

Synthesis and Characterization of Processible Polyaniline Derivatives for Corrosion Inhibition

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ABSTRACT: This article reports the synthesis and characterization of copolymers based on aniline and substituted anilines by using dodecylbenzene sulfonic acid as a dopant. The copolymers were soluble in organic solvents, such as methanol, ethanol, isopropanol, *N*-methylpyrrolidinone, dimethylsulphoxide, and have conductivity of the order of 1.5 to 10^{-7} S/cm depending upon the monomer ratios and extent of dopant used. The effect of substituents like 2-methyl, 2-ethyl, and 2-isopropyl groups on the electrochemical, conductivity, thermal stability, solubilization, and spectroscopic behavior of the copolymers has been evaluated.

The composition of the copolymers was determined by ¹H-NMR spectroscopy. Corrosion inhibition behavior of the copolymers in 1.0N HCl has been evaluated using linear polarization resistance method and Tafel extrapolation method. The corrosion efficiency depends upon the copolymer composition and it increased with increasing amount of 2-alkyl aniline in the feed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2328–2339, 2009

Key words: conducting polymer; polyaniline; poly(2-alkylaniline); copolymer; corrosion inhibitor

INTRODUCTION

Conducting polymers have become very popular in the field of material science due to their promising and novel electrical properties such as energy storage devices,^{1–3} gas sensors,^{4–6} EMI shielding,^{7–10} electrostatic charge dissipation,^{11–13} OLED and flexible display devices,^{14–18} anticorrosive materials,^{19–22} electrochromic materials,^{23–25} and electronic conducting fabrics.²⁶ Organic metals may offer a viable alternative to inorganic semiconductors because it is possible to control the conductivity of the polymer by altering the organic molecular structure by attaching substituents in the polymer backbone. Among conducting polymers, polyaniline^{27–33} has a special representation due to easy synthesis, environmental stability, simple nonredox doping by protonic acids, also chemical doping and undoping can reversibly control the electrical conductivity of the polymers and that is the reason for its extensive use as sensor material for toxic gases and hazardous vapors. However the commercial exploitation of

most of the applications based on polyaniline is closely linked to the ease of its processability, but polyaniline is insoluble in common organic solvents. Various attempts have been made to improve its processability. Heeger and coworkers³⁴ have reported the use of functionalized protonic acid. Two methods have been used in the present work to increase its processability. One of the methods is to use functionalized sulfonic acid such as dodecyl benzene sulfonic acid (DBSA), a bulky molecules containing a polar head and a long nonpolar chain which function both as surfactant and dopant.³⁵ Second one is the incorporation of bulky alkyl chain in the monomer moiety and by copolymerization in such a way that there is a variation in the torsion angle between adjacent phenyl rings of the polymer. Copolymerization of aniline with substituted anilines have been extensively reported^{36–43} in the literature though the conductivity of the copolymers was always lower than that of polyaniline itself. The present article is directed toward the synthesis of copolymers (aniline-co-2-alkyl anilines) having different composition of monomers, showing varying degrees of conductivity, solubility, and thermal stability.

Theoretical studies on polyaniline indicate that the bandgap and bandwidth are affected by the torsion angle between adjacent repeating units of the polymer chain. Thus the alkyl-substituted polyanilines have better solubility in organic solvents like ethanol

Additional Supporting Information may be found in the online version of this article.

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TABLE I
Electrochemical Peak Potential Data, Room Temperature Conductivity, and Thermal Stability of Doped Polyaniline, Poly(2-alkylaniline), and Copolymer of Aniline : 2-Alkylaniline in Different Mole Ratios

Ratio of aniline : 2-alkylaniline in the copolymer in DBSA medium	Abbreviations	Anodic peak potential (V) vs. SCE	Conductivity at room temperature (S/cm)	Thermal stability (°C)
Aniline : 2-alkylaniline (100 : 0)	PB0	0.139, 0.442, 0.669, 0.774	1.52	240
Aniline : 2-methylaniline (90 : 10)	MB1	0.142, 0.438, 0.518, 0.763	1.02	237
Aniline : 2-ethylaniline (90 : 10)	EB1	0.149, 0.437, 0.505, 0.758	9.60×10^{-1}	230
Aniline : 2-isopropylaniline (90 : 10)	PB1	0.164, 0.428, 0.755	3.57×10^{-1}	220
Aniline : 2-methylaniline (50 : 50)	MB5	0.200, 0.476, 0.674	8.4×10^{-3}	220
Aniline : 2-ethylaniline (50 : 50)	EB5	0.251, 0.479	6.21×10^{-5}	205
Aniline : 2-isopropylaniline (50 : 50)	PB5	0.260, 0.466	3.34×10^{-6}	195
Aniline : 2-methylaniline (0 : 100)	MB10	0.250, 0.614	1.21×10^{-4}	207
Aniline : 2-ethylaniline (0 : 100)	EB10	0.438	2.50×10^{-6}	198
Aniline : 2-isopropylaniline (0 : 100)	PB10	0.446	5.25×10^{-7}	175

and methanol than unsubstituted polyaniline primarily because of the stereo-electronic effects of the substituent on the torsion angle.⁴⁴ However, the incorporation of water in these solvents precipitates the otherwise soluble polyaniline, thus restricting its use as a corrosion inhibitor for iron and mild steel in acidic medium like HCl. Poly(2-isopropylaniline) and its copolymer with aniline are soluble in alcohol due to steric effect of isopropyl group. Solubility increases with increasing the molar ratio of 2-isopropyl aniline in copolymer feed. Corrosion inhibition performance of this polymer can be determined by dissolving the polymers in ethanol or methanol. Recently, Pawar et al.⁴⁵ have investigated corrosion protection performance of poly(aniline-*co*-*o*-toluidine) coatings on low carbon steel in aqueous 3% NaCl solutions. Earlier study by authors⁴⁶ has reported the corrosion inhibition effect of substituted polyaniline. DeBerry⁴⁷ has found that polyaniline films electrodeposited on stainless steel passivated the surface to corrosion in sulfuric acid solution. Since then there have been a lot of interest to study the corrosion inhibition properties of polyaniline⁴⁸⁻⁵³ and other conductive polymers.⁵⁴ Cook and coworkers⁵⁵ have shown that the protective properties of polyaniline containing suitable dopants like phosphonic or sulfonic acids can be used for corrosion

protection. Rahela and coworkers⁵⁶ investigated the mechanism of corrosion inhibition by polyaniline coated stainless steel in sulfuric acid solution.

The article describes the homopolymerization of 2-alkylaniline and its copolymerization with varying amounts of aniline. The mole ratio of aniline : 2-isopropylaniline was taken as 100 : 0, 90 : 10, 80 : 20, 70 : 30, 60 : 40, 50 : 50, 0 : 100 in the initial feed. The abbreviations of doped and undoped forms of these polymers are given in Tables I and II and the same code has been used throughout the rest of the article. Undoped polyaniline is abbreviated as UNP0 whereas undoped poly(2-methyl aniline), poly(2-ethylaniline), and poly(2-isopropylaniline) are represented as UNM10, UNE10, and UNP10, respectively. Their respective undoped copolymers where monomers aniline to 2-methyl aniline, 2-ethyl aniline, and 2-isopropylaniline in the ratio of 90 : 10 are represented as UNM1, UNE1, and UNP1, respectively. In the same manner copolymers having monomer ratio of aniline to alkyl anilines in 50 : 50 are represented as UNM5, UNE5, and UNP5, respectively. In the present work, dodecyl benzene sulfonic acid was used as dopant and the effect of dopant content and the copolymer composition on thermal stability, conductivity, morphology, and electrochemical behaviors was investigated. Corrosion

TABLE II
Composition of the Comonomers (Aniline : 2-Alkylaniline) in Copolymers by ¹H NMR Spectra in DMSO-*d*₆ Solvent, UV-visible Absorption Bands in NMP, and Thermal Stability of Undoped Copolymers

Comonomers (aniline : alkylanilines) feed ratio	Final composition of the comonomers in the copolymer from ¹ H-NMR	UV-visible absorption bands (nm) in NMP	Thermal stability (°C) of undoped copolymers
Aniline : 2-methylaniline (90 : 10) (UNM1)	84 : 16	324, 626	427
Aniline : 2-ethylaniline (90 : 10) (UNE1)	81 : 19	319, 622	424
Aniline : 2-isopropylaniline (90 : 10) (UNP1)	78 : 22	312, 619	420
Aniline : 2-methylaniline (50 : 50) (UNM5)	46 : 54	316, 618	280
Aniline : 2-ethylaniline (50 : 50) (UNE5)	39 : 61	307, 615	255
Aniline : 2-isopropylaniline (50 : 50) (UNP5)	36 : 64	301, 610	220

inhibition by chemically synthesized undoped as well as DBSA-doped poly(2-ethyl aniline) and poly(2-isopropylaniline) and their copolymers with aniline was evaluated using linear polarization resistance method and Tafel line extrapolation method. Determining the role of the bulky group in polymer matrix for getting proper processability, solubility, and corrosion inhibition was a primary aspect of our work.

MATERIALS

Aniline (Loba Chemie, India), 2-methyl aniline (Loba Chemie, India), 2-ethylaniline (Acros Organics, Belgium), and 2-isopropyl aniline (Acros Organics, Belgium) were used after distillation. Ammonium peroxydisulphate (Merck, India), dodecyl benzenesulphonic acid (DBSA, Aldrich, India), HCl (35.4% S D fine-chem, India), and Liq NH₃ (30%, Loba Chemie, India) were used as received. Methanol (Merck, India), chloroform (Merck, India), *N*-methyl pyrrolidinone (Merck, India), and dimethylsulphoxide (Merck, India) were used as solvents. Aqueous solutions were prepared from the double-distilled water having specific resistivity of 1 MΩ cm.

EXPERIMENTAL

The doped polyaniline, poly(2-alkylaniline), and their respective copolymers were chemically prepared by free radical oxidative polymerization route. The concentration of aniline and 2-alkylaniline was 0.1 mole and that of HCl was 1.0 mole. For the preparation of copolymers, aniline and 2-isopropylaniline were mixed in different molar ratios. Polymerization was initiated by the dropwise addition of ammonium persulphate solution (0.1 mole, (NH₄)₂S₂O₈ in distilled water). The polymerization was carried out at a temperature of 0–3°C for a period of 4–6 h. The synthesized polymer was isolated from reaction mixture by filtration and washed with distilled water to remove oxidant and oligomers. The above-synthesized powders were treated with 0.1 mole ammonium hydroxide and stirred for 2 h to remove the dopant from the polymer which is the undoped form of the respective polymer and copolymer. The undoped polymers were treated with 0.3 mole of DBSA in distilled water and after stirring at room temperature for 3–4 h, the doped polymers were collected by filtration followed by drying under vacuum oven at 50°C.

Electrochemical polymerization

The electrochemical polymerization of 0.1M aniline, 0.1M 2-alkylaniline, and their copolymers (of varying composition) in DBSA were carried out at 0.9 V on platinum electrode (working electrode) versus

saturated calomel electrode (SCE) (reference electrode) and Pt as counter electrode. The polymer films were also grown electrochemically on the platinum (working) electrode in DBSA medium of monomers and comonomers with various feed ratio at room temperature using cyclic potential sweep techniques. The potentials were swept continuously in the range of –0.2 to 0.90 V versus SCE at a scan rate of 20 mV/s.⁵⁷ Peak potential values of the corresponding polymers and copolymers were recorded in DBSA medium.

Corrosion studies of these copolymers were carried in a three electrode assembly using Solatron Electrochemical Analyzer (Model 1280 B) with pure iron of dimension 1 cm × 1 cm as working electrode embedded in araldite epoxy, Pt as counter electrode, and SCE as reference electrode. The cleaning of the working iron electrode was carried out by 1/0, 2/0, 3/0, and 4/0 grade emery papers which were then thoroughly cleaned with acetone and trichloroethylene to remove any impurities on the surface. The polarization measurements were carried out using Corrware Software (Scribner Associates, USA) from a cathodic potential of –0.2 V to anodic potential of +1.2 V with respect to the corrosion potential at a scan rate of 0.5 mV/s. The linear Tafel segments to the anodic and cathodic curves (–0.2 to +0.2 V versus corrosion potential) were extrapolated to corrosion potential to obtain the corrosion current densities.

Characterization

The electrochemical behavior of the samples was investigated by cyclic voltammetry (Autolab 30, Potentiostat/Galvanostat, The Netherlands). The UV-visible spectra of the samples were recorded using UV-visible spectrophotometer (Shimadzu UV-1601, Japan) in *N*-methylpyrrolidinone (NMP) as a solvent. The structure of the polymers was characterized by Fourier transform infrared (FTIR) spectrometer (Nicolet 5700 FTIR, USA) in KBr pellets in the range of 400–4000 cm^{–1}. ¹HNMR spectra of polyaniline and its copolymer with substituted aniline were recorded in DMSO-d₆ as a solvent on high resolution spectrometer (NMR; Bruker 300 MHz, Germany) using tetramethylsilane (TMS) as an internal standard. TGA (Mettler Toledo TGA/SDTA 851e, Switzerland) was used to investigate the thermal stability of polymers in nitrogen atmosphere. A heating rate of 10°C/min and a sample size (in the form of fine powder) of 10 ± 2 mg was used in each experiment. Micromorphology was observed using scanning electron microscopy (SEM; Leo S-440, Germany). Percent solubility of polymers was evaluated by dissolving a known amount of sample (after sieving using a mesh 0.45 μm) in different

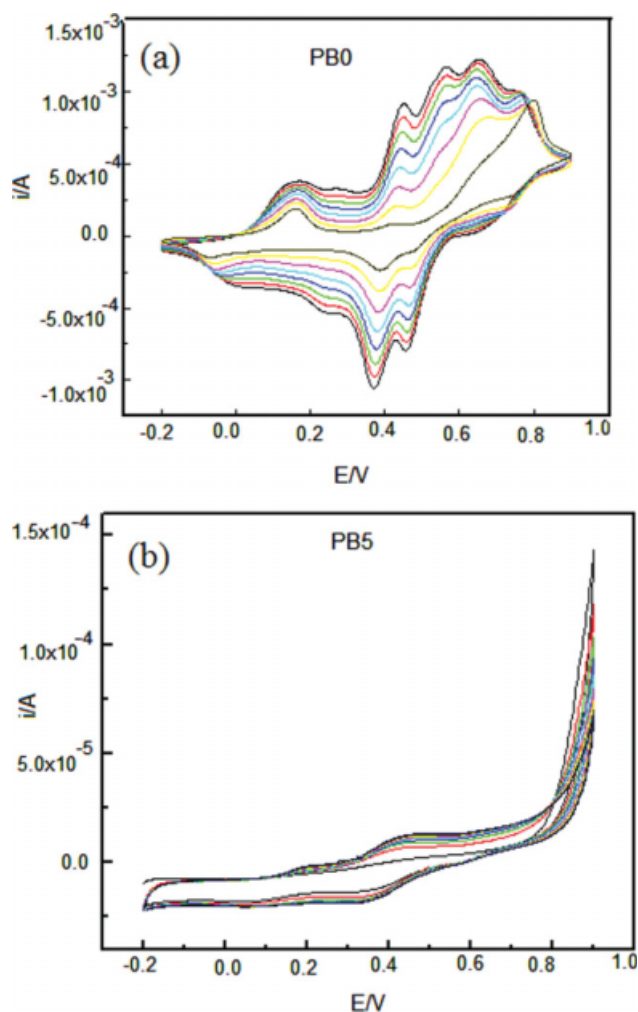


Figure 1 (a) Electrochemical growth behavior of 0.1M aniline in 0.3M DBSA on cycling potential between -0.2 and 0.9 V on platinum electrode versus SCE at a scan rate of 20 mV/s and (b) electrochemical growth behavior of aniline and 2-isopropylaniline (50 : 50) in DBSA medium on platinum electrode versus SCE at a scan rate of 20 mV/s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

solvents such as methanol, chloroform, *N*-methylpyrrolidinone (NMP), and dimethylsulphoxide. After 24 h, the solution was filtered and the insoluble fraction was calculated.

For the conductivity measurements, pellets of dimensions (length 13 mm, width 7 mm, thickness 1–2 mm) were prepared and the resistivities were measured by four-point probe technique using (Keithley 220 Programmable Current Source and 181 Nanovoltmeter, Germany).

Corrosion studies of the samples were carried on a Solatron Electrochemical Analyser (Model 1280 B) with pure iron (Johnson Matthey Ltd., UK) sample of dimension $1\text{ cm} \times 1\text{ cm}$ as working electrode embedded in araldite epoxy, Pt as counter electrode and SCE as reference electrode.

RESULTS AND DISCUSSION

The polymerization of aniline to polyaniline proceeds through the formation of a radical cation by an internal redox reaction, which causes the reorganization of electronic structure, to give two semiquinone radical cations. These radical cations through the coupling reaction lead to the formation of stable electrically conducting polymer. During the polymerization of substituted aniline and its copolymer in the presence of sulfonic acid, it has been observed that dopant gets attached to the anilinium ring and offers steric-hindrance affecting the polymer alignment, resulting in the formation of flexible and soluble conducting polymers.⁵⁸

Electrochemical behavior

The electrochemical polymerization of aniline, comonomers of aniline and 2-methyl aniline in 1 : 1 mole ratio (MB5), aniline and 2-ethylaniline in 1 : 1 mole ratio (EB5), and aniline to 2-isopropylaniline in 1 : 1 mole ratio (PB5) in DBSA medium was done by sweeping the potential in the potential range -0.2 to 0.9 V versus SCE on platinum electrode at a scan rate of 20 mV/s. On comparing the electrochemical growth behavior of aniline, Figure 1(a,b) comonomer of aniline and 2-isopropylaniline, it has been observed that the cyclic voltammogram of aniline growth in DBSA medium differs from the growth behavior observed for 2-alkylaniline and from the copolymer of aniline and 2-alkylaniline. Figure 2 shows the cyclic voltammogram of polyaniline and poly(2-alkylanilines) in DBSA medium. The cyclic voltammogram of copolymers by varying the molar ratio of 2-isopropyl aniline to aniline in the

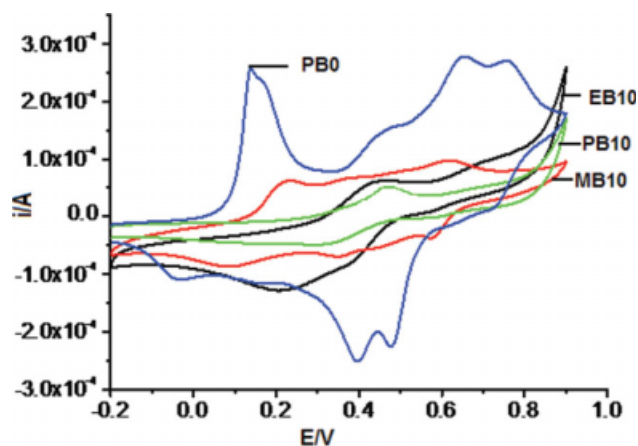


Figure 2 Cyclic voltammogram of polyaniline (PB0), poly(2-methylaniline) (MB10), poly(2-ethylaniline) (EB10), and poly(2-isopropylaniline) (PB10) in DBSA medium at a scan rate of 20 mV/s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

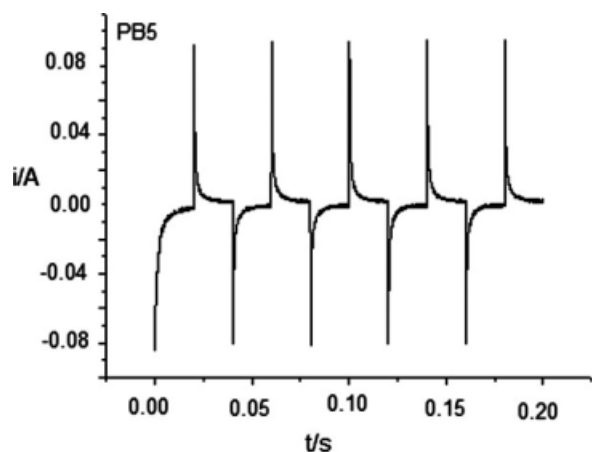


Figure 3 Chronoamperometric response of poly(aniline-co-2-isopropylaniline) PB5 film in DBSA medium.

electrolytic medium were also recorded and have been given as Supporting Information. The comparison of peak potential data indicates that the first redox value of polyaniline in DBSA medium lies at 0.139 V versus saturated calomel electrode (SCE), whereas the first peak potential value of poly(2-isopropylaniline) lies at 0.446 V. However, on increasing the mole ratio of isopropyl aniline in copolymers, the peak potential value shifts from 0.139 to 0.164 V in PB1 (0.9 : 0.1 mole ratio aniline : 2-isopropyl aniline) to 0.176 V in PB2 (0.8 : 0.2; aniline: 2-isopropylaniline) to 0.260 V in PB5 (0.5 : 0.5; aniline: 2-isopropylaniline). This implies that the copolymerization leads to larger peak potential shift, associated with electron transfer which implies that the presence of isopropyl group in the copolymer chain induce some nonplanar configurations that decrease the conjugation along the polymer backbone which is responsible for the positive shift in the oxidation potential. The electrochemical peak potential data of polyaniline, poly(2-isopropylaniline), and their copolymers are summarized in Table I. To compare the peak potential value of copolymer of aniline with other substituted anilines like 2-methylaniline and 2-ethylaniline, we have studied the cyclic voltammetric behavior of the copolymer in DBSA medium and the values have been incorporated in Table I. From Table I, it can be observed that the first anodic peak potential value which is observed at 0.139 V versus SCE in case of polyaniline in DBSA medium shifts to 0.142 V in case of copolymer where aniline and 2-methylaniline are present in 0.9 to 0.1 mole ratio (MB1) which further shifts to 0.149 V in case of copolymer of aniline to 2-ethylaniline (EB1). This value shifts to 0.164 V in case of PB1. This implies that the larger the substituent higher will be the peak potential shift, associated with electron transfer which implies that the presence of substituted group in the copolymer chain

induce some nonplanar configurations that decrease the conjugation along the polymer backbone which is responsible for the positive shift in the oxidation potential. On increasing the ratio of substituted aniline (2-methylaniline, 2-ethyl aniline, or 2-isopropylaniline) to aniline in the reaction mixture, first peak potential shifts to positive potential and reaches saturation level at 1 : 1 ratio which suggests the formation of copolymer.

The conducting polymer polyaniline film on electrode surface exhibits multiple color change on switching the potential from -0.2 to 0.8 V versus SCE. These changes correspond to different color oxidation state that appears on varying the potential. Figure 3 shows the chrono-amperometric response of poly(aniline-co-2-isopropylaniline) film in DBSA medium. The repetitive switching test to estimate the cyclic life of the electrochromic polyaniline film shows good stability provided the upper limit does not exceed 0.4 V. At higher potential, the oxidative degradation of the polymer occurs. After 10^5 cycles, the electrochromic activity of the conducting polymer film diminishes drastically as has been observed after recording the cyclic voltammogram of polyaniline film after the cycling period.

UV-visible spectroscopy

Figure 4 shows UV-visible absorption spectra of base form of homopolymers polyaniline, poly(2-alky

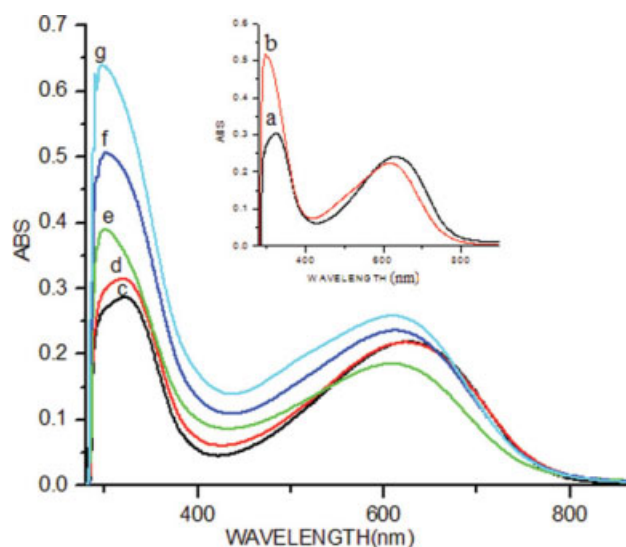


Figure 4 UV-visible absorption spectra of undoped copolymers of aniline and isopropylaniline synthesized in different molar ratios in NMP (c) UNP1(90 : 10); (d) UNP2 (80 : 20); (e) UNP3 (70 : 30); (f) UNP4 (60 : 40); and (g) UNP5 (50 : 50). Inset figure corresponds to UV-visible absorption spectra of (a) undoped polyaniline (UNP0) and (b) undoped poly(2-isopropylaniline) (UNP10). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

anilines), and their copolymers in *N*-methyl pyrrolidinone. Band in the range of 290–328 nm was assigned to the $\pi \rightarrow \pi^*$ transition which are associated due to extent of conjugation between adjacent phenyl rings in the polymer chain.^{59,60} It exhibited a hypsochromic shift from 328 to 290 nm when the 2-alkyl aniline content in the copolymer feed is gradually increased, indicating substantial reduction in the level of conjugation (i.e., an increase in the band gap) along the copolymer chain. The hypsochromic shift is due to the $-\text{CH}(\text{CH}_3)_2$ substituent which increases the torsional angle between the adjacent phenyl rings in the polymer backbone. The second absorption band which showed a blue shift from 628 nm in undoped polyaniline (EB) to 606 nm in undoped poly(2-isopropyl aniline). This could be due to the exciton transition related with the quinone-diimine structure, i.e., transition between HOMO orbitals of the benzenoid rings and LUMO orbitals of the quinoid rings. These blue shifts of the benzenoid absorption peak indicates the nonplanar conformation of the polymer backbone, since a more distorted ring conformation was indicative of reduction of conjugation length or blue shift of the absorption peak.⁶¹ UV-visible absorption bands of base form of poly(aniline-co-alkylanilines) are listed in the Table II. The table reveals that $\pi \rightarrow \pi^*$ transition and exciton bands exhibited the hypsochromic shift when bulkier substituents and its greater molar ratio were introduced in to the copolymer chain. DBSA-doped polyaniline and its copolymers with (2-isopropylaniline) were also soluble in NMP. The UV-visible absorption spectra exhibit two major absorption bands in the range of 330 to 303 nm, due to $\pi \rightarrow \pi^*$ transition which exhibited a blue shift with increasing amount of 2-isopropyl aniline in the comonomer feed. The second absorption band also shows blue shift from 635 to 586 nm. However, the doped polyaniline and its copolymers should not show this type of behavior. This means in the solvent, *N*-methyl pyrrolidinone which is a basic solvent, deprotonation of the doped form might have taken place which may be due to bond formation with the solvent resulting in the shifting of the absorption bands. On addition of dopant molecules in the solvent mixture containing the polymer, the color of the solution changes from blue to green, which indicates the redoping of the polymer chain resulting in the shifting of the bands from 635 to 810 nm in case of PANI and from 586 to 840 nm in case of copolymer of aniline and isopropyl aniline.

FTIR spectra

Figure 5 shows the FTIR spectra of homopolymers and copolymers. In the FTIR spectra, band around 815 cm^{-1} in doped polyaniline (PB0), 828 cm^{-1} in

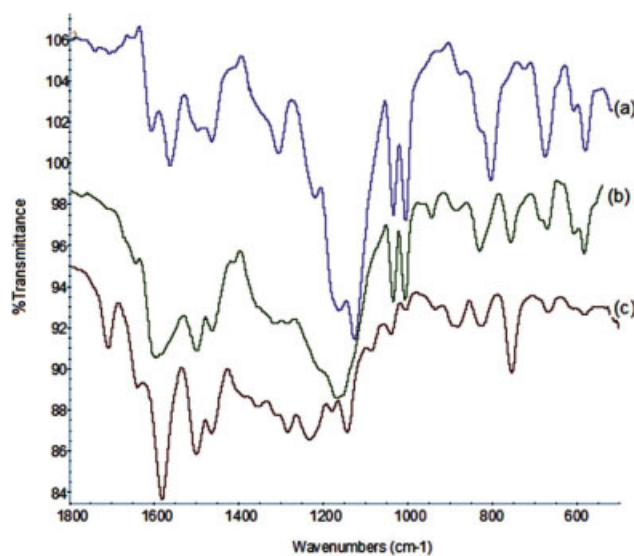


Figure 5 FTIR Spectra of DBSA-doped (a) polyaniline, (b) PB5, and (c) PB10. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

copolymer of aniline and isopropylaniline (PB5), and 826 cm^{-1} in poly(isopropylaniline) (PB10) is due to the out of the plane C–H bending vibrations and is indicative of the para coupling i.e., the polymerization occurs at 1–4 position. The band around 757 and 752 cm^{-1} is due to the out-of-plane $-\text{CH}-$ bending of 1, 2, 4-trisubstituted ring in case PB5 and PB10, respectively. Similar band has also been observed in UNP5 and UNP10. But this band is absent in undoped polyaniline and DBSA-doped polyaniline. The band at 1034 cm^{-1} corresponding to S=O stretching mode of the $-\text{SO}_3$ group of DBSA splits into two bands. Because of steric hindrance of bulky isopropyl group in PB10, the extent of doping is lower. Hence the S=O stretching band is weak in case of PB10 and these bands are absent in undoped polymers. The figure has been given in Supporting Information. The bands around 1126 and 1159 cm^{-1} are due to the symmetric SO_2 stretching and SO_3 stretching in PB0, PB5, and PB10. It was observed that there is only a weak shoulder in PB5 and PB10. Bands around 1563 and 1463 cm^{-1} are characteristic stretching bands of nitrogen quinoid (N=Q=N) and benzenoid (N-B-N) units, where B denotes the benzenoid and Q denotes quinoid ring and are due to the conducting state of the polymer. These bands generally show the blue shift of 20–30 cm^{-1} on the removal of dopant from the polymer.

NMR spectra

Figure 6 shows the ^1H -NMR spectra of the base forms of homopolymers and copolymers of aniline

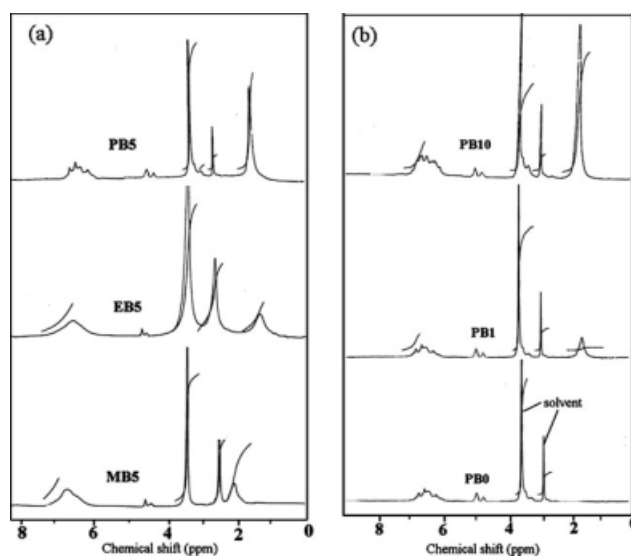


Figure 6 (a) $^1\text{H-NMR}$ spectra of base copolymers of aniline and 2-alkylanilines in 50 : 50 molar ratios in DMSO-d_6 and (b) $^1\text{H-NMR}$ spectra of base forms of polyaniline, poly(2-isopropylaniline), and their copolymer in DMSO-d_6 .

and 2-alkylaniline in DMSO-d_6 solvent. The $^1\text{H-NMR}$ spectra of the base forms of the polyaniline are characterized by the two signals. The signals in the region of 7.6–6.3 ppm are assigned to the aromatic protons and another weak signal at 4.6 ppm is due to the N–H protons. NMR spectrum of base forms of poly(2-methylaniline) and its copolymers with aniline, show three peaks at $\delta = 2.1$ ppm which are due to the $-\text{CH}_3$ and other two peaks have been observed at $\delta = 7.0$ –6.3 ppm and weak peak at $\delta = 4.9$ –5.0 ppm owing to the aromatic protons and $-\text{NH}$ protons, respectively. In the case of poly(2-ethylaniline), poly(2-isopropylaniline) and their copolymers with aniline show four types of protons. The signals in the region of 7.6–6.3 ppm are assigned to the aromatic protons and weak signals at $\delta = 4.85$ –1 ppm which are due to the $-\text{NH}$ protons and the resonance of the methylene protons ($-\text{CH}_2$) of poly(aniline-co-2-ethylaniline) and methyne protons ($-\text{CH}$) of poly(aniline-co-2-isopropylaniline) that appeared to overlap with that of the solvents (DMSO-d_6) and another peak at 0.9–1.5 ppm was attributed to the methyl protons ($-\text{CH}_3$) present in both copolymers chain. Moreover, the methyl protons of poly(aniline-co-2-methylaniline) were found to be more deshielded than poly(aniline-co-2-ethylaniline) and poly(aniline-co-2-isopropylaniline) because these protons are the closest to the aromatic ring. The intensity of signals (methyl protons) arising from 2-isopropylaniline unit increases with increasing the feed ratio of 2-isopropylaniline in the copolymer matrix as shown in the Figure 6. Therefore, the composition of copolymers can be

determined from the ratio of the integrated peak area of aromatic to methyl protons. The final compositions of the comonomers in the copolymers of aniline and 2-alkylanilines have been derived from the result and are listed in Table II. The result shows that if the initial feed of aniline: 2-alkylaniline was 90 : 10, the final composition of aniline : 2-alkylaniline in copolymer composition was found to be 84 : 16 in poly(aniline-co-2-methylaniline), 81 : 19 in poly(aniline-co-2-ethylaniline), and 78 : 22 in poly(aniline-co-2-isopropylaniline). If the initial feed ratio of aniline : 2-alkylaniline was 50 : 50, then the final composition of aniline to 2-alkylaniline in the copolymer was 46 : 54, 39 : 61, and 36 : 64 for poly(aniline-co-2-methylaniline), poly(aniline-co-2-ethylaniline), and poly(aniline-co-2-isopropylaniline), respectively. These results suggest that the soluble polymer in the DMSO consists mainly of substituted aniline units. Solubility increases with increasing alkylaniline in the copolymer and solubility of polyaniline unit in the copolymer is comparatively less than that of poly(*o*-alkylaniline) unit. Higher the ratio of bulky alkyl substituent in the copolymer, greater is the solubility. Hence isopropyl aniline shows better solubility in DMSO-d_6 and shows higher fraction in the copolymer than aniline as compared to initial feed. The monomers reactivity ratios were also calculated by Fineman-Ross method.⁶²

The reactivity ratio of the comonomers was calculated by the equation:

$$\frac{[m_1](M_2 - M_1)}{[m_2]M_1} = \frac{-M_2[m_1^2]r_1}{M_1[m_2^2]} + r_2$$

where $[m_1]$ and $[m_2]$ are the mole fraction of aniline and 2-alkylaniline in the initial feed, respectively, and $[M_1]$ and $[M_2]$ are mole fraction of aniline and 2-alkylaniline in the copolymer, respectively. A plot of the $[m_1](M_2 - M_1)/[m_2]$ versus $-M_2[m_1^2]/M_1[m_2^2]$ yield a straight line whose slope is r_1 and intercept is r_2 . From the plot, it was observed that the value of r_1 (reactivity ratio of aniline) was 0.35 and that of r_2 (reactivity ratio of 2-isopropylaniline) was 1.71. Hence $r_1 < 1$ and $r_2 > 1$ which indicates that 2-isopropylaniline is more reactive than aniline. This type of trend has also been observed in the case of other series of copolymers of aniline with 2-methylaniline and 2-ethylaniline.

Solubility

It was observed that PANI doped with inorganic protonic acid like HCl is rather insoluble in organic solvents. However, polyaniline doped with organic aromatic sulfonic acid like PTSA and DBSA is

soluble in chloroform, DMSO, DMF but rather insoluble in common organic solvents like ethylene glycol, isopropanol, ethanol, methanol, etc.³⁵ On the other hand, the copolymers of aniline and 2-substituted anilines doped with DBSA are soluble in common organic solvents. The solubility of synthesized copolymers of aniline with 2-alkylanilines increases with the increase in the bulky substituent proportion in the copolymer. This is due to the steric hindrance brought about by the introduction of substituted alkyl group in the polymer matrix. It was found that whereas undoped polyaniline is insoluble in methanol, the solubility of the copolymers present in various molar combinations increases with the increase in alkyl aniline. The solubility of undoped copolymer in the monomer ratios of aniline to 2-methylaniline of 90 : 10 (UNM1) is 48% in methanol and this solubility increases to 50% in aniline to 2-ethylaniline ratio of 90 : 10 (UNE1). The solubility of undoped copolymer (UNP1) where the monomer ratios of aniline to isopropylaniline is 90 : 10, increases to 60% in methanol. Moreover, the solubility of the undoped copolymer of aniline and 2-alkyl aniline in 50 : 50 (UNM5) increases from 70% in methanol to 86% for UNP5. However, the solubility of undoped poly(2-methylaniline) (UNM10) in CH₃OH is 75% which increases to 90% in case of poly(2-isopropyl aniline). Similarly, it was observed that the solubility of polyaniline doped with DBSA is almost negligible in methanol, the solubility increases to 50% in methanol in case of MB5 where aniline and 2-methylaniline are present in equimolar ratio which increases to 61 and 72% in case of EB5 and PB5, respectively. We have also studied the solubility behavior of the copolymers in other solvents like chloroform, *N*-methyl pyrrolidinone (NMP), and dimethylsulphoxide (DMSO). In the case of DBSA-doped polyaniline, the solubility in chloroform was found to be 54% whereas in NMP and DMSO, its solubility was 45 and 40%, respectively. However, DBSA-doped copolymers showed varying degree of solubility from 50 to 60% in NMP when comonomers were present in 90 : 10 molar ratio. The solubility of the copolymers was found to increase from 78 to 88% in the case of 50 : 50 molar ratios of comonomers. Moreover, the substituted homopolymers like MB10, EB10, and PB10 showed the maximum solubility in NMP up to 80, 89, and 91%, respectively. The solubility of these homopolymers in chloroform was found to be 81, 87, and 94%, respectively. All the data on solubility of homopolymers and copolymers has been tabulated and given as Supporting Information. The methanol medium was selected for our correlation studies because all the corrosion studies for iron were done for the copolymers in 1.0N HCl and since methanol was miscible with aqueous medium, it has not affected

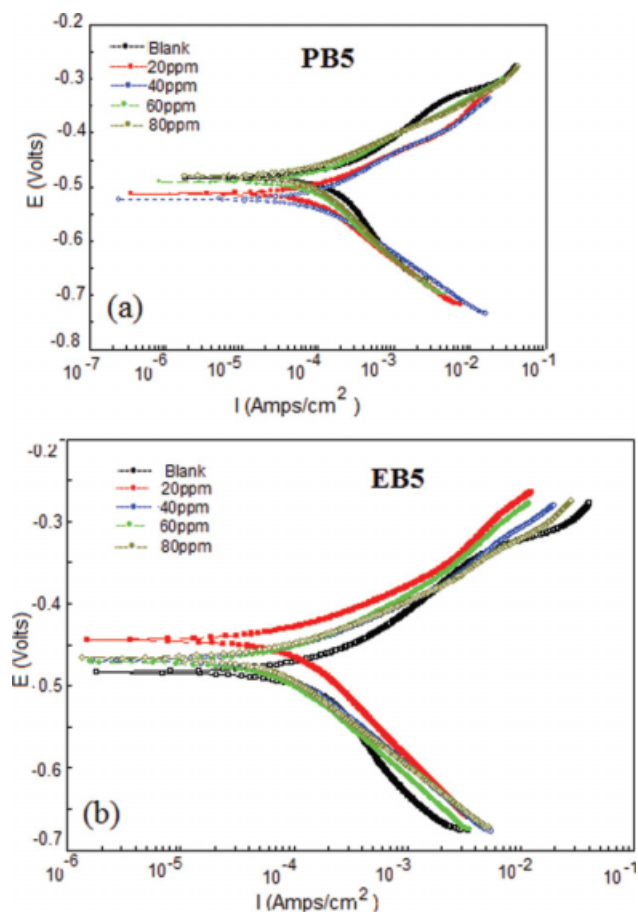


Figure 7 (a) Potentiodynamic polarization behavior of iron in 1N HCl with addition of different concentrations of PB5 and (b) potentiodynamic polarization behavior of iron in 1N HCl with addition of different concentrations of EB5. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the overall performance of the corrosion inhibition studies.

Thermogravimetric analysis

Thermograms of undoped polyaniline and its copolymers with different mole ratios of isopropyl aniline were also carried out to see the thermal stability of the various combinations. It was observed that the undoped polyaniline is thermally stable up to 430°C. The thermal stability of the copolymer decreased with increasing amounts of isopropyl aniline in the copolymers. It was found that in the copolymer combinations of aniline : 2-isopropylaniline (90 : 10) (UNP1), the thermal stability of the copolymer decreases to 420°C and it further decreased to 350°C in 80 : 20 monomer ratios in the copolymer (UNP2). The thermal stability of copolymer whose monomer ratios are 50 : 50 (UNP5) decreased further to 220°C whereas for undoped poly(2-isopropyl aniline), the thermal stability was

TABLE III
Corrosion Inhibition Efficiency of Alcohol-Soluble Polymers for Iron in 1.0N HCl

Copolymer compositions	Soluble fraction (%) of the polymers in methanol	Inhibitor concentration (ppm)	TAFEL extrapolation method				
			Corrosion current i_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion potential E_{corr} (V)	Inhibition efficiency (%)	LPR data R_p (Ωcm^2)	Corrosion inhibition efficiency (%)
Blank		–	185	–0.483	–	111.6	–
PB1	25	20	120	–0.491	41	122.91	9.21
		40	94	–0.516	49	48.917	25.0
		60	86	–0.512	54	178.99	37.6
		80	78	–0.515	56	205.17	45.5
PB5	72	20	91	–0.512	51	137.7	18.9
		40	88	–0.512	52	228.7	51.2
		60	84	–0.523	55	239.3	53.3
		80	76	–0.478	59	243.8	54.2
PB10	80	20	119	–0.4532	36	223.6	50.0
		40	68	–0.4899	63	236.3	52.6
		60	58	–0.4866	69	252.5	55.8
		80	52	–0.5130	72	254.5	56.1
UNP1	60	20	85	–0.5070	54	163.16	31.5
		40	80	–0.5019	57	167.45	33.3
		60	64	–0.4991	65	201.22	44.5
		80	63	–0.5258	66	271.0	58.8
UNP5	86	20	101	–0.5063	45	173.0	35.4
		40	74	–0.4873	60	187.0	40.3
		60	55	–0.5163	70	202.0	44.7
		80	52	–0.4929	72	272.1	58.9
UNP10	90	20	76	–0.520	59	172.0	35.0
		40	62	–0.514	66	260.7	57.1
		60	59	–0.528	68	277.1	59.7
		80	45	–0.508	76	326.4	65.8

found to be 210°C. This implies that introduction of isopropyl group in the aniline moiety and copolymerizing it with aniline decreases the thermal stability of the copolymer which is due to the steric hindrance brought by substituted aniline in the copolymer matrix. The thermal stability data of other copolymers composition of aniline and 2-methyl aniline and aniline and 2-ethylaniline have also been recorded and are given in Table II. This effect has also been observed when the electrochemical studies of the copolymer present in different mole ratios were carried out by cyclic voltammetric technique.

Similarly, the thermograms of DBSA-doped homopolymers like polyaniline (PB0), poly(2-methylaniline) (MB10), poly(2-ethylaniline) (EB10), and poly 2-isopropylaniline (PB10) were also carried out to see the thermal stability of the homopolymers and to see how the dopant introduced in the polymer backbone affects the thermal stability. It was observed that doped polyaniline (PB0) is thermally stable up to 240°C, whereas poly(2-methylaniline) (MB10) is thermally stable up to 207°C. Poly(2-ethylaniline) (EB10) is thermally stable up to 198°C, whereas poly(2-isopropylaniline) (PB10) is thermally stable up to 175°C. The above data has been given in Table I. This shows that introduction of bulky groups and large counter ion in the copolymer

brings about a change in the thermal stability of the copolymer which can again be correlated to the steric hindrance brought by introduction of ortho substituted group and bulky dopant in the aniline system. However, the copolymer of aniline and 2-methylaniline (MB5) is thermally stable up to 220°C, whereas copolymers of aniline and 2-ethylaniline (EB5) and copolymer of aniline to 2-isopropylaniline (PB5) are thermally stable up to 205 and 195°C, respectively. This shows that introduction of bulkier alkyl group in the copolymer brings about a change in the thermal stability of the copolymer which can again be correlated to the steric hindrance brought by introduction of alkyl group in the aniline system.

Conductivity studies

Room temperature conductivity values of polyaniline doped with aromatic sulfonate dopant and the copolymers of PANI with incorporation of different molar ratio of substituted monomers is given in Table I. The data reveals that copolymerization affected the conductivity of the parent polymer but it makes the copolymer more soluble in common organic solvents and this aspect has been utilized in studying the corrosion behavior of copolymers in highly corrosive medium. The values from the Table I

indicates that the conductivity changes from 1.52 S/cm in case of polyaniline to 1.02 S/cm in case of MB1 and this value changes to 0.96 and 0.35 S/cm in case of EB1 and PB1, respectively. Similarly, conductivity of the copolymer changes from 8.4×10^{-3} S/cm observed in case of MB5 to 3.34×10^{-6} S/cm in case of PB5. However, higher the bulky group attached in the copolymer matrix, more soluble is the copolymer in the organic solvents. Hence, we can select the copolymers for our further plan of action for corrosion inhibition studies as well as for blending with conventional polymers like low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS), etc.

Corrosion inhibition by polymers

Figure 7 shows the Tafel polarization curve for iron in 1.0N HCl with the addition of various concentrations of PB5 and EB5, respectively. The corrosion parameters obtained from Tafel curves are given in Table III. It is clear from the table that the corrosion current values (i_{corr}) decreased from $185 \mu\text{A}/\text{cm}^2$ of that of blank iron electrode to $52 \mu\text{A}/\text{cm}^2$ with the addition of 80 ppm concentration of copolymer (UNP5) and $45 \mu\text{A}/\text{cm}^2$ with the addition of 80 ppm concentration of UNP10. The inhibition efficiency was also found to increase from 59 to 72% by increasing the concentration of copolymer in the HCl medium.

Figure 8 shows the linear polarization resistance graphs of undoped copolymer of aniline to isopropylaniline in 1 : 1 ratio and DBSA-doped poly(2-isopropylaniline). These studies were also carried out to see the effect of copolymers concentration on the polarization resistance (R_p). From Table III, it was observed that the polarization resistance value was found to increase from $111 \Omega\text{cm}^2$ of that of blank iron electrode to $243 \Omega\text{cm}^2$ for 80 ppm of PB5, $254 \Omega\text{cm}^2$ for 80 ppm of PB10, $272 \Omega\text{cm}^2$ for 80 ppm concentration of UNP5, and $326 \Omega\text{cm}^2$ for 80 ppm concentration of UNP10, indicating that the polyaniline derivatives and its copolymers possess a good corrosion inhibiting property.

Poly(2-isopropylaniline) and its copolymers with aniline of being a conjugated polymer having plenty of π bonds along with the coexistence of quaternary nitrogen. Presence of delocalized π -electrons form co-ordination type of bonds with the iron surface and the iron in acidic medium is negatively charged, the existence of quaternary ammonium nitrogen acts as an anchoring unit which makes the polymer chain attached to the surface. For comparison, we have also evaluated corrosion inhibition behavior of copolymers on aniline with 2-ethylaniline by plotting Tafel polarization curve for iron in 1.0N HCl with the addition of various concentrations of copolymer

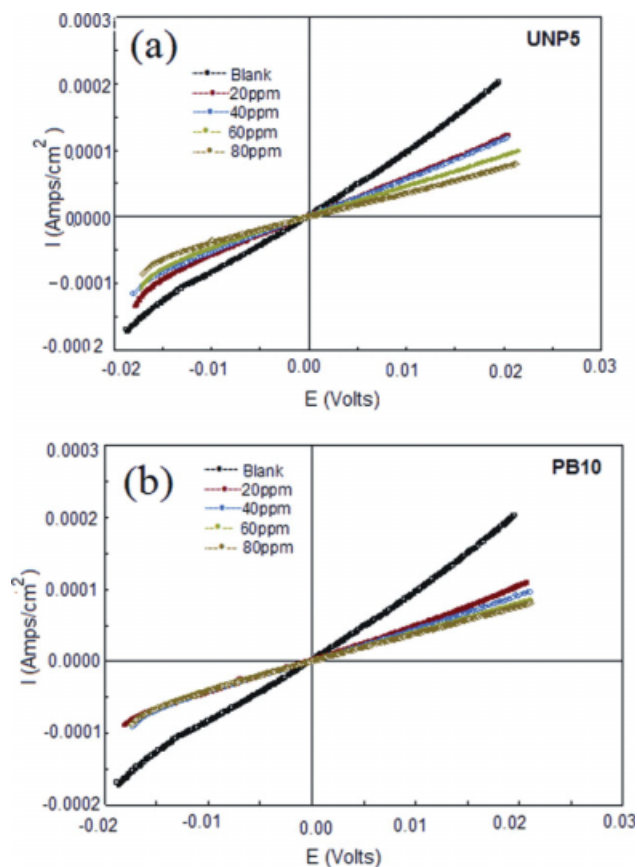


Figure 8 (a) Linear polarization behavior of iron in 1N HCl in the presence of different concentrations of UNP5 and (b) linear polarization behavior of iron in 1N HCl in the presence of different concentrations of PB10. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

UNE1, UNE5, and UNE10. It was observed that the corrosion current values (i_{corr}) decreased from $185 \mu\text{A}/\text{cm}^2$ of that of blank iron electrode to $66 \mu\text{A}/\text{cm}^2$ with the addition of 80 ppm concentration of UNE1, $55 \mu\text{A}/\text{cm}^2$ with the addition of 80 ppm concentration of copolymer UNE5, and $52 \mu\text{A}/\text{cm}^2$ with the addition of 80 ppm concentration of UNE10, whereas in the case of homopolymers and copolymers of 2-isopropylaniline, the corrosion current value decreased from $185 \mu\text{A}/\text{cm}^2$ of that of blank iron electrode to $63 \mu\text{A}/\text{cm}^2$ in UNP1, $52 \mu\text{A}/\text{cm}^2$ in UNP5, and $45 \mu\text{A}/\text{cm}^2$ at 80 ppm. Similar trend has been observed in their DBSA-doped polymers. The inhibition efficiency was found to increase in the case of homopolymer of 2-isopropylaniline and their copolymers with aniline. The bulkiness of substitution makes the cluster network on iron surface anchored more strongly resulting in good coverage of surface and enhanced inhibition efficiency. Solubility of the polymers in methanol is also an important parameter for their good corrosion inhibition efficiency.

Scanning electron microscopy

SEM micrographs of the DBSA-doped polyaniline (PB0), poly(2-isopropylaniline) (PB10), and their copolymer (PB5) show the globular morphologies. However, it was observed that when 2-isopropylaniline was copolymerized with aniline, morphology of the copolymer was affected due to combined effect of comonomers in the copolymer chain. These micrographs can be seen in the Supporting Information.

CONCLUSIONS

The synthesis of polyaniline, poly(2-alkylaniline), and its copolymer (aniline-co-2-alkylaniline) were carried out by chemical oxidative polymerization and electrochemical polymerization technique. On the basis of characterization of these polymers, the effect of alkyl group on thermal and electrochemical properties of conducting polyaniline has been observed. The electrochemical studies of these copolymers show a shift in the electrochemical peak potential values on increasing the substituted aniline ratio in the copolymer. Thin films of these polymers can be used as potentially viable electrochromic material since these films change their color on switching from reduced state to oxidized state. The solubility of conducting polyaniline could be enhanced by copolymerization with varying amount of 2-alkylanilines as comonomers. Moreover, by copolymerization, it is possible to obtain a processible and soluble conducting polymer without appreciable loss in electrical conductivity and thermal stability in selective comonomer ratios. These synthesized copolymers can then be easily melt-blended with other conventional polymers like LDPE, PP, etc. for various applications. From the above studies, it can be concluded that poly(2-isopropylaniline) and its copolymers with aniline can be used as effective corrosion inhibitors for iron and mild steel in highly corrosive medium like HCl.

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