European Polymer Journal 50 (2014) 223–234

Contents lists available at ScienceDirect

European Polymer Journal

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

Poly[2,7-(9,9-dioctylfluorene)-*alt*-(5,5′-bithiophene/permethylated β-cyclodextrin) main-chain polyrotaxane: Synthesis, characterization and surface morphology

Andreea Stefanache, Mihaela Silion, Iuliana Stoica, Adrian Fifere, Valeria Harabagiu, Aurica Farcas *

"Petru Poni" Institute of Macromolecular Chemistry, 700487 Iasi, Romania

ARTICLE INFO

Article history:
Received 22 May 2013
Received in revised form 25 October 2013
Accepted 5 November 2013
Available online 13 November 2013

Keywords:
Conjugated polymers
Complexation
Polyrotaxanes
Permethylated cyclodextrin
Mass spectra
Surface morphology

ABSTRACT

Poly[2,7-(9,9-dioctylfluorene)-alt-(5,5′-bithiophene/permethylated β-cyclodextrin) (**3·PMeβCD**) main-chain polyrotaxane was synthesized according to a Suzuki-type aryl-aryl coupling protocol, by reacting 9,9-dioctylfluorene-2,7-trimethylene diborate (**1**) with an inclusion complex of 5,5′-dibromo-2,2′-bithiophene (**2**)/permethylated-βCD (PMeβCD) (**2·PMeβCD**). The complexation ability of PMeβCD molecule towards monomer **2** was confirmed by MM+ and PM3 quantum-mechanics semi-empirical methods, ESI-MS, (ESI) MS/MS analysis, as well as FTIR and ^{1}H-NMR spectroscopy. A conjugated polyrotaxane copolymer with PMeβCD/structural unit ratio of about 1/3 and the number average molecular weight (*Mn*) value of 30600 was obtained by ^{1}H-NMR spectroscopy and gel permeation chromatography, respectively. The thermal, optical, surface morphology and the adhesion characteristics were investigated and compared to those of the non-rotaxane counterpart poly[2,7-(9,9-dioctylfluorene)-*alt*-(5,5′-bithiophene) (**3**).

1. Introduction

Conjugated polymers have received much consideration in the last two decades, due to their electro-optical properties, which made them suitable for use as active materials in optoelectronic devices [1–3]. Among the various π-conjugated polymers, polyfluorene and their derivatives (PFs) have been widely studied as promising candidates for the next generation of polymer light-emitting diodes (PLEDs) [4]. Major drawbacks for their application in PLEDs include the rather large band gap, photochemical degradation, morphology evolution process, low electron affinity and high ionization potential [5]. As a result, several approaches have been undertaken for the preparation of PFs with enhanced photoluminescence (PL) and electroluminescence (EL) properties [6–8]. The most successful approach is the copolymerization of fluorene monomers with other aromatic rings as alternating or statically repeating units. The resulting copolymers exhibited improved optoelectronic properties, which underlines their potential use as active materials for emissive layers [9–13]. Among them, the alternating copolymers containing fluorene and bithiophene units have proved to be one of the most promising π-conjugated polymers, due to their solution processability, excellent oxidation stability, high charge-transport properties and the ability to self-assemble into ordered nanoscale architectures at the surfaces [14–16].

Another attractive approach to obtain conjugated polymers with higher coplanarity of the polymer backbone, better solubility, film forming ability, and lower aggregation tendency is the construction of mechanically interlocked molecules, such as rotaxanes and polyrotaxanes [17–32]. A rotaxane is an assembly in which, the macrocyclic molecule (host) encircles an axle (guest), through

---

* Corresponding author. Tel.: +40 232 217454; fax: +40 232 21 1299.
E-mail address: auricafarcas@yahoo.com (A. Farcas).

0014-3057/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.eurpolymj.2013.11.001

non-covalent interactions [33]. Among the several known host molecules, cyclodextrins (CDs) are by far, the most intensively investigated macrocyclic molecules, in the synthesis of polyrotaxanes with π-conjugated polymers [17–27,29,32]. Such threading of CDs onto the conjugated chains does not disrupt the π-conjugation and additionally improves the solubility, as well as the photophysical characteristics of the conjugated macromolecular chains. As a result of the encapsulation into CDs cavities, many conjugated polyrotaxanes have been incorporated into light-emitting diodes [18,20,22]. Similar interest has also been emerged in the design of different supramolecular architectures by incorporating functionalized CDs [28,30,31]. In this context, permethylated CDs, which posses higher water solubility compared to native CDs [34], represents an alternative approach, for the encapsulation of π-conjugated molecules. In addition, better solubility in common organic solvents, easier processability and transparency of polyrotaxanes solid films represent noticeable advantages [28,30,31]. As a consequence, formation of polyrotaxanes with chemically-modified CDs versus native CDs, provides an opportunity for modification of physical and optical properties of conjugated copolymers, mostly in terms of water solubility, fluorescence efficiency enhancement and processability [28,30,31].

Therefore, for the construction of novel mechanically interlocked molecules with conjugated polymers, we decided to use PMeβCD as a host molecule, with improved aqueous solubility compared to native βCD and a highly hydrophobic cavity. Thus, poly[2,7-(9,9-dioctylfluorene)-*alt*-(5,5′-bithiophene/PMeβCD) (**3•PMeβCD**) main-chain polyrotaxane was synthesized by Suzuki cross-coupling reaction of 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (**1**) as a bulky molecule and 5,5′-dibromo-2,2′-bithiophene (**2**) as an inclusion complex with PMeβCD (**2•PMeβCD**) (Scheme 1). The complexation ability of PMeβCD molecule towards monomer **2** was confirmed by MM+ and PM3 quantum-mechanics semi-empirical methods, ESI-MS, (ESI) MS/MS analysis, as well as FTIR and ^{1}H-NMR spectroscopy. The chemical structures of copolymers were proved by FT-IR and NMR spectroscopy. The surface morphology, thermal, optical, as well as adhesion characteristics of the obtained rotaxane copolymer were compared to those of the non-rotaxane counterpart.

2. Experimental section

2.1. Materials

9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (97%) (**1**), 5,5′-dibromo-2,2′-bithiophene (99%) (**2**), tetrakis(triphenylphosphine) palladium (99%), bromobenzene (99%) (Br–Ph), sodium hydride (95%) (NaH) were purchased from Sigma-Aldrich and used as received. Iodomethane (99.5%) was purchased from Alfa Aesar GmbH. The solvents, chloroform ($CHCl_3$), toluene, methanol (CH_3OH), tetrahydrofuran (THF), dimethylformamide (DMF) and all other solvents were analytical grade and used as received.

2.2. Synthesis

2.2.1. Synthesis of PMeβCD

PMeβCD was synthesized from purified βCD, by similar experimental conditions described for αCD [35], except the purification steps (see experimental details, NMR and ESI-MS characterizations (Figs. S1–S3 in the Supplementary Material).

2.2.2. Synthesis of the inclusion complex **2•PMeβCD**

To prepare the inclusion complex **2•PMeβCD**, 0.297 g (0.21 mmol) of PMeβCD were dissolved in water (2.0 ml) and then, 0.0324 g (0.1 mmol) of monomer **2** were added and the mixture was sonicated for 20 min, at room temperature. To ensure the complete formation of the inclusion complex **2•PMeβCD**, the turbid solution was further stirred under argon atmosphere overnight. The solid product was collected by filtration, washed thoroughly with acetone (2 ml) and water (2 ml), dried under vacuum at 60 °C for 24 h to yield 0.176 g of **2•PMeβCD** as light-yellow powder (53.2% yield).

^{1}H-NMR (400 Mz, $CDCl_3$): δ 6.96–6.95 (d, J = 3.6 Hz, 2H, Ha′), 6.85–6.84 (d, J = 3.6 Hz, 2H, Hb′), 5.13–5.12 (d, J = 3.6 Hz, 7H, C(1)H), 3.87–3.75 (m, 14H, C(5)H, C(6)H), 3.65 (s, 21H, O(3′)CH_3), 3.57–3.64 (m, 14H, C(4)H, C(6)H), 3.45–3.36 (m, 28H, C(3)H, O(2′)CH_3), 3.39 (s, 21H, O(6′)CH_3), 3.19–3.17 (dd, J = 9.8 Hz, 7H, C(2)H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 137.75, 130.03, 124.11, 111.46 (aromatic carbons from bithiophene units), 98.94 (C1), 82.04 (C2), 81.69 (C3), 80.29 (C4), 71.40 (C6), 70.91 (C5), 61.42 (O(3′)–CH_3), 58.93 (O(6′)–CH_3), 58.49 (O(2′)–CH_3).

MS, m/z: 1451.36 [PMeβCD+Na]$^+$; 1754.62 [**2•PMeβCD**+H]$^+$; 1776.66 [**2•PMeβCD + Na**]$^+$.

2.2.3. Synthesis of **3•PMeβCD** polyrotaxane copolymer

A suspension of PMeβCD (0.247 g, 0.17 mmol) and monomer **2** (0.0324 g, 0.1 mmol) in water (2 ml) was sonicated for 20 min and vigorously stirred overnight. The flask was equipped with a condenser, evacuated and filled with argon several times to remove air traces. Then, monomer **1** (0.056 g, 0.1 mmol), 10 ml of toluene, 1 ml of 3 M sodium carbonate (Na_2CO_3) solution and 11.6 mg (1.0×10^{-2} mmol) of $Pd(PPh_3)_4$ as catalyst dissolved in 2 ml of degassed toluene were added. The mixture was protected in dark and argon atmosphere and stirred at 90–95 °C for 72 h. The polycondensation reaction was carried out with continuous removal of water from medium by azeotropic distillation with toluene. In order to obtain the macromolecular chains terminated with borate units [21], an excess of 0.0078 g (0.014 mmol) of monomer **1** dissolved in 3 ml of toluene was added and the reaction was continued for 12 h. Finally, 1 μl of Br–Ph was added, as end capper reagent and the reaction was continued for 10 h. The mixture was poured into water and extracted with toluene. The organic extracts were washed with water and dried over $MgSO_4$. The toluene solution was concentrated by rotary evaporation and precipitated in 50 ml of CH_3OH/deionized water 9/1 v/v mixture. The yellow polymer sample was filtered, washed with acetone, dried and purified by Soxhlet extraction with acetone for