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A.C.Conduction Mechanisms in Poly(1-Ethynylnaphtalene)

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Summary.The a.c.conduction mechanism in poly(1-ethynylnaphtalene) with various physical and isomeric(cis-cisoidal and trans-cisoidal) structures was investigated over the frequency and temperature ranges of 10-10^5Hz and 190-373°K respectively.The conduction mechanism depends on the isomeric structure of the polymer,and for the cis-cisoidal polymer supplementary on temperature and frequency.Over the whole frequency range(at 190°K) and above a critical frequency(at higher temperatures),which is temperature dependent,the quantum hopping mechanism is involved in cis-cisoidal polymer.Outside of this range the conduction process takes place by two parallel mechanisms:band and hopping mechanisms.In trans-cisoidal polymer the quantum hopping mechanism is involved over the whole frequency and temperature range considered.

Introduction.In spite of a great number of studies, the electric conduction process in disordered materials,including polymers,is far to be understood.To investigate the role of localized states(regularly found in these materials) in the conduction process, some authors used the a.c.conductivity technique (POLLAK,GEBALLE,1961;MOTT,1971;LEWIS,EDRIS,1975; DIACONU,at al.,1979;ROCKSTAD,1969;DIACONU,at al., 1980);intrinsec band conduction should be frequency independent,whereas conduction by hopping between localizes states should vary with frequency as ω^s with $0.5 \leqslant s \leqslant 1.0$ and ω -angular frequency.
In order to establish the conduction model in a.c. regim in poly(1-ethynylnaphtalene)(P1EN) of various physical and isomeric structures,the frequency and temperature dependence of the conductivity was investigated.The d.c.conductivity at certain selected temperatures was also measured.

Experimental.The investigated polymers had respectively cis-cisoidal(c-c)(80% crystallinity) and trans-cisoidal(t-c)(amorphous) structures(SIMIONESCU,at al.,

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1973).The conductivity measurements were carried out on disc-shaped samples($\emptyset$=13mm) in dry N_2or O_2at normal pressure,using a chamber already described(DIACONU, DUMITRESCU,1978).The discs were provided with vacuum evaporated gold electrodes of circular form($\emptyset$=10mm). Before starting the measurements,the samples were stored in a evacuated chamber(10^{-6}Torr) for three days.A General Radio 1621 bridge and a TR 2201 Orion teraohmmeter were used for a.c.(10-10^5Hz) and d.c.conductivity measurements respectively.

<u>Results and discussion</u>.Figure 1 shows the measured conductivity of P1EN$_{C-C}$ vs. frequency at various temperatures in N_2 atmosphere.On a separate axis the d.c.conductivity values, at the same temperatures,are indicated too. Over the temperature range considered the isomeric and physical structure of polymer do not alter (SIMIONESCU,1977). At 190°K,the a.c. conductivity varies with frequency as $\omega^{0.92}$ whereas at higher teperatures the same frequency dependence occurs only above a critical frequency which is temperature dependent. Below these frequencies, $\sigma(\omega)$ decreases smoothly with frequency to a frequency-independent value,which is very closed to that of the d c.conductivity, σ_0.

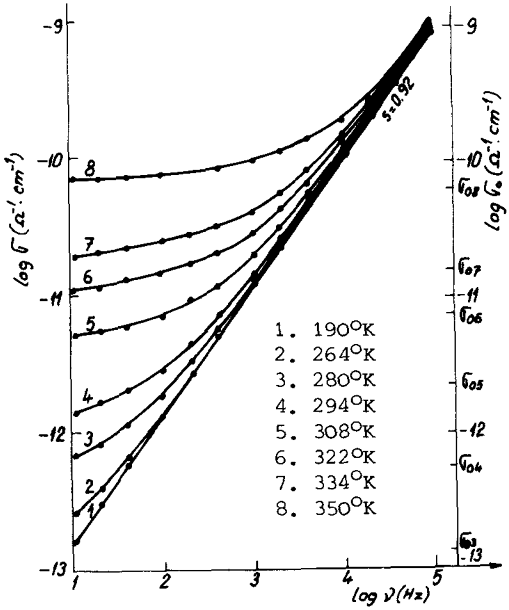

Fig.1.The frequency dependence of the measured conductivity of P1EN$_{C-C}$ in N_2 atmosphere.

If frequency is taken as a parameter and $\sigma(\omega)$ vs. 1/T is plotted,the curves presented in fig.2 were obtained. σ_0 vs. 1/T is also shown.

It may be seen that apparent activation energy increases with temperature and decreases with frequency.At high temperatures and low frequencies,the values of $\sigma(\omega)$ approach to those of σ_0 ,having the same temperature dependence.These facts provide strong evidence that the frequency independent component is in fact the d.c.conduc-

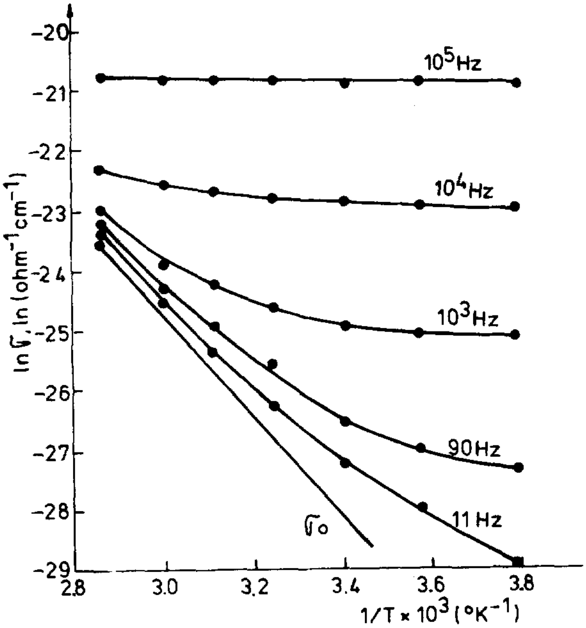

Fig.2.The temperature dependence of the a.c.conductivity $\sigma(\omega)$ (at various frequencies) and d.c. conductivity of P1EN$_{C-C}$ in N_2 atmosphere.

tivity.
Analising the temperature dependence of the frequency dependent component $\sigma_1(\omega)$,obtained by substracting $\sigma_0$from $\sigma(\omega)$,it was found that over the temperature and frequency range where s=0.92,$\sigma_1(\omega)$ depends sublinearly on temperature,whereas outside of this range a supralinear dependence occurs. POLLAK(POLLAK, 1964;POLLAK,1965; POLLAK,GEBALLE,1961 POLLAK,1971) found that,for hopping of charge between isolated pairs of randomly distributed localized states,a.c.conductivity varies with frequency as ω^s , where s decreases from 1.0(for single hops) to 0.5 for multiple hops.At higher temperatures,multiple hops frequently occur; at low temperatures single hops predominate.According to this model,the transfer of charge between localized states is single phonon assisted(quantum hopping model).As a result the a.c.conductivity depends linearly or sublinearly on temperature and the charge transport between localized states is mainly by tunneling through the potential barrier separating the sites.

PIKE(PIKE,1972) showed that as a a.c.conductivity depends supralinearly on temperature,the hopping of charge carriers between localized states over a potential barrier (classical hopping model) better explains his results. Comparing our data to the predictions of the quantum and classical hopping models,it may by concluded that over the frequency and temperature range where s=0.92 the electric conduction in P1EN$_{C-C}$ occurs almost entirely by single quantum hops.For the rest of the measuring range, where σ_0 is significant,it may be considered that conduction process takes place by two parallel mechanisms: band mechanism and hopping mechanism.As temperature increases and frequency decreases the contribution of the former mechanism increases as compared to the latter. The parallel hopping mechanism is a classical one. In a semicrystalline material such as $PlEN_{c-c}$, the shortest distance between states is found in amorphous regions. Therefore, in these regions, the quantum mechanism becomes most likly, whereas in crystalline regions the classical hopping mechanism is more probable.

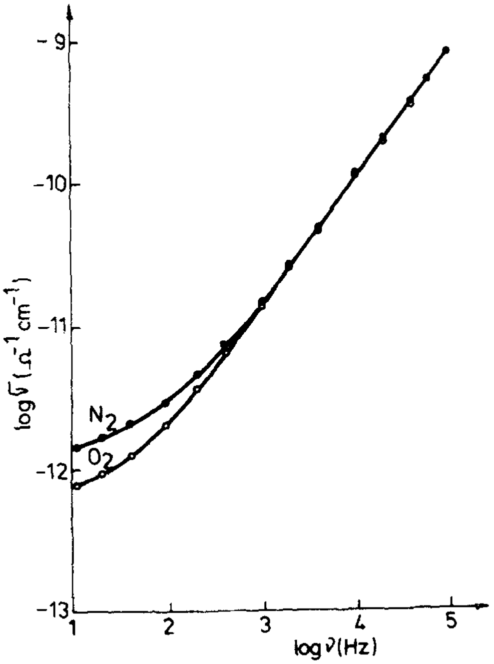

Fig.3. The frequency dependence of the conductivity of $PlEN_{c-c}$ in O_2 and N_2 atmospheres.

As compared with N_2, O_2 decreases the conductivity $\sigma(\omega)$ of $PlEN_{c-c}$ over the frequency and temperature range where σ_o is significant (Fig.3). It is suggested that the adsorbed oxygen delays the transfer of charge inside the energy band of the polymer.
The frequency dependence of the conductivity of PlEN is presented in figure 4. The values of σ_o are negligible as compared with the corresponding $\sigma(\omega)$ values over the whole frequency and temperature range. Analysing the values of s and the temperature dependence of $\sigma(\omega)$, it may be suggested that conduction process

in $P1EN_{t-c}$ takes place by single quantum hops.

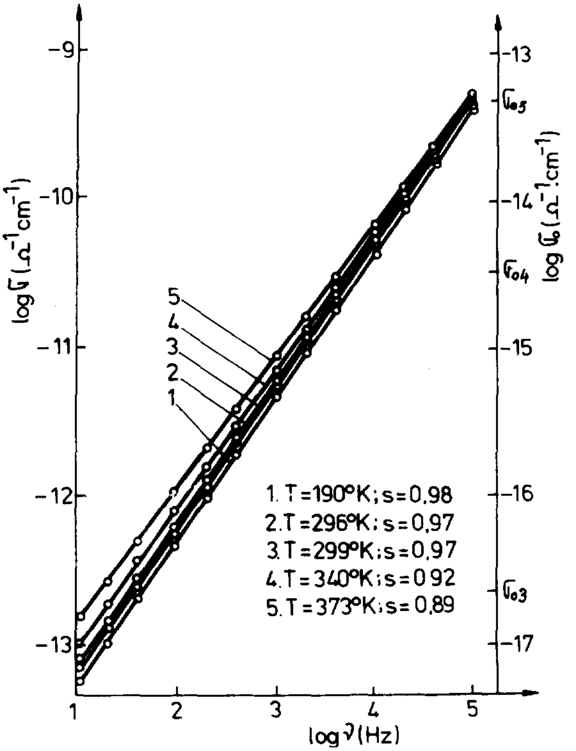

Fig.4.The frequency dependence of the measured conductivity of $P1EN_{t-c}$ in N_2 atmosphere.

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