



Synthesis and properties of electroactive aromatic polyimides with methyl- or trifluoromethyl-protecting triphenylamine units

High Performance Polymers
1–12

© The Author(s) 2016

Reprints and permission:

sagepub.co.uk/journalsPermissions.nav

DOI: 10.1177/0954008316653456

hip.sagepub.com

Sheng-Huei Hsiao¹ and Kai-Han Lin²

Abstract

Two series of new redox-active aromatic polyimides with methyl- ($-\text{CH}_3$) or trifluoromethyl ($-\text{CF}_3$)-protecting triphenylamine moieties were prepared from 4,4'-diamino-4''-methyltriphenylamine and 4,4'-diamino-4''-(trifluoromethyl)-triphenylamine with aromatic tetracarboxylic dianhydrides via the conventional two-step polycondensation technique. Flexible and strong polyimide films could be obtained via the thermal curing of their precursor poly(amic acid) films or direct solution cast from some organosoluble polyimides. The polyimides showed high glass-transition temperatures between 269°C and 312°C, and they did not show significant decomposition before 500°C in air or under nitrogen atmosphere. Cyclic voltammograms of the polyimide films on the indium–tin oxide-coated glass substrate exhibited a pair of reversible redox waves with half-wave oxidation potentials of 1.08–1.10 V (for the $-\text{CH}_3$ series) and 1.23–1.26 V (vs. silver/silver chloride; for the $-\text{CF}_3$ series) in acetonitrile solution. The polyimide films showed anodic electrochromism from pale yellow neutral state to purplish blue (for the $-\text{CH}_3$ series) and chrome yellow (for the $-\text{CF}_3$ series) when oxidized.

Keywords

Polyimides, triphenylamine, redox polymers, electrochemistry, electrochromism

Introduction

Aromatic polyimides are well-known high-performance polymeric materials for their excellent thermal, mechanical and electrical properties.^{1–4} They are commercially important materials used extensively as dielectric films and coatings in a wide range of high-technology applications. Incorporation of specific functionality into polyimide backbones leads to various advanced functional materials that exhibit certain advantageous properties, such as gas separation,^{5–8} highly refractive,^{9–11} photosensitive,¹² proton conducting,^{13–15} electrochromic^{16–19} and memory characteristics.^{20–23} Studies in the field of functionalization of polyimides continue to be actively developed, as is evident from the appearance of a large number of publications on this subject in the past few years. Tremendous efforts have also been made on the modification of the backbone structure of polyimides to obtain organosoluble or melt processable polyimides without much sacrificing their excellent thermal and mechanical properties.^{24–33}

Triphenylamine (TPA) and its derivatives with special propeller-shaped molecular structure are well-known for their ease in oxidation of the nitrogen core and the ability

to transport charge carriers via the radical cation species with high stability.^{34–36} Owing to their attractive electroactive and photoactive properties, various TPA derivatives and polymers are developed for optoelectronic applications, such as electrophotography, electroluminescent diodes, field-effect transistors, solar cells, memory devices and electrochromic devices.^{37,38} TPAs can be easily oxidized to form stable radical cations as long as the *para*-position of the phenyl rings is protected, and the oxidation process is always associated with a strong change of coloration. During the past decade, high-performance polymers (typically, aromatic polyamides and polyimides) carrying the redox-active TPA unit have been developed as a new and attractive family of electrochromic materials.^{17,39–47}

¹ Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei, Taiwan

² Department of Chemical Engineering, Tatung University, Taipei, Taiwan

Corresponding author:

Sheng-Huei Hsiao, Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 10608, Taiwan.

Email: shhsiao@ntut.edu.tw

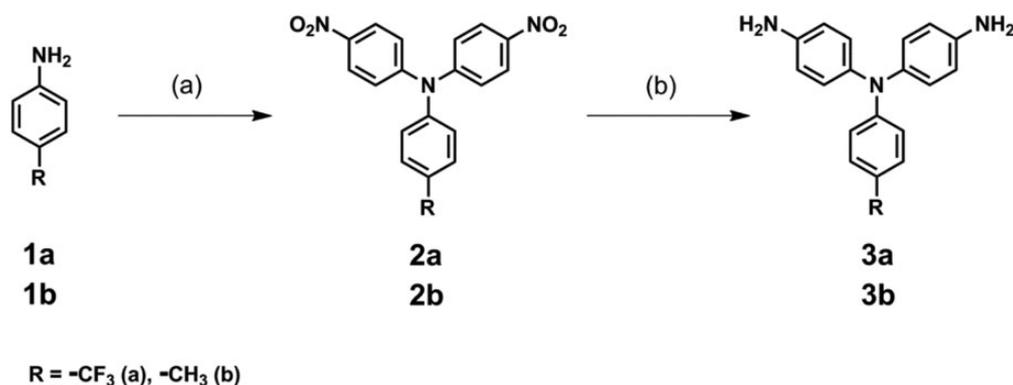


Figure 1. Synthetic route for the diamine monomers **3a** and **3b**: (a) *p*-fluoronitrobenzene, CsF, DMSO, 120°C, 20 h; (b) hydrazine, Pd/C, EtOH, reflux, 10 h. CsF: cesium fluoride; DMSO: dimethyl sulfoxide; Pd/C: palladium on charcoal; EtOH: ethanol.

Thin films of these polymers are generally colourless or near-colourless at their neutral state and then can change to multiple colours at their oxidized states, which is important property for neutral state colourless electrochromic device applications. To obtain a colourless regime, these types of materials do not need any potential or energy. In addition, the application of redox-active polymers as active electrode materials has attracted much attention in the area of secondary battery research during the past few decades.⁴⁸ For example, redox-active polytriphenylamine⁴⁹ and poly(*N*-vinylcarbazole)⁵⁰ have been evaluated as a cathode active material for use in rechargeable lithium batteries.

It is well-known that unsubstituted TPA undergoes dimerization to tetraphenylbenzidine (TPB) after the formation of a monocation radical.^{51,52} This is accompanied by the loss of two protons per dimer and the dimer is more easily oxidized than TPA and also can undergo further oxidations in two discrete one-electron steps to give TPB^{•+} and finally the quinoidal TPB²⁺. This side reaction may cause undesired colour change and deteriorate colour efficiency for the TPA-based electrochromic polymers. Incorporation of substituents at the *para* position of the TPA unit has been regarded as an effective way to prevent the side reaction.^{53–55} In this work, we therefore synthesize two TPA-based diamine monomers, 4,4'-diamino-4''-methyltriphenylamine and 4,4'-diamino-4''-(trifluoromethyl)-triphenylamine, and their derived aromatic polyimides with the -CH₃ or -CF₃ protecting TPA moieties. The effect of incorporating the -CH₃ and -CF₃ substituents on the thermal, electrochemical and electrochromic properties of the polyimides will be investigated. Although some polyimides based on 4,4'-diamino-4''-methyltriphenylamine have been reported,^{56,57} their properties have not been studied systematically yet.

Experimental

Materials

According to a well-established procedure,^{58,59} the TPA-based diamine monomers 4,4'-diamino-4''-(trifluoromethyl)

triphenylamine (**3a**) and 4,4'-diamino-4''-methyltriphenylamine (**3b**) were prepared from the fluoro-displacement reactions of *p*-fluoronitrobenzene with *p*-(trifluoromethyl)aniline (**1a**) and *p*-toluidine (**1b**), respectively, followed by Pd/C-catalyzed hydrazine reduction of the corresponding dinitro compounds, 4,4'-dinitro-4''-(trifluoromethyl)triphenylamine (**2a**) and 4,4'-dinitro-4''-methyltriphenylamine (**2b**). The synthetic route is outlined in Figure 1 and the synthetic details and characterization data of all the synthesized compounds have been reported in a separate paper.⁶⁰ Pyromellitic dianhydride (PMDA; **4a**; Aldrich, St. Louis, Missouri, USA) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA; **4c**; Aldrich) were purified by recrystallization from acetic anhydride. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA; **4b**; Oxychem, Austin, Texas, USA) and 4,4'-oxydiphthalic anhydride (ODPA; **4d**; Oxychem), 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA; **4e**; New Japan Chemical Co., Japan) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA; **4f**; Hoechst Celanese, Irving, Texas, USA) were heated at 250°C in vacuo for 3 h before use. Tetra-*n*-butylammonium perchlorate (TBAP; from Acros, Geel, Belgium) was recrystallized twice from ethyl acetate and then dried in vacuo before use. All other reagents and solvents were used as received from commercial sources.

Synthesis of polyimides

The polyimides were synthesized by the conventional two-step procedure via poly(amic acid) (PAA) precursors, followed by thermal or chemical imidization. The synthesis of polyimide **5a** is used as an example to illustrate the general synthetic route to produce the polyimides. The diamine monomer **3a** (0.6115 g and 1.78 mmol) was dissolved in 9.5 mL of *N,N*-dimethylacetamide (DMAc) in a 50 mL round-bottom flask. Then dianhydride **4a**, PMDA (0.3885 g and 1.78 mmol) was added to the diamine solution in one portion. Thus, the solid content of the solution is

Table 1. Inherent viscosity (η_{inh}) of PAAs and polyimides and average molecular weight of THF-soluble polyimides.

Code	η_{inh} of PAA (dL g ⁻¹) ^a	η_{inh} of polyimide (dL g ⁻¹) ^b	GPC data ^{b,d}		
			M_n	M_w	M_w/M_n
5a	1.02	— ^c	— ^e	—	—
5b	0.95	—	—	—	—
5c	0.88	—	—	—	—
5d	0.81	0.60	22,000	42,000	1.91
5e	0.80	0.48	18,000	36,000	2.00
5f	0.85	0.44	23,000	49,000	2.13
6a	1.60	—	—	—	—
6b	1.24	—	—	—	—
6c	1.08	—	—	—	—
6d	1.22	0.79	—	—	—
6e	0.95	—	—	—	—
6f	1.13	0.66	33,000	59,000	1.79

η_{inh} : inherent viscosity; PAA: poly(amic acid); THF: tetrahydrofuran; GPC: gel permeation chromatography; DMAc: *N,N*-dimethylacetamide.

^aMeasured at a concentration of 0.5 g dL⁻¹ in DMAc at 30°C.

^bPolyimide samples prepared by chemical imidization.

^cInsoluble in DMAc.

^dWith respect to polystyrene standards, with THF as the eluent.

^eInsoluble in THF.

chloride (AgCl), potassium chloride (sat.) reference electrode. Ferrocene was used as an external reference for calibration (+0.44 V vs. Ag/AgCl). UV-visible (UV-Vis) absorption spectra were measured with an Agilent 8453 UV-Vis spectrophotometer (Santa Clara, California, USA).

Results and discussion

Polymer synthesis

Polyimides **5a–5f** and **6a–6f** were prepared in conventional two-step method by the reactions of equal molar amounts of diamines **3a** and **3b** with various aromatic dianhydrides (**4a–4f**) to form the corresponding PAAs, followed by thermal or chemical cyclodehydration (Figure 2). As shown in Table 1, the inherent viscosities of the PAA precursors were in the range of 0.85–1.60 dL g⁻¹, indicating the formation of high-molecular weight polymers. All of the PAAs could be cast into flexible and tough films, which were subsequently converted into tough polyimide films by stage-by-stage heating at elevated temperatures. The PAAs also could be chemically cyclodehydrated to polyimides by treatment with a mixture of pyridine and acetic anhydride. Gel permeation chromatography analysis revealed that the weight-average molecular weight of the chemically imidized polyimides **5d–5f** and **6f** ranged from 36,000 to 59,000. The complete imidization of polymers was confirmed by IR spectroscopy. Figure 3 shows a typical pair of IR spectra for polyimide **5e** and its PAA precursor. All the polyimides showed the characteristic absorption bands of the imide ring near 1780 (asym C = O str.), 1720 (sym C = O str.), 1380 (C–N str.) and 740 cm⁻¹ (imide ring deformation). The disappearance of amide and carboxyl

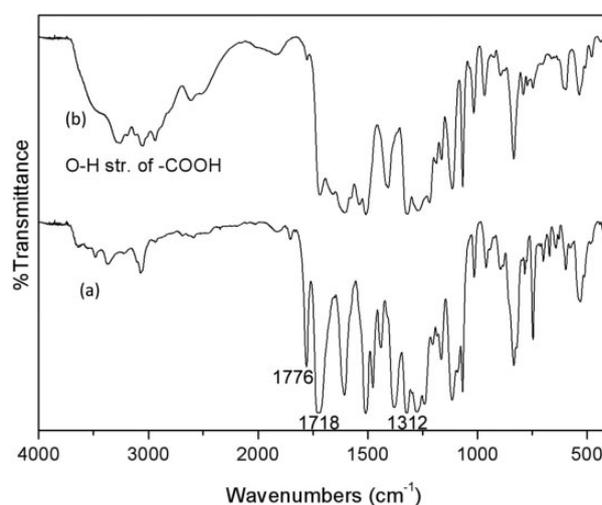


Figure 3. IR spectra (films) of (a) polyimide **5e** and (b) its PAA precursor. IR: infrared; PAA: poly(amic acid).

bands indicates a virtually complete conversion of the PAA precursor into polyimide.

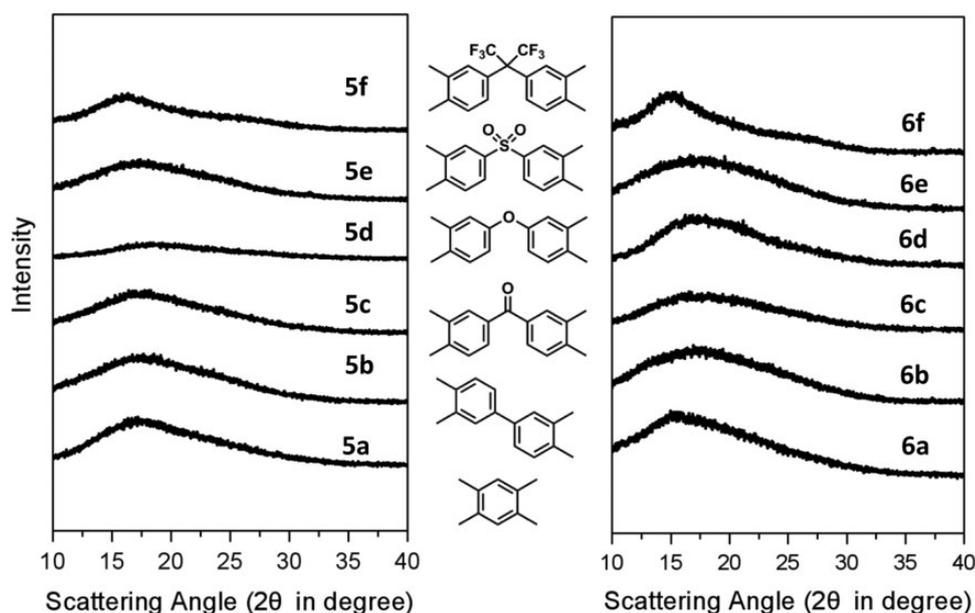
Solubility and film property

The solubility behaviours of the polyimides in several organic solvents at 10% (w/v) are summarized in Table 2. The polyimides derived from more rigid dianhydride components such as PMDA, BPDA and BTDA are insoluble in organic solvents. The DSDA- and 6FDA-derived polyimides **5e**, **5f**, **6e** and **6f** exhibited moderate or good solubility in the test solvents. When comparing the solubility behaviours between ODPA-derived polyimides **5d** and **6d**, the introduction of bulky –CF₃ substituent led to an

Table 2. Solubility behaviour of polyimides.

Polymer code	Solubility ^a						
	NMP	DMAc	DMF	DMSO	THF	m-Cresol	Chloroform
5a	–(–)	–(–)	–(–)	–(–)	–(–)	–(–)	–(–)
5b	–(–)	–(–)	–(–)	–(–)	–(–)	–(–)	–(–)
5c	–(–)	–(–)	–(–)	–(–)	–(–)	–(–)	–(–)
5d	+ (+)	+ (+)	+h (+)	–(+)	–(+)	+h (+)	–(–)
5e	+ (+)	+ (+)	+ (+)	+ (+)	+ (+)	+h (+)	+ (+)
5f	+ (+)	+ (+)	+ (+)	+ (+)	+ (+)	+ (+)	+ (+)
6a	–(–)	–(–)	–(–)	–(–)	–(–)	–(–)	–(–)
6b	–(–)	–(–)	–(–)	–(–)	–(–)	–(–)	–(–)
6c	–(–)	–(–)	–(–)	–(–)	–(–)	–(–)	–(–)
6d	–(–)	–(–)	–(–)	–(–)	–(–)	–(–)	–(–)
6e	+ (+)	+ (+)	+h (+)	+h (+h)	–(–)	+h (+h)	–(–)
6f	+ (+)	+ (+)	+ (+)	+h (+)	+ (+)	+h (+)	+ (+)

^aQualitative solubility was tested with 10 mg of a sample (chemically imidized) in 1 mL of the solvent. Data in parentheses are those of the polyimide samples prepared via chemical imidization. +: soluble at room temperature; +h: soluble on heating; –: insoluble. NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

**Figure 4.** X-ray diffractograms of polyimides **5a–5f** and **6a–6f**.

enhanced solubility possibly because it interferes with close chain packing. In addition, the chemically imidized samples generally revealed a higher solubility than those prepared by the thermal imidization method.

The X-ray diffraction patterns of all the thermally cured polyimide films are illustrated in Figure 4. The results indicate that all the polyimides are amorphous in nature. This is rationalized by the incorporation of packing-disruptive TPA units together with the $-\text{CH}_3$ and $-\text{CF}_3$ substituents. Figure 5 shows the photos of the thermally cured films of all the polyimides. The **5** series polymers exhibited a slightly less colour intensity as compared to the corresponding **6** series ones due to the bulky $-\text{CF}_3$ substituent.

The polyimides derived from PMDA, BTDA and DSDA generally displayed a darker colour than those derived from the other dianhydrides, possibly attributable to higher inter-chain charge transfer complexing. The colour of the polyimide films also depends on the imidization method. For example, as shown in Figure 6, the film directly cast from the chemically imidized sample of 6FDA-derived polyimide **5f** showed a lighter colour than that prepared from the thermally imidization of the PAA film. The mechanical properties of the polyimide films are summarized in Table 3. The polyimide films had a tensile strength of 89–134 MPa, an elongation at break of 8–15% and a tensile modulus of 2.0–2.7 GPa. Most of the polyimide films exhibited high



Figure 5. Photographs of the thermally cured films of polyimides **5a** → **5f** (top) and **6a** → **6f** (bottom) with film thickness of about 70 μm .



Figure 6. Photographs of the thermally (left) and chemically (right) imidized films of polyimide **5f**.

tensile strengths; thus, they could be considered as strong materials. The good mechanical properties are beneficial for their optoelectronic applications in flexible devices.

Thermal properties

The thermal properties of polyimides were examined by DSC, TMA and TGA techniques. The thermal behaviour data of the polyimides are included in Table 4. The glass transition temperature (T_g) values of the polyimides measured by DSC were recorded in the range of 269–312°C. The decreasing order of T_g generally correlated with that of chain flexibility. For example, the polyimides from ODPA showed the lowest T_g values (269°C for **5d** and 278°C for **6d**) because of the presence of flexible ether linkage between the phthalimide segments. As compared to the

Table 3. Tensile properties of polyimide films.^a

Polymer code	Strength at break (MPa)	Elongation at break (%)	Initial modulus (GPa)
5a	89	8	2.2
5b	134	10	2.6
5c	138	12	2.6
5d	124	9	2.4
5e	96	10	2.5
5f	92	9	2.0
6a	122	15	2.2
6b	133	15	2.4
6c	129	11	2.7
6d	133	11	2.5
6e	124	14	2.2
6f	119	9	2.5

^aSamples prepared by the thermal imidization method.

corresponding **6** series polyimides, the **5** series polyimides revealed a slightly lower T_g possibly attributable to the increased fractional free volume caused by the $-\text{CF}_3$ substituent. The softening temperatures (T_s) of the polymer films were determined with TMA by the penetration method. The T_s value was read from the onset temperature of the probe displacement on the TMA curve. A typical TMA trace for polyimide **6d** is shown in Figure 7. The T_s values of the polyimides are recorded in the range of 268–310°C, comparable to the T_g values determined by DSC. The thermal stability of polyimides was evaluated by TGA in both air and nitrogen atmospheres. Typical TGA curves for polyimide **6e** are shown in Figure 8. All of the polymers exhibited good thermal stability; the T_{ds} of these

Table 4. Thermal properties of polyimides.^a

Polymer code	T_g^b (°C)	T_s^c (°C)	T_d (°C) ^d at 5% weight loss		T_d (°C) ^d at 10% weight loss		Char yield ^e (%)
			In air	In N ₂	In air	In N ₂	
5a	302	300	561	566	594	599	62
5b	297	299	591	591	621	624	66
5c	303	298	564	574	596	602	65
5d	269	268	559	567	593	601	65
5e	291	293	510	519	561	558	52
5f	294	290	542	550	564	575	62
6a	312	310	543	564	572	589	68
6b	310	307	551	577	589	606	67
6c	307	303	532	548	574	583	63
6d	278	275	549	536	582	574	65
6e	302	298	465	481	508	512	59
6f	298	295	517	547	545	570	62

DSC: differential scanning calorimetry; TMA: thermomechanical analysis; TGA: thermogravimetric analysis; T_g : glass transition temperature; T_s : softening temperature; T_d : Decomposition temperature.

^aAll the polyimide samples were heated at 300°C for 1 h prior to DSC, TMA and TGA experiments.

^bThe midpoint temperature of heat capacity jump on the DSC heating trace (from 50 to 400°C at 20°C min⁻¹) was defined as T_g .

^cSoftening temperature measured by TMA using a penetration method.

^dDecomposition temperature, recorded via TGA at a heating rate of 20°C min⁻¹ and a gas flow rate of 30 cm³ min⁻¹.

^eResidual weight percentages at 800°C under nitrogen flow.

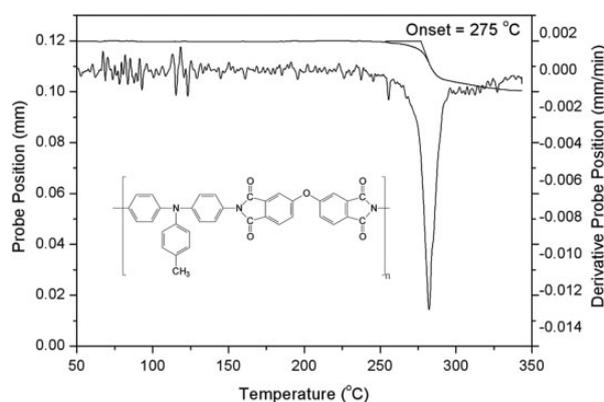


Figure 7. The TMA curve of polyimide **6d** with a heating rate of 10°C min⁻¹. TMA: thermomechanical analysis.

polyimides at a 10% weight loss were recorded in the range of 512–624°C in nitrogen and 588–621°C in air, respectively. The **5** series polyimides exhibited a slightly higher T_d as compared with their corresponding six counterparts, implying that the earlier weight loss is associated with the decomposition of the substituent on the TPA unit. The amount of carbonized residues (char yield) at 800°C under nitrogen atmosphere for all polyimides was in the range of 52–68 wt%. The high char yields of these polyimides can be attributed to their high aromatic content.

Optical and electrochemical properties

The optical and electrochemical properties of the organo-soluble polyimides **5d–f** and **6e, f** were investigated with

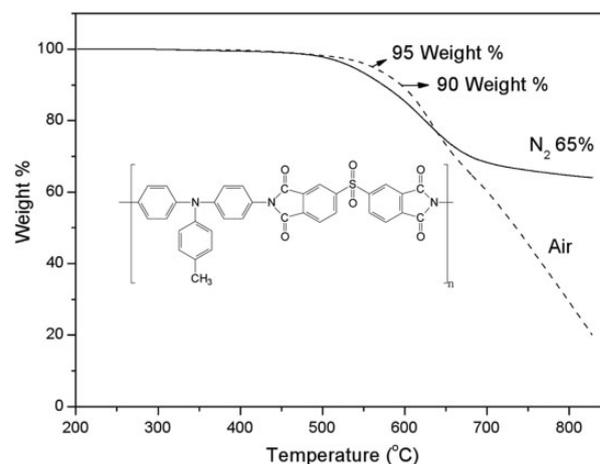


Figure 8. The TGA thermogram of polyimide **6e** at a scan rate of 20°C min⁻¹. TGA: thermogravimetric analysis.

UV-Vis spectroscopy and cyclic voltammetry (CV). The results are summarized in Table 5. The polymer films exhibited UV-Vis absorption λ_{max} at 302–316 nm, which were assignable to the π - π^* transition of the aromatic segments. They showed absorption edge (λ_{onset}) at 397–425 nm, corresponding to band gaps of 2.92–3.12 eV.

The redox behaviours of the polyimides were investigated by CV conducted for the cast films on an ITO-coated glass substrate as the working electrode in dry acetonitrile (CH₃CN) containing 0.1 M TBAP as an electrolyte under a nitrogen atmosphere. The typical CV diagrams for polyimides **5e** and **6e** are depicted in Figure 9. One reversible oxidation redox couple could be observed at $E_{1/2}$ value of

Table 5. Optical and electrochemical properties of the polyimides.

Polymer code	λ_{\max} (nm) ^a	λ_{onset} (nm) ^a	$E_{1/2}$ (V) ^b	Band gap (eV) ^c	HOMO (eV) ^d	LUMO (eV) ^d
5d	316	397	1.26	3.12	5.62	2.50
5e	307	420	1.23	2.95	5.59	2.64
5f	316	400	1.25	3.10	5.61	2.51
6e	305	425	1.08	2.92	5.44	2.52
6f	302	410	1.10	3.02	5.46	2.44

HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital; CV: cyclic voltammetry; Ag: silver; AgCl: silver chloride.

^aRead from the UV-Vis absorption spectra of the polymer films.

^bOxidation half-wave potential from CV (vs. Ag/AgCl).

^cThe data were calculated by the equation: Band gap = $1240/\lambda_{\text{onset}}$.

^dThe HOMO energy levels were calculated from the oxidation $E_{1/2}$ value of CV diagrams and were referenced to ferrocene (4.8 eV relative to vacuum energy level; $E_{1/2} = 0.44$ V in CH_3CN). HOMO = $E_{1/2} + 4.8 - 0.44$ (eV); LUMO = HOMO – band gap.

1.23 V for polyimide **5e** and at $E_{1/2} = 1.08$ V for polyimide **6e** in the oxidative scan. Upon oxidation, the polymer films of **5e** and **6e** changed colour from original pale yellow to chrome yellow and purplish blue, respectively. As can be seen from Table 5, polyimides **5d–f** displayed a higher $E_{1/2}$ value (1.23–1.26 V) in comparison with polyimides **6e** and **6f** (1.08–1.10 V), attributable to the electron-withdrawing trifluoromethyl substituent on the TPA unit. The energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the corresponding polyimides were estimated from the $E_{1/2}$ values. Assuming that the HOMO energy level for the ferrocene/ferrocenium (Fc/Fc^+) standard is 4.8 eV with respect to the zero vacuum level, the HOMO levels for these polyamides were calculated to be 5.44–5.62 eV. Their LUMO energy levels deduced from the band gap calculated from the absorption edge were 2.44–2.64 eV.

Spectroelectrochemical and electrochromic properties

The electrochromism of thin films from the polyimides was examined via the casting of polymer solutions onto an ITO-coated glass substrate, and their absorption spectra were monitored with a UV-Vis spectrometer at different applied potentials. The electrode preparation and solution conditions were identical to those used in CV. The typical spectral changes of polyimides **5e** and **6e** are shown in Figures 10 and 11, respectively. When the applied potential increased from 0.91 to 1.58 V, the absorption peak of polyimide **5e** at 308 nm decreased gradually, whereas two new bands grew at 358 and 747 nm because of the electron oxidation. Meanwhile, the film changed colour from pale yellow to chrome yellow at electrode potential of 1.50 V. Upon electro-oxidation at applied voltages higher than 0.71 V, the polymer film of **6e** showed new absorption bands at 368 and 710 nm, which appeared the complementary colour of blue after highly oxidized at 1.50 V.

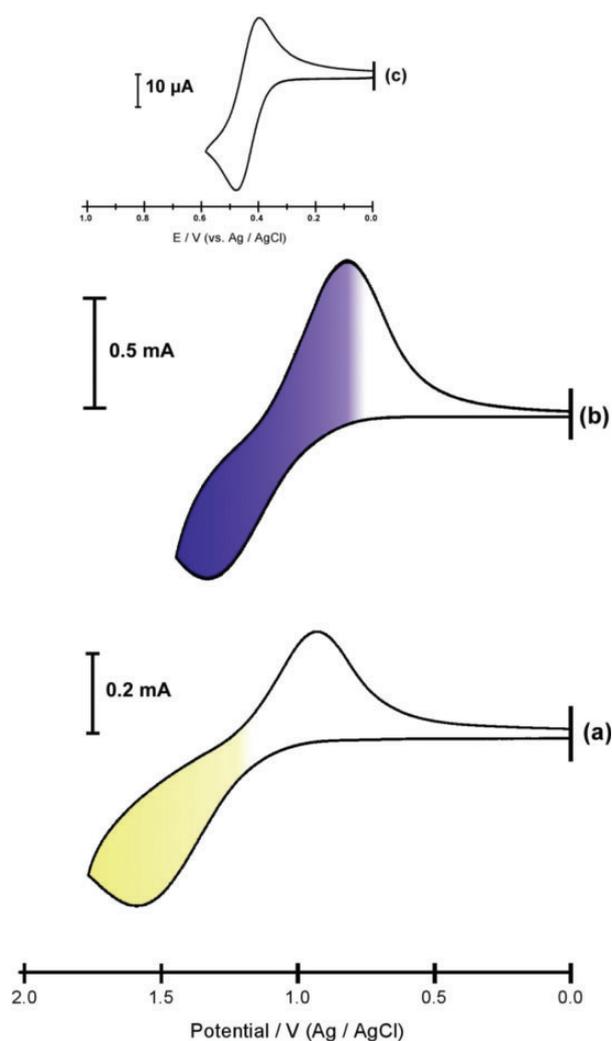


Figure 9. CV diagrams of the cast films of (a) polyimide **5e** (b) polyimide **6e** film on an ITO-coated glass substrate in 0.1 M TBAP/ CH_3CN at a scan rate of 100 mV s^{-1} . The CV diagram of ferrocene (c) was used as an external reference for calibration. CV: cyclic voltammetry; ITO: indium–tin oxide; CH_3CN : acetonitrile; TBAP: tetra-*n*-butylammonium perchlorate.

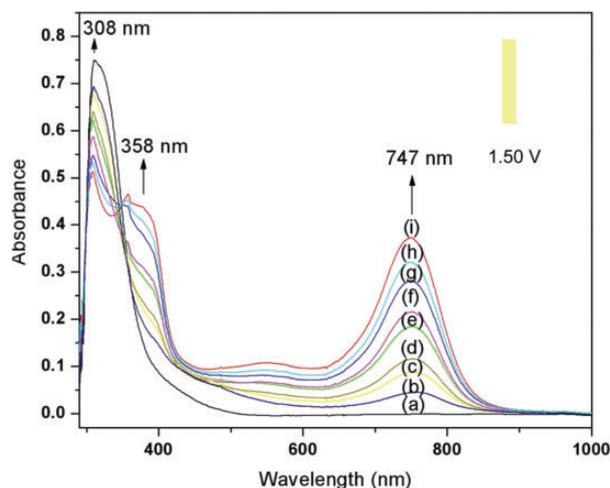


Figure 10. Electrochromic behaviour of polyimide **5e** thin film (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0.0, (b) 0.91, (c) 1.00, (d) 1.10, (e) 1.19, (f) 1.29, (g) 1.38, (h) 1.48 and (i) 1.58 V. CH_3CN : acetonitrile; TBAP: tetra-*n*-butylammonium perchlorate.

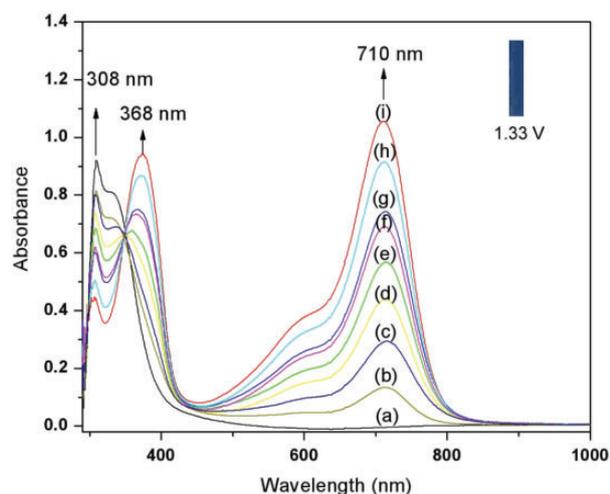


Figure 11. Electrochromic behaviour of polyimide **6e** thin film (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0.0, (b) 0.71, (c) 0.79, (d) 0.88, (e) 0.97, (f) 1.06, (g) 1.15, (h) 1.24 and (i) 1.33 V. CH_3CN : acetonitrile; TBAP: tetra-*n*-butylammonium perchlorate.

To explore the potential electrochromic application of the polyimide films, a square-wave potential step method coupled with UV-Vis spectroscopy were used to evaluate their switching stability. In Figure 12 are depicted the switching results obtained for polyimide **5e** film in TBAP/ CH_3CN for the colour change pale yellow D chrome yellow. The switching times estimated from the absorbance–time curves indicated in Figure 12 were determined by considering 90% of the full optical change. Thin films from polyimide **5e** would require 5 s for colouring after applying a voltage of 1.58 V and 3 s for bleaching after

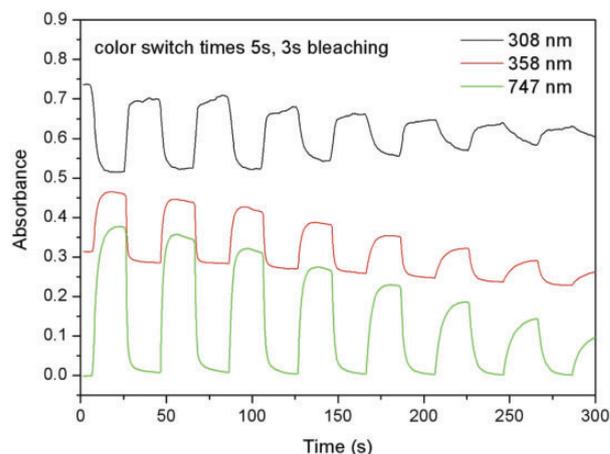


Figure 12. Potential step absorptometry of polyimide **5e** (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) by applying a potential step (0 V Δ 1.58 V). CH_3CN : acetonitrile; TBAP: tetra-*n*-butylammonium perchlorate.

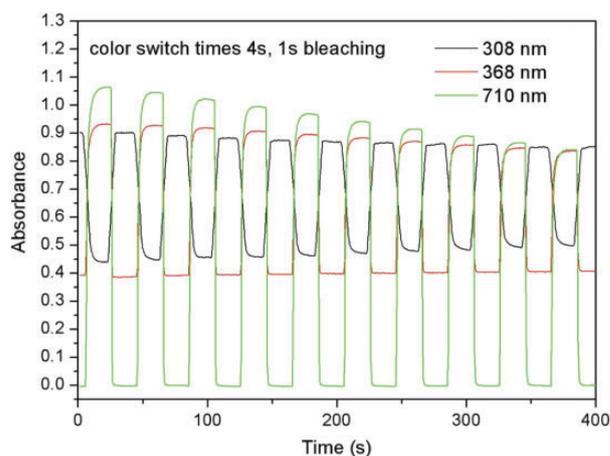


Figure 13. Potential step absorptometry of polyimide **6e** (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) by applying a potential step (0 V Δ 1.33 V). CH_3CN : acetonitrile; TBAP: tetra-*n*-butylammonium perchlorate.

switching off the potential. Because the electron-withdrawing $-\text{CF}_3$ group destabilizes the TPA radical cation formed upon oxidation, a considerable loss of optical contrast was observed after 10 redox switches for polyimide **5e**. Thin film from polyimide **6e** would require 4 s for colouring (at 1.33 V) and 2 s for bleaching (Figure 13). After 10 continuous cyclic scans between 0 V and 1.33 V, the polyimide **6e** film still did not show significant loss in optical contrast. It is reasonable that the CH_3TPA -functionalized **6** series polyimides exhibited much better electrochromic stability than the CF_3TPA -based **5** series polyimides because the former ones formed more stable TPA radical cations in the oxidative processes. Although the CF_3TPA -based **5** series polyimides showed a less electrochromic performance, the bulkiness of the $-\text{CF}_3$ group and their

good film quality make them potential application as gas separation membranes. Their other optoelectronic applications such as memory devices and charge storage materials are still deserved to be developed.

Conclusions

New triphenylamine-functionalized aromatic polyimides with methyl or trifluoromethyl protecting groups were synthesized from the polycondensation reactions of diamine monomers **3a** and **3b** with six commercially available aromatic dianhydrides. All the polyimides could afford flexible and strong films. The polyimides had T_g values higher than 269°C and were thermally stable with 10% weight loss temperature being recorded above 500°C under nitrogen atmosphere. Introduction of electron-withdrawing trifluoromethyl group increased the oxidation potential and decreased the electrochemical and electrochromic stability of the polyimides. The methyl-substituted TPA-containing polyimides exhibited good redox stability and might be good candidates for electrochromic applications.

Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This work was financially supported by the Ministry of Science and Technology, Taiwan (Grant no. MOST 104-2221-E-027-106).

References

1. Sroog CE. Polyimides. *Prog Polym Sci* 1991; **16**: 561–694.
2. Ghosh MM and Mittal KL. *Polyimides: Fundamentals and Applications*. New York: Marcel Dekker, 1996.
3. Liou GS and Yen HJ. Polyimides. In: Matyjaszewski K and Moller M (eds) *Polymer Science: A Comprehensive Reference*. Vol. 5. Amsterdam: Elsevier BV, 2012, pp. 497–535.
4. Liaw DJ, Wang KL, Huang YC, et al. Advanced polyimide materials: syntheses, physical properties and applications. *Prog Polym Sci* 2012; **37**: 907–974.
5. Li WM, Li SH, Zhang QY, et al. Synthesis of bis(amine anhydride)s for novel high T_g s and organosoluble poly(amine imide)s by palladium-catalyzed amination of 4-chlorophthalide anhydride. *Macromolecules* 2007; **40**: 8205–8211.
6. Maya EM, Garcia-Yoldi I, Lozano AE, et al. Synthesis, characterization, and gas separation properties of novel copolyimides containing adamantyl ester pendant groups. *Macromolecules* 2011; **44**: 2780–2790.
7. Yen HJ, Guo SM, Yeh JM, et al. Triphenylamine-based polyimides with trimethyl substituents for gas separation membrane and electrochromic applications. *J Polym Sci Part A: Polym Chem* 2011; **49**: 3637–3646.
8. Yen HJ, Wu JH, Huang YH, et al. Novel thermally stable and soluble triarylamine functionalized polyimides for gas separation. *Polym Chem* 2014; **5**: 4291–4226.
9. Liu JG, Nakamura Y, Shibasaki Y, et al. Synthesis and characterization of highly refractive polyimides from 4,4'-thio-bis[(*p*-phenylenesulfanyl)aniline] and various aromatic tetracarboxylic dianhydrides. *J Polym Sci A Polym Chem* 2007; **45**: 5606–5617.
10. Liu JG, Nakamura Y, Shibasaki Y, et al. High refractive index polyimides derived from 2,7-bis(4-aminophenylenesulfanyl)thianthrene and aromatic dianhydrides. *Macromolecules* 2007; **40**: 4614–4620.
11. Terraza CA, Liu JG, Nakamura Y, et al. Synthesis and properties of highly refractive polyimides derived from fluorene-bridged sulfur-containing dianhydrides and diamines. *J Polym Sci A Polym Chem* 2008; **46**: 1510–1520.
12. Fukukawa K and Ueda M. Recent progress of photosensitive polyimides. *Polym J* 2008; **40**: 281–296.
13. Rusanov AL, Bulycheva EG, Bugaenko MG, et al. Sulfonated polynaphthylimides as proton-conducting membranes for fuel cells. *Russ Chem Rev* 2009; **78**: 53–75.
14. Chen XB, Chen KC, Chen P, et al. Effects of tetracarboxylic dianhydrides on the properties of sulfonated polyimides. *J Polym Sci A Polym Chem* 2010; **48**: 905–915.
15. Saito J, Tanaka M, Miyatake K, et al. Proton conductive polyimide ionomer membranes: effect of NH, OH, and COOH groups. *J Polym Sci A Polym Chem* 2010; **48**: 2846–2854.
16. Cheng SH, Hsiao SH, Su TH, et al. Novel aromatic poly(amine-imide)s bearing a pendent triphenylamine group: synthesis, thermal, photophysical, electrochemical, and electrochromic characteristics. *Macromolecules* 2005; **38**: 307–316.
17. Kung YC and Hsiao SH. Solution-processable, high- T_g , ambipolar polyimide electrochromics bearing pyrenylamine units. *J Mater Chem* 2011; **21**: 1746–1754.
18. Yen HJ and Liou GS. Solution-processable triarylamine-based electroactive high performance polymers for anodically electrochromic applications. *Polym Chem* 2012; **3**: 255–264.
19. Wang HM and Hsiao SH. Ambipolar, multi-electrochromic polypyromellitimides and polynaphthalimides containing di(*tert*-butyl)-substituted bis(triarylamine) units. *J Mater Chem C* 2014; **2**: 1553–1564.
20. Ling QD, Chang FC, Song Y, et al. Synthesis and dynamic random access memory behavior of a functional polyimide. *J Am Chem Soc* 2006; **128**: 8732–8733.
21. Kuorosawa T, Chueh CC, Liu CL, et al. High performance volatile polymeric memory devices based on novel triphenylamine-based polyimides containing mono- or dual-mediated phenoxy linkages. *Macromolecules* 2010; **43**: 1236–1244.
22. Li YQ, Xu HH, Tao X, et al. Synthesis and memory characteristics of highly organo-soluble polyimides bearing a non-coplanar twisted biphenyl unit containing aromatic side-chain groups. *J Mater Chem* 2011; **21**: 1810–1821.

23. Yen HJ, Wu JH and Liou GS. High performance polyimides for resistive switching memory devices. In: Chen WC (ed) *Electrical Memory Materials and Devices*. RSC Polymer Chemistry Series No. 18. Croydon: CPI Group (UK) Ltd, 2015, Ch. 4, pp. 136–166.
24. Satoh A and Morikawa A. Synthesis and characterization of aromatic polyimides containing trifluoromethyl group from bis(4-amino-2-trifluoromethylphenyl)ether and aromatic tetracarboxylic dianhydrides. *High Perform Polym* 2010; **22**: 412–427.
25. Thiruvassagam P and Venkatesan D. Synthesis and characterization of processable aromatic polyimides. *High Perform Polym* 2010; **22**: 682–693.
26. Ghaemy M, Alizadeh R, Hashemi Nasr F, et al. Synthesis and properties of high performance polyimides derived from a novel diamine containing a *N*-octylcarbazole unit and two 3,5-diarylimidazole groups. *High Perform Polym* 2012; **24**: 262–273.
27. Wang JY, Liu C, Su GX, et al. Synthesis and characterization of organo-soluble polyimides containing phthalazinone and bicarbazole moieties in the main chain. *High Perform Polym* 2012; **24**: 356–365.
28. Shen J, Li XL, Zhang Y, et al. Synthesis and characterization of highly soluble and optically transparent polyimides derived from novel fluorinated pyridine-containing aromatic diamine. *High Perform Polym* 2013; **25**: 268–277.
29. Zheng HL, Pei XL, Chen GF, et al. Comparative studies on melt processable polyimides derived from 2,3,3',4'-oxydiphthalic anhydride and 2,3,3',4'-thioetherdiphthalic anhydride. *High Perform Polym* 2013; **25**: 454–463.
30. Lu YH, Xiao GY, Chi HJ, et al. Effects of *tert*-butyl substitutes of fluorinated diamine on the properties of polyimides. *High Perform Polym* 2013; **25**: 894–900.
31. Liu CT, Chen GF and Fang XZ. Preparation, characterization, and properties of poly(thioether ether imide)s from isomeric bis(chlorophthalimide)s and bis(4-mercaptophenyl) ether. *High Perform Polym* 2015; **27**: 112–121.
32. Nabeshima S and Morikawa A. Synthesis and properties of polyimides having a hexaphenylbenzene unit. *High Perform Polym* 2015; **27**: 772–781.
33. Saritha B and Thiruvassagam P. Synthesis of diol monomers and organosoluble fluorinated polyimides with low dielectric: study of structure–property relationship and applications. *High Perform Polym* 2015; **27**: 842–851.
34. Shirota Y. Organic materials for electronic and optoelectronic devices. *J Mater Chem* 2000; **10**: 1–25.
35. Shirota Y. Photo- and electroactive amorphous molecular materials – molecular design, syntheses, reactions, properties, and applications. *J Mater Chem* 2005; **15**: 75–93.
36. Shirota Y and Kageyama H. Charge carrier transporting molecular materials and their applications in devices. *Chem Rev* 2007; **107**: 953–1010.
37. Thelakkat M. Star-shaped, dendrimeric and polymeric triarylamines as photoconductors and hole transport materials for electro-optical applications. *Macromol Mater Eng* 2002; **287**: 442–461.
38. Iwan A and Sek D. Polymers with triphenylamine units: photonic and electroactive materials. *Prog Polym Sci* 2011; **36**: 1277–1325.
39. Liou GS, Hsiao SH and Chen HW. Novel high- T_g poly(amine-imide)s bearing pendent *N*-phenylcarbazole units: synthesis and photophysical, electrochemical and electrochromic properties. *J Mater Chem* 2016; **16**: 1831–1842.
40. Hsiao SH, Liou GS and Wang HM. Highly stable electrochromic polyamides based on *N,N*-bis(4-aminophenyl)-*N',N'*-bis(4-*tert*-butylphenyl)-1,4-phenylenediamine. *J Polym Sci A Polym Chem* 2009; **47**: 2330–2343.
41. Kung YC and Hsiao SH. Fluorescent and electrochromic polyamides with pyrenylamine chromophore. *J Mater Chem* 2010; **20**: 5481–5492.
42. Hsiao SH, Wang HM, Chang PC, et al. Synthesis and electrochromic properties of aromatic polyetherimides based on a triphenylamine-dietheramine monomer. *J Polym Sci A: Polym Chem* 2013; **51**: 2925–2938.
43. Yen HJ, Chen CJ and Liou GS. Flexible multi-colored electrochromic and volatile polymer memory devices derived from starburst triarylamine-based electroactive polyimide. *Adv Funct Mater* 2013; **23**: 5307–5316.
44. Wang HM and Hsiao SH. Enhancement of redox stability and electrochromic performance of aromatic polyamides by incorporation of (3,6-dimethoxycarbazol-9-yl)triphenylamine units. *J Polym Sci A Polym Chem* 2014; **52**: 272–286.
45. Hsiao SH and Cheng SL. New electroactive and electrochromic aromatic polyamides with ether-linked bis(triphenylamine) units. *J Polym Sci A Polym Chem* 2015; **53**: 496–510.
46. Wang YQ, Liang Y, Zhu JY, et al. High coloration efficiency and fast switching speed of poly(amic acid-imide)s containing triphenylamine in acidic electrolyte. *RSC Adv* 2015; **5**: 11071–11076.
47. Sun NW, Feng F, Wang DM, et al. Novel polyamides with fluorene-based triphenylamine: electrofluorescence and electrochromic properties. *RSC Adv* 2015; **5**: 88181–88190.
48. Janoschka T, Hager MD and Schubert US. Powering up the future: radical polymers for battery applications. *Adv Mater* 2012; **24**: 6397–6409.
49. Feng JK, Cao YL, Ai XP, et al. Polytriphenylamine: a high power and high capacity cathode material for rechargeable lithium batteries. *J Power Sources* 2008; **177**: 199–204.
50. Yao M, Senoh H, Sakai T, et al. Redox active poly(*N*-vinylcarbazole) for use in rechargeable lithium batteries. *J Power Sources* 2012; **202**: 364–368.
51. Seo ET, Nelson RF, Fritsch JM, et al. Anodic oxidation pathways of aromatic amines. Electrochemical and electron paramagnetic resonance studies. *J Am Chem Soc* 1966; **88**: 3498–3503.
52. Nelson RF and Adams RN. Anodic oxidation pathways of substituted triphenylamines. II. Quantitative studies of benzidine formation. *J Am Chem Soc* 1968; **90**: 3925–3930.

53. Chang CW, Liou GS and Hsiao SH. Highly stable anodic green electrochromic aromatic polyamides: synthesis and electrochromic properties. *J Mater Chem* 2007; **17**: 1007–1015.
54. Hsiao SH, Liou GS, Kung YC, et al. High contrast ratio and rapid switching electrochromic polymeric films based on 4-(dimethylamino)triphenylamine-functionalized aromatic polyamides. *Macromolecules* 2008; **41**: 2800–2808.
55. Hsiao SH, Hsiao YH and Kung YR. Highly redox-stable and electrochromic aramids with morpholinyl-substituted triphenylamine units. *J Polym Sci A Polym Chem* 2016; **54**: 1289–1298.
56. Takizawa K, Asai S and Ando S. Temperature dependence of electric conduction in polyimides with main chain triphenylamine structures. *Polym J* 2014; **46**: 201–206.
57. Lee SH, Bae J, Seo HM, et al. Electrochromism properties of polyimides possessing triphenylamine moieties with different substituents. *Mol Cryst Liq Cryst* 2014; **598**: 6–15.
58. Oishi Y, Takado H, Toneyama M, et al. Preparation and properties of new polyamides from 4,4'-diaminotriphenylamine and aromatic dicarboxylic acids. *J Polym Sci A Polym Chem* 1990; **28**: 1763–1769.
59. Imai Y, Ishida M and Kakimoto M. Synthesis and properties of new triphenylamine-containing aromatic polyimides based on *N,N'*-bis(4-aminophenyl)-*N,N'*-diphenyl-4,4'-biphenyldiamine. *High Perform Polym* 2003; **15**: 281–290.
60. Hsiao SH and Lin KH. A comparative study on the properties of aromatic polyamides with methyl- or trifluoromethyl-substituted triphenylamine groups. *J. Fluorine Chem* Available online 7 June 2016, DOI: 10.1016/j.jfluchem.2016.06.001