

SYNTHESIS AND CHARACTERISTICS OF POLY(ARYLENE ETHER DIKETONE)S

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Abstract Poly(arylene ether diketone)s were prepared by the aromatic nucleophilic displacement reaction of 4,4'-difluorobenzil with different bisphenols in the presence of anhydrous potassium carbonate in diphenylsulfone at elevated temperature. The polymers obtained had inherent viscosity of 0.51 ~ 0.63 dL/g, and exhibited glass transition temperature ranging from 136 ~ 217°C mainly depending on the bisphenols used in the polymer synthesis. Thermogravimetry of these polymers showed excellent thermal stability, indicating that 10% weight losses of the polymers were observed in the range above 428°C and 438°C in air and nitrogen, respectively. The mechanical properties of these polymers were also described and the permeability of five polymers for H₂, O₂ and N₂ was determined at 30°C.

Keywords Poly(arylene ether diketone); Thermal behavior; High-temperature polymers; Permeability

INTRODUCTION

Poly(aryl-ether-ether-ketone) is a tough aromatic polymer with unusual combination of properties, such as high chemical resistance, excellent thermal stability, and good mechanical strength^[1,2]. These properties make PEEK an attractive high performance polymer for potential adhesive and composite matrix applications.

It is also of interest to introduce the α -diketone groups into macromolecules of known polymers. However, few work^[3~6] focused on the study of poly(arylene ether diketone)s and recently Hedrick^[7,8] used this kind of polymers to synthesize poly(aryl ether)s containing heterocyclic functionalities.

The present work deals with the preparation of four new poly(arylene ether diketone)s (PEDK-1,5-DN, PEDK-2,7-DN, PEDK-PP, and PEDK-CP) via nucleophilic aromatic substitution polymerization and four known polymers were synthesized to compare with the new polymers. The thermal and mechanical properties of these

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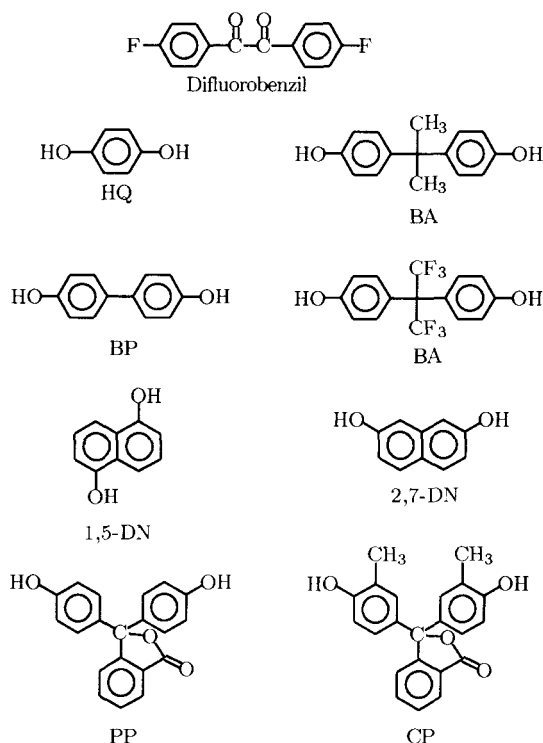
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polymers were also studied. In addition, the permeability of five polymers for H_2 , O_2 and N_2 was determined.

EXPERIMENTAL

Materials

The monomers used in this study are shown in Scheme 1. 4,4'-Difluorobenzil was prepared by a benzoin condensation^[9] of the *p*-fluorobenzaldehyde followed by a $CuSO_4$ -pyridine oxidation^[10]. Hydroquinone (HQ) (from H_2O), 1,5-dihydroxynaphthalene (1,5-DN) (from nitromethane), 2,7-dihydroxynaphthalene (2,7-DN) (from H_2O), and *o*-cresolphthalein (CP) (from AcOH) were purified by recrystallization. 4,4'-Biphenol (BP), 2,2'-bis(4-hydroxyphenyl)propane (BA), 2,2'-bis(4-hydroxyphenyl)hexafluoropropane (AF), and phenolphthalein (PP) were used as received without further purification.



Scheme 1

Polymerization

A typical example of the polymerization was illustrated as follows: To a 100 mL four-necked round-bottom flask equipped with a mechanical agitator, an argon gas

inlet, a thermometer, and an air condenser were placed 2.2475 g (9.13 mmol) of 4,4'-difluorobenzil and 16 g of diphenylsulfone. The mixture was heated to 180°C while being stirred, and at this temperature, under a stream of argon, 2.0838 g (9.13 mmol) of 2,2'-bis(4-hydroxyphenyl)propane and 1.2616 g (9.13 mmol) of anhydrous K_2CO_3 were introduced. The temperature was raised to 200°C, maintained for 1 h and then was gradually raised to 280°C in 1 h.

The polymerization ceased after the mixture has been kept for half an hour at 280°C. The mixture was poured into water, and the solid obtained was grounded and then boiled with ethanol and water for three times, respectively. After drying at 140°C for 4 h, product with quantitative yield was obtained. The inherent viscosity of the polymer in N-methyl-2-pyrrolidone (NMP) was 0.57 dL/g, measured at a concentration of 0.5 g/dL at 25°C.

Characterization

FT-IR spectra were measured on a Bruker IFS-113V FT-IR spectrometer. ^1H -NMR and ^{13}C -NMR spectra were recorded at 200 MHz using a Varian Unity 200 spectrometer in $DMSO-d_6$. Inherent viscosity was measured by using an Ostwald viscometer at 25°C at a concentration of 0.5 g of polymer in 100 mL NMP.

Glass transition temperature (T_g) was measured on a Perkin-Elmer DSC 7 differential scanning calorimeter at a heating rate of 20°C/min up to 330°C, cooling at about 200°C/min, and then reheating at 20°C/min. The T_g was taken at the midpoint of the change in slope of the base line.

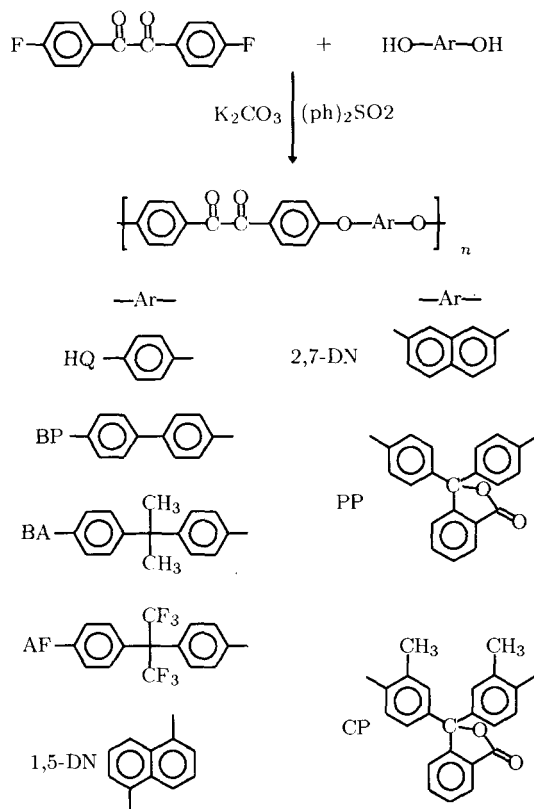
Thermal analysis was performed on a Du Pont 1090 thermal analyzer at a heating rate of 20°C/min for thermogravimetry (TG).

Mechanical properties of the cast films were examined by an Instron Universal Testing Instrument at a strain rate of 10 mm/min. The films were casted from NMP and dried in vacuum at 140°C for 8 h.

Permeability was measured using a K-315N-01 GTR Measurement Apparatus (RSK Rikaseiki Kogyo Co., Ltd.). The purity of the gases was 99.5% or higher.

RESULTS AND DISCUSSION

The poly(arylene ether diketone)s were successfully prepared by the aromatic nucleophilic displacement reaction of 4,4'-difluorobenzil with various bisphenols by using diphenylsulfone as solvent in the presence of anhydrous potassium carbonate (Scheme 2). The polymers has an inherent viscosity of 0.51 ~ 0.63 dL/g (cf. Table 1). The FT-IR spectrum of PEDK-2,7-DN (thin film) exhibits characteristic absorptions



Scheme 2

Table 1 Properties of poly(arylene ether diketone)s

Polymer	η (dL/g)	T_g ($^{\circ}\text{C}$)	T_d^a ($^{\circ}\text{C}$)	
			In Air	In N_2
PEDK-HQ	— ^b	160	492	527
PEDK-BP	— ^b	179	495	537
PEDK-BA	0.57	136	442	484
PEDK-AF	0.63	145	508	539
PEDK-1,5-DN	— ^c	179	458	504
PEDK-2,7-DN	0.60	146	455	496
PEDK-PP	0.51	207	470	489
PEDK-CP	0.55	217	428	438

a. Temperature at which a 10% weight was recorded by TG at a heating rate of $20^{\circ}\text{C}/\text{min}$, b. Insoluble in NMP, c. Partially soluble or swelling

at around 1680 and 1246 cm^{-1} due to the $\text{C}=\text{C}$ (α -diketone) and $\text{C}-\text{O}-\text{C}$ stretching, respectively (see Fig.1). Fig.2 was the FT-IR spectrum of PEDK-PP (thin film),

which shows similar characteristic absorptions with Fig.1 except for the strong peak at 1772 cm^{-1} and this peak can be attributed to the $\text{C}=\text{O}$ stretching of lactone. The most conclusive spectroscopic evidence for the proposed poly(arylene ether dike-tone)s were provided by ^1H -NMR and ^{13}C -NMR spectroscopy. The typical ^1H -NMR and ^{13}C -NMR spectra of PEDK-PP are shown in Fig.3 and 4.

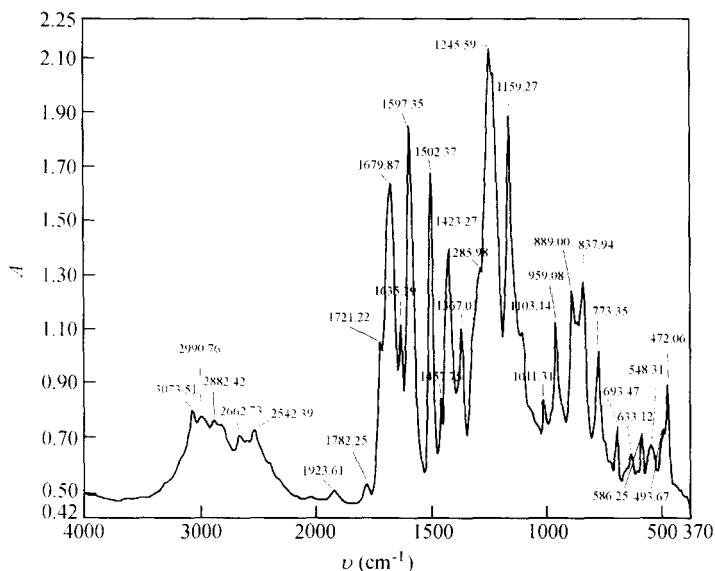


Fig.1 FT-IR spectrum of PEDK-2,7-DN (thin film)

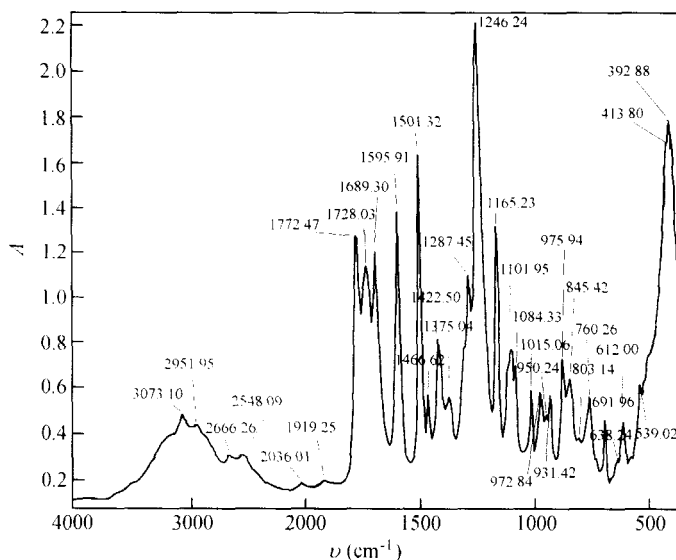


Fig.2 FT-IR spectrum of PEDK-PP (thin film)

The T_g and T_d (polymer decomposition temperature; 10% weight loss) of the various poly(arylene ether diketone)s are listed in Table 1. Since all the polymers are of sufficiently high molecular weights, T_g should not be affected by molecular weight variations. The melting endotherms of the resultant polymers are not observed except the PEDK-HQ, which shows $T_m = 304^\circ\text{C}$. The T_g value of these polymers range from 136 to 217°C depending on the monomers used in the synthesis, which was similar with the difluorobenzophenone based PEEKs containing the same bisphenol components.

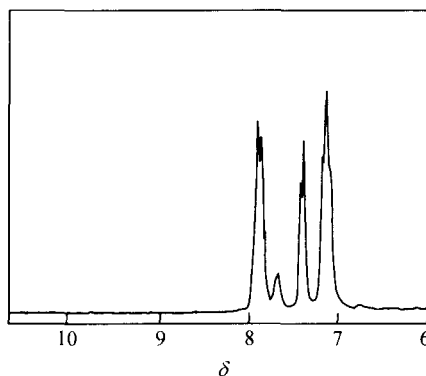


Fig.3 ^1H -NMR spectrum of PEDK-PP in $\text{DMSO}-d_6$

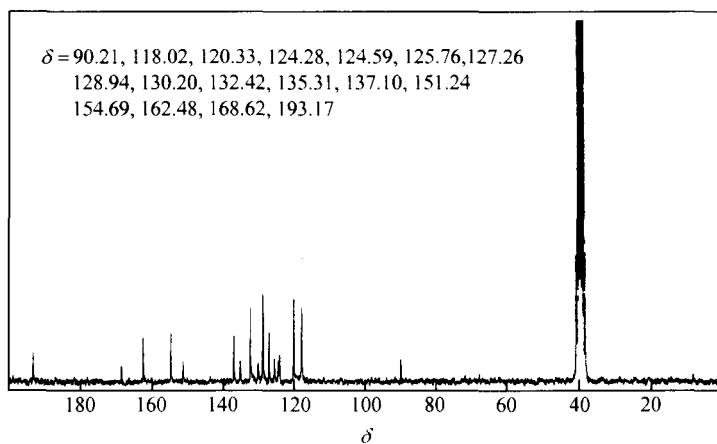


Fig.4 ^{13}C -NMR spectrum of PEDK-PP in $\text{DMSO}-d_6$

The poly(arylene ether diketone)s demonstrate excellent thermal stability with T_d exceeding 428°C and 438°C in air and under nitrogen, respectively. As can be seen from Table 1, the bisphenol components on the polymers significantly influenced thermal stability. The polymers based on AF and HQ exhibit higher decomposition temperatures than those of the other polymers. The lower thermal stability of PEDK-BA and PEDK-CP can be ascribed to the presence of methyl groups. Fig.5 shows the TG curves of PEDK-AF, a typical trace for the polymers, in N_2 and air, respectively. The curves indicate that PEDK-BF is stable both in nitrogen and air and that little degradation occurs at least up to

400°C. There is apparently relatively little difference in thermal stability of the

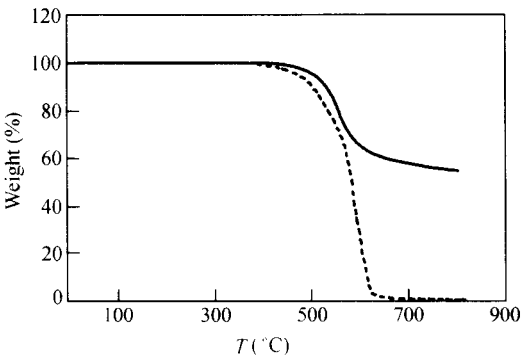


Fig.5 TG curves of PEDK-AF in air (---) and in nitrogen (—)

sample in either nitrogen or air below 500°C. In fact, the initial stages of degradation are not affected by the presence of oxygen and the thermal stability in nitrogen and air is very similar up to 570°C, above that temperature the weight loss in air becomes progressively larger than in nitrogen. In air, unlike in nitrogen, there is virtually no residue above 700 ~ 800°C whereas the weight loss in nitrogen is only about 45%. Since the influence of the atmo-

sphere of the thermogravimetry measurements on the thermal stability is great, the decomposition seems to take place mainly as an oxidative decomposition.

The solubility of the resulting polymers is shown in Table 2. Most of the polymers are soluble in DMSO, DMAc, NMP, pyridine, chloroform, and THF, however, the polymers of PEDK-HQ and PEDK-BP are insoluble even in NMP. So, it is apparent that the solubility of poly(arylene ether diketone)s is mostly dependent on the bisphenols.

Table 2 Solubility of poly(arylene ether diketone)s^a

Polymer	Solvent ^b							
	Acetone	THF	CHCl ₃	Toluene	Pyridine	DMSO	DMAc	NMP
PEDK-HQ	—	—	—	—	—	—	—	—
PEDK-BP	—	—	—	—	—	—	—	—
PEDK-BA	—	+	+	—	+	+	+	+
PEDK-AF	—	+	+	—	+	+	+	+
PEDK-1,5-DN	—	—	—	—	—	—	—	=
PEDK-2,7-DN	—	—	+	—	=	+	+	+
PEDK-PP	—	+	+	—	+	+	+	+
PEDK-CP	—	+	+	—	+	+	+	+

a. (+) Soluble, (=) partially soluble or swelling, (--) insoluble;
b. THF: tetrahydrofuran, DMSO: dimethylsulfoxide, DMAc: dimethylacetamide

All the measurements for the mechanical properties of these polymers were carried out by using cast films. Table 3 lists the mechanical properties of the poly(arylene ether diketone) films at room temperature. The results show that these polymers have same good mechanical properties as engineering plastics.

Table 3 Tensile properties of films of poly(arylene ether diketone)s^a

Polymer	Tensile strength (MPa)	Elongation at break (%)
PEDK-BA	99.4	16
PEDK-AF	120	17
PEDK-2,7-DN	107	18
PEDK-PP	76.7	14
PEDK-CP	92.2	16

a. At room temperature

Permeability (P) is often given as the product of diffusivity (D) and solubility (S) parameter^[11,12]. The approximate diffusivity can be measured by the time-lag method and then the solubility can be calculated^[13]. The ideal permselectivity ($\alpha_{A/B}$) may be obtained from the ratio of the respective permeabilities (P_A/P_B) and can also be conveniently considered as the product of diffusivity selectivity (D_A/D_B) and solubility selectivity (S_A/S_B)^[14]. The permeability, diffusivity, and solubility data measured for H₂, O₂ and N₂ for five polymers are summarized in Tables 4~6.

Table 4 Permeabilities^a of the polymers^b

Polymer	Permeability			Ideal permselectivity	
	H ₂	O ₂	N ₂	H ₂ /N ₂	O ₂ /N ₂
PEDK-2,7-DN	1.07	0.0481	0.00711	150	6.8
PEDK-BA	2.44	0.158	0.0248	98	6.4
PEDK-AF	3.12	0.210	0.0328	95	6.4
PEDK-PP	6.57	0.465	0.0911	72	5.1
PEDK-CP	7.01	0.508	0.102	69	5.0

a. Unit: Barrer; b. At 30°C and 10⁵Pa**Table 5** Diffusivities^a and diffusivity selectivities of the polymers^b

Polymer	Diffusivity			Ideal Diffusivity Selectivity	
	H ₂	O ₂	N ₂	H ₂ /N ₂	O ₂ /N ₂
PEDK-2,7-DN	161	1.99	0.509	316	3.9
PEDK-BA	295	3.84	0.986	299	3.9
PEDK-AF	414	6.01	1.79	231	3.4
PEDK-PP	808	13.0	4.92	164	2.6
PEDK-CP	891	14.1	5.05	176	2.8

a. Unit: 10⁻⁹cm²/s; b. At 30°C and 10⁵Pa

Referring to Tables 4, 5, and 6, it can be seen that the permeability of H₂, O₂

and N_2 in all the polymers studied decreases in the order of $P(H_2) > P(O_2) > P(N_2)$, which is the order of increasing kinetic molecular diameter, and also of decreasing diffusivity of these penetrants. Hence, the overall permeability appears to be largely controlled by the diffusivity selectivity and not by the solubility selectivity.

Table 6 Solubilities^a and solubility selectivities of the polymers^b

Polymer	Solubility			Ideal Solubility Selectivity	
	H ₂	O ₂	N ₂	H ₂ /N ₂	O ₂ /N ₂
PEDK-2,7-DN	0.665	2.42	1.40	0.475	1.7
PEDK-BA	0.827	4.11	2.52	0.328	1.6
PEDK-AF	0.752	3.29	1.83	0.412	1.8
PEDK-PP	0.813	3.59	1.85	0.439	1.9
PEDK-CP	0.786	3.61	2.02	0.389	1.8

a. Unit: $7.5 \times 10^{-7} \text{ cm}^3(\text{STP})/\text{cm}^3 \cdot \text{Pa}$; b. At 30°C and 10^5 Pa

Among the five polymers, PEDK-2,7-DN shows the lowest permeability for all gases but the largest permselectivity. This is probably due to the flat, rigid naphthalene segment existing in the main chain makes it possible for the intersegmental chain to pack more compact. At the same time, the segmental (rotational) mobility of the 2,7-DN moiety is prohibited by steric hindrance. Both of the two reasons above may benefit the polymer to discriminate between penetrant molecules of different sizes and shapes.

The introduction of BA moiety may cause a disruption of chain packing and some increase in the segmental motion, which increases the permeability of all gases (benefits the larger penetrants) and decreases the permselectivities. As a result, the permeability of PEDK-BA for H₂, O₂ and N₂ increases by 1.3, 2.3, and 2.5 times, respectively, while the permselectivity of H₂/N₂ and O₂/N₂ decreases by 35% and 6%, respectively. Compared with PEDK-BA, PEDK-AF possesses a larger increase in permeability for all the three gases and while there is no corresponding sharp decrease in permselectivity. The reason may be that substitution of the bulkier $-\text{C}(\text{CF}_3)_2-$ moiety for the $-\text{C}(\text{CH}_3)_2-$ moiety in the bisphenol segment leads to simultaneous packing disruption and inhibition of rotational motion. Thus, the permeability increases apparently while maintaining permselectivity without large decrease. This is just the same as the phenomena occurring in polyimides^[15,16].

The increased permeability of PEDK-PP may be primarily due to the disruption of chain packing. Since the large cardo-ring of phenolphthalein moiety may act as "spacers" in polymer backbone chain, the intersegmental chain packing is undoubtedly disrupted severely. The large group can also suppress the intrasegmental rota-

tion, which tends to raise the permselectivity. This results in a significant increase in permeability and relative small decrease in permselectivity. For example, its permeability of H_2 is 5.1 times than that of PEDK-2,7-DN, while the permselectivity of H_2/N_2 decreases by 52%. As shown in Table 4, the PEDK-CP is slightly more permeable than PEDK-PP. The reason is that the chemical structures are different between the two polymers, PEDK-CP has two methyl group. Usually, the introduction of methyl group in polymer will cause a large increase in permeability^[16]. However, no significant effect of methyl group on permeability is observed in this study. This may be due to the large phenolphthalein moiety already existing in the polymer. As the intersegmental packing is loose enough to penetrate the gas molecule for the "spacer" action of phenolphthalein moiety, the methyl group gives little contribution to disruption of chain packing. So, the permeability of PEDK-CP is somewhat similar with that of PEDK-PP.

CONCLUSION

Several poly(arylene ether diketone)s were prepared by the aromatic nucleophilic substitution polymerization of 4,4'-difluorobenzil with different bisphenols in the presence of anhydrous potassium carbonate in diphenylsulfone. The formation of the expected polymers can be proved by the FT-IR and NMR spectra. The solubility and glass transition temperature of these polymers are dependent on the bisphenols used in the synthesis. These polymers were characterized by excellent thermal stability together with good mechanical properties. Thus, poly(arylene ether diketone)s may be candidates for high-performance plastic materials. The permeability of the polymers for H_2 , O_2 and N_2 is also dependent on the bisphenol moiety. The increased permeability is primarily due to the disruption of chain packing. The large phenolphthalein moiety may act as a "spacer" to loose the chain packing, which results in a significant increase in permeability.

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