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Microgel-Stabilized Liquid Crystal Emulsions Enable Analyte-Induced Ordering Transition

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Experimental Section

Materials. N-isopropylacrylamide (NIPAM) (> 99.0%) and N,N'- methylenebisacrylamide (BIS) (>99.5%) were purchased from Acros Chemicals. The initiators potassium peroxodisulfate (KPS) (99.0%) and sodium dodecylsulfate (SDS) were obtained fromMerck and Fluka, respectively. 4-Cyano-4'-pentylbiphenyl (5CB) and 2,2-azobis(2-methylpropionamidine) dihydro-chloride (V50) were purchased from Sigma-Aldrich and methacryloxyethyl thiocarbamoyl rhodamine B (MRhB) from Polysciences Inc. All chemicals were used as received. Milli-Q water was used for all the syntheses and sample preparations.

Microgel Synthesis. *PNIPAM microgels.* Poly(N-isopropylacrylamide) (PNIPAM) microgels were synthesized by free radical precipitation polymerization.[1] Briefly, 5.0924 g of NIPAM, 0.3652 g of BIS and 0.0120 g of SDS were dissolved in 295 mL of water. This monomer solution was degassed with N_2 and preheated to 70 °C. Simultaneously, the initiator solution of 0.1265 g of KPS in 5 mL of water was degassed. The polymerization was started by adding the initiator solution at once into the monomer solution and let to proceed for 4 hours at 70 °C under constant stirring. The microgels were purified by threefold centrifugation at 30000 rpm and redispersion in fresh water. Lyophilization was applied before storage. These microgels were used for characterization of LC droplets by optical microscopy and for emulsion breaking experiments.
Fluorescently labeled PNIPAM-MRhB microgels. Fluorescent labeling was achieved through co-polymerization with methacryloxyethyl thiocarbamoyl rhodamine B (MRhB).[2] In a typical procedure, NIPAM (10.0 g) monomer, BIS cross-linker (0.68g; 5 mol% with respect to NIPAM) and MRhB dye (10.0 mg in 10 mL of water) were dispersed in water (420 mL) and stirred for one hour at 60 °C under nitrogen purging. The polymerization was initiated at 80 °C, by the drop-wise addition of V50 initiator solution (0.05 g in 10 mL of water). The reaction was run for 4 h at 80 °C, under constant stirring and nitrogen purging. The reaction mixture was then filtered through glass wool in order to remove particulate matter. The microgel suspension was further purified by three rounds of centrifugation (10000 rpm, 20 minutes), with decantation and redispersion in MilliQ water. These microgels were used only for Multi-confocal Laser Scanning Microscopy.

Characterization of the Microgels. The hydrodynamic radii (R_H) of the PNIPAM microgels were determined by dynamic light scattering (DLS) at a wavelength of 633 nm with an ALV-5000 DLS-setup. The samples were prepared in a flow box and filtered through syringe filters to avoid contamination by dust. The hydrodynamic radius was derived from the diffusion coefficient via cumulant analysis and the Stokes-Einstein equation. PNIPAM-MRhB microgels were carried out using a 3D LS spectrometer

from LS Instruments at a wavelength of 632.8 nm at 45° in a 3D cross correlation configuration equipped with a modulation unit.[3] The hydrodynamic radius was determined from a first cumulant analysis averaging over 3 consecutive 300 s measurements.

Preparation of the Liquid Crystal (LC) Emulsions. Typical emulsion batches were composed of 5 mL of aqueous phase containing microgels of different concentrations (0.01 to 1 wt %) and 10 μL of LC. This solution was then mixed with an Ultra Turrax T-25 with a 10 mm head (S25N-10G) at a speed of 8000 rpm for 30 sec. at room temperature. Bare LC emulsion was prepared using the same procedure without adding microgels.

Characterization of LC emulsions. *Multi-confocal Laser Scanning Microscopy (CLSM) with a Yogugawa spinning disc unit.* A commercial VisiScope Spinning Disk DC Confocal System (Visitron Systems GmbH, Puchheim) was used. The suspension (8 μl) was kept between a cover glass and bottom coverslip (thickness 170 μm) hermetically sealed by a 120 μm thick spacer with a 51 mm aperture (Secure Seal Imaging). The coverslip was placed onto a custom-made xy-piezo table (SmarAct GmbH, Oldenburg), mounted onto a commercial inverted microscope (Nikon Eclipse Ti-E). The fluorescence of rhodamine B was collected with a 100x/1.40 NA oil immersion objective (HP PLAN, Nikon), spectrally separated from the excitation laser light (561 nm) by a quad-line beamsplitter (Di01-T405/488/568/647, Semrock), and finally imaged onto the chip of an EMCCD camera (Andor iXON Ultra 888). Background light originating from the excitation laser was suppressed using a bandpass filter (ET605/70m, Chroma) placed in the emission path. All measurements were performed at 295 K.

Optical Microscopy. The size distribution and internal configuration of the LC emulsion droplets was characterized by direct imaging of the LC droplets using an optical microscope (Zeiss Axioskop) fitted with a 100x (NA 1.25) Zeiss Achrostigmat oil immersion objective under cross polarizer after dilution with water or SDS solutions of different concentration. Typically, a volume of 25 μL of SDS solution (or water for control) was added to a 500 μL aqueous dispersion of LC emulsions, prepared as described above, to produce a sample of desire SDS concentration. The sample was then kept for 30 min to allow complete adsorption of SDS molecules at the LC interface, and thus triggering an ordering transition in the microgel coated LC droplets.[4] An aliquot was then taken and the sample was prepared in a same way as described for confocal microscopy. The temperature was set by placing the samples on a metal cell connected to a thermostat. Images of about 100 droplets were analyzed, so that size distribution as well as the quantification of the configurational states of the LC droplets could be performed from statistical analysis.

Table S1. Hydrodynamic radius (R_H) of PNIPAM and PNIPAM-MRhB microgels obtained from DLS measurements

Microgel	R_H (nm) at 20 °C	R_H (nm) at 40 °C
PNIPAM[1]	223 ± 2	125 ± 2
PNIPAM-MRhB[2]	297 ± 2	193 ± 2

Table S2. Summary of Experiments for LC Stabilization by microgels*

Day	Min Diameter [μm]	Max Diameter [μm]	Ave Diameter [μm]
1	1.5, (1.6), [1.4]	12.2, (10.8), [6.0]	5.3, (4.8), [3.2]
3	2.1, (1.8), [1.5]	26.1, (9.3), [8.6]	8.7, (4.9), [3.5]
7	2.2, (1.8), [1.6]	29.6, (11.5), [9.5]	12.6, (6.0), [4.6]

** Data presented without bracket – no microgel, ( ) – 0.05 wt % microgel, [ ] – 1 wt % microgel*

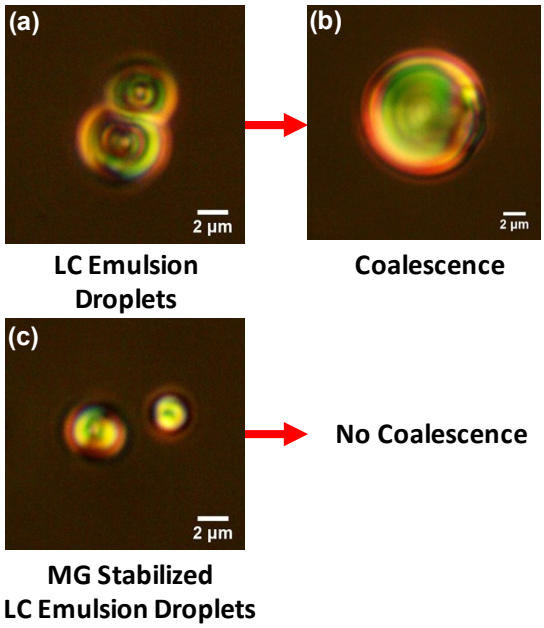

Fig S1. Optical images (polarized light) of bare LC droplets (a) that undergo coalescence to form a bigger droplet (b) and microgel stabilized LC droplets (c) that do not undergo coalescence.

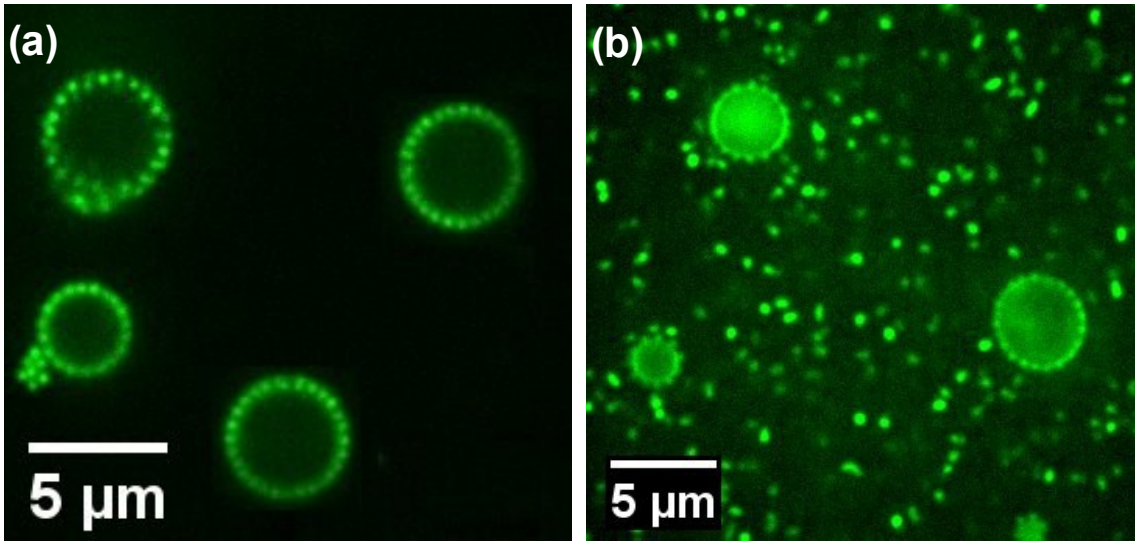

Fig S2. Multi-confocal spinning disc microscopy images of LC emulsion droplets stabilized by (a) 0.01 wt % and (b) 1 wt % microgels.

At low microgel concentration the droplets were formed by limited coalescence. In contrast, LC emulsions that were prepared with higher microgel concentration (1 wt %), directly led to stable and smaller droplets but with excess microgels in the aqueous phase.

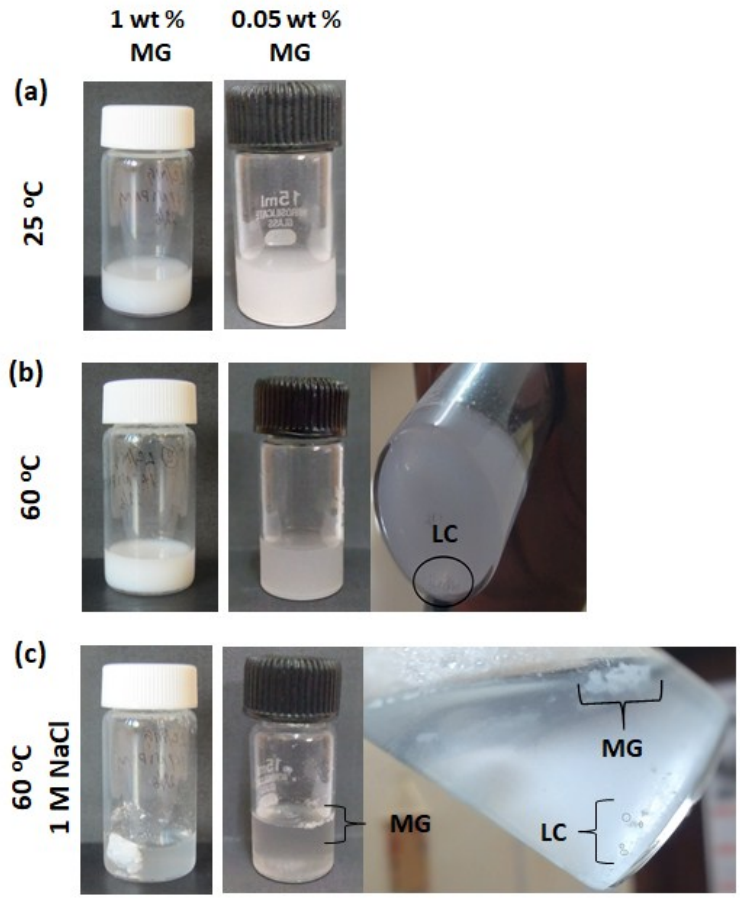

Fig S3. (a) Stable LC emulsions just after preparation at 25 °C, (b) temperature induced de-emulsification with the formation of stable colloidal particles at 60 °C for 30 min and (c) broken emulsions consisting of three distinct phases including collapsed aggregated microgels (flocculated), LC and a clear aqueous phase at 60 °C for 30 min and in presence 1 M NaCl.

Fig S3a showed the microgel stabilized LC emulsions just after their formation. The samples were heated at 60 °C for 30 min with a constant shaking of 200 rpm to investigate the effect of temperature increase on the LC emulsions. Under this condition, the LC emulsions were broken, while, microgels formed stable colloidal particles (collapsed microgels, Fig S3b). The temperature induced LC emulsion breaking was confirmed by the physical appearance of the LC phase, which was separated at the bottom after breakage. As a very small volume of LC (10 μL) was added to the aqueous solutions (5 mL) for the preparation of emulsions as described above, the separated LC phase was very small. Therefore, it was very difficult to image the tiny LC phase at high microgel concentration (1 wt %). The colloidal stability of the microgels was reduced upon addition of salt (1 M NaCl) at 60 °C, resulting in the formation of flocculated microgels (Fig S3c). Thus, three distinct phases such as collapsed aggregated microgels (flocculated), a LC phase at the bottom (as LC is denser than water) and a clear aqueous phase could be easily separated. The colloidal instability of the microgels was found to show no effect on the destabilization of the LC emulsions.

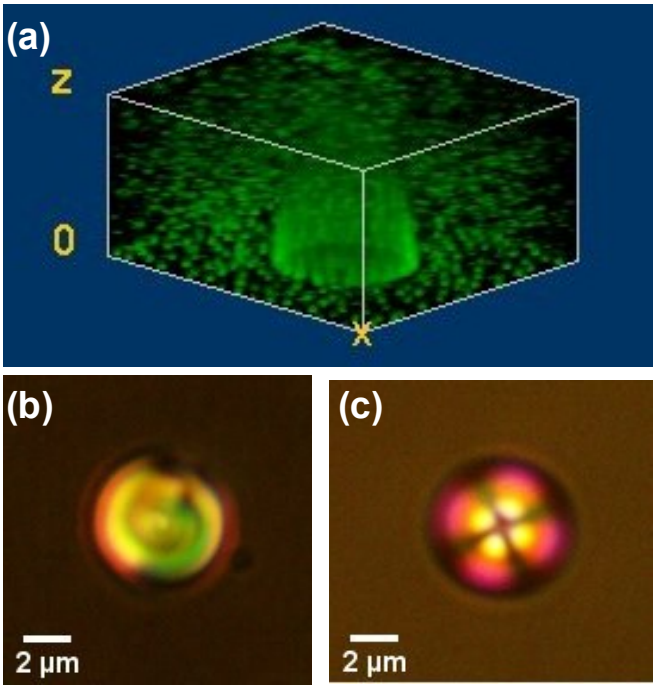

Fig S4. (a) 3D maximum intensity reconstruction (8 x 7 x 5 μm^3) of an LC droplet covered with PNIPAM-RhB microgels obtained from confocal microscopy after sedimentation and adsorption at the glass surface, (b) polarized light micrographs of a PNIPAM microgel stabilized LC droplet with bipolar optical signature after sedimentation from a SDS free aqueous solution, (c) polarized light image of a PNIPAM microgel stabilized LC droplet with radial optical signature deposited on the glass surface after exposure to 5 mM SDS solution.

While sedimentation and adsorption of LC droplets stabilized by microgels at the bottom wall leads to droplet deformation, no change of their initial bipolar or radial configuration was observed upon sedimentation. We concluded that such droplets were sufficiently protected by microgels to maintain their structure and therefore, the droplets undergoing sedimentation could also be taken into account for quantification of aqueous analytes, which is conversely not possible with unprotected bare LC droplets.

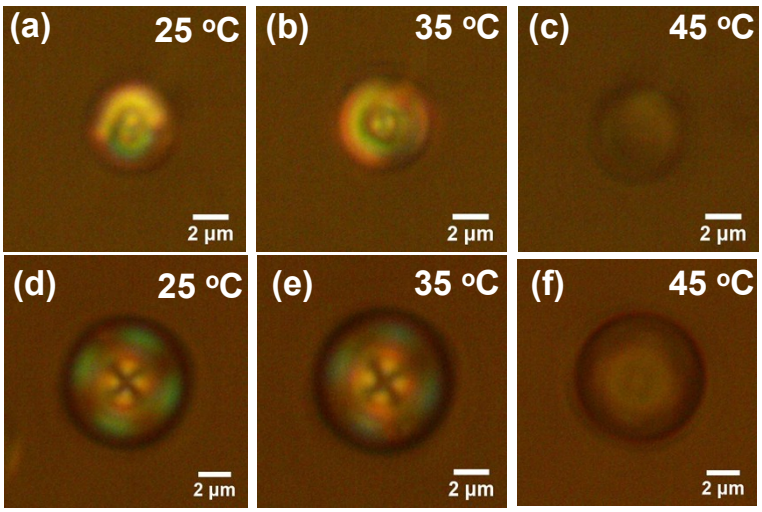

Fig S5. Optical micrographs (polarized light) of microgel stabilized LC droplets in SDS free water (a-c) and in presence of 5 mM SDS (d-f) with increasing temperature.

The nematic-isotropic transition temperature (T_c) for 5CB is 35.4 °C above which droplets undergo a phase transition and lose their optical signatures.

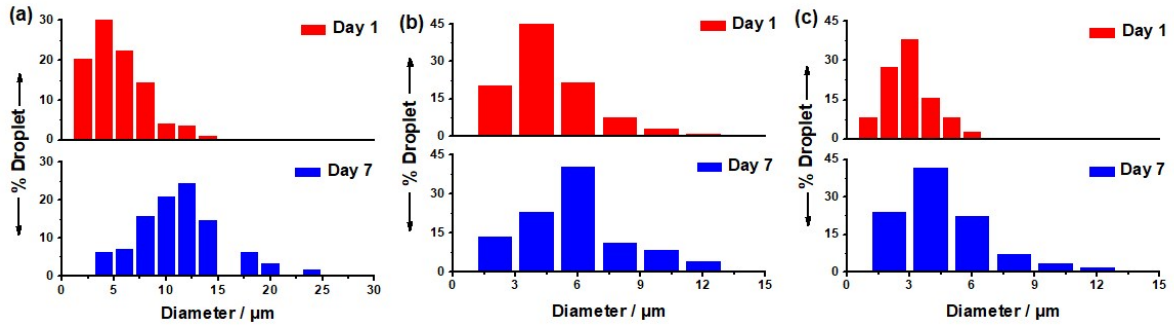

Fig S6. Size distributions of LC emulsion droplets with (a) no microgel, (b) 0.05 wt % and (c) 1 wt % microgel determined from the optical microscopy images after the adsorption of SDS (5 mM) at the LC-water interface.

Table S3. Summary of Experiments for LC Stabilization by microgels* after the adsorption of SDS (5 mM) at the LC-water interface.

Day	Min Diameter [µm]	Max Diameter [µm]	Ave Diameter [µm]
1	1.3, (1.5), [1.2]	12.2, (10.5), [6.1]	5.1, (4.6), [3.1]
7	2.0, (1.6), [1.5]	23.8, (11.0), [11.2]	11.1, (5.9), [4.6]

** Data presented without bracket – no microgel, ( ) – 0.05 wt % microgel, [ ] – 1 wt % microgel*

The stability of the microgels coated LC droplets in presence of excess SDS (5 mM) was investigated by measuring the droplet-size distributions over time using optical microscopy as shown in Fig S6 and summarized in Table S3. Similar to the results presented in Fig 2 and Table S2 (without SDS), the SDS adsorbed LC droplets without microgels (Fig S6a) underwent coalescence and formed larger droplets, while, the microgels coated droplets exhibited a remarkable stability over a period of 7 days after the addition of SDS (Fig S6a & S6b). No significant change in the droplet stability was observed upon SDS addition, indicating that the stability of the LC droplets was attributed to the irreversible adsorption of microgels only.

References

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4. T. Bera, J. Deng and J. Fang. *RSC Adv.,* 2015, **5**, 70094–70100.