Polymer 84 (2016) 65–71

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis, characterization, optical and electrochemical properties of spirobifluorene based polymers containing electron deficient moieties

Chin-Yang Yu*, Yuan-Ju Hsu

Department of Materials Science and Engineering, National Taiwan University of Science and Technology, 43, Section 4, Keelung Road, Taipei, 10607, Taiwan

ARTICLE INFO

Article history:
Received 27 May 2015
Received in revised form
19 December 2015
Accepted 24 December 2015
Available online 29 December 2015

Keywords:
Spirobifluorene
Conjugated polymer
Electron deficient moiety

ABSTRACT

2,7-linked or 2,2′-linked 9,9′-spirobifluorene based polymers containing electron deficient moieties such as naphthalene bisimide and/or benzothiadiazole were synthesized through Suzuki cross-coupling reaction. The molecular weights of the copolymers containing spirobifluorene and benzothiadiazole units are relative low due to the low solubility of the resulting polymers. In addition, all polymers derived from 2,2′-linked 9,9′-spirobifluorene and naphthalene bisimide and/or benzothiadiazole showed very low molecular weights due to the low reactivity of the active species. The UV–vis absorption spectrum of the polymers containing 2,7-linked 9,9′-spirobifluorene and naphthalene bisimide exhibited the longest absorption wavelength and very low quantum yield. Alternating polymers containing spirobifluorene and naphthalene bisimide moieties showed a low band gap relative to that of the spirobifluorene and benzothiadiazole containing polymers and their random copolymers presumably there is a strong charge transfer interaction between the alternating electron-donating spirobifluorene unit and the electron-accepting naphthalene bisimide.

1. Introduction

Conjugated polymers have been attracted much attention in their potential uses [1–4] in light emitting diodes, photovoltaic cells, fluorescent sensors and field effect transistors due to their fascinating optical properties, their tunable electronic properties and their facile solution processabilities. It is well known that conjugated copolymers comprising of the alternating electron rich and electron deficient moieties in the polymer main chain can lead to smaller bandgaps and higher performance in optoelectronics devices [5,6]. The introduction of fused-ring systems [7–10] such as cyclopentadithiophenes, dithienopyrroles, dithienosiloles, thienothiophenes and fluorenes can lead to further increase in planarity and extend the conjugation of the polymer backbone therefore reduce the bandgap of the polymer.

Fluorene derivatives have become one of the most promising candidates for blue-emitting materials due to their high efficiencies in photoluminescence and electroluminescence [11,12]. The C-9 position of the fluorene molecule can be readily functionalized which not only improves the solubility and processability but controls interchain interactions [13], cross-linking [14] and optical and electrochemical properties [15]. In addition, the structure of the C-9 functionalized fluorene can restrict the close packing and reduce the intermolecular interactions of the polymer chains therefore significant improve the solubility of the polymers which can minimize the formation of aggregation and/or excimers in the solid state [16]. Recently, the spirobifluorene have been attracted much attention [17–21] since it can be readily tuned by chemical modification which can alter the optical and electrochemical properties both in solution and in the solid state. In the spirobifluorene molecules, the two perpendicular conjugated moieties are connected with the sp^3-hybridized carbon atom. This structural feature can suppress the aggregation of polymers containing spirobifluorene units which lead to improve the solubility and processability. Furthermore, the spirobifluorene structure can prevent the possible photo and thermal oxidation of the C-9 position of the fluorene unit to form the undesired low energy ketonic defect [22]. This can be advantage for long lifetime use in polymer solar cells.

It has been reported the synthesis of spirobifluorene-linked oligomers and showed that the spiro oligomers have enhanced thermal and luminescent stabilities in comparison with those derived from dioctylfluorene units [23]. In addition, the spirobifluorene derivatives can also be used as a hole transport material in dye-sensitized solar cells [24,25]. Recently, the alternating

---

* Corresponding author.
E-mail address: cyyu@mail.ntust.edu.tw (C.-Y. Yu).

http://dx.doi.org/10.1016/j.polymer.2015.12.046

polymers containing fluorene and electron deficient moieties such as naphthalene bisimide and perylene bisimide have been demonstrated their potential uses as an n-type material in all polymer photovoltaics applications [26,27]. There have been a large number of publications on 9,9′-dialkylfluorene based donor acceptor alternating copolymers [28,29]. However, few literatures have been published on spirobifluorene-based donor acceptor alternating and random copolymers [30–32]. To the best of our knowledge, very few studies have appeared in the literature that report the synthesis, optical and electrochemical properties of the copolymers comprising of the two different linkages of spirobifluorenes such as 2,2′-linked and 2,7-linked spirobifluorene with electron deficient units such as naphthalene bisimide and/or benzothiadiazole.

Herein, we report the synthesis of alternating and random copolymers containing 2,2′-linked or 2,7-linked spirobiflourene and the electron deficient moieties such as naphthalene bisimide and/or benzothiadiazole by Suzuki cross-coupling reactions. In addition, the naphthalene diimide was functionalized with the 2-ethylhexyl substituents as the branched alkyl chain in order to increase the solubility of the resulting polymers. The comparison with 2,2′-linked or 2,7-linked spirobiflourene based donor acceptor copolymers enables us to clarify the role of the spiro units and electron deficient moieties in detail. We report a comparison of the optical and electrochemical properties of the six copolymers by UV–vis absorption, emission spectra and cyclic voltammetry measurement. In this research the lowest band gap polymers contained alternating strong donor–acceptor structures that enhance intramolecular charge transfer interactions. These polymers have been considered their potential uses as n-type or p-type materials for the active layers in photovoltaic devices.

2. Experimental

2.1. Instrumentation

^{1}H and ^{13}C NMR spectra were obtained using a Bruker 500 MHz or NMR 600 MHz instrument. Chemical shifts are expressed in parts per million (δ) using residual solvent as an internal standard. Molecular weights of polymers were obtained by gel permeation chromatography (GPC) using a Waters ACQUITY Advanced Polymer Chromatography with RI detector in THF solution calibrated with low polydispersity polystyrene standards. Cyclic voltammetry for all polymers was performed at 100 mV^{-1} in a BASI Epsilon electrochemical workstation with a three-electrode cell, Ag/AgCl as reference electrode, platinum wire as counter electrode and polymer film on a platinum plate as the working electrode in an argon-purged anhydrous acetonitrile solution containing 0.10 M tetra-n-butylammonium hexafluorophosphate (nBu_4NPF_6) at room temperature. UV–vis absorption spectra were recorded on a Jasco (V-670) UV–Vis–NIR spectrophotometer. Photoluminescence measurements were carried out on the Jasco FP-8500 fluorescence spectrophotometer. EI mass spectra were obtained on a Finnigan MAT 95 S mass spectrometer.

2.2. Materials

All chemicals and reagents were purchased from commercial sources (TCI, Alfa Aesar or Sigma Aldrich) and used without further purification unless otherwise noted. Solvents used for spectroscopic measurements were spectrograde. The monomers employed were based on 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-spirobifluorene **1**, *N,N*′-bis(2-ethylhexyl)-2,6-dibromonaphtalene-1,4,5,8-tetracarboxylic acid diimide **2**, 4,7-dibromobenzo[*c*] thiadiazole **3** and 2,2′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-spirobifluorene **4**. Monomer **3** was purchased from Sigma Aldrich. The details of syntheses and characterizations of monomers **1**, **2** and **4** can be found in the electronic supplementary information. Most of the reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates. Preparative separations were performed by column chromatography on silica gel grade 60 (0.040–0.063 mm) from Merck.

2.3. Synthesis of alternating copolymer *P1*

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-spirobifluorene **1** (0.114 g, 0.20 mmol) and *N,N*′-bis(2-ethylhexyl)-2,6-dibromonaphtalene-1,4,5,8-tetracarboxylic acid diimide **2** (0.130 g, 0.20 mmol), aqueous K_2CO_3 (2 M, 4.0 mL) were mixed in 1,4-dioxane (20 mL). After degas for 10 min, tetrakis(-triphenylphosphine) palladium (0.012 g, 5 mol %) was added under an argon atmosphere. The reaction mixture was heated at 110 °C for 48 h before cooling to room temperature. The solution was extracted with dilute aqueous hydrochloric acid and dichloromethane. The organic layer was combined, washed with brine, dried over anhydrous magnesium sulfate. After filtration, the residue was concentrated and poured into methanol and then the precipitate was collected by filtration. The solid was washed by a Soxhlet extraction with methanol and acetone for 24 h, respectively before being dissolved in hot chloroform. The residual was then dried under a vacuum to give a yield of 74%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.48 (2H), 8.02 (2H), 7.70 (2H), 7.45 (2H), 7.28 (2H), 7.13 (2H), 6.99 (2H), 6.71 (2H), 3.84 (4H), 1.61 (2H), 1.30–1.05 (16H), 0.82 (6H), 0.76 (6H) ppm. $M_n = 13300$, $M_w = 27500$, PDI = 2.06.

2.4. Synthesis of alternating copolymer *P2*

Similar procedure was used as that described by the synthesis of alternating copolymer **P1** using 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-spirobifluorene **1** (0.114 g, 0.20 mmol), 4,7-dibromobenzo[*c*] thiadiazole **3** (0.060 g, 0.20 mmol), aqueous K_2CO_3 (2 M, 4.0 mL), tetrakis(triphenylphosphine) palladium (0.012 g, 5 mol %) and 1,4-dioxane (20 mL). The product was dried under a vacuum to give a yield of 48%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.08 (2H), 8.01 (2H), 7.80 (2H), 7.39 (2H), 7.33 (2H), 7.09 (4H), 6.84 (2H). $M_n = 4500$, $M_w = 5600$, PDI = 1.22.

2.5. Synthesis of copolymer *P3*

Similar procedure was used as that described by the synthesis of alternating copolymer **P1** using 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-spirobifluorene **1** (0.114 g, 0.20 mmol), 4,7-dibromobenzo[*c*] thiadiazole **3** (0.030 g, 0.10 mmol), *N,N*′-bis(2-ethylhexyl)-2,6-dibromonaphtalene-1,4,5,8-tetracarboxylic acid diimide **2** (0.065 g, 0.10 mmol), aqueous K_2CO_3 (2 M, 4.0 mL), tetrakis(triphenylphosphine) palladium (0.012 g, 5 mol %) and 1,4-dioxane (20 mL). The product was dried under a vacuum to give a yield of 65%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.48 (2H), 8.09 (2H), 8.01 (4H), 7.75 (4H), 7.45 (4H), 7.30 (4H), 7.09 (6H), 6.92 (2H), 6.86 (2H), 6.72 (2H), 3.86 (4H), 1.62 (2H), 1.43–1.11 (16H), 0.86 (6H), 0.79 (6H) ppm. $M_n = 44000$, $M_w = 87000$, PDI = 1.98.

2.6. Synthesis of alternating copolymer *P4*

Similar procedure was used as that described by the synthesis of alternating copolymer **P1** using 2,2′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-spirobifluorene **4** (0.057 g, 0.10 mmol), *N,N*′-bis(2-ethylhexyl)-2,6-dibromonaphtalene-1,4,5,8-tetracarboxylic acid diimide **2** (0.065 g, 0.10 mmol), aqueous K_2CO_3 (2 M, 2.0 mL), tetrakis(triphenylphosphine) palladium (0.006 g,