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### CARDO POLYARYLETHERSULFONES AND POLYARYLETHETERKETONES BEARING ALKYL SUBSTITUENTS ON THE PHENYLENE UNIT

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# CARDO POLYARYLETHERSULFONES AND POLYARYLETHETERKETONES BEARING ALKYL SUBSTITUENTS ON THE PHENYLENE UNIT

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**Key Words:** Polyaryletherketone, Polyarylethersulfone, Substituents, Membrane materials Synthesis and Characterization, High Glass Transition Temperature

## ABSTRACT

A series of cardo polyaryletherketones and polyarylethersulfones containing alkyl substituents of a different kind, number and volume were synthesized from bis(4-nitrophenyl)ketone or bis(4-fluorophenyl)sulfone with various alkyl substituted phenolphthaleins by polycondensation using  $K_2CO_3$  as catalyst. Their chemical and aggregation structures were confirmed by FT-IR,  $^1H$ -NMR and WAXD. The resulting polymers were soluble in a variety of common polar solvents and, transparent, colorless, and tough films could be easily cast from 1,1,2-trichloroethane solution. Their tensile strength, elongation at break and tensile

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modulus were in the range of 70.5~97.1MPa, 4.49%~7.81%, and 1.69~2.27GPa, respectively. The prepared polymers had reasonably high glass transition temperatures at 207 to 269°C, and showed fairly good thermal stability with 5% thermal decomposition loss above 410°C.

## INTRODUCTION

Gas membrane separation technology has been found useful for numerous applications [1-4], such as hydrogen recovery from reactor purge gas, nitrogen enrichment, and water vapor removal from air, and stripping of carbon dioxide from natural gas, *et al.* Finding new membrane materials with high permeability and permselectivity is constantly essential to continue to advance this technology in the area listed above. Over the past decade, investigation on the synthesis of polymers for specific applications as gas separation membranes has become an active research field [5-8].

Polyaryletherketone (PEK-C) and Polyarylethersulfone (PES-C), obtained from phenolphthalein with bis(4-nitrophenyl)ketone and bis(4-chlorophenyl)sulfone, respectively, have been noted for their excellent mechanical toughness, electrical/insulating, thermo-oxidative stability, as well as high glass transition temperature (218°C and 259°C, respectively) [9], exhibiting potential used as coatings, adhesives, composites, molded parts, and toughening agents. In contrast to hydroquinone based polyetheretherketone(PEEK), which is insoluble even in polar aprotic solvent, PEK-C and PES-C are soluble in a few polar solvents such as DMF, NMP and chloroform. These characteristics enable PEK-C and PES-C to possibly serve not only as structural resins, but also as functional polymer membrane materials used in ultrafiltration, reverse osmosis, and high temperature gas separation.

The experimental results on gas permeability studies revealed that, in comparison with conventional glassy polymers, such as bisphenolA polysulfone [10], polycarbonate [11], and Polyimide (Kapton) [12], PEK-C and PES-C membranes possess better gas permeation properties [13], but from the viewpoint of practical application, their gas selectivity coefficient and permeability coefficient must be further improved.

In our previously reported paper [14], several chemical modifications were carried out to incorporate pendant amide and carboxyl groups onto the PEK-C backbone. The enhanced interchain interaction in the polymers due to intermolecular hydrogen bonds and ionic bonds leads to the polymers dense

packing density and restricted segmental motion, and thus results in extremely high gas permselectivity, but their permeability coefficients are also lowered to some extent.

The present work was undertaken to synthesize a series of new Polyaryl-ethersulfones and Polyaryletherketones via solution nucleophilic polycondensation. The systematic variations in chemical structure with different alkyl substituents on the phenylene unit were expected to result in interesting and useful physical properties, e.g., packing density and segmental motion of the polymer chain, and thus will significantly affect the gas permeation behavior through polymer membranes. Their thermal properties, solubilities, density and mechanical properties will also be described. For comparison, the unmodified PEK-C and PES-C were also prepared.

## EXPERIMENTAL

### Materials

Phenolphthalein (PPH) and 2',2''-dimethyl-phenolphthalein (DMPPH) were purchased from Beijing Chemical Works, and purified by recrystallization from 50:50(v/v) mixed solvent of ethanol and water, melting points are 262~263°C and 220~222°C, respectively; 2',2'',5',5''-tetramethyl-phenolphthalein (TMPPH) and 2',2''-diisopropyl-5',5''-dimethyl-phenolphthalein (IMPPH) were purchased from Fluka Chemical Corp., with melting points 239~240°C and 251~252°C, respectively, and used as received; bis(4-nitrophenyl) ketone (DNDPK) was prepared in our laboratory, m.p. 189~190°C; bis(4-chlorophenyl)sulfone (DCDPS) was purchased from Beijing Chemical Works, and purified by recrystallization from ethanol two times, m.p. 146~148°C; bis(4-fluorophenyl)sulfone (DFDPS) was purchased from Aldrich Chemical Corp., and used as received; dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF) were purified by vacuum distillation just before use; anhydrous potassium carbonate was finely powdered prior to use.

### Polymer Synthesis

#### *Synthesis of Polyaryletherketone Series Polymers*

The polyaryletherketones were prepared by the solution polycondensation of various bisphenols and DNDPK in DMSO. A typical procedure for PK-4 is presented as follows: 8.6108 g (0.02 mol) IMPPH, 5.4443 g (0.02 mol) DNBP, 2.9851 g (0.0216 mol) anhydrous K<sub>2</sub>CO<sub>3</sub>, 18 ml toluene and 16 ml DMSO were

added into a three-necked round bottom flask equipped with Dean-Stark trap, N<sub>2</sub> inlet, mechanical stirrer, and thermometer. A dark blue solution was formed. When the temperature was raised to 140°C, water began to be collected in the Dean-Stark trap. After toluene and water were distilled out, the reactant was heated gradually to 175°C, and allowed to react at this temperature for 12 hours to finally obtain a viscous pale green solution. The product was diluted with DMF, then precipitated in ethanol to separate white polymer. The polymer was dried at 100°C for 12 hours after the complete removal of inorganic salt by washing with boiling water for several times.

#### *Synthesis of Polyarylethersulfones*

A typical procedure for PS-2 is as follows: To a solution of 4.1462 g (0.03 mol) anhydrous K<sub>2</sub>CO<sub>3</sub>, 12 ml toluene and 11.8 ml DMSO, 4.8052 g (0.015 mol) DMPPH and 4.0833 g (0.015 mol) DFDPS were added. A slow stream of nitrogen was maintained throughout the whole reaction. The temperature was raised to 140°C to remove water formed by azeotropic distillation with toluene for about 2 hours, then the toluene was distilled out and the temperature was raised gradually to 175°C, allowed to react at this temperature for 4 hours and finally, a pale red viscous solution was obtained. After cooling, it was diluted with DMF and settled overnight. The supernatant liquid was coagulated in a mixed precipitant of ethanol and water to separate the white polymer. The polymer was washed successively with boiling water to remove the inorganic salt and dried in air at 100°C for 12 hours.

#### *Film Casting*

The polymer samples were dissolved in 1,1,2-trichloroethane(TCE) at a concentration of 8 wt%. The solution was cast onto a clean glass plate at room temperature for 8 hours, then the film was transferred to vacuum oven and dried further at 200°C and 10 mmHg for 48 hours. The film thickness is 35~40 μm.

#### **Measurements**

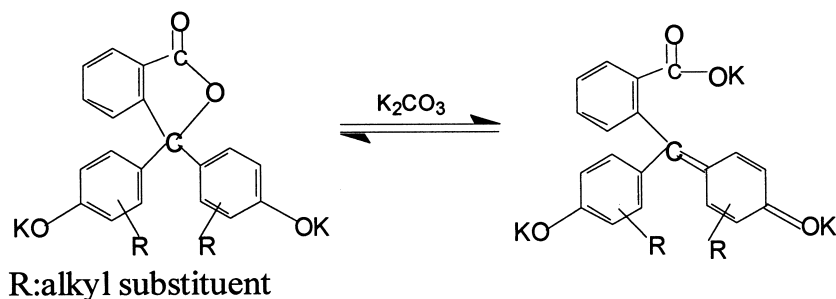
FTIR spectra were recorded on DIGLAB FTS-20E FTIR Spectrometer, and the film samples of 5μm in thickness were vacuum-dried at 180°C for at least 24 hours before measurement. <sup>1</sup>H-NMR spectra were obtained on a Unity-400 NMR spectrometer (Brucker). The samples were determined in DCCl<sub>3</sub>, using TMS as internal standard. Reduced viscosities were measured using a Ubbelohde Viscometer at a concentration of 0.5% (w/v) in DMF at 25±0.01°C. Wide-angle

X-ray diffraction (WAXD) measurements were performed on a D/Max-B X-ray diffractometer with Cu K $\alpha$  radiation having a wavelength of 1.54 Å. Glass transition temperatures ( $T_g$ ) were determined on Perkin-Elmer DSC-7, over a temperature interval of 100–400°C at a heating rate of 20°C/min. The  $T_g$ s were read at the middle of the change in the heating capacity. Thermogravimetric analyses (TGA) were made with Perkin-Elmer TGS-2 Instrument in the temperature of 50–650°C at a heating rate of 10°C/min in nitrogen atmosphere. Tensile properties were tested with a Instron-1211 Tension Tester at a strain rate of 5 mm/min at room temperature. The width and length of film samples were 5mm and 30mm, respectively.

## RESULTS AND DISCUSSION

Six new alkyl substituted cardo polyarylethersulfones and polyaryletherketones were easily synthesized by a solution of nucleophilic polycondensation of various bisphenols with bis((4-nitrophenyl)ketone or bis(4-halidephenyl)sulfone, using toluene to azeotrope the water formed (Scheme 1). In the process of polymerization reaction. All the above polymers were controlled to the same range of 0.52–0.72 dl/g so that an effective physical properties comparison could be made based only on the molecule structure. The conditions and results of the polymerization are listed in Table 1.

All three bisphenol monomers DMPPH, TMPPH, and IMPPH in this study contain phthalide groups, and are usually used as acid-base solution indicator like phenolphthalein (PPH). In the  $K_2CO_3$ /DMSO polymerization solution existed the following acid-base equilibrium (Scheme 2). These monomers presented in the form of quinoid and phenolic isomers and the equilibrium shift



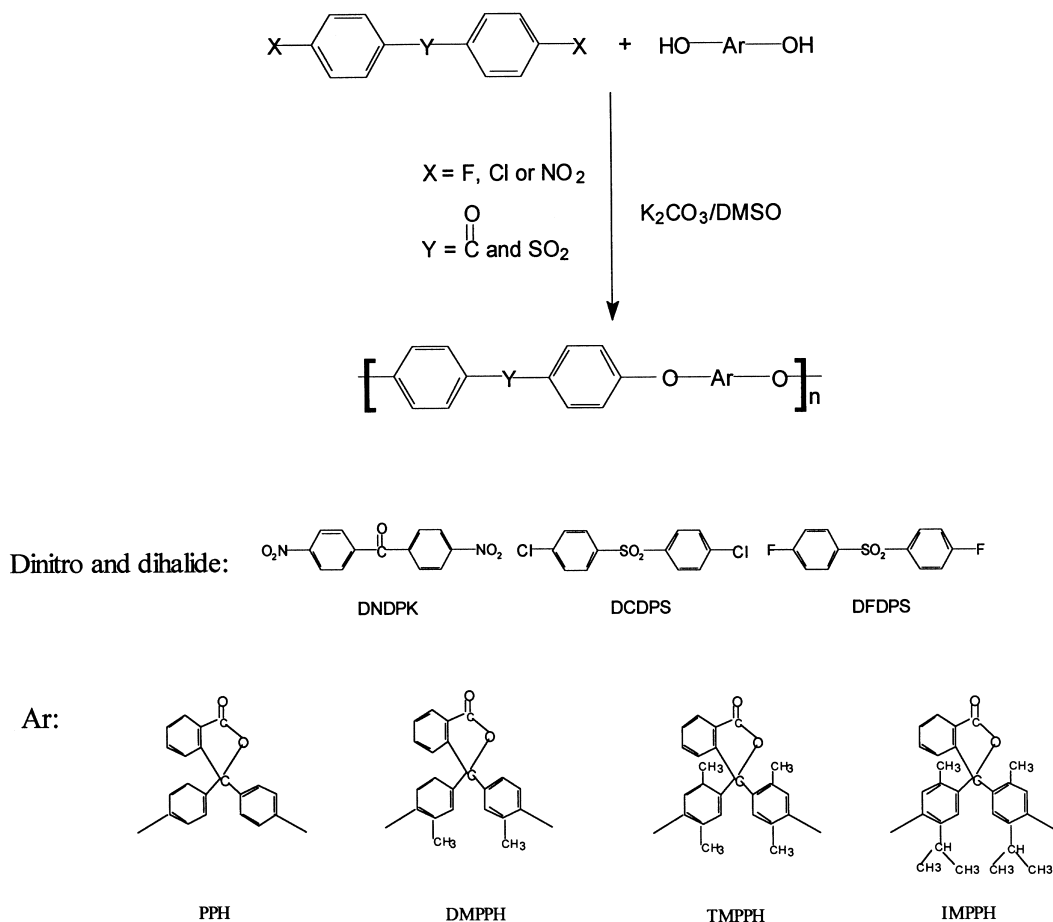
**Scheme 1.**

TABLE 1. Conditions and Results of Polymerization

Polymers	Monomers	Temp.	Time	$\eta_{RV}(\text{dl/g})$
PK-1	PPH + DNBP	175°C	3 hr	0.663
PK-2	DMPPH + DNBP	175°C	4 hr	0.625
PK-3	TMPPH + DNBP	175°C	8 hr	0.695
PK-4	IMPPH + DNBP	175°C	12 hr	0.518
PS-1	PPH + DCDPS	175°C	5 hr	0.619
PS-2	DMPPH + DCDPS	175°C	7 hr	0.722
PS-3	TMPPH + DCDPS	175°C	11 hr	0.629
PS-4	IMPPH + DFDPS	175°C	5 hr	0.574

toward the left with the polymerization proceeding. It was especially interesting to note that, for DMPPH and PPH, in the polymerization early stage, the reaction solution appeared purplish red, and the color gradually changed pale and become light red in the end. While for TMPPH and IMPPH, the solution color changed slowly from dark blue to pale green in the end. So, the observation of solution color change could be used as one of the simple methods to roughly judge the polymerization degree.

The replacements of hydrogen atoms with alkyl substituents *ortho* or *meta* to hydroxyl group were found to significantly decrease the bisphenols nucleophilic activities due to the steric hindrance effect, which was clearly reflected from the polymerization time and condition shown in Table 1. High molecular weight isopropyl substituted PK-4 polymer was formed through a 12 hour long reaction time from DNBP and IMPPH, whereas PS-4 could not be obtained from DCDPS and IMPPH even after 24 hours, polymerization, indicating that nitro group is more easily displaced than the chloro group. It has been reported that the difluoro monomer exhibit higher electrophilic activity than dichloro or dinitro monomer [15], which was also proved true in the polymerization of PS-4, as instead of DCDPS, the high molecular weight PS-4 was quickly formed from



Scheme 2.

DFDPS for only 2 hours. PS-1, as well as methyl substituted PS-2 and PS-3, could be successfully prepared from less expensive DCDPS. According to the polymerization time and conditions, the reactive activities of four monomers were estimated as PPH ~ DMPPH > TMPPH > IMPPH.

### Structure Characterization

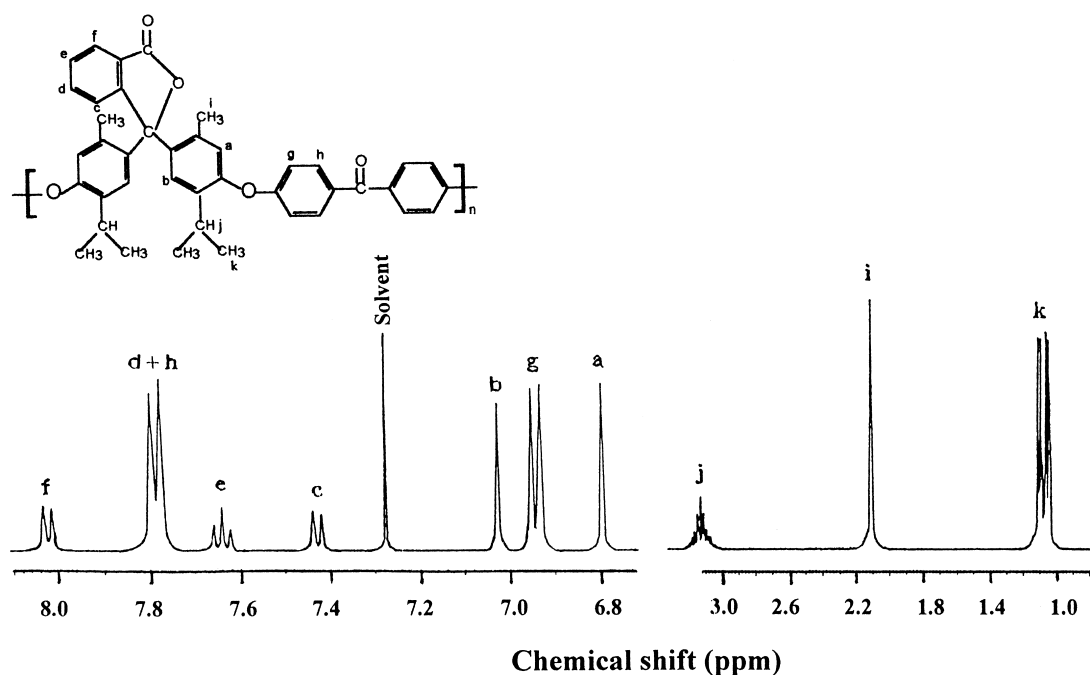
The formation of polyarylethersulfones and polyaryletherketones was confirmed from  $^1\text{H-NMR}$  and FTIR spectroscopy. The polymers exhibited characteristic IR absorptions of lactone carbonyl at  $1772\text{ cm}^{-1}$ , Ar-O-Ar at  $1245\text{ cm}^{-1}$ , Ar-CO-Ar at  $1645\text{ cm}^{-1}$  and  $\text{SO}_2$  at  $1320\text{ cm}^{-1}$ . Different from the unsubstituted PK-1 and PS-1, the steric hindrance of methyl and isopropyl made phenyl C=C



absorption split into a doublet at  $1592\text{ cm}^{-1}$  and  $1572\text{ cm}^{-1}$ , and Ar-O-Ar absorption also split into doublet at  $1232\text{ cm}^{-1}$  and  $1256\text{ cm}^{-1}$ . A typical  $^1\text{H-NMR}$  spectrum of PK-4 was presented in Figure 1. The heptet at  $3.094\text{ ppm}$  and the singlet at  $1.044\text{ ppm}$  were assigned to H atom of CH and  $\text{CH}_3$  in isopropyl group, respectively, and the singlet at  $1.075\text{ ppm}$  was attributed to the H atom of methyl meta to ether bond. The detailed IR and  $^1\text{H-NMR}$  data were listed in Tables 2 and 3.

An important point to note is that no ester carbonyl absorption at about  $1730\text{ cm}^{-1}$  was found in FT-IR spectra for all the prepared polymers, demonstrating that the pendant cardo phthalide groups of the polymers existed in the lactone form.

Wide-angle X-ray diffractograms of PEKs series polymers are illustrated in Figure 2. These polymers displayed amorphous nature due to the presence of the packing disruptive cardo phthalide groups and alkyl substituents. It could be seen from Figure 2 that the PK-2 and PK-1 had a similar reflection hump, but the humps of PK-3 and PK-4 broadened obviously, indicating that the packing regularity of the polymers decreased greatly with the increase of number and volume of alkyl substituents.







**Figure 1.**  $^1\text{H-NMR}$  spectrum of PK-4.

TABLE 2. Spectropy Data of the Polyaryletherketones Prepared

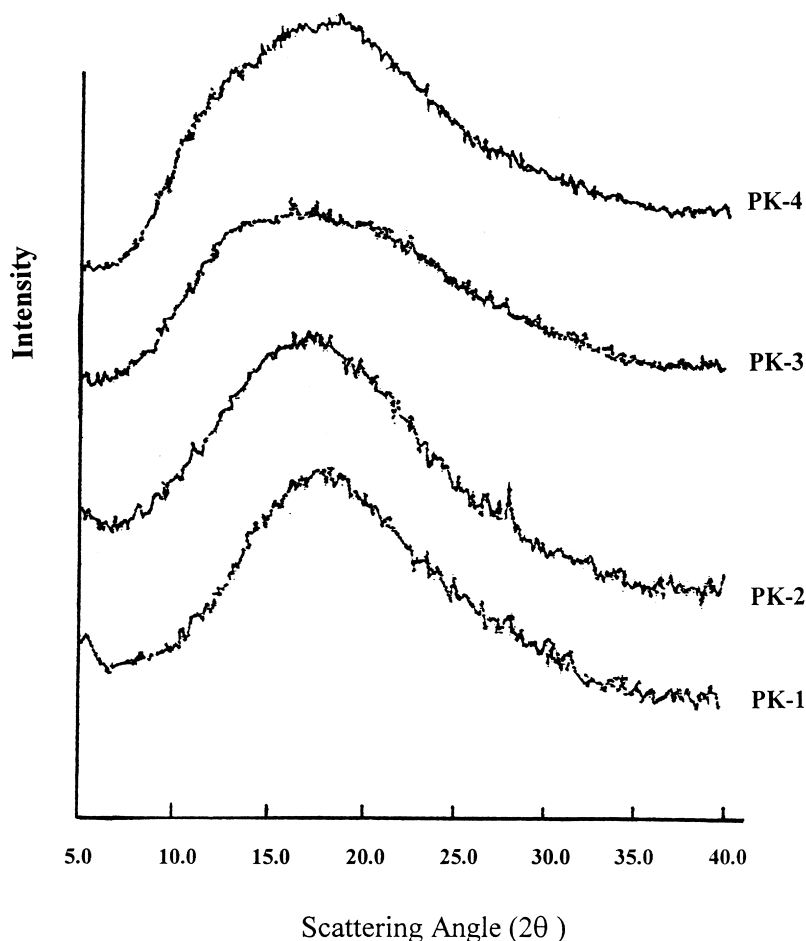
Polymer	IR(cm <sup>-1</sup> )	<sup>1</sup> H-NMR( $\delta$ , ppm)
PK-1	1773(Lactone carbonyl), 1654 (Ar-CO-Ar), 1242(C-O-C), 754 (1,2-Ar), 838(1,4-Ar).	6.91~7.89(m, 20 H, Ar-H).
PK-2	2923 and 2854(Ar-CH <sub>3</sub> ), 1773 (Lactone carbonyl), 1654(Ar- CO-Ar), 1241(C-O-C), 752(1,2 -Ar), 842(1,4-Ar), 813(1,2,4 -Ar).	2.2(s, 6H, CH <sub>3</sub> ), 6.94(s, 2H, Ortho to CH <sub>3</sub> ), 6.92 (d, 2H, ortho to -O-), Others(Ar-H).
PK-3	2923 and 2854(Ar-CH <sub>3</sub> ), 1773 (Lactone carbonyl), 1654(Ar- CO-Ar), 1263 and 1239(C-O-C), 752(1,2-Ar), 841(1,4-Ar), 892 (1,2,4,5-Ar).	2.2(s, 12H, CH <sub>3</sub> ), 6.94(s, 2H, Ortho to CH <sub>3</sub> and -O-), 6.82(s, 2H, Othor to CH <sub>3</sub> and quarterary atom), Others(Ar-H).
PK-4	2961, 2931 and 2869(CH <sub>3</sub> ), 1381 and 1366 (Isopropyl) 1773(Lactone carbonyl), 1654 (Ar-CO-Ar), 1269 and 1231 (C-O-C), 762(1,2-Ar), 853(1, 4-Ar), 898(1,2,4,5-Ar).	1.044(d, 12H, CH <sub>3</sub> ), 3.094 (m, 2H, CH of isopropyl), 1.075(s, 6H, Ar-CH <sub>3</sub> ), 7.017(s, 2H, Ortho to iso- propyl and quarterary carbon atom), 6.784(s, 2H, Ortho to -O- and isopropyl).

TABLE 3. FTIR Spectra Data of the Polymers Synthesized

PS-1		PS-2		PS-3		PS-4	
cm <sup>-1</sup>	group	cm <sup>-1</sup>	group	cm <sup>-1</sup>	group	cm <sup>-1</sup>	group
3030	Ar-H	3030	Ar-H	3030	Ar-H	3030	Ar-H
		2920	Ar-CH <sub>3</sub>	2925	Ar-CH <sub>3</sub>	2961	Ar-CH <sub>3</sub>
		2855		2866		2929	Isopropyl
						2869	
1771	C=O	1771	C=O	1771	C=O	1771	C=O
1585	phenylene	1585	phenylene	1592	phenylene	1593	phenylene
				1572		1568	
1323	SO <sub>2</sub>	1323	SO <sub>2</sub>	1323	SO <sub>2</sub>	1325	SO <sub>2</sub>
1244	Ar-O-A	1253	Ar-O-Ar	1260	Ar-O-Ar	1256	Ar-O-Ar
		1231		1230		1232	
1465		1465		1464		1464	
756	1,2-Ar	751	1,2-Ar	753	1,2-Ar	755	1,2-Ar
835	1,4-Ar	836	1,4-Ar	835	1,4-Ar	835	1,4-Ar
		813	1,2,4-Ar	893	1,2,4,5-Ar	896	1,2,4,5-Ar

### Physical Properties

The solubility of the polymers was evaluated qualitatively and the results are presented in Table 4. All the polymers prepared are easily soluble in Polar solvents such as NMP, DMF and chloroform at room temperature. With the incorporation of bulky alkyl substituents on the phenylene units, the polymers revealed an enhanced solubility. In addition to the above-mentioned high polar solvents, multiple- substituted polymers were also soluble in less polar solvent



**Figure 2.** Wide-angle X-ray diffraction patterns of polyaryletherketones.

such as THF. PK-4 and PS-4 were even soluble in acetone. This may be attributed to the existence of the bulky isopropyl groups that loosen the chain packing and allow the solvent molecules to diffuse into the polymer chain more easily.

These polymers could readily be cast into free-standing flexible, tough and colorless film from the 1,1,2-trichloroethane (TCE) solution. The tensile testing data measured at room temperature revealed that the flexible films possessed tensile moduli of 1690–2270MPa, tensile strength of 70.5–97.1MPa and the elongation at break of 4.49%–7.81%.

The thermal behavior of these polymers was evaluated by differential scanning calorimetry (DSC) and TGA under nitrogen atmosphere. As well known, the glass transition temperature ( $T_g$ ) can be corresponded to the onset of

TABLE 4. Solubilities of the Polymers

Solvent	DMF	NMP	HCCl <sub>3</sub>	TCE	THF	Acetone	CCl <sub>4</sub>	ethanol	Toluene
PK-1	++	++	++	++	+h	--	--	--	--
PK-2	++	++	++	++	+h	--	--	--	--
PK-3	++	++	++	++	++	+h	--	--	--
PK-4	++	++	++	++	++	++	+h	--	--
PS-1	++	++	++	++	+h	--	--	--	--
PS-2	++	++	++	++	+h	--	--	--	--
PS-3	++	++	++	++	++	+h	--	--	--
PS-4	++	++	++	++	++	++	+h	--	--

- a) Solubility: ++, soluble at room temperature; +h: soluble on heating; --, insoluble even on heating
- b) DMF: N,N-dimethylformamide; THF: tetrahydrofuran; NMP: N-methylacetamide; TCE: 1,1,2-trichloroethane

large-scale molecular motion and used as the measure of polymer chain rigidity. The data in Table 6 showed that the T<sub>g</sub>s of PESs series polymer were significantly higher than that of PEKs series, indicating that the SO<sub>2</sub> group resulted in stronger polymer chain rigid than CO group. Compared with the unmodified PS-1, dimethyl-substituted PS-2 displayed a slightly lower T<sub>g</sub> by 14°C, whereas PS-4, which has dimethyl and diisopropyl substituted simultaneously on the phenylene, exhibited the lowest T<sub>g</sub> at 230°C. This may be due to the fact that the existence of substituents forced the polymer chain apart from another, and the wider chain spacing was favorable for the polymer chain motion. However, different from PS-2 and PS-4, the PS-3, which has four methyl groups on a phenylene, showed an increased T<sub>g</sub> by 10°C. The reason why the tetramethyl-substituted polymers possess higher T<sub>g</sub> is not completely clear. Similar phenomenon

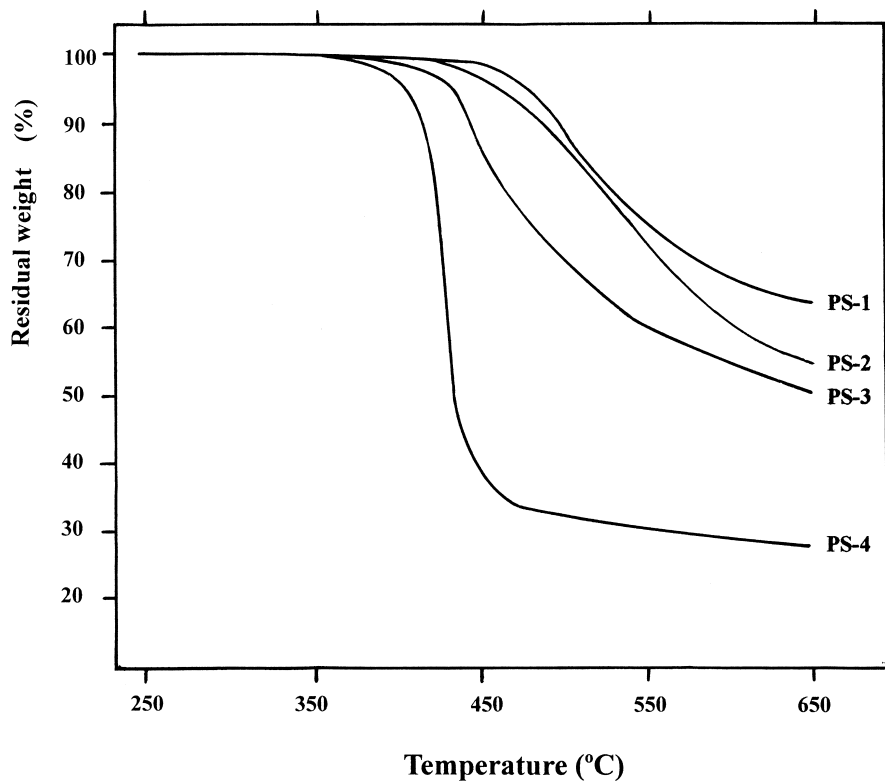
TABLE 5. Thermal Properties of Polymers Prepared

Polymer	T <sub>g</sub>	T <sub>5</sub>	T <sub>10</sub>	T <sub>30</sub>	RW(%)
PS-1	259	472	505	573	63
PS-2	245	459	486	552	54
PS-3	269	431	443	493	51
PS-4	230	410	421	426	28
PK-1	218	482	517	588	69
PK-2	207	462	491	567	57
PK-3	224	434	451	496	52
PK-4	210	426	436	454	31

T<sub>5</sub>, T<sub>10</sub> and T<sub>30</sub> are referred to the temperature at 5%, 10% and 30% weight loss, respectively; RW is referred to the residual weight percentage at 650°C.

had also been found from the substituted Bisphenol A polysulfone by Koros and Paul, who explained the reason as that the symmetric substitution resulted in a larger chain stiffening effect than the asymmetric substitution [16].

The TGA curves of PESs series polymers are illustrated in Figure 3. The influences of alkyl substitution on the thermal decomposition weight loss were presented in Table 6. These data indicated that the incorporation of alkyl group on phenylene led to a decrease in the decomposition temperature. For example, the temperature at 10% weight loss decreased from 505°C of unmodified PS-1 to 421°C of PS-4, and the residual weight at 650°C also decreased from 63% to 28%. In spite of this, these substituted polymers still possessed fairly good thermal stability and could be ranked among the heat-resistant functional polymer membrane materials.



**Figure 3.** Thermogravimetric curves of cardo polyarylethersulfones.

**TABLE 6.** Tension Properties of the Polymers

Polymer	Strength (MPa)	Elongation at break(%)	Moduli(GPa)
PK-1	97.1	7.81	2.27
PK-2	91.2	6.31	1.94
PK-3	89.8	6.04	1.82
PK-4	89.4	7.48	1.69
PS-1	91.3	6.99	2.20
PS-2	80.3	5.49	2.01
PS-3	81.7	5.07	1.92
PS-4	70.5	7.01	1.82

## CONCLUSION

Six linear high molecular weight cardo polyarylethersulfones and polyaryletherketones with various pendant alkyl substituents were readily prepared in the presence of potassium carbonate in DMSO without any side reaction. The prepared polymers had reduced viscosities in the range of 0.52–0.72 dl/g. The substituted polymers displayed obviously improved solubility in a variety of organic solvents and could be cast into flexible and tough films from their solution. These polymers have  $T_g$ s between 207°C–269°C, and showed fairly good thermal stability. The resulting polymers are expected to possess excellent gas permeation and separation properties, and thus will become a class of promising candidates for new high temperature gas separation membrane materials.

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