Fluorometric, Light Scattering and Atomic Force Microscopy Studies of Polystyrene-*block*-poly(2-vinylpyridine)-*block*-poly(ethylene oxide) Micelles

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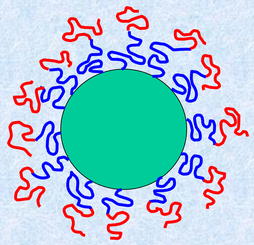
Introduction

The aim of the study is to investigate micellization of the triblock copolymer polystyrene-*block*-poly(2-vinylpyridine)-*block*-poly(ethylene oxide), PS–PVP–PEO, in aqueous solutions. Micelles of this triblock copolymer in an alkaline solution can be compared with so called "onion micelles"[1] which form by comicellization of PS–PVP micelles in an acid solution with PVP–PEO copolymer during alkalimetric titration.

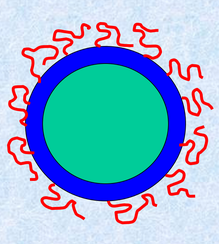
Since PVP is protonated and water-soluble in the pH range below 4.8, and in the pH range above 4.8 it is neutral and water-insoluble, we can assume two structures of the PS–PVP–PEO micelle in aqueous solutions:

pH < 4.8



micelles with the PS core and the PVPH$^+$/PEO shell

pH > 4.8



onion-type micelles with the PS core, the PEO shell and the PVP middle layer

Experimental

Characteristics of the copolymer sample

(purchased from Polymer Source, Inc., Canada)

M_n, 10^3 g mol^{-1}:	PS block	14.1
	PVP block	12.3
	PEO block	35.0
polydispersity index:		1.08

Preparation of micelles

PS–PVP–PEO cannot be dissolved in water directly (water is too strong a precipitant for polystyrene). Micelles are prepared as follows: (i) The copolymer is dissolved in 1,4-dioxane/methanol mixture (80 vol. % dioxane). (ii) Methanol is slowly added until 50 % methanol content is reached. (iii) 0.01 M HCl (sample A1) or 0.01 M NaOH (sample B1) is added until 50 % water content is reached. (iv) Organic solvent is removed by extensive dialysis against 0.01 M HCl (sample A1) or 0.01 M NaOH (sample B1). (v) Samples A2 and B2 are prepared by dialysis of sample B1 against 0.01 M HCl and sample A1 against 0.01 M NaOH, respectively.

Experimental techniques

- Static (SLS) and dynamic (DLS) light scattering – measurement of molar mass and hydrodynamic radius
- Fluorescence correlation spectroscopy (FCS) – measurement of molar mass and hydrodynamic radius
- Steady-state fluorometry – estimation of the polarity of the core (pyrene as a fluorescent probe)
- Atomic force microscopy (AFM) – imaging of the micelles or micellar aggregates

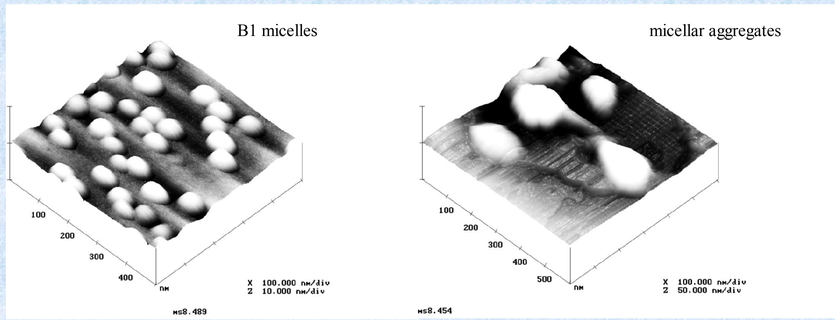
References

(1) Procházka, K.; Martin, T.J.; Webber, S.E.; Munk, P. *Macromolecules* **1996**, *29*, 6526.
(2) Humpolíčková, J.; Procházka, K.; Hof, M.; Tuzar, Z.; Špírková, M. *Langmuir* **2003**, *19*, 4111.
(3) Tsitsilianis, C.; Voulgaris, M.; Štěpánek, M.; Podhájecká, K.; Tuzar, Z.; Procházka, K. *Langmuir* **2000**, *16*, 6868.

Results and discussion

AFM imaging of micelles

micelles deposited on mica surface

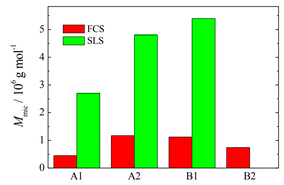


PS–PVP–PEO micelles tend to form aggregates in aqueous solutions at pH values above 4.8 at high ionic strength. (Aggregation in strongly acid solutions (pH below 4.8) at low ionic strength is suppressed by strong electrostatic repulsion between positively charged protonated PVP blocks.) Aggregation is very slow (occurs in the time scale of weeks) but it can be substantially accelerated by stirring, shaking or even by filtration of the sample through 0.2 μm filters. The latter is a complication for light scattering measurements and in case of PS–PVP–PEO micelles fluorescence correlation spectroscopy,[2] which does not require filtration, is much more convenient method for measurement of molar mass and hydrodynamic radius.

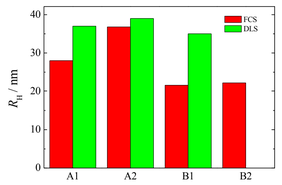
Characterization of micelles

Since the micelles are in a kinetically frozen state, different preparation recipes result in particles differing in mass and size.

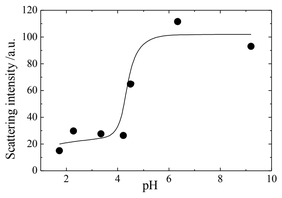
molar masses of the micelles measured by SLS and FCS



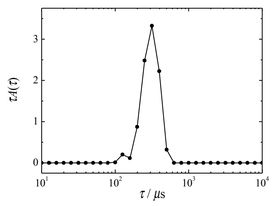
hydrodynamic radii of the micelles measured by SLS and FCS



scattering intensity change during alkalimetric titration of A1 micelles

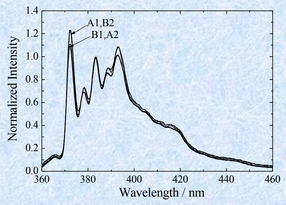


DLS relaxation spectrum of A1 micelles



Fluorometry

emission spectra of pyrene loaded in the micelles, normalized by the intensity of the third vibration band



Ratio of the first to the third vibration band intensity of pyrene emission spectrum, I_1/I_3, a well-known measure of microenvironment polarity, is 1.24 for the probe solubilized in A1 micelles and 1.12 for that in B1 micelles. Surprisingly, the I_1/I_3 values do not change during conversion of A1 and B1 micelles to B2 and A2 micelles. It clearly proves that the difference in I_1/I_3 is not connected with protonation of PVP blocks, instead, it is caused by a difference in a kinetically frozen structure of the core of A1 and B1 micelles. Since pyrene is much more soluble in PS than in PVP and I_1/I_3 values for PS and PVP are ca. 1.1 and 1.6, respectively, higher I_1/I_3 value for A1 micelles can indicate higher intermixing of PVP and PS chains.[3]

There is fairly good qualitative correlation between values of molar masses and hydrodynamic radii of the micelles, obtained from FCS (octadecylrhodamine B was used as a fluorescent marker) and SLS measurements. Quantitative differences are caused mainly due to partial aggregation of the micelles and also by the fact that molar masses obtained from FCS are number-averaged values, whereas those obtained from SLS are weight-averaged values. In case of B2 micelles, aggregation was so strong that it was not possible to filter the solution of B2 micelles for a light scattering measurement. (The resulting aggregates had molar mass of 3.6×10^7 g mol^{-1} and hydrodynamic radius of 60 nm.) On the other hand, it is possible to transfer B1 micelles to A2 micelles almost without a change of molar mass.

The molar mass of A1 micelles is lower than that of B1 micelles because of solubility of the PVP block in an acidic aqueous solution which decreases the number of unimers necessary for the stabilization of the PS–PVP–PEO micelle in aqueous media. On the contrary, the hydrodynamic radius of A1 micelles is higher than that of B1 micelles because of the stretching of positively charged PVPH$^+$ blocks due to repulsive electrostatic forces.

Conclusions

In this study, we have proven that triblock copolymer polystyrene-*block*-poly(2-vinylpyridine)-*block*-poly(ethylene oxide) forms, depending on pH, two types of spherical nanoparticles in aqueous solutions. Since the micelles tend to aggregate during filtration of the solutions, fluorescence correlation spectroscopy, which does not require filtration, is a suitable method for characterization of the micelles.

Acknowledgment

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