Photophysical Characterization of Polyelectrolytes in the Form of Polymerized Micelles from an Ionic Surfactant with a Terminal Double Bond

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ABSTRACT: A polymerized micelle poly(sodium undecenoate), PSUe, synthesized from an ionic surfactant with a terminal double bond has been studied by photophysical methods in aqueous solution. The data suggest that PSUe undergoes a conformational transition at pH around 8.5. At low pH < 8, the polymer forms a compact hydrophobic structure, at high > 10, the polymer tends to expand to a looser polymerized micelle, quite unlike PA-18K_2 and/or PMA. PA-18K_2 provides compact host structures for pyrene molecules over the entire pH range, while PMA tends to open in an extended form at pH > 5 and expose pyrene to the aqueous environment. The different pH effects are attributed to the different hydrocarbon side chains linked to the polymer backbone. In polymerized micelles compared to simple ionic sodium undecanoate micelles, USa, the movement of guest molecules is substantially restricted due to the screening effect of the polymer backbone: this occurs even in the looser polymer forms at higher pH. Different methods of synthesis do not lead to polymerized micelles of different structure but to polymers of different molecular weight, with one polymer molecule forming one polymerized micelle in the systems studied. The present studies demonstrate that tailoring of polymers to meet set needs may be achieved by changing the length of the hydrocarbon segment in the monomer surfactant.

Introduction

Polyelectrolytes are macromolecules carrying a large number of groups that may ionize in suitable solvents. The importance of studies on polyelectrolytes is well recognized. Turro and Barton have determined binding and spectroscopic parameters for a series of organometallic complexes binding to DNA.[1] This type of approach is useful in systematic studies of DNA recognization. Synthetic weak polyelectrolytes have attracted increasing attention in recent years not only for their own intrinsic interest but also for their resemblance to proteins. The hydrolyzed alternating copolymers of maleic anhydride and *n*-alkyl vinyl ethers, with intermediate-sized alkyl groups (C4–C8), undergo a conformational transition from hypercoiled to randomly coiled states with increasing pH. Copolymers have been studied by a covalently tagged dansyl probe.[2-4] A similar pH-induced transition from a compact coil to an extended form occurs around pH 4–5 in aqueous solutions of poly(methacrylic acid), PMA, and studies on this polymer by a wide variety of techniques have been reported in the literature.[5,6]

The weak anionic polyelectrolytes have been shown to form hydrophobic domains in strongly acidic solution, which can act as hosts for hydrophobic molecules. This condition disappears at high pH, due to uncoiling of the polymer. Strongly acidic solutions of polymers have been drawbacks for any practical use, and it is desirable to seek other ways of providing hydrophobic microdomains close to conditions of neutral pH. Modification of polyelectrolytes via covalent bonding with long hydrophobic chains provides an alternative route. A potassium salt of a 1:1 copolymer of maleic anhydride and 1-octadecene, PA-18K_2,[7] and the alternating copolymers of maleic acid with decyl and/or hexadecyl vinyl ether[8,9,10] were reported to form hydrophobic domains over the entire pH range. Increasing pH increases the ionization of the polyacids, which leads to a repulsive interaction of negatively charged carboxy groups and tends to expand the polymer. In hydrophobically modified polyelectrolytes, a strong hydrophobic interaction exists among the long hydrophobic side chains, which stabilizes the compact conformation even at high pH range. Such polymers have been called polysoaps or polymeric micelles.

The above polymeric micelles are covalently bound in the vicinity of the carboxylate head groups. Recently, a "glued micelle" was prepared by the polymerization of styrene in cetyltrimethylammonium bromide (CTAB) micellar solution.[11] Here the surfactant units are anchored or constrained close to the core of the micelle. Photophysical studies on polymeric micelles and glued micelles showed that the movement of pyrene and quencher molecules hosted by the systems is restricted compared to simple micelles. Of immediate interest is the construction and characterization of polymerized micelles where the polymer backbones are separated from carboxylate head groups by long hydrocarbon segments. Polymerized micelles of sodium undecenoate, an ionic surfactant monomer with a terminal double bond, may offer such an example, and a photophysical characterization of such a polymerized micelle, PSUe, is presented in this paper. The comparison of a polymerized micelle and a simple sodium undecanoate micelle is also reported in order to show the effect of the polymer backbone on the micellar structure and movement of molecules in the micelle.

Experimental Section

Fluorescent Probes and Quenchers. Pyrene, (1-pyrenylbutyl)trimethylammonium bromide (C_4PN^+), and 2-methylanthracene were employed as fluorescent probes. Nitromethane, oxygen, and 1-dodecylpyridinium chloride, DPC, were used as quenchers and were purified as in previous studies.[7,8]

Surfactants. Sodium undecanoate (SUa) was used as a conventional model micellar system. The concentration of surfactant was 0.2 M, while the cmc is 0.058 M.[12] The monomer surfactant sodium undecenoate (SUe) was used for synthesis of the polymer.[13] The sodium surfactant salt, SUa, and SUe were prepared by neutralizing the corresponding acid (Aldrich) with an equimolar quantity of sodium hydroxide. After refluxing for 2 h in anhydrous ethanol, the salts were crystallized from cooled solutions at −20 °C, washed with anhydrous acetone, and dried under vacuum.

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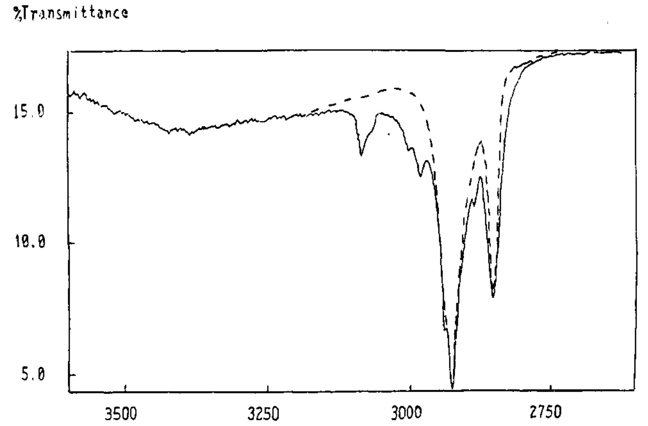

Figure 1. Infrared spectra of the monomer (—) and the product of polymerization (- - -).

Measurements. Steady-state absorption and emission spectra were recorded on Perkin-Elmer 552 UV-vis and MPF-44b fluorescence spectrophotometers, respectively. The fluorescence decay rate constant, k_0, and quenching rate constant, k_q, were measured with a PRA LN-100 nitrogen laser system with fast spectroscopic detection.[14] Prior to measurement, samples were deoxygenated by nitrogen bubbling, unless stated otherwise. Measurements of the degree of polarization and the pH of the sample solutions have been described in previous studies.[7,8]

Synthesis of PSUe. Undecenoic acid was obtained from Aldrich and neutralized with sodium hydroxide to give the sodium salt. Poly(sodium undecenoate), PSUe, used in this investigation was synthesized in aqueous solution in two different ways: (a) in micellar form by γ radiation (^{60}Co γ source at a dose rate of 21 krad/min for 2 h; monomer concentrations of 0.15–0.2 M were used) and (b) in liquid crystal form by using $K_2S_2O_8$ as an initiator, at 60 °C, following the method reported by Friberg[14,15] (here the monomer concentration was 2.5 M).

Results and Discussion

The IR spectra in Figure 1 show that the characteristic absorbance of the double bond at 3100 cm^{-1} was absent after polymerization of the monomer surfactant sodium undecenoate (SUe) in either micellar or liquid crystal form. Dilution of the reactant solutions with solutions of pyrene in water (concentration 6×10^{-7} M) to the concentration of surfactant well below cmc did not cause any loss of fine structure of the pyrene fluorescence spectra. This also indicates that SUe was polymerized. The earlier reports[12,13] of polymerizations of sodium undecenoate by γ radiation indicated that small polymers (10 monomer units, molecular weight 2000) were found. The present work produced polymers with much higher molecular weights. The different sizes of polymers obtained may be explained by the unique characteristics of the monomer surfactant. Several different transition regions were observed in plots of specific conductance vs concentration of monomer, corresponding to the formation of different types of aggregates or micelles.[12] Polymerization in dilute solution, 0.1 M > [SUe] > 0.043 M, leads to low molecular weight polymer, because polymerization occurs inside the core of the smaller surfactant aggregate (or premicelle) formed in this first transition region. The micellar size changes to larger aggregates from 0.15 to 0.2 M in the second transition region, thus leading to larger polymers. For the same reason, polymerization in larger liquid crystals also forms much larger polymers. The molecular weight of a polymer synthesized in the liquid form in the present studies is in good agreement with that obtained by Friberg.[16] The molecular weights of samples were measured by GPC in their acid form in tetrahydrofuran and calibrated with standard samples of polystyrene. The polymer synthesized by γ radiation was studied in detail, while the other polymer synthesized in the liquid crystal form was used for studying the molecular weight effect on the aggregation number of monomer units in polymerized micelles. The molecular weights of polymer samples were estimated to be 1.2×10^4 and 5.0×10^4 g/mol for methods a and b, respectively.

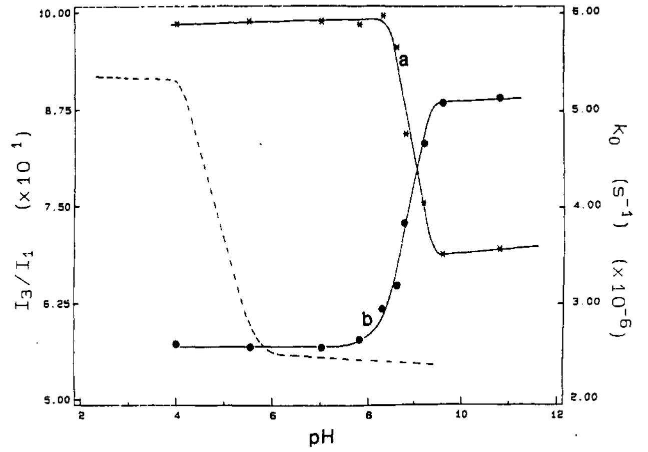

Figure 2. Plot of the intensity ratio, I_3/I_1 (a), and natural decay rate, k_0 (b), of pyrene fluorescence vs pH in aerated aqueous solutions. [pyrene] = 2×10^{-6} M. The dashed line is the plot of I_3/I_1 vs pH in PMA.

Fluorescence of Pyrene in PSUe. The pyrene fluorescene intensity ratio of peak 3 to peak 1 was used to monitor the environment of excited pyrene in polymeric micelles under various pH conditions. The results are given in Figure 2a and exhibit a pattern similar to that found in PMA (dashed line), but the transition induced by pH in PSUe solution occurs at much higher values than in PMA. The ratio I_3/I_1 of pyrene fluorescence in PSUe at pH < 8 is close to 1, indicating that pyrene is solubilized in a hydrophobic host structure. Increasing the pH leads to a sharp change in the I_3/I_1 ratio and the fluorescence decay constant, k_0. It is evident that the pyrene probe in aqueous solution of PSUe experiences a more polar environment at higher pH compared to that at low pH. The effect reaches a limit at pH 10, and the transition point of plots of I_3/I_1 vs pH and k_0 vs pH (shown in Figure 2b) is about pH 8.5. The transition at such high pH for PSUe compared to PMA is attributed to the ability of the hydrophobic interaction of the long hydrocarbon segments to stabilize the compact conformation of the polymerized micelle at higher pH. It is noteworthy that the ratios of I_3/I_1 in aqueous solutions of PSUe, even at pH ≥ 10, are substantially higher than those in water (0.68–0.7 vs 0.52). Consequently, the polymer at pH > 10 may be regarded as a loose hydrophobic structure and, unlike PMA at pH > 7, is not completely opened into an extended form: pyrene is still hosted in a hydrophobic structure at pH 10.

The ratio of I_3/I_1 in PSUe at pH < 8 is slightly lower than that in PA-18K$_2$ (1.1). It is reasonable to assume that the lower hydrophobicity of the compact polymerized micelle is due to the relatively short hydrocarbon side chain in PSUe. This also leads to the different effect of pH on polymer conformations. PA-18K$_2$ forms a compact structure over the entire pH range; conversely, PSUe undergoes a conformational transition from a compact to a loose micellar structure at pH above 8.

The time-dependent fluorescence measurements are consistent with the observations of changes of the I_3/I_1 ratio. The decay curves of pyrene fluorescence in PSUe are shown in Figure 3. The decays are single exponential either at pH 8 or pH 10 and fit first-order kinetics. The

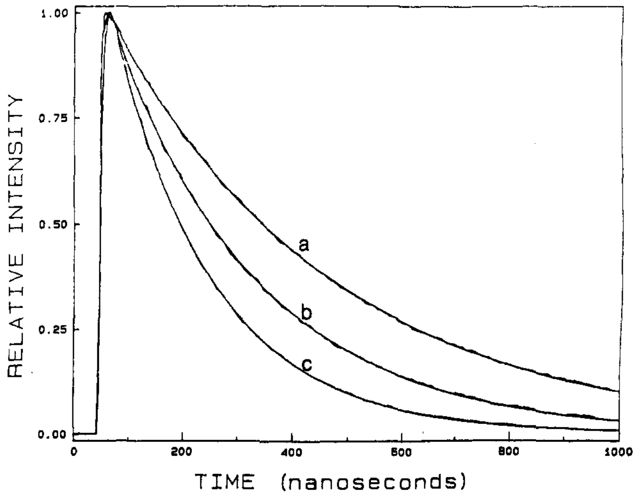

Figure 3. Decay curves of pyrene fluorescence in aqueous solutions of PSUe (a) at pH 7.6, (b) at pH 10, and (c) in distilled and deionized water. The concentration of pyrene in an aqueous solution of PSUe is 2×10^{-6} M; in pure water it is 6×10^{-7} M.

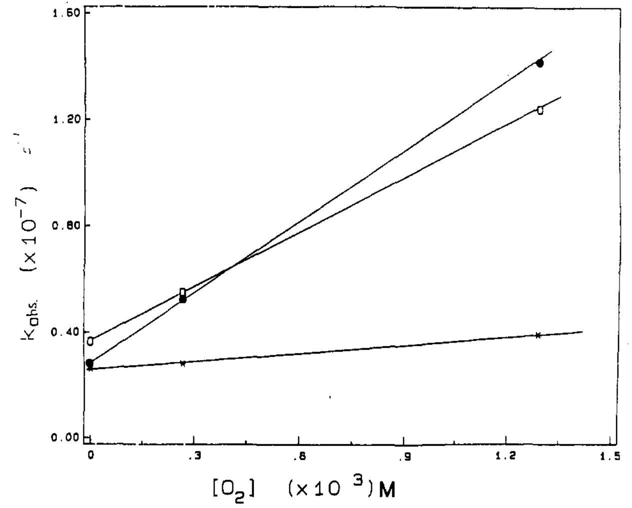

Figure 4. Observed decay rate constants, k_{obs}, for pyrene as a function of oxygen concentration in PSUe solution (*) at pH 7.6, (0) at pH 10, and (●) in a SUa micelle.

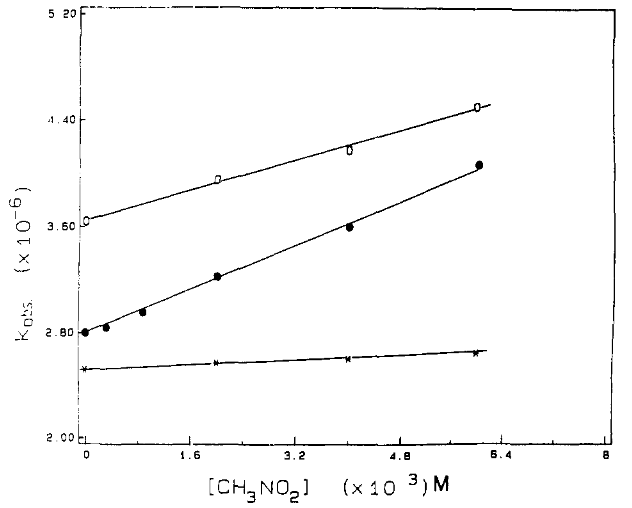

Figure 5. Observed decay rate constants, k_{obs}, for pyrene as a function of CH_3NO_3 concentration (symbols the same as in Figure 4).

Table I
Quenching Rate Constants of Pyrene[a] Fluorescence in Various Systems

	k_q, M^{-1} s^{-1}			
	PSUe[b]			
quencher	pH 7.6	pH 10	SUa[c]	water
decay constant in absence of quencher, s^{-1}	2.5×10^6	3.6×10^6	2.8×10^6	4.8×10^6
O_2	8.6×10^8	5.9×10^9	9.0×10^9	9.8×10^9
CH_3NO_2	1.8×10^7	1.4×10^8	2.0×10^8	9.5×10^8

[a] [Pyrene] = 2×10^{-6} M in micelle, [pyrene] = 6×10^{-7} M in water. [b] Poly(sodium undecenoate) synthesized by γ radiation in micellar form, 1 g/L. [c] Sodium undecanoate, 0.2 M (cmc = 0.058 M).[12]

first-order decay rates at pH < 8 (2.5×10^6 s^{-1}) and at pH 10 (3.7×10^6 s^{-1}) are both smaller than that observed for pyrene in water (5.0×10^6 s^{-1}).

Biomolecular Quenching. The change in the environment of the probe pyrene in the presence of PSUe can also be demonstrated by the restrictive effects that the polymer backbone impose on the approach of quencher molecules such as oxygen and nitromethane. Figures 4 and 5 present the Stern–Volmer quenching of pyrene fluorescence by oxygen and nitromethane in polymerized micelles of PSUe and in micellar SUa. The slopes of the plot of k_{obs} vs concentration of quencher yield quenching rate constants. Table I lists the data on the quenching of pyrene fluorescence in micellar PSUe and SUa systems, where the pyrene molecule is hosted in the polymerized micelle (at pH 7.6 and pH 10) and in a conventional ionic micelle. The quenching rates tend to increase on expansion of the compact polymerized micelle. For the oxygen quenching, there is an increase of 6-fold, on exposing pyrene in a looser polymeric micelle at high pH. The effect is larger in the case of nitromethane, where the increase is about 8-fold. The quenching kinetics are dynamic in nature, indicating that the quencher molecules diffuse in the micelle structure. The data illustrate that the penetration of quenchers to pyrene hosted in PSUe is more inhibited by the polymer at pH < 8 than in PSUe at pH > 10, thus confirming the conformational transition induced by pH.

Pyrene is also located in the hydrophobic region of simple SUa micelles, as seen by the higher I_3/I_1 ratio (0.95) and slower decay rate, k_0 (2.8×10^6 s^{-1}), of the pyrene fluorescence. However, the diffusion of quencher molecules was much less restricted in the unpolymerized micelle than in polymeric micelles. Consequently, quenching rates either at pH 7.6 or pH 10 in PSUe are smaller than those in SUe, as a consequence of the great restrictive effect of the polymer backbone on approach of quencher molecules to pyrene hosted in the compact polymerized micelle, a situation that also exists in the looser polymerized micelle at high pH.

The degree of fluorescence polarization of 2-methylanthracene, *P*, was measured in the above systems in order to gain information about the rigidity of the probe environment in these systems. The data show that *P*'s in PSUe at pH 8 (0.14) and in PSUe at pH > 10 (0.11) are much larger than that in SUa micelles (0.04). This confirms that the probe experiences a much more rigid environment in the polymerized micelle compared to a simple micelle.

Aggregation Number of Monomer in PSUe Micelle. Application of Poisson quenching kinetics in PSUe is only successful in aqueous polymer solutions at pH ≤ 8. Quenching of pyrene or C_4PN^+ by 1-dodecylpyridinium chloride DPC in PSUe at pH > 10 is static at a DPC concentration greater than 2×10^{-5} M, and the intensity decreased without any change of fluorescence lifetime. Quenching experiments in SUa exhibit similar kinetics.

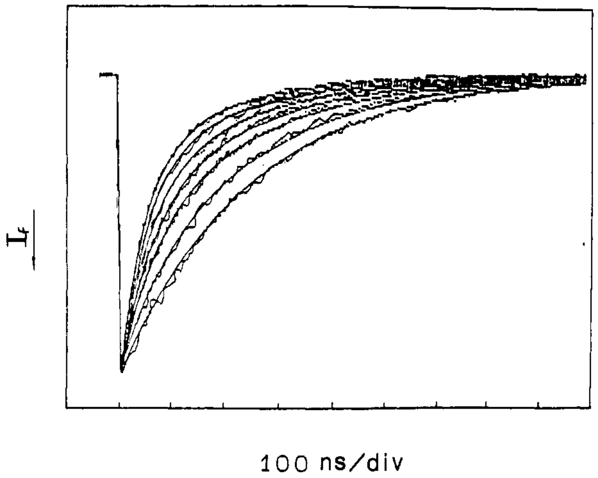

Figure 6. Transient decays for 2×10^{-6} M C_4PN^+ in 1 g/L of PSUe solution at pH 7.6 with 0, 2, 4, 6, 8, 10, and 12×10^{-5} M DPC. The smooth curves are the computer fittings of transient decays to Poisson kinetics.

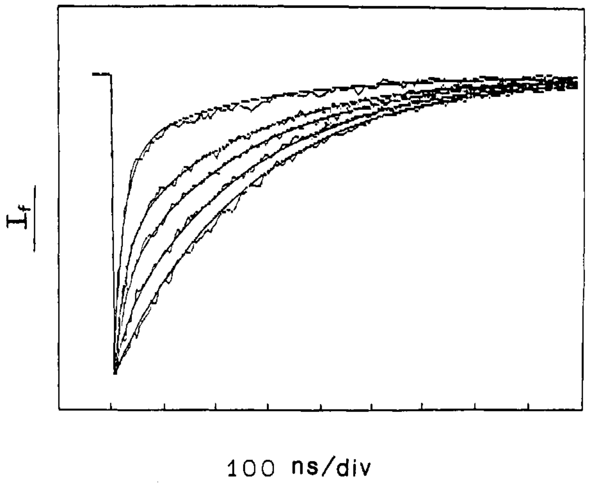

Figure 7. Transient decays for 2×10^{-6} M C_4PN^+ in 0.2 M SUa solution with 0, 1, 2, 3, and 5×10^{-3} M DPC. The smooth curves are as in Figure 6.

The transient decays and curve fittings to the Poisson scheme for 2×10^{-6} M C_4PN^+ in a PSUe micelle at pH 7.6 with various concentrations of DPC are provided in Figure 6. The decays for the SUa micelle are shown in Figure 7 for comparison. The fluorescence decay exhibits an initial sharp portion, which increases with an increase in the quencher concentration, a condition typical of Poisson kinetics. The curves are fitted to the Poisson formulation and provide values for k_0, k_q, and $\bar{n}$

$$I = I_0 \exp\{(-k_0 t) - \bar{n}[1 - \exp(-k_q t)]\} \tag{1}$$

where $\bar{n}$ denotes the average number of quencher molecules per polymerized micelle and k_0 and k_q are the first-order rate constants for the decay of probe in the absence and in the presence of quencher, respectively. The plots of $\bar{n}$ vs [DPC] in various PSUe solutions are linear (shown in Figure 8). The slope of this type of plot is equal to 1/[micelle], thus allowing the calculation of the aggregation number of monomer units, $\bar{N}$, in the polymeric micelle by the equation

$$\bar{N} = \frac{[\mathrm{PSUe}]_m - \mathrm{cmc}}{[\mathrm{micelle}]} \tag{2}$$

where $[\mathrm{PSUe}]_m$ is the concentration of polymer in monomer units, and the cmc is taken as zero as the polymeric micelle does not possess free monomer units. If the DPC quencher molecules are distributed in micelles according to the Poisson model, then the steady-state fluorescence should fit the equation

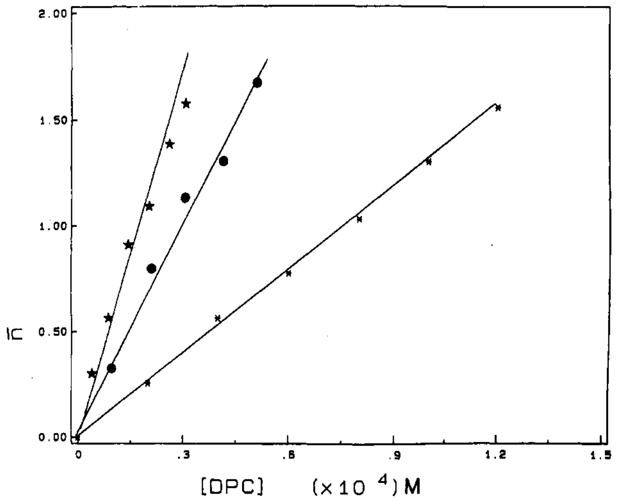

Figure 8. Plots of $\bar{n}$ from curve fitting of transient decays vs [DPC] in PSUe synthesized in micellar form for (*) 1 g/L and (●) 0.5 g/L and (★) in 1 g/L of PSUe synthesized in liquid crystal form.

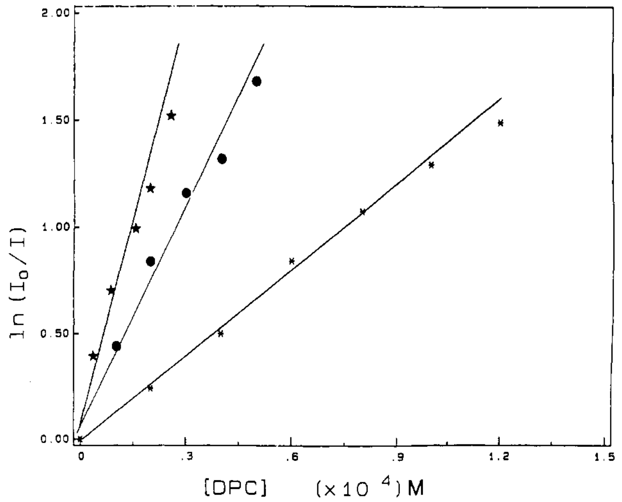

Figure 9. Steady-state quenching of pyrene fluorescence by DPC (symbols the same as in Figure 8).

$$\ln (I_0/I) = \frac{\mathrm{DPC}}{[\mathrm{micelle}]} \tag{3}$$

where I_0 and I are the fluorescence intensity in the absence of and in the presence of quencher. The linear plots of ln (I_0/I) vs [DPC] are given in Figure 9, the slopes of which again should be equal to 1/[micelle], providing another estimate of $\bar{N}$.

Table II summarizes the Poisson kinetics parameters from transient decay measurements and also steady-state measurements. The results from transient fits are in good agreement with those from steady-state measurement in PSUe. However, the data in the SUa micellar system show that $\bar{N}$ values determined from the transient measurements are slightly lower than those from the steady-state measurements. This may be due to some static component in the quenching kinetics. The data shown that one polymer molecule PSUe of molecular weight 1.2×10^4 or 5×10^4 forms one polymerized micelle. The Poisson quenching rate constant in polymerized micelles is 5-fold lower than that in SUa micelles, again indicating the greater rigidity of the polymerized micelle compared to the simple micelle. The PSUe sample synthesized in the

Table II
Poisson Parameters in Quenching of C_4PN^+ Fluorescence by DPC in Various Systems

	PSUe[a]		PSUe:[b]	SUa	
parameters	0.5 g/L	1 g/L	1 g/L	0.088 M	0.2 M
k_0	4.0×10^6	4.0×10^6	4.4×10^6	4.0×10^6	4.0×10^6
k_q	9.0×10^6	8.5×10^6	1.5×0^7	3.3×10^7	3.0×10^7
$\bar{N}$	65	61	267	35	37
$\bar{N}$ steady	67	63	280	37	42
$\bar{M}_w$	1.34×10^4	1.25×10^4	5.5×10^4		
$\bar{M}_w$(HPLC)	1.2×10^4		5.0×10^4		

[a] PSUe synthesized by γ radiation in micellar form. [b] PSUe synthesized in liquid crystal form. [c] $[C_4PN^+] = 2 \times 10^{-6}$ M.

liquid crystal form did not maintain a liquid crystal form in the polymer due to geometric changes on elimination of the double bond. A similar expansion of the compact conformation is observed in these samples on increasing pH > 10. Applications of Poisson quenching kinetics to the monomer SUe aggregate are not successful at this stage of study, because cmc values are uncertain at the different transition ranges.

Conclusion

Poly(sodium undecenoate), PSUe, synthesized from an ionic surfactant with a terminal double bond forms polymerized micelles in aqueous solution. The data suggest that PSUe undergoes a conformational transition at pH around 8.5. At low pH < 8, the polymer forms a compact hydrophobic structure, at high pH > 10, the polymer tends to expand as a looser polymerized micelle, quite unlike PA-18K_2 and/or PMA. PA-18K_2 provides compact host structures for pyrene molecules over the entire pH range, while the PMA polymer tends to open in an extended form at pH > 5 and exposes pyrene to the aqueous environment. The different pH effects are attributed to the different hydrocarbon side chains linked to the polymer backbone. In polymeric micelles compared to simple ionic sodium undecanoate micelles, SUa, the movement of guest molecules is substantially restricted due to the screening effect of the polymer backbone, this occurs even in looser polymer forms at higher pH. Different methods of synthesis did not lead to polymerized micelles of different structures but to different polymer molecular weight. One polymer molecule formed one polymerized micelle in the reported system. The present studies demonstrate that an alternative tailoring of polymer to meet set needs may be achieved by changing the length of the hydrocarbon segment in the monomer surfactant. Marked differences are observed for the two different polymerized micelles PSUe and PA-18K_2. However, a direct comparison of the two structures is not strictly valid due to the different hydrocarbon chain lengths of the surfactants.

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