Electrochemically and electrochromically stable polyimides bearing tert-butyl-blocked N,N,N',N'-tetraphenyl-1,4-phenylenediamine units

Hui-Min Wang (王惠民), Sheng-Huei Hsiao (蕭勝輝)*

Department of Chemical Engineering and Biotechnology (化學工程與生物科技系)

國立臺北科技大學
National Taipei University of Technology

ABSTRACT

A new class of electrochemically active polyimides with di-tert-butyl-substituted N,N,N',N'-tetraphenyl-1,4-phenylenediamine units were prepared from N,N-bis(4-aminophenyl)- N',N'-bis(4-tert-butylphenyl)-1,4-phenylenediamine and various aromatic tetracarboxylic dianhydrides via a conventional two-step procedure that included a ring-opening polyaddition to give poly(amic acid)s, followed by chemical or thermal cyclodehydration. Most of the polyimides are readily soluble in many organic solvents and can be solution-cast into tough and amorphous films. They had useful levels of thermal stability, with relatively high glass-transition temperatures (276-334 °C), 10 % weight loss temperatures in excess of 500 °C, and char yields at 800 °C in nitrogen higher than 60 %. Cyclic voltammograms of the polyimide films cast on the indium-tin oxide (ITO)-coated glass substrate exhibited two reversible oxidation redox couples at 0.70–0.74 V and 1.05–1.08 V versus Ag/AgCl in acetonitrile solution. The polyimide films revealed excellent stability of electrochromic characteristics, with a color change from colorless or pale yellowish neutral form to green and blue oxidized form at applied potentials ranging from 0.0 to 1.3 V. These anodically coloring polymeric materials exhibited high optical contrast of percentage transmittance change (Δ%T) up to 44 % at 413 nm and 43 % at 890 nm for the green coloration, and 98% at 681 nm for the blue coloration. After over 50 cyclic switches, the polymer films still exhibited good redox and electrochromic stability.
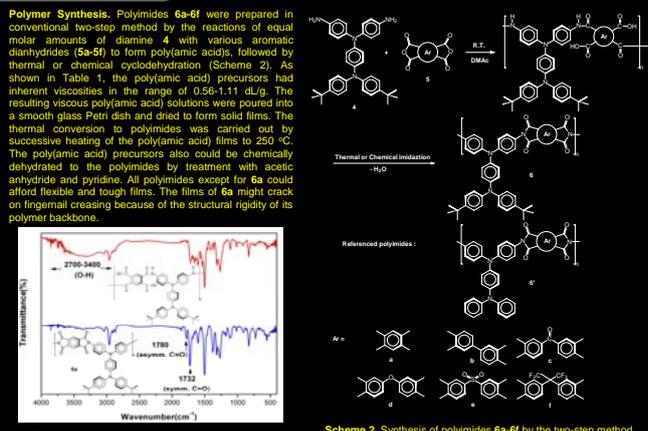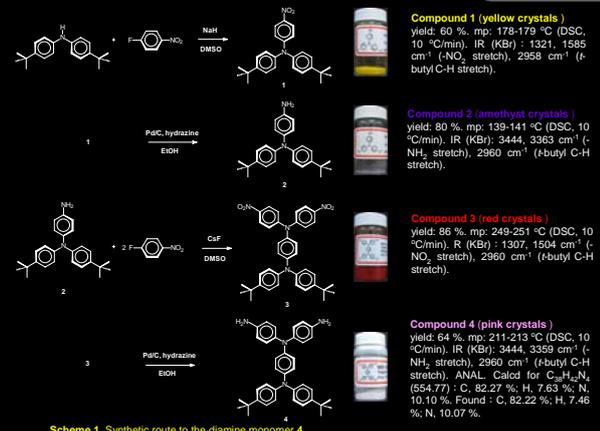
INTRODUCTION

Electrochromism is known as the evocation or alternation of color by passing a current or applying a potential.[1-3] This interesting property led to the development of many technological applications such as self-darkening rear-view mirrors, adjustably darkening windows, large-scale electrochromic screens, and chameleon materials. There are many chemical systems that are intrinsically electrochromic, such as metal oxides, metal-organic complexes, and conjugated conductive polymers. Conjugated electroactive polymers offer a broad set of new materials for electrochromic applications. These polymers exhibit ease of processability and useful mechanical properties (e.g. flexibility). However, the major advantage of these organic-based materials is that their electrochromic properties (switching speed, contrast ratio, and color) can be tuned through chemical structure modification.[4] The Reynolds group has carried out extensive studies on the design and synthesis of poly(3,4-alkylenedioxythiophene)s and poly(3,4-alkylenedioxypyrrole)s based polymers for electrochromic applications.[5,6]

It is well known that aromatic polyimides offer a combination of outstanding properties such as chemical and thermal stabilities, electric and mechanical properties, gas separation characteristics, etc; therefore, they have been widely used in microelectronics, optoelectronics, and aerospace engineering.[7] However, they are difficult to process in their fully imidized form because of high softening temperatures and limited solubility in commercially available solvents, thus possibly narrowing down their applicability. To overcome these limitations, polymer-structure modification becomes necessary. One of the common approaches for increasing solubility and processability of polyimides without sacrificing high thermal stability is the introduction of bulky, packing-disruptive groups into the polymer backbone. For example, the incorporation of three-dimensional, propeller-shaped triphenylamine (TPA) unit into the polyimide backbone led to an enhanced solubility.[8–10] Furthermore, triphenylamine-based polymers are widely used as the hole-transport layer in EL devices, but they also show interesting electrochromic behavior.[11]

The anodic oxidation pathways of TPA were also well studied.[12] The electrogenerated cation radical of TPA is not stable and could dimerize to form tetraphenylbenzidine by tail to tail coupling with loss of two protons per dimer. When the phenyl groups were incorporated by electron-donating substituents at the para-position of TPA, the coupling reactions were greatly prevented by affording stable cationic radicals and lowering the oxidation potenials. The redox properties, ion-transfer process, and electrochromic behavior of N,N,N',N'-tetraaryl-1,4-phenylenediamines are important for technological application. In this article, we therefore synthesized the new diamine, N,N-bis-(4-aminophenyl)-N',N'-bis(4-tert-butylphenyl)-1,4-phenylenediamine (4), and its derived polyimides containing the electroactive N,N,N',N'-tetraphenyl-1,4-phenylenediamine (TPPA) moiety. With such a configuration, the electrochemically active sites of the pendent phenyl groups are blocked, giving the polyimides extra electrochemical stability.

EXPERIMENTAL

Compound 1 (yellow crystals) yield: 60 %. mp: 178-179 °C (DSC, 10 °C/min). IR (KBr) : 1321, 1585 cm⁻¹ (-NO₂ stretch), 2958 cm⁻¹ (t-butyl C-H stretch).

Compound 2 (amethyst crystals) yield: 80 %. mp: 139-141 °C (DSC, 10 °C/min). IR (KBr): 3444, 3363 cm⁻¹ (-NH₂ stretch), 2960 cm⁻¹ (t-butyl C-H stretch).

Compound 3 (red crystals) yield: 86 %. mp: 249-251 °C (DSC, 10 °C/min). R (KBr) : 1307, 1504 cm⁻¹ (-NO₂ stretch), 2960 cm⁻¹ (t-butyl C-H stretch).

Compound 4 (pink crystals) yield: 64 %. mp: 211-213 °C (DSC, 10 °C/min). IR (KBr): 3444, 3359 cm⁻¹ (-NH₂ stretch), 2960 cm⁻¹ (t-butyl C-H stretch). ANAL. Calcd for $C_{38}H_{42}N_4$ (554.77) : C, 82.27 %; H, 7.63 %; N, 10.10 %. Found : C, 82.22 %; H, 7.46 %; N, 10.07 %.

Scheme 1. Synthetic route to the diamine monomer **4**.

Polymer Synthesis. Polyimides **6a-6f** were prepared in conventional two-step method by the reactions of equal molar amounts of diamine **4** with various aromatic dianhydrides (**5a-5f**) to form poly(amic acid)s, followed by thermal or chemical cyclodehydration (Scheme 2). As shown in Table 1, the poly(amic acid) precursors had inherent viscosities in the range of 0.56-1.11 dL/g. The resulting viscous poly(amic acid) solutions were poured into a smooth glass Petri dish and dried to form solid films. The thermal conversion to polyimides was carried out by successive heating of the poly(amic acid) films to 250 °C. The poly(amic acid) precursors also could be chemically dehydrated to the polyimides by treatment with acetic anhydride and pyridine. All polyimides except for **6a** could afford flexible and tough films. The films of **6a** might crack on fingernail creasing because of the structural rigidity of its polymer backbone.

Fig. 1. Typical IR spectra of the polyimide **6a** and its poly(amic acid) precursor.

Scheme 2. Synthesis of polyimides **6a-6f** by the two-step method.

RESULTS AND DISCUSSION

Table 1. Inherent viscosity and solubility behavior of polyimides prepared via thermal (-T) or chemical (-C) imidization

Polymer Code	η inh (dL/g) PAA	η inh (dL/g) Polyimide	NMP	DMAc	DMF	DMSO	m-Cresol	THF
6a-T	1.11	–	±	±	±	–	+	±
6a-C		–	±	±	±	–	±	±
6b-T	0.92	–	±	±	±	–	+	±
6b-C		–	±	±	±	–	±	±
6c-T	0.65	–	+	±	±	–	+	+
6c-C		–	++	±	±	–	++	+
6d-T	0.81	0.44	++	++	±	–	++	+
6d-C		0.40	++	++	±	–	++	++
6e-T	0.56	0.32	++	++	++	±	++	++
6e-C		0.40	++	++	++	±	++	++
6f-T	0.67	0.33	++	++	++	±	++	++
6f-C		0.57	++	++	++	±	++	++

ᵃ Inherent viscosity measured at a concentration of 0.5 dL/g in DMAc at 30 °C. PAA: poly(amic acid).
ᵇ The qualitative solubility was tested with 10 mg of a sample in 1 mL of stirred solvent. ++, soluble at room temperature; +, soluble on heating; ±, partially soluble; –, insoluble even on heating. NMP: N-methyl-2-pyrrolidone; DMAc: N,N-dimethylacetamide; DMF: N,N-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

Table 2. Thermal properties of polyimidesᵃ

Polymer code	Tg ᵇ (°C)	Tc ᶜ (°C)	Td d at 10 wt % loss (°C) In N₂	In air	Char yield ᵉ (wt %)
6a	334 (352)ᶠ	300 (327)	611 (614)	570 (595)	67 (72)
6b	311 (302)	291 (267)	632 (629)	584 (622)	75 (70)
6c	295 (294)	281 (251)	607 (618)	563 (589)	75 (63)
6d	276 (264)	262 (258)	613 (610)	585 (600)	67 (74)
6e	305 (305)	279 (281)	538 (568)	519 (582)	60 (67)
6f	294 (286)	273 (261)	608 (585)	578 (574)	65 (68)

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 ºC/min) of the sample after quenching from 400 to 50 ºC (rate = -200 ºC/min) in nitrogen.
ᶜ Softening temperature measured by TMA with a constant applied load of 10 mN at a heating rate of 10 ºC/min.
ᵈ Decomposition temperature, recorded via TGA at a heating rate of 20 ºC/min and a gas-flow rate of 30 cm³/min.
ᵉ Residual weight percentage at 800 ºC in nitrogen.
ᶠ Data in parentheses are those of structurally similar polyimides **6a'-6f'** without the tert-butyl substituent.

Table 3. Optical and electrochemical properties of the polyimides

Polymer code	In solution abs λmax (nm)ᵃ	In solution PL λmax (nm)ᵃ	In solution Φ_PL (%)	As film abs λmax (nm)	As film abs λonset (nm)	First E_onset	First E_1/2	Second E_1/2	E_g ᵈ (eV)	HOMOᵉ E_onset	HOMOᵉ E_1/2	LUMOᵉ E_onset	LUMOᵉ E_1/2
6a	302	396	–	344	430	0.57	0.73	1.07	2.84	4.93	5.09	2.09	2.25
6b	323	405	0.32	330	415	0.57	0.74	1.08	2.99	4.93	5.10	1.94	2.11
6c	312	378	0.50	326	423	0.64	0.74	1.07	2.93	5.00	5.10	2.07	2.17
6d	319	378	0.63	338	416	0.57	0.74	1.05	2.98	5.01	5.10	2.03	2.12
6e	307	374	0.52	316	428	0.60	0.73	1.06	2.90	4.96	5.09	2.06	2.19
6f	305	370	0.64	342	423	0.65	0.74	1.06	2.93	5.01	5.10	2.08	2.17
6'e	309	426	0.30	317	416	0.63	0.74	1.10	2.97	4.99	5.10	2.02	2.13

ᵃ Measured in dilute solution in NMP at a concentration of about 10⁻⁵ mol/L.
ᵇ The quantum yield in dilute solution was calculated in an integrating sphere with quinine sulfate as the standard (Φ_F = 54.6%).
ᶜ Oxidation potentials from cyclic votammograms.
ᵈ Energy gap = 1240/abs λ onset of the polymer film.
ᵉ The HOMO energy levels were calculated from E_onset or E_1/2 and were referenced to ferrocene (4.8 eV). LUMO = HOMO - E_g.

Table 4. Coloration efficiency of polyimide 6e

Cyclesᵃ	δ OD₈₉₀ ᵇ	Q (mC/cm²)ᶜ	η (cm²/C)ᵈ	Decay (%)ᵉ
1	0.366	1.71	214	0
10	0.351	1.66	211	1.4
20	0.337	1.61	209	2.3
30	0.319	1.54	207	3.3
40	0.301	1.46	206	3.7
50	0.284	1.40	203	5.1

ᵃ Times of cyclic scan by applying potential steps between 0 V and 1.0 V (vs. Ag/AgCl).
ᵇ Optical density change at 890 nm.
ᶜ Ejected charge, determined from the in situ experiments.
ᵈ Coloration efficiency is derived from the equation: η = δ OD890/Q.
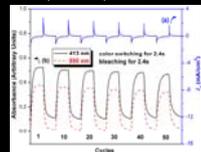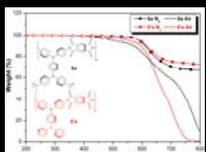ᵉ Decay of coloration efficiency after various cyclic scans.

Fig. 5. (a) Current consumption and (b) electrochromic switching between 0 V and 1.8 V and optical absorbance change monitored at 413 and 890 nm for polyimide **6e** in 0.1 M TBAP/CH₃CN with a cycle time of 18 s.

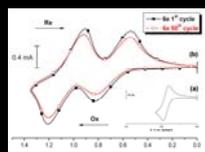**Fig. 2.** TGA curves of polyimides **6a** and **6'a** with a heating rate of 20 ºC/min.

Fig. 3. Cyclic voltammograms of (a) ferrocene and (b) the cast film of polyimide **6e** on the ITO-coated glass slide in CH₃CN containing 0.1 M TBAP at scan rate of 0.1 V/s.
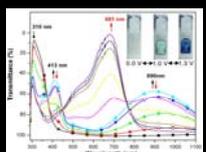
Fig. 4. Spectral change of the cast film of polyimide **6e** on the ITO-coated glass substrate (in acetonitrile with 0.1 M TBAP as the supporting electrolyte) along with increasing applied voltages: 0.0 (■), 0.7 (●), 0.8 (▲), 0.9 (▼), 1.0 (◆), 1.15 (△), 1.2 (○), 1.25 (□) and 1.3 V (◇) (vs. Ag/AgCl couple as reference).
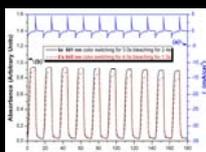
Fig. 6. (a) Current consumption and (b) electrochromic switching between 0 V and 1.0 V and optical absorbance change monitored at 681 and 645 nm for polyimide **6e** and **6'e** in 0.1 M TBAP/CH₃CN with a cycle time of 18 s.

REFERENCES

1. Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. Electrochromism: Fundamentals and Applications; VCH: Weinheim, Germany, 1995.
2. Rosseinsky, D. R.; Mortimer, R. J. Adv. Mater. 2001, 13, 783.
3. Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. Electrochromism and Electrochromic Devices, Cambridge University Press, Cambridge, UK, 2007.
4. Thompson, B. C.; Schottland, P.; Zong, K.; Reynolds, J. R. Chem. Mater. 2000, 12, 1563.
5. Groenendaal, L.; Zotti, G.; Aubert, P.-H.; Waybright, S. M.; Reynolds, J. R. Adv. Mater. 2003, 15, 855.
6. Walczak, R. M.; Reynolds, J. R. Adv. Mater. 2006, 18, 1121.
7. Ghosh, M. K.; Mittal, K. L. Eds. Polyimides: Fundamentals and Applications; Marcel Dekker: New York, 1996.
8. Cheng, S.-H.; Hsiao, S.-H.; Su, T.-H.; Liou, G.-S. Macromolecules 2005, 38, 307.
9. Hsiao, S.-H.; Chang, Y.-M.; Chen, H.-W.; Liou, G.-S. J. Polym. Sci. Part A: Polym. Chem. 2006, 44, 4579.
10. Liou, G.-S.; Hsiao, S.-H.; Chen, H.-W. J. Mater. Chem. 2006, 16, 1831.
11. Hsiao, S.-H.; Liou, G.-S.; Kung, Y.-C.; Yen, H.-J. Macromolecules 2008, 41, 2800.
12. Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. J. Am. Chem. Soc. 1966, 88, 3498.