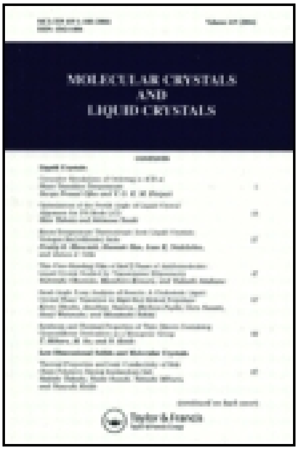

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Effect of Temperature on the Optical Properties of Conducting Polyaminoarenes and their Composites with Elastic Polymer Matrix

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Effect of Temperature on the Optical Properties of Conducting Polyaminoarenes and their Composites with Elastic Polymer Matrix

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In temperature interval 293–523 K the thermochromic effect in the films of sulfate-doped polyaminoarenes (polyaniline, polyorthotoluidine, and polyorthometoxyaniline) and their composites with elastic polyvinyl alcohol (PVA) matrix has been manifested and investigated. On the base of electronic spectroscopy, thermogravimetry and specific resistance temperature dependence data it is shown that changes in electron transition energy and film's optical density are caused by changing in macrochain conformation and connected with electronic properties of polymers. Thermochrom effect reserves in composite polyaminoarene-PVA films.

Keywords: absorption spectra; conducting polyaminoarenes; polymer composites; thermochromic effect

INTRODUCTION

Organic thermotropic materials, especially based on the liquid crystals, have a wide application in sensor devices and indicators [1]. It has been found that conjugated polymers such as poly-3-alkilthiophens [2,3] exhibit the state similar to liquid crystalline. They show a blue shift in absorption maximums and change in optical density at $T > 293\,K$. Study of temperature effect on the optical

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spectra of undoped polyanilines in solution and in solid state showed that thermochromic effect in these materials caused by the changing in polymer backbone conformation [4]. But in conducting (doped) forms of conjugated polyaminoarenes, excepting polyaniline doped by camphorosulfonic acid [5], this effect has a lack of study. In the present paper an effect of temperature on absorption spectra of sulfate-doped polyaminoarenes – polyaniline (PAN), polyorthotoluidine (POTI), poly-ortho-metoxyaniline (POMA) and their composites with polyvinyl alcohol (PVA) matrix has been studied.

EXPERIMENTAL

Preparation of polyaminoarene films was carried out in tree-compartment electrochemical cell by electrolysis of 0.1 M monomer solutions (*o*-toluidine, *o*-methoxyaniline, aniline) in 0.5 M H_2SO_4 at oxidative potential of monomers ($E = 0{,}8 - 1{,}0\,V$) during 60 min. The glass spin coated by SnO_2 working electrodes, Pt-wire counter electrodes and Ag/AgCl (in saturated KCl) as a reference were employed. The molecular structure of polymers supporting by IR-spectroscopy ("Specord M-80") for samples pressed in KBr pellets is similar to literature data [6,7] are presented in the Figure 1.

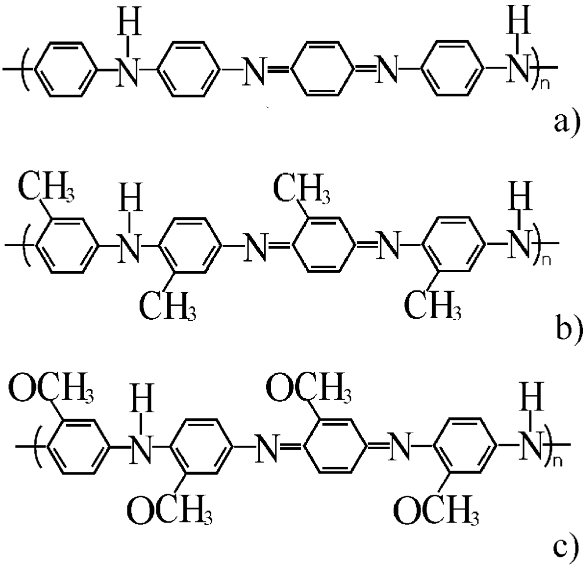

FIGURE 1 Chemical structure of conjugated polyaminoarenes: a) polyaniline, b) polyorthotoluidine, c) polyorthomethoxyaniline.

The UV-vis. absorption spectra ($\lambda = 320$–1000 nm) were obtained using the spectrophotometer SF-26 after 30 minutes of film heating at constant temperature (293 … 473 K). Investigation of polymer thermal stability was carried out on derivatograph Q-1500 D in temperature range 273–1273 K with Al_2O_3 standard and 10 K/min heating rate. The powder samples of polyaminoarenes prepared by polymerization of monomers in the presence of ammonium persulphate in 0.5 M sulfuric acid were used. Temperature dependence of the specific volume resistance was studied using a specially designed cell according to [8] in dynamic temperature regime, commensurable with the heating rate in thermogravimetry.

Composite polymer films were obtained by electrochemical polymerization of aminoarenes in the PVA film by 5 μm thickness on the SnO_2 electrode in 0.5 M sulfuric acid at $i = 0.5\,\mathrm{mA/cm^2}$ during 5–30 minutes. With increase of electrolysis time (Fig. 2) the optical density in the electron spectra of polymer composite film increases too.

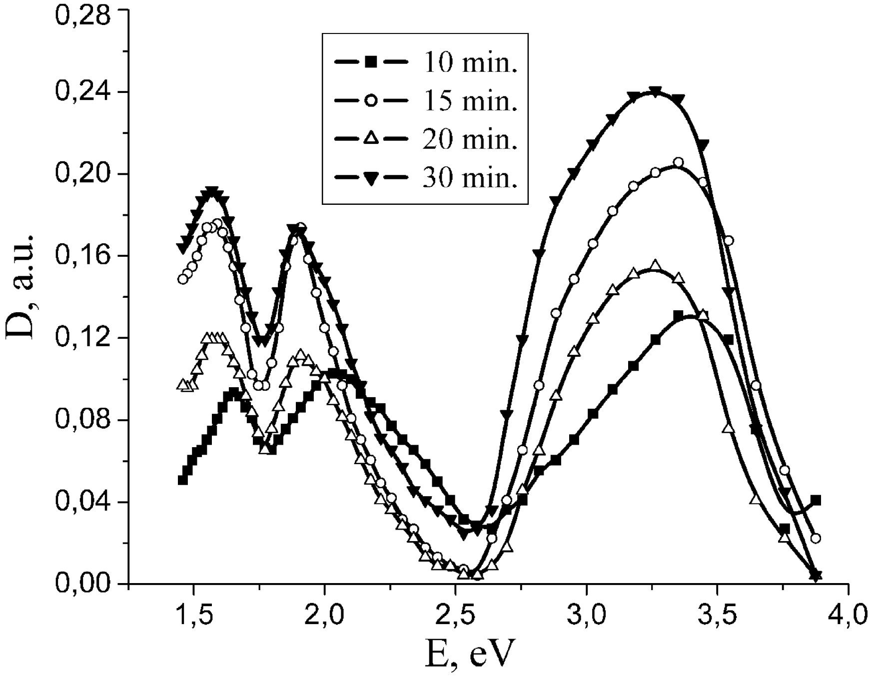

FIGURE 2 Electron spectra of PVA-PAN composite films on SnO_2 electrode at different time of electropolymerization of aniline in PVA matrix at $i = 0,5\,\mathrm{mA/cm^2}$ in 0,1 M solution of aniline in 0,5 M H_2SO_4.

RESULTS AND DISCUSSION

According to electron spectroscopy for all investigated films in near-UV and visible range of spectrum (Fig. 2, Fig. 3 a, b, c) three bands typical for absorption of polyaminoarenes are observed. The absorption maximum at 1,6–1,65 eV is characteristic of free charge carriers, delocalized along conjugated polymer chain [4]. Absorption near 1,9 eV is probably caused by n-π^* transition in imino-quinoide fragments of polyaminoarene chain. The band corresponding to energy interval 3,2–3,4 eV may be assigned to electron transition between π and π^* levels, which associated with energy of band-gap [4,5].

From the study of absorption spectra in the interval of $T = 293$–473 K a thermochromic effect in the films of POTI, PAN and POMA doped by sulfuric acid (level of doping is near 0,45 mol./aminoarene unit) has been manifested. Under temperature change the variations in the polymer films color are observed. In the optical spectra it's

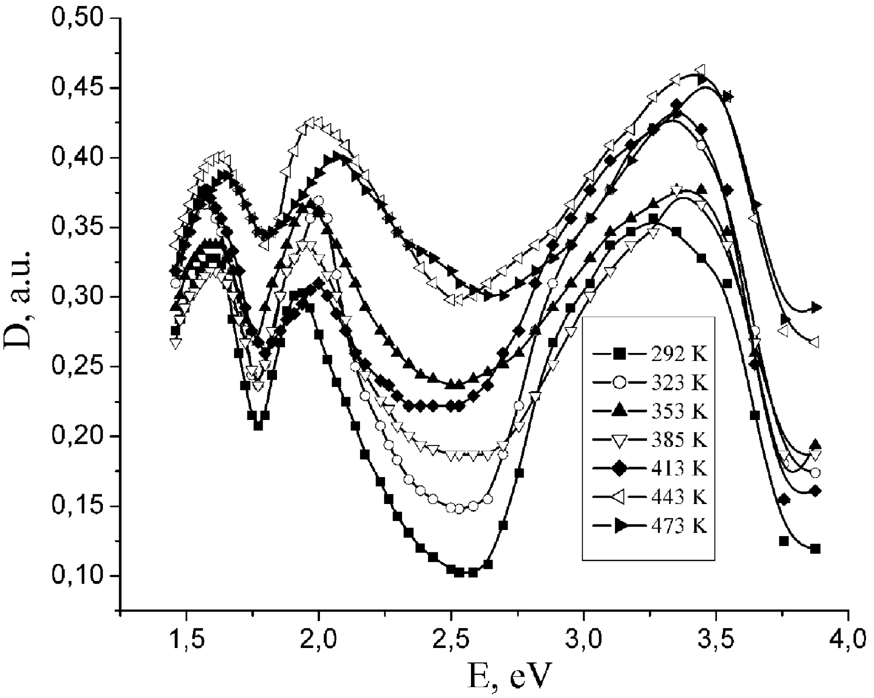

FIGURE 3 Absorption spectra of PAN a) POTI b) POMA c) POTI-PVA composite d) films heating at following temperatures.

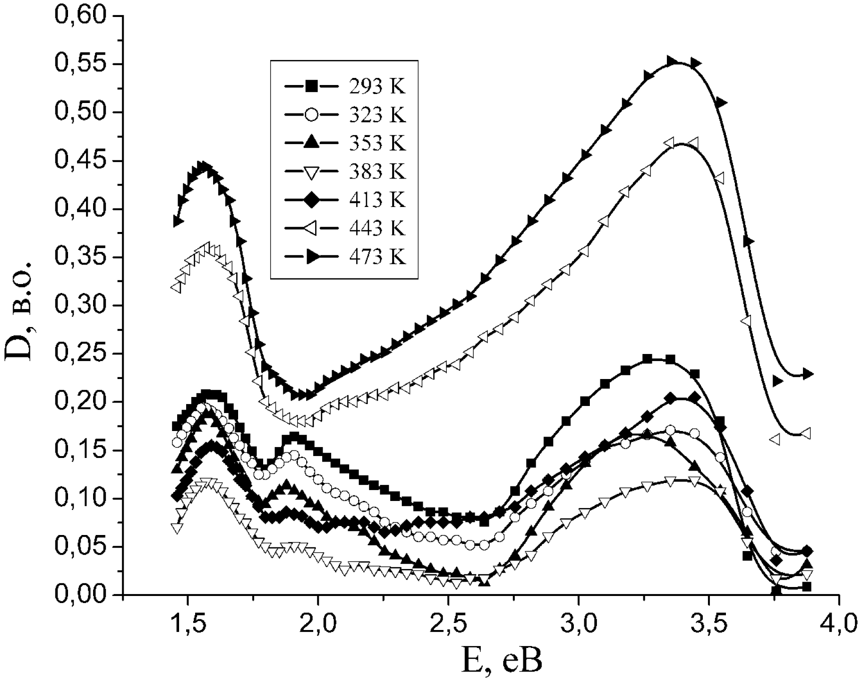

FIGURE 3 Continued.

developed in the "blue shift" of absorption maximums and in the changing of their intensity (Fig. 3). In polyaminoarene-PVA composites a thermochromic effect was also manifested. Under the thermal treatment the change of their coloration, and correspondently in absorption spectra are observed (Fig. 3d).

In electron spectra of POTI and POMA films (Fig. 3) the total decreasing of second absorption band and its almost full disappearance at T > 413 K is observed. This thermochromic change is in agreement with observations of Zheng and col [4]. for structure changes in undoped N-alkylated polyaniline films. The degradation of this band is connected with cross-linking processes flowing in the film under ambient temperature [4]. But in the case of doped PAN the intensity of this absorption band changes very small (Fig. 2a) indicating that crosslinking process requires more higher temperature.

During the study of polyaminoarene thermal stability at $T = 293$–773 K (Fig. 4) the series of peaks on DTG and DTA curves are fixed. In the case of sulfate-doped PAN it is found that endothermic maximum at $T = 403$–413 K is associated to loss of chemically

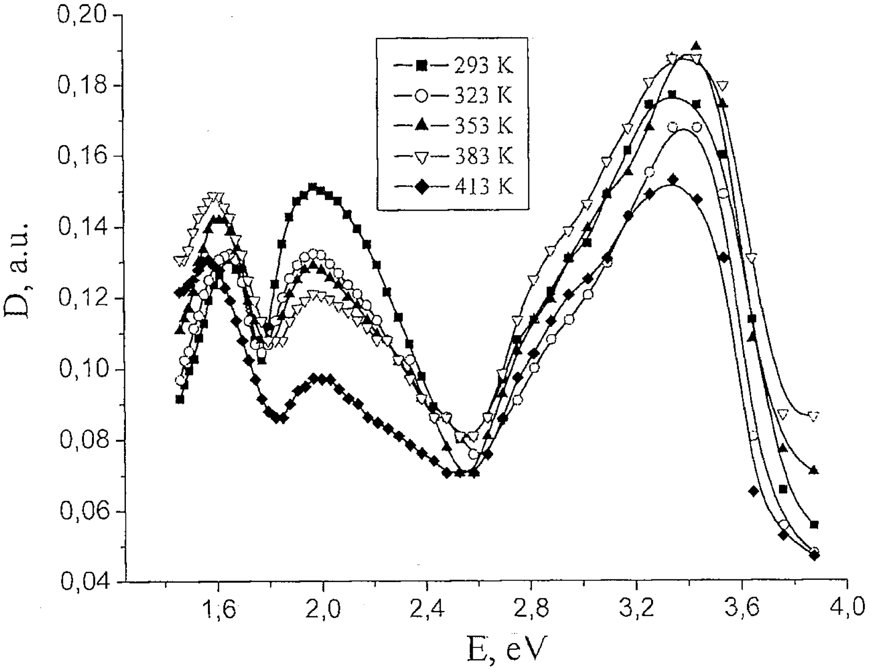

FIGURE 3 Continued.

absorption moisture. The exothermal peak at 453–473 K does not accompanied by significant mass loss and may be related to exothermal oxidation of amino-benzene fragments of polymer backbone to imino-quinoid ones [10]. At father rising of temperature the activation process of doping agents desorption (with maximum at $T = 553$ K) has proceed. It accompanied by crosslinking of PAN polymer chain [9].

In the case of POTI an endothermic maximum associated with loss of moisture is observed at $T = 373$ (DTG) and 393 K (DTA). Sequence of peaks on DTA and DTG curves in the region $T = 413$–600 K are evidences to thermo-oxidative destruction, cross-linking of polymer chains and simultaneously desorption of doping admixtures (with maximum at $T = 540$ K). Probably at these temperatures in POTI films structure changes in direct to space network formation take place. This decreases a kinetic mobility of polymer segments and brakes an internal rotation. That's why a thermochromic change in POTI films become irreversible and darkness of polymer film that causes an increasing of optical density is observed.

So far a cross-linking process in PAN films occurs at T > 493 K [8,9] but increasing of optical density observed in region 293–473 K, it may

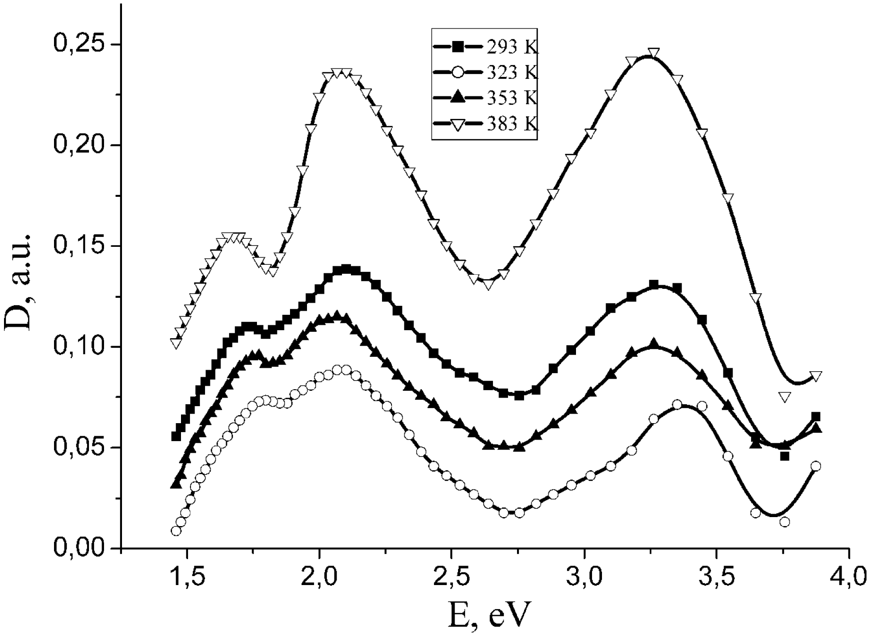

FIGURE 3 Continued.

be assume that color deepening of PAN films can be caused both by changing in polymer backbone conformation and thermal activation of charge carriers. For this examination the study of temperature dependence of polymer specific conductivity in the temperature region 293–523 K was carried out.

As shown previously [10] for temperature dependence of specific conductivity of polyaminoarenes in the region $T > 293\,\mathrm{K}$ the exponent low $\rho = \rho_0 exp(\varepsilon/2kT)$ may be used, where ε – activation energy of charge transport, ρ_0 – constant. The temperature dependence of polymers specific volume resistance, normalized to resistance defined at room temperature (ρ/ρ_{293}) for sulfate-doped PAN and POTI are shown in Figure 5. In the range 293–373 K (POTI) and 293–403 K (PAN) the linear dependence of $ln(\rho/\rho_{293}) - 1/T$ is observed, that gives a possibility to determine the value of $\varepsilon_\sigma = 0,490 \pm 0,01\,\mathrm{eV}$ (PAN) and $\varepsilon_\sigma = 0,876 \pm 0,015\,\mathrm{eV}$ (POTI). Therefore, presence of methyl substituent in the structure of POTI resulting in decreasing of linear region of $\ln(\rho/\rho_{293}) - 1/T$ dependence and considerable increasing in activation energy of conductivity for the PoTI in relation to PAN.

The temperature dependence of polyaniline–polyvinyl alcohol composite specific resistance was characterized by linear region in

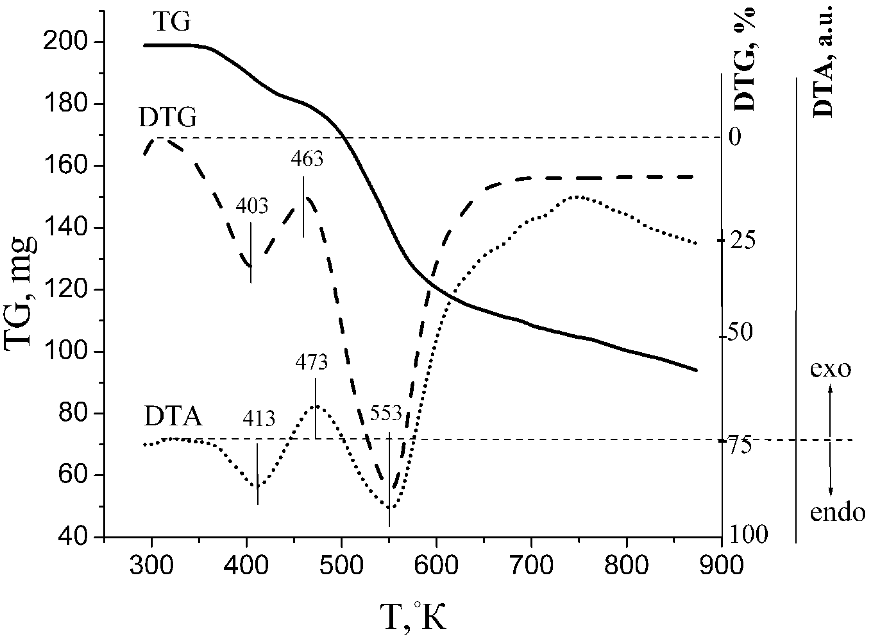

FIGURE 4 Termograms of decomposition of sulfate doped polyaniline (a) and polyorthotoluidine (b).

$ln(\rho/\rho_{293}) - 1/T$ coordinates. From obtained data the activation energy (0,53 ± 0,01 eV in temperature interval 293–353 K) was calculated. Therefore, polyaniline saves a charge transport properties, but temperature region of exponent low using is narrower.

From thermoinduced changes in optical spectra, thermal behavior and temperature dependence of specific volume resistance one can made some suppositions. It's known, that phenyl group disposition in polyaminoarenes lies under rotation angles, and phenyl ring may revolve around -C-N-bond. Since in solid state (in the film) the polymer chains mobility is considerably limited, in comparison with solution, absence of large lateral substitutes made impossible the creation of sufficient for conformation change free volume. That's why a thermochromic effect observed in the films connects not only with a polymer chains conformation but may be depended on electron properties of polyaminoarenes.

Calculations of spatial potential for non-conjugated polyaminoarenes (leucoemeraldine) suggested [11], that most probably for PAN rotation angle is increasing with temperature increasing. From this

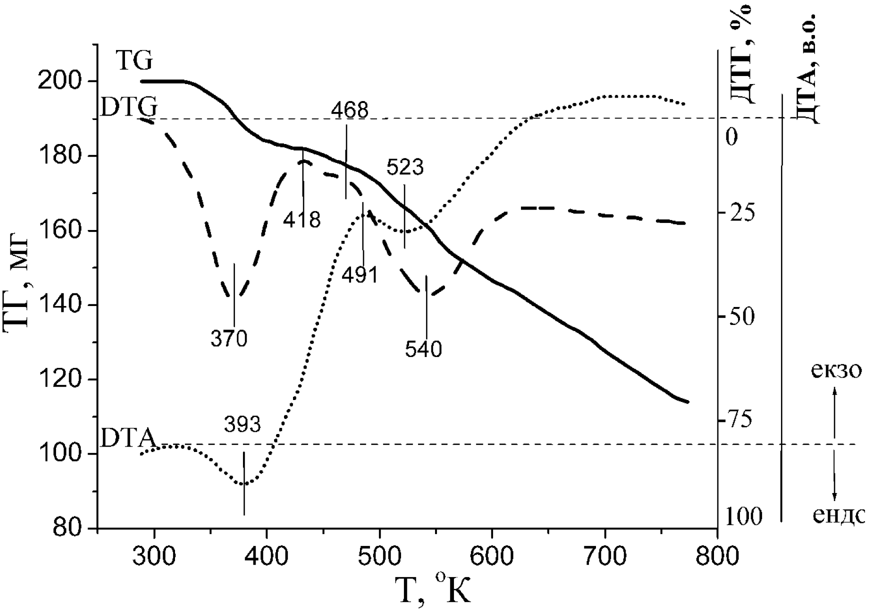

FIGURE 4 Continued.

it's necessary to wait thermo-induced increasing of optical transition energy with temperature increasing, that experimentally observed in present work. But character of optical density change in POTI, POMA and PAN films is noticeably different and requires more detail analysis.

In the presence of methyl or methoxy substitute in PoTI and PoMA macromolecules the increasing of spatial repulsion between phenyl rings and between neighboring chains [11] occurs in contrast to unsubstituted PAN. Increasing of macrochain repulsion leads to decreasing of conductivity in result of charge localization [12,13]. From the other hand this repulsion considerably relieves an internal rotation [11]. Therefore in the region of T = 293–403 K a thermochromic changes in mainly caused by change of polymer chains conformations and "enlightenment" of the films is observed. In the case of sulfate doped PAN, when doping lead to structure ordering [8,9] the difficulty of internal rotation take place. At this time an increasing of charge carries mobility along polymer chains occurs, that causes an increasing of PAN conductivity with low activation energy [12]. As support of this suggesting may be a dominating one-dimension charge transport defined by Epstein and MacDiarmid for salt forms of POTI and PAN

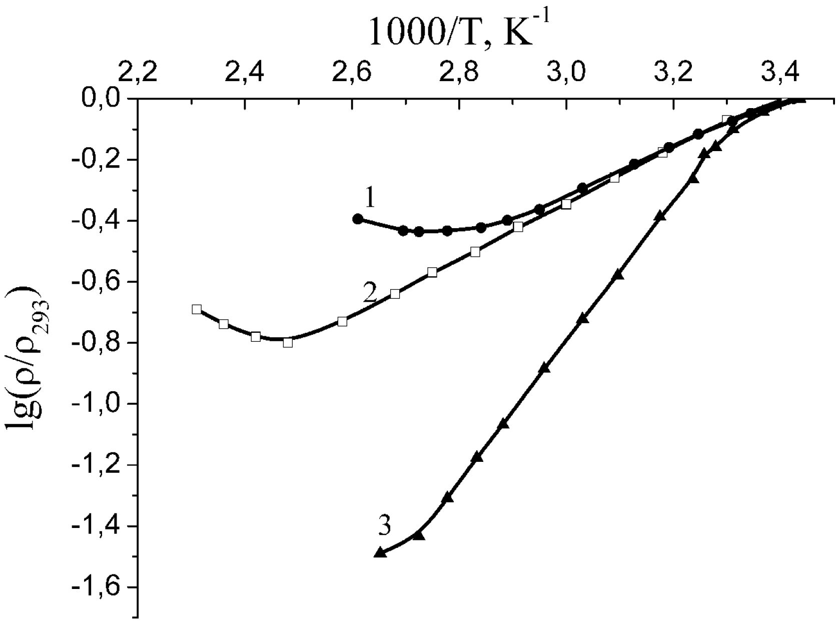

FIGURE 5 The temperature dependence of specific resistance for: 1 – polyaniline–polyvinyl alcohol composite, 2 – polyaniline, 3 – polyorthotoluidine.

[13]. Calculated from model of one-dimensional overlap a reverse lengh of localization for PoTI $\alpha^{-1} = 7{,}4\,\text{Å}$, is considerable less in relate to calculated for PAN : $\alpha^{-1} = 20\,\text{Å}$. Obviously in the case of doped PAN the influence of high temperature causes a carrier delocalization in result of "unfolding" of binding in spiral PAN macromolecule at $T > 413\,\text{K}$ [5], what causes a grows of current density in all region of temperature, before starting of macrochains thermal destruction.

As can see, the features of thermochromic transition in polyaminoarene-PVA composite films are reserved. For example, optical density of POTI films decreases in result of heating to 323 K (Fig. 3d), but at $T > 323\,\text{K}$ darkening of the films are observed. The increasing of optical absorption and "blue shift" of absorption maximum is observed. Since in PVA thermal destruction processes starting at lower temperature, thermochromic effect for composite film observed in narrower temperature interval. Films of PAN-PVA composite also change their coloration upon heating. This feature can be explained by conformation transition, which realize in polymer chains at studied temperature interval.

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