

Electrochemical and electrochromic properties of novel aromatic poly(amine–amide)s derived from *N,N'*-bis(4-carboxyphenyl)-*N,N'*-diphenyl-1,4-phenylenediamine

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Abstract

A series of novel triphenylamine-containing aromatic poly(amine–amide)s were prepared from the dicarboxylic acid, *N,N'*-bis(4-carboxyphenyl)-*N,N'*-diphenyl-1,4-phenylenediamine, and various diamines by direct phosphorylation polycondensation. All the poly(amine–amide)s were amorphous, soluble in a variety of 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 (195–280 °C). These polymers exhibited strong UV–Vis absorption bands at 330–346 nm and their photoluminescence showed maximum bands around 516–535 nm in NMP solution. The hole-transporting and electrochromic properties are examined by electrochemical and spectroelectrochemical methods. Cyclic voltammograms of the poly(amine–amide)s prepared by casting polymer solution onto an indium–tin oxide (ITO)-coated glass substrate exhibited two reversible oxidative redox couples at potential 0.73–0.78 V and 1.12–1.18 V, respectively vs Ag/AgCl in acetonitrile solution. All the poly(amine–amide)s exhibited excellent reversibility of electrochromic characteristics by continuous ten cyclic scans between 0.0 and 1.40 V, with a color change from original pale yellowish neutral form to the green and then to blue oxidized forms.

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1. Introduction

Triphenylamine (TPA) and its derivatives have been extensively made as hole-transporting layers (HTLs) in OLED devices due to their high carrier mobility and amorphous film-forming ability [1–4].

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 [5–10]. However, the morphological change resulted from deposited heat during processing and molecular migration promoted by the molecular motion near glass-transition temperature (T_g) would degrade the electroluminescence (EL) devices then shorten their lifetime. Therefore, the HTL materials

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with higher T_g and higher molecular weight are required for the long-term stability of the EL devices. 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 [11–21]. 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. The uses of polymeric materials also provide the possibility for various chemical design and modifications. However, little attention has been paid to the synthesis and electrochromic property of aromatic polyamides and polyimides containing triphenylamine moieties.

Wholly aromatic polyamides are well accepted as advanced materials for a thin-film application in microelectronic devices due to their outstanding mechanical, chemical, thermal and physical 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. These properties make them generally intractable or difficult to process, thus restricting their applications [22,23]. To overcome such a difficulty, polymer-structure modification becomes necessary. One of the common approaches for increasing solubility and processability of polyamides without sacrificing high thermal stability is the introduction of bulky, packing-disruptive groups into the polymer backbone. 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 [24,25], *N,N*-bis(4-carboxyphenyl)-*N'*,*N'*-diphenyl-1,4-phenylenediamine [26] and 2,4-diaminotriphenylamine [27], 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. In view of our continuing interest in the high-performance polymers with particular functions, this article describes the electrochemical and electrochromic behaviors of a series of novel triphenylamine-containing poly(amine–amide)s based on the aromatic dicarboxylic acid, *N,N'*-bis(4-carboxyphenyl)-*N,N'*-diphenyl-1,4-phenylenediamine [28]. The electro-

chemical and electrochromic properties of these polymers prepared by casting solution onto an indium–tin oxide (ITO)-coated glass substrate are investigated.

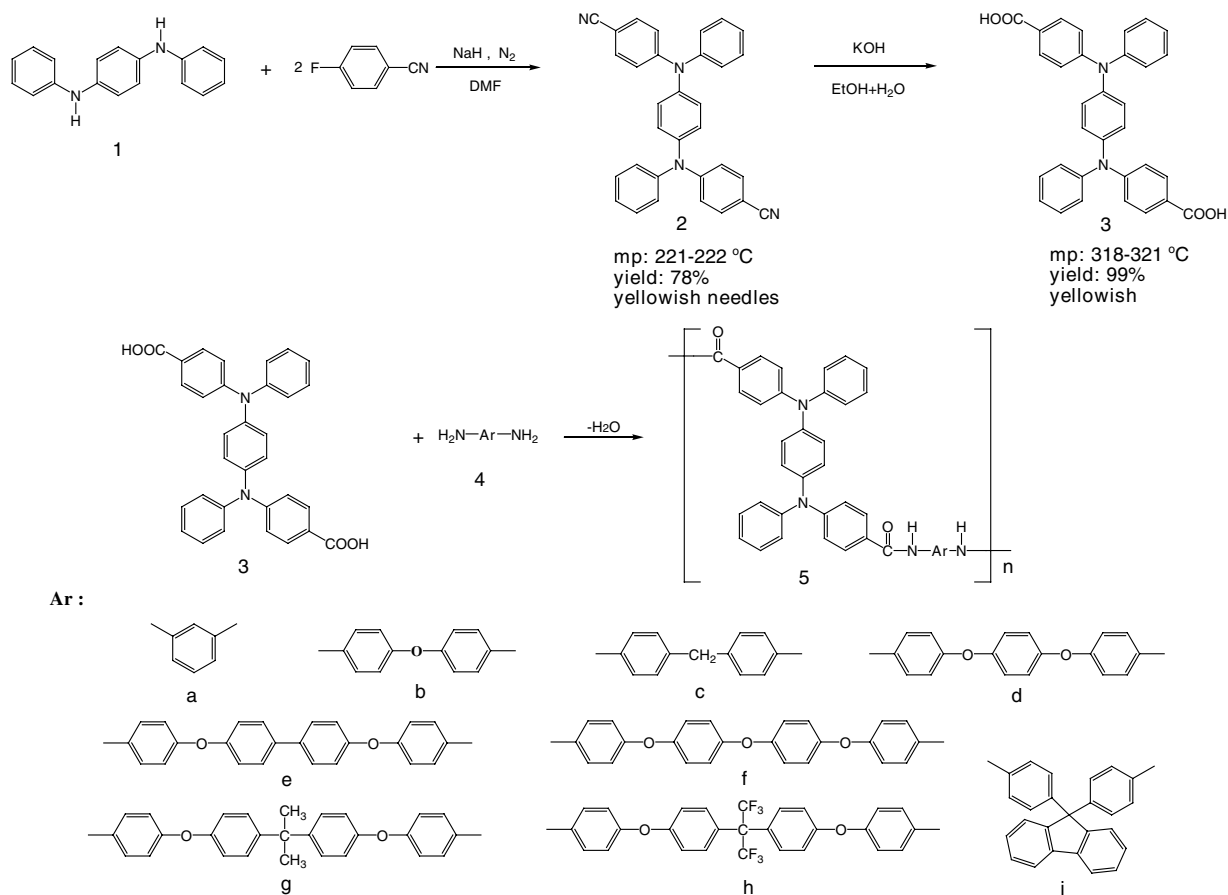
2. Experimental

2.1. Materials

N,N'-Bis(4-carboxyphenyl)-*N,N'*-diphenyl-1,4-phenylenediamine (mp: 318–321 °C) was synthesized by the condensation of *N,N'*-diphenyl-1,4-phenylenediamine with 4-fluorobenzonitrile in the presence of cesium fluoride, followed by the alkaline hydrolysis of the intermediate dinitrile compound as shown in Scheme 1 according to a previously reported procedure. The synthesis and characterization data of the strictly alternating poly(amine–amide)s were reported in a separate paper [28]. 4-Fluorobenzonitrile (Tokyo Chemical Industries), sodium hydride (95%, dry, Aldrich), potassium hydroxide (Tedia) were used as received. *N,N*-Dimethylacetamide (DMAc) (Tedia), *N,N*-dimethylformamide (DMF) (Acros), dimethyl sulfoxide (DMSO) (Tedia), *N*-methyl-2-pyrrolidinone (NMP) (Tedia), pyridine (Py) (Tedia), triphenyl phosphite (TPP) (Acros) were used without further purification. Bis[4-(4-aminophenoxy)phenyl]ether (**4f**) was prepared by the aromatic nucleophilic substitution reaction of 4,4'-oxydiphenol and *p*-chloronitrobenzene in the presence of potassium carbonate and by the subsequent reduction of the intermediate bis(*p*-nitrophenoxy) compound [29]. All the other commercially available aromatic diamines **4a–i** were purchased from Tokyo Chemical Industries and used as received. Commercially obtained anhydrous calcium chloride (CaCl_2) 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. Film preparation

A solution of polymer was made by dissolving about 0.6 g of the poly(amine–amide) sample in 10 mL of 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. The cast film was then released from the glass substrate and was further dried in vacuo at



Scheme 1.

160 °C for 8 h. The obtained films were about 70–100 μm in thickness and were used for transmission UV–Vis absorption analyses.

2.3. Measurements

Infrared spectra were recorded on a Perkin–Elmer RXI FT-IR spectrometer. ^1H and ^{13}C NMR spectra were measured on a Bruker Avance 500 MHz FT-NMR system. The X-ray crystallographic data were collected on an Enraf–Norius FR 590 CAD-4 diffractometer. Elemental analyses were run in an Elementar VarioEL-III. The inherent viscosities were determined at 0.5 g/dL concentration using a Tamson TV-2000 viscometer at 30 °C. Wide-angle X-ray diffraction (WAXD) measurements of the polymer films were performed at room temperature (ca. 25 °C) on a Shimadzu XRD-7000 X-ray diffractometer (40 kV, 20 mA) with a graphite monochromator, using nickel-filtered 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 conducted with a Perkin–Elmer Pyris 1 TGA. Experiments were carried out on approximately 6–8 mg film samples heated in flowing nitrogen or air (flow rate = 40 cm^3/min) at a heating rate of 20 °C/min. DSC analyses were performed on a Perkin–Elmer Pyris 1 DSC at a scan rate of 20 °C/min in flowing nitrogen (20 cm^3/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 $\text{cm} \times 0.5 \text{ cm}$) 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 homemade Ag/AgCl, KCl (satd) 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–Vis spectrophotometer. Photoluminescence spectra were measured with a Jasco FP-6300 spectrofluorometer.

3. Results and discussion

3.1. Polymer synthesis

A series of novel aromatic poly(amine–amide)s containing triphenylamine units were prepared from dicarboxylic acid **3** and various aromatic diamines **4a–i** by the phosphorylation polycondensation reaction [30] 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 poured the resulting polymer solutions under stirring into methanol. These poly(amine–amide)s were obtained in almost quantitative yields,










with inherent values in the range of 0.50–1.02 dL/g measured at a concentration of 0.5 g/dL in DMAc/5 wt % LiCl at 30 °C. The formation of poly(amine–amide)s was confirmed by elemental analysis and IR spectroscopy. They exhibited characteristic IR absorption bands of the amide group around 3316 (N–H stretching), 1668 cm⁻¹ (amide carbonyl).

3.2. Polymer properties

3.2.1. Optical and electrochemical properties

The optical and electrochemical behavior of the poly(amine–amide)s were investigated by UV–Vis, photoluminescence spectroscopy, and cyclic voltammetry. The results are summarized in Table 1. The UV–Vis absorption spectra of these polymers exhibited strong absorption bands at 330–350 nm in NMP solution, which are assignable to the π – π^* transition resulting from the conjugation between the aromatic rings and nitrogen atoms. Fig. 1 shows the UV–Vis absorption and photoluminescence spectra of poly(amine–amide)s **5c**, **5e** and **5g** for

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

Index	$\lambda_{\text{abs,max}}^{\text{b}}$ (nm)	$\lambda_{\text{abs,onset}}^{\text{b}}$ (nm)	$\lambda_{\text{PL}}^{\text{c}}$ (nm)	Oxidation (V) (vs Ag/AgCl)		HOMO–LUMO gap ^d (eV)	HOMO ^e (eV)	LUMO ^f (eV)
				First	Second			
5a 	346(344)	398(416)	520(500)	0.77	1.12	2.98	5.13	2.14
5b 	342(344)	398(420)	517(495)	0.78	1.15	2.95	5.14	2.19
5c 	341(338)	398(410)	516(496)	0.78	1.14	3.02	5.14	2.12
5d 	339(340)	397(404)	517(492)	0.78	1.16	3.07	5.14	2.07
5e 	336(340)	398(412)	519(495)	0.78	1.18	3.01	5.14	2.13
5f 	338(344)	398(418)	516(490)	0.78	1.14	2.97	5.14	2.17
5g 	333(344)	398(410)	517(493)	0.78	1.14	3.02	5.14	2.12
5h 	337(344)	399(422)	518(492)	0.78	1.15	2.94	5.14	2.20
5i 	340(347)	400(416)	517(497)	0.73	1.16	2.98	5.09	2.11

^a The color of these films was handed by media software.

^b UV–Vis absorption measurements in NMP (0.02 mg/mL) at room temperature, values in parentheses are polymer thin films.

^c PL spectra measurements in NMP (5 mg/mL) at room temperature, values in parentheses are polymer thin films.

^d The data were calculated from polymer thin films by the equation: gap = 1240/ λ_{onset} .

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

^f LUMO = HOMO – gap.

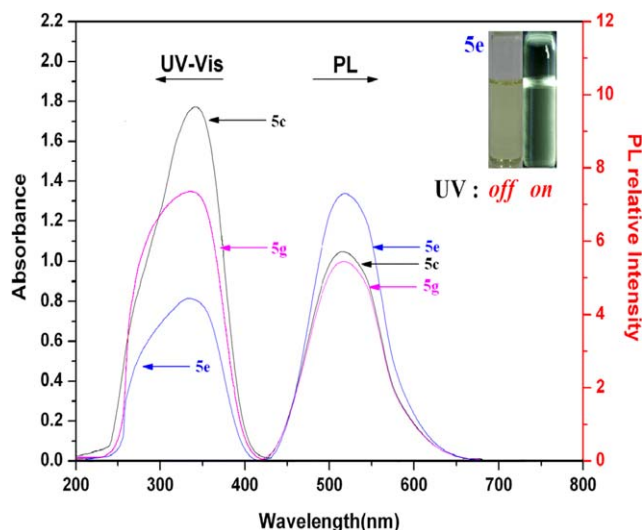


Fig. 1. Absorptions with a concentration of NMP (0.02 mg/mL) and PL with a concentration of NMP (5 mg/mL) spectra of some poly(amine–amide)s.

comparison. From the solution photoluminescence spectra, the emission for these polymers was in long wavelength green region (516–519 nm). This phenomenon possibly could be attributed to the large Stokes shift and this results in the lower emission quantum yield due to the greater number of conformations and a higher rate of radiationless decay. The electrochemical behavior of the poly(amine–amide)s was investigated by cyclic voltammetry performed for the cast film on an ITO-coated glass substrate as working electrode in dry acetonitrile (CH_3CN) containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere. The typical cyclic voltammogram for poly(amine–amide) **5a** is shown in Fig. 2. There are two reversible oxidation redox couples at $E_{1/2} = 0.77$ and 1.12 V corresponding to successive one electron removal from the nitrogen atoms at *N,N,N',N'*-tetraphenyl-1,4-phenylenediamine structure in each repeating unit to yield stable delocalized radical cation, poly(amine–amide)^{•+}, and another stable quinonoid-type dication, poly(amine–amide)²⁺ [31]. The triarylamine center at each *N,N,N',N'*-tetraphenyl-1,4-phenylenediamine structure of repeating unit is strongly coupled by the fact that the redox couple separation is 350 mV (1.12–0.77 V), which is larger than the statistical value for non-interacting center, where the separation of the first and the second oxidation redox couple is 35.6 mV [32]. Because of the good stability of the films and excellent adhesion between the polymer and ITO substrate, the poly(amine–

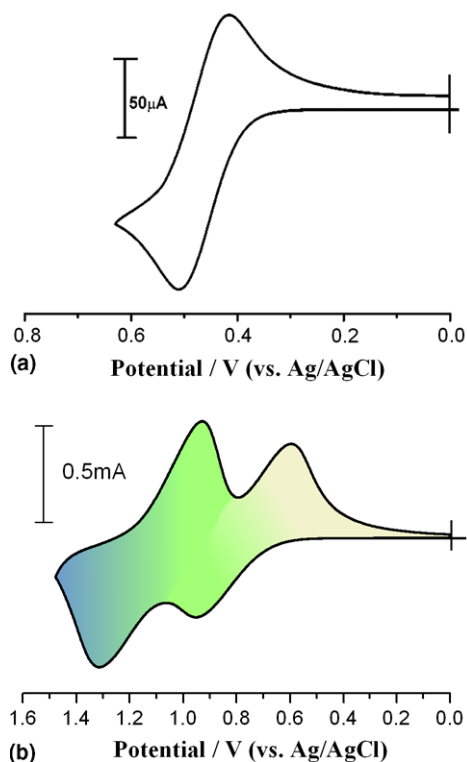


Fig. 2. Cyclic voltammogram of (a) ferrocene, (b) poly(amine–amide) **5a** film onto an indium–tin oxide (ITO)-coated glass substrate in CH_3CN containing 0.1 M TBAP. Scan rate = 0.1 V/s.

amide)s **5a** exhibited great reversibility of electrochromic characteristics by continuous ten cyclic

scans between 0.0 and 1.40 V, changing color from original pale yellowish to green, and then to blue. The energy of the HOMO and LUMO levels of the investigated poly(amine–amide)s can be determined from the oxidation half-wave potentials and the onset absorption wavelength and the results were listed in Table 1. For example, the oxidation half-wave potential for poly(amine–amide) **5a** has been determined as 0.77 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 poly(amine–amide) **5a** has been evaluated to be 5.13 eV.

3.2.2. Electrochromic characteristics

Electrochromism of the thin films from poly(amine–amide)s was determined by optically transparent thin-layer electrode (OTTE) coupled with a UV–Vis spectroscopy. The electrode preparations and solution conditions were identical to those used

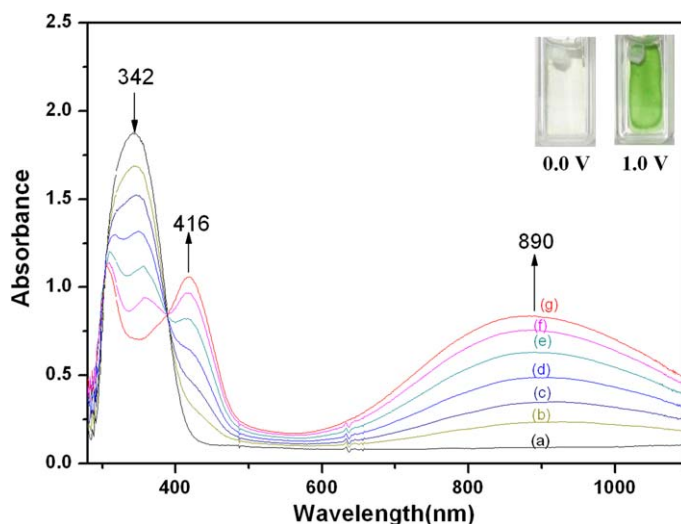


Fig. 3. Electrochromic behavior of poly(amine–amide) **5a** thin film (in CH₃CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0.00, (b) 0.15, (c) 0.30, (d) 0.50, (e) 0.65, (f) 0.80, (g) 1.00 V.

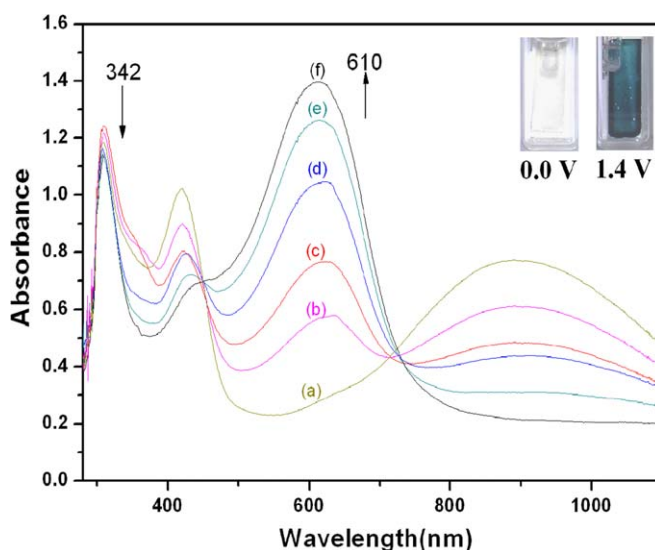


Fig. 4. Electrochromic behavior of poly(amine–amide) **5a** thin film (in CH₃CN with 0.1 M TBAP as the supporting electrolyte) at (a) 1.00, (b) 1.08, (c) 1.16, (d) 1.24, (e) 1.32, (f) 1.40 V.

in cyclic voltammetry. The typical electrochromic absorption spectra of poly(amine–amide) **5a** are shown as Figs. 3 and 4. When the applied potentials increased positively from 0 to 1.0 V, the peak of characteristic absorbance at 342 nm for neutral form poly(amine–amide) **5a** decreased gradually, while two new bands grew up at 416 and 890 nm due to the first electron oxidation. The new spectrum was assigned as that of the cationic radical poly(amine–amide)⁺, meanwhile complementary color of the

film turned into the green (as shown in Fig. 3). When a higher potential of 1.40 V was applied, the spectral change was shown as Fig. 4. The characteristic peaks for poly(amine–amide)⁺ in the first oxidation state disappeared and a new band grew up at 610 nm. The new spectrum was assigned as poly(amine–amide)²⁺ and the color of film became deep blue. Thus, this will be a good approach for facile color tuning of the electrochromic behaviors by attaching triphenylamine units to polymer main chain.

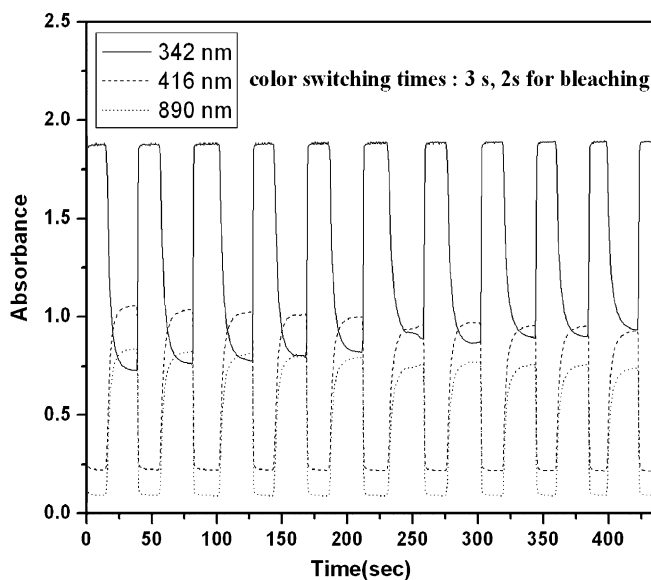


Fig. 5. Potential step absorptometry of poly(amine–amide) **5a** (in CH₃CN with 0.1 M TBAP as the supporting electrolyte) by applying a potential step (0–1.00 V).

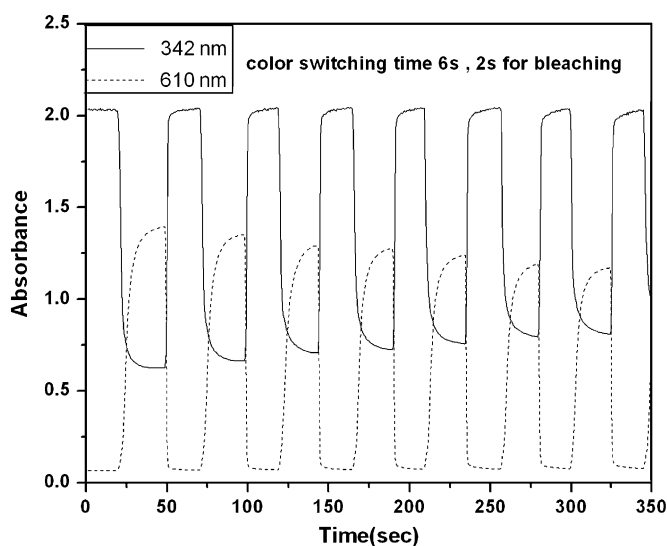


Fig. 6. Potential step absorptometry of poly(amine–amide) **5a** (in CH₃CN with 0.1 M TBAP as the supporting electrolyte) by applying a potential step (0–1.40 V).

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 required for reach 90% of the full change in absorbance after switching potential [33]. Thin films from poly(amine–amide) **5a** would require 3 s at 1.00 V for switching absorbance at 416 and 890 nm and 2 s for bleaching. When the potential was set at 1.40 V, thin films of poly(amine–amide) **5a** would require almost 6 s for coloration at 610 nm and 2 s for bleaching. After over 10 cyclic scans or color switching times, the polymer films still exhibited excellent stability of electrochromic characteristics.

4. Conclusions

A series of novel high-molecular-weight poly(amine–amide)s **5a–i** having triphenylamine units in polymer main have been readily prepared from the aromatic dicarboxylic acid, *N,N*-bis(4-carboxyphenyl)-*N,N'*-diphenyl-1,4-phenylenediamine and various aromatic diamines. By attaching bulky inherent electron-donating nature of triphenylamine units to polymer backbone, not only could be a good approach for facile color tuning of the electrochromic behaviors due to the oxidation potentials could be adjusted but also disrupt the coplanarity of aromatic units in chain packing which increases the between-chains spaces or free volume, thus most of the polymers were amorphous and exhibited excellent thin-film-forming ability. In addition to high glass transition temperatures and, good thermal stability, all the obtained poly(amine–amide)s also revealed excellent stability of electrochromic characteristics by the electrochemical and spectroelectrochemical methods, changing color from original pale yellowish to green, and then to blue. Thus, these novel triphenylamine-containing poly(amine–amide)s may find applications in electroluminescent devices as hole-transporting layer and electrochromic materials due to their proper HOMO values, excellent electrochemical and thermal stability.

Acknowledgements

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