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Electrochromic poly(N-alkyl-3,4-dihydrothieno[3,4-*b*][1,4]oxazine)s via electrosynthesis from green microemulsions

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ABSTRACT

In the era of miniaturization researchers are looking for electrochromic materials that combine cost-effective production technology, environmental stability and high performance. It has already been demonstrated that conducting polymers are ideal candidates for electrochromic applications. Herein, Electrosynthesis of poly(N-methyl-3,4-dihydrothieno[3,4-*b*][1,4]oxazine) (PMDTO) and poly(N-ethyl-3,4-dihydrothieno[3,4-*b*][1,4]oxazine) (PEDTO) were performed in green microemulsions (H_2O, EtOH (ethanol) and Mix (H_2O/EtOH)) containing $LiClO_4$ and poly(styrenesulfonic acid) (PSSH). The onset oxidation potentials (E_{onset}) of monomers in these microemulsions were lower than those in common organic electrolytes, but the addition of PSSH brought increased E_{onset} (ca. 0.15 V) versus direct electropolymerization in H_2O/$LiClO_4$ electrolyte. SEM images show that PMDTO and PEDTO films obtained in H_2O/PSSH/$LiClO_4$ present smooth, tight morphology. Spectroelectrochemistry results indicate that their electrochromic performance comparable with that in organic solvents, and significantly improved optical kinetic stability in H_2O electrolyte was observed, for which films under 1000s optical switching with little optical degradation. Based on these results, it is apparent that those polymers and systems have potential in electrochemical applications such as electrochromic devices and supercapacitors.

1. Introduction

Electrochromism is a phenomenon that materials display reversible color change upon electrochemical switching among various potentials [1–4]. Poly(thiophene)s are of particular interest as organic electrochromic materials due to their relative ease of chemical and electrochemical synthesis, environmental stability, and processability [2]. Among which poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives have been widely utilized because of their numerous superiority, such as cost effective, easily accessible, high color contrast and preferable coloration efficiencies [5–10]. What makes them extraordinary popular is that their aqueous dispersion (also known as PEDOT:PSS) obtained via chemical oxidation polymerization can be processed using printing techniques, typical of industrial scale onto different types of substrates [5,11–13]. Nevertheless, electrochemical polymerization has several advantages over chemical methods, for instance, requires a small amount of monomer, shorter polymerization time, easier control of polymerization parameters and thus adjustment of the films' microstructure. Up to now, major electrochemical synthesis of conducting polymer is carried out in non-aqueous solutions due to the monomer (precursor)'s poor solubility and high oxidation potential [6,14,15]. However, the crisis of global eco-environmental protection forces researchers to search electrochromic materials combined with cost-effective production technology, environmental stability and high performance. The use of aqueous solutions as a reaction medium can be welcomed as a sustainable chemistry way [16], and at the meantime

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polyelectrolytes serve as solubilizers or surfactants of the organic monomer [16−18]. Some investigations have showed that sulfonic polyelectrolytes have many positive effects on electrochemical and electrochromic performance of the as-prepared films, namely, lower the monomer' oxidation potential, accelerate the polymerization rate and increase the effective conjugate length, which mainly depend on structure, molecular weight and chain conformation of polymeric sulfonic acid [19−21].

To further investigate the electropolymerization of EDOTs in aqueous solutions and their electrochromic properties, we dwelt to study two nitrogen analogs of EDOT structure which have won great interest by our group and others [22−26], namely, N-methyl-3,4-dihydrothieno[3,4-*b*][1,4]oxazine (MDTO) and N-ethyl-3,4-dihydrothieno[3,4-*b*][1,4]oxazine (EDTO). They are synthesized by facile one-pot method with satisfying yield, which is beneficial to meet large-scale production. The alkyl group attached to the nitrogen atom has strong electro-donating effect, and subsequently gives the monomer lower oxidation potential and lower band gap. Such N-alkyl group can also enhance monomer solubility and polymer processibility. Moreover, the redox and electrochromic properties can be tuned via further structurally modification of the N-alkyl group, allowing more possible derivatives with respect to the monotonous structure of EDOT. Theoretically, the attached methyl and ethyl groups may have parallel contributions toward the overall chemical and optical performance. Moreover, such hydrophilic groups may give rise to strong intermolecular hydrogen-bonding (H-bonding) interactions with solvent and polyelectrolyte molecule, which will impose unexpected chain conformation and structure transformation.

In the majority of electrochemical polymerization studies on polyelectrolyte, numerous researches on PSSH (polystyrene sulfonic acid) and its sodium salt have been reported [18−20,27−29]. Compared with other polysulfonate materials, PSSH possesses advantages of low toxicity, high solubility and excellent dispersing capacity, and the high degree electrolytic activation of PSS^- in H_2O may also accelerated the electropolymerization rate. The PSSH in the complex has two functions, the first is to act as the source of the charge balancing counter ion to obtain doped PEDOT complex, and the second function is to keep PEDOT chain dispersed in the aqueous medium [5]. In this work, the electropolymerization of two nitrogen analogs was performed in H_2O, EtOH and their mixed microemulsions containing PSSH as surfactant [30]. Such electrolyte systems provide a prominent biological green, environmental friendly system for dissolving a variety of organic compounds. The structure and performance of the as-prepared PMDTO and PEDTO polymers were systematically studied by cyclic voltammetry, electrochemical impedance spectroscopy, FT-IR, Scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), spectroelectrochemical and electrochromic techniques. Experiments showed that the addition of PSSH into H_2O brought a slightly increased E_{onset}. As obtained PMDTO and PEDTO films exhibit disparate film morphology in different emulsions, and favorable EC contrast and significantly improved optical stability in aqueous microemulsion.

2. Experimental

2.1. Chemicals and instrumentation

Poly (styrene sulfonic acid) (PSSH, M.W. 75000, 30% w/v aq. soln, Alfa aesar), $LiClO_4$ (99%, Xiya Reagent Research Center), anhydrous ethanol (EtOH) (99%, J&K). All chemicals were used as received unless noted otherwise. All aqueous solutions were prepared using deionized water and were saturated with nitrogen prior to measurement.

Electrochemical and spectroelectrochemical studies were tested on a UV−vis spectrophotometer (SPECORD 200 PLUS) under control of an electrochemical workstation (Versa Stat 3). Infrared spectra were recorded using a Bruker Vertex 70 Fourier transform infrared (FT-IR) spectrometer with samples in KBr pellets. XPS measurements were detected on Thermo ESCALAB 250XI instrument with excitation energy of He I (21.22 eV). All electrochemical experiments were conducted after thorough degassing with a constant stream of purified nitrogen. All potentials stated were measured against Ag/AgCl.

2.2. Syntheses of MDTO and EDTO

N-methyl-3,4-dihydrothieno[3,4-b][1,4]oxazine (MDTO) and N-ethyl-3,4-dihydrothieno[3,4-b][1,4]oxazin (EDTO)were synthesized according to previously reported procedures [23]. The pure products were well characterized by ^{1}H NMR (see Fig. S1), and synthetic routes are briefly described in Fig. 1. Comparing with EDOT, the two nitrogen analogs were obtained via a facile one-step route, though the yields were not relatively high (59% for MDTO, and 54% for EDTO), further adjustment of experimental condition may improve the yield comparable to EDOT. Overall, the low toxicity of reagent, and the one step reaction route will facile the development of MDTO and EDTO for industrial application.

2.3. Electrochemistry test

While the monomers were only partly dissolved in H_2O and EtOH, stable microemulsion dispersions were formed upon adding PSSH as surfactants. 0.1 mmol of monomer (MDTO: 0.0155 g or EDTO: 0.0169 g) was added to 5 mL of solvent containing 0.1 mmol $LiClO_4$ (0.053 g) and 0.18 mL PSSH in glass beaker cell. Three kinds of solvents include H_2O, EtOH and H_2O-EtOH (volume ratio = 1:1) were utilized. The mixtures were ultrasonication (20 kHz, 22.6 W cm^{-2}) for 20 min, clear and transparent light yellow microemulsions were obtained for the following electrochemical polymerization.

The electrochemical tests and polymerization of the monomers were performed in a one compartment cell under computer control. For electrochemical tests, the working and counter electrodes were both platinum (Pt) wire ($\Phi = 1$ mm) and Ag/AgCl wire

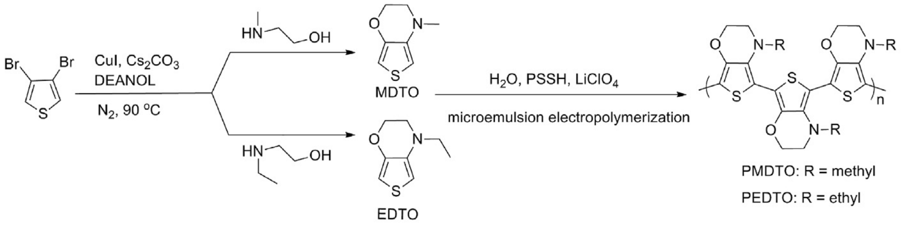

Fig. 1. Synthetic route and microemulsion electropolymerization of MDTO and EDTO.