

# Oxidative Copolymerization between Toluidine and Vinyl Acetate

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Received 21 July 2004; accepted 03 May 2005

DOI 10.1002/app.22822

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A series of copolymers between *o*-toluidine (OT) and vinyl acetate (VA) was synthesized by a chemically oxidative polymerization, which was carried out by three different methods: suspension solution precipitation, emulsion and inverse emulsion copolymerizations by using iron trichloride, and ammonium persulfate as oxidant. The progress in the copolymerization, polymerization yield, structure, and properties of the resulted OT/VA copolymers were systematically characterized by solution potential/temperature monitor, laser particle size, FTIR, UV-vis, and thermogravimetry techniques. The results show that the

diameter, spectral characteristics, solubility, film formability, electrical conductivity, and thermostability of the virgin polymer particles formed exhibit a nonmonotonic dependence on the OT/VA ratio, suggesting an occurrence of an oxidative copolymerization between OT and VA monomers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3562–3573, 2006

**Key words:** oxidative copolymerization; toluidine; vinyl acetate; electrical conducting copolymer; micrometer particle; structure; thermostability

## INTRODUCTION

Recently, a great interest in conducting polymers has arisen and most of the research work focused on the potential of conducting polymers in technological applications. In the year 2000, three scientists in this field won Nobel Prize for their inaugurating work in the conducting polymers.<sup>1–3</sup> Ever since then, more and more conducting polymers with some novel properties and extensive application potentials have been synthesized. The conducting polymers could be classified in four big groups according to the main-chain repeated units: polyacetylene, polyaniline (PAN), polypyrrole, and polythiophene. Among the four groups of conducting polymers, PAN and its derivatives showed better properties for their fairly high conductivities, environmental stability, and better solubility, especially better processibility. Therefore, the PAN and its many derivatives should be the most important conducting polymers displaying the most beautiful foreground. The oxidative copolymerization of aniline with aniline derivatives,<sup>4,5</sup> other aromatic amines,<sup>6,7</sup> and pyrrole<sup>8,9</sup> has been largely investigated

for a further improvement of the PAN performance in our laboratory. The copolymerization of aniline and available vinyl monomers might supply a preparing technique of inexpensive semiconducting polymers with a wide range of electrical conductivity. The copolymerization of the aniline and some vinyl monomers has also been studied and the electrical conductivity of the copolymers and reactivity ratio of the monomers were focused in the study.<sup>10</sup> However, the copolymerization yield, macromolecular structure, and many other important properties of the aniline/vinyl monomers copolymers have not been found till now.

In this paper, three oxidative copolymerization techniques, suspension solution, emulsion, and inverse emulsion, have been carried out and compared for the synthesis of a series of copolymers of *o*-toluidine (OT) and vinyl acetate (VA). The copolymerization yield, intrinsic viscosity, molecular structure, solubility, film formability, conductivity, and thermostability of the OT/VA polymers obtained were studied in detail by FTIR, UV-vis spectroscopies, solution casting method, and thermogravimetry. A significant relationship between the structure-properties of the polymers and the OT/VA ratio has been provided for the first time.

## EXPERIMENTAL

OT, VA, oxidant, initiator, solvent, and emulsifier are all commercially obtained and used as received.

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Contract grant sponsor: National Natural Science Fund of China; contract grant number: 20274030.

### Suspension solution copolymerization<sup>10</sup>

OT/VA copolymers were prepared by a suspension solution polymerization and a representative procedure for the preparation of OT/VA (50/50) is as follows: 80 mL CH<sub>2</sub>Cl<sub>2</sub> was mixed with 2.15 mL OT (0.02 mol) and 1.87 mL VA (0.02 mol) in a 150-mL beaker in ice-water bath. 6.5 g FeCl<sub>3</sub> and 100  $\mu$ L concentrated H<sub>2</sub>SO<sub>4</sub> were added into the monomer solution and then stirred vigorously by a magnetic stirrer for 24 h at 10°C. When the reaction completed, the OT/VA copolymer was isolated from the reaction mixture by filtration and washed with distilled water three times to remove oligomers and residual oxidants. The copolymers were separated into acetone-soluble and acetone-insoluble parts for the molecular structure investigation.

### Emulsion copolymerization

OT/VA copolymers were prepared by an emulsion copolymerization and a representative procedure for the preparation of OT/VA (50/50) is as follows: 80 mL 1M HCl was mixed with 2.15 mL OT (0.02 mol) and 1.87 mL VA (0.02 mol) in a 150-mL beaker at ambient temperature, which was magneto-stirred vigorously. 2 g (0.0057 mol) emulsifier, sodium dodecyl benzene sulfonate (SDBS), was added into the solution with stirring. 9.13 g (0.04 mol) ammonium persulfate, which was dissolved in 50 mL 1 mol/L HCl, was added dropwisely into the emulsion (the total molar ratio: oxidant/monomer = 1/1). After the mixture was stirred at 20°C for 24 h, 150 mL acetone was added into the resulting reactive solution to precipitate the OT/VA copolymers. They were washed with distilled water three times to remove the oligomers and residual reagents.

### Inverse emulsion copolymerization

OT/VA copolymers were also prepared by inverse emulsion copolymerization and a typical procedure for the preparation of OT/VA (50/50) is as follows: 50 mL toluene was mixed with 2.15 mL OT (0.02 mol) and 1.87 mL VA (0.02 mol) in a 250-mL glass flask at ambient temperature. 2 g emulsifier, DBSA, dissolved in 50 mL H<sub>2</sub>O, 5 g benzoyl peroxide (BPO) dissolved in 100 mL toluene, and 11.41 g ammonium persulfate dissolved in 50 mL 1 mol/L HCl were added into the monomer solution simultaneously and stirred by a magnetic stirrer for 24 h at 20°C. Then 150 mL 0.2M NH<sub>3</sub>·H<sub>2</sub>O was added into the solution to precipitate the OT/VA copolymers. They were washed with acetone and distilled water three times to remove the oligomers and residual reactants, and then dried in the oven at 60°C for 72 h.

### Measurement and characterization

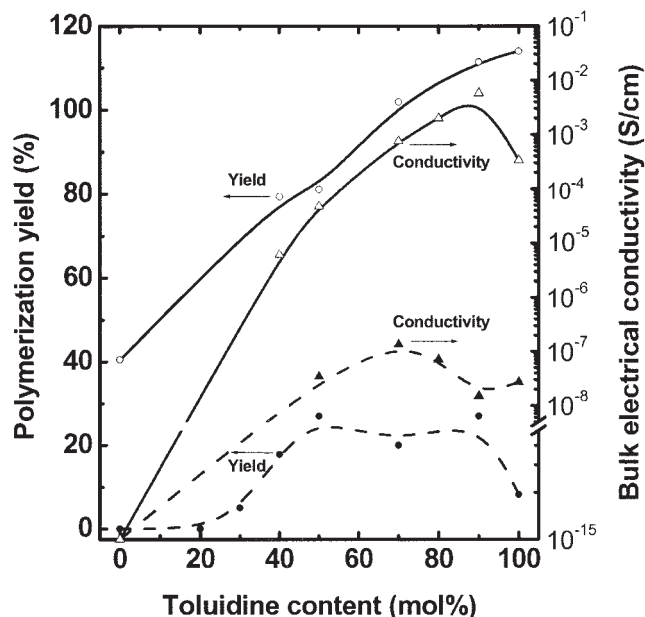
The real-time open-circuit potential (OCP) of the copolymerization solution was measured by an acidimeter, which connected a saturated calomel electrode (SCE) and a platinum electrode. The temperature of the copolymerization solution was real-time followed by a microthermometer. The solubility of the polymers was evaluated by the following method: a pinch of powder sample (about 5 mg) was added into the solvent of 2 mL at 20°C and dispersed thoroughly. After the mixture was swayed continuously for 2 h, the solubility of the sample was characterized. The intrinsic viscosity for the OT/VA copolymer in formic acid was measured with Ubbelodhe viscosimeter at 25  $\pm$  0.1°C. The IR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer with a resolution of 1 cm<sup>-1</sup> on KBr pellets. The UV-vis absorption of the copolymer solutions in formic acid at the concentration of 0.025 mg/mL was obtained by Perkin-Elmer Instruments Lambda 35 in a range of 190–900 nm at a scan rate of 480 nm/min. The size and its distribution of the as-prepared particles of the OT/VA copolymers in water were measured by LS230 Laser Particle Size Analyzer, Beckman Coulter Company. The film formability of the products in formic acid was tested by solution casting method onto a flat glass under a lamp of 40 W for 24 h. The bulk electrical conductivity of the copolymers as pressed pellets was measured by the two-disk method with a UT 70A multimeter at 20°C. The thermogravimetry of the dried products was performed in air on a Perkin-Elmer Thermal Analyzer at a heating rate of 10°C/min from 20 to 750°C with the sample size of 0.5–2.0 mg.

## RESULTS AND DISCUSSION

### Synthesis of the OT/VA copolymers

The OCP and temperature of the suspension solution during the copolymerization

The OCP of the suspension copolymerization solution with anhydrous FeCl<sub>3</sub> as oxidant at 10°C was found to be substantially constant during whole copolymerization process. However, the absolute value of the solution OCP depends on the OT/VA ratio and reaction temperature. The OCP is 500, 630, 890, and 1000 mV *versus* SCE for the OT/VA molar ratio of 100/0, 90/10, 50/50, and 40/60, whose comonomer solution OCPs in CH<sub>2</sub>Cl<sub>2</sub> are 486, 380, 336, 380, and 330 mV *versus* SCE, respectively, and FeCl<sub>3</sub> solution in CH<sub>2</sub>Cl<sub>2</sub> exhibits potential of 156 mV. Apparently, the higher OCP of the copolymerization solutions containing comonomers and oxidant should be due to the redox reaction between the comonomers and oxidant. The OCP increases with increasing VA content, possibly because of a decreased redox reaction mainly resulted from



**Figure 1** The product yield and electrical conductivity of the suspension solution copolymerization (---) at 15°C and FeCl<sub>3</sub>/monomer of 1/4 in CH<sub>2</sub>Cl<sub>2</sub> and emulsion copolymerization (—) at 20°C with different OT/VA molar ratios at (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/monomer molar ratio of 1/1 and emulsifier (SDBS)/monomer molar ratio of 22/88 and total monomer amount of 0.04 mol.

VA monomer. When the OT/VA molar ratio was constant at 50/50, the OCP of the copolymerization solutions changed from 820, 890, 580, and 510 to 900 mV versus SCE with elevating polymerization temperature from 5, 10, 15, and 20 to 25°C, whereas the OCPs of the comonomer solutions without adding anhydrous FeCl<sub>3</sub> were about 350–400 mV versus SCE. The OT/VA (50/50) copolymerization at 20°C produces a smallest increase in the solution OCP, implying that 20°C could be the optimal temperature for the copolymerization. In addition, the regular variation of the copolymerization solution OCPs with comonomer ratio and temperature indicates an occurrence of an interaction between OT and VA monomers, i.e., a real copolymerization of two monomers.

### Copolymerization

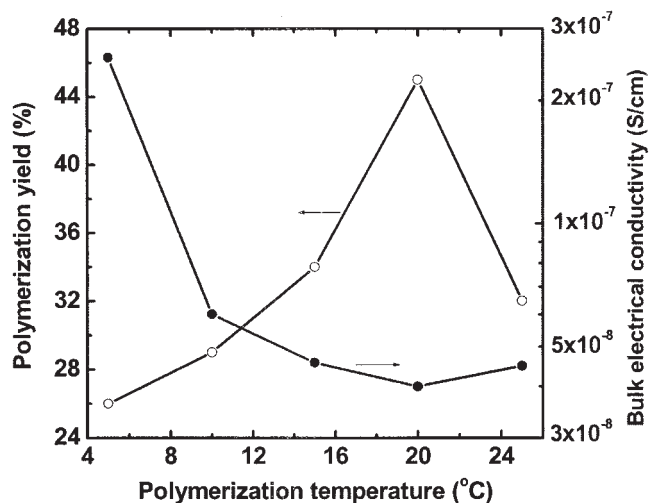
With the addition of the oxidants, either FeCl<sub>3</sub> or ammonium persulfate, the color of the polymerization

solutions changes from achromatically transparent to bluish-black in several seconds and finally turned black opaque. Black product indicates the formation of the polymer with continuous  $\pi$ -conjugated structure. A comparison between the polymer yields observed by suspension solution and emulsion copolymerizations at 10°C is shown in Figure 1. It seems that the copolymerization yield in the suspension solution increases substantially from 0 to 27% with increasing OT content from 20 to 50 mol %. The OT homopolymerization yield of down to 8.2% should be due to part solubility of pure OT homopolymer in CH<sub>2</sub>Cl<sub>2</sub>. Apparently, in the whole range of OT content, emulsion polymerization yield is always much higher than suspension polymerization yield. Furthermore, the emulsion polymerization yield observed increases monotonically from 40 to 114% with increasing OT content from 0 to 100%. These results strongly suggest that OT monomer exhibits much higher oxidative polymerizing activity than VA monomer. The yield higher than 100% may be due to the incorporation of the emulsifier that is not easy to be removed from the polymers. Apparently, the VA monomer exhibits an emulsion homopolymerizability to some extent if (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> served as oxidant, but no suspension homopolymerizability if FeCl<sub>3</sub> served as oxidant, because (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> can initiate both oxidative and radical polymerizations, whereas FeCl<sub>3</sub> can initiate only oxidative polymerization. However, the oxidative copolymerization of VA monomer could be initiated in the presence of a certain amount of OT cation radicals.

Note that the inverse emulsion polymerization yield at ammonium persulfate/monomer molar ratio of 1/1 is very low, as listed in Table I. But when ammonium persulfate/monomer molar ratio was reduced to 1/2 and no BPO was used as the initiator, the yield increases sharply to 36.9%. This shows that higher monomer concentration appears to advantage the oxidative copolymerization between OT and VA monomers in the inverse emulsion. In addition, polymerization yield is also influenced by the other polymerization conditions like polymerization temperature, as shown in Figure 2. The OT/VA (50/50) polymerization yield in suspension solution with the FeCl<sub>3</sub>/monomer of 1/1 displays a maximum of 45% at 20°C, implying that the optimal polymerization temperature could be 20°C. This result is coincident with that ob-

**TABLE I**  
The Polymerization Yield and Electrical Conductivity of OT/VA(50/50) Copolymers Obtained by Inverse Emulsion Copolymerization at 20°C with a Constant Emulsifier SDBS/Monomer Molar Ratio of 12/88 with Total Amount of Monomers of 0.04 Mol

BPO/monomer molar ratio	2/4	1/4	0/4	0/4
(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> /monomer molar ratio	1/1	1/1	1/1	1/2
Polymerization yield (%)	3.6	4.8	2.9	36.9
Electrical conductivity (S/cm)	$2.3 \times 10^{-6}$	$1.1 \times 10^{-4}$	$1.3 \times 10^{-4}$	$4.4 \times 10^{-4}$



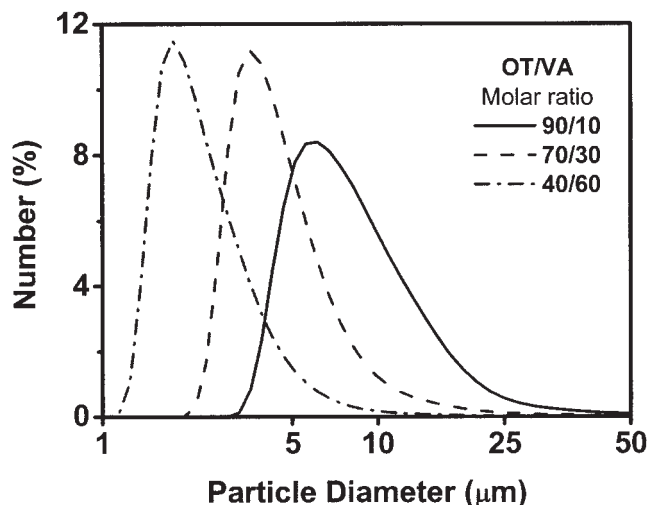
**Figure 2** The product yield and electrical conductivity of the suspension solution OT/VA (50/50) copolymerization at four polymerization temperatures with a fixed  $\text{FeCl}_3$ /monomer molar ratio of 1/1 in  $\text{CH}_2\text{Cl}_2$ .

served by solution OCP investigation. The intrinsic viscosity of the OT/VA polymers is listed in Table II. It appears that the intrinsic viscosity is too low, indicating that the molecular weight or chain rigidity of the polymers is not high.

### Structure of the OT/VA copolymers

The size and its distribution of the copolymer particles in water

The size distribution curves of the polymer particles obtained by suspension solution copolymerization at  $10^\circ\text{C}$  are drawn in Figure 3. The average particle diameter and its distribution of the polymer particles in water are listed in Table III. It can be seen that as the OT/VA molar ratio changes from 90/10 to 40/60, the number-average diameter decreases significantly (from 7.17 to  $2.21\ \mu\text{m}$ ) and so are all of the other three parameters. This indicates that the copolymer particles become smaller and also more narrowly distributed with increasing VA content. It seems that the VA units containing ester groups might act as internal stabilizer for the smaller particles.



**Figure 3** The particle size and its distribution of the products by suspension solution copolymerizations at  $10^\circ\text{C}$ .

FTIR spectra

Figures 4 and 5 show the FTIR spectra of all the OT/VA copolymers by suspension solution and emulsion copolymerizations. Apparently, the IR spectra of OT/VA copolymers systematically vary with OT/VA ratio, suggesting a systematical composition variation. For example, the vibration peaks at  $2920$  and  $2850\ \text{cm}^{-1}$  due to  $-\text{CH}_3$  in the VA units steadily become stronger with increasing VA content, although OT homopolymer also exhibits weak peaks at  $2920$  and  $2850\ \text{cm}^{-1}$  due to  $-\text{CH}_3$  in the OT units. It is seen from Figures 4 and 5 that the appearance of a shoulder peak at  $1718\ \text{cm}^{-1}$  ascribed to  $\text{C}=\text{O}$  for the acetone-insoluble part of OT/VA polymers with OT content of 0–50 mol % further confirms the presence of VA units in the dark polymers. On the other hand, there is a strong characteristic peak of  $\text{C}=\text{O}$  at  $1750\ \text{cm}^{-1}$  for the acetone-soluble part of the OT/VA (50/50) copolymer, an indication of VA units in the copolymer, and also medium peaks of aromatic  $\text{C}=\text{C}$  bond at  $1607$  and  $1497\ \text{cm}^{-1}$  that are an indication of VA units in the copolymer. These results suggest that insoluble part of the OT/VA copolymers obtained by suspension solution copolymerization usually consists of more OT and less VA units, but acetone-soluble part consists of

**TABLE II**  
The Intrinsic Viscosity, Film Formability, and Electrical Conductivity of Suspension Solution Copolymers with Different OT/VA Molar Ratios at a Fixed  $\text{FeCl}_3$ /Comonomer Molar Ratio of 1/1 in  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{SO}_4$  Medium at  $10^\circ\text{C}$

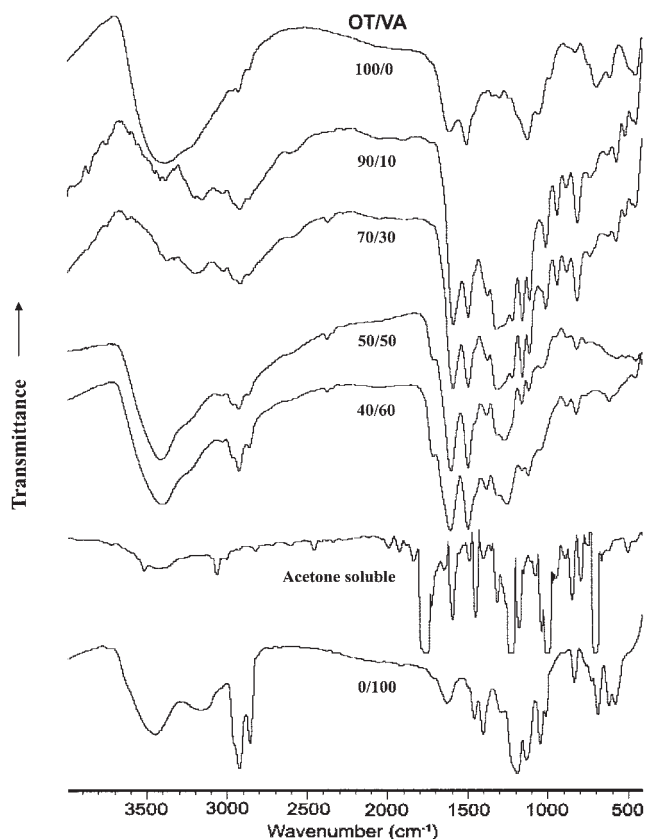
OT/VA molar ratio	90/10	70/30	50/50	40/60
$[\eta]$ (dL/g)	0.07	0.04	0.05	0.06
Film-forming ability	Fair	Nice	Good	Good
Conductivity (S/cm)	$3.1 \times 10^{-4}$	$2.8 \times 10^{-6}$	$6.0 \times 10^{-8}$	$1.4 \times 10^{-8}$
Film appearance	Black, smooth	Black, smooth	Black metal luster, smooth	Black metal luster, smooth

**TABLE III**  
The Size of Three Copolymer Particles in Water by Suspension Solution Copolymerization at 10°C

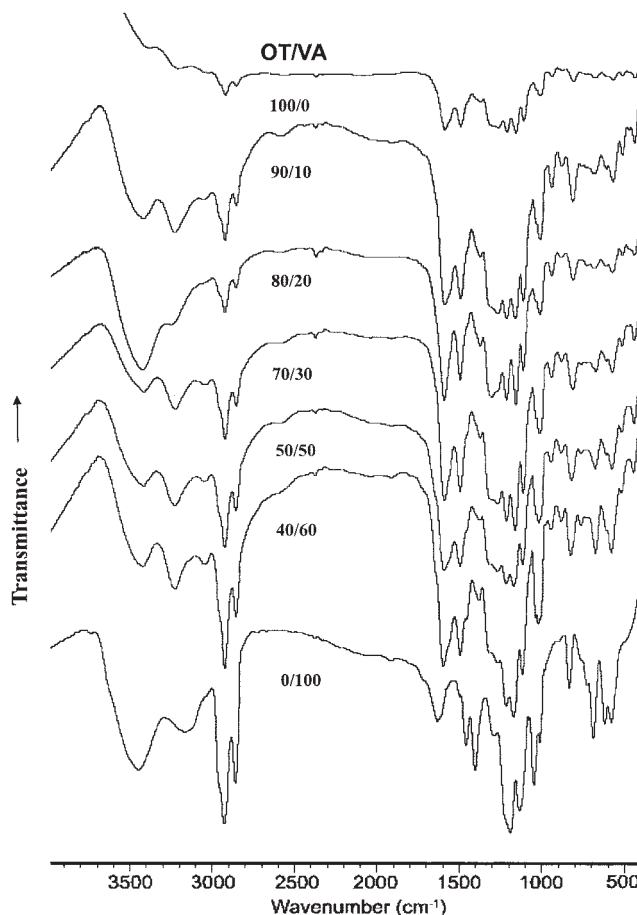
The size and distribution of OT/VA copolymer particles	90/10	70/30	40/60
Number-average diameter, $D_n$ ( $\mu\text{m}$ )	7.17	4.19	2.21
Standard deviation ( $\mu\text{m}$ )	6.11	4.01	1.91
Size polydispersity index, $D_w/D_n$	1.26	1.21	1.19

less OT and more VA units. In Figure 5, very strong peaks at 2920 and 1195  $\text{cm}^{-1}$  should be attributed to the residuum of emulsifier (SDBS) that has not been completely removed from the polymers.

The OT/VA copolymer structure is sometimes dependent on the polymerization condition. Figure 6 shows the FTIR spectra of the OT/VA (50/50) copolymers at different temperatures of suspension polymerization. All five polymers exhibit not only a similar shoulder peak at 1710  $\text{cm}^{-1}$  due to C=O group, but also nearly the same other peak characteristics. Therefore, the polymer structure appears independent of



**Figure 4** The FTIR spectra of OT/VA copolymers obtained by suspension polymerization from the top to bottom at the OT/VA molar ratios of 100/0, 90/10, 70/30, 50/50, 40/60, 0/100 and the gray acetone-soluble part of OT/VA (50/50) copolymer.

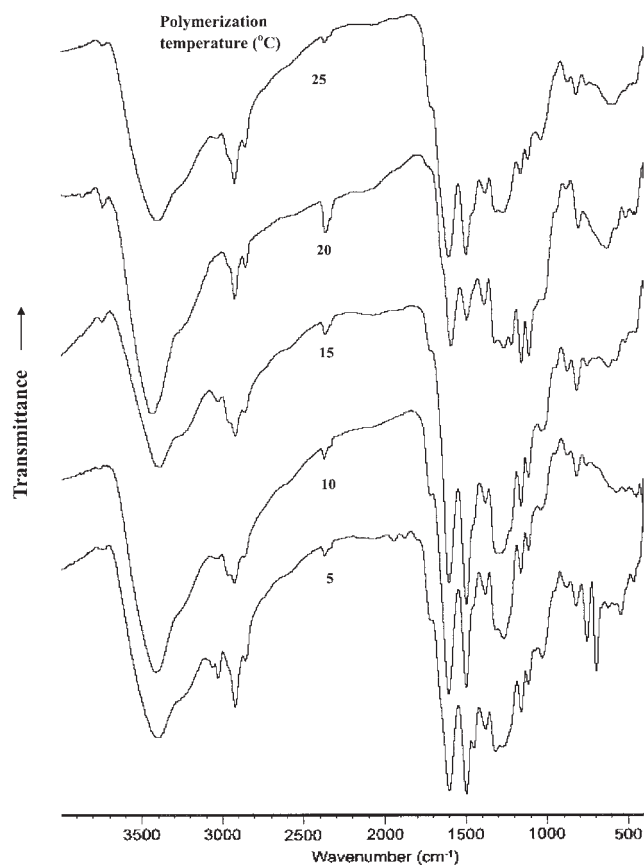


**Figure 5** The FTIR spectra of the products by emulsion copolymerizations and from top to bottom the OT/VA molar ratios of 100/0, 90/10, 80/20, 70/30, 50/50, 40/60, and 0/100 with total monomer amount of 0.04 mol.

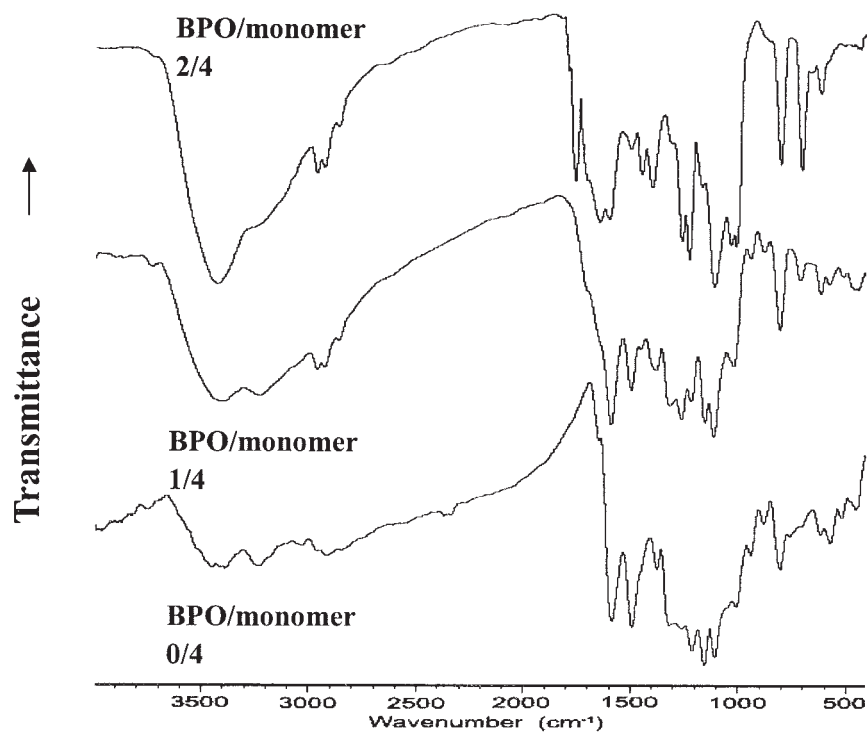
polymerization temperature. Figure 7 shows the FTIR spectra of the OT/VA (50/50) copolymer by inverse emulsion method with different BPO/monomer ratio. It seems that the characteristic peak of C=O group around 1700  $\text{cm}^{-1}$  gets stronger with increasing relative content of BPO as initiator. Two peaks at 1607 and 1497  $\text{cm}^{-1}$  due to aromatic rings also change significantly, i.e., the peak at 1607  $\text{cm}^{-1}$  becomes stronger and splits into a doublet with increasing BPO content, whereas the peak at 1497  $\text{cm}^{-1}$  steadily becomes weaker. It is concluded that the incorporation of BPO strongly influences the polymer structure because BPO is a traditional initiator for the radical polymerization of VA monomer, and also could be an oxidant for the oxidative polymerization of OT monomer. More BPO initiator could help the oxidative copolymerization of OT and VA by inverse emulsion copolymerization.

#### UV-vis spectra

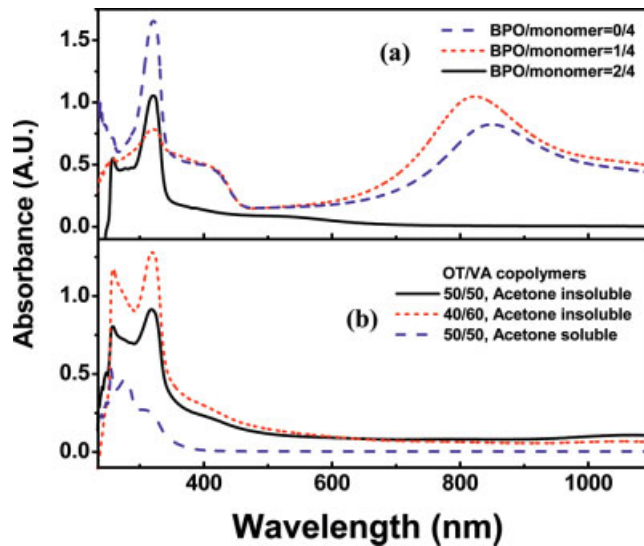
Figures 8 and 9 show the UV-vis absorption spectra of the typical OT/VA copolymers in formic acid by three



**Figure 6** The FTIR spectra of the OT/VA (50/50) copolymers by suspension solution copolymerization at different temperatures with the total monomer amount of 0.04 mol.

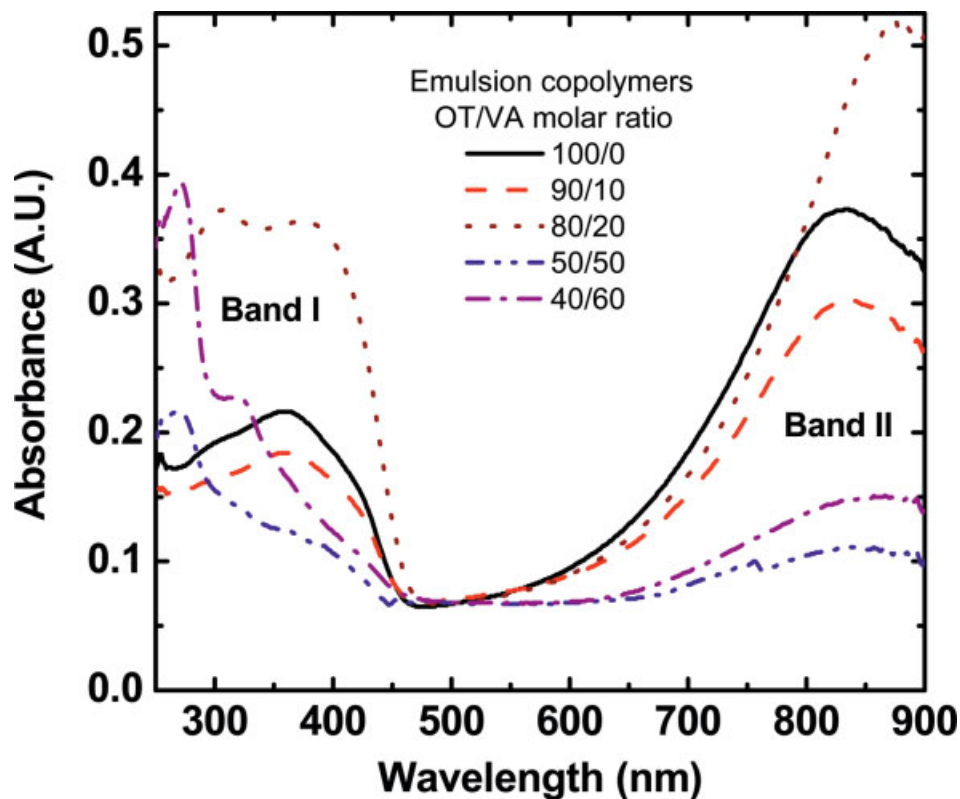


**Figure 7** The FTIR spectra of the OT/VA (50/50) copolymers by inverse emulsion copolymerizations with total monomer amount of 0.04 mol.



**Figure 8** The UV-vis spectra of the copolymers: (a) the OT/VA (50/50) copolymers of inverse emulsion copolymerization: GPO content varies from 5 to 0 g with the same other conditions and (b) the suspension solution copolymers with two OT/VA molar ratios. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

copolymerization methods. Characteristic absorption bands of the copolymers are listed in Table IV. The copolymers with OT content of 40–50 mol % exhibit a common peak around 255–270 nm and this peak be-



**Figure 9** The UV-vis spectra of the copolymers with five OT/VA molar ratios by an emulsion copolymerization. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

comes stronger with increasing VA content from 50 to 60 mol %, indicating that the peak is due to C=O bond and therefore the VA units indeed exist in the copolymers. All copolymers exhibit the peak around 316–325 nm corresponding to the  $\pi$ - $\pi^*$  transition and another peak around 358–420 nm. It is interesting that inverse emulsion OT/VA (50/50) copolymers with

BPO/monomer molar ratios of 1/4 and 0/4 exhibit a medium peak at 823–848 nm. Furthermore, all emulsion copolymers also demonstrate a typical peak at 834–879 nm. Especially, OT/VA (80/20) copolymer exhibits the strongest absorbance at the longest wavelength of 879 nm, which is similar to the electrical conductivity in Figure 1. Obviously, the absorbance

**TABLE IV**  
UV-vis Spectra in Formic Acid for the OT/VA Copolymers by Different Copolymerization Methods for Polymerization Time of 24 h

Copolymers	Wavelength (nm)
Inverse emulsion OT/VA (50/50) copolymers	
BPO/monomer = 2/4	256, 321 (Strongest), 520
BPO/monomer = 1/4	256, 321, 420, 823 (Strongest)
BPO/monomer = 0/4	258, 321 (Strongest), 420, 848
Suspension solution OT/VA copolymers	
Acetone-insoluble product of OT/VA (50/50)	258, 318 (Strongest), 420
Acetone-insoluble product of OT/VA (40/60)	259, 319 (Strongest), 420
Acetone-soluble product of OT/VA (50/50)	255 (Strongest), 277, 314
Emulsion OT/VA copolymers	
100/0	306, 358, 834 (Strongest)
90/10	302, 360, 837 (Strongest)
80/20	308, 375, 879 (Strongest)
50/50	269 (Strongest), 325, 365, 839
40/60	270 (Strongest), 316, 862

**TABLE V**  
**The Room-Temperature Solubility and Solution Color of the OT/VA Copolymers Obtained by Suspension Solution Copolymerization**

Solvents	Dielectric constant	Solubility of the copolymers with OT/VA molar ratio				
		100/0	90/10	70/30	50/50	40/60
H <sub>2</sub> SO <sub>4</sub>	101	SS,B	S,B	S,B	S,B	S,B
HCOOH	58	S,V	S,BI	S,BI	S,Br	S,Br
DMSO	47	PS,V	MS,BI	MS,BI	SS,BI	SS,Br
DMF	38	PS,V	PS,BI	PS,BI	PS,Br	PS,Br
NMP	32	PS,V	MS,BI	MS,BI	SS,Br	SS,Br
<i>m</i> -Cresol	12	SS,V	MS,BI	PS,BI	PS,Br	PS,Br
CH <sub>2</sub> ClCH <sub>2</sub> Cl	11	SS,V	SS,V	SS,V	SS,V	SS,V
CH <sub>2</sub> Cl <sub>2</sub>	9	SS,Br	SS,Br	SS,Br	SS,Br	SS,Br
THF	7	SS,V	SS,V	SS,V	SS,V	SS,V
CHCl <sub>3</sub>	5	SS,V	SS,V	SS,V	SS,V	SS,V
Benzene	2	SS,V	SS,V	PS,V	SS,V	SS,V

IS, insoluble; MS, mostly soluble; PS, partially soluble; S, soluble; SS, slightly soluble; B, black; BI, blue; Br, brown; G, green; O, orange; V, violet; Y, yellow.

peaks around 823–879 nm strongly imply very long  $\pi$ -conjugated backbone of the corresponding copolymers, which are very similar to that of protonation PAN emeraldine base showing a band at long wavelength of 880 nm.<sup>11</sup>

In addition, a regular variation of the intensity ratio of Band II (850 nm) over Band I (260–360 nm) of the copolymers with composition ratio was found. With increasing VA molar content from 0, 10, 20, and 50 to 60 mol %, the intensity ratio of Band II over Band I monotonically decreases from 1.73, 1.64, 1.38, and 0.52 to 0.38. This strongly suggests that the content of the long  $\pi$ -conjugated structure decreases steadily.

### Properties of the OT/VA copolymers

#### Solubility

One of the purposes to copolymerize OT and VA is to enhance the solubility or processability by adding the VA chain into the main chain of the OT polymers. The solubility of the OT/VA copolymers obtained by the three-polymerization techniques is listed in Tables V–VII. Nearly all the polymers are soluble in H<sub>2</sub>SO<sub>4</sub>

except for the OT homopolymer. The suspension solution and inverse emulsion polymers are all soluble in HCOOH, while the emulsion polymers are mostly soluble in HCOOH. On the contrary, the emulsion polymers are soluble in NMP and *m*-cresol, and inverse emulsion polymers are all soluble in DMF. Notethat the OT/VA polymers are only partly soluble in DMSO, slightly soluble in CH<sub>2</sub>ClCH<sub>2</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, THF, CHCl<sub>3</sub>, and benzene, and insoluble in xylene and toluene (not shown in Tables V and VI). It can be deduced that the OT/VA copolymers prefer to be soluble in the solvents with the solubility parameter of 23–27 J<sup>1/2</sup>/cm<sup>3/2</sup> or dielectric constant of 12–101. Apparently, the solubility of the polymers depends on the polymerization method and also the solvent, indicating that the polymer structure varies with the polymerization method. Note that the polymer solubility and solution color in most solvents appear to depend on the OT/VA and BPO/monomer ratios, indicating the change of the polymers. As expected earlier, the solubility of the emulsion polymers in benzene becomes steadily better with increasing VA content, because the presence of the VA units containing

**TABLE VI**  
**The Room-Temperature Solubility and Solution Color of the Copolymers by Emulsion Copolymerization**

OT/VA molar ratio	100/0	90/10	80/20	70/30	50/50	40/60	0/100
H <sub>2</sub> SO <sub>4</sub>	S,B	S,B	S,B	S,B	S,B	S,B	S,B
DMSO	PS,BI	PS,BI	PS,BI	PS,BI	PS,Br	PS,Br	PS
HCOOH	MS,B	MS,B	MS,G	MS,G	MS,Br	MS,Br	S
DMF	PS,BI	PS,BI	PS,BI	PS,G	PS,B	PS,B	MS
NMP	S,BI	S,BI	S,BI	S,BI	S,B	S,B	S
<i>m</i> -cresol	S,G	S,G	S,G	S,G	S,B	S,B	SS
CH <sub>2</sub> Cl <sub>2</sub>	SS,V	SS,V	SS,V	IS	PS,G	PS,G	S
THF	SS,BI	IS	SS,G	SS,G	S,B	S,G	MS
CHCl <sub>3</sub>	IS	IS	SS,B	IS	SS,B	S,B	S
Benzene	IS	IS	SS,G	SS,G	MS,G	MS,G	S



TABLE VII  
The Ambient Temperature Solubility of the OT/VA (50/50) Copolymers by Inverse Emulsion Copolymerizations

BPO/monomer molar ratio	2/4	1/4	0/4
H <sub>2</sub> SO <sub>4</sub>	S,Br	S,Br	MS,Br
HCOOH	S,O	S,G	S,G
DMF	S,Br	S,Bl	S,Bl
NMP	S,Br	S,Bl	MS,Bl
<i>m</i> -cresol	PS,Br	PS,Bl	PS,Bl
THF	PS,Br	SS,Br	SS,Br

acetate side groups will lead to the increase of the interchain distance, then the decrease of the interchain action, and finally the enhancement of the interaction between polymer chains and solvent molecules. In addition, a gradually enhanced solubility in CHCl<sub>3</sub>, benzene, and xylene of OT/VA copolymers with increasing VA feed content in Table VI qualitatively indicates the increase of true VA content in the copolymers.

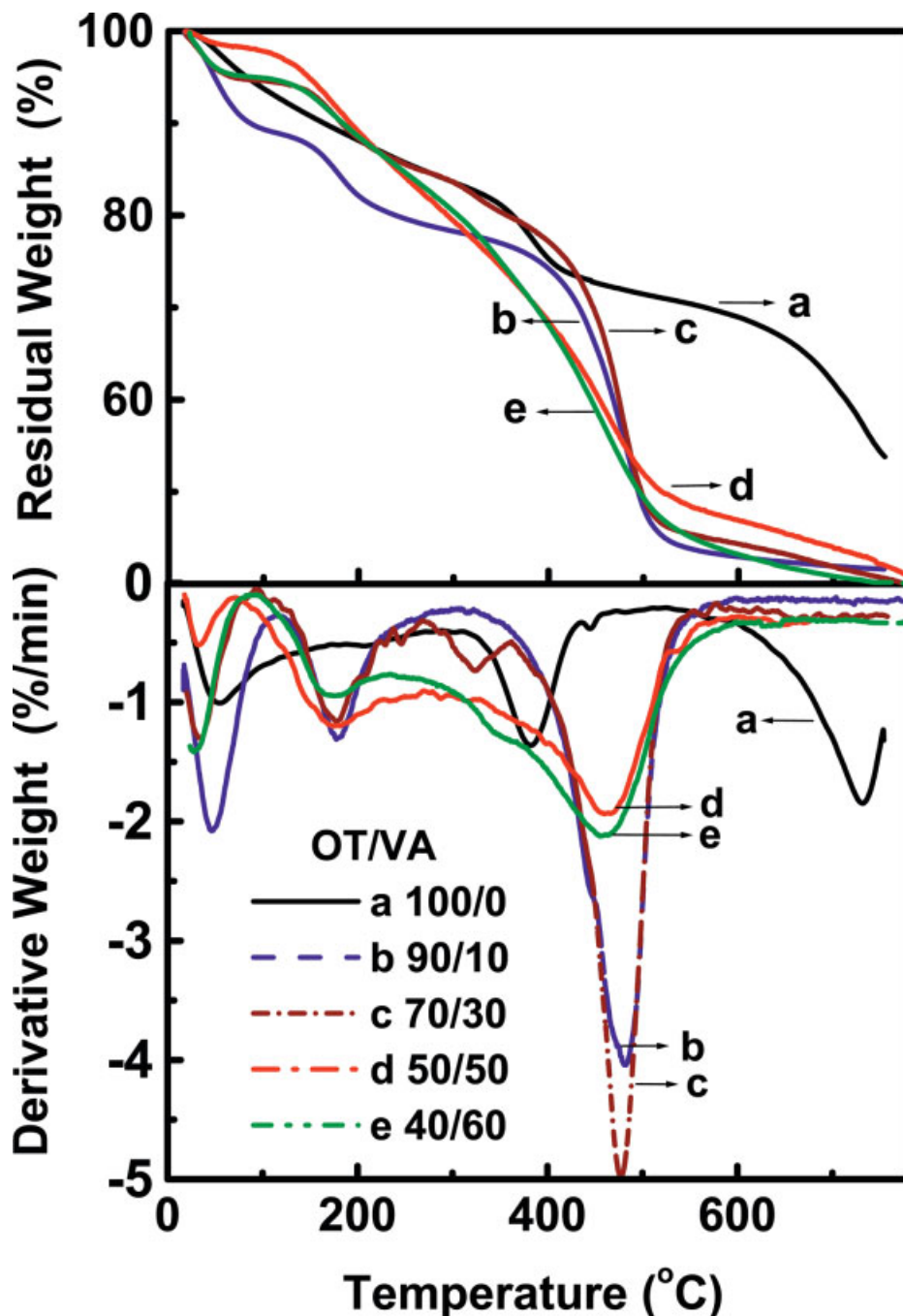


Figure 10 The thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of the OT/VA copolymers by suspension solution copolymerizations: the top one is TG curves and the bottom one the DTG curves. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE VIII**  
**The Kinetic Parameters of the Thermal Degradation of the Products by Suspension Solution Copolymerizations at different OT/VA Molar Ratio**

OT/VA molar ratio	$T_{\text{Water}}/T_{\text{dm1}}/$ $T_{\text{dm2}}/T_{\text{dm3}}$ (°C)	$(d\alpha/dt)_{\text{m1}}/(d\alpha/dt)_{\text{m2}}/$ $(d\alpha/dt)_{\text{m3}}$ (%/min)	$E$ (kJ/mol)	$n$
100/0	55/208/382/734	0.6/1.4/1.8	77.0	1.5
90/10	46/178/—/481	1.3/—/4.0	38.5	1.3
70/30	33/176/323/477	1.2/0.7/4.9	77.0	3.7
50/50	32/174/—/464	1.2/—/1.9	24.6	2.3
40/60	28/174/341/458	1.0/1.2/2.1	27.8	1.8

### Film formability

The film formability of the OT/VA polymers is listed in Table II. The film formability tends to become better with increasing VA content due to higher flexibility of VA units than OT units. However, it is not easy to understand why only OT/VA (50/50 and 40/60) polymers distinctly exhibit metallic luster, because the metallic luster of aromatic amine oxidative polymers should result from long-distance  $\pi$ -conjugated structure. Therefore, OT/VA (50/50 and 40/60) polymers exhibit stronger metallic luster than OT/VA (90/10 and 70/30) polymers because the relatively flexible VA units result in the smoother surface of the copolymer films.

### Bulk electrical conductivity

The electroconductivity of three types of virgin OT/VA copolymers obtained by three polymerization techniques is summarized in Tables I and II and Figures 1 and 2. The conductivity of the copolymers depends significantly on polymerization conditions. Usually, inverse-phase emulsion copolymers exhibit the highest conductivity, while suspension solution copolymers exhibit the lowest conductivity because of the much lower doping degree of the latter copolymers. It is seen from Table I that the conductivity of inverse emulsion copolymers seems to increase with decreasing BPO or  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  feed content possibly because of the enhancement of the copolymer molecular weight. Table II illustrates a monotonically increased conductivity from  $1.4 \times 10^{-8}$  to  $3.1 \times 10^{-4}$  S/cm for the suspension solution copolymers obtained at  $\text{FeCl}_3$ /comonomer molar ratio of 1/1 and 10°C, as the OT content increases from 40 to 90 mol %, apparently because of the lengthening conjugated bond. In particular, the suspension solution copolymers obtained at  $\text{FeCl}_3$ /comonomer molar ratio of 1/4 and 15°C in Figure 1 exhibit a maximum conductivity at OT content of 70 mol %. Similarly, the emulsion copolymers obtained at 20°C in Figure 1 also exhibit a maximum conductivity at OT content of 90 mol %. These results suggest that a small amount of VA monomer could promote the formation of OT poly-

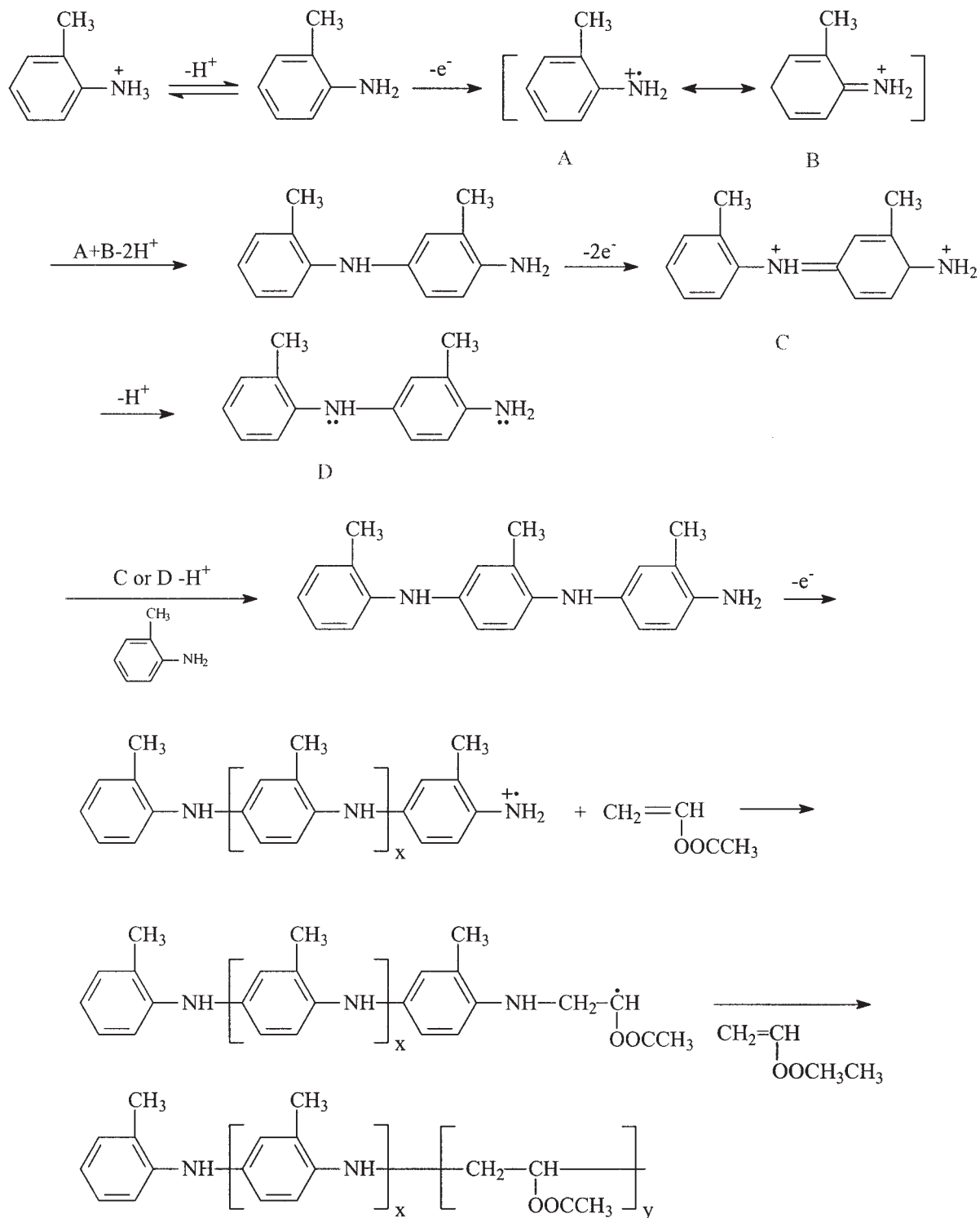
mers with higher conductivity, regardless of the electrical insulativity of VA homopolymer. The maximal conductivity and UV-vis absorbance wavelength (Fig. 9 and Table IV) at OT content of 70–90 mol % imply a clear and strong copolymerization effect between OT and VA monomers. The possible reason is that the copolymerization reactivity of OT with VA monomers is higher than their homopolymerization reactivity.<sup>12</sup> That is to say, the two types of monomers appear to activate each other, something like the copolymerization of aniline and chloroanilines.<sup>13</sup> This is another evidence that the polymer formed is a real copolymer. On the basis of a comparison of Table II and Figure 1, it can be found that the suspension solution copolymers obtained at 10°C exhibit much higher conductivity than at 15°C. Figure 2 also reveals an enhanced conductivity with lowering polymerization temperature from 25 to 5°C because of an increase in the molecular weight and, therefore, the conjugation length.

Besides the OT/VA ratio, polymerization method and temperature, emulsifier/monomer ratio, and acid species also remarkably influence the conductivity of the copolymers. If the emulsifier/monomer molar ratio changes from 12/88 to 22/78, the conductivity of the OT/VA (50/50) emulsion copolymer decreases from  $4.8 \times 10^{-5}$  to  $9.6 \times 10^{-7}$  S/cm, possibly owing to the presence of much insulative emulsifier as impurity. The OT/VA (50/50) suspension solution copolymer synthesized in  $\text{CH}_2\text{Cl}_2/\text{HNO}_3$  medium demonstrates higher conductivity ( $1.5 \times 10^{-6}$  S/cm) than that ( $6.0 \times 10^{-8}$  S/cm) in  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{SO}_4$  medium, since the copolymer obtained in  $\text{CH}_2\text{Cl}_2/\text{HNO}_3$  medium exhibits higher molecular weight and also much higher polymerization yield (77%).

### Thermal stability

The thermogravimetry (TG) and derivative thermogravimetry (DTG) curves are shown in Figure 10. The kinetic parameters of the thermal degradation of the copolymers were calculated by the Friedman technique using the equation:<sup>14–17</sup>

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



**Figure 11** One possible mechanism for chemically oxidative copolymerization between OT and VA monomers.

All the thermal degradation parameters are listed in Table VIII. The OT homopolymer exhibits higher thermostability than other polymers, but its degradation temperatures are much lower than those of the OT polymers obtained with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as oxidant.<sup>15</sup> With increasing VA content from 0 to 60, three decom-

position temperatures at the maximum weight-loss rate ( $T_{\text{dm}1}$ ,  $T_{\text{dm}2}$ ,  $T_{\text{dm}3}$ ) decrease steadily. These all indicate a decreasing tendency of the thermostability with increasing VA content. It is easily understood because aliphatic VA units, especially containing heat-sensitive ester groups, should be less thermostable

than aromatic OT units. On the other hand, three typical decomposition parameters, including maximum weight-loss rates  $[(d\alpha/dt)_{m3}]$ , activation energy ( $E$ ), and order ( $n$ ) all reach maximum at the OT/VA molar ratio of 70/30. This might reveal the fact that the polymer formed is a real OT/VA copolymer rather than a simple mixture of the OT and VA homopolymers because the properties of simple mixture should follow an additive principle. As regard to the mechanism of the copolymerizations of aniline or pyrrole,<sup>5-7,18</sup> possible block copolymerization mechanism of OT and VA monomers is shown in Figure 11. A gradual variation of the copolymer conductivity with OT/VA ratio in Table II and Figure 1 might be an evidence of the block copolymer formed by the suspension solution and emulsion polymerizations. If the copolymers are random, the copolymer conductivity could be dramatically decreased with a random incorporation of VA units into OT segments.

### CONCLUSIONS

A series of copolymers between OT and VA monomers have been successfully synthesized by chemically oxidative copolymerizations by three different copolymerization methods. The copolymers in water exist as stable fine particles with the number-average diameter of 2.21–7.17  $\mu\text{m}$  and a small size polydispersity index of 1.19–1.26. On the basis of FTIR and UV–vis spectra of the products, it is found that the OT/VA copolymerization significantly depends on the comonomer ratio: when OT molar content ranges from 40 to 50 mol %, the VA monomer will efficiently copolymerize into the main chain of OT polymer. The copolymerization effect also depends on the polymerization methods: emulsion polymerization technique will provide much higher yield than other two techniques. Inverse emulsion polymerization technique will provide a copolymer with the highest conductiv-

ity. Compared with the OT homopolymer, the solubility and electrical conductivity of the OT/VA copolymers are improved to some extent. It is surprising that the copolymers with OT content of 70–90 mol % exhibit higher conductivity than OT homopolymer. That is to say, the novelty of this article is that the introduction of around 10 mol % aliphatic VA unit into OT polymer can significantly enhance its electrical conductivity and solubility. Their thermal stability is also quite different from that of OT homopolymer. These results indicate the formation of a real copolymer between OT and VA monomers.

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