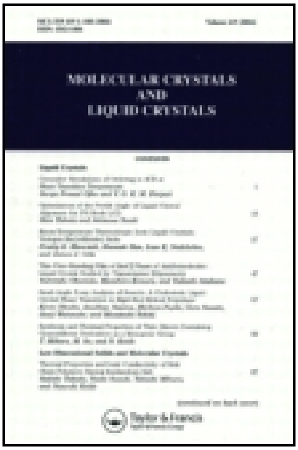

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Effect of electrosynthesis conditions on the structure and optical properties of the polyphenylacetylene films

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EFFECT OF ELECTROSYNTHESIS CONDITIONS ON THE STRUCTURE AND OPTICAL PROPERTIES OF THE POLYPHENYLACETYLENE FILMS

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The method of electrochemical synthesis of conducting polyphenylacetylene (PPA) layers on Pt, Cu, SnO_2, ITO-surfaces was developed. The influence of electrosynthesis conditions on the structure, morphology, optical spectra and conductivity of PPA films have been studied. The influence of electrosynthesis condition on the electron spectra of PPA films allow to propose the possibility of electrochemical generation in PPA films the free charge carriers by the mechanism of electrochemical doping.

Keywords: electrosynthesis; polyphenylacetylene; structure; absorption spectra; doping

INTRODUCTION

Polyphenylacetylene (PPA) belongs to peculiar π-conjugated polymers widely investigated because of its interesting electric and optical properties (photoconductivity, third-order non-linear optical response, sensitivity to relative humidity variation). Therefore PPA has a potential using in electrooptical devices [1–3]. However the PPA synthesis in the presence of metal-complex catalysts [2,3] lead to formation of stereo-regular *cis*-polymer with low electrical conductivity (10^{-10}–10^{-8} Sm/cm [4]). Under the thermal treatment (130°C) it transfer to *trans*-isomer. In result of *trans*-PPA doping by electron acceptors (J_2, AsF_5) and under illumination its

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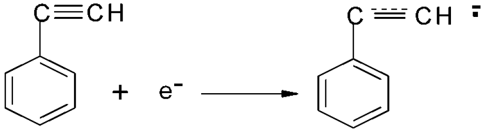
conductivity may be rising to 2–4 order [1,4]. In this report the possibility of the conducting PPA films direct formation at the transparent SnO_2, ITO and metallic surfaces, effect of electrosynthesis condition on the films structure and properties have been investigated.

EXPERIMENTAL

For experiments the phenylacetylene (PA) monomer with $n_D^{20} = 1.5491$, $d_4^{20} = 0,928\,g/cm^3$ was used. Electrolysis of PA solutions in dimethylformamide (DMFA), propylene carbonate (PC) and acetonitrile (AN) in the presence of $LiBF_4$, $LiClO_4$ and $N(Bu)_4ClO_4$ electrolytes was provided on the glass spin coated (SnO_2, ITO) and Pt, Cu electrodes with Ag/AgCl as reference electrode at the $T = 290\,K$. The potentiostat PI-50M was used as a power source. The IR-spectroscopy analysis was carried out by means of "Specord M-80" for polymer film on the KBr surface. The UV and UV-vis absorption spectra were recorded on spectrophotometer "Specord M-40" for the films on quartz and SnO_2 substrates. The films structure was investigated by scanning electron microscope "ISI DS-130". Element analysis on the lithium content was carried out by flame photometer "PFM-30-MZ" (sensibility$10^{-6} \div 10^{-9}$ g/l). For the conductivity measurements the four-probe method has been used.

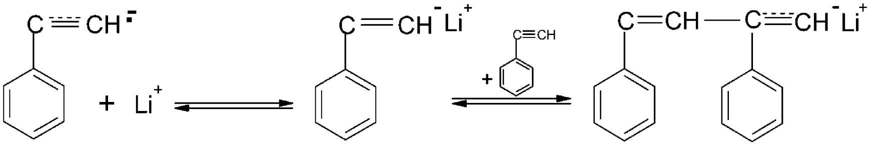
RESULTS AND DISCUSSION

The existence of electron-unsaturated bonds in the molecule of PA may be used for electrochemical initiation of the polymerization process by the direct electron transfer from electrode to monomer with formation of anion-radical particles



which are able to interact with monomer and excite the polymerization process. However, the known methods of PPA electrosynthesis allow to obtain the polymer mainly in the bulk with low yield (3–5%) and molecular mass $M \approx 500$ [5].

The cyclic voltammetry data of PA solutions containing 0,5 M $LiClO_4$ show the irreversible cathodic peak in the potential interval $E = -1.9 \div -2.2\,V$ rising with sweep cycle number, which indicate the electrochemical reducing of monomer, accompanied by electroactive polymer film formation [6]. The repetitive potential scanning in this potential region, potentiostatic or galvanostatic electrolysis cause the conducting polymer film formation at the electrode surfaces. The study of PPA electrochemical synthesis conditions showed its selectivity to the kind of electrolyte. The polymer film formation at the electrode surface takes place only in the presence of $LiClO_4$ or $LiBF_4$ electrolytes while in the presence of $N(Bu)_4ClO_4$ the polymer formation occurs only in the bulk [5,6]. This behaviour, together with the results of elemental and IR-spectroscopy analysis suggests the ion pair formation between PA anion-radicals and lithium cations during the electrosynthesis as presented in the scheme:



This circumstance leads to a particular compensation of the negative charge of the growing polymer chain, which made possible the polymer films formation at the cathodic surface. The charge dependence of the polymer film yield at different electrode surfaces (Fig. 1, Table) indicates the higher film formation rate on the metal electrode surface. However, at the prolonged electrolysis, the polymer yield remain constant, even can decrease. In this case the electrochemical destruction processes or films solvatation in the reaction medium may take place. At the same times, the decrease of PA polymerization rate may be connected with deactivation of active centers as a consequence of the intermolecular associates formation. Scanning electron microscopy investigation showed that electrolysis of PA solution in polar organic solvents in the presence of lithium salts, on Cu and

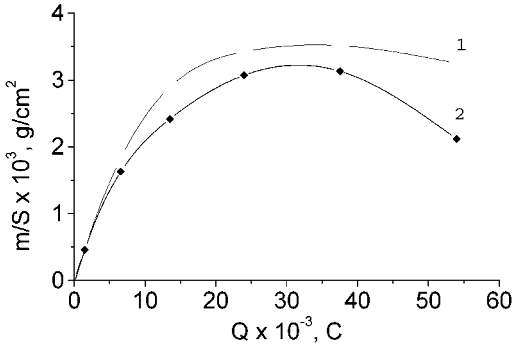


FIGURE 1 Charge dependence of polymer yield on the Cu (1) and SnO_2 (2) electrode surface.

TABLE Influence of Electrosynthesis Condition on the Properties of PPA Films

Electrolysis conditions					
Current density, MA cm^{-2}	2,0	2,0	2,0	5,0	2,5
Solvent, electrolyte	DMFA 0,1M $LiBF_4$	PC 0,1M $LiBF_4$	AN 0,1M $LiBF_4$	PC 0,1M $LiBF_4$	DMFA 0,1M $LiClO_4$
Electrode material	SnO_2	Pt	Cu	SnO_2	ITO
Synthesis duration, min	30	15	15	30	40
Properties of PPA-films					
Thickness, μm	0,280	0,450	0,930	0,230	0,330
Growth rate, mg cm^{-2}min^{-1}	0,08	0,28	0,76	0,08	0,13
Film structure	Fibrillate	Globular	Globular	Globular	Fibrillate

Pt or on SnO_2 electrodes at high current density ($i = 5$ mA/cm^2) leads to uniform films formation with a close packed globular structure (Fig. 2b). The assumption of $\ll$ slow-growing $\gg$ on SnO_2 or ITO electrodes allows to obtain the PPA films of fibrillar structure (Fig. 2a, Table).

According to IR spectroscopy data, the PPA electrosynthesized at the electrode surface has a molecular structure differed to that of bulk polymer [2,5]. It's found the absorption bands at 3060, 2960, 1604, 1490, 1400 cm^{-1} (v_{CH}– of benzene ring) and 1674–1660, 1646–1638 cm^{-1} ($v_{C=C}$) trans-substituted bond). Besides these it is proved by appearance of some supplementary low intensity maximums at 1320, 1250–1260, 1185, 1030, 1000, 706 cm^{-1} characteristics for deformation vibrations δ_{CH} bonds of mono-substituted and *para*-disubstituted benzene rings. This allow to suggest that a linkage of the monomer molecules may be realized between a phenyl-phenyl $\ll$ head-to-head $\gg$ and phenyl-alkine $\ll$ head-to-tail $\gg$ fragments. In the last case the formation of fragments like a poly-*para*-phenylene vinylene (PFV) structure [7] takes place.

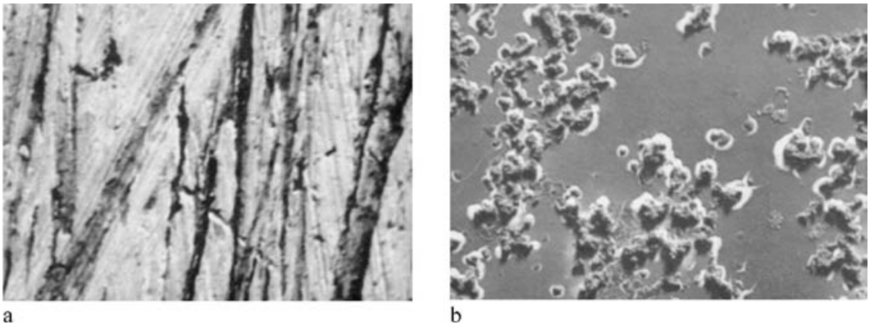
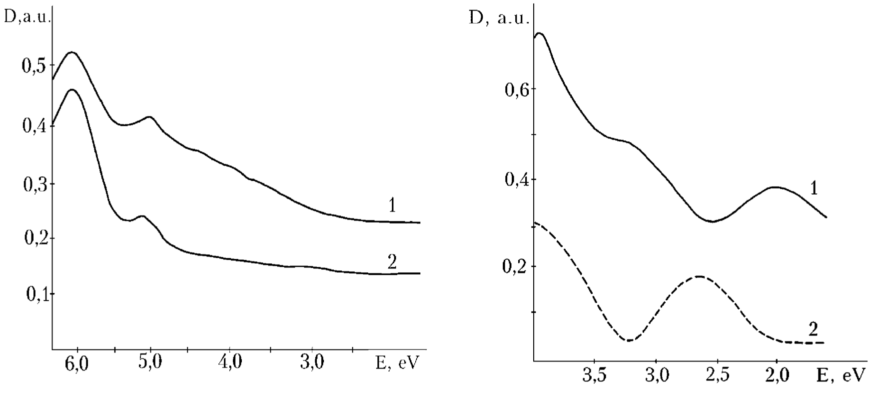


FIGURE 2 SEM of PPA layer on SnO_2 surface obtained at $i = 2$ (a) and 5 (b) mA/cm^2. [magnification: × 500 (a) and × 300 (b)].



a

b

FIGURE 3 The absorption spectra of chemically synthesized PPA casted on quartz (a) and electrochemically synthesized on SnO_2 surface at $i = 5\,mA/cm^2$ and electrolysis duration: (1) 15 min; (2) 40 min (b).

Process of charge transport during the film formation causes the change in electron properties of the resulting polymer. In PPA, obtained by the chemical synthesis under complex catalyst, dissolved in $CHCl_3$ and casting on the quartz, the absorption bands only in UV-region are observed (Fig. 3a). In the electron spectra of electrochemically prepared PPA (Fig. 3b) besides of the absorption band at 380 nm (typical to the π-π^* transition in conjugated systems) indicating in this PPA form the existence of PPA chain segments with delocalized π-electrons [2], the enough intensive absorption bands in visible region appeares (Fig. 3b).

With the increase of charge quantity passed during electrolysis these bands demonstrate the red shift. Taking into account that film thickness in this conditions slightly change (Fig. 1), one may suggest that through the electrochemical doping process the free carriers formation occurred. The charge generated by electron transport is delocalized on conjugated backbone and probably compensated by cations of lithium, according to the scheme:

$$[(-C_6H_5)CH{=}CH{-}]_n + mLi^+ + e \rightarrow [-(C_6H_5)-CH{=}CH{-}]_n^{m-}mLi^+$$

Proposed mechanism of electrochemical doping is in a good agreement with conductivity measurements and defining of the lithium concentration, which appeared 8–10 times higher in electrodeposited films in comparison to solution. Based on the provided experiments we elaborated a new method of PPA thin films electrochemical synthesis [6,8] with controlled surface structure by maintaining the corresponding electrolysis conditions.

REFERENCES

[1] Yang, M., Xu, J., & Hu, Q. (1995). *J. Photochem. Photobiol. A: Chem.*, *85*, 147.

[2] Tang, B. Z., Poon, W. H., Leung, S. M., et al. (1998). *Macromolecules*, *30*, 2209.

[3] Cametti, C., Codastefano, P., Amato, R. D., et al. (2000). *Synth. Metals*, *114*, 173.

[4] Simon, J. & Andre, J.-J. (1988). *Molecular semiconductors*. Moscow, Mir. (rus).

[5] Simionescu, Cr. I., Farafonov, V. V., & Grovu, M. (1979). *Revue Roumaine de Chimie.*, *24*, 379.

[6] Aksimentyeva, O. I., Lupshak, N., Kovalskyi, Ya., et al. (2001). *Ukr. Cmem. J.*, *67*, 363, N10.

[7] Vaeth, K. M. & Jensen, K. F. (1988). *Macromolecules*, *31*, 6789.

[8] Aksimentyeva, O. I., Lupsak, N., & Gavrysh, Yu. (2001). *Patent N 42130 (UA)*. Publ. Bul. No 8.