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ELECTRICAL CONDUCTIVITY IN POLYACRYLONITRILE AND PERBUNAN *

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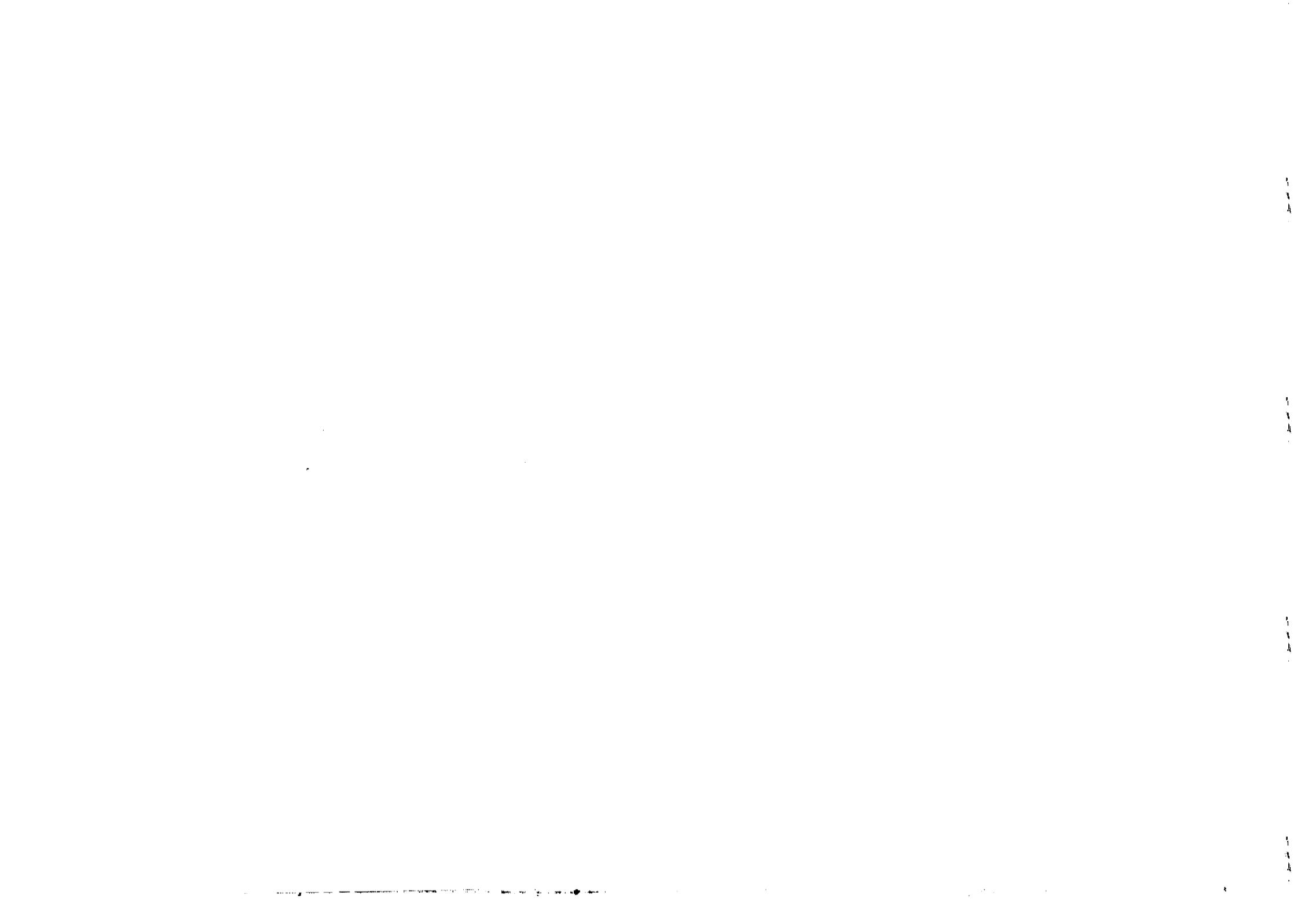Mansoura, Egypt,

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ABSTRACT

The electrical conduction in Ag-PAN-Ag and Ag-NBR-Ag
sandwich samples is studied measuring the dependence of cur-
rent on the applied voltage and temperature. The conduction
mechanism depends on the polymer type. A bulk polarization
contribution is suggested in the conduction mechanism at high
temperatures besides the Schottky emission in the case of PAN and
the
simple carrier jump model in/case of NBR at room temperature.
NBR(28) is proved to be more semiconducting than both NBR(38)
and PAN. This is attributed to the lowering of the nitrile
group content in NBR(28).

Investigations of the conduction mechanism in sandwich
systems with organic films have been performed. Nevertheless,
more studies are required to clarify the carrier transport mech-
anisms, especially in the polymeric semiconductors such as
polyacrylonitrile (PAN) and Perbunan[*]. Previous studies in
the case of PAN have suggested that different mechanisms might
operate. One group of authors [1),2)] has interpreted the con-
ductivity of the heat-treated PAN in terms of the band model.
Hirai and Nakada [3)] measured the electrical properties of thin
PAN films prepared by silent electric discharge in acryloni-
trile monomer vapour followed by the heat-treatment at dif-
ferent temperatures. Non-ohmic characteristics of the elec-
trical conduction were observed and this agreed with the
theoretical expression of the modified Poole-Frenkel effect.
On the other hand, thin films of PAN obtained by vacuum
deposition were made semiconductive by the heat-treatment in
nitrogen [4)]. The electrical conductivity measurements sug-
gested that the conduction should be understood in terms of
the hopping transport of charge carriers in the localized
states which are formed in the forbidden band by random
networks of conjugate double bond systems of carbon to carbon,
and carbon to nitrogen. Recently, Chutia and Barua [5)] pre-
pared PAN films by the isothermal immersion method. The
results permitted to rule out the Poole-Frenkkl type conduc-
tion mechanism and they concluded that the more appropriate
conduction mechanism is of the Schottky type.

[*)] Perbunan is a commercial name of trade mark of nitrile-
butadiene rubbers (NBR).

The present paper deals with the study of the electrical conductivity of PAN and nitrile-butadiene films prepared by the casting method. The results confirmed the possibility for transition from one mechanism to another by changing the sample temperature in one and the same system.

Experimental

Materials and film preparation

PAN was dissolved in N,N dimethyl formamide and NBR copolymer was dissolved in benzene. Films of PAN and NBR were obtained by casting the polymer solution onto a glass slide and evaporating the solvent. After casting, the films were dried at 35°C to remove the residual solvent. No heat treatment was done for the films. By this method different film thicknesses were prepared. The acrylonitrile content (%) in the rubber is 28±1 and 38±1 and hence these materials will be termed afterwards as NBR-28 and NBR-38.

D.C. conductivity measurements

Contacts were of highly conductive silver paste with an area of about 1 cm^2. These contacts are capable of injecting electrons freely up to a current density of at least 10^{-6}A.cm^{-2}. Electrical contact was made via metal props under slight spring loading. A d.c. conduction measurement was carried out

by using Levell type TM9BP (England) picoammeter with a smoothing adjustable power supply (0-1000 volts). A well-shielded thermostated oven containing an electrode system is used for temperature regulation from room temperature to about 150°C. All measurements were carried out at atmospheric air.

Results and Discussion

I-V characteristics at different temperatures

At low voltages the I-V characteristics are linear and correspond to the bulk conductivity of the polymer film separating the metal electrodes. By increasing the applied voltage, at room temperature, the I-V characteristics deviate more and more from Ohm's law for PAN only. In Fig.(1) the current-voltage characteristics (log I versus log V) at room temperature are shown for the three polymer PAN, NBR(38) and NBR(28) with film thickness 0.012; 0.05 and 0.05 cm respectively. At higher temperatures, deviation from Ohm's law was observed in the cases of NBR(38) and NBR(28). The type of I(V) dependence changes in different temperature regions, depending on the polymer. At the same time transition voltage, from linear to non-linear I(V) dependence, shifts towards smaller values with increasing temperature. It is clear that, on increasing the voltage, at room temperature, the log I vs log V plot, in case of PAN, is not linear, i.e., there is a deviation from Ohm's law.

Fig. (2) shows the log J vs $\sqrt{V}$ characteristics for PAN films at different constant temperatures. Similar results are reported in the literature and different conduction mechanisms have been taken in consideration. However, on the basis of the linear log J vs $\sqrt{V}$ characteristics of the system and the strong temperature dependence of the current, it is supposed that Schottky emission due to thermal excitation of carriers over the barrier is the main mechanism of electron transfer through the polymer film. It must be mentioned that at higher temperature (90°C), log I vs $\sqrt{V}$ characteristic is somewhat different and this may be attributed to the appearance of polarization processes.

On the other hand, Fig. (3) shows that the I-V characteristics at different constant temperatures for NBR(38) are linear and the ohmic behaviour predominates in the temperature range from 16 to 50°C. Similar results were obtained in the case of NBR(28). As the temperature is raised above 70°C, the slope of the relationships changes continuously to lower values, i.e., there is a deviation from Ohm's law. The ohmic behaviour for NBR samples, over a broad temperature range (16 to 50°C), indicates that the current density value is controlled by the thermal bulk generation of charge carriers. Above this temperature range, a deviation from Ohm's law is observed and this may be attributed to one of the following

two causes. The first reason is that the polymeric material structure changes to a new one of non-ohmic behaviour. The second reason is thought to be a change in the conduction mechanism.

On cooling a previously heated sample to room temperature and measuring the I-V characteristics, a similar behaviour was obtained. Thus the assumption of structural changes is ruled out.

The current as a function of increasing, decreasing, and reversed voltage, while keeping the temperature constant, for NBR(38), at 90°C is shown in Fig.(4). It is clear that for the forward biased sample the I-V characteristics obtained by increasing the applied voltage did not coincide with that obtained by decreasing the voltage. The same behaviour is seen in the reverse biasing. The shape of these characteristics has been observed only at relatively high temperatures ($\geqslant$90°C). At lower temperature the difference in the current obtained with increasing and decreasing voltages was found to be almost negligible. The non-coincidence of the current values can be explored on the basis that, at higher temperature, the polymer becomes an elastically isotropic solid with orientationally molecular dipoles. Hence when the voltage is applied to the samples, where the reduced internal viscosity of NBR samples appears to allow the dipoles to rotate freely [6],

dielectric polarization will influence the applied electric field. Thus the current at increasing voltage will not follow the same path as decreasing voltage. The decrease of the conducting current values, in/case of NBR(38), at 100°C than the values at 90°C is in favour of the polarization effects. Thus we can conclude that at high temperature the transient polarization currents are superimposed on the becoming weakly d.c. conducting currents and hence the conduction mechanism is influenced by polarization processes.

From Fig.(1) it can also be seen that the conducting current value of NBR(28) is greater than those observed for NBR(38) and PAN. These results would seem to cast doubts on the importance of the role of nitrile group (dipoles) concentration in conduction process. The importance of secondary forces between the molecules in controlling the packing and configuration of the molecules in the solid state was discussed [7)-9)] with emphasis on the fact that directional interactions such as forces between dipoles may reinforce or oppose each other, i.e., the electronic conduction depends on the correct spatial configuration of molecules. On the other hand, the transport in disordered organic polymeric solids is typically an unipolar one. However, NBR represents a long linear molecule, containing conjugate double bond system $>C = C<$, on which electrons were free to move. Further, the molecule

contains regularly (or not) spaced, highly polarizable CN-group on the side. So it is certain that electrical conductivity of NBR originates from π-electrons in the conjugate double bond systems. The simple carrier jump model seems to be applied to the conduction mechanism. A detailed discussion of the conduction mechanism will be reported elsewhere.

The nitrile groups (electron affinity about 2.26 e.v.) may act as electron trapping sites or at least influence the transfer of charge carriers due to polarization and alignment . opposing to the external applied electric field.

Temperature dependence of the D.C. electrical conductivity

Fig.(5) stands for the conductivity dependence on the reciprocal temperature for PAN, NBR(38) and NBR(28) samples, at constant applied voltage (25 volts). The Arrhenius relation for conductivity can be written as

$$\sigma = \sigma_0 \exp(- E_A/KT),$$

where σ_0 is a constant and E_A is the apparent activation energy. A linearity was observed in Fig.(5) in a limited range of temperature, depending on the sample type. On the other hand, a deviation from the Arrhenius relation was observed above 80, 70 and 55°C for PAN, NBR(38) and NBR(28) samples,

respectively. The apparent activation energies calculated for the different materials, from straight line portion, are listed in Table I. . The results show that the activation energy E_A depends on the type of polymeric material. The activation energy value for PAN is comparable with that given in literatures, 0.8 e.v [3]. From Fig.(5) it is observed that over a considerable range of temperature, two distinct regions are often found with two different values of E_A as listed in Table I. . The "break-point" in the $\ln\sigma - \frac{1}{T}$ curve for PAN takes place within the glass transition temperature range, i.e., from 80 to 104°C [15]. On the other hand, the break-points in the $\ln\sigma - \frac{1}{T}$ curves in the case of NBR samples did not agree with the glass transition temperatures for these samples. Since the break-point, termed T_b in what follows, may be of a physical significance due to some modification in the mode of the preparation of the polymer [10], thus it is important to discuss the dependence of T_b on the sample thickness and on the applied field. It is clear from Table II that, as the applied field increases, T_b decreases. This is consistent with the suggestion that the dipole rotation process becomes significant at lower T_b values as the applied field increases.

On the other hand, from Table III it is clear that the value of T_b increases as the film thickness increases. These results can be interpreted as follows. As the sample thickness increases, while the applied voltage is constant, the external field decreases so the process of dipole rotation predominates at higher T_b values. Since T_b is of film thickness and applied field dependence, it may represent the temperature, under the experimental conditions, at which the polarization process takes place.

The temperature dependence of the electrical conductivity for the materials, under investigation, may be discussed as follows: PAN films has two phase structures and phenomena such as glass transition, characteristic of the amorphous phase, are frequently quoted [11]-[13] for this polymer. On the other hand, Bohn et al [14] suggested a one phase structure. According to one phase model, the heat-treatment modifies the structure, probably due to the reorientation of the strongly interacted nitrile groups. Hence, above T_g, the decrease in the conductivity may be due to the increase in the dipole moment vector which opposes the external electric field vector [15]. For NBR samples it might be thought that the electronic conduction mechanism predominates below T_b, which is attributed to the creation of the negatively charged carriers and their motion through the bulk material under the effect of the applied field. At temperatures higher than T_b a change in the property of polymeric material allows for the appearance of

polarization process (or dipole reorientation). Thus the total electrical conductivity can be written as the sum of two terms :

$$\sigma_{tot} = \sigma_1 + \sigma_2 \; ,$$

where σ_1 is the electronic conductivity and

σ_2 is the polarization or dipolar conductivity.

In view of the above discussion it would be certain that a unique mechanism does not account for our results at different temperatures. It would seem clear however that the Schottky mechanism is involved in the case of PAN. On the other hand, the simple carrier mechanism operates in the case of NBR at room temperature. Moreover the nitrile group concentration influences the electrical conductivity of the polymer. The lower is the nitrile group concentration, as in NBR(28), the higher is the conductivity value. This phenomena was confirmed by the calculated activation energy (0.55 e.v.).

Acknowledgment

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Table I:

Apparent activation energy for different materials.

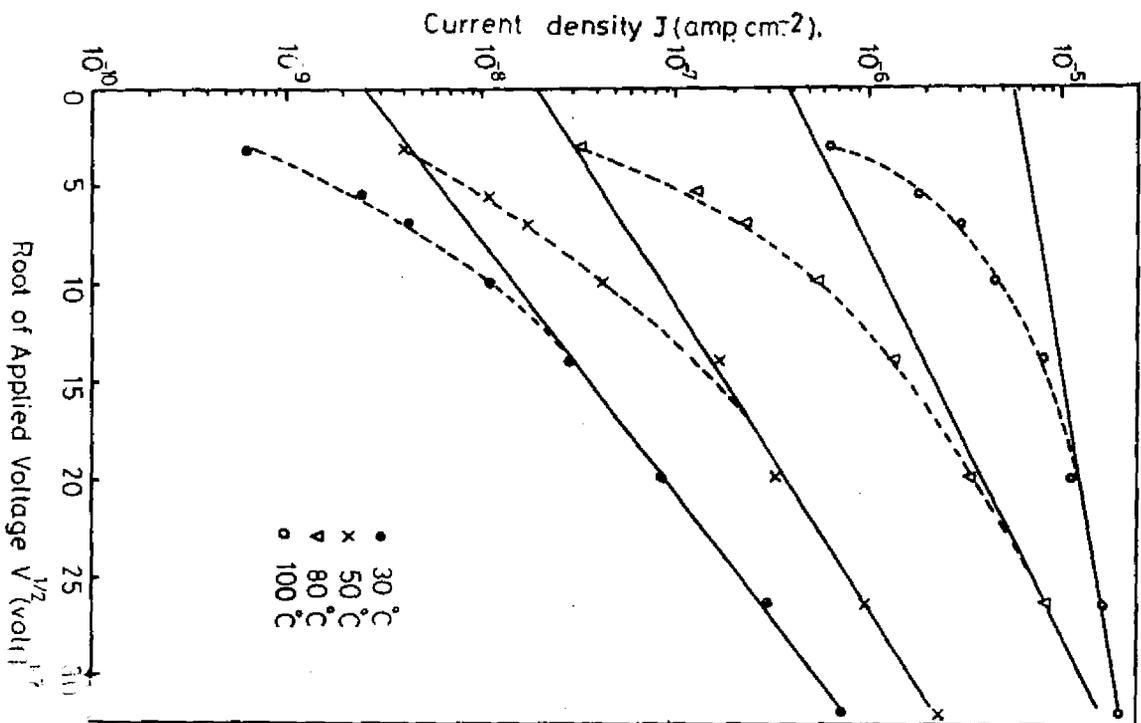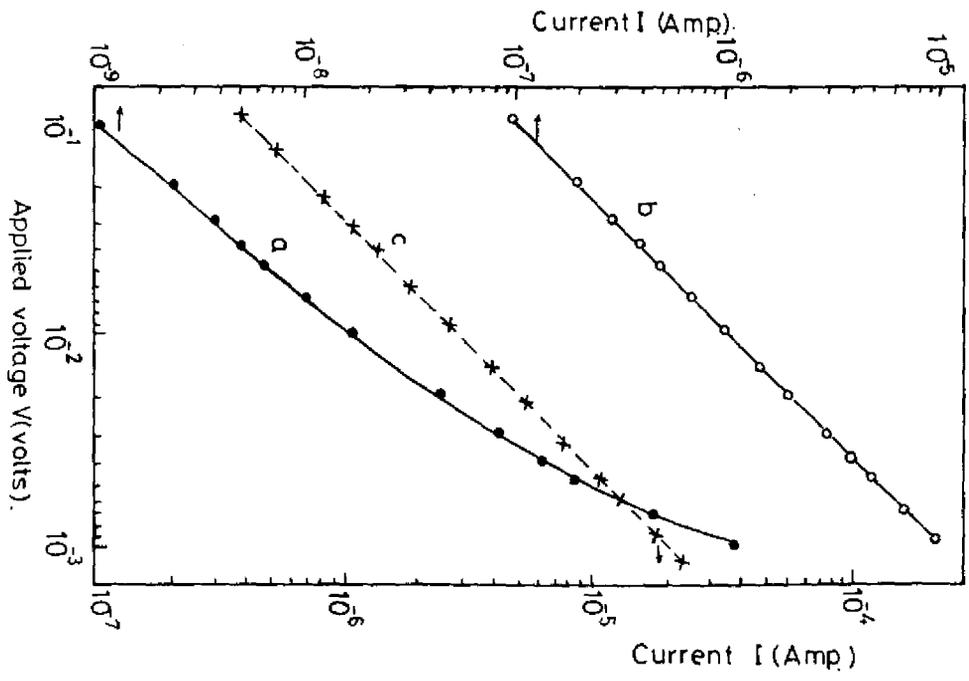| Polymer	$\Delta E(e.v.)$	
	Below T_b (or T_g)	Above T_b (or T_g)
PAN	0.86	0.2
NBR(38)	0.73	0.4
NBR(28)	0.55	0.3

Table II:

Dependence of T is on the applied voltage for NBR(38) at constant thickness; d = 0.03 cm.

Applied Voltage (volts)	T_b °C
25	57
50	54
100	50
500	43
1000	32

Table III:

Dependence of T_b on the NBR(38) sample thickness at constant applied voltage (25 volts).

Thick. d (cm)	$\Delta E(e.v.)$	T_b °C
0.02	0.76	50
0.03	0.76	57
0.05	0.73	80

Fig (1)

Fig (2)

Fig(3)

Fig(4)

Figure (left column)

Conductivity $(\Omega^{-1} \cdot Cm^{-1})$ [left axis]: 10^{-12}, 10^{-13}, 10^{-14}

Conductivity $(\Omega^{-1} \cdot Cm^{-1})$ [right axis]: 10^{-10}, 10^{-11}, 10^{-12}

Curves labeled: PAN, NBR(38), NBR(28)
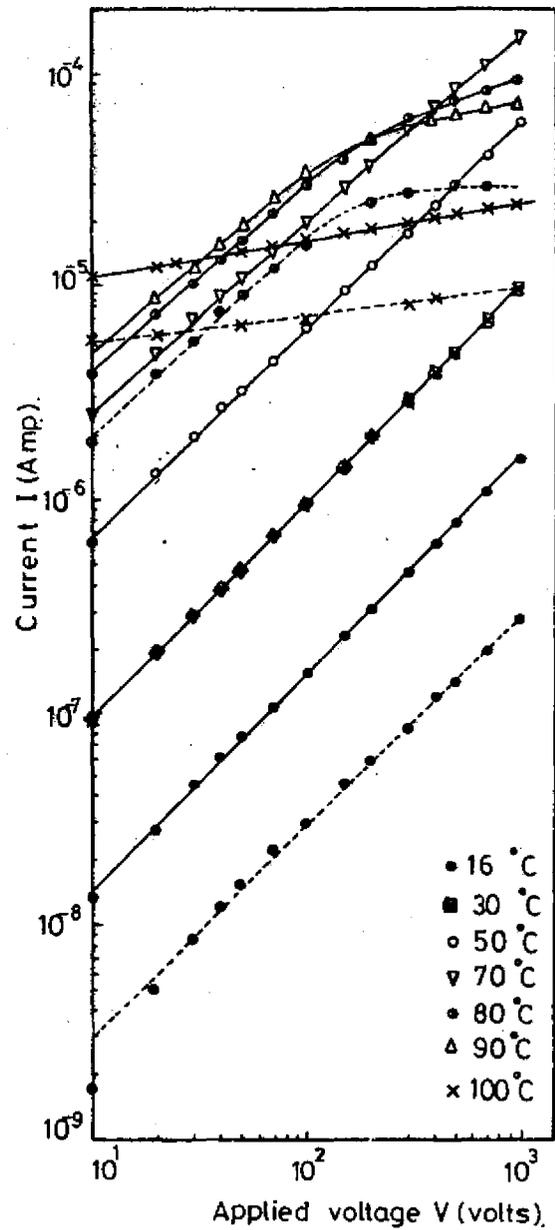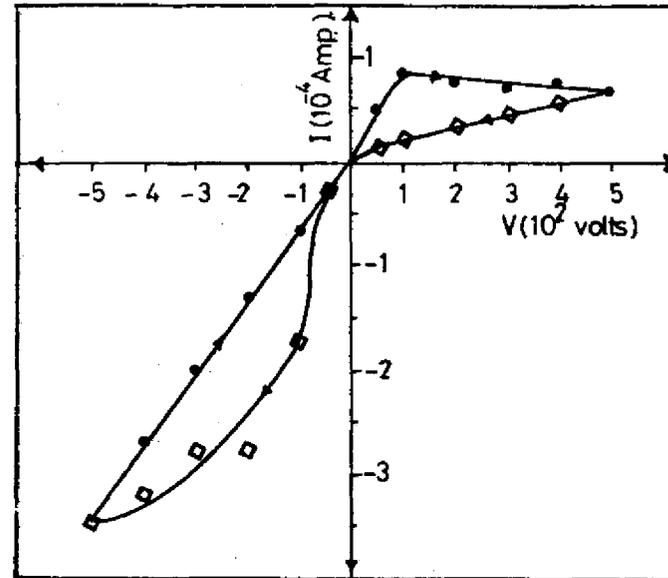
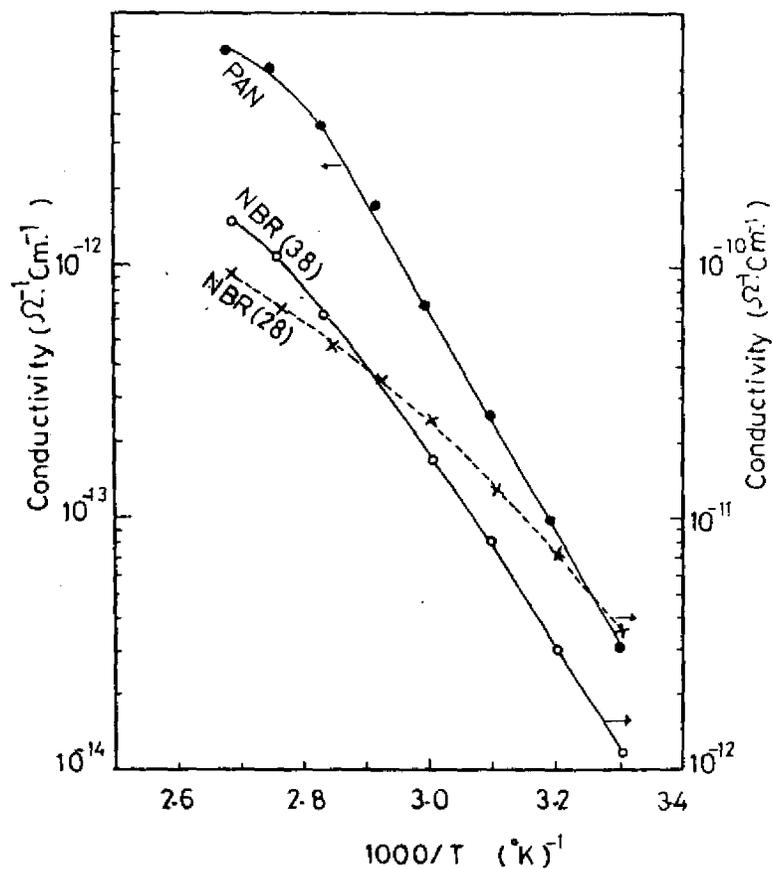X-axis: $1000/T$ $(^{\circ}K)^{-1}$ — 2·6, 2·8, 3·0, 3·2, 3·4

Fig (5)

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