

Synthesis and Characterization of Novel Electroactive Polyamides and Polyimides with 4-(1-Adamantoxy)triphenylamine Moieties

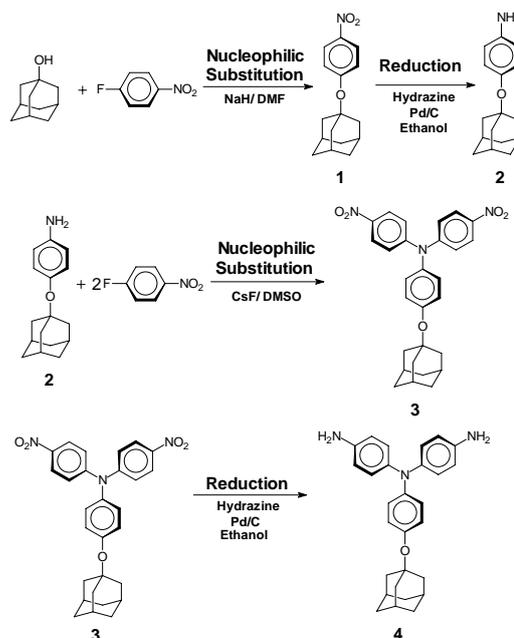
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Introduction. Electrochromism is known as the reversible change in optical absorption or transmittance upon redox switching.¹ This interesting property led to the development of many technological applications such as automatic anti-glazing mirror, smart windows, electrochromic displays, and chameleon materials.² Many different classes of electrochromic materials, such as organic systems, e.g., bipyridium salt (also known as viologens), electroactive conducting polymers (e.g., polyanilines, polythiophenes, polypyrroles), as well as inorganic systems based on transition metal oxides (e.g., WO₃) have been described. Conducting or conjugated polymers have been found to be more promising as electrochromic materials because of their better stability, faster switching speeds, and easy processing compared to the inorganic electrochromic materials, but the most exciting properties are multiple colors with the same material while switching between their different redox states,³ and fine-tuning of the color transition through chemical structure modification of the conjugated backbone.^{4,5} Considerable effort in the Reynolds group has been made on the understanding and the tailoring of electrochromic properties in conducting polymers such as poly(3,4-alkylenedioxythiophene)⁶ and poly(3,4-alkylenedioxyppyrole)⁷ and their derivatives.

Triarylamine derivatives are well known for photo- and electroactive properties that find optoelectronic applications as photoconductors, hole-transporters, and light-emitters. Triarylamines can be easily oxidized to form stable radical cations, and the oxidation process is always associated with a noticeable change of coloration. Thus, many triarylamine-based electrochromic polymers have been reported in literature.^{8,9} In recent years, we have developed a number of high-performance polymers (e.g., aromatic polyamides and polyimides) carrying the triphenylamine (TPA) unit as an electrochromic functional moiety.¹⁰⁻¹² Our strategy was to synthesize the TPA-containing monomers such as diamines and dicarboxylic acids that were then reacted with the corresponding comonomers through conventional polycondensation techniques. The obtained polymers possessed characteristically high molecular weights and high thermal stability. Because of the incorporation of packing-disruptive, propeller-shaped TPA units along the polymer backbone, most of these polymers exhibited good solubility in polar organic solvents. They may form uniform, transparent amorphous thin films by solution casting and spin-coating methods. This is advantageous for their ready fabrication of large-area, thin-film devices.

The anodic oxidation pathways of TPA are well studied. The unsubstituted TPA may undergo coupling-deprotonation to form tetraphenylbenzidine after the formation of the initial monocation radical. It has been well established that incorporation of electron-donating substituents such as methoxy group at the *para* position of TPA prevents the coupling reactions and affords stable radical cations. Therefore, we synthesized the diamine monomer, 4-(1-adamantoxy)-4',4''-diaminotriphenylamine (**4**), and its derived polyamides and polyimides containing electroactive TPA units with bulky electron-donating adamantoxy group *para* substituted on the pendent phenyl ring. The general properties such as solubility, crystallinity, and thermal properties are described. The electrochemical and electrochromic properties of these polymers are also investigated herein. It was expected that the polymers will present an enhanced solubility and decreased ionization potential because of the introduction of sterically bulky adamantoxy group.

Monomer Synthesis. The new diamine monomer **4** containing a 4-(1-adamantoxy)triphenylamine unit was synthesized by the multistep synthetic routes. In the first step, the intermediate compound, 4-(1-adamantoxy)nitrobenzene (**1**) was synthesized by nucleophilic aromatic displacement of 4-fluoronitrobenzene with 1-adamantanol using sodium hydride as the base. Reduction of the nitro compound by means of hydrazine and Pd/C gave 4-(1-adamantoxy)aniline (**2**). The target diamine monomer **4** was prepared by hydrazine Pd/C-catalyzed reduction of 4-(1-adamantoxy)-4,4''-dinitrotriphenylamine (**3**) resulting from *N,N*-diarylation of synthetic aniline with 4-fluoronitrobenzene in the presence of cesium fluoride.



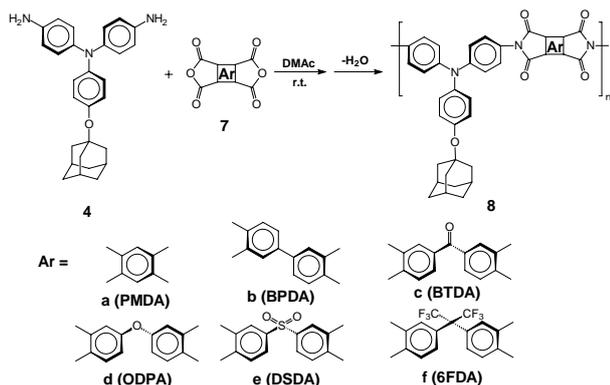
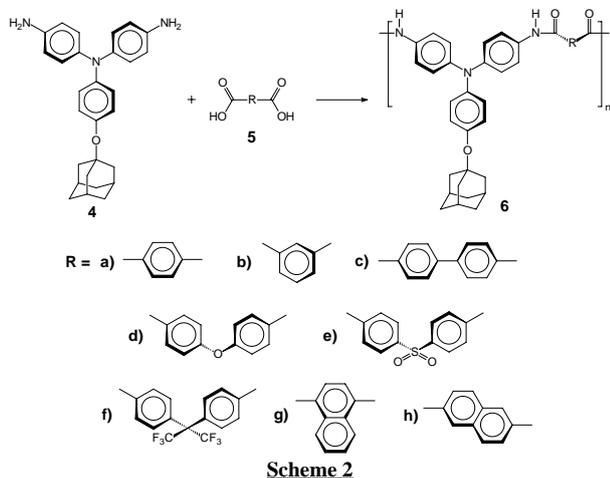
Scheme 1

Polymer Synthesis. According to the phosphorylation technique described by Yamazaki and co-workers,¹³ a series of novel TPA-based aromatic polyamides **6a-h** with bulky adamantoxy group *para* substituted on the pendent phenyl ring of the TPA unit were prepared from the diamine **4** and various aromatic dicarboxylic diacids (**5a-h**) by the direct polycondensation reaction with triphenyl phosphite (TPP) and pyridine as condensing agents (Scheme 2). The polyamides were produced with moderate to high inherent viscosities ranging from 0.45 to 0.82 dL/g (Table 1). The molecular weights of all the polyamides are sufficiently high to permit the formation of flexible and tough films by casting from their DMAc solutions. Polyimides **8a-f** were prepared in a conventional two-step method, i.e., by the reactions of equal molar amounts of diamine **4** with various aromatic dianhydrides (**7a-f**) to form poly(amic acid)s, followed by thermal or chemical cyclodehydration (Scheme 3).

General Properties of Polymers. All the polyamides were readily soluble in amide-type polar aprotic solvents (such as NMP, DMAc, and DMF). The high solubility of these polyamides is apparently due in part to the presence of the packing-disruptive TPA unit in the polymer backbone and the bulky adamantoxy pendent group in the side chain which resulted in increased chain packing distances and decreased intermolecular interactions. The solubility properties of the chemically imidized samples of polyimides **8c-f** were also easily soluble in polar solvents such as NMP and DMAc. All polymers could afford flexible and tough films, and they were amorphous in nature as evidenced by wide-angle X-ray diffraction (WAXD) patterns. The *T_g* values of all the polymers were observed in the range of 293-311 °C by DSC. All the polyimides exhibited good thermal stability with insignificant weight loss up to 450 °C in nitrogen, and the 10% weight-loss temperatures in nitrogen were recorded in the range of 460-529 °C. These polymers exhibited strong UV-vis absorption bands at 300~364 nm in NMP solutions, which were assignable to the π - π^* transition resulting from the conjugation between the aromatic rings and nitrogen atoms. Their PL spectra in NMP solution showed maximum bands around 358-456 nm in the violet-to-blue region.

Electrochemical and Electrochromic Properties. We undertook a study of the redox behaviors of all the synthesized polymers using cyclic voltammetry (CV). Electrochemical technique was conducted for a cast film on an ITO-coated glass substrate as working electrode in dry acetonitrile (CH₃CN) containing 0.1 M of tetrabutylammonium perchlorate (TBAP) as supporting electrolyte and saturated Ag/AgCl as reference electrode under nitrogen atmosphere. There is a pair of reversible redox couple observed on the first CV scans of all polymers. A typical CV curve for polyamide **6d** is shown in the inset of Figure 1, and the *E*_{1/2} values (average potential of the redox couple peaks) of all polymers are listed in Table 1. These polymers have *E*_{1/2} in the range of 0.78-0.83 V (for polyamides) and 0.97-1.05 V (for polyimides), respectively. All the adamantoxy-substituted polymers revealed a

lower oxidation potential than their corresponding analogues without the adamantoxy pendent group because of the electron-donating nature of the alkoxy substituent. The polyimides showed higher $E_{1/2}$ values than those of the polyamides because of the stronger electron-withdrawing nature of the imide group. Assuming that the HOMO energy level for the Fc/Fc⁺ standard is 4.80 eV with respect to the zero vacuum level, the HOMO energy levels for all polymers estimated from their $E_{1/2}$ values are also listed in Table 1. For the electrochromic investigations, all the polymer films were cast on an ITO-coated glass slide (a piece that fit in the commercial UV-visible cuvette), and a homemade electrochemical cell was built from a commercial UV-visible cuvette. The cell was placed in the optical path of the sample light beam in a commercial diode array spectrophotometer. This procedure allowed us to obtain electronic absorption spectra under potential control in a 0.1 M TBAP/CH₃CN solution. Typical result of the film of polyamide **6d** is presented in Figure 1 as a series of UV-vis absorbance curves correlated to electrode potentials. In the neutral form, at 0 V, the film exhibited strong absorption at wavelength around 336 nm, characteristic for triarylamine, but it was almost transparent in the visible region. Upon oxidation of the polyamide **6d** film (increasing applied voltage from 0 to 1.0 V), the intensity of the absorption peak at 336 nm gradually decreased while new peaks at 605 and 805 nm gradually increased in intensity, and the color of the film changed to pale green. We attribute this spectral change to the formation of a stable monocation radical of the triphenylamine moiety.



Conclusions. Two series of novel electroactive polyamides and polyimides have been prepared from the polycondensation reactions of a newly synthesized diamine monomer, 4-(1-adamantoxy)-4',4''-diaminotriphenylamine, with various dicarboxylic acids and dianhydrides, respectively. All the polymers could form morphologically stable and uniform amorphous films using solution-casting techniques. In addition to high T_g and T_s values, high thermal stability and good mechanical properties, the polymers also revealed electrochromic characteristics with color change from colorless or pale yellow neutral state to green or pale purple oxidized state. Thus, these polymers may find applications as new hole-transporting and electrochromic materials.

Table 1. Optical and electrochemical properties of the polymers

Polymer code	Abs λ_{\max} (nm) ^a	Abs λ_{onset} (nm) ^a	PL λ_{\max} (nm) ^b	$E_{1/2}$ (V) ^c (vs. Ag/AgCl)	E_g^d (eV)	HOMO/LUMO ^e (eV)
6a	360 (368)	434 (467)	456	0.78 (0.93)	2.66	5.14/2.48
6b	341 (349)	376 (411)	422	0.83 (0.91)	3.02	5.19/2.17
6c	352 (357)	398 (431)	443	0.79 (0.91)	2.88	5.15/2.27
6d	338 (342)	372 (404)	426	0.78 (0.94)	3.07	5.14/2.07
6e	364 (368)	453 (482)	452	0.80 (0.96)	2.57	5.16/2.59
6f	342 (347)	411 (448)	426	0.81 (0.95)	2.77	5.17/2.40
6g	313 (335)	399 (422)	402	0.83 (0.94)	2.94	5.19/2.25
6h	349 (352)	440 (475)	433	0.78 (0.95)	2.61	5.14/2.53
8a	312 (371)	399 (599)	394	0.97 (1.17)	2.07	5.33/3.26
8b	322 (328)	366 (382)	400	0.98 (1.17)	3.25	5.34/2.09
8c	300 (301)	387 (432)	359	1.02 (1.17)	2.87	5.38/2.51
8d	316 (329)	362 (412)	391	1.05 (1.14)	3.01	5.41/2.40
8e	302 (308)	380 (427)	358	0.98 (1.17)	2.90	5.34/2.44
8f	301 (303)	369 (393)	368	1.04 (1.18)	3.16	5.40/2.24

^a UV/vis absorption measured in NMP (1 x 10⁻⁵ mol/L) at room temperature. Values shown in parentheses are those measured as thin solid-film.

^b Photoluminescence measured in NMP (1 x 10⁻⁵ mol/L) at room temperature.

^c Oxidation half-wave potentials from cyclic voltammograms. Values shown in parentheses are those of structurally similar polyamides **6'** and polyimides **8'** without the adamantoxy substituent.

^d Energy gap = 1240 / Abs λ_{onset} of polymer film.

^e The HOMO energy levels were calculated from $E_{1/2}$ and were referenced to ferrocene (4.8 eV); LUMO = HOMO - E_g .

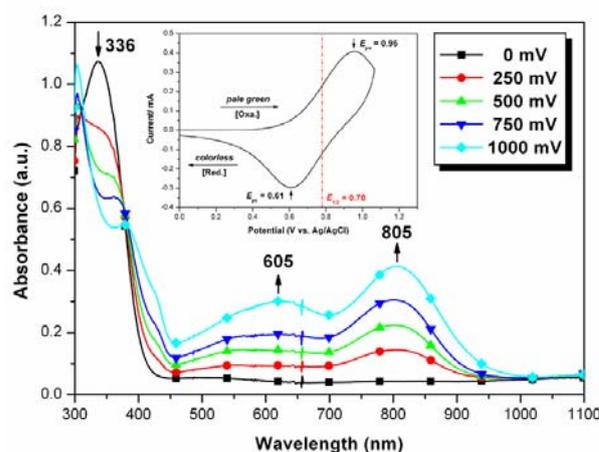


Figure 1. Spectral change of the cast film of polyamide **6d** on the ITO-coated glass substrate (in acetonitrile with 0.1 M TBAP as the supporting electrolyte) along with increasing applied voltages from 0 V to 1.0 V vs Ag/AgCl couple as reference. The inset shows the CV curve of polymer **6d**.

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Synthesis and Characterization of Novel Electroactive Polyamides and Polyimides with 4-(1-Adamantoxy)triphenylamine Moieties



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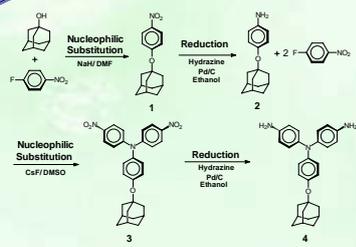
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ABSTRACT

A novel adamantoxy-substituted, triphenylamine-containing diamine monomer, 4-(1-adamantoxy)-4',4''-diaminotriphenylamine, was synthesized from readily available reagents and was reacted with various aromatic dicarboxylic acids and tetracarboxylic dianhydrides to produce two series of novel electroactive polyamides **6a-h** and polyimides **8a-f** with bulky adamantoxy pendent substituents. All polyamides were readily soluble in polar organic solvents and could be solution cast into tough and flexible films. The polyimide films were prepared via the thermal curing of their poly(amic acid) films. These polymers showed high glass transition and softening temperatures between 263 °C and 311 °C, and they were fairly stable up to a temperature above 480 °C (for polyamides) or 500 °C (for polyimides). All of these polymers showed one pair of reversible redox waves with $E_{1/2}$ values between 0.78-1.05 V. In addition, the polymers were observed to display electrochromic properties, with coloration change from colorless or pale yellowish neutral state to a dark blue or bluish green oxidized state.



Scheme 1. Synthetic route to target diamine monomer.

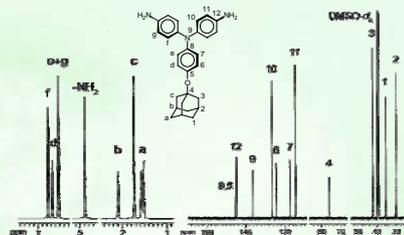


Figure 1. (a) ¹H NMR spectrum and (b) ¹³C NMR spectrum of monomer **4** in DMSO-*d*₆.

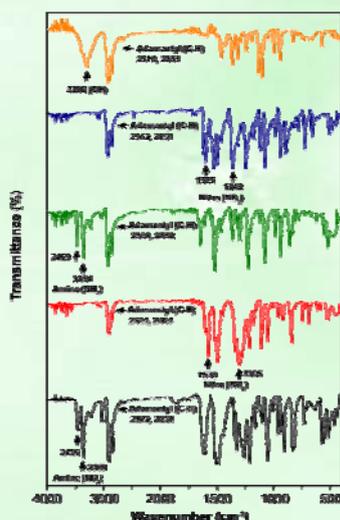
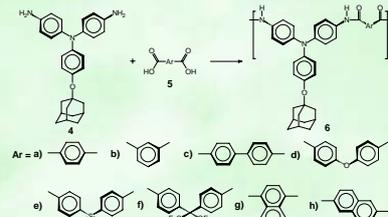
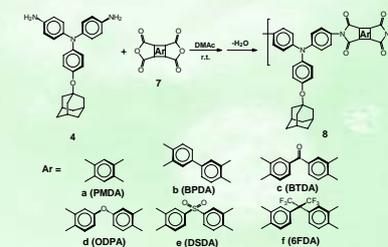


Figure 2. IR spectra of the raw material and all synthesized compounds.



Scheme 2. Synthesis of adamantoxy-based polyamides.



Scheme 3. Synthesis of adamantoxy-TPA containing polyimides.

Table 1. Inherent viscosity^a and solubility^b of polyamides and polyimides

Polymer Code	η_{inh}^a (dL/g)	Solvent ^c					
		NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
6a ^d	0.73	+++	+++	++	++	+++	---
6b	0.45	+++	+++	++	++	+++	---
6c	0.82	+++	+++	++	++	+++	---
6d	0.61	+++	+++	++	++	+++	---
6e	0.59	+++	+++	++	++	+++	---
6f	0.47	+++	+++	++	++	+++	---
6g	0.56	+++	+++	++	++	+++	---
6h	0.69	+++	+++	++	++	+++	---
8a	---	---	---	---	---	---	---
8b	---	---	---	---	---	---	---
8c	0.51	+++	++	++	++	+++	---
8d	0.60	+++	++	++	++	+++	---
8e	0.50	+++	++	++	++	+++	---
8f	0.44	+++	+++	++	++	+++	---

^a Inherent viscosity measured at a concentration of 0.5 dL/g in DMAc - 5 wt % LiCl at 30 °C.
^b Solubility: +++: soluble at room temperature; ++: partially soluble; +: soluble on heating; ---: insoluble even on heating.
^c Solvent: NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.
^d Values in parentheses are data of analogous polymer **6'**, ^d without adamantoxy substituent.

Table 2. Thermal behavior of polyamides and polyimides^a

Polymer code	T_g^b (°C)	T_d^c (°C)	T_d at 5 wt % loss ^d (°C)			Char yield ^e (%)	
			In N ₂	In air	In air		
6a	291 (295) ^f	285	445	448	500	495	72
6b	285 (290)	270	430	446	486	497	71
6c	294 (302)	290	459	456	502	509	71
6d	263 (273)	258	434	447	481	502	68
6e	284 (296)	276	442	449	484	486	65
6f	285 (295)	279	443	459	507	516	60
6g	283 (288)	278	454	460	500	406	65
6h	290 (307)	282	468	465	525	513	75
8a	---	286	480	489	503	538	50
8b	310 (331)	294	472	509	492	560	53
8c	311 (309)	292	488	506	522	547	64
8d	300 (326)	281	484	511	502	555	52
8e	307 (295)	304	436	477	460	503	43
8f	310 (316)	303	508	512	529	555	54

^a The polymer film samples were heated at 300 °C for 1 hr prior to all the thermal analyses.
^b The sample were heated from 50 to 400 °C at a scan rate of 20 °C/min followed by rapid cooling to 50 °C at -200 °C/min in nitrogen. The midpoint temperature of baseline shift on the subsequent DSC trace (from 50 to 400 °C at heating rate 20 °C/min) was defined as T_g .
^c Softening temperature measured by TMA using a penetration method.
^d Decomposition temperature at which a 5% or 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.
^e Residual weight percentages at 800 °C under nitrogen flow.

Table 3. Optical and Electrochemical Properties for Polyamides and Polyimides

Index x	$\lambda_{abs,max}$ (nm) ^a	$\lambda_{abs,onset}$ (nm) ^a	λ_{em} (nm) ^b	$E_{1/2}$ (V) ^c (vs. Ag/AgCl)	$E_{1/2}^{ox,d}$ (eV)	HOMO/LUMO (eV)
6a	360 (368)	434 (467)	456	0.78 (0.85) ^e	2.66	5.14/2.48
6b	341 (349)	376 (411)	422	0.80 (0.86)	3.02	5.16/2.14
6c	352 (357)	398 (431)	443	0.79 (0.86)	2.88	5.15/2.27
6d	338 (342)	372 (404)	426	0.78 (0.85)	3.07	5.14/2.07
6e	364 (368)	453 (482)	452	0.80 (0.87)	2.57	5.16/2.59
6f	342 (347)	411 (448)	426	0.81 (0.87)	2.77	5.17/2.40
6g	313 (335)	399 (422)	402	0.80 (0.86)	2.94	5.16/2.22
6h	349 (352)	440 (475)	433	0.78 (0.86)	2.61	5.14/2.53
8a	312 (371)	399 (599)	394	0.97 (1.17)	2.07	5.33/3.26
8b	322 (328)	366 (382)	400	0.98 (1.17)	3.25	5.34/2.09
8c	300 (301)	387 (432)	359	1.02 (1.17)	2.87	5.38/2.51
8d	316 (329)	362 (412)	391	1.05 (1.14)	3.01	5.41/2.40
8e	302 (308)	380 (427)	358	0.98 (1.17)	2.90	5.34/2.44
8f	301 (303)	369 (393)	368	1.04 (1.18)	3.16	5.40/2.24

^a Polymer concentration of 10⁻⁵ mol/L in NMP.
^b They were excited at absmax for both solid and solution states.
^c Half-wave potential vs Ag/AgCl in CH₂CN.
^d Optical energy gap was estimated from the absorption edge on the polymer film; $E_g^{opt} = 1240/\lambda_{onset}$.
^e The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV), LUMO = HOMO - 0.8 eV.
^f Values in parentheses are data of analogous polymer **6'**, ^d without adamantoxy substituent.

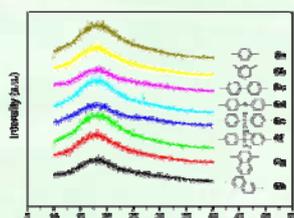


Figure 3. WAXD patterns of polyamide films.

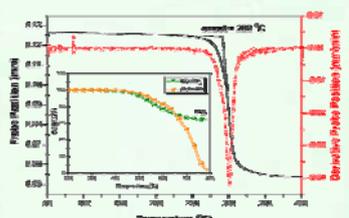


Figure 5. TMA and TGA curves of polyimide **8c** with heating rate of 10 and 20 °C/min.

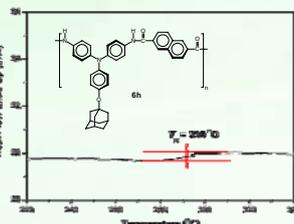


Figure 4. DSC trace of polyamide **6h** with heating rate of 20 °C/min.

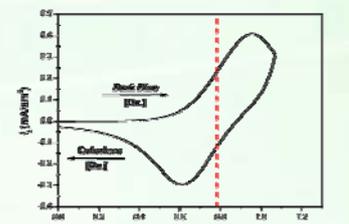


Figure 6. Cyclic voltammograms of polyamide **6d** film on an ITO-coated glass substrate in CH₂CN solutions containing 0.1 M TBAP at a scan rate of 50 mV/s. The arrows indicate the film color change during cyclic scan. $E_{1/2}$ values are indicated by dashed line.

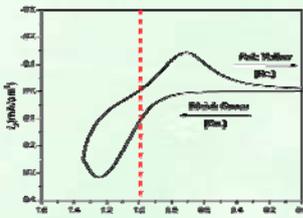


Figure 7. Cyclic voltammograms of polyamide **8e** film on an ITO-coated glass substrate in CH₂CN solutions containing 0.1 M TBAP at a scan rate of 50 mV/s. The arrows indicate the film color change during cyclic scan. $E_{1/2}$ values are indicated by dashed line.

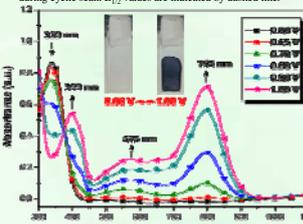


Figure 8. Electrochromic behavior of polyamide **6d** thin film (in CH₂CN with 0.1 M TBAP as the supporting electrolyte) at 0.00 (■), 0.65 (●), 0.70 (▲), 0.80 (▼), 0.90 (◆), and 1.00 (☆) (V vs. Ag/AgCl). The inset shows the photographic images of the film at indicated applied voltages.

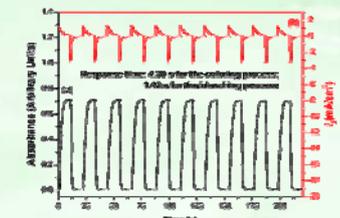


Figure 9. Potential step absorptometry and current consumption of polyamide **6d** by applying potential steps 0.00 to 0.10 (V vs. Ag/AgCl, coated area: 1 cm²).

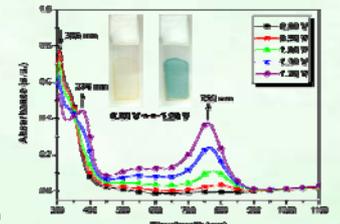


Figure 10. Electrochromic behavior of polyamide **8e** thin film (in CH₂CN with 0.1 M TBAP as the supporting electrolyte) at 0.00 (■), 0.90 (●), 1.00 (▲), 1.10 (▼), and 1.20 (◆) (V vs. Ag/AgCl).