

Synthesis and Properties of Novel Poly(phthalazinone ether ketone ketone)

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ABSTRACT: A novel poly(phthalazinone ether ketone ketone) was prepared via the nucleophilic substitution polycondensation of bis-1,4-(4-chlorobenzoyl)benzene and 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one. The synthesized polymer exhibited high glass-transition temperature, excellent thermooxidative properties, and fair rheological properties. The polymer was soluble in some polar solvents. Electronic friction and membrane properties are also discussed. The results indicate that the polymer falls in the class of high temperature resistance engineering plastics. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 823–826, 2001

Key words: poly(aryl ether ketone); heterocyclic polymer; phthalazinone; activated dichloride

INTRODUCTION

Poly(aryl ether ketone)s are an important class of high-performance thermoplastics, which have high-temperature resistance, excellent mechanical properties, radiation stability and flammability. These polymers can be used as materials for composite matrices, adhesives, and electronic parts. Because of their outstanding properties, a great deal of effort has been expended to develop poly(aryl ether ketone)s during the past several decades.^{1–4} The typical commercially available poly(aryl ether ketone)s include poly(ether ether ketone) (PEEK), commercialized by ICI in the late 1980s, and poly(ether ketone ketone) (PEKK), commercialized by BASF and Hoechst. These polymers contain rigid aromatic rings that give them high glass-transition temperature (T_g) and superior dimensional stability. However, before these materials find extensive use, many prob-

lems such as poor solubility and high cost must be resolved.

In recent years, the synthesis of poly(aryl ether ketone)s from activated dichloro monomers instead of difluoro monomers has received considerable attention.^{5–8} In previous reports, we described the synthesis of poly(phthalazinone ether)s from 4,4-difluorobenzophenone.^{9–11} In this study we describe polycondensation using bis-1,4-(4-chlorobenzoyl)benzene instead of the difluoro monomer, giving a poly(phthalazinone ether ketone ketone) (PPEKK) with a new chemical structure. The polymer's chemical and physical properties are discussed.

EXPERIMENTAL

Materials

4-(4-Hydroxyphenyl)-2,3-phthalazin-1-one (DHPZ) was synthesized and recrystallized from ethanol.¹² Bis-1,4-(4-chlorobenzoyl)benzene (BCBB) was synthesized according to Hergenrother et al.¹³ and recrystallized from *N,N*-dimethylacetamide (DMAc). Anhydrous potassium carbonate, reagent grade *N,N*-dimethylacetamide, and chlorobenzene (MCB) were used without further purification.

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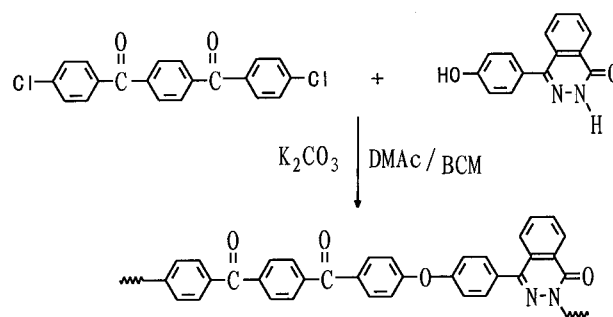
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Measurements

Infrared measurements were performed on a Perkin-Elmer 1600 FTIR spectrometer (Perkin-Elmer, Palo Alto, CA). The $^1\text{H-NMR}$ spectrum was recorded on a Varian Gemini 200 instrument (Varian Associates, Palo Alto, CA) using tetramethylsilane as an internal reference. The glass-transition temperature (T_g) was taken using a Du Pont 2000 differential scanning calorimeter (DSC; Du Pont, Wilmington, DE) at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen (200 mL/min). The T_g was taken as the midpoint of the change in the slope of the baseline. Thermal stability, as measured by weight loss, was determined using a Seiko TG/DTA 220 analyzer from 25 to 700°C at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen (200 mL/min). The inherent viscosity was determined using an Ubbelohde viscometer at a concentration of 0.5 g/dL in chloroform at 25°C . Wide-angle X-ray scattering (WAXS) was performed on a thin-film specimen with the X-ray diffractometer operating at 45 kV and 40 mA, using copper radiation with a flat sample holder and a graphite monochromator. The intensity was recorded on hard disc for the angular range $10\text{--}40^\circ\text{C}$ (2θ). The mechanical properties were determined at 25°C using a Shimadzu AG-2000A tester (Shimadzu, Japan) at a crosshead speed of 50 mm/min. The polymer was compression molded in a 55-mm^2 stainless mold using a hydraulic press equipped with heated platens. Five compact tensile specimens about $55 \times 6.0 \times 4.0$ mm were cut from the 55-mm^2 molding and tested, and the average value was reported. Surface resistivity and volume resistivity were tested on a ZC 36 electronic test instrument. A $55 \times 55 \times 4.0$ mm sample was prepared and used. The friction properties were performed on an M-200 friction test instrument and a $55 \times 6.0 \times 4.0$ mm sample was used. For the rheological tests, the polymer was dried in a vacuum oven at 140°C for 48 h prior to test. A Shimadzu AG-2000A capillary rheometer was used to perform the rheological characterization using a 20×2 mm [length (L) \times diameter (D) ($L/D = 10$)] capillary at a temperature range of $330\text{--}360^\circ\text{C}$. The shear rate range of $2\text{--}100$ mm/min was studied. The sample was added to the capillary as fast as possible and kept in the melt for 5 min before testing.

Polymer Synthesis

Polymerization was carried out as follows: to a 500-mL three-neck, round-bottom flask, equipped with a Dean-Stark trap, a thermometer, con-



Scheme 1

denser, nitrogen inlet/outlet, and stirrer, were added DMAc (350 mL), chlorobenzene (100 mL) as the azeotroping solvent, and anhydrous potassium carbonate as the catalyst (29.0241 g, 0.21 mol). A mixture of 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one (35.7360 g, 0.15 mol) and bis-1,4-(4-chlorobenzoyl)benzene (53.2815 g, 0.15 mol) were added to the reactor, then the mixture was heated to reflux by oil bath. After dehydration, the reaction was kept above 160°C for a further 10–30 h, until the desired viscosity polymer was obtained. The reaction mixture was filtered and slowly poured into a blender containing methanol while being well stirred. The obtained polymer was separated again by filtration. The polymer was dissolved in chloroform, filtered, and precipitated in methanol. The above-described purification procedure was repeated twice. The polymer was dried at 130°C under vacuum. The yield was generally higher than 87%.

RESULTS AND DISCUSSION

Polymer Synthesis

The high molecular weight poly(phthalazinone ether ketone) (PPEKK) with inherent viscosity of 0.61 dL/g was prepared by nucleophilic aromatic substitution polycondensation of bis-1,4-(4-chlorobenzoyl)benzene (BCBB) and 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one (DHPZ) as shown in **Scheme 1**. There are two kinds of active hydrogen in the asymmetric phthalazinone monomer, O—H and N—H. The phenolate anion and the aza nitrogen anion, formed by reaction with potassium carbonate as a base, underwent a nucleophilic displacement with bis-1,4-(4-chlorobenzoyl)benzene to form PPEKK. The nucleophilic displacement reaction was confirmed to proceed via a novel N—C coupling reaction by spectroscopic studies in an

Table I Properties of PPEKK

Property	Unit	Data
η_{inh}	dL/g	0.61
Glass-transition temperature	°C	245
5% Weight loss temperature in N ₂	°C	507
Tensile strength at yield	MPa	100.3
Tensile modulus	GPa	0.77
Flexural strength	MPa	167.6
Flexural modulus	GPa	2.9
Elongation at break	%	13.1
Surface resistivity	Ω	3.45×10^{15}
Volume resistivity	Ω cm	8.0×10^{16}
Melt index	g/10 min	<0.1
Vicat softening temperature	°C	242
Hardness	R	94
Density	g/cm ³	1.283

analogous system.¹⁴ In sharp contrast, formation of the N—C bond in aromatic systems usually proceeded under rather vigorous conditions.^{15,16}

The structure of PPEKK was confirmed by FTIR and ¹H-NMR. The FTIR spectrum of PPEKK showed a strong peak of the carbonyl group absorption at 1668 cm⁻¹; the peaks at 1592, 1496, and 1412 cm⁻¹ were phenyl group absorptions. The peak at 3200 cm⁻¹, attributed to the absorption of the hydroxy group of 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one, was not found. In the spectrum of PPEKK, the peak at 1095 cm⁻¹, attributed to the absorption of the C—Cl group of bis-1,4-(4-chlorobenzoyl)benzene, was very weak. The peak at 1240 cm⁻¹ was attributed to the C—O—C bond absorption. This implied that polycondensation had taken place, as expected. The ¹H-NMR spectrum of PPEKK showed three peaks from 7.1 to 8.6 ppm in chemical shift, which were assigned to the proton resonance of aryl groups.

The wide-angle X-ray scattering of PPEKK was compared to that of commercially available

Table II Solubility of PPEKK^a

Solvent	DMAc	CHCl ₃	DMF	DMSO	Pyridine
Solubility	±	+	±	-	+
Solvent	NMP	NB	TCE	THF	<i>o</i> -DCB
Solubility	+	+	+	±	-

^a +, fully soluble; ±, partially soluble; -, insoluble.

Table III Membrane Separation Property of PPEKK

Polymer	Water	PEG 12000 Rejection (%)
	Permeation Flux (kg m ² h ⁻¹)	
PPEKK	68	74

PEEK. Only a very broad diffraction trace was observed and no sharp peak was obtained. This demonstrates that PPEKK is amorphous in structure because of the incorporation of the phthalazinone moiety into the main chain. In this case, the regularity of the molecular chain is interrupted by the nonsymmetrical phthalazinone moiety, which provides better solubility but high melt viscosity.

Polymer Properties

Thermal properties of PPEKK were evaluated by thermogravimetry and DSC. PPEKK displayed good thermal stability. The temperature for 5% weight loss in nitrogen was 507°C. The T_g was found to be 245°C, which is much higher than that of PEEK, because of the incorporation of the rigid phthalazinone ring in its backbone. The tensile strength and flexural strength were tested with a Shimadzu AG-2000A tester. The results show that PPEKK has high tensile and flexural strength. The values of tensile and flexural strength were 100.3 and 167.6 MPa, respectively, which is a typical range for high-performance polymers. The test showed that surface resistivity and volume resistivity were $3.45 \times 10^{15} \Omega$ and $8.0 \times 10^{16} \Omega$ cm, respectively. Other properties of PPEKK are presented in Table I.

The solubility of PPEKK was tested at room temperature. Table II shows that PPEKK is soluble in chloroform, pyridine, nitrobenzene (NB), *N*-methyl pyrrolidinone (NMP), and 1,1,2,2-tetrachloroethane (TCE), but insoluble in dimethyl sulfoxide (DMSO)

Table IV Friction Properties of PPEKK

Polymer	Pressure (N)	μ	mm ³ N ⁻¹ m ⁻¹
PPEKK	100	0.42	4.03×10^{-5}
	200	0.55	
PTFE	100	0.21	6.84×10^{-3}
	200	0.22	
Nylon	100	0.40	3.30×10^{-3}
	200	0.50	

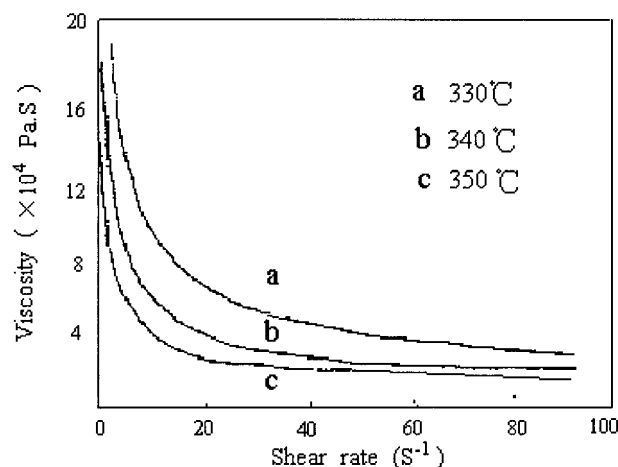


Figure 1 Melt viscosity of PPEKK.

and *o*-dichlorobenzene (*o*-DCB). A chloroform solution (10% solids) of PPEKK was centrifuged, and the decantate was positioned onto plate glass and dried at 25°C for 24 h to a tack-free film in a dust-proof chamber. After drying in a vacuum oven, a clean, tough, and flexible film was obtained.

The excellent solubility and film-forming properties of PPEKK make it potentially useful as a high-temperature membrane. A separation membrane of PPEKK was studied briefly and the results are presented in Table III. The separation membrane was prepared according to previously published methods,^{17,18} and water permeation flux was tested at room temperature. When the membrane was used to separate polyethylene glycol (PEG) with molecular weight 12,000 at room temperature, a high rejection was obtained. PPEKK has bright prospects as a potential material for high-temperature separation.

Under the same experimental conditions, compared with those of PTFE and nylon materials, the friction coefficient and friction wear coefficient of PPEKK were tested, the results of which are shown in Table IV. The study shows that the friction coefficient of PPEKK is almost the same as that of nylon, which is higher than that of PTFE, but the friction wear coefficient of PPEKK is much lower than that of PTFE and nylon.

The melt viscosity of PPEKK was measured at different temperature and shear rates.¹⁹ Figure 1 shows the melt viscosity curves at various run temperatures under different shear rates. PPEKK exhibits a high melt viscosity but, with increasing temperature and increasing shear rate, the melt

viscosity of PPEKK decreases quickly, and at 350°C PPEKK shows lower melt viscosity. Raising the process temperature above 350°C did not significantly change the melt viscosity.

CONCLUSIONS

A novel poly(phthalazinone ether ketone ketone) (PPEKK) containing the phthalazinone moiety in the polymer backbone was synthesized, which exhibited good mechanical properties, high glass-transition temperature, and excellent thermooxidative stability. The material has potential for use as a high-temperature separation membrane and friction wear resistance material.

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