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Polymer 42 (2001) 4099–4107

polymer

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Synthesis and characterization of *o*-phenylenediamine and xylidine copolymers

Xin-Gui Li[a,*], Mei-Rong Huang[a], Yuliang Yang[b]

[a]*Department of Polymer Materials Science & Engineering, College of Materials Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, People's Republic of China*

[b]*Department of Macromolecular Science, The Key Laboratory of Molecular Engineering of Polymers of the Ministry of National Education, Fudan University, Shanghai 200433, People's Republic of China*

Received 15 October 1999; received in revised form 14 March 2000; accepted 27 April 2000

Abstract

Chemically oxidative polymerization of *o*-phenylenediamine and 2,3-xylidine (XY) with three molar ratios was performed by using ammonium persulfate as an oxidant in boiling glacial acetic acid. The polymerization yield decreases significantly but the intrinsic viscosity of the polymers remains almost constant with increasing feed content of XY monomer. The resulting polymers were characterized by ^{1}H-nuclear magnetic resonance, UV–vis and Fourier transform infrared spectroscopies, wide-angle X-ray diffraction, and thermogravimetry methods. The results showed that the polymers are amorphous and exhibit a thermal decomposition temperature higher than 500°C, the maximum weight-loss rate lower than 5%/min in nitrogen and air. Char yield at 700°C for the polymers is larger than 32 wt% in nitrogen but nearly zero in air. The activation energy, order, and frequency factor of thermal decomposition for the copolymers were 43–53 kJ/mol, 0.4–1.3, and 13.5–181.3 min^{-1} in nitrogen and air. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*o*-phenylenediamine); 2,3-xylidine copolymer; Thermally oxidative polymerization

1. Introduction

Chemically oxidative polymerization has easily yielded various functional polymers. Typical polymers are polyaniline, polytoluidine, polypyrrole, polyaminopyridine, and polyphenylenediamine, showing high conductivity. Among them, polyphenylenediamine homopolymer has attracted attention recently because it has been reported to be a highly aromatic ladder and a partly ladder polymer containing the 2,3-diaminophenazine or quinoxaline repeat unit, and shows unusually high thermostability [1–3]. However, the conductivity and solubility of the phenylenediamine homopolymer are low [1–3]. It was reported that the solubility of polyphenylenediamine depends on solvent composition and on the oxidant that was used for polymerization. The polymerization of three phenylenediamine isomers was carried out using hydrogen peroxide as an oxidant and horseradish peroxidase as a catalyst in 1,4-dioxane and water mixture, and better solubility was found in NMP and DMF [4]. Note that the polyphenylenediamines obtained by horseradish peroxidase catalysis have considerable amounts of azo linkages [4], thus decreasing thermal stability. To improve the solubility and solution processability of the *o*-phenylenediamine (PDA) polymer and to retain the partly ladder phenazine-like structure and high thermostability, copolymerization of *o*-phenylenediamine (PDA) with 2,3-xylidine (XY) might be one of the best methods. However, no report about such copolymerization has been found until now.

Investigation on the X-ray diffraction and thermal degradation of the PDA homopolymer and copolymer with XY has also not been reported. The purpose of this paper is to synthesize an easily soluble copolymer by introducing methyl groups in the rigid poly(*o*-phenylenediamine) main chain, to describe the variations in yield, intrinsic viscosity, crystallinity, and thermostability with monomer ratio, and to explicate the structural and property modification induced by copolymerization of PDA with XY in boiling glacial acetic acid, with ammonium persulfate as an oxidant.

2. Experimental

2.1. Reagents

o-Phenylenediamine, 2,3-xylidine, ammonium persulfate,

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* Corresponding author.
E-mail address: xin-gui.li@263.net (X.-G. Li).

PII: S0032-3861(00)00661-3

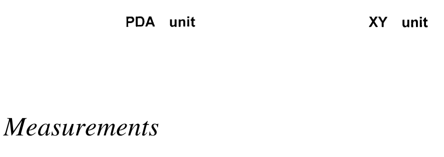
Table 1
Copolymerization of *o*-phenylenediamine (PDA) and 2,3-xylidine (XY) with monomer:ammonium persulfate of 1:3 in glacial acetic acid at 118°C for 72 h and their thermal stable parameters in a nitrogen flow at sample weight 1.0–1.1 mg

PDA/XY mol/mol	Polymn. yield (%)	Intrinsic viscosity (dl/g)	T_d (°C)	T_{dm} (°C)	$(d\alpha/dt)_m$ (%/min)	Char yield at 700°C (wt%)	E (kJ/mol)	n	ln Z (min^{-1})
In nitrogen									
100/0	96	0.12	562	677	2.7	39	43	1.0	2.6
90/10	72	0.13							
70/30	49	0.12	499	598	4.9	1	50	0.4	4.5
In air									
100/0	96	0.12	554	670	2.8	32	53	1.3	4.3
70/30	49	0.12	485	575	5.0	0	53	0.6	5.2

glacial acetic acid, dimethylsulfoxide, and other solvents were commercially obtained and used as received.

2.2. Polymerization

Polymers were prepared by oxidative polymerization according to Ref. [1]. A representative procedure for the preparation of the copolymer of *o*-phenylenediamine (PDA)/2,3-xylidine (XY) (70/30) is as follows: To 150 ml of glacial acetic acid at 40°C are added 1.54 g (0.014 mol) PDA and 0.73 ml (0.006 mol) XY in a 500 ml single-neck glass flask. 13.68 g (0.024 mol) ammonium persulfate [$(NH_4)_2S_2O_8$] was dissolved separately in 14 ml water to prepare an oxidant solution. The monomer solution was then stirred and treated with the oxidant solution added dropwise at an adding rate of one drop every three seconds for 30 min at 40°C (the total molar ratio: monomer/oxidant = 1/3). Immediately after the first few drops the reaction solution turns blue-violet. The reaction mixture was refluxed at 118°C for 72 h. The copolymer acetate was isolated from the reaction mixture by filtration and washed with an excess of distilled water to remove the oxidant and oligomers. A blackish violet solid powder was left to dry in ambient air for one week. The virgin copolymer of 1.2 g was obtained with a yield of ca. 49%. Deprotonation of the above virgin copolymers with excess 0.1 M NaOH aqueous solution at room temperature for 3 h gave a black powder. These copolymers exhibit the following nominal structure:



2.3. Measurements

The intrinsic viscosity for the polymers in DMSO was measured with an Ubbelodhe viscosimeter at 25°C. The solubility of the polymers was evaluated using the following method: polymer powder of 5 mg was added into 0.5 ml of the solvent and dispersed thoroughly. After the mixture was swayed continuously for 24 h at room temperature, the solubility of the polymers was characterized semi-quantitatively.

^{1}H NMR spectra were obtained in deuterated trifluoroacetic acid using a Bruker MSL-300 spectrometer operated at 300.13 MHz. ^{1}H NMR spectra in deuterated dimethylsulfoxide (DMSO-d_6) were obtained using a Bruker MSL-300 spectrometer operated at 300.13 MHz for virgin PDA homopolymer and using a Bruker AC200 spectrometer operated at 200 MHz for virgin PDA/XY (90/10) and (70/30) copolymers and for PDA/XY (100/0), (90/10), and (70/30) copolymers deprotonated by NaOH solution.

UV–vis spectra were recorded in dimethylsulfoxide on a Kontron Uvikon 860 spectrophotometer. IR spectra were recorded on a Nicolet Magna 550 FT-IR spectrometer made in USA, at 2 cm^{-1} resolution on KBr pellets. Wide-angle X-ray diffractograms were recorded using Rigaku RAX-10 diffractometry with monochromatized CuKα ($\lambda = 0.1541$ nm) radiation operated at 30 kV and 20 mA in a reflection mode. The scanning rate is 8°/min. The precision of the Bragg angle measurement is 0.01°. Thermogravimetry was carried out at a heating rate of 10°C/min in nitrogen (40 ml/min) and in static air with a sample size of 0.95–1.05 mg using a Netzsch-Geratebau GmbH Thermal Analyzer TG 209.

3. Results and discussion

3.1. Synthesis of the polymers from o-phenylenediamine and 2,3-xylidine

After copolymerization of *o*-phenylenediamine (PDA) and 2,3-xylidine (XY) with three molar ratios was carried out with ammonium persulfate as an oxidant in boiling glacial acetic acid for 72 h, a black precipitate was obtained as the product. It is found that the polymerization yield decreased from 96 to 49% with an increase in feed XY content from 0 to 30 mol%, as shown in Table 1. It appears that PDA easily homopolymerizes under the same polymerization condition, with the highest yield of 96%, and PDA is

Table 2
Solubility and solution color of *o*-phenylenediamine (PDA) and 2,3-xylidine (XY) polymers prepared at 118°C in organic solvents. S = soluble; MS = mainly soluble; PS = partially soluble; SS = slightly soluble; IS = insoluble. The letters in parentheses indicate the color of bipolymer solution in the solvents. BR = brown; B = black; G = gray. The color of the three solid polymers is black

PDA/XY (mol)	NMP	DMSO	TFA	Acetic acid	Benzene	Ethylene chloride	THF	$CHCl_3$	CCl_4	Acetone	Ethanol
100/0	S	S(BR)	MS(BR)	PS(B)	PS(B)	IS	SS(G)	SS(B)	SS(G)	IS	IS
90/10	S	S(BR)	S(BR)	MS(B)	PS(B)	PS(G)	SS(B)	PS(B)	PS(B)	PS(B)	SS(BR)
70/30	S	S(BR)	S(BR)	MS(B)	MS(B)	MS(B)	MS(B)	PS(B)	SS(B)	IS	IS

more polymerization reactive than XY. These results suggest 2,3-xylidine and oligo(2,3-xylidine)s act as an anticatalyst or anti-activator for the polymerization of *o*-phenylenediamine. This situation is nearly the same as that for the copolymerization of *o*-phenylenediamine with 2-pyrimidylamine (MA) [5].

Intrinsic viscosity of the copolymers remains nearly constant at 0.12 dl/g with the introduction of XY monomer, as listed in Table 1. The PDA/MA (90/10) copolymer shows the highest intrinsic viscosity of 0.26 dl/g. It can be seen that PDA/MA copolymers exhibit higher polymerization yield and larger intrinsic viscosity than the PDA/XY copolymers [5]. Therefore, MA monomer appears more copolymerizing reactive with the PDA monomer than the XY monomer. The lower polymerizing activity of the XY monomer could result from the greater spatial hindrance of two methyl groups on each XY monomer.

3.2. *Solubility of the polymers from o-phenylenediamine and 2,3-xylidine*

The PDA/XY polymers were almost completely soluble in NMP, DMSO, and trifluoroacetic acid at room temperature, but their solubility in other solvents exhibited an apparent composition dependency, as listed in Table 2. Among them, the PDA/XY (90/10) copolymer is mainly soluble in glacial acetic acid and PDA/XY (70/30) is mainly soluble in glacial acetic acid, benzene, ethylene chloride, and tetrahydrofuran.. In fact the solubility of the PDA/XY copolymers in most of the solvents in Table 2 gets better by introducing the XY unit in the poly(*o*-phenylenediamine) than in the PDA homopolymer and the PDA/MA copolymer [5]. Apparently, the good solubility of the copolymers results from the breaking of the regular semi-ladder chain structure containing the 2,3-diaminophenazine repeat unit. PDA/XY copolymers exhibit the same intrinsic viscosity and better solubility than the PDA homopolymer, suggesting that the solubility is primarily determined by molecular structure rather than by the intrinsic viscosity of the polymers [4,5].

In addition, better solubility was an evidence that the polymerization products were indeed copolymers containing the two monomer units rather than simple mixtures of two homopolymers [6].

3.3. *^{1}H NMR spectra of the polymers from o-phenylenediamine and 2,3-xylidine*

^{1}H NMR spectra of the virgin PDA/XY polymers in deuterated trifluoroacetic acid are characterized by three main signals, which correspond exactly to the three types of protons on the polymer chains, as shown in Figs. 1 and 2. The ^{1}H NMR spectra of the PDA/XY (100/0) and (70/30) polymers exhibit these three strong and sharp peaks at 6.851–6.8522, 6.883–6.892, and 6.933–6.942 ppm due to –NH-groups on the phenazine unit, the second strong broad peaks centered at 8.073, 8.126, 8.238, and 8.319 ppm ascribed to the aromatic protons on phenazine and disubstituted phenylene units, and the sharpest three singlets at 1.933–1.943, 1.993–1.996, and 2.182–2.191 ppm due to methyl groups on the XY unit for the PDA/XY copolymer and also on acetic acid (dopant) for the PDA homopolymer because the polymer products have not been deprotonated. The assignments of the NMR peaks of the copolymers are shown in Figs. 1 and 2 on the basis of a comparison of integrated peak areas and chemical shift of different protons.

Unfortunately, the spectrum of the PDA homopolymer in deuterated trifluoroacetic acid is less informative about the characterization of the number-average degree of polymerization of the PDA homopolymer because most of the NMR peaks from the –NH$_2$ on the polymer main chains disappear [1]. Note that the more active protons on –NH$_2$ will

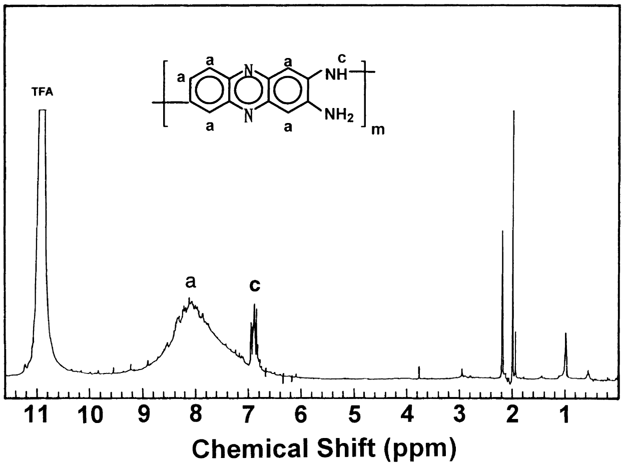


Fig. 1. ^{1}H NMR spectrum of virgin *o*-phenylenediamine (PDA) homopolymer (NS = 674) in deuterated trifluoroacetic acid at 300.13 MHz.

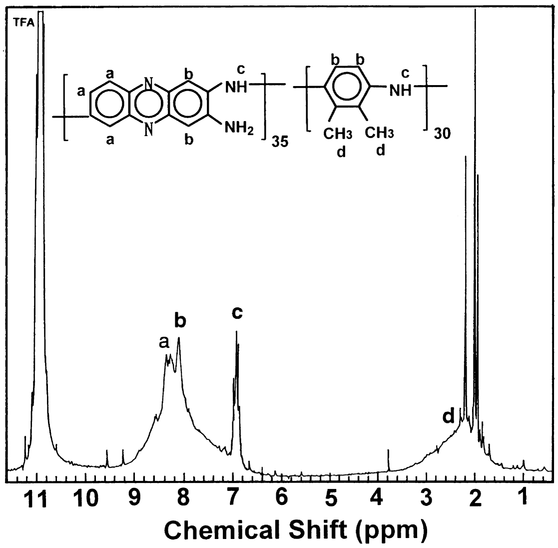


Fig. 2. ^{1}H NMR spectrum of the virgin polymer with *o*-phenylenediamine (PDA)/2,3-xylidine (XY) molar ratios of 70/30 (NS = 708) in deuterated trifluoroacetic acid at 300.13 MHz.

exchange with deuterated trifluoroacetic acid, but the calculation of the actual PDA/XY molar ratio in the PDA/XY (70/30, feed ratio) copolymer seems possible based on its NMR spectrum because the XY unit content could be calculated according to the area of the methyl protons. PDA unit content may be calculated by deducting the XY aromatic proton peak area from the total aromatic proton peak area. Based on this method, the PDA/XY molar ratio calculated from Fig. 2 is 72/28, which is very close to the feed ratio of 70/30. The slightly lower XY unit content than feed XY content could result from its lower polymerizing reactivity than the PDA monomer.

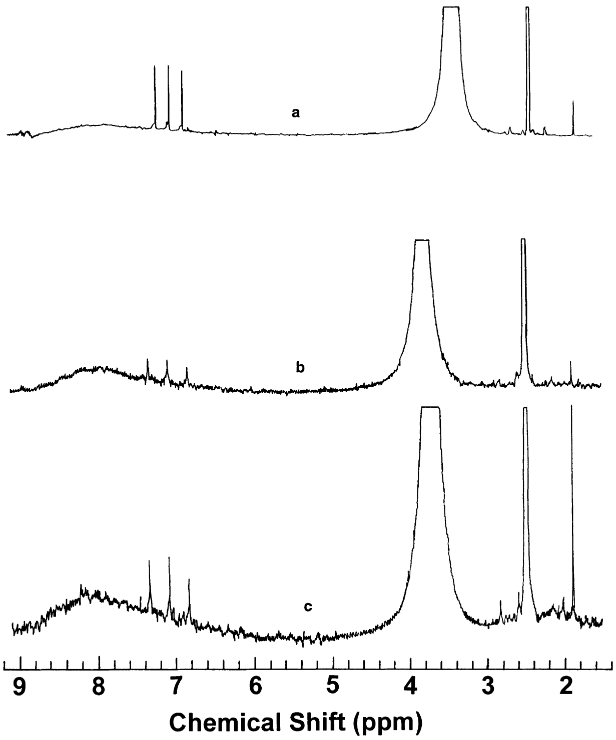


Fig. 3. ^{1}H NMR spectra in deuterated DMSO of the virgin polymers with *o*-phenylenediamine (PDA)/2,3-xylidine (XY) molar ratios of (a) 100/0 (NS = 128) at 300.13 MHz, (b) 90/10 at 200 MHz, and (c) 70/30 at 200 MHz.

In order to avoid the influence of trifluoroacetic acid on the NMR spectra, the ^{1}H NMR spectra of three virgin PDA/XY polymers in DMSO-d$_6$ were obtained and are shown in Fig. 3. Apparently, the same virgin PDA/XY polymers exhibit different ^{1}H NMR spectra in deuterated trifluoroacetic acid and DMSO-d$_6$ [5]. The aromatic proton peak at 6.5–9.0 ppm and methyl proton peak at 1.6–3.0 ppm in DMSO-d$_6$ are weaker and broader than those obtained in deuterated trifluoroacetic acid. Especially, the two strong singlets at 2.00 and 2.19 ppm in deuterated trifluoroacetic acid disappear completely upon using DMSO-d$_6$. A strong peak from the amino proton observed in deuterated trifluoroacetic acid becomes a triplet in DMSO-d$_6$. These difference should be due to the different interaction between the polymers and the two deuterated solvents. An additional factor could be the solubility of the homopolymer in the solvents. It has been found that the polymers are completely soluble in DMSO but only mainly soluble in trifluoroacetic acid, as listed in Table 2. It is reported that the number-average degree of polymerization of the PDA homopolymer could be evaluated and calculated on the basis of its NMR spectrum in DMSO-d$_6$ [5].

In the ^{1}H NMR spectra of the deprotonated polymers in DMSO-d$_6$(Fig. 4), there are only a broad peak between 6.2–9.0 ppm and a new and weak sharp doublet at 2.72 and

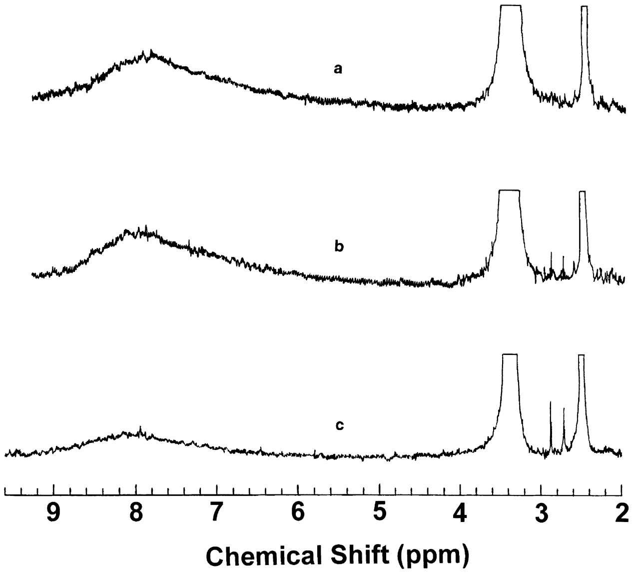


Fig. 4. ^{1}H NMR spectra in deuterated DMSO at 200 MHz for the deprotonated polymers with *o*-phenylenediamine (PDA)/2,3-xylidine (XY) molar ratios of (a) 100/0; (b) 90/10; and (c) 70/30.

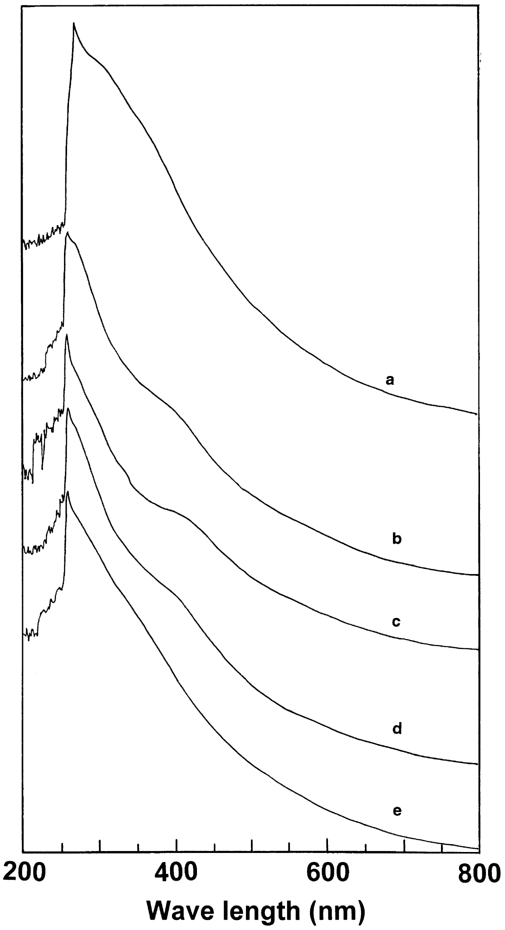


Fig. 5. UV–vis spectra of the copolymers of (a) virgin PDA/XY (90/10); (b) virgin PDA/XY (70/30); (c) deprotonated PDA/XY (100/0); (d) deprotonated PDA/XY (90/10); and (e) deprotonated PDA/XY (70/30) in DMSO.

2.88 ppm whose intensity becomes stronger with increasing XY unit content from zero to 30 mol%. Note that the medium triplet at 6.84, 7.10, and 7.35 ppm and a strong singlet at 1.91 ppm disappear upon deprotonation, which is similar to the result reported in Ref [1]. This implies that the amino proton can exchange with NaOH, and the singlet at 1.91 ppm is attributable to the methyl protons on the dopants (acetic acid).

3.4. UV–vis spectra of the polymers from o-phenylenediamine and 2,3-xylidine

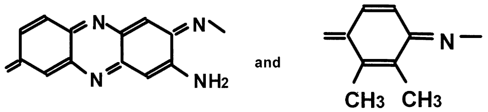
UV–vis spectra of the PDA/XY polymers in DMSO before and after deprotonation are compared in Fig.5. They all exhibit the strongest absorbance at 258–259 nm and a shoulder peak at 367–398 nm. The strongest peak remains almost at 258–259 nm regardless of polymer composition. These UV–vis spectra are different from those reported earlier [1] because there appears no absorbance between 500 and 700 nm. The absorbance at 258–259 nm could be ascribed to the quinonediimine-like phenazine units [3] (fully oxidative polyaniline–pernigraniline has the strongest absorbance at 273 nm). The smaller wavelength for PDA/XY copolymers as compared with polyaniline indicates a larger breakdown of the conjugation between repeat units [1].

It seems that the PDA homopolymer deprotonated with NaOH aqueous solution exhibits the strongest shoulder peak at about 393 nm. On the contrary, the PDA/XY (70/30) copolymer deprotonated with NaOH shows the weakest shoulder peak at about 367 nm. Obviously, with increasing XY unit content, the shoulder peak becomes weaker and shifts to a shorter wavelength on the basis of three spectra of the copolymers deprotonated by NaOH, and the content of the phenazine unit in the copolymer chains should decrease. Therefore, the shoulder peak could be due to the phenazine unit [1].

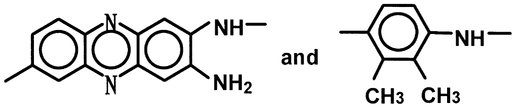
Upon deprotonation of the PDA/XY (70/30) copolymer with NaOH, only the shoulder peak shifts from ca. 398 to 367 nm. A similar phenomenon has been observed in the PDA homopolymer (protonated, 426 nm; deprotonated, 392 nm) [1].

3.5. FT-IR spectra of the polymers from o-phenylenediamine and 2,3-xylidine

Representative FT-IR spectra for the copolymers with PDA/XY molar ratios of 100/0 and 70/30 and PDA/MA (70/30) are shown in Fig. 6. A broad band centered at 3388–3401 cm^{-1} due to the characteristic free N–H stretching vibration suggests the presence of secondary amino groups (–NH–)[3]. A shoulder band at 3200 cm^{-1} corresponds to the hydrogen-bonded N–H vibration. A very weak shoulder peak at about 3050 cm^{-1} might be due to C–H stretching on aromatic phenazine and xylidine rings. Two very weak peaks at 2910 and 2850 cm^{-1} should be due to C–H stretching on the methyl groups of the xylidine units for the PDA/XY (70/30) copolymer and also acetic acid (dopant) for the PDA polymer. The two sharp IR absorptions in 1474–1695 cm^{-1} are associated with aromatic ring stretching. An additional absorption at 1695 cm^{-1} could be due to the 1,2,3,4-tetrasubstituted benzene ring of the xylidine unit [7] because the PDA homopolymer and the PDA/MA copolymer hardly ever exhibit this adsorption, but the aniline/2,3-xylidine (10/90) copolymer exhibits a medium adsorption at 1671 cm^{-1} [7]. It is believed that the peak at 1613–1616 cm^{-1} is assigned to the following quinoid ring



and the one at 1474–1481 cm^{-1} to the benzenoid ring.



The peak at 1613–1616 cm^{-1} is sharper but the peak at

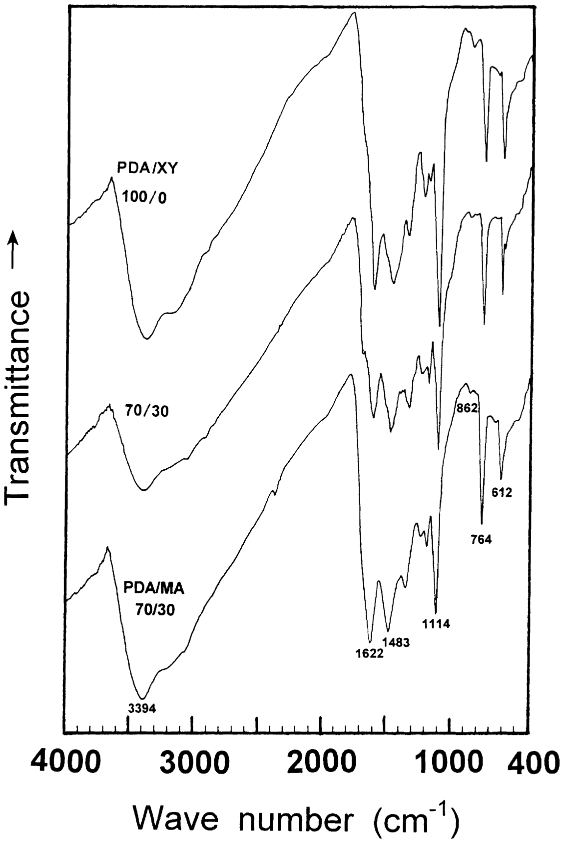


Fig. 6. FT-IR absorption spectra of the polymers with the *o*-phenylenediamine (PDA)/2,3-xylidine (XY) molar ratios of 100/0 (upper) and 70/30 (middle) and PDA/2-pyrimidylamine(70/30) copolymer (lower).

1474–1481 cm^{-1} is broader. The fact that the peak at 1613–1616 cm^{-1} shows nearly the same peak area as the peak at 1474–1481 cm^{-1} might suggest almost the same quinoid and benzenoid units in the copolymers. A weak peak at 1339–1352 cm^{-1} is attributable to the C–N stretching vibration in quinoid imine units. Two peaks at 1232–1238 and 614–619 cm^{-1} are ascribed to the C–N stretching in the benzenoid unit and out-of-plane bending vibration of the C–H bonds of the 1,2,4-trisubstituted benzene nuclei, respectively, and get weaker with introduction of the XY unit. With an increase in the XY unit content from 0 to 30 mol%, the IR absorption of the polymers exhibits a reduced intensity at 1111–1117 cm^{-1} and one at 858–868 cm^{-1}, which are due to the C–H in-plane bending vibration of 1,2,4-trisubstituted benzene ring and C–H out-of-plane bending vibration of the 1,2,4,5-tetrasubstituted benzene ring, respectively. These results indicate that the above mentioned four peaks are indeed attributed to the C–N and C–H vibrations of the substituted phenazine ring from the PDA monomer. Another two peaks at 1187–1189 and 764–765 cm^{-1} might be ascribed to the C–N stretching in the quinoid unit and the C–H out-of-plane bending of aromatic nuclei, respectively and get stronger with an introduction of the XY unit. Therefore, these two peaks should be due to both the aminophenazine unit and the xylidine unit. The assignments for the IR absorption bands for the PDA/XY and the PDA/MA polymers are listed in Table 3.

3.6. Wide-angle X-ray diffractograms of the poly(o-phenylenediamine-co-2,3-xylidine)

Wide-angle X-ray diffractograms of three PDA/XY polymer powders are shown in Fig. 7. The broad peak of the three diagrams is characteristic of the diffraction by an amorphous polymer. With increasing XY content, the PDA/XY polymers exhibit an increased Bragg angle of the major diffraction peak and a narrowed diffraction peak. Note that the intensity of the diffraction peak at a low Bragg angle of ca. 3° changed from the strongest to the lowest upon introducing XY unit content from 0 to 30 mol%. These results might demonstrate a quite different crystalline structure between the PDA homopolymer and the PDA/XY copolymers, suggesting that the polymers are actual copolymers of PDA and XY monomers rather than mixtures of two monomer homopolymers. The strongest diffraction peak at a low Bragg angle indicates that there is larger crystallite size in the PDA homopolymer, but an introduction of the XY unit makes the crystalline size smaller significantly and crystalline order better based on the narrowest major diffraction exhibited by the PDA/XY (70/30) copolymer. Introducing the XY unit into the PDA polymer will decrease both intermolecular chain spacing and amorphousness as compared with the PDA homopolymer despite the spatial hindrance of two methyl groups on each XY unit. Very similar variation in wide-angle X-ray diffraction diagrams was observed for the PDA/MA copolymer system [5].

3.7. Thermogravimetric analyses of the poly(o-phenylenediamine-co-2,3-xylidine)s

Figs. 8 and 9 show the thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of the PDA/XY polymer powders in flowing nitrogen and static air, respectively. The polymers exhibit two smaller weight-loss processes at 60 and 300–350°C and a single major decomposition starting at a temperature above 500°C in nitrogen and air. The first two losses should be due to water evaporation and thermal dedoping of the polymers (exclusion of acetic acid), respectively. The last, much greater loss is attributable to the thermal degradation of the polymer chains. Table 1 shows the stable and kinetic parameters of the thermal degradation of the polymers. It is found that three thermal decomposition temperatures (T_d and T_{dm}) and char yield at 700°C all decrease with introduction of the XY unit in nitrogen and air. The polymers exhibit an enhanced maximum weight-loss rate $(d\alpha/dt)_m$ with addition of the XY unit. These suggest that the XY unit is less thermostable, and displays a faster degradation rate and lower carbon-forming tendency than the aminophenazine unit. It is easily understood that the aminophenazine unit

Table 3

The assignments for the IR absorption bands for the PDA/XYand PDA/MA polymers. Abbreviations: b = broad; m = medium; s = strong; sh = sharp; vw = very weak; w = weak

Polymer	N–H/cm^{-1}	Aromatic C–H/cm^{-1}	Aliphatic C–H/cm^{-1}	Quinoid C–C/cm^{-1}	Benzenoid C–C/cm^{-1}	Quinoid C–N/cm^{-1}	Benzenoid C–N/cm^{-1}
PDA	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)
PDA/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)
PDA/MA (70/30)	3394(b,s) 3222(b)	3060(vw) 1114(s,sh) 862(w) 764(sh) 612(sh)		1622(s,sh)	1483(s)	1352(sh) 1188(m)	1236(w)

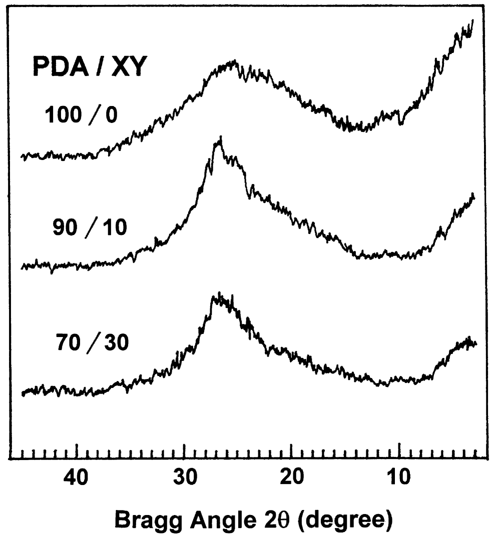


Fig. 7. Wide-angle X-ray diffraction diagrams of the copolymer powders with the *o*-phenylenediamine (PDA)/2,3-xylidine (XY) molar ratios of 100/0 (upper), 90/10 (middle), and 70/30 (lower).

possesses much more aromatics than the XY unit containing two methyl groups. Different thermostability was observed for the PDA/MA polymers [5].

The kinetic parameters of the thermal degradation for the copolymers are calculated [8–12] through Fig. 10 by the Friedman technique using Eq. (1)

$$\ln(\mathrm{d}\alpha/\mathrm{d}t) = \ln Z + n\ln(1-\alpha) - E/\mathrm{R}T \tag{1}$$

where $\mathrm{d}\alpha/\mathrm{d}t$ is the weight-loss rate that is obtained from the DTG curve; Z is the frequency factor of the degradation reaction; n is the degradation order; $1-\alpha$ is the residual weight of the sample at a certain temperature, which is obtained from the TG curve; E is the activation energy; and R and T are the gas constant and absolute temperature recorded on the thermogram, respectively. E and n values can be calculated from the plots of $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ or $\ln(1-\alpha)$ against reciprocal temperature. It can be seen that there is no regular dependency of activation energy E, decomposition reaction order n, and frequency factor $\ln Z$ values on the PDA/XY ratio. It should be noticed from Table 1 that the polymers possessing higher decomposition temperatures generally exhibit slightly lower activation energy and frequency factor of decomposition. The activation energy and frequency factor of thermal decomposition for the copolymers are larger in air than in nitrogen.

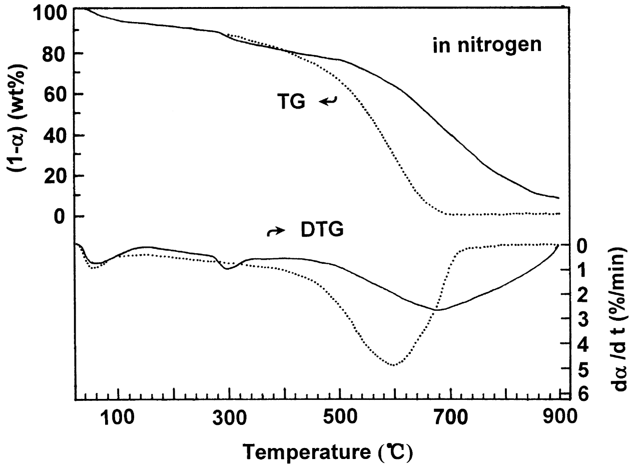


Fig. 8. Thermogravimetry (TG) and derivative thermogravimetry (DTG) of the polymer powders with the *o*-phenylenediamine (PDA)/2,3-xylidine (XY) molar ratios of 70/30 (···) and 100/0 (—) at a heating rate of 10°C/min in flowing nitrogen.

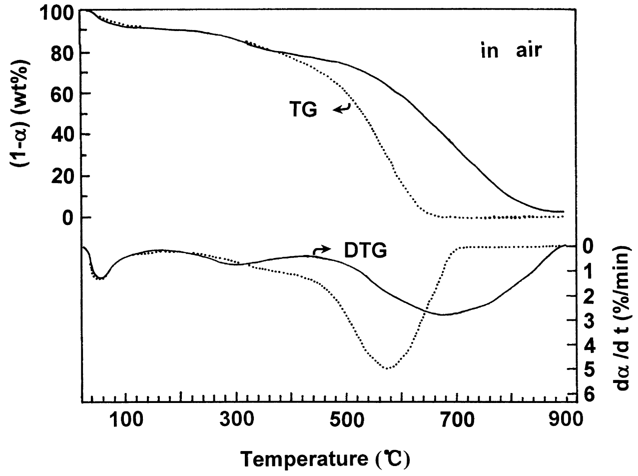


Fig. 9. Thermogravimetry (TG) and derivative thermogravimetry (DTG) of the polymer powders with *o*-phenylenediamine (PDA)/2,3-xylidine (XY) molar ratios of 70/30 (···) and 100/0 (—) at a heating rate of 10°C/min in static air.

3.8. Isothermal thermogravimetric thermograms of the copolymers

Fig. 11 is the isothermal TG curves at 400°C (673 K) predicted by the following equations, Eqs. (2) and (3), on

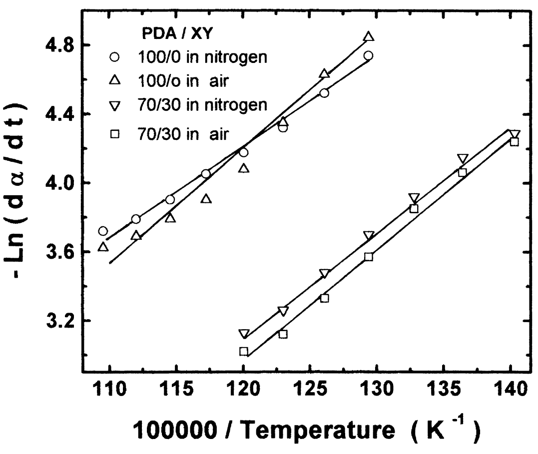


Fig. 10. The Friedman method (plot of $\mathrm{d}\alpha/\mathrm{d}t$ vs $1/T$) for calculation of the activation energy of the thermal decomposition of copolymer powders with *o*-phenylenediamine(PDA)/2,3-xylidine (XY) molar ratios of 100/0 (○) in nitrogen, 100/0 (△) in air, 70/30 (▽) in nitrogen, and 70/30 (□) in air.

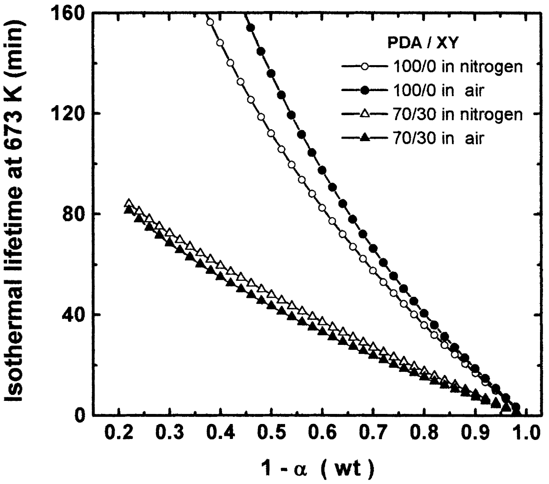


Fig. 11. Calculated isothermal TG curves for the copolymers with *o*-phenylenediamine (PDA)/2,3-xylidine (XY) molar ratios of 100/0 (○) and 70/30 (△) in nitrogen, and 100/0 (●) and 70/30 (▲) in static air based on the kinetic parameters listed in Table 1.

the basis of the kinetic parameters listed in Table 1 for non-isothermal degradation [13–15].

$$\text{Heating time} = [1 - (1 - \alpha)^{1-n}]\cdot\exp(E/\mathrm{R}T)/[Z(1 - n)] \times (n \neq 1) \qquad (2)$$

$$\text{Heating time} = [-\ln(1 - \alpha)]\cdot\exp(E/\mathrm{R}T)/Z\ (n = 1) \qquad (3)$$

The heating time is the lifetime of polymer to failure at the weight loss of α. It is found that the predicted TG curves are different as expected. The PDA/XY (100/0) polymer exhibits the highest and second highest isothermal stability in air and nitrogen, respectively. The PDA/XY (70/30) copolymer shows the third highest and lowest isothermal stability in nitrogen and air, respectively. The PDA/XY (100/0) polymer will lose 55 wt% after an isothermal heating time of 160 min in air but the PDA/XY (70/30) copolymer loses 80 wt% only after a heating time shorter than 80 min in air. These results might suggest that the PDA/XY (100/0) polymer is more isothermally stable in air than in nitrogen. However, a completely contrary phenomenon appeared for the PDA/XY (70/30) copolymer. This obvious difference of the isothermal stability for the two polymers could be due to the difference in their molecular structure. For example, two methyl groups on each XY unit will enhance the solubility of the polymers in common solvents, but the compromise is a significant reduction of the thermostability of the polymers.

4. Conclusions

o-Phenylenediamine and 2,3-xylidine can polymerize into a soluble amorphous copolymer with a high yield by oxidative polymerization for 72 h at 118°C in boiling glacial acetic acid. The polymers consist of the aminophenazine unit with quinoid and benzenoid formulae. The thermostability of the polymers decreases and the decomposition rate increases in both nitrogen and air with introduction of the XY unit. The PDA/XY copolymer shows a higher decomposition temperature, a larger char yield at 700°C, a slower maximum weight-loss rate, and a lower activation energy of decomposition in nitrogen compared with air.

Acknowledgements

The project is supported by the Phosphor Plan of Science Technology of Young Scientists of Shanghai China (98QE14027), by the National Natural Science Foundation of China (29804008), and by the Key Laboratory of Molecular Engineering of Polymers of Educational Ministry at Fudan University in Shanghai, China.

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