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Determination of the Macromolecular Dimensions of Hydrophobically Modified Polymers by Micellar Size Exclusion Chromatography Coupled With Multiangle Light Scattering

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The present work demonstrates that the use of a nonionic surfactant in the mobile phase together with light scattering coupled to size exclusion chromatography (SEC) provides an accurate determination of macromolecular dimensions of hydrophobically modified water-soluble polymer and polyelectrolyte, i.e., weight-average molar mass M_w and polydispersity I_p. This method, called micellar SEC, is based on the dissociation of the aggregates in aqueous solution and the formation of mixed micelles between the surfactant and the polymer hydrophobic groups. The methodology and its application are presented for synthetic sulfonated polyacrylamides (5 and 20 mol %) modified with three hydrophobic alkyl side groups (C8, C12, and C18) and with Triton X-100 as a nonionic surfactant and are discussed according to the associativity of polymers. The results are compared to those obtained by classical SEC in 0.1 M $NaNO_3$ and by static light scattering in formamide solution.

A hydrophobically modified water-soluble polymer (HMP) or polyelectrolyte (HMPE) consists of a hydrophilic polymer or polyelectrolyte chain that carries a small number of hydrophobic groups grafted onto the polymer or polyelectrolyte backbone. The sizes of the hydrophobic groups can vary, with linear or branched alkyl chains of various lengths, typically from 8 to 18 carbons (C8 to C18). These modified polymers are useful in a variety of applications. Aryl or alkylaryl groups can be applied for ultraviolet spectroscopy or fluorescence analysis, whereas fluorocarbon groups provide stronger hydrophobic interactions.[1−10] Additionally, hydrophobic monomers bearing a zwitterionic group[11] and thermoassociative groups have been considered in the literature.[12−14]

These hydrophobic groups tend to associate in aqueous solution, thus forming reversible intra- and intermolecular bonds. At low concentrations, intramolecular associations are dominant, leading the molecules to adopt compact conformations. At higher concentrations, intermolecular associations lead to the formation of a network held together by reversible cross-links, resulting in highly viscous solutions or physically cross-linked gels. The literature reports theoretical consideration of these intra- and intermolecular associations.[15,16] HMP(E)s are used extensively as thickeners of aqueous solutions, and many studies have described their rheological properties and the influence of added surfactants or salts on those properties.[17−19]

For more than 40 years, the aggregates present in HMP and HMPE solutions have presented a problem for the characterization of their macromolecular dimensions. Little information has been provided in the literature concerning molar mass determination because of the intra- and intermolecular association effects. For HMPEs, this is more important, since there are two opposing effects that act simultaneously: hydrophobic aggregation and

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Coulombic repulsion.[7,10] In the diluted regime, the first interactions lead to intramolecular associations, which decrease the polymer hydrodynamic volume, whereas the electrostatic forces tends to expand the polymer coils and thus the hydrodynamic volume. Adding salt can screen out the polyelectrolyte effect, but this will enhance the hydrophobic intramolecular associations.[20]

Some authors have reported static light scattering measurements by disrupting intermolecular hydrophobic associations with additives such as methanol[3,21] or with surfactants.[22] Biggs et al.[23] claimed that formamide can satisfy the HMP weight-average molar mass requirements, showing that the refraction increment index values (dn/dc) of a series of HMPs with different hydrophobic contents in formamide were equal to that of pure polyacrylamide. This was confirmed in our previous work[5] but was contradicted by Maia et al.,[24] whose conclusions indicated the presence of aggregation.

The most popular methods used to characterize the molar mass of polymers is size exclusion chromatography (SEC), which can be coupled with a multiangle light scattering detector (MALS).[25,26] SEC separates species according to their size in solution, i.e., their hydrodynamic volume.[27,28] These species may be single molecules, polymer coils, aggregates, or micelles. Hence, SEC can be applied to determine the molar mass of a polymer and to study the aggregation phenomena in solution.[29] In the case of HMPs, the determination of their molar masses by SEC under classical conditions is generally difficult because of their adsorption to the columns.[10] Blagodatskikh and co-workers[30−32] used SEC−MALS in a binary solvent (water/acetonitrile) to show that the dissolution of polymers with strongly interacting groups results in the formation of aggregates that are not disrupted during chromatographic separation.

Over the past 30 years, the interest for micellar-mediated separation has grown rapidly. In high-performance liquid chromatography, micellar mobile phases have been used to control retention and selectivity of various solutes (small molecules, peptides, proteins, ...) that would otherwise be inseparable or poorly resolved.[33−37] In addition, the use of ionic surfactant in capillary electrophoresis buffer solutions has extended the capabilities of electromigration techniques for the separation of uncharged solutes.[38,39] Micelles have also been used in other separation methods like ultrafiltration and cloud point extraction.[33] In the field of micellar-mediated separation, this work proposes a method based on the surfactant aided size exclusion separation of HMP(E) that can be called micellar SEC (MSEC) by analogy with the well-known micellar liquid chromatography[40] (MLC) and micellar electrokinetic capillary chromatography[41] (MECC or MEKC). The method is based on the disruption of aggregates by an excess of micelles and detection using an experimental setup with two detectors: a MALS device and a concentration-sensitive detector such as a refractometer (RI). The method was tested using a series of HMPEs with different numbers and properties of hydrophobic groups to ensure a balance between weakly and strongly interacting groups. More precisely, the polymers used in this work were synthetic sulfonated polyacrylamides, modified with alkyl hydrophobic side groups as shown in Figure 1. The chemical parameters investigated are the molar fractions of hydrophobic comonomers (0.1−1.0 mol % of C12 and 0.5−1.0 mol % of C18) and the size of the alkyl chains (0.5 mol % of C8, C12, and C18). HMPEs and their equivalent nonassociative polymers were synthesized using the micellar radical copolymerization technique.[3,4,7]

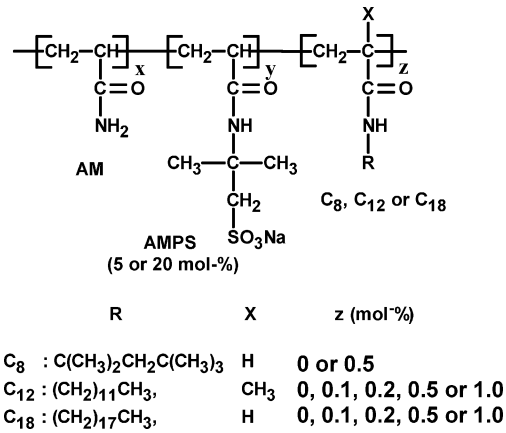

Figure 1. Chemical structure and composition of HMPEs used in the study.

MATERIALS AND METHODS

Materials. Acrylamide and sodium dodecyl sulfate (SDS) were obtained from ABCR. 2-Acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS), 2,2-azobis(2-methylpropionamidine)

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dihydrochloride, denoted VAZO56, 4-(1,1,3,3-tetramethylbutyl)phenyl-poly(ethylene glycol) (TritonX-100), denoted TXT, and sodium chloride salt (NaCl) were obtained from Aldrich, and ethanol was obtained from Sodipro. The hydrophobic monomers, *N*-dodecylmethacrylamide (C12), *N*-(*n*-octadecyl)acrylamide (C18), and *N-tert*-octylacrylamide (C8) were obtained from Polysciences, Inc. All of these products were of the highest commercially available grade and were used without any further purification. Salt-free Milli-Q water (resistivity: 18.3 MΩ·cm) was used to prepare all brines for polymer dissolution and all solutions used for SEC and MSEC analysis.

Synthesis. All polymers used in this work were synthesized according to the micellar copolymerization method as described by Candau and co-workers.[3,4,7] In this process, the hydrophobic monomers are solubilized within surfactant micelles, whereas the hydrophilic monomers are dissolved in the aqueous continuous medium. This microheterogeneity leads to copolymers with a largely blocklike distribution of the hydrophobic units along the backbone. The number of hydrophobic units per block is assumed to be equal to the number of hydrophobic monomers per micelle (N_H).

In this work, the surfactant was used at a large excess (0.26 mol/L) to ensure that N_H is constant and equal to one. For all samples, the total monomer concentration was kept at 0.5 mol/L with an initiator concentration equal to 0.001 mol/L. The concentration of NaCl was adjusted to maintain the total ionic strength ([NaCl] + [AMPS]) at 0.15 mol/L, and the temperature was kept constant at 60 °C. The monomers, SDS, and NaCl were placed in a five-necked 5 L reactor equipped with a thermostat, a nitrogen inlet/outlet, and a mechanical stirrer. The feed volume was adjusted to 1990 mL with Milli-Q water, and then degassed over 4 h with nitrogen. The initiator was dissolved in 10 mL of Milli-Q water and injected in the feed. The reaction proceeded for 10 h at 60 °C. The mixture was then precipitated in an excess of ethanol with a Waring laboratory blender 7009G, producing a fine white powder. This powder was washed several times with ethanol and dried in vacuo at 40 °C. The global yield of the reaction was higher than 95 wt %. Fourteen polymer samples were synthesized in two series. The first 12 samples were associative HMPEs with different hydrophobic units introduced at different contents. The last two were the nonassociative equivalent polymers and were prepared using the same procedure, including the same salt and surfactant concentrations.

Nomenclature. The samples were denoted using the following nomenclature. The nonassociative polyelectrolytes were named I*X*, where "I" indicates that the sample is ionic, referring to the AMPS (ionic) and "*X*" indicates the molar ratio of AMPS. The associative polyelectrolytes were named I*X*C*H-Y*, where "H" refers to the number of carbons in the hydrophobic monomer and "*Y*" refers to the content of hydrophobic units in mol %. For example, I20C12-0.5 is a polymer which contains 79.5 mol % of acrylamide, 20 mol % of AMPS, and 0.5 mol % of C12.

^{1}H NMR Measurements. The molar composition of each sample was determined by ^{1}H NMR (Bruker AVANCE 400 MHz) in D_2O. To improve the resolution, all the spectra were recorded at 85 °C with a delay time between each pulse of 5 s.[10] The purity of the final product was also confirmed (see spectra in the Supporting Information).

Rheological Measurements. The steady shear rheological properties of semidilute polymer solutions were determined using an MCR300 rheometer from Physica-Anton-Paar fitted with a Mooney−Ewart geometry (coaxial cylinders with cone and plate at the bottom) in the imposed strain mode. The temperature was set at 30 °C. The solutions were prepared at 10 g/L of polymer by dissolving a known amount of polymer powder in standard brine (20 g/L NaCl with 400 ppm of NaN_3 used as a bactericide). After 72 h of stirring, the solutions were allowed to stand until all bubbles disappeared, i.e., during 3 days.

Size Exclusion Chromatography Coupled to Multiangle Light Scattering. The weight-average molar mass (M_w), the polydispersity (I_p), and the radius of gyration (R_g) of the samples were determined by SEC using a Waters Alliance 2690 (U.S.A.) chromatograph equipped with two online detectors: a differential refractometer (Waters 2410) and a DAWN HELEOS II utilizing a 120 mW solid-state laser operating at 658 nm equipped with a K5 cell. Two different sets of chromatographic columns were used depending on the nature of the eluent. Four Shodex OHpak columns (SB-807HQ, SB-806HQ, SB-804HQ, and SB-802.5HQ) were used when the eluent was a classical solution of $NaNO_3$ at 0.1 M, whereas three Waters Ultrahydrogel columns (250, 500, 2000) were used for the MSEC analysis with a solution of 0.1 M $NaNO_3$ and 0.2 mg/mL TXT as the eluent. In both cases, the flow rate was set at 0.5 mL/min. The solutions for injection were prepared by dissolution of the polymer in 0.1 M $NaNO_3$ with or without surfactant (20 mg/mL TXT). The TXT concentrations used for the MSEC analysis, both in the solutions for injection and in the eluents, will be explained in the Results and Discussion section. After about 24 h of stirring, the solutions were filtered through a 0.45 μm filter (Millipore) and then injected. The injection volume (20−100 μL) was chosen to control the injected mass of polymer. The weight-average molar mass (M_w), the polydispersity (I_p), and the radius of gyration (R_g) were obtained from the data collected and analyzed using ASTRA SEC software (version 5.3, Wyatt Technology Corp., U.S.A.). The molar mass and the rms (root-mean-square) radius were calculated using the Zimm fit methods. The band-broadening correction was not considered[42] because this correction was not impacted the final results. The refractive index increments, dn/dc, were determined by SEC using the "RI peak areas" template of the Astra software. Delay volume, normalization and the RI calibration constant were determined using a monodisperse poly(ethylene glycol) sample ($M_w = 2 \times 10^4$ g/mol, $M_w/M_n = 1.05$, $dn/dc = 0.135$ mL/g) and bovine serum albumin (BSA).

Systematic errors occur because of incorrect values of dn/dc and the refractometer calibration factor k.[43] The effects of the RI calibration constant (k) and of the dn/dc on the weight-average molar mass M_w are proportional to k^{-1} and $(dn/dc)^{-1}$, respectively. For the M_w value, this systematic error can be prevented by using the same refractometer detector for the dn/dc and k determinations. The error limit of 8% on M_w is based on the average and standard deviation from multiple injections (4−8).

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The random errors inherent in each experiment are due to the baseline fluctuations of each detector.

Automatic Continuous Mixing Technique. The automatic continuous mixing (ACM) technique was used to determine the critical micelle concentration, cmc, and the aggregation number of the TXT in 0.1 M $NaNO_3$ according to a method described recently by our group.[44] The ACM technique has been previously described in detail by Strelitzki and Reed[45] and can be used to determine the mass-average molar mass (M_w), the radius of gyration (R_g), and the second virial coefficient (A_2) of polymer samples. For each sample, M_w, R_g, A_2, and dn/dc were measured in 0.15 M NaCl formamide solution with the same detectors used with the SEC−MALS system. The experiments were also carried out with a stepped gradient of polymer solutions of known concentrations. The dn/dc values used were 0.060 ± 0.002 and 0.066 ± 0.002 mL/g for the I20 and I5 samples, respectively.

Light Scattering Considerations for Micellar SEC. The intensity of scattered light from a binary polymer solution can be interpreted by the Zimm−Debye equation.[25] At the small-angle limit where interference effects can be neglected, this can be expressed as

$$\frac{K(\mathrm{d}n/\mathrm{d}c)^2c}{I(q,c)} = \frac{1}{M_w}\left(1 + \frac{q^2R_g^{\ 2}}{3}\right) + 2A_2c \qquad (1)$$

where M_w is the weight-average molar mass, A_2 is the second virial coefficient, $R_g^{\ 2}$ indicates the mean square radius, $I(q, c)$ is the excess Rayleigh ratio, dn/dc is the refractive index increment (mL/g), and K is the optical constant, which for vertically polarized incident light is given by

$$K = \frac{4\pi^2n^2}{N_A\lambda^4} \qquad (2)$$

where n is the refractive index of the solvent, C is the polymer concentration (g/mL), λ is the wavelength of the incident light, and N_A is Avogadro's number.

The scattering vector q is defined as

$$q = \left(4\pi\frac{n}{\lambda}\right)\sin(\theta/2) \qquad (3)$$

where θ is the scattering angle.

In the case where light scattering is coupled with SEC and a concentration detector such as a differential refractometer, the concentration C is determined by

$$c = k_{RI}\mathrm{RI}/(\mathrm{d}n/\mathrm{d}c) \qquad (4)$$

where k_{RI} is the instrumental constant of the refractometer and RI is the refractometer signal. Because the concentration of the sample in the chromatographic column is very low, the virial term can be neglected, $2A_2cM_w \ll 1$, and thus

$$\frac{K(\mathrm{d}n/\mathrm{d}c)^2c}{I(q,c)} = \frac{1}{M_w}\left(1 + \frac{q^2R_g^{\ 2}}{3}\right) \qquad (5)$$

Measurements at more than one angle can provide additional informations. In a plot of $Kc/I(q, c)$ versus q^2, M_w can be obtained from the intercept and the radius of gyration from the slope.

The theory of light scattering for a multicomponent system was first developed by Kirkwood and Goldberg[46] and Stockmayer.[47] From the point of view of scattering, the association of the surfactant and the polymer into a complex presents a similar problem to that of two comonomer species with different values of dn/dc, as described by Reed and co-workers in the case of polymer/surfactant assemblies studied by static light scattering.[48−50]

Here, the preferential interaction between the polymer and the surfactant components must be considered. Designating the polymer−surfactant complex as component ps, the polymer as component p, and the surfactant as component s, the light scattering equation for the polymer in the surfactant solvent is

$$\frac{K(\mathrm{d}n/\mathrm{d}c)_{ps}^{\ 2}c_{ps}}{I(q,c_{ps})} = \frac{1}{M_{w,ps}}\left(1 + \frac{q^2R_{g,ps}^{\ 2}}{3}\right) \qquad (6)$$

in which

$$M_{w,ps} = (1 + r)M_{w,p} \qquad (7)$$

where $M_{w,p}$ is the molar mass (weight-averaged) of the polymer component of the polymer−surfactant complex and r is the amount of surfactant associated with the polymer (in g/g).

$$c_{ps} = (1 + r)c_p \qquad (8)$$

where c_{ps} is the concentration of the polymer−surfactant complex (in g/mL) and can be measured directly if the value of r is known, e.g., by using a concentration-sensitive detector with an expression analogous to eq 4, and with

$$(\mathrm{d}n/\mathrm{d}c)_{ps} = \left(\frac{1}{1+r}\right)(\mathrm{d}n/\mathrm{d}c)_p + \left(\frac{r}{1+r}\right)(\mathrm{d}n/\mathrm{d}c)_s \qquad (9)$$

The specific refractive index increments of the polymer $(\mathrm{d}n/\mathrm{d}c)_p$ and of the surfactant $(\mathrm{d}n/\mathrm{d}c)_s$ are usually different, and therefore $(\mathrm{d}n/\mathrm{d}c)_{ps}$ can be calculated directly if r is known. Usually, because the value of r is unknown, it is not possible to directly determine the molar mass of the total polymer/surfactant complex according to eq 6. Fortunately, we are primarily interested in the molar mass of the polymer ($M_{w,p}$) in the polymer/surfactant complex. To obtain an expression for $M_{w,p}$, eqs 7−9 are inserted into eq 6, which is then solved for $M_{w,p}$:

$$\frac{K(\mathrm{d}n/\mathrm{d}c)_{app}^{\ 2}c_p}{I(q,c_{ps})} = \frac{1}{M_{w,p}}\left(1 + \frac{q^2R_{g,ps}^{\ 2}}{3}\right) \qquad (10)$$

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Table 1. Associative Characteristics (Viscosimetry) and Macromolecular Dimensions of HMPE Samples by Size Exclusion Chromatography (SEC), Classical Static Light Scattering (SLS), and Micellar Size Exclusion Chromatography (MSEC)

	viscosimetry	SEC−MALS 0.1 M $NaNO_3$[b]		SLS (formamide, 0.15 M NaCl)[c]		MSEC−MALS [TXT] = 0.2 g·L^{-1}[d]		
	η_0 (Pa·s) c_p = 10 g·L^{-1}[a]	$M_{w,p}$ (× 10^{-6} g·mol^{-1})	$R_{g,p}$ (nm)	$M_{w,p}$ (× 10^{-6} g·mol^{-1})	$R_{g,p}$ (nm)	$M_{w,p}$ (× 10^{-6} g·mol^{-1})	$R_{g,ps}$ (nm)	$(dn/dc)_{app}$ (mL·g^{-1})
I20	0.029	1.26	49	1.30	45	1.30	50	0.161
I20C12-0.1	0.022	1.30	51	1.31	45	1.33	51	0.161
I20C12-0.2	0.030	1.16	50	1.26	34	1.34	50	0.163
I20C12-0.5	12.2	ret		1.24	32	1.31	48	0.173
I20C12-1.0	ins	ins				1.40	53	0.194
I20C8-0.5	0.014	1.04	53	1.21	36	1.06	48	0.161
I20C18-0.5	>10^4	ret				1.10	46	0.173
I20C18-1.0	ins	ins				1.30	50	0.179
I5	0.020	1.34	52	1.30	39	1.30	50	0.177
I5C12-0.1	0.027	1.26	53	1.30	39	1.34	50	0.177
I5C12-0.2	0.034	1.21	47	1.37	34	1.25	47	0.177
I5C12-0.5	10^3	ret		1.30	39	1.38	45	0.180
I5C8-0.5	0.010	0.85	45	0.91	26	0.81	43	0.178
I5C18-0.5	ins	ret				1.28	42	0.215

[a] In 20 g/L NaCl at T = 30 °C; ins = insoluble. [b] $(dn/dc)_p$ = 0.161 and 0.177 mL·g^{-1} for the I20 and I5 series, respectively, and four Shodex OHpak columns were used (SB-807HQ, SB-806HQ, SB-804HQ, and SB-802.5HQ), T = 30 °C; re = retained on the columns, and ins = insoluble. [c] $(dn/dc)_p$ = 0.066 and 0.060 mL·g^{-1} for series I20 and I5, respectively. [d] Three Waters Ultrahydrogel columns (250, 500, 2000), T = 25 °C, M_w/M_n for all the samples is equal to 1.8 ± 0.1.

where $(dn/dc)_{app}$ is the apparent refractive index increment, which describes how the refractive index of the solution changes as function of the polymer concentration.

$$(dn/dc)_{app} = (dn/dc)_p + r(dn/dc)_s \quad (11)$$

$(dn/dc)_{app}$ can be measured directly by using the refractometer detector and an expression analogous to eq 4:

$$\left(\frac{dn}{dc}\right)_{app} = k\frac{S_{RI}}{m_{inj}} \quad (12)$$

In the equation above, the surface of the chromatographic peak (S_{RI}) is only proportional to the injected mass of polymer (m_{inj}), in cases where all the polymer is eluted and the amount of surfactant in the eluent is large enough to ensure a constant ratio r.

The molar mass of the polymer chain can be computed by the ASTRA software using $(dn/dc)_{app}$ and the calibration constant of the refractometer. This corresponds to eq 10 at $q = 0$.

$$\frac{K(dn/dc)_{app}{}^2 c_p}{I(0, c_{ps})} = \frac{1}{M_{w,p}} \quad (13)$$

The computation of $R_{g,ps}$ is independent of r and is simply given by

$$R_{g,ps}{}^2 = 3\frac{d\left(\frac{Kc_p}{I(q, c_{ps})}\right)}{dq^2}\frac{I(0, c_{ps})}{Kc_p} \quad (14)$$

RESULTS AND DISCUSSION

Basic Characterization of Polymers. The elucidation of molecular composition by ^{1}H NMR gives the molar composition in both the anionic sulfonated units and the hydrophobic groups (I and *Y*, respectively, in the chosen nomenclature).

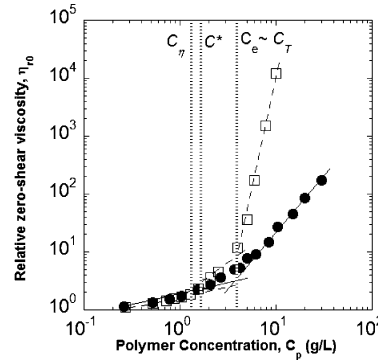

Figure 2. Relative zero-shear viscosity, η_{r0}, plotted as a function of polymer concentration for a nonassociative polymer (●, I20) and an associative polymer (□, I20C12-0.5). ([NaCl] = 20 g/L, T = 30 °C, see text for C_η and C^* definitions; lines are guides for the eyes).

According to previous studies,[2,10,19,51] the results confirm that it is possible to detect low contents of hydrophobic units with careful ^{1}H NMR characterization. In all the samples, the content of the hydrophobic units satisfactorily corresponds to the feed compositions, meaning that the hydrophobic monomers are almost completely incorporated in the polymer backbones. The 14 synthesized products are grouped together into two series according to their anionicity, with series I5 and I20 containing 5 and 20 mol % of the anionic AMPS comonomer, respectively (Table 1).

The associative characteristics of aqueous HMP solutions can be defined by the thickening efficiency compared to that of a nonassociative polymer, as shown in Figure 2. The thickening efficiency of HMP aqueous solutions depends on their concentration. Hydrophobic moieties in HMPs lead to coil contraction and a decrease in viscosity in dilute solutions. On the other hand, intermolecular associations occur at high enough concentrations, which may lead to an intermolecular physical network structure that causes an increase in viscosity. There is a concentration that

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depends on the molar mass of the polymer sample where an upward curvature can be observed in the graph of relative zero-shear viscosity as a function of polymer concentration. In the case of a nonassociative polymer, this upward increase in viscosity is due to the onset of the coil overlap concentration (C^*) and is therefore related to the molecular size. However, the viscosity increase observed in HMP cannot be attributed to chain overlap if the samples are within the same range of molar masses. The increase in viscosity is due to the formation of aggregates caused by hydrophobic intermolecular associations. In these cases, the concentration at which the viscosity increases can be identified as C_η, which is lower than C^*, the coil overlap concentration. The viscosity increase is expected to become more pronounced with an increase in the hydrophobic block size (N_H), and it takes effect even at lower concentrations.[52,53] Linear viscoelastic measurements performed on these systems revealed the existence of three distinct concentration regimes as in the case of nonassociating polymers. An illustration of this behavior is given in Figure 2.

(i) A dilute regime, $C < C_\eta$, where the chains are isolated and the viscosity is essentially controlled by intramolecular interactions. This regime does not significantly differ from that of unmodified polymers, i.e., C^* is close to C_η.

(ii) A semidilute unentangled regime, $C_\eta < C <$ CT. In this regime, the viscosity is enhanced with respect to that of the unmodified HMPE. The break between the first and second regimes is rather sharp with C_η depending on the molar mass.

(iii) A semidilute entangled regime, $C >$ CT. The break CT occurs at a concentration close to the critical concentration Ce where the unmodified polymer chains are entangled. In this regime, the viscosity is considerably enhanced with respect to that of the unmodified HMPE.[53] Similarly, aqueous solutions of HMPE provide a thickening efficiency according to the salinity of the solution. Generally, at low salt concentrations or in pure water, the polyelectrolyte effect predominates and matches the viscosifying properties.[7,20]

This work determined the associative characteristics of all the HMPEs by measuring the zero-shear viscosity, η_0, at 10 g/L in 20 g/L NaCl. The results are reported in Table 1. The polymers containing 0.5 mol % of C18 are highly associative. I20C18-0.5 behaves like a gel ($\eta > 10^6$ mPa·s), whereas I5C18-0.5 is insoluble in sodium chloride solution and forms a gel in pure water. The samples with 0.5 mol % of C12 present a classical associative behavior depending on anionicity: the viscosity of I5C12-0.5 is higher than I20C12-0.5. Note that 1 mol % of C12 or C18 forms insoluble polymers in 0.1 M $NaNO_3$ aqueous solution. For lower hydrophobic contents at C12 and C18 (<0.2 mol %) and for C8 conjugations, the measured viscosities are close to those of the corresponding nonassociative polymers. The slight observed difference can be explained by the differences in molar mass. As expected, the associativity increases with the size and content of the hydrophobic groups. The effect of the shear rate on the zero-shear viscosity for solutions of HMPE in pure water and in salt solutions as a function of the polymer concentration and the anionicity is outside the scope of this paper and will be described in detail in a forthcoming paper.

The first results obtained by classical SEC−MALS analysis in 0.1 M $NaNO_3$ show that it is not possible to characterize HMPEs with a high associativity (Table 1). For 0.5 mol % of C12 and C18, high amounts of the HMPEs were retained on the columns, and for 1 mol % of C12 and C18, the HMPEs were not soluble in salt solution. This is essentially due to the high hydrophobic content and the fact that the addition of salt induces hydrophobic aggregates between the polymer chains and the chromatographic support. However, it seems possible to disrupt the hydrophobic aggregates in salt solution for the less associative polymers, since some graft polymers present M_w values close to those obtained in SLS in 0.15 M NaCl formamide solutions. Note that even when using a water/methanol (70/30 in volume) or water/acetonitrile (70/30 in volume) cosolvent in 0.1 M NaCl with Shodex columns, high amounts of I20C12-0.5, I20C18-0.5, I20C12-1.0, and I20C18-1.0 were retained on the columns.

These results show that HMPs can be characterized by SEC−MALS in water or cosolvent mixtures depending on their associativity. According to the thickening efficiency, the aggregates cannot be disrupted during the chromatographic analysis procedure, and the hydrophobic groups adsorb on the columns to provide erroneous values of average molar masses and polydispersity. A similar trend has been observed by Blagodatskikh et al. for ionomers based on poly(dimethylsiloxane) with strongly interacting groups.[54]

Micellar SEC−MALS. The interactions between hydrophobically modified copolymers and surfactants have been intensively investigated.[55,56] Hydrophobically modified polymer solutions in the presence of surfactant are expected to show a maximum viscosity at a given surfactant concentration due to the formation of mixed micelles between the surfactant and the hydrophobic polymer groups.[18,57] The interactions between surfactants and polymers can be described by two critical concentrations. The first concentration is the critical binding concentration $C_{s,1}$. This corresponds to the onset of binding between surfactant and polymer, i.e., it represents the beginning of the formation of polymer/surfactant aggregation complexes. This concentration is normally lower than the cmc of the surfactant. As the surfactant concentration increases, the polymer chain becomes saturated with surfactant aggregates, and above this concentration, surfactant micelles appear in the aqueous solution and are in equilibrium with the polymer/surfactant complexes. At this polymer saturation point, PSP, the second critical concentration can be defined, $C_{s,2}$. This represents the surfactant concentration at which the polymer chains are saturated by surfactant molecules. Beyond this concentration, no additional interaction between the surfactants and the polymer chains

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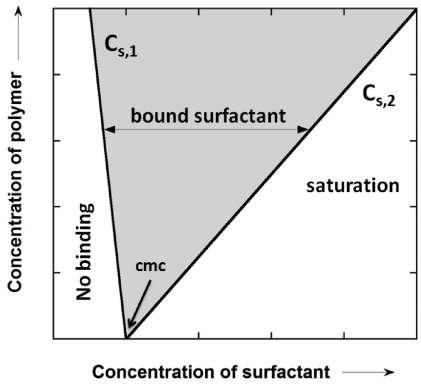

Figure 3. Schematic description of the association between an HMP(E) and a surfactant in different concentration domains.

occurs. Also in these systems, the difference between $C_{s,2}$ and $C_{s,1}$ decreases with polymer concentration. Figure 3 shows a schematic description of the association between an HMPE and a surfactant in different concentration domains: at low surfactant concentrations, there is no significant association at any polymer concentration; above $C_{s,1}$, the associations increase up to $C_{s,2}$, where the polymer chains become saturated.

Moreover, Hashidzume et al.[58] have shown by frontal analysis continuous capillary electrophoresis that the binding of a nonionic surfactant such as TXT to HMPE caused the dissociation of interpolymer aggregates.

Size exclusion chromatography is a useful tool in the study of size and binding equilibria of polymer−surfactant complexes,[29,59,60] but a number of difficulties arise in the quantitative interpretation of the results. Multiangle laser light scattering detection provides additional information above that available from typical concentration detectors. However, radius and molar mass measurements could be perturbed by fluctuations in the background scattering due to the presence of micelles in the mobile phase.[44] The best mobile phase concentrations for light scattering detection must be micellar, higher than the polymer saturation point ($C_{s,e} > C_{s,2}$) inside the columns, but low enough to respect the low background scattering from micelles in the mobile phase. In this case, the amount of surfactant associated with the polymer is constant, and the constant micelle concentration in the mobile phase minimizes fluctuations in background scattering. Taking these considerations into account, it is necessary to choose a surfactant with a weak interaction with the main chain and a low cmc value. The cmc's of nonionic surfactants are much lower than those of ionic surfactants. The relationship depends on the alkyl chain length, but 2 orders of magnitude is a rough estimation. Contrary to ionic surfactants, their physicochemical properties such as cmc and aggregation number are not really affected by the presence of electrolytes. A nonionic surfactant will interact strongly with the hydrophobic groups of the polymer and weakly with the main chain, in particular with the polyelectrolyte main chain.

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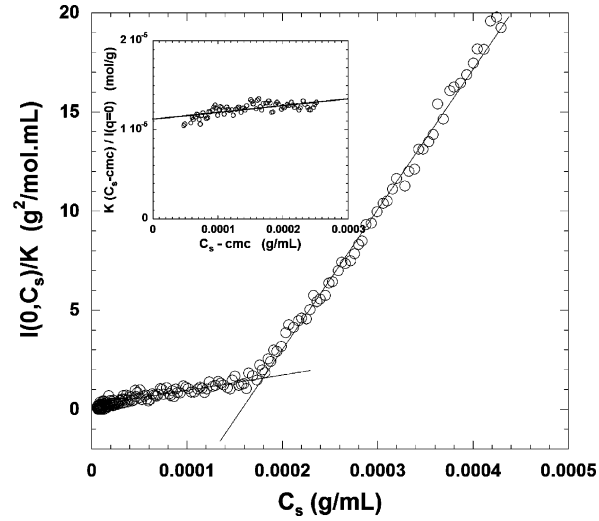

Figure 4. Light scattering data as a function of TXT concentration C_s in a 0.1 M $NaNO_3$ solution. Inset: determination of N_{ag} according to the literature (ref 44, eq 10 in this reference) for TXT in a 0.1 M $NaNO_3$ solution.

This work uses TXT as a surfactant. The cmc and aggregation number (N_{ag}) of the surfactant were determined in 0.1 M $NaNO_3$ using a method described in a previous study based on the combination of an ACM technique and static light scattering.[44] The collection and the subsequent data analysis of the data are both rapid and semiautomatic, which increases the precision, sensitivity, and range of applicability while substantially decreasing the amount of manual intervention required by the investigator. By treating the continuous data, the entire data set can be rapidly analyzed in the context of the closed association model to determine cmc = 0.178 mg/mL and N_{ag} = 143 for TXT as shown in Figure 4. The addition of $NaNO_3$ is useful to screen out the polyelectrolyte effect of HMPE.

As shown above, it is important to choose a surfactant concentration in the mobile phase, $C_{s,e}$, that provides a polymer saturation point in the micelles inside the elution volume of the chromatographic peak. By knowing the cmc of the surfactant in the eluent, $C_{s,e}$ can be higher to satisfy $C_{s,e} > C_{s,2} >$ cmc. For TXT, with $C_{s,e}$ = 0.2 mg/mL in the eluent, the light scattering intensity at 90° is 4 times higher than in pure 0.1 M $NaNO_3$ solvent, and it does not perturb the background scattering. Thus, from the TXT concentration in the mobile phase, $C_{s,e}$, we can estimate the maximal injected mass of copolymer, m_{inj}, which corresponds in the elution volume (V_{peak}) to a micelle concentration in the mobile phase ([mic] in mol/L) above the concentration of hydrophobic groups ([H] in mol/L). This ensures a polymer saturation point during the size exclusion of the sample.

In the mobile phase, the micelle concentration is higher than $(C_{s,e} - \text{cmc})/N_{ag}$, considering that N_{ag} is independent of the interaction between hydrophobically modified copolymers and surfactants. In the volume of the chromatographic peak, the hydrophobic group concentration is defined by

$$[H] = m_{inj} w_H / M_H V_{peak} \quad (15)$$

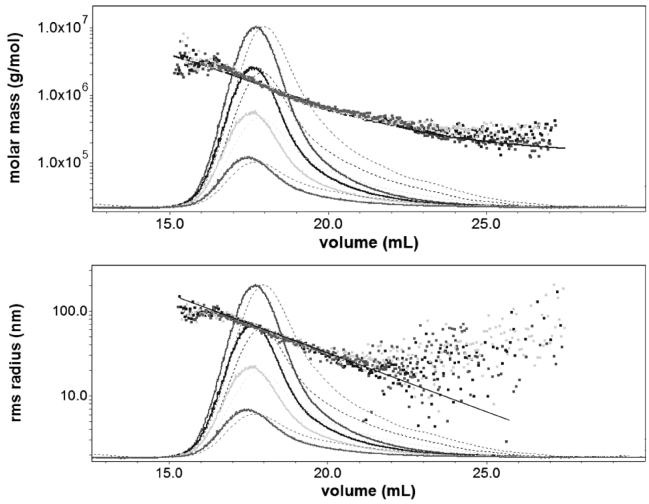

Figure 5. MSEC chromatograms for four injected masses of a highly associative HMPE (I20C18-0.5).

where w_H is the hydrophobic weight composition and M_H is the molar mass of the hydrophobic units.

To ensure [mic] > [H] in V_{peak} at $C_{s,e}$ in the mobile phase, the injected mass of polymer is the limiting factor:

$$m_{inj} < (C_{s,e} - \text{cmc})/N_{ag}M_H V_{peak} w_H \quad (16)$$

For example, if we consider the elution volume of the peak to be greater than 10 mL and the weight composition of the hydrophobic groups to be less than 4 wt % for C18, 3.1 wt % for C12, and 2.3 wt % for C8 (<1 mol % for each), the injected mass should be lower than 2.0 10^{-5} g for $C_{s,e} = 0.2$ mg/mL. This value is sufficient to allow for an accurate SEC analysis for a polymer with a molar mass around 10^6 g/mol.

The polymer concentration in the vial is higher than in the columns, so to ensure that the polymer saturation point is reached, it is necessary to dope the vial with an excess of surfactant. According to the same argument used in the case of the mobile phase, it is necessary to use a concentration of surfactant of 20 mg/mL in the vial for a polymer concentration lower than 1 mg/mL. In this way, saturation occurs and the dispersed sample can be injected in the mobile phase. The drawback of this is that the excess surfactant is delayed in the micellar eluent, and this elutes at volumes beyond the total column volume. The run times are thus lengthened (around 3 h), but the advantage is a feasible molar mass characterization of HMPE.

Figure 5 shows representative chromatograms obtained for the highly associative polymer I20C18-0.5 along with molar mass (M) and rms radius for four amounts of injected mass. The apparent dn/dc is determined by linearization of the refractometer surface signal and the injected mass according to eq 12. This value is used in the ASTRA software to extract the molar mass and the rms radius. Figure 5 reproduces M and the rms radius over the entire range of the peak. At high elution volumes, the light scattering intensities are too low to determine M and rms with good accuracy. At small elution volumes, the separation efficiency of the columns is reached.

Table 1 reports the calculated values $M_{w,p}$, $R_{g,ps}$, and $(dn/dc)_{app}$ for all the samples. The polydispersity index for all the samples is equal to 1.8 ± 0.1 and is not reported in Table 1. The observed values show that all the polymers can be analyzed, even highly associative polymers and HMPs that are insoluble in salt solution.

This method is based on the nonretention of the polymer complex on the columns. We assume that 100% of the injected mass is recovered. Although the measurement of $(dn/dc)_{app}$ for the polymer complex is found to be lower than the nonassociative equivalent due to the strong adsorption of polymers on the chromatographic support, it is impossible to check this assumption directly. Thus, an indirect method was used. We characterized some of the polymers by ACM in formamide solution. ACM is based on static light scattering as first described by Strelitzki and Reed[45] and was recently used in our laboratory.[44] The results are summarized in Table 1. The measured values of A_2 are close to zero ($\pm 10^{-6}$ mol/g^2·mL) and show that the formamide is a θ solvent. This explains why the radii of gyration determined here are slightly lower than those measured in 0.1 M $NaNO_3$ solution. The values of the weight-average molar mass are very close to those measured by MSEC. This comparison shows and confirms the nonretention of the surfactant−polymer complex on the columns. It may be noted for I20C18-0.5 that a mobile phase at surfactant concentration (i) higher than 0.2 mg/mL ($C_{s,e} = 0.3$ mg/mL) provides the same values of $M_{w,p}$, $R_{g,ps}$, and $(dn/dc)_{app}$ and (ii) lower than cmc ($C_{s,e} = 0.1$ mg/mL) maintains the retention on the columns observed without surfactant.

Aggregates present in HMP or HMPE solutions prevent accurate characterization of their macromolecular dimensions. Thus, the MSEC method reported here is a new alternative for determining molar masses and molar mass distributions. This method is based on the dissociation of aggregates in aqueous solution and the formation of mixed micelles between the surfactant and the polymer hydrophobic groups. MSEC requires a micelle concentration in the mobile phase ([mic] in mol/L) higher than the concentration of the hydrophobic groups ([H] in mol/L) in the elution volume (V_{peak}) of the chromatographic peak.

More generally for MSEC, the maximum of injected mass and the surfactant concentration in the mobile phase will be defined by the user with eq 16, according to the composition of HMPE or HMP and to the SEC device used.

Light scattering is one of the standard methods for the determination of weight-averaged molar masses of macromolecules. Its use is straightforward in the case of homopolymers but becomes considerably more complicated for copolymers. In this case, the apparent weight-averaged molar mass is measured as the sum of all the elements constituting the copolymer population. Recently, Reed and co-workers generalized the traditional scattering approach to the case of N comonomers and then derived a compact equation to determine the copolymer M_w that is readily and practically usable given a stream of continuous composition and light scattering data during copolymer synthesis, such as that provided by automatic continuous online monitoring polymerization (ACOMP). In the case of water-soluble polymers, these authors showed that the apparent weight-averaged molar mass obtained from the usual Zimm analysis method is not far from the true weight-average molar

mass in the case of a small to moderate drift in composition during copolymerization, and they are equal for no drift in composition. The copolymers poly(acrylamide-*co*-AMPS) do not have a drift in composition as described by Kujawa et al.,[3] and measurements for our copolymers were obtained in a similar way. The ratio of the hydrophobic unit is very low and can be neglected. Thus, the molar masses given in this paper can be considered to be the true values.

CONCLUSION

For more than 40 years, the aggregates present in HMP (associative polymers) solutions have presented a problem for the characterization of their macromolecular dimensions. This work demonstrates for the first time that the combined use of a nonionic surfactant in the mobile phase and light scattering coupled to SEC provide an accurate characterization of the macromolecular dimensions of such polymers. The MSEC method is a new alternative for determining molar masses and molar mass distributions. This method consists of the measurement of the $(dn/dc)_p$ of the nonassociative equivalent polymer and the $(dn/dc)_s$ of the surfactant in the mobile phase without surfactant, followed by injections of different masses to determine the apparent $(dn/dc)_{app}$ value of the polymer−surfactant complex in the mobile phase with surfactant. The measurements are performed using classical light scattering and concentration detectors such as MALS and refractometer instruments. On the basis of these results, we can consider that the determination of the macromolecular dimensions of HMP(E)s are within the reach of everyone, which will provide the basis for a meaningful comparison of their behaviors and properties in aqueous solution.

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SUPPORTING INFORMATION AVAILABLE

^{1}H NMR spectra of HMPE. This material is available free of charge via the Internet at http://pubs.acs.org.

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