



Solvent effects on the synthesis, characterization and electrochromic properties of acetic acid modified polyterthiophene



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ABSTRACT

The derivative of terthiophene oligomer 2-(2,5-di(thiophen-2-yl)thiophen-3-yl)acetic acid (TTAA) was synthesized, and its electropolymerization was researched comparatively by using three systems ($\text{CH}_3\text{CN}-\text{Bu}_4\text{NPF}_6$, $\text{CH}_2\text{Cl}_2-\text{Bu}_4\text{NPF}_6$, and BFEE). The effects of solvent on the electrochemical, morphology, redox stability, spectroelectrochemical properties and electrochromic performance of the achieved poly (2-(2,5-di(thiophen-2-yl)thiophen-3-yl)acetic acid) (PTTAA) films were studied in detail. PTTAA could be electrosynthesized in all the three systems facilely and displayed wonderful electroactivity and prominent redox stability in a wide potential window. The PTTAA films obtained in $\text{CH}_3\text{CN}-\text{Bu}_4\text{NPF}_6$ and $\text{CH}_2\text{Cl}_2-\text{Bu}_4\text{NPF}_6$ had similar electrochemistry property except morphology. PTTAA formed in BFEE had lower oxidation potential (0.4V) and better cycling stability. Also, it showed moderate response time (1.2 s) and excellent coloration efficiency ($391 \text{ cm}^2\text{C}^{-1}$), enhanced its possible application as electrochromic material. So compared with common solvents CH_3CN and CH_2Cl_2 , TTAA could electrochemical polymerization at a lower potential and got higher quality polymer films in the strong Lewis acid BFEE. And this also made PTTAA as-formed in BFEE had better redox stability and electrochromic performance.

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1. Introduction

Conducting polymers (CPs) have attracted widely research for various applications in organic light-emitting diodes (OLEDs) [1], electrochromic devices [2], supercapacitors [3], organic field effect transistors (OFETs) [4], photovoltaic cells [5], chemical sensors [6], and thermoelectric materials [7], owing to their excellent properties such as environmental stability, mechanical flexibility and ease in tuning their electronic and optical properties by structural versatility. Among them, the electrochromism of CPs is a much interesting topic and has various applications [8]. Compared with inorganic electrochromic materials, CPs offer the benefits of more colors, faster switching time, higher optical contrast, better processability, as well as their tunability of the band gap with structure modification [9–12].

Among the CPs, polythiophene is the most widely researched electrochromic material. And α -oligo/polythiophene [13–18] has

been considered to be promising candidates in developing and fabricating optoelectronic devices. As one kind of representative structures of α -oligo/polythiophene, the terthiophene (TT) structure has got researchers' attention for its outstanding performances and facile construction due to its several virtues (i) the polymers prepared from terthiophene exhibit high conductivity and environment stability; (ii) terthiophene substituted at the 3'-position can maintain during 2'- and 5''-positions coupling and allows its polymerization rapidly, relieving steric hindrance caused by the bulky functional group around the polymerization reaction site [19–27]. All above characteristics make terthiophene structure an ideal building block for constructing functional polymers.

Carboxyl group as a functional group grafting onto CPs backbone has important significance for research and application because of its excellent biocompatibility and solubility in water [28]. In addition, CPs can achieve donor-acceptor structure after attaching with the electron-withdrawing effect of carboxyl group [29]. These polymers have some characteristic features, like low-lying conduction bands and high electron affinity, which make them good candidates for *n*-type electrical conductors [30]. But so far, the carboxyl group still researched less about its influence on electrochromism.

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Based on above analysis, the polymer combined with carboxyl group as pendant and TT units as backbone may become a good candidate for organic electronic materials. In spite of great efforts were devoted basically to structural design, the factors influencing the optoelectronic properties of the polymers such as current density, applied potentials, solvents, supporting electrolytes, pH and temperature, meanwhile electropolymerization method were still researched in its early days [31]. In general, there are two methods for the polymerization of monomers: electrochemical polymerization and chemical oxidative polymerization. We used electrochemical polymerization here because of its easy control, simple operation, and high purity of the polymer.

Supporting electrolyte was reported easily dispersed in the polymer films to improve doping and contrast, thereby the polymer films could display better electrochromic performance [31]. And our group recent research found that compared with ionic liquid (BmimPF₆) and CH₂Cl₂, poly(thieno[3,4-b]-1,4-oxathiane) film showed higher electroactivity, superior stability, and higher coloration efficiency in the former [32]. Additionally, supporting electrolyte had great influence for CPs capacitance performance [33,34]. Thus, both solvent and supporting electrolyte may affect the synthesis, characterization, and electrochromic properties of polymer.

In this work, a terthiophene oligomer, 2-(2,5-di(thiophen-2-yl)thiophen-3-yl)acetic acid (TTAA) was synthesized. The effect of solvent-electrolyte systems (CH₃CN-Bu₄NPF₆, CH₂Cl₂-Bu₄NPF₆, and BFEE) on the electropolymerization behavior of TTAA was researched. Moreover, structure, electrochemical behavior of TTAA were systematically investigated. Besides, morphology, cycling stability and spectroelectrochemical properties, especially electrochromic performance of the as-prepared PTTAA films were studied.

2. Experimental

2.1. Materials

2-(Thiophen-3-yl)acetic acid, tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄), 2-thiopheneboronic acid and anhydrous Na₂CO₃ were purchased from Shanghai J&K Scientific Ltd. Anhydrous C₂H₅OH, n-bromosuccinimide (NBS) were purchased from Energy Chemical and used without further purification. CH₂Cl₂, boron trifluoride diethyl etherate (BFEE) and tetrahydrofuran (THF) were purified by distillation with CaH₂ and dried by 4 Å molecular sieves. Tetra-n-butylammonium hexafluorophosphate (Bu₄NPF₆; Energy Chemical) was dried for 24 h at 60 °C under

vacuum atmosphere before use. Other reagents and chemicals were purchased from Shanghai Vita Chemical Plant.

2.2. Synthesis of TTAA

TTAA was synthesized by the route displayed in Scheme 1 [35]. At last, the light yellow crystal TTAA was obtained in 62.7% yield. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.35 (d, J = 5.1 Hz, 1H), 7.24–7.17 (m, 3H), 7.13 (s, 1H), 7.09 (d, J = 8.7 Hz, 1H), 7.02 (s, 1H), 3.79 (s, 2H).

2.3. Electrosynthesis and electrochemical tests

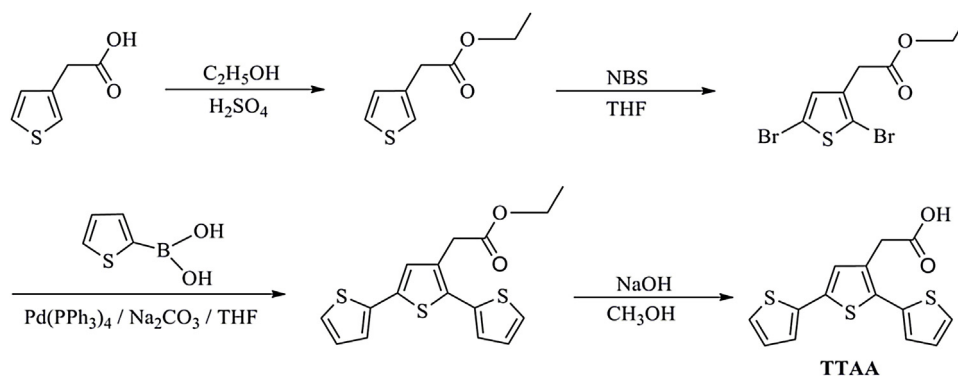
All the electrosynthesis and electrochemical tests performed by using Model 263A potentiostat/galvanostat (EG&G Princeton Applied Research) in a one-compartment cell. We used Pt wires (1 mm in diameter) as working and counter electrodes and Ag/AgCl as reference electrode for electrochemical tests. The three electrodes were placed 5 mm apart each other during the tests. Moreover, we used an indium tin oxide (ITO)-coated glass or a Pt sheet (surface areas of 3 cm²) and stainless steel sheets (surface areas of 6 cm²) as the working and counter electrodes to obtain enough polymer films for characterization. Every time before doing the experiments, the working and counter electrodes were burned and all the electrodes were polished with abrasive paper (1500 mesh) carefully (ITO-coated glass electrodes were soaked in ethanol for 6 h and then cleaned ultrasonically for 15 min), then dried in air after cleaning in acetone.

Electrochemical polymerization performed with 0.01 mol L⁻¹ TTAA in CH₃CN-Bu₄NPF₆, CH₂Cl₂-Bu₄NPF₆, and BFEE systems. All the experiments were carried out in the solution which was protected by dry nitrogen. And we washed the electrosynthesized polymer films with CH₃CN repeatedly to remove the electrolyte and oligomer/monomer.

2.4. Characterization

A Bruker AV 400NMR spectrometer was used for ¹H NMR spectra, CDCl₃ and tetramethylsilane were used as solvent and internal standard respectively. A Bruker Vertex 70 Fourier transform infrared (FTIR) spectrometer was used for the samples which was well-distribution in KBr pellet to infrared spectra measurements. After deposited the polymer film on the ITO-coated glass, we used a VEGA\\LSU scanning electron microscope (Tescan) to scanning electron microscopy (SEM) characterization.

A Specord 200 plus spectrophotometer was used for spectroelectrochemistry and kinetic research, and a Princeton Versa



Scheme 1. Synthetic route of TTAA.

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