Self-Assembled Liquid-Crystal Gels in an Emulsion†
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Self-assembled liquid-crystal (LC) gels in an emulsion (i.e., LC gel droplets dispersed in aqueous solution) were prepared and investigated for the first time. The aggregation of gelator molecules confined in the LC droplets results in the formation of circular and highly folded nanoscale fibers, in contrast to the extended ones formed in the bulk LC gel. Another manifestation of the confinement effect is that the electrooptical behavior (switching times and contrast) of single LC gel droplets is largely determined by the droplet size. By bridging LC gels and LC emulsions, this study introduces a new hybrid LC system and offers new possibilities of exploring functional LC materials.

Introduction

In recent years, more and more research effort on liquid crystals (LCs) has been directed to exploring their use in new materials aimed at applications other than liquid-crystal displays (LCDs). Among them, the LC-in-water emulsion (i.e., with LC droplets dispersed in aqueous solution) has received increasing attention.1-4 Though it has long been established that nematic LCs confined in small spherical cavities can display a rich variety of configurations determined by a number of factors such as the nature of LC molecular anchoring at the interface,5,6 most studies have been conducted in relation to polymer-dispersed liquid crystals (PDLC) where LC droplets are dispersed in a polymer matrix.3,7,8 Some recent work on the LC-in-water emulsion has shown potential. Most notably, Fernandez-Nieves et al. prepared a monodisperse nematic LC emulsion and obtained optically and geometrically anisotropic solid particles through photopolymerization that locked in the LC orientation inside the droplets; optical tweezing was used to rotate such particles, suggesting their use in microfluidic applications.3 Keeping in mind the exploitation of the large interface in LC emulsions for possible sensing applications, Abbott and co-workers succeeded in assembling a polyelectrolyte multilayer film at the droplet-water interface and showed that the transition of LC configurations inside the droplets could be sensitive to the adsorption of a surfactant (analyte).2

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cannot be utilized for an emulsion. To overcome this difficulty, we used a special gelator, 1-cyano-trans-1,2-bis(3,5-bis-trifluoromethyl-biphenyl)ethylene (CN-TFMBE). This gelator displays aggregation-induced enhanced emission (AIEE) by being highly fluorescent in the solid (aggregated) states but virtually nonfluorescent in the solubilized state.\textsuperscript{21} Previous studies found that CN-TFMBE is able to gel organic solvents\textsuperscript{22} and LCs\textsuperscript{23} while forming highly fluorescent fibrous aggregates as a result of the $\pi-\pi$ stacking interactions of the aromatic cores and the interactions induced by CF$_3$ units. The use of this peculiar property makes it possible to confirm the formation of fibrous aggregates inside emulsified LC droplets in aqueous solution. As will be shown, compared to the bulk LC gel, the LC gel in an emulsion exhibits different electrooptical behavior. Moreover, the gelation occurred inside the LC droplets under the confinement results in the formation of circular and highly folded fibrous aggregates, in contrast to the extended fibers formed in the bulk LC. By bridging LC gels and LC emulsions, this study demonstrates a new type of hybrid LC system and thus opens the door to exploring new functional LC materials.

**Experimental Section**

Figure 1 shows the chemical structures of the CN-TFMBE gelator and the nematic LC, E7 (purchased from Merck) having $T_{ni}$ $\approx$ 68 °C in the pure state. The typical procedure for preparing an LC gel emulsion is detailed as follows. Weighed E7 and CN-TFMBE (2 wt % with respect to the LC) were first dissolved in THF, after removal of the solvent (drying at 40 °C in a vacuum oven), an LC gel was formed at room temperature. Then, the as-prepared LC gel was heated to 140 °C to melt all aggregates of CN-TFMBE to obtain a homogeneous LC/gelator mixture. This mixture was then cooled to about 65 °C, at which temperature no aggregation of CN-TFMBE took place while E7 was still in the isotropic state. The warmed LC/gelator mixture was added to an aqueous solution of 2 wt % sodium dodecyl sulfate (SDS) under vigorous stirring at room temperature (the LC/gelator mixture in water while the solution was maintained at 40 °C to promote the aggregation process). The fluorescence emission from the droplets indicates that the LC gel emulsion was formed. The formation of LC droplets dispersed in aqueous solution (most diameters are in the range of 2–5 $\mu$m) and the aggregation of gelator molecules inside the droplets were revealed by optical and fluorescence microscopy (images in Supporting Information). The fluorescence emission from the droplets indicates that CN-TFMBE molecules are in an aggregated state inside the LC cavities. As will be shown later, the presence of a network of fluorescent fibrous aggregates inside the LC droplets is visible under the fluorescence microscope. Considering the fact that CN-TFMBE can gel bulk LCs upon aggregation,\textsuperscript{23} the observed droplets should be gelled E7. From the microscopy images, it can be noticed that fluorescent micrographs apparently show fewer water at room temperature, the LC gel needed to be in the homogeneous isotropic phase to be easily dispersible under stirring. However, when water was also heated to the same temperature (65 °C), part of the gelator was extracted from the solution, probably because of its different solubility in water as compared to that of the LC. Therefore, with the procedure that was used, the aggregation of the gelator took place upon cooling of the LC/gelator mixture in water while the solution was subjected to the vigorous stirring required for the dispersion; the aggregation process was basically completed after the emulsion was obtained. Observations on the LC gel emulsion were made within 1 day after the preparation, and the actual delay time had little effect on the results. Because of the preparation procedure, we were unable to investigate the kinetics of gelation inside the LC droplets.

The LC gel emulsions were observed using an optical microscope (Leitz DMR-P) both in bright field and under crossed polarizers. The microscope was also used to carry out the electrooptical measurements on single LC gel droplets by replacing the digital camera for photomicrographs with a high-speed photodetector (Melles Griot) that is connected to a digital oscilloscope (Tektronix, TDS 420A). The change in transmittance of the LC gel droplets could thus be measured in response to an electric field (1000 Hz ac field) provided by a high-voltage waveform generator (SWF6000, Circuit Test). More details on the measurements on single LC droplets will be given later. A fluorescence microscope (Leica DMRX) was used to observe the formation of fluorescent fibrous aggregates of CN-TFMBE inside the LC droplets. It was equipped with filters for 450–490 nm excitation and emission detection at $>510$ nm. The steady-state fluorescence emission spectra of LC gel emulsions were recorded using a fluorescence spectrophotometer (Varian Cary Eclipse) equipped with a single-cell Peltier for controlled-temperature measurements. Finally, fibrous aggregates formed inside the LC droplets and, for comparison, in the bulk LC were examined on a Hitachi S-4700 emission gun scanning electron microscope (SEM). In the case of LC gel emulsion, the sample that was used was prepared by first evaporating water at room temperature for 2 days, followed by the slow extraction of E7 in hexane. For the bulk LC gel, only the extraction of LC was required.

**Results and Discussion**

The formation of LC droplets dispersed in aqueous solution (most diameters are in the range of 2–5 $\mu$m) and the aggregation of gelator molecules inside the droplets were revealed by optical and fluorescence microscopy (images in Supporting Information). The fluorescence emission from the droplets indicates that CN-TFMBE molecules are in an aggregated state inside the LC cavities. As will be shown later, the presence of a network of fluorescent fibrous aggregates inside the LC droplets is visible under the fluorescence microscope. Considering the fact that CN-TFMBE can gel bulk LCs upon aggregation,\textsuperscript{23} the observed droplets should be gelled E7. From the microscopy images, it can be noticed that fluorescent micrographs apparently show fewer
Although there were no further increases in temperature so as to cause the varying focusing distances for the droplets located in different layers of the emulsion solution. However, it cannot be ruled out that no aggregation occurred in some LC droplets under the preparation conditions; those droplets were invisible under the fluorescence microscope.

To determine the stability of the fluorescent aggregates of the gelator inside the LC droplets, various-temperature fluorescence emission spectra of the LC gel emulsion were recorded ($\lambda_{ex} = 380$ nm). As can be seen from the spectra in Figure 2, with increasing temperature, the fluorescence intensity decreases, suggesting some thermally induced dissolution of gelator molecules in the LC host. However, the fluorescence emission remains even at 80 °C, which is above $T_{mi}$ of E7. This observation indicates that fibrous aggregates are present in the droplets of E7 in the isotropic phase, which likely gives rise to an isotropic gel. Although there were no further increases in temperature so as to avoid the evaporation of water, the results indicate that the aggregates inside the LC droplets have a melting temperature of $>80$ °C. This is no surprise considering the melting temperature of $\sim 130$ °C for the aggregates formed in bulk E7 (measured on the optical microscope). Upon subsequent cooling of the LC gel emulsion, the fluorescence intensity is only partially recovered, which can be seen from the spectrum recorded with the solution cooled to 25 °C. This suggests some irreversible structural or morphological changes of the aggregates during the thermal treatment, whereas the chromophore gelator could also undergo partial trans–cis isomerization caused and modulated by the ambient light and/or a thermal effect.\(^\text{24}\)

In a normal LC emulsion (without gelation inside the droplet), the LC configuration is determined by the anchoring of LC molecules at the aqueous interface. In an LC gel emulsion, the physical network formed by the fibrous aggregates should interact strongly with LC molecules and thus alter the LC director alignment. This indeed was observed on a polarizing optical microscope by comparing LC droplets with and without the CN-TFMBE gelator (polarizing photomicrographs in Supporting Information). For the LC emulsion without gelator, perpendicular anchoring of LC molecules at the interface results in the noticeable radial configuration for the LC droplets. By contrast, for the LC gel emulsion prepared under the same conditions, the radial configuration is no longer observable; only birefringent LC droplets could be recognized. It is no surprise that the fibrous aggregates inside the droplet disrupt the LC director alignment.

We were able to measure the change in optical transmittance in response to an electric field for single LC gel droplets of various diameters. The results have revealed the effect of droplet size on the electrooptical behavior of the LC gel. For this experiment, the initial LC gel emulsion was diluted (by a factor of 20) in an aqueous solution of 20 wt % PVA. The use of this high concentration of PVA was necessary to increase the viscosity of the emulsion so that a film with stable (immobilized) LC gel droplets could be obtained and sandwiched between two indium tin oxide (ITO)-coated glass slides. This was essential for single LC gel droplet electrooptical measurements. To prepare the film, a drop of the emulsion was cast on an ITO-coated glass slide and, after partial evaporation of water, a second slide was put on top to sandwich the LC gel emulsion film between the electrodes (the film had a thickness of about 66 μm and a surface area of about 25 mm\(^2\)). By placing the sample on the object stage of the optical microscope under crossed polarizers and using an appropriate magnification objective, a single LC droplet could be selected and positioned in the frame of the photomicrograph. Because only one birefringent LC droplet was viewed by the polarizing microscope, with the surrounding material being isotropic, the change in transmittance upon application of a voltage came from the electric field-induced reorientation of LC molecules inside the single droplet. Moreover, it should be emphasized that LC gel droplets of varying diameters were selected from the same emulsion film, ensuring that they were subjected to the same effective electric field strength, and the comparison of their electrooptical response is straightforward. Before discussing the results of the electrooptical measurements realized on single LC gel droplets of various sizes ranging from 12 to 55 μm in diameter (large droplets were selected to facilitate the single-droplet measurement), Figure 3 shows their polarizing photomicrographs in the field-off and field-on states (ac field, 1000 Hz, 5.3 V/μm, peak to peak) as well as their images recorded with the fluorescence microscope. Interesting observations can be made. First, under the same applied field strength, as the droplet size decreases, the remaining birefringence of the droplet is more prominent, indicating a more difficult field-induced reorientation of LC molecules inside the cavity. This behavior might be explained by an increasing confinement effect upon reducing the droplet size. Second, a similar network of fluorescent fibrous aggregates of CN-TFMBE is visible inside all of the LC gel droplets, suggesting that the basic aggregation process of gelator molecules remains the same under the increasingly severe confinement.

Figure 4 compares the change in transmittance as a function of applied voltage (ac field, 1000 Hz, peak to peak) for LC gel droplets of different sizes and, for comparison, the bulk LC gel. The bulk LC gel was prepared under the same conditions (2% CN-TFMBE in E7) except for being dispersed into droplets in water, and it was used to fill a 50 μm-gap ITO-coated cell for the electrooptical measurements. In all cases, the LC reorientation along the electric field direction gives rise to a drop in the transmittance. However, as compared to the bulk LC gel, the LC gel droplets have a higher threshold voltage and a lower apparent optical contrast (transmittance at field off is greater than that at 5.3 V/μm), and the effect of droplet size on electrooptical behavior is also clear: the threshold voltage increases and the optical transmittance decreases with decreasing size of the droplet. Moreover, in contrast to the bulk LC gel, the electric-field-induced reorientation inside the droplets develops gradually with the rise in voltage (the apparent shoulderlike change around 1.5 V/μm for

The electrooptical switching of the LC gel droplets is repeatable and similar to that of the bulk LC. Several cycles of transmittance change upon application (field on) and removal (field off) of a voltage (5.3 V/μm) results in no deterioration of the switching performance (an example of the measurement is given in Supporting Information). However, a close inspection reveals that their switching times are different and that the droplet size affects the switching times. Figure 5 shows (a) the decrease in transmittance upon application of an electric field of 5.3 V/μm and (b) the recovery of transmittance after turning off the field for the bulk LC gel and the LC gel droplets of different sizes; the calculated switching-on and switching-off times, defined as the time required for a transmittance change of between 10 and 90% of the initial and final levels, respectively, are indicated in parenthesis. On one hand, the comparison among the LC gel droplets shows that the switching-on time increases with decreasing droplet size, whereas the opposite trend is observed for the switching-off time. As the size of the LC gel droplet decreases, the increasing confinement renders the reorientation of LC molecules under the voltage more difficult to develop, which is also revealed by the decreasing contrast as already mentioned above. Apparently, when the field-induced reorientation is more difficult, the opposite process would be easier upon removal of the field, resulting in a faster relaxation of LC molecules returning to the initial state. On the other hand, the switching behavior of the bulk LC gel seems to be quite different from that of the LC gel droplets. Although the 55 μm droplet may be caused by data scattering related to experimental uncertainty).

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**Figure 3.** Photomicrographs for LC gel droplets of various diameters: (a) polarizing photomicrographs in the field-off state, (b) polarizing photomicrographs under a voltage (ac field, 1000 Hz, 5.3 V/μm, peak to peak), and (c) fluorescence images showing the presence of fibrous aggregates.

**Figure 4.** Change in optical transmittance vs applied voltage for the bulk LC gel and single LC gel droplets of different sizes.
switching-on time is of the same order of magnitude as for the droplets with a diameter of 30 μm or larger, the switching-off time is significantly longer than for all of the droplets.

The likely reason for the difference in electrooptical behavior between the bulk LC gel and the LC gel droplets may be the confinement effect that is absent for the former and present for the latter. Likewise, the differences among the LC gel droplets of various sizes also point to the confinement effect. However, the situation is complicated by the presence of fibrous aggregates in the LC gel droplets. Generally speaking, confinement refers to the effect arising from the curvature of the spherical cavity on the LC director and thus is mainly determined by the size of the LC droplet, regardless of the fibers inside, but at the same time, the presence of fibers obviously disrupts the LC director and creates a large interface between LC and the fibers, which can also affect the reorientation of LC molecules in response to an electric field. Therefore, for LC gel droplets, the confinement effect is coupled to both the distortion of the LC director by the fibers and the effect of fiber/LC interfacial interaction. More studies are needed to understand the coupling and interplay of the confinement effect and the effect arising from the presence of fibrous aggregates. Another point is worth mentioning. The electrooptical behavior of LC gel droplets (higher threshold voltage and lower contrast) suggests that they have limited potential for display-type applications, but sensing with LC gels in an emulsion may be of interest to explore in future work because the adsorption of an analyte at the LC gel droplet/water interface may cause a change in the electrooptical signal.

Whereas self-assembled LC gels can be prepared in the form of spherical droplets dispersed in aqueous solution, it is interesting to know how the confinement can affect the growth of fibrous aggregates of the gelator. An immediate consequence of the aggregation process occurring inside a small spherical cavity is that the straight section of a fiber cannot be longer than the diameter of the cavity and a growing long fiber must be folded to accommodate the geometry of the LC droplet. SEM was used to observe the fibrous aggregates of CN-TFMBE formed by the LC droplets. To do this, a drop of the gel emulsion was cast on a glass slide, dried at room temperature for 2 days to remove water, immersed in hexane to extract the E7 LC host, and dried again in air before the SEM observation. For comparison, a bulk LC gel was prepared under the same conditions using the same gelator and nematic LC; SEM observation was carried out on the fibrous aggregates after the extraction of E7 in hexane. The results are shown in Figure 6. In contrast to the long, extended fibrous aggregates formed in the bulk LC gel, the fibers resulting from the LC gel emulsion are highly folded, and they are also thinner than those in the bulk LC gel. Most striking is the formation of circular,
ringlike fibrous aggregates whose diameters correspond to the diameters of the LC gel droplets. The apparent fiber ring is intriguing. Because the fibrous aggregates are homogeneously dispersed inside the LC gel droplets in the emulsion (Figure 3c), the rings must be formed during the removal of the liquids (water and E7). It seems that in the course of drying, the fibrous aggregates coalesce and somehow move to and accumulate on the circumference of the droplets. At this point, we do not know how to explain this observation. With both the bulk and droplet LC gels, the fibrous aggregates are a bundle of primary fibers having a similar thickness (diameter) of about 100 nm, as can be seen from a magnified section in the inset. This result suggests that making LC gels in an emulsion, with aggregation occurring inside a small spherical cavity under confinement, might provide a way to shape the resulting fibrous aggregates in a circular form.

Conclusions

This work showed for the first time that self-assembled LC gels could be prepared in the form of micrometer-sized spherical droplets dispersed in aqueous solution. The aggregation of gelator molecules confined in spherical cavities leads to the formation of circular and highly folded fibrous aggregates, in contrast to the extended fibers formed in the bulk LC gel. The confinement also affects the electrooptical behavior, including switching times and optical contrast, of single LC gel droplets, which is largely determined by the droplet size. By building a bridge between LC emulsions and self-assembled LC gels, this study demonstrates a new hybrid LC system and thus offers new possibilities for exploring LC-based functional materials.

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Supporting Information Available: Optical and fluorescence microscope images of an LC gel emulsion, polarizing optical micrographs comparing an LC emulsion with an LC gel emulsion, and electrooptical switching data for a single liquid-crystal gel droplet. This material is available free of charge via the Internet at http://pubs.acs.org.