



CONDUCTIVITY AND SPECTRAL STUDIES ON HEAT TREATED POLY(ANILINE-CO-2-CHLOROANILINE) SALTS

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Abstract—Poly(aniline-co-2-chloroaniline)-*p*-toluenesulfonic acid and poly(aniline-co-2-chloroaniline)-formic acid salts were obtained by chemical oxidative copolymerization of aniline with *o*-chloroaniline. Copolymer salts were heat treated under a nitrogen atmosphere at 150, 200, 275 and 375°C. As prepared, the heat treated samples were characterized by IR, electronic absorption, and electron paramagnetic resonance spectra and conductivity measurements. The conductivity (2.7×10^{-2} S/cm) and yield (16.0 g) of poly(aniline-co-2-chloroaniline)-*p*-toluene sulfonate are less than those of poly(aniline-co-2-chloroaniline)-formate, 1.9×10^{-2} S/cm and 6.8 g, respectively. Poly(aniline-co-2-chloroaniline) salts primarily exist as polysemiquinone radical cation in which a free electron is localized on or near the nitrogen atom. The copolymer salts are stable up to 200°C and structural changes take place above 200°C. © 1997 Elsevier Science Ltd

INTRODUCTION

Conducting polymers in the highly extended conjugated electron systems in the main chain have recently attracted much attention from both fundamental as well as practical view points. Polyaniline is a promising candidate as an industrially important conducting polymer due to its stability and potentially attractive economics. Polyaniline has been described as the conducting polymer for technology, since all applications do not require conducting polymers with high conductivity in the region of 10–1000 S/cm. The semiconducting range of 10^{-4} – 10^{-1} S/cm can be used for EMI shielding and antistatic applications.

There have been several reports on the syntheses and properties of substituted polyanilines [1–4]. These polyaniline derivatives have improved solubilities and different electronic and electrochemical properties in comparison to those of polyaniline. Wei *et al.* [5] have studied the chemical and electrochemical copolymerization of aniline with alkyl ring substituted aniline. Chan *et al.* [6] have studied the copolymers of aniline with *o*-amino benzyl alcohol. Studies on copolymerization may lead to an understanding of the relationship between the reactivities and the chemical structure of the monomers and, therefore, to a better understanding of the mechanism of polymerization.

Serious disadvantages such as insolubility, infusibility and hence non-processibility often mask the great potential of conducting polymers. In order to address the question of processibility, attempts have been made to make blends with conventional thermoplastics, where the conducting polymer exists as the dispersed phase. Conventional thermoplastics are melt processed, usually several degrees above

their melting point or glass transition temperature. It means that the conductive polymer should be stable under the processibility conditions of the host thermoplastic polymers. The investigations on the thermal stability of conducting polymers are hence of great importance. Several workers [7–10] have studied the thermal stability of polyanilines both in the conducting and insulating forms by thermogravimetric and differential thermal analysis. This paper reports the thermal stability of poly(aniline-co-2-chloroaniline)-*p*-toluenesulfonate and poly(aniline-co-2-chloroaniline)-formate salts from conductivity and spectral studies.

The objectives of the present studies are (i) synthesis of poly(aniline-co-2-chloroaniline)-*p*-toluenesulfonate and poly(aniline-co-2-chloroaniline)-formate salts by chemical polymerization, (ii) characterization of the copolymer salts by IR, electronic and electron paramagnetic resonance (EPR) spectral measurements, and (iii) to study the effect of heat treatment at four different temperatures, between 150 and 375°C on the copolymer salts and the thermal behavior by conductivity and spectral methods.

EXPERIMENTAL

Materials

Aniline and 2-chloroaniline (reagent grade from E. Merck) were vacuum distilled under nitrogen prior to use. All other reagents from E. Merck were used as received.

Polymer sample preparation

The preparation of polyaniline salts were carried out as reported earlier [11]. Poly(aniline-co-2-chloroaniline) salts were prepared using the same procedure. Aniline (0.1 M) and *o*-chloroaniline (0.1 M) were dissolved in an aqueous

solution containing 0.1 M *p*-toluenesulfonic acid (or) 1.0 M formic acid and the reaction mixture was cooled to 5°C in an ice bath. An aqueous solution of ammonium persulfate (0.1 M) was added dropwise into the above solution and the reaction mixture (total volume 1000 ml) was kept aside for 24 hr. The precipitated polyaniline salt was recovered by filtration and it was washed with 3 L of distilled water, followed by methanol and acetone. The polymer salt was finally dried at 100°C until a constant mass was reached. The yield was 16.0 g poly(aniline-co-2-chloroaniline)-*p*-toluene sulfonic acid salt and 6.8 g poly(aniline-co-2-chloroaniline)-formic acid salt.

The copolymer salts were subjected to heat treatment at four different temperatures, 150, 200, 275 and 375°C. For this purpose, the sample was kept in an oven under a nitrogen atmosphere. The temperature of the oven was raised to the desired temperature and maintained at that temperature for about 10 min, the sample was then cooled to room temperature.

Characterization

Conductivity measurement, EPR, IR and electronic absorption spectroscopic techniques were used to characterize the polymer samples. Conductivity and spectral measurements on the as prepared and heat treated samples at 150, 200, 275 and 375°C were carried out at room temperature. No efforts were made to find out the copolymer compositions since the salts are not soluble in common organic solvents.

Conductivity measurements. Electrical conductivity (DC) of the samples was measured at room temperature using the four probe method on pressed pellets. The pellets were obtained, by subjecting the polymer samples to a pressure of 950 kg cm⁻². Resistance measurement was carried out using a Keithley Model 220 programmable current source and a Keithley Model 195A digital voltmeter. The reproducibility of the results was checked by measuring (i) the resistance value thrice for each pellet, (ii) the resistance for a batch of three pellets of each sample and (iii) the length and area five times. Since the mean values were used in the calculation of resistance, the total error may be less than 3%.

Electron paramagnetic resonance (EPR) spectra. The EPR spectra were obtained on a Varian E109 spectrometer operating in the X band. The samples were under vacuum when the spectra were recorded. The *g*-value and spin concentration were estimated using charred dextrose as the standard. The EPR spectra of the samples and charred dextrose were recorded under identical conditions. That is, the microwave frequency (9.05 GHz), microwave power (2 mW), modulation frequency (100 KHz), field set (3280 G), scan range (40 G), modulation intensity (1 G_{pp}), modulation time (0.064 sec) and scan time (200 sec) were kept constant. The spin concentration for the samples was calculated by comparing the area under the EPR signal of the sample with that of charred dextrose whose spin concentration is known. The calculated areas are likely to be within 10% of the true value.

Fourier-transform infrared spectra. Infrared spectra of the samples were recorded using a Bomem MB 100 FT-IR spectrometer in the range 400–4000 cm⁻¹. The KBr pellet technique was used to prepare the samples for recording the IR spectrum.

Electronic absorption spectra. Absorption spectra of the samples were recorded using a Hitachi U3400 spectrophotometer. Solution for the absorption spectra was prepared by dissolving the samples in *N,N*-dimethylformamide (DMF) and then filtering it using a filter paper. Absorption spectra of the dilute solutions were recorded in the range 200–840 nm at room temperature using a pair of matched 3 ml stoppered silica cells of 10 mm pathlength.

RESULTS AND DISCUSSION

Infrared spectra

The FT-IR spectra of the as prepared sample of (PANI-co-CA)-TSA and (PANI-co-CA)-HCOOH and the samples heat treated at 150, 200, 275 and 375°C recorded in the range 2000–400 cm⁻¹ are shown in Figs 1 and 2, respectively. The bands observed for the as prepared sample of (PANI-co-CA)-HCOOH salt can be explained on the basis of the normal modes of polyaniline; a band at 3280–3400 cm⁻¹ assigned to the NH stretch of the aromatic amine, the 2930 cm⁻¹ band to an aromatic CH stretch, 1575 and 1495 cm⁻¹ bands to benzene and/or quinone ring deformations, the 1290 cm⁻¹ band to the CN stretch of the secondary aromatic amine, and the 825 cm⁻¹ band to aromatic CH out-of-plane bending. In the region of 1010–1170 cm⁻¹, aromatic CH in-plane bending modes are usually observed. For (PANI-co-CA)-HCOOH, a strong characteristic band appears at 1130 cm⁻¹, which has been explained as an electronic band or a vibrational band of nitrogen quinone. The out-of-plane CH bending mode has been used as a key to identifying the type of substituted benzene. For the polymer salt this mode was observed as a single band at 825 cm⁻¹, which is in the range 800–860 cm⁻¹ reported for a 1,4-disubstituted benzene. Similar observations have been made by Inoue *et al.* [12] for polyaniline base obtained from polyaniline-perchloric acid salt. When compared to

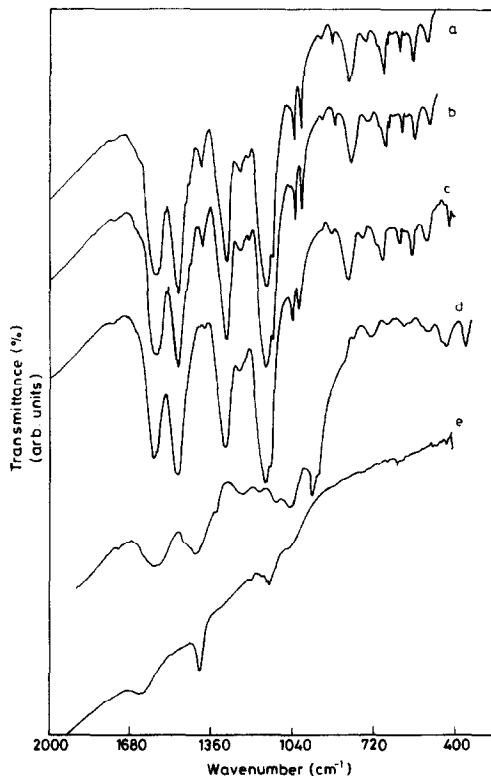


Fig. 1. Infrared spectra of poly(aniline-co-2-chloroaniline)-*p*-toluenesulfonic acid salt of (a) as prepared sample, sample heat treated at (b) 150°C, (c) 200°C, (d) 275°C and (e) 375°C.

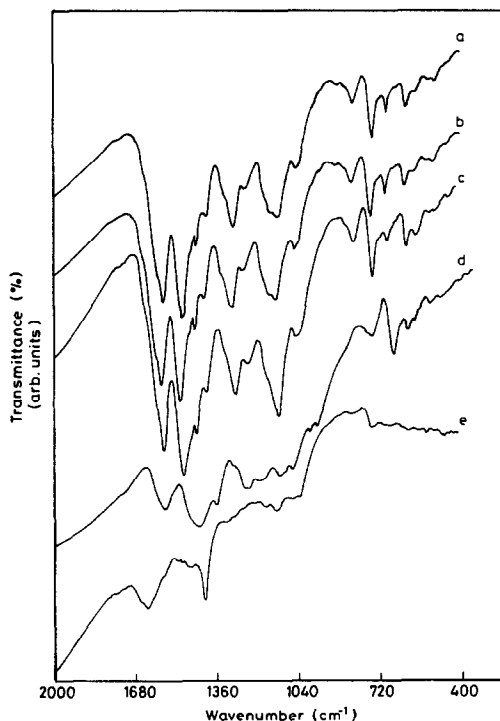


Fig. 2. Infrared spectra of poly(aniline-co-2-chloroaniline)-formic acid salt of (a) as prepared sample, sample heat treated at (b) 150°C, (c) 200°C, (d) 275°C and (e) 375°C.

(PANI-co-CA)-HCOOH, the IR spectrum of (PANI-co-CA)-TSA showed additional bands at 1035, 1010, 880, 565 and 510 cm^{-1} (Fig. 1). The bands at 1035 and 1010 cm^{-1} are assigned to aliphatic C-H deformation modes. The additional bands observed in the IR spectrum of (PANI-co-CA)-TSA are due to *p*-toluenesulfonic acid present in the (PANI-co-CA)-TSA salt.

The IR spectra of the as prepared sample and the samples heat treated at 150 and 200°C are very nearly the same (Figs 1 and 2). However, the IR spectrum of the sample heat treated at 275°C showed some difference. The IR spectrum of the sample heat

treated at 375°C shows only two peaks, a broad peak at 1630 cm^{-1} and another one at 1400 cm^{-1} . These observations suggest that complete structural changes have taken place in the case of the salt heat treated at 375°C and these changes may take place between 200 and 275°C.

Electronic absorption spectra

(PANI-co-CA)-TSA and (PANI-co-CA)-HCOOH salts were dissolved in DMF and only a very small quantity of the sample was soluble in DMF. The electronic absorption spectra of the solution were recorded and the results are reported in Table 1.

The electronic absorption spectra of polyaniline base and polyaniline salt have been reported in the literature. The absorption spectrum of polyaniline base [13–15] recorded in the range 850–350 nm shows a broad band around 610–650 nm depending on the preparation and/or processing of polyaniline. Polyaniline salt [16–18] obtained from the base by treatment with acid showed one band around 780–825 nm and the band at 610–650 due to polyaniline base disappeared completely.

The absorption spectrum of the as prepared sample of (PANI-co-CA)-TSA showed one broad band around 625 nm (Fig. 3), while (PANI-co-CA)-HCOOH showed only a broad hump around 540 nm (Fig. 4). This result suggests that the conjugation of the polymer chain is apparently more affected by the use of formic acid as counterion when compared to that of *p*-toluenesulfonic acid. It should be noted that no change in the absorption spectrum was observed even after the solution was left for 48 hr. The conspicuous absence of a band around 800 nm in the absorption spectra of (PANI-co-CA)-TSA and (PANI-co-CA)-HCOOH salts indicates that these salts are not soluble in dimethylformamide and only the base part is soluble in dimethylformamide.

Absorption spectra of (PANI-co-CA)-TSA and (PANI-co-CA)-HCOOH salts and the samples heat treated at 150 and 200°C are very nearly the same (Figs 3 and 4) and they showed a broad band around 610 and 540 nm, respectively. The samples heat treated at 275 and 375°C were not soluble in dimethylformamide and also in 98% sulfuric acid

Table 1. Conductivity, band maxima, *g*-value, linewidth and spin concentration of poly(aniline-co-2-chloroaniline) salts and the samples heat treated at 150, 200, 275 and 375°C

Salt	As prepared samples	Heat treated (°C)			
		150	200	275	375
Conductivity (S/cm)					
(PANI-co-CA)-TSA	2.7×10^{-2}	1.3×10^{-2}	1.2×10^{-3}	^a	^a
(PANI-co-CA)-HCOOH	1.9×10^{-7}	1.2×10^{-7}	$> 5 \times 10^{-8}$	^a	^a
Band maxima (nm)					
(PANI-co-CA)-TSA	625	620	620	^b	^b
(PANI-co-CA)-HCOOH ^c	550	550	550	^b	^b
<i>g</i> -value					
(PANI-co-CA)-TSA	2.0034	2.0032	2.0031	2.0032	2.0030
(PANI-co-CA)-HCOOH	2.0030	2.0030	2.0032	2.0035	2.0034
Line width (mT)					
(PANI-co-CA)-TSA	0.16	0.16	0.15	0.96	0.74
(PANI-co-CA)-HCOOH	0.20	0.22	0.23	1.10	0.86
Spin concentration (spins/g)					
(PANI-co-CA)-TSA	1.3×10^{21}	1.2×10^{21}	1.1×10^{21}	4.8×10^{20}	9.9×10^{20}
(PANI-co-CA)-HCOOH	2.6×10^{20}	2.5×10^{20}	1.7×10^{20}	6.3×10^{19}	1.3×10^{20}

^aPellets could not be prepared from the powder sample.

^bSamples not soluble in dimethylformamide.

^cOnly broad hump observed.

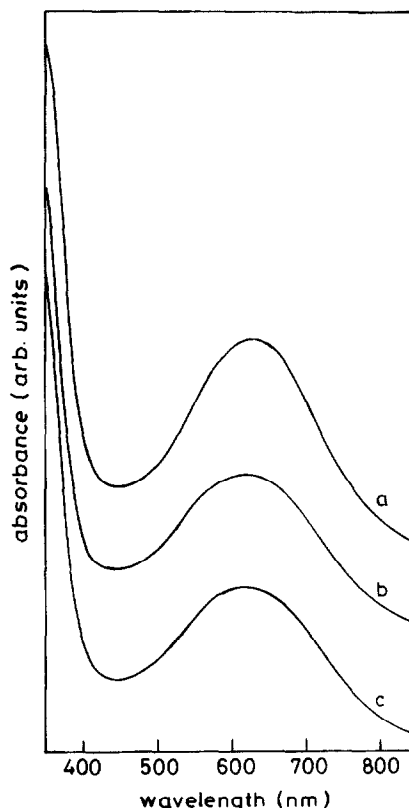


Fig. 3. Absorption spectra of poly(aniline-co-2-chloroaniline)-*p*-toluenesulfonic acid salt of (a) as prepared sample, sample heat treated at (b) 150°C, (c) 200°C, (d) 275°C and (e) 375°C.

indicating that cross linking of the polymer takes place.

Electron paramagnetic resonance spectra

The electron paramagnetic resonance (EPR) spectra of (PANI-co-CA)-TSA and (PANI-co-CA)-HCOOH samples and the samples heat treated at different temperatures showed a single signal without fine structure (Fig. 5). The *g*-value, linewidth and spin concentration are reported in Table 1.

The *g* values of (PANI-co-CA)-TSA and (PANI-co-CA)-HCOOH salts and the samples heat treated at different temperatures were nearly the same. The *g* value of all the salts lies between 2.0030 and 2.0035 compared to the free electron *g* value of 2.0023. It indicates that polyaniline salt exists primarily as polysemiquinone radical cation.

The line width and spin concentration of the salts and the samples heat treated at 150 and 200°C were nearly the same but changed drastically at 275 and 375°C. The line width of (PANI-co-CA)-TSA sample and the sample heat treated at 150 and 200°C is nearly the same (1.6, 1.6 and 1.5 G, respectively) and is rather small compared to those of the sample heat treated at 275°C (9.6 G). The narrower linewidth in the as prepared sample compared to the heat treated one at 275°C could be attributed to a lower degree of structural disorder in the former leading to reduced inhomogeneous linewidth. The spin concentration of (PANI-co-CA)-TSA salts and the samples

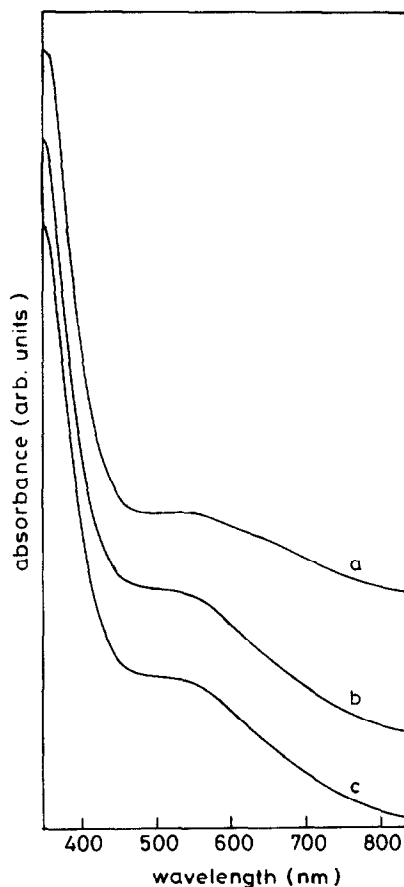


Fig. 4. Absorption spectra of poly(aniline-co-2-chloroaniline)-formic acid salt of (a) as prepared sample, sample heat treated at (b) 150°C, (c) 200°C, (d) 275°C and (e) 375°C.

heat treated at 150 and 200°C is also nearly the same, (correspondingly 1.3×10^{21} , 1.2×10^{21} and 1.1×10^{21}) and which decreased to 4.8×10^{20} at 275°C but increased to 9.9×10^{20} at 375°C. A similar

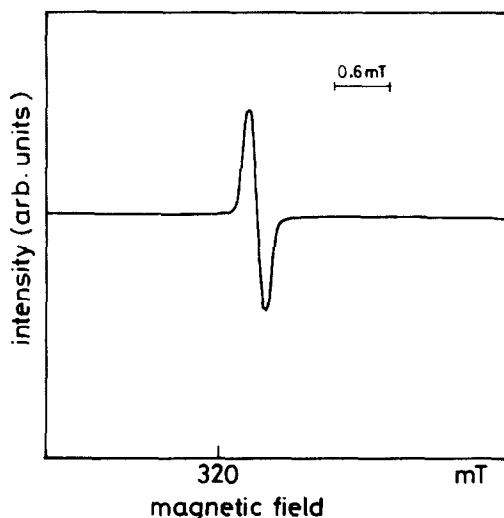


Fig. 5. Electron paramagnetic resonance spectra of poly(aniline-co-2-chloroaniline)-*p*-toluenesulfonic acid.

trend was observed for the (PANI-co-CA)-HCOOH system.

Electron paramagnetic resonance, electronic absorption and IR spectra of the as prepared samples of (PANI-co-CA)-TSA and (PANI-co-CA)-HCOOH and the heat treated samples up to 200°C are very nearly the same. This shows that no structural changes take place for the sample heat treated up to 200°C.

Conductivity

The conductivity of the copolymer samples and the samples heat treated at 150 and 200°C was measured using the four probe technique (Table 1). The conductivity of the samples heat treated at 275 and 375°C was not determined since the pellet could not be prepared from the sample. This suggests that the nature of the copolymer powder sample is changed when the samples are subjected to heat treatment at 275 and 375°C. The values of the conductivity and yield of copolymer salts were found to be dependent on the counterion used. The conductivity of (PANI-co-CA)-TSA was 2.7×10^{-2} S/cm which is five orders of magnitude lower than that of (PANI-co-CA)-HCOOH (1.9×10^{-7}). The yield of (PANI-co-CA)-TSA was 16.0 g which is also less than that of (PANI-co-CA)-HCOOH (6.8 g). These results suggest that the efficiency of oxidation and protonation of the monomers by formic acid to the copolymer salt is less when compared with that of *p*-toluenesulfonic acid.

Heat treatment decreases the conductivity, for example, the conductivity of (PANI-co-CA)-TSA was 2.7×10^{-2} , 1.3×10^{-2} and 1.2×10^{-3} for the sample as prepared and the samples heat treated at 150 and 200°C, respectively. A similar trend was observed for (PANI-co-CA)-HCOOH salt systems. Conductivity decreases with temperature and this may be due to the escape of a small amount of (unreacted) acid from the polymer surface.

CONCLUSIONS

The conductivity and yield of poly(aniline-co-2-chloroaniline)-*p*-toluenesulfonate are lower than that of poly(aniline-co-2-chloroaniline)-formate salt. Poly(aniline-co-2-chloroaniline) salts primarily exist

as polysemiquinone radical cation. No structural changes take place for the sample heat treated up to 200°C but complete structural changes occur at 375°C. Cross linking of the polymer take place near 275°C.

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