Charge transport and electrical conductivity studies on poly(aniline-co-p-nitroaniline)

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ABSTRACT

Copolymers of aniline with p-nitroaniline were synthesized for different molar ratio of the respective monomers in acidic medium using K2S2O8 as oxidant. The two probe electrical conductivity was measured on the pressed pellets of the polymers at frequencies of 100Hz and 10 KHz. The relative frequency dependence of electrical conductivity on the pH of the reaction media as well as on the copolymer composition and the temperature dependence of electrical conductivities were studied. All the copolymers showed lower electrical conductivity than that of polyaniline which decreased as the ratio of the nitroaniline units increased in the copolymer backbone. The electrical conductivity at the 10 KHz was greater than that measured at 100 Hz. The frequency dependence increased as the ratio of the nitroaniline units increased as well as with the increase in the pH of the reaction medium. The decrease of electrical conductivity is explained in terms of the decreased extent of conjugation, increase in the band gap caused by the increased phenyl ring torsional angles, decreased inter chain diffusion of the charge carriers and greater electron localization. The observation on frequency dependence of electrical conductivity suggested the evidence of greater electron localization in copolymers. We suggested that greater the electron localization greater will be frequency dependence of electrical conductivity. Temperature dependence of electrical conductivity showed that the effect of moisture on electrical conductivity has a negligible effect on both the polyaniline and copolymers and a combination of conduction mechanism are operating depending on the temperature ranges.   © 2008 Trade Science Inc. - INDIA

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INTRODUCTION

During the past two decades, polyaniline (PANI) has emerged as fascinating and promising conducting polymer owing to high electrical conductivity, environmental stability and processibility making it as potential candidate for electrical and electronic applications[1-4]. It was the first conducting polymer whose electronic properties could be reversibly controlled both by protonation and charge-transfer doping[5,6]. Polyaniline can be visualized as built up from reduced (B–NH–B–NH) and oxidized (B–N–Q–N) repeat units where 'B' and 'Q' denote benzenoid and quinonoid units respectively[7-9]. Depending upon the oxidation state it can exist in various unique structures. The unprotonated forms of polyaniline can be given by the formula,
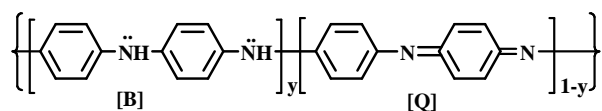
Where the oxidation state of the polymer increases with decreasing value of y. The average oxidation state **(1-y)** can be varied from zero corresponding to completely reduced polymer called leucoemeraldine to 0.5 to give the half oxidized emeraldine and to 1 to give completely oxidized pernigraniline. Polyaniline becomes highly conductive, only after a process called 'doping'. Doping of polyaniline with assisted control of electrical conductivity over a full range from insulator to metal is achieved either by chemically using a protonic acid or by electrochemical means and charge neutralility is maintained by the counter ions.

While discussing the charge conduction in polyaniline family of polymers, it is important to note that polyaniline, differs substantially from other conducting polymers. It is not charge conjugation symmetric i.e. the Fermi level and band gap are not formed in the centre of the π-bond so that the valence and conduction bands are very asymmetric[10]. Consequently, energy levels differ from other conducting polymers such as polypyrrol, polythiophene, polyacetylene etc.[11,12]. Secondly, the hetero-atom, nitrogen, is also within the conjugation path. Third,

the emeraldine base form of the polyaniline can be converted from insulating to metallic state if protons are added to –N= sites, while number of electrons in the chain held constant[8].

The electrical conduction mechanism, effect of disorder and one dimensionality of the polymers are still strongly debated. Chemical intuition suggests that the nitrogen lone pair orbital of N^{2-} would be highly susceptible to proton addition leading to charge transfer and thereby formation of delocalized polarons in the -orbital conduction band. A possibility of spinless bipolarons is also considered[13]. ESR signals observed during electrochemical preparation of conducting samples seems incompatible with spinless (bipolarons) model but could be interpreted in terms of conventional one dimensional electron density of state[14]. It has also been suggested that a "granular metal" model for polyanilines[15]. Alternatively, Wnek proposed that one electron free radical can provide a hopping mechanism for charge transport[16]. McManus et al.[17] found that the intermediate state responsible for the conductivity of polyaniline exhibited optical absorption features that were in excellent agreement with those of the radical state. Later work by Focke et al.[18] established qualitative agreement between the conductivity of electrochemically prepared polyaniline samples and the chemistry of free radical intermediate. Cowan et al. suggested[19] a simple model of electrical conductivity of polyaniline involving a three dimensional hopping model based on intermediate free radical state (among amine nitrogen sites), giving a reasonable quantitative description of the polymer conduction in all stages of oxidation and/or doping of polyaniline. In this article we report the electrical conductivity and charge transport behavior of copolymers of aniline with p-nitroanilne.

EXPERIMENTAL

Materials

Aniline, Ranbaxy Chemicals(distilled under reduced pressure). p-Nitroaniline(99%, Sisco Chemicals, recrystallized from alcohol and then from acetone),Potassium persulphate(99%, CDH Chemi-

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TABLE 1: Time taken for the initial colour change of the reaction mixture upon addition of oxidant and the electrical conductivity of the resulting polymers at two different frequencies

Polymer	Time taken for initial colour change (minutes)	Electrical conductivity (scm^{-1})	
		100Hz	10KHz
PANI	1-2	7.167×10^{-1}	7.168×10^{-1}
P(AcoPNA)2:1	4-5	5.4×10^{-2}	5.42×10^{-2}
P(AcoPNA)1:1	10-12	5.92×10^{-5}	6.48×10^{-5}
P(AcoPNA)1:2	12-14	6.04×10^{-7}	6.28×10^{-6}

cals, AR grade), Hydrochloric acid(Ranbaxy Chemicals, AR grade), Ammonia(CDH, AR grade) and Dimethylsulfoxide (DMSO) (99%, Merck India) were used as received.

Polymer synthesis

Polyaniline(PANI) and copolymers of aniline with p-nitroaniline for 2:1, 1:1 and 1:2 molar ratios of the respective monomers were synthesized using ammonium persulphate as an oxidant under acidic conditions[20]. In a typical procedure, the monomers were dissolved in 150ml of 1M HCl. A solution of $K_2S_2O_8$ (0.025mol) in 1M HCl was slowly added to it with constant stirring for 6 hours at a temperature of $28\pm2°C$. The dark viscous reaction mixture was filtered and washed with triply distilled water several times to remove the excess of oxidant and HCl present until the filtrate became colorless and acid free. The product was treated with methanol to remove low molecular weight oligomers. Finally, the product was washed with acetone, vacuum dried and kept at $50°C$ in an air oven for 3 days. The products were labeled as P(AcoPNA)2:1, P(AcoPNA)1:1, P(AcoPNA)2:1 respectively.

Charge transport and electrical conductivity studies

The polymers were finely powdered and made into pellets and the two probe electrical conductivity was measured using a RLC Digibridge (Genrad 1659 RLC Digibridge, USA) at two different frequencies, viz. 100Hz and 10KHz. The temperature dependence of electrical conductivity was also studied from room temperature up to $180°C$ at 10KHz by keeping the cell containing the pellets in an air oven and maintaining a heating rate of $1°C/min$.

To study the basic nature of charge transport,

the temperature dependence of conductivity data for P(AcoPNA)1:1 and P(AcoPNA)2:1 were fitted in to Variable Range Hopping Model and Arrhenius model[21,22]. The measured conductivity values were plotted logarithmically as a function of reciprocal of temperature.

RESULTS AND DISCUSSION

Polymer synthesis

The appearance of green color in the reaction mixture is taken as the indication of copolymerization. Polymerization of aniline into polyaniline was found to take place very quickly as observed by color change of the reaction mixture from pale → bluish green → green within two minutes of the addition of the oxidant. The copolymerization of aniline with p-nitroanilines was observed to be comparatively a slow process. TABLE 1 gives the time taken for the initial color change of reaction mixtures along with the % yield and electrical conductivities at two different frequencies of the products of formed.

It can be seen from the TABLE 1 that, the rate of reaction decreases as the ratio of nitroanilines increases in the reaction mixture. It was a qualitative indication that in presence of nitroanilines, the aniline monomers alone were not getting polymerized, rather, the nitroaniline units wereincorporated in the polymer backbone.

Electrical conductivity and charge transport studies

Despite of a wide range of applications and promising newer applications in future technologies, the electrical conductivity and charge transport in polyanilines have not yet fully understood[23]. Semicrystalline regions are embedded in the amorphous regions in the matrices of polyanilines. It is reported that metallic conduction may take place in the metallic regions whereas hopping conduction takes place in the amorphous regions in polyanilines[23,24]. However, there are inter and intra-fibrillar conduction and charge carriers hops from one chain to another within the metallic regions. Electrical conductivity generally increases with increase in temperature for hopping transport. It is also reported that some polyanilines
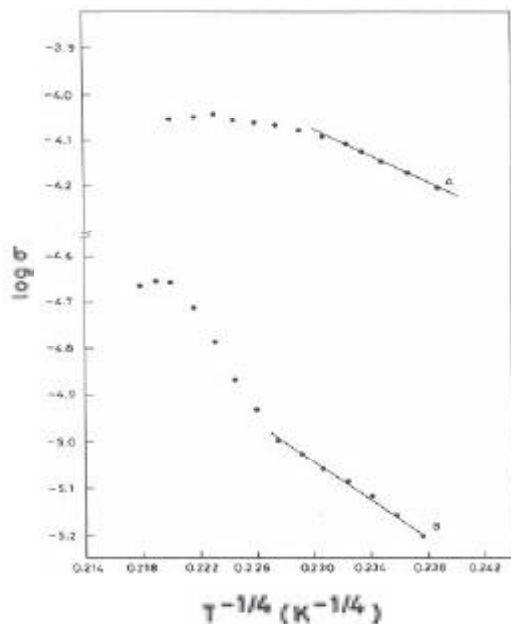
Figure 1: Application of variable range Hopping model for the electrical conductivity-temperature behavior for (A) poly(aniline-co-p-nitroaniline) 1:1 and (B) poly(aniline-co-p-nitroaniline) 1:2
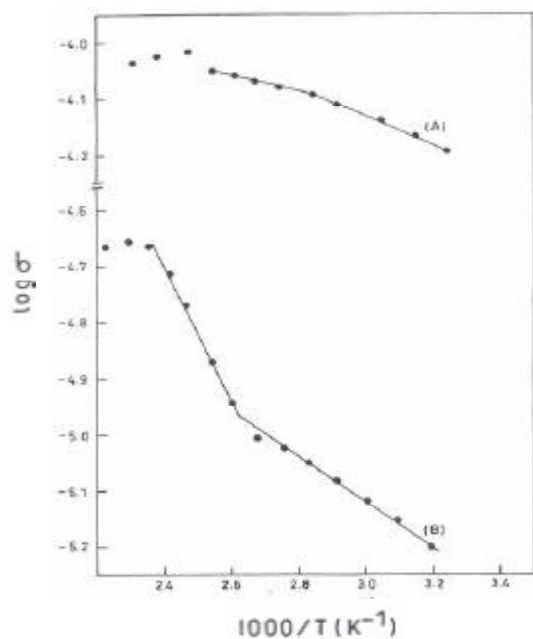

Figure 2: Arrhenius plot of log(σ) versus 1000/T(K^{-1}) for (A) poly(aniline-co-p-nitroaniline) 1:1 and (B) poly(aniline-co-p-nitroaniline) 1:2

exhibit many properties characteristic of the metallic state[25]. The whole process of charge transport in polyanilines is highly complex and no single model can explain it satisfactorily.

The two probe room temperature electrical conductivity measured on the pressed pellets of the polymers at frequencies of 100Hz and 10KHz are presented in TABLE 1 The dependence of electrical conductivity on pH of the reaction medium is given in TABLE 2. The temperature dependence of electrical conductivity of the polymers in the temperature range of 25°C-200°C is presented from figure 1 and figure 2. In order to understand the basic nature of charge transport, the temperature dependent electrical conductivity data were fitted to Arrhenius equation (band conduction) as well as to variable range hopping (VRH) model as shown through figure 1 and figure 2.

From TABLE 1, it can be seen that the copolymers showed lower electrical conductivity than that of polyaniline. The electrical conductivity was found to decease as the ratio of nitroaniline units increases in the copolymer backbone. The electrical conductivity measured at 10 KHz was found to be greater than that measured at 100Hz. This frequency dependence was more prominent in copolymers than in polyaniline. Frequency dependence of electrical conductivity was found to increase as the ratio of nitroaniline increases in the copolymer backbone. TABLE 2 shows that electrical conductivity was strongly dependent on pH of reaction mixture and the frequency dependence of electrical conductivity increases with increase in the pH of the reaction medium.

The lower electrical conductivity of the copolymers may be attributed to several factors. In general, the decrease of electrical conductivity of the copolymers can be explained in terms of the decreased extent of conjugation and an increase in the band gap caused by the increased phenyl ring torsional angles resulted from the steric repulsion between the adjacent phenyl rings due to the presence of -NO$_2$ groups on the phenyl rings[26]. This may also cause greater electron localization. Another possibility for the lower electrical conductivity is the decreased inter chain diffusion of the charge carriers in the copolymers[27]. This is induced by the increased separation of the polymer chains due to the presence of -NO$_2$ groups and lower crystallographic order and hence the reduced coherence between the

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TABLE 2: Dependence of electrical conductivity (Scm^{-1}) of the polymers on the pH of the reaction media for polymer synthesis

Polymer	Electrical conductivity (Scm^{-1})					
	pH=0		pH=0.5		pH=1	
	100Hz	10KHz	100Hz	10KHz	100Hz	10KHz
PANI	7.167×10^{-1}	7.168×10^{-1}	9.86×10^{-2}	9.92×10^{-2}	1.4×10^{-2}	1.55×10^{-2}
P(AcoPNA)2:1	5.4×10^{-2}	5.42×10^{-2}	3.9×10^{-2}	4×10^{-2}	6.9×10^{-3}	7.7×10^{-3}
P(AcoPNA)1:1	4.92×10^{-5}	6.48×10^{-5}	1.9×10^{-5}	4.6×10^{-5}	4×10^{-6}	1.68×10^{-5}
P(AcoPNA)1:2	6.04×10^{-7}	6.28×10^{-6}	1.7×10^{-7}	3.6×10^{-6}	3.2×10^{-8}	9.7×10^{-7}

chains. Also, the -NO$_2$ groups are likely to force the chain out of planarity by twisting the phenyl rings relative to one another to lower the overlap of orbitals along the conjugated systems. As a result, the conduction electron wave functions were expected to be substantially localized in the copolymers than those in polyaniline leading to lower mobility for the charge carriers. There are also possibilities for the strong electrostatic interactions such as hydrogen bonding between the -NO$_2$ groups and cationic radical nitrogen atoms to form some energetically favourable configurations. Such configurations can effectively localize the positive charge around the nitrogen atoms leading to a decrease in electrical conductivity [26].These factors were more predominant in copolymers containing greater number of -NO$_2$ groups. That is why the electrical conductivity followed the order PANI>P(AcoPNA)2:1>P(AcoPNA)1:1>P(AcoPNA) 2:1

TABLE 2 shows the dependence of electrical conductivity on pH of reaction media. It was observed that the electrical conductivity of polyaniline and the copolymers depends on the pH of the acid medium from which it is synthesized. When treated with acids, the amine nitrogen atoms of the polymers are protonated to form radical cation by an internal redox reaction[9]. The low electrical conductivity of the copolymers at higher pH level was due to lower degree of protonation as pH increased. Undoped imine nitrogen atoms and the associated quinoid units are expected to behave as a barrier for electrical conduction along the chains as well as between the chains resulting in pH dependent electrical conductivity[28]. It can also be seen from the TABLE 2 that the frequency dependence of electrical conductivity increases as pH increases.

A remarkable observation of our studies is the observation of frequency dependence of electrical

TABLE 3: Temperatures at which $\delta\sigma/\delta T \approx 0$ for different polymers

Polymer	Temperature at which $\delta\sigma/\delta T \approx 0$ (K)
PANI	398
P(AcoPNA)2:1	402
P(AcoPNA)1:1	410
P(AcoPNA)1:2	427

conductivity. From TABLE 1 and TABLE 2, it is clear that electrical conductivity measured at 10KHz was higher than that measured at 100Hz. We observed a strong frequency dependence of electrical conductivity for the copolymers though it was very feable in polyaniline. Frequency dependence became more prominent as the nitroaniline units increased in the polymer backbone. Epstein and coworkers[29] have performed the microwave conductivity of poly(o-toluidine) in order to characterize the effect of electron localization on the transport properties. In their work on dielectric constant and AC conductivity measurements at 10KHz on polyaniline and their derivatives, Pinto and coworkers[30] have pointed out that greater localization of charges leads to the reduced electrical conductivity and that the substitutents causes an increase in the disorder in the system. Our observation on frequency dependence of electrical conductivity suggests the evidence of greater electron localization in copolymers. We assume that greater the electron localization greater will be the frequency dependence of electrical conductivity.

The results of temperature dependent electrical conductivity measurements of the polymers are shown in figure 1 and figure 2. During the initial trial of the measurements irregular and non-reproducible results were observed because the pellets were found to be broken during the experiment at higher temperatures. The experiments were repeated by increasing the thickness of the pellets which yielded stable and reproducible results. Reproducible results

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were obtained if the pellets were cycled between 25°C and 90°C for several times, however, no reproducibility was observed when cycled between 25°C and 200°C.

The studies revealed a thermally activated conduction phenomena in the copolymers. We observed that the electrical conductivity increased linearly with increase in temperature up to a temperature at which $\delta\sigma/\delta T \approx 0$. After this temperature electrical conductivity decreased. The temperature at which $\delta\sigma/\delta T \approx 0$ for various copolymers are presented in TABLE 3. It can be seen that the temperature at which $\delta\sigma/\delta T \approx 0$ was lowest for poly(aniline-co-p-nitroaniline)2:1and highest for poly(aniline-co-*p*-nitroaniline)1:2.

It is an accepted fact that the electrical conductivity of highly conducting polyaniline is affected by environmental humidity and moisture[25,31]. Transport studies to understand the electrical conduction mechanism is generally carried out from low temperatures, 100K to room temperature. There are a fewer studies on temperature dependence of electrical conductivity above room temperature[21,25]. Similarly, not many studies have been carried out on the temperature dependence of electrical conductivity of substituted polyanilines[32]. In general, the electrical conductivity is given by, $\sigma = ne\mu$, where 'n' is the number of charge carriers per unit volume, 'e' is the electronic charge and 'μ' is the mobility of the charge carriers. In polyaniline, it is reported that the conduction band is partly filled and has a band width approximately an order of magnitude larger than kT[10]. It is also reported that the density of states function is approximately constant and electronic states are localized especially in low conducting samples of polyanilines[33]. The charge transport is then expected to take place via hopping mechanism. The localization of electronic states arises due to disorder and the presence of defects. The presence of moisture creates a dynamic disorder in the polymeric systems. At higher temperatures, when moisture is removed, it is expected that static defects such as chain ends and chemical defects control the charge transport.

In our studies, the effect of moisture on the electrical conductivity was found to have a negligible effect on both polyaniline and copolymers. A previous study of temperature dependence of electrical conductivity on highly conducting polyaniline[25] showed that, the electrical conductivity increased only up to 50°C after which conductivity decreased due to the loss of moisture. Interestingly, in all our samples, the electrical conductivity which falls in the semiconducting regime, increased up to 100°C. These results showed that temperature dependent electrical conductivity was not affected by the presence of moisture in semiconducting aniline based copolymers. The presence of moisture is reported to cause spin and charge delocalization, by solvating the Cl^- and thus by reducing the electrostatic interaction between the positive charges and Cl^-, thus reduces the polarity effect of anions. Loss of moisture leading to increased localization and thereby a reduction in conductivity was not operative in these polymers. This may be an indication that the static defects play an important role in the thermally activated conduction phenomena[33] in all these copolymers.

To understand the basic nature of charge transport, the data were fitted in Arrhenius equation as well as in the equation corresponding to Variable Range Hopping model. The results presented in figure 1 and figure 2 showed that a combination of conduction mechanisms is operating in these copolymers depending on the temperature range of the measurements. It can be seen that at higher temperature ranges, the charge transport is mainly through Arrhenius type and in the lower temperature range; the charge transport is through three dimensional variable ranges hopping. The electrical conductivity decreased after a temperature, corresponding to $\delta\sigma/\delta T \approx 0$, probably because of the degradation of polymers due to removal of dopants or due to some structural variation.

The observed conductivity-temperature relation is found to fit best in the variable range hopping model equation-

$$\sigma(T) = \sigma_0 \exp\left(\frac{T_0}{T}\right)^{1/4} \qquad (1)$$

where T_0 is the Mott's characteristic temperature and σ_0 is the electrical conductivity at room temperature in the low temperature range studied. At higher temperatures, the Arrhenius plot is found to be a good

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fit to the data following the equation-

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_A}{kT}\right) \qquad (2)$$

where, E_A is the energy of activation and k is the Boltzmznn constant. However, the data seemed to fit into Arrhenius equation in the low temperature range also but with different activation energies. This suggests that Arrhenius type conduction may also operative in the lower temperature range.

From our studies we conclude that a single mechanism can not be used to explain the charge transport in these copolymers in the entire temperature range studied. However, our limited studies do not point in to the exact conduction mechanism.

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