

Electrochromic properties of novel strictly alternating poly(amine–amide–imide)s with electroactive triphenylamine moieties

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Abstract

A series of novel triphenylamine-containing aromatic poly(amine–amide–imide)s (PAAIs) were prepared by the phosphorylation polyamidation reactions from the diamine, *N,N'*-bis(4-aminophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine, and various imide ring-preformed dicarboxylic acids. All the PAAIs were amorphous, had good solubility in many polar aprotic solvents, and exhibited excellent thin film forming capability with good mechanical properties. They displayed relatively high glass-transition temperatures (220–306 °C) and good thermal stability, with 10% weight-loss temperatures in excess of 522 °C in air or nitrogen and char yields at 800 °C in nitrogen higher than 66%. 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 0.63 and 1.01 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. © 2006 Elsevier Ltd. All rights reserved.

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

1. Introduction

Triarylamine- and triphenylamine-based derivatives 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

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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]. However, little attention has been paid to the synthesis and electrochromic property of aromatic polyamides and polyimides containing triphenylamine moieties.

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 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 polyimides and polyamides bearing triphenylamine units both in the main chain and side chain based on *N,N*-bis(4-aminophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine [34,35]. 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 triphenylamine-containing high-performance polymers, this article describes the electrochemical and electrochromic behaviors of a series of novel poly(amine–amide–imide)s based on the diamine, *N,N'*-bis(4-aminophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine, and various imide ring-

preformed dicarboxylic acids. The electrochemical and electrochromic, properties of these polymers prepared by casting solution onto an indium–tin oxide (ITO)-coated glass substrate are described herein.

2. Experimental

2.1. Materials

The novel triphenylamine-based diamine monomer, *N,N'*-bis(4-aminophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine, (mp = 261–262 °C) was prepared by the amination reaction of *N,N'*-diphenyl-1,4-phenylenediamine with 4-fluoronitrobenzene, followed by hydrazine Pd/C-catalytic reduction [36]. The synthesis and characterization data of the strictly alternating poly(amine–amide–imide)s were reported in a separate paper [37]. As reported previously [31–33], the imide ring-preformed dicarboxylic acids, 1,4-bis(trimellitimido)-2,5-dimethylbenzene, 2,5-bis(trimellitimido)toluene and 1,4-bis(trimellitimido)-2,5-dichlorobenzene were 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-pyrrolidinone (NMP) (Tedia), pyridine (Tedia), TPP (Acros) were also used as received. Commercially obtained anhydrous calcium chloride (CaCl₂) 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. Preparation of polymer films

A solution of polymer was made by dissolving about 0.7 g of the PAAI 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 transmission UV–visible absorption analyses.

2.3. Measurements

Infrared spectra were recorded on a PerkinElmer RXI FT-IR spectrometer. The inherent viscosities were determined at 0.5 g/dL concentration using an 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), using graphite-monochromatized Cu-K α radiation. Ultraviolet-visible (UV-vis) spectra of the polymer films were recorded on a Varian Cary 50 Probe spectrometer. Thermogravimetric analysis (TGA) was made on a PerkinElmer Pyris 1 TGA. 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. DSC analyses were performed on a PerkinElmer Pyris Diamond DSC at a scan rate of 20 °C/min in flowing nitrogen (20 cm³/min). Electrochemistry was performed with a CHI 611B electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry was performed with the use of a three-electrode cell in which ITO (polymer films area about 0.7 cm \times 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 Ag/AgCl, KCl (sat.) 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 were measured with a HP 8453 UV-visible spectrophotometer.

3. Results and discussion

3.1. Polymer synthesis

A series of novel PAAIs containing triphenylamine units in the main-chain were prepared from the diamine and various 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 PAAIs had inherent viscos-

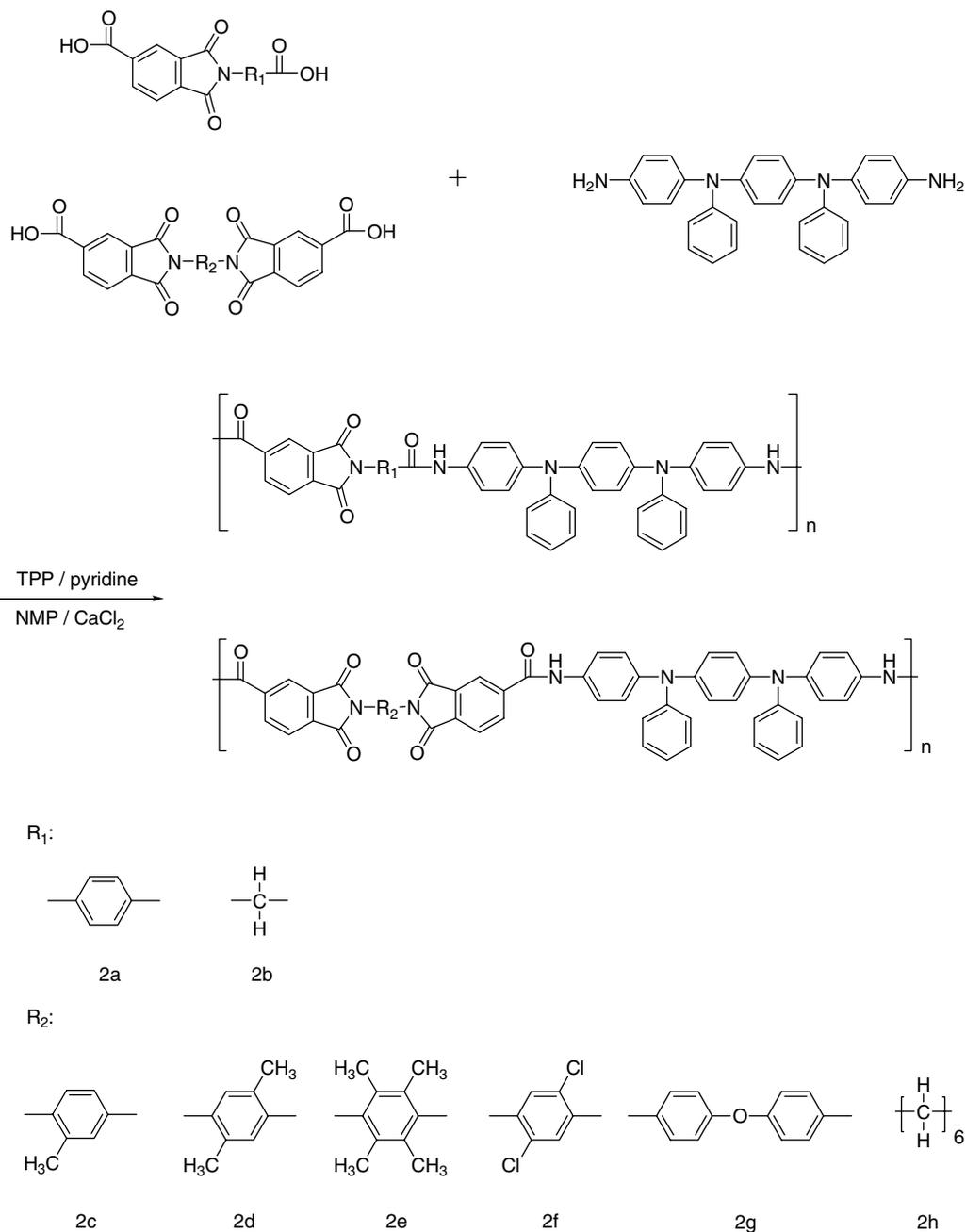
ities in the range of 0.37–0.80 dL/g. IR and NMR spectroscopy were used to confirm the formation of PAAIs. It exhibited characteristic IR absorption bands of the amide group around 3300 (N–H stretching), 1665 cm⁻¹ (amide carbonyl), imide absorption bands at 1779 (asymmetrical C=O), 1724 (symmetrical C=O), 1358 (C–N), and 726 cm⁻¹ (imide ring deformation). ¹H and ¹³C NMR spectra of polymers in DMSO-*d*₆, showed the exact peaks and have been readily assigned to the hydrogen and carbon atoms of the recurring unit.

3.2. Polymer properties

3.2.1. Optical and electrochemical properties

The optical and electrochemical properties of the PAAIs were investigated by UV-vis and cyclic voltammetry. The results are summarized in Table 1. The solutions of these polymers in NMP exhibited strong UV-vis absorption bands at 315 nm, assignable to the π - π^* 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; λ_0) read from the UV-visible transmittance spectra as shown in Fig. 1 were recorded in the range of 588–621 nm are also indicated in Table 1. It revealed that most of the visible light were absorbed by these PAAIs as indicated by their high λ_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 (CH₃CN) containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere. The typical cyclic voltammograms for **2a** and **2g** are shown in Fig. 2. There are two reversible oxidation redox couples at $E_{1/2}$ = 0.65 and 1.02 V, respectively, for **2a** in the oxidative scan. Because of the stability of the films and good adhesion between the polymer and ITO substrate, the polymer exhibited excellent reversibility of electrochromic characteristics by continuous ten cyclic scans between 0.0 to 1.35 V, changing color from original pale brownish to green, and then to blue at electrode potentials over 0.65 and



Scheme 1.

1.02 V, respectively. 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 1. For example (Fig. 2), the oxidation half-wave potential for 2a has been determined as 0.65 V vs. Ag/AgCl. The external ferrocene/ferrocenium (Fc/Fc⁺) redox standard $E_{1/2}$ is

0.44 V vs. Ag/AgCl in CH₃CN. Assuming that the HOMO energy for the Fc/Fc⁺ standard is 4.80 eV with respect to the zero vacuum level, the HOMO energy for 2a has been evaluated to be 5.01 eV.

3.2.2. Electrochromic behavior

Electrochromism of the thin films from the PAAIs was examined by casting their polymer solutions onto

Table 1
Optical and electrochemical properties for the aromatic poly(amine–imide–amide)s

Index	$\lambda_{\text{abs,max}}$ (nm) ^a	$\lambda_{\text{abs,onset}}$ (nm) ^a	λ_0 (nm) ^b	Oxidation (V) (vs. Ag / AgCl)		HOMO–LUMO Gap ^c (eV)	HOMO ^d (eV)	LUMO ^e (eV)
				First	Second			
2a	327 (321)	399 (420)	600	0.65	1.02	2.95	5.01	2.06
2b	325 (322)	387 (397)	596	0.65	1.01	3.12	5.01	1.89
2c	315 (318)	394 (419)	620	0.63	1.01	2.96	4.99	2.03
2d	315 (316)	397 (405)	619	0.63	1.01	3.06	4.99	1.93
2e	316 (317)	394 (406)	617	0.62	1.01	3.05	4.98	1.93
2f	313 (317)	403 (408)	620	0.63	1.01	3.04	4.99	1.95
2g	315 (315)	400 (403)	588	0.61	1.00	3.08	4.97	1.89
2h	315 (317)	392 (399)	621	0.68	1.00	3.11	5.04	1.93

^a UV/vis absorption measurements in NMP (0.02 mg/ml) at room temperature, values in parentheses are polymer thin film.

^b The cutoff wavelengths (λ_0) from the transmission UV/vis absorption spectra of polymer films.

^c The data were calculated from polymer films by the equation: $\text{gap} = 1240/\lambda_{\text{onset}}$.

^d The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).

^e LUMO = HOMO – gap.

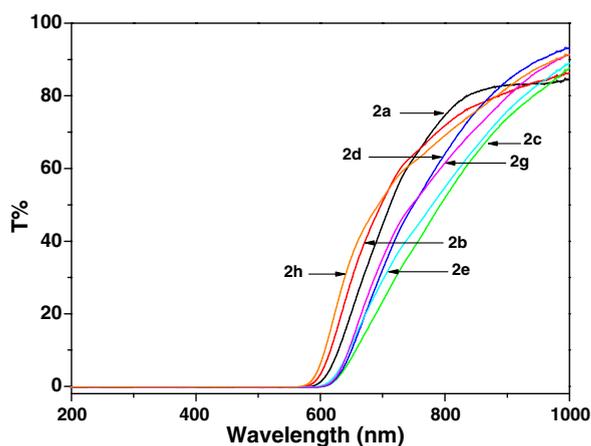


Fig. 1. Transmission UV–visible absorption spectra of some poly(amine–imide–amide)s film (thickness: 75–100 μm).

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 2a are shown in Figs. 3 and 5.

When the applied potentials increased positively from 0.56 to 0.86 V, the peak of characteristic absorbance at 319 nm for 2a decreased gradually while three new bands grew up at 422, 593 and 948 nm due to the first electron oxidation. The new spectrum was assigned as that of the cationic radical $\text{PAAI}^{\cdot+}$. Meanwhile the film color turned into the green (as shown in Fig. 3). When a higher potential of 1.24 V was applied, the spectral change was shown as Fig. 5. The characteristic peaks for $\text{PAAI}^{\cdot+}$ in the first oxidation state disappeared and a new band grew up at 787 nm. The new spectrum was assigned as PAAI^{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. 4 and 6). The switching time was defined as the time that required for reach 90% of the full change in absorbance after switching potential [38]. Thin films from 2a would require 4 s at 0.86 V for switching absorbance at 422, 593 and 948 nm and 3 s for bleaching. When the potential was set at 1.24 V, thin films of 2a would require almost 4 s for coloration at 787 nm and 4 s for bleaching. After over 10 cyclic scans or color switching times, the polymer films still exhibited excellent stability of electrochromic

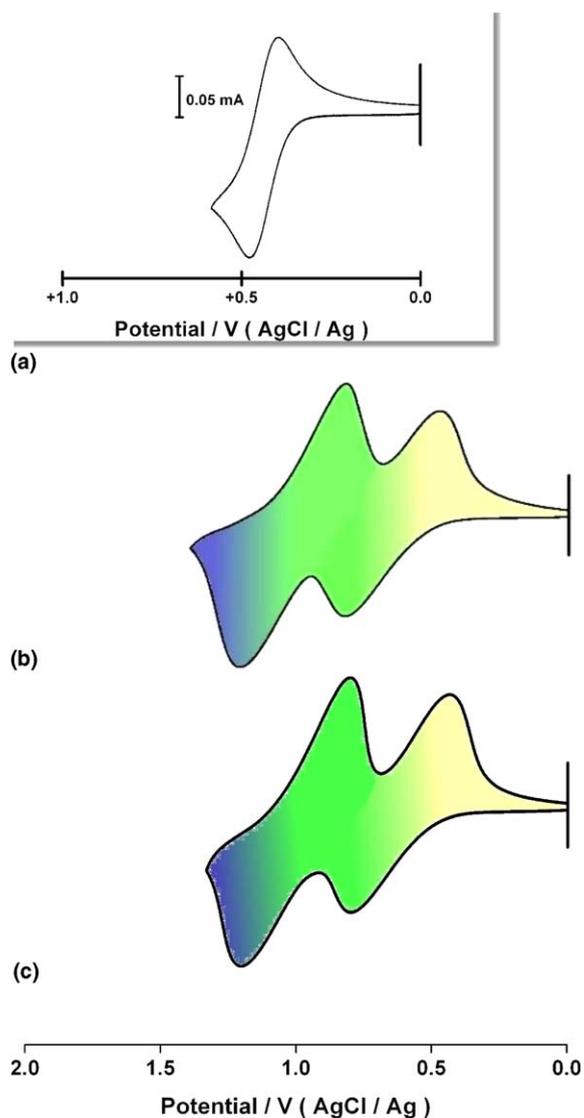


Fig. 2. Cyclic voltammograms of (a) ferrocene (b) poly(amine-imide-imide) **2a** (c) poly(amine-imide-imide)s **2g** film onto an indium-tin oxide (ITO)-coated glass substrate in CH_3CN containing 0.1 M TBAP. Scan rate = 0.1 V/s.

characteristics. Thus, the strictly alternating triphenylamine-based poly(amine-imide-imide)s derived from the diamine having triphenylamine unit and diimide-diacids showed better solubility and lower oxidation potentials than the corresponding poly(amine-imide) homopolymers with the same electrochromic mechanism.

4. Conclusions

A series of novel triphenylamine-containing poly(amine-imide-imide)s have been prepared

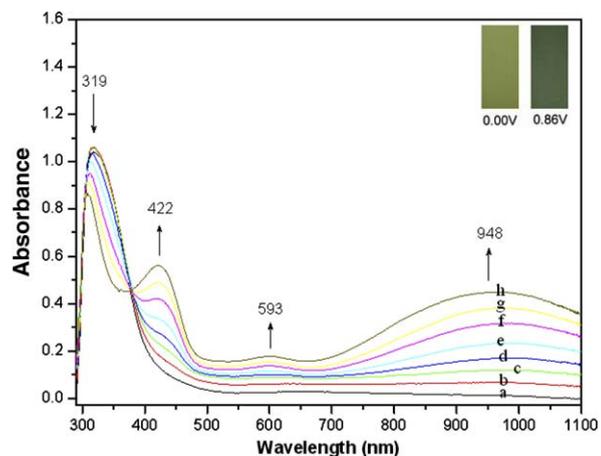


Fig. 3. Electrochromic behavior of poly(amine-imide-imide) **2a** thin film (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0, (b) 0.56, (c) 0.62, (d) 0.68, (e) 0.74, (f) 0.80 and (g) 0.86 V.

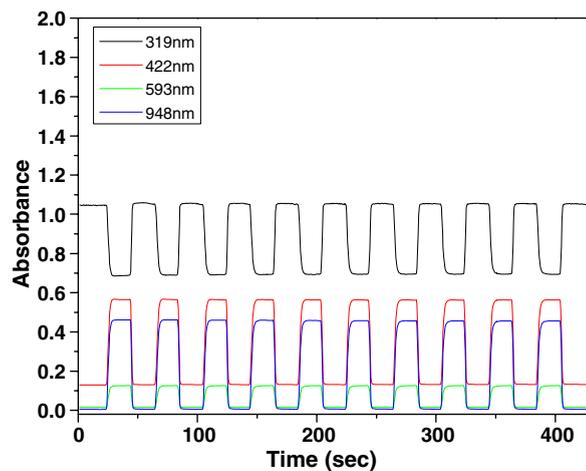


Fig. 4. Potential step absorptometry of poly(amine-imide-imide) **2a** (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) by applying a potential step (0 V \leftrightarrow 0.86 V).

from *N,N'*-bis(4-aminophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine and various diimide-diacids via the direct phosphorylation polycondensation. Because of the presence of the bulky inherent electron-donating nature of triphenylamine unit, the HOMO energy values could be decreased, and all the polymers were amorphous and exhibited excellent thin-film-forming ability in many polar aprotic solvents. In addition to moderately high T_g or T_s values, good thermal stability, and mechanical properties, all the obtained poly(amine-imide-imide)s were electrochemically active, with very stable elec-

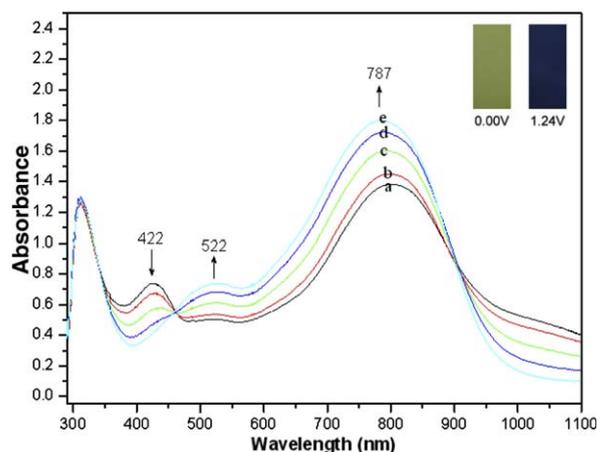


Fig. 5. Electrochromic behavior of poly(amine-imide-amide) **2a** thin film (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 1.00, (b) 1.06, (c) 1.12, (d) 1.18 and (e) 1.24 V.

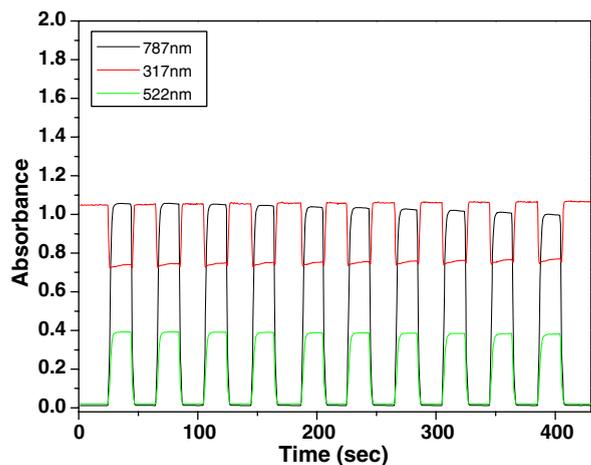


Fig. 6. Potential step absorptometry of poly(amine-imide-amide) **2a** (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) by applying a potential step (0 V \rightleftharpoons 1.24 V).

trochromic characteristics. Thus, these triphenylamine-containing poly(amine-imide-amide)s may be applied in OLED as hole-transporting layers and electrochromic materials due to their proper HOMO values, excellent electrochemical and thermal stability.

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