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Physical-and Technological Properties of the Sensor Materials Based on Conjugated Polyaminoarenes

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The physical and technological properties (temperature dependence of conductivity, thermal stability, optical absorption and structure) of the new sensor materials based on conjugated polyaminoarenes such as poly-*o*-toluidine, polyaniline, poly-*o,m*-aminophenols have been studied in temperature interval 273-773 K. It has been defined that change of inclination in temperature dependence of conductivity is caused by thermal decomposition of the polymers. The optical spectra of the polymer films exhibit an interesting temperature behavior in the range 293- 473 K connected with thermochromic transitions. By the X-ray powder diffraction it has been found that polyaminoarenes are amorphous-crystalline materials with content of crystalline phase from 20-22 % (undoped polymers) to 40-44 % (doped by inorganic acids) and with dimensions of crystallites 15-30 Å. For the technology application of such materials the temperature interval corresponded to the linear dependence of conductivity before the thermal decomposition temperatures has been recommended.

Ключові слова: polyaminoarenes, conductivity, thermal stability, thermochromic transitions, structure.

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Introduction

Conjugated polyaminoarenes such as polyaniline and its derivatives have a potential technological application in chemical power sources, electrochromic displays and recently attract a great attention as sensor materials [1-4]. These polymers change the resistance under gases (ammonium, water and alcohol vapor); their electrochemical response is applied to indicate the metallic ions (Ni^{2+} , Co^{2+} , Fe^{2+} and Ag^{+}), the films of polyaminophenols are used to define the concentration of organic compounds (ascorbic acid, hydroquinone) and complex $\text{K}_3\text{Fe}(\text{CN})_6$ [3,4]. The rate and mechanism of charge-transport in sensor materials based on polyaniline and its derivatives are connected with their functions, particularly, sensitivity to certain type of physical and chemical influence.

It's known that for conjugated polymers with hydrocarbon backbone (polyparaphenylene, polyacetylene) both donor (n-type) and acceptor (p-type) doping may be used, but the polyaniline and its derivatives achieve the high conductivity mainly in the case of strong proton acids using as doping agents [5]. In these polymers the positive polarons (cation-radicals) are considerate as possible charge carriers, under higher level of doping polarons may couple to bipolarons [1,5]. It's found that at the low temperatures ($T < 77$ K) the temperature dependence of polyaminoarene conductivity

may exhibit a metallic behavior (positive temperature coefficient of resistance, negative thermo-power and Pauli spin magnetism independent from temperature [1,5]). In temperature range 77-273 K character of polyaminoarene conductivity may be described in the frame of hopping model [1,5,8,]. However, at temperatures $T > 273$ K such model often does not adequate [1,5-8]. Since the most of polymer sensors operates at the room and higher temperatures, very important is information about changes in conductivity of polyaminoarenes during their application under these temperatures.

Temperature dependence of specific conductivity of some molecular semiconductors at $T > 273$ K has been described by exponent equation $\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{2kT}\right)$, in which ΔE -activation energy of charge transport, σ_0 – constant [7]. For the specific resistance of organic semiconductors this equation have a shape:

$\rho = \rho_0 \exp\left(\frac{\varepsilon_\sigma}{2kT}\right)$, where $\Delta E = \varepsilon\sigma$, $\rho_0 = 1/\sigma_0$ [7]. We

have studied the temperature dependence of conductivity; effect of temperature on the optical spectra, thermal stability and structure of polyaniline and its derivatives – poly-ortho-toluidine poly-ortho-aminophenol and poly-meta-aminophenol in temperature range 273-773 K.

I. Experimental

Preparation of polyaminoarene films was carried out in three-compartment electrochemical cell by galvanostatic electrolysis of 0.1M monomer solutions (*o*-toluidine, *o*-, *m*-aminophenol, aniline) in 0.5 M H₂SO₄ at oxidative potential of monomers ($E = 0,8 - 1,0$ V) during 60 min. The glass coated by SnO₂ working electrodes, Pt-wire counter electrodes and Ag/AgCl (in saturated KCl) as a reference were employed.

The powder samples of poly-*ortho*-aminophenol (PoAP), poly-*meta*-aminophenol (PmAP), poly-*ortho*-toluidine (PoTI) and polyaniline (PAN) were prepared by the oxidizing polymerization of aminoarene monomers in the presence of ammonium persulphate in 0,5 M sulfuric acid solution. Obtained product was neutralized by 5% ammonium solution, washed by distilled water, acetone and dried in dynamic vacuum at $T=353$ K during 8 hours. Acid doping was carried out by exposition of undoped PAN samples in 1N aqueous acid solutions (H₂SO₄, HClO₄, HCl) during of 24 hours. Obtained samples were filtered, washed by distilled water, acetone and dried in the same conditions..

Measurements of the specific volume resistance were carried out in dynamic temperature conditions, commensurable with the heating rate in thermogravimetric (TG) experiments. The sample in pressed pellet ($d=2$ mm, $h=2$ mm) was placed to quartz cylinder between two nickel disks with installed chromel-copal thermo-couple. During the measurements the sample was under pressure 100 kg/cm², where a resistance of organic semiconductors is approached to intrinsic value of specific volume resistance [7]. Studies of polyaminoarene thermal stability were carried out on derivatograph Q-1500 D in the temperature range 273-1273 K in the air and argon atmosphere, with Al₂O₃ standard at heating rate of 10 K/min.

IR-spectroscopy of polymer materials (pressed in KBr pellets) was carried out on spectrophotometer "Specord M-80" in the frequency range 400-4000 cm⁻¹. 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).

For structure investigations the method of X-ray powder diffraction at $T= 295$ K has been used (diffractometer DRON-3.0, FeK α -radiation). The degree of crystalline and crystallite size estimation were carried out in according to [8]. The dopant and moisture content have defined from the TG- and elemental analysis data as in [9]. The structure of the polymer films was investigated by means of transmission electron microscopy (UEMB-100K) and electronography (EG-100K).

II. Results and Discussion

A polymer formation in the process of polymerization of aminoarene monomers proceeds according to known scheme of oxidizing coupling

reaction of aromatic amines and includes the steps of monomer oxidation over aminogen with cation-radicals formation and its coupling accompanied by deprotonation. The IR-spectroscopy of powder polymer material showed the absorption bands at 3330, 3288, 1590, 1497, 1307, 1166 cm⁻¹, which is characteristics for emeraldine base of polyaminoarenes [1-3]. In the case of *o*-aminophenol the subsequent oxidation by two functional groups leading to formation of heterocycle [4]. This is confirmed by absorption bands at 1270-1200 cm⁻¹ (ether oxygen) and 3400-3200 cm⁻¹ (bound hydroxyl). The chemical structure of polyaminoarenes is presented in the Figure 1.

The temperature dependence of specific volume resistance of polymers demonstrate a behavior, which is typical for organic semiconductors [5-7], however the molecular structure of polymer chain and nature of doping acid has a strong effect on the shape of this

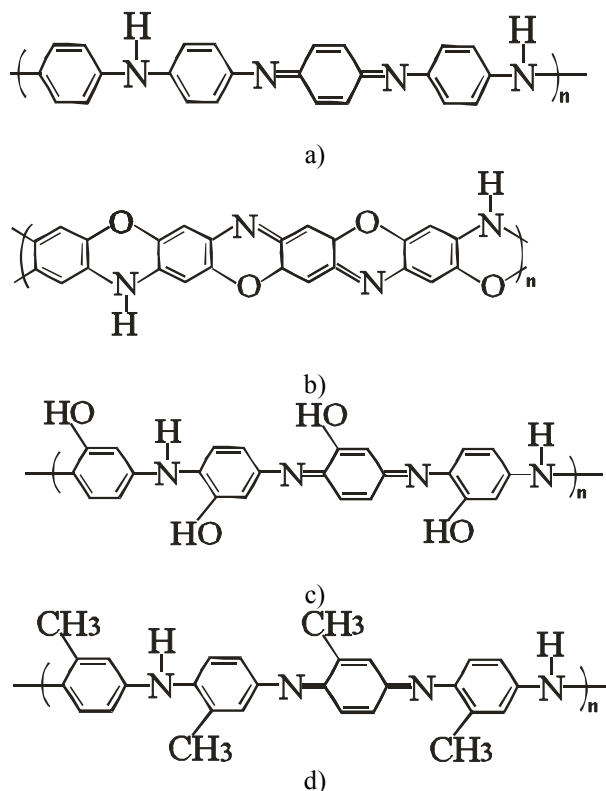


Fig. 1. Molecular structure of polyaminoarenes: (a) polyaniline; (b) poly-*ortho*-aminophenol, (c) poly-*meta*-aminophenol, (d) poly-*ortho*-toluidine

dependence. As shown in Figure 2, the change in specific resistance, normalized to resistance defined at room temperature, in the range 293-773 K includes some sections: the region of decreasing resistance, transition field and the region where the resistance rising.

At the first section the resistance of polyaminoarenes changes by known exponent law: $\rho = \rho_0 \cdot \exp\left(\frac{\varepsilon}{2kT}\right)$, where ε - activation energy of charge transport, ρ_0 - constant. Performance of resistance temperature

dependence in Arrhenius coordinates $\lg \rho - 1/T$ for the first section permits to calculate the value of activation energy

depended on the molecular structure of polymer and type of doping acid (Table 1)

Table 1

Parameters of charge transport in polyaminoarenes

Polymer	Doping level, mol/unit	σ_{293} , $S \cdot cm^{-1}$	ϵ , eV	Temperature interval, K
Polyaniline	-	$2 \cdot 10^{-8}$	$0,59 \pm 0,02$	293-423
Poly-o-toluidine	-	$3 \cdot 10^{-9}$	$0,88 \pm 0,02$	293-373
Poly-o-aminophenol	-	$5 \cdot 10^{-10}$	$1,59 \pm 0,03$	403-533
Poly-m-aminophenol	-	$7 \cdot 10^{-9}$	$1,61 \pm 0,03$	293-333
Polyaniline, doped by H_2SO_4	0,43	$3 \cdot 10^{-3}$	$0,35 \pm 0,03$	293-403
Polyaniline, doped by $HClO_4$	0,45	$7 \cdot 10^{-3}$	$0,49 \pm 0,02$	303-383

From the studies of thermal behavior of polyaminoarenes it is found that for all samples the endothermic maximum ($T=383-403$ K), associated with loss of chemisorbed moisture is observed. Following, the exothermal peak in the range 433-453 K typical for aminoarene polymers, is connected with processes of crosslinking of polymer chains [9]. This temperature region coincides with going out the temperature dependence of resistance on transition field (Figure 2). The thermal decomposition of doped polymers starts at temperatures 453-473 K depended on the type of doping agent. Attached to temperatures of this maximum the sign change of temperature coefficient of resistance can be observed, that have been associated with a loss of doping admixtures and starting the macrochains destruction processes [9]. In the case of polyaminophenols the complex character of DTA and DTG curves indicates the running of the structure phase transitions in polymer, which cause the sharp change in specific resistance. At temperatures of 413-433 K the extraction of chemisorbed moisture proceeds, at $T > 513$

K the significant mass loss is evidence to destruction of polyaminophenol macrochains [10].

The comparison of the data temperature dependence of conductivity and thermal stability permits to suggest that change in slope on temperature dependence of resistance is observed at temperatures corresponding to start of the polymer thermal decomposition. For poly-meta-aminophenol the change in slope of conductivity already at $T = 338$ K probably is caused by transformation of its molecular structure to ladder polymer (similar to PoAP) with low conductivity. So, for the technology application of such materials the temperature interval responded to the linear dependence of conductivity before the thermal decomposition temperatures as presented in Table 1 has been recommended.

According to electron spectroscopy for all investigated films in near-UV and visible range of spectrum (Figure 3) a three bands typical for absorption of polyaminoarenes are observed. The absorption at $\lambda = 750-850$ nm is characteristic of free charge carriers, delocalized along conjugated polymer chain. Absorption in the middle field is probably caused by $n-\pi^*$ transition in imino-quinoid fragments of polyaminoarene chains. The band corresponding to energy interval 380-440 nm may be assigned to the electron transition between π and π^* levels, which associated with energy of band-gap [1].

From the study of the temperature dependence of the absorption spectra in the interval of $T=293-473$ K a thermochromic effect in the films of polyaminoarenes doped by sulfuric acid has been manifested [11]. Under temperature change the variations in the polymer films color are observed. In all optical spectra it's developed in the "blue shift" of absorption maximums and in the changing of their intensity (Figure 3). The reversible lighting-darkness of the films takes place only when the heat temperature does not exceed the decomposition temperature of polymer.

According to structure study, obtained polyaminoarenes are paracrystalline materials with the different degree of the structural ordering. Diffraction spectra of obtained polymers are characterized by a broad

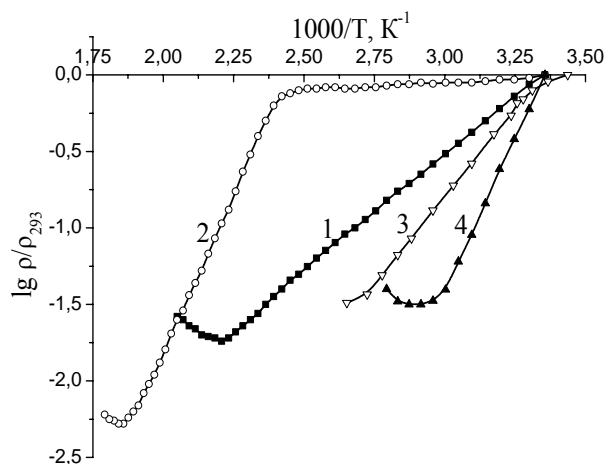


Fig. 2. Temperature dependence of specific volume resistance of undoped polyaniline (1), poly-*ortho*-aminophenol (2) poly-*ortho*-toluidine (3) and poly-*meta*-aminophenol (4)

amorphous halo and crystalline diffraction peaks in the range of $2\Theta = 10-60^\circ$. The parameters of structure, indexes of crystalline, calculated from the obtained X-ray diffractograms (Table 2) indicate that in result of acid doping a change of diffraction maximums position and

accordingly the interplane distances take a place. This is accompanied by a rising of the structural ordering level, probably caused by salt forms of polyaminoarenes formation.

Table 2

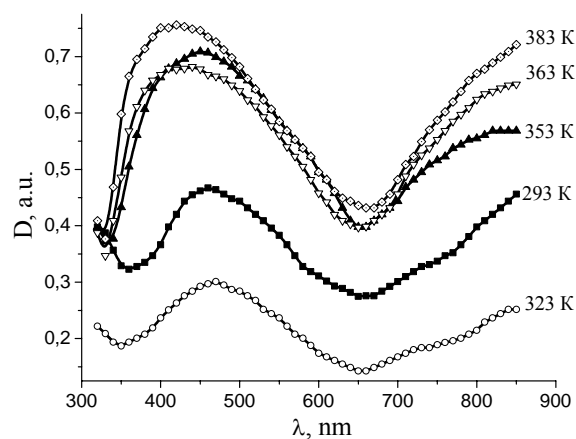
Parameters of X-ray diffraction, size of crystallites and degree of the crystalline of polyaminoarenes

Polymer	Interplane distance, $d, \text{\AA}$	Crystallite dimension, $l \pm 10\%, \text{\AA}$	Index of crystallinity, $I \pm 2\%$
Polyaniline (base)	4,47; 4,23; 3,58	15-20	25
Polyaniline doped by H_2SO_4	5,96; 5,00; 4,37; 3,49	25-30	41
Polyaniline doped by HCl	4,66; 4,31; 3,57	20-30	43
Poly- <i>meta</i> -aminophenol	5,19; 3,46; 3,26; 2,38; 2,38	15-20	23
Poly- <i>ortho</i> -aminophenol	7,18 ; 6,66; 5,69; 4,31; 3,56; 3,20; 2,82	10-15	41

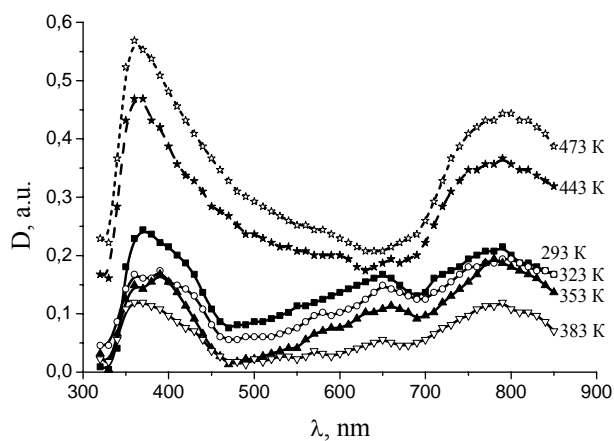
In the study of the conducting polymer films, electrochemically obtained on Pt surface, the two base structure types of macromolecular arrangement are observed. According to data of electronography at low angles scattering it is found that polymer film before 80

nm thickness is amorphous with a near order in disposition of structure elements. Follows to photometry of electronographic patterns the radial distribution of intensity as function of scattering vector $S=4\pi\sin\theta/\lambda$ has been obtained. From the disposition of low angle maximum the size of repetitive fragments (4,6 \AA) and length of conjugation in which the coplanar orientation of aromatic fragments is reserved (25-30 \AA) is calculated [12]. The observation of the film grows by electronic microscopy give the possibility to find, that with increasing of layer thickness from 80 to 3000 nm on the primary formed amorphous layer the dendrite crystals by 200-700 nm dimension are growing (Figure 4).

Obtained results permit to apply for doped polyaminoarenes the “domain” or “granular” model of the charge transport [5,12]. According to these performances the ordering areas (domain or crystallites) with high conductivity existence in the polymer. A charge transport between these domains occurred across the low-conductive amorphous layers, which create the energetic barrier to conductivity. At the high doping level in the amorphous phase the percolation bridges with high



a)



b)

Fig. 3. Absorption spectra of a) PoAP, b) POTI film heating at following temperatures

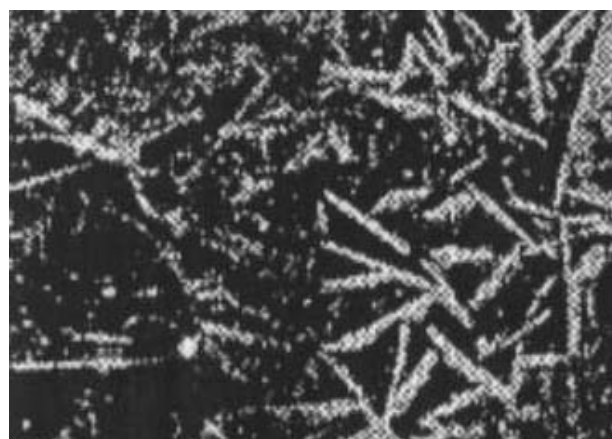


Fig. 4. Electron image of polyaniline film on Pt surface (x1000). Film thickness 3 μm .

conductivity are forming. When the percolation threshold achieved the polymer demonstrates the behavior similar to conductor. Attached to such small domains of crystalline in the polyaminoarenes the charge transport will be determined by resistance of disordered polymer phase.

Conclusion

Obtained results on conductivity and thermal stability suggest the significant effect of the polymers thermal destruction on charge transport processes and optical absorption.. In the case of studied polymers for temperature interval corresponding to linear section of resistance decreasing, the activation equation and some aspects of band theory may be used. The value of activation energy of charge transport is associated with effective band gap, constant ρ_0 - with function of carriers

free run [7]. The high specific resistance observed for polyaminiphenols in comparison to PAN is caused probably by existence of hydroxyl substitute in molecule structure of polyaminoarenes, which disturbs the system of conjugation along the polymer chain creating the significant energy barrier for charge transport. For the technology application of such materials the temperature interval before the temperature of thermal decomposition may be proposed.

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Фізичні та технологічні властивості сенсорних матеріалів на основі спряжених поліаміноаренів

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Вивчено фізичні та технологічні властивості (температурну залежність провідності, термічну стабільність, спектри поглинання та структуру) нових сенсорних матеріалів на основі спряжених поліаміноаренів, таких як поліортотолуїдин, поліанілін та поліамінофеноли в інтервалі температур 273-773 К. Встановлено, що зміна нахилу температурної залежності провідності відповідає температурам початку термічного розкладу поліаміноаренів. Оптичні спектри полімерних плівок виявляють цікаву температурну поведінку в межах 293-473 К, пов'язану з термохромними переходами. На основі Х-променевої дифракції показано, що поліаміноарени є аморфно-кристалічними матеріалами з вмістом кристалічної фази від 20-22 % (нелеговані зразки) до 40-44 % (леговані неорганічними кислотами), розміри кристалітів становлять 15-30 Å. Для технологічного застосування таких матеріалів рекомендовано інтервал температур, що відповідає лінійній ділянці зміни опору і не перевищує температуру термічного розкладу поліаміноаренів.