
Conjugated Polyaminoarenes as Electrochromic Layers for Non-Emissive Displays

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Abstract

Electrochromic properties of polyaminoarenes with different molecular structure, such as poly-*o*-aminophenol (POAP), poly-*o*-toluidine (POTI), poly-*o*-methoxyaniline (POMA) and polyaniline (PANI), are studied as potential materials for the three- and two-electrode construction of electrochromic devices.

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Introduction

From the family of non-emissive display materials, liquid crystals have been extensively used, since their intrinsic order is very sensitive to external fields [1,2]. As an alternative to liquid crystals, electrochromic (EC) inorganic or organic layers deposited on the transparent electrode surface have been recently proposed [3-8]. These layers are also sensitive to external electric fields and their colour changes are caused by a rebuilding of chemical or crystalline structure of the materials inside the film. Moreover, the application of the EC films built on transparent electrodes enables creating optoelectronic devices manifesting a long-term memory storage [6].

A number of constructions have been suggested for the EC displays, based on inorganic WO₃ layer in the acid electrolyte [6]. Such a layer may change its colour from white to blue, depending upon the quantity of positive ions (protons) and free electrons injected during formation of tungsten bronze under external electric field potential [2,6]. There are also the

known EC displays based on organic dyes, which harmonise with the background and are soft for human eyes, though their erasing-rewriting rate being low enough [3]. The latter may be increased by using conjugated layers of polyaminoarenes, such as polyaniline and its derivatives having electroactive chromophore groups [3-5].

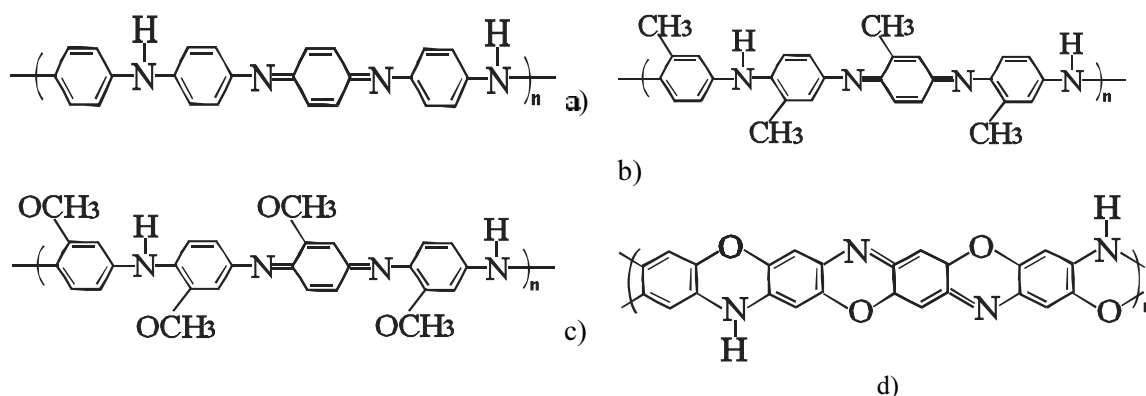
The conjugated polymers in thin layers still attract a profound interest because of their potential applications in the modified electrodes or sensors, electrode materials for the power cells and, recently, EC layers for the non-emissive displays [3-5,7,8]. In addition to a high colour contrast, the devices might manifest optical memory and stability, while subjected to a successive switching. This makes them competing with traditional inorganic displays [6]. By varying the oxidative state or the protonation level in the polymer structure, a wide range of colours could be controlled. The colour transitions (from a full colourless to yellow, green, blue, violet and purple, etc.) are observed as a function of electrode potential. A series of investigations have been carried out for

the EC polyaniline films in organic and aqueous electrolytes [3,5,7], but the EC devices basing on the conjugated polymer and operating as displays, screens or filters have not yet been developed.

In order to ground a choice of polymer material for the EC layer in three- or two-electrode operating EC devices, we have investigated optical and charge transport properties of polyaminoarenes with different molecular structure, including poly-*o*-aminophenol (POAP), poly-*o*-toluidine (POTI), poly-*o*-methoxyaniline (POMA) and polyaniline (PANI).

Experimental

Polyaminoarene films were prepared in a three-electrode electrochemical cell by electrolysis of 0.1 M solutions of purified monomers (*o*-toluidine, *o*-methoxyaniline, aniline and *o*-aminophenol) in 0.5 M H₂SO₄ [7]. Working SnO₂ electrode, Pt-wire counter electrode and Ag/AgCl (in the saturated KCl) as a reference were employed in this cell. Molecular structures of the polymers obtained by us are presented in Scheme 1.



Scheme 1. Molecular structure of the conjugated polyaminoarenes: (a) polyaniline (PANI), (b) poly-*o*-toluidine (POTI), (c) poly-*o*-methoxyaniline (POMA) and (d) poly-*o*-aminophenol (POAP).

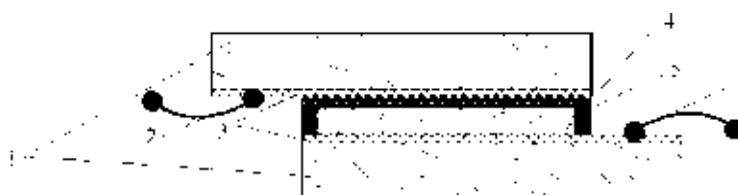


Fig. 1. Scheme of the two-electrode EC cell: 1, glass sheets; 2, metal electrodes; 3, transparent SnO₂ layer; 4, polymer film; 5, electrolyte solution.

The thickness of the films was measured with micro-interferometer MII-4. For the polymer-coated SnO₂ electrodes, the UV and visible absorption spectra were obtained “*in situ*” in the range of $\lambda=320\text{--}1000$ nm, using the quartz cell placed into the working camera of spectrophotometer SF-26 and connected with potentiostat PI-50M. Pt-wire electrode was employed in this cell as a reference. Cyclic voltammetry experiments were performed at the potential sweep rate of $v = 5\text{--}200$ mV/s.

The changes in the optical density in the region of light wavelengths $\lambda = 450\text{--}1000$ nm for the two-electrode EC cell (see Fig. 1) were studied with monochromator KSVU-6.

The optical properties of the element were measured in the spectral region mentioned above, under the voltage responsible for the colourless state ($U = -1.5$ V) and the dark ($U = 2.0$ V) colour of samples, as well as without any external voltage ($U = 0$ V).

Results and Discussion

The EC transitions in polyaminoarenes are associated with electrochemical processes of reducing-oxidation in the polymer layers, which

include electron transport from the electrode to the polymer film. It is found that the changes in the optical spectra of the investigated polyaminoarene films deposited on SnO_2 electrodes occur in the external potential $U = 0.1\text{--}2.0$ V (see Fig. 1 and 2). The optical density variations are observed in the absorption spectra of the polymers and the positions of the absorption bands are determined. These variations are accompanied with a reversible colour transition from the colourless state to the yellow, green, blue and violet colours (see Table 1).

Reducing of the chromophore groups in the polymer layers occurring at the potential $U = -0.2\text{--}0.1$ V (Ag/AgCl) leads to appearance of a colourless form of polyaminoarenes, with the absorption band being located at 340–420 nm

($\pi\text{--}\pi^*$ transition). This band corresponds to leucoemeraldine benzenamine polymer with a low conductivity [5]. The positive polarization of SnO_2 -polymer electrode at 0.2–0.6V causes green colour of the PANI, POMA and POTI films and rose-red colour of the POAP, as shown in Table 1. The polyaniline and its derivatives are present in conducting semi-oxidised states called as a “emeraldine” form [3,5]. The colour transitions are accompanied by appearance of a wide absorption maximum at $\lambda=700\text{--}850$ nm. For the polymers with linear macrochain structure such as POTI, POMA and PANI (see Scheme 1), the absorption at 340–400 nm and 700–800 nm may be assigned either to the polaron or bipolaron bands [9].

The polaron transition is dominant at lower

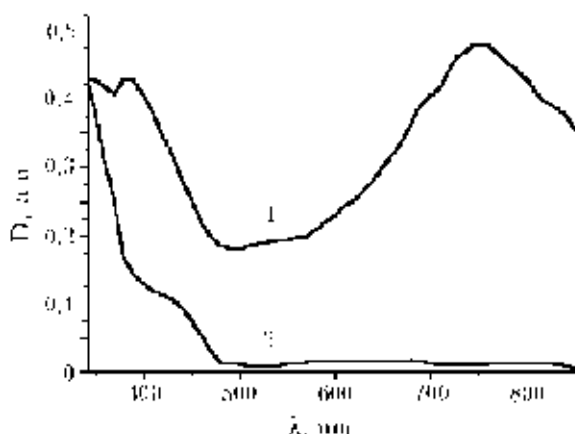


Fig. 2. Absorption spectra of the POMA film deposited on SnO_2 in 0.5M H_2SO_4 solution at $U = 0.5$ (1) and 0.2 V (2) (Ag/AgCl).

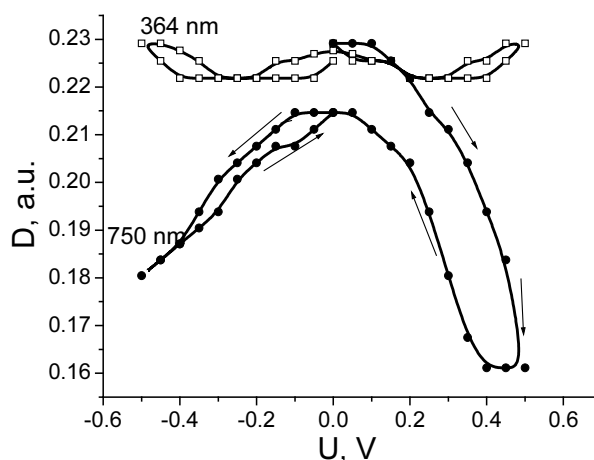


Fig. 3. Variations of optical density D for the PANI film at $\lambda=364$ nm and 750 nm under the potential ranging from $U = -0.5$ to 0.5 V (Pt) at $\nu=20$ mV/s.

Table 1. Potentials of EC transitions in the polyaminoarene films.

Conducting polymer layer on SnO ₂	Electrode potential, V (Ag/AgCl)													
	-0.2	-0.1	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	
Polyaniline														
Poly- <i>o</i> -aminophenol														
Poly- <i>o</i> -methoxyaniline														
Poly- <i>o</i> -toluidine														

polarising potentials, while the bipolaron one overwhelms at higher potentials. The blue (for PANI and POTI), violet (for POMA) and brown (for POAP) colours of the films are observed in the potential interval $U > 0.6\text{--}0.8$ V. They might be related to appearance of over-oxidised pernigraniline fragments in polyaminoarenes [5]. The colour variations become irreversible at still higher potentials ($U \geq 1.2$ V) and, furthermore, a loss of doping level and conductivity is observed.

To study the EC effect in the polymer films, we have studied the changes in the optical density (or the transition) taking place due to the applied potential for different light wavelengths corresponding to the absorption maxima. When sweeping the potential, the most remarkable changes are revealed to happen for the band located at 700–850 nm, which might be related to variations of free carrier concentration as a result of switching the potential (Fig. 2).

The studies for electrochemical behaviour

of polyaminoarene films in the aqueous electrolytes (HCl, HClO₄, H₂SO₄, HNO₃ and toluene sulfonic acid (TSA)) demonstrate that the charge transport across the film is limited by diffusion. The evidence for this is dependence of the peak current i_p on the square root of sweep rate ($i_p \sim \nu^{1/2}$) observed earlier [7,8]. The values of the effective diffusion coefficient (D_{ef}) and the transition diffusion time ($\tau_D = l^2/4D_{ef}$ [6], with l denoting the film thickness) calculated within the model of semi-infinite diffusion [10,11] are presented in Table 2. The obtained results suggest that the main factor influencing the charge transport across the film is molecular structure and segment mobility of the polymer chains.

The existence of electron-donating substitute in the polymer chain ($-\text{OCH}_3$ and $-\text{CH}_3$) leads to extend of the range of potentials needed for the colour transitions in the POMA and POTI films, when compare with the PANI [5]. Introduction of OH^- group to the monomer

Table 2. Charge transport parameters for the polyaminoarene films in 0.5 M H₂SO₄ electrolyte solution.

Conducting polymer layer	Film area S, cm^2	Film thickness $l, 10^{-4} \text{cm}$	Diffusion coefficient $D_{ef}, 10^{-9} \text{cm}^2/\text{s}$	Transition time τ_D, s
POTI	2.1	0.35	2.62 ± 0.06	0.5 ± 0.15
PANI	4.0	0.28	9.02 ± 0.05	0.02 ± 0.01
POMA	4.0	0.28	3.56 ± 0.07	0.8 ± 0.15
POAP	3.4	0.25	0.23 ± 0.04	6.4 ± 0.7

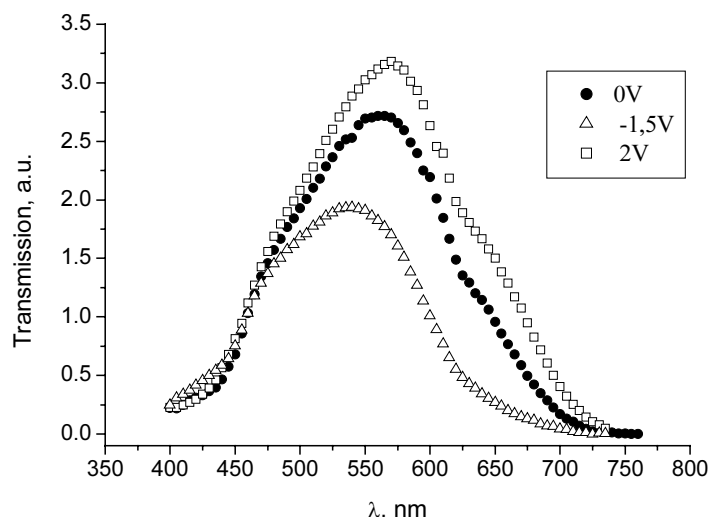


Fig. 4. Optical transmission spectra of the two-electrode optical elements with the PANI film in 0.5M H₂SO₄ solution.

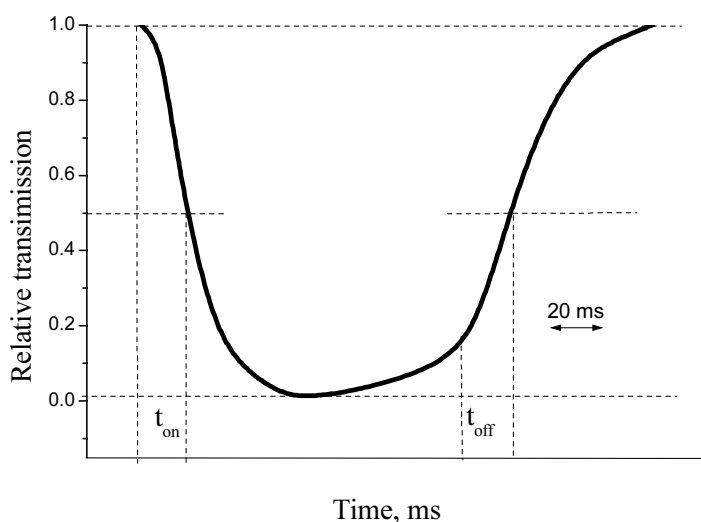


Fig. 5. EC response of the element with the PANI film in 0.5 M H₂SO₄ at $\lambda = 575$ nm and the applied voltage ranging from 0 to +1.5V.

molecule of *o*-aminophenol causes decreasing electron transport rate in the obtained POAP layer. In this case, formation of a rigid heterocyclic structure of the polymer [12] takes place (see Scheme 1, d). Issuing from the diffusion coefficient and transition time values, we conclude that the PANI and POTI films are the most attractive for the EC displays.

Optical elements operating according to three-electrode scheme allow controlling easily the colour transitions and the optical density of the films owing to small changes in the working potential. Nonetheless, this construction requires additional attachment for the third (reference)

electrode. For this reason, we have suggested the EC optical element with the PANI or POTI EC layer controlled by the two-electrode scheme (Fig. 1).

Clear changes in the shape of the absorption bands are observed in the two-electrode element when the voltage is applied (see Fig. 4), which evidence the EC effect in the polymer films in frame of the suggested switching scheme. The times for erasing and rewriting calculated from the temporal dependence of the EC response (Fig. 5) reach respectively 23 and 18 ms. These values are inside the range of speed of operation required

from the EC displays [6].

Moreover, the optical elements based on the conjugated polyaminoarenes do not generate noxious radiation and so may be used in home electronic appliances such as displays, light filters and sensor devices.

Conclusion

Basing on the results for the optical and charge transport properties of the conjugated polyaminoarenes, we have shown that the PANI and POTI layers represent the most attractive EC materials. The optical elements suggested by us are characterised by a high operating speed located in the range required for the EC displays.

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