Effect of Surfactant on the Intra- and Intermolecular Association of Hydrophobically Modified Poly(*N*,*N*-dimethylacrylamide)

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ABSTRACT: We prepared two copolymer precursors of *N*,*N*-dimethylacrylamide containing the reactive comonomer *N*-acryloxysuccinimide. One was obtained by conventional radical polymerization (M_n = 251 600 g·mol^{-1}; M_w/M_n = 2.20) and the other by controlled radical polymerization using the RAFT (reversible addition−fragmentation chain transfer) process (M_n = 49 200 g·mol^{-1}; M_w/M_n = 1.21). We used these precursors to prepare hydrophobically modified chains containing grafted dodecyl (DO) groups and fluorescent dyes: pyrene (PY), phenanthrene (PHE), or anthracene (AN). The interaction of these polymers with an anionic surfactant, sodium dodecyl sulfate (SDS), was studied by steady-state and time-resolved fluorescence. By following the formation of PY excimer and measuring the efficiency of energy transfer from PHE to AN labeled chains, we characterized the dynamics of association and the type and morphology of the resulting hydrophobic aggregates. We observed some aggregation of the poly(*N*,*N*-dimethylacrylamide) chains containing grafted DO and PY groups in water, which was enhanced by addition of a small amount of SDS. At high surfactant content, SDS micelles encapsulate individual hydrophobic groups, reducing their association. Using equivalent chains, some labeled with PHE and others with AN, we obtained direct proof of the formation of intermolecular aggregates and were able to characterize their evolution in number and size upon addition of SDS. The critical aggregation concentration (CAC) and aggregation number (N_{agg}) of the mixed SDS/polymer micelles are lower than the critical micelle concentration (cmc) and N_{agg} of SDS in water. This is due to the nucleation effect of the hydrophobic groups grafted to the polymer, which induce the aggregation of SDS at lower concentrations. We determined a lower CAC for the smaller polymer, which has a higher hydrophobic content.

Introduction

The complex interactions between water-soluble polymers and surfactants are primarily of interest for their influence in solution rheology. Water-born fluids containing mixtures of polymers and surfactants have been extensively studied, in part because of their many industrial applications, including coatings, oil recovery, cosmetics, food preparation, and pharmaceuticals.[1,2] In water, surfactant molecules aggregate to form micelles at the critical micelle concentration (cmc).[3] However, the presence of polymers induces the aggregation of surfactant micelles onto the polymer chains at a critical aggregation concentration (CAC) which is lower than the cmc of the surfactant in water.[2] In the case of nonionic polymers and ionic surfactants, micellelike aggregates are formed along the polymer chain above the CAC.[4,5]

One of the first water-soluble polymer/surfactant systems to be studied was poly(ethylene oxide) with sodium dodecyl sulfate (SDS).[6] The results showed the existence of two critical surfactant concentrations, both different from the cmc of the surfactant in pure water. The first is located below the cmc of SDS and corresponds to the surfactant concentration at which interaction with polymer first occurs (the CAC). The second is located above the cmc of the surfactant and corresponds to the concentration at which all the polymer sites available for interaction are saturated, with any further added surfactant forming free micelles in solution.[7] The CAC is largely independent of the polymer concentration, while the maximum amount of polymer-bound surfactant in the system increases linearly with the total polymer concentration.[8] Surfactant micelles bind to the polymer chain, which can be modeled as a "necklace" decorated with the surfactant micelles.[9] According to this model, the chain is elongated to reduce the electrostatic repulsion between the micelles. In fact, chain stretching[10] and polyelectrolyte behavior in viscosimetric measurements[11] have been observed in nonionic polymer/surfactant mixtures in water.

The interaction of surfactants with hydrophobically modified polymers has raised a great deal of attention.[7,12−21] These polymers are usually composed of a water-soluble backbone, decorated with hydrophobic groups. In water, they adopt a micellelike structure with the hydrophobic groups forming aggregates, which are protected from water by an outer layer of polymer segments.

Nonionic water-soluble polymers, containing a small number of hydrophobic alkyl or aryl groups as aggregation sites, show interesting rehological properties in solution,[7,22−25] and unique interactions with phospholipid bilayers and surfactants.[26] The hydrophobic groups, grafted to the polymer backbone or attached as end groups, favor intra- and interpolymer associations in order to minimize their exposure to water.[13] When the polymer concentration is increased above the overlap concentration C^* of the hydrophobically modified chain, interpolymer associations become more important than the associations between hydrophobic groups of the same chain, and can induce the formation of transient networks.[26,27]

In the presence of surfactants, the hydrophobic groups grafted to the polymer chains induce the nucleation of

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mixed polymer/surfactant aggregates at concentrations lower than the cmc of the surfactant in water.[7,22,23] The bridging of hydrophobe clusters by surfactant micelles reinforces interpolymer cross-links, increasing the viscosity as more surfactant is added. However, at high surfactant concentrations, the hydrophobes are separated into individual mixed micelles, disrupting the hydrophobic associations and decreasing the viscosity.[7,13] At even higher surfactant concentrations, the number of micelles equals or exceeds the number of hydrophobic groups of the polymer, and most interpolymer bridges are destroyed. The resulting repulsive interactions between the micelles decorating the chains tend to expand the polymer.[10−12]

Interactions between surfactant and hydrophobically modified hydroxyethylcellulose,[12] poly(ethylene oxide),[6−9,28−30] polyacrylamides,[7,22,23,31,32] poly(acrylic acid),[24,33] and their copolymers[34] and also thermosensitive polymers such as poly(*N*,*N*-diethylacrylamide)[35] and poly(*N*-isopropylacrylamide),[36−40] were studied by different methods, including fluorescence techniques with either external probes or covalently linked labels.[19,25,33,41−49] F. Winnik has reviewed the study of these interactions by fluorescence.[2]

In the present study, pyrene (PY), phenanthrene (PHE), and anthracene (AN) dyes are covalently linked to the polymer and, thus, are unable to diffuse freely in solution. From the emission of PY excimer we can detect the formation of hydrophobic aggregates very efficiently.[50−52] On the other hand, the electronic energy transfer from PHE labeled chains to AN labeled chains (occurring by a dipole−dipole coupling mechanism[53] that strongly depends on the donor−acceptor distance) was used to specifically detect intermolecular hydrophobic association and probe the size of the aggregates.[54,55] We report results obtained for aqueous mixtures of SDS and copolymers of *N*,*N*-dimethylacrylamide hydrophobically modified with a low fraction of dodecylamine and either pyrene, anthracene, or phenanthrene butyl derivatives (HM−polyDMA), at surfactant concentrations ranging from below to above its cmc in water. We describe steady-state and time-resolved fluorescence measurements of two HM−polyDMA chains, with different molecular weights and hydrophobic content. We determine the critical aggregation concentration (CAC) for the formation of mixed micelles of surfactant and polymer hydrophobic groups by following the fluorescence of PY labeled HM−polyDMA as a function of SDS concentration. Time-resolved fluorescence measurements of the same samples were used to obtain the aggregation number (N_{agg}) of the mixed micelles.

To distinguish between intra- and intermolecular association, we studied the energy transfer between two HM−polyDMA samples, one labeled with PHE and the other with AN. We detected the existence of intermolecular association even at relatively low polymer concentration and in the absence of SDS. Small amounts of SDS though, increase the number of mixed micelles containing hydrophobic groups from different chains. At surfactant concentrations above the CAC, we observed the disruption of intra- and intermolecular associations, with the polymer hydrophobic groups becoming isolated in different mixed micelles.

Experimental Section

Materials. *N*,*N*-Dimethylacrylamide (DMA, Aldrich, 99%) was distilled under reduced pressure (75 °C; 10 mmHg) to remove the inhibitor. The comonomer, *N*-acryloxysuccinimide (NAS), was synthesized as previously described.[56] 2,2′-Azobis(isobutyronitrile) (AIBN, Fluka, 98%) was purified by recrystallization from ethanol, and *tert*-butyl dithiobenzoate (*t*-BDB) was synthesized according to a previously published procedure.[57,58] *N*,*N*-Diisopropylethylamine (DIPEA, Aldrich, 99.5%), tetrahydrofuran (THF, Aldrich, 99%), *n*-hexane (LAB−SCAN, 95%), *tert*-butyl alcohol (Riedel-deHaën, 99+%) and dimethylformamide (DMF, Aldrich, 99.8%) were dried (under sodium or CaH_2) and distilled before use. 1,4-Dioxane (Acros, 99%) was distilled over $LiAlH_4$ (110 °C). All the purified chemicals were stored in the dark, at low temperature and under positive pressure of nitrogen. Dodecylamine (Aldrich, 98%), dimethylamine (Aldrich, 99+%), sodium dodecyl sulfate (SDS, SIGMA, 99%), trioxane (Acros, 99%), diethyl ether (SDS, 99.5%), and dichloromethane (SDS, 99.9%) were used without further purification. Details about the synthesis of the fluorophores used in this work, [4-(1-pyrenyl)butyl]amine hydrochloride, [4-(9-anthracenyl)butyl]amine hydrochloride and [4-(9-phenanthrenyl)butyl]amine hydrochloride, are reported elsewhere.[59] Spectroscopic grade methanol (MeOH, Merck, 99.9%) and Milli-Q water were used to prepare the solutions for the fluorescence measurements.

Table 1. DMA/NAS Random Copolymers

	poly(DMA_{250K}-*co*-NAS)	poly(DMA_{50K}-*co*-NAS)
no. av mol wt (M_n)[a]	251 600 g·mol^{-1}	49 200 g·mol^{-1}
polydispersity index (M_w/M_n)[a]	2.20	1.21
molar composition[b]	**DMA** 98 mol % **NAS** 2 mol %	**DMA** 77 mol % **NAS** 23 mol %

[a] Determined by aqueous SEC/LS. [b] DMA and NAS content determined by ^{1}H NMR.

Polymer Synthesis. Two random copolymers of *N*,*N*-dimethylacrylamide (DMA) and *N*-acryloxysuccinimide (NAS), were synthesized by radical polymerization using different techniques. The first DMA/NAS random copolymer, poly(DMA_{250K}-*co*-NAS), with $M_n \approx$ 250K and 2 mol % of reactive NAS units, was synthesized by conventional radical polymerization. The second, poly(DMA_{50K}-*co*-NAS), with $M_n \approx$ 50K and 23 mol % of NAS, was prepared by a controlled radical polymerization (reversible addition−fragmentation chain transfer, RAFT).[60] The RAFT technique offers a good control of molecular weight and composition, with small polydispersity index.[61−63] The characteristics of these two copolymers are summarized in Table 1.

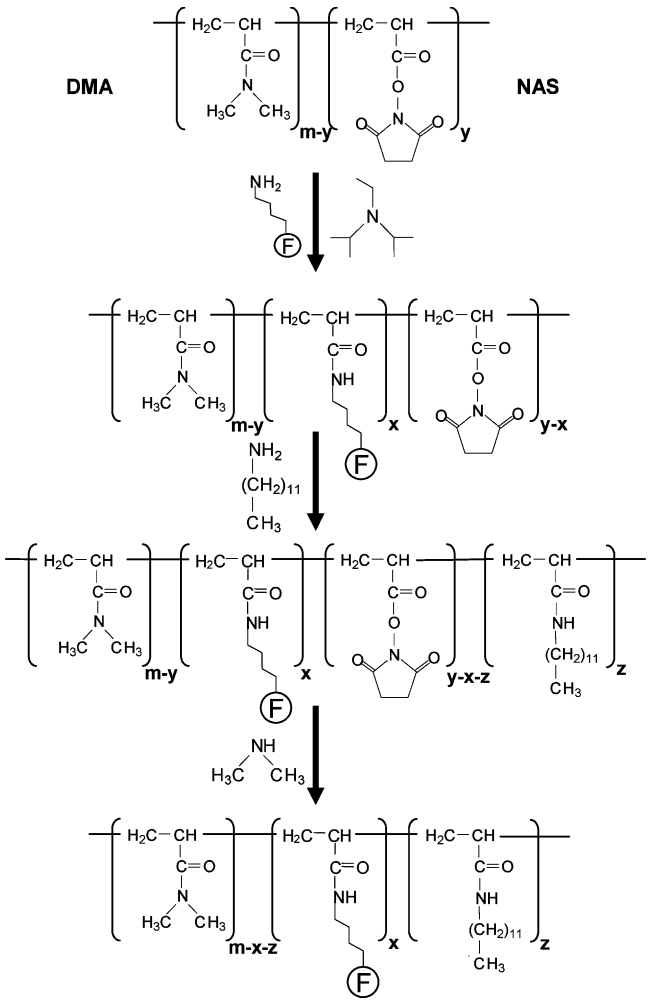
Poly(DMA_{250K}-*co*-NAS). This random copolymer was prepared by conventional radical copolymerization of DMA with NAS in *tert*-butyl alcohol, at 70 °C under nitrogen, using 2,2′-azobis(isobutyronitrile) initiator.[64,65]

Poly(DMA_{50K}-*co*-NAS). The lower molecular weight random copolymer poly(DMA_{50K}-*co*-NAS) was synthesized by RAFT-controlled radical copolymerization of DMA and NAS using 4,4′-azobis(isobutyronitrile) as initiator and *tert*-butyl dithiobenzoate as chain transfer agent (CTA). Details of this synthesis are described elsewhere.[66]

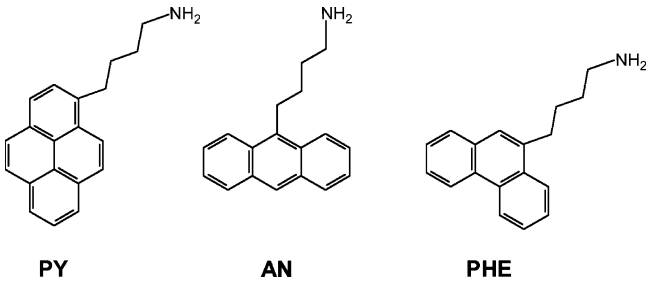
Polymer Labeling. Samples of hydrophobically modified poly(*N*,*N*-dimethylacrylamide) (HM−polyDMA) were prepared by labeling the reactive copolymers precursors poly(DMA_{250K}-*co*-NAS) and poly(DMA_{50K}-*co*-NAS) with dodecylamine (DO) and different fluorescent probes, according to the reactions represented in Scheme 1. We used three different fluorophores (shown in Scheme 2): [4-(1-pyrenyl)butyl]amine hydrochloride (PY), [4-(9-anthracenyl)butyl]amine hydrochloride (AN), and [4-(9-phenanthrenyl)butyl]amine hydrochloride (PHE).[59] The experimental conditions used in the labeling procedure are summarized in Table 2.

DIPEA was added to the solutions of the fluorophores (PY, AN or PHE) containing poly(DMA_{250K}-*co*-NAS) or poly(DMA_{50K}-*co*-NAS) in the appropriated solvent (either THF or DMF), in a round-bottom flask equipped with a magnetic stirrer. The reaction mixture was purged with nitrogen for several minutes and then placed in the dark, for 24 h. Whenever DMF was used, the reaction mixture was thermostated in an oil bath at

Scheme 1. Labeling of the Reactive Copolymer Precursors with Dodecylamine and Fluorescent Groups F = PY, AN, or PHE (described in Scheme 2)



Scheme 2. Fluorescent Dyes Used in the Labeling Reaction of the Copolymer Precursors



40 °C. For THF solutions, the reaction mixture was kept at room temperature. In the case of poly(DMA_{250K}-*co*-NAS), the polymer was then precipitated in *n*-hexane and dried to constant weight. A fraction (0.8 g) of the recovered polymer was added to dodecylamine (DO) dissolved in THF and kept for 48 h at room temperature, in the dark and under inert atmosphere. For the polymers obtained from poly(DMA_{50K}-*co*-NAS), DO was directly introduced in the reaction mixture, which was kept at room temperature for 24 h in the dark. Finally, unreacted NAS units were removed by bubbling dimethylamine into the reaction mixture. The modified polymers were recovered by precipitation in cold diethyl ether and purified by successive precipitations from a dichloromethane solution into cold diethyl ether and dried under vacuum up to constant weight.

Characterization of the Polymer Precursors. The polymerization kinetics of the RAFT polymer poly(DMA_{50K}-*co*-NAS) was followed through the monomer (DMA and NAS) conversions, determined by ^{1}H NMR (Bruker Avance 200 MHz spectrometer), using trioxane, which has no influence on the free radical process, as internal reference.[67] From the DMA and NAS conversion values, the molar composition of the final poly(DMA_{50K}-*co*-NAS) sample was obtained. For poly(DMA_{250K}-*co*-NAS) the conversion of the monomers was complete, and therefore, the final copolymer composition is equal to the feed composition: 98 mol % of DMA and 2 mol % of NAS.

The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of poly(DMA_{250K}-*co*-NAS) and poly(DMA_{50K}-*co*-NAS) were determined by aqueous size exclusion chromatography (SEC/LS) (borate buffer, pH = 9.3, 0.05 mol·L^{-1}, two Waters Ultrahydrogel columns 2000 and 500 Å, a DRI Waters 410 differential refractometer and a Wyatt three-angle MiniDAWN light scattering detector). Analyses were performed by injection of 200 μL of polymer solution (5 mg·mL^{-1}) in borate buffer. The specific refractive index increment (d*n*/d*c*) at 633 nm of polyDMA homopolymer and poly(DMA_{50K}-*co*-NAS) copolymer in borate buffer (0.157 and 0.150 mL g^{-1} respectively), were determined with a NFT ScanRef interferometer.[60]

From the RAFT polymerization kinetics of DMA/NAS copolymers, we calculated the DMA/NAS reactivity ratios $r_{DMA} = 0.36 \pm 0.04$ and $r_{NAS} = 0.6 \pm 0.3$, which led us to conclude that the copolymers are in fact random.[60]

Characterization of Hydrophobically Modified Polymers. The final content of dyes incorporated in the labeled polymers was calculated from the UV−vis absorption spectra measured in a Shimadzu UV-3101PC spectrometer. The presence of the alkyl chain groups in the polymers decrease their solubility in methanol and lead to dye aggregation that influences the correct determination of label content. To avoid this problem, the polymers were dissolved in 500 mM SDS aqueous dispersions, for which the surfactant concentration is well above its critical micelle concentration in pure water (8 mM).[68−70] The molar extinction coefficients of the free dyes PY (ϵ_{345nm} = 37 300 dm^3 mol^{-1}cm^{-1}), AN (ϵ_{351nm} = 3680 dm^3 mol^{-1}cm^{-1}), and PHE (ϵ_{299nm} = 10 600 dm^3 mol^{-1}cm^{-1}) were also obtained in 500 mM SDS aqueous dispersions.

The content in DO groups was determined by ^{1}H NMR in D_2O or $CDCl_3$, using a Bruker Avance 200 MHz spectrometer. The characteristics of the HM−polyDMA copolymers are summarized in Table 3. In Scheme 3, we show a schematic diagram stressing the differences between the two PY labeled polymers.

Sample Preparation. Stock solutions of each pyrene labeled HM−polyDMA (10 g·L^{-1}) and SDS (500 mM) were prepared by dissolving the polymers and the surfactant in Milli-Q water at room temperature, under magnetic stirring and in the dark for 24 h. From these, new solutions with constant polymer content (1 g·L^{-1}) and various surfactant concentrations (1−20 mM) were prepared. The 1 g·L^{-1} solution of poly(DMA_{250K}/PY_{12}/DO_{38}), in 500 mM of SDS, was prepared from the direct dissolution of the solid polymer into the SDS stock solution.

For the energy transfer measurements, stock solutions of poly(DMA_{50K}/PHE_3/DO_{10}) (1.33 g·L^{-1}) and poly(DMA_{50K}/AN_2/DO_{18}) (1.36 g·L^{-1}) were prepared in water. From these, we prepared mixtures of poly(DMA_{50K}/PHE_3/DO_{10})/SDS in water with a polymer concentration of 1 g·L^{-1}, surfactant concentrations from 0 to 15 mM, and a PHE to AN ratio of 1:3.

Prior to the measurements, the polymer/surfactant mixtures were equilibrated for 2 h. The measurements were made on aerated samples to avoid foaming.

Steady-State Fluorescence. Fluorescence spectra were recorded on a SPEX Fluorolog F112A fluorometer (bandwidths: 2.25 nm in excitation and 4.5 nm in emission). Fluorescence emission spectra of PY labeled polymer were recorded between 370 and 650 nm using 341 and 360 nm as excitation wavelengths. Excitation spectra were recorded between 260 and 360 nm with the fluorescence wavelength set at 377, 397, and 480 nm or 500 nm. The excimer-to-

Table 2. Experimental Conditions of the Polymer Labeling Reactions

	poly($DMA_{250K}/PY_{12}/DO_{38}$)	poly($DMA_{50K}/PY_2/DO_{18}$)	poly($DMA_{50K}/AN_2/DO_{18}$)	poly($DMA_{50K}/PHE_3/DO_{10}$)
poly(DMA_{250K}-*co*-NAS)	1.0000 g			
poly(DMA_{50K}-*co*-NAS)		0.6286 g	0.5290 g	0.5432 g
DIPEA	0.0258 g (0.2000 mmol)	0.0148 g (0.1150 mmol)	0.0237 g (0.1841 mmol)	0.0243 g (0.1887 mmol)
PY	0.0155 g (0.0500 mmol)	0.0085 g (0.0274 mmol)		
AN			0.0131 g (0.0458 mmol)	
PHE				0.0137 g (0.0479 mmol)
solvent	20 mL (THF)	20 mL (DMF)	20 mL (DMF)	20 mL (DMF)
DO	0.0222 g (0.1200 mmol)[a]	0.0500 g (0.2697 mmol)	0.0418 g (0.2255 mmol)	0.0430 g (0.2320 mmol)

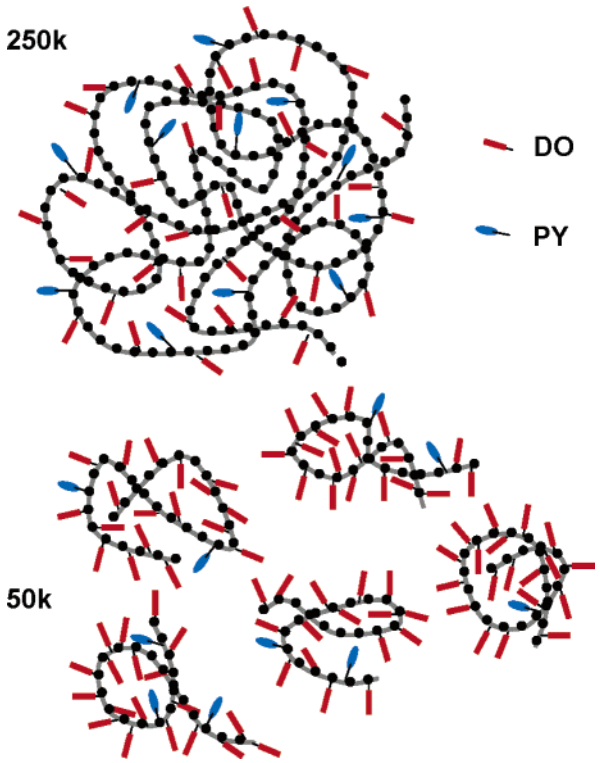
[a] Added to a THF solution containing 0.8 g of polymer obtained by precipitation in *n*-hexane and dried up to constant weight.

Table 3. Characteristics of the HM−PolyDMA

	label content[a]	hydrophobic content[b]
poly($DMA_{250K}/PY_{12}/DO_{38}$)	0.47 mol % PY (ca. 12 PY groups/chain)	1.50 mol % (ca. 38 DO groups/chain)
poly($DMA_{50K}/PY_2/DO_{18}$)	0.34 mol % PY (ca. 2 PY groups/chain)	3.56 mol % (ca. 18 DO groups/chain)
poly($DMA_{50K}/AN_2/DO_{18}$)	0.41 mol % AN (ca. 2 AN groups/chain)	3.74 mol % (ca. 18 DO groups/chain)
poly($DMA_{50K}/PHE_3/DO_{10}$)	0.62 mol % PHE (ca. 3 PHE groups/chain)	1.96 mol % (ca. 10 DO groups/chain)

[a] Determined by UV−vis spectroscopy. [b] Determined by ^{1}H NMR.

Scheme 3. Differences between Two 1 g L^{-1} Solutions in Methanol of Poly($DMA_{250K}/PY_{12}/DO_{38}$) (Top) and Poly($DMA_{50K}/PY_2/DO_{18}$) (Bottom)[a]



[a] For the same mass concentration of polymer, the molar concentration of PY is approximately the same, but the larger chain sample has half the hydrophobic groups (PY and DO).

monomer fluorescence intensity ratio (I_E/I_M) was calculated by dividing the emission intensity at 480 nm by the intensity at 377 nm, unless indicated otherwise. The ratio of the first and third vibronic peaks of pyrene (I_1/I_3) was determined from the intensities at 377 and 389 nm. Fluorescence spectra of the mixed solutions of AN and PHE labeled polymers were recorded between 310 and 580 nm, by excitation at 295 nm. The spectra were obtained using the right angle optical geometry at room temperature, unless indicated otherwise.

Time-Resolved Fluorescence Measurements. Fluorescence intensity decay curves with picosecond resolution were obtained by the single-photon timing technique using laser excitation. The system consists of a mode-locked Coherent Inova 440−10 argon ion laser synchronously pumping a cavity dumped Coherent 701−2 dye laser using either DCM or Rhodamine dyes, which delivers 5−6 ps pulses at a repetition rate of 460 kHz. Excitation light was frequency doubled using a BBO crystal. The fluorescence was observed using a polarizer at the magic angle, being the scattered light effectively eliminated by a cutoff filter. The fluorescence was selected by a Jobin-Yvon HR320 monochromator with a grating of 100 lines/mm and detected by a Hamamatsu 2809U-01 microchannel plate photomultiplier. To analyze the decay curves we developed software that uses a nonlinear least-squares reconvolution method based on the Marquard algorithm.[71]

Fluorescence intensity decay curves of PY labeled polymers were obtained by excitation light at 341 nm using the DCM dye laser, with emission detected at 378 nm (for the monomer) or 520 nm (for the excimer). For PHE labeled polymers, the excitation was set to 295 nm using the Rhodamine dye laser, and the emission was collected at 350 nm.

Results and Discussion

In Figure 1, we show the fluorescence spectra of 0.01 g·L^{-1} poly($DMA_{250K}/PY_{12}/DO_{38}$) in methanol (Figure 1A) and in water (Figure 1B) by excitation at 341 nm. The spectra present two separate emission bands. The one in the blue region is the characteristic emission of the excited pyrene monomer (with vibronic peaks at 376, 397, and 420 nm), while the other, centered around 480 nm, is the broad emission band of the pyrene excimer. At a polymer concentration of 0.01 g·L^{-1}, the bulk concentration of pyrene grafted to the chain is 4.8×10^{-7} M. This concentration is too low for free pyrene to form intermolecular excimer, so the presence of the band at 480 nm in our samples indicates that the excimer is formed between two PY groups belonging to same polymer chain or aggregate of chains.

Emission spectra of the polymer in water, obtained at excitation wavelengths of 341 and 360 nm (Figure 1B), show a band around 410 nm (more pronounced for 360 nm excitation) that is attributed to the emission of preassociated pyrene dimers.[51] The presence of dimers is confirmed by the wavelength shift observed in the excitation spectra recorded at 376 and 500 nm (Figure 1, insets). In methanol, a good solvent for the polymer and the hydrophobic groups, dimer formation is relatively low.

The presence of dimers can be more easily detected in the plot of excimer (500 nm) to monomer (376 nm) fluorescence intensity ratios vs excitation wavelength for 0.01 g·L^{-1} poly($DMA_{250K}/PY_{12}/DO_{38}$) in both methanol and water (Figure 2). In methanol, only a small increase in the I_E/I_M ratio is observed for wavelengths

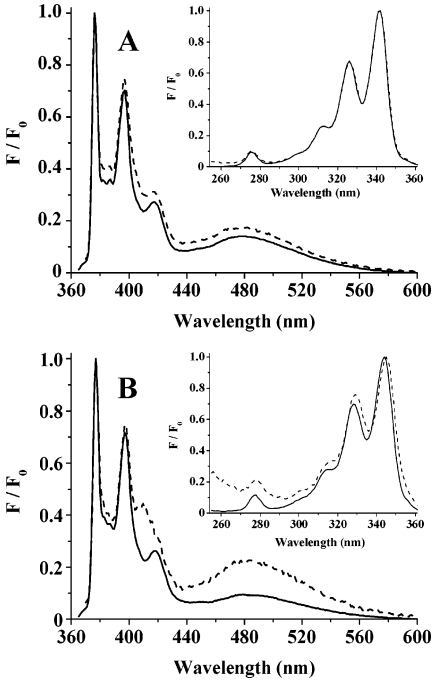


Figure 1. Fluorescence emission normalized at 376 nm of 0.01 g·L^{-1} poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$) in methanol (A) and water (B) by excitation at 341 nm (solid line) and 360 nm (dashed line). Inset: excitation spectra normalized at 341 nm, recorded at 376 nm (solid line) and 500 nm (dashed line).

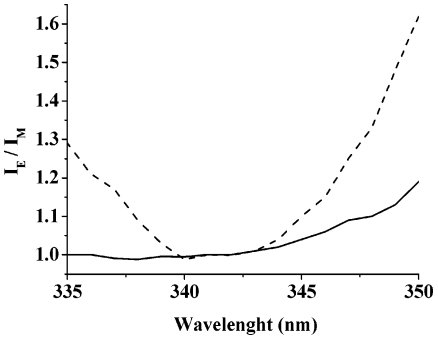


Figure 2. Excimer (500 nm) to monomer (376 nm) intensity ratio (I_E/I_M) normalized at 341 nm, of 0.01 g·L^{-1} poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$) in methanol (solid line) and water (dashed line).

above ca. 350 nm where the pyrene monomer absorption coefficient is lower. On the other hand, for water, there is a larger increase in I_E/I_M below ca. 340 nm and above ca. 350 nm, indicating that the emission at 500 nm has a much higher contribution from excimer that is produced from the direct excitation of preassociated dimers.

This behavior was already observed in a previous study of polyDMA in methanol, where the polymer was labeled with pyrenyl groups only.[65] It was concluded that even small amounts of pyrene (0.5−1.1 mol %) can induce the formation of microdomains in an organic solvent (supposed to be a good solvent for both polymer and dye), promoting the formation of ground-state pyrene aggregates.

The presence of grafted hydrophobic (PY and DO) groups in the water-soluble polyDMA chains induces an associative behavior in these polymers, similar to what was previously observed for other hydrophobically modified polymers in water.[72−82] This can be easily recognized by the increase in pyrene association with polymer concentration. The excimer-to-monomer intensity ratios (I_E/I_M) of poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$) and poly(DMA$_{50K}$/PY$_2$/DO$_{18}$) in water, with polymer concentration up to 60 g·L^{-1} for poly(DMA$_{50K}$/PY$_2$/DO$_{18}$) and up to 5 g·L^{-1} for poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$, are shown in Figure 3. The spectra were recorded using front face geometry due to the high optical density of these samples. The I_E/I_M ratio was calculated as the ratio of the emission intensities at 500 and 396 nm, since self-absorption significantly reduces the intensity of the first vibronic peak (376 nm) at high polymer concentration.

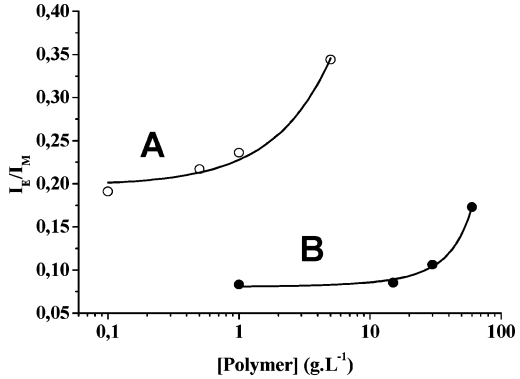


Figure 3. Excimer (500 nm) to monomer (396 nm) ratio (I_E/I_M) of poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$) (A) and poly(DMA$_{50K}$/PY$_2$/DO$_{18}$) (B) in water (λ_{ex} = 341 nm), as a function of polymer concentration.

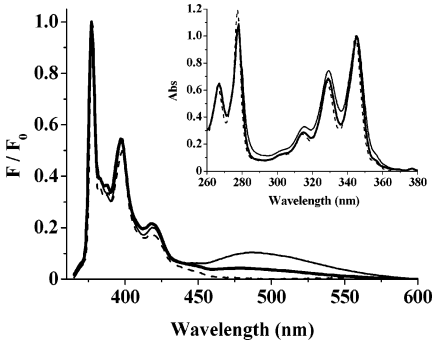


Figure 4. Fluorescence emission normalized at 376 nm obtained by excitation at 341 nm of 1 g·L^{-1} poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$) in water (solid line) and in 500 mM SDS aqueous solution (heavy line), compared with 5 × 10^{-6} M of free PY in 500 mM SDS (dashed line). The corresponding absorbance spectra (normalized at 345 nm) are shown in the insert.

The increase in I_E/I_M for poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$) is observed at much lower concentrations (ca. 1 g·L^{-1}) than for poly(DMA$_{50K}$/PY$_2$/DO$_{18}$) (ca. 10 g·L^{-1}), as expected from the relation between the molecular weight and the hydrophobic content of the two polymers. This increase is attributed to the higher ground-state dimer/monomer ratio due to intermolecular hydrophobic association. In fact, if the increase in association was only intramolecular, an increase in I_E/I_M with polymer concentration would not be observed.

To control the association behavior of our polymer in water, we used the anionic surfactant SDS. We have already described the use of a large concentration of SDS (500 mM) to reduce the hydrophobic associations between PY groups in HM−polyDMA water solutions, and thus quantify the chromophore content in each polymer by UV−vis absorption. Now, we will show that the use of lower concentrations of SDS can increase the association of the hydrophobic groups grafted to the polymer.

In Figure 4, we show the emission and absorption spectra of 1 g·L^{-1} poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$) in water and

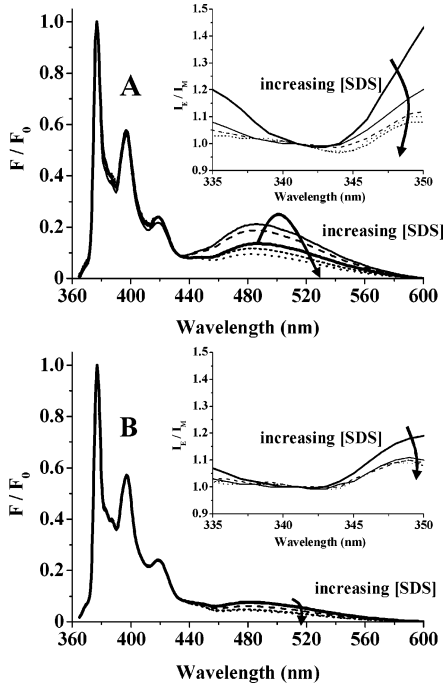


Figure 5. Fluorescence emission normalized at 376 nm (λ_{ex} = 341 nm) and I_E/I_M intensity ratios normalized at 341 nm, of 1 g·L^{-1} poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$) (A) and poly(DMA$_{50K}$/PY$_2$/DO$_{18}$) (B) in water (heavy line) and in 4 mM (solid line), 7 mM (dashed line), 10 mM (short dashed line) and 15 mM (doted line) SDS aqueous solutions.

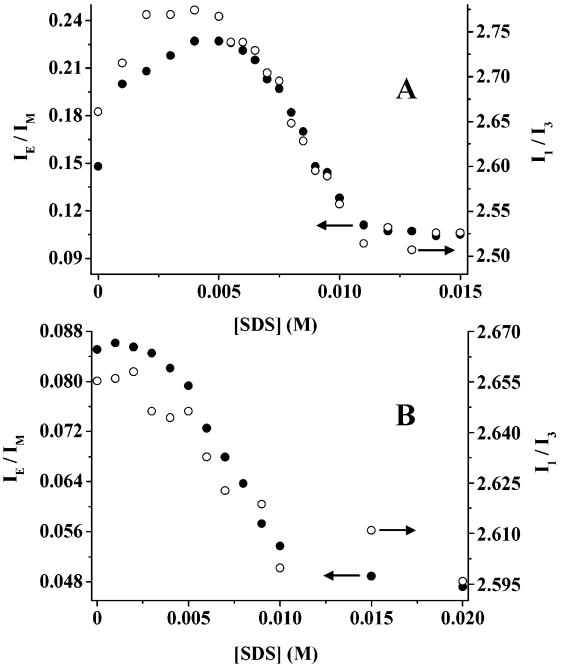


Figure 6. Plots of the I_E/I_M (full circles) and I_1/I_3 (open circles) intensity ratios of poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$)/SDS (A) and poly(DMA$_{50K}$/PY$_2$/DO$_{18}$)/SDS (B) mixtures at 1 g·L^{-1} polymer concentration.

in 500 mM SDS aqueous solution, compared to those of the free PY in 500 mM SDS aqueous solution. The pyrene excimer emission of poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$) is higher in water than in 500 mM SDS (a concentration much higher than the critical micelle concentration of SDS in water, cmc = 8 mM), indicating that the surfactant effectively isolates the hydrophobic groups of the polymer chain, reducing their association. The SDS micelles incorporate the PY and DO groups grafted to the polymer, isolating them, and disrupting the hydrophobic aggregates. We also note that the excimer fluorescence intensity of poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$) in 500 mM SDS aqueous solution is only slightly higher than that obtained for the free PY in the same conditions. While free PY is completely isolated inside the surfactant micelles, for poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$) a small fraction of the PY groups is still associated. This is attributed to the presence of PY groups that are incorporated into neighboring reactive NAS sites along the precursor chain. Since our poly(DMA-*co*-NAS) precursor copolymers have a random distribution of NAS active ester groups along the chains, a small fraction of the reactive sites can be close to each other.

In Figure 5, we present some of the normalized fluorescence emission spectra obtained for poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$) and poly(DMA$_{50K}$/PY$_2$/DO$_{18}$) mixtures with SDS (0−15 mM) in water. The emission spectra show that the effect of the interaction between surfactant micelles and the polymer is more pronounced for poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$) than poly(DMA$_{50K}$/PY$_2$/DO$_{18}$), with the smaller polymer showing less excimer emission for the full range of SDS concentrations. This is explained by the difference in molecular weight and number of (PY and DO) hydrophobic groups in the two polymers. Poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$) is 5 times larger than poly(DMA$_{50}$/PY$_2$/DO$_{18}$), and although it has a comparatively lower hydrophobic content (has 6 times more PY groups but only 2 times more DO groups), the constraints imposed by the larger chain lead to the formation of more excimer (the difference can be readily understood in Scheme 3).

The normalized excimer-to-monomer intensity ratios (Figure 5, inserts) show that for pure water, poly(DMA$_{250K}$/PY$_{12}$/DO$_{38}$) has a higher contribution of pre-associated PY groups to the excimer emission, as expected from its higher number of grafted PY groups relative to the DO content. While in aggregates containing both DO and PY the higher mobility of the PY groups allow them to adopt the more stable excimer configuration,[50] aggregates containing only PY are more likely to form dimers similarly to free PY in water.[51] Statistically, aggregates containing both DO and PY are more probable in poly(DMA$_{50K}$/PY$_2$/DO$_{18}$), so this polymer shows comparatively less dimer.

With the addition of small amounts of surfactant (to obtain less than 4 mM SDS), we noticed an increase in excimer-like pyrene emission, and a decrease in I_E/I_M corresponding to a lower contribution of pre-associated PY to excimer emission. In this concentration range (below the critical micelle concentration of SDS in water), the surfactant starts to interact with the hydrophobic microdomains of the polymer to form mixed aggregates. This nucleation process leads to changes in the volume and conformation of the aggregates. The resulting increase in pyrene mobility favors the rearrangement of dimers to form dynamic excimer, increasing excimer emission.[52]

A further increase in SDS concentration, leads to a decrease in the PY excimer emission because the formation of an increasing number of mixed micelles between the polymer hydrophobic groups and the surfactant tend to separate the PY groups. The increase in available SDS leads to the formation of more mixed micelar aggregates, isolating the PY and DO groups in different micelles.

In Figure 6, we show plots of I_E/I_M (measured 480 and 377 nm, respectively) and I_1/I_3 (377 and 389 nm, respectively) as a function of SDS concentration. The first ratio illustrates the relative importance of the emission of associated pyrene, while the second is a measure of the hydrophobicity of the pyrene environment. In the case of poly(DMA_{250K}/PY_{12}/DO_{38}), one can observe an initial increase in I_E/I_M for low surfactant concentrations. After reaching a maximum value around 4 mM, the increase in SDS concentration induces a decrease in I_E/I_M, which reaches a plateau at 10 mM. The same behavior is observed when analyzing the change in the I_1/I_3 ratio. For poly(DMA_{50K}/PY_2/DO_{18}), the changes in both I_E/I_M and I_1/I_3 are less pronounced: both ratios are almost constant up to 2 mM of SDS and after there is a decrease in the two ratios to reach a plateau at 10 mM. This plateau is located above the cmc of SDS in water and corresponds to the concentration at which all the polymer sites available for interaction are saturated and any further surfactant forms free micelles in solution.[7] In fact, since the mixed micelle aggregates are formed bellow the cmc of SDS in water, we can safely assume that in the mixtures with polymer the concentration of SDS unimer is kept bellow this value, and therefore no free SDS micelles are formed before the saturation point of the polymer hydrophobic groups (ca. 10 mM SDS). Above this point, the concentration of SDS unimers in solution increases and free SDS micelles are formed.

We have previously shown that ground-state pyrene dimers are partially responsible for the emission observed above 420 nm for poly(DMA_{250K}/PY_{12}/DO_{38}) in water. When a small amount of surfactant is added (ca. 2.5 mM), the hydrophobic aggregates containing PY and DO groups become larger, increasing the mobility of the PY groups and allowing the excited pyrene dimers to relax to the more stable excimer conformation. The relative excimer-to-monomer emission ratio is therefore increased. For poly(DMA_{50K}/PY_2/DO_{18}), this effect is not observed because the relative amount of ground-state PY dimers is much lower than for the longer polymer.

Above a certain concentration of SDS—ca. 4 mM for poly(DMA_{250K}/PY_{12}/DO_{38}) and ca. 2 mM for poly(DMA_{50K}/PY_2/DO_{18})—there is a strong decrease in both I_E/I_M and I_1/I_3 for the two polymers. This is due to the separation of the hydrophobic microdomains induced by the increase in SDS concentration. Pyrene groups become progressively more isolated inside different mixed micelles (I_E/I_M decreases), and sense a more hydrophobic media (I_1/I_3 decreases) as they are surrounded by more SDS and get further away from water.

The absolute values obtained for I_1/I_3 are higher than those published for isolated pyrene in water (1.84) and in SDS micelles (1.14).[83] This difference is related to the use of a PY derivative with a spacer arm to covalently attach the dye to the polymer backbone. It is well-known that pyrene substitution leads to a broadening of the vibrational fine structure, with an increase in I_1/I_3 and a decrease in the sensitivity of this ratio to the polarity of the dye environment[84] Nevertheless, even though the changes in I_1/I_3 reported in Figure 6 are quite small, this ratio is determined with high precision from the emission spectra.

In another experiment, we prepared a poly(DMA_{250K}/PY_{12}/DO_{38})/SDS mixture in water containing 4 g·L^{-1} of polymer and 10 mM of SDS (filled square in Figure 7). The increase in polymer concentration from 1 to 4 g·L^{-1},

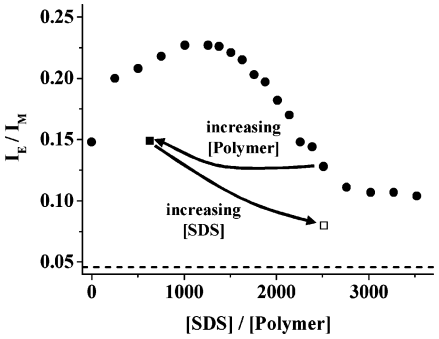


Figure 7. Excimer-to-monomer emission ratio of poly(DMA_{250K}/PY_{12}/DO_{38})/SDS mixtures in water as a function of the surfactant/polymer concentration ratio for polymer concentration of 1 g·L^{-1} (full circles) and 4 g·L^{-1} containing 10 mM SDS (full square) and 40 mM SDS (open square). The dashed line corresponds to 1 g·L^{-1} polymer and 500 mM SDS.

while maintaining a surfactant concentration of 10 mM (Figure 7), led to a slight increase in excimer emission compared to the monomer emission. While at 1 g·L^{-1} polymer and 10 mM SDS there are ca. 50 molecules of SDS per hydrophobic group grafted to the polymer chain (PY and DO), for the mixture with higher polymer concentration (4 g·L^{-1} polymer and 10 mM SDS), there are only ca. 12 SDS molecules per grafted hydrophobic group. Since the SDS aggregation number in water is around 62[68] and the hydrophobic groups act as nucleation sites for SDS aggregation, very few free micelles are expected to exist despite the SDS concentration being higher than its cmc in water. However, since for the mixture with 4 g·L^{-1} polymer and 10 mM SDS, there are less SDS molecules available for each grafted hydrophobic group, we expect that more grafted hydrophobic groups are present in each mixed micelle. This is supported by the slightly higher I_E/I_M ratio obtained for the higher polymer concentration: a fraction of the excess PY and DO groups are trapped together in mixed micelles.

When comparing the mixtures with the same [SDS]/[polymer] ratio, we observe that there is less association for 4 g·L^{-1} polymer and 10 mM SDS than for 1 g·L^{-1} polymer and 2.5 mM SDS. Although the number of SDS molecules per hydrophobic group is approximately the same for the two mixtures, the mixture with 4 g·L^{-1} polymer was prepared with an SDS concentration above its cmc in pure water, more effectively separating the PY groups and thus reducing the excimer to monomer intensity ratio.

Adding more surfactant to the solution with 4 g·L^{-1} polymer and 10 mM SDS, to get 40 mM of SDS (open square in Figure 7), the excimer-to-monomer ratio decreased to a value lower than that of the original sample with the same [SDS]/[polymer] $\approx$ 2500 ratio (1 g·L^{-1} polymer and 10 mM SDS). The added surfactant forms new SDS micelles, further separating the PY and DO groups and consequently decreasing the PY excimer emission.

Finally, in the presence of a very high concentration of surfactant (1 g·L^{-1} polymer, 500 mM SDS—dashed line in Figure 7), the I_E/I_M ratio is even smaller than the value of the plateau, meaning that at 15 mM of SDS and 1 g·L^{-1} of polymer ([SDS]/[polymer] $\approx$ 3500), the PY and DO groups of the polymer are not completely separated. One reason for this is that the solutions with 500 mM of SDS were prepared by dissolving directly the solid poly(DMA_{250K}/PY_{12}/DO_{38}) and SDS in water

instead of progressively increasing the SDS concentration in the polymer solution. This means that a fraction of the grafted hydrophobic groups become trapped together inside the mixed micelles and cannot be separated by stepwise addition of SDS. On the other hand, if free SDS micelles are already available when the mixture with polymer is prepared (as in the mixture of 500 mM SDS and 1 g·L^{-1} polymer), most of these groups are incorporated into separated micelles. We interpret this result to mean that some PY groups are associated in the form of ground-state dimers, which are not easily separated by the rearrangement of the SDS unimers and the fission of the mixed micelles (the predominant mechanism for hydrophobic solute exchange in SDS micelles in water).[85]

To analyze the room-temperature fluorescence decay curves of mixtures of PY labeled polymer and SDS in water ($\lambda_{ex} = 341$ nm; $\lambda_{em} = 378$ nm), we have to consider the structure of the polymer/surfactant hydrophobic aggregates. These are micellelike structures containing a small number of fluorescent groups, which can be described by a Poisson distribution since the chains are randomly labeled. Assuming that the exchange of grafted PY between mixed micelles in water is very limited (gradual addition of SDS to the polymer in water produces a higher I_E/I_M ratio than the mixture prepared from the solid components), the monomer fluorescence decay curves can be described by the Tachiya model for fluorescence quenching in micelles.[86,87] By excitation at 341 nm (where dimer excitation is very low), the excited pyrene monomer can either decay to the ground state with intrinsic lifetime τ_M or it can be quenched by a ground-state pyrene with a pseudo first-order rate constant k. The survival probability of the excited monomer is

$$I_M(t) = a_1 \exp\{-1/\tau_M - n_{PY}[1 - \exp(-kt)]\} \quad (1)$$

where a_1 is a factor that normalizes the total decay intensity and n_{PY} is the average number of pyrene groups per hydrophobic domain. We note that the model assumes a negligible rate for the dissociation of the excimer back to the excited monomer, which is usually valid for temperatures bellow 35 °C.[88]

The PY monomer decay curves calculated using initial guess parameters in eq 1 were convoluted with the experimental instrument response functions $L(t)$

$$I_M^{conv}(t) = \int_0^t L(s) I_M(t - s)\, ds \quad (2)$$

and then compared with the experimental decay curves to obtain the best fit parameters. A nonlinear least-squares method based on the Marquard algorithm was used,[71] and the quality of the fit was evaluated by the reduced χ^2, the weighted residuals, and the autocorrelation of the residuals. For different sets of initial guess parameters, we consistently obtained the same values of the fitting parameters for each solution, with $\chi^2 < 1.28$ for poly(DMA_{250K}/PY_{12}/DO_{38}) and $\chi^2 < 1.15$ for poly(DMA_{50K}/PY_2/DO_{18}), and homogeneously distributed weighted residuals and autocorrelation of the residuals.

In Figure 8, we show a fluorescence emission decay curve measured at 378 nm for a poly(DMA_{250K}/PY_{12}/DO_{38})/SDS mixture (1 g·L^{-1} polymer, 7 mM SDS) by excitation at 341 nm. The curve was analyzed with eq 1 yielding $n_{PY} = 0.647$ and $k = 10^7$ s^{-1} with $\chi^2 = 1.11$.

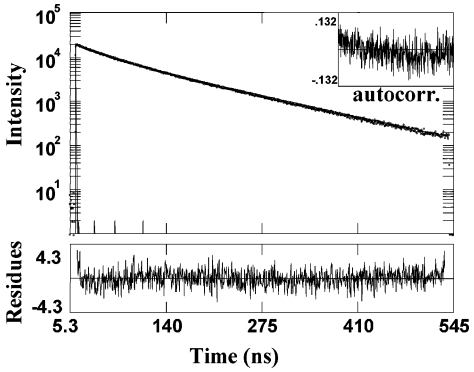


Figure 8. Fluorescence emission decay curve obtained at 378 nm for poly(DMA_{250K}/PY_{12}/DO_{38})/SDS mixture (1 g·L^{-1} polymer, 7 mM SDS) by excitation at 341 nm.

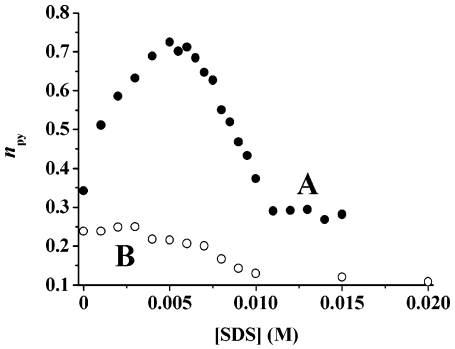


Figure 9. Average number of PY per hydrophobic aggregate obtained from eq 1 for poly(DMA_{250K}/PY_{12}/DO_{38})/SDS (A) and poly(DMA_{50K}/PY_2/DO_{18})/SDS (B) mixtures at 1 g·L^{-1} of polymer.

The values of the quenching rate constants k obtained for poly(DMA_{250K}/PY_{12}/DO_{38}) and poly(DMA_{50K}/PY_2/DO_{18}) over the full SDS concentration range are of the order of 1×10^7 s^{-1} to 2×10^7 s^{-1}, a value typical for pyrene excimer formation in SDS micelles.[89] In Figure 9, we show the average number of pyrene molecules per aggregate, n_{PY}, obtained from eq 1 for mixtures poly(DMA_{250K}/PY_{12}/DO_{38}) or poly(DMA_{50K}/PY_2/DO_{18}) with different SDS concentrations. The curve for the higher molecular weight polymer shows a maximum around 5 mM of SDS while for the smaller polymer, the number of PY per aggregate is constant in this range. The increase in n_{PY} observed for poly(DMA_{250K}/PY_{12}/DO_{38}) at low SDS concentrations is attributed to the disruption of PY dimers. This effect is not observed for the lower molecular weight polymer because the amount of ground-state PY dimers is much lower as we have seen before. For SDS concentrations higher than ca. 3 mM for poly(DMA_{50K}/PY_2/DO_{18}) and ca. 5 mM for poly(DMA_{250K}/PY_{12}/DO_{38}), both curves decrease until close to 10 mM SDS, after which the value is almost constant. This decrease is attributed to the increasing number of mixed micelles containing PY groups. At 10 mM SDS, a plateau is reached, suggesting that a maximum number of mixed micelles is obtained, with almost all PY groups being isolated. The subsequent increase in surfactant concentration, results in the formation of free SDS micelles.

The maximum value of n_{PY} is obtained for an SDS concentration lower than the cmc of SDS in water (8 mM) and corresponds to the onset of mixed aggregate formation of the polymers in the presence of SDS. This critical aggregation concentration (CAC) will be determined with more precision below.

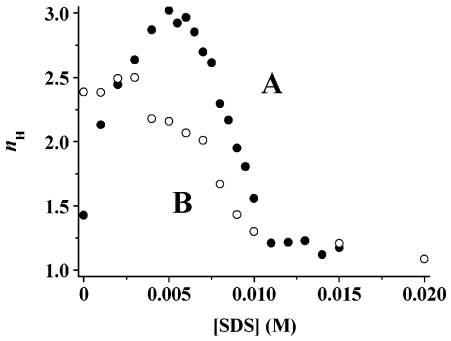


Figure 10. Average number of grafted hydrophobic groups n_H per aggregate for poly(DMA_{250K}/PY_{12}/DO_{38})/SDS (A) and poly(DMA_{50K}/PY_2/DO_{18})/SDS (B) mixtures at 1 g·L^{-1} of polymer.

From the values of n_{PY} and the hydrophobic content of the polymers, we can estimate the number of grafted (PY and DO) hydrophobic groups per mixed micelle n_H (Figure 10), which changes between 1 and 3 for both polymers over the range of SDS concentrations for which quenching of the monomer emission can be observed. This means that, although the number of PY groups per micelle is low, the micelles contain at least one hydrophobic group from the chain as expected.

At the saturation point (ca. 10 mM) there is only about one grafted hudrophobic group per mixed micelle. This corresponds to about 30 SDS molecules per hydrophobic aggregate in poly(DMA_{50K}/PY_2/DO_{18}) and 60 in poly(DMA_{250K}/PY_{12}/DO_{38}). We assume that no free SDS micelles are formed bellow 10 mM of SDS because, since the CAC is lower than the cmc of SDS in water (see Figure 6), the concentration of SDS unimers is lower than the cmc until no more polymer hydrophobic sites are available to form mixed micelar aggregates and free SDS micelles start to form. After the saturation point (ca. 10 mM SDS), the number of grafted hydrophobic groups per micelle is constant despite the increase in SDS, because all the polymer sites available for interaction are saturated, and the excess surfactant forms free micelles in solution (which are not detected by PY, since this is grafted to the polymer in our experiments).[7]

The average number of PY groups per mixed micelle correspond to the ratio of the PY concentration by the mixed micelle concentration:

$$n_{PY} = \frac{[PY]}{[\text{mixed micelles}]} \tag{3}$$

Since the mixed micelles are formed by SDS and hydrophobic groups (PY and DO) grafted to the polymer, their concentration is

$$[\text{mixed micelles}] = \frac{([SDS] + [PY] + [DO]) - CAC}{N_{agg}} \tag{4}$$

where CAC is the critical aggregation concentration for mixed micelles and N_{agg} is their aggregation number. For all concentrations above the CAC, the total concentration of SDS is much higher than the concentration of hydrophobic groups grafted to the polymer and therefore

$$1/n_{PY} \approx \frac{1}{[PY]} \times \frac{[SDS] - CAC}{N_{agg}} \tag{5}$$

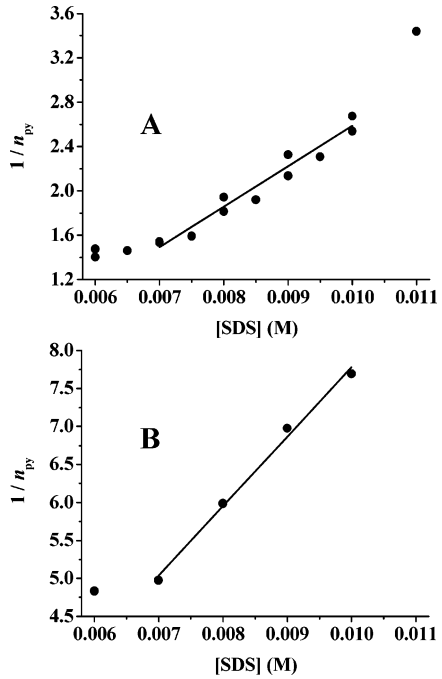


Figure 11. Inverse number of pyrene monomer groups per mixed micelle ($1/n_{PY}$) vs SDS concentration for 1 g·L^{-1} poly(DMA_{250K}/PY_{12}/DO_{38}) (A) and poly(DMA_{50K}/PY_2/DO_{18}) (B).

Table 4. Aggregation Number (N_{agg}) and cmc/CAC of SDS Micelles and Mixed Micelles (1 g·L^{-1} Polymer)

	poly(DMA_{250K}/PY_{12}/DO_{38})	poly(DMA_{50K}/PY_2/DO_{18})	SDS[68a]
N_{agg}	59 ± 10	32 ± 8	62
cmc/CAC (10^{-3} M)	3 ± 2	2 ± 2	8

From the linear region in the plot of $1/n_{PY}$ vs SDS concentration (Figure 11), we obtain the CAC and aggregation number of the polymer/SDS mixed micelles (Table 4). The CAC for poly(DMA_{250K}/PY_{12}/DO_{38}), 3 ± 2 mM, is slightly higher than for poly(DMA_{50K}/PY_2/DO_{18}), 2 ± 2 mM, but both values are lower than the cmc of SDS in water. This difference can be explained by the "nucleation" action of the hydrophobic groups grafted to the polymer chains, which promotes the formation of the mixed micelles at a lower concentration of surfactant.

The CAC values obtained by this approach are in agreement with those extracted from the I_E/I_M and I_1/I_3 plots (Figure 6) and from the n_{PY} plots (Figures 9 and 10). This value is smaller for the low molecular weight polymer which has twice the amount of hydrophobic groups for the same polymer concentration: 0.4 mM for poly(DMA_{50K}/PY_2/DO_{18}) and 0.2 mM for poly(DMA_{250K}/PY_{12}/DO_{38}) at 1 g·L^{-1} of polymer. The aggregation number N_{agg} follows the same trend, in agreement with our steady-state results (Figure 10) and those obtained by F. Winnik for PNIPAM/SDS mixtures.[36] The mixed micelles formed in poly(DMA_{250K}/PY_{12}/DO_{38})/SDS mixtures (N_{agg} = 59 ± 10) are larger than those of poly(DMA_{50K}/PY_2/DO_{18})/SDS mixtures (N_{agg} = 32 ± 8). The difference in aggregation number is related to the difference in the number of hybrophobic groups and size of the polymers: for the same amount of polymer, there are more hydrophobic groups in the smaller chain and these are more separated because there are about 5 times more chains (Scheme 3). Therefore, we think that since the available surfactant is distributed over a larger number of hydrophobic sites, mixed micelles of smaller

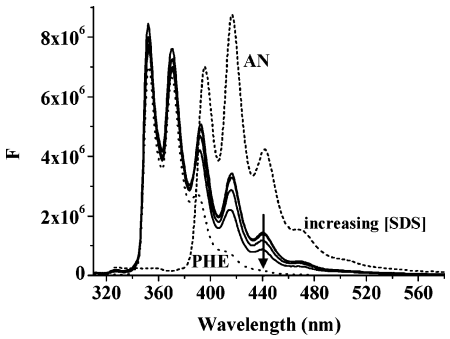


Figure 12. Fluorescence emission (by excitation at 295 nm) of SDS mixtures with 1 g·L^{-1} polymer for poly(DMA_{50K}/AN_2/DO_{18}) plus poly(DMA_{50K}/PHE_3/DO_{10}) (0, 1, 5, and 15 mM of SDS -solid lines); poly(DMA_{50K}/PHE_3/DO_{10}) corrected to the same PHE optical density (dashed line); and poly(DMA_{50K}/AN_2/DO_{18}).

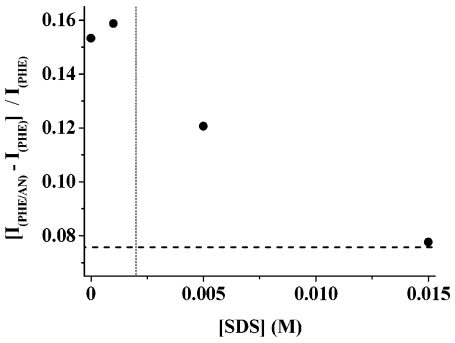


Figure 13. Fluorescence intensity ratio of AN (λ = 400 nm) to PHE (λ = 357 nm) for poly(DMA_{50K}/AN_2/DO_{18})/poly(DMA_{50K}/PHE_3/DO_{10}) 1 g·L^{-1} mixtures with SDS in water. The horizontal dashed line corresponds to an SDS concentration of 500 mM, and the vertical dotted line corresponds to the CAC obtained for poly(DMA_{50K}/PY_2/DO_{18})—Table 4.

aggregation number are formed. This is an indication that the hydrophobic groups grafted to the polymer act as effective nucleation sites for the formation of mixed micelles.

Pyrene fluorescence gave us relevant information on the hydrophobic aggregation processes of polymer/SDS mixtures. However, it cannot distinguishing between intramolecular (same polymer chain) and intermolecular (different chains) hydrophobic associations. To clarify the nature of this aggregation, we studied the resonance energy transfer in mixtures of SDS with donor and acceptor-labeled hydrophobically modified polyDMA. For this purpose, the poly(DMA_{50K}-*co*-NAS) chains obtained by RAFT were hydrophobically modified with dodecyl groups (DO) and either phenanthrene (PHE), poly(DMA_{50K}/PHE_3/DO_{10}), or anthracene (AN), poly(DMA_{50K}/AN_2/DO_{18}). The polymers, with the same M_n and M_w/M_n, differ in the type and level of dye and DO incorporation: an average of 3 PHE and 10 DO groups per chain for poly(DMA_{50K}/PHE_3/DO_{10} and 2 AN and 18 DO per chain for poly(DMA_{50K}/AN_2/DO_{18}).

For this donor/acceptor pair, direct nonradiative energy transfer (also called Förster resonance energy transfer or FRET) takes place by a dipole−dipole coupling mechanism.[53] The energy transfer rate is a very sensitive measure of the distance between donor and acceptor because it depends on the inverse sixth power of the separation between them. Energy transfer can occur at distances up to ca.three times a critical distance typical of each pair of dyes, called the Förster radius R_0. In our work we used phenanthrene (PHE) and anthracene (AN) as donor and acceptor respectively, and the Förster radius is R_0 = 2.4 nm. Therefore, in mixed solutions of poly(DMA_{50K}/PHE_3/DO_{10}) and poly(DMA_{50K}/AN_2/DO_{18}), energy transfer can only occur if PHE and AN are located in associated chains. Therefore, the amount of energy transfer reflects the extent of interpolymer association.[90]

Energy transfer measurements where performed for poly(DMA_{50K}/PHE_3/DO_{10}) and for mixtures of poly(DMA_{50K}/PHE_3/DO_{10}) and poly(DMA_{50K}/AN_2/DO_{18}) in water, with a polymer concentration of 1 g·L^{-1} and different SDS contents. The molar ratio of AN to PHE groups in the mixtures was fixed at 1.35 in order to have an optimum balance between the donor fluorescence intensity and the energy transfer efficiency.

The fluorescence spectra of poly(DMA_{50K}/PHE_3/DO_{10})/SDS mixtures in water obtained by excitation at 295 nm (Figure 12) are very similar to the spectrum of the same polymer in methanol, showing the characteristic phenanthrene emission band above ca. 350 nm. The intensity and shape of the spectra remain invariant with the increase in surfactant concentration.

For mixtures of poly(DMA_{50K}/AN_2/DO_{18}) and poly(DMA_{50K}/PHE_3/DO_{10}) with SDS in water (Figure 12), we observe a new band characteristic of AN emission, which is absent in mixtures of the two polymers in methanol. Also, under our experimental conditions, the emission of AN by excitation at 295 nm is not significant, so we conclude that energy transfer between PHE and AN occurs due to interpolymer association (Figure 12, solid lines). Therefore, even at relatively low polymer concentration (1 g·L^{-1}) some PHE and AN groups are close enough for FRET to occur. This is caused by the association of grafted hydrophobic groups from different chains.

To evaluate the amount of interchain aggregates, the ratio of AN (λ = 400 nm) to PHE (λ = 357 nm) emission intensities (corrected for the residual emission of PHE at 400 nm) is plotted as a function of SDS concentration (Figure 13). We observe that for SDS concentrations above the CAC—determined for poly(DMA_{50K}/PY_2/DO_{18})—there is a decrease in the amount of energy transfer, which is attributed to the disruption of mixed intermolecular micelles.

To discriminate between PHE groups that have an AN group in proximity and those that are isolated, we measured the fluorescence decay curves of the same poly(DMA_{50K}/AN_2/DO_{18})/poly(DMA_{50K}/PHE_3/DO_{10}) mixtures with SDS in water. The donor decay has contributions from PHE groups that are isolated in mixed micelles that do not contain any AN groups (these PHE decay with their intrinsic lifetime τ_D) and from PHE in mixed micelles containing AN, where energy transfer can occur. Since the two populations are independent (a PHE group is either in a micelle containing AN or in a micelle without AN), the overall donor decay function is a sum of the two contributions. If we assume that the distribution of AN groups around PHE is homogeneous, the decay of the PHE groups that are able to transfer energy to AN can be described by the Förster model. The overall donor decay is then given by

$$I_D(t) = a_1 \exp\left(-\frac{t}{\tau_D}\right) + a_2 \exp\left(-\frac{t}{\tau_D}\right) \exp\left[-P\left(\frac{t}{\tau_D}\right)^{0.5}\right] \quad (6)$$

where P is a parameter that reflects the local concentra-

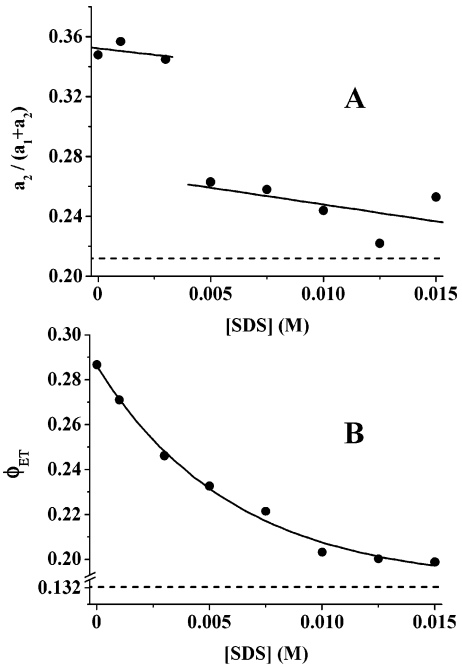


Figure 14. (A) Ratio of preexponentials $a_2/(a_1 + a_2)$ for 1.35:1 mixtures of poly($DMA_{50K}/AN_2/DO_{18}$) and poly($DMA_{50K}/PHE_3/DO_{10}$) in water with different SDS contents and total polymer concentration of 1 g·L^{-1}. (B) Efficiency of energy transfer for interchain aggregates containing both AN and PHE groups. The dashed line corresponds to an SDS concentration of 500 mM.

tion of AN groups around the excited PHE groups, and the pre-expontential factors a_1 and a_2 are proportional to the amount of isolated PHE and PHE/AN pairs, respectively. The use of the Förster model to describe energy transfer in mixed polymer/SDS micelles containing AN and PHE is an approximation that neglects the effect of the micelles restricted geometry and the possibility of dye diffusion during the donor decay time. While the system is too complex to use a model that accounts for the effect of the detailed morphology of the micelles on the donor decay function,[55] the effect of dye diffusion should be minor since PHE and AN are covalently bound to the polymer. These approximations are not expected to affect our conclusions.[55]

The fluorescence decay curves obtained for poly($DMA_{50K}/PHE_3/DO_{10}$) in water cannot be fitted with a single exponential function, contrarily to what we obtained for the same polymer in methanol. Besides the component of ca. 45 ns (equal to the one obtained in methanol), a short component with lifetime of 13 ns is recovered, which contributes with ca. 2.5% to the decay in water.[52] This short component does not disappear even for high surfactant concentrations, suggesting that a small amount of PHE groups are grafted to the chain in close proximity and can form aggregates similarly to what was observe for the PY labeled chain.

The experimental decay curves obtained for mixtures of poly($DMA_{50K}/AN_2/DO_{18}$) and poly($DMA_{50K}/PHE_3/DO_{10}$) with SDS in water were well fitted with eq 6, with $\chi^2 < 1.2$ and a random distribution of weighted residuals and autocorrelation of residuals.

The ratio of preexponentials factors, $a_2/(a_1 + a_2)$, shown in Figure 14A, reflect the fractional decrease of the number of PHE groups which are part of mixed intermolecular micelles that also contain AN groups. The decrease in this ratio above the CAC, shows that PHE and AN groups are incorporated into separated mixed micelles, with most PHE/AN pairs being separated, and the $a_2/(a_1 + a_2)$ ratio becoming approximately constant.

The energy transfer quantum yield for the fraction of PHE groups that are not isolated is defined as

$$\Phi_{ET} = 1 - \frac{\int_0^\infty I_D^e(t)\,dt}{\int_0^\infty I_D^0(t)\,dt} = \sqrt{\pi}\left(\frac{P}{2}\right)\exp\left(\frac{P}{2}\right)^2 \mathrm{erfc}\left(\frac{P}{2}\right) \qquad (7)$$

where $I_D^0(t)$ is the PHE decay in the absence of acceptors, $I_D^e(t)$ is the decay for PHE that can transfer their energy to AN groups and whose decay is given by the second term of eq 6, and erfc is the complementary error function. The efficiency of energy transfer initially decrease with the increase in SDS concentration (Figure 14B), reflecting the decrease in proximity of PHE/AN groups as the premicellar aggregates grow until the CAC is reached. After this point, the efficiency of energy transfer gradually stabilizes, because the size of the mixed micelles is constant and therefore the average PHE/AN distance is also constant.

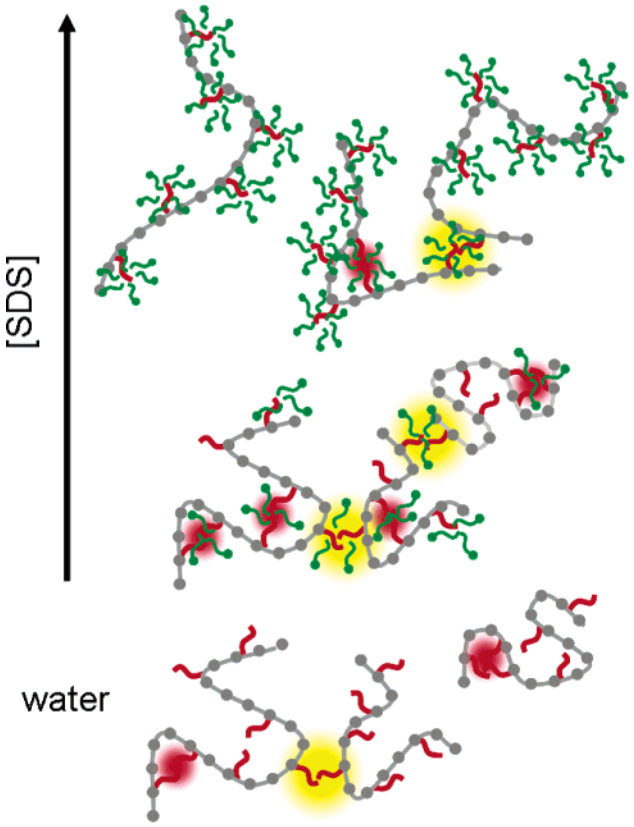
Time-resolved fluorescence results confirm the association of hydrophobic groups from different polymer chains. They also show that the addition of SDS to the polymer solution produces mixed aggregates of SDS and hydrophobic group grafted to the polymer. These grow until the CAC is reached. Above this concentration, SDS efficiently disrupts these hydrophobic aggregates, isolating most of the fluorophores in separated mixed micelles.

Conclusions

We prepared two copolymer precursors of poly(*N*,*N*-dimethylacrylamide) containing reactive NAS units, one by a conventional radical polymerization ($M_n = 251\,600$ g·mol^{-1}; $M_w/M_n = 2.20$) and another by controlled radical polymerization using the RAFT process ($M_n = 49\,200$ g·mol^{-1}; $M_w/M_n = 1.21$). These precursors were used to obtain hydrophobically modified poly(*N*,*N*-dimethylacrylamide) chains containing dodecyl and fluorescent groups. The resulting chains show a weak aggregation mechanism in water, which can be enhanced by addition of a small amount an anionic surfactant. The interaction of the hydrophobically modified chains with SDS was studied by steady-state and time-resolved fluorescence, by following both the formation of pyrene excimer and the resonance energy transfer occurring from phenanthrene to anthracene labeled chains.

From our results it is possible to draw a general aggregation mechanism of the hydrophobically modified polymer in water, with and without adding SDS (Scheme 4). In water, the polymer chains form hydrophobic clusters mainly by intrachain aggregation, although evidence for some association between different chains was also found. At very low surfactant concentrations, SDS molecules show already some interaction with the hydrophobic modified polyDMA. From the excimer formation results, we learned that SDS molecules incorporate into the hydrophobic aggregates, increasing their volume and leading to the relaxation of the pyrene aggregates, which form more dynamic excimer. Direct nonradiative energy transfer measurements showed that, at low SDS concentrations, part of these associations are intermolecular. Above the critical aggregation concentration, 3 ± 2 mM for poly($DMA_{250K}/PY_{12}/DO_{38}$)

Scheme 4. General Aggregation Mechanism of SDS (Green) and a Polymer Modified with Hydrophobic Groups (Red)[a]



[a] In water, the number of intra- (red shadow) and intermolecular (yellow shadow) contacts is limited. By addition of SDS, the number of intra- and intermolecular associations are increase due to the nucleation of mixed micelles. At high SDS concentration, the hydrophobic groups grafted to the polymer are separated into different mixed micelles and the chains are extended due to the repulsion between the negatively charged SDS micelles.

and 2 ± 2 mM for poly($DMA_{50K}/PY_2/DO_{18}$), mixed polymer/surfactant micelles are formed between the hydrophobic groups grafted to the polymer and SDS. The aggregation numbers obtained for the mixed micelles—59 ± 10 for poly($DMA_{250K}/PY_{12}/DO_{38}$) and 32 ± 8 for poly($DMA_{50K}/PY_2/DO_{18}$)—are lower than that for SDS alone, showing that the presence of polymer enhances micelle formation. Addition of more surfactant promotes the formation of more mixed micelles, leading to the separation of the mixed aggregates with the hydrophobic groups of the polymer becoming trapped inside different mixed micelles. Above 10 mM of SDS, there is an excess of SDS micelles that are not attached to polymer hydrophobic groups. Even though the grafted hydrophobic groups are almost completely separated into different mixed micelles (there is only ca. one hydrophobic group from the polymer per mixed micelle), some residual aggregation is still detected by energy transfer measurements.

Another effect of the increase in the number of mixed micelles is that the polymer chains become progressively more negatively charged, and thus are expected to acquire some polyelectrolyte character. This probably allows the polymer chains to adopt more extended conformations, due to their water solubility and the electrostatic repulsion by SDS micelles.

One difference observed between the 250K and the 50K polymers is that, for the larger (and more polydispersed) polymer, more ground-state pyrene dimers are formed in water. The dimers are converted into dynamic excimer by the addition of a small amount of SDS because the surfactant increases the mobility of the PY groups in the aggregates. Above a certain amount of SDS the excimer emission decreases because the PY groups become isolated in different micelles.

Finally, we expect the CAC to be independent of the molecular weight of the polymer since there is no interaction with the DMA units. However, this should depend on the number of hydrophobic groups of the chain. In fact, the hydrophobic content of the longer chain is two times lower (and the CAC is roughly two times higher) than of the 50K polymer. The decrease in CAC with the increase of hydrophobic content of the polymer is explained by the lower amount of SDS needed to form stable aggregates when more grafted hydrophobic groups are available to form mixed micelles.

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Supporting Information Available: Tables with the analysis results for the fluorescence decay curves of poly($DMA_{50K}/PY_2/DO_{18}$)/SDS, $DMA_{250K}/PY_{12}/DO_{38}$)/SDS mixtures and mixtures of poly($DMA_{50K}/AN_2/DO_{18}$) and poly($DMA_{50K}/PHE_3/DO_{10}$) with SDS in water. This material is available free of charge via the Internet at http://pubs.acs.org.

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