Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Layer-by-layer assembly and thermal sensitivity of poly(3,4-ethylenedioxythiophene) nanofilms

O. I. Konopelnyk, O. I. Aksimentyeva, Yu. Yu. Horbenko, D. O. Poliovyi & I. Ye. Opaynych

To cite this article: O. I. Konopelnyk, O. I. Aksimentyeva, Yu. Yu. Horbenko, D. O. Poliovyi & I. Ye. Opaynych (2016) Layer-by-layer assembly and thermal sensitivity of poly(3,4-ethylenedioxythiophene) nanofilms, Molecular Crystals and Liquid Crystals, 640:1, 158-164, DOI: 10.1080/15421406.2016.1257327

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1257327

Published online: 14 Dec 2016.

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 640, 158–164
http://dx.doi.org/10.1080/15421406.2016.1257327

Taylor & Francis
Taylor & Francis Group

Layer-by-layer assembly and thermal sensitivity of poly(3,4-ethylenedioxythiophene) nanofilms

O. I. Konopelnyk[a], O. I. Aksimentyeva[a], Yu. Yu. Horbenko[a], D. O. Poliovyi[b], and I. Ye. Opaynych[a]

[a]Ivan Franko National University of Lviv, Lviv, Ukraine; [b]Ivan Horbachevsky Ternopil State Medicine University, Ternopil, Ukraine

ABSTRACT

The functional nanofilms of poly(3,4-ethylenedioxythiophene) – poly(styrenesulfonate) (PEDOT:PSS) anionic complex were prepared on the transparent substrates by layer-by-layer (LBL) assembly with N-cetylpyridinium bromide (CPB) as cationic surfactant. It has studied dependence of films thickness on the number of bilayers of PEDOT:PSS/CPB and on initial concentration of PEDOT:PSS in colloid solution. The LBL films of PEDOT:PSS/CPB demonstrate the thermal sensitivity of optical absorption in visible and near IR range of spectrum which promises their application in sensor devices.

KEYWORDS

layer by layer assembly; PEDOT:PSS; absorption spectra; thermochromic behavior

Introduction

Conjugated polymers combine the optical properties of semiconductors with flexibility, thermoplastic processing and lightness of polymers [1, 2]. The development of the new generation of materials for organic displays, flat panels, smart windows and sensors requires a working out the effective methods to obtain the nanosize functional films sensitive to external influence namely electric field, temperature, radiation and adsorption of chemical substances [3–7]. One of the most promising conducting polymer is poly(3,4-ethylenedioxythiophene) (PEDOT), especially doped with polystyrene sulfonic acid (PSS). It characterized by high conductivity, flexibility and interesting optical properties in visible, near-UV and NIR spectral range, whereas is perspective for the optical application [8–11].

For the preparation of PEDOT:PSS films electropolymerization, spin coating and imprinting methods [3–10] are widely employed, but process of self-assembling in layer by layer (LBL) deposition is not quite studied. This method is preferable for obtaining of ultrathin conducting polymer and hybrid films due to its simplicity and possibility of direct control of film thickness by number of the pair layers (bilayers) [11–15]. An important advantage of the method is the possibility to obtain functional films on virtually any surface [11, 16].

The formation of multilayered polymer films via the LBL assembly utilizes the electrostatic interaction between oppositely charged molecules – anionic and cationic types. The PEDOT:PSS is anionic complex of PEDOT where polystyrene sulfonate acts both as dopant for PEDOT and anionic surfactant. The cationic surfactant creates a positive charge on the surface. It is selected, as rule, from series of polyelectrolytes: polydiallyldimethyl ammonium

CONTACT O. I. Konopelnyk konopel@ukr.net

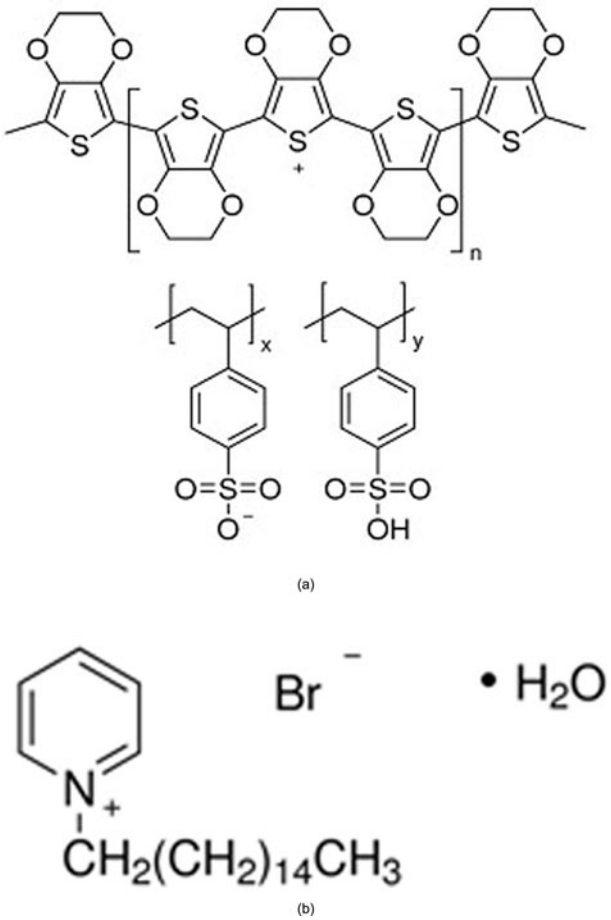

Figure 1. (a) Structure formula of poly(3,4-ethylenedioxythiophene): polystyrene sulfonic acid complex; (b) Structure formula of cationic surfactant – N-cetylpyridinium bromide.

chloride, polyallylamine hydrochloride, etc [14–16]. An inclusion of the inert polymer particles into the functional polymer material decreases an optical transmittance of the film due to light dissipation or light absorption by inert polyions [14, 15]. For improving the optical characteristics of PEDOT:PSS films we proposed to use N-alkylpyridinium chloride as low-molecular surfactant [12]. It has been found that compact uniform films of PEDOT:PSS on the indium-tin-oxide (ITO) surface with regular thickness (10–60 nm) were deposited in result of 5–40 routes of alternative adsorption of cationic surfactant (cetylpyridinium chloride) and anionic polymer complex PEDOT:PSS. Obtained films demonstrate certain electrochemical activity and may be used for the development of electrochromic devices. However, widening area of application of PEDOT:PSS for sensors, plastic electronics, conductive textile and paper is needed to obtain functional nanofilms on the surface of different nature – glass, quartz, plastic, etc. Beside this the thermal behavior of conducting polymer spectra is a subject of specific interest, but for PEDOT:PSS films obtained by LBL method this subject has a lack of study.

In the present work we investigated a process of layer-by-layer assembly of PEDOT:PSS nanofilms on the transparent dielectric surface of the glass "Corning" and study their sensitivity to external factor such as temperature.

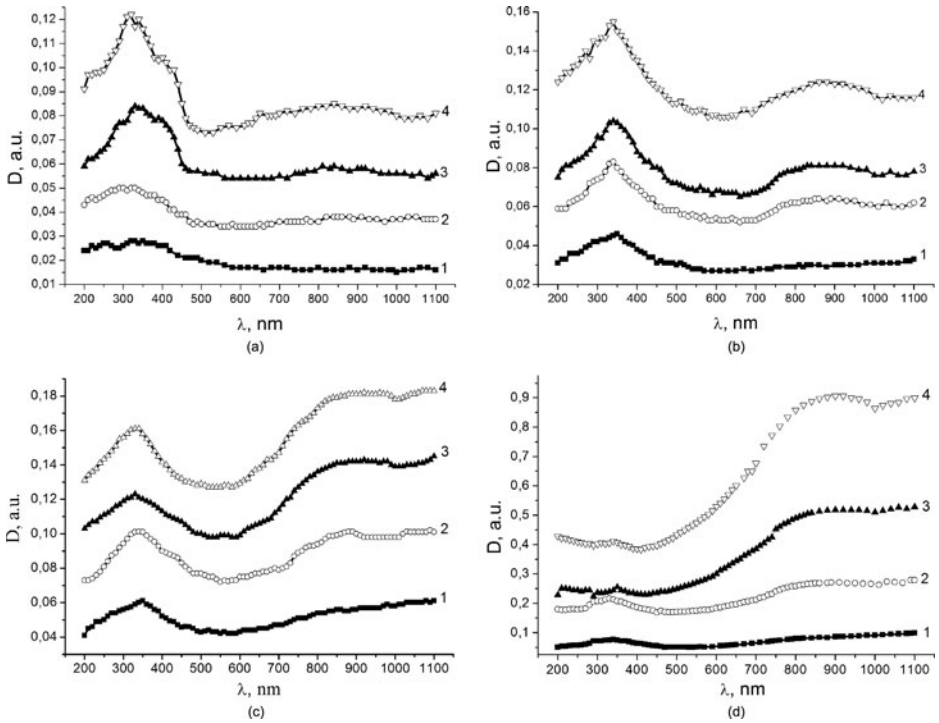

Figure 2. Absorption spectra of the PEDOT:PSS/CPB nanofilms deposited on glass "Corning" by the LBL method. Concentration of PEDOT:PSS 0,05 (a), 0,1 (b), 0,2 (c) and 0,4 wt.% (d). Number of bilayers: 10 (1), 20 (2), 25 (3); 30 (4).

Experimental

Materials

The poly(3,4-ethylenedioxythiophene) used in the form of aqueous suspension of polymer stabilized by anionic surfactant – polystyrene sulphonic acid, with content of PEDOT:PSS 1.3 wt. %. PSS content is 0.8 wt. % PEDOT content is 0.5 wt. %.

As cationic active surfactant used the high purity N-cetylpyridinium bromide (CPB) monohydrate (98%). All reagents were purchased from the Sigma-Aldrich. Chemical structures of the anion stabilized polymer and cationic surfactant are presented in Fig. 1.

All solutions were prepared on the twice distilled water at room temperature. The concentration of CPB was 0.05 wt. %. Water dispersion of PEDOT:PSS was diluted to concentrations from 0.05 to 0.4 wt. %. Films were assembled on the transparent surface of "Corning" optically clear cover glasses. Before coating slides were washed, placed in glacial acetic acid for 10 minutes and rinsed with distilled water. After acid treatment and rinsing glass slides were treated with N-(2-aminoethyl)-3-aminopropyl-trimethoxysilane to make the substrate surface hydrophilic.

Method of film formation

The LBL films of PEDOT:PSS/CPB were prepared by alternative electrostatic-absorption process as described in [11, 17]. The molecules of CPB in water form the cationic surfactant

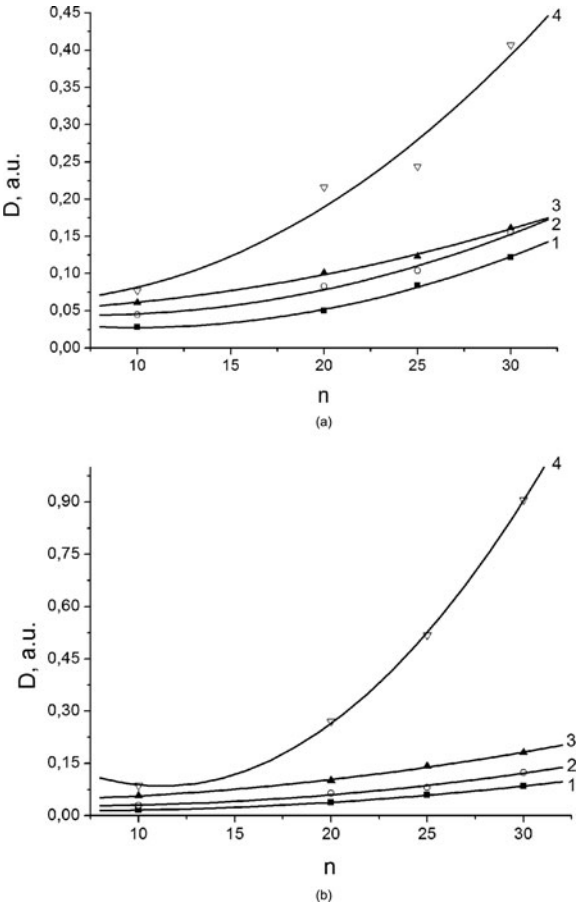

Figure 3. The relationship between optical absorption and the number of PEDOT:PSS/CPB bilayers at a) 350 nm, b) 850 nm. The numbers indicated PEDOT:PSS concentration: 1 – 0.05%, 2 – 0,1%, 3 – 0,2% and 4 – 0.4% (by wt.).

particles $[C_nH_{2n+1}NC_5H_5]^+$ which adsorb on the surface of a glass plate and give it a positive charge. After washing and drying a plate was immersed to PEDOT:PSS solution and expose during 10 minutes. In this route takes place in front of the adsorption process of contrary charged anionic layer and forms a double layer (bilayer). The next cycles of deposition include alternative immersion of the plate in CPB solution, in water, then in solution of anionic polymer, water and drying in beam of nitrogen. In result of 8–30 cycles of deposition the smooth uniform layers with thickness of 10–50 nm were formed.

Instrumentation

Optical absorption spectra in UV-visible-near-IR region were obtained with spectrophotometer SP-46 at the temperatures T = 293, 323 and 343 K in air atmosphere.

Film thickness was measured with laser zero-ellipsometer LEF-3M-1 (λ = 632.8 нм), by 4-bands technique as early described in [12].

Results and discussion

As showed by electron spectroscopy, increasing of the bilayers number during the process of film formation leads to arising in optical absorption of polymer layer and correspondingly, in

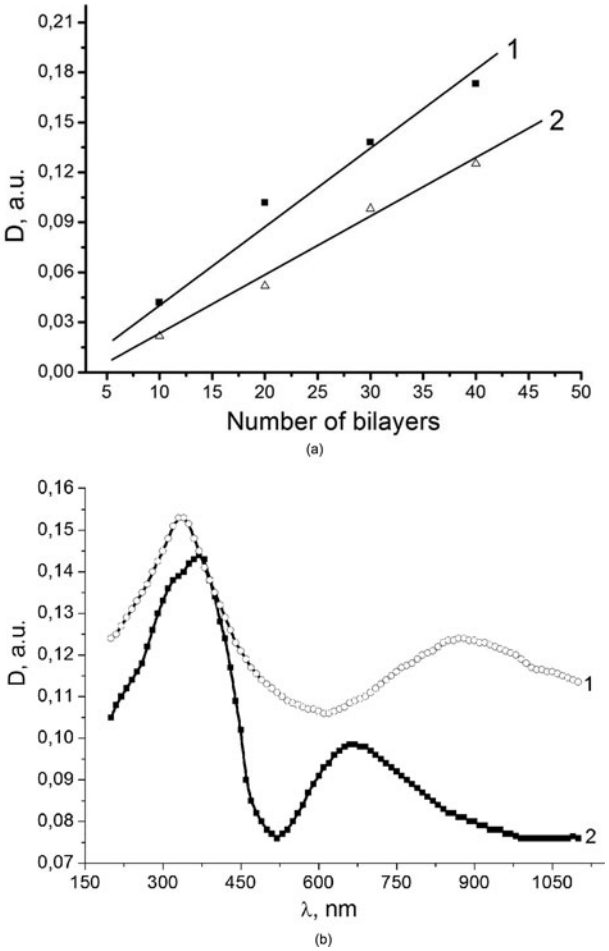

Figure 4. (a) The relationship between optical absorption of the PEDOT:PSS/CPC films on ITO surface and the number of bilayers at λ = 380 (1) and 660 nm (2) [12]; (b) Absorption spectra of PEDOT:PSS/CPB LBL film on "Corning" glass (1) and ITO (2) surface (N = 30 bilayers).

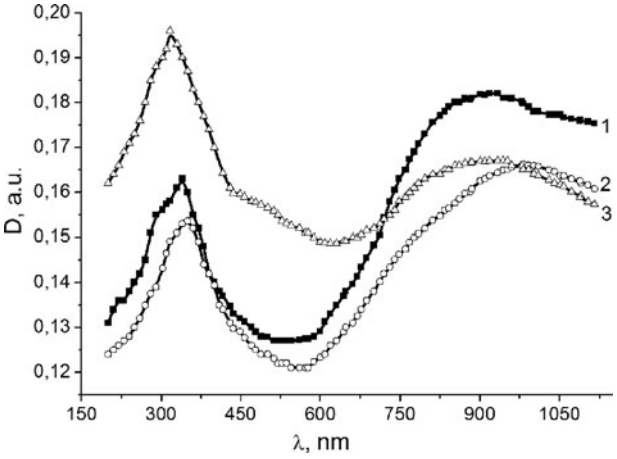

Figure 5. Absorption spectra of PEDOT:PSS/CPB film on "Corning" glass at T = 293 (1). 323(2) and 343 K (3) for N = 30, C = 0,2 wt. %.

thickness of the self-assembled film. An increasing in optical absorption of polymer layer has not significant effect on the position and relative intensity of the absorption bands (Fig. 2).

PEDOT:PSS/CPB films, obtained from 10 and more bilayers on the "Corning" glass surface characterized by absorption at 340–360 nm indicates the existence of localized polarons, and broad band at 780–920 nm attributes to vibronic coupling and indicates the inter-chain π-stacking interaction of thiophene rings [18]. With increasing number of layer, along with common rising absorption, the peak position of the first and second bands have a non significant shift. For films obtained at PEDOT:PSS concentration 0,2 and 0,4% (wt) the optical absorption at $\lambda > 800$ nm extended to near IR region (Fig. 2,c,d). It may be attributed to both polarons and bipolarons with formation of their own band [1, 18].

The dependence of optical absorption of indicated maximums in spectra of LBL films on number of bilayer (N) is described by parabolic functions (see Fig. 3 a, b) which is different than for LBL films obtained on the ITO substrates with cetylpyridinium chloride (CPC) surfactant, where this dependence is similar to linear up to 40 bilayers (see Fig. 4, a [12]).

The shape of the optical spectra of the LBL films assembled on "Corning" glass and ITO surface also have some differences (Fig. 4, b). As one can see the film on glass demonstrates a blue shift of the first band and a red shift for the second as compared to the film on ITO surface. Such peculiarities may be connected with roughness of ITO surface and its semiconducting nature [16].

Influence of temperature on the absorption spectra of PEDOT:PSS/CPB films was investigated in the interval of $T = 293–373$ K. It has been found that under temperature change the variations in the polymer films color are observed. In the optical spectra it's developed in the shift of absorption maximums and in the changing of their intensity (Fig. 5).

Thermo-induced changes in the optical spectra of PEDOT:PSS nanolayers may be connected with conformation rotation of segments in polymer chains and probably with change in electronic properties of conjugated polymer system [19, 20]. 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 [21]. 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 may be connected not only with a polymer chains conformation but also depended on electron delocalization of π-conjugated polymer backbones.

Conclusion

So, we studied a process of LBL films assembly from anionic complex PEDOT:PSS and cationic surfactant cetylpyridinium bromide. It has found that process of film formation is depended on concentration of PEDOT-PSS in colloid solution, number of bilayers and type of the substrate. Thermal behavior of optical spectra of PEDOT:PSS/CPB films deposited on the glass surface in the temperature interval of 293–343 K demonstrate the thermochromic effect probably connected with conformation of polymer backbone and change in the length of electron delocalization.

References

[1] Heeger, A. J. (2002). *Synth. Metals*, *123*, p. 23.
[2] Cao, Z., Chen, Z., & Escoubas, L. (2014). *Optical Materials Express*, *4*(12), 2532.
[3] Carpi, F., & De Rossi, D. (2006). *Optics&Laser Technology*, *38*, 292.

[4] Aksimentyeva, O. I., Konopelnyk, O. I., & Poliovyi, D. O. (2011). *Mol. Cryst. Liq. Cryst.*, *536*, 392.
[5] Hou, S., Zhibin, Lv, & Wu, H. et al. (2012). *Mater. Chem*, *22*, 6549.
[6] Karbovnyk, I., Olenych, I., & Aksimentyeva, O. et al. (2016). *Nanoscale Research Letters*, *11*, 84. DOI 10.1186/s11671-016-1293-0, 5p.
[7] Gavgani, J. N., Hasani, A., Nouri, M., Mahyari, M., & Saleh, A. (2016). *Sensors and Actuators B*, *229*, 239.
[8] Han, Y., Guo, Y., Shen, M., Duan, P., Yuan, Z., & Zhang, M. (2014). *High Performance Polymers*, *26*(5), 499.
[9] Malki, Z. E., Hasnaoui, K., & Bejjit, L. et al. (2010). *Journal of Non-Crystalline Solids.*, *356*(9), 467.
[10] Li G., Shrotriya, V., Huang, J., Yao, Y., & Moriarty, T. (2005). *Nature Materials*, *4*, 864.
[11] Aba, L., Yusuf, Y., & Mitrayana, Triyana K.. (2012). *J. Mod. Phys.*, *3*, 529.
[12] Konopelnyk, O. I., Aksimentyeva, O. I., Dyakonov, V. P., Piechota, S., Opaynych, I. Ye., & Szymczak, H. (2013). *Functional Materials*, *20*(2), 248.
[13] Kitamura, K., & Shiratori, S. (2011). *Nanotechnology*, *22*(19), 195703.
[14] Kim, S., Shim, N., Lee, H., & Moon, B. (2012). *J. Mater. Chem.*, *22*, 13558.
[15] De Saint-Aubin C., & Hemmerlé, J., Boulmedais et al. (2012). *Langmuir*, *28*(23), 8681.
[16] DeLongchamp, D. M., Kastantin, M., & Hammond, P. T. (2003). *Chem. Mater.*, *15*, 1575.
[17] Aksimentyeva, O., Konopelnyk, O., Opaynych, I., & Horbenko, Yu. (2014). Patent № 90790 (UA).
[18] Lock, J. P., Lutkenhaus, J. L., & Zacharia, N. S. et al. (2007). Synth. *Metals*, *157*, 894.
[19] Seeboth A., & Lötzsch. D. (2008). *Thermochromic Phenomena in Polymers / Smithers Rapra Technology Limited*. UK.
[20] Konopelnik, O. I., Aksimentyeva, O. I., & Martynyuk, G. V. (2005). *Mol. Cryst. Liq. Cryst.*, *427*, 37.
[21] Ouyang, J., Xu, Q., Chu, C. -W., Yang, Y., Li, G., & Shinar, J. (2004). *Polymer*, *45*, 8443.