Synthesis and Photoluminescent and Electrochromic Properties of Aromatic Poly(amine amide)s Bearing Pendent *N*-Carbazolylphenyl Moieties

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Received 23 March 2006; accepted 23 April 2006
DOI: 10.1002/pola.21517

ABSTRACT: A series of novel poly(amine amide)s (**IIa**–**IIl**) with pendent *N*-carbazolylphenyl units having inherent viscosities of 0.25–1.06 dL/g were prepared via direct phosphorylation polycondensation from various dicarboxylic acids and a carbazole-based aromatic diamine. Except for poly(amine amide) **IIc**, derived from *trans*-1,4-cyclohexanedicarboxylic acid, all the other amorphous poly(amine amide)s were readily soluble in many polar solvents, such as *N,N*-dimethylacetamide and *N*-methyl-2-pyrrolidone (NMP), and could be cast into transparent and flexible films. The aromatic poly(amine amide)s had useful levels of thermal stability associated with relatively high glass-transition temperatures (268–331 °C), 10% weight loss temperatures in excess of 540 °C, and char yields at 800 °C in nitrogen higher than 60%. These polymers exhibited maximum ultraviolet–visible absorption at 293–361 nm in NMP solutions. Their photoluminescence in NMP solutions exhibited fluorescence emission maxima around 362 and 448–499 nm for aromatic–aliphatic poly(amine amide)s **IIa**–**IIc** and aromatic poly(amine amide)s **IId**–**IIl**, respectively. The fluorescence quantum yield in NMP solutions ranged from 0.34% for **IIj** to 4.44% for **IIa**. The hole-transporting and electrochromic properties were examined with electrochemical and spectroelectrochemical methods. Cyclic voltammograms of the poly(amine amide) films cast onto an indium tin oxide coated glass substrate exhibited reversible oxidation at 0.81 V and irreversible oxidation redox couples at 1.20 V versus Ag/AgCl in acetonitrile solutions, and they revealed excellent stability of the electrochromic characteristics, with a color change from yellow to green at applied potentials ranging from 0.00 to 1.05 V. © 2006 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 44: 4108–4121, 2006
Keywords: electrochemistry; functionalization of polymers; high performance polymers; polyamides; redox polymers; step-growth polymerization

INTRODUCTION

Triarylamines have attracted considerable interest as hole-transport materials for use in multilayer organic electroluminescence (EL) devices because of their relatively high mobilities and low ionization potentials.[1–5] The feasibility of using spin-coating and ink-jet-printing processes for large-area EL devices and the possibility of various chemical modifications (to improve emission efficiencies and allow patterning) make polymeric materials containing triarylamine units very attractive.[6–14] To enhance the hole-injection ability of polymeric emissive materials such as poly(1,4-phenylenevinylene)s (PPVs) and polyfluorenes (PFs), there have been several reports

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 44, 4108–4121 (2006)

on PPV and PF derivatives involving hole-transporting units such as triarylamine or carbazole groups in the emissive π-conjugated core/main chains,[15–20] grafting them as side chains in a polymer,[21–23] or attaching them onto the polymer chain ends or outer surface of dendritic wedges.[24,25]

Carbazole is another well-known hole-transporting and EL unit. Polymers containing carbazole moieties in the main chain or side chain have attracted much attention because of their unique properties, which allow various optoelectronic applications such as photoconductive, EL, and photorefractive materials.[26,27] In the field of EL, carbazole derivatives are often used as the materials for hole-transporting and light-emitting layers. Moreover, carbazole derivatives are used as layers because of their high charge mobility and thermal stability, and they show blue EL because of the large band gap of the improved planar biphenyl unit by the bridging nitrogen atom.[28] From a structural point of view, carbazole differs from diphenylamine in its planar structure because it can be further imagined as bonded diphenylamine; the thermal stability of materials with the incorporation of carbazolyl units therefore is improved. Carbazole also can be easily functionalized at the (3,6)-,[29–31] (2,7)-,[32] or N-positions[33–35] and then covalently linked into polymeric systems, both in the main chain[36–42] as building blocks and in the side chain as pendent groups.[43–47] It is thus worthwhile to design a carbazole-based aromatic diamine as a starting monomer for the preparation of a high-performance polyamide system with novel optoelectronic functions.

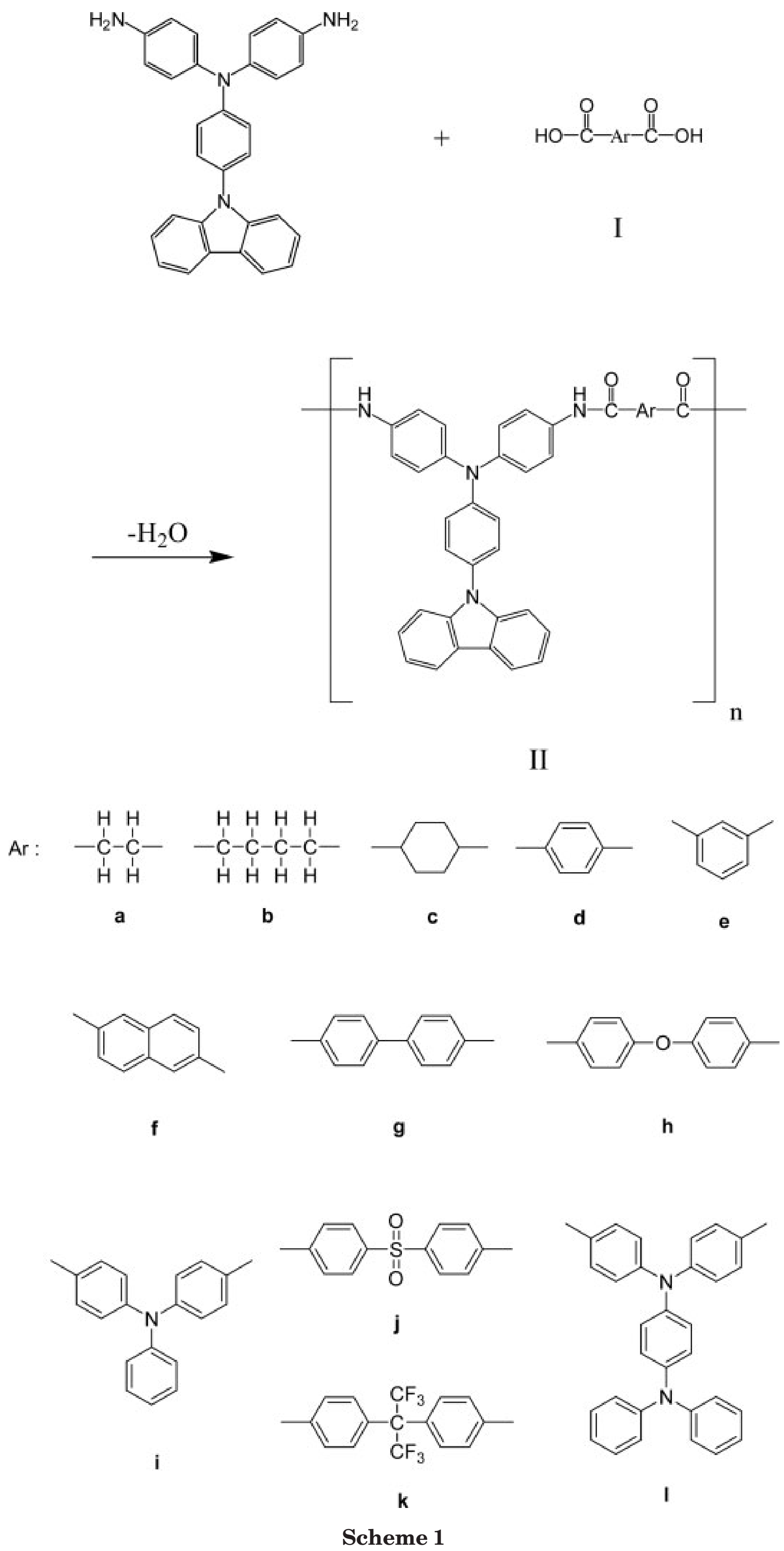
Wholly aromatic polyamides are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties. However, the rigidity of the backbone and strong hydrogen bonding result in high melting temperatures or glass-transition temperatures (T_g's) and limited solubility in most organic solvents, thus restricting their applications in some fields.[48,49] 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.[50–56] 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[57] and *N,N*-bis(4-aminophenyl)-*N′,N′*-diphenyl-1,4-phenylenediamine.[58] 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.

The electrochemistry of triphenylamine in aprotic solvents has been well studied.[59] The triphenylamine cationic radical of the first electron oxidation is not stable; the chemical reaction therefore follows to produce tetraphenylbenzidine by tail-to-tail (para positions) coupling with the loss of two protons per dimer. When the phenyl groups are incorporated by electron-donating substituents at the para position of triarylamines, the coupling reactions that afford stable cationic radicals are greatly prevented.[60] In this study, we synthesized a series of novel poly(amine amide)s containing electron-rich triphenylamine groups with carbazolyl para-substituted on the pendent phenyl ring from a carbazole-based diamine monomer, 4,4′-diamino-4″-*N*-carbazolyltriphenylamine (**4**), and various dicarboxylic acids. The incorporation of bulky *N*-carbazolylphenyl moieties would interrupt the intermolecular hydrogen bonding of the polyamides and generally disturb the coplanarity of the aromatic unit to reduce stacking efficiency and crystallinity. The general properties, such as the solubility, crystallinity, thermal, and mechanical properties, are described. The electrochemical, electrochromic, and photoluminescence (PL) properties of these polymers prepared by the casting of a solution onto an indium tin oxide (ITO) coated glass substrate are also described here.

EXPERIMENTAL

Materials

N,N-Bis(4-carboxyphenyl)-*N′,N′*-diphenyl-1,4-phenylenediamine[61] (**Il**; mp = 274–277 °C) and 4,4′-dicarboxytriphenylamine[62] (**Ii**; mp = 313–315 °C) were synthesized by the condensation of 4-aminotriphenylamine and aniline with 4-fluorobenzonitrile in the presence of cesium fluoride or sodium hydride, followed by the alkaline hydrolysis of the intermediate dinitrile compounds. The carbazole-based aromatic diamine **4**[63] was synthesized by the cesium fluoride-mediated condensation of *N*-(4-aminophenyl)carbazole with 4-fluoronitrobenzene, followed by a palladium-catalyzed hydrazine reduction. *N,N′*-Dimethylacetamide (DMAc;



Scheme 1

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

Poly(amine amide)s		Elemental Analysis (%)					
Code	η_{inh} (dL/g)[a]	Formula (Molecular Weight)		C	H	N	S
IIa	0.48	$(C_{34}H_{26}N_4O_2)_n$ [$(522.60)_n$]	Calcd.	78.14	5.01	10.72	
			Found	77.53	5.06	10.61	
IIb	0.31	$(C_{36}H_{30}N_4O_2)_n$ [$(550.65)_n$]	Calcd.	78.52	5.49	10.17	
			Found	77.85	5.54	10.12	
IIc	0.34	$(C_{38}H_{32}N_4O_2)_n$ [$(576.69)_n$]	Calcd.	79.14	5.59	9.72	
			Found	78.50	5.63	9.64	
IId	0.58	$(C_{38}H_{26}N_4O_2)_n$ [$(570.64)_n$]	Calcd.	79.98	4.59	9.82	
			Found	79.20	4.62	9.74	
IIe	0.32	$(C_{38}H_{26}N_4O_2)_n$ [$(570.64)_n$]	Calcd.	79.98	4.59	9.82	
			Found	79.45	4.52	9.75	
IIf	1.06	$(C_{42}H_{28}N_4O_2)_n$ [$(620.70)_n$]	Calcd.	81.27	4.55	9.03	
			Found	80.82	4.49	9.05	
IIg	0.99	$(C_{44}H_{30}N_4O_2)_n$ [$(648.75)_n$]	Calcd.	81.71	4.68	8.66	
			Found	81.25	4.59	8.56	
IIh	0.75	$(C_{44}H_{30}N_4O_3)_n$ [$(662.73)_n$]	Calcd.	79.74	4.56	8.95	
			Found	79.36	4.52	8.86	
IIi	1.01	$(C_{50}H_{35}N_5O_2)_n$ [$(737.85)_n$]	Calcd.	81.39	4.78	9.49	
			Found	80.86	4.73	9.43	
IIj	0.60	$(C_{44}H_{30}N_4O_4S)_n$ [$(710.79)_n$]	Calcd.	74.35	4.25	7.88	4.51
			Found	73.84	4.21	7.90	4.45
IIk	0.62	$(C_{47}H_{30}F_6N_4O_2)_n$ [$(796.76)_n$]	Calcd.	70.85	3.80	7.03	
			Found	70.31	3.72	6.94	
IIl	0.25	$(C_{62}H_{44}N_6O_2)_n$ [$(905.05)_n$]	Calcd.	82.28	4.90	9.29	
			Found	81.85	4.91	9.22	

[a] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C (**IIl** was measured in NMP).

Tedia), *N,N′*-dimethylformamide (DMF; Acros), dimethyl sulfoxide (DMSO; Tedia), *N*-methyl-2-pyrrolidone (NMP; Tedia), pyridine (Tedia), and triphenyl phosphite (TPP; Acros) were used without further purification. Commercially available aromatic dicarboxylic acids such as succinic acid (**Ia**; Acros), adipic acid (**Ib**; Showa), *trans*-1,4-cyclohexanedicarboxylic acid (**Ic**; TCI), tereph-

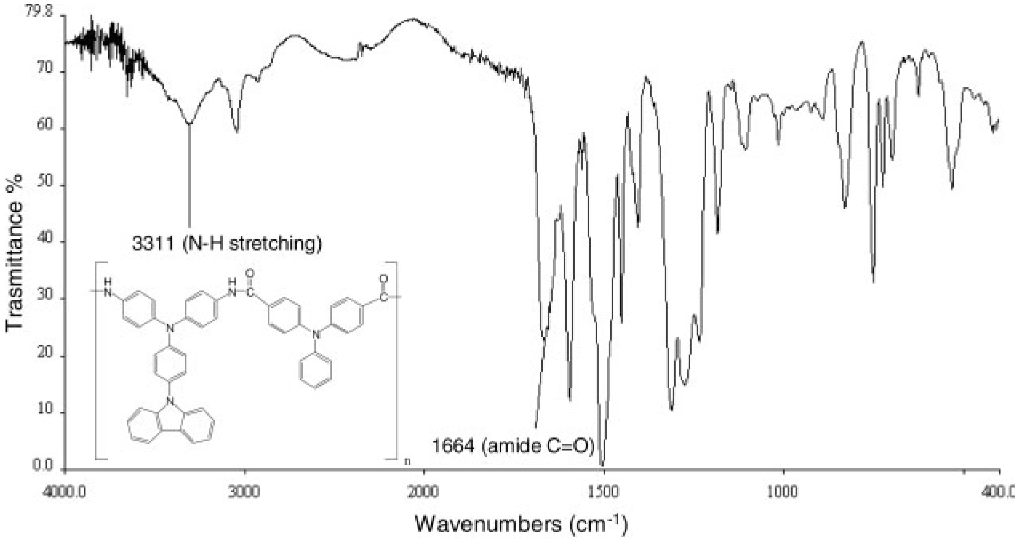


Figure 1. IR spectrum of a poly(amine amide) **IIi** film.

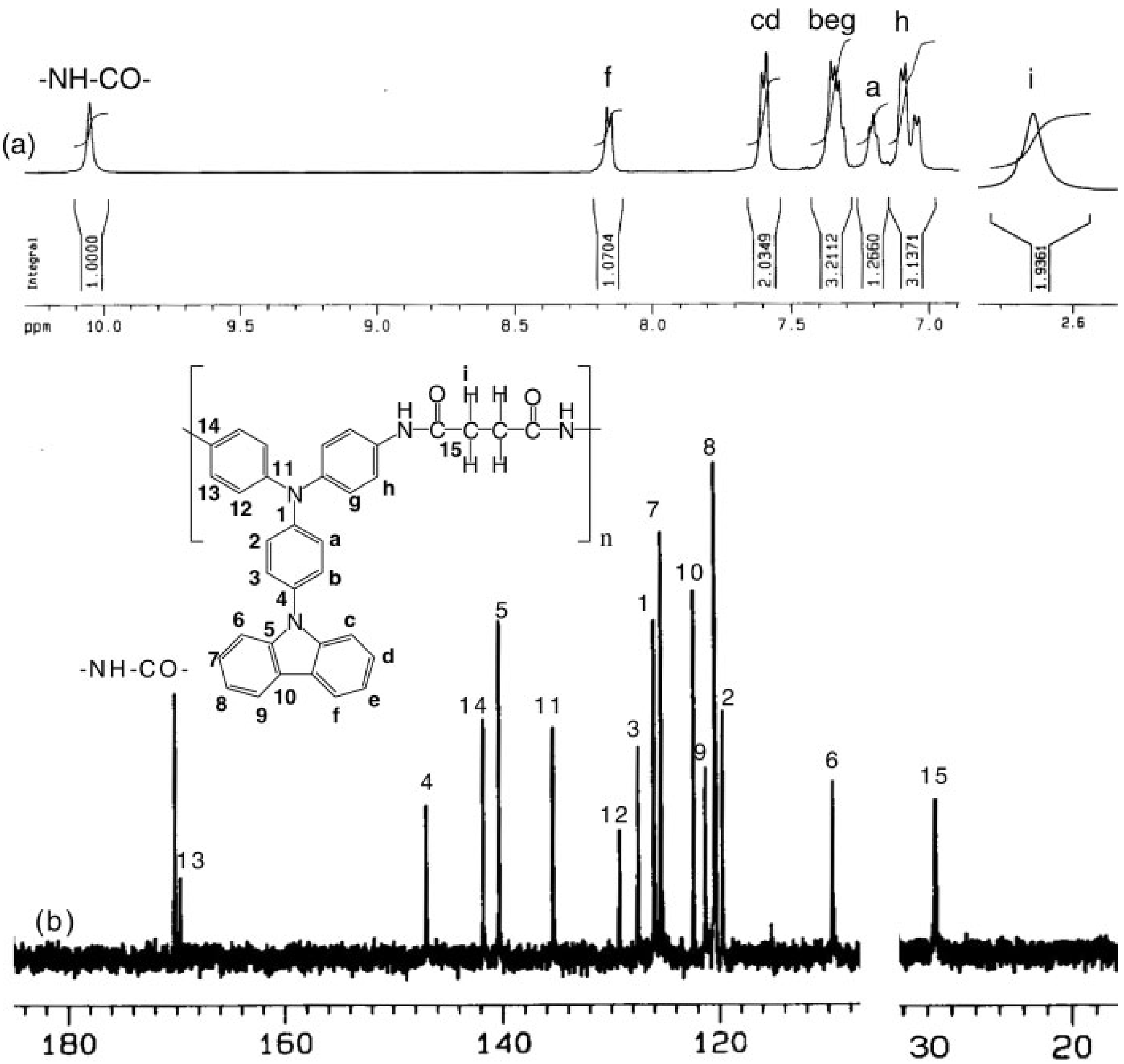


Figure 2. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of poly(amine amide) **IIa** in DMSO-d_6.

thalic acid (**Id**; TCI), isophthalic acid (**Ie**; TCI), 2,6-naphthalenedicarboxylic acid (**If**; TCI), 4,4′-biphenyldicarboxylic acid (**Ig**; TCI), 4,4′-oxydibenzoic acid (**Ih**; TCI), 4,4′-sulfonyldibenzoic acid (**Ij**; New Japan Chemical Co.), and 2,2′-bis(4-carboxyphenyl)hexafluoropropane (**Ik**; TCI) were used as received. 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 Poly(amine amide) IIf by Direct Polycondensation via the Phosphorylation Reaction

The synthesis of poly(amine amide) **IIf** is used as an example to illustrate the general synthetic route used to produce the poly(amine amide)s. A mixture of 0.55 g (1.25 mmol) of diamine **4**, 0.27 g (1.25 mmol) of **If**, 0.15 g of calcium chloride, 0.9 mL of TPP, 0.63 mL of pyridine, and 2.5 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. The precipitate was dissolved in 8 mL of DMAc, and the homogeneous solution was poured into a 9-cm glass culture dish, which was placed in a 90 °C oven for 12 h to remove the solvent. Then, the obtained film was further dried *in vacuo* at 180 °C for 8 h. The inherent viscosity of the obtained poly(amine amide) (**IIf**) was 1.06 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

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

	Solvent						
Polymer	NMP	DMAc	DMF	DMSO	*m*-Cresol	Tetrahydrofuran	Chloroform
IIa	++	++	++	++	−	−	−
IIb	++	++	++	++	++	±	−
IIc	++	±	−	−	−	−	−
IId	++	++	++	++	+	−	−
IIe	++	++	++	++	+	−	−
IIf	++	++	++	++	−	−	−
IIg	++	++	±	±	−	−	−
IIh	++	+	+	+	+	−	−
IIi	++	++	++	−	++	−	−
IIj	++	++	++	++	+	−	−
IIk	++	++	++	++	++	++	−
IIl	++	++	++	+	++	±	−

[a] The qualitative solubility was tested with a 1-mg sample in 1 mL of a stirred solvent. ++ = soluble at room temperature; + = soluble on heating; ± = partially soluble; − = insoluble even on heating.

Elem. Anal. Calcd. for $(C_{42}H_{28}N_4O_2)_n$ $(620.70)_n$: C, 81.27%; H, 4.55%; N, 9.03%. Found: C, 80.82%; H, 4.49%; N, 9.05%.

Preparation of the Films

A solution of the polymer was made by the dissolution of about 0.7 g of the poly(amine amide)s sample in 10 mL of DMAc or NMP. The homogeneous solution was poured into a 9-cm glass Petri dish, which was placed in a 90 °C oven overnight to remove most of the solvent; then, the semidried film was further dried *in vacuo* at 180 °C for 8 h. The obtained films were about 50–80 μm thick and were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

Table 3. Mechanical Properties of the Poly (amine amide) Films

Polymer	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
IIa	85.6	6.6	2.5
IIb	57.9	4.8	1.7
IId	85.0	19.8	2.6
IIe	60.6	9.9	1.9
IIf	67.6	5.9	2.3
IIg	69.7	11.6	2.2
IIh	87.6	24.5	2.2
IIi	74.9	11.1	2.0
IIj	73.3	14.7	2.1
IIk	71.6	25.2	1.9

RESULTS AND DISCUSSION

Polymer Synthesis

According to the phosphorylation technique first described by Yamazaki and coworkers,[64,65] a series

Table 4. Thermal Properties of the Poly (amine amide)s

		T_d at a 5% Weight Loss (°C)[b]		T_d at a 10% Weight Loss (°C)[b]		
Polymer	T_g (°C)[a]	N_2	Air	N_2	Air	Char Yield (wt %)[c]
IIa	183	416	351	470	436	64
IIb	137	402	388	419	420	31
IIc	290	415	394	460	443	43
IId	331	491	455	573	546	77
IIe	278	489	459	566	525	77
IIf	318	515	506	578	575	72
IIg	323	504	494	577	574	75
IIh	291	486	465	541	547	69
IIi	302	524	490	593	564	77
IIj	314	508	476	553	526	72
IIk	305	519	507	557	550	71
IIl	268	511	502	567	595	61

[a] Midpoint temperature of the baseline shift on the second DSC heating trace (rate = 20 °C/min) of the sample after quenching from 400 °C.

[b] Decomposition temperature recorded via TGA at a heating rate of 20 °C/min and a gas flow rate of 20 cm^3/min.

[c] Residual weight percentage at 800 °C in nitrogen.

Table 5. Optical and Electrochemical Properties for the Poly(amine amide)s

	λ (nm)											
	Solution[a]			Film				$E_{1/2}$ (V; vs Ag/AgCl in CH_3CN)				
Index	Absorption Maximum[b]	PL Maximum	Φ_F (%)[c]	λ_0[d]	Absorption Maximum	Absorption Onset	PL Maximum[e]	First	Second	E_g (eV)[h]	HOMO (eV)[i]	LUMO (eV)[j]
IIa	294	362	4.44	385	326	377	407	0.86	1.28[f]	3.29	5.20	1.91
IIb	293	362	3.08	382	326	373	409	0.85	1.30[f]	3.32	5.21	1.89
IIc	293	362	3.93	344	326	374	410	0.81	1.26[f]	3.32	5.17	1.85
IId	345	449	0.48	443	345	428	518	0.87	1.37[f]	2.90	5.23	2.33
IIe	342	454	0.51	553	344	396	503	0.85	1.35[f]	3.13	5.21	2.08
IIf	344	449	0.44	486	342	454	523	0.83	1.29[f]	2.73	5.19	2.46
IIg	345	451	0.51	465	340	433	533	0.84	1.30[f]	2.86	5.20	2.34
IIh	341	458	0.34	444	344	392	517	0.83	1.30[f]	3.16	5.19	2.03
IIi	358	482	0.36	408	353	400	493	0.84	1.33[f]	3.10	5.20	2.10
IIj	340	449	0.34	508	342	488	562	0.89	1.31[f]	2.54	5.25	2.71
IIk	343	448	0.47	449	345	396	524	0.93	1.31[f]	3.13	5.29	2.16
IIl	349	499	0.48	435	347	421	508	0.90	1.20[g]	2.95	5.26	2.31

[a] Spectra in NMP (concentration = 10^{-5} mol/L).
[b] Excitation wavelength.
[c] Quantum yield in a dilute solution [calculated by the integration of a sphere with quinine sulfate as the standard ($\Phi_F = 0.546$].
[d] Cutoff wavelength from the UV–vis transmission spectra of polymer films.
[e] Excited at the same wavelength for the solid and solution states.
[f] The second oxidation redox couple is irreversible.
[g] The third oxidation redox couple is irreversible at 1.68 V for **IIl**.
[h] The data were calculated as follows: Gap = 1240/Onset wavelength of the polymer film. E_g = energy gab between HOMO and LUMO.
[i] The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).
[j] LUMO = HOMO − Gap.

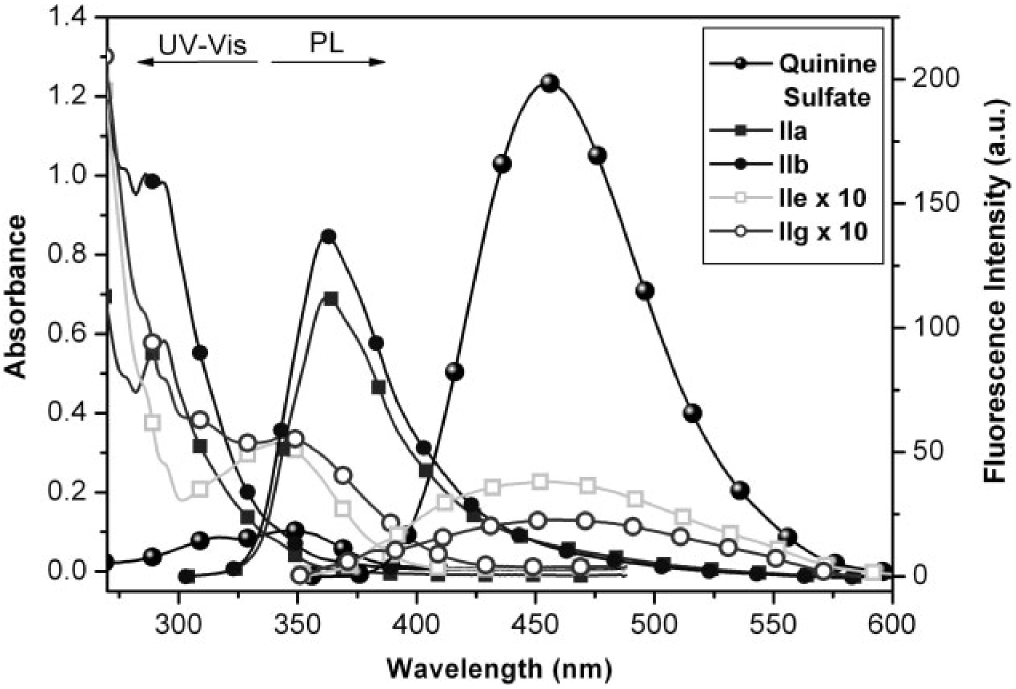


Figure 3. UV–vis absorption and PL spectra of poly(amine amide)s **IIa**, **IIb**, **IIe**, and **IIg** in NMP solutions (10^{-5} M). Quinine sulfate dissolved in 1 N aqueous H_2SO_4 with a concentration of 10^{-5} M was used as the standard (quantum yield = 0.546).

of novel poly(amine amide)s (**IIa–III**) with pendent *N*-carbazolylphenyl units were synthesized from diamine **4** and various dicarboxylic acids, as shown in Scheme 1. The polymerization was carried out via solution polycondensation with TPP and pyridine as condensing agents. The polymerization pro-

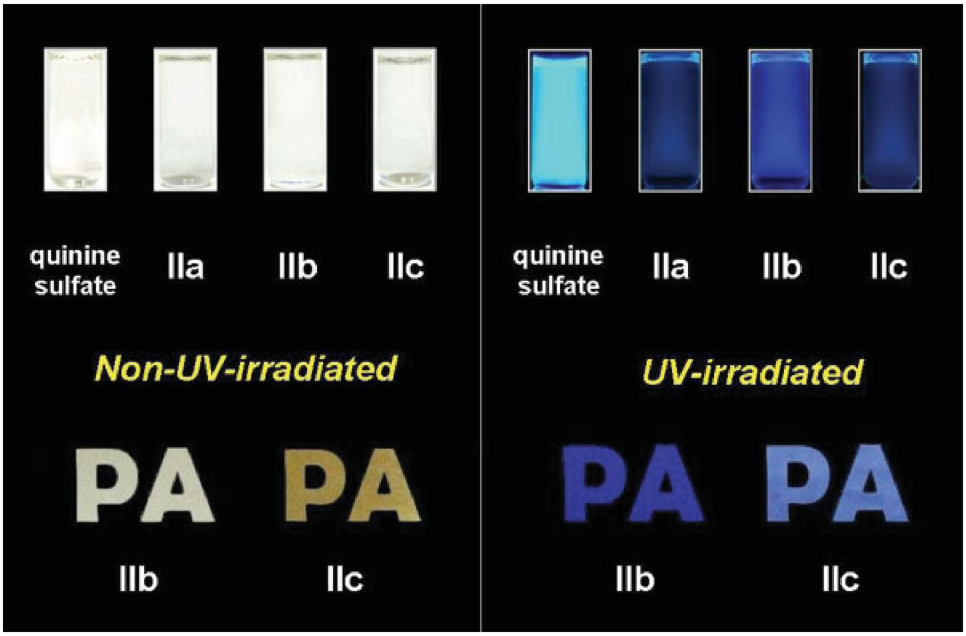


Figure 4. PL of polymer **IIa**, **IIb**, and **IIc** solutions (10^{-5} M) and **IIb** and **IIc** thin films (thickness = 4–10 μm) by UV irradiation (excited at 365 nm). Quinine sulfate dissolved in 1 N aqueous H_2SO_4 (10^{-5} M) was used as the standard (quantum yield = 0.546).

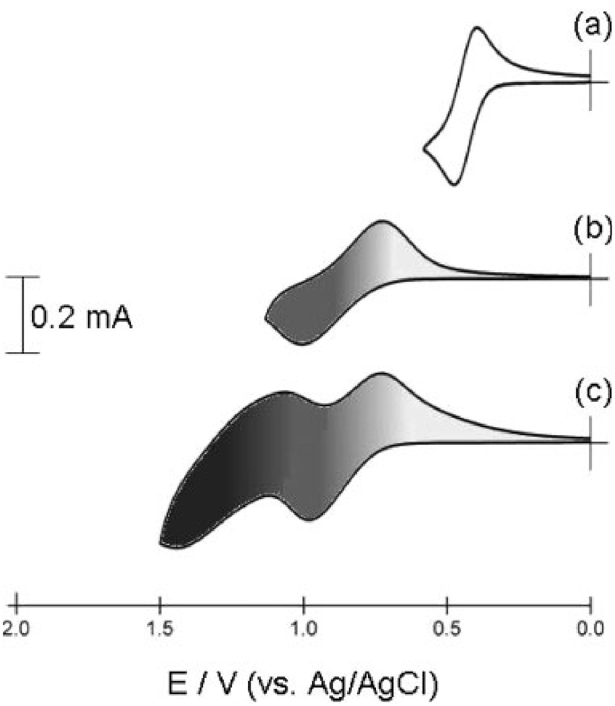


Figure 5. Cyclic voltammograms of a poly(amine amide) **IIj** film on an ITO-coated glass substrate in CH_3CN containing 0.1 M TBAP (scan rate = 0.1 V/s): (a) ferrocene, (b) first reversible oxidation redox of poly(amine amide) **IIj**, and (c) first and second oxidation redoxes of poly(amine amide) **IIj.**

ceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. All the polymers precipitated in a tough, fiberlike form when the resulting polymer solutions were slowly poured into methanol. The obtained poly(amine amide)s had inherent viscosities of 0.25–1.06 dL/g, and the results of elemental analysis are summarized in Table 1.

For obtaining light-colored polyamides, a lower capability of charge transfer is indispensable. An effective way of depressing the charge transfer of polymers is introducing nonconjugated segments into the backbone. Thus, we synthesized poly(amine amide)s **IIa**, **IIb**, and **IIc** from aliphatic diacids **Ia**, **Ib**, and **Ic**, respectively. This could effectively reduce the conjugation and capability of charge transfer and led to enlarged band gaps of the polyamides. The formation of poly(amine amide)s was confirmed with IR and NMR spectroscopy. Figure 1 shows a typical IR spectrum for poly(amine amide) **IIi**. It exhibits characteristic IR absorption bands of the amide group around 3311 (N—H stretching) and 1664 cm^{-1} (amide carbonyl). As a typical example, the structure of poly(amine amide) **IIa** was also confirmed by solution NMR. Figure 2 shows a typical set of ^1H and ^{13}C NMR spectra of poly(amine amide) **IIa** in deuterated dimethyl sulfoxide (DMSO-d_6); all the peaks were readily assigned to the hydrogen and carbon atoms of the recurring unit.

Polymer Properties

Basic Characterization

All the carbazole-based poly(amine amide)s, except **IIc**, showed amorphous patterns by wide-angle X-ray diffraction diagrams. The high crystallinity of conventional polyamides and aromatic polyamides mostly disappeared with the introduction of bulky pendent *N*-carbazolylphenyl groups in the repeat unit. The amorphous nature of these carbazole-based poly(amine amide)s was also reflected in their good solubility.

The solubility behavior of aromatic–aliphatic poly(amine amide)s **IIa–IIc** and aromatic poly(amine amide)s **IId–IIl** was tested qualitatively, and the results are presented in Table 2. All the aromatic poly(amine amide)s were soluble in NMP. Even poly(amine amide)s **IId** and **IIg** obtained from rigid monomers **Id** and **Ig** were also organic-soluble. The good solubility can be attributed to the bulky pendent *N*-carbazolylphenyl group in the polymer backbone. In the aromatic–aliphatic poly(amine amide)s, the solubility in common organic solvents increased with an increase in the aliphatic chain length from 2 in **IIa** to 4 in **IIb**. For example, polymer **IIa** was insoluble in *m*-cresol, whereas polymer **IIb** dissolved in this solvent at room temperature. The fact that **IIc** did not show good solubility may be due to its crystalline nature, as indicated by X-ray diffractograms.

Transparent, flexible, and amorphous films could be cast from NMP solutions of all the poly(amine amide)s, expect for **IIc** and **IIl**, and they were subjected to tensile testing. Table 3 summarizes the tensile properties of the poly(amine amide) films, which showed tensile strengths of 57.0–87.6 MPa, elongations to break of 4.0–25.2%, and initial moduli of 1.7–2.6 GPa. As the aliphatic chain length increased from 2 in **IIa** to 4 in **IIb**, the tensile strength decreased from 85.6 to 57.9 MPa, and the tensile modulus decreased from 2.5 to 1.7 GPa; this implied an increase in the flexibility of the polyamide backbone.

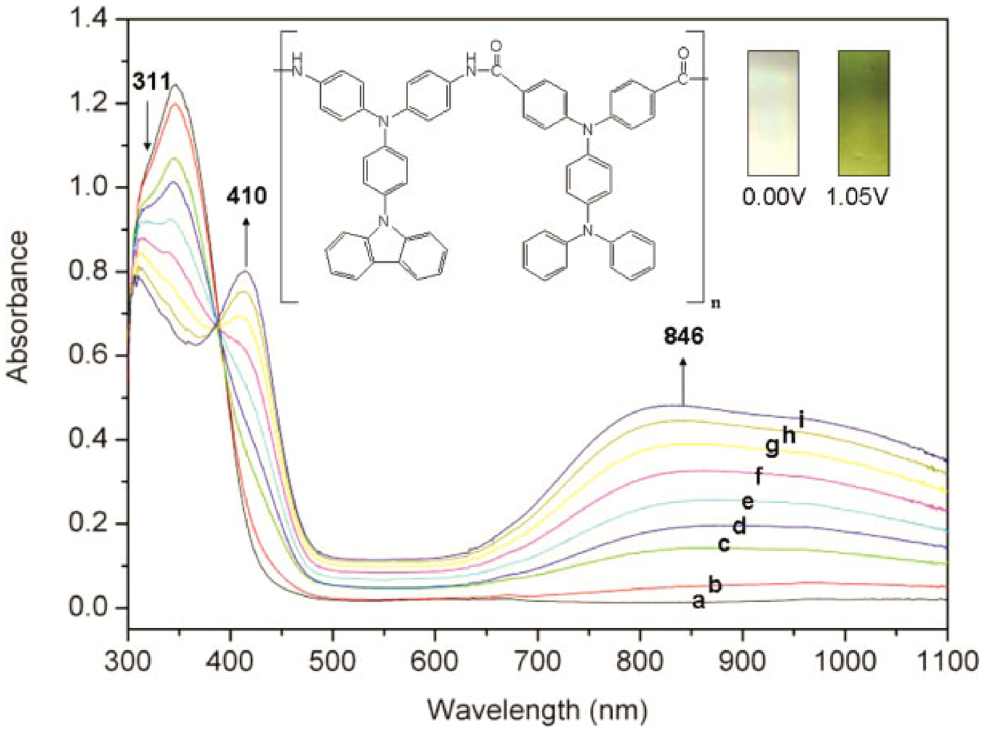


Figure 6. Electrochromic behavior of a poly(amine amide) **IIl** thin film (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0.00, (b) 0.70, (c) 0.75, (d) 0.80, (e) 0.85, (f) 0.90, (g) 0.95, (h) 1.00, and (i) 1.05 V.

The thermal properties of the poly(amine amide)s were investigated with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results are summarized in Table 4. All the aromatic poly(amine amide)s exhibited good thermal stability with insignificant weight loss up to 400 °C in nitrogen. The 10% weight loss temperatures of the aromatic poly(amine amide)s in nitrogen and air were recorded in the range of 541–593 and 525–595 °C, respectively. The amount of carbonized residue (char yield) of these polymers in a nitrogen atmosphere was more than 61% at 800 °C. The high char yields of these polymers could be ascribed to their high aromatic content. The T_g values of all the aromatic poly(amine amide)s could be easily measured in the DSC thermograms; they were observed in the range of 268–331 °C and decreased with decreasing rigidity and symmetry of the dicarboxylic acids. The aromatic–aliphatic poly(amine amide)s had T_g values in the range of 137–183 °C. As expected on the basis of the chemical structures, the T_g values decreased with an increase in the aliphatic chain length. The polymers indicated no clear melting endotherms up to the decomposition temperatures on the DSC thermograms (Table 4).

Optical and Electrochemical Properties

The optical properties of the carbazole-based poly(amine amide)s are summarized in Table 5. These polymers exhibited maximum ultraviolet–visible (UV–vis) absorption at 293–358 nm in NMP solutions because of the π–π^* transitions of the aromatic chromophores (e.g., carbazole units and triphenylamine rings). In the solid state, the UV–vis absorption of carbazole-based poly(amine amide)s **IIa–IIl** is nearly identical and shows a single absorbance at 326–353 nm. Figure 3 shows the UV–vis absorption and PL spectra of poly(amine amide)s **IIa**, **IIb**, **IIe**, and **IIg** measured in NMP (concentration = 10^{-5} mol/L). Aromatic–aliphatic poly(amine amide)s **IIa–IIc** and aromatic poly(amine amide)s **IId–IIl** exhibited fluorescence emission maxima around 362 and 448–499 nm in NMP solutions. The fluorescence quantum yield in NMP solutions ranged from 0.34% for **IIj** to 4.44% for **IIa**. The blueshift and higher fluorescence quantum yield of aromatic–aliphatic poly(amine

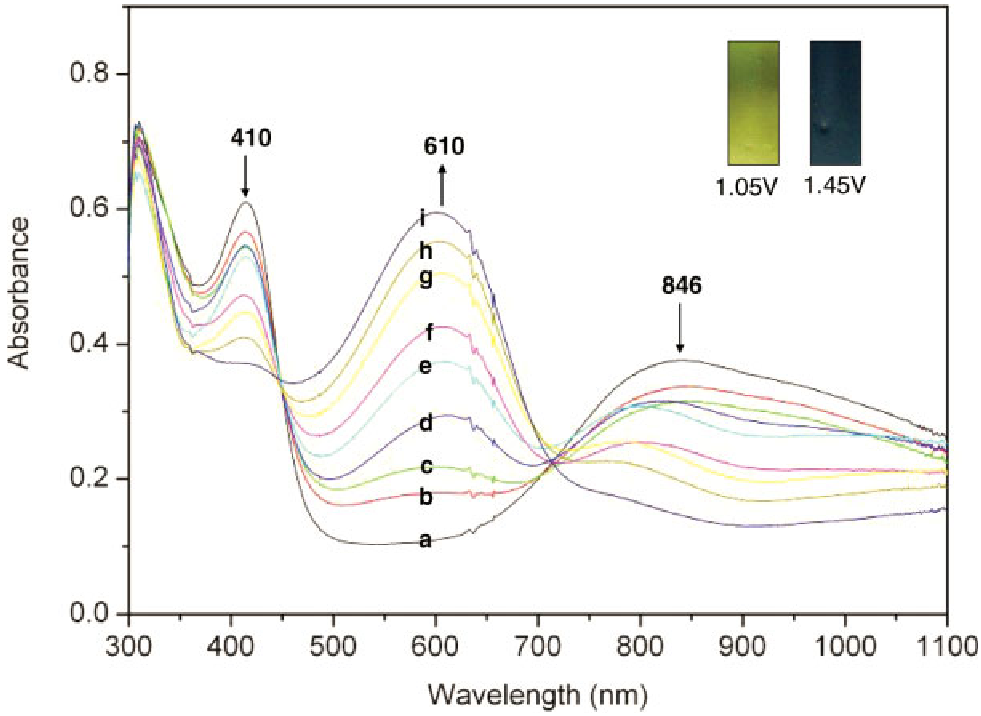


Figure 7. Electrochromic behavior of a poly(amine amide) **IIl** thin film (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 1.05, (b) 1.10, (c) 1.15, (d) 1.20, (e) 1.25, (f) 1.30, (g) 1.35, (h) 1.40, and (i) 1.45 V.

amide)s **IIa–IIc**, compared with aromatic poly (amine amide)s **IId–IIl**, could be attributed to the effectively reduced conjugation and capability of charge-transfer-complex formation by aliphatic diacids in comparison with the electron-donating amino unit and the strongly electron-accepting aromatic diacid unit.[66] PL of some polymer solutions and thin films of **IIa**, **IIb**, and **IIc** by UV irradiation is also shown in Figure 4. The thin films of **IIa–IIc** and **IId–IIl** exhibited violet-blue and green fluorescence, respectively. The cutoff wavelengths (absorption edge) from UV–vis transmittance spectra were in the range of 344–553 nm. Because of the lower capability of charge transfer, poly(amine amide)s **IIa–IIc** showed a light color and high optical transparency with cutoff wavelengths in the range of 344–385 nm.

The redox behavior of the poly(amine amide) **II** series was investigated by cyclic voltammetry conducted for the cast films on an ITO-coated glass substrate as a working electrode in dry acetonitrile (CH_3CN) containing 0.1 M TBAP as an electrolyte under a nitrogen atmosphere. The typical cyclic voltammograms for poly(amine amide) **IIj** underwent reversible oxidation processes at $E_{1/2}$ (average potential of the redox couple peaks) = 0.89 V and irreversible oxidation processes at $E_{1/2} = 1.31$ V, as shown in Figure 5. The first stable cation radical N^+ for poly(amine amide) is assumed to occur at the nitrogen center of triphenylamine, which is linked to three electron-rich phenyl groups in a propeller-like geometry.[60] The energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the investigated poly(amine amide)s could be determined from the oxidation half-wave potentials and the onset absorption wavelength,[67] and the results are listed in Table 5. For example, the oxidation half-wave potential for poly(amine amide) **IIj** was determined to be 0.89 V versus Ag/AgCl. The external ferrocene/ferrocenium (Fc/Fc^+) redox standard $E_{1/2}$ value (Fc/Fc^+) was 0.44 V versus Ag/AgCl in CH_3CN. Assuming that the HOMO energy for the Fc/Fc^+ standard was 4.80 eV with respect to the zero vacuum level, we determined the HOMO energy for poly(amine amide) **IIj** to be 5.25 eV.

Electrochromic Characteristics

The electrochromism of the thin films from the poly(amine amide)s was examined by the casting

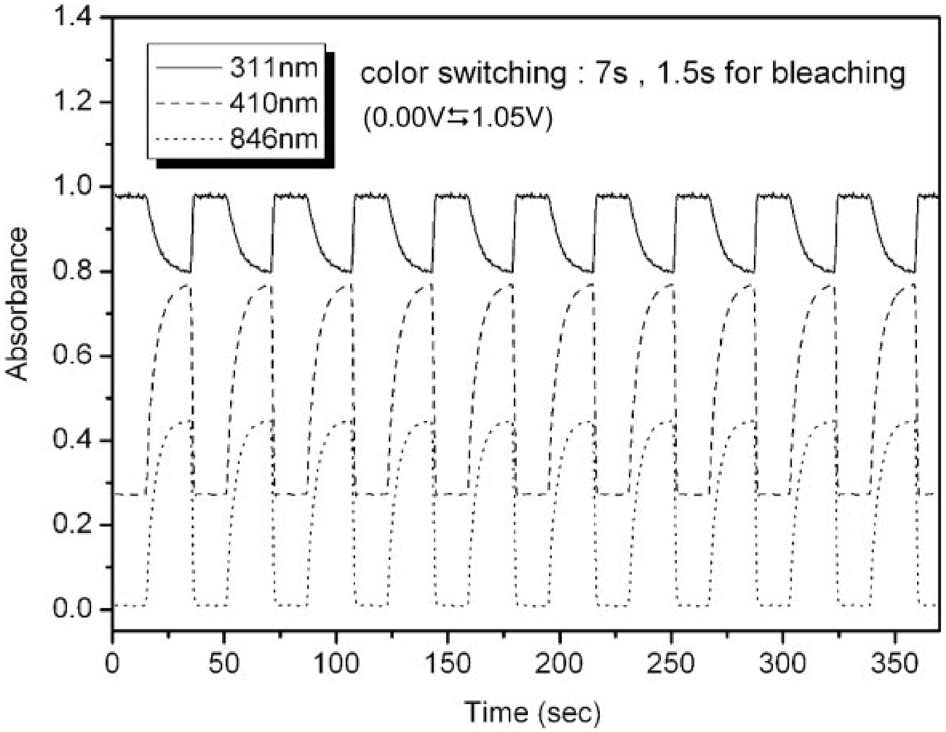


Figure 8. Potential step absorptometry of poly(amine amide) **III** (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) by the application of a potential step (0.00 V → 1.05 V).

of polymer solutions onto an ITO-coated glass substrate, and their 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 absorption spectra of poly (amine amide) **III** are shown in Figures 6 and 7. When the applied potentials increased positively from 0.00 to 1.05 V, the peak of the absorbance at 311 nm, characteristic for poly(amine amide) **III**, decreased gradually, whereas new bands grew up at 410 and 846 nm because of the first electron oxidation. When the potential was adjusted to a more positive value of 1.45 V, corresponding to the second electron oxidation, the peak of the characteristic absorbance decreased gradually, whereas one new band grew up at 610 nm. Meanwhile, the color of the film changed from the original yellow to green and then to a dark blue oxidized form.

The color switching times were estimated by the application of a potential step, and the absorbance profiles were followed (Figs. 8 and 9). The switching time was defined as the time required to reach 90% of the full change in absorbance after the switching of the potential. Thin films from poly(amine amide) **III** required 7 s at 1.05 V for switching the absorbance at 311, 410, and 846 nm and 1.5 s for bleaching. When the potential was set at 1.45 V, thin films from poly(amine amide) **III** required almost 10 s for coloration at 610 nm and 4 s for bleaching.

CONCLUSIONS

A series of new poly(amine amide)s were readily prepared from diamine **4** and various aromatic dicarboxylic acids via direct phosphorylation polycondensation. The introduction of the electron-donating carbazole group not only stabilized triphenylamine cationic radicals but also disrupted polymer chain packing, and thus excellent thin-film-forming ability was exhibited. The aromatic–aliphatic poly(amine amide)s had a light color and high optical transparency with a cutoff wavelength in the range of 344–385 nm, and they exhibited violet-to-blue emissions in the solid state. The poly (amine amide) films showed good adhesion behavior and were electroactive. As for the multicolor electrochromic behavior, the polymer films exhib-

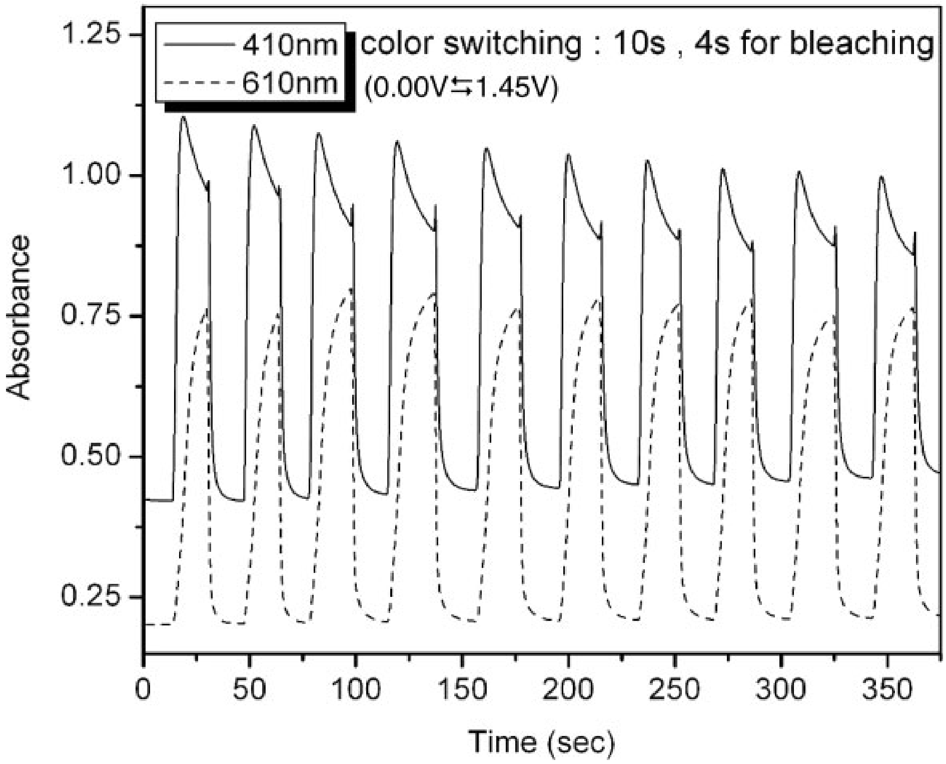


Figure 9. Potential step absorptometry of poly(amine amide) **III** (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) by the application of a potential step (0.00 V → 1.45 V).

ited pale yellow, green, and blue colors when various potentials were applied. All the obtained poly(amine amide)s revealed good stability of electrochromic characteristics for the first oxidation state, changing color from the yellowish neutral form to the green oxidized forms when positive potentials were scanned from 0.00 to 1.05 V. Thus, these poly(amine amide)s could be employed as potential candidates for the development of dynamic electrochromic and EL devices because of their proper HOMO values, excellent thermal stability, and reversible electrochemical behavior.

The authors are grateful to the National Science Council of the Republic of China for its financial support of this work.

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