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Synthesis and spectroscopic characterization of fluorescently labeled hydrocarbon- and/or fluorocarbon-modified poly(sodium 2-acrylamido-2-methylpropanesulfonates)

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Dedicated to Professor I. Yamazaki, a long time collaborator and dear friend, on the occasion of his retirement from Hokkaido University.

Abstract

Fluorescently labeled amphiphilic polyelectrolytes bearing naphthalene (Np) or pyrene (Py) chromophores, hydrocarbon and/or fluorocarbon chains have been prepared by free-radical polymerization using azobis(isobutyronitrile) (AIBN) as an initiator in *N*,*N*-dimethylformamide (DMF). The five different Py labeled polymers prepared are (i) a copolymer of sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) and *N*-*n*-dodecyl-*N*-[4-(1-pyrenyl)butyl]acrylamide (PyDodAm) in a molar ratio of 95:5, (ii) two terpolymers of NaAMPS, PyDodAm, and *N*-*n*-dodecylacrylamide (DodAm) in 90:5:5 and 80:5:15 molar ratios, and (iii) two terpolymers of NaAMPS, *N*-*n*-^{1}H,^{1}H-perfluorooctyl-*N*-[4-(1-pyrenyl)butyl]acrylamide (PyOctAm), and *N*-*n*-^{1}H,^{1}H-perfluorooctylacrylamide (OctAm) or DodAm in a molar ratio of 80:5:15. The four different Np labeled polymers are terpolymers of NaAMPS, *N*-*n*-dodecyl-*N*-[2-(1-naphthyl)ethyl]acrylamide (NpDodAm) or *N*-*n*-^{1}H,^{1}H-perfluorooctyl-*N*-[2-(1-naphthyl)ethyl]acrylamide (NpOctAm), and DodAm or OctAm in a molar ratio of 80:5:15. The polymers were characterized by FTIR, ^{1}H and ^{19}F NMR, and fluorescence spectroscopy. Their solution properties in water and in NaCl solutions have been studied by surface tension and dynamic light scattering measurements. Fluorescence depolarization determinations indicate that local motions of Np are more restricted in the hydrophobic nanodomains formed by fluorocarbon chains than in those formed by hydrocarbon chains. Experiments based on the non-radiative energy transfer from excited Np (Np*) to Py in mixed solutions of the singly labeled polymers, which bear either Np or Py chromophores, reveal the absence of interpolymeric micelles. All polymers exhibit a low activity on the air/water interface even for solutions of polymer concentrations up to $10\,\mathrm{g\,L^{-1}}$ (~$55\,\mathrm{mN\,m^{-1}}$). In aqueous solutions, the polymers form polymeric micellar structures with an average diameter of ~20 nm (20 °C, $1\,\mathrm{g\,L^{-1}}$).

Keywords: Amphiphilic polyelectrolyte; Fluorescence spectroscopy; Fluorocarbon; Polymeric micelles; Non-radiative energy transfer

1. Introduction

Amphiphilic polyelectrolytes exhibit a range of attractive characteristics in aqueous solutions, as a result of the presence of both ionizable groups, which are responsible for their good solubility in water, and hydrophobic moieties, which tend to self assemble, leading to the formation of inter- or intrachain assemblies [1]. Even when their concentration is very low, they have a marked effect of the rheology of their solutions, which often exhibit shear thinning and/or shear thickening properties. Thus, amphiphilic polyelectrolytes have found numerous practical applications in drug delivery systems, enhanced oil recovery fluids, and water borne paints [2,3]. The conformation and assembly of amphiphilic polyelectrolytes in water are controlled by two opposed forces: (i) the attraction of the hydrophobic substituents driven by the hydrophobic interactions among alkyl groups brought in contact with water and (ii) the electrostatic repulsion between the charged units of the polymer chain. If the hydrophobic group content is sufficiently low and if the groups are distributed randomly along the backbone, the polyelectrolyte main chain adopts a relatively extended conformation. As the hydrophobic group content increases, the polyelectrolytes will tend to contract and form compact structures consisting of hydrophobic nanodomains surrounded by hydrophilic charged chain fragments, known as unimolecular polymeric micelles or “unimers”. Extensive

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studies by Morishima et al. have established that random copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) and *n*-dodecylmethacrylate [4] exhibit a strong tendency for interpolymeric association. On the contrary, random copolymers of NaAMPS and *N*-*n*-dodecylmethacrylamide, in which the *n*-dodecyl chains are linked to the polymer backbone via an amide bond, show a strong preference for intrapolymeric associations and form compact unimers, even in solutions of high polymer concentrations [5]. Experimental results based on NMR and fluorescence spectroscopy, together with viscosity and surface tension measurements led Morishima et al. to conclude that the mobility of the ionizable groups and the nature of the hydrophobic groups are critical factors which control unimer formation [6]. Copolymers of NaAMPS and methacrylamides of rigid bulky groups, such as 1-adamantyl or cyclododecyl moieties, show a particularly strong tendency to form unimers [7].

Surprisingly, copolymers of NaAMPS and perfluoroalkyl-substituted methacrylamides have not yet been reported, although other perfluoroalkyl-substituted polyelectrolytes have been investigated and shown to exhibit a more pronounced tendency towards aggregation than their hydrocarbon counterparts. Examples include the cationic copolymers of choline methacrylate and ^{1}H,^{1}H,^{2}H,^{2}H-perfluorooctylmethacrylate [8], cationic terpolymers of acrylamide, *N*-(acryloxyethyl)-*N*,*N*,*N*-trimethylammonium chloride, and a fluorocarbon-containing acrylate [9], ionenes consisting of poly(*N*,*N*′-dimethyl-1,6-hexanediamine) quaternized with semifluorinated alkyl bromides [10], derivatives of poly(sodium acrylate) prepared by modification of poly(acrylic acid) with perfluoroalkylamine [11] or by free radical copolymerization of acrylic acid and a fluorocarbon-containing methacrylate [12], and anionic terpolymers of acrylic acid, *n*-octadecylacrylate, and a fluorocarbon-containing methacrylate [13]. Amphiphilic polyelectrolytes bearing a high content of fluorocarbon chains [14] or both fluorocarbon and hydrocarbon chains [15] tend to assemble in water via interpolymeric association, although cationic polysoaps [16], in particular the cationic ionenes developed by Kotzev and Laschewsky [17], exist preferentially in water in the form of unimers.

Water soluble polymers carrying *both* hydrocarbon and fluorocarbon groups are expected to exhibit unique properties in aqueous media, as a result of the inherent lipophobic nature of fluorocarbons, which leads to incompatibility of fluorinated and hydrogenated chains. Conceptually, such copolymers may form multicompartment micelles, a phrase coined by Lehmann and Ringsdorf [18] and de Gennes [19], who compared the assembly of such copolymers to that of multidomain proteins. Examples of such hybrid amphiphilic polymers include hydrophobically-modified (HM) polyacrylamides [20], polysoaps carrying fluorocarbon and hydrocarbon side chains in a block copolymer structure [16], poly(*N*-acylethyleneimine) end-capped with a fluorocarbon and a hydrocarbon chain [21], and HM-poly(*N*-isopropylacrylamides) [22]. In the latter case, it was shown that in water the polymers form interpolymeric micelles with cores consisting of fluorocarbon-rich and hydrocarbon-rich nanodomains.

We report here the preparation and solution properties of a series of amphiphilic PAMPS bearing moderate amounts (5–20 mol%) of alkyl and/or perfluoroalkyl chains (Fig. 1). The polymers were labeled with low levels (5 mol%) of either pyrene or naphthalene chromophores. In all cases, each chromophore and either an alkyl or a perfluoroalkyl chain are linked to the same monomer unit. This approach differs from most spectroscopic studies monitoring the formation of fluorocarbon nanodomains, which are based on the use of a fluorocarbon-substituted pyrene probe. This molecule self assembles in aqueous solutions of extremely low concentration ($\sim 10^{-7}$ M) [23]. It interacts with amphiphilic polymers dissolved in water, but the precise localization of the chromophore within the hydrophobic nanodomains is uncertain, as pyrene is poorly compatible with fluorocarbon-rich nanodomains [24,25]. The photophysics of a chromophore linked to the same monomer unit as the hydrocarbon or fluorocarbon substituent of the polyelectrolyte provide a closer look into the formation of polymeric fluorocarbon nanodomains and eventual segregation of fluorocarbon and hydrocarbon nanodomains, as demonstrated in earlier studies of HM-PNIPAM [26–28].

The hybrid amphiphilic polyelectrolytes studied were obtained by free-radical polymerization in homogeneous solutions, taking advantage of the solubility in dimethylformamide (DMF) of all monomers. The copolymers were characterized by ^{1}H and ^{19}F NMR spectroscopy. Their solution properties in water were studied by fluorescence spectroscopy, using three methodologies: (i) formation of pyrene excimer as a means to assess the formation of hydrophobic nanodomains, (ii) non-radiative energy transfer (NRET) between excited naphthalene and pyrene chromophores to test the occurrence of interpolymeric micelles, and (iii) depolarization of naphthalene fluorescence to probe the microviscosity of the hydrophobic nanodomains. Further support for the formation of polymeric micelles in aqueous solutions of hybrid HM-PAMPS was gathered from surface tension and dynamic light scattering measurements. We study the effects of gradually substituting the hydrocarbon chains of HM-PAMPS with fluorocarbon chains on the properties of their aqueous solutions, including the tendency of intrapolymeric hydrophobic associations. Our results confirm the formation of unimers in aqueous solutions of HM-PAMPS bearing only hydrocarbon chains. We demonstrate that HM-PAMPS bearing fluorocarbon chains only also form unimers in water. Finally, we present compelling evidence suggesting that HM-PAMPS bearing *both* fluorocarbon and hydrocarbon chains also form unimolecular micelles, in which fluorocarbons and hydrocarbons cohabit.

2. Experimental

2.1. Materials

Dicholoromethane was purified by distillation from calcium hydride (CaH_2) under nitrogen (N_2) immediately before use. Dimethylformamide was dried over CaH_2 overnight, distilled under reduced pressure and kept under N_2 prior to use. Tetrahydrofuran (THF) was distilled from sodium and

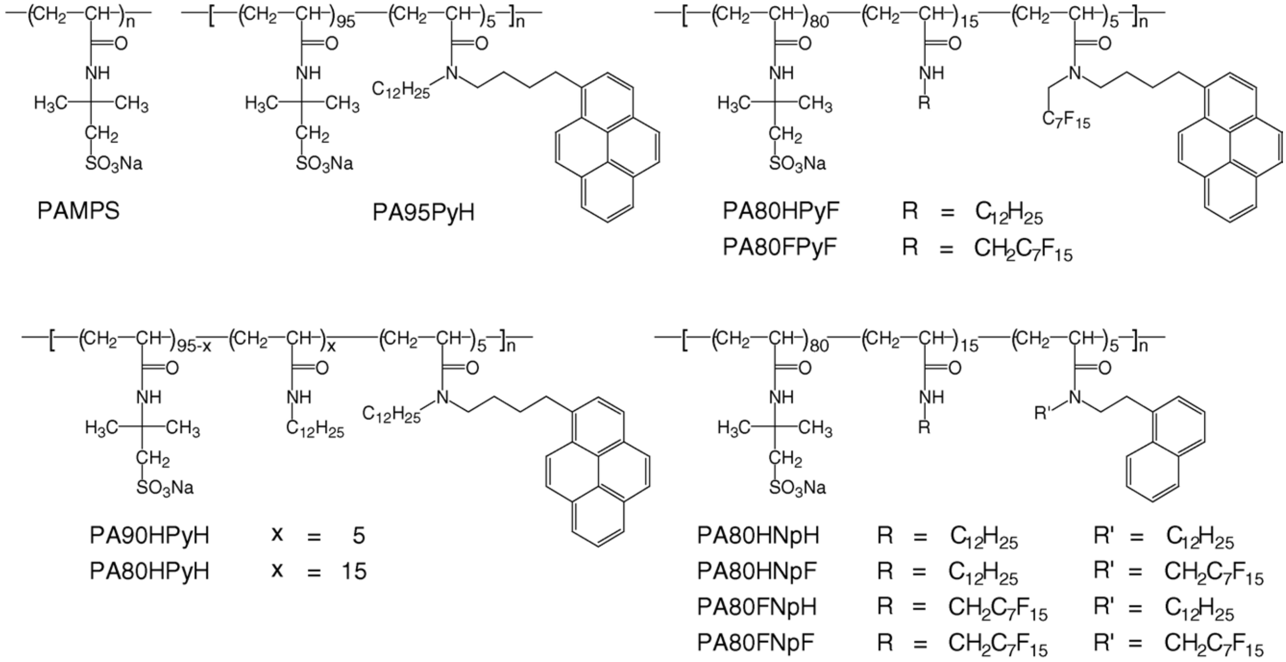

Fig. 1. Structure of the polymers used in this study.

triethylamine (Et_3N) was distilled from sodium hydroxide (NaOH) under N_2 before use. Water was deionized with a Millipore Milli-Q Water System. DMF and THF were obtained from Anachemia Canada Inc. and J.T. Baker, respectively. *N*,*N*-Azobis(isobutyronitrile) (AIBN), acryloyl chloride, borane-dimethyl sulfide complex (2.0 M solution in THF), *N*,*N*′-carbonyldiimidazole, 1-naphthylacetic acid, and 4-(1-pyrenyl)butyric acid (PBA) were obtained from Aldrich Chemical Co. Inc. and were used as received. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) and *n*-dodecylamine were obtained from Sigma Chemical Co. and were used without further purification. ^{1}H,^{1}H-Perfluorooctylamine was obtained from Lancaster synthesis. *N*-*n*-Dodecylacrylamide (DodAm) was prepared as described previously from *N*-*n*-dodecylamine and acryloyl chloride with an improved yield of 80% [29], and *N*-*n*-^{1}H,^{1}H-perfluorooctylacrylamide (OctAm) was prepared from *n*-^{1}H,^{1}H-perfluorooctylamine and acryloyl chloride following the same conditions with an improved yield of 77% [22]. Details on the preparation and spectroscopic characteristics of *N*-*n*-dodecyl-*N*-[2-(1-naphthyl)ethyl]acrylamide (NpDodAm), *N*-*n*-^{1}H,^{1}H-perfluorooctyl-*N*-[2-(1-naphthyl)ethyl]acrylamide (NpOctAm), *N*-*n*-dodecyl-*N*-[4-(1-pyrenyl)butyl]acrylamide (PyDodAm), and *N*-*n*-^{1}H,^{1}H-perfluorooctyl-*N*-[4-(1-pyrenyl)butyl]acrylamide (PyOctAm) are provided as supporting information.

Moisture- and oxygen-sensitive reactions were carried out in flame-dried glassware under N_2. Solvents for chromatography (hexane and THF) were distilled prior to use. FAB high resolution mass spectra were obtained from McMaster Regional Centre for Mass Spectrometry of McMaster University and the mass spectrometry laboratory at Université de Montréal. Combustion analyses were performed by the laboratory of elemental analysis of the Université de Montréal.

2.2. *Polymerizations*

2.2.1. *Pyrene labeled copolymer (PA95PyH)*

To a solution of AMPS (19 mmol) in DMF (50 mL), sodium carbonate (Na_2CO_3) (10 mmol) was added at 0 °C under N_2. The suspension was stirred for 6 h and was slowly warmed up to room temperature. PyDodAm (1 mmol) and AIBN (0.084 mmol) were added, and the polymerization mixture was gently stirred and bubbled with N_2 for 1 h. The mixture was then immersed into an oil bath and the stirring was continued for 48 h at 60 °C under N_2. The polymer was isolated by adding the reaction mixture slowly into diethyl ether (2 L) with vigorous stirring. The white solid was redissolved in methanol (MeOH) (50 mL) and the clear solution was added dropwise into diethyl ether (2 L) with vigorous stirring. The precipitation from MeOH (50 mL) into diethyl ether (2 L) was repeated two times, and the final white solid was collected by filtration and dried under vacuum overnight. The aqueous solution of the crude polymer (50 mL) was dialysed against deionized water until the conductivity of water became constant. The polymer solution was concentrated under vacuum and the polymer was isolated by lyophilization in a conversion yield of 90%. The polymer was then characterized and was used without further purification.

2.2.2. *Pyrene labeled terpolymers (PA90HPyH and PA80HPyH)*

These polymers were prepared in a conversion yield of 90% by following the procedure described above, starting from AMPS (20 mmol), PyDodAm (1.11 mmol for PA90HPyH or 1.25 mmol for PA80HPyH), and *n*-dodecylacrylamide (DodAm) (1.11 mmol for PA90HPyH or 3.75 mmol for PA80HPyH).

2.2.3. Pyrene labeled fluorinated terpolymers (PA90HPyF and PA80FPyF)

The polymers were prepared in a conversion yield of 90% according to the same polymerization procedure for PA95PyH, starting from AMPS (16 mmol), PyOctAm (1 mmol), and DodAm (3 mmol) or OctAm (3 mmol).

2.2.4. Naphthalene labeled fluorinated terpolymers (PA80HNpF, PA80FNpH, and PA80FNpF)

The polymers were prepared in a conversion yield of 90% as described for the preparation of PA95PyH, starting from AMPS (16 mmol), NpOctAm (1 mmol), and DodAm (3 mmol) or OctAm (3 mmol).

2.3. Instrumentation

Dynamic laser light scattering was performed on a Brookhaven laser light scattering instrument equipped with a BI9000 AT digital correlator and an Uniphase μBlue laser with an output power of 125 mW, which supplies vertically polarized light with a wavelength of 532 nm. The data were collected by monitoring the scattered light intensity at a 90 °C scattering angle at 25 °C. The cell was thermostated with a Neslab water circulating bath, and measurements were performed using polymer solutions filtered through membranes of 0.45 μm pore size directly into scintillation vials of 1.5 cm diameter prior to measurements. Data were analyzed using the software provided by the manufacturer (CONTIN calculations). Gel permeation chromatography (GPC) measurements were performed with a Waters 590 programmable HPLC system equipped with a Waters 486 UV detector and a Waters 410 differential refractometer. Poly(ethylene glycol) standards were used for calibration. FT-IR spectra were measured on a Bruker Vector 22 spectrometer. NMR spectra were recorded on a Bruker ARX-400 400 MHz spectrometer. Surface tensions were measured with a Future Digital Scientific DCAT11 tensiometer using the Du Noüy Ring method and the Wilhelmy Plate method. Temperature control within 0.1 °C was achieved using a Neslab RTE-9DD refrigerated bath circulator. All solutions for surface tension measurements were prepared at least 24 h in advance of measurements to ensure that equilibrium was reached. The platinum–iridium ring was thoroughly cleaned by washing with Milli-Q water, methanol and acetone, rinsing in Milli-Q water, and flaming until red-hot before each measurement. Surface tension values were recorded until the standard deviation between 50 consecutive values was less than 0.01 mN m^{-1}. The reproducibility between measurements on different samples of the same polymer was ±1 mN m^{-1}. UV–vis spectra were measured with a Hewlett-Packard 8452A photodiode array spectrometer.

2.4. Steady-state fluorescence spectroscopy

Steady-state fluorescence was recorded on a Fluorolog Tau 3 spectrometer operated by a GRAM/32 data system. Temperature control of the sample was achieved using a water-jacketed cell holder connected to a NESLAB circulating bath. Excitation spectra were measured in the ratio mode. Emission spectra were not corrected. They were recorded with an excitation wavelength of 344 nm (pyrene) and 290 nm (naphthalene). Emission and excitation slit widths were both set at 0.5 mm. Solutions in water were not degassed. In all solutions, the polymer concentration was kept low, in order to ensure that the maximum absorbance of a solution at the excitation wavelength remains below 0.07, thus avoiding undesirable inner filter effects and self quenching.

2.5. Fluorescence depolarization

Fluorescence anisotropy (r) was measured on a SPEX Fluorolog 212 spectrometer equipped with a polarizer (excitation side) and an analyzer (detection side) and operated by a GRAM/32 data system. Fluorescence spectra for the naphthalene-labeled polymers were obtained at 25 °C by excitation at 290 nm and monitored at 340 nm. Both the excitation and emission slits widths were maintained at 10.0 nm. The r-value was calculated from

$$r = \frac{I_{\mathrm{VV}} - gI_{\mathrm{VH}}}{I_{\mathrm{VV}} + 2gI_{\mathrm{VH}}} \tag{1}$$

where I_{VV} and I_{VH} are the fluorescence intensities measured with parallel and perpendicular orientations of the excitation and emission polarizers, respectively, and g is the factor for instrumental correction [30]:

$$g = \frac{I_{\mathrm{HV}}}{I_{\mathrm{HH}}} \tag{2}$$

2.6. Non-radiative energy transfer (NRET)

Aqueous mixtures of HM-PAMPS-Py (PA95PyH, PA90HPyH, PA80HPyH, PA80HPyF, or PA80FPyF) (0.01 g L^{-1}) with various HM-PAMPS-Np (PA80HNpH, PA80HNpF, or PA80FNpF) concentrations (0–0.1 g L^{-1}) were excited at 290 nm and the spectra were recorded in the wavelength range from 300 to 600 nm. The naphthalene monomer and pyrene excimer emission intensities, I_{Np} and I_{Py}, respectively, were estimated at 340 and 480 nm, respectively. To obtain an accurate value of I_{Py} in the emission of mixed solutions, the contribution from the naphthalene emission at 375 nm was subtracted from each spectrum, using I_{Np} (375 nm) measured upon excitation of solutions of Np-labeled HM-PAMPS (0.01–0.1 g L^{-1}).

2.7. Time-resolved fluorescence spectroscopy

Fluorescence lifetimes were measured on a Fluorolog Tau 3 multi-frequency phase modulation fluorometer (Jobin-Yvon Horiba Inc.). The excitation light from a 450 W xenon lamp was modulated with a Pockels cell. Phase and modulation values were determined relative to a glycogen aqueous solution. The excitation wavelength was set at 344 nm (pyrene) or 290 nm (naphthalene). Pyrene monomer and excimer emissions were monitored at 375 and 480 nm, respectively, and naphthalene monomer emission was monitored at 340 nm. The frequency of the analyzing light was chosen in the range of 0.1–10 MHz.

All measurements were carried out at 25 °C. Data were analyzed with the Datamax spectroscopy software based on a GRAM/32 data system (Galactic Inc.). Data were fit to a multi-exponential decay law:

$$F(t) = \sum a_i \, e^{-t/\tau_i} \tag{3}$$

where a_i and τ_i are the pre-exponential factors and the lifetime of the ith component, respectively. The goodness of the fit was determined by the χ^2 value ($\chi^2 < 1.1$) and examination of the residuals. The pre-exponential factors a_i are related to the observed fractional intensity contribution f_i by the relation:

$$f_i = \frac{a_i \tau_i}{\sum_j a_j \tau_j} \tag{4}$$

The average lifetime $\langle\tau\rangle$ was calculated from:

$$\langle\tau\rangle = \sum f_i \tau_i \tag{5}$$

2.8. Determination of the spectroscopic parameters

The fluorescence of HM-PAMPS-Py in aqueous solutions consists of two contributions: a well-resolved spectrum with the [0,0] band at 375 nm, attributed to the emission of spatially isolated pyrene groups (pyrene monomer emission, intensity I_M) and a broad featureless band centered at 480 nm attributed to pyrene excimer emission (intensity I_E). Dynamic excimer emission requires that an excited pyrene (Py^*) and a pyrene in the ground state come in close proximity during the Py^* lifetime. On the other hand, formation of pyrene/pyrene aggregates before excitation results in static excimer emission [31,32]. The pyrene excimer-to-monomer ratio (I_E/I_M) was taken as the ratio of the intensity (peak height) at 480 nm to the intensity at 375 nm. Mixed solutions of HM-PAMPS-Py and HM-PAMPS-Np excited at 290 nm show a complex emission consisting of the direct emission from excited naphthalene and the emission of pyrene excited through non-radiative energy transfer (NRET) from excited naphthalene. Pyrene and naphthalene are known to interact as energy donor (naphthalene) and energy acceptor (pyrene) by NRET with a characteristic distance (R_0) of 29 Å [33]. The extent of pyrene emission due to NRET from naphthalene to pyrene was assessed by recording the ratio (I_{Py}/I_{Np}) of the emission intensity at 375 nm (pyrene) to the emission intensity at 340 nm (naphthalene), after correcting for emission due to direct pyrene excitation at 290 nm. In this case, the correction was performed by subtracting from each spectrum the emission spectrum of HM-PAMPS-Py, excited at 290 nm, of identical pyrene concentration.

2.9. Sample preparation

Stock solutions of HM-PAMPS-Py and HM-PAMPS-Np were prepared by dissolving each polymer separately in water (0.2 g L^{-1}) and stirring at room temperature in the dark overnight to ensure complete dissolution of the polymers, and were then kept still for 3 h before use. Polymer solutions used for spectroscopic analysis were made by diluting aliquots of the stock solutions to the desired concentration. Mixed polymer solutions for NRET experiments were obtained by combining the HM-PAMPS-Py stock solution with various amounts of stock solution of HM-PAMPS-Np, while keeping the HM-PAMPS-Py concentration constant (0.01 g/L) in each sample, and diluting with water. All polymer solutions were allowed to equilibrate and stir overnight, and stand for another 3 h at room temperature prior to fluorescence measurements.

3. Results and discussion

3.1. Polymer synthesis and characterization

All polymers were synthesized by azobis(isobutyronitrile) (AIBN) initiated free radical polymerization of sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) and the respective hydrocarbon- and/or fluorocarbon-modified acrylamides. Two pyrene-labeled monomers bearing either an *n*-dodecyl chain or an *n*-^{1}H,^{1}H-perfluorooctyl chain and two naphthalene-labeled monomers bearing either an *n*-dodecyl chain or an *n*-^{1}H,^{1}H-perfluorooctyl chain were prepared from 4-(1-pyrenyl)butyric acid or 1-naphthylacetic acid and the corresponding alkylamine or perfluorinated alkylamine via a three-step synthesis, involving: (i) a one-pot two-step *N*,*N*′-carbonyldiimidazole catalyzed coupling of the amine and carboxylic acid [34–36] to the corresponding amides, (ii) a borane-dimethyl sulfide complex reduction of the amide producing quantitatively the corresponding amines [37], and (iii) a reaction of the amines with acryloyl chloride [38,39]. In all cases, the reaction yields were comparable, independently of the reactant identity (see scheme and detailed procedures in Supplementary data).

The polymerizations were carried out in freshly distilled *N*,*N*-dimethylformamide, a solvent in which both monomers and polymers are soluble. These conditions were used to favor the statistical growth of polymers and to control the polymer composition by the initial monomer feed ratios [40]. All polymers were purified by repeated precipitations from methanol in diethyl ether and dialysis in water. The polymer molecular weight was estimated from GPC measurements, using a 0.2 M solution of $LiClO_4$ in methanol as an eluent and standard poly(ethylene glycol) samples for calibration (Table 1).

The polymer chemical composition was determined by ^{1}H NMR and UV–vis spectroscopy (Table 1). The ^{1}H NMR spectrum of PA80HPyF in CD_3OD (Fig. 2) presents a sharp singlet at δ 0.91 ppm attributed to the resonance of the terminal methyl protons of the *n*-dodecyl chain, a broad singlet at δ 2.36 ppm due to the resonance of the main chain methine protons, and a multiplet centered at δ 8.1 ppm attributed to the resonance of the pyrenyl protons. These three signals were used jointly to determine the incorporation level of *n*-dodecyl group (15 mol% or $\sim 6 \times 10^{-4}$ mol g^{-1} polymer) and of *N*-*n*-^{1}H,^{1}H-perfluorooctyl-*N*-4-(1-pyrenyl)butyl group (5 mol% or $\sim 2 \times 10^{-4}$ mol g^{-1} polymer). The latter value was confirmed by UV absorption data of the polymer solution in methanol, using the pyrene-labeled monomer, PyOctAm ($\varepsilon_{344} = 34{,}900$ cm^{-1} mol^{-1} L), as a reference compound.

Table 1
Molecular characteristics of the polymers prepared

Polymer	Chemical composition (mol%)					Physical properties		
	NaAMPS[a]	$C_{12}H_{25}$[a]	$CH_2C_7F_{15}$	Np[c]	Py[c]	M_n[d]	M_w[d]	M_w/M_n[d]
PA95PyH	95	5			5	36000	80000	2.2
PA90HPyH	90	10			5	38000	103000	2.7
PA80HPyH	80	20			5	28000	81000	2.9
PA80HPyF	80	15	5		5	37000	92000	2.5
PA80FPyF	80		20[b]		5	33000	86000	2.6
PA80HNpH	80	20		5		31000	77000	2.5
PA80HNpF	80	15	5	5		28000	59000	2.1
PA80FNpH	80	5	15[b]	5		50000	129000	2.6
PA80FNpF	80		20[b]	5		29000	66000	2.3

[a] From ^1H NMR measurements.
[b] From monomer feed ratios.
[c] From UV absorbance measurements.
[d] From GPC measurements.

The same approach was used to determine the hydrophobe incorporation level for the analogous naphthalene labeled polymer, PA80HNpF, and the four polymers that contain only hydrocarbon chains (PA95PyH, PA90HPyH, PA80HPyH, and PA80HNpH) (results not shown). In the cases of PA80FPyF, PA80FNpF and PA80FNpH that contain the *N*-*n*-^1H,^1H-perfluorooctylacrylamide (OctAm) monomer unit, it was not possible to determine the total level of perfluorinated alkyl chain incorporation from the respective ^1H NMR spectra, due to the unfortunate overlap of the NaAMPS methylene protons and the perfluorinated *n*-octyl methylene protons resonances at δ 3.33 ppm. For all polymers bearing fluorocarbon chains, evidence for the presence of *n*-^1H,^1H-perfluorooctyl groups was provided by the ^{19}F NMR spectrum of the polymer solutions in CD_3OD. The total level of fluorocarbon incorporation was taken to be identical to the monomer feed ratio, an assumption deemed acceptable given the excellent relationship, in the case of hydrocarbon-containing monomers, between monomer feed ratios and the compositions of the copolymers obtained by analysis of their ^1H NMR spectra (see above).

3.2. Micellar properties of the polymers

While the ^1H and ^{19}F NMR spectra of the polymer solutions in CD_3OD were well-resolved, ^1H NMR spectra acquired with the polymer solutions in D_2O exhibited significant broadening of certain signals (Fig. 3). These included the singlet at δ 0.91 ppm and the multiplet centered at δ 8.1 ppm, which are due to the resonances of the terminal methyl protons of the *n*-dodecyl chains and the polycyclic aromatic groups, respectively. The loss of resolution indicates that the motions of the hydrocarbon and polycyclic aromatic groups are highly restricted. These phenomena clearly suggest association of these hydrophobic groups to form hydrophobic nanodomains and the existence of polymeric micelles [41]. The formation of micellar structures was supported by dynamic light scattering

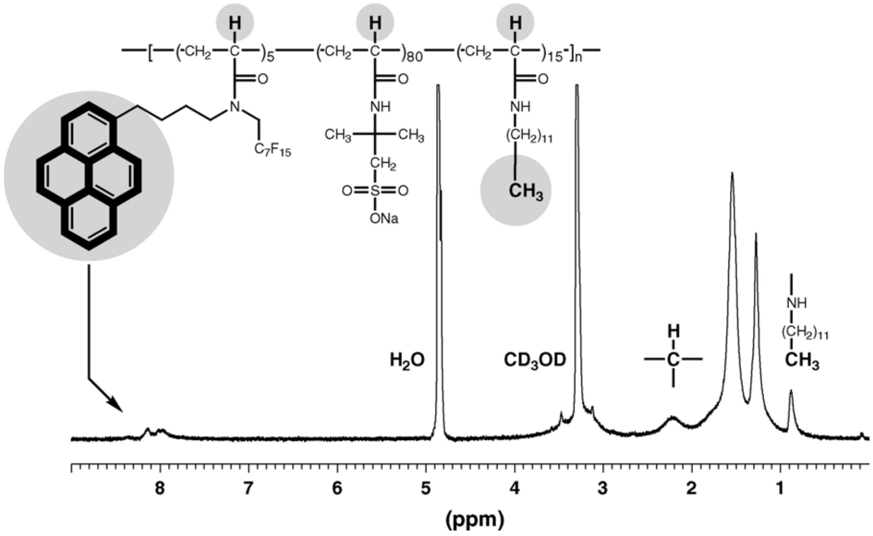

Fig. 2. ^1H NMR spectrum of PA80HPyF in CD_3OD.

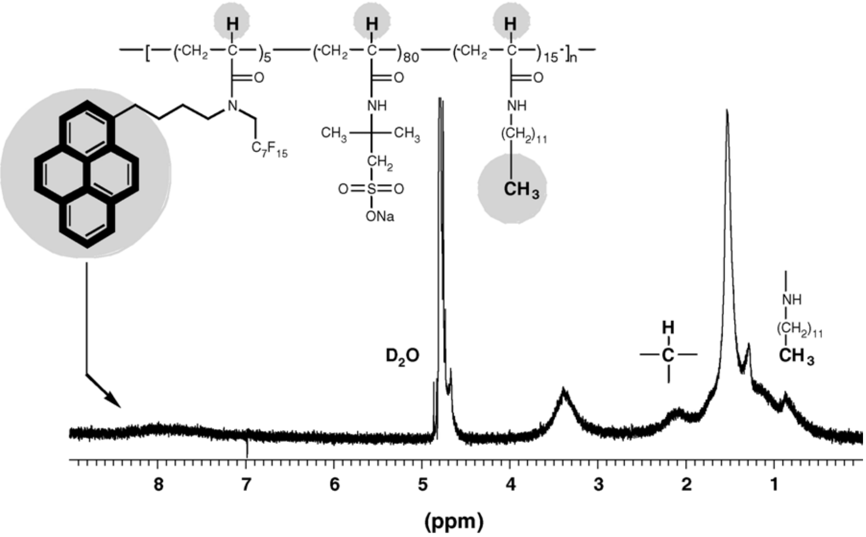

Fig. 3. ^{1}H NMR spectrum of PA80HPyF in D_2O.

measurements (20 °C, 1 g L^{-1}) for these hydrophobically modified PAMPS (HM-PAMPS). The effective hydrodynamic diameter of the polymeric micelles, as determined by a cumulative analysis of the data, ranges from 15 to 25 nm depending on the nature of the hydrophobic substituent. It did not vary significantly with polymer concentration within the concentration range (0.5–2.0 g L^{-1}) for which the polymeric micelles were detectable.

Further information on the aggregation of the hydrophobes of HM-PAMPS in water was provided by surface tension measurements carried out at 25 °C (Fig. 4). Hydrocarbon-, fluorocarbon-, and mixed hydrocarbon/fluorocarbon-modified PAMPS behave similarly at the air/water interface. The surface tension of all polymer solutions remained constant for solutions of low polymer concentrations (0.01–0.1 g L^{-1}). It decreased monotonically with increasing polymer concentration, from ∼0.5 to 10 g L^{-1}, with no sharp break point, that would indicate the attainment of a critical aggregation concentration (cac), similar to the detection of the critical micellar concentration of surfactants [42]. The surface activity of all polymers, even in concentrated solutions, remained weak. For instance, the surface tension of a 10 g L^{-1} aqueous solution of PA80HPyH, which has a *n*-dodecyl concentration of 8.2 mM, was ∼60 mN m^{-1}, a value significantly higher than the surface tension of ∼40 mN m^{-1} recorded for an aqueous solution of sodium dodecylsulfate (SDS) at a concentration above the cmc (10 mM). The surface tension of HM-PAMPS solutions is also significantly higher than that of an aqueous solution of poly(sodium acrylate) grafted with 3 mol% of *n*-dodecyl chains, 38 mN m^{-1}, polymer concentration: 2 g L^{-1} [43]. The latter polymer is known to associate in water via predominantly *interpolymeric* hydrophobic interactions [44]. Our results suggest that the hydrophobes grafted on the HM-PAMPS main chains are not available for adsorption at the air/water interface, but rather buried inside the polymeric micelles.

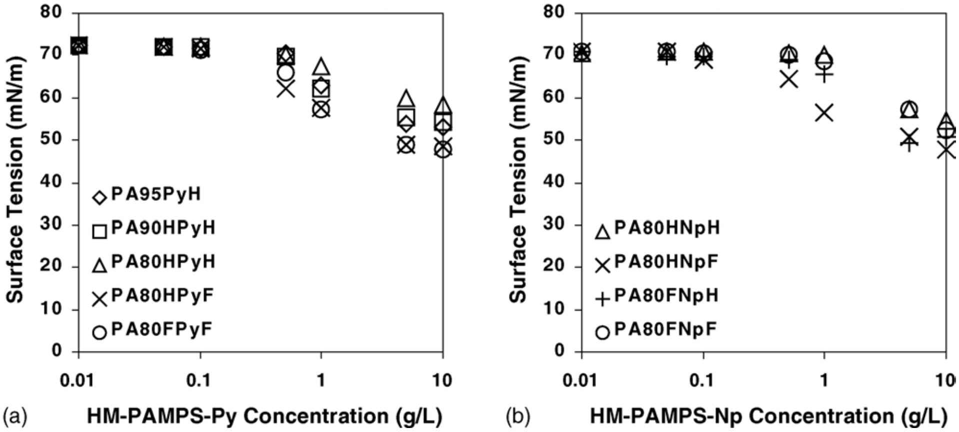

Fig. 4. Plot of the changes in surface tension for aqueous solutions of HM-PAMPS-Py, and HM-PAMPS-Np as a function of polymer concentration; temperature = 25 °C.

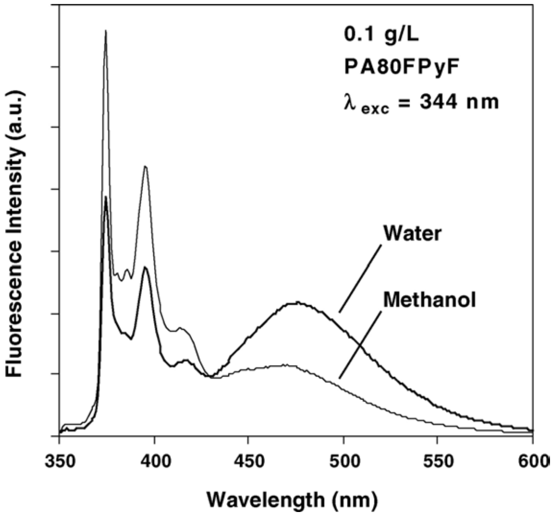

Fig. 5. Fluorescence spectra of solutions of PA80FPyF in methanol and in water; $\lambda_{exc} = 344$ nm; polymer concentration = 0.1 g L^{-1}.

3.3. *Photophysical properties of the polymers*

3.3.1. *Pyrene-labeled HM-PAMPS*

Steady-state emission spectra were acquired for pyrene-labeled HM-PAMPS (HM-PAMPS-Py) in methanol and water, and in aqueous NaCl solutions of increasing ionic strength. The polymers in water show a characteristic well-resolved emission due to the locally isolated excited pyrenes (Fig. 5), with the (0,0) band located at 375 nm (monomer emission, intensity I_M) as well as a strong, broad, featureless emission centered at 480 nm (intensity I_E) attributed to the emission of pyrene excimers. This strong pyrene excimer emission implies that the pyrene groups are in close spatial proximity. This may be due to either a non-statistical distribution of the pyrene groups along the polymer chain or the formation of hydrophobic nanodomains that bring together pyrene groups attached to monomer units well separated along the polymer chain. It seems unlikely that the pyrene-containing units are clustered in blocks, since the polymerization was conducted under conditions previously shown to lead to HM-PAMPS-Py having random monomer unit distributions along the main chain [45] Moreover, the spectrum of the same polymers in methanol (Fig. 5), a good solvent for HM-PAMPS-Py, presents a weaker excimer emission, contrary to what would be expected to occur if these pyrene groups were attached to neighboring monomer units.

Spectra of all HM-PAMPS-Py were recorded for solutions of polymer concentration ranging from 0.002 to 0.5 g L^{-1}. The ratio $[I_E/I_M]^{Py}$ was insensitive to changes in polymer concentration: $[I_E/I_M]^{Py} = 0.141 \pm 0.006$, PA95PyH; $[I_E/I_M]^{Py} = 0.205 \pm 0.010$, PA90HPyH; $[I_E/I_M]^{Py} = 0.297 \pm 0.009$, PA80HPyH; $[I_E/I_M]^{Py} = 0.276 \pm 0.021$, PA80HPyF; $[I_E/I_M]^{Py} = 0.345 \pm 0.010$, PA80FPyF. This observation can be taken as an indication that unimers exist in solutions of all HM-PAMPS-Py, independently of the degree of modification and of the chemical nature of the hydrophobic substituents. Comparing the $[I_E/I_M]^{Py}$ values recorded for these polymers, we note that the ratio increases not only with the incorporation level of hydrocarbon chains, but also with the substitution level of fluorocarbon chains. Time resolved fluorescence measurements were performed on all polymer solutions in water (Table 2). No growing-in component was detected in the profile recorded for the excimer, indicating the occurrence of a “static excimer” [31]. This excimer formation mechanism is supported also by features of the excitation spectra monitored for the pyrene monomer and excimer emissions (Fig. 6, right panel). They present the same overall shape, but the former is red-shifted by ca. 2 nm. Also, the peak-to-valley ratio computed for the excimer excitation spectrum (1.31) is smaller than that obtained from the monomer excitation spectrum (1.79) [31].

Next, the emission spectra of HM-PAMPS-Py were measured in aqueous solutions of increasing salt concentration. Most noticeable is the salt-induced *increase in pyrene excimer emission intensity*, relative to the pyrene monomer emission intensity. This effect is illustrated in Fig. 6 (left panel), which presents the change of the ratio $[I_E/I_M]^{Py}$ for PA80FPyF solutions of increasing ionic strength. The ratio increases sharply in the low ionic strength domain (0–0.2 M) and continues to increase slightly in solutions of higher ionic strength. The spectroscopy of HM-PAMPS-Py undergoes an additional minor, but revealing, change easily detectable by steady-state fluorescence. The differences between the excitation spectra recorded for the excimer and monomer emissions are enhanced, diagnostic of the predominance of the “static excimer” formation mechanism in solutions of high ionic strengths. Taken together, these features point to a significant contraction of the unimolecular micelles in solutions of high salt concentrations. Increasing the ionic strength enhances the folding or coiling of the polymer main chains (screening effect) [46], and thus, brings more pyrene groups into close proximity.

3.3.2. *Naphthalene labeled HM-PAMPS*

Naphthalene (Np) groups covalently linked to a polymer backbone are often used as fluorescence depolarization probes to monitor the dynamics and conformations of polymers in solution [47]. In the case of aqueous solutions of a Np-labeled amphiphilic polyelectrolyte, the incorporation of the Np groups in the hydrophobic nanodomains formed by the non-polar alkyl chains restricts the local motions of these chromophores [48]. Thus, the fluorescence anisotropy (r) is an index of the rigidity of the hydrophobic nanodomains [49]. The fluorescence anisotropy of Np was determined for all Np-labeled HM-PAMPS (HM-PAMPS-Np) dissolved in water over a wide polymer concentration range (0.05–1.0 g L^{-1}). Different r-values were recorded, depending on the nature of the hydrophobic group linked to the polymer, but for a given polymer, r remained constant over the entire concentration range probed. The averaged r-value was 0.030 for PA80HNpH solutions and 0.047 for PA80FNpF solutions, implying a lower mobility of the chromophores in the latter case. This effect might be taken as an indication of an enhanced clustering of the Np groups as a result of the incompatibility between fluorocarbon chains and hydrocarbon aromatic groups [50]. In the case of HM-PAMPS-Np bearing both fluorocarbon

Table 2
Fluorescence lifetimes of pyrene and naphthalene in aqueous solutions of PA80HPyH, PA80HPyF, PA80FPyF, PA80HNpH, and in mixed polymer solutions

Sample	λ_{exc} (nm)	λ_{em} (nm)	τ_1 (ns)	a_1	τ_2 (ns)	a_2	$\langle\tau\rangle$ (ns)
PA80HPyH	344	375	25.6	0.20	103.3	0.80	87.8
		480	63.4	1.0			
PA80HPyF	344	375	27.7	0.24	111.7	0.76	91.5
		480	65.2	1.0			
PA80FpyF	344	375	32.0	0.20	115.3	0.80	98.6
		480	61.3	1.0			
PA80HNpH	290	340	43.7	1.0			
PA80HPyH + PA80HNpH ([Py]/[Np] = 1)	290	340	47.3	1.0			
		375	28.6	0.22	109.9	0.78	92.0
		480	65.1	1.0			
	344	375	29.0	0.25	109.2	0.75	89.2
		480	70.3	1.0			
PA80HPyF + PA80HNpF ([Py]/[Np] = 1)	290	340	39.5	1.0			
		375	26.0	0.23	108.5	0.77	89.5
		480	61.7	1.0			

and hydrocarbon chains, the averaged *r*-value was higher in the case of PA80HNpF (0.039), compared to PA80FNpH (0.032). These spectroscopic results parallel the photophysical properties of HM-PAMPS-Py, particularly the facts that $[I_E/I_M]^{Py}$ is independent of polymer concentration and that it is higher in the case of PA80FPyF solutions, compared to PA80HPyH solutions.

Steady-state fluorescence spectra of HM-PAMPS-Np were also recorded for polymer solutions in water and in methanol. In methanol, the polymers exhibited a structured spectrum with a maximum at 340 nm (I_{Np}), characteristic of locally isolated excited naphthalenes. No excimer emission was observed. In contrast, polymer solutions in water present spectra with a significant contribution from naphthalene excimer emission ($\lambda_{max} = 400$ nm). This emission persists in solutions of very low concentration ($[I_E/I_M]^{Np} = 0.24 \pm 0.01$, PA80FNpF, water, 0.05 g L^{-1}). Thus, the spectroscopic data also support the formation of unimolecular micelles in aqueous solutions of HM-PAMPS-Np.

3.3.3. Mixed solutions of pyrene labeled and naphthalene labeled HM-PAMPS

The pyrene and naphthalene chromophores are known to interact as a pair of energy donor (Np) and energy acceptor (Py) by non-radiative energy transfer (NRET), with a characteristic distance, R_0, of 29 Å [51]. Under circumstances where Py and Np groups are in close enough proximity to satisfy the NRET requirements, excitation at 290 nm will result in a complex emission consisting of an emission from the excited naphthalene (Np^*, 310–400 nm) and an emission of pyrene (Py^*) excited by transfer of energy from Np^*. Excitation of a mixed solution of Np- and Py-labeled polymers with a light of 344 nm will result exclusively in the direct excitation of Py with no contribution via NRET from Np, which does not absorb light of this wavelength. The occurrence of energy transfer can be confirmed also by the fluorescence lifetimes of the pyrene and naphthalene chromophores [26]: (i) the decay of Np^* is faster, compared to the fluorescence lifetime of Np^* that does not undergo energy transfer, and (ii) the time-dependent profile of Py^* presents a

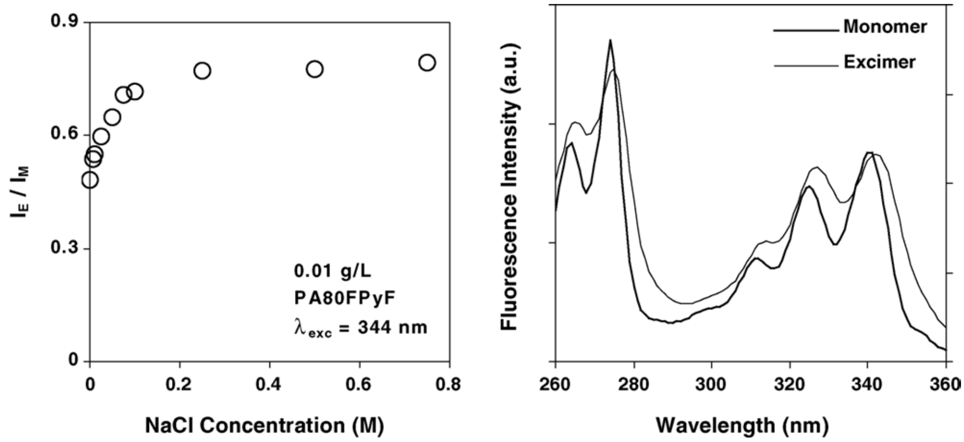

Fig. 6. (Left) Changes in the ratio I_E/I_M for aqueous solutions of PA80FPyF as a function of NaCl concentration: $\lambda_{exc} = 344$ nm; polymer concentration = 0.01 g L^{-1}. (Right) Excitation spectra of PA80FPyF in water: thick line, $\lambda_{em} = 375$ nm (pyrene monomer); thin line, $\lambda_{em} = 480$ nm (pyrene excimer); polymer concentration = 0.1 g L^{-1}.

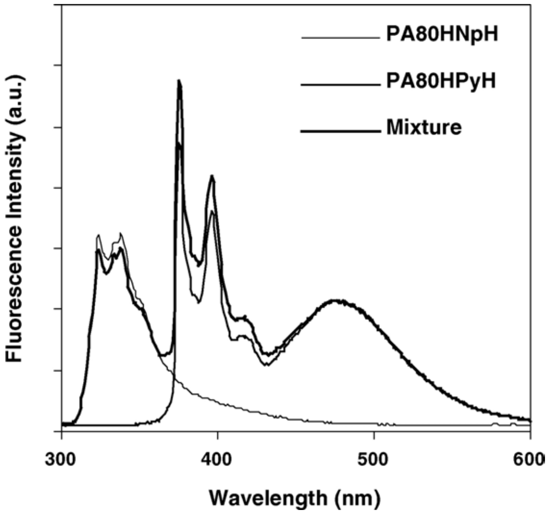

Fig. 7. Fluorescence spectra of aqueous solutions of PA80HPyH (0.01 g L^{-1}), PA80HNpH (0.01 g L^{-1}), and of a mixture of the two polymers (total polymer concentration = 0.02 g L^{-1}): λ_{exc} = 290 nm.

short-lived growing-in component corresponding to the energy transfer process.

Excitation of Np (λ_{exc} = 290 nm) in a mixed solution of PA80HPyH and PA80HNpH resulted in an emission with contribution from Np^* (maximum at 340 nm), and weak contributions from the pyrene monomer (360–400 nm) and pyrene excimer (maximum at 480 nm). By comparing this emission to the spectra recorded for solutions of individual polymers, one observes concurrently a small quenching of the naphthalene emission and a weak enhancement of the pyrene monomer emission (Fig. 7), implying that the efficiency of the NRET process in the mixed solution is poor. Note (Fig. 7) that the differences detected via steady state measurements are minimal, barely above the expected experimental uncertainties. Time-resolved fluorescence measurements performed on mixed solutions with [Py]/[Np] = 1 yielded no support for the occurrence of NRET between Np^* and Py: (i) the profile of the Py^* monomer (λ_{exc} = 290 nm) in mixed solutions of PA80HPyH and PA80HNpH features no rising component (Table 2); (ii) the fluorescence decay lifetime of Np^* was the same in mixed solutions and in solutions of HM-PAMPS-Np alone.

Further NRET experiments were performed under the same conditions for other pairs of HM-PAMPS-Py and HM-PAMPS-Np, to determine the hydrophobe effect on the interpolymeric hydrophobic associations of HM-PAMPS. No significant NRET occurred between PA80HNpH and either PA95PyH or PA90HPyH in aqueous solutions. In the cases of HM-PAMPS-Py bearing fluorocarbon chains (PA80HPyF and PA80FPyF), HM-PAMPS-Np with the same content of fluorocarbon chains (PA80HNpF and PA80FNpF, respectively) were selected for the NRET experiments. Neither the mixed PA80HPyF/PA80HNpF solutions nor the mixed PA80FPyF/PA80FNpF solutions showed any significant NRET, even in solutions containing up to a 10-fold excess of HM-PAMPS-Np. The inefficiency, or non-existence, of NRET implies that the pyrene groups of HM-PAMPS-Py and the naphthalene groups of HM-PAMPS-Np are incorporated in separated hydrophobic nanodomains, supporting the formation of unimolecular micelles in water.

Since fluorocarbon groups are known to exhibit poor compatibility with both hydrocarbon groups and aromatic polycyclic groups, the observations for the fluorocarbon/hydrocarbon hybrid HM-PAMPS in mixed PA80HPyF/PA80HNpF solutions deserve further comments. Laschewsky et al. have reported that an ionene carrying both alkyl and fluorinated alkyl side chains in the form of a statistical copolymer behaves as an associating polyelectrolyte and forms interpolymeric aggregates. On the contrary, the ionene bearing both alkyl and fluorinated alkyl side chains in the form of a block copolymer, and the ionenes bearing either alkyl or fluorinated alkyl side chains all show a strong tendency of intrapolymeric hydrophobic associations. We suggest that the strong preference for intrapolymeric hydrophobic associations for PA80HPyF and PA80HNpF may be due to the high mobility of the sulfonate groups of NaAMPS, which remarkably reduces the rigidity of the highly charged polymer main chain and can accommodate the conformation of an unimolecular micelle.

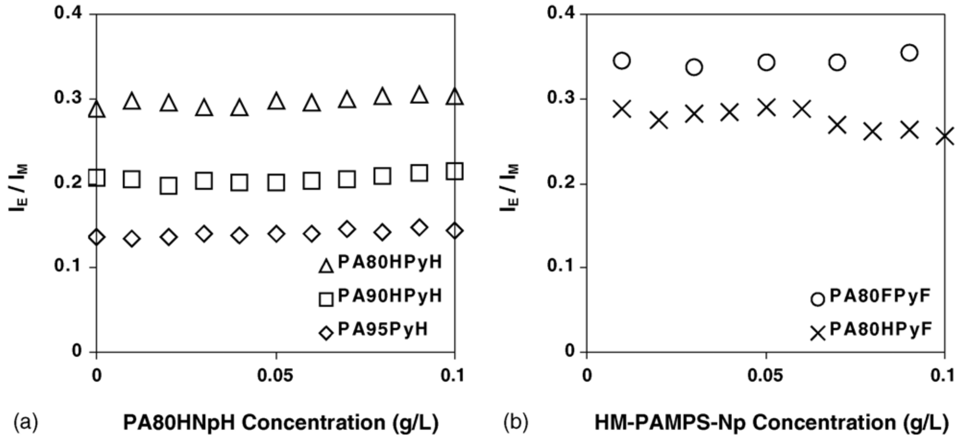

Fig. 8. (a) Changes as a function of increasing PA80HNpH concentration of the ratio I_E/I_M for aqueous mixtures of PA95PyH and PA80HNpH (◇), PA90HPyH and PA80HNpH (□), and PA80HPyH and PA80HNpH (△): λ_{exc} = 344 nm and (b) changes as a function of increasing HM-PAMPS-Np concentration of the ratio I_E/I_M for aqueous mixtures of PA80HPyF and PA80HNpF (×), and PA80FPyF and PA80FNpF (◯): λ_{exc} = 344 nm.

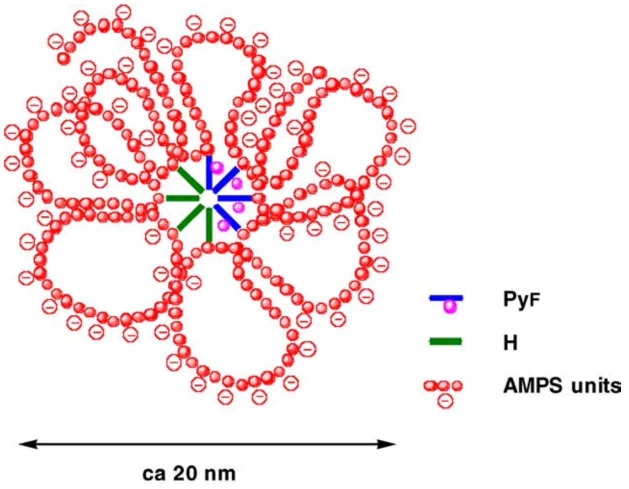

Fig. 9. Conceptual representation of the hybrid unimer micelle.

Next, the pyrene emission of HM-PAMPS-Py in aqueous solutions ($\lambda_{exc} = 344$ nm, 0.01 g L^{-1}) was assessed as a function of added HM-PAMPS-Np. The presence of HM-PAMPS-Np did not affect the fluorescence of HM-PAMPS-Py. The monomer emission and the excimer emission remained constant. These results are presented in Fig. 8, where the values of the ratio $[I_E/I_M]^{Py}$ are plotted as a function of HM-PAMPS-Np concentration. The ratio remains constant upon addition of HM-PAMPS-Np, even in solutions containing up to a 10-fold excess of HM-PAMPS-Np. These spectroscopic observations reveal the absence of dilution of the hydrophobic core of HM-PAMPS-Py micelles by HM-PAMPS-Np *n*-dodecyl chains, which could provide a solubilizing environment for the pyrene chromophores. In mixed polymer micelles, the pyrene groups would separate from each other, and with sufficient added *n*-dodecyl chains, they would be kept apart from each other at distances too large for efficient excimer formation. The failure of HM-PAMPS-Np to alter the emission of HM-PAMPS-Py is a consequence of the incompatibility of the hydrophobic cores of HM-PAMPS-Py and of HM-PAMPS-Np. The absence of changes in the excitation spectra of the Py chromophores in response to added HM-PAMPS-Np brings further support to this conclusion.

We tested the reluctance to mix of these two types of fluorescently labeled polymeric micelles by subjecting the mixed solutions of HM-PAMPS-Py and HM-PAMPS-Np to prolonged standing in the dark at room temperature (up to 36 h) or by heating them to 60 °C. Neither treatment resulted in a change in the emission of HM-PAMPS-Py, independently of the total polymer concentration or the number of heating/cooling cycles.

4. Conclusions

The fluorescence label experiments as well as the dynamic light scattering and surface tension measurements give convincing evidence that HM-PAMPS carrying as few as 5 mol% of *N*-*n*-dodecyl-*N*-4-(1-pyrenyl)butyl groups along the polymer main chain preferentially form *intrapolymeric* micellar structures, even in solutions of high polymer concentrations. The fluorescently labeled HM-PAMPS form polymeric micelles with an averaged diameter of 20 nm, as a result of the associations of hydrophobes in aqueous solutions. The micellar structure consists of a hydrophobic core that captures the naphthalene or pyrene chromophores, with the polyelectrolyte main chain surrounding this hydrophobic nanodomain (Fig. 9). In contrast to the observations of Laschewsky et al. in their investigations of aqueous solutions of ionenes randomly grafted with fluorocarbon and hydrocarbon groups, we found no evidence for interpolymeric aggregation in the aqueous solutions of HM-PAMPS bearing fluorocarbon and hydrocarbon groups. To our knowledge, this is the first example of fluorocarbon/hydrocarbon hybrid amphiphilic polyelectrolytes that show a strong tendency of intrapolymeric hydrophobic associations to form unimolecular micelles in water. The detailed structure of these hybrid unimolecular micelles, in which the alkyl and the fluorinated alkyl chains may, or may not, demix, remains an open question that is under current investigation.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2005.10.026.

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