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High glass transition and thermal stability of new pyridine-containing polyimides: Effect of protonation on fluorescence

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Abstract

A new diamine monomer containing heterocyclic pyridine and triphenylamine groups, 4-(4,4′-diaminotriphenylamine)-2,6-bis(4-methylphenyl)pyridine (**4**), was synthesized by Chichibabin and nucleophilic fluoro-displacement reactions. The diamine was used to prepare a series of novel polyimides via polycondensation with various aromatic tetracarboxylic dianhydrides in *N*-methyl-2-pyrrolidinone. The polyimide **4a** derived from the diamine **4** with 4,4′-hexafluoroisopropylidenediphthalic anhydride and having high T_g (313 °C), mechanical, and thermal properties was soluble in various organic solvents, such as *N*-methyl-2-pyrrolidinone, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, pyridine, chloroform, tetrahydrofuran, at room temperature. The polyimide (**4a**) could be cast into a self-standing film from DMAc solution and was thermally converted into tough and flexible film. The film had high tensile modulus of 2.2 GPa and exhibited excellent thermal stability in both nitrogen and air ($T_d^{10} > 550$ °C). The pristine polymer exhibited the UV–vis absorption bands in the region 240–400 nm and protonated polymer exhibited absorption in the region 390–500 nm. The protonated polymer possessed strong orange fluorescence (around 600 nm) in THF solution after protonation with acids as excited at 438 nm. The fluorescent intensity was influenced by the acid concentrations and the chemical structure of conjugated bases. The fluorescent intensity at 600 nm increased as acid concentration from a lower to a moderate concentration and decreased at higher concentrations.

Keywords: Polyimide; Protonation; Pyridine

1. Introduction

Aromatic polyimides have been studied extensively as high performance materials for applications in integrated electronic circuits, aerospace devices, microelectronics, optoelectronics, composites and so on, due to their excellent properties, such as outstanding thermal and thermo oxidative stabilities, chemical resistance, mechanical and electrical properties [1–11]. However, most of them have high melting, softening temperatures or low optical transparency and are insoluble in organic solvents. These properties make them generally intractable or difficult to process, thus limiting their applications. In order to overcome this drawback, special structures, such as bulky lateral substituents, flexible alkyl side chains, unsymmetric, alicyclic or kinked structures have been attached along the backbone [12–20]. In recent years, the rigid rod polyimides with high organic solubility have attracted some research efforts. These efforts have been focused on synthesizing new rigid diamines that resulted in soluble and processable polyimides without deteriorating their positive properties.

The polyimides containing triphenylamine possess photochemical and electronic properties as well as high thermal stability because of the triphenylamine conjugated system [21,22]. Moreover, polyimides with triphenylamine groups may be applied in organic electroluminescent elements because light-emitting triphenylamine derivatives were reputed to be hole-transporting layer materials and showed increasing potential

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as active components for a wide range of photoelectronic and electronic devices [23–31]. Moreover, the bulky triphenylamine units can increase the solubility of polymers [22]. On the other hand, recently, some reports have concerned the introducing of pyridine and its derivatives into polymeric frames to increase thermal stability of polymers [6,27,32–34]. Pyridine is an electron-rich aromatic heterocycle, with a localized lone pair of electrons in sp^2 orbital on the nitrogen atom. Consequently, the derived polymers can increase electron affinity to improve electron-transporting properties and offer the possibility of protonation or alkylation of the lone pair electrons as a way of modifying their properties [35–38]. Therefore, polymers containing pyridine and triphenylamine groups are expectable to have good solubility and excellent thermal properties.

This work explores the synthesis and characterization of aromatic polyimides containing pyridine and triphenylamine groups by the polymerization of 4-(4,4′-diaminotriphenylamine)-2,6-bis(4-methylphenyl)pyridine (**4**) with various commercially available aromatic dianhydrides. The solubility, thermal, mechanical and optical properties of the obtained polyimides were investigated as well as the effect of protonation on fluorescence.

2. Experimental

2.1. Materials

The materials, 4-nitrobenzaldehyde (from Aldrich), 4′-methylacetophenone (from Acros), 4-fluoronitrobenzene (from Acros), cesium fluoride (from Aldrich), ammonium acetate (from SHOWA), glacial acetic acid (from SHOWA), hydrazine monohydrate (from Alfa Aesar), and 10% palladium on activated carbon (from Merck), were used as-received. The solvents, *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO), were purchased from TEDIA, and tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF) were purchased from ECHO. These solvents were purified by distillation over calcium hydride and stored over 4 Å molecular sieves. Acetic anhydride and pyridine were purchased from Acros and used as-received. The aromatic tetracarboxylic dianhydrides, 4,4′-hexafluoroisopropylidenediphthalic anhydride (6FDA, **a**; from CHRISKEV), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, **b**; from CHRISKEV), 4,4′-sulfonyldiphthalic anhydride (DSDA, **c**; from TCI), 4,4′-oxydiphthalic anhydride (ODPA, **d**; from TCI), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA, **e**; from TCI) and pyromellitic dianhydride (PMDA, **f**; from CHRISKEV) were sublimated before use.

2.2. Measurements

Infrared (IR) spectra were recorded on a Perkin–Elmer GX FTIR spectrometer. NMR spectra were recorded using a Bruker DRX-500 NMR (^{1}H at 500.13 MHz and ^{13}C at 125.76 MHz) spectrometer. Elemental analyses were made on a Perkin–Elmer 2400 instrument. The inherent viscosity of polyimides was measured by Ubbelohde viscometer. Thermogravimetric data were obtained on a Perkin–Elmer Pyris 6 TGA under nitrogen or air flowing condition at a rate of 20 $cm^3\ min^{-1}$ and a heating rate of 20 °C min^{-1}. Differential scanning calorimetric analysis was performed on a Perkin–Elmer Pyris DSC 6 under nitrogen flowing condition at a rate of 20 $cm^3\ min^{-1}$ and a heating rate of 10 °C min^{-1}. Weight-average (M_w) and number-average (M_n) molecular weights were determined by gel permeation chromatography (GPC). Four Waters (Ultrastyragel) columns (300 × 7.5 mm, guard, 10^5, 10^4, 10^3, and 500 Å in a series) were used for GPC analysis with tetrahydrofuran (THF, 1 mL min^{-1}) as the eluent. The eluents were monitored with a UV detector (JMST Systems, VUV-24, USA) at 254 nm. Polystyrene was used as the standard. Tensile properties were determined from stress–strain curves obtained with an Orientec Tensilon with a load cell of 10 kg. A gauge of 2 cm and a strain rate of 2 cm min^{-1} were used for this study. Absorption spectra were measured with a UV 500 UV–vis spectrometer at room temperature in air. Photoluminescence (PL) spectra were measured with a Perkin–Elmer LS 55 luminescence spectrometer. Cyclic voltammetry (CHI model 619A) was conducted with the use of a three-electrode cell in which ITO (the polymer film area was ca. 0.7 cm × 0.5 cm) was used as a working electrode. The spectroelectrochemical cell was composed of a 1-cm cuvette, ITO as a working electrode, a platinum wire as an auxiliary electrode, and an Ag/AgCl reference electrode.

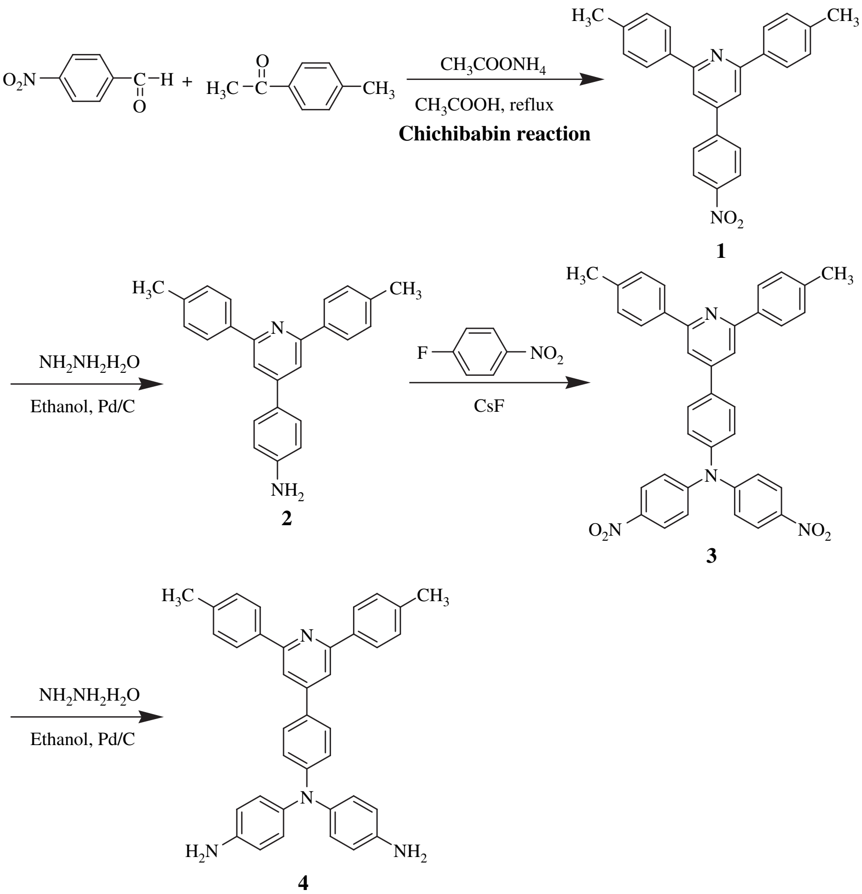
2.3. Synthesis of monomer (Scheme 1)

2.3.1. 4-(4-Nitrophenyl)-2,6-bis(4-methylphenyl) pyridine (*1*)

In a 500 mL round-bottomed flask, a mixture of 9.0 g (60 mmol) of 4-nitrobenzaldehyde, 16.0 g (120 mmol) of 4-methylacetophenone, 91.7 g (1.2 mol) of ammonium acetate and 300 mL of glacial acetic acid was refluxed for 18 h. Upon cooling, the precipitated orange solid was collected by filtration and washed with ethanol. The yield of the crude product was 10.1 g (89%). The crude product was recrystallized from DMSO twice to afford yellowish solid; m.p. 226 °C (by DSC); FTIR (KBr): 1513 and 1343 cm^{-1} (NO_2). Elemental analysis calcd for $C_{25}H_{20}N_2O_2$: C, 78.93; H, 5.30; N, 7.36. Found: C, 77.88; H, 5.18; N, 7.72.

2.3.2. 4-(4-Aminophenyl)-2,6-bis(4-methylphenyl) pyridine (*2*)

In a 500 mL three-necked flask, a mixture of 10.0 g (26.3 mmol) of nitro compound **1**, 0.5 g of 10% Pd/C, 13.3 mL of hydrazine monohydrate and 300 mL of tetrahydrofuran was refluxed with stirring for 20 h. The mixture was then filtered to remove Pd/C and dried by using rotation vapor to afford the crude product. The yield of the crude product was 8.8 g (95%). The crude product was purified by column chromatography (eluent: chloroform) to afford the pure product **2**; m.p. 216 °C (by DSC); FTIR (KBr): 3454 and 3319 cm^{-1} (NH_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 8.13–8.12 (d, 4H), 7.81 (s, 2H), 7.61–7.59 (d, 2H), 7.35–7.33 (d, 4H), 6.80–6.78 (d,



Scheme 1. Synthesis of the new diamine, 4-(4,4′-diaminotriphenylamine)-2,6-bis(4-methylphenyl)pyridine (**4**).

2H), 2.46 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 157.2, 149.6, 147.36, 138.7, 137.4, 129.3, 128.8, 128.1, 126.9, 115.6, 115.3, 21.3. Elemental analysis calcd for $C_{25}H_{22}N_2$: C, 85.68; H, 6.33; N, 7.99. Found: C, 85.33; H, 6.29; N, 7.95.

2.3.3. 4-(4,4′-Dinitrotriphenylamine)-2,6-bis(4-methylphenyl)pyridine (*3*)

In a 500 mL round-bottomed flask, a mixture of 7.0 g (20 mmol) of amino compound **2**, 5.7 g (40 mmol) of 4-fluoronitrobenzene, 6.1 g (40 mmol) of cesium fluoride and 100 mL of dimethyl sulfoxide was heated with stirring at 130 °C for 18 h. After cooling, the mixture was poured into 1000 mL of water, and the precipitate was collected by filtration and washed thoroughly with water. The crude product was then washed with hot ethanol and dried at 100 °C. The yield of the yellow product **3** was 9.8 g (83%); m.p. 351 °C (by DSC); FTIR (KBr): 1580 and 1318 cm^{-1} (NO_2). Elemental analysis calcd for $C_{37}H_{28}N_4O_4$: C, 74.99; H, 4.76; N, 9.45. Found: C, 74.38; H, 4.74; N, 9.31.

2.3.4. 4-(4,4′-Diaminotriphenylamine)-2,6-bis(4-methyl phenyl)pyridine (*4*)

In a 500 mL three-necked flask, a mixture of 9.0 g (15 mmol) of dinitro compound **3**, 0.45 g of 10% Pd/C, 7.4 mL of hydrazine monohydrate and 300 mL of tetrahydrofuran was refluxed with stirring for 20 h. The mixture was then filtered to remove Pd/C and dried by using rotation vapor to afford the crude product. The crude product was purified by column chromatography twice (eluent: chloroform and ethyl acetate, respectively) to afford the pure product **4**; yield: 6.9 g (85%); m.p. 255 °C (by DSC); FTIR (KBr): 3440 and 3361 cm^{-1} (NH_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 8.12–8.11 (d, 4H), 7.82 (s, 2H), 7.57–7.56 (d, 2H), 7.34–7.32 (d, 4H), 7.04–7.00 (t, 6H), 6.66–6.65 (d, 4H), 3.40 (s, 4H), 2.45 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 157.2, 150.0, 149.5, 143.0, 138.6, 137.1, 129.3, 129.0, 127.4, 127.2, 126.9, 118.9, 116.1, 115.5, 21.2. Elemental analysis calcd for $C_{37}H_{32}N_4$: C, 83.43; H, 6.06; N, 10.52. Found: C, 83.12; H, 6.02; N, 10.47.

2.4. Synthesis of polymers (Scheme 2)

To a stirred solution of 0.40 g (0.75 mmol) of compound **4** in 4 mL of *N*-methyl-2-pyrrolidinone (NMP), 0.334 g (0.75 mmol) of 4,4′-hexafluoroisopropylidenediphthalic anhydride (**a**) was gradually added. The mixture was stirred at ambient temperature for 4 h to form the poly(amic acid). Chemical imidization was carried out by addition of 1 mL of acetic anhydride and 0.5 mL of pyridine into the above-mentioned poly(amic acid) solution and then heating at 110 °C for 4 h. The polymer solution was poured slowly into 300 mL of methanol. The precipitate was filtered, washed with methanol, and

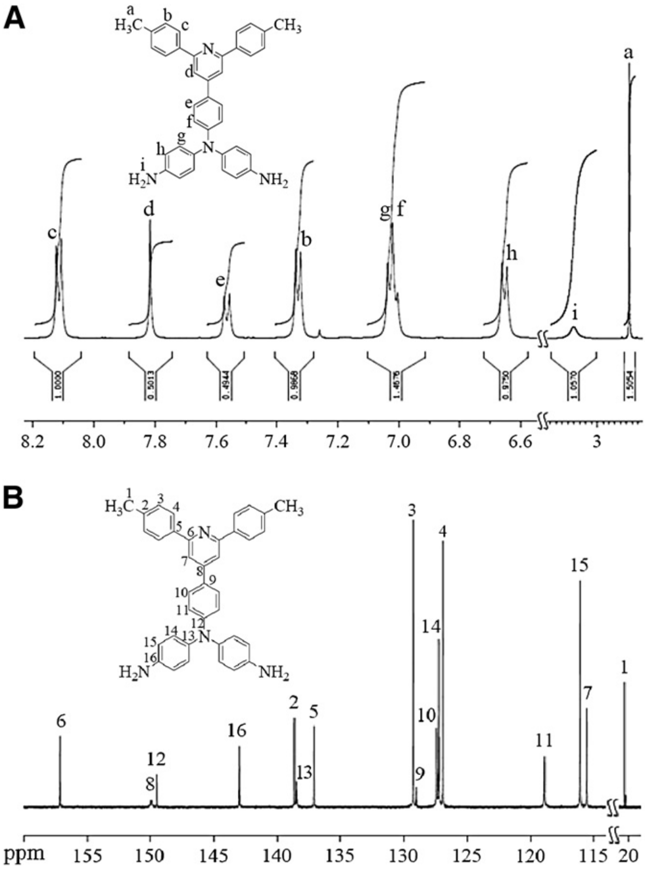


Fig. 1. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of the new diamine **4**.

dried at 100 °C under vacuum. FTIR (film): 1784, 1724, 1378, 722 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 8.10–7.33 (m, 28H), 2.42 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 166.1, 166.0, 157.3, 149.1, 147.0, 139.1, 138.9, 136.7, 135.9, 134.3, 132.3, 129.3, 128.3, 127.5, 127.0, 126.1, 125.2, 125.1, 124.5, 124.1, 122.2, 116.0, 21.2.

In the same way, the other polyimides were polymerized from compound **4** and BTDA, DSDA, ODPA, BPDA, and PMDA, respectively.

3. Results and discussion

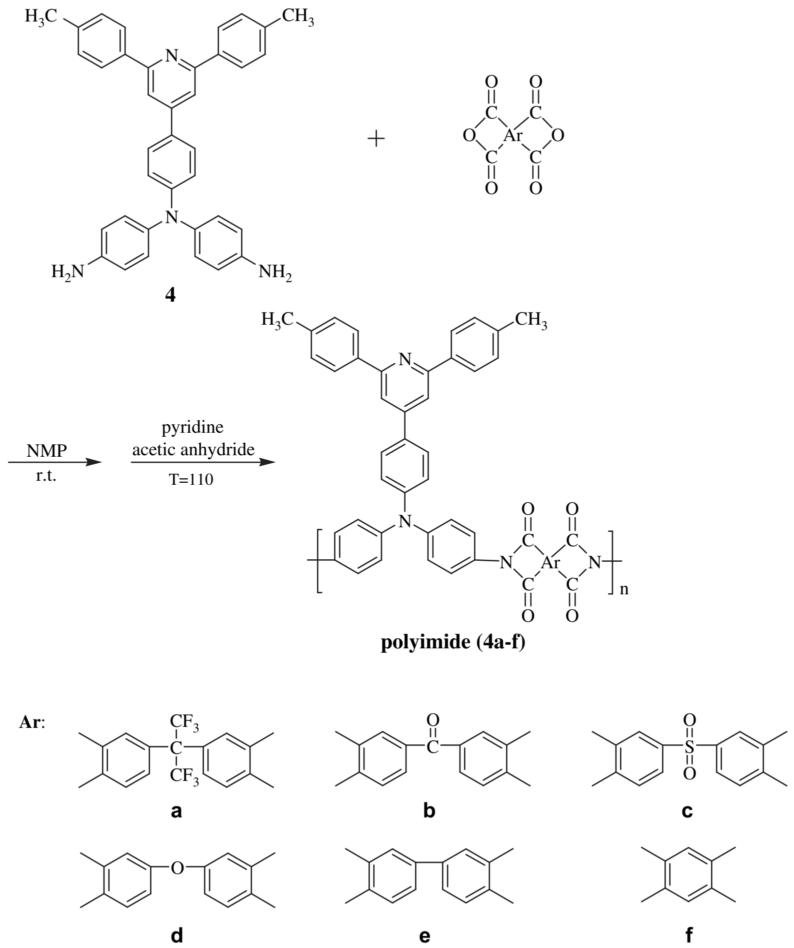
3.1. Monomer synthesis

The synthesis of the novel diamine containing heterocyclic pyridine and triphenylamine groups, 4-(4,4′-diaminotriphenylamine)-2,6-bis(4-methylphenyl)pyridine (**4**), is shown in Scheme 1. The nitro compound **1** containing heterocyclic pyridine was synthesized with a modified Chichibabin reaction, which was a facile way for the preparation of substituted pyridine [39–41]. In particular, the condensation of 4-nitrobenzaldehyde with 4′-methylacetophenone in the presence of ammonium acetate afforded the nitro compound **1** in one step. The FTIR spectra of nitro compound **1** showed characteristic bands of the nitro group at 1347 and 1513 cm^{-1} and methyl groups from 2800 to 3100 cm^{-1}. In addition, C=C and C=N bands of phenyl and pyridine rings at 1424, 1547 and 1593 cm^{-1} were observed. Reduction of the nitro derivative (**1**) in tetrahydrofuran with hydrazine monohydrate in the presence of catalytic amount of palladium on activated carbon at 70 °C produced the new compound **2** (Scheme 1). Elemental analysis, IR, and NMR spectra confirmed the structures of compound **2**. The characteristic absorptions of the nitro groups disappeared and new absorptions at 3319 and 3454 cm^{-1} (N–H stretching) appeared. In ^{1}H NMR spectrum, compound **2** has a new singlet peak (3.84 ppm) due to amino proton, and in ^{13}C NMR spectrum, the signals appeared at 157.2, 147.4 and 115.6 ppm confirming the formation of heterocyclic pyridine ring. These results clearly confirm that compound **2** synthesized herein is consistent with the proposed structure. Condensation reaction of compound **2** and 4-fluoronitrobenzene in the presence of CsF afforded the dinitro compound **3** (Scheme 1). The FTIR spectrum of nitro compound **3** showed characteristic bands of nitro groups at 1318 and 1580 cm^{-1}. Reduction of the nitro derivative (**3**) in tetrahydrofuran with hydrazine monohydrate in the presence of catalytic amount of palladium on activated carbon at 70 °C produced the new compound **4**. The characteristic absorptions of nitro groups disappeared and new absorptions at 3361 and 3440 cm^{-1} (N–H stretching) appeared. The ^{1}H NMR and ^{13}C NMR spectra of compound **4** are clearly illustrated in Fig. 1. When the dinitro compound **3** was reduced to diamine, a new signal at 3.40 ppm which is characteristic of amino groups appeared in the ^{1}H NMR spectrum. Elemental analysis, IR, and NMR spectra clearly confirm that compound **4** synthesized herein is fully consistent with the proposed structure.

3.2. Preparation of polyimides

Polyimides were prepared by the conventional two-step polymerization method, as shown in Scheme 2, involving ring-opening polyaddition forming poly(amic acid)s and subsequent chemical imidization. Reaction of dianhydride with diamine (**4**) at ambient temperature gave viscous poly(amic acid) solutions. The chemical imidization of poly(amic acid)s with a dehydrating agent such as a mixture of acetic anhydride and pyridine was also effective in obtaining polyimides. Besides, precipitated solids occurred in chemical imidization when ODPA, BPDA and PMDA were used as dianhydrides.

The polymer structures were confirmed by elemental analysis, IR and/or NMR spectra. The elemental analysis values of the polyimides were in agreement with their respective structures. The FTIR spectra (Fig. 2) of the polyimides exhibited characteristic absorption bands at around 1780 and 1720 cm^{-1} due to the asymmetric and symmetric stretches of carbonyl group of imide. The polyimides exhibited a band at around 1370 cm^{-1} due to the formation of imidization (C–N). The yields, inherent viscosities and molecular weights of all polyimides are summarized in Table 1. The polyimide **4a** obtained by chemical imidization had inherent viscosity of 0.64 dL g^{-1} in DMAc. Its number-average (M_n) and weight-average (M_w) molecular weights were 4.6×10^4 and 6.5×10^4, respectively, and the polydispersity index (PDI = M_w/M_n) was 1.42, as measured by gel permeation chromatography (GPC), relative to polystyrene standards.



Scheme 2. Synthesis of polyimides.

3.3. Properties of polymers

The solubility of polyimides is summarized in Table 2. Among these polyimides, **4e** and **4f** showed poor solubility due to the presence of rigid phenylene and biphenylene units. The polyimide **4a** exhibited excellent solubility as compared to the others as it was readily soluble in a variety of solvents such as tetrahydrofuran, *N*-methyl-2-pyrrolidinone, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, pyridine and chloroform at room temperature. The excellent solubility of **4a** is due to 6FDA (fluorine effect) [4,32,34].

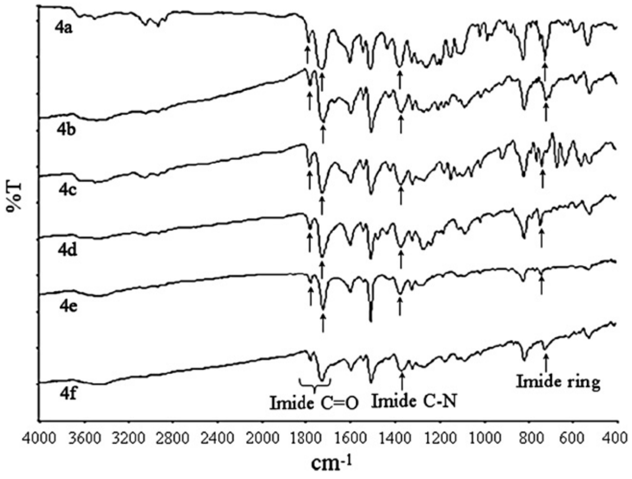


Fig. 2. FTIR spectra of polyimides.

The thermal properties of the polyimides were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results are summarized in Table 3. The glass transition temperatures (T_gs) of the polyimides were found to be in the range of 307–373 °C. The polyimide **4d**, obtained from ODPA, showed the lowest T_g (307 °C)

Table 1
Yield, inherent viscosity and molecular weight of polyimides

Polymer code	Yield (%)	η_{inh}[a] (dL g^{-1})	$M_w \times 10^{-4}$[b]	$M_n \times 10^{-4}$[b]	PDI[c]
4a	98	0.64	6.5	4.6	1.42
4b	99	0.37	–[e]	–[e]	–[e]
4c	96	0.63	2.0	0.77	2.55
4d	98	–[d]	–[e]	–[e]	–[e]
4e	93	–[d]	–[e]	–[e]	–[e]
4f	91	–[d]	–[e]	–[e]	–[e]

[a] Measured in DMAc at a concentration of 0.5 g dL^{-1} at 30 °C.
[b] Measured by GPC in THF; polystyrene was used as standard.
[c] PDI = M_w/M_n.
[d] The polymer is insoluble in DMAc at room temperature.
[e] The polymer is insoluble in THF at room temperature.

Table 2
Solubility of polyimides

Polymer code	Solubility[a]						
	THF	NMP	DMAc	DMF	DMSO	Pyridine	$CHCl_3$
4a	++	++	++	++	+−	++	++
4b	+−	+	++	+−	+−	+	−
4c	++	+	++	+	+−	+	−
4d	−	+−	+−	+−	−	+−	+−
4e	+−	+−	+−	+−	+−	+−	−
4f	−	+−	−	−	−	−	−

Abbreviations: NMP, *N*-methyl-2-pyrrolidinone; DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

[a] Solubility: ++, soluble at room temperature; +, soluble on heating at 70 °C; +−, partially soluble on heating at 70 °C; −, insoluble on heating at 70 °C.

because of the presence of flexible ether linkage between the phthalimide units. The polyimide **4f**, obtained from PMDA, showed the highest T_g (373 °C) due to the presence of rigid phenylene unit [4,6]. The thermal stability of the polyimides was evaluated by TGA measurements in both nitrogen and air atmosphere at a heating rate of 20 °C min^{-1}. The temperatures for 10% weight loss of polyimides in nitrogen and air atmosphere were in the range of 533–614 °C and 520–598 °C, respectively. The polyimides exhibited high thermal stability and glass transition temperatures due to the rigid pyridine group [6,27,32–34,41]. The polyimide **4c**, obtained from DSDA, exhibited the lowest T_d^{10} in comparison with other polyimides because the C–S bond of dianhydride might be degraded easily with heating. The char yields at 800 °C in nitrogen for polyimides were in the range of 63–73 wt%. The high char yield of these polyimides in nitrogen could be ascribed to their high aromatic content. Compared with the polyimides shown in Scheme 3, the polyimide **4a** has equal glass transition temperature with the polyimide **Ref-1** [42] derived from triphenylamine and 6FDA, but higher thermal degradation temperature (Table 3) than **Ref-1**, which suggests that the heterocyclic pyridine group could improve thermal stability of polymers. On the other hand, polyimide **4a** also has higher thermal stability than the polyimides (**Ref-2** [32] and **Ref-3** [34]) with pyridine group in the main chain. It suggests that the triphenylamine group also could improve thermal stability of polymers [21,22,27].

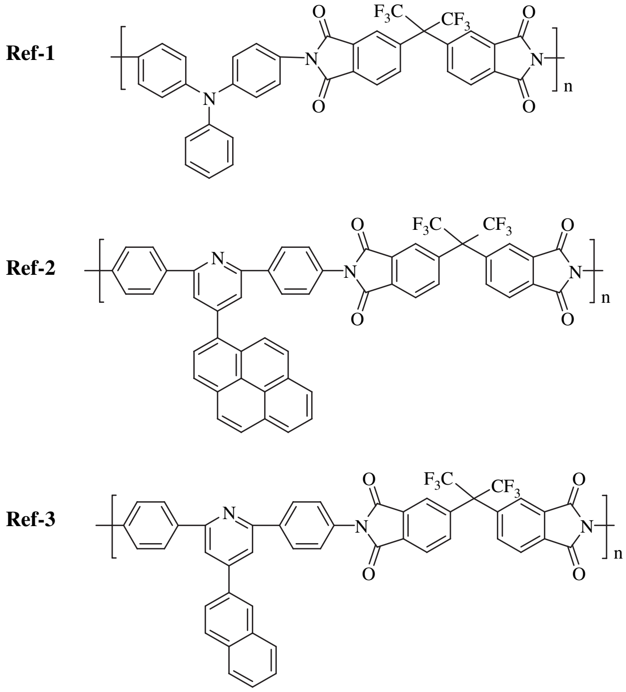
Table 3
Thermal properties of polyimides

Polymer code	T_g[a] (°C)	T_d at 5% weight loss[b] (°C)		T_d at 10% weight loss[b] (°C)		Char yield[c]	
		In N_2	In air	In N_2	In air	In N_2	In air
4a	313	538	520	565	550	63	0
4b	311	540	505	586	556	68	0
4c	321	461	462	533	520	67	18
4d	307	570	562	606	598	73	10
4e	327	581	469	614	529	71	0
4f	373	573	529	587	571	71	28
Ref-1	316	–	–	527	524	59	–
Ref-2	–	–	–	544	529	–	–
Ref-3	–	–	–	532	527	–	–

[a] Glass transition temperature measured by DSC at a heating rate of 10 °C min^{-1}.

[b] Decomposition temperature recorded on TGA at a heating rate of 20 °C min^{-1}.

[c] At 800 °C.



Scheme 3. Structures of reference polyimides.

The mechanical properties of the polyimide films are summarized in Table 4. Two polyimides (**4a** and **4c**) could be cast into color lightness, optically transparent, tough and flexible films from DMAc solution. The tensile modulus is in the range of 1.7–2.2 GPa and the elongation is in the range of 5.5–6.0%. Other polyimides could not be cast into self standing films due to their poor solubility.

The optical properties of the polyimides **4a** were investigated by UV–vis and photoluminescence spectroscopies in THF with a polymer concentration of 1 mg/10 mL. The polyimide in THF solution exhibited maximum absorption (λ_{max}) at 338 nm due to the π–π* transition, as shown in Fig. 3. The absorption spectra of the protonated polyimide with HCl (hydrogen chloride) and MSA (methanesulfonic acid) are functions of acid concentrations. It is obvious that the absorption bands of the protonated polymer are the same with the

Table 4
Mechanical properties of polyimides

Polymer code	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)	Film state
4a	74	6	2.2	Flexible
4b	–[a]	–[a]	–[a]	Brittle
4c	46	5.5	1.7	Flexible
4d	–[b]	–[b]	–[b]	–[b]
4e	–[b]	–[b]	–[b]	–[b]
4f	–[b]	–[b]	–[b]	–[b]

[a] The polymer film is too brittle to be measured.

[b] The solubilities of polymer are too poor to prepare the film.

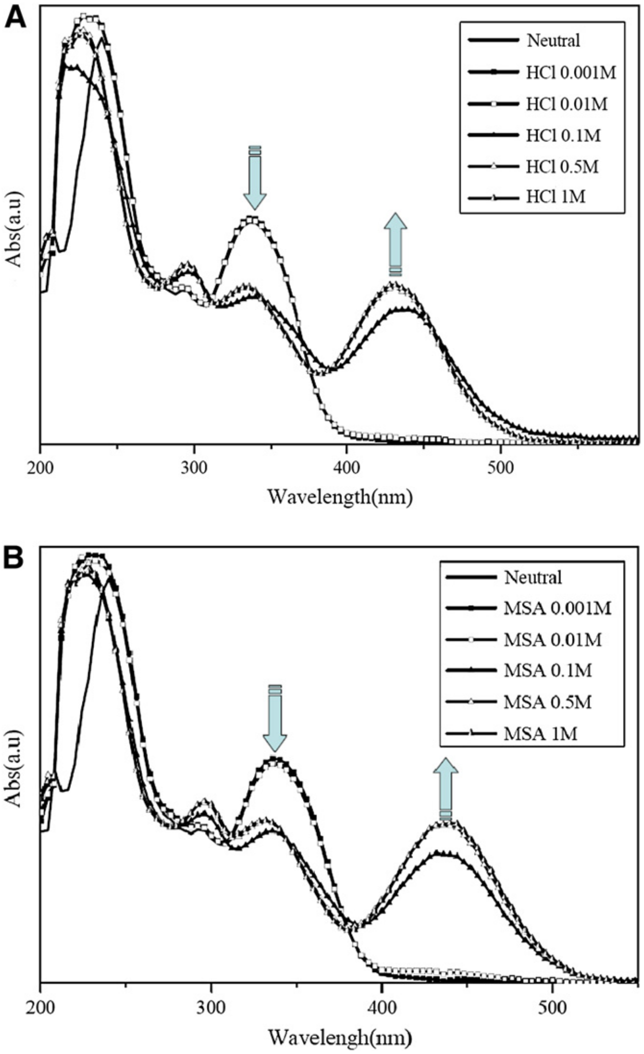


Fig. 3. Absorption spectra of the polyimide **4a** protonated with (A) HCl and (B) MSA.

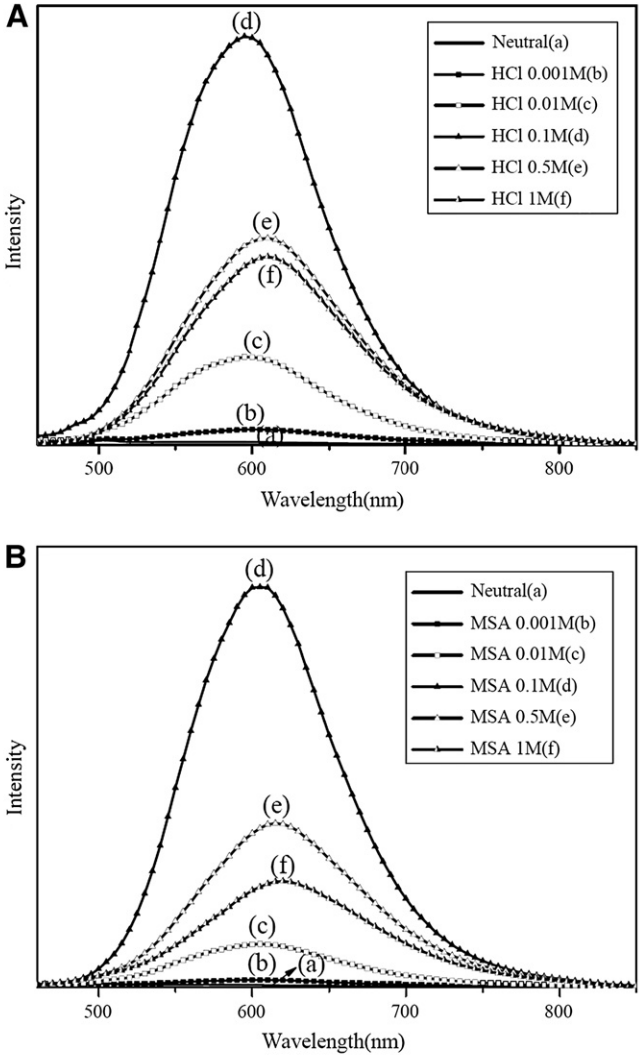
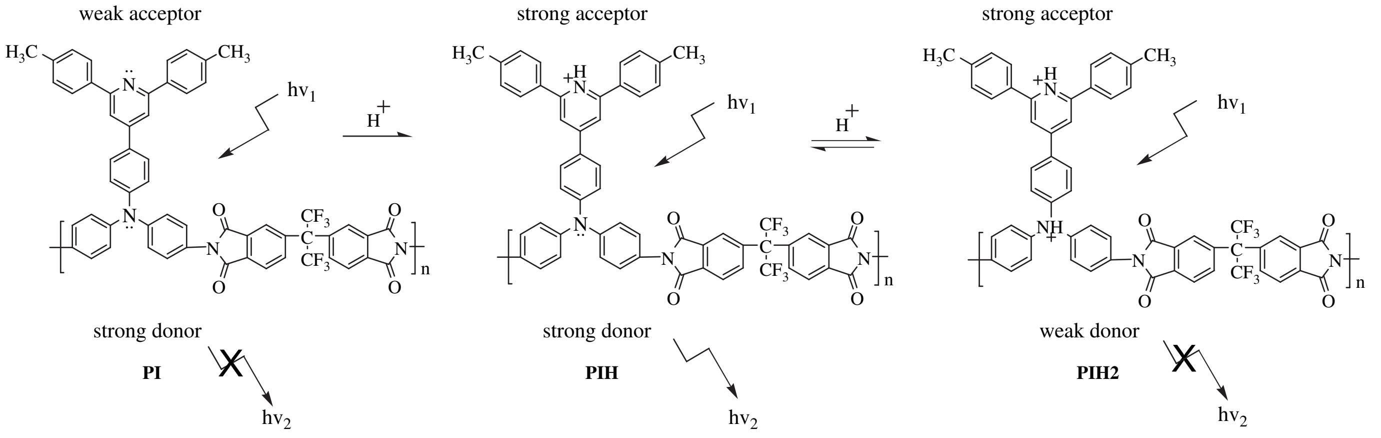


Fig. 4. Emission spectra of the polyimide **4a** protonated with (A) HCl and (B) MSA.

pristine polyimide at low acid concentrations. From the UV spectrum of polyimide **4a** protonated with HCl (Fig. 3A), the intensity of the absorptions at 338 nm decreases and a new absorption band forms at 438 nm when HCl concentration is higher than 0.01 M. The absorption intensity at 338 nm (π−π*) decreases after protonation, because the lone pair electron of the nitrogen on pyridine is quaternated by protic acid. The intensity of new band at around 438 nm



Scheme 4. Proposed protonation of the polyimide **4a**.

depends on the HCl concentration. The polymer protonated by higher HCl concentration exhibits stronger absorption at 438 nm. The spectral behavior suggests that a lower π–π* transition occurs for the quaternated polymer. The absorption peak at 338 nm decreased but does not disappear even at high concentration of 1 M HCl. Considering the big difference between p*K*a values of pyridine and its conjugated acid, it is likely that most pyridine groups are protonated. Therefore, we think the π–π* absorption at 338 nm is not completely contributed by the pyridine. The same phenomenon was also observed in the protonation with MSA (Fig. 3B). However, from the comparison with Fig. 3A, the absorption band of protonated polymer with MSA exhibits a slight red-shift (from 438 to 448 nm) and its absorption intensity is little bit stronger than that of obtained with HCl for the same acid concentration. These observations reveal that the absorption characteristics of the quaternated form of the polymer are affected by the conjugated base of acids.

Fig. 4 shows the emission spectra of protonated polyimide with HCl (A) and MSA (B). In the case of protonation with HCl (Fig. 4A), there was no fluorescence observed at around 600 nm in neutral polymer solution when the solution was excited at 438 nm. A new strong fluorescence at around 600 nm was observed when acid concentration increased. Two interesting emission features caused by different acid concentrations are observed. The first is the emission intensity of protonated polymer exhibits an acid concentration dependent increase in the concentration range 0.001–0.1 M and decreases at the acid concentrations beyond 0.1 M. The second is the spectral shift in the emission maxima to longer wavelength as the acid concentration increases from 0.001 to 1 M. The proposed protonation of this polyimide (**PI**) is shown in Scheme 4. Because the pyridine group is more basic than triphenylamine group, the lone pair electron of the nitrogen on pyridine was quaternated by protic acid at first to form quaternated polymer (**PIH**) and then the lone pair electron of the nitrogen on triphenylamine was further quaternated by protic acid to form **PIH2** as acid concentration increases. The triphenylamine is a well-known electron donor and the pyridine is a weak electron acceptor [43], therefore the neutral **PI** is nonfluorescence as excited at 438 nm. However, the quaternated pyridine becomes a stronger acceptor as protic acid attached to the pyridine, and then a strong emission occurs between triphenylamine and quaternated pyridine groups (**PIH**). Furthermore, the quaternated triphenylamine changes into a weak donor as protic acid attached to the nitrogen on triphenylamine (**PIH2**). But the emission does not disappear at very high acid concentration (1 M). It means that this protonation is an equilibrium transformation. This statement coincides with the first feature of emission spectrum, which shows a maximum intensity protonated by 0.1 M HCl. The two features were also observed when protonation was carried out by MSA (Fig. 3B).

The electrochemical property of the polymer **4a** was carried out by cyclic voltammetry (CV). The result shows two redox couples, where the reduction values are at −0.66 and −1.65 V and the oxidation values at 1.20 and 2.34 V (Fig. 5). The two redox couples result from the nitrogen atoms of pyridine and triphenylamine groups [21,22].

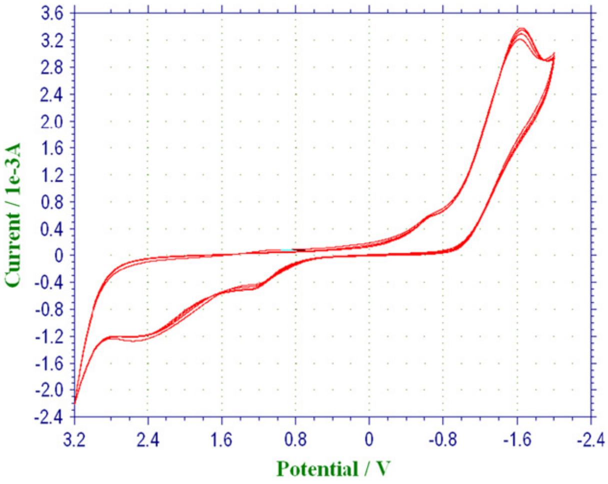


Fig. 5. The cyclic voltammogram (CV) of polymer **4a** coated on an ITO glass substrate in acetonitrile containing 0.1 M TBAP. Scanning rate = 0.1 V s^{-1}.

4. Conclusion

In the present study, a new aromatic diamine, 4-(4,4′-diaminotriphenylamine)-2,6-bis(4-methylphenyl)pyridine (**4**), containing pyridine and triphenylamine groups was successfully synthesized. All the novel polyimides derived from this diamine showed high thermal stability due to the pyridine and triphenylamine groups. The polyimide **4a** exhibited good solubility not only in polar aprotic solvents such as NMP, DMAc, and DMF, but also in some low boiling point solvents such as THF and chloroform. After protonation with protic acid, a strong emission at around 600 nm was observed and the intensity of emission depended on the concentration and conjugated base of acids. The response to protonation caused dynamic shifts in the emission spectra, providing evidence for a stepwise intramolecular charge-transfer switching phenomenon. These characteristics indicate that the new polyimides containing pyridine and triphenylamine groups are promising materials for acid sensor and optoelectric applications.

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