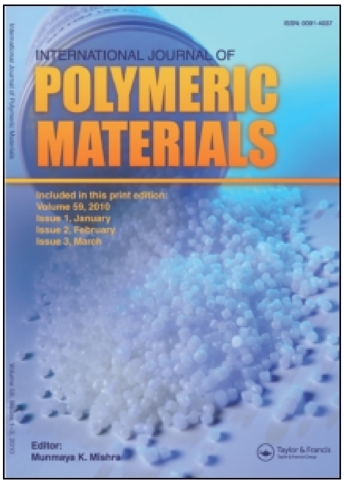

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Kulkarni, Milind V. , Viswanath, Annamraju Kasi and Khanna, P. K.(2006) 'Synthesis and Characterization of Poly(o-anisidine) Doped with Polymeric Acids', International Journal of Polymeric Materials, 55: 7, 501 — 512

To link to this Article: DOI: 10.1080/00914030500210358

URL: http://dx.doi.org/10.1080/00914030500210358

International Journal of Polymeric Materials, 55:501–512, 2006
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ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/00914030500210358

Synthesis and Characterization of Poly(o-anisidine) Doped with Polymeric Acids

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Conducting poly(o-anisidine) doped with polymeric acids [viz, poly(styrene sulphonic acid) (PSSA), poly(vinyl sulphonic acid) (PVSA) and poly(acrylic acid) (PAA)] was synthesized by in-situ chemical polymerization method using ammonium persulphate as an oxidizing agent. This is a single-step polymerization process for the direct synthesis of emeraldine salt phase of the polymer. The polymers were characterized by using UV-Vis., FT-IR spectroscopy, thermal analysis, and conductivity measurements. Formation of mixed phases of polymer together with conducting emeraldine salt phase are confirmed by spectroscopic techniques. Thermal analysis shows that PAA doped poly(o-anisidine) undergoes three stage decomposition pattern similar to unsubstituted polyaniline. While, in PSSA and PVSA, doped sample splitting up of the second weight loss stage is observed leading to a four-step decomposition pattern. Room temperature conductivity measurements show less conductivity in poly(o-anisidine) than in polyaniline, due to the cumulative steric as well as electronic effects of the bulky methoxy substituent present at ortho position on the benzene ring. Increase in conductivity with increase in temperature is observed by high temperature conductivity measurements, showing "thermally activated behavior."

Keywords: polymers, chemical synthesis, spectroscopy, thermal stability, conductivity, poly(o-anisidine)

Received 13 May 2005; in final form 27 May 2005.

The authors are thankful to Dr. B. K. Das, Executive Director, C-MET, Pune for his constant encouragement.

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INTRODUCTION

Polymer systems with special properties are a field of increasing scientific and technical interest, offering the opportunity to polymer and synthetic organic chemists to synthesize a broad variety of promising new materials, with a wide range of electrical and magnetic properties. A great deal of research on conducting polymers has been cited in the literature in the last two decades because of their applications in electronics, optoelectronics, and energy storage devices [1–3]. Among the conducting polymers, polyaniline (Pani) has been the most widely studied material as a unique member of the conducting polymers family for the following reasons: (1) It is the only conducting polymer whose electronic structure and electrical properties can be reversibly controlled by both oxidation and protonation and (2) It has interesting electrochemical behavior and very high environmental stability [4] and conductivity together with the ease of preparation [5–7].

However, the industrial development of polyaniline is considerably hampered by its infusibility, insolubility in common organic solvents, and low mechanical strength. Incorporation of polar functional groups or long and flexible alkyl chains in the polymer backbone is a common technique to prepare Pani type polymers that are soluble in water and/or organic solvents. For example, polytoluidines, polyanisidines, or N-methyl and N-ethyl anilines are more soluble in common organic solvents than the unsubstituted polyaniline, but at a cost of low conductivity. Figure 1 shows the structures of polyaniline and of poly (o-anisidine) and its reduced and oxidized forms. The conductivity in these polymers can be varied by doping they with different protonic acids or by using functionalized protonic acids, which makes the polymers conducting as well as soluble in organic solvents.

One problem associated with short-chain protonic acid dopants is ease of dedoping by aging or by contact with water and consequently the loss of its electrical conductivity. It is believed that the dopant species are so small that they may evaporate or sublime out of the polymer [8–9]. To overcome this drawback, several polymeric acids have been used as dopants, such as polyacrylic acid and polystyrene sulphonic acid [10].

The authors have taken up a systematic investigation of conducting polymers [11–16] and polymers doped with suitable molecules for the development of humidity sensors [17–18]. The present work reports the in-situ chemical oxidative polymerization method for polymeric acids–doped poly(o-anisidine), and its characterization by various analytical techniques.

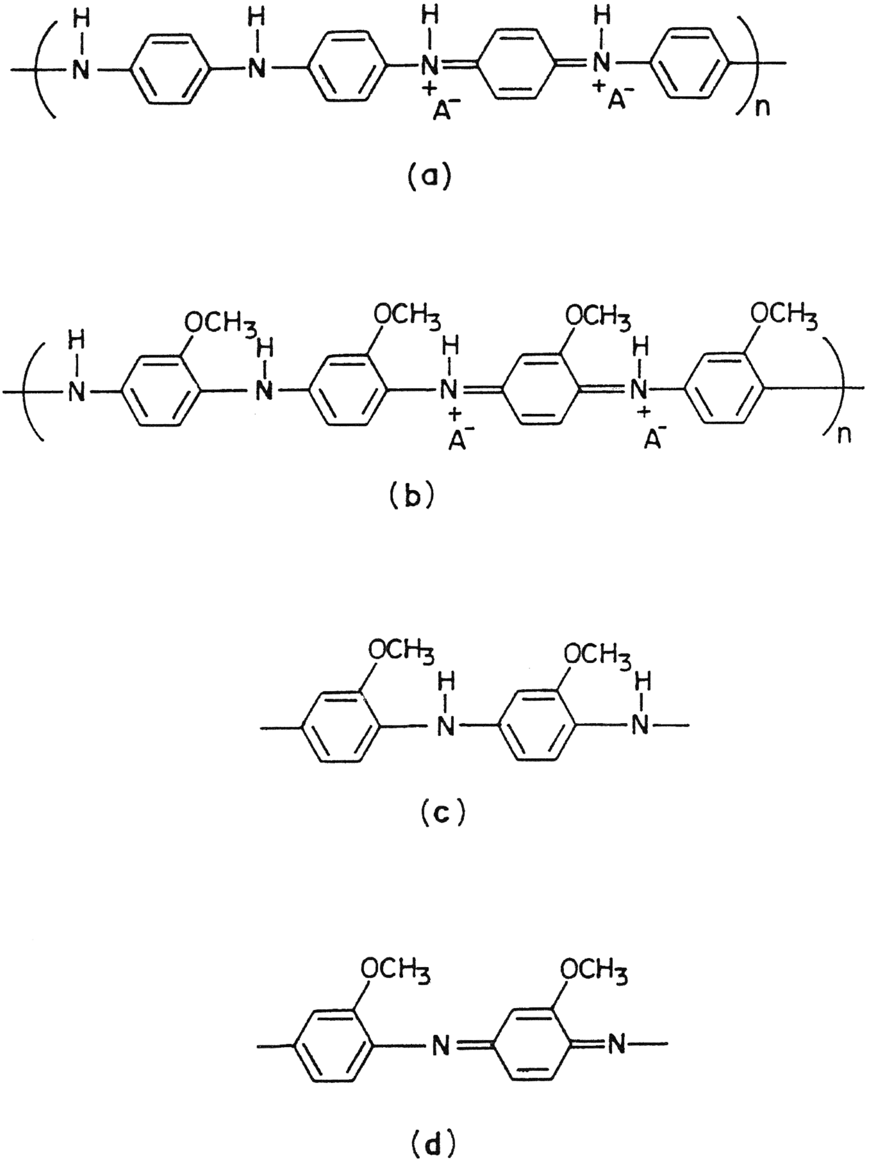

FIGURE 1 Structures of polyaniline (a), poly(o-anisidine) (b) and its reduced (c) and oxidized (d) forms.

MATERIALS AND METHODS

All chemicals used were of analytical reagent (AR) grade and used as received. The polymerization of the monomer, o-anisidine (0.62 ml) was initiated by the dropwise addition of the oxidizing agent, ammonium persulphate (1.26 gm) in an acidified solution (containing 0.1 gm of PSSA or PAA and 0.1 ml of PVSA) prepared under constant stirring at 0–5°C using doubly distilled water. The monomer to oxidizing agent ratio was kept as 1:1. After complete addition of the oxidizing agent the reaction mixture was kept under constant stirring for 24 h. The precipitated polymer was filtered and washed with distilled water until the filtrate was colorless. Finally, the polymer was dried in an oven at 70°C for 12 h.

The UV-visible spectra of the polymer solution in m-cresol were recorded by using Hitachi-U3210 spectrophotometer in the range of 300–900 nm. FT-IR spectra of the polymer were taken on a Perkin-Elmer-Spectrum 2000 spectrophotometer between 400–4000 cm^{-1}. The samples were prepared in a pellet form using spectroscopic grade KBr powder. Thermograms of the polymer samples were recorded using a Mettler-Toledo 851 thermogravimetric analyzer in N_2 atmosphere from RT to 900°C with a heating rate of 10°C/min. Room temperature conductivity of the samples was measured by two probe method. Dry powdered samples were made into pellets using a steel die of 1.5 cm diameter in an hydraulic press under a pressure of 7 tons. Temperature-dependent electrical conductivity of the polymer samples was studied by using a laboratory made set up. The electrical contacts were made by using platinum foils. The controlled heating of the sample was carried out by the heater placed near the sample. The change in resistance was recorded with increase in the temperature. The conductivity values were calculated directly from the measured resistance and sample dimensions.

RESULTS AND DISCUSSION

Figure 2 represents the UV-Vis. spectra of the poly (o-anisidine) doped with polymeric acids using m-cresol as a solvent. As can be seen in the figure there is a strong peak at 320 nm and small humps at 420 and 540 nm together with a broad peak at 820 nm in all three polymer samples.

The strong peak at 320 nm represents the π-π^* transition of the benzenoid rings. The humps at 420 and 540 nm represent the bipolaronic peak and insulating pernigraniline phase of the polymer, respectively. The presence of conducting emeraldine salt phase in the polymer is

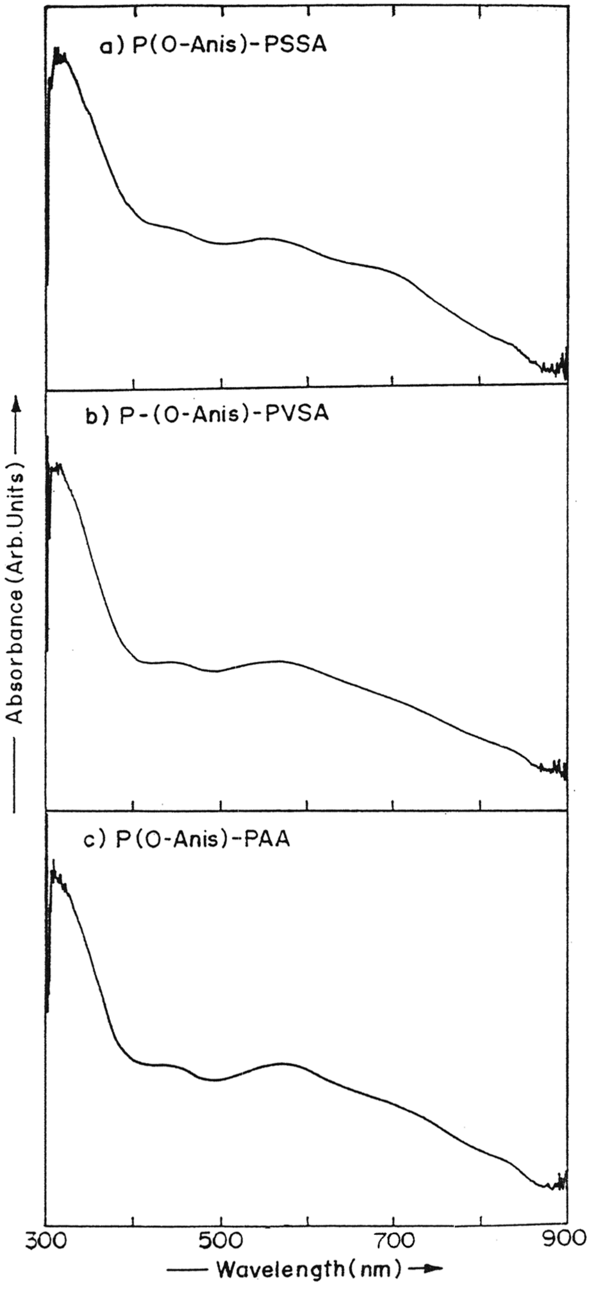

FIGURE 2 UV-Visible spectra of poly(o-anisidine) doped with PSSA, PVSA, and PAA recorded using m-cresol as a solvent.

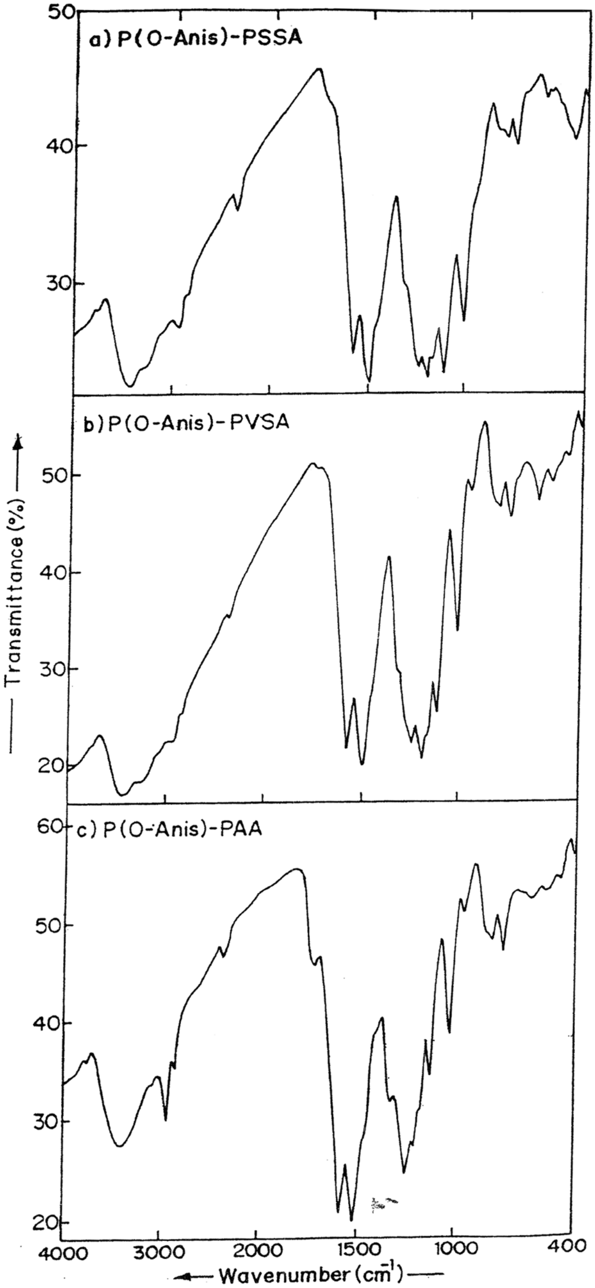

FIGURE 3 FT-IR spectra of poly(o-anisidine) doped with PSSA, PVSA, and PAA.

identified by a broad peak at 820 nm [11]. Thus, from the UV-Visible spectroscopic measurements it is observed that the sample is composed of mixed phases (conducting and insulating) of the polymers.

The FT-IR spectra of the polymer samples were recorded by using spectroscopic grade KBr and are shown in Figure 3. The peak positions and their assignments are listed in Table 1. The strong bands in the vicinity of the 1500 cm^{-1} and 1600 cm^{-1} are assigned to the non-symmetric C_6 ring stretching modes. The higher frequency vibrations at 1600 cm^{-1} has a major contribution from the quinoid ring whereas the lower frequency mode at 1500 cm^{-1} depicts the presence of the benzenoid ring units. The presence of both these bands clearly shows that the polymer is composed of the amine and the imine units. Further, it supports the earlier interpretation that different oxidation states of the polymer coexist, as observed by the UV-visible spectroscopic analysis. The presence of vibration band of the dopant ion and other characteristic bands confirm that the polymer is in the conducting emeraldine salt phase.

Thermal stability of the polymer samples was evaluated by thermogravimetric analysis and shown in Figure 4. The details of the decomposition pattern are quoted in Table 2. A typical three-stage decomposition pattern is observed in the poly(acrylic acid) doped poly(o-anisidine) sample, similar to that of unsubstituted polyaniline, whereas poly(o-anisidine) doped with PSSA and PVSA shows four-stage decomposition pattern. The first stage weight loss, practically

TABLE 1 Characteristic Frequencies of Chemically Synthesized poly(o-anisidine) Doped with PSSA, PVSA, and PAA

Wavenumber (cm^{-1})			
PSSA	PVSA	PAA	Band characteristics
801.84	806.59	807.24	Paradisubstituted aromatic rings indicating polymer formation
610.13	612.92	613.82	C–H out of plane bending vibration
1120.80	1123.99	1124.26	C–H in plane bending vibration
1329.03	1329.00	1329.03	Aromatic C-N stretching indicating secondary aromatic amine group
1500.43	1501.16	1516.39	C–N stretching of benzenoid rings
1583.91	1583.58	1583.22	C–N stretching of quinoid rings
—	—	1721.23	ν(C=O) of polyacrylic acid
2929.88	2929.88	2928.06	Aliphatic C–H stretching vibration in substituted methoxy group
3225.09	3210.33	3212.18	The aromatic C–H stretching
3419.92	3415.09	3387.54	>N–H stretching vibration

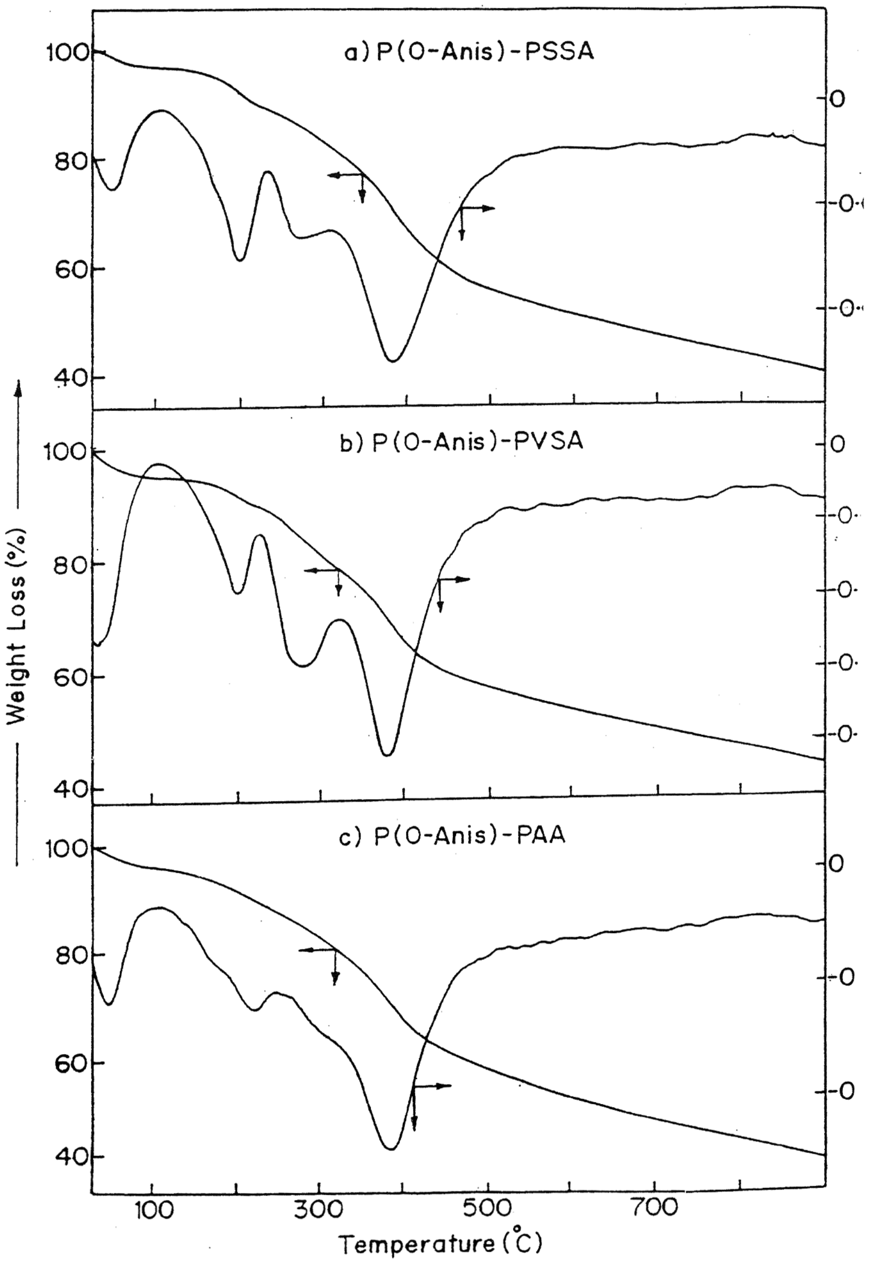

FIGURE 4 Thermograms (TGA/DTG) of poly(o-anisidine) doped with PSSA, PVSA, and PAA.

TABLE 2 Weight Loss of Chemically Synthesized Polymeric Acid Doped poly(o-anisidine) Over Different Temperature Ranges

Sr. No.	Polymer	Temperature range (°C)	Weight loss (%)
1.	P(o-Anis)—PSSA	RT-106	4.0
		110–233	8.0
		205–310	8.0
		314–624	30.0
2.	P(o-Anis)—PVSA	RT-105	5.0
		110–227	5.3
		230–320	11.0
		323–536	23.0
3.	P(o-Anis)—PAA	RT-105	4.5
		120–248	9.5
		255–550	31.0

starting from RT to 120°C is due to the loss of water present in the polymer matrix. The second stage weight loss, starting from 120°C to 300°C is responsible for the loss of the dopant ion from the polymer (thermal dedoping). The third step loss from 300°C to 900°C is attributed to the decomposition and complete degradation of the polymer backbone [11]. The splitting of the second step loss in PSSA and PVSA may be due to the separate loss of styrene and vinyl moiety of the dopant followed by the thermal decomposition of sulphonic acid from the polymer matrix, respectively. DTG analysis also supports this interpretation and shows four peaks in the thermogram of PSSA and PVSA doped poly(o-anisidine). On the other hand, poly(acrylic acid) doped sample shows three peaks in the DTG spectrum. Thus, depending on the type of the polymeric acid used for doping of the poly(o-anisidine), a variation is observed in the second stage of the weight loss in TGA/DTG analysis. However, the first and third stage weight loss are found to be identical in all three samples.

The room temperature solid-state conductivities were measured on pressed pellets having a diameter of 1.5 cm using two-probe technique. Table 3 gives the values for the same. In the case of poly(o-anisidine)

TABLE 3 Room Temperature Conductivity Values of poly(o-anisidine) Doped with PSSA and PVSA

Polymer	Conductivity S/cm
poly(o-anisidine)—PSSA	5.54×10^{-5}
poly(o-anisidine)—PVSA	1.90×10^{-5}

doped with PAA the conductivity is found to be very low (the resistance of the pellet is very high, i.e., greater than 40 MΩ), which is beyond the authors' instrument limit. The lower conductivity relative to polyaniline may be explained by an increase of the interchain distance and diluting effect of the charge carriers caused by the presence of bulky

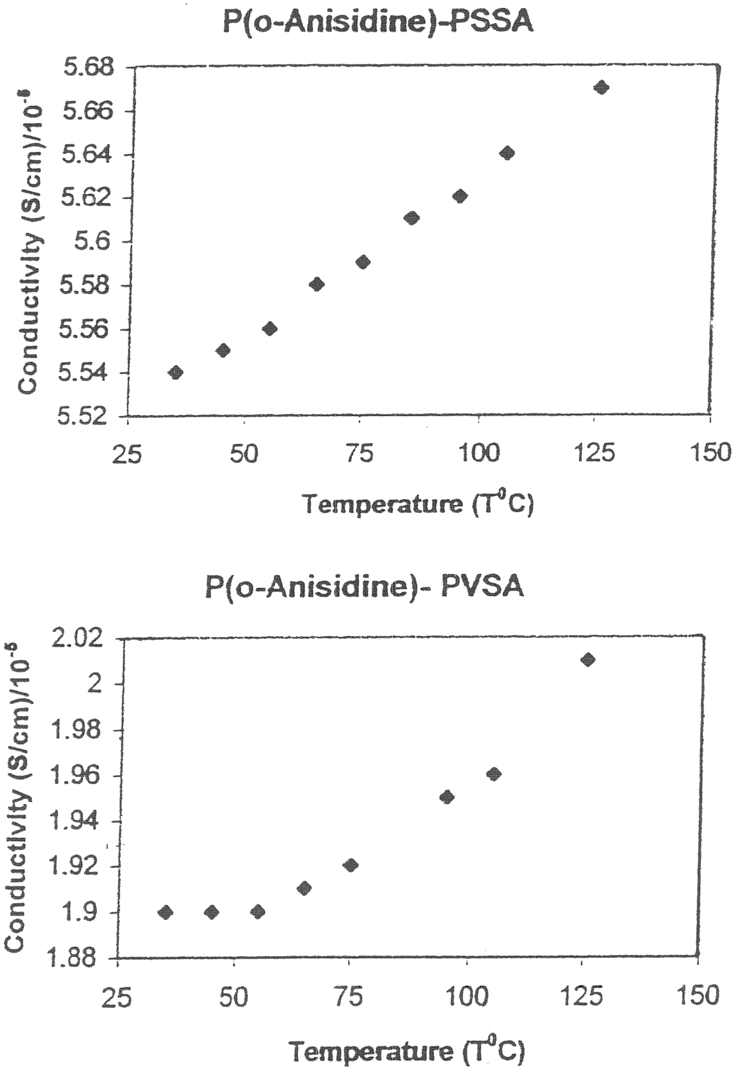

FIGURE 5 Temperature-dependent conductivity plots of poly(o-anisidine) doped with PSSA and PVSA.

methoxy group in the polymer. Furthermore, the substituent present at the ortho position of the benzene ring forces a greater torsion angle between the repeat units. This, in turn, results in a decrease of the degree of conjugation and hence a decrease in conductivity. This explains the observed decrease in the conductivity [19]. Also, due to the large size of the polymeric acids the easy migration of the charge carriers is hampered, resulting in the decrease of conductivity.

Figure 5 shows the temperature-dependent conductivity of poly (o-anisidine) doped with PSSA and PVSA. From the figure it is observed that the conductivity increases with temperature for both samples. The increase in conductivity with increase in temperature is the characteristic of "thermally activated behavior." The increase in conductivity is due to the increase of efficiency of charge transfer between the polymer chains and the dopant with increase in temperature [20–21]. It can also be suggested that, there may be molecular rearrangement on heating, which makes the molecular conformation favorable for electron delocalization [22].

CONCLUSIONS

In-situ chemical oxidative polymerization of poly(o-anisidine) offers the formation of mixed oxidation state phases of polymers together with conducting emeraldine salt phase. The formation of different oxidation states of the polymer was confirmed by UV-Visible and FT-IR spectroscopic analysis. TGA/DTG studies reveal the three stage decomposition pattern similar to that of unsubstituted polyaniline for PAA doped poly(o-anisidine). However, a four-stage decomposition pattern is observed in PSSA- and PVSA-doped samples. The lower room temperature conductivity in polymeric acids doped poly (o-anisidine) than in polyaniline is due to the cumulative steric as well as electronic effects of the bulky methoxy substituent. The improvement in the conductivity of these materials together with an advantage of high solubility in common organic solvents may make them useful for various technological applications.

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