

Supporting Information

Time-dependent heterogeneity in viscoelastic properties of worm-like micelle solutions

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1. Materials

Cetyl trimethyl ammonium bromide (CTAB) was purchased from Kishida Chemical Co., Ltd. (Osaka, Japan) and purified by recrystallization from a 1:1 mixture of methanol and acetone (v:v). Sodium salicylate (NaSal) and polyethylene glycol (PEG) with a weight-average molecular weight of 300 – 500k were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and used without further purification. Water, after deionization with a Milli-Q Lab (Millipore, Billerica, MA, USA) system, was used to prepare the aqueous solution of worm-like micelles. The specific resistance of the purified water was greater than 18 M Ω cm. For the microrheological studies, polystyrene microspheres containing a fluorescent dye, Fluoresbrite Polychromatic Red Microsphere, commercially available as a 2.5 wt% aqueous suspension, was purchased from Polysciences, Inc. (Warrington, PA, USA). The radius of the microspheres was 548 ± 14 nm as provided by the commercial source.

2. Microrheology

2-1. Setup and calibration of the optical tweezers. The setup of our optical tweezers was based on an inverted microscope, a Nikon ECLIPSE *Ti*, with an NA 1.30 oil-immersion objective lens. The light with a wavelength of 1064 nm was generated by a Nd:YAG laser (Furukawa Electric Co., Ltd., Tokyo, Japan), which was used to trap and manipulate the probe particles. The position of the laser beam was sinusoidally oscillated at a frequency in the range of 0.05 – 2.0 Hz using a piezo-driven mirror, which was controlled by a function generator (33210A, Agilent Technologies Co., Ltd., Santa Clara, CA, USA). A halogen lamp was used to illuminate the sample, and a charge-coupled device (CCD) camera (DS-Qi1Mc, Nikon Instech Co., Ltd., Tokyo, Japan) to acquire images of particles trapped in the sample, at a frame rate of 31 Hz. Commercial imaging software, NIS-Elements AR-3.2 (Nikon Instech Co., Ltd.), was used to track the particle during oscillation. The displacement of the particle was detected as a function of time using a quadrant photodiode (OP711, SENTEC Co., Ltd., Osaka, Japan). The signals from the function generator and the photodiode were introduced into a lock-in amplifier (7260, EG&G Co., Ltd., Oak Ridge, TN, USA) to obtain the phase lag between them.

Since the laser intensity had a Gaussian profile, Hooke's law with an apparent spring constant, k_{OT} , was applied to represent the force of the optical trap. The k_{OT} value was determined by a hydrodynamic method^{1,2} based on Stokes and Hooke's laws:

$$k_{OT} = \frac{6\pi\eta r v}{d} \quad (1)$$

where η , r , v , and d are the viscosity of the medium, particle radius, velocity of the solution flow, and distance between the particle and the center of the laser beam, respectively. To evaluate the spring constant for the optical trap, a typical Newtonian fluid (water) was used. A particle was optically trapped using a given laser power, and then water flow was produced by moving the substage.² When the water flow, alternating in direction, was applied, the particle position shifted, showing an approximately square wave response. The step height in the response of the particle position corresponded to twice the distance of the particle from the center of the laser beam, $2d$. The distance d , together with the known parameters, η , r , and v gave k_{OT} value at that laser power. The k_{OT} value was linearly proportional to the laser power with a linear coefficient of $0.115 \text{ pN} (\text{nm}\cdot\text{W})^{-1}$. In this study, all experiments were performed at a laser power of 1.0 W , meaning k_{OT} of $0.115 \text{ pN}\cdot\text{nm}^{-1}$. Assuming that the spring constant obtained was retained in the transparent worm-like micelle and PEG solutions, the viscoelastic moduli could be determined.³

2-2. Determination of storage and loss moduli. The storage (G') and loss (G'') moduli in the viscoelastic medium are given by the following equations:^{4,5}

$$G' = \frac{k_{OT}}{6\pi r} \left(\frac{A_L}{A_P} \cos\delta - 1 \right) \quad (4)$$

$$G'' = \frac{k_{OT}}{6\pi r} \left(\frac{A_L}{A_P} \sin\delta \right) \quad (5)$$

where r is the radius of a probe particle, k_{OT} is the apparent spring constant of optical trapping, A_L and A_P are the amplitude of the sinusoidal movements of the laser and particle, and δ is the phase lag between the two sinusoidal signals. The values of A_P and δ were experimentally obtained. The particle displacement was detected using the CCD camera. To determine the A_P value, the particle displacement creating three sinusoidal pattern was recorded (see Figure 2b in the main text) and then a curve-fitting analysis for it was made.

This procedure was performed three times and the average value of A_p obtained was used for the calculation of the G' and G'' values. The δ value was detected with a lock-in amplifier, where two signals from the function generator and the photodiode were introduced. The δ value was monitored for 60 sec and was obtained by averaging over those values. To examine the spatial heterogeneity in the viscoelastic properties, G' and G'' were measured at 10 different locations in the same solution.

2-3. Measurements. The latex particle solution with a volume of 0.5 μL was mixed into 1 mL of aqueous 200 mM-CTAB solution. Then, 1 mL of NaSal aqueous solution was stirred in the CTAB solution containing the particles. The concentration of the NaSal solution was varied at 50, 100, 150, and 200 mM. Each solution was aged for more than 3 hours at room temperature. The resulting solution was poured into a glass bottom dish (Matsunami Glass Ind. Ltd., Osaka, Japan). The sample was aged for 30 minutes at room temperature protected with a cover glass prior to the measurements using optical tweezers.

A particle in the worm-like micelle solution was optically trapped and then was sinusoidally oscillated in Y position with an amplitude in the range of 70 – 2500 nm at 1.0 Hz. Figure S1 shows the laser-position amplitude dependence of the amplitude difference between the laser and particle movement. Each value was normalized against the laser-position amplitude. As the laser amplitude approached 400 nm, the difference started to decrease. This implies that the aggregated state of worm-like micelles was, in part, broken by the particle movement (non-linear effects associated with the failure of linear response), and that the extent of the destruction became more significant with increasing laser amplitude. Thus, an amplitude of 320 nm, where the structural destruction was trivial, was adopted for further study. In fact, the mean values of G' and G'' obtained at all frequencies were in excellent accord with the bulk values by a conventional rheometer.

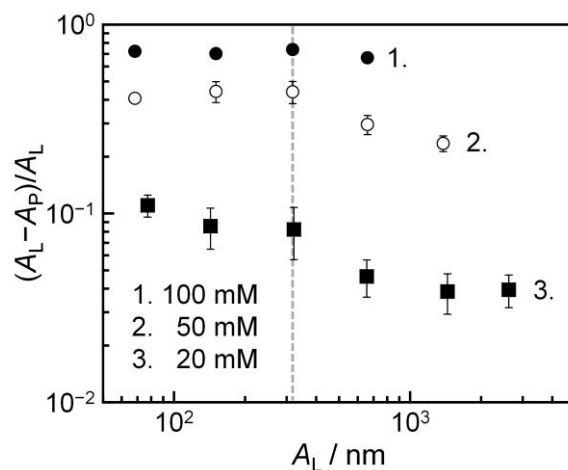


Figure S1 Relationship between the laser amplitude and the amplitude difference between laser and particle movement, $(A_L - A_P)/A_L$. A_L and A_P are the amplitudes of the sinusoidal movements of the laser and the particle, respectively. The experimental conditions were as follows: frequency = 1.0 Hz and temperature = 298 K.

Figure S2 shows the particle position amplitudes and phase lags measured for the worm-like micelle solution. Both values varied widely, depending on the location of the particles. The coefficient of variation (CV) was 12 % for A_P and 9.9 % for δ , respectively. These CV values here observed led to the fluctuations in the G' and G'' values of the worm-like micelle solution.

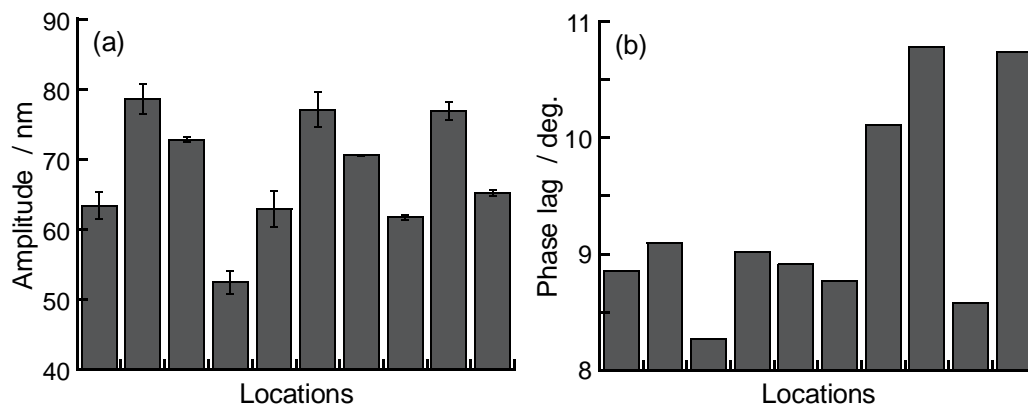


Figure S2 (a) The amplitudes and (b) phase lags acquired at 10 different locations in the aqueous solution of worm-like micelles. The experimental conditions were as follows: frequency = 1.0 Hz, laser amplitude = 320 nm, temperature = 298 K and [CTAB] = [NaSal] = 100 mM.

The effective values of CV, here denoted as CV_{eff} , were determined by deconvolution with the contribution of the experimental errors arising from the detection of A_P and δ . The contribution of the fluctuations in the A_P and δ values to those of G' and G'' was written from Eqs. (4) and (5) on the basis of the error propagation rules.⁶

$$\sigma_{G'} = \frac{k_{OT}A_L}{6\pi rA_P} \sqrt{\left(\frac{\cos\delta}{A_P}\sigma_{A_P}\right)^2 + \left(\sin\delta\sigma_\delta\right)^2} \quad (6)$$

$$\sigma_{G''} = \frac{k_{OT}A_L}{6\pi rA_P} \sqrt{\left(\frac{\sin\delta}{A_P}\sigma_{A_P}\right)^2 + \left(\cos\delta\sigma_\delta\right)^2} \quad (7)$$

where $\sigma_{G'}$, $\sigma_{G''}$, σ_{A_P} and σ_δ were standard deviations of G' , G'' , A_P and δ , respectively. Assuming that the σ_{A_P} and σ_δ values obtained for a homogeneous liquid, namely pure water, corresponded to the experimental errors, the $\sigma_{G'}$ and $\sigma_{G''}$ values arising from the errors (σ_{err}) can be determined. When the probability distributions in the G' and G'' values are expressed using a Gaussian function, the effective values of σ , (σ_{eff}) can be calculated using:

$$\sigma_{\text{eff}} = \sqrt{\sigma^2 - \sigma_{\text{err}}^2} \quad (8)$$

Thus, normalizing σ_{eff} by the mean value gave CV_{eff} .

3. Bulk rheology

Bulk rheological measurements were performed using a conventional rheometer, Physica MCR-301 (Anton Paar, GmbH, Graz, Austria). Each of the samples was held between the sample stage and a cone-type plate with a diameter of 50 mm and a tilt angle of the cone-type plate was 1°. A piece of paper wetted with water was laid around the sample to prevent water evaporation from the sample during the measurement.

An aqueous solution of worm-like micelles was mounted on the sample stage, which was controlled at 298 K. A strain sweep was performed to investigate the linear response in the viscoelastic properties of the worm-like micelle solution. As shown in Figure S3, the G' and G'' values were almost constant at strain amplitudes below *ca.* 40 %. Thus, a strain amplitude of 10 % was applied for further study.

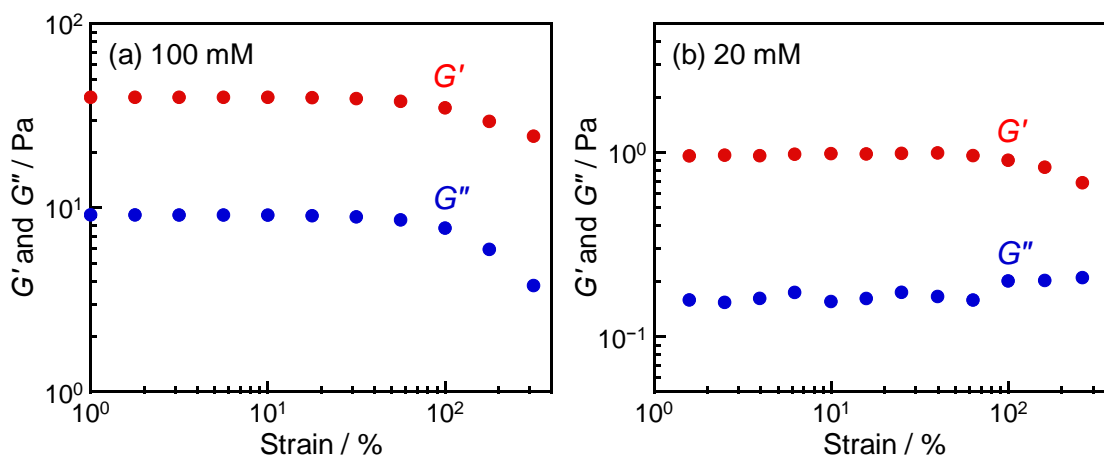


Figure S3 Strain dependence of viscoelastic moduli for a worm-like micelle solution with a concentration of (a) 100 mM and (b) 20 mM. The experimental conditions were as follows: frequency = 1.0 Hz and temperature = 298 K.

To determine the aging time of the worm-like micelle solution, changes in rheological properties were monitored after adding one equivalent of NaSal into the CTAB solution. Figure S4 shows the time dependence of the viscoelastic moduli for the CTAB solution with a concentration of 20 mM and 100 mM. For the 20 mM, G' and G'' increased with increasing aging time, and then became constant. This observation is assignable to a structural change from spherical to worm-like micelles.⁷ When the concentration was increased to 100 mM, the same concentration used for the optical tweezers measurements, the increase in G' and G'' was not observed. This is probably because the structural change for the 100 mM solution was much faster than for the 20 mM. Hence, to avoid such structural changes during the optical tweezers measurements, the solution of CTAB and NaSal were aged for 3 hours at room temperature prior to the measurements.

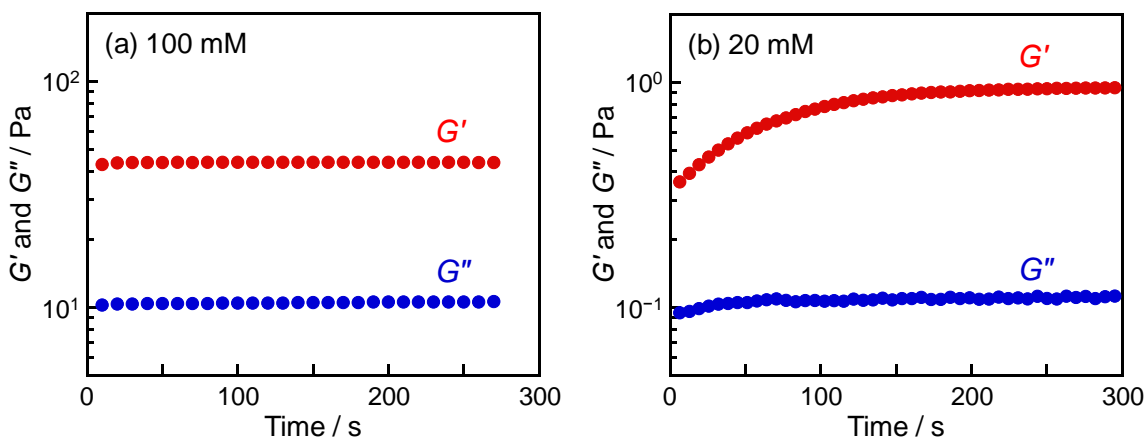


Figure S4 Time dependence of the viscoelastic moduli for the CTAB solution with a concentration of (a) 100 mM and (b) 20 mM immediately after adding one equivalent of NaSal. The experimental conditions were as follows: frequency = 1.0 Hz, strain amplitude = 10 % and temperature = 298 K.

Figure S5(a) shows the frequency dependence of the viscoelastic moduli for the worm-like micelle solution. G' and G'' were found to be proportional to ω^2 and ω at lower frequencies. At higher frequencies, on the other hand, G' reached a plateau and G'' was proportional to ω^{-1} . Also, a Cole-Cole plot with semicircular shape was observed, as shown in Figure S5(b). These are clear signatures that a Maxwell model with a single relaxation process can be applied to analyze the results. According to the model, G' and G'' are given by:

$$G' = G_0 \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (9)$$

$$G'' = G_0 \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (10)$$

where G_0 and τ are the plateau modulus and relaxation time, respectively. The values of G_0 and τ were determined to be 42.9 Pa and 0.72 s, respectively, on the basis of curve-fitting analyses for the data points in Figure 5(a), with Eqs. (9) and (10). As seen in Table S1, the average of the values obtained via optical tweezers is in good agreement with those here obtained by bulk rheological study, as well as those reported by other researchers.⁸⁻¹⁰ This indicates that the bulk viscoelastic properties of the worm-like micelle solution can be understood by averaging local properties.

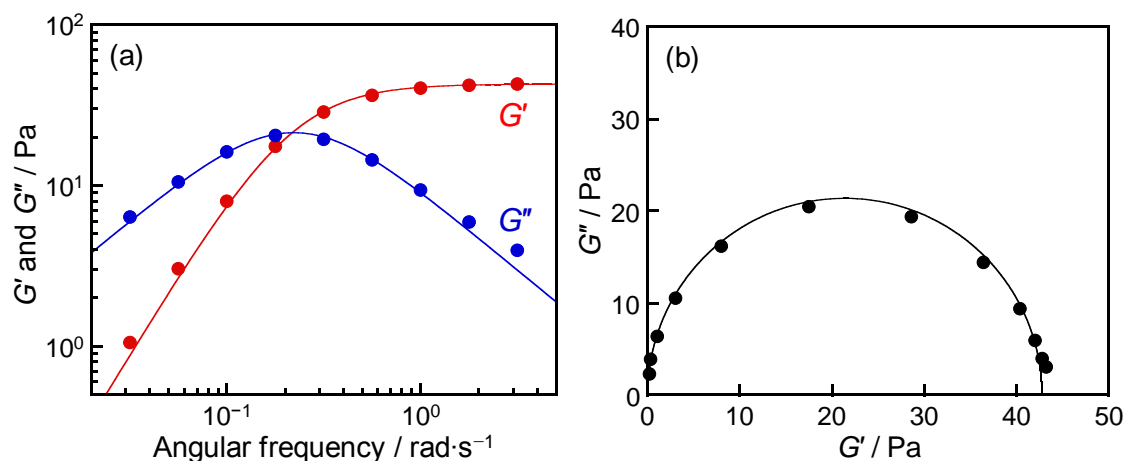


Figure S5 (a) Frequency dependence of viscoelastic moduli for the worm-like micelle solution and (b) a Cole-Cole plot of the G' and G'' data. Solid lines denote the best-fit curves obtained using a Maxwell model with a single relaxation. The experimental conditions were as follows: strain amplitude = 10 %, temperature = 298 K and [CTAB] = [NaSal] = 100 mM.

Table S1 Plateau modulus (G_0) and relaxation time (τ) obtained by curve-fitting based on a Maxwell model.

| | G_0 / Pa | τ / s |
|---------------------------|-------------------|-------------------|
| Experimental ^a | 46.2 ± 1.9 | 0.72 ± 0.02 |
| Experimental ^b | 42.9 | 0.72 |
| References ^c | 48 - 56 | 0.75-0.80 |

^a data obtained via optical tweezers, ^b data obtained via rheometer, ^c data taken from refs. 7-9

4. References

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