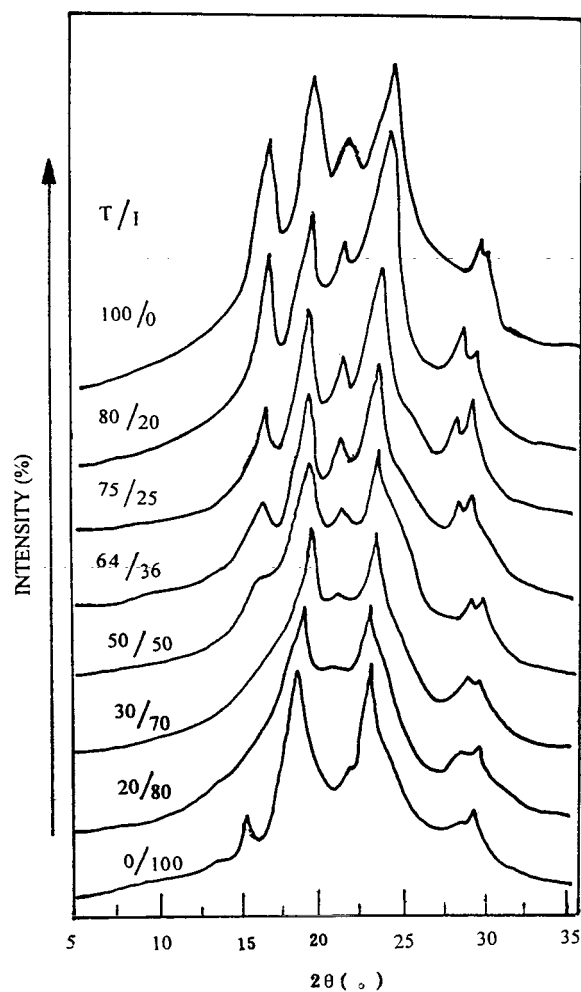

Figure 12 WAXD patterns of PEKK (T/I) copolymers crystallized at 230°C for 1.5 h from the glassy state.
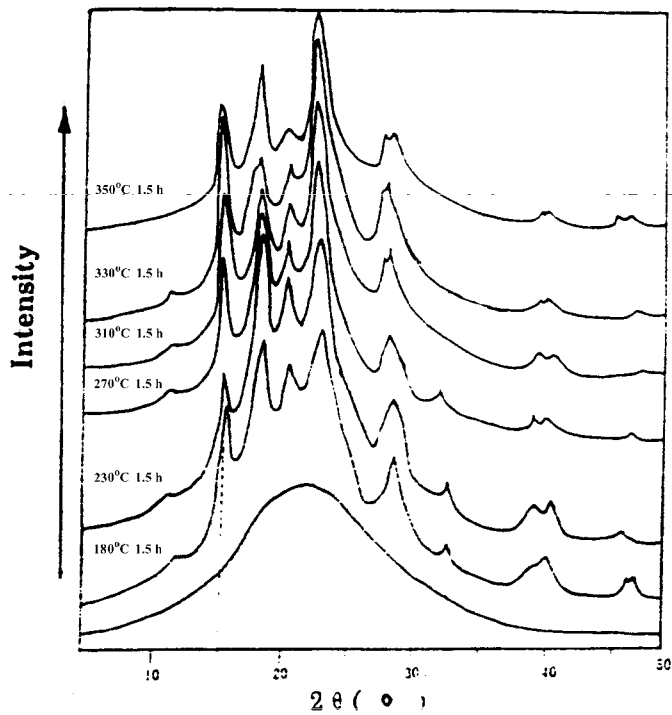
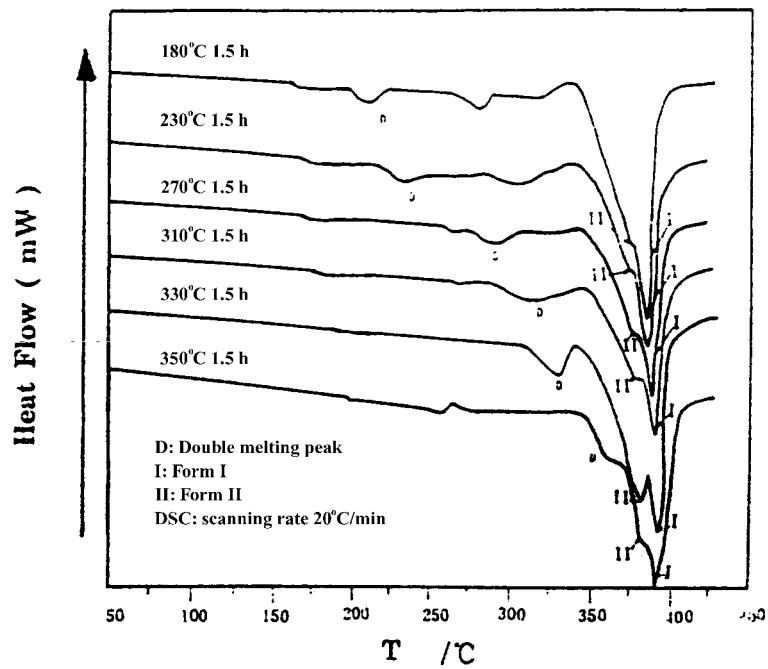**Figure 13** WAXD patterns of PEKK crystallized at different temperatures for 1.5 h from the glassy state.

Figure 14 DSC scanning of PEKK samples crystallized at different temperatures for 1.5 h from the glassy state.
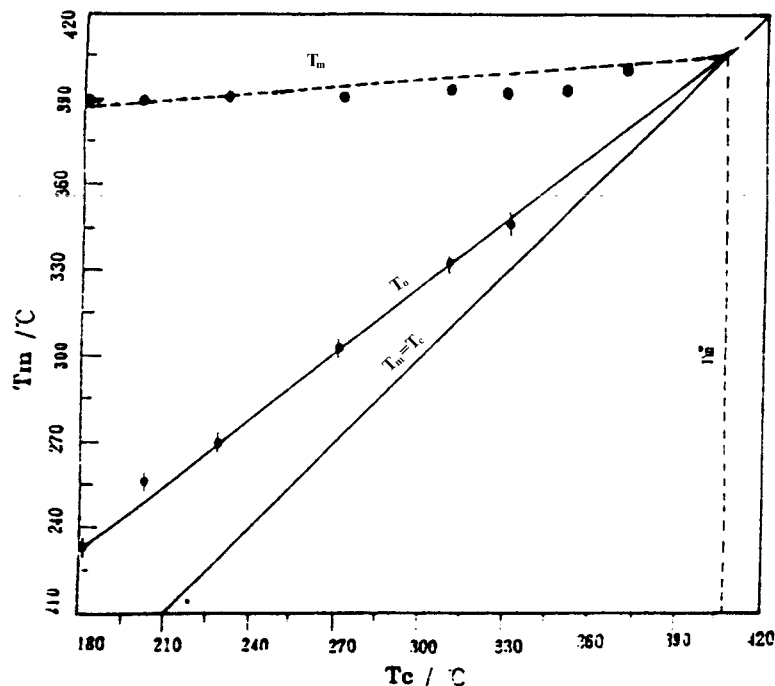
Figure 15 Plot of the melting point of PEKK system with the crystallization temperature, together with the Hoffman−Weeks plot to show the equilibrium melting point.

while some quite different diffraction patterns (polymorphism) are found in all these obtained samples. These will be further discussed elsewhere. Polymorphism often exists in the PEKK systems from both E and N. The appearance and the content of form II depends not only on the preparation route but also on the crystallization conditions as well. Polymorphism is a factor affecting the properties of the obtained polymers.

PREPARATION EXAMPLES

Polymer PEKK

DPFBB, 0.05 mol (16.12 g), and 95 g DPS were melted at 150°C, mixed with 0.05 mol (15.92 g)

DPHBB and 0.0505 mol (0.6969 g) K_2CO_3 with 0.04545 mol (4.8177 g) Na_2CO_3. The mixture was heated at 160°C for 1 h, 270–280°C for 2 h, and 340°C for 4 h. Then, the hot mixture was poured into pure cold water. The precipitate was crushed and washed with hot water for 2 h three times, then refluxed with fresh acetone.

Monomers of KS_5 and MK_5

A 500 mL three-necked flask was equipped with a mechanical stirrer, N2 gas inlet, thermometer, and glass trap for collecting water. Then, 0.10 mol (32.2 g) DPFBB, 0.20 mol (32.2 g) DFBB, 0.20 mol (18.80 g) phenol, 0.30 mol (41.1 g) dried K_2CO_3, 270 mL DMAc, and 60 mL toluene were added into

Table V Optimization Results of PEKK Synthesis by Different Routes

Route	t (h)	Catalyst	Solvent	AL/KT	Na/K	Solid (%)	CN/KT	DF/KT
E	≥ 8	$ALCL_3$	$C_2H_4Cl_2$ o-DCB	1.3–1.5	—	$20 \sim 30$	$2 \sim 4$	$2 \sim 4$
N	≤ 8	$NaCO_3$ K_2CO_3	DPS	—	9/1	$20 \sim 30$	—	—

t, reaction time (h); o-DCB, o-dichlorobenzene; AL/KT, molar ratio of $AlCl_3$ to ketone group; Na/K, molar ratio of $NaCO_3$ to K_2CO_3; CN/KT or DF/KT, molar ratio of CH_3NO_2 or DF to ketone group.
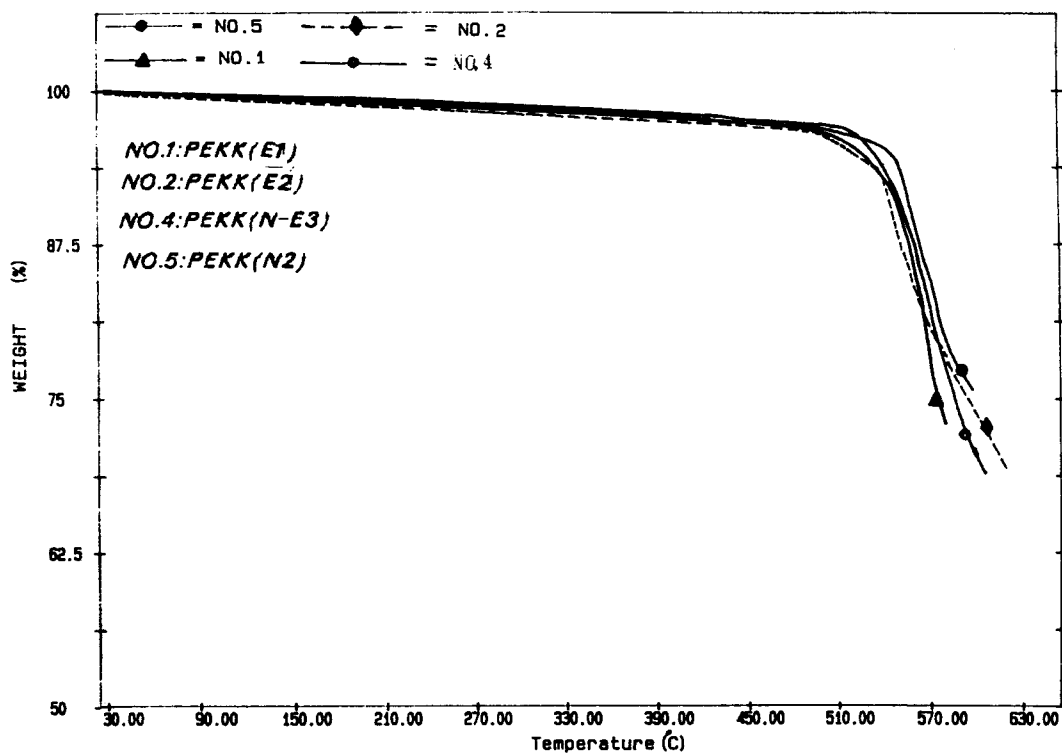
Figure 16   Thermal degradation behavior of PEKK samples from different preparation routes.

the flask. The mixture was reacted with the temperature gradually, increasing up to 158°C for 1 h. Then, water was collected. The reaction mixture was kept at 158°C for 1 and 2 h at 162°C. The reaction mixture was poured into pure water and the precipitate was filtered and dried under air for 24 h at 108°C. Recrystallization from toluene twice gave a KS_5 with an mp of 224°C and a yield of 90% is obtained compared with 215°C in the literature.[10]

For MK_5, the reaction process was the same as in the preparing process of KS_5. The T_m for MK_5 is 169°C. For the monomer of 4,4′-di(meta-florobenzoyl)benzene (DMFBB), one may refer to the literature.[10]

Monomer of DPHBB

TPC, 0.1 mol (20.3 g) was mixed in 100 mL phenyl methyl ether ($ArOCH_3$, Ar–phenyl group). Then, the mixture was dropped into another mixture of 1600 mL $ArOCH_3$ and 0.26 mol (34.71 g) $AlCl_3$ for 1 h. The mixture was reacted at 5–30°C for 5 h. After that, the mixture was poured into ice water slowly. The precipitate was washed with cold water several times and diluted chlorohydrolic acid

twice, then dried at 100°C for 24 h. This dried compound was put into a 1000 mL flask which contains 300 mL chclorobenzene and 0.30 mol (40.5 g) $AlCl_3$. The mixture was refluxed for 6 h to get rid of the —CH_3 group and gave the sample of DPHBB with an mp of 300–301°C. The element analysis results are C 75.11%, H 4.49% (observed) and C 75.46, H 4.43% (calculated). The ^{13}C-NMR of DPHBB have chemical shifts of C1, 160.8; C2, 114.0; C3, 131.2; C4, 127.0; C5, 195.0; C6, 139.5, and C7, 128.2 in the solvent of DMSO-d_6. The ^{13}C-NMR of DPFBB have chemical shifts of C1, 164.6; C2, 114.4; C3, 131.5; C4, 133.0; C5, 192.8; C6, 139.5; and C7, 128.2 in DMSO-d_6 (see molecular figures in Fig. 1).

When DPFBB was adopted to obtain DPHBB, the hydration of DPFBB also gave a sample of DPHBB with an mp of 304–305°C. This can follow the synthesis route: 0.10 mol (32.2 g) DPFBB with 0.30 mol (16.8 g) KOH was put into a 1000 mL high-pressure reaction container. The mixture was added to 200 mL of water, 1 mL nitrobenzene, and 10–20 mL NMP, then placed into a stove with a constant temperature from 149 to 260°C (pressure from 2–6 atm or so).

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