A New Approach to Soluble Polyaniline and Its Copolymers with Toluidines

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ABSTRACT: Homopolymers of aniline, toluidines and their copolymers were synthesized by chemical oxidative polymerization using different ratios of monomers in the feed in H_2SO_4 medium. The synthesized polymers were characterized by employing Fourier transform infrared, UV-visible, proton nuclear magnetic resonance, X-ray diffraction techniques for understanding the details of the structure of the synthesized polymers. Morphological, thermal, and electrical conductivity of the as synthesized polymers were also studied by employing scanning electron microscopy, thermogravimetric analysis, and dc electrical conductivity, respectively. From the SEM images rod shaped nanoparticles were observed in PANI and spherical shaped nanoparticles were observed for copolymers. A three-step thermal degradation was observed for all the polymers. The electrical conductivities of the copolymers were less compared with PANI, and at higher temperature the conductivities of all the polymers were more or less same. It was observed that yield and intrinsic viscosity of copolymers are not regularly dependant on monomer concentration in the feed. The copolymers show better solubility but lower conductivity than PANI. Properties of homopolymers and copolymers are also pointed out. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1350–1360, 2010

Key words: homoploymers; copolymers; synthesis; solubility; thermogravimetric analysis

INTRODUCTION

Conductive polymeric materials containing conjugated bonds have attracted much interest in scientific and technological areas in recent years. A key property of a conductive polymer is the presence of conjugated double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localized "sigma" (σ) bond, which forms a strong chemical bond. In addition, every double bond also contains a less strongly localized "pi" (π) bond which is weaker. However, conjugation is not enough to make the polymer material conductive. In addition, charge carriers in the form of extra electrons or "holes" have to be injected into the material. And this is what the dopant does.

Among the conducting polymers, polyaniline (PANI) has a specific situation owing to its simple synthesis, good environmental stability, and ability to dope with protonic acids.[1,2] However, conductive form of PANI is difficult to process, as it is insoluble in common organic solvents and unstable at melt processing temperatures, has restricted its applications. To overcome this, several substituted PANI homopolymers (single type of monomers involved) soluble in organic solvents have been prepared such as alkyl[3] and alkoxy[4] as well as alkyl-N-substituted polyanilines.[5] Another approach followed is copolymerization (more than one type of monomers involved) of aniline with suitable substituted aniline. Using the latter method, Chen and Hwang[6] have synthesized the first water soluble self-acid doped PANI, poly(aniline-co-N-propanesulphonicacidaniline). Heeger et al.[7] have prepared soluble PANI in its conducting form by doping it with functionalized surfactants such as camphorsulphonic acid and dodecylbenzenesulphonic acid. Among substituted PANIs, polytoluidines have attracted considerable attention as they exhibit better solubility[8] in many organic solvents and better processability[9] than PANI with moderate to good conductivity. However, the methyl substitutions on the phenyl ring

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increases the steric repulsion between rings along the polymer chain, consequently polytoluidines show less conductivity than PANI. To combine the high conductivity of PANI with the good solubility of the PANI derivatives, copolymerization received greater attention as it helps to tailor-make a material with specifically desired properties, such as excellent electrical, optical, and mechanical properties.

Although there are reports on the copolymers of aniline with o- and m-toluidines,[10–12] however, these studies were focused on the copolymer bases and not the salts. Such materials were only partially characterized.[10,13] Sathyanarayana and Savitha[13] reported conductivity, spectral, and thermal properties of salts, but morphology and viscosity are not reported. Moreover, homopolymers and copolymers reported to be soluble in solvents like dimethyl sulphoxide (DMSO), N -methylpyrrolidone (NMP), N,N-dimethylformamide (DMF), and tetrahydrofuran (THF), which are hazardous, costly and out of some are also viscous. As our main aim of the study was to obtain copolymer salts with improved solubility and better processability compared to PANI and early reported PANI derivatives. We synthesized copolymers which are soluble in most common, economical, nonviscous, comparatively safe, nonhazardous solvent like ethyl alcohol, which helps in making films. In this research program homopolymers of aniline, toluidines and their copolymers [poly(aniline-co-o/m-toluidines)] of different compositions have been synthesized by chemical polymerization in acidic (H_2SO_4) medium. Resulted homopolymers and copolymers were characterized by ultraviolet-visible (UV-Vis), Fourier transform infrared (FTIR), proton nuclear magnetic resonance (^{1}H-NMR), and X-ray diffraction (XRD) techniques. We have evaluated their conductivity (dc electrical conductivity), thermal properties (thermogravimetric analysis (TGA)), morphology (scanning electron microscopy (SEM)), and viscosity. We also made an effort to understand the effect of having electron-donating methyl group in the polymer chain and noted the differences between the homopolymers and copolymers.

EXPERIMENTAL

Materials

Aniline, o-/m-toluidines (Merck) were distilled twice and all other chemicals viz., sulfuric acid, ammonium persulphate, dimethyl sulphoxide (DMSO), N-methylpyrrolidone (NMP), N,N-dimethylformamide (DMF), tetrahydrofuran (THF), toluene, propanol, chloroform, and ethyl alcohol, etc., of analytical grade were used as procured.

Synthesis of homopolymers

In a typical experiment, aqueous solution of 0.1 M oxidizing agent, ammonium persulphate was added dropwise into 1.0 M H_2SO_4 solution containing 0.1 M aniline at a temperature of 0–5°C. The oxidation of aniline is highly exothermic and therefore, the rate of addition of the oxidant was adjusted to prevent any increase in the temperature of the reaction mixture. After the addition of oxidant, the reaction mixture was left stirring at constant temperature for 4 h. The precipitated PANI was filtered and then washed with distilled water until the washing liquid was colorless. To remove oligomers and other organic byproducts, the precipitate was washed with methanol until the methanol solution was colorless. Finally, the resulting polymer salt was dried at 100°C till a constant mass [Scheme I(a)]. PANI base was prepared by dedoping polyaniline-sulfate salt (1 g), with constant stirring at ambient temperature in 100 mL sodium hydroxide solution (1 M) for 12 h. The resultant solid was filtered and washed with water, followed by acetone and finally dried at 100°C till a constant mass.

Substituted polyaniline homopolymers, poly-o-toluidine (POT) and poly-m-toluidine (PMT) salts [Scheme 1(b)] and their bases were prepared similarly.

Synthesis of copolymers

Copolymers of aniline with o/m-toluidines were synthesized in various molar fractions using ammonium persulphate as oxidizing agent and H_2SO_4 as acid medium. A typical procedure for the preparation of copolymers 50 : 50 ratio of aniline and o/m-toludines is as follows.

1 M H_2SO_4 solution containing o-/m-toluidine (0.05 M) and aniline (0.05 M) maintained at 0°C, an aqueous solution of ammonium persulphate (0.1 M) was added drop wise, stirred for 4 h and then kept at room temp for about 15 h. The green precipitate of copolymer salt obtained was filtered and washed with distilled water several times and then washed with acetone and subsequently dried at 100°C till a constant mass (Scheme 2). The copolymer base was obtained by stirring 1 g of salt in 100 mL of 1.0 M NH_4OH for 12 h. The resultant solid was filtered and washed with water, followed by acetone and finally dried at 100°C till a constant mass.

Characterization techniques and studies used

A weighed amount (10 mg) of the homopolymer and copolymer was added separately to 2 mL of the solvent with stirring. Additional solvent was added at the rate 1 mL per 10 min till the copolymer was
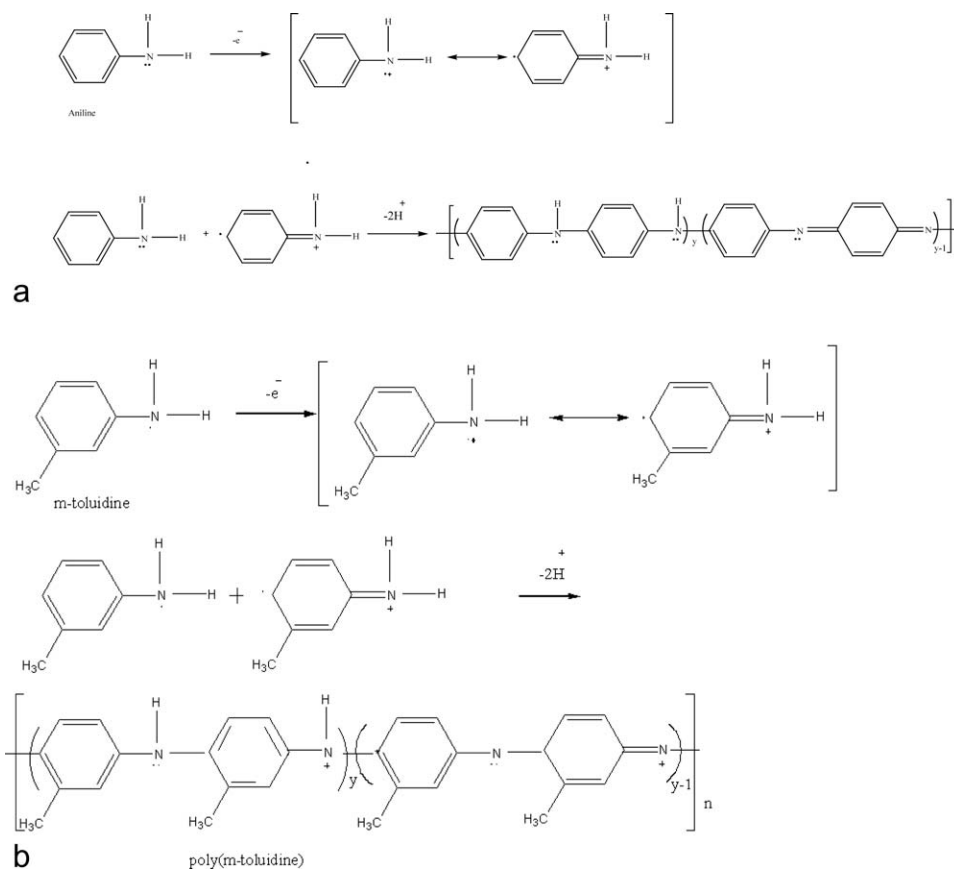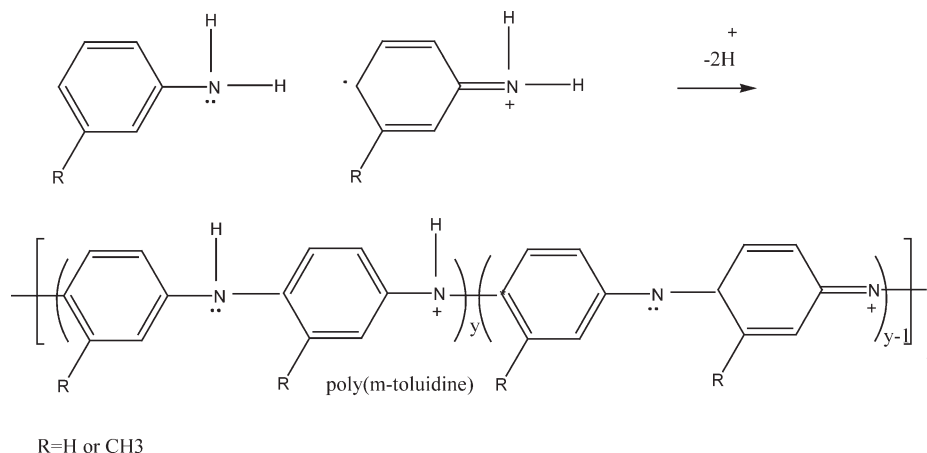
Scheme 1 a) Homopolymerisation of aniline, (b) Homopolymerisation of *m*-toluidine.

completely dissolved. This procedure was continued for 30 min, left for 3 h and then filtered; the polymers which did not dissolve completely during this period were taken as "partially soluble".

The FTIR spectra of the polymers were recorded on a JASCO FTIR-5300 instrument in the range 4000–400 cm^{-1} at a resolution of 4 cm^{-1} by making KBr pellets. For UV-Vis, the samples were prepared by dissolving the polymers in the dimethylsulphox-

ide (DMSO). The filtrate was used for recording the UV-Vis spectrum using a UV-visible 5704SS ECIL spectrophotometer operated at 1 nm resolution from 200–800 nm. UV-vis spectra were also recorded for C_2H_5OH, NMP, and THF. ^{1}H-NMR spectra were recorded with a Bruker AMX 400 MHz instrument using DMSO as an internal reference. The XRD patterns were obtained employing a JEOL JDX-8p spectrometer using Cu Kα radiation (λ = 1.54 Å). The

R=H or CH3

Scheme 2 Copolymerisation of aniline with *m*-toluidine.

TABLE I
Yield, Intrinsic Viscosity, and Conductivity of homoploymers and copolymers

Polymer	Yield (%)	Intrinsic viscosity (dl/g)	Conductivity (S/cm)
PANI	95	0.69	10^{-2}
PMT	98	0.85	$10^{-4}-10^{-2}$
POT	97	0.78	$10^{-4}-10^{-2}$
PAPMT13	97	0.85	$10^{-4}-10^{-2}$
PAPMT11	99	1.73	$10^{-4}-10^{-2}$
PAPMT31	98.5	0.45	$10^{-4}-10^{-2}$
PAPOT13	97	0.77	$10^{-4}-10^{-2}$
PAPOT11	98.5	1.804	10^{-3}
PAPOT31	98	0.65	10^{-3}

X-ray generator was operated at 30 kV and 20 mA. The scanning range, $2\theta/\theta$ was selected. The morphologies of the polymers were studied by using coupling JSM-840A scanning electron microscope. The electron microscope was operated at 20 kV.

The thermogravimetric analysis (TGA) measurements were made using a Mettler Toledo Star System at a heating rate of 10°C per min under nitrogen atmosphere. The intrinsic viscosity of the copolymers was measured at 35°C with an Ostwald's viscometer. Conductivity measurements were done at room temperature by two-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 sources and a Keithely model digital 195A voltammeter was less than 2%.

RESULTS AND DISCUSSION

Homopolymers, of aniline is denoted as PANI and those of o-toluidine and m-toluidine as POT and PMT, respectively. Copolymer, poly(aniline-co-o-toluidine) (PAPOT) synthesized with various molar fractions of aniline and o-toluidine in the feed ranging from 0.25, 0.5, and 0.75 M are denoted here as PAPOT13, PAPOT11, and PAPOT31, respectively. Poly(aniline-co-m-toluidine) (PAPMT) copolymers of aniline and m-toluidine are similarly identified as PAPMT13, PAPMT11, and PAPMT31.

Yield

Homopolymers, PANI, PMT, POT yield is improved by keeping oxidant to monomer 1 : 1. Copolymers yield is more than individual homopolymer. Wei et al.[12] have previously utilized a lower molar ratio (0.25:1) of the oxidant to monomer and had obtained copolymers in low yields (<15%). However, in this work the copolymers were obtained in high yields by keeping an oxidant to monomer ratio of 1 : 1. Yields of the copolymers were found to increase with an increase in the amount of aniline in the feed for most of the copolymers (Table I). The steric hindrance in toluidines, which predominates over the effect of electron-donating groups may reduce the yield of the copolymers slightly when the amount of toluidine in the monomer feed ratio is higher.[13] m-toluidine copolymers are generally obtained in higher yields compared to those of o-toluidine.

Solubility

Solubility of conducting polymers is always a matter of discussion and many reports have been published in literature discussing the solubility of PANI.[14–17] Normally, when a pinch of PANI doped with mineral or organic acid is added to highly polar solvents such as DMSO or NMP, part of the polymer material (presumably oligomeric or of low molecular weight) is dissolved but a residual mass is always present in the mixture. Such a mixture is filtered and the solubility of PANI (g/L) is calculated by weighing the residual mass. In this article, when we quote 'completely soluble' we mean, that the PANI is dissolved in the solvent without leaving any solid residue. PANI produced in the present way is completely soluble with dark bluish violet color in polar solvents like DMSO, NMP, DMF, and THF, partially soluble with light bluish color in less polar solvents like chloroform, and insoluble in ethyl alcohol and benzene. In 2 : 1 mixture of toluene+2-propanol, it gives a clear green solution, which can be spin- or drop-coated on metallic and glass substrates.[11]

It is well known that copolymerization of aniline and toluidine improves the solubility of PANI, especially PANI-EB (emeraldine base) form, in solvents such as NMP, DMSO, and THF.[11,12] A partial solubility of copolymers in their ES (emeraldine salt) form in DMSO, DMF, NMP, THF, CHCl$_3$ etc., has also been reported.[18] In most cases, the partial solubility of ES form of the copolymer arises from the undoped segments of the polymer backbone and can be easily confirmed from the UV-vis spectra where strong band characteristic of EB form is observed.[13]
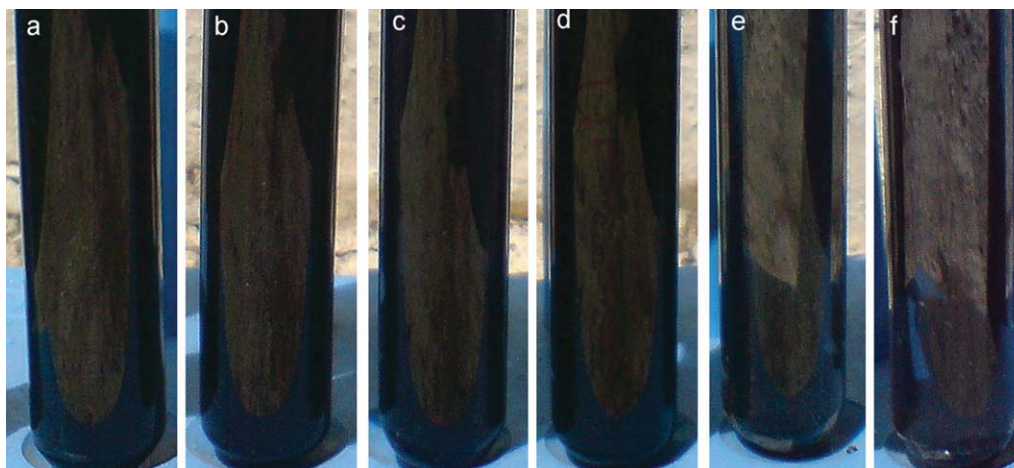
Figure 1 (a–e): Solubility of copolymers in ethyl alcohol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Substituted polyaniline homopolymers POT, PMT, and poly(aniline-co-o-toluidine)s, synthesized using the present protocol, were clearly soluble in aforementioned solvents as well as common solvents like ethyl alcohol, chloroform, and other solvents. In ethyl alcohol, soluble with viscous dark bluish violet color to nonviscous blue color and in 2 : 1 mixture of toluene+2-propanol with green color. Among copolymers, PAPOT11, PAPMT11, PAPOT13, and PAPMT13 are clearly soluble and PAPOT31 & PAPMT31 are sparingly soluble because of high feed of aniline ratio. Good copolymer solubility results from the presence of a large number of methyl substituents on the aniline ring and an amorphous structure, which increases the distance between the macromolecular chains and then significantly reduces the interaction between the copolymer chains.[11] In addition, better solubility is evidence that the polymerization product produced is indeed copolymer containing two monomers rather than a simple mixture of two homopolymers.[19] The intrinsic viscosity of the copolymers is comparable to that of PANI, but the solubilities of the copolymers and PANI are much different from each other. These results indicate that solubility is primarily determined by molecular structure rather than by the intrinsic viscosity of the polymers.[20,21]

Copolymers also show partial solubility in dichloromethane. Strong green colouration of the solution indicates that solubility is mainly due to ES form of the polymer backbone. A clear green solution of the copolymer can be easily spin or drop-coated on a glass or metal substrate to get a coherent thin/thick film.[11] It is well established that solubility of copolymer increases with increase in the feed concentration of o-toluidine.[11] To find out the solubility, constant known amount of each copolymer was added to 5 mL of solvent, stirred for 2 min and

filtered. The difference in the solubility is evident from the photographs of their solution as shown in Figure 1.

UV–visible spectroscopy studies

The UV–visible spectra of the homopolymers, as well as the copolymers, were studied in detail and their solvatochromic behavior was noted. All polymer solutions exhibited dark bluish violet to violet color. Absorption spectra were recorded in DMSO, NMP, DMF, THF, and C_2H_5OH. Present the UV–visible spectral data obtained for the homopolymers, namely PANI, POT, and PMT, and their copolymers recorded in different solvents. Two main absorption bands were observed for PANI in all of the five solvents—one around 310 nm assigned to the $\pi - \pi^*$ transition of the phenyl ring and another around 620 nm assigned to the $n-\pi^*$ transition. The absorption peaks in the 300–320 nm region and that at 550–610 nm region, respectively, correspond to excitation of amine nitrogen of the benzenoid segments and imine nitrogen of the quinoid segments.[10,22–24] These peaks shifts to 346–354 nm and 606–607 nm for POT and PMT, respectively, hence revealing a decrease in the extent of conjugation and an increase in the band gap. The copolymers of both o-toluidine and m-toluidine with aniline also show such hypsochromic shifts to 343–408 nm and 606–607.5 nm. However, the absorption bands of the o-toluidine copolymers lie close to those of POT, while the copolymers of m-toluidine show absorption peaks nearer to those of PANI. The blue shifts observed in the copolymers are smaller when compared to those of the homopolymers POT and PMT, as previously observed by Dhawan and Trivedi[10] and Sathyanarayana and Savitha.[13] A solvatochromic shift was observed for PANI, POT, and PMT, and in the
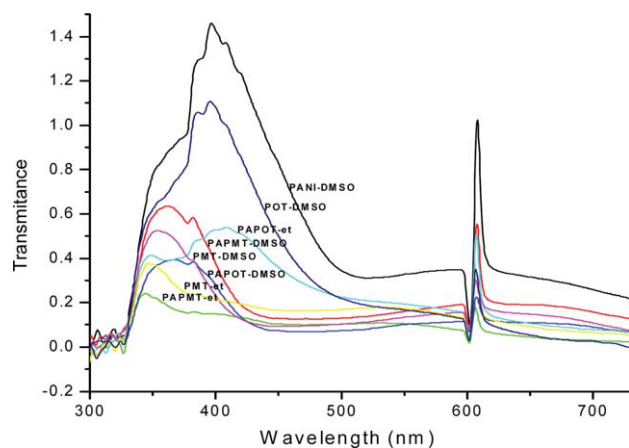
Figure 2 UV-Vis spectra of PANI, PMT, POT, PAPMT11, PAPOT11 in DMSO, and C_2H_5OH (et). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

copolymers, which was studied by using the exciton band at 620 nm. This spectral band of the polymer can be related to the dielectric constant of the solvent by the following equation.

$$-\Delta E = \mu_g(\mu_e - \mu_g)f(\varepsilon)/a^3 \qquad (1)$$

where ΔE denotes the energy of the transition, μ_g and μ_e are the dipole moments of the solute in the ground and excited states respectively, a is the spherical radius of the volume occupied by a solute molecule and $f(\varepsilon)$ is a function of the dielectric constant, given by $f(\varepsilon) = 2(\varepsilon - 1)/(2\varepsilon + 1)$.[25] The effect of the refractive index is ignored in this equation as it does not vary as much as the dielectric constant for the chosen solvents.

Figure 2 shows the absorption spectra of the polymers in DMSO and C_2H_5OH solvents. A plot of the energy corresponding to the λ_{max} versus $f(\varepsilon)$ gives a linear relationship, as predicted by eq. (1). The deviations from the straight line can be traced to the variation in the refractive indices of the solvents, which is neglected in eq. (1). Interestingly, the plot for the copolymer of PAPOT11 deviates towards that of POT while that of the corresponding copolymer of *m*-toluidine and aniline deviates towards PANI. These trends may be due to the higher content of *o*-toluidine compared to that of aniline in the copolymer, whereas in the case of the copolymer of aniline with *m*-toluidine, the reverse is probably true. It has also been observed that both the bands around 330 and 620 nm in the spectra of salts show a blue shift when a solvent of higher dielectric constant (e.g. DMSO) is changed to a solvent of lower dielectric constant (e.g. THF). This result was observed for almost all of the five solvents. However, for the copolymer base of PAPOT, Dhawan and Trivedi[10]

from a study of the spectra in just two solvents, namely NMP and THF, reported a red shift for the 330 nm and a blue shift for the 630 nm bands on going from higher dielectric constant (NMP, $\varepsilon = 32.0$) to lower dielectric constant (THF, $\varepsilon = 7.5$).

FTIR spectroscopy studies

The characteristic IR peaks of PANI, POT, PMT and the copolymer salts PAPOT11 and PAPOT13 are shown in Figure 3. The present studies made for the copolymer salts offer a clear advantage over the copolymer bases to estimate approximately, the amount of toluidine in the copolymers (as discussed later). An accurate quantitative determination of the compositions of the copolymers is rendered difficult due to the overlap of the absorption bands where the spectra of the polytoluidines differ from that of PANI,[12] especially in the case of copolymers which have low toluidine contents. The characteristic bands in the IR spectrum of the PANI salt occur at 1562, 1487, 1302,1240, 1107, and 798 cm^{-1}. A broad band at 3440 cm^{-1} was assigned to the free N—H stretching vibration. The bands at 2920 and 2850 cm^{-1} was assigned to vibration associated with NH part in $C_6H_4NH_2C_6H_4$. The high-frequency bands at 1562 and 1487 cm^{-1} are assigned to the C=C ring stretching vibrations of the benzenoid ring and the C—N stretching of the quinoid ring, respectively. The bands at 1302 and 1240 cm^{-1} correspond to the N—H bending and symmetric component of the C=C (or C—N of the benzenoid ring) stretching modes. The remaining bands at 1107 and 798 cm^{-1}
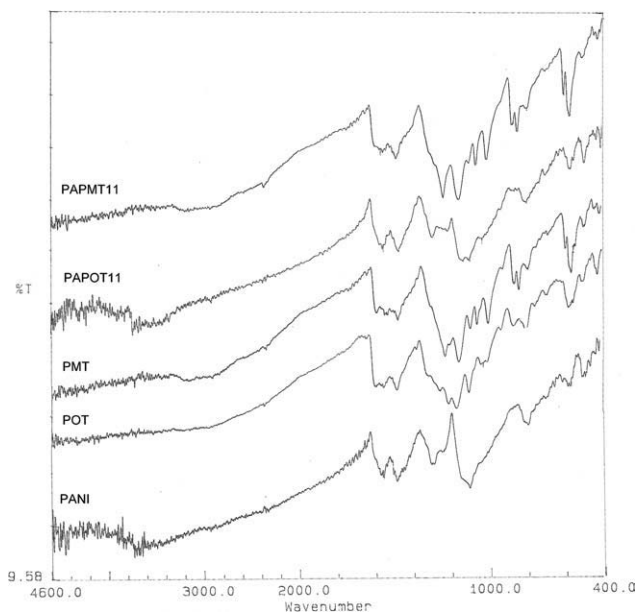

Figure 3 FTIR spectra of PANI, PMT, POT, and PAPMT11and PAPOT11.

could be attributed to the in-plane and out-of plane C–H bending modes respectively. The C—H out-of-plane bending mode has been used as a key to identify the type of substituted benzene. For PANI salt, this mode was observed as a single band at 798 cm^{-1}, which was almost nearer to the range 800–860 cm^{-1} reported for 1,4-substituted benzene.[26] The IR spectra of POT and PMT are similar to those of the PANI salt with the bands showing slight shifts to higher frequencies. A new band which is not present in PANI appears in the spectra of both in POT at 1172 cm^{-1} and in PMT at 1167 cm^{-1}, which could be attributed to the –CH$_3$ rocking mode. Approximate estimations of the copolymer compositions can be made by utilizing the intensity of this new band at around 1160 cm$^{-1.}$

The characteristic IR spectral bands of the salts of the homopolymers and the copolymers are shifted from those of the polymer base. For example, the spectrum of the PANI base shows an intense band at 1157 cm^{-1}, which shifts to 1107 cm^{-1} in the spectrum of the salt. The IR spectra of the POT and PMT bases show a band at 1150 cm^{-1}, due to the rocking mode of the —CH$_3$ group. It should be noted that the PANI base and the bases of the copolymers of aniline and toluidine have a band near at 1150 cm^{-1}, overlapping with the band arising from the —CH$_3$ rocking mode and makes it difficult to estimate the toluidine contents in the copolymers. On the other hand, the spectrum of the PANI salt has no infrared absorption at around 1160 cm^{-1}, as mentioned above. Thus, the infrared spectra of the copolymer salts help us to estimate roughly, the amounts of toluidine present in the copolymers. The spectral characteristics of the copolymers are similar to those of PANI and polytoluidines (Fig. 3). It was noticed that the spectra of the PAPMT copolymers show a greater similarity to the spectra of PMT. The IR absorptions at 1489–1595 cm^{-1} are associated with aromatic ring stretching. The peak at 1577 cm^{-1} assigned to the quinoid ring and peak at 1489 cm^{-1} to the benzenoid ring and the intensity of the peak near 1160 cm^{-1} increases as the amount of m-toluidine in the feed increases. The same is true for the PAPOT copolymers. Our findings are consistent with the findings of Wei et al.[12] and Sathyanarayana and Savitha.[13]

^{1}H-NMR spectroscopy studies

The ^{1}H-NMR spectra of PANI, PMT, POT and copolymers PAPOT11 and PAPMT11 salts in DMSO are shown in Figure 4. The ^{1}H-NMR spectra of the PANI exhibits sharp signals near δ 7.4–6.9 ppm due to the aromatic benzenoid and quinoid protons. A peak at δ 3.5 ppm arises from the —NH protons. The ^{1}H-NMR spectrum of the PMT salt is character-
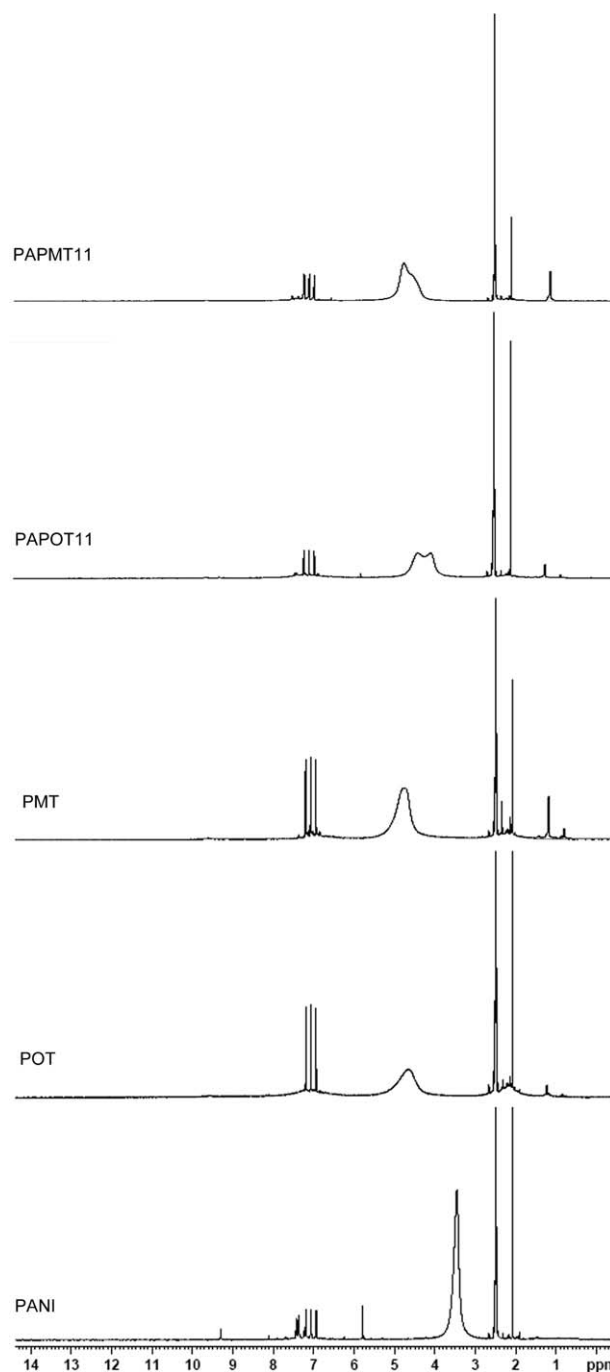

Figure 4 ^{1}H-NMR spectra of PANI, PMT, POT, and PAPMT11 and PAPOT11.

ized by the presence of main signals in the region of δ 7.4–6.9 ppm are due to the protons of the aromatic rings, while the signal at δ 4.65 ppm is due to the protons of the —NH group. The resonances in the region of δ 2.07 ppm could be assigned to the methyl protons of the quinoid ring and those in the region δ 1.91 ppm to the methyl protons of the benzenoid ring. The spectrum of POT is very similar to that of PMT. The ^{1}H-NMR spectra of

polytoluidines show signals due to the methyl protons, which are absent in the spectrum of PANI.[12] The spectrum of the PAPMT11 copolymer in its salt form exhibits peaks in the regions of δ 7.5–6.9 ppm for the aromatic benzenoid and quinoid protons, δ 4.6 and 4.8 ppm for —NH protons of PANI unit and —NH protons of toluidine unit, respectively, δ 2.01 ppm for methyl protons of quinoid ring and δ 1.25 ppm for methyl protons of benzenoid ring. The spectrum of the PAPOT11 copolymer in its salt form exhibits peaks in the regions of δ 7.4–6.9 ppm for the aromatic benzenoid and quinoid protons, δ 4.0 and 4.5ppm for —NH protons of PANI unit and —NH protons of toluidine unit respectively. δ 2.08 ppm for methyl protons of quinoid ring and δ 1.25 ppm for methyl protons of benzenoid ring. The ^{1}H-NMR spectrum of the corresponding copolymer base, on the other hand, shows a considerable shift in the position of methyl protons from that of the salt and has peaks at δ 7.4–6.9 ppm, 3.4 and 3.9 ppm, 1.8 and 0.8 ppm. The peaks due to the methyl on quinoid shift upfield by δ 0.28 ppm while the benzenoid peaks shift by δ 0.45 ppm. The peaks at δ 4.0 and 4.5 ppm in the spectra of the salts also undergoes a shift to δ 3.4 and 3.9 ppm as the transition from the doped to the undoped —NH protons occur.[13] Due to the difference in the solubilities, the amount of toluidines could not be estimated by spectral data. However, an increasing intensity of the methyl protons with an increase in the amount of toluidine in the feed could clearly be seen. Wei et al.[12] observed, for the copolymer base in DMSO, the signals arising from the methyl protons in the region of δ 1.8–2.1 ppm. Huang et al.[11] observed, the spectrum of the copolymer base in CDCl₃ show sharp peaks in the regions 2.14–2.19 ppm and 1.65–1.75 ppm, which are assigned to methyl protons of quinoid and benzenoid, respectively, Sathyanarayana and Savitha[13] observed large shifts for the spectra of the copolymers due to the combined effects of protonation and change of solvent. Our spectral data is consistent with literature[23] and also with the findings of Satyanarayana and Savitha.[13] Spectra obtained by us have better resolution when compared to the spectra obtained by earlier workers and our spectra clearly explained that there are two peaks for —NH protons in copolymers one is —NH of PANI unit and —NH of toluidine unit (Fig. 4).

X-ray diffraction studies

Figure 5 shows the X-ray diffraction patterns of homopolymers and copolymers. The PANI exhibits three broad peaks at 2θ angles around 10.3°,19.5°, and 25.5°, 2Θ = 25.5° is characteristics of the van der Waals distances between stacks of phenylene rings (polyaniline ring).[24,27] These broad peaks indi-
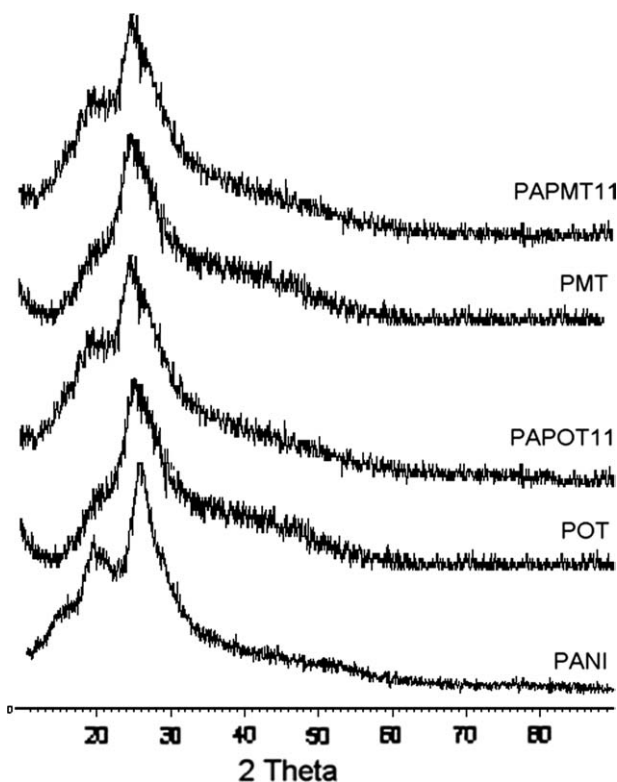

Figure 5 XRD patterns of PANI, PMT, POT, and PAPMT11 and PAPOT11.

cate crystalline domains in the amorphous structure of PANI The chain length of PANI is about 4.355AU.[28] The POT and PMT show broad peak at 25.5° and a weak broad peak at 19° while the copolymers, PAPOT and PAPMT show two broad peaks at 19.2° and 25°, the two broad peaks indicates amorphous structure of copolymers.[27] More broadness and decreased intensity in peaks was observed in copolymers when compared to PANI. This suggests that in copolymers, introduction of methyl group on an aniline unit increases the intramolecular chain spacing and amorphousness as compared with the pure PANI.

Morphological studies

SEM images of homopolymers (PANI, POT, and PMT) and their copolymer salts (PAPMT and PAPOT) are shown in Figure 6 (a–e), respectively. Nanorods PANI bundles made of agglomerated with typical sizes around 100 to 200 nm observed. POT, PMT and their copolymer salts exist as highly agglomerated globular particles with typical sizes around 100–500 nm. Somewhat sponge type appearance is observed in PMT and PAPMT particles. Similarity in shape and appearance is observed in POT and PAPOT images.
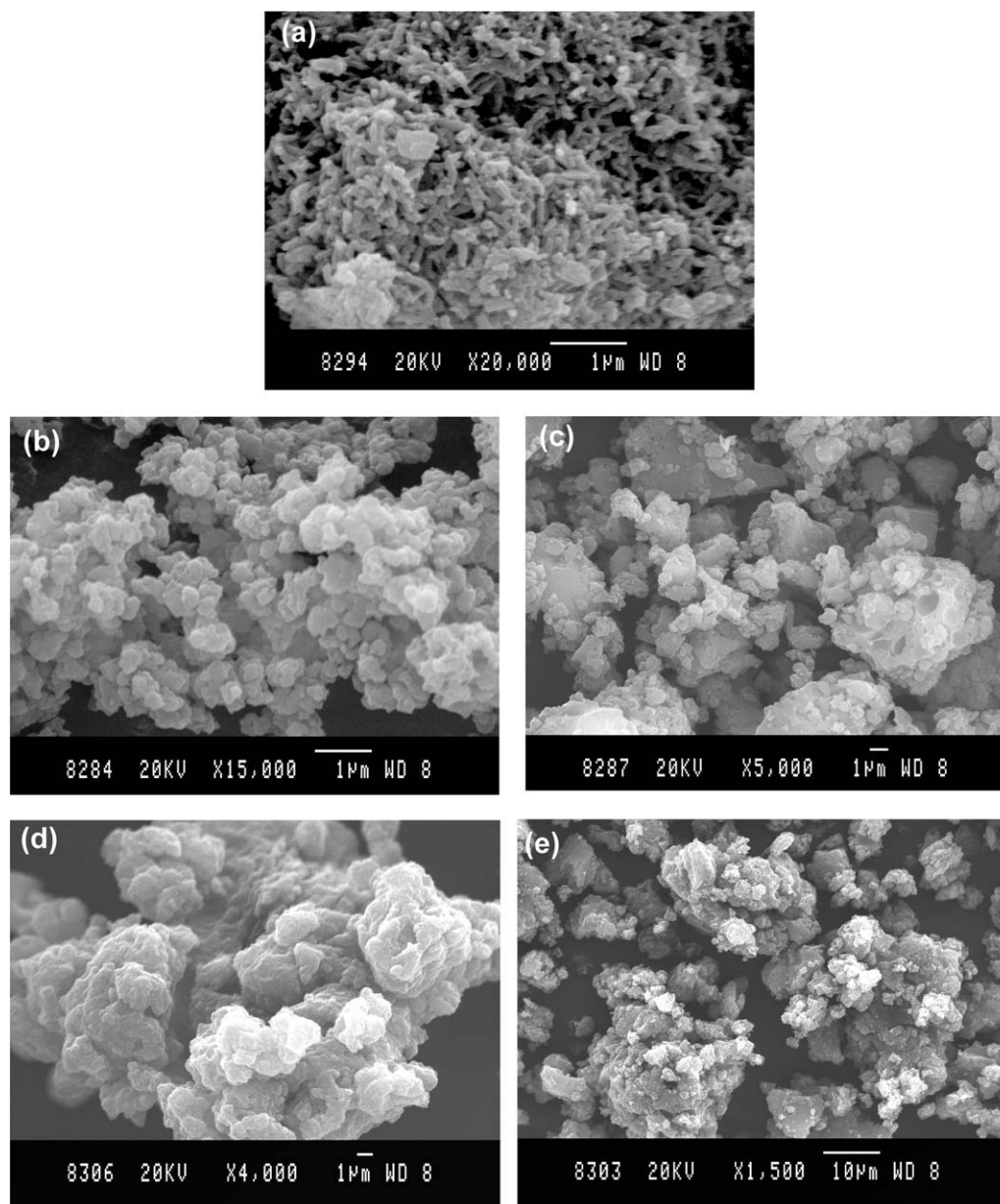
Figure 6   SEM images of (a) PANI, (b) PMT, (c) POT, (d) PAPMT11, and (e) PAPOT11.

Thermogravimetric analysis

Thermogravimetric analysis of PANI, POT, and PMT, and their copolymers were performed in an air atmosphere, employing a heating rate of 10°C min^{-1}. The TGA curve for the PANI salt shows a three-step weight loss. The weight loss up to 150°C due to the loss of moisture is about 6%. The 4.5% weight loss occurring up to 395°C is attributed to the loss of the dopant H_2SO_4. The final step starts at around 400°C, leads to the complete degradation of the PANI salt.[9] The thermograms of the POT and PMT salts also show similar three-step degradation, but at lower temperatures. Figure 7 shows the representative TGA trace of the homopolymer, PMT and copolymer PAPMT11.

The PAPMT11 copolymer salt also shows a three-step weight loss similar to that of PANI, POT, and PMT. The first weight loss in the range of 50–140°C is due to loss of moisture is about 18%,the second stage 180–280°C due to loss of dopant H_2SO_4 is about 27%, third step starts from 300°C corresponds to the degradation of the copolymer. However, the copolymers have their degradation steps starting at lower temperatures when compared to that of PANI. Huang et al.[11] have reported a two-step degradation process for the copolymer bases in air, with the lowest degradation temperature being observed for the POT homopolymer base. They also reported that the copolymer of aniline–o-toluidine with a very high content of aniline in the feed (90%) had the
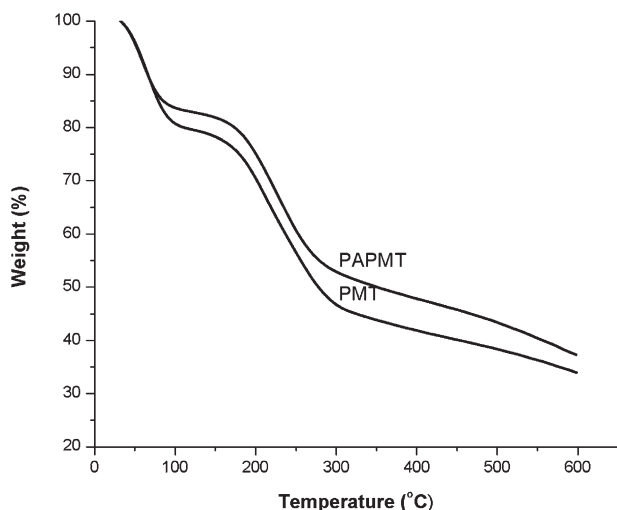
Figure 7   TGA of PMT and PAPMT11.

maximum stability. This has also been observed in the case of the salts, with the copolymer of 75% aniline content showing a degradation temperature very nearer to that of PANI. It was also noticed that the thermal stabilities of all of the copolymers, with the exception of the PAPOT31 systems, were lower than that of both POT and PMT and that the stabilities of the copolymers decrease as the amount of *o*-toluidine increases in the feed.

Conductivity measurements

The conductivities of the homopolymers and copolymers were measured by using the two-probe method (Fig. 8). It was noticed that as the amount of toluidine increases in the copolymers, the conductivity decreases. The presence of even 0.25 *M* toluidine in the feed drastically decreases the conductivity. The conductivities of POT and its copolymers are lower than those of PMT and its copolymers at lower temperatures but at high temperatures, conductivity of PMT was lower. The difference in the conductivity of PMT and POT may be due to small differences in the orientation of the phenyl rings and lowering of the conductivity in polytoluidines, and the copolymers of toluidines with aniline, may be due to the decrease in conjugation caused by the steric hindrance of the methyl group in the toluidine unit and the variation in the molecular conformation. However, at higher temperature the conductivities of all the polymers are more or less of the same magnitude. The higher conductivities of the copolymers, when compared to those of POT and PMT, could be explained as being due to the formation of block copolymers which facilitates faster charge transport by bipolarons.[10]

Viscosity studies

Intrinsic viscosity of the copolymers varied irregularly with the monomer ratio, as listed in Table I. It is interesting that the PAPMT11 copolymer showed the highest intrinsic viscosity, 1.804 dL/g. On the contrary, the PAPMT31 copolymer had the lowest intrinsic viscosity, 0.45 dL/g. Viscosity was increased with increase in the concentration (wt of polymer in grams per 100 mL of solvent), which is characteristic property of high molecular weight polymers.

CONCLUSION

To make soluble and processable PANI, substituted PANI homopolymers and copolymers were synthesized by chemical polymerization with easily available reagents, which in addition assures a good reaction yield. The resulting product exhibits reasonable conductivity with excellent solution processing properties. However, conductivity of copolymers is lower compared to PANI but higher than that of POT and PMT. At higher temperatures all polymers tend to have almost same conductivity. Morphology of PANI salt showed nano-rods with average diameter of 100–200 nm size, whereas copolymers showed 100–500 nm size particles. This processable form of PANI salt and its copolymers could be widely applicable to coatings, to making thin films, preparation of clay composites and solution blending with other
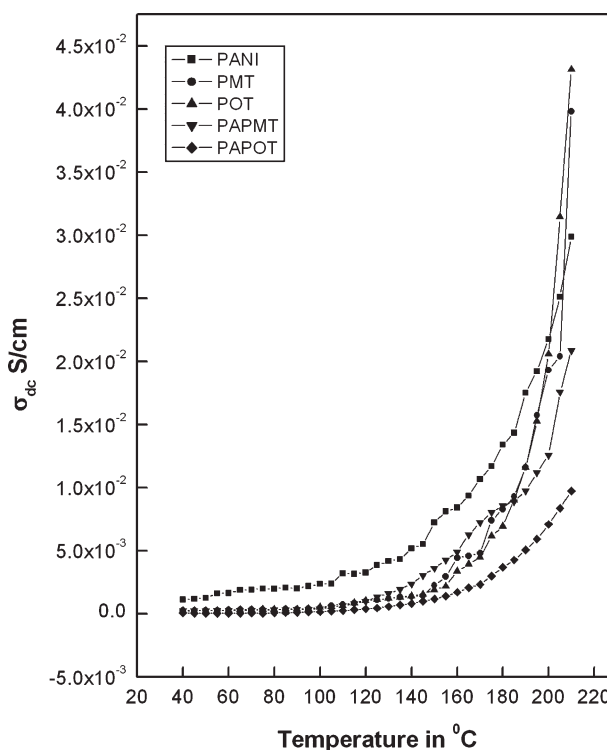

Figure 8   Conductivity of PANI, PMT, POT, and PAPMT11 and PAPOT11.

commodity polymers. Still much research work is necessary to improve the quality of the materials to make commercially viable products.

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