

## INFLUENCE OF STRUCTURAL DEFECTS ON THE THERMOPHYSICAL AND MAGNETIC PROPERTIES OF POLYANILINE

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*The temperature dependences of the thermophysical and paramagnetic properties of polyaniline that contains variously structured impurity centers have been investigated. The results obtained have been explained on the basis of the theory of phase transitions of second order.*

Current-conducting polymer materials represent a new class of materials widely used in electronics [1–3]. Many fundamental aspects of the electronic and structural properties of current-conducting polymer materials are still poorly known, since these are rather complex systems whose properties are largely determined by the low dimension, the disorder factor, and the significant phonon-electron interaction.

Among the wide class of current-conducting polymer materials, polyaniline (PANI) is characterized by highly stable electrophysical properties and a comparatively accessible technology of synthesis. Moreover, PANI is characterized by a fundamentally new type of doping (protonation with acids) in which the number of electrons in the backbone polymer chain remains constant. The structural, electrophysical, optical, and thermophysical properties of PANI have been investigated and described in [4–6]. However we emphasize that there has been no consensus of opinion on the interrelation between the structural properties of PANI and its thermophysical, electrophysical, and magnetic parameters until the present time. In this connection, in the present work we give new experimental results on the thermodynamic and magnetic properties of PANI.

The technology of synthesis of PANI and the doping conditions have been given in [7] in detail. The thermophysical properties have been investigated on a universal low-temperature thermophysical standard setup; the determination error was no higher than 0.4% for the specific heat and 4% for the thermal conductivity.

**Thermophysical Properties. Thermal Conductivity.** The temperature dependence of the thermal conductivity of the initial PANI [ $\lambda(T)$ ] has a "classical" form for amorphous polymers. In its doping, we observe a substantial deviation of [ $\lambda(T)$ ] from the classical form, and an activation addition to the thermal conductivity  $\Delta\lambda$  appears, which strongly depends on both the concentration of the dopant and the dopant temperature (Fig. 1). In investigating the concentration dependence of  $\Delta\lambda$  of PANI samples, it has been revealed that the sharpest increase in  $\Delta\lambda$  corresponds to the region of temperatures 180–200 K, i.e., we observe the characteristic temperature  $T_c$  of appearance of  $\Delta\lambda$ ; the location of  $T_c$  and the height of the jump (i.e., the absolute value of  $\Delta\lambda$ ) were substantially dependent on the dopant concentration — as the latter increased, we revealed a shift of  $T_c$  to the region of high temperature. It is noteworthy that the [ $\lambda(T)$ ] given earlier [5] and investigated by us in detail follow the analogous thermal-conductivity curves. Since thermal conductivity and electrical conductivity are kinetic parameters and the mechanisms of transfer of heat and charge are qualitatively interrelated, let us consider them. The transfer of charge and heat carriers in current-conducting polymer materials is usually activation-type, just as in other disordered systems. The analysis of the models of jump-like and tunneling activation transitions shows that the first model is more preferable. The influence of the ionized states of molecular media on the electron-phonon interaction can result in self-localization in which, due to the polarization of the molecules by the carriers, they themselves are left in the potential wells produced. In this case, transition to the next site requires the activation energy to overcome the barrier whose value is equal to the binding energy of the defect. It is common knowledge that PANI is a simple molecular system and, because of the nondegenerate state, it be-

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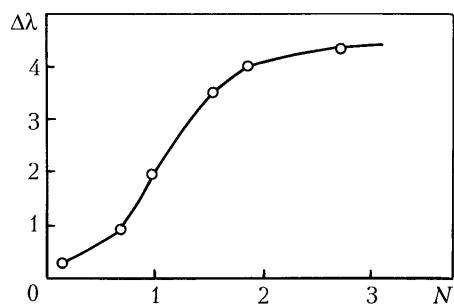


Fig. 1. Activation thermal conductivity vs. concentration of the dopants.  $\Delta\lambda$ , W/(m·K);  $N$ , mole/g.

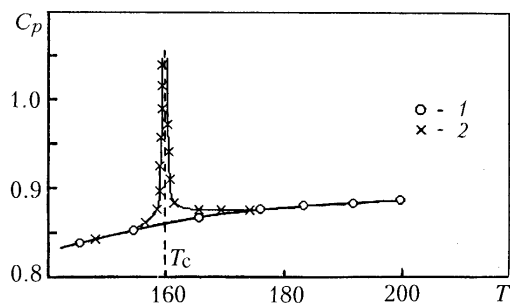


Fig. 2. Temperature dependence of the specific heat of PANI: 1) initial PANI and 2) doped PANI ( $N = 0.2$  mole/g).  $C_p$ , kJ/(kg·K);  $T$ , K.

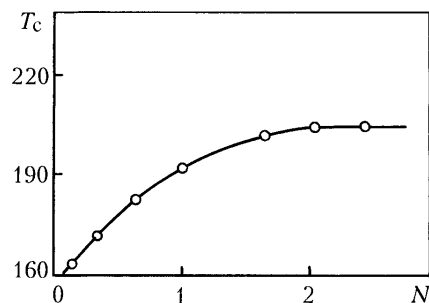


Fig. 3. Characteristic temperature of the anomaly of the specific heat of PANI vs. concentration of the dopants.  $T_c$ , K;  $N$ , mole/g.

longs to the class of combined Peierls dielectrics in which the elementary excited states can be polarons or solitons representing the defects of the polymer structure. It has been established in x-ray structural investigations [6] that PANI has both amorphous and polycrystalline regions the boundary between which is very indistinct. The presence of blocks and regions of various size determines the spread in electronic levels; levels with different polarization energies occur, which results in the localization of electronic states. Therefore, we may assume that charge carriers are transferred by thermally activated jumps of variable length between the localized states. Within the conjugate chain, the carriers are moving as in a single potential well with a periodic potential determined by the polymer chain. Analysis of the experimental results obtained on electrical conductivity [6] with the use of the Mott theory shows that electrical conductivity is well described by this theory only at temperatures higher than  $T_c$ , which suggests a change in the mechanisms of charge transfer at  $T_c$ . Investigations of the temperature dependence of the permittivity of PANI in a wide frequency range [7] have shown that the dimensions of the crystalline regions monitor the properties of a microwave to transfer charge at low temperatures. At the same time, the nature of the amorphous bond between crystalline domains enhances the delocalization of the charge, which is observed with increase in the temperature, and it can depend on the local structure (taken by the dopant in the PANI chain) and in the degree of paracrystallinity. Therefore, we may assume that the observed features of the thermal conductivity of PANI at  $T_c$  are related to the change in the structural defects of PANI. The calculations show that this is due to the appearance of the so-called polaron heat conduction.

*Specific Heat.* The temperature dependence of the specific heat of the initial PANI has a classical character, just as the thermal conductivity, but, in doped PANIs,  $\lambda$ -like peaks are superimposed on the linear character of the temperature dependence of the specific capacity in the temperature range 170–200 K (Fig. 2); the presence of these peaks can be explained as the structural phase transition of second order [6] related to the change in the PANI structure. We note that the increase in the dopant concentration, which results in a growth of 8 to 10 orders of magnitude in the electrical conductivity, exerts a substantial influence on both the absolute value of the specific capacity of PANI and the values of  $T_c$  (Fig. 3). It has been established by x-ray structural investigations that, depending on the doping level, the PANI structure takes the following different states at temperatures higher than  $T_c$ : amorphous state with un-

TABLE 1. Magneto-resonance Parameters of the EPR Spectra of PANI in Undoped and Doped States

PANI	$g$ factor	PMC·10 <sup>19</sup> , spin/G	$\Delta H_{pp}$ , G	$A/B$
Undoped	2.00316	6.6	5.30	0.94
Doped	2.0029	8.4	0.75	1.20

bound metal islands, a polycrystal with unbound metal islands, and a polycrystal with weakly bound metal islands. Therefore, the dependence of  $T_c$  on the doping level and its shift toward the higher-temperature region are attributable to the fact that the crystallinity of the polymer increases four to five times in this case, and this increases the probability of interaction between polymer chains.

Thus, by the investigations of specific heat, thermal conductivity, and electrical conductivity we have established the presence of reversible phase transitions which are due to the transformation of the defect states of the PANI polymer chain and to the change in the intermolecular interactions between them.

**Electron-Paramagnetic-Resonance (EPR) Spectra.** The temperature dependences of the EPR spectra of PANI were recorded on an ESP-300 spectrometer of the three-centimeter-range (Brooker Company) with an ESP-1600-computer-based control and data processing system [7].

The EPR spectra of PANI samples in undoped and doped states represent single signals whose parameters are given in Table 1. The second PANI differs from the first one by a low value of the line width  $\Delta H_{pp}$ , a high concentration of paramagnetic centers (PMCs), a nearly Dyson signal shape (characteristic of metals), and a  $g$  factor closer to the  $g$  factor of a free electron. These differences are determined by the contribution (increasing in doping) of the Pauli paramagnetism in the conducting state.

The integral dependence of the intensity of an EPR signal on the temperature for PANI has a nonmonotone character, just as in the case of electrophysical and thermodynamic characteristics, and it shows an inflection at  $T_c$ . The detected extrema of the temperature dependences of the intensity and width of the EPR signal of the PANI samples are, apparently, attributable to the following fact. The linear character of the dependence of the intensity of the signal in the range of temperatures lower than  $T_c$  indicates that the concentration of the paramagnetic centers in this temperature interval is constant. At a temperature higher than  $T_c$ , the slope of the curve begins to smoothly change up to 300 K. This can occur only in the case where one observes a constant (throughout the indicated temperature range, i.e.,  $T \geq T_c$ ) change in the concentration of the paramagnetic centers and, in particular, in conformation transformations in the molecular chain. Similar reasoning can lead us to the assumption that an increase in the temperature above  $T_c$  in the absence of any conformation changes would result in a narrowed width of the signal. However in our case a conformation change at  $T_c$  brings about new paramagnetic centers while a decrease in the signal width enables us to assume that here we have a growth in the contribution of mobile spins. Investigation of the concentration dependence of the EPR spectra of PANI shows that, as the concentration of dopants increases, there is an increase in the degree of crystallinity of the polymer and accordingly a growth in the concentration of paramagnetic centers.

## CONCLUSIONS

1. Change in the degree of imperfection of PANI in doping results in different structures of the polymer and accordingly different values of the temperature  $T_c$ .
2. Change in the structure of polymeric defects under different conditions of synthesis, doping, and temperature determines the observed features of the temperature dependences of the electrophysical, thermophysical, magnetic, and optical properties of PANI.
3. Taking into account the results of the earlier investigations, we can point to the identity of the physical processes observed in PANI, i.e., phase transitions of the disorder–order type.

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## NOTATION

$\lambda(T)$ , temperature dependence of the thermal conductivity;  $\Delta\lambda$ , activation additional thermal conductivity;  $C_p$ , specific heat at constant pressure;  $N$ , concentration of the dopants;  $T$ , temperature;  $\Delta H_{pp}$ , EPR line width;  $g$ , wave

vector of a free electron;  $A$  and  $B$ , low and high-field components of the signal. Subscripts:  $c$ , critical (temperature);  $pp$ , notation in EPR, marking the experimental features.

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