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Synthesis and characterization of malonic acid-doped polyaniline

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The conductive form of polyaniline was synthesized by the anodic and chemical oxidation of aniline in malonic acid medium. The conductivity of polyaniline doped with malonic acid changed from 1.62×10^{-6} to $2.5 \times 10^{-5}\,\mathrm{S\,cm^{-1}}$ depending on the way it was synthesized. The polymer growth rate was observed to be very slow in malonic acid compared with H_2SO_4. Thermogravimetric data revealed that the maximum thermal reaction rate of PANI doped with malonic acid was at 200 °C and 520 °C compared with 290 °C and 530 °C of the polymer doped with H_2SO_4.

1. Introduction

There have been numerous studies on the synthesis, characterization and use of conductive polymers such as polypyrrole, poly(*N*-vinylcarbazole) and polythiophene [1–4]. Polyaniline (PANI) has received much attention due to its environmental stability, ease of synthesis and cheapness.

PANI can be synthesized both chemically using suitable oxidants such as $FeCl_3$ [5] and $(NH_4)_2S_2O_8$ [6] in solutions containing mineral or organic acids, and electrochemically, in which it is directly oxidized on a suitable electrode [7–9]. In both methods PANI is converted into a highly conducting metallic state with no gap in the electronic band structure.

Some properties of conducting PANI are closely related to the type of anion doped into it. For instance, the solubility of PANI, which is an important criterion for the processability and characterization, can be improved by doping it with big anions such as camphor sulphonic acid [10] and 5-sulphosalicylic acid [11]. It was reported that the dopant anions which improve PANIs solubility generally contain carboxyl groups [12].

The use of polymer electrolyte dopants also promotes the solubility. PANI doped with poly (styrene sulphonic acid) was observed to dissolve in water [13] as well as in some organic solvents [14]. It was reported that the film growth rate increased and the surface morphology of the PANI film showed a dramatic change by the addition of polymer electrolytes [7]. In a different study, it was shown that PANI obtained in poly(styrene sulphonic acid) media had a globular morphology while the polymer obtained in poly(vinyl sulphonic acid) had a fibrous network structure [15].

The conductivity of PANI synthesized electrochemically was dependent on the redox state of the polymer, the solution pH, water content and, to a lesser extent, the type of dopant anion [16]. The type of dopant anion also affects the stability of the conductivity in PANI at different atmospheres and at temperatures [17]. Changing the nature of the anion also has a significant influence on the kinetics and conversion in the electrochemical polymerization of aniline [18].

The synthesis and characterization of PANI doped with different anions is critical, since many properties of the final polymer are influenced by the nature of the dopant anion. There is no literature data related to malonic acid being used as dopant for PANI. In the present work, the chemical and electrochemical synthesis and characterization of malonic acid-doped PANI were studied.

2. Experimental details

2.1. *Materials*

Aniline(BDH) was doubly distilled under vacuum. Other chemicals such as malonic acid, H_2SO_4, and dimethylsulfoxide (DMSO) were used as received from Merck.

2.2. *Procedures*

The chemical polymerization was carried out by rigorous stirring of the 4 M aqueous malonic acid solution containing 0.4 M double distilled aniline and adding $FeCl_3$ dropwise. The polymerization temperature was 0 °C. Following stirring for 2 h the mixture was kept at 0 °C for 24 h and the dark green product was filtered, washed with water then with

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1 M malonic acid and dried under vacuum at 50 °C for two days.

The electropolymerization was carried out in an H-type three electrode cell equipped with a 1.5 cm^2 Pt foil working electrode and a 2 cm^2 Pt foil counter electrode. The reference electrode was Ag/Ag^+. The cell was filled with 50 mL 4 M aqueous malonic acid containing aniline (0.4 M) and the system was purged with nitrogen for 20 min prior to electrolysis. The polymer sample taken from the electrode surface at the end of the electrolysis was washed with water, then with 1 M malonic acid and dried under vacuum at 50 °C for two days.

The cyclic voltammograms (CV) were obtained using a three electrode cell having 1 mm long Pt wire working electrode, 2 cm coiled Pt wire counter electrode, and Ag/Ag^+ reference electrode.

All the electrolysis and CV experiments were performed using a Bank Elektronik ST 88 potentiostat, a Bank Elektronik VSG 2000 function generator, and a Karl Kolb Servagor X-Y recorder.

An undoped PANI sample was prepared by stirring doped PANI in dilute NH_4OH for twenty four hours [6].

The infrared spectra of undoped and doped PANI samples were taken in KBr pellets using a Matsonn 1000 FTIR spectrometer.

The u.v.-visible spectra were recorded using a Shimadzu 160 A spectrophotometer. PANI solutions at different pH values were prepared by adding malonic acid into undoped PANI solutions in DMSO and the u.v. spectra were taken using DMSO solutions of malonic acid at the same pH values as reference. The reference used in the u.v. spectra of undoped PANI in DMSO was DMSO itself.

Thermogravimetric analysis was carried out between 25 °C and 700 °C with a flow rate of 10 mL min^{-1} and a heating rate of 10 °C min^{-1} under a helium atmosphere. The thermograms were taken using a Linseis model thermal analyser.

Micrographs of malonic acid-doped PANI were obtained from the polymers removed from electrode by an adhesive tape. Scanning electron microscopy (SEM) studies were performed on a Jeol JM-100 CX II microscope.

The samples to be used in conductivity measurements were prepared by grinding PANI and forming 1 mm thick 1.3 cm diameter pellets. The measurements were made by a standard four probe method.

3. Results and discussion

3.1. *Cyclic voltammetry*

Figure 1 shows the cyclic voltammograms of 4 M aqueous malonic acid and 4 M aqueous malonic acid containing 0.4 M aniline in the potential range −0.4 V to 1.4 V. There is no peak for 4 M malonic acid solution up to 20 cycles (Fig. 1(a)). On the other hand when aniline (0.4 M) was added to the medium a broad band appeared at 1.0 V in the first scan which decreased considerably in the second scan and totally vanished in further cycles (Fig. 1(b)).

CV curves in Fig. 1(b) are typical and aniline was found to show similar behaviour in systems containing various acids such as H_2SO_4, HCl and 5-sul-

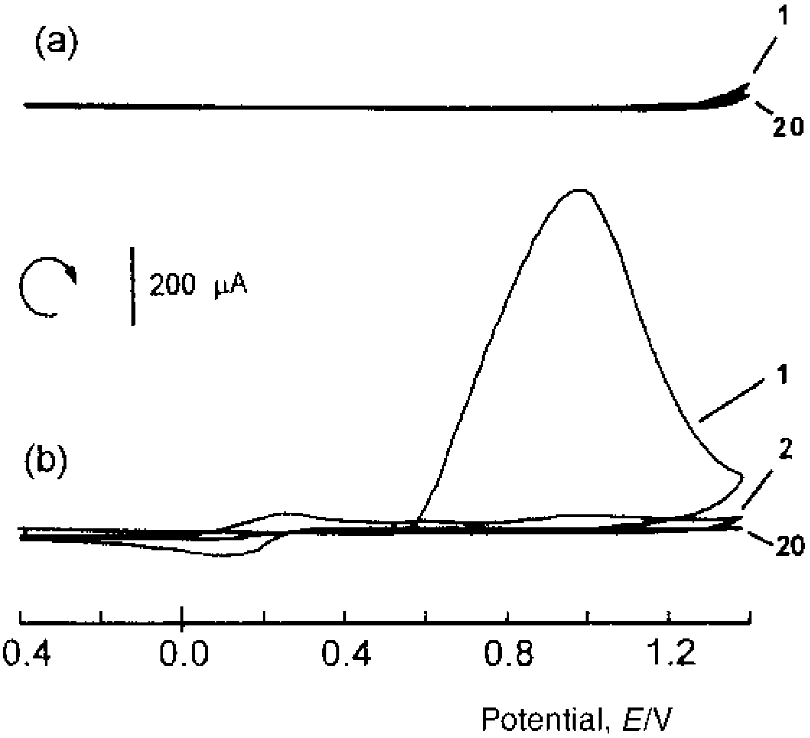


Fig. 1. Cyclic voltammograms between −0.4 V and 1.4 V in (a) 4.0 M malonic acid, (b) 4.0 M malonic acid + 0.4 M aniline at a sweep rate of 50 mV s^{-1} on Pt electrode. The numbers show the cycling.

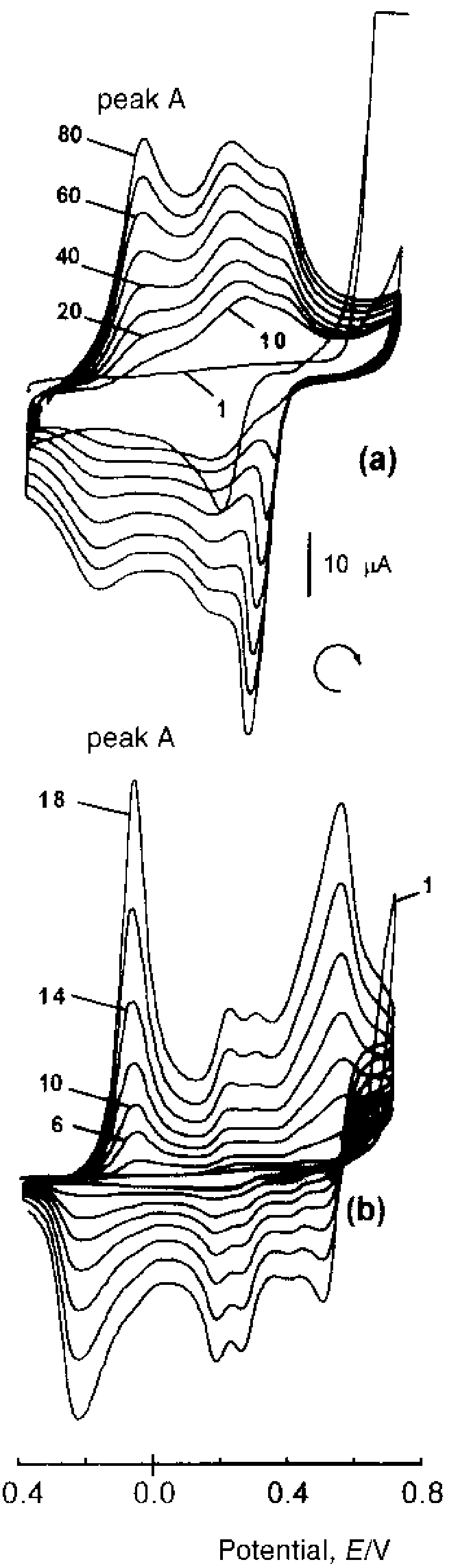


Fig. 2. Cyclic voltammograms between −0.4 V and 0.7 V in (a) 4.0 M malonic acid + 0.4 M aniline and (b) 1.0 M H_2SO_4 + 0.1 M aniline at a sweep rate of 50 mV s^{-1} on Pt electrode. The numbers show the cycling.

phosalicylic acid [11, 19]. This shows that aniline forms an anilium radical cation by anodic oxidation through direct electron transfer in malonic acid solution.

In the potential range −0.4 V to 0.7 V voltammograms obtained at higher sensitivity in 4 M malonic acid containing 0.4 M aniline are given in Fig. 2(a). The magnitude of peak A is a measure of the amount of polymer formed [20]. Figure 2(a) and 2(b) clearly illustrate that the rate of PANI growth in malonic acid is much slower than in H_2SO_4.

Figure 3 shows the CV of H_2SO_4- and malonic acid-doped PANI. Peak B is attributed to the quinone/hydroquinone couple forming during the polymerization of aniline and absorbed into the polymer matrix and adsorbed on the electrode surface as suggested elsewhere [11]. The magnitude of peak B in malonic acid-doped PANI is higher than in H_2SO_4-doped PANI. This proves that amount of quinone/hydroquinone contaminants absorbed into PANI matrix synthesized in malonic acid is higher than those absorbed into the PANI matrix obtained in H_2SO_4.

The conductivity of chemically and electrochemically synthesized malonic-acid doped PANI

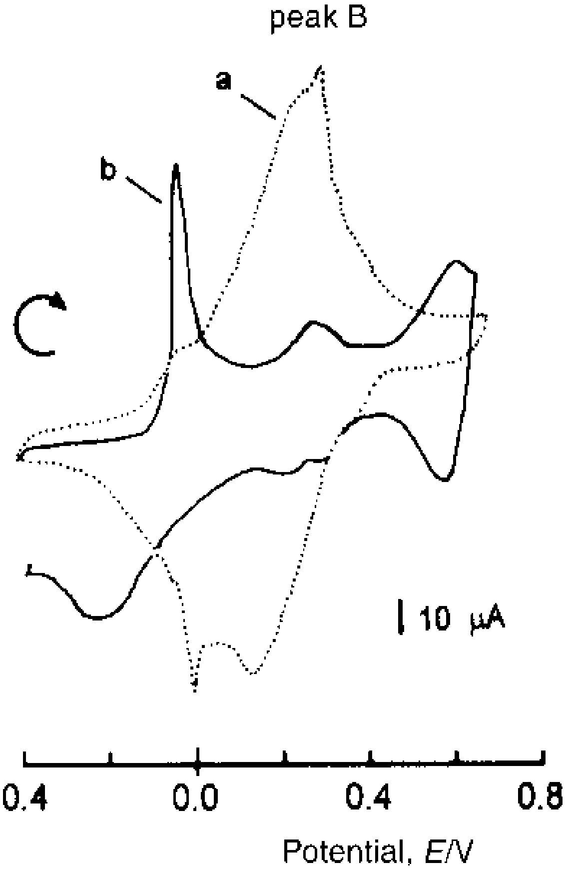


Fig. 3. Cycling voltammograms of PANI film-coated Pt electrodes: (a) PANI film obtained at 0.8 V in 4.0 M malonic acid + 0.4 M aniline and CV recorded in 4.0 M malonic acid and (b) PANI film obtained at 0.8 V in 1.0 M H_2SO_4 + 0.4 M aniline and CV recorded in 1.0 M H_2SO_4.

were 1.6×10^{-6} S cm^{-1} and 2.5×10^{-5} S cm^{-1}, respectively. On the other hand, the conductivity of electrochemically synthesized H_2SO_4-doped PANI was found to be 0.2 S cm^{-1}. The conductivity values of malonic acid-doped PANI is smaller compared with this value.

3.2. *Dependence of rate of polymer growth on aniline concentration*

The plot of the anodic peak current for peak A against the number of scans (i.e., time) at different aniline concentrations indicates the relationship between the polymer growth rate and the aniline concentration; the order of reaction with respect to aniline concentration can be determined [18, 20].

Figure 4 shows the change of current values of peak A with the number of cycles between –0.4 V and 0.7 V at 25 °C and a scan rate of 50 mV s^{-1}. The increase in aniline concentration increases the height of peak A. This increase is especially rapid up to the first 10 cycles. Further cycles result in morphological characteristics which retard the subsequent increase [18].

The polymer growth rate at a certain point can be determined from the slope of the curve at specified points. When the slopes were measured for each aniline concentration at different scan numbers the plots of Fig. 5 were obtained. The linearity of these plots indicates that the polyaniline growth rate is first order with respect to aniline concentration in malonic acid solution.

3.3. *UV-visible spectra*

Figure 6 shows the u.v.-visible spectra of chemically synthesized malonic acid-doped and undoped PANI between wavelengths of 300–1100 nm. Curve a in Fig. 6 is the spectrum of undoped PANI in DMSO (pH 6.2) and shows two fundamental absorption bands at 323 and 630 nm. If the pH of this solution is gradually decreased by the addition of malonic acid the original blue colour of the solution turns green and decreases the intensity of the band at 630 nm and forms new bands at 445 and 900 nm. Curve b in Fig. 6 is the spectrum taken at pH 4.3, showing all these bands together. We observed that the band at 630 nm

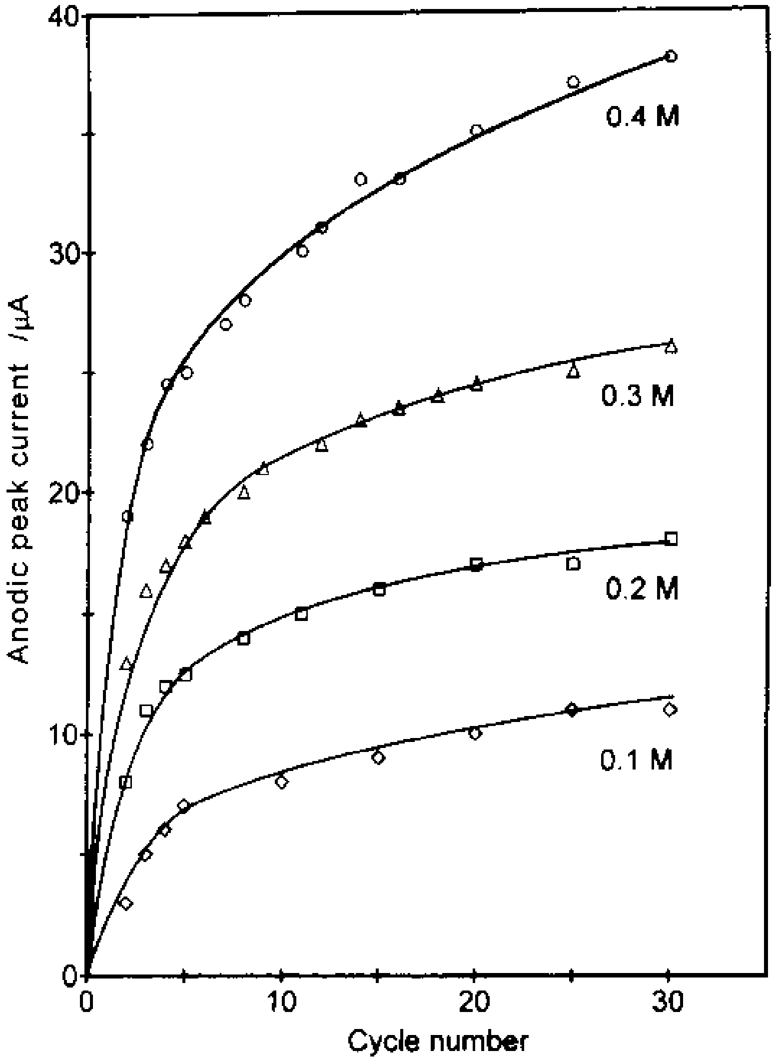


Fig. 4. Dependence of anodic peak current on cycle number at various aniline concentrations at a scan rate of 50 mV s^{-1}: (◇) 0.1 M, (□) 0.2 M, (△) 0.3 M, (○) 0.4 M.

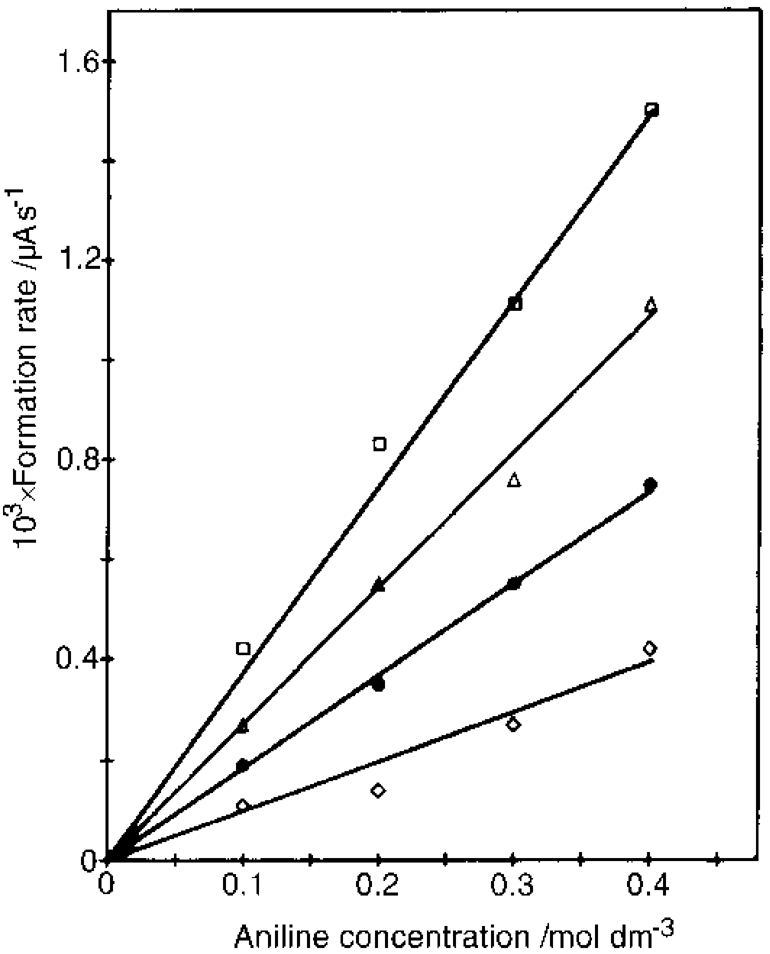
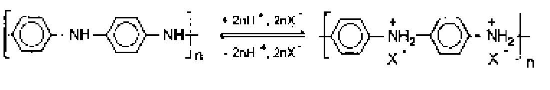


Fig. 5. Rate of polymer formation at various anodic peak current values against concentration of aniline.

completely disappeared at pH values below 4.3 (curve c) and the bands at 445 and 900 nm remained.

The change in colour of the solution from blue to green with pH decrease is due to the loss of protons from the polymeric molecules, and an acid-base equilibrium occurs at pH 4–5.



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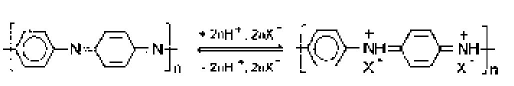

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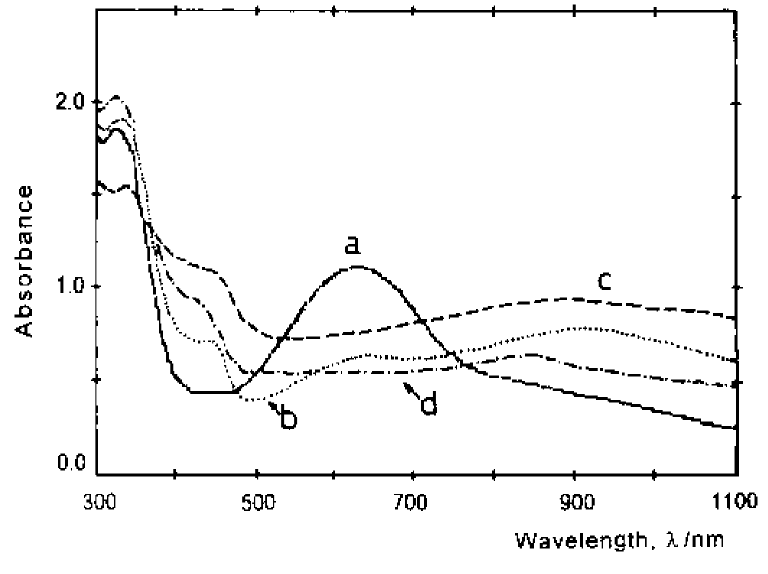

Fig. 6. u.v.-visible spectra of chemically obtained (a) undoped PANI in DMSO, (b) at pH 4.3 and (c) at pH 3.6; (d) u.v.-visible spectrum of electrochemically obtained PANI in DMSO at pH 3.8 (pH values are reached by adding malonic acid).

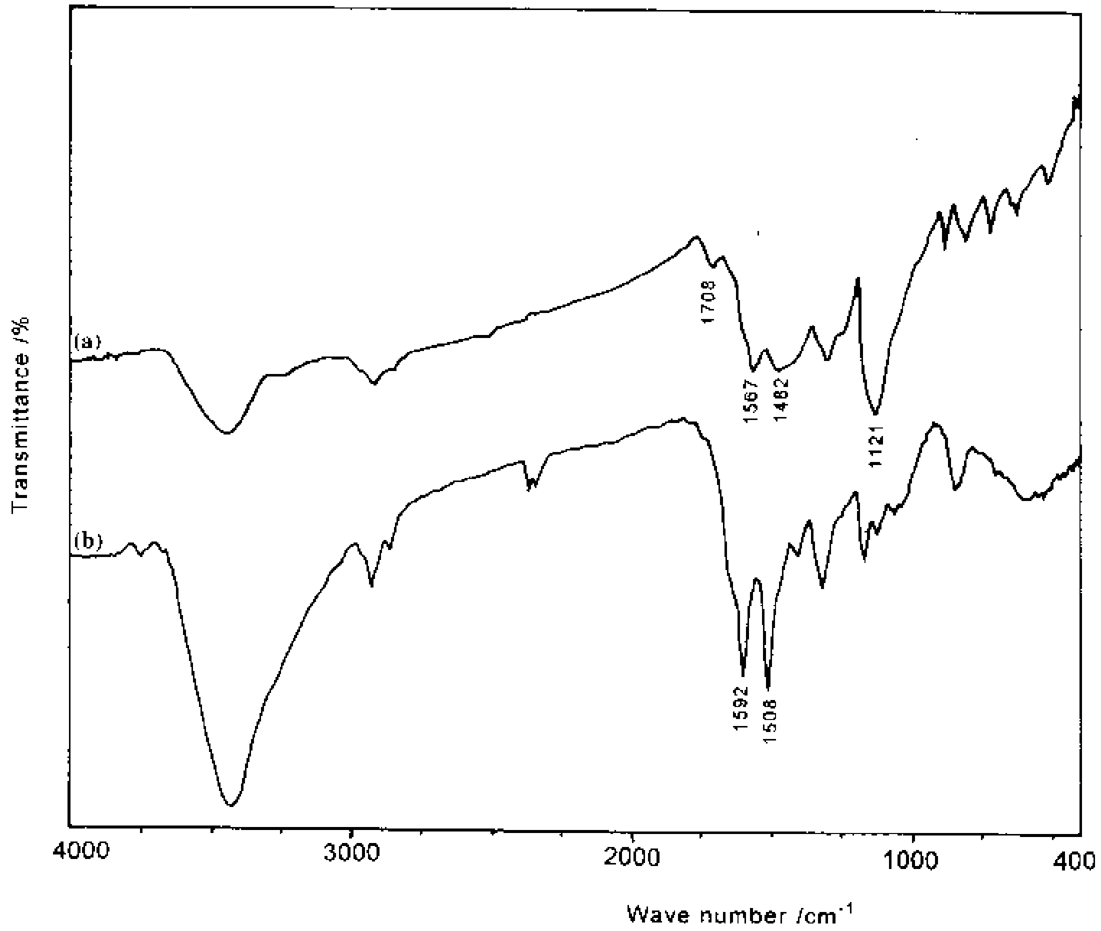

Fig. 7. Fourier transform i.r. spectra of (a) chemically obtained malonic acid-doped PANI and (b) undoped PANI.

The band observed at 445 nm at low pH results from the species on the right side of Equation 2, and the band about 320 nm is due to species on both sides in Equation 1 [21].

PANI synthesized electrochemically showed similar adsorption behaviour. As seen from the spectrum in Fig. 6 (curve d) for electrochemically synthesized PANI solution in DMSO (pH 3.8) there are characteristic bands at 318, 436 and 838 nm similar to chemically synthesized PANI. The shift in band positions to lower values in the electrochemically synthesized sample may be attributed to differences in chain length.

3.4. *Infrared spectra*

Figure 7 shows the Fourier transform i.r. spectra of undoped PANI and chemically synthesized PANI doped with malonic acid. The bands observed at 1592 and 1508 cm^{-1} for undoped PANI (spectrum b) show a shift in doped PANI. These bands are located at 1567 and 1482 cm^{-1} in chemically synthesized PANI (spectrum b). The observed shift is likely due to quinoid rings in PANI being converted into benzenoid rings [11].

The broad and intense band observed at 1121 cm^{-1} in the doped form is also characteristic for conductive PANI and is due to charge delocalization on the polymer backbone [22]. The intensity of this peak is a measure of the delocalization of the electrons or the conductivity [23]. It disappears after the removal of the dopant (spectrum b).

Similarly, the band at 1708 cm^{-1} in doped PANI is due to carboxyl groups present in the dopant and it disappears as the dopant is removed.

3.5. *Scanning electron microscopy*

A SEM micrograph of the electrode side of the electrochemically obtained malonic acid-doped PANI is given in Fig. 8. The surface is not smooth and uniform but contains macrogranular structures formed by the aggregation of small globular structures.

3.6. *Thermogravimetric analysis*

The thermograms of malonic acid and H_2SO_4-doped PANI samples between 25 °C and 700 °C are given in Fig. 9. The weight losses of malonic acid and H_2SO_4-doped PANI at 700 °C were found to be 41.9 % and 53.0 %, respectively.

The thermal reaction rates (dW/dt) determined from the thermograms are separately shown in Fig. 10. The reaction rate calculation range was chosen as 150–700 °C to eliminate the weight loss due to the

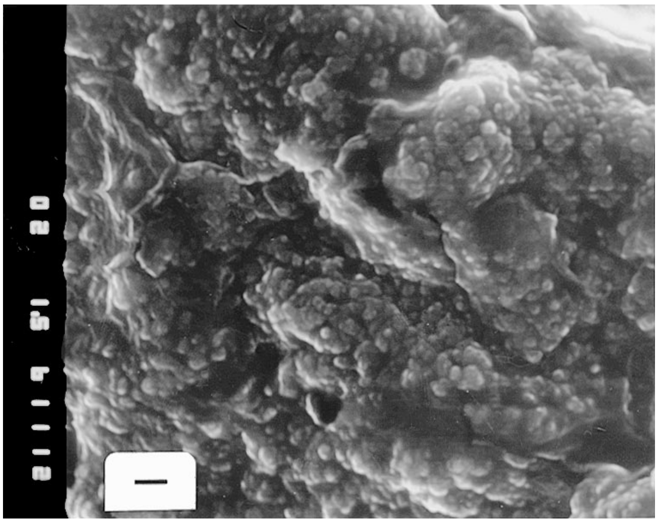

Fig. 8. SEM micrograph of malonic acid-doped PANI (electrode side) (bar indicates 5 μm).

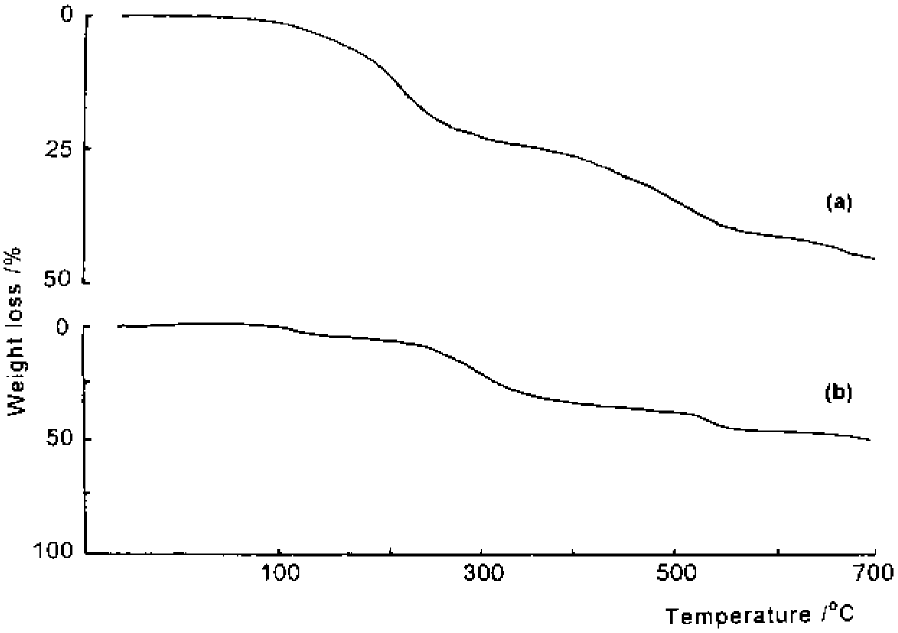

Fig. 9. TGA curves of (a) malonic acid-doped PANI and (b) H_2SO_4-doped PANI.

removal of water. The highest thermal reaction rate was observed at 200 and 520 °C for malonic acid, and 290 and 530 °C for H_2SO_4-doped PANI samples. These results indicate that, the nature of the dopant anion influences the thermal properties of PANI.

4. Conclusion

A conductive PANI can be synthesized in malonic acid solution using both chemical and electrochemical routes.

The electrochemical polymer growth rate in malonic acid media is much lower than that observed in H_2SO_4. Similarly, the conductivity of PANI samples obtained in malonic acid media is much lower than those synthesized in H_2SO_4.

The cyclic voltammetric investigation of PANI revealed that the samples synthesized in malonic acid media contained a quinone/hydroquinone type contaminant in large amount.

Finally, based upon thermogravimetric analysis, the nature of the dopant influences the thermal behaviour of PANI to a certain extent.

Acknowledgement

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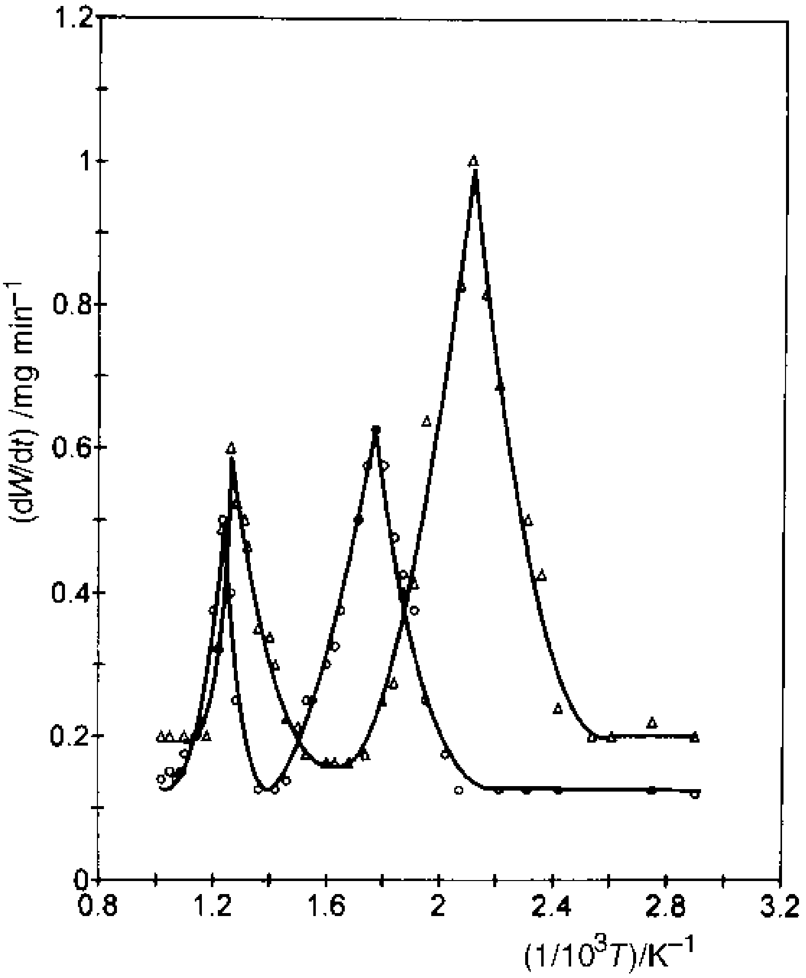

Fig. 10. The temperature dependencies of the reaction rate of (△) malonic acid-doped PANI and (○) H_2SO_4-doped PANI.

References

[1] M. S. Satch, S. Tanaka and K. Kaeriyama, *J. Chem. Soc. Chem. Commun.* (1986) 873.

[2] M. Saçak, U. Akbulut, C. Cheng and D. N. Batchelder, *Polymer* **35** (1994) 2495.

[3] A. F. Diaz and K.K. Kanazawa, *J. Chem. Soc., Chem. Commun.* (1979) 635.

[4] K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt and G. B. Street, *ibid.* (1974) 854.

[5] A. Yasuda and T. Shimidzu, *Polymer J.* **25** (1993) 329.

[6] J. C. Chiang and A.G. MacDiarmid, *Synth. Met.* **13**(1986) 193.

[7] K. Hyoda, M. Omea and Y. Kagami, *Electrochim. Acta* **36** (1991) 87.

[8] L. H. C. Mattoso, R. M. Faria, L. O. S. Bulhoes and A. G. MacDiarmid, *Polymer* **35** (1994) 5104.

[9] D. E. Stilwell and S. M. Park, *J. Electrochem. Soc.* **136** (1989) 427.

[10] Y. Cao, P. Smith and A. J. Heeger, *Synth. Met.* **48** (1992) 81.

[11] D. C. Trivedi and S.K. Dhawan, *ibid.* **58** (1993) 309.

[12] K. Tzou and R. Gregory, *ibid.* **53** (1993) 365.

[13] K. Shannon and J.E. Fernandez, *J. Chem. Soc. Chem. Commun.* (1994) 643.

[14] Y. Li, Y. Cao and Z. Xue, *Synth. Met.* **20** (1987) 141.

[15] J. H. Hwang and C. Yang, *ibid.* **29** (1989) E271.

[16] W. W. Focke, G.E. Wnek and Y. Wei, *J. Phys. Chem.* **91**(1987) 5813.

[17] Y. Wang and M. F. Rubner, *Synth. Met.* **47** (1992) 255.

[18] P. Nunziante and G. Pistoia, *Electrochim. Acta* **34** (1989) 223.

[19] D. E. Stilwell and S.M. Park, *J. Electrochem. Soc.* **135** (1988), 2254.

[20] Y. Wei, Y. Sun, G.W. Jang and X. Tung, *J. Polym. Sci., Polym. Lett.* **28** (1990) 81.

[21] R. Jiang and S. Dong, *Synth. Met.* **24** (1988) 255.

[22] Y. H. Kim, C. Foster, J. Chiang and A.J. Heeger, *ibid.* **26** (1988) 49.

[23] J. Tang, X. Jing, B. Wang and F. Wang, *ibid.* **24** (1988) 231.