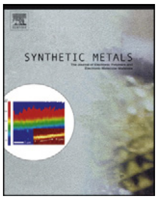
Synthetic Metals 161 (2011) 72–78

Contents lists available at ScienceDirect

Synthetic Metals

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



Synthesis and properties of phenothiazylene vinylene and bithiophene-based copolymers for organic thin film transistors

Jun-Ho Kim[a], Young-Hoon Seo[a], Woo-Hyung Lee[a], Yongtaek Hong[b], Sang Kyu Lee[c], Won-Suk Shin[c], Sang-Jin Moon[c], In-Nam Kang[a,*]

[a] *Department of Chemistry, The Catholic University of Korea, Yeokgok 2-dong, Wonmi-gu, Bucheon, Gyeonggi-do 420-743, Republic of Korea*
[b] *Department of Electrical Engineering and Computer Science, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151-744, Republic of Korea*
[c] *Energy Materials Research Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong, Daejeon 305-600, Republic of Korea*

ARTICLE INFO

Article history:
Received 25 June 2010
Received in revised form 21 October 2010
Accepted 30 October 2010
Available online 20 November 2010

Keywords:
Organic thin film transistor
Phenothiazine
Bithiophene
Semiconducting polymer
Conjugated polymer

ABSTRACT

A series of new phenothiazylene vinylene and thiophene copolymers (P1, P2, and P3) have been synthesized via Yamamoto and Stille coupling reactions. The number-averaged molecular weights (M_n) of P1, P2, and P3 were found to be 12,000, 10,000, and 8200, with polydispersity indices of 3.5, 1.4, and 1.6, respectively. The UV–visible absorption spectra of the polymers contain two strong absorption bands in the ranges 306–325 nm and 430–480 nm, which arise from the absorptions of the phenothiazine segments and the conjugated main chains respectively. Solution-processed field-effect transistors (FETs) fabricated with these polymers exhibit p-type organic thin film transistor characteristics. The field-effect mobilities for P1, P2, and P3 were measured to be 1.8×10^{-4}, 5.7×10^{-4}, and 2.5×10^{-7} cm^2 V^{-1}s^{-1}, respectively, with the corresponding on/off ratios of 5×10^2, 1×10^4, and 5×10^2.

1. Introduction

Organic semiconducting polymers have been used in applications such as polymer light-emitting diodes (PLEDs) [1,2], organic thin-film transistors (OTFTs) [3–5], and organic photovoltaics (OPVs) [6,7]. The use of OTFTs based on solution-processable organic semiconductors in low-cost memory devices, large-area display devices, and flexible electronic devices is increasing. Many studies have performed chemical modifications on the conjugated moieties or incorporated new conjugated building blocks into the polymer chains [8,9]. Of the conjugated polymers tested to date, polythiophenes [10,11], fluorene-based copolymers [12,13], and poly(p-phenylene vinylene) derivatives [14,15] exhibit high performances in OTFT applications. The molecular design and synthesis of new conjugated semiconducting polymers with high charge carrier mobilities might enable the realization of high performance solution-processable OTFTs. With this aim, the use of phenothiazine-based conjugated polymers in various electronic devices has been investigated because they exhibit good electron-donation and transport behaviors due to the presence of electron-rich sulfur and nitrogen atoms [16,17]. In previous studies, we synthesized several phenothiazine-based conjugated polymers for PLED, OTFT, and OPV applications [18,19]. However, the mobility of these polymers is low, which is possibly due to their non-optimized chemical structures. To modify the electronic properties of phenothiazine-based polymers, we introduced bithiophene linkages into the π-conjugated systems, and thus fabricated a new building block for organic semiconductors.

Here we report the synthesis and characterization of a new class of phenothiazylene vinylene and thiophene-based semiconducting polymers (P1, P2, and P3), which function as p-type semiconductors in OTFTs (Schemes 1 and 2). To increase the solubility of the polymers, an easily accessible dialkoxy-substituted phenylene ring was incorporated into the phenothiazine units. The effects of molecular ordering on the organic devices were studied by introducing structurally rigid bithiophene and flexible alkylbithiophene units into the polymer backbones to control the intrachain and interchain π–π interactions. The influence of structural variation on the field-effect mobility of the OTFTs was also investigated.

2. Experimental

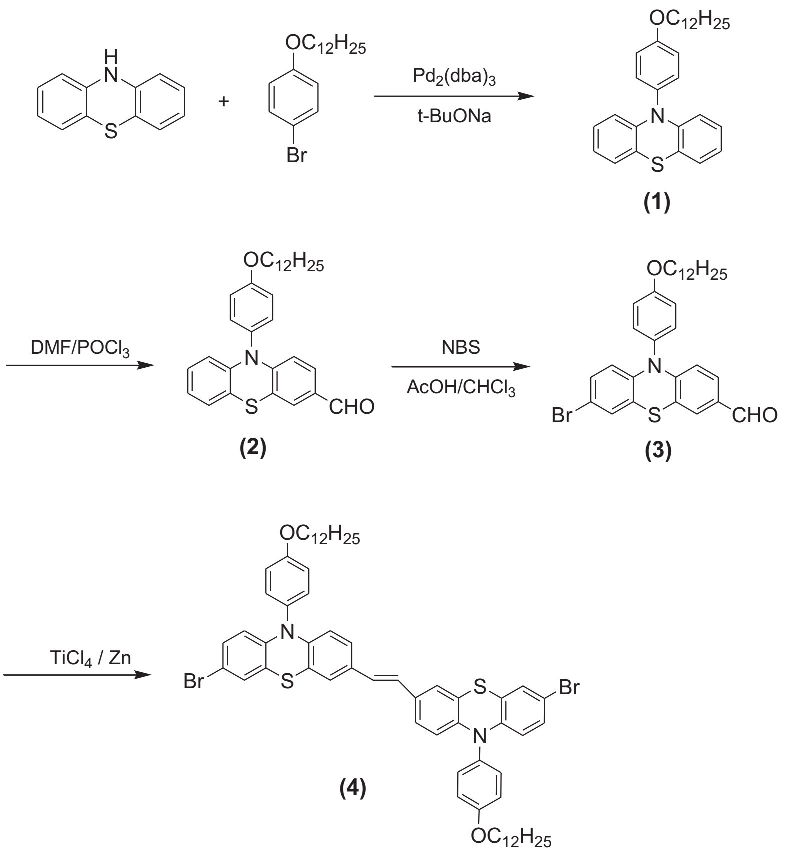
2.1. Materials

n-Butyllithium, *N*-bromosuccinimide (NBS), and *N*,*N*-dimethylformamide (DMF) were purchased from Aldrich. All reagents purchased commercially were used without further purification except for tetrahydrofuran (THF), which was dried

---

[*] Corresponding author. Tel.: +82 0 2 2164 4334; fax: +82 0 2 2164 4764.
E-mail address: inamkang@catholic.ac.kr (I.-N. Kang).

0379-6779/$ – see front matter. Crown Copyright © 2010 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2010.10.036



Scheme 1. Synthetic routes to the monomers.

over sodium/benzophenone. 1-Bromo-4-(dodecyloxy)benzene, 2-(trimethylstannyl)-5-(5-(trimethylstannyl)thiophen-2-yl) thiophene, and 3-hexyl-2-(3-hexyl-5-(trimethylstannyl)-thiophen-2-yl)-5-(trimethylstannyl)thiophene were prepared with previously described methods [20–22].

2.2. Instrumentation

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer, with tetramethyl silane as an internal reference. The optical absorption spectra were measured on a Shimadzu UV-3100 UV–VIS–NIR spectrometer. The number- and weight-averaged molecular weights of the polymers were determined with gel permeation chromatography (GPC) on a Viscotek T60A instrument by using tetrahydrofuran (THF) as the eluent and polystyrene as a standard. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were carried out with a TA Q100 instrument operated under a nitrogen atmosphere. Cyclic voltammetry (CV) was performed on an AUTOLAB/PG-STAT12 model system with a three-electrode cell in an acetonitrile solution of 0.1 M n-Bu_4NBF_4 at a scan rate of 50 mV s^{-1}. Polymer film coatings on Pt wire electrodes were formed by dipping electrodes into the appropriate polymer solutions. The electrical characteristics of the TFTs were measured under ambient conditions by using Keithley 2400 and 236 source/measure units. All measurements were obtained with a channel length (L) of 100 μm and a channel width (W) of 1000 μm. Field-effect mobility was extracted in the saturation regime from the slope of the source–drain current.

2.3. Fabrication of the organic thin film transistor devices

Thin-film transistors were fabricated on silicon wafers by using a top contact geometry (channel length L = 100 μm, width W = 1000 μm) under ambient conditions without taking special precautions to exclude air, moisture, or light. A heavily n-doped silicon wafer with a 300 nm thermal silicon dioxide (SiO_2) layer was used as the substrate/gate electrode, with the top SiO_2 layer serving as the gate dielectric. The SiO_2 surface of the wafer substrate was first cleaned with piranha solution (H_2O_2/H_2SO_4) at 130 °C for 20 min, and then was immersed in a solution of 1.0 mM octyltrichlorosilane (OTS-8) in toluene at room temperature for 2 h under nitrogen. The semiconductor layer was spin-coated at 2000 rpm from a 0.5 wt.% $CHCl_3$ solution, to a thickness of 60 nm. Subsequently, a series of gold source/drain electrode pairs were deposited by vacuum evaporation through a shadow mask. Silicon oxide on the back of the silicon wafer of the TFT device was removed with HF to provide a conductive gate contact.

2.4. Synthesis of the monomers and polymers

2.4.1. Synthesis of 10-(4-(dodecyloxy)phenyl)-10H-phenothiazine (1)

Phenothiazine (10.0 g, 50 mmol), 1-bromo-4-dodecyloxybenzene (20.5 g, 60 mmol), $Pd_2(dba)_3$[tris(dibenzylidineacetone) dipalladium(0)] (2.29 g, 2.4 mmol), sodium *tert*-butoxide (7.4 g, 72 mmol), and tricyclohexylphosphine (0.98 g, 3.6 mmol) were dissolved in 200 mL of toluene and kept under nitrogen at 130 °C for 5 h. When the reaction had finished, the reaction mixture was cooled to room temperature, quenched by the addition of 200 mL of water, and then extracted three times with dichloromethane and water. The organic layer was separated and dried with anhydrous magnesium sulfate, and then the solvent was removed by using a rotary evaporator. The crude product was purified with column chromatography by using a cosolvent (toluene:hexane = 1:2 [v/v]) as the eluent. The product yield was 86% (19.7 g). ^{1}H NMR (300 MHz,