

Synthesis and Electrochromic Properties of Aromatic Polyamides with Main-Chain 4-(Dimethylamino)triphenylamine Units

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ABSTRACT

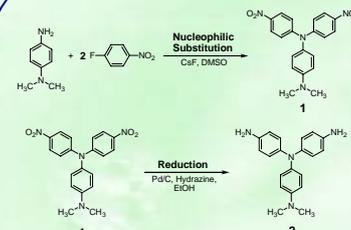
A new triphenylamine-based aromatic diamine monomer, 4,4'-diamino-4''-(dimethylamino)triphenylamine, was synthesized in high purity and high yields from readily available reagents. A series of novel 4-(dimethylamino)triphenylamine [(NMe₂)TPA]-functionalized aromatic polyamides were readily prepared from the newly synthesized diamine monomer with various aromatic dicarboxylic acids via the phosphorylation polyamidation reaction. These polyamides are readily soluble in many organic solvents and can be solution-cast into tough and amorphous films. The polyamides showed glass-transition temperatures (*T_g*) in the range of 277–298 °C (by DSC). Decomposition temperatures for 10% weight loss all occurred above 500 °C in both air and nitrogen atmospheres. The polymer films showed reversible electrochemical oxidation accompanied by strong color changes with high coloration efficiency, high contrast ratio, and rapid switching time. The polymers also displayed low ionization potentials as a result of the (NMe₂)TPA moieties. Cyclic voltammograms of the polyamide films on the indium-tin oxide (ITO)-coated glass substrate exhibited a pair of reversible oxidation waves with very low onset potential of 0.35 V (vs Ag/AgCl) in acetonitrile solution.

INTRODUCTION

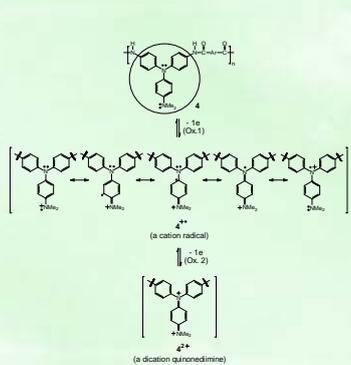
Electrochromism is known as the reversible change in optical absorption or transmittance upon redox switching.¹ This interesting property led to the development of many technological applications such as automatic anti-glazing mirror, smart windows, electrochromic displays, and chameleon materials.² Many different classes of electrochromic materials, such as organic systems, e.g., bipyridium salt (also known as viologens),³ electroactive conducting polymers (e.g., polyanilines,⁴ polythiophenes,⁵ polypyrroles),⁶ as well as inorganic systems based on transition metal oxides (e.g., WO₃)⁷ 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 the display of multiple colors with the same material while switching between their different redox states⁸ and fine-tuning of the color transition through chemical structure modification of the conjugated backbone.^{9,10} 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)¹¹ and poly(3,4-alkylenedioxyppyrole)s¹² and their derivatives. Triarylamines are well known for photo- and electroactive properties that find optoelectronic applications as photoconductors, hole-transporters, and light-emitters.¹³ 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 triarylamines-based electrochromic polymers have been reported in literature.¹⁴ 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.¹⁵ 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.

In order to be useful for applications, electrochromic materials must exhibit long-term stability, rapid redox switching, and large changes in transmittance (large Δ*T*%) between their bleached and colored states.¹⁴ As an electrochromic functional moiety, the TPA unit has two basic properties: (1) the easy oxidizability of the nitrogen center and (2) its hole-transporting ability via the radical cation species. However, unsubstituted TPA undergoes coupling-deprotonation to form tetraphenylbenzidine after the formation of the initial monoaradical.¹⁵ The oxidation potential and the π-π* bandgap of the product, generally called triaryldiamine, are different from that of the starting material. Therefore, the small concentration of the product may cause an unstable color change of the electrochromic material during redox switching. The formation of protons as by-products may deteriorate the coloration efficiency of the electrochromic devices through undesirable side reactions. It has been well established that incorporation of electron-donating substituents such as methoxy group at the para position of TPA prevents the coupling reaction and affords stable radical cations.^{16–18} It has also been demonstrated that carbazole derivatives with dimethylamino (NMe₂) groups para to the carbazole nitrogen could afford quite stable radical cations in the first one-electron oxidation process and reasonably stable dication quinonoidimines could also be generated by a second one-electron process. Therefore, we synthesized the diamine monomer, 4,4'-diamino-4''-(dimethylamino)triphenylamine [(NMe₂)TPA-diamine; 2], and its derived aromatic polyamides containing electroactive TPA units with electron-donating NMe₂ para substituted on the pendent phenyl ring. The NMe₂ substituents are expected to reduce the oxidation potential and increase the electrochemical stability and electroconductivity of the polyamides. We anticipated that the electrochromic films prepared from the present polyamides would be very stable to multiple redox switching and exhibit enhanced optical response times. For a comparative study, some properties of the present polyamides will be compared with those of structurally related ones based on 4,4'-diamino-4''-(diphenylamino)triphenylamine [(NPh₂)TPA-diamine; 2'] that has been reported previously.¹⁹

EXPERIMENTAL SECTION



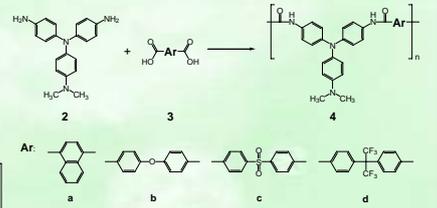
Scheme 1



Scheme 2

Compound 1 (dark red crystals) yield: 94%. mp: 182–183 °C (DSC, 2 °C/min). IR (KBr): 1577, 1340 cm⁻¹ (NO₂ stretch). ¹H NMR (DMSO-*d*₆, δ, ppm): 2.95 (s, 6H, methyl), 6.81 (d, 2H, H₂), 7.08 (d, 2H, H₃), 7.17 (d, 4H, H₄), 8.16 (d, 4H, H₅). ¹³C NMR (DMSO-*d*₆, δ, ppm): 40.3 (methyl), 61.5 (C¹), 121.4 (C²), 125.4 (C³), 128.6 (C⁴), 132.3 (C⁵), 141.4 (C⁶), 149.3 (C⁷), 151.8 (C⁸). Anal. Calcd (%) for C₁₈H₁₈N₄O₂ (378.38): C, 63.49; H, 4.79; N, 14.81. Found: C, 63.37; H, 4.85; N, 14.75.

Compound 2 (pale-green crystals) yield: 85%. mp: 177–178 °C (DSC, 2 °C/min). IR (KBr): 3417, 3340 cm⁻¹ (N-H stretch). ¹H NMR (DMSO-*d*₆, δ, ppm): 2.77 (s, 6H, methyl), 4.74 (s, 4H, -NH₂), 6.47 (d, 4H, H₂), 6.61 (d, 2H, H₃), 6.65 (d, 4H, H₄), 6.72 (d, 2H, H₅). ¹³C NMR (DMSO-*d*₆, δ, ppm): 40.8 (methyl), 113.7 (C¹), 114.7 (C²), 122.6 (C³), 124.6 (C⁴), 138.1 (C⁵), 139.5 (C⁶), 143.4 (C⁷), 145.2 (C⁸). Anal. Calcd (%) for C₂₀H₂₂N₄ (318.42): C, 75.44; H, 6.96; N, 17.60. Found: C, 75.43; H, 6.93; N, 17.64.



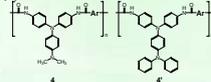
Polymer Synthesis. The synthesis of polyamide 4b was used as an example to illustrate the general synthetic route used to produce the polyamides. A mixture of 0.318 g (1.0 mmol) of the (NMe₂)TPA-diamine monomer 2, 0.258 g (1.0 mmol) of 4,4'-oxydibenzoic acid (3b), 0.1 g of calcium chloride, 1.0 mL of triphenyl phosphite (TPP), 0.5 mL of pyridine, and 2.0 mL of *N*-methyl-2-pyrrolidone (NMP) was heated with stirring at 110 °C for 3 h. The obtained polymer solution was poured slowly into 300 mL of stirred methanol giving rise to a stringy, fibrous precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried under vacuum at 100 °C. Reprecipitations of the polymer by *N,N*-dimethylacetamide (DMAc)/methanol were carried out twice for further purification. The inherent viscosity of the obtained polyamide 4b was 1.64 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

RESULTS AND DISCUSSION

Table 1. Inherent Viscosity, Film Color and Solubility Behavior of Polyamides

| Polymer | Solubility in various solvents ^a | | | | | | | | |
|---------|---|---------------|-----|------|-----|------|------------------|-----|------------|
| Code | η_{inh}^b (dL/g) | Color of film | NMP | DMAc | DMP | DMSO | <i>m</i> -Cresol | THF | Chloroform |
| 4a | 1.15 | yellow | ++ | ++ | ++ | ++ | ++ | ++ | ++ |
| 4b | 1.64 | yellow | ++ | ++ | ++ | ++ | ++ | ++ | ++ |
| 4c | 0.89 | yellow | ++ | ++ | ++ | ++ | ++ | ++ | ++ |
| 4d | 0.77 | yellow | ++ | ++ | ++ | ++ | ++ | ++ | ++ |
| 4e | 0.53 | yellow | ++ | ++ | ++ | ++ | ++ | ++ | ++ |
| 4f | 0.53 | yellow | ++ | ++ | ++ | ++ | ++ | ++ | ++ |
| 4g | 0.53 | yellow | ++ | ++ | ++ | ++ | ++ | ++ | ++ |

^a Structures of the polymers:



^b Measured at a polymer concentration of 0.5 g/dL in DMAc: 5 wt % LiCl at 30 °C.

^c The photographs are the appearance of the polymer films (thickness: 1.5–2 μm).

^d The solubility was determined with a 1 mg sample in 1 mL of a solvent. ++, soluble at room temperature; +, soluble on heating; --, partially soluble or swelling; ---, insoluble even on heating.

Table 2. Thermal Properties of Polyamides^a

| Polymer code ^b | <i>T_g</i> (°C) | <i>T_g</i> at 5 wt % loss (°C) | <i>T_g</i> at 10 wt % loss (°C) | Char yield (%) |
|---------------------------|---------------------------|--|---|----------------|
| 4a | 283 | 492 | 466 | 25.8 |
| 4b | 277 | 514 | 491 | 56.9 |
| 4c | 295 | 475 | 485 | 51.4 |
| 4d | 298 | 504 | 520 | 56.6 |
| 4e | 263 | 504 | 502 | 54.6 |
| 4f | 287 | 486 | 489 | 54.9 |

^a The polymer film samples were heated at 300 °C for 1 h prior to all the thermal analyses.

^b Midpoint temperature of baseline shift on the heating DSC trace (from 50 to 400 °C at 20 °C/min).

^c Decomposition temperature at which a 5% or 10% weight loss was recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 20 cm³/min.

^d Residual weight percentages at 800 °C under nitrogen flow.

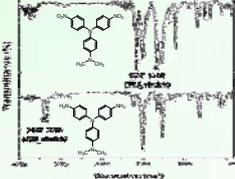


Figure 1. IR spectra of compounds 1 and 2.

Table 3. Redox Potentials and Energy Levels of Polyamides

| Polymer | UV-vis absorption of the polymer films (nm) | | Oxidation potential (V vs. Ag/AgCl in CH ₂ Cl ₂) | | HOMO (eV) | LUMO (eV) |
|---------|---|-----------------|---|------------------------------------|-----------|-----------|
| | λ_{max} | λ_{cut} | <i>E</i> ₁ ^a | <i>E</i> ₂ ^b | | |
| 4a | 320 | 460 | 0.44 | 0.88 | 0.32 | 2.70 |
| 4b | 343 | 440 | 0.47 | 0.91 | 0.38 | 2.82 |
| 4c | 320 | 490 | 0.41 | 0.91 | 0.37 | 2.53 |
| 4d | 346 | 454 | 0.45 | 0.91 | 0.35 | 2.73 |
| 4e | 348 | 398 | 0.63 | 1.00 | 0.53 | 2.95 |
| 4f | 321 | 467 | 0.65 | 1.03 | 0.52 | 2.51 |

^a *E*₁: (Average potential of the redox couple peaks).

^b The data were calculated from polymer films by the equation: *E*₂ = 1240/λ_{cut} (energy gap between HOMO and LUMO).

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

Table 4. Coloration Efficiency of Polyamide 4b

| Cycles ^a | ΔOD ₅₀₀ ^b | Q (cm ² /cm ²) ^c | η (cm ² /Cf) ^d | Decay (%) ^e |
|---------------------|---------------------------------|--|--------------------------------------|------------------------|
| 1 | 0.176 | 0.727 | 242 | 0 |
| 50 | 0.191 | 0.802 | 238 | 1.7 |
| 100 | 0.185 | 0.797 | 232 | 4.1 |
| 150 | 0.182 | 0.801 | 227 | 6.2 |
| 200 | 0.176 | 0.796 | 221 | 8.7 |
| 250 | 0.168 | 0.770 | 218 | 9.9 |
| 300 | 0.169 | 0.793 | 213 | 12.0 |
| 350 | 0.176 | 0.842 | 209 | 13.6 |
| 400 | 0.173 | 0.848 | 204 | 15.7 |
| 450 | 0.168 | 0.848 | 198 | 18.2 |
| 500 | 0.168 | 0.870 | 193 | 20.2 |

^a Times of cyclic scan by applying potential steps: 0.00 ↔ 0.55 V (vs. Ag/AgCl).

^b Optical density change at 805 nm.

^c Ejected charge, determined from the *in situ* experiments.

^d Coloration efficiency is derived from the equation: η = ΔOD₅₀₀/Q.

^e Decay of coloration efficiency after cyclic scans.

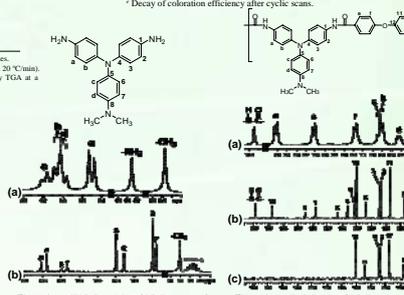


Figure 2. (a) ¹H NMR and (b) ¹³C NMR spectra of (NMe₂)TPA-diamine monomer 2 in DMSO-*d*₆. (c) DEPT-135 spectra of polyamide 4b in DMSO-*d*₆.

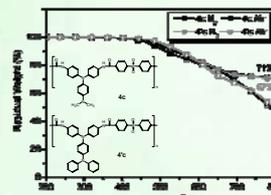


Figure 3. TGA thermograms of polyamides 4c and 4e at a scan rate of 20 °C/min.

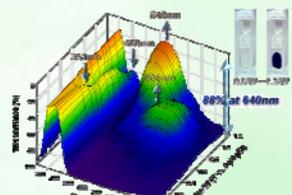


Figure 4. 3-D spectroelectrochemical behavior of the 4b thin film on the ITO-coated glass substrate in CH₂Cl₂ with 0.1 M TBAP as the supporting electrolyte from 0 to 1.2 V (vs. Ag/AgCl).

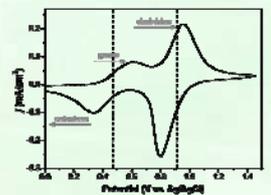


Figure 5. Cyclic voltammograms of the polyamide 4b film on an ITO-coated glass substrate in CH₂Cl₂ solutions containing 0.1 M TBAP at a scan rate of 50 mV/s. The arrows indicate the film color change during CV scan. *E*₁ and *E*₂ values are indicated by dashed lines.

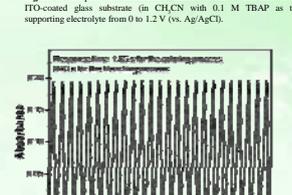


Figure 6. (a) Potential step absorptometry and (b) current consumption of the polyamide 4b film on the ITO-coated glass substrate (coated area: 1 cm²) during the continuous cycling test by switching potentials between 0 and 0.55 V (vs. Ag/AgCl).

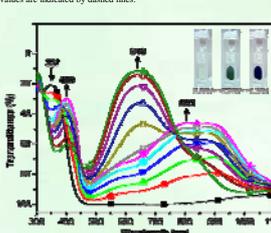


Figure 7. Spectral change of 4b thin film on the ITO-coated glass substrate (in CH₂Cl₂ with 0.1 M TBAP as the supporting electrolyte) along with increasing of the applied voltage: (●) 0.40, (○) 0.50, (▲) 0.55, (▼) 0.60, (◇) 0.70, (★) 0.80, (□) 0.90, (△) 0.95, (▽) 1.00, (◇) 1.10, (○) 1.20 V (vs. Ag/AgCl) couple as reference. The inset shows the photographic images of the film at indicated applied voltages.

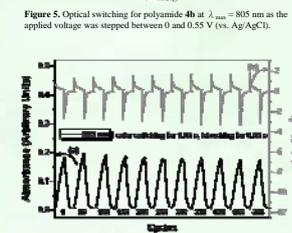


Figure 8. (a) Potential step absorptometry and (b) current consumption of the polyamide 4b film on the ITO-coated glass substrate (coated area: 1 cm²) during the continuous cycling test by switching potentials between 0 and 0.55 V (vs. Ag/AgCl).

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