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Conducting polymers

Part IV *Electrical conductivity of poly(4,4′-N,N-diiminosulphoxide diaminophenol ether)*

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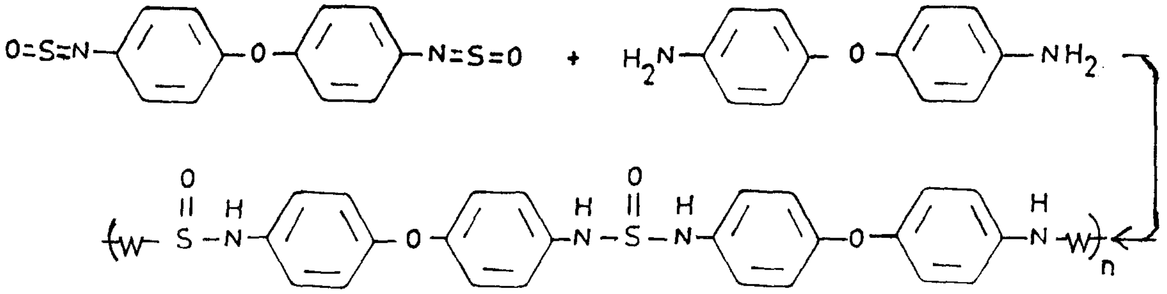
Poly(4,4′-N,N-diiminosulphoxide diaminophenyl ether) was prepared by Michael addition of 4,4′-disulphinyl diphenyl ether with 4,4′-diaminodiphenyl ether at 150 °C. The thermal and electrical behaviours of the polymer have been studied. The polymer is found to have increased conductivity possibly due to the participation of lone pair of electrons on nitrogen and sulphur atoms with σ bond of the macrochain.

1. Introduction

During recent years, several conducting polymers have been synthesized and their electrical conductivities measured. It is well established that the electrical properties depend on the presence of delocalized π-electron system resulting from SP^2 hybridization of the carbon atoms along the polymer chain [1–3]. Such polymers have attracted great interest both fundamentally and for practical application to batteries [4], optical switching elements [5] and sensors [6]. Polymers containing the N–S linkage are of interest because of superior electrical conduction [7, 8]. Kresze *et al.* [9, 10] reported that amino compounds, both aliphatic and aromatic, when treated with thionyl chloride give N-sulphinyl compounds containing –N=S=O group. In our previous papers [3, 11, 12], we reported the electrical conductivities of poly-(bis-p-phenylenediaminosulphoxide) and poly(bis-2,6-diaminopyridinesulphoxide). The present paper deals with the synthesis of poly(4,4′-diiminosulphoxide diaminosulphenyl ether) on reacting 4,4′-disulphinyl diphenyl ether by Michael addition with 4,4′-diaminodiphenyl ether:



Thermal stability and a.c. electrical conductivity at different frequencies and temperatures of the polymer were studied.

2. Experimental details

2.1. Materials

4,4′-diaminodiphenyl ether (Aldrich Chemical Co., Inc.), was purified by recrystallization from ethanol to give brown crystals. Thionyl chloride was freshly distilled. All other chemicals and solvents were purified by standard procedures.

2.2. Preparation of 4,4′-disulphinyl diphenyl ether

Recrystallized 4,4′-diaminophenyl ether (0.1 mol) was placed in a flask fitted with a dropping funnel containing thionyl chloride (0.3 mol) and a thermometer. The flask was kept in an ice bath and thionyl chloride was added dropwise so that the temperature was kept below 0 °C. The flask was then allowed to attain room temperature and then the reaction mixture was refluxed for 5 to 6 h. Unreacted thionyl chloride was removed by distillation under reduced pressure; the last traces were removed by addition of dry benzene and distillation when a dark brown solid was formed. The crude product was purified by dissolving in chloro-

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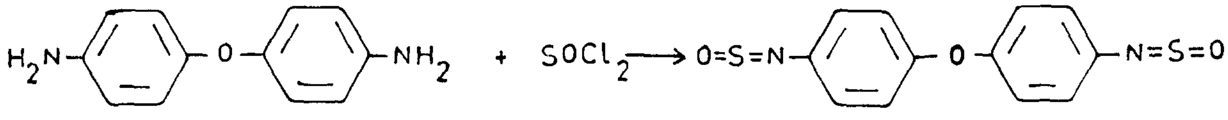
form and precipitating pure crystals by addition of petroleum ether.

2.3. Preparation of poly(4,4′-N,N-diiminosulphoxide diphenyl ether)

4,4′-disulphinyl diphenyl ether was dissolved in DMF in a flask and warmed with stirring in nitrogen atmosphere to give a dark red solution. Equimolecular amounts of 4,4′-diaminodiphenyl ether solution in DMF and 4,4′-disulphinyl diphenyl ether solution were mixed with stirring. The reaction mass was allowed to reflux for 10 h at 180 to 200 °C in a slow stream of nitrogen. A viscous deep red material was obtained. It was cooled to room temperature and poured in ice-water to obtain a black precipitate. It was filtered, washed thoroughly with water and dried. The crude product was purified by dissolving in dimethylformamide (DMF) and precipitating with absolute alcohol.

2.4. Characterization of monomer and polymer

Sulphur contents were estimated using the Schoniger combustion method [13]. Three values of sulphur content for the monomer and polymer were obtained from the Analytical Unit at Cairo University.



IR spectra were recorded on a Perkin–Elmer 257 grating spectrometer with the sample in the form of a KBr disc.

NMR spectra were obtained from a Perkin–Elmer R 32 90 MHz spectrometer using DMSO as solvent and TMS as internal standard. Chemical shifts were expressed in p.p.m. as δ values.

Thermogravimetry (TG) 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}). The sample holder was boat-shaped, $10 \times 5 \times 2.5$ mm^3 deep, and the temperature-measuring thermocouple was placed at a distance of 1 mm from the sample holder. The initial rate of degradation, d*n*/d*t*, of the polymer was found using TG at different intervals and the activation energy was measured by using the Arrhenius relationship.

Viscosity measurement was carried out for 0.5% (w/v) solution in DMF at 30 °C using an Ubbelhode level viscometer.

The electrical conductivity $\sigma_{a.c.}$, dielectric permittivity ε' and dielectric loss (tan δ) were measured at various temperatures. The polymer was pressed at 5 ton cm^{-2} to form circular discs of diameter 12 mm and thickness 1.25 mm. The sample was rubbed with silver paste on both surfaces of the pellet to ensure good electrical contact with the brass electrodes. The sample was inserted between the electrodes in a temperature test chamber. This chamber was evacuated to a pressure lower than 10^{-2} Pa using a diffusion pump to avoid the large enhancement of conductivity of the polymer due to absorbed water [2]. The temperature was measured to better than ± 1 °C with a calibrated Ni–Cr thermocouple set close to one of the electrodes. AC electrical measurements of the polymer were made with a computer controlled lock-in technique 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 (10 Hz to 100 kHz) and temperature (304 to 460 K).

3. Results and discussion

3.1. Identification of the monomer and the polymer

4,4′-disulphinyl diphenyl ether was prepared by refluxing 4,4′-diaminodiphenyl ether with excess of thionyl chloride at 80 °C. The IR spectrum of the monomer indicates the characteristic bands at 1305 and 1270 cm^{-1} due to the –N=S=O group, as reported by Parshall *et al.* [14]. The calculated analysis for $C_{12}H_8O_3N_2S_2$ (M.W. 292.3); C, 49.31; H, 2.74; O, 16.41; N, 9.59 and S, 21.94% and that found C, 49.18; H, 2.80; O, 16.29; N, 9.75 and S, 21.75%.

Poly(4,4′-N,N-diiminosulphoxide diaminophenyl ether) was prepared by Michael addition mechanism of 4,4′-disulphinyl diphenyl ether with 4,4′-diaminodiphenyl ether. The inherent viscosity of the polymer was found to be 0.22 dl g^{-1}, indicating that the polymer is of relatively low molecular weight as was reported in our previous articles [3, 11, 12].The NMR spectrum contains two signals in the region 8.18 and 6.90 p.p.m. due to NH protons and aromatic protons, respectively. The IR spectrum of the polymer shows an absorption band at 3450 cm^{-1}, due to the NH group. Microanalytical data for the polymer calculated C, 58.5; H, 4.06; O, 12.99; N, 11.38; S, 13.02% and found C, 58.2; H, 4.2; O, 12.7; N, 11.5; S, 12.7%.

3.2. Thermogravimetry (TG)

TG curves of poly(4,4′-N,N-diiminosulphoxide diaminophenyl ether) are shown in Fig. 1. Degradation starts at about 443 K and shows two stages. T_{max} of the peaks are 488 and 573 K, shown by derivative equipped with the TG apparatus. It is evident from the TG curve that the polymer is somewhat more stable than other conducting polymers [15]. The effective activation energy for the thermal degradation of the polymer was determined from the temperature dependence of the initial rate, d*n*/d*t*, using TG thermogram. Fig. 2 gives a plot of ln (d*n*/d*t*) against 1/*T*, from which the activation energy is 10 kcal mol^{-1}.

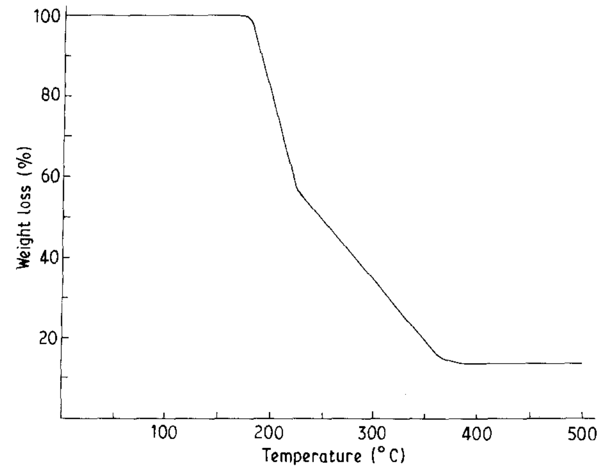


Figure 1 TG curve for poly(4,4′-N,N-diiminosulphoxide diaminophenyl ether).

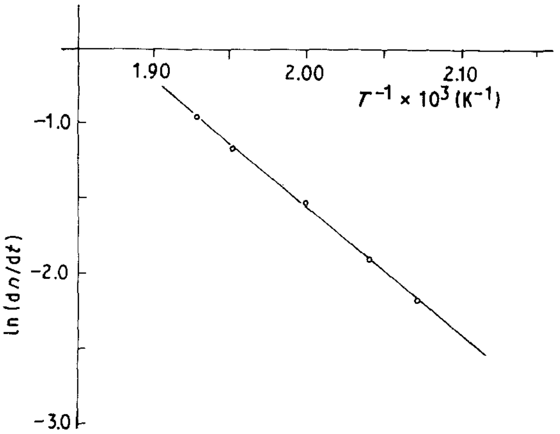


Figure 2 Plot of ln (initial rate of degradation) against $1/T$ of poly(4,4′-N,N-diiminosulphoxide diaminophenyl ether).

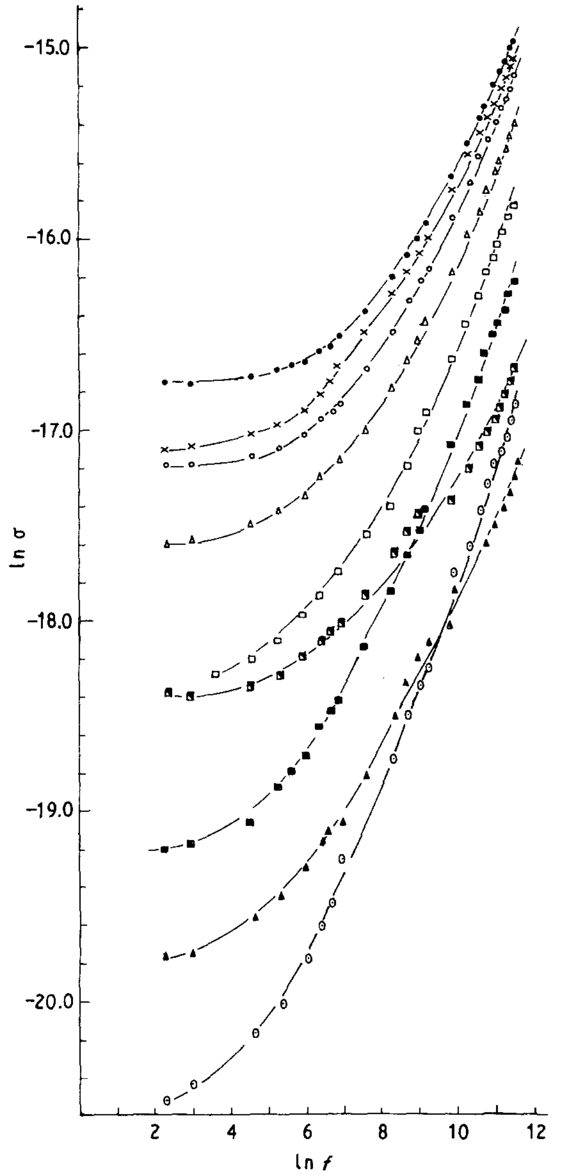


Figure 3 Relationship between $\ln\sigma$ and $\ln f$ at different temperatures. (⊙ 304 K, ▲ 315 K, ■ 325 K, ◨ 335 K, □ 345 K, △ 361 K, ○ 391 K, × 415 K, ● 460 K).

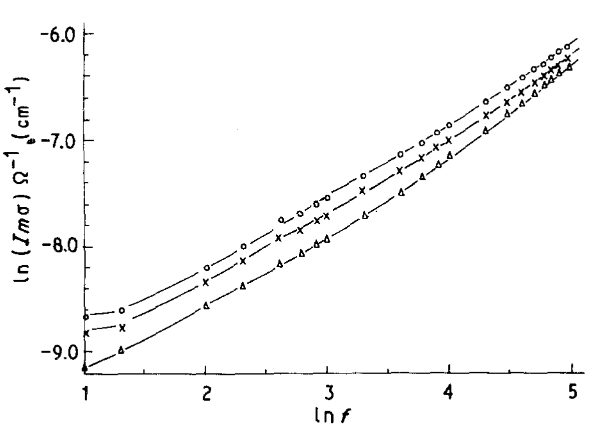


Figure 4 Plot of $\ln \mathrm{Im}\,\sigma l$ against $\ln f$ frequency at various temperatures. (△ 304 K, × 335 K and ○ 345 K).

3.3. Electrical conductivity of the polymer

The a.c. conductivity and dielectric data for poly(4,4′-N,N-diiminosulphoxide diaminophenyl ether) in the range 304 to 460 K at 10 to 10^5 Hz are shown in Figs 3, 4, 5, 6 and 7. The frequency dependence of the real $\sigma_{a.c.}$ and imaginary ($\mathrm{Im}\ \sigma(\omega)$) parts of the apparent a.c. conductivity, in the above temperature range, are shown in Figs 3 and 4. It is seen that $\ln\sigma_{a.c.}$ increases with increasing temperature (T), reaches a maximum value at 345 K, then decreases reaching its minimum value at 390 K and then increases again. This indicates conclusively the presence of a glass transition region between 345 and 360 K. This result is confirmed by differential thermal analysis (DTA) of the polymer indicating a glass transition temperature ($T_g = 355$ K). The temperature dependence curve, shown in Fig. 7, shows a sudden change in the conductivity at T_g. This result is in a good agreement with polymer behaviour since a change in the physical properties of polymers can occur at T_g [16]. There are basically two plateaux in the $\ln\sigma_{a.c.}$ against ln frequency plots at all values of temperatures. The first plateau corresponds to $\sigma_{a.c.}$ measured at low frequencies, 10 to 10^3 Hz, exhibits temperature dependence and is nearly frequency insensitive due to onset of ionic d.c. conduction [17, 18]. On the other hand, the values of conductivity obtained from the second plateau, frequency exceeding 10^3 Hz, display a strong frequency dependence and weak temperature dependence. The implication of both frequency and temperature dependence of a.c. conductivity is that poly(4,4′-N,N-diiminosulphoxide diaminophenyl ether) follows

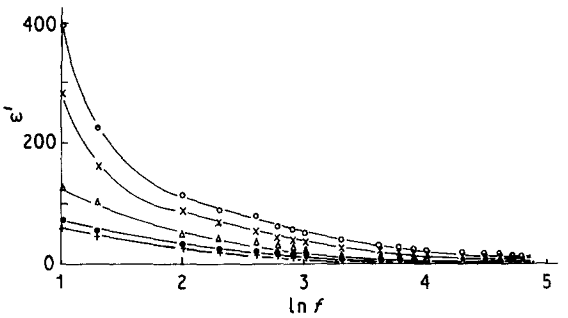


Figure 5 Relationship between ε' and ln f at various temperatures. (+ 304 K, ● 315 K, △ 325 K, × 335 K, ○ 345 K).

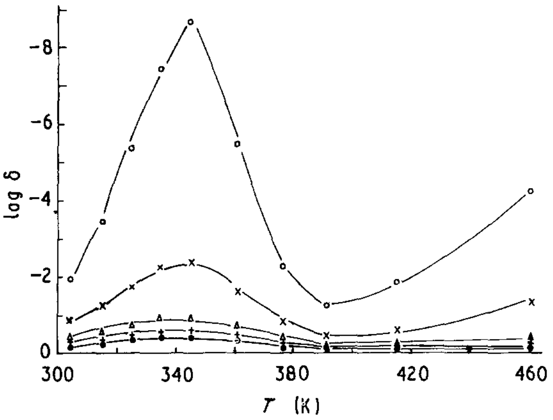


Figure 6 Relationship between tan δ and T at various frequencies. (○ 10^2 Hz, × 10^3 Hz, △ 10^4 Hz, + 4 × 10^4 Hz, ● 10^5 Hz).

the frequency dependence given by power law [2, 19]

$$\sigma_{a.c.}(\omega) = \sigma_0(T) + A(T)\omega^n(T)$$

where $\sigma_0(T)$ is the d.c. conductivity contribution equal to $\sigma_{a.c.}$ When $f \rightarrow 0$ [19], A is a constant very slightly temperature dependent in our case, and the exponent n nearly equal to 0.6 in all temperature ranges except at T_g is slightly higher. This is confirmed well by results obtained for most disordered materials associated with the presence of hopping conduction by electrons [17, 20].

The plots of permittivity ε' against ln frequency f at different temperatures for poly(4,4'-N,N-diiminosulphoxide diaminophenyl ether) are shown in Fig. 5. This plot shows that the dielectric constant decreases markedly with increasing frequency and reaches a constant value of about 11.5. Even this value of ε' is very high in magnitude compared with dielectric constant of conventional polymers. This residual value of ε' is neither temperature nor frequency dependent. A plot of dielectric loss (tan δ) of the polymer against temperature, Fig. 6, exhibits a broad peak, at high frequencies, at a temperature just below T_g. This result is in agreement with the behaviour for most polymers [2].

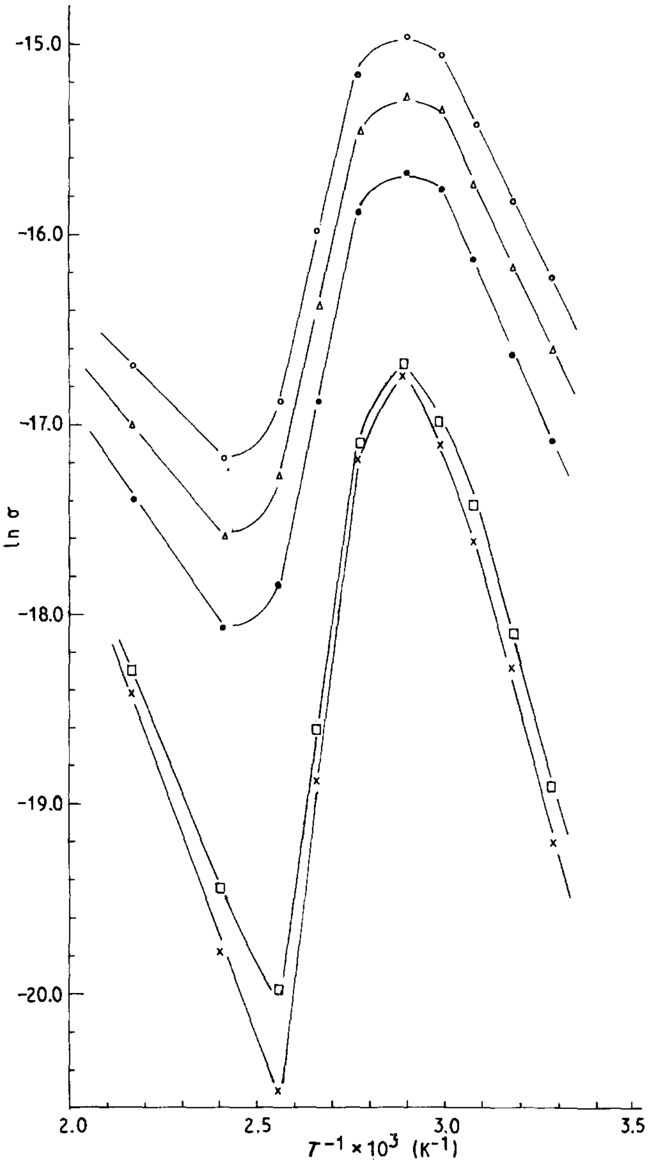
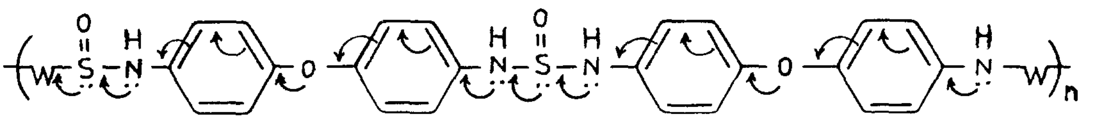


Figure 7 Relationship between ln σ and $1/T$ at various frequencies. (× 20 Hz, □ 200 Hz, ● 2 × 10^4 Hz, △ 5 × 10^4 Hz, ○ 10^5 Hz).

The temperature dependence of $\sigma_{a.c.}$ of the polymer is shown in Fig. 7; three distinct regions can be seen. The feature of the first, at low temperature ($T < 350$ K), and third region, at high temperature ($T > 390$ K), is that the value of ln $\sigma_{a.c.}$ decreases with decreasing temperature and gives a linear relationship with $1/T$, obeying the Arrhenius relation. Thermal activation energy calculated for the first region was found to decrease with increasing the frequency (14.2 kcal mol^{-1}) at 10 Hz to 7.5 kcal mol^{-1} at 10^5 Hz). This may be due to facile delocalization of electrons at higher frequency in the macrochain. It seems that the a.c. conduction of poly(4,4'-N,N-diiminosulphoxide diaminophenyl ether) can be attributed to the hopping of bipolarons (lone pair of electrons) sitting on sulphur and nitrogen atoms in the macrochain as



The second region shows decrease of $\ln\sigma$ with increase of temperature, which is similar to the metal-like structure behaviour. This region is characterized by thermal activation energy ranging from 31.2 kcal-mol^{-1} at 10 Hz to 15.9 kcal mol^{-1} at 10^5 Hz. However, some articles show a break in the relationship of $\ln\sigma$ against $1/T$ for polymeric semiconductors [21, 23], and ascribed to the effect of impurities, included oxygen or to glass transition temperature. In poly(4,4′-N,N-diiminosulphoxide diaminophenyl ether) the first deflection of $\ln\sigma$ against $1/T$ relationship at about 357 K, is clearly due to glass transition temperature, while the second deflection, at about 392 K, may be attributed to thermal degradation taking place at this temperature which is conformed by the TG curve in Fig. 1. At this temperature the formed broken bonds may act as sites of delocalization of charge carries [24, 25]. The increase in the conduction again in the third region, may be due to the charge carriers transferring from one such site to another.

As a conclusion, it seems that the electrical conductivity of the polymer is controlled by the participation of lone pairs of electrons sitting on nitrogen and sulphur atoms with the σ-bond in the macrochain. Increasing the frequencies increase the movement of the electrons.

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