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Electrochromic behavior of poly(pyridinium triflates) films: Electrolyte ions influence

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ABSTRACT

Electrochromic properties of two poly(pyridinium) salts (PV1 and PV2 with additional methyl substituent) in different supporting electrolytes were investigated. KCl, NaCl, LiCl and KBr supporting electrolytes were used to analyze the ions transfer due to ions size variation. The electrochromic properties of polymer films were examined by electrochemical and spectroelectrochemical methods. Both polymers demonstrate reversible redox process in all studied supporting electrolytes. In general, replacement of K^+ ions by Li^+ or Na^+ ions leads to deterioration in the optical contrast and coloring time in contrast to bleaching time which is improved for both studied polymers. The reason behind this is thought to be an increasing cation size obstructing the cation transport in redox reactions. Comparing the relative changes in polymer electrochromic characteristics by the electrolyte replacement is less significant for PV2 films. The replacement of supporting electrolyte anions has practically no effect on the electrochromic properties of both polymers.

1. Introduction

Electrochromic materials (EMs) are capable of reversibly changing color under applied voltage. It is explained by undergoing redox reactions generating of new electronic absorption transitions in the visible region. EMs usually turn from transparent to colored or between two colored states (multicolored). This optical change is usually induced by small potential variation (~1 V) [1]. There are a lot of promising applications of EMs: electrochromic displays and earth-tone chameleon materials, various indicators and smart windows with controllable transmission/reflection [2–4]. To use EMs in commercial applications fast response time, high value of optical contrast and long-term stability are favorable [5]. There are several types of EMs: inorganic, low molecular-weight organic and high molecular-weight organic (polymers). They are used in electrochromic devices [6], but most promising EMs are polymers possessing high optical contrast and extremely short switching times. Chemical and physical properties of polymer EMs may be easily tuned by changes in chemical structure of monomer unit [7–14] and strongly depend on the ionic composition of the system [15–22] (electrolyte ions and film counterions). Recently, it was shown [23,24] that conducting polymer/noble metal hybrid films have better conductivity, coloration efficiencies and switching times relative to control films [24]. Such influence of metal cations on the electrochemical and optical properties of conducting polymers could be used to create sensors based on them [25].

Monomer unit structure affects the electrochromic properties due to the distortion of the π-conjugated backbone by steric interactions with the addition of functional groups or due to direct interaction (inductive and/or mesomeric) of functional groups with the charged π-conjugated system [7]. Even short alkyl side chains may significantly alter electrochromic behavior [8,9]. For example, substitution of side chains in the structure of poly(3-ethyl-2-(2-thienyl)-1H-pyrrole) from ethyl to propyl leads to the peak shift of optical absorption by more than 100 nm, and also to noticeable changes in the switching times of electrochromic films. With the propyl introduction, the coloring times increase and the bleaching times of samples decrease, which is attributed to limitations of ion diffusion [9]. The influence of side alkyl substituents on the electrochromic properties of ProDOT was studied [8]. It was shown that both ethyl and methyl groups distort the planarity of the π-conjugated backbone. As a result, films deposited from ProDOT-Me_2 and ProDOT-Et_2 have more open morphology compared to ProDOT, which facilitates ion transport in the system and leads to the improvement of electrochromic contrast, coloration efficiency, stability and switching times.

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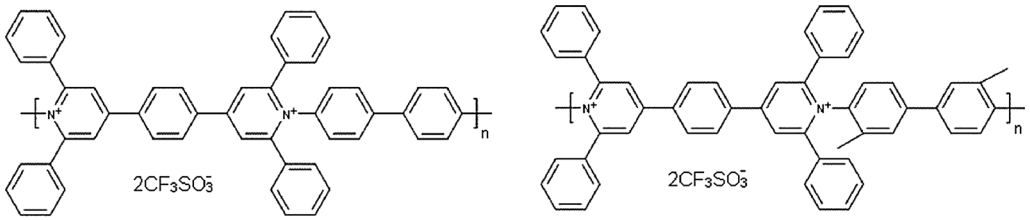

PV1 PV2

Scheme 1. Schematic structure of poly(pyridinium triflate).

Many features associated with the chemical structure of polymer are strongly manifested in cyclic voltammograms (CVs). For example, the electron-donating or accepting substituents shift positions of redox potentials [8–10]. Also it was shown, that minor changes in chemical structure, e.g. increase of alkyl spacers length in polyviologen molecules, led to self-organization of macromolecules reflecting on the redox peak half-width decrease [11].

Ion composition of the system plays an important role in redox processes. Redox reactions are accompanied by the formation of the additional charges in the bulk of the film which have to be neutralized. Charge neutralization may be achieved either by penetration of ions into the polymer film or by transferring ions into solution, or a combination of both [15]. Ion transport between the film and the electrolyte maintains electrical neutrality of the system [7,16].

The role of ion transport in redox processes is analyzed in a number of works [16–22]. In some of them it was demonstrated [16–19] that anion transport is dominating over cation one. Electrochemical activity of the polyviologen film depends on the anion size of the supporting electrolyte [17,18]. It was shown that typical redox process was observed in a solution containing a smaller anion in comparison with the anion used in electropolymerization. The growth of the anion size of the supporting electrolyte resulted in inactivation of the redox process. This ion-controlled electrochemical behavior (the structural memory effect [26]) demonstrates the role of the ion transport in redox processes.

There are a number of works where the cation transport has overwhelming influence [21,22]. For example, there is a linear correlation between switching times of polyaniline in the presence of poly(2-acrylamido-2-methyl-1-propanesulfonic acid) and the hydrated cation size in the buffer solution [22]. Smaller cations efficiently penetrate into the film, thus accelerating the oxidation process. According to [19], with the increase of ion diffusion coefficient in 3D ordered macroporous films of polyaniline the switching time of electrochromic materials is improved.

One can suggest that both cation and anion transport may be involved in the redox processes [7]. Thus, a review of published papers shows that the analysis of ion transport still presents a challenge problem.

In this study we investigate two poly(pyridinium triflates) (PV1 and PV2) (so-called polyviologens) with different side substituents. It is expected that the addition of methyl substituents (PV2) will affect the electrochromic properties due to their electron-donating properties and their steric effect on the π-conjugated system. Since the backbones of both polymers consist of para-catenated aromatic rings, they can only rotate around the axis of the backbones. The model of the PV1 dimer shows [27] that it is a rigid-rod. To minimize the potential energy, two central aromatic rings of the PV1 are twisted (15 degrees) along its axis. Poly(pyridinium) salts are electrochromic, transparent in a neutral state and blue in colored state [28–30]. Redox switching gives rise to new optical absorption bands together with transfer of electrons/counterions. This research is focused on the analysis of the electrochromic properties of thin poly(pyridinium triflates) films in supporting solutions of various electrolytes. Comparative analysis of the general electrochromic parameters, such as switching time and optical contrast, obtained in supporting electrolytes containing cations and anions of various sizes assess the role of ion transport. We study the influence of electrolyte ions on the electrochromic properties of two polymers containing the same functional groups inside the principal polymer chain but with different side substituents, thus examining electron-donating and steric effects of methyl groups.

2. Methods

2.1. Materials

Poly[4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium)triflate] ((polypyridinium) triflate) PV1 and poly[4,4′-(2-methyl-1,4-phenylene) bis(2,6-diphenylpyridinium) triflate] PV2 (Scheme 1) were prepared and characterized using the procedure reported in [26]. The synthetic route involves the following stages: synthesis of 3,3′-(p-phenylene)bis (1,5diphenyl-1,5pentanedione) (yield 98%; IR (KBr cm^{-1}):1685 (C = O); 159,214,411,271. ^{1}H-NMR (DMSO-d_6), δ, ppm): 8.19–7.23 (m, 24H, Ar-H); 2.95 (d, 8H, CH_2); 2.82(m, 2H, CH). Anal. Calcd for $C_{40}H_{34}O_4$, %: C, 83.02; H,5.92. Found,%: 82.64; H,5.71) and synthesis of 4,4′-(p-phenylene)bis(2,6-diphenylpyrylium)triflate (PPPT) ((yield 95%; IR (KBr cm^{-1}):1271 (C-F); ^{1}H-NMR (DMSO-d_6), δ, ppm): 9.37 (s, 4H,pyrylium, Ar-H), 7.51–9.00 (broad, 24H, Ar-H). Anal. Calcd for $C_{42}H_{28}F_6S_2O_8$, %: C, 60.13; H,3.36. Found, %: 59.84; H,3.11). PV1 was synthesized by polymerization of PPPT with 4,4′-diaminodiphenyl in *N*,*N*-dimethylformamide (DMF)/toluene mixtures at elevated temperatures (IR (KBr cm^{-1}):1271 (C-F); ^{1}H-NMR (DMSO-d_6), δ, ppm): 9.31–8.85 (broad, 4H, pyrylium, Ar-H), 7.11–8.70 (broad, 32H, Ar-H). Anal. Calcd for $C_{52}H_{36}N_2F_6S_2O_6$, %: C, 64.86; H,3.77;.N,2.91; F,11.84; S,6.66. Found, %: 64.17; H,3.51; N,2.41; F,11.12; S,6.00. Inherent viscosity was measurement at concentration of 0.1 g/dl at 25 °C in DMSO η_{inh} =7.1 dl/g.). PV2 was prepared by polymerization of PPPT with 3,3′-dimethylbenzidine (IR (KBr cm^{-1}):1270 (C-F); ^{1}H-NMR (DMSO-d_6), δ, ppm):, Ar-H), 7.51–9.20 (broad, 34H, Ar-H, pyrylium, Ar-H), 2.2 (s, 6H,CH_3). Anal. Calcd for $C_{54}H_{40}$ $N_2F_6S_2O_6$,%: C, 65.45; H,4.07;. N,2.83; F,11.50; S,6.47. Found,%: 64.81; H,3.81; N,2.32; F,11.10; S,6.14. Inherent viscosity was measurement at concentration of 0.1g/dl at 25 °C in DMSO η_{inh} = 6.2 dl/g.) Both polymers were obtained in a quantitative yield.

Polymer solutions were prepared in *N*,*N*-Dimethylformamide (DMF) (Sigma-Aldrich). PV1 and PV2 solutions concentration (in DMF) were 5 mg/mL. It was established experimentally that this concentration is optimal for the production of thin and homogeneous films.

0.1 M aqueous solutions of KCl (Fluka), LiCl (Fluka), KBr (Fluka) and NaCl (Fluka) were used as supporting electrolytes. For preparation of all solutions was used deionized water (Millipore, resistivity of 18 MΩcm).

2.2. Films preparation

The electrochromic films were formed by spin-coating technique (10,000 rpm for 3 min) over a cleaned 1.75 cm × 1.75 cm indium tin oxide electrode (ITO). For polymer films manufacture Spincoater SCV-