

# Synthesis and Electrochromism of Novel Organosoluble Polyarylates Bearing Triphenylamine Moieties

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**ABSTRACT:** A series of novel aromatic polyarylates with triphenylamine units in the main chain and as the pendent group were prepared from the dicarboxylic acid monomer, *N,N*-bis(4-carboxyphenyl)-*N'*, *N'*-diphenyl-1,4-phenylenediamine (1), and various bisphenols. These polyarylates were amorphous and readily soluble in common organic solvents. They had excellent levels of thermal stability associated with moderately high  $T_g$  values (182–263 °C). These polymers exhibited strong UV–vis absorption bands at 357–360 nm in toluene solution and the photoluminescence spectra showed maximum bands around 493–503 nm in the green region. The hole-transporting and electrochromic properties were examined by electrochemical and spectroelectrochemical methods. Cyclic voltammograms of the polyarylates exhibited two reversible oxidation redox couples in acetonitrile solution at  $E_{\text{onset}}$  0.77–0.79 V and 1.12–1.14 V, respectively. The typical polymer **3b** film revealed good stability of electrochromic characteristics, with color change from colorless to green and blue at applied potentials ranging from 0.00 to 1.24 V. These anodically polymeric electrochromic materials not only showed excellent reversible electrochromic stability with good green coloration efficiency ( $CE = 159 \text{ cm}^2/\text{C}$ ) and blue coloration efficiency ( $CE = 154 \text{ cm}^2/\text{C}$ ) but also exhibited high contrast of optical transmittance change ( $\Delta T\%$ ), 54% in 895 nm for green color and up to 84% in 595 nm for blue color. After over 100 cyclic switches, the polymer films still exhibited excellent stability of electrochromic characteristics. © 2007 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 45: 2004–2014, 2007

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## INTRODUCTION

Electrochromic materials and devices have been studied for years because of their scientific and technological interest. Electrochromism involves electroactive materials that present a reversible change in optical properties when the material

is electrochemically oxidized or reduced. Several applications have been envisaged for systems based on electrochromic devices, for example, light and overheating protection windows, mirrors, glazing, smart sunglasses, temperature indicators, safeguarding systems, optical filters, and display panels. Nowadays, there are two commercial applications: one is the power-triggered dimming rear-view mirrors available in some top-of-the line automobiles, whose largest manufacturer is Gentex Corp. (USA); the second

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application is the electrochromic smart window which is being developed worldwide.<sup>1</sup>

It is well known that wholly aromatic polyesters (polyarylates) possess high thermal stability, optical transparency in visible light region, and excellent mechanical properties.<sup>2</sup> Interest in molecular engineering of physical properties for high-performance polymers persists because small alternation of molecular structure of a polymer can dramatically influence performance and processing properties. So far, however, most studies have focused on their high-performance applications. There has been no application using these polymers as photonic/electronic device materials. Thus, modulation of their photo-physical and electrical properties by means of a simple condensation synthetic method may be an impressive challenge in terms of new development of polymeric light-emitting diodes (PLEDs) and electrochromic materials.<sup>3</sup>

The anodic oxidation pathways of triphenylamine (TPA) were well studied.<sup>4</sup> The electrogenerated cation radical of TPA<sup>+</sup>• is not stable and could be dimerized to form tetraphenylbenzidine by tail to tail coupling with loss of two protons per dimer. When the phenyl groups were incorporated by electron-donating substituents at the para-position of TPA, the coupling reactions were greatly prevented that afforded stable cationic radicals.<sup>5,6</sup> TPA and its derivatives have been extensively investigated because of their high charge mobility and electrochromism. The main disadvantage, which often makes application difficult, is their insufficient morphological stability and susceptibility to crystallization or phase separation. To solve this problem, attempts to introduce TPA units into the main or side chain of the polymer backbone were undertaken intensively, and some important results have been obtained.<sup>7–14</sup> Furthermore, the uses of polymeric materials also provide the possibility for various chemical design and modifications.

However, many of these high performance polymers are insoluble in common solvents and are infusible at temperatures below the polymer decomposition temperature which make them generally intractable or difficult to process, thus restricting their applications. To overcome such a difficulty, polymer structure modification becomes necessary. We have reported the synthesis of aromatic polyimides,<sup>15–17</sup> polyamides,<sup>18–20</sup> and polyhydrazides and polyoxadiazoles<sup>21–23</sup> bearing TPA units in the main chain. Because of the incorporation of bulky, three-dimensional TPA

moieties along the polymer backbone, all the polymers were amorphous and had good solubility in many aprotic solvents. Recently, we have initiated a study to obtain TPA-containing anodic electrochromic polymers that exhibited green and blue colors in the oxidized states and were transparent in the neutral state.<sup>24–27</sup> However, to the best of our knowledge, there is no literature dealing with the structures and properties of polyarylates with chromophoric triarylamine unit. It is thus worthy to explore the feasibility of new high-performance polyarylate system with novel optoelectronic functions. In addition, the prepared TPA-containing polyarylates may find application in anodically polymeric electrochromic materials and organic electroluminescent elements. Therefore, this article deals with the preparation and basic characterization of a new class of polyarylates from the direct polycondensation reaction of *N,N*-bis(4-carboxyphenyl)-*N,N'*-diphenyl-1,4-phenylenediamine(**1**) with various bisphenols. The general properties such as solubility, crystallinity, and thermal properties are described. The electrochemical and electrochromic properties of these polymers are also investigated herein.

## EXPERIMENTAL

### Materials

*N,N*-bis(4-carboxyphenyl)-*N,N'*-diphenyl-1,4-phenylenediamine (mp 274–277 °C) was synthesized by the condensation of 4-aminotriphenylamine with 4-fluorobenzonitrile in the presence of sodium hydride, followed by alkaline hydrolysis of the intermediate dinitrile compound according to a reported procedure.<sup>25</sup> Diphenylamine (ACROS), palladium on charcoal (Pd/C; Fluka), sodium hydride (95%; dry, Aldrich), 4-fluorobenzonitrile (TCI), *N,N*-dimethylacetamide (DMAc) (TEDIA), *N,N*-dimethylformamide (DMF) (ACROS), *N*-methyl-2-pyrrolidinone (NMP) (TEDIA), pyridine (Py) (TEDIA), and diphenyl chlorophosphate (DPCP) (ACROS) were used without further purification. Commercially obtained anhydrous lithium chloride was dried under vacuum at 150 °C for 10 h. The bisphenol monomers that include 4,4'-isopropylidenediphenol (**2a**) (bisphenol A) (ACROS), 9,9-bis(4-hydroxyphenyl)fluorene (**2b**) (TCI), phenolphthalein (**2c**) (Aldrich), and 2,2-bis(4-hydroxyphenyl)hexafluoropropane (**2d**) (TCI) were purified by recrystallization from solvents. Tetrabutylammonium perchlorate (TBAP) was

obtained from ACROS and recrystallized twice from ethyl acetate and then dried *in vacuo* prior to use. All other reagents were used as received without further purification.

### Preparation of Polyarylates via Direct Polycondensation<sup>28</sup>

A typical example of polycondensation is described as follows. A solution of diphenylchlorophosphate (DPCP) (0.69 g), LiCl (0.08 g), and pyridine (4.0 mL) was stirred at room temperature for 30 min and then added dropwise for 20 min to a hot solution (preheated at 120 °C for 5 min) containing 0.501 g (1.00 mmol) of *N,N*-bis(4-carboxyphenyl)-*N',N'*-diphenyl-1,4-phenylenediamine (**1**) and 0.228 g (1.00 mmol) of bisphenol A in pyridine (2.0 mL). The final solution was heated at 120 °C for 3 h under stirring. The obtained polymer solution was poured slowly into 300 mL of stirred methanol giving rise to a stringy, fiber-like precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried under vacuum at 100 °C. Reprecipitations of the polymer by chloroform/methanol were carried out twice for further purification.

ELEM. ANAL values of the polymer **3a** are calculated for  $(C_{47}H_{36}N_2O_4)_n$  (692.80)<sub>n</sub>: C, 81.48%; H, 5.24%; N, 4.04%. Found: C, 79.74%; H, 5.34%; N, 3.98%. IR (film): 2965, 2925, 2853 (—CH<sub>3</sub>, C—H stretch), 1734 (C=O stretch), 1200–1250 cm<sup>-1</sup> (C—O stretch). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 1.72 (s, 3H, —CH<sub>3</sub>), 7.04–7.08 (m, 8H, H<sub>c</sub> + H<sub>g</sub> + H<sub>d</sub>), 7.08–7.17 (t, 8H, H<sub>i</sub> + H<sub>e</sub>), 7.21 (d, 4H, H<sub>b</sub>), 7.29 (t, 8H, H<sub>f</sub> + H<sub>h</sub>), 8.10 (d, 4H, H<sub>a</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 31.0 (—CH<sub>3</sub>), 42.5 (C<sup>17</sup>), 121.1 (C<sup>15</sup>), 122.1 (C<sup>3</sup>), 123.3 (C<sup>1</sup>), 123.3 (C<sup>12</sup>), 124.3 (C<sup>7</sup>), 124.6 (C<sup>10</sup>), 127.8 (C<sup>6</sup>), 127.9 (C<sup>14</sup>), 129.4 (C<sup>11</sup>), 131.7 (C<sup>2</sup>), 139.5 (C<sup>8</sup>), 145.7 (C<sup>5</sup>), 147.4 (C<sup>9</sup>), 147.9 (C<sup>16</sup>), 148.9 (C<sup>4</sup>), 151.4 (C<sup>13</sup>), 164.7 (C=O). The other polyarylates **3b–3d** were synthesized by a similar procedure described as earlier.

### Measurements

Infrared spectra were recorded on a PerkinElmer RXI FT-IR spectrometer. <sup>1</sup>H- and <sup>13</sup>C NMR spectra were measured on a Bruker Avance 300 MHz FT-NMR system. Elemental analyses were run in an Elementar VarioEL-III. Gel permeation chromatography (GPC) was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Waters 5-μm

Styragel HR-2 and HR-4 columns (7.8 mm i.d. × 300 mm) were connected in series with tetrahydrofuran (THF) as the eluent at a flow rate of 1 mL/min and were calibrated with narrow polystyrene standards. Wide-angle X-ray diffraction (WAXD) measurements of the polymer films were performed at room temperature (ca. 25 °C) on a Shimadzu XRD-7000 X-ray diffractometer (40 kV, 20 mA) with a graphite monochromator, using nickel-filtered Cu Kα radiation. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Varian Cary 50 Probe spectrometer. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 6–8-mg film samples heated in flowing nitrogen or air (flow rate = 40 cm<sup>3</sup>/min) at a heating rate of 20 °C/min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 20 °C/min in flowing nitrogen (20 cm<sup>3</sup>/min). Electrochemistry was performed with a CHI 611B electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downward. Cyclic voltammetry was performed with the use of a three-electrode cell in which indium-tin oxide (ITO) (polymer films area about 0.7 cm × 0.5 cm) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of a homemade Ag/AgCl, KCl (sat.) reference electrode. Absorption spectra in the spectroelectrochemistry experiments were measured with a HP 8453 UV–Visible spectrophotometer. Coloration efficiency is derived from the equation  $\eta = \Delta OD / Q$ , where  $\Delta OD$  is the optical density change at specific absorption wavelength and  $Q$  is the ejected charge determined from the *in situ* experiments. Photoluminescence spectra were measured with a Jasco FP-6300 spectrofluorometer. The fluorescence quantum yields ( $\Phi_{PL}$ ) of polymer solution were determined in toluene against quinine sulfate (ACROS) in 1 N H<sub>2</sub>SO<sub>4(aq)</sub> as the standard ( $\Phi_{PL} = 0.546$ ).

## RESULTS AND DISCUSSION

### Polymer Synthesis

A series of novel aromatic polyarylates **3a–3d** having the TPA unit in the main chain and as the pendent group were prepared from the dicarboxylic acid, *N,N*-bis(4-carboxyphenyl)-*N',N'*-

diphenyl-1,4-phenylenediamine (**1**), and various bisphenols by the direct polycondensation reaction with DPCP and pyridine as condensing agents (Scheme 1). All the polymerizations proceeded homogeneously throughout the reaction and afforded clear and viscous polymer solutions. These polyarylates were obtained in almost quantitative yield. The GPC curves of polyarylates indicated that weight-average molecular weight ( $M_w$ ) values were in the range of 10,000–14,000 relative to standard polystyrene, and polydispersity (PDI) values, a measure of molecular weight distribution, were 2.0–2.1 (Table 1). Considering the data for  $M_n$ , only oligomers could be obtained because just 7–9 repeating units are present in the polymers. The formation of polyarylates was confirmed by means of IR and NMR spectroscopy. The typical FTIR spectrum of polyarylate **3a** (Fig. 1) exhibited characteristic ester absorption band around  $1734\text{ cm}^{-1}$  (C=O stretching) and in the region of  $1200\text{--}1300\text{ cm}^{-1}$  (C–O–C stretching). Figure 2 illustrates the  $^1\text{H}$ - and  $^{13}\text{C}$  NMR spectra of the polyarylate **3a**. Assignments of each carbon and proton are assisted by the two-dimensional C–H HMQC NMR spectrum shown in Figure 3,

**Table 1.** Average Molecular Weights<sup>a</sup> of Polyarylates

Polymer Code	$M_w$	$M_n$	PDI
<b>3a</b>	12,000	5700	2.1
<b>3b</b>	12,500	6000	2.1
<b>3c</b>	10,000	5000	2.0
<b>3d</b>	14,000	6700	2.1

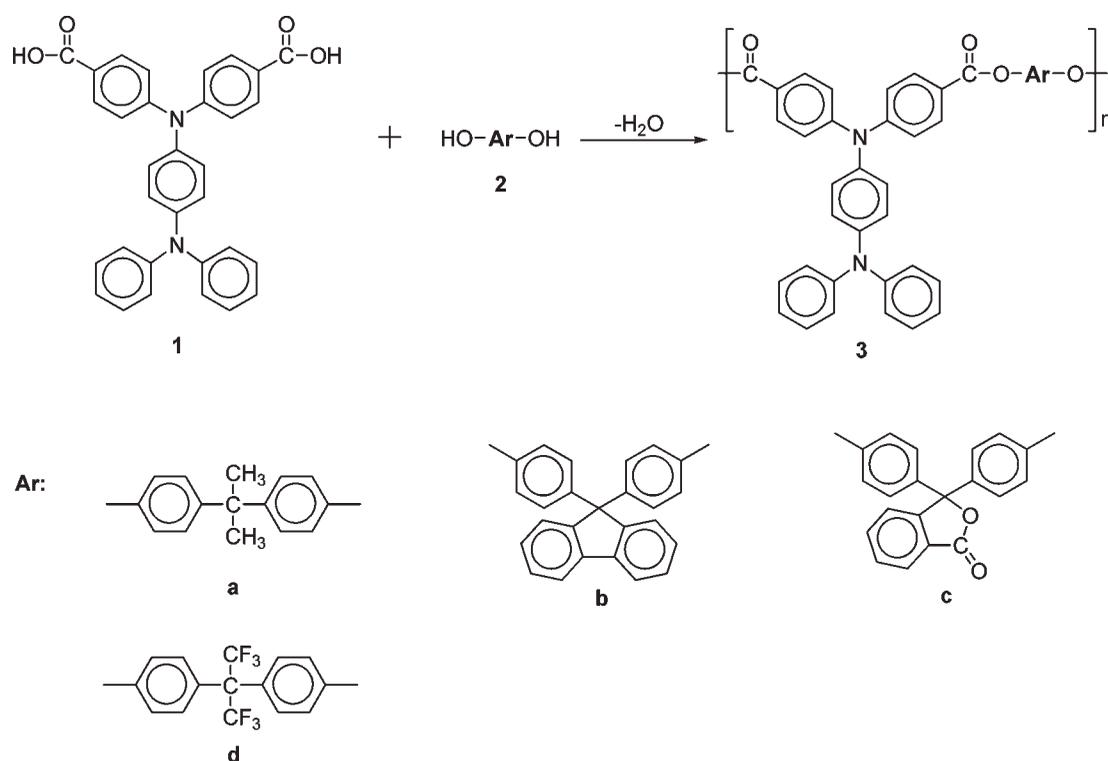
<sup>a</sup> Relative to polystyrene standards, using THF as the eluent.

and agree well with the proposed molecular structure of polyarylate **3a**.

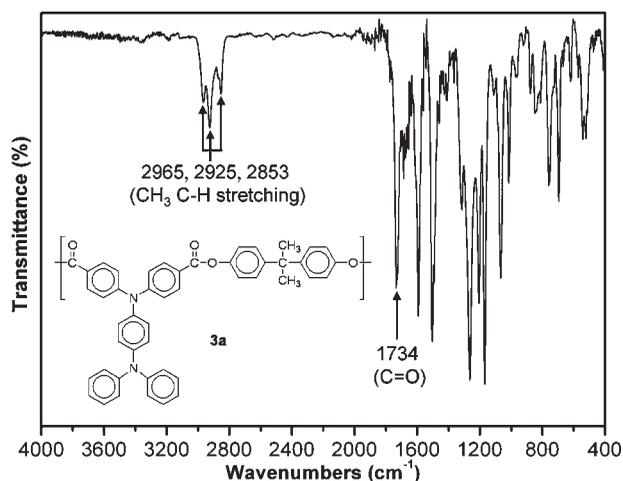
## Polymer Properties

### Basic Characterization

The qualitative solubility of the polyarylates was studied in various solvents, and the results are summarized in Table 2. All these polyarylates were highly soluble in common solvents such as NMP, DMAc, and even in chloroform and THF. X-ray diffraction results, as discussed later, revealed that all polymers were amorphous. The solubility behavior was consistent with the X-ray diffraction studies because of



**Scheme 1.** Synthesis of polyarylates.

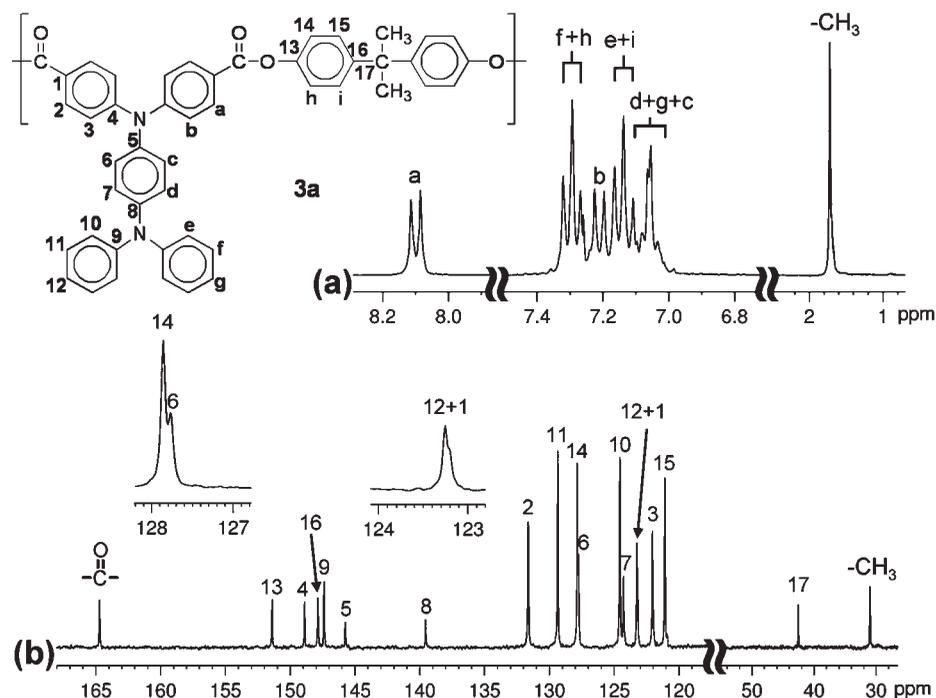


**Figure 1.** The FTIR spectrum of polyarylate **3a**.

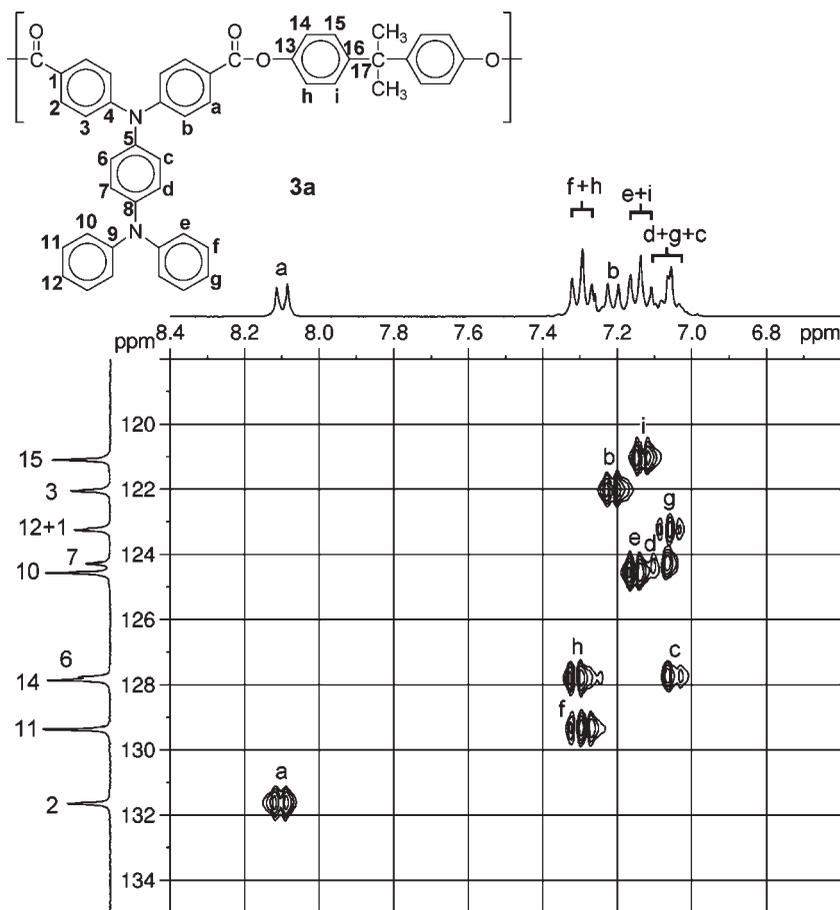
introduction of the bulky TPA core in the repeat unit. Thus, the excellent solubility makes these polymers for practical applications by cast processes to afford transparent and almost colorless free-standing films. The structural characterization was made first by X-ray measurement with the prepared films. The WAXD patterns of these polyarylates indicate that the polymers are essentially amorphous, revealing that the TPA-containing polymers do not form a well-packed

structure. Thus, the amorphous nature of these polymers was reflected in their excellent solubility, which is in agreement with the general rule that solubility decreases with increasing crystallinity.

The thermal properties of all the obtained polymers were investigated by DSC and TGA. The results are summarized in Table 3. All the polymers indicated no clear melting endotherms up to the decomposition temperatures on the DSC thermograms. This result supports the amorphous nature of the TPA-containing polymers. The glass transition temperatures ( $T_g$ ) of these polyarylates could be easily measured in the DSC charts of the second heating trace, and observed in the range of 182–263 °C, depending on the structure of the bisphenol component, and decreased with decreasing rigidity of the polymer backbone, or with introduction of flexible linkages in the polymer main chain. The  $T_g$  values are substantially higher than those of 4,4'-bis[*N,N*-(*m*-tolyl)phenylamino]biphenyl (TPD) (63 °C), indicating that the use of these polymers may greatly improve the device durability, which relates to the  $T_g$  of the materials as reported by Tokito et al.<sup>29,30</sup> Representative TGA curves of polyarylate **3d** under both air and nitrogen atmospheres are shown in Figure 4. All the polyarylates exhibited good thermal sta-



**Figure 2.** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectra of polyarylate **3a** in chloroform-*d*.



**Figure 3.** C–H HMQC spectrum of polyarylate **3a** in chloroform-*d*.

bility without significant weight losses up to 470 °C under nitrogen. The 10% weight-loss temperatures ( $T_d^{10}$ ) of these polyarylates under nitrogen and air were recorded in the range of 485–535 and 480–525 °C, respectively. The amount of carbonized residue (char yield) of these polymers under nitrogen atmosphere was above 50% at 800 °C. The high char yields of

these polymers can be ascribed to their high aromatic content.

#### Optical and Electrochemical Properties

The electrochemical and optical properties of the polyarylates were investigated by cyclic voltammetry and UV–vis and photoluminescence (PL)

**Table 2.** Solubility<sup>a</sup> of Polyarylates

Polymer Code	Solvent							
	NMP	DMAc	DMF	<i>m</i> -Cresol	THF	CHCl <sub>3</sub>	Toluene	MeCN
<b>3a</b>	++	++	++	+	++	++	++	–
<b>3b</b>	++	++	++	+	++	++	±	–
<b>3c</b>	++	++	++	+	++	++	±	–
<b>3d</b>	++	++	++	+	++	++	++	–

NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; THF, Tetrahydrofuran; CHCl<sub>3</sub>, Chloroform; MeCN, Acetonitrile.

<sup>a</sup> The solubility was determined by using 1 mg sample in 1 mL of solvent. ++, soluble at room temperature; +, soluble on heating; ±, partially soluble or swelling on heating; –, insoluble even on heating.

**Table 3.** Thermal Properties of Polyarylates<sup>a</sup>

Polymer Code	T <sub>g</sub> (°C) <sup>b</sup>	T <sub>d</sub> at 5% Weight Loss (°C) <sup>c</sup>		T <sub>d</sub> at 10% Weight Loss (°C) <sup>c</sup>		Char Yield (wt %) <sup>d</sup>
		N <sub>2</sub>	Air	N <sub>2</sub>	Air	
<b>3a</b>	182	490	470	515	495	50
<b>3b</b>	263	515	500	535	525	62
<b>3c</b>	235	465	460	485	480	62
<b>3d</b>	189	470	465	485	480	58

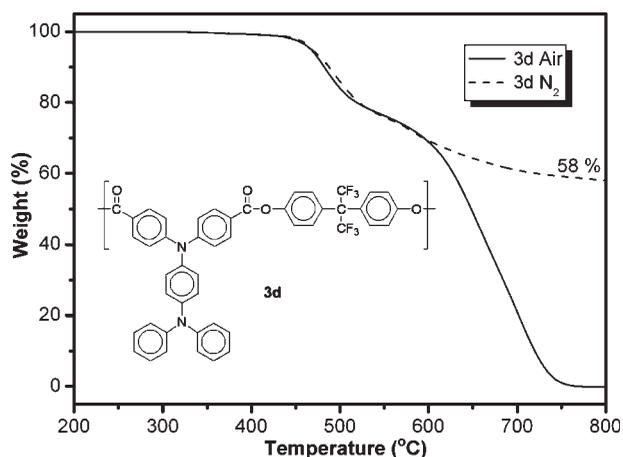
<sup>a</sup> The polymer film samples were heated at 200 °C for 1 h prior to all the thermal analyses.

<sup>b</sup> Midpoint temperature of baseline shift on the second DSC heating trace (rate 20 °C/min) of the sample after quenching from 400 °C.

<sup>c</sup> Decomposition temperature, recorded via TGA at a heating rate of 20 °C/min and a gas-flow rate of 30 cm<sup>3</sup>/min.

<sup>d</sup> Residual weight percentage at 800 °C in nitrogen.

spectroscopy, and the results are summarized in Table 4. Molar absorptivity ( $\epsilon$ ) and PL spectra of representative polyamides, measured in toluene (Conc., 10<sup>-5</sup> mol/L), and the solid thin films are shown in Figure 5. These polymers **3a–3d** exhibited UV–vis absorption bands at 355–356 nm in toluene solution, which are assignable to the  $\pi$ – $\pi^*$  transition resulting from the conjugation between the aromatic rings and nitrogen atoms, and showed PL emission maxima around 493–503 nm in the green region with fluorescence quantum yield ranging from 5.2% for **3d** to 7.9% for **3a**. The cast films of these polymers also showed UV–vis absorption peaks and PL emission maxima similar to those of their toluene solutions, which means these polymers are not able to form a  $\pi$ -stacking structure in the

**Figure 4.** TGA thermograms of polyarylate **3d** at a scan of 20 °C/min.**Table 4.** Optical and Electrochemical Properties of Polyarylates

Index	Solution $\lambda$ (nm) <sup>a</sup>			Film $\lambda$ (nm)			Oxidation (V vs. Ag/AgCl)			HOMO <sup>f</sup> (eV)	LUMO <sup>g</sup> (eV)	
	Abs max	PL max <sup>b</sup>	PL (%) <sup>c</sup>	$\lambda_0$ <sup>d</sup>	Abs max	Abs onset	PL max <sup>b</sup>	First E <sub>onset</sub>	Second E <sub>1/2</sub>			E <sub>g</sub> <sup>e</sup> (eV)
<b>3a</b>	357	493	7.87	377	356	414	498	0.78	1.13	3.00	5.12	2.12
<b>3b</b>	360	494	7.64	381	354	415	500	0.78	1.12	2.99	5.12	2.13
<b>3c</b>	360	500	6.35	377	357	414	508	0.77	1.12	3.00	5.11	2.11
<b>3d</b>	360	503	5.14	378	356	413	505	0.79	1.14	3.00	5.13	2.13

<sup>a</sup> Polymer concentration of 10<sup>-5</sup> M in toluene at room temperature.

<sup>b</sup> They were excited at abs<sub>max</sub> for both solid and solution states.

<sup>c</sup> These values were measured by using quinine sulfate (dissolved in 1 N H<sub>2</sub>SO<sub>4</sub> (aq) with a concentration of 10<sup>-5</sup> M, assuming  $\Phi_{PL}$  of 0.546) as a standard at 24–25 °C.

<sup>d</sup> The cutoff wavelengths ( $\lambda_0$ ) from the transmission UV/vis absorption spectra of polymer films (thickness, 1–3  $\mu$ m).

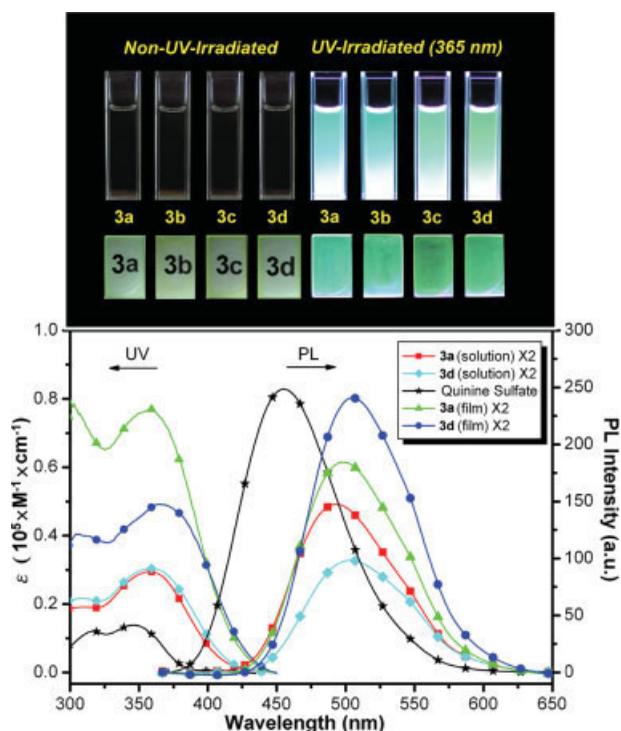
<sup>e</sup> The data were calculated by the following equation: gap = 1240/ $\lambda_{onset}$  of polymer film.

<sup>f</sup> The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).

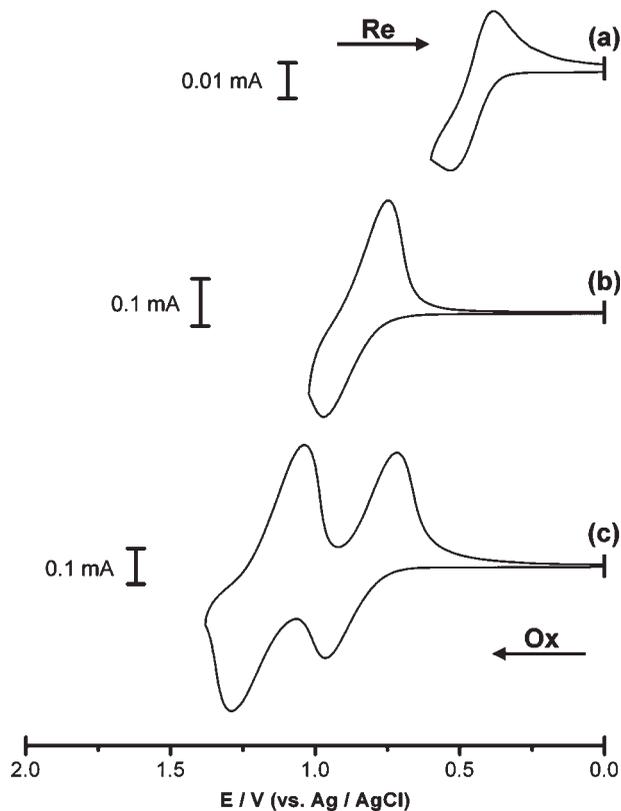
<sup>g</sup> LUMO = HOMO-gap.

solid state because of the twisted triarylamine moieties. The toluene solution and thin films of the polymers were almost colorless and gave a green PL under irradiation with a general UV lamp ( $\lambda = 365$  nm) as also shown in Figure 5. These polymer films were also measured for optical transparency using UV-vis transmittance spectroscopy. The cutoff wavelengths (absorption edge,  $\lambda_0$ ) in the range of 377–381 nm revealed light-color and high optical transparency from the UV-vis spectra are also indicated in Table 4.

The electrochemical behavior of these polyarylates was investigated with cyclic voltammetry conducted by the cast film on an ITO-coated glass substrate as working electrode in dry acetonitrile containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere. The cyclic voltammograms for these polyarylates exhibited two reversible oxidation redox couples at  $E_{\text{onset}} = 0.77$ – $0.79$  V and  $E_{1/2} = 1.12$ – $1.14$  V, respectively. The typical cyclic voltammogram for polymer **3b** is shown in Figure 6. There are two reversible



**Figure 5.** Absorption and PL spectra of polyarylates with a concentration of toluene ( $10^{-5}$  M) and polymer films. Photoluminescence of polyarylates in toluene solution ( $10^{-5}$  M) and thin films (thickness, 1–3  $\mu\text{m}$ ) by UV irradiation (Excited at 365 nm).



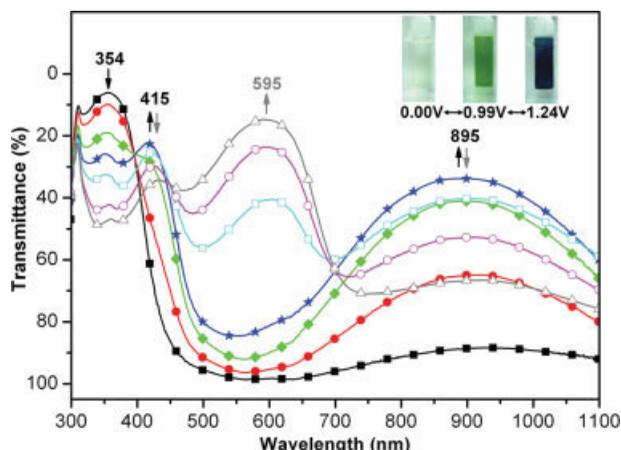
**Figure 6.** Cyclic voltammograms of (a) ferrocene, (b) the first oxidation redox of polyarylate **3b**, and (c) the first and second oxidation redox of polyarylate **3b** film onto an indium-tin oxide (ITO)-coated glass substrate in  $\text{CH}_3\text{CN}(\text{aq})$  containing 0.1 M TBAP. Scan rate = 0.1 V/s.

oxidation redox couples for polyarylate **3b** at  $E_{\text{onset}} = 0.78$ , and  $E_{1/2} = 1.12$  V, corresponding to successive one electron removal from the nitrogen atoms at  $N,N,N',N'$ -tetraphenyl-1,4-phenylenediamine structure in each repeating unit to yield one stable delocalized radical cation, polyarylate<sup>+</sup>, and one stable quinonoid-type dication, polyarylate<sup>2+</sup>, respectively. The triarylamine centers at  $N,N,N',N'$ -tetraphenyl-1,4-phenylenediamine structures of repeating unit are strongly coupled by the fact that the separation of the first and the second oxidation redox couple is much larger than 35.6 mV.<sup>31</sup> Because of the good stability of the films and excellent adhesion between the polymer and ITO substrate, the polyarylates **3b** exhibited excellent reversibility of electrochromic characteristics by continuous over one hundred cyclic scans between 0.00 and 1.24 V, changing color from original transparent to green, and then to blue. In addition, the first electron removal for polyarylates is assumed to occur at the

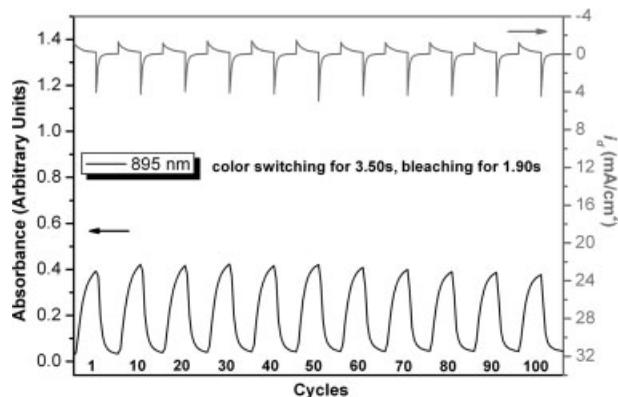
nitrogen atom on the pendent TPA unit, which is more electron-rich than the N atom on the main-chain TPA group surrounded by two phenyl groups with ester linkages. The energy of the HOMO and LUMO levels of the investigated polyarylates can be determined from their oxidation onset potentials and the onset absorption wavelength, and the results are listed in Table 4. For example, the oxidation onset potential for polyarylate **3b** has been determined as 0.78 V versus Ag/AgCl. The external ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox standard  $E_{1/2}$  is 0.46 V versus Ag/AgCl in CH<sub>3</sub>CN. Assuming that the HOMO energy for the Fc/Fc<sup>+</sup> standard is 4.80 eV with respect to the zero vacuum level, the HOMO energy for polyarylate **3b** has been evaluated to be 5.12 eV.

### Electrochromic Characteristics

Electrochromism of these polyarylates thin films was examined by casting polymer solution onto an ITO-coated glass substrate, and their electrochromic absorption spectra were monitored by a UV-vis spectrometer at different applied potentials. The electrode preparations and solution conditions were identical to those used in CV. All these polyarylates exhibited similar electrochromic properties, and the typical electrochromic transmittance spectra of polymer **3b** are

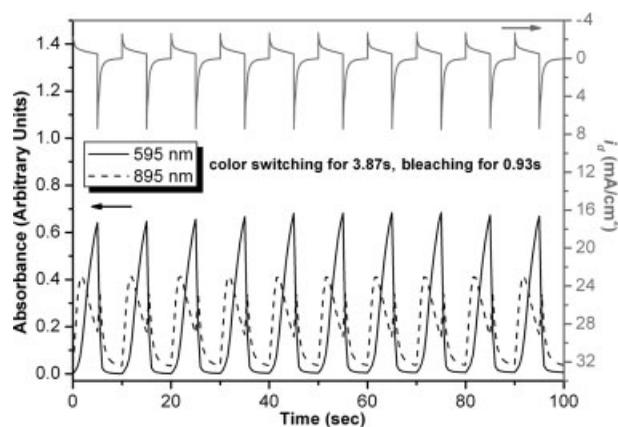


**Figure 7.** Electrochromic behavior of polyarylate **3b** thin film (in CH<sub>3</sub>CN with 0.1 M TBAP as the supporting electrolyte) at (■) 0.00 (●) 0.80 (◆) 0.90 (★) 1.00 (□) 1.10 (○) 1.20 (△) 1.24 V. **3b**<sup>+</sup>: first oxidation state of polyarylate **3b** (solid symbol with black solid arrow); **3b**<sup>2+</sup>: second oxidation state of polyarylate **3b** (hollowly symbol with gray solid arrow). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 8.** Potential step absorptometry and current consumption of polyarylate **3b** for 100 cyclic scans by applying potential steps 0.00–0.99 (V vs. Ag/Ag<sup>+</sup>), (coated area, 1 cm<sup>2</sup>) and cycle time 10s for coloration efficiency (159 cm<sup>2</sup>/C).

shown in Figure 7. When the applied potentials increased positively from 0.00 to 0.99 V, the peak of absorption at 354 nm, characteristic for neutral form polymer **3b**, decreased gradually, while two new bands grew up at 415 and 895 nm due to the first stage oxidation. When the potential was adjusted to a more positive value of 1.24 V, corresponding to the second step oxidation, the peak of characteristic absorbance decreased gradually while one new band grew up at 595 nm. Meanwhile, the film changed from original colorless to green and then to a blue oxidized form. Polymer **3b** exhibited highly contrast of optical transmittance change ( $\Delta T\%$ ) up to 84% in 595 nm. The coloration efficiency



**Figure 9.** Potential step absorptometry and current consumption of polyarylate **3b** for 10 cyclic scans by applying potential steps 0.00–1.24 (V vs. Ag/Ag<sup>+</sup>), (coated area, 1 cm<sup>2</sup>) and cycle time 10 s for coloration efficiency (154 cm<sup>2</sup>/C).

**Table 5.** Optical and Electrochemical Data Collected for Coloration Efficiency Measurements of Polyarylate **3b**

Cycle <sup>a</sup>	$\Delta OD_{895}$ <sup>b</sup>	$Q$ (mC/cm <sup>2</sup> ) <sup>c</sup>	$\eta$ (cm <sup>2</sup> /C) <sup>d</sup>	Decay (%) <sup>e</sup>
1	0.352	2.32	152	0
20	0.377	2.37	159	0
40	0.372	2.34	159	0
60	0.365	2.37	154	3.1
80	0.346	2.31	150	5.7
100	0.334	2.24	149	6.3

<sup>a</sup> Times of cyclic scan by applying potential steps: 0.00  $\leftrightarrow$  0.99 (V vs. Ag/Ag<sup>+</sup>).

<sup>b</sup> Optical density change at 895 nm.

<sup>c</sup> Ejected charge, determined from the *in situ* experiments.

<sup>d</sup> Coloration efficiency is derived from the equation  $\eta = \Delta OD/Q$ .

<sup>e</sup> Decay of coloration efficiency after cyclic scans.

at 595 nm is as fair as about 154 cm<sup>2</sup>/C with high optical density change ( $\delta OD_{595}$ ) up to 0.64, determined from the *in situ* experiments.<sup>32</sup> The color switching times were estimated by applying a potential step, and the absorbance profiles are shown in Figures 8 and 9. The switching time was defined as the time that required for reach 90% of the full change in absorbance after switching potential. Thin film from polyarylate **3b** would require 3.50 s at 0.99 V for switching absorbance at 895 nm and 1.90 s for bleaching. When the potential was set at 1.24 V, thin film **3b** would require almost 3.87 s for coloration at 595 nm and 0.93 s for bleaching. After over 100 cyclic scans for green color (Fig. 8), the polymer films still exhibited good stability of electrochromic characteristics. The electrochromic coloring efficiency ( $\eta = \Delta OD_{895}/Q$ ) ranged from 152 cm<sup>2</sup>/C for the first cycle to 149 cm<sup>2</sup>/C for the 100th cycle. After over 10 cyclic scans for blue color (Fig. 9), the electrochromic coloring efficiency ( $\eta = \Delta OD_{595}/Q$ ) ranged from 154 cm<sup>2</sup>/C for the 1st cycle to 149 cm<sup>2</sup>/C for the 10th cycle. These electrochromic behavior and coloring efficiency decay of polyarylate **3b** were also calculated,<sup>33</sup> and the results are summarized in Table 5.

## CONCLUSIONS

A series of stable anodic green electrochromic polyarylates with high contrast of optical transmittance change ( $\Delta T\%$ ) up to 84% in 595 nm have been readily prepared from the *N,N*-bis(4-

carboxyphenyl)-*N,N'*-diphenyl-1,4-phenylenediamine and various bisphenols. The introduction of the bulky intrinsic electron-donating TPA group could not only increase the HOMO energy levels but also disrupt the coplanarity of aromatic units in chain packing, which increase the between-chains spaces or free volume and enhance solubility of the polyarylates. Thus, all of the polymers were amorphous with good solubility in common solvents. In addition to moderate high  $T_g$  values and good thermal stability, these anodically polymeric electrochromic materials also showed excellent cyclic stability of electrochromic characteristic with good coloration efficiency from 152 cm<sup>2</sup>/C for first cycle to 149 cm<sup>2</sup>/C for 100th cycle, changing color from the original transparent neutral form to the green oxidized forms when scanning potentials positively from 0.00 to 0.99 V. After over 100 cyclic switches, the polymer films still exhibited excellent reversibility of electrochromic characteristics.

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