Poly (α-toluidine-co-α-chloroaniline) copolymers: Effect of polymerization conditions on the properties of the copolymers

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Received 30 December 2003

Fully substituted polyaniline derivatives are synthesized by chemical copolymerization of α-toluidine with α-chloroaniline by three different methods to note the effect of synthesis conditions. The structures of the copolymers have been determined by IR, Raman, NMR and their conductivity data. The copolymer compositions have been determined by proton NMR spectroscopy. The copolymers are completely soluble in DMSO and their conductivity is generally higher than that of the homopolymers, poly(α-toluidine) and poly(α-chloroaniline).

In the past few years, aromatic conducting polymers such as polyaniline, polypyrrole, polythiophene, etc have attracted much attention. Among these polymers, polyaniline (PANI) has been described as the 'Conducting Polymer for Technology'. It is easily synthesized and exhibits good environmental and thermal stability. As a result, polyaniline and its derivatives can be used as active electrode materials in microelectronics and electrochromic display devices. However, applications of polyaniline are limited by poor solubility in common organic solvents. To increase the processibility of the polymer, the use of substituted polyanilines is attractive.

Many properties of the ring and N-substituted polyanilines differ from those of the parent polyaniline. For example, substituted polyanilines are considerably more soluble than polyaniline. Substituted PANI can be synthesized by modifying the polymer chain in the following ways: (i) the post-substitution of the parent PANI, (ii) the chemical and electrochemical homopolymerization of aniline derivatives, and, (iii) copolymerization of aniline with ring and N-substituted derivatives.

Studies on the synthesis and characterization of the homopolymer, poly(α-toluidine) have been reported from this laboratory. Chemical polymerization of aniline with electronegative substituents has been little reported. Chemical synthesis of poly(α-chloroaniline) has been achieved using only a stronger oxidizing agent namely chromic acid in aqueous HCl solution and conductivity in the region of \(10^{-5} - 10^{-7}\) S/cm has been reported. The aim of the present work is to synthesize polyaniline derivatives with two different substituents present simultaneously in the polymer chain by chemical copolymerization of α-toluidine with α-chloroaniline. Three different methods have been tried to note the effect of the synthesis conditions. The copolymers have been synthesized using solution, emulsion and inverse emulsion methods. The effect of temperature, the solvent used to carry out the polymerization and the oxidant employed have been investigated using spectroscopic, thermal and electrical methods.

**Materials and Methods**

α-Toluidine (Merck) was distilled twice before use. α-Chloroaniline (Aldrich) and all other chemicals were used as procured.

**Preparation of the copolymers**

**Emulsion method**

Chloroform (or toluene) (100 mL) was taken in a 500 mL beaker and 2.25g of sodium lauryl sulphate (emulsifier) in 50 mL of water (0.1 M) was added to it with constant stirring to obtain a milky white emulsion. α-Toluidine (0.05 M, 1.3 mL) and α-chloroaniline (0.05
M, 1.3 mL) were then added to it followed by the dropwise addition of 50 mL of the 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 with stirring. The organic phase was separated and washed repeatedly with water. It was then added to a beaker containing 600 mL of a non-solvent, namely, acetone when the copolymer precipitated out. After 10 h, the precipitate was filtered, washed with some more acetone and dried under vacuum for 72 h.

Inverse emulsion method

A solution of 0.2 M of the oxidant, benzoyl peroxide (12.1 g), was taken in 100 mL of the solvent and 0.1 M of sodium lauryl sulphate (emulsifier) in 50 mL of water was added to it with vigorous stirring to obtain a milky white emulsion. Then, 0.05 M of o-chloroaniline was added followed by 0.05 M o-toluidine. Then, 100 mL of 1 M HCl was added to it dropwise and the polymerization was allowed to proceed for 24 h. The product was precipitated using acetone. It was collected and purified as mentioned above.

Solution method

In a typical experiment, a mixture of 1.3 mL of o-toluidine (0.05 M) and 1.3 mL of o-chloroaniline (0.05 M) was dissolved in 100 mL of 1 M HCl. An aqueous solution of 0.1 M ammonium persulphate (5.7 g) was added to it dropwise over a period of 20 minutes with continuous stirring. The total volume of the reaction mixture was kept at 250 mL. The reaction was allowed to proceed for 24 h with stirring. The resulting dark green precipitate was filtered, washed repeatedly with distilled water until the filtrate became colourless. It was then washed with methanol followed by acetone. The product was dried at room temperature for 72 h under vacuum. The reaction also carried out at 0°C.

The UV-visible absorption spectra were recorded using a Hitachi U-3400 spectrophotometer for solutions prepared in DMSO. FT-IR spectra for solid samples were obtained with a Bruker-IFS 55 instrument using the KBr pellet technique. FT-Raman spectra were recorded with a Bruker RFS-100/S spectrometer for the powdered polymers using a Nd<sup>3+</sup>-YAG laser having a laser power of 100 mW at the sample. <sup>1</sup>H NMR spectra in DMSO-<sup>d6</sup> were obtained using a Bruker AMX 400 MHz spectrometer with tetramethyl silane as an internal reference. Conductivity measurements were made using the four-probe technique on pressed pellets obtained by subjecting the powder to a pressure of 50 kN. Thermogravimetric (TGA) measurements were made using a Mettler Toledo Star System at a heating rate of 10°C per minute under air atmosphere. Solubility of the copolymers in their salt form in DMSO was evaluated as the amount of solvent required to dissolve 10 mg of the copolymer.

Results and Discussion

Copolymers of o-toluidine and o-chloroaniline at varying ratios were chemically synthesized to form poly(o-toluidine-co-o-chloroaniline). Figure 1 shows the general structure of the copolymers formed.

The names of the copolymers have been abbreviated on the basis of the temperature, the oxidant, the solvent, and the method used for their synthesis. For example, the copolymer synthesized employing 1:1 feed ratio of the comonomers o-toluidine (OT) and o-chloroaniline (OC) by solution method (S) at 0°C (L) is denoted as OTOC11SL while the copolymer synthesized at room temperature (R) is denoted as OTOC11SR. The copolymer synthesized by the emulsion technique employing ammonium persulphate (A) as the oxidant and chloroform as the

![Fig. 1- Repeat unit of the copolymer, poly (o-toluidine-co-o-chloroaniline)](image_url)
Solvent (C) is denoted as OTOC11AC, whereas OTOC11AT denotes a copolymer synthesized under similar conditions in toluene (T) as the solvent. Similarly, the copolymer OTOC11BC was synthesized using benzoyl peroxide (B) as the oxidant in chloroform (C) medium.

Solubility of the copolymers synthesized by different methods was determined in DMSO. Most of the copolymers showed fairly good solubility in DMSO as shown in Table 1 except for the copolymer OTOC11SL prepared by the solution method at 0 °C and that prepared in toluene medium by the inverse emulsion method, OTOC11BT. The former copolymer has lower o-chloroaniline content as seen from the IR and NMR studies discussed below. The insoluble nature of OTOC11BT could not be understood. The copolymer OTOC11AT which has a rather high o-chloroaniline content shows the highest solubility. Irrespective of the method of synthesis, the yield of the copolymers calculated on the basis of the monomers taken was between 32 and 37% except in one case. The yield was exceptionally high for the copolymer synthesized in toluene medium by the inverse emulsion method.

Although homopolymerization of o-chloroaniline requires a stronger oxidizing agent, i.e., chromic acid in HCl medium, interestingly the copolymers of o-chloroaniline with toluidine could be prepared with milder oxidizing agents, viz., ammonium persulphate and benzoyl peroxide.

### Conductivity

The conductivity of the copolymers is considerably higher than those of the corresponding homopolymers, poly(toluidine) and poly(chloroaniline). The conductivity of the copolymers varies over the range $2.8 \times 10^{-2} - 8 \times 10^{-4} \text{ S cm}^{-1}$. The copolymer synthesized at room temperature exhibits a lower conductivity than that synthesized at 0°C for the same comonomer feed ratio. This may be due to the larger number of defects which may occur in the copolymer synthesized at ambient temperature. On the other hand, the copolymers synthesized by the emulsion method show higher conductivity compared to those obtained by the inverse emulsion method. Interestingly benzoyl peroxide which has a lower oxidation potential supports the copolymerization of o-chloroaniline to a relatively greater degree. It results in lower conjugation and hence lower conductivity. The copolymers prepared in toluene medium exhibit higher conductivity than those prepared in other solvents demonstrating the effect of the solvent medium on the structure of the polymer chain formed and on doping as verified from the presence of the polaron peak around 800 nm in the absorption spectra of the copolymers OTOC11AT and OTOC11BT discussed.
DMSO electron donating effect of the -CH₃ groups increases copolymers conductivity. Sometimes they are higher than those of copolymers with moderate o-chloroaniline content assigned to the Table 1. The spectra consist of four major absorption bands. The first band in the region 311-316 nm is assigned to the π-π* transition of the benzenoid ring based on the earlier studies on polytoluidines⁴,⁶,¹⁰. It is related to the extent of conjugation between the phenyl rings along the polymer chain. The second absorption at 600-618 nm is assigned to the “exciton” transition from HOMO of benzenoid to LUMO of quinoid ring. It is sensitive to the overall oxidation state of the polymer. Both the 430 and 800 nm absorptions are assigned to the polaron transitions. They are observed only when the degree of doping and solubility of the copolymer in the salt form are considerably high since they are weak absorptions. Most of the copolymers exhibit a band around 800 nm. The 450 nm absorption band is observed as a very weak band and small shifts of the neighboring peaks lead to overlapping. Thus, the weak band near 450 nm is often not observed since it may merge with the high intensity 315 nm peak or the 600 nm peak depending upon its position in the spectrum.

A noticeable feature of the spectra of the copolymers is a small bathochromic shift of the 600 nm peak when compared to that of pure POT (where it occurs at 602 nm). This shift may be due to the lowering of the band gap of the copolymer due to the presence of o-toluidine (with a donor -CH₃ group) alternating to o-chloroaniline (with an acceptor -Cl group)¹¹ as shown in Fig.1. However, the bathochromic shift is not observed for the copolymers synthesized by the inverse emulsion method. Since benzoyl peroxide is a milder oxidizing agent than ammonium persulphate, probably a higher amount of o-chloroaniline is incorporated into the copolymer as noted earlier, significantly decreasing the electron density on the ring and hence copolymers with diminution in conjugation are obtained.

The temperature at which the solution polymerization is carried out seems to influence the absorption spectra. The copolymer synthesized at 0°C displays increased bathochromic shift of the exciton band (which occurs at 602 nm in POT) probably due to smaller amount of o-chloroaniline segments in the copolymer. The solvent used to carry out the copolymerization by emulsion and inverse emulsion methods does not seem to have any significant effect on the absorption spectra.

**Absorption spectra**

Figure 2 shows the UV-visible spectra of the copolymers OTOC11AC and OTOC11SL recorded in DMSO solution as typical of copolymers. The spectral bands for all the copolymers investigated are listed in Table 1. The spectra consist of four major absorption bands. The first band in the region 311-316 nm is assigned to the π-π* transition of the benzenoid ring based on the earlier studies on polytoluidines⁴,⁶,¹⁰. It is related to the extent of conjugation between the phenyl rings along the polymer chain. The second absorption

**FT-IR spectra**

In the IR spectra of OTOC11SL and OTOC11BC as typical of copolymers, a small weak band at ~3200 cm⁻¹ in poly(o-toluidine) spectra corresponding to the hydrogen bonded N-H vibrations is found shifted to
normally infrared-inactive mode becomes active when a protonation process induces conformational changes in the polymer chain, i.e., forming polarons or bipolarons. The spectra of the copolymers exhibit a fairly intense absorption at 758-764 cm\(^{-1}\) due to the characteristic C-Cl stretching which occurs as a strong absorption at 746 cm\(^{-1}\) in the monomer indicating the presence of o-chloroaniline units in the copolymers.

The strong C-H out of plane bending vibrations of the 1,2,4-trisubstituted benzenes appear around 880 and 810 cm\(^{-1}\) indicating that the monomers in the copolymers are bonded head to tail in agreement with the expected structures. The IR spectra of o-toluidine and o-chloroaniline copolymers show the quinoid and benzenoid absorptions at about 1580 and 1495 cm\(^{-1}\) for the doped structure. The IR spectra of the copolymers show characteristic bands of the functional group$^7$-CH$_3$ at ca.1005 cm\(^{-1}\).

An intense C-Cl absorption was found in the spectra of the copolymers OTOC11AC and OTOC11BC which were synthesized in chloroform medium using ammonium persulphate and benzoyl peroxide respectively as the oxidants. The spectra of the other copolymers and particularly the spectrum of OTOC11AT show a weak band for C-Cl stretching. It clearly indicates that the amount of o-chloroaniline copolymerized depends on the synthesis conditions.

**FT-Raman spectra**

The FT-Raman spectrum of the homopolymer POT exhibits intense peaks at 1610, 1498, 1361 and 1257 cm\(^{-1}\). These bands are found in the o-toluidine - o-chloroaniline copolymers with small shifts supporting the presence of o-toluidine units in the copolymer. The band at 1610 cm\(^{-1}\) is attributed to the C=C stretching and the peak at 1498 cm\(^{-1}\) to the C=N stretching of the quinoid and benzenoid rings respectively. The spectrum of o-chloroaniline shows strong bands at 1025, 838, 680 and 563 cm\(^{-1}\). The spectra of the copolymers exhibit these characteristic peaks with small shifts indicating the presence of o-chloroaniline units in the copolymer. As noted earlier from the IR spectra, the intensity of the peaks arising from o-chloroaniline is highest when the synthesis was carried out in chloroform as the solvent medium. The spectra of both OTOC11AC and OTOC11BC show more intense Raman bands arising from
α-chloroaniline units consistent with the FT-IR studies.

**1H NMR spectra**

The 1H NMR spectra consist of resonance peaks in the region of 0.8-1.0 ppm and 1.8-2.2 ppm corresponding to the methyl protons of the quinoid and benzenoid rings respectively of POT demonstrating the presence of α-toluidine segments in the copolymer. The resonance peaks of -NH protons along the polymer chain occur at 3.6 ppm, while the monomeric or chain end -NH₂ protons are found at 5.2 ppm. The aromatic protons of α-chloroaniline occur in the region of 6.8-7.2 ppm and those of α-toluidine occur at 7.4-8.0 ppm. For the copolymers prepared by the emulsion/inverse emulsion method, the quinoid protons are masked by the surfactant impurities. On the other hand, the copolymers prepared by the solution method show peaks due to the monomeric -NH₂ protons which are totally absent in other copolymers. This could be due to the presence of a larger number of low molecular weight chains which are not completely removed by washing.

The effect of synthesis conditions on the composition of the copolymers could be observed from the NMR spectra. 1H NMR spectra of the copolymers OTOCl11SR, OTOCl11AC and OTOCl11BC showed fairly intense aromatic signals arising from α-chloroaniline, whereas the other copolymers exhibited signals chiefly of α-toluidine showing that the synthesis carried out at 0°C as well as in toluene medium provide copolymers with low α-chloroaniline content.

The compositions of the copolymers were semiquantitatively verified from 1H NMR spectra by comparing the intensities of the aromatic protons of α-toluidine and α-chloroaniline. The highest intensity of α-chloroaniline peaks is observed for the copolymer OTOCl11BC which has an α-toluidine to α-chloroaniline copolymer composition ratio of 2.3:1. The copolymer OTOCl11R had α-toluidine and α-chloroaniline in the ratio of 4.2:1, whereas the composition ratio of OTOCl11E was 7:1. For OTOCl11AT, OTOCl11SL and OTOCl11BT, the α-chloroaniline content was very low (less than 5%).

Thus, the spectroscopic studies reveal the formation of true copolymers and not a mixture of the homopolymers.

### Thermogravimetric analysis

The TGA curves for the copolymers show a three-step weight loss; the results are summarized in Table 2. The weight loss up to ~130°C is due to the loss of moisture. The second weight loss step occurring up to ~300°C is attributed to the loss of substituent/dopant Cl/HCl. The final step which starts around 400°C leads to the complete degradation of the copolymer chain. The copolymers thus have better thermal stabilities when compared to the homopolymer POT for which the degradation temperature is 335°C. The copolymer synthesized by the solution method at 0°C was found to have a higher thermal stability. This could be due to the formation of highly ordered and strongly conjugated structures of high molecular weight at low temperatures. Among the copolymers synthesized at room temperature, OTOCl11AC has a higher stability, while the copolymer OTOCl11BC is the least stable. The lower stability could be the result of the diminution in conjugation due to the electron withdrawing effect of the chlorine substituent. At the same time, the presence of moderate level of α-chloroaniline units (as in the copolymer OTOCl11AC) could lead to a higher degree of hydrogen bonding as well as inter chain linking due to the presence of -Cl as the ring substituent and hence increase in the thermal stability.

### Conclusion

Electronic and steric effects of the aniline substituents markedly affect the copolymerization of 2-substituted aniline derivatives namely α-toluidine and α-chloroaniline. Although homopolymerization of α-chloroaniline requires a stronger oxidising agent (chromic acid in HCl), the copolymers of

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp. range, °C (wt. loss, %)</th>
<th>1st step</th>
<th>2nd step</th>
<th>3rd step</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTOCl11SL</td>
<td>50–133 (10)</td>
<td>158–308 (16)</td>
<td>444</td>
<td></td>
</tr>
<tr>
<td>OTOCl11SR</td>
<td>50–117 (3)</td>
<td>127–227 (9)</td>
<td>381</td>
<td></td>
</tr>
<tr>
<td>OTOCl11AC</td>
<td>50–138 (8)</td>
<td>187–300 (15)</td>
<td>413</td>
<td></td>
</tr>
<tr>
<td>OTOCl11AT</td>
<td>50–127 (7)</td>
<td>188–281 (7)</td>
<td>404</td>
<td></td>
</tr>
<tr>
<td>OTOCl11BT</td>
<td>50–144 (10)</td>
<td>223–358 (21)</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>OTOCl11BC</td>
<td>50–129 (5)</td>
<td>185–300 (18)</td>
<td>362</td>
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</table>
α-chloroaniline with toluidine could be readily synthesized using milder oxidants, viz., benzoyl peroxide and ammonium persulphate. The conductivity of the copolymers range from $2.8 \times 10^{-2} - 7.2 \times 10^{-4}$ S cm$^{-1}$, which is higher than that of the homopolymers, poly(α-toluidine) and poly(α-chloroaniline). The copolymer, OTOC11BC, synthesized by the inverse emulsion method using chloroform as the solvent has a higher α-chloroaniline content, but its thermal stability and conductivity are low. On the other hand, the copolymer OTOC11AC synthesized by emulsion method also possesses higher α-chloroaniline content but exhibits higher thermal stability and conductivity.

References