Studies on biphenyl disulphonic acid doped polyanilines: Synthesis, characterization and electrochemistry

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Abstract. In this article, we report on the results obtained for the efforts we made to bring processability to the conducting polyaniline and substituted polyanilines by designing and synthesizing a new disulphonic acid with a biphenyl moiety as spacer group, viz. 4,4′-biphenyldisulphonic acid (BPSA). When doped, the disulphonic acid acts as a spacer group between the polyaniline chains and facilitates increase in solubility and conductivity. The spacing effect is maximized when BPSA is used as doping agent in *in situ* polymerization reactions. The conductivity of polyaniline doped by BPSA is 4 S/cm and for the substituted polyanilines it ranged from 2×10^{-5} to 8×10^{-4} S/cm.

1. Introduction

Conducting polymers (CPs) (Skotheim 1986) have attracted the scientific community ever since when polyacetylene was first synthesized by Shirakawa *et al* (1977). The advantage of most of these 'organic metals' is their thin film formation on various conducting substrates for construction of devices by simple electrochemical techniques. They are also attractive due to their reversible doping-dedoping (redox activity) process, tuning of conductivity levels and electrochromism. Particularly, attention has been given on polyaniline (PAni) due to its environmental stability, film forming property with tunable conductivity and commercial viability. Polyanilines have been studied extensively due to the fundamental interest in reaction mechanisms and for their applications to practical devices for energy storage, electrochemical sensors, electrochromic devices, EMI shielding, corrosion protection and others (Kobayashi *et al* 1984; DeBerry 1985; Kitani *et al* 1986; Genies *et al* 1988; Zhou *et al* 1990; Baxskai *et al* 1993; Chen *et al* 1996; Hugot-Le-Goff 1997; MacDiarmid 1997; Park 1997; Trivedi 1997; Malinauskas 1999; Wang and Jing 2005). Application of CPs in energy storage devices is well known (Conway 1999) and recent studies (Hughes *et al* 2002; Gupta and Miura 2005; Martha *et al* 2005; Peng *et al* 2006) in this area gave impetus to fundamental and applied research on CP-based new materials.

First known as 'aniline black' (Letheby 1862), the chronological developments in the history of conducting polyanilines research possess many milestones (Skotheim 1986;

Hugot-Le-Goff 1997; Park 1997; Trivedi 1997). Mineral acid doped PAni is not proccessable due to its metal like conductivity and hence foremost priority was given for achieving proccessability for the otherwise intractable conducting polyaniline. The technological significance for processing polyaniline into films and fibres (Menon *et al* 1993) arised mainly due to two strategies: (i) by synthesizing functionalized protonic acids, such as camphorsulfonic acid, dodecyl-benzene sulfonic acid, *para*-toluene sulfonic acid, benzene sulfonic acid, sulfanilic acid, sulfamic acid, octyl-benzene sulfonic acid, sulfosalicylic acid or methane sulfonic acid as dopants (Epstein *et al* 1987; Li *et al* 1987; Dhawan and Trivedi 1991, 1992; Kobayashi *et al* 1992; Trivedi and Dhawan 1993; Sanjai *et al* 1997) and (ii) the second strategy is to introduce substituent groups in the ring giving polymers such as alkyl polyanilines (Maccines and Funt 1988), alkoxy polyanilines (Gazotti and De Paoli 1996), sulfonic acid ring-substituted polyanilines (SPAN) (Yue *et al* 1991; Wei *et al* 1996). With respect to the parent polymer PAni, substituted polyanilines exhibit better solubility in common organic solvents and this facilitates their improved processability for various applications. However, the conductivity is lowered to a large extent due to decrease in conjugation length owing to changes in the planarity of the phenyl rings of the polymer chains owing to the substitutions.

Thus, it has been observed that the electronic, magnetic, optical and redox properties including processability of the polyanilines are greatly influenced by structure, electronegativity, solvation and orientation of the counter anion (Trivedi 1988, 1999). In the present communication, we report the synthesis of newly functionalized sulphonic acid

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used as dopant, viz. 4,4′-biphenyl disulphonic acid (BPSA), which acts as a spacer group between two PAni polymer chains when doped. It is hoped that the spacing of polymer chain would influence the solubility, processability and other properties of the doped polymer. The results on the synthesis, characterization, electrochemistry of the conducting polyaniline and its substituted derivatives doped by BPSA are presented and discussed.

2. Experimental

2.1 *Materials and methods*

All chemicals used were of analytical (CDH Chemicals, India) grade and used as received. Polyaniline, as emeraldine base, was synthesized and purified as per the literature procedure (Trivedi 1997). SEM measurements were performed on a Hitachi-3000H microscope. X-ray diffraction patterns (XRD) were obtained with PANalytical MPD diffractometer using Cu K_α radiation. FT–IR spectra of KBr powder-pressed pellets were recorded on a model no. Paragon-500 from Perkin-Elmer spectrometer. Cyclic voltammetry was performed on a AUTOLAB 302 electrochemical system using three-electrode assembly consisting of a platinum foil (2×2.5 mm) working electrode, a platinum wire auxiliary electrode and SCE as reference electrode. Conductivity of the samples were measured by four-probe method using KEITHLEY nanovoltmeter after pressing the samples into 1 cm dia, 1·5 mm thick pellets under 3 ton pressure. TGA experiments were performed with TA instruments Inc., on model SDT Q600 by heating under air at 20°C per min. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer (model no. AVance 400 digital).

2.2 *Synthesis of 4,4′-biphenyldisulphonic acid [BPSA]*

Concentrated sulphuric acid (35 ml, 98%) was added to biphenyl (3·5 g, 0·0227 mol) in a 50 ml conical flask and slowly heated to 90 °C for 4 h with stirring. The reaction mixture was cooled to room temperature first and further cooled in an ice-water mixture for 3–4 h. The crystallized 4,4′-biphenyldisulphonic acid (BPSA) was filtered through sintered crucible using vacuum. Analytically pure samples were obtained from the crude after several washings with hexane and chloroform. As the acid was highly hygroscopic, formation and purity of disulphonic acid was checked by recording C,H,N,S elemental analysis for the disodium salt of the acid. ^{1}H NMR of the acid BPSA gave (DMSO-d_6, δ, ppm) a quartet 7·707, 7·687, 7·662 and 7·641 for biphenyl protons (4H) and a broad signal centred at 7 for sulphonic acid protons. The ^{13}C spectrum of this symmetric molecule showed four signals; a doublet carbon signal at 126·62, 126·83 and two singlets at 140·49 and 146·84 ppm. The corresponding elemental analysis obtained for disodium salt was C:40·09%, H:2·15%, S:17·84% as against the calculated

values of C:40·22%, H:2·23%, S:17·87% with a molecular formula of $C_{12}H_{10}S_2O_6Na_2$.

2.3 *Synthesis of substituted polyanilines*

Poly(N-methylaniline), poly(2-methylaniline) and poly(2-methoxyaniline) were synthesized by adopting a general procedure and the procedure for poly(N-methylaniline) is as follows: To an aqueous 1M HCl solution(150 ml) of N-methylaniline(20 g, 0·186 mol) maintained at 5°C, was added ammonium persulphate (APS) (42 g, 0·186 mol) dissolved in 1M HCl (100 ml) drop wise within 20–30 min. The contents were stirred for 4–6 h and the resulting precipitates were filtered and dried at 60–80°C. The de-doping of the polymers was performed by stirring the conducting polymers in diluted NH$_4$OH solution maintained at pH 9 for 4 h. Further, the emeraldine base forms (EB) of the polymers were purified by refluxing in copious amounts of methanol followed by benzene for 4 h and filtering. As one of the methods, conducting polyanilines were obtained by thorough mixing of powdered EBs with BPSA (1:0·5 mole ratios) in a mortar.
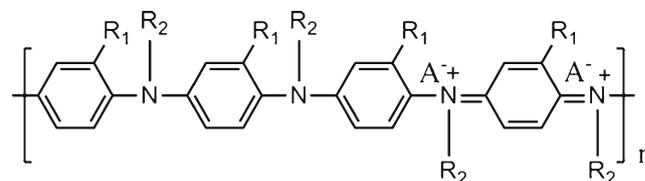
Polymer	R_1	R_2	A^-
P(A)-BPSA	H	H	BPSA
P(NMeA)-BPSA	H	Me	BPSA
P(2-MeA)-BPSA	Me	H	BPSA
P(2-OMeA)-BPSA	OMe	H	BPSA

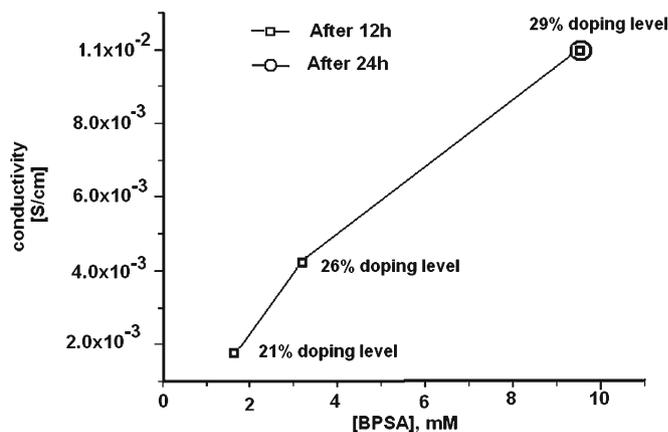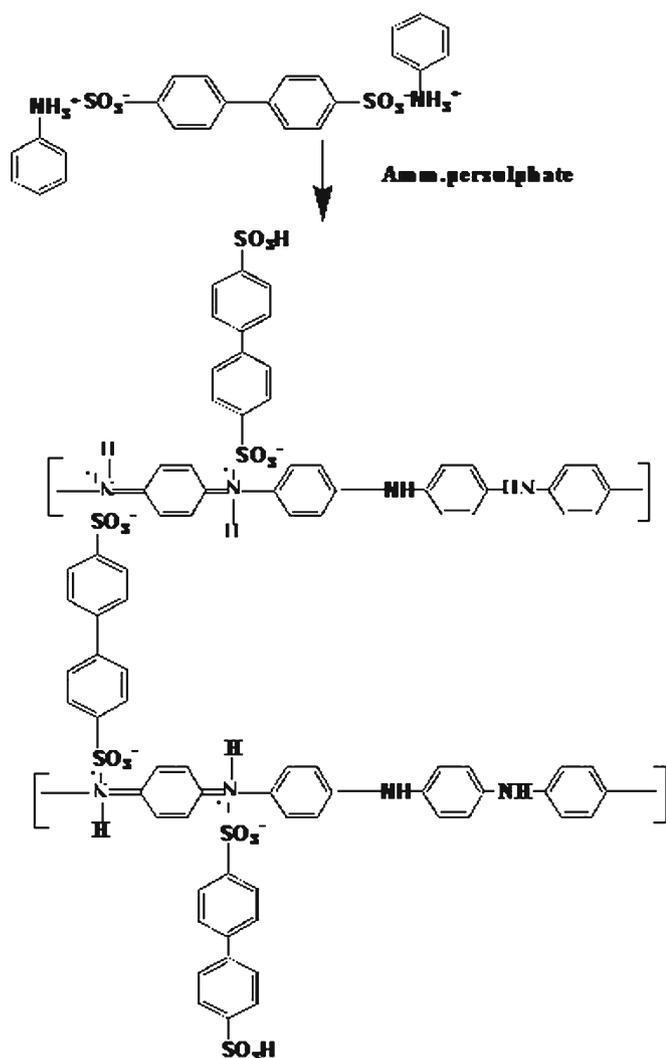**Figure 1.** Structures of synthesized conducting polyanilines.

Figure 2. Conductivity of polyaniline doped by BPSA at different concentrations in water.

3. Results and discussion

3.1 *Synthesis of disulphonic acid and polyanilines*

Disulphonic acid (BPSA) containing biphenyl as spacer group, is obtained in a straightforward reaction in about 70–80% yield by sulphonation of biphenyl in excess sulphuric acid as described in the experimental section. The purity and formation of diacid are confirmed by NMR and elemental analysis.

Figure 1 shows structure of the conducting polyanilines prepared from aniline, *N*-methylaniline, 2-methylaniline and 2-methoxyaniline in this study. They are abbreviated as P(A)–BPSA, P(NMeA)–BPSA, P(2-MeA)–BPSA and P(2-OMeA)–BPSA, respectively. Among the substituted polyanilines, P(NMeA) is most studied in literature because (i) to know more about reaction mechanism of polymerization and (ii) it is expected to be different from the parent polyaniline. This is partly because the proton exchange sites on nitrogen are blocked by the methyl group and only one proton available for removal in the course of the polymerization reaction. As a result, the deprotonation of the imine group occurring during the second oxidation step of PANI is not likely to occur in P(NMeA). In other words, P(NMeA) can be prevented from going to the pernigraniline state by which the degradation by hydrolysis during the electrochemical oxidation (Barbero *et al* 1991; Yano *et al* 1994) can be greatly reduced.

BPSA doped polyanilines are obtained in two different methods. The first method consists of including BPSA in the feed of aniline polymerization reaction. In this case, *in situ* doping of BPSA into the polymer occurs. The second method consists of preparation of emeraldine base using a conventional mineral acid and an oxidizing agent such as HCl and APS, followed by solid state doping of BPSA by thorough mixing in a mortar or water. The two types of polymers exhibited few differences in their properties, particularly in conductivity. The conductivity of the *in situ* doped sample is found to be higher than the sample obtained by doping with pre-formed EB with BPSA in water. The conductivity increases with increase in the concentration of BPSA (figure 2); it reached a maximum value of 1×10^{-2} S/cm in 12 h at a doping level of 29%. Increase of concentration of BPSA or doping time did not influence the conductivity of the sample. The low value of conductivity has aroused because, the P(A)–EB is not soluble in water and hence the big molecule BPSA is not able reach the active sites, i.e. imine nitrogens (=N–) in the closely packed emeraldine base (EB) polymer chain. For the same reason, the second sulphonic acid functionality in BPSA may not participate in doping reaction.

Scheme 1. Schematic representation of spacing effect by BPSA doping for P(A)–BPSA polymer.

Table 1. Conductivity and XRD data of various polyanilines doped by BPSA.

Polymer	Conductivity (S/cm) (EB doped)	Conductivity (S/cm) (as prepared)	XRD peaks (2θ)
P(A)–BPSA[a]	1×10^{-2}	4·0	18·17, 25·12
P(N-MeA)–BPSA[b]	8×10^{-5}	2×10^{-5}	18·34, 23·33
P(2-MeA)–BPSA[b]	$4·4 \times 10^{-3}$	$7·9 \times 10^{-4}$	14·94, 18·81, 25·01
P(2-OMeA)–BPSA[b]	$1·1 \times 10^{-2}$	$1·2 \times 10^{-4}$	13·52, 15·14, 24·8, 25·6

[a] Doping is carried out by mixing solids in water up to 24 h; [b] doping is carried out by mixing solids in a mortar with a pestle for about 0·5 h

Table 2. FT–IR and UV-Vis spectral data of polyanilines.

Polymer	FT–IR (KBr pellet)							UV–Vis (DMF)nm
	$C-H_{op}$	$R-SO_3^-$	$C-N$	$N-B-N$	$N=Q=N$	$C-H_{(arom)}$	$N-H$	
P(A)–BPSA	823	1047	1235	1460	1135, 1637	2930	3466	378, 550, 984
P(N-MeA)–BPSA	821	1047	1236	–	1140, 1618	2920	–	428, 572, 1096
P(2-MeA)–BPSA	816	1047	1240	1460	1136, 1637	2933	3414	441, 549, 1090
P(2-OMeA)–BPSA	819	1056	1236	1450	1135, 1637	2930	3471	446, 549, 1144

The above situation does not arise in the case of *in situ* doping where it is believed that the doping by two sulphonic acid groups would take place almost instantly as the polymer chains are not closely packed in the solution. The situation is schematically shown scheme 1. First, one sulphonic acid group from two BPSA molecules involves in the doping process at the active site of the polyaniline chain. Because the BPSA acts as a rigid rod, when its second sulphonic acid group involves in doping process, the second polyaniline chain would be kept at a distance (of the length of biphenyl molecule). It means to say that BPSA would act as a spacer between two conducting polyaniline chains. This would result in less coiling (or more straightening) of the polymer, higher conductivity and higher solubility. This is indeed observed. The conductivity of P(A)–BPSA is 4 S/cm which is found to be higher than the structural analogue of BPSA, which cannot offer spacer effect, i.e. benzenesulphonic acid(BSA) doped polyaniline P(A)–BSA (2 S/cm) (Trivedi and Dhawan 1993). The polymer P(A)–BPSA is soluble in DMF, DMSO and *m*-cresol/chloroform systems which suggests increased processability. The BPSA doped substituted polymers are also more processable. Upon contact with BPSA, EB form of substituted polymers became doped and formed dark brown/black rubbery and sticky materials which can be drawn as thin films on glass slides. These films, including P(A)–BPSA, are moisture sensitive and should be stored in desiccators.

The conductivity exhibited by the polymers is shown in table 1. It is clear that the conductivity of substituted polyanilines obtained by physically mixing of EBs and BPSA (1:0·5 mM) in solid forms showed higher conductivity than samples made by *in situ* polymerization method. This may be ascribed to lower level of doping due to losses of BPSA (as it may decompose to biphenyl for prolonged exposure to water and highly oxidizing conditions) in latter method compared to former method where all the BPSA is effectively used. The NMR spectra of these conducting substituted polyanilines (obtained by solid state mixing) showed high intense signals due to BPSA alone, suppressing the EB signals. This suggests that part of BPSA is not used for doping.

The data on the main bands observed in the FT–IR spectra of PAni–BPSA and substituted PAni–BPSA recorded in the region of 4000–400 cm^{-1} are given in table 2 with their possible assignments. The bands at 1023–1056 cm^{-1} are assigned to the symmetric –SO$_3^-$ stretching, and are the characteristic bands of a sulphonate group, present in the dopant
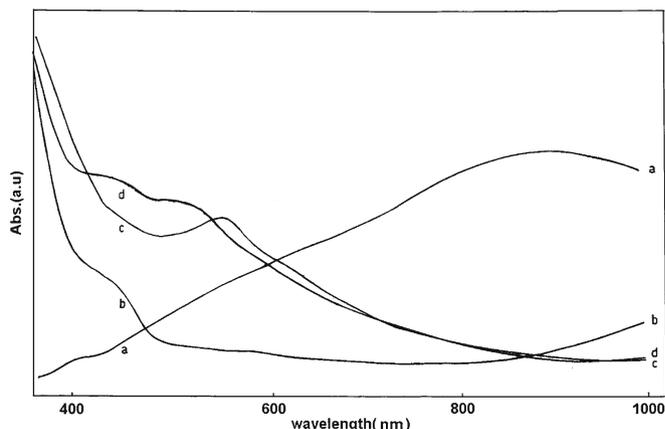
Figure 3. UV-Vis spectra of conducting polyanilines in DMF/DMSO solvent. (**a**) P(A)–BPSA, (**b**) P(N-MeA)–BPSA, (**c**) P(2-MeA)–BPSA and (**d**) P(2-OMeA)–BPSA.

BPSA. The band at 783–824 cm^{-1} indicates that there is a head to tail coupling in polymer and is assigned to C–H$_{op}$. The band at 1140 cm^{-1} shown by all the polyaniline samples is due to charge delocalization on the polymer backbone; the intensity of this band is significantly lowered in the de-doped EB spectra due to removal of charges. Bands due to aromatic ring breathing mode are observed in the region 1637–1400 cm^{-1}. Band at 1480 cm^{-1} is the characteristic band assigned to N–B–N and the band at 1632 cm^{-1} is due to nitrogen quinoid (N=Q=N). The C–N stretching is observed between 1235 cm^{-1} (Epstein and MacDiarmid 1988; Furukawa *et al* 1988; Sariciftci *et al* 1990; Trivedi 1997). The N–H band is observed as a broad band centred at 3467 cm^{-1} and is absent for P(*N*-MeA)–BPSA. The aromatic C–H stretching is observed around 2930 cm^{-1}. Overall, FT–IR studies confirm the formation of polyanilines in their conducting form.

3.2 *Electronic and NMR spectral analysis*

The polymers are characterized by UV-Vis electronic spectroscopy by recording their absorption bands in DMF/or DMSO solvent and the data is shown in table 2. The spectra are shown in figure 3. P(A)–BPSA showed bands at 378 nm, 550 nm and 984 nm (figure 3a). In the IR region, it showed one main band at 1432 nm. The absorption peaks
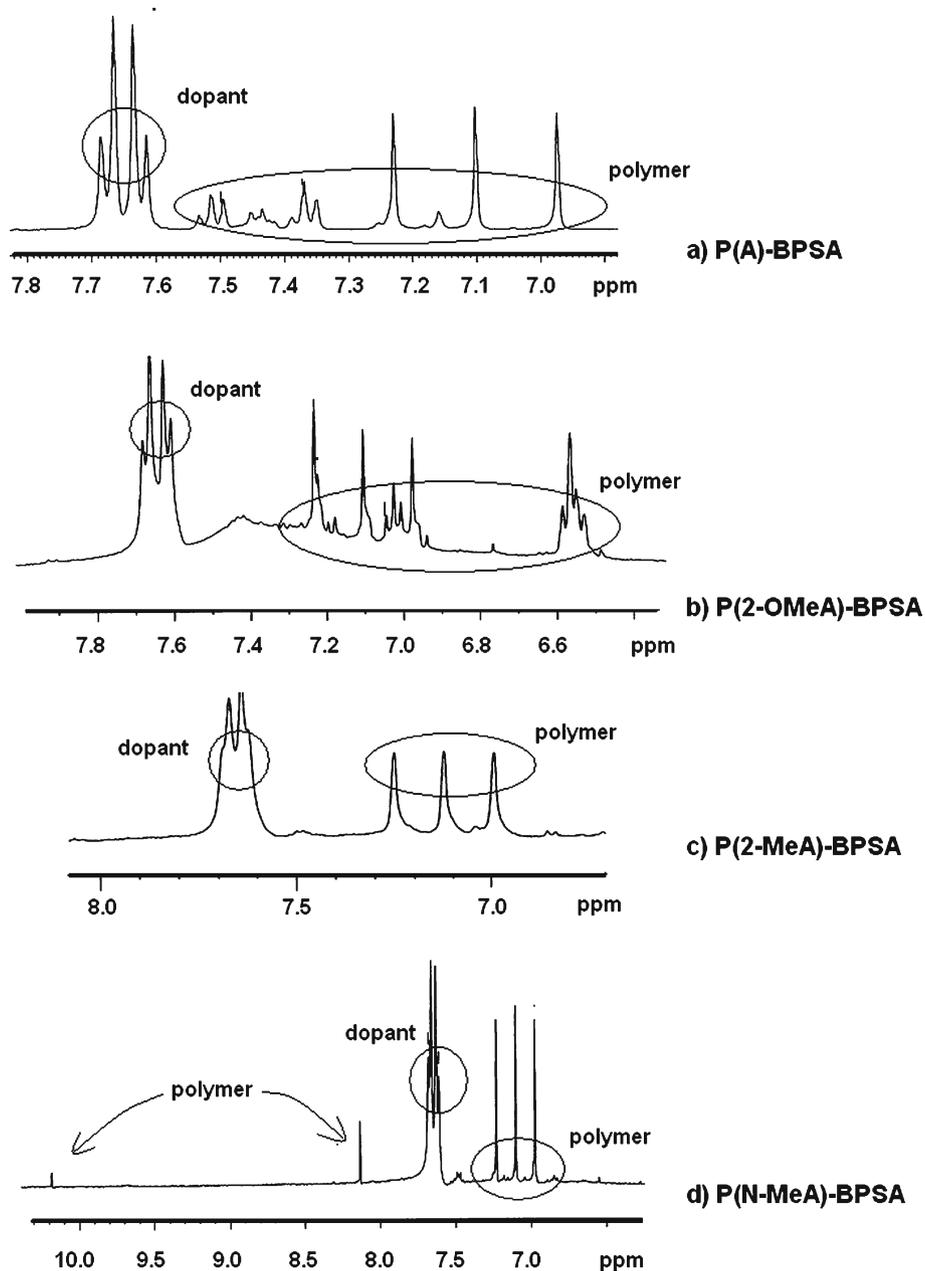
Figure 4. ^{1}H NMR spectra of conducting polyanilines in d_6-DMSO solvent.

observed at 378 nm is assigned due to Π–Π* transition associated with benzenoid ring. The band due to cation radicals is seen at 550 nm. The band observed at higher wavelength, i.e. 980 nm, is due to charge carriers. The tail of this band extended to infrared region (1432 nm) indicating that charge carriers are bipolarans. The UV-Vis bands for P(NMeA)–BPSA are seen at 428 nm, 572 nm and 1096 nm. The band at 572 nm is due to n–Π* (Falcou *et al* 2005). The band at 1096 nm is due to bipolaron charge carriers and existence of this band together with the band at 428 nm, suggests that the polymer is in pernigraniline oxidation state (Blomquist *et al* 2006). For P(2-MeA)–BPSA and P(2-OMeA)–BPSA, the spectra showed bands at 441 nm, 549 nm, 1090 nm

and 446 nm, 549 nm, 1144 nm, respectively and a similar explanation for P(NMeA)–BPSA can be given.

Figure 4(a) shows ^{1}H NMR spectrum of polymer P(A)–BPSA. The three individual singlets having equal intensities at δ 6·97, 7·106 and 7·23 are originating from free radical NH proton; because of the presence of ^{14}N with unit spin, the signal of the proton is split into three lines. This type of splitting is not detected in the NH proton of polyaniline–EB, in which only a single broad peak at 7·39 attributed to NH was observed, similar to an observation known in literature (Zhang *et al* 2007). A quartet, with an intensity ratio of 1:2:2:1 is observed at δ 7·62 and is attributed to the dopant BPSA protons. Figure 4(b–d) shows condensed ^{1}H NMR

Table 3. Electrochemical data (V vs SCE) of polymers.

Polymer	First cycle (Radical cation formation)	Second cycle		Characterization cycle	
		Oxidation peaks	Reduction peaks	Oxidation peaks	Reduction peaks
P(A)–BPSA	1·0	0·210, 0·495, 0·766	0·105, 0·454, 0·629	0·213, 0·487, 0·766	0·147, 0·410, 0·721
P(N-MeA)–BPSA	0·903	0·466, 0·603	0·521, 0·421	0·379	0·308
P(2-MeA)–BPSA	1·02	0·416	0·337	0·237, 0·450	0·198, 0·542
P(2-OMeA)–BPSA	0·873	0·383	0·315	0·363	0·305
P(A)–SA[a]	–	–	–	0·090, 0·360, 0·625	–
P(A)–BSA[b]	–	–	–	0·100, 0·400, 0·700	–

SA: sulphuric acid: BSA: benzene sulphonic acid; [a] Trivedi *et al* (1993) and [b] Dhawan *et al* (1994).
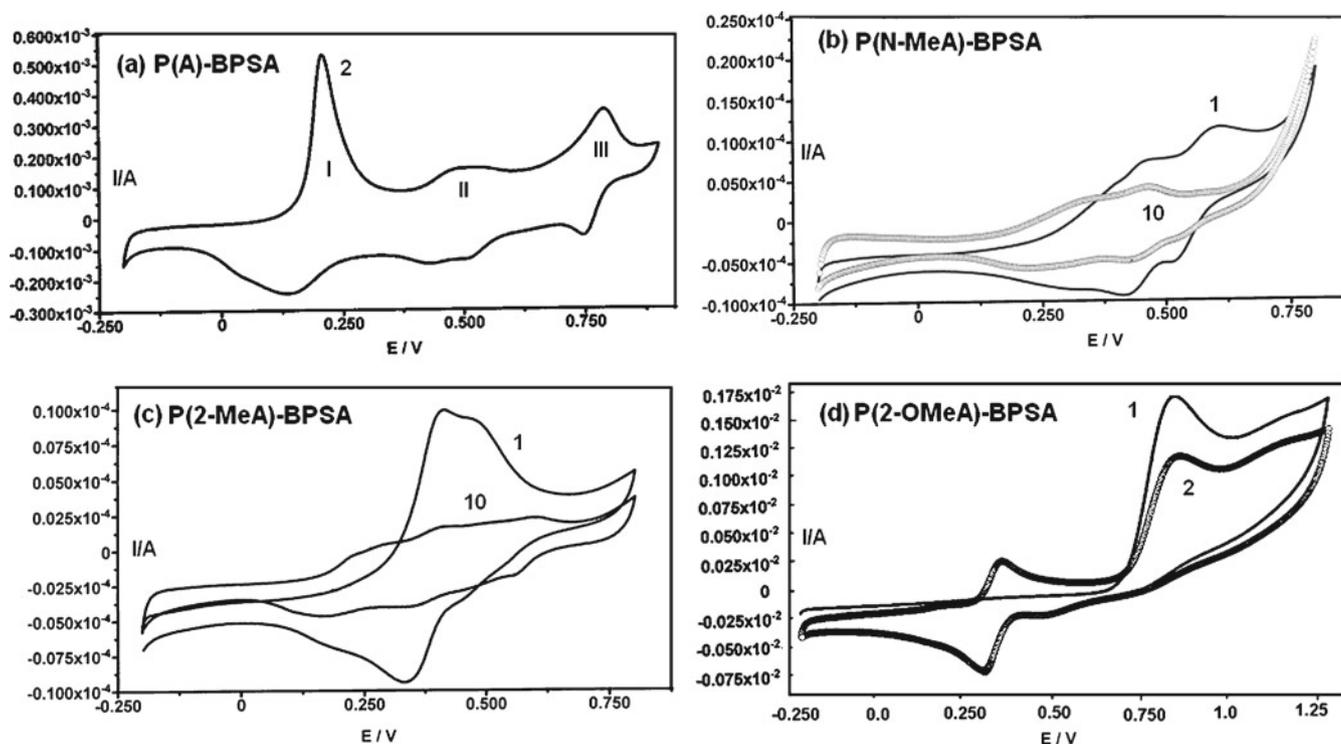
Figure 5. Cyclic voltammograms (with cycle numbers) of polyanilines at a scan rate of 50 mV/s.

spectra of the P(2-OMeA), P(2-MeA) and P(N-MeA) polymers made by *in situ* doping method. All samples showed a triplet at 2·5 due to DMSO(*d*6) solvent and a quartet due to dopant. All substituted polymers showed intense peak due to methyl protons around 3·5 which is also coupled with moisture peaks in the polymer/solvent. Similar to P(A) system, three well separated singlets due to ^{14}N–H splittings are also seen for substituted polymers.

3.3 *Electrochemical studies*

The electrochemical polymerization behaviour of the monomers, viz. aniline, *N*-methylaniline, 2-methylaniline and 2-methoxyaniline, is investigated by using cyclic voltammetry technique. The electrochemical data has been shown

in table 3. Figure 5 shows cyclic voltammogram of aniline monomer polymerization in 0·5 M BPSA solution obtained when the potential is cycled between –0·2 and 1 V at a scan rate of 50 mV/s. The radical cation formation took place at 1 V (vs SCE). From the second cycle onwards, three oxidation peaks at 0·210, 0·495, 0·766 V in forward scan and three reduction peaks at 0·629 V, 0·454 V, 0·105 V in reverse scan are observed. The formation of radical cations is seen as first peak which on further coupling, is seen as third peak. The peak current increases continuously with successive potential scans, suggesting the build up of electroactive P(A)–BPSA on the electrode surface. In monomer free BPSA electrolyte, the film exhibited oxidation peaks at 0·213, 0·487, 0·766 and reduction peaks at 0·721 V, 0·410 V, 0·147 V. The formation of radical cations at peak I, are subsequently oxidized into imines at peak III. The peak II is essentially due to adsorption

of quinone/hydroquinone, generated during the growth of the polymer film due to degradation of radical cations, which gets strongly adsorbed in the polymer matrix. It is found that the potentials of radical cation formation (polarons) (peak I) and their transformation into bipolarons (peak III) for the P(A)–BPSA system are shifted to more positive values compared to polyaniline–sulphuric acid (Trivedi and Dhawan 1993) (0·090 V, 0·360 V, 0·625 V, table 3) and polyaniline–benzenesulphonic acid (Dhawan and Trivedi 1991) system (0·100 V, 0·400 V, 0·700 V, table 3). It suggests that cation formation and their transformation is energetically more demanding when the size (bulkiness) of the counter ions increases (from sulphate to benzene sulphonate to biphenyldisulphonate).
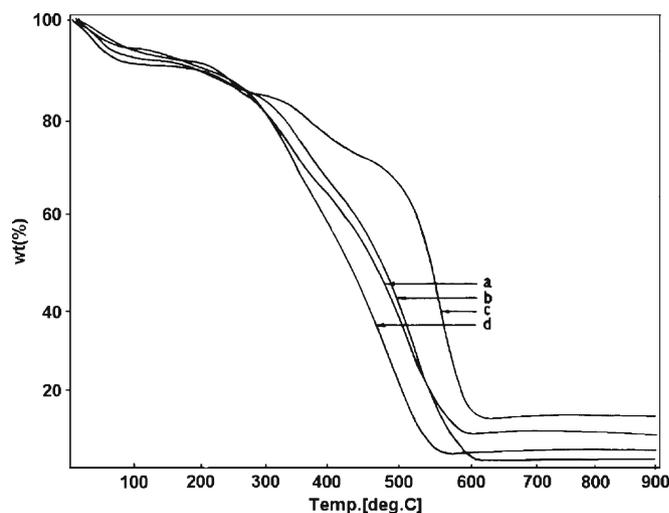
The cyclic voltammogram exhibited during the growth of *N*-methylaniline is shown in figure 5(b). Several authors described synthesis, morphology and electrochemical behaviour of P(N-MeA) in various electrolytes (Sivakumar and Saraswathi 2003, 2004; Yano *et al* 2003; Blomquist *et al* 2006; Wei *et al* 2006). It is observed that redox chemistry is highly dependent on the electrolytes used. For example,
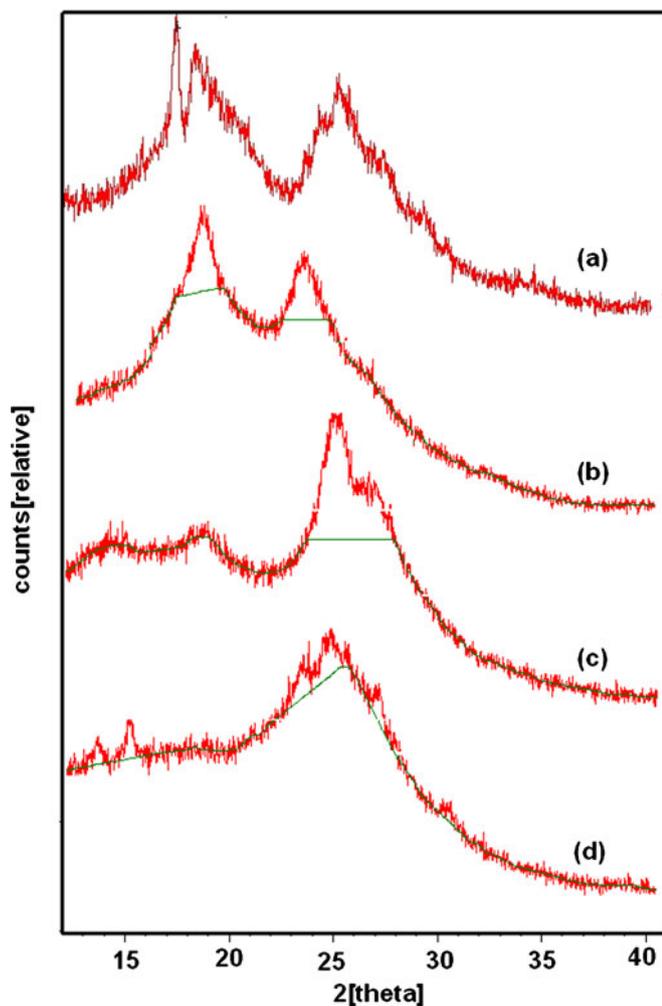
only one clear anodic peak at 0·39 V and a diffusion limiting region at 0·85 V are observed for polymerization of *N*-methylaniline (Sivakumar and Saraswathi 2003) in sulphuric acid. In the present study, the radical cation is formed at 0·903 V in the first cycle. From second scan onwards two anodic peaks at 0·466 V, 0·603 V in the forward scan and two cathodic peaks at 0·521 V, 0·421 V in the reverse scan are observed. When the number of scans is increased (say 10), the two anodic and two cathodic peaks coalesce to a single anodic and a cathodic peak at 0·466 V and 0·424 V with decreased intensity suggesting that impure oligomeric species are dissolved during these scans. These values are slightly shifted positively, compared to the films generated in sulphuric acid (Sivakumar and Saraswathi 2003), owing to the bulky nature of the ingressed biphenyl sulphonate ions. The pure film in BPSA solution (characterization curve) exhibited one broad peak each in forward (centred at 0·339 V) and reverse (centred 0·250 V) scans at 50 mV/s. These two potentials are slightly shifted to 0·340 V and 0·305 V, respectively with increased scan rate (100, 250, 200 mV/s).

Figure 5(c,d) shows cyclic voltammograms obtained during the synthesis and characterization of P(2-MeA)–BPSA and P(2-OMeA)–BPSA electroactive polymers. In electropolymerization of 2-Me-aniline, the radical cation forms at 1·02 V in the first scan and a redox couple observed at 0·416 V and 0·337 V in the subsequent scans. The dissolution of the formed oligomeric polymeric species is observed for several scans and is also evident from the decrease in current values. The potential was also found to drift with increasing number of scans. After 10 scans (from –0·2 V to 0·8 V), the voltammogram showed three anodic peaks at 0·225 V, 0·403 V, 0·6 V and three cathodic peaks at 0·132 V, 0·353 V, 0·566 V. The same film in BPSA solution (without monomer) exhibited only two anodic peaks at 0·237 V, 0·450 V and two cathodic peaks at 0·542 V, 0·198 V.


Figure 6. XRD spectrum of (**a**) P(A)–BPSA, (**b**) P(N-MeA)–BPSA, (**c**) P(2-MeA)–BPSA and (**d**) P(2-OMeA)–BPSA.

Figure 7. TGA curves for (**a**) P(A)–BPSA, (**b**) P(N-MeA)–BPSA, (**c**) P(2-MeA)–BPSA and (**d**) P(2-OMeA)–BPSA.

The electrochemical polymerization of 2-methoxyaniline to yield P(2-OMeA)–BPSA exhibited a anilinium cation formation at 0·873 V and one anodic and one cathodic peak at 0·383 V and 0·315 V during first and second cycle onwards in their CV pattern (figure 5). The pure film in BPSA solution showed a redox couple at 0·363 and 0·305 V. Overall, the electrochemical studies showed that stable P(A), P(N-MeA), P(2-MeA) and P(2-OMeA) polymers doped by BPSA can be electrochemically generated on the platinum electrode.

3.4 *XRD, thermal, SEM and AFM studies*

The XRD profiles of the polymers are shown in figure 6 and the data is shown in table 1. Overall, all the four polymers showed main 2 to 4 peaks between $2\Phi = 10$–40 which are broad suggesting amorphous nature of the polymers (Trivedi 1997). It is interesting to note that the position of the peaks for $P(A)$ is comparable with P(N–Me) and that for P(2-MeA) is with P(2-OMeA). The peak at
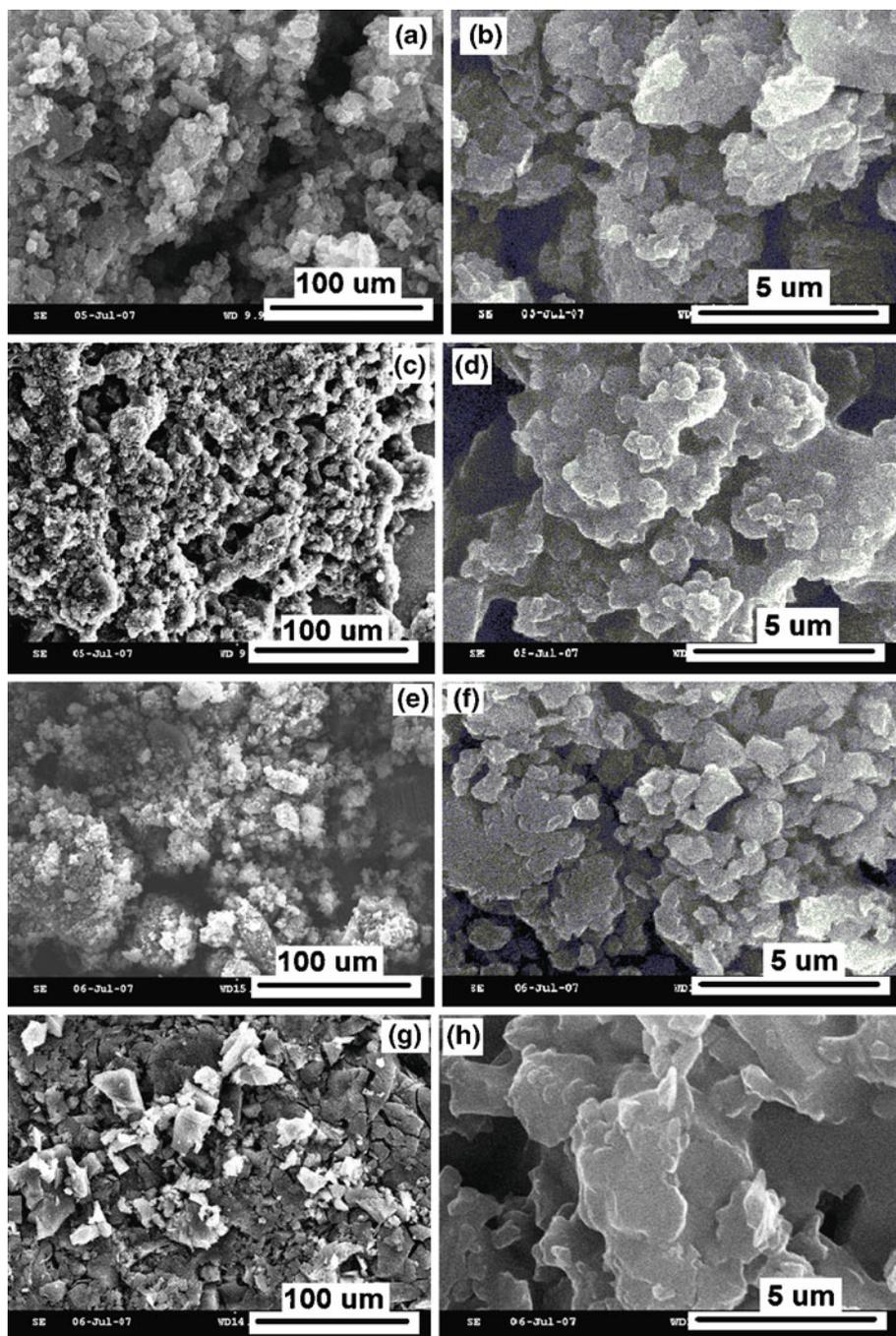
Figure 8. SEM pictures of chemically prepared polymers at different magnifications: (**a**, **b**): P(A)–BPSA; (**c**, **d**): P(N-MeA)–BPSA; (**e**, **f**): P(2-MeA)–BPSA and (**g**, **h**): P(2-OMeA)–BPSA.

$2\theta = 9.58(d \sim 9.302$ Å) which is generally observable (Pouget *et al* 1994; Abdiryim *et al* 2007) for conducting polyaniline is not observed in the present case due to the technical limitation of the diffractometer, can be considered as the distance between two stacks in the 2D stacking arrangement of polymer chains with intervening dopant ions between stacks (Pouget *et al* 1994). The peak centred at $2\theta = 18.92$ may be ascribed to periodicity parallel to the polymer chain, while the peaks at $2\theta = 25.12$ may be caused by the periodicity perpendicular to the polymer chain (Moon *et al* 1989). This peak also represents the characteristic distance between the ring planes of benzene rings in adjacent chains or the close-contact interchain distance (Pouget *et al* 1995).

Thermal analysis of the samples (figure 7) shows that the polymers are stable up to 250–300°C in doped state. The trapped moisture loss for the polymers occurs at 91°C, 92°C, 96°C, 94.4°C, respectively. In general, the dopant expulsion/decomposition starts above 300°C for the polymers and continues up to 600–650°C, recording total weight losses of about 90–95% which includes about 30–40 % loss as dopant.

The surface morphology of these conducting polymers prepared by both chemical and electrochemical polymerization methods have been investigated by scanning electron microscope (SEM) and atomic force microscope (AFM),

respectively. Figure 8 shows surface morphology of the four conducting polymers synthesized chemically using BPSA as acid medium as seen by SEM at ×2000 (100 μm scale bar) and ×10 K (5 μm scale bar) magnification. P(A) and P(NMeA) shows similar structural morphology with porous and sponge like appearance. The polymers P(2-MeA) and P(2-OMeA) showed slightly crystalline appearance which appear to be less porous. Among all the polymers, less soluble P(A) is composed of small particles (figures 8a,b). The more soluble polymers P(NMeA), P(2-MeA) and P(2-OMeA) are less porous as the particles are glued to one another to give lump type structures (figures 8d,h).

Figure 9 shows surface morphology of thin films of polymers synthesized electrochemically on Pt foils obtained after ten scans. The cross-section analysis (not shown in the figure) of the AFMs showed that the thickness of the films are ~150 nm, 100 nm, 180 nm and 100 nm, respectively for P(A)–BPSA, P(N-MeA), P(2-MeA) and P(2-OMeA). All the polymers formed almost smooth surface except for few wrinkles formed mostly due to the rough surface of the Pt foil. The topography of the films showed that the surface is rough with up-downs (about 50 nm). The surface of P(N-MeA) film consisted of small and also overgrown, closely packed islands of about 200×500 nm which made the surface rough. The surface of the film, P(2-MeA), mostly consists of
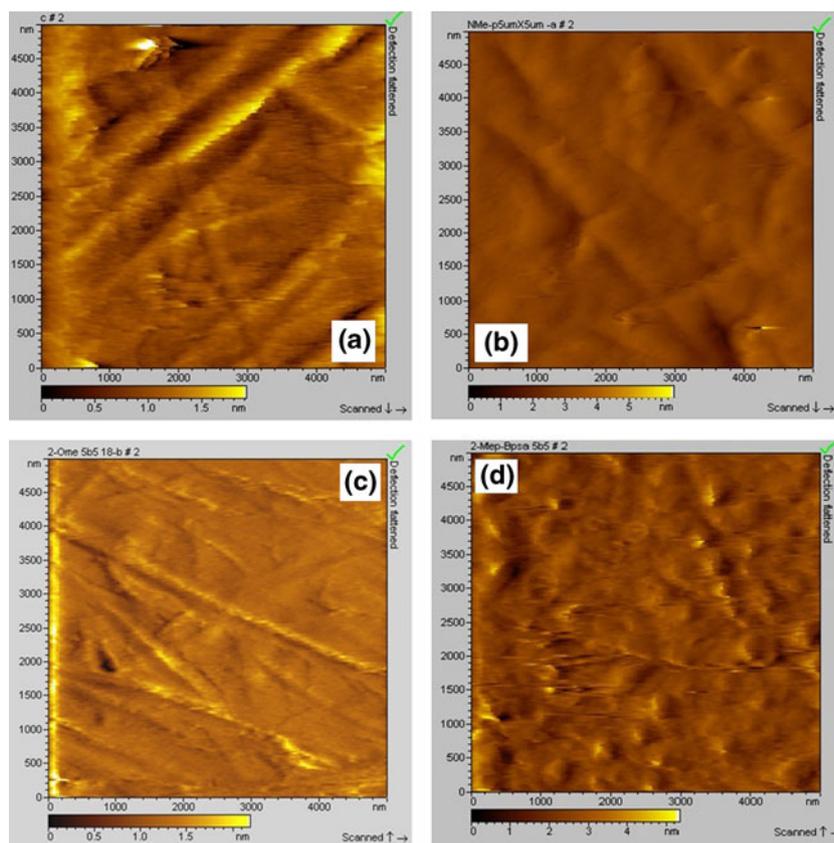
Figure 9. AFM pictures of electrochemically synthesized polymer samples on Pt electrode: (**a**) P(A)–BPSA, (**b**) P(N-MeA)–BPSA, (**c**) P(2-MeA)–BPSA and (**d**) P(2-OMeA)–BPSA.

uniform globular structures of size 100–200 nm. The appearance of film of P(2-OMeA) is not smooth and resembles more like P(A) film.

4. Conclusions

A new disulphonic acid, viz. 4,4′-biphenyldisulphonic acid (BPSA), is synthesized. It is demonstrated that this dopant yielded high conducting polyanilines with increased processability. The conducting polyaniline and its substituted derivatives are more soluble due to spacing effect of the dopant. The spacing effect is maximized when BPSA is used as doping agent in *in situ* polymerization reactions. The conductivity of polyaniline doped by BPSA is 4 S/cm and for the substituted polyanilines it ranged from 2×10^{-5} to 8×10^{-4} S/cm. The electrochemical studies showed that deposition of substituted polyanilines are more difficult due to highly soluble nature of doped polyanilines.

References

Abdiryim T, Jamal R and Nurulla I 2007 *J. Appl. Polym. Sci.* **105** 576

Barbero C, Miras M C, Haas O and Kotz R 1991 *J. Electroanal. Chem.* **310** 437

Baxskai J, Kertesz V and Inzelt G 1993 *Electrochim. Acta* **38** 393

Blomquist M, Lindfors T, Vahasalo L, Pivrikas A and Ivaska A 2006 *Synth. Metals* **156** 549

Chen S A, Chuang K R, Chao C I and Lee H T 1996 *Synth. Met.* **82** 207

Conway B E 1999 *Electrochemical supercapacitors—Scientific fundamentals and technology applications* (New York: Kluwer Academic Plenum)

DeBerry D W 1985 *J. Electrochem. Soc.* **132** 1022

Dhawan S K and Trivedi D C 1991 *Polym. Int.* **25** 55

Dhawan S K and Trivedi D C 1992 *J. Appl. Electrochem.* **22** 563

Epstein A J and MacDiarmid A G 1988 *Mol. Cryst. Liq. Cryst.* **160** 165

Epstein A J, Ginder J M, Zuo F, Bigelow R W, Woo H S, Tanner D B, Richter A F, Huang H S and MacDiarmid A G 1987 *Synth. Met.* **18** 303

Falcou A, Duchene A, Hourquebie P, Marsacq D and Balland-Longea A 2005 *Synth. Metals* **149** 115

Furukawa Y, Ueda F, Hyoda Y, Harada I, Nakajima T and Kawagoe T 1988 *Macromolecules* **B21** 1297

Gazotti Jr W A and De Paoli M A 1996 *Synth. Met.* **80** 263

Genies E M, Hany P and Santier Ch 1988 *J. Appl. Electrochem.* **18** 751

Gupta V and Miura N 2005 *Electrochem. Solid State Lett.* **8** A630

Hugot-Le-Goff A 1997 *Handbook of organic conductive molecules and polymers* (ed.) H S Nalwa (Chichester: Wiley) **Vol 3**

Hughes M, Chen G Z, Shaffer M S P, Fray D J and Windle A H 2002 *Chem. Mater*. **14** 1610

Kitani A, Kaya M and Sasaki K 1986 *J. Electrochem. Soc.* **133** 1609

Kobayashi A, Xu X, Ishikawa H, Satoh M and Hasegawa E 1992 *J. Appl. Phys.* **72** 5702

Kobayashi T, Yoneyama H and Tamura H 1984 *J. Electroanal. Chem.* **177** 293

Letheby H 1862 *J. Am. Chem. Soc.* **15** 161

Li S, Cao Y and Xue Z 1987 *Synth. Met.* **20** 141

Maccines D and Funt L B 1988 *Synth. Met.* **25** 235

MacDiarmid A G 1997 *Synth. Met.* **84** 27

Malinauskas A 1999 *Synth. Met.* **107** 75

Martha S K, Hariprakash B, Gaffoor S A, Trivedi D C and Shukla A K 2005 *Electrochem. Solid State Letts* **8** A353

Menon R, Yoon C O, Moses D, Heeger A J and Cao Y 1993 *Phys. Rev.* **B48** 17685

Moon Y B, Cao Y, Smith P and Heeger A J 1989 *Polym. Commun.* **30** 196

Park S M 1997 *Handbook of organic conductive molecules and polymers* (ed.) H S Nalwa (Chichester: Wiley) **Vol 3**

Peng C, Snook G A, Fray D J, Shaffer M S P and Chen G Z 2006 *J.C.S. Chem. Commun.* **44** 4629

Pouget J P *et al* 1994 *Synth. Met.* **65** 131

Pouget J P, Hsu C H, Mac Diarmid A G and Epstein A J 1995 *Synth. Metals* **69** 119

Sanjai B, Raghunathan A, Natarajan T S, Rangarajan G, Thomas S, Prabhakaran P V and Venkatachalam S 1997 *Phys. Rev.* **B55** 10734

Sariciftci N S, Kuzmany H, Neugebauer H and Neckel A 1990 *J. Chem. Phys.* **92** 4530

Shirakawa H, Louis L J, McDiarmid A G, Chang C K and Heeger A J 1977 *J.C.S. Chem. Commun.* **16** 578

Sivakumar R and Saraswathi R 2003 *Synth. Metals* **138** 381

Sivakumar S R and Saraswathi R 2004 *J. Power Sources* **137** 322

Skotheim T A 1986 *Handbook of conducting polymers* (New York: Marcel Dekker)

Trivedi D C 1988 *J. Solid State Electrochem.* **2** 85

Trivedi D C 1997 *Handbook of organic conductive molecules and polymers* (ed.) H S Nalwa (Chichester: Wiley) **Vol 2**

Trivedi D C 1999 *Bull. Mater. Sci.* **22** 447

Trivedi D C and Dhawan S K 1993 *Synth. Met.* **58** 309

Wang Y and Jing X 2005 *Polym. Adv. Technol.* **16** 344

Wei D, Kvarnstrom C, Lindfors T, Kronberg L, Sjoholm R and Ivaska A 2006 *Synth. Metals* **156** 541

Wei X L, Wang Y Z, Long S M, Bobeczo C and Epstein A J 1996 *J. Am. Chem. Soc.* **118** 2545

Yano J, Kokura M and Ogura K 1994 *J. Appl. Electrochem.* **24** 1164

Yano J, Takamura F, Masaoka K, Yamasaki S, Ota Y and Kitani A 2003 *Synth. Metals* **135** 417

Yue J, Wang Z H, Cromack K R, Epstein A J and MacDiarmid A G 1991 *J. Am. Chem. Soc.* **113** 665

Zhang J, Shan D and Mu S 2007 *Polymer* **48** 1269

Zhou T A, Nie L H and Yao S Z 1990 *J. Electroanal. Chem.* **293** 1