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STUDIES ON SUBSTITUTED POLYANILINE EFFECT OF POLYMERIZATION CONDITIONS ON TRANSPORT PROPERTIES

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ABSTRACT

The temperature dependance of the transport properties of polyaniline, poly(o-methoxyaniline) and poly(N-phenylaniline) prepared under different conditions was investigated. The results show that the localization of conducting electrons is least in case of polyaniline and it increases with substituents and with polymerization temperature. The data show that such polymers are a class of 1-D disorder conductor between localization state associated by proton exchange.

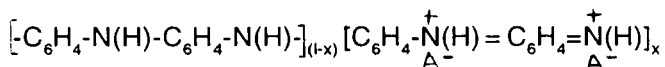
INTRODUCTION

The polymerization of aniline and its substituted derivatives is reported to take place through oxidation to a radical cation and subsequent addition of a radical cation to oligomer. The polymer energy bandgap is affected by solvent, amount of oxidant used for polymerization and temperature at which polymerization is carried out. It was found that polymer prepared at 0° C when the monomer oxidant ratio is 1:1.15 respectively in strongly acidic medium has the lowest energy band gap and maximum electrical conductivity¹.

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The emeraldine salt of polyaniline is believed to have the composition



where, A⁻ is counter ion and the chain consists of reduced [-C₆H₄-N(H)-C₆H₄-N(H)] and oxidized [C₆H₄-N=C₆H₄=N] repeat units.²

Extensive studies have demonstrated that material differs critically from earlier studied conducting polymers such as polyacetylene, polypyrrole and polythiophene, because of important role of the aromatic ring together with the presence of hetroatom, N, within the conjugation path³. It is also reported that polyaniline emeraldine salt (PAN-ES) represents a class of quasi-1D disorder conductor which consists of bundles of coupled parallel chains in which the electron wave function are 3-D delocalized⁴⁻⁶. These bundles are the crystalline regions of the polymer separated from one another by amorphous regions and the formation of bundles is attributed to interchain coupling⁷. Thus, the results suggest that improvement of interchain coupling is an important strategy to achieve high conductivity. In this communication we report the effect of the substituents in ring as well as N atom and the temperature of polymerization on the transport properties of polyaniline.

METHODS

Synthesis of Polymer

Polymers were prepared by peroxodisulphate oxidation of aniline, o-methoxyaniline and N-phenylaniline using (NH₄)₂S₂O₈ as oxidant and 1 N HCl and mixture of 1 N HCl : CH₃CN as solvent in different ratios.

The peroxodisulphate oxidation was carried out at temperature 0, 15 and 30°C, using 1:1.15 monomer oxidant mol ratio¹.

Elemental Analysis

C, H, and N analysis of the polymer samples was carried out by microanalytical techniques using a Carlo-Erbastrum DP-200 instrument at the R.S.I.C., C.D.R.I., Lucknow.

Electrical Conductivity and Dielectric Constant

DC electrical conductivity of samples was measured as a function of temperature as resistivity and capacitance. DC conductivity of the pelletized samples, having higher resistivity and capacitance were measured by the two probe technique on a DC resistance bridge LCR meter 926 at a heating rate 1 K min⁻¹.

The conductivity of material having lower resistivity was measured by the four probe technique model DEP-92 at the temperature from

295 to 395 K at a heating rate of 1 K min⁻¹. The measured resistance and capacitance were converted to conductivity and dielectric constant from pellet dimensions.

RESULTS

The results of elemental analysis of polymers together with the theoretical values are recorded in Table-1.

The theoretical values (in bracket) have been calculated using 4 ring monomer units and is found to fit with empirical repeat unit as shown in Fig. 1.

The discrepancy in calculated and experimental values may be due to the different levels of counterion and protonation since elemental analysis is not a reliable criteria for unequivocally establishing the presence or absence of H atom. At lower temperature, complete protonation is assumed while at higher temperature it is less.

The temperature dependance of conductivity was fitted to an Arrhenius type equation.

$$\sigma(T) = \sigma_0 \exp(-E_a/2kT) \quad \dots (1)$$

and the measured values were plotted semilogarithmically as a function of reciprocal of temperature in Fig. 2. (a)

The conductivity is found to increase with temperature; however there are deviations at lower temperature and in some case at higher temperature. The reason for deviation is not known but the data fit in a smaller temperature range where Arrhenius behaviour is regarded as a good approximation to band theory. The activation energy for conductivity E_a is less than the band width found by optical investigations⁷. The explanation lies in the fact that we are dealing with a material already oxidized to some extent and during chemical peroxidation the creation of intermediate states connected with increased conductivity, lowers the activation energy. Thus appropriate charge carriers are generated by partial oxidation. The oxidation creates a positive charge defect as a result the electron assumes a polaron state, the energy of which lies in the bandgap. For the present data the temperature dependance is fitted to equation⁸.

$$\sigma(T) \propto \exp(-T_0/T)^{1/2} \quad \dots 2$$

as shown in Fig. 2(b) in the temperature range of studies. In Eq. (2) T_0 is defined as

$$T_0 = 8 \alpha / N(E_f) Z k \quad \dots 3$$

where, $N(E_f)$ is the density of states at the Fermi energy which is taken as 1.6 eV states per two ring units suggested for poly

TABLE - 1

Elemental analysis of polyaniline and substituted polyaniline.

Polymer	Temperature of polymerization, °C	Elemental analysis found (Calculated)%		
		C	H	N
Polyaniline	0	56.16 (56.63)	4.19 (4.21)	10.47 (11.21)
	30	53.72 (53.83)	4.27 (3.71)	9.91 (10.46)
Poly (o-methoxy-aniline)	0	55.31 (57.04)	4.47 (4.75)	8.77 (9.50)
	30	52.98 (53.84)	5.21 (4.48)	8.07 (8.97)
Poly (N-phenylaniline)	0	75.86 (78.04)	4.42 (4.87)	7.15 (7.58)
	30	72.01 (74.51)	3.75 (4.65)	6.88 (7.24)

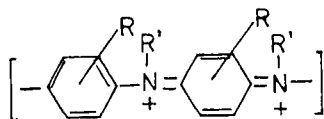


Fig.1. Repeat unit in polyaniline and substituted polyaniline. where $R = \text{OCH}_3$, and $R' = \text{H}$ for ring substituted; $R = \text{H}$ and $R' = \text{C}_6\text{H}_5$ for N (substituted).

$(\text{aniline})^{4-6,9}$ and Z is the number of the nearest neighbour chains (~ 4).

T_0 is calculated from Fig. 2(b). Eq (3) can be used to estimate charge localization α^{-1} , most probable hopping distance R , and hopping energy w , defined by Eq (4) and (5)^{9,10}.

$$R = \alpha^{-1} (T_0 / 16 T)^{1/2} \quad \dots 4$$

$$w = Zk T_0 / 16 \quad \dots 5$$

The T_0 for polyaniline and its substituted derivative as well as the α^{-1} , R , and w are recorded in table 2. It is observed from table 2 that T_0 for poly (N-phenylaniline) is about 100 times more compared

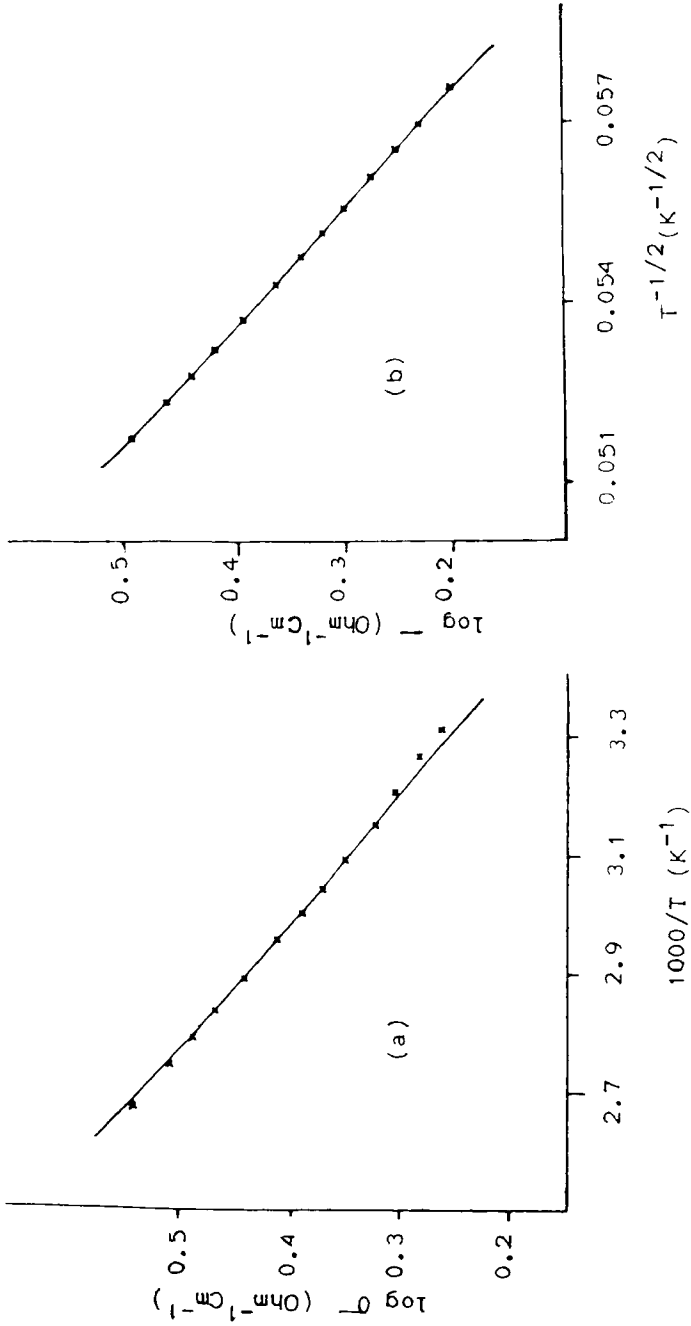


Fig. 2 : Temperature dependence of electrical conductivity of poly(aniline) according to (a) Arrhenius equation (1) (b) equation (2).

TABLE 2
Transport properties of polyaniline and its derivatives

HCl: CH ₃ CN	Temp.	σ (300)K Ohm ⁻¹ cm ⁻¹	T _p ,K	λ^{-1} , nm	R _{nm}	w,eV	ϵ	
a) Polyaniline								
HCl	0	1.186	3.98x10 ³	5.93	5.33	0.085	1.83x10 ²	
HCl	30	0.305	1.10x10 ⁴	2-10	3.25	0.240	4.13x10 ²	
1:1	0	0.285	4.10x10 ³	5.73	5.51	0.089	8.23x10 ²	
1:1	30	0.037	3.71x10 ⁴	0.64	1.78	0.080	4.06x10 ⁴	
b) Poly(o-methoxyaniline)								
HCl	0	2.59x10 ⁴	1.56x10 ⁴	1.52	2.75	0.34	2.85x10 ²	
HCl	15	1.89x10 ⁴	3.73x10 ⁴	0.63	1.78	0.80		
HCl	30	1.18x10 ⁵	9.77x10 ⁴	0.24	1.10	2.15	5.84x10 ²	
1:1	0	1.08x10 ⁵	8.8x10 ⁴	0.27	1.16	1.89	3.12x10 ²	
1:1	15	1.98x10 ⁷	1.59x10 ⁴	1.41	2.72	0.34		
1:1	30	1.28x10 ⁸	5.86x10 ⁴	0.04	0.44	12.62	6.18x10 ²	
c) Poly (N-phenyl aniline)								
	3:1	0	2.30x10 ⁷	1.29x10 ⁵	0.21	1.02	2.43	2.96x10 ²
	3:1	30	2.79x10 ⁷	1.6x10 ⁵	0.15	0.86	3.46	3.12x10 ²
	1:3	0	2.40x10 ⁷	1.13x10 ⁵	0.21	1.02	2.44	
	1:3	30	1.35x10 ⁸	1.65x10 ⁵	0.14	0.84	3.56	3.89x10 ²

to polyaniline and it is about 10 times more than the value for poly(o-methoxyaniline). The T_p for polyaniline prepared at 0°C is 3980 which is less than the polymer prepared at higher temperature. Therefore, correspondingly the localization length, average charge hopping distance and hopping energy varies with the substituents. The temperature of polymerization also affects the localization length, charge hopping distance, and hopping energy. There is no much effect by the change of solvent for polymerization. This

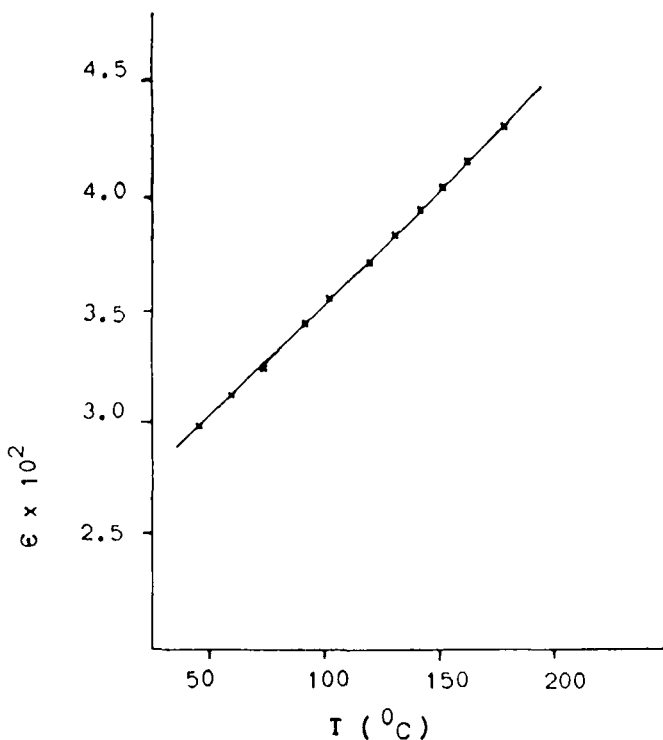


Fig. 3 Temperature dependence of the dielectric constant of poly (N - Phenyl aniline)

increase in electron localization with bulkier substituent is due to the adjacent torsion in ring angle which is increased to avoid the strong steric repulsion from substituent on the ring¹¹. This reduces the overlap of the π -electron wave function and hence the band width¹².

Dielectric Behaviour

The dielectric constant (ϵ) of polyaniline and substituted derivatives of polyaniline is also given in Tables 2. This shows that ϵ is maximum for polyaniline and as the bulkiness of substituent increases it decreases. With the increase in temperature ϵ increases as shown in Fig 3. The polymer prepared in highly acidic media has low ϵ and as the amount of CH_3CN in polymerization solvent increases ϵ is found to increase. Similarly the increase in temperature of polymerization also affects ϵ .

Thus dielectric constant depends on temperature of polymerization, solvent used for polymerization, nature of substituent group and its size.

The dielectric constant is a measure of the capacitive coupling of conducting islands separated by insulating barriers. So on heating barrier between the conducting grains continue to widen (localization of electron increases). This will increase the dielectric constant with the temperature.

GENERAL DISCUSSION

The temperature dependance data Fig. 2(b) suggest that the localization length is maximum in polyaniline and is less in substituted derivatives. This shows that electron is more delocalized in polyaniline than in substituted derivatives. From localization length, the most probable hopping distance is about (0.4 - 5 nm) which is much large than the interchain separation (0.35 - 0.49 nm) probably due to contribution from misaligned chains. It may also suggest that effective 1-D unit in which charge can hop from one state to another is not a single chain but a bundle of misaligned polymer chains with dimensions nearly equal to coherence length¹³.

The origin of the formation of metallic bundles in polyaniline salt is attributed to the significant interchain coupling and coherence in the crystalline region. The difference between polyaniline and its substituted derivatives in electron localization can be understood in terms of Q- dimensionality of electron states. The metallic bundles in polyaniline are similar to 3-D thin metallic wire and in case of derivatives, the disorder due to strain and steric hinderance or nonplanarity of aromatic rings, is larger and electron localization is more. The interchain coupling and coherence are suppressed due to side group and are nonmetallic even within the crystalline regions.

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REFERENCES

1. Umare S.S., Huque M.M., Gupta M.C., and Vishwanath S.G. Poly Commun. (communicated 1994)., Gupta M.C., Umare S.S., *Macromolecules* - (1992) 25, 138.
2. Huang W.S., Humphry B.D. and MacDiarmid A.G., *J.Chem.Soc. Faraday Trans I*, (1986) 82, 2385.

3. Epstein A.J., 'Conjugated polymers : the Novel Science and Technology of Conducting and Non-linear Materials' edited by J.L.Bredas and R.Silbey (Kluwer Academic Publisher NY) 1992.
4. Wang Z.H., Li, C., Scherr E.M., MacDiarmid A.G., and Epstein A.J., Phys. Rev. Lett. (1991) 66, 1745,
5. Gogolin A.A., Phys. Rep. (1988), 5, 269.
6. Heeger A.J., Kivelson S.A., Schreffer J.R. and Su W.P., Rev. Mod. Phys. (1988), 60, 781.
7. Kivelson S.A., and Heeger A.J., Synth. Met. (1988), 22, 371.
8. Shante V.K.S., Varma C.M., Bloch A.N., Phys. Rev. (1973) B-8, 4885.
9. Jozefowicz M.E., Laversanne R., Javadi H.H.S., Epstein A.J., Pouget J.P., Tang X. and MacDiarmid A.G., Phy.Rev. (1989) B-39, 12598.
10. Pouget J.P., Jozefowicz M.E., Epstein A.J., Tang X., and MacDiarmid A.G., Macromolecules (1991) 24, 779.
11. Wei Y, Focke W.W. Wnek G.E., Ray A. and MacDiarmid A.G., J.Phys.Chem. (1989) 93, 495, Ray A., MacDiarmid A.G., Ginder J.M. and Epstein A.J., Proc Mater Res.Soc. (1990) 173, 353.
12. Ginder J.M., Epstein A.J. and MacDiarmid A.G.Solid State Commun. (1989) 72, 697. Ginder J.M. and Epstein A.J., Phys.Rev. (1990) B-41, 10674.
13. Sindhimeshram D.C. and Gupta M.C., Ind. J. Chem. (in press) (1994).