

Novel Electrochromic Aromatic Poly(amide-imide)s Based on the Diimide-Diacid Condensed from *N,N*-bis(4-aminophenyl)-*N,N'*-bis(4-tert-butylphenyl)-1,4-phenylenediamine and Trimellitic Anhydride

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Abstract

A new imide ring-preformed, triphenylamine-containing dicarboxylic acid monomer, *N,N*-bis(4-tert-butylphenyl)-*N,N'*-bis(4-trimellitido)-1,4-phenylenediamine (**2**), was synthesized from the condensation of *N,N*-bis(4-aminophenyl)-*N,N'*-bis(4-tert-butylphenyl)-1,4-phenylenediamine (**1**) and two equivalent amount of trimellitic anhydride (TMA). A series of new poly(amide-imide)s were prepared from the diimide-diacid **2** with various aromatic diamines by the phosphorylation polyamidation reaction. All the polymers were readily soluble in many organic solvents and could be solution-cast into tough and flexible polymer films. They displayed relatively high glass-transition temperatures (280–320 °C) and good thermal stability, with 10% weight-loss temperatures in excess of 470 °C in nitrogen and char yields at 800 °C in nitrogen higher than 64%. Cyclic voltammograms of the poly(amide-imide) films cast onto an indium-tin oxide (ITO)-coated glass substrate exhibited two reversible oxidation redox couples at 0.68–0.69 V and 1.06–1.10 V vs. Ag/AgCl in acetonitrile solution, and they revealed high redox and electrochromic stability with a color change from colorless neutral form to yellow and blue oxidized forms at applied potentials ranging from 0.0 to 1.3 V. Cyclic voltammograms of the poly(amide-imide) **4g** prepared from diimide-diacid **2** and diamine **1** exhibited four reversible oxidation redox couples in acetonitrile solution at $E_{1/2}$ = 0.63, 0.69, 0.95, and 1.04 V, respectively. Because there are more than two redox states are electrochemically accessible from poly(amide-imide)s **4a** and **4g**, they could form tristable and even tetra-stable color species and thus could display several colors upon oxidation at varying applied voltages. Their films could change color from colorless in the neutral form to yellow or green and then blue at different oxidized stages. The poly(amide-imide) **4c** showed excellent reversible electrochromic stability with good coloration efficiency of yellow (CE = 268 cm²/C). After cycling for 100 times, the polymer films still exhibited excellent electrochemical and electrochromic stability.

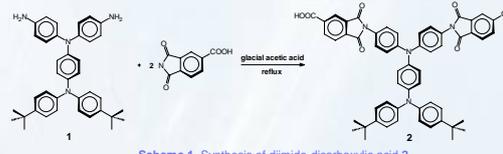
Introduction

Electrochromic materials exhibit a change in optical absorption or transmittance upon redox switching. There are many chemical systems that are intrinsically electrochromic, such as transition metal oxides, inorganic coordination complexes, organic molecules, and conjugated polymers.¹ Traditionally, interest in electrochromic materials has been directed towards optical changes in the visible region, leading to many technological applications such as variable reflectance mirrors, tunable windows, and electrochromic displays. Of the available electrochromic materials, conjugated conducting polymers such as poly(3,4-alkylenedioxythiophene)s and poly(3,4-alkylenedioxy-pyrrole)s derivatives have become widely researched electrochromic materials because of their fast switching speeds, improved processability, and color tenability through structural modification.² In recent years, the Liou group has carried out extensive studies on the design and synthesis of triarylamine-based high-performance polymers such as aromatic polyamides and polyimides for electrochromic applications.³ The electrochromic function of these polymers came from the triarylamine core which can be easily oxidized and the resulting radical cation is stable enough and can undergo a long-term redox cycles.

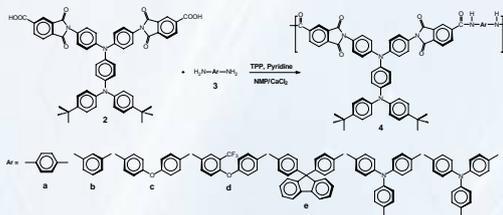
Aromatic poly(amide-imide)s (PAIs) possess balanced characteristics between polyamides and polyimides such as high thermal stability and good mechanical properties together with easy processability. Since we successfully applied the Yamazaki-Higashi phosphorylation reaction⁴ to the direct synthesis of high-molecular-weight PAIs from the TMA-derived imide ring-bearing dicarboxylic acids and aromatic diamines using triphenyl phosphite (TPP) and pyridine as condensing agents,⁵ this efficient synthetic route has proved to exhibit significant advantages in preparing operations as compared with conventional acid chloride or isocyanate methods. Thus, many novel PAIs have been readily prepared by this convenient technique in our and other laboratories. Furthermore, this synthetic procedure can offer us the option of the incorporation of specific functionalities between amide or imide groups in the PAI backbone. The incorporation of such functional groups may provide a method of controlling certain physical properties or special functions of the resulting PAIs.

In our recent publications,⁶ we have reported the synthesis of electrochromic aromatic polyamides and polyimides functionalized with the *N,N,N,N*-tetraphenyl-1,4-phenylenediamine (TPPA) unit. Because of the incorporation of bulky, butterfly-shaped TPPA units along the polymer backbone, all the polyamides and most polyimides were amorphous, showed good solubility in many aprotic solvents, good film-forming capability, and exhibited high thermal stability. However, the polyimides derived from less flexible dianhydrides such as pyromellitic dianhydride (PMDA) and 3,4,3',4'-biphenyltetracarboxylic dianhydride (BPDA) revealed a less solubility, possibly due to the rigid nature of the polymer main chain. As a continuation of our efforts in developing easily processable high-performance functional polymers with the triarylamine group, the present study describes the synthesis of novel electrochromic PAIs based on a new diimide-dicarboxylic acid condensed from **1** and TMA. The active sites of the TPPA unit are blocked with bulky *tert*-butyl substituent, and as a result, the present PAIs are expected to exhibit an enhanced solubility and extra electrochromic stability.

Experimental



Scheme 1. Synthesis of diimide-dicarboxylic acid **2**.



Scheme 2. Synthesis of PAIs **4a-4g**.

Polymer Synthesis

A series of new *tert*-butyl-blocked TPPA containing PAIs **4a-4g** were prepared from the diimide-dicarboxylic acid **2** and various aromatic diamines (**3a-3g**) by the direct polycondensation reaction using triphenyl phosphite (TPP) and pyridine as condensing agents (Scheme 2). The polymerization proceeded homogeneously throughout the reaction and afforded highly viscous polymer solutions, and precipitated in a tough fibrous form when pouring the resultant polymer solutions into methanol. The obtained PAIs had inherent viscosities in the range of 0.33–0.78 dL/g, and the formation of these polymers was confirmed by IR, and NMR spectroscopy.

Compound 1 (pink powder)
yield: 64%. mp: 211–213 °C (DSC, 10 °C/min).
IR (KBr): 3444, 3359 cm⁻¹ (N–H stretch), 2960 cm⁻¹ (*t*-butyl C–H stretch).

Compound 2 (brown powder)
yield: 80%. mp: 321–323 °C (DSC, 10 °C/min).
IR (KBr): 2700–3400 (O–H stretching), 2964 (*t*-butyl C–H stretch), 1778, 1724 cm⁻¹ (imide C=O stretching).

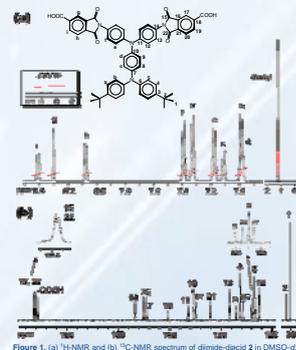


Figure 1. (a) ¹H-NMR and (b) ¹³C-NMR spectrum of diimide-diacid **2** in DMSO-*d*₆.

Film Preparation of PAIs

A solution of polymer was made by dissolving about 0.6 g of the polymer sample in 10 mL of DMAc. The homogeneous 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. The obtained film with the thickness of about 50–60 μm were used for solubility tests, thermal analyses, optical and electrochromic properties measurements.

Basic Characterization

Table 1. Inherent viscosity and Solubility of PAIs

Polymer Code	η_{inh}^a (dL/g)	Solubility in various solvents ^b					
		NMP	DMAc	DMF	DMSO	m-Cresol	THF
4a	0.61	++ (+)	++ (-)	++ (-)	++ (-)	++ (-)	++ (-)
4b	0.47	++ (+)	++ (+)	++ (+)	++ (+)	++ (+)	++ (+)
4c	0.39	++ (+)	++ (+)	++ (+)	++ (+)	++ (+)	± (S)
4d	0.70	++ (+)	++ (+)	++ (+)	++ (+)	++ (+)	± (S)
4e	0.34	++ (+)	++ (+)	++ (+)	++ (+)	++ (+)	++ (-)
4f	0.78	++ (+)	++ (+)	++ (+)	++ (+)	++ (+)	++ (-)
4g	0.33	++	++	++	++	++	±

^a Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.
^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.
^c Values in parentheses are data of analogous polyamides **4'** having the corresponding diacid residue as in the **4** series.



Figure 2. (a) TMA and (b) TGA curves of PAI **4a** with a heating rate of 10 and 20 °C/min, respectively.

Table 2. Thermal properties of PAI^a

Polymer code	T_g^b (°C)	T_d^c at 5 wt % loss (°C)		T_d^c at 10 wt % loss (°C)		Char yield ^d (wt %)	
		In N ₂	In air	In N ₂	In air		
4a	314	290	423	434	470	493	64
4b	299	272	453	455	512	515	65
4c	280	260	447	451	495	515	66
4d	284	250	449	451	523	498	64
4e	320	289	486	481	535	540	68
4f	293	278	477	463	533	521	69
4g	282	255	477	516	532	523	70

^a Midpoint temperature of the baseline shift on the second DSC heating trace (rate=20 °C/min) of the sample after quenching from 400 to 50 °C (rate=200 °C/min) in nitrogen.
^b Softening temperature measured by TMA with a constant applied load of 10 mN at a heating rate of 10 °C/min.
^c Decomposition temperature at which a 5% or 10% weight loss was recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 20 cm³/min.
^d Residual weight percentage at 800 °C in nitrogen.

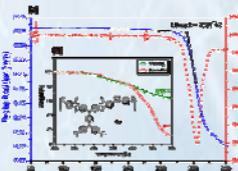


Figure 2. (a) TMA and (b) TGA curves of PAI **4a** with a heating rate of 10 and 20 °C/min, respectively.

Optical, Electrochemical and Electrochromic Properties

Table 3. Optical and electrochemical properties of PAIs

Polymer code	In solution		As film		Oxidation potential ^a (V) vs. Ag/AgCl in CH ₃ CN				$E_{1/2}^b$ (eV)	HOMO ^c (eV)		LUMO ^d (eV)			
	abs	PL	abs	abs	First	Second	Third	Fourth		E_{onset}	$E_{1/2}$				
	λ_{max} (nm)	λ_{max} (nm)	λ_{max} (nm)	λ_{max} (nm)	E_{onset}	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$		E_{onset}	$E_{1/2}$				
4a	312	369	0.53	306	417	0.44	0.68	1.07	—	2.97	4.80	5.04	1.83	2.07	
4b	313	373	0.47	307	405	0.46	0.69	1.06	—	3.06	4.82	5.05	1.76	1.99	
4c	306	376	0.46	306	401	0.42	0.69	1.04	—	3.09	4.78	5.05	1.69	1.96	
4d	311	385	0.23	307	401	0.47	0.68	1.07	—	3.09	4.83	5.04	1.74	1.95	
4e	311	371	0.47	311	400	0.45	0.69	1.10	—	3.10	4.81	5.05	1.71	1.95	
4f	310	370	0.37	317	428	0.47	0.69	0.89	1.05	2.89	4.83	5.05	1.94	2.16	
4g	313	376	0.26	316	460	0.42	0.63	0.69	0.95	1.04	2.70	4.78	4.99	2.08	2.29
4'c	304	368	0.22	301	400	0.82	1.00	—	—	3.10	5.18	5.36	2.08	2.26	

^a Measured in dilute solution in NMP at a concentration of about 10⁻⁴ mol/L. ^b The quantum yield in dilute solution was calculated in an integrating sphere with quinine sulfate as the standard ($\phi_f = 54.6\%$). ^c Oxidation potentials from cyclic voltammograms. ^d Energy gap = 1240 (Abs.)_{onset} of the polymer film. ^e The HOMO energy levels were calculated from $E_{1/2}$ and were referenced to ferrocene (4.8 eV). ^f LUMO = HOMO + E_g .

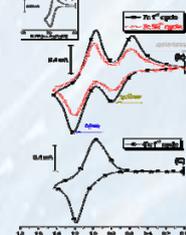


Figure 3. Cyclic voltammograms of (a) ferrocene and the cast films of (b) PAI **4c** and (c) PAI **4c** on the ITO-coated glass substrate in CH₃CN containing 0.1 M TBAP at a scan rate of 0.05 V/s.

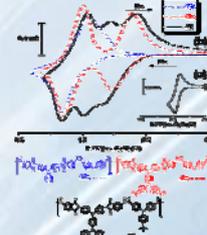


Figure 4. Cyclic voltammograms of (a) ferrocene and the cast films of (b) PAI **4c**, **4f** and (c) PAI **4g** on the ITO-coated glass substrate in CH₃CN containing 0.1 M TBAP at a scan rate of 0.05 V/s.

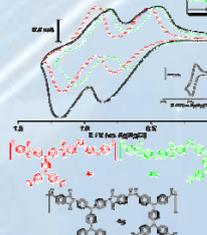


Figure 5. Cyclic voltammograms of (a) ferrocene and the cast films of (b) PAI **4c**, **4f** and (c) PAI **4g** on the ITO-coated glass substrate in CH₃CN containing 0.1 M TBAP at a scan rate of 0.05 V/s.

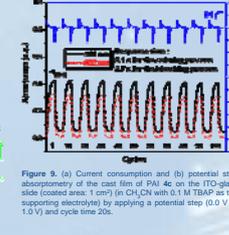


Figure 6. Electrochromic behavior of PAI **4c** thin film in CH₃CN with 0.1 M TBAP as the supporting electrolyte at 0.0 (□), 0.8 (■), 0.9 (●), 1.0 (▼), 1.1 (◇), 1.2 (▲), 1.3 (△) and 1.5 (▽) V (vs. Ag/AgCl).

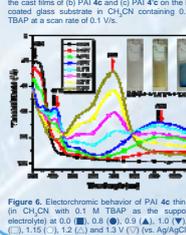


Figure 7. Polyelectrochromic behavior of PAI **4f** thin film in CH₃CN with 0.1 M TBAP as the supporting electrolyte at 0.0 (□), 0.8 (■), 1.0 (▲), 1.3 (△) and 1.5 (▽) V (vs. Ag/AgCl).

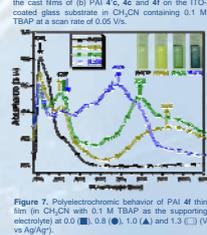


Figure 8. Polyelectrochromic behavior of PAI **7g** thin film in CH₃CN with 0.1 M TBAP as the supporting electrolyte at 0.0 (□), 0.8 (■), 1.0 (▲), 1.15 (▼), 1.3 (△) and 1.5 (▽) V (vs. Ag/AgCl).

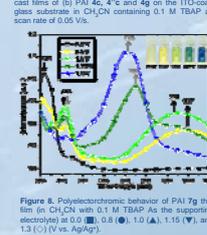


Figure 9. (a) Current consumption and (b) potential step absorbometry of the cast film of PAI **4c** on the ITO-glass slide (coated area: 1 cm²) in CH₃CN with 0.1 M TBAP as the supporting electrolyte by applying a potential step (0.0 V to 1.0 V) and cycle time 20s.

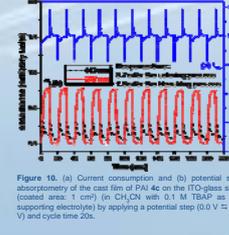


Figure 10. (a) Current consumption and (b) potential step absorbometry of the cast film of PAI **4g** on the ITO-glass slide (coated area: 1 cm²) in CH₃CN with 0.1 M TBAP as the supporting electrolyte by applying a potential step (0.0 V to 1.3 V) and cycle time 20s.

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