Facile Synthesis and Properties of Semicrystalline Copoly(Arylene Ether Ketone) Containing Hydroquinone and Phthalazinone

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ABSTRACT: Two series of novel copoly(arylene ether ketone) were successfully synthesized from hydroquinone or bisphenol A, bis(4-fluorophenyl)ketone and 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one with anhydrous potassium carbonate as the catalyst. The synthesized polymers exhibited high glass-transition temperatures together with excellent thermooxidative stability. The chain structure of these polymers was studied by means of ^{13}C-nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry (DSC), and wide-angle X-ray diffraction (WAXD) techniques. The experimental results showed that these "as-made" copolyaryleneketones containing hydroquinone moieties exhibited a multiblock chain structure with long segments that mainly consisted mainly of hydroquinone and bis(4-fluorophenyl)ketone at the middle of the molecular chain. These long segments exhibited crystallites in the produced polymers. The synthesized copolyaryleneketone containing 90 mol % hydroquinone possessed a glass-transition temperature higher than that of commercial PEEK. The synthesized polymers also exhibited either fair processability or solubility. The glass-transition temperatures, solubility, and tensile strengths of the two series of copolyaryleneketones tended to increase with increasing phthalazinone moiety content. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2687–2695, 2001

Key words: copoly(arylene ether ketone); bisphenol A; phthalazinone; hydroquinone; semicrystalline

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a high-performance aromatic polymer that can be used as a material in aerospace, electronics, and nuclear industries.[1,2] It possesses excellent mechanical, thermooxidative, and chemical resistance properties. These characteristics permit PEEK to be used in many engineering applications, often in harsh environments.[3] For example, PEEK finds application as a high-performance matrix for fiber-reinforced composites and cable insulators.

PEEK is a semicrystalline polymer with a glass-transition temperature of 143°C and a melting point of 334°C; it is insoluble in organic solvents at room temperature.[4] The synthesis of

commercial PEEK is generally performed at an elevated temperature very close to its melting point in diphenylsulfone. Compared with soluble polymer, the purification of such a polymer is difficult because it contains a high amount of inorganic salt. Moreover, PEEK suffers from creep behavior above its lower glass-transition temperature (T_g); hence, the synthesis of semicrystalline poly(arylene ether ketone) (PAEK) with higher T_g is of particular interest. It is well known that the incorporation of bulky groups into the main molecular chain, or pendant bulky groups onto the side-chain of the main molecule can lead to an increase in T_g. From this point of view, modified PEEK containing heterocyclic moieties[5] and pendant aromatic groups on main molecular chain[7–9] have been prepared by the nucleophilic or electrophilic displacement methodologies. Low crystalline or amorphous PAEK are often obtained in this procedure.

We previously synthesized an amorphous poly(phthalazinone ether ketone) (PPEK)[5,6] with very high T_g (263°C) and excellent mechanical properties. However, the processability[9] of the PPEK is relatively poor due to its rigid amorphous molecular structure. As an exclusive subject of the synthesis of poly(arylene ether) containing the phthalazinone moiety, two series of PAEK containing the phthalazinone moieties are synthesized by solution nucleophilic polycondensation in this work. The synthesized PAEK containing hydroqinone exhibit both high T_g and crystallinity. The molecular structure is investigated by nuclear magnetic resonance (^{13}C-NMR), differential scanning calorimetry (DSC), and wide-angle X-ray diffraction (WAXD) techniques. The mechanical, rheological, and thermal properties are also characterized and discussed.

EXPERIMENTAL

Materials

4-(4-hydroxyphenyl)-2,3-phthalazin-1-one (DHPZ) was synthesized according to the procedure reported by Berard and Hay,[11] except that the solvent is a mixture of sulfolane and chlorobenzene (1/4 v/v). Bis(4-fluorophenyl)ketone (BFK) was obtained from Jilin University (China) and was purified by recrystallizing it from ethanol. Anhydrous potassium carbonate, bisphenol A (BPA), hydroquinone (HQ), the reagent-grade sulfolane, and chlorobenzene solvents were used without further purifica-
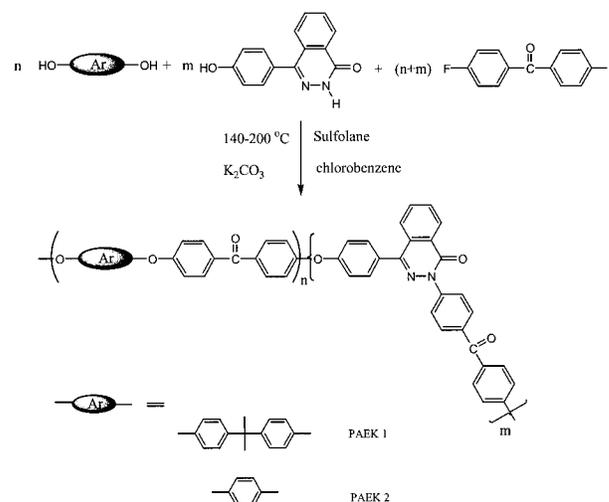

Figure 1 Synthetic scheme of poly(arylene ether ketone) (PAEK).

tion. Commercial PEEK was also kindly supplied by Jilin University.

General Procedure for Synthesis of PAEK

As depicted in Figure 1, the synthesized PAEK were designated as PAEK 1 and PAEK 2, respectively. The synthetic procedure of PAEK containing BPA and phthalazinone moieties (PAEK 1) was similar to that of poly(phthalazinone ether solfone ketone) (PPESK) as reported in previous work,[6] except that the solvent used was sulfolane and the polycondensation temperature employed was 180°C. The synthetic procedure of PAEK containing hydroquinone and phthalazinone moieties (PAEK 2) was also similar to that of PPESK, except for the purifying procedure for the polymers produced. For the purification of PAEK 2, a small amount of phenol was added to the reaction flask to endcap PAEK 2 at the end of polycondensation. The reaction mixture was diluted three times with sulfolane, and then the viscous solution was slowly poured into a vigorously stirred mixture of ethanol and water (3:1 vol ratio). The PAEK 2 was precipitated, and the resulting dispersion solution was filtered. The PAEK 2 filtrate obtained was boiled in water for 1 h, followed by filtering. The filtrate was boiled in acetone for 1 h, again followed by filtering. Subsequently, the above boiling purification procedures in water and acetone were repeated four times. Finally, the purified PAEK 2 was dried at 130°C under vacuum, and the white powder product was obtained. The yield was generally higher than 95%.

Table I Thermal and Mechanical Properties of PAEK 1

DHPZ/BPA (molar ratio)	25/75	50/50	75/25	100/0
IV (dL/g)	1.06	1.05	1.70	0.45
T_g (°C)	212	229	245	263
5% wt loss temperature (°C)	493	483	490	500
Tensile strength at break (MPa)	78.0	89.4	102	109
Strain at break (%)	8.5	8.8	8.9	9.5

Instrumentation

The inherent viscosities (IV) of PAEK 2, except for PAEK 2 (100/0), were determined using an Ubbelohde viscometer at a concentration of 0.5 g/dL in a mixed solvent of chloroform and phenol (10/3 v/v) at 25°C. The IV of PAEK 1 and PAEK 2 (100/0) were determined at a concentration of 0.4 g/dL in chloroform at 25°C. The T_g were determined using a Perkin–Elmer differential scanning calorimeter (model DSC-7) at a heating rate of 20°C/min under nitrogen flow, and the reported T_g values were recorded from the second scan after first heating and quenching. The thermogravimetric analysis was performed with a Perkin–Elmer TGA-7 at a heating rate of 10°C/min in nitrogen atmosphere. The structure of the as-cast and annealed samples was examined by means of WAXD. The ^{13}C-NMR spectrum of the PAEK 2 was recorded using a Varian Gemini-200 NMR instrument operated at 110 MHz. The polymers were dissolved in a mixed solvent of CDCl$_3$ and trifluoroacetic acid (TFA), to give a 10 wt % solution. The mechanical properties of PAEK were determined at 23°C, using a Shimadzu AG-2000A tester at a cross-head speed of 50 mm/min. The samples, with dimensions of $0.2 \times 6.0 \times 50$ mm^3, were prepared by the solution casting method in a mixed solvent of chloroform and phenol (10/3 v/v). At least five samples for each composition were tested, and the average value was reported.

For the rheological tests, the PAEK in powder form were dried in a vacuum oven at 140°C for 48 h before testing. A Shimadzu AG-2000A capillary rheometer with a 2-mm-long and 1-mm-diamr capillary (L/D=2) was used to perform the rheological characterization at various temperatures. The shear rate range studied was within 10–200 S^{-1}. Rabinowitch correction and entrance effect were taken into consideration because of the short capillary employed. The samples were added to the capillary as fast as possible and kept in the molten state for 5 min before testing.

RESULTS AND DISCUSSION

Synthesis and Properties of PAEK 1

The synthesis of PAEK 1 was conducted according to the procedure shown in Figure 1. The synthesized PAEK 1 with various compositions are expressed as PAEK 1 (DHPZ/BPA). For example, the PAEK 1 containing 25 mol % phthalazinone is written as PAEK 1 (25/75). The polycondensation temperature is controlled below 180°C because the formed PAEK 1 and bisphenolic salt can decompose at temperatures higher than 180°C in the presence of alkali catalyst, which can then produce oligomers with very low molecular weight (IV). From Table I, it can be seen that the synthesized PAEK 1 exhibit very high IV. It is noted when the molar phthalazinone content in PAEK 1 equals 100 mol %, the copolymer PAEK 1 corresponds to homopolymer PPEK.[9] Table I also lists the thermal and mechanical properties of the produced PAEK 1. It is apparent that the T_g for PAEK 1 increase linearly with increasing phthalazinone moiety content. The incorporation of the rigid phthalazinone moiety in the main chain leads to an increase of molecular rigidity in PAEK because of the whole aromatic structure of phthalazinone moiety, which increases the segment size in the PAEK molecular chain. The variation of T_g values with molar phthalazinone content fits the rule of random copolymers. Furthermore, the thermogravimetric data as shown in Table I shows that the synthesized PAEK 1 are thermooxidatively stable and that all 5% weight loss temperatures are >480°C. Moreover, it is evident that the tensile strength for PAEK 1 increases with increasing molar phthalazinone content because of the introduction of rigid phthalazinone moieties (Table I). Generally, the naphthalene ring within the polymer backbone contributes more to the mechanical strength than the phenylene ring or biphenylene ring and the aliphatic carbon in a main molecular chain (from BPA moiety) also results in poorer mechanical
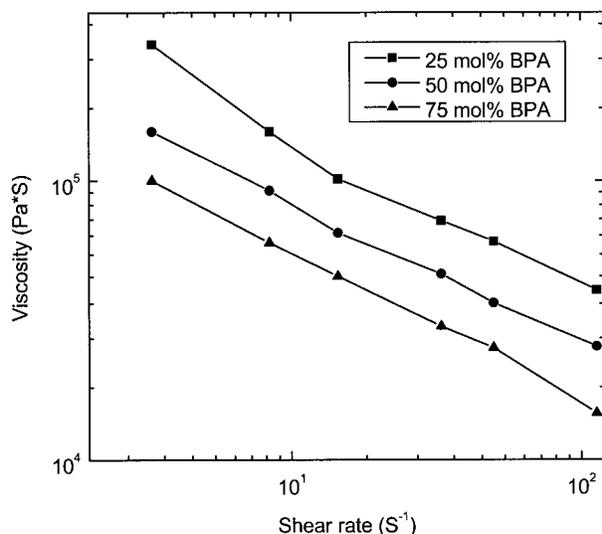
Figure 2 Melt viscosity versus shear rate for poly-(arylene ether ketone) (PAEK) 1 with various DHPZ content at 320°C.

properties compared with the whole aromatic structure. The incorporation of the phthalazinone moieties, however, leads to a slight decrease in strain at break.

Figure 2 shows the melt viscosity versus shear rate for PAEK 1 with various compositions at 320°C. The rigidity of the BPA is much smaller than that of the phthalazinone monomer. In this regard, the copolymerization of DHPZ with BPA should improve the processability of PPEK. Apparently, the melt viscosities for PAEK 1 decrease with increasing molar BPA content, indicating that the processability of PPEK homopolymer can be improved considerably by the incorporation of a flexural BPA moiety.

Synthesis and Properties of PAEK 2

The synthesis of PAEK 2 was also conducted according to the procedure shown in Figure 1. The

polycondensation is carried out at 200°C, and the polycondensation times are reduced from 20 to 8 h with increasing molar phthalazinone content since the solubility of the polymers produced in sulfolane tend to increase with the increase of molar phthalazinone content. For the synthesis of PAEK 2 with hydroquinone molar content higher than 80%, the produced polymers precipitate out directly from the polymerization solution because of their poorer solubility.

The thermal and mechanical properties of the PAEK 2 obtained are presented in Table II. The results demonstrate that the formed PAEK 2 generally have high molecular weight or IV. The high IV of synthesized PAEK 2 copolyketones result from the greater reaction activity of hydroquinone. When the molar phthalazinone content in PAEK 2 (based on HQ and DHPZ) equals 0 mol %, the copolyketone produced corresponds to commercial PEEK, and PAEK 2 with 100 mol % DHPZ corresponds to the homopolyketone PPEK synthesized in previous work.[5,6] As is evident in Table II, all PAEK 2 exhibit high T_g, and the T_g values increase monotonically with increasing molar phthalazinone content. Moreover, the variation of T_g values with molar DHPZ content basically fits the rule of random copolymers. The T_g for PAEK 2 show a dramatic increase when the molar phthalazinone content reaches $\geq 80\%$. Thermogravimetric properties were investigated by means of TGA, and the results show that the PAEK 2 are thermooxidatively stable (Table II).

The static mechanical properties of PAEK 2 demonstrate that all PAEK 2 exhibit high tensile strength (>80 MPa). Tensile strength tends to increase significantly with increasing molar phthalazinone content, owing to the incorporation of the bulky phthalazinone moiety into the molecular chain. However, the values of strain-at-break are basically constant ($\sim 10\%$) and are not dependent on molar DHPZ content. It is apparent that

Table II   Thermal and Mechanical Properties of PAEK2

DHPZ/HQ (molar ratio)	0/100	10/90	20/80	35/65	50/50	80/20	90/10	100/0
IV (dL/g)	1.00	0.86	0.77	0.98	1.18	1.53	1.67	0.45
T_g (°C)	143	160	177	189	202	223	258	263
T_m (°C)	334	315	291[a]	307[a]	312[a,b]	—	—	—
5% wt loss temperature (°C)	500	512	508	485	483	462	516	500
Tensile strength at break (MPa)	—	—	—	83.5	89.8	106	126	134
Strain at break (%)	—	—	—	11.3	11.1	13.6	10.7	9.90

[a] The peak disappeared in second scan.
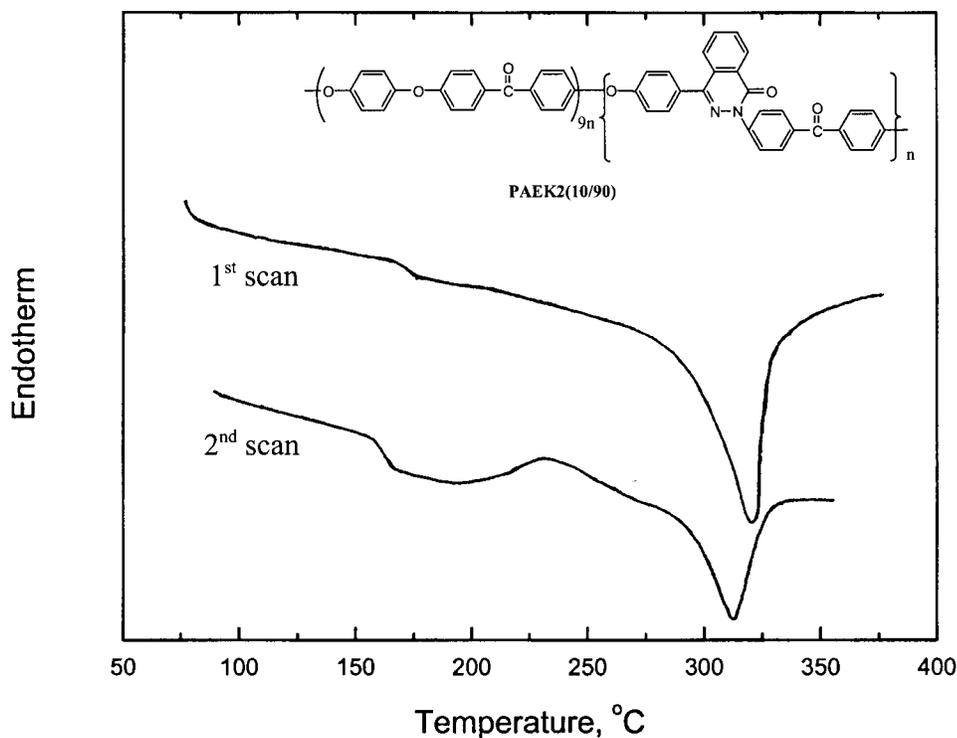[b] Not clear even in first scan.

Figure 3   Differential scanning calorimetry (DSC) curves for poly(arylene ether ketone) (PAEK) 2 (10/90) sample.

the synthesized PAEK 2 show superior mechanical strength. Moreover, it is worthy to note that the synthesized PAEK 2 containing phthalazinone moieties higher than 20 mol % are soluble in some common organic solvents such as chloroform, N,N'-dimethylacetamide, N-methylcaprolactam, and nitrobenzene. Such solubility enables PAEK 2 to be used as high-performance composite matrices, high temperature membranes and adhesives, as well as cable insulators.

Chain Structure of PAEK 2

As shown in Table II, it is very interesting to note that the PAEK 2 with phthalazinone moieties of <50 mol % tend to include both a T_g and a melting point (T_m). Figure 3 displays the DSC plots for the synthesized PAEK 2 (10/90). The sample exhibits both a glass-transition zone and a sharp crystalline melting point in the first scan curve. Both crystallization peak (located at 231°C) and a melting point (located at 315°C) are observed within the investigated temperature range in the second scan curve. This behavior obviously demonstrates that the synthesized PAEK 2 contains some crystallites. The crystallinity of the PAEK 2 can be calculated based on the following equation:

$$X_c = \Delta H_m^{\circ}$$

where X_c is the degree of crystallinity, ΔH_m is the heat of fusion of PAEK 2, and ΔH_m° is the heat of fusion of pure PEEK, i.e.

$$\Delta H_m^{\circ} = 130 \ \text{J/g}$$

Thus, the crystallinities of PAEK 2 (20/80) and PAEK 2 (10/90) are equal to ~3.5% and 19.6%, respectively, whereas the crystallinity of pure PEEK is ~30%. These crystallites in PAEK 2 are believed to be thermodynamically stable, as the crystalline melting point can be seen in the second scan. Moreover, the melting point of PAEK 2 (10/90) is 315°C, which is 18°C lower than that of commercial PEEK. In this case, it implies that PAEK 2 (10/90) may exhibit better processability.

Figure 4 shows the WAXD traces for the synthesized PAEK 2. It is apparent that the PAEK 2 copolyketones exhibit several sharp peaks in WAXD traces, indicating the formation of the crystalline structure within the samples. This is direct proof of the existence of a crystalline melt endotherm. The diffraction intensities of PAEK 2 crystalline peaks tend to decrease with increasing
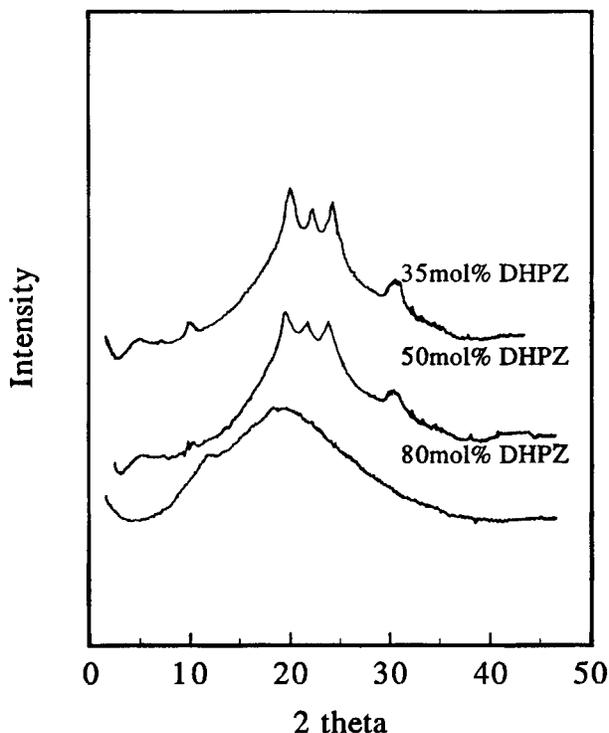
Figure 4 Wide-angle X-ray diffraction traces for synthesized poly(arylene ether ketone) (PAEK) 2 with various DHPZ content.

Figure 5 ^{13}C-NMR spectrum of synthesized poly(arylene ether ketone) (PAEK) 2 containing 80 mol % DHPZ in the mixed solvent of CDCl$_3$ and trifluoroacetic acid at 30°C.

molar phthalazinone content, and they can not be detected when the molar phthalazinone content is higher than 80% (Fig. 4). The diffraction peaks are the same as those for commercial PEEK,[12,13] indicating that the structure of the crystallites in PAEK 2 is similar to that of PEEK resin, i.e., an orthorhombic structure.[12,13]

On the basis of these experimental results, it is believed that the structure of PAEK 2 is a copolymer containing PEEK segments. The PEEK segments in the molecular chain basically consist of BFK and HQ, which have the same structure as that of commercial PEEK, as evident in Figure 4. The creation of these segments within the PAEK 2 copolyketones results from the large difference in reaction activity between hydroquinone and phthalazinone. Therefore, the increase in T_g value is mainly contributed by the amorphous domains of PAEK 2 and the Tm value is produced by its crystalline domains.

Figure 5 shows a typical ^{13}C-NMR spectrum of the PAEK 2 containing 80 mol % DHPZ. The peaks of 116.991 and 117.991 ppm are assigned as carbon-a and carbon-b on the basis of the structural formula shown in Figure 5. From the relative peak heights of these two characteristic
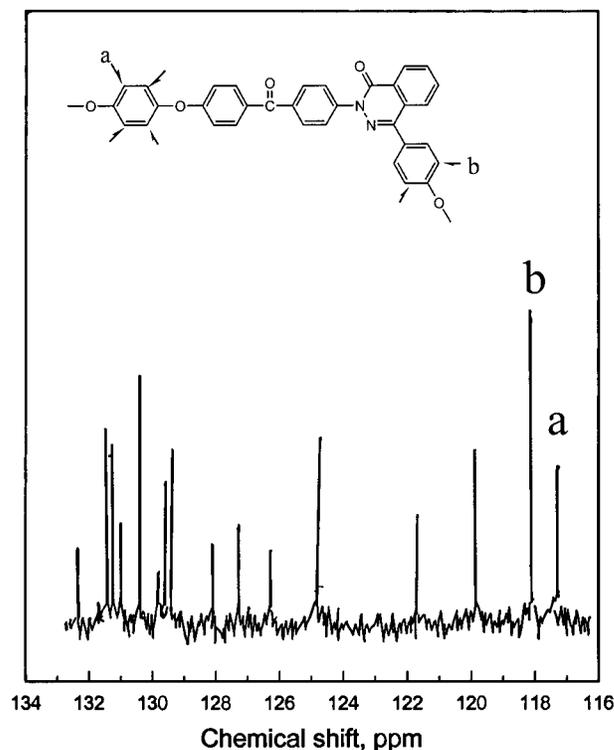
peaks, the compositions of PAEK 2 (molar ratio of DHPZ content to HQ content) can be readily calculated, and the results are listed in Table III. It can be seen that the compositions of copolymers are essentially equal to those of charged materials. Thus, the obtained PAEK 2 does not contain the BFK and HQ homopolymers because the homopolymer or PEEK is insoluble in organic solvents.

Many attempts[7,14,15] have been made to raise the T_g of the rigid amorphous phase in commer-

Table III Composition of Synthesized PAEK 2 Determined by ^{13}C-NMR Technique

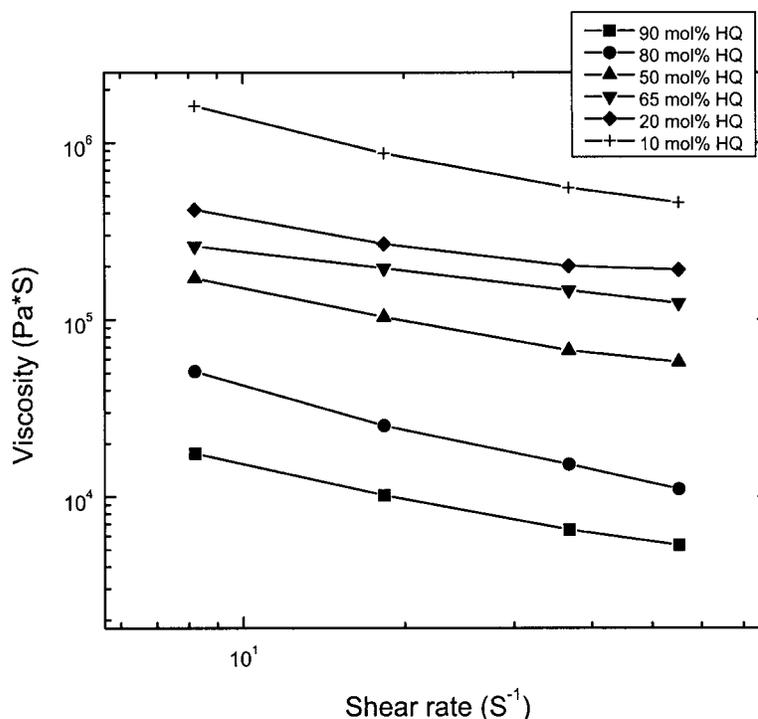| Charge DHPZ Content (mol %)	Peak Height (a)	Peak Height (b)	DHPZ Moiety Content in PPEK 2 (mol %)
80	1.9	3.8	80.0
50	7.3	3.9	51.5
35	28.5	7.9	35.7

Figure 6 Relationship between the melt viscosity and shear rate for poly(arylene ether ketone) (PAEK) 2 with various HQ contents at 320°C.

cial PEEK in order to improve its creep resistance at elevated temperature. Some patents concerning these copolymers including block copolyketones containing PEEK oligomer have been reported[16-18]; however, several steps are needed to achieve the synthesis. From this work, the incorporation of DHPZ into PEEK molecular chain can be considered as an easy and effective alternative approach for this purpose. At least two positive results can be derived from this alternative route. First, a modified PEEK with a higher T_g could be synthesized, and, second, the synthetic process for PAEK 2 (with lower polycondensation temperature and easier purification of the polymers produced) is much easier than those of PEEK and copolycondensation using other PAE oligomers.[15] Thus, it is possible to perform polycondensation for producing PAEK at an ambient temperature.

Rheological Properties of PAEK 2

Figure 6 shows the relationship between the melt viscosity and shear rate for PAEK 2 with various DHPZ contents at 320°C. As is evident, all PAEK 2 exhibit a pseudoplastic behavior. In this context, the melt viscosity tends to decrease with increasing shear rate, i.e., shear thinning. It can

also be seen that the melt viscosities of PAEK 2 decrease dramatically with increasing molar HQ content, indicating that the long segments consisting of HQ and BFK tend to act as plasticizers for PAEK 2. The higher melt viscosity of the PAEK 2 (90/10) results from the rigid amorphous and DHPZ moiety-rich phases. However, all PAEK 2, except PAEK 2 (20/80) and PAEK 2 (10/90), have very high melt viscosity ($>10^5$ PaS) and are difficult to process at the investigated temperature of 320°C. It should be noted that when shear rate exceeds 20 S^{-1}, the melt viscosity of PAEK 2 (10/90) is lower than 10^4 PaS, indicating that it is processable by injection molding.

To investigate the effect of temperature on melt viscosity, the PAEK 2 (80/20) was selected and tested. Figure 7 shows that increasing the test temperatures from 340 to 370°C generally leads to a reduction in melt viscosity. However, it is interesting to see that the melt viscosity at 380°C is considerably higher than those at other test temperatures. It is believed that this behavior is caused by the crosslinking and chain-extending reactions of PAEK 2 at temperatures higher than 360°C due to the presence of trace
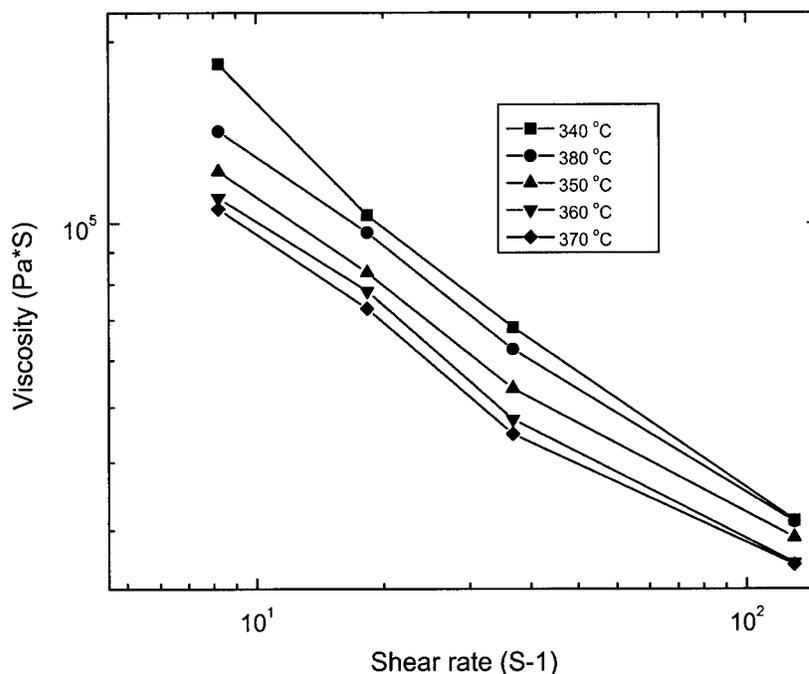
Figure 7 Relationship between the melt viscosity and shear rate for poly(phthalazinone ether ketone) (PPEK) 2 at various temperatures.

un-endcapped end groups and catalyst.[19] The gel contents of PAEK 2 (80/20) can be determined by extracting the samples using a mixed solvent of chloroform and phenol (10/3 v/v) for 24 h (Table IV). The results show that the gel contents increase slightly at 350 and 360°C, but they tend to increase significantly at temperatures of ≥370°C. The value of gel content at 380°C is close to 30 wt %, which in turn leads to a dramatic increase in the melt viscosity. The results of the gel content calculation are in good agreement with those of the melt flow curves (Fig. 7). Based on the above results, we assume that the PAEK 2 can be processed at a temperature of ~350°C; in this case the melt viscosity is lower than 10^4 PaS. For PAEK 2 (10/90), it can be melt processed at a temperature as low as 320°C, which is equivalent to that of commercial PEEK.

Table V presents the melt viscosities for homopolymer PPEK and PAEK copolymer at 320°C and various shear rates. On the basis of these data, it appears that PAEK 1 and PAEK 2 exhibit much lower melt viscosities than PPEK. Hence the processability of PPEK can be improved via copolymerization with HQ or BPA bisphenols. In addition, the degree of improvement in the processability for PAEK containing HQ or BPA bisphenols is basically identical.

CONCLUSIONS

Two series of novel copoly(arylene ether ketone) are synthesized from bis(4-fluorophenyl)ketone and 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one with hydroquinone or bisphenol-A in the presence of anhydrous potassium carbonate as catalyst. The synthesized polymers exhibit high T_g together with excellent thermooxidative stability. The chain structure of synthesized polymers is studied by means of ^{13}C-NMR spectroscopy, DSC, and WAXD technique. The experimental results show that these "as-made" copolyaryleneketones with hydroquinone exhibit a chain structure containing PEEK segments, consisting mainly of hydroquinone and bis(4-fluorophenyl)ketone. The PEEK segments are semicrystalline with the same crystalline structure as that of commercial PEEK. These polymers

Table IV   Gel Content of PAEK 2 (20/80) Formed at Various Temperatures

Temperature (°C)	340	350	360	370	380
Gel content (wt %)	0.00	0.40	4.80	12.1	29.2

Table V   Melt Viscosities of PPEK and PAEK at Various Shear Rates

Shear rate s^{-1}	3.34	8.35	16.7	33.4	50.1	167
PAEK $\eta_a * 10^{-5}$						
PPEK	18.4	14.2	6.15	5.80	5.02	4.62
PAEK 1 (50/50)	1.60	1.02	0.68	0.51	0.34	0.23
PAEK 2 (50/50)	3.20	2.00	1.30	0.82	0.60	0.39

Shear rate (s^{-1}); $\eta_a * 10^{-5}$.

also exhibit fair processability, solubility, and mechanical properties. The synthetic method in this paper provides an effective and novel approach to fabricate semi-crystalline PAEK with high T_g.

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