

HETEROAROMATIC POLYMERS — HIGH TEMPERATURE POLYPYRROLONES DERIVED FROM 2,6-BIS(3',4'-DIAMINOPHENYL)- 4-BIPHENYLPYRIDINE AND VARIOUS AROMATIC DIANHYDRIDES*

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Abstract A new type of aromatic tetraamine containing biphenyl moiety in the side chain was synthesized *via* a modified Chichibabin's reaction. 3-Nitro-4-acetamidoacetophenone was reacted with 4-phenyl benzaldehyde in the presence of ammonium acetate to obtain 2,6-bis(3',4'-diaminophenyl)-4-biphenyl pyridine (DPPA). A series of polypyrrolones (PPys) were prepared using tetraamine and various aromatic dianhydrides *via* a two-step cyclization procedure. All the PPys show excellent high temperature stabilities with the initial decomposition temperatures of 530–549°C and residual weight ratio of 49%–80% at 750°C in nitrogen. The polymers exhibit no apparent glass transition temperatures (T_g s) except PPy-1 ($T_g = 327^\circ\text{C}$), which is derived from tetraamine DPPA and 2,2-bis[4-(3',4'-dicarboxyphenoxy)-phenyl]propane dianhydride (BPADA). In addition, the polymers have acceptable mechanical properties with the tensile strength of 65–94 MPa. The PPy films show excellent hydrolysis-resistance in alkaline aqueous medium and could maintain most of the properties even after boiling in 10% aqueous sodium hydroxide solution for a week.

Keywords: Tetraamine; Polypyrrolone; Pyridine; High temperature polymers; Film; Hydrolysis-resistance.

INTRODUCTION

Polypyrrolones (PPys) are typical heteroaromatic polymers derived from the conventional two-step procedure including the reaction of aromatic dianhydrides and tetraamines followed by thermal cyclization. The first-stage polymer obtained from the reaction of the monomers in aprotic solvent, such as *N*-methyl-2-pyrrolidinone (NMP) and *N,N*-dimethylacetamide (DMAc), is soluble precursor, poly(amino acid amide) (PAAA), which can be pyrrolonized *via* two dehydration reactions. The obtained PPy possesses a repeat unit with two benzene rings joined by two fused five-membered rings, imparting a great degree of thermal and chemical resistance^[1–3]. The excellent combined properties of the PPys have attracted much attention for applications such as gas separating membrane, packaging materials in microelectronics and conducting materials^[4–6].

Now, the development of PPys is mainly focused on the improvement of processability in order to find new applications as functional materials in high-tech fields. Generally speaking, introduction of flexible segments or bulky pendent groups into the heteroaromatic polymer backbones can obviously modify its processability^[7, 8]. However, the influences of these groups on the intrinsic properties of polymers are varied. In most cases, they will damage the thermal stability of the polymers more or less. For instance, Sek and his co-workers reported the processable polypyrrolones with flexible ester segments in the main chain. The poly(esterimidazopyrrolone)s has been synthesized by one-step high temperature polycondensation because of its good solubility in *m*-cresol or *p*-chlorophenol. However, the thermal stability of the polymers was greatly damaged and the temperatures of

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10% weight loss ($T_{10\%}$) were less than 350°C^[9]. Therefore, a combination of rigid polymer chains and processability is a crucial factor in designing the functional high temperature polymers.

In the present work, in order to investigate the influences of the bulky pendent groups on the properties of the PPys, a new tetraamine monomer, 2,6-bis(3',4'-diaminophenyl)-4-biphenylpyridine (DPPA) was synthesized and the thermal and mechanical properties of the new polymers derived from the tetraamine and various aromatic dianhydrides were evaluated in detail.

EXPERIMENTAL

Materials

4-Phenylbenzaldehyde (Acros), *p*-amino acetophenone, ammonium acetate, glacial acetic acid and absolute ethanol (Beijing Chemical Reagents Corp.) were used as received. 4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA, Hoechst Celanese Corp.) was recrystallized from acetic anhydride and dried at 160°C overnight prior to use. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA), 2,2-bis[4-(3,4-dicarboxyphenoxy) phenyl] propane dianhydride (BPADA) and 4,4'-oxydiphthalic anhydride (ODPA) were synthesized in our laboratory and recrystallized from acetic anhydride prior to use. 3-Nitro-4-acetamidoacetophenone^[10] was synthesized according to the literature and was purified by recrystallization from absolute ethanol to give off-white powders (m.p.:136–137°C). Commercially available *N*-methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation over CaH₂ prior to use.

Characterization

Inherent viscosity was measured using an Ubbelohde-viscometer with 0.5 g • dL⁻¹ NMP solution at 30°C. FT-IR spectra were obtained with a Perkin-Elmer 782 Fourier transform spectrometer. ¹H-NMR and ¹³C-NMR spectra were performed on a Varian Unity 200 spectrometer operated at 300 MHz in DMSO-*d*₆. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Perkin-Elmer 7 series thermal analysis system at a heating rate of 10 K/min. Water uptakes were determined according to the following procedure. The PPy sample (3.0 cm × 1.0 cm × 0.005 cm) was immersed in boiling deionized water (100°C) in a 250 mL round-bottomed flask fitted with a condenser for 24 h, which was then dried immediately and weighted to determine the water uptakes according to Eq. (1).

$$W_{\text{uptake}} = \frac{W_2 - W_1}{W_1} \times 100\% \quad (1)$$

where W_{uptake} stands for the water uptake ratio, W_2 stands for the weight of the film samples after immersed in water and W_1 the initial weight of the samples. Mechanical properties of the polymer films were measured with an Instron model 1130 tensile tester with a 5 kg load cell at a crosshead speed of 5 cm • min⁻¹ on strips of 30–40 μm thickness and 0.5 cm width with a 2 cm gauge length.

The alkaline hydrolytic resistance of PPys was qualitatively investigated according to the following method. The PPy film sample (3.0 cm × 1.0 cm × 0.005 cm) was immersed in boiling 10% aqueous NaOH solution in a 250 mL round-bottomed flask fitted with a condenser. The times of initial (t_i) and complete (t_w) hydrolysis were recorded. t_i was defined as the time when cloudy substance appeared in the solution and t_w as the time when the test film was completely disappeared.

Monomer Synthesis

2,6-Bis[(3'-nitro-4'-acetamido)phenyl]-4-biphenyl pyridine (1)

A 250 mL three-necked flask equipped with a mechanical stirrer and a reflux condenser was charged with 266.4 g (1.2 mol) of 3-nitro-4-acetamidoacetophenone, 109.3 g (0.6 mol) of 4-phenyl benzaldehyde, 600 g (7.8 mol) ammonium acetate and 1500 mL glacial acetic acid. The solution was refluxed with stirring for 3 h. Then the yellow solid precipitate was filtered off and washed thoroughly with water to give a crude product 1, which was purified by recrystallization in ethanol to give 71.4 g pale yellow crystals **1** with the yield of 40.5%,

m.p.: 317–319°C. $^1\text{H-NMR}$ (300 MHz, in DMSO-d_6): 2.11 (s; 6H, H_a), 7.42 (d; 1H, H_9), 7.50 (t; 2H, H_8), 7.80 (m, 4H, H_6 , H_7), 7.85 (d; 2H, H_5), 8.19 (d; 2H, H_3), 8.40 (s; 2H, H_4), 8.64 (q; 2H, H_2), 8.84 (s; 2H, H_1) and 10.42 (s; N—H). MS (EI): 587 (15.6%), 545 (19.2%), 503 (45%), 457 (10.6%) and 410 (7.2%). Elemental analysis: Calc. for $\text{C}_{33}\text{H}_{25}\text{N}_5\text{O}_6$ (%): C 67.45, H 4.29, N 11.92%. Found (%): C 67.12, H 4.40, N 11.49.

2,6-Bis[(3'-nitro-4'-amino)phenyl]-4-biphenyl pyridine (2)

A solution of 12.74 g of KOH in 60 mL methanol was added dropwise, with vigorous stirring, to a mixture of 38.78 g (0.066 mol) of **1** in 200 mL methanol over a period of 0.5 h, and then KOH of more than 6.54 g was added. The reaction mixture was stirred and refluxed for 6 h and cooled to room temperature, and then poured into 500 mL deionized water to give yellow solid, which was collected and washed thoroughly with water. The precipitate was collected and dried under vacuum overnight to give 33.10 g of **2**. Yield: 99.6%, m.p.: 321–322°C. $^1\text{H-NMR}$ (300 MHz, in DMSO-d_6): 7.19 (d; 2H, H_3 ; $^3J_{\text{H}_3-\text{H}_2} = 9.0$ Hz), 7.55 (m; 3H, H_6 , H_7 ; $^3J_{\text{H}_6-\text{H}_5} = 7.7$ Hz), 8.01 (d; 2H, H_5 ; $^3J_{\text{H}_5-\text{H}_6} = 7.7$ Hz), 8.04 (s; 2H, H_4), 8.36 (q; 2H, H_2 ; $^3J_{\text{H}_2-\text{H}_3} = 9.0$ Hz, $^4J_{\text{H}_2-\text{H}_1} = 1.3$ Hz), 8.92 (s; 2H, H_1) and 7.74 (N—H). MS (EI): 503 (100%), 457 (15.7%), 410 (16.0%). Elemental analysis: Calc. for $\text{C}_{29}\text{H}_{21}\text{N}_5\text{O}_4$ (%): C 69.18, H 4.20, N 13.91. Found (%): C 68.89, H 4.32, N 13.84.

2,6-Bis(3',4'-diaminophenyl)-4-biphenyl pyridine (DPPA)

Hydrazine monohydrate (15 mL) was added dropwise at 75–80°C over a period of 1.5 h to a mixture of **2** (5.0352 g, 10 nmol), ethanol (150 mL) and a catalytic amount of 5% Pd/C (0.24 g) placed in a 250 mL three-necked flask. The reaction mixture was refluxed for 24 h, and then the mixture was filtered hot to remove Pd/C. Brown-red powder, precipitated from the cold filtrate, was collected, washed with water and then dried under vacuum overnight. Yield: 3.73 g (84.0%), m.p. 236–238°C. FT-IR (KBr, cm^{-1}): 3381, 3314, 3030, 1590, 1545, 1517, 1452, 1622, 1518, 870, 836, 812, 765 and 697. $^1\text{H-NMR}$ (300 MHz, in DMSO-d_6): 4.58 (N—H), 4.82 (N—H), 6.65 (d; 2H, H_3 ; $^3J_{\text{H}_3-\text{H}_2} = 8.0$ Hz), 7.42 (d; 3H, H_2 , H_9 ; $^3J_{\text{H}_2-\text{H}_3} = 8.0$ Hz, $^3J_{\text{H}_9-\text{H}_8} = 7.5$ Hz), 7.52 (t; 2H, H_8 ; $^3J_{\text{H}_8-\text{H}_7} = 7.5$ Hz; $^3J_{\text{H}_8-\text{H}_9} = 7.5$ Hz), 7.55 (d; 2H, H_1 ; $^4J_{\text{H}_1-\text{H}_2} = 1.1$ Hz), 7.75 (s; 2H, H_4), 7.76 (d; 2H, H_7 ; $^3J_{\text{H}_7-\text{H}_8} = 8.9$ Hz), 7.85 (d; 2H, H_6 ; $^3J_{\text{H}_6-\text{H}_5} = 8.2$ Hz) and 8.00 (d; 2H, H_5 ; $^3J_{\text{H}_5-\text{H}_6} = 8.2$ Hz). $^{13}\text{C-HMR}$ (300 MHz, in DMSO-d_6): 113.5 (C_6), 113.9 (C_3), 114.9 (C_8), 117.6 (C_4), 127.5 (C_{11}), 128.1 (C_{11}), 128.2 (C_{12}), 128.6 (C_{15}), 129.0 (C_{16}), 129.9 (C_5), 135.3 (C_2), 137.5 (C_1), 138.4 (C_{14}), 140.2 (C_{10}), 141.3 (C_{13}), 148.5 (C_9) and 157.9 (C_7). MS (EI): 443 (100%). Elemental analysis: Calc. for $\text{C}_{29}\text{H}_{25}\text{N}_5$ (%): C 78.53, H 5.68, N 15.79. Found (%): C 78.37, H 5.72, N 15.68.

Polymer Synthesis

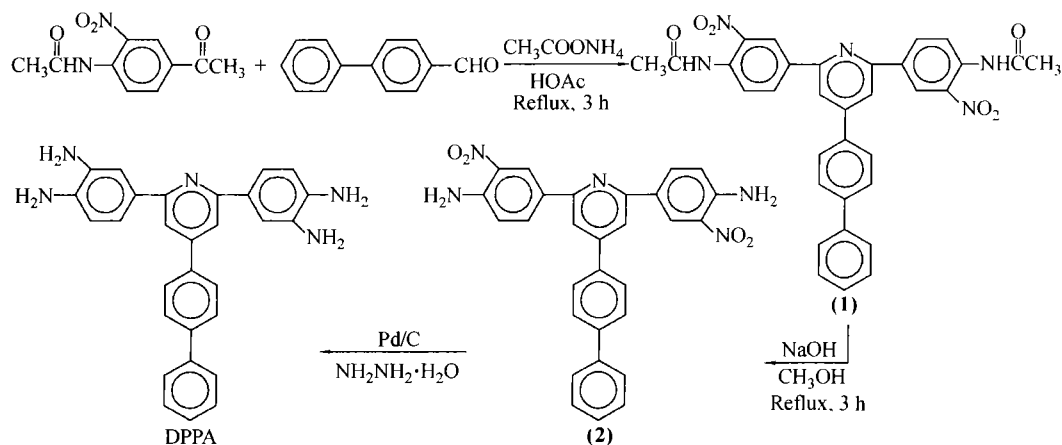
The general procedure for the reaction of dianhydrides with DPPA can be illustrated by the preparation of PPy-1. In a typical experiment, DPPA (4.4355 g, 10 mmol) was added with stirring to 50 mL newly-distilled NMP placed in a 100 mL three-necked flask equipped with a mechanical stirrer, a dropping funnel, a dry nitrogen inlet and a thermometer. The reaction system was cooled in an ice-salt bath and the temperature was maintained at -15°C . BPADA (5.2012 g, 10 mmol) dissolved in 30 mL NMP was added dropwise to the system over a period of 1 h. The reaction mixture was stirred at -10°C for 5 h and then 12 h at room temperature to yield a viscous poly(amino acid amide) (PAAA) solution. The brown solution was then filtered through a 0.2 μm Teflon syringe filter to remove any particulates that might affect the quality of the film. The PPy-1 film was obtained by thermal curing the PAAA solution by the following heating procedure: 80°C , 1 h; 150°C , 1 h; 250°C , 1 h; 300°C , 1 h and 350°C , 3 h. PPy-1 film was deep brown in color. FT-IR (film, cm^{-1}): 1762, 1600, 1385, 1220 and 820.

PPy-2(DPPA/ODPA), PPy-3(DPPA/BTDA) and PPy-4(DPPA/6FDA) were prepared by adopting the similar procedure with different dianhydrides.

RESULTS AND DISCUSSION

Monomer Synthesis

The pyridine-bridged aromatic tetraamine DPPA was synthesized through a three-step procedure as shown in Scheme 1. 3-Nitro-4-acetamidoacetophenone was reacted with 4-phenyl benzaldehyde using the similar pathway reported by Weiss^[11]. After hydrolysis and reduction reaction of the intermediate, DPPA was obtained as a brown-red powder with a total yield of about 34%. The structure of the tetraamine monomer was confirmed by FT-IR, ¹H-NMR, ¹³C-NMR, mass spectroscopy, and elemental analysis. The results of the elemental analysis agree well with the calculated values for the proposed structure of the DPPA.



Scheme 1 Synthetic route for the preparation of tetraamine DPPA

Figure 1 shows the FT-IR spectra of DPPA and dinitro compound **2**. Absorption bands at 1580 and 1336 cm^{-1} assigned to the asymmetric and symmetric stretching vibration of $-\text{NO}_2$ group in the dinitro compound **2** disappeared in the spectrum of DPPA. The characteristic double absorption bands of N—H symmetric and asymmetric stretching vibrations at 3300–3500 cm^{-1} region of the DPPA spectrum verify the formation of primary amine structures. In addition, absorption at *ca.* 1590 cm^{-1} attributed to the stretching vibration of C=C and C=N bonds in phenyl and pyridine rings and the band at *ca.* 836 cm^{-1} due to the C—H stretching vibration of pyridine ring are observable.

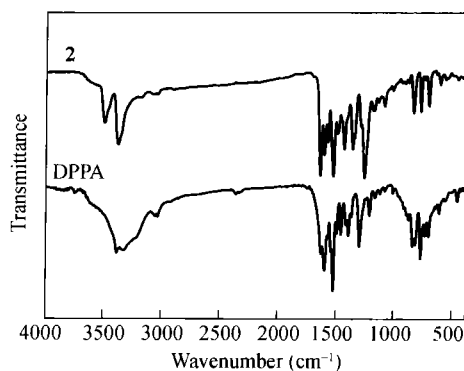


Fig. 1 FT-IR spectra of **2** and DPPA (KBr sample)

The ¹H-NMR and ¹³C-NMR spectra of DPPA are shown in Fig. 2. In the ¹H-NMR spectra, the protons of amino groups or ortho to amine groups (H_3) appear at the farthest upfield of the spectrum. The signal at 8.00 corresponds to H_5 , which appears at the farthest downfield of the spectrum. The ¹³C-NMR spectrum of DPPA reveals 17 signals, which agrees well with the predicated structure of DPPA.

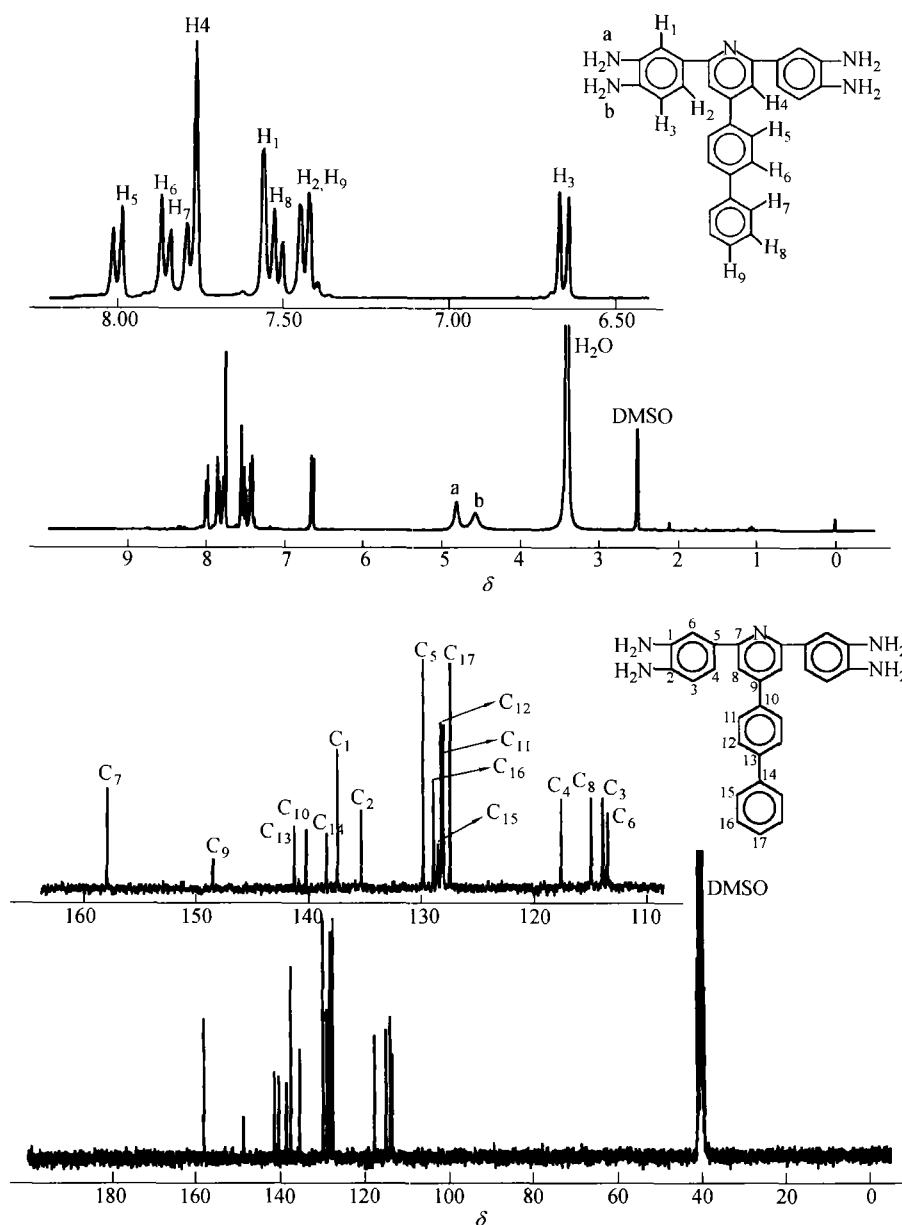
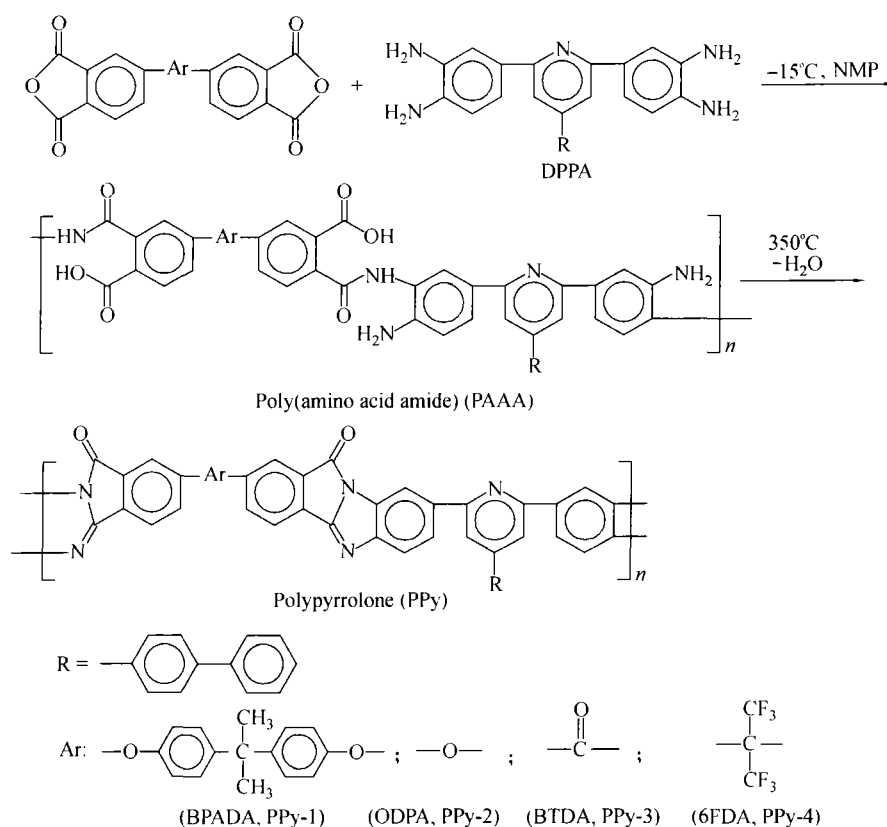


Fig. 2 ^1H -NMR and ^{13}C -NMR spectra of DPPA (DMSO- d_6 , 300 MHz)

Polymer Synthesis

PPys were prepared by two-step thermal cyclization of the precursor poly(amino acid amide)s (PAAA)s, which were prepared by polycondensation of aromatic dianhydride with aromatic tetraamine in NMP at low temperature (Scheme 2). The reaction was strongly affected by the stoichiometry, adding sequence and adding interval of the monomers. For example, the reaction mixture would easily gel during the reaction when dianhydride was overfed or when the adding interval was too short. Therefore, an exact stoichiometry of dianhydride and tetraamine and a long addition interval were necessary in the synthesis of the PAAA solution. It was found that the [dianhydride]/[tetraamine] mole ratio close to 1.00 was required to yield a PAAA solution with reasonable viscosity which could produce a strong and flexible polymer film by casting the polymer solution on a glass substrate followed by thermal curing at temperatures up to 350°C.



Scheme 2 Synthesis of polypyrrolones from the polycondensation of aromatic dianhydride with DPPA

The inherent viscosities of PAAA solutions measured by Ubbelohde-viscometer with $0.5 \text{ g} \cdot \text{dL}^{-1}$ NMP solution at 30°C were in the range of $0.55\text{--}0.84 \text{ dL} \cdot \text{g}^{-1}$ (Table 1), which indicated the moderate molecular weight of the polymers. The inherent viscosity of PPy-4 prepared from 6FDA was lower than those of the other three dianhydrides, which was mainly attributed to the low reaction activity under the polymerization condition of 6FDA. The polymer films exhibited water uptakes of $1.82\%\text{--}1.93\%$, a bit higher than those of the aromatic polyimides^[11], which might be attributed to the larger free volume of the molecular chains of the former. Crystallinity of the PPy films was examined by wide-angle X-ray diffraction analysis with 2θ ranging from $3\text{--}60^\circ$. As shown in Fig. 3, all the polymers exhibited amorphous natures.

Table 1. Inherent viscosity of PAAAs and film properties of PPys

PAAAs	$\eta_{\text{inh}}^a (\text{dL} \cdot \text{g}^{-1})$	PPys	Film quality ^b	Water uptakes (%)
1	0.84	1	F&T	1.93
2	0.73	2	F&T	1.38
3	0.68	3	F&T	1.82
4	0.55	4	B	— ^c

^a $0.5 \text{ g} \cdot \text{dL}^{-1}$ NMP solution measured at 30°C

^b F: flexible; T: tough; B: brittle

^c not measured

Figure 4 shows the FT-IR spectra of PPy-1 (BPADA/DPPA) thermally cured at different temperatures. When the curing temperature was lower than 180°C , the characteristic absorptions of imide (*ca.* 1778 cm^{-1} and *ca.* 1718 cm^{-1}) were observed, demonstrating that poly (amino imide) (PAI) was the major curing product. When the curing temperature was higher than 200°C , the imide characteristic absorptions disappeared and a new absorption band at *ca.* 1756 cm^{-1} appeared, which was assigned to the characteristic stretching vibration of $\text{C}=\text{O}$

in pyrrolone groups^[12]. At a temperature higher than 200°C, a second thermal cyclization between the imide groups and the α -NH₂ in the aromatic rings occurred and pyrrolone segments were produced.

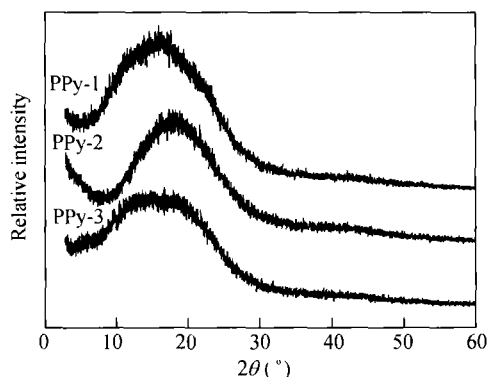


Fig. 3 X-ray diffraction patterns of PPY films

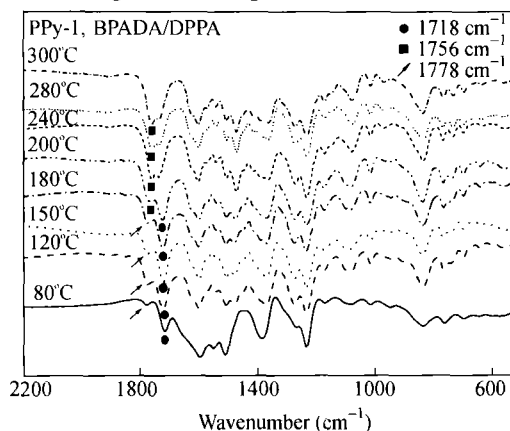


Fig. 4 Thermal curing of PPY-1 monitored by FT-IR spectra (film samples)

Thermal Properties

Thermal stabilities of PPys were measured by TGA and evaluated by temperature of 10% weight loss ($T_{10\%}$) and residual weights at 750°C (R_w). The results are summarized in Fig. 5 and Table 2. Thermal analysis revealed that the PPys were stable up to 530°C, as it could be seen from the onset decomposition temperature (T_{ds}) ranged from 530–549°C. The $T_{10\%}$ temperature, which is usually defined as the criterion of the thermal stability for high-temperature polymers, is all higher than 570°C. The thermal stabilities of PPys depend on the aromatic dianhydrides employed and decrease in the following order: ODPA (635°C) > BPADA (612°C) > BTDA (603°C) > 6FDA (571°C). The residual weight ratios at 750°C of the PPys decrease in the order of PPY-1 > PPY-2 > PPY-3 > PPY-4. The excellent thermal stabilities of the PPys could be interpreted by the stable multiaromatic conjugated structures in the polymers' backbones.

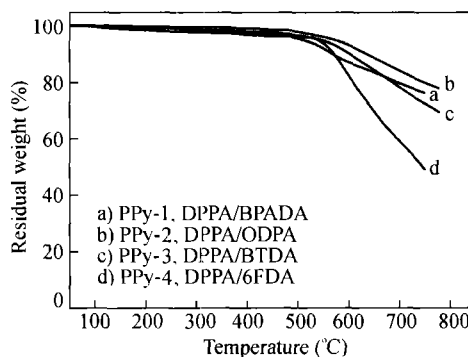


Fig. 5 TGA curves of PPys
In nitrogen; Heating rate: 10 K/min

Table 2. Thermal properties of PPY films

PPys	T_d^a (°C)	$T_{5\%}^b$ (°C)	$T_{10\%}^b$ (°C)	T_g^c (°C)	R_w^d (%)	t_i^f (h)	t_w^g (h)
1	540	531	612	327 (337 ^h)	81	19	>168 h
2	537	569	635	— ^e	80	18	>168 h
3	530	545	603	— ^e	73	16	>168 h
4	549	537	571	— ^e	49	14	>168 h

^a Initial thermal decomposition temperature; ^b Temperature at 5% and 10% weight loss, respectively

^c Glass transition temperatures; ^d Residual weight at 750°C; ^e No apparent T_g in the measurement;

^f Initial hydrolyzing time; ^g Wholly hydrolyzing time; ^h T_g measured by DMA

The glass transition behavior of the PPys was evaluated by DSC measurement (Fig. 6). The results reveal that all the PPys show no apparent glass transition at a scan rate of 10 K/min^{-1} except PPy-1. The high T_g (327°C) of PPy-1 is mainly attributed to the strong inter- and intra-molecular interactions of the polymer chains. The typical result of a DMA measurement of PPy-1 is shown in Fig. 7, where the tensile storage modulus (E') and tensile loss modulus (E'') are plotted against the temperature. As it can be observed from the E' plot, PPy-1 retains its mechanical properties up to nearly 330°C . The T_g obtained from the peak of the DMA loss modulus was 337°C , which was 10°C higher than that measured by DSC measurement (327°C).

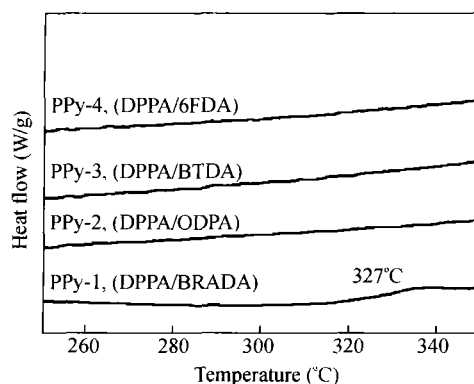


Fig. 6 DSC curves of PPys
In air; Heating rate: 10 K/min

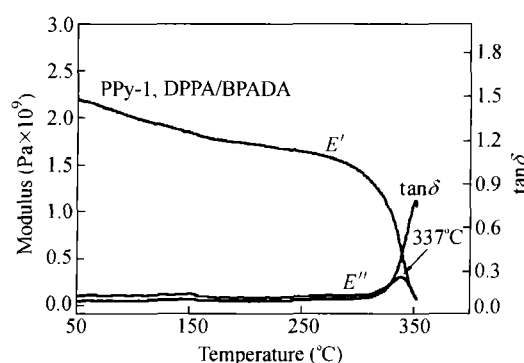


Fig. 7 DMA curve of PPy-1
In air; Heating rate: 10 K/min

Hydrolysis Resistance Properties

Experimental results demonstrated that PPys possess good hydrolysis resistance in alkaline aqueous solution (Table 2) although aromatic polyimides possess good combined physical and chemical properties including high thermal stability, high mechanical property and high environmental stability. Their hydrolysis resistances, especially in alkaline aqueous solution, were generally poor due to the inherent chemical structures in the polymer backbones, *i.e.* imide bonds could be easily broken and decompose by the OH^- attack. It was reported that Kapton[®] film would be completely hydrolyzed after boiling in hydrazine to produce two initial monomers, pyromellitic anhydride and 4,4'-oxydianiline quantitatively^[13].

As it can be seen from Table 2, the PPy films cured at 350°C could stand 14–19 h in 10% boiling NaOH aqueous solution before hydrolysis was initially observed. After boiling for 7 days, the PPy films could remain most of their original shapes and toughness. The excellent alkaline hydrolysis resistance for PPys could be probably attributed to the more fused multiaromatic structures.

Mechanical Properties

The tensile properties of the PPy films except PPy-4, which was too brittle to be measured, are summarized in Table 3. The films had tensile strength of 65–94 MPa, elongation at break of 4%–8% and initial modulus of 0.68–0.84 GPa. PPy-1, derived from BPADA and DPPA, shows the best tensile properties compared with the other two systems, which could be attributed to the flexible isopropylidene and ether bonds in the dianhydride moiety. The inferior tensile properties of PPy-4 film (6FDA/DPPA) are mainly due to the low reactivity of dianhydride 6FDA.

Table 3. Mechanical properties of PPy films

PPys	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (GPa)
1	92	8	0.84
2	94	6	0.82
3	65	4	0.68

CONCLUSIONS

New tetraamine monomer 2,6-bis(3',4'-diaminophenyl)-4-biphenyl pyridine was synthesized and characterized, and was further reacted with different dianhydrides to obtain a series of novel PPys. The synthesized polymers exhibit good thermal stability up to 530°C in nitrogen. The amorphous polymers show no apparent glass transition during heating except PPy-1. The PPy films had acceptable mechanical properties with tensile strength of higher than 60 Mpa, and they also exhibit excellent alkaline hydrolysis resistance. The films could maintain their shapes and toughness even after boiling in 10% sodium hydroxide aqueous solution for 7 days. The valuable properties of the PPys make them good candidate for electric or electronic applications.

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