



Electrochromism of interpolyelectrolyte poly(pyridinium) – Poly(styrene sulfonate) complexes



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ABSTRACT

This paper represents a synthesis method of both soluble and insoluble interpolyelectrolyte complexes due to interaction of poly(4,4-(1,4-phenylene)bis(2,6-diphenylpyridinium) triflate) (PV) and sodium polystyrene sulfonate (PSS). Systematic evaluation of electrochromic properties of the both type complexes is given compared to the pristine electrochromic PV. The complexes composition and properties were studied as a function of polyanion and polycation concentrations and their ratios. It was demonstrated that non-stoichiometric insoluble complexes PV/PSS with an excess of PSS are formed in the initial mutual solvent DMF/H₂O 5/1. Films prepared from that mixtures exhibit slower response times and deteriorated electrochromic stability. Non-stoichiometric interpolymer complexes PV/PSS with an excess of PV remain soluble in the initial solvent. Corresponding films have a superior electrochromic contrast than films obtained from the solution of pristine PV under identical conditions. Thus, optimum mixture ratios were found to obtain soluble interpolymer complexes with the advanced properties that may open up new possibilities for making novel electrochromic devices.

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1. Introduction

Electrochromism is a change, evocation, or bleaching, of color as effected either by an electron-transfer (redox) process or by a sufficient electric potential [1]. Electrochromism is typical for many chemical species, including both inorganic metal oxides and metal coordination complexes as well as organic compounds such as bipyridinium salts also known as viologens and conjugated polymers [2]. Viologens are particularly attractive since radical cations formed upon reduction are stable under ambient conditions and intensely colored, with high molar absorption coefficients [1].

There are a lot of promising applications of electrochromic materials (EM) such as electrochromic displays, chameleonic fabrics, different indicators and widely discussed smart windows with controllable light transmission/reflectance suitable for use in cars (anti-glare mirrors), aircrafts and buildings [3–7]. The electrochromic performance of EM can be assessed with respect to three key characteristics: response time, optical contrast and electrochromic stability. For commercial applications an electrochromic device needs a fast response time, high contrast and long-term

stability [8]. All these characteristics can be controlled and enhanced by modulating electrochromic composition and morphology with use of different blends and composites. Blending of two polymers is very attractive due to the abilities to reinforce their physical characteristics, combine electrochromic properties (e.g. color), and even introduce new properties based on the morphological modification or electronic interaction between the two polymers. Moreover, it is not necessary to be an electrochromic for one of the blending polymer. In that case, it serves to act as a matrix for morphological stabilization of the active material during electrochemical reaction and suppression of its agglomeration. Layer-by-layer assembly technique (LBL) is widely used for this purpose. Indium tin oxide coated glass (ITO substrate) is alternatively exposed to positively and negatively charged polyelectrolytes, with spontaneous polymer deposition via Coulombic interactions. For instance, different polyviologen multilayer films with enhanced electrochromic properties were prepared in this manner [9,10].

Matrix polymerization is one of the techniques used for preparation of specific polymer blends or the so-called interpolymer complexes. For instance, polymerization of 3,4-ethylenedioxythiophene (EDOT) in presence of poly(styrenesulfonate) (PSS) leads to polyelectrolyte PEDOT/PSS

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complex formation with partially ordered structure of conductive PEDOT chains and good electrochromic properties [11]. The polymerization of the aniline in the presence of anionic polyelectrolyte (different polysulfonic acids) also leads to the electrochromic interpolymer complex formation, which becomes water-soluble, while pristine PANI is insoluble in water [12].

A number of studies are focused on researching electrochromic properties of interpolymer complexes, prepared by simple mixing of an appropriate solutions [13,14]. Interpolymer complexes can be formed by hydrogen bonds, electrostatic interactions, van der Waals forces and donor-acceptor interactions [15]. However, there is no systematic research, wherein electrochromic characteristics of different polymer blends were given in comparison with characteristics of pristine electrochromic polymer whereas this approach is very helpful for assessing the roles of different nonconductive additives on properties of EM.

We perform systematic study of different electrochromic polymer blends based on poly(4,4-(1,4-phenylene)bis(2,6-diphenylpyridinium) triflate) PV (Scheme 1) to reveal the interpolymer interaction influence on the electrochemical and optical properties of the PV. We recently reported the electrochromic characteristics of PV/poly(*N*-vinylcaprolactam) (PVCa) blends [16]. PV/PVCa films demonstrate electrochromic contrast enhancement and at the same time exhibit slower switching time suggesting restrictions of counterion diffusion during charging/discharging processes. These changes in PV electrochromic behavior in the presence of PVCa were attributed to the interaction between PVCa amide groups and PV radical cations induced by electrochemical reaction.

The present work is a systematic study of PV/PSS interpolyelectrolyte complexes (IPEC) electrochromic properties, both in their soluble and insoluble form. To study electrochromic properties of PV/PSS IPEC thin films were deposited from solutions with various compositions by spin-coating technique. The electrochemical and optical properties of PV and PV/PSS films were studied using a variety of electrochemical and spectroscopic techniques, i.e. cycling voltammetry, chronoamperometry, UV–Vis absorption spectroscopy and in situ monitoring of absorbance during electrochemical switching (so-called spectroelectrochemistry). An in-depth characterization of pristine PV film including evaluation of PV concentration on electrochemistry and electrochromic properties of PV is performed.

2. Experimental

2.1. Materials

Poly[4,4-(1,4-phenylene)bis(2,6-diphenylpyridinium) triflate] ((polypyridinium) triflate) PV was synthesized and characterized according to the reported procedure [17]. Poly(styrenesulfonate)

sodium salt (PSS) (Mw = 70 000, Sigma-Aldrich) was used without any further purification. For preparation of the interpolymer complex PV/PSS the mutual solvent DMF/H₂O 5/1 was experimentally found. *N,N*-Dimethyl formamide (DMF) and acetonitrile (ACN) were purchased from the Sigma-Aldrich. All solutions were made with deionized water (Millipore, resistivity of 18 MΩcm). Indium-tin-oxide-coated (ITO) glass (Nominal resistance 5–20 Ohm/cm²) is washed with deionized water and then dried by at 40–50 °C in the drying oven.

2.2. Selection of the mutual solvent

PV is soluble in DMF, DMSO and other organic solvents, while PSS is water-soluble. Therefore, for preparation of IPEC mutual solvent for both polymers had to be selected. To serve this purpose, the volume fractions of DMF and water were varied and solubility of polymers in this mixture was viewed. Its optimal composition was chosen with the following considerations.

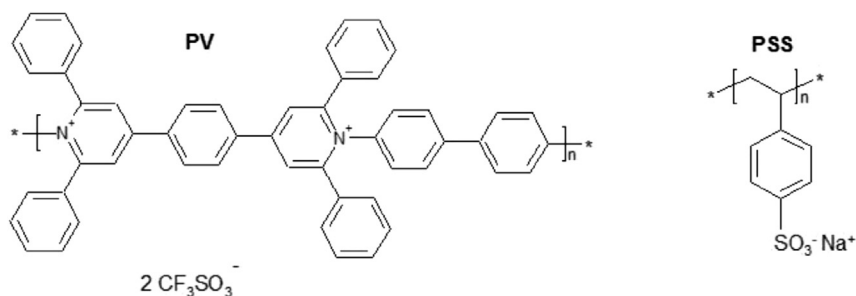
- (i) In mutual solvent PSS concentration can be obtained up to 2 mg mL⁻¹ and up to 25 mg mL⁻¹ for PV (these concentrations are needed to prepare interpolymer complexes with desired composition).
- (ii) Water content in mixture should be minimized (water negatively affects film-forming properties of solution).

In accordance with these requirements, the mixture of DMF/Water with volume ratio 5/1 is turned to be the optimal composition.

2.3. Interpolyelectrolyte complex preparation

Interpolyelectrolyte complex was prepared by adding of the PSS solution dropwise (0.1–0.5 mL drop) to the PV solution (both in mutual solvent DMF/H₂O 5/1) till the required composition of PV/PSS was formed. For example, 5.39 mL of PSS solution (concentration 1.8 mg mL⁻¹) was added to 3.39 mL of PV solution (concentration 1.8 mg mL⁻¹) to prepare PV/PSS blend with molar ratio 1/1. After the each drop of PSS the solution was stirred for 15 min. With the increase of PSS fraction the resulting mixture became turbid. The precipitant (insoluble complex) of PV/PSS was separated by centrifugation (12 000 rpm for 15 min) and dried in vacuum at 60 °C. Mass of the dried precipitant and supernatant volume were measured. The supernatant was characterized by IR and UV–vis absorption spectroscopy. UV–vis–NIR spectrophotometer (UV-3600, Shimadzu) was used to measure UV–vis absorbance spectra of the studied systems to calculate concentration of PV in the system.

All measurements of electrochromic characteristics were performed for both PV/PSS blends and supernatants.



Scheme 1. Monomer unit structure of poly(4,4-(1,4-phenylene)bis(2,6-diphenylpyridinium) triflate) PV and poly(styrenesulfonate) PSS. The molecular weight of the PV monomer unit is 986 mg mL⁻¹. The molecular weight of the PSS monomer unit is 206 mg mL⁻¹.

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