

Feature Article

MICROSCOPIC HETEROGENEITY IN VISCOELASTIC PROPERTIES OF MOLECULAR ASSEMBLED SYSTEMS*

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Abstract An important step in understanding molecular assembled systems is to examine the structure and physical properties at various length scales and clarify the correlation between them. However, while the structures of these systems have been extensively studied from nanoscopic to macroscopic scales, their viscoelastic properties have been often limited to bulk rheological measurements. By using optical tweezers and particle tracking, we here show the local viscoelastic properties and their spatial distributions for the following systems: worm-like micelle solution, supramolecular hydrogel and lyotropic liquid crystal, which are formed by self-assembly of amphiphilic molecules in water. We found that all systems studied possessed a spatial heterogeneity in their viscoelastic properties and this was originated from the heterogeneous structures. It is interesting to note that there is the heterogeneity with the characteristic length scale of sub-micrometer or micrometer scale, thereby structures, although the systems are formed by molecules with nanometer size. The findings of these studies should lead to a better understanding of the dynamics of such systems.

Keywords: Optical tweezers; Soft materials; Heterogeneity; Hierarchical structure; Rheological properties.

INTRODUCTION

The phenomenon of molecular assembly is a key concept in various fields of science^[1, 2]. Common examples include the formation of micelles, vesicles, bilayers and liquid crystal phases by amphiphilic molecules in a polar medium which is utilized in various scientific, technological and industrial applications^[3–5]. Molecular assembled systems generally possess hierarchical structures with different length scales ranging from nanometer to millimeter. The driving force for the formation of these structures is non-covalent bonds such as hydrogen bonding, hydrophobic effect, van der Waals interactions, π - π interactions and/or electrostatic interactions. These characteristics increase the complexity in the dynamics of molecular assembled systems^[6, 7]. For example, the systems behave like solid and liquid states, depending on the space and time scales of observations^[7]. Thus, to understand the dynamics of molecular assembled systems, it is necessary to examine their structures and physical properties at various length scales, and clarify the correlation. Such approach also should lead to the understanding how the nano- and microscopic structures and viscoelastic properties are related to the macroscopic physical properties.

The aggregated structures of various length scales have been well-studied using established experimental techniques like nuclear magnetic resonance spectroscopy^[8], X-ray scattering measurements^[9, 10] and electron

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microscopy^[11, 12], to name a few. However, this is not the case for the study of the viscoelastic properties of molecular assembled systems, which have been limited to bulk rheological measurements. One of the major reasons for this is the limited number of available techniques for space- and time-resolved rheological measurements. Recently, the measurement of local rheological properties has become possible by the development of various techniques which have come to be collectively referred to as microrheology. In microrheology, probe particles with sub-micrometer or micrometer size were dispersed in a medium to be measured. Information on the local properties can be obtained by detecting their thermal motion (passive) or their responsive movement toward an external force (active), since the movement of the particle reflects the viscoelastic properties of the surrounding medium^[13–15]. Although there are several techniques in microrheology, we focus on the use of an accessorized optical microscope such as optical tweezers and particle tracking. This is because these techniques make it possible to determine the time- and spatial-distributions of local viscoelastic functions in materials by observing individual particles^[16, 17]. In this feature article, we review the local viscoelastic properties of self-assembled systems of amphiphilic molecules in water, in particular a worm-like micelle solution^[18], a supramolecular hydrogel^[19] and a lyotropic liquid crystal^[20]. In these studies, we found that there exists a spatial heterogeneity in their viscoelastic properties and the characteristic length scale of the heterogeneity is on the sub-micrometer or micrometer scale.

EXPERIMENTAL

Optical tweezers have been applied in examining dynamic viscoelastic properties on the micrometer scale in polymer solutions^[21], micelle solutions^[22], gels^[23], *etc.* In this method, a dispersed probe particle in a medium to be measured is trapped by a laser beam and sinusoidally oscillated. The responsive movement of the particle reflects the viscoelastic properties of the surrounding medium^[24]. Such technique is referred to as active microrheology^[13–15]. From the sinusoidal oscillations of the trapped particle, the storage (G') and loss (G'') moduli of the viscoelastic medium can be determined using the following equations^[25, 26]:

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

$$G'' = \frac{k_{OT}}{6\pi r} \left(\frac{A_L}{A_P} \sin \delta \right) \quad (2)$$

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 amplitudes of the sinusoidal movements of the laser and the particle, respectively; and δ is the phase lag between the two sinusoidal signals. For our setup, the value of k_{OT} was estimated to be 0.13 pN nm⁻¹ by a hydrodynamic method^[27] using a Newtonian medium, namely pure water.

Figure 1 shows a schematic illustration of our optical tweezers instrument^[19]. The displacement of a particle was detected as a function of time by a charge-coupled device (CCD) camera and a quadrant photodiode. By curve-fitting the plot of the particle displacement against time, the A_P value was determined. The δ value was detected with a lock-in amplifier, where two signals from the function generator and the photodiode were introduced. G' and G'' were measured at 10 different locations in the same solution to examine the spatial heterogeneity in the viscoelastic properties.

In the case of the particle tracking technique, the thermal fluctuations of the embedded probe particles (without being optically trapped as opposed to the above procedure) in a medium to be measured were monitored. This technique is known as passive microrheology^[13–15]. Information on local viscoelastic properties can be obtained from mean square displacement (MSD), which is calculated from the trajectory of the particle. The diffusion of individual particles was followed using our optical tweezers setup mentioned above. A halogen lamp was used to illuminate the sample, and a CCD camera acquired images of the particles in the samples, at a frame rate of 31 Hz. The tracking of the particle trajectories in the samples was analyzed using a commercial imaging software.

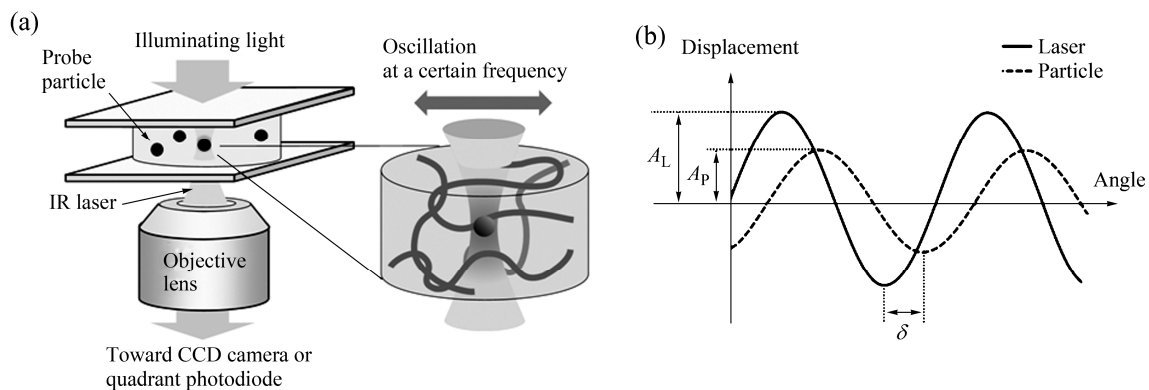


Fig. 1 (a) Schematic illustration showing measurement of the local viscoelastic properties in molecular assembled systems by using optical tweezers; (b) Plot of the displacement of the particle and the laser, observed during laser oscillation at a certain frequency

RESULTS AND DISCUSSION

Worm-like Micelle Solution

Surfactant molecules often form micelles with a large aspect ratio, so called “worm-like” micelles, leading to the formation of a three-dimensional network based on their entanglements. The local viscoelastic properties of an aqueous solution of worm-like micelles composed of cetyl trimethyl ammonium bromide (CTAB) and sodium salicylate (NaSal) were examined by optical tweezers. In the absence of NaSal, the CTAB molecules form spherical micelles at a relatively low concentration (typically 100–400 mmol/L)^[28], but complexation with this salt leads to the formation of worm-like micelles^[29]. Polystyrene (PS) particles having a radius of 550 ± 10 nm were used as probes to examine the viscoelastic properties. A worm-like solution ($[\text{CTAB}] = [\text{NaSal}] = 100$ mmol/L) containing the particles was mounted on the substage of an optical tweezers setup. Figure 2(a) shows an optical microscopic image of a particle dispersed in the solution. The worm-like micelles and/or their bundles were not observed because of their small size and transparency. The particles moved thermally without remaining in an optical trap. When an infrared laser (IR) with a wavelength of 1064 nm was focused on a particle in the worm-like micelle solution and then sinusoidally oscillated at 1.0 Hz, the particle followed the stimulus motion of the laser beam, as shown in Fig. 2(b). The amplitude of the sinusoidal movement of the particle ($A_p = 78$ nm) was smaller than that of the laser movement ($A_L = 320$ nm), where the destruction of worm-like micelles was trivial if any. This is probably because the network structure in the worm-like micelle solution suppressed the particle motion.

Figure 2(c) shows the G' and G'' obtained at 10 different locations in the worm-like micelle solution. It behaves more like an elastic solid than a viscous liquid under the measurement conditions as shown by larger G' than G'' at any given location. The average values obtained were $G' = 45 \pm 8$ Pa and $G'' = 10 \pm 2$ Pa. These values are quite close to the bulk moduli obtained using a traditional oscillatory rheometer ($G' = 40$ Pa and $G'' = 9.4$ Pa). This comparison indicates that the bulk viscoelastic properties of worm-like micelles can be understood by averaging local properties. It is of note that the values of G' and G'' varied widely, depending on the location of the particles. The coefficient of variation (CV), which is defined as the value of the standard deviation (σ) divided by the mean value, was 17% for G' and 21% for G'' . These values are higher than those obtained from an experiment made on a polyethylene glycol (PEG) solution (CV = 6.5% for G' and 8.0% for G'' at 1.0 Hz), which is commonly used as a benchmark of a homogeneous system^[30]. The relatively larger CV values of G' and G'' for the worm-like micelle solution clearly indicate the heterogeneity in the viscoelastic properties. The scale of the characteristic length of the heterogeneity should be on the order of the particle size, namely the sub-micrometer scale, similar to that observed in physical gels^[26, 31].

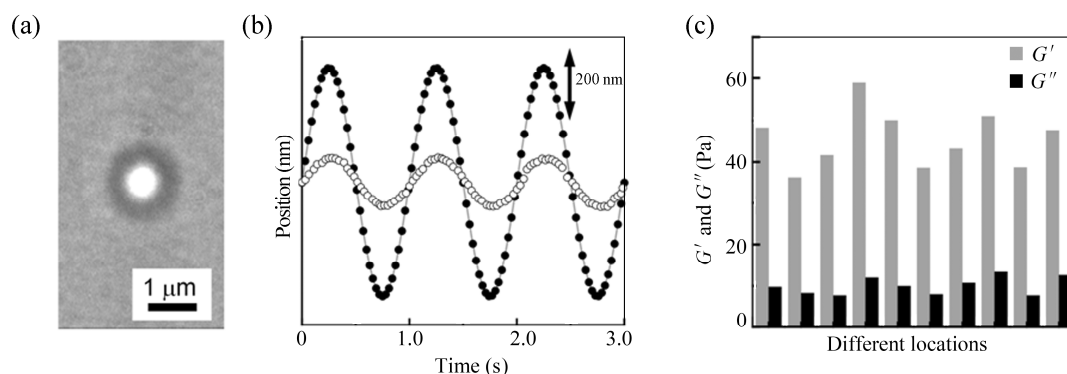


Fig. 2 (a) Optical microscopic image of the probe particle incorporated into the worm-like micelle solution; (b) Plot of the displacement of the particle (open circles) and laser (solid circles), obtained during oscillation; (c) Storage (G' , gray bars) and loss moduli (G'' , black bars) acquired at 10 different locations in the aqueous solutions of worm-like micelles. The experimental conditions were as follows: frequency = 1.0 Hz, amplitude of laser displacement = 320 nm, temperature = 298 K and [CTAB] = [NaSal] = 100 mmol/L. (Reproduced by permission of The Royal Society of Chemistry [18])

These results motivated us to explore the origin of the heterogeneity. Figure 3(a) shows the frequency dependence of G' and G'' , shown here as average values of those measured at 10 different locations in the worm-like micelle solution. A Maxwell model with plateau modulus (G_0) and relaxation time (τ) could express the viscoelastic behavior of the solution as shown by the best-fit curves (chi-square value, $\chi^2 = 0.29$ for G' and 0.32 for G'') in Fig. 3(a). The values of G_0 and τ were determined to be 46 ± 2 Pa and 0.72 ± 0.02 s, respectively. A bulk rheological study with an oscillatory rheometer confirmed identical behavior with G_0 of 43 Pa and τ of 0.72 s^[32]. Here, it should be noted that the location-dependent variation of G' and G'' depends on the frequency, as shown in Fig. 3(b). The CV values (CV = 9.1% for G' and 5.5% for G'' at 0.1 Hz) are comparable to those obtained for the PEG solution at lower frequency. However, the CV values increased when the frequency went beyond τ^{-1} ^[33]. This plot makes it clear that the heterogeneity in the viscoelastic properties of the worm-like

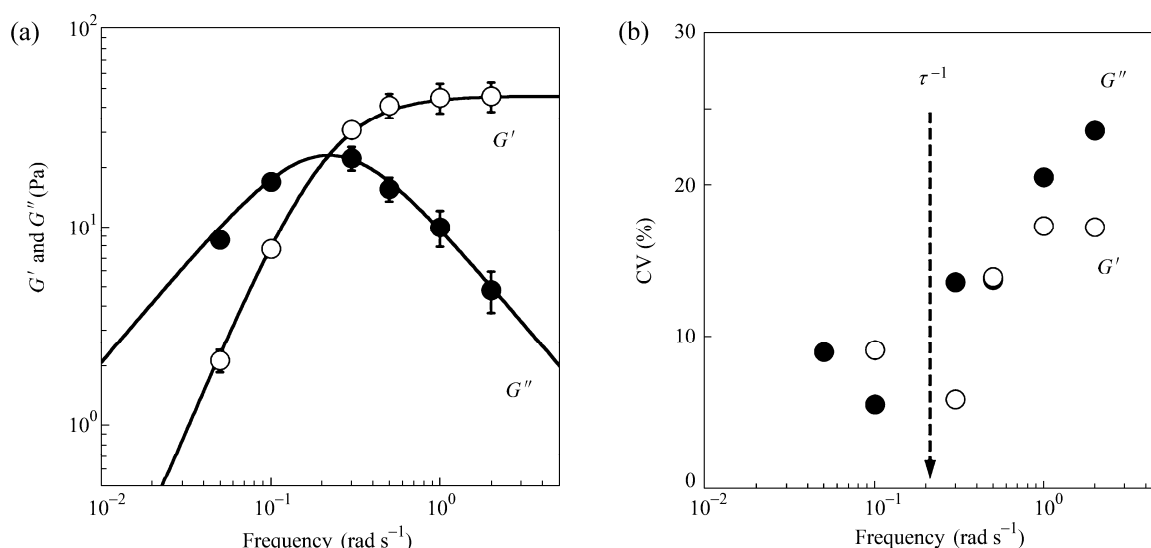


Fig. 3 (a) Frequency dependence of storage (G') and loss moduli (G''), expressed as average values of those acquired at 10 different locations in the worm-like micelles (Solid lines denote the best-fit curves obtained using a Maxwell model with a single relaxation.); (b) Correlation between frequency and the CV values for G' and G'' . The experimental conditions were as follows: amplitude of laser displacement = 320 nm, temperature = 298 K and [CTAB] = [NaSal] = 100 mmol/L. (Reproduced by permission of The Royal Society of Chemistry [18])

micelle solution became more striking with increasing frequency (decreasing measurement time), and is related to the relaxation time. This is the demonstration of time-dependent heterogeneity in the viscoelastic properties of worm-like micelle solutions.

Two major models were proposed to explain the single relaxation process of worm-like micelles. One is based on reptation model with reversible chain association and scission reaction^[34], and another is phantom-crossing model in which two entangled worm-like micelles were in part fused and then re-formed into individual micelles^[35, 36]. In both models, the entanglement of worm-like micelles, which behave as a cross-linking point in the network structure, dissolves after time τ . At lower frequency, where time is longer than τ , entanglement dissolution occurs, and the entanglement does not contribute to the viscoelastic properties, resulting in $G' < G''$. However, this is not the case at higher frequency, where time is shorter than τ . In this case, the entanglement is essentially preserved and dominant in the viscoelastic properties, leading to $G' > G''$. As mentioned above (Fig. 3b), the heterogeneity in the viscoelastic properties predominates at frequencies above τ^{-1} . Thus it can be claimed that the heterogeneity in the viscoelastic properties of the worm-like micelle solution originates from a heterogeneous network based on the micelle entanglements.

Supramolecular Hydrogel

A number of peptide-based amphiphiles have been reported to self-assemble in aqueous media and achieve macroscopic hydrogelation. We used a *N*-palmitoyl-Gly-Gly-Gly-His trifluoroacetate (PalG₃H) as a hydrogelator^[37]. PalG₃H formed a hydrogel based on a micelle-like self-assembly to produce a fibrous network as schematically illustrated in Fig. 4(a). Figure 4(b) shows photographs containing the variation in the physical state of a mixture of PalG₃H and water. An aqueous dispersion of PalG₃H with a concentration of 0.2 wt% was heated at 363 K for 10 min, leading to a clear solution. Cooling this solution to room temperature (298 ± 1 K) and then aging for 1 h gave a hydrogel. When shaken to physically break the gel, it transformed into a fluid state without any precipitate. Letting this undisturbed for 72 h, it returned to a non-fluid state. Such re-gelation behavior has been discussed on the basis of re-assembly of the gelator molecules^[38, 39]. Also, we serendipitously found that heating at 333 K, as an alternative to 363 K, also gave a clear solution but unlike in the above case, it did not form any gel state even after aging for a few weeks. Thus, these observations highlight that a difference in dissolution temperature (by 30 K in this case) significantly affect the resultant physical states.

These led us to investigate, by optical tweezers, the local viscoelastic properties and assembled structures for the gel and sol states obtained by heating at 363 K and 333 K, respectively. In the measurements using optical tweezers, PS particles having a radius of 540 ± 10 nm were used as probes. To examine the spatial heterogeneity in the viscoelastic properties, G' and G'' were measured at 10 different locations in the same sample. When the measurements were made at a frequency of 1 Hz, the average values were $G' = 0.98 \pm 0.4$ Pa and $G'' = 0.16 \pm 0.05$ Pa for the gel state, and $G' = 0.24 \pm 0.1$ Pa and $G'' = 0.093 \pm 0.04$ Pa for the sol state, respectively. In both states, G' was larger than G'' , meaning that the media are elastic. An important fact is that the location-dependent variation of G' and G'' was more striking in the gel state ($\sigma = 0.4$ for G' , 0.05 for G'') than in the sol state ($\sigma = 0.1$ for G' , 0.04 for G''). It is clear that the temperature used to dissolve a gelator into a solvent not only affects the macroscopic physical state but also the heterogeneity of the viscoelastic properties in supramolecular hydrogels.

To address the origin of the heterogeneity, Fourier-transform infrared (FTIR) spectroscopic measurements for the gel and the sol states were made. Figure 5 shows FTIR spectra of PalG₃H in the gel, the sol and the dimethyl sulfoxide (DMSO) solution, where all the samples were prepared by using deuterated solvents. In the spectrum of the gel, the symmetric and antisymmetric C—H stretching vibrations of CH₂ groups were observed at 2849 and 2919 cm⁻¹, respectively. These values were smaller than those obtained for the DMSO solution, in which PalG₃H was molecularly dispersed. This indicates that the alkyl chains in PalG₃H are ordered in the gel state^[40]. Also, the absorption peak assignable to the C=O stretching vibration, namely amide I band, was split into two peaks at 1645 and 1632 cm⁻¹ for the gel. On the contrary, the DMSO solution gave the corresponding absorption peak at 1670 cm⁻¹, including the contribution from trifluoroacetate^[41]. Such a red-shift of amide I

band is characteristic of a hydrogen bonding^[42]. Importantly, there was no substantial difference between the FTIR spectra for the gel and the sol. From these information, it is clear that PalG₃H forms a micelle-like assembly, which was accompanied by the alkyl-chain ordering and hydrogen bonding both in the gel and the sol states. Thus, the difference in the physical state and the heterogeneity between the gel and the sol states cannot be explained in terms of the molecular assembled states of PalG₃H.

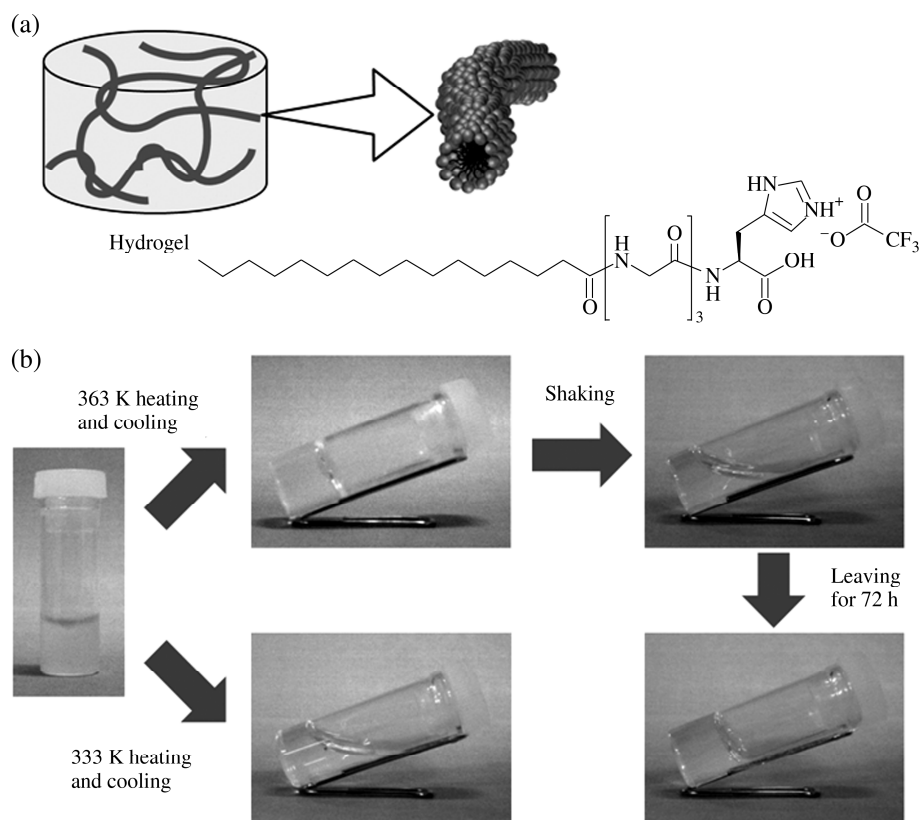


Fig. 4 (a) Schematic illustration of supramolecular hydrogel formed by PalG₃H; (b) Photographs showing the variation in the physical state for a mixture of PalG₃H and pure water, [PalG₃H] = 0.2 wt% (Reproduced by permission of The Royal Society of Chemistry [19])

To examine the assembled states of PalG₃H at a larger size scale, fluorescence microscopic observation for the gel and the sol states was made. A fluorescent probe, 8-anilino-1-naphthalene-sulfonate sodium salt (ANS), was used for the observation. The stronger emission of ANS in a hydrophobic environment compared with that in a hydrophilic one makes it possible to stain the hydrophobic core in micelles^[43]. The fluorescence spectra of ANS in the gel and the sol confirmed the intensification in emissions relative to that in pure water, indicating a micelle-like assembly. Figure 6 shows the fluorescence microscopic images of the ANS-containing gel and sol. Both the gel and the sol were found to contain fibrils with a diameter below 1 μm . However, the fibril length and dispersity were not the same. In the case of the sol, the fibrils were shorter and monodispersed. On the other hand, longer fibrils existed in addition to shorter ones in the gel. Longer molecules such as polymer chains generally form a network with stronger mechanical properties due to entanglements. Assuming that such a notion of entanglements is effective even for supramolecular hydrogel, it is quite reasonable that the system shown in the panel (a) of Fig. 6 did not flow, as shown in the panel (b) of Fig. 4. Of course, a network mainly composed of shorter fibrils, which is relatively weak mechanically, is present even in the gel. Thus, it can be claimed that the heterogeneity in the viscoelastic properties of the supramolecular hydrogel originates from a

heterogeneous network based on the fibril entanglements. It is noteworthy that both of the gel and the sol did not behave as a phantom-crossing model^[35] which was confirmed by the bulk rheological study with an oscillatory rheometer. This might be due to the fact that the fibrils were formed by the micelle-like assembly based on relatively strong interactions (hydrogen bonding) among the PalG₃H molecules, which should suppress a micelle fusion in a phantom-crossing process.

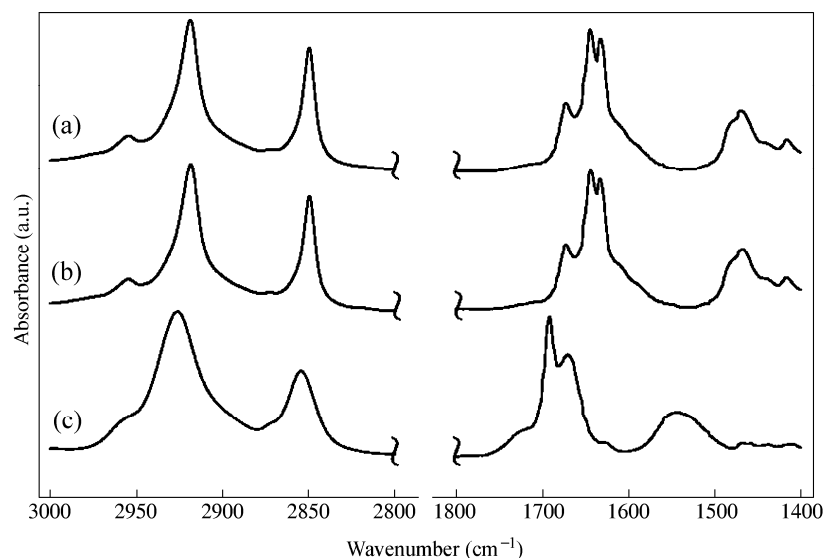


Fig. 5 FTIR spectra of PalG₃H in (a) the gel state, (b) the sol state and (c) the solution state at 298 K [PalG₃H] = 1.0 wt%. All the samples were prepared by using the deuterated solvents. (Reproduced by permission of The Royal Society of Chemistry [19])

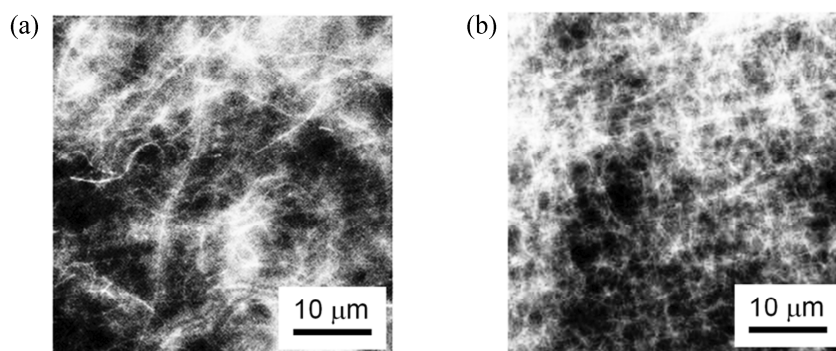


Fig. 6 Fluorescence microscopic images of ANS-containing gel (a) and sol (b) [ANS] = 30 μmol/L and [PalG₃H] = 0.2 wt% (Reproduced by permission of The Royal Society of Chemistry [19])

Lyotropic Liquid Crystal

Liquid crystalline mesophases represent an exciting physical system where different self-assembled structures can be obtained simply by changing the surfactant concentration and/or the temperature^[44]. For example, it is known that non-ionic surfactant, hexaethylene glycol (C₁₂E₆), in water self-assembles into various kinds of mesophases by varying the C₁₂E₆ concentration: isotropic at 20 wt%, hexagonal at 50 wt% and lamellar at 80 wt%^[45]. This fact motivated us to explore a spatial heterogeneity in these mesophases by a particle tracking technique. The probes used were PS particles having a radius (r) of 250 ± 5 nm. The diffusion of individual particles dispersed into the liquid crystals was tracked using our optical tweezers setup as shown in Fig. 1. Figure 7(a–c) shows typical two-dimensional trajectories of individual particles dispersed in the C₁₂E₆-water

mixtures with three concentrations of 20 wt%, 50 wt% and 80 wt%. In the figure, x - y displacements of 9 representative particles were sampled from a larger set acquired at 298 K for each sample concentration. The motion of the particles dispersed in 20 wt% (isotropic) and 80 wt% (lamellar) $C_{12}E_6$ suggests a typical thermal diffusion as shown by the erratic, non-directional trace of the particle movement. This is not the case, however, in 50 wt% (hexagonal phase) $C_{12}E_6$. Aside from some particles exhibiting thermal diffusion, other particles showed restricted motion as evidenced by the almost stationary position.

From the trajectories, the coordinates of the probe particle being tracked were transformed into MSD (symbolically represented here as $\langle \Delta r^2(t) \rangle$) traces^[46]. From the slope (γ) of the double logarithmic plot of the $\langle \Delta r^2(t) \rangle$ for the individual probe particles against the lag time (t) shown in Figs. 7(d–f), the type of diffusion of the probes in the solution can be known. A normal diffusion can be inferred with a logarithmic slope unity ($\gamma = 1$) while an anomalous diffusion is described by $\gamma \neq 1$ ($\gamma < 1$, subdiffusion; $\gamma > 1$, superdiffusion)^[47, 48]. The γ is close to unity at concentrations of 20 wt% (isotropic) and 80 wt% (lamellar), indicating that the probe particles diffused normally in these solutions and the solutions behaved as viscous liquids. Interestingly, two types of slopes can be observed in the $\langle \Delta r^2(t) \rangle$ versus t plots for the particles in 50 wt% solution (hexagonal). The slope of one set of particle populations is close to unity ($\gamma = 1$), suggesting the thermal diffusion for these particles while the other set of tracer populations has a $\gamma < 1$, inferring subdiffusion. Less than unity ($\gamma < 1$) indicates that an elastic trapping of the particles happened within the self-assembled structures^[49].

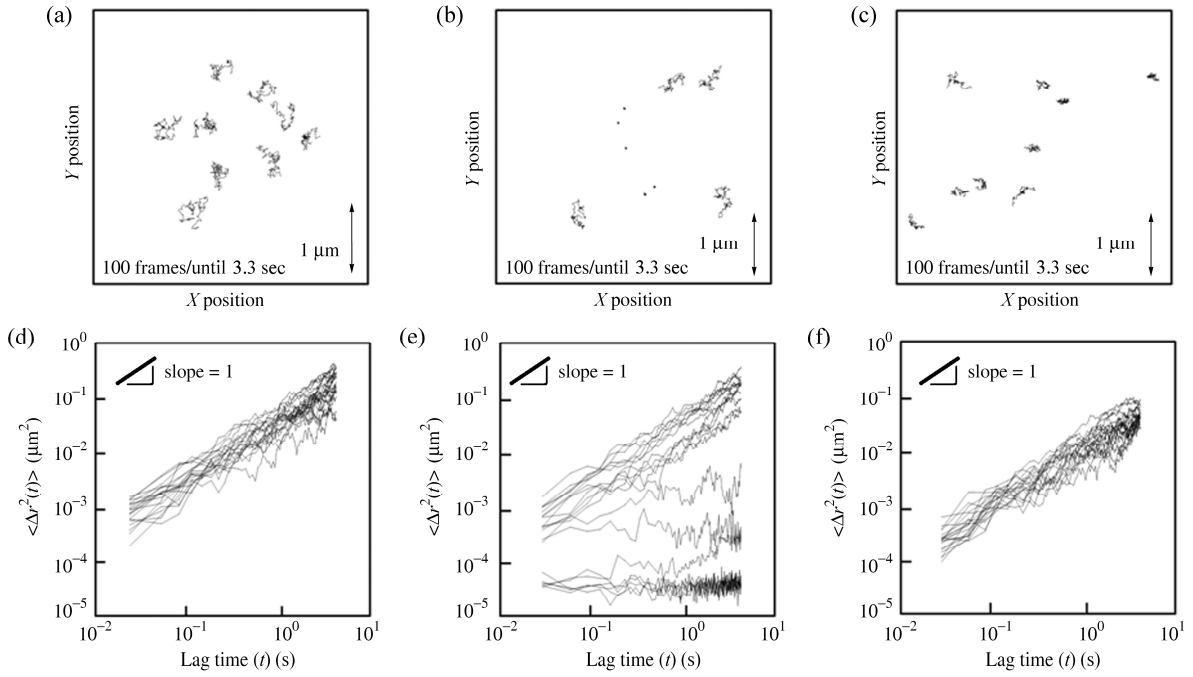


Fig. 7 (a–c) Typical trajectories of nine representative particles and (d–f) the plots of $\langle \Delta r^2(t) \rangle$ against lag time (t) for probe particles dispersed in (a and d) isotropic, 20 wt%, (b and e) hexagonal, 50 wt% and (c and f) lamellar, 80 wt% $C_{12}E_6$ aqueous solutions, respectively (Reproduced by permission of the PCCP Owner Societies [20])

To address the origin of the heterogeneity in the hexagonal phase, we decided to extract the local viscosity from the MSD profiles of the probe particles, and compare that to the bulk viscosity obtained using a conventional viscometer. For a normally diffusing particle ($\gamma = 1$), its diffusion coefficient (D) could be obtained by the relation of $\langle \Delta r^2(t) \rangle \propto 4Dt$ in two dimensions. The Stokes-Einstein's equation relates the D value to the local viscosity, η , as shown below^[50]:

$$\eta = \frac{k_B T}{6\pi r D} \quad (3)$$

where k_B is Boltzmann constant, T is absolute temperature, r is radius of the probe particle. We also applied the same procedure to determine the local and the bulk viscosities of water and 85 wt% aqueous glycerol solution as well, as representatives for a non-viscous and a viscous Newtonian liquid samples, respectively. Table 1 summarizes the values determined by the viscosity measurements. The local viscosities of water and the glycerol solution are in excellent agreement with the bulk ones. The same case can be seen for the 20 wt% solution (isotropic) that has a bulk viscosity of 5.0×10^{-2} Pa s and a local viscosity of 7.1×10^{-2} Pa s. However, this is not the case with that of 50 wt% solution (hexagonal) where the bulk and the local viscosities were significantly different. Compared to its bulk viscosity value of 4.6 Pa s, the local viscosity for the 50 wt% solution was 4.5×10^{-2} Pa s. The determined local value is interestingly close to the local and the bulk values of the 20 wt% solution (isotropic), suggesting that the local environment probed by these particles is isotropic-like rather than hexagonal-like in the 50 wt% solution. From these results, we made an assumption on the origin of the two sets of probe populations observed in 50 wt% $C_{12}E_6$ solution, as shown in Fig. 8. In this figure, the gray-colored area represents the predominantly hexagonal phase in the system while the area in white represents the isotropic-like environment surrounded by the hexagonal domains. In the predominantly hexagonal phase, the motion of an embedded probe particle (solid circles drawn in Fig. 8) should be restricted simply because of the high viscosity of the hexagonal phase. A particle located in the isotropic-like environment, on the other hand, should thermally diffuse because of a relatively lower viscosity ($\eta = 4.5 \times 10^{-2}$ Pa s). Thus, the origin of the spatial heterogeneity observed in the 50 wt% $C_{12}E_6$ solution can be associated to the heterogeneous structures composed of the hexagonal domains with isotropic-like regions.

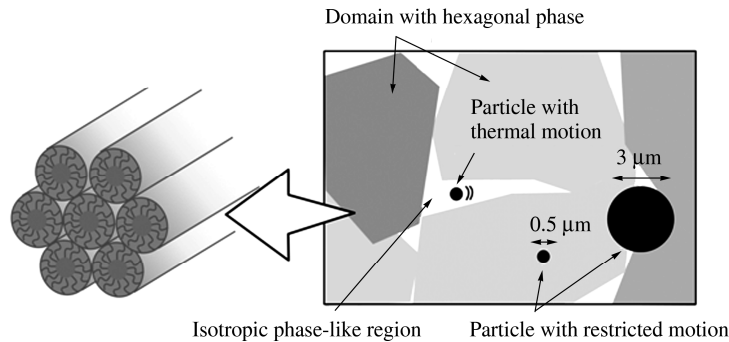


Fig. 8 Schematic illustration showing the origin of heterogeneity in the responses of the local environment in the hexagonal liquid crystal

Table 1. Viscosity values of the $C_{12}E_6$ -water mixtures determined using the particle tracking and bulk viscosity measurements

	Viscosity (Pa s)	
	Local	Bulk
Pure water	0.95×10^{-3}	1.0×10^{-3}
85 wt% glycerol	8.6×10^{-2}	8.7×10^{-2}
20 wt% $C_{12}E_6$ (isotropic)	7.1×10^{-2}	5.0×10^{-2}
50 wt% $C_{12}E_6$ (hexagonal)	4.5×10^{-2}	4.6

A qualitative information on the structural length scale in soft materials can be obtained by varying the size of the probe particle^[51]. Hence, we used probe particles that are larger ($r = 1.6 \pm 0.05 \mu\text{m}$) than that were previously used ($r = 250 \pm 5 \text{ nm}$) to determine the size scale of the isotropic-like regions in the hexagonal phase. Using the relatively larger size particles in the 50 wt% $C_{12}E_6$ solution, only restricted motion ($\gamma < 1$) was

observed. Why this is so is probably because the larger particles could not be incorporated into the isotropic-like region. Thus, by varying the probe particle size, we estimate the size of the isotropic-like regions should be on the sub-micrometer or micrometer scale.

CONCLUSIONS

By using optical tweezers and particle tracking, we have determined the local viscoelastic properties and their spatial distributions for the worm-like micelle solution, supramolecular hydrogel and lyotropic liquid crystal which were composed of amphiphilic molecules and water. All systems studied possessed a spatial heterogeneity in their viscoelastic properties. This arises from the heterogeneous structures based on the three-dimensional networks or intermediate regions between the self-assembled domains. It should be emphasized that the characteristic length scale of the heterogeneity was commonly on the sub-micrometer or micrometer scale, although the systems was formed by molecules with nanometer size. A heterogeneity with a length scale of nanometer may also exist, however, this cannot be observed under existing setup capability due to the inability to optically track probe particles having a few nanometers in size. We believe that the microscopic heterogeneity is a key feature to characterize molecular assembled systems. The findings of these studies should lead to a better understanding of the dynamics of such systems.

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