



Truly solid state electrochromic devices constructed from polymeric ionic liquids as solid electrolytes and electrodes formulated by vapor phase polymerization of 3,4-ethylenedioxythiophene



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ABSTRACT

Using polymeric ionic liquids, namely poly[1-(2-(2-(2-(methacryloyloxy)ethoxy)ethoxy)ethyl)-3-methylimidazolium]bis(trifluoromethylsulfonyl)imide or tetracyanoborate, and poly(3,4-ethylenedioxythiophene) (PEDOT) as an ion conductor and electrodes, respectively, the all-polymer-based thin-film symmetrical electrochromic devices (ECDs) have been constructed and tested. The proposed architecture serves as a prove of concept that polymeric ionic liquids (PILs) can be themselves used as solid electrolytes thus avoiding any electrolyte leakage since the ionic liquid species are grafted on the polymer backbone. Three different methods for the synthesis of PEDOT electrode films, including two new approaches consisted in vapor phase polymerization of 3,4-ethylenedioxythiophene (EDOT) in the presence of ionic monomer and poly(ethylene glycol)(di)methacrylates, have been investigated. Two oxidants, $\text{Fe}[(\text{CF}_3\text{SO}_2)_2\text{N}]_3$ and $\text{Fe}[(\text{CN})_4\text{B}]_3$, bearing the same anions as PILs were prepared for the first time and utilized in the vapor phase polymerization of EDOT. It was found that the more compact structure and the highest conductivity are achieved for PEDOT electrodes prepared by vapor phase polymerization of EDOT in the presence of ionic monomer and poly(ethylene glycol)(di)methacrylates, followed by radical polymerization of the latters. The simplicity of ECDs assembly, their fast switching times (3–5 s), high coloration efficiency (up to $430 \text{ cm}^2/\text{C}$), satisfactory optical contrast (up to 28.5%), absence of any liquids and good performance in air and in vacuum were found among the advantages of the proposed technology.

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1. Introduction

Poly(ionic liquid)s, or polymeric ionic liquids (PILs), refer to a novel subclass of polyelectrolytes having ionic liquid (IL) species in each monomer repeating unit, connected through a polymeric backbone to form a macromolecular architecture [1–6]. PILs cause increasing genuine interest because they combine all beneficial properties of ILs with those of classical polyelectrolytes. Since PILs offer great ability in the designing of cationic and anionic structures and their combinations, one can in principle manipulate their properties as desired and enhance their ionic conductivity to a high level (10^{-11} – 10^{-5} S/cm at 25°C [2]). Thus, one of the motivations

for the study of PILs is their potential application as solid polymer electrolytes in various modern nascent technologies such as lithium batteries, fuel cells, actuators, dye-sensitized solar cells, field-effect transistors, light-emitting electrochemical cells, etc. [7–18].

Another intriguing field for PILs possible application is their utilization in electrochromic devices (ECDs) for the development of information displays, cathode ray tubes, storage devices, electromagnetic shutter and mirrors [19–22]. The main objective to be solved is the creation of simple and reliable technology for ECDs production that can promote their adaptation for wide glazing and displays manufacture. To achieve this it is necessary to fulfill several conditions: for easy assembling the quantity of layers must be reduced from 7–9 to 3–5; for the rejection of complicated sealing the presence of liquid containing electrolyte (salt solution in organic solvent or polymer gel electrolyte) should be avoided;

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finally, for best performance in air the all-solid-state composition is preferable [20,22,23].

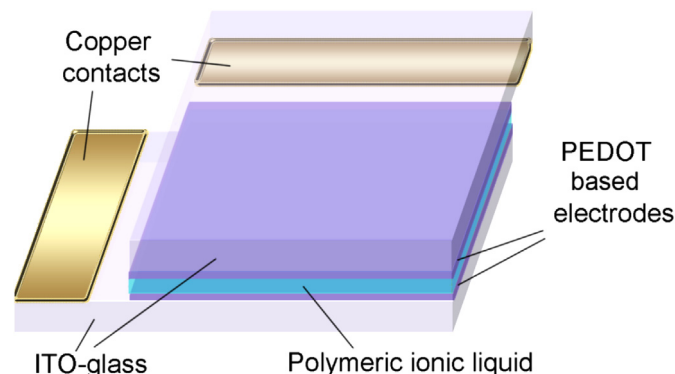
One of the perspective approaches is the creation of all-polymer ECDs. Usually, the electronically conducting polymers such as polypyrrole, polyaniline, polythiophene, etc. and their derivatives are considered as promising ECDs electrode materials [24–26]. Among the others, poly(3,4-ethylenedioxythiophene) (PEDOT) has gained special attention because it can be easily prepared by standard oxidative chemical or electrochemical polymerization, it has well defined polymer backbone structure, it demonstrates high electrochemical stability compared to the thiophene analogs and it was found to be almost transparent or light blue in oxidized (p-doped) state or dark blue in its dedoped state [27–31]. For these reasons PEDOT was intensively used in the construction of various ECDs [21–23,32].

The present work deals with several directions of the research: 1) it represents the continuation of the development of synthetic methods for well-defined PILs with high ionic conductivity [33–38]; 2) development of new methods for 3,4-ethylenedioxythiophene (EDOT) polymerization and subsequent characterization of the obtained thin films by means of cyclic voltamperometry, scanning electron microscopy and four-point impedance spectroscopy; 3) synthesis of novel oxidants, namely, $\text{Fe}(\text{CF}_3\text{SO}_2)_2\text{N}_3$ ($\text{Fe}(\text{TFSI})_3$) and $\text{Fe}(\text{CN})_4\text{B}_3$ ($\text{Fe}(\text{TCB})_3$), having the same anions as PILs and their application in vapor phase polymerization (VPP [39–42]) of EDOT for the obtaining of PEDOT films with the enhanced electric conductivity; 4) first time creation of novel electrode materials by means of EDOT's VPP in the presence of ionic liquid like monomers (ILMs) and poly(ethylene glycol)(di) methacrylates (PEGDM and PEGM) with the sequential radical polymerization of the latter; 5) utilization of the synthesized PILs and PEDOT based films in the construction of truly all-solid state thin-film ECDs [43] having symmetrical structure (Scheme 1).

2. Experimental

2.1. Materials

Poly(ethylene glycol) dimethacrylate (PEGDM, $M_n = 750$ g/mol, Aldrich), poly(ethylene glycol) methyl ether methacrylate (PEGM, $M_n = 475$ g/mol, Aldrich), $\text{Fe}(\text{III})$ tosylate (55 wt.% solution in *n*-butanol, $\text{Fe}(\text{TsO})_3$, Bayer AG), 4-methoxyphenol (99%, Acros), phosphorus pentoxide (98%, Alfa Aesar), ethanol (HPLC grade, Carlo Erba), *n*-butanol (99+%, extra dry, Acros), *N,N*-dimethylformamide (DMF, anhydrous 99.8%, Acros), 2-[2-(chloroethoxy)-ethoxy] ethanol (98+%, TCI Europe), lithium chloride (99+%, Acros), 1-methyl-3-ethylimidazolium tetracyanoborate ([1-Me-3-Etim]



Scheme 1. Schematic representation of symmetrical PEDOT/PIL/PEDOT electrochromic device.

$\text{B}(\text{CN})_4$, 99%, Merck), silver nitrate (99+%, Acros), silver bis(trifluoromethylsulfonyl)imide (99%, Solvionic), lithium bis(trifluoromethylsulfonyl)imide (LiTFSI , 99+%, Solvionic) and $\text{Fe}(\text{III})$ chloride (98+%, anhydrous, Acros) were used without further purification. Methacryloyl chloride (Fluka, 98%) was distilled over linseed oil, while *N*-methylimidazole (99%, Acros) was distilled under inert gas over CaH_2 . Dichloromethane, acetonitrile, ethyl acetate and diethyl ether were distilled over P_2O_5 . 2,2'-Azobisisobutyronitrile (AIBN, 98%, Acros) was recrystallized from methanol. 3,4-Ethylenedioxythiophene (EDOT, Bayer) was distilled under vacuum. ITO-coated glass slides (14×50 mm, sheet resistance $30 \Omega \text{ cm}^{-2}$) were purchased from Solems S.A. and treated prior to use by sonication in acetonitrile.

2.2. Characterization

NMR spectra were obtained on Bruker AMX-400 spectrometer at 25°C in the indicated deuterated solvent and are listed in ppm. The signal corresponding to the residual protons of the deuterated solvent was used as an internal standard (^1H , ^{13}C relative to tetramethylsilane), H_3BO_3 and CHCl_2F were utilized as an internal standards for ^{11}B and ^{19}F NMR, respectively. A Nicolet Magna-750 Fourier IR-spectrometer was used to record IR spectra at a resolution of 2 cm^{-1} and with the scan number equal to 128 (KBr pellets).

Intrinsic viscosities $[\eta]$ of PILs were measured in Ubbelohde type capillary viscometer at 25.0°C , using 0.5 M $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ and 0.5 M [1-Me-3-Etim] $\text{B}(\text{CN})_4$ solutions in DMF for **PIL TFSI** and **PIL TCB**, respectively. The molecular weights (M_n , M_w) and polydispersity index (M_w/M_n) of the same PILs transformed to the water soluble chloride form were determined at 30°C on an LC-20AD gel permeation chromatograph (GPC, Shimadzu Corporation, Japan) equipped with a Tosoh TSK-GEL G6000 PW_{XL}-CP column and a refractive index detector. 0.5 M NaNO_3 aq. solution was used as an eluent with a flow rate of 0.5 mL/min. The calibration was performed with pullulan standards (Shodex P-82).

The study of ILMs and PILs by differential scanning calorimetry (DSC) was performed on a Q100 isothermal differential calorimeter (TA Instruments, USA) in the range of $-90 \div +100^\circ\text{C}$ at a heating rate of 2.0 or $5.0^\circ\text{C}/\text{min}$ for ILMs and PILs, respectively. Glass transition temperature (T_g) of PIL was determined by thermomechanical analysis (TMA) using Q400 analyzer (TA Instruments, USA) at a heating rate of $5^\circ\text{C}/\text{min}$ and a constant load of 0.08 MPa. Thermogravimetric analysis (TGA) was performed in air on a Q50 model (TA Instruments, USA) applying a heating rate of $5^\circ\text{C}/\text{min}$.

Dielectric spectroscopy studies of PILs were run on a Novocontrol Broadband Dielectric Spectrometer equipped with an Alpha analyzer and a Quatro temperature controller (Novocontrol GmbH, Germany). Thin polymer films (0.15–0.20 mm) were cast directly on the gold-coated brass electrodes from acetonitrile solutions, dried at $80^\circ\text{C}/1 \text{ mmHg}$ in vacuum oven for 4 h, whereupon two electrodes were pressed together and put into the measuring cell. The experiments were carried out at 25°C in the 10^{-1} – 10^7 Hz frequency range in air. Ionic conductivities were duplicated by complex impedance analysis using impedance analyzer VSP (Bio-Logic Science Instruments, France). PILs were pressed into a thin film (0.2 mm) between stainless steel electrodes and were put in a cell with pressure contact. The runs were performed in inert atmosphere (Ar or N_2), varying the frequency from 10^{-2} to 10^8 Hz. Conductivity of PEDOT thin films was measured using a four-point probe connected to a EG&G 273A (Princeton Applied Research, USA) potentiostat/galvanostat in the $100 \mu\text{A}$ – 1 mA current range according to the procedure described in Ref. [40]. The electronic

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