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Preparation of cholesteric liquid crystal microcapsules for application in colour image storage media

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Cholesteric liquid crystal (CLC) microcapsules for application in image storage media can be obtained via a diffusion-controlled polymerization method (DPM). To improve the swelling of the CLC seed particle, in poly(methylmethacrylate) (PMMA), a polymerizable acrylate based on a cholesterol moiety was synthesized and copolymerized with MMA to prepare the seed particle. As a result, monodispersed and CLC core/shell-structured microcapsules may be obtained. The resulting CLC microcapsules selectively, absorbed visible light at around 660 nm, and so appeared blue in the mesophase. Polymer dispersed cholesteric liquid crystal (PDCLC) cells were prepared using the CLC microcapsules, and were used as an image storage medium in reversible writing/erasing experiments.

1. Introduction

Polymer dispersed cholesteric liquid crystals (PDCLCs), that consist of a micron-sized cholesteric liquid crystal (CLC) droplet dispersion within a polymer matrix, have been investigated intensively and have application potential in electro-optic devices [1–5]. The optical properties of a PDCLC depend on the applied electric field which changes the CLC alignment from planar, focal-conic to homeotropic [6]. A CLC aligned perpendicularly to the direction of light propagation (planar texture) can selectively reflect visible light. The texture is changed to a focal-conic which shows light scattering, and to homeotropic, which is transparent on applying the electric field. Furthermore, since these textures are maintained even after the removal of the electric field, PDCLCs are widely used for colour display and information storage media [5].

It is technologically important not only to store and erase the full colour information reversibly, but also to enhance the recording density. However, most research is focused on aspects of tuning the colour; Broer and Lub [7] reported on tuning the colour by changing the ratio of monomers in the copolymer matrix. Stohr and Strohriegl [8] investigated tuning the colour by changing the crosslinked network formation. There has been little or no investigation on achieving a high resolution image storage medium.

In a previous study [9–11], we prepared highly monodispersed nematic LC microcapsules incorporated in a mono-sized LC domain via a diffusion-controlled polymerization method (DPM) and studied this as part of an electro-optical device. In this work, DPM is used in an attempt to control the size and size distribution of CLC droplets in microcapsules. To improve the affinity between the CLC and the polymer particle, a cholesterol-based acrylate (ChA) was synthesized and used as comonomer during seed preparation. Selective absorption was measured using a UV-Vis spectrophotometer; and by executing a writing/erasing process repeatedly, the possibility for application of this type of material to reversible image storage media was investigated [12].

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2. Experimental

2.1. *Materials*

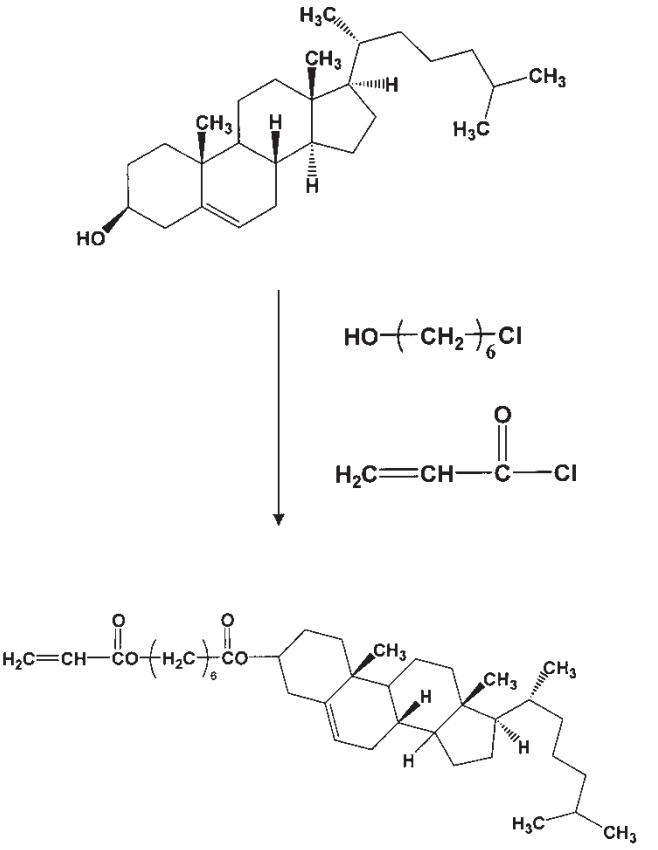
To prepare PMMA seed particles, methylmethacrylate (MMA, Junsei Chemicals), methanol (99.9%, Mallinckrodt Co.), aerosol-OT solution (AOT, Sigma Chemicals) and polyvinylpyrrolidone (PVP, $M_w = 4.0 \times 10^4\,g\,mol^{-1}$, Sigma Chemicals) were used as received. Azobis(isobutylonitrile) (AIBN, Junsei Chemicals) and benzoyl peroxide (BPO, Junsei Chemicals) were used after recrystallization. ChA was synthesized using cholesterol and 6-chlorohexanol (TCI Chemicals), acryloyl chloride (Sigma Chemicals), tetrahydrofuran (THF, Mallinckrodt Co.) and triethylamine (TEA, Junsei Chemicals). In the DPM process, sodium dodecyl sulfate (SDS, Yakuri Chemicals), ethanol (99.95%, Baker Co.), distilled deionized water (DDI water), styrene (St, Junsei Chemicals), sodium nitrite ($NaNO_2$, Junsei Chemicals) and polyvinylalcohol (PVA, $M_w = 8.8 \times 10^4$–$9.2 \times 10^4\,g\,mol^{-1}$, 87–89% hydrolyzed) were used. The low molar mass LCs, cholesterol oleyl carbonate (COC, $T_{NI} = 38^\circ C$) and MLC-2039 ($T_{NI} = 91^\circ C$, $\Delta\varepsilon = -4.1$), were purchased from Merck Co.

2.2. *Synthesis of cholesterol-based acrylate (ChA)*

ChA was synthesized by the successive reactions of cholesterol, 6-chlorohexanol and acryloyl chloride in THF at 60°C for 5 h. After the evaporation of THF, ChA was obtained. The synthesis route is illustrated in scheme 1. The reaction was monitored using FTIR spectroscopy and these results are shown in figure 1. The hydroxyl peak at around $3350\,cm^{-1}$ in the spectrum of cholesterol, Figure 1 (*a*), disappeared and two peaks around 1750 and $1250\,cm^{-1}$, which indicate the carbonyl group and C–C double bond, respectively, appeared after reaction was complete, Figure 1 (*b*).

2.3. *Preparation of PMMA and poly(ChA-co-MMA) seed particles*

Monodispersed PMMA and poly(ChA-co-MMA) seed particles were prepared via dispersion polymerization. PVP, AIBN, AOT, MMA, ChA and methanol were mixed homogeneously and polymerized at 58°C for 24 h with 40 rpm stirring in a dry nitrogen atmosphere. The polymer seed particles were recovered after washing with water and methanol repeatedly, and dried at room temperature. The detailed process for dispersion polymerization is described in our previous papers [13, 14]. Details for the dispersion polymerizations are shown in table 1.



Scheme 1. ChA synthesis route.

2.4. *Encapsulation of CLC in poly(MMA-co-ChA) seed particles by DPM*

Encapsulation was carried out by employing the DPM process. Firstly, the seed particles were dispersed in 40 g of SE solution, which consisted of 0.25 wt% SDS solution/ethanol = 4/1. A homogeneous mixture

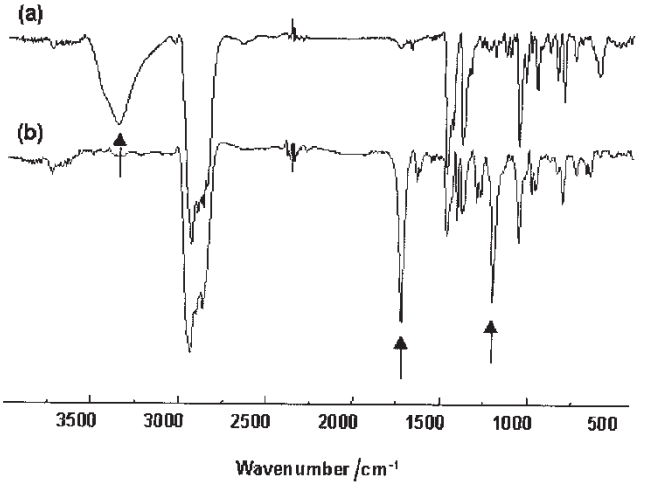


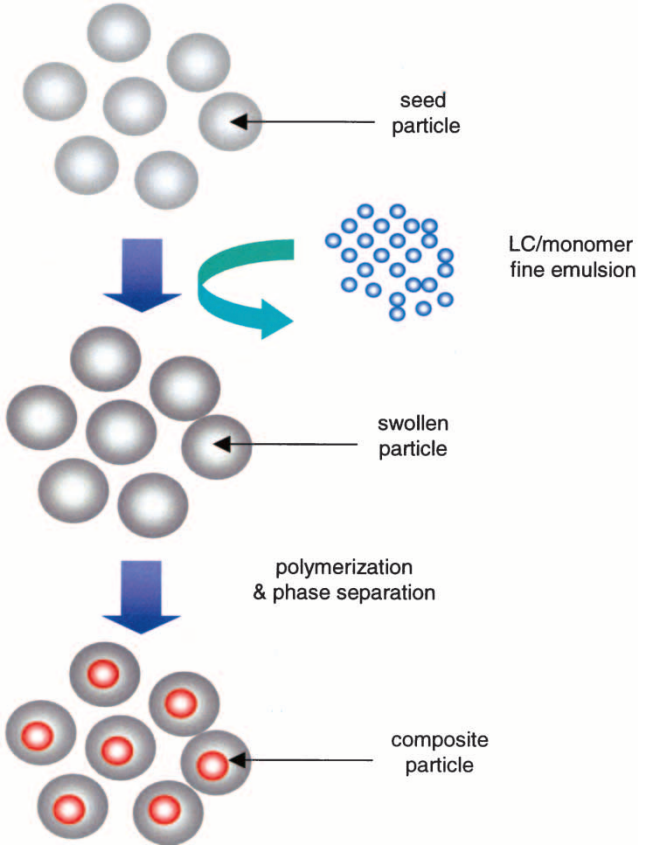
Figure 1. The FTIR spectrum of (*a*) cholesterol and (*b*) ChA.

Table 1. Details for preparation of PMMA and poly(ChA-co-MMA) seed particles[a].

Components	PMMA/g	Poly(MMA-co-ChA)/g
MMA	10	9.7–9.9
ChA[b]	—	0.3–0.1
PVP[c]	4	4
AOT	0.45	0.45
AIBN[d]	0.1	0.1
Methanol	85.45	85.45

[a]58°C, 24 h; 10 wt % of monomer concentration based on total weight.
[b]The wt % of ChA was based on MMA (1–3 wt %).
[c]4 wt % of PVP ($M_w = 4.0 \times 10^4$ g mol^{-1}) based on total weight.
[d]1 wt % of AIBN based on monomer weight.

emulsion of MMA, St, CLC (COC and MLC-2039) and BPO in 15 g of SE solution was poured into seed particle dispersion. Polymerization was then carried out at 50°C for 10 h to phase-separate the CLC into microcapsules—polymerization-induced phase separation (PIPS). A schematic representation and the details of the DPM process are shown in scheme 2 and table 2,



Scheme 2. Schematic representation of the DPM procedure.

Table 2. Procedure for the LC capsules and composition for the DPM process[a].

Components	Weight/g			
	CM-1-2	CM-1-3	CM-1-5	CM-2-3
Seed dispersion process				
Seed particles	0.2	0.3	0.5	0.3
SE solution[b]		40		
Diffusion process				
MMA		0.4		
St		0.3		
COC	0.15	0.15	0.15	0.2
MLC-2039	0.15	0.15	0.15	0.1
BPO		0.007		
SE solution		15		
Polymerization process				
$NaNO_2$ solution[c]		50		
PVA solution[d]		10		

[a]The amount of monomer for DPM is fixed to 1 g.
[b]Ethanol 0.25 wt % SDS solution = 1/4.
[c]0.2 wt % $NaNO_2$ solution.
[d]5 wt % PVA solution.

respectively. More detailed information of the DPM process is given in previous papers [9–11].

2.5. *Characterization*

The synthesis of ChA was monitored using Fourier transform infrared spectroscopy (FTIR, Nicolet, Mahgna IR-550). The morphology of the seed particles was observed using scanning electron microscopy (SEM, Hitachi), optical microscopy (OM, Olympus BH-2) and using a polarizing optical microscope (POM, Olympus BH-2) equipped with an image analyser. Selective absorption was measured using a UV-Vis spectrophotometer (Shimadzu UV-2101 PC).

3. Results and discussion

To prepare highly mono-sized microcapsules having a single mono-sized COC and MLC-2039 (negative anisotropy nematic LC) domains, dispersion polymerization and DPM were used. Dispersion polymerization [9, 10] is widely used to produce monodispersed micron-sized polymer particles. Monodispersed polymer particles are used to prepare the functionalized materials by swelling of a second monomer emulsion into the polymer seed particles, and this method has been widely investigated by several groups [15–17]. In particular, Suh *et al.* [18, 19] have reported on the application of DPM for the preparation of many functionalized materials. Dispersed seed particles can be swollen efficiently using a finely emulsified second monomer by a diffusion process using Ostwald ripening [20–22]. This mechanism can be controlled by changing

the affinity between the polymer particles and the second monomer, the solubility of the monomer in the medium, surfactant concentration, etc.

The conditions for DPM were determined in detail in previous work [11]. Because the CLC used in our system is very hydrophobic and has a larger molar volume than PMMA homopolymer seed particles, complete swelling could not be achieved using PMMA seed particles. To swell the CLC and monomer mixture effectively, ChA, which contains a cholesterol moiety, was synthesized and copolymerized with MMA. ChA in the polymer particles improves the affinity between the seed particles and CLC, due to their similar chemical structure. In addition, the bulky cholesterol moiety in the seed particles enlarges the free volume of the seed particles. These factors enable the complete swelling of CLC in the seed particles. The optimum condition for copolymer seed particle preparation was determined to be at the ratio of MMA/ChA = 9.8/0.2. The affinity between the seed particles and CLC is not enhanced when 1 wt% of ChA is used. For 3 wt% of ChA, the affinity between the seed particle and CLC is largely enhanced; however, swollen CLC in microcapsules was not effectively phase-separated in the process of polymerization. Given these results, the change in swelling behaviour of microcapsules with the preparation step is illustrated in figure 2. The CLC emulsion was incompletely swollen into the PMMA homopolymer seed particle, figure 2 (*a*). However fine emulsion droplets in the aqueous phase could not be detected, indicating that CLC and monomer mixture emulsion was completely swollen into poly(MMA-co-ChA) seed particles, figure 2 (*b*).

In a PDCLC, the interfacial properties between the polymer and CLC are most important factors in determining electro-optical properties. In particular, because the character of the polymer matrix largely affects the phase separation and the electro-optical properties, we investigated the mesomorphism of poly(ChA) using POM, with the results illustrated in figure 3. In this figure, poly(ChA) shows a smectic mesophase at room temperature, a cholesteric mesophase at 80–130°C, and the isotropic phase above 130°C. However, because the content of poly(ChA) in the copolymer is very low, no mesophase is seen for the copolymer seed particles. Although a small amount of the ChA moiety in the seed particles does not affect the mesomorphism of the polymer matrix, it does significantly affect the phase separation of CLC in the seed particles.

For a more precise observation, the morphology of the seed particles and CLC microcapsules were observed using SEM, see figure 4. In figure 4 (*a*), linear poly(MMA-co-ChA) seed particles show a high monodispersity. The microcapsules, figure 4 (*b*), became slightly larger than the seed particles due to the incorporation of CLC. However, the shape of the microcapsules does not change and remains monodisperse even after the DPM process.

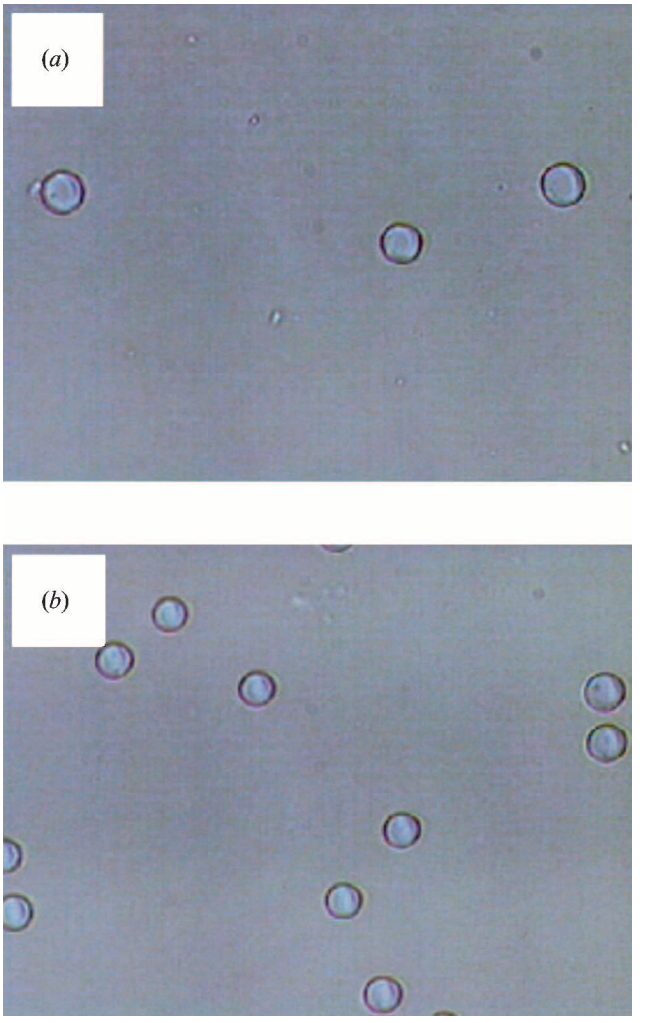


Figure 2. Microphotographs after DPM completion: (*a*) PMMA seed particle, (*b*) linear poly(ChA-co-MMA) seed particle.

The optical properties of the CLC microcapsules were measured using a UV-Vis spectrophotometer for different seed particle to CLC ratios. Selective absorption spectra of some CLC microcapsules and pure CLC were recorded, see figure 5. The selective absorption (λ_m) of pure CLC is seen at around 600 nm; but other microcapsules show a λ_m at about 660 nm, which is in the red region. The DPM process leads to a considerable shift in the selective light absorption peak to the long wavelength region of the spectrum, i.e. the interaction between the CLC and polymer seed particle

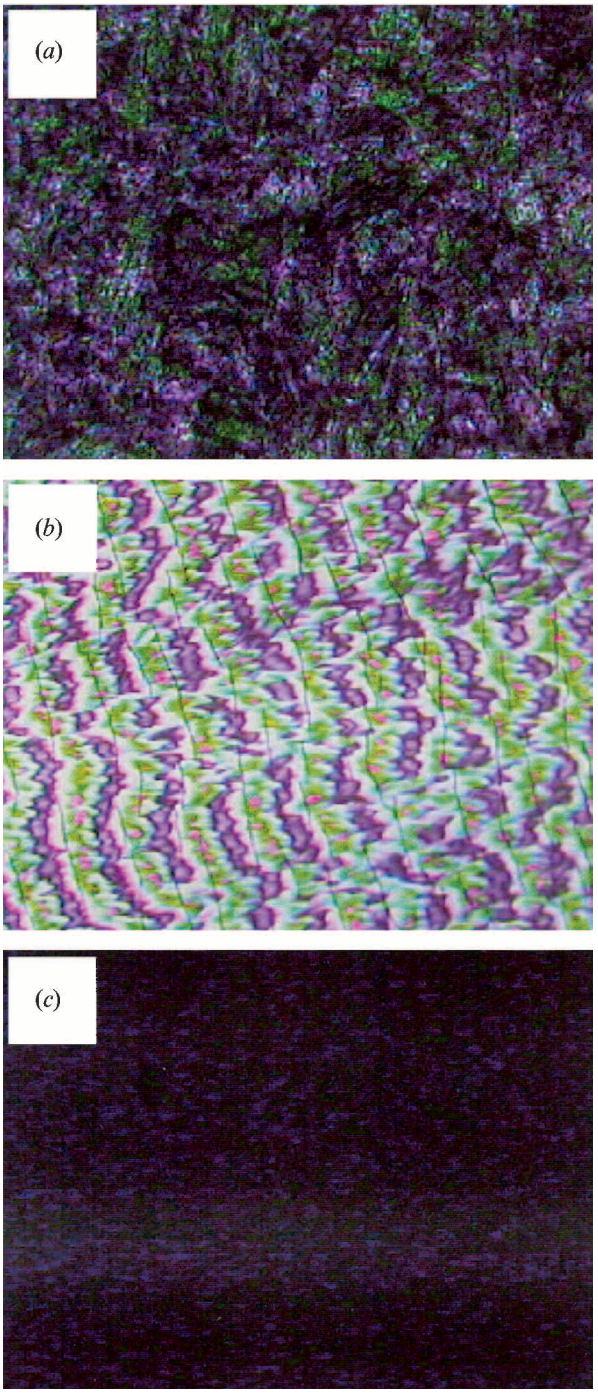


Figure 3. Observation of poly(ChA) mesomorphism using POM: (*a*) smectic phase (at room temperature), (*b*) cholesteric phase (80°C), (*c*) isotropic phase (130°C).

changes the cholesteric helix. It is confirmed that the interaction between the CLC and seed particle increases on increasing the CLC ratio, as this results in the bandwidth of the absorption peak broadening. All CLC microcapsules absorbed light at around 660 nm; that is,

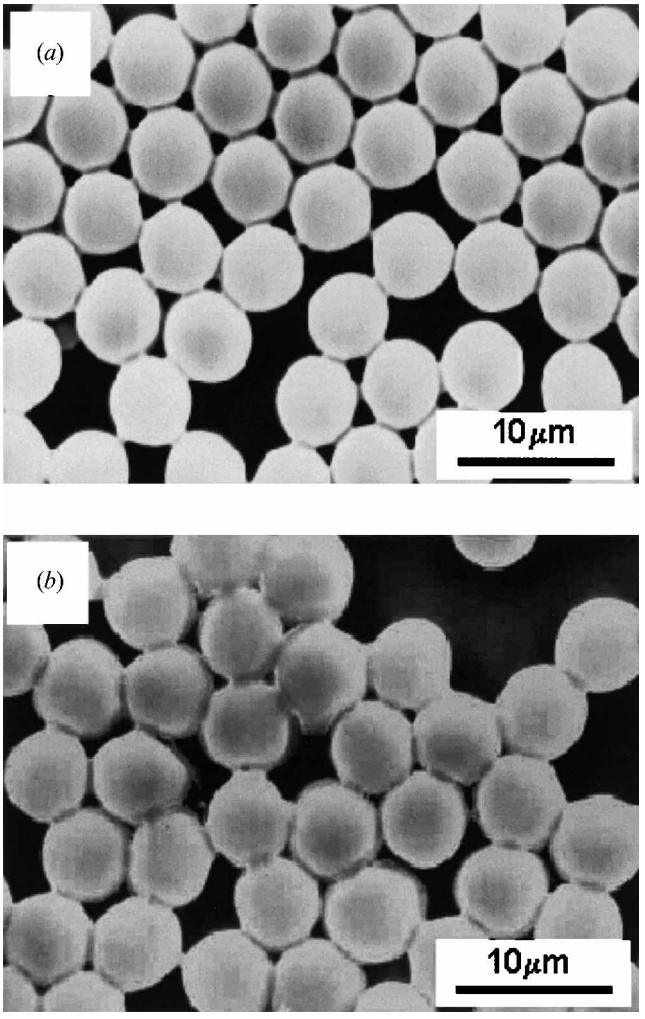


Figure 4. SEM photomicrographs: (*a*) poly(ChA-co-MMA) seed, (*b*) CLC microcapsules.

the CLC particles selectively reflect blue colour in the aligned condition.

To investigate the possibility of using these materials in a colour image storage device, a PDCLC was fabricated using CLC microcapsules and polyurethane acrylate binder. Their reversible image storage/erasing process is shown in figure 6. The as-prepared samples show a blue colour at 50°C. The samples appear white at 0°C in the crystalline state. The writing process is achieved by locally heating to the isotropic temperature using a heating pen (100°C). After annealing at room temperature, the isotropic phase becomes the mesophase and the written region appears blue. Blue colour images were stored until heating to 100°C (erasing process). This reversible storage/erasing process shows that the CLC microcapsules can be applied in image storage media.

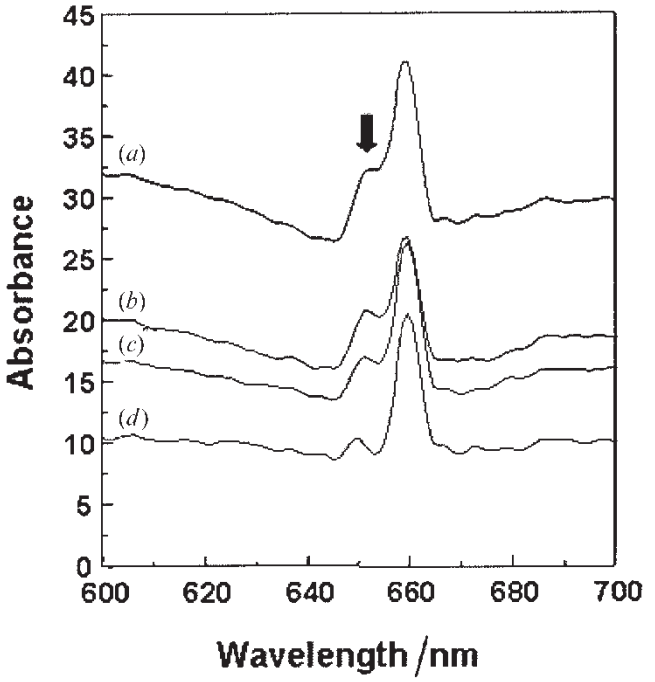


Figure 5. Selective absorption band measurement using UV-Vis spectrometer: (*a*) CM-1-2, (*b*) CM-1-3, (*c*) CM-1-5 and CM-2-3.

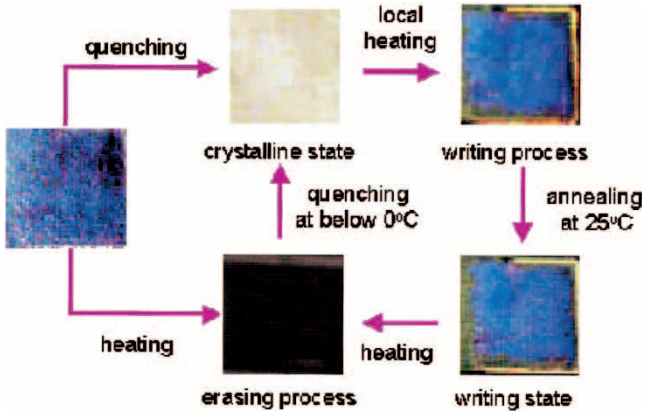


Figure 6. The reversible storage/erasing process.

4. Conclusion

A CLC was encapsulated in polymer seed particles through DPM to prepare mono-sized CLC microcapsules. In the process of DPM, ChA was synthesized and copolymerized with MMA in dispersion polymerization. The ChA moiety in poly(MMA-co-ChA) stimulated CLC swelling, due to the enhancement of affinity and enlargement of free volume of seed particles. With this process, we obtained stable CLC microcapsules and these selectively reflected in the blue colour region. A PDCLC prepared using CLC microcapsules appeared blue and we showed the possibility of using these in a reversible storage/erasing cycle via the application of heat.

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References

[1] Brehmer, M., Lub, J., and Witte, P., 1998, *Adv. Mater.*, **17,** 1438.
[2] Barannik, A. V., Zyryanov, V. Y., and Shabanov, V. F., 1998, *J. opt. Technol.*, **65,** 577.
[3] Yang, D. K., Doane, J. W., Yaniv, Z., and Glasser, J., 1994, *Appl. Phys. Lett.*, **64,** 1905.
[4] Kato, K., Tanaka, K., Tsuru, S., and Sakai, S., 1993, *Jpn. J. appl. Phys.*, **32,** 4600.
[5] Priestley, E. B., Wojtowicz, P. J., and Sheng, P., 1976, *Introduction to Liquid Crystals* (New York: Plenum Press).
[6] Hwang, J. C., Liang, S. C., and Liang, K. H., 1993, *Jpn. J. appl. Phys.*, **38,** 131.
[7] Broer, D. J., and Lub, J., 1995, *Nature*, **378,** 467.
[8] Stohr, A., and Strohriegl, P., 1997, *Mol. Cryst. liq. Cryst.*, **299,** 211.
[9] Li, K., and Stover, H. D. H., 1993, *J. polym. Sci. A: polym. Chem.*, **31,** 2473.
[10] Kim, J. W., and Suh, K. D., 2000, *Polymer*, **41,** 6181.
[11] Park, N. H., Park, S. I., and Suh, K. D., 2001, *Colloid polym. Sci.*, **279,** 1082.
[12] Palffy-Muhoray, P., and Singer, K. D., 1995, *Optics and Photonics News*, **17**.
[13] Kim, J. W., and Suh, K. D., 1999, *Colloid Polym. Sci.*, **277**, 66.
[14] Shen, S., Sudol, E. D., and El-aasser, M. S., 1994, *J. polym Sci. A: Polym. Chem.*, **32,** 1087.
[15] Higuchi, W. I., and Misra, J., 1962, *J. pharm. Sci.*, **51,** 459.
[16] Ugelstad, J., and Mork, P. C., 1980, *Adv. colloid interface Sci.*, **13,** 101.
[17] Ugelstad, J., 1978, *Makromol. Chem.*, **179**, 815.
[18] Park, J. G., Kim, J. W., and Suh, K. D., 2001, *Colloid Surface A*, **191,** 193.
[19] Park, J. G., Kim, J. W., and Suh, K. D., 2000, *Colloid Polym. Sci.*, **279,** 638.
[20] Taylor, P., 1998, *Adv. colloid interface Sci.*, **75**, 107.
[21] Weiss, J., Hermann, N., and McClements, D. J., 1999, *Langmuir*, **15,** 6652.
[22] Binks, B. P., Clint, J. H., Fletcher, P. D. I., and Rippon, S., 1998, *Langmuir*, **14,** 5402.
[23] Kajiyama, T., Miyamoto, A., and Kikuchi, H., 1989, *Chem. Lett.*, 813.
[24] Park, N. H., Cho, S. A., Kim, J. Y., and Suh, K. D., 2000, *J. appl. polym. Sci.*, **77,** 3178.