

Synthesis and Characterization of Poly(aniline-co-xylidine)s

Xin-Gui LI,[†] Mei-Rong HUANG, and Yuliang YANG*

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

*Department of Macromolecular Science, Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, People's Republic of China

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ABSTRACT: Copolymers were synthesized by oxidative polymerization of aniline and 2,3-xylylidine (XY) at five monomer ratios using ammonium persulfate as an oxidant in HCl medium. The yield and intrinsic viscosity of the copolymers were significantly dependent on monomer ratio. The copolymers were characterized by Fourier transform Infrared spectroscopy, ¹H nuclear magnetic resonance spectroscopy, wide-angle X-ray diffraction, DSC, and thermogravimetry. The results showed that the actual content of XY unit in the copolymers is much higher than feed XY unit content but 2,3-xylylidine cannot homopolymerize under the same condition. The copolymers are amorphous and exhibit thermal decomposition temperature higher than 395°C, char yield larger than 22 wt% at 900°C in nitrogen. The activation energy of thermal decomposition for the copolymers decreased monotonically from 124 kJ mol⁻¹ to 42 kJ mol⁻¹ with increasing XY unit content from 10 to 90%.

KEY WORDS Xylylidine Copolymer / Oxidative Copolymerization / Soluble Aniline Terpolymer / Nuclear Magnetic Resonance Spectrum / Thermostability / Degradation Kinetics /

Nitrogen-containing conductive polymers, polyaniline, polypyrrole, polyaminopyridine, and polypyridine, have attracted attention recently because they exhibit high gas separation ability¹ and lyotropic liquid crystalline behavior.² Polyaniline is the most attractive because of its easier preparation, higher air stability and highest oxygen / nitrogen separation factor up to 30.¹ Polyaniline is mainly soluble in a few organic solvents with high boiling point such as *N*-methyl-2-pyrrolidone (NMP), *N*, *N*-dimethylacetamide, and dimethylsulfoxide. Therefore, investigation on the structure and processability of polyaniline is difficult. It is important to prepare soluble polyaniline in common organic solvents. The purpose of this paper is to synthesize a soluble copolymer in chloroform, benzene, ethylene chloride, and tetrahydrofuran through introducing two methyl groups on the phenylene ring in rigid polyaniline main chain, discuss the variation in yield, intrinsic viscosity, crystallinity, thermostability with monomer ratio, and explain the structural and property modification induced by copolymerization of aniline (AN) with 2,3-xylylidine (XY), because no report about the copolymerization of AN with XY has been found hitherto.

EXPERIMENTAL

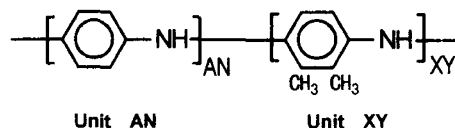
Reagents

Aniline, 2,3-xylylidine, ammonium persulfate, LiCl·H₂O, and *N*-methyl-2-pyrrolidone were commercially obtained and used as received.

Copolymerization

Copolymers were prepared by oxidative polymerization of two monomers by using a previously described method.³ A typical procedure for the preparation of the copolymer from aniline / 2,3-xylylidine (50/50) is as fol-

lows: To 200 mL of a 1 M HCl solution were added 60 g (0.5 mol) LiCl·H₂O, 9.4 mL (0.1 mol) aniline, and 12.3 mL (0.1 mol) 2,3-xylylidine in a 500 mL two-neck glass flask. Ammonium persulfate [(NH₄)₂S₂O₈] 11.4 g (0.1 mol) was dissolved separately in 100 mL 1 M HCl to prepare an oxidant solution. Both solutions were cooled in an ice/sodium chloride (2/1, wt) bath to -8°C. The monomer solution was then treated with the oxidant solution added dropwise at -8°C in *ca.* 2 h (the total molar ratio: monomer/oxidant = 1/4). Immediately after the first thirty drops the reaction solution turned blue-violet. The reaction mixture was vigorously stirred for 48 h at -8°C. The copolymer hydrochloride salt was isolated from the reaction mixture by filtration and washed with an excess of distilled water to remove the oxidant and oligomers. The hydrochloride salt was subsequently neutralized twice in 0.1 M ammonium hydroxide for 24 h to obtain the copolymer base. The copolymer base was washed with excess water. A blackish violet solid powder was left to dry in ambient air for one week. The copolymer of 2.3 g was obtained with the yield of *ca.* 9%. This copolymer exhibits the following nominal structure:



Measurements

The intrinsic viscosity for the copolymers in NMP was measured with a Ubbelohde viscosimeter at 25°C. The solubility of the polymers was evaluated using the following method: Polymer powder sample of 5 mg was added into the solvent of 0.5 mL and dispersed thoroughly. After the mixture was swayed continuously for

[†]To whom correspondence should be addressed (E-mail: Li_xingui@hotmail.com).

Table I. Copolymerization of aniline(AN) and 2,3-xylydine(XY) with monomer/ammonium persulfate of 4 / 1 in 1 M HCl and LiCl aqueous solution at -8°C for 48 h and their thermal stable parameters in a nitrogen flow

AN / XY	Polymn. Yield	Intrinsic viscosity	T_d	T_{dm}	$(d\alpha/dt)_m$	Char yield at 900°C	E	n	$\text{Ln } Z$	r^a
mol%	%	dL g^{-1}	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$\% \text{ min}^{-1}$	wt%	kJ mol^{-1}		min^{-1}	
100 / 0 ^b			430	520		60				
90 / 10	16	0.81	428	457,484	5.0, 6.0	35	124	2.9(1.6) ^c	19	0.993
70 / 30	12	0.79	427	455	3.9	—	—	—	—	—
50 / 50	9	0.70	416	454	4.5	27	121	2.8(1.7) ^c	20	0.989
30 / 70	6	0.65	395	455	4.8	31	79	1.8(1.1) ^c	12	0.994
10 / 90	2	0.20	418	455	3.4	23	42	1.8(1.0) ^c	4.4	0.998
0 / 100	0.1	—	—	—	—	—	—	—	—	—

^a r is linear correlation coefficient. ^b From ref 13. ^c Data were calculated by Kissinger equation based on the 2DTG curves.

24 h at room temperature, the solubility of the polymers was characterized semi-quantitatively. IR spectra were recorded on a Nicolet FT-IR 5DXC Spectrometer made in USA at 2 cm^{-1} resolution on KBr pellets. ^1H NMR spectra were obtained in deuterated chloroform using a Bruker MSL-300 spectrometer operated at 300.13 MHz. Wide-angle X-ray diffractograms were recorded using Rigaku RAX-10 diffractometry with monochromatized $\text{Cu-K}\alpha$ ($\lambda = 0.1541 \text{ nm}$) radiation operated at 30 kV and 20 mA in the reflection mode. The scanning rate was $8^{\circ} \text{ min}^{-1}$. The precision for the measurement of Bragg angle was 0.01° . Differential scanning calorimetry (DSC) measurement was performed using a DSC unit of a TA Instrument 2000 with the sample size of 6–8 mg. Thermogravimetry was carried out at a heating rate $10^{\circ}\text{C min}^{-1}$ in nitrogen (40 mL min^{-1}) with the sample size of 1.0–1.1 mg using a TGH Perkin-Elmer 7 series.

RESULTS AND DISCUSSION

Synthesis of Copolymers from Aniline and 2,3-Xylydine

The copolymerization of aniline and 2,3-xylydine with ammonium persulfate as oxidant in 320 mL 1 M HCl aqueous solution afforded black precipitates as products. Aniline and 2,3-xylydine at five monomer ratios copolymerized in 1 M HCl at -8°C for 48 h. Polymerization yield decreased linearly with increase in feed XY content from 10 to 100 mol%, as shown in Table I and Figure 1. The copolymerization yield of aniline with *o*-ethylaniline was found to be low, 16–20%.⁴ It appears that 2,3-xylydine hardly ever homopolymerizes under the same reaction conditions, although the polymerization solution became bluish-black after the stirring of 48 h. Similar results were observed for the homopolymerization of 2- and 3-cyanoanilines,⁵ nitro-aniline,⁵ 3-ethylaniline,⁶ 2-propylaniline,⁶ 2- and 3-fluoroanilines.⁷ Note that 2,3-xylydine is less homopolymerization-reactive than 3-ethylaniline and 2-propylaniline.⁶ These results suggest aniline and oligoanilines act as catalysts for the polymerization of 2,3-xylydine.⁵

Intrinsic viscosity of the copolymers was significantly influenced by the monomer ratio. As listed in Table I, the intrinsic viscosity decreased from 0.81 dL g^{-1} to 0.21 dL g^{-1} with increasing XY content from 10 mol% to 90 mol%, which is probably due to low polymerization reactivity of 2,3-xylydine in the reaction condition, reducing the propagation ability of copolymer molecular chains.

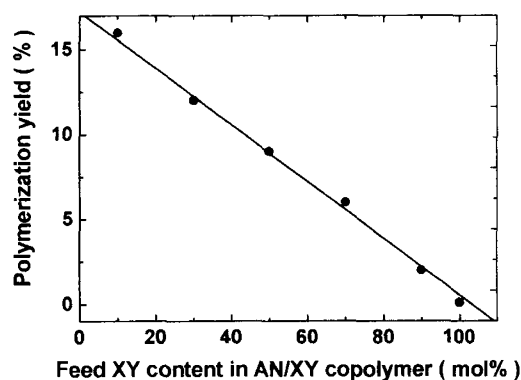


Figure 1. Dependency of polymerization yield of aniline (AN) with 2,3-xylydine (XY) on feed molar content of XY unit in the AN/XY copolymers with ammonium persulfate as oxidant in 1M HCl solution at -8°C for 48 h.

Solubility of the Copolymers

When the AN/XY polymer concentration was *ca.* 1 g / 100 mL solvent, the polymers were almost completely soluble in NMP, dimethyl sulfoxide (DMSO) and chloroform, and mainly soluble in tetrahydrofuran, ethylene chloride, benzene, tetrachloromethane, and acetone, as shown in Table II. But these polymers are only partially soluble in glacial acetic acid and absolute ethanol. The solubility of the polymers becomes higher with increasing content of XY unit. Apparently, good solubility of the copolymers results from the presence of a large number of methyl substituents on the aniline ring and amorphous supermolecular structure which increase the distance between the macromolecular chains and significantly reduces interactions between the chains of copolymers. The intrinsic viscosity of the copolymers was comparable to that of polyaniline, but the solubilities of the copolymers and polyaniline were much different from each other. Solubility may thus be primarily determined by molecular structure rather than intrinsic viscosity of the polymers.^{8,9}

It should be noticed that better solubility was evidence that the polymerization products were indeed copolymers containing the two monomers rather than a simple mixture of two homopolymers.⁴

FT-IR Spectra of Poly(aniline-co-2,3-xylydine)s

Representative FT-IR spectra for the copolymers with AN / XY molar ratios of 50 / 50 and 10 / 90 are shown in

Table II. Solubility and solution color of aniline (AN) and 2,3-xylylidine (XY) bipolymer bases prepared at -8°C in organic solvents

AN/XY mol/mol	NMP	DMSO	CHCl_3	THF	Ethylene chloride	Benzene	Acetone	CCl_4	Acetic acid	Ethanol
90/10	S (BV)	S	S(V)	MS(BV)	MS(RV)	MS(BV)	MS(BV)	MS(RV)	PS(DG)	PS(BV)
70/30	S (BV)	S	S(V)	MS(BV)	MS(RV)	S(BV)	MS(BV)	MS(RV)	PS(DG)	PS(RV)
50/50	S (BV)	S	S(V)	MS(BV)	MS(RV)	MS(BV)	MS(BV)	MS(RV)	PS(DG)	PS(RV)
30/70	S (BV)	S	S(V)	MS(BV)	MS(RV)	PS(BV)	MS(BV)	MS(RV)	PS(DG)	PS(BV)
10/90	S (BV)	S	S(B)	S(BB)	S(RB)	S(RB)	MS(RB)	SS(LV)	S(RB)	PS(RB)

S = soluble; MS = mainly soluble; PS = partially soluble; SS = slightly soluble. The letters in parentheses indicate color of bipolymer solution in the solvents. B = brown; BB = blackish brown; BV = bluish violet; DG = dark green; LV = light violet; RB = reddish brown; RV = reddish violet; V = violet. The color of the first four solid bipolymers is blackish violet but the last AN/XY(10/90) bipolymer shows black color.

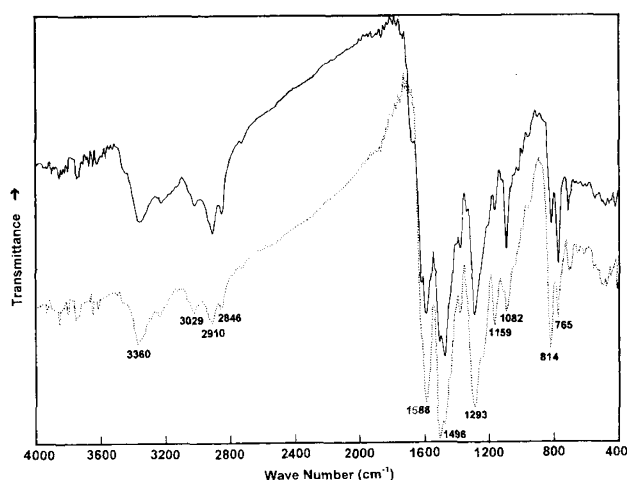


Figure 2. FT-IR absorption spectra of the copolymers with the aniline (AN)/2,3-xylylidine (XY) molar ratios of 10/90 (—) and 50/50 (.....).

Figure 2. A broad band centered at 3360 cm^{-1} due to the characteristic free N-H stretching vibration suggests the presence of primary and secondary amino groups ($-\text{NH}_2$ and $-\text{NH}-$)⁸ and becomes stronger with increase in XY unit content from 50 mol% to 90 mol%, indicating the molecular weight becomes lower. This is the same as intrinsic viscosity listed in Table I. A small shoulder band at 3231 cm^{-1} corresponded to the hydrogen-bonded N-H vibration. The peak at about 3029 cm^{-1} might be due to C-H stretching on benzene ring. The peaks at 2910 cm^{-1} and 2846 cm^{-1} are attributed to the C-H stretching vibration in methyl groups and get stronger with increasing XY unit content from 50 mol% to 90 mol%. The IR absorption in $1490\text{--}1590\text{ cm}^{-1}$ are associated with aromatic ring stretching. The peak at 1588 cm^{-1} was assigned to the quinoid ring



and 1496 cm^{-1} to the benzenoid ring.



That the peak at 1496 cm^{-1} has the higher intensity than the peak at 1588 cm^{-1} suggests more benzenoid unit in the copolymers. This is verified by the following $^1\text{H NMR}$ study. A weak peak at 1377 cm^{-1} is attribut-

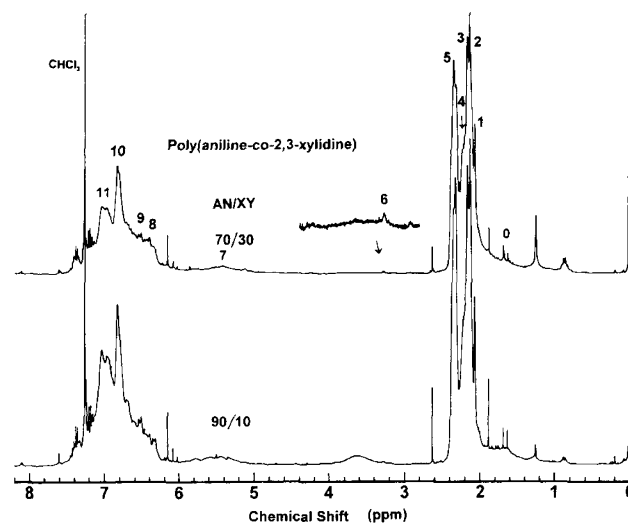


Figure 3. $^1\text{H NMR}$ spectra of copolymer with aniline (AN)/2,3-xylylidine (XY) molar ratios of 70/30 (upper, numbers of summation = 184) and 90/10 (lower, numbers of summation = 334) in deuterated chloroform at 300.13 MHz.

able to the C-N stretching vibration in quinoid imine units. A strong peak at 1293 cm^{-1} is due to the C-N stretching vibration in alternating unit of quinoid-benzenoid-quinoid. This indicates that there are more alternating quinoid-benzenoid sequences, also confirmed by the $^1\text{H NMR}$ study. A similar sequential structure was observed in polyaniline.¹⁰ A shoulder peak at 1249 cm^{-1} was ascribed to the C-N stretching in the benzenoid-benzenoid-triad sequence. The IR absorption of the copolymers exhibits enhanced intensity at 1159 cm^{-1} and 814 cm^{-1} with increase in AN unit content from 10 mol% to 50 mol%, indicating that the both peaks are indeed attributed to the C-H in-plane and C-H out-of-plane bending vibration of 1,4-disubstituted benzene ring on AN unit, respectively. The peaks at 1082 cm^{-1} and 765 cm^{-1} should be due to the C-H in-plane and C-H out-of-plane bending vibration of 1,2,3,4-tetrasubstituted benzene ring



on the XY unit, respectively, because the intensity of both peaks increase significantly with increasing XY unit content from 50 to 90 mol% and both peaks were not observed in the FT-IR spectra of polyaniline base.^{10,11} The presence of these disubstituted AN units

Table III. Possible assignments of ^1H NMR peaks of aniline(AN) / 2,3-xylylidine (XY) copolymers in CDCl_3 at 300.13 MHz

Peak	Feature	Chemical Shift/ppm	Structural	Assignments
0	Weak	1.63, 1.69		
1	Sharp	2.06		
2	Strongest sharp	2.13		
3	2nd strongest sharp	2.16		
4	Broad	2.20		
5	3rd strongest sharp	2.27		
6	Weak broad	3.26		
7	Very broad	5.4 — 5.5		
8	Broad	6.33 — 6.65		
9	Sharp	6.65 — 6.75		
10	4th strongest sharp	6.82		
11	Strong broad	6.97 — 7.04		

and tetrasubstituted XY units and secondary amino groups suggests the formation of polymers.

^1H NMR Spectra of the Copolymers

^1H NMR spectra of the AN/XY copolymers are characterized by four main signals, which exactly corresponded to the four protons on the copolymer chains. The ^1H NMR spectra of AN/XY(90/10) and (70/30) copolymers exhibit strongest sharp peaks at 2.13 and 2.27 ppm due to methyl groups, a medium broad peak centered at 6.82 and 7.03 ppm due to protons on phenylene and disubstituted phenylene units, and two weak broad peaks centered at 5.4 and 3.26 ppm due to $-\text{NH}-$ group and $-\text{NH}_2$ end group respectively, as shown in Figure 3. Note that a broad peak centered at 3.63 ppm may be due to the water protons bonded by $-\text{NH}-$ and $-\text{NH}_2$ groups. These spectra are informative for evaluation and calculation of sequence distribution of the comonomer units. After comparison of peak area and chemical shift, the assignments of the resonance peaks of the copolymers are listed in Table III. Peaks 0—4 are attributed to the methyl groups on benzenoid unit and peak 5 attributed to the methyl groups on quinoid unit. Therefore, the ratio of benzenoid to quinoid units in the copolymer is 2.18 : 1.00 for AN/XY(90/10) and 2.26 : 1.00 for AN/XY (70/30). Top of broad peak from phenyl protons for both copolymers was observed at 6.82 ppm due to the protons of *p*-disubstituted phenylene. This suggests a linear structure of the copolymers synthesized by oxidative copolymerization.

Although the average length of sequential AN units could not be calculated based on Figure 3 and Table III, the number-average sequence lengths $L_{\text{XY-XY}}$ of consecu-

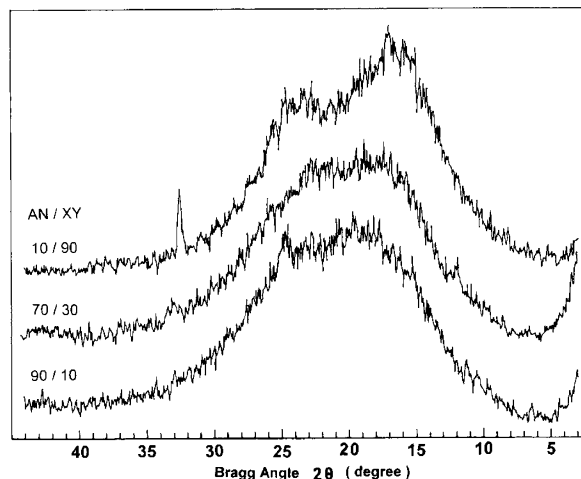


Figure 4. Wide-angle X-ray diffraction diagrams of the copolymer powders with aniline(AN)/2,3-xylylidine (XY) molar ratios of 10/90 (upper), 70/30 (middle), and 90/10 (lower).

tive XY-XY diads could be given by the equation¹²

$$L_{\text{XY-XY}} = 1 / (1 - P_{\text{XY-XY}}) \quad (1)$$

Where $P_{\text{XY-XY}}$ is the probability of unit XY being bonded to another unit XY, *e.g.*,

$$P_{\text{XY-XY}} = (2S_0 + S_1) / (2S_0 + S_1 + S_2 + S_3) \quad (2)$$

Where S_0 , S_1 , S_2 , and S_3 are the areas of peaks Nos. 0, 1, 2, and 3, respectively. $L_{\text{XY-XY}}$ calculated by eq 1 and 2 on the basis of Figure 3 and Table III are 1.93 for AN/XY (90/10) and 2.11 for AN/XY(70/30) copolymers.

Through comparison of areas of phenyl and methyl protons, the actual AN/XY molar ratios in the copolymers are 50/50 for the feed ratio of 90/10 and 41/59 for the feed ratio of 70/30. Actual XY content is much larger than the feed XY content. A very similar result was observed for the aniline/*o*-ethylaniline copolymers.³

Although resonance peaks from $-\text{NH}-$ and $-\text{NH}_2$ protons are very weak, the number-average degree of polymerization could be roughly calculated by the following equation :

$$(\text{DP})_n = [2 \times (\text{NH peak area}) + (\text{NH}_2 \text{ peak area})] \div (\text{NH}_2 \text{ peak area}) \div \text{content of benzenoid unit} \quad (3)$$

if the content of all benzenoid unit from AN and XY units is assumed 50%, the $(\text{DP})_n$ calculated is 76 for the AN/XY(90/10) and 62 for AN/XY(70/30). The variation of molecular weight of the copolymers with XY content from 10 to 30 mol% is in agreement with that of their intrinsic viscosities listed in Table I.

Wide-Angle X-Ray Diffractograms of the Copolymers

Wide-angle X-ray diffractograms of AN/XY copolymer powders are shown in Figure 4. Three copolymers with AN/XY ratios of 90/10, 70/30, and 10/90 exhibit a broad peak at $2\theta = 19.6^\circ$ for AN/XY(90/10), 18.8° for AN/XY (70/30), and 17.0° for AN/XY(10/90) and a very broad shoulder peak at $2\theta = 23-24.8^\circ$. This broad peak is characteristic of diffraction by an amorphous polymer. The strongest broad peak of polyaniline base is located at $2\theta = 19-20^\circ$.¹¹ These results indicate that the introduction of two methyl groups on aniline unit increases

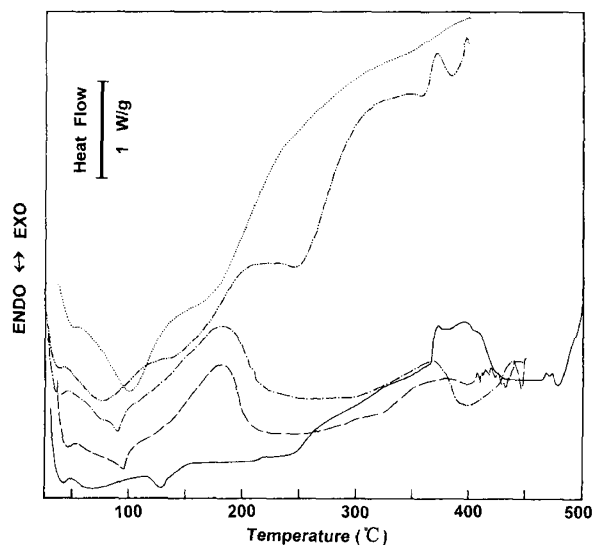


Figure 5. DSC thermograms of the copolymer powders with aniline (AN)/2,3-xylydine (XY) molar ratios of 90/10 (.....), 70/30 (-·-·-), 50/50 (- - - -), 30/70 (— — —), and 10/90 (—) at a heating rate of 20 °C min.

intermolecular chain spacing and amorphousness as compared with polyaniline.

DSC Thermograms of the Copolymers

DSC traces of AN/XY copolymer powders show two endothermic transition peaks at ca. 50°C and 80–129°C, as shown in Figure 5. These two peaks are due to evaporation of water molecules trapped inside the copolymers, but the peak at 129°C for AN/XY(10/90) copolymer should be due to dedoping of HCl, which agrees with TG measurement. It should be noted that there are one or two broad exothermic peaks at temperature above 180°C to 370°C. These exotherms could be attributed to complex chemical reactions, involving bond scissioning (such as the exclusion of methyl groups), followed immediately by new bond formation and crosslinking.⁴ This reaction process was confirmed by the weight loss results discussed later in this article. Continuously increasing exotherms in the region from 180 to 370°C are observed in DSC thermograms of the copolymers prepared at feed monomer ratios AN/XY 90/10 and 70/30. Possible explanations are as follows: The exclusion of methyl groups from the copolymers is endothermic but subsequent crosslinking reaction should be exothermic. Because there are relatively fewer methyl groups in AN/XY(90/10) and (70/30) copolymer chains among five copolymers, the exothermic crosslinking could be predominant as compared with endothermic exclusion of methyl groups. A similar exotherm was observed in the DSC pattern of aniline and *o*-ethylaniline copolymers.⁴

Thermogravimetric Thermograms of the Copolymers

Figure 6 shows the thermogravimetry (TG), derivative thermogravimetry (DTG), and second derivative thermogravimetry (2DTG) curves of AN/XY copolymer powders in a flowing nitrogen. The copolymers exhibit a two or three stage decomposition. The initial weight loss occurring of 2–10% may be explained by vaporating water molecules trapped by polymer chains. The second weight

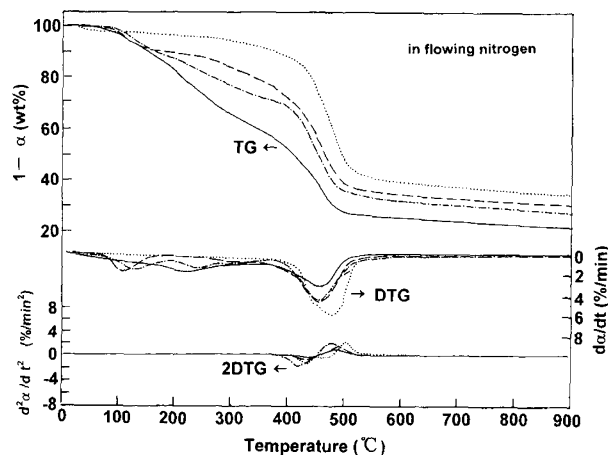


Figure 6. Thermogravimetry (TG), derivative thermogravimetry (DTG), and the second derivative thermogravimetry (2DTG) of the copolymer powders with aniline (AN)/2,3-xylydine (XY) molar ratios of 90/10 (.....), 50/50 (-·-·-), 30/70 (- - - -), and 10/90 (—) at a heating rate of 10 °C min⁻¹ in a flowing nitrogen.

loss in a range 180–370°C in the TG curve of AN/XY copolymer is due to chemical reactions of copolymers, such as exclusion of methyl groups and hydrogen and subsequent crosslinking between copolymer chains. An exception is that a big weight loss at the temperature centered at 225°C results from the dedoping of HCl. The final stage of decomposition starting at 400°C is attributable to the thermal degradation of copolymer chains.

Table I shows the stable and kinetic parameters of the thermal degradation of the copolymers. The thermal decomposition temperature T_d of AN/XY copolymers decreased first and increased with XY content from 0 to 90 mol%.¹³ The lowest degradation temperature was 395°C for AN/XY(30/70) copolymer. AN/XY copolymers are significantly less stable than polyaniline¹⁴ because a large number of methyl groups on the copolymer chains is easily excluded from the chains at an elevated temperature. A very similar dependency of thermal decomposition temperature on the copolymer composition was observed for the aniline/*o*-ethylaniline copolymer.⁴ AN/XY(90/10) copolymer exhibits slightly higher intrinsic viscosity (Table I) and larger T_d than AN/XY(70/30) copolymer. This is due to slightly shorter sequential length of XY unit and then more rigid chain in AN/XY(90/10) than AN/XY(70/30). It is interesting that nearly all the copolymers exhibit the same temperature T_{dm} (455°C) at maximum weight-loss rate. There are no regular variation of maximum decomposition rate $[(d\alpha/dt)_m]$ and char yield at 900°C with AN/XY ratio. Note that the char yields at 900°C for the AN/XY copolymers are higher than 23–35 wt%, which could be valuable for the preparation of carbon composite.

The kinetic parameters of the thermal degradation for the copolymers are calculated^{15–17} through Figure 7 by Friedman technique by eq 4

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

and Kissinger technique by eq 5

$$n = | (d^2\alpha/dt^2)_{L_{max}} | / | (d^2\alpha/dt^2)_{R_{max}} | \quad (5)$$

The activation energy E , decomposition reaction order n ,

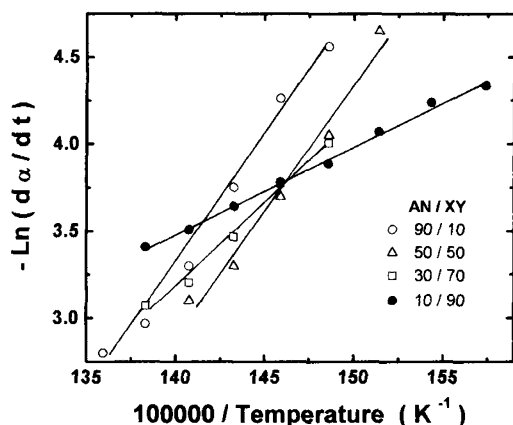


Figure 7. Friedman method (plot of $d\alpha/dt$ vs. $1/T$) for calculation of the activation energy of the thermal degradation of the copolymer powders with aniline (AN)/2,3-xylydine (XY) molar ratios of 90/10 (\circ), 50/50 (\triangle), 30/70 (\square), and 10/90 (\bullet) in a flowing nitrogen.

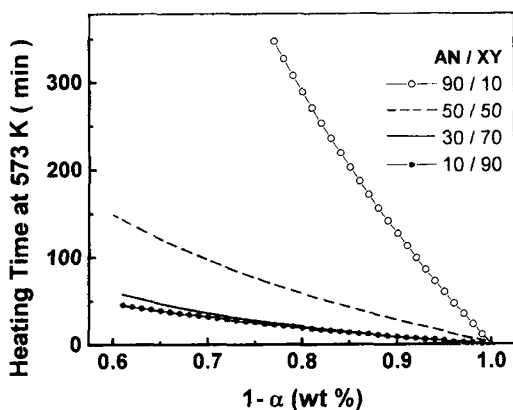


Figure 8. Predicted isothermal TG at 573 K based on average kinetic parameters listed in Table I for copolymers with AN/XY molar ratios of 90/10 (\circ), 50/50 (\square), 30/70 (\square), and 10/90 (\bullet) in nitrogen through the equation: Heating time = $[1 - (1 - \alpha)^{1-n}] \exp(E/RT) / [Z(1-n)]$ ($n \neq 1$).

and frequency factor $\ln Z$ all decrease with increasing XY content. All these results suggest that the thermostability and decomposition rate decrease as XY content increases.

The predicted isothermal TG curves for the four AN/XY copolymers based on average kinetic parameters listed in Table I was shown in Figure 8. The estimated isothermal stability at 573 K increases with AN unit content in the order: 10/90 < 30/70 < 50/50 < 90/10. AN/XY(10/90) copolymer exhibits 39% weight loss after a heating time of 45 min at 573 K but AN/XY(90/10) copolymer shows only 23% weight loss after heating

time of 347 min at the same temperature.

CONCLUSIONS

Aniline and 2,3-xylydine can polymerize into amorphous and soluble copolymer with low yield by oxidation polymerization, but pure 2,3-xylydine hardly ever forms any polymer by chemical oxidation even if the reactants are kept for 48 h at -8°C with stirring. Actual XY unit content of the AN/XY copolymer soluble in CDCl_3 determined by NMR spectra is higher than feed XY content of corresponding copolymer. The thermostability and decomposition rate decrease as XY unit content increases.

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REFERENCES

1. M. R. Anderson, B. R. Mattes, H. Reiss, and R. B. Kaner, *Science*, **252**, 1412 (1991).
2. Y. Cao and P. Smith, *Polymer*, **34**, 3139 (1993).
3. X.-G. Li, M.-R. Huang, G.-F. Gu, W. Qiu, and J.-Y. Lu, *J. Appl. Polym. Sci.*, **74**, (1999).
4. J. A. Conklin, S. C. Huang, S. M. Huang, T. Wen, and R. B. Kaner, *Macromolecules*, **28**, 6522 (1995).
5. M. Ranger and M. Leclerc, *Synth. Met.*, **84**, 85 (1997).
6. M. Leclerc, J. Guay, and L. H. Dao, *Macromolecules*, **22**, 649 (1989).
7. A. H. Kwon, J. A. Conklin, M. Makhinson, and R. B. Kaner, *Synth. Met.*, **84**, 95 (1997).
8. D. Ichinohe, T. Muranaka, T. Sasaki, M. Kobayashi, and H. Kise, *J. Polym. Sci., Part A, Polym. Chem.*, **36**, 2593 (1998).
9. X.-G. Li, M.-R. Huang, and L.-X. Gu, in submission.
10. E. T. Kang, K.G. Neoh, and K. L. Tan, *Prog. Polym. Sci.*, **23**, 277 (1998).
11. M. J. Chang, Y. H. Liao, A. S. Myerson, and T. K. Kwei, *J. Appl. Polym. Sci.*, **62**, 1427 (1996).
12. X.-G. Li, M.-R. Huang, G. H. Guan, and T. Sun, *Angew. Makromol. Chem.*, **227**, 69 (1995).
13. D. K. Moon, K. Osakada, T. Murayama, and T. Yamamoto, *Makromol. Chem.*, **193**, 1723 (1992).
14. J. Yue, A. J. Epstein, Z. Zhong, P. K. Gallagher, and A. G. MacDiarmid, *Synth. Met.*, **41-43**, 765 (1991).
15. X.-G. Li, *Polym. Degrad. Stab.*, **65**, 473 (1999).
16. X.-G. Li and M.-R. Huang, *J. Macromol. Sci., Pure Appl. Chem.*, **A36**, 859 (1999).
17. X.-G. Li, M.-R. Huang, and H. Bai, *J. Appl. Polym. Sci.*, **73**, 2927 (1999).