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EFFECT OF DOPING ON THERMO-OPTICAL BEHAVIOR OF POLY-3,4-ETHYLENEDIOXYTHIOPHENE FILMS

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The temperature dependences of optical absorption spectra of the conducting polymer films of poly-3,4-ethyledioxythiophene (PEDOT) doped with potassium ferricyanide complex $K_3[Fe(CN)_6]$ have been studied in the interval of T = 80–380 K. It has shown that doping of polymer by $K_3[Fe(CN)_6]$ leads to increasing of intensity of absorption band at λ = 610–780 nm. Change of temperature from 80 to 380 K causes a decrease in optical absorption of PEDOT films in all temperature range, however characteristics of thermochromic effects are vary under polymer doping by ferricyanide.

Key words: thermooptical behavior, poly-3,4-ethylenedioxythiophene, doping, potassium ferricyanide, thermochromics.

Numerous organic substances exhibit a possibility to change their optical characteristics (and color) under action of external physical and chemical factors. Generally the color change is based on alteration of the electron states of molecules, especially the π- or d-electron state [1, 2]. This phenomenon is induced by various external stimuli which can alter the electron density of substances. A great attention now attracts the conjugated polymers with intrinsic electron conductivity such as polyaniline [2, 3] and polythiophene derivatives [4–8] because of its environmental stability, interesting electro-optical properties, and high conductivity. Action of temperature, magnetic or electric fields, adsorption of gases or ions changes the electronic properties of conjugated polymers – energy of band gap, concentration of charge carriers or their mobility [1, 2]. This provides a development of the new generation of materials for organic displays, panels, sensors, "smart windows", which integrates the optical properties of semiconductors with flexibility, thermoplastic processing and lightness of polymers [5–9]. To enhance the performance of optical devices based on conducting polymer, especially contract ratio, sensitivity, long cycle life and coloration efficiency often used process of polymer doping by metal oxide (WO_3, V_2O_5, RuO_2, etc.) or metal complexes [2, 6–8, 10].

Among the metal complexes a grate attention is attracted to group of Prussian complex salts, especially to potassium ferro- and ferricyanide [6–8]. Potassium ferricyanide is used in many amperometric biosensors as an electron transfer agent [6]. Doping of conjugated polymers with these complexes leads to change their electrooptical characteristics [2, 8]. The specific capacitance of PEDOT hydrogel was efficiently increased by the doping with $K_3[Fe(CN)]_6$ that may be use for supercapacitor applications [7]. However effect of doping by $K_3[Fe(CN)_6]$ complex on the thermochromic behavior of conjugated polymers for today is not studied.

The thermochromic properties of conducting polymers are a subject of specific interest. It has been found that conjugated polymers such as poly-3-alkilthiophens [1, 11] exhibit the state similar to liquid crystalline. Study of temperature effect on the optical spectra of undoped polyanilines in solution and in solid state showed that thermochromic effect in these materials caused by the changing in polymer backbone conformations [12, 13]. From the study of absorption spectra it found that under temperature change the variations in the polymer films color are observed [1, 13]. In the optical spectra it's developed in the "blue shift" of absorption maximums and in the changing of their intensity. However in conducting (doped) forms of conjugated polymers, especially when the metal complex doping agents are used, this effect has a lack of study.

The goal of the present paper is study effect of doping on the temperature dependence of the optical spectra of poly-3,4-ethylenedioxythiophene (PEDOT), doped with $K_3[Fe(CN)_6]$ complex.

The monomer – 3,4-ethylene dioxythiophene (EDOT) purchased from the Aldrich, USA (assay 97 %) were used. Films were obtaining by electropolymerization method on the transparent surface of tin-oxide (SnO_2) glass (SCHOTT, Korea) with resistance of 20 Ohms/sq. with a visible transmission of >80 %. Preparation of PEDOT films on the SnO_2 glass working electrodes by area of 1 cm^2, Pt-network counter electrodes was carried out by electrolysis 0,1 M solution of EDOT in water-ethanol (1:1) mixture contained 0,05 M $LiClO_4$ at current density i = 0.1 mA/cm^2 during 10 min at T = 293 K [5]. Obtained samples were washed by distilled water and dried in dynamic vacuum at T = 333 K. Films thickness determined with interferometer MII-4 was 440 ± 12 nm.

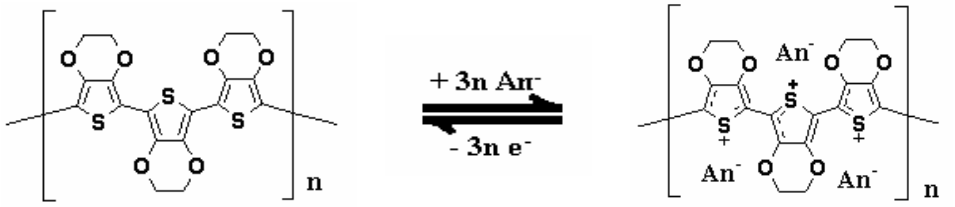
The PEDOT coating deposited from an aqueous solution containing the EDOT monomer and $LiClO_4$ as supporting electrolyte was used as a "reference" material The chemical structure of elementary link for PEDOT is well known from literature [2, 4–8] and in our study was confirmed by FTIR spectroscopy as described in [5]. Doping of the polymer films by complex $K_3[Fe(CN)_6]$ (analytical grade, purchased from the "Sfera Sim") was realized in the process of ion exchange reactions [14–16] by exposition of the films in 0,01 M solution of $K_3[Fe(CN)_6]$ in 0,1 M KCl by 2 h.

The value of thermochromic effect (%) is calculated as the difference in absorbance D_{80} at very low (80 K), and the highest temperature D_{380} (380 K) divided by D_{80} relative: $((D_{80}-D_{380})/D_{80})\times 100$ %.

Optical absorption measurements were performed in a temperature range from 80 to 380 K using the cryostat with the ITC4 programmed temperature controller (Au/Fe-chrome thermocouple). The spectra were analyzed with a Zeiss model SPM2 grating monochromator (setting to a spectral bandwidth of 2 cm^{-1}) detected by a cooled photomultiplier. The SRS 250 boxcar integrator has averaged the resulting signal. A continuous flow helium cryostat (Oxford, model CF 1104) was used for temperature measurements. All measurements were curried out in Institute of Physics of Polish Academy of Science.

Conducting polymers including PEDOT are prepared by oxidizing polymerization of corresponding monomers. They have positive charges every three to five monomer units (ethylene dioxythiophene rings) along polymeric backbone [2, 4, 18]. The positively charged ensembles (polarons and bipolarons) work as a charge carrier for conduction. During electrochemical synthesis, counter-anions called dopants are introduced into the conducting polymers to neutralize the positive charges of backbones (Fig. 1). In our case perchlorate anion ClO_4^- acts as a dopant in PEDOT.

Process of PEDOT doping by potassium ferricyanide complex may be realized in some ways: on the stage of the synthesis (self-doping [7]), by redox reactions [6] and in result of ion-exchange reaction [14–16]. The small-sized dopant molecules are efflux from the films in presence of large-sized dopants such as $[Fe(CN)_6]^{3-}$ [6–8].



PEDOT
insulator

[PEDOT^{+}] nAn-
conductor

Fig. 1. Chemical structure of elementary link for neutral PEDOT (insulator) and for electrodeposited PEDOT ($An^- – ClO_4^-$).

Doping process in the ion-exchange reaction is followed by the scheme:

$$[PEDOT^{\cdot 3+}]\ 3An^- + Fe(CN)_6^{3-} \leftrightarrow [PEDOT^{3+}]\ Fe(CN)_6^{3-} + 3An^- \quad (1)$$

Due to reducing of ferricyanide ion in a result of electron transfer from non-oxidized links of PEDOT, the formation of ferrocyanide anion takes a place [17]:

$$[Fe(CN)_6]^{3-} + e \leftrightarrow [Fe(CN)_6]^{4-} \quad (2)$$

Reaction is reversible and proceeds until the equilibrium state achieves. In result a redox pair $[Fe(CN)_6]^{-3/-4}$ acts as an ion-dopant for PEDOT: So, introducing of $K_3Fe(CN)_6$ into PEDOT film causes the doping effect of anionic ferricyanide/ferrocyanide couple [7] known as a redox probe [6].

UV-vis optical absorption spectra of PEDOT films at room temperature before and after doping are shown in Fig. 2.

The spectrum of PEDOT film at T = 300 K contains absorption bands with maximum at about 385, 620 and 692 nm. The absorption bands appear at λ = 380–400 nm due to π-π* transition in the double bonds of polymer backbone and band at λ = 620 nm can be attributed to interchain interaction [18], while absorption at λ > 690 nm was assignable to charge carriers, so-called polarons (polaron band). These are typical absorption shapes for the PEDOT [3, 18–20].

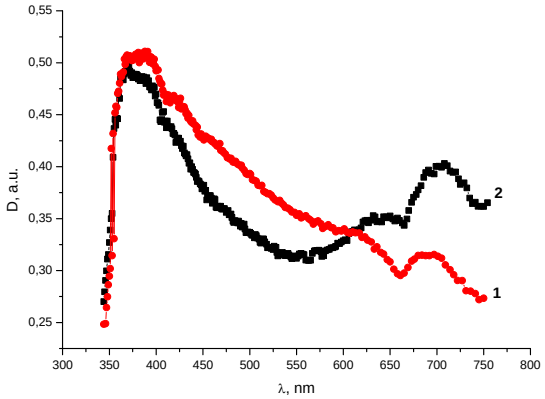


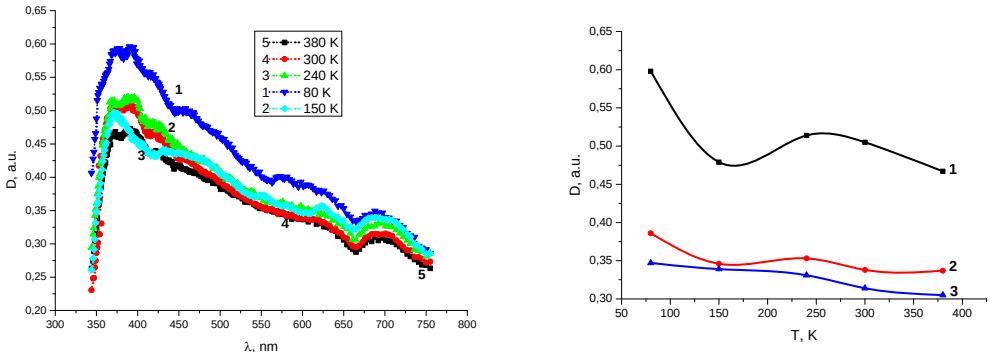
Fig. 2. Optical absorption spectrum of undoped PEDOT film (1) and PEDOT, doped with $K_3[Fe(CN)_6]$ (2) at T = 300 K.

Doping of PEDOT by $K_3[Fe(CN)_6]$ complex causes a change in color of the film from blue to purple and correspondently – in absorption spectrum of the film. Some decrease of absorption intensity in the range 360–400 nm and simultaneous narrowing of the band wideness is observed due to change in configuration of energy levels. Two other bands in absorption spectrum are shifted on 10–15 nm in long-wave range of spectrum and have a higher intensity in comparison with pristine PEDOT film. This phenomenon indicates a greater length of the electron delocalization of PEDOT doped by ferrycianide in result of additional oxidation of conjugated polymer backbone by $[Fe(CN)_6]^{3-}$ according to equation (2).

The increase of the absorption band intensity with maximum near 700 nm in a result of doping is evidence of structural ordering of macrochains and increase the polaron states in result of doping [15–17].

It has been found that shape of the optical spectra PEDOT film at different temperatures is similar (see Fig. 3, 4). At low temperature (80–240 K) they contain four absorption bands with maximum at about 375, 391, 600 and 692 nm. When temperature rising the first two bands coalescence to one broad band at λ = 375–390 nm. However an influence of temperature on the optical absorption of PEDOT films has a tendency to lightness – decrease in optical density over visible spectral range, indicating thermochromic effect.

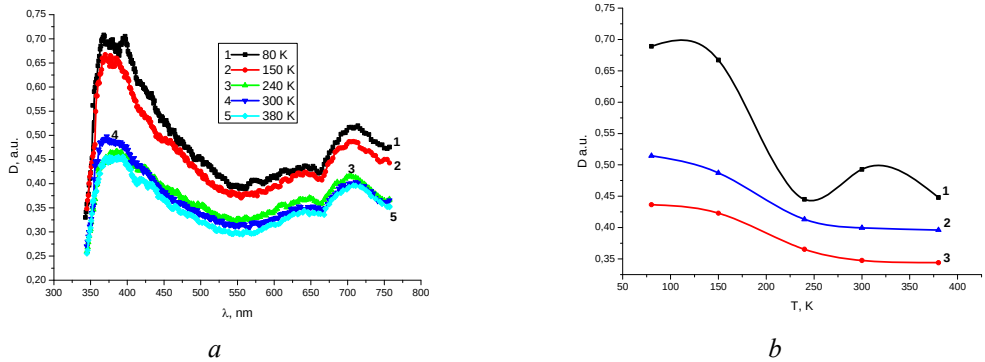
As one can see from Fig. 3, *a*, *b* the intensity of the absorption is decreasing with growth of temperature in the range of 80–380 K. But most significant changes in optical absorption are observed for bands in the range of λ = 360–400 nm. Simultaneously a small shift of π-π* transition band (on 5–10 nm) to the higher energies ("blue" or hypsochromic shift) was observed. More significant termochromic effect in PEDOT film (24,8 %) under rising of temperature from 80 to 380 K is attributed namely to this band. For polaron band (698 nm) termochromic effect is 11,7 %.



a *b*

Fig. 3. *a* – optical absorption spectra of PEDOT film on SnO_2 surface at different temperatures, K: 80 (1); 150 (2); 240 (3); 300 (4); 380 (5); *b* – temperature dependence of optical absorption of PEDOT film at λ = 385 (1); 620 (2); 692 nm (3).

For the films of PEDOT doped with $K_3[Fe(CN)_6]$ the intensity of the absorption in optical spectra also decreased when temperature rising. As shown in figure 4, doping of PEDOT by ferricyanide complex causes stronger temperature dependence in the optical absorption in comparison to reference PEDOT film. The thermochromic effect for doped film is significantly higher and for π-π* transition band achieves 34,3 %. For polaron band (708 nm) thermochromic effect is 25,0 %.



a *b*

Fig. 4. *a* – optical absorption spectra of PEDOT film doped with $K_3[Fe(CN)_6]$ on SnO_2 surface at different temperatures, K: 80 (1); 150 (2); 240 (3); 300 (4); 380 (5); *b* – temperature dependence of optical absorption of doped PEDOT film at 370 (1), 640 (2) and 708 nm (3).

Thermo-induced changes in the optical spectra of polymers may be connected both with conformation rotation of segments in polymer chains and change in electronic properties of conjugated polymer system [1, 11]. It known that PEDOT backbone has a high ability to conformation changes and modify its configuration from compressed coil to expanded chain under different factors – temperature, doping, solvent and others [19]. A developed blue shift of absorption maximum of π-π* transition under temperature rising and decrease of their intensity may be evidence of conformation changing in polymer backbone [11, 20]. But in solid state (in the film) the polymer chain mobility is considerably limited in comparison with solution, that's why a thermochromic effect observed in the films connects not only with a polymer chains conformation but also depended on electron properties of polymers.

Effect of doping by ferricyanide complex on the optical absorption of PEDOT also develops in the significant shift of temperature induced minimum of π-π* transition band from 150 K to 250 K (Fig. 3, b and Fig.4, b). This may be caused by a change in electron structure of conjugated chain in results of macromolecular structure ordering.

So, for the first time we studied a temperature behavior of optical spectra of PEDOT films electrodeposited on the SnO_2 surface in the temperature interval of 80–380 K. It has been found that thermochromic effect in PEDOT film is attributed mainly to π-π* transition band. Doping of PEDOT by ferricyanide complex causes stronger temperature dependence in the optical absorption. Most significant relative changes in optical adsorption are observed in near UV-spectral range and for doped films this value is 34,8 %, while for reference – 24,8 %.

Acknowledgments

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ВПЛИВ ЛЕГУВАННЯ НА ТЕРМООПТИЧНУ ПОВЕДІНКУ ПЛІВОК ПОЛІ-3,4-ЕТИЛЕНДІОКСИТІОФЕНУ

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Вивчено температурну залежність оптичних спектрів поглинання електропровідних полімерних плівок полі-3,4-етилендіокситіофену (ПЕДОТ), легованих комплексом калій гексаціаноферату (III) $K_3[Fe(CN)_6]$ в інтервалі $T = 80–380$ K. Плівки отримували методом електрохімічної полімеризації розчину мономеру 3,4-етилендіокситіофену у водно-етанольній (1:1) суміші, що містила 0,05 M $LiClO_4$ за густини струму $i = 0{,}1$ мА/см^2 протягом 10 хв при $T = 293$ K. Полімерні плівки легували реакцією іонного обміну за витримки плівки у 0,01 M розчині $K_3[Fe(CN)_6]$ протягом 2 год за кімнатної температури. Легування полімеру комплексом $K_3[Fe(CN)_6]$ веде до збільшення оптичного поглинання плівок ПЕДОТ в інтервалі $\lambda = 610–780$ нм. Водночас підвищення температури від 80 до 380 К спричиняє зменшення оптичного поглинання у всьому температурному діапазоні. Термоіндуковані зміни в оптичних спектрах ПЕДОТ можна пояснити високою здатністю цього полімеру до конформаційного обертання сегментів полімерного ланцюга та зміною електронних властивостей спряженої полімерної системи, про що свідчить наявність "синього зсуву" максимуму поглинання π-π^*-переходу в разі підвищення температури та зменшення його інтенсивності. Виявлено суттєвий вплив легування на термохромний ефект у плівках ПЕДОТ: найбільші відносні зміни оптичного поглинання простежуються в ближній УФ ділянці, причому для легованих плівок це значення становить 34,8 %, а для нелегованих – 24,8 %.

Ключові слова: полі-3,4-етилендіокситіофен, легування, калій гексаціаноферат (III), термохромність.

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