Complex Ordering of Supramolecular Dendrimers in Confined Geometries.

Dong Ki Yoon[1], Myung Chul Choi[2,3] , Yun Ho Kim[1], Mahn Won Kim[2], Hee-Tae Jung[,1]*

[1] Department of Chemical and Biomolecular Eng., KAIST, Daejeon 305-701, Korea
[2] Department of Physics, KAIST, Daejeon 305-701, Korea
[3] MRL, UCSB, Santa Barbara, CA93106, USA
heetae@kaist.ac.kr

The self-assembly of supramolecular dendrimers allows the rapid construction of nanosized structures with regularly ordered features that depend on the shape of the molecules and the relative strength of the intra- and intermolecular interactions. Recently, it has been reported that the defects of smectic (Sm) LCs can make well ordered patterns in a confined area. Defect of LCs were extensively studied theoretically and experimentally not only in the efforts on minimizing defects, including by using microstructures (grooves and gratings) in technological applications such as displays and optical switches, but also by the interest in the unique rheological and optical properties. However, the defect domains possess unique rheological and optical properties, which could potentially be exploited to make novel materials. The prerequisite for doing so would be the control of the type, size, and spatial distribution of the defects, which had not been well addressed in previous studies. In this work, we present the control of the size and spatial distribution of toroidal defects in the Sm LC dendrimers by using surface modified microchannels. By changing the feature size of the micro-scale channels with a controlled surface, we were able to generate very uniform toroidal defects in size with 2D ordered regular patterns.

This process is analogous to colloidal crystallization, except here the "colloids" are the "soft" micro-sized defects within the LC. The defect ordering results from the competition between the boundary conditions and the elasticity of the Sm phase, whereas the ordering in colloids is caused by interparticle interactions. The electric field driven elliptic disclination loops, the undulating paired disclinations in bulk cell, or point radial hedgehogs in Sm LC droplet suspended on planar matrix, have been made by using polarized optical microscopy (POM). The direct imaging of electron microscopy (EM) of a novel defect topology of interconnections between defects, which is a network of bilayers in a hydrogel, were reported The vesicles of nonzero genus have been investigated, since the formation of wormholes has been observed first in multi-lamellar vesicles of binary lipid-water systems and studied with the curvature model.

Here, we present defect ordering formed over large areas (~10 mm) of the microchannel with perfect persistence. The order and orientation of supramolecular dendrimers can be controlled by surface anchoring in confined geometries. POM, SEM, TEM, AFM and XRD results show that the molecules form the complicated defect-ordering in the microchannels with different feature sizes. We show that these defect domains are strongly influenced by the boundary and feature size of the surfaces. This technique can be used to create a grain size in the plane of the film that is much larger than that which can be achieved using previously reported soft-material based pattering.

To recognize the complex LC ordering in the channels, we used various experimental tools such as SEM, FF-TEM and GIWXAS from the micrograph of an area on an unconfined area of the droplet. At thermal transition point, the materials begin to form Sm phase cooling from isotropic melt. Interestingly, specific gaping holes were formed by changing surface treatment. In this work, we found that boundary condition plays a important role in forming focal conic LC defects on the modified surfaces. The difference of stiffness between hole and layer structure cause to anisotropic split, therefore, and we could observe that the LC (**F7A)** droplet is arranged into stacked-lamellar microstructure (Figure 1 (c)). Based on the direct observation, we recognize that planar lamellar sheets of LC material at the bottom changes into the homeotropic orientation at the top.

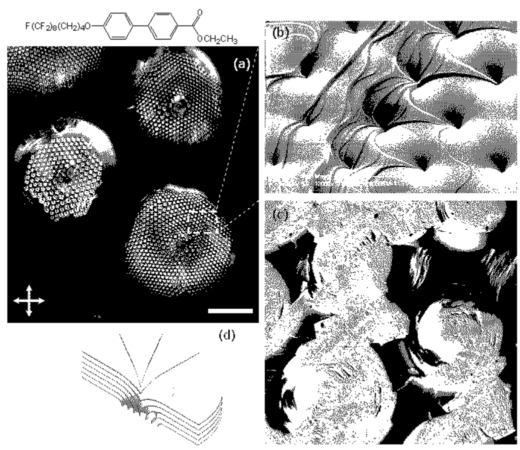

Figure 1. Molecular structure of **F7A** (a) POM image of **F7A** droplet on a flat Teflon-AF coated Si wafer surface. The LC droplet is densely populated by toroidal defects that have a small size distribution. (b) SEM image of an area on an unconfined area of F7A droplet populated by nearly mono-dispersed toroidal defects. (c) Internal structure of F7A droplet shows stacked lamellar sheets clearly. (d) A side cut view of a toroidal defect. Lamellar sheets become hollow, which change from planar orientation at the bottom to the homeotropic orientation at the top.

Interestingly, the defect ordering is clearly appeared over the entire length (~10 mm) of the microchannel with very high persistence. The defects in the channels adopt well defined sizes, with the average diameter of the circular defect approximately equal to the critical dimension of the channel. Moreover, the defects appear to be arranged in periodic lattices perfectly in the ~5μm channel with one-dimensional symmetry.

The ordering of the uniform defect domains into quasiperiodic patterns can be qualitatively understood by considering the elastic and interfacial energies. The toroidal defects arising from a combination of boundary layer conditions with lower surface energies have stored elastic energy, and can essentially be considered as "hard" objects. Defect domains interact with each other through long-range elastic interactions mediated by the connecting Sm layers. When the concentration of defects becomes sufficiently large, the distribution of the defects into ordered patterns becomes energetically favorable This is due to the fact that it lowers the elastic distortion energy in regions between defects. A detailed theoretical understanding of the size selection and spatial ordering of the defects must take into account the interplay between surface and bulk elastic energies.

The patterning of uniform-sized defects described here offers tantalizing hints to the novel physical properties and possible applications of this material. In terms of its mechanical properties, it is expected that the ordered defects behave as a quasi-2D solid with an in-plane elastic modulus, analogous to colloidal crystals. The ordering of the highly birefringent defects opens the way to harnessing the unique nonlinear optical properties in the LC defect domain. It would be possible to use the ordered patterns as templates for new materials, which would open up many potential applications such as opto-electronics, chemical and gene carriers.