ARTICLE IN PRESS

European Polymer Journal xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

European Polymer Journal

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

Novel conjugated polyelectrolytes based on polythiophene bearing phosphonium side groups

Sviatoslav Hladysh [a,*], Dmitrij Bondarev [b], Jan Svoboda [a], Jiří Vohlídal [a], David Vrbata [a], Jiří Zedník [a]

[a] Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, CZ-12840 Prague 2, Czech Republic
[b] Department of Polymer Engineering, Tomas Bata University in Zlín, Faculty of Technology, Vavrečkova 275, CZ-762 72 Zlín, Czech Republic

ARTICLE INFO

Article history:
Received 20 April 2016
Received in revised form 20 July 2016
Accepted 25 July 2016
Available online xxxx

Keywords:
Conjugated polymers
Polyelectrolytes
Polythiophene
Luminescence

ABSTRACT

The synthesis and photophysical properties of poly{3-[6-(triethylphosphonium)hexyl]-thiophene-2,5-diyl bromide} and poly{3-[6-(triphenylphosphonium)hexyl]-thiophene-2,5-diyl bromide} are reported in the present contribution. Three various polymer precursors (poly[3-(6-bromohexyl)thiophene-2,5-diyl]s) with molecular weights 7.2, 11.8 and 13.2 kg mol^{-1} respectively and head to tail regioregularity from 62% to 94% were prepared and consecutively transformed into the corresponding polyelectrolytes by a simple quaternization reaction with appropriate phosphines. Synthesized polyelectrolytes exhibited solvatochromism. Detailed aggregation experiments via changing water/DMSO ratio have been performed. Photoluminiscence spectra of the polyelectrolyte solutions indicate that the emission maxima are red-shifted gradually with the increasing solvent polarity. Fluorescence quenching has been studied by interaction with model quenchers: $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ in water using Stern-Volmer methodology.

1. Introduction

Conjugated polymers (CPs) have attracted attention of many researchers because of the wide variety of applications, for example: light-emitting diodes [1,2], electrochemical cells [3], plastic lasers [4], solar cells [5], field-effect transistors [6,7], and sensors [8–10] in the last few decades. There are various polymer types belonging to the conjugated polymers family. Polythiophenes (PTs) represent one of the most important groups of conjugated polymers. PTs possess high charge carrier mobility, high absorption in the visible spectral range and also the possibility to tune their properties by the choice of substituents or the main-chain composition. In particular, poly(3-hexylthiophene-2,5-diyl) exhibited good properties in photovoltaic cells [11,12].

There are many pathways of PTs preparation described in the literature. The simplest known procedure is represented by the oxidative polymerization of thiophene [13]. Despite the easy way of polymerization, this method does not usually lead to high-molecular weight polymers and head-to-tail (H-T) regioregularity of the main chain is also low (50%) [14]. There are several routes known how to get PTs with higher molecular weight (MW) and better (H-T) regioregularity [15]. The mentioned parameters (high H-T regioregularity and MW) result in better conductivity and charge carrier mobility due to the enhanced π-stacking and consequent better organization of polymer chains in the solid state [16]. One of the most important

---

* Corresponding author.
E-mail address: sviatoslavhladysh@gmail.com (S. Hladysh).

http://dx.doi.org/10.1016/j.eurpolymj.2016.07.019
0014-3057/© 2016 Elsevier Ltd. All rights reserved.

Please cite this article in press as: S. Hladysh et al., Novel conjugated polyelectrolytes based on polythiophene bearing phosphonium side groups, Eur. Polym. J. (2016), http://dx.doi.org/10.1016/j.eurpolymj.2016.07.019

routes for PTs preparation is represented by Grignard metathesis polymerization denoted as GRIM in further text [17]. GRIM polymerization is described as a general method. Hence, the conditions of the reaction can be modified in order to obtain PTs with tailored properties.

An important subclass of conjugated polymers is represented by conjugated polyelectrolytes (CPEs). Water/alcohol soluble CPEs [18] found, except of the above mentioned applications, usage as chemosensors and biosensors [8,19–24].

Water solubility of CPEs derived from PTs can be achieved by various approaches. An example of the most feasible one is the incorporation of ionic moiety as the polymer side/pendant groups to the hydrophobic polythiophene backbone (such as sulfonate (SO_3^-) [25], carboxylate (COO^-) [26] or ammonium (NR_4^+) groups [27–30]. The first example of water soluble conductive (CPEs) derived from PTs was published in 1987 by Wudl, Heeger and co-workers [31]. Water soluble PTs based polyelectrolytes are subject of investigation also in our research group [32].

The present contribution is aimed at preparation of novel polythiophene-based cationic CPEs, namely poly {3-[6-(triethyl phosphonium)hexyl]-thiophene-2,5-diyl bromide}, poly {3-[6-(triphenylphosphonium)hexyl]-thiophene-2,5-diyl bromide}. Variation of (i) molecular weight (MW) and (ii) H-T regioregularity and consequent effects on the optical properties are the main goals of the present study. The advanced study of polymer aggregation in various solvents and fluorescence quenching (by ionic quenchers) are presented also.

2. Experimental

2.1. Materials

Methanol, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), hexane, toluene and starting materials 3-bromothiophene, 1,6-dibromohexane, *n*-butyllithium (BuLi), methylmagnesium bromide, *N*-bromosuccinimide (NBS), triphenylphosphine, triethylphosphine, [1,3-Bis(diphenylphosphino)-propane]dichloronickel(II) ($Ni(dppp)Cl_2$) were purchased from Sigma-Aldrich. THF was distilled from $LiAlH_4$ under argon before use and transferred by a whole glass syringe and stainless-steel capillary. Hexane was dried over molecular sieves 4A. Other chemicals were used as received without further purification.

2.2. Measurements

^1H and ^{13}C NMR spectra were recorded on a Varian ^{UNITY}*INOVA* 400 or Varian NMR SYSTEM 300 instruments and referenced to the solvent signal: 7.25 ppm (for $CDCl_3$), 3.31 ppm (CD_3OD), 2.50 ppm (d_6-DMSO) for ^1H spectra and 77.23 ppm ($CDCl_3$), 49.15 ppm (CD_3OD) or 39.51 ppm (d_6-DMSO) for ^{13}C spectra. Coupling constants, J (in Hz), were obtained by the first-order analysis. UV/vis spectra were recorded on Shimadzu UV-2401PC or Specord DAD UV/vis apparatus using methanol, DMSO or water solutions of prepared compounds. Solid state samples were prepared using coating via slow solvent evaporation technique on the surface of the quartz plate (obtained by disassembling of four windows luminescence cuvette). $CHCl_3$ and methanol (for polyelectrolytes) were used for thin films preparation. Photoluminescence spectra were measured on a Fluorolog 3-22 Jobin Yvon Spex instrument (Jobin Yvon Instruments S.A., Inc., USA) in solutions using four-window quartz cuvette (1 cm). Samples prepared in thin film were measured using the methodology mentioned above for UV/vis spectra. The emission spectra were excited using the wavelength, λ_{ex}, equal to the position of the absorption maxima of particular compound. Quantum luminescence yields, ϕ_F, of photoluminescence were measured using integration sphere Quanta-ϕ F-3029 Horriba Jobin Yvon. SEC analyses were performed on a Spectra Physics Analytical HPLC instrument fitted with two SEC columns Polymer Labs (Bristol, UK) Mixed-D, Mixed-E and THERMO UV6000 DAD detector, using THF as mobile phase; apparent molar mass averages related to the polystyrene standards are reported.

2.2.1. Stern-Volmer study

We utilized our CPEs as fluorophores with potassium ferrocyanide or potassium ferricyanide respectively as luminescence quenchers. A set of various quencher (Q) concentrations was prepared (for detailed information concerning quencher concentrations see ESI info – Table S1). Concentration of polymeric fluorophore was maintained constant (10^{-3} M with respect to polymer repeating units (RU)). Emission spectra were recorded at excitation wavelength corresponding to absorption maxima and at constant slit width.

In order to obtain the quantitative value of the fluorescence quenching, we used the Stern-Volmer equation (1):

$$PL^0/PL = 1 + K_{SV}[Q] \tag{1}$$

To measure K_{SV} – the Stern-Volmer constant, where PL^0 and PL are the integrated fluorescence intensity without and with quencher, respectively, [Q] – is the concentration of the quencher. After plotting (PL^0/PL) against [Q], determined slope gives us the meaning of K_{SV}.

2.2.2. Aggregation study

To study aggregation, we considered a set of poly{3-[6-(triethylphosphonium)hexyl]-thiophene-2,5-diyl bromide}s (**PH-EtP⁺** - polyelectrolyte with the highest H-T regioregularity and MW) solutions with different percentage of DMSO and water. Firstly, the solution of **PH-EtP⁺** (concentration was set to 0.1 M with respect to polymer repeating units) in water

Please cite this article in press as: S. Hladysh et al., Novel conjugated polyelectrolytes based on polythiophene bearing phosphonium side groups, Eur. Polym. J. (2016), http://dx.doi.org/10.1016/j.eurpolymj.2016.07.019