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Synthesis and Characterization of Conducting Polyaniline Doped with Polymeric Acids

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Conducting polyaniline doped with polymeric acids was synthesized by a in situ chemical polymerization method. The synthesized polymers were characterized by using UV-Visible, FT-IR spectroscopy and SEM analysis. Thermal stability of these polymers was evaluated by using TGA/DSC analysis. Among the three polymeric acids used for doping purpose, poly(vinyl sulphonic acid) doped polyaniline is found to be more conducting than those doped with other acids. From the temperature dependent conductivity measurements, an increase in conductivity with increase in temperature was observed.

Keywords conducting polyaniline, chemical synthesis, spectroscopy, conductivity

Introduction

Polyaniline (Pani) is one of the most extensively studied conducting polymers and represents a class of macromolecules whose electrical conductivity can be varied from insulating to metallic state by either electrochemically (by oxidation/reduction) or chemically (by protonation/deprotonation). The conducting emeraldine salt state can be achieved by the protonation of the imine nitrogen (=N-) in 50% emeraldine salt using aqueous acids such as HCl, H_2SO_4 or some organic sulphonic acids (1–5). The protonated polymer is a polysemiquinone radical cation consisting of two separated polarons. The spreading out of the polaron wave function on to the neighboring rings results in the formation of a delocalized half filled polaron energy band. Figure 1 shows the protonation of emeraldine base via protonation of its imine sites with a sufficiently strong acid and its transformation to render all rings equivalent and strongly favors charge delocalization.

There are still several problems to be solved in order to achieve high quality polyanilines.

a) Small acid dopants (especially HCl) could be evaporated from the polymer matrix at higher temperature or by ageing and consequently, the loss of its electrical conductivity (6).

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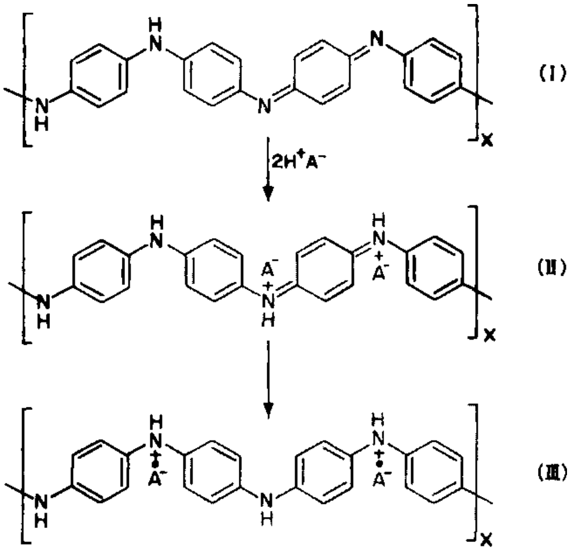


Figure 1. Protonation of emeraldine base and its transformation.

b) When polyaniline is used as a cathode in a secondary battery diffusion of dopant anion during redox or doping/undoping processes results in short life cycles (7).

To overcome this drawback, several polymeric acids have been used as dopants such as poly (acrylic acid), and poly (styrene sulphonic acid) (8–11). Polyaniline with these dopants were synthesized by an electrochemical method however, little attention has been given to the *in situ* synthesis of these polymers. Also, complete characterization of the resulting polymers was lacking. To our knowledge, this is the first report on the direct chemical synthesis and characterization of polyaniline doped with a number of polymeric acids. Recently, we have started a systematic investigation of conducting polymers (12–17) and polymers doped with suitable dyes for the development of humidity sensors (18–22).

In the present work, we report the *in situ* chemical polymerization of aniline using poly(styrene sulphonic acid) PSSA, poly(vinyl sulphonic acid) PVSA, and poly(acrylic acid) PAA as dopants and their characterization by using UV-vis and FT-IR spectroscopy, SEM, TGA/DSC and conductivity measurements.

Experimental

All chemicals used were of Analytical Reagent (AR) grade. The solutions were prepared in twice-distilled water. The oxidizing agent (ammonium persulphate (1.26 gm) dissolved separately in distilled water) was added dropwise in an acidified solution (containing 0.1 gm of PSSA or PAA or 0.1 ml of PVSA) of monomer, aniline (0.53 ml) under constant stirring at low temperature between 0–5°C. The monomer to oxidizing agent ratio was kept as 1:1. After complete addition of an oxidizing agent, the reaction mixture was kept under constant stirring for 24 h. The greenish -black precipitate of the polymer was isolated by filtration and conditioned by washing and drying in an oven. UV-Vis. spectra of the polymer solution in m-cresol were recorded by using a 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 the pellet form using a spectroscopic grade KBr powder.

Morphological studies were performed with the help of a Philips XL-30 Scanning Electron Microscope. Thermograms of the polymer samples were recorded using a Mettler-Toledo 851Thermogravimetric analyzer in the presence of N_2 atmosphere from RT to 900°C at a heating rate of 10°C/min.

DSC studies were performed using a Mettler-Toledo 821 system in the presence of N_2 atmosphere up to 400°C at a heating rate of 10°C/min. Temperature dependent electrical conductivity of the polymer samples were measured by using a home built instrument by a two probe method.

Results and Discussion

UV-Visible Spectroscopy

The electronic absorption spectra of the polymers were recorded by dissolving the polymers in m-cresol as a solvent. Figure 2 depicts the spectra of these polymers, the polymer exhibits a sharp peak at 420 nm and a small shoulder at 800 nm. The sharp and intense peak at 420 nm represents the localized polarons, which are characteristics of the protonated polyanilines (14, 15). Whereas, a shoulder at 800 nm can be assigned to the conducting emeraldine salt phase of the polymer. A very similar feature is observed in the UV-Vis. spectrum of the polyanilines doped with three polymeric acid dopants.

FT-IR Characterization

Figure 3 represents the FT-IR spectra of the polyaniline doped with PSSA, PVSA and PAA, respectively. Similar bands were observed in all three polymers characteristic of the conducting emeraldine salt phase of the polyaniline. The peak positions and their assignment are presented in Table 1. The presence of bands at 1040 cm^{-1} representing O=S=O stretching vibration, the S-O stretching band at 700 cm^{-1} and 630 cm^{-1} for C-S stretching vibration mode in polyanilines doped with PSSA and PVSA confirm the presence of the SO_3^- group from the sulphonic acids attached to the polymeric backbone. On the other hand, the polyacrylic acid doped polyaniline shows the presence of a sharp peak at 2900 and 2800 cm^{-1}, which can be attributed to the C-H stretching vibrations of acrylic acid. Also, it is important to note the presence of non-protonated $-COO^-$ groups as a stretching band at 1700–1740 cm^{-1}. Strong peaks at 1238 cm^{-1} and at 1410 cm^{-1} for -C-O stretching and -C-OH in plane bending reveal the presence of free acrylic acid in the polymer matrix.

Scanning Electron Microscopy

Figure 4 shows the scanning electron micrographs of the polyanilines doped with PSSA, PVSA and PAA recorded at the magnification of 4000 X. The morphology of the polymeric acids doped polyaniline is quite different from that of the polyaniline doped with small size acids. Liu and Yang (10) and Hwang and Yang (11) have reported that the polyacids strongly controls the polymer morphology. Polymer electrolytes such as

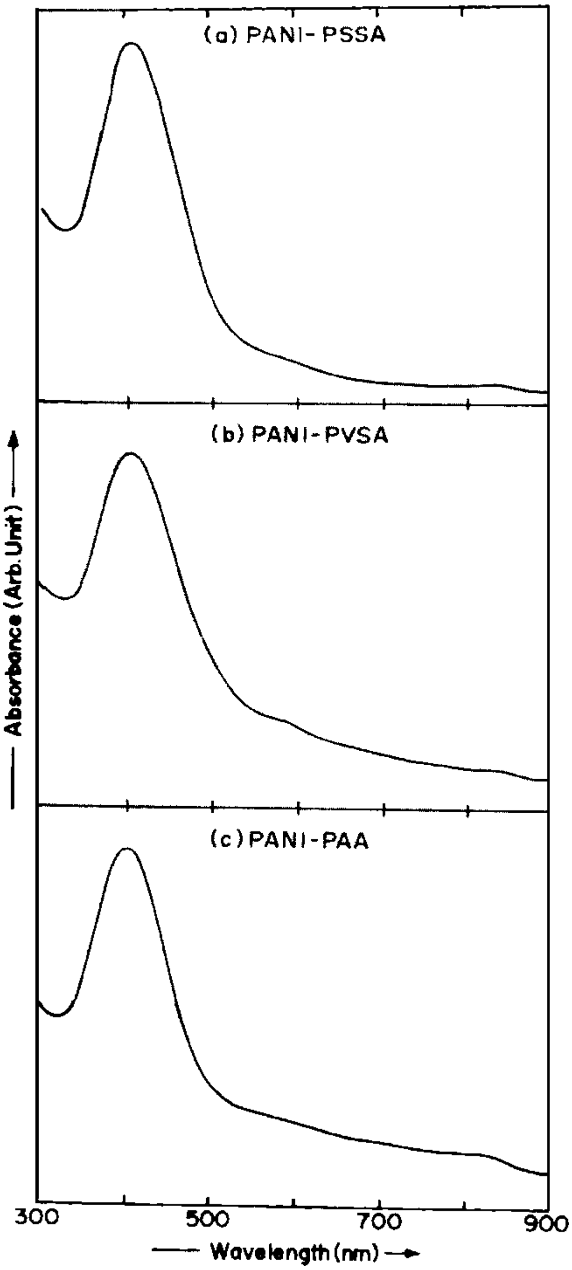


Figure 2. UV-Vis. spectra of polyaniline doped with a) PSSA, b) PVSA and, c) PAA.

those used in the present study are known to bind small molecules or ions by one or more of the following process:

A) Columbic attraction of positive ions by the ionized anionic polymer.
B) Hydrogen bonding of a base molecule to the unionized acid group in the polymer and

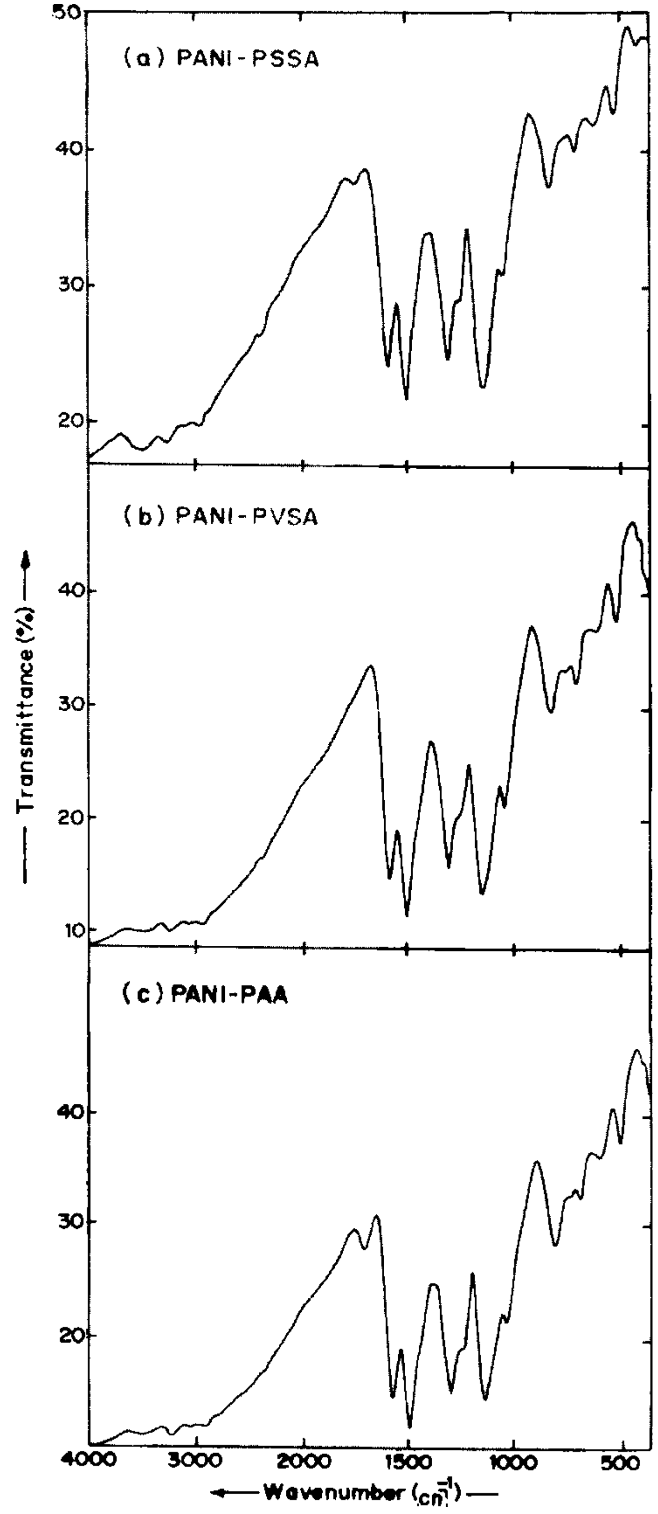


Figure 3. FT-IR spectra of polyaniline doped with a) PSSA, b) PVSA and, c) PAA.

Table 1
Characteristic frequencies of chemically synthesized polymeric acid doped polyanilines

Wavenumber (cm^{-1})			
PSSA	PVSA	PAA	Band characteristics
818.39	816.62	814.99	Paradisubstituted aromatic rings indicating polymer formation
698.61	694.50	698.23	C-H Out of plane bending vibration
1143.67	1141.01	1140.74	C-H in plane bending vibration
1300.76	1299.09	1298.24	Aromatic C-N stretching indicating secondary aromatic amine group
1496.65	1497.91	1498.38	C-N stretching of benzenoid rings
1576.75	1576.76	1576.92	C-N stretching of quinoid rings
2929.88	2928.30	2918.20	The aromatic C-H stretching
3239.85	3238.80	3238.80	>N-H stretching vibration

C) Hydrophobic interaction between the organic groups of the polyelectrolyte and small molecules.

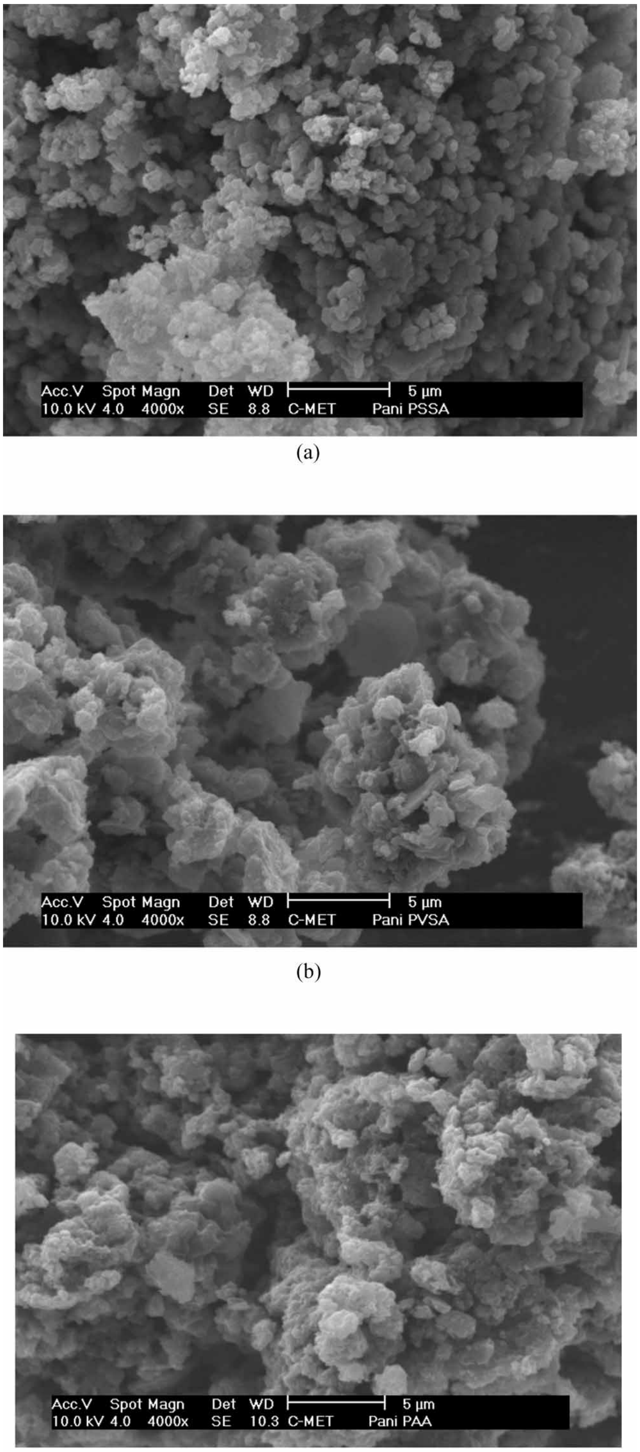
The observed strong morphological control suggests a template guides chemical polymerization process that involves the binding of the monomer aniline onto the polyacids, followed by polymerization of the monomers attached to the polyacid template.

When the template molecule is an extended linear chain of poly(acrylic acid), the morphology of the polymer is that of the long fibers. When the template molecule is poly(styrene sulphonic acid), the random coil conformation of the template-monomer complex leads to globular morphology.

Columbic attraction is important when the degree of ionization of the polymer acid is high. This is the case for the acid/base equilibrium between poly(vinyl sulphonic acid) and aniline, leading to a least distinctive morphology. In accordance with the above discussion, our SEM results also shows the similar variation in the morphology depending upon the polyelectrolyte used for the doping purpose. A globular structure composed of the aggregation of the small granules is observed in polyanilines doped with PSSA and PVSA. However, there is a difference in the shape and size of the globules. In PSSA doped polyaniline, the size of the globule is small compared to that of the PVSA doped material. A sponge-like structure with less void space, composed of an entangled and closely packed long polymer chains is observed in the poly(acrylic acid) doped polyaniline. The observed variation in the morphology is consistent with the variation in the binding of aniline to different polymeric acids. It is also observed that the morphology could be strongly modified by using the polymer acids as dopants instead of conventional inorganic acids.

Thermogravimetric Analysis

Figure 5 represents the thermogramms of polyanilines doped with polymeric acids. Continuous weight loss was observed above the room temperature although this may be



(a)

(b)

(c)

Figure 4. Scanning electron micrographs of polyaniline doped with a) PSSA, b) PVSA and, c) PAA.

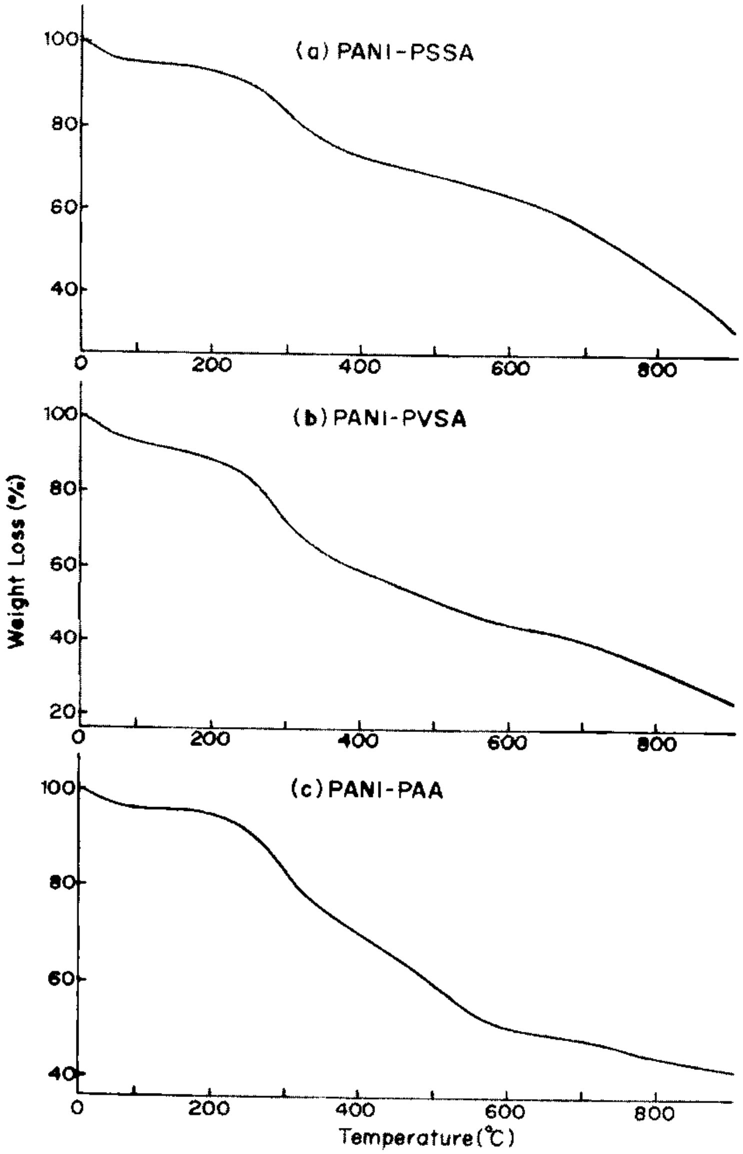


Figure 5. Thermogram of polyaniline doped with a) PSSA, b) PVSA and, c) PAA.

broken down into three steps of decomposition. The three steps in the decomposition curve can be attributed to the loss of water molecules (at 100°C) present in the polymer matrix, loss of the dopant ion (at 200°C) and complete decomposition and degradation of the polymer backbone (at 300°C and above) after removal of the dopant ion from the polymer matrix (dedoping).

Among the three steps of decomposition, the first and the last step are quite distinct exhibiting rapid weight loss with respect to the temperature, while the second step shows a very small weight loss over a broad temperature range. The loss of water molecule is found to be ~2–4% in all three polymers. The second step loss related to

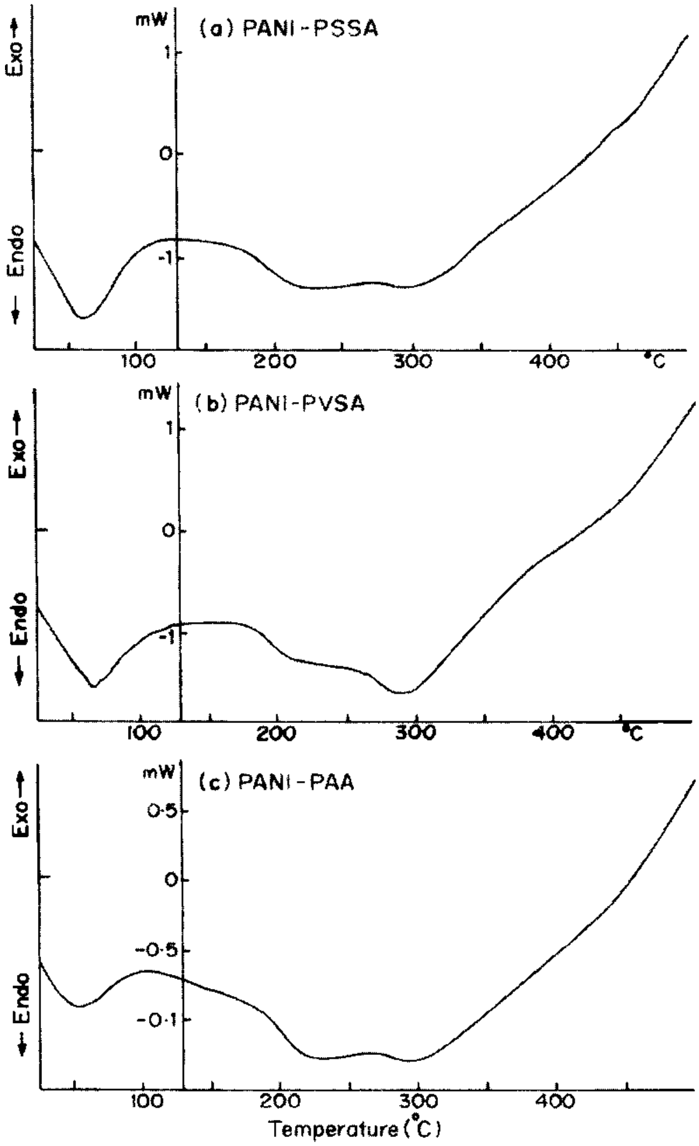


Figure 6. DSC thermogram of polyaniline doped with a) PSSA, b) PVSA and, c) PAA.

dedoping is found to be ~11%. The third step loss is found to be varied depending upon the dopant used for the synthesis. About 50% of the original weight of the polymer is observed up to 700°C in the polyaniline doped with PSSA and PAA. However, only ~40% of the original weight of the polymer is observed up to 700°C in the case of poly(vinyl sulphonic acid) doped polyaniline suggesting the less thermal stability of the polymer. Our studies on a number of polyanilines have shown that the degradation temperature depends on the kind of counterion used for the doping purpose. It was also observed in the literature that the polyaniline doped with organic acids having long alkyl chain show increased thermal stability (23–25).

Differential Scanning Calorimetry

Figure 6 shows the DSC thermograms of polyaniline doped with different polymeric acids. The thermogram exhibits only one endotherm, which is a common feature in all three acids. The endotherm completes at 120°C and is attributed to the expulsion of the loosely bound water molecule present in the polymer matrix (26). The peak at 210°C is due to the loss of the dopant ion (thermal dedoping) from the polymer chains, whereas, the endotherm at 300°C is responsible for the complete decomposition and degradation of the polymer backbone. These results are well in agreement with our thermal studies (TGA) described in the previous section. The thermograms also confirm the absence of any glass transition (Tg) and melting (Tm) temperature for the polyaniline salt system. It should be noted that the melting of polyaniline is not observed in DSC thermogramms possibly because of its early decomposition. Our thermal studies results agree with those generally observed in polyanilines (25–29).

Conductivity Measurements

The room temperature conductivity measurements were carried out on pressed pellets using a two-probe conductivity measurement technique using a homemade system. Table 2 quotes the values for the same. Among the three acids used for doping purpose, the conductivity of poly(acrylic acid) doped polyaniline is found to be lower than that doped with PSSA and PVSA. Since, PAA is a considerably weaker acid, which in turn is unable to dope the polyaniline efficiently. This partial doping of polyaniline results in less conductivity of the polyacrylic acid doped polyaniline than that doped with PSSA and PVSA and, is in good agreement with that suggested in the literature (3, 6, 10). Also, it is reported in the literature (6), that the confinement of the carboxylic acid groups on the flexible polymer chains of PAA leads to a non-uniform and inefficient doping, such that some of the acid groups are unable to participate in the doping and PAA is mainly distributed in the region, where PAA-doped Pani sub chain aggregate and the undoped PAA forms another phase, though the acid-base interaction promotes the miscibility between PAA and Pani. Thus, partial undoping of Pani occurs and the conductivity of the blend is 2.9×10^{-4} S/cm for the composition of the blend is 1/1. The similar trend might also have been observed for other polymeric acids. This value of conductivity is much less. However, the*in situ* doping of polyaniline by poly(acrylic acid), the method followed by us, leads to an increase in the conductivity by a magnitude of two order and is found to be 5.66×10^{-2} S/cm. This high value of conductivity clearly indicates the efficient doping of the polyaniline with poly(acrylic acid) by the *in situ* polymerization process rather than that of the doping-undoping and

Table 2
Room temperature conductivity values of polyaniline doped with polymeric acids

Polymer	Conductivity S/cm
Pani-PSSA	6.54×10^{-2}
Pani-PVSA	8.86×10^{-2}
Pani-PAA	5.66×10^{-2}

redoping polymerization method. In order to examine the thermal stability of the electric conduction, temperature dependence was investigated under atmospheric conditions.

Figure 7 shows the temperature dependent conductivity of polyanilines doped with different polymeric acids. From the figure, it is observed that the conductivity is found to be increased with an increase in temperature in all the polyanilines. This increase in conductivity with an increase in temperature is characteristic of "thermal activated

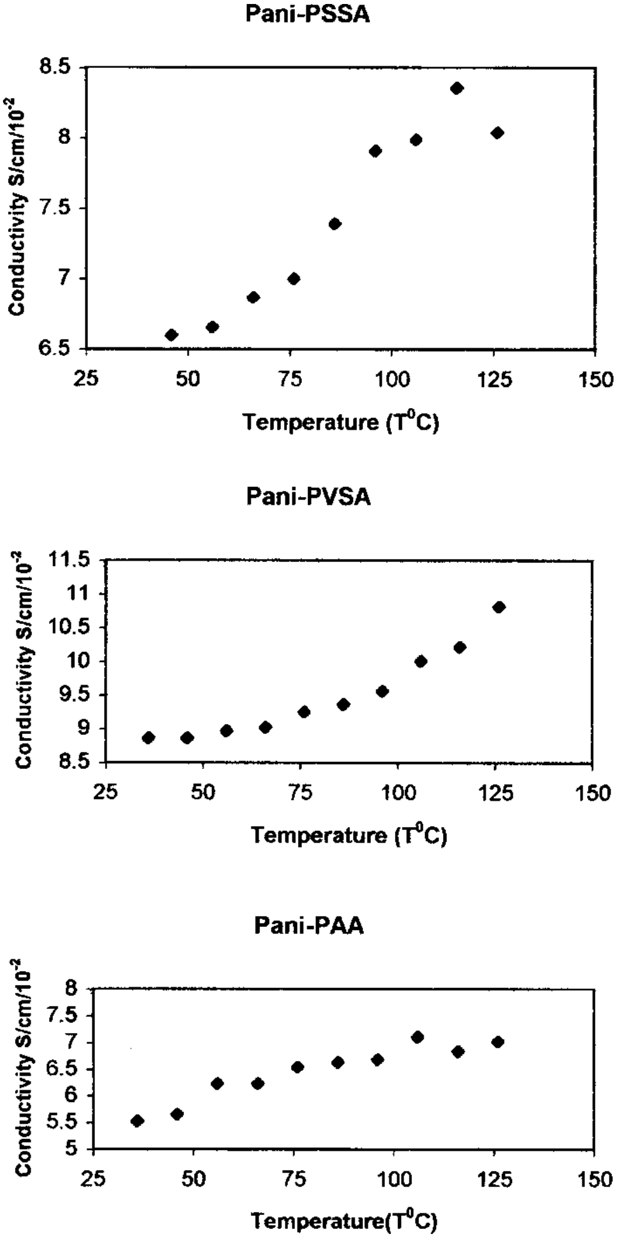


Figure 7. Temperature dependent conductivity plot of polyaniline doped with a) PSSA, b) PVSA and, c) PAA.

behavior". The increase in conductivity would be due to the increase of efficiency of charge transfer between the polymer chains and the dopant with an increase in temperature. The conductivity of polyaniline doped with polymeric acids increases slowly upto 130°C. Critical temperature to which conductivity increased monotonously means that there had to be molecular rearrangement on heating, which made the molecular conformations favorable for electron delocalization. It is in good agreement with the increase of conductivity after mild curing, reported in the literature (30, 31). Also, it should be expected that the molecular motion becomes non-negligible in the high temperature range, which leads to the recombination and/or relocation of the dopant ion.

Conclusions

Very good quality polyaniline doped with various polymeric acids were synthesized by direct chemical methods for the first time. From the spectroscopic and thermal studies, it is observed that the physico -chemical properties of the polyaniline are found to be affected by the nature of the dopant ion used for the doping purpose. Among the three polymeric acids used for doping, polyaniline doped with poly(vinyl sulphonic acid) has higher conductivity than the other two acids.

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References

1. Chiang, J.C. and MacDiarmid, A.G. (1986) *Synth. Met.*, 13: 193.
2. MacDiarmid, A.G., Chiang, J.C., and Richter, A.F. (1987) *Synth. Met.*, 18: 285.
3. Kang, E.T., Neoh, K.G., and Tan, K.L. (1994) *Polymer*, 35: 3193.
4. Athawale, A.A., Deore, B.A., and Kulkarni, M.V. (1999) *Mater. Chem. and Phys.*, 60: 262.
5. Angelopoulos, M., Ray, A., MacDiarmid, A.G., and Epstein, A.J. (1987) *Synth. Met.*, 21: 21.
6. Chen, S.A. and Lee, H.T. (1995) *Macromolecules*, 28: 2858.
7. Moon, D.K., Padias, A.B., Hall, H.K., Huntoon, T., Jr., and Calvert, P.D. (1995) *Macromolecules*, 28: 6205.
8. Shannon, K. and Fernandez, J.E. (1994) *J. Chem. Soc. Chem. Comm.* 643.
9. Orata, D. and Buttry, D.A. (1994) *J. Electroanal. Chem.*, 71: 257.
10. Liu, J.M. and Yang, S.C. (1991) *J. Chem. Soc. Chem. Comm.*, : 1529.
11. Hwang, J.H. and Yang, S.C. (1989) *Synth. Met.*, 29: E 271.
12. Kulkarni, M.V. and Viswanath, A.K. (2004) *European Polymer Journal*, 40 (2): 379.
13. Kulkarni, M.V., Viswanath, A.K., Marimuthu, R., and Seth, T. (2004) *Polymer Engineering and Science*, 44: 1676.
14. Kulkarni, M.V., Viswanath, A.K., Marimuthu, R., and Seth, T. (2004) *J. Polymer Science A: Polymer Chemistry*, 42: 2049.
15. Kulkarni, M.V. and Viswanath, A.K. (2004) *J. of Macromol. Sci., Part A: Pure and Appl. Chem.*, 41: 1173.
16. Kulkarni, M.V., Viswanath, A.K., Marimuthu, R., and Mulik, U.P. (2004) *J. Mater. Sci., Mater. in Electro.*, 15: 781.
17. Kulkarni, M.V., Viswanath, A.K., and Mulik, U.P. (2005) *Mater. Chem. and Phys.*, 89: 1.
18. Somani, P.R., Viswanath, A.K., Aiyer, R.C., and Radhakrishnan, S. (2001) *Sensors and Actuators B.*, 80: 141.

19. Somani, P.R., Viswanath, A.K., Aiyer, R.C., and Radhakrishnan, S. (2001) *Organic Electronics*, 2: 83.
20. Kulkarni, M.V. and Viswanath, A.K. (2005) *Sensor and Actuators B.*, 107 (2): 791.
21. Somani, P.R., Marimuthu, R., Viswanath, A.K., and Radhakrishnan, S. (2003) *Polymer Degradation and Stability*, 79: 77.
22. Kulkarni, M.V. and Athawale, A.A. (2001) *J. Appl. Polym. Sci.*, 81: 73.
23. Neoh, K.G., Pun, M.Y., Kang, E.T., and Tan, K.L. (1995) *Synth. Met.*, 73: 209.
24. Lee, Y.H., Lee, J.Y., and Lee, D.S. (2000) *Synth. Met.*, 114: 347.
25. Palaniappan, S. and Narayana, B.H. (1994) *J. Polym. Sci. A Polym. Chem.*, 32: 2431.
26. Wei, Y. and Hsueh, K.F. (1989) *J. Polym. Sci. A, Polym. Chem.*, 27: 4351.
27. Choi, K.M., Lee, E.J., Park, J.W., and Kim, K.H. (1991) *J. Appl. Polym. Sci.*, 42: 2129.
28. Choi, K.M. and Kim, K. (1992) H. *J. Appl. Polym. Sci.*, 44: 751.
29. Somani, P.R., Marimuthu, R., and Mandale, A.B. (2001) *Polymer*, 42: 2991.
30. Han, M.G. and Im, S.S. (1998) *J. Appl. Polym. Sci.*, 67: 1863.
31. Han, M.G. and Im, S.S. (1999) *J. Appl. Polym. Sci.*, 71: 2169.