

Molecular scale organized poly(MDMO-*p*-phenylene vinylene)–heteropolyacid composites

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Abstract

In this study, the interaction of phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) with poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene] (MDMO-PPV) has been investigated by the methods of optical absorbance and luminescence spectroscopy, electrochemical, EPR and chemical analysis. It is shown that the interaction between MDMO-PPV and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ leads to the formation of charge-transfer complex, which involves one heteropolyanion per four monomer units of the polymer chain. We have demonstrated that this interaction causes reversible changes in the electronic structure of the polymer as well as the appearance of an additional line in a long-wavelength region of optical absorbance spectra, a sharp decrease of the efficiency of luminescence and the emergence of pronounced EPR signal.

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1. Introduction

Recently considerable attention has been given to the conjugated polymers, such as polyaniline [1–8], polypyrrole [8–12] and polythiophene [13–15] doped by heteropolyanions, with special emphasis on the elaboration of alternative electrodes for the electrochemical batteries [7], electrochemical sensors [10], catalysts and electrocatalysts [3–6] as well as on the preparation of polymer materials with a controlled conductivity [4]. In these studies, the most frequently used dopants were Keggin-type polyoxometalates (heteropolyacids)— $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$ and others. The procedures for obtaining doped materials were a combined electrodeposition of the polymer and heteropolyacid or of the polyoxometalate salt of the polymer, and an interaction of pre-prepared polymer film with heteropolyacid.

This paper examines the interaction of phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) with a soluble derivative of poly(*p*-phenylene vinylene)–poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene] (MDMO-PPV). In recent years this polymer, along with other analogs, such as, e.g. MEH-PPV, has attracted considerable interest due to the prospects for its using in photovoltaic [16–19], light-emitting diodes [20–22] and light-emitting electrochemical cells [23–25].

2. Experimental

We used in this work a commercial phosphomolybdic acid $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (Aldrich). To investigate the interaction of the polymer and heteropolyacid in solutions, we used MDMO-PPV solutions with a concentration of 0.01 mol/l (calculated for a monomeric unit) and 0.04 mol/l $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ solutions in methanol/chloroform mixture (1:1, v/v). MDMO-PPV films with a thickness of about 10 μm were deposited onto quartz supports (for optical measurements) and onto optically transparent conductive SnO_2 electrodes (for electrochemical investigations)

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from 5% polymer solution in chlorobenzene, which was previously demonstrated to be the most suitable solvent for obtaining high-quality MDMO-PPV films [18].

Photoluminescence spectra were recorded with Spex Fluorolog-3 spectrofluorometer, optical absorbance spectra—with Specord M-40 spectrophotometer. For the electrochemical measurements, we used PI-50-1 potentiostat with PR-8 programmer and standard three-electrode cell equipped by saturated Ag/AgCl reference electrode and Pt counter electrode.

EPR spectra were recorded on a Varian E-3 X-band spectrometer at 77 K. The standards for the calculation of g -factor values were a DPPH sample ($g = 2.0036$) and Mn^{2+} ions in MgO matrix, where positions of the third and fourth EPR lines and the splitting value between them is equal to $g_3 = 2.0328 \pm 0.0002$, $g_4 = 1.9812 \pm 0.0002$, $\Delta H_{3-4} = 86.76 \pm 0.05$ G [26]. The content of paramagnetic centres in the samples was measured by double integration of the spectra with subsequent comparison with the standard ($CuCl_2 \cdot 2H_2O$ monocrystal) with a known number of spins, as it has been done in ref. [26].

3. Results and discussion

The mixing of chloroform–methanol solutions of MDMO-PPV and $H_3PMO_{12}O_{40}$ in 1:1 molar ratio leads to an immediate formation of black gel deposit which turns metallic dark green after drying. Being placed on a glass support and dried, this deposit appears bluish grey in transmitted light. Contrary to the starting materials, this deposit is practically insoluble in chloroform, alcohols, dichloroethane, tetrahydrofuran and toluene, hence it can be cleaned from the non-reacted initial components by washing with appropriate solvents. A prolonged stirring of the deposit in chloroform does lead to dissolving a small amount of the polymer that is detected by the appearance of a corresponding weak absorption in the optical spectrum of resulted chloroform solution. After that, being treated with methanol, the deposit liberates the respective portion of heteropolyacid. By repetitive washing with chloroform and methanol, one can gradually destroy a marked part of initially deposited compound.

According to the data of chemical elemental analysis, an organic (combustible) part of the deposit resulted from the interaction of MDMO-PPV and $H_3PMO_{12}O_{40}$ solutions in a molar ratio of 1:1 contains 78.8% C, 9.74% H, the values being in a good consistency with a calculated chemical composition of MDMO-PPV (79.1% C, 9.79% H). These data of elemental analysis testify that the interaction between MDMO-PPV and $H_3PMO_{12}O_{40}$ does not lead to a crude destructive oxidation of the polymer by the heteropolyacid, the fact being not so evident taking into account a strong oxidative activity of $H_3PMO_{12}O_{40}$. Once such an oxidation takes place, it should more markedly affect C and H percentage.

An annealing of the MDMO-PPV/heteropolyacid deposit in air at 900 °C gives a solid (21%, w/w), which represents pure MoO_3 . These data indicate that, issuing from the starting heteropolyacid/polymer molar ratio of 1:1 calculated as a number of heteropolyacid molecules per one monomer unit of a polymer chain in the initial solutions, we obtain the product of

heteropolyacid/MDMO-PPV interaction with a corresponding ratio of about 1:4. Excess heteropolyacid is easily removed with methanol.

Similar to the interaction between MDMO-PPV and $H_3PMO_{12}O_{40}$ solutions, a reaction accompanied by notable changes in color proceeds under the treatment of polymer films deposited on quartz supports with heteropolyacid solutions. To accomplish this reaction with the whole film, we used the solutions of heteropolyacid in chloroform/methanol mixtures enriched by chloroform. In pure methanol only the very thin surface layer of polymer film undergoes transformations because of very pure solubility of MDMO-PPV in this solvent, while chloroform favors swelling and partial dissolution of the polymer surface layer.

One can observe drastic changes in optical absorbance spectra of MDMO-PPV films after treating the polymer with heteropolyacid solution consisted in the appearance of additional wide maximum in a long-wavelength region, which is more pronounced on the spectrum normalized on maximal absorbance (Fig. 1).

The treatment of polymer films with heteropolyacid solution also brings about significant changes in the photoluminescence spectra. From Fig. 2, it is seen that the intensity of luminescence is about two orders of magnitude lower as compared with the initial one; the shape of spectrum also changes—the main peak at 593 nm is practically disappeared. Accordingly, dramatic changes are observed in the photoluminescence excitation spectra (Fig. 3) registered at two different wavelengths corresponding to the maximums on photoluminescence spectrum of initial MDMO-PPV. It should be noted that both optical and luminescent properties of the resulted films are determined namely by the properties of polymer-heteropolyacid composite whereas the input of pure heteropolyacid or the products of its reduction was below the limits of experimental error for these measurements as was clear from the spectra of the films successively treated with polar solvents for exhaustive removal of heteropolyacid and its derivatives.

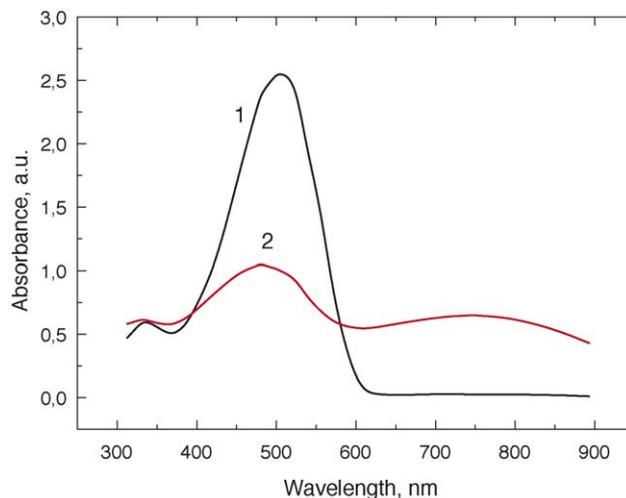


Fig. 1. Optical absorbance spectra of MDMO-PPV films (1) as deposited, and (2) after treatment with $H_3PMO_{12}O_{40}$ chloroform-methanol solution.

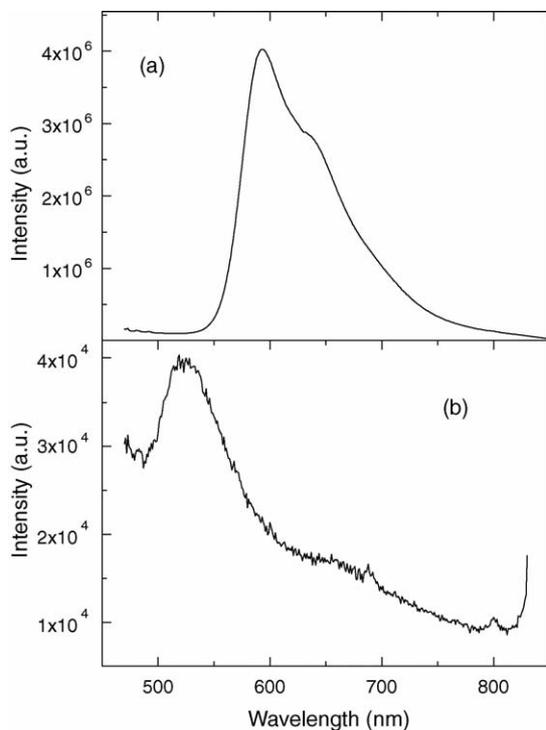


Fig. 2. Photoluminescence spectra of MDMO-PPV film (a) as deposited, and (b) after treatment with $\text{H}_3\text{PMO}_{12}\text{O}_{40}$ chloroform-methanol solution. $\lambda_{\text{exc}} = 420$ nm.

It should be also stressed that at the interaction of MDMO-PPV with $\text{H}_3\text{PMO}_{12}\text{O}_{40}$ one molecule of heteropolyacid per four structural unit of the polymer is sufficient for producing significant changes in absorbance and luminescence spectra of the polymer. These changes are indicative of the transforma-

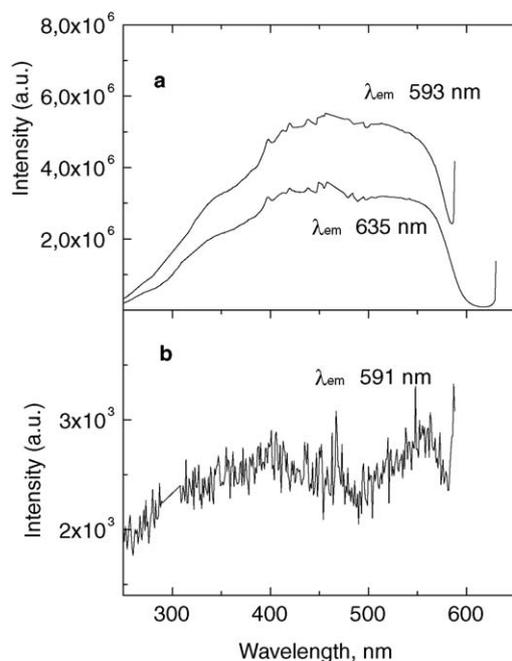


Fig. 3. Photoluminescence excitation spectra of MDMO-PPV film (a) as deposited, and (b) after treatment with $\text{H}_3\text{PMO}_{12}\text{O}_{40}$ chloroform-methanol solution for different wavelengths of emitting light (λ_{em}).

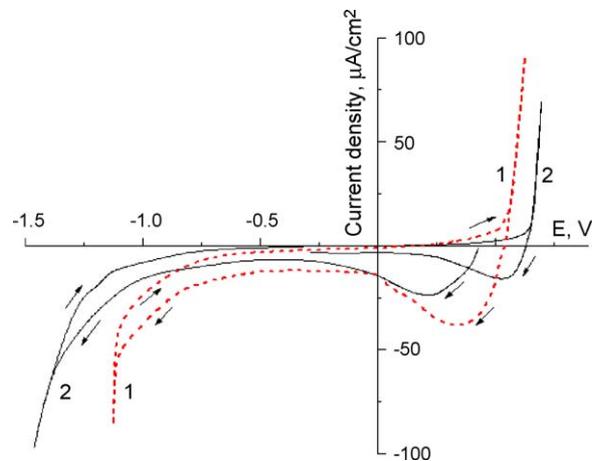


Fig. 4. Cyclic voltammograms at 10 mV s^{-1} of MDMO-PPV films (2) before and (1) after treatment with $\text{H}_3\text{PMO}_{12}\text{O}_{40}$ chloroform-methanol solution. The electrolyte is $0.1 \text{ M } (\text{C}_4\text{H}_9)_4\text{NBF}_4$ in acetonitrile. Scan rate 10 mV/s .

tions proceeded in the conjugated polymer chain, which might affect the charge-transfer processes. This is sustained by the results of the electrochemical measurements with MDMO-PPV film electrodes, which comprise the polymer layer (before and after treating with heteropolyacid) deposited onto the optically transparent electroconductive support ($\text{SnO}_2/\text{quartz}$). In these experiments, we knowingly did not introduce additional redox species into the electrolyte solution to ensure flowing current to be primarily determined by the redox processes involving the components of electrode material.

As is seen from cyclic voltammograms of MDMO-PPV electrodes before and after treatment with $\text{H}_3\text{PMO}_{12}\text{O}_{40}$ solution (Fig. 4), under negative going potential scan a wide peak of cathodic current appears at -0.1 to $+0.6 \text{ V}$. In the case of anodically pre-treated MDMO-PPV electrode, the location of this peak shifts to the positive direction ($+0.3$ to $+0.7 \text{ V}$). In the range of highly negative potentials of MDMO-PPV electrode, a sharp increase of cathodic current is observed at $E < -1$ to -1.3 V . After treating the polymer film with heteropolyacid solution the peak of current at -0.1 to $+0.6 \text{ V}$ rises markedly, and a sharp growth of cathodic current in the range of highly negative electrode potentials is seen at lower by 0.2 V bias (Fig. 4, curve 1).

Thus, MDMO-PPV/heteropolyacid composite is more reactive than pure polymer, that is, in general, not surprising when taking into account the pronounced redox properties of polyoxometalates. After passing cathodic charge through the composite film under highly negative potentials ($E < -1 \text{ V}$), turn bluish grey color of the film turns to yellowish orange inherent to the pure MDMO-PPV. Then, after passing anodic charge through the electrode system at the potentials higher than $+0.7$ to $+1.2 \text{ V}$, red color of the film transforms again to bluish grey characteristic of MDMO-PPV/heteropolyacid composite. Such reversibility may serve as another substantial argument in favor of assumption that the interaction of MDMO-PPV with heteropolyacid does not lead to non-reversible destructive chemical transformations of the polymer in spite of strong alterations in its chromophore system.

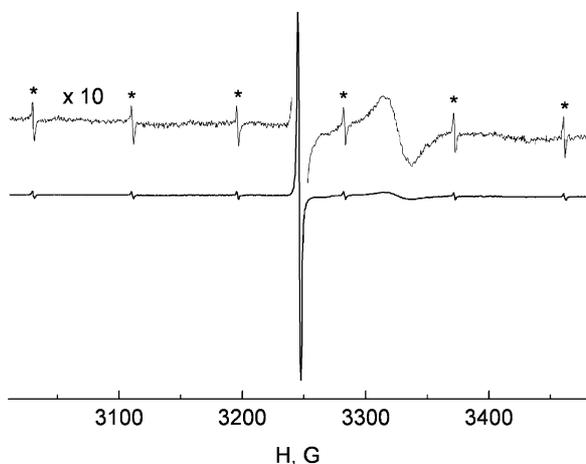


Fig. 5. ESR spectra of MDMO-PPV/ $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ composite at 77 K (1) and at higher gain (2). Six asterisks * depicts lines of Mn^{2+} ions in MgO matrix.

It is known from literature and was checked ourselves that neither MDMO-PPV nor $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ have ESR spectra at 298 or 77 K. Fig. 5 shows typical ESR spectra of the composite system MDMO-PPV/ $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ at 77 K, which appears just after mixing solutions of these two components. Fig. 5 presents two types of paramagnetic centers in the sample. An intensive narrow single line with a g -factor equal to 2.0025 ± 0.0003 and the line width $\Delta H = 1.1 \pm 0.1$ G is characteristic for the unpaired electron localized in a conjugated polymer matrix. The second signal with $g = 1.9545 \pm 0.0005$ and $\Delta H = 20 \pm 0.5$ G should be attributed to Mo^{5+} ions. At room temperature, only “radical” spectrum is observed with parameters similar to those at 77 K.

Indeed, at studies of photoinduced charge transfer in MDMO-PPV/CdSe semiconductor composites under illumination with the 514 nm line of an Ar^+ -laser at room temperature, a strong line with $g = 2.0025$ has been observed due to the polymer cation radicals [27]. Authors did not observe any ESR signals in pure MDMO-PPV and CdSe with and without optical excitation. Also, two overlapping light-induced electron spin resonance (LESR) lines were observed from positive polarons on the conjugated polymer chains (MDMO-PPV) with $g = 2.0025$ and negative charges on the fullerene moieties, denoted as PCBM, with $g = 1.9995$ [28]. Microwave power saturation studies showed different relaxation times for these two spins.

A broad single line at higher magnetic field (Fig. 5) evidently belongs to Mo^{5+} ions in POMs: its g -value is in a good correlation with those mentioned in the introduction and reported in [29] ($g = 1.945$). Some difference in measured g -values (≈ 0.01) can be connected with slight changes in $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ structure surrounded with MDMO-PPV polymer matrix.

It should be mentioned that the value of ΔH does not practically change with variation of $[\text{H}_3\text{PMo}_{12}\text{O}_{40}]/[\text{PPV}]$ ratio in the range between 0.02 and 1.0. This fact (the absence of broadening with the increase of POMs concentration in composites) allows us to conclude that there is no dipole–dipole interaction between stabilized electrons and Mo^{5+} centers in POMs, i.e. that the mean distance between the neighboring paramagnetic centers is larger than 25–30 Å [30]. It is possible to assume that at shorter distances the recombination reactions between unpaired

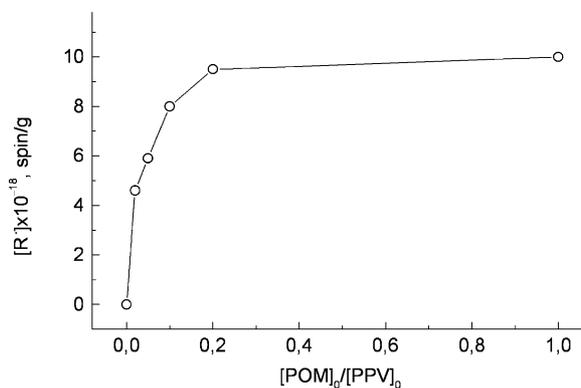


Fig. 6. Concentration of the stabilized unpaired electron $[\text{R}^x]$ vs. relative content of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and MDMO-PPV at the synthesis of polymer/heteropolyacid composites.

electrons can be more effective, and such close $\text{R}^\bullet\text{--Mo}^{5+}$ pairs are not observed, i.e. they are not stable enough at conditions of our experiment.

We have conducted a series of experiments on the synthesis of MDMO-PPV/heteropolyacid composites in solutions with varying molar ratio of the starting components. Fig. 6 shows a concentration plot of the stabilized unpaired electron in MDMO-PPV on the molar ratio $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{MDMO-PPV}$ (calculated on a monomer unit) used in the synthesis of the composites. As is seen from the plot, the concentration of paramagnetic centers grows with increasing content of heteropolyacid in reaction mixtures up to the ratio MDMO-PPV/ $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ equal approximately to 4:1. As indicated above, namely this ratio of the components was obtained from the data of chemical analysis for MDMO-PPV/ $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ composite prepared at the ratio of the starting components equal to 1:1.

In these conditions, if the content of heteropolyacid in the reaction mixture is higher than one molecule per four monomer units of the polymer, the abundant $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ will not react with the polymer and thus will not cause increasing concentration of paramagnetic centers. Hence, the EPR data, along with results of chemical analysis, testify on a distinct relation between the content of heteropolyacid and polymeric components in the composites under investigation.

4. Conclusion

Relying on optical absorbance and luminescence spectra, electrochemical and EPR measurements as well as on the data of chemical analysis, we conclude that the interaction of MDMO-PPV with $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ leads to the formation of strong charge-transfer complex including approximately one heteropolyanion per four monomer units of the polymer chain. This interaction does not cause non-reversible destructive transformations in the polymer chain that is confirmed by the return of composite film color to red after the cathodic reduction of MDMO-PPV/ $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ composite. We have demonstrated that the introduction of heteropolyanions into MDMO-PPV matrix does not amount to classical acid–basic doping well-known in polyaniline/heteropolyacid system [1–8], but causes

reversible changes in the polymer electronic structure, which lead to the appearance of an additional line in optical absorbance spectra, to a sharp decrease of the efficiency of luminescence and to the emergence of pronounced EPR signal.

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