

# One-Pot Synthesis of Polyetherimides from Bis(chlorophthalimide) and Dichlorodiphenylsulfone in Diphenylsulfone

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**ABSTRACT:** Polyetherimides and copolymers have been synthesized in one pot from bis(chlorophthalimide), dichlorodiphenylsulfone, and bisphenolate using diphenylsulfone as the solvent. The inherent viscosities of the obtained polyimides are in the range of 0.32–0.72 dL/g, and the structures of polyimides were confirmed by IR and elemental analyses. All of the polyimides have good solubility in common organic solvents. The 5% weight-loss temperatures of the polyimides were 429–507°C in air. The glass transition temperatures ( $T_g$ ) of 4,4'-(9-fluorenylidene) diphe-

nol-based polyimides are in the range of 253–268°C. The  $T_g$  of bisphenol A-based polyimides is in the range of 198–204°C, while the  $T_g$  change inconspicuously when the ratios of diphenylsulfone increase. The wide-angle X-ray diffraction showed that all polyimides prepared are amorphous. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4584–4588, 2006

**Key words:** polyetherimide; bis(chlorophthalimide); diphenylsulfone; dichlorodiphenylsulfone; one-pot synthesis

## INTRODUCTION

Aromatic polyimides, as a class of high-performance polymers, have unique thermal, mechanical, and electrical properties as well as outstanding chemical resistance at elevated temperature. Therefore, they are widely used as films, wire enamels, coatings, molding resins, and matrix resins for composites in the aerospace, transportation, and electrical and electronic industries.<sup>1–3</sup> However, their applications are often limited because of the high cost and their poor solubility and high processing temperature partly due to the rigid molecular chain and the strong interchain interaction. To overcome these limitations, many efforts have been made to decrease the cost and improve the processability of polyimides while maintaining their excellent properties.<sup>4,5</sup> Utilizing bis(chlorophthalimide) as the monomer for the preparation of polyimides is an attractive route, because the starting material chlorophthalic anhydride should be an inexpensive product.<sup>6–8</sup> Incorporation of heat-resistant units into polyimides to form copolyimides is an effective method to improve the processability. Many copolyimides have been studied, such as poly(amide-imide), poly(etherketone-imide),

poly(ester-imide), poly(siloxane-imide), and poly(sulfone imide). These copolyimides have not only enhanced processability but also many other properties, which homopolyimide cannot own.<sup>9–25</sup>

To introduce ether units into polyimide as the most important modification for polyimides has been receiving great attention as they may provide good processability owing to the presence of flexible ether links. Polyetherimides can be synthesized via the two-step method using dianhydrides, which contain ether unit and diamines, or by the nucleophilic displacement of bisphenolate and bis(chlorophthalimide)s or bis(nitrophthalimide)s. The latter is more favorable because of its low cost.<sup>2,6,26–32</sup> However, it is difficult to obtain a polyetherimide with high molecular weight polyimides owing to the instability of bisphthalimide in alkaline conditions and insoluble of the obtained polymer.<sup>27</sup> In this article, we synthesized poly(etherimide-co-ether sulfone) using diphenylsulfone as the solvent. Because of the immiscibility of diphenylsulfone with water, it is easy to get high-molecule-weight polymers and good reproducibility for the reaction. The structures, thermal and mechanical properties of the copolyimides were also discussed.

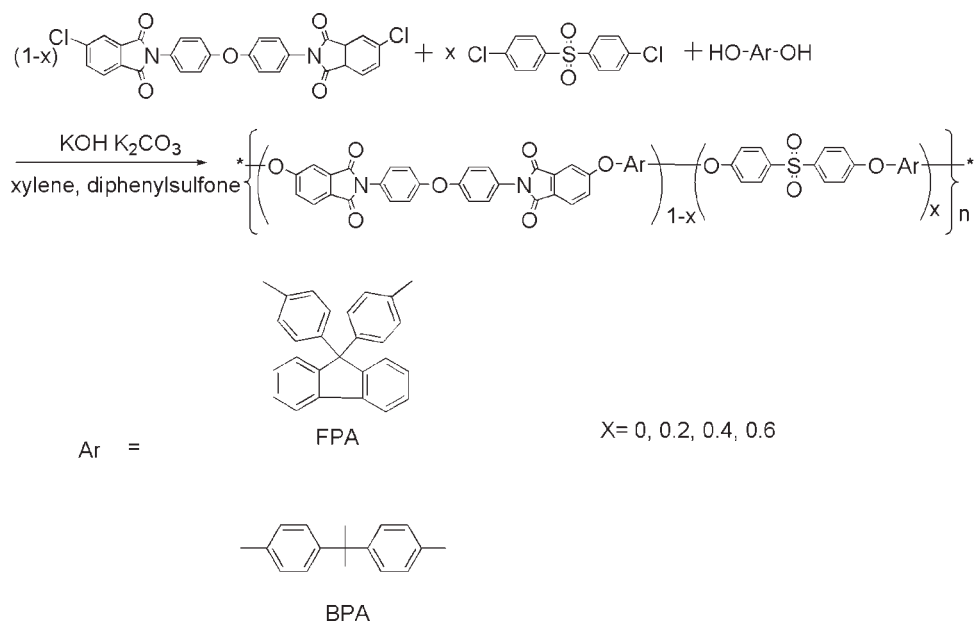
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## EXPERIMENTAL

### Materials

4-Chlorophthalic anhydride (99%) and 1,4-bis(4-aminophenoxy) benzene were synthesized in our laboratory.



**Scheme 1** Synthesis of poly(ether sulfone-*co*-ether imide).

Bis(4-chlorophenyl)sulfone, bisphenol A, 4,4'-(9-fluorenylidene) diphenol, and 4,4'-(9-fluorenylidene) dianiline were purchased from Aldrich Chemical (Milwaukee, WI), and 4,4'-Bis-(4-chlorophthalimido)diphenyl ether was prepared as reported in the literature,<sup>8</sup> mp 238–240°C. All other reagents were purchased from Shanghai Chemical Reagent Plant (Shanghai, China). 4,4'-Diamino-diphenyl ether (ODA) was purified by sublimation in vacuum. Diphenylsulfone was recrystallized from acetone and dried at 100°C. Other reagents were of analytical grade and used as received.

### Characterizations

Fourier transform infrared (FTIR) spectra were determined with a Bio-Red Digilab Division FTS-80 spectrometer. <sup>1</sup>HNMR spectra were recorded on a Varian Unity spectrometer at 400 Hz with tetramethylsilane as an internal standard. Elemental analyses were per-

formed on an elemental analyzer MOD-1106 (Italy). Melting points were determined on an XT-4 melting point apparatus (Beijing Taike Apparatus), and were uncorrected. Inherent viscosities were determined at 30°C with an Ubbelodhe viscometer, and the concentration was 0.5 g/dL in *p*-chlorophenol. Thermogravimetric analyses were obtained at a heating rate of 10°C/min under nitrogen atmosphere with a Perkin-Elmer TGA-2 thermogravimetric analyzer. Dynamic mechanical thermal analysis (DMTA) was performed on dynamic mechanical thermal analyzer V (Rheometric Scientific) in a tension mode at a heating rate of 3°C/min and a frequency of 1 Hz. The wide-angle X-ray diffraction (WAXD) measurements were undertaken on a Rigaku max 2500V PC X-ray diffractometer (Japan) with Cu K $\alpha$  radiation (40 kV, 200 mA) at a scanning rate of 2°C/min from 2 to 50°C. The tensile measurements were carried out on an Instron model 1122 at room temperature.

**TABLE I**  
Inherent Viscosities, Yields, and Elemental Analysis Results of Polyimides

Polyimides	$\eta_{inh}^a$ (dL/g)	Yield (%)	Elemental analyses (%)							
			C		H		N		S	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
ODA-FPA-0	0.65	97	79.22	79.31	3.67	3.664	3.42	3.441	0.00	0.000
ODA-FPA-20	0.61	94	78.88	78.89	3.80	3.812	2.96	2.968	0.84	0.825
ODA-FPA-40	0.58	99	78.85	78.83	3.89	3.896	2.37	2.381	1.80	1.851
ODA-FPA-60	0.72	96	78.81	78.80	3.99	3.978	1.70	1.711	2.90	2.942
ODA-BPA-0	0.32	93	75.44	75.46	4.09	4.10	4.09	4.10	0.00	0.00
ODA-BPA-20	0.45	95	75.14	75.17	4.22	4.22	3.52	3.55	1.00	1.05
ODA-BPA-40	0.38	95	74.80	74.86	4.36	4.35	2.86	2.87	2.18	2.21
ODA-BPA-60	0.33	96	74.39	74.38	4.53	4.52	2.0	2.10	3.56	3.57

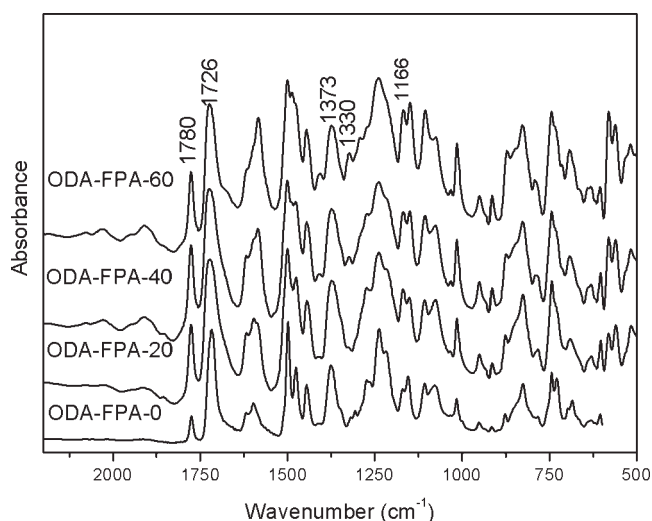


Figure 1 FTIR spectra of FPA-based polyimides.

### Polymer synthesis

The representative polymerization procedure is given below. In a three-necked, 250 mL, round-bottomed flask equipped with a mechanical stirrer, a Dean-Stark trap, and nitrogen inlet and outlet, 4,4'-(9-fluorenylidene) diphenol (3.5041 g, 0.01 mol), potassium hydroxide (1.122 g, 0.02 mol), anhydrous potassium carbonate (0.4146 g, 0.003 mol) diphenylsulfone (25 g), and xylene (50 mL) were placed. The mixture was heated to 160°C and stirred under nitrogen atmosphere. When no water was collected in the Dean-Stark trap, 20 mL xylene was distilled out and another 20 mL fresh xylene was added. After the mixture was refluxed for another 3 h, the most of residual xylene was distilled off. Then 4,4'-Bis-(4-chlorophthalimido)-diphenyl ether (5.2963 g, 0.01 mol) was added in one portion, and the mixture was stirred at 200°C for 10 h. The resulted viscous solution was poured slowly into 500 mL dilute hydrochloric acid. The precipitates were collected by filtration, extracted with acetone in a Soxhlet extractor for 24 h to remove the solvent diphenylsulfone. The polymer remained was dried at

200°C in vacuum for 4 h to afford powder of polyimide with the yield of 95%.

## RESULTS AND DISCUSSIONS

### Synthesis of polyimides

The synthesis of polyimides via nucleophilic displacement of bisphenolate and bis(chlorophthalimide) or bis(nitrophthalimide) is a valuable route for the low cost. The important chemistry was reported in a series of papers and patents by the researchers of GE.<sup>6,27–32</sup> In 1974, the researchers in GE reported the synthesis of PEI from biphenol and bis(chlorophthalimide), but the molecular weight was very low.<sup>31</sup> Li et al. reported the similar reaction in 1986.<sup>6</sup> In 1996, Schmidhauser reported the synthesis of polyimides with moderate molecular weight from disodium bisphenolate and bis(chlorophthalimide), however, the yield of disodium biphenolate was only 50%.<sup>32</sup> In this work, we successfully prepared polyimides and the copolymers with moderate molecular weight from disodium biphenolates, which were synthesized *in situ* (Scheme 1), and using diphenyl sulfone as the solvent. The immiscibility of diphenyl sulfone with water may be the critical point for obtaining high molecular weight. Because, the hydrolysis of bis(phthalimide) in the reaction medium where usually contain trace of water is the main problem for the polymerization. It is interesting that in this system the stoichiometry of base was not a critical fact, it may cause for the immiscibility of diphenyl sulfone with water, so the excess base is not able to react with bis(phthalimide). The inherent viscosities, yields, and elemental analyses of polyimides are shown in Table I. We also found that the molecular weight of polyimides form is the higher molecular weight of polyimides based on 4,4'-(9-fluorenylidene) diphenol than that on bisphenol A may contribute to the better solubility of the disodium of 4,4'-(9-fluorenylidene) diphenolate in diphenylsulfone.

The structures of polyimides are confirmed by IR and elemental analysis. Figure 1 shows the FTIR spectra of FPA-based polyimides. All the polymers showed

TABLE II  
Solubility Behavior of Polyimides

Polyimides	CHCl <sub>3</sub>	TCE <sup>a</sup>	THF	DMAc	DMSO	NMP	<i>m</i> -cresol	<i>p</i> -chlorophenol
ODA-FPA-0	–	–	–	+	+	+	+	+
ODA-FPA-20	+	+	±	+	+	+	+	+
ODA-FPA-40	+	+	±	+	+	+	+	+
ODA-FPA-60	±	+	±	+	+	+	+	+
ODA-BPA-0	+	+	+	+	+	+	+	+
ODA-BPA-20	+	+	+	+	+	+	+	+
ODA-BPA-40	+	+	+	+	+	+	+	+
ODA-BPA-60	+	±	+	+	+	+	+	+

<sup>a</sup> TCE = 1,1,2,2-tetrachloroethane.

Key: +, fully soluble at room temperature; ±, partially soluble; –, insoluble on heating.

**TABLE III**  
**Thermal and Mechanical Properties of Polyimides**

Polyimides	$T_g$ (°C) <sup>a</sup>	$T_{5\%}$ (°C) <sup>b</sup>	Tensile strength (MPa)	Modulus (MPa)	Elongation (%)
ODA-FPA-0	257	482	112	2080	7.5
ODA-FPA-20	253	481	124	2100	8.9
ODA-FPA-40	256	507	110	2040	6.9
ODA-FPA-60	268	429	65	1900	3.5
ODA-BPA-0	— <sup>c</sup>	495	— <sup>c</sup>	— <sup>c</sup>	— <sup>c</sup>
ODA-BPA-20	204	493	117	2200	7.5
ODA-BPA-40	198	476	100	2090	5.2
ODA-BPA-60	203	437	72	1340	6.0

<sup>a</sup> Obtained from DMTA at heating rate of 3°C/min at 1 Hz.

<sup>b</sup> Five percent weight loss obtained from TGA at a heating rate of 10°C/min in air.

<sup>c</sup> The film is too brittle to be measured.

the characteristic absorption bands of the imide ring near 1780 (asym C=O str), 1726 (sym C=O str), 1373 (C—N str), and 730  $\text{cm}^{-1}$  (imide ring deformation), and the characteristic absorption bands of the imide ring near 1330 (asym O=S=O str), 1160  $\text{cm}^{-1}$  (sym O=S=O str), and their intensities increased as the ratio of dichlorodiphenylsulfone increased. The elemental analysis results of polyimides also agreed well with the theoretical values of the proposed structures.

## Properties of polyimides

### Solubility

The solubility of the copolyimide powders was summarized in Table II. It can be seen that all of the polyimides have good solubility in phenolic solvents and polar aprotic solvents, such as NMP, DMAc, DMSO, and even in THF,  $\text{CHCl}_3$ , and TCE. The solubility of 4,4'-(9-fluorenylidene) diphenol based polyimides was further enhanced by copolymerization with dichlorodiphenylsulfone. However, the copolyimides based on bisphenol A have similar solubility.

### Thermal and mechanical properties

The thermal and mechanical properties of polyimides were summarized in Table III. The temperatures of 5% weight loss ( $T_{5\%}$ ) of polyimides in air are in the range of 429–507°C. The thermoxidative stability decreases with the increase of the content of dichlorophenylsulfone because of the limited stability of sulfone unit in the polymer chain.

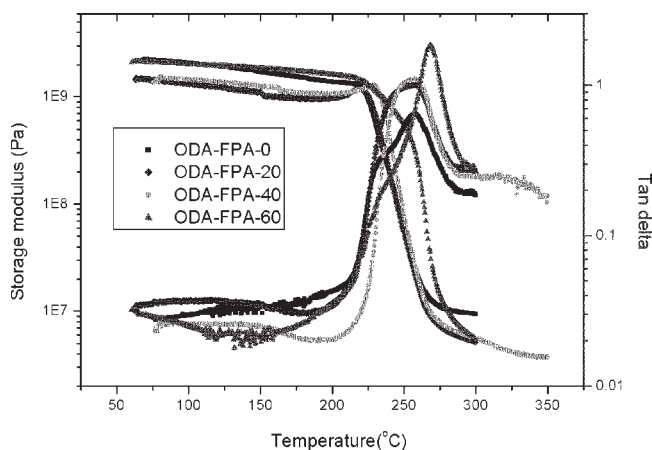
All of the polymer films were cast from the 10% (w/v) solutions in DMAc, and dried at 80°C for 12 h and 250°C for 3 h. The film of ODA-FPA-0 is tough, flexible, but opaque. The film of ODA-BPA-0 is highly brittle because of its lower molecular weight. The films cast from copolyimides are tough, flexible, and transparent. The tensile strengths, moduli, and elongations at break of the polyimides are 67–124 MPa,

1.34–2.48 GPa, and 3.5–8.9%, respectively. When the content of dichlorophenylsulfone increases, the tensile strengths decrease rapidly.

The DMTA results of the polyimides are shown in Figure 2. The original storage modulus ranged from 1.36 to 3.16 GPa. Regarding the peak temperature in the  $\tan \delta$  curves as the glass transition temperature ( $T_g$ ), no obvious change of  $T_g$  for copolymers can be found when the content of dichlorophenylsulfone differs.

### X-ray diffraction

As shown in Figure 3, the crystallizability of polyimides is examined by wide angle X-ray diffraction. All of the polymers show amorphous patterns. It was well-known that poly(ether sulfone) have a strong tendency to crystallize,<sup>31</sup> which decreases the mechanical properties and the ability of film-forming. However, by copolymerization with bis(chlorophthalimide), the crystallizability was depressed successfully.



**Figure 2** DMTA curves of FPA-based polyimides.

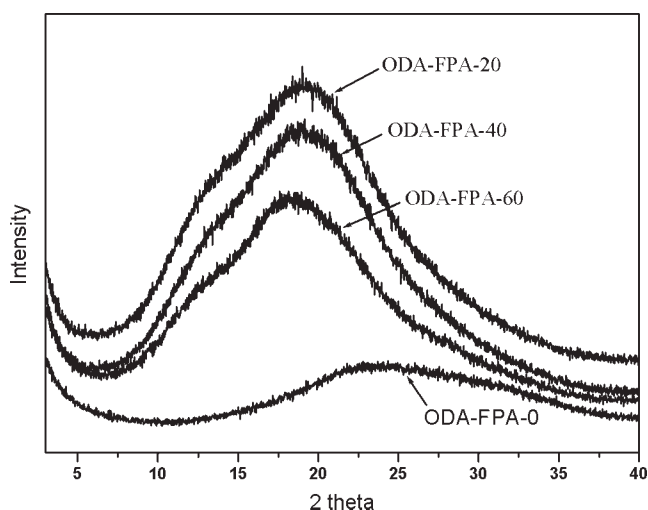


Figure 3 WAXD diagram of FPA-based polyimides.

### CONCLUSIONS

Polyetherimides using bis(chlorophthalimide)s as the monomer and copolymers with dichlorodiphenylsulfone were synthesized by a one-pot procedure in diphenylsulfone to obtain moderate molecular weight. The immiscibility of diphenyl sulfone with water for diphenylsulfone may depress the hydrolysis of bis(chlorophthalimide), and therefore the reaction has good reproducibility. The polyimides prepared are all exhibit good solubility in common solvents. Flexible and transparent films can be cast from the copolyimides.

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