

# Novel Polyaryletherketones Containing Various Pendant Groups. I. Synthesis and Characterization

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**ABSTRACT:** Novel high glass transition temperature polyaryletherketones, containing pendant amido, alkyl, and carboxyl groups with reduced viscosity above 0.54 dL/g, were synthesized via solution nucleophilic polycondensation reaction of phenolphthalin, 2',2''-diisopropyl-5',5''-dimethylphenolphthalin, and 3,3'-bis(4-hydroxyphenyl)isobenzopyrrolidone with bis(4-nitrophenyl)ketone in the presence of potassium carbonate. By ion exchange with Na<sup>+</sup> and K<sup>+</sup>, four ionomers were also prepared. A new monomer simultaneously containing carboxyl and alkyl substituents was synthesized by reduction reaction of 2',2''-diisopropyl-5',5''-dimethyl-phenolphthalein. The resulting polymers were soluble in a few polar aprotic solvents; transparent, colorless, and tough films could easily be cast from DMF or DMSO solution. The mechanical properties of the films were excellent; and their tensile strength, elongation at break, and tensile moduli were in the range of 67.1–97.1 MPa, 7.8–165%, and 1.47–2.27 GPa, respectively. The prepared polymers showed fairly good thermal stability and reasonably high glass transition temperatures above 210°C. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1127–1135, 1997

## INTRODUCTION

In stiff-chain glassy polymers, separation of smaller molecules such as hydrogen from larger molecules such as nitrogen through the membrane is mainly affected by the packing density of the polymer chains, which determines the diffusibility of the gas molecules. Investigation of the synthesis of polymers for specific use as gas separation membranes has become an active research area in recent years.<sup>1–5</sup>

Phenolphthalein (PPH) based polyaryletherketone (PEK-C) is an amorphous polymer (prepared in our laboratory<sup>6</sup>) that exhibits excellent mechanical properties, thermal stability, high glass transition temperature ( $T_g$ ), as well as good

solubility in polar aprotic solvents such as DMF, DMSO, and chlorohydrocarbons. These characteristics enable the PEK-C to possibly serve not only as structural materials but also as functional polymer materials.

Several modifications based on PEK-C have been reported previously,<sup>7,8</sup> including sulfonation, bromination, and quaternarization; some of them have been used for microfiltration and ultrafiltration membranes. The experimental results on gas permeability studies revealed that, in comparison with conventional glassy polymers, such as bisphenol-A polysulfone, polycarbonate, and polyimide (Kapton), PEK-C possesses better gas permeation properties.<sup>9</sup> But its gas selectivity coefficient and permeability coefficient must be further improved for practical application in nitrogen enrichment and hydrogen recovery fields.

For this reason, the present work was undertaken to synthesize a series of novel PEK-Cs con-

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taining various pendant groups. For comparison, the unmodified PPH based PEK-C was also prepared. The introduction of amido, alkyl, carboxyl, and carboxylate groups was expected to result in interesting and useful properties, for example, high glass transition temperature, good solubility, good mechanical properties, and excellent gas permeation properties. And the last feature might offer possible application in the gas separation membrane field.

## EXPERIMENTAL

### Materials

PPH was purchased from Beijing Chemical Works and was purified by recrystallization from a 50 : 50 (v/v) mixed solvent of ethanol and water (mp 262–263°C). 2',2''-Diisopropyl-5',5''-dimethyl-phenolphthalein (IMPPH) was purchased from Fluka Chemical Corp. (mp 251–252°C) and was used as received. Bis(4-nitrophenyl)ketone (DNBP) was prepared in our laboratory (mp 189–190°C). DMSO and DMF were purified by vacuum distillation just before use. Anhydrous potassium carbonate was finely powdered prior to use.

### Monomer Synthesis

#### IMPPL

IMPPL (42.8 g), 45 g solid NaOH, 400 mL distilled water, and 35 g zinc powder were charged into a round bottom flask, fitted with a mechanical stirrer and thermometer, to form a purplish red solution. The reaction mixture was stirred at room temperature for 1 h, heated to 60°C, and stirred for an additional hour. It was observed that the solution faded gradually to being colorless. Upon cooling, the product was poured into aqueous hydrochloric acid and filtered to separate the white solid. The white solid was extracted with 200 mL boiling distilled water for 0.5 h and hot filtered. By cooling the filtrate the white floccy precipitate was collected and dried.<sup>10</sup> The yield was 85.1%.

The synthesis of PPL was similar to that of IMPPL.

#### 3,3'-Bis(4-hydroxyphenyl)isobenzopyrrolidone

PPH (100 g) was dissolved in 1000 mL of 28% aqueous ammonia and allowed to stand at room temperature for 20 days. When the color changed

to nearly colorless, the solution was poured into a mixture of ice and concentrated hydrochloric acid and the product was washed with water to neutrality. The product was recrystallized from a 50 : 50 (v/v) mixed solvent of ethanol and water, and the yield was 91%.<sup>11</sup>

### Polymer Synthesis

#### PEK-HPP

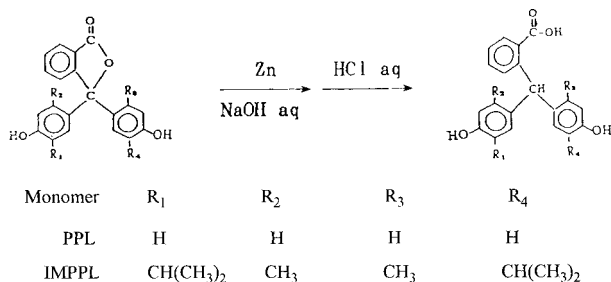
HPP (6.3468 g, 0.02 mol), 5.4443 g (0.02 mol) DNBP, 2.9851 g (0.0216 mol) anhydrous K<sub>2</sub>CO<sub>3</sub>, 18 mL toluene, and 16 mL DMSO were added into a three-necked round bottom flask equipped with a Dean–Stark trap, N<sub>2</sub> inlet, mechanical stirrer, and thermometer. A dark blue solution was formed. When the temperature was raised to 140°C, water began to be collected in the Dean–Stark trap. After toluene and water was distilled out, the reactant was heated gradually to 175°C and allowed to react at this temperature for 3 h to finally obtain a viscous solution. The product was diluted with DMF, then precipitated in ethanol to separate the white polymer. The polymer was dried at 100°C for 12 h after complete removal of inorganic salt by washing with boiling water several times. There was a 96% yield.

#### PEK-pPL

PPL (4.8052 g, 0.015 mol) 4.0833 g (0.015 mol) DNBP, 4.1462 g (0.03 mol) anhydrous K<sub>2</sub>CO<sub>3</sub>, 12 mL toluene, and 11.8 mL DMSO were added into a 150-mL three-necked round bottom flask to make a solution of about 25% solid content. 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 h. Then the toluene was distilled out and the temperature was raised gradually to 175°C. It was allowed to react at this temperature for 4 h and finally a 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 hydrochloric acid 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 10 h (yield 94%).

The synthesis of IMPEK-L was similar to that of PEK-L.

To obtain Na<sup>+</sup>-type and K<sup>+</sup>-type ionomers



**Scheme 1** Synthesis and structures of two bisphenols containing a carboxyl group.

PEK-L and IMPEK-L were first ground into powder, then they were soaked with aqueous solutions of sodium hydroxide or potassium hydroxide. After equilibrating the polymer with the solution for about 24 h, the solid was rinsed with distilled water to remove the excess electrolytes and then dried.

### Film Casting

The polymer samples, except PEK-Na<sup>+</sup> and PEK-K<sup>+</sup>, were dissolved in DMF at a concentration of 8 wt %. The solution was cast onto a clean glass plate at 60°C in an oven for 8 h, then the film was transferred to vacuum oven and dried further at 200°C and 10 mmHg for 48 h. For PEK-Na<sup>+</sup> and PEK-K<sup>+</sup>, the samples were dissolved in DMSO at a concentration of 10 wt %. The solution was cast onto a glass plate and dried at 100°C for 10 h, then at 200°C and 10 mmHg in a vacuum oven for additional 48 h. The films were 35–40 μm thick.

### Measurements

Elemental analyses were performed on an 1106 elemental analysis instrument (Italy).

FTIR spectra were recorded on Digilab FTS-20E FTIR spectrometer. Film samples of 5-μm thickness were vacuum dried at 180°C for at least 24 h before measurement.

Glass transition temperatures were determined on a Perkin–Elmer DSC-7, over a temperature interval of 100–400°C at a heating rate of 20°C/min.

Reduced viscosities were measured using a Ubbelohde viscometer at a concentration of 0.5% (w/v) in DMF at 25 ± 0.01°C.

Thermogravimetric analyses (TGA) were made with a Perkin–Elmer TGS-2 instrument at the temperature of 50–650°C at a heating rate of 10°C/min in a 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 the film samples were 5 and 30 mm, respectively.

## RESULTS AND DISCUSSION

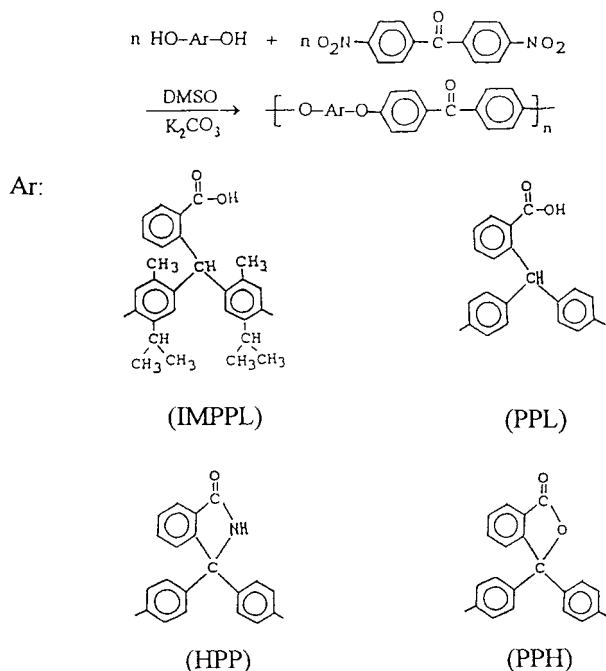
### Monomer Synthesis

As shown in Scheme 1, PPL and a new polymerization-grade monomer, IMPPL, were prepared by the reduction of PPH and IMPPH with zinc powder in aqueous NaOH solution, followed by neutralization with dilute hydrochloric acid.

The chemical structures of the three monomers synthesized (HPP, PPL, and IMPPL) were assigned on the basis of elemental analysis and FTIR. The disappearance of C=O absorption corresponding to a lactone group indicated that the reduction reactions of PPH and IMPPH were very complete. The physical characteristics and spectra data are given in Table I.

**Table I** Physical Characteristics and Spectra Data of Bisphenols Synthesized

Bisphenols	Yield (%)	mp (°C)	Elemental Analysis			FTIR (cm <sup>-1</sup> )
				C (%)	H (%)	
HPP	90.6	283–284	Calcd	75.70	4.76	1711 (C=O of lactam)
			Found	75.73	4.74	1462 (quarternary carbon)
PPL	85.1	236–237	Calcd	74.99	5.04	1694 (C=O of associated carboxyl group), 1600 (Ar)
			Found	75.08	4.98	
IMPPL	82.7	209–210	Calcd	78.85	6.15	1690 (C=O of associated carboxyl group), 1600 (Ar)
			Found	78.91	6.17	2927 and 2869 (Ar—CH <sub>3</sub> ), 2960 (CH <sub>3</sub> of isopropyl)



**Scheme 2** Synthesis of the polyaryletherketones.

### Polymer Synthesis

Unmodified PPH based PEK-C and three novel PEKs containing various pendant groups were synthesized by the conventional solution nucleophilic polycondensation reaction of corresponding bisphenols with dinitro monomer (DNBP), using toluene to azeotrope the water formed (see Scheme 2). The results of polymerization are summarized in Table II.

In the process of the polymerization reaction, all the above polymers were controlled to almost the same molecular weight so that an effective comparison could be made based only on the molecule structure. According to the polymerization time, the reaction activities of four monomers were estimated as PPH ~ HPP ~ PPL ≫ IMPPL. The fact that IMPPL was far less active than the other three monomers could be due to the steric

hindrance of isopropyl and methyl substituents ortho or meta to the hydroxyl group. Considering the carboxyl group in every PPL or IMPPL molecule, in order to synthesize high molecular weight PEK-L and IMPEK-L, potassium carbonate must be in excess of at least 100% to ensure all hydroxyl groups became phenoxide.

### Structural Characteristics

The structures of the polymers synthesized were confirmed from FTIR spectroscopy. The IR spectra of PEK-C exhibited the characteristic absorption of a lactone group at  $1772 \text{ cm}^{-1}$ . For PEK-L and IMPEK-L it was observed that the C=O band of the carboxyl group was split into a doublet. The peak at  $1725 \text{ cm}^{-1}$  was assigned to the C=O of the free acid form; the other at  $1694 \text{ cm}^{-1}$  corresponded to the C=O of the hydrogen-bonded carboxyl group. The experimental result showed the intramolecular and intermolecular hydrogen bond in PEK-L and IMPEK-L. Because no ester group was found in the IR spectra, this meant in the DMSO/ $\text{K}_2\text{CO}_3$  system, the  $\text{COO}^-$  did not participate in the nucleophilic polycondensation reaction with the activated dinitro monomer (DNBP). Furthermore, if  $\text{COO}^-$  could also participate in the polymerization like the phenoxide group, PPL and IMPPL would behave as a trifunctional monomer and a crosslink reaction would have taken place during the nucleophilic polycondensation of PPL and IMPPL with DNBP. But in fact, the PEK-L and IMPEK-L obtained were high molecular weight linear polymers. The detail IR spectra data are listed in Table III.

To elucidate the occurrence of a hydrogen bond in PEK-H, the differential temperature FTIR spectra are given in Figure 1. The  $1716 \text{ cm}^{-1}$  absorption was attributed to the free C=O stretching vibration of lactam. As the interaction between the hydrogen atom and the oxygen atom of the lactam group lowered the force constant of the

**Table II** Synthesis of Polyaryletherketones

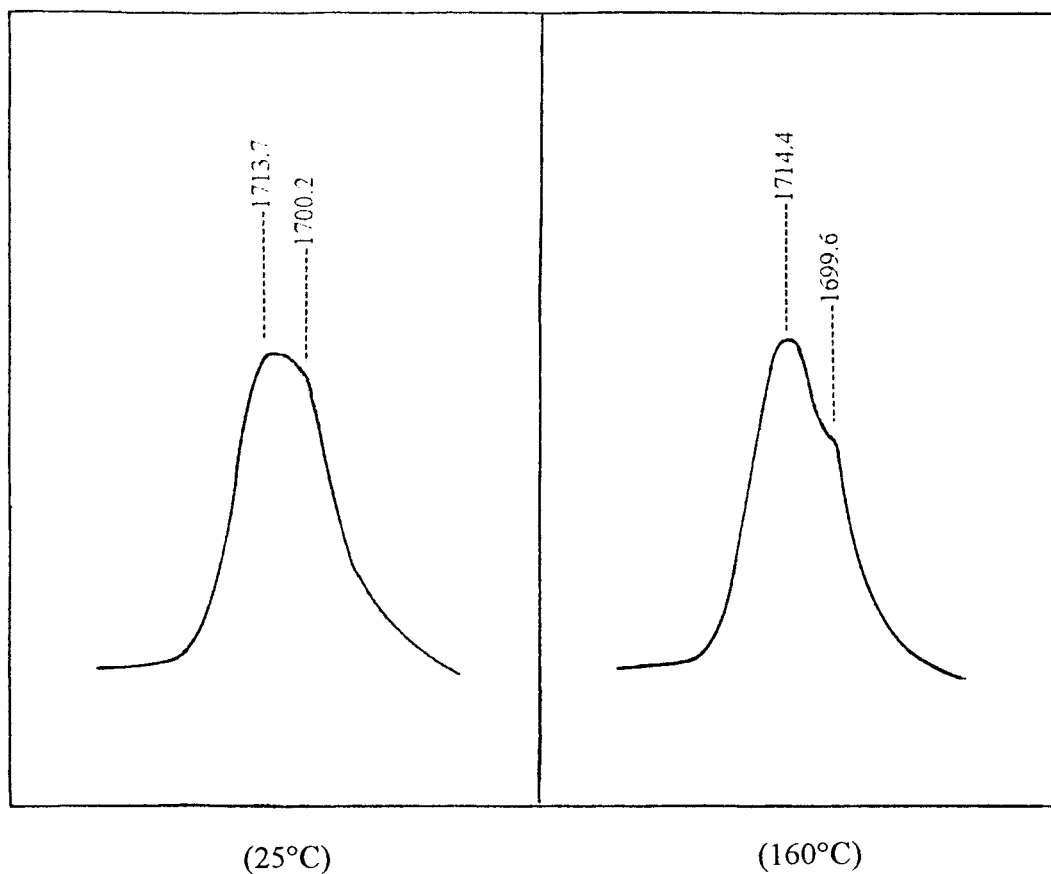
Polymer	Monomer	Reaction Time (h)	RV (dL/g)	Yield (%)	Color
PEK-C	PPH + DNBP	3	0.663	95	White
PEK-H	HPP + DNBP	3	0.544	91	White
PEK-L	PPL + DNBP	3	0.681	96	White
IMPEK-L	IMPPL + DNBP	10	0.622	96	White

RV, reduced viscosity.

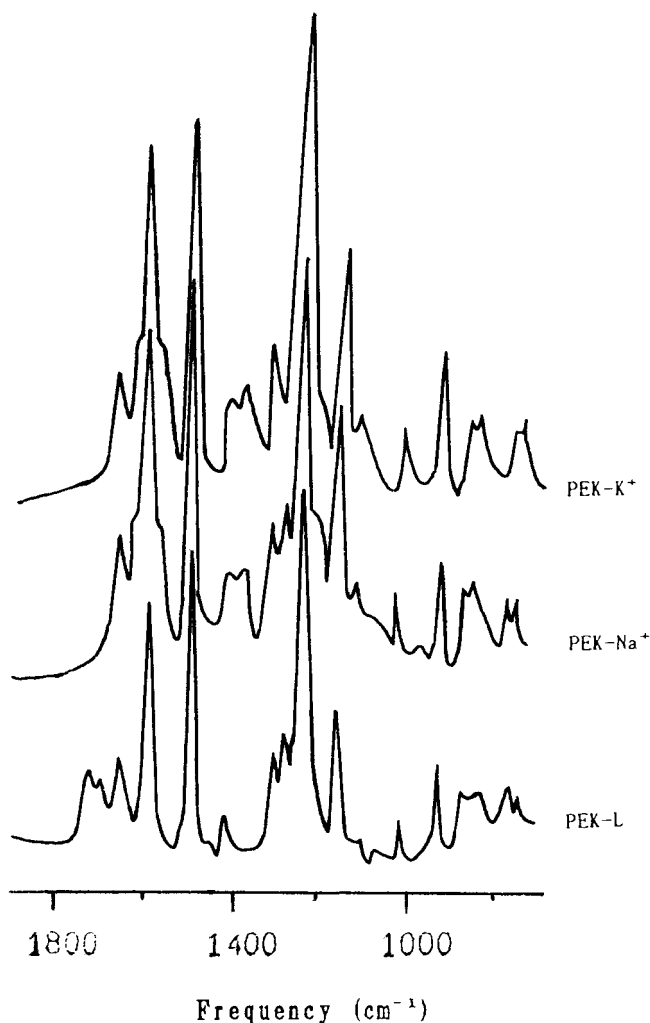
**Table III FTIR Spectra Data of Polymers Synthesized**

PEK-C		PEK-H		PEK-L		IMPEK-L	
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
				2928	(Ar) <sub>3</sub> CH	2960	iso CH <sub>3</sub> <sup>a</sup>
						2927	Ar—CH <sub>3</sub>
						2869	
1773	C=O of lactone	1716	Free C=O	1722	Free C=O	1725	Free C=O
		1691	Bonded C=O	1702	Bonded C=O		Bonded C=O
1586	Ar	1593	Ar	1592	Ar	1599	Ar
1488		1498		1499		1575	
1245	Ar—O—Ar	1242	Ar—O—Ar	1244	Ar—O—Ar	1262	Ar—O—Ar
						1229	
762	1,2-Ar	763	1,2-Ar	764	1,2-Ar	766	1,2-Ar
838	1,4-Ar	853	1,4-Ar	843	1,4-Ar	852	1,4-Ar
						898	1,2,4,5-Ar

<sup>a</sup> CH<sub>3</sub> of isopropyl.



**Figure 1** Differential temperature FTIR spectra of PEK-H.



**Figure 2** FTIR spectra of PEK-L and its ionomers.

C=O bond, the absorption shifted toward a lower wave number. As shown in Figure 1, a new peak at  $1699\text{ cm}^{-1}$  appeared. When the measurement temperature was raised from 25 to  $160^{\circ}\text{C}$ , the en-

hanced molecular mobility allowed the partial hydrogen bond to be broken, so that the absorption peak corresponding to the hydrogen-bonded carbonyl group decreased significantly.

A comparison of IR spectra of PEK-L as well as its  $\text{Na}^+$ -type and  $\text{K}^+$ -type ionomers is given in Figure 2. The disappearance of the original doublet at  $1725$  and  $1694\text{ cm}^{-1}$  after the  $\text{H}^+$  exchange with  $\text{Na}^+$  or  $\text{K}^+$  illustrated that the doublet corresponded to the C=O of the carboxyl group but not the ester group, and that the ion exchange with  $\text{Na}^+$  or  $\text{K}^+$  was rather complete. The new absorptions at  $1550\text{--}1610$  and  $1350\text{--}1430\text{ cm}^{-1}$  were attributed to the asymmetric stretching vibration ( $\text{COO}^-$ ) and symmetric stretching vibration ( $\text{COO}^-$ ), respectively.

### Solubility Behavior of Polymers

The data in Table IV clearly reveal the influence of interchain interaction on the solubility of the polymers in different solvents. For example, PEK-C could readily dissolve in chloroform and tetrahydrofuran (THF); but PEK-H, PEK-L, and their ionomers capable of formation of an interchain hydrogen bond and ionic bond did not dissolve in them. They were soluble in more polar aprotic solvents. As shown in Table IV, PEK-H and PEK-L could dissolve in DMF, *N,N'*-dimethylacetamide (DMAc), and *N*-methylpyrrolidone (NMP), whereas PEK- $\text{Na}^+$  and PEK- $\text{K}^+$  were only soluble in DMSO. This might be attributed to the fact that the ionic bond was stronger than the hydrogen bond.

As for IMPEK-L and its ionomers series, it could be seen that the substitution with bulk isopropyl was highly effective in reducing the packing density of the polymer chain, and thus contributed to the polymer solubility. In spite of the exis-

**Table IV** Solubilities of Polyaryletherketones

Solvent	PEK-C	PEK-H	IMPEK-L			PEK-L		
			$\text{H}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{H}^+$	$\text{Na}^+$	$\text{K}^+$
DMSO	+	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	-	-
DMAc	+	+	+	+	+	+	-	-
NMP	+	+	+	+	+	+	-	-
THF	+	-	+	-	-	-	-	-
Chloroform	+	-	+	-	-	-	-	-

(+) soluble, (-) insoluble.

**Table V Thermal Properties of Polymers Prepared**

Polymer	$T_g$ (°C)	$T_{side}$ (°C)	$T_5^a$ (°C)	$T_{10}^a$ (°C)	$T_{30}^a$ (°C)	RW (%) at 650°C
PEK-C	218	—	480	495	584	63
PEK-H	263	—	447	472	582	62
PEK-L	221	—	433	450	543	58
PEK-Na <sup>+</sup>	—	270	338	418	494	56
IMPEK-L	228	—	402	412	429	31
IMPEK-Na <sup>+</sup>	—	265	370	412	429	38

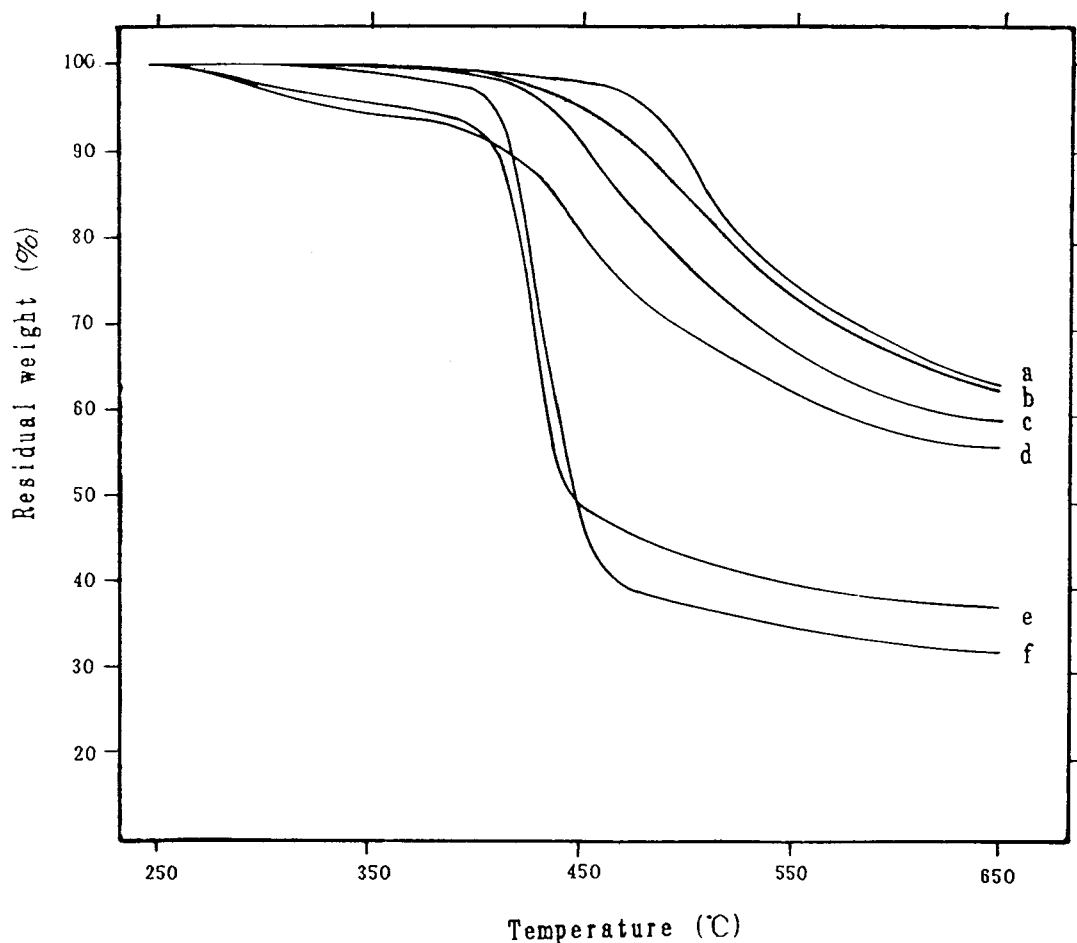
$T_{side}$ , decarboxylation temperature; RW, residual weight.

<sup>a</sup>Temperature of 5, 10, and 30% weight lose.

tence of the interchain hydrogen bond, IMPEK-L displayed almost the same solubility as PEK-C. After the ion exchange of H<sup>+</sup> with Na<sup>+</sup> and K<sup>+</sup>, IMPEK-Na<sup>+</sup> and IMPEK-K<sup>+</sup> were insoluble in chlorohydrocarbons, but could still dissolve in DMF and NMP, etc. This was of vital importance for the casting of asymmetric membranes.

### Thermal Behavior of Polymers

The thermal behaviors of these polymers were evaluated by differential scanning calorimetry (DSC) and TGA in N<sub>2</sub> atmosphere. The thermal properties are summarized in Table V. The  $T_g$ s of PEK-H, PEK-L, and IMPEK-L increased from the



**Figure 3** Thermogravimetric curves of the polymers prepared: (a) PEK-C, (b) PEK-H, (c) PEK-L, (d) PEK-Na<sup>+</sup>, (e) IMPEK-Na<sup>+</sup>, (f) IMPEK-L.

**Table VI Tension Properties of Polymers Prepared**

Polymer	Tensile Strength (MPa)	Tensile Moduli (GPa)	Elongation at Break (%)
PEK-C	97.7	2.27	7.81
PEK-H	82.7	1.86	97.7
PEK-L	79.2	1.89	147
PEK-Na <sup>+</sup>	63.7	1.33	165
IMPEK-L	78.6	1.65	8.81
IMPEK-Na <sup>+</sup>	67.1	1.47	13.3

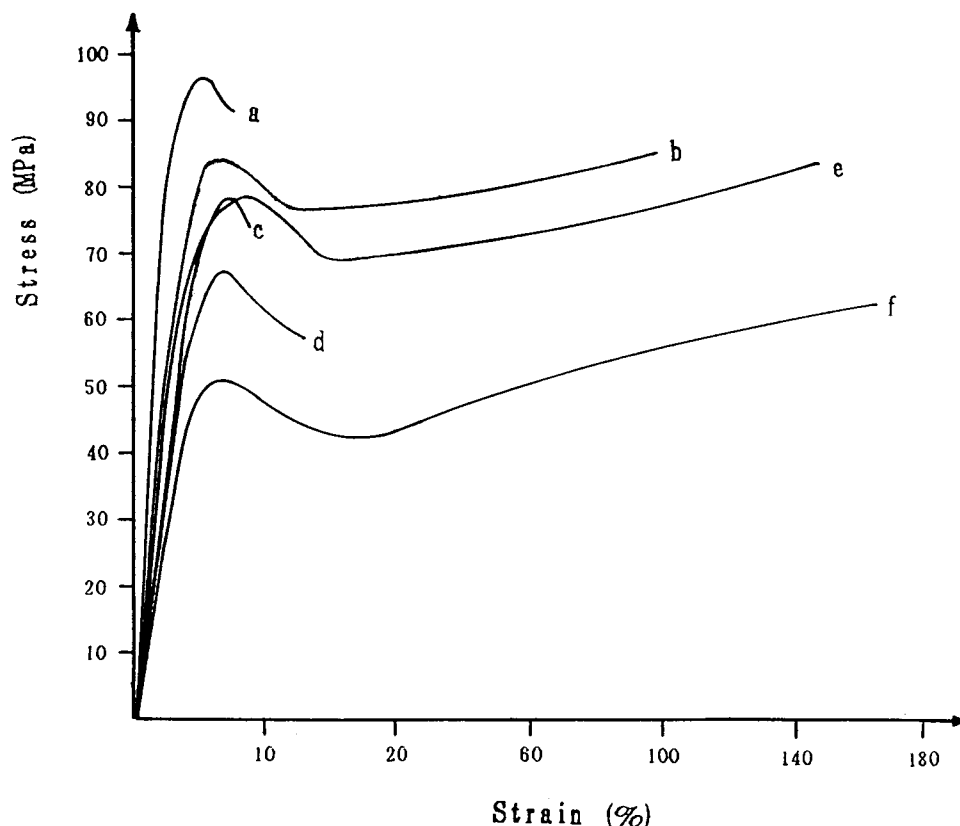
218°C of the unmodified PEK-C to 263, 220, and 228°C, respectively. This was attributed to the affect of interchain hydrogen bonds. In particular for PEK-Na<sup>+</sup> and IMPEK-Na<sup>+</sup>, no glass transitions were observed in a temperature interval of 100–400°C, indicating that the strong intermolecular interaction led to a stiffer polymer segment and the glass transition should take place at a temperature higher than 400°C. Similar phenomena were observed for sulfonated poly(phen-

ylene oxide), polyethersulfones, and polyetherketones,<sup>12–16</sup> as explained in terms of the increasing interchain association through the polar ionic sites, that is, an ionomer effect.

The traces of TGA of the polymers are illustrated in Figure 3, and the influence of various pendant groups on the thermal decomposition weight loss are given in Table VI. These data indicated that there was a decrease in the decomposition temperature with the introduction of alkyl and carboxyl groups. The TGA curves of PEK-Na<sup>+</sup> and IMPEK-Na<sup>+</sup> displayed two thermal decomposition steps. One took place at about 270°C, corresponding to the decarboxylation process; another was at about 450°C, corresponding to the decomposition of the polymer main chain.

### Mechanical Properties

Transparent, colorless, and tough films could be cast from DMF or DMSO solution of the PEK-Cs. Figure 4 exhibits the stress–strain curves of the polymer films prepared. Compared with that of PEK-C, the introduction of physical crosslink,



**Figure 4** Stress–strain curves of the polymer films: (a) PEK-C, (b) PEK-H, (c) IMPEK-L, (d) IMPEK-Na<sup>+</sup>, (e) PEK-L, (f) PEK-Na<sup>+</sup>.



that is, interchain hydrogen bond or ionic bond, could significantly enhance the mechanical properties of the polymers. For instance, the elongation at break of PEK-H, PEK-L, and PEK-Na<sup>+</sup> increased from 7.81% for PEK-C to 98, 147, and 165%, respectively. This finding could be explained by the similar affect described above in the solubility section.

## CONCLUSION

Our studies demonstrated that linear high molecular weight PEKs containing various pendant amido, alkyl, and carboxyl groups were readily prepared by the nucleophilic polycondensation of corresponding bisphenols with bis(4-nitrophenyl)ketone in the presence of potassium carbonate in DMSO without any side reaction. The polymers synthesized have reduced viscosities in the range of 0.54–0.68 dL/g. Compared with the introduction of the same pendant groups by a polymeric reaction, this method was advantageous in obtaining polymers with the specific position and content of pendant groups as expected. The resulting polymers showed higher  $T_g$ , excellent mechanical properties, and good solubility in moderate solvents as well.

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