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Confined Liquid Crystals

Size-Dependent Ordering of Liquid Crystals Observed in Polymeric Capsules with Micrometer and Smaller Diameters**

Jugal K. Gupta, Sri Sivakumar, Frank Caruso, and Nicholas L. Abbott**

It is widely appreciated that the supramolecular ordering of polymers, surfactants, and liquid crystals (LCs) can be impacted by confinement. In many cases, however, these effects remain poorly understood. This is particularly true for LCs, for which confinement-induced ordering in natural systems (e.g., containing DNA and proteins[1–2]) underlies remarkable material properties such as the strength of spider silk,[3] and confinement in synthetic systems[4–6] influences the design of LC-based sensors,[7–10] directed assembly of microscopic[11,12] and nanoscopic[13] objects, and the interactions of light with LCs.[14,15] Although it is generally accepted that size-dependent ordering of LCs reflects a subtle competition between bulk and interfacial physicochemical factors,[16–21] for the important and prototypical case of LC droplet systems, the absence of experimental approaches that permit precise variation of LC droplet size (in a relevant size range) with rigorous control over interfacial chemistry, temperature, and other key parameters of the system has prevented elucidation of the effects of confinement. Herein we report that it is possible to extend previously reported methods[22] for the preparation of aqueous dispersions of polymer-encapsulated LC droplets into the sub-micrometer range. We use the capability to prepare micrometer and sub-micrometer LC droplets with precise control over size and interfacial chemistry to unmask size-dependent changes in LC ordering. In particular, we reveal that previous theoretical predictions of LC ordering in the limit of sub-micrometer droplet size are not realized experimentally, and we propose an alternative physical picture to account for our observations. We also report that the effects of size-dependent ordering can be exploited to manipulate LC ordering transitions that are triggered by the assembly of amphiphiles at the surfaces of the LC droplets, suggesting new principles for the design of LC-based technologies, including chemical and biological sensors.[7,8]

Although indirect observations reported in the past hint at size-dependent ordering within LC droplets,[17,20,21] direct characterization of the effects of confinement on LC droplets has not been reported. Furthermore, no prior theoretical[16,18,19,21] study has unambiguously established the effect of droplet size on LC ordering. Order-of-magnitude thermodynamic arguments that describe competing bulk and surface effects have been proposed, and these lead to the widely held but untested prediction that the ordering of LCs within small droplets will be uniform throughout the droplets[16,17,21] (see below for details). Previously, we reported the preparation of aqueous dispersions of monodisperse droplets of the nematic LC 4′-pentyl-4-cyanobiphenyl (5CB) with diameters ranging from 3 to 10 μm that were wrapped in nanometer-thick, multilayered polymeric shells.[22] Control over the LC droplet size was achieved by using monodispersed polymer shells, prepared by sequential adsorption of poly(styrene sulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) onto sacrificial silica template particles[23,24] (Figure 1 A). Herein, we report that this synthetic procedure can be extended to smaller droplets than those reported previously and most importantly to sub-micrometer-sized droplets where size-dependent ordering of LC droplets is unmasked for the first time. Figure 1 B–G shows bright-field images of 5CB-filled polymer shells with diameters ranging from 10.0 ± 0.22 to 0.7 ± 0.08 μm, demonstrating that precise control over LC droplet size extends from the micrometer-range into the sub-micrometer range. The droplets are encapsulated by identical polymeric layers, thus giving rise to identical physicochemical interactions at the interfaces of the droplets.[25] Because a large population of droplets (more than 10^9 droplets per mL) of the same size can be easily prepared, this approach enables definitive experimental observations (with high statistical confidence) regarding the size-dependence of LC ordering within the droplets. We note that microfluidic-based approaches[26] for the preparation of monodisperse droplets are relatively low in throughput and have been limited so far to droplets with diameters larger than 3 μm. As discussed below, droplets with sizes greater than 3 μm do not show size-dependent ordering of LCs.

Thermodynamic arguments reported in the past for micrometer-sized LC droplets predict that the orientation-dependent interfacial energy scales with the square of the droplet radius (ca. WR^2; W is the anchoring strength coefficient) whereas the bulk elastic energy of the LC droplet

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[*] S. Sivakumar, Dr. F. Caruso
Centre for Nanoscience and Nanotechnology
Department of Chemical and Biomolecular Engineering
The University of Melbourne, Victoria 3010 (Australia)
Fax: (+61) 3-8344-4153
E-mail: fcaruso@unimelb.edu.au
J. K. Gupta, Dr. N. L. Abbott
Department of Chemical and Biological Engineering
University of Wisconsin-Madison
1415 Engineering Drive, Madison WI 53706 (USA)
Fax: (+1) 608-262-5434
E-mail: abbott@engr.wisc.edu

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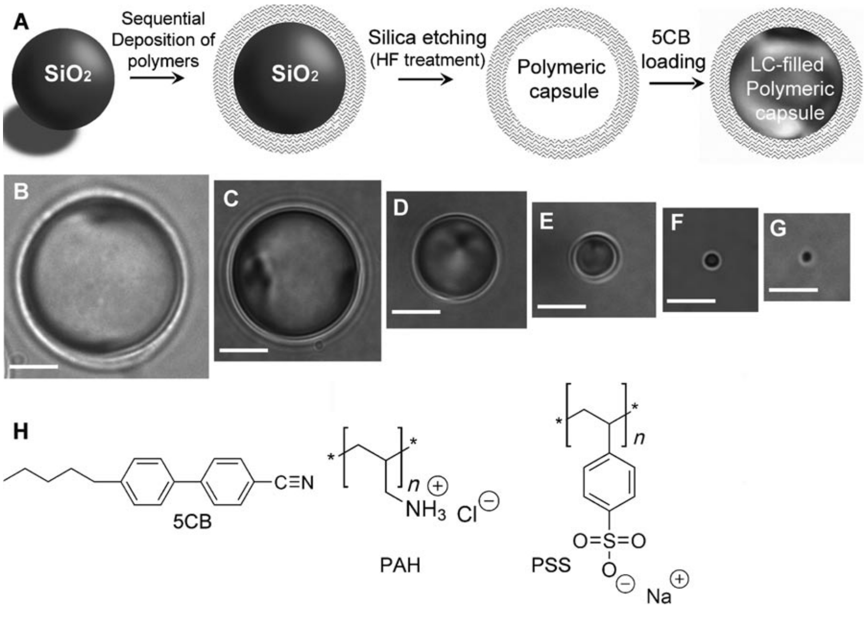

Figure 1. A) Preparation of LC droplets of predetermined sizes within polymeric multilayer shells. Polymeric shells were prepared by sequential deposition of PSS and PAH onto silica templates and subsequent etching of the silica (see also Figure S1 in the Supporting Information). The resulting polymeric shells were filled with LCs. B–G) Bright-field micrographs of polymer-encapsulated 5CB droplets obtained using silica templates with diameters of 10 ± 0.22, 8 ± 0.20, 5 ± 0.19, 3 ± 0.18, 1 ± 0.04, and 0.7 ± 0.08 μm, respectively. The scale bars in all images correspond to 3 μm. H) Structures of molecules used in this study.

scales linearly with droplet radius (ca. KR; K is the elastic constant of the LC).[16–18,21] These thermodynamic considerations lead to the prediction that LC droplets with $R \ll K/W$ will avoid spatial variation of the orientation of the LC within the droplet ($n(r) = \text{constant}$; n is the so-called director of the LC) (as shown in Figure 2B).[16,17,21] To test this prediction, we synthesized LC droplets of different sizes, but with identical surface chemistry, by using the above described procedure (Figure 1). Figure 2C,D shows polarized light and bright-field micrographs, respectively, which permit identification of the ordering of LC within droplets prepared using the 8.0 ± 0.2 μm silica template. These micrographs are consistent with two point defects at the poles of the droplet, referred to as a bipolar director configuration (Figure 2E, and Supporting Information—Section B).[21] We also observed LC-filled shells prepared from templates with diameters of 10 ± 0.22, 5.0 ± 0.19, and 3.0 ± 0.18 μm to exhibit an optical appearance identical to the 8.0 ± 0.2 μm LC droplets, thus being consistent with the presence of the two boojums (data not shown). In contrast to the larger LC droplets, bright-field images of droplets with diameters of 1.0 ± 0.04 μm (Figure 2G,I) exhibited only one point defect. The apparent location of the point defect ranged from the droplet center (Figure 2G) to the droplet edge (Figure 2I), with the majority (90%) lying between these limits (see Figure S2A in the Supporting Information). When combined with the polarized light micrographs in Figure 2F,H, these bright-field images lead us to conclude that the LC ordering within the 1 μm LC droplet corresponds to a single point defect lying on the droplet surface (Figure 2J; the apparent locations of the defects in Figure 2G,I depend upon the angles at which the droplets are viewed). This ordering of the LC is described as being "preradial".[16,27] Identification of the preradial ordering of the 1 μm-sized LC droplets was further assisted by the preradial ordering also observed with bigger LC droplets decorated with the anionic surfactant, sodium dodecyl sulfate (SDS) (see Figure S3 in the Supporting Information). Polarized-light micrographs of the smallest droplets used in our study (diameters of 0.70 ± 0.08 μm) reveal a third type of optical signature (Figure 2K) corresponding to a radial director configuration (Figure 2M). We note that the bright-field image of the 0.70 ± 0.08 μm droplet in Figure 2L does not show a point defect at the droplet center because of the far-field resolution limits of optical microscopy (see Figure S2 in the Supporting Information). Although the synthesis of droplets smaller than 0.7 μm is within the capabilities of the methods reported above, with far-field optical microscopy,

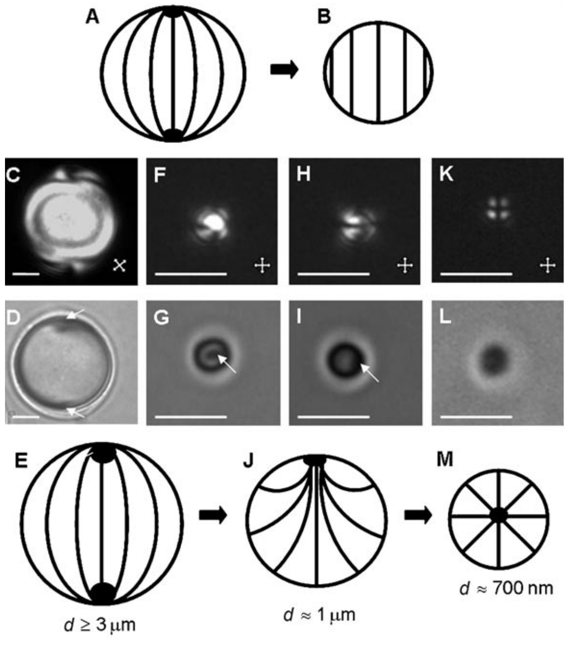

Figure 2. A) Bipolar and B) homogeneous director configurations. C, F, H, K) Polarized and D, G, I, L) bright-field optical micrographs of polymer-encapsulated 5CB droplets (see Figure 1 for details) with C, D) diameters of 8.0 ± 0.2 μm and bipolar LC ordering, F–I) diameters of 1.0 ± 0.2 μm and preradial LC ordering (F and G show the end-on views of the preradial ordering whereas H and I show side views), and K, L) diameters of 0.70 ± 0.08 μm and radial LC ordering. Point defects in the LCs are indicated by white arrows. Cartoons in E, J, and M show bipolar, preradial, and radial ordering of the LC droplets, respectively. The scale bars are 2 μm for C, D, and F–I and 1 μm for K and L. See Methods Section in the Supporting Information for details.

it is not possible to characterize the ordering of LC within droplets with diameters less than 0.7 μm.

The results above reveal for the first time that the ordering of LCs within droplets with constant interfacial chemistry changes with decreasing droplet size from bipolar (Figure 2E) to preradial (Figure 2J) and then to a radial ordering (Figure 2M). The observation of bipolar ordering in the limit of large droplet size indicates that the preferred alignment (easy axis) of the LC at the surface of each droplet is parallel to the droplet surface.[28] Our experimental observation of radial ordering in the smallest LC droplets is, therefore, surprising in light of the above-described prediction of a uniform LC orientation within small droplets (Figure 2B). To provide insight into the above observations, we considered the possible effects of saddle-splay and splay-bend elastic energies,[29] both of which were ignored in the arguments leading to the prediction shown in Figure 2B. The energetic effects of saddle-splay (K_{24}) and splay-bend (K_{13}) elasticity can be described by the Frank–Oseen elastic energy density,[21] and minimization of this energy density (Section C in the Supporting Information) leads us to conclude that radial ordering of a LC droplet (Figure 2M) is stable relative to uniform ordering (Figure 2B) when the following constraint is satisfied: $K_{11}+K_{13}+WR/6<K_{24}/2$ (K_{11} is splay elastic constant of LC). This relationship predicts that for droplets with $R<6K^{*}/W$ ($K^{*}=K_{24}/2-K_{13}-K_{11}$), uniform ordering will not be observed (relative to radial ordering). Estimates of K_{24} and K_{13} for 5CB are $K_{24}\approx 3.1\,K_{11}$[30] and $K_{13}\approx -0.2\,K_{11}$,[31] leading to $K^{*}\approx 0.75\,K_{11}$, and the conclusion that LC droplets with radial ordering are stable in the limit of small LC droplet size, as seen in our experiments. We emphasize that our experiments and our refined thermodynamic argument indicate that uniform ordering of LC within droplets should not be expected in the limit of small droplet size (provided continuum descriptions of the LC remain valid). More broadly, by tuning size at constant interfacial chemistry, our results demonstrate the subtle balance between bulk and surface energetics that controls the ordering of LC within droplets.

In addition to allowing size-dependent ordering to be identified within LC droplets with precisely controlled interfacial chemistry, the experimental system described above also enables ordering induced by changes in interfacial chemistry to be studied in LC systems of well-defined size. Here we focus on LC ordering transitions induced by SDS, as past studies have demonstrated that SDS can permeate through the polymer shell to change the orientation of the LC from parallel to perpendicular.[28] We also note that prior reports have established that a range of adsorbates (e.g., lipids,[5,6] polymers,[32] and proteins[7,9]) can trigger changes in the ordering of LCs in contact with aqueous solutions. To determine if control of the size of LC droplets might provide the basis of a simple and general method to tune LC ordering transitions triggered by interfacial adsorbates,[7,8] we investigated the bulk concentration of SDS needed to cause radial ordering of LC droplets as a function of droplet size. Figure 3 reveals that the concentration of SDS that triggers radial ordering of the LC decreases continuously with decreasing droplet size. Other results revealed that for a given concentration of SDS, LC droplets exhibit size-dependent ordering. Overall, these results led us to conclude that control over LC droplet size in the micrometer-to-sub-micrometer range does allow the ordering response of LCs to interfacial adsorbates to be tuned, and that it holds particular promise as a means to control the sensitivity and dynamic range of LC-based chemical and biological sensors.[7,8]

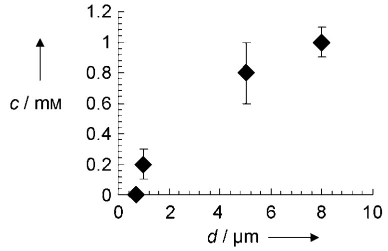

Figure 3. Size-dependent response of polymer-encapsulated LC droplets to concentration of model analyte (SDS). The SDS concentration (*c*) that causes radial ordering of the LC droplet is plotted as a function of droplet size (*d*).

In conclusion, this study establishes the feasibility of synthesizing polymer-encapsulated LC droplets with diameters in the micrometer-to-sub-micrometer range. This capability is significant because it is in the micrometer-to-sub-micrometer size range that size-dependent ordering of LCs is observed. Our observations reveal that previous theoretical predictions of uniform LC orientations in the limit of small droplet size are not realized experimentally. More broadly, our experiments resolve ambiguities in prior experimental observations regarding the effects of size and interfacial chemistry on the ordering of LCs within droplets.[17,20] Our methods also provide scalable quantities of monodisperse LC-filled polymeric shells that may be technologically useful. The size and interfacial chemistry of these LC-filled shells can be controlled at a level that has not previously been possible, and thus they open up a range of technological opportunities whereby size-dependent ordering of LCs can be exploited. For example, the interaction of light with LCs is influenced by the ordering of the LC; control of the size of LC droplets provides a general approach to manipulate this interaction. In addition, a particularly promising set of opportunities revolve around the design of LC materials that respond to chemical and biological molecules, as the response of the LCs can be tuned by subtle changes in size and interfacial conditions (e.g., binding events). In future studies we plan to explore the effects of electric and magnetic fields and additional interfacial adsorbates on LC systems with defined size and interfacial chemistry.

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