Structure of Hydrogen and Hydrophobically Bonded Amphiphilic Copolymer with Poly(methacrylic acid) Complexes as Revealed by Small Angle Neutron Scattering

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Summary: We study by SANS the structure of intermolecular complexes formed through hydrogen bonding and hydrophobic interactions between poly(methacrylic acid) (PMA) and a neutral copolymer surfactant (PEO-PPO-PEO). The contrast variation method enables us to probe the structure factor of each polymer in the complex and their cross structure factor. The number of copolymer chains, which results from the cooperative action of hydrogen bonding and hydrophobic interactions increases as the charge of the polyacid decreases. The aggregation preserves the micellar core-corona organization of the copolymer and shrinks the polyacid chains which adopt a similar compact structure. Finally, the structure of the aggregates is compared to that of PEO-PMA homopolymer complex observed by SANS.

Keywords: amphiphiles; SANS; surfactants

Introduction

Intermolecular forces that drive self association in biological or soft condensed matter systems in water are mainly the electrostatic, the hydrogen bonding and the so-called hydrophobic interaction. In most of cases, these effects operate together in a cooperative way [1,2,3,4], and it is difficult to estimate the contribution and the effect of each type of interaction on the structure of the complex. For that reason, we decided to investigate the structure of a polymer complex stabilized simultaneously via hydrogen binding and hydrophobic interactions. Our choice was fixed on a complex formed by an amphiphilic copolymer (PEO-PPO-PEO) [2] and poly(methacrylic acid) that can form hydrogen bonds between the hydroxyl groups of the polyacid and the oxygen of the poly(ethylene oxide) (PEO) or the poly(propylene oxide) (PPO) [1-3-4]. Furthermore, the hydrophobicity of PPO

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and non ionized parts of poly(methacrylic acid) that depend essentially on temperature can also promote aggregation. Beside, the repulsive electrostatic interactions and the entropy of the counterions act on the opposite way and resist aggregation. In order to sort out these relative contributions to the final structure of the complex, we decided to study the structure of the complex using Small Angle Neutron Scattering (SANS) and more specifically, the contrast variation method which allows to probe the structure of each polymer and their mutual interactions[3]. We focus our attention on the effect of the polyacid neutralization degree α on the structure of the complex.

Materials and methods

Fully deuterated poly(methacrylic acid)(PMA-D, M_w=370000 g/mol) was synthesized by radical polymerization of deuterated methacrylic acid. The degree of neutralization of the polyacid (α=[COO^-]/([COO^-]+ [COOH])) was adjusted by adding the required quantity of NaOH. The copolymer, known by its trade name as Pluronic® (P105, EO_{37}-PO_{56}- EO_{37}) was a gift from BASF (France). It was used without further purification.

The scattering experiments were performed at Laboratoire Léon Brillouin on the spectrometer PACE. The range of scattering vector was 10^{-2} Å^{-1}< q < 0.11 Å^{-1}. The measured normalized scattering intensity I(q) (in cm^{-1}) is related to the partial structure factors of the sample constituants by the equation.

$$I(q)= (n_a-n_w)^2S_{aa}(q)+ (n_a-n_w)(n_b-n_w)S_{ab}(q)+ (n_b-n_w)^2S_{bb}(q) \quad (1)$$

n_a, n_b and n_w are respectively the scattering length densities of PMA(D), the copolymer and of the solvent. The partial structure factors S_{ij} are defined as usual by $S_{ij}(q)= \int d^3r \langle \delta\Phi_i(0)\delta\Phi_j(r)\rangle e^{iqr}$, where $\Phi_i(r)$ is the local volume of constituent *i* and $\delta\Phi_i(r)$ the local deviation from the average value in the sample volume. The partial structure factors $S_{ii}(q)$ are related to the structure of each polymer in the complex, whereas the cross structure factor $S_{ab}(q)$ gives information on the interaction between the constituents of the complex. The contrast variation experiments were performed by measuring the scattering intensity of the solutions prepared with three proportions of heavy water and the three partial structure factors are obtained by solving eq. 1 for these three compositions of the solvent [4]. SANS experiments were performed at 30°C; the copolymer concentration was 2.5% (w/v) and the ratio [PEO]/[PMA]=2.

Results and discussion

At 30°C, well above the critical micellization temperature (about 20°C), the copolymer form micelles with a dry core of PPO surrounded by a hydrated coronna of PEO [2]. The intensity scattered by the micelles is fitted using a hard sphere interaction structure factor and a core-corona form factor [4]. The fitting procedure is based on four fitting parameters: N_a: the micelle association number, R_1: the core radius, R_2: the corona radius and R_{hs}: the hard sphere interaction distance. The result of the scattered intensity fit is displayed on figure 1, giving R_{hs}= 100 Å, R_1= 42.5 Å and R_2= 59.1 Å. The intermicellar interaction radius is 60% larger than the micelle radius, indicating that the micelles are well separated from each other [4].

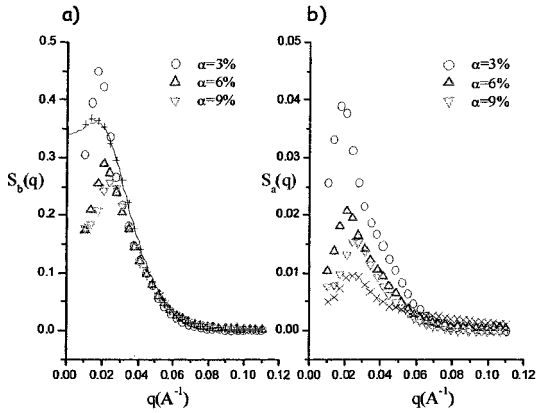

Figure 1. a) Structure factor of the copolymer in the complex for three values of α. The solid line represents the best fit of the structure factor of the pure copolymer in water (+). b) Structure factor of the PMA(D) in the complex for three values of α and alone in water for α = 6% (□).

The study of the increasing of the scattered intensity remains the simplest way of characterizing aggregation as the association proceeds, and usually, the larger the intensity, the larger the aggregates. This is indeed what we observe in figure 1 where we compare the structure factors of PMA and the copolymer chains in the complex with their

counterparts in the pure equivalent solution. Precisely, we observe that the intensity scattered by each polymer in the complex increases as the degree of neutralization α decreases. In other words, the aggregation number of each polymer in the complex increases with the density of non ionized (complexable) hydroxyl groups along the polyacid chains. This is confirmed by the positive cross structure factors $S_{ab}(q)$ (figure 3) which indicates that the interaction between the copolymer and the PMA is attractive. In addition, this attractive interaction increases with the density of available carboxyl groups as reflected by the evolution of $S_{ab}(q)$ with α.

The number of PMA chains in the complex decreases with the density of complexable monomers along the polyacid chains and the comparison of the scattered intensities allows to give an estimation of this number that varies from 2 chains (α=9%) to 4 chains (α=3%) per aggregate.

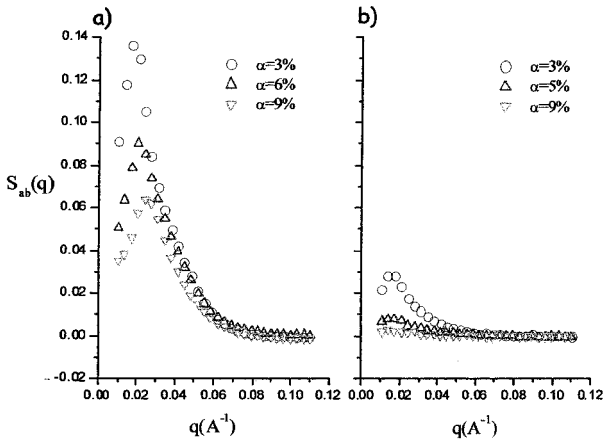

Figure 2. a) Cross structure factor of the copolymer-PMA(D) complex in water for three values of α. b) Cross structure factor of PEO-PMA(D) in the complex in water for three values of α.

The number of copolymer chains per aggregate also decreases with the density of complexable groups on PMA chains. More precisely the scattered intensities indicate that this number is divided by a factor of about 2 in the range of variation of α. It is interesting to notice that at high neutralization, the number of copolymer chains is surprisingly lower in the complex than in the micelles. An additional interesting feature is that the copolymer

correlation peak is not only shifted in comparison with the micelle peak position, but its shape changes from a smooth correlation peak reflecting the hard sphere interaction potential to a sharp electrostatic peak due to long range Coulombic interactions between aggregates. Furthermore, for a given α value, the position of the electrostatic peak observed on the three partial structure factors is that of the free PMA chains at the same concentration, indicating that the aggregates repel each other via electrostatic interactions as free PMA chains [4].

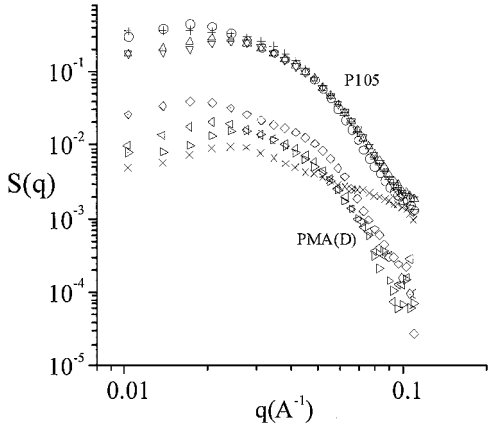

Figure 3. Structure factor of the copolymer in the complex for three values of α (⌡:α=9%, ⌠:α=6%, |:α=3%) and alone in water (+). Structure factor of the PMA(D) in the complex for three values of α (≅:α=9%, 0:α=6%, ≀:α=3%) and alone in water for α = 6% (□).

The shape of the polymer partial structure factors at large scattering vector is related to the local structure of the chains within the complex. Beyond the correlation peaks, the intensity scattered by the copolymer in the micelles or in the complex is the same whatever the value of α (Figure 3). It appears that the complexation does not change the organization of the copolymer compared with the micelles whatever the strength of the interaction (i.e. the value of α). The preservation of the core-corona structure of the copolymer in the presence of PMA is confirmed by dynamical information obtained by NMR [4,5], showing that the PEO block dynamics is not affected by complexation and forms the hydrated corona, whereas the PPO block dynamics is strongly hindered by the association with PMA, forming the dry core of the aggregate. One can notice that, unlike

the copolymer, the structure of PMA chains in the presence of copolymer and alone in water are very different (Figure 3). Precisely, in the high q regime, the intensity scattered by PMA decreases more rapidly for the complex than for free chains, showing that the association process modifies the local structure of the polyacid up to the molecular scale by shrinking the chain. The scattered intensity decay does not depend on α and is very similar to that of copolymer chains, indicating that the core-corona picture is also valid to describe polyacid chains organization within the complex [4]. In that scheme, most of non-dissociated carboxyl group sequences are complexed with the PPO, forming the dense hydrophobic core of the complex. This core is surrounded by a hydrated corona formed with free ionized polyacid sequences and PEO blocks.

It is interesting to compare the structure of the copolymer-PMA complex with that of PEO-PMA homopolymer complex obtained with the same contrast variation method [3]. Such a comparison allows to estimate the respective influence of the hydrophobic and the hydrogen bonding attractive interaction on the formation and the structure of the complex. The PEO-PMA complex was composed with the same polyacid and with a poly(ethylene oxide) (M_w=100000 g/mol) purchased from Aldrich [3]. In both cases, the aggregation number of each polymer and the size of the aggregates increase when α diminishes. These observations are confirmed by the increase of the cross structure factors as α decreases (Figure 2.), indicating that the attractive hydrogen bonding interaction increases with the density of complexable (non dissociated) carboxyl groups. The comparison between cross structure factors displayed in fig. 3 shows that, as the polyacid charge is higher than 9 %, there is no interaction between homopolymers ($S_{ab}\approx 0$) whereas the copolymer-PMA interaction is attractive ($S_{ab}>0$). For the copolymer, the combined action of hydrogen bonding and hydrophobic effects allow to overcome the repulsive interactions. This is no more the case with the homopolymer for which the hydrophobic interactions are absent and the hydrogen bonding is too weak to overcompensate the repulsion between the polymers. Another important difference that deserves to be discussed between the two complexes is the evolution of the structure of each polymer in the aggregates when α decreases. Contrary to the copolymer-PMA complex, the structure of each polymer in the homopolymer complex depends on the degree of neutralization α [3]. For α=9%, no complexation occurs and the structure factors of the polymers is close to that of their counterparts alone in water at the same concentration. As α decreases, the structure factors

of the free and complexed chains become progressively different, and for the lower values of α, the PEO and PMA chains appear to be zipped together, adopting the same compact structure [3]. The proportion of hydrophobic sequences formed with non dissociated PMA blocks and PEO increases as the neutralization of the polyacid decreases, leading to a progressive shrinking of the chains. Contrary to the complex formed with the copolymer, the local structure of the chains within the aggregates is very sensitive to the PMA neutralization.

Conclusion

The contrast variation method is a powerful tool to probe the structure of the intermolecular complex formed with a polyacid and a copolymer. Above the cmt, the aggregation number of each polymer increases when the density of ionized PMA groups decreases. The aggregation number of the copolymer decreases below that of pure micelles if the polyacid charge exceeds 3-4%. It appears that the complexation preserves the core-corona organization of the copolymer and shrinks the PMA chains that adopt a similar core-corona structure. Contrary to what happens with PEO-PMA homopolymer complexes, the structure of both constituents is not sensitive to the polyacid charge. Whatever the neutralization, the non dissociated PMA blocks associate with PPO to form the dry core of the complex whereas the PEO and ionized blocks of PMA form the stabilizing hydrated corona. This polymeric system gives a particular demonstrative example of interaction between a surfactant and a polymer. Furthermore, it can help us to understand the association between biological polymers like DNA and Pluronic used in gene therapy [6]. Finally, at higher micellar concentration, clusters of interconnected micelles with long polyacid chains appear [7], leading to the formation of a novel class of pH and temperature sensitive gels.

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