JOURNAL OF APPLIED ELECTROCHEMISTRY **22** (1992) 563–570

Synthesis and properties of polyaniline obtained using sulphamic acid

S. K. DHAWAN, D. C. TRIVEDI

Central Electrochemical Research Institute, Karaikudi 623 006, India

Recieved 16 May 1991; revised 29 August 1991

The results of investigations of the chemical and electrochemical polymerization of aniline in sulphamic acid medium and its characterization by electrochemical and spectroscopic techniques are presented. The investigations reveal that sulphamic acid medium affects, not only the polymerization process, but also its electrochemical characteristics.

1. Introduction

Even though the understanding of conduction in many organic polymers is limited, very many applications using these materials have been envisaged [1–7]. The polyaniline family of polymers has been known for more than a century [8, 9]. The efforts of MacDiarmid and his coworkers has made polyaniline (PAn), one of the most thoroughly studied conducting polymers [10, 11, 19]. But there still remains scope to exploit the synthesis of polyaniline, which largely depends upon the synthetic ability to manipulate its molecular structure.

Other reports tell that PAn can be made soluble in 80% acetic acid [11], concentrated H_2SO_4 [12] and by the use of organic proton acids [13–15]. The solubilization in 80% acetic acid or concentrated H_2SO_4 shows that it is possible to induce dipole polarization in the macromolecular system to yield a soluble polymer. If this is the case then it should be possible to achieve solubilization of PAn by synthesizing it in the presence of acids which can form strong H-bonding with the polymer [13]. Sulphamic acid (SMA) is one such acid whose pKa in water is 1.04 [16] and which exists in the following principle equilibrium:

$$NH_2SO_3H \rightleftharpoons \overset{+}{N}H_3SO_3^- \rightleftharpoons NH_2SO_3^- + H^+ \qquad (1)$$

Equation 1 depicts only the principle equilibrium whereas various species like $NH_2SO_3^{\cdot}$, $NH_2^{\cdot}$, $NH_3^+SO_3^{\cdot}NH_3^+$; SO_3^- also exist along with the principle equilibrium. The existence of free radicals and radical ions make sulphamic acid one of the best catalysts in polymerization processes (for example, in the manufacture of isoprene, polystyrene, polyvinyl alcohol etc) [17]. In DMSO (dimethyl sulphoxide) solution, sulphamic acid has a pKa of 6.5. The lower acid strength has been attributed to partially weak solvation of the sulphamate ion [18].

This acid, which is milder than H_2SO_4, may prove to be a better agent for the formation of H-bonds due to the $-NH_2$ group. With this in mind, the polymerization of aniline was carried out in a sulphamic acid medium by both persulphate oxidative and electrochemical routes. Thus, by both these methods the PAn obtained is soluble in NMP (N-methyl pyrrolidinone), DMSO and DMF (dimethyl formamide). In this paper we present studies on the chemical and electrochemical synthesis of polyaniline and its characterization by cyclic voltammetry, chronoapmerometry, u.v. visible, FTIR studies and 1H NMR of the soluble PAn synthesized in sulphamic acid medium.

2. Experimental details

The polymerization of aniline in aqueous sulphamic acid solution (SMA) was carried out by two methods: (i) by chemical oxidative polymerization using ammonium persulphate; and (ii) by anodic polymerization at platinum, indium tin oxide (ITO) and stainless steel electrodes.

2.1. *Chemical polymerization*

The chemical oxidative polymerization of a 0.1 : 1 molar ratio of aniline and sulphamic acid was carried out by adding 0.1 mol of ammonium persulphate solution drop by drop. (For stoichiometry 0.2 mol are required). Stirring of the reaction mixture was continued for 2 h to ensure the completion of the reaction which was indicated by the stabilization of the temperature of the reaction mixture. The reaction mixture was then filtered and washed repeatedly with distilled water and finally with 1.0 M sulphamic acid. The polymer so obtained was dried under vacuum at 40 °C for 24 h.

2.2. *Electrochemical preparation*

The electrochemical polymerization was carried out from 0.1 M monomer in 1.0 M sulphamic acid aqueous solution. Prior to polymerization, the solution was deoxygenated by passing argon gas for 30 min. The polymerization was carried out at 0.72 V against a saturated calomel electrode (SCE) on either a platinum electrode, an ITO coated glass plate (resistivity: 20–50 Ω cm) or stainless steel electrodes (charged passed, Q: 0.32 C cm^{-2}). The polymer film growth was

0021-891X/92

also studied by sweeping the potential between −0.2 to +0.8 V at a scan rate of 50 mV s^{-1}.

The chronoamperometric studies of the polyaniline film (thickness: ~1.0 μm) obtained by a potentiodynamic method were carried out on a Bio-analytical System Inc., USA (BAS 100 A), by switching the potential from −0.2 V to +0.8 V and back to −0.2 V.

The cyclic voltammetry studies were carried out using a Tacussel bipad potentiostat coupled with an *X–Y* recorder and a BBC microcomputer, (model SE-780) and universal programme PARC 175. The u.v.-visible absorption spectra were recorded on an Hitachi-3400 spectrophotometer and FTIR spectra on a Nicolet spectrometer. The 1H–NMR of PAn in DMSO-d6 was recorded at 22 °C on a Bruker FX 90Q NMR spectrometer using TMS (tetramethyl silane) as standard.

3. Results and discussion

3.1. *Synthesis*

The polmerization of aniline to conducting polyaniline (PAn) by chemical and electrochemical methods in mineral acids has been widely studied [10–12]. However, the study on the synthesis of PAn and its properties in organic acids is limited [13–15]. In the present investigation, a dimethyl sulphoxide (DMSO), dimethylformamide (DMF) and N-methylpyrrolidinone (NMP) soluble doped conducting polyaniline is obtained when oxidative polymerization of aniline is carried out in sulphamic acid medium, contrary to its insoluble nature when it is synthesized using mineral acids [19–20].

The characteristics of PAn obtained in various media is tabulated in Table 1. This reveals that the variation in the solubility of the doped polymer in active solvents like DMSO depend upon the dopant. This observation indicates the possible interaction of dopant with polymer. Therefore, in the present study the interaction of $-SO_2OH$ of sulphamic acid with the chemically flexible amine (–NH–) group of polyaniline cannot be ruled out to give a polymer solution. This suggests that the solubility of these polymers in active solvent is due to dopant induced interaction of the polymer with the dipole end of the solvent. Hence the maximum solubility is observed in DMSO where the sulphoxide group is capable of interacting with the sulphonate attached to the polymer as a dopant. These types of interactions are less likely in the solvents devoid of active groups like CCl_4, $CHCl_3$, etc.

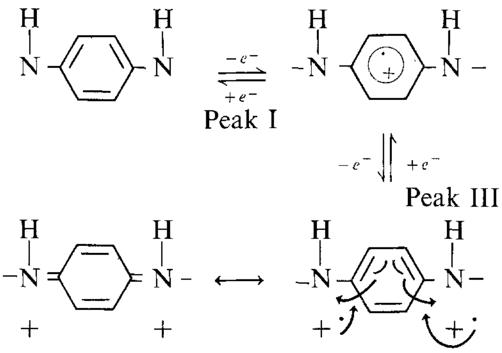
Although the PAn obtained by either of the methods has identical environmental stability, the electrochemical method leads to formation of a thin film on the electrode surface which can be used for electrochromic display and for various other electrochemical studies.

3.2. *Cyclic voltammetric studies*

The electrochemical polymerization of aniline in sulphamic acid medium is obtained by sweeping the potential in three different potential ranges: from −0.2 to +0.8 V (curve a of Fig. 1), from −0.2 to 1.0 V (curve b of Fig. 1) and from −0.2 to 1.4 V (curve c of Fig. 1). This indicates that the peak appearing at 1.05 V (SCE) in the first cycle corresponds to oxidation of aniline whereas the corresponding peak in H_2SO_4 medium appears at +0.80 V (Fig. 2). This suggests that the intermediate species involved in the polymerization of aniline in SMA medium is not a simple radical cation but is possibly bound to the SMA.

In the subsequent cycles, new oxidation peaks II and III appear indicating that these radical cations undergo further coupling to give the polymer at the anode surface as indicated by the increase in the intensity of peak I (Fig. 1). The slight shift in potential of peak I is attributed due to the presence of oligomeric species adsorbed at the electrode surface. These oligomeric species are further polymerized in the next few sweeps as indicated by the stabilization of peak potential after twelve scans (curve a of Fig. 1). On increasing the upper potential limit from 0.8 to 1.4 V (curves b and c of Fig. 1) well defined peaks of higher current intensity appear, implying fast growth of the polymer.

Figure 3 shows the cyclic voltammogram for PAn films obtained by potential sweeping in a blank 1.0 M SMA medium (not containing the monomer). It shows two main redox couples at +0.125 V (peak I) and +0.670 V (peak III). In order to explain the electrochemical behaviour of polyaniline, the formation of radical cations near peak I, which are subsequently oxidized into imines near peak III, has been suggested [21, 22] and can be represented as follows:



The peak II (Fig. 3) in the cyclic voltammogram is essentially due to adsorption of quinone/hydroquinone, generated during the growth of the polymer film which is strongly adsorbed in the polymer matrix and this peak II persists even in fresh electrolyte. The intensity of peak II further increases in the presence of quinone and hydroquinone added externally in the electrolyte. Our suggetion that peak II is essentially due to the quinone/hydroquinone couple has support from studies on chemically modified electrodes which report the strong adsorption of the quinone/hydroquinone couple on the electrode surface [23].

The redox potentials of the various peaks of the PAn systems in different electrolytes are shown in

Table 1. Characteristics of PAn in different media

Medium	Method of preparation	Conductivity/Scm^{-1}	Solubility/g $(100 ml)^{-1}$ DMSO	I.r. absorption bands/cm^{-1}	U.v.-visible spectra		Ref.
					Solid reflectance/nm	Solution absorption/nm	
SMA NH_2SO_2OH	Chemical	0.2	1.1	1571, 1483, 1303, 1261, 1144 (s), 1111, 1021 and 803	419 and 672	320, 420 and 618	This work
SMA NH_2SO_2OH	Electrochemical	2.0	0.8	1570, 1481, 1301, 1260, 1160 (s), 1119, 1021, 801	419 and 682	303, 332, 447 and 639	This work
H_2SO_4	Chemical	0.7	Nil	1578, 1493, 1300, 1246, 1140 and 810	420 and 800	–	[29]
H_2SO_4	Electrochemical	1.2	Nil	–	420 and 820	–	[30]
BSA* $C_6H_5SO_2OH$	Electrochemical	2.0	0.820	1572, 1492, 1301, 1261, 1170, 1137, 1025 and 801	416 and 662	336, 449 and 646	[13]
PTSA* $CH_3C_6H_4SO_2OH$	Electrochemical	5.0	0.850	1568, 1489, 1302, 1260, 1160, 1130, 1040 and 798	417.8 and 686.0	343, 453 and 662	[14]

* BSA, benzene sulphonic acid, PTSA, p-toluene sulphonic acid.

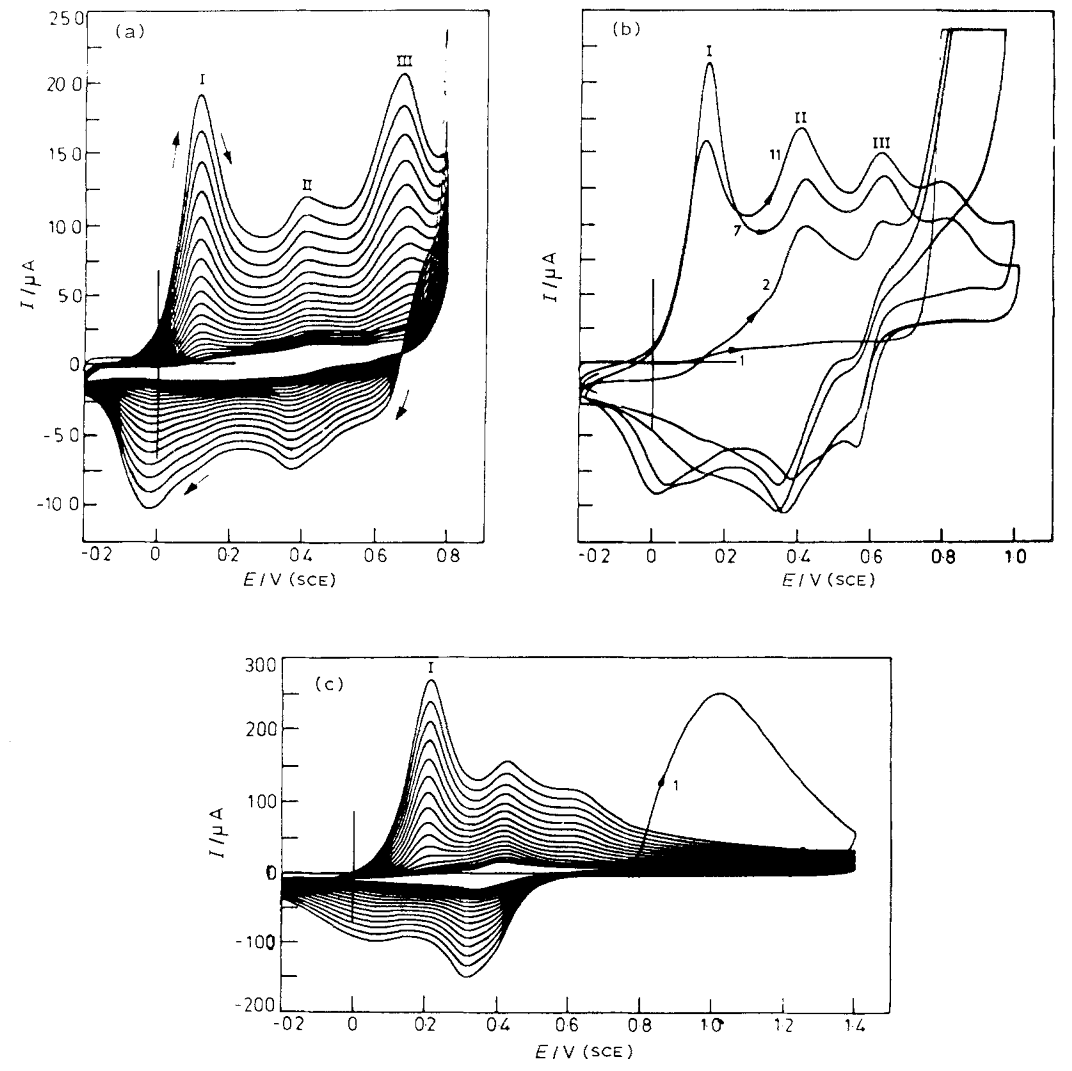


Fig. 1. Electrodeposition of PAn in 1 M sulphamic acid solution + 0.1 M aniline by potential sweeping between: (a) −0.2 to +0.8 V; (b) −0.2 to +1.0 V and (c) −0.2 to +1.4 V on a platinum electrode (0.25 cm^2) against SCE at a scan rate of 50 mV s^{-1}. (cycle (1 and 2) at 2.5 μA, seventh cycle (7) at 5 μA, and eleventh cycle (11) at 10 μA curve b).

Table 2. It is clear that the polymerization potential is essentially dependent on the electrolytic medium and hence a change in peak potentials of the redox couple is observed.

On comparing these results we find that in sulphuric acid medium the peak potential of the PAn film corresponding to I and III anodic peak is at +0.110 and +0.630 V whereas the corresponding peak potential values in SMA medium lies at +0.125 and +0.670 V. The shift in potential can be attributed due to an interaction of the $NH_2SO_3^-$ anion with the polymer (as is evident also from solubility and spectral studies).

3.3. *Dependence of rate of polymer formation on monomer concentration*

It has been observed that the anodic current of peak I corresponding to the growth of PAn films and therefore the amount of the polymer varies as a function of cycle number i.e., the reaction time (Fig. 4). The amount of polymer growth on the electrode surface was determined by calculating the charge under peak I [24] of Fig. 1a. This observation reveals that the rate of formation of polymer increases with increase in concentration of aniline. The slope of these curves at any point gives the rate of polymer formation [25] at the corresponding reaction time. Figure 5 gives the rate of polymer deposition obtained from the slope of Fig. 4 against the concentration of aniline at different anodic current values. These plots, being linear, imply that the rate of polymer formation is of first order with respect to aniline concentration.

3.4. *Cyclic voltammogram of polyaniline solution*

Figure 6 shows the cyclic voltammogram of the 0.8 g dm^{-3} of PAn solution in DMSO where two c.v. peaks are observed which are not sharp, but on the addition of sulphamic acid (curve b of Fig. 6) a well defined redox behaviour in the cyclic voltammogram is obtained.

3.5. *Cyclic voltammogram of PAn cast film from DMSO solution*

The PAn film obtained by evaporation (in vacuum) of PAn soluton in DMSO on a platinum electrode (0.25 cm^2) (the process being repeated twice) gave a cyclic voltammogram (curve c of Fig. 6) having peak potential values at +0.13 and +0.510 V (SCE). However, the middle peak, observed in the usual cyclic

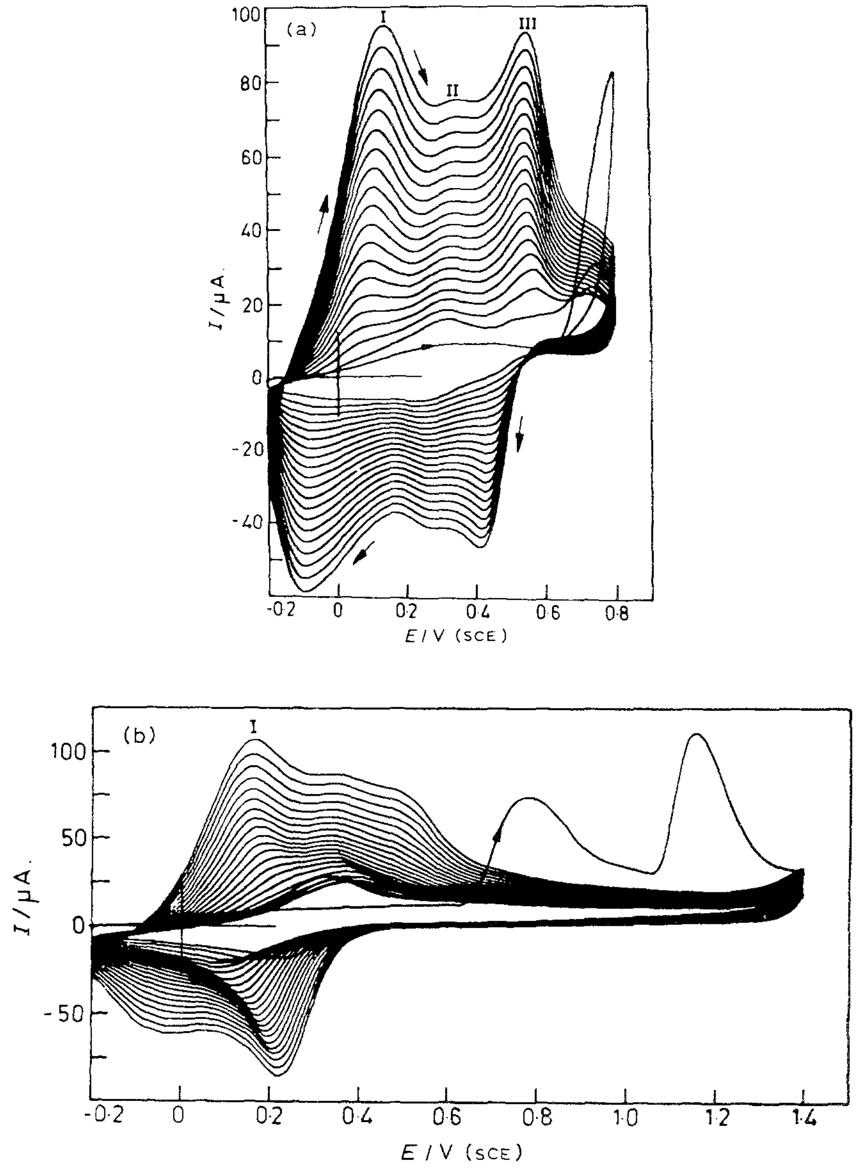


Fig. 2. Electrodeposition of polyaniline (1.0 M sulphuric acid + 0.1 M aniline) by potential sweeping between: (a) − 0.2 to + 0.8 V and (b) − 0.2 to 1.4 V on a platinum electrode (0.25 cm^2) against SCE at a scan rate of 50 mV s^{-1}.

voltammogram of PAn in SMA medium due to quinone/hydroquinone, was missing. This indicates that a DMSO solution cast polyaniline film is free from other impurities like quinone/hydroquinone.

3.6. *U.v.–visible spectra*

Figure 7 shows the diffuse reflectance spectra of electrochemically prepared PAn film on ITO (indium tin oxide) substrate in SMA medium. A dark green coloured film (thickness: ~ 1.0 μm) showed two absorption bands at 419 and 682 nm whereas the PAn film prepared in H_2SO_4 medium gives absorption bands at

Table 2. Redox potentials of polyaniline film

PAn deposited	$E_{p.ox}$/V(SCE)		
	1st peak	2nd peak	3rd peak
SMA medium	*+ 0.125*	*+ 0.400*	*+ 0.670*
H_2SO_4 medium	*+ 0.110*	*+ 0.370*	*+ 0.630*

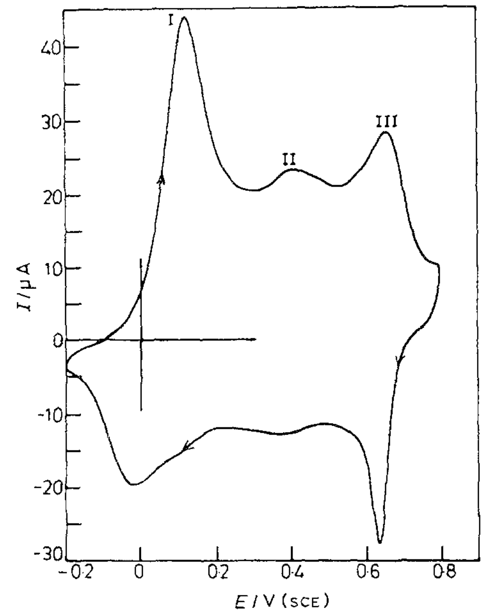


Fig. 3. Cyclic voltammogram of PAn in 1.0 M SMA at 50 mV s^{-1}.

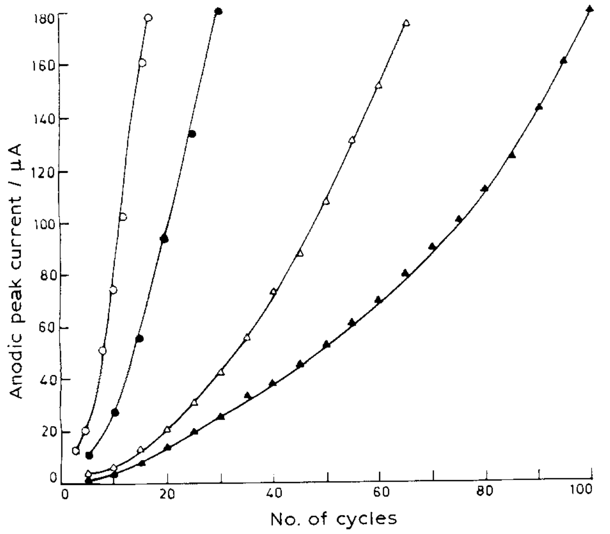


Fig. 4. Dependence of anodic peak current on cycle number at various aniline concentrations at a scan rate of $50 \mathrm{mV\,s^{-1}}$: (○) 0.3, (●) 0.2, (△) 0.1 and (▲) 0.05 M.

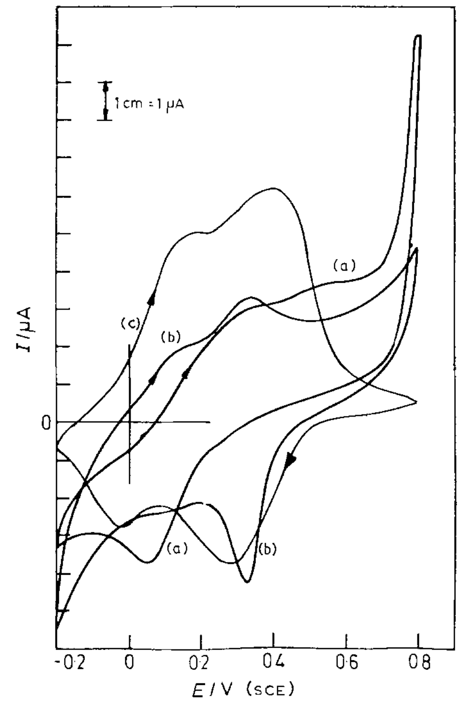


Fig. 6. Cyclic voltammogram of (a) PAn solution in DMSO ($0.8 \mathrm{g\,dm^{-3}}$) (b) 1 ml of 1.0 M SMA solution in the above solution and (c) PAn film on a platinum electrode ($0.25 \mathrm{cm^2}$) cast by evaporation of PAn-DMSO solution in 1.0 M SMA at a scan rate of $50 \mathrm{mV\,s^{-1}}$ against SCE.

320, 420 and 800 nm [26]. The neutralized blue colour PAn film prepared from H_2SO_4 medium gave a broad spectrum with $\lambda_{max} = 620$ nm. These observations indicate that in the present case there is a blue shift in the absorption spectrum compared to PAn prepared in the presence of H_2SO_4. This indicates a possible interaction of the dopant with the polymer to give new active sites for solubilization of the polymer with DMSO. The differences in elecronic spectra may also be attributed to fewer quinoneimine moieties in the polymer synthesized in the presence of SMA medium than the polymer prepared in sulphuric acid medium [27].

The electronic spectra of PAn solution in DMSO synthesized chemically and electrochemically are shown in curves c and d of Fig. 7. A DMSO solution of electrochemically synthesized polyaniline shows absorption bands at 303, 332, 447 and 639 nm whereas for the chemically prepared polymer the absorption bands are observed at 320, 440 and 618 nm. The reason for the higher wavelength maximum in the electrochemically prepared polyaniline in DMSO is due to long range order. This is also evident from its higher conductivity ($\sim 2 \mathrm{S\,cm^{-1}}$), whereas for the chemically synthesized polymer the conductivity is $0.2 \mathrm{S\,cm^{-1}}$ (Table 1). This type of behaviour has also been reported for poly-(para phenylene) [28]. The reason for not observing the absorption bands, characteristic of doped PAn, may be due to the fact that sulphamic acid in the presence of moisture may be hydrolysed to ammonium bisulphate. However, on addition of SMA solution to either of these solutions or to the DMSO

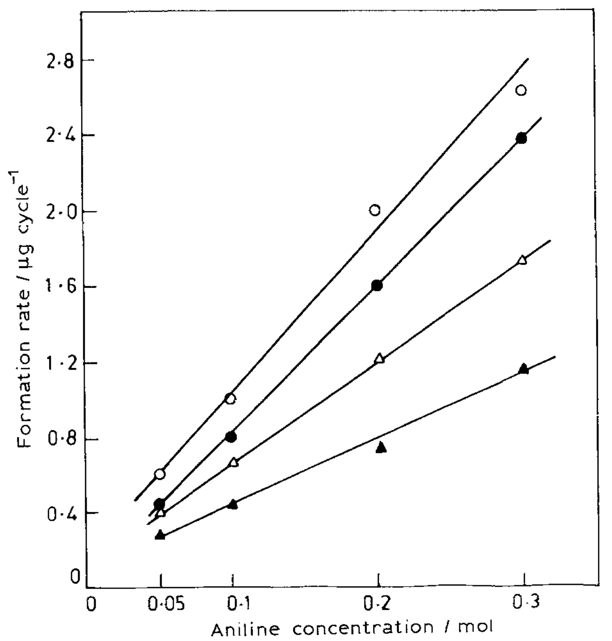


Fig. 5. Rate of polymer formation (values obtained as slope from Fig. 4) at various anodic peak current values against concentration of aniline (in 1.0 M SMA).

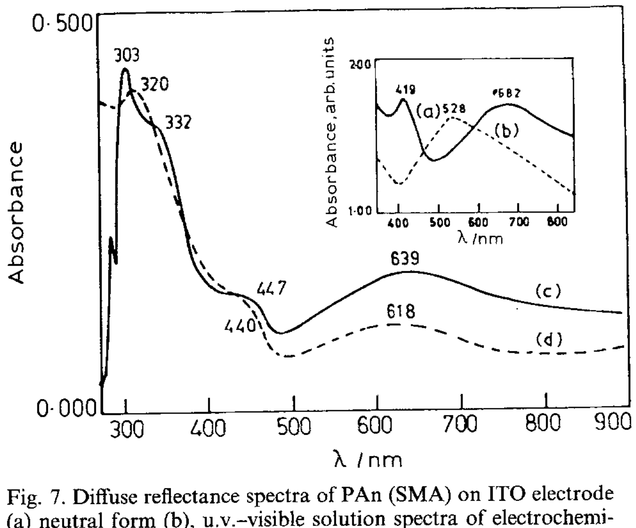


Fig. 7. Diffuse reflectance spectra of PAn (SMA) on ITO electrode (a) neutral form (b), u.v.-visible solution spectra of electrochemically prepared PAn-SMA solution in DMSO (c), Chemically prepared PAn-SMA solution in DMSO (d).

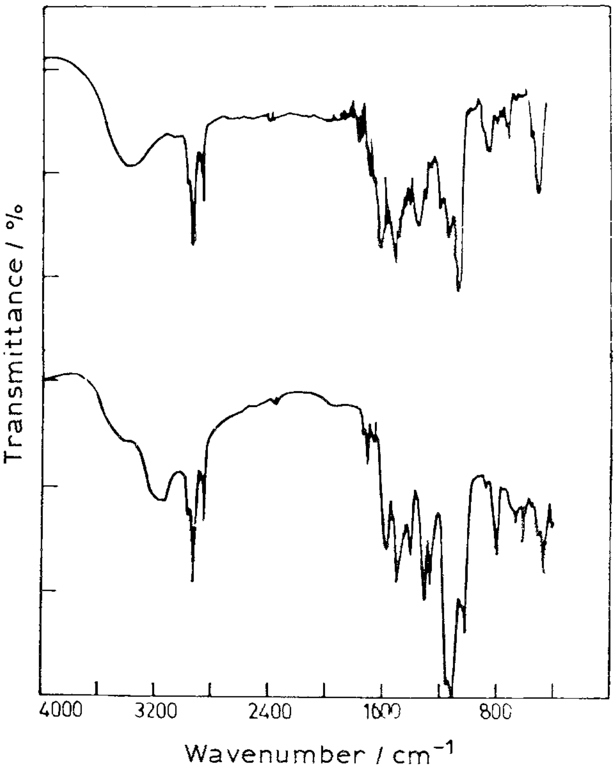


Fig. 8. FTIR spectra of polyaniline in KBr. Top curve: undoped PAn; bottom curve: doped PAn.

solution of compensated or undoped PAn (absorption bands observed at 320 and 600 nm), the absorption bands due to doped PAn are observed at 320, 427 (shoulder) and 840 nm.

3.7. *I.r. spectra*

Principal absorption bands observed in the FTIR spectra of PAn–SMA are given in Table 1. An almost identical spectrum was observed to that of usual PAn as synthesized in the presence of mineral acid. In the region 1650–1400 cm^{-1}, bands due to aromatic ring breathing, N–H deformation and C–N stretching are observed. The bands at 1571 and 1483 cm^{-1} are characteristic bands of nitrogen quinoid and benzenoid and are present due to the conducting state of the polymer. These bands show the blue shift from 1571 to 1603 cm^{-1} and from 1483 to 1501 cm^{-1} on removal of the dopant from the polymer (Fig. 8). These changes are indicative of the conversion of the benzenoid (B) ring to quinoid (φ) rings in the PAn matrix. The absorption band at 1140 cm^{-1} in PAn–sulphuric acid system is the characteristic band and is due to charge delocalization on the polymer [10] because in the undoped polymer the intensity of this band becomes very weak. In the present system too a very strong band at 1111 cm^{-1} and having a shoulder at 1144 cm^{-1} can be assigned due to the characteristic mode of B–NH–Q or B–NH–B [29]. The band at 1144 cm^{-1} in the doped sample can also be assigned due to –SO_3 stretching vibrations which is missing in the undoped sample. However, it was very difficult to assign bands for –SO_3 stretching vibrations in the present system as the involvement of the sulphamate anion in the polymer may give rise to complex bands which may have a cumulative effect on the other i.r. bands.

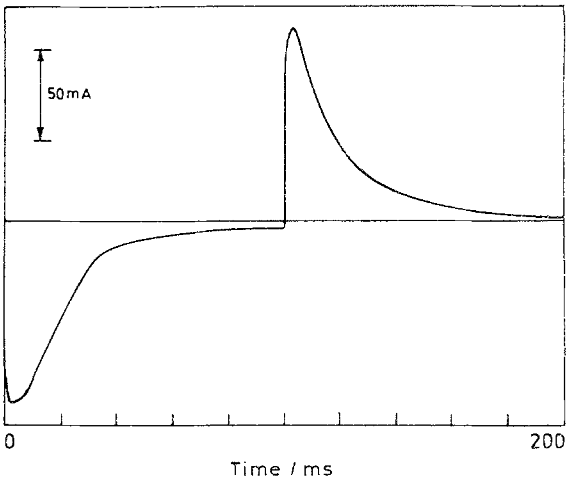


Fig. 9. Chronoamperometric curve for PAn film in 1.0 M SMA. Conditions: E/mV = −200 (init.) 800 (high) and −200 (low); pulse width/ms = 100; and SMPL INT/μs = 100.

3.8. *N.m.r. spectra*

The 1H-n.m.r. spectra of sulphamate anion doped polyaniline gave a signal at 8.2 p.p.m. due to aromatic protons. This signal is shifted to 7.0 p.p.m. on the removal of the dopant. This strong downfield shift indicates the interaction of dopant with the polymer matrix to yield active sites which are responsible for solubilizing of polymer in its doped state.

3.9. *Chronoamperometric studies*

PAn film in blank sulphamic acid medium exhibits a multiple colour change (pale yellow–green) on switching the potential from −0.2 to 0.8 V to −0.2 V (SCE). (Beyond 0.8 V (SCE) the film turns blue.) These changes correspond to the different oxidation states of PAn that appear upon varying the potential. Figure 9 shows the electrochromic response of a 1 μm thick PAn film. The response times are different for oxidizing (50 ms) and reducing (40 ms) steps which can be explained on the basis of different electrical conductivities of the two states. We have also observed that, on increasing the film thickness, the response time increases. The repetitive switching tests to estimate the cyclic life of the electrochromic nature indicates good stability, provided the upper limit does not exceed 0.6 V. At higher potential the oxidative degradation of the polymer occurs. After 3×10^6 cycles the electrochromic activity of the polymer diminishes drastically as has been observed by recording the cyclic voltammogram of the polymer modified electrode.

4. Conclusion

It has been shown that by judiciously manipulating the dopant it is possible to achieve solubilization of the protonic conducting form of polyaniline. It has also been observed that polyaniline synthesized in sulphamic acid medium is quite stable and does not deteriorate on cycling and may therefore find applications in electrochromic devices.

References

[1] E. M. Genies, A. A. Syed and C. Tsintavis, *Mol. Cryst. & Liq. Cryst.* (*GB*) **121** (1985) 181.

[2] A. G. MacDiarmid, S. L. Mu, N. L. D. Somasiri and W. Wu, *ibid.* **121** (1985) 187.

[3] A. Kitani, M. Kaya and K. A. Sasaki *J. Electrochem. Soc.* **133** (1986) 1069.

[4] F. Garnier, G. Tourillon, M. Gazand and J. E. Dubois *J. Electroanal. Chem.* **148** (1983) 299.

[5] T. Kobayashi, H. Yoneyama and M. Tamura, *ibid.* **161** (1984) 419.

[6] E. M. Genies and M. Lapkowski *Synth. Metals* **24** (1988) 67.

[7] E. M. Genies, M. Lapkowski, C. Santier and E. Viril, *ibid.* **18** (1987) 631.

[8] H. Letheby, *J. Chem. Soc.* **15** (1862) 161.

[9] A. G. Green and A. E. Woodhead, *ibid.* **97** (1910) 2388.

[10] A. G. MacDiarmid, J. C. Chiang, A. F. Richter and A. J. Epstein, *Synth. Metals* **18** (1987) 285.

[11] M. Angelopoulos, A. Ray, A. G. MacDiarmid and A. J. Epstein, *ibid.* **21** (1987) 21.

[12] Y. Cao and A. J. Heeger, *ibid.* **26** (1988) 303.

[13] S. K. Dhawan and D. C. Trivedi, *Polym. Intn.* **25** (1991) 55.

[14] S. K. Dhawan and D. C. Trivedi, *Bull. Electrochem.* **5** (1989) 208.

[15] S. Li, Y. Cao and Z. Xue, *Synth. Metals* **20** (1987) 141.

[16] C. B. Monk and M. F. Amira, *J. Chem. Soc. Faraday Trans.* **I** (1978) 1170.

[17] E. B. Bell, *in* Kirk-Othmer 'Encyclopedia of Chemical Technology', Vol. 21 (3rd), John Wiley and Sons, New York (1983) pp. 949–60.

[18] J. Courtet-Coupez and M. LeDemezet, *Bull. Soc. Chim. Fr.* (1969) 1033.

[19] E. M. Genies, M. Lapkoswki and J. F. Penneau, *J. Electroanal. Chem.* **249** (1988) 97.

[20] A. Kitani, M. Kaya, J. Yano, K. Yoshikawa and K. A. Sasaki, *Synth. Metals* **18** (1987) 341.

[21] S. H. Glarum and J. H. Marshall, *J. Electrochem. Soc.* **134** (1987) 2160.

[22] D. E. Stilwell and S. M. Park, *ibid.* **135** (1988) 2254.

[23] J. Joseph and D. C. Trivedi *Bull. Electrochem.* **4** (1988) 469.

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

[25] Yen Wei, Y. Sun and X. Tang, *ibid.* **93** (1989) 4878.

[26] Y. Cao, P. Smith and A. J. Heeger, *Synth. Metals* **32** (1989) 263.

[27] D. Vachon, R. O. Angus, F. L. Lu, M. Nowak, Z. X. Liu, H. Schaffer, F. Wudl and A. J. Heeger, *ibid.* **18** (1987) 297.

[28] D. C. Trivedi, *J. Chem. Soc. Chem. Comm.* (1989) 544.

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

[30] S. Stafstrom and B. Sjorgren, *ibid.* **16** (1986) 31.