Synthesis and Characterization of Electrically Conducting Poly(*o-/m-* toluidine-*co-o-/m*-aminoacetophenone) copolymers

P SAVITHA, D.N.SATHYANARAYANA

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

ABSTRACT: A series of poly(*o-/m*-toluidine-*co-o-/m*-aminoacetophenone) copolymers combining the features of high conductivity and processibility have been synthesized and characterized by a number of techniques including ^{1}H nuclear magnetic spectroscopy (^{1}H NMR), thermogravimetry (TGA/DTA), infrared, Raman and UV-visible spectroscopy, scanning electron microscopy and X-ray diffraction. The copolymers were synthesized by the emulsion and inverse emulsion methods using conventional ammonium persulphate and a new oxidant namely benzoyl peroxide respectively. The influence of the polymerization conditions such as the monomer feed ratios, solvent and the non-solvent has been investigated. The composition of the resulting copolymers has been determined by ^{1}H NMR analysis. The conductivity of the copolymers varies with the aminoacetophenone content in the feed and on the polymerization conditions. Interestingly, the conductivity of the copolymers is higher than that of the corresponding homopolymers. The results have been rationalized on the basis of the effect of the -$COCH_3$ substituent on the polymer structure.

Keywords: conducting polymer, copolymerization, poly(*o-/m*-toluidines), poly(*o-/m*-aminoacetophenone)s, emulsion and inverse emulsion polymerization

---

Correspondence to: D.N.Sathyanarayana (E-mail: dns@ipc.iisc.ernet.in)

INTRODUCTION

In the past few years polyaniline (PANI) has been one of the most widely studied material in the search for commercially viable conducting polymers because of its unique reversible proton dopability, chemical stability, easy synthesis and variable electrical conductivity.[1] PANI can be used in applications as an electrode material, in the fabrication of secondary batteries, in microelectronics, as antistatic material and as chemical sensor.[2] However the commercial use of PANI has been hampered by its intractable nature because of its insolubility in common organic solvents. The use of substituted polyaniline has been attempted mainly to increase the processibility of polyaniline but this approach usually results in the lowering of conductivity. Recent methods to improve the processibility of doped polyaniline include the preparation of polymer composites and blends as well as copolymers. The copolymerization of aniline with a suitable solubilizing comonomer should lead to a copolymer which is soluble and conducting.

Our laboratory has been focussing on this strategy of the synthesis and characterization of copolymers as new conducting polymeric materials with improved processibility.[3,4] The copolymerization of toluidine and aniline monomers has been studied in recent years.[5,6,7]. They possess higher solubility but lower conductivity than that of polyaniline. Copolymers of toluidines with aniline derivatives having electron withdrawing sulphonic acid substituent groups were found to exhibit better conductivity than aniline-toluidine copolymers.[8] In this context copolymers of toluidines with aminoacetophenones are of interest; they may exhibit good solubility and higher conductivity than polytoluidine homologues and hence possess improved processibility. They may also provide information regarding the structure-property relationships governing conductivity.

It is known that emulsion polymerization increases the interaction between the oxidant, dopant and the monomers since the reaction occurs in a large number of loci dispersed in a continuous phase providing a larger surface area for polymerization to take place.[9] Inverse emulsion polymerization offers an alternative method. Here a novel oxidizing agent namely benzoyl peroxide which is a milder oxidant than ammonium persulphate has been employed. As an oxidizing agent, benzoyl peroxide has been shown to yield polymers of higher purity and better solubility.[10]

In this paper we report the chemical syntheses of copolymers of various compositions of *o-/m*-toluidine with *o-/m*-aminoacetophenone by two methods - emulsion as well as inverse emulsion - using ammonium persulphate and benzoyl peroxide as the oxidants respectively using various feed ratios of the monomers. The resulting copolymers have been characterized by UV-visible, IR, Raman and NMR techniques. Thermal stability has been determined by TGA/DTA measurements. The morphology of the materials and electrical conductivity have been investigated. The composition of the copolymers by ^{1}H NMR analyses is also determined. Results are discussed on the basis of electron withdrawing and steric effects of the -$COCH_3$ side chain.

EXPERIMENTAL

Materials

o-/m-Toluidine (Merck) was distilled twice and *m*-aminoacetophenone (Merck) was recrystallised from ethanol before use. *o*-Aminoacetophenone (Aldrich) and all other chemicals (analytical grade) were used as procured.

Chemical Synthesis of the copolymers.

Emulsion method: *m*-Aminoacetophenone (1.7 g, 0.05M) was dissolved in 100 mL of the solvent (chloroform or toluene). An aqueous solution of sodium lauryl sulphate (2.25 g in 50mL of water, 0.1 M) was added to it under constant stirring to obtain a milky white emulsion. *o-/m*-Toluidine (1.1 mL, 0.05M) was afterwards added to it followed by the dropwise addition of 50 mL of dopant HCl (1 M) and 50 mL of an aqueous solution of the oxidant (ammonium persulphate, 5.7 g, 0.1 M). The reaction was allowed to proceed for 24 h. The organic phase was separated and washed repeatedly with water. It was then added to 600 mL of a non-solvent namely acetone or petroleum ether to precipitate the copolymer. After 10 h, the precipitate was filtered under suction, washed with excess of the non-solvent and dried under vacuum for 72 h.

Inverse emulsion method: A solution of benzoyl peroxide (12.1 g, 0.2 M) in 100 mL of the solvent was taken. An aqueous solution of sodium lauryl sulphate (2.25 g in 50 mL of water, 0.1 M) was added to it under constant stirring to obtain a milky white emulsion. *m*-Aminoacetophenone (1.8 g, 0.05 M) was then added to it followed by the addition of *o*-toluidine (1.1 mL, 0.05 M). To the resulting mixture, 100 mL of 1 M HCl was added dropwise and the polymerization reaction was allowed to proceed for 24 h. The organic phase was separated and washed repeatedly with water. It was then added to 600 mL of acetone as a non-solvent when the copolymer precipitates out. After 10 h, the precipitate was filtered under suction, washed with acetone and dried under vacuum for 72 h.

Measurements

UV-visible absorption spectra of the copolymers were recorded with a Hitachi U-3400 spectrophotometer for the solutions prepared in DMSO. FT-IR spectra were measured with a Bruker-IFS 55 instrument by the KBr pellet technique. FT-Raman spectra were recorded with a Bruker RFS-100/S spectrometer for the powder sample with a Nd^{3+}-YAG laser with a laser power of 60 mW at the sample. ^1H NMR spectra were recorded with a Bruker AMX 400 MHz instrument using tetramethyl silane as an internal reference. Conductivity was measured at room temperature by four-probe method on pressed pellets obtained by subjecting the powder to a pressure of 50 kN. The error in resistance measurements under galvanostic conditions with a Keithley model 220 programmable current source and a Keithely model digital 195A voltammeter was less than 2%. The TGA/DTA measurements were made using a Mettler Toledo Star System at a heating rate of 10°C per minute under nitrogen atmosphere. The scanning electron microscopic (SEM) measurements were carried out using a JEOL JSM 5600 L scanning electron microscope. The X-ray diffractograms (XRD) were recorded for the powdered materials with a Siemens D5005 X-ray diffractometer. A weighed amount of the copolymer (10 mg) was added to 2 mL of the solvent with magnetic stirring. Additional solvent was added at the rate 1 mL per 10 min till the copolymer was completely dissolved. This procedure was continued for 2 hr and the copolymers which did not dissolve completely during this period was taken as “partially soluble”.

Abbreviations for the copolymers synthesised

The copolymers of different compositions have been synthesized using three different molar ratios of the monomers, toluidine: aminoacetophenone of 1:3, 1:1 and 3:1 or 2:1, 1:1 and 2:1 when the monomer ratio of 1:3 did not yield the desired copolymers. *m*-Toluidine copolymers were synthesized only with *m*-aminoacetophenone for the monomer feed ratio of 1:1. The names of the copolymers have been abbreviated on the basis of the comonomer feed ratios, the oxidant, the solvent, and the non-solvent used for the copolymer synthesis. For example, OTMAP11CP refers to a copolymer synthesized employing a 1:1 monomer feed ratio of *o*-toluidine (OT) and *m*-aminoacetophenone (MAP). The solvent and the non-solvent were chloroform (C) and petroleum ether (P) respectively. Similarly OTMAP11C denotes an analogous copolymer where the non-solvent used was acetone (no abbreviation employed). For OTMAP11T, the solvent used was toluene while the copolymer OTOAP11CP was prepared employing *o*-toluidine and *o*-aminoacetophenone (OAP). For the copolymer OTMAP11BC synthesized by the inverse emulsion method, the oxidant used was benzoyl peroxide (B) and the solvent was chloroform (C). Similarly, MTMAP11BT refers to a copolymer synthesized using a 1:1 monomer feed ratio of *m*-toluidine and *m*-aminoacetophenone with toluene (T) as solvent. In the inverse emulsion method, the non-solvent used was always acetone. The homopolymer of OT and MT is denoted as POT and PMT respectively.

RESULTS AND DISCUSSION

Several poly (aniline-*co*-aminoacetophenone) copolymers synthesized are listed in Table 1 along with the various comonomer feed compositions used. The general structure of the copolymer salt is given in Figure1.

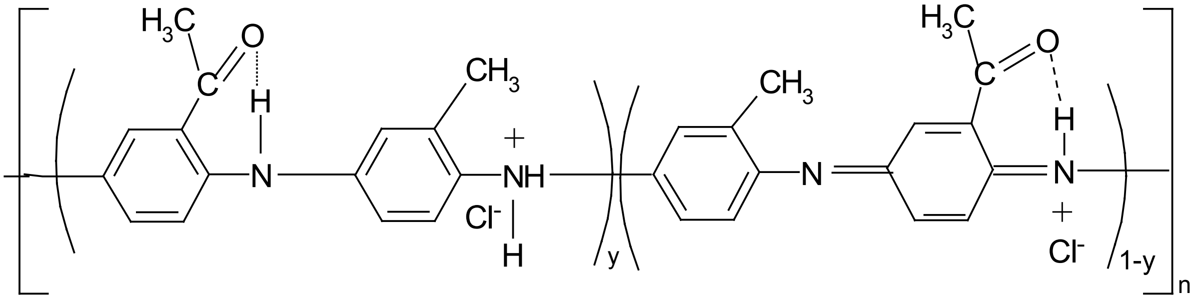


Figure 1

Yield

The yield of the copolymers generally decreases as the amount of *m*- or *o*-aminoacetophenone units in them increases (Table 2). This could be traced to the steric hindrance of the substituent $-COCH_3$ group. Higher yields of the copolymers were obtained when petroleum ether was used as a solvent compared to that when acetone was used. It may be due to petroleum ether leaving the oligomers undissolved. Further a higher proportion of the polymer chains particularly those containing greater *m*-aminoacetophenone units seems to dissolve in acetone as noted from FT-IR studies discussed later. *m*-Toluidine copolymers are generally obtained in higher yields compared to those of *o*-toluidine. However, by the inverse emulsion method, the reverse holds true. Further, better yield of the copolymers realized when chloroform was used as a solvent to carry out the reaction by inverse emulsion method may be due to the higher solubility of benzoyl peroxide in chloroform than in toluene.

Absorption Spectra

The UV-visible spectra of the copolymers OTMAP11BT and MTMAP11BT dissolved in DMSO are shown in Figure 2. The spectrum of *m*-aminoacetophenone exhibits two bands at 262 and 349 nm while that of *o*-aminoacetophenone in DMSO also shows two bands at 261 and 402 nm. The spectrum of the homopolymer poly(*o*-toluidine) in the emeraldine salt form consists of four bands at 311,443,608 and 790 nm. The absorption spectrum of poly(*m*-toluidine) - HCl salt is similar and the bands are found at 303, 423, 586 and 859 nm.

The spectra of all the copolymers generally show three or four absorption bands. The spectra of the copolymers for e.g. OTMAP11BT show four absorption bands. The first band at 313 nm is assigned to the $\pi - \pi^*$ transition of the phenyl rings based on earlier studies.[11] It is related to the extent of conjugation between the phenyl rings in the polymer chain. The extended conjugation of π orbitals is said to be responsible for conductivity which requires coplanarity of the atoms involved in π-electron delocalization for maximum resonance interaction.[12] Thus a small bathochromic shift of the 313 nm band relative to the band at 311 nm for poly(o-toluidine) implies a very small increase in the extent of conjugation for this copolymer. The second absorption band at 620 nm is assigned to the exciton transition caused by the interchain or intrachain charge transfer.[13] It is sensitive to the overall oxidation state of the polymer. This band in the copolymer also shows a bathochromic shift with respect to the homopolymer poly(*o*-toluidine). The remaining two bands at 436 and 846 nm are due to the polaronic transitions.[14]: The polaronic bands are found only in the spectrum of the salt and their presence indicates greater solubility of the copolymer salt in the solvent used since the intensity of these bands are very low. The peak at 850 nm in polyaniline has been assigned to $-NH_2^+-$ species which is generated on doping and a correlation between the intensity of this peak and the conductivity of the sample seems to exist.[4] The intensity of this peak at 846 nm is seen to be greater in the spectra of this copolymer OTMAP11BT which has the highest conductivity among all the copolymers.

The hypsochromic shift of the 315 nm band in some of the copolymers especially those synthesized using petroleum ether as non-solvent implies diminution in conjugation. The second absorption band in the region 540-620 nm show both hypsochromic and bathochromic shifts in the copolymers showing subtle changes in conjugation due to steric repulsion between the bulky $–COCH_3$ group and the phenyl ring hydrogens. It can be seen that the polaronic band is not observed in all the cases mainly due to the low solubility of the salt form of the copolymer in DMSO. The 450 nm absorption band is inherently very weak in intensity and small shifts of the neighbouring peaks may cause overlapping rendering it indistinguishable. The intensity of the peak around 800 nm is seen to be greater in the spectra of the copolymers of *o-/m*-toluidine with *m*-aminoacetophenone compared to that of the homopolymers.

Infrared spectra

The FT-IR spectra of the copolymers OTMAP11C and OTMAP11CP are shown in Figure 3. The FT-IR studies reveal the formation of the copolymers and help to obtain qualitatively their compositions. The infrared spectra of the copolymers synthesized by the two methods are nearly the same. The copolymer OTMAP11C shows a weak band at 3213 cm^{-1} assigned to $–NH_2^+$ stretching. The two main bands centered at 1600 and 1483 cm^{-1} in the spectrum correspond respectively to the ring-stretching vibrations of the quinoid and benzenoid rings. A band near 1383 cm^{-1} is assigned to the C-N stretching adjacent to the quinoid structure while the bands around 1180 and 1105 cm^{-1} are attributed to C-H deformation modes. These bands confirm the presence of poly(toluidine) segment in the copolymer backbone. The carbonyl bands of *m*-aminoacetophenone, at 1678 and 688 cm^{-1} assigned to the stretching and bending mode occur in the spectra of the copolymers confirming the presence of poly(*m*-aminoacetophenone) segments. The carbonyl bands of MAP are shifted to higher wavenumbers in the copolymer. The copolymers prepared using toluene as the solvent medium to carry out the reaction show more intense carbonyl peaks of *m*-aminoacetophenone when compared with those prepared in chloroform. Thus the extent of polymerization of *m*-aminoacetophenone is dependent on the nature of the medium. The intensity of the C=O bands is relatively low in the FT-IR spectra of the copolymer precipitated using acetone as a non-solvent for a given comonomer feed ratio (Figure 3) compared to that when petroleum ether was used as a nonsolvent. Acetone apparently dissolves the polymer segments having higher amount of *m*-aminoacetophenone units. The bands in the FT-IR spectra of *m*-toluidine-aminoacetophenone copolymers are shifted to higher frequencies compared to those of OT copolymers and the carbonyl stretching band for example shifts by nearly 11 cm^{-1}.

The spectra of the copolymers of *o*-toluidine with *o*-aminoacetophenone show the carbonyl peaks at 1643 and 669 cm^{-1} corresponding to the bands at 1647 and 701cm^{-1} respectively in the spectrum of the monomer OAP. The shift to lower wavenumbers of these bands indicates increased conjugation. Intramolecular hydrogen bonding in OAP may change to intermolecular hydrogen bonding on copolymer formation.

Raman Spectra

The Raman spectra support the formation of copolymers as deduced from the infrared spectra. The Raman band at 1610 cm^{-1} in the spectrum of the copolymer OTMAP11C is attributed to the C=C ring stretching vibration of the quinoid ring and that at 1490 cm^{-1} to C-C ring stretching vibration of the benzenoid ring. The 1366 and 1259 cm^{-1} bands are assigned to the N-H and C-H bending modes respectively. A band at 1311 cm^{-1} is assigned to the C (ring)-N stretching mode. These bands which are also found in the FT-Raman spectra of the homopolymer PMT/POT confirm the presence of POT/PMT segments in the copolymer. The intensities of the characteristic *m*-aminoacetophenone peaks at 1604, 1322, 948 and 547 cm^{-1}increase with the increasing amount of *m*-aminoacetophenone in the comonomer feed qualitatively revealing the composition of the copolymer. The copolymers of *o*-aminoacetophenone show very low intensity bands arising from *o*-aminoacetophenone units suggesting that in the copolymer the amount of OAP present is small. The copolymers obtained by the inverse emulsion method using chloroform as solvent show higher intensities for *m*-aminoacetophenone peaks than those prepared in toluene. The spectra of *m*-toluidine- *m*-aminoacetophenone copolymers show low intensity of *m*-aminoacetophenone peaks consistent with the IR spectra.

NMR Spectra

Figure 4 gives the NMR spectra of two copolymers OTOAP11CP and OTMAP11CP. The ^1H NMR spectra of the homopolymers POT-HCl / PMT-HCl salts consist of four main signals. The signals in the spectrum, for example of POT, in the region of δ 6.8 - 7.4 ppm correspond to the protons of the aromatic rings. The signal at δ 3.4 ppm arises from the -NH group. The bands in the region δ1.8 - 2.1 and 1.1 - 1.3 ppm are assigned to the protons of the methyl group on the quinoid and the benzenoid rings respectively. The spectrum of *m*-aminoacetophenone consists of a signal at δ 2.58 ppm due to methyl protons of the $-COCH_3$ group, another at δ 5.35 ppm due to the $-NH_2$ protons and two signals due to the aromatic protons at δ 6.8 and at 7.1 ppm. For *o*-aminoacetophenone, these resonances appear at 2.7, δ 6.4, 6.6,7.2 and 7.6 ppm respectively.

The ^1H NMR spectra of resemble the spectrum of POT/PMT. In the ^1H NMR spectrum of the copolymer OTMAP11CP for example the methyl protons of the quinoid ring of POT are shifted downfield from 2.03 to 2.25 ppm whereas the methyl protons of *m*-aminoacetophenone hardly show any shift. The signals due to the methyl protons of the benzenoid ring of the POT overlap with those of the surfactant impurity. The -NH proton resonance shifts downfield by 0.2 ppm to 3.6 ppm. The peaks due to the aromatic rings of toluidine and *m*-aminoacetophenone units occuring in the region of 6.9 to 8.1 ppm overlap. Thus the ^1H NMR spectrum supports the presence of polytoludine and polyaminoacetophenone segments. When the copolymer was precipitated using acetone, the intensity of the methyl peaks of *m*-aminoacetophenone decreased and the peaks of POT in the aromatic region were strengthened. It supports the inference drawn from the FT-IR spectra that acetone dissolves copolymers containing greater *m*-

aminoacetophenone segments. Similarly, the copolymers obtained when polymerization was carried out in toluene have higher intensity of *m*-aminoacetophenone peaks which is in accord with the FTIR spectra. The effect of the solvent and non-solvent used for the copolymerization on the spectra of the MT copolymers is similar to that noted for the OT copolymers.

The ^{1}H NMR spectra of the copolymers of toluidine with *o*-aminoacetophenone showed very low intensity peaks arising from *o*-aminoacetophenone indicating that *o*-aminoacetophenone undergoes polymerization to a lesser extent compared to *m*-aminoacetophenone due to steric hindrance of the $-COCH_3$ group and the intramolecular hydrogen bonding (Figure 4) consistent with the finding from IR spectra.

The copolymers prepared using chloroform as solvent medium by the inverse emulsion method showed distinct peaks for the aromatic protons of OT and *m*-aminoacetophenone (OT protons occur from 6.9 to 7.2 ppm and those of *m*-aminoacetophenone from 7.5 to 7.95 ppm). As noted from the FT-IR spectra, here too the intensity of the signals arising from *m*-aminoacetophenone protons was found to be higher when the polymerization was carried out in toluene than when chloroform was used. This clearly reflects the influence of the solvent used for polymerization in the inverse emulsion method. The spectra of the copolymers of *m*-toluidine with *m*-aminoacetophenone show that *m*-aminoacetophenone polymerizes more in the presence of MT when compared to the corresponding OT copolymers.

Composition of the copolymers: Compositions of the copolymers were determined by comparing the intensities for the methyl protons of $-COCH_3$ group (from aminoacetophenone) and the aromatic protons of the copolymer. Since the methyl protons of aminoacetophenone occurs at 2.6 ppm which is very close to the protons of the solvent DMSO (2.5 ppm) determination of the compositions of the copolymer was difficult in several cases due to overlapping. However the copolymers whose compositions could be determined clearly demonstrates the low reactivity of aminoacetophenone monomer compared to that of the toluidines. It also confirms the observation made from the NMR as well as IR spectra that acetone dissolves polymer chains containing greater aminoacetophenone segments.

Thermogravimetric analysis

The first weight loss step in the thermogravimetric analysis curves of the copolymers around 50-140 °C corresponds to the loss of moisture, volatilization of the solvent and adsorbed HCl. The second step in the TGA curves between 160 and 260 °C is due to the loss of dopant and concurrent evolution of CO_2. The third step occurring between 400 and 600 °C corresponds to the final degradation of the polymer. The first endothermic peak in the DTA curve correlates to the loss of adsorbed HCl and moisture in the TG study. The second endothermic peak between 250 and 300 °C can be attributed to the morphological changes and disruption of inter and intramolecular hydrogen bonding and loss of dopants. The exotherm denoting the final degradation step occurs around 525 °C.

The thermal stability of the copolymer increases when the amount of *m*-aminoacetophenone in the comonomer feed is higher. For example, when the *m*-aminoacetophenone content in the feed is varied from 0.033 M to 0.066 M (leading to the formation respectively of OTMAP21C and OTMAP12C) the degradation temperature increases significantly from 386 to 453 °C. It suggests extensive interchain linking and hydrogen bonding in these copolymers owing to the presence of the substituent $-COCH_3$ group. The copolymers of *m*-toluidine and *m*-aminoacetophenone show higher thermal stability than those of *o*-toluidine with *m*-aminoacetophenone. The copolymers synthesized by the inverse emulsion method have a higher thermal stability over those synthesized by the emulsion method. The solvent used to carry out polymerization seems to influence the thermal stability, for example, the degradation temperature of OTMAP11BC (458 °C) is slightly higher than that of OTMAP11BT(438 °C).

Scanning electron microscopy

The SEM micrographs have shown sharp edged granular particles with lamellar structure on one side and a smoother pattern on the other, similar to that of polyaniline salts.[10,15] The size of the particles increase with increasing *m*-aminoacetophenone content as noted from Figure 5. The size of the particles is smaller for *o*-aminoacetophenone-toluidine cpolymers than those of *m*-aminoacetophenone-toluidine copolymers. PMT and the copolymers of *m*-toluidine with aminoacetophenone have smaller particle size when compared to those of POT and the copolymers of *o*-toluidine-aminoacetophenone. The copolymers synthesized in toluene as well as those precipitated out using petroleum ether also have smaller particle size.

The conductivity of the copolymers was observed to be related to the particle size. For example, the copolymers OTMAP11BT and OTMAP11C which had larger particles than OTMAP11T and OTMAP11BC were seen to be more conductive.

X-ray diffraction studies

The diffraction patterns were typical of crystalline/amorphous copolymers. The crystalline regions in the copolymers are shown by the presence of relatively sharp peaks. The amorphous regions are visible by the broad low intensity halo Accordingly, the copolymer OTMAP21P is more crystalline than OTMAP11CP and OTOAP11CP. The more amorphous nature of PMT and the copolymers of *m*-toluidine with *m*-aminoacetophenone than those of POT and the copolymers of *o*-toluidine with *m*-aminoacetophenone was inferred from their diffraction patterns.

The position of the Bragg's peaks (2θ) also gives information on the morphology of the copolymers. The copolymers exhibit their strongest peak at 2θ = 23-25°, their second strongest peak at 8-10°, a medium intensity peak at 17-19° and a weak peak at 31-35°. The diffraction angle tends to be slightly smaller with increasing aminoacetophenone content. The number of diffraction peaks in the wide angle X-ray diffractogram also decreases. These results indicate that the introduction of aminoacetophenone units into polyaniline as in the copolymer increases intermolecular chain spacing and the amorphous nature of the copolymer because of the steric hindrance of the -$COCH_3$ group.

Conductivity

To avoid any dependence of the electrical conductivity of the copolymers on the post synthesis treatment, the washing procedure and the drying time of the polymer powders were verified to be identical. The conductivities of both copolymers and homopolymers are listed in Table 2. One does not see sharp variations in the magnitude of the conductivity when the comonomer feed compositions or polymerization conditions are varied. The measured conductivities remain relatively high and vary in a narrow region (10^{-2} to 10^{-3} S cm^{-1}).

The conductivity of the copolymers given in Table 2 is generally higher than that of the homopolymer either POT or PMT. Aminoacetophenone does not homopolymerize. The conductivity of the copolymers prepared using inverse emulsion method is generally high. The conductivity is probably determined by the number of carriers and the conjugation length along the polymer backbone. When the non-solvent used to precipitate the copolymer was petroleum ether, the conductivity decreases with increase in MAP units. However when the non-solvent used was acetone, a reverse trend was observed. The copolymers of *o*-toluidine with *o*-aminoacetophenone generally have lower conductivity than the corresponding copolymers with *m*-aminoacetophenone. The copolymers synthesized in toluene as solvent medium show higher conductivity than those synthesized using chloroform. This significant difference in conductivity could be due to the aromatic rings of toluene having $\pi-\pi^*$ type of interaction with the phenyl rings, inducing coplanarity of the phenyl ring chains leading to a higher conjugation and conductivity. This observation is also in accord with the large bathochromic shifts of the bands at 608 and 587 nm of POT and PMT respectively in the spectra of these copolymers as discussed earlier. The copolymers of *m*-toluidine have relatively lower conductivity than those of the OT copolymers. However the copolymer MTMAP11T shows a rather significantly higher conductivity. Similar trends in conductivity were noticed for the copolymers synthesized by the inverse emulsion method.

CONCLUSION

The effect of comonomer feed compositions and polymerization conditions on the conducting copolymers of *o-/m*-toluidine and *o-/m*-aminoacetophenone synthesized using emulsion and inverse emulsion techniques have been studied. Characterization of the copolymers by a host of techniques supports their proposed structure. The compositions of some of the copolymers have been determined by ^{1}H NMR analysis. These copolymers exhibit increased conductivity as well as solubility when compared to those of the homopolymers poly(*o*-toluidine) or poly(*m*-toluidine) . The copolymers synthesized using toluene as solvent medium by both the methods are more conducting than those synthesized using chloroform. Aminoacetophenones does not homopolymerize, however copolymers of aminoacetophenones with toluidines are readily obtained.

REFERENCES AND NOTES

1. Nguyen, M.T.; Kasai, P.; Miller, J. L.; Diaz, A.F. Macromolecules 1994, 27**,** 3625.

2. Chan,H.S.O.; HO, P.K.H; Ng, S.C.; Tan, B. T. G; Tan, K.L. J Am Chem Soc 1995, 117*,* 8517.

3. Rao,P.S.; Sathyanarayana, D.N. Polymer 2002, 43(18), 5051.

4. Rao,P.S.; Sathyanarayana, D.N. Synth Met 2003,138(3), 519.

5. Huang, M-.R.; Li, X.-G.; Yang, Y.-L.; Wang, X.-S.; Yan, D. J. Appl Polym Sci 2001, 81. 1838.

6. Wei, Y.; Hariharan, R; Patel, S.A. Macromolecules 1990,23,758.

7. Savitha, P.; Sathyanarayana, D.N. Polym Int 2004, 53, 106.

8. Rao, P.S.; Sathyanarayana, D.N. J Polym Sci Polym Chem 2002, 40, 4065.

9. Ruckenstin,E.; Sun, Y. Synth Met 1995,74,107.

10. Rao, P.S.; Sathyanarayana, D.N.; Palaniappan, S. Macromolecules 2002, 35*,* 4988.

11. Trivedi, D.C. In Handbook of Organic Conductive Molecules and Polymers: Nalwa, H.S., Ed.; John Wiley & Sons: Chichester, 1993; Vol 2, 505.

12. Chan, H.S.O ; Ng, S.C; Sim, W.S.; Tan, K.L.;, Tan, B.T.G. Macromolecules 1992*,* 25*,* 6029.

13. Kim, Y.H.; Foster, C.; Chiang, J.; Heeger, A.J. Synth Met 1989, 29, 285.

14. Tzou, K.; Gregory, R.V. Synth Met 1993, 53, 365.

15. Zhang, A.Q.; Cui, C.Q.; Lee, J.Y. Synth. Met. 1995, 72, 217.

Table 1. The copolymers of *o-/m*-toluidine (M_1) and *o-/m*-aminoacetophenone (M_2)

Sample	Solvent	Non-solvent	Monomer feed ratio, M_1/M_2	Copolymer composition, M_1/M_2
M_1=OT, M_2 = *m*-aminoacetophenone , oxidant: Ammonium persulphate				
POT	$CHCl_3$	Pet.ether	-	-
OTMAP13CP	$CHCl_3$	Pet.ether	1:3	#
OTMAP11CP	$CHCl_3$	Pet.ether	1:1	1:2
OTMAP31CP	$CHCl_3$	Pet.ether	3:1	3:1
OTMAP12C	$CHCl_3$	Acetone	1:2	#
OTMAP21C	$CHCl_3$	Acetone	2:1	11:1
OTMAP11C	$CHCl_3$	Acetone	1:1	#
OTMAP11T	Toluene	Acetone	1:1	#
M_1 = OT, M_2 = *o*-aminoacetophenone				
OTOAP11CP	$CHCl_3$	Pet.ether	1:1	#
OTOAP31CP	$CHCl_3$	Pet.ether	3:1	#
M_1 = OT, M_2 = *m*-aminoacetophenone, oxidant: Benzoyl peroxide				
OTMAP12BC	$CHCl_3$	Acetone	1:2	#
OTMAP21BC	$CHCl_3$	Acetone	2:1	#
OTMAP11BC	$CHCl_3$	Acetone	1:1	#
OTMAP11BT	Toluene	Acetone	1:1	#
M_1=MT, M_2 = *m*-aminoacetophenone , oxidant: Ammonium persulphate				
PMT	$CHCl_3$	Pet.ether	-	-
MTMAP13CP	$CHCl_3$	Pet.ether	1:3	#
MTMAP11CP	$CHCl_3$	Pet.ether	1:1	#
MTMAP31CP	$CHCl_3$	Pet.ether	3:1	3.3:1
MTMAP11C	$CHCl_3$	Acetone	1:1	#
MTMAP11T	Toluene	Acetone	1:1	5:1
M_1= MT, M_2 = *m*-aminoacetophenone , oxidant: Benzoyl peroxide				
MTMAP11BC	$CHCl_3$	Acetone	1:1	#
MTMAP11BT	Toluene	Acetone	1:1	#

'#' - could not be determined.

Table 2. Yield, conductivity, UV-visible spectra and solubility of the copolymers

Sample	Yield (%)	Conductivity (x 10^{-3} Scm^{-1})	Absorption spectra λ_{max}(nm) (in DMSO)	Solubility (g/l of DMSO)
POT	70	1.1	311, 443, 608, 790	–
OTMAP13CP	#	#	306, 541	–
OTMAP11CP	33	0.56	309, 576	2.9
OTMAP31CP	47	1.76	316, 611	–
OTMAP12C	19	5.22	311, 615, 816	3.3
OTMAP21C	33	1.82	312, 614, 780	–
OTMAP11C	17	1.83	314.0, 617, 798	–
OTMAP11T	18	7.69	311, 621, 814	2.5
OTOAP11CP	60	0.22	310, 593	2
OTOAP31CP	58	1.46	311, 442, 609, 826	–
OTMAP12BC	13	0.39	310, 603, 825	10
OTMAP21BC	36	2.34	314, 430, 609, 842	2.5
OTMAP11BC	31	9.2	315, 612, 831	3.3
OTMAP11BT	9	34	313, 436, 620, 846	2.5
PMT	80	0.51	303, 413, 587, 859	–
MTMAP13CP	#	#	-	–
MTMAP11CP	65	#	296, 555	5
MTMAP31CP	84	0.35	303, 424, 580	2
MTMAP11C	23	0.81	303, 428, 598, 802	4
MTMAP11T	15	31	313, 607, 845	–
MTMAP11BC	20	6.2	306, 590	3.3
MTMAP11BT	8	8.0	312, 605	–

couldnot be determined.

Table 3. Data for thermogravimetric analysis of the copolymers

Sample	Temperature range (°C) & weight loss (%)		
	1st step	2nd step	3rd step
OTMAP11CP	43-110 (3)	147 - 347 (32)	410
OTMAP21C	44-150 (9)	207 - 317 (15)	386
OTMAP11C	45-145 (5)	160-370 (34)	400
OTMAP12C	43-123 (5)	190-365 (21)	453
OTMAP11T	46-150 (6)	171-344 (27)	405
MTMAP11P	43-138 (6)	188 - 370	458
OTOAP11CP	50-140 (4)	183-360 (35)	420
OTMAP11BC	40-130 (8)	205-380 (26)	458
OTMAP11BT	43-124 (8)	180-347 (18)	438

Legends to Figures:

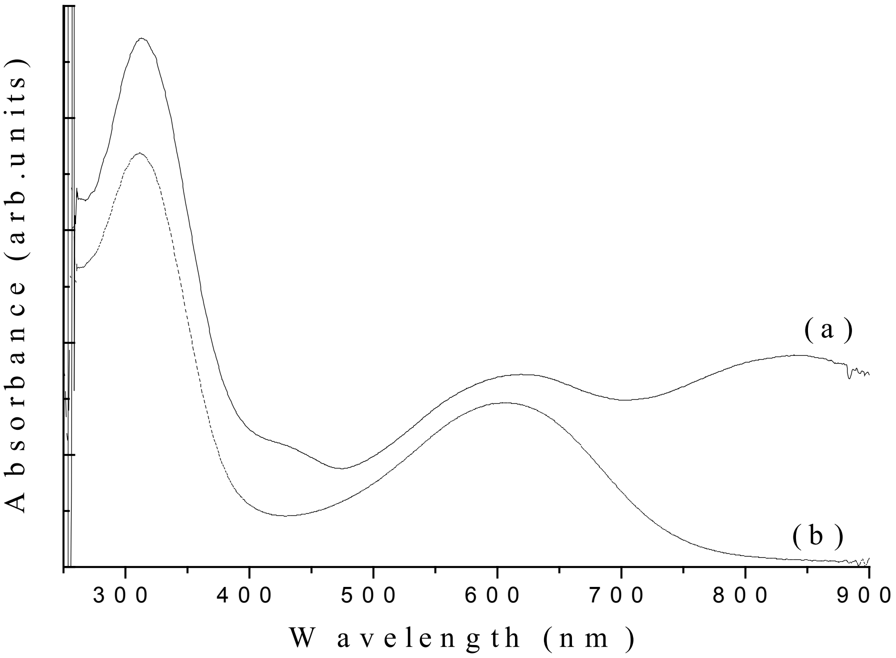
Figure 1. Schematic representation of the structure of the copolymer salt

Figure 2. UV-visible spectra of (a) OTMAP11BT and (b) MTMAP11BT

Figure 3. FT-IR spectra of (a) OTMAP11C and (b) OTMAP11CP

Figure 4. ^{1}H NMR spectra of (a) OTOAP11CP and (b) OTMAP11CP

Figure 5. SEM Micrographs of (a) OTAP11BC and (b) OTAP12BC



Absorbance (arb.units)
(a)
(b)
300
400
500
600
700
800
900
Wavelength (nm)

Figure 2.

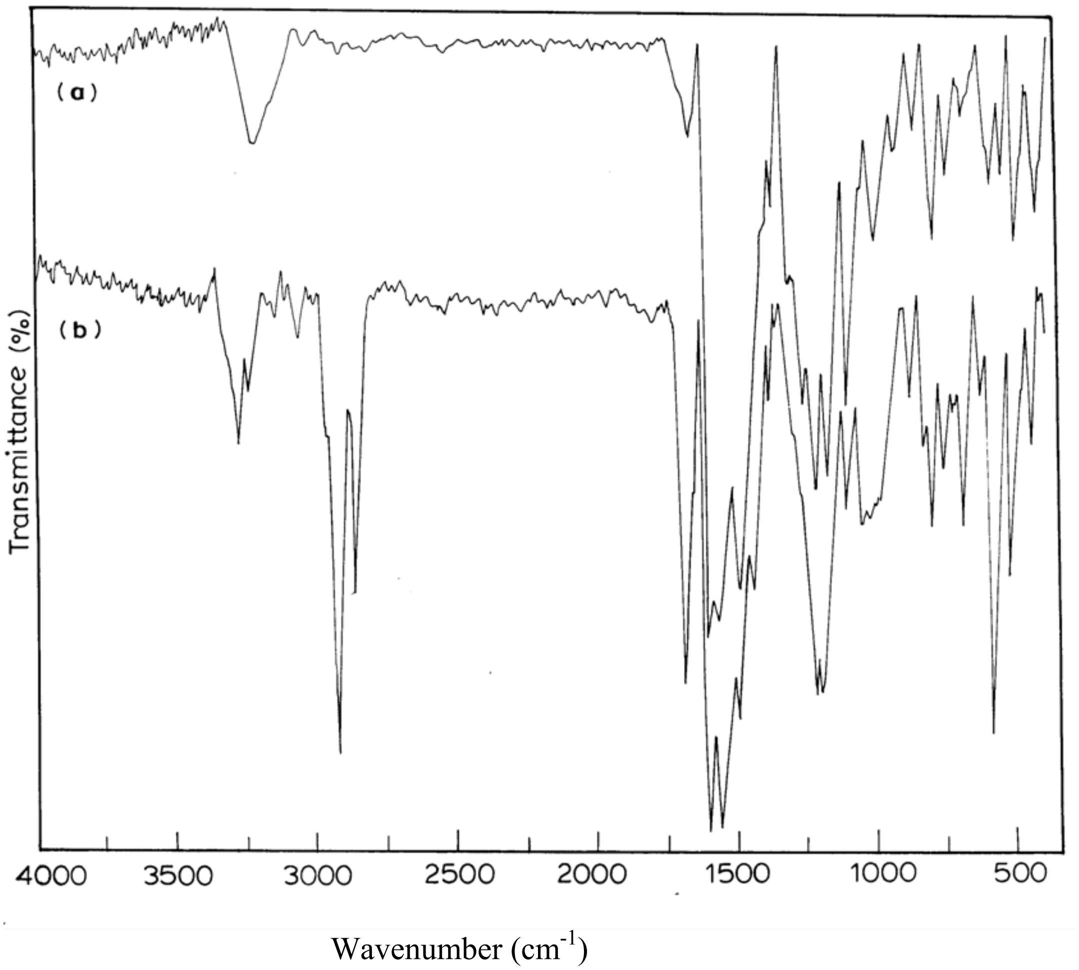

(a)
(b)
Transmittance (%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

Figure 3.

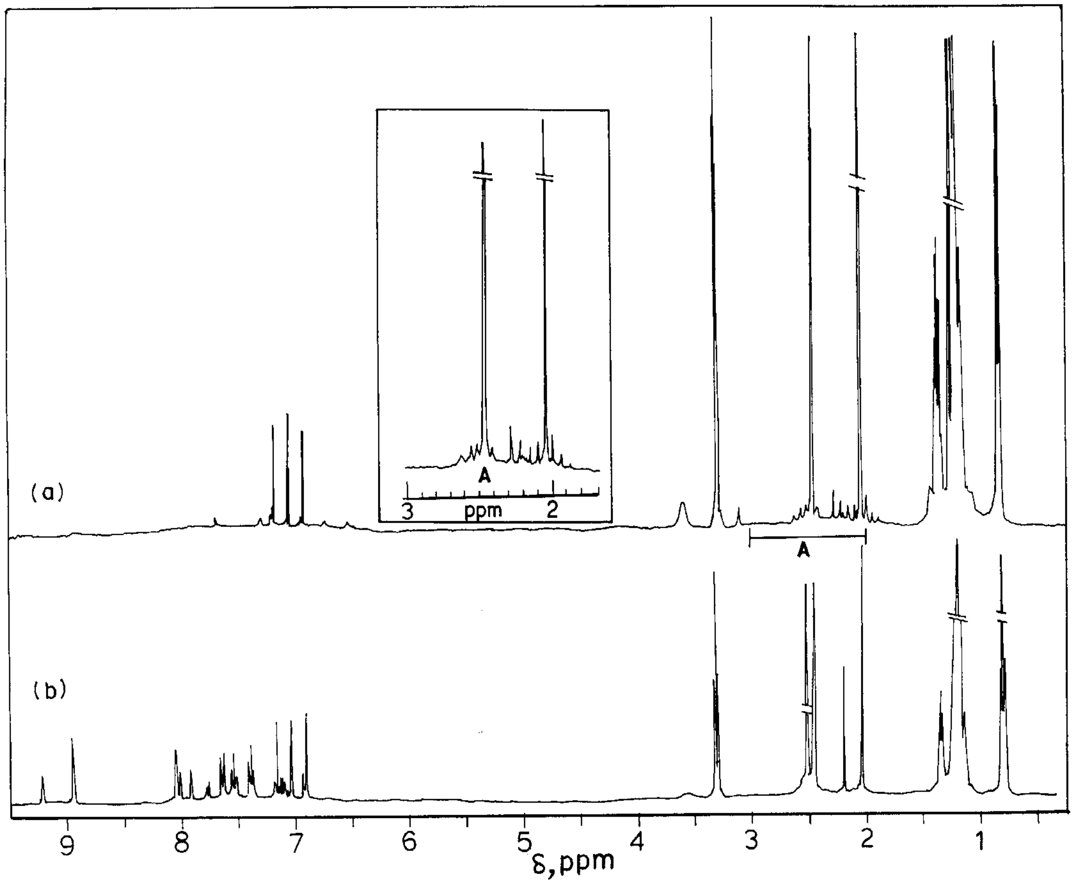
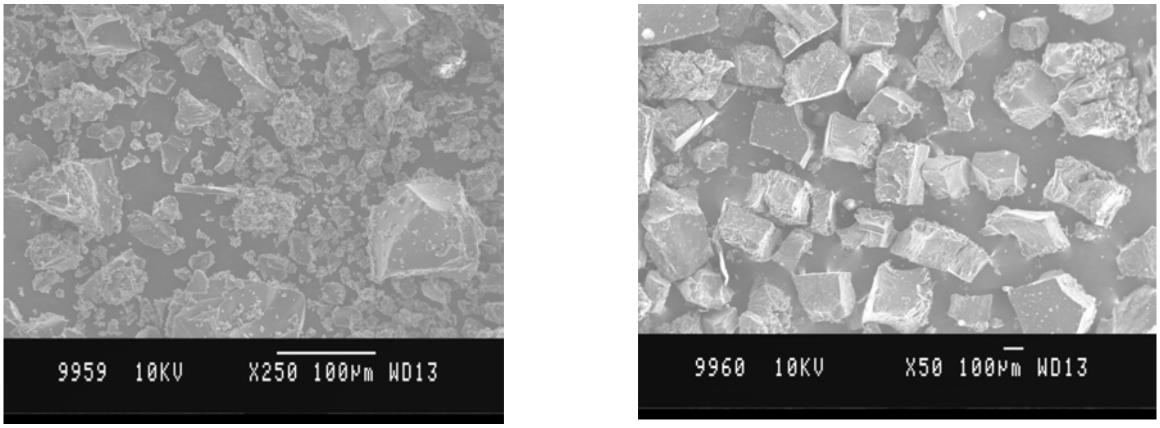


Figure 4



(a) (b)

Figure 5.