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On the interesting optical transitions observed in polyaniline films in the conducting and insulating states

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Systematic optical absorption investigations have been carried out on polyaniline (PANI) films. The samples investigated include emeraldine base(EB) form of polyaniline cast from N-Methyl Pyrrolidinone(NMP) and m-cresol and hydrochloric(HCl) acid doped polyaniline and HCl doped polyaniline-Multiwalled Carbon Nano Tube(MWNT) composite films, both cast from m-cresol. Corresponding to the indirect transition, negative energy gaps are observed in PANI (HCl) and PANI (HCl)-MWNT films, which are in the conducting state, whereas the negative energy gap is not observed in the EB films (insulating). This is a new observation in polyaniline films. The structural confirmation is achieved from Fourier Transform Infra Red (FTIR) spectroscopic studies and Transmission Electron Microscopic (TEM) studies.

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1. Introduction

Polyaniline (PANI) is one of the highly pursued conducting polymers owing to its good air stability, ease of synthesis, electrical conductivity that could be tuned from the insulating to the metallic regime and the availability of cost effective monomer and precursors [1-4].We have observed comparably high room temperature D.C electrical conductivity with negligible temperature variation (303K-413K) in the pellet samples of acid doped PANI and PANI-MWNT composite. Though extensive investigations have been reported on the electrical conductivity behaviour of doped PANI both in bulk and thin film forms [5, 6, 7, 8] detailed investigations on the optical characterization of PANI thin films are scanty. Reports on the room temperature D.C electrical conductivity of acid(sulphuric acid, camphor sulphonic acid, toluene sulphonic acid etc) doped PANI in the form of pressed pellets is reported to lie in the range 0.5-2S/cm[9,10,11]. We have carried out D.C electrical conductivity measurements on PANI pellets doped with hydrochloric acid(HCl),Camphor Sulphonic acid(CSA) and ortho phosphoric acid(H3PO4) and have observed a maximum conductivity of 2.2S/cm in HCl doped PANI.In HCl doped PANI-MWNT composite pellet samples, the highest room temperature D.C electrical conductivity of 28 S/cm has been observed in HCl doped PANI-MWNT composite with 50% MWNT loading. The room temperature D.C electrical conductivity values observed in thin films of HCl doped PANI and HCl doped PANI-MWNT composite both cast from m-cresol is about 10 S/cm and 40 S/cm respectively. In the present work, we have attempted a comparative study of the optical transitions of HCl doped PANI, HCl doped PANI-MWNT composite and the emeraldine base (EB) form of PANI, all in thin film forms. The first two samples constitute the conducting state and the third sample constitutes the insulating state of PANI. Such an investigation has been carried out mainly because of 1.HCl doped PANI and HCl doped one.

PANI-MWNT composite samples show quite high room temperature D.C electrical conductivity and 2. though extensive investigations have been reported on the electrical conductivity behaviour of acid doped PANI samples and their various composites[6,7,8,10], a comparative study on the various optical transitions in PANI films in the conducting and insulating forms is quite scanty.

2. Experimental

2.1 Synthesis of bulk samples

PANI doped with HCl, is synthesized in bulk form as already reported [1].

5 ml of monomer aniline is dissolved in 1.5M HCl.3M ammonium peroxidisulphate (APS) aqueous solution is used as the oxidant**.** APS dissolved in water is added drop wise to the mixture with continuous stirring for 4-5 hours. The precipitate obtained is filtered, washed and dried. HCl doped PANI-MWNT powder is prepared by adding MWNT to the mixture of aniline and hydrochloric acid, with aniline to MWNT feed ratio maintained at 1:0.5(weight/weight). All other synthesis conditions remain the same. PANI(EB) is prepared by dedoping HCl doped PANI salt with 1.5M NH_4OH.

2.2 Film preparation

0.2 g of the polymer sample in powder form is dissolved in 2 ml of m-cresol by stirring continuously for about 12 hours. The obtained solution is spread uniformly on ultrasonically clean glass substrates and allowed to dry in a hot air oven kept at 70 degrees. The same procedure is adopted for preparing thin films of all the samples.

2.3 Film thickness measurement

Film thickness is recorded using a DEKTAK 6M STYLUS PROFILER working in the range 0.005 μm to 262 μm.The recorded thickness of all the films falls in the range 35 μm to 45 μm.

2.4 Investigations using FTIR and TEM

The Fourier Transform Infra Red Spectra of the samples are recorded using an Avatar 370 spectrometer employing a DTGS KBr detector.

The TEM images of HCl doped PANI and HCl doped PANI-MWNT composite are obtained using a JOEL JEM 2200 FS electron microscope using an accelerating voltage of 200 KV.

2.5 UV-VIS- NIR Studies

UV-VIS- NIR spectra of the films are recorded in the range 190cm-1 to 1800 cm-1 using a Jasco V 570UV/VIS/NIR spectrophotometer employing a deuterium lamp, halogen lamp and a single monochromator.

3. Results and discussion

3.1Structural confirmation using FTIR and TEM

The FTIR spectrum of PANI (EB) is shown in Fig. 1.

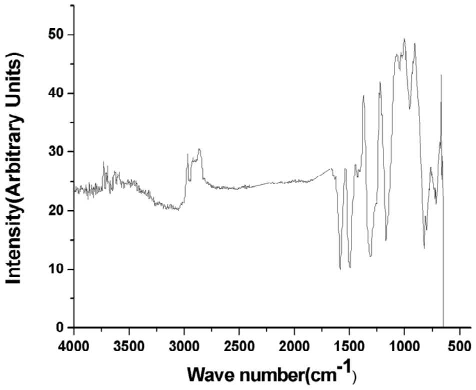

Fig. 1. FTIR spectrum of PANI (EB).

The major peaks observed at 1584 cm^{-1}, 1488 cm^{-1},1308cm^{-1},1171cm^{-1}and 827cm^{-1} are in good agreement with the already reported peaks of PANI (EB) confirming its formation [12, 13].A comparison of the FTIR spectra of PANI (HCl) and PANI (HCl)-MWNT is shown in Fig. 2.

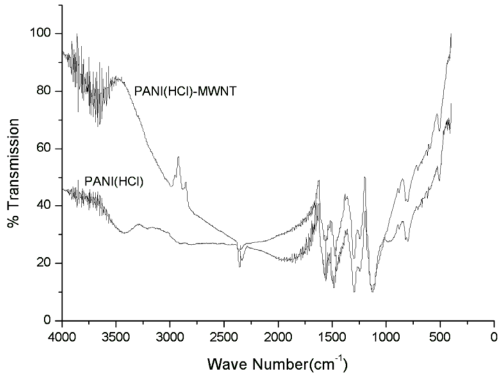

Fig. 2. FTIR spectra of PANI (HCl) and PANI (HCl)-MWNT (1:0.5) composite.

The two spectra resemble each other closely with only small shifts in absorption wave numbers. Both the spectra show all the characteristic vibrations of HCl doped PANI. [1]However it is observed that the NH stretching vibration occurs around 3500cm^{-1} in HCl doped PANI, whereas the NH stretching vibration seems to have shifted to 3000cm^{-1} in HCl doped PANI-MWNT composite. This could be due to the interaction of MWNT with the lone pair electrons of nitrogen. Since the characteristic C=C vibrations of MWNT are more or less in the same frequency range as those in HCl doped PANI, the presence of MWNT in the composite cannot be clearly established from the FTIR spectra. However its presence in the composite can be established from the TEM images (Fig. 3 & Fig. 4)

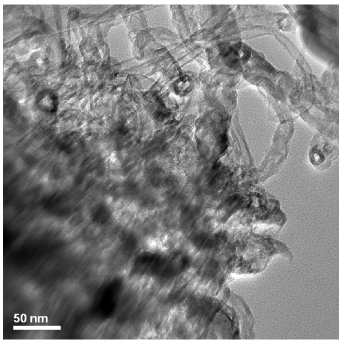

Fig. 3. TEM image of PANI (HCl).

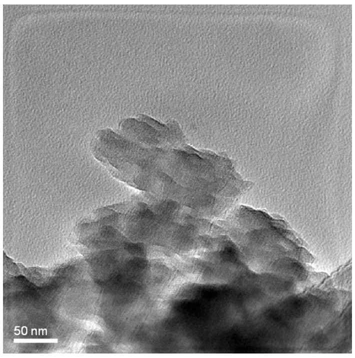

Fig. 4. TEM image of PANI(HCl)-MWNT(1:0.5) composite.

The TEM image of HCl doped PANI is shown in Fig. 3. Fig. 4 depicts the TEM image of HCl doped PANI-MWNT composite synthesized in the aniline monomer to MWNT feed ratios 1:0.5(weight/weight).

Fig. 4 clearly indicates the presence of both PANI and MWNT in the composite. The rod-like structures of MWNT is clearly seen in the TEM image, which confirms the formation of PANI-MWNT composite.

3.2 Optical absorption studies

The optical absorption spectra of PANI (EB) cast from NMP, PANI (EB) cast from m-cresol, PANI (HCl) and PANI (HCl)-MWNT both cast from m-cresol are shown in Figs. 5-8.

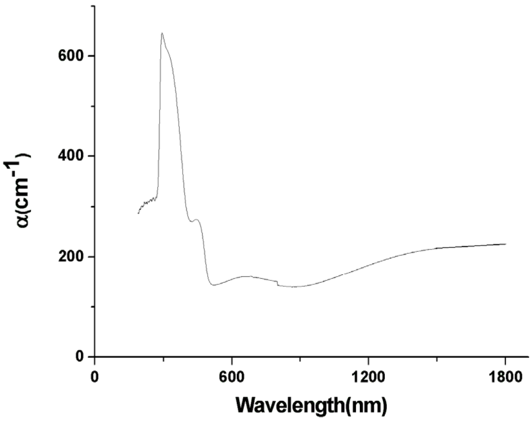

Fig. 5. Optical absorption spectrum of PANI (EB) cast from NMP.

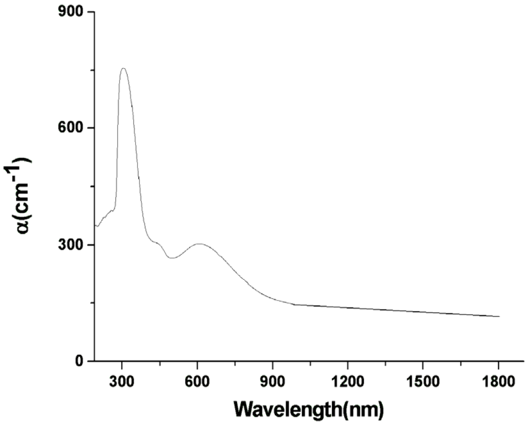

Fig. 6. Optical absorption spectrum of PANI(EB) cast from m-cresol.

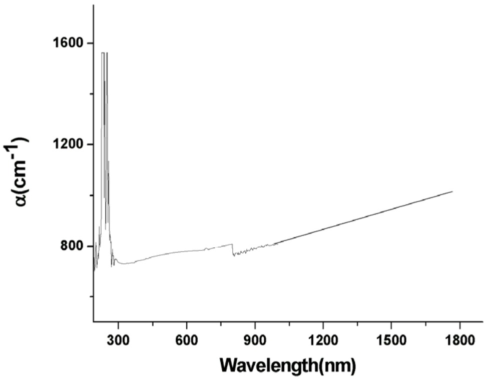

Fig. 7. Optical absorption spectrum of PANI(HCl).

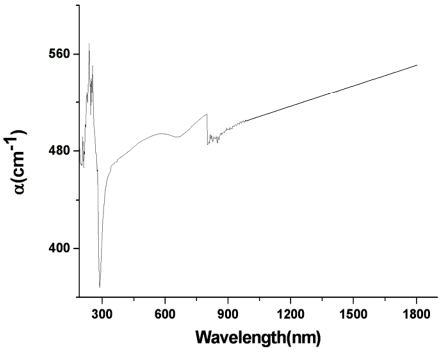

Fig. 8. Optical absorption spectrum of PANI(HCl)-MWNT(1:0.5) composite.

There are clear differences between the absorption spectra of PANI(EB) cast from NMP and m-cresol(Fig. 5 and Fig. 6). PANI(EB) cast from NMP exhibits peaks at 306nm and 615 nm, quite close to the reported values[14,15]. The peak at 306 nm corresponds to Π- Π^* transition and that at 615 nm corresponds to exciton band formed due to charge transfer exciton like electronic transition from the highest occupied molecular orbitals(HOMO) centered on the benzenoid rings to the lowest unoccupied molecular orbitals(LUMO) centered on the quinonoid rings[14,16]. The Π- Π^* transition peak of PANI(EB) cast from m-cresol(289 nm) is very close to that observed for PANI(EB) cast from NMP, while the exciton band of EB decreases in intensity for the sample cast from m-cresol. The transition peak at 458nm which corresponds to polaron to Π^* transition is more intense in the PANI(EB) film cast from m-cresol as compared to PANI(EB) film cast from NMP.The reason for the observed difference between the two spectra is that PANI takes a random coil conformation in solvents such as NMP.In solvents such as m-cresol, the acidity of the phenol group facilitates the proton exchange between m-cresol and the imine nitrogen atoms, showing the nature of a protonic acid doped system[14]. Fig. 7 and Fig. 8 show the absorption spectrum of PANI(HCl) and PANI(HCl)-MWNT composite films(both cast from m-cresol) respectively. Polaron to Π^* transition is observed in both the doped films at around 480nm as a low intensity kink Both the spectra exhibit absorption peak at around 790nm which corresponds to Π to polaron transition[14]. The peak corresponding to Π- Π^* transition has been reduced to a very weak kink in both PANI(HCl) and PANI(HCl)-MWNT films. A free carrier tail extending to the near infrared (NIR) region is observed in HCl doped PANI and HCl doped PANI-MWNT composite films which is characteristic of a highly conducting state [14]. However a similar free carrier tail is also observed in the EB film cast from m-cresol, possibly due to the moderate doping effect of m-cresol [14]. In the EB film cast from NMP, the free carrier tail is not observed.

The photon absorption in many amorphous materials is found to obey the Tauc relation given by, $(\alpha h\upsilon) = B (h\upsilon - E)^n$

Here α is the absorption coefficient in $eVcm^{-1}$, hυ the photon energy, B a constant and the index n is connected with the distribution of the density of states. For direct allowed transition energy gap, n=1/2 and for indirect allowed transition energy gap, n=2 $(\alpha h\upsilon)^2$ as a function of photon energy hυ gives direct allowed transition energy gap. $(\alpha h\upsilon)^{1/2}$ as a function of photon energy hυ gives indirect allowed transition energy gap [17]. The direct allowed transition energy gaps of PANI(EB) cast from NMP and PANI(EB) cast from m-cresol are shown in Figs. 9 and 10 respectively.

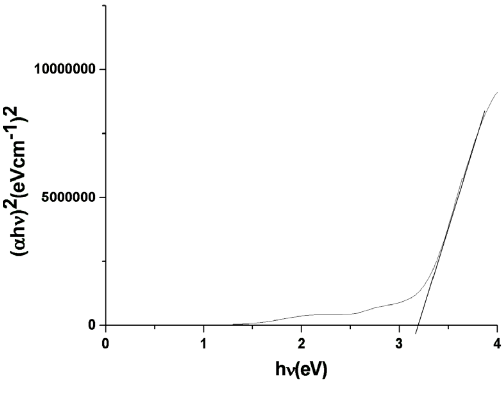

Fig. 9. Direct allowed transition energy gap of PANI(EB) cast from NMP.

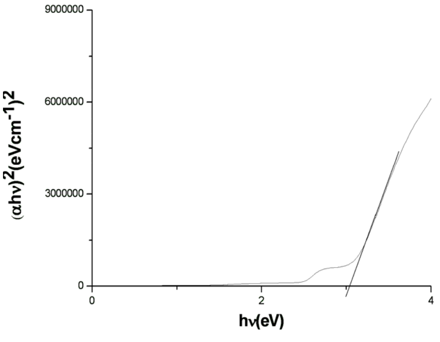

Fig. 10. Direct allowed transition energy gap of PANI(EB) cast from m-cresol.

The direct allowed transition energy gap of PANI (EB) cast from NMP falls at 3.12 eV(Π- Π^* transition), while that corresponding to PANI(EB) cast from m-cresol falls at 3.0 eV and 2.508 eV(polaron to Π^* transition). The indirect allowed transition energy gaps of PANI(EB) cast from NMP and PANI(EB) cast from m-cresol are shown in Figs. 11 and 12.

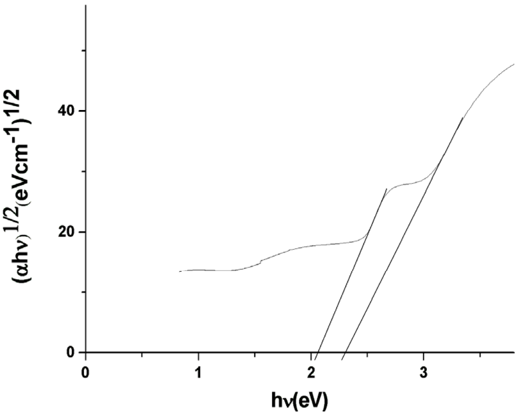

Fig. 11. Indirect allowed transition energy gap of PANI(EB) cast from NMP.

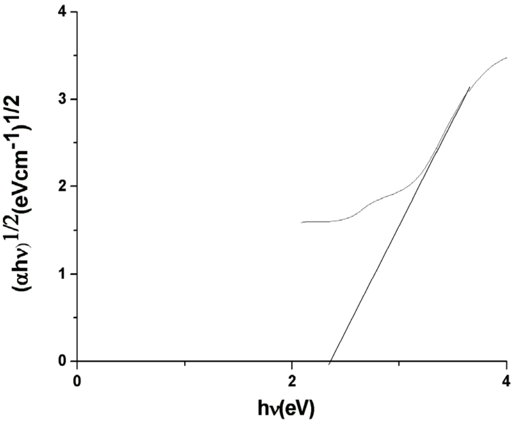

Fig. 12. Indirect allowed transition energy gap of PANI(EB) cast from m-cresol.

The indirect allowed transition energy gap of PANI (EB) cast from NMP is at 2.38 eV (Π- Π^* transition) and that corresponding to PANI(EB) cast from m-cresol falls at 2.33eV(Π- Π^* transition) and 2.05 eV(polaron to Π^* transition).The obtained values closely matches with those obtained for undoped plasma polymerized PANI films[17].Polaron to Π^* transition is not observed in PANI(EB) films cast from NMP and plasma polymerized films of undoped PANI. The presence of polaron to Π^* transition in PANI(EB) film cast from m-cresol is possibly due to the moderate doping effect of m-cresol. Obviously both the direct allowed and indirect allowed transition energy gaps decrease for PANI (EB) films cast from m-cresol.PANI (EB) takes up a random coil conformation in NMP due to twist defects between aromatic rings while such twist defects are removed in PANI (EB) cast from m-cresol solution. The moderate doping effect due to increased polymer-solvent interaction in m-cresol results in more extended conformation of polymer chains. The free carrier tail in the NIR region indicates the presence of intra band transitions within the half-filled polaron band [14].

The direct allowed and indirect allowed transition energy gaps of PANI (HCl) and PANI (HCl)-MWNT (both cast from m-cresol) are shown in Figs. 13-16.

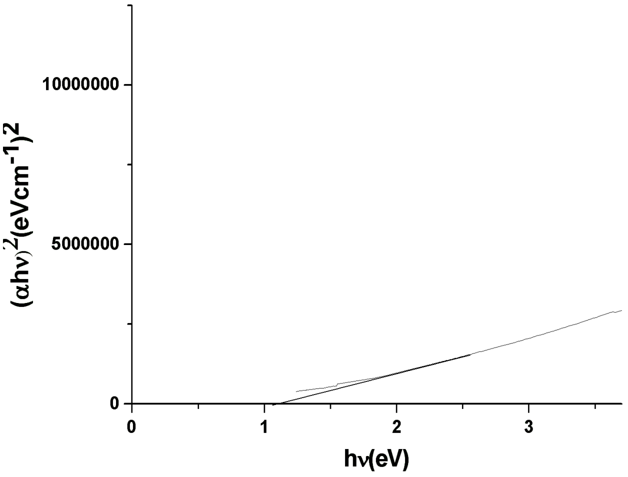

Fig. 13. Direct allowed transition energy gap of PANI(HCl).

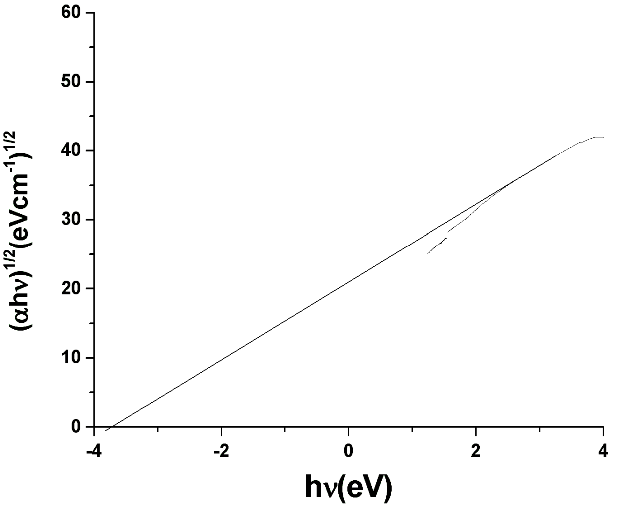

Fig. 14. Indirect allowed transition energy gap of PANI(HCl).

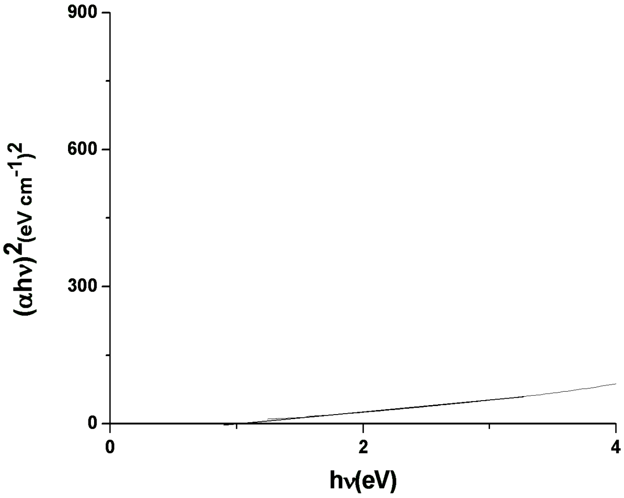

Fig. 15. Direct allowed transition energy gap of PANI(HCl)-MWNT(1:0.5) composite.

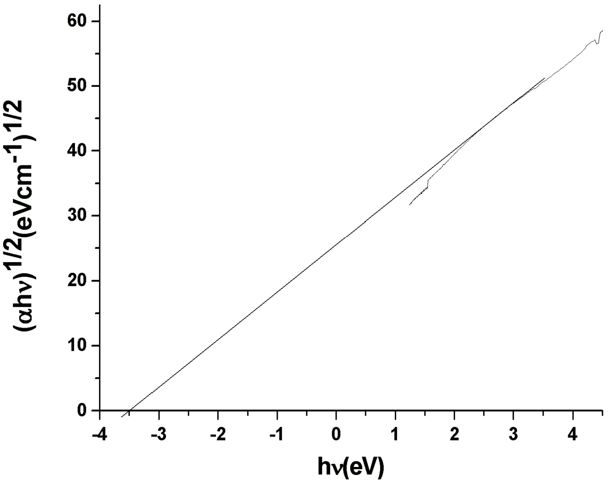

Fig. 16. Indirect allowed transition energy gap of PANI(HCl)-MWNT(1:0.5) composite.

As the polaron band gets more dispersed in energy, Π-Π* transition becomes very weak due to the elimination of band gap between Π band and polaron band[14]. In that case the transition energy gap corresponds to that between polaron band and Π* band. The direct allowed transition energy gap of PANI(HCl) cast from m-cresol is 1.09eV while the indirect transition energy gap is -3.7eV. The direct allowed transition energy gap of PANI(HCl)-MWNT film cast from m-cresol is 0.91147eV and indirect allowed transition energy gap is -3.58eV.Negative energy gap has already been reported in inorganic systems such as InN_xSb_{1-x},$Hg_{1-x-y}Cd_xMn_yTe$ and HgTe-CdTe[18-20]. Techniques like XPS,HREELS,magneto phonon resistance and magneto transport measurements have been employed to establish the presence of negative energy gap. According to reports, in negative energy gap materials, Valance Band Maximum (VBM) lies below Conduction Band Minimum (CBM) [18]. But we have not come across any reports of negative energy gap in doped polymers. Since the energy band structure of conducting polymers is different from that of conventional inorganic semimetals, more detailed investigations are necessary to bring out the origin of negative energy gap in doped polymers showing semi metallic behaviour. In the present work, negative energy gap has been observed in the indirect allowed transitions for the HCl doped PANI and HCl doped PANI-MWNT composite films which are in the semi metallic state(as given earlier, the D.C electrical conductivity values of HCl doped PANI and HCl doped PANI-MWNT composite films are 10S/cm and 40S/cm respectively.). Both the PANI (EB) films, which are in the insulating state, do not show any negative energy transition. The existence of the negative energy transition is a consequence of the semi metallic state of the polymer, which is in agreement with the earlier observation of negative energy gap in semi metallic inorganic systems. Moreover the negative energy transition is observed only in the indirect allowed transition whereas it is absent in the direct allowed transition. Thus phonons do play a significant role in the origin of negative energy transition. The origin and nature of such a transition in highly conducting doped polymers can be clearly established only after detailed investigations employing more sophisticated techniques.

4. Conclusions

In the indirect allowed transitions, a negative energy transition has been observed in HCl doped PANI and HCl doped PANI-MWNT films, both of which are in the highly conducting, semimetallic state. Such a transition is absent in the PANI (EB) films which are in the low conducting, insulating state. The origin of the negative energy transition is a consequence of the semi metallic state, brought about by phonon assisted processes. The present work extends ample scope for future investigations in these directions, since the origin and nature of the negative energy transition in highly conducting polymer systems can be clearly established only after detailed investigations using more sophisticated techniques.

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