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

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ABSTRACT: A novel adamantoxytriphenylamine-containing diamine monomer, 4-(1-adamantoxy)-4,40,400-diaminotriphenylamine, was synthesized from readily available reagents. Two series of novel electroactive aromatic polyamides and polyimides with bulky 4-(1-adamantoxy)triphenylamine moieties were prepared from the newly synthesized diamine monomer with various aromatic dicarboxylic acids and tetracarboxylic dianhydrides, respectively. All the resulting polyamides and most of the polyimides were readily soluble in polar organic solvents and could be solution cast into tough and flexible films. These polymers showed moderate to high glass transition temperatures in the range of 263–311 °C, and they were fairly stable up to a temperature above 480 °C (for polyamides) or 500 °C (for polyimides). Cyclic voltammograms of the polyamides and polyimides showed one pair of reversible redox waves with oxidation half-wave potentials ($E_{1/2}$) in the range of 0.78–0.81 and 0.97–1.05 V, respectively, versus Ag/AgCl in an acetonitrile solution. In addition, the polymers were found to display stable electrochromic properties by repeated cyclic scans between 0.0 and 1.1–1.2 V, with coloration change from a colorless or pale yellowish neutral form to a dark blue or bluish green oxidized form. © 2009 Wiley Periodicals, Inc.

Keywords: adamantane; electrochemistry; electrochromism; polyamides; polyimides; triphenylamine

INTRODUCTION

Aromatic polyamides and polyimides are well-known high-performance polymers that have excellent thermal, mechanical and electrical properties as well as outstanding chemical resistance. However, most of them have high melting or softening temperature and are insoluble in most of organic solvents because of the rigidity of the backbone and strong interchain interactions. These properties make them generally intractable or difficult to process; thus, their applications are restricted in some fields. To overcome these limitations, many efforts have been made to improve the processing characteristics of these intractable polymers while other advantageous properties are...
been several reports on PPV and PF derivatives (polyphenylenevinylene)s (PPV) and polyfluorenes (PF), there have been emissive materials such as poly(1,4-phenylenevinylene) (PVP) and polyfluorenes (PF), which exhibit high thermal stability.\(^{17-24}\) In recent years, we have reported that many TPA-based polymides and polyamides show interesting electrochromic properties and some of them are very stable toward redox cycling, which makes them potential candidates for commercial device applications.\(^{25-35}\)

TPA derivatives are easily oxidized and so they are interesting materials for hole-transport function in various electro-optical applications.\(^{36-40}\) To improve the hole-transporting ability of polymeric emissive materials such as poly(1,4-phenylenevinylene) (PPV) and polyfluorenes (PF), there have been several reports on PPV and PF derivatives incorporating TPA or triarylamino moiety in the emissive \(\pi\)-conjugated core/main chains or attaching them onto the polymer backbone because of their electron-rich property.\(^{41-46}\) In the electrochemical oxidation of TPAs in acetonitrile, it has been proposed that the initial step is the formation of the cation radical; two of these then couple in solution to form a substituted tetraphenylbenzidine.\(^{47}\) Quantitative data have been obtained for several 4-substituted TPAs in the form of second-order coupling rate constants, and it was generally found that electron-donating substituents such as methoxy group tended to stabilize the cation radicals whereas electron-withdrawing groups had the opposite effect.\(^{48}\)

Adamantane (tricyclo[3.3.1.1\(^{8,7}\)]decane) is a highly symmetrical tricyclic hydrocarbon, which consists of fused chair-form cyclohexane rings.\(^{49}\) The unique structure of this substance is reflected in highly unusual physical and chemical properties such as thermal and oxidation stabilities, low surface energy, and high hydrophobicity. The incorporation of adamantyl groups into aromatic polyamides and polyimides has been reported to improve solubility or dielectric properties while retaining high thermal stability and glass transition temperatures.\(^{50-57}\) The improvement of solubility and thermal properties of adamantyl containing polymers results from the rigidity and the bulkiness of the adamantyl moiety, which greatly reduce the chain mobility and inhibit chain packing. In the present study, we therefore synthesized the new diamine monomer, 4-(1-adamantoxy)-4’,4’’-diaminotriphenylamine, and its derived aromatic polyamides and polyimides containing electroactive TPA units with bulky electron-donating adamantoxo group para substituted on the pendant 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, electron-donating adamantoxo group.

**EXPERIMENTAL**

Materials

\(N,N\)-Dimethylacetamide (DMAc) (Tedia), \(N,N\)-dimethylformamide (DMF) (Tedia), pyridine (Py) (Wako) and \(N\)-methyl-2-pyrrolidone (NMP) (Tedia) were dried over calcium hydride for 24 h, distilled under reduced pressure, and stored over 4 Å molecular sieves in a sealed bottle. The commercially available aromatic dicarboxylic acids that included terephthalic acid (5a) (Wako), isophthalic acid (5b) (Wako), 4,4’-biphenyldicarboxylic acid (5c) (TCI), 4,4’-dicarboxydiphenyl ether (5d) (TCI), bis(4-carboxyphenyl) sulfone (5e) (New Japan Chemicals.), 2,2-bis(4-carboxyphenyl)hexafluoropropane (5f) (TCD), 1,4-naphthalenedicarboxylic acid (5g) (Wako), 2,6-naphthalenedicarboxylic acid (5h) (TCD) were used as received. Commercially obtained calcium chloride was dried under vacuum at 180 °C for 8 h before use. Commercially available aromatic tetraacarboxylic dianhydrides such as pyromellitic dianhydride (PMDA; 7a, from Aldrich) and 3,3’,4,4’-benzophenonetetracarboxylic dianhydride (BTDA; 7c, from Aldrich) were purified by recrystallization from acetic anhydride. 3,3’,4,4’-Biphenyltetraacarboxylic dianhydride (BPDA; 7b, from Oxychem), 4,4’-oxydiphthalic anhydride (ODPA; 7d, from Oxychem), 3,3’,4,4’-diphenylsulfonetetracarboxylic dianhydride (DSDA; 7e, from New Japan Chemical.), and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA; 7f, from Hoechst Celanese) were heated at 250 °C in vacuo for 3 h before use. Tetrabutylammonium perchlorate (TBAP) (TCI) was recrystallized twice by ethyl acetate under nitrogen atmosphere and then dried.
in vacuo before use. All other reagents were used as received from commercial sources.

Synthesis of Adamantoxo-TPA Diamine Monomer 4

4-(1-Adamantoxo)nitrobenzene (1)

A mixture of 6.0 g (0.15 mol) of sodium hydride (NaH) (60% in mineral oil) and 22.8 g (0.15 mol) of 1-adamantanol in 120 mL of anhydrous DMF was stirred at room temperature for about 30 min. Then, 21.9 g (0.16 mol) of 4-fluoronitrobenzene were added to the suspension solution, and the mixture was heated with stirring at 120 °C for 18 h. After cooling to room temperature, the reaction solution was poured into 800 mL of stirred methanol, and then the precipitated product was filtered and dried to afford 26.7 g (65% in yield) of pale yellow crystals with a mp of 134–135 °C.

FT-IR (KBr): 2912, 2851 cm⁻¹ (adamantyl C-H stretch), 1585, 1342 cm⁻¹ (nitro N=O stretch), 1228, 1055 cm⁻¹ (Ar-O-Ar stretch). ¹H NMR (500 MHz, DMSO-d₆, δ, ppm): 1.61 (s, 6H, Hₐ), 1.92 (s, 6H, Hₐ), 2.17 (s, 3H, Hₐ), 7.21 (d, J = 8.6 Hz, 2H, Hₐ), 8.16 (d, J = 8.6 Hz, 2H, Hₐ). ¹³C NMR (125 MHz, DMSO-d₆, δ, ppm): 30.3 (C₂), 35.3 (C₁), 41.8 (C₃), 79.8 (C₄), 123.3 (C₆), 124.9 (C₇), 142.4 (C₈), 160.6 (C₉).

4-(1-Adamantoxo)aniline (2)

In a 300-mL three-neck round-bottomed flask, a mixture of 19.1 g (0.07 mol) of nitro compound 1, 10 mL of hydrazine monohydrate, and 200 mL of ethanol was stirred at a reflux temperature under nitrogen atmosphere for about 10 h. The solution was filtered while hot to remove Pd/C, and the filtrate was washed thoroughly by methanol and water, and recrystallized twice from DMF/methanol to afford 16.0 g (94% in yield) of pure amino compound 2 with a mp of 176–177 °C.

FT-IR (KBr): 3469, 3354 cm⁻¹ (N-H stretch), 2908, 2852 cm⁻¹ (adamantyl C-H stretch), 1211, 1060 cm⁻¹ (C=O stretch). ¹H NMR (500 MHz, DMSO-d₆, δ, ppm): 1.51, 1.57 (two AB doublets, J = 12.0 Hz, 6H, Hₐ), 1.71 (broad singlet (brs), 6H, Hₐ), 2.09 (brs, 3H, Hₐ), 4.73 (s, 2H, -NH₂), 6.44 (d, J = 8.6 Hz, 2H, Hₐ), 6.60 (d, J = 8.6 Hz, 2H, Hₐ). ¹³C NMR (125 MHz, DMSO-d₆, δ, ppm): 30.0 (C₂), 35.7 (C₁), 42.3 (C₃), 75.4 (C₄), 113.9 (C₅), 124.9 (C₆), 143.2 (C₇), 144.6 (C₈).

4-(1-Adamantoxo)-4’,4”-dinitrotriphenylamine (3)

To a solution of 12.2 g (0.05 mol) of compound 2 and 14.3 g (0.1 mol) of 4-fluoronitrobenzene in 120 mL of dried dimethyl sulfoxide (DMSO), 15.3 g (0.1 mol) of cesium fluoride (CsF) was added with stirring all at once, and the mixture was heated at 150 °C for 18 h under nitrogen atmosphere. The mixture was poured into 800 mL of stirred methanol slowly, and the precipitated compound was collected by filtration, washed thoroughly by methanol and water, and recrystallized twice from DMF/methanol to afford 20.2 g (83% in yield) of golden crystals with a mp of 200–201 °C.

FT-IR (KBr): 2914, 2854 cm⁻¹ (adamantyl C-H stretch), 1579, 1305 cm⁻¹ (nitro N=O stretch), 1220, 1055 cm⁻¹ (nitro N=O stretch). ¹H NMR (500 MHz, DMSO-d₆, δ, ppm): 1.60 (two overlapped AB doublets, J = 12.4 Hz, 6H, Hₐ), 1.85 (brs, 6H, Hₐ), 2.15 (brs, 3H, Hₐ), 7.08 (d, J = 8.6 Hz, 2H, Hₐ), 7.17 (d, J = 8.6 Hz, 2H, Hₐ), 7.19 (d, J = 9.0 Hz, 2H, Hₐ), 8.18 (d, J = 9.0 Hz, 4H, Hₐ). ¹³C NMR (125 MHz, DMSO-d₆, δ, ppm): 30.2 (C₂), 35.5 (C₁), 42.2 (C₃), 77.6 (C₄), 122.0 (C₁₀), 125.5 (C₁₁), 125.9 (C₈), 128.1 (C₇), 139.4 (C₉), 141.8 (C₁₂), 151.6 (C₈), 152.8 (C₅).
4-(1-Adamantoxy)-4',4'-diaminotriphenylamine (4)

In a 500-mL three-neck round-bottomed flask equipped with a stirring bar under nitrogen atmosphere, 20.0 g (0.04 mol) of dinitro compound 3 and 0.2 g of 10% Pd/C were dissolved/suspended in 250 mL of ethanol. The suspension solution was heated to reflux, and 12 mL of hydrazine monohydrate was added slowly to the mixture, then the solution was stirred at reflux temperature. After a further 8 h of reflux, the solution was filtered to remove Pd/C, and the filtrate was cooled under a nitrogen flow to grow crystals. The crystals were collected by filtration and dried in vacuo at 80°C; yield = 14.2 g (81%), mp = 177–178°C.

FT-IR (KBr): 3456, 3369 cm⁻¹ (N–H stretch), 2912, 2850 cm⁻¹ (adamantyl C–H stretch), 1215, 1057 cm⁻¹ (C–O stretch). ¹H NMR (500 MHz, DMSO-d₆, δ, ppm) [for the proton assignments, see Fig. 1(a)]: 1.52, 1.57 (two AB doublets, J = 12.2 Hz, 6H, Hₐ), 1.73 (s, 6H, Hₓ), 2.09 (brs, 3H, Hₜ), 4.88 (s, 4H, –NH₂), 6.52 (d, J = 8.6 Hz, 4H, Hₖ), 6.53 (d, J = 8.9 Hz, 2H, Hₜ), 6.67 (d, J = 8.9 Hz, 2H, Hₓ), 6.76 (d, J = 8.6 Hz, 4H, Hₖ). ¹³C NMR (125 MHz, DMSO-d₆, δ, ppm) [for the carbon assignments, see Fig. 1(b)]: 30.1 (C⁴), 35.6 (C¹), 42.3 (C⁶), 76.0 (C⁴), 114.7 (C¹¹), 117.5 (C⁶), 124.6 (C⁸), 126.7 (C¹⁰), 136.6 (C⁸), 145.0 (C¹²), 145.2 (C⁸), 145.5 (C⁶). Anal. Calcd (%) for C₂₈H₃₁N₃O (425.57): C, 79.02; H, 7.34; N, 9.87. Found: C, 78.96; H, 7.35; N, 9.84.

Synthesis of Polyamides

The synthesis of polyamide 6a was used as an example to illustrate the general synthetic route used to produce the polyamides. A mixture of 0.510 g (1.2 mmol) of diamine monomer 4, 0.199 g (1.2 mmol) of terephthalic acid (5a), 0.2 g of anhydrous calcium chloride, 1.2 mL of triphenyl phosphate (TPP), 0.4 mL of pyridine, and 2.0 mL of N-methyl-2-pyrrolidone (NMP) was heated with stirring at 120 °C for 3 h. The obtained polymer solution was poured slowly into 300 mL of stirred methanol giving rise to a stringy, fiber-like precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried under vacuum at 100 °C. Reprecipitation of the polymer from DMAc/methanol was performed twice for further purification. The inherent viscosity of the obtained polyamide 6a was 0.73 dL/g, measured at a concentration of 0.5 g/dL in DMAc-5 wt % LiCl at 30 °C.

¹H NMR (500 MHz, DMSO-d₆, δ, ppm) [for the proton assignments, see Fig. 2(a)]: 1.56 (two overlapped AB doublets, 6H, Hₐ), 1.79 (brs, 6H, Hₓ), 2.12 (brs, 3H, Hₜ), 6.73-6.99 (m, 8H, Hₖ+Hₜ+Hₓ), 7.67 (d, 4H, H₉), 8.06 (s, 4H, H₆), 10.32 (s, 2H, amide protons).

Preparation of the Polyamide Films

A solution of polymer was made by dissolving about 0.7 g of the polyamide sample in 12 mL of DMAc. The homogeneous solution was poured into a 9-cm glass Petri dish, which was placed in a 90 °C oven for 5 h to remove most of the solvent; then the semidried film was further dried in vacuo at 180 °C for 8 h. The obtained films were about 80–100 μm in thickness and were used for X-ray diffraction measurements, solubility tests, and thermal analyses.

Synthesis of Polyimides

A typical procedure is as follows. The diamine monomer 4 (0.489 g, 1.15 mmol) was dissolved in 9.5 mL of CaH₂-dried DMAc in a 50-mL round-bottom flask. Then dianhydride 7f, 6FDA (0.511 g, 1.15 mmol) was added to the diamine solution in one portion. Thus, the solid content of the solution is approximately 10 wt %. The mixture was stirred at room temperature for about 3 h to yield a viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) was 1.16 dL/g, measured in DMAc at a concentration of 0.5 g/dL at 30 °C. The poly(amic acid) film was obtained by casting from the reaction polymer solution onto a glass Petri-dish and drying at 90 °C overnight. The poly(amic acid) in the form of solid
film was converted to polyimide 8f by successive heating under vacuum at 150 °C for 30 min, 200 °C for 30 min, and then 250 °C for 1 h. The inherent viscosity of polyimide 8f was 0.49 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C. The IR spectrum of 8f (film) exhibited characteristic imide absorption bands at 1785 cm⁻¹ (asymmetrical C=O stretch) and 1726 cm⁻¹ (symmetrical C=O stretch).

¹H NMR (500 MHz, CDCl₃, δ, ppm) [for the proton assignments, see Fig. 2(b)]: 1.64 (two overlapped AB doublets, 6H, Hₐ), 1.90 (brs, 6H, Hₐ), 2.20 (brs, 3H, Hₐ), 6.96 (d, 2H, H₂), 7.11 (d, 2H, H₃), 7.22 (d, 4H, H₄), 7.29 (d, 4H, H₅), 7.86 (d, 2H, H₆), 7.96 (s, 2H, H₇), 8.04 (d, 2H, H₈).

For the chemical imidization method, 4 mL of acetic anhydride and 2 mL of pyridine were added to the polyamic acid solution obtained by a similar process as above, and the mixture was heated at 100 °C for 1 h to effect a complete imidization. The homogenous polymer solution was poured slowly into 200 mL of stirring methanol giving rise to yellow precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried. A polymer solution was made by the dissolution of about 0.5 g of the polyimide sample in 10 mL of hot DMAc. The homogenous 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.

**Measurements**

Infrared spectra were recorded on a Horiba FT-720 FT-IR spectrometer, and the ¹H and ¹³C NMR spectra on a 500 MHz instrument (Bruker AVANCE-500 FT-NMR system) using DMSO-d₆ as the solvent and tetramethylsilane as the internal standard. Elemental analyses were run in a Heraeus VarioEL-III CHNS elemental analyzer. The inherent viscosities of the polymers were determined at 0.5 g/dL concentration using a Cannon-Fenske or Ubbelohde viscometer at 30 °C. Weight-average molecular weights (Mw) and number-average molecular weights (Mn) were obtained via gel permeation chromatography (GPC) on the basis of polystyrene calibration using Waters 2410 as an apparatus and THF as the eluent. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (≈25 °C) on a Shimadzu XRD-6000 X-ray diffractometer (40 kV, 20 mA), using graphite-monochromatized Cu-Kα radiation. Thermogravimetric analyses (TGA) were conducted with a PerkinElmer Pyris 1 TGA. Experiments were performed on approximately 3–5 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm³/min) at a heating rate of 20 °C/min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 20 °C/min in flowing nitrogen (20 cm³/min). Thermomechanical analyses (TMA) were conducted with a PerkinElmer TMA 7 instrument. The TMA experiments were
conducted from 50 to 350 °C at a scan rate of 10 °C/min with a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures (\(T_s\)) were taken as the onset temperatures of probe displacement on the TMA traces. Cyclic voltammetry (CV) was performed with a CH Instruments 600C electrochemical analyzer using ITO as a working electrode (the coating area of the polymer film is approximately 1 cm\(^2\), 0.8 cm × 1.25 cm) and a platinum wire as an auxiliary electrode at a scan rate of 100 mV/s against a Ag/AgCl reference electrode in acetonitrile (CH\(_3\)CN) solution of 0.1 M tetrabutylammonium perchlorate (TBAP) under a nitrogen atmosphere. Spectroelectrochemical experiments were performed in a cell built from a commercial UV-visible cuvette using an Agilent 8453 UV-visible diode array spectrophotometer. The 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.

**RESULTS AND DISCUSSION**

**Monomer Synthesis**

The new diamine monomer, 4-(1-adamantox)-4',4''-diaminotriphenylamine (4) was prepared by a four-step reaction sequence, as shown in Scheme 1. In the first step, the intermediate compound 4-(1-adamantox)nitrobenzene (1) was
synthesized by the nucleophilic aromatic fluoro-displacement reaction of 4-fluoronitrobenzene with the sodium salt of 1-adamantanol formed in situ by treatment of sodium hydride. Then, catalytic reduction of the nitro compound by means of hydrazine and Pd/C gave 4-(1-adamantoxy)aniline (2). The target adamantoxyl-TPA diamine monomer 4 was prepared by the CsF-promoted N-arylation reaction of 2 with two equivalent 4-fluoronitrobenzene, followed by catalytic reduction of the intermediate dinitro compound 4-(1-adamantoxy)-4',4''-dinitrotiophenylamine (3) using Pd/C and hydrazine in refluxing ethanol. Elemental analysis, IR, 1H NMR and 13C NMR spectroscopic techniques were used to identify structures of the intermediate compounds and the target diamine monomer 4. Figure S1 (see Supporting Information) shows the FT-IR spectra of all the synthesized compounds together with the starting 1-adamantanol. In the IR spectrum of compound 1, the absorption band at 3286 cm$^{-1}$ for the hydroxyl group of 1-adamantanol disappeared and new bands appeared at 1585 and 1342 cm$^{-1}$ due to N=O stretching vibrations in nitro group. After reduction, the characteristic absorptions of the nitro group disappeared and the primary amino groups showed the typical absorption pair at 3469 and 3354 cm$^{-1}$ due to N–H stretching as shown in the IR spectrum of compound 2. Similar absorption changes could also be observed in the IR spectra of dinitro-compound 3 and the target diamine monomer 4. The absorption bands appeared in the 2800–3000 cm$^{-1}$ region were attributed to the adamantyl C–H stretching vibrations. Figure 1 illustrates the 1H NMR and 13C NMR spectra of the diamine monomer 4. Assignments of each carbon and proton assisted by the two-dimensional NMR spectra (see Fig. S2) are also given in these figures, and these spectra agree well with the proposed structure of 4. The 1H NMR spectra confirm that the nitro groups have been completely transformed into amino groups by the high-field shift of the aromatic protons and by the resonance signals at around 4.88 ppm corresponding to the amino protons. The resonance signals appeared at 1.50–2.10 ppm in the 1H NMR spectra and 30.1–76.0 ppm in the 13C NMR spectra are peculiar to the adamantoxyl group.

**Polymer Synthesis**

According to the phosphorylation technique first described by Yamazaki et al., a series of novel aromatic polyamides 6a–6h bearing main-chain adamantoxyl-TPA units were synthesized from the diamine monomer 4 with various aromatic dicarboxylic acids 5a–5h (Scheme 2). The polymerization was performed via solution polycondensation using triphenyl phosphite and pyridine as condensing agents. All polymerization reactions proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. All the polyamides precipitated in a tough fiber-like form when slowly pouring the resulting polymer solutions into stirred methanol.

**Scheme 2.** Synthesis of adamantoxyl-TPA polyamides.
Table 1. Inherent Viscosity and Solubility Behavior of Polyamides

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>(\eta_{inh}) (dL/g)</th>
<th>NMP</th>
<th>DMAc</th>
<th>DMF</th>
<th>DMSO</th>
<th>m-Cresol</th>
<th>THF</th>
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<td>++ (+)</td>
<td>++ (+)</td>
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<td>++ (++)</td>
<td>++ (+)</td>
<td>++ (+)</td>
<td>++ (+)</td>
<td>++ (+)</td>
<td>-- (-)</td>
</tr>
<tr>
<td>6c</td>
<td>0.82</td>
<td>++ (+)</td>
<td>++ (+)</td>
<td>++ (+)</td>
<td>++ (+)</td>
<td>++ (+)</td>
<td>-- (-)</td>
</tr>
<tr>
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<td>++ (+)</td>
<td>++ (+)</td>
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</tbody>
</table>

\(\eta_{inh}\) values are shown in parentheses. Models are those of structurally similar polyamides 6 without the adamantoyx substituent.

Values shown in parentheses are those of structurally similar polyamides 6 without the adamantoyx substituent.

Polyamides 6a–6f were prepared in conventional two-step method by the reactions of equal molar amounts of diamine 4 with various aromatic dianhydrides (7a–7f) to form poly(amic acid)s, followed by the thermal or chemical cyclodehydration (Scheme 3). As shown in Table 2, the inherent viscosities of the poly(amic acid) precursors were in the range 1.16–1.82 dL/g, indicating the formation of high-molecular-weight polymers. All of these poly(amic acid)s could be solution cast into flexible and tough films, which were subsequently converted into tough polyimide films by extended heating at elevated temperatures. The poly(amic acid)s also could be chemically cyclodehydrated to polyimides by treatment with a mixture of pyridine and acetic anhydride. The complete imidization of polymers could be confirmed by IR and NMR spectroscopy. Figure S3(a) shows a typical IR spectrum for polyamide 6a. The characteristic IR absorption bands of the amide group appeared at around 3298 cm\(^{-1}\) (N-H stretch) and 1653 cm\(^{-1}\) (amide carbonyl). The \(^1\)H NMR spectrum of polyamide 6a is reproduced in Figure 2(a) and agrees well with the desired polymer structure. The resonance signal appearing at 10.32 ppm also supports the formation of amide linkages.

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Polyimide. The thermally or chemically imidized polyimides exhibited inherent viscosities between 0.44 and 0.63 dL/g. The GPC data of two THF-soluble polyimides 8e–C and 8f–C indicated that they exhibited weight-average and number-average molecular weights of 73,600–75,500 and 48,000–52,500, respectively, relative to the polystyrene standards (see Table S1 in Supporting Information). The organosoluble polyimides such as 8c–8f could be solution cast into strong films in the fully imidized form.

**Polymer Properties**

**Solubility and Film Property**

The solubility properties of polyamides 6a–6h and polyimides 8a–8f in several organic solvents at 10% (w/v) are also summarized in Tables 1 and 2, respectively. Except for the polyimides derived from more rigid dianhydrides such as PMDA and BPDA, the other polyimides and all polyamides exhibited good solubility in polar solvents such as NMP, DMAc, DMF, DMSO, and m-cresol at room temperature or upon heating at 70 °C. Polyamide 6f and polyimide 8f also showed good solubility in less polar solvents like THF because of the additional contribution of the hexafluoroisopropylidene (–C(CF3)2–) fragment in the polymer backbone. In general, these polymers revealed an enhanced solubility with respect to conventional aromatic polyamides and polyimides and their triphenylamine-based analogues without the pendent substituent (the 6′ and 8′ series polymers as shown in the footnotes of Tables 1.

![Figure 2. 1H NMR spectra of (a) polyamide 6a in DMSO-d6 and (b) polyimide 8f in CDCl3 (* the solvent peak). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]](url)
Table 2. Inherent Viscosity and Solubility Behavior of Polyimides

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>( \eta_{inh} ) (dL/g)</th>
<th>Solubility in Various Solvents (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PAA</td>
<td>Polyimide</td>
</tr>
<tr>
<td>8a–T</td>
<td>1.60</td>
<td>–</td>
</tr>
<tr>
<td>8a–C</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>8b–T</td>
<td>1.82</td>
<td>–</td>
</tr>
<tr>
<td>8b–C</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>8c–T</td>
<td>1.36</td>
<td>0.53</td>
</tr>
<tr>
<td>8c–C</td>
<td>–</td>
<td>0.51</td>
</tr>
<tr>
<td>8d–T</td>
<td>1.61</td>
<td>0.63</td>
</tr>
<tr>
<td>8d–C</td>
<td>–</td>
<td>0.60</td>
</tr>
<tr>
<td>8e–T</td>
<td>1.23</td>
<td>0.52</td>
</tr>
<tr>
<td>8e–C</td>
<td>–</td>
<td>0.50</td>
</tr>
<tr>
<td>8f–T</td>
<td>1.16</td>
<td>0.49</td>
</tr>
<tr>
<td>8f–C</td>
<td>–</td>
<td>0.44</td>
</tr>
</tbody>
</table>

\( ^{a}\) The polyimide samples prepared via thermal imidization were coded with –T, and those via chemical imidization with –C.

\( ^{b}\) Inherent viscosity measured at a concentration of 0.5 dL/g in DMAc at 30 °C. PAA = Poly(amic acid)

\( ^{c}\) Qualitative solubility was tested with 10 mg of a sample in 1 mL of a stirred solvent. ++: soluble at room temperature; +: soluble on heating; –: insoluble even on heating. NMP: \( N \)-methyl-2-pyrrolidone; DMAc: \( N, N \)-dimethylacetamide; DMF: \( N, N \)-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

\( ^{d}\) Values shown in parentheses are those of structurally similar polyimides 8 without the adamantoxy substituent.


\( 8' \)
and 2). Therefore, the good solubility makes these polymers potential candidates for practical applications in spin-coating and inkjet-printing techniques to afford high performance thin films for optoelectronic devices. As mentioned earlier, all the polymers could afford flexible and tough films. The films exhibited ultimate tensile strengths of 83–102 MPa, elongations to break of 6–14%, and initial moduli of 2.0–2.6 GPa. The WAXD studies of these film samples indicated that all the polymers were essentially amorphous. The WAXD patterns for the 6 series polyamides are illustrated in Figure S4. Their high solubility and amorphous properties can be attributed in part to the incorporation of bulky, three-dimensional adamantoxy-TPA moiety along the polymer backbone, which results in a high steric hindrance for close packing, and thus reduces their crystallization tendency and interchain interactions.

**Thermal Properties**

For the creation of useful devices based on organic light-emitting and charge-transporting materials, long-term durability and high-quality amorphous glassy materials are required. The thermal properties of the polyamides and polyimides were investigated by TGA, DSC, and TMA techniques. Table 3 summarizes the thermal behavior data of these polymers.

Typical TGA curves of the representative polyimide 8c in both air and nitrogen atmospheres are shown in the inset of Figure 3. Even with the incorporation of adamantoxy groups, polyimide 8c exhibited high thermal stability without significant weight loss up to 450 °C under nitrogen or air atmosphere. The decomposition temperatures \( T_d \) at a 10% weight loss of these polymers in nitrogen and air were recorded in the range of 481–529 °C and 406–555 °C, respectively. All the polymers exhibited a lower \( T_d \) value as compared with their corresponding counterparts without the adamantoxy substituent.

### Table 3. Thermal Properties of Polyamides and Polyimides

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>( T_g ) b (°C)</th>
<th>( T_s ) c (°C)</th>
<th>In N(_2)</th>
<th>In Air</th>
<th>Char Yield(^e) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>291 (295)(^f)</td>
<td>285</td>
<td>500 (546)(^f)</td>
<td>495 (526)(^f)</td>
<td>72</td>
</tr>
<tr>
<td>6b</td>
<td>285 (290)</td>
<td>270</td>
<td>486 (554)</td>
<td>497 (513)</td>
<td>71</td>
</tr>
<tr>
<td>6c</td>
<td>294 (302)</td>
<td>274</td>
<td>502 (573)</td>
<td>509 (528)</td>
<td>71</td>
</tr>
<tr>
<td>6d</td>
<td>263 (273)</td>
<td>258</td>
<td>481 (581)</td>
<td>502 (523)</td>
<td>68</td>
</tr>
<tr>
<td>6e</td>
<td>284 (296)</td>
<td>276</td>
<td>484 (515)</td>
<td>486 (504)</td>
<td>65</td>
</tr>
<tr>
<td>6f</td>
<td>285 (295)</td>
<td>279</td>
<td>507 (544)</td>
<td>516 (525)</td>
<td>60</td>
</tr>
<tr>
<td>6g</td>
<td>293 (288)</td>
<td>278</td>
<td>500 (564)</td>
<td>506 (532)</td>
<td>65</td>
</tr>
<tr>
<td>6h</td>
<td>291 (307)</td>
<td>282</td>
<td>525 (569)</td>
<td>513 (535)</td>
<td>75</td>
</tr>
<tr>
<td>8a</td>
<td>– (–)</td>
<td>299</td>
<td>503 (606)</td>
<td>538 (596)</td>
<td>50</td>
</tr>
<tr>
<td>8b</td>
<td>310 (331)</td>
<td>294</td>
<td>492 (613)</td>
<td>560 (619)</td>
<td>53</td>
</tr>
<tr>
<td>8c</td>
<td>311 (309)</td>
<td>292</td>
<td>522 (590)</td>
<td>547 (590)</td>
<td>64</td>
</tr>
<tr>
<td>8d</td>
<td>300 (295)</td>
<td>281</td>
<td>502 (608)</td>
<td>555 (611)</td>
<td>52</td>
</tr>
<tr>
<td>8e</td>
<td>307 (326)</td>
<td>304</td>
<td>490 (546)</td>
<td>523 (577)</td>
<td>52</td>
</tr>
<tr>
<td>8f</td>
<td>310 (316)</td>
<td>303</td>
<td>529 (581)</td>
<td>555 (571)</td>
<td>54</td>
</tr>
</tbody>
</table>

\(^a\)The polymer film samples were heated at 300 °C for 1 h before all the thermal analyses.

\(^b\)The samples were heated from 50 to 400 °C at a scan rate of 20 °C/min followed by rapid cooling to 50 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 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.

\(^f\)Values shown in parentheses are those of structurally similar polyamides 6 and polyimides 8 without the adamantoxy substituent.
The glass-transition temperatures \(T_g\) of polyamides 6a–6h could be easily determined in the DSC thermograms; they were observed in the 263–294 \(^\circ\)C range, depending upon the rigidity of the polymer chain. The lowest \(T_g\) value of 6d in the 6 series polyamides can be explained in terms of the flexible ether linkage in its diacid component. No discernible glass transition was observed for polyimide 8a by DSC, possibly because of the rigid backbone caused by the pyromellitimide segment. The range of \(T_g\) values for the other 8 series polyimides (8b–8f) was 300–311 \(^\circ\)C. All of the polyamides and polyimides indicated no clear melting endotherms up to the decomposition temperatures on the DSC traces. This result also supports the amorphous nature associated with these polymers. As can be seen from Table 3, almost all the 6 and 8 series polymers revealed a slightly lower \(T_g\) when compared with their respective 6' and 8' analogues. This result implies that the bulky adamantoxyl substituent in the former leads to an increase in steric hindrance for close chain packing and an enhanced fractional free volume between polymer chains.

The softening temperatures \(T_s\) (or may be referred as apparent \(T_g\)) of the polymer films were examined by the TMA method using a loaded penetration probe. They were read from the onset temperature of the probe displacement on the TMA trace. As a representative example, the TMA trace of polyimide 8c is illustrated in Figure 3. As listed in Table 3, the \(T_s\) values of the 6 series polyamides and the 8 series polyimides were in the range of 258–285 \(^\circ\)C and 281–304 \(^\circ\)C, respectively. The trend of \(T_s\) variation with the chain stiffness was similar to that of \(T_g\) observed in the DSC measurements. However, in all cases the \(T_s\) values obtained by TMA were slightly lower than the \(T_g\) values measured by the DSC.

**Table 4.** Optical and Electrochemical Properties of Polyamides and Polyimides

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Abs (\lambda_{\text{max}}) (nm)(^a)</th>
<th>Abs (\lambda_{\text{onset}}) (nm)(^a)</th>
<th>PL (\lambda_{\text{max}}) (nm)(^b)</th>
<th>(E_{1/2}) (V)(^c) (vs. Ag/AgCl)</th>
<th>(E_{\text{opt}}) (eV)(^d)</th>
<th>(E_{\text{HOMO}}/E_{\text{LUMO}}) (eV)(^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>360 (368)</td>
<td>434 (467)</td>
<td>460</td>
<td>0.78 (0.85)</td>
<td>2.66</td>
<td>5.14/2.48</td>
</tr>
<tr>
<td>6b</td>
<td>341 (349)</td>
<td>376 (411)</td>
<td>442</td>
<td>0.80 (0.86)</td>
<td>3.02</td>
<td>5.16/2.14</td>
</tr>
<tr>
<td>6c</td>
<td>352 (357)</td>
<td>398 (431)</td>
<td>454</td>
<td>0.79 (0.86)</td>
<td>2.88</td>
<td>5.15/2.27</td>
</tr>
<tr>
<td>6d</td>
<td>338 (342)</td>
<td>372 (404)</td>
<td>455</td>
<td>0.78 (0.85)</td>
<td>3.07</td>
<td>5.14/2.07</td>
</tr>
<tr>
<td>6e</td>
<td>364 (368)</td>
<td>453 (482)</td>
<td>465</td>
<td>0.80 (0.87)</td>
<td>2.57</td>
<td>5.16/2.59</td>
</tr>
<tr>
<td>6f</td>
<td>342 (347)</td>
<td>411 (448)</td>
<td>446</td>
<td>0.81 (0.87)</td>
<td>2.77</td>
<td>5.17/2.40</td>
</tr>
<tr>
<td>6g</td>
<td>313 (335)</td>
<td>399 (422)</td>
<td>432</td>
<td>0.80 (0.86)</td>
<td>2.94</td>
<td>5.16/2.22</td>
</tr>
<tr>
<td>6h</td>
<td>349 (352)</td>
<td>440 (475)</td>
<td>454</td>
<td>0.78 (0.86)</td>
<td>2.61</td>
<td>5.14/2.53</td>
</tr>
<tr>
<td>8a</td>
<td>312 (371)</td>
<td>399 (449)</td>
<td>394</td>
<td>0.97 (1.17)</td>
<td>2.76</td>
<td>5.33/2.57</td>
</tr>
<tr>
<td>8b</td>
<td>322 (328)</td>
<td>366 (382)</td>
<td>400</td>
<td>0.98 (1.17)</td>
<td>3.25</td>
<td>5.34/2.09</td>
</tr>
<tr>
<td>8c</td>
<td>300 (301)</td>
<td>387 (432)</td>
<td>395</td>
<td>1.02 (1.17)</td>
<td>2.87</td>
<td>5.38/2.51</td>
</tr>
<tr>
<td>8d</td>
<td>316 (329)</td>
<td>362 (412)</td>
<td>391</td>
<td>1.05 (1.14)</td>
<td>3.01</td>
<td>5.41/2.40</td>
</tr>
<tr>
<td>8e</td>
<td>302 (308)</td>
<td>380 (427)</td>
<td>385</td>
<td>0.98 (1.17)</td>
<td>2.90</td>
<td>5.34/2.44</td>
</tr>
<tr>
<td>8f</td>
<td>301 (303)</td>
<td>369 (393)</td>
<td>368</td>
<td>1.04 (1.18)</td>
<td>3.16</td>
<td>5.40/2.24</td>
</tr>
</tbody>
</table>

\(^a\)UV/vis absorption measured in NMP (10\(^{-5}\) M) at room temperature. Values shown in parentheses are those measured as thin solid-film.

\(^b\)Photoluminescence measured in NMP (10\(^{-5}\) M) 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 adamantoxyl substituent.

\(^d\)Optical energy gap, \(E_{\text{opt}} = 1240/\lambda_{\text{onset}}\) of the polymer film.

\(^e\)The HOMO energy levels were calculated from \(E_{1/2}\) and were referenced to ferrocene (4.8 eV); \(E_{\text{LUMO}} = E_{\text{HOMO}} − E_{\text{opt}}\).
experiments. These differences may also be attributed to the different heating story of the samples and the distinct nature of these two testing methods.

**Optical Properties**

The optical properties of these polymers were investigated by UV-vis and photoluminescence (PL) spectroscopy. The absorption $\lambda_{\text{max}}$ and $\lambda_{\text{onset}}$ (absorption edge) and PL $\lambda_{\text{max}}$ data are reported in Table 4. The polyamides exhibited strong UV-vis absorption bands at 313–364 nm in NMP solution ($10^{-5}$ M), assignable to the $\pi-\pi^*$ transition resulting from the adamantoxy-TPA moieties. Their PL spectra in NMP solution showed emission peaks around 432–465 nm in the blue region. Figure 4 shows the UV-vis absorption and PL spectra of some typical polyamides 6a, 6c, 6e, and 6f. Optical band gap ($E_{\text{opt}}$) determined from the $\lambda_{\text{onset}}$ values of the solid-state absorption spectra of the polyamides were found to be 2.61–3.07 eV. The polyimides present similar spectra in dilute NMP solutions and in the solid state, with $\lambda_{\text{max}}$ at 300–322 nm. They exhibited significantly less detectable fluorescence than the polyamides. We propose that the observed quenching of PL that occurs in the polyamides is due to re-absorption by the charge transfer complexing between the donor triphenylamine and acceptor imide units.

**Electrochemical Properties**

Charge transport in organic materials is believed to be governed by the hopping process involving the redox reaction of charge transport molecules. To probe the redox properties of the synthesized polymers, cyclic voltammetry (CV) was conducted for a cast film on an ITO-coated glass substrate as working electrode in dry acetonitrile ($\text{CH}_3\text{CN}$) 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 CV scans of all polymers. Typical CV curves for polyamide 6d and polyimide 8e are shown in Figure 5, and the half-wave potentials ($E_{1/2}$; average potential of the redox couple peaks) of all polyamides and polyimides are also presented in Table 4. The polyamides exhibited $E_{1/2}$ values in the range of 0.78–0.81 V, corresponding to TPA oxidation. The color of the polyamide films changed from colorless to deep blue because of electrochemical oxidation of the polymers. The oxidative and electrochromic reversibility is maintained on repeated scanning between 0 and 1.1 V (vs. Ag/AgCl). This result confirms that para-substitution of the adamantoxy group on the TPA unit leads considerable stability to the radical cation species. The oxidation of polyimides started to occur at higher potentials than the polyamides because of the electron-withdrawing effect arising from the...
imide group. Their $E_{1/2}$ values were recorded in the 0.97–1.05 V range. The color of the polyimide films turned from pale yellow to bluish green upon oxidation. However, the polyimide samples revealed a less redox stability with respect to the polyamide ones. They generally lost redox and electrochromic reversibility after some repeated CV scans. The $E_{1/2}$ value of ferrocene/ferrocenium ($\text{Fc/Fc}^+$) is known to be 4.8 eV below the vacuum level and was used as a calibration reference. The highest occupied molecular orbital (HOMO) energy levels of the 6 series polyamides and the 8 series polyimides estimated from their $E_{1/2}$ values were in the range of 5.14–5.17 eV and 5.33–5.41 eV, respectively; these HOMO levels were comparable to those of small hole-transporting molecules.36

**Spectroelectrochemical and Electrochromic Properties**

Spectroelectrochemical experiments were performed to probe the optical change upon oxidation. 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/CH$_3$CN solution. Typical result of the film of polyamide 6d is presented in Figure 6 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 339 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 1.00 V), the intensity of the absorption peak at 339 nm gradually decreased whereas new peaks at 399, 575, and 795 nm gradually increased in intensity, and the color of the film changed to dark blue (as shown in Fig. 6). The spectral changes were clearly due to the formation of the cationic states of polyamide 6d.

For optical switching studies, polymer films were cast on ITO-coated glass slides in the same manner as described above, and each film was potential stepped between its neutral (0 V) and oxidized (+1.00 V) state. When the films were switched, the absorbance at 795 nm was monitored as a function of time with UV-vis-NIR spectroscopy. The switching time was calculated at 90% of the full switch because it is difficult to perceive any further color change with naked eye beyond this point. As depicted in Figure 7, thin film of polyamide 6d required 4.30 s at 1.00 V for coloring and 1.42 s for bleaching, reflecting the different reaction rates between the neutral and oxidized forms of the film of 6d. Switching data

**Figure 6.** Spectral change of polyamide 6d thin film on the ITO-coated glass substrate (in CH$_3$CN with 0.1 M TBAP as the supporting electrolyte) along with increasing of the applied voltage (vs. Ag/AgCl couple as reference). The inset shows the photographic images of the film at indicated applied voltages. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

**Figure 7.** Calculation of optical switching time for polyamide 6d thin film at $\lambda_{\text{max}}$ = 795 nm as the applied voltage was stepped between 0 and 1.00 V (vs. Ag/AgCl). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
for the cast film of polyamide 6d are given in Figure 8. After continuous several cyclic scans between 0 and 1.00 V, the polyamide film still exhibited good electrochromic stability.

The typical absorption spectral change of polyimide 8e is shown in Figure 9. In the neutral form, at 0 V, the film exhibited strong absorption at wavelength around 306 nm and weak absorption tail in the region 400–500 nm and thus appeared in pale yellow. Upon oxidation of the polyimide 8e film (increasing applied voltage from 0 to 1.20 V), the intensity of the absorption peak at 306 nm gradually decreased whereas new peaks at 374 and 759 nm gradually increased in intensity, and the color of the film changed to bluish green (as shown in Fig. 9). The new spectrum was assigned as that of the formation of a cationic radical state of the polyimide 8e. However, the stability of all the polyimides was not as good as the polyamides.

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'-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 good thermal stability, the polymers also revealed interesting electrochromic characteristics with color change from colorless or pale yellow neutral state to dark blue or bluish green oxidized state. The polyamides generally revealed a higher electrochemical and electrochromic stability in comparison with the polyimides. These adamantoxy-TPA polymers may find optoelectronic applications as new hole-transporting or electrochromic materials.

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REFERENCES AND NOTES
