J. Am. Chem. Soc. **2000,** *122,* 6801−6802

Toroidal Droplet Formation in Polymer-Dispersed Liquid Crystal Films

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Received May 11, 2000

Polymer-dispersed liquid crystal (PDLC) thin films find applications as light shutters in a range of optical devices.[1,2] Comprised of micron sized LC droplets encapsulated in optically transparent polymers, these materials strongly scatter light in their natural state, making them translucent. They are switched to an optically transparent state by application of an electric field normal to the film surface. To completely understand their functional properties, a clear understanding of the types of LC droplets formed is required.

Both droplet shape and LC configuration play important roles in governing the light-scattering properties of the film. It is most often assumed that the droplets take on a spheroidal (or oblate spheroidal) shape,[2] and many physical models published to date have been developed under this assumption. Such droplets yield a range of nematic-like LC organizations, depending on the LC elastic constants and the surface anchoring conditions.[2] These include bipolar, axial, radial, and toroidal configurations.[2] The toroidal configuration is only expected in LC with a small ratio of bend and splay elastic constants.[3] Tangential alignment of the LC at the polymer interface is also required. However, in recent near-field scanning optical microscopy studies it was shown that the toroidal configuration is routinely observed in PDLC materials having a relatively large bend-to-splay ratio.[4] These materials are comprised of E7 (a eutectic nematic LC mixture) and poly(vinyl alcohol) (PVA). The toroidal configuration is likely induced in these solid films by the formation of toroidal polymeric cavities, as deduced from topographic images.[4] The mechanism for formation of the toroidal cavities was not explored in this previous work. Indeed, it is possible that these cavities resulted from near-field-probe-induced changes in film morphology.

In this communication, the formation of toroidal droplets in thin PDLC films is studied in detail by multiphoton-excited fluorescence microscopy.[5] The results show that the toroidal droplets form spontaneously by collapse of the polymer shell covering the droplet. Toroidally shaped objects are not specific to PDLC systems but are also found in other materials, such as vesicles and micelles,[6] and are therefore of general importance. The reasons for their formation are addressed here via studies of the dependence of droplet shape on the concentration of added surfactant. As the polymer shell covering the droplet is weakened by interfacial adsorption of surfactant, a dramatic increase in the population of toroidal droplets is observed.

PDLC films were prepared by well-known encapsulation methods.[7] They were spin cast onto glass substrates from aqueous emulsions (prepared from 18 MΩcm water) of 5% (by weight) PVA and 2% (by weight) E7, forming films of ≈1 μm average thickness. Sodium dodecyl sulfate (SDS) was used as the surfactant and was added to the initial emulsion at various concentrations prior to film casting.

Fluorescence from the LC droplets was excited by focusing ≈1 mW of 810 nm light from a mode locked Ti:sapphire laser to a diffraction-limited spot in the sample, using the 100×, 1.3 numerical aperture objective of a sample-scanning confocal microscope.[8] The fluorescence was detected with a single photon counting photomultiplier tube. In these experiments, the LC simultaneously absorbs three photons of light and subsequently emits into a broad spectrum centered near 400 nm. Proof that excitation is by three-photon absorption is obtained from the power-dependence of the fluorescence. log−log plots of signal vs incident power are linear and have a slope of 2.9 ± 0.1. It is believed LC fluorescence comes from excimers.[9] The experimental details and the spectral and temporal characteristics of the emission are given elsewhere.[10] To the authors' knowledge, this study represents the first demonstration of multiphoton-excited fluorescence imaging of PDLC materials. These methods are much less invasive than the previously applied near-field methods,[4] and extremely soft materials may be imaged, without a substantial loss of spatial resolution.[11]

Figures 1a,b show two fluorescence images of the same droplet recorded with different incident polarizations. This droplet was found in a film prepared without added surfactant and is typical of the majority of droplets in such films. Images recorded at different focus depths show the droplet to be of oblate spheroidal shape. Multiphoton excitation processes are strongly polarization dependent,[12] and LC organization is readily deduced from these images. For the uniaxial LC studied here, the intensity of the fluorescence scales as $\cos^6\theta$, where θ is the angle between the polarization vector of the incident light and the local nematic axis. The images shown prove the LC is organized in the well-known bipolar configuration,[13] shown schematically in Figure 1c. Note that the LC aligns tangential to the polymer/LC interface in the E7/PVA system.

While droplets of spheroidal shape and bipolar configuration are expected, droplets with the unexpected[3] toroidal configuration are also observed. Figures 1d,e,f show typical images and a model for such droplets. A bipolar droplet with its average nematic orientation normal to the film plane could yield optical images similar to those shown; however, the bright lobes would be rotated by 90° in the sample plane, under the polarization conditions employed. In films with no added surfactant, approximately 8% of droplets have a toroidal configuration, the remainder being predominantly bipolar. In all samples, droplet shape and LC configuration are also observed to depend on droplet size. Small droplets (i.e. <2−3 μm diameters) are predominantly spheroidal while larger droplets can be toroidal. The toroidal droplets are believed to form via collapse of the polymer shell covering the droplet,[4] thus forming a toroidal cavity in the film. Fluorescence images recorded at different focus depths indeed show little fluorescence from the droplet center, as expected for such droplets.

Studies of films prepared with varying concentrations of SDS provide valuable evidence as to the origins of the toroidal droplets. They also provide evidence supporting the conclusion that they are formed by collapse of the polymer shell. Addition of

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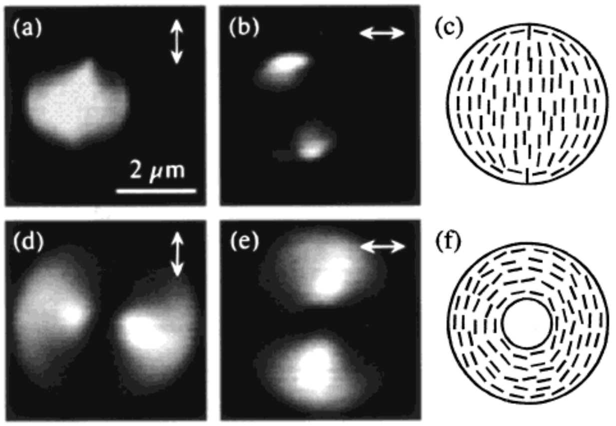

Figure 1. (a and b) Three-photon-excited fluorescence images of a spheroidal droplet in a PDLC thin film prepared in the absence of SDS. The white arrows indicate the direction of the incident polarization (±5°). (c) Schematic of the LC organization. (d and e) Three-photon-excited fluorescence images of a toroidal droplet. The polarization dependence proves the LC is organized in a toroidal fashion. (f) Model for the LC organization.

surfactants has been proposed previously as a good method for stabilizing PDLC dispersions and controlling LC anchoring at the polymer wall,[14] but no mention of its effects on droplet shape in solid films has been found.

Films prepared from emulsions containing 5 mM SDS (below the critical micelle concentration, CMC, of SDS in water) show a significant increase in the fraction of toroidal droplets. Images similar to those shown in Figures 1d,e are typically observed. Approximately 42% of the droplets in these films appear to be of toroidal shape. At even higher surfactant concentrations of 24 mM (above the CMC), more droplets with profoundly narrower toroidal cavities (i.e. having a smaller internal diameter) are found. Figures 2a,b show images of such a droplet. Approximately 32% of the droplets are found to be of similar shape. The smaller number of toroidal droplets in this sample is due to the decrease in average droplet radius brought about by the surfactant. Finally, the spheroidal droplets in the film were found to incorporate complex LC configurations, as shown in Figures 2c,d.

From the surfactant concentration dependence, it may be concluded that the toroidal configuration is induced by the collapse of the polymer shell covering the droplet, under the mass of supported polymer. An approximately toroidal cavity results. In all cases, collapse of the shell likely results from LC leakage from within the droplet. Such leakage may occur via evaporation through pores in the shell after the film has been cast, or via mechanical (shear) rupturing of the shell during spin casting. As surfactant is added, interfacial polymer is displaced by surfactant, weakening the shell. As a result, the shell becomes more fragile and more permeable, readily leaking encapsulated LC. Toroidal droplets may also result from film shrinkage during drying. As the polymer shrinks, the cavity diameter grows (in the film plane), causing the droplet (of constant volume) to collapse in the center. It is likely that both mechanisms play a role as toroids are observed in films prepared without spin casting (simple evaporation) as well; at present, it is difficult to determine which of the two mechanisms is dominant.

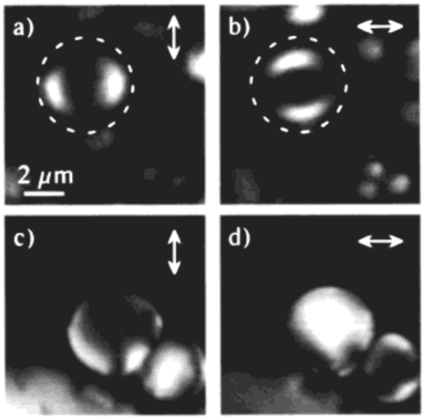

Figure 2. (a and b) Toroidal droplet in a thin film prepared from an aqueous emulsion with 24 mM surfactant (inside dashed circle). (c and d) Complex LC configuration in spheroidal droplets in the same film. The white arrows indicate the direction of the incident polarization (±5°).

It may also be concluded that the extent of shell collapse is highly dependent on the strength of the polymer shell. As the shell collapses in systems with low surfactant concentration, the relatively strong polymer shell bends in a large radius. Toroidal droplets with "smooth" surfaces result. The droplet walls (outer circumference) partially support the shell covering the droplet; therefore, it only collapses in the center. At higher surfactant concentrations, because the shell is significantly weaker, it collapses further. As shown in Figures 1d,e and 2a,b, the internal diameter of the toroidal cavity is dramatically smaller, as evidenced by the narrower "ring" of fluorescence in Figures 2a,b. At high surfactant concentrations the shell may also fold or wrinkle. The LC then takes on a complex organization as a result of the complex shell structure and (possibly) altered polymer/LC interfacial interactions.[14]

The presence of LC droplets of toroidal shape in PDLC films contributes to the broad range of optical properties often observed in PDLCs.[1] While toroidal droplets have been shown to form spontaneously, the results presented here also suggest droplet shape in solid films can be controlled by addition of surfactants. Using such methods, it may be possible to fabricate films comprised entirely of toroidal droplets, allowing for their optical properties to be exploited in PDLC devices.

Acknowledgment. The authors thank the National Science Foundation (CHE-9701509 and CHE-9709034), 3M Corporation, and Kansas State University for financial support. Jesus E. Hernandez, Maryanne M. Collinson, and the reviewers are thanked for their contributions to this paper.

JA001617J

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