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Aggregation of associating polymers studied by ^{19}F n.m.r.

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The aggregation in aqueous solution of a hydrophobically modified polyelectrolyte was investigated by ^{19}F n.m.r. The polymer studied was a poly(sodium acrylate) of average molecular weight 5000 bearing 8 mol% of $-CH_2C_7F_{15}$ pendant alkyl chains. The ^{19}F n.m.r. spectra of the modified polymer displayed the characteristic features of slow exchange between the free and the aggregated states for the alkyl chains. It is therefore possible to determine the respective fractions of free and aggregated $-CH_2C_7F_{15}$ groups by direct integration of the n.m.r. signals. This behaviour is opposite to the fast exchange occurring for classical surfactants (sodium pentadecafluorooctanoate, SOF). The exchange process in the polymer case is at least three orders of magnitude slower than in the surfactant system. © 1997 Elsevier Science Ltd.

(Keywords: amphiphilic polymers; n.m.r.; association)

Introduction

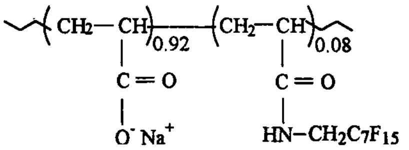
Associating polymers are water-soluble polymers bearing a low fraction of very hydrophobic groups such as, for instance, long pendant alkyl chains. In aqueous solution the hydrophobic moieties associate and form hydrophobic microdomains which can act as reversible crosslinks between the polymer chains provided their backbone is long enough[1–9]. Hence very viscous solutions and even gels can be obtained.

Over the past years associating polymers have attracted increasing interest because of their use in aqueous formulations. Several experimental techniques have been used to characterise the hydrophobic microdomains at a molecular level by their aggregation number (i.e. the average number of hydrophobic groups involved in an aggregate) and their size. The most widely used have been fluorescence spectroscopy[10–13], pulsed gradient spin echo n.m.r.[14–16] and, to a lesser extent, electron spin resonance[17]. The fractions of free and aggregated hydrophobic groups are key parameters in the characterisation of the hydrophobic microdomains. However, to our knowledge, these have never been measured.

In previous works[1,18–20] we investigated the solution properties of hydrophobically modified poly(sodium acrylate) (HMPA). In this study we report on the possibility of determining the fractions of free and aggregated alkyl chains by simple n.m.r. experiments. The polymer used here is a HMPA bearing perfluorinated alkyl side chains.

Experimental

The copolymer studied has a random structure and contains 8 mol% of hydrophobic units:



$$-(CH_2-\underset{\underset{O^-Na^+}{|}}{\underset{C=O}{|}}{CH})_{0.92}-(CH_2-\underset{\underset{HN-CH_2C_7F_{15}}{|}}{\underset{C=O}{|}}{CH})_{0.08}-$$

It was obtained via a modification reaction of poly(acrylic acid) (Fluka) of average molecular weight 5000. Its synthesis and characterisation are described elsewhere[1,18,21]. This polymer is referred to as PA 5 8C8F. It was shown that this polymer has the same tendency to self-assemble as homologous derivatives of higher molecular weight[22]. However, owing to its low molecular weight, this derivative does not form viscous aqueous solutions, at least until 20 wt%. It is therefore easy to prepare and handle solutions of relatively high polymer concentration.

Sodium pentadecafluorooctanate (SOF) was purchased from Aldrich in the acid form and was neutralised by 1 M NaOH before use.

The solutions were prepared by diluting the proper amount of polymer or surfactant in D_2O at least 18 h before use. Polymer concentrations are given in weight per cent.

^{19}F n.m.r. 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 the delay times were 0.85 and 2 s, respectively. Depending on the polymer concentration, 100 to 2000 scans were recorded. Sodium trifluoromethane sulfonate (Aldrich) was used as an internal reference ($\delta = -80.8$ ppm)[23].

Results and discussion

Surfactants (fast exchange). ^{19}F and ^{13}C n.m.r. measurements have been used to determine the critical micellar concentration (*CMC*) of fluorinated and hydrogenated surfactants and, in some cases, their aggregation number[24–29]. In fact, the chemical shifts of the fluorine atoms depend on the environment experienced by the surfactant molecules. This environment changes appreciably from highly polar aqueous (free surfactant) to a low polarity one (micellar surfactant).

Figure 1 displays part of the ^{19}F n.m.r. spectrum of SOF for two surfactant concentrations: $C = 0.01$ M and $C = 0.05$ M, which are respectively below and above the *CMC* ($CMC = 0.031$ M)[27]. Only the signal of the CF_3 group is given which splits into a triplet owing to spin–spin coupling

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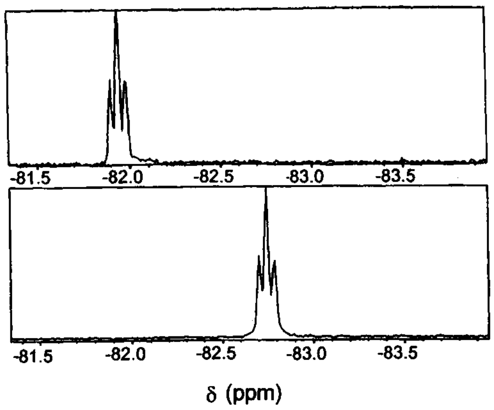

Figure 1 ^{19}F n.m.r. spectra corresponding to the CF_3 group of sodium pentadecafluorooctanoate at two different surfactant concentrations. Top: $C = 0.01$ M; bottom: $C = 0.05$ M

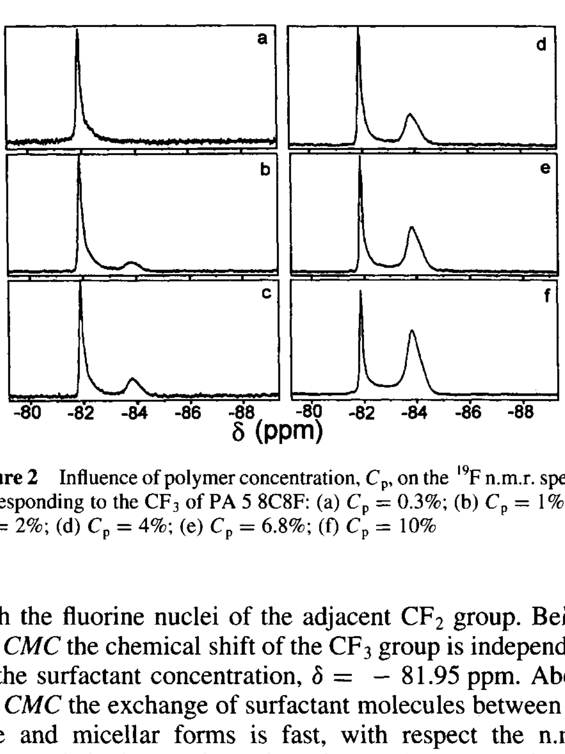

Figure 2 Influence of polymer concentration, C_p, on the ^{19}F n.m.r. spectra corresponding to the CF_3 of PA 5 8C8F: (a) $C_p = 0.3\%$; (b) $C_p = 1\%$; (c) $C_p = 2\%$; (d) $C_p = 4\%$; (e) $C_p = 6.8\%$; (f) $C_p = 10\%$

with the fluorine nuclei of the adjacent CF_2 group. Below the *CMC* the chemical shift of the CF_3 group is independent of the surfactant concentration, $\delta = -81.95$ ppm. Above the *CMC* the exchange of surfactant molecules between the free and micellar forms is fast, with respect the n.m.r. characteristic time scale, and the CF_3 peak moves upfield. It has been shown[24] that in the phase separation model, the chemical shift above the *CMC* is given by:

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

where δ_f and δ_m are the intrinsic chemical shifts of free and milellar surfactant, respectively. According to equation (1) and *Figure 1*, with $CMC = 0.031$ M, $C = 0.05$ M and $\delta = -83.72$ ppm we obtain $\delta_m = -84.00$ ppm.

Hydrophobically modified poly(sodium acrylate) (slow exchange). Figure 2 displays the ^{19}F n.m.r. spectra obtained with PA 5 8C8F at different polymer concentrations ranging between 0.3% and 10%. Once again, only the signal of the CF_3 group is given but the same phenomenon can also be observed with the other fluorine atoms of the alkyl chain, especially with the CF_2 adjacent to the CF_3. For a polymer concentration of 0.3% a peak is observed at −81.91 ppm. Because of the lower resolution of the polymer spectrum the triplet form of the peak is not observed here. When the polymer concentration is increased a second peak appears and grows at −83.87 ppm. By comparison with the surfactant spectrum (*Figure 1*) the first peak can be attributed to the free alkyl chains and the second one to the aggregated alkyl chains.

The data of *Figure 2* lead us to the following conclusions.

(1) For the hydrophobically modified polymer, the exchange rate between the free and aggregated forms is slow with respect to the ^{19}F n.m.r. characteristic time, τ_{nmr}. Thus the n.m.r. experiment can distinguish between the two species. τ_{nmr} is given by the relationship[30]:

$$\tau_{nmr} = \frac{\sqrt{2}}{\pi \Delta \nu} \qquad (2)$$

where $\Delta\nu$ is the frequency difference between the aggregated and free forms. For our polymer $\Delta\nu = 461.3$ Hz, which gives $\tau_{nmr} = 1$ ms. Therefore the exchange characteristic time for our sample is higher than 1 ms. For equivalent surfactants we expect[31] characteristic times of the order of 10^{-3} ms. The difference with respect to the surfactant behaviour reveals that there is a considerable slowing down of the association dynamics because of the polymer backbone, which limits the molecular motions of the pendant alkyl chains.

(2) There is a threshold polymer concentration, C_p^0, below which no hydrophobic aggregates are detected (only one peak is observed for a polymer concentration of 0.3%). This C_p^0 lies between 0.3% and 0.6%. Rheological data obtained on a similar polymer of high molecular weight have also indicated that aggregation starts above this threshold polymer concentration[20].

(3) The fractions of free and aggregated alkyl chains can be directly obtained by integration of the n.m.r. signal. It was checked that, under the experimental conditions employed, all the ^{19}F nuclei were fully relaxed and therefore the peak areas can be compared qualitatively. The variation in the fraction of aggregated alkyl chains as a function of polymer concentration is given in *Figure 3*. Below C_p^0 all the alkyl chains are free in an aqueous environment. Above C_p^0, the fraction of aggregated alkyl chains first increases rapidly and then seems to reach a plateau value around 60–70%. This latter phenomenon can be explained by steric hindrance, arising from the poly(sodium acrylate) backbone, preventing some of the alkyl chains from associating.

It is noteworthy that the free alkyl signal at −81.91 ppm is asymmetrical even at the lowest polymer concentration (*Figure* 2a). This might be due to the formation of some small 'pre-aggregates' in which the alkyl chains

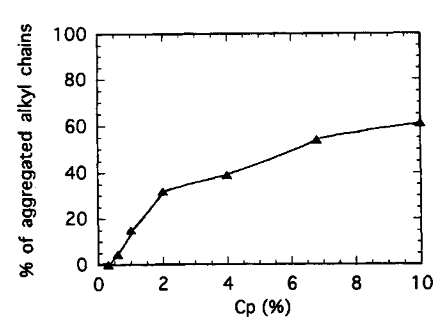

Figure 3 Fraction of aggregated alkyl chains *versus* polymer concentration for PA 5 8C8F. For this polymer C_p^0 lies between 0.3 and 0.6%

exchange faster with the free form. The presence of small fast-exchanging aggregates presumably explains the partial overlap between the signals of free and aggregated alkyl chains at higher polymer concentration (for instance, see *Figure* 2f). Nevertheless, their contribution to the total area of the peaks remains small and does not influence significantly the estimated value of the aggregated fraction.

Conclusion

In this work we have demonstrated that the fractions of free and aggregated alkyl chains of an associating polymer can be obtained directly from simple n.m.r. experiments. A more detailed study of the association mechanism of these systems will be given in a forthcoming paper. Determination of the aggregated fraction is a prerequisite for a precise estimation of the aggregation number (number of alkyl chains per aggregate) which can be obtained in combination with other techniques, namely fluorescence spectroscopy or small-angle X-ray or neutron scattering.

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