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Effect of Pyrene Chain End Labeling on the Interaction of Poly(ethylene oxide) with Sodium Dodecyl Sulfate in Aqueous Solution

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ABSTRACT: The photobehavior of pyrene chain end labeled poly(ethylene oxide) (PEOPy) in aqueous solution is strongly modified by sodium dodecyl sulfate (SDS) addition. At low surfactant concentrations the excimer/monomer emission intensity ratio increases with SDS addition, a result explained in terms of PEOPy incorporation into aggregates comprising two or more end-labeled chains. The aggregation of the surfactant onto the end-labeled chains takes place at SDS concentrations considerably lower than those required to produce its micellization onto the unlabeled poly(ethylene oxide) chains. At higher surfactant concentrations, the excimer/monomer emission intensity ratio decreases as a consequence of dilution of the polymer molecules into an increasing number of micelles.

Introduction

The interaction of poly(ethylene oxide) with sodium dodecyl sulfate (SDS) in aqueous solution has been extensively investigated. Studies on the interaction were performed by following solution properties such as viscosity,[1] surface tension,[2] and dialysis equilibrium,[3] as well as by employing spectroscopic techniques, in particular, NMR,[4] ESR,[5] neutron scattering,[6] and fluorescence.[7-11] From these studies it is well-known that poly(ethylene oxide) interacts with SDS by inducing the micellization of the surfactant on the polymer chains at concentrations well below that corresponding to its critical micelle concentration in pure water. The micelles formed on the polymer are some kind of mixed micelles comprising surfactant monomers and polymer strands. These micelles have smaller aggregation numbers[11] and a more open structure than those of the SDS micelle itself.[8] The currently accepted description of the whole aggregates, at least at large surfactant/poly(ethylene oxide) ratios, corresponds to several micelle-like aggregates supported by a single polymer chain. There is no evidence at present pointing to aggregates comprising several polymer chains. This kind of aggregates could be particularly important in solutions at low surfactant/polymer ratios. In principle, end labeling of the poly(ethylene oxide) chains with pyrene groups could provide information regarding the number of polymer chains that pertain to each supramacromolecular structure, due to the possibility of excimer emission when two or more polymer chains are incorporated to a given aggregate. This work was aimed at investigating the feasibility of this approach for studying the effect of the polymer concentration on its interaction with the surfactant.

Experimental Section

The pyrene end labeled poly(ethylene oxide) (PEOPy) employed was obtained by esterification of a poly(ethylene oxide) sample (Unilever, Research Laboratories, Welwyn, U.K.; nominal molecular weight, 2×10^4) with 4-(3-pyrenyl)butyric acid (PBA; Koch-Light). The estrification was performed by following the procedure described by Cuniberti and Perico,[12] but employing a very small [PBA]/[polymer] stoichiometric ratio in order to obtain single labeling of the chain ends. The degree of substitution of the polymer chain ends was determined by UV spectroscopy. The absorption spectra of dilute solutions of the polymer in tetrahydrofuran were the same as those of PBA and methyl 4-(3-pyrenyl)butyrate (MPB). The extinction coefficient for the peak at 330 nm was equal to 3×10^4 M^{-1} cm^{-1} for both PBA and MPB. This value was employed for the end-group analysis of the polymer. The number of pyrene groups per chain so obtained was 0.6.

Sodium dodecyl sulfate (SDS) (BDH, specially pure) was employed without treatment. Ruthenium tris(bipyridyl) chloride hexahydrate $[Ru(bpy)_3]^{2+}$ and 9-methylanthracene (9-MA) were obtained from Sigma.

Absorption spectra were recorded on a Shimadzu 160 spectrophotometer. Fluorescence spectra and intensities were registered on a Perkin-Elmer LS5 luminescence spectrometer.

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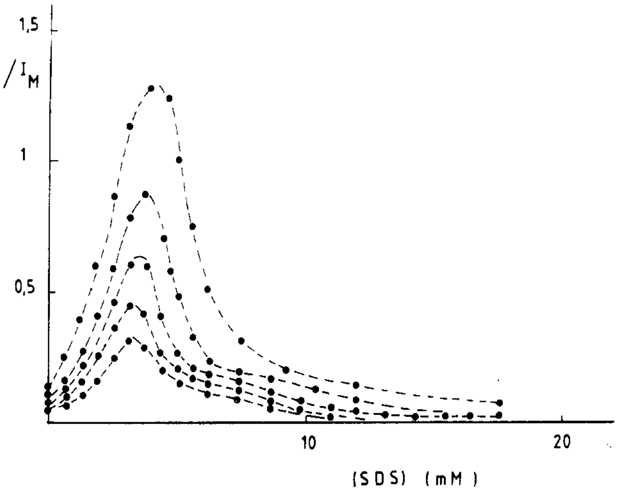

Figure 1. Effect of SDS addition on the I_E/I_M ratio for different PEOPy concentrations. Polymer concentration (from bottom to top): 0.0125%; 0.025%; 0.05%; 0.1%; 0.2%.

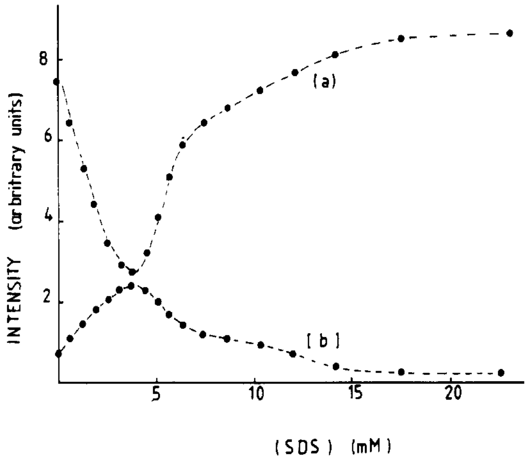

Figure 2. Effect of SDS addition on the monomer (a) and excimer (b) emission intensities of PEOPy (0.1%).

Fluorescence lifetimes were measured by following the fluorescence intensity decay after excitation with the pulse of a Nitromite LN100 nitrogen laser.

All experiments were carried out at room temperature in air-equilibrated solutions.

Results and Discussion

Emission spectra of PEOPy were measured at five different concentrations (from 0.0125% to 0.2%) in pure water and in the presence of SDS. The results obtained are shown in Figures 1 and 2. In Figure 1, the ratio of the intensities of monomer and excimer emission value, I_E/I_M, is plotted against the surfactant concentration. It is seen that for all the polymer concentrations employed, the I_E/I_M dependence with surfactant concentration shows the typical pattern of a micellar catalysis operating on the excimer-forming process; i.e., as the SDS concentration increases, the I_E/I_M ratio increases, reaches a maximum, and then decreases. The data given in Figure 2 show that at low SDS concentrations, the excimer emission increases at the expense of the monomeric fluorescence and that the opposite occurs beyond the SDS concentration at which I_E/I_M reaches its maximum. These results clearly indicate that SDS is being adsorbed on the polymer by forming some kind of aggregates which involves the polymer chain ends carrying the pyrene group. A remarkable consequence of these data is that the interaction of PEOPy with SDS is much stronger than that of poly(ethylene oxide) itself. The onset of SDS adsorption on poly(ethylene oxide) with formation of micelles on the polymer has been reported to occur at 4×10^{-3} M.[2,6a] Our own measurements of the "apparent critical micelle concentration" for the unlabeled poly(ethylene oxide)/SDS system obtained by surface tension measurements gave a value of 3.2 mM. The PEOPy–SDS interaction occurs (even for the lowest polymer concentration employed) at SDS concentrations below ca. 0.5 mM. This is a remarkable but not surprising result, since, although present as a small part of the total mass of the polymer, the much higher hydrophobicity of the pyrene moiety relative to that of the oxyethylene units makes the polymer chain ends the best binding sites for the surfactant. We believe that the interaction between PEOPy and SDS starts by adsorption of the surfactant at the chain ends.

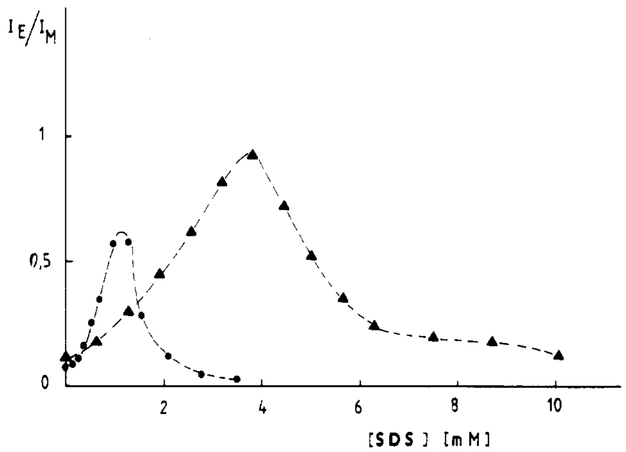

Figure 3. Effect of salt addition on the interaction of PEOPy with SDS: (▲) no salt; (●) in the presence of 0.1 M sodium chloride. Polymer concentration: 0.1%.

The fact that the surfactant aggregation onto PEOPy starts at an SDS concentration much lower than that at which SDS aggregates onto unlabeled poly(ethylene oxide) indicates that the labeled polymer must be considered as a different species. This is specially relevant when a drastic change in structural characteristics occurs, such as in the present case where a large apolar group is introduced at the end of a mostly polar chain. These considerations imply that care must be taken in the use of labeled polymers to deduce properties of the unlabeled species.[13]

The increase of the I_E/I_M ratio as more surfactant is added occurs up to a SDS concentration that, depending on the polymer concentration, is in the 3–4 mM range. Beyond this concentration, further addition of SDS decreases the I_E/I_M ratio, indicating that pyrene chain ends are diluted among the new aggregates. It is remarkable that the maximum value of the I_E/I_M ratio occurs at a SDS concentration that nearly corresponds to the onset of mixed-micelle formation on the main chain of unlabeled poly(ethylene oxide). We interpret this behavior as indicative of (i) an increase of the number of chain ends acting as a nucleus for micelle formation as more surfactant is added until most pyrene groups are micelle associated (behavior below the maximum) and (ii) a dilution of the local concentration due to incorporation of the chain ends into the new mixed micelles formed (probably) on the polymer main chain (after the maximum). These considerations are supported by the results obtained in the presence of added salt. The data given in Figure 3 show that the amount of SDS required to reach the I_E/I_M maximum decreases to nearly 1 mM in a 0.1 M NaCl solution containing 0.1% PEOPy. This concentration also corresponds to the onset of mixed-micelle formation on the main chains of unlabeled poly(ethyl-

Table I
Number of Micelles and Average Number of PEOPy Chains[a]

[SDS], mM	$1 - f^*$	f	[micelles], 10^{-6} M	n
0.7	0.14	0.12	0.4	1.06
1.7	0.30	0.33	0.94	1.0
3.3	0.54	0.60	1.60	1.06
3.8	0.7	0.65	2.23	1.02

[a] f^* is the intensity of the long component (extrapolated to zero time) relative to that measured in the absence of SDS; f is the intensity of the monomeric emission relative to that measured in the absence of SDS. PEOPy concentration; 0.1%.

ene oxide) in the presence of 0.1 M NaCl.

To further characterize the type of aggregates formed between PEOpy and SDS, we carried out experiments to quantify the average number of PEOPy molecules incorporated in each microaggregate. Excitation spectra for the monomer and excimer emissions (registered at observation wavelengths of 378 and 500 nm, respectively) were very similar and satisfactorily matched the UV absorption spectrum. This would indicate that no significant interaction is taking place in the ground state. Excimer formation must then be attributable to a dynamic process involving diffusion together of the excited- and ground-state pyrene groups and/or the rearrangement of nearest-neighbor pyrene groups lacking the proper geometry to give the excimer. Time-resolved emission measurements were performed at 0.1% PEOPy concentration. In the absence of SDS (a condition under which the emission consists of only monomeric fluorescence), the decay is monoexponential with a lifetime of 130 ns.[14] At 0.05 M SDS (conditions under which all pyrene can be considered micelle associated and the spectrum consists of only monomeric emission) the decay is also monoexponential with a lifetime of 135 ns. For all SDS concentrations below 3.8 mM the decay is more complex but is dominated by a long component with a lifetime of 130 ns. Extrapolation of this long component to time = 0 provides the fraction of pyrene groups in the aqueous solution (if emission arising from micelles bearing a single chain end is disregarded). The results obtained are shown in Table I. The amount of pyrene incorporated into the aggregates can also be estimated from the decrease of the intensity of the monomeric emission following the surfactant addition. This procedure assumes that the contribution to the monomeric emission from the micelles, either comprising one or several PEOPy chains, is negligible. The data obtained from this treatment are also included in Table I. The agreement between both determinations would support the procedures employed in their evaluation. To estimate the average number of pyrene groups in the aggregates it is necessary to know the number of micelles. These numbers were estimated following the method based on the quenching of $[Ru(bpy)_3]^{2+}$ luminescence by 9-MA.[15] Figure 4 shows the ln (I^0/I) vs [9-MA] plots obtained for SDS concentrations of 1.7, 3.3, 6, and 10 mM. From these plots the micelle concentrations given in Table I are obtained. These data allow calculation of the number of pyrene chain ends per aggregate, which are summarized in Table I. These numbers, although they can be underestimated due to the assumptions involved, indicate that each micelle contains a small number of PEOPy chain ends. The relatively large excimer emission must then be due to a very favorable excimer formation, even in those micelles bearing two PEOPy chains. In this regard, it is interesting to note that while at high (>3.8 mM) SDS concentration the excimer formation is a rather slow process taking place with a rise time of ca. 25 ns, at low SDS the excimer formation takes place in a time scale shorter than our detection limit (ca. 10 ns). If we consider that there are no preformed pairs and that the average number of pyrenes per micelle is rather low, these results would suggest a very small size for the micelles formed on the PEOPy chains at low SDS concentrations. At larger SDS concentrations, both the decrease in the average number of pyrene groups per micelle and a larger size of the aggregates must contribute to the observed change in the excimer emission rise time.

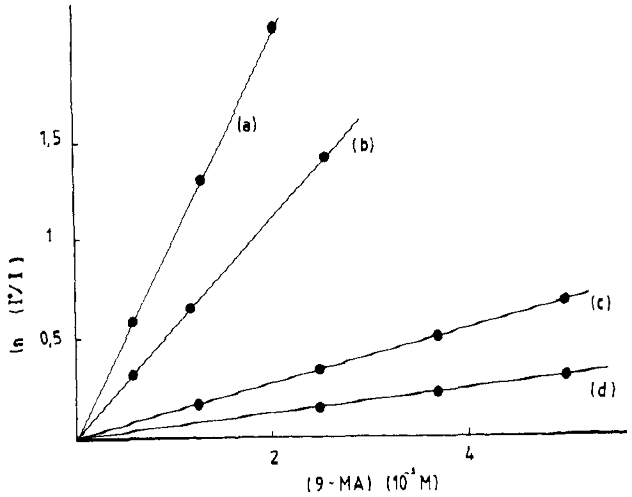

Figure 4. Quenching plot for the effect of 9-MA addition on the luminescence of $[Ru(bpy)_3]^{2+}$ in a 0.1% solution of PEOPy at SDS concentrations corresponding to 1.7 (a), 3.3 (b), 6 (c), and 10 mM (d). I^0 and I are the emission intensities of the ruthenium complex in the absence and presence of 9-MA, respectively.

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