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Effect of charge transfer interaction and disorderness on transport properties of polyaniline systems

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Films of pure polyaniline and polyaniline-tetracyanoquinodimethane have been prepared. The optical absorption spectra of both the samples in the emeraldine base forms are explained in light of the three-dimensional exciton model. A temperature dependence study of the electrical conductivity of the samples shows an interesting crossover phenomenon ($T_c = 143$ K) which may be considered as competition of the two oppositely directed factors, namely, charge transfer interaction and the disorderness parameter (r). While charge transfer interaction is evident from optical absorption spectroscopy, the extent of disorderness is reflected by the results of CHN microanalysis and temperature dependent electrical conductivity measurement. © 2000 American Institute of Physics. [S0021-9606(00)71141-X]

I. INTRODUCTION

Electrically conducting conjugated polymers have attracted substantial attention in recent years because of their many potential applications and unique electrical and optical properties.¹⁻⁴ The effect of doping on electronic states, conductivity and optical properties of such polymers has been widely investigated over the last two decades, leading to the proposal that these properties are tremendously affected by polaron, bipolaron or soliton type defects generated in the neutral polymer chain.⁵⁻⁹

Of the many conducting polymers identified so far polyaniline (PANI) and its derivatives have been studied extensively because of its many promising properties, viz., its fast switching rates with the ability to switch reversibly from the insulating to the conducting state either by electrochemical or chemical doping, environmental stability and processability.^{10,11} The conductivity of PANI can be affected by the degree of oxidation of the polymer, percentage of protonation and the nature of the protonic acid.^{12,13} The conductivity may also be affected by the extent of the water content which has profound effect on the interchain charge transport phenomenon.¹⁴ It seems instructive to consider that PANI doped with protonic acid segregates into either an isolated conducting chain in an insulating polymer matrix or into granular three-dimensional (3D) metallic islands circumvallated by amorphous regions.^{15,16} Such a conclusion

can be derived from the various experimental findings of its magnetic susceptibility, conductivity and spin dynamics.¹⁶

Over the past few years several attempts have been made to modify the electronic and optoelectronic properties of PANI with a view to finding its potential worth in making microelectronics and molecular electronic devices.¹⁷⁻²¹ Several illustrative ideas have been put forth to account for it. Cao *et al.*¹⁹ studied the effect of the oxidizing agent and its strength on the various electrophysical properties of PANI and they found that the nature of the oxidizing agent and its strength have a minor effect on the electrical and optoelectrical properties of the same. On the other hand, many research workers have observed that both ring-substituted and *N*-substituted poly(alkyl aniline) have poor electrical conductivity with respect to pure polyaniline.^{20,21} The major achievement of their investigation is the fact that the addition of side groups to PANI has enhanced its solubility in common organic solvents and hence its processability.²⁰ Since pure PANI is soluble in different protonic acids (up to 20% w/w), such as methyl sulfonic acid, camphor sulfonic acid, etc., without any detectable degradation,¹⁹ one has to pay more attention to the development of more electrically conducting PANI.

Employing the aforesaid findings we have initiated a systematic investigation aimed at improving the electrical and optoelectrical properties of PANI so as to make it more useful and meaningful in preparing different electrochromic devices.

In the present work we propose to prepare a charge

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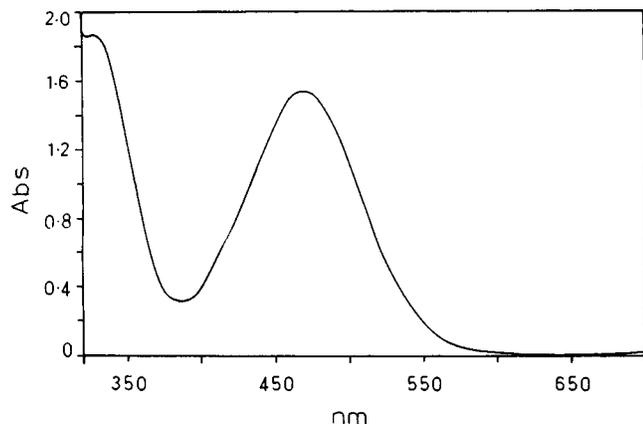


FIG. 1. UV-vis absorption spectrum of the CT complex (ANI-TCNQ).

transfer complex using aniline as a donor and tetracyanoquinodimethane (TCNQ) as an acceptor. After polymerization of the resulting complex we intend to find out how the various electrophysical properties of PANI are influenced in the new procedure of synthesis. These properties have been assessed using ultraviolet-visible (UV-vis) spectroscopy and temperature dependent four-probe conductivity measurements.

II. EXPERIMENT

A. Materials

Aniline (Merck, Germany) was distilled at a reduced pressure of 65 mm of Hg and a middle fraction was collected and stored under N_2 atmosphere at $-10^\circ C$. Ethyl alcohol (Bengal Chemical & Pharmaceutical Works, India), ammonium peroxydisulfate (Merck, Germany), TCNQ (Merck, Germany) and hydrochloric acid (International, India) were procured as the highest grade obtainable and used without further purification.

B. Synthesis

A typical route for synthetics is described here for the preparation of polyaniline. The distilled aniline acidified with 1.5 mol HCl solution was placed in a freezing mixture bath. The temperature of the medium was maintained at $-5^\circ C$. An aqueous solution of ammonium persulfate was added dropwise to the mixture, keeping the ratio of aniline to persulfate concentration at 1.25. The whole mixture was stirred magnetically for 2 h. The green precipitation of polyaniline salt was filtered out and washed with de-ionized water. The wet filter cake was dedoped with 3% NH_4OH aqueous solution for 2 h as suggested by Cao *et al.*,¹⁹ then filtered, washed with de-ionized water and methanol and dried under vacuum at room temperature for 12 h.

To prepare the PANI-TCNQ sample, a charge transfer complex (CTC) (1:1) using aniline as a donor and TCNQ as an acceptor was prepared in ethanol medium. The CTC shows an absorption peak with $\lambda_{max}=450$ nm (Fig. 1). The resulting complex was then polymerized following the same method as that in the case of PANI synthesis. It was observed that the induction period for the formation of a new

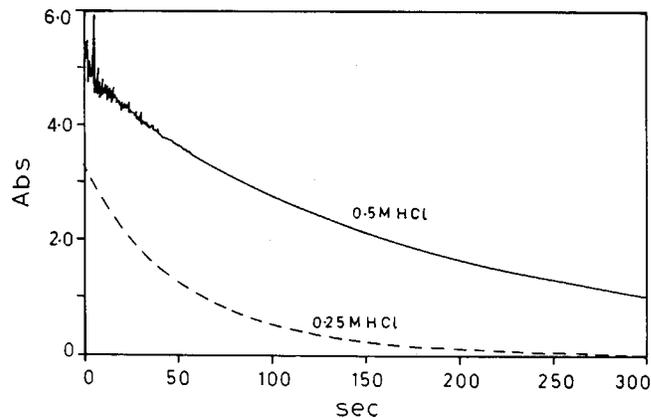


FIG. 2. Kinetic decay of absorbance of the blue colored material (peak at 580 nm).

polymer was almost double that of PANI. The dedoped polymer was collected following the same route just mentioned above. The most interesting feature of PANI-TCNQ synthesis was the formation of a deep blue color which followed exponential decay, shown in Fig. 2. The blue colored material is electron spin resonance (ESR) inactive which indicates that the color has no relation to the spin of the system. Moreover, it has also been observed that color which is otherwise transient can be trapped in the liquid nitrogen atmosphere. Hence the appearance of the blue color as a consequence of proton tunneling is also ruled out. Keeping all these possibilities in mind one can surmise that diffusion of the proton in various positions of the rings is associated with the transient emergence of the blue color.

C. Film formation

The solutions of dedoped polymer samples were prepared in DMSO and filtered twice to ensure the removal of large suspended particles. The true solutions were then kept in a 100 ml beaker without being disturbed for one week. Due to slow evaporation of the solvent, homogeneous films having thickness of $0.1 \mu m$ formed at the surface of the solutions. The films thus prepared were collected carefully and placed in HCl vapor for 2 h. The acidified green colored films were used for resistivity measurements.

D. UV-vis-near-infrared spectroscopy

UV-vis-near-infrared (NIR) spectra were recorded with a Hitachi U-3501 spectrophotometer. Films of HCl doped and dedoped PANI and PANI-TCNQ were prepared by *in situ* growth of the samples in quartz cells.

E. Resistivity measurements

The electrical resistivities of acidified films of PANI and PANI-TCNQ were measured in the temperature range of $25 K \leq T \leq 300 K$ using a Keithley electrometer (model 236). The low temperature measurement was performed using a closed cycle helium cryostat. Electrical contact was made with highly conducting silver paint.

TABLE I. Results of CHN microanalysis.

Sample	C (%)	H (%)	N (%)
PANI	52.24	4.87	10.61
PANI-TCNQ	54.63	3.75	14.52

F. CHN microanalysis

The weight percentage of the CHN of PANI and PANI-TCNQ was determined by elemental analysis using a CHN analyzer (2400 series II, Perkin Elmer), and the results are presented in Table I.

III. RESULTS AND DISCUSSION

The optical absorption spectra, recorded for the pure PANI and PANI-TCNQ films both in emeraldine base (EB) and emeraldine salt (ES) form, are shown in Figs. 3 and 4, respectively. The EB form of pure PANI shows a sharp absorption peak with $\lambda_{\max}=630$ nm while for the corresponding ES form an absorption band with $\lambda_{\max}\approx 930$ nm has been observed. But the appearance of a relatively less sharp peak having λ_{\max} at 600 nm with a prominent shoulder at 690 nm for the EB form and relatively narrow absorption band with $\lambda_{\max}=800$ nm for the ES form of PANI-TCNQ system is quite interesting. Moreover, it is clearly evident from Figs. 3 and 4 that, in comparison to pure PANI system, a conspicuous blueshift occurs for both the EB and ES forms of PANI-TCNQ system. While the optical absorption spectra for both EB and ES films at room temperature are very similar to those observed by Monkman and Adams,²² a remarkable departure has been observed for the spectra of PANI-TCNQ system.

The optical absorption spectra of the polyaniline system have been a matter of controversy over the last two decades although several luciferous ideas have been proposed to account for these observations.^{23,24} Early investigations²⁵ led to the proposal that low energy absorption maxima of EB and ES appear due to a $\pi-\pi^*$ transition in the separate conjugated fragments (CFs). It has also been suggested that a charge transfer exciton (CTE) appears in the polymer material upon photoexcitation and that the charge carriers are delocalized over several CFs surrounding the excited CF. Since

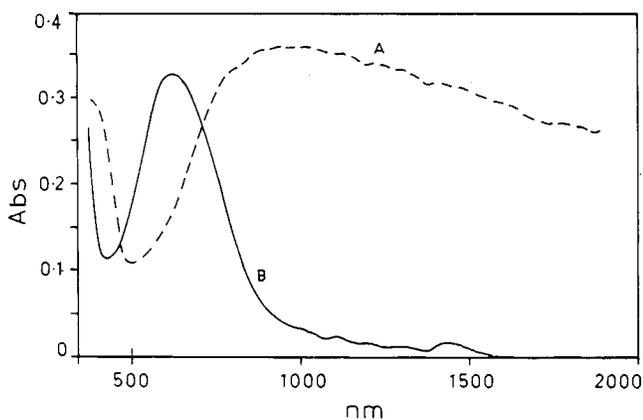


FIG. 3. UV-vis-NIR absorption spectra of PANI in its EB and ES forms.

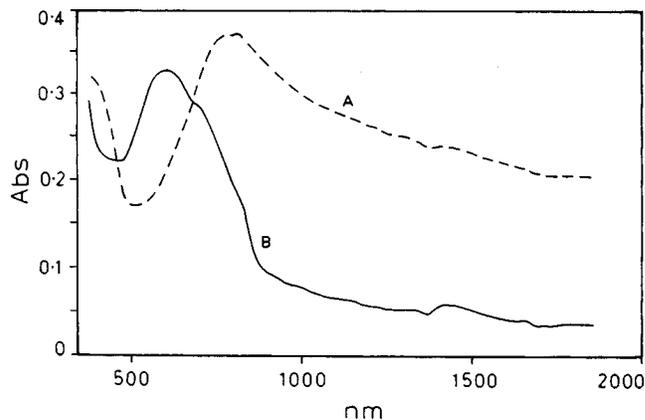


FIG. 4. UV-vis-NIR absorption spectra of PANI-TCNQ in its EB and ES forms.

all the CFs are not equivalent the excitation cannot propagate through the polymer sample like crystalline material. The state of a localized CTE involves the excited state of one CF and also the states where one of its electrons is transferred from its highest occupied molecular orbital (MO) to the lowest unoccupied MO of a neighboring CF.

These states appear when one photon with energy $h\nu = E \approx 2$ eV is absorbed. To make such a transfer possible, the following energy relation has to be satisfied:

$$I - A - 2E_d \approx \Delta E, \quad (1)$$

where I is the ionization energy of the CF, A is the electron affinity of the CF and E_d is the polarization energy. From an analysis of the data available on I , A and E_d for macromolecules with conjugated bonds, one finds that in polyaniline $I=6.6$ eV, $A \approx 1$ eV and $E_d \approx 1.5$ eV.^{26,27} Thus one obtains about 2 eV which is the energy required for generation of two separate charges located on the CFs.

Since the modified polymer contains a charge transfer agent (TCNQ) as evidenced from CHN microanalysis (Table I) it is quite obvious that the ionization energy of the CF corresponding to the new polymer should be higher compared to that for the pure PANI system. This makes the observed blueshifts in the ΔE values of the PANI-TCNQ system come into good agreement with that obtained from this model. Although the theoretical models²³⁻²⁵ are successful in many respects, none of them could provide any explanation for the presence of an additional shoulder at 690 nm in the EB form of the PANI-TCNQ system. Probably it appears due to transfer of charge from the conjugated fragment with delocalized π electrons to the acceptor molecule TCNQ.

The temperature dependence of conductivity $\sigma(T)$ in the absence of a magnetic field of the PANI and PANI-TCNQ samples is presented in Fig. 5. The conductivity decreases with a decrease in temperature, indicating the semiconducting behavior in the whole range of temperatures, $25 \text{ K} \leq T \leq 300 \text{ K}$. The room temperature conductivity of pure PANI is 24 S cm^{-1} but the conductivity changes to a somewhat higher value (39 S cm^{-1}) for the PANI-TCNQ system. The conductivity ratio²⁸ $r = \sigma(300 \text{ K})/\sigma(T')$ (T' represents the

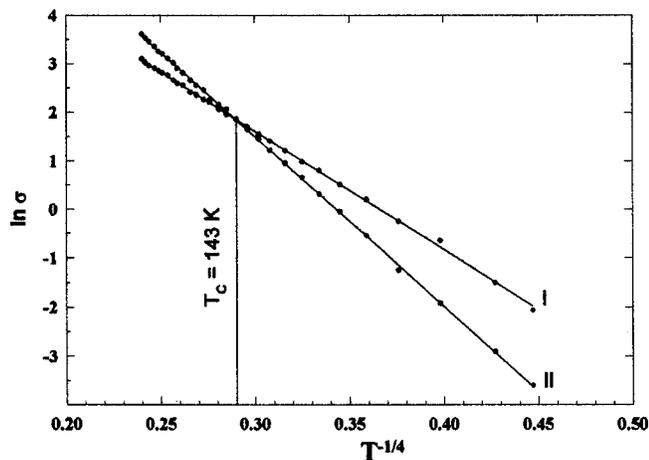


FIG. 5. Mott plot for PANI and PANI-TCNQ systems.

lower temperature limit) is different for the two samples. It is quite obvious that the higher the value of r of a sample, the stronger its $\sigma(T)$ dependence will be.

The electrical properties of doped polymers are strongly dependent on the extent of disorderness present in the material.²⁹ The term disorderness is a vector of many aspects including (i) the nonequivalence of conjugated fragments, (ii) the presence of both crystalline and noncrystalline phases, (iii) impurities, (iv) substitution at the monomer unit, etc. Besides, conducting polymers are regarded as a randomly distributed polaron/bipolaron lattice which in fact gives the quantum picture of disorderness.³⁰ When disorder is introduced into a system electronic states change fundamentally. Incorporation of disorderness would lead to a scattering process that would decrease the amplitude for the electron to move from one end of the material to the other.^{30–32}

The extent of disorderness is generally characterized in terms of the temperature dependence of the conductivity, more specifically in terms of the conductivity ratio.^{28,29,33} In the present context, the higher value of r for PANI-TCNQ ($r=1370$) implies that the disorderness present in it is larger than that of the pure PANI ($r=175$) system. The results of CHN microanalysis and optical spectra of the samples which indicate the presence of TCNQ in the PANI lattice corroborate the findings.

The temperature dependence of the electrical conductivity of amorphous semiconducting samples can be explained in terms of the variable range hopping (VRH) of polarons and bipolarons.³⁴ The phonon assisted hopping conduction can be expressed by the following:

$$\sigma = \sigma_0 \exp(-A/T^{1/4}), \quad (2)$$

where

$$A = 2.1[\alpha^3/kN(E_F)]^{1/4}, \quad (3)$$

where α^{-1} and $N(E_F)$ represent electron localization length and density of states at the Fermi surface, respectively. Following Eq. (2) we have plotted $\ln \sigma$ vs $T^{-1/4}$ for both samples in Fig. 5 which emphasizes the validity of the three-dimensional VRH model. The VRH parameters are shown in Table II.

TABLE II. Experimental values of Mott's VRH parameters.

Sample	σ (300K) (S cm ⁻¹)	$r = \sigma(300 \text{ K})/\sigma(25 \text{ K})$	α^{-1} (Å)	$N(E_F)$ (eV ⁻¹ cm ⁻³)
PANI	24	175	56	2.52×10^{19}
PANI-TCNQ	39	1370	36	2.78×10^{19}

The striking feature of the plots in Fig. 5 is the crossover phenomenon at $T_c = 143$ K. From Fig. 5, it is clearly evident that

$$\sigma_{II} > \sigma_I \text{ at } T > T_c,$$

$$\sigma_{II} = \sigma_I \text{ at } T = T_c,$$

$$\sigma_{II} < \sigma_I \text{ at } T < T_c,$$

where pure PANI and PANI-TCNQ are denoted by I and II, respectively.

Considering the results of CHN microanalysis and the optical absorption spectra as mentioned earlier, one can argue that at $T > T_c$ the higher σ_{II} value over σ_I is due to extra charge transport apart from the normal hopping transport through polarons and bipolarons. But when $T < T_c$, σ for the PANI-TCNQ system falls off more rapidly than for the pure PANI system. It appears true that at $T < T_c$, a charge transfer band transition which plays a significant role in the high temperature domain practically freezes and disorder induced localization of the charge carrier dominates. Finally, competition between these two opposing factors leads to the appearance of the crossover temperature (T_c).

IV. CONCLUSIONS

In summary, we have presented detailed results from a series of experiments through which we have investigated the role of the charge transfer agent in modifying the energy band structure of PANI and the concomitant change in the electrophysical properties of the same. The major findings of these experiments are (i) the appearance and subsequent decay of a deep blue color just after the addition of HCl in aniline-TCNQ solution indicates that the protons may have occupied different positions before they finally settle in the ring, (ii) the room temperature conductivity of the modified polymer is somewhat greater than that of pure PANI, (iii) the spectral linewidth of the acidified thin film of PANI-TCNQ is shorter in comparison to that of pure PANI and thus can be regarded as a promising material for low noise light emitting devices and (iv) the crossover phenomenon ($T_c = 143$ K) observed in the temperature dependence study of electrical conductivity of the samples suggests the possibility of the dominance of disorderness rather than the extra charge transfer process in the lower temperature region.

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