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Poly(2,5-dihexyloxyphenylene vinylene-*alt*-2,2-dibutylpropylenedioxythiophene): Synthesis and characterization for photovoltaic applications

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ABSTRACT

A thiophene/phenylene vinylene-based polymer (P1) was synthesized and its properties compared with those of a previously described analogous polymer (P2-CN) which contains CN substituents in the vinyl moieties. In solution, the P1 polymer absorbed in a range from UV to near 600 nm and, compared to P2-CN, exhibited a band gap energy that was larger, from 1.7 to 2.0 eV, and the energy levels of LUMO and HOMO lower, by 0.2 and 0.5 V, respectively. However, the power conversion efficiencies (PCE, 0.30%) of photovoltaic devices fabricated using a blend of P1 and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) appeared to be slightly higher than the reported PCE (0.15%) for P2-CN devices fabricated in the same configuration.

1. Introduction

Of the various types of polymer-based, bulk, heterojunction, photovoltaic devices, the most efficient, with power conversion efficiencies (PCEs) up to ~5%, have been fabricated using a blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as an electron-donor and electron-acceptor, respectively [1–6]. However, the PCE values of these polymer-based solar cells need to be significantly enhanced over the current values to be useful in practical applications.

For the development of high efficiency polymer solar cells, it is necessary to shift the absorption spectra of the electron-donor polymers toward the red region of the visible spectrum, meaning that new polymers should have lower band gap energies than P3HT (~2.0 V) [7,8]. Recently, various types of low band gap polymers have been synthesized for application in photovoltaic devices [9] and the PCEs of devices fabricated using these low band gap polymers have not exceeded those of P3HT-based devices due to some important factors. For example, the charge mobility in the polymer film is an important parameter which affects photovoltaic device performance [10] and, of course, the energy levels of the electron-donors and electron-acceptor should be optimized for efficient charge separation of excitons.

Recently, Reynolds and coworkers synthesized a low band gap polymer (P2-CN, Fig. 1), which is based on a thiophene and phenylene vinylene derivative with CN substituents in the vinyl groups, and reported its optical and electrochemical properties and photovoltaic device characterization [11]. Even though the band gap energy of this polymer was relatively low (1.7 eV), the PCE of its photovoltaic devices was not satisfactory (0.1%) because of its low fill factor.

The very strong electron-withdrawing effect of the CN group significantly affects the charge separation and charge transfer processes as well as the band gap energy. Thus, in this research group, a similar conjugated polymer (P1), but lacking CN groups, was synthesized in order to observe changes in the properties related to photovoltaic device performance. This paper describes the synthesis and general characterization of this polymer with respect to optical, thermal, and electrochemical properties. A polymer blend of P1 with PCBM (1:4) was employed in the fabrication of photovoltaic devices and the preliminary result regarding the performance of these devices is described.

2. Experimental

2.1. Materials

2,2′-Thiodiacetic acid (98%), diethyl oxalate (≥99%), 2,2-dibutyl-1,3-propanediol (97%), diethyl-azodicarboxylate solution (40 wt% in toluene), lithium aluminum hydride (reagent grade, 95%,

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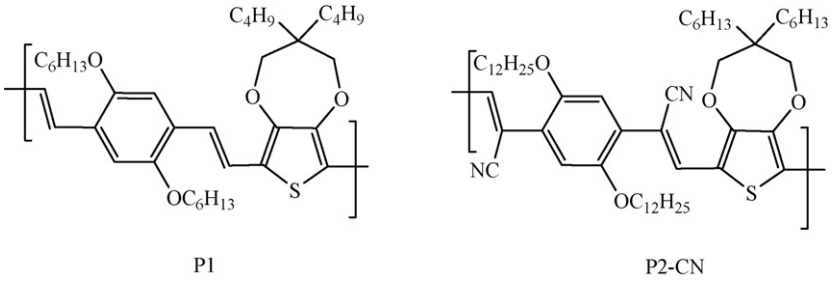


Fig. 1. Chemical structures of (a) P1 and (b) P2-CN.

powder), pyridinium dichromate (PDC) (98%), α,α′-dibromo-*p*-xylene (97%), triethyl phosphate (≥99.8%) were purchased from Aldrich. Potassium *tert*-butoxide (≥97.0%) and hydroquinone (≥98.0%) were purchased from Purum. Triphenylphosphine (PPh_3, ≥98.5%) was purchased from Fulka. All chemicals were used as received.

2.2. Synthesis

2.2.1. 3,3-Dibutyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-dicarbaldehyde (1)

3,3-Dibutyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepine-6,8-dicarbaldehyde (compound **1**) was synthesized from 2,2′-thiodiacetic acid using a reported four-step procedure [11]. ^{1}H NMR ($CDCl_3$): δ 10.0 (s, 2H), 4.0 (s, 4H), 1.2–1.33 (m, 12H), and 0.96 (t, 6H).

2.2.2. 1,4-Dibromomethyl-2,5-dihexyloxybenzene (2)

1,4-Dibromomethyl-2,5-dihexyloxybenzene (compound **2**) was synthesized from hydroquinone with a reported two-step procedure [11,12]. ^{1}H NMR ($CDCl_3$): δ 6.85 (s, 2H), 4.52 (s, 4H), 4.0 (t, 4H), 1.33–1.82 (m, 16H), and 0.9 (t, 6H).

2.2.3. 1,4-Bis(diethylphosphine)-2,5-bis(hexyloxy)benzene (3)

Compound **2** (4.0 g, 8.62 mmol) was reacted with excess triethylphosphite (10 g) at 150 °C for 5 h in a nitrogen atmosphere. A white solid product was obtained after removal of triethylphosphite by vacuum distillation and recrystallization from diethyl ether with 76% yield. ^{1}H NMR (DMSO-d_6): δ 7.4 (s, 2H), 4.47 (m, 12H), 3.6 (d, 4H), 2.25 (m, 4H), 1.6–1.9 (m, 24H), and 1.3 (t, 6H).

2.2.4. Poly(2,5-dihexyloxyphenylene vinylene-alt-2,2-dibutylpropylenedioxythiophene) (P1)

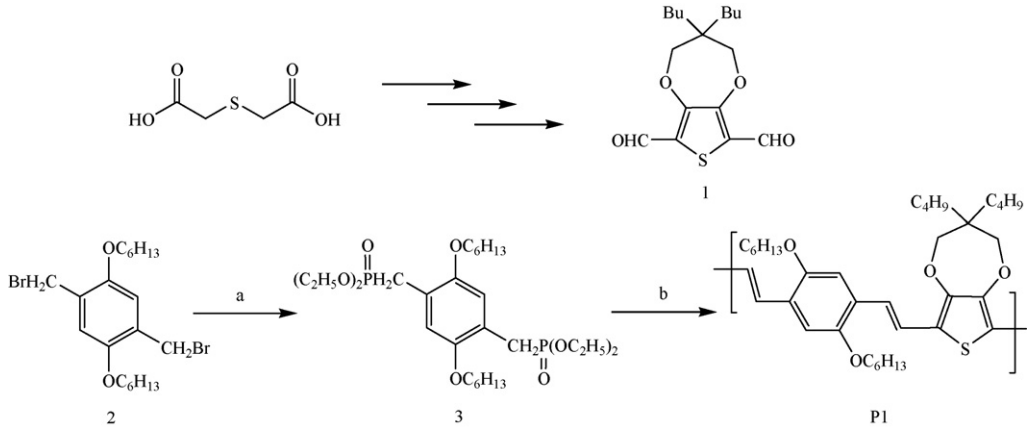
Compound **3** (0.25 g, 0.432 mmol) and potassium *tert*-butoxide (0.116 g, 10.37 mmol) were added to a solution of compound **1** (140 mg, 0.432 mmol) in 30 mL THF. The mixture was refluxed for 48 h and then precipitated by adding excess methanol, redissolved in chloroform, and precipitated three times with methanol to obtain P1 (0.22 g, 58% yield). ^{1}H NMR ($CDCl_3$): δ 7.15 (bm, 2H), 6.9 (bm, 2H), 3.9 (bm, 4H), 3.8 (bm, 4H), 1.2–1.5 (bm, 28H), and 0.87 (bm, 12H).

2.3. Measurement

The ^{1}H NMR spectra were recorded using a JEOL FT-NMR (400 MHz) spectrometer, the UV–vis spectra obtained using a Shimadzu UV-2550 spectrophotometer, and photoluminescence (PL) emission spectra of films or solutions in chloroform (1×10^{-5} M) obtained using a FP-6500 spectrofluorometer (JASCO). Thermogravimetric analysis (TGA) of the polymer was performed on a TA instrument Q-50, at a heating rate of 20 °C/min under nitrogen. Cyclic voltammetry (CV) analyses were performed on a VersaSTAT3 (METEK) in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.10 M) in dichloromethane under argon, at a scan rate of 50 mV/s at room temperature, and a Pt wire and Ag/Ag^+ used as a counter and reference electrode, respectively.

2.4. Fabrication of photovoltaic devices

Photovoltaic devices were fabricated with the configuration of ITO/PEDOT:PSS/polymer:PCBM/LiF/Al, possessing an active area of 12 mm^2. Patterned ITO glasses were cleaned with acetone and isopropanol using an ultrasonicator, and then treated with O_2-plasma. PEDOT:PSS was spin-coated to a thickness of about 40 nm onto the top of the ITO glass, and dried at 110 °C for 10 min. The active layer



Scheme 1. Synthetic route to P1: (a) triethylphosphite, 150 °C, 5 h and (b) compound 1, t-BuOK, reflux 48 h.