

# Stably anodic green electrochromic aromatic poly(amine–amide–imide)s: Synthesis and electrochromic properties

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## Abstract

A series of new poly(amine–amide–imide)s with pendent 4-methoxy-substituted triphenylamine (TPA) units having inherent viscosities of 0.35–0.45 dL/g were prepared from various aromatic bis(trimellitimide)s and the 4-methoxy-substituted triphenylamine-based aromatic diamine, 4,4'-diamino-4''-methoxytriphenylamine (**I**), by direct polycondensation. All the polymers are readily soluble in polar organic solvents. Flexible and amorphous films of these poly(amine–amide–imide)s could be obtained by solution-casting, and showed excellent thermal stability, 10% weight-loss temperatures in excess of 515 °C, and char yields at 800 °C in nitrogen higher than 58% associated with high glass-transition temperatures (297–305 °C). These polymers exhibited a maximum UV–vis absorption at 302–304 nm with fluorescence emission maxima around 360–376 nm in *N*-methyl-2-pyrrolidinone (NMP) solution. The hole-transporting and electrochromic properties were examined by electrochemical and spectroelectrochemical methods. Cyclic voltammograms of the poly(amine–amide–imide) films cast onto an indium–tin oxide (ITO)-coated glass substrate exhibit a reversible oxidation at 0.79–0.80 V vs. Ag/AgCl in acetonitrile solution, and reveal good stability of electrochromic characteristics with a color change from yellow to green at applied potentials ranging from 0.00 to 0.95 V. These anodically polymeric electrochromic materials not only showed excellent reversible electrochromic stability with good green coloration efficiency (CE = 395 cm<sup>2</sup>/C) but also exhibited high contrast of optical transmittance change ( $\Delta T\%$ ) up to 78% in 768 nm. After over 100 cyclic switches, the polymer films still exhibited stable electrochromic characteristics.

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**Keywords:** Poly(amine–amide–imide)s; Triphenylamine; Electrochromic materials; Coloration efficiency

## 1. 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

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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, and aircraft canopies for the military, and glare-reduction systems for offices and smart windows used in cars and buildings [1–3].

The first studies and commercial interests in electrochromic materials started with inorganic compounds such as tungsten trioxide ( $\text{WO}_3$ ) and iridium dioxide ( $\text{IrO}_2$ ) [4]. Later, organic materials (i.e., viologens, metallophthalocyanines and conjugated polymers) have received more attention than inorganics for electrochromic applications because of the different colors observed with these compounds while switching among their redox states [1,5,6]. Although conjugated polymers (CPs) in particular have several advantages over inorganic compounds; i.e., outstanding coloration efficiency, fast switching ability, high stability, fine-tuning of the band gap (and the color) through chemical structure modification, multiple colors with the same material [7], thin film flexibility, and cost effectiveness, they have not received enough attention in terms of applications. One of the main reasons for this was the deficient third leg (green) of color space in conjugated polymers (CPs) until first report about a green-colored neutral conjugated polymer (CP) was published [8]. For green color, at least two chromophores are required that absorb at red and blue wavelengths in the neutral form, and should also deplete together when the polymer is oxidized.

Aromatic polyimides are an important class of high performance materials because of their excellent thermo-oxidative stability, mechanical strength, electrical properties, and solvent resistance. However, the intractable characteristics have been major problems as a result of high melting point and insolubility. To overcome this drawback, various copolyimides and polymer-structure modification have been developed [9]. For example, a poly(amide–imide) (PAI) has been developed as an alternative material offering a compromise between excellent thermal stability and processability. Another common approach for increasing solubility and processability of polymers without sacrificing high thermal stability is the introduction of bulky, packing-disruptive groups into the polymer backbone [10–17]. A

number of PAIs have been synthesized through two main routes: via amide–imide-forming reaction from trimellitic anhydride, and through amide-forming reaction from imide-containing monomers such as imide-preformed dicarboxylic acid or their acid chlorides [18]. One of the more facile approaches to prepare PAIs with high molecular weights is the direct polycondensation between imide-bearing dicarboxylic acids with aromatic diamines following the Yamazaki–Higashi phosphorylation technique [19–22]. The direct polycondensation route avoids using moisture-sensitive acid chlorides or isocyanates and provides significant advantages in laboratory preparation of PAIs as well as aromatic polyamides. Recently, we have reported some TPA-containing polyamides and polyimides from 4,4'-diamino-4''-*N*-carbazolyltriphenylamine [23,24], 4,4'-dicarboxy-4''-*N*-carbazolyltriphenylamine [25], and 4,4'-dicarboxy-4''-methoxytriphenylamine [26], respectively. Because of the incorporation of bulky, propeller-shaped TPA units along the polymer backbone, all the polymers were amorphous with high thermal stability, good solubility in many aprotic solvents, and thin-film-forming capability. Recently, we have initiated a study to obtain TPA-containing anodic electrochromic polymers which exhibited green light in the oxidized state and were transparent in the neutral state [27–30].

The anodic oxidation of TPA in aprotic solvents has been well studied [31]. The oxidation product, the TPA radical cation, is not stable and the following chemical reaction produces tetraphenylbenzidine by tail to tail (*para* position) coupling, with the 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 that afforded stable radical cations [32,33]. In this article, we therefore synthesized a diamine, 4,4'-diamino-4''-methoxytriphenylamine (**I**), and its derived poly(amine–amide–imide)s containing TPA groups with electron-rich pendent 4-methoxy phenyl ring which permits tuning the solubility and redox potential of the polymers. The general properties such as solubility and thermal properties are described. The electrochemical and electrochromic properties of these polymers are also described herein and are compared with those of structurally related ones from 4,4'-diaminotriphenylamine without 4-methoxy substituent.

## 2. Experimental

### 2.1. Synthesis

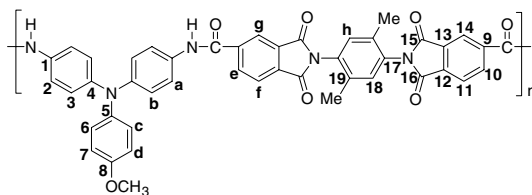
#### 2.1.1. Materials

A 4-methoxy-substituted TPA-containing aromatic diamine, 4,4'-diamino-4''-methoxytriphenylamine (**I**), was synthesized by the cesium fluoride-mediated condensation of *p*-anisidine with 4-fluoronitrobenzene, followed by palladium-catalyzed hydrazine reduction of the dinitro intermediate according to a previously reported procedure [34–36]. 4,4'-Diaminotriphenylamine (mp = 186–187 °C) [37], 2,5-Bis(trimellitimido)toluene [38] (**II-M**), 1,4-bis(trimellitimido)-2,5-dimethylbenzene [39] (**II-2M**), and 1,4-bis(trimellitimido)-2,5-dichlorobenzene [40] (**II-2Cl**) were prepared as previously reported procedures. *N,N*-dimethylacetamide (DMAc) (TEDIA), *N,N*-dimethylformamide (DMF) (ACROS), *N*-methyl-2-pyrrolidinone (NMP) (TEDIA), pyridine (Py) (TEDIA), and triphenyl phosphite (TPP) (ACROS) were also used as received. Tetrabutylammonium perchlorate (TBAP) (ACROS) was recrystallized twice from ethyl acetate and then dried under vacuum prior to use. All other reagents were used as received from commercial sources.

#### 2.1.2. Polymer synthesis through direct polycondensation via the phosphorylation reaction

The synthesis of poly(amine–amide–imide) **PAI-2M** is used as an example to illustrate the general synthetic route: A mixture of 0.382 g (1.25 mmol) of diamine, 4,4'-diamino-4''-methoxytriphenylamine (**I**), 0.606 g (1.25 mmol) of 1,4-bis(trimellitimido)-2,5-dimethylbenzene (**II-2M**), 0.30 g of calcium chloride, 0.9 mL of triphenyl phosphite, 1.2 mL of pyridine, and 5 mL of NMP was heated with stirring at 105 °C for 3 h. The obtained polymer solution was poured slowly into 300 mL of stirred methanol giving rise to a stringy, fiber-like precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried under vacuum at 100 °C. Reprecipitations from DMAc into methanol were carried out twice for further purification. The inherent viscosity of the obtained poly(amine–amide–imide) **PAI-2M** was 0.45 dL/g, measured at a concentration of 0.5 g/dL in NMP at 30 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ, ppm): 2.10 (s, 6H, CH<sub>3</sub>), 3.75 (s, 3H, OCH<sub>3</sub>), 6.97–7.05 (m, 8H, H<sub>d</sub> + H<sub>b</sub> + H<sub>c</sub>), 7.48 (s, 2H, H<sub>h</sub>), 7.73 (d, 4H, H<sub>a</sub>), 8.15 (d, 2H, H<sub>f</sub>), 8.42 (d, 2H, H<sub>e</sub>), 8.48 (s, 2H, H<sub>g</sub>), 10.59 (s, 2H, NH–CO).

<sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, δ, ppm): 17.2 (CH<sub>3</sub>), 55.5 (OCH<sub>3</sub>), 115.2 (C<sup>7</sup>), 122.0 (C<sup>2</sup>), 122.6 (C<sup>14</sup>), 122.9 (C<sup>3</sup>), 124.0 (C<sup>11</sup>), 126.7 (C<sup>6</sup>), 131.4 (C<sup>18</sup>), 131.7 (C<sup>17</sup>), 132.1 (C<sup>1</sup>), 133.3 (C<sup>19</sup>), 134.0 (C<sup>13</sup>), 134.6 (C<sup>10</sup>), 135.0 (C<sup>4</sup>), 140.3 (C<sup>12</sup>), 140.7 (C<sup>5</sup>), 144.2 (C<sup>9</sup>), 155.9 (C<sup>8</sup>), 163.4 (NH–CO), 166.5 (C<sup>15</sup>), 166.7 (C<sup>16</sup>). Anal. Calcd. for (C<sub>45</sub>H<sub>31</sub>N<sub>5</sub>O<sub>7</sub>)<sub>n</sub> (753.76)<sub>n</sub>: C, 71.71%; H, 4.15%; N, 9.29%. Found: C, 69.70%; H, 4.28%; N, 9.11%. The other poly(amine–amide–imide)s were synthesized by an analogous procedure.



#### 2.1.3. Preparation of the films

A solution of polymer was made by dissolving about 0.7 g of the poly(amine–amide–imide)s sample in 10 mL of DMAc, and the homogeneous solution was poured into a 9-cm diameter glass culture dish which was heated at 90 °C for 2 h and 160 °C for 8 h to slowly release the solvent under vacuum. The obtained flexible films were about 50–70 μm in thickness and were used for inherent viscosity tests, solubility tests, and thermal analyses.

## 2.2. Measurements

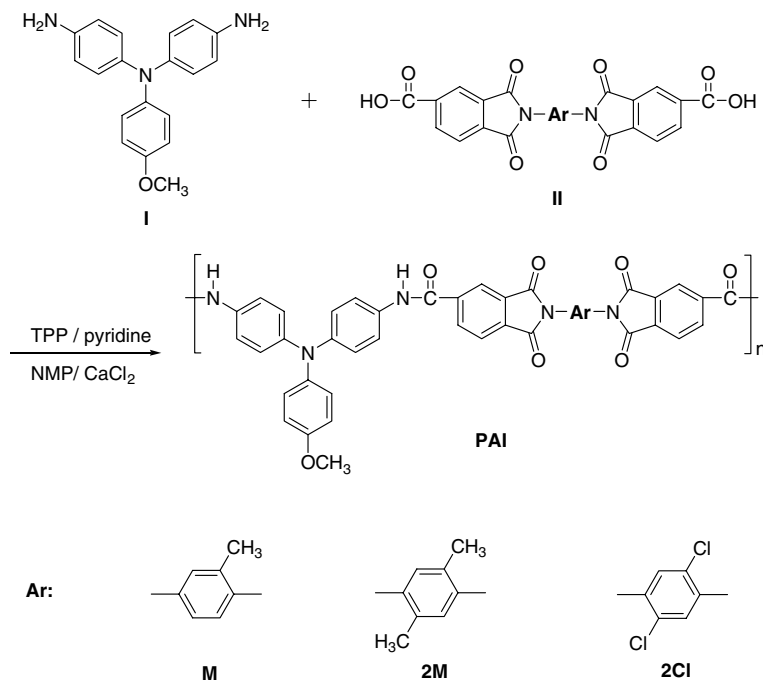
Infrared spectra were recorded on a PerkinElmer RXI FT-IR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker Avance 300 MHz FT-NMR system. Elemental analyses were run in an Elementar VarioEL-III. Wide-angle X-ray diffraction (WAXD) measurements of the polymer films were performed at room temperature (≈25 °C) on a Shimadzu XRD-7000 X-ray diffractometer (40 kV, 20 mA) with a graphite monochromator, using nickel-filtered Cu-Kα radiation. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Varian Cary 50 Probe spectrometer. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 6–8 mg film samples heated in flowing nitrogen or air (flow

rate = 40 cm<sup>3</sup>/min) at a heating rate of 20 °C/min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 20 °C/min in flowing nitrogen (20 cm<sup>3</sup>/min). Electrochemistry was performed with a CHI 611B electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry was performed with the use of a three-electrode cell in which ITO (polymer films area about 0.7 cm × 0.5 cm) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of a homemade Ag/AgCl, KCl (sat.) reference electrode. Absorption spectra in the spectroelectrochemistry experiments were measured with a HP 8453 UV–Visible spectrophotometer. Coloration efficiency is derived from the equation:  $\eta = \Delta OD / Q$ ,  $\Delta OD$  is optical density change at specific absorption wavelength and  $Q$  is ejected charge determined from the *in situ* experiments. Photoluminescence spectra were measured with a Jasco FP-6300 spectrofluorometer. The fluorescence quantum yields ( $\Phi_{PL}$ ) of polymer solution were determined in toluene against quinine sulfate (ACROS) in 1 N H<sub>2</sub>SO<sub>4(aq)</sub> as the standard ( $\Phi_{PL} = 0.546$ ).

### 3. Results and discussion

#### 3.1. Polymer synthesis

A series of new intrinsic alternating 4-methoxy-substituted TPA-containing poly(amine–amide–imide)s were successfully prepared from the diamine, 4,4'-diamino-4''-methoxytriphenylamine (**I**), and various aromatic diimide–diacids by the direct polycondensation reaction using triphenyl phosphite and pyridine as condensing agents (Scheme 1). The polymerization proceeded homogeneously throughout the reaction and afforded highly viscous polymer solutions, and precipitated in a tough fiber-like form when pouring the resultant polymer solutions into methanol. The obtained poly(amine–amide–imide)s had inherent viscosities in the range of 0.35–0.45 dL/g, and the formation of these polymers was confirmed by elemental analysis, IR, and NMR spectroscopy. Fig. 1 shows a typical IR spectrum for poly(amine–amide–imide) **PAI-2M**, and exhibits characteristic IR absorption bands of the amide group at 3371 (N–H) and 1655 cm<sup>-1</sup> (amide carbonyl), imide absorption bands at 1777 (asymmetrical C=O), 1721 (symmetrical C=O), 1358 (C–N), and 726 cm<sup>-1</sup> (imide ring deforma-



Scheme 1. Synthesis of poly(amine–amide–imide)s.

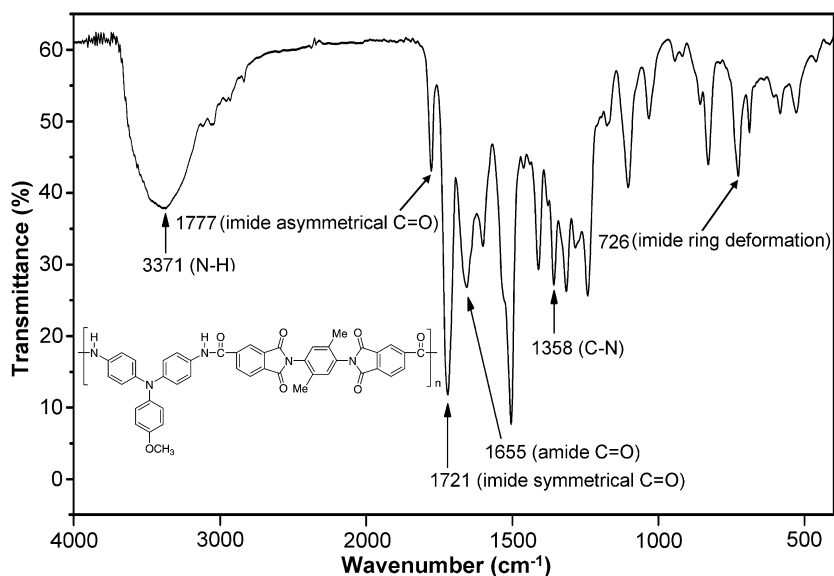


Fig. 1. IR spectrum (film) of poly(amine–amide–imide) **PAI-2M**.

tion). Fig. 2 shows a typical set of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **PAI-2M** in deuterated dimethyl sulfoxide ( $\text{DMSO}-d_6$ ), where all the peaks have been readily assigned to the hydrogen and carbon atoms of the recurring unit. Assignments of each carbon and proton are assisted by the two-dimensional H–H COSY and C–H HMQC NMR spectrum shown in Figs. 3 and 4, and these spectra agree well with the proposed molecular structure of **PAI-2M**. For a comparative study, a referenced poly(amine–amide–imide) **PAI-2M'** was also synthesized from 4,4'-diaminotriphenylamine and the corresponding diimide–diacid **II-2M**.

### 3.2. Polymer properties

#### 3.2.1. Basic characterization

As indicated by the (WAXD) patterns shown in Fig. 5, all the polymers were essentially amorphous. The qualitative solubility of the amorphous poly(amine–amide–imide)s in various solvents is shown in Table 1. These polymers show excellent solubility in aprotic dipolar solvents such as NMP, DMAc, DMF, and DMSO, and even in less polar *m*-cresol. The solubility behavior of the **PAI-2M** was compared with the **PAI-2M'** derived from 4,4'-diaminotriphenylamine and corresponding diimide–diacid **II-2M** in Table 1. The enhanced solubility of **PAI-2M** can be attributed to the introduction of bulky pendent 4-methoxytriphenylamine group in the repeat unit.

The results of inherent viscosity and thermal properties of the poly(amine–amide–imide)s are summarized in Table 2. The obtained polymers have inherent viscosities in the range of 0.35–0.45 dL/g and could afford flexible polymer films. Their 10% weight-loss temperatures in nitrogen and air are recorded in the range of 515–525 and 525–555 °C, respectively. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere is more than 58% at 800 °C. The high char yields of these polymers can be ascribed to their high aromatic content. The softening temperatures ( $T_s$ ) of the polymer film samples are determined by the TMA method with a loaded penetration probe. They are obtained from the onset temperature of the probe displacement on the TMA trace. A typical TMA thermogram for poly(amine–amide–imide) **PAI-2CI** is illustrated in Fig. 6. In all cases, the  $T_s$  values obtained by TMA are comparable to the  $T_g$  values measured by the DSC experiments (Table 2).

#### 3.2.2. Optical and electrochemical properties

The optical and electrochemical properties of the poly(amine–amide–imide)s are investigated by UV–vis, photoluminescence spectroscopy, and cyclic voltammetry, and the results are summarized in Table 3. These polymers exhibit strong UV–vis absorption bands at 302–304 nm in NMP solution, which are assignable to the  $\pi$ – $\pi^*$  transition resulting from the conjugation between the aromatic rings

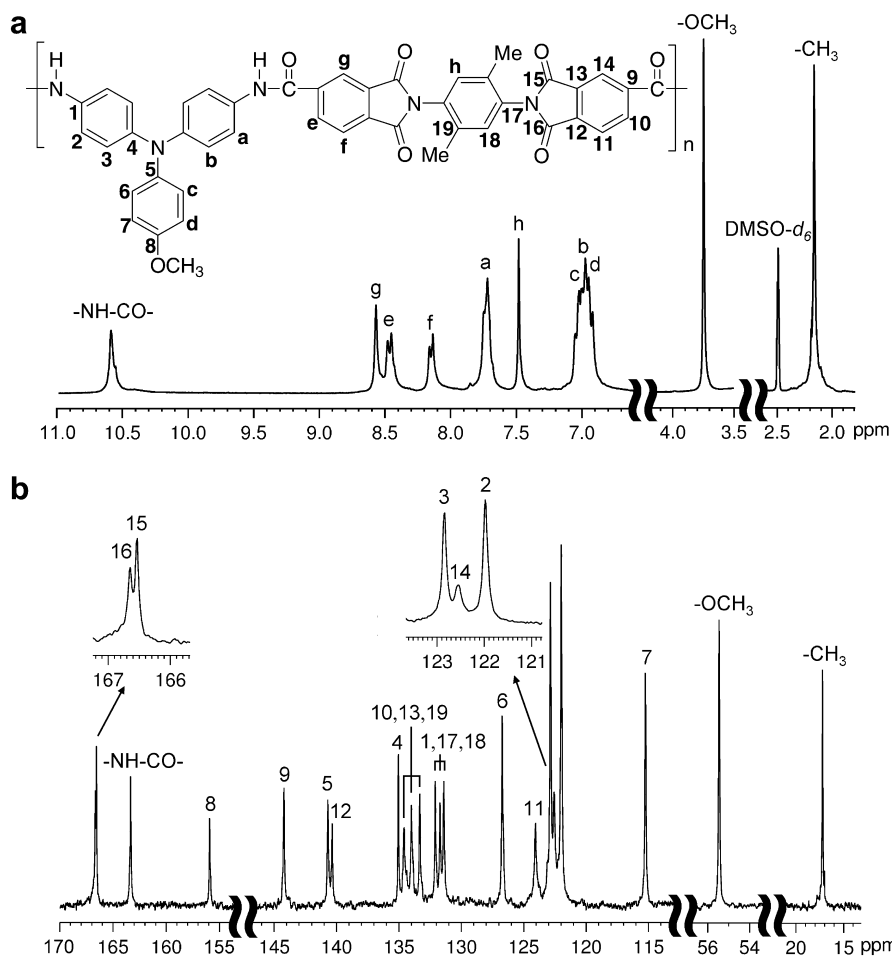


Fig. 2. (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectra of poly(amine–amide–imide) PAI-2M in  $\text{DMSO-}d_6$ .

and nitrogen atoms. In solid state, the UV–vis absorptions of poly(amine–amide–imide)s are nearly identical and show absorbance around 301–312 nm. These 4-methoxy-substituted TPA-based poly(amine–amide–imide)s exhibited fluorescence emission maxima around 360–376 nm in NMP solution with extremely low fluorescence quantum yield ranging from 0.02% for PAI-2Cl to 0.06% for PAI-M due to intramolecular charge transfer self-quench effect. The polymer films are measured for optical transparency using UV–vis transmittance spectroscopy and the cut-off wavelengths (absorption edge:  $\lambda_0$ ) in the range of 476–496 nm.

The redox behavior of the poly(amine–amide–imide)s PAI and PAI' series have been investigated by cyclic voltammetry conducted for the cast film on an ITO-coated glass substrate as working electrode in dry acetonitrile ( $\text{CH}_3\text{CN}$ ) containing 0.1 M of

TBAP as an electrolyte under nitrogen atmosphere. The typical cyclic voltammograms for PAI-2M (with 4-methoxy-substituted) and PAI-2M' (without 4-methoxy-substituted) are shown in Fig. 7 for comparison. Electrochemical oxidation (or p-doping) of the polymer PAI-2M started at about 0.66 V ( $E_{\text{onset}}$ ) with a reversible oxidation processes at  $E_{1/2}$  (average potential of the redox couple peaks) 0.79 V vs. Ag/AgCl. After continuous 100 cyclic scans between 0.0 and 1.04 V, the polymer films still exhibited excellent electrochemical stability. The oxidation of PAI-2M occurred at nitrogen center of TPA unit, which is incorporated by electron-donating methoxyl substituents at the *para*-position of phenyl rings in a propeller-like geometry. The introduction of electron-donating methoxyl substituents into the *para*-position of TPA not only greatly stabilize the cationic radicals but also lower the oxidation

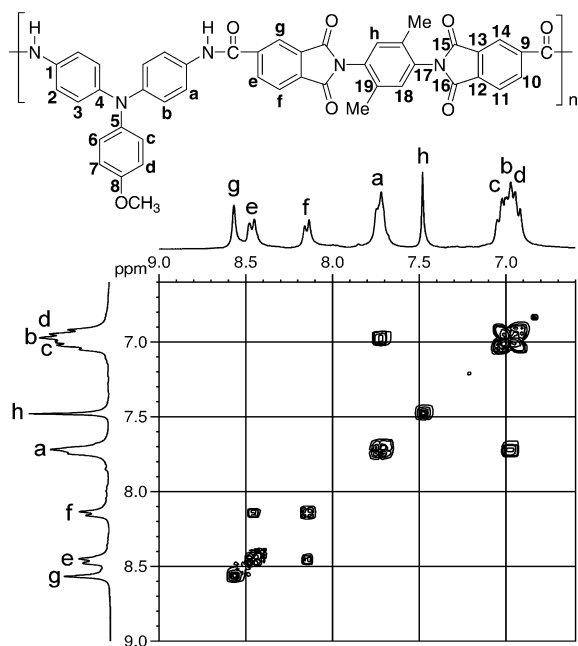


Fig. 3. H-H COSY spectra of poly(amine–amide–imide) **PAI-2M** in  $\text{DMSO-}d_6$ .

potentials of the electroactive poly(amine–amide–imide)s **PAI** as compared with the corresponding **PAI'** without methoxyl substituent. The energy of

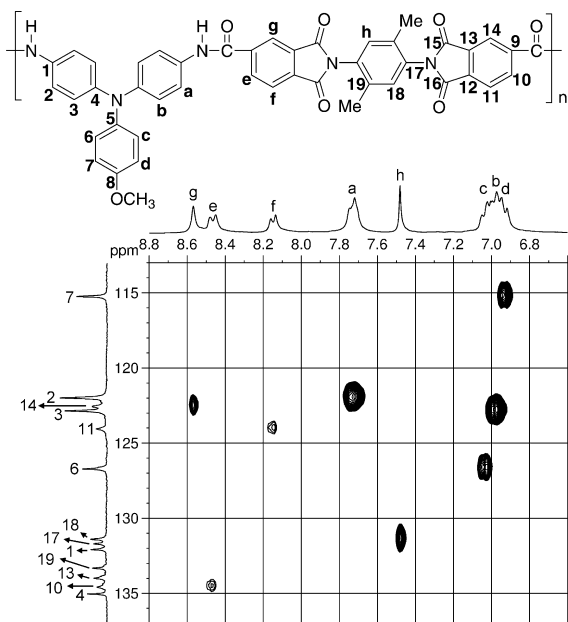


Fig. 4. C-H HMQC spectra of poly(amine–amide–imide) **PAI-2M** in  $\text{DMSO-}d_6$ .

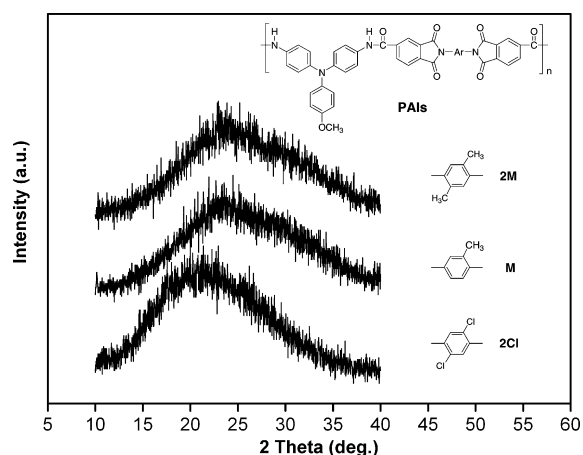


Fig. 5. WAXD patterns of poly(amine–amide–imide) films.

the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the investigated polymers could be determined from the oxidation onset or half-wave potentials and the onset absorption wavelength of polymer films, and the results are also listed in Table 3. For example, the oxidation half-wave potential for **PAI-2M** has been determined as 0.79 V ( $E_{\text{onset}} = 0.66$  V) vs. Ag/AgCl. The external ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox standard  $E_{1/2}$  ( $\text{Fc}/\text{Fc}^+$ ) is 0.44 V vs. Ag/AgCl in  $\text{CH}_3\text{CN}$ . Assuming that the HOMO energy for the  $\text{Fc}/\text{Fc}^+$  standard is 4.80 eV with respect to the zero vacuum level, the HOMO energy for poly(amine–amide–imide) **PAI-2M** has been evaluated to be 5.15 eV.

### 3.2.3. Electrochromic characteristics

Electrochromism of the poly(amine–amide–imide) thin films was examined by optically transparent thin-layer electrode (OTTE) coupled with a UV–vis spectroscopy. The electrode preparation and solution condition were identical to those used in cyclic voltammetry. The typical electrochromic transmittance spectra of poly(amine–amide–imide) **PAI-2M** are shown in Fig. 8. When the applied potentials increased positively from 0.00 to 0.95 V, the peak of absorption at 312 nm, characteristic for neutral form for poly(amine–amide–imide) **PAI-2M** decreased gradually, while two new bands grew up at 395 and 768 nm, respectively. The new spectrum patterns were assigned as that of the cation radical poly(amine–amide–imide) **PAI-2M**, by electron removal from the lone pair electron of nitrogen atom on the TPA structure. Meanwhile,

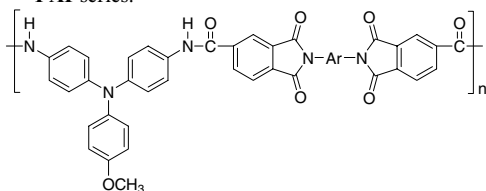
Table 1  
Solubility<sup>a</sup> of aromatic poly(amine–amide–imide)s

Polymer code <sup>b</sup>	Solvents						
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF	CHCl <sub>3</sub>
PAI-M	++	++	++	++	–	–	–
PAI-2M	++	++	++	++	–	–	–
PAI-2CI	++	++	++	++	–	±	–
PAI-2M'	+	+	+	+	–	–	–

++: Soluble at room temperature; +: soluble on heating; ±: partial soluble; –: insoluble even on heating.

<sup>a</sup> The solubility was determined by using 1 mg sample in 1 mL of solvent.

<sup>b</sup> PAI series:



PAI' series:

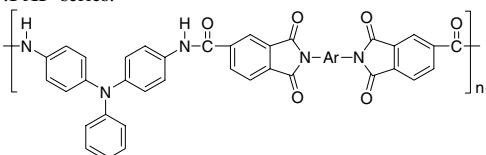


Table 2  
Inherent viscosities and thermal properties of aromatic poly(amine–amide–imide)s

Polymer code	$\eta_{inh}^a$ (dL/g)	$T_g$ (°C) <sup>b</sup>	$T_s$ (°C) <sup>c</sup>	$T_d$ at 5% weight loss (°C) <sup>d</sup>		$T_d$ at 10% weight loss (°C) <sup>d</sup>		Char yield (wt.%) <sup>e</sup>
				N <sub>2</sub>	Air	N <sub>2</sub>	Air	
PAI-M	0.45	305	301	490	505	525	555	62
PAI-2M	0.45	303	281	485	480	515	525	58
PAI-2CI	0.35	297	301	475	480	515	525	61

<sup>a</sup> Measured at a polymer concentration of 0.5 g/dL in NMP at 30 °C.

<sup>b</sup> Midpoint temperature of baseline shift on the second DSC heating trace (rate 20 °C/min) of the sample after quenching from 400 °C.

<sup>c</sup> Softening temperature measured by TMA with a constant applied load of 10 mN at a heating rate of 10 °C/min.

<sup>d</sup> Decomposition temperature, recorded via TGA at a heating rate of 20 °C/min and a gas-flow rate of 30 cm<sup>3</sup>/min.

<sup>e</sup> Residual weight percentage at 800 °C in nitrogen.

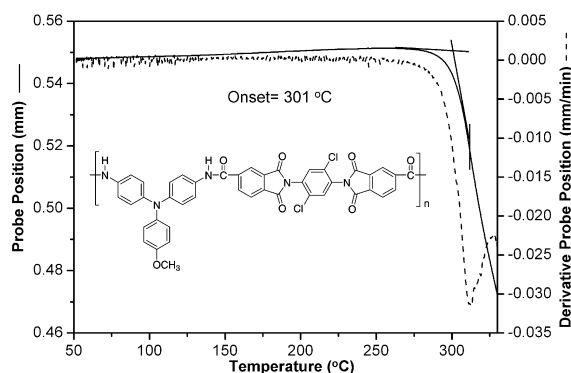


Fig. 6. TMA curve of poly(amine–amide–imide) PAI-2CI with a heating rate of 10 °C/min.

complementary color of the PAI-2M film changed from yellow to green with high contrast of optical transmittance change ( $\Delta T\%$ ) up to 78% at 768 nm (as shown in Fig. 8).

The color switching times were estimated by applying a potential step, and the absorbance profiles were followed (Fig. 9). The switching time was defined as the time that required for reach 90% of the full change in absorbance after applying potential. Thin films from poly(amine–amide–imide) PAI-2M would require 3.0 s at 0.95 V for switching absorbance at 395 and 768 nm and 2.5 s for bleaching. The color switching times of PAI-2M are also shown in Fig. 9. After over 100



Table 3  
Optical and electrochemical properties for poly(amine–amide–imide)s

Index	Solution $\lambda$ (nm) <sup>a</sup>			Film $\lambda$ (nm)			$E_{1/2}/V$ (vs. Ag/AgCl in CH <sub>3</sub> CN)		$E_g^c$ (eV)	HOMO <sup>f</sup> (eV)		LUMO <sup>g</sup> (eV)		
	Abs max	PL <sub>max</sub> <sup>b</sup>	$\Phi_F$ (%) <sup>c</sup>	$\lambda_{\lambda_0}$ <sup>d</sup>	Abs max	Abs onset <sup>e</sup>	PL <sub>max</sub> <sup>b</sup>	$E_{1/2}$		$E_{onset}$	$E_{1/2}$	$E_{onset}$	$E_{1/2}$	$E_{onset}$
PAI-M	302	360	0.06	494	308	417	–	0.79	0.67	2.97	5.15	5.03	2.18	2.06
PAI-2M	304	376	0.05	476	312	427	–	0.79	0.66	2.90	5.15	5.02	2.25	2.12
PAI-2Cl	303	374	0.02	496	301	416	–	0.80	0.66	2.98	5.16	5.02	2.18	2.04
PAI-2M'	308	363	0.08	444	325	413	–	0.93	0.77	3.00	5.29	5.13	2.29	2.13

<sup>a</sup> Polymer concentration of  $10^{-5}$  M in NMP at room temperature.

<sup>b</sup> Excited at the absorption maximum for both the solid and solution states. –: No discernible PL<sub>max</sub> was observed.

<sup>c</sup> The quantum yield in dilute solution was calculated in an integrating sphere with quinine sulfate as the standard ( $\Phi_F = 0.546$ ).

<sup>d</sup> The cutoff wavelength from the UV–vis transmission spectra of polymer films.

<sup>e</sup> The data were calculated by the equation:  $gap = 1240/\lambda_{onset}$  of polymer film.

<sup>f</sup> The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).

<sup>g</sup> LUMO = HOMO –  $E_g$ .

cyclic scans, the polymer films still exhibited good stability of electrochromic characteristics. The high electrochromic coloring efficiency ( $\eta = \Delta A/Q$ ) ranging from 395 cm<sup>2</sup>/C for first cycle to 379 cm<sup>2</sup>/C for

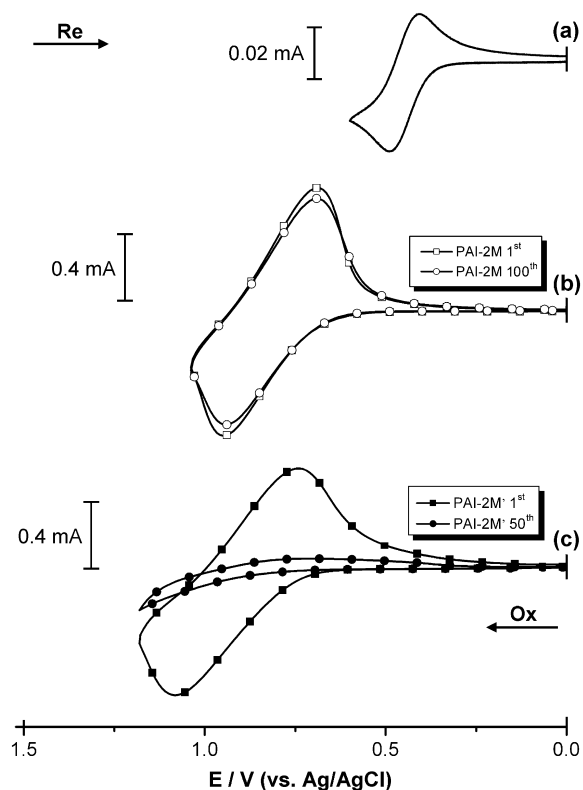


Fig. 7. Cyclic voltammograms of (a) ferrocene, (b) poly(amine–amide–imide) PAI-2M and (c) PAI-2M' films onto an indium–tin oxide (ITO)-coated glass substrate over 100 and 50 cyclic scanning in CH<sub>3</sub>CN containing 0.1 M TBAP at scan rate = 0.05 V/s.

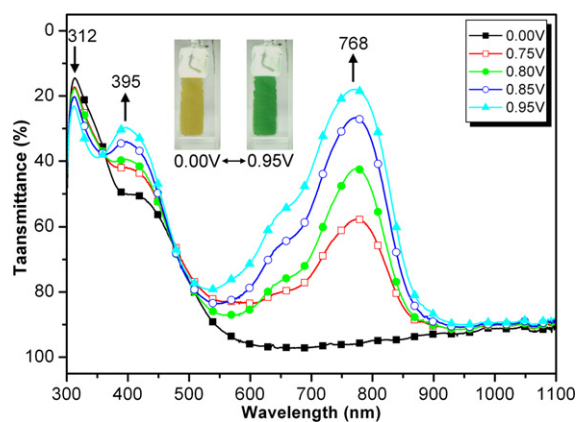


Fig. 8. Electrochromic behavior of poly(amine–amide–imide) PAI-2M thin film (in CH<sub>3</sub>CN with 0.1 M TBAP as the supporting electrolyte) at (■) 0.00 (□) 0.75 (●) 0.80 (○) 0.85 (▲) 0.95.

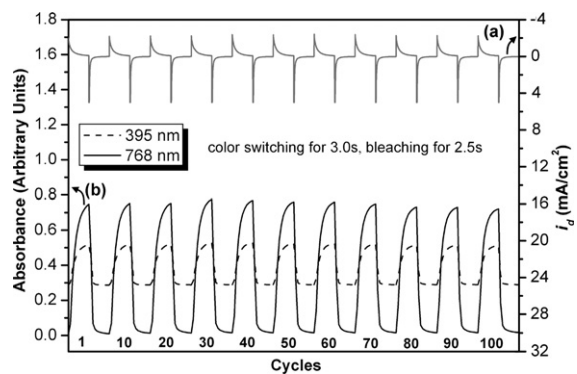


Fig. 9. (a) Current consumption and (b) potential step absorptometry of polyamide PAI-2M (in CH<sub>3</sub>CN with 0.1 M TBAP as the supporting electrolyte) by applying a potential step (0 V ↔ 0.95 V), (coated area: 1 cm<sup>2</sup>) and cycle time 10 s for coloration efficiency from 395 cm<sup>2</sup>/C (first cycle) to 379 cm<sup>2</sup>/C (100th cycle).

Table 4

Coloration efficiency with optical and electrochemical properties of poly(amine–amide–imide) **PAI-2M**

Cycles <sup>a</sup>	$\Delta A_{768}$ <sup>b</sup>	$Q$ (mC cm <sup>-2</sup> ) <sup>c</sup>	$\eta$ (cm <sup>2</sup> C <sup>-1</sup> ) <sup>d</sup>	Decay (%) <sup>e</sup>
1	0.738	1.86	395	0.0
20	0.738	1.88	392	0.8
40	0.754	1.92	391	1.0
60	0.744	1.94	382	3.3
80	0.716	1.88	380	3.8
100	0.703	1.85	379	4.0

<sup>a</sup> Times of cyclic scan by applying potential steps: 0.00 ↔ 0.95 (V vs. Ag/Ag<sup>+</sup>).

<sup>b</sup> Optical density change at 768 nm.

<sup>c</sup> Ejected charge, determined from the in situ experiments.

<sup>d</sup> Coloration efficiency is derived from the equation:  $\eta = \Delta A/Q$ .

<sup>e</sup> Decay of coloration efficiency after cyclic scans.

100th cycle and decay of the **PAI-2M** were calculated [41] and the results are summarized in Table 4.

#### 4. Conclusions

A series of stable anodic green electrochromic poly(amine–amide–imide)s with high contrast of optical transmittance change ( $\Delta T\%$ ) up to 78% in 768 nm have been readily prepared from the diamine, 4,4'-diamino-4''-methoxytriphenylamine (**I**), and various aromatic diimide–diacids via the direct phosphorylation polycondensation. Because of the incorporation of electron-donating methoxy substituents at the *para*-position of TPA, not only the electrochemical oxidative coupling reactions could be greatly prevented that afforded stable cationic radicals but also lower the oxidation potentials of the electroactive poly(amine–amide–imide)s. In addition to enhanced solubility and thin film formability, high  $T_g$  values, and good thermal stability, these anodically polymeric electrochromic materials also showed excellent continuous cyclic stability of electrochromic characteristic with good coloration efficiency from 395 cm<sup>2</sup>/C for first cycle to 379 cm<sup>2</sup>/C for 100th cycles, changing color from the yellow neutral form to the green oxidized forms when scanning potentials positively from 0.00 to 0.95 V. After over 100 cyclic switches, the polymer films still exhibited excellent reversibility of electrochromic characteristics. Thus, the 4-methoxy-substituted TPA-based poly(amine–amide–imide)s could be good candidates as anodic electrochromic materials due to their proper oxidation potentials, excellent electrochemical and thermal stability.

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