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Polystyrene - poly(ethylene oxide) diblock copolymers micelles in water

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Summary

Micellization in water of polystyrene-poly(ethylene oxide) diblock copolymers is achieved by the stepwise dialysis technique in order to prepare micellar solutions for copolymers with a wide range of molecular parameters. Hydrodynamic radii, determined by quasielastic light scattering, are correlated with the molecular parameters, e.g. molecular weight and composition, and compared with the theory. Two couples of phenanthrene and anthracene labelled copolymers are used to prepare micellar solutions by mixing them before and after dialysis. The non radiative energy transfer is determined on these solutions to prove that polystyrene-poly(ethylene oxide) diblock copolymers micelles in water are “frozen” micelles even when heated near the Tg of polystyrene.

Introduction

Block and graft copolymers are of great interest in liquid systems such as emulsions, dispersions as well as in the solid state (1,2). The presence in the same molecule of two or more incompatible sequences leads to a microphase separation and the block copolymers are able to spontaneously form micelles in a selective solvent for one block (3).

However, the formation of micelles is governed by a thermodynamic equilibrium in which unimers can exchange with copolymer molecules in the micelles. Such stable solutions can be currently achieved by simple dissolution, heating or stripping common solvent for both blocks from a mixture of common and selective solvent.

Among many known block copolymers, the polystyrene-poly(ethylene oxide) block copolymers (PS-PEO) exhibit micellar properties in organic medium like cyclopentane (4) and in water (5), due to the presence of hydrophobic (PS) and hydrophilic (PEO) sequences. In comparison to classical low molecular weight surfactants, like sodium dodecylsulfate, it could sometimes be difficult to solubilize directly in water such block copolymers, which are polymeric surfactants. An alternative procedure avoiding aggregate formation is to prepare micellar solutions by the stepwise dialysis technique (6,7). This technique which can be considered as a series of successive equilibrium states should lead to a “true” micellar system with possible exchange between unimers and micelles.

However all these dissolution techniques do not lead systematically to equilibrium micelles as mentioned recently by Munk (8). For this author, equilibrium conditions are respected during micelles formation only if selective solvent is poor enough for the core forming block to avoid anomalous micellization, but good enough for the same core to swell it, and to allow the mobility of the chains and consequently the exchange between unimers and micelles. For nonequilibrium micellar systems, two cases have to be considered:

- existence of individual micelles with inappropriate size essentially due to an absence of

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sufficient mobility of the core; this situation can occur even in dialysis technique.

- existence of clusters formed by individual micelles connected together by insoluble blocks; evaporation and crystallisation of solvent can cause an increase in copolymer concentration and then lead to such a system.

The characterization of a micellar system can be made by the critical micelle concentration (cmc), the aggregate number (Z), the hydrodynamic radius (R_H) and sometimes the unimer exchange rate. Various techniques like nonradiative energy transfer (9-13), static (14) and dynamic light scattering (6,14,15) are currently used to determine these micellar parameters. Finally, theoretical relations based on the thermodynamic equilibrium of the micelles have been elaborated to correlate micellar parameters with molecular characteristics of the block copolymers (16-20).

The aim of this article is mainly to check if PS-PEO diblock copolymers form in aqueous medium “true” or “frozen” micelles. For this purpose, we use the dialysis technique to prepare micellar solutions of copolymers having very different molecular characteristics. These solutions are analyzed by dynamic light scattering (DLS) and the obtained R_H values are tested by different theories for the relation with molecular weights of the sequences. Furthermore, nonradiative energy transfer (NRET) experiments on two couples of copolymers are realized to verify the possible exchange between unimers and micelles.

Experimental

Block copolymers

PS-PEO diblock copolymers are synthesized by sequential anionic polymerization in tetrahydrofuran under nitrogen at -78°C using cumylpotassium as an initiator. The copolymers are characterized by size exclusion chromatography and nuclear magnetic resonance (21). A special series called HH_i with exactly the same PS sequence are also prepared to show the influence of the hydrophilic block. Two couples of phenanthrene and anthracene labelled diblock copolymers (C15-C17 and C20-C21) are prepared especially to analyze the exchange between unimers and micelles. The details of their synthesis is given in reference 22.

Micellar solutions

The solutions are prepared by dissolving the copolymer in a common solvent for both blocks such as tetrahydrofuran (THF), adding methanol (MeOH) to prevent precipitation with water and completing with distilled water so that the final composition of the medium is THF / MeOH / H_2O 50:25:25 volume %. This mixture is then dialyzed with a large amount of distilled water. This procedure, the details of which are given in reference 21, leads to micellar solutions without aggregates for a large compositional and molecular range of block copolymers.

Micellar size measurements

The hydrodynamic radius of a micellar solution is determined by quasielastic light scattering using a Coultronics N4 apparatus. Typically, the solution is filtrated over 0.2 µm DynaGuard filter to remove any dust and the radius is then the average of ten reproducible measurements.

Nonradiative energy transfer measurements

The fluorescence spectra are obtained on a Perkin-Elmer LS-5B luminescence spectrometer according to the procedure described in reference 22.

Results and discussion

Quasielastic light scattering measurements

Results of the quasielastic light scattering measurements are given in table 1. This table shows that there is a dependence between hydrodynamic radii and molecular parameters of the block copolymers. As expected, any increase in one molecular parameter leads to an increase of R_H. This tendency is especially observed for HHi series which have exactly the same PS block. One can also notice that the R_H values are in the same range as those of classical polymeric micelles. Apparently, no clusters with higher hydrodynamic radii have been formed during the dialysis process.

Table 1: Molecular characteristics of the diblock copolymers
and hydrodynamic radius of the micelle obtained by dialysis procedure

Copolymer	M_nPS	M_nPEO	% PS (wt)	R_H (nm)
H19	50600	44000	53.5	34.3
H17	42500	15300	73.5	32.4
28	31300	51200	38.0	23.1
29	31300	80100	28.1	27.6
34	15800	24500	39.2	20.4
36	15800	58000	21.4	22.8
35	15800	261400	5.7	41.6
30	14200	29400	32.5	20.6
31	14200	53700	20.9	24.3
18	13400	22100	37.7	20.2
H13	4600	3000	60.6	13.8
37	4200	10100	29.3	11.8
38	4200	19000	18.1	14.6
39	4200	30800	12.0	19.3
HH1	4000	3950	50.0	9.2
HH2	4000	6500	38.0	11.4
HH3	4000	11000	27.0	14.5
HH4	4000	19600	17.0	16.6
HH5	4000	30800	11.0	17.9
41	3700	19800	15.6	16.2
RS1465	1015	1015	50.0	7.4
C15 Phe	10000	15000	40.0	19.0
C17 Ant	12000	16000	43.0	21.9
C20 Phe	8000	106000	7.0	40.2
C21 Ant	8000	106000	7.0	41.2

Theoretical relations between molecular characteristics and micelle size

Several theories can describe micellar systems with relationships between the structural parameters of the micelles and the molecular characteristics of the copolymers. These theories are based on different models; each of them have their restrictions but are elaborated from the same concept: the thermodynamic equilibrium of the micelle during and after his formation.

We have tried to apply the Noolandi and Hong theory (18) as well as the Halperin theory (20) to our system (21) but it does not work as predicted by these authors. In our case, the relationships should be $R_H = K\ (N_{PS} + N_{PEO})^{2/3}$ and $RH = K'\ N_{PEO}^{\ 3/5}\ N_{PS}^{\ 3/25}$ respectively. As an example, we give in figure 1 the results obtained from the Noolandi and Hong theory; it can be seen that the dependence between experimental and theoretical R_H values is not linear for all our copolymers. Similar results are obtained for the

Halperin theory. Nevertheless, it is possible to determine experimental linear relationships ($R_H = 1.79\ (N_{PS} + N_{PEO})^{0.36}$ and $R_H = 1.77\ N_{PS}^{0.09}\ N_{PEO}^{0.31}$ respectively) as mentioned in reference 21, but it is not adapted to all the copolymers of the table 1.

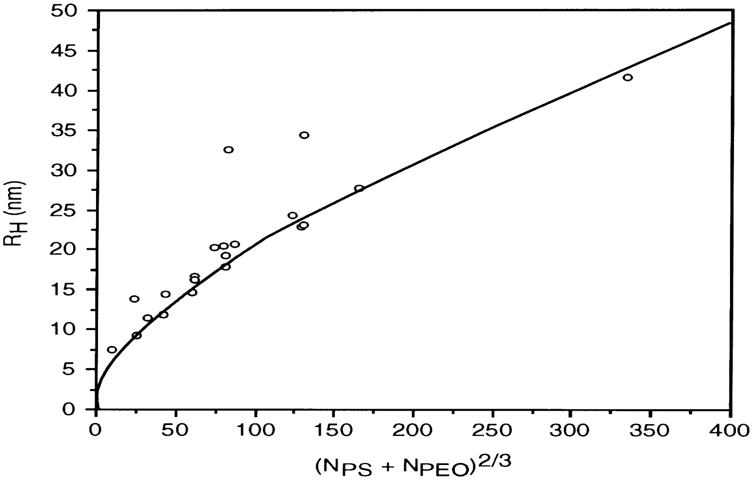

Figure 1: Relationship of the Noolandi and Hong theory for diblock copolymers micelles

This is a first indication that the PS-PEO copolymers micelles can not be described by these theories based upon thermodynamic equilibrium.

Despite this, we have chosen to apply the Nagarajan and Ganesh (19) theory for which the relationship depends on the copolymer/solvent system and seems correspond to a larger range of molecular characteristics of the copolymers.

Indeed, for these authors, the R_H value can be expressed as the sum of two terms, the first one for the core of the micelle and the second one for the shell. If we consider N_A an N_B the numbers of repeating units in soluble and insoluble blocks respectively, the expression of R_H is:

$$R_H = K_1\, N_A^{\alpha_1}\, N_B^{\beta_1} + K_2\, N_A^{\alpha_2}\, N_B^{\beta_2} \qquad (1)$$

K_i, α_i, β_i are constants depending on the copolymer/solvent interaction parameters.

To apply this relation to diblock copolymers, two restrictions must be respected:

$$0.1 \leq N_A / N_B \leq 10 \text{ and } 50 \leq (N_A + N_B) \leq 2500 \qquad (2)$$

At present, the PS and PEO/water interaction parameters are unknown and it seems impossible to apply directly the theory to our system. Nevertheless, we have selected the example given by the authors for the PPO-PEO diblock copolymer/water system (PPO: polypropylene oxide) and we assume that $\alpha 1$ and $\alpha 2$ coefficients for PEO are the same in a PS-PEO block copolymer as in a PPO-PEO block copolymer.

Thus the Nagarajan and Ganesh expression becomes for our system:

$$R_H = K_1\, N_{PEO}^{-0.17}\, N_{PS}^{\alpha} + K_2\, N_{PEO}^{0.74}\, N_{PS}^{\beta} \qquad (3)$$

To determine the values of K1, K2, α and β, we have respected the above restrictions and selected two series of copolymers with a constant PS content. In this case, the expression

(2) becomes: $RH / NPEO^{-0.17} = K_3 + K_4 N_{PEO}^{0.91}$ (4)

where $K_3 = K_1 N_{PS}\alpha$ and $K_4 = K_2 N_{PS}^{\beta}$.

For each series, K_3 and K_4 can be determined by plotting $R_H / N_{PEO}^{-0.17}$ against $N_{PEO}^{0.91}$ as described in table 2.

Table 2: K_3 and K_4 determination from $R_H / N_{PEO}^{-0.17} = f(N_{PEO}^{0.91})$

Copolymer	N_{PS}	N_{PEO}	N_{PEO}/N_{PS}	$N_{PEO}+N_{PS}$	R_H	K_3	K_4	r^a
34	152	557	3.66	709	20.4	42.36	0.055	0.9674
36	152	1318	8.67	1470	22.8			
30	136	668	4.91	804	20.6			
31	136	1220	8.97	1356	24.3			
37	40	229	5.72	269	11.8	15.69	0.109	0.9332
38	40	432	10.8	472	14.6			
HH1	38	90	2.36	128	9.2			
HH2	38	148	3.89	186	11.45			
HH3	38	250	6.57	288	14.55			

a : linear regression coefficient

To determine K_1, K_2, (α and β values, we consider the average values of N_{PS} for each series of copolymers (144 and 39 respectively), and use the following expressions

$$\log K_3 = \log K_1 + \alpha \log N_{PS} \text{ and } \log K_4 = \log K_2 + \beta \log N_{PS}$$

which finally give: $\alpha = 0.75$ $\beta = -0.53$ $K_1 = 0.98$ $K_2 = 0.76$

The relation between the hydrodynamic radius and the molecular characteristic of the diblock copolymer can now be written as:

$$R_H = 0.98\, N_{PEO}^{-0.17}\, N_{PS}^{0.75} + 0.76\, N_{PEO}^{0.74}\, N_{PS}^{-0.53} \quad (5)$$

To check the validity of this empiric relationship, we have plotted on the same graph the straight line of the expression (5) and the experimental value of R_H, which appears on the figure 1. Three types of symbols are used to distinguish the copolymers:

- the copolymers which were used to determine the relation (5): series 1
- the copolymers which were not used for this determination due to the restrictions given by Nagarajan and Ganesh in the relation (2): series 2
- five copolymers which were independently analyzed by Winnik's group (23): series 3.

The molecular characteristics of the series 3 copolymers are given in table 3.

Table 3: Molecular characteristics of the series 3 copolymers

Copolymer	N_{PS}	N_{POE}	N_{POE}/N_{PS}	$N_{POE}+N_{PS}$	R_H
32	113	886	7.84	999	23.0
23	108	398	3.68	506	22.0
41	35	450	12.8	485	19.0
40	35	236	6.74	271	15.0
JLM5	16	154	9.62	170	10.0

Figure 2 shows clearly that the copolymers of series 2 are very close to the straight line determined by copolymers of series 1, especially for high and low values of R_H for which the other theories (16-18, 20) are not satisfactory (21). One also notices a strong agreement with Winnik's values which are determined independently. Further to this, it appears that, despite the difference of structure compared to classical diblock copolymers, the two couples of labelled copolymers verify approximatively the relation (5).

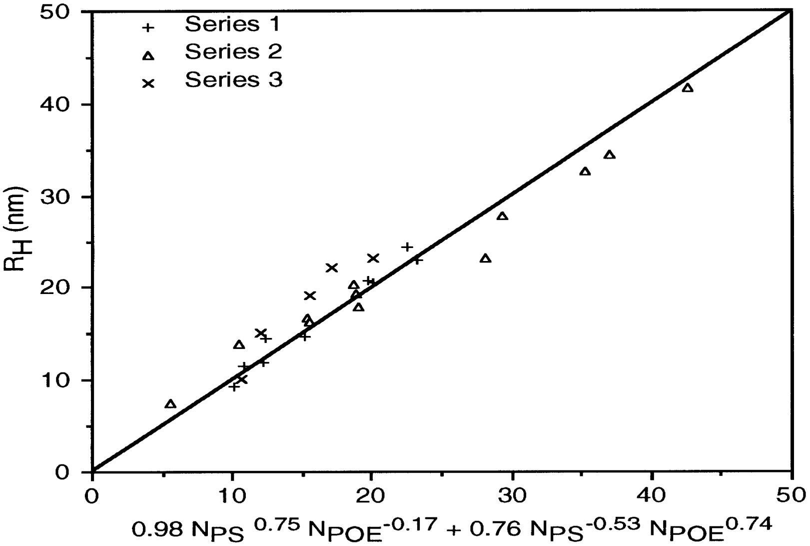

Figure 2: Relationship between R_H and (N_{PEO}, N_{PS}) for diblock copolymers micelles

Finally, it seems that it is possible to correlate the molecular characteristics of PS-PEO diblock copolymers with their micelle sizes for a large range of molecular weight and compositions such as $2000 \leq M_{nCOP} \leq 95000$ and $5 \leq PS \leq 75$.

Nevertheless, the relation that we found supports the analogy between PPO-PEO and PS-PEO systems for the coefficients corresponding to PEO sequences. It is also important to note that the non correlation with other theories in which all coefficients are clearly defined according to thermodynamic equilibrium indicates that PS-PEO copolymers micelles seem in fact to be “frozen” micelles.

Non radiative energy transfer measurements

Non radiative energy transfer measurements have been realized on C15-C17 and C20-C21 couples of diblock copolymers in water, in order to show the formation of micelles and to determine the critical micelle concentration (13).

We also show in this paper that the energy transfer is practically negligeable if the mixture of donor and acceptor copolymers is made after dialysis. Indeed, as shown in the figure 3, if the C20 and C21 copolymers, as well as the C15 and C17 copolymers, are dialyzed separately and mixed afterwards, the fluorescence spectra a and c respectively correspond in each case to that of the phenanthrene group, e.g. the donor. On the other hand, if the mixture is made before dialysis, the micelles are composed of donor and acceptor labelled copolymers and the fluorescence signal of the donor decreases while that of the acceptor increases (figure 3). It is evident that the dialyse which is realized separately on C20 and C21 does not lead after mixing to C20 and C21 containing micelles. The exchange between C20 containing micelles and C21 containing micelles is not possible in these conditions.

The absence of exchange also observed by Wang et al. (10) on PS-PEO copolymer micelles is apparently not specific to this chemical nature of block copolymers. Indeed, the same observation is reported by Meyer et al. (12) for poly(acrylic acid)-poly(methyl methacrylate) block copolymers/water system on the time scale of weeks. Similarly, no exchange is detected by Zhang et al. (6) for polystyrene-poly(acrylic acid) block copolymers in aqueous medium. For these authors, the high value of the Tg of the PS sequence is responsible for the “frozen” state of the micelles. The glassy nature of polystyrene is also mentioned in reference 10 to justify the absence of exchange.

Accordingly, it seems interesting to repeat the same experiments as in our previous work, but at more elevated temperatures e.g. nearer the Tg of polystyrene. Then we have tried but without any success to measure significant signal of fluorescence of acceptor groups after mixing two different labelled solutions of copolymers and heating them to 60°C, 65°C and 80°C on a time scale of about a hundred hours. We can easily conclude that the PS-PEO block copolymers micelles'formation in water, even by the stepwise dialysis technique, follows a dynamic equilibrium at the beginning of the dialysis, but becomes a kinetically “frozen” equilibrium when the content of non solvent reaches a critical value. This conclusion is partially in agreement with the experiments of Wang et al (10) who do not observe any exchange with the same system at room temperature and a very low exchange at 60°C at the rate of about 10^{-5} s^{-1}. This value is practically negligible like that measured by Jerome et al. (11) for the poly(sodium methacrylate)-poly((dimethylamino)ethyl methacrylate)/water system (10^{-3} s^{-1}) as compared to the rate of classical surfactants which is about 10^{6} - 10^{8} s^{-1}.

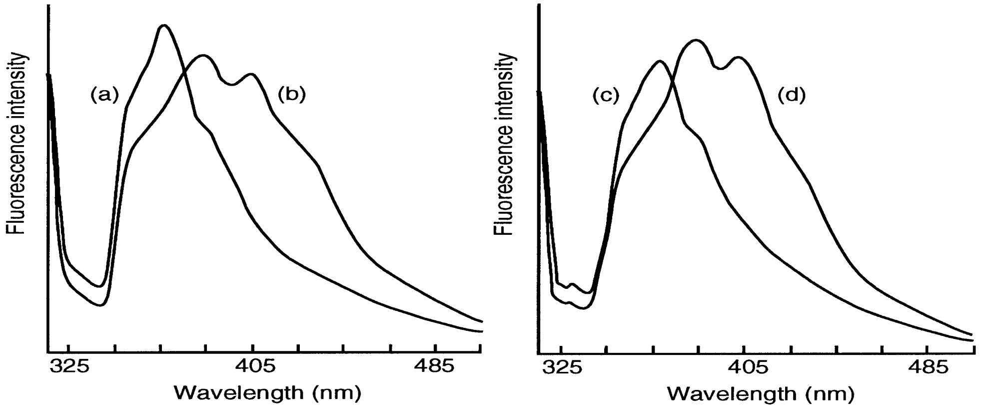

Figure 3: Fluorescence spectra of mixtures of copolymers in water
The copolymers are dialyzed separatly and mixed afterwards:
(a) C20-C21 (c) C15-C17
The copolymers are mixed then dialyzed together
(b) C20-C21 (d) C15-C17

Conclusion

Micelles of PS-PEO block copolymers with a wide range of molecular parameters are realized in water by the stepwise dialysis technique. The hydrodynamic radii are measured by quasielastic light scattering and do not follow the different theories proposed for diblock copolymers. As a consequence, this means that the micelles'formation doesn't follow a dynamic equilibrium along the dialysis. Nevertheless, it seems possible to correlate the hydrodynamic radius of a micelle to the molecular characteristics of the containing copolymer, and this for the range $2000 \leq M_{nCOP} \leq 95000$ and $5 \leq PS \leq 75$.

In addition, we show by nonradiative energy transfer measurements that the "frozen" state of the micelles after dialysis doesn't change with increasing temperature in the time range of the experiments.

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