

Synthesis, Photoluminescence, and Electrochromism of Aromatic Polyamides Based on 4,4'-Dicarboxy-4''-(3,6-di-*tert*-butylcarbazol-9-yl)triphenylamine

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ABSTRACT

A new carbazole-derived, triphenylamine-containing aromatic dicarboxylic acid monomer, 4,4'-dicarboxy-4''-(3,6-di-*tert*-butylcarbazol-9-yl)triphenylamine (**5**), was synthesized by a well known chemistry from readily available reagents. A series of novel aromatic polyamides with main-chain triphenylamine and pendent 3,6-bis(*tert*-butyl)carbazole units were prepared from the newly synthesized dicarboxylic acid monomer and various aromatic diamines by the Yamazaki-Higashi phosphorylation polyamidation technique. These polyamides were amorphous with good solubility in many organic solvents and could be solution-cast into flexible polymer films. They had useful levels of thermal stability associated with relatively high glass-transition temperatures (282–335 °C), 10% weight loss temperatures in excess of 480 °C, and char yields at 800 °C in nitrogen higher than 66%. These polymers exhibited strong UV-vis absorption maxima at 346–352 nm, and their photoluminescence showed emission peaks around 457–505 nm with quantum yields up to 32% in dilute NMP solution. The hole-transporting and electrochromic properties were examined by electrochemical and spectro-electrochemical methods. Cyclic voltammograms of the polyamide films prepared by casting polymer solution onto an indium-tin oxide (ITO)-coated glass substrate exhibited two reversible oxidative redox couples at 1.00–1.11 V and 1.34–1.41 V versus Ag/AgCl in acetonitrile solution. The polyamide films revealed excellent stability of electrochromic characteristics, with a color change from colorless or pale yellowish neutral form to green and blue oxidized forms at applied potentials ranging from 0.0 to 1.5 V.

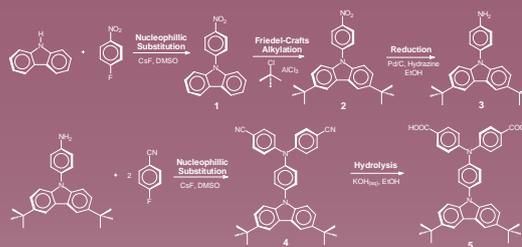
INTRODUCTION

Electrochromism is defined as a reversible and visible change in the transmittance and/or reflectance of a material as the result of electrochemical oxidation or reduction.¹ The property of electrochromism is not unique to conducting polymers but is found in a variety of organic and inorganic materials. The drastic change in the optical absorption spectrum of conducting polymers upon doping makes these materials useful for the construction of electrochromic devices. Significant effort has been put forth on electrochromic devices based on inorganic electrochromic systems such as tungsten oxide (WO₃). In general, a higher coloration efficiency and enhanced processibility of organic polymers suggest these materials may prove even more useful. Considerable effort in the Reynolds group has been focused on the understanding and the tailoring of electrochromic properties in conducting polymers such as poly(3,4-alkylenedioxythiophene)s and poly(3,4-alkylenedioxy pyrrole)s.² These conjugated polymers have demonstrated fast switching capabilities and a high degree of color tailorability.

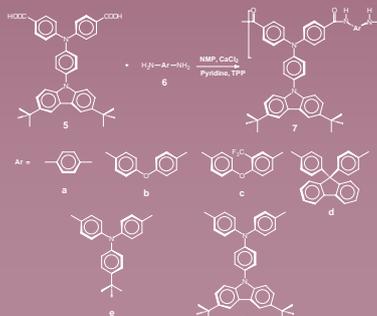
Triarylamine derivatives are well known for photo- and electroactive properties that find optoelectronic applications as photoconductors, hole-transporters, and light-emitters.³ Triarylamines can be easily oxidized to form stable radical cations, and the oxidation process is always associated with a noticeable change of coloration. 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.⁴ 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 the polymers exhibit good solubility in polar organic solvents and could be easily solvent cast into morphologically stable films.

Carbazole is another well-known hole-transporting and electrochromic unit. Polymers containing carbazole moieties in the main chain or side chain have attracted much attention because of their unique properties, which allow various optoelectronic applications such as photoconductive, electroluminescent, and photorefractive materials.⁵ We recently reported on the polyamides bearing main-chain triphenylamine and pendent carbazole units from the dicarboxylic acid monomer 4,4'-dicarboxy-4''-*N*-carbazolyltriphenylamine.^{6(a)} The polyamides could afford amorphous and high-*T_g* films with useful mechanical properties (e.g., flexibility). They also reveal good redox stability for the first oxidation state, and the oxidation process is always associated with a noticeable change of the coloration. However, the second oxidation process of these polymers is not reversible, possibly due to the electrochemical coupling of carbazoles through the active C-3 and C-6 sites. In this study, a molecular-design strategy to retain the useful properties of such polymers while enhancing the redox stability by substitution of the C-3 and C-6 positions of the carbazole unit with bulky *tert*-butyl groups is reported. Thus, a novel carbazole-derived, TPA-containing dicarboxylic acid monomer **5** was synthesized and led to a series of novel aromatic polyamides with main-chain TPA and pendent 3,6-bis(*tert*-butyl)carbazole units. The *tert*-butyl groups are expected to increase the solubility and to give extra electrochemical stability of the resulting polymers.

EXPERIMENTAL



Scheme 1. Synthesis of dicarboxylic acid monomer **5**.



Scheme 2. Synthesis of polyamides **7a-7f**.

Compound 1 (yellow crystals)

yield: 97 %; mp: 208–209 °C;
IR (KBr): 1594, 1326 cm⁻¹ (NO₂ stretch).

Compound 2 (yellow crystals)

yield: 98 %; mp: 234–235 °C;
IR (KBr): 2952 cm⁻¹ (t-butyl C–H stretch),
1594, 1326 cm⁻¹ (NO₂ stretch).

Compound 3 (white powders)

yield: 86 %; mp: 221–222 °C;
IR (KBr): 3442, 3336 cm⁻¹ (N–H stretch)

Compound 4 (yellowish needles)

yield: 60 %; mp: 338–341 °C;
IR (KBr): 2217 cm⁻¹ (C=N stretch)

Compound 5 (yellowish powders)

yield: 82 %; mp: 364–366 °C;
IR (KBr): 2400–3400 cm⁻¹ (O–H stretch),
1687 cm⁻¹ (C=O stretch).

Polymer Synthesis

According to the phosphorylation technique described by Yamazaki and co-workers,⁶ a series of novel aromatic polyamides (**7a–7f**) with 3,6-di-*tert*-butylcarbazol-9-yl-substituted TPA units were synthesized from the dicarboxylic acid monomer **5** and aromatic diamines **6a–f** using triphenyl phosphite (TPP) and pyridine as condensing agents (Scheme 2). As shown in Table 1, the obtained polyamides had inherent viscosities in the range of 0.26–0.63 dL/g and could be solution-cast into flexible and tough films, indicating the formation of high molecular weight polymers.

Film Preparation of Polyamides

A solution of polymer was made by dissolving about 0.6 g of the polymer sample in 10 mL of DMAc. The homogeneous solution was poured into a 9-cm glass Petri dish, which was placed in a 90 °C oven overnight for the slow release of the solvent, and then the film was stripped off from the glass substrate and further dried in vacuum at 160 °C for 6 h. The obtained film with the thickness of about 50–60 μm were used for solubility tests, thermal analyses, optical and electrochemical properties measurements.

RESULTS AND DISCUSSION

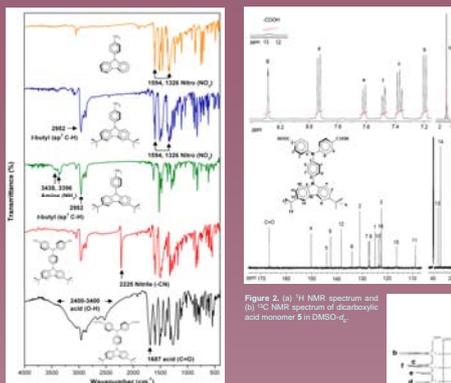


Figure 1. IR spectra of all the synthesized compounds **1-5**.

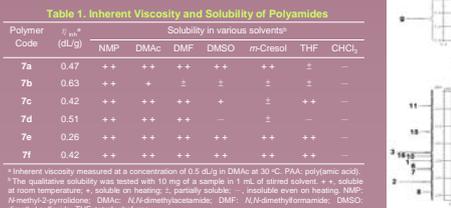


Figure 2. (a) ¹H NMR spectrum and (b) ¹³C NMR spectrum of dicarboxylic acid monomer **5** in DMSO-*d*₆.

Figure 3. (a) ¹H COSY and (b) C–H HMBC spectra of monomer **5** in DMSO-*d*₆.

Table 2. Thermal Properties of Polyamides^a

| Polymer code | <i>T_g</i> ^b (°C) | <i>T₅</i> ^c (°C) | <i>T₁₀</i> ^d at 10 wt % loss (°C) | | Char yield ^e at 800 °C (wt %) |
|--------------|--|--|---|--------|--|
| | | | In N ₂ | In air | |
| 7a | 335 | 303 | 518 | 503 | 71 |
| 7b | 282 | 265 | 482 | 507 | 66 |
| 7c | 293 | 282 | 482 | 482 | 66 |
| 7d | 352 | 308 | 541 | 541 | 68 |
| 7e | 323 | 295 | 505 | 518 | 68 |
| 7f | 320 | 295 | 546 | 537 | 69 |

^a The polymer film samples were heated at 300 °C for 30 min prior to all the thermal analyses.
^b Midpoint temperature of the baseline shift on the second DSC heating trace (rate = 20 °C/min) of the sample after quenching from 400 to 50 °C (rate = 200 °C/min) in nitrogen.
^c Softening temperature measured by TMA with a constant applied load of 10 mN at a heating rate of 10 °C/min.
^d Decomposition temperature, recorded by TGA at a heating rate of 20 °C/min and a gas-flow rate of 30 mL/min.
^e Residual weight percentage at 800 °C in nitrogen.

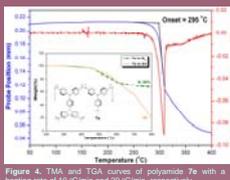


Figure 4. TMA and TGA curves of polyamide **7e** with a heating rate of 10 °C/min and 20 °C/min, respectively.

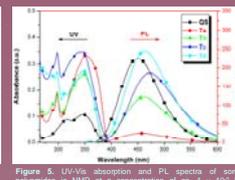


Figure 5. UV-Vis absorption and PL spectra of some polyamides in NMP at a concentration of ca. 1×10^{-4} M. References: quinine sulfate (ca. 1×10^{-4} M) in 1 N H₂SO₄.

Table 3. Optical and Electrochemical Properties of Polyamides

| Polymer code | In solution | | As film | | Oxidation potential ^a (V) (vs. Ag/AgCl in CH ₃ CN) | | | | <i>E₁</i> ^c (eV) | HOMO ^d (eV) | LUMO ^e (eV) | | | | |
|--------------|-----------------------------------|-----------------------------------|----------------------|----------------------|--|------------------------|------------------------|------------------------|--|------------------------|------------------------|------|------|------|------|
| | abs | PL | abs | abs | First | Second | Third | Fourth | | | | | | | |
| | λ_{max} (nm) ^b | λ_{max} (nm) ^b | λ_{max} (nm) | λ_{max} (nm) | <i>E_{ox1}</i> | <i>E_{ox2}</i> | <i>E_{ox3}</i> | <i>E_{ox4}</i> | | | | | | | |
| 7a | 298, 352 | 457 | 2.9 | 298, 350 | 389 | 0.91 | 1.10 | 1.41 | — | — | 3.19 | 5.27 | 5.47 | 2.09 | 2.28 |
| 7b | 298, 351 | 462 | 17.0 | 299 | 386 | 0.97 | 1.09 | 1.34 | — | — | 3.21 | 5.33 | 5.45 | 2.12 | 2.24 |
| 7c | 298, 348 | 466 | 21.3 | 298, 346 | 400 | 0.92 | 1.04 | 1.32 | — | — | 3.10 | 5.28 | 5.40 | 2.18 | 2.30 |
| 7d | 298, 348 | 465 | 32.8 | 300, 347 | 394 | 0.91 | 1.03 | 1.30 | — | — | 3.15 | 5.27 | 5.39 | 2.12 | 2.24 |
| 7e | 298, 351 | 505 | 0.4 | 303 | 392 | 0.60 | 0.70 | 1.10 | 1.34 | — | 3.16 | 5.06 | 5.17 | 1.90 | 2.02 |
| 7f | 298, 351 | 493 | 0.5 | 300 | 421 | 0.65 | 0.71 | 1.14 | 1.25 | 1.38 | 2.95 | 5.07 | 5.20 | 2.12 | 2.25 |

^a Measured in dilute solution in NMP at a concentration of about 10^{-4} mol/L. ^b The quantum yield in dilute solution was calculated in an integrating sphere with quinine sulfate as the standard ($\Phi_f = 54.6\%$). ^c Oxidation potentials from cyclic voltammograms. ^d Energy gap = 1240 Åbs. ^e onset of the polymer film. ^f The HOMO energy levels were calculated from *E_{ox1}* and were referenced to ferrocene (4.8 eV). LUMO = HOMO - *E_g*.

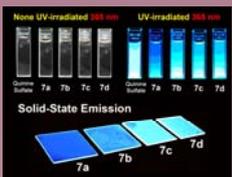


Figure 6. PL images of the dilute solutions and thin film of polyamides **7a-7d** before and upon UV exposure (excited at 365 nm).

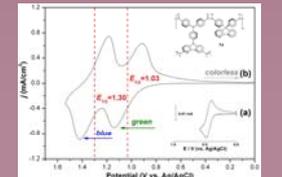


Figure 7. Cyclic voltammograms of (a) ferrocene and (b) polyamide **7d** at 0.1 V/s in 0.1 M TBAP in acetonitrile. The arrows indicate the film color change during CV scans. *E_{ox1}* values are indicated by dashed lines.

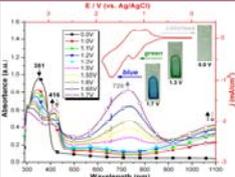


Figure 8. Electrochromic behavior of polyamide **7a** thin film in CH₃CN with 0.1 M TBAP as the supporting electrolyte at 0.0 (A), 0.5 (B), 1.0 (C), 1.5 (D), 2.0 (E), 2.5 (F), and 3.0 (G) V (vs. Ag/AgCl).

CONCLUSION

The new carbazole-based aromatic dicarboxylic acid monomer, 4,4'-dicarboxy-4''-(3,6-di-*tert*-butylcarbazol-9-yl)triphenylamine (**5**) was successfully synthesized in high purity and good yield. Novel blue-light-emitting aromatic polyamides bearing pendent *N*-phenylcarbazole units were readily prepared from the newly synthesized dicarboxylic acid monomer and various aromatic diamines by direct phosphorylation polycondensation. All the polyamides were amorphous with high *T_g* and exhibited excellent thermal stability. These polymers exhibited blue photoluminescence both in film and in solution with quantum yield up to 32%. All obtained polyamides revealed good stability of electrochromic characteristics for oxidation state, changing color from the original pale yellowish to green, and then to deep blue. Thus, these polyamides can be employed as potential candidates in the development of electrochromic and EL devices due to their suitable HOMO values, excellent thermal stability and reversible electrochemical redox behavior.

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