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ELECTRICAL, ELECTRONIC AND THERMAL STUDIES ON POLY(ANILINE-Co-N-PHENYLANILINE) COPOLYMERS

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ABSTRACT

Poly(aniline-co-N-phenylaniline)copolymers have been synthesized through the chemically oxidative copolymerization of aniline and N-phenylaniline in aqueous hydrochloric acid medium under nitrogen atmosphere at 0-4^{0}C. The molar feed ratio of monomers is varied to prepare copolymers of different compositions. These copolymers are characterized by the various techniques like C, H and N analysis, FTIR, UV-visible spectroscopy and TGA. The electrical conductivity of copolymers is less than polyaniline but processability has been improved significantly. These copolymers exhibit improved solubility in organic solvents like 1-methyl-2-pyrrolidone (NMP), dimethyl sulphoxide (DMSO) and dimethyl formamide (DMF). Copolymers have been observed to be thermally more stable than polyaniline.

Key words: Polyaniline, Copolymers, Conductivity, Poly (aniline-co-N-phenylaniline) FTIR, TGA.

INTRODUCTION

Electrically conducting organic polymers are a novel class of synthetic metals that combine the chemical and mechanical properties of polymers with the electronic properties of metals and semiconductors. These polymers become conductive upon partial oxidation or reduction; a process commonly referred to as doping. These novel polymers are under intensive research and development world wide both in the academic world and in the chemical and electronic industries. During the last two decades, polyaniline(PANI) has been studied extensively[1-4] PANI has emerged as a potential conductive material due to its comparatively fair environmental stability, ease of preparation[5] and wide areas for its applications.

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PANI is made up of combination of fully reduced (B-NH-B-NH) and fully oxidized (B-N=Q=N-) repeating units, where B denotes a benzenoid and Q denotes a quinoid ring. Thus, differents ratios of these fully reduced and fully oxidized units yield various forms of PANI, such as leucoemeraldine (100% reduced form), emeraldine base (50% oxidized form) and pernigraniline (fully oxidized form). However, all of these forms are electrically insulating in nature. Doping of emeraldine base with a protonic acid converts it into conducting form protonated emeraldine (emerdine salt). The main issue with PANI is processing difficulties due to its infusibility and relative insolubility in common organic solvents. It can be made processable/soluble either by polymerizing functionalized anilines[6,7] or by copolymerizing aniline with substituted monomers[7-10]. The copolymerization is a powerful method to improve processability of conducting polymers. In general, solubility of substituted PANIs in organic solvents is significantly higher than PANI. However, their thermal stability and electronic conductivities are substantially lower than doped PANI. In order to maintain balance between conductivity, stability and processability, copolymerization has been done.

In this paper, poly(aniline-co-N-phenylaniline) copolymers have been synthesized by chemical peroxidation method. These copolymers are characterized by the various techniques like C, H and N analysis, FTIR, UV-visible spectroscopy and TGA. Their electronic conductivities have been measured by two-probe technique.

EXPERIMENTAL

Aniline (S.D.Fine Chem.) was distilled before use. N-Phenylaniline (S.D.Fine Chem.) and all other chemicals were used as purchased.

Synthesis of homopolymers

(a) Polyaniline (PANI) was chemically synthesized[11-13] using ammonium peroxodisulphate as an oxidant in an aqueous 1 M HCl in nitrogen atmosphere at 0-4^{0}C.

(b) Poly(N-phenylaniline) (PNPANI) was chemically synthesized[11-13] using ammonium peroxodisulphate as an oxidant in an aqueous 1 M HCl and CH_3CN (1 : 1 ratio) in nitrogen atmosphere at 0-4^{0}C.

Synthesis of copolymers

Poly(aniline-co-N-phenylaniline) (PANI-co-PNPANI) copolymers were chemically copolymerized[14-16] from the monomers, aniline and N-phenylaniline using ammonium peroxodisulphate as an oxidant in an aqueous 1M HCl and CH_3CN (1 : 1ratio) in nitrogen atmosphere at 0-4^0C. The molar feed ratio of starting aniline monomer was varied to result in copolymers of different compositions. The homopolymers and copolymers obtained from reaction medium were filtered. These were washed with distilled water and methanol several times to remove unreacted monomers and then dried in an air oven at 70^0C for 8 hours.

Characterization

The solubility of the homopolymers and copolymers 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 G_4. The room temperature solubility was recorded. The density of homopolymers and copolymers was measured at 30^0C using hydrometer by flotation method in the mixture of benzene and carbon tetrachloride.

C, H and N analysis of homopolymers and copolymers was carried out by microanalytical technique at RSIC, Central Drug Research Institute, Lucknow using a Carlo-Erbastum DP-200 instrument. UV-Visible spectra of homopolymers and copolymers were recorded at room temperature in NMP, DMF and DMSO 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} at RSIC, Nagpur University, Nagpur. TGA of homopolymers and copolymers was recorded on TGA / SDTA 851 Mettler Toledo in nitrogen atmosphere with heating rate of 15^0C/min.

DC electrical conductivity of polymer samples was measured by the two probe technique in the temperature range of 298-398 K. Dry powdered samples were made into a pellet under hydraulic press IEBIG and placed between electrodes in a cell. Resistance was measured on a DC resistance bridge LCR Meter 926. The conductivity value was calculated from the measured resistance and sample dimensions.

RESULTS AND DISCUSSION

The solubility and density of homopolymers and copolymers are presented in Table 1. PANI and PNPANI homopolymers show low and high solubility as compared to copolymers, which indicates the incorporation of the substituted monomer units in the copolymer, which gives a solubility intermediate between the corresponding homopolymers. The substituent introduce flexibility into the rigid PANI backbone structure as a result, copolymers shows higher solubility than PANI. The density of copolymers is intermediate between their homopolymers. In the copolymerization process, substituted aniline may affect the crystallinity and growth of the chain and hence, the copolymer density is lesser than the PANI. The elemental data of homopolymers and copolymers along with calculated values are presented in Table 2. Theoretical values are calculated considering two anions in four ring monomer units[17] for homopolymers and four anions in eight ring monomer units for copolymers.The discrepancies in calculated and experimental values are due to the different levels of counter ion and protonation. While calculating these values, the complete protonation has been assumed at lower temperature that may not be the same in all cases and also the monomer reactivity of aniline and N-phenylaniline is different in copolymerization reactions. The empirical repeat unit for homopolymers and copolymers is shown in Figs. 1 and 2.

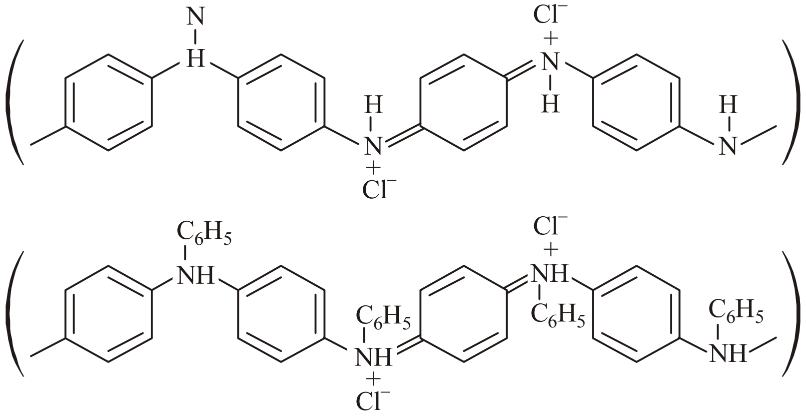

Fig. 1: Repeat unit for homoolymers (a) PANI (b) PNPANI

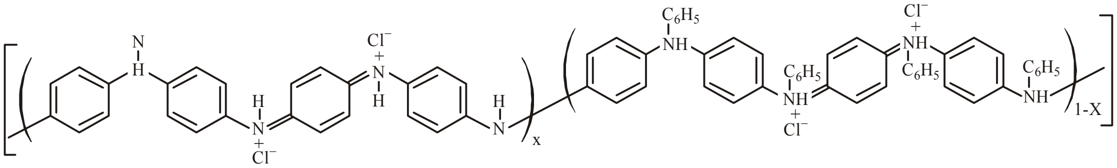

Fig. 2: Repeat unit for copolymers

Table 1: Solubility, density and electrical conductivity at room temperature of homopolymers and copolymers

Polymer/Copolymer σ (S/cm)	Solubility (g/dL)	Density (g/cm^3)	Conductivity
PANI	0.0414	1.3140	6.55 x 10^{-2}
PNPANI	0.0732	1.2430	1.026 x 10^{-9}
PANI-co-PNPANI (60 : 40)	0.0560	1.2590	2.191 x 10^{-7}
PANI-co-PNPANI (30 : 70)	0.0625	1.2200	1.517 x 10^{-8}

Table 2: Elemental analysis data of homopolymers and copolymers

Polymer/Copolymer	Experimental (Calculated) (%)		
	C	H	N
PANI	59.90 (66.20)	4.63 (4.59)	10.50 (12.87)
PNPANI	73.84 (77.94)	4.42 (4.87)	7.20 (7.57)
PANI-co-PNPANI (60 : 40)	68.62 (64.24)	5.05 (4.20)	7.73 (8.92)
PANI-co-PNPANI (30 : 70)	75.28 (68.11)	5.37 (4.34)	6.60 (7.79)

The absorption bands of homopolymers and copolymers in NMP, DMF and DMSO were recorded. The corresponding bands are recorded in Table 3. There are two absorption bands in the electronic spectra of homopolymers and copolymers. The bands around 290-330 nm (4.278-3.760 eV) is assigned to π - π^* (band gap) transition (which is related to the extent of conjugation between the adjacent rings in the polymer chain) and the band above 540 nm (exciton band) is due to inter band charge transfer associated with excitation of benzenoid to quinoid moieties[18](formation of exciton). These bands change with solvents. The π - π^* band of copolymers shows hypsochromic shift with the increase in dielectric constant of the solvent[19]. The exciton band shows the bathochromic shift with an increase in dielectric constant of the solvent. The excitation leads to formation of molecular exciton (positive charge on the adjacent benzenoid units and negative charge centred on quinoid unit)[20]. This interchain charge transfer from HOMO to LUMO may lead to the formation of positive and negative polarons. A polymer in a solvent of high dielectric constant may exist in coil like conformation (decrease in conjugation) and a less polar solvent provides thermodynamically more stable chain conformation and restricts the polymer to lower energy high planarity state. Such shift may increase the conjugation of the system, which yields a lower energy transition; a red shift[21]. The band in copolymers shifts to the lower wavelength as the percentage of N-phenylaniline in copolymer increases. It may be due to addition of more phenyl groups, which twist the torsion angle and are expected to increase the average band gap in the conjugated polymer chain.The continuous variation of the wavelength and intensity of the UV-VIS bands may have resulted from the copolymerization effect of N-phenylaniline and aniline. In other words, the polymer formed by the oxidative polymerization of N-phenylaniline with aniline is the copolymer of two monomers rather than a mixture of two homopolymers.

Table 3: UV-VIS Absorption bands of homopolymers and copolymers

Polymer/Copolymer	**UV- Visible Absorption band (nm)**					
	NMP		**DMF**		**DMSO**	
PANI	330	628	328	618	314	618
PNPANI	314	600	310	610	310	600
PANI-co-PNPANI (60 : 40)	292	560	298	560	294	580
PANI-co-PNPANI (30 : 70)	290	560	296	540	290	580

The FTIR spectra of homopolymers and copolymers are shown in Fig. 3 and spectral data are recorded in Table 4. The FTIR spectra of PANI shows a broad band at 3431 cm^{-1}; characteristics of N-H stretching. The band in the range 810-819 cm^{-1} may be assigned to 1,4-substituted aromatic ring indicating the bonding in polymers and copolymers were through 1,4-position. The bands at 1569 cm^{-1} and 1492 cm^{-1} are assigned to quinoid nitrogen (N=Q=N) and benzenoid (N-B-N) ring stretching. In the spectra of copolymer, there appears an absorption band at 1310 cm^{-1} (C-N stretching) and 1500 cm^{-1} (benzenoid stretching) indicating the existence of phenyl group on a benzene ring. The relative intensity of 1600-1500 cm^{-1} is between those of PNPANI and PANI, and so the coexistence of N-phenylaniline and aniline units in the copolymer was further confirmed.

Table 4: FTIR Spectral data of homopolymers and copolymers

Polymer/Copolymer	**Wavenumber (cm^{-1})**						
PANI	819	1145	1246	1300	1492	1569	3431
PNPANI	810	1160	1250	1315	1510	1560	
PANI-co-PNPANI (60 : 40)	813	1141	1242	1310	1485	1556	

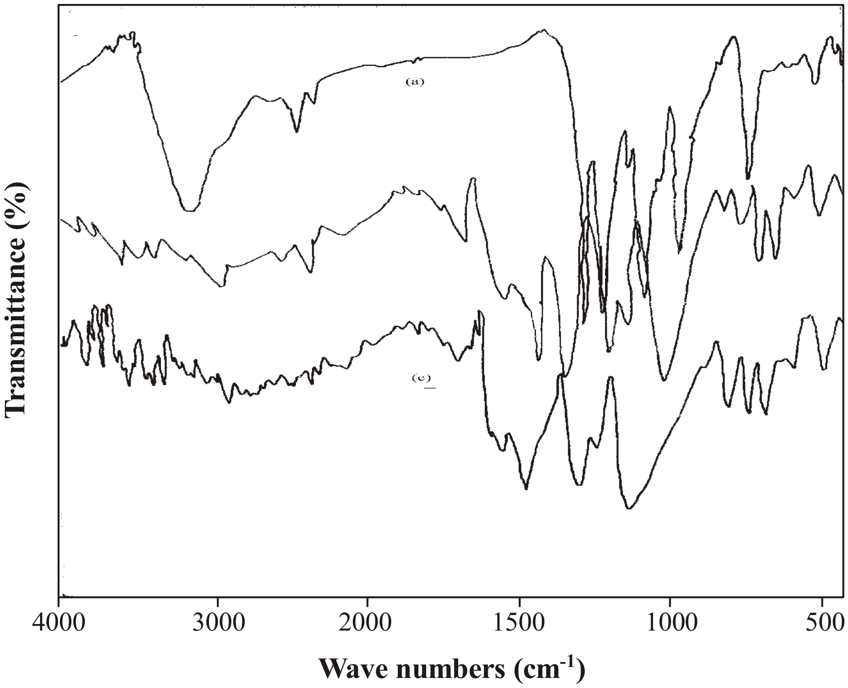

Fig. 3: FTIR Spectra of (a) PANI (b) PNPANI (c) PANI-co-PNPANI (60 : 40)

The TG thermograms of homopolymers and copolymers (Fig. 4) in nitrogen atmosphere shows three distinct stages of mass loss. In the first stage, mass loss is due to the loss of moisture (absorbed water), the second stage of mass loss is due to loss of some low molecular mass and the third stage of mass loss may be due to the decomposition of sample. The decomposition pattern of homopolymers and copolymers is given in Table 5. The copolymers; thus, have better thermal stabilities when compared to the PNPANI for which the degradation temperature is 420^{0}C. The stability decreases with an increase in the amount of N-phenylaniline in copolymer.

The electrical conductivity of copolymer salts were measured and compared to that of homopolymers, the results are summarized in Table 1. The PANI shows conductivity of order of 6.55 x 10^{-2} S cm^{-1} and it is 1.026 x 10^{-7} S cm^{-1} for PNPANI, while copolymer shows lower conductivity than PANI, which indicates the ionization potential, band gap and bandwidth are affected by torsion angle between adjacent phenyl rings to relieve steric strain in polymer chain. The conductivity of copolymer decreases with increasing the content of N-phenylaniline in copolymers. The temperature dependence of electrical conductivity data was fitted to an Arrhenius equation i.e. $\sigma(T) = \sigma_o \exp -Ea/2kT$ and the measured values were plotted semilogarithmically as a function of reciprocal of temperature (Fig. 5).

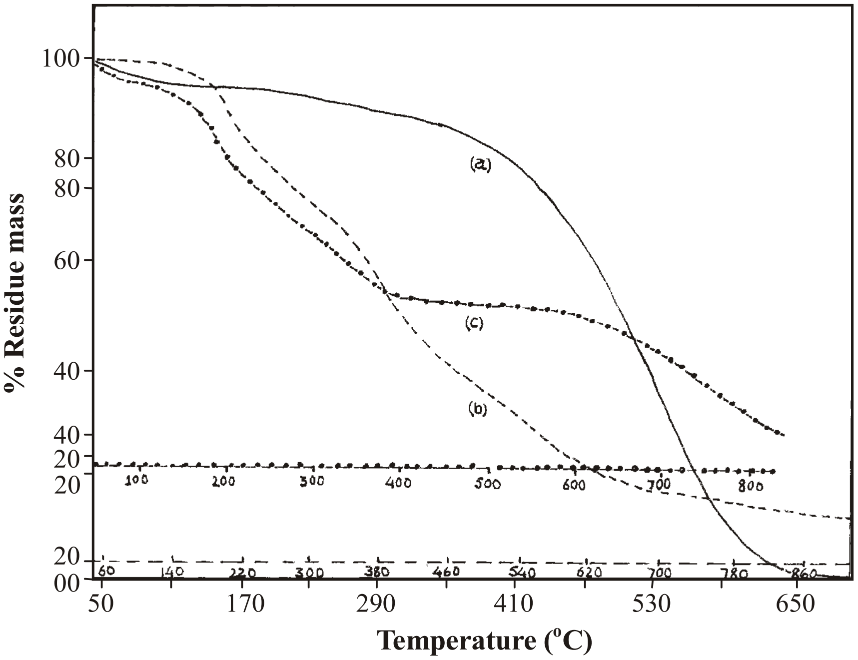

Fig. 4: TGA curve of (a) —— PANI (b) ······ PNPANI and (c) -•-•- PANI-co-PNPANI (60 : 40) in N_2 atmosphere

Table 5: Decomposition pattern of homopolymers and copolymers

Polymer/ Copolymer	Temp. range (°C)	%Mass loss Obs. (Theo.)	Constituent lost & comment	Max. decomp. temp. (°C)
PANI	165	5.2	H_2O	500
	165-380	11.4	Low molecular wt.	
	650	2.0	polymer Residual mass	
PNPANI	160	6.10	H_2O & CH_3CN	520
	160-260	9.80 (9.74)	-C_6H_5 Residual mass	
	860	20.0		
PANI-co-PNPANI (60 : 40)	210	24.86	H_2OCH_3CN & Low mol.	600
	210-520	16.36 (12.26)	wt. copolymer	
	820	26.0	2-C_6H_5 Residual mass	

The conductivity is found to increase with temperature; however, there are deviations at lower temperature. In the present studies, the temperature dependence of

$\sigma(T)$ is fitted to the Zeller equation[22] i.e. $\sigma(T) \alpha$ exp - $(To/T)^{½}$ Fig. 6 decribes the interchain conductivity where only the neighbour variable range hopping (VRH) of charge (which is quasi 1-dimensional) is considered.[23] From temperature dependence, it is suggested that the conduction mechanism in copolymers is possibly a polaron hopping conduction similar to homopolymers[24].

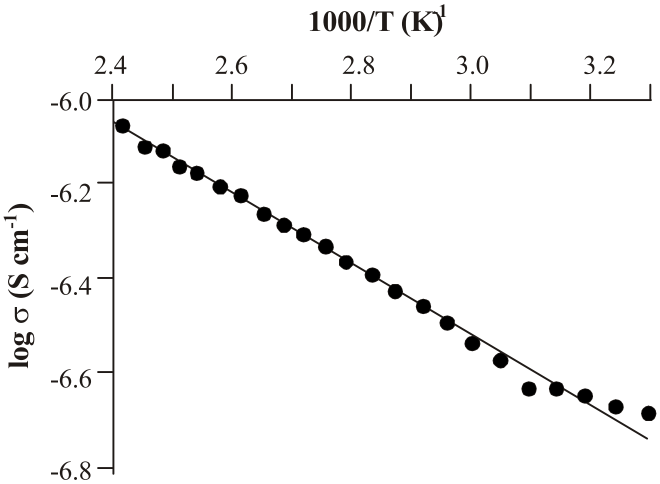

Fig. 5: Temperature dependence of electrical conductivity of PANI-co-PNPANI (60 : 40) (Arrhenius equation)

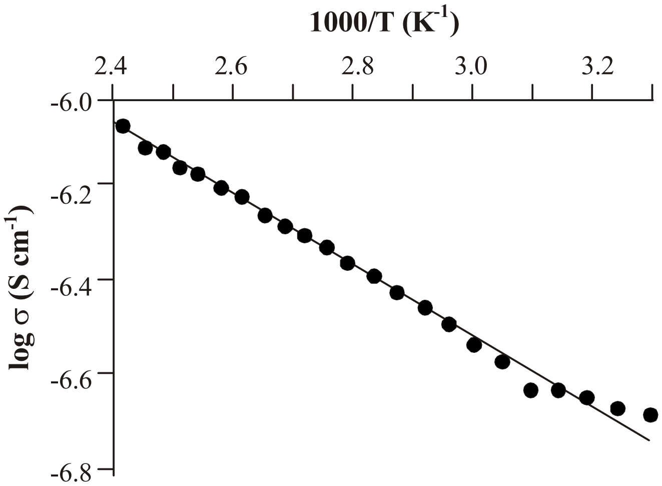

Fig. 6: Temperature dependence of electrical conductivity of PANI-co-PNPANI (60 : 40) (Zeller equation)

CONCLUSIONS

The chemical copolymerization of aniline with N-phenylaniline has been carried out. The ratio of the two monomers has influence on the copolymerization process due to different reactivities of monomers. Elemental analysis data infer that one anion is substituted for every two phenyl rings for complete protonation. Spectroscopic information indicates the presence of both the comonomers in the polymer chain. The temperature dependence of conductivity suggests that the conduction is quasi 1 D variable range hopping between nearest neighboring chains. The substituent group decreases the conductivity of copolymers and the coplanarity of the polymer chain gets disrupted. It also reduces the mobility of the charge carriers along the main chain.

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