Synthesis, Photoluminescence, and Electrochromic Properties of Wholly Aromatic Polyamides Bearing Naphthylamine Chromophores

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ABSTRACT: A series of novel polyamides with pendent naphthylamine units having inherent viscosities of 0.15–1.02 dL/g were prepared via direct phosphorylation polycondensation from various diamines and a naphthylamine-based aromatic dicarboxylic acid, 1-[N,N-di(4-carboxyphenyl)amino]naphthalene. These amorphous polyamides were readily soluble in various organic solvents and could be cast into transparent and tough films. The aromatic polyamides had useful levels of thermal stability associated with high glass-transition temperatures (268–355 °C), 10% weight loss temperatures in excess of 480 °C, and char yields at 800 °C in nitrogen higher than 60%. These polymers showed maximum ultraviolet–visible absorption at 350–358 nm and exhibited fluorescence emission maxima around 435–458 nm in N-methyl-2-pyrrolidinone solutions with fluorescence quantum yields ranging from 0.4 to 15.0%. The hole-transporting and electrochromic properties were examined with electrochemical and spectroelectrochemical methods. Cyclic voltammograms of the polyamide films cast onto an indium tin oxide coated glass substrate exhibited one oxidative redox couple around 1.08–1.16 V (oxidation onset potential) versus Ag/AgCl in an acetonitrile solution and revealed good stability of the electrochromic characteristics, with a color change from colorless to green at applied potentials ranging from 0 to 1.6 V. © 2006 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 44: 6094–6102, 2006

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INTRODUCTION

The first report of polymeric light-emitting diodes based on poly(p-phenylenevinylene)[1] triggered a large amount of interest in emitting polymer layers.[2–4] The advantages of emitting polymer materials over their molecular counterparts, first reported in 1987 by Tang and VanSlyke,[5] are an easy process for the formation of films by spin coating and a drastic decrease in the potential for crystallization of the films, which is quite common among small organic molecules. Organic light-emitting diodes are readily available in all three primary colors. However, blue light-emitting materials remain an area of intense research activity in competition with GaN-based inorganic light-emitting diodes. Furthermore, in full-color displays, a polymer with a large energy band gap that can efficiently emit blue light and also serve as an energy-transfer donor in the presence of low-energy fluorophores is highly desirable. The polymer approaches to blue electroluminescent

devices are generally categorized into fully conjugated polymers and partially conjugated polymers with isolated chromophores that are attached to the main chain or side chain of the polymers. However, the solubility of many highly conjugated polymers is low, particularly for blue-emitting species. These targeted blue-emitting polymers therefore often bear large alkyl, alkoxy, or aryloxy groups to improve the solubility, which lower their glass-transition temperatures and thermal stability.

Many blue-emitting polymers, however, have low quantum yields for solid-state emissions or sizable solid-state emission wavelength shifts with respect to solution-phase emission spectra because of the presence of intramolecular charge transfer[6,7] and interchain interactions such as aggregation, excimer formation, and polaron pair formation.[8,9] There are some effective approaches to minimizing these undesirable effects. For example, the introduction of an asymmetric meta linkage in the main conjugated chain of the polymer can limit interchain interactions and constrain exciton migration to the quenching site.[10,11] The greater the torsion angle is, the more interrupted the effective conjugated length is or the more reduced the interchain interaction is. Another approach is to use bulky substituents to limit close packing between aromatic chromophores in the solid state.[12]

Wholly aromatic polyamides are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties. However, the rigidity of the backbone and strong hydrogen bonding result in high melting temperatures or glass-transition temperatures and limited solubility in most organic solvents.[13,14] These properties make them generally intractable or difficult to process, thus restricting their applications in some fields. To overcome these limitations, polymer-structure modification becomes necessary. One of the common approaches for increasing the solubility and processability of polyamides without sacrificing high thermal stability is the introduction of bulky, packing-disruptive groups into the polymer backbone.[15–27] Recently, we reported the synthesis of soluble, aromatic poly(amine amide)s bearing triphenylamine units in the main chain based on N,N'-bis(4-aminophenyl)-N,N'-diphenyl-1,4-phenylenediamine[28] and 4,4'-diamino-4''-N-carbazolyltriphenylamine,[29] respectively. Because of the incorporation of bulky, propeller-shaped triphenylamine units along the polymer backbone, all the polymers were amorphous, showed good solubility in many aprotic solvents and good film-forming capability, and exhibited high thermal stability.

Therefore, in this study we synthesized a series of new aromatic polyamides from a naphthylamine-based diacid monomer, 1-[N,N-di(4-carboxyphenyl)amino]naphthalene. The incorporation of bulkier 1-naphthyldiphenylamine moieties should effectively interrupt the intermolecular hydrogen bonding between the polyamides and greatly disturb the coplanarity of the aromatic rings to reduce stacking efficiency for obtaining blue-light-emitting polymers without significant π–π interaction aggregation between the polymer chains. The general properties, such the as solubility, crystallinity, and thermal properties, are reported. The electrochemical, electrochromic, and photoluminescence (PL) properties of these polymers are also described herein.

EXPERIMENTAL

Materials

A naphthylamine-based aromatic dicarboxylic acid, 1-[N,N-di(4-carboxyphenyl)amino]naphthalene, was synthesized by the sodium hydride mediated condensation of 1-aminonaphthalene with 4-fluorobenzonitrile, followed by the alkaline hydrolysis of the intermediate dinitrile compound.[30] N,N'-Dimethylacetamide (DMAc; Tedia), N,N'-dimethylformamide (DMF; Acros), dimethyl sulfoxide (DMSO; Tedia), N-methyl-2-pyrrolidinone (NMP; Tedia), pyridine (Py; Tedia), and triphenyl phosphite (TPP; Acros) were used without further purification. Commercially available aromatic diamines such as p-phenylenediamine (**1a**; TCI), 4,4'-oxydianiline (**1b**; TCI), and 9,9-bis(4-aminophenyl)fluorene (**1c**; TCI) were used as received. 2,2'-Bis(4-amino-2-trifluoromethylphenoxy)biphenyl (**1d**) and 2,2'-bis(4-amino-2-trifluoromethylphenoxy)-1,1'-binaphthyl (**1e**) were prepared by a reported procedure.[31] Tetrabutylammonium perchlorate (TBAP; Acros) was recrystallized twice from ethyl acetate and then dried *in vacuo* before use. All other reagents were used as received from commercial sources.

Preparation of the Polyamides by Direct Polycondensation via the Phosphorylation Reaction

The synthesis of polyamide **Ib** is used as an example to illustrate the general synthetic route
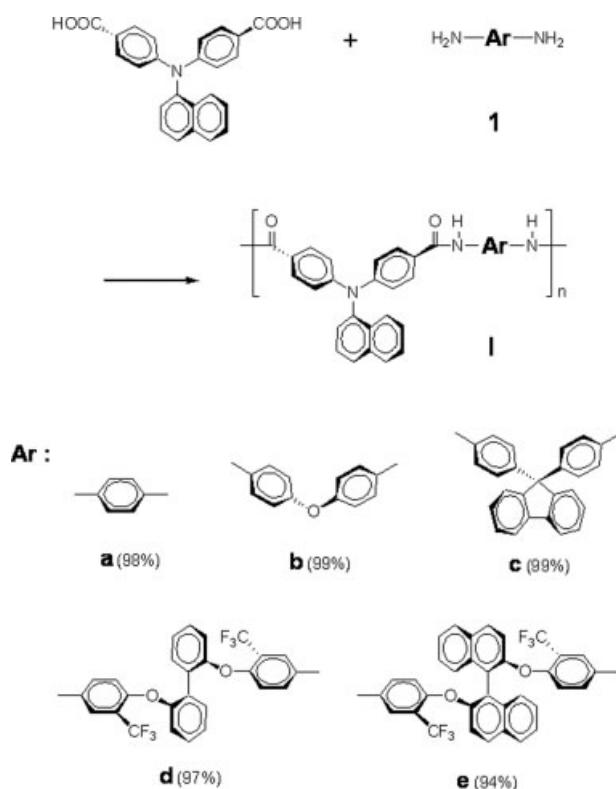
Scheme 1. Synthesis of poly(amine-amide)s with percentage yields.

used to produce the polyamides. A mixture of 0.38 g (1 mmol) of dicarboxylic acid, 1-[*N*,*N*-di(4-carboxyphenyl)amino]naphthalene, 0.20 g (1 mmol) of **1b**, 0.12 g of calcium chloride, 0.7 mL of TPP, 0.5 mL of Py, and 1 mL of NMP was heated with stirring at 105 °C for 3 h. The obtained polymer solution was poured slowly into 300 mL of stirred methanol, giving rise to a stringy, fiberlike precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried *in vacuo* at 100 °C. Reprecipitation from DMAc into methanol was carried out twice for further purification to give 0.54 g (99% yield). The inherent viscosity of the obtained polyamide (**Ib**) was 0.96 dL/g, measured at a concentration of 0.5 g/dL in NMP at 30 °C.

^{1}H NMR (DMSO-d_6, δ, ppm): 6.97 (d, 4H, H$_b$), 7.06 (d, 4H, H$_k$), 7.46–7.47 (m, 2H, H$_c$ + H$_d$), 7.55 (t, 1H, H$_h$), 7.63 (t, 1H, H$_g$), 7.71 (d, 4H, H$_j$), 7.80 (d, 1H, H$_e$), 7.85 (d, 4H, H$_a$), 8.00 (d, 1H, H$_f$), 8.05 (d, 1H, H$_i$), 10.11 (amide–NH). ELEM. ANAL. Calcd. for $(C_{36}H_{25}N_3O_3)_n$ [(547.6)$_n$]: C, 78.96%; H, 4.60%; N, 7.67%. Found: C, 77.87%; H, 4.85%; N, 7.70%.

The other polyamides were prepared by an analogous procedure.

Preparation of the Films

A solution of a polymer was made by the dissolution of about 0.50 g of a polyamide sample in 8 mL of DMAc. The homogeneous solution was poured into a 9-cm glass Petri dish, which was heated at 50 °C for 1 h, at 100 °C for 2 h, and at 160 °C for 8 h to slowly release the solvent *in vacuo*. The obtained films were about 40–50 μm thick and were used for X-ray diffraction measurements, solubility tests, thermal analyses, and measurements of the optical and electrochemical properties and electrochromic characteristics.

Measurements

IR spectra were recorded on a PerkinElmer RXI Fourier transform infrared spectrometer. Elemental analyses were run on a Elementar Vario EL-III. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV-500 FT-NMR system. The inherent viscosities were determined at a 0.5 g/dL concentration with a Tamson TV-2000 viscometer at 30 °C. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (ca. 25 °C) on a Shimadzu XRD-7000 X-ray diffractometer (40 kV, 20 mA) with graphite-monochromatized Cu Kα radiation. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on
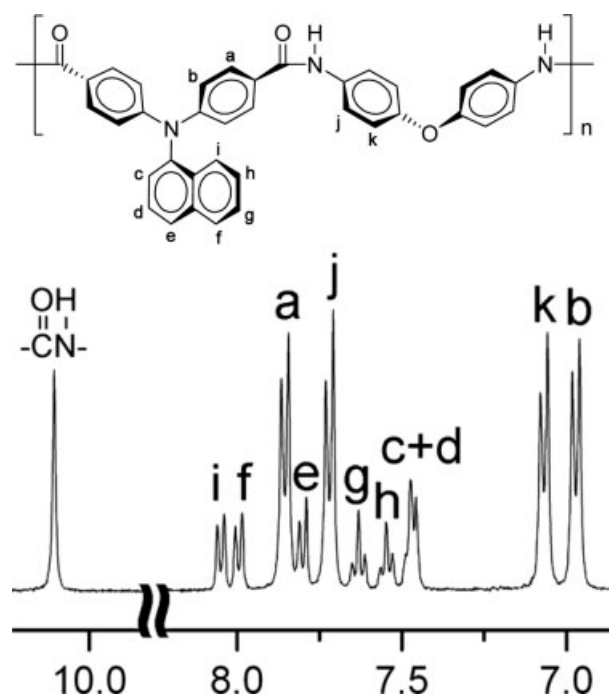

Figure 1. ^{1}H NMR spectrum of poly(amine amide) **Ib** in DMSO-d_6.

Table 1. Inherent Viscosity (η_{inh}) and Solubility of the Poly(amine amide)s

Polymer			Solvent[c]						
Code	η_{inh} (dL/g)[a]	Film[b]	NMP	DMAc	DMF	DMSO	m-Cresol	Tetrahydrofuran	Chloroform
Ia	1.02		++	+	+	+	++	+−	+−
Ib	0.96		++	++	++	++	+	+−	+−
Ic	0.66		++	++	++	++	+	+−	+−
Id	0.25		++	++	++	++	++	++	+−
Ie	0.15		++	++	++	++	++	++	+−

[a] Measured at a polymer concentration of 0.5 g/dL in NMP at 30 °C.
[b] Photographs of the polyamide films (1–3 μm thick).
[c] ++ = soluble at room temperature; + = soluble on heating; +− = partially soluble or swelling; − = insoluble even on heating.

a Varian Cary 50 probe spectrometer. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA instrument. Experiments were carried out on approximately 6–8-mg film samples heated in flowing nitrogen or air (flow rate = 20 cm³/min) at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer Pyris Diamond differential scanning calorimeter at a scanning rate of 20 °C/min in flowing nitrogen (20 cm³/min). Cyclic voltammetry was performed with a Bioanalytical System model CV-27 potentiostat and a BAS X–Y recorder with indium tin oxide (ITO; polymer film area ≈ 0.7 cm × 0.5 cm) as a working electrode and a platinum wire as an auxiliary electrode at a scanning rate of 100 mV/s against a Ag/AgCl reference electrode in a solution of 0.1 M TBAP/acetonitrile (CH₃CN). Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downward. All cell potentials were taken with the use of a homemade Ag/AgCl, KCl (saturated) reference electrode. The spectroelectrochemical cell was composed of a 1-cm cuvette, ITO as a working electrode, a platinum wire as an auxiliary electrode, and a Ag/AgCl reference electrode.

Absorption spectra in spectroelectrochemical analysis were measured with an HP 8453 UV–vis spectrophotometer. PL spectra were measured with a Jasco FP-6300 spectrofluorometer. The fluorescence quantum yield (Φ_F) values of the samples in NMP were measured with quinine sulfate in 1 N H_2SO_4 as a reference standard (Φ_F = 0.546).[32] All corrected fluorescence excitation
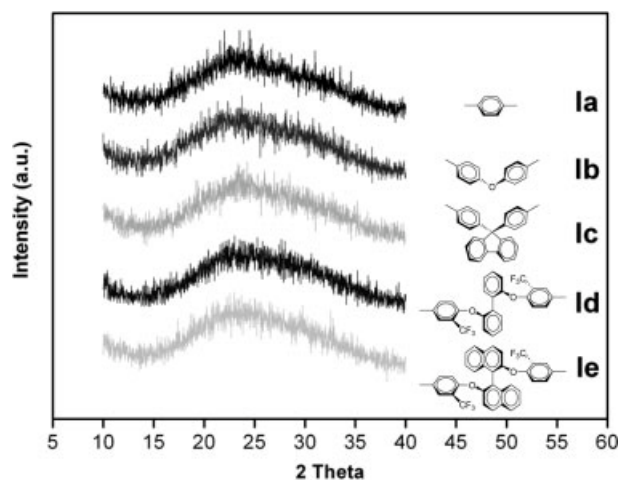

Figure 2. WAXD patterns of the polyamide films.

Table 2. Thermal Properties of the Poly(amine amide)s[a]

Polymer	T_g (°C)[b]	T_d^5 (°C)[c]		T_d^{10} (°C)[d]		Char Yield (wt %)[e]	
		N$_2$	Air	N$_2$	Air	N$_2$	Air
Ia	294	483	487	542	551	65	12
Ib	304	496	498	538	548	65	14
Ic	355	476	480	519	525	67	17
Id	268	454	446	498	486	58	—[f]
Ie	320	417	399	479	461	66	4

[a] The polymer film samples were heated at 300 °C for 1 h before all the thermal analyses.
[b] Midpoint temperature of the baseline shift on the second DSC heating trace (rate = 20 °C/min) of the sample after quenching from 400 to 50 °C (rate = 200 °C/min) in nitrogen.
[c] Temperature at which 5% weight loss occurred, recorded via TGA at a heating rate of 20 °C/min and a gas flow rate of 20 cm^3/min.
[d] Temperature at which 10% weight loss occurred.
[e] Residual weight percentage at 800 °C in nitrogen.
[f] There was no residual weight at 800 °C in air.

spectra were found to be equivalent to their respective absorption spectra.

RESULTS AND DISCUSSION

Polymer Synthesis

According to the phosphorylation technique first described by Yamazaki and coworkers,[33,34] a series of novel polyamides (**I**) with pendent naphthylamine units were synthesized from a dicarboxylic acid, 1-[*N,N*-di(4-carboxyphenyl)amino]-naphthalene, and various aromatic diamines, as shown in Scheme 1. The polymerization proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. Most of the polymers precipitated in a tough, fiberlike form when the resulting polymer solutions were slowly poured into methanol. The obtained polyamides had inherent viscosities of 0.15–1.02 dL/g, which decreased as the steric hindrance and electron-withdrawing ability of the diamine structures increased.

The chemical structures of the polymers were characterized with IR and NMR spectroscopy and elemental analysis. In the IR spectra of these polyamides, the characteristic absorption bands of the amide group appeared at 3307 (N—H stretching) and 1654 cm^{-1} (amide carbonyl). As a typical example, the structure of polyamide **Ib** was also confirmed by solution NMR. Figure 1 shows a typical ^{1}H spectrum of polyamide **Ib** in DMSO-d_6; all the peaks have been readily assigned to the hydrogen atoms of the recurring unit.

Polymer Properties

Basic Characterization

The solubility behavior of the aromatic polyamides (**I**) was qualitatively tested, and the results are summarized in Table 1. These light-colored polymers exhibited good solubility in a variety of solvents, such as NMP, DMAc, DMF, and *m*-cresol. Even polyamide **Ia** obtained from rigid **1a** was organosoluble. The enhanced solubility can be attributed to the introduction of the bulky, asymmetric, and noncoplanar 1-naphthyldiphenylamine group into the repeat unit, which reduces interchain interactions and increases the between-chain spaces or free volume. Thus, the excellent solubility makes these polymers good
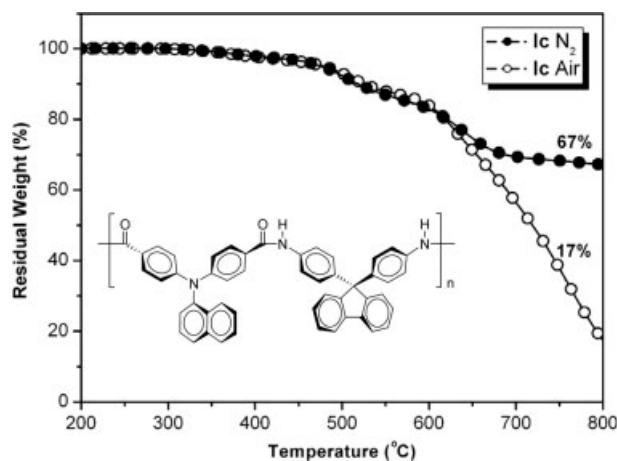
Figure 3. TGA thermograms of poly(amine amide) **Ic** at a scanning rate of 20 °C/min.

Table 3. Optical and Electrochemical Properties of the Poly(amine amide)s

| Index | Solution Wavelength (nm)[a] | | | | Film Wavelength (nm) | | | E_{onset} (V)[e] | E_g (eV)[f] | HOMO (eV)[g] | LUMO (eV)[h] |
	Absorption Maximum	PL Maximum[b]	Φ_F (%)[c]	λ_0[d]	Absorption Maximum	Absorption Onset	PL Maximum[b]				
Ia	361	468	0.4	403	356	405	468	1.08	3.06	5.44	2.38
Ib	351	424	1.4	387	358	402	444	1.10	3.09	5.46	2.37
Ic	350	422	5.3	390	356	397	440	1.13	3.12	5.49	2.37
Id	351	431	14.4	401	351	396	437	1.08	3.13	5.44	2.31
Ie	350	434	15.0	389	353	405	445	1.16	3.06	5.42	2.46

[a] The polymer concentration was 10^{-5} mol/L in NMP.
[b] Excited at the absorption maximum for both the solid and solution states.
[c] Quantum yield in a dilute solution calculated in an integrating sphere with quinine sulfate as the standard ($\Phi_F = 0.546$).
[d] Cutoff wavelength from the UV–vis transmission spectra of polymer films (1–3 μm thick).
[e] Oxidation onset potential versus Ag/AgCl in aqueous CH_3CN.
[f] Band-gap energy calculated from the polymer film with the following equation: $E_g = 1240/\lambda_{onset}$, where λ_{onset} is the onset wavelength.
[g] Calculated from cyclic voltammetry and referenced to ferrocene (4.8 eV).
[h] LUMO = HOMO − gap.

candidates for practical applications by spin- or dip-coating processes.

The WAXD patterns of the naphthylamine-based polyamides given in Figure 2 indicate that the polymers are essentially amorphous, revealing that the naphthylamine-based triarylamine-containing polymers do not form a well-packed structure. The amorphous nature of these naphthylamine-based polyamides is reflected not only in their good solubility but also in the UV–vis data for the polymers, which show that the UV–vis absorption peaks of the polymers do not shift from the solutions to the films, implying that there is no significant π–π interaction aggregation between the polymer chains.

Thermal Properties

The thermal properties of the polyamides were investigated with TGA and DSC. The results are summarized in Table 2. Typical TGA curves of a representative polyamide (**Ic**) in both air and nitrogen atmospheres are shown in Figure 3. All the aromatic polyamides exhibited good thermal stability with insignificant weight loss up to 460 °C in nitrogen. The 10% weight loss temperatures of these polymers in nitrogen and air were recorded in the range of 480–540 and 525–550 °C, respectively. The concentration of carbonized residue (char yield) of these polymers in a nitrogen atmosphere was more than 58% at 800 °C. The high char yields of these polymers can be ascribed to their high aromatic content. The glass-transition temperatures of all the aromatic polyamides

could be easily measured in the DSC thermograms; they were observed in the range of 268–355 °C and decreased with decreasing rigidity and symmetry of the diamines. All the polymers indicated no clear melting endotherms up to the decomposition temperatures on the DSC thermograms. This result supports the amorphous nature of these triarylamine-containing polymers.

Optical Properties

The optical properties of the polyamides were investigated with UV–vis and PL spectroscopy, and the results are summarized in Table 3. The molar absorptivity (ε) and PL spectra of polyamides measured in NMP (concentration = 10^{-5} mol/L)

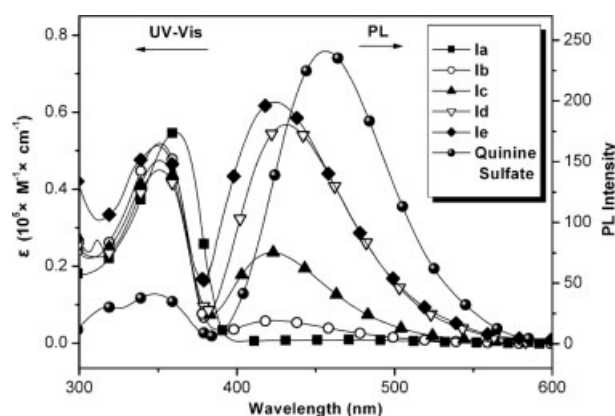**Figure 4.** ε and PL spectra of polyamides in NMP solutions (10^{-5} M). Quinine sulfate dissolved in 1 N aqueous H_2SO_4 (10^{-5} M) was used as the standard ($\Phi_F = 0.546$).
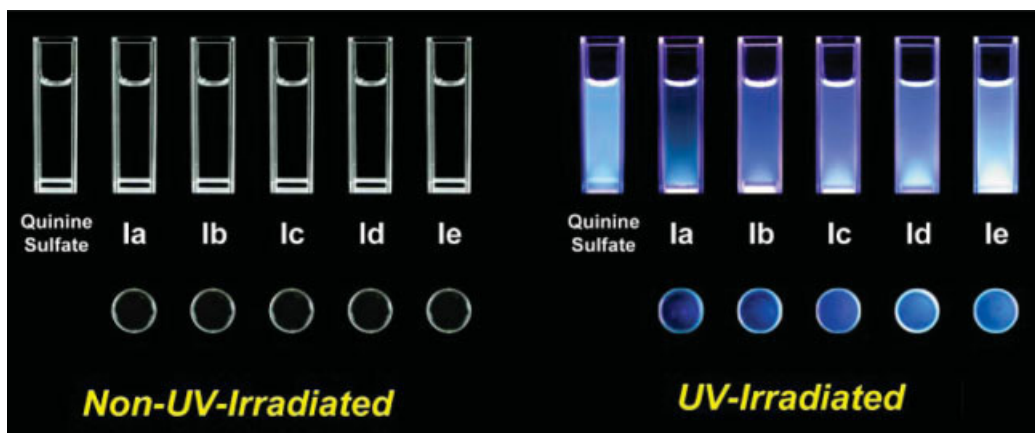
Figure 5. PL of polyamide solutions (10^{-5} M) and thin films (1–3 μm thick) by UV irradiation (excited at 365 nm). Quinine sulfate dissolved in 1 N aqueous H_2SO_4 (10^{-5} M) was used as the standard ($\Phi_F = 0.546$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

are shown in Figure 4. The cast films of these polymers showed UV–vis absorption peaks similar to those of their NMP solutions, with the maximum absorption at 350–358 nm; this means these polymers are not able to form a π-stacking structure in the solid state because of the twisted triarylamine moieties. These aromatic polyamides exhibited fluorescence emission maxima around 435–458 nm in NMP solutions, with Φ_F ranging from 0.4% for **Ia** to 15.0% for **Ie**. The NMP solution and thin films of the polymers were almost colorless and gave strong blue PL under irradiation with a general UV lamp (wavelength = 365 nm), as shown in Figure 5. The transmission UV–vis spectra of the polyamide films are shown in Figure 6, and the cutoff wavelengths (absorption edge) in the range of 387–403 nm revealed a light color and high optical transparency.

Electrochemical Properties

The electrochemical behavior of the polyamides **I** series was investigated by cyclic voltammetry conducted with cast films on an ITO-coated glass substrate as the working electrode in dry CH_3CN containing 0.1 M of TBAP as an electrolyte under a nitrogen atmosphere. A typical cyclic voltammogram for polyamide **Ia** is shown in Figure 7. The electrochemical oxidation (or p-doping) of polymer **Ia** starts at about 1.08 V (oxidation onset potential) versus Ag/AgCl. The energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the investigated polyamides can be determined from the oxidation onset potentials and the onset

absorption wavelength,[35] and the results are listed in Table 3. For example, the oxidation onset potential for polyamide **Ia** was determined to be 1.08 V versus Ag/AgCl. The external ferrocene/ferrocenium (Fc/Fc^+) redox standard $E_{1/2}$ (the average potential of the redox couple peaks) is 0.44 V versus Ag/AgCl in aqueous CH_3CN. Assuming that the HOMO energy for the Fc/Fc^+ standard was 4.80 eV with respect to the zero vacuum level, we evaluated the HOMO energy for polyamide **Ia** to be 5.44 eV.

Electrochromic Characteristics

The electrochromism of the thin films from polyamides was examined by the casting of a polymer solution onto an ITO-coated glass substrate,
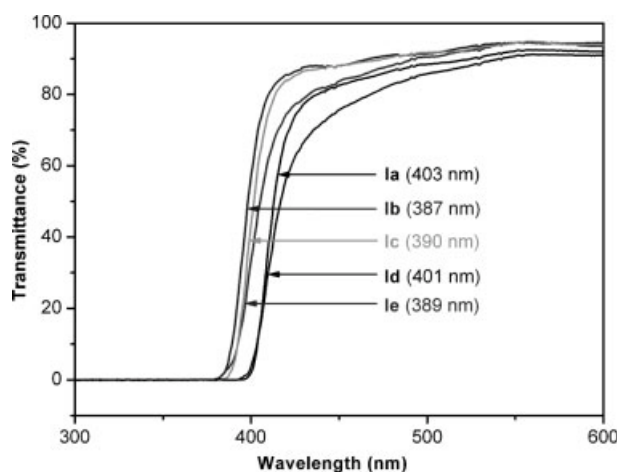

Figure 6. UV–vis transmission spectra of some polyamide films (1–3 μm thick).
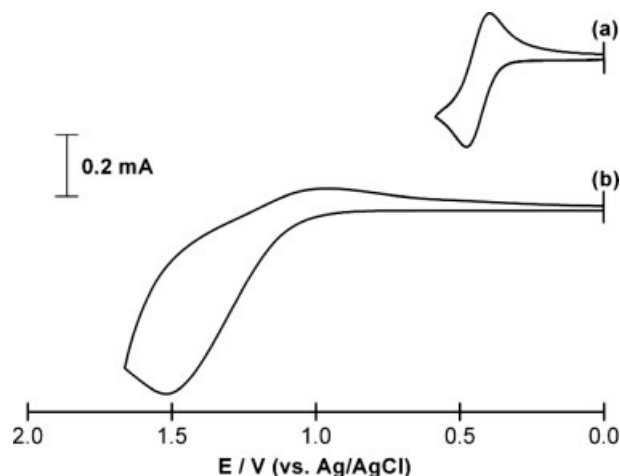
Figure 7. Cyclic voltammograms of a poly(amine amide) **Ia** film on an ITO-coated glass substrate in CH$_3$CN containing 0.1 M TBAP (scan rate = 0.1 V/s): (a) ferrocene and (b) an oxidation redox of **Ia**.

and the electrochromic absorption spectra were monitored with a UV–vis spectrometer at different applied potentials. The electrode preparations and solution conditions were identical to those used in cyclic voltammetry. The typical electrochromic spectra of two polyamides are shown in Figures 8 and 9. When the applied potentials increased positively from 0.00 to 1.60 V, the peak of characteristic absorbance at 345 nm, characteristic for polyamide **Ib**, decreased gradually, whereas one new band grew in at 696 nm. Meanwhile, the color of the film changed from colorless to green, as shown in Figure 9. Similar elec-
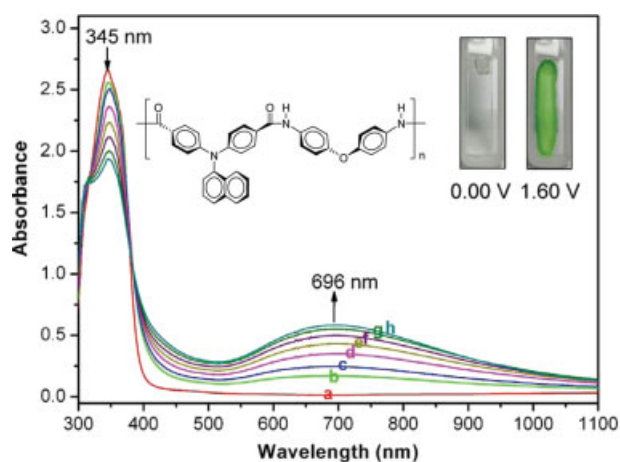

Figure 8. Electrochromic behavior of a polyamide **Ib** thin film (in CH$_3$CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0.00, (b) 1.10, (c) 1.20, (d) 1.30, (e) 1.40, (f) 1.50, (g) 1.55, and (h) 1.60 V.

Figure 9. Electrochromic behavior of a polyamide **Ic** thin film (in CH$_3$CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0.00, (b) 1.10, (c) 1.20, (d) 1.30, (e) 1.40, (f) 1.50, (g) 1.55, and (h) 1.60 V.
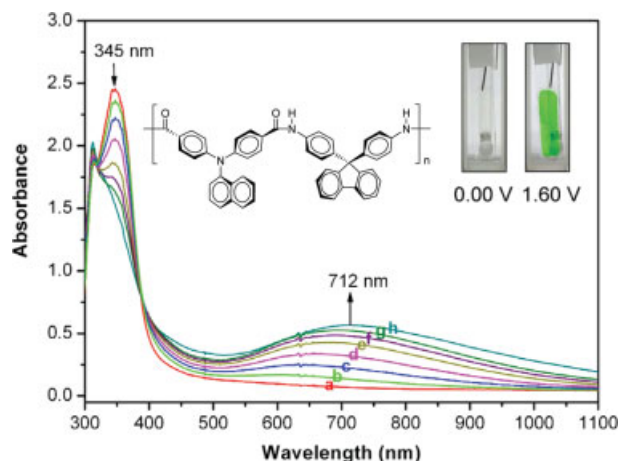
trochromic characteristics of polyamide **Ic** are also shown in Figure 9.

CONCLUSIONS

A series of new aromatic polyamides have been successfully prepared from a dicarboxylic acid, 1-[*N,N*-di(4-carboxyphenyl)amino]naphthalene, and various aromatic diamines via direct phosphorylation polycondensation. The introduction of the bulky naphthalene group into the polymer backbone disrupts the coplanarity of aromatic rings in chain packing, and this increases the between-chain spaces or free volume, thus enhancing the solubility of the formed polyamides. All the polymers are amorphous with high optical transparency according to UV–vis transmittance measurements, with a cutoff wavelength in the range of 387–403 nm, and exhibit a blue emission maximum around 437–458 nm in the solid state. Φ_F in NMP solutions ranges from 0.4% for **Ia** to 15.0% for **Ie**. The polyamides also reveal electrochromic characteristics, changing color from the colorless, neutral form to the green, oxidized forms when potentials are scanned positively from 0.00 to 1.60 V. Thus, these novel naphthylamine-based polyamides have great potential to be widely applied in polymer light-emitting diodes as a new class of hole-transporting-layer and blue-light-emitting materials because of their proper HOMO values, excellent thermal stability, solubility, and electrochemical behavior.

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