Aggregation Mechanism of Amphiphilic Associating Polymers Studied by ^{19}F and ^{13}C Nuclear Magnetic Resonance†

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The association in aqueous solution of hydrophobically modified polyelectrolytes was investigated by ^{19}F and ^{13}C NMR. The polymers studied were poly(sodium acrylate) of average molecular weight ranging between 5 000 and 150 000 and bearing few mole percent of $-CH_2C_7F_{15}$ or $-C_{12}H_{25}$ pendant alkyl chains. The ^{19}F and ^{13}C NMR spectra of these polymers display the characteristic features of slow exchange between the free and aggregated states for the alkyl chains. It is therefore possible to determine the respective fractions of free and aggregated side groups by direct integration of the NMR signals. Thanks to this determination the association mechanism and the dynamics of these systems were studied at a molecular level and compared to what is observed with classical surfactants.

Introduction

Over the last years many studies have been devoted to associating polymers due to their interest in numerous formulations. These materials are hydrophobically modified water-soluble polymers mainly constituted of a hydrophilic backbone and a low fraction of very hydrophobic side or end chains, as, for instance, long alkyl chains. In aqueous solution, the hydrophobic moieties associate into hydrophobic microdomains. These hydrophobic aggregates can act as reversible cross-links between the macromolecules provided their backbone is long enough.[1−9] Hence very viscous solutions and even gels displaying a shear thinning behavior can be obtained.

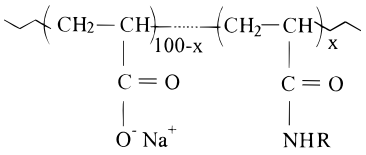
To achieve a clear understanding of the rheological behavior of such systems, the hydrophobic microdomains as well as the association mechanism must be characterized at a molecular level. Several parameters are fundamental in this molecular description: (1) the aggregation number, i.e., the average number of hydrophobic groups involved in an aggregate, (2) the shape of the aggregates, (3) the fractions of free and aggregated alkyl chains, (4) the ratio between intra- and interchain associations, and (5) the average lifetime of an alkyl chain into a hydrophobic aggregate.

The aggregation number and the size of the hydrophobic microdomains were studied by several techniques, the most widely used being fluorescence spectroscopy,[10−13] pulsed gradient spin−echo NMR,[14−16] and to a lesser extent electron spin−echo resonance.[17] The ratio beween intra- and interchain associations was qualitatively studied by fluorescence spectroscopy with polymers bearing fluorescent moieties as the hydrophobic grafts.[18−24] Estimations of the average lifetime of a hydrophobic chain into an aggregate could be provided by rheological measurements[25−28] and pulsed gradient spin−echo NMR.[29]

Very recently, we have reported on the possibility of directly measuring the fraction of aggregated alkyl chains by simple NMR experiments.[30] This information is essential to the understanding of the association mechanism and to the estimation of the aggregation number, when combined with data obtained by other techniques (fluorescence spectroscopy, SAXS, or SANS). In this paper we propose a thorough study of the association mechanism of hydrophobically modified poly(sodium acrylate) with this NMR technique. The polymers studied are polyelectrolytes bearing either hydrogenated (HMPA-H) or perfluorinated (HMPA-F) side chains. Comparisons are drawn between these systems and simple surfactant molecules.

Experimental Section

The HMPA-H and HMPA-F studied are random copolymers with the following structure:



where x is the modification degree and R is a hydrogenated or perfluorinated alkyl chain. These polymers are obtained via a modification reaction of poly(acrylic acid) samples of average molecular weight 150 000, 50 000, or 5 000. Their synthesis and characterization are described elsewhere.[1,31,32] For HMPA-H the following designation is used: PA 150 3C12 is a derivative obtained from a PA of average molecular weight 150 000 and containing 3 mol % of dodecyl alkyl chains. PA 5 10C12 is a derivative obtained from a precursor of average molecular weight 5 000 bearing 10 mol % of dodecyl side groups. For HMPA-F the same notations are adopted except that C8F refers to a $-CH_2C_7F_{15}$ alkyl side chain. The different polymers used in this study are gathered in Table 1.

Sodium decanoate (SD) was purchased from Fluka and was used as received. The solutions were prepared at least 18 h before use by diluting the proper amount of polymer or

† This paper is dedicated to the memory of Dr. Roland Audebert who died in July 1997. He played a great part in the study of associating polymers in our group. His comments and suggestions were always illuminating. The authors greatly appreciated his scientific competence as well as his human qualities and learned a lot from him.

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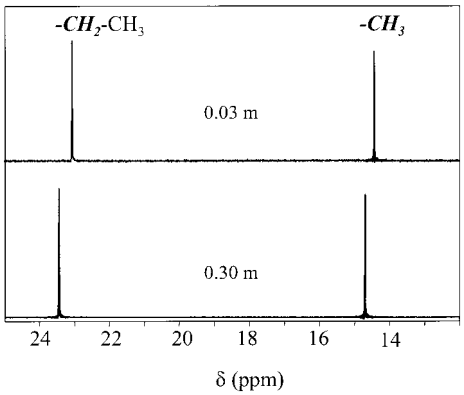

Figure 1. ^{13}C NMR spectra corresponding to the $-CH_3$ and $-CH_2CH_3$ groups of SD at two different surfactant concentrations: top, $C = 0.030$ *m*; bottom, $C = 0.300$ *m*.

TABLE 1: HMPA-H and HMPA-F Derivatives Used in This Study

	alkyl side chain	
molecular weight	$-C_{12}H_{25}$	$-CH_2C_7F_{15}$
150 000	PA 150 3C12	PA 150 3C8F
	PA 150 7 C12	PA 150 7C8F
	PA 150 10C12	
50 000	PA 50 10C12	
5 000	PA 5 10C12	PA 5 8C8F

surfactant in D_2O for NMR experiments and in deionized water for the rheological studies.

^{19}F NMR spectra were run on a Bruker WP 250 spectrometer operating at 235.4 MHz. A spectral width of 19 000 Hz and a flip angle of 30° were used. The acquisition and delay times were 0.85 and 2 s, respectively. Depending on polymer concentration 100−2000 scans were recorded. Sodium trifluoromethane sulfonate (Aldrich) was used as an internal reference ($\delta(CF_3SO_3Na) = -80.8$ ppm[33]). Proton-decoupled ^{13}C NMR spectra were recorded on a Bruker ARX 250 spectrometer operating at 62.9 MHz. The spectral width was 15 000 Hz, the flip angle was 90°, and the acquisition and delay times were 1 and 10 s, respectively. Due to the poor abundance of ^{13}C nuclei (1.108%), many more scans were needed in order to obtain a good signal-to-noise ratio. Methanol was used as an internal reference ($\delta(CH_3OH) = 49.9$ ppm[34]). The rheological measurements were performed at 25.0 °C with a Contraves low-shear 30 viscometer.

Results and Discussion

Analysis of the Spectra. *Surfactant: Fast Exchange*. In ^{19}F or ^{13}C NMR, the chemical shifts of the nuclei (fluorine or carbon) of the hydrophobic tail of a surfactant depend on the environment experienced by the molecule. This environment changes appreciably whether the surfactant molecule is free in solution (polar aqueous environment) or aggregated within micelles (low-polarity environment). This property was used to determine the critical micellar concentration (CMC) of hydrogenated or fluorinated surfactants and in some cases their aggregation number.[35−40]

On Figure 1 a part of the ^{13}C NMR spectra of SD is displayed for two surfactant concentrations, $C = 0.030$ *m* (mol/kg of D_2O) and $C = 0.300$ *m*, which are respectively below and above the CMC of this surfactant (CMC = 0.099 *m*). Only the signals of the last two carbon atoms of the alkyl chain are given. Below the CMC the chemical shifts of these nuclei are independent of the surfactant concentration ($\delta_f(-CH_3) = 14.44$ ppm and $\delta_f(-CH_2CH_3) = 23.07$ ppm). Above the CMC, the surfactant molecules exchange between the free and micellar forms. As this exchange is fast with respect to the NMR characteristic time scale, average peaks of the free and aggregated forms are obtained. Both the $-CH_3$ and the $-CH_2CH_3$ signals move upfield. It has been shown[35] that in the phase separation model the chemical shifts above the CMC are given by:

$$\delta = \delta_m + \frac{CMC}{C}(\delta_f - \delta_m) \quad (1)$$

where δ_f and δ_m are the intrinsic chemical shifts of free and micellar surfactant, respectively. According to eq 1, with CMC = 0.099 *m*, $C = 0.300$ *m*, $\delta(-CH_3) = 14.69$ ppm, and $\delta(-CH_2CH_3) = 23.44$ ppm, we obtain $\delta_m(-CH_3) = 14.84$ ppm and $\delta_m(-CH_2CH_3) = 23.59$ ppm. Similar results were obtained by ^{19}F NMR with a perfluorinated surfactant (sodium perfluorooctanoate).[30]

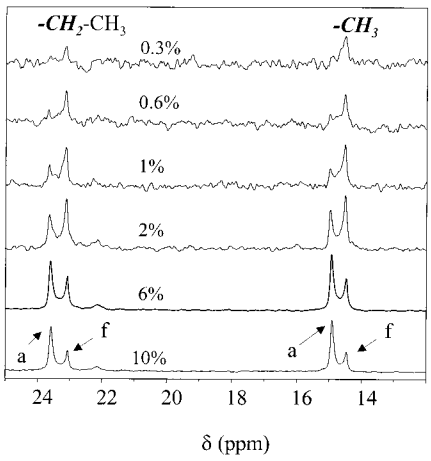

Figure 2. Influence of polymer concentration on the ^{13}C NMR spectra corresponding to the $-CH_3$ and $-CH_2CH_3$ groups of PA 5 10C12. $\delta(-CH_3) = 14.48$ ppm and $\delta(-CH_2CH_3) = 23.08$ ppm for the free alkyl chains (f), whereas $\delta(-CH_3) = 14.80$ ppm and $\delta(-CH_2CH_3) = 23.48$ ppm for the aggregated alkyl chains (a).

HMPA-H and HMPA-F: Slow Exchange. Figure 2 displays the ^{13}C NMR spectra obtained with PA 5 10C12 at different concentrations ranging between 0.3% and 10%. As for SD only the signals of the $-CH_3$ and the $-CH_2CH_3$ are given. The signal-to-noise ratio at the lowest polymer concentration is poor. However we observed two peaks at $\delta(-CH_3) = 14.48$ ppm and $\delta(-CH_2CH_3) = 23.08$ ppm. When the polymer concentration increases a second peak appears and grows next to each of the former signals at $\delta = 14.80$ and 23.48 ppm. By comparison to the surfactant spectra, the first two peaks can be attributed to the free alkyl chains and the second ones to the aggregated alkyl chains. Similar results were obtained by ^{19}F NMR with PA 5 8C8F (see Figure 3).

From these spectra several remarks can be made. First of all, with HMPA-H and HMPA-F, ^{13}C and ^{19}F NMR can distinguish between the free and aggregated forms, which means that the exchange rate between these two species is slow with respect to the NMR characteristic time. We will further discuss this point in a later section of this paper. Moreover, at low polymer concentration ($C_p = 0.3\%$) only the peak corresponding to the free alkyl chains is obsverved. This is especially clear for HMPA-F thanks to the good signal-to-noise ratio of the ^{19}F NMR spectra. It means that there is a threshold polymer concentration C_p^0 below which no hydrophobic aggregates are detected. Last but not least, the fraction of free and aggregated

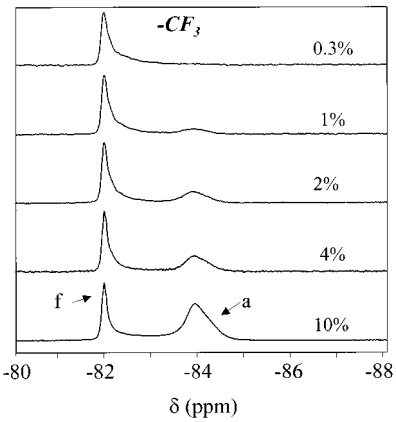

Figure 3. Influence of polymer concentration on the ^{19}F NMR spectra corresponding to the $-CF_3$ group of PA 5 8C8F. $\delta(-CF_3) = -81.91$ ppm for the free alkyl chains (f), and $\delta(-CF_3) = -83.87$ ppm for the aggregated alkyl chains (a).

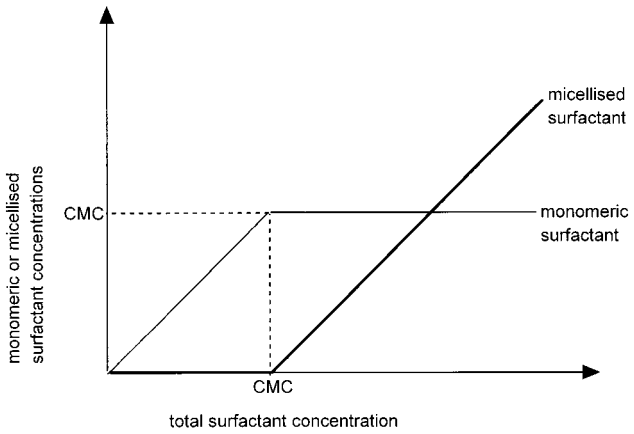

Figure 4. Typical variations of the free and aggregated surfactant concentrations as a function of the total surfactant concentration.[41]

alkyl chains can be directly obtained by integration of the signal. It was checked that under the used experimental conditions all the ^{19}F nuclei (^{19}F NMR) and the ^{13}C nuclei (^{13}C NMR) were fully relaxed. For some samples, ^{13}C NMR spectra were run under gated decoupling conditions (without NOE), and it was checked that proton decoupling does not influence the integration ratio between the free and aggregated forms. Moreover the integration of the $-CH_3$ and $-CH_2CH_3$ signals leads to the same value of the aggregated fraction.

The analysis of the spectra thus allows us to study the association mechanism and its dynamics as well as the influence of several parameters such as the modification ratio and the polymer molecular weight.

Association Mechanism. *Comparison with Surfactants.* For small surfactant molecules micelle formation is a cooperative phenomenon.[41] Typical variations of the free and aggregated surfactant concentrations as a function of the total surfactant concentration are schematically shown in Figure 4. Below the CMC all the surfactant molecules are free. At the CMC a sharp transition is observed. The free surfactant concentration reaches a plateau and remains approximatively constant over a wide range of concentrations while the aggregated surfactant concentration starts to increase. The situation is quite different with HMPA. Figures 5 and 6 display the same kind of plots obtained with PA 5 8C8F and PA 5 10C12, respectively. With both polymers a transition is observed, but it is much smoother than for surfactants. Moreover the concentration of free aggregated alkyl chains keeps increasing above C_p^0. This is clear evidence

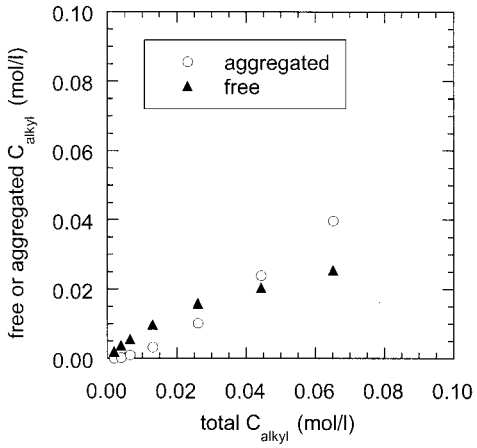

Figure 5. Concentrations of the free and aggregated alkyl side chains as a function of the total alkyl chain concentration for PA 5 8C8F.

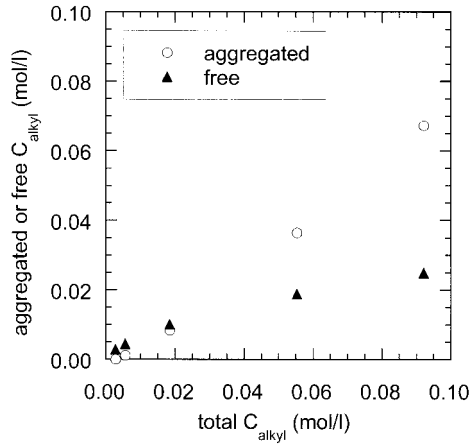

Figure 6. Concentrations of the free and aggregated alkyl side chains as a function of the total alkyl chain concentration for PA 5 10C12.

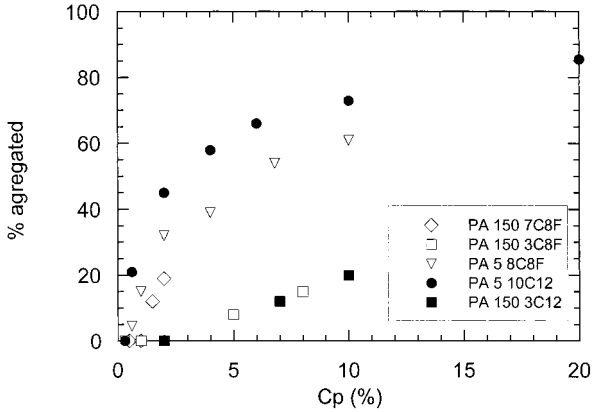

Figure 7. Fraction of aggregated alkyl chains as a function of polymer concentration for several HMPA.

of a more progressive and less cooperative association mechanism than observed with small surfactant molecules. It is also noteworthy that in agreement with this conclusion the free alkyl chain signal at $\delta = -81.95$ ppm for PA 5 8C8F (see Figure 3) is asymmetrical even at the lowest polymer concentration. This is probably due to the formation of some small "preaggregates" in which the alkyl chains exchange faster with the fully free form.

Influence of Polymer Concentration. Figure 7 displays the fraction of aggregated alkyl chains as a function of polymer concentration for several HMPA derivatives. For the most

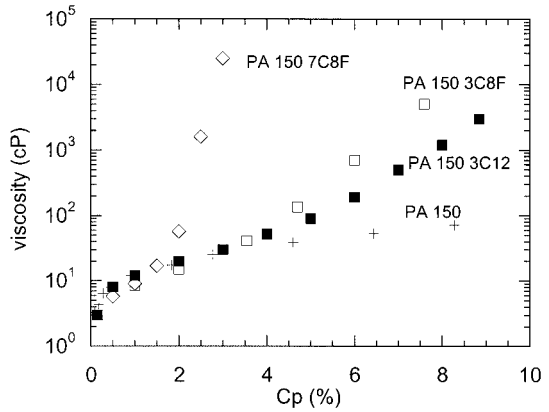

Figure 8. Viscosity as a function of polymer concentration for the high-molecular-weight samples of Figure 7 (shear rate = 0.06 s^{-1}).

TABLE 2: Comparison of the Threshold Polymer Concentration C_p^0 Determined from NMR and Viscometric Measurements for Several HMPA

	C_p^0 (%)	
polymer	NMR	viscometry
PA 150 3C12	3	3
PA 150 3C8F	3	3
PA 150 7C8F	1	1

modified polymers the fraction of aggregated alkyl chains first increases rapidly and then reaches a slowly increasing regime which seems to end at a plateau value around 70−90% depending on the polymer (see also below the data obtained in the presence of salt). This latter phenomenon can be explained by the steric hindrance due to the poly(sodium acrylate) backbone preventing some of the alkyl chains from associating. As expected, the higher the modification degree of the polymer, the lower C_p^0 and the sharper the initial increase of the curve. This is in good agreement with the rheological measurements (see Figure 8). The viscosity curve of the modified polymers starts to increase above that of the nonmodified polymers for a threshold polymer concentration C_p^0 which is very close to the one obtained from the NMR experiments (see Table 2).

It is also interesting to note that a relatively low fraction of aggregated alkyl chains is needed in order to obtain a subsequent rheological effect. For instance, the viscosity of a PA 150 3C8F solution, at C_p = 8%, is about 2 decades higher than the viscosity of a solution of the nonmodified PA at the same concentration, yet, only 15% of the alkyl side chains are aggregated.

Influence of Salt. Figure 9 displays the fraction of aggregated alkyl chains as a function of the sodium chloride concentration for different polymers, at C_p = 2%. As expected, salt favors the alkyl chain association. However, once again with the systems investigated, the aggregated fraction reaches a plateau value around 60−80%. This leveling off is attributed to the steric hindrance of the polymer backbone. The NMR experiments by themselves do not allow us to determine the relative contributions of intra- and interchain associations. However by combining the results obtained by NMR and viscometry, it is possible to evaluate qualitatively their contributions as a function of salt concentration. On Figure 10 the viscosities of the modified polymers divided by the viscosity of the non modified polymer, measured under the same conditions, are shown as a function of the fraction of aggregated alkyl chains. When the salt concentration is increased, the fraction of aggregated side chains increases. At first, this phenomenon is accompanied by a sharp increase of the normalized viscosity and then by a decrease (eventually followed by phase separation). This variation is evidence that interchain associations dominate the behavior at low salt concentration, whereas intrachain associations progressively prevail at higher salt concentration.

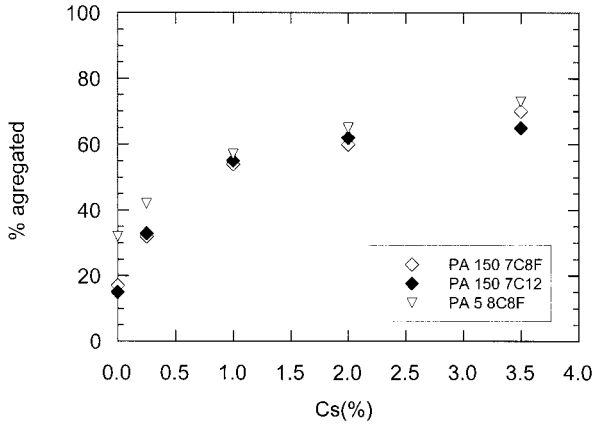

Figure 9. Fraction of aggregated alkyl chains as a function of sodium chloride concentration for different polymers at C_p = 2%.

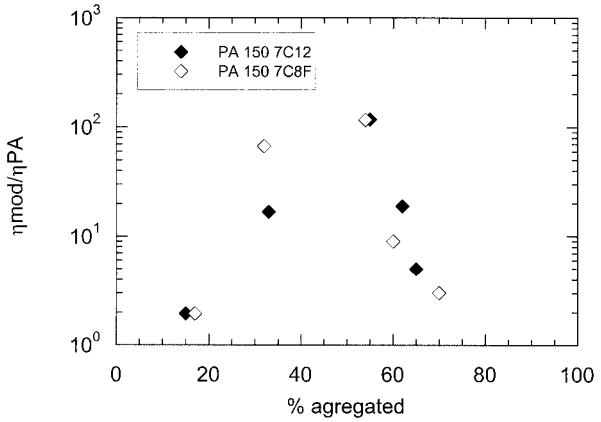

Figure 10. Viscosity of PA 150 7C12 and PA 150 7C8F divided by the viscosity of the nonmodified PA, measured in the same conditions, as a function of the fraction of aggregated alkyl chains.

Comparison between HMPA-H and HMPA-F. In a previous study[42] it was shown that a polymer bearing $-CH_2C_7F_{15}$ side groups has roughly the same associative behavior as a polymer containing the same amount of $-C_{12}H_{25}$ alkyl chains. The observation of Figures 7 and 9 confirms that this analogy between HMPA-F and HMPA-H is also valid at a molecular level.

Influence of the Polymer Molecular Weight. The comparison of the curves obtained with PA 5 8C8F and PA 150 7C8F (Figures 7 and 9) shows that the molecular weight of the polymer backbone has little influence on the association of the hydrophobic side chains. This result is also corroborated by the fraction of aggregated alkyl chains measured, at C_p = 2%, for PA 150 10C12 (50% aggregated), PA 50 10C12 (44% aggregated), and PA 5 10C12 (45% aggregated), see Table 3. High- and low-molecular-weight polymers have the same tendancy to self-assemble. However, with low-molecular-weight polymers, the hydrophobic aggregates are not connected via the polymer backbone over a wide range of polymer concentration, which explains the low viscosity of these systems with respect to the corresponding high-molecular-weight HMPA. A schematic illustration of the aggregates is given in Figure 11.

Some Dynamic Aspects of the HMPA Association. It was previously shown that, for all the HMPA studied, the exchange rate between the free and aggregated alkyl forms is slow with respect to the NMR characteristic time τ_{NMR}. It means that τ,

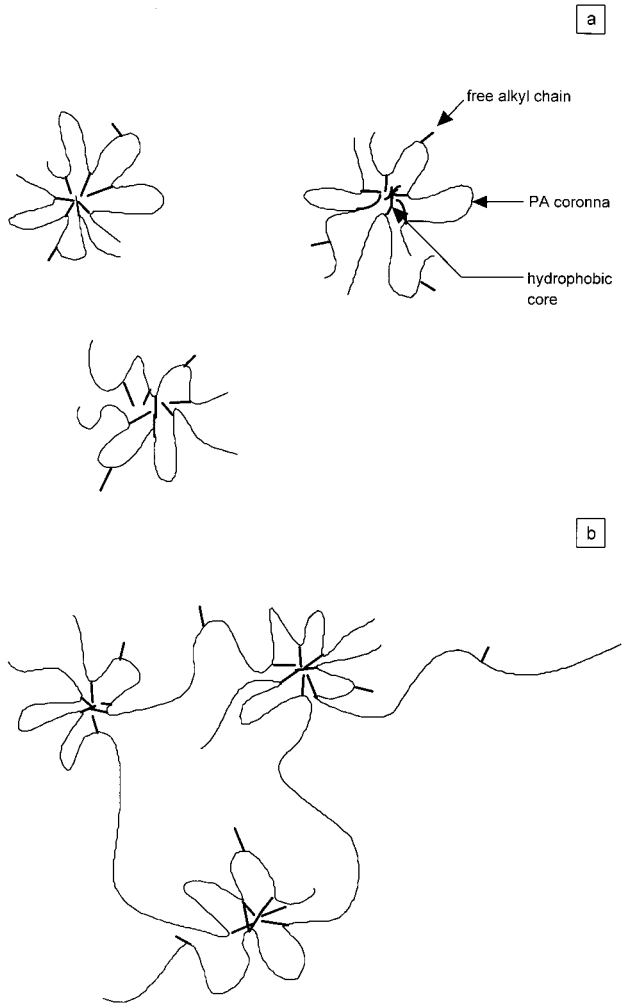

Figure 11. Schematic illustration of the hydrophobic aggregates: (a) low-molecular-weight HMPA, the hydrophobic aggregates are not interconnected; (b) high-molecular-weight HMPA, the hydrophobic aggregates are interconnected. In both cases a macromolecular chain participates in a given hydrophophobic aggregate by several alkyl chains.

TABLE 3: Evaluation of τ_{NMR} for Different Systems with an Aggregated Fraction Close to 50%

sample	% aggregated	$\Delta\nu$ (Hz)	τ_{NMR} (ms)
PA 5 8C8F, $C_p = 4\%$	40	456	1
PA 5 8C8F, $C_p = 6.8\%$	54	461	1
PA 5 8C8F, $C_p = 2\%$, NaCl (0.25%)	42	456	1
PA 5 8C8F, $C_p = 2\%$, NaCl (1%)	57	473	1
PA 150 7C8F, $C_p = 2\%$, NaCl (1%)	54	463	1
PA 5 10C12, $C_p = 2\%$	45	34	13
PA 50 10C12, $C_p = 2\%$	44	32	14
PA 150 10C12, $C_p = 2\%$	50	32	14
PA 150 7C12, $C_p = 2\%$, NaCl (1%)	54	32	14

the exchange characteristic time between the free and aggregated states, is higher than τ_{NMR}. Thus, the NMR experiment can distinguish between the two species. The situation where $\tau = \tau_{NMR}$ would correspond to the coalescence of the free and aggregated signals. When the probability for the studied nucleus is the same in the free or aggregated state (i.e., when the fractions of free and aggregated side chains are equal) τ_{NMR} is given by:[43]

$$\tau_{NMR} = \frac{\sqrt{2}}{\pi\Delta\nu} \quad (2)$$

where $\Delta\nu$ is the frequency difference between the free and aggregated forms. τ_{NMR} was evaluated from eq 2 for several systems with an aggregated fraction close to 50%. These values are gathered in Table 3. (In fact the exact value of the NMR time scale is a matter of definition. In a more general way $\tau_{NMR} \approx 1/\Delta\nu$, and therefore the values given in Table 3 should be considered as a first approximation.)

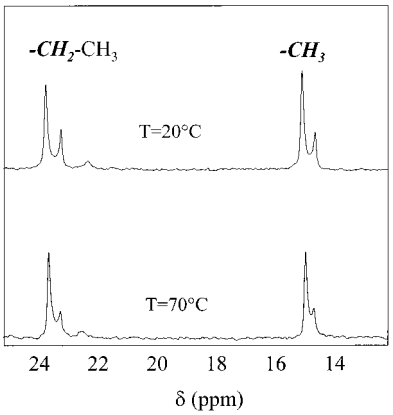

Figure 12. Influence of temperature on the ^{13}C NMR spectra corresponding to the $-CH_3$ and $-CH_2CH_3$ groups of PA 5 10C12: top, $T = 20$ °C; bottom, $T = 70$ °C.

From the data of Table 3 we can conclude that the exchange characteristic time τ is longer than 1 ms for HMPA-F and longer than 14 ms for HMPA-H. For equivalent surfactants we expect exchange characteristic times of the order of 10^{-3} ms.[44] The difference with the surfactant behavior entails that there is a considerable slowing down of the association dynamics due to the polymer backbone which limits the molecular motions of the pendant alkyl chains. Note that in the case of end-capped associating polymers the association process is still fast as compared to τ_{NMR}.[45]

It is noteworthy that τ represents an average exchange characteristic time. Actually HMPA exhibit a large spectrum of exchange times, and some hydrophobic side chains exchange faster than others. This phenomenon explains the partial overlap between the signals of the free and aggregated alkyl side chains (for instance, see Figures 2 and 3). Nevertheless the contribution of the fast exchanging chains to the total area of the peaks remains small and does not influence significantly the estimated value of the aggregated fraction.

To accelerate the exchange and try to reach the coalescence of the free and aggregated peaks, we performed some NMR experiments at a higher temperature ($T = 70$ °C). Figure 12 displays the ^{13}C NMR spectra obtained with PA 5 10C12, $C_p = 10\%$, at $T = 20$ and 70 °C. When the temperature is increased, the free and aggregated peaks get closer; however, we did not observe their coalescence. This result confirms that at room temperature the dynamics of HMPA is very slow with respects to the NMR characteristic times.

Conclusion

The fraction of free and aggregated alkyl chains of HMPA can be directly obtained from simple NMR experiments. From this determination it is possible to thoroughly study the association mechanism of such systems and compare it to the association of small surfactant molecules. It was found that below a certain polymer concentration no hydrophobic aggregates were detected neither by NMR experiments nor by viscometric measurements. However some very small aggregates with a very low lifetime may be formed in the first instance. The association mechanism of HMPA is thus less cooperative

and more progressive than micellization of classical surfactants. We found that the molecular weight of the polymer backbone has little influence on the polymer tendancy toward self-association. Besides, the same analogy between HMPA-H and HMPA-F was found at a molecular level as the one observed macroscopically by viscometric measurements. Even at high polymer concentrations or in the presence of salt, a significant number of alkyl chains are in the free state. In fact, the steric hindrance of the PA segments between two consecutive alkyl chains prevents them from being fully aggregated.

It was also shown that the average lifetime of an alkyl chain in an aggregate is higher than 1 ms for HMPA-F and higher than 14 ms for HMPA-H. The exchange process is thus much slower than what is reported for classical surfactants. The polymeric backbone thus entails a considerable slowing down of the dynamics of such systems. This slowing down of the exchange process certainly contributes to the high viscosities encountered with these systems. Beside the study of the association mechanism, a good estimation of the aggregated fraction is also a prerequisite for a determination of the aggregation number which can be obtained in combination with other techniques, namely, fluorescence spectroscopy or small-angle X-ray scattering, as will be presented in forthcoming papers.

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