

SANS Evidence for the Cross-Linking of Wormlike Micelles by a Model Hydrophobically Modified Polymer

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Certain surfactants are known to self-assemble in aqueous solution into very long threadlike or wormlike micelles (WLM), which can endow the fluid with remarkable stimuli-sensitive rheological properties.¹ Such systems find applications in diverse fields ranging from personal care products to drilling fluids for enhanced oil recovery. Addition of hydrophobically modified water-soluble polymers (HMP) can enhance the zero shear rate viscosity of a WLM solution by several orders of magnitude, at sufficiently low concentrations that neither the WLM nor the HMP alone would exert much effect. This phenomenon raises the possibility of significantly reducing the amount of additive required to achieve a desired rheological profile, with concomitant advantages in both cost and environmental impact. The detailed mechanism underlying this “viscoelastic synergy” remains to be completely established, but the most plausible explanation involves a transient cross-linking of the WLMs by intercalation of hydrophobic “stickers” (typically linear alkyl groups on the HMP) into the micellar cores.^{2–6} In the pioneering work the HMPs used to achieve this effect were based on structurally ill-defined macromolecular frameworks (guar,³ polyacrylamide,⁴ and chitosan⁶), which might limit the possibilities for elucidating the mechanism and optimizing the outcome.

We recently described the synthesis and characterization of a series of well-defined HMPs, comprising narrow distribution poly(ethylene oxide) (PEO) chains with alkyl stickers installed at the chain ends.⁵ The PEO molecular weights ranged from 10^4 to 10^5 , with sticker lengths of C_{14} , C_{18} , and C_{22} . In addition, the HMP architecture was varied from “diblock” (one sticker) to “triblock” (two stickers) to 3-arm star (three stickers). These HMPs were combined in varying concentrations with a 1% solution of cetyltrimethylammonium tosylate (CTAT), a system well-known to form WLMs.^{7–10} The steady shear viscosity, η , and the dynamic shear moduli, G' and G'' , were examined in detail.⁵ In many of the mixtures η was 2–3 orders of magnitude larger than either of the separate WLM and HMP solutions, and the G' and G'' profiles indicated greatly enhanced longest relaxation times, τ , and well-defined gel-like plateaus in G' . The longest relaxation time was most sensitive to the sticker length; a C_{22} -terminated triblock would impart a relaxation time $\sim 10^3$ times longer than the same PEO with C_{14} stickers. Increasing the PEO molecular weight also increased τ , either at constant sticker concentration or at constant polymer concentration. There was little difference in effect between the triblocks and 3-arm stars, whereas the diblock only reduced the viscosity of the CTAT solution. This last observation is consistent with the idea

of the HMP cross-linking the WLMs, since a monofunctional diblock cannot link two WLMs. The observed drop in η was attributed to a shortening of the average WLM length, possibly due to stabilization of the WLM end-caps by the intercalated chains. In an analogous system of WLMs and added HMP diblocks, the end-cap energy was found to decrease with added HMP.¹¹

In this report we focus on one representative solution, containing 1% CTAT and 0.25% of a 3-arm star, in which each arm molecular weight is 44 kg mol^{-1} and each sticker is C_{22} . The solvent was substituted with D_2O , and the solutions were examined by small-angle neutron scattering (SANS) to gain insight into the underlying mechanism. SANS measurements were performed at NIST, on the ExxonMobil/University of Minnesota beamline NG7. Neutrons of wavelength $\lambda = 6.0 \text{ \AA}$ were used, with a distribution $\Delta\lambda/\lambda = 0.11$; the sample cells were 1 mm thick. Three different sample-to-detector distances were employed to extend the accessible range of the scattering vector, $q (= (4\pi/\lambda) \sin(\theta/2))$. The scattering data were corrected for sample transmission, empty cell, solvent, and background scattering, and detector response. Absolute intensity curves $I(q)$ were then obtained by the direct beam method, followed by azimuthal averaging. Rheological measurements were performed on a Rheometrics RFS II rheometer with a cup-and-bob geometry (34 mm cup and 32 mm bob). The temperature was controlled using a fluid circulating system. The applied frequency was varied between 10^{-2} and 10^2 rad s^{-1} , and care was taken to ensure that the strain was small enough to be in the linear response regime.

The elastic modulus, G' , and the loss modulus, G'' , are plotted as functions of frequency for the 1% CTAT solution, the 0.25% HMP solution, and the WLM/HMP mixture in Figure 1. The three solutions are remarkably different. For the WLMs alone, the viscoelastic response is that of a high molecular weight, flexible polymer on the dilute/semidilute boundary; it is not entangled. These results are fully consistent with those reported by other groups: the viscosity of CTAT/water solutions undergoes a very rapid increase at concentrations above 1%.^{7,9,12} At this concentration, however, there is no suggestion of a plateau in G' that would be the signature of entanglement. The 0.25% HMP solution has no measurable G' and exhibits a viscosity close to that of the solvent. In contrast, the ternary mixture exhibits $G' > G''$ across the accessible frequency range, indicative of gel-like behavior, and indeed the sample does not flow when in an inverted vial.¹³ As shown in our previous report, this viscoelastic response can be reasonably well described by the superposition of a single Maxwell element time (in this case with $\tau \approx 90 \text{ s}$ and a network mesh size $\xi \approx 700 \text{ \AA}$) and the Rouse-like modes of the WLMs.⁵ We further proposed that the value of τ was set by the average “pullout” time of a sticker from a WLM.¹⁴

A cartoon depicting the formation of a transient gel is given in Figure 2. Here the WLMs are represented as thick green filaments, the PEO blocks as thin blue coils, and the hydrophobic domains as red circles. In dilute solution by themselves, the HMPs are expected to form flowerlike micelles, in which the PEO corona blocks form loops originating and terminating in a single micellar core.^{14,15} However, there is always a finite possibility of bridging, whereby a single PEO block extends from one micellar core to another, or of dangling ends, in which the hydrophobe is exposed to solvent.^{16,17} As suggested in Figure

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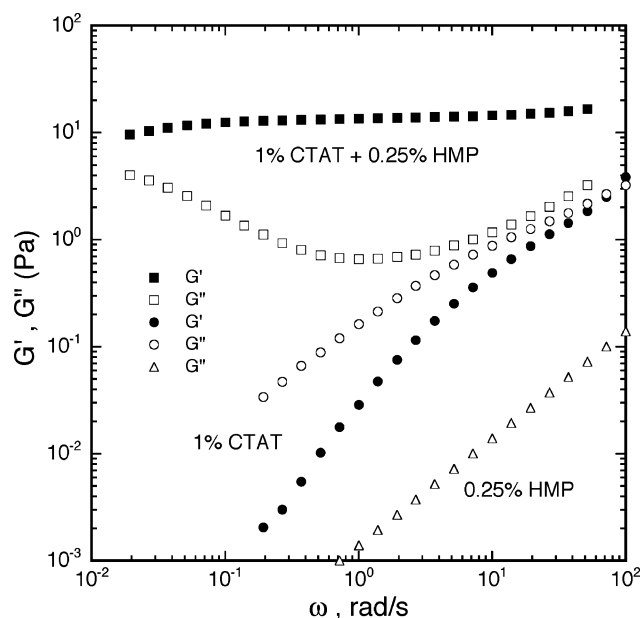


Figure 1. Dynamic shear moduli for a 1% CTAT solution, an 0.25% solution of the 3-arm star PEO with C_{22} stickers, and a mixture containing both 1% CTAT and 0.25% of the 3-arm star PEO with C_{22} stickers.

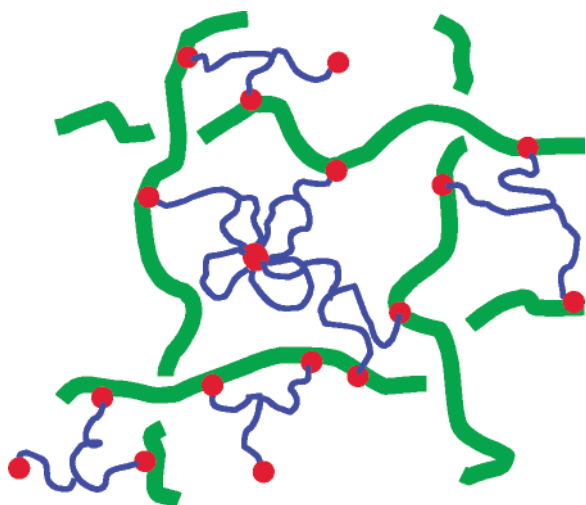


Figure 2. A cartoon suggesting how wormlike micelles (green) can be cross-linked by intercalation of stickers (red) attached to PEO chains (blue). One flowerlike micelle is also shown.

2, when the WLMs and HMPs are combined, a substantial fraction of stickers insert into the WLMs while some may remain in the cores of HMP micelles. We found that approximately one sticker/ ξ^3 corresponded to the “gel point”, i.e., the HMP concentration at which a well-defined plateau in G' became evident. This result hints that the fraction of stickers intercalated in WLMs is relatively high.

Despite the appealing simplicity of the picture depicted in Figure 2, it is by no means the only possible explanation to consider. In fact, at least four distinct possibilities might be envisioned. These include:

A. HMPs cross-link the WLMs. As described above, the stickers intercalate into the WLMs, forming a network that can relax at long times due to sticker pullout. A similar mechanism has recently been proposed to describe the viscoelastic response on combining WLM and telechelic HMP; in the work of Ligoure and co-workers the WLM concentration was nearly an order of

magnitude larger than here, and thus the WLM solution was entangled prior to addition of HMP.²

B. The surfactants cross-link the HMPs. In this scenario, the WLMs break down and re-form as spherical (or much shorter cylindrical) micelles, in order to shield the stickers completely from solvent. The PEO chains thus act as bridges between surfactant micelles.

C. The WLMs thread through the loops of the flowerlike HMP micelles, forming a so-called “slide-ring” gel.¹⁸

D. Phase separation. The intercalation of stickers into the WLMs leads to a “bundling” process, in which the WLMs cluster as fibers or filaments, which gel due to increased stiffness. This is reminiscent of the mechanism of gelation proposed for other associating polymers, such as methylcellulose.¹⁹ It is known that HMPs similar in design to those studied here will phase separate in water, albeit at concentrations higher than those we employ.²⁰ Also, in the system recently described by Ramos and Ligoure phase separation was found, but at significantly higher concentrations of added HMP.² Moreover, the low concentration of HMP employed here may not provide enough attractive interaction to compensate the repulsive electrostatic (Coulombic) interactions between the micelles.²¹

The SANS results we now describe serve to eliminate mechanism B, and strongly disfavor mechanism D. Mechanism C is neither favored nor disfavored by the SANS data, but on purely entropic grounds it seems highly unlikely that the WLMs (with a diameter of 42 Å, see below) would often find their way into the PEO corona loops (with estimated size ≈ 150 Å). In one study surfactant vesicles were shown to form a gel with hydrophobically modified chitosan via a similar combination of rheology and SANS to that employed here;⁶ these results also weigh against mechanism C.

Three SANS curves are shown in double-logarithmic format in Figure 3a: the 0.25% HMP in D_2O , 1% CTAT in D_2O , and the mixture. The HMP scattering is rather weak, as expected for such a low concentration, but the results are broadly consistent with the flowerlike micelle hypothesis. In particular, the lack of any kind of power law behavior argues against any well-defined fractal structure, and the absence of a low q plateau clearly reveals the presence of aggregates with radius much larger than 250 Å ($\approx 1/q_{\min}$, where q_{\min} is the low q limit of the experiment). Well-defined spherical micelles from these polymers would not be as large as 250 Å in radius, and so some association of micelles via bridging is indicated. The scattering curve from the CTAT solution is much richer. Very similar curves have been reported previously,^{8,10} so the interpretation is well established. In particular, the distinct peak in $I(q)$ is due to the polyelectrolyte effect.²² The WLMs are charged objects and thus show the low q depression in scattering due to the high osmotic penalty for large spatial scale fluctuations in charge density. At scattering angles beyond the peak, however, the scattering is described almost quantitatively by a cylindrical form factor (smooth curve, eq 1^{2,23}), with radius $R = 21$ Å (fixed by the distinct minimum in $I(q)$ that occurs near 0.2 Å^{-1}) and contour length $L = 1000$ Å. The fit is not sensitive to the value of L because the low q plateau is not achieved.

$$P(q) = \left(\frac{\phi}{V_{\text{cyl}}} \right) (\rho_{\text{cyl}} - \rho_{\text{sol}})^2 V_{\text{cyl}}^2 \times \int_0^{\pi/2} \frac{\sin^2 \left(\frac{qL \cos \alpha}{2} \right)}{\left(\frac{qL \cos \alpha}{2} \right)^2} \left(\frac{2J_1(qr \sin \alpha)}{qr \sin \alpha} \right)^2 (\sin \alpha) d\alpha \quad (1)$$

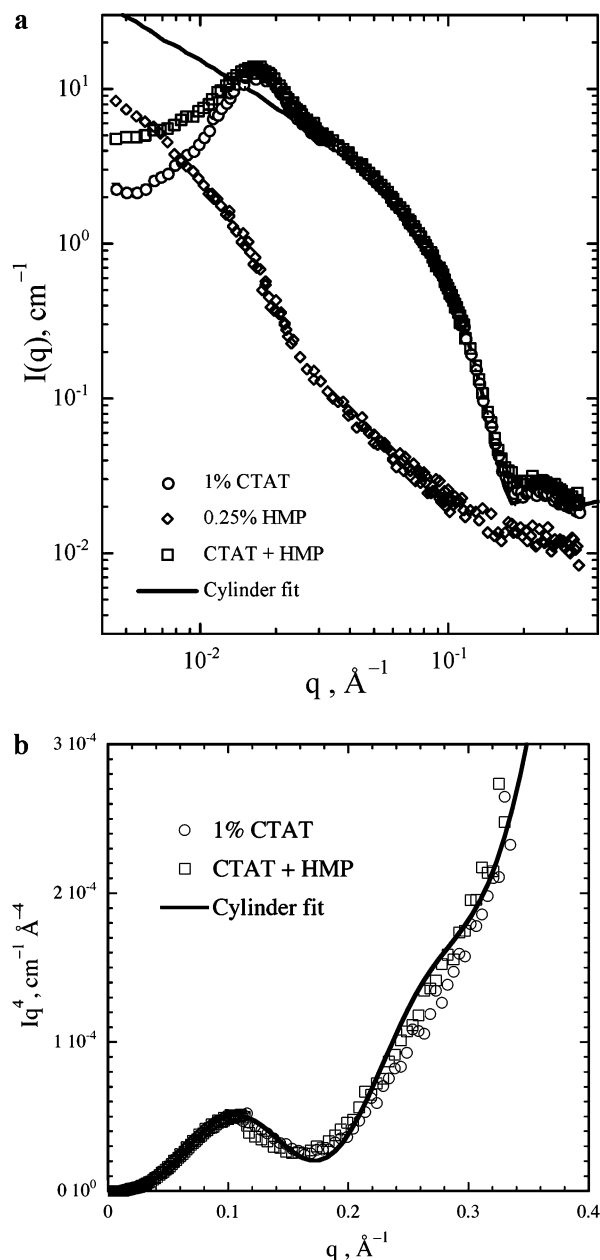


Figure 3. SANS data for D₂O solutions of CTAT, HMP, and their mixture; the smooth curve is a fit to the form factor of a cylinder with radius 21 Å, as described in the text. (a) I vs q in a double-logarithmic format; (b) Iq^4 vs q .

Here $J_1(x)$ is the first-order Bessel function and α is the angle between the cylinder axis and the scattering vector (q). Φ is the volume fraction of cylinders of length L and radius r . The scattering length density (ρ) of CTAT is $2.5 \times 10^9 \text{ cm}^{-2}$, assuming a bulk density of 1.0 g cm^{-3} and based on the surfactant structure ($\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{SO}_3\text{C}_6\text{H}_4\text{CH}_3$).

The principal result in this work is the SANS curve for the WLM/HMP mixture in Figure 3a,b (open squares). The scattering is indistinguishable from that for the CTAT alone, within the experimental uncertainty, from the q position of the peak to the highest value of q measured. The point is reinforced by replotting the data in the Porod format (Iq^4 vs q), emphasizing the higher q portion, as shown in Figure 3b. This is clear evidence that the structure of the WLMs over this range of length scale is unchanged by the addition of the HMP, eliminating mechanism B from further consideration. In a related

SANS study on a different WLM plus amphiphilic copolymer system, a similar conclusion was reached, namely that the local cylindrical structure of the WLMs is unaffected by the added copolymer.²⁴ At low q in Figure 3a there is some modest enhancement of scattering relative to CTAT alone, but most importantly the scattering is lower in intensity than that of HMP alone and shows no sign of a strong upturn. Therefore, there is no indication of any kind of phase separation or clustering as posited in mechanism D. Furthermore, these samples are optically clear and visually indistinguishable from the 1% CTAT solution, which also argues against phase separation on larger length scales than accessed by SANS. The fact that the low q intensity is higher than for CTAT alone is consistent with a general observation in polymeric gels, that the cross-linking locks in some extra spatial heterogeneity.²⁵ The SANS measurements described in this note provide strong evidence in favor of the proposed cross-linking mechanism that leads to massive viscoelastic synergy in mixtures of wormlike micelles and hydrophobically modified polymers; the alkyl tails of the HMP insert into the WLM, acting as long-lived cross-links.

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