

# Synthesis and Characterization of Readily Soluble Polyarylates Derived from Either 1,1-bis(4-hydroxyphenyl)-1-Phenylethane or Tetramethylbisphenol A and Aromatic Diacid Chlorides

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**ABSTRACT:** A series easily soluble polyarylates were synthesized from either 1,1-bis(4-hydroxyphenyl)-1-phenylethane or tetramethylbisphenol A with various aromatic diacid chlorides by the two-phase interfacial polycondensation. These polyarylates have the inherent viscosities in the range of 0.36–0.97 dL/g, and their number-average and weight-average molecular weights determined by gel permeation chromatography are 14,200–43,200 and 31,900–102,500, respectively. All these polyarylates are readily soluble in a wide range of organic solvents, thus these polymers can be convenient to process into heat resistance films by cast, spin- or dip-coating. The polyarylates have the glass transition temperatures in the

range of 165.0–201.6°C. The pendent phenyl-containing polyarylates reveal excellent thermal stability, and their initial degradation temperatures are all above 480°C and char yields at 700°C are 37.97–40.53% in nitrogen atmosphere. However, the polymers prepared from tetramethylbisphenol A have a large decrease in thermal stability, and their initial degradation temperatures in nitrogen are only about 440°C. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1923–1930, 2011

**Key words:** polyarylates; 1,1-bis(4-hydroxyphenyl)-1-phenylethane; tetramethylbisphenol A; solubility; thermal properties

## INTRODUCTION

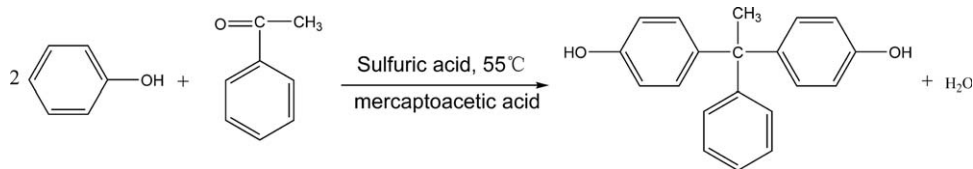
Polyarylates are high-performance engineering materials with an unusual combination of properties such as excellent heat resistance and thermal stability, high mechanical properties and antiultraviolet, and good flame retardant. The polyarylates can be applied in various industries as fibers, coatings, membranes, molded components, composites, and so on. However, the fully aromatic polyarylates need high processing temperature and have poor solubility in organic solvents because of their extended rigid structures and low melting entropies, which greatly limited their development and application. Thus, improvement of the processability is necessary, but this is often accompanied by lowering thermal stability.<sup>1–3</sup>

In the past few years, much effort was made to improve the processability of the polyarylates.<sup>1–22</sup> The main methods for improving their processability were reported as follows: (1) introduction of bulky

pendent groups in the repeating unit; (2) introduction of flexible structures in the backbone; and (3) introduction of asymmetric units in the main chains. The representative examples are enumerated as following: Akutsu et al.<sup>1</sup> introduced 4, 4'-*o*-terphenyldiyl structure to the main chains of polyarylate. The results showed the introduction of this bulky group improved the solubility and maintained the thermal stability of the polyarylates. Jeong et al.<sup>2</sup> synthesized a new class of polyarylates containing tetraphenylfuran units using 2,5-bis(4-hydroxyphenyl)-3,4-dipheylfuran as a new monomer. These polyarylates exhibited excellent solubility in various common organic solvents and also had good thermal stability as well as  $T_g$  around 220°C. Bhowmik and Han<sup>3</sup> prepared a series polyarylates derived from either phenyl-substituted 4,4'-biphenols or 1,1'-binaphthyl-4,4'-diol and 2-bromoterephthalic acid or 2-phenylterephthalic acid by acidolysis condensation polymerization. They found that all of the substituted polymers had either low  $T_m$  or lower  $T_f$  values than those of the respective unsubstituted homopolymers and had the thermal initial degradation temperature in the range of 445–485°C in nitrogen.

In this article, the pendent phenyl-containing polyarylates were synthesized from 1,1-bis(4-hydroxyphenyl)-

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Scheme 1

1-phenylethane and various aromatic diacid chlorides by interfacial polycondensation to improve the processability of polyarylates. The properties of these polyarylates were characterized by a series of experimental methods, such as gel permeation chromatography, differential scanning calorimetry, dynamic mechanical analyses, thermogravimetric analyses, and so on. For a comparative study, the polyarylates derived from either tetramethylbisphenol A or bisphenol A were also prepared and characterized, respectively.

## EXPERIMENTAL

### Materials

Phenol, acetophenone, 2,6-dimethylphenol, acetone, sulfuric acid, mercaptoacetic acid, hydrochloric acid, chloroform, dichloromethane, benzyltriethylammonium chloride (BTEAC), ethanol, methanol, and sodium hydroxide (all from KELONG), which were analytically pure, were used as received. Terephthaloyl chloride (II<sub>a</sub>, from aladdin) and isophthaloyl chloride (II<sub>b</sub>, from aladdin) were recrystallized from petroleum ether before use.

### Monomer synthesis

#### 1,1-Bis(4-hydroxyphenyl)-1-phenylethane (I<sub>a</sub>)

I<sub>a</sub> was prepared by the acid catalyzed condensation of phenol with acetophenone (Scheme 1). A typical procedure for that is given as follows. 0.4 mol of phenol, 46 mL of 13.0 mol/L sulfuric acid solution, and a few drops mercaptoacetic acid as assistant catalyst were added in a three-neck, 250 mL round-bottom flask equipped with a condenser and a stirring bar. The flask was immersed in a thermostat water bath with stirring at 40°C. After the phenol was dissolved, 0.1 mol of acetophenone was added dropwise to the flask over a period of 30 min, and the temperature was then raised to 55°C. The mixture

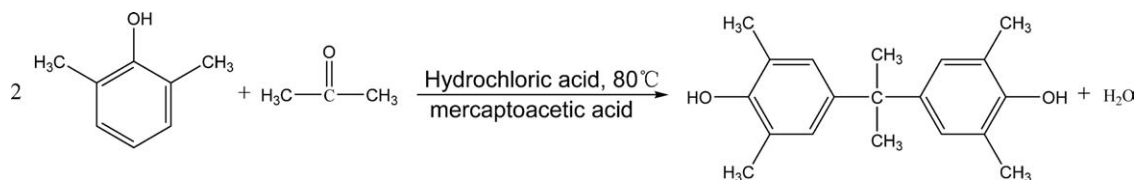
was stirred for 8 h at that temperature, and the carmine and viscous solid was collected by filtration when the reaction finished. The crude product was washed repeatedly by boiling water and dichloromethane, respectively, and then dried at 40°C under vacuum. White and pure powder of I<sub>a</sub> was obtained. The yield was 60.0%. m.p. 172–173°C; IR (KBr): 3275 ( $\nu_{\text{O-H}}$ ), 2973 ( $\nu_{\text{C-H}}$ ), 1371 ( $\nu_{\text{C-H}}$ ), 833, 725, 699 ( $\nu_{\text{Ar}}$ ,  $\delta_{\text{C-H}}$ )  $\text{cm}^{-1}$ . <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 2.01 (s, 3H, H<sub>a</sub>), 6.65 (d, 4H, H<sub>e</sub>), 6.80 (d, 4H, H<sub>f</sub>), 7.02 (d, 2H, H<sub>b</sub>), 7.18 (t, 1H, H<sub>d</sub>), 7.25 (t, 2H, H<sub>c</sub>), 9.25 (s, 2H, H<sub>g</sub>). <sup>13</sup>C-NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 30.77 (C<sup>2</sup>), 51.10 (C<sup>1</sup>), 114.93 (C<sup>9</sup>), 126.06 (C<sup>6</sup>), 128.16 (C<sup>5</sup>), 128.67 (C<sup>4</sup>), 129.67 (C<sup>8</sup>), 139.96 (C<sup>3</sup>), 150.34 (C<sup>7</sup>), 155.65 (C<sup>10</sup>).

#### Tetramethylbisphenol A (I<sub>b</sub>)

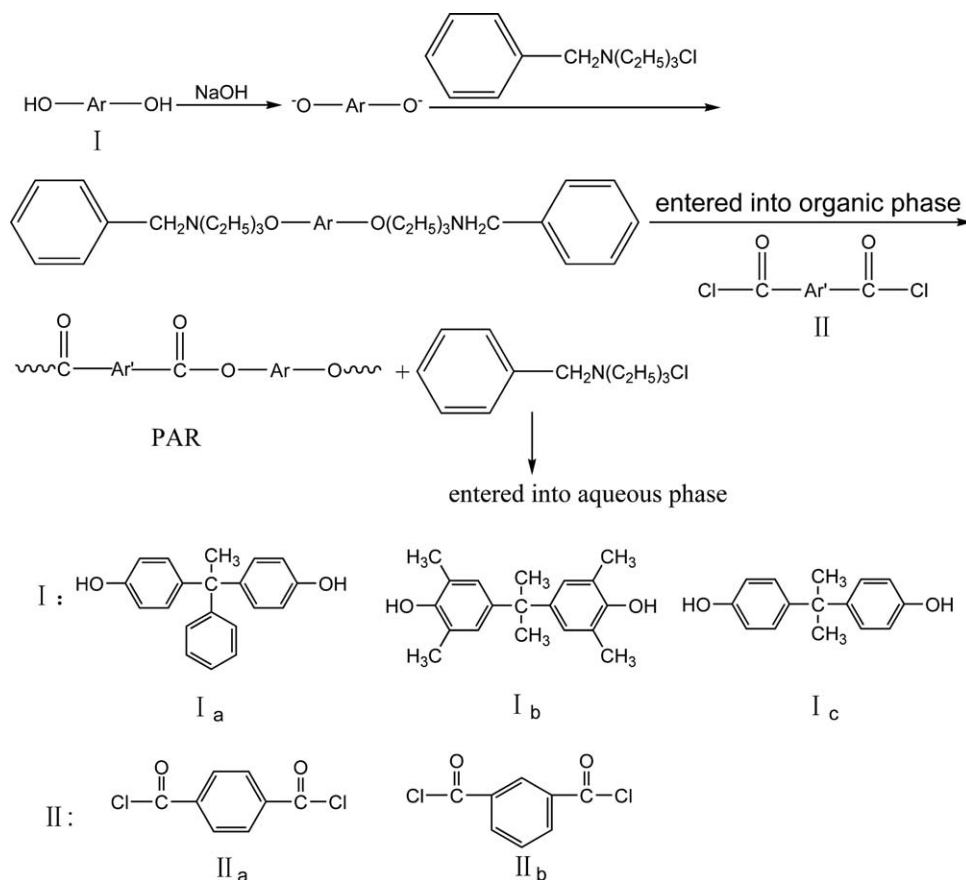
I<sub>b</sub> was synthesized from 2,6-dimethylphenol with acetone by a similar procedure described as earlier (Scheme 2). The main differences from the preparation of I<sub>a</sub> were in the following: the catalyst was the condensed hydrochloric acid, and the reaction temperature was raised to 80°C, and the crude product was washed repeatedly by boiling water and cyclohexane, respectively. The yield of I<sub>b</sub> was 50.0%. IR (KBr): 3350 ( $\nu_{\text{O-H}}$ ), 1359, 1380 ( $\nu_{\text{C-H}}$ ,  $\delta_{\text{C-H}}$ )  $\text{cm}^{-1}$ . <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 1.488 (s, 6H, H<sub>a</sub>), 2.085 (s, 12H, H<sub>c</sub>), 6.708 (s, 4H, H<sub>b</sub>), 7.891 (s, 2H, H<sub>d</sub>). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 1.585 (s, 6H, H<sub>a</sub>), 2.200 (s, 12H, H<sub>c</sub>), 4.458 (s, 4H, H<sub>b</sub>), 6.827 (s, 2H, H<sub>d</sub>).

### Polymerization

Polyarylates were synthesized by interfacial polymerization shown in Scheme 3. The synthesis of PAR-2 was used as an example to illustrate the general synthetic route. In a three-neck, 250-mL round-bottom flask equipped with a mechanical stirrer and



Scheme 2



Scheme 3

a condenser, 3.625 g (12.5 mmol) of  $I_a$ , 25 mg of BTEAC were placed, and dissolved in 30 mL of 1M aqueous sodium hydroxide with stirring. A solution of 1.776 g (8.75 mmol) of  $II_a$  and 0.761 g (3.75 mmol) of  $II_b$  in 75 mL dichloromethane was added dropwise to the flask over a period of 20 min with vigorous stirring, and the reaction mixture gradually became white and viscous. The two-phase mixture was stirred for 3 h at room temperature, and poured into ethanol for precipitation. The precipitated polymer was collected by filtration, and washed with hot water thoroughly, and then dried at 100°C under vacuum. The yield was 95.8%. The FTIR spectrum (film) showed absorptions at 1740  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ), 1300–1200  $\text{cm}^{-1}$  ( $\delta_{\text{C-O-C}}$ ). The inherent viscosity of the PAR-2 was 0.97 dL/g, measured at a concentration of 0.5 g/dL in chloroform at 30°C.

All polymers were prepared from bisphenols with the corresponding diacid chlorides by a similar procedure described as earlier (Table I).

#### Preparation of polyarylate films

Polyarylate films were prepared by casting chloroform solutions containing 10 wt % polymer onto glass plates and then dried for 1 h at 70°C. Then, the films were peeled off and further vacuum dried for

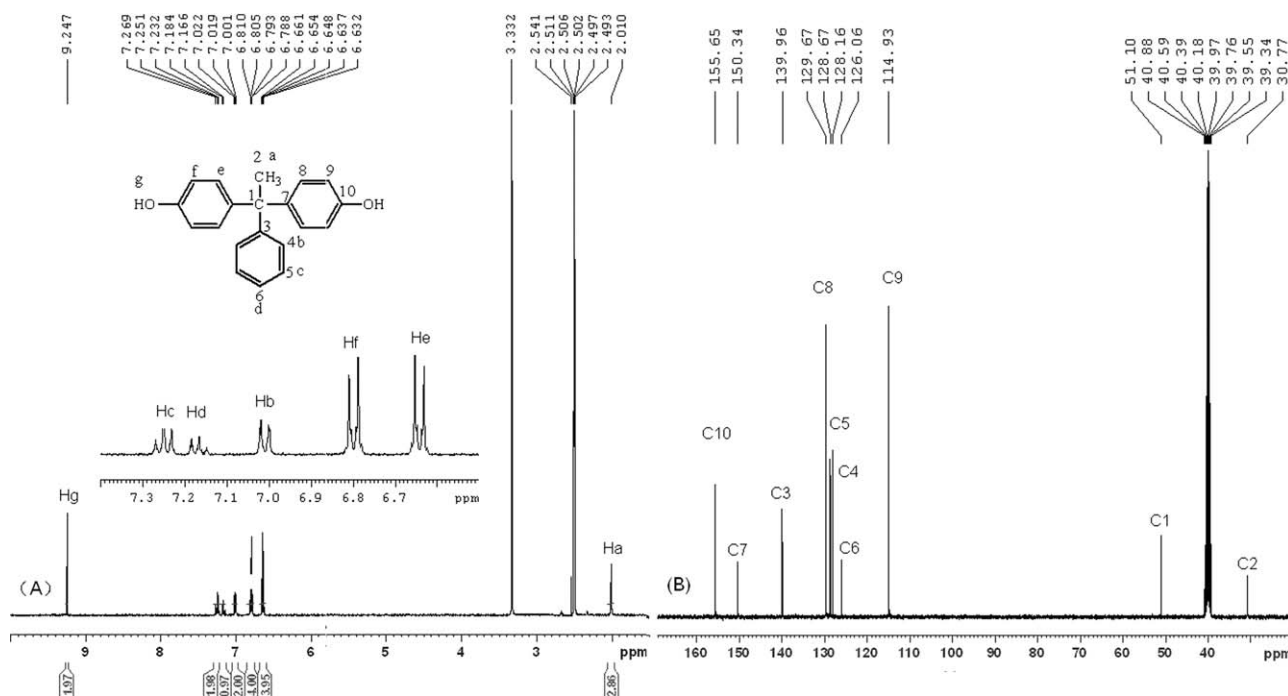
12 h at 70°C to ensure the complete removal of the solvent. The obtained films were about 0.2 mm in thickness and were used for FTIR spectra measurements and DMA tests.

#### Measurements

The infrared (IR) spectra were recorded on a Nicolet 560 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were measured with a Bruker 400 MHz Ultra Shield NMR spectrometer. The chemical shifts were calibrated using tetramethylsilane (TMS) as an internal standard, and the peak multiplicity was described as follows: s, singlet; d,

TABLE I  
Identification of Polymers Studied in this Study

Polymer code	Bisphenol	Aromatic diacid chloride
Series 1	PAR-1	$II_a$
	PAR-2	$II_a$ (70%) + $II_b$ (30%)
	PAR-3	$II_b$
Series 2	PAR-4	$II_a$
	PAR-5	$II_a$ (70%) + $II_b$ (30%)
	PAR-6	$II_b$
Series 3	PAR-7	$II_a$
	PAR-8	$II_a$ (70%) + $II_b$ (30%)
	PAR-9	$II_b$



**Figure 1**  $^1\text{H}$ -NMR (A) and  $^{13}\text{C}$ -NMR (B) spectra of 1,1-bis(4-hydroxyphenyl)-1-phenylethane in  $\text{DMSO-}d_6$ .

doublet; t, triplet; m, multiplet. The inherent viscosities of polyarylates were determined with an Ubbelohde capillary viscometer ( $4 - \phi 0.5$ ) at  $30^\circ\text{C}$ . Gel permeation chromatography (GPC) was carried out on a Waters 1515 chromatography. All GPC analyses were performed using a polymer/THF solutions at a flow rate of 1 mL/min and calibrated with narrow polystyrene standards. Differential scanning calorimetry (DSC) was carried out using a NETZSCH DSC 204F1 at a heating rate of  $10^\circ\text{C}/\text{min}$  in flowing nitrogen ( $20 \text{ cm}^3/\text{min}$ ). The temperature and heat enthalpy were calibrated with indium standard before the equipment running. Dynamic mechanical analyses (DMA) were made with a TA Q800 DMA. The storage modulus  $G'$  and  $\tan \delta$  were studied when the polyarylate films was subjected to the temperature scan mode at a heating rate  $10^\circ\text{C}/\text{min}$  from 30 to  $300^\circ\text{C}$  at a frequency of 1 Hz. A sample 50 mm in length, 10 mm in width, and 0.2 mm in thickness was used. Thermogravimetric analyses (TGA) were measured with a TA SDT Q600 thermal analyzer using a heating rate of  $20^\circ\text{C}/\text{min}$  in  $\text{N}_2$  at a flow rate of  $100 \text{ cm}^3/\text{min}$ .

## RESULTS AND DISCUSSION

### Monomer synthesis

The pendent phenyl-containing bisphenol  $\text{I}_a$  was obtained by the acid catalyzed condensation of acetophenone and excess phenol, according to the typical Ketol reaction. The synthetic route is shown in Scheme 1. The crude product was pink because of

the by-product formed by the side reaction in phenol sulfonation, but these by-products could be removed easily by dichloromethane. The structure of pure  $\text{I}_a$  was confirmed by FTIR and NMR spectra. Characteristic IR absorption bands of hydroxyl O—H stretching vibration, methyl C—H stretching and deformation vibrations, symmetrically substituted and mono-substituted phenyl C—H deformation vibrations can be observed around  $3275$ ,  $1973$ ,  $1371$ ,  $833$ ,  $725$ , and  $699 \text{ cm}^{-1}$ , respectively. Figure 1 represents the  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of  $\text{I}_a$ . It is found that the chemical shifts of H and C are completely consistent with the structure of  $\text{I}_a$ .

As shown in Scheme 2,  $\text{I}_b$  was also obtained according to the Ketol reaction. The reaction temperature was higher than that of  $\text{I}_a$  because of the lower reactivity of 2,6-dimethylphenol. Therefore, we used hydrochloric acid as the catalyst instead of sulfuric acid to reduce the side reaction. The structure of  $\text{I}_b$  was also demonstrated by FTIR and NMR spectra (Fig. 2).

### Preparation of polyarylates

According to a well-known technique, PAR-1–PAR-9 were prepared from three bisphenol monomers ( $\text{I}_a$ ,  $\text{I}_b$ , and  $\text{I}_c$ ) with the corresponding aromatic diacid chlorides by the two-phase polycondensation in a dichloromethane-aqueous sodium hydroxide solution system using BTEAC as the phase transfer catalyst. All polyarylates were obtained in almost quantitative. The formation of polymers was confirmed

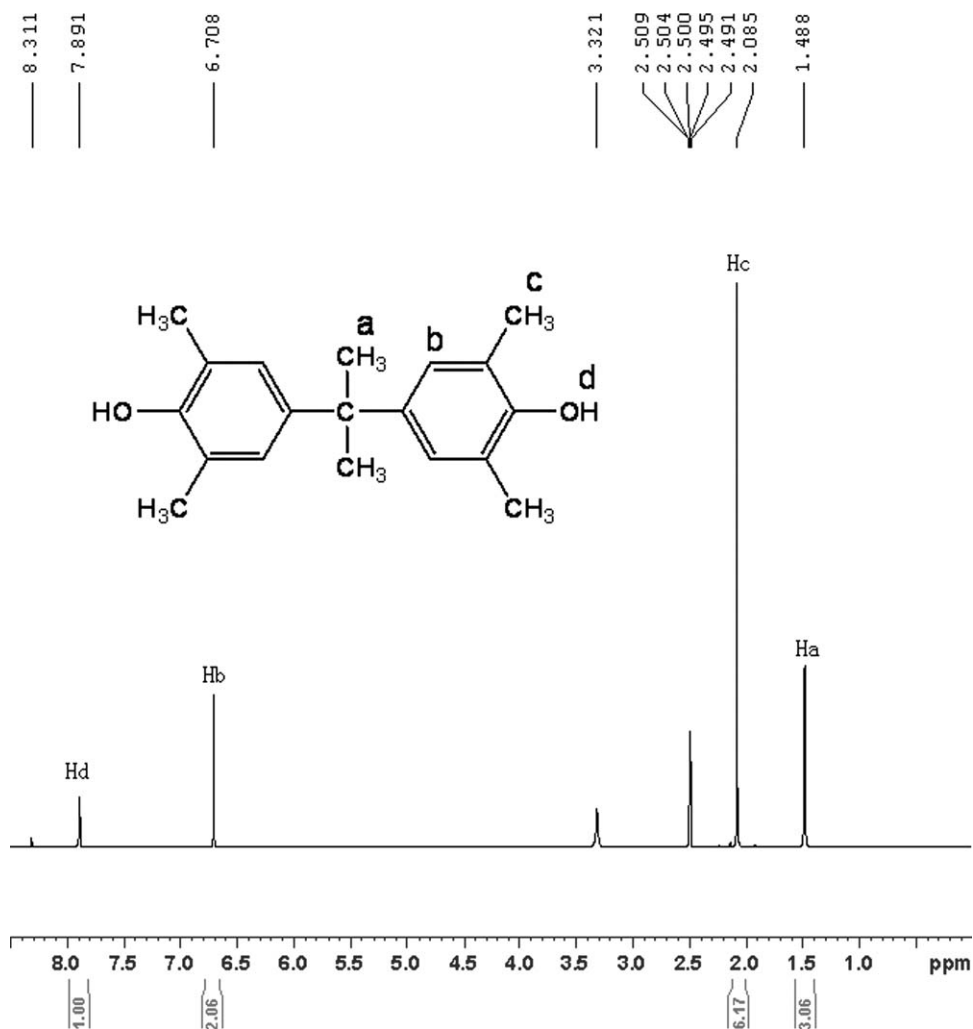


Figure 2  $^1\text{H-NMR}$  spectrum of tetramethylbisphenol A in  $\text{DMSO-}d_6$ .

by means of IR spectroscopy. The typical FTIR spectra of representative polymers PAR-2, PAR-5, and PAR-8 (Fig. 3) exhibit characteristic ester absorption band around  $1740\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretching) and in the region of  $1300\text{--}1200\text{ cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$  stretching).

The inherent viscosities and molecular weights of PAR-1–PAR-6 are listed in Table II. These polyarylates have  $\eta_{\text{inh}}$  in the range of 0.36–0.97 dL/g, and their  $M_n$  and  $M_w$  determined by GPC are 14,200–43,200 and 31,900–102,500, respectively. The inherent viscosities and molecular weights of Series 2 polymers are lower than that of Series 1 polymers. This may be explained by the lower reactivity of  $\text{I}_b$  because of the steric hindrance and electron-donating effects of the methyl groups. All polyarylates can be solution-cast into transparent and colorless films. However, PAR-4–PAR-6 films are very brittle owing to their low inherent viscosities and molecular weights. Meanwhile, it is found that PAR-2 has higher molecular weights than PAR-1 and PAR-3. The reason for that may be the flexibility of backbone is increased when a

few isophthalic ester groups are introduced. The polyarylates obtained from  $\text{I}_b$  also show the similar tendency.

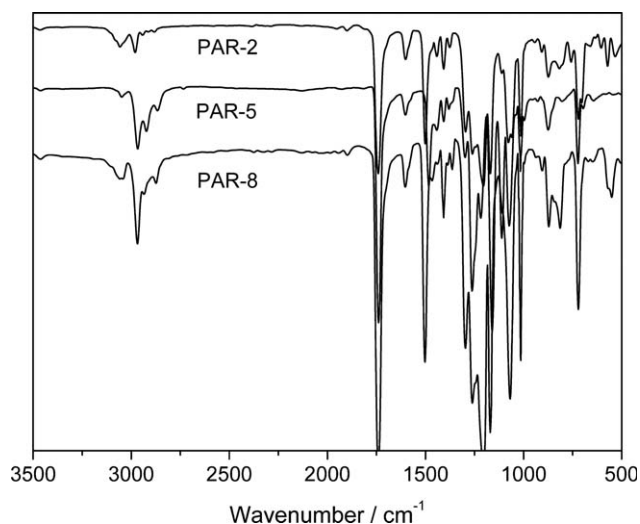


Figure 3 The FTIR plots of the representative polyarylates.

**TABLE II**  
Inherent Viscosities<sup>a</sup> and Molecular Weights<sup>b</sup> of Polyarylates

Polymer code	$\eta_{inh}$ (dL/g)	Molecular weights			PDI <sup>c</sup>
		$M_n$	$M_w$	$M_z$	
PAR-1	0.60	27,000	54,000	80,700	2.00
PAR-2	0.97	43,200	102,500	141,900	2.37
PAR-3	0.64	21,900	81,300	118,500	3.71
PAR-4	0.36	14,200	31,900	53,200	2.25
PAR-5	0.43	18,500	47,900	79,600	2.59
PAR-6	0.41	15,900	43,900	70,700	2.76

<sup>a</sup> Measured at a polymer concentration of 0.5 g/dL in chloroform at 30°C.

<sup>b</sup> Calibrated with polystyrene standards, using THF as the eluent at a constant flow rate of 1 mL/min.

<sup>c</sup> Polydispersity index ( $M_w/M_n$ ).

### Properties of polymers

The qualitative solubility of the polyarylates was studied in various solvents, and the results are summarized in Table III. The polymers PAR-7–PAR-9 reveal a relatively poor solubility and are only soluble or partial soluble in  $\text{CHCl}_3$ , Py, and NMP on heating because of their closely packed structures. PAR-1–PAR-6 are readily soluble in a wide range of organic solvents such as toluene, chloroform, dichloromethane, THF, Py, NMP, and DMF at room temperature or on heating. However, all polymers are entirely insoluble in methanol. Their high solubility is attributed to the loose packed structures. The introduction of bulky pendent phenyl in the repeating unit or tetra-substitution of methyl groups on the BPA phenyl rings surely play an important role to increase free volume in the polymer chains and decrease packing density so as to allow much solvent to come in. Thus, the excellent solubility makes these polymers convenient to processing into products by cast, spin- or dip-coating.

The thermal properties of these polyarylates were evaluated by means of DSC, DMA, and TGA. The results are listed in Table IV. Since the residual solvent or water and the different thermal history may influence the first heating run of DSC, samples were cooled from 400 to 100°C at a cooling rate of 10°C/min and the DSC data was determined by the second heating. The semicrystalline polymer PAR-7 shows an obvious melting endotherm peak at 356°C in the second DSC heating trace. However, the other polyarylates do not have melting endotherm peaks up to 400°C on the DSC heating curves, suggesting these polyarylates are amorphous. The polyarylates prepared from I<sub>a</sub>, I<sub>b</sub>, and I<sub>c</sub> have the glass transition temperatures of 167.0–195.1°C, 165.0–201.6°C, and 153.7–154.5°C, respectively. The two former Series polymers exhibit higher  $T_g$  values than the latter Series, probably due to the increase of steric hindrance effect caused by the introduction of bulky pendent phenyl in the repeating unit or tetra-substitution of methyl groups on the BPA phenyl rings.

**TABLE III**  
Qualitative Solubility<sup>a</sup> of Polyarylates

Polymer code	Solvent <sup>b</sup>										
	$\text{CCl}_4$	Toluene	$\text{CHCl}_3$	$\text{CH}_2\text{Cl}_2$	THF	Acetone	Py	NMP	DMF	DMSO	MeOH
PAR-1	--	+h	++	++	++	--	++	++	++	--	--
PAR-2	--	+t	++	++	++	--	++	++	++	--	--
PAR-3	--	+t	++	++	++	--	++	++	++	--	--
PAR-4	++	++	++	++	++	+-	++	++	++	+-	--
PAR-5	++	++	++	++	++	+-	++	++	++	+-	--
PAR-6	++	++	++	++	++	+-	++	++	++	+-	--
PAR-7	--	--	+t	--	--	--	--	--	--	-	--
PAR-8	--	--	+t	--	--	--	+-	+-	--	--	--
PAR-9	--	--	+t	--	--	--	+h	+h	--	--	--

<sup>a</sup> Qualitative solubility was determined by using 10 mg sample in 1 mL of solvent. ++, soluble in a short time at room temperature; +t, soluble in a long time at room temperature; +h, soluble on heating; +-, partial soluble or swelling on heating; --, insoluble on heating.

<sup>b</sup> Solvent: THF, tetrahydrofuran; Py, pyridine; NMP, *N*-methyl-2-pyrrolidone; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; MeOH, methanol.

**TABLE IV**  
Thermal Properties Data of Polyarylates

Polymer code	$T_g^a$ (°C)	$T_{id}^b$ (°C)	$T_{md}^b$ (°C)	$T_{fd}^b$ (°C)	Char yield <sup>c</sup> (%)
PAR-1	167.0	480.9	504.6	530.2	37.97
PAR-2	195.1	481.7	504.6	533.8	40.53
PAR-3	169.4	483.2	504.5	526.8	33.28
PAR-4	187.4	446.0	482.8	518.3	26.47
PAR-5	201.6	440.5	484.7	517.8	24.14
PAR-6	165.0	449.0	488.6	518.5	24.56
PAR-7	-	491.3	511.3	533.2	28.73
PAR-8	154.5	487.4	507.1	526.7	29.01
PAR-9	153.7	486.5	499.5	515.2	28.98

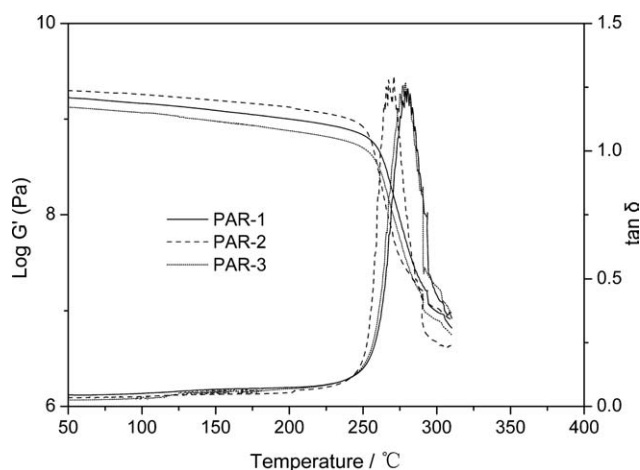
<sup>a</sup> Samples were cooled from 400 to 100°C at a cooling rate of 10°C/min and  $T_g$  data was determined by the second heating DSC curve.

<sup>b</sup>  $T_{id}$ ,  $T_{md}$ , and  $T_{fd}$  represent the initial, the maximum, and the final decomposition temperature, respectively.

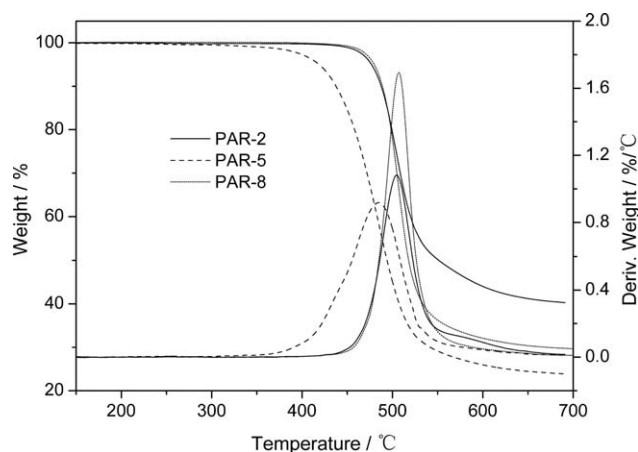
<sup>c</sup> Residual weight percentage at 700°C in nitrogen.

Figure 4 shows the DMA curves of PAR-1, PAR-2, and PAR-3 films at a heating rate of 10°C/min. The peak of  $\tan \delta$  was identified as the glass transition temperature of polymer because of a large decrease in storage modulus ( $G'$ ) occurred at this point. The  $T_g$  values of PAR-1, PAR-2, and PAR-3 were 280.2, 270.4, and 280.5°C, respectively. It is found that the  $T_g$  value determined by DMA is higher than that determined by DSC. All the pendent phenyl-containing polyarylates maintain good mechanical properties ( $G' \geq 10^8$  Pa) when the temperature is below 270°C.

Thermal stabilities of these polyarylates were evaluated by TGA under nitrogen atmosphere. Typical TGA curves of the representative polymers PAR-2, PAR-5, and PAR-8 are shown in Figure 5. The pendent phenyl-containing polyarylates exhibit good resistance to thermal and their initial decomposition temperatures ( $T_{id}$ ) are all above 480°C, which approximate to the  $T_{id}$  values of Series 3. Moreover,



**Figure 4** DMA curves for PAR-1–PAR-3 films.



**Figure 5** TGA-DTA curves of the representative polyarylates.

the char yields of the series 1 at 700°C have a slight increase, which range from 37.97 to 40.53% because of the increase of the phenyl density in the repeating unit. However, the polyarylates derived from  $I_b$  reduce approximate 40°C of the  $T_{id}$  values compared to that of the other series. The results indicate that the introduction of bulky pendent phenyl in the repeating unit and tetra-substitution of methyl groups on the BPA phenyl rings both can significantly improve the solubility of the polyarylates, but the latter polymers have a large decrease in thermal stability while the former ones have no effect.

## CONCLUSIONS

A series easily soluble polyarylates were synthesized from either tetramethylbisphenol A or 1,1-bis(4-hydroxyphenyl)-1-phenylethane. The introduction of bulky pendent phenyl or tetra-substitution of methyl groups on the BPA phenyl rings increases free volume in the polymer chains and decrease packing density so as to allow much solvent to come in. Thus, the polyarylates have good solubility, and are readily soluble in a wide range of organic solvents. Moreover, the bulky pendent phenyls do good for preserving the thermal stability of the polyarylates, the glass transition temperatures of the pendent phenyl-containing polyarylates range from 165.0 to 201.6°C by DSC, and the initial decomposition temperatures in nitrogen are all above 480°C and char yields at 700°C are 37.97–40.53%. However, the polymers prepared from  $I_b$  have a large decrease in thermal stability.

## References

- Akutsu, F.; Inoki, M.; Takahashi, K. I.; Yonemura, T.; Kasashima, Y.; Naruchi, K. *Polym J* 1996, 28, 1107.
- Jeong, H. J.; Kakimoto, M. A.; Imai, Y. *J Polym Sci Polym Chem* 1991, 29, 1293.

3. Bhowmik, P. K.; Han, H. *Macromolecules* 1993, 26, 5287.
4. Wang, C. S.; Yang, R. W.; Hsu, K. R. *J Polym Sci Polym Chem* 1998, 36, 645.
5. Ellzey, K. A.; Ranganathan, T.; Zilberman, J.; Coughlin, E. B.; Farris, R. J.; Emrick, T. *Macromolecules* 2006, 39, 3553.
6. Wang, C. S.; Hsuan, L. C. *Polymer* 1999, 40, 4387.
7. Cai, R.; Prestone, J.; Samulski, E. T. *Macromolecules* 1992, 25, 563.
8. Liou, G. S.; Chern, Y. T. *J Polym Sci Polym Chem* 1999, 37, 645.
9. Krigbaum, W. R.; Hakemi, H.; Kotek, R. *Macromolecules* 1985, 18, 965.
10. Bhowmik, P. K.; Atkins, E. D. T.; Lenz, R. W. *Macromolecules* 1993, 26, 440.
11. Hsiao, S. H.; Chiang, H. W. *Eur Polym J* 2004, 40, 1691.
12. Liou, G. S.; Lin, S. M.; Yen, H. *J Eur Polym J* 2008, 44, 2608.
13. Liou, G. S.; Chang, C. W.; Huang, H. M.; Hsiao, S. H. *J Polym Sci Polym Chem* 2007, 45, 2004.
14. Han, X.; Padias, A. B.; Hall, H. K. *J Polym Sci Polym Chem* 1999, 37, 2891.
15. Zadrozna, I.; Parzuchowski, P.; Brzozowski, Z. K.; Milburn, G. H. W. *J Appl Polym Sci* 1999, 71, 1017.
16. Kharul, U. K.; Kulkarni, S. S.; Kulkarni, M. G.; Houde, A. Y.; Charati, S. G.; Joshi, S. G. *Polymer* 1998, 39, 2011.
17. Karadkar, P. B.; Kharul, U. K.; Bhole, Y. S.; Badhe, Y. P.; Tambe, S. S.; Kulkarni, B. D. *J Membr Sci* 2007, 303, 244.
18. Guzman-Gutierrez, M. T.; Ruiz-Trevino, F. A.; Zolotukhin, M.; Hernandez-Lopez, S.; Scherf, U. *J Membr Sci* 2007, 305, 347.
19. Eastmond, G. C.; Paprotny, J.; Irwin, R. S. *Polymer* 1999, 40, 469.
20. Ohishi, H.; Ohwaki, T.; Nishi, T. *J Polym Sci Polym Chem* 1998, 36, 2839.
21. Lenz, R. W.; Jin, J. I. *Macromolecules* 1981, 14, 1405.
22. Sinta, R.; Gaudiana, R. A.; Minns, R. A.; Rogers, H. G. *Macromolecules* 1987, 20, 2374.