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Smart shell membrane prepared by microfluidics with reactive nematic liquid crystal mixture

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ABSTRACT

Smart, uniform-sized, solid-state nematic liquid crystal (NLC) (NLC_{solid}) shell membranes were successfully fabricated from a reactive mesogen mixture (RMM727) and 4-cyano-4′-pentylbiphenyl (5CB) using a microfluidic method that combines flow-focusing and co-flow glass capillary geometries after UV curing and 5CB extraction. The NLC shells having planar anchoring with poly(vinyl alcohol) (NLC_p shells) showed unavoidable defects as per the Poincaré theorem, with a total of +2 defect strengths on the top of the shell (often the weakest point of the shell), and were usually ripped during UV curing. The NLC shells having homeotropic anchoring with sodium dodecyl sulfate/polysorbate 80 (1/1, w/w) (NLC_h shells) had a defect-free structure and could be formed into NLC_{solid} shells without ripping when the density of the RMM727/5CB mixture matched that of the aqueous medium in the microfluidic channel (controlled using a glycerol/water mixture). The thin part of the NLC_h shell was easily ripped during UV curing without density matching. The thus-produced NLC_{solid} shells exhibited good swelling/shrinkage properties depending on the solvent quality and temperature, which could be further utilized for encapsulating/releasing Rhodamine 6G in/from the core of the NLC_{solid} shell. The pores in the NLC_{solid} shell (the size of which was controlled by the 5CB content of the RMM727/5CB mixture) were completely closed in a poor solvent and open in a good solvent. The encapsulation/release properties were studied based on the fluorescence intensity of encapsulated Rhodamine 6G. This study provides a method for preparing uniform-sized and robust NLC_{solid} shell membranes that can be used for several applications, such as in smart actuators, sensors, and parts of microelectromechanical systems.

1. Introduction

Uniform-sized liquid crystal (LC) shells were realized after recent developments in microfluidic methods, and the effects of the LC shells on defect structures, anchoring conditions [1–5], transitions [3,6,7], and theoretical simulations [8–13] have been investigated. In particular, topological defects of nematic liquid crystal (NLC) shells have been found to depend on the anchoring conditions [1,5,14–18]. The topological defects occur on the surface; thus, defects on both the inner and outer interfaces between the NLCs and the isotropic liquid should be considered for NLC shells. The anchoring conditions at the interface can be easily controlled using coating materials [19] like poly(vinyl alcohol) (PVA) [20,21] and sodium dodecyl sulfate (SDS) [22], which introduce planar and homeotropic orientations against the interface, respectively. NLC shells with planar anchoring on both the inner and outer surfaces show defect structures with a total defect strength (s) of 2, according to the Poincaré theorem [23,24]. In this case, defects on the inner surface are located at the same position as those on the outer surface, such that only one set of defects is visible. The pairs of surface defects are located at the top of the shell because of the inhomogeneous thickness of these shells, which are thinnest at the top, precisely where the defects are found [25]. When the anchoring is perpendicular with SDS on both the surfaces, no defects are required anywhere inside the shell and the Maltese cross pattern is observed. Hybrid anchoring with planar outer and homeotropic inner surfaces (or vice versa) is also possible. The two +1 defects on the planar hybrid anchoring surface are separated at the opposite poles in this hybrid anchoring [25]. A recent study revealed that the NLC shell with homeotropic anchoring (controlled by only SDS during the production of the NLC shell in the microfluidic channel) is easily ruptured into a single NLC droplet [25]. This instability of the homeotropic NLC shell was overcome by using a mixture of SDS/polysorbate 80 (TWEEN80) instead of SDS. NLC droplets can also be obtained in the PDLC system wherein the size and morphology can be regulated accurately [26,27].

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However, most studies of NLC shells are focused on the configuration of the NLC shell with defects and are limited to low-molecular-weight, non-polymerizable NLCs [4,6,28,29]. Solid-state NLC shells (NLC_{solid} shells) are highly desirable for real applications of NLC shells under robust conditions. Zentel et al. reported the fabrication of one-piece micropumps from NLC core-shell elastomer particles using a microfluidic double-emulsion process [30]. The flow-induced orientation of the mesogens is made permanent by UV-initiated polymerization and crosslinking. The NLC elastomer shell contains a liquid core, which is reversibly pumped into and out of the particle by actuation of the liquid crystalline shell in a jellyfish-like motion. However, since they used the melt state of the reactive monomer mixture to be processed in the microfluidic channel, their study requires a customized heat-resistant microfluidic device with temperature-tolerant silicone oil as the outer continuous phase [31]. Another way to make NLC_{solid} droplets (not shells) in the microfluidic channel at room temperature without a heating device is to use a mixture of reactive mesogen (RM) and NLC [32–34]. Complete NLC_{solid} droplets can be obtained after UV irradiation and extracting the non-reactive NLC [35]. The ordered NLC within the droplets functions as a template for polymerization reactions, thus leading to the generation of micrometer-sized anisotropic polymeric networked particles. However, the produced solid-state particle changed its initial configuration after UV curing and NLC extraction. Recently Abbott et al. reviewed the shape change of polymeric networked particles templated from chemically patchy, anisometric, and mesoporous NLC droplets [36]. Photopolymerization of RM is accompanied by a large volume change; therefore, the change in droplet shape is unavoidable [34,39]. In particular, the NLC_{solid} shell made from the RM/NLC mixture has not yet been reported because of these manufacturing difficulties. A commercial RM mixture (RMM) can be formed into thin birefringent films through in-situ polymerization without any significant dimensional changes. If the RMM has sufficient flow ability, it can be used as a dispersion phase without a solvent in a microfluidic channel. This flow ability (measured from viscosity) can be controlled by mixing the RMM with NLC. After the non-reactive NLC extraction, the fully polymerized NLC droplets (or shells) can be obtained and the internal orientation of the solid-state NLC droplets (or shells) is retained after NLC extraction. They can be stored over long periods in the dry state and be used when needed. Thus, well-defined NLC_{solid} droplets (or shells) have many advantages over NLC droplets obtained without polymerization.

In this study, uniform NLC_{solid} shells were fabricated from a RMM727 and 4-cyano-4′-pentylbiphenyl (5CB) mixture using a microfluidic method that combines flow-focusing and co-flow glass capillary geometries after UV curing and 5CB extraction. The non-reactive 5CB was easily extracted after UV irradiation to obtain NLC_{solid} shells. We investigated the effects of the surface anchoring conditions and the 5CB content of the mixture (ϕ) on the structure and stability of the NLC_{solid} shell. The fabricated NLC_{solid} shells showed good swelling/shrinkage depending on the solvent quality and temperature, which can be further utilized for encapsulating/releasing materials in/from the core of the NLC_{solid} shell. In this paper, we describe a method for preparing uniform and robust solid–state shells, which can have several applications, such as smart actuators, sensors, small reactors, and parts of microelectromechanical systems.

2. Experimental

2.1. Materials

RMM727 (reactive LC mesogen mixture, Merck, UK), 5CB (Synthon, Germany), PVA (Yakuri, Japan), SDS (DC chemical Co., Ltd, Korea), polysorbate 80 (TWEEN 80, Sigma-Aldrich, America), *n*-hexane (Junsei, Japan), and methanol (Junsei, Japan) were used as received. Toluene, benzene, tetrahydrofuran (THF), pyridine, dichloromethane (DCM), ethanol, and acetone were purchased from Duksan (South Korea) and were used as received. Predetermined amounts of RMM727 and 5CB were mixed at 60 °C for 12 h by magnetic stirring followed by cooling to 25 °C, after which the transparent mixture turned milky. The 5CB content of the mixture of RMM727 and 5CB is denoted as ϕ. The NLC_{solid} shells in water and pyridine were freeze-dried with a freeze dryer (fd-1000, EYELA, Japan).

2.2. Preparation of NLC_{solid} shell using microfluidics

A micro-capillary device, consisting of two tapered, round glass capillaries (tapered ends pointed toward each other) enclosed in a square glass capillary, was used to prepare the NLC shells from RMM727 mixed with 5CB, as shown in Figure SI 1. The detailed experimental method can be found in Text SI 1. To stabilize the NLC shells and prevent them from rupturing, the two aqueous phases must contain either a surfactant or polymer that adsorbs at the NLC/aqueous interface; we selected PVA and a SDS/TWEEN80 mixture for planar and homeotropic anchorings, respectively. The NLC shells were collected in a vial at the end of the outlet tubing. The produced droplets were cured by UV irradiation at 365 nm with alternate 5-s sequences of turn-on and turn-off for 20 min using a UV curing machine (Innocure 100N, Lichtzen, South Korea). Thus, the total UV exposure time was 10 min. The UV-cured NLC_{solid} shells were washed 10 times with acetone to extract 5CB. UV curing caused slight shrinkage of the NLC shell, and consequently, the initial configuration was sometimes deteriorated. We employed the sequential (on/off) UV irradiation condition for UV curing because this method affords NLC_{solid} shells with almost the same configuration as that of the NLC shells before curing. This is possibly because the chains were relaxed in the off state so that the original configuration of the NLC shells did not show any notable change.

2.3. Measurements

The formation of NLC shells on a chip was imaged using a high-speed digital video-recording camera (MotionBlizt Cube4, Mikroton, Germany) with an inverted microscope (JSP-20T, Samwon, South Korea). The NLC (and NLC_{solid}) shells were examined using a polarized optical microscope (POM, ANA-006, Leitz, Germany) under crossed polarizers using a charge-coupled device (CCD) camera (STC-TC83USB, Samwon, South Korea). An image of the surface of the NLC_{solid} shell was obtained using a field-emission scanning electron microscope (FE-SEM; SU8220, Hitachi, Japan) operated at an accelerating voltage of 3 kV. The samples for SEM were prepared by coating the surface of the NLC shell with Pt. Attenuated total-reflection Fourier-transform infrared (ATR-FTIR) spectra were obtained from 600 to 4000 cm^{-1} at 4 cm^{-1} resolution by averaging 64 scans (FTIR-4100, Jasco, Japan).

2.4. Measurement of density of RMM727/5CB mixture

A floating method was used to determine the density of the RMM727/5CB mixture. The droplet can be in the middle of the fluid when its density is the same as that of the fluid. The density of the fluid was controlled by the mixing ratio of glycerol and water. The glycerol content in the mixture is denoted as φ. Images of vials containing NLC droplets at ϕ = 20, 40, 60, and 80 wt% at different values of φ are shown in the supporting information (Figures SI 2a–2d). For example, the NLC droplet (ϕ = 20 wt%) floats at φ_{float} = 45 vol%; however, it lies at the bottom of the vial at φ = 44 vol% and at the top of the vial at φ = 46 vol%, indicating that the density of the NLC