

Synthesis of Redox-Stable Aromatic Polyamides with Pendent Triphenylamine Group for Electrochromic Applications

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Abstract

Three series of electroactive polyamides with pendent triphenylamine (TPA) units were prepared *via* the phosphorylation polyamidation reactions from three diamine monomers, namely 4-(3,5-diaminobenzamido)triphenylamine (**4**), 4-(3,5-diaminobenzamido)-4',4''-di-*tert*-butyltriphenylamine (***t*-Bu-4**) and 4-(3,5-diaminobenzamido)-4',4''-dimethoxytriphenylamine (**OMe-4**), with three aromatic dicarboxylic acids. These polyamides were amorphous with good solubility in many organic solvents and showed useful levels of thermal stability. The polyamide films exhibited reversible electrochemical oxidation, accompanied by strong color changes with high coloration efficiency and contrast ratio, which can be switched through potential modulation. The electrodimerization of the TPA groups in the polyamides derived from diamine **4** at potentials below 0.8 V was confirmed by cyclic voltammetry and spectroelectrochemical studies.

1. Introduction

Electrochromism is the phenomenon displayed by some materials of reversibly changing color resulting from the oxidation or the reduction of the material in response to an externally applied potential by electrochemical means.¹ This interesting property led to the development of many technological applications such as automatic antiglazing mirrors, smart windows for cars and buildings, electrochromatic displays, and chameleon materials. Among the most studied electrochromic materials we can include metal coordination complexes, metal oxide (especially tungsten oxide), viologens (4,4'-bipyridium salts), and conducting polymers (such as polyanilines, polypyrroles, and polythiophenes). The use of conjugated polymers as active layers in electrochromic devices became popular due to the advantageous properties such as fast switching time, ease of synthesis, and wide range of colors.² For efficient operation of an electrochromic device, it is necessary to take a number of properties into consideration: electrochromic efficiency, optical contrast, response time, stability and durability. The difficulty in achieving satisfactory values for all these parameters at the same time stimulates the development of new methods of preparation of electrochromic films, new materials and components for the devices.³

Triarylamine derivatives are well known as their photo and electroactive properties that may find optoelectronic applications as photoconductors, hole-transporters, light-emitters, or memory devices.⁴ Electron-rich triarylamines can be easily oxidized to form stable radical cations, and the oxidation process is always associated with a noticeable change of coloration. Thus, triarylamine-based polymers are promising materials for use in electrochromic devices.⁵ In recent years, Liou's and our groups have developed many high-performance polymers (e.g., aromatic polyamides and polyimides) bearing the TPA unit as an electrochromic functional moiety.⁶

It is well known that the electrogenerated cation radical of TPA is not stable and could dimerize to form tetraphenylbenzidine by tail to tail coupling with loss two protons per dimer.⁷ Blocking the *para* coupling sites of the TPA unit with appropriate substituents such as *tert*-butyl and methoxy groups greatly prevents the coupling reactions. In this work, we therefore synthesized the diamines monomers, ***t*-Bu-4** and **MeO-4**, and their derived aromatic polyamides containing electroactive TPA units with

para-substituted methoxy or *tert*-butyl groups on the pendent phenyl rings. The electrochemical and electrochromic properties of these polyamides are compared with those of their parent polyamides derived from diamine **4**. These polyamides are expected to exhibit high thermal stability due to their aryl amide backbones, together with good solubility and redox-activity because of the laterally attached TPA groups. Furthermore, the incorporation of electron-donating methoxy or *tert*-butyl substituents is expected to give extra electrochemical and electrochromic stability of the resulting polyamides.

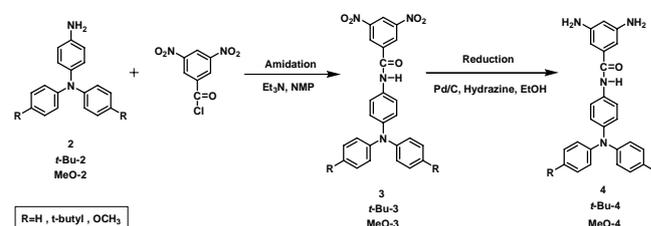
2. Experimental

2.1 Materials

According to well-known chemistry,^{6(e-g)} 4-amino-4',4''-dimethoxytriphenylamine (**MeO-2**) (mp = 133–134 °C) was synthesized by hydrazine Pd/C-catalytic reduction of 4-nitrotriphenylamine (**MeO-1**) resulting from the Ullmann C-N coupling reaction of 4-nitroaniline with iodoanisole. 4-Aminotriphenylamine (**2**) (mp = 148–149 °C) and 4-amino-4',4''-di-*tert*-butyltriphenylamine (***t*-Bu-2**) (mp = 139–141 °C) were synthesized by hydrazine Pd/C-catalytic reduction of 4-nitrotriphenylamine (**1**) and 4,4'-di-*tert*-butyl-4''-nitrotriphenylamine (***t*-Bu-1**) respectively resulting from the fluoro-displacement reaction of *p*-fluoronitrobenzene with the sodium amides of aniline and bis(4-*tert*-butylphenyl)amine formed *in situ* by treatment with sodium hydride.

2.2 Monomer synthesis

Three new TPA-pendent diamine monomers, **4**, ***t*-Bu-4** and **OMe-4**, were successfully synthesized by hydrazine Pd/C-catalyzed reduction of the dinitro compounds 4-(3,5-dinitrobenzamido)triphenylamine (**3**), 4-(3,5-dinitrobenzamido)-4',4''-di-*tert*-butyltriphenylamine (***t*-Bu-3**) and 4-(3,5-dinitrobenzamido)-4',4''-dimethoxytriphenylamine (**OMe-3**), that were prepared by acylation of the amino group of compounds **2**, ***t*-Bu-2** and **MeO-2**, respectively, with 3,5-dinitrobenzoyl chloride in NMP in the presence of triethylamine (Scheme 1).

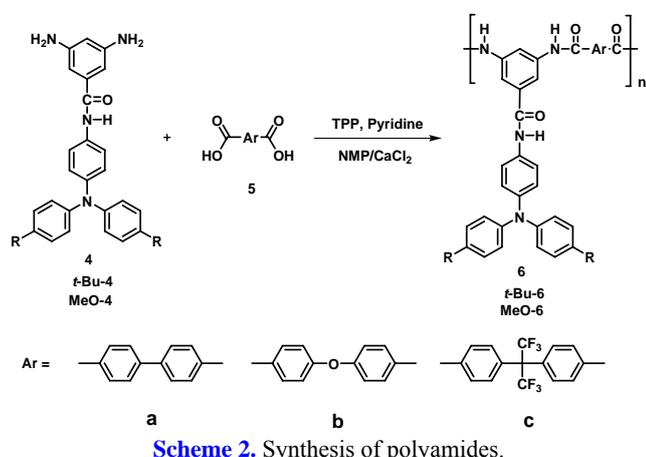


Scheme 1. Synthetic route to diamine monomers **4**, ***t*-Bu-4** and **MeO-4**.

2.3 Polymer synthesis

According to the phosphorylation polyamidation technique described by Yamazaki and coworkers,⁸ all the **6** series of aromatic polyamides were synthesized from the diamines **4**, ***t*-Bu-4**, and **MeO-4** with three dicarboxylic acids **5a-5c** using triphenyl phosphite (TPP) and pyridine as condensing agents (Scheme 2). All the polymerizations proceeded homogeneously throughout the reaction and afforded clear and highly viscous polymer solutions, which precipitated in a tough, fiber-like form when the resulting

polymer solutions were slowly poured into stirring methanol. As shown in the Table 1, the obtained polyamides had inherent viscosities in the range of 0.32–0.81 dL/g and all of them could be solution-cast into flexible and tough films, indicating high molecular weight polymers.



3. Results and discussion

3.1 Solubility and film property

The solubility behavior of polyamides was tested qualitatively, and the results are summarized in Table 1. All the polyamides were highly soluble in polar solvents such as NMP, DMAc, DMF, and DMSO, and the high solubility could be attributed to the introduction of the bulky pendent TPA moiety into the repeat unit. Thus, the excellent solubility makes these polymers potential candidates for practical applications by common solution processes to afford high performance thin films for optoelectronic devices.

3.2 Thermal properties

The thermal properties of the polyamides were investigated by TGA and DSC techniques. The thermal behavior data are also included in Table 1. Their decomposition temperatures (T_d) at a 10 % weight-loss in nitrogen and air were recorded at 490–556 and 489–554 °C, respectively. These polyamides left high carbonized residue (char yield) in excess of 50% at 800 °C in an inert atmosphere, due to their high aromatic content. Polyamides *t*-Bu-6 and MeO-6 series exhibited a lower T_d value as compared with the parent 6 series without substituents on the pendent phenyl rings. This is reasonable when considering the less stable aliphatic segments. The glass-transition temperatures (T_g) of all the

polyamides were observed in the range of 269–294 °C by DSC. All the polymers indicated no clear melting endotherms up to the decomposition temperatures on the DSC thermograms. The thermal analysis results revealed that these polyamides exhibited good thermal stability, which in turn is beneficial to increase the service time in device application and enhance the morphological stability to the spin-coated film.

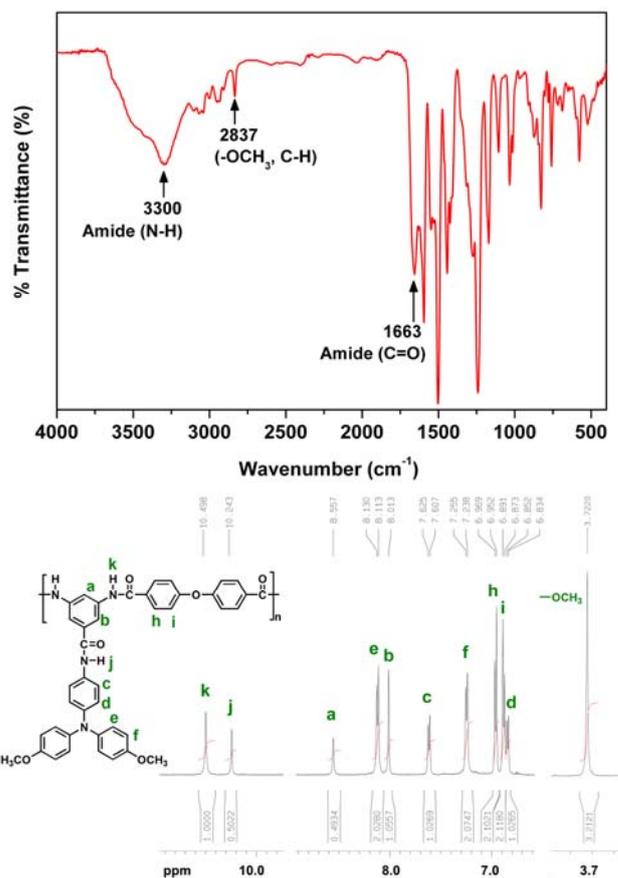


Figure 1. IR and ^1H NMR spectra of polyamide MeO-6b.

Table 1 Inherent Viscosity, Solubility Behavior and Thermal Properties of the Polyamides

Polymer code	$\eta_{\text{inh}}^{\text{a}}$ (dL/g)	Solubility in various solvents ^b						T_g (°C) ^c	T_d at 10 wt% (°C) ^d		Char yield (wt %) ^e
		NMP	DMAc	DMF	DMSO	<i>m</i> -cresol	THF		In N ₂	In air	
6a	0.93	+	+	+-	+	-	-	294	556	554	70
6b	0.83	++	++	++	++	+	+-	274	543	537	70
6c	0.39	++	++	++	++	+	++	283	553	543	68
<i>t</i> -Bu-6a	0.78	++	++	++	+	+-	-	287	475	489	56
<i>t</i> -Bu-6b	0.49	++	++	++	++	+	++	294	501	534	50
<i>t</i> -Bu-6c	0.32	++	++	++	++	+	++	291	493	524	58
MeO-6a	0.80	++	++	++	++	+	-	- ^f	490	501	67
MeO-6b	0.72	++	++	++	++	+-	-	269	492	503	62
MeO-6c	0.32	++	++	++	++	+	++	276	496	499	61

^a Measured at a polymer concentration of 0.5 g/dL in DMAc–5 wt % LiCl at 30 °C. ^b The qualitative solubility was tested with 10 mg of a sample in 1 mL of stirred solvent. Notation: ++, soluble at room temperature; +, soluble on heating; +-, partially soluble; -, insoluble even on heating. ^c Midpoint temperature of the baseline shift on the second DSC heating trace (rate = 20 °C/min) of the sample after quenching from 400 °C to 50 °C (rate = -200 °C/min) in nitrogen. ^d Decomposition temperature, recorded *via* TGA at a heating rate of 20 °C/min and a gas-flow rate of 30 cm³/min. ^e Residual weight percentage at 800 °C in nitrogen. ^f No discernible transition was detectable by DSC.

3.3 Electrochemical properties

The electrochemical behavior of the polyamides was investigated by cyclic voltammetry (CV) conducted for the cast

film on an ITO-coated glass substrate as working electrode in dry acetonitrile (CH₃CN) containing 0.1 M of Bu₄NClO₄ as an electrolyte under nitrogen atmosphere. One pair of reversible redox

waves was observed in the first CV scan of these polymers. Figure 2 compares the CV curves of polyamides **6b**, *t*-Bu-**6b**, and MeO-**6b**. As expected, the oxidation potential of MeO-**6b** ($E_{pa} = 0.83$ V) is lower as compared with those of **6b** ($E_{pa} = 0.95$ V) and *t*-Bu-**6b** ($E_{pa} = 1.12$ V) because of the electron-donating methoxy groups on the pendent phenyl rings of the TPA unit. The repetitive CV curves for polyamides **6b** and MeO-**6b** are compared in Figure 3. In the case of **6b**, a new redox couple was observed around 0.80 V in the second and the later scans indicating the tetraphenylbenzidine (TPB) formation during oxidation of the TPA moieties of polyamide **6b** (Scheme 3). The CV trace of **6b** is in agreement with the behavior of a typical TPA oxidation. The TPA oxidation produces a dimer (TPB) that has a more extended π -conjugation. As a result, TPB is easier to oxidize than the parent TPA unit. Because the TPB unit undergoes two oxidation processes at different potentials, in the case of **6b**, the newly formed redox couple could be ascribed to the first oxidation of TPB, and the second one overlaps with the principal peak of **6b**. As shown in the inset of Figure 3, the plot of the anodic current at 0.8 V was linearly proportional to the number of scans, confirming the occurrence of the oxidative coupling at the *para*-position of TPA in polyamide **6b**. The redox potentials of the polyamides as well as their respective highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (on the basis of ferrocene/ferrocenium is 4.8 eV below the acuum level with $E_{1/2} = 0.44$ V) estimated from their oxidation or reduction in CV experiments are summarized in Table 2.

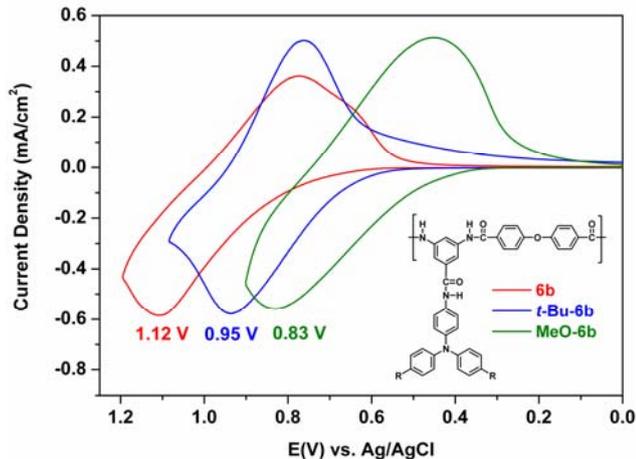


Figure 2. Cyclic voltammograms of the cast films of polyamides **6b**, *t*-Bu-**6b**, and MeO-**6b** on an ITO-coated glass substrate in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$ solution at a scan rate of 50 mV/s.

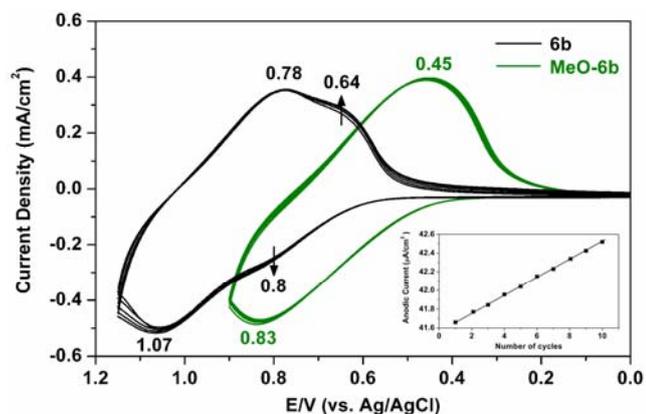
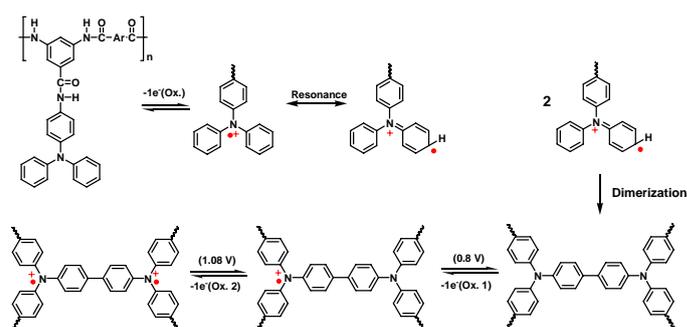


Figure 3. Repetitive cyclic voltammograms of: polyamide **6b** and MeO-**6b** films on an ITO-coated glass substrate in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$ solution at a scan rate of 50 mV/s. The inset showed a linear plot of the anodic current grown at 0.8 V vs. the number of scans.



Scheme 3. Proposed electro-dimerization reaction of the pendent TPA units

in the **6** series polyamides.

Table 2. Redox Potentials and Energy Levels of Polyamides

Polymer code	Thin film		Oxidation potential (V) ^a		E_g (eV) ^b	HOMO ^c /LUMO ^d
	λ_{max}	λ_{onset}	E_{onset}	$E_{1/2}^{ox}$		
6a	302	368	0.77	0.93	3.37	5.29/1.92
6b	296	370	0.77	0.94	3.35	5.30/1.95
6c	299	392	0.80	0.91	3.16	5.27/2.11
<i>t</i> -Bu- 6a	304	375	0.63	0.84	3.31	5.20/1.89
<i>t</i> -Bu- 6b	293	338	0.63	0.85	3.67	5.21/1.54
<i>t</i> -Bu- 6c	294	339	0.63	0.87	3.66	5.23/1.57
MeO- 6a	309	370	0.51	0.69	3.35	5.01/1.66
MeO- 6b	301	346	0.51	0.70	3.58	5.03/1.45
MeO- 6c	305	386	0.53	0.72	3.21	5.06/1.85

^a Oxidation potentials from cyclic voltammograms (vs. Ag/AgCl in CH_3CN).

^b Energy gap = $1240/\lambda_{onset}$ of the polymer film. ^c $E_{HOMO} = -(E_{1/2}^{Ox} + 4.8)$ (eV)

^d $E_{LUMO} = E_{HOMO} - E_g$

3.4 Spectroelectrochemical and electrochromic properties

The electro-optical properties of the polymer films were investigated using the changes in electronic absorption spectra at various applied voltages. The result of the **6b** film upon electro-oxidation is presented in Figure 4a as a series of UV-vis-NIR absorption curves correlated to electrode potentials. In the neutral form, at 0.0 V, polyamide **6b** exhibited strong absorption at λ_{max} of 311 nm, characteristic for TPA, but it is almost transparent in the visible region. As the applied voltage was stepped from 0.0 to 1.2 V, the intensity of the absorption peak at 311 nm decreased gradually, and new peaks at 400, 760 and 920 nm gradually increased in intensity. In the same time, the film turned into a greenish-blue color. We attribute these spectral changes to the formation of a stable cation radical of the side-chain TPA moiety. After the first electrochemical series of polyamide **6b** was recorded from 0.00 V to 1.10 V and then back to 0 V, we re-applied the electrode voltage. As shown in Figure 4b, when the applied voltage was stepped from 0.0 V to 0.7 V, the characteristic absorbance at long-wavelengths decreased significantly, whereas a new small absorption at 483 nm appeared. Meanwhile, the film changed color from greenish-blue to orange-yellow. An additional orange-yellow oxidized state has been observed in the re-scan film at applied voltage of 0.7 V. The film showed a multicolored electrochromism from colorless neutral state to orange-yellow, and then greenish-blue oxidized states. This phenomenon persisted for several subsequent scans. The new orange-yellow oxidized state may be attributed the oxidation of the TPB unit resulted from the coupling reaction occurred on the active sites of the side-chain TPA unit (Scheme 3).

For a comparative study, the spectral changes of the polyamides *t*-Bu-**6b** and MeO-**6b** with *tert*-butyl or methoxy substituents on the TPA unit are presented in Figures 4c and 4d, respectively. In their neutral states, these films exhibited strong absorptions at wavelengths around 324 and 309 nm, characteristic for the TPA moiety, but they were almost transparent in the visible region.

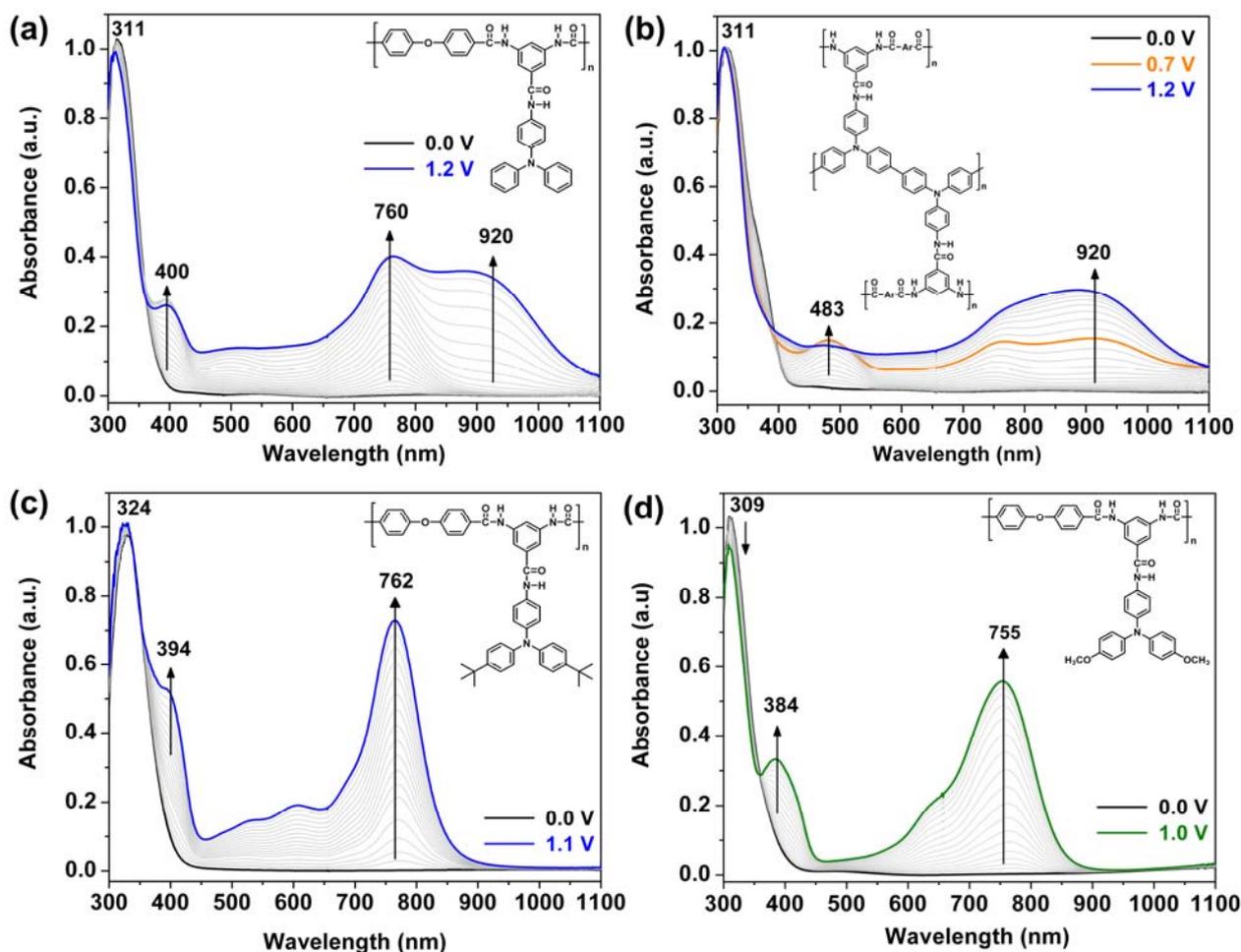


Figure 4. Spectral changes of the cast films of polyamides (a) **6b** (b) **6b** after the first scan (c) *t*-**Bu-6b** (d) **MeO-6** on an ITO-coated glass in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$ at various applied potentials (vs Ag/AgCl).

When the applied voltage was stepped from 0 to 1.0 or 1.1 V, new peaks at 762 and 755 nm gradually increased in intensity. The intensity is much higher than that observed for polyamide **6b** at the fully oxidized state. This result may be explained by the introduction of bulky *tert*-butyl or electron-donating methoxy group which greatly prevents the coupling reaction. Thus, the effect of *tert*-butyl or methoxy substitution on the enhancement of electrochemical and electrochromic reversibility and optical contrast ratio is very clear.

4. Conclusions

Three series of novel aromatic polyamides with pendent TPA units were readily prepared from the newly synthesized aromatic diamine monomer **4**, *t*-**Bu-4**, and **MeO-4** with three aromatic dicarboxylic acids via the phosphorylation polyamidation reaction. Introduction of bulky *tert*-butyl or electron-donating methoxy substituents at the *para*-positions of TPA not only could prevent the electrochemical oxidative coupling reactions but also could decrease the oxidation potentials of the polyamides. All the obtained polyamides revealed good electrochemical and electrochromic stability along with strong coloration changes. These polyamides also showed good film-forming ability and high thermal stability. Thus, these characteristics suggest that this new class of polyamides has great potential for use in optoelectronics applications such as electrochromic devices.

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