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Synthesis of electrically conducting copolymers of aniline with *o*/*m*-amino benzoic acid by an inverse emulsion pathway

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Abstract

Copolymers of aniline and *ortho*/*meta*-amino benzoic acid were synthesized by chemical polymerization using an inverse emulsion pathway. The copolymers are soluble in organic solvents, and the solubility increases with the amino benzoic acid content in the feed. The reaction conditions were optimized with emphasis on high yield and relatively good conductivity (2.5×10^{-1} S cm^{-1}). The copolymers were characterized by a number of techniques including UV–vis, FT-IR, FT-Raman, EPR and NMR spectroscopy, thermal analysis, SEM and conductivity. The influence of the carboxylic acid group ring substituent on the copolymers is investigated. The spectral studies reveal that the amino benzoic acid groups restrict the conjugation along the polymer chain. The SEM micrographs of the copolymers reveal regions of amorphous and crystalline domain. Thermal studies indicate a marginally higher thermal stability for poly(aniline-*co*-*m*-amino benzoic acid) compared to poly(aniline-*co*-*o*-amino benzoic acid). © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(aniline-*co*-*o*/*m*-amino benzoic acid); Inverse emulsion; Benzoyl peroxide

1. Introduction

Polyaniline, one of the oldest of the conjugated conducting polymers, has always been at the forefront in the search for conducting polymers for commercial applications because of its unique reversible proton dopability, excellent redox recyclability, environmental stability, variable electrical conductivity, which can be 'tuned', low cost and easy synthesis. Polyaniline can be used as an electrode material [1,2], an electronic material [3] and in microelectronics [4]. Technological applications in the area of recordable optical disks [5] and sensors have also been realized [6]. The commercial applications of polyaniline, however, are limited owing to its poor processability and intractable nature [7]. In the last few years considerable progress has been made in the processing of polyaniline by preparing copolymers of polyaniline with suitable aniline derivatives (alkyl, alkoxy, halide, etc.) [8,9], preparation of blends and composites, etc. In general, an increase in the solubility is achieved at the expense of conductivity. Polyaniline polymers with sulphonic acid groups either on the ring or on the nitrogen atoms, are more soluble and usually show relatively higher conductivity depending on the substitution [10–12]. Incorporation of the acidic groups like carboxylic [13,14], sulphonic [15,16] and phosphonic [17] acids as substituents in the ring influences the acidity constants of the amine groups and appears to offer advantages in less acidic medium, since the conductivity does not fall off dramatically with increase in the pH as in the case of polyaniline. Self-doping could result from the polymerization of a mixture of aniline and an acid group substituted aniline.

Poly(*o*-amino benzoic acid), an aniline based polymer capable of self-doping is of interest as a soluble derivative of polyaniline. Poly(*o*-amino benzoic acid) is soluble in aqueous alkaline solutions, and in polar solvents such as *N*-methylpyrrolidone, dimethylsulphoxide, etc. Copolymers of aniline and amino benzoic acids have been synthesized by chemical [18–20] and electrochemical routes [13,21]. Chan et al. [18] and Nguyen et al. [19] have reported the synthesis of the copolymers of aniline and amino benzoic acid in acidic medium while Yan et al. [20] have employed alkaline medium. The yield obtained by the former method was low while improved yields have been reported by the latter method. These copolymers are potential precursors of polyaniline, which on losing the carboxylic acid group yield polyaniline [20].

In this paper, a novel route for the synthesis of poly(aniline-*co*-amino benzoic acid) copolymers exhibiting

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relatively higher conductivity and better yields is reported. To elucidate the effect of the substituent on the resulting polymer, aniline derivative with carboxylic acid substituent at the *o*/*m*-position has been copolymerized with aniline. The influence of the reaction temperature and the ratio of the two monomers in the feed have been studied. The synthesis was carried out using inverse emulsion method in the presence of an organic oxidant, namely benzoyl peroxide, in a heterogeneous medium of chloroform and water. Classical oxidative polymerization of aniline using ammonium persulphate in aqueous solution requires harsh reaction conditions. Since ammonium persulphate is a strong oxidizing agent and polymerization of aniline being exothermic, controlling the reaction temperature is rather difficult and consequently polymers with wide distribution of molecular weights may result. The removal of inorganic by-product (ammonium sulphate) from the polymer produced is also difficult. To overcome these limitations a mild organic oxidant namely benzoyl peroxide is used and the excess of oxidant can easily be removed using solvents such as acetone, which is used as a non-solvent in the inverse emulsion process.

Inverse emulsion polymerization consists of an aqueous solution of the monomer, which is emulsified, in a non-polar organic solvent and the polymerization is initiated with an oil-soluble initiator. The inverse emulsion process has several distinct advantages. The reaction takes place in a large number of loci dispersed in a continuous external phase in a heterogeneous system. The physical state of the emulsion system makes it easier to control the process. Thermal and viscosity problems are much less significant here than in bulk polymerization. The product of an emulsion polymerization can in many instances be used directly as a solution in the organic solvent without further processing. The copolymers are characterized by spectral, electrical and thermal studies.

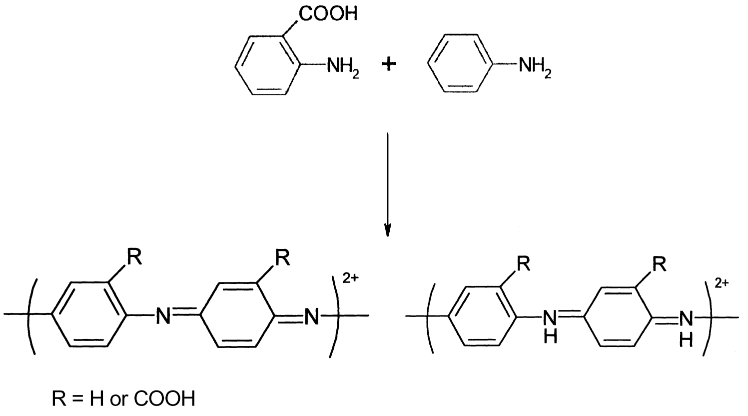
2. Experimental

2.1. Materials

Aniline (Merck) was distilled twice under reduced pressure. *o*-Amino benzoic acid (anthranilic acid) and *m*-amino benzoic acid (Fluka) were recrystallized from methanol. All other chemicals were analytical grade reagents and were used as procured.

2.2. Synthesis of poly(aniline-co-amino benzoic acid) copolymers

A typical synthesis under inverse emulsion procedure is as follows. 2.25 g of the emulsifier (sodium lauryl sulphate) in 30 ml of water and 3.43 g (0.1 M) of *o*-amino benzoic acid in 120 ml of water, which constitutes the continuous phase were added one after another with stirring to 12.12 g (0.2 M) of the oxidant (benzoyl peroxide) in 50 ml of chloroform. Aniline (2.4 ml, 0.1 M) was then added. To the resulting milky white emulsion, 50 ml of aqueous 1 M hydrochloric acid was added dropwise with continuous stirring over a period of half-an-hour. The emulsion gradually turns green. The reaction was allowed to proceed for 24 h. The organic phase was separated and washed repeatedly with water. The dark green polyaniline solution was then treated with anhydrous sodium sulphate to remove the excess of water. The viscous organic solution was then added to 1 l of acetone in order to break the emulsion and precipitate the copolymer. The product was filtered to obtain a dark green powder, which was washed with acetone and dried in vacuum for 36 h. The copolymers were synthesized at three different temperatures and the feed ratio of the two monomers was also varied. The synthesis of the copolymer of aniline with *m*-amino benzoic acid (in equimolar ratio) was also carried out employing the above procedure.



2.3. Characterization

For recording the UV–vis absorption spectra, a Hitachi U-3000 spectrophotometer was used. The solutions of the copolymer in dimethylsulphoxide (DMSO), *N*-methylpyrrolidone (NMP) and dimethylformamide (DMF) were used for recording the spectrum. The spectra were measured at three different concentrations and checked for consistency. The FT-IR spectra were recorded using a Bruker Equinox 55 instrument by the KBr pellet technique. The FT-Raman spectra were obtained using a Bruker RFS 100/S spectrometer using Nd^{3+}/YAG laser with 30–40 mW power at the sample. The EPR spectra were recorded using a Varian E109 spectrometer operating in the X-band. The sample tube was evacuated to remove the moisture before recording the spectrum. To obtain the g value and spin concentration, the EPR spectra of the samples and charred dextrose as a standard were recorded under identical conditions of microwave frequency (9.05 GHz), microwave power (2 mW), modulation frequency (100 kHz), fieldset (3280 G), scan range (100 or 200 G), modulation intensity (1 Gpp), modulation time (0.064 s) and scan time (200 s). The spin concentration was determined by comparing the area under the EPR signal of the polyaniline sample with that of charred dextrose. The calculated areas are likely to be within 5% of the true value [22]. The ^1H NMR and ^{13}C spectra were measured on a Bruker AMX 400 MHz spectrometer in DMSO-d_6 using TMS as an internal reference. The electrical conductivities (dc) were measured at ambient temperature by the four-probe method. The copolymers were pressed into pellets by applying a pressure of 50 kN. The error in the resistance measurements under galvanostatic condition using a Keithley model 220 programmable current source and a Kiethley model 195A digital voltammeter is less than 2%. The consistency in the measurements was checked by measuring the resistance twice for each pellet and for a batch of two pellets for each sample. The SEM measurements were carried out with a JEOL JSM 480A scanning electron microscope. The TGA and DTA were recorded up to 800 °C using a SDTA 851E thermal analyser at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. The C, H, N analysis was carried out using Heraeus D-6450 elemental analyser.

3. Results and discussion

Poly(aniline-*co*-amino benzoic acid) copolymers synthesized by the inverse emulsion polymerization have higher solubility in organic solvents such as NMP, DMSO and DMF. The copolymers synthesized presently are of high purity since the excess of benzoyl peroxide is readily removed with acetone, which is used to break the emulsion. The copolymers of aniline and *o*-amino benzoic acid synthesized at 0, room temperature and 60 °C with equimolar quantities of the two monomers in the feed are designated as C11OZ, C11O and C11OR, respectively, when the ratio of aniline to *o*-amino benzoic acid (anthranilic acid) is 1:2 and 2:1 as C12O and C21O, respectively, and the copolymer of aniline with *m*-amino benzoic acid obtained with a feed ratio 1:1 as C11M. The elemental analyses of the copolymers given in Table 1 are in good agreement with the copolymers of nearly the same composition prepared by the solution method [18] and the yields of the copolymers obtained presently are relatively higher. The conductivity of C11O (2.5×10^{-1} S cm^{-1}) prepared by the present method is higher compared to that obtained by the solution polymerization at the same temperature with sodium persulfate as the oxidant (7×10^{-3} S cm^{-1}) [18].

Table 1
Yield, conductivity and elemental composition of poly(aniline-*co*-amino benzoic acid) polymers

Sample	Yield (%)	Conductivity (S cm^{-1})	C, H, N analysis
Polyaniline–HCl salt		2.31	$C_{6.04}H_{8.12}N$
C11OZ	18.0	1.57	$C_{5.98}H_{8.04}N$
C11O	84.0	2.5×10^{-1}	$C_{6.85}H_{5.44}N$
C11OR	53.0	1.82×10^{-2}	$C_{7.23}H_{5.59}N$
C11M	75.4	1.91×10^{-1}	$C_{6.54}H_{5.19}N$
C12O	36.1	6.25×10^{-3}	$C_{7.64}H_{5.81}N$
C21O	78.8	8.10×10^{-1}	$C_{6.92}H_{5.89}N$

The yield decreases with increase in the amount of amino benzoic acid in the feed. It is consistent with the mechanism of polymerization proposed by Chan et al. [18]. The electron-withdrawing carboxylic acid group coupled with the steric factors deactivate the aromatic system retarding the polymerization of amino benzoic acid compared to that of aniline. Due to this electronic effect a higher potential is need to oxidize amino benzoic acid monomer.

3.1. Absorption spectra

Absorption spectroscopy is a valuable tool to detect the presence or otherwise of polyaniline salt and its base. The absorption maxima for the copolymers in three different solvents namely, dimethylsulphoxide (DMSO), dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP) are listed in Table 2. As representatives of the copolymers, the absorption spectra of C11O, C11OZ and C11M in DMSO are shown in Fig. 1.

The absorption spectrum of amino benzoic acid exhibits a band at 320 nm and a more intense band at 270 nm. The polyaniline–HCl salt in DMSO has fairly strong absorptions at 326, 433 and 630 nm and a weak one at 820 nm. The former peak is ascribed to the $\pi-\pi^*$ transition of the benzene rings and it is also present in the absorption spectrum of amino benzoic acid. The 630 nm absorption band has been attributed as due to excitonic transition ($n-\pi^*$) between the HOMO of the benzenoid ring (non-bonding nitrogen lone pair) and the LUMO (π^*) of the

Table 2
Absorption maxima for the copolymers in different solvents

Sample	λ_{max} (nm)												
	NMP			DMF				DMSO					
Polyaniline–HCl									326	433		630	820
C11OZ	279	323	560	275	328		584	288	328	442		620	
C11O	272	324	560	272	330		575	269	331	431		623	870
C11OR	269	300	550	272			557	269	320		560		
C12O	280	333	530	272	332	390	540	299	322	430		637	884
C21O	272	340	535	270	330		630	274	332	393	545		
C11M	268	350	525	267	353		541	274		380	575		

quinoid ring [23]. The remaining peaks at 430 and 820 nm have been assigned as due to the polaron transitions [24]. These bands are characteristic of the polyaniline salt and do not occur in the spectrum of the base.

The spectra of the copolymers show bands around 270 and 320 nm with varying intensities depending on the amount of amino benzoic acid in the copolymer. The copolymers have two different monomer units and the variation in a given monomer content along the polymer chain results from the difference in the reactivities between the two monomers and the rate of polymerization. The steric effect of the –COOH group causes loss of coplanarity of the π system obstructing charge delocalization along the chains resulting in decreased conductivity (Table 1) [18]. The exciton band around 630 nm therefore undergoes a hypsochromic shift when the amount of amino benzoic acid in the feed is enhanced and also when the temperature at which the reaction is carried out is higher (Table 2). Increased rate of polymerization of amino benzoic acid is expected at a higher temperature. The band at 623 nm in the copolymer C11O is blue shifted in the analogous copolymer of aniline and *m*-amino benzoic acid indicating that the quinone diimine content in the latter is relatively lower than in the former (Fig. 1) [20]. A weak to medium intensity band at 850 nm is observed for the copolymers, C11O and C21O (Fig. 1). The 850 nm band attributed to the polaron transition in the polyaniline salt is absent in the spectrum of the base [24]. There is a small amount of base always associated with the polyaniline salt. Therefore, the bands at 850 and 430 nm appear in the solution spectra only when the salt is more soluble. Hence, due to the higher solubility of the copolymers in DMSO, the peak at 850 nm is observed (Table 2).

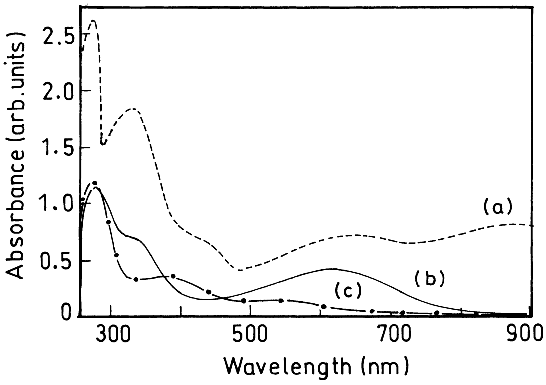


Fig. 1. The electronic absorption spectrum of (a) C11O, (b) C11OZ and (c) C11M in DMSO.

The absorption peak around 630 nm undergoes a blue shift when the solvent is changed from dimethylsulphoxide to dimethylformamide and to *N*-methylpyrrolidone (Table 2). For example, the 560 nm band of C11OR in dimethylsulphoxide shifts to 557 and 550 nm in dimethylformamide and *N*-methylpyrrolidone, respectively. With decreasing dielectric constant of the solvent (ε, DMSO 46.68. DMF 36.71 and NMP 32.21), the absorption band undergoes a hypsochromic shift [25]. This can be explained on the ability of the solvent to interact with the amine group as hydrogen bond acceptors thus replacing the interchain hydrogen bonding between the amine group acting as donors and the imine groups of the adjacent chains as acceptors.

3.2. FT-IR and FT-Raman spectra

The assignments of the infrared and Raman bands of the copolymers are based on those of aniline, *p*-diaminobenzene and *p*-benzoquinone which are supported by the ab initio molecular orbital calculations of the vibrational spectra [26–28]. The IR spectra of C11O and C21O recorded as KBr pellet are shown in Fig. 2. The FT-IR spectra of poly(aniline-*co*-*o*-amino benzoic acid) copolymers display an intense band at 1580 cm^{-1}, which is assigned to the C–C ring stretching vibrations of the benzenoid ring. The strong band near 1450 cm^{-1} is due to C–N stretching mode of the quinoid ring, which arises due to the protonation of polyaniline by the dopant (HCl as well as –COOH of amino benzoic acid). The peak at 1295 cm^{-1} (strong) corresponds to N–H bending. The medium intensity band at 1235 cm^{-1} in the spectra corresponds to C–N stretching modes of the benzenoid ring. A fairly strong band at 935 cm^{-1} is assignable to the ring-breathing mode of the quinoid group, which becomes active on protonation. The 708 cm^{-1} band is due to NH_2 wagging of the protonated group. The bands at 1295, 1235 and 708 cm^{-1} observed in the spectrum of the polyaniline salt remain unshifted in the spectra of the copolymers. However, the bands at 1560 and

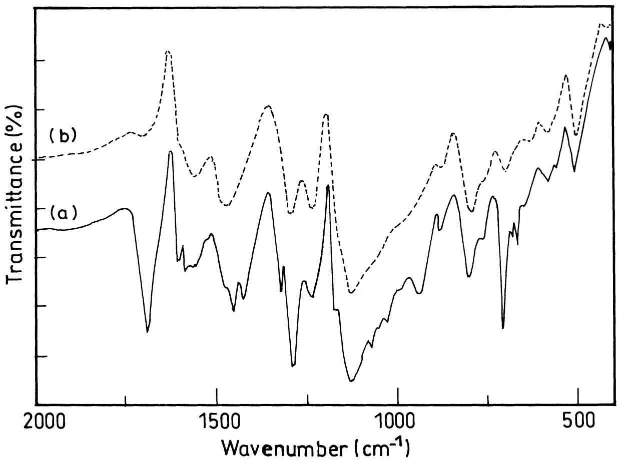


Fig. 2. The FT-IR spectra of (a) C11O and (b) C21O.

1479 cm^{-1} observed in the polyaniline salt spectrum are shifted to higher and lower wavenumbers, respectively, by nearly 20 cm^{-1} in the spectra of copolymers. A shift of nearly 6 cm^{-1} occurs for the band at 935 cm^{-1} in the copolymer spectra. The shifts are somewhat larger when the amount of amino benzoic acid in the copolymer is higher.

The copolymers give rise to new bands at around 1690 and 668 cm^{-1} due to C=O stretching and bending modes, respectively, of amino benzoic acid. The spectra of C11O, C11OR and C12O show an intense band at 1690 cm^{-1} while in the spectrum of C21O, it is of moderate intensity and weak in the spectrum of C11OZ. The intensity of this band increases with increase in the amount of amino benzoic acid in the feed (Fig. 2). A similar trend was observed for the band at 668 cm^{-1}. They serve as a measure of amino benzoic acid content in the copolymer. A new band observed in the spectra of copolymers at 755 cm^{-1} corresponds to the C–H out-of-plane bending vibration of the trisubstituted benzene ring. In addition, all the copolymers show an infrared band around 875 cm^{-1} which was observed by Thiemann and Brett [21] for the electrochemically synthesized poly(aniline-*co*-*o*-amino benzoic acid) copolymer films. The spectra of poly(aniline-*co*-*o*-amino benzoic acid) and poly(aniline-*co*-*m*-amino benzoic acid) are similar.

The FT-Raman spectrum of the polyaniline salt exhibits characteristic bands around 1617, 1589, 1535, 1499, 1358, 1335, 1256, 1171, 513 and 410 cm^{-1}. The amino benzoic acid shows an intense band at 770 cm^{-1} apart from other relatively strong bands at 3082, 1623, 1563, 1348 and 1240 cm^{-1}. The Raman spectrum of amino benzoic acid contains bands in the same region as that of the polyaniline salt. Hence, they are not very prominent in the spectra of the copolymer. However, the spectra of the copolymers do show additional splitting in the overlapping regions with appearance of weak to medium intensity bands. For example, the spectrum of C11O shows split bands around 1330 and 1500 cm^{-1}. For the copolymers synthesized at 60 °C, the band at 1617 cm^{-1} in the spectrum of polyaniline salt attributed to a Raman active –C=C– ring stretching vibration of the quinoid structure decreases in intensity due to decreased conjugation with increase in amino benzoic acid content. The 1358 cm^{-1} band corresponding to the C–H bending mode shifts by about 10 cm^{-1} and narrows in the spectra of the copolymers synthesized at a higher temperature. The intensity of the 1250 cm^{-1} peak due to N–H bending increases and shifts by nearly 8 cm^{-1}. Similar observations have been made for the absorption at 1589 cm^{-1} and the less intense band at 1499 cm^{-1} broadens which are assigned to the C–C ring stretching vibrations of the quinoid and benzenoid rings, respectively. Moderately intense bands at 524 and 417 cm^{-1} in the spectra of polyaniline salts assignable to the out-of-plane ring bending modes decrease in intensity in the copolymer with increase in the temperature at which synthesis is carried out. The Raman band at 780 cm^{-1} in the amino benzoic acid shifts to around 810 cm^{-1} in the copolymer and its intensity varies with the amount of amino benzoic acid in the feed. Similar changes were found in the Raman spectra of the copolymers when the feed ratio of amino benzoic acid to aniline was varied. The Raman spectrum of C11M is similar to that of C11O, however, the medium intensity peak at 1233 cm^{-1} shifts to 1244 cm^{-1} and the peak at 1505 to 1512 cm^{-1} in the former. Thus due to the different conformation of the polymer and the extent of doping, the frequency of the C–C stretching vibration varies. The shift in the frequencies of the peaks in the Raman spectra of the copolymers increase with increase in the amount of amino benzoic acid in the copolymer indicating interaction between aniline and amino benzoic acid units of the copolymer.

The strong intramolecular interaction between COO$^-$ groups and polaronic nitrogen atoms or hydrogen bonding can give rise to favourable five or six membered chelates, in which the movement of electrons is more localized. Therefore self-doping by carboxylate group is much less effective than external doping by HCl. The steric effect of the carboxylate group due to intermolecular interaction between COO$^-$ group and hydrogen on the adjacent phenyl is likely to force the aromatic rings out of the plane relative to each other lowering the degree of conjugation. The torsional angle between the aromatic rings may increase in order to relieve steric strain. Evidence for restrictions to π-conjugation has been obtained from UV–vis and FT-IR spectroscopy and cyclic voltammograms of poly(aniline-*co*-*o*-amino benzoic acid). Chan et al. [18] have obtained evidence for self-doping from X-ray photoelectron spectroscopy and have reported a steady decrease in the Cl$^-$/N$^+$ ratio for the copolymers of aniline with *o*-amino benzoic acid with an increasing proportion of aminobenzoic acid in the copolymer feed. This therefore implies that some of the nitrogen atoms have been self-doped to maintain charge neutrality and self-doping by the carboxylate group seems to be very much less effective than the corresponding doping by HCl. The conductivity was found to be dependent on the type of proton involved. Nguyen and Diaz [19] also

Table 3
EPR data for the poly(aniline-*co*-amino benzoic acid) copolymers

Sample	Spin concentration (spins g^{-1})	g value	A/B ratio	ΔH (G)
C11OZ	1.186×10^{20}	2.0027	0.98	2.25
C11O	2.379×10^{19}	2.0034	1.03	2.75
C11OR	3.459×10^{19}	2.0026	1.01	4.75
C11M	1.833×10^{20}	2.0060	1.04	2.75
C12O	9.453×10^{18}	2.0044	0.99	3.50
C21O	2.566×10^{19}	2.0037	1.02	2.50

observed a decrease in conductivity from 5.2 for polyaniline salt to 10^{-8} S cm^{-1} for poly(*o*-amino benzoic acid) as the amount of amino benzoic acid increases in the copolymer. The decrease in conductivity is attributed to the decrease in the number of charge carriers and conjugation length.

3.3. EPR spectra

The spin concentration, line width (ΔH), g value and the A/B ratio (i.e. the ratio of the height of positive to the negative peak) for poly(aniline-*co*-amino benzoic acid) copolymers are given in Table 3. The ambient temperature EPR signals of the copolymers display a single signal without any hyperfine structure. The g value of the copolymers lies in the range 2.0026–2.0044, which is close to that of the free electron. The A/B ratio is nearly unity, indicating that the spins are free electron type. The g value and the A/B ratio do not reveal the nature of polyaniline (salt or base) present. The spin concentration and line widths help to detect the salt/base form of polyaniline. For polyaniline salts, the spin concentration is high and lie around 10^{19}–10^{20} spins g^{-1} and the value of ΔH is low, lies between 2.0 and 3.5 G. The value of ΔH for the copolymers is close to that of the polyaniline salt. However, the spin concentration for the copolymers decreases with increase in the amount of amino benzoic acid in the feed as noted for C11O and C12O, for which the spin concentration decreases from 10^{19} to 10^{18} spins g^{-1}. The extent of polymerization of amino benzoic acid at low temperature is low and hence the conductivity and spin concentration of C11OZ is high (1.57 S cm^{-1} and 1.186×10^{20}, respectively).

3.4. NMR spectra

The proton NMR spectrum of polyaniline–HCl salt synthesized at room temperature exhibits signals near δ 7.3 and 6.95 ppm due to the aromatic protons of the quinoid (doped state) and the benzenoid rings, respectively. As representative of the copolymers, the proton NMR spectra of C11O is shown in Fig. 3. The proton NMR spectra of both *ortho* and *meta*-amino benzoic acid show signals in the aromatic region. While the spectrum of *o*-amino benzoic acid shows resonances at δ 7.89, 7.33, 7.27, 6.71 and 6.62 ppm, that of *m*-amino benzoic acid exhibits signals at δ 7.37, 7.32, 7.17, 6.87 and 6.30 ppm. The spectra of the copolymers display signals due to both polyaniline salt and amino benzoic acid with some shifts in the position of the peaks. The peak at $\delta = 11.0$ ppm assignable to the OH proton of *m*-amino benzoic acid is shifted to nearly 9.6 ppm in the spectrum of C11M. The protons at 3 and 6 positions of *o*-amino benzoic acid appearing at 7.86 and 6.71 ppm, respectively, shift to 7.96 and 7.04 ppm in the spectra of C11O and C11OR. Similar shifts are also observed in the spectrum of C11M in the aromatic region. The shifts indicate the formation of copolymers from the polymerization of the two monomers. The signal at δ 3.81 ppm in the spectrum of polyaniline salt assigned to the N–H shifts to 3.5 ppm in the copolymers. In order to confirm this assignment the spectrum was recorded in DMSO-d_6 after adding a drop of D_2O. Due to exchange between D_2O and N–H proton, the intensity of the signal at 3.5 ppm decreases dramatically demonstrating its origin from N–H proton.

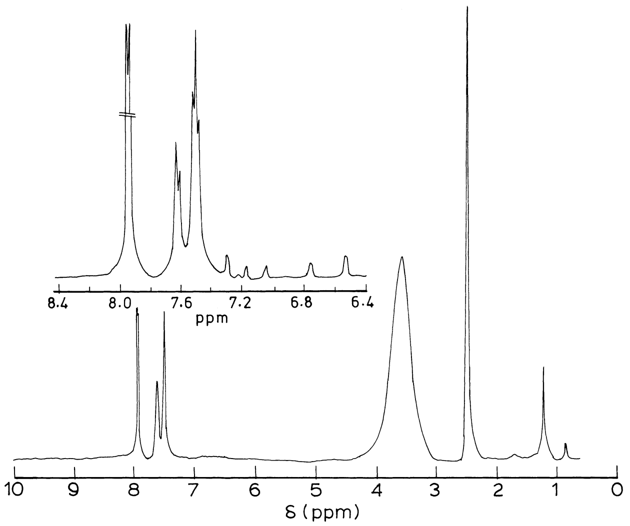


Fig. 3. The ^1H NMR spectra of C11O.

The ^{13}C spectra exhibit resonances supporting the presence of amino benzoic acid and polyaniline salt in the copolymers. Several peaks are found in the region, δ 120–170 ppm. The copolymer C11OR due to its higher solubility gives a better spectrum than C11O. The moderately intense signal at δ 136.9 ppm corresponding to the –CH carbon of the quinoid rings of polyaniline [29] occur around 135 ppm in the copolymers. The signals at δ 129.8 and 128.2 ppm attributed to the C–H carbons of the benzenoid rings [30] register small shifts in the spectra of the copolymers. The signal due to the carboxylate carbon of amino benzoic acid at 169.5 ppm shifts to around 167 ppm in the spectra of C11O, C11OR and C11M. This band is not observed in the other copolymers due to the weak signal intensity of the quaternary carbon. These shifts once again indicate chemical interaction possibly of hydrogen bonding type between the monomers in the polymer.

3.5. Conductivity

The conductivity of the copolymers given in Table 1 varies over a wide range from 1.57 to 6.25×10^{-3} S cm^{-1} depending on the temperature at which synthesis of the copolymer is carried out and the feed ratio of the monomers. The conductivity decreases from 0.81 to 6.25×10^{-3} S cm^{-1} when the feed ratio of the monomers, aniline/*o*-amino benzoic acid is changed from 2:1 to 1:2, respectively. The decrease in conductivity with increase in the amount of amino benzoic acid in the feed could be attributed to an increase in the band gap owing to decreased conjugation along the chain as inferred from the absorption spectra. A similar decrease in conductivity was noted when the polymerization was carried out at a higher temperature (Table 1). It may be due to an increased rate of polymerization of amino benzoic acid at a higher temperature. The position of the carboxylate group apparently does not seem to significantly affect the conductivity since both C11O and C11M have nearly the same conductivity. The conductivity of the copolymers is lower than that of the polyaniline–HCl salt. Therefore self-doping by the carboxylate group seems to be much less effective than external doping by HCl as discussed earlier.

The conductivity of C11O (2.5×10^{-1} S cm^{-1}) synthesized presently is two orders magnitude higher than that of the copolymer obtained by the solution method with ammonium persulphate and sodium persulphate as the oxidant which shows a conductivity of 4.5×10^{-5} and 7×10^{-3} S cm^{-1}, respectively [18,19]. Similarly the conductivity of C12O prepared by solution method shows a conductivity of 2×10^{-5} S cm^{-1} [18] which is lower by two orders of magnitude than the copolymer of the same composition synthesized by the present method using the inverse emulsion process (Table 1). The higher conductivity of polyaniline obtained by the present method could be attributed as due to a more homogenous protonation of the imine nitrogen and a more ordered chain conformation of the copolymer. It is known that a more ordered chain conformation leads to higher conductivity [31,32].

3.6. Morphology

The SEM micrographs were used to investigate the morphology of the copolymers. Polyaniline shows an amorphous morphology. The copolymers, however, display two features, one of amorphous and the other of crystalline domain. The crystalline morphology may result from intramolecular hydrogen bonded amino benzoic acid units [20]. The particles are sharp edged with lamellar structure on one side. The copolymer particles show rough pattern on one side and a comparatively smoother one on the other side (Fig. 4). The difference in morphology between polyaniline and its copolymers with amino benzoic acid as shown in Fig. 4 may be associated with different reactivities of the two monomers [21].

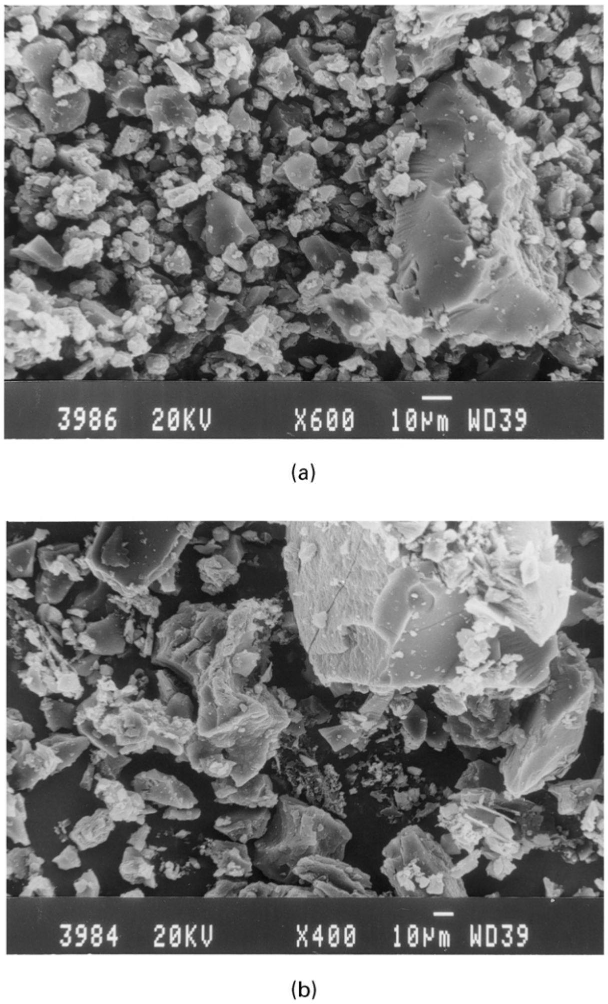


Fig. 4. The SEM micrograph of (a) C11M and (b) C11O.

3.7. Thermal studies

The TGA profiles of C11O and C11M are shown in Fig. 5 as representatives of the copolymers. The TGA of polyaniline–HCl salt shows a three-step weight loss commencing at 50, 130 and 430 °C. The weight loss in the first and second steps corresponds to the loss of moisture and the dopant, respectively. A slow and somewhat gradual weight loss profile after 430 °C is due to the degradation of the salt.

The TGA curves of the copolymers, like the polyaniline salt, also exhibit a three-step weight loss. In the first step beginning around 50 °C, the weight loss is attributed to the loss of moisture, volatilization of solvent or adsorbed HCl. The second step that starts around 165 °C accounts for the loss of the dopant along with the evolution of carbon dioxide. The third step around 425 °C is attributed to the decomposition of the copolymers. When the amount of *o*-amino benzoic acid in the feed is higher, the commencement of the second step occurs at a higher temperature and the weight loss is also higher. For example, the second step for the copolymer C11O occurs at 162 °C with a weight loss of 16%, while for C12O it occurs at 210 °C with a weight loss

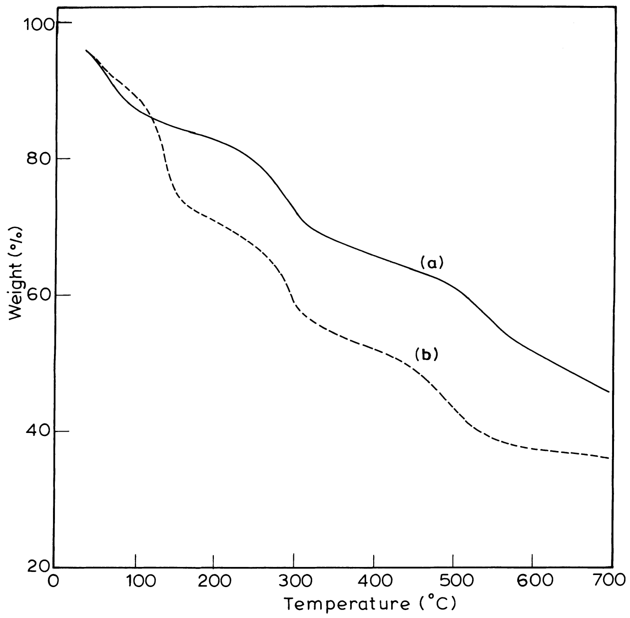


Fig. 5. The TGA profiles of (a) C11O and (b) C11M.

of 22.4%. The copolymers, however, do not offer any advantage regarding the thermal stability as noted from an earlier study too [18]. Yan et al. [20] observed that the weight loss at 100 °C is lower in the copolymers and they associated it to the copolymer being less doped by HCl and hence contain fewer binding water molecules. This was, however, not noticed in the present study. The copolymer C11M degrades at a marginally higher temperature (444 °C) than the corresponding *o*-amino benzoic acid copolymer C11O (413 °C).

4. Conclusions

Poly(aniline-*co*-*o*/*m*-amino benzoic acid) copolymers which show relatively higher electrical conductivity were synthesized in high yields by chemical polymerization of aniline and *o*/*m*-amino benzoic acid using an inverse emulsion pathway. The rate of polymerization of amino benzoic acid, which is relatively lower than that of aniline, increases if the synthesis is carried out at a higher temperature. The solubility of the copolymer increases with the amount of amino benzoic acid in the feed. Evidence for the presence of amino benzoic acid and aniline segments in the copolymer has been obtained by IR, Raman and NMR spectra. The EPR spectra of the copolymers indicate a decrease in spin concentration when the amount of amino benzoic acid content in the copolymer is higher. The steric effect of the −COOH group along the polymer chain possibly causes loss of coplanarity of the π system obstructing charge delocalization along the chains resulting in decreased conductivity. The SEM micrographs of the copolymers reveal regions of amorphous and crystalline domain. The thermal stability of *m*-amino benzoic acid copolymer with aniline is marginally higher than that of its analogous *o*-amino benzoic acid copolymer.

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