



Investigation of the electrochromic properties of tri-block polyaniline-polythiophene-polyaniline under visible light

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ABSTRACT

This paper describes the synthesis and electrochromic properties of a novel soluble polyaniline-polythiophene-polyaniline tri-block copolymer. The measurements of optical absorbance as a function of voltage and time on tri-block copolymer thin films demonstrated an improvement in stability at ambient conditions and visible light irradiation during the application of voltages. Switching experiments showed an improvement of stability of tri-block copolymer up to 3 times in comparison to the polythiophene block only. A comparison of optical absorbance characteristics for the tri-block copolymer relative to the polythiophene block indicated that the polyaniline blocks substantially increased film stability and therefore has influence on the optical and electrochemical properties of tri-block polyaniline-polythiophene-polyaniline.

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1. Introduction

The synthesis of conjugated polymers for high performance electrochromic devices for controllable windows, sun glasses, and screens has been continually developed through different synthetic approaches such as electropolymerization and copolymerization [1–3]. Polythiophene and polyaniline are important representative classes of conjugated polymers used as active conducting layers in electrochromic devices [4–6]. Polyaniline is commonly used for the development of photovoltaic devices [7,8], supercapacitors [9,10], organic light emitting diodes (OLEDs) [11,12], photocatalysts [13,14], and electrochromic devices [15,16]. Polyaniline is very chemically and oxidatively stable under visible light irradiation [13,14] and has unique electrochemical properties through an oxidative or protonated doping process. Polyaniline is insoluble in common organic solvents but the solubility of polyaniline can be improved through the incorporation of alkyl groups into the main chain, copolymerization with

alkylated polythiophene monomers [17–21], or water soluble functional groups such as sulfonic acid or carboxylic acid [22–24]. Polyaniline in doped states has very high conductivity compared with other conjugated polymers such as polypyrrole and polythiophene [25]. Polythiophene and its derivatives are known to be applicable for photovoltaics [26,27], OLEDs [28], and electrochromic devices [29–31] due to its high thermal stability, atmospheric stability, ease of chemical tuning for solubility, and good electrochemical stability. However, the ease of oxidation of polythiophene can lead to the over-oxidation and the degradation of the polymers under light irradiation [32].

To address some of the limitations of polythiophene and polyaniline, chemical and electrochemical polymerizations of polythiophene and polyaniline for novel copolymers with suitable properties (e.g. good conductivity, ease of solubility, and good stability with application of voltages) have been developed [33–39]. The copolymerization of monomers and/or oligomers of thiophene and aniline units was shown to produce copolymers with intermediate properties between the parent polymers, polythiophene, and polyaniline. Various copolymerization approaches such as the polymerization of a thiophene-aniline monomer [33–36] the post-functionalization of oligomer aniline units have been reported [35,38,39]. However, with such

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approaches, the random copolymers that are produced limited the performance of the devices due to random distribution of the copolymer units and the side chains [35].

The problems of the random distribution of the copolymer were improved with the alternative design of copolymers with the tri-block (A-B-A) system. The use of tri-block copolymers has shown to have a better control of the polymer chain orientation which improved the performance of conjugated polymer based devices [40–42]. For example, the tri-block copolymers of polyaniline-polyfluorene-polyaniline used as an active layer in photovoltaic devices and OLEDs improved the performance of the devices due to the formation of good controlled structure on a substrate [41,42]. The copolymer made from two distinct polymer blocks should exhibit a unique set of optical and electrochemical properties [42].

By applying this strategic copolymerization of two polymer blocks to improve the properties of polythiophene and polyaniline, we reported a soluble A-B-A tri-block copolymer with polyaniline as the A block and alkyl functionalized polythiophene as the B block as a promising candidate for the electrochromic active material. We investigated the electrochromic properties of our newly synthesized tri-block copolymer via cyclic voltammetry, spectroelectrochemistry, and stability during repeated on-off switching cycles with applied voltage. The polyaniline blocks increased the stability of the tri-block copolymer up to 3 times during switching experiments under visible light irradiation and at ambient conditions.

2. Experimental methods

2.1. General

All reactions were carried out under an argon atmosphere. The starting materials and reagents were purchased from commercial sources, which were listed in details. [1,3-Bis(diphenyl phosphino)propane]dichloronickel(II) (Ni(dppp)Cl₂), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄), *N*-Bromosuccinimide (NBS), ammonium persulfate ((NH₄)₂S₂O₈), 3,4-dibromothiophene, 4-bromoaniline, ethylenediaminetetraacetic acid (EDTA), aniline, tetrabutylammonium hexafluorophosphate (TBAPF₆), acetonitrile were purchased from Sigma Aldrich. 1-bromododecane, magnesium turnings, diethyl ether (99.5%, extra dry over molecular sieve, stabilized), tetrahydrofuran; THF (99.5%, extra dry over molecular sieve, stabilized), toluene (99.85%, extra dry over molecular sieve), and methanesulfonic acid were purchased from Acros.

¹H NMR and ¹³C NMR spectra were obtained on Bruker Biospin DPX-300 and Bruker AVANCE 400 NMR spectrometers. CDCl₃ and C₂D₂Cl₄ were used as NMR solvents. NMR spectra were listed in Supporting information. The molecular weight of each polymer (**P1** and tri-block **P2**) was determined on a Jasco gel permeation chromatographic (GPC) analyzer and was measured against polystyrene standard. The UV/Vis spectra were recorded on a Perkin Elmer Lambda 650 UV-vis spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA 851 with a heating rate of 20 °C min⁻¹ up to 650 °C using alumina crucibles under ambient conditions.

2.2. Synthesis of monomers

3,4-Didodecylthiophene (**1**): 1-Bromododecane (3.09 g, 12.4 mmol) was added dropwise to a suspension of magnesium turning (iodine etched) (0.3 g, 12.4 mmol) in diethyl ether (20 mL). The reaction mixture was refluxed for 1 h. With a syringe, the dodecylmagnesium bromide solution was slowly transferred to a solution of 3,4-dibromothiophene (1 g, 4.13 mmol) and Ni(dppp)Cl₂ (13 mg, 0.24 mmol) in diethyl ether (30 mL). The mixture was

refluxed for 16 h. After the completion of the reaction, it was cooled down to room temperature and quenched with 2 M HCl (20 mL). The organic layer was separated and then washed with water. The organic layer was then dried over Na₂SO₄ and concentrated under reduced pressure. Then, the yellow liquid was purified by column chromatography using silica gel with hexane as an eluent to obtain the product (1.5 g, 86%). ¹H NMR (400 MHz, CDCl₃, δ): 6.86 (2H), 2.47 (4H), 1.59 (4H), 1.24 (36H), 0.86 (6H). ¹³C NMR (100 MHz, CDCl₃, δ): 142.12, 119.85, 31.92, 29.68, 29.36, 28.81, 22.69, 14.12.

2,5-Dibromo-3,4-didodecylthiophene (**2**): A mixture of (**1**) (1.738 g, 4.13 mmol) and NBS (2.205 g, 12.39 mmol) in THF (30 mL) was stirred at 50 °C for 16 h in the dark. After the completion of the reaction, the mixture was cooled to room temperature and concentrated under reduced pressure. The reaction residue was dissolved in hexane and purified by column chromatography using silica gel and heptane as an eluent. After solvent evaporation, a yellow solid was obtained (3.35 g, 97%). ¹H NMR (400 MHz, CDCl₃, δ): 2.47 (4H), 1.23 (40H), 0.85 (6H). ¹³C NMR (100 MHz, CDCl₃, δ): 141.46, 107.78, 31.92, 29.66, 29.53, 29.35, 28.95, 22.69, 14.12.

2,5-Bis(trimethylstannyl)thiophene (**3**): The monomer was prepared from the reaction of thiophene with *n*-butyllithium, followed by treatment with trimethyltin chloride according to the literature resulting in a white solid (3.30 g, 68%) [43]. ¹H NMR (400 MHz, CDCl₃, δ): 7.35 (2H), 0.34 (18H). ¹³C NMR (100 MHz, CDCl₃, δ): 143.41, 136.20, -7.70.

2.3. Synthesis of polymers

4-Aminophenyl-terminated Poly(9,9-dioctyl)thiophene (**P1**): (**2**) (1.3748 g, 2.37 mmol), (**3**) (1.555 g, 2.82 mmol), 4-bromoaniline (77 mg, 0.45 mmol) and Pd(PPh₃)₄ (120.8 mg, 0.104 mmol) were refluxed in toluene (40 mL) under argon atmosphere for 3 days in the dark. After the reaction did not progress any further, it was allowed to cool down and aqueous 2 M HCl (~20 mL) was added. The reaction mixture was then extracted with chloroform and the organic layer was washed with a saturated aqueous solution of EDTA, saturated aqueous solution of NaHCO₃, and DI water, respectively. The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The remaining residue was dissolved in CHCl₃ and precipitated out in a mixture of methanol/2 M HCl (10:1 v/v). The obtained solid was then purified by Soxhlet extraction with methanol, acetone, ethyl acetate, and chloroform, respectively. The chloroform phase was collected and evaporated under reduced pressure. The obtained solid was precipitated in methanol/2 M HCl (10:1 v/v) and the final dark red solid was filtered off and dried under vacuum. **P1** (341.6 mg, 27%). ¹H NMR (400 MHz, C₂D₂Cl₄, δ): 7.34 (4H), 7.05 (2H), 6.80 (4H), 6.09 (4H), 2.07 (4H), 1.18 (40H), 0.79 (6H). ¹³C NMR (100 MHz, C₂D₂Cl₄, δ): 151.9, 140.6, 140.0, 128.7, 127.1, 126.1, 121.7, 119.9, 55.3, 40.1, 31.7, 30.0, 29.0, 24.1, 22.5, 13.9.

Poly(9,9-didodecylthiophene)-*b*-polyaniline (**P2**): **P1** (140 mg) was dissolved in 10 mL of dry toluene. A solution of aniline (101.7 mg, 1.09 mmol) in 3.2 mL of THF, methanesulfonic acid (0.16 mL) in H₂O (1.1 mL), and (NH₄)₂S₂O₈ (1244 mg, 5.45 mmol) in H₂O (1.6 mL) were added by syringe into the solution of **P1**, respectively. The reaction was stirred for 3 days at room temperature. After the reaction was completed, toluene (40 mL) was added into the reaction mixture. The organic layer was collected and washed with brine, saturated Na₂CO₃, and then brine. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. A mixture of methanol/2 M HCl (10:1 v/v) was used to precipitate out the solid polymer. The polymer was purified by Soxhlet extraction with acetone and toluene. The toluene layer was collected and concentrated. The polymer was re-precipitated in

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