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Microencapsulation of Cholesteric Liquid Crystal by Combined Method of Solvent Evaporation and Photopolymerization

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In this article, UV-curable liquid CBU226 was firstly employed as the shell material to microencapsulate cholesteric liquid crystals (CLCs) by a combined technique of solvent evaporation and photopolymerization. Microcapsule properties depend on the sequence of photopolymerization and solvent evaporation process during preparation. Solvent-evaporation-induced-phase-separation–photopoly-merization process could produce microcapsules with high core loading and spherical core/shell structure. Specifically, spherical CLC microcapsules with mononuclear structure, smooth surface, and high CLC loading (97.34 wt%) were prepared. After drying, the microcapsules could easily deform to nonspherical geometry and exhibit vivid color, showing great potential for the application of display devices.

Keywords Cholesteric liquid crystals; microcapsules; photopolymerization; reflection characteristics; solvent-evaporation–induced phase separation

Introduction

Reflective displays based on cholesteric liquid crystals (CLCs) have attracted much attention due to their pure reflective nature, bistability, low power consumption, high brightness, and contrast [1–3]. Microencapsulation of CLCs could protect it from adverse environmental effects and permit the use of flexible plastic substrates [4], which prevent erasure of images during flexing or handling the display [5]. Solute codiffusion method/diffusion-controlled swelling method (SCM/DSM) [6,7], coacervation phase separation [8], and polymerization-induced phase separation [9] were employed to prepare liquid crystal microcapsules. But the liquid crystal loadings hardly achieved a high value. Excessive leakage of liquid crystal molecules occurred in the microcapsules with 75 wt% core loading by SCM/DSM [10,11]. However, the core loading is important to the switching behavior of the composite systems. The outstanding contrast ratio, low threshold, and driving voltage for a display film can be achieved with higher content of CLCs in the polymer matrix [10].

Moreover, microcapsules with a low core loading always have a thick shell, resulting in spherical geometry after drying especially when the shell is poly(methyl methacrylate)

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(PMMA) [6,9–14]. The geometry of CLC microcapsules is significant to its reflection characteristics. Both experimental [3] and theoretical [14] studies showed that nonspherical CLC droplets such as flattened spherical were crucial to achieve the outstanding reflective properties needed for CLC displays. Hence it is an interesting issue how to prepare nonspherical CLC microcapsules with high core loading.

Previously, we have prepared flattened spherical PMMA/E7 microcapsules and PMMA/CLC microcapsules with a core loading above 90 wt% by solvent-evaporation–induced phase separation (SIPS) [14,15]. But the microcapsules cracked easily and hardly prepared the flexible display devices. UV-curable liquids have been used to prepare the polymer stabilized liquid crystal displays [16–18]. Thin films prepared by photopolymerization of CBU226 are transparent, flexible, and tough and believed to be a good substitute for PMMA shell.

In this article, the UV-curable liquid CBU226 was firstly employed as the shell materials and CLCs were microencapsulated by a combined method of SIPS and photopolymerization. Different microcapsule formation processes were investigated and compared in detail. The CLC loadings, morphologies, and reflection characteristics of the microcapsules were also discussed.

Experiment

Materials

CBU226 (refractive index $n = 1.403$, after polymerization) was from Kunshan Richang Huaxin electronic materials Co. Ltd. Red CLC (refractive index of ordinary light $n_o = 1.51$, refractive index of extraordinary light $n_e = 1.49$, mean reflection wavelength $\lambda_0 = 640$ nm) was obtained from Shijiazhuang Chengzhi Yonghua Display Material Company. Poly(vinyl alcohol) (PVA, Average molecular mass $Mw = 8.8 \times 10^4$–9.2×10^4 g/mol, 88% hydrolyzed) was purchased from Tianjin Keruisi Reagent Company. Organic solvents such as dichloromethane (DMC, Guangfu Chemicals), acetone (Guangfu Chemicals), and ethanol (Guangfu Chemicals) were reagent grade and used without further purification.

Preparation of CLC Microcapsules by SIPS-Photopolymerization Process

CBU226 (about 0.05 g) and CLCs (about 0.5 g) were first dissolved in a mixture of 4.5 mL DMC and 0.5 mL acetone. Then the solution was added into 40 mL 3 wt% PVA aqueous solution. The stirring rate was kept at 1500 rpm for 20 min to form an Oil/Water emulsion. Then the stirring rate was reduced to 300 rpm and another 40 mL of 3 wt% PVA aqueous solution was added to dilute the emulsion. Afterward, the mixture was heated to and kept at 35°C for 5 h to evaporate the solvent. The whole process was kept in the dark place. Then the mixture was exposed to UV lights (365 nm, 900 μw/cm^2) for another 2 h. Finally, the obtained microcapsules were repeatedly washed with deionized water via decantation, and then concentrated.

Characterizations of Microcapsules

Structures of CLC microcapsules and CLC/CBU226 droplets were observed using an optical microscope (OM, Lv-UEPI, JP-Nikon). Reflection characteristics of CLC microcapsules were shown on a stereo microscope (SMZ1500, JP-Nikon). The anisotropy characteristics

of CLCs inside CLC/CBU226 droplets were characterized by polarization optical microscope equipped with an image analyzer (POM, Lv-UEPI, JP-Nikon). The scanning electron microscope (SEM) image of fractured microcapsule was obtained with a SEM (S4800, JP-Hitachi Limited). The morphologies of CLC microcapsules were examined by environment SEM (ESEM, XL-30, NL-Philips). To determine microcapsule sizes and size distributions, about 600 microcapsules were measured at random by the optical microscope.

Certain amount of dried microcapsules was cracked by squeezing, and then the CLCs were extracted with ethanol (10 mL × 5). The residual shells were collected, dried, and weighed. The CLC loading in the microcapsules ($C_c\%$) is calculated as follows:

$$C_c\% = (1 - W_p/W_t) * 100\%, \tag{1}$$

where W_p and W_t are the weights of the residual shell and the dried microcapsules, respectively.

Result and Discussion

Formation of CLC Microcapsules

CLC microcapsules could be prepared by emulsion and direct phase separation (DPS) using CBU226 and CLCs. CBU226, a liquid composed of acrylate monomers, oligomers, and photoinitiator, can dissolve in the CLCs only when the temperature is above the clearing temperature (62°C). So CLCs and CBU226 were mixed together at 65°C and the emusification process was done at 65°C. Afterward, the emulsion was allowed to cool down to the room temperature, which induced primary phase separation for a declined compatibility of CLCs and CBU226. Then the mixture was exposed to UV lights and CBU226 gradually converted into the polymer – CBU-polymer—inducing further phase separation. Spherical microcapsules were obtained. But the CLC loading was found lower than 60 wt% (see Table 1) and the encapsulation efficiency was very low (19.4 wt%). Moreover, the CLC leakage was very heavy after drying. These could be easily explained by the low migration of CBU226 and CBU-polymer to droplet surfaces during phase separation [19].

Employment of solvents could enhance this migration during the SIPS [20]. So DMC was introduced into the system as the solvent of oil phase. When a mixture of

Table 1. Comparison of CLC microcapsules prepared by various processes

Samples	Preparation process	CLC content[a] (%)	$Cc\%$[b] (%)	CLC leakage after drying
1	DPS	77	55	Much CLC leakage
2	Photopolymerization-SIPS	91	69	Much CLC leakage
3	SIPS-plus-photopolymerization	91	80	Little CLC leakage
4	SIPS-photopolymerization	91	91	No CLC leakage

[a]Initial CLC content, which is the ratio of the weight of the initial addition of CLCs to the total addition of CLC and CBU226.

[b]CLC loading in microcapsules calculated from Eq. (1).

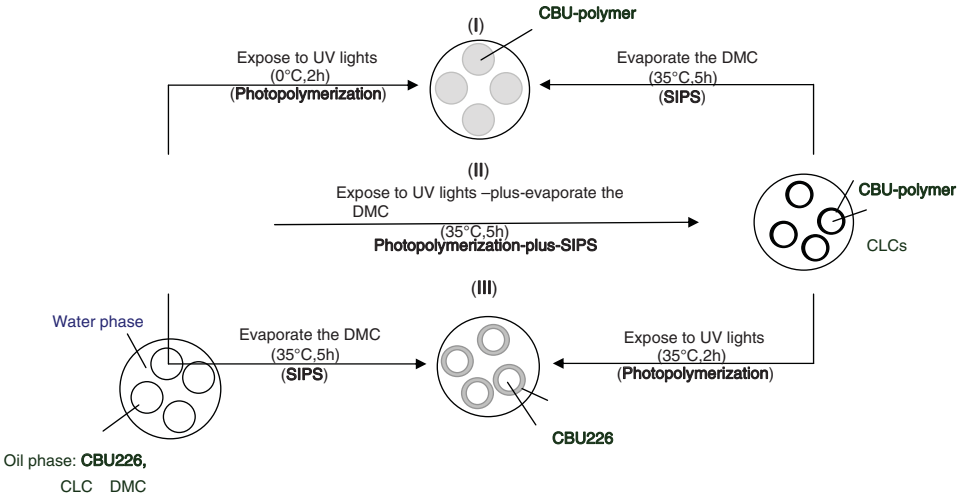

Figure 1. Schematic diagram of CLC microcapsule formation processes during photopolymerization-SIPS (I), SIPS-plus-photopolymerization (II), and SIPS-photopo-lymerization processes (III).

CLCs, CBU226, and DMC was dispersed in water, the droplet phase was homogeneous, and this indicated that the components mixed practically in the initial dispersion state. As the solvent evaporated, both CBU226 and CBU-polymer could separate from CLC phase for their low compatibility at room temperature. Hence, photopolymerization process could occur before, with or after the solvent evaporation process, which were designated as photopolymerrization-SIPS, SIPS-plus-photopoly-merization and SIPS-photopolymerization process respectively (see Fig. 1).

All microcapsules prepared by three different processes have a spherical core/shell structure in the aqueous solution [see Fig. 2(a)]. Since the geometries of CLC microcapsules are relating to their color [3,14], additional image from stereomicroscope can further confirm the shape and structure of CLC microcapsules. As shown in Fig. 2(b), the microcapsules in water are red at the center, change to green moving away from the center and are colorless at the fringes, corresponding to a spherical geometry of CLC microcapsules [14].

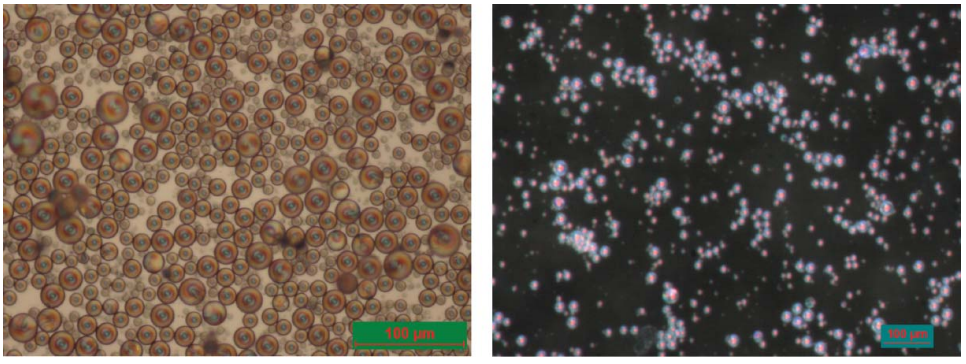

Figure 2. OM (a) and stereomicroscope (b) images of CLC microcapsules dispersed in water.

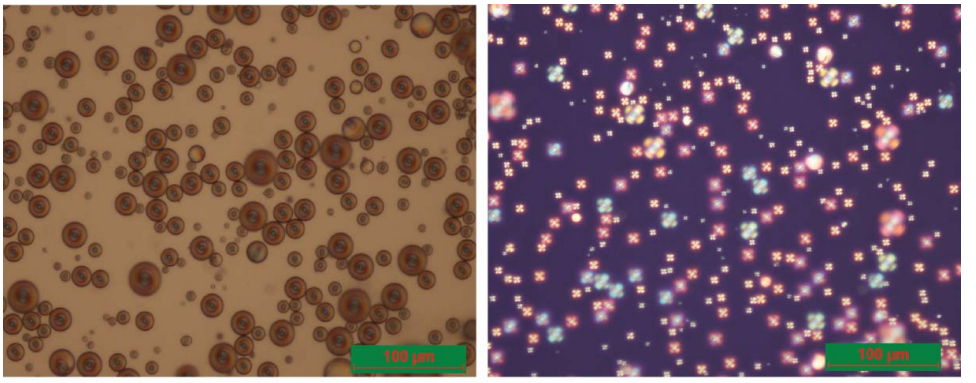

Figure 3. OM (a) and POM (b) images of CLC/CBU226 droplets formed after SIPS but before exposing to the UV lights (SIPS-photopolymerization process).

However, the core loading varies with different processes. As shown in Table 1, sample 4 – microcapsules obtained via SIPS-photopolymerization process – shows a CLC loading as high as 91 wt%, which is in good agreement with the initial CLC content. But CLC loadings of microcapsules prepared by photopolymerization-SIPS and SIPS-plus-photopolymerization process (samples 2 and 3) are obviously lower than their initial CLC contents. Moreover, sample 1 cracked easily and much CLCs leaked after drying. Some microcapsules of sample 2 were also found broken after drying. It is interesting that sample 4 shows no CLC leakage after drying.

Studies of microcapsule formation processes (see Fig. 1) might reveal the underlying mechanism. During SIPS-photopolymerization process, spherical core/shell structure droplets were found with a clear anisotropy characteristic of CLCs inside CLC/CBU226 droplets by OM and POM images (see Fig. 3) after solvent evaporation process but before photopolymerization process. This indicates that the phase separation between CLCs and CBU226 has been realized first by solvent evaporation. Then microcapsules were produced after the CBU226 photopolymerized completely [see Fig. 1(III)]. But for photopolymerization-SIPS process, CBU226 was changed to CBU-polymer first and then the phase separation occurred between CLCs and CBU-polymer [see Fig. 1(I)]. In our prior experiments, the CBU-polymer films prepared directly by the photopolymerization of CBU226 were flexible and tough. But when CBU-polymer was dissolved in DMC and then coated on the PET substrates, the obtained films were susceptible to be scraped though flexible. This might be attributed to the weakened polymeric cohesive energy [21]. So tough shell of microcapsules obtained via SIPS-photopolymerization process ensures the sealing of CLCs even after drying.

When solvent evaporation and photopolymerization took place simultaneously in SIPS-plus-photopolymerization process, partial CBU226 had migrated to droplet surfaces before complete conversion into CBU-polymer. This could enhance the polymeric cohesive energy of shells in comparison with the photopolymerization-SIPS process. Thus the CLC loading improved and CLC leakage after drying reduced.

CLC Loading and Shell Thickness of CLC Microcapsules

By SIPS-photopolymerization process, CLC microcapsules with various CLC loadings could be prepared by adjusting the ratio of CBU226 to CLCs. Results were listed in Table 2.

Table 2. Properties of microcapsules prepared via SIPS-photopolymerization process

Samples	Initial addition CBU226(g)	Initial addition CLCs(g)	CLC content[a] (%)	*Cc*%[b] (%)	Average size (μm)	Shell thickness[c] (μm)
5	0.3026	0.5015	62.50	62.28	11.03	1.0115
6	0.1008	0.4998	83.33	83.61	10.72	0.4116
7	0.0507	0.5009	90.91	91.35	10.11	0.2029
8	0.0253	0.5023	95.24	95.30	10.08	0.1095
9	0.0152	0.5019	97.09	97.34	9.82	0.0603

[a]Initial CLC content, which is the ratio of the weight of the initial addition of CLCs to the total addition of CLC and CBU226.
[b]CLC loading in microcapsules calculated from Eq. (1).
[c]Shell thickness calculated from Eq. (2).

An extremely good agreement was clearly found between the CLC loading (*Cc*%) and the initial CLC content. This is consistent with previous results obtained by solvent evaporation method [22,23]. Herein the CLC loading could be achieved as high as 97.34 wt%, which is far higher than that of reported microcapsules [10,11,14,15].

For mononuclear CLC microcapsules with a core loading of *Cc*%, the shell thickness (t) can be calculated using Eq. (2), where R is the microcapsule radius and ρ_c and ρ_m are the densities of the CLC cores and CBU-polymer shells respectively. Thus, the microcapsule shell thickness of sample 5 could be predicted as 1.0115 μm (see Table 2). As shown in the SEM image of fractured microcapsule (see Fig. 4), the shell thickness of Sample 5 was evaluated as about 1 μm. This agrees well with the predicted value.

$$t = \left[1 - \left(\frac{C_c\%/\rho_c}{(1 - C_c\%)/\rho_m + C_c\%/\rho_c}\right)^{1/3}\right] R. \tag{2}$$

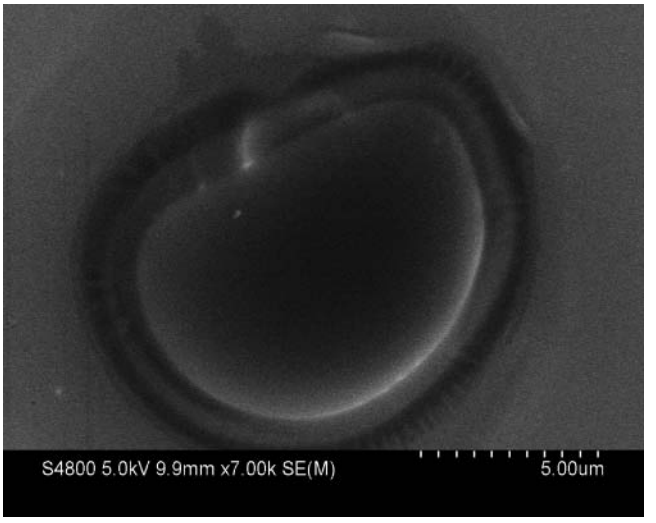

Figure 4. SEM image of the fractured CLC microcapsule of sample 5.

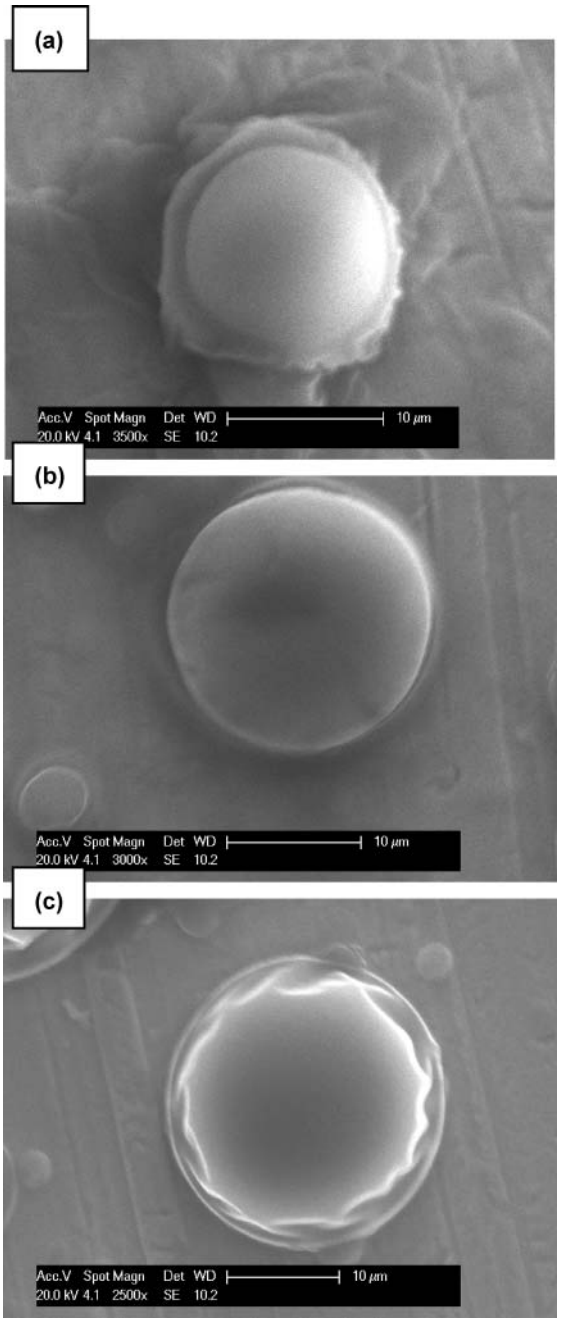

Figure 5. ESEM images of dried CLC microcapsules with different core loadings: 62.28 wt% (a, sample 5); 83.61 wt% (b, sample 6); and 91.35 wt% (c, sample 7).

Furthermore, spherical microcapsules of sample 5 could still deform to a nonspherical geometry after drying (see Fig. 4). This indicates that CLC microcapsules incline to deform to nonspherical geometries because of the flexibility of the shell material, which will benefit its reflection characteristics.

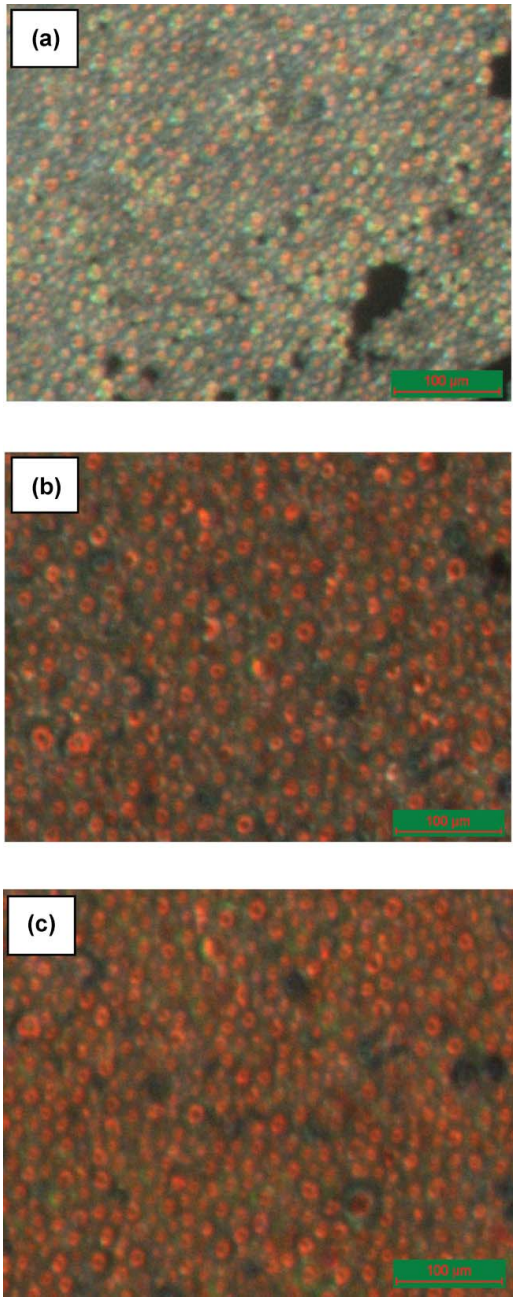

Figure 6. Stereomicroscope images of dried CLC microcapsules with different core loadings: 62.28 wt% (a, sample 5); 83.61 wt% (b, sample 6); and 91.35 wt% (c, sample 7).

Morphology and Reflection Characteristics of CLC Microcapsules

The morphologies of the dried microcapsules were observed by ESEM images in Fig. 5 and show that all microcapsules have smooth surface. However, the morphologies vary with the different core loadings. As shown in Fig. 5(a), a perfect spherical geometry is shown

for dried sample 5. Clear flattened spherical geometries are shown for dried sample 6 (83.61 wt%) and 7 (91.35 wt%). Moreover, clear folds are found at the spherical shell edge of dried sample 7. Combining with Fig. 4, it could be explained by the different deformation degrees relating to the shell thickness. The low core loading of sample 5 (62.28 wt%) leads to a thick shell that can greatly withstand the spherical CLC droplets.

Furthermore, the core loading affects the reflective properties of microcapsules. Stereomicroscope images of dried CLC microcapsules (See Fig. 6) show a clear red section in the center in comparison with that of CLC microcapsules dispersed in water. It is reported that a clear red section in the center is relating to a nonspherical geometry of CLC microcapsules [14]. A nonspherical geometry has been proved crucial to achieve the outstanding reflective properties needed for CLC displays [3–5,24–28]. The fringes of dried sample 5 still show a narrow section with changing color from green to colorless. But Figs. 6(b) and (c) show only red sections in the center, which correspond to a flattened geometry of dried sample 6 and 7. The high core loadings in sample 6 and 7 could result in thin microcapsule shells. The thinner the shell, the higher the deformation degree of dried microcapsules, leading to a vivid red color of the microcapsules. Similar phenomena were also found with sample 8 and 9. But some CLC leakages occurred in processing due to the thin shell (below 110 nm).

Conclusion

A combined technique of the SIPS and photopolymerization that can be applied to microencapsulate CLCs into CBU-polymer with high loadings has been presented. The CLC loadings and microcapsule properties depend on the sequence of two processes. By SIPS-photopolymerization process, the microencapsulation technique described in this study provided great usefulness in producing spherical core/shell microcapsule structure. CLC loading in microcapsules is easy to be controlled by the initial addition amount and the shell thickness of microcapsules could be precisely predicted. Due to the flexibility of CBU-polymer shell material, CLC microcapsules incline to deform to nonspherical geometries after drying. The deformation degree is relating to the shell thickness. Specifically, spherical CLC microcapsules with mononuclear structure, smooth surface, and high CLC loading (91.35 wt%) were prepared. After drying, the microcapsules could easily deform to flattened spherical geometry and exhibit vivid color. And the tough shell promises its processing ability, showing great potential for the application of display devices.

References

[1] Yang, D. K., & Doane, J. W. (1992). *SID Intl. Symp. Digest Tech. Papers*, *23*, 759.
[2] Yang, D. K., West, J., Chien, L. C., & Doane, J. W. (1994). *J. Appl. Phys.*, *76*, 20.
[3] Shiyanovskaya, I., Barua, S., Green, S., Khan, A., Greg, M., & Marhefka, D. (2007). *SID Intl Symp. Digest Tech. Papers*, *38*, 65.
[4] Schneider, T., Davis, D. J., Franklin, S., Venkataraman, N., Daniel, D. M., & Nicholson, F. (2007). *Proc. SPIE*, *6487*, 64870J-5.
[5] Khan, A., Shiyanovskaya, I., & Montbach, E. (2006). *Proc SPIE*, *13*, 1.
[6] Park, N. H., Park, S. I., & Suh, K. D. (2001). *Colloid. Polym. Sci.*, *279*, 1082.
[7] Cho, S. A., Park, N. H., Kim, J. W., & Suh, K. D. (2002). *Colloids. Surface A.*, *196*, 217.
[8] Hodson, T. L., Cartmell, J. V., Kettering, D. C., &, Jones, J. W. (1971). Patent US No. 3,585,381.
[9] Ju, K. H., Kim, J. W., Han, S. H., Chang, I. S., King, H. K., Kang, H. H., Lee, O. S., & Suh, K. D. (2002). *Colloid. Polym. Sci.*, *280*, 879.
[10] Ryu, J. H., Choi, Y. H., & Suh, K. D. (2006). *Colloids Surface A*, *275*, 126.
[11] Ryu, J. H., Lee, S. G., & Suh, K. D. (2004). *Liq. Cryst.*, *31*, 1587.

[12] Park, S. I., Park, K. D., & Suh, K. D. (2002). *Liq. Cryst.*, *29*, 6783.
[13] Kim, J. W., Lee, K. S., & Ju, H. K. (2004). *J. Polym. Sci. A*, *42*, 2202.
[14] Lv, K., Liu, D. Z., Li, W., Tian, Q. X., & Zhou, X. Q. (2012). *Dyes and Pigments.*, *94*, 452.
[15] Lv, K., Liu, D. Z., Li, W., Tang, S., & Zhou, X. Q. (2012). *Mol. Cryst. liq. Cryst.*, *557*, 217.
[16] Held, G. A., Dierking, I., Kosbar, L. L., Lowe, A. C., Grinstein, G., Afzali-ardakani, A., Lee, V., & Miller, R. D. (1999). *Mol. Cryst. Liq. Cryst.*, *329*, 473.
[17] Ma, J., Shi, L., & Yang, D. K. (2010). *Appl. Phys. Express 3*, *021702*, 1.
[18] Ko, T. C., Fan, Y. H., Shieh, M. F., Fuh, A.Y. G., Huang, C. Y., Tsai, M. S., & Jiang, I. M. (2001). *J. Appl. Phys.*, *40*, 2255.
[19] Amundson, K., Blaaderen, A., & Wiltzius, P., (1997). *Phys. Rev. E: Stat. Phys. Plasma. Fluids*, *55*, 1646.
[20] Nwabunma, D., & Kyu, T. (1998). *Macromolecules*, *32*, 664.
[21] Dowding, P. J., Atkin, R., Vincent, B., & Bouillot, P. (2005). *Langmuir*, *21*, 5278.
[22] Salaun, F., Devaux, E., Bourbigot, S., & Rumeau, P. (2010). *Carbohyd. Polym.*, *79*, 964.
[23] Freitas, S., Merkle, H. P., & Gander, B. (2005). *J. Controlled Release*, *102*, 313.
[24] Shiyanovskaya, I., Green, S., Khan, A., Magyar, G., Pishnyak, O., & Doane, J. W. (2008). *J. SID.*, *16*, 113.
[25] Huiji, N., & Yamamoto, S. (2010). Patent US No. 7,662,444.
[26] Khan, A., Schneider, T., Miller, N., Ernst, T., Nicholson, F., & Doane, J. W. (2005). *Proc. SPIE.*, *5744*, 1.
[27] Shiyanovskaya, I., Khan, A., Green, S., Magyar, G., Pishnyak, O., & Doane, J. W. (2005). *Proc. SPIE.*, *5801*, 204.
[28] Khan, A., Shiyanovskaya, I., Schneider, T., Miller, N., & Ernst, T. (2005). *J. SID.*, *13*, 469.