

Comparison of Poly(*o*-anisidine) and Poly(*o*-anisidine-*co*-aniline) Copolymer Synthesized by Chemical Oxidative Method

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ABSTRACT: In this study, poly(*o*-anisidine) [POA], poly(*o*-anisidine-*co*-aniline) [POA-*co*-A], and polyaniline [PANi] were chemically synthesized using a single polymerization process with aniline and *o*-anisidine as the respective monomers. During the polymerization process, *p*-toluene sulfonic acid monohydrate was used as a dopant while ammonium persulfate was used as an oxidant. *N*-methyl-pyrrolidone (NMP) was used as a solvent. We observed that the ATR spectra of POA-*co*-A showed features similar to those of PANi and POA as well as additional ones. POA-*co*-A also achieved broader and more extended UV-vis absorption than POA but less than

PANi. The chemical and electronic structure of the product of polymerization was studied using Attenuated Total Reflectance spectroscopy (ATR) and UV-visible spectroscopy (UV-vis). The transition temperature of the homopolymers and copolymers was studied using differential scanning calorimetry and the viscosity average molecular weight was studied by using dilute solution viscometry. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3123–3130, 2010

Key words: chemical synthesis; poly(*o*-anisidine-*co*-aniline); poly(*o*-anisidine); *p*-toluene sulfonic acid; ammonium persulfate; ATR; UV-vis; DSC; DSV and NMP

INTRODUCTION

The need to discover new materials with better properties than their predecessors is the driving force for many scientific and technological ventures. In the last two decades, the area of conducting polymers has attracted immense attention from several branches of science: physics, chemistry, and several engineering disciplines. The desirable electrical, chemical, and electrochemical properties of conducting polymers have made their applicability in many technological applications possible.^{1–6}

However; much of these studies have focused on understanding the nature of polyaniline as a superior material for use in applications such as coatings,⁷ biosensors,⁸ light emitting diodes,⁹ batteries,¹⁰ and microelectronic devices¹¹ mainly because of its good electrochemical properties. But despite its superior electrical conductivity, polyaniline has a downside to it which is primarily its insolubility in many organic solvents like *N*-methyl-pyrrolidone (NMP); therefore, posing a problem as far as processing is concerned. With this in mind, a renewed effort has been dedi-

cated to exploring other alternative conducting polymers such as poly(*o*-anisidine),^{12–14} poly(*N*-ethyl-aniline),^{15–17} and others. These substituted polyaniline derivatives (as shown in Scheme 1) have other advantages over polyaniline such as solubility in common organic solvents which leads to better processability.

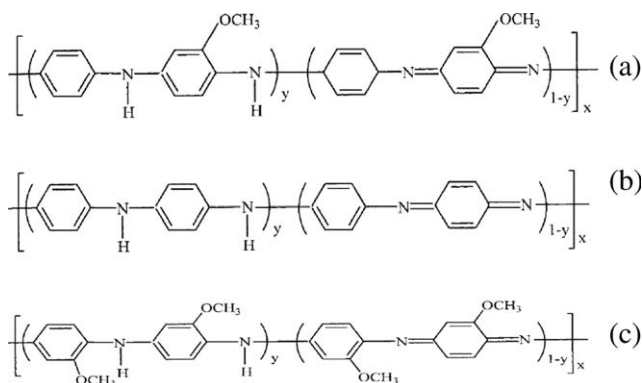
Earlier studies on chemically generated conducting copolymers have been on pyridine,¹⁸ benzene, and biphenyl,¹⁹ to mention a few. Electrochemically generated conducting copolymers have also been obtained from pyrrole¹⁴ derivatives²⁰ and thiophenes.²¹ In regard to polyaniline-derived copolymers, initial studies have been done by Wei et al.^{22,23}

Their studies have shown that the copolymerization of aniline with *o*-toluidine enables the conductivity to be controlled in a broad range. Langer has also reported the successful copolymerization of aniline with *N*-methylaniline.²⁴ Electrochemical copolymerization of aniline with *o*-anisidine has also been reported by Motheo et al.²⁵ Additional studies on copolymerization of aniline with *o*-anisidine and *o*-toluidine have been done by Borole et al.²⁶ who studied the effect of organic sulfonic acids on optical, electrochemical, and conductivity properties of poly(aniline-*co*-*o*-anisidine-*co*-*o*-toluidine).

Not much literature is present on the chemical synthesis of poly(*o*-anisidine-*co*-aniline) due to the fact that alternative methods like cyclic voltammetry are well established and very efficient at generating the copolymer than the former. Wang et al.²⁷

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Scheme 1 Illustration of (a) poly(*o*-anisidine-*co*-aniline), (b) polyaniline, and (c) poly(*o*-anisidine), where $0 \leq y \leq 1$ and $y = 0.5$ corresponds to polyaniline emeraldine base, $y = 1$ corresponds to leucoemeraldine and $y = 0$ corresponds to pernigraniline.

chemically synthesized poly(*o*-anisidine-*co*-aniline) at various temperatures and monomer compositions; and they found that the copolymer exhibits lower conductivity and tensile strength than polyaniline synthesized by chemical method. Ozdemir et al.²⁸ also studied chemically synthesized poly(*o*-anisidine-*co*-aniline).

The goal of this study is to use the single chemical oxidative polymerization method to synthesize soluble and easily processable copolymers and homopolymers based on aniline and its derivatives with adequate optical properties. The chemical oxidative method has some important advantages over the electrochemical synthesis method. For example, unlike the electrochemical method, the chemical synthesis method results in very high yield and the monomers are completely consumed at the end of the reaction. Also because of the significantly high yield and easy processability associated with the chemical method, large amounts of the products can be formed at a relatively lower cost. And after doing so, thin films or membranes can be cast on any substrate unlike the electrochemical method in which the film is cast solely on a conducting substrate. Chemical oxidative polymerization allows us to explore in detail, the optical, chemical, thermal, electronic, and rheological properties of the products of polymerization.

EXPERIMENTAL

Reagents

o-anisidine (99% purity), aniline (98% purity), and NMP (99% purity) were purchased from Sigma-Aldrich Company. Ammonium persulfate (99% purity) and *p*-toluene sulfonic acid (*p*TSA) monohydrate were also purchased from Sigma-Aldrich. All

the reagents listed above are all analytical grade; AR. Doubly distilled and deionized water were also used in this process.

Synthesis of copolymer POA-*co*-A

Chemical synthesis of the copolymer was achieved by a single polymerization process, which is known to offer good physical and chemical properties.

Sample 1 (POA-*co*-A-01) was synthesized by using 12.480 g (0.098 mol) of *o*-anisidine and 9.246 g (0.0993 mol) of aniline. The reaction mixture was ultrasonicated for 2 min after which stirring was continued using a magnetic stirrer. A total of 45.760 g (0.2003 mol) of ammonium persulfate was dissolved in 100 mL of doubly distilled water and added to the *o*-anisidine-aniline mixture dropwise until completion while the reaction mixture was being stirred vigorously with a magnetic stirrer. Reaction temperature was maintained at 25°C. Stirring was continued for 1.5 h after which the product was filtered using a suction pump. The resultant solid mass was washed using deionized water and then dried in a vacuum oven at 120°C for 3 h.

Sample 2 (POA-*co*-A-02) was synthesized by using similar quantities of *o*-anisidine and aniline as in the above except that, 8.05 g (0.02146 mol) of *p*TSA was dissolved in 50 mL of doubly distilled water and then added to the *o*-anisidine-aniline mixture followed by ultrasonication for 2 min. A similar set of procedures was followed as in the preparation of sample number one.

Samples 3 (POA-*co*-A-03) was prepared exactly as Sample 2 except that the dopant level was increased to 12.098 g.

Synthesis of homopolymer POA

Sample 1 (POA-01) was synthesized as follows: 12.514 g (0.985 mol) of *o*-anisidine was added to a beaker. A total of 22.7 g (0.996 mol) of ammonium persulfate was dissolved in 100 mL of doubly distilled water and added to the *o*-anisidine dropwise until completion while constant stirring was performed by means of a magnetic stirrer. After 1.5 h the product was filtered, washed with deionized water, and dried in a vacuum oven at 120°C for 1.5 h.

Sample 2 (POA-02) was synthesized as follows: 12.517 g (0.985 mol) of *o*-anisidine was measured and added to a beaker. A total of 4.05 g (0.0108 mol) of *p*TSA was dissolved in 50 mL of doubly distilled water and then added to the beaker containing *o*-anisidine. The mixture was ultrasonicated for 2 min after which 22.7 g (0.985 mol) of ammonium persulfate was dissolved in 100 mL of doubly distilled water added dropwise while continuously

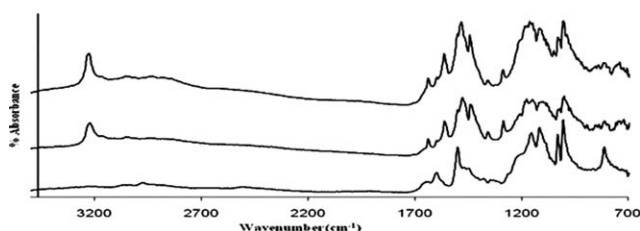


Figure 1 ATR spectrum of (a) undoped-POA-co-A-01 (bottom), (b) POA-co-A-02, and (c) POA-co-A-03 (top).

stirring with a magnetic stirrer. After 1.5 h the product was filtered, washed with deionized water, and dried in a vacuum oven at 120°C for 1.5 h.

Sample 3 (POA-03) was synthesized in the same way as Sample 2 except that 6.065 g (0.03192 mol) of *p*TSA was used.

Synthesis of homopolymer PANi

Polyaniline (PANi), homopolymer, was prepared exactly in the same way as POA by using 0.985 mol of aniline and 0.966 mol of ammonium persulfate. Sample 1 PANi-01 was synthesized with no dopant. Sample 2, PANi-02, was prepared using 4.05 g of dopant while Sample 3, PANi-03, was prepared using 6.05 g.

Characterization method

Nicolet 6700 FTIR instrument (Smart Orbit ATR accessory with diamond crystal) was used to determine the chemical structure of the homopolymers and copolymers. ATR was performed over a wavenumber range of 4000 cm^{-1} to 400 cm^{-1} . Samples were prepared by solution casting on aluminum plates followed by drying at 120°C for 1.5 h. ATR samples used were of 5% concentration.

UV-visible spectroscopy was used to study the electronic transition in the UV-vis region of the EM spectrum. Measurements were performed by using a U-3000 series spectrometer with wavelength range of 190–900 nm. UV-vis samples were prepared from 0.5 mg per 10 mL of NMP.

Dilute solution viscometry (DSV) was also used to determine the intrinsic viscosity of the polymers. Measurements were done using an Ubbelohde viscometer Kilmax, USA, size 100 and a stop watch.

Differential scanning calorimetry (DSC) tests were also conducted using DSC, TA Instrument 2010 Series. The tests were conducted in two steps. The first step involved heating the samples at 20°C/min from 25 to 250°C, and cooling back to room temperature. The second step involved reheating the samples to 400°C.

RESULTS AND DISCUSSION

ATR spectroscopy

Figure 1(a) shows the ATR spectrum of the undoped copolymer, POA-co-A-01. A prominent peak corresponding to the aromatic C–H stretching is observed at 3230 cm^{-1} . Characteristic peaks for the polymers are also observed at 1570 cm^{-1} and 1480 cm^{-1} due to C–N stretching of quinoid and benzenoid groups, respectively (see summary in Table I). Figure 1(b,c) shows the ATR spectra of doped copolymers POA-co-A-02 and POA-co-A-03 with dopant concentrations of 11 and 15 wt %, respectively. One of the striking differences between the undoped copolymer POA-co-A-01 and the doped copolymers POA-co-A-02, POA-co-A-03 is the increasing intensity of the quinoid and benzenoid peaks in the order: POA-co-A-03 > POA-co-A-02 > POA-co-A-01, with respect to increasing dopant concentration. Also, the dopant seems to cause a shift in the position of the quinoid and benzenoid peaks with the two peaks being at 1600 cm^{-1} and 1500 cm^{-1} in the undoped copolymer and 1570 cm^{-1} and 1480 cm^{-1} in the doped copolymer. According to the literature,²⁹ the intensity ratio of the peaks at $\sim 1600 \text{ cm}^{-1}$ to $\sim 1500 \text{ cm}^{-1}$ can be used to estimate the degree of oxidation of polyaniline and its derivatives:

$$\text{The ratio } R = \frac{1600 \text{ cm}^{-1} \text{ Intensity}}{1500 \text{ cm}^{-1} \text{ Intensity}}$$

The values calculated from the ATR data are $R = 0.276, 0.475,$ and 0.520 for undoped-POA-co-A-01, POA-co-A-02, and POA-co-A-03, respectively. Also, $R = 0.760, 0.820,$ and 0.920 for PANi-01, PANi-02, and PANi-03, respectively. Finally, $R = 0.230, 0.376,$ and 0.472 for POA-01, POA-02, and POA-03, respectively. All values of R are shown in Table II. The value of R is less than 1.0 in all the cases, indicating that there are more benzene units in the polymer structure than there are quinoid units. A value of 1.0 defines the emeraldine base (EB) structure of

TABLE I
Characteristic Band Assignment of
Poly(*o*-anisidine-co-aniline)

Peak position		Band characteristics
POA-co-A-01	POA-co-A-02 and POA-co-A-03	
3230	3230	Aromatic C–H stretching
1600	1640	C–N stretching of quinoid ring
–	1570	C–N stretching of quinoid ring
1500	1480	C–N stretching of benzenoid ring
1440	1440	C–N stretching of benzenoid ring
1160	1160	C–N in plane bending vibrations
1120	1120	C–N in plane bending vibrations
997	997	O-methoxy group
818	818	Paradisubstituted aromatic ring

TABLE II
Ratio of $\sim 1600\text{ cm}^{-1}$ to $\sim 1500\text{ cm}^{-1}$

Polymer	Ratio of $\sim 1600/\sim 1500$
POA-co-A-01	0.276
POA-co-A-02	0.475
POA-co-A-03	0.520
PANi-01	0.760
PANi-02	0.820
PANi-03	0.910
POA-01	0.230
POA-02	0.376
POA-03	0.472

polyaniline, which makes it more conductive.²² This means that copolymer POA-co-A-03, for example, is half as oxidized as polyaniline in the EB. Based on the ratios of the $\sim 1500\text{ cm}^{-1}$ to the 1600 cm^{-1} peak, the degree of oxidation follows the order: PANi > POA > POA-co-A, which agrees with conductivity values found in literature,³⁰ mainly because steric as well as electronic effects of the bulky methoxy groups hinder effective doping.

Figure 2(a) shows the ATR spectrum of the undoped homopolymer PANi. There is a distinctly broad peak around $\sim 3100\text{ cm}^{-1}$, which is due to aromatic C–H stretching. The characteristic peaks at 1620 cm^{-1} , 1530 cm^{-1} , and 1470 cm^{-1} were also observed. The ATR peak at 1620 cm^{-1} is due to C–N stretching in the quinoid ring while the peaks at 1530 cm^{-1} and 1470 cm^{-1} are due to C–N stretching in the benzenoid structure (see summary in Table III). Figure 2(b,c) shows the ATR spectra of the doped homopolymers, PANi-02 and PANi-03, which were synthesized with 11 and 16 wt % dopant concentration. The characteristic peaks at 1620 cm^{-1} and 1530 cm^{-1} are due to the quinoid and benzenoid structure, respectively. The quinoid peak around 1470 cm^{-1} decreased with increasing dopant concentration. A prominent peak was also observed at 1400 cm^{-1} , which increased with increasing dopant amount in the order: PANi-03 > PANi-02 > PANi-01. A broad peak at $\sim 1020\text{ cm}^{-1}$ in PANi is due to symmetric and asymmetric S=O stretching of the SO_3^- group in *p*TSA. This peak increases with increasing dopant concentration as was expected.

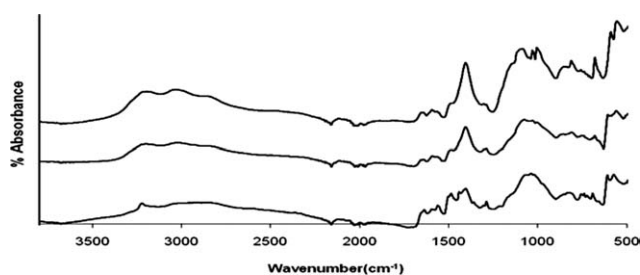


Figure 2 ATR spectrum of (a) undoped-PANi-01 (bottom), (b) PANi-02, and (c) PANi-03 (top).

TABLE III
Characteristic Band Assignment for Polyaniline

Peak position	Band characteristics
PANi-01,02,03	
3100	Aromatic C–H stretching
1620	C–N stretching of quinoid ring
1530	C–N stretching of benzenoid ring
1470	C–N stretching of benzenoid ring
1400	C–C in-ring stretching
1020	S=O stretching of SO_3^- group
808	Paradisubstituted aromatic ring

Figure 3(a) shows the ATR spectrum of undoped homopolymer POA-01. Characteristic peaks are observed at 1550 cm^{-1} and 1460 cm^{-1} due to the quinoid benzenoid groups, respectively. The broad peak at $\sim 2900\text{ cm}^{-1}$ is due to C–H stretching in the aromatic ring (see summary in Table IV). Figure 3(b,c) shows the ATR spectra of POA-02 and POA-03. Characteristic peaks occurring at 1560 cm^{-1} and 1470 cm^{-1} are due to quinoid and benzenoid groups, respectively.

Based on the ATR results POA-co-A can be shown to be a copolymer of aniline and *o*-anisidine monomers by looking at the differences between the copolymer and homopolymer spectra. For example, the peak due to C–H aromatic stretching is observed at $\sim 3230\text{ cm}^{-1}$ in POA-co-A, $\sim 3100\text{ cm}^{-1}$ in PANi, and $\sim 2900\text{ cm}^{-1}$ in POA. Also, the peak at $\sim 1160\text{ cm}^{-1}$ is present in the copolymer but absent in PANi and POA, which confirms the occurrence of copolymerization as opposed to mixing of PANi and POA. More so the relative intensity of the $\sim 1600\text{ cm}^{-1}$ and $\sim 1500\text{ cm}^{-1}$ peaks in PANi and POA differ greatly from those in the copolymer, which further confirms that the polymer in question is a copolymer and not a mixture of PANi and POA.

UV-vis spectroscopy

Figures 4–7 show the UV-vis spectra of aniline, anisidine, poly(*o*-anisidine), polyaniline, and poly(*o*-anisidine-co-aniline), respectively, in NMP. All the three

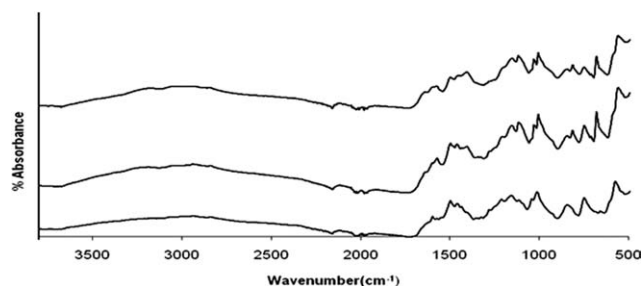


Figure 3 ATR spectrum of (a) undoped-POA-01, (b) POA-02, and (c) POA-03.

TABLE IV
Characteristic Band Assignment for Poly(*o*-anisidine)

Peak position	Band characteristics
POA-01,02,03	
2900	Aromatic C–H stretching
1560	C–N stretching of quinoid ring
1470	C–N stretching of benzenoid ring
1390	C–C in-ring stretching
1120	C–N in plane bending vibrations
997	O-methoxy group
804	Paradisubstituted aromatic ring

POA polymers show a large peak at ~ 280 nm (Fig. 4), which is attributed to π - π^* transitions in the benzenoid structure. The area under the ~ 280 nm peak increases with dopant concentration and is believed to be due to an increase in conjugation length of the polymers. The three polymers also show UV absorbance at around ~ 420 and ~ 560 nm. The absorption peak at ~ 420 nm is associated with polaron- π^* transitions, while the peak at around ~ 560 nm is (see summary in Table V) believed to be due to n - π^* transitions in the quinoid structure of the polymer backbone. Figure 5 shows the UV-vis spectra of *o*-anisidine and aniline monomers. Both monomers show a sharp peak at ~ 290 nm. The narrowness of the peak at ~ 290 nm is associated with the low-molecular weight nature of the monomers.

The UV-vis spectrum of polyaniline (Fig. 7) shows a strong absorption peaks at ~ 274 – 330 nm and a broad weak peak at ~ 600 nm. The strong peak at ~ 330 nm is believed to be due to π - π^* transition in the benzenoid structure while the broad peak at ~ 600 nm is believed to be due to n - π^* transition in the quinoid structure of the polymer backbone. The peaks at ~ 330 and ~ 600 nm are characteristics of the EB form of polyaniline.³¹

Figure 6 shows the UV-vis spectra of the copolymer. The undoped copolymer POA-co-A-01 shows a strong peak at ~ 264 nm and a weak and broad peak

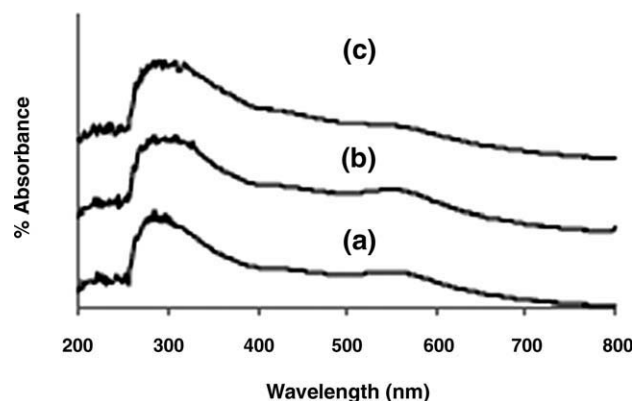


Figure 4 UV-vis spectrum of (a) undoped-POA-01 (bottom), (b) POA-02, and (c) POA-03 (top).

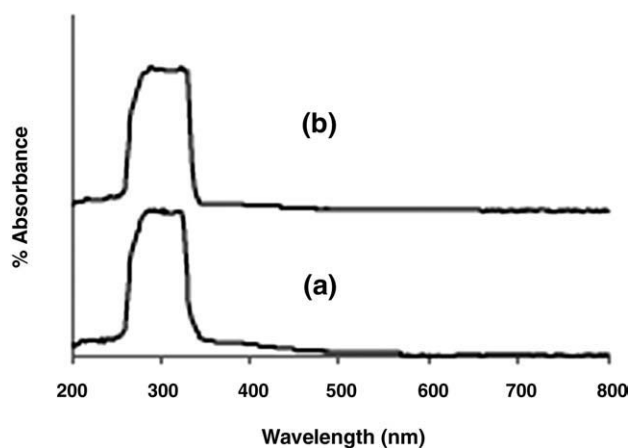


Figure 5 UV-vis spectrum of (a) *o*-anisidine (bottom) and (b) aniline (top).

at 550 nm. The copolymer POA-co-A-02 has a strong peak at ~ 274 nm and a weak and broad peak at ~ 560 nm. The copolymer POA-co-A-03 also has a strong peak at ~ 274 nm and a weak and broad peak at ~ 530 nm. The peak at ~ 260 – 270 nm that becomes broader with increasing dopant concentration is attributed to π - π^* transition in the benzenoid ring and carbonyl (C=O) structure on the methoxy group, while the broad peak at ~ 560 nm is believed to be due to n - π^* transitions of the quinoid group. The PANi peak at ~ 600 nm has shifted to 560 nm in the copolymer, which confirms that the polymer in question is indeed a copolymer and not a mixture of PANi and POA. Another evidence of copolymerization is that both PANi and POA have three UV-vis peaks while POA-co-A has only two peaks. This decrease in the number of peaks points to a decrease in conjugation.

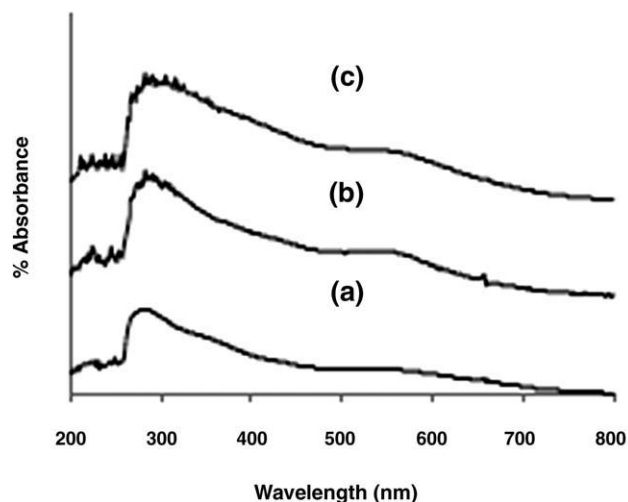


Figure 6 UV-vis spectrum of (a) undoped-POA-co-A-01 (bottom), (b) POA-co-A-02, and (c) POA-co-A-03 (top).

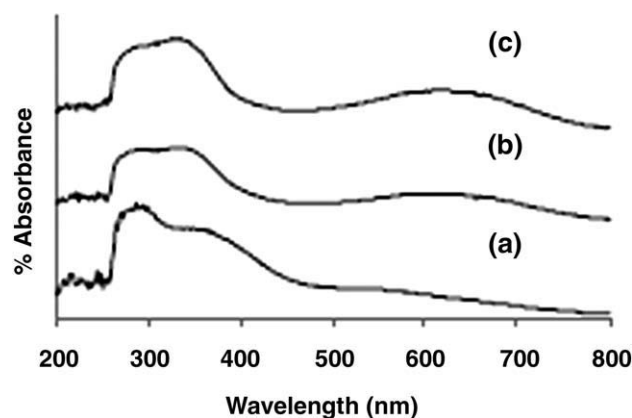


Figure 7 UV-vis spectrum of (a) undoped-PANi-01 (bottom), (b) PANi-02, and (c) PANi-03 (top).

DSC studies

Figures 8–10 show the second run DSC thermograms of POA-co-A, PANi, and POA, respectively. The glass transition temperature (T_g s) and melting temperature (T_m) are summarized in Table VI. Sample POA-co-A-01 shows two T_g s at 60°C and 148.8°C and one T_m at 242.2°C. Sample POA-co-A-02 also shows two T_g s at 114.7°C and 150.2°C and one T_m at 245.6°C. Sample POA-co-A-03 shows two T_g s at 118.5°C and 139.8°C and one T_m at 233.6°C. The presence of both glass transition and melting temperatures indicating that the copolymer is semicrystalline. The appearance of multiple T_g s and T_m s could be attributed to the effect of thermal history on the polymer structure. The samples were heated to 250°C during curing and this is believed to have caused the rearrangement of the polymer chains, and hence affecting the transition temperatures.

On the other hand, PANi and POA have single glass transition temperatures and multiple melting temperatures except PANi-02, which has only one melting temperature.

Dilute solution viscometry

The intrinsic viscosity $[\eta]$ of the POA-co-A, POA, and PANi were obtained by using an Ubbelohde viscometer. The intrinsic viscosity was obtained from a plot of $\text{Log}(\text{Rel } \eta)/C$ and $\text{Sp } \eta/C$ versus C . Where C is the concentration in g/dL and η is a measure of

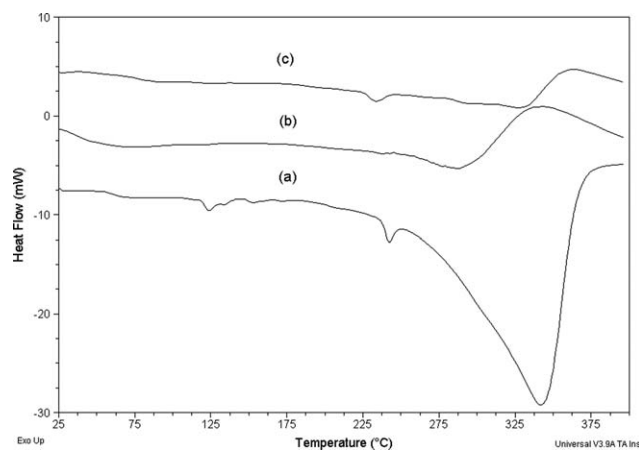


Figure 8 DSC thermogram of (a) POA-co-A-01, (b) POA-co-A-02, and (c) POA-co-A-03.

the viscosity. The intrinsic viscosity values for the samples are as follows: 1.02, 0.501, and 0.320 dL/g for POA-co-A-01, POA-co-A-02, and POA-co-A-03, respectively, as shown in Figure 11. Intrinsic viscosity values for polyaniline formed under varying reaction condition are 1.18, 1.12, and 0.76 dL/g for PANi-01, PANi-02, and PANi-03, respectively. The intrinsic viscosities of poly(*o*-anisidine) are 0.956, 0.6726, and 0.535 dL/g for POA-01, POA-02, and POA-03, respectively.

$$\text{Relative viscosity (rel } \eta) = t/t_0 \quad (1)$$

$$\text{Specific viscosity (Sp } \eta) = (t - t_0)/t_0 \quad (2)$$

where t is the elution time for solution and t_0 is the elution time for solvent.

By extrapolating the reduced viscosity plots to zero concentration, as shown in Figure 11, we obtained the intrinsic viscosity, which in turn is used to calculate the viscosity average molecular weight by using the Mark-Houwink equation:

$$[\eta] = KM^a$$

where the parameters K and a are the Mark-Houwink constants, which depend on the polymer-solvent system. Based on the Mark-Houwink equation, the molecular weights of the copolymer decrease in the order: POA-co-A-01 > POA-co-A-02

TABLE V
Summary of UV-vis Peaks

	POA-co-A-01	POA-co-A-02	POA-co-A-03	PANi-01	PANi-02	PANi-03	POA-01	POA-02	POA-03
Strong peaks (nm)	264	274	274	278	272	274	280	284	286
	–	–	–	340	328	324	–	–	–
	–	–	–	–	–	–	–	–	–
Weak peaks (nm)	–	–	–	–	–	–	420	420	420
	550	530	560	550	600	600	560	560	560

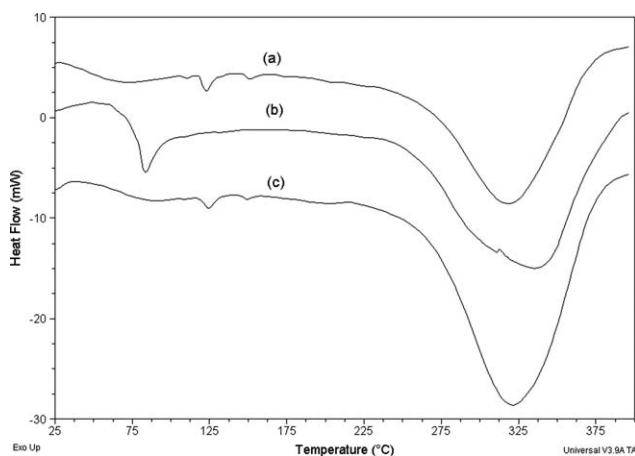


Figure 9 DSC thermogram of (a) PANi-01, (b) PANi-02, and (c) PANi-03.

> POA-co-A-03, suggesting that a decrease in degree of polymerization occurs with increasing dopant concentration.

CONCLUSION

We synthesized polyaniline, poly(*o*-anisidine), and poly(*o*-anisidine-co-aniline) by chemical oxidative polymerization and characterized it by using ATR spectroscopy, UV-vis spectroscopy, DSC, and DSV.

The ATR spectra of the copolymers show characteristic peaks similar to those of poly(*o*-anisidine) and polyaniline as well as additional ones, which indicate the presence of a copolymer rather than a mixture of the two homopolymers. The intensity of the quinoid and benzenoid peaks is very sensitive to dopant concentration and is attributed to oxidation state. The ratio of the $\sim 1600\text{ cm}^{-1}$ peak to the $\sim 1500\text{ cm}^{-1}$ peak gives a measure of the degree of oxidation and increases in the order: POA-co-A < POA < PANi, which concurs with conductivity values found in literature.³⁰

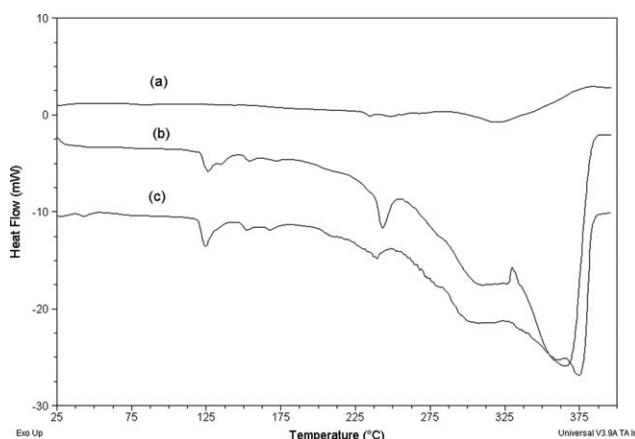


Figure 10 DSC thermogram of (a) POA-01, (b) POA-02, and (c) POA-03.

TABLE VI
Glass Transition Temperatures and Melting Points of POA-co-A, POA, and PANi

1st T_g	2nd T_g	1st T_m	2nd T_m
POA-co-A-01			
60	148.8	124.13	242.15
POA-co-A-02			
114.7	150.2	245.6	–
POA-co-A-03			
118.5	139.8	233.6	–
PANi-01			
107.1	–	122.7	151.1
PANi-02			
89.5	–	83.9	–
PANi-03			
107.1	–	124.6	149.2
POA-01			
77.2	–	143.09	234.6
POA-02			
150	–	160	240
POA-03			
150	–	160	240

The broadness of the UV-vis absorption of the copolymer in the ~ 250 to ~ 420 nm region is between that of poly(*o*-anisidine) and polyaniline. This broadening of the UV-vis absorption peak between 250 and 420 nm is associated with increased conjugation length, which is sensitive to the dopant concentration.

The intrinsic viscosities of the POA-co-A and PANi were found to decrease with increasing dopant concentration, signifying a decrease in molecular weight with increasing dopant concentration. Also PANi has higher intrinsic viscosity than POA-co-A and POA pointing to lower molecular weight in POA-co-A and POA due to possible steric hindrance effect of the bulky methoxy group on polymerization.

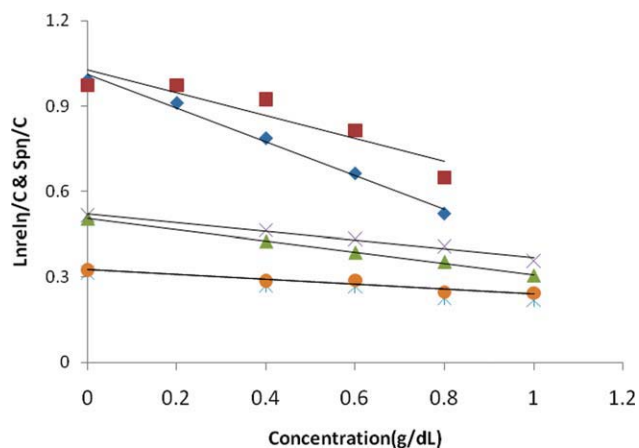


Figure 11 Dilute solution viscosity plot of (a) POA-co-A-01 (top), (b) POA-co-A-02, and (c) POA-co-A-03 (bottom). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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