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Water Dispersible Low Band Gap Conductive Polymer Based on Thieno[3,4-*b*]thiophene

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Abstract

Herein we describe the synthesis and properties of poly(thieno[3,4-*b*]thiophene) (PT34bT), a new low band gap polymer that shows high optical transparency in oxidized conductive state. Thieno[3,4,*b*]thiophene was polymerized in water using chemical oxidants in the presence of poly(styrenesulfonic acid). Since poly(styrenesulfonic acid) is water soluble and there are strong interactions between poly(styrenesulfonate) and the oxidized PT34bT, the resulting polymer system is rendered a colloidal dispersion. PT34bT-PSS has a band gap of ca. 1.08 eV (1150nm) depending on oxidants used as determined by the onset of the π to π^* from the Vis-NIR spectrum with a peak at an energy of 1.63 eV (760 nm). Diluted PT34bT-PSS dispersions are transmissive green in the oxidized form and become transmissive blue in reduced state. Electrical conductivities for these polymers are dependent on chemical oxidants used and are varied from 0.01 to 10^{-4} S/cm.

Keywords: Poly(thieno[3,4-*b*]thiophene), Intrinsically conductive polymer, Optically transparent polymer

1. Introduction

Commercialization of many intrinsically conducting polymers (ICP) has not been successful due to their inherent insolubility in common inexpensive solvents, and lack of both tractability and environmental stability. For the few ICPs that do fit this set of stringent criteria, typically their optical properties coupled to their electrical conductivities are the limiting factors for their ultimate use in either electrical or electro-optical applications. Appending flexible side groups to the backbone has circumvented poor solubility of many ICPs [1]. Especially, self-doped conducting polymers which have ionic side chains covalently bonded to its backbone show good water solubility and alleviate processing problems in many conducting polymers [2]. A more practical approach to achieve water solubility/dispersibility has been to carry out the polymerization of the monomer in an aqueous electrolyte solution via chemical oxidation in the presence of a suitable template [3]. To date, the largest commercial success in the field of ICPs is poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS) presently marketed under the tradename Baytron-P. Baytron-P is primarily used as an antistatic coating for photographic films [4] and its application areas are being extended to optically transparent electrodes [5], sensors [6], electrochromic windows [7], use as hole transport layers in light emitting diodes[8], and its utilization in solid-state capacitors [9]. The success of PEDOT-PSS can be attributed to several key features. PEDOT-PSS is sky blue with high optical transparency in the oxidized state and has been demonstrated to exhibit high environmental stability [10]. In the reduced state, Baytron-P is deep blue exhibiting a λ_{max} at 650 nm. The monomer, 3,4-ethylenedioxythiophene (EDOT or Baytron-M), has a fairly low oxidation potential due to two electron-rich oxygens on positions three and four and, therefore, the monomer has an elevated HOMO with only two coupling sites available for polymerization. In essence, this translates to polymerization under nondegradative conditions to produce a linear polymer without β-defects. EDOT has been polymerized via suspension in water in the presence of a chemical oxidant and a polymeric acid such as poly(styrenesulfonic acid), PSSA [4,11]. The resulting PEDOT-PSS has been reported to exhibit

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electrical conductivities as high as 80 S/cm [12] whereas blends and composites of PEDOT-PSS have conductivities ranging from 0.2 to 360 S/cm [13].

Recently, we have reported the first oxidative electrochemical polymerization of thieno[3,4-*b*]thiophene (T34bT) [14]. Poly(thieno[3,4-*b*]thiophene) (PT34bT) shows a very low band gap of 0.85 eV and, as such, can be both p- and n-doped at low positive and negative potentials, respectively. Due to its long-term redox stability, high oxidative stability, and the ability to switch between an optically transparent colorless oxidized state and a blue reduced state, PT34bT would be an excellent candidate for use as hole transport layers, electrochromic devices, and transparent charge dissipation coatings.

2. Experimental

2.1. Materials

Thieno[3,4-*b*]thiophene (T34bT) was synthesized in accordance to literature procedure from 3,4-dibromothiophene [15]. Ferric sulfate hydrate (iron content 21.7 wt%), ammonium persulfate, and hydrazine monohydrate were purchased from ACROS and were used as received. Chloroform was purchased from ACROS and purified by distillation over calcium hydride. Hydrogen peroxide (35wt% solution in water) were purchased from Aldrich and used as received. Poly(styrenesulfonic acid) (30 wt% in water, MW 70,000) was purchased from Polysciences Inc. and used without further purification. For all the suspension polymerization, 18 MΩ Millipore de-ionized water was used as a solvent.

2.2. Instrumentation

Optical properties of polymer dispersion and film were measured by a Perkin-Elmer Lambda 900 UV-Vis-NIR spectrometer. Polymer film thickness was measured on glass substrate with Zygo New View 3-D surface profilers. Dynamic light scattering measurements were made with a Brookhaven BI9000-AT autocorrelator. The light source was a Coherent Innova 70-3 Ar^+ laser operating at 514.5 nm. Conductivities were measured using four gold coated leads across the entire width of the polymer 0.25 cm apart from each other. Current was applied across the outer leads and voltage was measured across the inner leads. To test whether the polymer films follow Ohm's law, a minimum of three different currents are applied (between $1e^{-6}$ A and $1e^{-4}$ A) and the resistance values are found to be the same at these different current levels within 1-2% error. Conductivity (σ) is calculated from $\sigma = l/twR$ where l is the distance between leads, w is the width of the film, and t is the thickness of the film. Humidity is kept constant at 65% within our laboratory and the temperature is approximately 25 ±2°C. Films were prepared by drop casting PT34bT-PSS onto a glass slide and allowing for slow evaporation over a period of 24 hours to yield a 5 micrometer thick film.

2.3. Preparation of PT34bT-PSS dispersion via chemical oxidation

To a 25 ml one neck flask, 50.0 mg (0.36mmol) of T34bT and 418.0 mg of 30 wt% PSSA aqueous solution were added. To this suspension 159.0 mg of $Fe_2(SO_4)_3.nH_2O$ was added. The total mass of all the reactants was adjusted to 10 g by adding appropriate amount of de-ionized water. The reaction was carried out for 24 hours with vigorous stirring at room temperature. Other oxidants used for the polymerization are 113.0 mg (0.48 mmol) of $(NH_4)_2S_2O_8$ along with 0.9 mg (1.74×10^{-3} mmol) of $Fe_2(SO_4)_3.nH_2O$ or 113.0 mg of $(NH_4)_2S_2O_8$ or 67.34 mg of 35 wt% of an aqueous solution of hydrogen peroxide (0.693 mmol). After polymerization, the resulting aqueous dispersions were purified by passing them through cation and anion exchange columns (Lewatit K-2629 and Lewatit K-7333).

3. Results and Discussion

3.1. Chemical polymerization of T34bT in the presence of polyelectrolyte

T34bT was polymerized in water using several different chemical oxidant systems such as ferric sulfate hydrate, ammonium persulfate, ammonium persulfate/ferric sulfate hydrate mixtures, hydrogen peroxide, and ferric sulfate hydrate/ hydrogen peroxide mixtures in the presence of PSSA as shown in Fig. 1. Unlike EDOT, T34bT has three positions α to heteroaromatic sulfurs that are available for coupling to produce conjugated pathways.

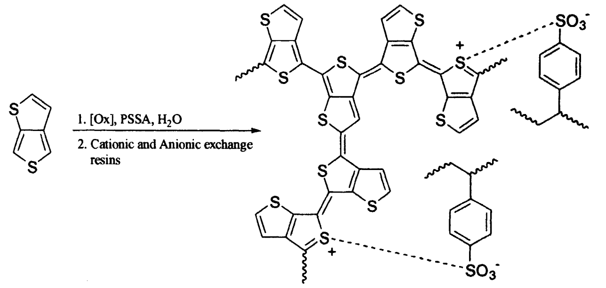

Fig. 1. Preparation of PT34bT-PSS

Polymerization through each of these α positions could result in crosslinked or branched material as illustrated in Scheme 1. It is known that coupling through the 4,6 positions produces a conductive polymer; however, only recently we have reported the oxidative polymerization of a 6-substituted T34bT that produced a 2,4 coupled conjugated PT34bT having a bandgap of 1.55 eV [16]. In