SUPPORTING INFORMATION

for

Growth of Wormlike Surfactant Micelles Induced by Embedded Polymer: Role of Polymer Chain Length

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NMR-Spectroscopy. Figure S1 shows ^{1}H NMR spectrum of solution of P4VP-228 in deuterated DMSO. The peak assignments are given on the spectrum. It is seen that the both peaks of the pyridine ring are much less broadened than those of P4VP embedded into potassium oleate micelles (Figure 2). At the same time, the peaks are still significantly broader than in case of 4-methylpyridine in D_2O

(Figure 2), which indicates to the restricted mobility of the monomer units of the polymer chain in the coil in comparison with low-molecular weight model of the monomer unit.

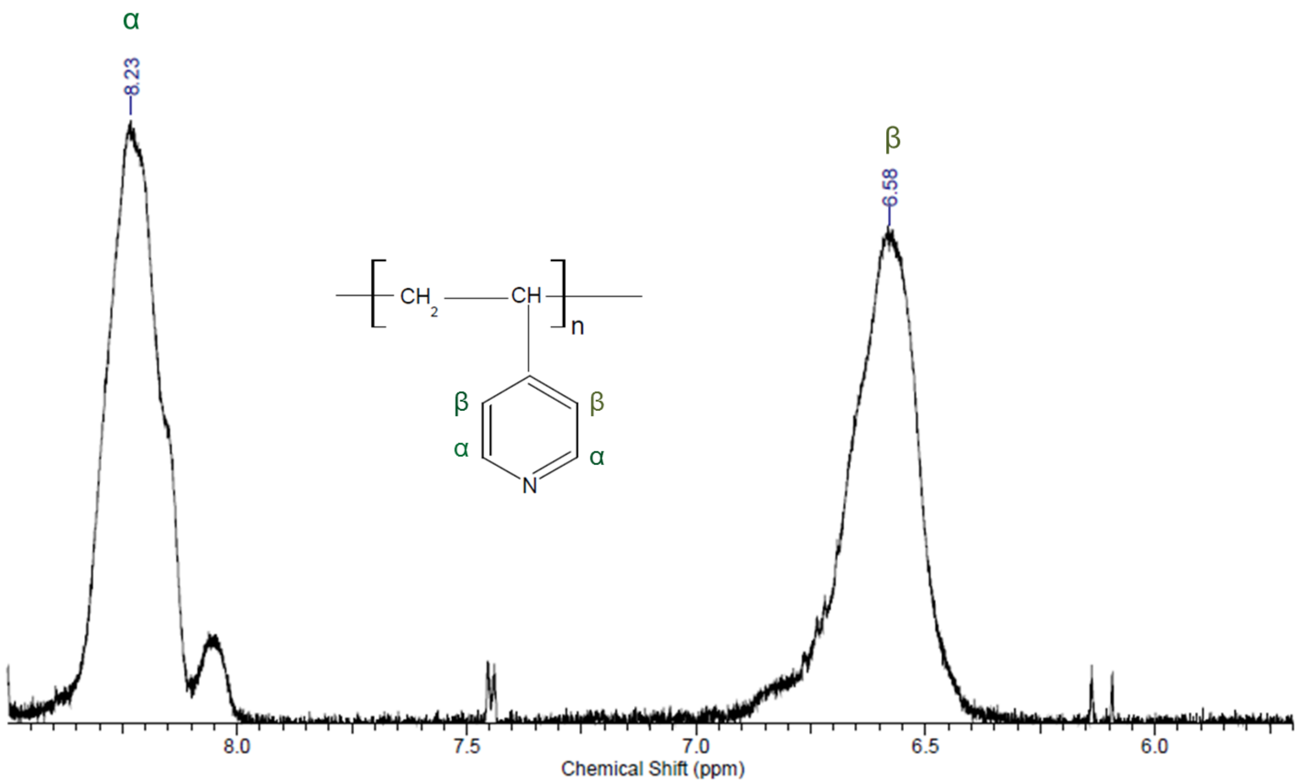


Figure S1. ^{1}H NMR spectrum in the range 5.7-8.5 ppm for 0.019 monomol/L P4VP-228 solution in deuterated DMSO at 22^{0}C.

SANS Study of Surfactant-Polymer Mixtures. SANS curves for the free potassium oleate micelles and surfactant/P4VP-228 complexes saturated with polymer obtained upon matching the scattering from the polymer are presented in Figure S2. They demonstrate that in the complexes, the molecules of the surfactant keep their cylindrical packing, since the scattering intensity in the low-Q range varies as $I \sim Q^{-1}$.[1]

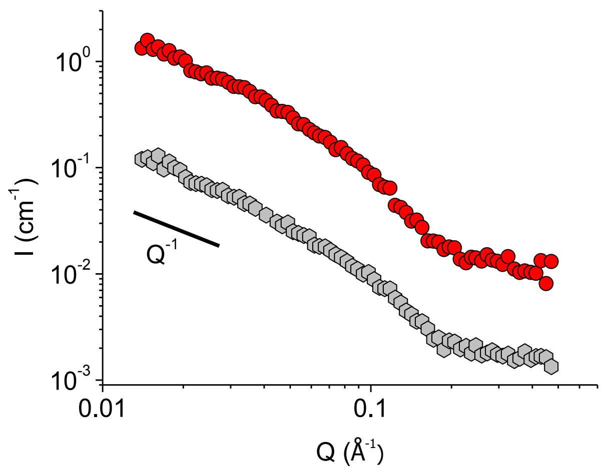
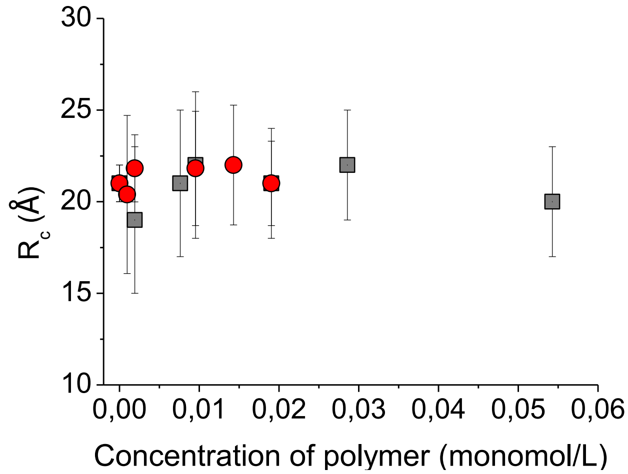


Figure S2. SANS curves of neat surfactant micelles in 0.047 M potassium oleate without polymer (circles) and of saturated surfactant-polymer complexes in 0.047 M potassium oleate with 0.019 monomol/L P4VP-228 (hexagons) obtained by matching the scattering from the polymer (solvent: 0.08 M KCl in 37/63 (v/v) D_2O/H_2O, pH 11). The data for solution without polymer are absolute values; the curve with polymer is shifted by factor of 10 for clarity. The solid line shows the slope of a $I \sim Q^{-1}$ dependence.

Since the form of micelles in surfactant/polymer complexes stays cylindrical the curves of the dependences of ln(IQ) on Q^2 obtained from the SANS data represent straight lines.[2] From the slope and the intercept of these dependences, the values of radius R_c and mass of the surfactant per unit length M_L of the micelles were obtained. They are plotted as a function of the concentration of added polymers on Figure S3. It is seen that the R_c value does not change with the increase of the concentration of solubilized P4VP of both molecular weights being equal to 2 nm. As to M_L value, it slightly decreases with increasing content of polymer.

a)



b)

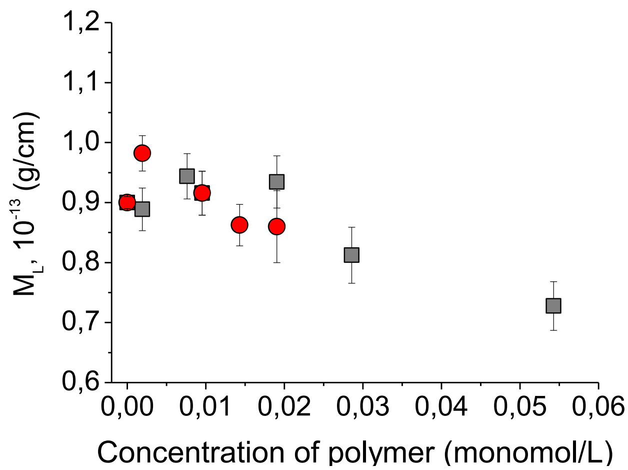


Figure S3. Radius R_c (a) and mass per unit of length M_L (b) of wormlike micelles as a function of the concentration of added polymer P4VP-77 (red circles) or P4VP-228 (gray squares) in 0.047 M potassium oleate solution obtained by matching the scattering from the polymer (solvent: 0.8 M KCl in 37/63 (v/v) D_2O/H_2O, pH 11).

The SANS curves of the polymer in hybrid micelles saturated by P4VP-77 and P4VP-228 obtained under matching the scattering from the surfactant are presented in Figure S4. They show two distinct slopes, which intersect at Q^* of 0.06 Å^{-1}. From the Q^* value the persistence length l_p of polymer was estimated as $l_p = \frac{6}{\pi Q^*}$.[3] It was shown that the l_p values of both polymers P4VP-77 and P4VP-228 in the complexes are the same and equal to 3.2 nm.

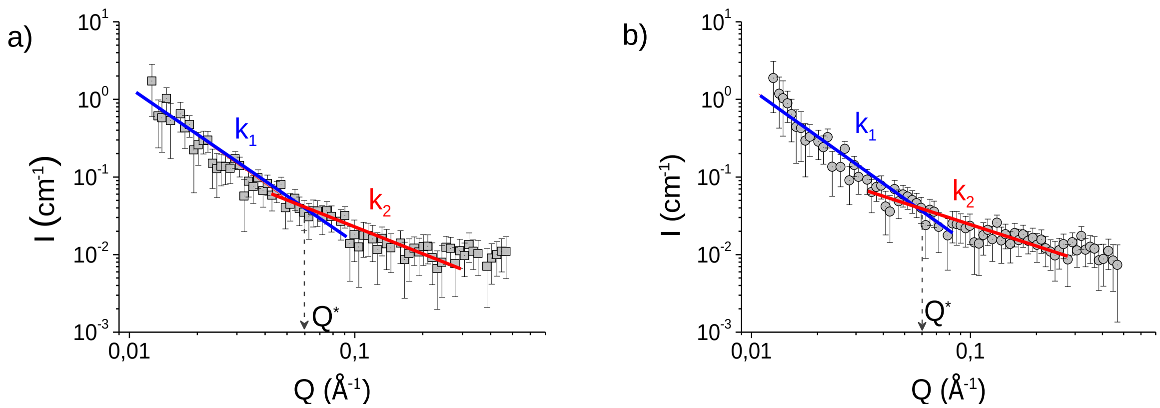


Figure S4. SANS curves in double logarithmic scale for 0.047 M solutions of potassium oleate saturated (a) with P4VP-77 (concentration of polymer - 0.054 monomol/L) or (b) P4VP-228 (concentration of polymer - 0.019 monomol/L) obtained under matching the scattering from the surfactant (solvent: 0.8 M KCl in D_2O/H_2O 10/90 v/v, pH 11). Straight solid lines with slopes $-k_1$ and $-k_2$ show power-laws in low-Q and high-Q regions, dashed lines - their intersection Q^*.

Flow Curves of Surfactant-Polymer Mixtures. Flow curves of aqueous solutions of potassium oleate at different concentrations of added polymer P4VP-228 are presented in Figure S5. It is seen that the zero-shear viscosity η_0 decreases upon addition of P4VP-228.

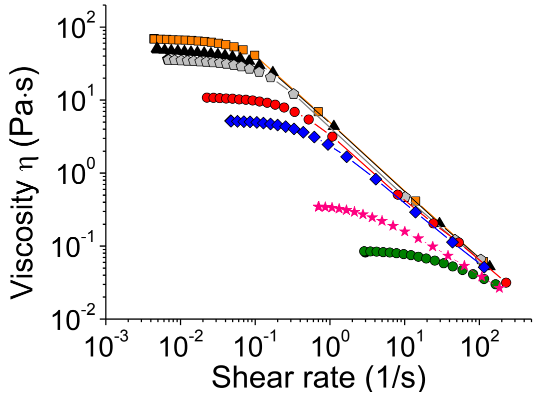


Figure S5. Flow curves of 0.047 M aqueous solutions of potassium oleate at different concentrations of added polymer P4VP-228: 0 (orange squares), 0.0008 monomol/L (black triangles), 0.0023 monomol/L (gray pentagons), 0.006 monomol/L (red circles), 0.009 monomol/L (blue diamonds). Solvent: 0.8 M KCl in water, pH 11.

Determination of the Scission Energy from Rheological Data. The scission energy E_{sc}, which controls the shortening of the length of micelles $\bar{L}$ at heating, was estimated from the dependence of $\frac{\bar{L}}{l_e}$ on the inverse temperature $1/T$. The $\frac{\bar{L}}{l_e}$ value is related to the ratio of two experimentally measurable quantities - the plateau modulus G_0 and the storage modulus at its minimum value at high frequencies G''_{min} through: [4]

$$\frac{\bar{L}}{l_e} \approx \frac{G_0}{G''_{\min}},$$

where l_e is the entanglement length. Since l_e does not vary with T, [5] the temperature dependence of the ratio $\frac{G_0}{G''_{\min}}$ will be the same as that of $\frac{\bar{L}}{l_e}$. The Arrhenius plots of $\frac{\bar{L}}{l_e}$ (i.e. $\frac{G_0}{G''_{\min}}$) versus $1/T$ give straight lines with the slope equal to $E_{sc}/2k_B$, where k_B is the Boltzmann constant. Some of these plots are presented in Figure S6, the determined scission energies are summarized in Table S1.

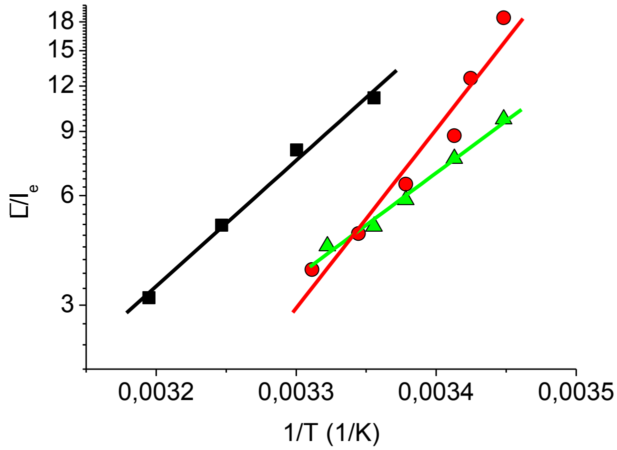


Figure S6. Arrhenius plots of $\frac{\bar{L}}{l_e}$ versus *1/T* for 0.047 M solutions of potassium oleate containing different amounts of added P4VP-228: no polymer (squares), 0.011 monomol/L (circles), 0.0023 monomol/L (triangles). Solvent: 0.8 M KCl in water, pH 11.

Table S1. Scission Energies of WLMs of Potassium Oleate with and without Embedded Polymer P4VP-228 in 0.047 M Surfactant Solutions in the presence of 0.8 M KCl

P4VP-228 concentration, $\cdot 10^{-3}$ monomol/L	0	1.1	2.3
Scission energy, kJ/mol	140±12	190±12	109±8

Molecular Dynamics Simulations of Polymer-Loaded WLMs under the Shear Flow. To study the effect of shear deformation on WLMs with embedded polymer we performed non-equilibrium molecular dynamics simulations. Figure S7 shows the time evolution of WLM elongated by flow with embedded longer polymer chain (N=60). As is seen some sections of WLM become more narrow and break resulting in 3 sections of WLM at the steady state condition. The WLM break occurs near the "weak spots", i.e. boundaries between polymer-containing and polymer-free sections.

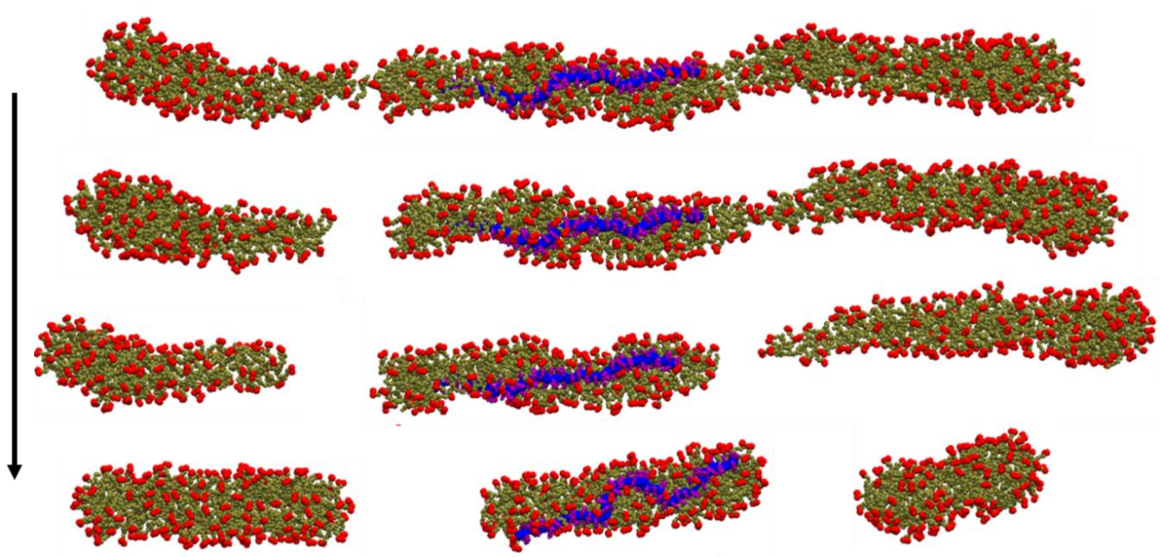


Figure S7. MD simulation snapshots of the time evolution (from top to bottom) of a wormlike micelle with an embedded longer P4VP polymer (60 repeat units) under shear deformation (shear rate of 1.67 ns^{-1}).

Figure S8 shows time evolution of WLM containing two shorter P4VP chains (N=30). As is seen, the WLM splits into a larger number of short sections. Initially the WLM sections containing two short P4VP chains remain intact, but with time they also become separated into two parts each containing one short P4VP chain. The WLMs containing short and long P4VP chains consist of exactly the same number of surfactant molecules.

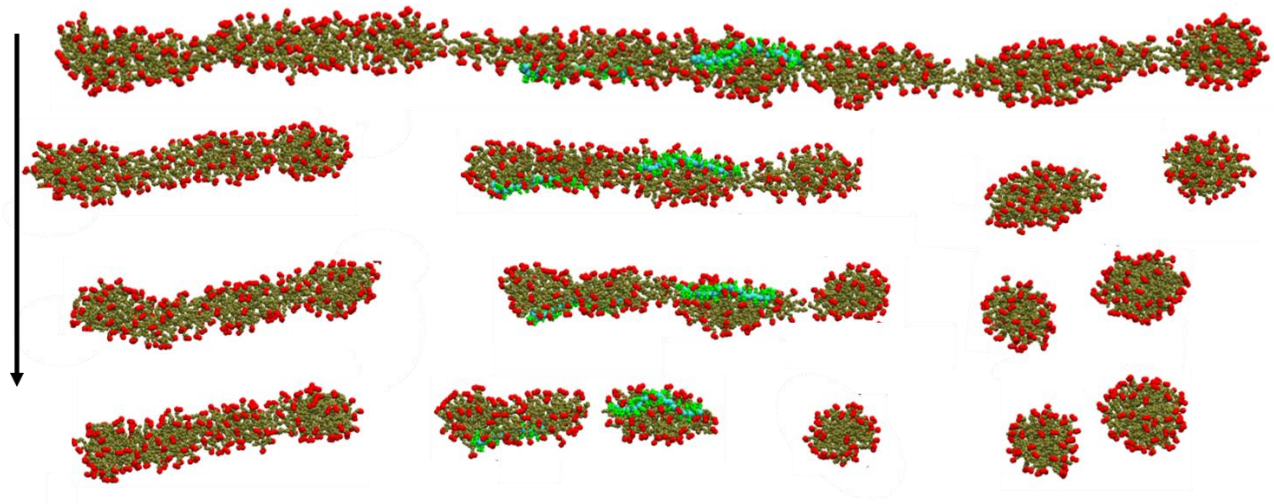


Figure S8. MD simulation snapshots of the time evolution (from top to bottom) of a wormlike micelle with two embedded short P4VP polymers (30 repeat unit) under shear deformation (shear rate of 1.67 ns^{-1}).

Estimation of the Amount of Macromolecules Embedded in One Micelle. The aggregation number of WLMs of maximum length N_{surf} can be estimated by using the following formula:

$$N_{surf} = \frac{N_a}{M_{surf}} M_L \bar{L},$$

where $\bar{L}$ is maximum average contour length of WLMs, M_L is mass of the surfactant per unit length, M_{surf} is molecular weight of potassium oleate, N_a is Avogadro number.

As value of M_L changed only slightly in the range of concentrations of embedded polymer from 0 to 0.019 monomol/L (Figure S3), in the calculation the average value of M_L equal to $0.9 \cdot 10^{-13}$ g/cm was used. The values of maximum average contour length of WLMs loaded with P4VP-77 and P4VP-228 were taken from Figure 9.

Finally, the amount of macromolecules of P4VP-77 and P4VP-228 N_{P4VP}, embedded in one micelle was calculated from the following formula:

$$N_{P4VP} = \frac{c_{surf} N_{surf}}{c_{P4VP} P},$$

where C_{surf} is the concentration of potassium oleate, equal 0.047 M, C_{P4VP} is the concentration of monomer units of P4VP-77 and P4VP-228 in hybrid micelles with maximum $\bar{L}$, P is the degree of polymerization of P4VP-77 and P4VP-228.

The calculations show that maximum length of micelles is reached, when the amount of P4VP-77 and P4VP-228 macromolecules embedded in one micelle is equal to 0.56 and 0.58, respectively, which corresponds roughly to 1 macromolecule per 2 micelles.

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