Novel Organosoluble Poly(pyridine−imide) with Pendent Pyrene Group: Synthesis, Thermal, Optical, Electrochemical, Electrochromic, and Protonation Characterization

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ABSTRACT: A new diamine containing a pyridine heterocyclic group and a pyrene substituent, 4-(1-pyrene)-2,6-bis(4-aminophenyl)pyridine (**PBAPP**), was synthesized and used in a preparation of poly(pyridine−imide) by direct polycondensation with 4,4′-hexafluoroisopropylidenediphathalic anhydride (6FDA) in *N*-methyl-2-pyrrolidinone (NMP). The poly(pyridine−imide) derived from diamine (PBAPP) was highly soluble in several solvents such as THF, NMP, DMAc, DMF, pyridine, DMSO, and cyclohexanone at room temperature or upon heating at 70 °C and exhibited good thermal stability both in nitrogen and air ($T_d^{10} > 520$ °C) and a high dielectric constant of 4.32 at 1 kHz. The poly(pyridine−imide) could be cast into a flexible and tough film from DMAc solution. The poly(pyridine−imide) film had a tensile strength of 118 MPa and a tensile modulus of 2.2 GPa. The optical properties exhibited the UV−vis absorption bands at the region of 200−400 nm and possessed strong orange fluorescent (560 nm) after protonated with protic acid.

Introduction

Polyimides constantly attract wider interest because of their unique mechanical properties, thermal stability, and morphological properties.[1−7] Conventional polyimides like Kapton produced by DuPont have been applied to microelectronic devices and aerospace fields. However, these polyimides are generally insoluble in organic solvent, exhibit low optical transparency, and have an intense yellow color. Soluble polyimides are needed as coating materials on specific space components. In order to overcome this drawback, either bulky lateral substituents, flexible alkyl side chains, unsymmetric, alicyclic or kinked structure have been attached along the backbone.[8−14] The rigid-rod polyimides with high organic solubility have attracted some research efforts in recent years. These efforts have been focused on designing and synthesizing new rigid diamines that resulted in soluble and processable polyimides without deterioration of their positive properties.

In particular, polymers have attracted considerable attention because of their good scalability, mechanical strength, flexibility, and most important of all, ease of processing. In the recent years, there has been a considerable interest in the photoluminescent and electroluminescent properties of conjugated polymers.[15−17] These polymer materials are used for several electronic applications, including light-emitting devices (LEDs), transistors, photovoltaic cells, polymer memory, and switches.[16,18−24] However, certain non-conjugated polymers, e.g., polyimides, in combination with electron transporting layers, also rank among efficient electroluminophores.[22−24] Recently, some reports have concerned the incorporation of pyridine and its derivatives into polymeric frameworks.[25] Compared to a benzene ring, pyridine is an electron-deficient aromatic heterocycle, with a localized lone pair of electrons in sp^2 orbital on the nitrogen atom; consequently, the derived polymers have increased electron affinity,[26] improved electron-transporting properties,[27] and offer the possibility of protonation or alkylation of the lone pair electrons as a way of modifying their properties.[28,29] On the other hand, the pyrene unit is an efficient fluorescent probe because it has a long singlet lifetime and readily forms excimer.[30] A literature survey revealed that there are a limited number of investigations concerning the attachment of pyrene to polyimides.[31,32] Pyrene containing polymers have been used as acceptors for energy transfer from various donors.[33,34] Additionally, the bulky condensed aromatic ring of pyrene is expected to enhance the solubility and thermal stability of polyimides.

The present investigation deals with the synthesis and characterization of a new poly(pyridine−imide) derived from a new monomer, 4-(1-pyrene)-2,6-bis(4-aminophenyl)pyridine (**PBAPP**), containing heterocyclic pyridine and pyrene substituents. The solubility, electrochemical stability, mechanical, thermal and optical properties of the obtained poly(pyridine−imide) were investigated.

Experimental

Materials. The materials, 1-pyrenecarboxaldehyde, 4′-nitroacetophenone, ammonium acetate, hydrazine monohydrate, and 10% palladium on activated carbon were purchased from Merck and used as received. Glacial acetic acid was purchased from Aldrich Chemical Co. and used as received. 4,4′-Hexafluoroisopropylidenediphathalic anhydride (6FDA, TCI) was recrystallized twice from acetic anhydride, and then sublimated before use. The solvents, *N*-methyl-2-pyrrolidinone (NMP), tetrahydrofuran (THF), *N*,*N*′-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF) were purchased from Merck and purified by distillation under reduced pressure over calcium hydride and store over 4 Å molecular sieves. Acetic anhydride and pyridine were also purchased from Merck but used as received.

Synthesis of Monomer (Scheme 1). 4-(1-Pyrene)-2,6-bis(4-nitrophenyl)pyridine (PBNPP, 1). In a 500 mL, round-bottomed

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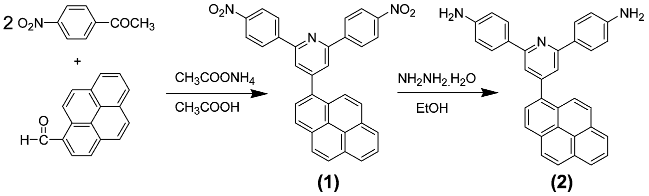
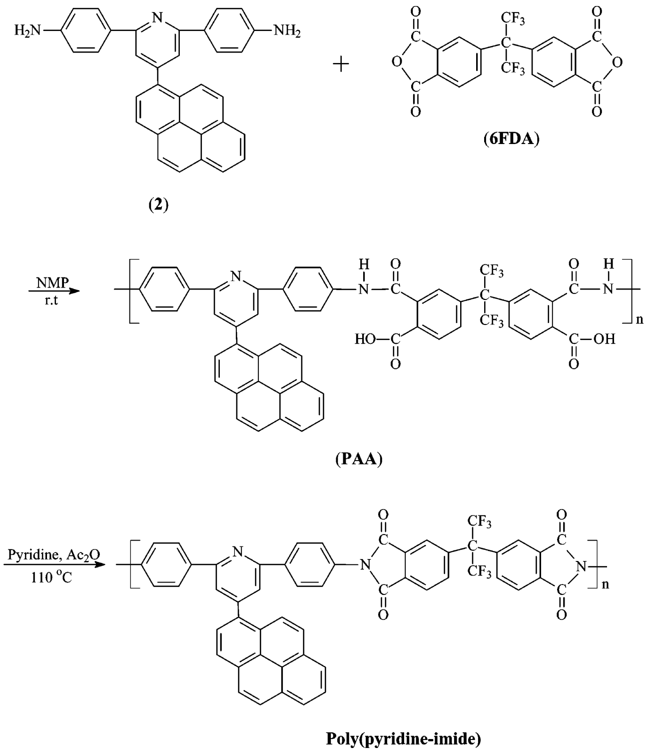
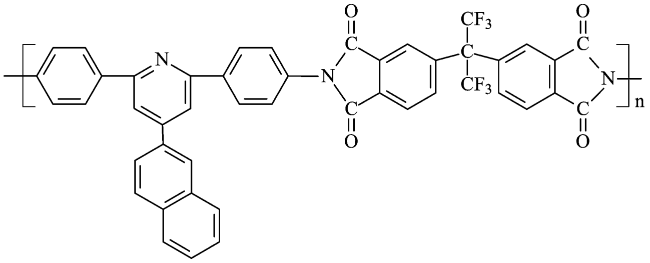
Scheme 1. Synthesis of New Monomer 4-(1-Pyrene)-2,6-bis(4-aminophenyl)pyridine (2)



Scheme 2. Preparation of Poly(pyridine-imide)



Scheme 3. Ref-1



flask, a mixture of 15 g (65 mmol) of 1-pyrenecarboxaldehyde, 21.5 g (130 mmol) of 4′-nitroacetophenone, 100.4 g (1.3 mol) of ammonium acetate, and 300 mL of glacial acetic acid was refluxed for 16 h. Upon cooling, the precipitated light yellow solid was collected by filtration and washed with cold *N*,*N*′-dimethylacetamide (DMAc). The crude product was recrystallized from DMAc five times to afford 8.1 g (57%) of light yellow needles; mp 333 °C (by DSC). FTIR (KBr): 1523 and 1345 cm^{-1} (NO_2). ^{1}H NMR (500 MHz, DMSO-d_6): δ8.67−8.65 (d, 4H), 8.50 (s, 2H),8.48 (s, 1H), 8.42−8.40 (d, 4H), 8.39 (s, 1H), 8.37−8.35 (d, 1H), 8.31 (s, 2H), 8.30−8.29 (d, 1H), 8.26−8.24 (d, 2H), 8.16−8.13 (t, 1H). Anal. Calcd for $C_{33}H_{19}N_3O_4$: C, 76.00; H, 3.67; N,8.06. Found: C, 76.00; H, 3.86; N, 7.98.

4-(1-Pyrene)-2,6-bis(4-aminophenyl)pyridine (PBAPP, 2). A mixture of 2.7 g (5.1 mmol) of **PBNPP**, 0.13 g of 10% Pd/C, 2.5 mL of hydrazine monohydrate, and 200 mL of ethanol was placed in a flask. The reaction was heating at 90 °C for 24 h and then removed the ethanol under reduce pressure. THF (50 mL) used as a solvent was added to the mixture, filtered to remove Pd/C and removed the THF using rotation evaporator. The light yellow solid was recrystallized from THF/ethanol (10/1, v/v) twice and dried under vacuum. The yield was 67%; mp 266 °C (by DSC). FTIR (KBr): 3472, 3379, 1247 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.40−8.38 (d, 1H), 8.33−8.31 (d, 1H), 8.28−8.26 (d, 1H), 8.23 (s, 2H), 8.17−8.14 (m, 3H), 8.10−8.06 (t, 1H), 8.03−8.02 (d, 4H), 7.75 (s, 2H), 6.71−6.70 (d, 4H), 5.45 (s, 4H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 156.1, 150.0, 149.4, 135.6, 130.9, 130.7, 130.4, 128.1, 127.8, 127.7, 127.6, 127.3, 127.2, 126.5, 126.4, 125.5, 125.2, 125.0, 124.3, 124.1, 124.0, 116.5, 113.7. Anal. Calcd for $C_{33}H_{23}N_3$: C, 85.87; H, 5.03; N, 9.10. Found: C, 85.94; H, 5.01; N, 9.05.

Synthesis of Poly(pyridine−imide). To a stirred solution of 0.6183 g (1.3 mmol) of (**PBAPP**) in 5 mL of *N*-methyl-2-pyrrolidinone (NMP), 0.5775 g (1.3 mmol) of 4,4′-hexafluoroisopropylidenediphathalic anhydride were gradually added. The mixture was stirred at ambient temperature overnight (ca. 12 h) to form the poly(amic acid). Chemical cyclodehydration 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 with stirring at room temperature for 1 h, and then heating at 110 °C for 4 h (Scheme 2). The polymer solution was poured into methanol. The precipitate was filtered, washed with methanol, and dried at 100 °C under vacuum. The inherent viscosity of the polymer in *N*,*N*-dimethylacetamide was 0.58 dL·g^{-1}, measured at a concentration 0.5 g dL^{-1} at 30 °C. FTIR (KBr): 1784, 1724, 1372 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.46 (s, 4H), 8,27−8.08 (m, 15H), 7.91 (s, 2H), 7.65−7.64 (d, 4H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 166.6, 157.0, 152.1, 139.6, 139.4, 136.8, 136.7, 136.1, 134.3, 134.0, 133.9, 132.5, 132.0, 129.3, 129.2, 128.9, 128.4, 128.2, 128.1, 127.4, 127.2, 126.5, 126.2, 125.9, 125.8, 125.7, 125.4, 124.7, 123.7, 121.7, 121.4, 66.3. Anal. Calcd for $C_{52}H_{25}N_3O_4F_6$: C, 71.81; H, 2.90; N, 4.83. Found: C, 70.68; H, 3.29; N, 4.97.

Measurements. FTIR spectra were recorded in the range 4000−400 cm^{-1} for the synthesized monomers and polymers in an KBr disk (Bio-Rad Digilab FTS-3500). Elemental analysis was made on a Perkin-Elmer 2400 instrument. The inherent viscosity of polyimide was measured using Ubbelohde viscometer. NMR spectra were recorded using a Bruker Avance 500 NMR (^{1}H at 500.13 MHz and ^{13}C at 125.77 MHz). Weight-average (M_w) and number-average molecular weights (M_n) were determined by gel permeation chromatography (GPC). Calibration was made by using polystyrene as standard with molecular weight in the range of 1680−402100 g/mol. Four Waters (UltraStyragel) columns (300 × 7.7 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. Thermogravimetric data were obtained on a TA Instruments Dynamic TGA 2950 under nitrogen and air flowing condition at a rate of 50 cm^3 min^{-1} and a heating rate of 10 °C min^{-1}. Melting points of monomers and glass transition temperature of polymer were performed on a differential scanning calorimeter (TA Instruments TA 910) under nitrogen flowing conditions at a rate of 50 cm^3 min^{-1} and a heating rate of 10 °C min^{-1}. Dielectric constants of polyimide thin film were measured by the parallel−plate capacitor method using a dielectric analyzer (TA Instrumenents DEA 2970) at the range of frequency 1−10 kHz. Gold electrodes were vacuum-deposited on both surfaces of dried film, and measurement were made at 25 °Cunder N_2 atmosphere. Average tensile properties were determined at room temperature with five specimens from the stress−strain curve obtained with an Orientec Tensilon with a load cell of 10 kg. A gauge of 2 cm was used for this study in a strain rate of 2 cm min^{-1}. UV−vis spectra of the polymer film were recorded on a V-550 spectrophotometer at room temperature. The fluorescence spectra were recorded by a Shimadzu RF-5031 spectrophotometer. Electron micrographs were recorded with a JEOL JSM-6500 scanning electron microscope (SEM) at 20 kV.

Results and Discussion

Monomers Synthesis. Scheme 1 shows the synthesis of the novel diamine compound, 4-(1-pyrene)-2,6-bis(4-aminophenyl) pyridine (**PBAPP**). The dinitro compound (**PBNPP**) containing a pyridine heterocyclic ring and a pyrene pendent group was synthesized with a modified Chichibabin reaction, which was a facile way for the preparation of substituted pyridine.[35,36]The condensation of 1-pyrenecarboxaldehyde with 4′-nitroacetophenone in the presence of ammonium acetate afforded dinitro (**PBNPP**) in one step. Reduction of the dinitro derivative (**PBNPP**) in ethanol with hydrazine monohydrate in the presence of catalytic amount of palladium on activated carbon at 90 °C produced a new diamine compound (**PBAPP**). Elemental analysis, FTIR, and NMR spectroscopes confirmed the structures of these compounds. As shown in the experimental part, the ^{1}H NMR spectra indicated the formation of the pyridine heterocyclic group present at 8.50 ppm for dinitro (**PBNPP**) and 7.75 ppm for diamine (**PBAPP**). When the dinitro compound was reduced to diamine, a new signal at 5.45 ppm due to the amino group in the ^{1}H NMR spectrum appeared. These results clearly confirm that the diamine (**PBAPP**) prepared herein is consistent with the proposed structure.

Preparation of Poly(pyridine−imide). In this study, we synthesized only one poly(pyridine−imide) from 6FDA. As described in experimental part, recrystallization has to be carried out from DMAc five times in order to get the pure dinitro compound. The solubility of this dinitro compound is also very poor. Furthermore, the pure diamine has to be recrystallized two times and the preservation is also hard due to denaturalization. Therefore, we choose 6FDA dianhydride to synthesize a poly(pyridine−imide), because many papers reported that polyimides containing 6FDA show good thermal and mechanical properties and good solubility as well as and colorless films.[37,38] Colorless and transparent are important factors for optoelectrical materials. Poly(pyridine−imide) was prepared by the conventional two-steps polymerization method, as shown in Scheme 2, involving ring-opening polyaddition forming poly(amic acid) and subsequent chemical imidization. Reaction of dianhydride with diamine at ambient temperature gave a viscous poly(amic acid) solution. The chemical imidization of poly(amic acid) with a dehydrating agent such as a mixture of acetic anhydride and pyridine was effective in obtaining the desired polyimide. The polyimide obtained by chemical imidization had inherent viscosity of 0.58 dL·g^{-1} in DMAc. The number-average molecular weights ($\bar{M}_n$) and weight-average molecular weights ($\bar{M}_w$) of poly(pyridine−imide) measured by GPC relative to polystyrene standards were 2.5×10^4 and 5.7×10^4 g/mol, respectively. The molecular weight of poly(pyridine−imide) was sufficient to cast a tough and flexible film. The elemental analysis values of the poly(pyridine−imide) was in agreement with its respective structure. The FTIR spectrum exhibited characteristic absorption bands around 1784 and 1724 cm^{-1} due to the asymmetric and symmetric stretches of carbonyl group of imide, and a band around 1371 cm^{-1} for the C−N bond. The FTIR spectrum confirms the formation of the imide due to imidization. The chemical structure of the poly(pyridine−imide) was also verified by ^{1}H and ^{13}C NMR.

Polymer Properties. The solubility of the polymer was determined by dissolving 1 mg of polymer in 1 mL of solvent at room temperature or upon heating. The poly(pyridine−imide) exhibited excellent solubility in various solvents such as THF, NMP, DMAc, DMF, γ-butyrolactone at room temperature, and pyridine, dimethyl sulfoxide, cyclohexanone upon heating to 70 °C. The bulky pendent pyrene group in the pyridine unit and trifluoromethyl group in the dianhydride reduce packing force and result in good solubility of the polyimide.

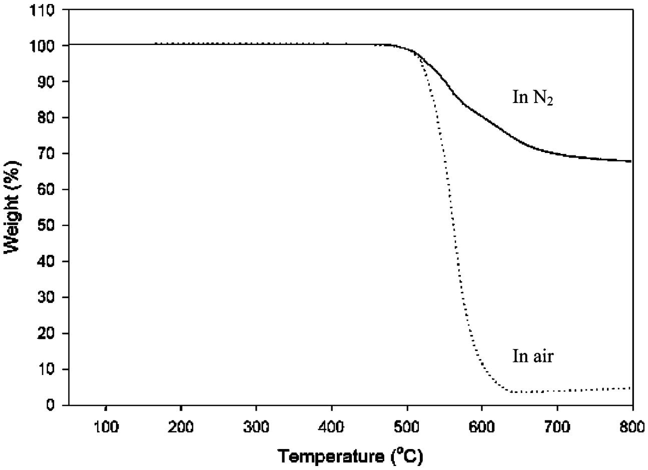


Figure 1. TGA curves of poly(pyridine−imide) in nitrogen and air atmosphere at a heating rate of 10 °C·min^{-1}.

The thermal properties of the poly(pyridine−imide) were evaluated in powder form by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The poly(pyridine−imide) did not show any glass transition up to 350 °C. The thermal stability of the poly(pyridine−imide) was evaluated by TGA measurements in both air and nitrogen atmospheres at a heating rate of 10 °C min^{-1}. The TGA curve for poly(pyridine−imide) is showed in Figure 1. The poly(pyridine−imide) almost shows no degradation below 500 °C in air and nitrogen. The temperatures for 10% weight loss of poly(pyridine−imide) in nitrogen and air were 544 and 529 °C, respectively. The good thermal stability of poly(pyridine−imide) is due to the presence of rigid pyridine heterocyclic diamine in the polymer backbone and a pyrene group in the pedant.[39]

The poly(pyridine−imide) could be cast into a film from DMAc solution and the film was color lightness, optically transparent, flexible and tough. The film exhibited ultimate tensile strengths of 118 MPa, elongation to break of 14%, and tensile modulus of 2.2 GPa. The polymer film exhibited high tensile strength; thus it could be considered as a strong material.

Figure 2 illustrates the UV−vis absorption and fluorescence emission spectra of the poly(pyridine−imide) in dilute THF solution (Figure 2a,c), and solid film (Figure 2b,d) with thickness of 87 μm. The poly(pyridine−imide) exhibited absorption maximum (λ_{max}) at 283 nm due to the n−π* transition of the pyridine group, and the π−π* transitions in the region of 300−400 nm. The photoluminescence spectra, which are attributed to fluorescence on account of the short lifetime of the excited states,[41] were obtained by irradiative excitation at the wavelength of maxima absorption. Moderate blue fluorescence resulted with emission maxima at 396 nm. This *indicates* that photoluminescence took place by migration of electrons in a conduction band (π* level) to a valence band (π level). The solid poly(pyridine−imide) was prepared by spin-coating on a quartz plate from solution of poly(pyridine−imide). The absorption band shows very similar behavior to the solution phase. Comparing the absorption spectrum of poly(pyridine−imide) in solution with that of poly(pyridine−imide) in the solid state, it could be observed that a broadened peak and long wavelength tail appeared in the UV−vis spectra. The fluorescence maxima of the solid film shifted toward longer wavelength than in solution due to the formation of aggregates.[40]

Figure 3 and Figure 4 show the absorption spectra of the protonated poly(pyridine−imide) with HCl (hydrogen chloride)

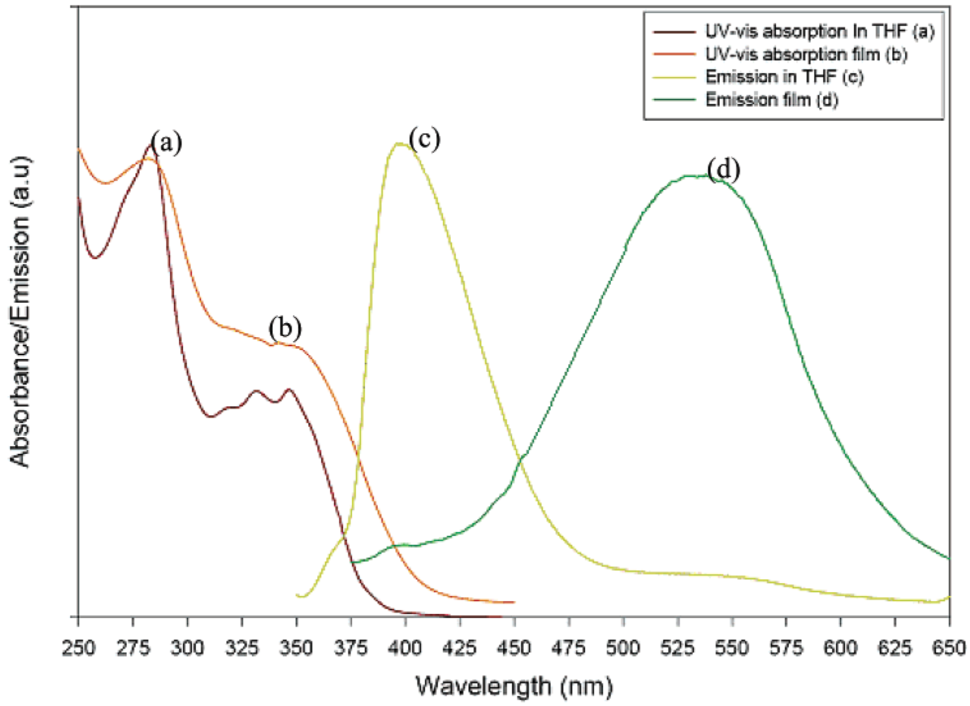


Figure 2. UV−vis spectra of poly(pyridine−imide) in THF solution and solid film.

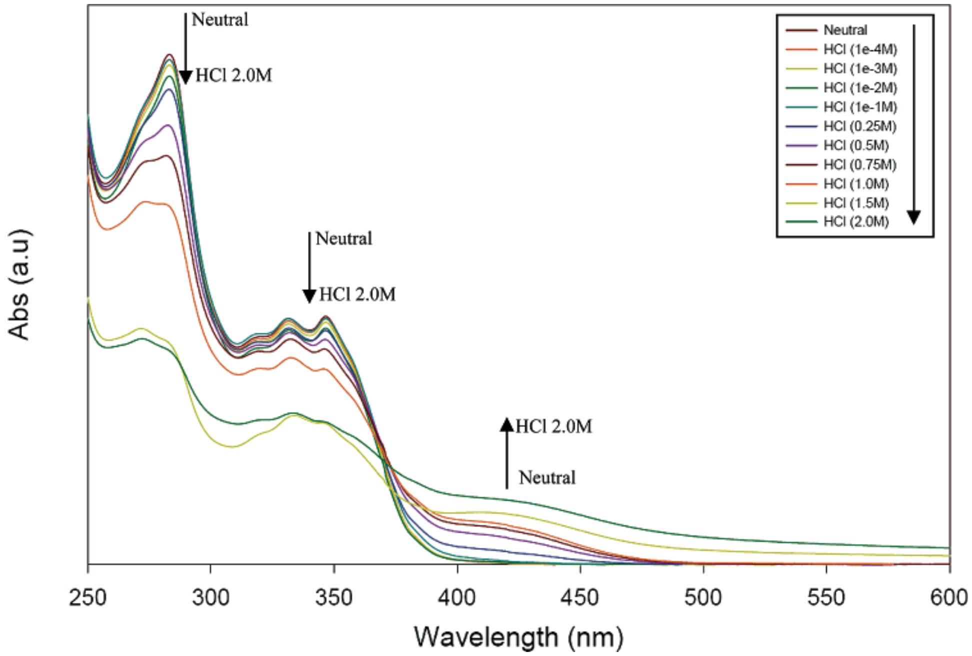


Figure 3. Absorption spectra of poly(pyridine−imide) as a function of HCl concentration.

and MSA (methanesulfonic acid), respectively, as a function of acid concentration. In Figure 3, it is obvious that at low protonated concentrations the absorption bands are the same as neutral poly(pyridine−imide). When the acid concentration was increased, a new band appeared at 430 nm. This phenomenon was similar to the poly(2,5-pyridylene) (PPY), which has been reported in the literature.[29, 41,42] On protonated by HCl or MSA, the absorption intensity at 283 nm (n−π*) decreased depending on concentration of protic acid, because of the lone pair electron of the nitrogen on pyridine was quaternated by protic acid. The presence of an isosbestic point in the UV−vis spectra at low degree of protonation indicates the coexistence of protonated and neutral segments in the poly(pyridine−imide). At high degree of protonation, the isosbestic point is lost due to repulsion between the charged pyridinium fragments. As shown in Figure 2, no abosorption band at 430 nm appears in solution as well as in solid state. Therefore, the new band at 430 nm could be a characteristic absorption band of the protonated polymer. The spectral behavior suggest a lower π−π* transition energy for the protonated polymer. When the protonation was carried out with MSA, a similar trend was also observed (Figure 4). Comparing Figure 3 with Figure 4, the poly(pyridine−imide) protonated with MSA exhibited a higher absorption intensity at 430 nm. The differences depend on the strength of protic acid used.

The transparency of the poly(pyridine−imide) film (87 μm) could also be elucidated from the cutoff wavelength observed in the UV−visible transparent spectra. As shown in Figure 5,

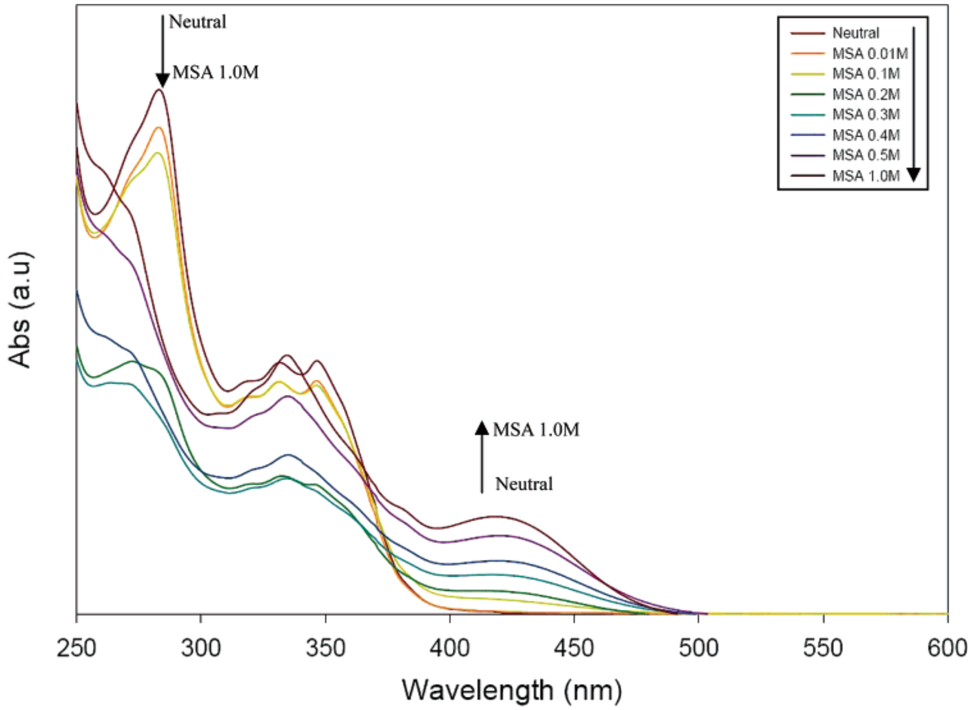


Figure 4. Absorption spectra of poly(pyridine−imide) as a function of MSA concentration.

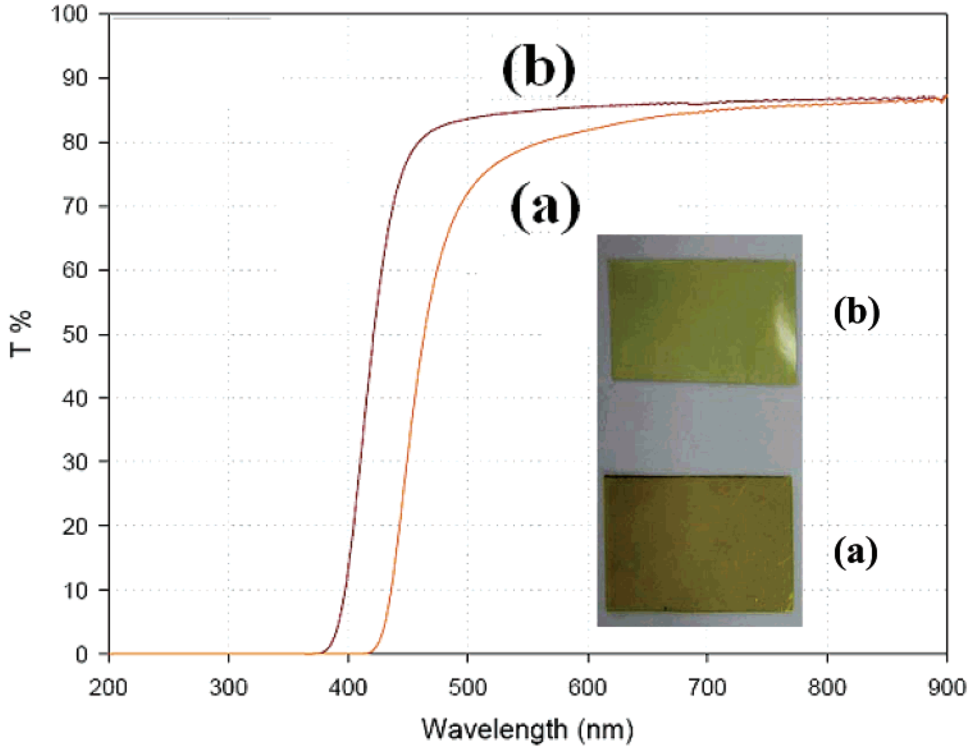


Figure 5. Transparent spectra and film states of (a) poly(pyridine−imide) in this research and (b) **Ref-1**.

the poly(pyridine−imide) film exhibited the cutoff wavelength and the 80% transmission wavelength at 423 and 563 nm, respectively. Comparing this poly(pyridine−imide) film with **Ref-1** (Scheme 3) (84 μm) containing naphthalene group, this poly(pyridine−imide) has higher cutoff wavelength and 80% transmission wavelength than **Ref-1** (380 and 459 nm). These results were attributed to the presence of pyrene substituent in the diamine **PBAPP**, which increased the electron-donating of diamine segment and then improved both intra- and intermolecular charge-transfer (CT) interactions.[38,42]

Figure 6 shows the emission spectra of poly(pyridine−imide) protonated with HCl. Nevertheless, when the HCl concentration was increased from 1×10^{-4} to 2.0 M, the emission at 396 nm intensity diminished and a new strong orange fluorescence at around 560 nm appeared and increased rapidly after HCl concentration reaching 0.5 M. The emission band at 396 nm results from unprotonated polymer as shown in Figure 2. The intensity of emission peak at 560 nm is stroner than the peak at 396 nm when HCl concentration higher than 0.5 M. The phenomenon suggested a relocation of the proton in the

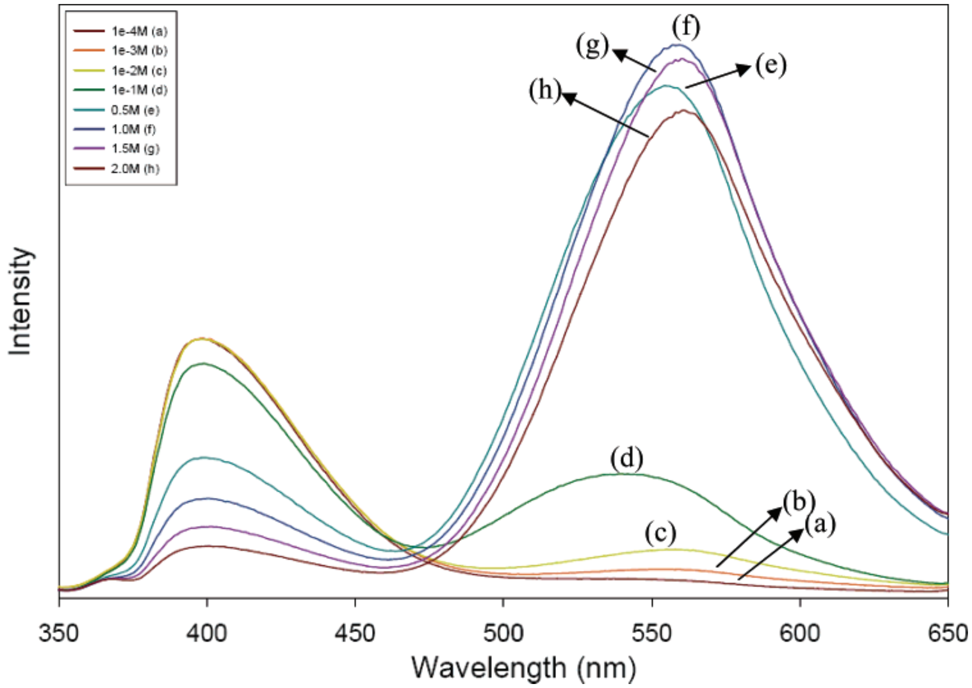


Figure 6. Emission spectra of poly(pyridine−imide) as a function of HCl concentration.

equilibrium excited state.[44] As observed in fluorescence spectra, both protonated and unprotonated forms were present, and it can be interpreted as evidence of incomplete ionization equilibrium being established during the lifetime of the excited state. In addition, two redox pairs were observed in cyclic voltammogram of the polymer where the reduction values are at −0.63 and −1.08 V and the oxidation values are at −0.2 and −0.85 V (see Supporting Information).

The electrical insulating properties, measured on the parallel−plate capacitor method using a dielectric analyzer on a thin film. The poly(pyridine−imide) exhibited relatively high dielectric constant of 4.53−4.26 in the frequency region of 1 to 10 kHz. The dielectric constant of poly(pyridine−imide) at 1 kHz (4.32, 87 μm) is higher than that of commercially available polyimide film, **Kapton HN** (3.50, 125 μm, 1 kHz). This poly(pyridine−imide) also has a higher dielectric constant than the polyimides (3.05, 87 μm, 1 kHz;[37] 3.58, 74 μm, 1 kHz)[38] derived from 6FDA. The result of higher dielectric constant is due to the presence of aryl-substituted pyridine heterocylic group and π-conjugation of pyrene structure in the polymer backbone, which increased the polarizability of the polymer under electric field.

The morphology of the poly(pyridine−imide) was observed by scanning electron micrographs (SEM). Thin films were obtained by depositing a drop of the polymer solutions onto a glass slide. The SEM micrograph of poly(pyridine−imide) from THF reveal that the surface of polymer is homogeneous with irregular shaped granules that are neatly packed close to each other (Figure 7a). For comparison with the protonated polymer, we also prepared SEM sample by the same way from a THF/HCl (1.0 M) solution of the poly(pyridine−imide), as shown in Figure 7b, which clearly exhibited a large size of granules. This may be attributable to the interaction of poly(pyridine−imide) and HCl which resulted in aggregation of the polymer.

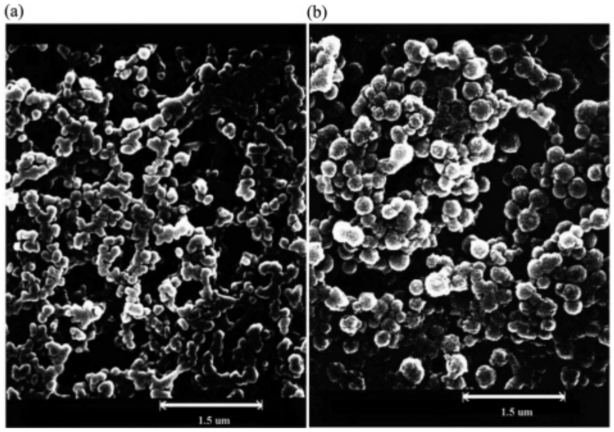


Figure 7. SEM of poly(pyridine−imide) depositing a drop of the polymer solutions onto a glass slide: (a) THF as solvent and (b) THF/HCl (1.0 M) as solvent.

Conclusion

In the present study, a novel poly(pyridine−imide) containing a heterocyclic pyridine and a pyrene substituent derived from new diamine 4-(1-pyrene)-2,6-bis(4-aminophenyl) pyridine (**2**) was successfully prepared. The obtained poly(pyridine−imide) exhibits good solubility in common organic solvents, such as THF, DMAc, DMF, NMP, etc. The poly(pyridine−imide) possessed a high dielectric constant and showed good thermooxidative stability higher than 500 °C and excellent mechanical properties. This investigation showed that the polymer possessed blue emission in neutral solution and orange emission after protonation. After protonation with protic acid, the poly(pyridine−imide) exhibited a bathochromic shift. These characteristics indicate that pyrene-containing poly(pyridine−imide) is a promising material for optoelectric applications.

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Note Added after ASAP Publication. This article was published ASAP on April 7, 2007. Corrections have been made to Scheme 2, Scheme 3, and the Table of Contents graphic. The correct version was posted on April 20, 2007.

Supporting Information Available: Figures showing NMR spectra and cyclic voltammogram. This material is available free of charge via the Internet at http://pubs.acs.org.

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