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ELECTRO-AND THERMOPHYSICAL PROPERTIES OF POLYANILINE

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The electrophysical and thermophysical properties of electrically conducting polyaniline are investigated in a wide temperature range (77–500 K). Possible mechanisms of polyaniline electrical conductivity depending on the synthesis conditions, doping level, and temperature are analyzed.

Introduction. Polyaniline (PANI) is a well studied polymer and can, as polyacetone, be considered a classical representative of conducting polymers with a network of conjugate bonds.

A specific feature of PANI, as compared to other conducting polymers, is the high stability of its conducting properties. PANI is a rather easily synthesized (both chemically and electrochemically) polymer, and its electrical conductivity in a doped state reaches $10^2\ \Omega^{-1}\cdot\text{cm}^{-1}$. Moreover, PANI has a radically new type of doping: protonation by acids, in which the number of electrons in the major chain of the polymer does not change, as it does in other conducting polymers.

In [1-3] it is shown that PANI conductivity depends equally on the degrees of both oxidation and protonation. It is also noted that σ has a higher value in the intermediate PANI form, since intermediate radical-cations are more stable in an aqueous solution than in oxidized and reduced forms. The structural, electrochemical, and optical properties of PANI as well as its conductivity mechanisms are well studied theoretically and described in [4-6]. However, it should be noted that so far there is no unified opinion concerning the relationship between the specific structural features of PANI and its electrical and other properties. Investigation of the physical properties of PANI in a wide temperature range depending on the synthesis conditions and the degree of doping is, in our opinion, of both theoretical (understanding of the conductivity mechanism) and practical (creation of various devices) interest. Therefore in this work we report the results of investigations of the electrophysical and thermophysical properties of PANI in the temperature range of 77–500 K.

1. Electrophysical Properties. Polyaniline was synthesized by aniline oxidation with ammonium persulfate in an aqueous solution of hydrochloric acid [7]. Doping of the PANI films was accomplished by holding them for 24 h in solutions of hydrochloric acid with different concentrations. The increase in conductivity in the case of HCl treatment is attributable to the fact that in the polymer, which can be represented as a copolymer consisting of diamine and diimine links, protonation processes with the formation of radicals of semiquinoid structure take place [8]. Electrical measurements were made by two- and four-probe methods. Determination of the volt-ampere characteristics (VAC) and temperature measurements were accomplished in a special cryostat in the dark, and the contacts to the samples were obtained by applying silver paste to the latter. The VACs of these samples (Fig. 1a) are lineara and not related to the lay-out of the contacts. This points to spatial homogeneity of the samples investigated in the form of both tablets and films. With an increase in the degree of doping, we observed current build-up in the sample (Fig. 1a, curves 2 and 3). In this case, the ratio of dark currents of the undoped and doped (in 1.0 N HCl) PANI at $U = 10$ V was ~10^6.

From the viewpoint of thermal stability it was interesting to study the influence of temperature on the PANI electrophysical properties. We investigated the influence of the current running through the PANI at a constant voltage in the temperature range of 20–150°C (Fig. 1b). It was found that, depending on the degree of doping,

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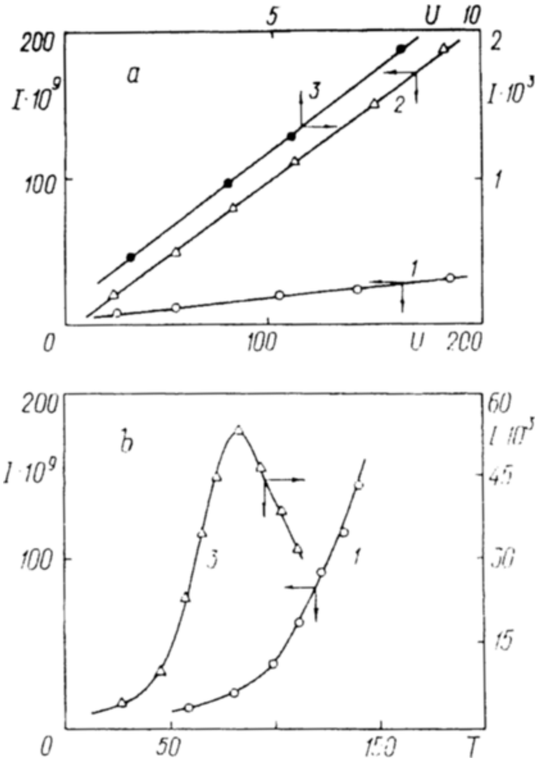


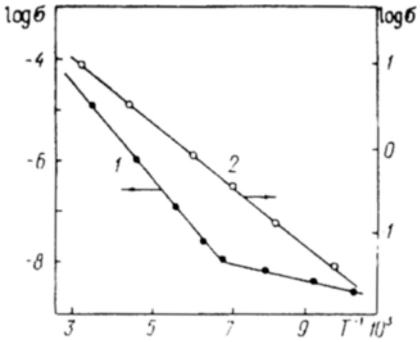
Fig. 1. Volt-ampere characteristics of polyaniline (a) and temperature dependence of direct current in it (b): 1) undoped; 2, 3) doped in $5 \cdot 10^{-2}$ and 1.0 N HCl, respectively. I, A; U, V; T, °C.

the films had different levels of conductivity and temperature curves (Fig. 1b, curves 1 and 3). Thus, when a film was doped in 1.0 N HCl at a temperature higher than 80°C, the conductivity decreased, which was probably attributable to dehydrochlorination, i.e., the release of a certain part of the HCl from the PANI. This is also confirmed by the fact that with film cooling to room temperature, the conductivity falls by a factor of four as compared to its initial value before heating. With a decreasing degree of polymer doping, the changes in conductivity due to dehydrochlorination are less pronounced. We conclude that with a decrease in the degree of PANI doping, it becomes difficult for HCl to leave the polymer.

In the case of undoped PANI film, the temperature dependence of current shows the opposite trend, i.e., for one cycle of annealing the film conductivity undergoes more than a two-fold increase. This is apparently due to partial conformational ordering of the olygomeric chains of the PANI or to film sorption of moisture, CO_2, and other dopants during heat treatment in air.

To refine the above assumptions by the derivatography method, we investigated PANI behavior in the temperature range of 15–350°C. As the thermogravimetric analysis showed, the weight of the undoped PANI was practically unchanged at temperatures up to 300°C. With an increased degree of doping in the interval of 50–175°C, the samples lost weight, with the loss percentage increasing in proportion to the dopant concentration in the initial polymer, which can be explained by the fact that HCl leaves the polymer. With a further temperature increase to 300°C, no changes in the polymer weight were found, but starting from 325°C we observed considerable losses in the sample weights, which were apparently attributable to polymer destruction. In this case, the losses were inversely proportional to the HCl content in the initial polymer. These studies confirm the conclusions about the decrease in electrical conductivity as the dopant leaves the samples on their heating.

Some interesting features of the temperature dependence of σ were found when investigating $\sigma = f(T)$ at low temperatures $T = 77-300$ K. Measurements were made for alternating and direct currents using an E9-4 bridge or an E7-30 electrometer voltmeter at $E = 50$ V/cm.



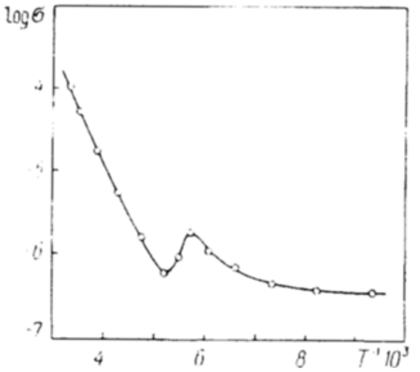


Fig. 2. Temperature dependence of electrical conductivity of undoped (1) and doped in 2.0 N HCl (2) PANI in a constant electric field; T, K.

Fig. 3. Temperature dependence of σ of undoped PANI synthesized in formic acid in electric field at $f = 1$ kHz.

Figure 2 shows σ versus temperature for undoped (curve 1) and 1.0 N HCl doped PANI samples measured with direct current. In the case of the undoped PANI two characteristic regions of σ variation are seen. In the first region, σ depends slightly on T, and this dependence is identical for both tablets and films. In the second region, i.e., at higher temperatures, the slope of the $\sigma = f(T)$ curve changes, thus pointing to a change in the energy of the process. The position of the transition of bending from the first to the second region ($T \sim 175$ K) depended on the doping level, which with a increase in the latter shifted to the region with a higher temperature. Figure 2 (curve 2) shows that as PANI passes into a highly conducting state, these charactetistic regions disappear and σ changes according to an exponential law with activation energy $\Delta E = 0.2$ eV. As follows from these curves, the character of the temperature dependences of σ for doped and undoped PANI is apparently attributable to differences in the electrical conductivity mechanisms for different temperature ranges. Though the temperature dependence of σ for the doped PANI is well described by

$$\sigma = \sigma_0 \exp\left(-\Delta E/kT\right), \tag{1}$$

for the undoped PANI formula (1) does not hold, since it pertains to impurity conduction. For this, two straight sections with the same E_σ must be observed in the $\ln\sigma \sim 1/T$ plots, with lower E_σ corresponding to the impurity conduction region, higher E_σ to the intrinsic conduction region, and the transition between them to depletion of the doping impurity. Though such behavior is observed in the undoped PANI, it does not confirm the impurity nature of conduction, since polyconjugate systems must have a slightly higher E_σ [9].

The temperature dependence of the conductivity of semiconducting polymers in a wide temperature range corresponds to the Mott law [10]

$$\sigma = \sigma_0 \exp\left[-(T_0/T)^x\right], \tag{2}$$

which was proposed to describe disordered systems in which carriers are transferred by thermally activated jumps of variable length between localized states. It can be assumed that within the limits of the conjugation chain the carriers move as in a common potential well with a periodic potential specified by the chain structure. The presence of polyconjugation blocks and regions of different size is responsible for the spread of electronic levels, which gives rise to levels with different ionization energies. The spread of levels causes localization of electronic states, while thermal localization makes electrons jump between these localized states, thus initiating electrical conductivity.

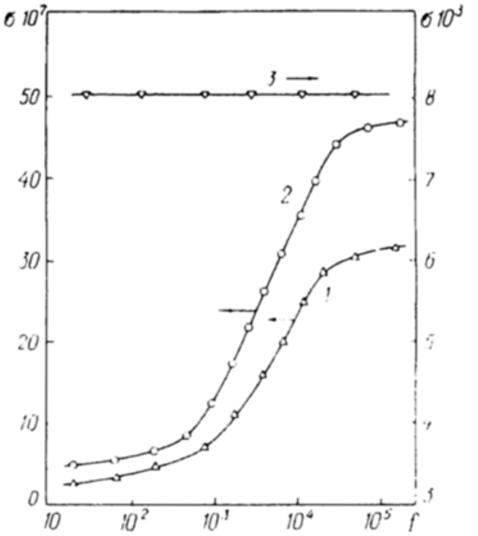
An analysis of $\sigma = f(T)$ using ordinary methods of mathematical statistics to process the results (checking of fulfillment of one of the two dependences at $x = 0.25$ and $x = 0.5$) has shown that $\sigma = f(T)$ is described well only in the second region after the bend with $x = 0.25$. This case corresponds to the random distribution of localized states [11]. The first region of $\sigma = f(T)$ does not obey the Mott law. From the aforesaid we can assume that the changes in $\sigma(T)$ are attributable to changes in the mechanisms of carrier transfer due to structural rearrangement of the polymer chain at the transition temperature T_{tr}. The dependence of T_{tr} on the doping level and its absence in strongly doped PANI indicates clearly that the assumption is correct.

A structure itself of conducting polymers, which is characterized by microinhomogeneity, forecasts changes in an alternating field, where conductivity variance must be manifested in a temperature range determined by the properties of the polymer structure. Indeed, some interesting features have been found in the temperature dependence of σ measured with alternating current with a frequency of 1 kHz and higher. As is seen in Fig. 3, the behavior of σ of undoped PANI synthesized in formic acid is anomalous at $T \sim 180$ K. With a temperature rise from 90 to 180 K, σ is practically unchanged, which is probably due to strong localization of the charge carriers in the polymer chain. At a temperature near ~180 K, σ grows and then has a bend point. It should be noted that such anomalous behavior of σ is dependent on the doping level, and in the case of strong doping, $\sigma = f(T)$ becomes a linear dependence.

This regularity manifested in undoped PANI in $\sigma = f(T)$ investigations conducted with both direct and alternating currents makes it possible to conclude that the anomalous behavior near 180 K can be attributable either to conformational changes in the polymer structure or reorientation of defect states in the polymer chains.

The frequency dependence of polyaniline conductivity was investigated in the range of from 10^1 to 10^5 Hz at room temperature (Fig. 4). As is seen, it is rather peculiar. In the undoped PANI, the dependence is weak up to a frequency of 10^3 Hz, but after this frequency, it increases. In the section after 10^3 Hz, the $\sigma \sim f^s$ regularity, with s lying within 0.8–0.92, is observed. Our results are in good agreement with the data or [12], where an increase in σ of the initial PANI by an order of magnitude was observed in the frequency range of $10^3 - 10^5$ Hz. In the case of PANI synthesized in formic acid, the increase in σ in the same frequency range is greater. Such a specific feature of the frequency dependences of σ for PANI obtained in hydrochloric and formic acids can be explained by differences in packing density and structure ordering. As x-ray analysis has shown, PANI synthesized in formic acid has a close-packed structure similar to a "crystalline" one. From this it is inferred that the frequency dependence of σ is determined by an increase in the probability of carrier jumping from one macromolecule to another [13]. Indeed, at low frequencies up to 10^3 Hz, the share of intermolecular transitions of carriers is low and practically independent of frequency. With increasing frequency, the polymer macrochains undergo reorientation, and, as a consequence, the activation energy of barriers decreases and the probability of jumping, and, consequently, the electrical conductivity increases. In this case, the barrier mechanism of σ is confirmed not only by an increase in electrical conductivity depending on the packing density of the polymer but also by the fact that in the case of strong doping, i.e., opening a conduction "channel," σ does not depend on frequency in the entire range investigated (Fig. 4, curve 3).

2. Thermophysical Properties. As shown above, investigation of the temperature-dependent PANI conductivity has revealed a change in the mechanism that is attributable to structural rearrangement. Therefore, a complete understanding of such structural changes, i.e., molecular processes, requires experimental evidence. Note that thermophysical data are especially valuable in the interpretation of transitions in which simple "order-disorder" effects prevail [14], while thermophysical methods can be employed as a structure-sensitive tool for investigation of such effects. Therefore, we report the results of investigations of thermophysical properties, i.e., the temperature-dependent thermal conductivity and heat capacity, of PANI with different levels of doping.



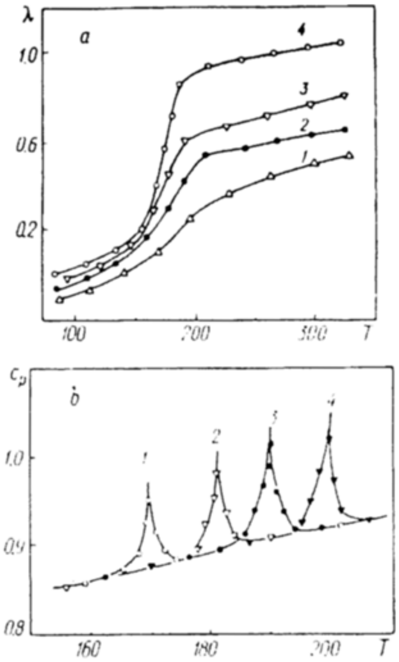


Fig. 4. Frequency dependences of σ of PANI synthesized in hydrochloric (1) and formic (2) acids. Curve 3 pertains to the doped PANI. f, Hz.

Fig. 5. Temperature dependences of thermal conductivity (a) and heat capacity (b) of PANI: 1) undoped; 2, 3) doped in 0.5 and 2.0 N HCl, respectively; 4) PANI obtained in formic acid. λ, W/m·K; c_p, kJ/kg·K.

Thermal conductivity λ was determined by the pulsed probe method [15]. A tungsten probe was placed between two identical polymer tablets in a thermostat. Measurements were made in an inert N_2 atmosphere. The system was controlled and data were acquired and processed by an Élektronika 1103 computer. The error of the method was not more than ~5%.

Figure 5a shows a temperature dependence of λ of the PANI. It is seen that λ increases with temperature. For the all polymers investigated, the dependence $\lambda = f(T)$ shows two regions of temperature coefficient variation with a characteristic region of T_{tr} where a jump in $\lambda(T)$ occurs. It should be noted that with a change in the degree of doping, the character of the jump remains unchanged; only its amplitude and the temperature range of its manifestation change. The jump in $\lambda(T)$ is apparently due to the glass transition process, i.e., to conformation and configuration changes in the structure and, consequently, to a change in the conditions of heat transfer through the sample. The further increase in $\lambda(T)$ described by the expression [16]

$$\lambda = 1/3 \sum \int c_{vi}(w)\, \bar{v}_{si}\, \bar{l}_i(w)\, dw\,, \tag{3}$$

where $c_{vi}(w)$ is the heat capacity, $\bar{v}_{si}$ is the mean sound velocity, and $\bar{l}_i$ is the mean free path length of the i-th phonon, is apparently due to a linear increase in $c_p(T)$. From (3) it follows that an insignificant change in $\bar{v}_{si}$ or $\bar{l}_i(w)$ which can be calculated from

$$\bar{l} = \frac{3\lambda}{c_v \bar{v}_s} \sim 10^{-9} \ \text{m}\,,$$

will exert an influence on λ. The obtained $\bar{l}$ value is determined by the length of the polymer chain for this temperature range. As the calculated free path length of phonons and our experimental data obtained for PANI show, phonon scattering depends on the packing density of the polymer. In polymers with strong intermolecular interaction, phonons are scattered over great lengths, and, as a consequence, in this case energy transfer proceeds more intensely. Therefore, the character of the temperature dependence of λ, namely, its increase with temperature, is determined by the intensity of thermal motion as well as by changes in intermolecular interaction. As a result, in the PANI synthesized in formic acid the increase in λ in the 200–300 K range is greater (Fig. 5a, curve 4), since its structure is much denser than that of the PANI obtained in HCl.

A temperature-dependent c_p was measured by a vacuum-adiabatic calorimeter [17] with an error of 0.5%.

The measurements revealed that in the investigated temperature range of 80–300 K the temperature dependence of heat capacity is linear for the all polymers obtained. However, in the 170–200 K range for the polymers with an amorphous structure the linear trend is disturbed by Λ-shaped peaks (Fig. 5b), the presence of which can be characterized as a structural phase transition of the second kind. It should be noted that doping of the initial PANI-HCl compounds with different concentrations, resulting in an increase in electrical conductivity by 8–10 orders of magnitude, exerts a substantial influence on the absolute c_p value. Figure 5b shows that as the degree of PANI doping increases, the Λ-shaped peak on the $c_p(T)$ curve is shifted toward higher temperatures. In the heat capacity curve corresponding to PANI synthesized in the presence of formic acid, there is a peak, even without doping, observed at a higher temperature (Fig. 5b, curve 4). Considering that the PANI obtained in formic acid is more crystalline than that obtained in HCl, the peak displacement toward the high-temperature region could be naturally due to structure ordering of the polymer. The peak displacement with respect to temperature, depending on the degree of PANI doping in HCl, can be explained by the fact that with an increase of the latter the polymer crystallinity undergoes a 4–5-fold increase, thus increasing the probability of interaction between molecular chains.

Thus, the measurements of $\sigma(T)$, $c_p(T)$, and $\lambda(T)$ have revealed a reversible structural rearrangement in the PANI. Note that different methods determine, within the limits of error, a constant transition temperature for the same sample, which depends on the degree of doping and crystallinity of the samples. Correlation of the transition temperature in the dependences of σ, λ, and c_p shows that the only mechanism that lies behind the anomalies found is the structural rearrangement of the defect states in the PANI chain and changes in the intermolecular interactions between them.

NOTATION

σ, electrical conductivity; T, temperature, K; λ, thermal conductivity; c_p, heat capacity at constant pressure; U, voltage; E, activation energy; K, Boltzmann constant.

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