

Novel Electrochromic Aromatic Polyamides and Polyimides Having 2,3-Dimethylindole-substituted Triphenylamine Pendent Group

NSC 95-2221-E-036-028

Wei-Dun Jhuang (莊為敦), Yi-Chun Kung (龔義群), Sheng-Huei Hsiao (蕭勝輝)*
Department of Chemical Engineering, Tatung University (大同大學化學工程學系)

Department of Chemical Engineering and Biotechnology, National Taipei University of Technology
(國立臺北科技大學化學工程與生物科技系)

Tel: +886-2-27712171 ext. 2548; Fax: +886-2-27317117

E-mail: shhsiao@ntu.edu.tw



Abstract

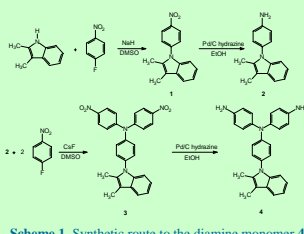
A new indole-derived, triphenylamine-containing diamine monomer, 4,4'-diamino-4''-(2,3-dimethyl-N-indolyl)triphenylamine, was synthesized from readily available reagents and was reacted with various aromatic dicarboxylic acids and tetracarboxylic dianhydride to produce two series of novel triphenylamine-based polyamides **6a-h** and polyimides **9a-f** with pendent 2,3-dimethyl-indolyl substituents. All polyamides were readily soluble in polar organic solvents and could be solution cast into tough and flexible films. The polyimide films were prepared via the thermal curing of their poly(amic acid) films. These polymers showed high glass transition and softening temperatures between 255 °C and 314 °C, and they were fairly stable up to a temperature above 500 °C (for polyamides) or 600 °C (for polyimides). The redox behaviors of the polymers were examined using cyclic voltammetry. Most of these polymers showed one reversible oxidation process. In addition, the polymers were observed to display electrochromic properties, with coloration change from a pale yellowish neutral state to a dark green oxidized state.

Introduction

Triphenylamines have attracted considerable interest as hole transport materials for its multilayer organic electroluminescence (EL) devices due to their relatively high mobilities and their low ionization potentials.¹ The feasibility of utilizing spin-coating and ink-jet printing process for large-area EL devices and possibilities of various chemical modifications (to improve emission efficiencies and allow patterning) make polymeric materials containing triphenylamine units very attractive.² To enhance the hole injection ability of polymeric emissive materials such as poly(1,4-phenylenevinylene)s (PPV) and polyfluorenes (PF), there have been several reports on PPV and PF derivatives involving hole-transporting units such as triphenylamine in the emissive π -conjugated core/main chains³ or grafting them as side chains in a polymer⁴ or attaching them to the polymer chain-ends or the outer surface of dendritic wedges.⁵ Aromatic polyamides and polyimides are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties.⁶ However, rigidity of the backbone and strong interchain interactions result in high melting or glass-transition temperatures (T_g) and limited solubility in most organic solvents. These properties make them generally intractable or difficult to process, thus restricting their wide-spread applications. To overcome such a difficulty, polymer-structure modification becomes necessary. One of the common approaches for increasing solubility and processability of aromatic polyamides and polyimides without sacrificing high thermal stability is the introduction of bulky, packing-disruptive groups into the polymer backbone.⁷ We have demonstrated that aromatic polyamides and polyimides containing bulky, propeller-shaped triphenylamine unit are amorphous, have good solubility in organic solvents, and exhibit excellent thin-film-forming capability and high thermal stability.⁸ Furthermore, many triphenylamine-based polymers also show interesting light-emitting and electrochromic behavior.^{9,14} In this article, we synthesized the novel 2,3-dimethylindole-based diamine monomer, 4,4'-diamino-4''-(2,3-dimethyl-indolyl)triphenylamine (**4**), and its derived polyamides and polyimides containing electron-rich triphenylamine groups. The properties of these polymers are investigated herein.

Monomer Synthesis

The new diamine monomer **4** containing a 4-(2,3-dimethyl-indolyl)triphenylamine unit was synthesized by the synthetic route outlined in Scheme 1. In the first step, the intermediate compound, 2,3-dimethyl-N-(4-nitrophenyl)indole (**1**) was synthesized by nucleophilic aromatic displacement of 4-fluoronitrobenzene with 2,3-dimethylindole using sodium hydride as the base. Reduction of the nitro group of compound **1** by means of hydrazine and Pd/C gave 2,3-dimethyl-N-(4-aminophenyl)indole (**2**). The target diamine monomer **4** was prepared by hydrazine Pd/C-catalyzed reduction of 4-(N-(2,3-dimethyl-indolyl)-4'-nitrophenyl)aniline (**3**) resulting from *N,N*-diarylation of compound **2** with 4-fluoronitrobenzene in the presence of cesium fluoride. Fig. 2 illustrates the ¹H NMR and ¹³C NMR spectra of the diamine monomer **4**. Assignments of each carbon and hydrogen are assisted by the two-dimensional NMR spectra, and these spectra agree well with the proposed molecular structure of compound **4**.



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

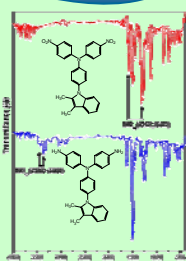


Figure 1. IR spectra of compound **3** and **4**.

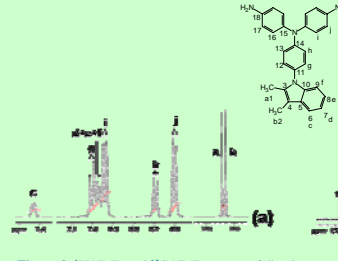
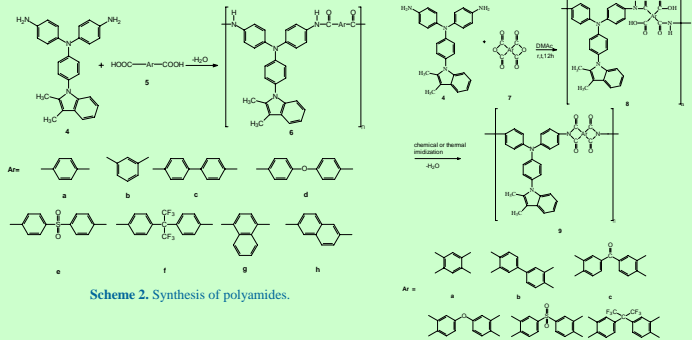


Figure 2. ¹H NMR and ¹³C NMR spectra of diamine monomer **4** in DMSO-*d*₆.

Polymer Synthesis and Solubility Behavior



Scheme 2. Synthesis of polyamides.

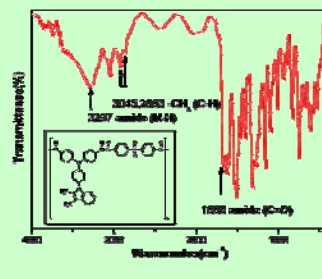


Figure 3. Typical IR spectra of polyamide **6e**.

Scheme 3. Synthesis of polyimides

Table 1. Inherent viscosity and solubility of polyamides and polyimides

Polymer code	η_{inh}^a (dL/g)	Solubility ^b					
		NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
6a	0.35	+	+	+	+	+	+
6b	0.19	+	+	+	+	+	+
6c	0.80	+	+	+	+	+	+
6d	0.50	+	+	+	+	+	+
6e	0.60	+	+	+	+	+	+
6f	0.48	+	+	+	+	+	+
6g	0.68	+	+	+	+	+	+
6h	0.38	+	+	+	+	+	+
9a	0.77	+	+	+	+	+	+
9b	2.77	+	+	+	+	+	+
9c	1.42	+	+	+	+	+	+
9d	2.10	+	+	+	+	+	+
9e	0.92	+	+	+	+	+	+
9f	1.33	+	+	+	+	+	+

^a Inherent viscosity measured at a concentration of 0.5 g/dL in DMAc-5wt% LiCl at 30 °C. ^b Solvent: NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran. Solubility: +: soluble at room temperature; +h: soluble on heating at 100 °C; -: insoluble even on heating.

Thermal Properties

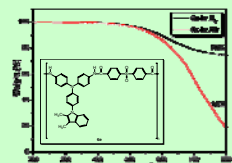


Figure 4. TGA thermogravimetry of polyimide **6e** with heating rate of 20 °C/min.

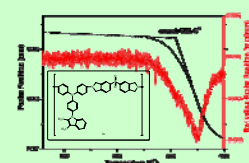


Figure 5. TMA trace of polyimide **9e** with a heating rate of 10 °C/min.

Table 2. Thermal behavior of polyamides and polyimides^a.

Polymer code	T_g^b (°C)	T_s^c (°C)	T_d at 5% weight loss (°C)	T_d at 10% weight loss (°C)	Char yield ^d (%)	Air		N ₂	
						T_d at 5% weight loss (°C)	T_d at 10% weight loss (°C)	T_d at 5% weight loss (°C)	T_d at 10% weight loss (°C)
6a	290	280	555	555	631	607	79	—	—
6b	—	—	—	—	—	—	—	—	—
6c	288	280	598	560	653	619	81	—	—
6d	286	255	545	529	631	593	79	—	—
6e	282	273	544	530	595	576	76	—	—
6f	285	266	542	551	581	607	70	—	—
6g	284	261	545	555	614	612	79	—	—
6h	287	283	510	519	582	609	81	—	—
9a	296	272	531	495	590	549	73	—	—
9b	295	284	568	550	618	596	74	—	—
9c	303	287	532	528	592	578	65	—	—
9d	289	279	552	549	610	591	68	—	—
9e	314	306	463	465	512	524	68	—	—
9f	292	291	550	530	582	564	62	—	—

^a The polymer film sample were heated at 300 °C for 1 h prior to all the thermal analyses.
^b The sample was heated from 50 to 400 °C at a scan rate of 20 °C/min followed by rapid cooling to 50 °C 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 5% or 10% weight loss was recorded by TGA at heating rate of 20 °C/min.
^e Residual weight percentages at 800 °C under nitrogen flow.

Optical, Electrochemical, and Electrochromic Properties

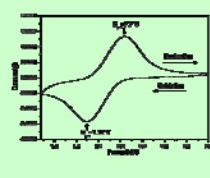


Figure 6. Cyclic voltammograms of polyamide **6a** film on an ITO-coated glass substrate in CHCN solutions containing 0.1 M TBAP at a scan rate of 100 mV/s.

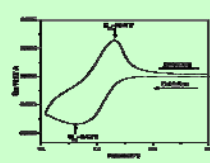


Figure 7. Cyclic voltammograms of polyimide **9a** film on an ITO-coated glass substrate in CHCN solutions containing 0.1 M TBAP at a scan rate of 100 mV/s.

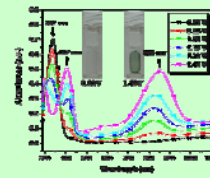


Figure 8. Electrochromic behavior of polyamide **6d** thin film in CHCN with 0.1 M TBAP as the supporting electrolyte at 0.00 V, 0.85 V, 1.00 V, 1.10 V, 1.20 V, 1.40 V (vs. Ag/AgCl).

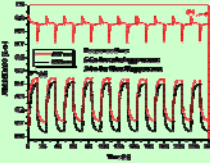


Figure 9. Potential step absorbometry and current consumption of **6d** by applying potential steps 0.00 to +1000 (mV vs. Ag/AgCl) (coated area: 1 cm²).

Table 3. Optical and Electrochemical Properties for Polyamides and Polyimides

Index	Solution ^a (mol/L in NMP)			Thin film ^b (nm)			Oxidation (V) (vs. Ag/AgCl)		E_g^c (eV)	HOMO/LUMO ^d (eV)
	Abs.	PL	Abs.	Abs.	PL	Abs.	E_{ox}^1	E_{ox}^2		
6a	348	420	305	437	0.94	1.11	2.84	5.32/2.53	—	—
6b	336	414	313	405	0.96	1.19	3.06	5.32/2.27	—	—
6c	344	418	300	433	0.97	1.11	2.86	5.33/2.43	—	—
6d	336	408	333	398	0.96	1.13	3.12	5.32/2.18	—	—
6e	306	369	308	485	0.92	1.01	2.56	5.28/2.69	—	—
6f	340	417	332	415	0.95	1.21	2.99	5.31/2.25	—	—
9g	322	411	306	457	0.96	1.18	2.71	5.29/2.26	—	—
9h	302	367	317	402	0.93	1.06	3.08	5.29/2.09	—	—
9i	317	456	313	423	1.07	1.45	2.92	5.43/2.51	—	—
9j	323	448	314	388	1.07	1.46	3.20	5.43/2.23	—	—
9k	314	454	310	390	1.08	1.44	3.18	5.44/2.26	—	—
9l	320	454	313	384	1.06	1.44	3.23	5.42/2.19	—	—
9m	309	454	308	397	1.05	1.38	3.12	5.41/2.29	—	—
9n	320	448	307	386	1.07	1.39	3.21	5.42/2.21	—	—

^a Polymer concentration of 10⁻⁵ mol/L in NMP.
^b They were excited at above for both solid and solution states.
^c Half-wave potential vs. Ag/AgCl in CH₂Cl₂.
^d Energy gap was estimated from the absorption edge on the polymer film; $E_g = 1240/\lambda_{cut-off}$ of film.
^e The HOMO level levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV). LUMO = HOMO - gap.

REFERENCES

- Shirota, Y. *J. Mater. Chem.* **2005**, *15*, 79.
- Cho, J.-S.; Kimoto, A.; Higuchi, M.; Yamamoto, K. *Macromol. Chem. Phys.* **2005**, *206*, 635.
- Wu, F.-I.; Shih, P.-I.; Shia, C.-F.; Tang, Y.-L.; Chi, Y. *Macromolecules* **2005**, *38*, 9028.
- Liang, F.-S.; Kazan, T.; Nishida, H.; Kido, J. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 5765.
- Pu, Y.-Q.; Li, Y.-L.; Yan, S.-K.; Bo, Z.-S. *Macromolecules* **2004**, *37*, 6395.
- Ghosh, M. K.; Mitra, K. L., Eds. *Polyimides: Fundamentals and Applications*; Marcel Dekker: New York, **1996**.
- Myung, B. Y.; Ahn, C. J.; Yoon, T. H. *Polymer* **2004**, *45*, 3185.
- Hsiao, S.-H.; Chen, C.-W.; Lion, G.-S. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 3302.
- Cheng, S.-H.; Hsiao, S.-H.; Su, T.-H.; Lion, G.-S. *Macromolecules* **2005**, *38*, 307.
- Su, T.-H.; Hsiao, S.-H.; Lion, G.-S. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 2085.
- Hsiao, S.-H.; Chang, Y.-M.; Chen, H.-W.; Lion, G.-S. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 4579.
- Liou, G.-S.; Hsiao, S.-H.; Chen, H.-W. *J. Mater. Chem.* **2006**, *16*, 1831.
- Liou, G.-S.; Hsiao, S.-H.; Fung, Y.-K. *Electrochim. Acta* **2006**, *51*, 1533.
- Liou, G.-S.; Hsiao, S.-H.; Hsu, N.-K.; Yang, Y.-L. *Macromolecules* **2006**, *39*, 5337.
- Liou, G.-S.; Chen, H.-W.; Yen, H.-J. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 4108.