



Polythiophene-based conjugated polyelectrolyte: Optical properties and association behavior in solution



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ABSTRACT

Conjugated polyelectrolyte with polythiophene main chain and imidazolium side groups, poly{3-[6-(1-methylimidazolium-3-yl) hexyl]thiophene-2,5-diyl bromide}, is investigated. Polymer architecture with hydrophobic main chain and hydrophilic side groups is responsible for the inconvenient behavior of the polymer in solution. Absorption and emission characteristics and supramolecular assembling are investigated by spectroscopic, microscopic and light-scattering methods. We report significant solvatochromism which is observable by a naked eye. Water solutions and mixed solvent systems exhibit most interesting features: supramolecular assembling was investigated by DLS, AFM and TEM techniques and common spectroscopic methods such as UV–vis and fluorescence spectroscopy. Moreover, slow relaxation processes take part in water as it is evidenced by time evolution of absorption spectra. It is a result of vanishing of inter- and intramolecular interactions. These interactions are responsible for extraordinary solution behavior of the ionic polythiophene.

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1. Introduction

Conjugated polyelectrolytes (CPEs) are polymers comprising conjugated main chains and ionic and/or ionizable groups. These materials have attracted a lot of interest in the last decades because of wide range of potential applications such as fluorescence sensors for biomolecules [1], active layers in light emitting diodes [2], active components in electrochromic devices [3], or active components in photovoltaic cells [4,5]. In spite of such interest, the studies of solution properties are surprisingly rare although it is known that aggregates present in the solution can be transferred into the solid state. In other words, the memory of polymer main-chain conformation can determine the photo-physical properties of the polymer in solid state [6]. Conformations and intermolecular interactions are fixed by strong electrostatic forces when transferred from solution to solid state. It can be even more pronounced, e.g., in the fabrication of layer-by-layer assemblies of the polyelectrolytes of the opposite charge [7], or in the composites

with charged surfaces such as nanoparticles [8–11]. Ionic polythiophenes are a peculiar group among other CPEs because optical properties of polythiophenes are strongly influenced by two parameters. First parameter: it is the covalent structure of the polymer, i.e., head-to-tail regioregularity and the molecular weight (MW). It was shown for the poly(3-alkylthiophenes) that the HT-regioregularity is a key parameter determining spectral properties [12]. More recently it was reported that small (4–6%) difference in the regioregularity can cause significant (10 nm and more) change in the absorption spectra [13]. The importance of sufficiently high MW is obvious. Saturated conjugation length cannot be reached in low-MW sample even if the strictly HT-architecture is achieved. Moreover, the MW governs the mechanical properties which are important in thin film applications [14]. Second type of parameters influencing optical properties are adjustable parameters such as temperature, solvent or concentration. These adjustable parameters affect current conformations and consequently the delocalization of π -electrons which is manifested in absorption or emission characteristics. The higher the delocalization the higher the values of absorption and emission maxima and edges. Delocalization is influenced by torsion angles between adjacent main-chain units (the more

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coplanar architecture the more delocalized π -electrons) [15]. It is clear that HT-regioregular samples show lower barrier to the planarization than head-to-head connections with more serious steric hindrances. The changes in torsion angles are caused by the action of side groups, e.g., additional electrostatic repulsion in the case of ionic polythiophenes [16–18]. Intermolecular interactions can take part as well. In early 90s, the X-ray experiments revealed that polythiophenes with regioregular main-chain architecture undergo side-chain-induced self-assembly resulting in intermolecular π -stacking and lamellar structures in the solid state which are allowed by planarization of main-chain units [19,20]. Such organization promotes bathochromic shift followed by developing of fine vibronic structures. These red-shifted peaks located at ~ 520 nm ~ 560 nm and ~ 610 nm were detected also in the solution/colloidal systems and they were attributed to the formation of π -stacked intermolecular aggregates [21]. Authors proposed the presence of columnar aggregates with hydrodynamic radius ca. 50 nm according to the light scattering measurements. Moreover, it was shown that the π - π^* transitions at 520 nm and 560 nm reflect the most planarized conformations of single polymer chains present in the systems with molecularly dissolved polymer because the absorption edge in such systems is located at appr. 560 nm and absorption below this wavelength must be a result of intramolecular processes [22]. On the other hand, the absorption at 610 nm must originate from the intermolecular π -stacked assemblies with extended delocalization of π -electrons [22–24]. Polythiophenes exhibit one of the highest differences between the solution and solid state absorption maxima, up to 100 nm. For example in polyfluorene (*co*) polymers these differences hardly exceed 5 nm [25,26]. The large differences between solution and solid state absorption and emission testifies for the strong solid-state-induced interactions between polymer main chains which result in effective packing, strong π - π interactions and induced conformational ordering. In the present study we deal in detail with optical and association properties of the amphiphilic polythiophene with hydrophobic HT-regioregular polymer main chain and hydrophilic side groups. It should be noted that amphiphility is observed in the diblock copolymers more frequently. Recently some data were reported on polymers combining amphiphilic polythiophene polyelectrolyte blocks with fully hydrophobic blocks [27], and copolymers with non-ionic blocks of different hydrophobicity [28,29]. Most recently, the study of amphiphilic block copolymers with cationic side groups was published [30] in which the solvatochromic effects are also contributed. Another important field is the interaction of ionic conjugated polymers with oppositely charged species such surfactants and DNA which cause substantial chromatic changes [31,32] due to the influence of oppositely charged species on the inter- and intramolecular interactions within polythiophene main chains. Nevertheless, the solution behavior of conjugated polyelectrolytes is still a challenging topic. We performed the investigation of both absorption and emission characteristics of polythiophene polyelectrolyte in various solvents. In addition, we performed experiments illustrating the association behavior: dynamic light scattering, atomic force microscopy and transition electron microscopy. We also report on the time-dependent processes in solutions as the dynamics of de-association processes are reported only rarely [33,34].

2. Experimental

2.1. Techniques

Size-exclusion chromatography (SEC) measurements were performed using an Agilent HT 220 equipped with Waters 2414 differential refractometer with a THF as an eluent.

^1H and ^{13}C NMR spectra were measured on a Bruker AVANCE III 500 MHz spectrometer in CDCl_3 , D_2O or CD_3OD solutions. Chemical shifts are reported in ppm (δ) relative to tetramethylsilane (^1H) or the solvent peak (for ^{13}C ; 77.00 ppm for CDCl_3 and 49.3 ppm for CD_3OD). Estimation of HT-regioregularity was based on the ratio of signals of ^1H NMR spectra at 6.98 ppm (HT-connections) and 7.0 ppm (the rest).

UV/vis absorption spectra were recorded on a spectrophotometer Cary 300, Varian Inc. using quartz cuvettes and spectroscopic grade solvents. Temperature dependence of UV/vis spectrum of PMIT-Br was done using a double beam PerkinElmer Lambda 950 spectrophotometer using a thermostated sample holder, temperature was measured with Pt-100 resistance thermometer. The aging of solution was carried out in cuvettes. For concentration 1 mg/ml the cuvette with 1 mm pathlength was used, for concentration 0.1 mg/ml 1 cm pathlength, respectively. During the aging, cuvettes were kept under controlled atmosphere to avoid evaporating of solvents and thus solution thickening.

Fluorescence emission spectra were measured on a FSL 920 fluorimeter from Edinburg Instruments using four-window quartz cuvette (1 cm).

DLS measurements were performed on Zetasizer Nano ZS apparatus (Malvern Instruments, UK) at the scattering angle 173° and with 632.8 nm as the wavelength of the incident laser light. In practice, the size distribution histograms were obtained from the auto-correlation curves by the Contin algorithm, a method based on the inverse Laplace transformation of the DLS data. ACD software was used to calculate refractive index, n , utilizing semi-empirical methods.

Colloidal particles were prepared by injection of 30 μl of stock solution (6.5 mg/ml or 1.64 mg/ml) of PMIT-Br into the 2.97 ml of THF or THF/MeOH mixture. Addition of THF to the polymer solution in methanol led to the precipitation. For topographic characterization, Atomic force microscopy (AFM) was performed using the PeakForce Tapping mode on Dimension ICON from Bruker Corporation. Measurements were performed at laboratory conditions (temperature and atmosphere). The ScanAsyst-Air probe from Bruker Corporation was used for AFM measurement, with the nominal spring constant 0.2 N/m, Scanning rate was 1 Hz. The mica-substrates were covered by drop cast method from MeOH, MeOH/THF (1/1000 vol/vol, prepared by addition of 10 μl of MeOH solution into the 990 μl of THF and ten-times dilution with THF) and water solutions.

TEM and cryo-TEM observations were performed on a Tecnai G2 Spirit Twin 120 kV (FEI, Czech Republic), equipped with cryo-attachment (cryo-specimen holder, Gatan) using a bright field imaging mode at accelerating voltage 120 kV. 2 μl of the aqueous or THF/MeOH 100/1 vol/vol solutions were dropped onto a copper TEM grid (300 mesh), which was coated with thin, electron-transparent carbon film. The solution of water was removed out by touching the bottom of the grid with filtering paper. This fast removal of the solution was performed after 1 min in order to minimize oversaturation during the drying process. Both samples were left to dry completely at room temperature, transferred to the TEM microscope and observed as described above. Cryo-TEM: 3 μl of the sample solution was applied to an electron microscopy grid covered with holey carbon supporting film (C-flat 2/1-4C, Electron Microscopy Science) after hydrophilization by glow discharge (Expanded Plasma Cleaner, Harrick Plasma, USA). The excess of the solution was removed by blotting (Whatman no. 1 filter paper) for ~ 1 s, and the grid was immediately plunged into liquid ethane held at -181°C . The frozen sample was immediately transferred into the microscope and observed at -173°C under the conditions described above.

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