Transport Properties of Copolymer of Aniline and M-Methylaniline

A.D. Borkar

NabiraMahavidyalaya, KatolDistt. Nagpur 441302,India
arun.borkar@rediffmail.com

Abstract

Poly(aniline-co-m-methylaniline) has been synthesized by chemical peroxodisulphate oxidation method on aqueous hydrochloric acid.UV-visible spectra of copolymer shows hypsochromic shift with increase in dielectric constant of the solvent and due to substitution in the aromatic ring. From temperature dependence of electrical conductivity, charge localizatiom length and hopping distance are calculated. The introduction of substituent group in a ring produces space hinderance to internal rotation. Conduction mechanism has been found to be 3D-VRH in case of pure HCl-doped polyaniline and 1D-VRH for copolymer.The room temperature conductivities of doped polyaniline and poly(aniline-co-m-methylaniline)are found to be 6.550×10^{-2} and 3.785×10^{-5} S Cm^{-1} respectively. The increase in activation energy of copolymer is noticed that it would be a conducting material. The temperature dependence of dielectric constant and conductivity suggests that copolymer is 1D-disordered state composed of 3D-metallic crystalline region and 1D-localized amorphous region.

Keywords: Polyaniline,Copolymer,Conductivity, Transport properties.

Introduction:

In general, conducting polymers are a special class of organic polymers that have alternate single-double bond conjugation and can conduct electricity. Among all the conducting polymers polyaniline (PANI) demonstrates outstanding properties due to its environmental stability, redox reversibility, high electrical conductivity and ease of synthesis which drives it towards potential electrical device applications[1-5]. Polyaniline is made up of combination of fully reduced (B-NH-B-NH) and oxidized (B-N=Q=N-) repeating units, where B denotes a benzenoid and Q denotes, a quiniod ring. Thus, different rations of these fully reduced and fully oxidized units yield various forms of polyaniline,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 protonic acid converts it into conducting form protonated emeraldine(emeraldine salt). The main issue with polyaniline 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[8-10]. Electronic properties of these synthetic metals can be tailored by carrying out the polymerization under the controlled conditions and in the presence of specific dopants.

In the present study, the copolymerization of aniline in presence of m-methylaniline as comonomer to prepare conducting copolymer of poly(aniline-co-m-methylaniline) type via the chemical oxidative polymerization route has been reported. The copolymer was characterized by the various techniques like UV-Visible

spectroscopy and FTIR and their electronic conductivity has been measured by two- probe technique, where resistivity and conductivity varies with temperature.

Polymerization

The doped polyaniline substituted polyaniline and their processable copolymer was chemically prepared by free radical oxidative polymerization route[11]. The concentration of both of aniline and substituted aniline was 0.1M and that of HCl was 1.0 M for the copolymer, aniline and substituted aniline were mixed in the mole ratio 60 : 40 polymerization was initiated by the drop wise addition of ammonium peroxodisulphate 0.1M $(NH_4)_2SO_4$ in 100 ml H_2O). The polymerization was carried out at a temperature of 0-4^{0}C and over a period of 4-6 hrs. Then the doped polymer powder was obtained by the process of precipitation, filtration, rinsing and drying, successively. The above synthesized powder was treated with 0.1M aqueous ammonia and stirred for 2hrs to obtain their base (undoped) forms.

Measurements

FTIR spectra were recorded on Shimadzu FTIR-8101A spectrophotometer. UV-Visible spectra were recorded on Shimadzu UV-1601.Temperature dependent DC conductivity measurements were carried out with the samples in the temperature range from 30 to 140^{0}C. The resistance was measured on DC resistance bridge LCR meter 923. The conductivity value was calculated from the measured resistance and sample dimensions.

Results and Discussion:

FTIR Spectra

The FTIR spectra ofcopolymer was obtained. The vibrational peak at 1587 cm^{-1} assigned to the stretch of thequinoid ring and a peak at 1485 cm^{-1} assigned to the stretch of the benzenoidring. The stretching peak of N-H appeared in the range 3500-3100 cm^{-1}. In the spectra of the salt form copolymer, absorption peak at 1260 cm^{-1} and 1490 cm^{-1}, indicates the existence of the methyl group on the benzene ring.

UV- Visible absorption spectra

The absorption band of copolymer was recorded in NMP DMF and DMSD solvents. There are two peaks in the UV –Visible range one around 310 nm is due toп-п* transition (band gap) and is directly related to the extent of conjugation. The other peak 610 nm is due to the molecular excition associated with the quinine-diimine structure[12], i.e transition between HOMO orbitals of benzenoid rings and LUMO orbitals of the quinoidrings.The UV- visible data reveals thatп-п* band in copolymer shifts to the lower wavelength(hypsochromic shift) which can be attributed to the addition of more side groups which alters the torsional angle and leads to the lower conjugation lengths. The degree of hypsochromic shift is directly related to the size of the substituent.

Conductivity

The temperature dependence of electrical conductivity of copolymer was estimated in the range of applicability of Arrhenius type equation

$$\sigma_{(T)} = \sigma_0[\exp^{Ea/2kT}] \tag{1}$$

andthe measured valued was plotted semilogarithmetically as a function of reciprocal of temperature (Fig.1).The conductivity increases exponentially with temperature.Also tried to fit the appropriate model for the variation of conductivity of material with temperature. For the above model considered thatsample follow the VRH model. In the VRH regime, temperature dependence of conductivity(σ) follow the generalized relation.

$$\sigma = \sigma_0[\exp^{-(T_0/T)^{1/r}}] \tag{2}$$

where T_0 is the Mott characteristics temperature and is a measure of the hopping barrier.   The σ_0 is the conductivity at infinite temperature. Their values are determined by density of states, localization length and average hopping distance. The value of r is related to the dimensionality (d) of the system as r =(d+1). For the one, two and three-dimensional systems,d is equal to the 1,2 and 3 respectively and corresponding values of r are 2,3 and 4 respectively.The temperature dependence of electrical conductivity (Fig.1 (b))for copolymer, which suggests that the charge conduction is 1D-VRH between nearest neighbouring chains[13].In case of HCl doped polyanilineCl[-1] ions are small and the interchain separation is small,resulting in appreciable coupling interaction between the chains. Thus, charge carriers could easily hop from one chain to other to give of 3D-VRH conduction[14]However in the case of copolymer although the charge carriers hop between granular particles as 3D-VRH but interchain hopping has been strongly inhibited leading to 1D-VRH.

In Zeller equation, T_0 is related to delocalization length (α^{-1}), most probable hopping distance (R) and hopping energy (w) by the relations (3), (4) and (5).

$$T_0 = 8\alpha/N(EF)ZK \tag{3}$$

$$R = (T_0/T)^{1/2} \alpha^{-1/4} \tag{4}$$

$$w = ZKT_0/16 \tag{5}$$

where Z is the number of nearest neighbouring chains (~4), K the Boltzmann constant and N(Ef) the density of states at Fermi energy for sign of spin which is taken as 1.6 states per eV (2-ring unit suggested for PANI).

The temperature dependence of electrical conductivity indicates that the observed semiconducting nature is due to only small fraction of delocalized carriers. Using equation (l) activation energies are determined for samples(Table1). These activation energy values suggested that the hopping conduction is the prominent conducting mechanism in these types of systems. Hopping mechanism requires low activation energy with higher dielectric permittivity. Due to this Ea, electrical conductivity is expected to be weakly temperature dependent around 300 K[15]. The transport properties of PANI, PmMANIandPANI-co-PmMANIare reported in Table 1.

Conductivity data clearly shows that the copolymer is less conducting relative to the polyaniline. The conductivity decreases both due to decrease in conjugation length as well as less doping level achieved.

Dielectric Behaviour

The dielectric constant and dielectric loss of PANI,PmMANI and PANI-co-PmMANI are reported in Table 2. From table2 it is observed that the dielectric constant and dielectric loss values of PANI are greater than those of PmMANI and PANI-co-PmMANI. The lower values of dielectric constant and dielectric loss of PmMANI and PANI-co-PmMANI may be due to bulkiness of substituents present on the chain also in copolymer. The dielectric constant and dielectric loss decrease with increase in the content of substituted aniline monomer, also found to be depends on the nature and size of the substituent.
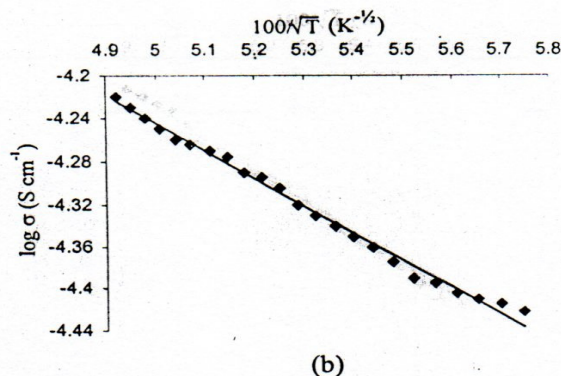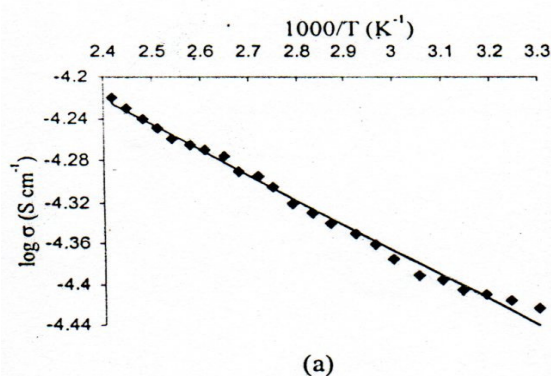
Further the dielectric constant and dielectric loss both increase with temperature as shown in Fig.2.The dielectric constant is a measure of the capacitance of the sample and is due to the capacitative coupling of conducting islands separated by insulating barriers. So on heating, barrier between the conducting grains continue to widen (localization of electrons increases) or develop a larger barrier potential. This increase in localization will increase the dielectric constant.

Table. 1- Transport properties of PANI, PmMANI and PANI-co-PmMANI

Polymer/Copolymer	σ(S/cm)	T_0 (K)	α^{-1}(nm)	R(nm)	w(eV)	Ea(eV)	
PANI	6.550×10^{-2}	3.315×10^3	6.995	5.736	0.071	0.047	
PmMANI	1.240×10^{-5}	1.434×10^4	1.617	2.758	0.308	0.102	
PANI-co-PmMANI	3.785×10^{-5}	6.120×10^3	3.788	4.221	0.101	0.062	

Table. 2- Dielectric constant and dielectric loss ofPANI, PmMANI and PANI-co-PmMANIat 303 K

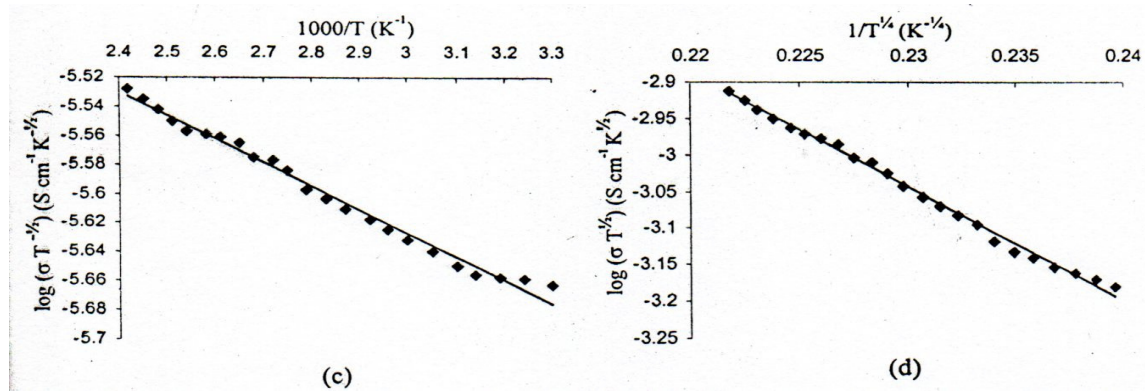| Polymer/Copolymer	Dielectric constant	Dielectric loss
PANI	6.40×10^3	4.80×10^2
PmMANI	3.20×10^2	2.30×10^1
PANI-co-PmMANI	4.80×10^2	2.94×10^1

(a)   (b)

Figure.1- Electrical conductivity plots of poly(aniline-co-m-methylaniline)

(a) Band Theory (b) Tunneling Conduction
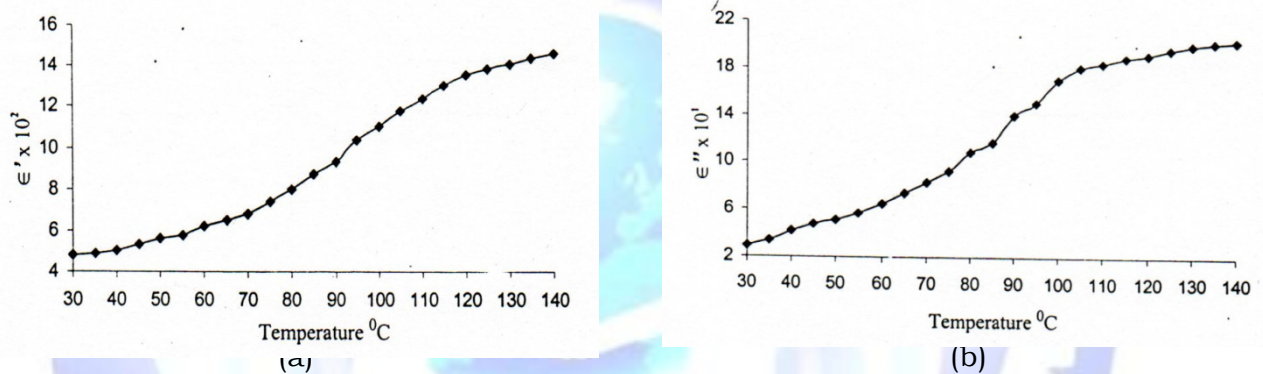
(c) Grain Boundary (d) HopingMechanism

Figure. 2- Temperature dependence of dielectric constantand dielectric loss of poly(aniline-co-m-methylaniline) (a) Dielectric constant (b) Dielectric loss

Conclusions:

Conducting copolymer of poly(aniline-co-m-methylaniline) type have been prepared. The electrical conductivity of copolymer increases with decreasing reaction temperature and is optimum at stiochiometric ratio of oxidant,dopant and monomer.The temperature dependence of dielectric constant and conductivity suggests that homopolymer and copolymer are 1D-disordered state composed of 3D-metallic crystalline region and 1D-localized amorphous regions.Conductivity plots suggest that 3D-VRH is proper model for HCl-doped polyaniline whereas for copolymer 1D-VRH seems to be apt choice. Activation energy being an empirical parameter is employed to characterize the exponential temperature dependence of the change in the conductivity. The increase in activation energy of copolymer is noticed that it would be a conducting material.

References:

1. **R.Valaski, F.Muchenski, R.M.Q.Mello, L.Micaroni, L.S.Roman and I.A.Hummelgen (2006)**J.Solid State Electrochem.,1024.

2. **K.F.Seidel,L.Rossi,R.M.Q.Mello and I.A.Hummelgen(2012)**J.Mat.Sci.,24(3),1052.

3.**M.Kandyla,C.Pandis,S.Chatzandroulis,P.PissisandI.Zergioti,   (2012)**App.Phy.,110(3), 623.

4. **J.Bhadra and D.Sarkar (2010)** Ind. J.Phy.,84(6) 693.

5. **L.Grigore and M.C. Petty (2003)** J. Mat.Sci., 14(5).389.

6. **L.H.Dao, M.Leclerc, J.Guay and J.W.Chevalier,(1998)**Synth.Met., 29,377.

7. **M.Leclerc, (1990)** J. Electroanal. Chem., 296,93.

8. **S.K. Dhawan and D.C. Trivedi, (1991)**Electrochem. Soc.ExtendedAbstract 682.

9.   **L.H.C.Mattoso,R.M.Faria,L.O.S.Bulhoes,A.G.MacDiarmidandA.J.   Epstein (1994)**J.Polym.Sci.&Polym. Chem. 32,2147.

10. **P. Savitha, S.P. Rao and D.N. Sathyanarayan, (2005)**Polym. Int. 54, 1243.

11.**A.D.Borkar,M.C.Gupta and S.S.Umare(2001)**Polym.Plast.Techno.Eng., 40(2),225.

12.**L.H.C.Mattoso,R.M.Faria,J.G.Masters and A.G.MacDiarmid(2004)** Synth.Met.,146.

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

14.**J.Li,K.Fang,Q.Hong,S.Li and W. Mao. (2004)** Synth.Met.,142,107.

15. **K.Morii, H.Kawano, I.Fuji, T.Matsui and Y. Nakayama (1995)** J. App. Phy.,78(3),1914.