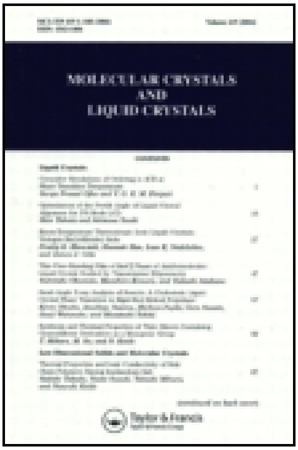


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Thermo-Vacuum Deposition and Electrooptical Properties of Polyaniline Thin Films

O. I. Aksimentyeva [a], V. M. Beluh [a], D. O. Poliovyi [a], V. V. Cherpak [b], P. Y. Stakhira [b] & D. Y. Volynyuk [b]

[a] Ivan Franko Lviv National University, Lviv, Ukraine

[b] Lviv Polytechnic National University, Lviv, Ukraine

To cite this article: O. I. Aksimentyeva, V. M. Beluh, D. O. Poliovyi, V. V. Cherpak, P. Y. Stakhira & D. Y. Volynyuk (2007): Thermo-Vacuum Deposition and Electrooptical Properties of Polyaniline Thin Films, Molecular Crystals and Liquid Crystals, 467:1, 143-152

To link to this article: http://dx.doi.org/10.1080/15421400701221336

Mol. Cryst. Liq. Cryst., Vol. 467, pp. 143–152, 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701221336

Thermo-Vacuum Deposition and Electrooptical Properties of Polyaniline Thin Films

O. I. Aksimentyeva
V. M. Beluh
D. O. Poliovyi
Ivan Franko Lviv National University, Lviv, Ukraine

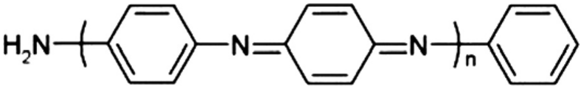
V. V. Cherpak
P. Y. Stakhira
D. Y. Volynyuk
Lviv Polytechnic National University, Lviv, Ukraine

The effect of vacuum deposition temperature on the structure and electrooptical properties of polyaniline (PAN) thin films has been studied. In ellipsometry investigations, it has been found that films deposited at 300–400°C at a pressure of 1×10^{-6} Torr with 20–40 nm thickness possess an optical anisotropy. The films obtained at a deposition temperature of 450°C are characterized by a high electrochemical and electrooptical activity. They have an improved morphology and oxidation-reduction stability as compared to those of the films formed by the electrochemical polymerization method.

Keywords: electrooptical activity; optical anisotropy; polyaniline, vacuum deposition

INTRODUCTION

Due to its unique electronic and optical properties, polyaniline (PAN) is an important conductive polymer, which leads to its wide application in electrochromic devices, batteries, and chemical sensors [1–5]. The general formula of polyaniline in its base form is:



Formula of polyaniline

Address correspondence to P. Y. Stakhira, Lviv Polytechnic National University, 12, S. Bandery Str., Lviv 79013, Ukraine. E-mail: stakhira@polymet.ua

The formation of the PAN films on the optical transparent electrodes is generally carried out from a PAN solution by the solvent evaporation and by the oxidative or electrochemical polymerization of aniline [2–5]. On the other hand, a thermo-vacuum deposition is a promising method of formation of a perfect polymer film on the both conductive and dielectric surfaces. In many works, the PAN thin films were deposited onto different substrates by heating a PAN powder from 180 to 500°C at a pressure of about 1×10^{-6} Torr [6–15]. These vacuum-deposited films are characterized by a low conductivity due to the formation of the non-conjugated leucoemeraldine-like form of PAN in the deposition process [6]. It is suggested [6,7] that the evaporation of polyaniline at a temperature over 325°C causes the formation of defective films. But, at a lower deposition temperature (275–325°C), the obtained films may be converted into the conductive emeraldine form of PAN in the course of a complex doping process. However, the systematic investigations on the effect of deposition temperature on the structure, optical anisotropy, and electrooptical properties of vacuum-deposited PAN films have not been carried out.

The aim of this article is to ground the conditions of thermo-vacuum deposition of conductive and electroactive PAN films. Therefore, the thermal behavior of the polymer in the range of 20–700°C and the effect of temperature deposition on the structure, optical, electrochemical, and electrooptical properties of PAN thin films have been studied.

EXPERIMENTAL

Polyaniline was synthesized in the emeraldine base form by oxidative polymerization of aniline as described in [3]. The obtained powder was pressed into pellets and placed in a molybdenum crucible. Before the deposition, PAN was heated up to a temperature of 100°C during 30 min under vacuum. The deposition of films was carried out in the temperature interval 180–500°C at a residual pressure of 5×10^{-6} Torr, and the temperature of the substrate was 100°C. The PAN films were deposited onto different substrates: glass plates, ITO-electrodes, quartz, single crystal silicon (for ellipsometric studies). The film deposition time was chosen depending on the deposition temperature and was 40 min for the deposition temperatures of 360–500°C and 4 hours for 180°C.

The thermal behavior of polyaniline was studied using a derivatograph Q-1500D of the Paulic-Paulic-Erdey type in quartz crucibles in the temperature range 20–700°C at a heating rate of 5°C/min. Standard–Al_2O_3. Spectral characteristics of the films were studied using a "SPECORD M-40" spectrophotometer in the interval of wavelengths of 350–1000 nm. The film thickness and the optical anisotropy were determined by means of ellipsometry techniques by a laser zero-ellipsometer LEF-3M-1 ($\lambda = 632.8$ nm) using a 4-zone technique. The morphology of the obtained films was studied using a metallomicroscope MIM-8 at a magnification of 1250.

Electrochemical and electrooptical characteristics of the films were studied by the cyclic voltammetry and spectroelectrochemical methods in a 3-electrode quartz cell with an ITO-PAN working electrode (1 cm^2), the platinum wire was a counter electrode, and the Pt/H_2 electrode was a reference one. For the electrooptic investigation, a 2-electrode cell described in [4] was used. As an electrolyte, a 0.5 M solution of sulfuric acid was employed.

RESULTS AND DISCUSSION

Polyaniline is known to be a semicrystalline material, in which the crystalline phase content varies from 25 to 44% [2,3]. Due to peculiarities of the molecular and crystalline structure, the conjugated PAN cannot be processed in a melt, because it decomposes at temperatures below the melting point [2]. At heating, a polymer undergoes the thermal and thermooxidative destruction [3,16]. But, in the inert atmosphere and at low pressure, it can sublimate in a certain temperature range, which makes possible its vacuum deposition.

The thermogravimetric studies (Fig. 1a, b) showed that, for both doped and undoped PAN samples, the endothermic maximum at

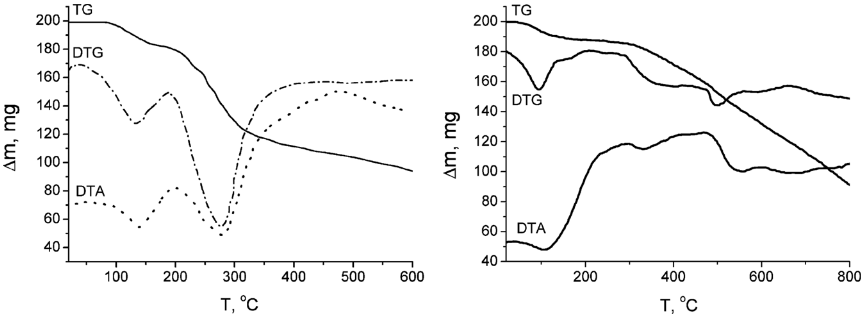


FIGURE 1 Thermograms of decomposition of sulfate-doped samples of polyaniline (a) and of undoped polyaniline (b).

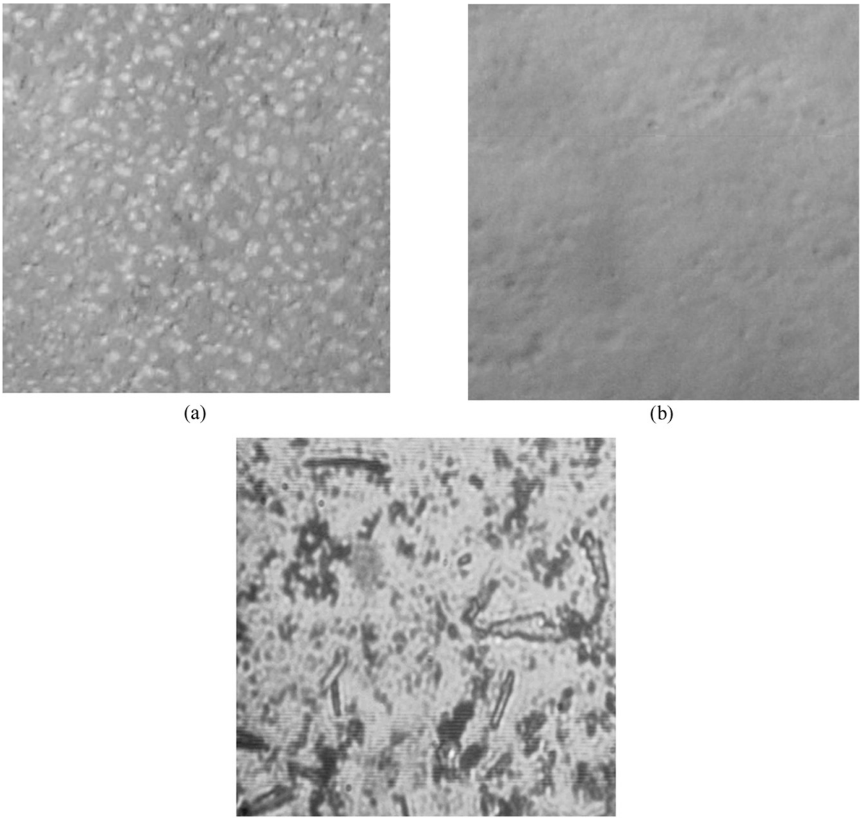
$T = 110$–130°C associated with desorption of a chemosorbed moisture is observed. The exothermal peak on the DTA curves at $T = 160$–180°C may be attributed to the cross-linking processes in the polymer [16], and the mass loss in the interval of $T = 200$–300°C is due to the removal of a dopant [3]. At a further temperature increase within the range of 350–450°C, the curve of mass loss (TG) assumes a stable character without abrupt phase transitions up to $T = 500$–510°C, following which the processes of thermal and thermooxidative destruction become more intense. In the argon atmosphere, as well as in vacuum, the processes of thermooxidative destruction occur only in a small degree [16,17], and the main mass losses within the range 350–450°C are caused by evaporation (i.e., sublimation) of macromolecular globules of the conjugated polymer. In accordance with the determined temperatures of the main points of mass losses, a vacuum deposition of PAN was carried out at $T = 180$, 360, 450, and 500°C.

It was determined that the deposition temperature essentially affects the whole complex of the physical and chemical properties of films, i.e., the structure, morphology, spectral and chemical properties.

The PAN films obtained by vacuum deposition are characterized by uniformity and homogeneity (Fig. 2a, b). The morphology of deposited films is considerably improved as compared with those of electrochemically polymerized PAN films (Fig. 2c). At the same time, depending on the technological conditions of the deposition, the essential difference in the morphology and dyeing of the polymer films is observed The films obtained at relatively low temperatures (180°C) have got an island-like character and a light yellow color which is characteristic of the insulating leucoemeraldine form of PAN having a low degree of conjugation [2,4,5]. If the deposition temperature increases up to 450°C, a compact monolithic film is formed, whose light green color indicates the presence of PAN in the conductive emeraldine form. The films obtained at $T = 500$°C have got a dark grayish-brown color and are nonuniform.

The studies of optical spectra of the PAN films show a strong dependence of the position and intensity of the absorption bands on the vacuum deposition temperature (Fig. 3a).

The positions of absorption peaks of the PAN films obtained at the temperatures of 180 and 360°C correspond to the characteristics of the leucoemeraldine form of PAN [7]. These films turned out to be incapable of the proton doping and thus are liable to environmental effects. In the case of the PAN films deposited at higher temperatures (450°C), the acid doping in an HCl solution provides the restoration of many properties essential to conventional PAN (Fig. 3b). One can observe that the absorption grows within the spectral range of about



(a) (b) (c)

FIGURE 2 Photos of the PAN films on surface of ITO obtained by means of vacuum deposition at $T = 180°C$, $\tau = 240$ min. (a), $T = 450°C$, $\tau = 40$ min (b), electrochemical polymerization ($j = 0{,}01\,mA/cm^2$, $\tau = 20$ min) (c). Magnification ×1250 ($50 \times 50\,\mu m$).

400 nm (usually assigned to the absorption of localized cation-radicals-polarons [20]) and near 800 nm (delocalized polaron and bipolaron absorption) in the absorption spectra of the films deposited at $T = 450°C$. A growth of the band near 800 nm is far more intense in this case than that observed earlier in [21].

It is shown [22] that free-standing PAN films fabricated by both the casting and spin coating procedures with a subsequent drawing possess a distinctly defined optical anisotropy. While the optical symmetry axis is located strongly within the film plane, the in-plane birefringence increases with the film extension. Thus, following the drawing process, the films become anisotropic and uniaxial.

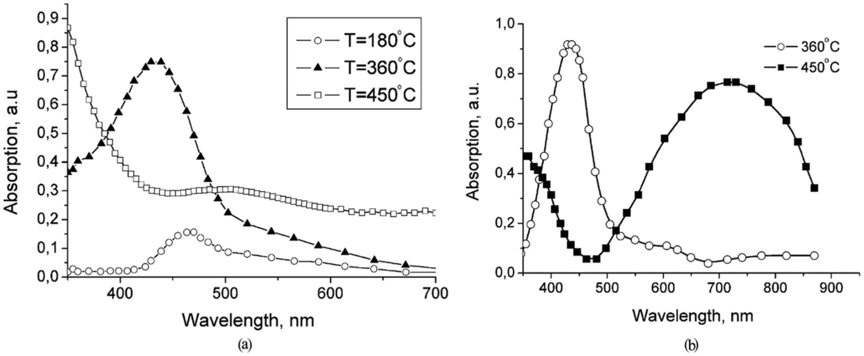


FIGURE 3 Absorption spectra of undoped (a) and doped (b) PAN films obtained using the techniques of vacuum deposition at various temperatures.

Hence, it is very important to compare the structure of our films obtained by means of vacuum deposition with that of the films deposited onto silicon substrate [22]. To this end, we have used the ellipsometry techniques. Changing the orientation of the films relatively to the incidence plane of the laser beam from an ellipsometer (angle α), as well as the incidence angle of the laser beam (angle φ), we were able to determine the refraction index of PAN (n) for various orientations of the light spreading. The mode of changes of the refraction index made it possible to make a certain conclusion concerning the structure of the deposited films. Moreover, we have determined the films thickness by means of ellipsometric measurements.

In order to analyze the results of ellipsometric measurements, the "transparent uniform film – absorption substrate" model was used. A transmission coefficient of PAN films deposited at temperatures of

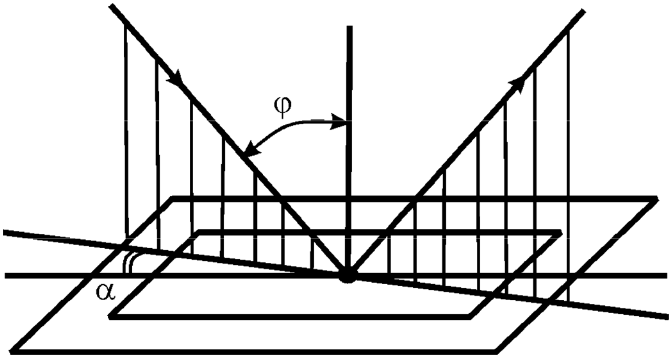


FIGURE 4 Spatial orientation of the laser beam relatively to the film position.

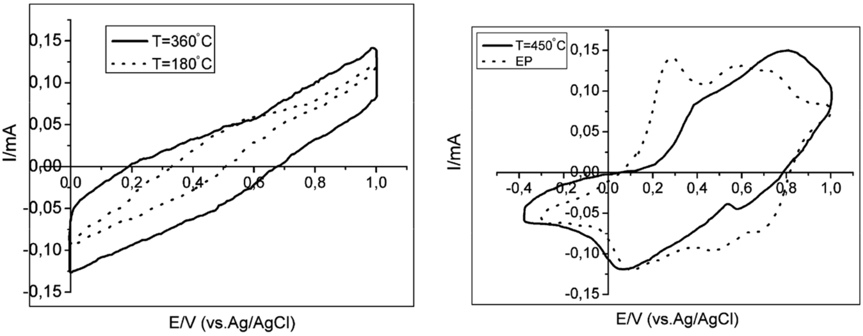
180, 360, and 400°C is at least 90% (Fig. 3a). Thus, the neglect of a slight absorption causes small errors at determining the films thickness (of the order of one Ångström).

The obtained results show that the uniformity in the thickness of vacuum-deposited PAN films is characterized by the deviation from the average value not worse than $\pm 1.5\,\mathrm{nm}$ (and in majority of samples even better). The film deposition speed at the same duration of the process increases with the deposition temperature. Particularly, the films thickness deposited at the temperature $T = 180^\circ\mathrm{C}$ during $\tau = 4$ hours is $d = 21 \pm 1.5\,\mathrm{nm}$; at $T = 360^\circ\mathrm{C}$ and the deposition time $\tau = 40\,\mathrm{min}$, $d = 36 \pm 0.5\,\mathrm{nm}$; and at $T = 450^\circ\mathrm{C}$ and $\tau = 40\,\mathrm{min}$, $d = 40.5 \pm 0.5\,\mathrm{nm}$. The films deposited at 500°C for $\tau = 40\,\mathrm{min}$ absorb at $\lambda = 632.8\,\mathrm{nm}$ much stronger, and, moreover, they have apparently an uneven structure in the depth. That is why the "transparent homogeneous film – absorbing substrate" model cannot be used in determining the films thickness and the refractive index.

Having used "transparent homogeneous film – absorbing substrate" model in order to analyze the measurement results, we have obtained the dependence of the refractive index of a material (n) on the film orientation relatively to the incidence plane of the laser beam of an ellipsometer, that is $n = f(\alpha)$. In this dependence, the distinct maximum and minimum values of the refractive index n decrease with increase of the film deposition temperature.

Thus, for $T = 180^\circ\mathrm{C}$ and $\tau = 4$ hours, $n_{\max} = 1.856$, $n_{\min} = 1.692$; for $T = 360^\circ\mathrm{C}$ and $\tau = 40\,\mathrm{min}$, $n_{\max} = 1.820$, $n_{\min} = 1.735$; for $T = 400^\circ\mathrm{C}$ and $\tau = 40\,\mathrm{min}$, $n_{\max} = 1.799$, $n_{\min} = 1.745$. For the film deposited at $T = 450^\circ\mathrm{C}$ for $\tau = 40$ min, we have not observed a distinct dependence $n = f(\alpha)$; the maximum and minimum of the reflective index of a film was observed in all the cases approximately in mutually perpendicular orientations. However, the orientations of these mutually perpendicular axes $n_{\max}$–$n_{\min}$turn out to be different at different points on the film surface. At separate points on the surface of a PAN film deposited at $T = 180^\circ\mathrm{C}$ and $\tau = 4$ hours, we observed a smooth change of the refraction index in the dependence $n = f(\varphi)$ which is characteristic of crystalline materials. However, in most cases, the refractive index n was changed chaotically or almost was not changed at a change of the angle φ.

These results mainly confirm the conclusion [6,7,13] that a destructive form of the polymer under thermovacuum deposition is formed, which particularly concerns the films deposited at temperatures over 400°C. However, having analyzed the films deposited at low temperatures ($T = 180^\circ\mathrm{C}$ and $\tau = 4$ hours), we may assume that a high content of the crystalline phase is present therein.



(a) (b)

FIGURE 5 (a) CVA of PAN films obtained on the ITO electrode using vacuum deposition at T = 180°C and 360°C; (b) CVA of PAN films obtained on the ITO electrode at T = 450°C during 40 min and (c) electrochemical polymerized (EP) at j = 0.1 mA during $\tau = 10$ min. Background is 0.5 M H_2SO_4.

In order to evaluate the functional properties of the deposited PAN films, the comparative studies of their electrochemical activity have been carried out using the techniques of cyclic voltamperotering (CVA) in a 0.5 M water solution of sulfate acid. It can be seen from the CVA curves in Figure 5 that the obtained PAN films at deposition temperatures of 180°C and 360°C possess a low electrochemical activity and are not subjected to the electrochemical doping at the superimposition of consecutive cycles of the potential sweep.

At the same time, the PAN films obtained by means of vacuum deposition at 450°C show a distinct electrochemical activity (Fig. 5b). Comparing the CVA curves with ones obtained for electrochemically polymerized films, we can observe some difference in the form of the voltamperograms, though the oxidation-reduction currents remain on the some level in general. The switching of optical elements by the three-electrode scheme allows us to accurately control the color change and the optical density of the films by means of a small change of the operating potential in relation to the reference electrode. However, this construction turns out to be somewhat inconvenient in use and requires an additional device for the reference electrode. For this reason, a two-electrode circuit of the electrochromic optical element with a PAN electrochromic layer is proposed for practical realization [4]. The operating voltage between two (SnO_2–polymer/SnO_2) electrodes is $U = \pm 0.6$ V.

Based on the spectroelectrochemical research carried out in the water solutions of sulphate acid according to a two-electrode circuit

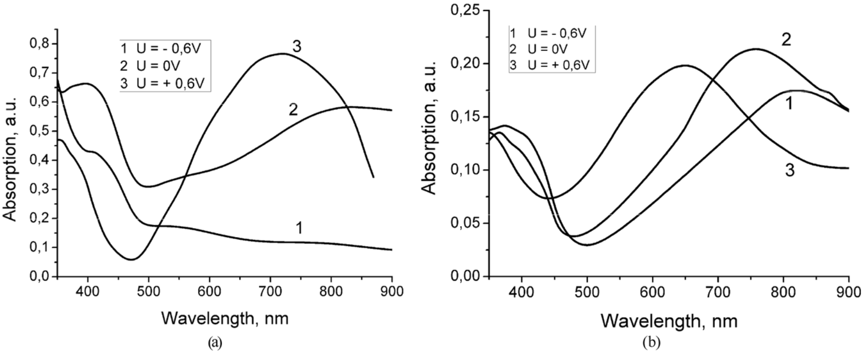


FIGURE 6 Absorption spectra of vacuum deposited PAN films at 450°C (a) and electrochemically polymerized (b) on the surface of ITO electrodes under the action of the external polarization at the mentioned potentials. Electrolyte –0.5 M H_2SO_4.

(Fig. 6), it has been established that PAN films obtained by thermovacuum deposition at a temperature of 450°C reveal the electrochromic behavior similar to that of the electrochemically polymerized films of polyaniline [9,23]. Particularly, the essential alteration of spectral properties is observed for PAN films at the superimposition of the outer potential from -0.6 to $+0.6$ V. Similarly to the case of the electrochemically polymerized films of PAN, the film is almost transparent at $E = -0.6 \ldots -0.4$ V, and the adsorption spectrum corresponds to the leucoemeraldine form of PAN having an absorption maximum hear 400 nm. An increase of the positive charge on the electrode corresponds to the formation of dyed forms of PAN. This is accompanied by an increase of the absorption in the visible and near infrared region with a maximum of 720 nm that corresponds to electron transitions in the polaron band [5,8].

It can be seen from the data on absorption spectra (Fig. 6) that the electrochromic elements based on vacuum-deposited PAN films at $T = 450$°C are characterized by a much better contrast range as compared with the electrochromic elements formed based on electrochemically polymerized PAN films.

CONCLUSIONS

Based on the results of studies of the surface morphology and the film thickness and on the spectral analysis of vacuum-deposited PAN films, the choice of the "transparent uniform film – absorbing substrate" model has been proposed in order to determine the refractive index of the formed films using the techniques of laser ellipsometer measurements. The obtained refractive indices showed that, at the deposition, the PAN films possess an optical anisotropy within the film plane. The optical anisotropy disappears with increase in temperature.

The acid treatment of the vacuum-deposited polyaniline films in HCl showed that the films deposited at low temperatures (180 and 360°C) are chemically stable. But, at higher temperatures (450°C), they are characterized by a considerably higher electrochemical activity as compared with electrodeposited films.

Thus, it is possible to control the optical properties of the films by varying the technological regime of the PAN deposition.

REFERENCES

[1] Kahol, P. K., Ho, J. C., Chen, Y. Y., Wang, C. R., Neeleshwar, S., Tsai, C. B., & Wessling, B. (2005). *Synth. Met.*, *151*, 65.

[2] Genies, E. M., Boyle, A., Lapkowski, M., & Tsintavis, C. (1990). *Synth. Met.*, *36*, 139.

[3] Aksimentyeva, O. I., Grytsiv, M. Ya., & Konopelnik, O. I. (2002). *Functional Materials*, *9*, 251.

[4] Aksimentyeva, O., Konopelnik, O., Cherpak, V., Stakhira, P., Fechan, A., & Hlushyk, I. (2005). *Ukr. J. Phys. Opt.*, *6*, 27.

[5] Konopelnik, O. I., Aksimentyeva, O. I., & Grytsiv, M. Ya. (2002). *Mat. Sci.*, *20*, 49.

[6] Ivanov, V. F., Nekrasov, A. A., Gribkova, O. L., & Vannikov, A. A. (1996). *Synth. Met.*, *83*, 249.

[7] Nekrasov, A. A., Ivanov, V. F., Vannikov, A. A. (2001). *Electrochim. Acta*, *46*, 3301.

[8] Dillingham, T. R., Cornelison, D. M., Bullock, E. (1994). *J. Vac. Sci. Technol. A*, *12*(4), 2436.

[9] Hong Qiu, Hui Li, Kun Fang, Jing Li, Weimin Mao, & Sheng Luo. (2005). *Synth. Met.*, *148*, 71.

[10] Dixit, V., Misra, S. C. K., & Sharma, B. S. (2005). *Sensors and Actuators B*, *104*, 90.

[11] Plank, R. V., Wei, Y., DiNardo, N. J., & Vohs, J. M. (1996). *Chem. Phys. Lett*, *263*, 33.

[12] Plank, R. V., DiNardo, N. J., & Vohs, J. M. (1997). *Synth. Met.*, *89*, 1.

[13] Nekrasov, A. A., Ivanov, V. F., Gribkova, O. L., & Vannikov, A. V. (1996). *J. Electroanal. Chem.*, *412*, 133.

[14] Plank, R. V., DiNardo, N. J., & Vohs, J. M. (1997). *Phys. Rev. B*, *55*, R10 241.

[15] Misra, S. C. K., Ram, M. K., Pandey, S. S., Malhotra, B. D., & Chandra, S. (1992). *Appl. Phys. Lett.*, *61*, 1219.

[16] Chan, H. S. O., Teo, M. Y. B., Khor, E., & Lim, C. N. (1989). *J. Term. Anal.*, *35*, 765.

[17] Aksimentyeva, E. I. (1999). *Ukr. Khim. Zh.*, *65*, 60.

[18] Lee Hsun-Tsing, Liao Chien-Shiun, & Chen Show-An. (1993). *Makromol. Chem.*, *194*, 2443.

[19] Chan, H. S. O., Teo, M. Y. B., Khor, E., & Lim, C. N. (1989). *J. Term. Anal.*, *35*, 765.

[20] Stilwell, D. E., Park, S. -M. (1989). *J. Electrochem. Soc.*, *136*, 427.

[21] Nekrasov, A. A., Ivanov, V. F., Gribkova, O. L., & Vannikov, A. V. (1994). *Synth. Met.*, *65*, 71.

[22] Cha Cheol, Samuels, R., Hardaker, S., & Gregory, R. (1997). *Synth. Met.*, *84*, 743.

[23] Yang, C. H., Chong, L. W., Huang Lee, Y. L., & Wen, T. C. (2005). *Mater. Chem. Phys.*, *91*, 154.