Influence of copolymer composition on the transport properties of conducting copolymers: poly(aniline-co-o-anisidine)

S S UMARE*, A D BORKAR[†] and M C GUPTA[†]

Department of Chemistry, Visvesvaraya Regional College of Engineering, Nagpur 440 011, India
[†]Department of Chemistry, Nagpur University, Nagpur 440 010, India

Abstract. The effect of different compositions of monomers on the transport properties of copolymers by various techniques such as optical, electrical and magnetic has been investigated and compared with the homopolymers. The UV-visible absorption spectra show a hypsochromic shift with an increase in the o-anisidine content in copolymers indicating a decrease in the extent for conjugation (i.e. an increase in the bandgap). From temperature dependence of electrical conductivity the transport parameters such as charge localization length and average hopping distance are calculated and also the effect of the monomeric composition on the coherence length has been discussed. The magnetic studies show the paramagnetic and diamagnetic nature of homopolymers and copolymers. The X-ray diffraction pattern indicates that the copolymers are of amorphous nature.

Keywords. Polyaniline; poly(aniline-co-o-anisidine); transport properties.

1. Introduction

Polyanilines (PA) constitute a large family of polymers which can be synthesized by electrochemical method (Genies *et al* 1985; Genies and Tsintavis 1986) or by chemical oxidative polymerization of aniline (MacDiarmid *et al* 1985; MacDiarmid and Epstein 1989; Gupta and Borkar 1990; Gupta and Umare 1992). The chemical synthesis of polyaniline usually involves the oxidative polymerization of aniline in HCl by $(NH_4)_2S_2O_8$ to result in emeraldine hydrochloride salt. The emeraldine hydrochloride salt can be converted to emeraldine base by treating with NH_4OH. The emeraldine base corresponds to 50% oxidized poly(*para*phenyleneamineimine) $[(-C_6H_4-NH-C_6H_4-NH)_y-(C_6H_4-N=C_6H_4=N-)_{1-y}]_x$ (Neoh *et al* 1990). When emeraldine base is equilibrated in a large excess of aqueous acid solution, protonation occurs at imine repeat unit to produce emeraldine salt of polyaniline (PA–ES) believed to have the composition (Umare *et al* 1995; Trivedi 1999)

$$[(C_6H_4-NH-C_6H_4-NH)_y-(C_6H_4-\overset{+}{N}H=C_6H_4=\overset{+}{N}H)_{1-y}]_x,$$
$$\underset{A^-}{|} \qquad \underset{A^-}{|}$$
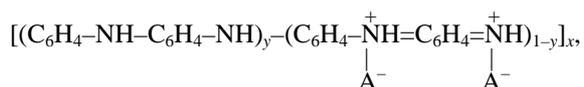
where A^- is the anion and consists of equal number of reduced $[C_6H_4-NH-C_6H_4-NH]$ and oxidized $[C_6H_4-N=C_6H_4=N-]$ repeat units. This results in the increased conductivity. However, conductivity is affected by the protonation, level of oxidation, moisture content, poly-

merization condition, solvent used etc (Gupta and Umare 1992; Umare *et al* 1996). The electrical conductivity of chemically synthesized poly(o-anisidine) (PoA) has been studied. It is observed that the electrical conductivity is substantially less than that of PA (Gupta *et al* 1993; Umare *et al* 1995, 1996) which may be due to steric constraints imposed by methoxy group that could induce additional deformation along the polymer backbone as well as increase the interchain distance. Both factors reduce the mobility of the carriers and as a result lower conductivity is exhibited.

PA represents a class of quasi-1-dimensional disordered conductor which consists of bundles of well coupled chains instead of isolated chains as in conventional quasi-1-dimensional conductors and within these bundles the electron is 3-dimensionally delocalized (Heeger *et al* 1988; Wang *et al* 1991). Thus the electron state in PA–ES is 3-dimensional metallic state in the ordered crystalline regions of the polymers separated from one another by amorphous regions and the formation of bundles is attributed to interchain transfer (Kivelson and Heeger 1988). However, in amorphous regions, the interchains transfer rate is suppressed by disorder, so that the electron is still localized in essentially isolated chain while in PoA inter chain coupling and coherence transfer rate are suppressed due to the presence of $-OCH_3$ group which is non-metallic within crystalline regions.

The copolymerization of aniline and o-anisidine has been performed by chemical oxidation (Umare *et al* 2000). It has been observed that the amount of o-anisidine incorporated in the copolymer chain is more than

---

*Author for correspondence

aniline monomer due to its higher reactivity. In the present paper we have studied experimentally the effect of the o-anisidine content, on the optical, transport properties and X-ray diffraction patterns of copolymers of PA and PoA.

2. Experimental

2.1 *Preparation of copolymers*

Poly(aniline-co-o-anisidine) (PA-co-PoA) copolymers were chemically copolymerized (Siyu *et al* 1997; Borkar *et al* 2001) from the monomers, aniline and o-anisidine, using ammonium peroxodisulphate as an oxidant in acid aqueous medium. The molar feed ratio of the starting aniline monomer was varied to result in copolymers of different compositions. The copolymerization was carried out in N_2 atmosphere at 0–4°C.

UV-visible spectra of the homopolymers and copolymers were recorded at room temperature in different solvents viz. 1-methyl-2-pyrrolidone (NMP) (32·4), dimethylformamide (DMF) (36·7), dimethylsulphoxide (DMSO) (46·7) in 190–700 nm range using a UV-240 Shimadzu automatic recording double beam spectrophotometer. The magnetic susceptibility of the polymeric samples was determined by Gouy's method (Inoue and Yanagisawa 1974) at room temperature using mercury tetrakis(thiocyanato)cobaltate (II), $Hg[Co(CNS)_4]$ as reference material. Magnetic susceptibility value per two-ring mole was computed from the change in mass of the sample under applied magnetic field of different strengths between 2300 and 9800×10^{-4} T. Diamagnetic corrections for the compound and counter ion were applied. X-ray diffractograms were recorded on Philips PW-700 automatic X-ray diffractometer using Cu K$_a$ radiation of wavelength, $l = 0.154060$ and 0.154434 nm. The diffractometer was operated at 35 kV and 20 mA. Electrical conductivity of the polymeric samples was measured as a function of temperature as resistivity by two-probe method. Powdered samples were made into pellets under a pressure of 5 metric tons cm^{-2}. The resistance was measured as a function of temperature using LCR meter.

3. Results and discussion

3.1 *Electronic spectra*

The absorption bands of homopolymers and copolymers in NMP, DMF and DMSO are recorded. The corresponding bands are given in table 1. There are two absorption bands in the electronic spectra of homopolymers and copolymers. The band around 308–330 nm (4·03–3·76 eV) is assigned to $p \to p^*$ (bandgap) transition (which is related to the extent of conjugation between the adjacent rings in the polymer chain) and the band above 600 nm

(exciton band) is due to inter band charge transfer associated with excitation of benzenoid to quinoid moieties (formation of exciton). These bands change with solvents. The $p \to p^*$ band of copolymers shows hypsochromic shift with the increase in dielectric constant of the solvent. Ghosh and Kalpagam (1990) tried to explain such shift on the basis of dielectric constant of the solvent. Macroscopic parameters such as the dielectric constant and refractive index cannot always fully explain the solvatochromism, as it is dependent on many other factors like geometry as well as electronic structures of both solute and solvent. However, the exciton band shows a bathochromic shift with an increase in dielectric constant of the solvent in which the UV-visible absorption spectra were taken. In the case of exciton band the absorption is interchain. The excitation leads to formation of molecular exciton (positive charge on the adjacent benzenoid units and negative charge centred on quinoid unit) (Ginder and Epstein 1990). This interchain charge transfer from HOMO to LUMO may lead to the formation of positive and negative polarons (Stafstrom *et al* 1987).

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 (Zho *et al* 1991). The $p \to p^*$ band in copolymers shifts to the lower wavelength as the percentage of o-anisidine in copolymer increases which may be due to addition of more methoxy groups which twist the torsion angle, which are expected to increase the average bandgap in the conjugated polymer chain.

3.2 *Magnetic susceptibility*

Magnetic susceptibility, c_m, per two-ring unit mole and the magnetic moment data are recorded in table 2. The data show that both the homopolymers PA and PoA show paramagnetism whereas copolymers show diamagnetic

Table 1. UV-visible absorption bands of copolymers and homopolymers.

Polyaniline derivative base form	UV-visible absorption band (nm)					
	DMSO		DMF		NMP	
PA	314	620	328	618	329	620
PA-co-PoA10	318	–	328	614	328	630
PA-co-PoA20	320	620	324	610	332	620
PA-co-PoA40	322	628	322	606	328	620
PA-co-PoA60	322	624	320	600	324	620
PA-co-PoA70	322	620	318	600	322	614
PoA	316	620	308	604	312	622

nature. The homopolymers have large magnetic moments (3–4 unpaired electrons or holes per chain unit). This is equal to 0·75/1·0 electrons/holes per monomer unit in the chain. The change in magnetic susceptibility of the copolymers may be due to change in unpaired spin concentration (polaron/bipolaron) in the chain units. In the study of the spin dynamics of PA it has been proposed that polaron–polaron reaction or polaron ionization to bipolaron (spin-less charge defects) could change the spin concentration in the sample and hence the magnetic susceptibility (Mizoguchi 1990). The polarons in the p-conjugated systems could interact with each other or with neighbouring chains leading to spin-less charged states or hole states (Jozefowicz *et al* 1989; Ginder and Epstein 1990). This state may be free or delocalized depending on the Coulomb forces between the interacting moieties. They can also remain localized in the vicinity of charged counterion formed in inter or intramolecular chains.

3.3 X-ray diffraction

X-ray diffractograms of copolymers show broadening of peaks which indicates copolymers are of amorphous nature while PA is crystalline. The d-spacing calculated from angular positions of the reflections is given in table 3 and from reflection broadening ($2q$), the coherence length (L) of the crystalline order in the sample is calculated using Scherrer formula (Guinior 1963)

$$L = 0.9 \; l/\Delta \, 2(q) \cos q. \tag{1}$$

From table 3 it is observed that there is increase of d-spacing and decrease of coherence length as the fraction of o-anisidine increases in the copolymer composition. On increasing the amount of o-anisidine in the copolymer the crystallite size decreases which may be due to the presence of methoxy group on the aromatic ring which increases disorder and decreases crystal size. Thus, in copolymers the increased charge localization may be due to the reduction of interchain diffusion of charge, decrease of interchain band width which is caused by the large transverse unit cell length and decrease in coherence between the chains caused by greater disorder in interchain separation within crystalline region, due to the existence of the side group ($-OCH_3$) along the main copolymer chain.

3.4 Electrical conductivity

The temperature dependence of conductivity was fitted to an Arrhenius type equation

$$s_{(T)} = s_0 \exp(- Ea/2kT), \tag{2}$$

and the measured values were plotted semilogarithmically as a function of reciprocal of temperature (figure 1a). The conductivity is found to increase with temperature, however, there are deviations at lower temperatures. The reason for the deviation is not known but the results relate to a small temperature range where Arrhenius behaviour can be regarded as a good approximation to band theory. In the present studies the temperature dependence is fitted to the Zeller equation (Shante *et al* 1973). Figure 1b describes the interchain conductivity where only the neighbour variable range hopping (VRH) of charge (which is quasi-1-dimensional) is considered

$$s_{(T)} \; a \exp[- (T_0/T)^{1/2}]. \tag{3}$$

In Zeller equation, T_0 is related to delocalization length (a^{-1}), most probable hopping distance (R) and hopping

Table 2. Magnetic susceptibility of homopolymers and co-polymers.

Polyaniline derivative hydrochloride salt	Magnetic susceptibility, c_m (emu/2 ring unit)	$\mu_{eff.}$, B.M.
PA	6.813×10^{-3}	4.103
PA-co-PoA10	$- 4.345 \times 10^{-3}$	Diamag.
PA-co-PoA20	$- 3.458 \times 10^{-3}$	Diamag.
PA-co-PoA40	$- 2.306 \times 10^{-3}$	Diamag.
PA-co-PoA60	$- 2.908 \times 10^{-3}$	Diamag.
PA-co-PoA70	$- 2.400 \times 10^{-3}$	Diamag.
PoA	3.781×10^{-3}	3.072

Table 3. Characteristics of X-ray diffraction pattern.

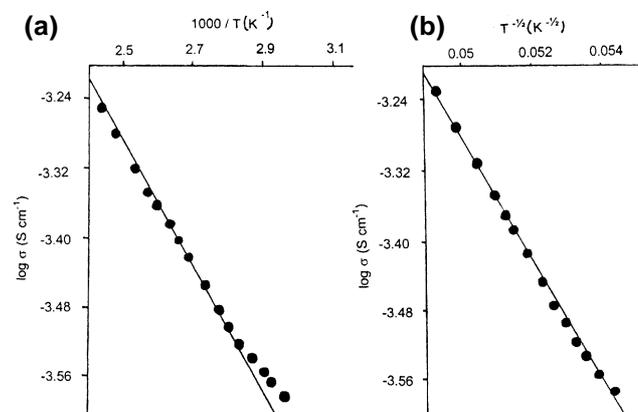| Polyaniline derivative HCl salt	Coherence length (L), (Å)	d-spacing (Å)
PA	8.15	3.53
PA-co-PoA10	8.03	3.52
PA-co-PoA20	8.00	3.54
PA-co-PoA40	3.40	3.56
PA-co-PoA60	4.13	3.59
PA-co-PoA70	6.90	3.63
PoA	5.90	3.59

Figure 1. Temperature dependence of electrical conductivity of PA-co-PoA60 (a) arrhenius equation and (b) zeller equation.

Table 4. Transport properties of copolymers and homopolymers.

Polyaniline derivative HCl salt	s (S/cm)	T_0 (K)	a^{-1} (nm)	R (nm)	w (eV)
PA	$6\cdot5 \times 10^{-2}$	$0\cdot509 \times 10^4$	$4\cdot55$	$4\cdot66$	$0\cdot110$
PA-co-PoA10	$2\cdot7 \times 10^{-2}$	$1\cdot027 \times 10^4$	$2\cdot26$	$3\cdot29$	$0\cdot221$
PA-co-PoA20	$3\cdot4 \times 10^{-3}$	$1\cdot197 \times 10^4$	$2\cdot31$	$3\cdot50$	$0\cdot305$
PA-co-PoA40	$1\cdot6 \times 10^{-3}$	$0\cdot989 \times 10^4$	$2\cdot36$	$3\cdot36$	$0\cdot210$
PA-co-PoA60	$3\cdot4 \times 10^{-4}$	$1\cdot379 \times 10^4$	$1\cdot97$	$2\cdot83$	$0\cdot297$
PA-co-PoA70	$2\cdot2 \times 10^{-4}$	$1\cdot673 \times 10^4$	$1\cdot89$	$2\cdot04$	$0\cdot375$
PoA	$4\cdot1 \times 10^{-4}$	$1\cdot973 \times 10^4$	$1\cdot17$	$2\cdot36$	$0\cdot424$

energy (w) by the relations (4), (5) and (6) (Jozefowicz *et al* 1989; Pouget *et al* 1991).

$$T_0 = 8\ a/N\ (E_F)\ Zk, \tag{4}$$

$$R = (T_0/T)^{1/2} \cdot a^{-1}/4, \tag{5}$$

$$w = ZkT_0/16, \tag{6}$$

where Z is the number of nearest neighbouring chains (~ 4), k the Boltzmann constant and $N(E_F)$ the density of states at fermi energy for sign of spin which is taken as $1\cdot6$ states per eV (2-ring unit suggested for PA) (Jozefowicz *et al* 1989). The value of T_0 is determined graphically from log $s_{(T)}$ vs $T^{-1/2}$ (figure 1b) and other parameters are computed from the data (table 4). It is observed that T_0 for PoA is more than PA (maximum localization length). Therefore, correspondingly the localization length and average charge hopping distance decrease on increasing the amount of o-anisidine in copolymer chain. This increase in the electron localization is due to the presence of –OCH$_3$ group in one of the aromatic rings in the copolymer chain which increases the adjacent torsion in the ring angle to avoid strong steric repulsion from the –OCH$_3$ on the ring and T_0 value increases with more incorporation of o-anisidine in copolymer composition. The temperature dependence of the electrical conductivity fits (3) (figure 1b) for homopolymers and copolymers, which suggests that the charge conduction is quasi-1D VRH between nearest neighbouring chains (Heeger *et al* 1988; Wang *et al* 1991). From the values of T_0 (table 4), the localization length is found to decrease and is in the same order as the coherence length (table 3) obtained from the X-ray diffractogram. This shows that the electrons are delocalized within the crystalline regions, the localization length of copolymers is found to be intermediate between those of homopolymers.

4. Conclusions

WAXRD studies on homopolymer and copolymer show that they are largely amorphous but the crystalline region belongs to orthorhombic crystalline lattice and the inter-chain spacing and coherence length are affected by the percentage of o-anisidine in copolymer chain. The electrical conductivity behaviours of the copolymers show intermediate characteristics, between those of homopolymer PA and PoA. The values of T_0 of the copolymers are dependent on the amount of o-anisidine incorporated in copolymer chain. Temperature dependence of electrical conductivity suggests that the copolymers are a class 1-D disorder conductor between the localization state associated by proton exchange as that of homopolymers. Increased electron localization in copolymer can be explained by increased interchain spacing and interchain disorder in copolymer.

References

Borkar A D, Gupta M C and Umare S S 2001 *Polym. Plast. Technol. Eng*. **40** 225

Genies E M and Tsintavis C 1986 *J. Electro and Chem*. **200** 127

Genies E M, Syed A A and Tsintavis C 1985 *Mol. Cryst. Liq. Cryst*. **121** 181

Ghosh S and Kalpagam V 1990 in *Polymer science contemporary themes*, (ed.) S Sivaram (New Delhi: Tata MaGraw Hill) Vol. II p. 819

Ginder J M and Epstein A J 1990 *Phys. Rev.* **B41** 15 10674

Guinior A 1963 *X-ray diffraction in crystals, imperfect crystals and amorphous bodies* (San Francisco: W H Freeman)

Gupta M C and Borkar A D 1990 *Indian J. Chem.* **A29** 631

Gupta M C and Umare S S 1992 *Macromolecules* **25** 138

Gupta M C, Warhadpande S V and Umare S S 1993 *Indian J. Chem.* **A32** 298

Heeger A J, Kivelson S A, Schrieffer J R and Su W P 1988 *Rev. Mod. Phys.* **60** 781

Inoue H and Yanagisawa S J 1974 *Inorg. Nucl. Chem.* **36** 1409

Jozefowicz M E, Laversana R, Javadi H S, Epstein A J, Pouget J P, Tang X and MacDiarmid A G 1989 *Phys. Rev.* **B39** 12598

Kivelson S A and Heeger A J 1988 *Synth. Met.* **22** 371

MacDiarmid A G and Epstein A J 1989 *Faraday Discuss. Chem. Soc.* **88** 317

MacDiarmid A G, Chiang J C, Halporn M H, Hvang W S, Mu S L, Somasiri N L, Wu W and Yaniger S I 1985 *Mol. Cryst. Liq. Cryst.* **121** 173

Mizoguchi K 1990 *Macromol. Chem. Macromol. Symp.* **37** 53

Neoh K G, Kang E T and Tan K L 1990 *Eur. Polym. J.* **26** 403

Pouget J P, Jozefowicz M E, Epstein A J, Tang X and MacDiarmid A G 1991 *Macromolecules* **24** 779

Shante V K S, Verma C M and Bloch A N 1973 *Phys. Rev.* **138** 4885

Siyu Y, Do N T, Dao L H and Vijh A K 1997 *Synth. Met.* **65** 88

Stafstrom S, Bredas J L, Epstein A J, Woo H S, Taner D B, Huang W S and MacDiarmid A G 1987 *Phys. Rev. Lett.* **59** 1464

Trivedi D C 1999 *Bull. Mater. Sci.* **22** 447

Umare S S, Huque M M, Gupta M C and Viswanath S G 1995 *Macromol. Rep.* **A32** 281

Umare S S, Huque M M, Gupta M C and Viswanath S G 1996 *Macromol. Rep.* **A33** 381

Umare S S, Borkar A D and Gupta M C 2000 *Phy. Chem. Chem. Phys.* (communicated)

Wang Z H, Li C, Scherr E M, MacDiarmid A G and Epstein A J 1991 *Phys. Rev. Lett.* **66** 1745

Zho W S, Cromak K and MacDiarmid A G 1991 *J. Am. Chem. Soc.* **113** 2665