Journal of Photochemistry and Photobiology A: Chemistry 328 (2016) 33–41

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Self-aggregation of the pyrene labeled poly(acrylic acid) in nanoscopically crowded environments

Gabriela Stîngă, Adriana Băran, Alina Iovescu, Elena Livia Simion, Ludmila Aricov, Dan-Florin Anghel*

Colloid Chemistry Laboratory, "Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, 202 Spl. Independentei, 060021 Bucharest, Romania

A R T I C L E I N F O

Article history:
Received 20 November 2015
Received in revised form 27 May 2016
Accepted 28 May 2016
Available online 29 May 2016

Keywords:
Fluorescent polymer
Pyrene excimer
Reverse micelle

A B S T R A C T

The paper investigates the behavior of pyrene labeled poly(acrylic acid) with various graft content in sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles (RMs) at various hydration degrees (w_0). The work is carried out by UV–vis, steady-state and time-resolved fluorescence as well as dynamic light scattering (DLS). The report indicates new insights regarding the interactions and dynamics of the fluorescent labeled polymer in the nanoscopic aqueous host. It was found that the spectral properties of the polymer depend on the H-bonds and π-π interactions. The efficiency of pyrene excimer formation indicated the "on-off" control of the polymer chain in RMs by triggering of w_0. The constriction of the polymer coil in different nanocages of RMs influenced the formation of excimers. At low w_0, the pyrene labeled poly(acrylic acid) senses the micellar interface. At higher hydration degree, the grafted polymer resides in the water pool of RMs with elevated polarity similar to that in the bulk water. The study discloses the ability of the pyrene-labeled polymer to sense the crowded nano-environments.

1. Introduction

Fluorescent materials with multifunctional properties have been obtained using one of the most widespread hydrophobic fluorophore, namely pyrene (Py) [1–4]. Pyrene-based materials are of major interest to design organic electronic devices such as sensors, light emitting diodes, dye sensitized solar cells or to shed light on the structure of proteins, peptides, lipid membranes, etc. Polyelectrolytes including the poly(acrylic acid) (PAA) are renowned for their bio-related features and technical applications [5–9]. PAA can be chemically modified with dye-substituted alkylamines to obtain pyrene-labeled poly(acrylic acid)s. These fluorescently labeled polymers have been previously proposed to mimic the hydrophobically modified water soluble polymers used as rheology and viscosity modifiers in water-borne fluids, flocculating agents in water plants, stabilizing agents of nanoparticles (NPs) in conductive inks, etc. [6,10–14]. Pyrene labeled poly(acrylic acid)s have intriguing properties in bulk water [11,12,15]. The presence of carboxylic groups confers solubility in water and the polyion conformation can be controlled by different external stimuli like pH, electrolyte, surfactant, cyclodextrin [12,14,15], etc. The emissive response of fluorophore is one of the first challenges to infer information about the conformation and interactions of fluorescent polymers in different micro-environments. In water, the Py labels are maintained by hydrophobic interactions in close contact and mostly promote the formation of ground-state dimers also known as pre-associated monomers or static excimers [16–19]. Good organic solvents for Py solvate the labels, which cannot associate as ground-state dimers and the excimers are primarily formed between excited-state and ground-state monomers. The process is controlled by diffusion and gives rise to dynamic excimers [18,19].

Although there are many reports on the behavior of polymers in aqueous solutions without and with surfactant or in pure organic solvent, much less is known about their association in reverse micelles (RMs). The water from RMs mimics very well the nanoscopically confined water from the cellular membranes and proteins or from the nonbiological systems (i.e., minerals, zeolites, fuels, etc.). Moreover, RMs have many other applications being employed in significant processes including drug delivery [20], synthesis of artificial light-harvesting systems [21] or NPs [22,23], etc. In RMs, the surfactant molecules cluster with the polar head groups toward the nano-sized water droplets and the hydrocarbon tails delimit the organic phase [24]. For RMs with spherical morphology, the size of aqueous core depends on the molar ratio of

---

* Corresponding author.
E-mail address: danflorin.anghel@gmail.com (D.-F. Anghel).

http://dx.doi.org/10.1016/j.jphotochem.2016.05.021
1010-6030/© 2016 Elsevier B.V. All rights reserved.

water molecules per surfactant molecule or the hydration degree (w_0) [25–27]. The micellar system formed by self-assembly of anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) in non-polar solvents has been used to highlight the unique properties of water at the micellar interface [28–30].

This study investigates the photophysical properties of the poly (acrylic acid)s randomly labeled with 3% mol Py (PAAPy) and 0.4% mol Py (PAAPy1) in AOT RMs. The present work designs a supramolecular self-assembling system of host-guest type and brings novel information about the polymer dynamics and its interactions in nano-environments containing confined water. Fluorescent molecular probes (pyronin, pyranine, 1-anthracene sulphonate, coumarins, acridine orange, etc.) have been often used to explore the specific properties of RMs [27,31–33]. New perspectives are open when the RMs will be explored with the fluorescent polymers. On the one hand, it is likely to investigate the photophysical properties of the polymer in restricted micro-environments. One the other hand, the fluorescent label gives the possibility to assess the polymer effect on the specific properties of such micellar host.

2. Experimental

2.1. Materials

Reagent grade sodium bis(2-ethylhexyl) sulfosuccinate (Scheme 1) from Aldrich was used as received. *n*-Hexane of spectroscopic grade was purchased from Aldrich. The pyrene was supplied by Sigma-Aldrich. The 25% aqueous solution of poly (acrylic acid) (PAA) with molecular weight of 150000 was supplied by Wako Chemicals. The solid PAA was recovered by freeze drying and randomly labeled with 3% mol pyrene (Py) (PAAPy) and respectively, 0.4% mol Py (PAAPy1). *N*-Methyl-2-pyrrolidone anhydrous (NMP, 99.5%), 1-pyrenylmethylamine hydrochloride (PyMA, 95%) triethylamine (TEA, 99%,) and N,N'-dicyclohexylcarbodiimide (DCC, 99%) were purchased from Sigma-Aldrich. Details about synthesis and the characterization of PAAPy were presented in [2,11].

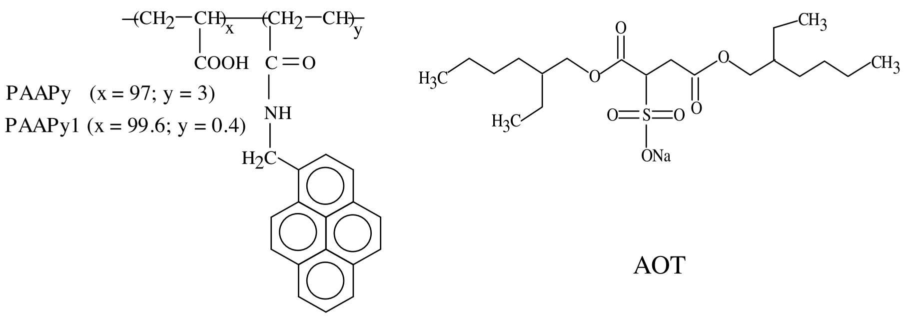
The level of Py labeling determined by UV absorption and ^{1}H NMR was of 3% mol. The synthesis of PAAPy1 is presented in the Supporting Information. The content of grafted pyrene on PAAPy1 was of 0.4% mol as determined by UV in methanol using 1-pyrenylmethylamine hydrochloride ($\varepsilon = 37500\,M^{-1}\,cm^{-1}$ at $\lambda = 342$ nm in methanol) as a model compound. The structures of PAAPy and PAAPy1 are given in Scheme 1.

2.2. Construction of RMs with pyrene labeled poly(acrylic acid)s

An appropriate volume of aqueous solution containing the polymer was added to the AOT/*n*-hexane stock solution. The rest of the water and non-polar solvent were injected into RMs solution to obtain the desired concentration of water, AOT and polymer. The hydration degree was calculated using the molar ratio of water to the surfactant ($w_0 = [H_2O]/[\text{surfactant}]$). The following w_0 values are considered: 5, 7, 10 and 15. The surfactant and polymer stock solutions were prepared at room temperature with 24 h before measurements. The working concentrations were for AOT of 0.1 M, for PAAPy of 0.014 g/L (and its dilutions of 0.0070 g/L, 0.0023 g/L and 0.0014 g/L) and for PAAPy1 of 0.014 g/L. Millipore water was used throughout the experiments to prepare solutions.

2.3. Methods

Absorption spectra was recorded on a Varian Cary 100 Bio spectrophotometer. The RMs solutions of corresponding w_0 and without polymer were used as references in the absorption measurements. P_A parameter was calculated using the peak-to-valley absorption ratio of the lower energetic electronic transition ($S_0 \rightarrow S_2$) in the absorption spectra of PAAPy [34]. Dynamic light scattering (DLS) measurements were performed on a ZetaSizer, Nano ZS, Malvern Instruments to determine the hydrodynamic diameter of the RMs. The analysis was accomplished at a laser wavelength of 633 nm and an angle of 173°. The quality of the obtained DLS results is reflected by the polydispersity index (PDI). The PDI values, for systems without and with polymer, are in accepted range for monodisperse samples (PDI = 0.05–0.21). Steady-state fluorescence measurements were carried out with a Horiba Jobin Yvon Fluoromax 4P spectrofluorimeter. Excitation spectra was registered in-between 250 and 360 nm, the emission being fixed at 374 nm for the monomer (M) and at 480 nm for the excimer (E). The slits for the excitation and emission were of 2 nm and respectively, 1 nm. P_M and P_E parameters were calculated using the peak-to-valley emission ratio of the $S_0 \rightarrow S_2$ transition in the M and E excitation spectra [34]. For emission spectra, the excitation wavelengths were 344 nm and 350 nm for pyrene labeled poly (acrylic acid) and 335 nm for pyrene probe. The Py emission was monitored in-between 360 and 600 nm with slits of 2 nm (excitation) and 1 nm (emission). The excimer-to-monomer intensity ratio, I_E/I_M, was determined by dividing the fluorescence intensity of excimer (at about 480 nm), I_E, to that of monomer (taken as semi-sum of fluorescence intensities at 374 and 395 nm), I_M. To calculate the I_1/I_3 ratio, the fluorescence intensity at 374 nm (I_1) was divided to that at 385 nm (I_3). The fluorescence lifetime measurements were carried out on an Edinburgh Instruments FLSP 920 spectrofluorimeter using the time-correlated single photon counting technique. The excitation wavelength was of 344 nm, and the source was a picosecond pulsed diode laser at 338.2 nm. The fluorescence emissions were collected at 374 nm (Py monomer) and 480 nm (Py excimer). A Ludox solution was used to determine the instrument response function. The intensity decays were solved in terms of a multiexponential model given by $I(t) = \sum_{i=1}^{n} B_i e^{-t/\tau_i}$, where the pre-exponential factor, B_i, is the



Scheme 1. Molecular structures of pyrene labeled poly(acrylic acid) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT).