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SENSORY SENSITIVITY OF THIN LAYERS OF POLY-ORTHO-TOLUIDINE

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The influence of vapors of organic solvents (dimethylformamide, tetrahydrofuran, chloroform) on the optical properties of thin layers of poly-ortho-toluidine obtained on the glass surface coated with tin (IV) oxide were investigated. Areas of polymer layer spectral sensitivity to the action of organic solvents, the nature of which depends on their physical and chemical parameters, especially, polarity, were identified. Based on the received data, it was proved that chemically synthesized film of poly-ortho-toluidine on optically transparent substrates can be used to determine the vapors of organic solvents, and the highest sensor responsiveness is observed on the action of dimethylformamide.

Key words: poly-ortho-toluidine, optical spectra, organic solvents, polarity, sensor sensitivity.

The optical properties of conjugated polymers are the subject of many theoretical and experimental studies, and include a wide range of phenomena associated with changes in the electronic structure of conjugated chains, energy optical transitions, including optical absorption (transmission) radiation (photo-, electro-, thermoluminescence) [1–5]. The most interesting optical phenomena that have conjugated polyaminoarenes and form part of their specific properties, is the ability to optical changes, namely, change optical absorption spectra under the influence of external factors, including gas adsorption [4, 6]. Also are interesting optical properties of conjugated polymer systems, which are both in the visible range of the spectrum and in the infrared and near ultraviolet area.

Poly-ortho-toluidine (POTI) has similar structure of polyaniline, but the presence of electron donor substitute – methyl group in ortho position relatively to the aminogroup, leads to some interesting physical and chemical properties of the polymer. It is known that the thin POTI films show electrochromic effect, can change its color under the influence of an applied potential [3, 5] and are able to change the optical spectra under influence of different types of gases [4, 6, 7, 8].

According to published data, it is known, that poly-ortho-toluidine can be used for designing resistive gas sensors [9] and diode structures [10]. Instead, the possibility of using this polymer as substance sensitive to vapors of organic substances is not fully discovered.

The aim of this work was to study the influence of vapors of organic solvents different nature to change the optical absorption spectra of chemically synthesized films of poly-ortho-toluidine and prediction on this data their possible use in optical sensors.

For the synthesis of conductive polymer poly-ortho-toluidine were used as initial materials: o-toluidine – mark “cp”; ammonium persulfate – mark “pfa”; sulfuric acid – mark “p”. All solutions for synthesis were prepared in distilled water.

As organic solvents we used dimethylformamide (DMFA), tetrahydrofuran (THF) and chloroform. Basic physical and chemical characteristics of the studied solvents are presented in Table 1.

For the formation of poly-ortho-toluidine films were used glass plates, coated by SnO₂, 10×20×0.1 mm size, surface resistance – 20 Ohms/cm². Cleaned and defatted plate was placed in a solution of 0.5 M sulfuric acid, containing 0.1 M solution of o-toluidine and 0.1 M solution of ammonium persulfate.

Table 1

Physicochemical characteristics of organic solvents

Name	n_D^{20}	ϵ	μ	η^{25} , mPa·s	Donor number	Acceptor number
DMFA	1.4304	36.7	3.82	0.796	26.6	16.0
THF	1.4050	7.6	1.63	0.48	20.0	8.0
Chloroform	1.4455	4.806	1.15	0.542	–	23.1

Oxidative polymerization of o-toluidine was carried out at room temperature for 60 minutes, according to the method described in [11]. After washing the sample with distilled water to remove residual of monomer and oxidant, it was dried at room temperature for 2 hours and kept in desiccators.

During polymerization thin films of poly-ortho-toluidine, formed on the surface of SnO₂, are uniform and had light purple color. As one can see from Fig. 1, in amorphous polymer matrix of the film are embedded the microcrystalline domains (Fig. 1). Such morphology of the film is typical for polyaminoarenes, particularly, for poly-ortho-toluidine [2, 10].

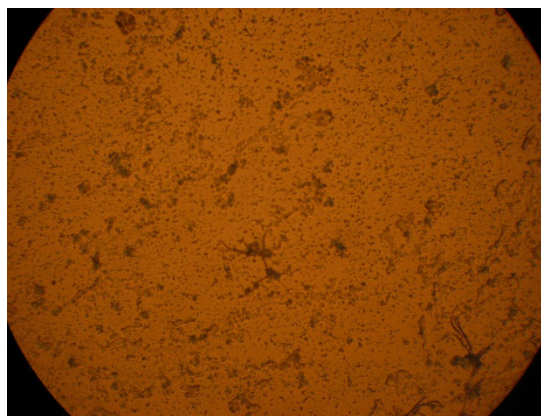


Fig. 1. Microphoto of the POTI film, obtained by chemical deposition on SnO₂ surface (zooming ×150)

The thickness of the films was measured by an interference microscope MII-4 and was 300 ± 20 nm.

Poly-ortho-toluidine film of the same thickness on the surface of SnO₂, was obtained by electrochemical polymerization of 0.1 M o-toluidine solution in 0.5 M sulfuric acid in terms of cyclic potential sweep from 0 to 1.35 V (Ag/AgCl) at scan rate $v = 50$ mV/s and the number of cycles $N = 50$. As the power source was used PI-50 potentiostat paired with the digital controller MTech CON-PI-50-2.

Sensory sensitivity of the films were studied for change their optical absorption after exposition of the film in the hermetic chamber by volume of 4 cm³ with vapor of the organic solvent during 5 minutes. In all tests a quantity of the solvent in vapor phase was the same (1 mg) at 293 K.

Optical absorption spectra of films were obtained with a spectrophotometer SF-46 (spectral range of $\lambda = 200$ –1100 nm) and photoelectrocolorimeter CFC-3. The operating range of wavelengths is from 400 to 900 nm. The pure plate of glass with SnO₂ coating was used as a reference.

Typical spectral dependence of optical absorption (A) for films of poly-ortho-toluidine in the wavelength range of 300–1100 nm is shown in Fig. 2. For both chemically and electrochemically deposited film the spectra are characterized by intense absorption band in the range $\lambda = 380$ –420 nm, resulting π - π^* transitions in conjugated aromatic system. In literature this band is associated with electronic transitions that match the energy difference of HOMO and LUMO orbital [1, 3]. The second broad intense absorption band for chemically obtained film is observed in the range 580–600 nm and is associated with the $n \rightarrow p$ transitions in benzoquinoid system of polymer chain. Maximum of second absorption band in the case of electrochemical polymers is observed at a wavelength of 720 nm, which corresponds to the absorption of delocalized charge carriers [3]. If you compare the spectra of the POTI films obtained by chemical polymerization with spectra of the POTI films obtained by electrochemical polymerization (Fig. 2, curves 1 and 2), it can be noted, that the resulting chemical deposition of POTI film has hypsochromic shift of the second band. Absorption in the range of 620–640 nm is the evidence that in the structure of the polymer dominates not oxidized formations.

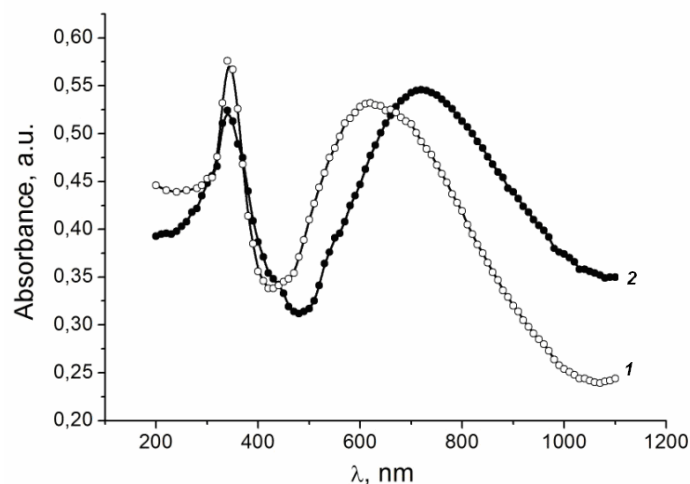


Fig. 2. Absorption spectra of POTI films, obtained by chemical (1) and electrochemical (2) method on the surface of SnO₂

This allows us to assume that thin layers of POTI obtained by chemical deposition, are able to both oxidation and reduction under adsorption of gas molecules of donor or acceptor type [12]. Under vapors of organic solvents are observed considerable changes in the optical spectra of chemically synthesized POTI films, as it can be seen from the results presented in Fig. 3 and 4.

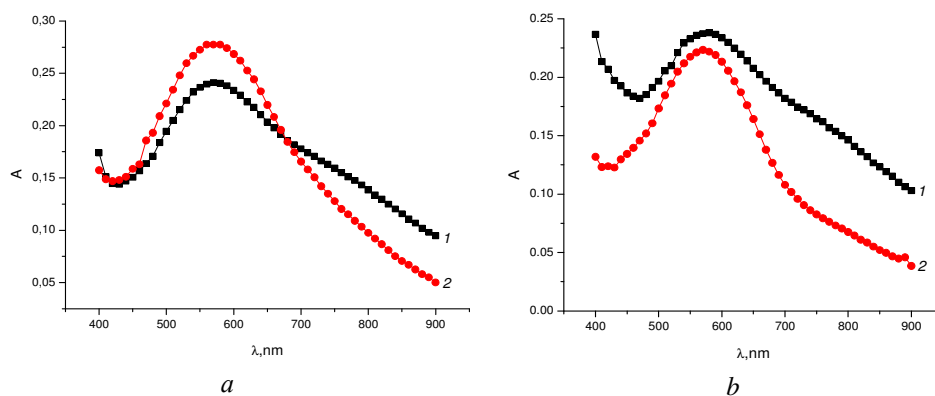


Fig. 3. Optical spectra of POTI films: *a*) 1 – original film; 2 – after influence of DMFA vapors, *b*) 1 – original film; 2 – after influence of THF vapors

In particular, under DMFA vapors is observed growth of optical absorption in the range 550–580 nm, but its maximum position remains unchanged. Instead, in $\lambda > 750$ nm there is a decrease in optical absorption (Fig. 3, *a*). A similar trend is observed under the fumes of chloroform.

If the POTI film is under the influence of THF, the biggest changes happen in optical absorption spectral range of 400–500 nm and 650–900 nm, and different from the effect of DMFA and chloroform (Fig. 3 *b*). Comparative sensory sensitivity to the action films of organic solvents, determined as $\Delta A/A$, is shown in Table 2.

Table 2

Sensor sensitivity of POTI films to the action of organic solvents

Solvent	λ , nm	A_0 , r. u.	A_g , r. u.	ΔA , r. u.	$\Delta A/A_0$, %
DMFA	450	0.140	0.150	-0.010	-7.1
	570	0.241	0.277	-0.036	-14.9
	850	0.125	0.070	0.055	44.0
Chloroform	450	0.115	0.110	0.005	4.34
	570	0.110	0.14	-0.03	-27.3
	850	0.05	0.04	0.01	20.0
THF	450	0.185	0.135	0.05	27
	570	0.230	0.220	0.01	4.34
	850	0.120	0.052	0.04	33.3

As can be seen from the table, the action of organic solvents is observed as a positive or negative deviation from the original values. But the general trend is the presence of significant differences in the optical absorption in the spectral range on the border of the visible and near infrared range, namely at $\lambda > 750$ nm. At $\lambda = 850$ nm spectral sensitivity to the vapors of DMFA is 44.0 %, to THF fumes – 33.3 %, to chloroform vapors – 20.0 %. It should be noted, that in the maximum absorption $\lambda = 570$ nm for chloroform maximum sensitivity is 27.3 %, comparing to THF – 4.34 % and DMFA – 14.9 %.

As for band of π - π^* transition near the 420 nm the highest sensitivity is observed to vapor THF (27 %), while under the influence of chloroform and DMFA these values are 4.34 and 7.1 %, respectively. The spectral sensitivity of the sensor films is shown in Fig. 4.

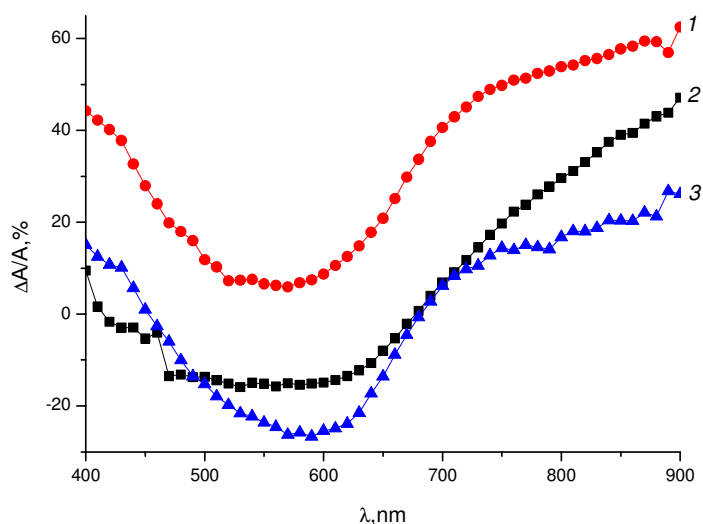


Fig. 4. Spectral dependence of sensor sensitivity of POTI film to the action of organic solvents vapors: 1 – THF; 2 – DMFA; 3 – chloroform

We can assume that the differences in the sensitivity of the POTI film to various solvents are associated with their physical and chemical properties. The highest values of the dielectric constant and dipole moment is of characterized DMFA, indicates its high capacity for solvation and dissolution of substances of different nature. Its interaction with the surface of the film is complex, and causes an increase in the maximum of absorption of a significant reduction in the near infrared area. To polar solvents we may also include THF, the action of which, also cause an increase in the optical absorption in the near infrared area. As for chloroform, this solvent has less impact on optical spectra of POTI, which is probably due to its lower polarity.

The spectral dependence of the optical absorption of thin layers of poly-ortho-toluidine in vapors of organic solvents (dimethylformamide, tetrahydrofuran, chloroform) was studied. The presence of the main absorption bands in the range of 380–420 and 580–620 nm, which correspond to electronic transitions in conjugated electronic system, was identified. During the action of vapors of organic solvents, it was observed both

positive and negative deviation of values relatively to the original optical signal. The nature of the spectral sensitivity of poly-ortho-toluidine to the action of vapors of organic solvents depends on their polarity, and the highest sensory responsiveness is observed under action of DMFA. Discovered influence of solvents on the optical spectra of poly-ortho-toluidine provides for possibility of selective detection of studied solvents with the application of thin layers of POTI as a sensitive element of optical sensors.

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СЕНСОРНА ЧУТЛИВІСТЬ ТОНКИХ ШАРІВ ПОЛІОРТОТОЛУЇДИНУ**А. Степура, Ю. Горбенко, О. Конопельник, О. Аксіментьєва**

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Мета праці – вивчити вплив парів органічних розчинників різної природи на зміну оптичних спектрів поглинання плівок поліортотолуїдину (ПОТІ) та прогнозувати на цій основі їх можливе застосування в оптичних сенсорах.

Для формування тонких шарів ПОТІ використано хімічну й електрохімічну полімеризацію о-толуїдину в середовищі 0,5 М сульфатної кислоти на поверхні SnO₂, товщина плівок становила 300±20 нм.

На основі дослідження впливу парів органічних розчинників (диметилформаміду, тетрагідрофурану, хлороформу) на оптичні характеристики тонких шарів хімічно синтезованого поліортотолуїдину визначено область спектральної чутливості полімерних шарів до дії органічних розчинників, характер якої залежить від їхніх фізико-хімічних параметрів. На основі отриманих даних доведено, що плівки ПОТІ на оптично-прозорих субстратах можуть бути використані для визначення випарів органічних розчинників, найвища сенсорна чутливість простежується стосовно диметилформаміду.

Виявлений ефект впливу досліджуваних розчинників на оптичні спектри ПОТІ має суттєву відмінність у характері їхньої взаємодії, що передбачає можливість селективного визначення розчинників під час застосування ПОТІ як чутливого елемента оптичних сенсорів.

Ключові слова: поліортотолуїдин, оптичні спектри, органічні розчинники, полярність, сенсорна чутливість.

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