Study of Self-Associating Amphiphilic Copolymers and Their Interaction with Surfactants

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Received October 26, 1995; Revised Manuscript Received March 11, 1996[⊗]

ABSTRACT: The self-association of copolymers of *N*-isopropylacrylamide and *N*-*n*-octadecylacrylamide (Pnipam-C18) in aqueous solutions was studied by means of time-resolved fluorescence quenching. The discrete domains consist of several polymer chains interacting through their hydrophobic side chains, since the number of aliphatic side chains involved in the microdomain formation (aggregation number) is larger than the number of aliphatic side chains per polymer. By means of titration microcalorimetry, the interaction of the copolymer with surfactants was studied. Strong association between the copolymer and the cationic surfactants *N*-cetylpyridinium chloride (C16PyCl) and cetyltrimethylammonium bromide (CTAB) occurs by partitioning of the surfactants in a noncooperative mechanism. Prior to mixed-micelle formation, individual surfactant molecules adsorb to collapsed polymer coils as can be seen from the large exothermal contribution in the enthalpy curves which result from microcalorimetric titration of surfactant into aqueous Pnipam-C18 solutions.

Introduction

Taking into account the numerous applications of hydrophobically modified polyacrylamides,[1−3] it is of importance to unravel in a systematic way their structure in aqueous solution and to study how their solution structure is affected by the presence of additives, such as surfactants, salts, alcohols, etc.

Two different structural archetypes of associating polymers have emerged: the telechelic associating polymers, in which hydrophobic modifiers are located only at the ends of the water-soluble polymer backbone, and the comb-type associating polymers, in which hydrophobic modifiers are distributed randomly along the polymer backbone. A well-known class of telechelic associating polymers are the urethane-coupled poly(ethylene oxide)s (PEO's) with hydrophobic end groups, often referred to as HEUR-type polymers.[4−6] These associating polymers form micellar clusters or "rosettes" consisting of looped polymer chains with their hydrophobic groups sequestered into a micelle-like core.[7] As the polymer concentration increases, bridging chains begin to link the rosettes into supraclusters, eventually forming a network over the whole solution. Another type of telechelic associating polymers are end-alkylated poly(*N*-isopropylacrylamide)s (Pnipam-$(C18)_2$'s) prepared by free-radical polymerization of the isopropylacrylamide monomer using the lipophilic initiator 4,4′-azobis(4-cyano-*N*,*N*-dioctadecylpentanamide). The end-alkylated poly(*N*-isopropylacrylamide) derivatives form multipolymeric micelles, consisting of a rigid core of octadecyl chains and a diffuse corona of solvated Pnipam chains.[8] The comb-type associating polymers, on the other hand, are believed to experience predominantly intramolecular associations at low polymer concentrations, with a transition to intermolecular association occurring at a concentration which depends on molecular details such as the length of the hydrophobic modifier and the degree of hydrophobic modification.[9,10] Fluorescence studies reported in this paper have yielded information regarding the degree of association and the aggregation number, describing how many aliphatic side chains are involved in the microdomain formation by comb-type hydrophobically modified Pnipam copolymers. The aggregates are depicted as multipolymeric even in dilute solutions, a result corroborating conclusions reached by Ringsdorf et al.[11] from a study of differently labeled similar amphiphilic Nipam copolymers in experiments based on the photophysical process of direct nonradiative energy transfer between two chromophores.

The interaction of Pnipam-C18 with the cationic surfactants CTAB and C16PyCl is analyzed using titration microcalorimetry as the experimental technique. It is known that cationic surfactants interact with polymers, provided that the latter are sufficiently hydrophobic. No interaction with poly(vinylpyrrolidone) (PVP) and poly(ethylene oxide) (PEO) has been detected,[12,13] but interaction does occur with poly(propylene oxide) (PPO), poly(vinyl methyl ether) (PVME), or poly(vinyl alcohol-*co*-vinyl acetate) (PVOH-Ac) due to the reduction in Gibbs energy concomitant with the transfer of hydrophobic polymer segments to the micellar phase.[14−16]

Experimental Section

Experimental Methods. Fluorescence decay curves were obtained by making use of a mode-locked argon ion laser pumping synchronously a cavity-dumped DCM (4-(dicyanomethylene)-2-methyl-6-(*p*-(dimethylamino)styryl)-4*H*-pyran) dye laser (excitation wavelength after frequency doubling: 330 nm). All fluorescence decay curves were observed under the magic angle (54.44°), contained 8×10^3 peak counts, and were collected in $^1/_2$K data points of the multichannel analyzer. All samples used for fluorescence measurements were degassed by repeated freeze−pump−thaw cycles. The global analysis method used in the analysis of the fluorescence decays has been discussed extensively in previous papers.[17,18] It is well-known that the global analysis method, i.e., when data from

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

S0024-9297(95)01615-9 CCC: $12.00

Table 1. Physical Properties of the Polymers

polymer	composition[a] Nipam:C_{18}	M_n[b]	M_w[b]	M_w/M_n[b]	LCST[c]/°C	T_g[d]/°C
A. Pnipam-C18/100	60:1	50000	88000	1.76	29.5	
B. Pnipam-C18/100	68:1	83500	100000	1.20	27.8	(1) 117 (2) 107 (3) 100

[a] By ^{1}H-NMR: the intensity of the signal corresponding to the septet of the isopropyl proton at $\delta = 4$ is compared to the signal of the octadecylmethylene protons at $\delta = 1.25$ (15 methylene groups have been taken into consideration instead of 17). [b] By GPC (relative to polystyrene). [c] Absorbances at 400 nm (A) and at 550 nm (B) versus temperature. [d] DSC scanning rates of respectively 20, 10, and 5 °C/min. It is possible through the analysis of the glass transition behavior to predict the nature of the copolymer: whereas block or graft copolymers normally have multiple glass transition temperatures which are near the values of T_g for each constituent homopolymer, random or statistical copolymers usually have a single T_g between that of the corresponding homopolymers. Assuming that in the copolymer the free volumes add in proportion to the weight fractions w_A and w_B of the comonomers A and B and using the formula $1/T_{gco} = w_A/T_{gA} + w_B/T_{gB}$, using T_g values for the homopolymers from literature,[24,25] one can calculate Nipam:C18 ratios of 130:1 (DSC, 20 °C/min), 70:1 (DSC, 10 °C/min), or 50:1 (DSC, 5 °C/min).

several different experiments are analyzed simultaneously with common model parameters partly or totally linked, is generally superior to single-curve analysis. Data from time-resolved fluorescence measurements are well-suited for global analysis, a method that has been much used since its introduction.[19,20] Alternative methods are available to analyze decay curves, such as the maximum entropy method (MEM), which is used when the governing kinetic model is not a priori known.[21] Steady-state spectra were recorded with a SPEX Fluorolog 212. Absorbance spectra were taken with a PU8700 series UV−vis spectrophotometer. The hydrodynamic radius and diffusion coefficients of the polymer aggregates in water were determined by photon correlation spectroscopy using the 488 nm line of an argon ion laser as light source and a digital correlator to determine the intensity correlation function. The aqueous polymer solutions were made dust-free by filtering them with 450 nm membrane filters (Millipore, HV 13). To ensure reproducibility and to prevent shear-induced degradation of the polymer chains, this filtration process was carried out slowly. The microcalorimetric measurements were performed using an Omega isothermal titration microcalorimeter (Microcal, Northampton, MA).[22,23] The degassed sample solutions were stirred to ensure complete mixing. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AMX 400 spectrometer with TMS as external reference. The glass transition temperature was measured using a Perkin-Elmer DSC7.

Chemicals. Probes and Quencher. Pyrene (99% Py, Aldrich Chemical Co.) was purified by repeated recrystallization from ethanol and subsequent sublimation. 1-Ethylpyrene was purchased from Molecular Probes, Inc. *N*-Cetylpyridinium chloride monohydrate (98% Aldrich Chemical Co.) was purified by Soxhlet extraction with diethyl ether.

Polymers. Poly(*N*-isopropylacrylamide-*co*-*N*-*n*-octadecylacrylamide) (Pnipam-C18/*x*) was obtained by radical copolymerization in dioxane at 60 °C under an argon atmosphere with azobis(isobutyronitrile) (AIBN) as initiator.[24] The monomers isopropylacrylamide and *n*-octadecylacrylamide were purchased from Kodak and Norticon, respectively. The polymers were recovered from dioxane (40 mL) by precipitation in diethyl ether (800 mL) and filtered. The unreacted monomers were extracted from the polymer by Soxhlet extraction with diethyl ether (the polymer being insoluble in diethyl ether) until no signals from the monomer could be observed in the ^{1}H-NMR spectra (three doublets of doublets at the δ values around 6.25, 6.1, and 5.6 ppm refer to the monomer protons of the double bond, respectively, in the cis, geminal, and para position of the amide group; the three signal groups are superimposed on a broad signal of the polymer amide group). The removal of unreacted acrylamide is necessary before performing time-resolved fluorescence experiments, since residual acrylamide monomer could quench the fluorescence of pyrene.[25,26] The dried polymers were dissolved in water and lyophilized. Water was deionized by means of a Millipore Milli-Q water purification system.

Polymer Samples. Pnipam-C18/*x* of two different syntheses has been used. Their physical properties are summarized in Table 1.

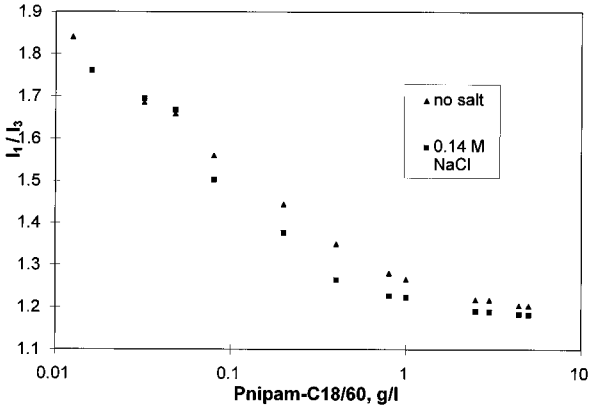

Figure 1. I_1/I_3 ratio of pyrene solubilized in aqueous Pnipam-C18/60 solutions, differing from each other in concentration (from 0.012 to 5 g/L); the presence of 0.14 M NaCl has no effect on the observed ratio.

Study of Self-Association of Pnipam-C18 Studied by Means of Fluorescence Techniques

Stationary Fluorescence. The sensitivity of the vibrational fine structure of pyrene to the polarity of its environment makes it an interesting fluorophore to study the hydrophobicity of aggregating systems such as micelles, domain-forming polymers, or polymer/surfactant clusters.[29] In particular, the intensity (I_1) of the (0,0) band increases in polar solvents whereas that (I_3) of the (0,2) band is essentially unaffected. As a consequence, the ratio $(I_1/I_3)^{py}$ is sensitive to solvent polarity and has been shown to correlate well with other scales of solvent polarity. In water its value is ca. 1.90 whereas in hydrocarbon solvents it has a value of 0.70. In Figure 1 the $(I_1/I_3)^{py}$ ratio is monitored as a function of copolymer concentration. Already at very low concentrations the ratio is much smaller than the value monitored for pyrene in water. The low value of $(I_1/I_3)^{py}$ indicates that by itself the copolymer provides pyrene with hydrophobic domains into which it is entirely solubilized (Figure 1).

Time-Resolved Fluorescence Quenching. 0.25 and 0.5 w/v % Pnipam-C18/68 Solutions. The fluorescence decays of 1-ethylpyrene, solubilized in aqueous Pnipam-C18/68 solutions (2.5 or 5 g/L) and quenched by the immobile quencher *N*-cetylpyridinium chloride,[30] are described by the equation

$$I(t) = A_1 \exp[-A_2 t - A_3(1 - \exp(-A_4 t))] \qquad (1)$$

where $A_1 = I(0)$, assuming δ-pulse excitation at $t = 0$, $A_2 = k_0$, the monomolecular decay constant of the excited probe, $A_3 = [Q_m]/[M]$ (=$\langle n \rangle$, the average occupa-

Table 2. Global Analysis of the Fluorescence Decays of 1-Ethylpyrene (5×10^{-6} M), Solubilized in 0.25 and 0.50 w/v % Pnipam-C18/68 Solutions, in the Absence or Presence of *N*-Cetylpyridinium Chloride[a]

[Q]/mM	$A_3 = [Q]/[M] \pm \sigma$	k_q (10^6 s^{-1})	[M]/mM $\pm \sigma$	χ^2
	0.25 w/v % Pnipam-C18/68			
0.01	0.457 ± 0.03	3.4	0.0219 ± 0.0015	0.94
0.02	0.928 ± 0.03		0.0215 ± 0.0008	1.04
0.03	1.358 ± 0.04		0.0221 ± 0.0007	1.16
0.05	2.297 ± 0.05		0.0218 ± 0.0005	1.13
	0.50 w/v % Pnipam-C18/68			
0.02	0.62 ± 0.07	2	0.032 ± 0.030	1.16
0.04	1.14 ± 0.08		0.035 ± 0.002	1.11
0.06	1.72 ± 0.09		0.035 ± 0.002	1.10
0.08	2.33 ± 0.11		0.034 ± 0.002	1.01

[a] Equation 1 was used for the fitting of the decay curves (DCM laser, λ_{ex} at 330 nm, time increment 1.53 ns (time window 783 ns), $T = 20$ °C).

tion number), with $[Q_m]$ the concentration of quenchers solubilized in the microdomains and [M] the microdomain concentration, and $A_4 = k_q$, the first-order intramicellar quenching rate constant for a micelle with one quencher and one probe (s^{-1}). From Infelta's[31] and Tachiya's treatments,[32] it follows that the model is valid under certain conditions: (i) the aggregates are of equal size, (ii) the probes and quenchers distribute in a Poissonian way among the micelles, (iii) the probe is stationary in its host aggregate during the fluorescence process, and (iv) the quenchers do not interact with each other. Condition (iii) can be fulfilled by the choice of probe, e.g., 1-ethylpyrene, which is, due to its low water solubility, stationary in the host micelle within the excited-state lifetime. The last condition implies that the quenching rate is proportional to the number of quenchers in the aggregate and that the entry and exit rates for a quencher between the bulk and the aggregate are independent of the number of quenchers located in the aggregate. In the case of mobile quenchers, migrating between the aggregates, the model also holds but the physical meaning of the parameters A_1-A_4 will be diferent, a situation which has been investigated both theoretically[33,34] and experimentally.[35,36]

The model parameters A_2 and A_4 were linked within the same experimental series and were obtained by simultaneous analysis of four decay curves. The fitting of the fluorescence decay curves to eq 1 provides statistically acceptable fits (Table 2). In this paper, two different time increments were used, to allow the development of the quencher-concentration-independent part of the decay. It is known from other measurements[37] that when the quenching is slow or the probe or quencher migrates, a too narrow time window can lead to wrong conclusions. (A longer time increment leads to a more pronounced exponential tail and gives more accurate estimates of the aggregation number.)

In the copolymer poly(*N*-isopropylacrylamide-*co*-*N*-*n*-octadecylacrylamide), Pnipam-C18/68, the number 68 refers to the fact that for each 68 monomers there is 1 octadecylacrylamide unit incorporated. The molecular weight of this repeating unit, expressed in grams per mole, is 8007. Using a 0.5 w/v % Pnipam-C18/68 solution, the concentration of aliphatic side chains amounts to (5 g/L)/(8007 g/mol) or 0.6 mM. The aggregation number is than 0.6 mM/0.035 mM or 17 (±1). For the 0.25 w/v % Pnipam-C18/68 solution, the domain concentration, recovered from the A_3 parameter, amounts to 0.0218 mM, whereas the concentration of aliphatic side chains is (2.5 g/L)/(8007 g/mol) or 0.3 mM. This

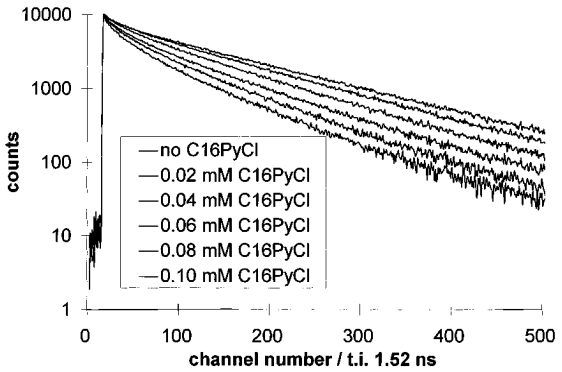

Figure 2. Time-resolved fluoresence decay traces for ethylpyrene (10^{-5} M) in a 0.5 w/v % Pnipam-C18/68 solution in the absence or presence of *N*-cetylpyridinium chloride.

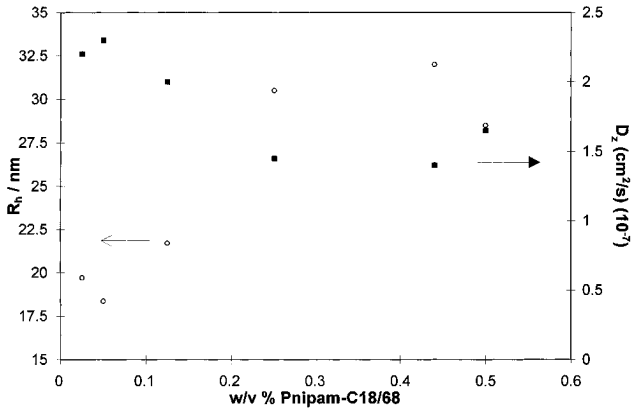

Figure 3. Hydrodynamic radius R_h (nm, error ±1 nm) (left *y*-axis, open circles) and translational diffusion coefficient (cm^2/s (10^{-7}), error ±0.2 cm^2/s (10^{-7})) (right *y*-axis, solid squares) plotted versus Pnipam-C18/68 concentration (w/v %).

gives an aggregation number of 0.3 mM/0.0218 mM or 14 (±1). Taking into account that the molecular weight M_w in tetrahydrofuran is 100 000 (Table 1) and that the molecular weight of the repeating unit is 8000, we conclude that for both polymer solutions more than one polymer chain is involved in the microdomain formation process or, in other words, that microdomain formation results both from intra- and interpolymer side chain interactions.

N-Cetylpyridinium chloride, which was used as a quencher, is also a surfactant and forms in the absence of polymer micelles at a concentration of 1 mM. The observation that quenching occurs at a concentration of 0.01 mM indicates that in the three-component system (water/Pnipam-C18/surfactant) detergent molecules start to interact with the polymer at a concentration much lower than the critical micelle concentration (cmc).

Study of Pnipam-C18/68 Aggregates in Water by Quasielastic Light Scattering

In Figure 3 the translational diffusion coefficient (cm^2/s) (black squares, right *y*-axis) is plotted versus Pnipam-C18 concentration (w/v %). Its value decreases with increasing concentration. The white circles refer to the hydrodynamic radius (nm) (left *y*-axis). The observed increase of the hydrodynamic radius with increasing polymer concentration suggests the formation of interpolymeric aggregates at higher concentration. The hydrodynamic radius of the aggregates in a 0.025 w/v % Pnipam-C18/68 solution is 19.7 nm. This value is 2.5 times smaller than the one for the Pnipam homopolymer

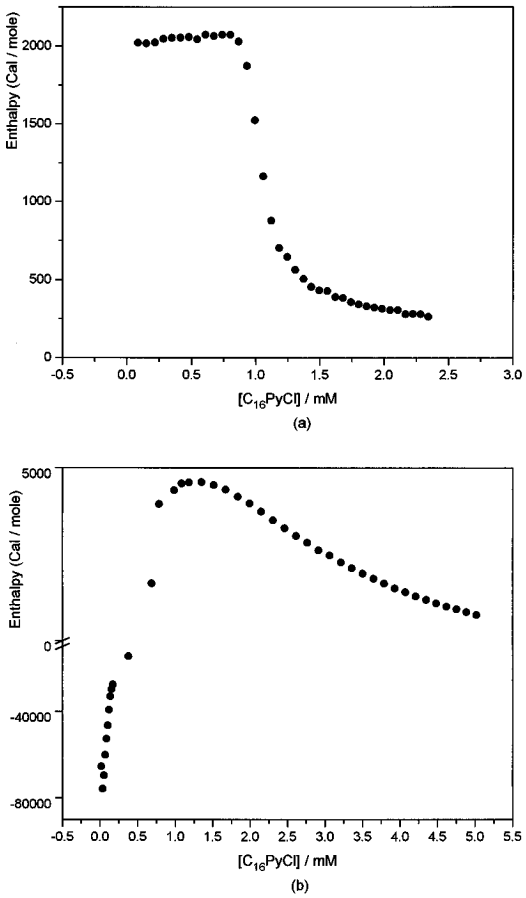

Figure 4. (a) Enthalpy of dilution (cal/mol) of C16PyCl in water. (b) Enthalpy of dilution (cal/mol) of C16PyCl in an aqueous Pnipam-C18 solution (0.5 w/v %) at 30 °C.

(0.01 w/v %) and indicates a more compact polymer coil conformation when the Pnipam polymer has hydrophobic aliphatic side chains.

Interaction between Pnipam-C18/68 and Cationic Surfactants Studied by Titration Microcalorimetry

The microcalorimetric measurements were carried out using an Omega isothermal titration calorimeter containing two cell compartments: a sample cell and a reference cell. The calorimetric titration experiments consisted of series of consecutive additions of concentrated surfactant solutions (concentration ≫ cmc, but < critical rod concentration (crc)) to the calorimeter sample vessel initially containing aqueous Pnipam-C18/*x* solutions (between 0.05 and 0.5 w/v %). The heat absorbed or evolved was recorded, and after thermal equilibrium was reached, the next injection was given. The resulting enthalpy curves (obtained by integrating the signal peaks) and cumulative enthalpy curves provide detailed information about polymer−surfactant interactions and are compared to the curves resulting from titration of surfactant in water only.

The microcalorimetric titration curve for C16PyCl in water (Figure 4a) can be essentially characterized by three regions.[39] In a premicellar region I, the injected micelles disintegrate completely and the enthalpy change for the demicellization and loss of intermicellar interactions is recorded. Region II is the transition region around the cmc. In the post-transition region III, the injected micelles remain intact and only a very small enthalpy change for reduction of intermicellar interaction is recorded. The enthalpy of micellization is calculated as the difference in dilution enthalpy between regions I and III. The micelle formation is essentially a cooperative process, requiring simultaneous participation of an ensemble of amphiphilic molecules. The enthalpy curve for the binary system C16PyCl/H_2O has the typical sigmoidal shape.

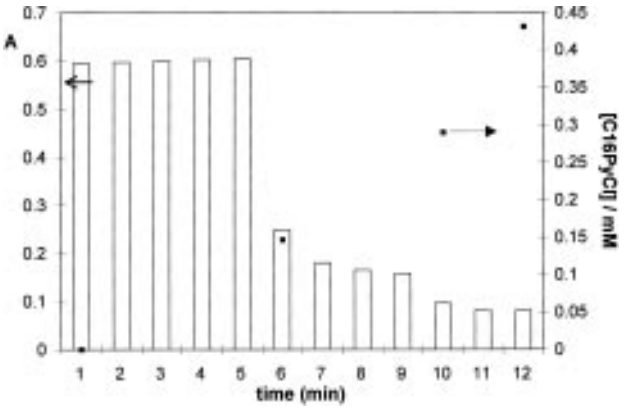

Figure 5. Absorbances at 29.5 °C (large white rectangles, left *y*-axis) plotted versus time in the absence or presence of C16PyCl (small black squares, right *y*-axis).

The enthalpy curves for the ternary systems SURF/H_2O/Pnipam-C18 are far more complex due to the specific polymer−surfactant interactions. It is essential to keep in mind that a number of experiments have been performed at 30 °C, a temperature at which phase separation of Pnipam-C18 has occurred prior to the titration. Adding surfactant results in an increase of the LCST as can be observed in Figure 5. Absorbances (left *y*-axis, large white rectangle) of a 0.2 w/v % polymer solution were recorded as a function of time at 29.5 °C, in the absence or presence of different C16PyCl concentrations (right *y*-axis, small black squares).

The events during the titration of an initial two-phase system Pnipam-C18/H_2O with detergent C16PyCl (Figure 4b) can be summarized as follows. At the first additions of surfactant resulting in final molarities below the critical micelle concentration (cmc), the added micelles are diluted and break up to yield monomers in solution which interact with the collapsed multipolymeric demixed phase. The recorded enthalpy is a superposition of multiple effects: dilution of micelles, adsorption of surfactant monomer to the collapsed entangled polymer coils (milky demixed polymer-rich phase), mixing of the polymer subphase, etc. The net result is an initial exothermal part. When more monomer is added, the interaction becomes endothermal. This is probably due to ion−ion interactions of added monomer, being more important at higher surfactant concentrations (endothermal part). From the top of this endothermal contribution, mixed-micelle formation is believed to take place. The shape of the enthalpy curves for the ternary systems indicates a noncooperative type of binding and suggests an equilibrium between adsorbed micelles and free micelles that is shifted toward the latter at higher surfactant concentration. In Figure 6 the cumulative enthalpy is given as a function of added surfactant. The upper curve refers to an experiment performed at 25 °C. Almost no exothermal effect is observed at this temperature. The two lower curves were obtained at 30 °C. The observed minimum in the initial part denotes the point where the balance between exothermal and endothermal contributions shifts in favor of the latter.

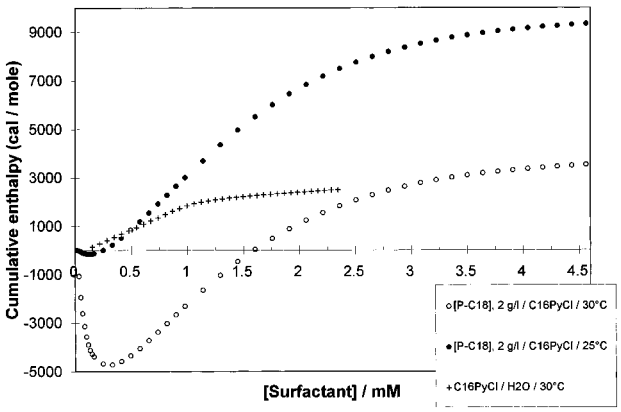

Figure 6. Cumulative enthalpy of dilution versus [C16PyCl] (mM) present in an aqueous Pnipam-C18 solution (0.2 w/v %) at 25 °C (●) and 30 °C (○); for comparison the cumulative enthalpy of dilution versus [C16PyCl] (mM) in water at 30 °C is shown (+).

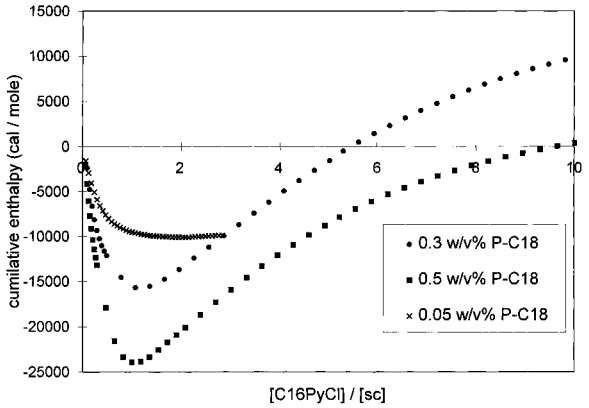

Figure 7. Cumulative enthalpy of dilution plotted versus the molar ratio [C16PyCl]:[hydrophobic side chains] at 30 °C resulting from injection of aliquots (μL) of (a) a 0.635 mM C16PyCl solution in an aqueous 0.05 w/v % Pnipam-C18 solution (×), (b) a 23 mM C16PyCl solution in an aqueous 0.3 w/v % Pnipam-C18 solution (●), and (c) a 23 mM C16PyCl solution in an aqueous 0.5 w/v % Pnipam-C18 solution (■).

In Figure 7 the cumulative enthalpy is plotted against the molar ratio [C16PyCl]:[hydrophobic side chains]. The initial exothermal part in the cumulative enthalpy curve reaches a minimum at a molar ratio [C16PyCl]:[hydrophobic side chains] of 1 irrespective of the polymer content, suggesting the formation of a 1/1 complex.

That the initial exothermal part results from surfactant monomer−polymer interaction is demonstrated in an additional experiment (the upper cumulative enthalpy curve in Figure 7) where a 0.05 w/v % Pnipam-C18 solution was titrated with C16PyCl surfactant monomer (concentration of surfactant in syringe: 0.635 mM < cmc). Instead of a minimum, the cumulative enthalpy curve asymptotically levels off to a value that is reached at the same molar ratio [C16PyCl]:[side chains]. The concentration of surfactant at the end of the experiment (0.14 mM) is too small for micelle formation or polymer−micelle cluster formation to take place.

Conclusion

Based on results from time-resolved fluorescence quenching experiments, it was possible to define an aggregation number, describing how many aliphatic side chains are involved in the microdomain formation. Since this value is greater than the number of side chains per polymer, this inevitably leads to the conclusion that the discrete domains consist of several polymer chains interacting through their hydrophobic side chains. An important feature relates to the absence of exchange of probe and quencher during the decay of the excited state and is visualized by the parallel linear tails of these decays for different quencher concentrations at longer times. The distinct initial nonexponential decay indicates a sufficient quenching of *N*-cetylpyridinium chloride. The latter is both a quencher and a surfactant and forms in a polymer-free aqueous solution micelles at a concentration of 1 mM. The observation that quenching of ethylpyrene (solubilized in the hydrophobic domains) already occurs at a quencher concentration of 0.01 mM indicates that for this three-component system (water/Pnipam-C18/surfactant) the surfactant monomers start to interact with the polymer at a concentration much lower than the cmc. The possibility for binding of surfactant monomers or very small aggregates to the polymer at concentrations below the cmc has been indicated in several papers.[40,41] Clearly, there is always a distribution equilibrium for the surfactant monomers between the polymer and the bulk. The structural details of such a "preassociation" are difficult to measure due to the extremely low concentrations of preassociated molecules. The enthalpy curves and cumulative enthalpy curves, obtained from microcalorimetric experiments, clearly denote an initial exothermal interaction between surfactant monomer and collapsed polymer coils. The observation that the initial exothermal part in the cumulative enthalpy curve reaches a minimum that occurs at a molar ratio [C16PyCl]:[hydrophobic side chains] of 1 suggests the formation of a 1/1 complex. Further addition of surfactant results in endothermal contributions (probably ion−ion interactions) up to a surfactant concentration at which polymer−micelle cluster formation can take place. The titration curves obviously indicate a strong noncooperative association of C16PyCl to the hydrophobic copolymer. The polymer−micelle clusters will be further investigated at different temperatures using time-resolved fluorescence quenching.

Acknowledgment. H.F. is a predoctoral fellow of the Vlaams Instituut voor de Bevordering van het Wetenschappelijk-Technologisch Onderzoek in de Industrie (IWT). The DWTC is gratefully acknowledged for financial support through IUAP-II-16 and IUAP-III-040. Dr. E. Hendrickx, Dr. M. Triest, and Prof. Dr. A. Persoons are thanked for the assistance in the use of their quasielastic light scattering instrumentation.

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MA951615X