

Polyimides Derived from Novel Unsymmetric Diamine Containing N-aminonaphthalimide Group

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ABSTRACT: Novel polyimides derived from an unsymmetric diamine containing N-aminonaphthalimide and several dianhydrides such as pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 4,4'-oxydiphthalic anhydride (ODPA), 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA) have been synthesized by one-step polymerization in *m*-cresol. It was found that these polyimides possess high T_g values (≥ 302 °C), ultra low moisture absorption ($\leq 0.20\%$), low dielectric constants of 2.76 – 3.03 at 1 MHz, and green fluorescence property. The polyimides also show high modulus, improved solubility in common organic solvents, and well thermal stability in nitrogen.

1. Introduction

Structure-property relationships, as in any other polymers, have been extensively investigated as a main subject for practical applications in polyimide (PI) systems.^[1-3] In all the structures that in general mean the chemical structure of the PIs chains, unsymmetric characteristic is an important factor of property. It is apparent that geometric unsymmetry of the polymer will result in less efficient chain packing and an increase in the free volume of the polymer. So polyimides containing unsymmetric structure, compared to the corresponding polyimides containing symmetric structure, show better solubility, low dielectric constant, melt processability and other advantages without much deteriorating their inherent excellent properties because close chain stacking and intermolecular interactions are restricted while the main-chain rigidity of the polyimide can also be maintained.^[4-14]

At the same time, an increasing need for polymers with various specific properties such as high glass transition temperature, improved processability, and long-term thermal stability is still a major driving force for the development of new monomers. This allows the incorporation of aromatic heterocyclic groups such as phthalimide,^[15-17] naphthalimide,^[18-20] perylenetetracarboxylic diimide,^[21] benzimidazole^[22-24] and other heterocyclic moieties^[25-32] into the polymer chains to get polyimides with high glass transition temperature. Another modification allows the incorporation of the monomers containing hydrazine^[15-21]. Hydrazine is the simplest diamine, and its unstable derivatives from phthalic anhydride have been known for many years.^[33,34] On the contrary, the product of hydrazine and naphthalic anhydride is very stable, which makes the synthesis of monomers and the corresponding polyimides derived from six-member-ring N-aminonaphthalimide very feasible. There are some polyimides based on hydrazine, showing high T_g s, excellent thermal stability, and good solubility.^[15-21]

Based on these improvements, we herein report new polyimides derived from a novel unsymmetric diamine, 4-(4-aminophenylthio)-N-amino-1,8-naphthalimide (**2**).

2. Experimental Part

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2.1. Materials

4-Bromo-1,8-naphthalic anhydride, 4-amino-benzenethiol were purchased from Aldrich Chemical Co. and used as received. 4,4'-(4,4'-Isopropylidenediphenoxy)bis(phthalic anhydride) (BPADA) and 4,4'-oxydiphthalic anhydride (ODPA) purified by recrystallization from acetic anhydride. Pyromellitic dianhydride (PMDA) and 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA) were sublimated before use. The other reagents used in this study were purchased from Shanghai Chemical Reagent Plant.

2.2. Instrumentation

The ^1H NMR spectra were measured at 400 MHz on a Bruker 400 AVANCE III spectrometer, using dimethyl sulfoxide- d_6 (DMSO- d_6) or CDCl_3 as solvent. Melting points were determined on an XT4-100B melting point apparatus (Beijing Keyi Elec-opti instrument) and were uncorrected. The Fourier transform infrared spectra (FTIR) were obtained with a Thermo Nicolet 6700 FTIR spectrometer, where the sample was prepared with KBr pellets. The UV-vis spectra were recorded on a PerkinElmer lambda 950 spectrophotometer at room temperature in the absorption mode. The fluorescence spectra were obtained from a Shimadzu RF-5301PC spectrofluorometer. Elemental analyses were carried out on a PerkinElmer model 2400 II C, H, N, S analyzer. The inherent viscosities were measured with an Ubbelodhe viscometer at 30 ± 0.1 °C in m-cresol at a concentration of 0.5 g/dL. Thermogravimetric analysis (TGA) was recorded on a Perkin-Elmer Diamond TG/DTA instrument at a heating rate of 10 °C /min under nitrogen atmosphere (flow rate of 50 mL/min). Differential scanning calorimetry (DSC) was carried out using Mettler Toledo DSC at a heating rate of 20 °C /min under nitrogen atmosphere with 50 mL/min gas flow, and T_g was reported as temperature at the middle of the thermal transition from the second heating scan. The tensile measurements were tested five PI film samples by an Instron model 5567 at room temperature, and the results were averaged. Dielectric property of the polymer films was tested by the parallel-plate capacitor method using a HP-4194A Impedance/Gain Phase Analyzer at 1 MHz frequency. Silver electrodes were fired on both surface of the 15 ~ 20 μm thick, 2 cm × 2 cm dried films, followed by measuring at room temperature at 70% relative humidity. The equilibrium water absorption was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 100 h.

2.3. Monomer synthesis

2.3.1. 4-Bromo- N-amino-1,8-naphthalimide (**1**)

A mixture of 4-bromo-1,8-naphthalic anhydride (2.77 g, 10 mmol), hydrazine hydrate (1.50 g, 30 mmol) and 50 ml ethanol was stirred at 80 °C for 4 h under argon atmosphere. After cooling to room temperature, the yellow precipitate was filtered off, washed with 50 ml ethanol and dried in vacuum at 80 °C for 24 h. A yellow solid (2.76 g, 95%) was obtained, which needed no further purification.

2.3.2. 4-(4-Aminophenylthio)-N-amino-1,8-naphthalimide (**2**)

4-Bromo- N-amino-1,8-naphthalimide (14.55 g, 50 mmol), 4-amino-benzenethiol (6.89 g, 55 mmol), and triethylamine (5.57 g, 55 mmol) were placed in a 500-mL, three-necked, round-bottom flask containing 200 mL of N,N-dimethylformamide (DMF). The mixture was heated to 90 °C and stirred for 12 h in a nitrogen atmosphere. After it was cooled to room temperature, the resulting yellow mixture was poured into 1 L of water and then filtered. After recrystallization from pyridine/water (v/v = 5/2) three times, a reddish brown powder (11.68 g, 69.68 %) was obtained.

2.3.3. Polymerization

The polyimides were prepared from monomer **2** with four dianhydrides. One-step polymerizations of diamine **2** with various aromatic dianhydrides **3a-d** were then carried out in m-cresol in the presence of a

small amount of isoquinoline at 200 °C. The synthetic procedure for all polyimides is described as a typical example. The diamine **2** (1.0061 g, 3 mmol), ODP A **3(C)** (0.9306 g, 3 mmol), and *m*-cresol (22.0 mL) were added to a three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a distillation head. Isoquinoline (0.50 ml) was added to the flask. After the mixture was heated at 100 °C for 6 h, then 200 °C for 20 h. Water was continuously distilled from the reaction mixture. The solution was cooled to room temperature and subsequently poured into a methanol (300 mL). The precipitated polymer was collected, filtered and then extracted using methanol in a Soxhlet extractor overnight. After drying under a high vacuum at 150 °C for 24 hours, polyimide 4(c) was obtained as a white powder (1.7921 g, yield: 98.0%). The inherent viscosity of 4(c) was 0.51 dL/g, as measured at a concentration of 0.5 g/dL in *m*-cresol at 30 °C. IR (KBr): 1780, 1749, 1727, 1700, 1336, 1112, 744 cm⁻¹.

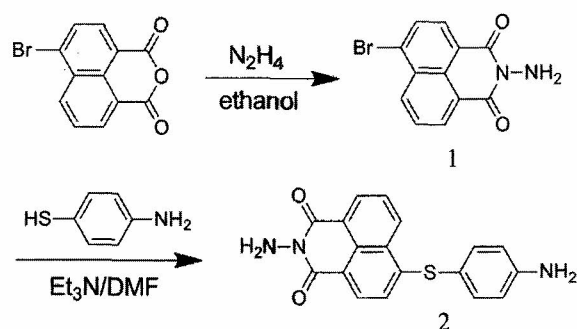
2.3.4. Film Casting

All the polymer films were cast from *m*-cresol solutions. A typical procedure for film casting was as follows. The purified and dried polymer (0.8–1 g) was dissolved in 15–18 mL of *m*-cresol (some of the polymers needed to be heated to dissolve rapidly). The solution was filtered to remove dust particles and then cast on a leveled clean glass plate. The casting films were dried in an oven at 130 °C for 6 h, 180 °C 1 h, 230 °C 1 h and last at 300 °C 1 h. The film was removed from the glass by immersion in water and then dried at 100 °C for 6 h.

3. Results and Discussion

3.1 Monomer Synthesis

The reactions of hydrazine, as the simplest diamine, with aromatic anhydrides have been investigated since 1930s.[33,34] The products of hydrazine with phthalic anhydride are *N*-aminophthalimide and phthalhydrazide; the former is unstable and has the tendency to convert into its six-membered ring isomer, phthalhydrazide. Nevertheless, the product of hydrazine with naphthalic anhydride is much more stable *N*-aminonaphthalimide. So, as shown in **Scheme 1**, 4-Bromo-*N*-amino-1,8-naphthalimide (**1**) was obtained by reacting of 4-bromo-1,8-naphthalic anhydride with hydrazine hydrate. Monomer diamine **2** was prepared smoothly by the nucleophilic displacement of **1** with 4-amino-benzenethiol in the presence of base, such as potassium carbonate or triethylamine. The ¹H NMR spectra of **2** are presented in **Figure 1** with assignments of all peaks. The IR spectra of the diamine **2** exhibit C=O absorptions around 1654-1724 cm⁻¹ characteristic of the imide ring and around 3318-3342 cm⁻¹ for the amino (N-H) stretching vibration. In addition, the elemental analysis results agree well with the calculated values. These results clearly support the structure of diamine **2**.



Scheme 1 Synthesis of unsymmetric diamine **2**

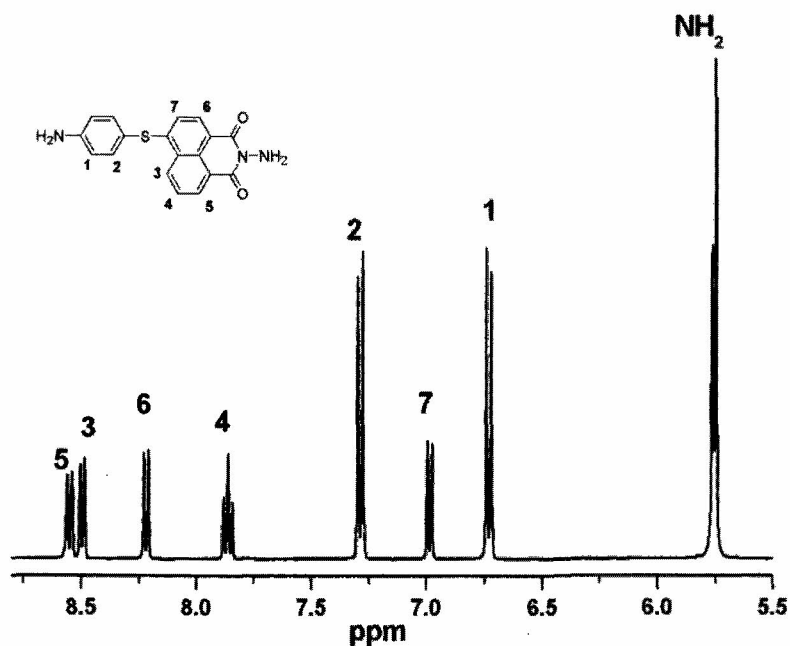
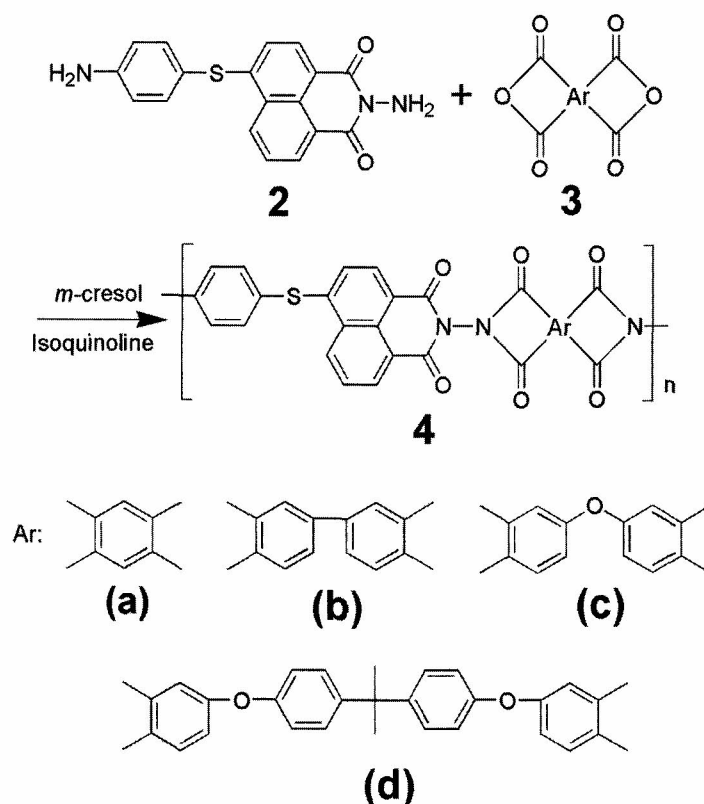


Figure 1. ^1H NMR spectrum of diamine **2** in $\text{DMSO-}d_6$

3.2 Synthesis of Polyimides

A conventional two-step method in NMP for synthesis of targeted polyimides is very difficult to proceed because of the low reactivity of the amino groups. However, high-molecular-weight polymers could be easily prepared in all cases via the one-step polymerization in *m*-cresol. As shown in **Scheme 2**, the polyimides were prepared by the one-step polymerization in *m*-cresol at 200 °C in the presence of a small amount of isoquinoline. As shown in **Table 1** the inherent viscosities of novel polyimides **4a-d** derived from unsymmetric diamine containing naphthalimide **2** were 0.39~1.22 dL/g in *m*-cresol at 30 °C, indicating the formation of high molecular weight polymers. Furthermore, all the polyimides **4a-d** could be cast into flexible and tough film.

The formation of polyimides was confirmed with FT-IR (**Figure 2**) and elemental analysis. The IR spectrum of polyimide **4(a)** showed four peaks at 1780, 1754, and 1728, 1701 cm^{-1} for the naphthalic and phthalic imides. The two peaks at 1780 and 1728 cm^{-1} are assigned to asymmetric and symmetric C=O stretching of the phthalimide respectively, while the other two peaks at 1754 and 1701 cm^{-1} can be assigned to asymmetric and symmetric C=O stretching of the naphthalimide respectively. The formation of the imide groups can also be confirmed by the peaks 1335 (C-N stretching) and 744 cm^{-1} (C=O bending). The peak at 1109 cm^{-1} is assigned to the N-N stretching. All the results above are consistent with the characteristic absorption bands of hydrazine-based imide groups. In addition to the IR spectra, the elemental analysis results of polymers also generally agreed well with the calculate values for the proposed structures (**Table 2**).



Scheme 2. Preparation of polyimides

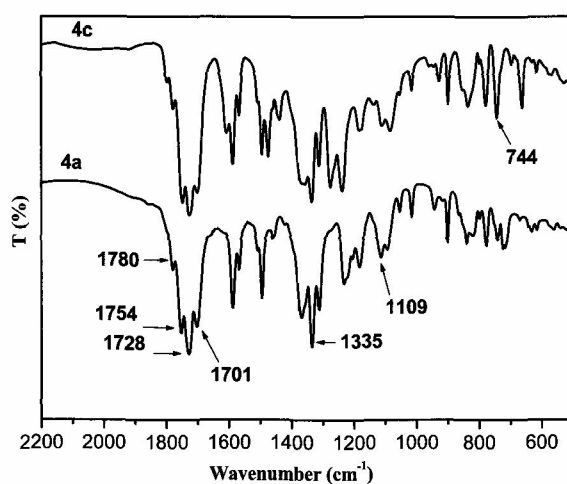


Figure 2. FT-IR spectrum of PI 4a and 4c

3.3. Polymer solubility

The solubility of the polyimide derived from unsymmetric diamine **2** was summarized in **Table 1**. The polymers based on unsymmetric diamine **2** show good solubility in phenols at room temperature, and the polyimide based on BPADA and ODPa are soluble in NMP and TCE, and the polyimide based on BPADA even can be readily soluble in chloroform. Compared to the polyimide made from ODPa and ODA, the polyimides derived from unsymmetric diamine **2** show improved solubility, which can be attributed to unsymmetric naphthalimide-phthalimide structure and flexible thioether kink structure that decrease chain packing and intermolecular interactions of the polymer.

Table 1. Inherent Viscosity (η_{inh}), Thermal properties and Solubility Behavior of the Polyimides

Polymer	η_{inh}^a	Solubility ^{b)}					T _g (°C) ^{d)}	T _{5%} (°C) ^{e)}
		DMAc	NMP	TCE ^{c)}	CHCl ₃	<i>m</i> -cresol		
4a	0.39	G	G	G	±	+	N/O	474
4b	1.22	G	G	G	±	+	417	481
4c	0.51	±	+	+	±	+	353	480
4d	0.56	+	+	+	+	+	302	467
Ref 1 ^{f)}	0.50	±	±	+	±	+	262	493

^{a)} Inherent viscosity measured in *m*-cresol at 30 °C. ^{b)} Qualitative solubility was tested with 20 mg of a sample (powder) in 2 mL of the solvent. + soluble; ± partially soluble on heating; G Gelation. ^{c)} TCE= 1,1,2,2-tetrachloroethane. ^{d)} Obtained from the second DSC scan at a heating rate of 20 °C/min in nitrogen. N/O = not observed. ^{e)} Temperature at which 5% weight loss recorded by thermogravimetry at a heating rate of 10 °C/min in nitrogen. ^{f)} Made from 4,4'-ODPA and ODA.

3.4. Thermal properties of the polyimides

DSC and TGA were used to investigate the thermal properties of the polyimide films, and some of the thermal behavior data were tabulated in **Table 1**. The glass transition temperatures (T_g s) were determined by DSC; all PIs based on unsymmetric diamine **2** had high T_g (>302 °C) (see **Figure 3**). In comparison with the T_g (262 °C) of the polyimide derived from ODPA and ODA, the T_g value of the analogue polyimide 4(c) increased by 91 °C. Evidently, the increase in T_g was attributed to the large and rigid naphthalimide unit in the polymer. The polyimides based on unsymmetric diamine **2** exhibited good thermal stability up to 450 °C. Their 5% weight-loss temperatures in nitrogen were recorded at 467-481 °C (see **Figure 4**), which was slightly inferior to the thermal stability of polyimides based on bis(phthalic anhydride)s, such as the polyimides derived from 4,4'-ODPA and ODA (whose $T_{5\%}$ is 493 °C in nitrogen atmospheres), and this may be attributed to the low bond energy of the N-N bond (the bond energy of the N-N bond is 159 kJ/mol, whereas that of the C-C bond is 332 kJ/mol).

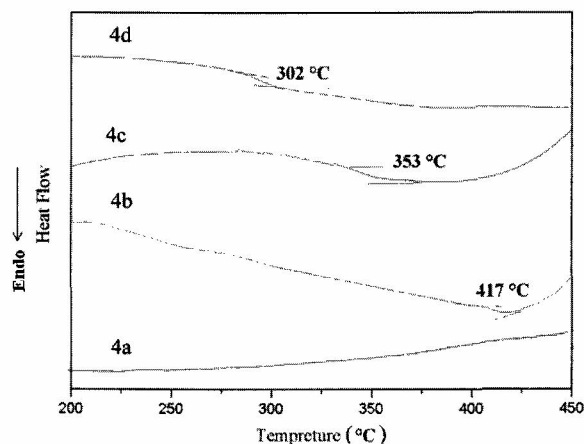


Figure 3. DSC curves of PI films (in nitrogen atmosphere, 20 °C/ min)

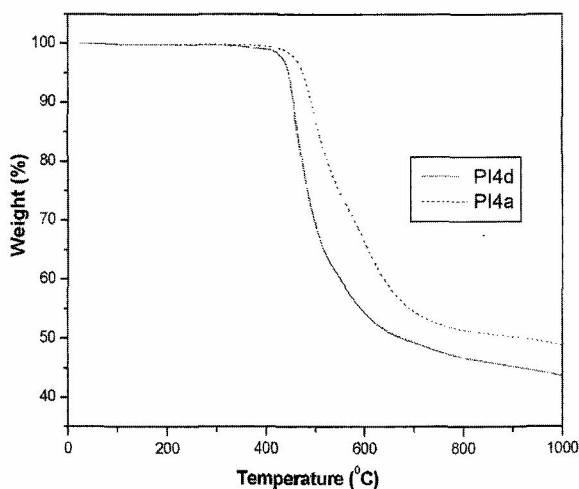


Figure 4. TGA curves of polyimides **4a** and **4d** at a scan rate of 10 °C/min in N₂

3.5. Mechanical properties

The tensile properties of the polyimides derived from unsymmetric diamine **2** measured with an Instron model 5567 analyzer are tabulated in **Table 2**. All of the polyimides are able to be cast as transparent, flexible, and tough films that had good mechanical strength. These films have tensile strengths of 85.1–142.9 MPa, elongations at break of 4.7–5.9 %, and tensile modulus of 2.67–4.11 GPa, which indicate excellent mechanical properties of the polyimides.

Table 2. Physical Properties of Polyimide Films

Polymer	Initial Modulus (GPa)	Strength@Break (MPa)	Elongn.@Break (%)	H ₂ O% absorptn. ^{a)}	Dielectric const. (1 MHz)
4a	4.11	142.9	5.5	0	2.90
4b	2.94	126.0	5.9	0	3.03
4c	2.86	100.2	5.7	0	2.76
4d	2.67	85.1	4.7	0.20	2.96
Ref 2 ^{b)}	1.32	142.0	58	2.58	3.30

^{a)} Moisture absorption of polyimide films were measured immersing films of these polyimides in distilled water at 25 °C for 100 h. ^{b)} A poly(ether imide) was synthesized from 4,4'-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) in our laboratory. The inherent viscosity of its poly(amic acid) precursor was 0.98 dL/g.

The tensile strength of the polyimides derived from unsymmetric diamine **2** is close to those derived from commercial diamines such as PI(OPDA/ODA). However, the values of tensile modulus are far larger than those polyimides derived from commercial diamines, and are within the range of those derived from

4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride.[35] Evidently, the increase in tensile modulus is attributed to the large and rigid naphthalimide unit in the polymer backbone. Even though increasing the free volume, weakening the intermolecular force and packing ability of polymers generally decreases modulus and glass transition temperature, the large and rigid naphthalimide unit in the polymer backbone compensates the disadvantage.

3.6. Dielectric properties and Moisture uptakes

The polyimide films derived from unsymmetric diamine **2** show good dielectric properties, and possess low dielectric constants of 2.76–3.03 at 1 MHz at room temperature and 70% relative humidity (**Table 2**). The polyimides **4a-d** with unsymmetric diamine groups reveal a decreasing dielectric constant in comparison with that of the corresponding analogues of the polyphthalimide such as PMDA/ODA ($\epsilon = 3.30$). The low dielectric constant is attributed to the fact that the introduction of the unsymmetric diamine groups leads to the formation of configuration isomers of repeat units in the polymer backbone and causes the decrease in the intermolecular force and packing ability of the resulting polymers. These results suggest that the PIs containing unsymmetric groups loosen the polymer packing and increased the free volume, subsequently leading to reducing dielectric constant. Polyimides derived from unsymmetric diamine **2** also have low moisture absorption even zero moisture absorption, which is tested in distilled water at 25 °C for 100 h. The polyimides derived from PMDA, BPDA and ODPA displayed excellent water proofing, which is rarely reported. The ultra low moisture absorption is attributed to the fact that the polyimides **4a-d** contained N-N bond and naphthalimide moiety in the polymer backbone. The N-N bond, as the simplest diamine, can weaken the inter- and intra- chain interactions and then result in low polarization. The water proofing effect of the naphthalimide groups in the polyimide which is more stable than phthalimides can also lead low absorption. The ultra low water uptakes ensured that the PIs had stable dielectric constants.

3.7 Optical properties

The UV-visible spectrum of diamine **2** dissolved in DMF (5×10^{-5} mol L⁻¹) exhibits a broad featureless absorption with the lowest energy absorption maximum at ca. 401 nm. The substitution of donor groups 4-aminophenylthioether to the bay position of naphthalene core leads to enlargement of p- π conjugation. The UV-Vis absorption spectra of the polyimides **4a-d** in NMP at dilute concentration (1×10^{-5} mol L⁻¹) are shown in **Figure 5**. In the UV-Vis spectra, all the four polyimides show typical naphthalimide absorption peak around 400 nm with high coefficients. It seems that the conjugation is only slightly broken at the imide linkage. The offset of absorption bands shifted to longer wavelength due to better chain packing in the polyimide film compared to solution (see **Figure 6**). The absorption peaks of the polymer films are observed around 430 nm. The fluorescence spectra of PIs are shown in **Figure 7**. These polyimides show green fluorescence excited at 380 nm. The emission of the unsymmetric diamine **2** excited at 380 nm is in the range of 380 to 500 nm, and monomer **2** shows intense fluorescent maxima at 420 nm. In contrast, the emission of the polyimides excited at 401 nm is in the range of 450 to 650 nm, and the polyimides also show intense fluorescent at about 520 nm. The concentration of the 4-aminophenylthioether moiety increases from the PI based on BPADA to the PI based on PMDA, whereas the intensity of fluorescence decreases from the PI based on BPADA to the PI based on PMDA; the tendency may result from the decreasing electrophilicity of 4-aminophenylthioether moiety in the polymer backbone.

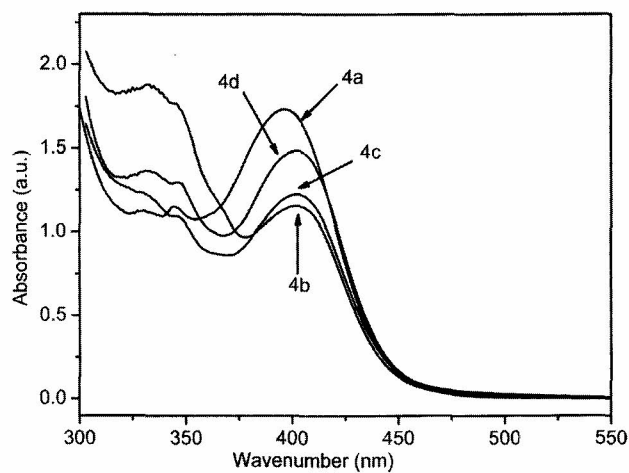


Figure 5. UV-vis spectra of the polyimide **4a-d** in NMP (1×10^{-5} mol L⁻¹).

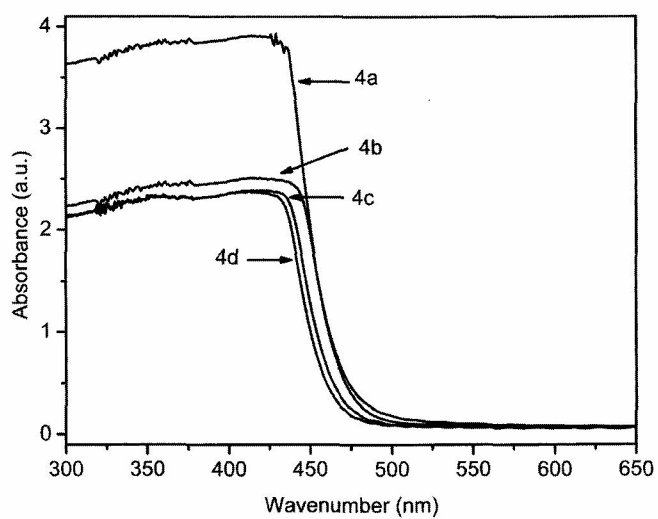


Figure 6. UV-vis spectra of the polymer films **4a-d**.

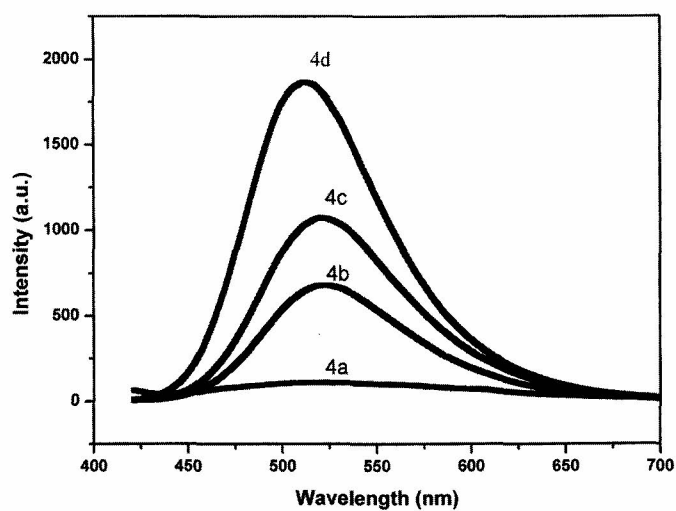


Figure 7. Fluorescence spectra of the polyimide **4a-d**.

4. Conclusion

In this work, new polyimides were successfully prepared through a “one-pot” polymerization approach via an unsymmetric diamine containing naphthalimide moiety, in which the N-N bond moiety was part of the polymer backbone. These polyimides show improved solubility, high T_g value, high modulus, low dielectric constant, ultra low moisture absorption and green fluorescence because of the unsymmetric naphthalimide-phthalimide structure and the thioether kink in the main chain. The excellent properties exhibited in the novel unsymmetric diamine based PIs demonstrate a promising potential for future advanced material applications.

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(more Refs see p140)