Oxidative Copolymers of Aniline with *o*-Toluidine: Their Structure and Thermal Properties

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ABSTRACT: Chemically oxidative polymerization of aniline and *o*-toluidine (OT) with 6 molar ratios was performed using ammonium persulfate as an oxidant in a HCl medium at $-18°C$. It was observed that the copolymers were not regularly dependent on the monomer ratio for yield and intrinsic viscosity. The resulting copolymers were characterized by Fourier transform IR spectroscopy, ^{1}H-NMR spectroscopy, wide-angle X-ray diffraction, differential scanning calorimetry, and several thermogravimetry methods. The results showed that the actual content of the OT unit in the copolymers was much higher than the feed content of the OT unit. Given the same reaction conditions, *o*-toluidine showed a larger tendency toward homopolymerization rather than toward copolymerization with aniline. The copolymers were amorphous and exhibited thermal decomposition temperatures higher than 440°C and a char yield larger than 39 wt % at 900°C in nitrogen. The activation energy of thermal decomposition for the copolymers was 40–244 kJ/mol in nitrogen and 32 kJ/mol in air, respectively. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1838–1847, 2001

Key words: polytoluidine; toluidine copolymer; oxidative polymerization; nuclear magnetic resonance spectra; thermogravimetric analysis

INTRODUCTION

Chemically oxidative copolymerization is a very useful technique for the designed synthesis of various functional polymers. Typical oxidative polymers are polyaniline, polypyrrole, polyaminopyridine, and polyphenylenediamine, which display such unique properties as high conductivity and liquid crystalline behavior. Unfortunately, except for *N*-methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide, which have high boiling points, these polymers all are insoluble in common solvents, resulting in difficult processability that restricts their applications. Recently, polytoluidine

has attracted attention because it has been reported to exhibit better solubility[1] and processibility[2] than polyaniline.[3,4] Copolymerization of aniline with toluidine might be one of the best methods to modify the solubility of polyaniline and to combine the advantages of polytoluidine with polyaniline. However, there are only a few reports about copolymerization in the literature.[5] The purpose of this study was to synthesize an easily soluble copolymer by introducing methyl groups on the phenylene ring in the rigid polyaniline main chain; to describe the variations in yield, intrinsic viscosity, crystallinity, and thermostability from variations in the monomer ratio; and to explain the structural and property modifications induced by copolymerization of aniline (AN) with o-toluidine (OT) for the first time.

EXPERIMENTAL

Chemical Reagents

Aniline, o-toluidine, ammonium persulfate, $LiCl \cdot H_2O$, and N-methyl-2-pyrrolidone were commercially obtained and used as received.

Oxidative Copolymerization

Copolymers were prepared by oxidative copolymerization of two monomers using a previously described method.[6–7] A typical procedure for the preparation of a copolymer from 50:50 aniline–o-toluidine is as follows: To 100 mL of a $1M$ HCl solution in a 250-mL two-neck glass flask were added 29 g of $LiCl \cdot H_2O$, 4.7 mL (0.05 mol) of aniline, and 5.4 mL (0.05 mol) of o-toluidine. An oxidant solution was prepared separately by dissolving 5.5 g (0.024 mol) ammonium persulfate [$(NH_4)_2S_2O_8$] in 50 mL of $1M$ HCl. Both solutions were cooled in an ice–sodium chloride (2:1 wt %) bath to $-18°C$. The monomer solution was then treated with the oxidant solution, which was added dropwise for about 2 h at a rate of 1 drop every 3 sec at $-18°C$ (total molar ratio of monomer:oxidant = 4:1). After the first few drops the reaction solution immediately turned bluish violet. The reaction mixture was vigorously stirred for 40 h at $-18°C$. 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 150 mL of $0.1M$ 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 1 week.

The yield, of about 13%, produced about 1.2 g of copolymer, which exhibited the following nominal structure:

AN unit   **OT unit**
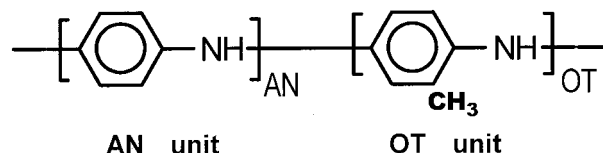
Measurements

The intrinsic viscosity of the copolymers in NMP was measured at 25°C with a Ubbelohde viscosimeter.

The solubility of the polymers was evaluated using the following method: 5 mg of polymer powder was added to 0.5 mL of solvent and dispersed thoroughly. After the mixture was swayed intermittently for 24 h at room temperature, the solubility of the polymers could be characterized semiquantitatively.

IR spectra were recorded on a Nicolet FTIR 5DXC spectrometer (made in the United States) at a resolution of 2 cm^{-1} on KBr pellets.

^{1}H-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 a Rigaku RAX-10 diffractometer with monochromatized $CuK\alpha(\lambda = 0.1541$ nm) radiation operated at 30 kV and 20 mA in a reflection mode. The scanning rate was 8°/min, with the Bragg angle (2ϕ) measured to a precision of 0.01°.

Differential scanning calorimetry (DSC) measurements were performed on 6–8 mg samples using a TA Instruments (New Castle, DE) Thermal Analyst 2000 System along with an IBM PC computer Model 55 SX.

Nonisothermal thermogravimetry was done on 1.0–1.1 mg samples at a heating rate of 10°C/min in nitrogen (40 mL/min) using a TGH Perkin Elmer 7 series and on 0.93 mg samples in static air using the Netzsch-Geratebau GmbH TG 209 thermal analyzer. Isothermal thermogravimetry was carried out on 0.9–1.1 mg samples at 300°C for 310 min with a heating rate 50°C/min in nitrogen (40 mL/min) using the same Netzsch-Geratebau thermal analyzer.

RESULTS AND DISCUSSION

Synthesis of Copolymers from Aniline and o-Toluidine

The copolymerization of aniline and o-toluidine using ammonium persulfate as an oxidant in a

Table I Copolymerization of Aniline (AN) and *o*-Toluidine (OT) with Monomer and Their Thermal Stable Parameters at Sample Weights of 0.8–1.1 mg

AN–OT Mol %	Polymer- ization Yield (%)	Intrinsic Viscosity (dL/g)	T_d (°C)	T_{dm} (°C)	$(d\alpha/dt)_m$ (%/min)	Char Yield at 900°C (wt %)	E (kJ/mol)	n	Ln Z (min^{-1})	r[a]
In nitrogen										
100 : 0[b]			430	520		60				
90 : 10	11	0.59	490	620	3.0	63	57	1.8 (1.8)[c]	4.6	0.995
70 : 30	10	0.12	466	483	12.1	39	244	2.4 (1.5)[c]	38	0.996
50 : 50	13	1.70	480	600	3.5	57	52	1.3	3.4	0.987
30 : 70	11	0.77	440	470	10.7	42	185	2.1 (1.4)[c]	29	0.994
30 : 70[d]	11	0.77	440	540	2.3	52	81	5.8	10	0.989
10 : 90	11	0.85	449	485	7.9	44	120	1.9 (2.0)[e]	17	0.998
0 : 100	34	0.52	434	474	4.1	57	90	3.2 (2.1)[e]	12	0.981
In air										
100 : 0[e]			445	473	7.3	0	38	0.5	3.8	0.996
50 : 50[f]	13	1.70	490	628	1.1	48	32	3.5	0.47	0.997
30 : 70[f]	11	0.77	478	610	4.1	1	48	0.6	3.8	0.994

Ammonium persulfate 4 : 1 in 1*M* HCl and LiCl aqueous solution at −18°C for 40 h.

[a] *r* value is linear correlation coefficient.

[b] From Moon et al.[13]

[c] Data were calculated using Kissinger equation based on the 2DTG curves.

[d] Sample weight is 0.9 mg at a nitrogen flowing rate of 10 mL/min, and the TG/DTG curves were obtained by Netzsch–Geratebau GmbH thermal analyzer.

[e] Its TG and DTG curves were obtained from that in Cham et al.[14]

[f] Sample weight is 0.8–0.9 mg in static air, and the TG/DTG curves were obtained by Netzsch–Geratebau GmbH thermal analyzer.

1*M* HCl aqueous solution generated black precipitates as products. At 6 different ratios of monomer, aniline and *o*-toluidine copolymerized at −18°C for 40 h. It was found that the polymerization yield varied over a narrow range, 10%–13%, with an increase in feed OT content from 10 mol % to 90 mol %, as shown in Table I. It appears that *o*-toluidine easily homopolymerized under the same reaction condition, producing a higher yield, 34%. The *o*-toluidine was more reactive than aniline.[5] These results suggest aniline and oligoanilines act as anticatalyst or antiactivator for the polymerization of *o*-toluidine. This situation is totally contrary to that for the copolymerization of aniline with 2,3-xylidine.[7]

Intrinsic viscosity of the copolymers varied irregularly with the monomer ratio, as listed in Table I. It is interesting that the 50:50 AN–OT copolymer showed the highest intrinsic viscosity, 1.7 dL/g. On the contrary, the 70:30 AN–OT copolymer had the lowest intrinsic viscosity, 0.15 dL/g. These results were further confirmed by the following thermogravimetric study.

Solubility of Poly(aniline-*co*-*o*-toluidine)

AN–OT copolymers were almost completely soluble in NMP and dimethyl sulfoxide (DMSO) and exhibited better solubility in chloroform, as listed in Table II. But these polymers were partially soluble in tetrahydrofuran, ethylene chloride, benzene, and acetone and were slightly soluble or even insoluble in glacial acetic acid, tetrachloromethane, and absolute ethanol. In fact, the solubility of the copolymers in NMP and DMSO was improved with increasing OT unit content in the copolymers. Apparently, good copolymer solubility results from the presence of a large number of methyl substituents on the aniline ring and an amorphous supermolecular structure, which increases the distance between the macromolecular chains and then significantly reduces the interaction between the copolymer chains. The intrinsic viscosity of the copolymers is comparable to that of polyaniline, but the solubilities of the copolymers and polyaniline are much different from each other. These results indicate that solubility is primarily determined by the molecular structure rather than by the intrinsic viscosity of the polymers.[8,9]

In addition, better solubility is evidence that the polymerization product produced is indeed copolymer containing two monomers rather than a simple mixture of two homopolymers.[10]

Table II   Solubility and Solution Color of Aniline (AN) and o-Toluidine (OT) Bipolymer Bases Prepared at −18°C in Organic Solvents

AN–OT (mol/mol)	NMP	DMSO	CHCl$_3$	THF	Ethylene Chloride	Benzene	Acetone	CCl$_4$	Acetic Acid	Ethanol
90: 10	S (BV)	MS	MS (V)	PS (BV)	SS (RV)	PS (BV)	SS (BV)	IS	IS	IS
70: 30	S (BV)	MS	MS (V)	PS (BV)	MS (BV)	PS (BV)	PS (BV)	SS (BV)	SS (LB)	SS (LB)
50: 50	S (BV)	MS	MS (V)	PS (BV)	PS (BV)	PS (BV)	PS (BV)	SS (BV)	SS (LB)	SS (LB)
30: 70	S (BV)	S	MS (V)	PS (BV)	MS (BV)	PS (BV)	PS (BV)	SS (BV)	SS (B)	SS (LB)
10: 90	S (BV)	S	MS (V)	PS (BV)	SS (RV)	PS (BV)	PS (BV)	SS (BV)	SS (B)	SS (LB)
0 :100	S (BV)	S	MS (V)	PS (BV)	PS (BV)	PS (BV)	PS (BV)	SS (BV)	PS (B)	SS (LB)

1. S = soluble; MS = mainly soluble; PS = partially soluble; SS = slightly soluble; IS = insoluble.
2. The letters in parentheses indicate the color of the bipolymer solution in the solvents: B = blue; BV = bluish violet; LB = light blue; RV = reddish violet; V = violet.
3. The color of the six solid polymer bases is blackish violet.

FTIR Spectra of Poly(aniline-*co*-o-toluidine)

Representative FTIR spectra for the copolymers with AN–OT molar ratios of 90:10 and 0:100 are shown in Figure 1. The broad band centered at 3367 cm^{-1}, a result of the characteristic free N—H stretching vibration, suggests the presence of secondary amino groups (—NH—)[8] and becomes stronger with an increase in the OT unit content from 10 mol % to 100 mol %, indicating that the molecular weight becomes lower. This is the same as the intrinsic viscosity result (Table I). A small shoulder band at 3293 cm^{-1} corresponds to the hydrogen-bonded N—H vibration. The peak at about 3029 cm^{-1} might be because of C—H stretching on the benzene ring. The peak at 2917 cm^{-1} can be attributed to the C—H stretching vibration in methyl groups and gets a little bit stronger with OT unit content increasing from 10

Figure 1   FTIR absorption spectra of the copolymers with the AN–OT molar ratios of 0:100 (——) and 90:10 (· · · ·).

mol % to 100 mol %. The IR absorptions at 1489–1595 cm^{-1} are associated with aromatic ring stretching. The peak at exactly 1595 cm^{-1} can be assigned to the quinoid ring
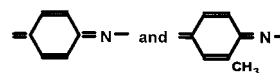
and the one at 1489 cm^{-1} to the benzenoid ring.
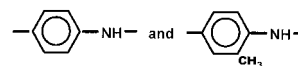
The higher intensity of the peak at 1489 cm^{-1} compared to the one at 1595 cm^{-1} suggests more benzenoid units in the copolymers. This result was verified by the following ^{1}H-NMR study. A weak peak at 1379 cm^{-1} can be attributed to the C—N stretching vibration in the quinoid imine units. A strong peak at 1314 cm^{-1} is because of the C—N stretching vibration in the alternative unit of quinoid–benzenoid–quinoid. This indicates additional alternative quinoid–benzenoid sequences, which was also confirmed by the ^{1}H-NMR study. A similar sequential structure can be observed in the polyaniline.[11] A weak peak at 1241 cm^{-1} can be ascribed to the C—N stretching in the benzenoid–benzenoid–benzenoid triad sequence. The IR absorption of the copolymers exhibits an enhanced intensity at 1145 cm^{-1} and 800 cm^{-1} with an increase in the AN unit content from 0 mol % to 90 mol %, indicating both peaks can indeed be attributed to, respectively, the C—H in-plane and the C—H out-of-plane bending vibration of the 1,4-disubstituted benzene ring on the AN unit. The peaks at 1113 cm^{-1} and 890 cm^{-1} should be the result of, respectively, the
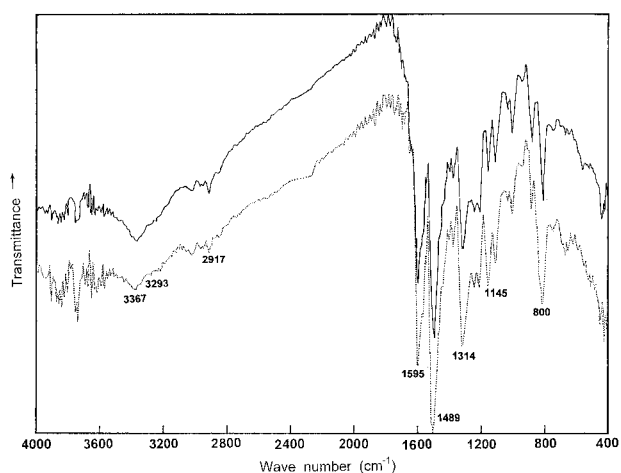
C—H in-plane and C—H out-of-plane bending vibration of the 1,2,4-trisubstituted benzene ring —⌬— on OT unit because the intensity of both peaks increases slightly with the OT unit content increasing from 10 mol % to 100 mol % and because both peaks were almost never observed in the FTIR spectra of the polyaniline base.[11,12] The presence of these disubstituted AN units and trisubstituted OT units and secondary amino groups suggests the formation of polymers.

^{1}H-NMR Spectra of Poly(aniline-*co-o*-toluidine)

The ^{1}H-NMR spectra of the soluble fraction of the AN–OT copolymers in deuterated chloroform can be characterized by four main signals, which correspond exactly to the four types of protons on the copolymer chains. As shown in Figure 2, the ^{1}H-NMR spectra of the 70:30, 10:90, and 0:100 AN–OT copolymers exhibit the strongest sharp peaks at, respectively, 2.19, 2.16, and 2.18 ppm because of the methyl groups on the quinoid unit; the second-strongest sharp peaks at, respectively, 1.78, 1.75, and 1.65 ppm because of the methyl groups on the benzenoid unit; and a medium broad peak centered at, respectively, 6.82, 6.83, and 6.83 ppm because of the protons on the phenylene and substituted phenylene units. There are also two weak broad peaks centered at 5.44–5.51 ppm as a result of —NH— groups in the ^{1}H-NMR spectra of the three copolymers and 4.81–4.79 ppm because of the —NH₂ end group in the ^{1}H-NMR spectra of the 70:30 and 10:90 AN–OT copolymers. These spectra are very informative for calculating and evaluating the sequence distribution of the comonomer units. The assignments of the NMR peaks of the copolymers are shown in Table III as a comparison of the integrated peak areas and the chemical shifts of different protons. The top of the broad peak from phenyl protons for both copolymers can be observed at 6.82–6.83 ppm because of the protons of the *p*-disubstituted phenylene. This suggests that copolymers synthesized by oxidative copolymerization have a linear structure.

Through a comparison of methyl protons to phenyl protons of the integrated area, it was possible to determine that the actual AN–OT molar ratio in a soluble fraction of AN–OT (70:30, feed ratio) copolymer in chloroform is 8:92. This result suggests that the soluble polymer in chloroform consists mainly of *o*-toluidine units but that the insoluble fraction consists of aniline unit because the solubility of pure polyaniline in chloroform is about 10%. For both polymers, with AN–OT feed
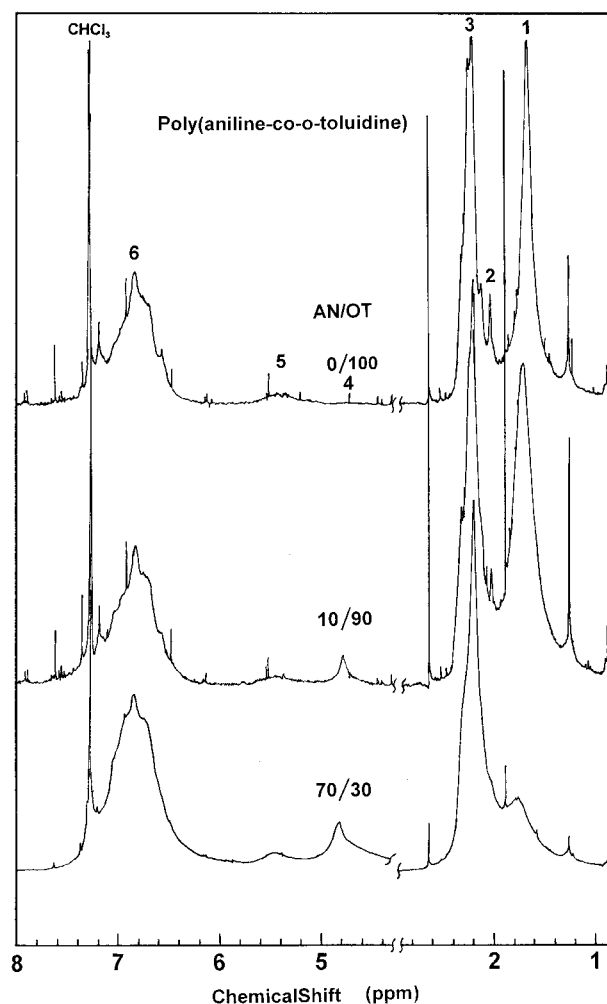

Figure 2 ^{1}H-NMR spectra of copolymers with AN–OT molar ratios of 70:30 [lower, numbers of summation (NS) = 350], 10:90 (middle, NS = 300), and 0:100 (upper, NS = 248) in deuterated chloroform at 300.13 MHz.
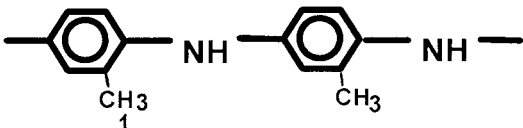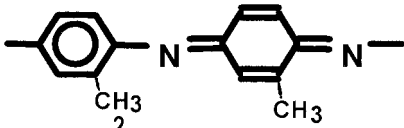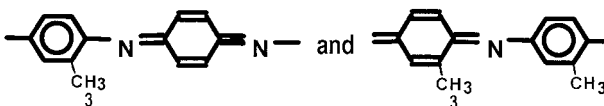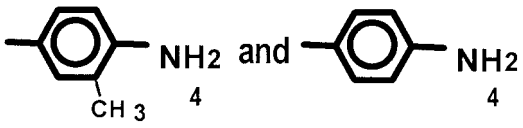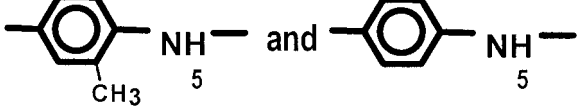
ratios of 10:90 and 0:100, their ratios of the integrated NMR area of methyl protons to phenyl protons are 2.43 and 1.99, respectively—that is, the actual OT content is much higher than the feed OT content. A very similar result was observed for the aniline–*o*-ethylaniline copolymers.[10]

Although the resonance peaks from —NH— and —NH₂ protons are very weak, the number-average degree of polymerization of the copolymer base could be roughly calculated by the following equation:

$$(DP)_n = 2 \times (2 \times (\text{NH peak area})$$
$$+ (\text{NH}_2 \text{ peak area}))/(\text{NH}_2 \text{ peak area}) \quad (1)$$

where the $(DP)_n$ calculated is 5 for the AN–OT (70:30, feed ratio), 8 for AN–OT (10:90, feed ratio),

Table III   Assignments of ¹H-NMR Peaks of Aniline–o-Toluidine (AN–OT) Copolymers in CDCl₃ at 300.13 MHz

Peak	Feature	Chemical Shift (ppm)	Structural	Assignments
1	Strong Sharp	1.65, 1.75		
2	Weak Sharp	2.02		
3	Strong Sharp	2.14, 2.19		
4	Broad	4.8		
5	Weak Broad	5.4		
6	Broad	6.56 ~ 7.4	The protons on aniline and toluidine rings	

and 62 for 0:100 AN–OT polymers. The very low $(DP)_n$ for the 70:30 and 10:90 AN–OT copolymers might be a result of its low solubility in CDCl₃. In fact, only low-molecular-weight copolymer can dissolve in CDCl₃, and the —NH— and —NH₂ protons in high-molecular-weight copolymers containing more AN units cannot be detected. Therefore, a low $(DP)_n$ indicates that only the soluble fraction of the copolymers has a low molecular weight, while the actual molecular weight of the copolymers with an OT content of 50–90 mol % is high on the basis of their intrinsic viscosity, listed in Table I.

In addition, the ¹H-NMR spectra of the aniline–toluidine copolymer and the o-toluidine homopolymer reported in this article are quite different from those reported by Wei et al.,[5] whose findings did show a strong peak at 1.65–1.75 ppm in the spectra.[5] Possible explanations for this are:

1. The solvents are different. The solvent used in the current research was deuterated chloroform, while Wei et al.[5] used deuterated DMSO.
2. The NMR spectrometers and magnetic field frequency are different. The ¹H-NMR spectra in this investigation were obtained at 300.13 MHz, while Wei et al.[5] obtained theirs at 250 MHz.
3. The polymerization temperature and time are different. The temperature used in this study was lower and the time longer.

Wide-Angle X-ray Diffractograms of Poly(aniline-co- o-toluidine)

Wide-angle X-ray diffractograms of four AN/OT polymer powders are shown in Figure 3. The broad peak of four diagrams is characteristic of diffraction by an amorphous polymer. Only the 50:50 AN–TO copolymer shows its strongest broad peak at a low Bragg angle, 17°, and a very broad peak at 21.6°, suggesting that the structure of this copolymer should be the most random and the spacing between the copolymer chains the biggest among the four polymers. The other two polymers, those with AN–OT ratios of 90:10 and 0:100, exhibit their strongest broad peak at $2\theta = 22°$, while the 100:0 AN–OT polymer exhibits a double peak, at 21.0° and 24.4°. The very different
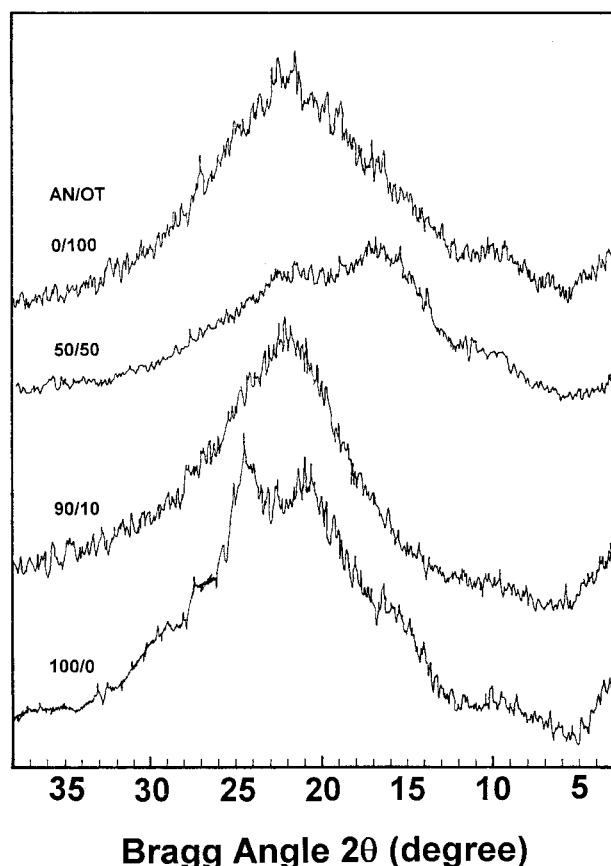
Figure 3 Wide-angle X-ray diffraction diagrams of the copolymer powders with AN–OT molar ratios of 0:100 (upper), 50:50 (upper middle), 90:10 (lower middle), and 100:0 (lower).

diffractograms of the four polymers indicate their different crystalline structures. An introduction of methyl groups on an aniline unit increases the intermolecular chain spacing and amorphousness as compared with pure polyaniline.

DSC Thermograms of Poly(aniline-*co-o*-toluidine)

DSC traces of AN–OT copolymer powders show one endothermic transition peak at about 100°C and an exothermic peak at about 250°C, as shown in Figure 4. The endothermic peak is a result of the evaporation of water molecules trapped inside the copolymers, but the exothermic peak should be attributed to a series of complex chemical reactions, involving bond scissioning (such as the exclusion of methyl groups), followed immediately by new bond formation and crosslinking.[10] Similar exotherms were observed in the DSC pattern of aniline and 2,3-xylidine or *o*-ethylaniline copolymers.[7,10]

Nonisothermal Thermogravimetric Thermograms of Poly(aniline-*co-o*-toluidine)

Figures 5 and 6 show the thermogravimetry (TG), derivative thermogravimetry (DTG), and second derivative thermogravimetry (2DTG) curves of AN–OT copolymer powders in flowing nitrogen and static air, respectively. The copolymers exhibit a single-stage decomposition in nitrogen, attributable to the thermal degradation of the copolymer chains and two-stage decomposition in air. Table I shows the stable and kinetic parameters of the thermal degradation of the copolymers. No regular relationship between the thermal stable parameters [T_d, T_{dm}, $(d\alpha/dt)_m$, char yield], and the AN–OT ratio was found with increasing OT content from 0 to 100 mol %. The lowest degradation temperature was 434°C, for the 0:100 AN–OT polymer, while the highest degradation temperature for the 90:10 AN–OT polymer was 490°C. The 50:50 AN–TO copolymer had the higher degradation temperatures, which re-
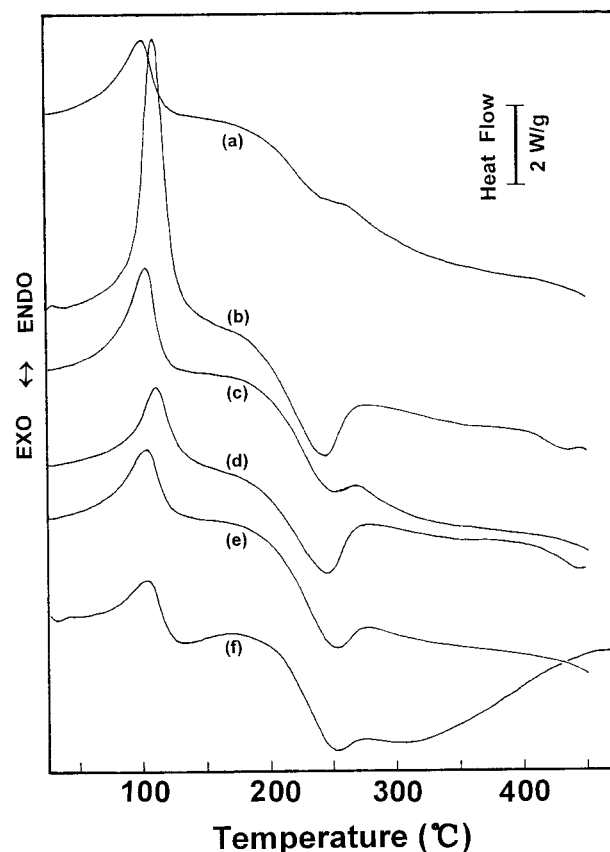

Figure 4 DSC thermograms of the copolymer powders with AN–OT molar ratios of (a) 0:100, (b) 10:90, (c) 30:70, (d) 50:50, (e) 70:30, and (f) 90:10 at a heating rate 20°C/min.
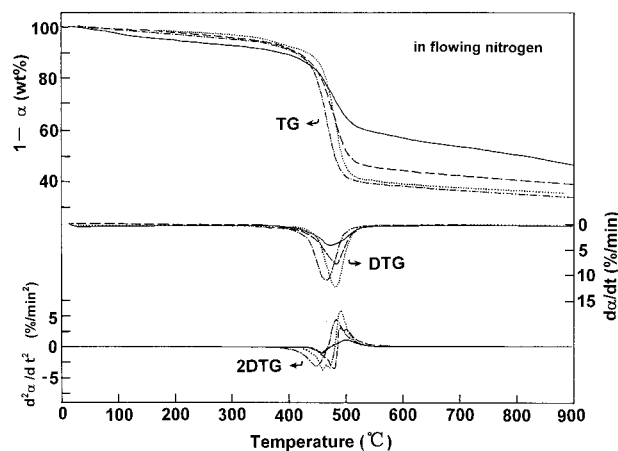
Figure 5 Thermogravimetry (TG), derivative thermogravimetry (DTG), and the second derivative thermogravimetry (2DTG) of the copolymer powders with AN–OT molar ratios of 70:30 (····), 30:70 (—·—·—), 10:90 (– – –), and 0:100 (——) at a heating rate of 10°C/min in flowing nitrogen.

sulted from its having the highest intrinsic viscosity. Decreasing the nitrogen flow rate from 40 mL/min to 10 mL/min will increase the degradation temperature and char yield but decrease the weight-loss rate because a decrease in the nitrogen flow rate can decrease the rate of evaporation of gaseous degradation product from the polymer samples. It is interesting that the char yields at 900°C in nitrogen for the AN–OT copolymers were greater than 39–63 wt %, which could be very valuable for the preparation of carbon composites. Note that AN–OT copolymers exhibit higher thermostability in static air than in flowing nitrogen. A comparison of the decomposition temperatures of the AN–OT copolymer with AN–*o*-ethylaniline copolymers,[10] AN–2,3-xylidine copolymers,[7] and pure polyaniline,[13,14] revealed the
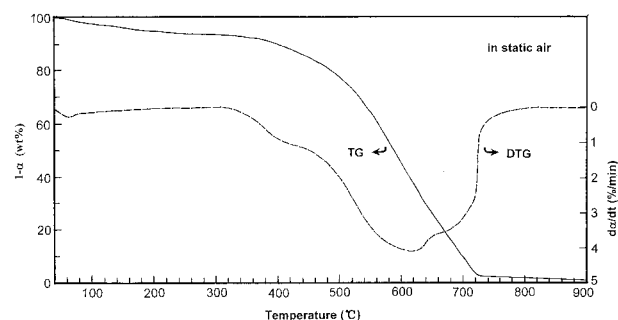

Figure 6 Thermogravimetry and derivative thermogravimetry of copolymer powder with an AN–OT molar ratio of 30:70 at a heating rate of 10°C/min in a static air.
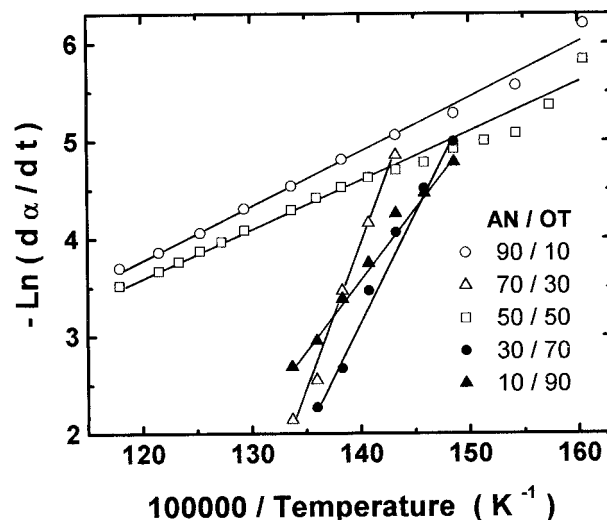

Figure 7 Friedman method (plot of $d\alpha/dt$ vs. $1/T$) for the calculation of the activation energy of the thermal degradation of copolymer powders with AN–OT molar ratios of 90:10 (○), 70:30 (△), 50:50 (□), 30:70 (●), and 10:90 (▲) in flowing nitrogen.

order of increasing thermal stability of the polymers as: AN–2,3-xylidine polymer < AN–o-ethylaniline polymer < polyaniline ≤ AN–OT polymer.

The kinetic parameters of the thermal degradation of the copolymers were calculated[15–20] through Figures 7 and 8 by the Friedman technique using eq. (2)

$$\mathrm{Ln}(d\alpha/dt) = \mathrm{Ln}\, Z + n\, \mathrm{Ln}(1 - \alpha) - E/RT \quad (2)$$
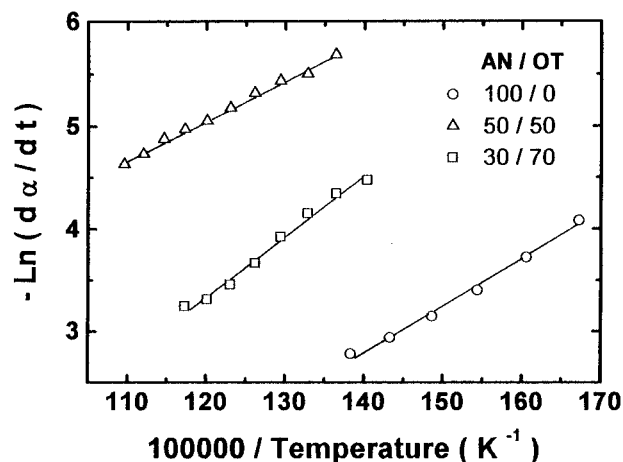

Figure 8 Friedman method (plot of $d\alpha/dt$ vs. $1/T$) for the calculation of the activation energy of the thermal degradation of copolymer powders with AN–OT molar ratios of 100:0 (○), 50:50 (△), and 30:70 (□) in air.
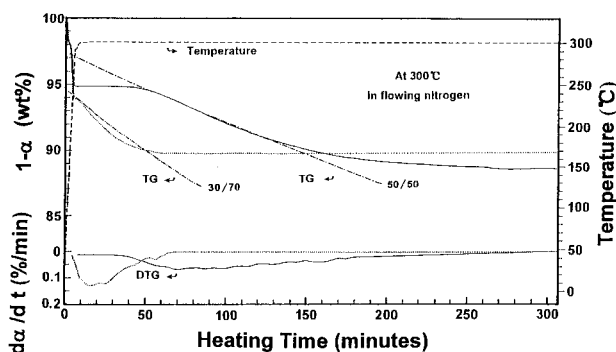
Figure 9 Isothermal TG and DTG curves for copolymers with AN–OT molar ratios of 50:50 (——) and 30:70 (····) in nitrogen and calculated isothermal TG curves (—·—·—) based on the kinetic parameters listed in Table I.

and by the Kissinger technique using eq. (3)

$$n = |(d^2\alpha/dt^2)_{L-\max}|/|(d^2\alpha/dt^2)_{R-\max}| \quad (3)$$

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 AN–OT ratio. It should be noted that the polymers possessing higher decomposition temperatures generally exhibit lower activation energy and frequency factor of decomposition. The activation energy and frequency factor of thermal decomposition for the copolymers are larger in nitrogen than in air.

Isothermal Thermogravimetric Thermograms of Copolymers

The weight losses of the copolymers with AN–OT molar ratios of 50:50 and 30:70 during isothermal heating under nitrogen were measured at 300°C, as shown in Figure 9. The copolymers exhibited rapid weight losses of 5% for the 50:50 AN–OT copolymer and 6% for the 30:70 AN–TO copolymer in an increasing temperature range from room temperature to 300°C during the initial 7 min. This rapid weight loss could be the result of the volatilization of residual water and HCl dopant inside the copolymers. The 50:50 AN–OT copolymer rarely exhibited any significant weight loss during the heating time from 7 to 50 min and then exhibited 6.3% weight loss during the heating time from 50 to 260 min until a char yield of 88.7%. The behavior of isothermal degradation for the 30:70 AN–OT copolymer was different. The 30:70 AN–OT copolymer exhibited 4.5%

weight loss during isothermal heating time from 7 to 60 min until a constant char yield of 89.7%. The isothermal heating time at the maximum weight-loss rate for 50:50 AN–OT copolymer was longer than that for 30:70 AN–OT copolymer, indicating that the 50:50 AN–TO copolymer has higher thermostability than the 30:70 AN–OT copolymer. This thermostable result is agreement with that of nonisothermal weight loss listed in Table I.

The point-dotted lines shown in Figure 9 are the isothermal TG curves at 300°C predicted by eq. (4) on the basis of the kinetic parameters listed in Table I for the nonisothermal degradation:

$$\text{Heating time} = [1 - (1 - \alpha)^{1-n}]$$
$$\times \exp(E/RT)/[Z(1-n)] \quad (n \neq 1) \quad (4)$$

The heating time is the lifetime of polymer to fail at weight loss α. It was found that the predicted TG curves were very close to those observed experimentally during the major weight-loss period. This indicates that the major isothermal degradation reaction of the copolymers might follow the same mechanism as that in the nonisothermal degradation reaction. However, an obvious difference between the experimental and predicted TG curves was found when the isothermally heating time was longer than 150 min for the 50:50 AN–OT copolymer and 50 min for the 30:70 AN–OT copolymer, suggesting that the subsequent isothermal decomposition process is different from nonisothermal decomposition process. A similar result has been observed for the thermotropic liquid crystalline aromatic oxybenzoate–ethylene terephthalate–benzamide copolymer.[18]

CONCLUSIONS

Aniline and *o*-toluidine can polymerize oxidatively into an amorphous copolymer with low yield for 40 h at −18°C with stirring. The actual OT unit content in the AN–OT copolymer soluble in CDCl$_3$ is much higher than the feed OT content in the corresponding copolymer. The thermostability and decomposition rate of the copolymers appear to vary irregularly with the AN–OT molar ratio, which could also be a result of the variation of the molecular weight of the copolymers. The copolymers show lower decomposition temperatures but larger char yield at 900°C and higher

activation energy of decomposition in nitrogen than in air.

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