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Room-Temperature Fabrication of Mono-dispersed Liquid Crystalline Shells with High Viscosity and High Melting Point

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We propose a new method to fabricate mono-dispersed liquid crystalline (LC) microcapsules with shells consisting of LC materials showing high viscosity and/or high melting point at room temperature. In this method, it is important to control the state of the shell phase by the addition and removal of agents inducing LC-to-isotropic phase transitions at the right times.

Core-shell double emulsions (liquid microcapsules) show various functions suitable to widespread applications owing to their capabilities to dissolve any molecules and to disperse any particles in each of the core and shell phases.^{1–3} The fabrication techniques of liquid microcapsules have been sophisticated. In particular, glass microcapillary systems⁴ enable us to easily combine a variety of fluids into mono-dispersed tailor-made liquid microcapsules; e.g., photonic microcapsules with a shell of colloidal suspensions,⁵ microcapsules tagged with colourful quantum dots and/or magnetic nanoparticles,⁶ magnetically controllable microcapsules with a shell or core of the suspension of magnetic nanoparticles,⁷ magnetically controllable antioxidative microcapsules with a shell of a nitroxide radical liquid,⁸ and microcapsules sensing H₂O₂ with a core of a luminol solution showing chemiluminescent reaction.⁹

Since the first example of nematic liquid crystalline (NLC) double emulsions with NLC shells was reported,¹⁰ LC microcapsules have attracted a great deal of attention in physics¹¹ because LC materials confined in 3D geometries show unique properties and functions.¹² LC phases have molecular orientational ordering, whose direction is called director. Thus, when LC materials are confined in a spherical shell, topologically-inevitable defects emerge in their director fields.^{11,13–16} Such topological defects have recently been

vigorously investigated as promising systems for generating functional colloidal arrays.¹⁷ Furthermore, a lot of functional NLC microcapsules have been reported; NLC elastomer shells containing a liquid core act as reversible micropumps rendering micromachining techniques¹⁸ and pH-responsive NLC microcapsules coated with a pH-responsive polyelectrolyte block copolymer are potentially promising for LC-based biosensors.¹⁹ In addition to NLC microcapsules, cholesteric LC (CLC) microcapsules act as photonic microcapsules such as phototunable omnidirectional laser resonators,^{15,20} unclonable patterns for secure authentications²¹ and highly sensitive H₂O₂ sensors.⁹ In these cases, CLC shells enhance emission intensities of both photoluminescence of dyes and chemiluminescence of luminol reaction. These functions are attributed to their 3D alignment of the director.

One of unique properties of LC microcapsules is that the core-shell structure can be stabilized without adding any surfactants to the shell phase owing to the LC orientational elastic forces.¹⁰ Of course, in general the addition of appropriate surfactants to outer and shell phases is needed to stabilize the liquid microcapsules. In contrast, since the most stable director fields in LC microcapsules have one of the local minima of the elastic energy, the rupture of the LC shells accompanied with the deformation of LC director fields is avoided. Moreover, since most of surfactants are incompatible with LC materials, such surfactants dispersed in the shell phase simply work as impurities in the LC director fields and make the LC microcapsules unstable. Therefore, LC microcapsules with a low-viscosity LC shells can be easily prepared by the glass microcapillary devices; the fabrications and properties of NLC and CLC microcapsules with low-viscosity materials have been reported.^{9,11,13–16,19–21} In contrast, most of LC materials show high viscosity and/or high melting points; it is extremely difficult to fabricate microcapsules with a shell consisting of higher-ordered smectic and columnar LC materials using the microcapillary systems at room temperature.

To treat substances showing high viscosity or crystalline (Cr) phase in the microcapillary systems, heating and solvent

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addition have been reported to be effective; microspheres consisting of oil with high melting points^{22,23} and polymersomes²⁴ with a shell of solid polymers can be produced by using the microcapillary systems. As temperature increases, solid-to-liquid phase transitions occur and viscosities decrease.^{22,23} In fact, the fabrication of smectic A (SmA) and smectic C (SmC) LC microcapsules by using such heating systems have been reported.^{25–28} However, since we cannot heat the system above the boiling point of water when we fabricate microcapsules with aqueous phases, it is impossible to use LC materials that cannot flow under 100°C. Meanwhile, when the appropriate solvent is added, solid-to-liquid phase transitions occur and viscosities decrease. Core-shell structures are fabricated with the liquid phase induced by using the solvent. In the previous reports, after the encapsulation, the solvent is removed slowly by the phase separation with the shell material.²⁴ Thus, surfactants are needed to stabilize the core-shell structure in the encapsulation and solvent removal processes. However, as mentioned above, surfactants dispersed in LC phases disturb the orientational ordering in the LC phases. As far as we know, there have never been any reports on the fabrication of LC microcapsules by using an LC material dissolved in a solvent.

Here, we describe the microfluidic fabrication methods of mono-dispersed LC microcapsules at room temperature with an LC material showing high viscosity and/or higher melting points than room temperature neither by heating nor by adding surfactants but by using a small amount of Excipient Liquid Instantly eXcluded Into Rushing outer phase "elixir". Shell phases added the elixir show isotropic (Iso) phases until contacting with inner and outer phases. And then, the elixir is removed instantly during the encapsulations, the Iso-to-LC phase transition occurs, and the LC orientational elastic force recovers to stabilize the core-shell structure.

First, we tried to fabricate LC microcapsules with a shell of a well-known high-viscosity SmA compound, 4-cyano-4'-octylbiphenyl (8CB, Fig. 1a and b), which have been previously fabricated by the heating method,^{25–28} by using an elixir at room temperature. 10 wt% poly(vinyl alcohol) (PVA; MW: 13 000–23 000 g/mol, 87–89% hydrolyzed) aqueous solution was employed as the inner and outer phases to stabilize LC shells with tangential aligning boundary condition. We added acetone (20 wt%) as the elixir to 8CB. In fact, the addition of the elixir induced SmA-to-Iso phase transition; 8CB with the elixir shows the fluidity suitable for microcapillary systems (Fig. 2). In the emulsification process, the shell phase was transparent before contacting the aqueous phases, and then, it became opaque immediately after the encapsulation as shown in Fig. 2b and Movie S1. At the same time, the birefringence observed under a polarizing microscope (Fig. 2c and Movie S2) indicates that the Iso-to-LC phase transition occurs, and the recovered elastic forces stabilize the mono-dispersed 8CB microcapsules as shown in Fig. 3.

The size of the 8CB microcapsules is controllable by changing the flow rate of the shell phase from 0.5 to 1.3 mL/h, when the flow rates of the inner and outer aqueous phases are kept constant at 1.0 and 8.0 mL/h, respectively. The outer diameter

of the shells varied from 590 to 610 μm , whereas the shell thickness varied from 20 to 50 μm (Fig. 4).

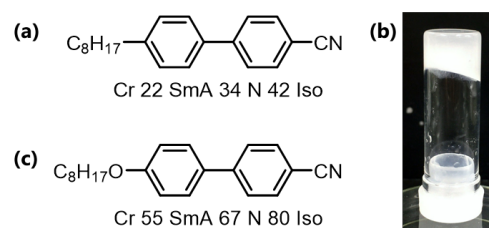


Fig. 1 Molecular structure of (a) 8CB. (b) Photograph of 8CB in a vial at room temperature. (c) Molecular structure of 8OCB. Transition temperatures ($^{\circ}\text{C}$) are shown with standard notation of the phases: crystalline (Cr), smectic A (SmA), nematic (N) and isotropic (Iso) phases.

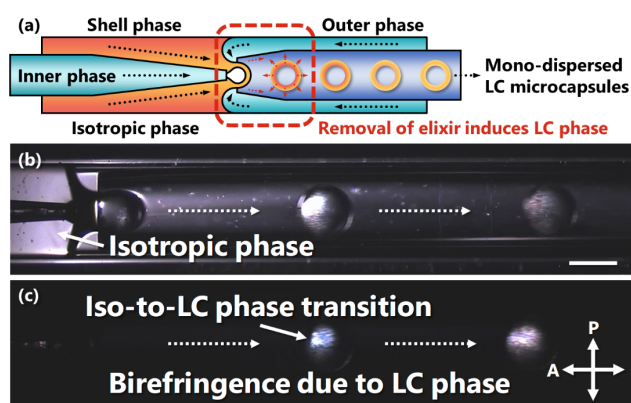


Fig. 2 (a) Schematic of the mechanism of the formation of LC microcapsules with the elixir. LC materials miscible with the elixir show isotropic phase before the encapsulation. Immediately after the shell formation, the added elixir diffuses from the shell phase to the outer aqueous phase. Swift diffusion of the elixir to the outer aqueous phase induces Iso-to-LC phase transition of shells, which stabilizes the core-shell structure. (b), (c) Fabrication of 8CB shells at room temperature (b) under a bright field microscope and (c) under a polarizing microscope. The mixture of 8CB and acetone shows isotropic phase before the shell formation, and then, 8CB shows the LC phase and birefringence after the shell formation. Scale bar corresponds to 500 μm . The orientations of polarizer (P) and analyzer (A) are shown.

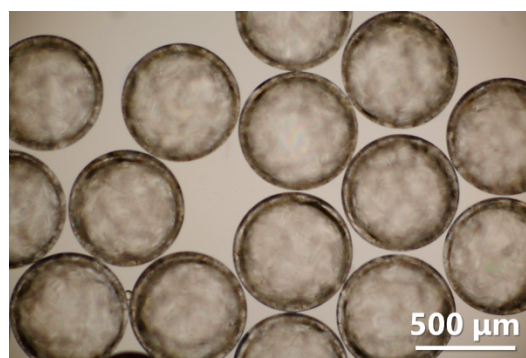


Fig. 3 Mono-dispersed 8CB microcapsules fabricated at room temperature.

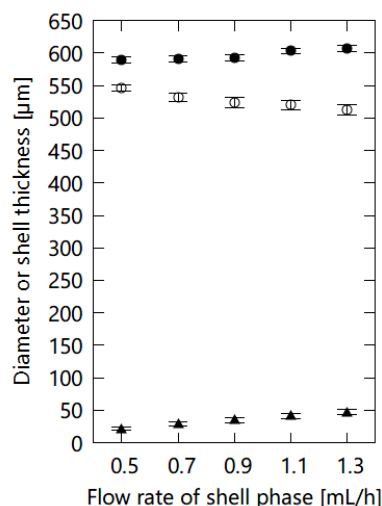


Fig. 4 Plots of the outer diameter (closed circle), inner diameter (open circle) and shell thickness (closed triangle) of 8CB shells as a function of the flow rate of the shell phase. These values are the mean values at each flow rate. The error bars represent the standard deviation of the diameter of shell thickness for each set of flow rates.

We can sum up the estimated mechanism of our fabrication method as follows. The mixture of 8CB and acetone shows the Iso phase before contacting with the aqueous phases. Since acetone is well soluble in water, it diffuses rapidly from the shell phase to the aqueous phases at a moment of the shell formation. Then, the Iso-to-SmA phase transition occurs during the shell formation (Fig. 2), and the LC orientational elastic force needed to stabilize the core-shell structure is recovered.

After the removal of the elixir by substituting the outer phase for 10 wt% PVA aqueous solution several times, to make the domain size of the director field grow larger, we heated the fabricated 8CB shell, and observed it under a crossed polarizing microscope. In PVA aqueous solution, a texture with stripes in a herring-bone-like arrangement (herring-bone-like texture²⁸) was developed at 32 °C in the cooling process, where 8CB shows the N-to-SmA phase transition, as shown in Fig. 5. Since the same texture has been reported for the SmA shells with tangentially aligning conditions,^{25–28} the results indicate that the director of 8CB is well aligned in the shell and the elixir is estimated to be completely removed from the shell phase.

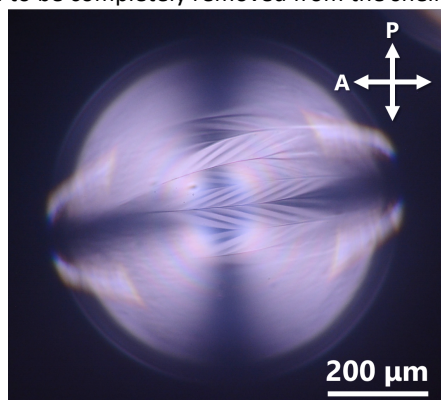


Fig. 5 Planar-aligned 8CB shell observed under a crossed polarizing microscope at 32 °C. 8CB shell shows a herring-bone-like texture with stripes. The orientations of polarizer (P) and analyzer (A) are shown.

To confirm that our method is also applicable to room-temperature-crystalline LC compounds in general, we tried to fabricate LC microcapsules with a shell of 4-cyano-4'-octyloxybiphenyl (8OCB, Fig. 1c), which shows a supercooled SmA phase at room temperature, in the same way. 10 wt% PVA aqueous solution was employed as the inner and outer aqueous phases. We added the mixture of acetone and tetrahydrofuran (THF) as the elixir to 8OCB (23 and 12 wt%, respectively). The elixir disturbs the molecular packing and induce Cr-to-Iso phase transition; the mixture of 8OCB and the elixir is no longer solid at room temperature and we can fabricate the 8OCB microcapsules at room temperature by using microcapillary devices. During the fabrication of microcapsules the elixir diffused into the aqueous phases; the diffusion of the elixir into the outer phase is observable owing to the difference in refractive index as shown in Fig. 6a and Movie S3. Immediately after the removal of the elixir, 8OCB did not crystallize; 8OCB showed the birefringence and fluidity in the device, indicating that Iso-to-supercooled SmA phase transition occurred soon after the encapsulation at room temperature (Fig. 6b and Movie S4). As a result, we have obtained mono-dispersed 8OCB microcapsules. The size of the 8OCB microcapsules is also controllable by changing the flow rate of the shell phase from 1.0 to 1.6 mL/h, when the flow rates of the inner and outer aqueous phases are kept constant at 1.3 and 12.0 mL/h, respectively (Fig. 7). We heated the fabricated 8OCB shells after the substitution of the outer phase with the elixirs for 10 wt% PVA aqueous solution several times, and observed them under a crossed polarizing microscope. They show a herring-bone-like texture²⁸ at 65 °C in the cooling process, where 8OCB shows the N-to-SmA phase transition, as shown in Fig. 8a. These results indicate the complete the removal of the elixir. Furthermore, 8OCB finally crystallized at room temperature remaining the core-shell structure. The crystallized 8OCB shells can be picked up stably from the PVA solution into the air (Fig. 8b), and the core-shell structure is confirmed to remain by observing broken shell (Fig. 8c). By heating up the crystallized 8OCB shells in the PVA solution, they show the SmA phase again, and furthermore, this process is repeatable. Even after 3 months of storage of the crystallized 8OCB shells at room temperature, this process works well.

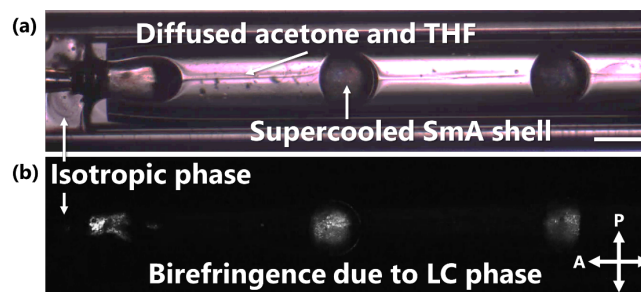


Fig. 6 (a),(b) Fabrication of 8OCB shells at room temperature (a) under a bright field microscope and (b) under a polarizing microscope. After removal of the elixirs, 8OCB shows supercooled SmA phase, whose orientational elastic forces stabilize the shell structure. Scale bar corresponds to 500 μm. The orientations of polarizer (P) and analyzer (A) are shown.

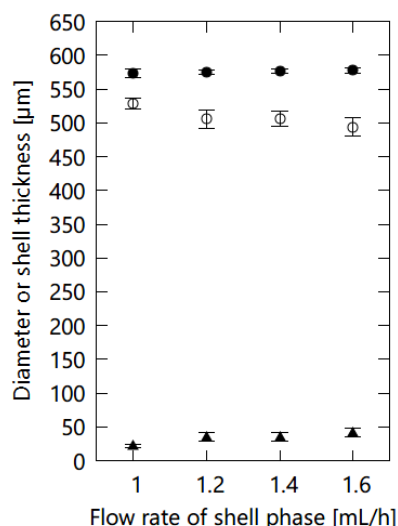


Fig. 7 Plots of the outer diameter (closed circle), inner diameter (open circle) and shell thickness (closed triangle) of 8OCB shells as a function of the flow rate of the shell phase. These values are the mean values at each flow rate. The error bars represent the standard deviation of the diameter or shell thickness for each set of flow rates.

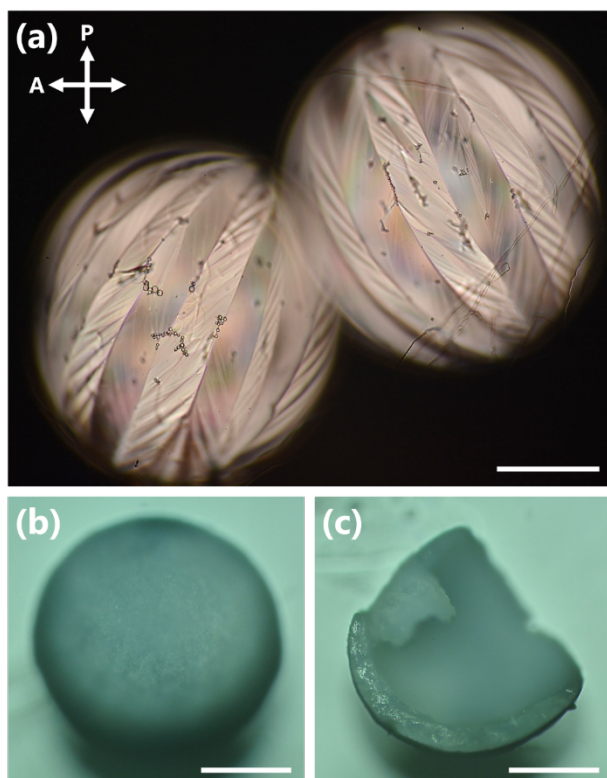


Fig. 8 (a) Planar-aligned 8OCB shells observed under a crossed polarizing microscope at 65 °C. The orientations of polarizer (P) and analyzer (A) are shown. (b) Crystallized 8OCB shell picked up from the PVA solution into the air. (c) Broken crystallized 8OCB shell indicates that the core-shell structure remains the same. Scale bars correspond to 200 μm.

The following three criteria are essential for the elixirs of the above-mentioned method. (1) Even a little amount of the elixir can induce LC-to-Iso or Cr-to-Iso transitions to obtain low-viscosity Iso phases. It effectively disturbs the orientational ordering in the LC phases and/or the molecular packing in the

Cr phases. (2) The elixir is highly soluble in water. To stabilize the core-shell structure by LC orientational elastic forces, the elixir should be removed from the shell phase instantly; swift diffusion of the elixir occurs when the elixir has high solubility in aqueous phases. (3) The elixir should be highly volatile because it should be removed completely from the system not to destabilize the core-shell structure. For example, acetone, THF, dioxane, diethyl ether, lower alcohols, acetonitrile and ethyl acetate meet the requirements for the elixir.

Conclusions

We developed a new method to prepare LC microcapsules with a shell of SmA or Cr phases at room temperature by using glass microcapillary systems. In this method, a specific excipient, “elixir”, is added to the shell phase, and it is instantly removed during the encapsulation process. The initial Iso phase is suitable for the fabrication of the core-shell structure, whereas the final LC phase stabilizes the structure. We need neither use any heating systems nor add any surfactants to the shell phase. Furthermore, mono-dispersity and size-controllability of this method remain the same as those of the conventional methods.²⁹ We call this method to fabricate microcapsules by Encapsulating with a Little amount of eliXir Instantly Removable “ELIXIR method”. The ELIXIR method enables us to fabricate various LC microcapsules with a shell of LC materials showing high viscosity and/or high melting point, such as smectic, columnar and other functional LC materials. Thus, this method could open up completely new research fields; material sciences and physics of topological defects.^{11,17,30}

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