Novel Family of Triphenylamine-Containing, Hole-Transporting, Amorphous, Aromatic Polyamides with Stable Electrochromic Properties

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ABSTRACT: We report the preparation and characterization of a series of novel electrochromic, aromatic poly(amine amide)s with pendent triphenylamine units. The synthesis proceeded via direct phosphorylation polycondensation between a novel diamine, *N,N*-bis(4-aminophenyl)-*N′,N′*-diphenyl-1,4-phenylenediamine, and various aromatic dicarboxylic acids. All the poly(amine amide)s were amorphous and readily soluble in many common organic solvents and could be solution-cast into transparent, tough, and flexible films with good mechanical properties. They exhibited good thermal stability and 10% weight-loss temperatures above 540 °C. Their glass-transition temperatures were 263–290 °C. These polymers in *N*-methyl-2-pyrrolidinone solutions exhibited strong ultraviolet–visible absorption peaks at 307–358 nm and photoluminescence peaks around 532–590 nm in the green region. The hole-transporting and electrochromic properties were studied with electrochemical and spectroelectrochemical methods. Cyclic voltammograms of poly(amine amide) films prepared by the casting of polymer solutions onto an indium tin oxide coated glass substrate exhibited two reversible oxidation redox couples at 0.65 and 1.03 V versus Ag/AgCl in an acetonitrile solution. All the poly(amine amide)s showed excellent stability with respect to their electrochromic characteristics; the color of the films changed from pale yellow to green and then blue at 0.85 and 1.25 V, respectively. © 2005 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 43: 2085–2098, 2005

Keywords: aromatic polyamides; electrochromic; hole-transporting; *N,N*-bis(4-aminophenyl)-*N′,N′*-diphenyl-1,4-phenylenediamine; poly(amine amide)s; triphenylamine

INTRODUCTION

Triarylamine- and triphenylamine-based derivatives have been used as hole-transporting molecules in optoelectronics, in both photoreceptor devices[1] and organic light-emitting diodes.[2,3] The redox properties, ion-transfer process, electrochromism, and photoelectrochemical behavior of *N,N,N′,N′*-tetrasubstituted 1,4-phenylenediamines are important for technological application.[4–7] A new material with a longer life, higher efficiency, and appropriate highest occupied molecular orbital (HOMO) energy level is in increas-

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ing demand. In recent years, intensive research efforts have been focused on the development of new charge-transport polymers because of the promising commercial advantages over low-molecular-weight counterparts.[8–10] One of the perceived benefits is that polymer films can be more easily deposited over a larger area, and they are often flexible. Furthermore, the prevention of crystallization and phase separation may improve the device performance. Because triarylamine derivatives have been widely used as hole-transport compounds in organic photoconductors and electroluminescent devices,[11–14] many triarylamine macromolecules have been developed, and some important results have been obtained.[15–22] For the development of amorphous polymer materials that exhibit good hole-transporting ability and high thermal stability, it is important to design a novel polymer with high performance.

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.[23,24] These properties make them generally intractable or difficult to process, thus restricting their applications in some fields. To overcome such difficulties, 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.[25–32] Recently, we reported the synthesis of some triphenylamine-based monomers, such as *N,N*′-bis(4-aminophenyl)-*N,N*′-diphenyl-1,4-phenylenediamine,[33,34] *N,N*′-bis(4-carboxyphenyl)-*N,N*′-diphenyl-1,4-phenylenediamine,[35] and 2,4-diaminotriphenylamine,[36] and their derived aromatic polyamides and polyimides bearing triphenylamine units in the main chain. Because of the incorporation of bulky, three-dimensional triphenylamine units along the polymer backbone, all the polymers were amorphous, had good solubility in many aprotic solvents, and exhibited excellent thin-film-forming capability.

In view of our continuing interest in the synthesis of triphenylamine-containing high-performance polymers, this work describes the synthesis of a series of novel poly(amine amide)s containing both main-chain and side-chain triphenylamine groups from *N,N*-bis(4-aminophenyl)-*N*′*,N*′-diphenyl-1,4-phenylenediamine and various aromatic dicarboxylic acids. The general properties, such as the solubility, crystallinity, thermal, and mechanical properties, are reported. The electrochemical, electrochromic, and photoluminescence (PL) properties of these polymers, which were prepared by the casting of solutions onto an indium tin oxide (ITO) coated glass substrate, are also described here and are compared with those of structurally related ones from 4,4′-diaminotriphenylamine.

EXPERIMENTAL

Materials

4,4′-Diaminotriphenylamine (mp = 186–187 °C) was synthesized through the hydrazine Pd/C-catalyzed reduction of 4,4′-dinitrotriphenylamine resulting from the condensation of aniline with 4-fluoronitrobezene in the presence of cesium fluoride (CsF) according to a previously reported procedure.[37] A novel aromatic diamine with a bulky pendent triphenylamine group, *N,N*-bis(4-aminophenyl)-*N*′*,N*′-diphenyl-1,4-phenylenediamine (mp = 245–248 °C), was prepared through the CsF-mediated nucleophilic displacement reaction of 4-aminotriphenylamine with 4-fluoronitrobenzene, followed by hydrazine Pd/C-catalyzed reduction.[38] *N,N*-Dimethylacetamide (DMAc; Tedia), *N,N*-dimethylformamide (DMF; Acros), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidinone (NMP; Tedia), pyridine (Py; Tedia), and triphenyl phosphite (TPP; Acros) were used without further purification. Commercially available aromatic dicarboxylic acids such as terephthalic acid (**Ia**; TCI), isophthalic acid (**Ib**; TCI), 2,6-naphthalenedicarboxylic acid (**Ic**; TCI), 4,4′-biphenyldicarboxylic acid (**Id**; TCI), 4,4′-oxydibenzoic acid (**Ie**; TCI), and 4,4′-sulfonyldibenzoic acid (**If**; New Japan Chemical Co.) were used as received. Tetrabutylammonium perchlorate (TBAP) was obtained from Acros and was recrystallized twice from ethyl acetate and then dried *in vacuo* before use.

Polymer Synthesis

The synthesis of poly(amine amide) **IIc** is used as an example to illustrate the general synthetic route. The typical procedure was as follows. A mixture of 0.553 g (1.25 mmol) of *N,N*-bis(4-

aminophenyl)-N',N'-diphenyl-1,4-phenylenediamine, 0.276 g (1.25 mmol) of **Ic**, 0.3 g of calcium chloride, 0.9 mL of TPP, 1.2 mL of Py, and 5 mL of NMP was heated with stirring at 105 °C for 3 h. The polymer solution was poured slowly into 300 mL of stirring methanol, and this gave rise to a stringy, fiberlike precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried *in vacuo* at 150 °C for 15 h *in vacuo*; the yield was 0.771 g (99%). Precipitations from NMP into methanol were carried out twice for further purification. The inherent viscosity of **IIc** was 0.52 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C. The IR spectrum of **IIc** (film) exhibited characteristic amide absorption bands at 3310 (N—H stretching) and 1654 cm^{-1} (amide carbonyl).

ELEM. ANAL. Calcd. for $(C_{42}H_{30}N_4O_2)_n$ $(622.71)_n$: C, 81.01%; H, 4.86%; N, 9.00%. Found: C, 78.14%; H, 4.87%; N, 8.63%.

The other poly(amine amide)s were prepared by an analogous procedure.

Preparation of the Films

A solution of the polymer was made through the dissolution of approximately 0.6 g of the poly(amine amide) 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 160 °C for 8 h. The obtained films were about 40–80 μm thick and were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

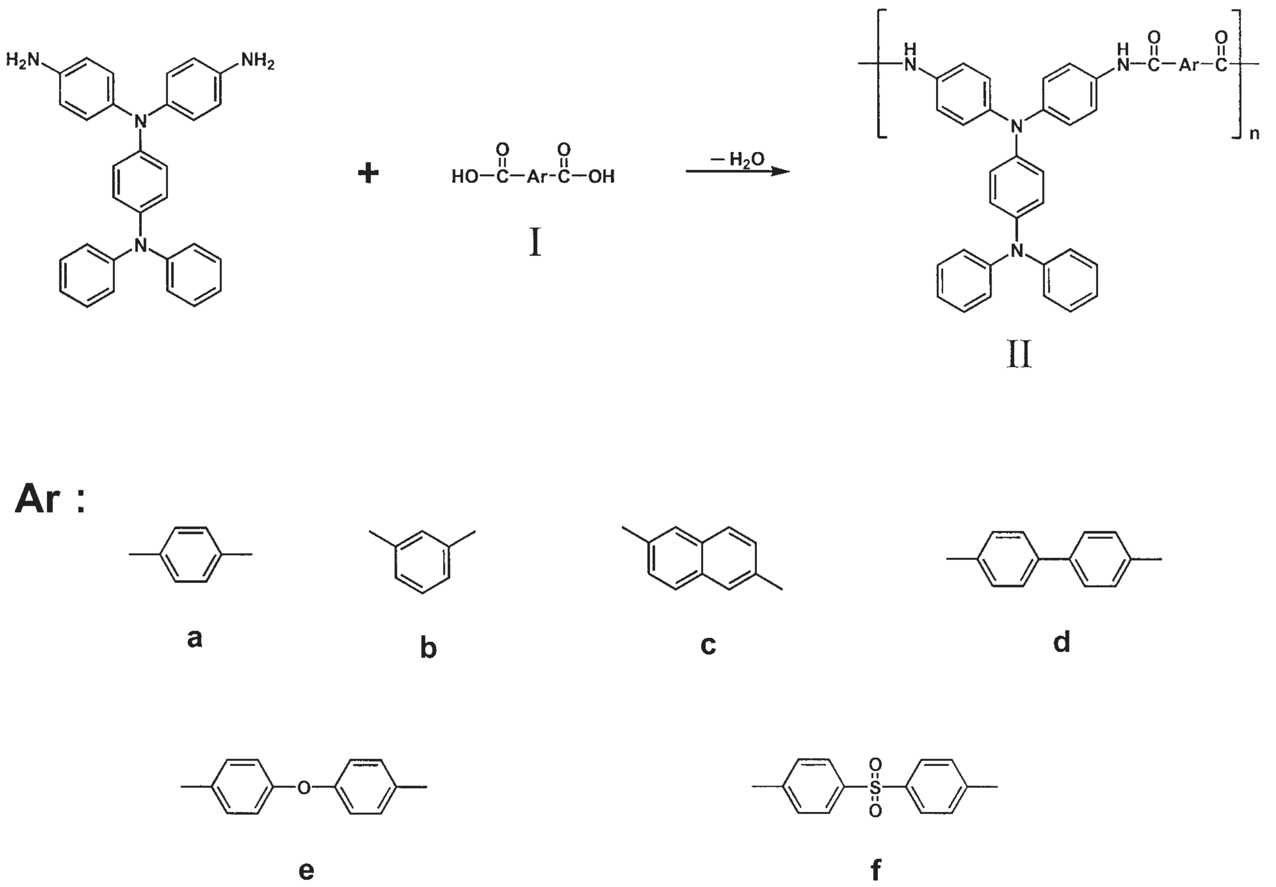
Measurements

IR spectra were recorded on a PerkinElmer RXI FTIR spectrometer. Elemental analyses were run in an Elementar Vario EL-III. ^1H and ^{13}C NMR spectra were measured on a Varian Unity Inova 600 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 and 20 mA) with graphite-monochromatized Cu Kα radiation. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Varian Cary 50 Probe spectrometer. An Instron model 4400R universal tester with a load cell of 5kg was used to study the stress–strain behavior of the samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. The measurements were performed at room temperature with film specimens (0.5 cm wide and 6 cm long), and an average of at least three replicates was used. Thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer Pyris 1 TGA instrument. Experiments were carried out on approximately 6–8-mg film samples heated in flowing nitrogen or air (flow rate = 20 cm^3/min) at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer Pyris Diamond DSC instrument at a scanning rate of 20 °C/min in flowing nitrogen (20 cm^3/min). Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 instrument. The TMA experiments were conducted from 50 to 350 °C at a scanning rate of 10 °C/min with a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures (T_s's) were taken as the onset temperatures of probe displacement on the TMA traces. Electrochemistry was performed with a Bioanalytical System model CV-27 potentiostat and a BAS X–Y recorder. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downward. Cyclic voltammetry was conducted with the use of a three-electrode cell in which ITO (the polymer film area was ca. 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 (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 an Ag/AgCl reference electrode. Absorption spectra were measured with an HP 8453 UV–vis spectrophotometer. PL spectra were measured with a Jasco FP-6300 spectrofluorometer.

RESULTS AND DISCUSSION

Polymer Synthesis

According to the phosphorylation technique first described by Yamazaki and coworkers,[39,40] a series of novel aromatic poly(amine amide)s (**IIa–IIf**) with pendent triphenylamine units were synthesized from the diamine, *N,N*-bis(4-aminophe-



Scheme 1

nyl)-*N′*,*N′*-diphenyl-1,4-phenylenediamine, and various aromatic dicarboxylic acids, as shown in Scheme 1. The polymerization was carried out via solution polycondensation with TPP and Py as condensing agents. The polymerization proceeded 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 under stirring into methanol. As shown in Table 1, the obtained poly(amine amide)s had inherent viscosities of 0.27–0.88 dL/g. All these polymers could be solution-cast into flexible and tough films, and this was indicative of high-molecular-weight polymers. The results of elemental analyses are also included in Table 1. The elemental analyses were in a good agreement with the proposed structures, missing only the values found for C percentages, which were always slightly lower than the calculated ones. That possibly can be attributed to the very aromatic nature of these polymers, which commonly leave a small coal residue under the standard conditions of microanalysis. 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) **IIc**. It exhibited characteristic IR absorption bands of the amide group around 3310 (N—H stretching) and 1654 cm^{-1} (amide carbonyl). Figure 2 shows a typical set of ^{1}H and ^{13}C NMR spectra of poly(amine imide) **IIc** in DMSO-d_6; all the peaks were readily assigned to the hydrogen and carbon atoms of the recurring unit. The resonance peaks appearing at 10.49 ppm in the ^{1}H NMR spectrum and at 165.0 ppm in the ^{13}C NMR spectrum also support the formation of amide linkages. For a comparative study, a series of referenced poly(amine amide)s (**II′a–II′f**) were also synthesized from 4,4′-diaminotriphenylamine and dicarboxylic acids **Ia–If** by the same technique used for the **II** series polymers.

Polymer Properties

Basic Characterization

Morphological information about the polymer films was obtained with WAXD measurements.

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

Poly(amine amide)s		Elemental Analysis (%) of Poly(amine amide)s					
Code	η_{inh} (dL/g)[a]	Formula (Formula Weight)		C	H	N	S
IIa	0.60	$(C_{38}H_{28}N_4O_2)_n$	Calcd.	79.70	4.93	9.78	
		$(572.65)_n$	Found	77.00	4.99	9.49	
IIb	0.27	$(C_{38}H_{28}N_4O_2)_n$	Calcd.	79.70	4.93	9.78	
		$(572.65)_n$	Found	76.86	4.97	9.45	
IIc	0.52	$(C_{42}H_{30}N_4O_2)_n$	Calcd.	81.01	4.86	9.00	
		$(622.71)_n$	Found	78.14	4.87	8.63	
IId	0.88	$(C_{44}H_{32}N_4O_2)_n$	Calcd.	81.46	4.97	8.64	
		$(648.75)_n$	Found	78.74	4.98	8.36	
IIe	0.53	$(C_{44}H_{32}N_4O_3)_n$	Calcd.	79.50	4.85	8.43	
		$(664.75)_n$	Found	77.20	4.84	8.10	
IIf	0.53	$(C_{44}H_{32}N_4O_4S)_n$	Calcd.	74.14	4.52	7.86	4.50
		$(712.81)_n$	Found	71.15	4.55	7.57	4.46

[a] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.

The reflection pattern was featureless, showing only a broad, amorphous halo. This result indicated that all the polymers were essentially amorphous. The solubility behavior of poly(amine amide)s was tested qualitatively, and the results are presented in Table 2. All the poly(amine amide)s were highly soluble in polar solvents such as NMP, DMAc, DMF, and DMSO, and the enhanced solubility could be attributed to the introduction of the bulky pendent triphenylamine group into the repeat unit. Thus, the excellent solubility makes these polymers potential candidates for practical applications with spin- or dip-coating processes.

All the aromatic poly(amine amide)s could afford flexible and tough films via solvent casting. These films were subjected to tensile testing, and the results are given in Table 3. The tensile strengths, elongations to break, and initial moduli of these films were 78–111 MPa, 8–40%, and 2.1–2.8 GPa, respectively. Polymers **IIa** and **IId** necked during tensile testing and showed a moderate extension to break; this indicated strong and ductile materials.

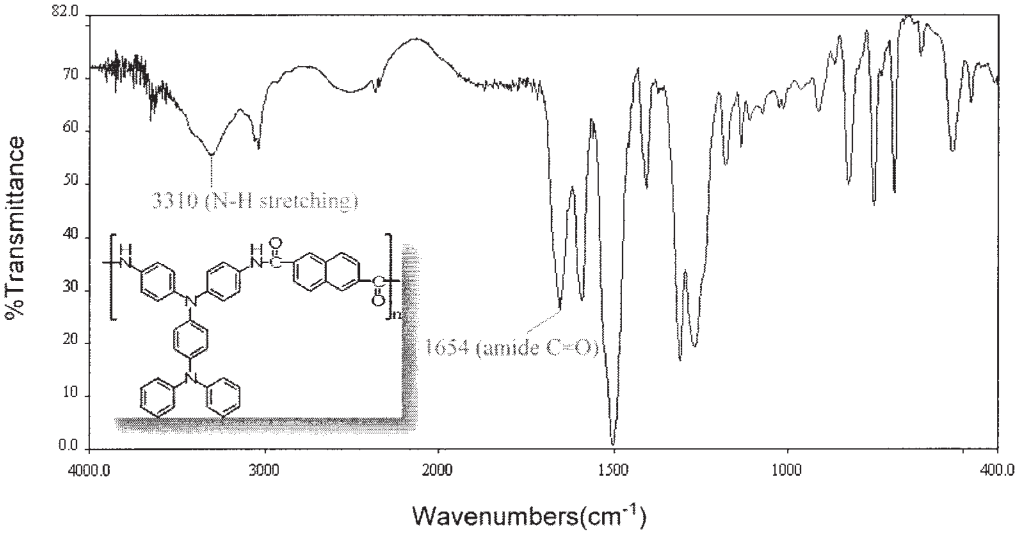


Figure 1. IR spectrum (film) of poly(amine amide) **IIc**.

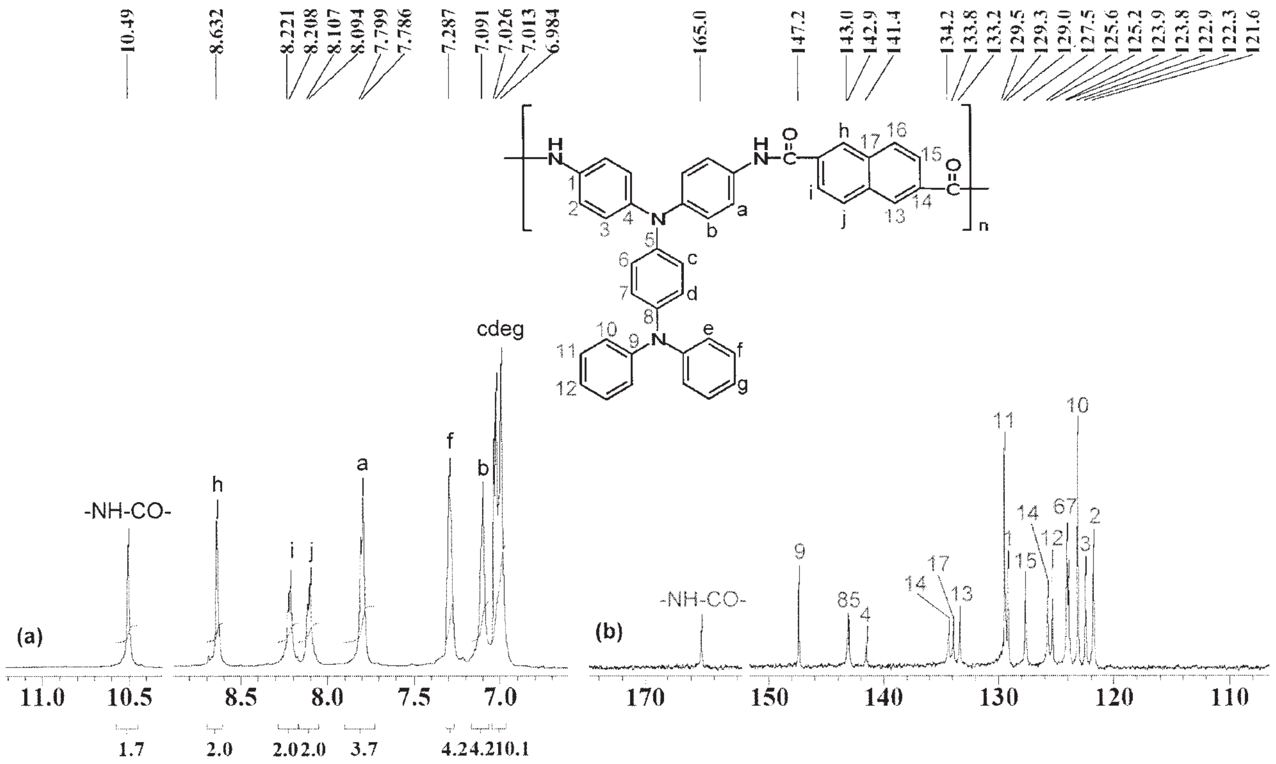


Figure 2. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of poly(amine amide) **IIc** in DMSO-d_6.

The thermal properties of the poly(amine amide)s were investigated with TGA, DSC, and TMA. The results are summarized Table 4. Typical TGA curves of representative poly(amine amide) **IIa** in both air and nitrogen atmospheres are shown in Figure 3. All the poly(amine amide)s exhibited good thermal stability, with insignificant weight loss up to 400 °C in nitrogen. Their 10% weight-loss temperatures in nitrogen and air were recorded at 546–592 and 537–576 °C, respectively. The concentration of carbonized residue (char yield) of these polymers when they were heated to 800 °C in nitrogen was more than 67%. The high char yields of these polymers could be ascribed to their high aromatic content. The T_g values of all the polymers could be easily measured in the DSC thermograms; they were observed in the range of 263–290 °C and decreased with decreasing rigidity and symmetry of the dicarboxylic acids. In comparison with the corre-

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

	Solvent					
Polymer	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF
IIa	+	+	+	+	+h	±
IIb	+	+	+	+	+	±
IIc	+	+	+	+	+h	±
IId	+	+	+	+	+h	±
IIe	+	+	+h	+	±	−
IIf	+	+	+	+	+h	±

[a] + soluble at room temperature; +h soluble on heating; ± partially soluble or swelling; − insoluble even on heating.

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

Polymer	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
IIa	99	29	2.1
IIb	100	9	2.8
IIc	96	8	2.6
IId	105	40	2.4
IIe	111	8	2.4
IIf	78	14	2.1

sponding poly(amine amide) series **II′** (Table 4), the **II** series of poly(amine amide)s showed a slightly decreased T_g that could be attributed to the increased conformational flexibility or free volume caused by the lateral attachment of the bulky triphenylamine group along the polymer backbone. None of the polymers indicated clear melting endotherms up to the decomposition temperatures on the DSC thermograms. This result also supports the amorphous nature of these triphenylamine-containing polymers. The T_s values of the polymer film samples were determined by the TMA method with a loaded penetration probe. They were obtained from the onset temperature of the probe displacement on the TMA trace. A typical TMA thermogram for poly(amine amide) **IIb** is presented in Figure 4. In most cases, the T_s values obtained by TMA were comparable to the T_g values measured by the DSC experiments (Table 4).

Optical and Electrochemical Properties

The optical and electrochemical properties of the poly(amine amide)s were investigated with UV–vis and PL spectroscopy and cyclic voltammetry. The results are summarized Table 5. These polymers exhibited strong UV–vis absorption bands at 307–358 nm in NMP solutions, which were assignable to the π–π^* transition resulting from the conjugation between the aromatic rings and nitrogen atoms. Their PL spectra in NMP solutions showed maximum bands around 532–590 nm in the green region. The cutoff wavelengths (absorption edge) read from the UV–vis

Table 4. Thermal Properties of Poly(amine amide)s[a]

Polymer	T_g (°C)[b]	T_s (°C)[c]	T_d at 5% Weight Loss (°C)[d]		T_d at 10% Weight Loss (°C)[d]		Char Yield (wt %)[e]
			N_2	Air	N_2	Air	
IIa	276 (295)[f]	273 (297)[f]	514	486	574	549	68
IIb	265 (289)	260 (271)	500	491	562	557	77
IIc	276 (307)	261 (315)	525	509	592	567	80
IId	290 (302)	283 (304)	530	513	591	576	75
IIe	263 (273)	248 (269)	504	502	546	537	71
IIf	287 (295)	280 (292)	486	489	549	551	67

[a] The polymer film samples were heated at 300 °C for 1 h before all the thermal analyses.

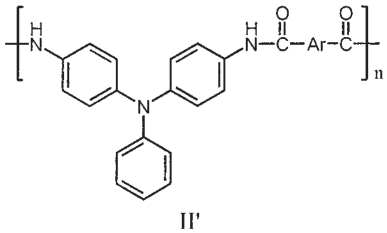
[b] Midpoint temperature of the baseline shift in the DSC heating trace (rate 20 °C/min).

[c] Measured by TMA with a constant applied load of 10 mN at a heating rate of 10 °C/min.

[d] Decomposition temperature recorded via TGA at a heating rate of 20 °C/min and a gas-flow rate of 30 cm^3/min.

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

[f] The values in parentheses are those of analogous polyamides (**II′**) with the corresponding —Ar— unit as in the **II** series:



II'

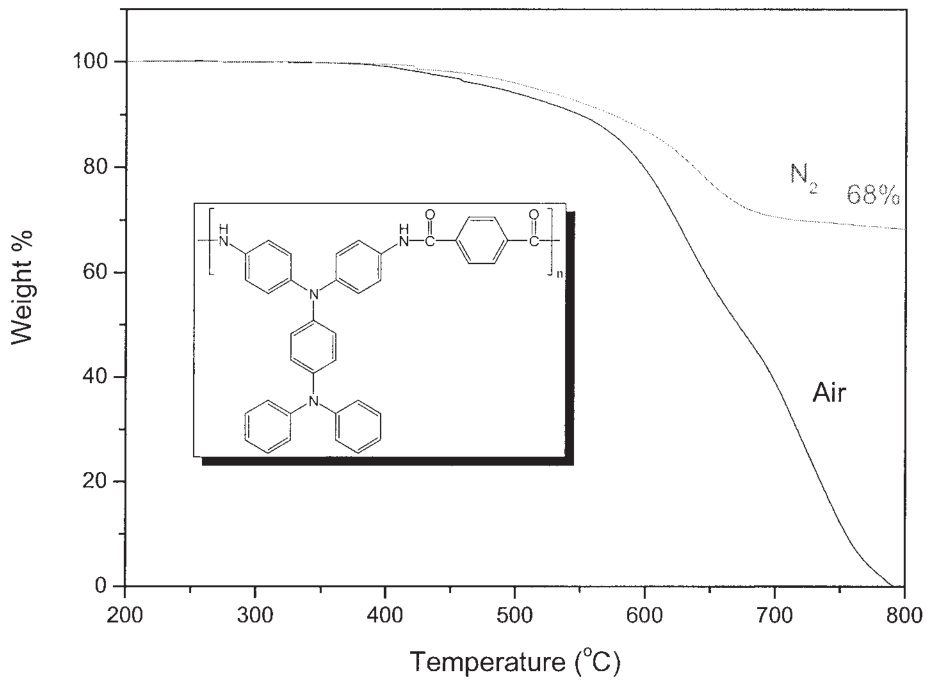


Figure 3. TGA thermograms of poly(amine amide) **IIa** at a scanning rate of 20 °C/min.

transmittance spectra are also indicated in Table 5 and were recorded in the range of 431–533 nm. The cutoff wavelengths of the poly(amine amide)s increased with increasing electron affinity of the corresponding diacid residue, and this suggested that the coloration of the polymer films was caused by charge-transfer (CT) interactions. The Stokes shifts [PL wavelength (λ_{PL}) − absorp-

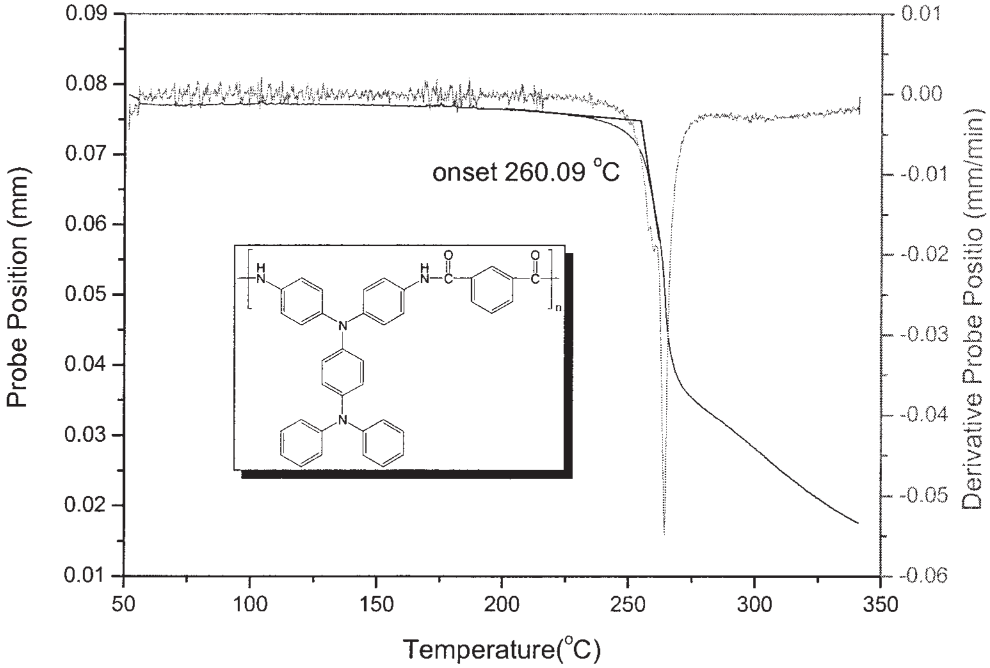


Figure 4. TMA curves of poly(amine amide) **IIb** at a heating rate of 10 °C/min.

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

Polymer	$\lambda_{abs,max}$ (nm)[a]	$\lambda_{abs,onset}$ (nm)[a]	λ_{PL} (nm)[b]	λ_0 (nm)[c]	Oxidation (V; vs Ag/AgCl)		HOMO–LUMO Gap (eV)[d]	HOMO (eV)[e]	LUMO (eV)[f]
					First	Second			
IIa	358 (317)	442 (469)	556	508	0.58	0.96	2.64	4.89	2.25
IIb	349 (341)	409 (429)	546	464	0.58	0.96	2.89	4.89	2.00
IIc	310 (331)	449 (477)	590	512	0.58	0.95	2.60	4.89	2.29
IId	307 (322)	435 (450)	557	494	0.63	1.00	2.76	4.94	2.18
IIe	348 (341)	398 (421)	532	446	0.63	1.00	2.95	4.94	1.99
IIf	321 (324)	467 (494)	572	533	0.65	1.03	2.51	4.96	2.45
II′e	342 (339)	392 (409)	527	431	0.85	—	3.03	5.16	2.13
II′f	282 (311)	447 (468)	603	511	0.87	—	2.65	5.18	2.53

[a] UV–vis absorption measurements in NMP (0.02 mg/mL) at room temperature. The values in parentheses are for polymer films.

[b] PL spectroscopy measurements in NMP (5 mg/mL) at room temperature.

[c] Cutoff wavelengths from the transmission UV–vis absorption spectra of polymer films.

[d] The data were calculated in the film state by the following equation: gap = $1240/\lambda_{onset}$.

[e] The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).

[f] LUMO = HOMO − gap.

tion wavelength (λ_{abs})] of the poly(amine amide)s in solution or film were around 200 nm or even higher. This phenomenon could be attributed to the CT interactions between intrinsic electron-donating triphenylamine-containing diamine and various aromatic dicarboxylic acids as electron-acceptor moieties. In general, the PL bands were located in a lower energy region than the corresponding CT absorption band as a result of the Stokes shifts.[41] Figure 5 shows UV–vis absorption and PL spectra of poly(amine amide)s **IIe**, **IIf**, **II′e**, and **II′f** for comparison. These polymers exhibited similar spectrograms, whereas the PL intensity of the poly(amine amide) **II′** series was

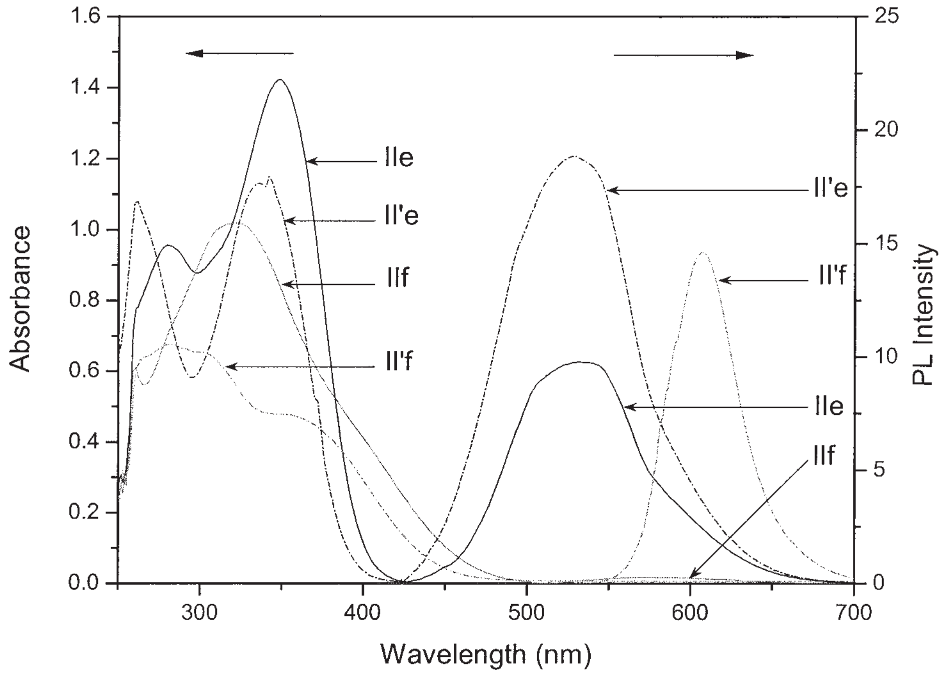


Figure 5. Absorption and PL spectra of poly(amine amide)s **IIe**, **IIf**, **II′e**, and **II′f** in NMP solutions.

greater than that of the poly(amine amide) **II** series. This may be explained by the increased conformational mobility of the latter caused by the introduction of pendent triphenylamine units. It is well known that one part of a less rigid molecule can undergo low-frequency vibrations with respect to its other parts; such motions undoubtedly account for some energy loss and, therefore, a consequent increase for nonradiation deactivation. In addition to conformational mobility, the characteristics of CT PL by excitation within the CT absorption bands are a spectral redshift and a fluorescence yield decrease with an increase in CT ability; this means that the PL intensity has a tendency to decrease as the peak positions shift toward lower energy. For this reason, poly(amine amide) **IIf**, derived from a sulfone-containing diacid having a higher electron affinity and a lower ionization energy diamine, *N,N*-bis(4-aminophenyl)-*N′,N′*-diphenyl-1,4-phenylenediamine, showed a very weak PL intensity in comparison with that of **IIe** and **II′f**.[41] The redox behavior of the poly(amine amide) **II** and **II′** series was investigated by cyclic voltammetry conducted for the cast films on an ITO-coated glass substrate as the 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)s **IIf** and **II′f** are shown in Figure 6. There are two reversible oxidation redox couples at $E_{1/2}$ values of 0.65 and 1.03 V for poly(amine amide) **IIf** and only one reversible oxidation redox couple at $E_{1/2} = 0.87$ V for poly(amine amide) **II′f** in the oxidative scan. Because of the stability of the films and the good adhesion between the polymer and ITO substrate, poly(amine amide) **IIf** exhibited excellent reversibility of electrochromic characteristics in five continuous cyclic scans between 0.0 and 1.35 V, changing color from pale yellow to green and then blue at electrode potentials over 0.65 and 1.03 V, respectively. Comparing the electrochemical data, we found that poly(amine amide) **IIf** was much more easily oxidized than poly(amine amide) **II′f** (0.65 vs 0.87 V). The first electron removal for poly(amine amide) **IIf** was assumed to occur at the N atom on the main-chain triphenylamine unit, which was more electron-rich than the N atom on the pendent triphenylamine group. The energy of the HOMO and lowest unoccupied molecular orbital levels of the investigated poly(amine amide)s could be determined from the oxidation half-wave potentials and the onset absorption wavelength, and the results are listed in Table 5. For example (Fig. 6), the oxidation half-wave potential for poly(amine amide) **IIf** was determined to be 0.65 V versus Ag/AgCl. The external ferrocene/ferrocenium (Fc/Fc^+) redox standard $E_{1/2}$ (Fc/Fc^+) was 0.49 V versus Ag/AgCl in CH_3CN. Under the assumption that the HOMO energy for the Fc/Fc^+ standard was 4.80 eV with respect to the zero vacuum level, the HOMO energy for poly(amine amide) **IIf** was evaluated to be 4.96 eV.

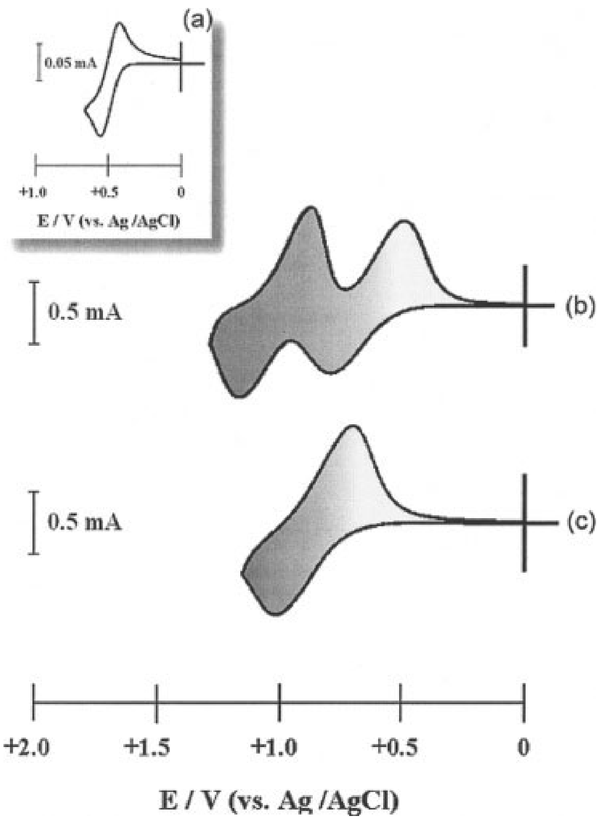


Figure 6. Cyclic voltammograms of (a) ferrocene, (b) poly(amine amide) **IIf**, and (c) **II′f** film on an ITO-coated glass substrate in CH_3CN containing 0.1 M TBAP. The scanning rate was 0.1 V/s.

Electrochromic Characteristics

The electrochromism of thin films from the poly(amine amide)s was examined via the casting 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 preparation and solution conditions were identical to those used in cyclic voltammetry. The typical electrochromic absorption spectra of poly-

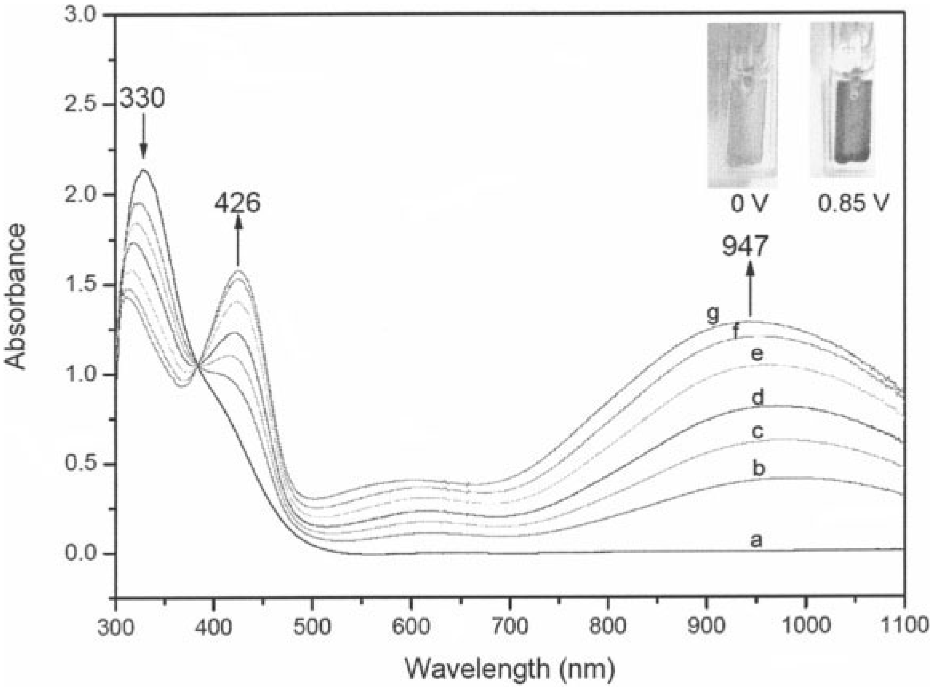


Figure 7. Electrochromic behavior of poly(amine amide) **IIf** thin films (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0, (b) 0.55, (c) 0.60, (d) 0.65, (e) 0.70, (f) 0.80, and (g) 0.85 V.

(amine amide)s **IIf** and **II′f** are shown in Figures 7–9. When the applied potentials increased positively from 0.55 to 0.85 V, the peak of the absorbance at 330 nm, characteristic of poly(amine amide) **IIf**, decreased gradually, whereas two new bands grew at 426 and 947 nm because of the first electron oxidation. The new spectrum was assigned to the cationic radical poly(amine amide)$^{+\cdot}$. Meanwhile, the film color became green (as shown in Fig. 7). Then, the potentials were adjusted to more positive values, corresponding to the second electron oxidation, and the spectral changes are shown as Figure 8. The characteristic peaks for poly(amine amide)$^{+\cdot}$ disappeared, and a new band grew at 720 nm. The new spectrum was assigned to poly(amine amide)$^{2+}$, and the color of film **IIf** became deep blue. The electrochromic characteristics of poly(amine amide) **II′f** are also shown in Figure 9. When the applied potential was swept from 0.70 to 1.10 V, the absorbance at 313 nm, characteristic of poly(amine amide) **II′f**, decreased gradually, whereas new bands grew at 398, 802, and 945 nm. The new spectrum was assigned to the cationic radical poly(amine amide)$^{+\cdot}$ and showed the complementary color of deep green.

The color switching times were estimated by the application of a potential step, and the absorbance profiles were followed (Figs. 10 and 11). The switching time was defined as the time required to reach 90% of the full change in the absorbance after the potential was switched. Thin films from poly(amine amide) **IIf** required 3 s at 0.85 V for switching absorbance at 426 and 947 nm and 2 s for bleaching. When the potential was set at 1.25 V, thin films from poly(amine amide) **IIf** required about 4 s for coloration at 720 nm and 2 s for bleaching. After five continuous cyclic scans between 0.0 and 1.25 V, the polymer films still exhibited excellent stability with respect to their electrochromic characteristics.

CONCLUSIONS

A series of high-molecular-weight poly(amine amide)s were readily prepared from *N,N*-bis(4-aminophenyl)-*N′,N′*-diphenyl-1,4-phenylenediamine and various aromatic dicarboxylic acids via direct phosphorylation polycondensation. The introduction of the bulky intrinsic electron-donating triphenylamine group reduced the HOMO en-

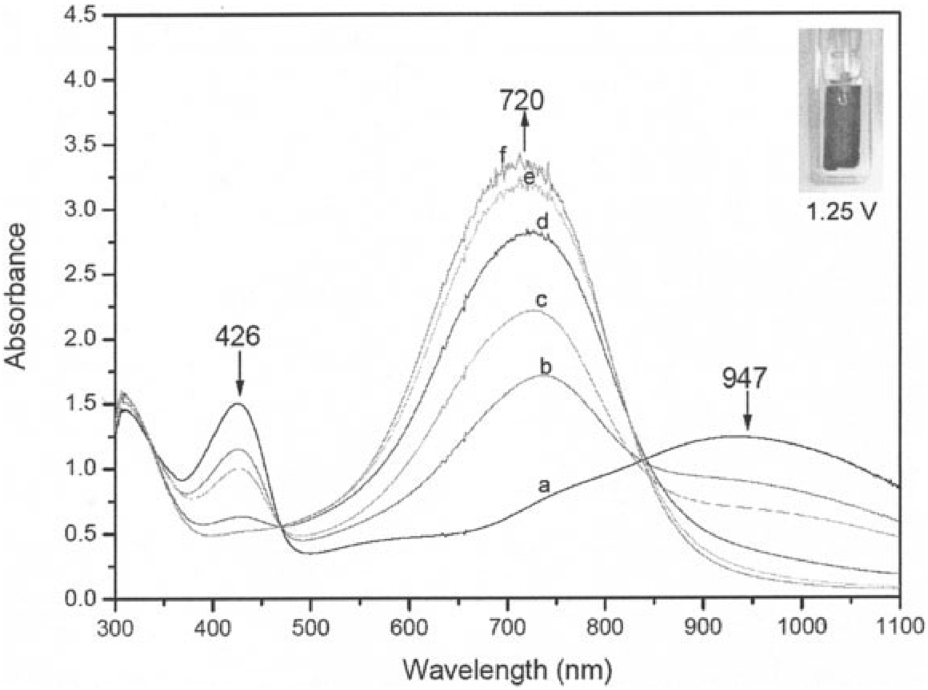


Figure 8. Electrochromic behavior of poly(amine amide) **IIf** thin films (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0.90, (b) 0.96, (c) 1.03, (d) 1.10, (e) 1.18, and (f) 1.25 V.

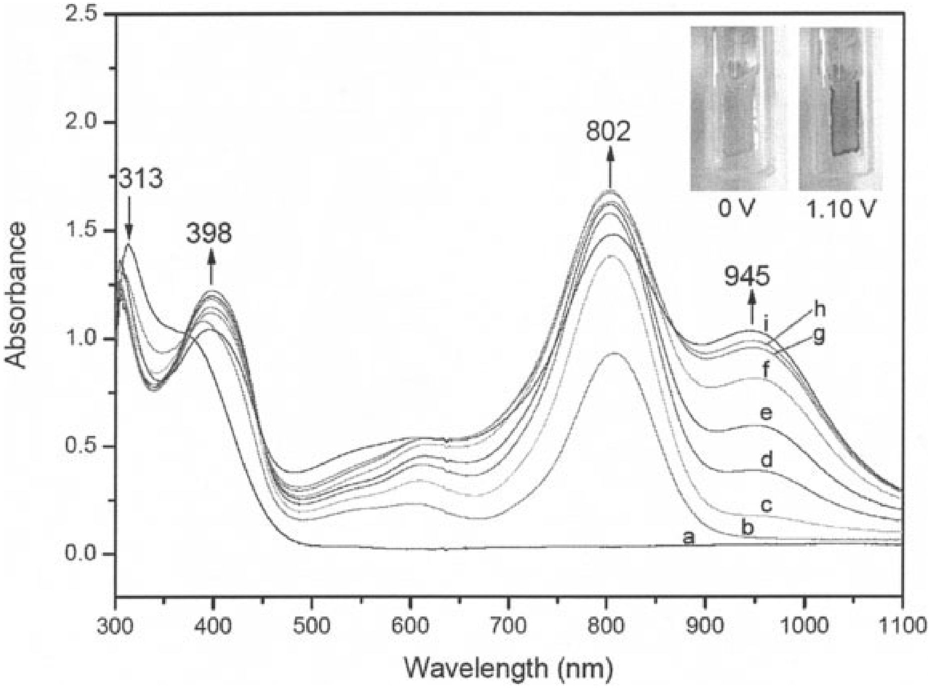


Figure 9. Electrochromic behavior of poly(amine amide) **II′f** thin films (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0, (b) 0.70, (c) 0.75, (d) 0.80, (e) 0.87, (f) 0.94, (g) 1.01, (h) 1.03, and (i) 1.10 V.

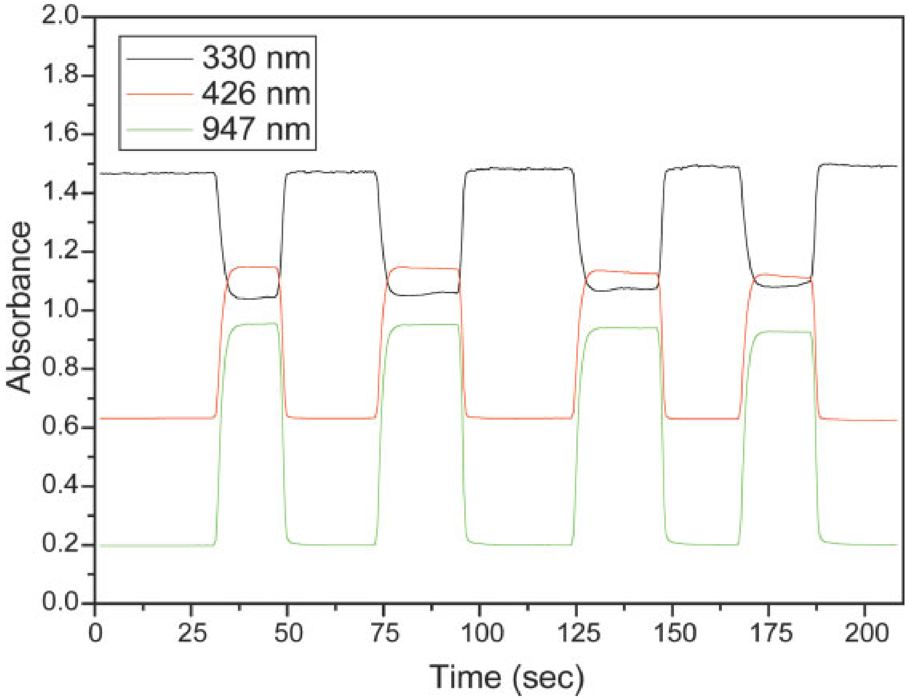


Figure 10. Potential step absorptometry of poly(amine amide) **IIf** (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) by the application of a potential step (0 V ⇆ 0.85 V).

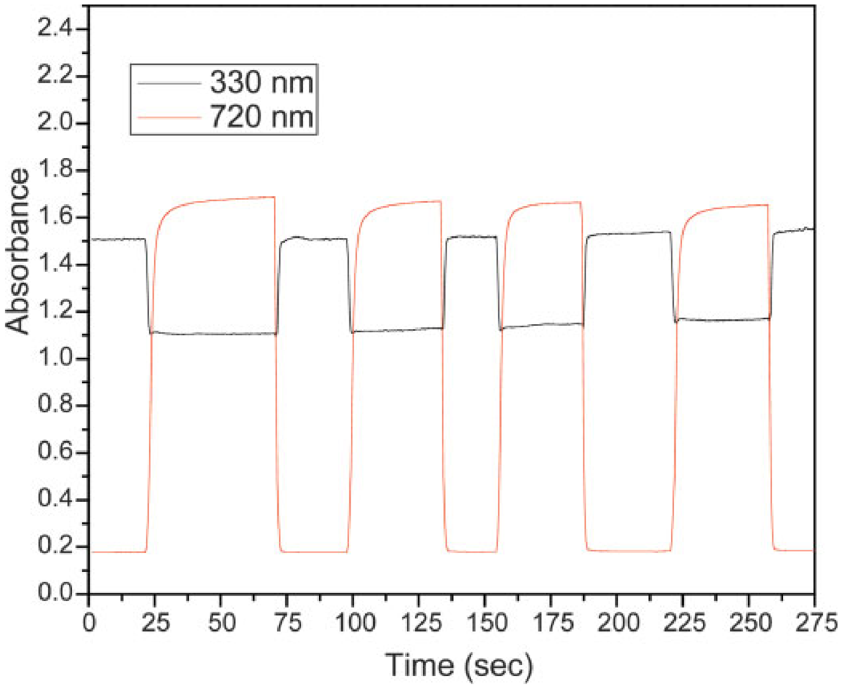


Figure 11. Potential step absorptometry of poly(amine amide) **IIf** (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) by the application of a potential step (0 V ⇆ 1.25 V).

ergy levels and disrupted the coplanarity of aromatic units in chain packing; this increased the between-chain spaces or free volume, and so all the polymers were amorphous with good solubility in many polar aprotic solvents and exhibited excellent thin-film-forming ability. In addition to moderately high T_g or T_s values and good thermal stability and mechanical properties, the poly(amine amide)s also showed excellent stability with respect to their electrochromic characteristics, changing color from the pale yellowish neutral form to the green and blue oxidized forms when potentials were scanned positively from 0.65 to 1.25 V. Thus, these novel triphenylamine-containing poly(amine amide)s have great potential as new types of hole-transporting and electrochromic materials because of their proper HOMO values and excellent electrochemical and thermal stability.

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