



Research Article

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Effect of copolymer composition on solubility and electrical conductivity of poly(aniline-co-o-chloroaniline)

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ABSTRACT

Chemically oxidation copolymerization of aniline and o-chloroaniline with 4 molar ratios have been synthesized using ammonium persulphate as an oxidant in HCl medium at 0-4 °C. The molar feed ratio of monomers is varied to prepare copolymers of different composition. The solubility and spectroscopic analysis suggest that the product is a copolymer of aniline and o-chloroaniline. The electrical conductivity of the compressed pellets was measured by two probe method. The electrical conductivity of copolymer is found to be less than polyaniline but processibility has been improved significantly in solvents like NMP, DMSO and DMF. The electrical conductivity of the copolymer is lower than polyaniline due to diminution in π conjugation along the chain caused by the steric effect of the -Cl group.

Keywords: Conducting copolymers; Polyaniline and derivatives; Conductivity and Solubility.

INTRODUCTION

Electrically conducting polymers are novel class of synthetic metals that combine the chemical and mechanical properties of polymers with the electronic properties of metals and semiconductors [1]. Polyaniline is an important member in the class of electrically conducting polymers due to the easy doping-dedoping process and its thermal and environmental stabilities. The conjugation mechanism of polyaniline is unique among other conducting polymers, owing to a combination of benzenoid and quinoid rings leading to three different oxidation states [2]. Polyaniline and its derivatives can be used as active electrode materials in microelectronics and electrochromic display devices [3]. However, applications of polyaniline are limited by poor solubility in common organic solvents. To increase the processibility of the polymer, the use of substituted polyaniline is attractive.

The aim of the present work is to synthesize copolymers by chemical copolymerization of aniline with o-chloroaniline. The effect of copolymer composition on solubility and electrical conductivity have been studied.

EXPERIMENTAL SECTION

Synthesis of Homopolymers

Polyaniline (PANI), Poly(o-chloroaniline) (PoClANI) were chemically synthesized [4-6] using ammonium peroxydisulphate as an oxidant in aqueous 1M HCl at 0-4 °C.

Synthesis of Copolymers

Poly(aniline-co-o-chloroaniline) (PANI-co-PoClANI) copolymers were chemically copolymerized [7-10] from the monomers, aniline and o-chloroaniline using ammonium peroxydisulphate as an oxidant in aqueous 1M HCl at 0-4 °C.

The homopolymers and copolymers obtained from reaction mixture were filtered and washed with distilled water and methanol to remove unreacted monomers and then dried in an air oven at 70 °C for 8 hours.

Characterization

The solubility of the homopolymers and copolymers salt form was tested by dissolving each material in DMF. The mixture was kept for 24 h at room temperature, after which the solution was filtered through sintered glass crucible G₄. The room temperature solubility was determined. UV-Visible spectra of homopolymers and copolymers were recorded at room temperature in NMP in 190-700 nm range using UV-240 Shimadzu Automatic Recording Double Beam Spectrophotometer. FTIR spectra of homopolymers and copolymers were recorded on 550 series II, Nicolet, using KBr pellet technique in the range of 400-4000 cm⁻¹. DC electrical conductivity of polymer samples was measured by two probe method. The resistance was measured as a function of temperature using LCR meter 926.

RESULTS AND DISCUSSION

The solubility of homopolymers and copolymers are presented in Table 1. PANI and PoClANI homopolymers show low and high solubility as compared to copolymers, which indicates that the incorporation of the substituted monomer units in the copolymer which gives a solubility intermediate between the corresponding homopolymers. The substituent introduces flexibility into the rigid PANI backbone structure as a result copolymers show higher solubility than PANI.

Table 1 Solubility and Electrical Conductivity at room temperature of polymer samples

Polymer/Copolymer	Solubility, g/dl	Conductivity σ , (S/cm)
PANI	0.0614	6.550×10^{-2}
PoClANI	0.6780	2.026×10^{-8}
PANI-co-PoClANI (80:20)	0.4020	5.191×10^{-4}
PANI-co-PoClANI (60:40)	0.5120	3.517×10^{-4}
PANI-co-PoClANI (40:60)	0.5780	1.860×10^{-4}
PANI-co-PoClANI (20:80)	0.5970	1.226×10^{-4}

The absorption bands of homopolymers and copolymers in NMP are recorded. The corresponding bands are given in (Table 2). There are two absorption bands in the electronic spectra of the homopolymers and copolymers. The band around 265-330 nm (4.6792-3.7575 eV) is assigned to $\pi \rightarrow \pi^*$ (bandgap) transition (which is related to the extent of conjugation between the adjacent rings in the polymer chain) and the band above 630 nm (exciton band) is due to inter band charge transfer associated with excitation of benzenoid to quinoid moieties [11] (formation of exciton).

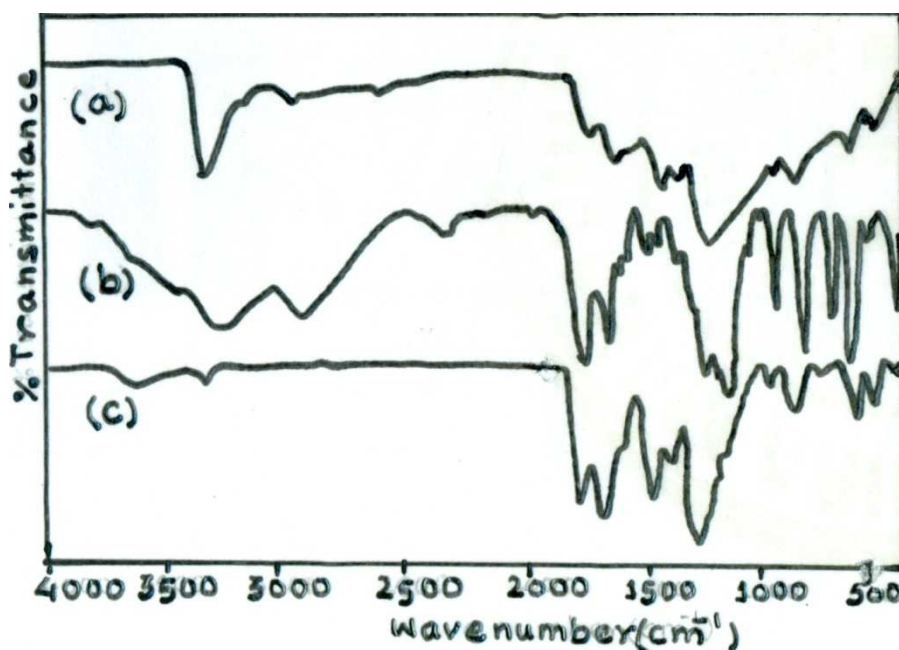


Figure 1 FTIR Spectra of (a) PANI (b) PoClANI (c) PANI-co-PoClANI (40:60)

Table 2 UV-Vis. absorption bands of polymer samples.

Polymer/Copolymer	UV-vis. absorption band nm (eV) in NMP	
	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
PANI	330 (3.7575)	630 (1.9682)
PoClANI	283(4.3816)	596 (2.0840)
PANI-co-PoClANI (80:20)	265 (4.6792)	570 (2.1754)
PANI-co-PoClANI (60:40)	265 (4.6792)	590 (2.1016)
PANI-co-PoClANI (40:60)	270 (4.5925)	605 (2.0495)
PANI-co-PoClANI (20:80)	300 (4.1333)	610 (2.0327)

Figure 1(a, b and c) present the FTIR spectra of PANI, PoClANI and PANI-co-PoClANI (40:60). FTIR spectra of PANI (Fig.1(a)) exhibits band at 1780 cm^{-1} and 1450 cm^{-1} corresponds to the C-C ring stretching vibration of the quinonoid and benzenoid form. The band at 1250 cm^{-1} is assigned to the C-H bending mode. The band at 1200 cm^{-1} is assigned to the C-N stretching, 1122 cm^{-1} correspond to in plane C-H bending mode, 3310 cm^{-1} - NH stretch. The band at $1618\text{ -}1534\text{ cm}^{-1}$ is assigned to the quinonoid and benzenoid phenyl ring.. The spectral characteristics of PANI-co-PoClANI(40:60) (Fig.1(c)) are similar to PANI and PoClANI. The FTIR spectra of PANI-co-PoClANI resembles the C = C stretching of the benzene ring appear at 1480 cm^{-1} and C-N stretching[12] at 1300 cm^{-1} that of PoClANI and with the increase in amount of oClANI in copolymer chain, the intensity of -NH₂ band increases.

The electrical conductivity of copolymer salts are measured and compared to that of homopolymers, the results are summarized in Table 1. The PANI shows conductivity of order of $6.550 \times 10^{-2}\text{ S cm}^{-1}$ and $2.026 \times 10^{-8}\text{ S cm}^{-1}$ for PoClANI while copolymer shows lower conductivity than PANI which indicates the ionization potential, bandgap and bandwidth are affected by torsion angle between adjacent rings on substituents. The conductivity of copolymers decreases with increasing the content of o-chloroaniline in copolymers is due to the incorporation of chloroaniline which may be restricting the mobility of electrons.

CONCLUSION

The chemical oxidative copolymerization of aniline with o-chloroaniline has been carried out. The ratio of the two monomers has influence on the copolymerization process due to different reactivity of monomers. The solubility of the copolymers increases with increasing the content of o-chloroaniline in copolymers. However, their electrical conductivities are lower than PANI.

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