PHYSICS AND CHEMISTRY
OF SOLID STATE
V. 25, No. 3 (2024) pp. 579-586

Section: Chemistry

DOI: 10.15330/pcss.25.3.579-586

*Vasyl Stefanyk Precarpathian
National University*

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 25, № 3 (2024) С. 579-586

Хімічні науки

UDC: 541.64

ISSN 1729-4428 (Print)
ISSN 2309-8589 (Online)

O.I. Aksimentyeva[1], B.R. Tsizh[2,3], Yu.Yu. Horbenko[1], M.I. Chokhan[3],
A.L. Stepura[1], V.I. Baluk[4]

Influence of the Toxic Vapors on the Gas Sensitivity and Structure of Poly(o-toluidine)

[1]*Ivan Franko National University of Lviv, Ukraine;* Olena.Aksimentyeva@lnu.edu.ua;
[2]*Kazimierz Wielki University in Bydgoszcz, Bydgoszcz, Poland;* tsizhb@ukw.edu.pl;
[3]*Stepan Gzytskyi National University of Veterinary Medicine and Biotechnologies Lviv, Ukraine;* tsizhb@ukr.net;
[4]*National University "Lvivska Polytechnyka", Lviv, Ukraine;* vasyl1850@gmail.com

In the present work, we investigated the influence of the toxic vapors (ammonia, chloroform, tetrahydrofuran, dimethylformamide, nitrobenzene, toluene) on the specific resistance, optical absorption, and structure of conducting polymer poly-o-toluidine (PoT) obtained by oxidative polymerization of o-toluidine in toluene sulfonic acid (TSA) solution. This polymer has a high level of crystallinity and is thermal stable to 473 K (200 ^{0}C). The action of organic solvent vapors causes an increase in PoT-TSA resistance by 1.3-1.4 times, while after the action of ammonia, the resistivity increases almost 500 times. The activation energy of charge transfer E_a also increases from 0.21 to 0.71 eV under the action of ammonia due to the deprotonation of the polymer and its transformation to the resistive base form. When the organic solvents are used, the observed phenomena have a different direction (resistance increase or decrease) due to the peculiarities of polymer-solvent molecular interaction. This phenomenon may be used for selective detection of solvents.

Keywords: poly(o-toluidine), structure, specific resistance, organic vapors, ammonia action.

Received 27 February 2024; Accepted 4 August 2024.

Introduction

In the modern world, the issue of a clean environment and resources (water, land, etc.) is one of the most important ones that humanity is trying to solve. As a result of the built environment and military actions, the world is on the verge of an ecological disaster. Therefore, there is a need to create devices to monitor changes in the state of the environment, the atmosphere in workplaces, and everyday life. Low energy and resource consumption, high efficiency, speed of operation, the shortest response time, and small size are the main requirements for sensors. Currently, a significant part of the scientific interests of researchers is to improve and modify many devices, detectors, and sensors already existing [1-9].

Essential for environmental monitoring are chemical or chemosensors that selectively react to a particular object and are used for qualitative or quantitative determination of the analyzed substance (analyte). The main issue in the operation of such sensors is the selection of an indicator substance that responds to the action of chemicals (analytes) by changing its physical properties [10-12].

The most sensitive and easy to use are resistive sensors changing electrical resistance in response to the external signal [1, 4]. Structurally, resistive-type sensors consist of a sensitive film applied to the substrate, a heater in the form of a resistive film on the other side of the substrate, and electrodes. The physical principle underlying the operation of the sensors is the change in the resistance caused by the gas adsorption on its surface. So, resistive-type sensors are characterized by the value of the response, defined as the ratio of the resistance under the action of the gas to the initial one [3-5].

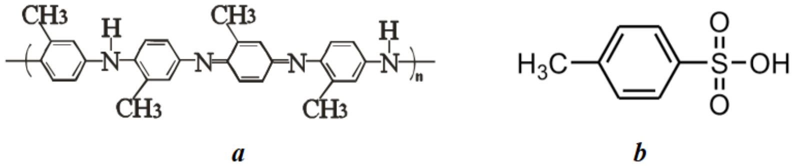


Fig. 1. Chemical structure of the elementary unit of poly(o-toluidine) (*a*) and toluenesulfonic acid (*b*).

Semiconductor sensors have minimal dimensions and a simple design, consume little power, and are manufactured using group microelectronic technology, ensuring their relatively low cost and compatibility with electronic devices for further signal processing [3, 5]. The disadvantages of such sensors include their low stability and selectivity, as well as the high operating temperature of the sensitive element. The latest materials for sensitive elements of sensors working at room temperature without special heating equipment are conjugated polymers with electronic conductivity or composites based on them with metal or semiconductor nanoparticles [2, 5-9].

Conducting polymers are organic semiconductors promising for the sensitive element creation for both resistive and optical types of sensors [2, 6]. Numerous papers are devoted to sensors of ammonia and inorganic gases [2, 5, 9], while the influence of vapors of toxic organic and inorganic substances on the electrical resistance of organic semiconductor films today is poorly studied [10, 11].

Currently, resistive and optical sensors based on polyaniline (PAn) are being actively researched [2, 5, 6, 9]. Along with PAn as sensor material, its derivatives, namely poly(o-anisidine) [12] and poly(o-toluidine) [13-16] and their copolymers [17] are studied. Due to the alkyl substituent in the aromatic ring, these conducting polymers have improved solubility compared to polyaniline, simplifying the process of making films by non-destructive, non-energy-intensive methods.

Poly(o-toluidine) (PoT) has an elementary link structure quite similar to polyaniline (Fig. 1), but the presence of an electron-donating substituent – a methyl group in the ortho position to the amino group determines a number of interesting physical and electrochemical properties of this polymer [13-16].

It is reported that PoT is used in diode structures [18], as an electrochromic material of organic displays [19], as a component of sensor media for gas detection [13-15]. PoT belongs to the conjugated polymers with intrinsic electronic conductivity, which occupy an intermediate position between insulators and metals. As a result of doping with substances of the acceptor or donor type, the "insulator-metal" transition occurs, and the specific conductivity of conjugated polymers, including PoT, increases by several orders of magnitude [20]. A particular type of doping of conjugated polymers is proton (or acid) doping under the action of strong acids, leading to the highly conductive salt formation. The control of the functional properties of conducting polymers allows the choice of a volatile agent. Toluenesulfonic acid (TSA) is especially promising among the acidic dopants. Due to the mobile sulfonic group in the *para*-position and an aromatic ring (Fig. 1,b), it acts as an electrolyte, a dopant, and a plasticizing agent, providing high conductivity and processability of polymers.

We investigated several organic and inorganic materials and their composites to select sensitive elements of resistive sensors for gaseous substance recognition and detection [2, 5, 9, 17]. The effect of different types of gas environments on the change in the specific resistance of poly(o-toluidine) doped with TSA is reported in this paper to show the possibility of this material's use in resistive-type gas sensors.

I. Experimental technique

The chemical synthesis of PoT was carried out by the method of oxidative polymerization of a 0.1M solution of o-toluidine under the action of an equimolar amount of the oxidant ammonium persulfate in a medium of 0.1 M TSA as described in [16]. The base (undoped) form of PoT was prepared by neutralization of PoT-TSA precipitate by 5 % ammonia solution. The obtained products were dried to a constant mass under a dynamic vacuum at a temperature of 60 °C.

The films of PoT-TSA were obtained by the "in situ" chemical oxidative polymerization of monomer in TSA solution on the transparent surface of the glass plates coated by tin oxide. For the deposition of polymeric films, plates of 10 × 30 × 0.1 mm in size were used. The cleaned plate was placed in a 0.1 M TSA solution containing 0.1 M o-toluidine and 0.1 M ammonium persulfate at room temperature for 60 min according to the method described in [12, 14]. During polymerization, thin poly(o-toluidine) films of light purple color formed on the surface of SnO_2. After washing the sample with distilled water to remove monomer and oxidant residues, it was dried at room temperature for 2 hours and stored in a desiccator. The thickness of the films measured with MII-4 interference microscope was 300 ± 20 nm.

Dimethylformamide (DMF), tetrahydrofuran (THF), chloroform, nitrobenzene, and toluene, obtained from Sigma-Aldrich, were used as organic solvents. The physical and chemical parameters of the solvents are shown in Table 1.

The molecular structure of the obtained samples was confirmed by Fourier transform IR spectroscopy using an Avatar 320 spectrometer in the wave number range of 400 - 4000 cm^{-1}. Optical absorption of PoT films was studied with spectrophotometer SF-46 in the 350 – 1100 nm range.

The structure was investigated by powder X-ray diffraction using a STOE STADI P diffractometer, Cu $K\theta_1$ radiation. Film morphology was studied with optical Nikomed microscope and scanning electron microscopy

Table 1.

The physical and chemical parameters of the solvents [21]

Solvent	M_r, g/mol	ρ^{20}, g/cm^3	n_D^{20}	E	μ, D	η^{25}, MPa×s	Donor number	Acceptor number
DMF	73.09	0.95 (25°C)	1.4304	36.7	3.82	0.796	26.6	16.0
THF	72.11	0.889	1.4050	7.6	1.63	0.48	20.0	8.0
Chloroform	119.4	1.488	1.4455	4.81	1.15	0.542	—	23.1
Nitrobenzene	123.1	1.199	1.5562	34.9	4.0	1.838	8.1	14.8
Toluene	92.14	0.867	1.4969	2.38	4.22	0.5516	0.1	—

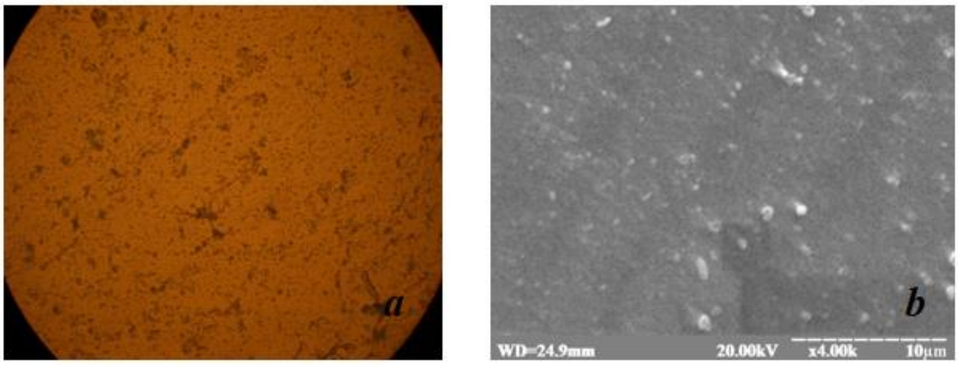


Fig. 2. (*a*) Photomicrograph (×120) and SEM image (*b*) of the PoT-TSA film obtained by oxidative polymerization on the glass surface.

using REMMA-102-02.

The study of the thermal behavior of the samples was carried out with the derivatograph "Q-1500-D" of the Paulik-Paulik-Erdey system in an air atmosphere using corundum crucibles in the temperature range of 273 - 1073 K at a heating rate of 10 K/min, Al_2O_3 was used as a standard.

The specific resistance of PoT-TSA before and after the action of the indicator gas was determined by the standard 2-contact method at a temperature of 293 K. The temperature dependence of the resistance was studied under the conditions of a dynamic temperature change at a rate of 5 K/min. A sample in the compressed tablet form was placed between two nickel disk contacts in a quartz cylinder. The temperature was controlled using a chromel-copel thermocouple mounted in a quartz cylinder. The specific resistance was calculated according to the formula:

$$R = (\rho \times l) / S,$$

where S – the cross-sectional area of the cylindrical sample, l – the height, R – the measured resistance value, and ρ – the specific resistance. The relative error of determining σ for a series of parallel measurements did not exceed 5 %.

To study the sensitivity of PoT to the action of toxic vapors the special clamber with input and output clamps was used. The sensory sensitivity of the PoT-TSA powder pressed in pellets and films was studied for change their resistance (or optical absorption) after exposition of the sample in the hermetic chamber by volume of 4 cm^3 with vapor of the organic solvent during 30, 60, 120, 180 and 300 s. In all tests a quantity of the solvent in vapor phase was the same (1 mg) at 293 K which corresponds to 0.25 mg/cm^3.

II. Results and Discussion

To study the molecular and crystalline structure of poly(o-toluidine) doped with toluenesulfonic acid, a complex of physicochemical methods was used: FTIR, X-ray diffraction, thermogravimetric analysis, UV-visible-NIR spectroscopy.

As we showed recently [16], the IR spectrum of the synthesized polymer is characterized by the absorption bands. The absorption band at 3017 cm^{-1} (N–H valence vibrations of the secondary amine); 1485 and 1598 cm^{-1} (valence vibrations of the benzene and quinoid rings, respectively). The band at 1386 cm^{-1} is caused by symmetric deformation vibrations of the methyl group. Three bands at 1008, 873, and 812 cm^{-1} belong to the out-of-plane vibrations of the C–H bond, the 1,2,4-substituted benzene ring and the in-plane C–H vibrations in the quinoid ring, respectively. The characteristic absorption bands of PoT samples concur with the known IR spectra of PoT salts [13, 16, 18] and confirm the molecular structure of polyaminoarene.

Conjugated polyaminoarenes have an amorphous-crystalline structure and represent an amorphous matrix with interspersed "domains" of the crystalline phase with sizes from 0.3 to 1 μm. The content of this phase or the level of crystallinity depends significantly on the type of dopant and the level of polymer doping [20]. This structure is characteristic of PoT-TSA films obtained by chemical deposition on the surface of conductive glass (Fig. 2).

The study of the crystal structure of PoT-TSA made it possible to establish that doping with this TSA unlike other doping acids (for example, H_2SO_4 [16]), leads to the appearance of several crystal reflexes belonging to the salt products of the interaction of TSA with PoT functional groups (Fig. 3, curve 1).

Thermogravimetric curves indicate that the studied polymer doped with TSA and in the base form is sufficiently stable up to T = 250 ˚C. A little loss of mass associated with the moisture removal (2 - 2.5 %) is observed at 80 - 100 C. As the temperature rises to 150 ˚C, adsorbed (bound) moisture is removed. Small extremes on the DTG curve correspond to these processes (Fig. 4). The most significant mass loss begins when the temperature reaches 250 ˚C. At the same time, the thermal behavior of the doped and undoped base samples is different. There is an insignificant mass loss in the base form, while in the doped form – about 10 %.

With increasing temperature from 250 to 350 ˚C, a sharp inflection of the TG curve is observed (Fig. 4,*a*), according to an intense extremum on the DTG curve with a maximum of T = 296 ˚C. This process corresponds to a series of endothermic maxima on the DTA curve (Fig. 4, *b*)

Analyzing these data, it can be stated that there is a loss of dopant, i. e. a process of dedoping associated with the alloying impurity removal, in the area of 250 - 350 ˚C. For the PoT base, such a section does not appear. Thermal decomposition occurs at a constant rate up to 850 ˚C. So, summarizing the above material, we can assume that the area of reliable thermal stability of PoT is the temperature range up to 200 - 250 ºC.

According to the studies, TSA-doped poly(o-toluidine) at room temperature and in the air has a relatively small value of specific resistance of 19.2 Ω•m (Table 2). As the temperature increases from 293 to 373 K, the resistance of the PoT-TSA sample decreases according to the exponential law:

$$\rho = \rho_0 \cdot \exp\left(E_a/2kT\right),$$

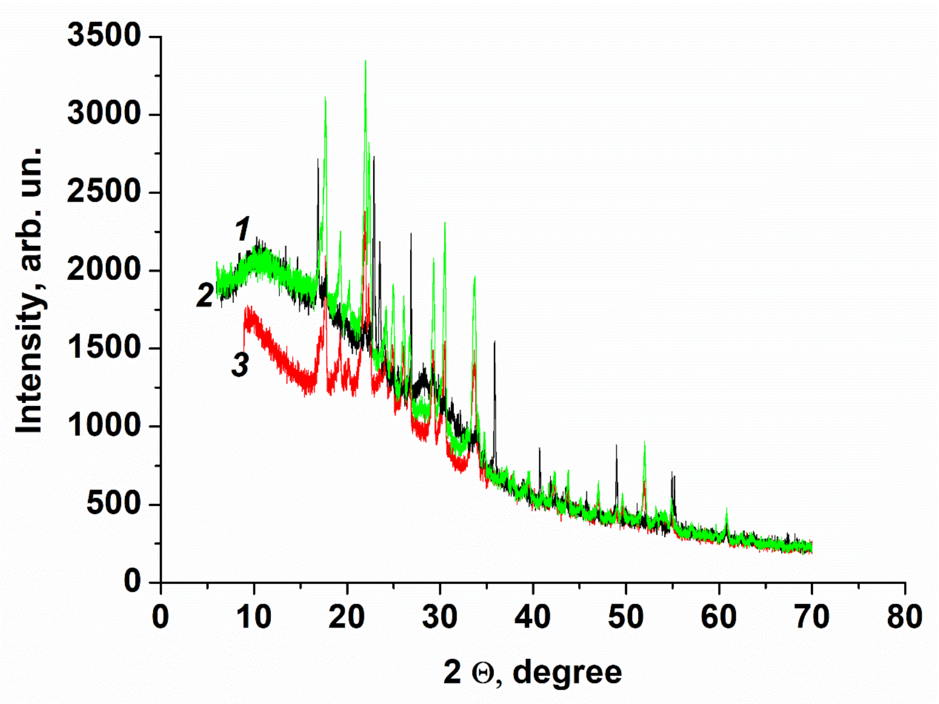


Fig. 3. X-ray diffractograms of PoT-TSA:
1 – before the action of ammonia, *2* – after the action of ammonia, *3* – after the action of ammonia and heating.

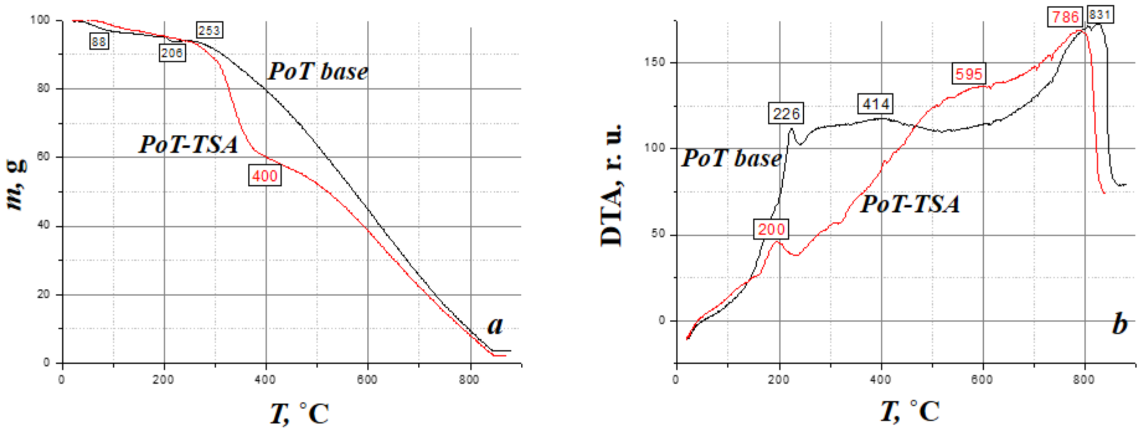


Fig. 4. Thermogravimetric (*a*) and DTA curves (*b*) of PoT base and PoT-TSA samples.

Table 2.

Parameters of charge transfer for PoT-TSA under the influence of gaseous media during 30 s

Gas	ρ^{293}, Ohm×m	ρ_0, Ohm×m	$\sigma = 1/\rho$, S/m	E_a, eV	Sensitivity, R/R_o
-	19.2	0.018	0.0520	0.206	-
Ammonia	9020.6	$1.16\cdot10^{-6}$	0.000110	0.708	470
Nitrobenzene	18	0.0046	0.0555	0.277	0.94
Toluene	13.4	0.118	0.0746	0.227	0.70
Chloroform	25	0.001	0.0395	0.255	1.30
DMF	26	0.0277	0.0384	0.180	1.35
THF	26	0.0630	0.0384	0.139	1.35

where E_a – charge transfer activation energy, ρ_0 – specific resistance, k – Boltzmann's constant, T – temperature.

Representation of the data in the coordinates of the Arrhenius equation $\ln(R/R_0 = f(1/T))$ showed that temperature dependence is described by a straight line (Fig. 5), which indicates the possibility of applying the band theory of conductivity to the studied polymers.

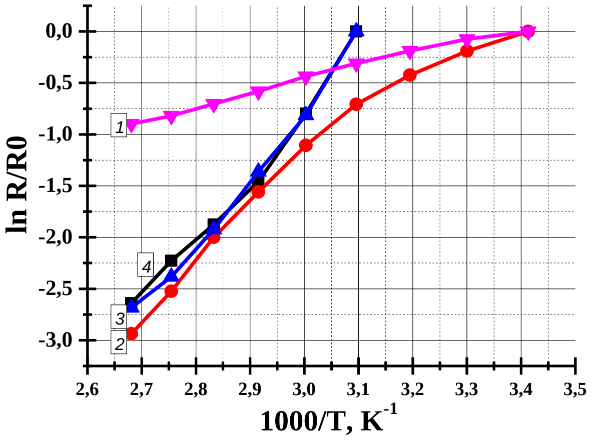


Fig. 5. (*a*) Dependence of the logarithm of the normalized resistance on the inverse temperature for the PoT-TSA in the air (*1*), and after exposure to ammonia vapors for 30 s (*2*), 1 min (*3*) and 5 min (*4*).

The values of charge transfer parameters calculated according to the above equation for linear dependences in the temperature interval of 313 - 373 K (40 - 100 °C) are shown in Table 2. The activation energy of charge transfer for PoT-TSA is $E_a = 0.206 \pm 0.002$ eV. Doping of PoT with TSA provides high conductivity compared to other acids, for example, sulfate [16], probably due to a high level of structure ordering.

After the action of ammonia, the specific resistance of PoT-TSA increases significantly, almost 500 times (Table 2), and the activation energy of conductivity also increases from 0.206 to 0.708 eV. It can be assumed that as a result of the interaction of ammonia molecules with acid-doped polyaminoarene, the deprotonation of the polymer occurs with the formation of an unstable ammonium complex, causing a significant decrease in the concentration of charge carriers and, accordingly, an increase in specific resistance.

In the interaction with ammonia, the intensity of crystal reflexes in the XRD of PoT-TSA samples increases, which indicates the chemical interaction of the gas with the acid groups of PoT-TSA (Fig. 3, curve 2) with the formation of crystalline salt form. After heat treatment of the films, a slight decrease in reflexes was observed due to ammonia desorption (Fig. 3, curve 3). However, the observed changes are insignificant, indicating sufficient reproducibility of the PoT-TSA structure, i.e., amorphization of the crystal structure, typical for most polymers, does not occur.

The influence of the organic solvent on the resistance of PoT-TSA depends on the physical and chemical characteristics of the solvent. As can be seen from the data in Table 2 and the temperature dependence of the resistance, the nature of the solvent causes a change in the specific resistance, the E_a value, and the constant ρ_0. However, the effect is much lower compared to the action of ammonia.

When exposed to vapors of polar aprotic solvents – DMF, THF, and chloroform various effects of exposure are observed (Fig. 6).

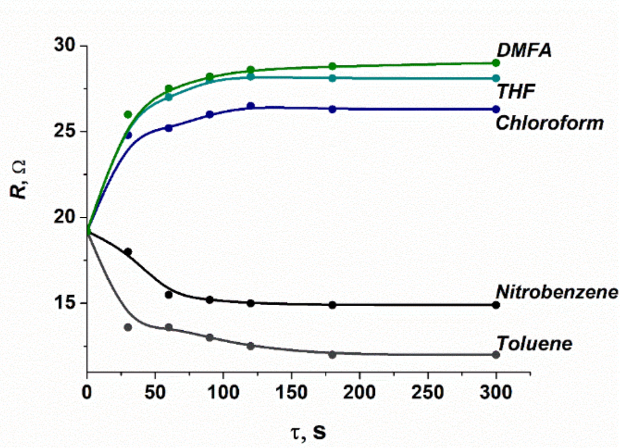
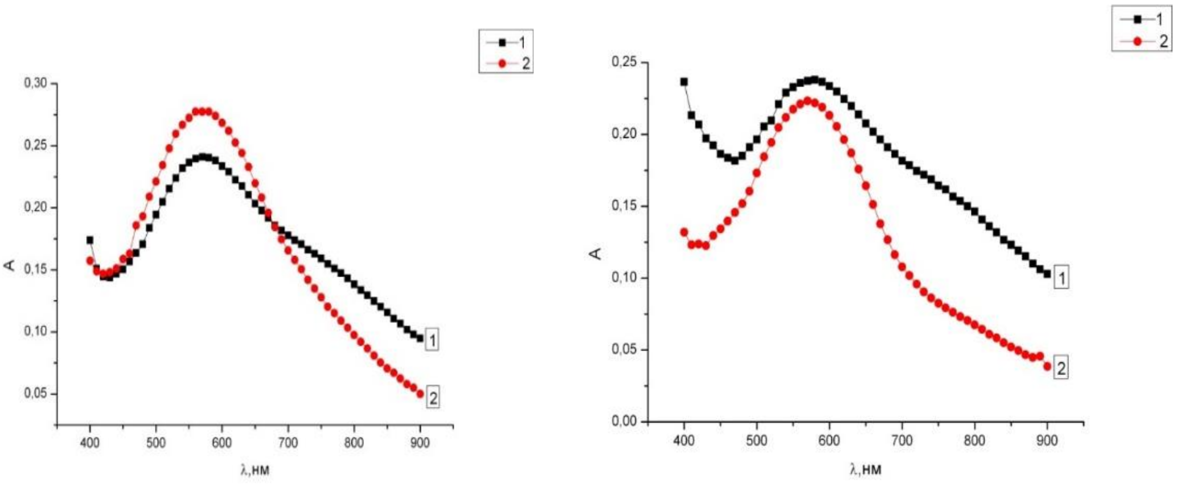


Fig. 6. Temporal dependence of the resistance of PoT-TSA under action of organic vapors: 1- DMF; 2 – THF; 3 – chloroform; 4 - nitrobenzene; 5 – toluene.

In general, the effect of the vapors of the above-mentioned solvents causes an increase in resistance by 1.3 - 1.4 times. The values of the activation energy under



a b

Fig. 7. Optical spectra of PoT-TSA films: a) 1 − original film; 2 − after influence of DMF vapors, b) 1 − original film; 2 − after influence of THF vapors.

the action of polar solvents DMF and TGF decrease. Probably, the observed phenomena are due to the peculiarities of the polymer-solvent molecular interaction.

The decrease in resistance and an insignificant increase in the activation energy of conductivity are observed when vapors of an organic solvent with a chemical structure similar to PoT - aromatic compounds with a substituent on the benzene ring, i.e. nitrobenzene and toluene, act on the sensor film (Table 2, Fig. 6). Probably, the process of physical adsorption of solvent molecules occurs which does not significantly affect the electronic properties of the polymer.

In addition, there is a some correlation between the physicochemical parameters of the solvent and its influence on the nature of the resistance change. Solvents with a high donor number (d.p.) and less dipole moment (μ), such as DMF, THF, and chloroform (Table 1), cause an increase in the resistance of PoT-TSA, and with a low d.p. and higher μ - decrease. Recent experiments have determined that the forces associated with charge transfer are weak and yet they can cause intermolecular interactions in addition to the nonspecific van der Waals forces [22].

The optical absorption spectra of PoA film obtained by “in situ” chemical polymerization were characterized by absorption near 360 - 410 nm (π-π^* transition) and a broad band in the range of 520 - 750 nm, which can be attributed to the n-π^* transition in amino-quinoid fragments of the polymer system (Fig. 7, curves 1). The influence of organic vapors causes changes in films coloration that correspond to spectral changes in the visible and NIR range of the spectrum.

Under DMF vapors, optical absorption growth is observed in the 550 - 580 nm range, but its maximum position remains unchanged. Instead, in $\lambda > 750$ nm, there is a decrease in optical absorption (Fig. 7,a). A similar trend is observed under the fumes of chloroform and THF (Fig. 7,b). However, the optical absorption is lower in all spectral intervals studied.

Therefore, the obtained results confirm the presence of intermolecular polymer-gas interaction under the action of different types of gases, the nature of which is determined by the physicochemical parameters of the organic solvent. Charge transfer forces between molecules are formed during the interaction between electron donors with low ionization energy and electron acceptors with high electron affinity. The donor strength of a solvent is characterized by the ability to dissolve compounds with ionic and covalent bonds and cause solute ionization. It may explain the higher sensitivity of THF, DMF, and chloroform characterized by larger donor ability (d.p.) compared to other solvents studied. The results indicate the possibility of using PoT-TSA in resistive ammonia sensors and for selective recognition of organic gas media of different polarities.

Conclusions

Films and bulk samples of conducting polymer PoT doped with TSA were obtained by oxidative chemical polymerization. Their structure and physicochemical properties were studied. The presence of a bulk dopant (TSA anion) with a mobile proton of a sulfonic group causes an improvement in the physicochemical properties of the PoT-TSA, namely higher electrical conductivity and thermal stability compared to PoT doped with other protonic acids. The sensitivity of PoT-TSA to the different gas mediums was tested. It was found that the highest resistance change occurs under the action of ammonia vapors. In the case of organic solvent vapours, the process of physical adsorption of solvent molecules occurs, which does not significantly affect the electronic properties of the polymer. The resistance change under the organic solvent vapors depends on their molecular structure and physicochemical parameters (donor number, dipole moment). The obtained results can be helpful in the development of gas sensors based on organic sensing media.

Acknowledgment

The research results presented in this article were obtained with grant funding from the National Research Foundation of Ukraine under the competition «Science for strengthening the defense capability of Ukraine» within the framework of the project 2023.04/0133 “Development of detectors for express control of toxic substances in polluted areas” (2024-2025).

Aksimentyeva O.I. - doctor of chemical sciences, professor, chief researcher, professor of the department of physical and colloidal chemistry;
Tsizh B.R. - doctor of technical sciences, professor, head of the department of general technical disciplines;
Horbenko Yu.Yu. - candidate of chemical sciences, senior researcher, senior researcher, associate professor of the department of physical and colloidal chemistry;
Chokhan M.I. - candidate of technical sciences, associate professor, associate professor of the department of general technical disciplines;
Stepura A.L. - master of chemistry, engineer of the department of physical and colloidal chemistry
Baluk V.I. - engineer of the 1st category of the department of applied physics and nanomaterials science.

[1] B. Adhikari, P. Kar, eds.: G. Korotcenkov, *Polymers in Chemical Sensors*, Chemical Sensors (Momentum Press, LLC, New Jersey, USA, 2010).
[2] B. Tsizh, O. Aksimentyeva, *Ways to improve the parameters of optical gas sensors of ammonia based on polyaniline*, Sens. Actuator A Phys. 442 (2020); https://doi.org/10.1016/j.sna.2020.112273 0924-4247.
[3] S. Wilson, R. Jourdan, Q. Zhang et al., *New materials for micro-scale sensors and actuators. An engineering review*, Mater. Sci. Eng. Rep., 56, 1 (2007); https://doi.org/10.1016/j.mser.2007.03.001.
[4] A. Ghoorchian, N. Alizadeh, *Chemiresistor gas sensor based on sulfonated dye-doped modified conducting polypyrrole film for high sensitive detection of 2,4,6-trinitrotoluene in air*, Sens. Actuators B Chem., 255(1), 826 (2018); https://doi.org/10.1016/j.snb.2017.08.093.
[5] O. Aksimentieva, B. Tsizh, M. Chokhan, Sensors of control of gaseous media in the food industry and the environment (Lviv, Pyramida, 2018).
[6] H. Bai, G. Shi, *Gas sensors based on conducting polymers*, Sensors, 7, 267 (2007); https://doi.org/10.3390/S7030267.
[7] C.-W. Hu, Y. Yamada, K. Yoshimura. *A new type of gasochromic material: conducting polymers with catalytic nanoparticles*, Chem. Commun., 53, 3242 (2017); https://doi.org/10.1039/C7CC00077D.
[8] D.A. Pomogailo, S. Singh, M. Singh, *Polymer-matrix nanocomposite gas-sensing materials*, Inorg. Mater., 50(3), 296 (2014); https://doi.org/10.1134/S0020168514030108.
[9] O.I. Aksimentyeva, B.R. Tsizh, Yu.Yu. Horbenko, O.I. Konopelnyk, G.V. Martynyuk, M.I. Chokhan’, *Flexible elements of gas sensors based on conjugated polyaminoarenes*, Mol. Cryst. Liq. Cryst., 670(1), 3 (2018); https://doi.org/10.1080/15421406.2018.1542057.
[10] T. Lamarque, P.Le Barny, E. Obert, E. Chastaing, B. Loiseaux, I. Leray, *Detection of nitro-aromatic compounds by optical gas sensors based on sensitive or photoluminescent polymers*, Proc. of SPIE, 6189 (2006); http://dx.doi.org/10.1117/12.664032.
[11] B.A. Farooqi, M. Yar, A. Ashraf, U. Farooq, Kh. Ayub, *Graphene-polyaniline composite as superior electrochemical sensor for detection of cyano explosives*, Eur. Polym. J., 138, 109981 (2020); https://doi.org/10.1016/j.eurpolymj.2020.109981.
[12] D. Anaklı, S. Çetinkaya1, M. Karakışla, M. Sacak, *Synthesis and characterization of conductive poly(o-anisidine)/talc composite*, Journal of the Faculty of Engineering and Architecture of Gazi University, 33(2), 403 (2018) 403; https://doi.org/10.17341/gazimmfd.416349.
[13] B.R. Tsyzh, M.R. Dzeryn, Yu.Yu. Horbenko, *Gas sensitivity of poly-ortho-toluidine films*, Scientific Messenger LNUVMBT named after S. Z. Gzhytskyj, 19(75), 59 (2017); http://dx.doi.org/10.15421/nvlvet7512.
[14] A. Stepura, Yu. Horbenko, O. Konopelnyk, O. Aksimentyeva, *Sensor sensitivity of thin layers of polyorthotoluidine*, Visnyk of the Lviv University. Ser. Chem., 58(2), 368 (2017).
[15] A.A. Khan, S. Shaheen, *Electrical conductivity, isothermal stability and amine sensing studies of a synthetic poly-o-toluidine/multiwalled carbon nanotube/Sn(IV) tungstate composite ion exchanger doped with p-toluenesulfonic acid*, Anal. Methods, 7, 2077 (2015); https://doi.org/10.1039/C4AY02911A.
[16] A.L. Stepura, O.I. Aksimentyeva, P.Yu. Demchenko, *Features of the Structure and Physical-Chemical Properties of Poly-Ortho-Toluidine Doped with Toluenesulfonic Acid*, Physics and Chemistry of Solid State, 20(1), 77 (2019); https://doi.org/10.15330/pcss.20.1.77-82.
[17] B. Tsizh, Yu. Horbenko, M. Dzeryn, O. Aksimentyeva, *Combined polymer sensitive elements for gas sensors*, Mol. Cryst. Liq. Cryst., 716(1), 112 (2021); https://doi.org/10.1080/15421406.2020.1859701.
[18] A. Elmansouri, A. Outzourhit, A. Oueriagli, A. et al., *Spectroscopic characterization of electrodeposited poly(o-toluidine) thin films and electrical properties of ito/poly(o-toluidine)/aluminum schottky diodes*, Act. Pass. Electron. Compon., 2007 (2007); https://doi.org/10.1155/2007/17846 .
[19] O.I. Aksimentyeva, O.I. Konopelnyk, M.Ya. Grytsiv, G.V. Martyniuk, *Charge transport in electrochromic films of polyorthotoluidine*, Funct. Mater., 11(2), 300 (2004);
[20] A. MacDiarmid, *‘Synthetic metals’: a novel role for organic polymers*, Curr. Appl. Phys. 1, 269 (2001); https://doi.org/10.1016/S0379-6779(01)00508-2.
[21] Common Solvents Used in Organic Chemistry: Table of Properties. https://organicchemistry data.org/solvents.

[22] M.F.J. Mabesoone, A.R.A. Palmans, E.W. Meijer, *Solute–Solvent Interactions in Modern Physical Organic Chemistry: Supramolecular Polymers as a Muse*, J. Am. Chem. Soc., 142(47), 19781 (2020); https://doi.org/10.1021/jacs.0c09293.

О.І. Аксіментьєва[1], Б.Р. Ціж[2,3], Ю.Ю. Горбенко[1], М.І. Чохань[3],
А.Л. Степура[1], В.І. Балук[4]

Вплив токсичних парів на газочутливість і структуру полі(о-толуїдину)

[1]*Львівський національний університет імені Івана Франка, Україна;* Olena.Aksimentyeva@lnu.edu.ua;
[2]*Університет Казимира Великого у Бидгощі, Бидгощ, Польща,* tsizhb@ukw.edu.pl;
[3]*Львівський національний університет ветеринарної медицини і біотехнологій імені С.З. Гжицького, Львів, Україна;* tsizhb@ukr.net;
[4]*Національний університет "Львівська політехніка", Львів, Україна;* vasyl1850@gmail.com

Досліджено вплив токсичних парів (аміаку, хлороформу, тетрагідрофурану, диметилформаміду, нітробензолу, толуолу) на питомий опір, спектри поглинання і структуру електропровідного полімеру полі-о-толуїдину (ПоТ), отриманого окисною полімеризацією о-толуїдину в розчині толуолсульфокислоти (ТСК). Встановлено, що цей полімер має високий рівень кристалічності і термостабільний до 473 К. Дія парів органічних розчинників викликає підвищення опору ПоТ-ТСК в 1,3-1,4 рази, тоді як після дії аміаку питомий опір зростає майже в 500 разів. Енергія активації переносу заряду Еа також зростає від 0,21 до 0,71 еВ під дією аміаку за рахунок депротонування полімеру та його перетворення в резистивну форму емеральдинової основи. При використанні органічних розчинників спостережувані явища мають різну спрямованість (підвищення або зменшення опору) через особливості молекулярної взаємодії полімер-розчинник. Це явище можна використовувати для вибіркового виявлення розчинників.

Ключові слова*:* полі(о-толуїдин), структура, питомий опір, органічні пари, дія аміаку.