

Highly Stable Anodic Electrochromic Polyamides Containing Dimethoxy-Activated Triphenylamine Moiety



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ABSTRACT

A new triphenylamine-containing diamine monomer, 2,4-dimethoxy-4',4''-diaminotriphenylamine (2), was synthesized from readily available reagents and was reacted with various aromatic or aliphatic dicarboxylic acids to produce a series of polyamides (4a-f) containing 2,4-dimethoxy-activated triphenylamine units. All the resulting polyamides were readily soluble in polar organic solvents and could be solution cast into tough and flexible films. These polymers exhibited good thermal stability with glass-transition temperatures of 243–289 °C and softening temperatures of 235–280 °C, 10% weight-loss temperatures in excess of 500 °C in nitrogen, and char yields at 800 °C in nitrogen higher than 65%. The redox behaviors of the polymers were examined using cyclic voltammetry (CV). Most of these polymers showed two reversible oxidation processes in the first CV scan. The polymers also displayed low ionization potentials as a result of their 2,4-dimethoxy-activated triphenylamine moieties. In addition, the polymers displayed excellent stability of electrochromic characteristics with coloration change from a pale yellowish neutral state to a green or blue-violet oxidized state. After over 2000 cyclic scans, the polymer films still exhibited good electrochemical and electrochromic stability.

INTRODUCTION

Electrochromism can be defined as the reversible change in optical properties of a material resulting from electrochemically induced redox states. Color changes are commonly between a transparent state, where the chromophore only absorbs in the UV region, and a colored state, or between two colored states in a given electrolyte solution. The electrochromic material may exhibit several colors and be termed polyelectrochromic. Electrochromic anti-glare car rear-view mirrors have already been commercialized, with other proposed applications of electrochromic materials including their use in controllable light-reflective or light-transmissive devices for optical information and storage, sunglasses, protective eyewear for the military, controllable aircraft canopies, and glare-reduction systems for offices and smart windows for use in cars and buildings.^{1,2}

Triarylamines have attracted considerable interest as hole transport materials for use in multilayer organic electroluminescence (EL) devices due to their relatively high mobilities and their low ionization potentials.³ 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 triarylamines units very attractive. 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 triarylamine in the emissive π -conjugated core/main chains or grafting them as side chains in a polymer or attaching them onto the polymer chain-ends or the outer surface of dendritic wedges.⁴⁻⁶

Aromatic polyamides are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties.⁷ 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 without sacrificing high thermal stability is the introduction of bulky, packing-disruptive groups into the polymer backbone. We have demonstrated that aromatic polyamides containing bulky, propeller-shaped triphenylamine (TPA) unit are amorphous, have good solubility in organic solvents, and exhibit excellent thin-film-forming capability and high thermal stability.^{8,9} Furthermore, many TPA-based polymers also show interesting light-emitting and electrochromic behavior.^{10,11}

The anodic oxidation pathways of TPA are well studied.¹² The unsubstituted TPA may undergo coupling-deprotonation to form tetraphenylbenzidine after the formation of the initial monocation radical. It has been well established that incorporation of electron-donating substituents such as methoxy group at the para position of TPA prevents the coupling reactions and affords stable radical cations.^{13,14} Therefore, we synthesized the diamine monomer, 4,4''-diamino-2,4''-dimethoxytriphenylamine (2), and its derived polyamides containing electroactive TPA units with electron-donating methoxy groups *para* and *ortho* substituted on the pendent phenyl ring. We anticipated that the electrochromic films obtained from the present polyamides would be stable to multiple redox switching.

MONOMER SYNTHESIS

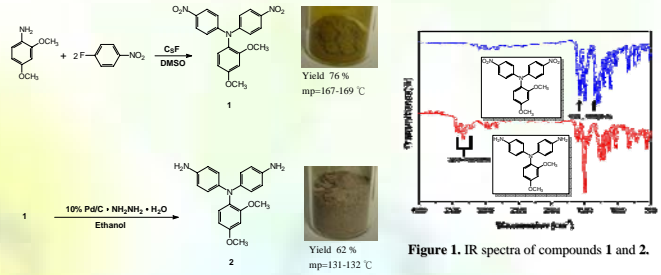


Figure 1. IR spectra of compounds 1 and 2.

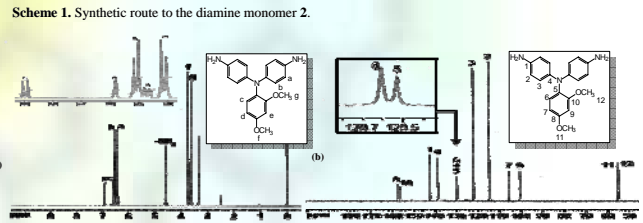
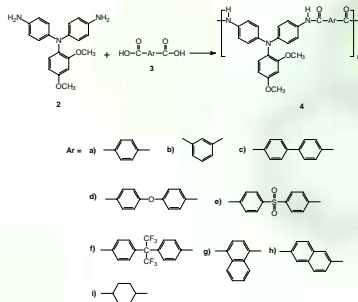


Figure 2. (a) ¹H NMR and (b) ¹³C NMR spectra of diamine monomer 2 in DMSO-*d*₆.

POLYMER SYNTHESIS AND SOLUBILITY



Scheme 2. Synthesis of polyamides.¹⁵

Table 1. Inherent viscosities and solubility of the polyamides

Polymer	η_{inh} (dL/g)	Solubility ^a						
		NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF	
4a	0.089	++	++	++	++	++	++	
4b	0.22	++	++	++	++	++	++	
4c	0.298	++	++	++	++	++	++	
4d	1.62	++	++	++	++	++	++	
4e	0.73	++	++	++	++	++	++	
4f	0.69	++	++	++	++	++	++	
4g	0.68	++	++	++	++	++	++	
4h	0.68	++	++	++	++	++	++	
4i	0.59	++	++	++	++	++	++	

^a Measured in DMAc containing 5 wt % LiCl at 30 °C on 0.5 g/dL.

^b Qualitative solubility was tested with 10 mg sample in 1 mL solvent. Symbol: ++, soluble at room temperature; +, soluble on heating at 100 °C; ±, partially soluble or swelling on heating; -, insoluble even on heating. NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

THERMAL PROPERTIES

Table 2. Thermal properties of the polyamides

Polymer	T _g (°C)	T _{5%} (°C)	T _{10%} (°C)		Char yield (%)
			loss ^a	loss ^b	
4a	239	264	409	457	49.7
4b	245	246	457	472	48.9
4c	285	281	460	463	48.6
4d	254	282	445	429	49.9
4e	276	276	449	479	50.2
4f	277	289	429	399	50.9
4g	288	284	424	403	47.7
4h	265	269	429	411	43.5
4i	245	232	425	437	47.7

^a 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 .

^b Softening temperature measured by TMA using a penetration method.

^c Decomposition temperature at which a 5% or 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.

^d Residual weight percentages at 800 °C under nitrogen flow.

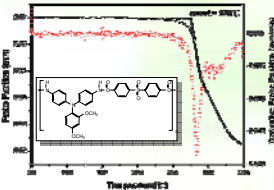


Figure 3. TMA curve of polyamide 4e with a heating rate of 10 °C/min.

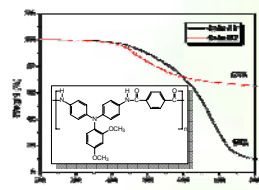


Figure 4. TGA thermograms of polyamide 4a with a heating rate 20 °C/min.

OPTICAL AND ELECTROCHEMICAL PROPERTIES

Table 3. Optical and electrochemical properties of the polyamides

Polymer	Absorption ^a		Emission ^b		E _{onset} (V)		E _{1/2} (V)		E _{onset} (V)	
	λ_{max}	λ_{max}	λ_{max}	λ_{max}	E ₁	E ₂	E ₁	E ₂	E ₁	E ₂
4a	275	265	426	425	0.65	0.72	0.91	1.24	2.38	2.64
4b	275	265	426	425	0.65	0.72	0.91	1.24	2.38	2.64
4c	275	265	426	425	0.65	0.72	0.91	1.24	2.38	2.64
4d	275	265	426	425	0.65	0.72	0.91	1.24	2.38	2.64
4e	275	265	426	425	0.65	0.72	0.91	1.24	2.38	2.64
4f	275	265	426	425	0.65	0.72	0.91	1.24	2.38	2.64
4g	275	265	426	425	0.65	0.72	0.91	1.24	2.38	2.64
4h	275	265	426	425	0.65	0.72	0.91	1.24	2.38	2.64
4i	275	265	426	425	0.65	0.72	0.91	1.24	2.38	2.64

^a Spectra measured in NMP (1 × 10⁻³ mol/L).

^b The data were calculated by the equation: $E_g = 1240 / \lambda_{em} \times \lambda_{exc}$ of polymer film.

^c The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).

^d LUMO = HOMO - E_g .

^e Values in parentheses are data of analogous polyamides 4' having the corresponding diacid residue as in the 4 series.

^f Values in parentheses are data of analogous polyamides 4'' having the corresponding diacid residue as in the 4 series.

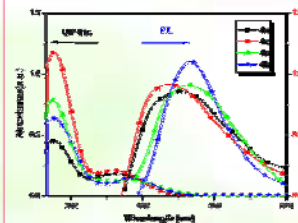


Figure 5. UV-Vis absorption and PL spectra of polyamides 4a, 4c, and 4h, with a concentration of about 10⁻³ M in NMP.

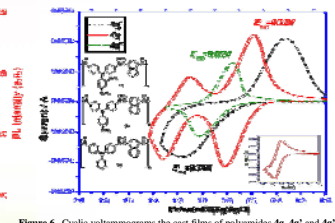


Figure 6. Cyclic voltammograms of the cast films of polyamides 4g, 4e, and 4g'' on an ITO-coated glass substrate in CH₃CN containing 0.1 M TBAP at a scan rate of 100 mV/s. The inset shows the CV curve of ferrocene as the standard.

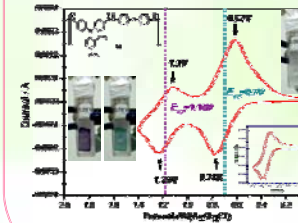


Figure 7. Cyclic voltammogram of the cast film of polyamide 4d on an ITO-coated glass substrate in CH₃CN containing 0.1 M TBAP at a scan rate of 100 mV/s.

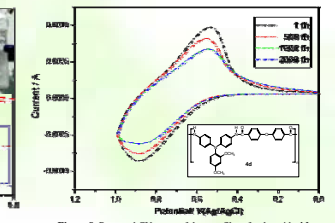


Figure 8. Repeated CV scans of the cast film of polyamide 4d on an ITO-coated glass substrate in CH₃CN containing 0.1 M TBAP with a scanning rate of 100 mV/s.

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