Colloid Polym Sci 279:1082–1089 (2001)

ORIGINAL CONTRIBUTION

N.-H. Park
S-Il Park
K-Do Suh

A novel method for encapsulation of a liquid crystal in monodisperse micron-sized polymer particles

Received: 22 November 2000
Accepted: 12 March 2001

N.-H. Park · S.-I. Park · K.-D. Suh (✉)
Department of Industrial Chemistry
College of Engineering
Hanyang University
Seoul 133-791, Korea
e-mail: kdsuh@email.hanyang.ac.kr
Tel.: +82-2-22900526
Fax: +82-2-22952102

Abstract Liquid crystals (LCs) encapsulated in monodisperse micron-sized polymer particles were prepared to control the size and size distribution of LC droplets in polymer-dispersed LCs. The poly(methyl methacrylate) (PMMA) seed particles were swollen with the mixture of liquid crystal, monomers (methyl methacrylate and styrene) and initiator by using a diffusion-controlled swelling method. A single LC domain was produced by the phase separation between PMMA and LC through polymerization. The optical microscopy and scanning electron microscopy showed that the particles are highly monodisperse with core–shell structure. Moreover, monodisperse LC core domains were confirmed from polarized optical microscope observations. The final particle morphology was influenced by the cross-linking of the seed particle. When linear PMMA particles, which are not cross-linked, were used as a seed, the microcapsules were distorted after annealing for a few days; however, in the case of cross-linked PMMA particles, the core–shell structure was sustained stably after annealing.

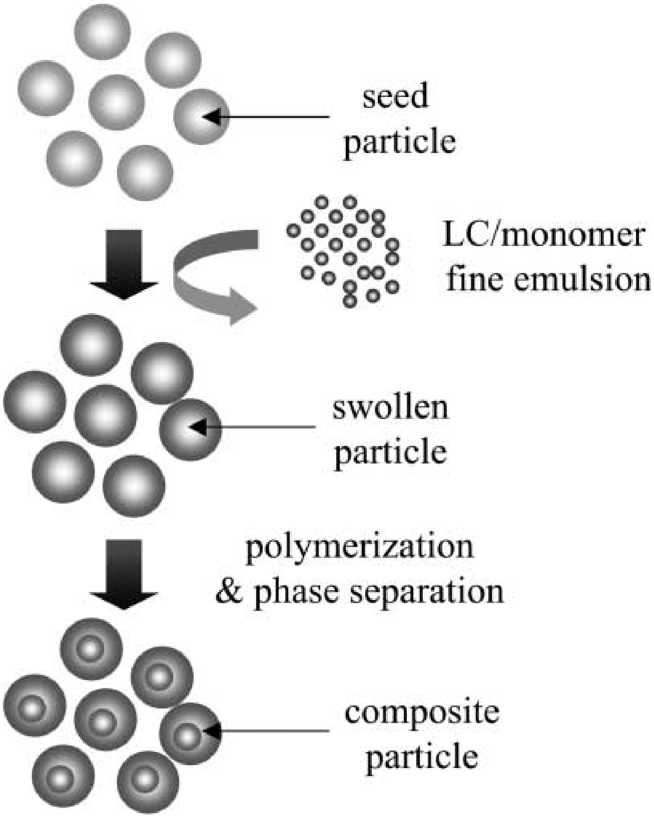
Key words Liquid crystal · Encapsulation · Polymer-dispersed liquid crystal · Poly(methyl methacrylate) seed · Diffusion-controlled swelling method

Introduction

A polymer-dispersed liquid crystal (PDLC) that consists of a micron-sized liquid crystal (LC) droplet dispersion and a polymer matrix is investigated intensively and applied to special types of materials for electrooptic devices [1–6]. The principle of PDLC operation [1, 2, 5] is based on the field-controlled light scattering [7, 8] from nematic microdroplets. When the electric field is applied to a PDLC film, the refractive index of the aligned LC along the direction of the electric field and the polymer matrix is matched, which cause the film to change from an opaque state to a transparent state.

Since PDLC is produced using the phase separation between polymer and LC, there are difficulties in controlling the size and size distribution of LC droplets that affect the electrooptical properties of PDLC. Many researchers reported the effect of LC droplet size in PDLC. Fuh and Caporaletti [9] investigated the effect of LC droplet size on electrooptical properties in the process of phase separation of a LC and polymers (or polymer precursors). Ono and Kawatsuki [10] reported the encapsulation of LC with water-soluble polymers and the effect of encapsulated LC droplet size on PDLC properties. Through many investigations, it is known that the size of the LC droplets significantly affects the electrooptical properties of the final PDLC films. Especially, PDLC having 2–3 μm of LC droplets shows the best electrooptical properties, owing to the balance between transmittance and scattering of incident light by multiple scattering of LC droplets [11, 12]. One of the factors which affect the electrooptical properties is the size distribution of the LC droplets. The broad size distribution induces the slow change in transmittance (broadness of driving voltage) and hysteresis [13] due to the divergence of aligning and relaxing the LC molecules in LC droplets anchored by the polymer wall. So, it is expected that controlling the LC droplet size and the monodispersity of LC droplets in PDLC will improve the electrooptical properties, such as removing hysteresis, the sharpness of the driving voltage, fast response time, and so on.

In this article, a novel method for encapsulation of a LC in polymer particles was attempted to control the size and size distribution of LC droplets in PDLC. To attain the mono-sized LC microcapsules, monodisperse micron-sized poly (methyl methacrylate) (PMMA) seed particles were swollen with a mixture of LC, methyl methacrylate (MMA) and styrene (St) using a diffusion-controlled swelling method (DSM) [14, 15], and the schematic representation of the DSM is illustrated in Scheme 1. During the DSM process, medium solvency, the concentration of surfactant used and the polymerization rate were adjusted. In addition, the final morphology of the encapsulated LC was determined by scanning electron microscopy (SEM) and polarized optical microscopy.



Scheme 1 The graphical representation of the diffusion-controlled swelling process

Experimental

Materials

To prepare PMMA seed particles, MMA (Junsei Chemicals), methanol (99.9%, Mallinckrodt), aerosol-OT 10% solution (AOT, Sigma Chemicals) and poly(vinylpyrrolidone) (PVP, M_w = 40,000 gmol^{-1}, Sigma Chemicals) were used as received. Azobis(isobutylonitrile) (AIBN, Junsei Chemicals) was used after recrystallization using absolute methanol. The cross-linker was synthesized using poly(propylene glycol) (PPG, M_w = 2,000 gmol^{-1}, Polyol), acryloyl chloride (Sigma Chemicals), tetrahydrofuran (THF, Mallinckrodt) and magnesium sulfate (Junsei Chemicals). In the diffusion-controlled swelling and polymerization process, sodium dodecyl sulfate (SDS, Junsei Chemicals), ethanol (99.95%, Baker), distilled deionized water St (Junsei Chemicals), $NaNO_2$ (Junsei Chemicals) and poly(vinyl alcohol) (PVA, $M_w = 8.8 \times 10^4$–9.2×10^4 gmol^{-1}, 87–89% hydrolyzed) were used without further purification. The low-molecular-weight LC E7, which is a mixture of cyanobiphenyls and cyanoterphenyls, was purchased from Merck.

Synthesis of PPG diacrylate as cross-linker

The cross-linker could be synthesized by the reaction of PPG and acryloyl chloride in THF below 5 °C for 4 h and then at 50 °C for 5 h. The product solution could be separated using water and chloroform. Then, the organic layer was extracted using a separating funnel and was dried with $MgSO_4$. The chloroform was evaporated using a rotary evaporator. In this process, PPG diacrylate could be obtained.

Preparation of PMMA seed particles

To prepare monodisperse cross-linked PMMA seed particles, dispersion polymerization was used [16, 17]. PVP, AOT and methanol were weighed in a four-necked round flask equipped with a reflux condenser, a nitrogen inlet apparatus and a mechanical stirrer. After mixing for 30 min, AIBN, MMA and PPG diacrylate were poured into the reactor and were stirred vigorously to mix the reactants homogeneously. The mixture was reacted at 55 °C for 24 h with 50 rpm stirring. The product was purified three times through centrifugation at 2,500 rpm for 10 min and washing with water to remove the surface-anchored PVP molecules. Then, the particles were dried at room temperature. The recipe of the dispersion polymerization is shown in Table 1.

Encapsulation of LC in PMMA seed by the DSM

Encapsulation was executed by swelling cross-linked seed particles with the LC and monomer mixture using the DSM [14, 15]. Firstly, cross-linked PMMA seed particles were dispersed in 40 g SM solution, which was composed of 1:4 ethanol/0.25 wt% SDS solution, via sonication and mechanical stirring. A homogeneous mixture of MMA, St, E7 and benzoyl peroxide (BPO) was emulsified in 15 g SM solution using a homogenizer at 20,000 rpm for 5 min with sonication. The seed dispersion was swollen with the emulsion at room temperature with 200 rpm stirring. The DSM process was continued until the emulsion disappeared completely. Then, 10 g 5 wt% PVA solution and 50 g 0.2 wt% $NaNO_2$ solution were added slowly and the swollen particles were polymerized at 55 °C for 7 h. After this procedure, monodisperse polymer/LC microcapsules incorporating a mononuclear LC droplet were obtained, owing to phase separation by polymerization (PIPS). Then, the microcapsules obtained were washed with water repeatedly and dried at room temperature. The recipe for the DSM is represented in Table 2.

Table 1 The standard recipe for dispersion polymerization: 55 °C, 24 h; 10 wt% of monomer concentration based on total weight

Ingredients	Linear poly (methyl methacrylate) (g)	Cross-linked poly(methyl methacrylate) (g)
Methyl methacrylate	10	9.8
Poly(propylene glycol) diacrylate	–	0.2
Poly(vinylpyrrolidone)[a]	4	4
Aerosol-OT	0.45	0.45
Azobis(isobutylonitrile)[b]	0.1	0.1
Methanol	85.45	85.45

[a] 4 wt% of poly(vinylpyrrolidone) (M_w = 40,000 gmol^{-1}) based on total weight

[b] 1 wt% of azobis(isobutylonitrile) based on monomer weight

Measurements

The synthesis of PPG diacrylate was monitored using a Fourier transform IR (FT-IR)spectroscope (Nicolet, Mahgna IR-550). The morphology of the particles was observed using a scanning electron microscope (SEM, Hitachi) and a polarized optical microscope (POM, Olympus BH-2) equipped with an image analyzer. The degree of phase separation between the polymer and E7 in the particles was estimated using a differential scanning calorimeter (DSC, TA Instruments). All DSC measurements were carried out from 25 to 100 °C at 5 °C/min elevation temperature.

Results and discussion

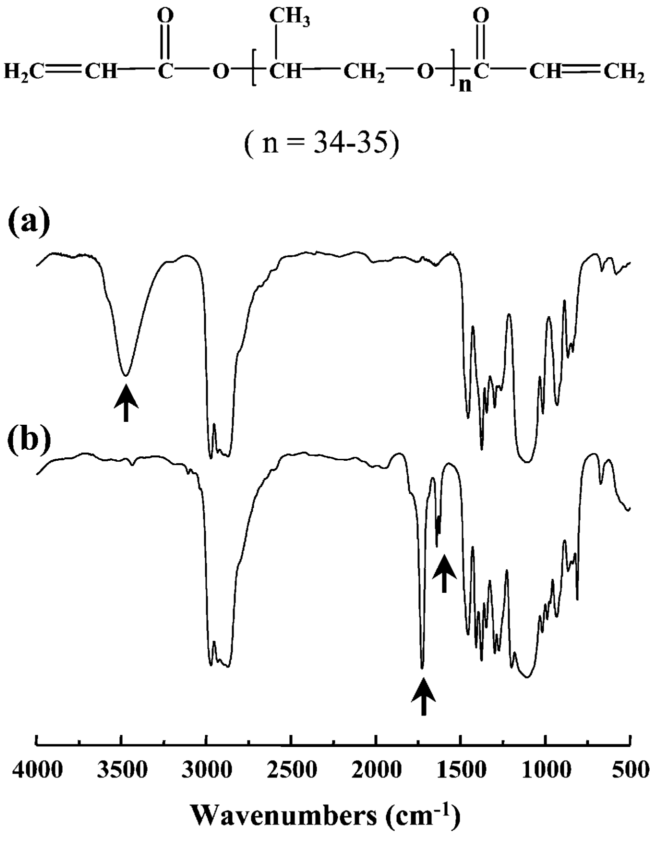
Dispersion polymerization [14–6] is widely used to produce monodisperse micron-sized polymer particles, owing to the ease of obtaining highly monodisperse micron-sized polymer particles and the simplicity of preparation. However, monomer-swellable, highly monodisperse cross-linked polymer particles cannot be obtained using conventional low-molecular-weight cross-linkers such as divinylbenzene and ethylene glycol dimethacrylate, etc. In our previous studies, highly monodisperse cross-linked particles were prepared using special cross-linkers [17–19], such as urethane acrylate, PPG diacrylate and poly(ethylene glycol)–PPG–poly(ethylene glycol) diacrylate. These particles could be swollen by a second monomer, owing to the flexible chains in the cross-linkers. In our study, to prepare monomer-swellable cross-linked PMMA particles, PPG-based diacrylate was synthesized using PPG 2000. The molecular structure and FT-IR spectra of PPG diacrylate are illustrated in Fig. 1.

The spectrum in Fig. 1, trace a is the IR chart of PPG and the peak around 3500 cm^{-1} indicates the hydroxyl

Table 2 The recipe for the preparation of poly(methyl methacrylate)/liquid crystal composite particles. The amount of monomer for diffusion-controlled swelling is fixed at 1 g

Ingredients	Weight (g)
Seed dispersion process	
Poly(methyl methacrylate) seed	0.2–0.5
SM solution[a]	40 g
Diffusion-controlled swelling process	
Methyl methacrylate	0.4–0.7
Styrene	0–0.3
E7	0.3
Benzoyl peroxide	0.007
SM solution	15 g
Polymerization process	
$NaNO_2$ solution (0.2 wt%)	50
Poly(vinyl alcohol) solution (5 wt%)	10

[a] 1:4 ethanol: 0.25 wt% sodium dodecyl sulfate solution



$$H_2C{=}CH{-}\overset{O}{\overset{\|}{C}}{-}O{-}[\overset{CH_3}{\overset{|}{C}H}{-}CH_2{-}O]_n{-}\overset{O}{\overset{\|}{C}}{-}CH{=}CH_2$$

Fig. 1 The molecular structure and Fourier transform IR spectra of poly(propylene glycol) (PPG) based cross-linker: *a* PPG spectrum, *b* PPG diacrylate spectrum groups in PPG. After reaction with acryloyl chloride, the hydroxyl peak of PPG disappeared and two peaks appeared around 1750 and 1650 cm^{-1}, which indicate the carbonyl group and C = C double bond, respectively (Fig. 1, trace b). As a result of the FT-IR measurements, we could confirm the reaction. By using the synthesized cross-linker, we can obtained the monomer-swellable cross-linked seed particles.

When the cross-linked seed particles were swollen with second monomers, we called this swelling process a DSM [14, 15]. In our studies, polymer/LC microcapsules were prepared using dispersion polymerization and the DSM. Methods for swelling a second monomer emulsion in polymer seed particles have been investigated by several researchers; Higuchi and Misra [20] investigated the degradation of an emulsion in the aqueous phase by diffusion. Ugelstad and Mork [21, 22] developed the procedure for the preparation of slightly water soluble acrylic monomer emulsions and determined their diffusion rate, etc. Park et al. [23] reported the application of the DSM for the preparation of many functionalized materials. Dispersed seed particles can be swollen efficiently using finely emulsified monomer by diffusion of monomer to seed particles in the aqueous phase via Ostwald ripening [24–26]. Ostwald ripening is an emulsion degradation process, which is due to the chemical potential gradient between large and small droplets and/or particles. As a result, small particles become smaller and large particles become larger. This mechanism could be controlled by the solubility of the monomer in the medium, the difference between the size of the seed particles and the monomer emulsion droplet, the temperature, the stirring speed, the surfactant concentration etc. So, we determined the swelling condition of PMMA seed particles with LC and monomer mixture emulsions by the change in the medium solvency and the surfactant, SDS, concentration.

To adjust the medium solvency with respect to the LC and monomer mixture, an ethanol/water mixture was used as the medium in our experiments. The optimum condition was determined at the ratio of ethanol/water of 1/4. In the case of 1/3, the solvency was so high that large amounts of LC and monomer mixture emulsions were dissolved in the aqueous medium, with the result that the LC and monomer mixture did not diffuse toward the polymer seed particles efficiently and existed in aqueous medium. However, in the case of 1/5, the solvency was so low that the mixture emulsions remained in medium even after swelling for a few days above ambient temperature. The micellar concentration was determined at 0.25 wt% by testing the degree of swelling over 1 day. In the case of a nonionic surfactant, it is generally known that the swelling rate increases significantly with the increase in concentration [24]. However, the droplet state is stabilized in the aqueous phase at a high concentration of anionic surfactants, so the emulsion does not diffuse toward the seed particles.

We carried out the diffusion-controlled swelling in accordance with the conditions previously mentioned, and then the polymerization was executed. LC domains are separated with polymer during the polymerization (PIPS). The stability and the final morphology of the microcapsules are significantly affected by the polymerization condition; therefore, several experiments, such as the addition of stabilizer, polymerization inhibitor and polymerization temperature, were carried out. PVA (10 g 5 wt% solution) and $NaNO_2$ (50 g 0.2 wt%) were added before the polymerization to stabilize the microcapsules during the polymerization and to inhibit the polymerization in an aqueous medium. The polymerization temperature was determined at 55 °C to prevent the drastic shrinkage during the polymerization. The LC was drained into the aqueous phase during the polymerization when the polymerization was carried out at higher temperature, owing to shrinkage. All the experiments were carried out in SM solution at room temperature.

The degree of polymerization is one of the important factors in PDLC preparation because unreacted monomer and oligomer have a significant influence on the electrooptical properties. The unreacted components in the LC droplet prohibit the alignment of the LC in the electrically on and off states, resulting in the increase in the threshold voltage, the increase in the response time, the decrease in the contrast ratio, and so on. To investigate the polymerization and the phase-separation behavior, the degree of polymerization was measured by a gravimetric method. The test was executed with an MMA/St/E7/BPO weight ratio of 0.4/0.3/0.3/0.007 using an emulsion polymerization method [27, 28] and the results are illustrated in Fig. 2.

The polymerization conversion was similar to that of conventional emulsion polymerization; however, the final conversion was slightly lower owing to the existence of LCs in the polymerizing system. About 85% conversion could be obtained after 7-h polymerization (conventional emulsion polymerization: 90%). Almost all the PDLC systems showed incomplete phase separation, irrespective of high polymerization conversion, owing to the natural affinity between the polymer and the LC. The phase separation between the LC and the polymer was observed by polarized optical microscope measurement with polymerization time. In our system, the phase separation was observed above 70% conversion after 2-h polymerization.

The degree of phase separation was investigated using DSC measurements. The T_{NI} of pure E7 is 61 °C and the enthalpy change at the transition temperature was 3.249 Jg^{-1}; however, E7 in the PMMA particles showed different results in comparison with pure E7. The T_{NI} of

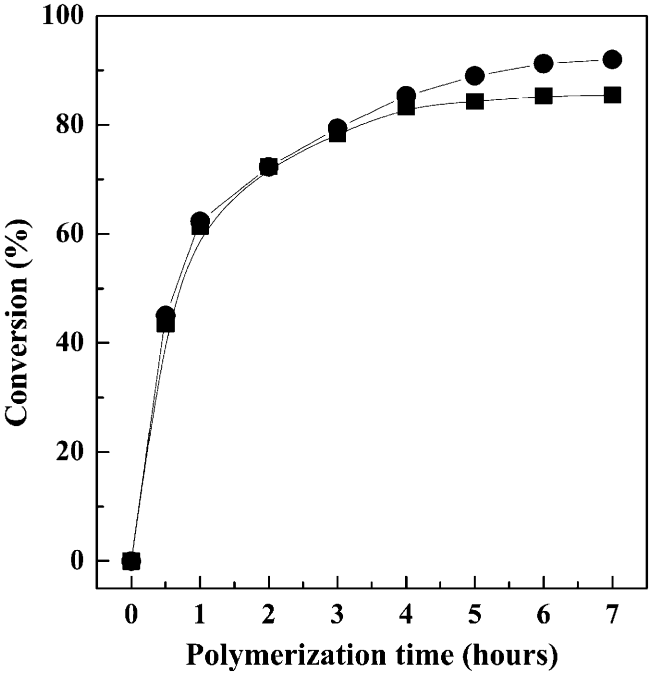


Fig. 2 The polymerization conversion of an E7, methyl methacrylate (*MMA*) and styrene (*St*) mixture in emulsion polymerization (MMA/St/benzoyl peroxide = 0.4/0.3/0.007, -■-: with E7, -●-: without E7)

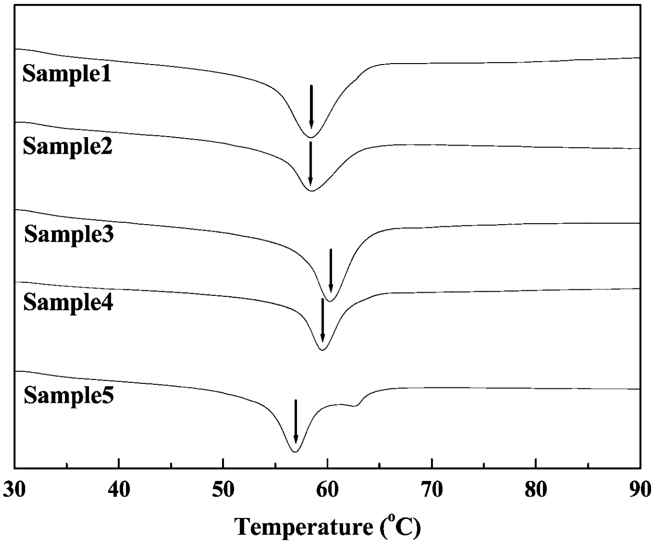


Fig. 3 Differential scanning calorimetry thermograms of poly(methyl methacrylate) (*PMMA*)/liquid crystal (*LC*) composite particles

E7 in microcapsules and the enthalpy change decreased because the anchoring of the polymer/LC boundary stimulates the transition of the LC from the nematic to the isotropic phase. Generally, it is reported that the small amount of low-molecular-weight LC is dissolved in the polymer matrix, and dissolved LC has an influence on the thermal properties and the electrooptical properties of PDLC. So, the evaluation of the phase separation of a LC in a polymer matrix is required and the criteria of this phenomenon can be evaluated by following equations [29, 30].

$$\alpha = \frac{\Delta H_{\mathrm{NI(obs)}}}{\phi \Delta H_{\mathrm{NI(LC)}}} \ ,$$

$$\phi = \frac{m_p}{m_{\mathrm{LC}} + m_{\mathrm{P}}} \ ,$$

where α is the amount of low-molecular-weight LC in the LC droplet. $\Delta H_{\mathrm{NI(obs)}}$ and $\Delta H_{\mathrm{NI(LC)}}$ are the observed transition enthalpy and the transition enthalpy of the pure LC, respectively. m_{P}, m_{LC} and ϕ are the weight of the polymer and the LC in PDLC and the weight fraction of the polymer matrix in PDLC, respectively. The transition enthalpy was measured using DSC. DSC thermograms and the degree of phase separation (α) are shown in Fig. 3 and in Table 3.

The transition temperature and the enthalpy change by transition of the LC capsules were relatively low in comparison with pure E7, indicating that the phase separation does not occur completely. However, the cross-linked particle was relatively well phase separated. This fact could be evaluated by the α value. As seen in Table 3, as the amount of LC incorporated increased, α increased firstly owing to the increase of well-separated LCs and then deceased owing to the increase of dissolved LCs in the matrix. As a consequence, it is suggested that the large amount of LC in the PMMA particles exists in the form of droplets. It is predicted indirectly that the final morphology of microcapsules is E7 (core)–poly(MMA-*co*-St) (shell) type.

Table 3 The degree of phase separation of poly(methyl methacrylate)/liquid crystal composite particles

	T_{NI} (°C)	ΔH (Jg^{-1})	ϕ	α
Pure E7	61	3.249	–	–
Sample 1[a]	58.49	2.629	0.769	1.052
Sample 2[b]	59.29	3.169	0.8	1.219
Sample 3[c]	60.30	3.231	0.786	1.279
Sample 4[d]	59.50	2.976	0.769	1.19
Sample 5[e]	56.97	2.010	0.75	0.825

[a] Sample 1: linear seed (0.3 g), methyl methacrylate (0.4 g), styrene (0.3 g), E7 (0.3 g)
[b] Sample 2: cross-linked seed (0.5 g), methyl methacrylate (0.4 g), styrene (0.3 g), E7 (0.3 g)
[c] Sample 3: cross-linked seed (0.4 g), methyl methacrylate (0.4 g), styrene (0.3 g), E7 (0.3 g)
[d] Sample 4: cross-linked seed (0.3 g), methyl methacrylate (0.4 g), styrene (0.3 g), E7 (0.3 g)
[e] Sample 5: cross-linked seed (0.2 g), methyl methacrylate (0.4 g), styrene (0.3 g), E7 (0.3 g)

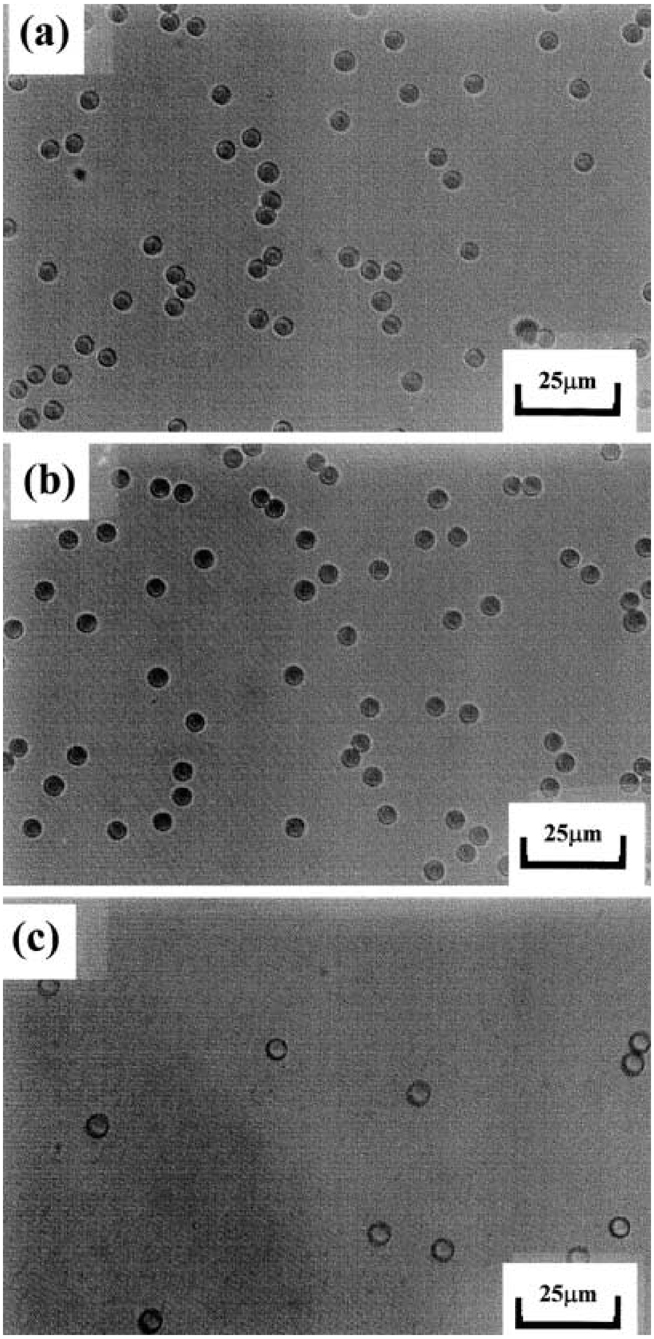


Fig. 4 Photographs of the morphology changes with manufacturing process using an optical microscope (*OM*): **a** seed particles; **b** swollen particles (before polymerization); **c** microcapsules (after polymerization)

The morphology change of the seed particles and the microcapsules with manufacturing step is illustrated in Fig. 4.

Cross-linked seed particles show monodisperse spherical shape (Fig. 4a). After the DSM process with the LC and monomer mixture, the morphology was maintained and the particle size increased slightly. Any fine emulsion droplets in the aqueous phase could not be detected (Fig. 4b) and this means that the LC and monomer mixture emulsion was completely swollen into the seed particles. Monodisperse spherical morphology was sustained after polymerization (Fig. 4c).

The morphology of the seed particles and the microcapsules was observed using SEM and the SEM photographs are illustrated in Fig. 5.

The cross-linked PMMA seed particles show high monodispersity (Fig. 5a). Their size is about 3.772 μm and the polydispersity is 1.003. The microcapsules became slightly larger than the seed particles owing to

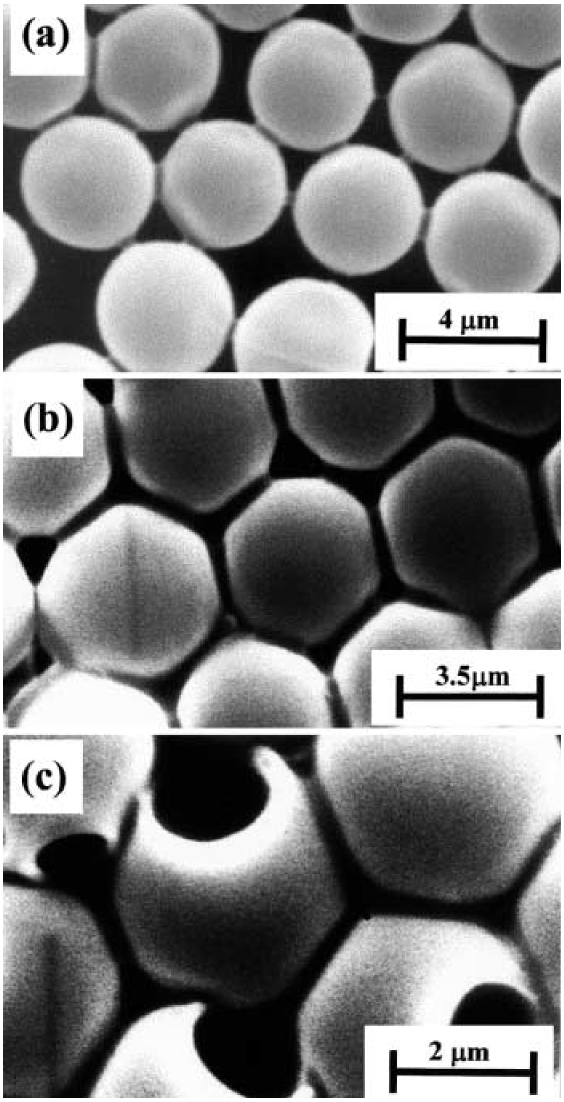


Fig. 5 Scanning electron microscope photographs of seed particles and PMMA/LC microcapsules: **a** cross-linked PMMA seed particles; **b** PMMA/LC microcapsules (using cross-linked PMMA seed); **c** PMMA/LC microcapsules after extraction with methanol

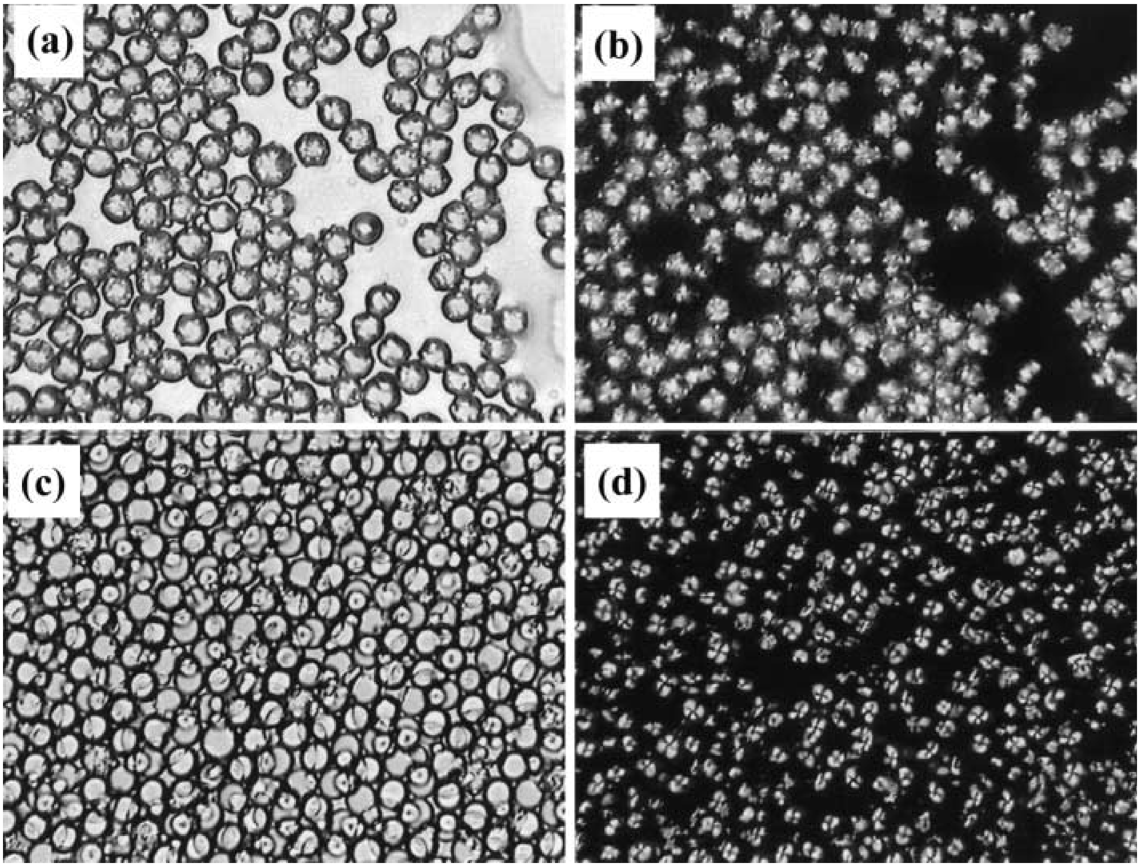


Fig. 6 Photographs of PMMA/LC composite particles using a polarized optical microscope (*POM*): **a**, **b** OM and POM photographs of sample 1; **c**, **d** OM and POM photographs of sample 4

the incorporation of poly(MMA-*co*-St) and LC. However, the shape of the microcapsules does not change and maintains the monodispersity even after a few days. The morphology of the microcapsules after extraction with methanol for 1 day is shown in Fig. 5c. The LC core was extracted through the weak point of the shell; as a result, an internal cavity per particle was observed. This picture indicates that the single-domain LC core was formed in a microcapsule; however, the LC domain existed near the shell, owing to the interaction between the aqueous phase/LC and the LC/cross-linker which has slight hydrophilicity. In this method, the morphology of the microcapsules could be investigated; however, the internal structure and the existence of LCs could not be confirmed directly using SEM; therefore, we used the POM with crossed polarizers. The POM photographs are shown in Fig. 6.

The LC phase is shown spherically in microcapsules in Fig. 6. In the case of using linear particles, though the microcapsules show monodispersity when using the optical microscope, the LCs in the seed particles are squeezed out onto the surface of the seed particles with time (Fig. 6a, b). After annealing for 2–3 days in aqueous solution, the LC is squeezed out into the aqueous phase and the the microcapsules becomes acorn-shaped. However, in the case of cross-linked PMMA seed particles, the morphology of the LC core and the PMMA shell structure was maintained. That is, we could obtain stable core–shell-structured microcapsules by using the cross-linked particles. We expected that the monodispersity of the LC droplets would improve the electrooptical properties, such as the removal of the hysteresis effect and the sharpness of the operating voltage, and various optical properties can be obtained by introducing various types of LC and by controlling the composition and properties of the matrix polymers.

Conclusions

LCs were encapsulated in PMMA seed particles by the DSM process to prepare mono-sized LC microcapsules. The optimum condition for the DSM process was 1:4 ethanol/0.25 wt% SDS solution at room temperature. After polymerization at 55 °C, monodisperse polymer/LC microcapsules could be obtained. In the case of using linear PMMA particles, the morphology was distorted with annealing at ambient temperature, owing to the incomplete phase separation between PMMA and E7, i.e., a relatively large amount of LC dissolves in the PMMA seed particle. This dissolved LC lowers the glass-transition temperature of the polymer matrix. However, when cross-linked PMMA particles were used as a seed, mononuclear LC domains were observed and were sustained stably after annealing.

Acknowlegement This work was supported by the Brain Korea 21 Project.

References

1. Craighead HG, Cheng J, Hackwood S (1982) Appl Phys Lett 40:22
2. Kawatsuki N, Ono H (1995) J Appl Polym Sci 55:911
3. Shimada E, Uchida T (1992) Jpn J Appl Phys 31:352
4. Doane JW, Golemme A, West JL, Whitehead JR, Wu BG (1988) Mol Cryst Liq Cryst 65:511
5. Pane S, Caporusso M, Hakemi H (1997) Liq Cryst 23:861
6. Chien LC, Lin C, Fredley DS, McCargar JW (1992) Macromolecules 25:133
7. Doane JW, Vaz NA, Wu BG, Zumer S (1986) Appl Phys Lett 48:269
8. Zumer S, Doane JW (1986) Phys Rev A 34:3373
9. Fuh A, Caporaletti O (1989) J Appl Phys 66:5278
10. Ono H, Kawatsuki N (1995) Jpn J Appl Phys 34:L54
11. Montgomery GP, Vaz NA (1987) Appl Opt 26:738
12. Seeboth A (1993) Thin Solid Films 223:140
13. Ono H, Kawatsuki N (1995) Kobunshi Runbunshu 52:195
14. Li K, Stover HDH (1993) J Polym Sci Part A Polym Chem 31:2473
15. Kim JW, Suh KD (2000) Polymer 41:6181
16. Kim JW, Suh KD (1999) Colloid Polym Sci. 277:66
17. Shen S, Sudol ED, El-Aasser MS (1994) J Polym Sci Part A Polym Chem 32:1087
18. Kim JW, Kim BS, Suh KD (2000) Colloid Polym Sci 278:591
19. Kim JW, Suh KD (1998) Colloid Polym Sci 276:870
20. Higuchi WI, Misra J (1962) J Pharm Sci 51:459
21. Ugelstad J, Mork PC (1980) Adv Colloid Interface Sci 13:101
22. Ugelstad J (1978) Makromol Chem 179:
23. Park JG, Kim JW, Suh KD (2000) Colloid Polym Sci
24. Taylor P (1998) Adv Colloid Interface Sci 75:107
25. Weiss J, Hermann N, McClements DJ (1999) Langmuir 15:6652
26. Binks BP, Clint JH, Fletcher PDI, Rippon S (1998) Langmuir 14:5402
27. Bardran AS, Ayoub MMH, Abd MA, El-Ghaffar; Naser HE, Abd AA, El-Hakim (1997) Eur Polym J 33:537
28. Cochin D, Laschewsky A, Nallet F (1997) Macromolecules 30:2278
29. Kajiyama T, Miyamoto A, Kikuchi H (1989) Chem Lett 813
30. Park NH, Cho SA, Kim JY, Suh KD (2000) J Appl Polym Sci 77:3178