Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
polymer
Polymer 47 (2006) 699–708
www.elsevier.com/locate/polymer

Electronic structure and properties of alternating donor–acceptor conjugated copolymers: 3,4-Ethylenedioxythiophene (EDOT) copolymers and model compounds

Chia-Ling Pai [a], Cheng-Liang Liu [a], Wen-Chang Chen [a,b,*], Samson A. Jenekhe [c]

[a] *Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan, ROC*
[b] *Institute of Polymer Science and Engineering, National Taiwan University, Taipei 106, Taiwan, ROC*
[c] *Department of Chemical Engineering and Department of Chemistry, University of Washington, Seattle, WA 98195-1750, USA*

Received 28 September 2005; received in revised form 24 November 2005; accepted 28 November 2005
Available online 20 December 2005

Abstract

The electronic structure and properties of 3,4-ethylenedioxythiophene (EDOT) based alternating donor–acceptor conjugated copolymers and their model compounds were studied by the density functional theory (DFT) at the B3LYP level with 6-31G or 6-31G** basis set. The acceptors investigated include thiazole (Z), thiadiazole (D), thienopyrazine (TP), thienothiadiazole (TD), thiadiazolothienopyrazine (TPD), quinoxaline (BP), benzothiadiazole (BD), pyrazinoquinoxaline (BPP), benzobisthiadiazole (BDD), and thiadiazoloquinoxaline (BDP). The torsional angle, intramolecular charge transfer, bridge bond length, and bond length alternation were analyzed and correlated with the electronic properties. It was found that the geometries of the donor–acceptor materials were significantly affected by the ring size and intramolecular charge transfer. The HOMO level, LUMO level, and band gap of the model compounds were well correlated with the acceptor strength. However, the electronic properties of the copolymers did not vary systematically with the acceptor strength due to the change in geometry from model compound to polymer. The aromatic geometry of EDOT–TP model compound is transformed to quinoid in the corresponding copolymer and results in a small band gap (E_g) of 0.97 eV. Large intramolecular charge transfer and the small bond length alternation in the EDOT–BDP copolymer resulted in an E_g of 0.7 eV. Hence, these two polymers could have potential applications for transparent conductors or photovoltaic devices. The small effective masses and large HOMO and LUMO bandwidths of PEDOT–TP and PEDOT–BDP make them potential materials for ambipolar thin film transistors. The theoretical results suggest that both the acceptor strength and the stable geometry contribute significantly to the electronic properties of alternating donor–acceptor conjugated copolymers.

Keywords: 3,4-Ethylenedioxythiophene; Theoretical electronic properties; Donor–acceptor

1. Introduction

Conjugated polymer systems with donor–acceptor architecture [1–3], including alternating copolymers, blends, and multilayers, have been widely studied for applications as transparent conductors [1–3], light-emitting diodes [4,5], thin film transistors [6,7], and photovoltaic devices [8,9]. We are particularly interested in the alternating donor–acceptor copolymers since their electronic and optoelectronic properties can be tuned efficiently by intramolecular charge transfer (CT) [1–13]. The interaction between the electron donor (D) and acceptor (A) moieties in such an alternating donor–acceptor copolymer can result in the hybridization of the high-lying HOMO energy level of the donor and low-lying energy levels of the acceptor, leading to a relatively small band gap polymer semiconductor with novel electronic structure and ambipolar charge transport properties. The small band gap is of interest for near-infrared light-emitting diodes [4] whereas the ambipolar charge transport feature of such polymers is of interest in developing ambipolar organic thin film transistors [6,7].

Poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives are widely studied conjugated polymers due to their relatively low ionization potential, high conductivity when doped, and good stability [14,15]. PEDOT homopolymer is widely used as a conducting and hole-injecting electrode in organic light emitting diodes (OLEDs) [4,5]. Several EDOT-based donor–acceptor conjugated polymers with small band

---

* Corresponding author. Address: Department of Chemical Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Rd, Taipei 106, Taiwan, ROC. Tel.: +886 2 236 28398; fax: +886 2 236 23040.
E-mail address: chenwc@ntu.edu.tw (W.-C. Chen).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.11.083

gaps have been reported, including EDOT–pyridine [16,17], EDOT–(4-dicyanomethylene-4H-cyclopenta[2,1-b;3,4-b′]dithiophene) [18,19], EDOT–thienopyrazine [20,21], EDOT–benzothiadiazole [22], and EDOT–(*N*′2′-ethylene-4,5-dicarboxylic imide benzothiophene) [23]. The optical or electrochemical band gap of these alternating copolymers were either around 1.0 eV or less and thus transparent conductors or electrochromic applications have been suggested. The electronic properties of these donor–acceptor copolymers varied significantly with the acceptor moiety. A comprehensive understanding of the electronic structures and the electronic properties of these EDOT-based donor–acceptor alternating conjugated polymers would help to further develop this and other classes of donor–acceptor copolymers for electronic applications.

In this paper, we report a theoretical study of the electronic structure and properties of EDOT-based alternating donor–acceptor conjugated polymers (**4**) and their model compounds (**2**) whose molecular structures are shown in Fig. 1. Ten copolymers and 10 model compounds were investigated, corresponding to ten different electron acceptors. The 10 electron acceptors can be grouped into different backbone ring structure: (a) five-member ring: thiazole (Z), thiadiazole (D), thienopyrazine (TP), thienothiadiazole (TD), thiadiazolothienopyrazine (TPD); and (b) six-member ring: quinoxaline (BP), benzothiadiazole (BD), pyrazinoquinoxaline (BPP), thiadiazoloquinoxaline (BDP), and benzobisthiadiazole (BDD). The model compounds and their corresponding polymers are named as dEDOT (**1**), EDOT-acceptor (**2**), PEDOT (**3**), PEDOT-acceptor (**4**), respectively. For example, the model compound of 3,4-ethylenedioxythiophene-thienopyrazine and its corresponding polymer are named as EDOT–TP and PEDOT–TP, respectively. The series of ten acceptors provide a basis for a comprehensive understanding of the effects of the backbone ring, heteroatom, and fused rings on the geometric and electronic properties of the model compounds and copolymers. The electronic structure and properties were investigated by the density functional theory (DFT) at the B3LYP level and 6-31G or 6-31G** basis set. The bond length of the EDOT-acceptor bridge, bond length alternation, and intramolecular charge transfer of the materials were analyzed and correlated with their chemical structures. The effects of the acceptor strength on the electronic properties, including the HOMO level, LUMO level, band gap, bandwidth, and effective mass were also studied.

2. Theoretical analysis

2.1. Methodology

The ground-state geometries and electronic structures of the EDOT-based conjugated polymers and their model compounds were optimized by means of the hybrid density functional theory (DFT) method, using periodic boundary conditions, at the B3LYP level of theory with the 6-31G or 6-31G** basis set performed on Gaussion03 program package [24]. In the case of the model compounds, both basis sets (6-31G and 6-31G**) were used in the analysis. The comparison of the theoretical results from the 6-31G and 6-31G** basis sets suggests that both methods give rise to similar theoretical results for

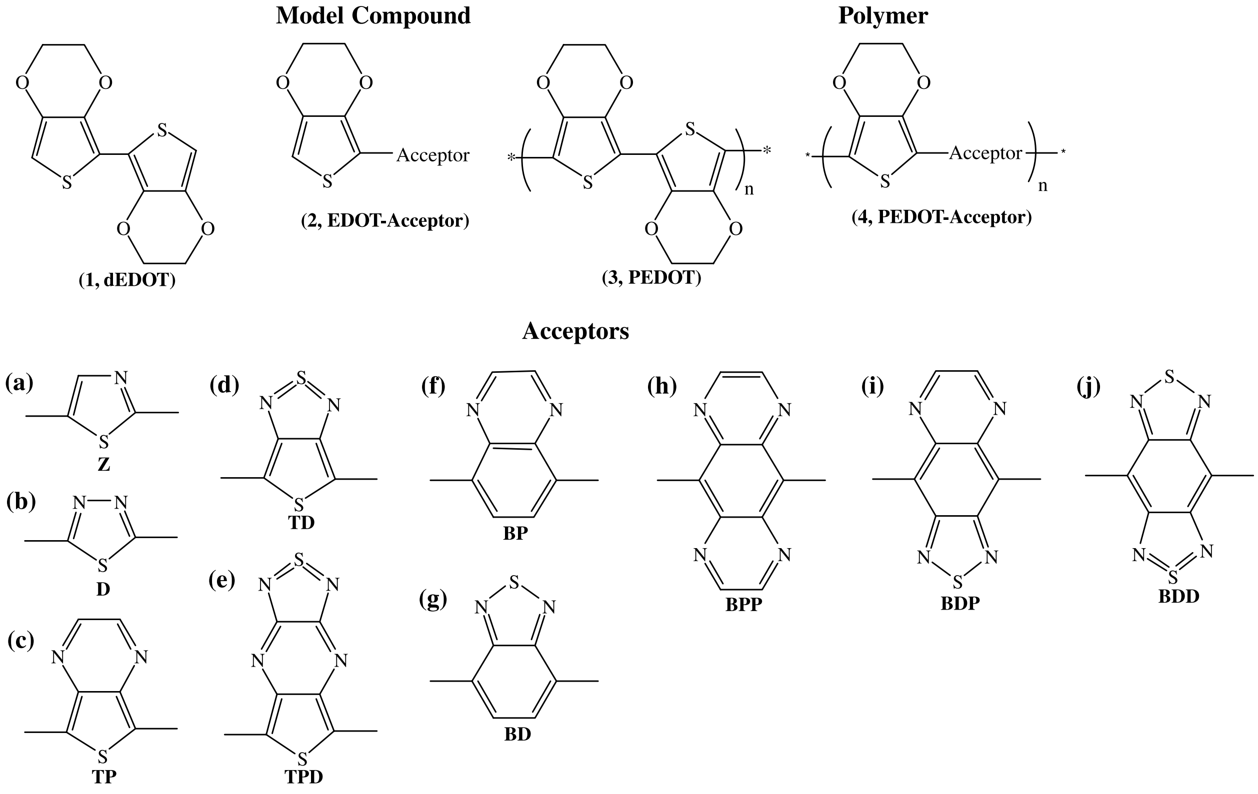

Fig. 1. Molecular structures of EDOT-based alternating donor–acceptor conjugated copolymers and their model compounds.