Liquid crystalline cellulose-based nematogels

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Physical properties of composite materials can be pre-engineered by controlling their structure and composition at the mesoscale. However, approaches to achieving this are limited and rarely scalable. We introduce a new breed of self-assembled nematogels formed by an orientationally ordered network of thin cellulose nanofibers infiltrated with a thermotropic nematic fluid. The interplay between orientational ordering within the nematic network and that of the small-molecule liquid crystal around it yields a composite with highly tunable optical properties. By means of combining experimental characterization and modeling, we demonstrate submillisecond electric switching of transparency and facile responses of the composite to temperature changes. Finally, we discuss a host of potential technological uses of these self-assembled nematogel composites, ranging from smart and privacy windows to novel flexible displays.

INTRODUCTION

Composite materials exhibit physical properties that depend on their structure and composition at the mesoscale. However, the approaches to controlling the mesoscopic structure and the ensuing properties are limited and rarely scalable. This is especially true for a broad family of materials, called "gels," which finds important technological and scientific applications, ranging from biomedical uses of hydrogels to applications of aerogels in thermal insulation and detection of Cherenkov radiation (1–). Despite large diversity, these materials share a common feature of having three-dimensional (3D) networks of nanoparticles or molecules surrounded by a fluid- or a gas-like medium. These networks are often anisotropic in nature, that is, made of rodlike or ribbon-like and other kinds of anisotropic building blocks ( ). Sol-gel transitions are often accompanied by various types of

exchange of the fluid within the gel, which includes the replacement of water with isopropanol and then with the nematic LC 4-cyano-4′-pentylbiphenyl (5CB), transforms this gel solid first into an ordered organogel and then into a nematogel (Fig. 1, C, D, G, and H), as described in detail in Materials and Methods.

The phase behavior of the nematogel as a composite is substantially different from that of the pristine bulk 5CB LC. This new behavior is caused by paranematic ordering of 5CB molecules induced by the network of nanofibrils, with surfaces prompting their tangential orientation with respect to the nanofibers, similar to nematic LCs in other confinement geometries (–1). The thermodynamic phase behavior of condensed matter is often modified by external fields and confinement so that material systems can exhibit ordered states even at temperatures at which they cannot be thermodynamically stable without fields or nanoconfinement (1). In the case of nematic LCs, the paranematic state is such a state that typically can exist in the presence of fields or confinement even at temperatures above the nematic-isotropic phase transition temperature. For example, these effects of confinement-induced paranematic ordering have been studied previously in polymer-dispersed LCs and other nanoscale confinement geometries (10–1). Optical observations, including light transmission and polarizing microscopy textures, reveal that the nematogel composite formed by 5CB

of nematic-isotropic transition T_{NI} of the pristine 5CB nematic fluid and just above T_{PNI} of the nematogel composite (Fig. 2, B and E). The CNF network preserves its nematic-like order and shows birefringence under POM at temperatures not only above T_{NI} of 5CB but even above T_{PNI} of the nematogel composite (Fig. 2, C and F). Even above T_{PNI}, optical anisotropy due to the nematic network of CNFs is additionally enhanced by the short-range paranematic ordering induced by the CNF-5CB interfaces (*1*), as already discussed above.

At temperatures above T_{PNI}, the nematogel exhibits high transparency across a wide range of the visible and near-infrared spectrum, even higher than that of the original cellulose-based hydrogel or organogel

of the CNF network, yields the equilibrium director configurations within the nematogel at different fields, albeit the high-field behavior cannot be easily accounted for analytically (1,) and requires numerical studies. We therefore first consider this problem at the onset the Fréedericksz transition, at the lowest threshold field when the dielectric torque overcomes the elastic and surface anchoring torques in prompting the director realignment (1,). This problem can be treated for the LC nematogel cell of gap thickness along the applied field direction, assuming that it can then be extended to understand the realignment transition in each of the identical rectangular nematogel domains confined by the CNF network. The total bulk free energy density (per unit volume within each compartment) of the nematic LC can be expressed as

$$ = \frac{}{2}\left[\left(\frac{q}{}\right)^2 + \left(\frac{q}{y}\right)^2\right] - \frac{1}{2}e_0 De\ ^2 \sin^2 q \qquad (1)$$

where q ($_{,y}$) is the distortion angle of the nematic director with respect to the axis, is the average Frank elastic constant of the LC, e_0 is the vacuum permittivity, De is the LC dielectric anisotropy, and is the electric field ( ). With finite surface anchoring on the perimeter of each of the rectangular director domains, the geometric parameters and have to be modified to account for the finite-strength boundary conditions at the CNF-5CB interfaces. For this, we assume that the

boundary conditions are tangentially degenerate and that the surface anchoring energy per unit area can be expressed in the Rapini-Papoular form: $= \sin^2 q/2$, where is the polar surface anchoring strength coefficient characterizing director-CNF coupling at the surfaces in the cot(t)0Tc1.93(ngm7Tc1ed)-1d8Tc1e8.3(ng)-3939-9.46T attrg

times. Because the falling time is $t_{\text{falling}} \quad {}^2_c = g/(e_0 De)$

19. , . , , ., ..., Principles of Condensed Matter Physics (, ... , ... , 2000).

20. . . , . . , ... , . . . , . . . , ... , ... Nano Lett. **10**, 1347–1353 (2010).

21. . . , . . , Introduction to the Theory of Soft Matter: From Ideal Gases to Liquid Crystals (. . . . , 2015).

22. . . . . , A. . . . . Chem. Soc. Rev. **40**, 3941–3994 (2011).

23. . . . . . . , ... , Comprehensive Cellulose Chemistry: Fundamentals & Analytical Methods (. . , . . 1, 1998).

24. . . . . Mol. Cryst. Liq. Cryst. **100**, 327–340 (1983).

25. . . . . Liq. Cryst. **31**, 989–992 (2004).

26. . . . . Phys. Rev. Lett. **69**, 2094–2097 (1992).

27. . . . (1992). . . . . 593.1(. .)-341(. .)-337.6. . . . . 0.4970 . . (. 77(. 5(0.5(. 3 . . -336. . .) . 01 . . (. .)-336. .). 34. . . . .)-329.7(.)-336.7 . 8 . . 01-1.3781 . .)-

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