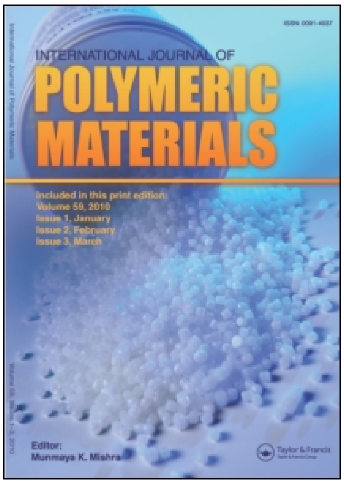

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Alternating current conductivity and dielectric properties of newly prepared poly(bis thiourea sulphoxide)

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To cite this Article Atta, A.(2003) 'Alternating current conductivity and dielectric properties of newly prepared poly(bis thiourea sulphoxide)', International Journal of Polymeric Materials, 52: 5, 361 — 372

To link to this Article: DOI: 10.1080/00914030304922

URL: http://dx.doi.org/10.1080/00914030304922

International Journal of Polymeric Materials, 52: 361–372, 2003
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0091-4037/03 $12.00 +.00
DOI: 10.1080/00914030390119578

ALTERNATING CURRENT CONDUCTIVITY AND DIELECTRIC PROPERTIES OF NEWLY PREPARED POLY(BIS THIOUREA SULPHOXIDE)

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Poly(bis-thiourea sulphoxide) was prepared by Michael addition mechanism of thiourea with bis-sulphinyl thiourea, which in turn, was prepared by the reaction of thiourea with thionyl chloride. The formed polymer was identified by microchemical analysis and IR spectrum. Thermogravimetric analysis shows that it is stable up to 490°K, and having thermal activation energy 11.2 K cal·mol^{-1}. It is of relatively low molecular weight as found from the inherent viscosity value (0.242 dLg^{-1}).Alternating conductivity measurements at different temperatures and frequencies exhibited that the prepared polymer is a highly polarized material. The relaxation time of the orientational process is about 9×10^{-11} second and the activation energy of this process is 0.387 eV. The conduction mechanism could be attributed to the correlated barrier hopping (CBH) model.

Keywords: poly(bis thiourea sulphoxide), synthesis, conductivity

1. INTRODUCTION

It is well established that the electrical properties of polymers depend on the presence of delocalized π-electron system resulting from SP^2 hybridization of the carbon atoms along the polymer chain [1, 2]. On the other hand, some polar polymers manifest dielectric absorption caused by internal rotation of a substituent around bond joining it to the main chain by internal rotation of groups within the side chain [3, 4]. Such polymers have attracted great interest both fundamentally and for practical application to batteries [5], optical switching elements [6], sensors [7] and electrets [8].

Received 20 January 2001; in final form 29 January 2001.

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Polymers containing the N-S linkage are of interest because of superior electrical conduction [9, 10]. Kresze *et al.* [11, 12] reported that the amino compounds, both aliphatic and aromatic, when treated with thionyl chloride give N-sulphinyl compounds containing $-N{=}S{=}O$ group.

Substantial work have been done by Reicha and his group [13−16] on structure and electrical properties of conducting polymers derived from various aromatic amines.

Radiation-induced and electroinitiated polymerization of allylurea [17] and allylthiourea [18, 19] have been reported. However, no attempts seems to have been made to study the synthesis, characterization and thermal stability of aliphatic polymers containing $-N{=}S{=}O$ group. In the present investigation, the electrical conductivity of novel prepared poly(bis-thiourea sulphoxide) was measured at different frequencies and temperatures. The dielectric constant, dielectric loss, relaxation time, and thermal stability of the polymer were determined.

2. EXPERIMENTAL DETAILS

2.1. Materials

Thiourea (Aldrich Chemical Co., Inc.) was purified by recrystallization from hot ethanol and filtering, light brown crystals, m.p. 176°C. Thionyl chloride was freshly distilled all other chemicals and solvents were purified by standard procedures.

2.2. Preparation of the Monomer and Polymer

Bis(-N-sulphinyl thiourea) and poly (bis thiourea sulphoxide) were prepared by the method described in a previous paper [13].

2.3. Characterization of the Monomer and Polymer

Sulphur contents were estimated using the Schoniger combustion method [20]. Three values of sulphur content for the monomer and polymer were obtained from the analytical unit at Cairo University.

IR spectra were recorded on Mattson 5000 FTIR spectrometer with the sample in the form of KBr disc.

Visible and UV optical measurements were carried out using very thin films of polymer sample on planar quartz plates. Optical transmission measurements of these films as function of wave length were performed in the range 200−900 nm using a dual beam

Unicom-UV2-100 UV/visible spectrometer V3-32 at normal incidence. Direct determination of optical band gap is possible by technique described elsewhere [21], without need for thickness determination.

2.4. Thermogravimetry (T_D)

Thermogravimetry measurements were made with a DU Pont 950 thermobalance. 10 mg of sample was heated at 10° min^{-1} in a dynamic nitrogen atmosphere (70 ml min^{-1}). T_D curve of polymer sample is shown in Figure 1a. Degradation starts at 490°K and shows one stage. It is evident from the T_D curve that the polymer is somewhat more stable than other aromatic polymers [19].

The effective activation energy for thermal degradation of the polymer was determined from the temperature dependence of the initial rate, dn/dt, using T_D thermograms. Figure 1b gives a plot of ln(dn/dt) against 1/T, from which the activation energy is 11.2 Kcal·mol^{-1}.

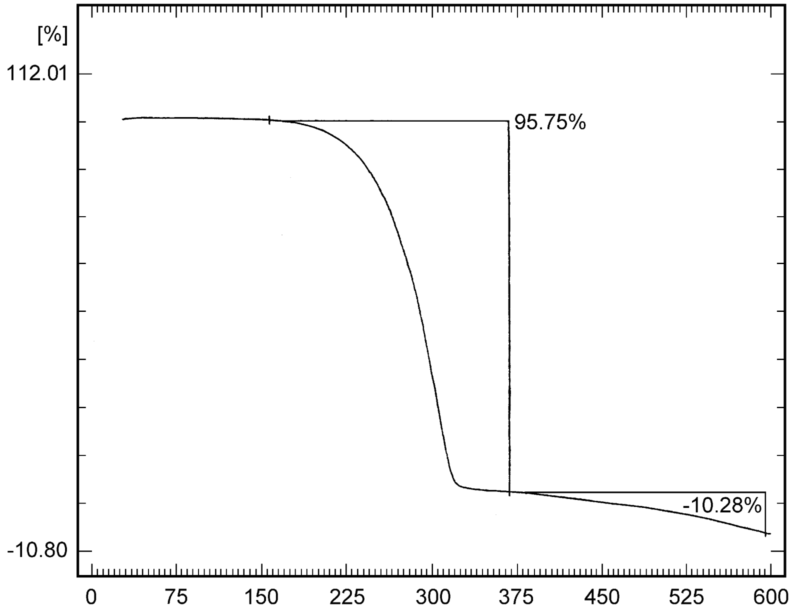


FIGURE 1a TGA curves of poly(bis-sulphoxide thiourea).

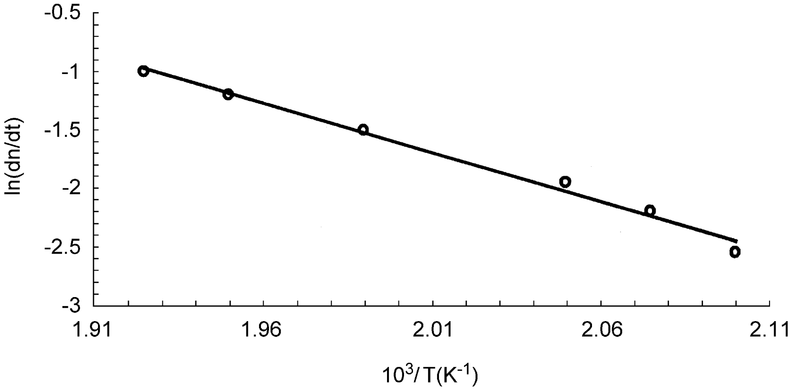


FIGURE 1b Plot of ln (initial rate of degradation) against 1/T of poly(bis-thiourea sulphoxide).

2.5. The Electrical Conductivity $\sigma_{a.c.}$, Dielectric Permittivity ε' and Dielectric Loss ($\tan\delta$) Measurements

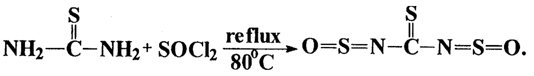
The polymer was pressed at 10 ton cm^{-2} to form circular disc of 12 mm diameter and 1.25 mm thickness. The sample was rubbed with silver paste on both surfaces of the pellet to ensure good electrical contact with silver electrodes. The sample was inserted between the electrodes in a temperature test chamber. This chamber was evacuated to a pressure lower than 10^{-3} Torr using rotary pump to avoid the large conductivity enhancement of the polymer due to absorbed water [22]. The temperature was controlled and measured to better than ±1°C by using a computerized heating system (Cole-Parmer Instrument Co. Model 89000-15).

AC electrical measurements of the polymer were made with a computer controlled lock-in technique (STANFORD RESEARCH SYSTEM MODEL SR830) in order to avoid thermoelectric voltage and polarization effect. Appropriate correction was made for stray capacitance. The measurements were carried out as a function of frequency (20 Hz to 100 KHz) and temperature ranged from 300 K to 510°K.

3. RESULTS AND DISCUSSION

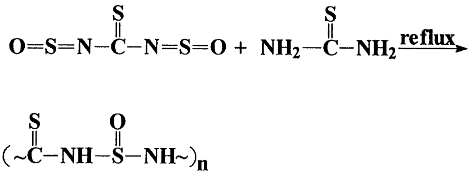
3.1. Identification of the Monomer and the Polymer

Bis-sulphinyl thiourea was prepared by refluxing thiourea with excess thionyl chloride at 80°C.



$$\mathrm{NH_2-\overset{\overset{S}{\|}}{C}-NH_2 + SOCl_2 \xrightarrow[80^{\circ}C]{reflux} O=S=N-\overset{\overset{S}{\|}}{C}-N=S=O.}$$

The product formed yellowish crystals, m.p. 162°C. The I.R. spectrum of the monomer indicates the characteristic peaks at 1468 and 1380 cm^{-1} due to $-N=S=O$ as reported by Parshall *et al.* [23]. The calculated analysis for $CN_2S_3O_2$ (M.W., 168.24); C: 7.14; N: 16.65; S: 57.19; O_2: 19.02 and that found C: 7.19; N: 16.62; S: 57.16 and the remaining is oxygen 19.03%. Poly(bis thiourea sulphoxide) was prepared by Michael addition mechanism of bis-sulphinyl thiourea with thiourea.



$$\mathrm{O=S=N-\overset{\overset{S}{\|}}{C}-N=S=O + NH_2-\overset{\overset{S}{\|}}{C}-NH_2 \xrightarrow{reflux}}$$

$$\mathrm{(\sim\overset{\overset{S}{\|}}{C}-NH-\overset{\overset{O}{\|}}{S}-NH\sim)_n}$$

Inherent viscosity of the polymer was measured and found to be 0.242 dLg^{-1}, indicating that the polymer is relatively low molecular weight. The I.R. spectrum of the polymer shows an absorption band at 3202 and 3355 cm^{-1} due to imino groups. A strong band at 1605 cm^{-1} in the polymer spectrum assignable to δ(NH).

The free ligand band at 1506 cm^{-1} is attributed to ν(CN) mode of the thioamidic part of the polymer with some contribution from ν(SCN) mode. The ligand band occurring at 800 cm^{-1} is due to ν(CS) frequency [24]. The I.R. spectrum of the polymer shows no characteristic absorption assignable to NH_2 function. This confirms the formation of the poly(bis-thiourea sulphoxide). Microanalytical data calculated for the polymer $(CH_2N_2S_2O)_n$(M.W., 122.19); C: 9.83; N_2: 22.93; H_2: 1.65; S: 52.49; O_2: 13.09 and that found C: 9.81; N_2: 22.96; H_2: 1.68; S: 52.50 and the remaining oxygen 13.05%.

3.2. The Optical Absorption

Figure (2a) shows that the total absorption could be due to one optical transition which fitted to relation [25]

$$\alpha h\nu = C_o(h\nu - E_g^{opt.})^n$$

with $n = 3/2$. Generally the exponent value $n = 3/2$ is a characteristic of the forbidden direct transition between parabolic bands, $E_g^{opt.}$ being the optical energy gap [26, 27].

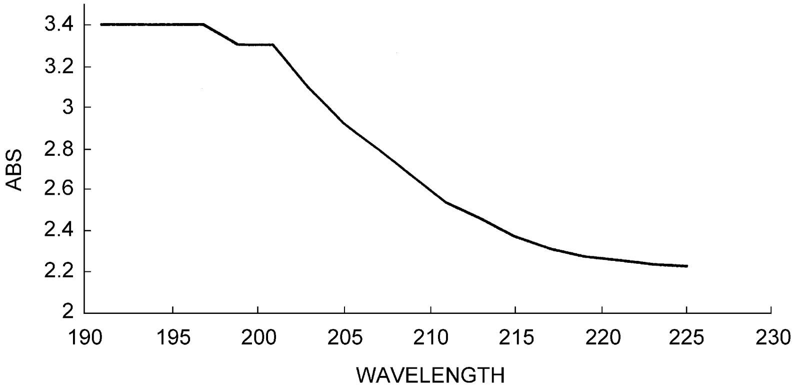


FIGURE 2a UV spectrum of poly(bis-thiourea sulphoxide).

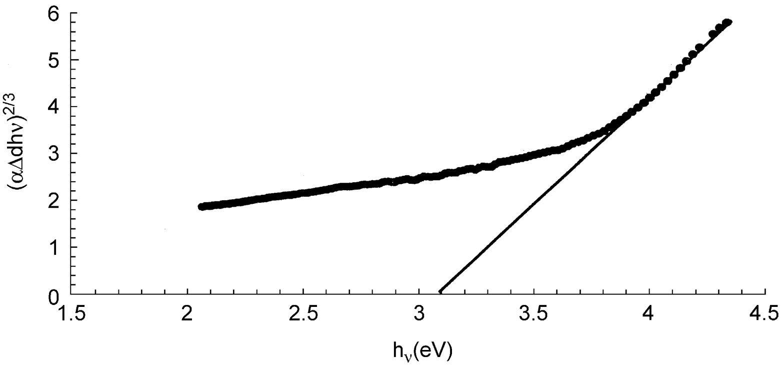


FIGURE 2b Variation of $(\alpha\Delta dh\nu)^{2/3}$ *vs.* hν.

Figure (2b) shows the absorption coefficient variation with the photon energy plotted as $(\alpha\Delta dh\nu)^{2/3}$ *vs.* hν. The least square fit yielded straight line given by

$$(\alpha\Delta dh\nu)^{2/3} = 4.7847\,h\nu - 15.027$$

The mean value of the calculated E_g^{opt} is found to be 3.1 ev. It is to be noted that the curve is characterized by the presence of an potentially decaying tail at the low photon energy which is usually found in amorphous materials [27].

3.3. Electrical Behavior

Figure (3a) shows plots (on logarithmic scale) of the real part of the a.c. conductivity plotted *versus* frequency.

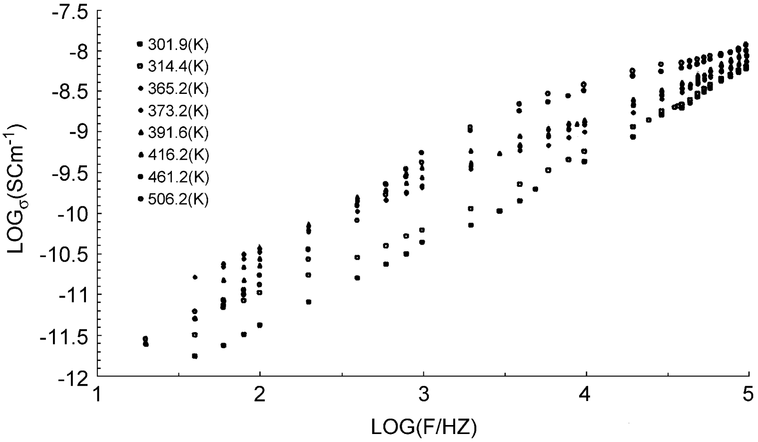


FIGURE 3a Relationship between real part of A.C conductivity of the polymer sample as a function of frequency at different temperatures (logarithmic scale).

The conductivity was measured at various frequencies (20-10^5 HZ) with temperature varying from ~ 302 to 506 K. The obtained results do not follow exactly the universal power low relation [28]

$$\sigma = \sigma_o + A(T)\omega^{S(T)}$$

It can be seen that the d.c. part in the universal power low can be neglected in the temperature range (302–375 K) and slightly depends on the temperature increase above this range.

This means that the temperature dependence of conductivity is negligible and the most probable dependence is the frequency dependence, reflecting that the polymer under investigation is of the highly polarized type.

It is generally assumed that measurement at sufficiently high frequency gives rise to polarization conductivity. We think that in the present case it is a good approximation for quantitative approach, considering the frequency range selected (10^3–10^5 HZ). The real part of the polarization conductivity $\sigma'(\omega)$ behaves as ω^s (Figure 3b), s being a parameter $0<s<1$. In this case s is temperature dependent.

The value of $s \approx 1$ at 300°K decreases gradually with increasing temperature down to a value of ≈ 0.4 in a well fitted linear form as in Figure (3c).

Variation of s with temperature was noticed for other materials and explained as $s = 1-4 \ln (1/\omega\tau_o)$ for electron tunnelling model [29] and $s = 1 - 6\, K_BT/W_M$ for the model of two electron hopping

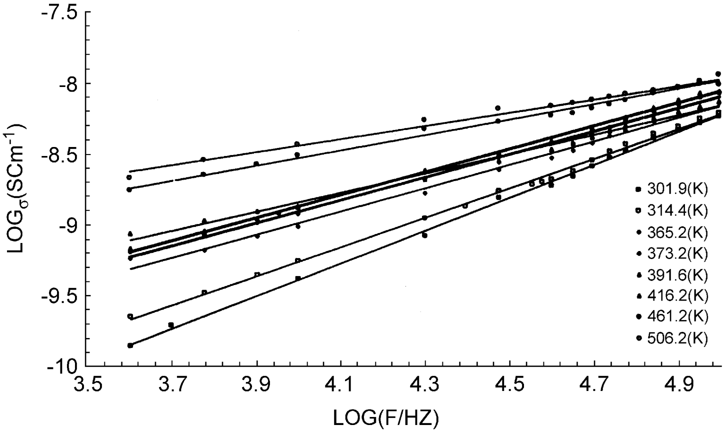


FIGURE 3b Real part of polarization conductivity, $\sigma'(\omega)$, as a function of frequency at different temperatures (logarithmic scale).

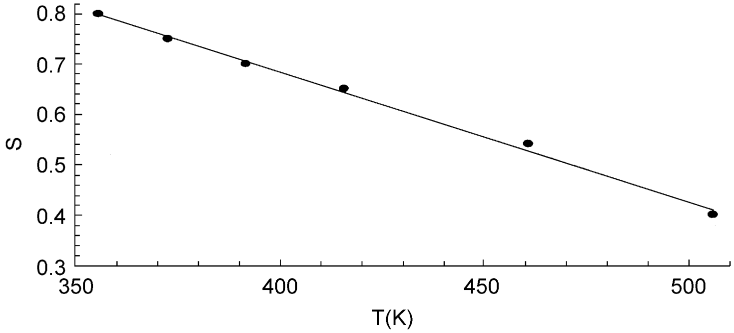


FIGURE 3c Temperature dependence of the exponent S calculated from the straight line portion of the log(conductivity) and (frequency).

simultaneously [30]; the large-polaron tunnelling mode [31] predicts that s decreases initially with increasing temperature. However, it is clear from Figure 3c that for the present investigated material there is a conflict with the prediction of the above models. The use of the correlated barrier hopping (CBH) model can be applied in this case if we take boundary condition $W_M \gg 6$ KT at temperatures ranged from 0°K up to room temperature, and $W_M \leqslant 6$ KT for very high temperatures. For the first boundary condition it depends upon the presence of polar groups presented in the main chain. Therefore, the value of W_M, the energy required to remove two electrons from a localized site to the conduction band often equated to the energy band gap, could be calculated and found to be 0.318 ev, comparable with that determined from optical band gap, and indicating that the prepared polymer is of a highly polarized type.

3.4. Dielectric Constant Results

Figure 4 represents the relation of the real part of the dielectric constant ε' with frequency at specific temperatures. As can be seen ε' varies very slightly in the temperature range from (300–506) with varying frequency.

The typical dependence of the dielectric loss (tanδ) on a simultaneous change of both temperature and frequency is illustrated in Figure 5. As the temperature rises, the maximum value of tan δ shifts toward higher frequencies. The relaxation time of the orientational process τ could be estimated using the relation

$$\omega_0 \tau = 1$$

where ω_o is the frequency value corresponding to maximum of tan δ. Figure 6 represents the correlation between τ and temperature, which exhibits the exponential temperature dependence

$$\tau = \tau_0 \varepsilon^{\mathrm{Ea/RT}}$$

with $E_a = 0.3867$ ev, is the activation energy for the relaxation process and R the universal gas constant.

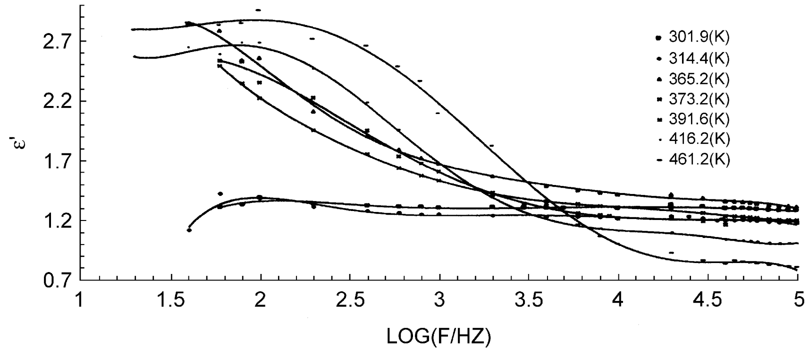


FIGURE 4 Variation of the dielectric constant ε' with log(frequency) at different temperatures.

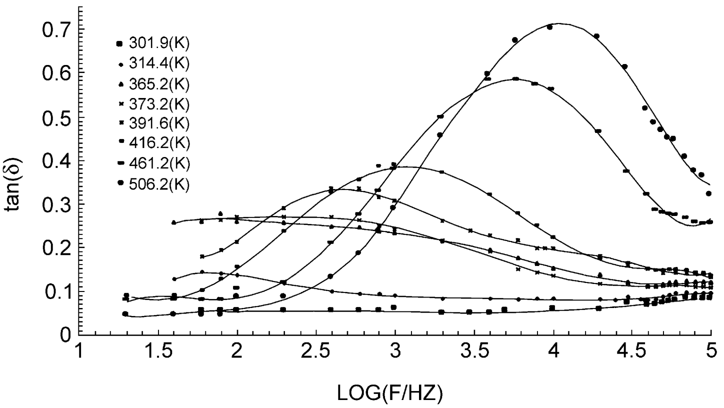


FIGURE 5 Variation of the dissipation factor tan(δ) with log(frequency) at different temperatures.

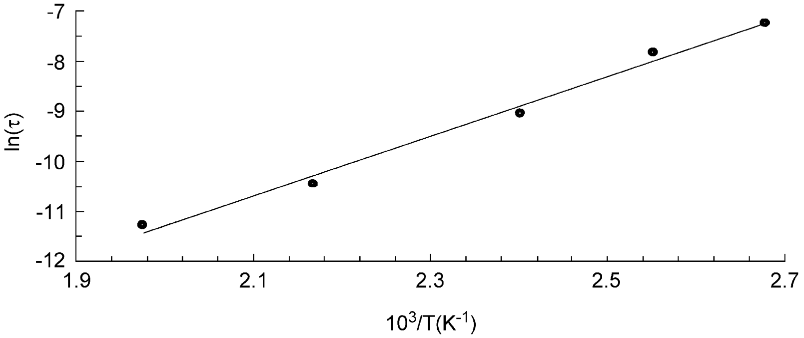


FIGURE 6 Arrhenius-type representation of the relaxation time (τ) with (1/T) for poly(bis-thiourea sulphoxide).

4. CONCLUSION

In summary, we have shown that thiourea reacts with thionylchloride yielding Bis(-N-sulphinyl thiorea) which in turn reacts with thiourea to give poly(bis thiourea sulphoxide), having the following interesting physical properties:

(1) It has low molecular weight as indicated from the viscosity measurements (0.242 dLg^{-1}).
(2) It is thermally stable as indicated from T_D curve and the value of thermal activation energy $E = 11.2$ Kcal mol^{-1}, and has an amorphous structure.

(3) It is a highly polarized material as indicated from the lack contribution of dc part of an a.c. conductivity and the prodominance of the dielectric part $A\omega^S$.
(4) The correlated barrier hopping (CBH) model is capable of explaining the conduction.

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