

Supporting Information

Spatial heterogeneity in lyotropic liquid crystal with hexagonal phase

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1. Materials

The non-ionic surfactant, hexaethylene glycol dodecyl ether ($C_{12}E_6$) was purchased from Wako Pure Chemical Industries, Ltd. and was used as received. Water after deionization with a Milli-Q Lab (Millipore) system was used to prepare the aqueous solutions of $C_{12}E_6$. The specific resistance of the purified water was greater than $18\text{ M}\Omega\text{ cm}$. For particle tracking studies, an aqueous dispersion of polystyrene (PS) microspheres containing fluorescence probes, the so-called Fluoresbrite Yellow Green Microsphere, with a concentration of 2.5 wt% was purchased from Polysciences Inc. The diameter (d) of the PS particles was found to be $504 \pm 10\text{ nm}$ as measured by dynamic light scattering (DLS) measurements.

2. Microrheology

2-1. Instrument for particle tracking.

The setup of instrument for particle tracking, as previously reported elsewhere,¹ is based on an inverted microscope, Nikon ECLIPSE Ti, with an NA 1.30 oil-immersion objective lens. A halogen lamp was used to illuminate the sample and a charge-coupled device (CCD) camera (DS-Qi1Mc, Nikon Instech Co., Ltd.) acquired images of the particles in the samples, at a frame rate of 31 Hz. An imaging software, NIS-Elements AR-3.2 (Nikon Instech Co., Ltd.) was used for the analysis of the trajectory for the particle diffusion.

2-2. Sample preparation. The aqueous solutions of $C_{12}E_6$ with three concentrations were prepared: 20 wt%, 50 wt% and 80 wt% where the surfactant molecules are known to self-assemble into isotropic, hexagonal and lamellar structures, respectively.²

For microrheological measurements, the probe particles were well-dispersed in the non-ionic surfactant solutions. For example, the particle latex solution with a volume of $1\text{ }\mu\text{L}$ was added into 1 mL of the 20 wt% $C_{12}E_6$ solution and then was well-dispersed using a vortex mixer (Taitec Ltd.). For the relatively more viscous solutions of 50 wt% and 80 wt% $C_{12}E_6$, the solutions were heated up to 353 K (80 °C) in a water bath before the particle latex solution were added.³ All sample containing the particles aged for several hours prior to the measurements.

2-3. Particle tracking observation. About $40\text{ }\mu\text{L}$ of each of the mixtures was placed on a glass bottom dish (Matsunami Glass Inc. Ltd.) and then it was covered with a

glass slide. This was placed on the stage of the instrument mentioned above. Samples were allowed to equilibrate for an hour or several hours depending on the viscosity of the samples. To perform particle tracking experiments on these samples, the microscope was initially focused on particles deposited on the bottom surface of the sample dish. Then, the focusing was adjusted some distance away from the bottom. The diffusion of individual probe particles embedded in the liquid crystal was then observed. A total of 20 probe particles were tracked in each sample with each particle being monitored 20 times. Each video tracking contains 100 frames at 0.03 second per frame, corresponding to 31 Hz frame rate.

3. Dynamic light scattering (DLS).

The stock solution of the particles with a volume of 10 μL was diluted with 10 mL of water. The water used for the dilution was initially passed through a membrane filter with a pore size of 0.45 μm (Advantec MFS, Inc.). A volume of 4 mL of this solution was placed in the DLS tube. The particle size was measured using a DLS-7000 Spectrophotometer (Photal Otsuka Electronics Co, Ltd). The detection angle used was 90°. He-Ne laser with a wavelength of 633 nm was used as the light source in the measurements conducted at 298 K. The determination of hydrodynamic diameters and its distribution was based on the cumulant method.

4. Viscosity measurements.

The bulk viscosity measurements of the sample solutions were performed using an oscillation viscometer, Viscomate VM-10A (Sekonic Co.). The sensing cylinder of the viscometer was inserted to the sample solution in a glass vial, which was placed in a water bath kept at 298 K. A parafilm was wrapped around the mouth of the vial to prevent the water evaporation from the sample during the measurements.

5. References

1. A. Shundo, K. Mizuguchi, M. Miyamoto, M. Goto and K. Tanaka, *Chem. Commun.*, 2011, **47**, 8844-8846.
2. P. Oswald and M. Allain, *J. Colloid and Interface Sci.*, 1988, **126**, 45-53.
3. K. P. Sharma, G. Kumaraswamy, I. Ly and O. Mondain-Monval, *J. Phys. Chem. B*, 2009, **113**, 3423-3430.

6. Figures

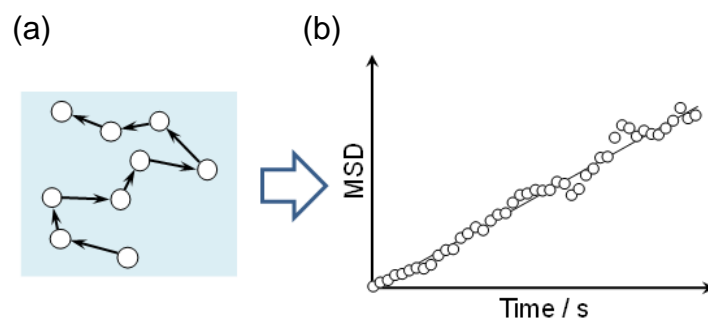


Figure S1 (a) The schematic illustration of a diffusion path for a particle in a liquid sample; (b) plot of the mean square displacement (MSD) against time showing their linear relationship for a particle that follows normal diffusion.

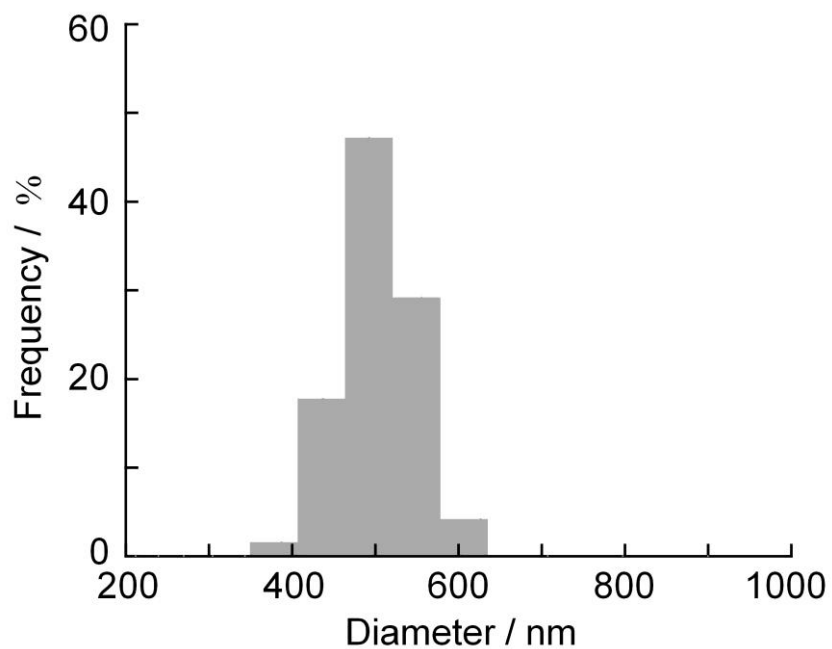


Figure S2 Size distribution of the polystyrene probe particles ($d = 504 \pm 10$ nm) as measured by dynamic light scattering. The detection angle used was 90° and the measurement was done at 298 K.

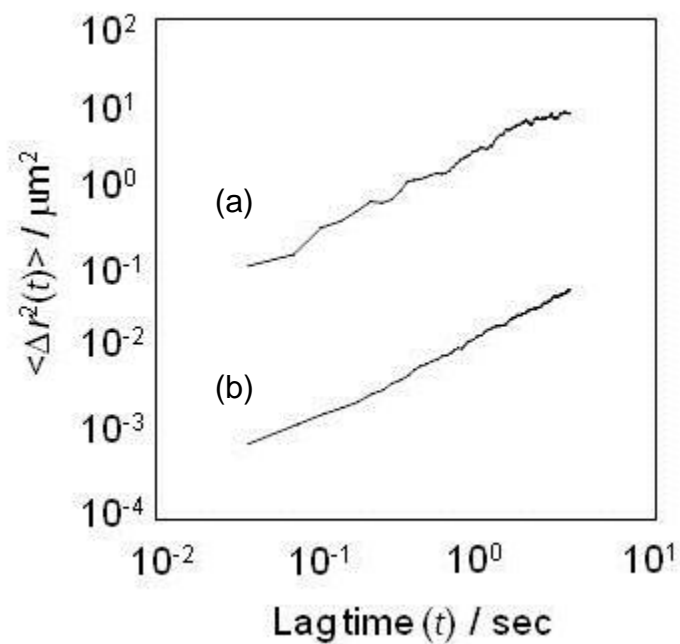


Figure S3 The plot of the mean square displacement, $\langle \Delta r^2(t) \rangle$ and lag time, t , of the polystyrene probe particles ($d = 504 \pm 10$ nm) dispersed in (a) water and (b) 85 wt% glycerol. The two liquids are used as benchmark comparison for homogeneous liquid with the former and the latter as non-viscous and viscous Newtonian liquids, respectively. The measurements were done at 298 K.

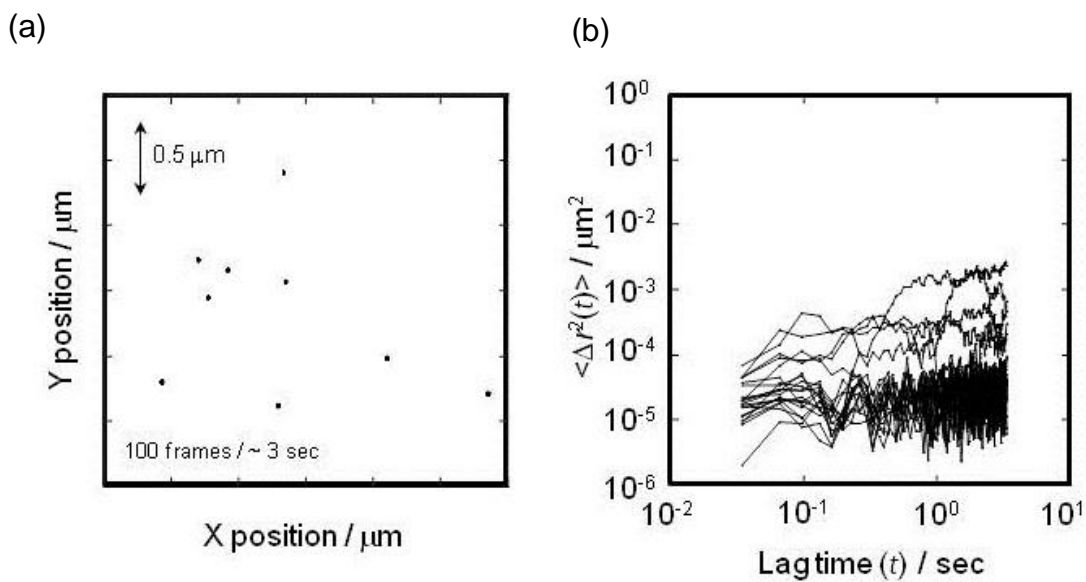


Figure S4 (a) The typical trajectories (nine representative particles) of the polystyrene probe particles ($d = 3.14 \pm 0.09 \mu\text{m}$) embedded in 50 wt% aqueous solution of C_{12}E_6 (hexagonal); (b) the plot of mean square displacement, $\langle \Delta r^2(t) \rangle$, and lag time, t , for panel (a).