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Charge transport and magnetic properties in polyaniline doped with methane sulphonic acid and polyaniline-polyurethane blend

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Charge transport in polyaniline protonated fully with methane sulphonic acid (MSA) and polyaniline (MSA)-polyurethane [PANI(MSA)-PU] blend has been investigated through measurements of temperature (T) and electric field (E) dependence of conductivity (σ), temperature dependence of thermoelectric power and magnetic susceptibility and electron spin resonance at room temperature. PANI(MSA) exhibits a three-dimensional variable-range hopping (VRH) type of conduction, which is not the case with HCl-doped PANI and the electric field dependence of its conductivity is also consistent with VRH behavior. The thermopower in PANI(MSA) shows metallic behavior. The blend follows a one-dimensional VRH type of conduction and the electric field dependence of its conductivity exhibits the Poole-Frenkel effect. The temperature-dependent magnetic susceptibility measurements indicate the presence of Pauli and Curie spins in both the samples. From electron spin resonance measurements the percentage of Lorentzian and Gaussian spins have been estimated. In PANI-MSA a larger number of spins are found to be delocalized. The conduction mechanism in PANI-PU blend is discussed in comparison to other commercial conducting polymer blends. [S0163-1829(97)02412-0]

I. INTRODUCTION

The development of environmentally stable, processible conducting polymer with good mechanical properties opens up the possibility of new applications for polymers. Polyacetylene doped with iodine or AsF_5 can attain conductivity comparable to that of metals.[1] Owing to their instability, they have limited usefulness in applications. Polyaniline (PANI) has emerged as one of the most promising conducting polymers.[2] PANI is inexpensive, environmentally stable and it exhibits relatively high conductivity. It is processable when doped with organic acids. While the room-temperature conductivity (σ) of paratoluene-sulphonic-acid–doped PANI (PANI-PTSA) is 5 S/cm and sulpho-salicylic-acid–doped PANI (PANI-SSA) is 1 S/cm,[3] conductivity as high as 10^2 S/cm has been obtained by doping PANI with camphor sulphonic acid (PANI-CSA).[4] The present work focuses on the study of methane-sulphonic-acid–doped PANI (PANI-MSA) and PANI-polyurethane blend. (S denotes siemens, 1 S=1 A/volt.)

The carriers generated in the process of doping in conducting polymers are known to be self-trapped by the conjugated polymeric chains in the form of polarons or bipolarons. Hopping or tunneling conduction is the usual transport seen in conducting polymers. One-dimensional variable-range hopping[5] (VRH) and charging energy limited tunneling[6] (CELT) conduction are characterized by a temperature dependence of the form $\exp[-(T_0/T)^{1/2}]$ where T_0 is a constant. Charge transport in PANI-PTSA and PANI-SSA has been found to follow CELT conduction from temperature-dependent conductivity $[\sigma(T)]$ and thermopower $[S(T)]$ measurements. A distinction between CELT and one-dimensional (1D) VRH conduction can be made if the electric field (E) dependence of conductivity at different temperatures, $\sigma(E,T)$, is measured. $\ln[\sigma(E,T)]$ should vary as E and E^{-1} for VRH and CELT, respectively.[5,6]

Blending PANI with other nonconducting polymers improves the mechanical properties of PANI.[7,8] It has been found that PANI® (VERSICON, Allied Signals Corporation, USA)–poly vinyl chloride (PVC) blends show a temperature dependence of conductivity that is quite different from that of unblended doped PANI®.[9] As the temperature is decreased, the blends show a much smaller decrease of conductivity than the unblended PANI®. It is found to be even more pronounced in the case of PANI®–poly methyl methacrylate (PMMA) blends than in PANI®-PVC blends. It is said that the conduction barriers around PANI® particles appear to be reduced in height.[10] The blends of PANI with a copolyester of polyethylene terephthalate (PETG) show a flattening in σ at high temperatures in a manner similar to PANI®-PMMA blend and the decrease in conductivity as the temperature is reduced is larger.

In these blends, from 250 to 10 K a temperature dependence characteristic of either 1D VRH or CELT at low field, is observed. Even in the case of PANI-CSA/PMMA blends[11] a temperature dependence characteristic of VRH transport, viz., $\sigma(T)\propto\exp[-(T_0/T)^\gamma]$ with the exponent γ increasing from $\gamma=0.25$ to 1, has been found upon decreasing the volume fraction of PANI up to the percolation threshold, below which $\gamma=0.5$, as in the case of granular metals.

While at high temperatures $\ln(\sigma)$ varies as $T^{-1/2}$ for PANI®-PMMA and PANI®-PVC blends, at millikelvin temperatures they are found to exhibit a fluctuation-induced tunneling (FIT) conduction.[12] For the PANI®-PETG blends $\sigma(E,T)$ exhibits a CELT conduction.[13] It has been found that the method of synthesis and the insulating polymer used for blending play a vital role in deciding the morphology and conduction mechanism in a polymer blend containing the same mole fraction of PANI in a given insulating polymer matrix.[14] In an attempt to improve the mechanical properties of pure PANI-MSA, in the present case it has been blended with the insulating polymer, viz., polyurethane.

A correlated study of transport and magnetic properties provides better insight into the conduction mechanisms. The transport and magnetic properties of doped PANI-MSA and its blend with polyurethane [PANI(MSA)-PU] are discussed in the present work. The plan of this paper is as follows: In Sec. II, the synthesis and characterization of polyaniline and its blend and the experimental details are described. Charge transport studies include temperature-dependent (i) dc electrical conductivity, (ii) electric-field-dependent conductivity, and (iii) thermoelectric power measurements. The magnetic properties investigated are temperature-dependent dc magnetic susceptibility and electron-spin-resonance absorption. The relevant theoretical models are briefly discussed in Sec. III. The results are presented in Sec. IV followed by a discussion in Sec. V and conclusions in Sec. VI.

II. EXPERIMENT

A. Synthesis and characterization

Polyaniline was prepared by chemical oxidation of aniline using ammonium persulphate in the presence of methane sulphonic acid.[15] The prepared polymers were purified by repeated washing with water and methanol. NCO terminated polyurethane was prepared by condensation of polyoxypropylene glycol and toluene diisocyanate by the procedure reported by Francis, Thomas, and Gupta.[16] PANI was powdered well and blended with solutions of polyurethane in toluene. The concentration of PANI was set to 50% by weight. Thin films were cast on clean glass surfaces and were allowed to cure at room temperature.

B. Experimental details

Unblended PANI-MSA pellets of diameter 8 mm and thickness 1 mm were used for conductivity (σ) and thermoelectric power (S) measurements while for the PANI(MSA)-PU(50%) blend, flexible sheets of dimensions 1 cm×1 cm ×0.1 cm were used. For unblended PANI-MSA $\sigma(T)$ was measured by the Van der Pauw method[17] using a Keithley constant current source Model No. 225 and a Keithley 191 Nanovoltmeter. For the PANI(MSA)-PU(50%) blend a two-probe method was used as the sample resistance was high. Gold was deposited on both sides of the sample to avoid any interactions of PANI with the contact material. A constant voltage was applied using a Keithley 617 electrometer and the current was measured in the low-field Ohmic region of the sample. The sample was mounted in a Cu block using GE varnish (General Electric, Oxford Instruments, England). A Janis closed-cycle refrigerator model CCS-500 was used for these measurements. The temperature was controlled by a Lakeshore temperature controller model 330 and it was measured using a calibrated silicon diode sensor. During the electric-field–dependent conductivity measurements the sample temperature was monitored carefully to avoid any self-heating in the sample beyond a certain value of applied voltage. Thermoelectric power was measured by the differential method.[18] Magnetic susceptibility was measured using a commercial Quantum Design Superconducting quantum interference device magnetometer model MPMS-5 in the temperature range 300–5 K in a magnetic field of 500 G. Room-temperature ESR spectra of the sample were recorded at X band using a Varian E110 spectrometer.

III. THEORY

A. Transport properties

1. Conductivity

Conducting polymers are predominantly polycrystalline or amorphous in character and have a substantial amount of disorder. As a result, hopping or tunneling conduction is generally observed and the dependence of conductivity on temperature (T) and electric field (E) help to identify the exact conduction mechanism.

(a) Variable range hopping conduction.[5] In a disordered material when the charge carriers are localized due to random electric fields, instead of band conduction, charge transport takes place via phonon-assisted hopping between localized sites. Since the localized states have quantized energies extending over a certain range, an activation energy is required for each hop.

The quasi-1D VRH model[19] predicts a temperature-dependent conductivity given by

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

According to the 1D VRH model, Mott's characteristic temperature is given by

$$T_0=8\alpha/k_BN(E_F)Z, \tag{2}$$

where α^{-1} is the localization length, $N(E_F)$ is the density of states at the Fermi energy, k_B is the Boltzmann constant, and Z is the number of nearest-neighbor chains which is 4 for PANI.[20]

The range of hopping (R_{hop}) and activation energy for hopping (W_{hop}) for 1D VRH are expressed as

$$R_{\mathrm{hop}}=[\alpha\pi k_BTN(E_F)]^{-1/2}, \tag{3}$$

$$W_{\mathrm{hop}}=[\pi R_{\mathrm{hop}}N(E_F)]^{-1}. \tag{4}$$

The inverse localization length for the strong localization is given by

$$\alpha=(2m^*V/\hbar^2)^{1/2}, \tag{5}$$

where m^* is the effective mass of the charge carriers, $\hbar=h/2\pi$, where h is Planck's constant, and V is the effective barrier height between localized sites.

For variable-range hopping in three dimensions (3D VRH), the temperature dependence of conductivity follows the relation

$$\sigma\propto\exp[-(T_0/T)^{1/4}], \tag{6}$$

where T_0 is the characteristic Mott temperature in 3D and is given as

$$T_0=16\alpha^3/k_BN(E_F). \tag{7}$$

The expressions for the range of hopping and the activation energy for hopping in three dimensions are given by

$$R_{\mathrm{hop}}=[9/8\pi k_B T\alpha N(E_F)]^{1/4}, \tag{8}$$

$$W_{\mathrm{hop}}=k_B(T_0T^3)^{1/4}. \tag{9}$$

(b) Charging energy limited tunneling.[6] In a disordered material when the insulating barrier between two conducting regions is sufficiently thin, electron tunneling occurs between small surface areas. A tunnel junction can be approximated by a parallel plate capacitor (C) and a resistance (R). When the conducting segments are large, the total capacitance (C_0) between the conducting segments is large and therefore the charging energy ($e^2/2C_0$) becomes negligible and the conduction is due to fluctuation-induced tunneling.[21] When the size of the conducting segments is small and the isolated metallic grains are dispersed in a dielectric matrix, the charging energy plays a dominant role. Electrons and holes are transported from one isolated metallic grain to the next by tunneling. The effects of charging energy are seen in both the temperature and electric field dependence of conductivity. The low-field charging energy limited conductivity is of the form

$$\sigma\propto\exp[-(D/k_BT)^{1/2}], \tag{10}$$

where D is a constant.

2. Electric-field-dependent conductivity

A nonlinear relationship between current and voltage implies that either mobility or carrier concentration, or both, in PANI vary with the applied field. From $\sigma(E)$ measurements at a particular temperature it is possible to distinguish between 1D VRH and CELT.

(a) Variable-range hopping. The electric field dependence of conductivity according to the VRH model in any dimension[5] is given by

$$\sigma\propto\exp(eRE/k_BT), \tag{11}$$

where R is the range of hopping.

(b) CELT. In the high field non-Ohmic regime, the CELT model predicts[6]

$$\sigma=\sigma_0'\ \exp(-E_0/E), \tag{12}$$

where E is the electric field. Here σ_0' and E_0 are some constants only weakly dependent on T and E. The most probable separation between the centers of two metallic grains ω is given by

$$\omega=k_BD/4eE_0, \tag{13}$$

$$\text{or}\quad \omega=k_BT/eE_t,$$

where D is a constant and E_t is the threshold electric field above which σ increases rapidly according to equation (12).

(c) Poole-Frenkel effect. The Poole-Frenkel effect is the field-assisted thermal ionization occurring in insulators and semiconductors.[22] This can be explained by treating the semiconductor as a system of neutral atoms and not as a system of electrons moving in a self-consistent periodic potential. After ionization of impurity atom, the electron moves in the medium of a polarizable atom and in the field of a positive ion.

If the electrons are localized in an effective potential $V(r)$ centered at $r=0$, when an electric field E is applied, $V(r)$ is given by

$$V(r)=-e^2/4\pi\epsilon_0\epsilon r-erE, \tag{14}$$

where ϵ_0 is the permittivity of free space and ϵ is the relative permittivity of the material. Hence the maximum height $V_{\max}$ between adjacent sites will be lowered by

$$\delta V=(e^3/\pi\epsilon_0\epsilon)^{1/2}E^{1/2}, \tag{15}$$

since α changes according to Eq. (5), using Eq. (1) and expanding V leads to

$$\ln(\sigma)\propto(1/4V)(T_0/T)^{1/2}(e^3/\pi\epsilon_0\epsilon)^{1/2}E^{1/2},$$

i.e.,

$$\ln(\sigma)=KE^{1/2}, \tag{16}$$

where

$$K=(T_0^{1/2}/4V)(e^3/\pi\epsilon_0\epsilon)^{1/2}T^{-1/2}, \tag{17}$$

or

$$K=K'T^{-1/2},\quad K'=(T_0^{1/2}/4V)(e^3/\pi\epsilon_0\epsilon)^{1/2}. \tag{18}$$

3. Thermoelectric power

The sign of thermoelectric power (S) shows the type of majority carriers present in the material at a particular temperature. In fully doped polyanilines a small and linear temperature dependence of S is observed that is characteristic of metals and is given by the Mott expression

$$S=[\pi^2k_B^2T/3e][\delta(\ln\ \sigma(E_F))/\delta E]_{E=E_F}, \tag{19}$$

where S is related to the energy derivative of the electrical conductivity at the Fermi level. The 3D VRH model gives the temperature dependance of thermopower on the other hand as

$$S\propto T^{1/2}. \tag{20}$$

B. Magnetic properties

1. dc magnetic susceptibility (χ)

In disordered conducting polymers the presence of polarons and bipolarons gives rise to temperature-independent paramagnetic susceptibility apart from the temperature-dependent Curie susceptibility.[23–25] Experimental χ_{spin} can be resolved into Pauli and Curie contributions according to the expression

$$\chi_{\mathrm{spin}}=\chi_P+C/T, \tag{21}$$

where C is Curie constant and χ_P is Pauli susceptibility expressed as

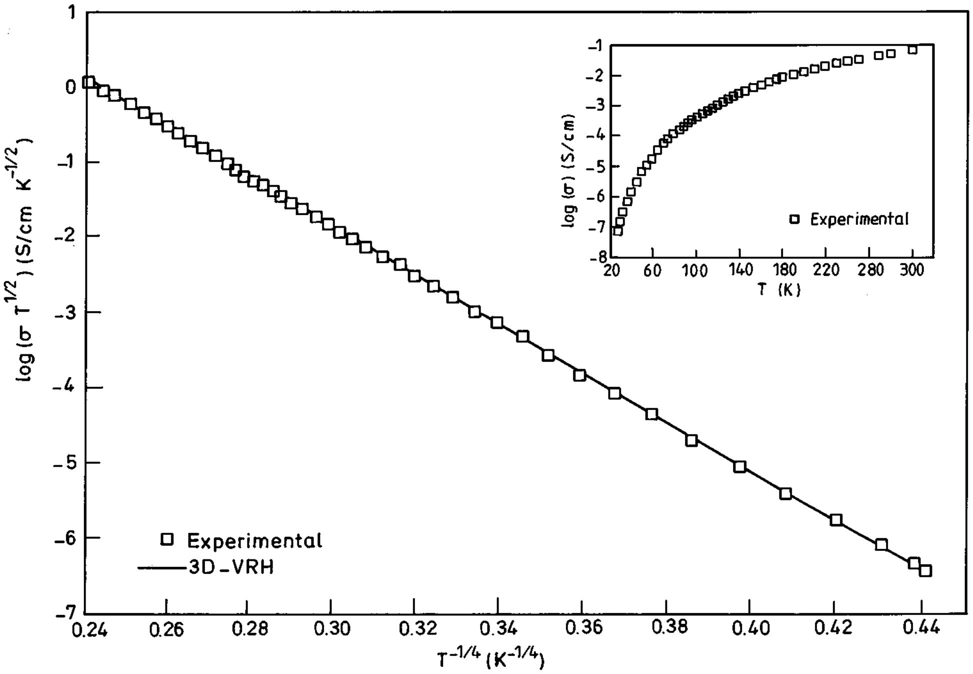

FIG. 1. Temperature dependence of dc conductivity of PANI-MSA showing a fit to 3D VRH (solid line). The inset shows a plot of the experimental data.

$$\chi_P = \mu_B^2 N(E_F), \tag{22}$$

where μ_B is the Bohr magneton. The measurement of χ_{spin} therefore helps in determining $N(E_F)$.

2. Electron spin resonance

Electron spin resonance measurements give information regarding the g factor, linewidth, and line shape. These ESR parameters can be analyzed in terms of static and dynamic characteristics of the paramagnetic centers. Deviations from free-electron g values are mainly due to coupling of electron spins with the orbital angular momenta. The linewidth measures the interaction between the unpaired electrons of different nature namely, conduction and localized electrons.[26] The presence of localized spins gives rise to a Gaussian shape given by the function[27]

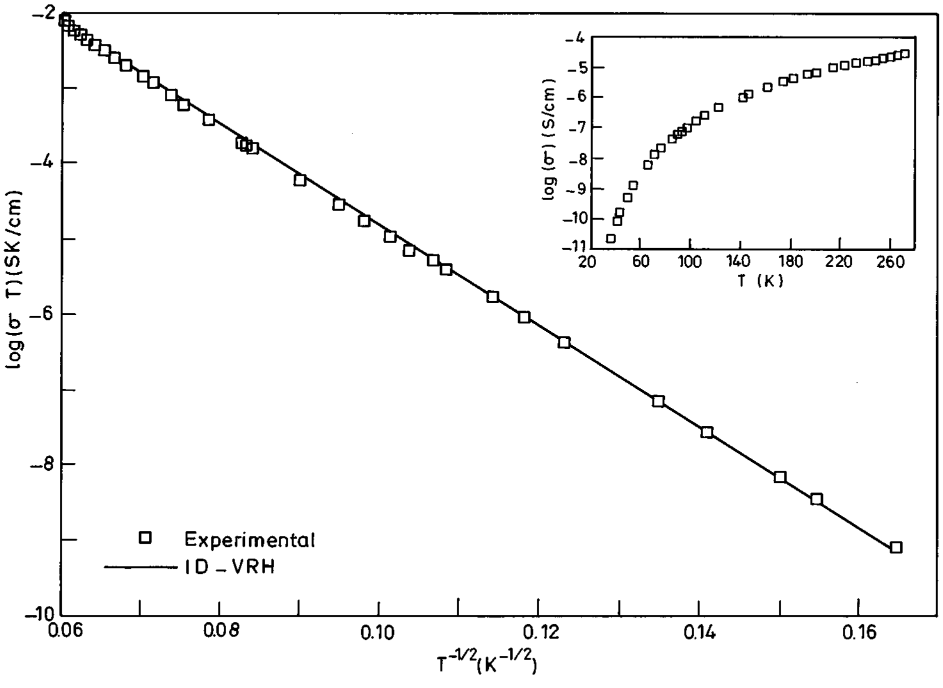

FIG. 2. Temperature dependence of dc conductivity of PANI(MSA)-PU blend showing a fit to 1D VRH (solid line). The inset shows a plot of the experimental data.

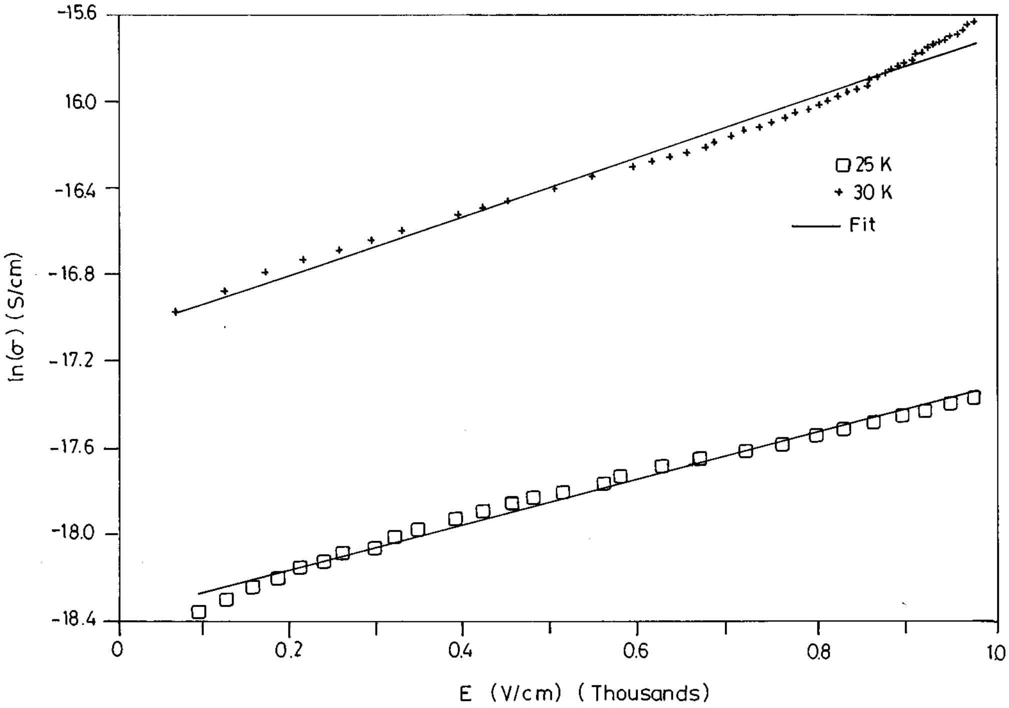

FIG. 3. Electric field dependence of conductivity of PANI-MSA at 25 K (□) and 30 K (+) showing a fit to VRH conduction.

$$f_G(H)=1/\Delta(2\pi)^{1/2}\exp\left[-\frac{\overline{(H-H_0)^2}}{(2\Delta^2)}\right], \qquad (23)$$

where Δ is the rms linewidth and H_0 is the resonance field. The presence of delocalized spins gives rise to a Lorentzian shape given by the normalized function[27]

$$f_L(H)=(\gamma/\pi)\{1/[\gamma^2+\overline{(H-H_0)^2}]\}, \qquad (24)$$

where γ is the linewidth. In many cases the actual line shape is a combination of Lorentzian and Gaussian distributions.

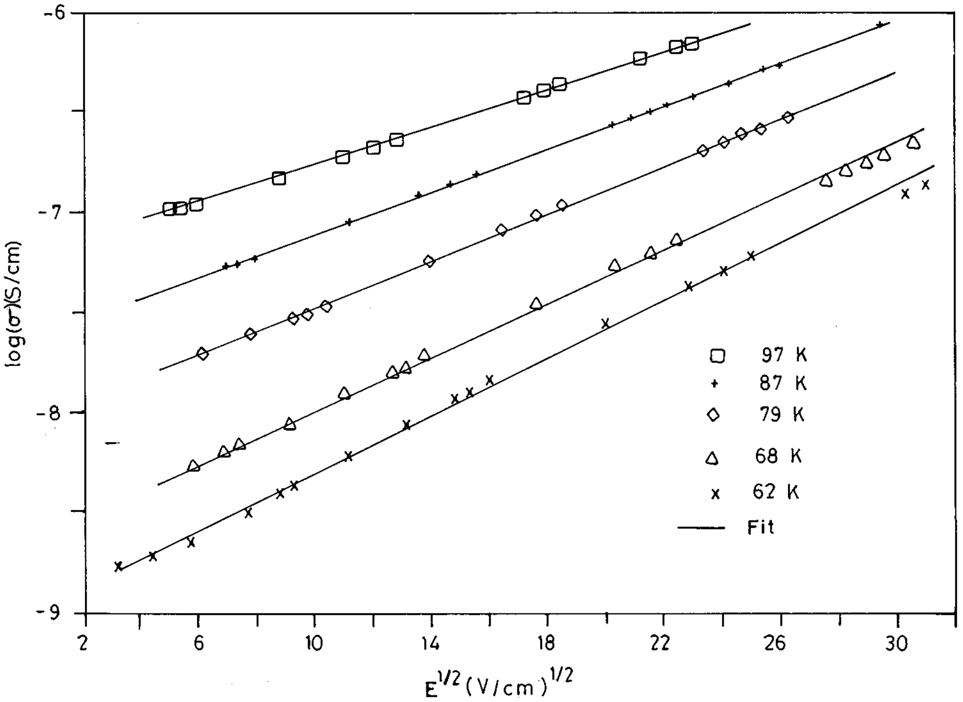

FIG. 4. Electric field dependence of conductivity of PANI(MSA)-PU blend at 97 K (□), 87 K (+), 79 K (◇), 68 K (△), 62 K (×), and the solid line is the fit to the Frenkel-Poole effect.

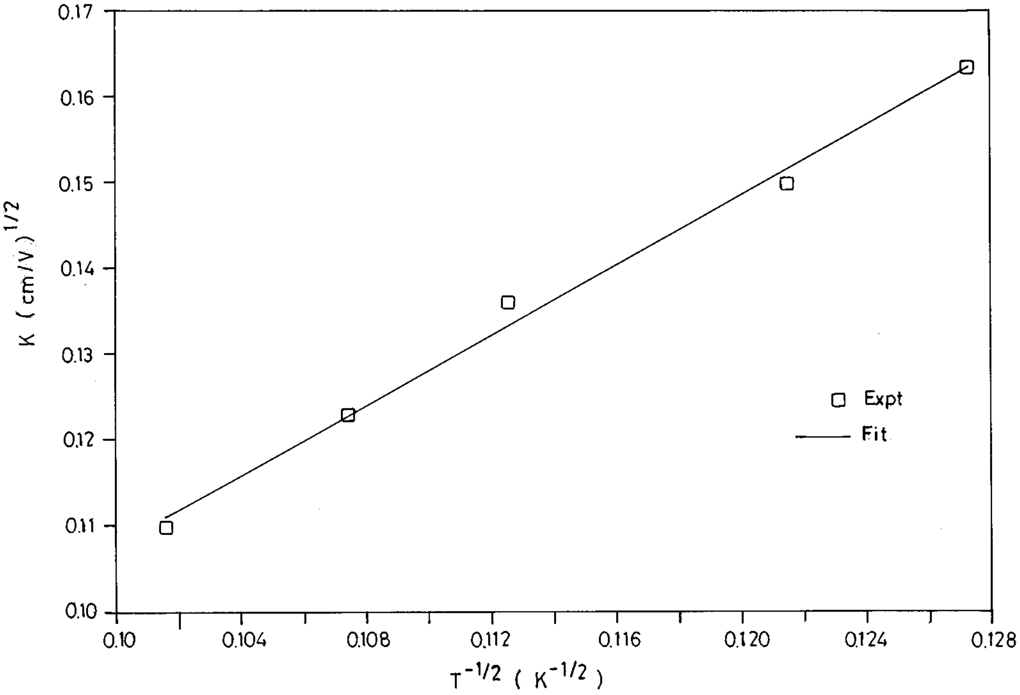

FIG. 5. A plot of K vs $T^{-1/2}$ from Eq. (12) and the solid line is the fit to calculate the value of K' from Eq. (18).

IV. RESULTS

A. Temperature dependence of conductivity $\sigma(T)$

1. Unblended PANI-MSA

The room-temperature conductivity of the sample is found to be 0.1 (S/cm). $\sigma(T)$ is found to follow a behavior characteristic of 3D VRH given as

$$\sigma(T)=\sigma_0 T^{-1/2}\exp[(-T_0/T)^{1/4}].$$

$\sigma(T)$ data are shown in Fig. 1 in the form of $\log_{10}(\sigma T^{1/2})$ versus $T^{-1/4}$ plot. The inset of Fig. 1 shows a plot of $\log_{10}(\sigma)$ versus T. The value of the Mott characteristic temperature T_0 obtained from the slope of Fig. 1 is found to be 3.2×10^7 K.

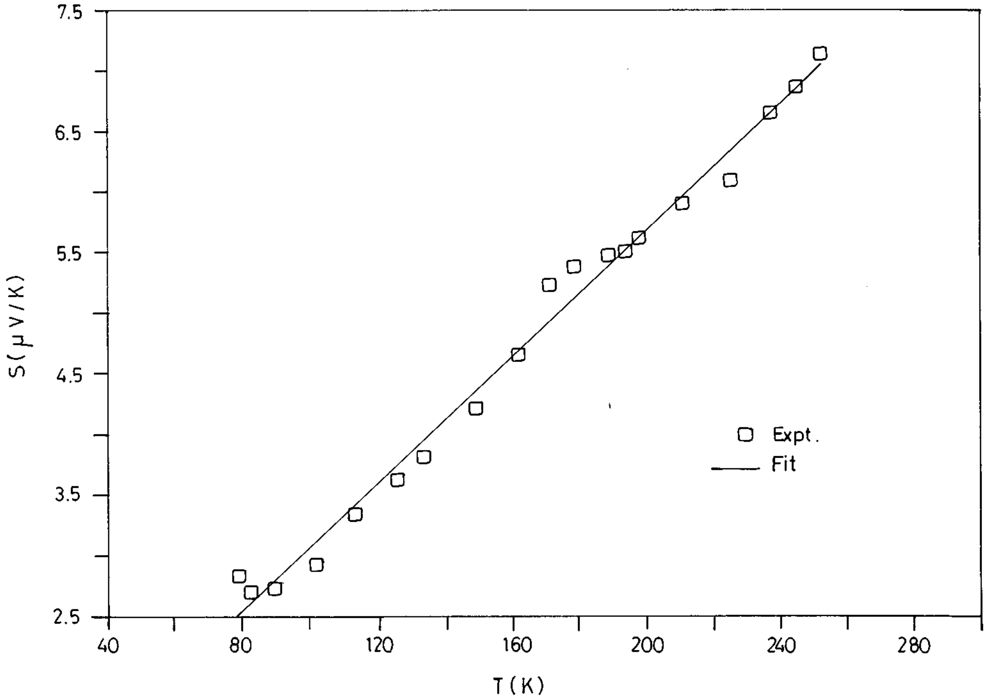

FIG. 6. Temperature dependence of thermoelectric power of PANI-MSA where □ denotes experiment and − is the fit to Eq. (19).

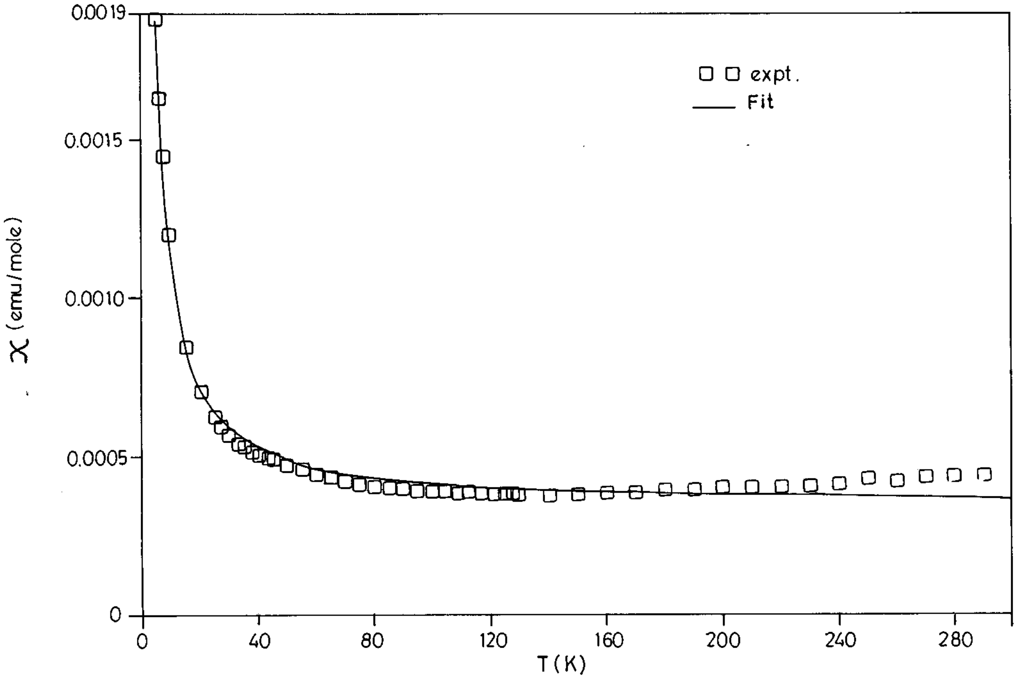

FIG. 7. Temperature dependence of dc magnetic susceptibility of PANI(MSA) where □ denotes experiment and − is the fit to Eq. (21).

2. PANI(MSA)-PU(50%) blend

The room-temperature conductivity of the blend is found to be 10^{-3} (S/cm). $\sigma(T)$ data from 300 to 50 K are shown in Fig. 2 in the form of a $\log_{10}(\sigma)$ versus $T^{-1/2}$ plot. The inset of Fig. 2 shows a plot of $\log_{10}(\sigma)$ versus T. This behavior is characteristic of variable-range hopping in one dimension[5] or charging energy limited tunneling in the low-field regime.[6] The value of T_0 is found to be 2.4×10^4 K.

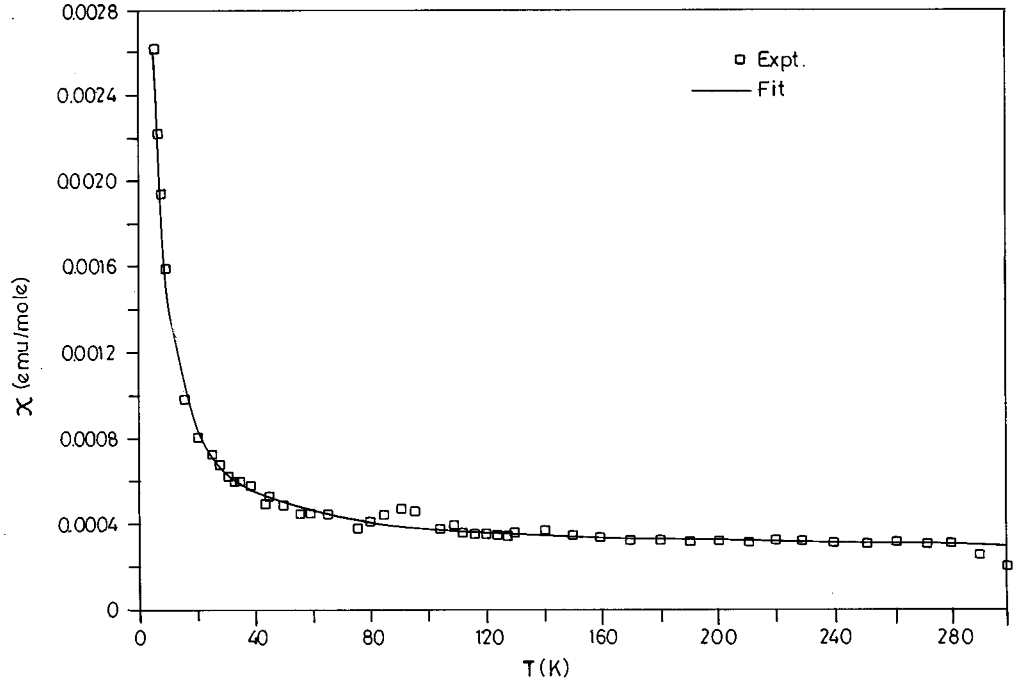

FIG. 8. Temperature dependence of dc magnetic susceptibility of PANI(MSA)-PU blend where □ denotes experiment and − is the fit to Eq. (21).

TABLE I. Parameters of PANI materials evaluated from theory.

Sample	Hopping dimension	Mott temp. T_0 (K)	α^{-1} (A)	χ_p (emu/mole)	C (emu K/mole)	N (E_F)	R_{hop} (A) at 100 K	W_{hop} (eV) at 100 K
Unblended PANI-MSA	3D	3.2×10^{7}	0.71	330×10^{-6}	77×10^{-4}	3.3×10^{22} states/eV cm^3	5.5	0.15
PANI (MSA)-PU blend	1D	2.4×10^{4}	80	255×10^{-6}	117×10^{-4}	1.22×10^{22} states/ev cm^3	500	0.05

B. Electric field dependence of conductivity $\sigma(E,T)$

1. Unblended PANI-MSA

A plot of $\ln(\sigma)$ versus E for PANI-MSA is shown in Fig. 3 for different temperatures. It follows a behavior characteristic of variable-range hopping according to Eq. (11).

2. PANI(MSA)-PU(50%) blend

The results of electric-field–dependent conductivity measurements performed at different temperatures are shown in Fig. 4 in the form of a $\log_{10}(\sigma)$ versus $E^{1/2}$ plot. They are found to follow a behavior according to Eq. (16), which is characteristic of the Frenkel-Poole effect. Slope (K) of the lines in Fig. 4 versus $T^{-1/2}$ is found to be linear and is shown in Fig. 5. The value of the potential barrier V determined from the slope (K') of Fig. 5 according to Eq. (18) is found to be 1.56 eV [the value of ϵ is taken as 4.3 (Ref. 28)].

C. Thermoelectric power (S)

Unblended PANI-MSA. An S versus T graph is shown in Fig. 6. S is found to be linear with T characteristic of metals. For the blended polymer, because of high resistance of the sample, S could not be measured.

D. dc magnetic susceptibility (χ)

χ for a two-ring repeat unit is shown as a function of temperature in Figs. 7 and 8 for unblended PANI-MSA and PANI(MSA)-PU(50%), respectively. The experimental values have been corrected for diamagnetic contributions from the atomic cores (χ_{core}) using Pascal constants.[29] The values of χ_{core} for unblended PANI-MSA and PANI(MSA)-PU(50%) are -153×10^{-6} and -244×10^{-6} emu/mole, respectively. The corrected susceptibility could be fitted to Eq. (21). The values of χ_P and $N(E_F)$ are given in Table I.

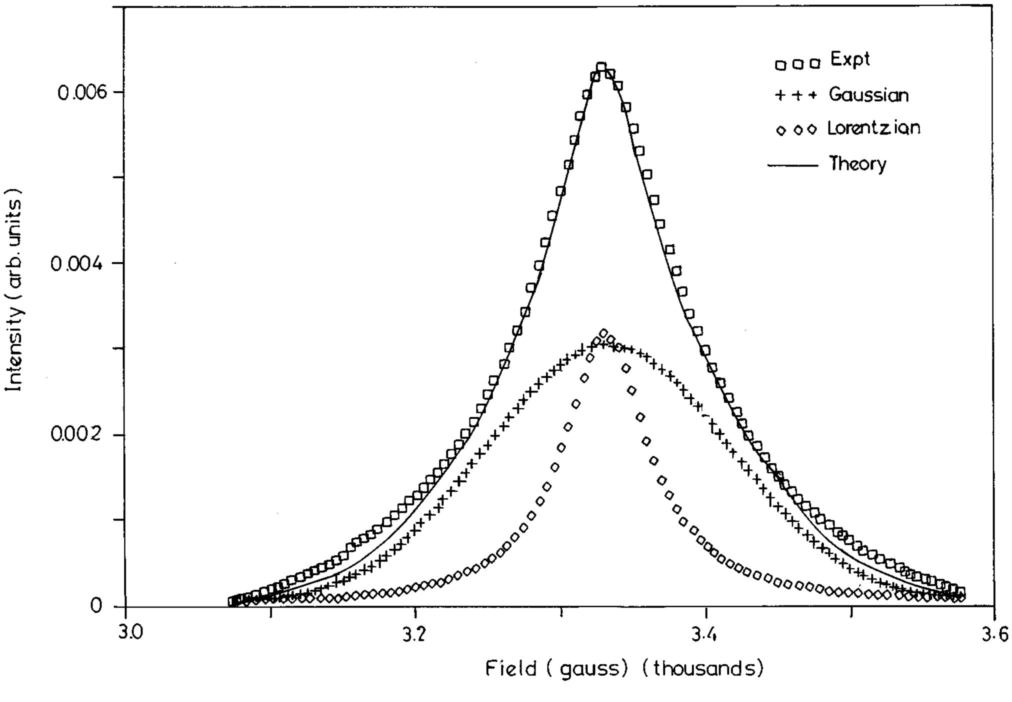

FIG. 9. Room-temperature ESR spectra PANI(MSA) where □ denotes experiment, + denotes Gaussian fit, ◇ denotes Lorentzian fit, and – denotes combination of Gaussian and Lorentzian.

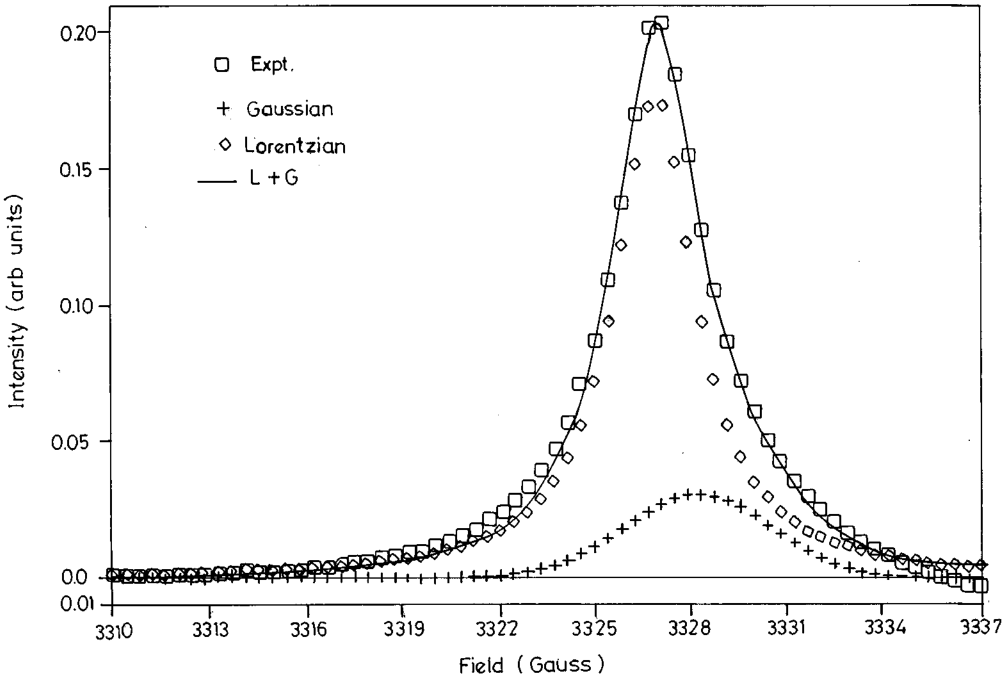

FIG. 10. Room-temperature ESR spectra of PANI(MSA)-PU blend where □ denotes experiment, + denotes Gaussian fit, ◇ denotes Lorentzian fit, and − is the combination of Gaussian and Lorentzian.

E. ESR

The experimental X-band ESR spectra of both unblended PANI-MSA and PANI(MSA)-PU(50%) could be resolved into a Lorentzian and a Gaussian line shape and are shown in Fig. 9 and Fig. 10, respectively. The various parameters obtained from the spectra are given in Table II.

V. DISCUSSION

For the unblended PANI-MSA, a ln(σ) versus $T^{-1/4}$ variation is observed that is characteristic of 3D VRH instead of 1D VRH, which is normally observed in fully doped polyanilines.[30] This could probably be due to a better interchain coupling upon doping with MSA due to which more sites are available for hopping in three-dimensions. The electric-field–dependent conductivity also shows a variation characteristic of VRH. While a hopping conduction characteristic of disordered material is seen from temperature-dependent conductivity measurements, a small and linear temperature dependence of S, which is characteristic of a metal is observed (Fig. 6) instead of a $1/T$ variation expected for hopping conduction. A small temperature-dependent Pauli susceptibility is observed in addition to χ_{Curie}, which also supports the metallic character in the material. The temperature-dependent Pauli susceptibility above 150 K indicates the existence of a finite Fermi density of states of spin carriers. A similar observation has been made in polypyrrole doped with BF_4.[31] The authors observe that this could be due to the microcrystalline regions of the polymer embedded in amorphous matrix apart from the different lengths of the chains of the polymer due to which magnetic species can coexist with nonmagnetic species in a chaotic state. The exact reasons for such a behavior in PANI(MSA) are not clear.

In PANI(MSA)-PU(50%) blend, the value of σ (300 K) is found to be decreased from that of unblended PANI-MSA by 2 orders of magnitude unlike PANI®-PVC (Ref. 9) and PANI®-PMMA where the conductivities are either comparable to or higher than that of pure PANI®.[10] While a $T^{-1/2}$ variation reminiscent of either 1D VRH or CELT is observed from $\sigma(T)$ measurements, $\sigma(E,T)$ behavior is in accordance with quasi-1D VRH of electrons among localized sites where the electrons have an effective Coulombic barrier between adjacent sites. The effective barrier height is lowered by an

TABLE II. Parameters obtained from the ESR spectra.

Sample	ΔH_{expt} (G)	ΔH_G (G)	ΔH_L (G)	G%	L%	g_{G}	g_L
Unblended PANI-MSA	1.4	2.2	1.5	18	82	2.0231	2.023 89
PANI (MSA)-PU blend	126	199	72	68	32	2.0077	2.0185

applied electric field and hence the conductivity increases with E and a Poole-Frenkel effect is observed similar to the case of polytoluidine (POT-ES).[32] Hence $\sigma(E,T)$ measurements confirm that the conduction mechanism in PANI(MSA)-PU(50%) blend is 1D VRH and not CELT.

From the value of T_0 and $N(E_F)$ the localization length α^{-1} is calculated using Eq. (2) for PANI-PU(50%) blend and Eq. (7) for unblended PANI-MSA and are given in Table I. Other Mott parameters R_{hop} and W_{hop} are determined using Eqs. (8) and (9) for unblended PANI-MSA and Eqs. (3) and (4) for PANI-PU(50%). The polyurethane chains in PANI(MSA)-PU blend might increase the average chain separation between adjacent PANI chains and this reduces the interchain transfer of charge carriers. Hence an additional random potential may be present in this material because of blending with insulating PU. The value of the localization length is 80 Å for the blend while for the unblended doped PANI-MSA it is 0.71 Å. This variation in localization length cannot be used to conclude that the charge carriers in the case of blends are more delocalized as the conduction in this case is 1D VRH whereas in the unblended PANI-MSA it is 3D VRH. It is difficult to compare these two polymers on the basis of α^{-1} alone. The thermopower of PANI-MSA is proportional to temperature indicating a metallic character. The linear thermopower is a signature of very high intrinsic conductivity in PANI-MSA. Such metallic thermopower also indicates that the thermal resistance of the barriers that dominates the electrical resistance is small.

From Table II it can be seen that the area under the Lorentzian and Gaussian line shapes are 32% and 68%, respectively, for the PANI-PU(50%) blend, which indicates the presence of more localized spins in the material as compared to PANI-MSA. The linewidth of the experimentally observed, Gaussian, and Lorentzian line shapes are 126G, 199G and 72.5G, respectively for PANI(MSA)-PU(50%) blend. These values are about 2 orders of magnitude higher than those for unblended PANI-MSA and other doped PANI.[3,33] This indicates that there is no significant motional narrowing and there is line broadening due to the localized spins because of blending with polyurethane. This result is qualitatively consistent with the values of the Curie constant as given in Table I for both the samples.

It has been confirmed by our measurements that the commercial blends [PANI doped with organic acid(VERSICON) and blended with insulating polymers] containing 60% by weight of copolyester of polyethylene terephthalate (PETG) exhibit conduction by the CELT mechanism.[13] This indicates that the insulating polymer used alters the morphology of the conducting regions in the material. The size of the metallic regions may be more and the barrier width may be less in the PANI-PETG blend when compared to pure PANI-MSA doped with HCl, which shows a 1D VRH behavior.[31] The use of polyurethane for blending seems to increase the disorder in PANI-MSA, which is reflected in an increased value of ESR linewidth and a greater number of Curie spins per unit volume when compared to unblended PANI-ES. The insulating polymer used and the exact method of synthesis play a vital role in determining the morphology and the conduction mechanism in conducting polymer blends.

VI. CONCLUSIONS

A 3D VRH conduction is observed in pure PANI-MSA, while in the case of PANI doped with inorganic acids, so far only a 1D VRH type of conduction has been observed.[30] This could be due to better interchain coupling in PANI-MSA. In the case of the PANI(MSA)-PU blend the conduction is by 1D VRH. In order to distinguish between 1D VRH and CELT, since in both the cases $\ln(\sigma)$ varies as $T^{-1/2}$, electric-field–dependent conductivity measurements have been carried out. From these measurements it has been confirmed that both PANI-MSA and PANI(MSA)-PU follow a VRH type of conduction and not CELT. In the blended polymer a Frenkel-Poole effect is observed where the intersite potentials, assumed to be Coulombic, are lowered by the applied electric field. The localized charges hop from one localized site to another along the chain. The effective potential barrier height is 1.56 eV. The metallic character in the polymers is seen from a linear temperature dependence of $S(T)$, the presence of Pauli spins from $\chi(T)$ measurements and the Lorentzian component of the ESR absorption. The larger ESR linewidth in the PANI(MSA)-PU blend when as compared to the unblended PANI(MSA) qualitatively indicates greater localization of charge carriers in the blended polymer.

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