

# Electrochemical behavior of $N,N,N',N'$ -tetraphenyl-1,4-phenylenediamine moiety on novel aromatic polyamides and their electrochromic properties

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## Abstract

A series of novel aromatic polyamides with  $N,N,N',N'$ -tetraphenyl-1,4-phenylenediamine units were prepared from the diamine,  $N,N'$ -bis(4-aminophenyl)- $N,N'$ -diphenyl-1,4-phenylenediamine, and various aromatic dicarboxylic acids via the direct phosphorylation polycondensation. All the polyamides were amorphous, readily soluble in many organic solvents and could be solution cast into transparent, tough, and flexible films with good mechanical properties. They had useful levels of thermal stability associated with relatively high glass-transition temperatures (257–287 °C). These polymers exhibited strong UV–vis absorption bands with a maximum at 320–336 nm in NMP solution. The hole-transporting and electrochromic properties are examined by electrochemical and spectroelectrochemical methods. Cyclic voltammograms (CV) of these films prepared by casting polymer solution onto an indium-tin oxide (ITO)-coated glass substrate exhibited two reversible oxidation redox couples at potentials 0.61–0.64 and 0.99–1.07 V, respectively, vs Ag/AgCl in acetonitrile solution. All obtained polyamides revealed excellent stability of electrochromic characteristics, changing color from original pale yellowish to green, and then to blue at electrode potentials 0.65 and 1.10 V, respectively.

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**Keywords:** Aromatic polyamides;  $N,N,N',N'$ -Tetraphenyl-1,4-phenylenediamine; Triphenylamine; Redox polymers; Electrochromic polymers

## 1. Introduction

Triarylamine- or 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-phenylenediamine are of importance for technological applications [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 because of the promising commercial advantages over low molecular weight counterparts [8]. One of the perceived benefits 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 polyamides are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties. However, rigidity of the backbone and strong hydrogen bonding results in high melting or glass-transition temperatures ( $T_g$ 's) and limited solubility in most organic solvents [20–21]. These properties make them generally intractable or difficult to process, thus restricting their applications. To overcome such a difficulty, polymer-structure modification becomes necessary. Recently, we have reported the synthesis of soluble aromatic polyamides bearing triphenylamine units in the main chain based on  $N,N'$ -bis(4-aminophenyl)- $N,N'$ -diphenyl-1,4-phenylenediamine [22]. Because of the incorporation of bulky, three-dimensional

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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 functional properties of the triphenylamine-containing high-performance polymers, this article describes the electrochemical and electrochromic behaviors of the novel polyamides based on the diamine, *N,N'*-bis(4-aminophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine. 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

*N,N'*-Bis(4-aminophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine was prepared by the condensation of 4-fluoronitrobenzene with *N,N'*-diphenyl-1,4-phenylenediamine in a dipolar solvent in the presence of a base, followed by hydrazine Pd/C-catalytic reduction [22]. The crude product was purified by recrystallization from toluene to give white-beige crystals. The synthesis and characterization data of the strictly alternating polyamides were reported in a separate paper [22]. *N,N'*-Diphenyl-1,4-phenylenediamine [from Tokyo Chemical Industry (TCI)], 4-fluoronitrobenzene (from TCI), and 10% Pd/C (from Lancaster or Fluka) were used without further purification.

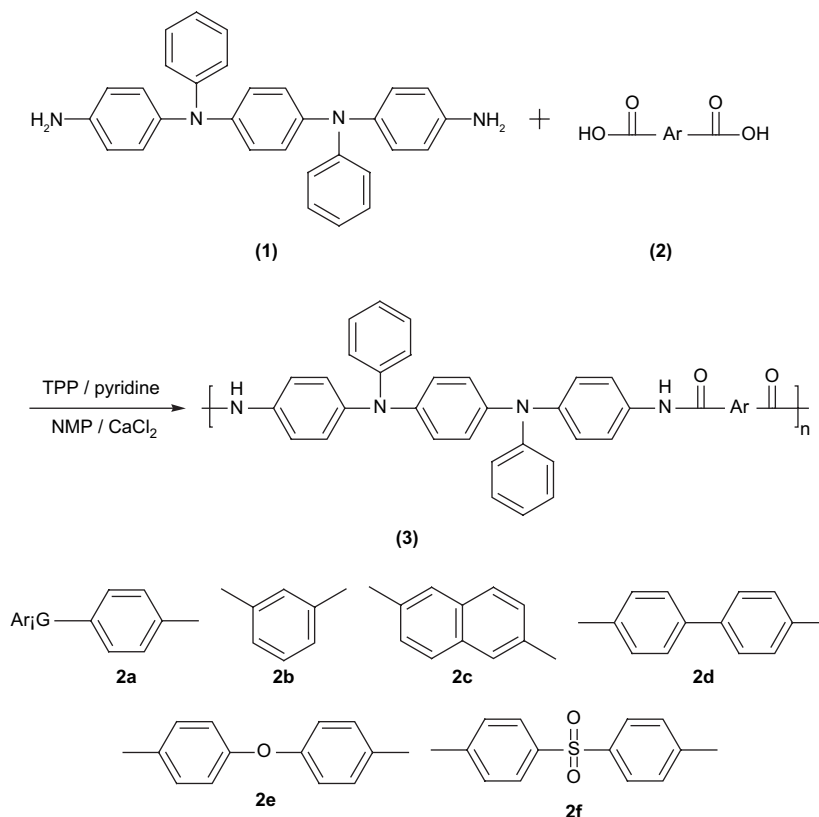
Commercially available aromatic dicarboxylic acids such as terephthalic acid (**2a**) (TCI), isophthalic acid (**2b**) (TCI), 2,6-naphthalenedicarboxylic acid (**2c**) (TCI), 4,4'-biphenyldicarboxylic acid (**2d**) (TCI), 4,4'-oxydibenzoic acid (**2e**) (TCI), and 4,4'-sulfonyldibenzoic acid (**2f**) (New Japan Chemical Co.) were used as received.

### 2.2. Preparation of polymer films

Typical procedure for the synthesis of triphenylamine-containing polyamide **3a** is as follows. A mixture of 0.553 g (1.25 mmol) of diamine **1**, 0.208 g (1.25 mmol) of terephthalic acid **2a**, 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: 0.711 g (99%). The inherent viscosity of the obtained polyamide **3a** was 0.54 dL/g measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30 °C (Scheme 1).

### 2.3. Measurements

IR spectra were recorded with a Horiba FT-720 Fourier transform infrared spectrometer. Elemental analyses were performed by a Perkin–Elmer model 2400 CHN analyzer. <sup>1</sup>H and



Scheme 1.

$^{13}\text{C}$  NMR spectra were measured on a JEOL EX 400 spectrometer with perdeuteriodimethyl sulfoxide ( $\text{DMSO-}d_6$ ) as the solvent and tetramethylsilane as the internal reference. The inherent viscosities were determined at a concentration of 0.5 g/dL in concentrated sulfuric acid using a Cannon–Fenske viscometer at 30 °C. Thermogravimetric analysis (TGA) was conducted with a Perkin–Elmer Pyris 1 TGA. Experiments were carried out with 3–5-mg samples heated in flowing nitrogen or air (30  $\text{cm}^3/\text{min}$ ) at a heating rate of 20 °C/min. DSC analyses were performed on a Perkin–Elmer Pyris 1 DSC in flowing nitrogen (20  $\text{cm}^3/\text{min}$ ) at a heating rate of 20 °C/min. Thermomechanical analysis (TMA) was conducted with a Perkin–Elmer TMA 7 at a scan rate of 10 °C/min with a penetration probe of 1.0 mm diameter under an applied constant load of 10 mN. Wide-angle X-ray diffractograms were obtained on a Siemens Kristalloflex D5000 X-ray diffractometer with nickel-filtered  $\text{Cu K}_\alpha$  radiation (40 kV, 15 mA), and the scanning rate was 2°/min. Measurements were performed with film specimens of about 0.1 mm in thickness. 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  $\text{cm} \times 0.5 \text{ cm}$ ) 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  $\text{Ag}/\text{AgCl}$ ,  $\text{KCl}$  (sat.) reference electrode. The spectroelectrochemical cell composed of a 1 cm cuvette, ITO as a working electrode, a platinum wire as an auxiliary electrode, and a  $\text{Ag}/\text{AgCl}$  reference electrode. Absorption spectra were measured with an HP 8453 UV–visible spectrophotometer.

### 3. Results and discussion

#### 3.1. Polymer synthesis

A series of novel polyamides containing  $N,N,N',N'$ -tetraphenyl-1,4-phenylenediamine units in the main chain were prepared from the diamine (**1**) and various 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 polyamides had inherent viscosities in the range of 0.43–0.73 dL/g. The IR spectra of the polymers, which showed characteristic amide absorptions at 3400–3300 and 1650  $\text{cm}^{-1}$ , supported the formation of the polyamides. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of polymers in  $\text{DMSO-}d_6$ , 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 polyamides were investigated by UV–vis and cyclic voltammetry. These polymers exhibited strong UV–vis absorption bands at 320–339 nm in NMP solution, assignable to the  $\pi$ – $\pi^*$  transition resulting from the conjugation between the aromatic rings and nitrogen atoms. The results are summarized in Table 1. The cutoff wavelengths (absorption edge;  $\lambda_0$ ) read from the UV–vis transmittance spectra of polymer films (thickness 10–20  $\mu\text{m}$ ) as shown in Fig. 1 were recorded in the range of 402–459 nm and are also summarized in Table 1. It revealed that some of the visible light was absorbed by these polyamides as indicated by their high  $\lambda_0$  values and brown color. The brown color of these polyamide films is probably attributable to the formation of charge transfer complex between electron-donating triphenylamine unit and electron-accepting diacids unit. All the polyamides did not reveal the discernible PL peaks probably due to reabsorption caused by between-chain charge transfer. The redox behavior of polyamides 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 polyamide **3f** are shown in

Table 1  
Optical and electrochemical properties for the aromatic polyamides

Index	$\lambda_{\text{abs, max}}$ (nm) <sup>a</sup>	$\lambda_{\text{abs, onset}}$ (nm) <sup>a</sup>	$\lambda_0$ (nm) <sup>b</sup>	Oxidation (V) (vs $\text{Ag}/\text{AgCl}$ )		HOMO–LUMO gap <sup>c</sup> (eV)	HOMO <sup>d</sup> (eV)	LUMO <sup>e</sup> (eV)
				First	Second			
<b>3a</b>	339 (332)	460 (443)	430	0.63	1.00	2.69	4.96	2.27
<b>3b</b>	339 (335)	438 (405)	411	0.61	1.07	2.83	4.94	2.11
<b>3c</b>	320 (320)	470 (430)	431	0.61	0.99	2.64	4.94	2.30
<b>3d</b>	321 (305)	456 (420)	436	0.62	0.99	2.72	4.95	2.23
<b>3e</b>	343 (336)	419 (409)	402	0.64	1.00	2.96	4.97	2.01
<b>3f</b>	338 (325)	470 (432)	459	0.62	1.01	2.64	4.95	2.31

<sup>a</sup> UV–vis absorption spectra of these films prepared by casting polymer solution onto an indium–tin oxide (ITO)-coated glass substrate. Values in parentheses are polymer solutions in NMP.

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

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

<sup>d</sup> The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).

<sup>e</sup>  $\text{LUMO} = \text{HOMO} - \text{gap}$ .

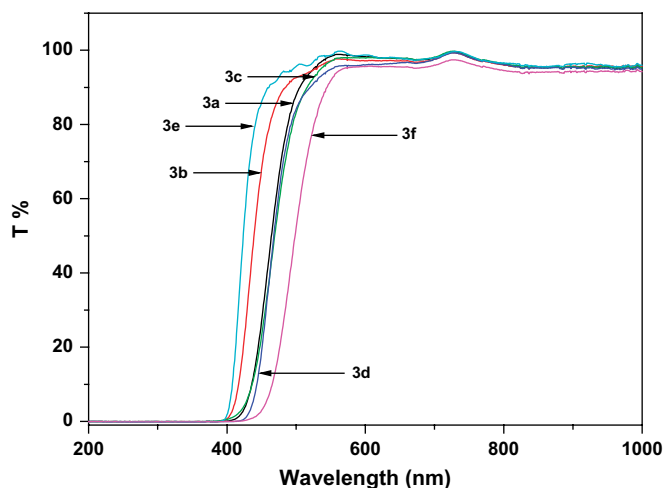


Fig. 1. Transmission UV-vis absorption spectra of some polyamides film (thickness: 10–20  $\mu\text{m}$ ).

Fig. 2. There are two reversible oxidation redox couples at  $E_{1/2} = 0.62$  and 1.01 V, respectively, in the oxidative scan. The polyamide **3f** exhibited excellent reversibility of electrochromic characteristics by continuous 10 cyclic scans between 0.0 and 1.30 V, changing color from original pale yellowish to green, and then to blue at electrode potentials over 0.65 and 1.03 V, respectively. The energy of the HOMO and LUMO levels of the investigated polyamides can be determined

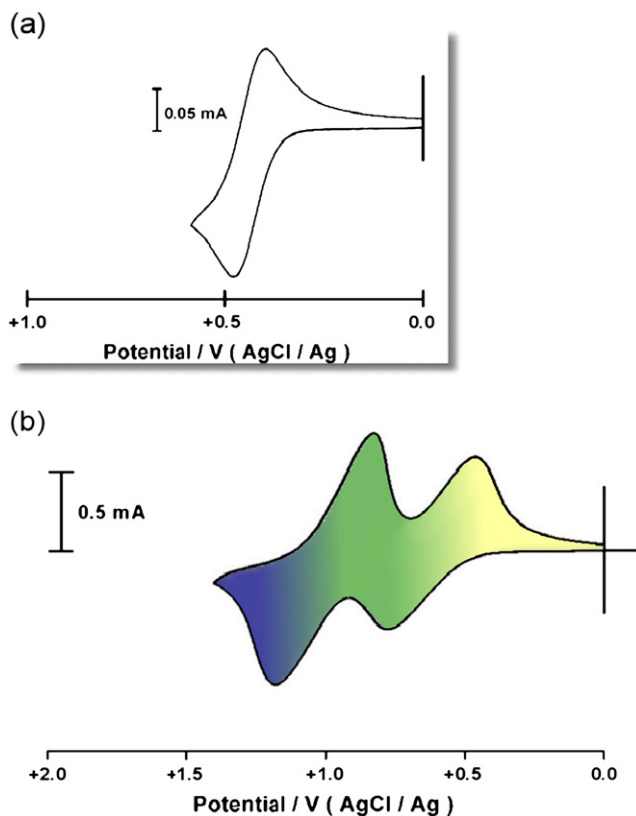


Fig. 2. Cyclic voltammograms of (a) ferrocene and (b) polyamide **3f** film onto an indium-tin oxide (ITO)-coated glass substrate in  $\text{CH}_3\text{CN}$  containing 0.1 M TBAP. Scan rate = 0.1 V/s.

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 **3f** has been determined as 0.62 V vs Ag/AgCl. The external ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox standard  $E_{1/2}$  is 0.47 V 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 **3f** has been evaluated to be 4.95 eV.

### 3.2.2. Electrochromic behavior

Electrochromism of the thin films from the polyamides 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 first and second electrochromic absorption spectra of polyamide **3f** are shown in Figs. 3 and 4, respectively. When the applied potentials increased positively from 0.54 to 0.90 V, the peak of characteristic absorbance at 329 nm, characteristic for polyamide **3f** decreased gradually while the two new bands grew up at 424 and 956 nm due to the first electron oxidation. When the potentials were adjusted to more positive values, corresponding to the second electron oxidation, the spectral change was shown in Fig. 4. The characteristic peaks for poly(amine–amide) $^{+}$  disappeared and new bands grew up at 528 and 787 nm. The new spectrum was assigned as poly(amine–amide) $^{2+}$  and the color of film **3f** became deep blue. The color switching times were estimated by applying a potential step, and the absorbance profiles were followed (Figs. 5 and 6). The switching time was defined as the time that is required to reach 90% of the full change in absorbance after switching potential. Thin films from polyamide **3f** would require 2 s at 0.90 V for switching absorbance at 424 and 956 nm and 1 s for bleaching. When

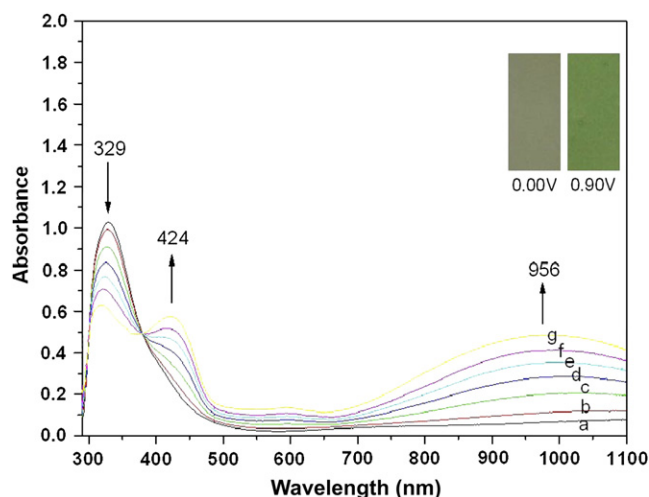


Fig. 3. Electrochromic behavior of polyamide **3f** thin film (in  $\text{CH}_3\text{CN}$  with 0.1 M TBAP as the supporting electrolyte) at (a) 0.00, (b) 0.54, (c) 0.62, (d) 0.66, (e) 0.70, (f) 0.74, and (g) 0.90 V.

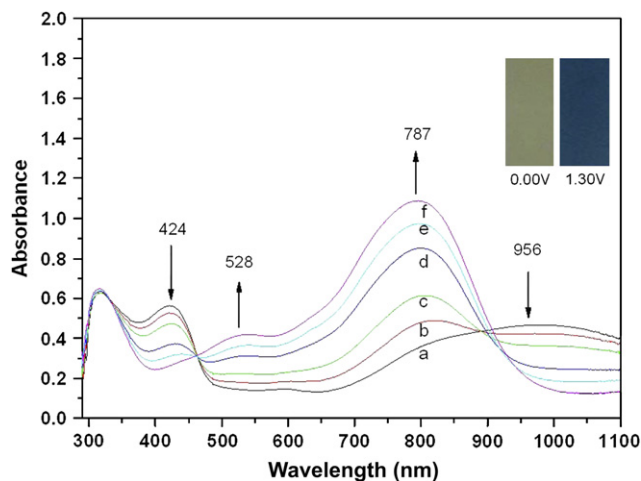


Fig. 4. Electrochromic behavior of polyamide **3f** thin film (in  $\text{CH}_3\text{CN}$  with 0.1 M TBAP as the supporting electrolyte) at (a) 0.95, (b) 0.99, (c) 1.03, (d) 1.07, (e) 1.11, and (f) 1.30 V.

the potential was set at 1.30 V, thin films from polyamide **3f** would require about 3 s for coloration at 787 nm and 2 s for bleaching. On continuous 10 cyclic scans between 0.0 and 1.30 V, the polymer films still exhibited excellent stability of the electrochromic characteristics.

#### 4. Conclusions

A series of high molecular weight polyamides have been readily prepared from the diamine,  $N,N'$ -bis(4-aminophenyl)- $N,N'$ -diphenyl-1,4-phenylenediamine, and various aromatic dicarboxylic acids. The introduction of the bulky intrinsic electron-donating triphenylamine group could decrease the HOMO values and disrupt the coplanarity of aromatic units

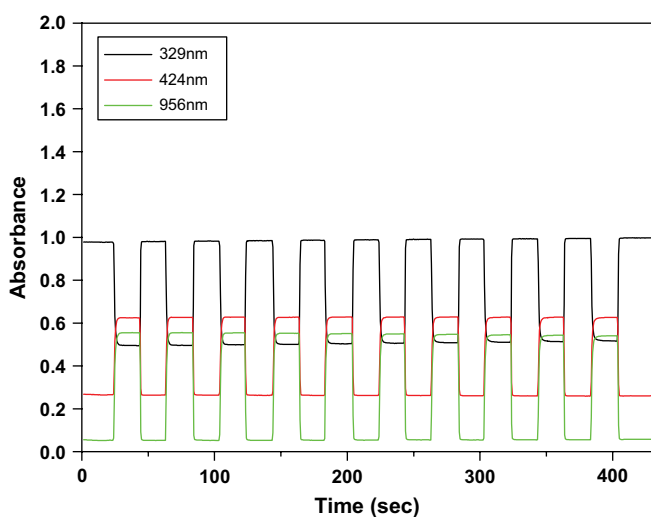


Fig. 5. Potential step absorptiometry of polyamide **3f** (in  $\text{CH}_3\text{CN}$  with 0.1 M TBAP as the supporting electrolyte) by applying a potential step ( $0 \text{ V} \rightleftharpoons 0.90 \text{ V}$ ). The switching time was defined as the time that is required to reach 90% of the full change in absorbance after switching potential. Thin films from polyamide **3f** would require 2 s at 0.90 V for switching absorbance at 329, 424 and 956 nm and 1 s for bleaching.

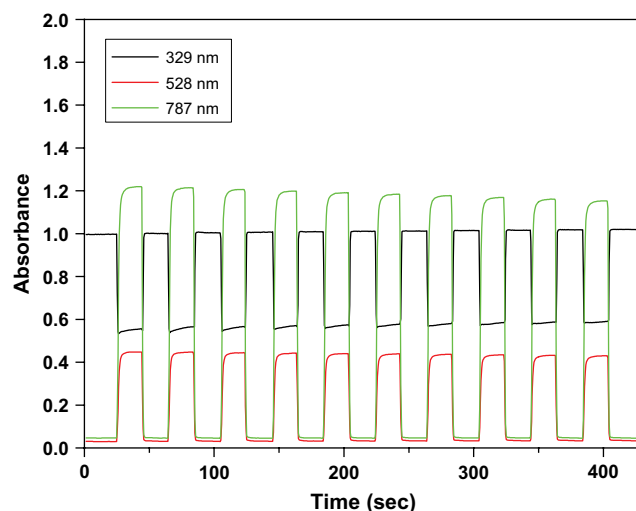


Fig. 6. Potential step absorptiometry of polyamide **3f** (in  $\text{CH}_3\text{CN}$  with 0.1 M TBAP as the supporting electrolyte) by applying a potential step ( $0 \text{ V} \rightleftharpoons 1.30 \text{ V}$ ). The switching time was defined as the time that is required to reach 90% of the full change in absorbance after switching potential. Thin films from polyamide **3f** would require 3 s at 1.30 V for switching absorbance at 329, 528 and 787 nm and 2 s for bleaching.

in chain packing which increases the between-chains spaces or free volume, thus 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  $T_g$  values, good thermal stability, and mechanical properties, the polyamides also revealed excellent stability of electrochromic characteristics, changing color from the pale yellowish neutral form to the green and then to blue oxidized forms when scanning potentials positively from 0.65 to 1.30 V. Thus, these novel triphenylamine-containing polyamides have a great potential as a new type of hole-transporting and electrochromic materials due to their proper HOMO values, excellent electrochemical and thermal stabilities.

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