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Conductivity of Poly (Vinylmercaptobenzothiazole) Iodine Complex

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ABSTRACT

A non-conjugated polymer poly (vinylmercaptobenzothiazole) (PVMBT) shows semi conducting properties in presence of electron acceptor-iodine. The enhancement of conductivity is presumably due to the formation of charge transfer (CT) complexes between iodine and the lone pair of the nitrogen atom of the polymer. This CT complex is characterized through FTIR, UV, ESR, electrical conductivity measurement and dependence of conductivity on temperature. The thermal properties of PVMBT have also been studied with the help of DSC and TGA.

Key words: UV spectrophotometer; DSC; TGA; ESR; FTIR; Doping.

INTRODUCTION

The report on the exceptional electrical properties of the doped Polyacetylene in 1977 [1] has generated a rapidly increasing interest in conducting polymers. Numerous studies have been carried out on polyconjugated systems as well as polyheterocycles such as Polypyrrole and Polythiophene [2-5]. Most of the polyconjugated conducting polymers are not environmentally stable and non-processible properties which are not conducive to their industrial utilization. Recently, however, a class of polymers with non-conjugated backbone structure have been reported which shows properties similar to conducting polymers [6-9]. Polyisoprene derivatives are prototypical of this class and when doped with I₂ or Br₂, they form conducting complexes having conductivity in the range of 10⁻² Mho/cm. In view of this background it was thought that non-conjugated polymers with heterocyclic pendant groups may lead to the development of a processible and stable conducting polymer.

The present study deals with the exploration of the conducting properties of a non-conjugated, heterocyclic polymer, polyvinylmercaptobenzothiazole (PVMBT), after doping with I_2 . The doped polymer is stable at ambient temperature and is soluble in dimethyl sulfoxide (DMSO). Charge transfer (CT) complexes of PVMBT at different dopant levels were investigated in the light of FTIR, UV-visible absorption spectroscopy, ESR, DSC, TGA and conductivity measurements.

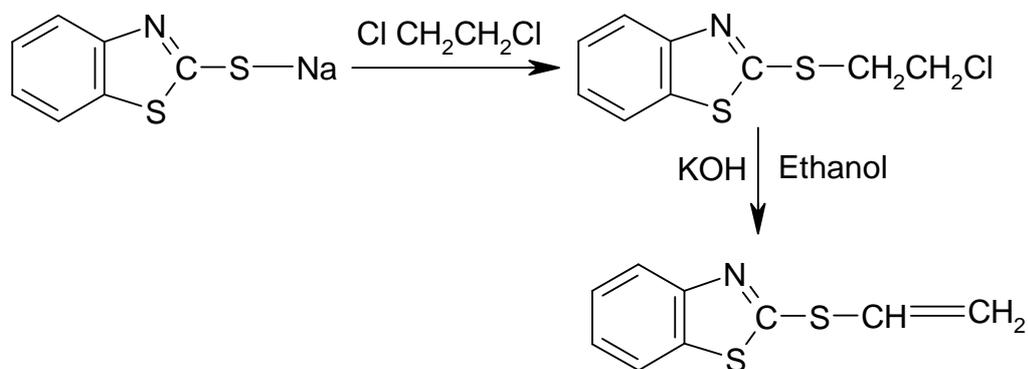
EXPERIMENTAL SECTION

Materials

Mercaptobenzothiazole (MBT) was supplied by Bayer India Ltd., Calcutta as a gift sample and was used as received. Solvents were freshly distilled by the method described elsewhere [10].

Synthesis of Polyvinyl Mercaptobenzothiazole (PVMBT)

The method of Otsu *et al.* [11] was used for the preparation of monomeric vinylmercaptobenzothiazole and its polymerization. The scheme of reaction is shown in Scheme 1. PVMBT was purified by repeated precipitation from benzene using methanol as non-solvent.



Scheme 1 Synthesis of polyvinyl Mercaptobenzothiazole (PVMBT).

Doping with Iodine

Doping was accomplished by direct exposure of the polymer to the vapor of oxidative iodine as dopant. Dry powdered samples were kept in evacuated desiccators into which iodine was introduced. Polymer samples with different dopant concentrations were prepared by allowing different times of exposure. Doping is characterized by the change of color and the polymer gradually turned black with the progression of doping. Repeated evacuation was done to remove traces of free iodine until a constant weight was attained. Dopant concentrations were determined gravimetrically.

Spectral analysis

Fourier-transform infrared (FTIR) measurements were carried out on a Perkin Elmer 1600 series FTIR instrument with the polymer dispersed in KBr. UV-visible spectra were recorded on a Hitachi U 3200 series spectrophotometer using chloroform as solvent. The spectra were scanned over the wave number range of 4000 to 500 cm^{-1} .

ESR

ESR measurements were carried out in a Varian X – band spectrometer with 100 KHz field modulation.

Thermogravimetric Analysis

TGA measurements were carried out on a Perkin Elmer Delta series TGA-7 instrument and DSC measurements were carried out in a Perkin Elmer DSC-4 instrument under nitrogen atmosphere. Indium standards were used to calibrate the differential scanning calorimetry (DSC) temperature and enthalpy scale. The samples were hermetically sealed in aluminum pans. The heating rates employed were 10 °C /min for DSC and 20 °C /min for TGA study.

Conductivity Measurements

For electrical conductivity measurements, polymer samples were pressed into thin circular pellets (0.3 – 0.5 mm thick, 1.2 cm diameter) in a hydraulic press at a pressure of 6 tons/m². Electrical conductivities were measured by the standard four probe technique.

For each sample with same thermal history, four pellets were tested and the conductivity of each pellet was measured four times at different positions of the pellet. The average of 16 measurements was taken as the conductivity of each sample. The resistivity, ρ can be calculated by Equation:

$$\rho = 2 \pi S (V/I) \quad (1)$$

where, S is the probe spacing (mm), which was kept constant, I is the supplied current in (mA), and the corresponding voltage was measured in (mV). Conductivity can be computed using the

Equation: $\sigma = 1/\rho$ (2)

where σ and ρ are conductivity ($\Omega^{-1} \text{ cm}^{-1}$) and resistivity ($\Omega \text{ cm}$), respectively. The electrical conductivity measurements were carried out at intervals of 20 min. All the measurements were repeated three times at intervals of 20 min.

RESULTS AND DISCUSSION

Elemental Analysis

Conductivity values of PVMBT samples at different dopant concentrations are shown in Table 1, while the elemental analysis of the polymer (PVMBT) and the doped polymer (S6) are shown in Table 2. The electric conductivity is influenced by the dopant level. It has been clearly observed that by increasing the level of dopant, electric conductivity increased, simultaneously. The chemical analytical data confirm that the charge transfer (CT) complexes are composed of polymer units and the iodine dopant. The chemical analytical data of the polymer at other dopant levels are not shown as these follow the same trend.

Table 1 Effect of dopant level on electric conductivity of PVMBT.

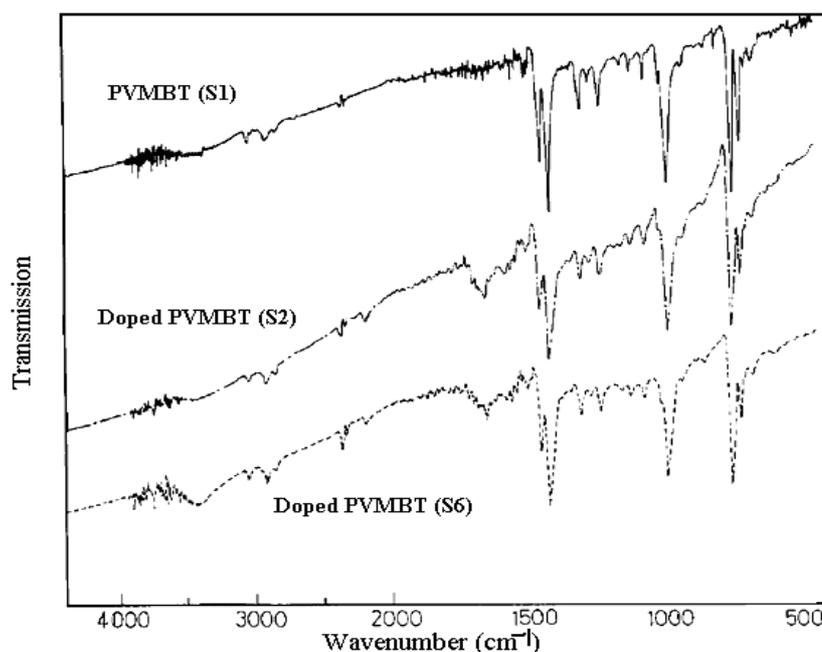
Sample No.	Iodine/Polymer	Conductivity ($\Omega^{-1} \text{ cm}^{-1}$)
S1	0.0	1.53×10^{-15}
S2	0.0579	3.22×10^{-11}
S3	0.1740	3.14×10^{-9}
S4	0.2826	1.36×10^{-8}
S5	0.4034	2.75×10^{-6}
S6	0.5073	2.32×10^{-5}
S7	0.6053	4.03×10^{-5}

Table 2 Elemental analysis of sample nos. 1 and 6.

Sample No.	Chemical composition	
	Found %	Calculated %
S1	C – 56.28, H- 3.70 N- 7.20, S-32.85	C – 55.92, H – 3.65 N – 7.25, S – 33.17
S6	C – 37.09, H – 2.39 N – 4.80, S – 21.98 I – 33.06	C – 37.12, H – 2.41 N – 4.81, S – 22.00 I – 33.66

FTIR Spectra

FTIR Spectra of PVMBT and the doped PVMBT samples are presented in Figure 1. It is observed that on doping an additional band is generated at around 1654 cm^{-1} . No doping action of iodine on polystyrene is observed which indicates that the benzene ring is not involved in the formation of charge transfer complexes with iodine. Thus, doping with iodine may be presumed to take place at the heterocyclic ring. The C=N stretching usually appears between $1550 - 1505\text{ cm}^{-1}$ but moves to a lower wave number when influenced by conjugation. The C=N stretching in the original polymer appears at 1458 cm^{-1} [12] indicating extensive delocalization of C=N bond with benzene ring. On doping, the intensity of C=N stretching decreases and a new peak appears at around 1654 cm^{-1} . A strong absorption at 1630 cm^{-1} is attributed to C=N^+ stretching is reported [13]. Consequently, the new peak at 1654 cm^{-1} is related to C=N^+ stretching in the iodine complex of the polymer. It was also observed that with increasing dopant concentration, the peak at 1654 cm^{-1} is split into two with an additional peak appearing at around 1590 cm^{-1} . This peak is also presumably related to C=N stretching with the influence of different anions representing CT complex formation between the polymer and iodine [14].

**Figure 1** FTIR spectra of PVMBT and doped PVMBT

UV- visible Spectroscopy

Evidence of CT interaction is provided by UV visible spectroscopy which indicates the generation of new CT band [15-16]. The spectra of the polymer and its doped state are shown in Figure 2. Iodine in chloroform shows an absorption at 499 nm which shifts to 511 nm on addition of PVMBT and the color of the solution changes from violet to orange. In the UV region, the polymer exhibits some characteristic adsorption with higher extinction coefficient but, on addition of iodine, the absorption value increases. In other words, the molar extinction coefficient increases, though the relative position of the peaks remains unchanged. But, at the same time a new peak at around 364 nm is observed which indicates the generation of I_3^- species in the system [17-18]. It provides the evidence for the oxidation-reduction doping process of PVMBT with iodine.

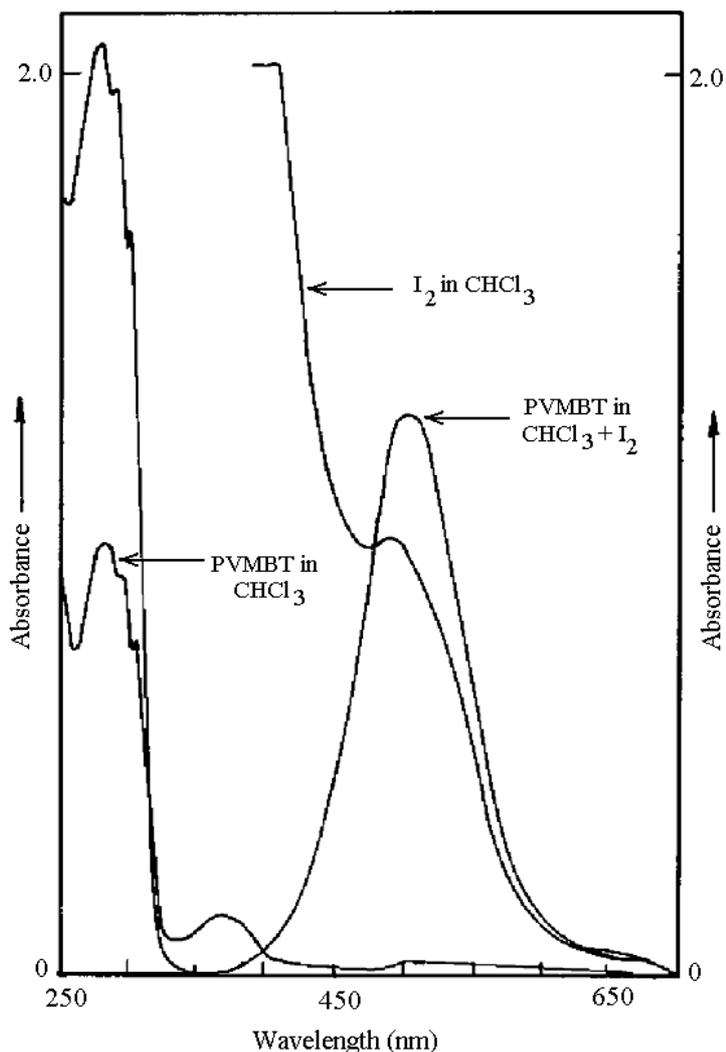


Figure 2 UV- vis spectra of Iodine, PVMBT and doped PVMBT.

ESR Spectra

The ESR spectra of doped PVMBT are shown in Figure 3. The appearance of a signal in electron spin resonance spectra after exposure to iodine also proves the redox reaction of doping [19-20]. As expected, the undoped polymer is diamagnetic. Free iodine and the polymer themselves don't show any ESR signal. Hence, its appearance in the doped state is an indication of the generation of radical cation within the polymer during doping due to electron transfer to iodine. The observed g value of PVMBT – I_2 complex is 2.0055 in comparison to diphenyl picrylhydrazyl which is significantly higher than that of 2.0026 observed for the radicals located

on the carbon atom in polyphenylene [21]. Further, it is much less than that of 2.0070 – 2.0075 for the radical cation located on the sulphur atom in Poly (p-phenylene sulphide) [22]. Thus, it may be deduced that the unpaired electron in PVMBT $-I_2$ is probably not located on carbon or sulphur atom, the other obvious site is the nitrogen atom.

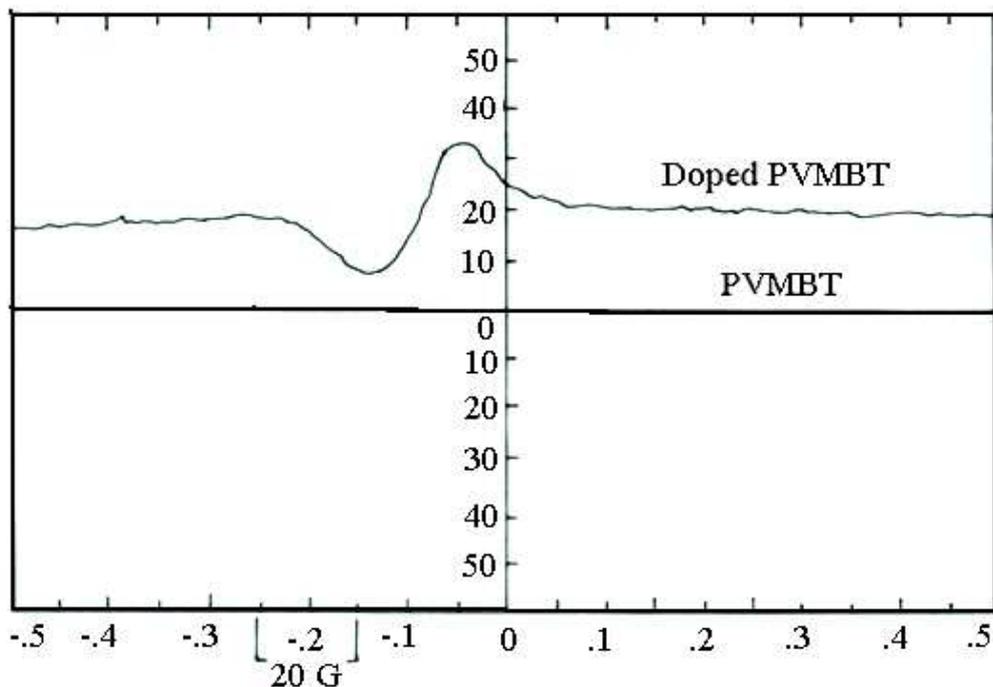


Figure 3 ESR spectra of PVMBT and doped PVMBT.

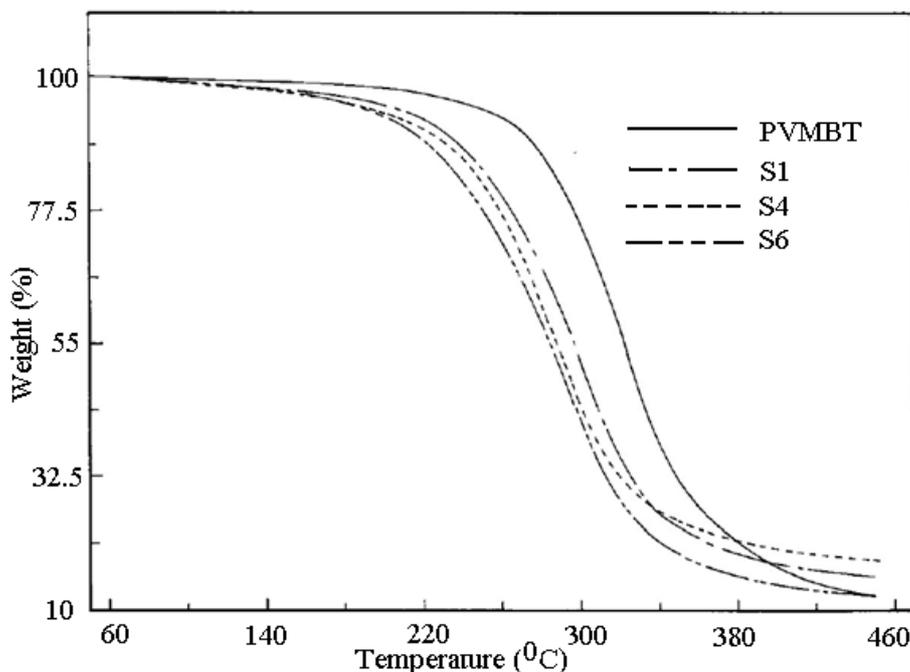


Figure 4 TGA analysis of PVMBT and doped PVMBT.

Thermal Properties

Thermal properties of PVMBT and its doped state are examined in the light of TGA and DSC studies. Figure 4 illustrates the weight (%) as a function of temperature. From TGA curves, we

can see that the weight loss of PVMBT and doped PVMBT (sample S6) are about 22.5 % and 57 %, respectively. This heavy weight is associated with the degradation and evaporation of dopant. In other words, the thermal stability of the polymer gradually decreases with an increase in the dopant concentration which is a general observation in the case of most halogen-doped polymers. From the temperature scan data, it is apparent that the doped samples (S1, S4 and S6) are relatively stable at temperatures below 100 °C.

To further investigate the thermal stability of doped polymer, DSC scans were performed and the results are shown in Figure 5. A thermal transition of the polymer is observed at 55 °C which is increased on doping (S6) to around 70 °C. This anti-plasticization effect may also be attributed to the CT-complex formation on doping [23]. The anti-plasticization process may be related to the bonding of chain segments by the dopant. The CT interaction in which the dopant acts as the acceptor, in the system D-A-D (D stands for donor or polymer chain segments and A for the dopant-acceptor) causes virtual crosslinking of the polymer thus decreasing chain mobility.

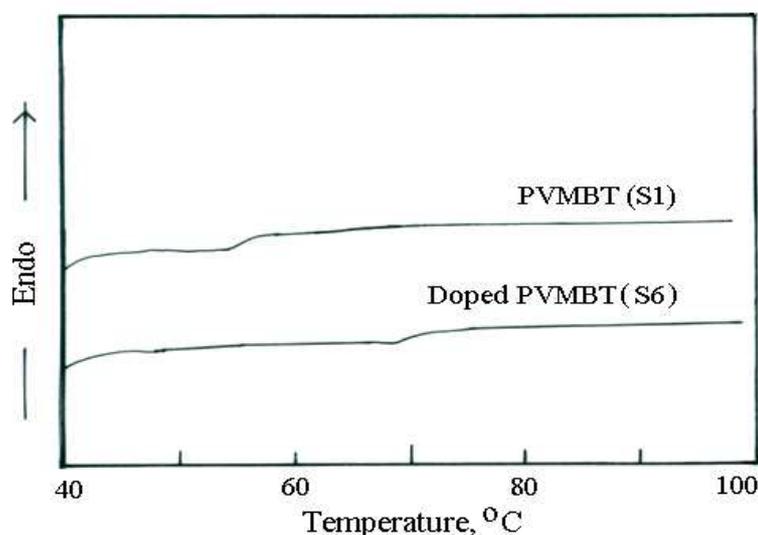


Figure 5 DSC scans showing thermal transition of PVMBT and doped PVMBT (S6) at 55 °C and 70 °C, respectively.

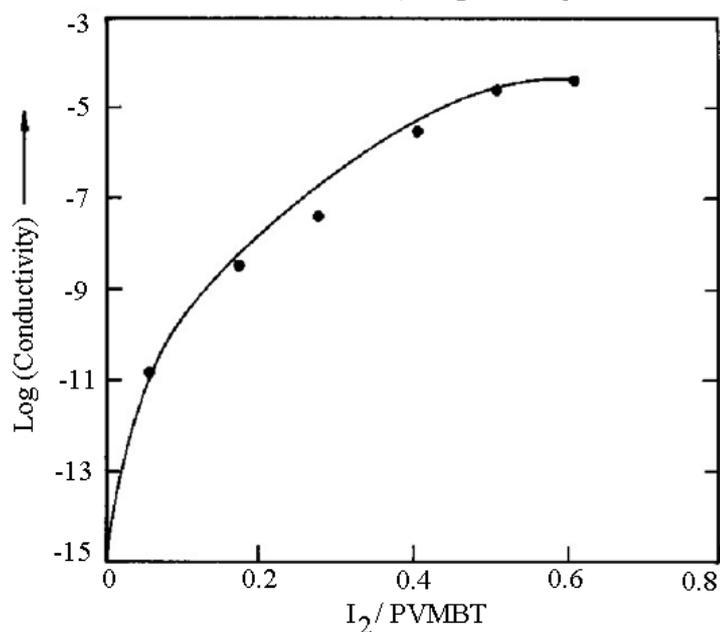


Figure 6 Effect of concentration of dopant on conductivity of PVMBT.

Electrical Properties and Conduction Mechanism

The electrical properties of PVMBT-dopant system are explained on the basis of current-voltage characteristics curve, temperature dependence of current voltage characteristics, conductivity measurements and activation energy calculations. The undoped polymer (PVMBT) is an insulator having conductivity of $1.53 \times 10^{-15} \Omega^{-1} \text{cm}^{-1}$ which increases to $2.322 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ on

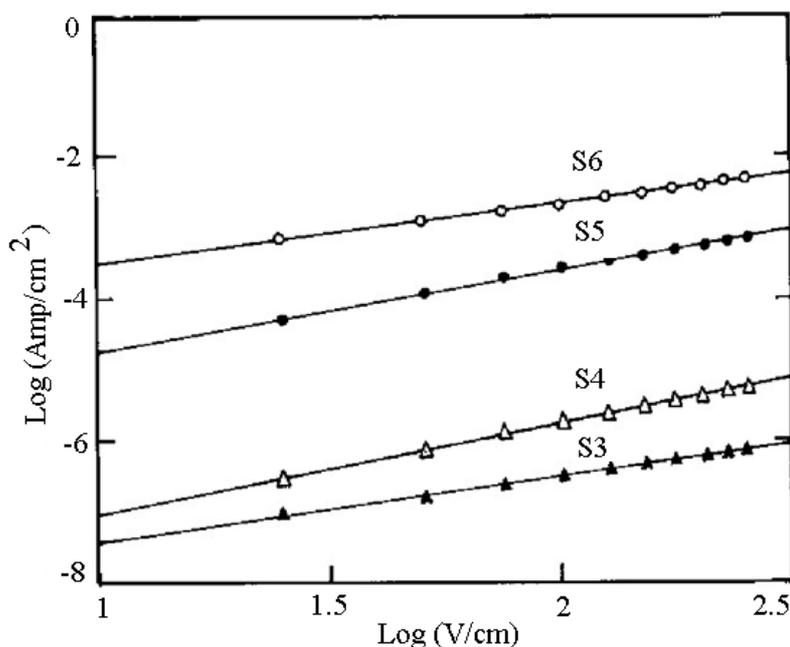


Figure 7 Current density of doped polymers (S3, S4, S5 and S6) as a function of electric field strength.

doping to a dopant level of about 50 % (iodine/polymer). The plots of $\log \sigma$ versus iodine/polymer ratio are shown in Figure 6. It has been observed that conductivity changes from $2.322 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ to $4.025 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ on changing the dopant concentration from 50 to 60 %. The plots of current density versus field strength of the samples (S3, S4, S5 and S6) are shown in Figure 7. Linear plots indicate the pure ohmic characteristics at room temperature (27 °C).

Study of the current-voltage characteristics of all the samples at different temperatures is also carried out revealing their ohmic characteristics. Such a plot of current density versus field strength at different temperatures (S6) is shown in Figure 8. It is well known that the conductivity, σ of the polymer varies with the absolute temperature, T according to the relation,

$$\sigma = \sigma_0 e^{-\frac{E_a}{kT}} \quad (3)$$

where, E_a is the activation energy, σ_0 the conductivity at infinite temperature and k is Boltzmann constant. In Figure 9, the results of measured conductivity values of sample S6 are plotted semilogarithmically as a function of the reciprocal of temperature, $1/T$ (K^{-1}). It is observed from the results that the plot deviates from linearity at lower values of temperature.

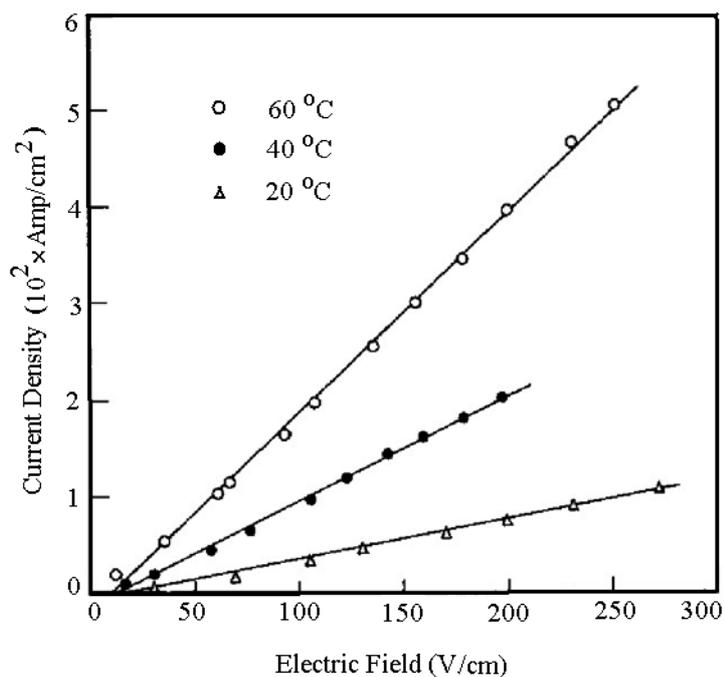


Figure 8 Current density versus field strength plots of doped PVMBT (S6) at different temperatures.

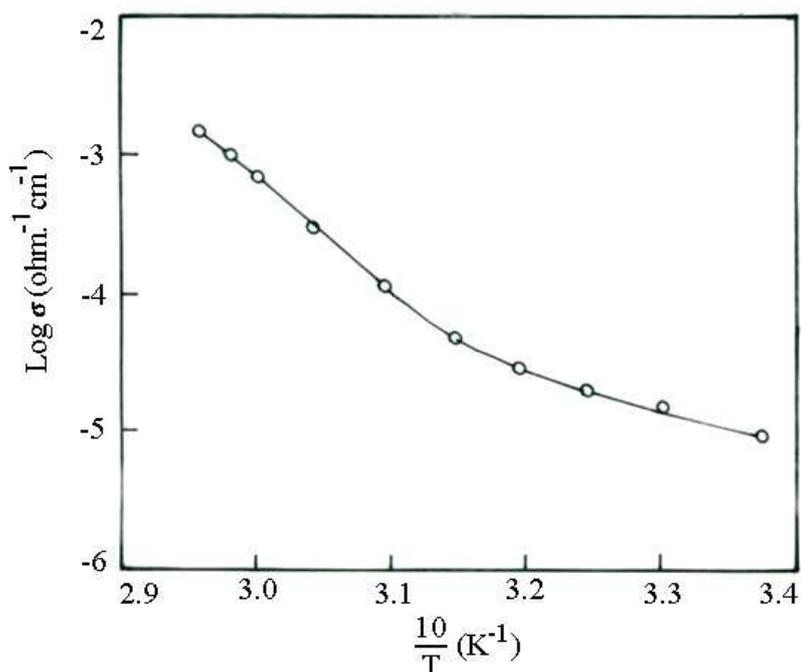


Figure 9 Conductivity of doped PVMBT (S6) as a function of reciprocal of temperature (1/T)

Many equations are suggested to explain the mechanism of conduction and the cause of jump of conductivity which are relevant to various modes of conduction [24-26]. The Greaves Equation is valid for variable range hopping mode of conduction and can be written as

$$\sigma T^{1/2} = e^{-\frac{B}{T^{3/4}}} \quad (4)$$

where, B is a constant. The plot of $\log(\sigma T^{1/2})$ versus $1/T^{3/4}$ is shown in Figure 10 for sample S6. It is observed that the results follow the Greaves Equation, above and below the temperature at which the sudden jump of conductivity occurs. It indicates that the variable range hopping mode

of conduction is operative. Since the polymer is non-conjugated, it is expected that in the CT complexes the conduction process may follow the interchain hopping mechanism. The first derivative of $\log \sigma$ versus $1/T$ in Figure 11 shows that the temperature at which the jump occurs is 53 °C. From the DSC study, it is observed that the doped polymer shows a thermal transition at around 70 °C. UV and FTIR studies conducted earlier confirmed that some ionic impurities (I_1 , I_3) are formed in the doped system. It is reported that the ionic conductivity generally increases after the start of the segmental motion of the polymer chains. It is therefore, reasonable to assume that the enhancement of electrical conductivity is due to the increase of ionic mobility above the T_g [27-29] of the polymer. Thus, ionic contribution is thought to be the main cause of this deviation. There is a difference of about 15 °C between the T_g 's indicated by the DSC study and the thermal

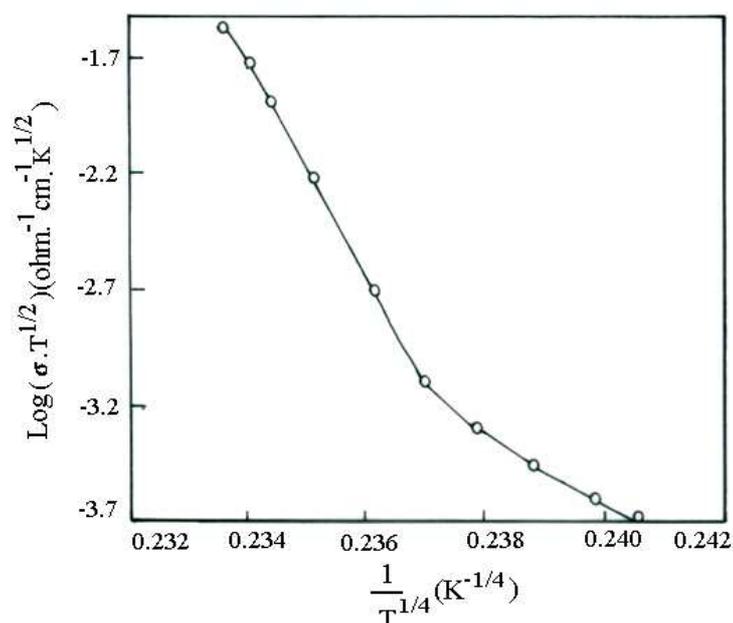


Figure 10 The plot of $\log(\sigma T^{1/2})$ versus $1/T^{1/4}$ for doped PVMBT (S6), calculated from Greaves Equation.

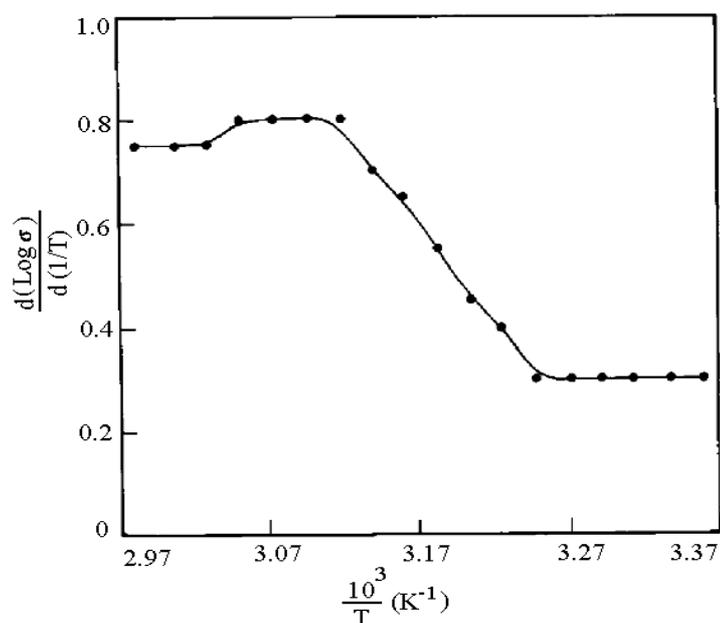


Figure 11 The first derivative of $\log \sigma$ versus $1/T$ curve for doped PVMBT (S6).

transition temperature values from conductivity measurements. This is reasonable because the thermal transition (T_g) is a kinetically controlled process and its value depends on the frequency of the measurement. The frequencies of DSC and conductivity measurements are very different

CONCLUSIONS

In the present study, a non-conjugated polymer PVMBT is successfully doped with I_2 . It is evident that the dopant iodine forms CT complexes with the polymer PVMBT and during the formation of CT complex; it generates some defects in the system which are responsible for the electrical conductivity of the doped polymer. In the CT complex, iodine reacts with the nitrogen atom of the mercapto group of the polymer. The conduction mechanism in the present system is of the variable range hopping mode. But, increased ionic mobility after thermal transition is the main cause for the deviation from variable range hopping mechanism as denoted by the Greaves Equation. The ionic contribution, before and after the thermal transition of the doped polymer remains the same. It only affects the thermal transition zone.

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