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Transport of Charge Carriers in Organic Disordered Semiconductors Based on Polyacrylonitrile

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The conductivity and static permittivity of heat-treated polyacrylonitrile products with polyconjugation regions were obtained in the vicinity of the percolation threshold. It was observed under the values of this threshold, the experimentally obtained dependencies of conductivity and static permittivity on the volumetric content of polyconjugation regions in these materials differ from the dependencies calculated within the framework of the percolation theory. The reason of this controversial data is analyzed in terms of the spatial-structural hierarchical model proposed by Balberg *et al.* for composites. Analysis of the temperature dependence of conductivity within the framework of the local activation energy shows the formation of a continuous spatial structure from tunnel-connected polyconjugation regions.

Keywords: Semiconductor, Pyrolyzed, Polyacrylonitrile, Electrical conductivity, Dielectric constant, Local activation energy, Pyropolymers, Conductivity

INTRODUCTION

In recent years, disordered systems containing conductive fibrous fillers (nanotubes, nanofibers, nanowires, *etc*.) have been of particular interest, both from a fundamental and applied point of view. For example, a recently published review article by I. Balberg [1] shows that the existing classical theories of percolation, continuous percolation and effective medium theory can explain all the features of the dependency of the electrical conductivity on the content of fibrous filler in such systems, and also provides a number of areas of their practical application. On the other hand, semiconductor materials with a chain structure (organic semiconductors based on doped conjugated polymers, molecularly doped polymers, polymer composites with inclusions of carbon nanotubes, heat-treated products of a number of polymers with polyconjugated regions, *etc*.) are also of interest [2-4]. We have shown [5,6] that the formation of heat-treated products of a number of polymers (pyropolymers), including polyacrylonitrile, can be represented to a first approximation as a process of filling the dielectric with fibrous nanodispersed conductive particles-polyconjugation regions. Therefore, composites containing conductive fibrous fillers, as well as semiconductor materials with a chain structure, including heat-treated polyacrylonitrile products, can be included in one general class of heterogeneous systems. Unlike composites containing conductive fibrous fillers in pyropolymers, highly electrically conductive polyconjugated areas arise under the influence of heat treatment as a result of complex chemical transformations and are in a chemically bonded state with non-conducting areas.

Therefore, clarifying the mechanism of charge carrier transfer in organic conducting pyropolymers within the framework of modern theories of inhomogeneous systems has again become relevant.

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Objects and methods of research. The object of study was heat-treated powdered (grain diameter of the order of 0.5-1 μm) polyacrylonitrile (PAN). Heat treatment of the samples was carried out in a vacuum in the temperature range (200-1100) °C for three hours at each temperature with an interval of 50 °C. Conductivity in constant and alternating fields was measured under a pressure of about 0.35 GPa in a fixed pressure chamber [7], in a vacuum of about 10^{-3} mm. rt. Art. This made it possible, by excluding contact phenomena between powder particles, to study the properties of a monolithic compound. Conductivity was determined by measuring resistance, and dielectric constant was calculated by measuring the electrical capacitance of the samples. Methods for measuring the resistance and capacitance of samples are described in [8]. The determination of the volume fraction of polyconjugation regions is described in [5]. The size of the polyconjugation length was determined by small-angle X-ray diffraction, which we used for different composite materials containing nickel nanoparticles [9].

In works [5,6] it is shown that pyropolymers, a typical representative of which are heat-treated PAN products, are dielectric at low heat treatment temperatures (T_t) ≤ 200 °C, and at $T_t \geq 200$ °C they acquire semiconductor properties. Responsible for the electrical properties of semiconductor PAN are the polyconjugation regions that appear at $T_t \geq 200$ °C.

They are denser, highly conductive nanowires with a linear size of ≤ 20 nm compared to the original polymer, and their cross-sectional diameter is estimated to be about 0.5 nm [10], in which the charge carriers are π electrons of double bonds, similar to those in organic conducting polymers, for example, polyaniline or polypyrrole. Less dense and therefore wider gap gaps between the conjugation regions represent potential barriers for electrons.

The purpose of this work is to study the dependence of the behavior of conductivity and static dielectric constant on the volumetric content of polyconjugated regions in PAN-based pyropolymers within the framework of the modern theory of disordered systems [1,11], as well as to analyze the results obtained on the study of the temperature dependence of conductivity within the framework of the local activation energy of electrical conductivity, to clarify a mechanism of charge carrier transfer in them.

Results and discussion. Heat-treated PAN product, at 200 °C ≤ T_t ≤ 600 °C, when the volume of polyconjugation areas increases (Fig. 1) due to an increase in their number, semiconductor PAN is an electronically inhomogeneous system. At $T_t \geq 600$ °C, the growth and unification of conjugation regions occur, as a result of which the pyropolymer is already a single-phase system formed by an infinite cluster of polyconjugation regions [5].

According to the percolation theory, the conductivity σ of systems containing metal particles randomly distributed in a dielectric matrix, under the boundary conditions ($V_1 = 0$ и $V_1 = 1$), is described by the following formulas:

$$\sigma(V_1) = \sigma_2\,(V_c - V_1/V_c)^{-q} \quad \text{at } V_1 < V_c \tag{1}$$

$$\sigma(V_1) = \sigma_1\,(V_1 - V_c/1 - V_c)^{t} \quad \text{at } V_1 > V_c \tag{2}$$

here σ_1 - is an electrical conductivity of metal particles; σ_2 - electrical conductivity of the dielectric matrix; V_c - is the critical concentration (percolation threshold) at which an infinite cluster (IC) of filler particles is first created; t and q are parameters called critical indices.

For the studied pyropolymers, V_c was determined by differentiating lgσ with respect to V_1. The critical index t was obtained from experimental data, representing them as a graph in coordinates $\lg\sigma - \lg[(V_1 - V_c)/(1 - V_c)]$, the slope of the graph is t. The value of σ_1 was calculated by extrapolating this graph to $V_1 = 1$. It was found that $V_c = 0{,}50$ ($T_t = 600$ °C) and $t = 2.20$.

Figure 1 shows that for the studied pyropolymers, the correspondence between the calculated and experimental data is observed at $V_1 > V_c$. Consequently, for the resulting pyropolymers the value of V_c is much greater than the theoretical value of the percolation threshold [1], but for ceramic materials with highly dispersed nickel particles $V_c = 0{,}443$ [8] is close.

The existence of a threshold at a concentration higher than that predicted by the theory of percolation in pyropolymers indicates, as shown in [1,12], a high degree of asymmetry between the characteristic shapes of conducting and non-conducting regions.

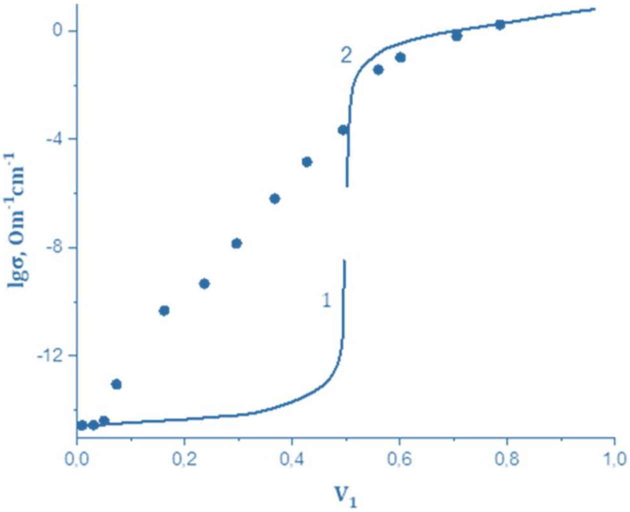

Fig. 1. Comparison of experimental (dots) and calculated (solid curves) conductivity values as a function of the volumetric content of nanofibrous “conducting” particles - polyconjugation regions (V_1). 1- $\sigma_{ras.}$ according to (1), 2- $\sigma_{ras.}$ according to (2).

The deviation of the experimental dependence of the electrical conductivity of pyropolymers shows that they have an additional contribution to the electrical conductivity below V_c. It can be explained based on the model of electrical conductivity in composites proposed by Balberg in [11].

According to this model, all metal particles in composites with randomly distributed metal particles in a dielectric matrix are electrically coupled, and the electrical conductivity of these composites is determined by both the tunneling of charge carriers between adjacent particles and the tunneling between particles located at a distance. Percolation behavior can be observed when the contribution of tunneling between particles separated from each other to macroscopic conductivity is negligible. This occurs when the particle radius (b) significantly exceeds the tunneling region parameter (or tunneling decay parameter) (d).

In case where b ~ d, tunneling of charge carriers between non-neighboring particles contributes to macroscopic conductivity along with tunneling between neighboring particles, and the dependence of macroscopic conductivity on the concentration of metal-containing particles differs from that of explained by classical percolation theory. It can be seen that the conductivity behavior of the studied pyropolymers described above is consistent with these model predictions.

As shown in [11], in such composites there are two percolation thresholds, one of them is observed at high values of V_1, and it is the percolation threshold V_c defined above. Another of them (additional percolation threshold V_{cd}) is observed at low values of V_1 and it is the critical fractional volume of metal particles that initiates the first infinite cluster of tunnel-connected conductors. By adjusting the section (for $V_1 < V_c$) of experimental curve 1 (Fig. 1) for the pyropolymer, it was established that $V_{cd} = 0.05$.

Figure 2 shows the experimental and theoretical dependences of the static dielectric constant ε on V_1 for the materials under study. The static dielectric constant was calculated from data on the frequency dependence of the dielectric constant in the region of 20-200 Hz by extrapolating this dependence to zero frequency.

Theoretical dependencies are calculated using the following equation:

$$\varepsilon(V_1) = \varepsilon_d \left(\frac{V_c - V_1}{V_c}\right)^{-q}, \quad V_1 < V_c, \qquad (3)$$

where ε is the dielectric constant of PAN, and the index q is the same as in (1). This equation, using the boundary condition $V_1 = 0$, was studied from the expression for the static dielectric constant near the percolation threshold, which has the form [13].

$$\varepsilon(V_1) = \frac{\varepsilon_d}{|V_1 - V_c|^q}, \quad \omega = 0 \qquad (4)$$

The calculation was performed with the same values of V_c that were obtained from the experimental dependences of σ on V_1, as described above.

Figure 2 shows that for pyropolymers, the experimental dependence of ε on V_1 does not agree with the dependence calculated using this formula and shows an additional contribution to ε. It is noteworthy that for this pyropolymer the V_1-dependence curve for ε is similar to the V_1-dependence curve for σ.

Based on the qualitative interpretation of the sharp increase in ε near the percolation threshold [13] and physical concepts of the “hierarchy” of electrically connected spatial structures in composites [11], taking into account that for the corresponding composite materials studied here, the V_1-dependence curves for ε and σ are similar, we can offer the following interpretations of the behavior of ε.

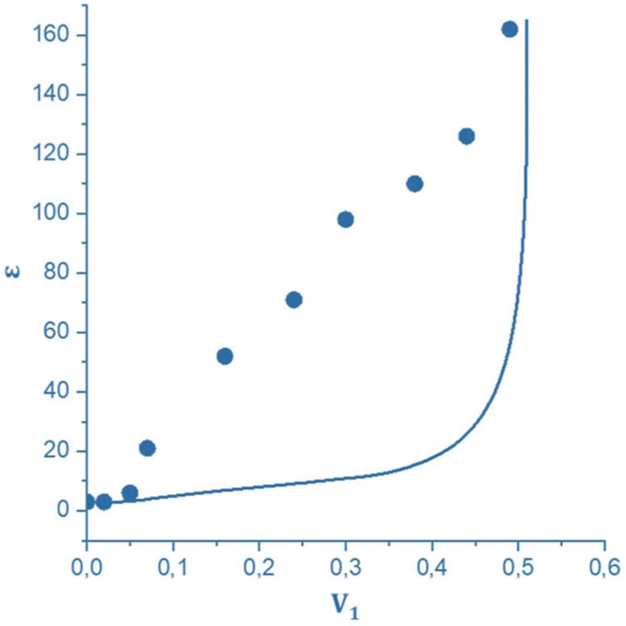

Fig. 2. Comparison of experimental (dots) and calculated (solid curve) values of static dielectric constant as a function of the volumetric content of nanofibrous “conducting” particles-polyconjugation regions (V_1). 1- ε_{dis}. according to (3).

In the pyropolymers under study, as V_1 increases, clusters of polyconjugation regions are formed, which are separated by the dielectric material of the matrix. Each pair of these clusters forms a capacitor. In our case, the presence of a characteristic feature in the V_1 dependence for ε at the additional percolation threshold V_{cd} discussed above allows us to conclude that capacitors that include non-nearby clusters contribute to the macroscopic capacitance along with capacitors that include nearby clusters.

The change in the course of the curve of ε *versus* V1 for this composite in the Vcd region can be attributed to the process of formation of a continuous spatial structure of tunnel-connected conductors.

To clarify the formation of a continuous spatial structure of tunnel-connected conductors in pyropolymers, we studied their temperature dependences of conductivity.

It is known that relatively low-temperature ($T \leq 450$ K) electrical transfer in semiconductor PAN is carried out by Mott hopping conduction with a variable hop length (Variable range hopping, VRH) [14].

$$\sigma = \sigma_0 \exp[-(To/T)^x] \qquad (5)$$

where the numerical value of the indicator x - 0.25 was confirmed in [5] by the rectification method in pre-selected coordinates 1gσ - $T^{-1/4}$. However, our analysis based on the data from these works shows that rectification is also possible on other scales with no less accuracy. Therefore, the question arises about the exact determination of the exponent x in (5), and ultimately the energy variation of the density of localized states $g(\varepsilon) = g_0 (\varepsilon - \varepsilon_F)^n$ near the Fermi energy ε_F, since the relation $x = n+1/n+d+1$, where d is the dimension of space.

The results of measurements of σ*(T)* for a series of PAN samples are shown in Fig. 3. To determine x in Eq. (5) in pyropolymers, the method of analyzing the temperature dependence of the reduced activation energy of conductivity was used. We used this processing method to study the temperature dependence of the conductivity of composite ceramic and polymer materials containing nickel nanoparticles [15,16].

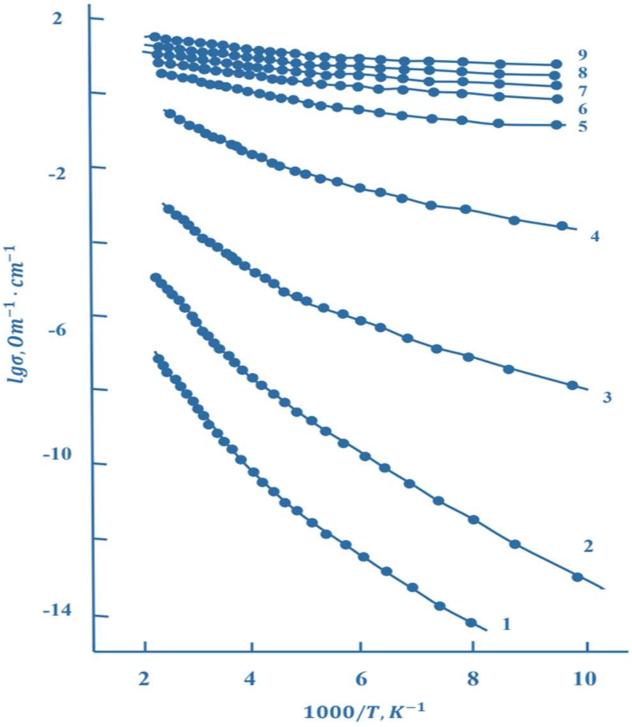

Fig. 3. Electrical conductivity of pyro-PAN, heat-treated at T_t, °C: 1-350, 2-450, 3-550, 4-650, 5-750, 6-850, 7-900, 8-1000, 9-1100.

In [17] it is shown that to determine x one can use the equation

$$Lg\omega = B - x\lg T$$

$$\omega = -\frac{1}{T}\frac{\partial \lg\sigma}{\partial T^{-1}} = \frac{\partial \lg\sigma}{\partial \lg T} \tag{6}$$

where B = const, ω-reduced activation energy of conductivity.

Figure 4 shows the temperature dependence of ω for the samples, obtained by graphically differentiating the curves in Fig. 3 in coordinates lgσ - lgT.

It can be seen that there are three characteristic regions: high and low temperature, separated by a transition region. In the high-temperature region to the right of curve a, in Fig. 4 *lgω* - *lgT*, which corresponds to $x = 1$ in (5), *i.e.* conductivity with constant activation energy Δε.

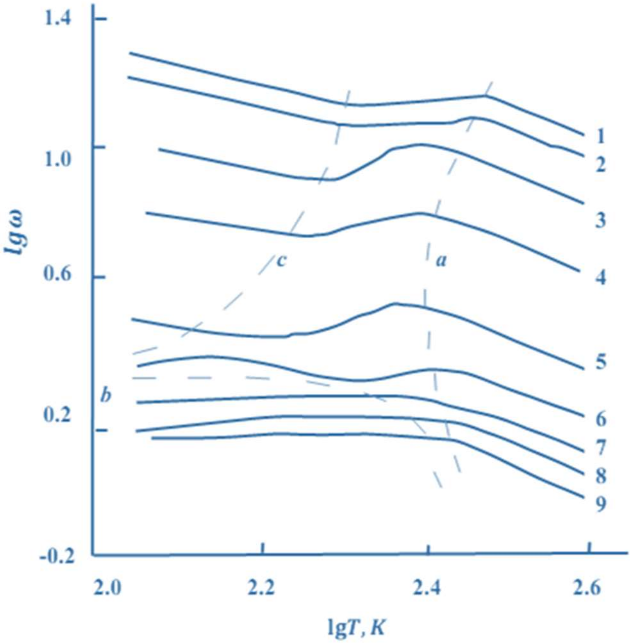

Fig. 4. Dependence of the reduced activation energy of pyro-PAN on temperature. Designations as in Fig. 3.

$$\sigma = \sigma'_0 \exp(\Delta\varepsilon/kT) \tag{7}$$

At relatively low temperatures (to the left of the c curve) *lgω-x lgT c* x ~ 0.5. This corresponds to a special case of law (1) for conductivity with variable activation energy (Fig. 4).

$$\sigma = \sigma''_0 \exp[-(To/T)^{1/2}] \tag{8}$$

Analysis of the temperature dependence of electrical conductivity within the framework of the local activation energy of conductivity shows that in semiconductor pyropolymers based on polyacrylonitrile in the region below the classical percolation threshold of percolation, in the high-temperature region, the main contribution to electrical conductivity comes from tunneling of charge carriers between the nearest-neighbor and non-nearest-neighbor polyconjugation regions with constant conduction activation energy.

At relatively low temperatures, electrical transfer in such systems is also carried out by tunneling charge carriers between nearest-neighboring and non-nearest-neighboring polyconjugation regions, but is characterized by the so-called "sliding" activation energy, *i.e.* the jump length (r) increases with decreasing temperature according to the law r ~ $T^{-1/2}$ [17]. In the transition region, both of these conduction mechanisms smoothly transition from one to the other.

CONCLUSIONS

Conductivity σ and static permittivity ε from the fractional content of polyconjugation regions V of heat-treated polyacrylonitrile products were measured in the vicinity of the percolation threshold. It has been established that below this threshold, the experimentally obtained dependences of conductivity and static permittivity on the volumetric content of polyconjugated regions in these materials differ from the dependences calculated within the framework of the percolation theory, with the fact that the curve of this dependence for ε is similar to the curve for σ.

It is concluded that in the studied pyropolymers the process of percolation-tunneling, which is considered (Balberg *et al.*) as the cause of the "low" percolation threshold V_{cd} and determines the behavior of σ in the region below the classical percolation threshold, also determines the behavior of ε in this region. Based on an analysis of the temperature dependence of conductivity in them within the framework of the local activation energy of conductivity, the formation of a continuous spatial structure from tunnel-connected polyconjugation regions was confirmed.

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