

# Preparation and Characterization of Poly(*p*-phenylenediamine-*co*-xylylidine)

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**ABSTRACT:** *p*-Phenylenediamine (PPDA) homopolymer and its copolymers with 2,3-xylylidine (XY) were synthesized by oxidative polymerization using potassium persulfate as an oxidant in HCl medium at room temperature. The yield, intrinsic viscosity, and solubility of the polymers were significantly dependent on the monomer ratio. The resulting polymers were characterized by Fourier transform IR spectroscopy, <sup>1</sup>H-NMR spectroscopy, wide-angle X-ray diffraction, and thermogravimetry methods. The results showed that the number-average degree of polymerization of the PPDA homopolymer was 33 and the actual content of XY units in the copolymer was slightly higher than the feed XY unit content. The polymers were substantially amorphous and showed the strongest diffraction at a Bragg angle of 3°. The polymers exhibited a thermal decomposition temperature higher than 436°C, the maximum weight-loss rate was slower than 4%/min, and the char yield was larger than 24 wt % at 600°C in nitrogen. The activation energy of thermal decomposition for the polymers increased from 19 to 25 kJ/mol with increasing XY unit contents from 0 to 10 mol %. The polymers showed higher thermostability but lower activation energy of decomposition in nitrogen than in air. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3107–3116, 2001

**Key words:** *p*-phenylenediamine homopolymer; xylylidine-containing copolymer; oxidative polymerization; IR spectrum; NMR spectrum; thermostability; degradation kinetics

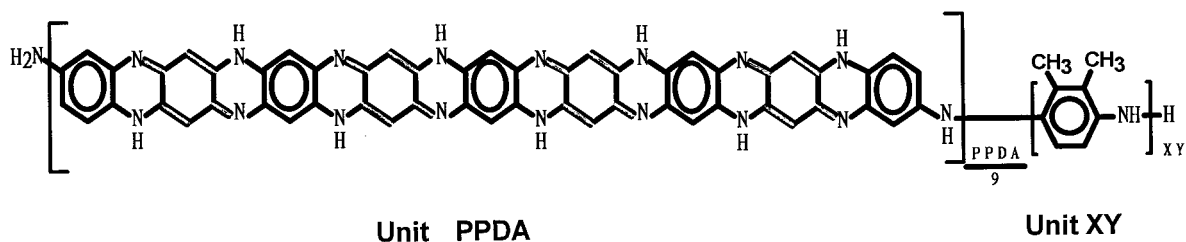
## INTRODUCTION

Conductive polymers, such as polyaniline, polypyrrole, polyaminopyridyl, polypyridyl, polypyrimidyl,

and polyphenylenediamine, have attracted attention recently because they exhibit high gas separation ability<sup>1</sup> and lyotropic liquid crystallinity.<sup>2</sup> Conjugated polyaniline is the most attractive one because of its easier preparation, higher air stability, and highest oxygen/nitrogen separation factor up to 30.<sup>1</sup> It is reported that polyphenylenediamines synthesized by chemically oxidative polymerization with sodium, potassium, or ammonium persulfate as an oxidant exhibit ladder and ladder-like structures consisting of highly aromatic nitrogenous heterocycles.<sup>3–5</sup> This nitrogenous heterocyclic ladder structure is expected to be of great benefit to the preparation of advanced air separation membranes.<sup>6</sup> However, the polyphenylenediamines are

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Scheme 1

slightly soluble in most of the common organic solvents with relatively low boiling points. Only a few studies on oxidative homopolymerization of three phenylenediamine isomers were reported<sup>3-5,7</sup> and no report on copolymerization of phenylenediamine with xylylene diamine was found up to now. The purpose of this study was to synthesize soluble copolymers in dimethylsulfoxide (DMSO), trifluoroacetic acid (TFA), and tetrahydrofuran (THF) through introducing dimethylaniline units on the ladder-like polymer main chain; to describe the variations in yield, intrinsic viscosity, solubility, crystallinity, and thermostability with monomer ratio; and to elaborate for the first time the structural and property modification induced by copolymerization of *p*-phenylenediamine (PPDA) with 2,3-xylylene diamine (XY).

## EXPERIMENTAL

The PPDA, XY, potassium persulfate, and DMSO and other solvents were used as received.

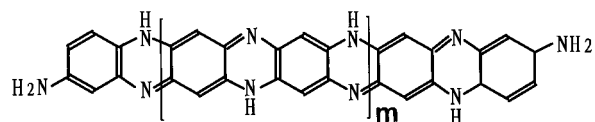
### Polymerization

Copolymers were prepared by oxidative polymerization of two monomers according to an earlier report.<sup>3</sup> A typical procedure for the preparation of PPDA/XY (90/10) copolymer is as follows: 1.779 g (16.4 mmol) of PPDA and 0.223 mL (1.84 mmol) of XY were added to 125 mL of a 1.36M HCl solution in a 250-mL glass flask in a water bath at 25°C. Potassium persulfate (3.8 g, 14.1 mmol) was dispersed in 40 mL of 1M HCl to prepare an oxidant solution. The monomer solution was magnetically stirred and treated with the oxidant solution added dropwise at a rate of one drop every 3 s for about 1 h (the total molar ratio of monomer/oxidant = 1.3/1.0). In order to compare the difference in the way that the monomer and oxidant solution were added, 0.889 g (8.2 mmol) of PPDA in 60 mL of 1.36M HCl aqueous solution was added dropwise to a mixture of 0.1115 mL (0.92 mmol) of XY and 1.9 g (7 mmol) of potassium persulfate in 40

mL of 1.36M HCl aqueous solution in a 125-mL glass flask in a water bath at 30.5°C for about 30 min. Immediately after the initial 3 min of adding the reactants, the reaction solution turned light violet and then black for the two methods. This solution turned dark black after the reactant solution was completely added. The solution temperature increased slightly during the addition of the oxidant or PPDA solution. The reaction mixture was vigorously stirred with a magnetic stirrer for 24 h at 25 or 30°C. The copolymer HCl salt was isolated from the reaction mixture by filtration and washed with water to remove the oxidant and oligomers. The HCl salt was subsequently neutralized in 100 mL of 0.2M NH<sub>4</sub>OH for 24 h to obtain the copolymer base. This base was washed with excess water. Blackish violet copolymers weighing 0.4 and 0.1 g were obtained with yields of 21 and 10% when adding the oxidant and PPDA solutions, respectively, which exhibited the nominal structure found in Scheme 1. Based on the results reported earlier,<sup>3</sup> the chain structure of PPDA homopolymer could be as shown in Scheme 2.

### Measurements

The intrinsic viscosity for the polymers in DMSO was measured with an Ubbelohde viscosimeter at 25°C. The solubility of the polymers was characterized using the following method. A 5-mg polymer powder sample was added to 0.5 mL of solvent and dispersed thoroughly. After the mixture was continuously lightly shaken for 24 h at room temperature, the solubility of the polymers was determined semiquantitatively. IR spectra were



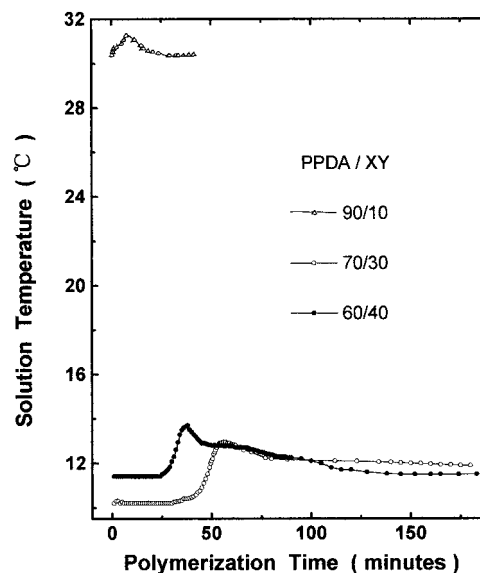
Scheme 2

recorded on a Nicolet Magna FTIR 550 spectrometer at  $2\text{ cm}^{-1}$  resolution on KBr pellets. The  $^1\text{H-NMR}$  spectrum was obtained in deuterated DMSO for the PPDA homopolymer and in deuterated TFA for the PPDA/XY (90/10) copolymer using a Bruker MSL-300 spectrometer operated at 300.13 MHz. The deuterated TFA for the  $^1\text{H-NMR}$  measurement of the PPDA/XY (90/10) copolymer was used to prevent the interference of the methyl groups in DMSO. Wide-angle X-ray diffractograms were recorded using Rigaku RAX-10 diffractometry with monochromatized  $\text{CuK}\alpha$  ( $\lambda = 0.1541\text{ nm}$ ) radiation operated at 30 kV and 20 mA in a reflection mode. The scanning rate was  $8^\circ/\text{min}$ . The precision for the measurement of the Bragg angle was  $0.01^\circ$ . Thermogravimetry (TG) was carried out at a heating rate of  $10^\circ\text{C}/\text{min}$  in nitrogen (10 mL/min) and in static air with sample sizes of 0.91–1.04 mg for the PPDA homopolymer and 0.74–0.77 mg for the PPDA/XY (90/10) copolymer using a Netzsch-Geratebau GmbH thermal analyzer (TG 209).

## RESULTS AND DISCUSSION

### Synthesis of PPDA Homopolymer and Its Copolymer with XY

The homopolymerization of PPDA and its copolymerization with XY with potassium persulfate as an oxidant in HCl aqueous solution at ambient temperature for 24 h afforded black precipitates as products. The progress in the copolymerization reaction was followed by testing the solution temperature and observing the solution color. The variation of the polymerization solution temperature with polymerization time is shown in Figure 1. We found that when dropping the oxidant solution slowly and regularly the polymerization solution temperature remained almost constant at the starting temperature for about 27 min, then it increased rapidly up to the highest temperature, and finally decreased and reached a nearly constant temperature. The highest temperature a polymerization solution can reach depends on the starting solution temperature (Fig. 1). The enhancement of the solution temperature is generally  $2.5\text{--}3^\circ$ . The PPDA/XY (70/30) polymerization solution turned green with a polymerization time of 32 min, it turned black at 35 min, and it turned blackish violet at 52 min. The variation of the reaction solution color for PPDA/XY (60/40) copolymerization was very similar. The appearance of a black solution implies the forma-

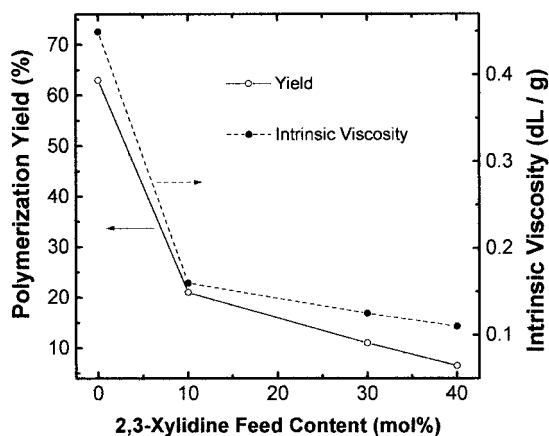


**Figure 1** The variation of the polymerization solution temperature with the polymerization time during the oxidative copolymerization of *p*-phenylenediamine (PPDA) with 2,3-xylydine (XY) with the PPDA/XY molar ratios of ( $\Delta$ ) 90/10 by adding the PPDA solution dropwise, ( $\circ$ ) 70/30, and ( $\bullet$ ) 60/40 by adding a potassium persulfate solution dropwise.

tion of copolymer. These phenomena demonstrated that the induction period of the copolymerization was about 27 min, the copolymerization was exothermic, and the polymerization reached the fastest rate at a reaction time of about 30 min and a steady slower rate after 80–100 min. The longer induction period of polymerization and smaller temperature enhancement of the reaction solution were because of the slower adding rate of the oxidant solution and lower reactivity of the XY monomer.

The polymerization yield decreased dramatically when adding 10 mol % XY monomer first and then decreased continuously and slowly with increasing XY feed content from 10 to 40 mol %, as shown in Figure 2. The copolymerization yield of *o*-phenylenediamine (OPDA)/XY was also found to be lower than the OPDA homopolymer yield.<sup>8</sup> It appears that XY and its oligomers acted as anticatalysts for the polymerization of PPDA or OPDA, which was possibly due to the steric hindrance of the two methyl groups on the XY monomer.<sup>9</sup>

The intrinsic viscosity of the PPDA/XY polymers was also significantly influenced by the monomer ratio. As shown in Figure 2, the intrinsic viscosity decreased from 0.45 to 0.15 dL/g with increasing XY feed content from 0 to 10 mol %,



**Figure 2** The variation of the polymerization yield and polymer intrinsic viscosity with the 2,3-xylidine (XY) feed content in the *p*-phenylenediamine (PPDA) with XY copolymers.

which was probably due to the low polymerization reactivity of XY in the reaction condition, reducing the propagation ability of the polymer molecular chains.

It appears that the yield and intrinsic viscosity at 0% XY were determined by the polymerization condition; but at 10, 30, and 40% XY they were determined by the XY concentration in addition to the polymerization condition because there was a linear relationship between the yield/viscosity and XY concentration, which is shown in Figure 2. It seems that the PPDA homopolymer could be terminated by the XY unit. Note that some polymer did form when a PPDA solution was added dropwise to a mixture solution of XY/potassium persulfate with a relatively low yield. This implied that the PPDA homopolymer terminated by the XY unit could copolymerize further with the PPDA monomer.

### Solubility of PPDA Homopolymer and Its Copolymer with XY

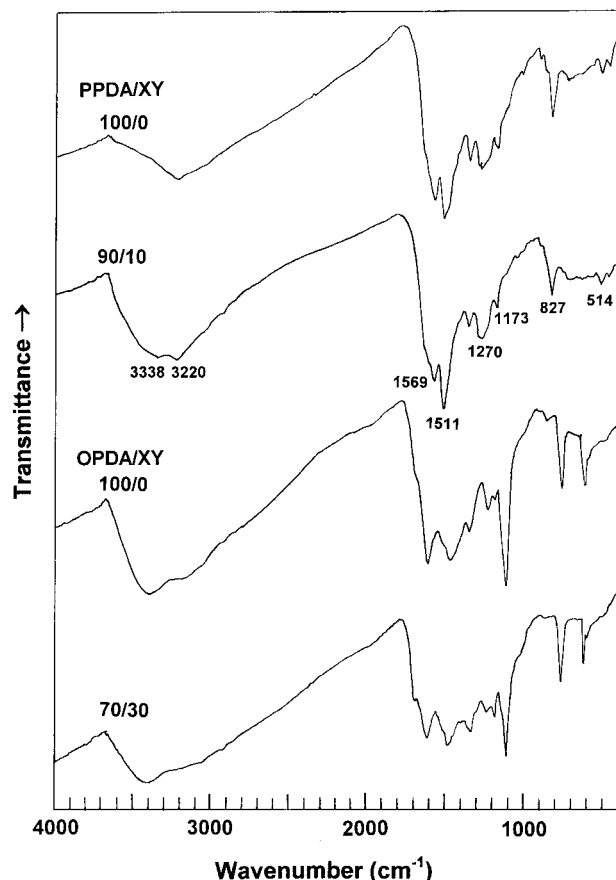
When the polymer concentration was about 1 g/100 mL solvent, the PPDA homopolymer was almost completely soluble in NMP and mainly soluble in DMSO. With inducing 10 mol % of the XY unit, the solubility of the PPDA/XY copolymer in DMSO and TFA became much better. However, when the XY feed content reached 30–40 mol %, the PPDA/XY copolymers were nearly soluble in TFA and THF, mainly soluble in acetone, and partially soluble in chloroform, acetic acid, and ethylene chloride. The polymers were insoluble in tetrachloromethane and water, as shown in Table I. Obviously, the better solubility of the PPDA/XY copolymers resulted from the break in the rigid-rod-like ladder structure, the presence of a small amount of methyl substituents on the polymer chain, and an amorphous supermolecular structure that increased the distance between the macromolecular chains and then significantly reduced the interaction between the polymer chains. It should be noted that the enhanced solubility of the copolymers could be relative to their lower intrinsic viscosity. It can be concluded that the variation of copolymer solubility and yield was evidence that the polymerization product was indeed a copolymer containing the two monomers rather than a simple mixture of two homopolymers, because the XY monomer did not homopolymerize at the same reaction condition.<sup>8,9</sup> In addition, the fact that the PPDA monomer could be dissolved in water and the XY monomer was soluble in benzene suggested that these two monomers oxidatively polymerized into copolymers that were insoluble in water and slightly soluble in benzene. The PPDA/XY polymers exhibited poorer solubility than the OPDA/XY polymers, because the former consisted mainly of a ladder

**Table I** Solubility and Solution Color of *p*-Phenylenediamine (PPDA) and 2,3-Xylidine (XY) Copolymer Bases in Organic Solvents

Feed PPDA/XY (mol/mol)	Feed					Acetic		Ethylene		Benzene	CCl <sub>4</sub>
	NMP	DMSO	TFA	THF	Acetone	Acid	CHCl <sub>3</sub>	Chloride	Ethanol		
100/0	S	MS (B)	PS (B)	SS	IS	SS	SS	IS	IS	SS	IS
90/10	S	S	MS (B)	SS	IS	SS	SS	IS	IS	SS	IS
70/30	S	S	S (B)	MS (RV)	PS (RV)	PS (DV)	IS	IS	SS	IS	IS
60/40	S	S	S (B)	S (RV)	MS (RV)	PS (DV)	PS (RV)	PS (RV)	SS	SS	IS

IS, insoluble; MS, mainly soluble; PS, partially soluble; S, soluble; SS, slightly soluble. The letters in parentheses indicate the color of the polymer solution in the solvents: B, brown; RV, reddish violet; DV, deep violet.

The four solid polymers are black in color.



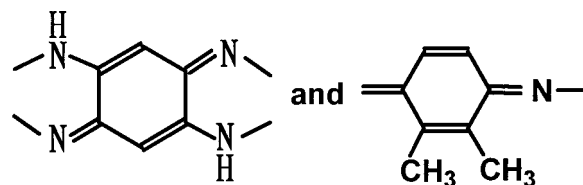
**Figure 3** FTIR absorption spectra of the polymers with the *p*-phenylenediamine (PPDA)/2,3-xylydine (XY) molar ratios of 100/0 and 90/10 and the *o*-phenylenediamine (OPDA)/XY molar ratios of 100/0 and 70/30.

structure with higher aromaticity while the latter consisted of a partial ladder structure with a lot of  $\text{—NH}_2$  groups.<sup>8</sup>

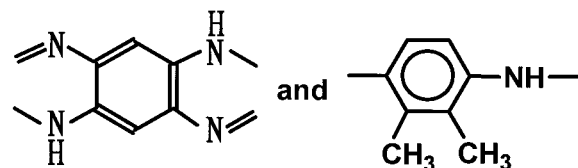
#### FTIR Spectra of PPDA Homopolymer and Its Copolymer with XY

FTIR spectra for the polymers with PPDA/XY molar ratios of 100/0 and 90/10 are shown in Figure 3. The FTIR spectra for the polymers with OPDA/XY molar ratios of 100/0 and 70/30 are also shown in Figure 3 for a convenient comparison.<sup>8</sup> Apparently, there were some differences between the FTIR spectra of the PPDA/XY and OPDA/XY polymers. A broad band centered at  $3338\text{ cm}^{-1}$  for PPDA/XY copolymer due to the characteristic free N—H stretching vibration suggested the presence of secondary amino groups ( $\text{—NH—}$ ).<sup>8</sup> Note that the PPDA homopolymer did not exhibit the absorption at  $3338\text{ cm}^{-1}$ , which was indicative that there were almost no free secondary amino

groups in the PPDA homopolymer chains. A broad band at  $3218\text{--}3220\text{ cm}^{-1}$  corresponded to the hydrogen-bonded N—H vibration and became stronger with added XY units. A very weak shoulder peak at  $3031\text{ cm}^{-1}$  for both PPDA/XY polymers might have been due to C—H stretching on the aromatic quinoxaline and xylydine rings. Two very weak peaks at  $2928$  and  $2857\text{ cm}^{-1}$  were observed for the PPDA/XY (90/10) copolymer and should have been due to C—H stretching on the methyl groups of the XY units. This result suggested that there were indeed XY units in the polymer chains. Two shoulder peaks at  $1608$  and  $1638\text{ cm}^{-1}$  and two sharp peaks in  $1511\text{--}1570\text{ cm}^{-1}$  were associated with C—C stretching on the aromatic rings. It is believed that the peak at  $1569\text{--}1570\text{ cm}^{-1}$  is assigned to the following quinoid ring<sup>3–5</sup>:



and that at  $1511\text{ cm}^{-1}$  is assigned to the benzenoid ring:



The fact that the peak at  $1569\text{--}1570\text{ cm}^{-1}$  showed nearly the same peak area as the peak at  $1511\text{ cm}^{-1}$  suggested the same quinoid and benzenoid units in the polymers. The peak at  $1511\text{ cm}^{-1}$  was the strongest in the FTIR spectra of the PPDA/XY polymers, but the peak at  $1111\text{--}1117\text{ cm}^{-1}$  was the strongest for the OPDA/XY polymers. On the other hand, the difference between the wave numbers of the two peaks at  $1569\text{--}1570$  and  $1511\text{ cm}^{-1}$  was  $58\text{--}59\text{ cm}^{-1}$ , which was much smaller than the difference ( $132\text{--}142\text{ cm}^{-1}$ ) between the wave numbers of the two peaks at  $1613\text{--}1616$  and  $1474\text{--}1481\text{ cm}^{-1}$ . These results indicated an apparent structure difference between PPDA/XY and OPDA/XY polymers. A medium peak at  $1346\text{--}1349\text{ cm}^{-1}$  was attributable to the C—N stretching vibration in quinoid imine units and became weaker with added XY units. Broad peaks at  $1270$ ,  $1286$ , and  $1293\text{ cm}^{-1}$  were

**Table II** Assignments for IR Absorption Bands for PPDA/XY and OPDA/XY Polymers

Polymer	H—H ( $\text{cm}^{-1}$ )	Aromatic C—H ( $\text{cm}^{-1}$ )	Aliphatic C—H ( $\text{cm}^{-1}$ )	Quinoid C—C ( $\text{cm}^{-1}$ )	Benzenoid C—C ( $\text{cm}^{-1}$ )	Quinoid C—N ( $\text{cm}^{-1}$ )	Benzenoid C—N ( $\text{cm}^{-1}$ )
PPDA	3218 (b, s)	3031 (vw) 899 (s, sh) 825 (s)		1570 (s, sh)	1511 (s)	1346 (sh) 1169 (m)	1293 (m) 1286 (m)
PPDA/XY (90/10)	3338 (b, s) 3220 (b, s)	3031 (vw) 899 (s, sh) 827 (s)	2929 (vw) 2857 (vw)	1569 (s, sh)	1511 (s)	1349 (sh) 1173 (m)	1273 (m)
OPDA	3388 (b, s) 3180 (b)	3060 (vw) 1117 (s, sh) 858 (w) 764 (sh) 614 (sh)	2910 (vw) 2850 (vw)	1616 (s, sh)	1474 (s)	1352 (sh) 1189 (w)	1232 (sh)
OPDA/XY (70/30)	3401 (b, s) 3200 (b)	3050 (vw) 1111 (s, sh) 868 (w) 765 (sh) 619 (sh)	2910 (vw) 2850 (vw)	1613 (s, sh) 1695 (m)	1481 (s)	1339 (sh) 1187 (m)	1238 (w)

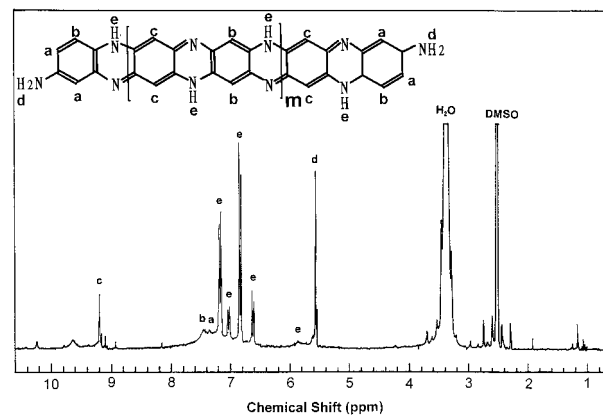
b, broad; m, medium; s, strong; sh, sharp; vw, very weak; w, weak

ascribed to the C—N stretching in the benzenoid unit. A weak peak at 1169–1173  $\text{cm}^{-1}$  might be ascribed to the C=N stretching in the quinoid unit. There was no adsorption at about 1115  $\text{cm}^{-1}$ , suggesting that there was no 1,2,4-trisubstituted benzene ring in the PPDA/XY polymers. This is quite different from OPDA/XY polymers.<sup>8</sup> A much stronger peak at 825–827  $\text{cm}^{-1}$  for PPDA/XY polymers than the peak at 858–868  $\text{cm}^{-1}$  for OPDA/XY polymers was observed, which was due to the C—H out of plane bending vibration of the 1,2,4,5-tetrasubstituted benzene ring. The peak at 825–827  $\text{cm}^{-1}$  became weaker when adding XY units. These results indicated that the PPDA/XY polymers consisted mainly of a ladder structure with a continuous quinoxaline ring from the PPDA monomer. The assignments for the IR absorption bands for the PPDA/XY and OPDA/XY polymers are summarized in Table II.

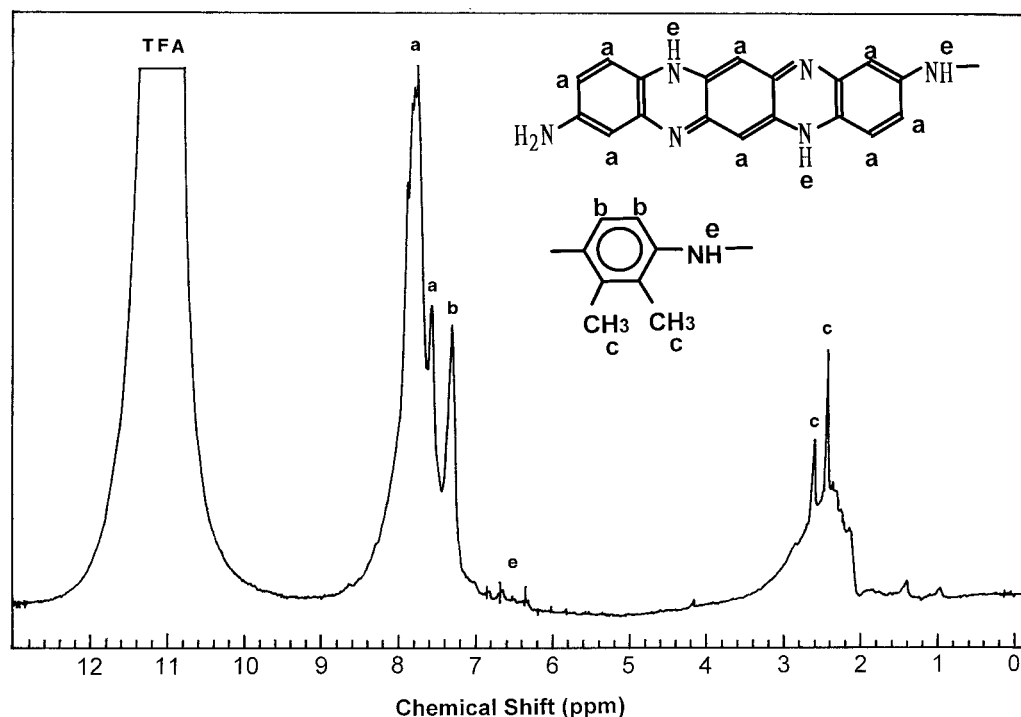
#### <sup>1</sup>H-NMR Spectra of PPDA Homopolymer and Its Copolymer with XY

<sup>1</sup>H-NMR spectra of the PPDA homopolymer and PPDA/XY copolymer are shown in Figures 4 and 5. We found the spectra to be quite different from each other. The <sup>1</sup>H-NMR spectrum of the PPDA homopolymer was characterized by four major signals, which exactly corresponded to the four

types of protons on the polymer chains. The <sup>1</sup>H-NMR spectrum of the PPDA polymer exhibited the sharpest peak at 5.55 ppm due to —NH<sub>2</sub> end groups; a weak broad peak centered at 5.84 ppm and four doublets at 6.58, 6.61, 6.81, 6.83, 6.99, 7.02, 7.14, and 7.17 ppm due to —NH— groups; two broad weak peaks centered at 7.35 and 7.44 ppm; and the weak peaks at 9.17 and 9.62 ppm due to the protons on 1,2,4,5-tetrasubstituted benzene rings. This spectrum provided information on the evaluation and calculation of the num-



**Figure 4** A <sup>1</sup>H-NMR spectrum of *p*-phenylenediamine homopolymer (numbers of summation = 864) in deuterated DMSO at 300.13 MHz.



**Figure 5**  $^1\text{H-NMR}$  spectrum of copolymers with a *p*-phenylenediamine (PPDA)/2,3-xylidine (XY) molar ratio of 90/10 (numbers of summation = 512) in deuterated trifluoroacetic acid (TFA) at 300.13 MHz.

ber-average degree of polymerization. It is found from Figure 4 that the area ratio of  $-\text{NH}-$  and  $-\text{NH}_2$  proton peaks to aromatic proton peaks is 1.89. Thus, there was a relationship between the area ratio and number-average degree of polymerization for the PPDA homopolymer with the macromolecular chain structure shown in Scheme 2, which is expressed as follows:

$$1.89 = [8 + 4m]/[6 + 2m] \quad (1)$$

where  $m = 15$ ; therefore,

$$(\text{DP})_n = 3 + 2m = 33 \quad (2)$$

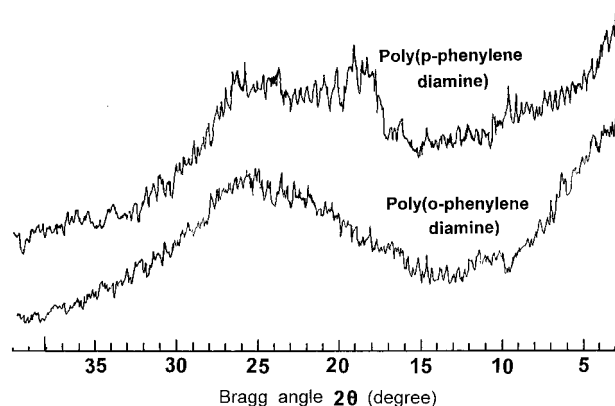
Another calculating method for the estimation of the number-average degree of polymerization  $[(\text{DP})_n]$  for the PPDA homopolymer is end-group analysis. According to this method, the  $(\text{DP})_n$  can be roughly calculated by the following equation:

$$(\text{DP})_n = \frac{[-\text{NH}- \text{ peak area} + (-\text{NH}_2 \text{ peak area}/4)]}{(-\text{NH}_2 \text{ peak area}/4)} \quad (3)$$

The value of  $(\text{DP})_n$  calculated through eq. (3) is also 33.

Additionally, the  $^1\text{H-NMR}$  spectrum of the PPDA homopolymer reported in this article is different from that in Cataldo's study<sup>3</sup> because the sharpest peak at 5.55 ppm due to  $-\text{NH}_2$  end groups, as well as the two sharpest doublets at 6.81, 6.83, 7.14, and 7.17 ppm due to  $-\text{NH}-$  groups, became broader in the spectrum in that study.<sup>3</sup> On the contrary, the strongest and broadest peak centered at 4.5 ppm due to  $-\text{NH}-$  and  $-\text{NH}_2$  protons and a small peak at 7.85 ppm reported by Cataldo<sup>3</sup> were not observed in the spectrum in the present article. A possible explanation was that the molecular weight of our PPDA homopolymer was higher than that in Cataldo's study,<sup>3</sup> thus causing much smaller peaks from  $-\text{NH}-$  and  $-\text{NH}_2$  protons. The higher resolution of the spectrum in our study was ascribed to the higher magnetic frequency (300.13 MHz) than that used in the literature (200 MHz).<sup>3</sup>

The  $^1\text{H-NMR}$  spectrum of the PPDA/XY (90/10) copolymer shown in Figure 5 was characterized by four main signals, which corresponded to the four types of protons on the polymer chains. Two



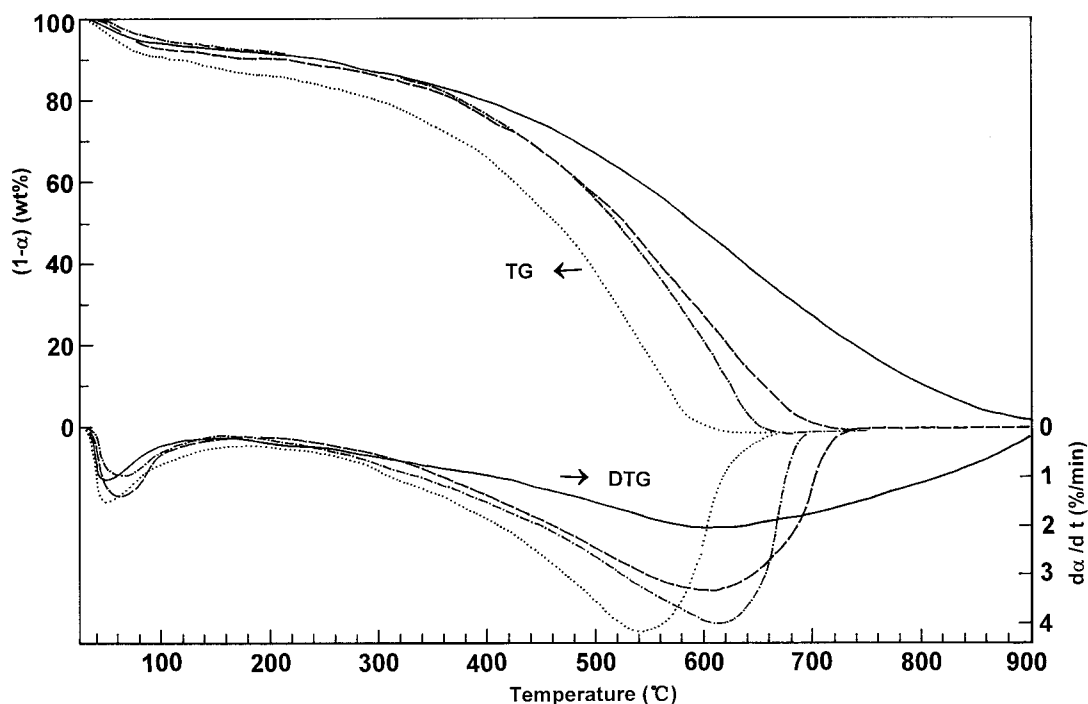
**Figure 6** Wide-angle X-ray diffraction diagrams of the powders of poly(*p*-phenylenediamine) (upper) and the poly(*o*-phenylenediamine) (lower).

medium peaks centered at 2.404 and 2.587 ppm were attributed to two kinds of the methyl groups on the XY units, the weakest peak at 6.2–7.1 ppm was due to —NH— groups, a sharp peak at 7.291 ppm was due to aromatic protons on the XY units, and the two strongest peaks centered at 7.555 and 7.742 ppm were due to two types of aromatic protons on the quinoxaline units formed by PPDA monomer through oxidative polymerization. No

resonance peak for —NH<sub>2</sub> protons was observed because these protons exchanged with deuterated TFA.<sup>8</sup> Therefore, it was difficult to calculate the number-average degree of polymerization of the PPDA/XY (90/10) copolymer from Figure 5. However, this spectrum was quite informative for the calculation of the actual monomer ratio. Through a comparison of the area of the phenyl protons on the quinoxaline unit from the PPDA monomer and the methyl protons on the XY units, the actual PPDA/XY molar ratio in the copolymer was found to be 89/11 for a feed ratio of 90/10. This means that the actual XY content in the copolymer was nearly the same as the feed XY content. A very similar result was observed for the OPDA/XY (70/30) copolymer.<sup>8</sup>

#### Wide-Angle X-Ray Diffractograms of Polymers

Wide-angle X-ray diffractograms of PPDA and OPDA homopolymer powders are shown in Figure 6. Two homopolymers appeared to exhibit the strongest diffraction intensity at  $2\theta \leq 3^\circ$  and a medium broad peak centered at  $2\theta = 25^\circ$ , which is characteristic of the diffraction by an amorphous polymer. Note that the PPDA homopolymer



**Figure 7** Thermogravimetry (TG) and derivative thermogravimetry (DTG) traces of (—) the base powders of *p*-phenylenediamine (PPDA) homopolymer in nitrogen, (---) the PPDA homopolymer in air, (- · -) PPDA/2,3-xylydine (XY) (90/10) in nitrogen, and (· · ·) PPDA/XY (90/10) in air at a heating rate of 10°C/min.



**Table III Thermal Stability of Polymers from *p*-Phenylenediamine (PPDA) with 2,3-Xylidine (XY) at Monomer : Potassium Persulfate Ratio of 1 : 1 in 1M HCl for 28 h at 23–25°C**

Feed PPDA/XY (mol/mol)	$T_d$ (°C)	$T_{dm}$ (°C)	$(d\alpha/dt)_m$ (%/min)	Char Yield at 600°C (wt %)	$E$ (kJ/mol)	$n$	$\ln Z$ ( $\text{min}^{-1}$ )
In nitrogen							
100/0	436	603	2.1	47	19	0.7	-0.7
90/10	452	614	4.0	24	25	0.1	0.4
In air							
100/0	429	601	3.3	27	25	0.4	0.5
90/10	418	540	4.2	2.0	29	0.3	1.5

showed an additional strong peak centered at  $2\theta = 19^\circ$ . This result indicated that the supermolecular structure of the PPDA homopolymer was different than that of the OPDA homopolymer because they exhibited quite different macromolecular structures, which was verified by FTIR and NMR spectra.<sup>8</sup>

### TG Thermograms of Polymers

Figure 7 shows the TG and derivative (DTG) of PPDA/XY polymer powders in flowing nitrogen and static air. The polymers exhibited a two-stage weight loss. The initial weight loss of 5–9% may be explained by the evaporating of water molecules trapped by polymer chains. The second weight loss starting at about 300°C was attributable to the thermal degradation of polymer chains.

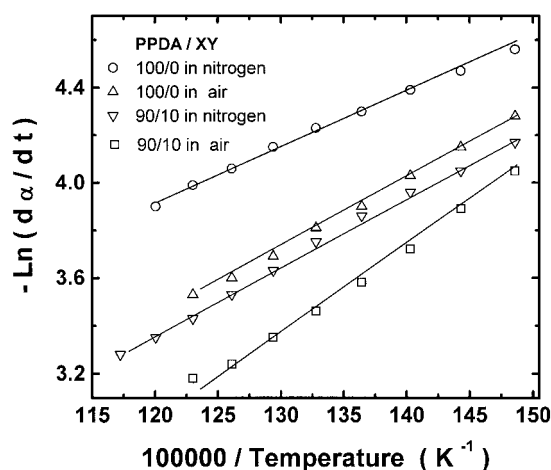
Table III shows the thermostable and kinetic parameters of the thermal degradation of the polymers. The thermal decomposition temperatures ( $T_d$ ) and the temperature at the maximum decomposition rate ( $T_{dm}$ ) of the PPDA/XY polymers were found to increase in nitrogen but decrease in air with an introduction of 10 mol % XY units. However, the maximum weight-loss rate  $(d/dt)_m$  increased and the char yield at 600°C decreased in both nitrogen and air with adding XY units. Note that the char yields at 600°C for the PPDA homopolymer were higher than 47 wt %, which could be valuable for the preparation of carbon composites.

The kinetic parameters of the thermal degradation for the polymers were calculated<sup>10–15</sup> through Figure 8 by the Friedman technique in eq. (4).

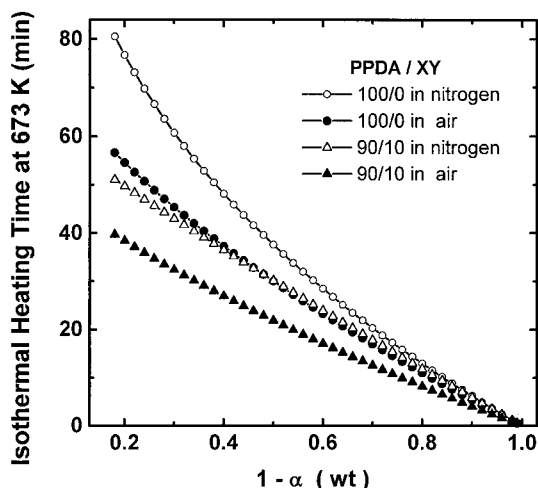
$$\ln(d\alpha/dt) = \ln Z + n \ln(1 - \alpha) - E/RT \quad (4)$$

where  $d\alpha/dt$  is the weight-loss rate,  $R$  is the gas constant (8.3136), and  $T$  is the absolute temperature. It can be seen from Table III that the activation energy  $E$  and frequency factor  $\ln Z$  values both increased but the decomposition order  $n$  decreased with introduced XY units. Note that the PPDA/XY polymers exhibited a lower decomposition temperature and a lower decomposition activation energy than the OPDA/XY polymers.<sup>8</sup> This result implied that PPDA/XY polymers were significantly less thermostable than OPDA/XY polymers,<sup>8</sup> possibly because of the lower molecular weight of the PPDA/XY polymers verified by NMR.

The predicted isothermal TG curves<sup>13–18</sup> for the PPDA/XY polymers on the basis of the average kinetic parameters listed in Table III are shown in Figure 9. We found that the estimated



**Figure 8** The Friedman method (plot of  $d\alpha/dt$  vs.  $1/T$ ) for the calculation of the activation energy of the thermal degradation of the PPDA homopolymer in (○) nitrogen and (△) air and PPDA/XY (90/10) in (▽) nitrogen and (□) air.



**Figure 9** The predicted isothermal thermogravimetry at 673 K based on the average kinetic parameters listed in Table III for the polymers with PPDA/XY molar ratios of (○) 100/0 and (△) 90/10 in nitrogen and (●) 100/0 and (▲) 90/10 in air through the following equation:

$$\text{heating time} = [1 - (1 - \alpha)^{1-n}] \times \exp(E/RT)/[Z(1-n)] \quad (n \neq 1)$$

isothermal stability at 673 K for the PPDA/XY polymers decreased in the order 100/0 in nitrogen > 100/0 in air > 90/10 in nitrogen > 90/10 in air. The PPDA/XY (100/0) polymer exhibited 80% weight loss after a heating time of 80 min at 673 K in nitrogen, but the PPDA/XY (90/10) copolymer showed 80% weight loss after a shorter heating time of 40 min at the same temperature in air.

## CONCLUSIONS

PPDA could be polymerized into an amorphous ladder polymer-polyquinoxaline with medium yield by the oxidation polymerization method with potassium persulfate as the oxidant at room temperature, but when 10–40 mol % XY was added, PPDA and XY polymerized to copolymers with much lower yield and lower intrinsic viscosity because of the anticatalyst activity of XY to the oxidative polymerization of PPDA. The poly-

merization yield and intrinsic viscosity of the polymers were linearly correlated with the feed XY concentration. The PPDA homopolymer might have been terminated by the XY unit. The PPDA/XY polymers exhibited very different molecular and supermolecular structures and thermal decomposition characteristics as compared with OPDA/XY polymers based on their FTIR and NMR spectra, wide-angle X-ray diffractograms, and TG analyses. The number-average degree of polymerization was 33 for the PPDA homopolymer obtained. The actual PPDA/XY ratio of the copolymers exhibited better solubility, reduced thermostability, and increased decomposition rate as the XY unit was added.

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