

# Novel electrochromic aromatic poly(amine–amide–imide)s with pendent triphenylamine structures

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Received 9 November 2004; received in revised form 23 April 2005; accepted 17 May 2005

Available online 21 June 2005

## Abstract

Three new aromatic poly(amine–amide–imide)s (PAAIs) having pendent triphenylamine units were prepared from the phosphorylation polyamidation reactions of a newly synthesized diamine, *N,N*-bis(4-aminophenyl)-*N',N'*-diphenyl-1,4-phenylenediamine, with three imide ring-preformed dicarboxylic acids. These PAAIs had inherent viscosities of 0.54–0.86 dL/g, and they were amorphous and readily soluble in many organic solvents and could be solution cast into transparent, tough, and flexible films with good mechanical properties. They displayed relatively high glass-transition temperatures (279–287 °C) and good thermal stability, with 10% weight-loss temperatures in excess of 522 °C in nitrogen and char yields at 800 °C in nitrogen higher than 67%. The solutions of polymers in NMP exhibited strong UV–vis absorption bands with a maximum around 315 nm. The hole-transporting and electrochromic properties were examined by electrochemical and spectroelectrochemical methods. Cyclic voltammograms of the PAAIs prepared by casting polymer solution onto an indium-tin oxide (ITO)-coated glass substrate exhibited two reversible oxidation redox couples at 0.67 and 1.08 V vs. Ag/AgCl in acetonitrile solution. All the PAAIs revealed very stable electrochromic characteristics, changing color from original pale brownish to green, and then to blue at 0.67 and 1.08 V, respectively.

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**Keywords:** Aromatic poly(amine–amide–imide)s; Triphenylamine; Redox polymers

## 1. Introduction

Semiconducting, conducting, and light-emitting organic materials are showing increasing potential as active components for a wide range of electronic and optoelectronic devices. Arylamine-containing aromatics have been used as hole-transporting molecules in the optoelectronic fields, both in photoreceptor devices [1] and organic light emitting diodes (OLEDs) [2,3]. The redox properties, ion transfer process, electrochromism and photoelectrochemical behavior of *N,N,N',N'*-tetrasubstituted-1,4-phenylenediamines are of importance for technological application [4–7]. A new material with longer life, higher efficiency and appropriate HOMO energy level is in increasing demands. In recent years, intensive research efforts have been focused

on the development of new charge transport polymers, since they promise a number of commercial advantages over low molecular weight counterparts [8]. One of the perceived advantages is that polymer films can be more easily deposited over a larger area and they are often flexible. Furthermore, prevention of crystallization and phase-separation may improve the device performance. Since triarylamine derivatives have been widely used as hole-transport compounds in organic photoconductors and electroluminescent devices [9–12], many triarylamine macromolecules have been developed, and some important results have been obtained [13–19].

Wholly aromatic poly(amide–imide)s (PAIs) are an important class of materials having excellent resistance to high temperatures and favorable balance of other physical and chemical properties [20,21]. However, these polymers are generally intractable and lack the properties essential for successful fabrication into useful forms due to their high melting or glass transition temperatures and limited solubility in organic solvents. Conventionally, trimellitic anhydride (TMA)-based PAIs could be prepared in several

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ways such as two-step polycondensation from the acid chloride of TMA with aromatic diamines involving polyaddition and subsequent cyclodehydration [22], low-temperature solution polycondensation of TMA-derived imide ring-preformed diacid chlorides and aromatic diamines [23–26], polycondensation of TMA or TMA-derived imide ring-containing dicarboxylic acids with diisocyanates [27–29]. The phosphorylation polyamidation reaction [30] of imide-containing dicarboxylic acids with aromatic diamines using triphenyl phosphite (TPP) and pyridine as condensing agents is another efficient method to prepare high-molecular-weight PAIs [31–33].

Recently, we have reported the synthesis of soluble aromatic polyamides and polyimides bearing triphenylamine units in the main chain based on *N,N'*-bis(4-aminophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine [34, 35], *N,N'*-bis(4-carboxyphenyl)-*N,N'*-diphenyl-1,4-phenylenediamine [36] and 2,4-diaminotriphenylamine [37], respectively. 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. As part of an effort to develop triphenylamine-containing aromatic polymers, the present article reports the synthesis of novel triphenylamine-containing poly(amine–amide–imide)s bearing pendent triphenylamine groups based on a novel diamine, *N,N'*-bis(4-aminophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine (**I**), and three TMA-derived, imide ring-preformed dicarboxylic acids by means of TPP and pyridine. The general properties such as solubility, crystallinity, thermal, and mechanical properties are reported. The electrochemical, electrochromic, and photoluminescence properties of these polymers prepared by casting solution onto an indium-tin oxide (ITO)-coated glass substrate are also described herein.

## 2. Experimental

### 2.1. Materials

The novel triphenylamine-based diamine monomer **I** (mp = 245–248 °C) was prepared by the amination reaction of 4-aminotriphenylamine with 4-fluoronitrobenzene, followed by hydrazine Pd/C-catalytic reduction. The synthetic details and characterization data of **I** were reported in a separate paper [38]. As reported previously [31–33], the imide ring-preformed dicarboxylic acids, 1,4-bis(trimellitimidido)-2,5-dimethylbenzene (**II-2M**), 2,5-bis(trimellitimidido)toluene (**II-M**) and 1,4-bis(trimellitimidido)-2,5-dichlorobenzene (**II-2Cl**) was synthesized via the two-stage procedure that included ring-opening addition of 2,5-dimethyl-1,4-phenylenediamine, 2-methyl-1,4-phenylenediamine dihydrochloride and 2,5-dichloro-1,4-phenylenediamine, respectively, with two equivalent amount of trimellitic anhydride, followed by cyclodehydration to the

imidodicarboxylic acid by toluene–water azeotropic distillation. *N,N*-Dimethylacetamide (DMAc) (Tedia), *N,N*-dimethylformamide (DMF) (Acros), *N*-methyl-2-pyrrolidone (NMP) (Tedia), pyridine (Tedia), TPP (Acros) were also used as received. Commercially obtained anhydrous calcium chloride (CaCl<sub>2</sub>) was dried under vacuum at 180 °C for 8 h. 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 from commercial sources.

### 2.2. Polymer synthesis

The synthesis of **PAAI-2M** is used as an example to illustrate the general synthetic route. A mixture of 0.553 g (1.25 mmol) of diamine **I**, 0.606 g (1.25 mmol) of diimide-diacid **II-2M**, 0.3 g of calcium chloride, 0.9 mL of TPP, 1.2 mL of pyridine, 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 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; yield: 1.10 g (99%). The polymer that precipitated was collected by filtration, washed thoroughly with hot methanol, and dried at 150 °C for 15 h in vacuo. Precipitations from NMP into methanol were carried out twice for further purification. The inherent viscosity of the obtained **PAAI-2M** was 0.86 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C. The IR spectrum of **PAAI-2M** (film) exhibited characteristic amide absorption bands at 3300 (N–H stretching), 1665 cm<sup>-1</sup> (amide carbonyl), imide absorption bands at 1779 (asymmetrical C=O), 1724 (symmetrical C=O), 1358 (C–N), and 726 cm<sup>-1</sup> (imide ring deformation).

The other two PAAs (**PAAI-M** and **PAAI-2Cl**) were prepared by an analogous procedure.

### 2.3. Preparation of polymer films

A solution of polymer was made by dissolving about 0.7 g of the PAAs 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 70–100 μm in thickness and were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

## 3. Results and discussion

### 3.1. Polymer synthesis

Three new PAAs containing triphenylamine units both in the main-chain and side-chain were prepared from

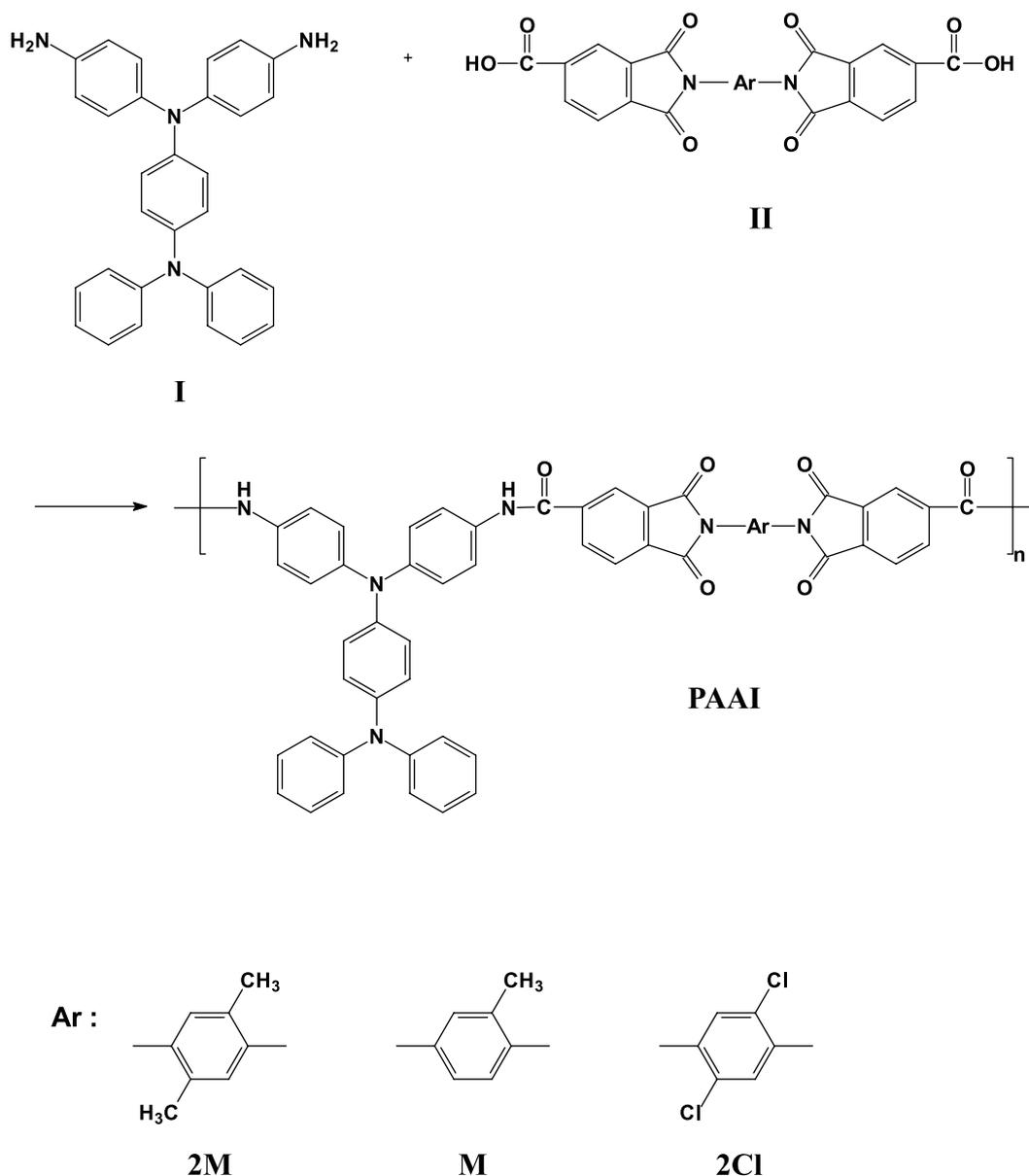
diamine **I** and three aromatic diimide–diacids by the direct polycondensation reaction using TPP and pyridine as condensing agents (Scheme 1). The polymerization proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. All the polymers precipitated in a tough fiber-like form when slowly pouring the resulting polymer solutions under stirring into methanol. The obtained PAAs had inherent viscosities in the range of 0.54–0.86 dL/g. IR and NMR spectroscopy confirmed the formation of PAAs. Fig. 1 shows a typical IR spectrum for **PAAI-2M**. It exhibited characteristic IR absorption bands of the amide group around 3300 (N–H stretching), 1665  $\text{cm}^{-1}$  (amide carbonyl), imide absorption bands at 1779 (asymmetrical C=O), 1724 (symmetrical C=O), 1358 (C–N), and 726  $\text{cm}^{-1}$  (imide ring deformation). Fig. 2 shows a typical set of  $^1\text{H}$

and  $^{13}\text{C}$  NMR spectra of **PAAI-2M** in  $\text{DMSO-}d_6$ , and all the peaks have been readily assigned to the hydrogen and carbon atoms of the recurring unit.

### 3.2. Polymer properties

#### 3.2.1. Basic characterization

As indicated by the WAXD patterns shown in Fig. 3, all the polymers were essentially amorphous. The solubility behavior of PAAs was tested qualitatively, and the results are presented in Table 1. All the PAAs were highly soluble in polar solvents such as NMP, DMAc and dimethyl sulfoxide (DMSO), and the enhanced solubility can be attributed to the introduction of bulky pendent triphenylamine group in the repeat unit. Thus, the excellent solubility



Scheme 1. Synthesis of poly(amine–amide–imide)s.

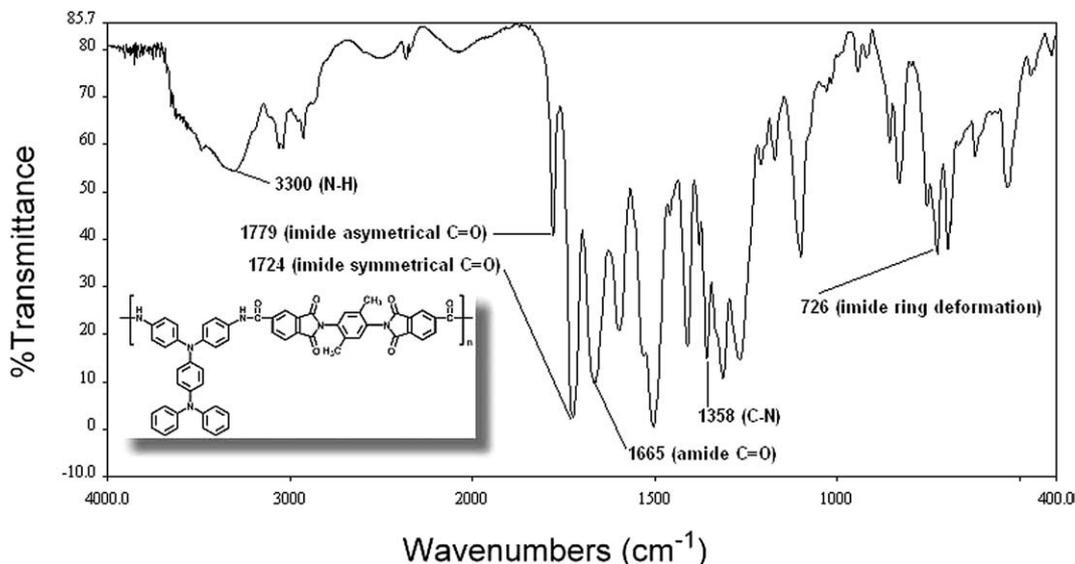


Fig. 1. The IR spectrum (film) of PAAI-2M.

Table 1  
Inherent viscosity and solubility of PAAIs

Polymer	$\eta$ inh <sup>a</sup> (dL/g)	Solubility <sup>b</sup>						
		NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF	Chloroform
PAAI-2M	0.86	+	+	±	+	–	+h	–
PAAI-M	0.66	+	+	±	+	–	+h	–
PAAI-2CI	0.54	+	+	+	+	±	+h	–

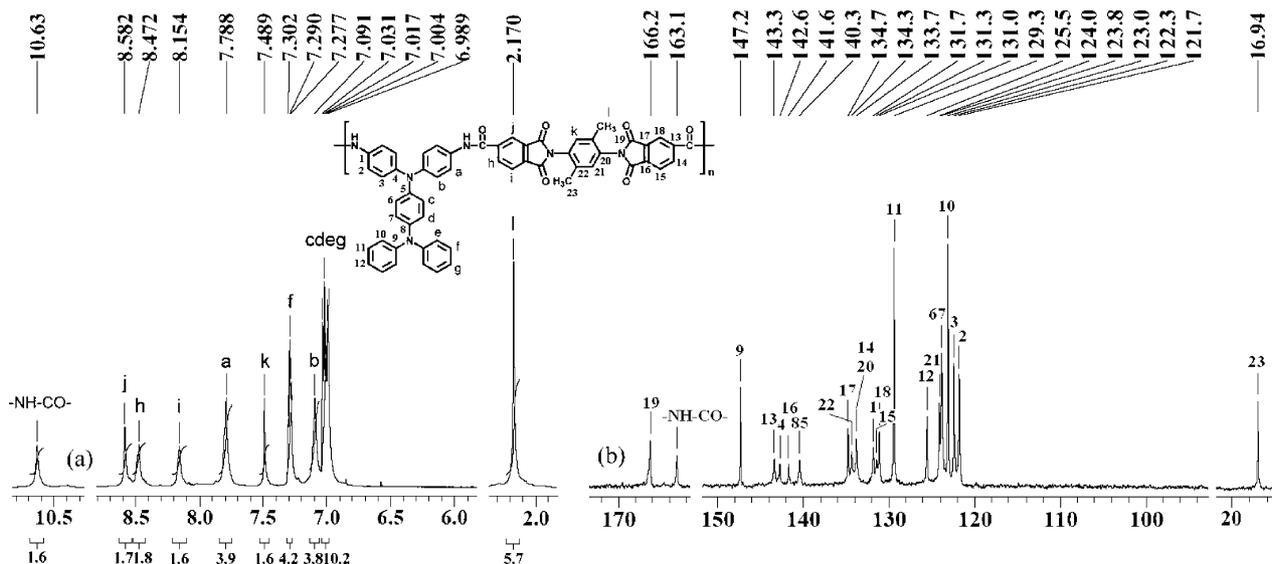
<sup>a</sup> Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.

<sup>b</sup> Solubility: +, soluble at room temperature; +h, soluble on heating; ±, partially soluble or swelling; –, insoluble even on heating.

makes these polymers as potential candidates for practical applications by spin- or dip-coating processes.

PAAI-2M and PAAI-M could afford flexible and tough films via solution casting. These films were subjected to tensile testing, and the results are given in Table 2. The

tensile strengths, elongations to break, and initial moduli of these films were in the ranges of 87–110 MPa, 9–11% and 1.8–2.3 GPa, respectively. The cast film of PAAI-2CI revealed some brittleness; thus, it was not subjected to the tensile test. TGA, DSC, and TMA were employed to

Fig. 2. (a) <sup>1</sup>H NMR and (b) <sup>13</sup>C NMR spectra of PAAI-2M in DMSO-*d*<sub>6</sub>.

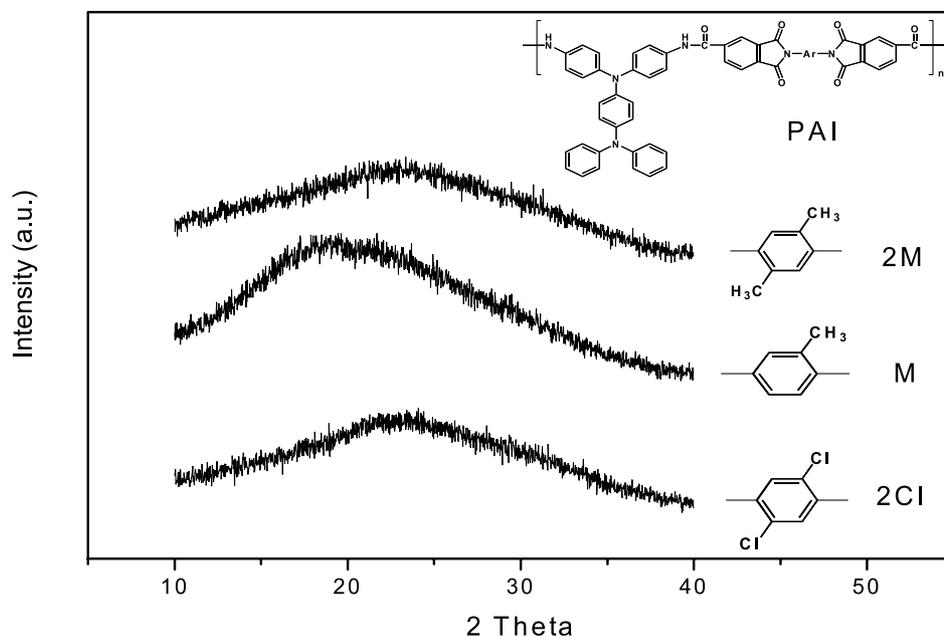


Fig. 3. WAXD patterns of PAAI films.

investigate the thermal properties of the PAAIs. The results are summarized in Table 3. The results of TGA analyses revealed that all the polymers exhibited good thermal stability with insignificant weight loss up to 400 °C in nitrogen. The 10% weight-loss temperatures of the polymer in nitrogen and air were recorded in the range of 522–544 and 525–538 °C, respectively. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere was more than 67% at 800 °C. The high char yields of these polymers can be ascribed to their high aromatic content. The  $T_g$ s of all the polymers could be easily measured in the DSC thermograms; they were observed in the range of 279–287 °C. All the polymers indicated no 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 softening temperatures ( $T_s$ ) 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 PAAI-2Cl is illustrated in Fig. 4. In all cases, the  $T_s$  values obtained by TMA are slightly lower than the  $T_g$  values measured by the DSC experiments (Table 4). These differences may be attributed to the different heating stories and the distinct natures of these two testing methods.

Table 2  
Mechanical properties of PAAI films

Polymer code	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (GPa)
PAAI-2M	110	9	2.3
PAAI-M	87	11	1.8

### 3.2.2. Optical and electrochemical properties

The optical and electrochemical properties of the PAAIs were investigated by UV–vis and photoluminescence spectroscopy and cyclic voltammetry. The results are summarized in Table 4. The solutions of these polymers in NMP exhibited strong UV–vis absorption bands at 315 nm, assignable to the  $\pi$ – $\pi^*$  transition resulting from the conjugation between the aromatic rings and nitrogen atoms. The polymer thin films were also measured for optical transparency using UV–vis spectroscopy. The cutoff wavelengths (absorption edge;  $\lambda_0$ ) read from the UV–vis transmittance spectra were recorded in the range of 608–647 nm are also indicated in Table 4. It revealed that most of the visible light were absorbed by these PAAIs as indicated by their high  $\lambda_0$  values and dark red brown color. The dark red brown color of these PAAI films is probably attributable to the formation of charge transfer complex between electron-donating triphenylamine unit and strongly electron-accepting trimellitimide unit. All the PAAIs did not revealed discernible PL peaks probably due to reabsorption caused by between-chain charge transfer.

The redox behavior of PAAIs was investigated by cyclic voltammetry conducted for the cast film on an ITO-coated glass substrate as working electrode in dry acetonitrile ( $\text{CH}_3\text{CN}$ ) containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere. The typical cyclic voltammograms for PAAI-2M was shown in Fig. 5. There are two reversible oxidation redox couples at  $E_{1/2} = 0.67$  and 1.08 V, respectively, for PAAI-2M in the oxidative scan. Because of the stability of the films and good adhesion between the polymer and ITO substrate, the PAAI-2M exhibited excellent reversibility of electrochromic characteristics by continuous five cyclic scans between 0.0 and 1.35 V,

Table 3  
Thermal properties of PAAIs

Polymer	$T_g$ (°C) <sup>a</sup>	$T_s$ (°C) <sup>b</sup>	$T_d$ at 5% weight loss (°C) <sup>c</sup>		$T_d$ 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>PAAI-2M</b>	279	260	495	483	522	525	70
<b>PAAI-M</b>	287	265	498	501	527	538	68
<b>PAAI-2Cl</b>	287	275	494	480	544	531	67

The polymer film samples were heated at 300 °C for 1 h prior to all the thermal analyses.

<sup>a</sup> Midpoint temperature of baseline shift on the DSC heating trace (rate 20 °C/min).

<sup>b</sup> Softening temperature measured by TMA with a constant applied load of 10 mN at a heating rate of 10 °C/min.

<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.

Table 4  
Optical and electrochemical properties for the PAAIs

Code	$\lambda_{\text{abs,max}}$ (nm) <sup>a</sup>	$\lambda_{\text{abs,onset}}$ (nm) <sup>a</sup>	$\lambda_{\text{PL}}$ (nm) <sup>b</sup>	$\lambda_0$ (nm) <sup>c</sup>	Oxidation (V) (vs. Ag/AgCl)		HOMO-LUMO gap <sup>d</sup> (eV)	HOMO <sup>e</sup> (eV)	LUMO <sup>f</sup> (eV)
					1st $E_{1/2}$ ( $E_{\text{onset}}$ )	2nd $E_{1/2}$			
<b>PAAI-2M</b>	315 (321)	397	–	610	0.67 (0.52)	1.08	3.12	4.94 (4.94)	1.82 (1.82)
<b>PAAI-M</b>	315 (316)	396	–	608	0.68 (0.53)	1.08	3.13	4.95 (4.95)	1.82 (1.82)
<b>PAAI-2Cl</b>	315 (316)	393	–	647	0.68 (0.54)	1.08	3.16	4.95 (4.96)	1.79 (1.80)

<sup>a</sup> From UV/vis absorption spectra measured in NMP solution (0.02 mg/mL) at room temperature. Values in parentheses are those measured in polymer films.

<sup>b</sup> PL spectra measured in NMP solution (5 mg/mL) at room temperature. No discernible PL peak was observed.

<sup>c</sup> The cutoff wavelengths ( $\lambda_0$ ) from the transmission UV/vis absorption spectra of polymer films.

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

<sup>e</sup> The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV). Values in parentheses are calculated from  $E_{\text{onset}}$ .

<sup>f</sup> LUMO = HOMO-gap. Values in parentheses are calculated from  $E_{\text{onset}}$ .

changing color from original pale brownish to green, and then to blue at electrode potentials over 0.67 and 1.08 V, respectively. The first electron removal for **PAAI-2M** is assumed to occur at the N atom on the main-chain triphenylamine segment, which is electron-richer than the

N atom on the side-chain triphenylamine unit. The energy of the HOMO and LUMO levels of the investigated PAAIs can be determined from the oxidation onset or half-wave potentials and the onset absorption wavelength, and the results are listed in Table 4. For example (Fig. 6), the

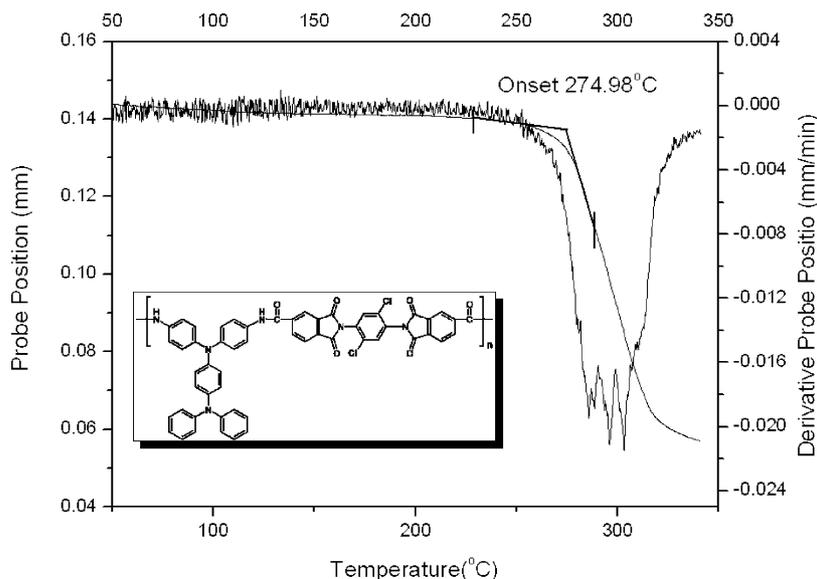


Fig. 4. TMA curve of **PAAI-2Cl** with a heating rate of 10 °C/min.

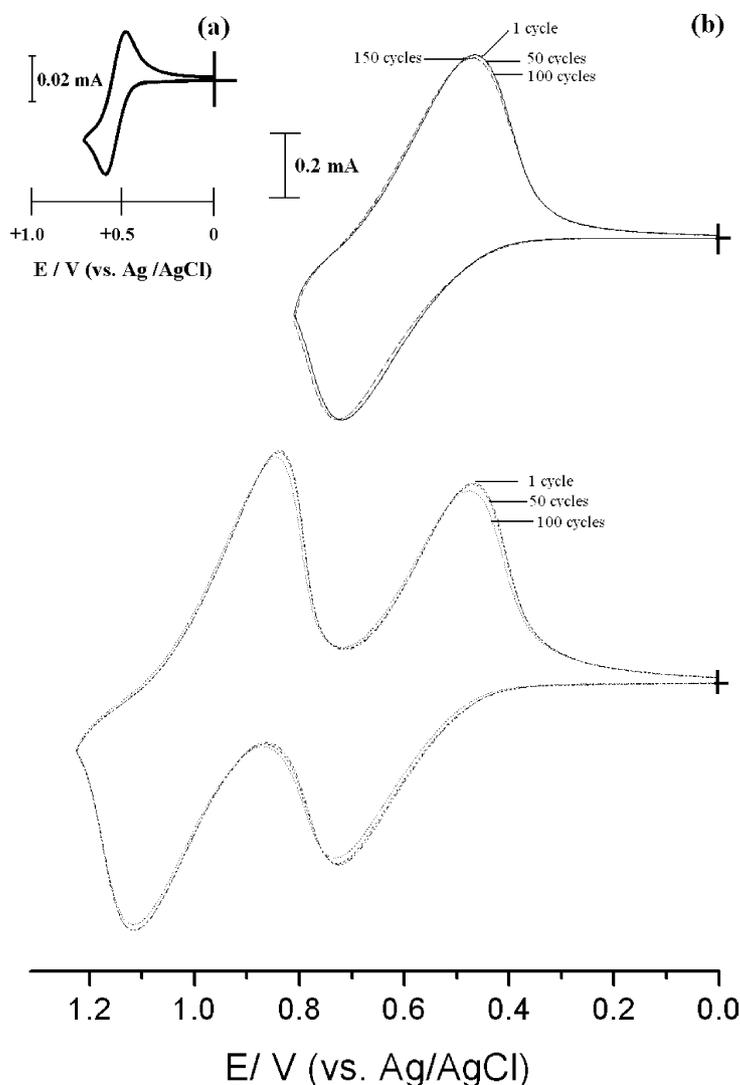


Fig. 5. Cyclic voltammograms of (a) ferrocene (b) **PAI-2M** film onto an indium-tin oxide (ITO)-coated glass substrate in  $\text{CH}_3\text{CN}$  containing 0.1 M TBAP. Scan rate = 0.1 V/s.

oxidation onset and half-wave potential for **PAI-2M** has been determined as 0.52 and 0.67 V, respectively, vs Ag/AgCl. The external ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox standard  $E_{\text{onset}}$  and  $E_{1/2}$  are 0.38 and 0.53 V, respectively, vs Ag/AgCl in  $\text{CH}_3\text{CN}$ . Assuming that the HOMO energy for the  $\text{Fc}/\text{Fc}^+$  standard is 4.80 eV with respect to the zero vacuum level, the HOMO energy for **PAI-2M** has been evaluated to be 4.94 eV.

### 3.2.3. Electrochromic behavior

Electrochromism of the thin films from the PAIs was examined by casting their polymer solutions onto an indium-tin oxide (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 cyclic voltammetry. The typical electrochromic

absorption spectra of **PAI-2M** are shown in Figs. 6 and 7. When the applied potentials increased positively from 0.58 to 0.85 V, the peak of characteristic absorbance at 321 nm, characteristic for **PAI-2M** decreased gradually while three new bands grew up at 421, 612 and 948 nm due to the first electron oxidation. The new spectrum was assigned as that of the cationic radical  $\text{PAI}^{\cdot+}$ . Meanwhile the film color turned into the green (as shown in Fig. 6). When a higher potential of 1.35 V was applied, the spectral change was shown as Fig. 7. The characteristic peaks for  $\text{PAI}^{\cdot+}$  in the first oxidation state disappeared and a new band grew up at 718 nm. The new spectrum was assigned as  $\text{PAI}^{2+}$  and the color of film became deep blue.

The color switching times were estimated by applying a potential step, and the absorbance profiles were followed (Figs. 8 and 9). The switching time was defined as the time that required for reach 90% of the full change in absorbance

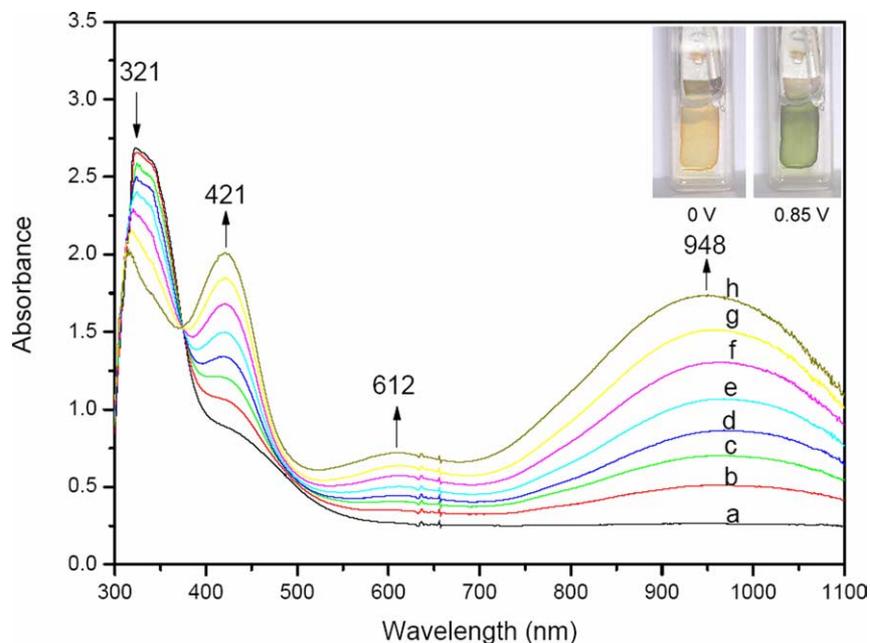


Fig. 6. Electrochromic behavior of **PAA-2M** thin film (in  $\text{CH}_3\text{CN}$  with 0.1 M TBAP as the supporting electrolyte) at (a) 0.0 (b) 0.58 (c) 0.61 (d) 0.64 (e) 0.67 (f) 0.70 (g) 0.76 (h) 0.85 V.

after switching potential. Thin films from **PAAI-2M** would require 3 s at 0.85 V for switching absorbance at 421, 612 and 948 nm and 2 s for bleaching. When the potential was set at 1.35 V, thin films of **PAAI-2M** would require almost 5 s for coloration at 718 nm and 2 s for bleaching. After over 100 cyclic scans (Fig. 5) or color switching times (Fig. 8), the polymer films still exhibited excellent stability of electrochromic characteristics. The electrochromic efficiency ( $\eta = \Delta A/Q$ ) and decay of the absorption changes to

100 cycles were calculated [39] and the results are summarized in Table 5.

#### 4. Conclusions

Three poly(amine–amide–imide)s have been successfully prepared from the novel diamine, *N,N*-bis(4-aminophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine, and three

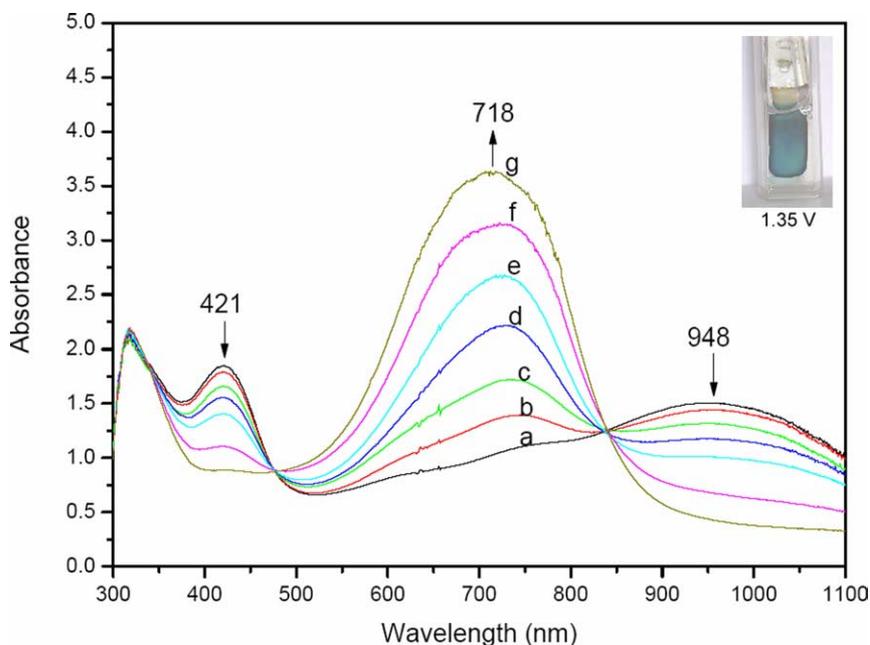


Fig. 7. Electrochromic behavior of **PAAI-2M** thin film (in  $\text{CH}_3\text{CN}$  with 0.1 M TBAP as the supporting electrolyte) at (a) 0.98 (b) 1.00 (c) 1.03 (d) 1.08 (e) 1.13 (f) 1.18 (g) 1.35 V.

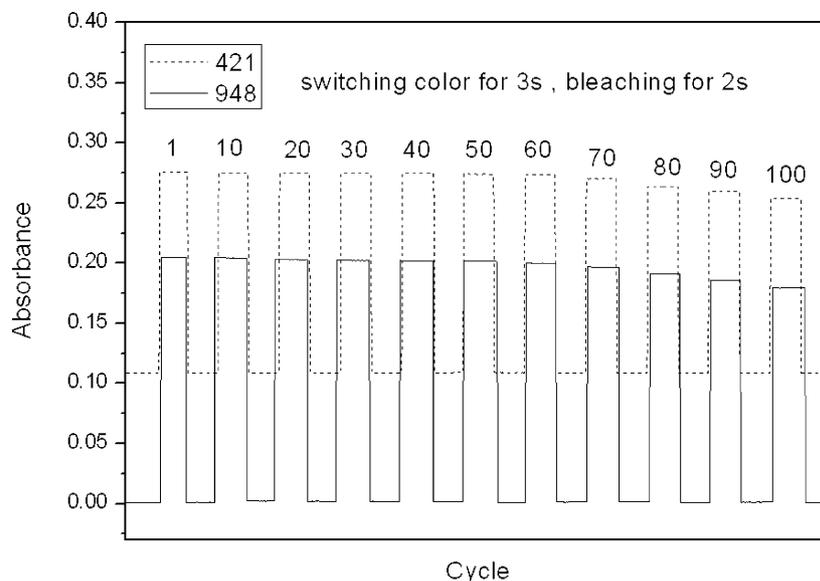


Fig. 8. Potential step absorptometry of **PAAl-2M** (in  $\text{CH}_3\text{CN}$  with 0.1 M TBAP as the supporting electrolyte) by applying a potential step ( $0 \rightleftharpoons 0.85$  V).

Table 5  
Optical and electrochemical data collected for coloration efficiency measurements

Cycle	$\Delta A$	$Q$ ( $\text{mC cm}^{-2}$ )	$\eta$ ( $\text{cm}^2 \text{C}^{-1}$ )	Decay (%)
1	0.202	0.664	304	0
10	0.202	0.662	305	0
20	0.202	0.663	305	0
30	0.202	0.662	305	0
40	0.201	0.662	304	0
50	0.202	0.661	305	0
60	0.200	0.661	302	0.5
70	0.196	0.664	295	3.0
80	0.190	0.663	287	5.6
90	0.186	0.664	280	7.9
100	0.180	0.664	272	10.5

aromatic diimide-diacids via the direct phosphorylation polycondensation. Because of the presence of the bulky inherent electron-donating nature of triphenylamine unit, the HOMO energy levels could be decreased, and all the polymers were amorphous, had 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, good thermal stability, and mechanical properties, all the obtained poly(amine–amide–imide)s were electrochemically active, with very stable electrochromic characteristics. Thus, these triphenylamine-containing poly(amine–amide–imide)s may be applied in OLED as hole-transporting layers and electrochromic materials due to their proper HOMO values, excellent electrochemical and thermal stability.

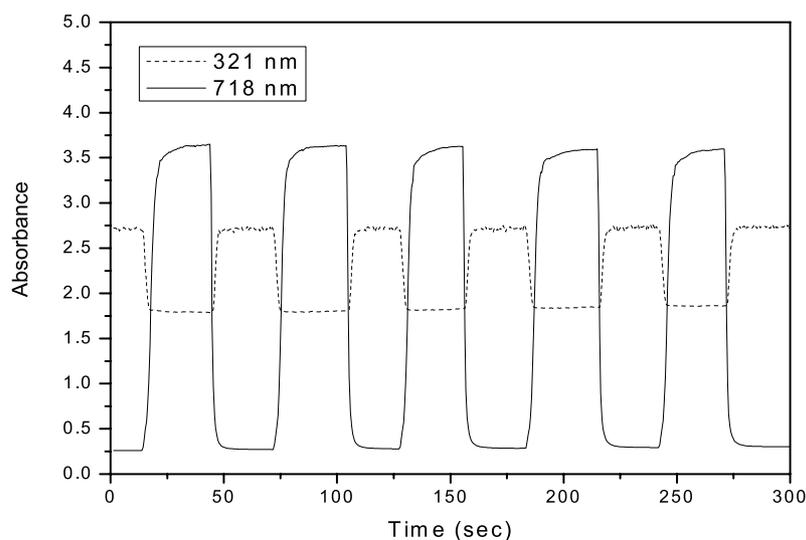


Fig. 9. Potential step absorptometry of **PAAl-2M** (in  $\text{CH}_3\text{CN}$  with 0.1 M TBAP as the supporting electrolyte) by applying a potential step ( $0 \rightleftharpoons 1.35$  V).

## Acknowledgements

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

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