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Improvement of Conductivity of Electrochemically Synthesized Polyaniline

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ABSTRACT: The electrochemical polymerization of aqueous solution of aniline and HCl was carried out in a single compartment electrochemical cell. After 2 h of the polymerization reaction, polarity of the electrodes was reversed and kept for 1 h. By this process the conductivity of the polyaniline (PAni) formed was found to increase dramatically from 1.1×10^{-4} to 3.0×10^{-1} S/cm. The PAni samples obtained both by reversing the polarity ("PANI-R") and without reversing the polarity ("PANI") were characterized by the infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), ultraviolet spectroscopy (UV), Hall effect experiment, X-ray analysis (XRD) and scanning electron microscope (SEM). The results show that the increase in the conductivity of PAni through the rever-sion of polarity is due to the partial reduction of over oxidized sample giving more emeraldine base and hence more polaron formation with increased charge carrier density and its mobility. The degree of crystallinity and the crystallite size is decreased marginally and the *d*-spacing is increased marginally due to this reduction. The PAni behaves like a *p*-type semiconductor that means the majority current carriers are holes. A plausible reduction mechanism due to reversal of polarity during electrochemical polymerization is also proposed. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 57–64, 2008

Key words: conducting polymers; FTIR; synthesis; thermogravimetric analysis (TGA)

INTRODUCTION

Polyaniline (PAni) is regarded as one of the conducting polymers with very high potential in commercial applications because of its ease of synthesis and novel properties.[1–5] However, there are still many unresolved problems concerning their structures, properties, and efficient means of modification. There is still good amount of complexity in macro- and micro-structures obtained by different synthesis conditions and post-synthesis treatments.[6] The degrees of doping and oxidation levels are two crucial factors which affect the electrical conductivity and other properties of polyaniline.[7–9] The half oxidized polyaniline with ~50% doping is expected to exhibit high conductivity.[10,11] The conductivity of PAni also depends upon the type of dopant. The doping percentage can be controlled easily by controlling the acid concentration (pH) of the reaction mixture[11–13] or by de-doping and re-doping process.[1] But the control of polymer structure which is most important to achieve high conductivity in PAni seems to be critical. Therefore, the most important part of the synthesis of PAni is the control of structural parameters and oxidation state during synthesis. The literature dealing with the control of the oxidation state, which means preparation of 50% oxidized polyaniline during chemical or electrochemical synthesis, is scanty. In our previous report we have shown that the PAni containing more emeraldine structure can be prepared by partial reduction using chemicals like stannous chloride which acts as a reducing agent.[1]

The present report is based on the development of a new technique of partial reduction during electrochemical synthesis by reversing the polarity of the electrodes to control the structure of PAni with more emeraldine form. To find out the reasons for the difference in the conductivity of the normal PAni and reduced PAni, the oxidation level was determined from the IR analysis, the thermal stability of different PAni was determined from the thermo gravimetric analysis (TGA), the ease of polaron/bipolaron transition was concluded from the UV analysis. The density of the charge carriers, their mobility and the type of charge carriers were analyzed from the Hall effect experiment. The change in the degree of crystallinity, crystallite size, *d*-spacing, and inter-chain separation was estimated from the XRD analysis and the structural morphology was studied from scanning electron microscope (SEM) analysis.

EXPERIMENTAL

Materials and electrochemical cell

Aniline (Merck, Mumbai, India) and hydrochloric acid (Ranbaxy, India) of analytical grade were used

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as received. A glass container of 30.0 cm height and 3.5 cm diameter was used as single compartment electrochemical cell. A graphite rod of 0.7 cm diameter and 15.0 cm length was used as working electrode; a stainless steel rod of 13.0 cm length, 2.0 cm width, and 0.03 cm thickness was used as counter electrode and a saturated calomel electrode (SCE) was used as reference electrode.

Electrochemical synthesis and reduction of PAni

The electrochemical polymerization was carried out in a single compartment cell as mentioned earlier. An aqueous solution of aniline (0.15M) and HCl (1.0M) were taken in the electrochemical cell. A constant potential difference of 1.3 V vs. SCE was applied across the two electrodes at room temperature. The reaction was carried out for different period of time. The PAni particles formed at the graphite electrode were collected and washed thoroughly with distilled water, filtered, and dried in a vacuum oven at room temperature.

In next experiments, same procedure was followed and the reactions were carried out for 2 h (the reason of carrying the reaction for 2 h is explained in the respective section) but before the collection of PAni samples the polarity of the electrodes was reversed and kept for different period of time under the same condition (potential difference = −1.3 V). Then the PAni samples were collected and dried as usual.

Characterization of PAni

The DC conductivity was measured with the Milli-Ohm Meter, GOM 802, GW Instek, Taiwan. Sample pellet from PAni powder was prepared with the help of a Perkin Elmer hydraulic device using a pressure of 15 tons.

The FTIR spectra of the PAni samples were recorded using FTIR Spectrometer, Spectrum RX 1, USA. The samples were compressed to the thin pellet form with the help of a Perkin Elmer hydraulic device after mixing the PAni Powder with KBr by the ratio 1 : 10. The areas under different IR peaks were calculated using Perkin Elmer applications software.

The TGA analysis was carried out using TGA, Q50, TA Instruments, USA, under N_2 atmosphere from room temperature to 800°C at the heating rate 20°C/min.

The UV analysis was performed using UV–visible spectrophotometer, UV-1601, Shimadzu Corpn., Japan. Measurement was made using only the soluble fraction of PAni in DMF.

To calculate charge carrier concentration and its mobility the Hall Effect experiment was carried out

using Hall Effect Equipment 662, Lake Shore, USA, at a temperature of 0.0 K under the vacuum of 0.5 mb.

The XRD analysis was carried out using X Pert PRO, PANalytical instrument, USA, with Cu detector using 1.54 Å wavelength of the X-ray. The d-spacing of different samples was determined by Debye-Scherrer (powder) method using Bragg's relation,[14,15] the crystallite size was determined from Scherrer relation[16] and the inter-chain separation was determined from the relation given by Klug and Alexander.[17]

The morphology of different PAni synthesized was investigated using scanning electron microscopy SEM, JSM 5800, Jeol, Japan. The surface of the PAni particles was coated with gold prior the investigation under microscope.

RESULTS AND DISCUSSION

Effect of reaction time on the conductivity and yield

The electrochemical polymerization of aniline was carried out for 1, 2, and 3 h under normal polarity condition, i.e. graphite as a working electrode and stainless steel as a counter electrode and maintaining other reaction conditions constant as mentioned earlier. When the reaction was carried out for 1 h, both the conductivity and yield was low. It is found that at lower time of reaction, the chain length of PAni obtained is not sufficient for long-range π electron delocalization giving rise to lower conductivity and yield of PAni.[18] This is mainly because the long-range delocalization of the charge carriers does not occur until the molecule attains a definite size.[4,18] It is found that after 2 h of reaction the yield of PAni is substantial and with further increase of reaction time the change in yield is marginal. Moreover with increase in reaction time the conductivity of PAni formed increases up to 2 h, and in fact beyond 2 h there is marginal decrease in the conductivity as shown in Figure 1. This may be due to the over oxidation of PAni. The conductivity of PAni depends much on its oxidation states. The protonated and 50% oxidized, i.e. half oxidized/half reduced emeraldine base (EB) form is highly conducting, whereas the fully reduced leucoemeraldine base (LEB) and the fully oxidized pernigraniline base (PNB) are mainly insulating in nature, and rests are in between.[1,18–22] Hence, the initial reaction time of 2 h under normal polarity condition is fixed and the PAni obtained at this condition is designated as ''PANI.'' The DC conductivity of ''PANI'' is 1.1 × 10^{-4} S/cm.

After 2 h of the reaction under normal polarity condition, the polarity of the electrodes was reversed
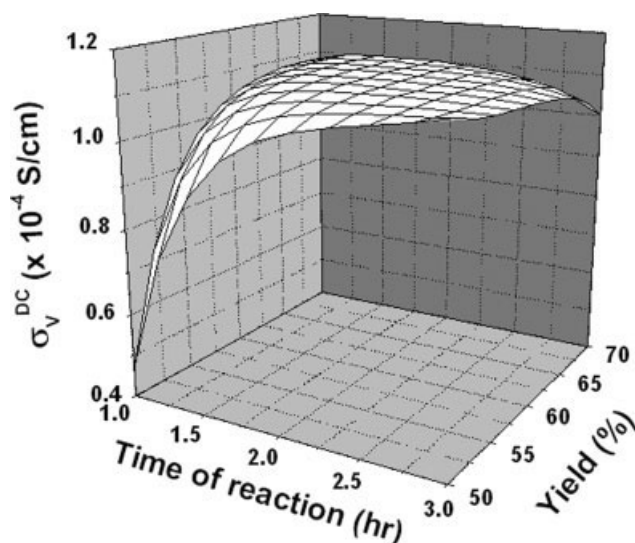
Figure 1 Effect of time of electrochemical reaction under normal polarity of the electrodes on the yield and DC conductivity of PAni.

keeping other reaction parameters unchanged and the reaction was again carried out for 0.5, 1.0, and 1.5 h. It is found that the PAni obtained after 3 h of total reaction (2 h under normal polarity condition and 1 h under reversed polarity condition) is showing substantial increase in DC conductivity (Fig. 2). Hence, the reaction time of 2 h under normal polarity and one hour under reversed polarity condition is taken and the PAni obtained at this condition is designated as "PANI-R." The DC conductivity of "PANI-R" is 3.0×10^{-1} S/cm.

The electropolymerization of PAni is anodic oxidation process.[23] After deposition of PAni if the polarity of the applied potential is reversed, the reduction of the deposited PAni is expected. This reduction

may increase or decrease the conductivity of the resultant PAni depending on its oxidation state. The increase in conductivity of the PAni after electrochemical reduction may be due to the fact that the PAni obtained under normal condition was over oxidized. When the reaction was carried out for 0.5 h under reversed polarity condition the reduction might not be sufficient whereas for 1.5 h over reduction might take place. When the reaction was carried out for 1 h under reverse polarity condition fraction of reduction was right to form PAni containing maximum EB structure and hence conductivity is also the maximum.

Oxidation level of "PANI" and "PANI-R" (FTIR analysis)

The FTIR spectra of the "PANI" and "PANI-R" are presented in Figure 3. The IR peaks at 1572 cm^{-1} and 1488 cm^{-1} are due to the ring stretching vibration of quinoid (Q) and benzenoid (B) respectively, while the peaks at 1294 cm^{-1} and 1136 cm^{-1} are due to the stretching vibration of C—N—C and B—NH$^+$=Q respectively.[1,18,21,22] The ratio of area under these two peaks at 1572 cm^{-1} and 1488 cm^{-1} is proportional to the ratio of population of quinoid to benzenoid structure in "PANI" and "PANI-R". When this ratio approaches to unity, the PAni structure assumes EB form. The Q/B ratio in "PANI" is 1.2 whereas the Q/B in "PANI-R" is 1.0. This result indicates that "PANI" contains more quinoid rings "PANI-R" contains equal quinoid and benzenoid rings. So, "PANI-R" contains more EB structure and hence its conductivity is also more. In our earlier work[1] it was observed that the chemically synthesized PAni, if subjected to reducing agent like stannous chloride an appreciable increase in the conductivity is observed. The partial reduction causes over
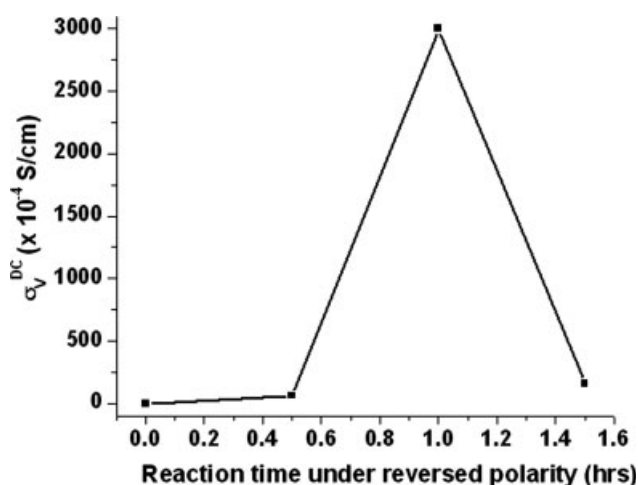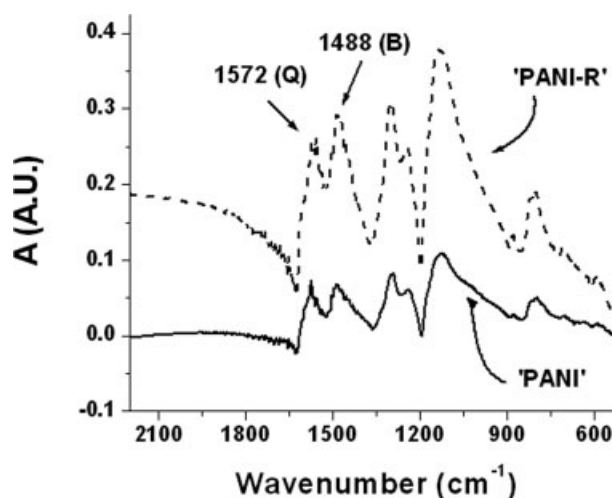

Figure 2 Effect of time of electrochemical reaction under reversed polarity of the electrodes (after 2 h of reaction under normal polarity) on the DC conductivity of PAni.

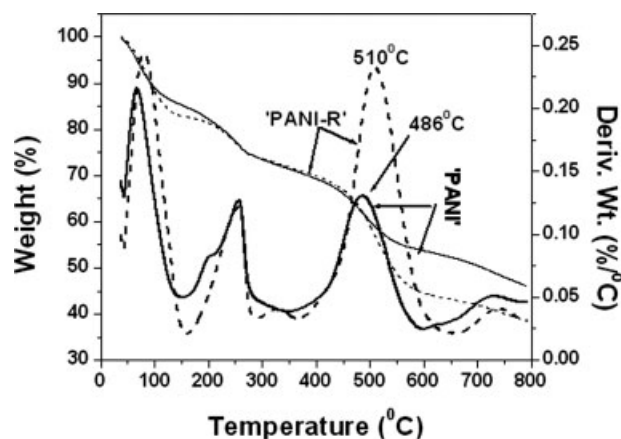**Figure 3** FTIR spectra of "PANI" and "PANI-R."

Figure 4 TGA and DTG curves of ''PANI'' and ''PANI-R.''

oxidized PAni to attain appropriate level of oxidation containing more EB structure, leading to the increase in conductivity.

Thermal stability (TGA analysis)

The TGA curve of different PAni (Fig. 4) exhibits four step weight loss processes. The 1st step of weight loss taking place over the temperature range 40–150°C may be due to the loss of moisture. The PAni always shows high moisture loss as it is highly hygroscopic in nature and even after vacuum drying some moisture still remains.[18,24,25] The 2nd step of weight loss over 150–350°C may be due to loss of bound water acting as a secondary dopant and/or counter anion of dopant and/or low molecular weight oligomers.[24,25] The 3rd step of weight loss over the temperature range 350–650°C may be due to the actual thermal decomposition of doped PAni into some chemical form and the final step of weight loss over 650–790°C may be due to the final carbonization of intermediate chemicals formed in the 3rd step.[18,21,22,26,27] The decomposition temperature of ''PANI'' is found to be around 486°C where as the decomposition temperature of ''PANI-R'' is around 510°C. The increase in the decomposition temperature again indicates that the partial reduction of PAni due to reversion of polarity of the electrodes, as the stability of benzenoid ring is more than that of quinoid one.[6] Choi et al. found that the thermal stability of PAni decreases with increase in the polymerization temperature.[25] They carried out the reaction from −1°C to 5°C and got the decomposition temperature of PAni above 700°C. Our electrochemical polymerization was carried out at room temperature and this may be reason for lower decomposition temperature of ''PANI'' and ''PANI-R.'' So, this difference in decomposition temperature may be accounted for the polymer produced under different

condition leading to some difference in the polymer chains.

Plausible electrochemical polymerization mechanism of aniline and reduction mechanism of polyaniline

Electrochemical synthesis of PAni from aniline is an oxidative anodic reaction[23] as schematically presented in Figure 5. The reaction goes in following fashion, the aniline molecules gets converted into aniline cation radicals after discharging their electron on anode (here graphite electrode). Two cation radicals combine and release protons to form dimer. Dimer in turn reacts with another cation radical forming trimeric cation radical, followed by formation of quadramer with release of proton and so on. Thus the process continues to generate PAni as shown schematically.

After the polymerization of aniline for a specific period of time (here 2 h) when the polarity of the electrodes is changed the graphite rod is converted to cathode which can now donate electron. The electron is taken up by the quinoid benzene ring of the deposited PAni and subsequently converted to the carbanion radical (a), nitranion radical (b), nitrogen radical (c), nitranion (d) which consequently takes up another proton to get converted itself to benzenoid ring as depicted in Figure 6.

It is worth mentioning here that when the over oxidized PAni is partially reduced, the possibility of formation of alternate arrangement of quinoid and benzenoid rings in PAni is more. Because in that
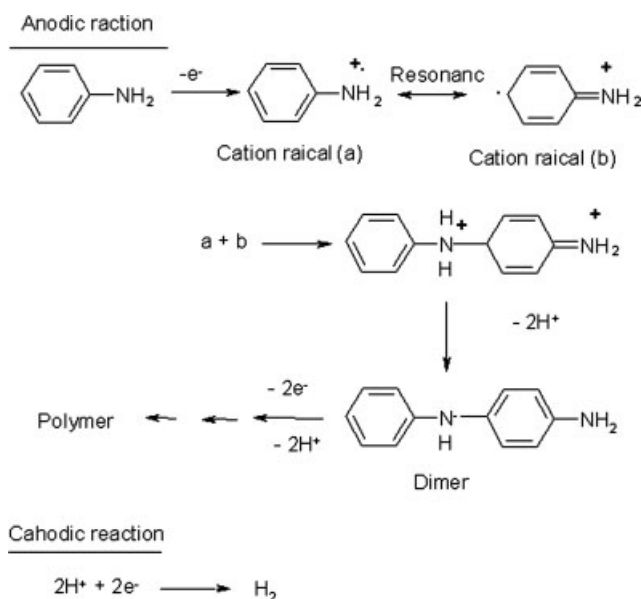

Figure 5 Plausible mechanism for the electrochemical polymerization of aniline.

Anodic reaction

$$2HCl \rightleftharpoons 2H^+ + 2Cl^-$$

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$
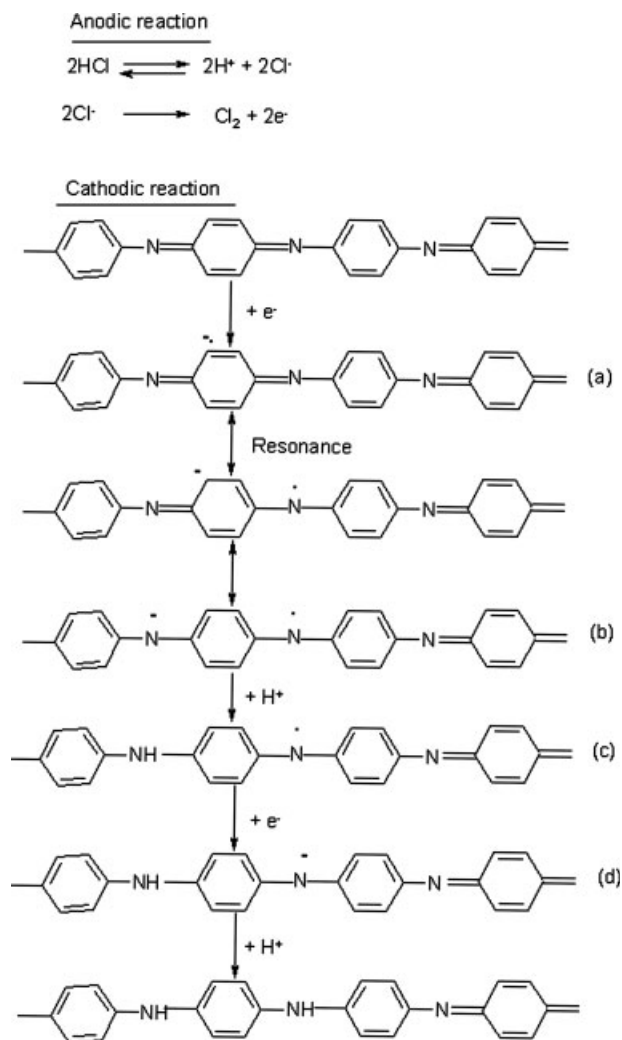
Cathodic reaction

Figure 6 Plausible mechanism for the partial electrochemical reduction of PAni.

case one of the consecutive quinoid rings is more prone to reduction as in that case the formed product is more stable due to more π electron delocalization via the formation of polarons in presence of protonic acids.

The charge transport in PAni occurs mainly through the formation of polarons[28,29] and their movement along a polymer chain or among the chains by hopping mechanism.[30,31] The polarons are formed in presence of protonic acids from the EB form of PAni where alternative quinoid and benzenoid rings are present. For the PAni chains containing consecutive benzenoid or quinoid rings, polaron formation is not possible. The conduction mechanism in terms of polaron formation and its movement was discussed elaborately in previous report.[1] So, the alternate arrangement of quinoid and benzenoid rings in PAni seems to be the most important factor for the attainment of high level of conductivity.

Band gap energy for electronic transition (UV analysis)

The characteristics of the π bonds are the source of semi-conducting properties. The π orbital produces the valance band and π* forms the conduction band. The difference in energy between these two ground and excited orbital is called band gap or band energy, determines both the electrical and optical properties of semi conducting polymers. Lower the band gap energy easier will be the electronic transition and it is expected that the system will show higher conductivity. In acidic condition, the UV spectra show three characteristic absorption bands, 250–280, 340–370, and 550–650 nm (Fig. 7). The first absorption (a) is due to the excitation of the nitrogen in the benzenoid segments (π–π* transition) while the second (b) and the third (c) ones are ascribed to polaron/bipolaron transition that occurs in doped PAni.[32,33] The band energies of the ''PANI'' and ''PANI-R'' for the 1st (a) and 2nd (b) band are almost same. The band energies for the third electronic transition (c) are 2.17 eV for ''PANI'' and that for ''PANI-R'' 1.96 eV. The lower band energy for the ''PANI-R'' indicates relatively easier polaron/bipolaron transition occurring in it which is responsible for its higher conductivity. This may be due to the formation of ''PANI-R'' with more EB structure via the partial reduction process as discussed earlier.

Density, mobility and type of charge carrier in PAni (Hall effect measurement)

The behavior of electrically conducting materials under the influence of a magnetic field applied at right angle to that of electric field is termed as Hall effect. A Hall effect can be used to determine the charge carrier concentration, their mobility and type (*n*-type or *p*-type) of semiconductors.[34–36] For
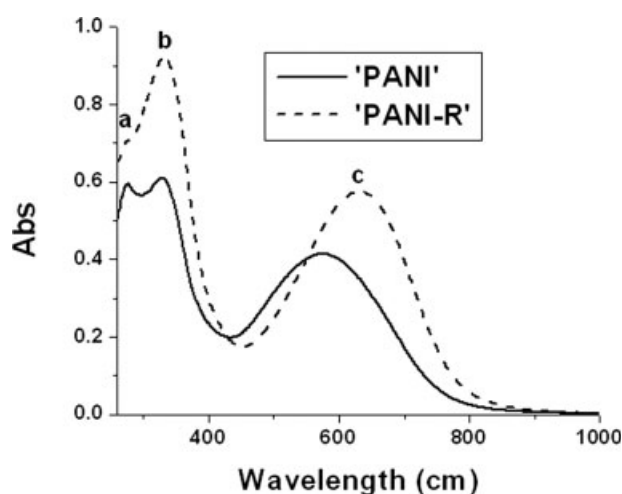

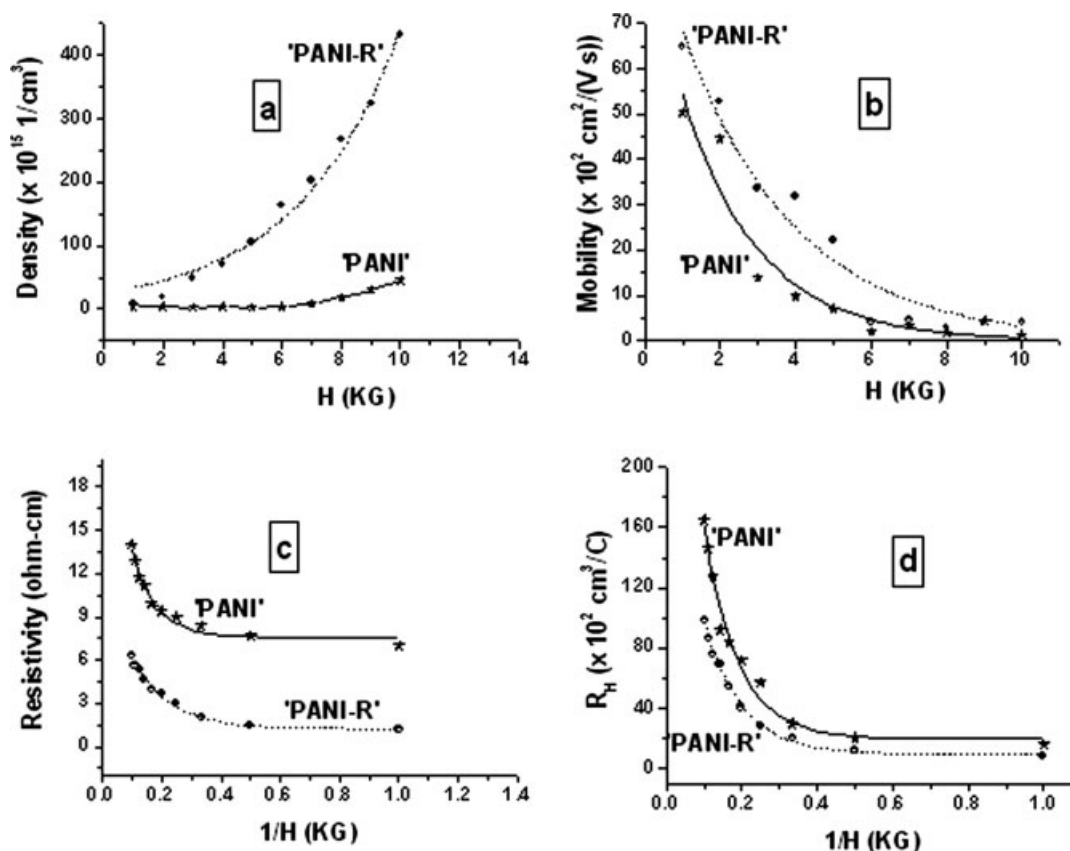**Figure 7** UV spectra of ''PANI'' and ''PANI-R.''

Figure 8 Results of Hall effect experiment of ''PANI'' and ''PANI-R'': change in the (a) charge carriers density, (b) charge carriers mobility, (c) resistivity and (d) Hall coefficient with change in the applied magnetic field strength.

negatively charged carriers (n-type semiconductors) the Hall voltage as discussed below is positive and for positively charged carriers (p-type semiconductors) the Hall voltage is negative. The Hall voltage is defined as

$$V_H = \frac{R_H \times I \times H}{t} \quad \text{or } R_H = \frac{V_H \times t}{I \times H}$$

where R_H is the Hall coefficient, I is the current, H is the magnetic field strength and t is the sample thickness. Hence in the R_H vs. $1/H$ plot for the n-type semiconductors the slope will be positive and for the p-type semiconductors the slope will be negative.

The Hall effect results of ''PANI'' and ''PANI-R'' are plotted in Figure 8. The charge carrier density is found to increase with the increase in the applied magnetic field strength as shown in Figure 8(a). This effect is ascribed to the fact that an opposite force exerted by the applied magnetic field on the charge carriers normal to the direction of the current flow causes deflection and hence the mobility of the charge carriers [Fig. 8(b)] is reduced with increase in the magnetic field strength. The increase in the resistivity with the increase in magnetic field strength

[Fig. 8(c)] is due to the decrease in the mobility of the charge carriers. It can be seen from the [Fig. 8(d)] that R_H vs. $1/H$ is giving a negative slope which indicates that the majority charge carriers are holes and hence it may be concluded that ''PANI'' and ''PANI-R'' exhibit p-type conduction. At a particular field strength, the carrier density and carrier
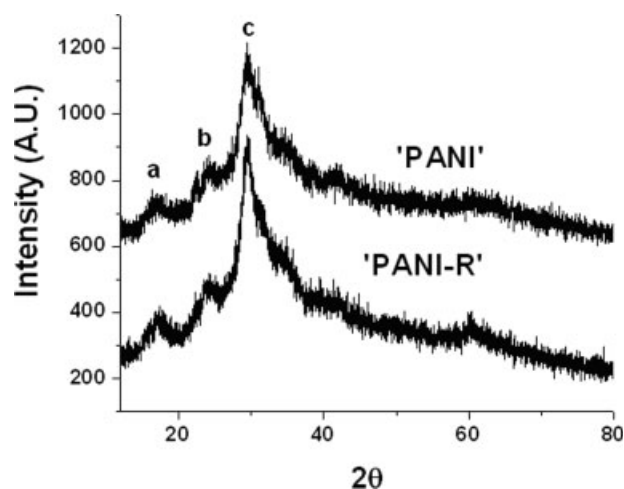

Figure 9 XRD curve of ''PANI'' and ''PANI-R.''

The d-Spacing, Crystallite Size, Percent Crystallinity, and the Inter-Chain Separation of "PANI" and "PANI-R"

Sample	d_a (Å)	t_a (Å)	PC_a (%)	R_a (Å)	d_b (Å)	t_b (Å)	PC_b (%)	R_b (Å)	d_c (Å)	t_c (Å)	PC_c (%)	R_c (Å)	TC (%)
"PANI"	5.1	50.8	1.1	6.36	3.6	46.4	2.4	4.56	3.0	15.0	26.6	3.77	30.1
"PANI-R"	5.4	45.5	0.9	6.74	3.7	36.9	2.5	4.59	3.0	15.5	25.2	3.78	28.6

d_a, d_b, d_c are the d-spacings, t_a, t_b, t_c are the crystallite sizes, PC_a, PC_b, PC_c are the percentages of crystallinity, and R_a, R_b, R_c are the inter-chain separations corresponding to the peaks a, b, and c, respectively; TC is the total percentage of crystallinity.

mobility are higher where as the resistivity and Hall coefficient are lower for "PANI-R" compared to that of "PANI." This may be due to the probability of more polaron formation in the "PANI-R" compared to that in PAni.

Crystallinity, d-spacing, crystallite size, and inter-chain separation (XRD analysis)

Figure 9 represents the XRD curve of "PANI" and "PANI-R." There are three crystalline peaks named as a, b, and c corresponds to three different crystal planes exist in the system.[25] The percentage of crystallinity, crystallite size, d-spacing, and inter-chain separation corresponding to each peak was calculated[1,18,21,22] from the XRD curve as shown in Table I. The degrees of crystallinity, the crystallite size are less and the d-spacing and inter-chain separations are more for "PANI-R" compared to that of the "PANI." This may be due to the slight loosening of the structure during the partial reduction.

The regularity and organized structure which is defined in terms of crystallinity is a favorable factor mainly for intra-molecular mobility of charged species along the chain and to some extent intermolecular hopping because of better and more close packing. Hence, the increase in the crystallinity is expected to increase the conductivity. Again with

decrease in the d-spacing or inter-chain separation the probability of inter-chain hopping will increase and hence the conductivity is expected to increase. The net conductivity is not only due to the intra-chain mobility of electron and hole but also the inter-chain mobility of the same. According to this concept the conductivity of "PANI" should be more compared to "PANI-R," but in reality it is reversed. This may be due to the formation of more EB structure in "PANI-R" with alternative arrangement of quinoid and benzenoid rings after partial reduction and hence more polaron formation in presence of protonic acid.

Morphology study from SEM

The morphology of "PANI" and "PANI-R" was studied from the photograph of SEM. The morphology and the structural pattern of PAni depend on the method of synthesis.[37–39] From the SEM photographs it is clear that the particles of "PANI" (Fig. 10) are like that of a long fiber where as in "PANI-R" (Fig. 11) it is found to be agglomeration of PAni particles. This may be due to the fact that some disorderness might have generated in "PANI-R" due to the slight loosening of the crystalline structure during the partial reduction. So, the conductivity of
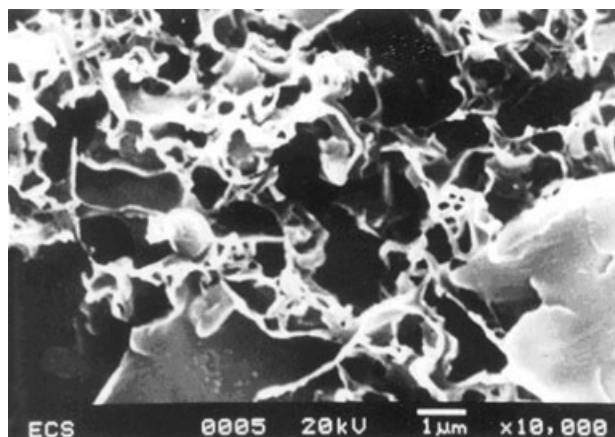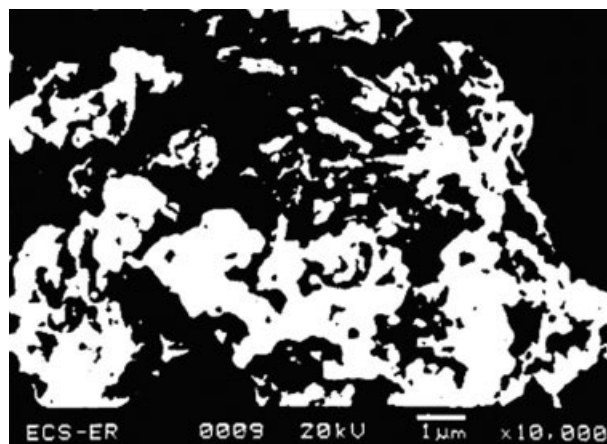

Figure 10 SEM photograph of "PANI."

Figure 11 SEM photograph of "PANI-R."

''PANI'' should be more compared to ''PANI-R,'' but in reality it is reversed. This may be due to the more polaron formation in ''PANI-R'' as discussed earlier.

The conductivity of PAni mainly depends on the (i) oxidation state or molecular structure and arrangement, (ii) degree of doping, (iii) degree of crystallinity, (iv) d-spacing or inter-chain separation, and (v) molecular weight or chain length.[1,18,21,22] If there is no EB structure in PAni then other factors as mentioned earlier may not play significant role towards the control of conductivity as in such case polaron formation will not take place in presence of protonic acid and there will be hardly any charge transport. So, alternate arrangement of quinoid and benzenoid rings in PAni seems to be the most important factor to achieve high level of conductivity. The suitable way to form this type of structure may be partial reduction of over oxidized PAni.

CONCLUSIONS

The most important part for the synthesis of highly conductive PAni is to control the oxidation state, molecular structure, and arrangement. The alternate arrangement of quinoid and benzenoid rings in PAni seems to be the most important factor for the attainment of high level of conductivity which is possible by reducing the over oxidized PAni.

The reversion of polarity of the electrodes during the electrochemical synthesis of PAni caused dramatic improvement in conductivity of PAni. This may be due to the partial reduction of some repeated quinoid ring to alternate quinoid and benzenoid rings that means there is formation of PAni having more EB structure. This results in more polarons formation in presence of protonic acid where carrier density and its mobility are more and hence conductivity is more. The Hall effect study reveals that the PAni is p-type semiconductor that means charge carriers are holes. The electrochemical reduction may lead to the marginal decrease in the crystallinity and crystallite size and slight increase in the d-spacing but still the conductivity is found to improve mainly due to more polaron formation.

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