Structure of a New Type of Transient Network: Entangled Wormlike Micelles Bridged by Telechelic Polymers

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ABSTRACT: The thermodynamics and structural behavior of a new type of transient network are reported. The network is obtained by adding in a solution of entangled surfactant wormlike micelles a telechelic triblock copolymer whose hydrophobic ends anchor into the micelles and whose hydrophilic tails are swollen in the aqueous solvent and reversibly link the entangled cylindrical micelles. For comparison, we have also studied the same surfactant system decorated with an amphiphilic diblock copolymer which corresponds exactly to a triblock telechelic copolymer cut into two identical diblock copolymers. We find that the addition of telechelic polymers induces an effective attraction of entropic origin between the surfactant that may result, in equilibrium, in the coexistence of a dilute phase and a connected network, as predicted by theory. Small-angle neutron scattering experiments show first that the locally cylindrical structure of the micelles is maintained upon copolymer addition over a wide range of copolymer-to-surfactant molar ratio. On the other hand, the addition of telechelic polymer correlates with (i) the emergence of a broad peak in the structure factor at a finite scattering vector, *q*, due to the short-range steric repulsion induced by the polymer between the cylinders, and (ii) the large rise of the scattered intensity at low *q*'s (for small enough surfactant concentration), which indicates an increase of the osmotic compressibility of the solution due to the effective attractive interaction between cylinders provoked by the telechelic polymers linking them.

Introduction

Examples of equilibrium network-forming systems include surfactant solutions, aqueous gels of biological molecules, or synthetic polymers. Among them, two classes of materials have been the subject of numerous publications from academic and industrial groups in the past two decades. These are entangled solutions of long and flexible surfactant cylinders (wormlike micelles)[1] and solutions of associated water-soluble polymers with hydrophobic end blocks (telechelic polymers).[2] These systems are particularly interesting because of their ability to form highly viscous solutions with relatively simple viscoelastic behavior, since they are very often characterized by a single relaxation time.

More recently, huge synergetic effects have been evidenced when solutions of cylindrical surfactant assemblies are mixed with hydrophobically modified polymers. Previous studies[3−6] have indeed demonstrated that the polymers considerably modify the viscoelasticity of the samples; in particular, the viscosity of the mixtures can be up to 4 orders of magnitude higher than the viscosities of the pure component solutions,[4−6] suggesting that the hydrophobic blocks of the polymers anchor into wormlike micelles and bridge them. However, all these studies were carried out with macromolecules for which hydrophobic stickers are randomly distributed along a water-soluble backbone. Our aim is to investigate a simpler experimental configuration in order to be able ultimately to quantitatively model the effect of the polymers on the rheological properties. We therefore use a so-called telechelic polymer, where a hydrophobic sticker is grafted at each extremity of a hydrophilic polymer. Very generally, when a telechelic polymer is added to a surfactant solution (for a surfactant concentration above the critical micellar concentration), it can either anchor its two stickers into one given surfactant assembly and form a loop or bridge two distinct surfactant assemblies. Equilibrium or out-of-equilibrium exchange of telechelic ends between neighboring self-assemblies controls the interactions between the micelles and *in fine* the viscoelastic properties of the composite materials. However, the exact calculation of the explicit entropic interaction between colloids reversibly linked by telechelic polymers is a difficult problem of polymer physics and has been addressed only in the planar[7,8] and spherical geometry.[9−12]

Mixtures of telechelic polymers and spherical surfactant assemblies, including micelles,[13] microemulsion droplets,[14−19] or vesicles,[20] have been previously investigated. In all cases, telechelics have been shown to eventually induce a transient network by reversibly bridging the surfactant assemblies and hence convert the initial fluid sample into a viscoelastic medium. However, to the best of our knowledge, mixtures of very long and entangled wormlike micelles and telechelic polymers have not been investigated so far. Such a model systems present interesting analogies with gels of rigid actin filaments.[21]

In this paper, we present experimental results on the phase behavior of, and on the interactions at play in, a model transient network comprising entangled surfactant wormlike micelles reversibly linked by telechelic polymers. For comparison, we have also studied the thermodynamics and phase behavior of the same surfactant system decorated with an amphiphilic copolymer, whose structure corresponds exactly to the triblock telechelic copolymer cut into two identical diblock copolymers.

Experimental Section

Materials. We use surfactant solutions composed of a mixture of cetylpyridinium chloride $[H_3C-(CH_2)_{15}]-C_5H_4N^+-Cl^-$ (CpCl) and sodium salicylate (NaSal), with a constant molar ratio [NaSal]/[CpCl] = 0.5, diluted in brine [NaCl] = 0.5 M (NaCl). This system is known to form long and flexible micelles even at low concentration.[22] CpCl is received from Fluka and is purified by successive

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recrystallizations in water and acetone. NaSal and NaCl are used as received. We add to this host phase di- or triblock copolymers, which are synthesized in our laboratory. The polymer is poly(ethylene oxide) (PEO), and it has been hydrophobically modified and purified in the laboratory using the method described in refs 23 and 24. The molecular weight of the starting PEO is determined by size-exclusion chromatography. The hydrophobically modified PEO contains an isocyanate group between the alkyl chain and the ethylene oxide chain. Two copolymers have been prepared: a triblock "telechelic" polymer, $C_{18}-PEO_{10K}-C_{18}$ with a $C_{18}H_{37}$ aliphatic chain grafted at each extremity of the central PEO chain of molecular weight 10 000 g/mol, and a diblock "amphiphilic" $PEO_{5K}-1C18$ copolymer, constituted of a poly(ethylene oxide) (PEO) central block, of molecular weight 5000 g/mol, grafted at one extremity with a $C_{18}H_{37}$ aliphatic chain. Hence, the amphiphilic copolymer corresponds exactly to the triblock telechelic copolymer cut into two identical diblock copolymers. After modification, the degrees of substitution of the hydroxyl groups were determined by NMR using the method described in ref 25 and are found to be larger than 98%. The radius of gyration of the POE block is respectively 37 and 24 Å[26] for the telechelic and amphiphilic polymer, respectively. Experiments are performed at a temperature of 30 °C. The samples are characterized by the mass fraction of surfactant $\phi = (m_{\mathrm{CPCl}} + m_{\mathrm{Sal}})/m_{\mathrm{tot}}$, where m_{CpCl}, m_{Sal}, m_{tot} are respectively the mass of CpCl, the mass of salicylate, and the total mass of the sample, and by the sticker ($C_{18}H_{37}$) over surfactant molar ratio β. The samples are prepared by weight. We first incorporate the surfactant CpCl and the hydrophobically modified PEO in brine until complete dissolution of the polymer (this requires one night or more). After addition of NaSal to the homogeneous mixture, the sample is stirred several times for homogenization and then left undisturbed at 30 °C for several days. In the following, since the densities of all components are nearly identical, we identify mass and volume fractions when H_2O is used. For the neutron scattering experiments, H_2O is replaced by deuterated water, D_2O, and a correction is applied to the composition to account for their difference in molar weight. We have moreover checked that the use of deuterated instead of hydrogenated water does not significantly modify the phase diagrams of the mixtures.

SANS Experiments. Small-angle neutron scattering (SANS) experiments have been performed on the spectrometer PAXE at the Laboratoire Léon Brillouin (Saclay, France) and on the D11 beamline at the Institut Laue Langevin (Grenoble, France). The scattered intensity, I, is systematically measured on a large range of scattering vectors q, from 5×10^{-3} to 0.3 $\mathrm{Å}^{-1}$. Data are treated and put on an absolute scale according to standard procedures. Deuterated water is used in order to obtain only one contrast factor, namely the contrast between the deuterated compounds and the hydrogenated compounds (surfactant and polymer). As the surfactant polar heads are hydrated and the POE blocks are swollen in water, this method is sensitive to the contrast between the hydrophobic core of the micelles and the D_2O solvent.

Results

Phase Diagram. The phase diagram of the CpCl−NaSal mixture in brine has been extensively studied by Rehage et al.[22] and Berret et al.[27] Without copolymer, the micellar solutions are homogeneous and isotropic for surfactant weight fraction up to 36%. In the ranges of values investigated for the two parameters ϕ and β ($0.025\% < \phi < 16\%$ and $0 < \beta < 3\%$), we have checked that the phase diagram is not modified by the addition of amphiphilic copolymer (one sticker): the mixture remains a transparent isotropic phase. These results are consistent with our previous findings with the same surfactant system and another amphiphilic polymer where phase separation was observed for surfactant concentration always larger than 18%.[28] We have previously shown[28,29] that this type of sample comprises a semidilute solution of surfactant hairy wormlike micelles.

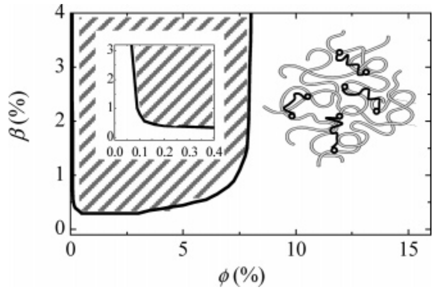

Figure 1. Phase diagram in the plane (ϕ, β), with ϕ the surfactant concentration and β the sticker over surfactant molar ratio. The shaded area represents the two-phase region. Inset: (left) zoom up of the phase diagram in the low ϕ region; (right) cartoon of the expected structure of the soft composite material in the one-phase region, for ϕ larger than the overlap concentration $\phi^* = 0.3\%$.

By contrast, the phase diagram (with the same ranges of values investigated for ϕ and β ($0.025\% < \phi < 16\%$ and $0 < \beta < 3\%$) is markedly affected by the addition of telechelic polymers, as shown in Figure 1. While for sufficiently low amounts of telechelic polymers (up to $\beta = 0.25\%$), a one-phase region is obtained for all surfactant concentrations, for higher β, phase separation occurs in a wide range of surfactant concentration. In the low-ϕ zone (inset of Figure 1), phase separation occurs at lower ϕ as β increases and always before the overlap concentration of naked micelles $\phi^* = 0.3\%$. The overlap concentration of the naked micelles is obtained from the crossover between a Einstein behavior in the dilute regime and a power-law behavior in the semidilute regime for the variation of the static viscosity of the solution with the surfactant concentration.[22,30,31] In the high-ϕ region, phase separation occurs at higher ϕ when β increases and saturates at about 8% for β larger than 1.5%. The biphasic region comprises two isotropic and transparent phases, one being a rather stiff gel and the other being a fluid of low viscosity. In a large domain of the phase diagram, however, the mixed system remains homogeneous and isotropic and consists of a solution of wormlike micelles presumably both decorated and bridged by telechelic polymers, as inferred from the scattering experiments described below.

We note that the phase diagram of wormlike micelles and telechelic polymers (Figure 1) is analogous to the phase diagram of mixtures of microemulsion droplets and telechelic polymers[19] but also to the theoretical phase diagram for long filaments and cross-linkers molecules.[32] Indeed, as demonstrated by Zilman and Safran,[32,33] a generic phase behavior is expected for mixed systems of self-assembled aggregates and polymeric cross-linkers: an entropically driven, first-order thermodynamic phase transition is predicted to occur even in the absence of any specific interactions at the mean-field level. The configurational entropy of polymer junctions induces indeed an effective attraction that can result in an equilibrium between a dilute phase and a connected network.

Structure. We use small-angle neutron scattering (SANS) in order to evaluate how the polymer modifies the interactions between the wormlike micelles. We note that the persistence length $l_p \approx 190$ Å of the naked micelles has been measured[28,31] from SANS experiments using the method developed in ref 34 on a sample at the overlap concentration. However, it is not possible to measure the persistence length for the micelles decorated or bridged by polymers because of the presence of a correlation peak in the scattering patterns as discussed below. We presume that it is not strongly modified by the presence of polymers. We first check that the incorporation of telechelic polymer does not modify the local cylindrical structure of the

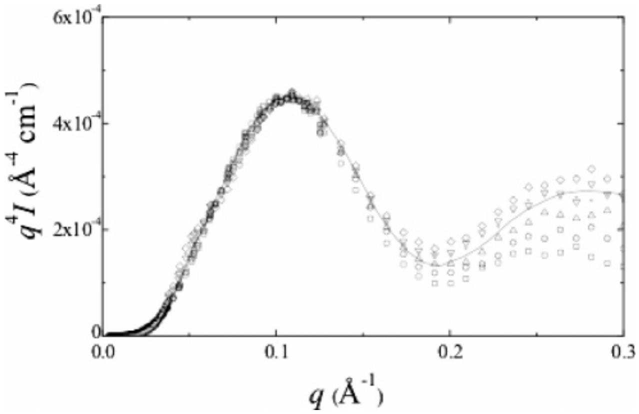

Figure 2. Porod representation, q^4I vs q, with I the scattered intensity and q the scattering vector, for naked wormlike micelles (squares), wormlike micelles with amphiphilic polymer with $\beta = 2\%$ (gray-filled down triangles), and wormlike micelles with telechelic polymers with $\beta = 0.5\%$ (circles), $\beta = 1\%$ (up triangles), $\beta = 2\%$ (down triangles), and $\beta = 3\%$ (diamonds). The line is the best fit of the form factor of a rigid cylinder with a radius of 21.5 ± 2 Å, taking into account the apparatus fonction (see ref 28 for details). The surfactant concentration is $\phi = 8\%$.

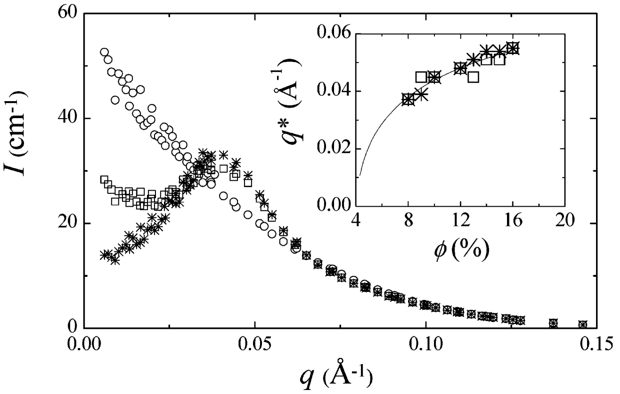

Figure 3. Scattered intensity for a semidilute solution of naked micelles (circles) and of micelles with amphiphilic polymer (stars) and with telechelic polymer (squares). The surfactant volume fraction is $\phi = 8\%$, and the sticker over surfactant molar ratio is $\beta = 2\%$. Inset: peak position as a function of ϕ, for $\beta = 2\%$, for micelles with amphiphilic polymer (stars) and with telechelic polymer (squares). The line is a fit of the data using the equation $q^* = (\sqrt{2}/\delta)\sqrt{\ln(\phi/\phi_c)}$,[29] with $\phi_c = 4.1\%$ and $\delta = 30.5$ Å.

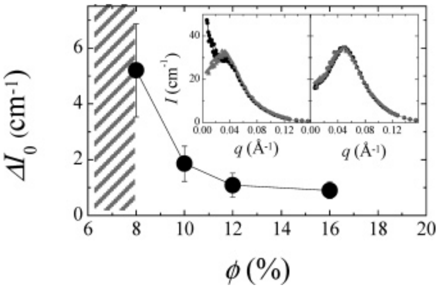

Figure 4. Difference between the scattered intensity at small angle for a solution of wormlike micelles with telechelic polymer and a solution of wormlike micelles with amphiphilic polymer, as a function of the surfactant concentration, ϕ. The shaded area marks the biphasic region. Inset: scattered intensity as a function of the wave vector for wormlike micelles with amphiphilic polymer (gray symbols) and with telechelic polymers (black symbols). The sticker over surfactant molar ratio is $\beta = 1\%$ and $\phi = 8\%$ (left) and 16% (right).

micelles. As can be seen in Figure 2 on a Porod representation (q^4I vs q), the form factor of naked wormlike micelles superimposes with those of micelles with telechelic polymers, in the whole range of β investigated. In particular, the maxima and minima of the form factor are located at exactly the same q position. A fit of the data with the expression for the form factor of rigid cylinders,[28,31] which takes into account both the apparatus function and a polydispersity of the cylinder radius on the order of 3 Å, gives in all cases a radius of the hydrophobic core of the cylindrical micelles of 21.5 Å, a value which is very close to the maximal length $l_{\max} \approx 21.8$ Å for a saturated hydrocarbon chain with 16 carbons.[35] We note nevertheless a slight difference in the intensity at large q's between naked micelles and micelles with polymer, which can be easily detected in the first minima and in the second maxima of the form factor as a continuous increase as β increases. This probably reflects the contribution of the polymer layer that covers the micelles. The superposition is however perfect for sample with amphiphilic and telechelic polymers with a same β, as expected if the difference in intensity is due to the POE shell.

Figure 3 compares, for samples with $\phi = 8\%$, the scattered intensity of mixtures of wormlike micelles and amphiphilic diblock copolymers or triblock telechelic polymers with that for naked micelles. While the scattering intensity of naked wormlike micelles is monotonically decreasing with q, the two spectra measured with copolymers exhibit a peak at a finite scattering vector. The peak indicates the existence of repulsive interactions between the micelles which are mediated by the copolymer. In the whole range of surfactant concentration and polymer amount investigated (for which the telechelic/surfactant mixture does not phase-separate), both the position and the intensity of the peaks are found equal with amphiphilic and telechelic polymers. Interestingly, we note that such a correlation peak is not observed for wormlike micelles mixed with associating polymers.[6] As an illustration, we show in the inset of Figure 3 the variation of the peak position, q^*, with the surfactant concentration for both amphiphilic and telechelic polymers, for samples with $\beta = 2\%$. The data obtained with the two types of copolymer are found to collapse onto a single master curve, which suggests that the repulsive interactions due to the copolymer layer that surrounds the micelles are very comparable (see also insets of Figure 4). We have previously modeled the repulsive interaction between wormlike micelles induced by the addition of amphiphilic copolymers and quantitatively shown that it results from steric repulsion due to the soft and short-range polymer layer covering the micelles.[28] This model uses the random phase approximation (RPA) to compute the structure factor $S(q)$ of a solution of wormlike micelles interacting through a repulsive Gaussian potential describing the steric repulsion. It predicts that above a threshold polymer concentration, ϕ_c, whose magnitude is essentially controlled by the range of the potential δ, $S(q)$ exhibits a peak whose position q^* is given by $q^* = (\sqrt{2}/\delta)\sqrt{\ln(\phi/\phi_c)}$. Using this approach, which was used successfully for another system,[28,29,31] we evaluate from a fit of q^* vs ϕ (an example of such a fit is shown in the inset of Figure 3) that the steric polymer layer that covers the micelles has a thickness $h = 30$ Å for $\beta = 2\%$ and $h = 53$ Å for $\beta = 3\%$, for both amphiphilic and telechelic polymers. These results are consistent with h being on the order of the radius of gyration of the POE block and increasing with β and are moreover in agreement with our previous measurements obtained with another type of amphiphilic polymer.[29]

By contrast, the intensities scattered at small wave vector, I_0, are markedly different for the two types of copolymer. Assuming a binary system, I_0 is proportional to the osmotic compressibility of the solution. As a consequence, a higher intensity for mixtures of micelles and telechelic copolymer than for mixtures of micelles and amphiphilic copolymer reveals that the telechelic polymer indeed creates bridges between the micelles, hence inducing an attractive interaction, as in the case of bridged droplets.[10−12] As reported in Figure 4, the difference between I_0 for telechelic polymers and I_0 for amphiphilic polymers continuously decreases as the surfactant concentration increases. In this plot, the error bars result from an average of the experimental values obtained for several β values, from 1 to 3%. This observation is in agreement with the following simple expectation: the telechelic-mediated attraction between the micelles is effective when the mean distance between the micelles (the mesh size or correlation length of the semidilute solution, ξ) is of the order of magnitude or larger than the radius of gyration of the POE unit, R_g. Reversibly, when the surfactant concentration increases, the mesh size decreases and eventually becomes shorter than R_g. Hence, the attraction vanishes and I_0 becomes equal for amphiphilic and telechelic copolymers. This attractive interaction is also responsible for the phase separation observed at smaller surfactant concentration, similarly to what is found for mixtures of spherical micelles with telechelic polymers.[19] For the naked wormlike micelles solution, the mesh size is of the order of 100 Å for $\phi = 8\%$,[30] the surfactant concentration below which phase separation occurs for large amounts of telechelics, a numerical value in reasonable agreement with the radius of gyration of the water-soluble backbone of the telechelic polymers.

Predicting the structure factor of bridged wormlike micelles from the RPA theory is however more complex than for the case of wormlike micelles decorated by amphiphilic copolymers and remains still to be done.

Conclusion

We have shown that adding telechelic copolymers to a semidilute solution of surfactant wormlike micelles induces both an effective attractive interaction between the micelles, due to the bridging of the micelles, and a repulsive interaction, due to the steric repulsion between the micelles induced by the water-soluble POE shell that decorates the micelles. The attractive interaction is at the origin of the associative phase separation observed experimentally. This novel and original system is an example of materials exhibiting two interconnected transient networks, one arising from the entangled wormlike micelles and the other one from the telechelic polymer, which create sliding junctions between the micelles. The unusual linear rheological properties of these materials will be reported elsewhere.

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