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The effect of poly(N-vinylcaprolactam) on the electrochromic properties of a poly(pyridinium triflate)

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ABSTRACT

Electrochromic properties of poly(pyridinium triflate) PV and its polymer blend with poly(N-vinylcaprolactam) (PV/PVCa) are reported. PV films change their color from transparent slight yellow to blue in a reversible and reproducible manner upon application of potentials within the limits of 0.4 V and −1.2 V vs Ag/AgCl in a 3.5 KCl (aqu) solution. The main electrochromic properties of PV and PV/PVCa were evaluated by a series of cyclic voltammetry and chronoabsorptometry experiments of identical thin films. PV/PVCa films demonstrate electrochromic contrast enhancement ($\Delta T = 32\%$ for pure PV and 40% for PV/PVCa) and narrowing of a colored cation absorbance peak. At the same time, PV/PVCa thin films exhibit slower switching time suggesting restrictions of counterion diffusion during charging/discharging processes. Coloring (transmittance change of 97–70% at 700 nm) and bleaching times for PV films are 0.26 and 0.77 s, respectively. The same values for PV/PVCa films (transmittance change of 97–61% at 700 nm) are about 1.20 and 13.50 s. Dramatic changes in electrochromic behavior of PV in the presence of PVCa can be attributed to the interaction between PVCa amide groups and PV radical cations induced by electrochemical reaction.

1. Introduction

Electrochromism is a reversible and visible change in transmittance and/or reflectance that is associated with an electrochemically induced oxidation–reduction reaction [1]. Electrochromism is typical for many chemical species, including both inorganic metaloxides and metal coordination complexes as well as organic compounds such as conjugated polymers (polypyrroles, polythiophenes, polyanilines, etc.) and bipyridinium salts (also known as viologens), which are particularly attractive since radical cations formed upon external voltage application are highly colored and stable under ambient conditions [2–4].

There are a lot of promising applications of electrochromic materials (EM) such as EC displays, so-called chameleonic fabrics, EC indicators (for instance, state-of-charge or frozen-food monitoring indicators) and particularly widely discussed smart windows with controllable light transmission/reflectance suitable for use in cars (anti-glare mirrors), aircrafts and buildings [5–10].

Visible electrochromism is useful for all these purposes if only colors of oxidized and reduced states are markedly different [11]. Color control strategies are of great importance in establishing new devices. Nowadays, there exist several major color control strategies used with EM [12].

First method is based on monomer unit structure modification, in this instance EC properties can be controlled with induced steric and electronic effects of donor/acceptor substituents [13]. The other approach involves distinct monomers copolymerization or homopolymerization of hybrid monomers with several EC units, which can also lead to an interesting combination of corresponding substances [14].

Finally, third main method is use of different blends, laminates and composites, which, similar to copolymers, combine EC properties of several systems [15]. For this purpose layer-by-layer (LBL) assembly technique is widely used. In this case the 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 conductive properties were prepared in this manner [16–18].

On the other hand, a number of studies are focused on researching various properties of polymer complexes with conductive and EC polymers [19]. It has been known that polymerization of 3,4-ethylenedioxythiophene (EDOT) in presence of poly(styrenesulfonate) (PSS) leads to polyelectrolyte PEDOT/PSS complex formation with partially ordered structure of conductive PEDOT chains [20]. The preparation of polyelectrolyte complexes with polyviologen during mixing aqueous solutions of poly(xyly1

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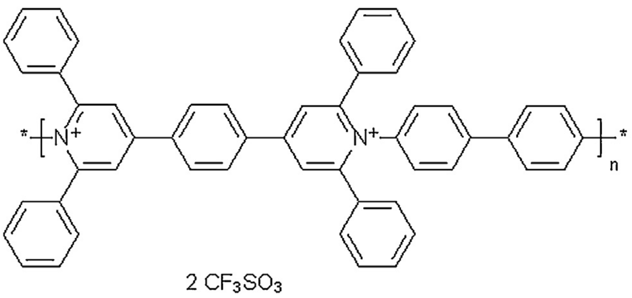


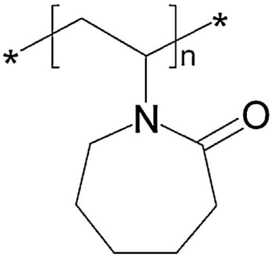
Scheme 1. Chemical structure of poly(pyridinium triflate) PV.

viologen dibromides) (PXV-Br) and PSS [21] or dropwise adding the poly(alkylene) viologen aqueous solution into the PSS aqueous solution [22], has been also reported.

Despite the great number of papers researching different ways of EC improvement, many aspects of such modifications and even coloration processes which occur during redox reactions are still unclear [23]. There is no systematic research on the influence of non-conductive additives on EM properties or nature of forces which lead to conductive polymer complexes formation.

The present work is a systematic study of poly(pyridinium triflate) (Scheme 1) electrochemical and electrochromic properties both with and without electrochromically inactive poly(N-vinylcaprolactam) (PVCa, Scheme 2). There are several reasons PVC was chosen to study effects of weak intermolecular interactions, their ability to conduct electrons along the polymer chain, and the importance of free pyridine chromophore position in the electrochromic system. First, PVCa presumably interacts with PV due to formation of weak bonds between PVCa amide groups and PV pyridinium rings, PVCa methylene groups and PV phenylene and phenyl rings while PVCa steric restrictions may also affect PV electrochromic properties. The second important point is that monomer units of the PVCa contain the amide groups in the lactam ring. It is known [24] that poly(pyridinium salt)s readily undergo photodecomposition in amide solvents. Therefore, analysis of PV electrochromic properties in presence of a polymer containing amide groups allows to deepen understanding of interaction between PV cation radicals and amide groups.

In this study electrochromic films were obtained by spincoating method from solutions of polymer blends with various compositions. The electrochemical and optical properties of PV and PV/PVCa thin films were then studied using a variety of voltammetric and spectroscopic techniques, i.e. cycling voltammetry, voltage stepping and in situ monitoring of absorbance during switching. An in-depth characterization of pure PV film including evaluation of temperature and thickness influence on electrochemistry and EC properties of PV is performed. PV films have highly transmissive neutral state and can constitute the working electrode of an electrochromic display.



Scheme 2. Chemical structure of poly(N-vinylcaprolactam).

2. Experimental

2.1. Materials

Poly[4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium) triflate] (PV) was synthesized according to the reported procedure [24]. Total yield of poly(pyridinium triflate) was 75%. PV was soluble in dimethylformamide (DMF), dimethylsulfoxide (DMSO), propylene carbonate and acetonitrile (particularly). The FTIR spectra contained a strong aromatic stretch band at 1619 cm^{-1}, C—N stretch band at 1492 cm^{-1}, and a C—F stretch band at 1274 cm^{-1}. IR (KBr) (cm^{-1}) 3062, 1664, 1619, 1597, 1552, 1492, 1452, 1394, 1360, 1259, 1225, 1157, 1030, 842, 779, 763, 727, 700, 638, 609.

Poly(N-vinylcaprolactam) (PVCa, polymerization degree 20,000) was synthesized according to the reported procedure [25]. Dimethyl formamide (DMF) was purchased from the Chimmed Group, potassium chloride (KCl) was purchased from Aldrich and used as is. Indium-tin-oxide-coated (ITO) glass (Nominal resistance 5–20 Ω/cm^2) was purchased from Sigma–Aldrich. It was washed with ethanol and deionized water (Milli-Q RG, Millipore) in the drying oven at 50 °C.

2.2. Films preparation

Films preparation was accomplished with use of the spincoating method (Spincoater SCV-10 Novocontrol Technologies) with ITO glass substrates (2×2 cm^2) as the optically transparent electrodes. For film deposition PV solutions in DMF (concentration 5 mg/ml) were prepared. 0.2 ml of the solution was then deposited on an ITO substrate (rotating at 3000 rpm per minute) for 3 minutes. Then films have been dried for 10 min. The polymer blend was prepared by dropwise adding (0.1 ml drop) of the PV DMF solution to the PVC DMF solution with 10 min stirring after each drop. PV Concentration in all solutions was 5 mg/ml, and PV/PVC molar ratio was 2/1, 1/1 and 1/2.

2.3. Electrochemical and spectroscopic measurements

Electrochemical measurements of PV films were recorded under inert atmosphere conditions with potenstiostat/galvanostat (Autolab, model μAutolab) and carried out in a homemade Teflon cell with quartz windows under the three-electrode cell scheme. ITO-coated glass was used as a working electrode, platinum wire as a counter electrode, and Ag/AgCl wire in a 3.5 M KCl (aqu) solution as a reference electrode. The electrolyte was 0.1 M aqueous solution of KCl. PV is insoluble in water under room temperature while PVCa is insoluble in water at 35–40 °C degrees and so all electrochemical measurements were carried out at 40 °C degree. Scan rate was 100 mV/s. The operating potential was scanned between −1.2 V and 0.4 V vs Ag/AgCl, in different supporting electrolytes. This range was selected in accordance with limits of electrochemical processes in aqueous electrolytes and partially irreversible second stage of reduction process in poly(pyridinium) salts [26].

A nitrogen gas was passed through the solutions to remove dissolved oxygen before the measurements and over the solutions during the measurements.

All analyzed cyclic voltammograms were collected in the second or third subsequent scan to avoid the memory effect connected with the polymer pretreatment before cycling [23].

It was also shown that absorbance spectra of polypiridinium salts in amide solvents dramatically change after UV–vis irradiation [24]. So all other experiments were carried out in low-light conditions (solutions were prepared and stored in a darkened conditions and then polymer films were spincoated under normal daylight conditions).