



Influence of covalent structure and molecular weight distribution on the optical properties of alternating copolymers and oligomers with 1,2,3-triazole and 1,3,4-oxadiazole side groups



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ARTICLE INFO

Article history:

Received 11 May 2017

Received in revised form

14 July 2017

Accepted 17 July 2017

Available online 18 July 2017

Keywords:

Conjugated polymers

Size exclusion chromatography (SEC)

Luminescence

UV–vis spectroscopy

ABSTRACT

Series of alternating conjugated copolymers of thiophene-based monomers substituted with bulky and electron withdrawing 1,2,3-triazole and 1,3,4-oxadiazole pendant groups was synthesized and characterized. Either a Suzuki coupling approach with 1,4-phenylene, 2,5-bis(octyloxy)-1,4-phenylene and 9,9-Dioctylfluorene-2,7-diyl boronates or the Stille reaction with 2,5-thiophenediyl stannane was used for polymer synthesis. The choice of the arylene or thiophene comonomers gives the opportunity to tune solubility, molecular weight and final optical/electrochemical properties of prepared polymers. We achieved improvements of the energetic levels (HOMO, LUMO and band gap). Moreover experiments comparing not only effects of polymer covalent structure but also evaluating the effect of molecular weight distribution on the optical properties using the SEC apparatus equipped by Diode Array Detector (SEC-DAD) and Fluorescence (FLD) detectors were performed.

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1. Introduction

Conjugated polymers have been subject of investigation for several decades because of many potential applications like light emitting diodes [1], organic solar cells [2], non-linear optics [3], sensors [4], thin-film transistors [5], materials for gas separation and storage [6], etc.

One of the most important pathways of polymer properties tailoring is the variation (tuning) of the polymer's covalent structure. Luminescence properties or energetic levels of HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) represent important aspects of conjugated polymer design. Luminescence and band-gap position in conjugated polymers can be modified, for example, by: i) selection of the covalent structure of the conjugated polymer main chain (i.e. composition, conformation, length) or ii) by a choice of side groups attached to the polymer main-chain.

Polythiophenes PTs are very promising candidates for mentioned applications [7]. Alternating copolymers of thiophene in combination with fluorene [8] or phenylene [9] units represent one of the most suitable choices, allowing simple tailoring of the desired polymer system, because they represent a combination of units with different band-gap values. Lack of long-time stability of mentioned materials delimits their use in desired applications [10]. Although, mentioned aspect is more pronounced in solution, it plays also remarkable role in thin solid films. Limited oxidative stability of various poly(monosubstituted acetylene)s [11] and poly(phenylenevinylene)s [12] was previously studied by our group. On the other hand poly(disubstituted acetylene)s [13] and other conjugated polymers are usually stable or almost stable in solution, as well as in thin solid films [14]; however, they still exhibit slow degradation upon strong illumination, thermal or electrical loads, i.e. under conditions of active devices. Consequently, long term stability of conjugated polymers is one of the most important aspects that have to be taken into account during systems tailoring.

In general, all the properties could be tuned either by the covalent structure of the polymer's main chain or by the introduction of suitable low molecular weight components (either organic or inorganic) into the polymer matrix. However, simple mixing of

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polymer with low molecular weight admixtures is not advantageous because of probable phase separation of the components [15].

Despite mentioned phase separation, oxadiazole-based compounds are recently widely reported [16,17] in Polymer Light Emitting Diodes (PLEDs) as low molecular weight admixtures. However, introduction of appropriately modified or designed chemical moieties as: (i) part of the main chain or (ii) as side groups covalently bound to the polymer backbone, represent primary option in system architecture design. Oxadiazole groups used as a part of the polymer main chain [18–21] or a pendant group covalently attached to the polyarylene/polyheteroarylene backbone [22–25] served as electron withdrawing groups (EWG) influencing HOMO/LUMO levels in the prepared conjugated polymers. Various triazole derivatives (also EWG) are also known from the literature [26–29]. 1,2,3-triazole has been already reported as a main-chain unit [30]. 1,2,3-triazoles used as side groups in polythiophene polymers including basic luminescence and electrochemical properties have been also recently reported by various researchers [31,32]. To the best of our knowledge copolymers utilizing both triazole and oxadiazole groups as side groups are still rare in the literature and their comparative study is not known at all. In the present work, we report the synthesis and characterization of copolymers derived from thiophene monomers carrying oxadiazole or triazole groups polymerized with phenylene, fluorene and thiophene comonomers. We paid particular attention to the influence of M_w distribution on electronic spectra (absorption and emission).

2. Results and discussion

2.1. Synthesis of monomers

The synthesis of monomers and their codes are shown in Chart 1. Synthetic procedures and analytical data are available in supplementary information file. Triazole-containing compound **TA1** was prepared by the standard Huisgen Cu(I)-catalyzed 3 + 2 dipolar cycloaddition (“click” reaction) in high yield (94%). NMR analysis did not show any by-product formation. Bromination of **TA1** with *N*-bromosuccinimide gave **TA3** in a good overall yield of 68%. Compounds **Ox1** and **Ox3** were synthesized by the reaction of

carboxylic acid chlorides with substituted tetrazoles. These reactions also gave high yields and purity of oxadiazole derivatives (66%–78%). All compounds were characterized by NMR and IR spectroscopy (see supporting information file).

2.2. Oxidative polymerizations

Compounds **TA1** and **Ox1** were treated with FeCl_3 and $(\text{NH}_4)_2\text{S}_2\text{O}_7$ in anhydrous chloroform according to standard procedures for oxidative polymerization [33]. SEC analysis showed only low M_w material and, in both cases, the FTIR and ^1H NMR analyses confirmed that isolated compounds were identical to the starting compounds. Electron withdrawing groups such as nitrile disable oxidative polymerization because of the increased oxidative potential of such substituted thiophene-based monomers compared to the unsubstituted thiophene or thiophene with an electron donating group like octyl, as is known from the literature [34]. A steric effect of triazole and oxadiazole groups probably was not to be the main obstacle to polymerization because bulky phenyl-substituted polythiophenes are known [35]. Oxadiazole and triazole side-groups are not only bulky, but they are also electron withdrawing group – EWG. Therefore, a difference in electron densities caused by the EWGs could very probably explain the disinclination of compounds **TA1** and **Ox1** to oxidative polymerization. A similar effect was also reported in the literature [31,32]. Mentioned papers describe the synthesis of triazole-substituted polythiophene in a similar system.

2.3. Catalytic polymerizations

Structures of polymers and reaction pathways are depicted in Chart 2. Suzuki-Miyaura and Stille cross-coupling reactions were successfully utilized and alternating copolymers were obtained in yields from 52% to 93%. Four different comonomers (see Chart 1) were reacted with **TA3** and **Ox3** and eight different alternating copolymers were prepared. Results are summarized in Table 1 (polymer yield, M_w). Nature of catalytic copolymerization used in the synthesis did not allow the detailed control of the regio-regularity of prepared alternating copolymers. The steric hindrance was only the effect which could influence the position of bulky oxadiazole/triazole pendant group in 3-thienyl repeating

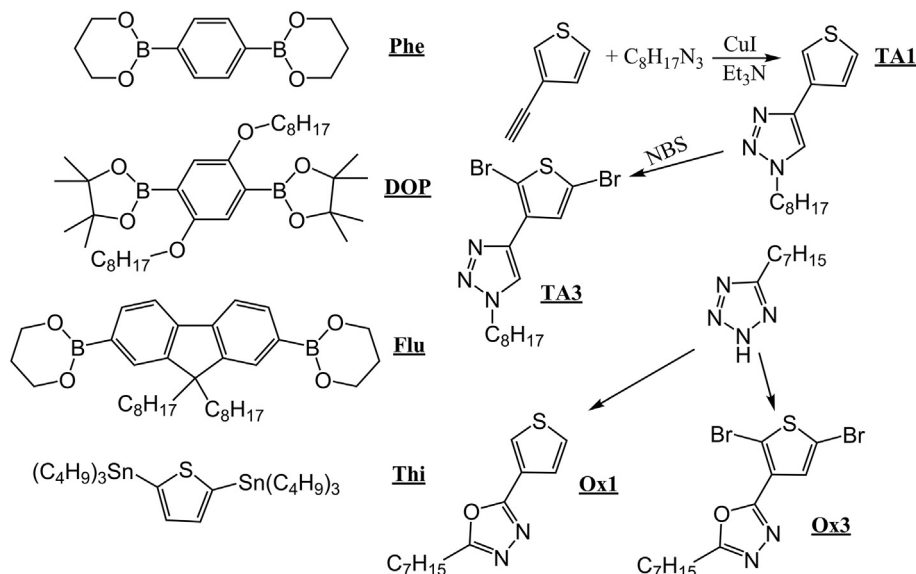


Chart 1. Monomer's codes and synthesis.

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