

Electroactive Polyimides Derived from Amino-Terminated Aniline Trimer

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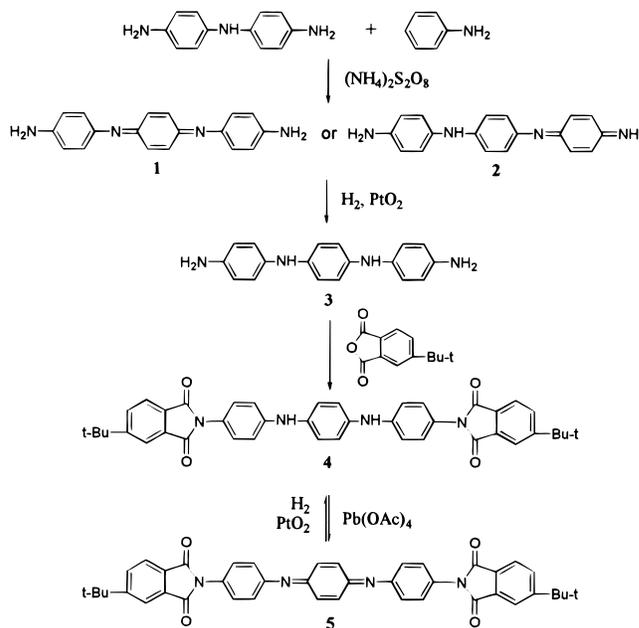
In connection with research on conductive polyaniline,¹ aniline oligomers have been studied as model compounds and explored as new electroactive materials.² Many linear aniline oligomers are known, including amino-terminated oligomers such as *N,N*-bis(4'-aminophenyl)-1,4-quinonediimine (**1**) and its reduced analogue **3** (*N,N*-bis(4'-aminophenyl)-1,4-phenylenediamine).³ Conceivably, the terminal-functionalized aniline oligomers are valuable building blocks for making polyaniline-like, new electroactive polymers. However, multistep synthesis and instability of aniline oligomers in the reduced (leuco) form hampered the large-scale preparation of a functionalized oligomer as a monomer.

A general one-step approach was recently established by Wei et al. for the synthesis of the aniline trimer and other trimeric analogues from inexpensive materials.⁴ Accordingly, trimer **1** could be easily obtained in large quantity by oxidative coupling of 4,4'-diaminodiphenylamine or *p*-phenylenediamine and aniline (Scheme 1).^{5,6} The availability of the amino-terminated aniline trimer allowed us to exploit a variety of potentially electroactive polymers such as polyimides and polyamides. In this paper, we report for the first time the synthesis and characterization of *electroactive, high molecular weight, film-forming polyimides* derived from the amino-terminated aniline trimer.

Both oxidized and reduced trimers **1** and **3** can be considered diamine monomers. Before polymerization was attempted, model reactions using 4-*tert*-butylphthalic anhydride were carried out in order to test the polymerizability of trimers **1** and **3**. Direct imidization using trimer **1** was unsuccessful in producing the corresponding diimide in high yield, presumably due to the presence of the mono-amino tautomer **2** in solution.^{2b} Although being more prone to air oxidation, diamine **3** could be obtained by reduction of **1** (or **2**) with hydrazine^{4,6} or by catalytic hydrogenation prior to use. Thus, hydrogenation of **1** in *N*-methyl-2-pyrrolidinone (NMP) gave diamine **3**, which was subsequently reacted with 4-*tert*-butylphthalic anhydride to afford model diimide **4** in high yield (Scheme 1).⁷

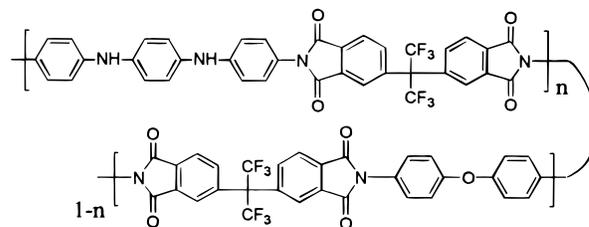
Following a successful model reaction, three copolyimides were prepared using 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), diamine **3**, and 4,4'-oxydianiline (ODA) in different feed ratios.⁸ One-step polymerization was carried out in *m*-cresol at 200 °C

Scheme 1. Synthesis of Aniline Trimers **1** and **3** and Redox Reaction of Diimides **4** and **5**.



under nitrogen. Diamine **3**, freshly prepared from **1** by hydrogenation, was added to a refluxing *m*-cresol solution of 6FDA and ODA. It was found that the stoichiometry of all monomers could be readily achieved by slow addition of diamine **3** to the reaction medium upon observation of a significant increase in solution viscosity.

All the copolymers were characterized by spectroscopic means (UV-vis, NMR, and IR). The carbonyl peak at 1725 cm⁻¹ and characteristic peak near 1300 cm⁻¹ due to the C–N stretching^{2a} were found in the IR spectra of these copolyimides. Similar to model compound **4**, copolyimides **7–9** had a maximum absorbance



- 6:** $n = 0.00$
7: $n = 0.29$
8: $n = 0.57$
9: $n = 0.65$
10: $n = 1.00$

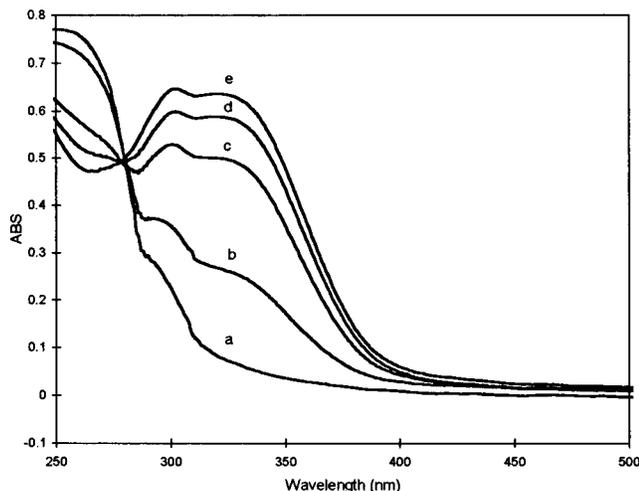
(λ_{\max}) at 340 nm, indicating the presence of the leuco aniline trimer or the 1,4-bis(phenylamino)benzene moiety in the polymer backbone. The mole ratio of the aniline trimer to ODA in the copolymers was determined to be in a range 29–65% from the ¹H NMR spectra (Table 1). Apparently, the measured trimer content in copolyimides **7–9** was different from the feed ratio but obeyed Beer's law, as shown by a fairly tight isosbestic point in the absorption spectra (Figure 1). All copolyimides were of high molecular mass and had inherent viscosity values ranging from 0.72 to 0.89 dL/g

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Table 1. Characterizations of Polyimides 6–10

	6	7	8	9	10
n in feed ^a	0.00	0.20	0.40	0.80	1.00
n in polymer ^b	0.00	0.29	0.57	0.65	1.00
η_{inh} , dL/g ^c	0.52	0.89	0.72	0.73	0.39 ^d
T_d , °C ^e	535	500	510	517	524

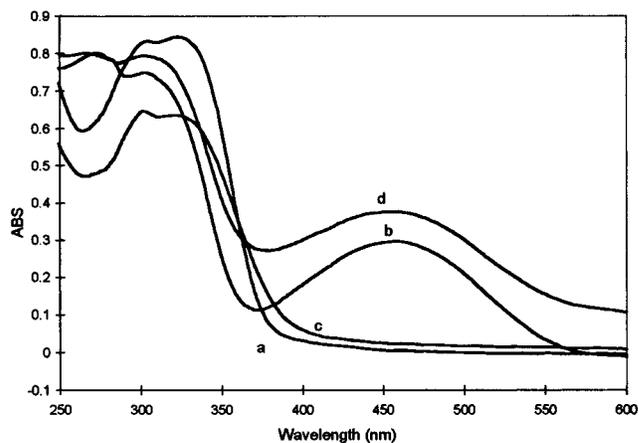
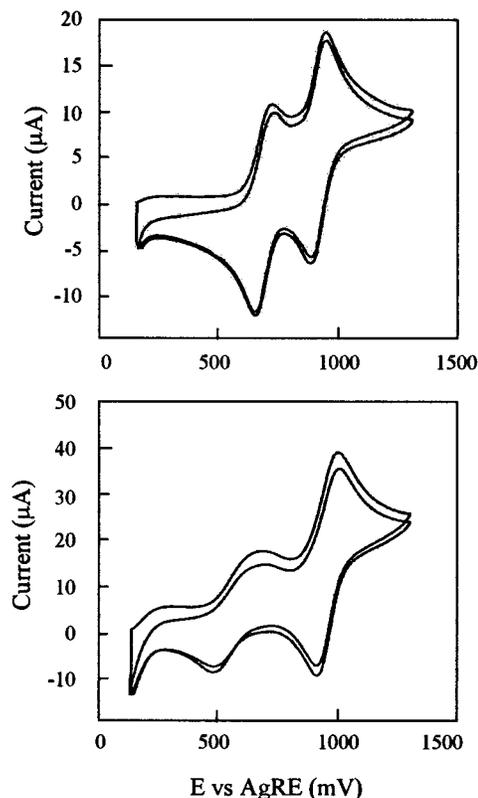
^a Mole fraction of monomer **3** in feed. ^b Mole fraction of monomer **3** in polymers determined by NMR. ^c Inherent viscosity (0.5 g/dL in THF) measured at 30 °C. ^d $\eta_{inh} = 0.83$ dL/g in NMP at 30 °C. ^e Onset temperature for 5% weight loss in nitrogen determined by TG at a heating rate of 10 °C/min.

**Figure 1.** UV-vis spectra of polyimides **6** (a), **7** (b), **8** (c), **9** (d), and **10** (e).

(Table 1). Copolyimide **7** had a weight-average molecular weight of 199 700 relative to polystyrene and a polydispersity index of 2.04. These copolyimides showed good solubility in common organic solvents such as tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and NMP and could be cast into tough thin films. A glass transition temperature (T_g) was detected to be near 300 ± 5 °C by differential scanning calorimetry (DSC) for all copolyimides and the onset temperature for 5% weight loss in nitrogen was above 500 °C, as assessed by thermogravimetry (TG).

Two homopolyimides **6** and **10** were also prepared for comparison with copolyimides. Nonelectroactive polyimide **6** was obtained in high molecular weight ($M_w = 98\,500$, $M_n = 51\,800$, relative to polystyrene) by one-step polymerization of 6FDA and ODA in *m*-cresol. Polymerization of 6FDA and diamine **3** in NMP at 180 °C afforded polyimide **10**, which contained less than 5% of the amic acid units. The "as-prepared" polyimide **10** was soluble in THF, DMF, DMSO, and NMP and became insoluble in these solvents upon further thermal imidization. The IR and UV-vis spectra of polyimides **6** and **10** were consistent with their structures. Polyimides **6** and **10** had similar T_g values around 305 °C.

The redox nature of these polyimides was demonstrated by chemical oxidation of model diimide **4** and polyimide **10**. Although inert to ammonium persulfate and silver(I) oxide, diimide **4** was readily oxidized by lead tetraacetate to the corresponding diimide **5** containing the benzoquinoneimine moiety (Scheme 1),⁹ as evidenced by the λ_{max} at 450 nm in the UV-vis spectrum (Figure 2, curve b). Similarly, treatment of polyimide **10** with lead tetraacetate gave the oxidized polymer that had the λ_{max} at the same wavelength (Figure 2, curve d) due to the $\pi-\pi^*$ transition of the quinoid unit.

**Figure 2.** UV-vis spectra of model compounds **4** (a) and **5** (b), polyimide **10** (c), and its oxidized imine analogue (d).**Figure 3.** Cyclic voltammograms (two scans) of model **4** (top) and polyimide **10** coated on a Pt electrode (bottom) in a solution of $\text{Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$ containing 2.34×10^{-2} M HClO_4 .

Chemical reduction of the model compound or polymer was easily achieved by hydrogenation in the presence of platinum oxide catalyst (e.g., **5** to **4**, Scheme 1).

According to a proposed mechanism for the electrochemical redox reaction of the aniline oligomers,^{2a} the electrochemical behavior of the model compound and the polyimides was examined in a strongly acidic electrolyte composed of tetrabutylammonium perchlorate and hydrogen perchlorate in acetonitrile. Under these conditions, the cyclic voltammograms of model **4** and polyimide **10** displayed two distinct reversible waves (Figure 3). However, for both **4** and **10** the first oxidation wave occurred at a higher potential (near 600 mV) than those (ca. 300 mV) of the reported dimer and tetramer without the terminal substituents.^{2a} The electrochemistry of polyimide **10** (Figure 3, bottom) appears very similar

to that of model **4**, except for a slightly higher potential for its second oxidation wave. This observation confirms that there is no extended conjugation in these electroactive polyimides. The high oxidation potential, because of the electron-withdrawing imido group, is consistent with the observed resistance of model **4** and polyimide **10** toward chemical oxidation.

In conclusion, a series of high molecular weight, film-forming, electroactive polyimides have been prepared using a readily available amino-terminated aniline trimer. Unlike polyaniline and the aniline oligomers, these electroactive polyimides show a high oxidation resistance. Further investigation of the electrochemical and mechanical properties of these polyimides is ongoing.

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References and Notes

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- (5) Modified synthesis of **1** is as follows: 4,4'-Diaminodiphenylamine sulfate (23.65 g, 0.796 mol) and aniline (7.40 g, 0.796 mol) were dissolved in aqueous HCl solution (1.0 M, 800 mL) containing 75 g of NaCl. A solution of ammonium persulfate (18.00 g, 0.789 mol) in aqueous HCl (1.0 M, 200 mL) was added via a dropping funnel into the above solution at $-5\text{ }^{\circ}\text{C}$ at the rate of approximately 60 drops/min. The reaction mixture was stirred for 1 h at $-5\text{ }^{\circ}\text{C}$. The resulting precipitate was collected by filtration and washed with aqueous HCl solution (1.0 M, 400 mL) precooled to $0\text{ }^{\circ}\text{C}$. The solid product was washed with 10% NH_4OH solution (100 mL) and a large amount of distilled water and then dried in a vacuum oven at $50\text{ }^{\circ}\text{C}$ overnight. Trimer **1** was obtained as a red solid: 11.8 g (51.5%). The melting point and spectroscopic data were consistent with those reported before.^{4,6}
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- (7) Trimer **1** (1.885 g, 6.540 mmol) in 50 mL of NMP was reduced to diamine **3** with hydrogen at 40 lbs/in.² over 0.12 g of platinum oxide for 2 h. The NMP solution was then transferred via a syringe into a 250 mL, three-neck round-bottomed flask containing 4-*tert*-butylphthalic anhydride (2.803 g, 1.370 mmol) and 10 mL of NMP under nitrogen. The reaction mixture was heated to reflux for 3 h, and during this period of time about 50 mL of NMP was allowed to distill off. After cooling to room temperature, 100 mL of ethanol was added to the reaction flask. The resulting precipitate was collected by filtration, washed with ethanol, and dried at $200\text{ }^{\circ}\text{C}$ under vacuum for 5 h. Diimide **4** was obtained as a brown-yellow powder: 4.20 g (97%); mp $334.4\text{ }^{\circ}\text{C}$ (DSC); IR (KBr) 3397, 2968, 1773, 1774, 1615, 1539, 1506, 1378, 1316, 1226, 1186, 1086, 819, 685 cm^{-1} ; ^1H NMR (200 MHz, $\text{DMSO-}d_6$) δ 1.40 (s, 18 H), 7.06 (d, 4H), 7.15 (s, 4H), 7.22 (d, 4H), 7.93 (m, 6H), 8.21 (s, 2H); ^{13}C NMR (50 MHz, $\text{DMSO-}d_6$) δ 31.10, 35.79, 114.98, 120.39, 120.50, 122.42, 123.47, 128.69, 129.38, 131.67, 132.17, 136.64, 145.09, 158.59, 167.58, 167.89; MS (FAB, *m/e*, relative intensity %) 663 ($\text{M} + \text{H}^+$, 11).
- (8) A typical polymerization procedure is as follows: To a 100 mL, three-necked, round-bottomed flask equipped with a dropping funnel were added 6FDA (888.5 mg, 2.000 mmol), ODA (320.4 mg, 1.600 mmol), and *m*-cresol (15 mL). The reaction mixture was heated to $180\text{ }^{\circ}\text{C}$ under nitrogen. A solution of diamine **3** in THF, freshly prepared from trimer **1** (136.9 mg, 0.470 mmol) by hydrogenation over PtO_2 catalyst (6.8 mg) in THF (50 mL), was added to the reaction flask via a dropping funnel under nitrogen. The half portion of diamine **3** was added quickly at an approximate rate of 1 drop/2 s and the rest was added slowly (e.g., 1 drop/40 s). THF was allowed to distill off during polymerization at $180\text{ }^{\circ}\text{C}$. After 18 h, the hot reaction solution was poured into methanol (100 mL). The resulting polymer **7** was collected by filtration, redissolved in THF (50 mL), and then precipitated into methanol (300 mL). After drying at $150\text{ }^{\circ}\text{C}$ under vacuum (5 mmHg) for 2 days, polyimide **7** was obtained as red fibrous solids: 825 mg (66%).
- (9) Compound **5**: mp $288.0\text{ }^{\circ}\text{C}$ (DSC); λ_{max} (THF) 450 nm; ^1H NMR (200 MHz, $\text{DMSO-}d_6$) δ 1.39 (s, 18 H), 6.80–7.20 (4 d, 8H, *cis/trans* isomers), 7.50 (q, 4H), 7.95 (m, 6H); MS (EI, *m/e*, relative intensity %) 660 (M^+ , 3.0).

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