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ORIGINAL CONTRIBUTION

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Phase separation behavior of encapsulated liquid crystals in monodispersed acetalized poly(methylmethacrylate) particles

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Abstract To improve the degree of phase separation between polymer and LC in LC microcapsules, poly(methylmethacrylate-*co*-vinylacetate) substrate particles were acetalized by using aldehydes having a different chain length. LC microcapsules were prepared by the solute co-diffusion method (SCM). The phase separation behavior was evaluated with a differential scanning calorimeter (DSC). The degree of phase separation between LC and substrate particles modified with butyl aldehyde was relatively high in comparison with those modified with hexanal and octanal. This means that poly(vinylbutyral) (PVB) moiety in substrate particles causes the complete phase separation and a single LC domain formation. On the contrary, as the aldehyde chain lengthened, the phase separation of LC domain was inhibited.

Keywords Liquid crystal · Polymer-dispersed liquid crystal · Acetalization · Phase separation · Microcapsule

Introduction

Polymer/liquid crystal (LC) composites have been the focus of an immense number of investigations because of their potential applications. Recently, polymer-dispersed liquid crystals (PDLC) [1, 2, 3, 4, 5, 6] and polymer-stabilized liquid crystals (PSLC) [7, 8] have been intensively investigated and applied in the field of display devices due to advantages such as polarizer-free, alignment layer-free, fast response time, simple preparation, and so on. Generally, they are fabricated by phase separation methods such as thermal-induced phase separation, solvent evaporation-induced phase separation, and polymerization-induced phase separation [1, 2, 3, 4, 5, 6, 7, 8]. Because the morphology of LC domain in polymer matrix depends largely on the condition during the phase separation process and significantly affects the electro-optical properties, many researchers have investigated the phase separation behavior of LC domain theoretically and experimentally [9, 10]. The morphology of LC domain depends largely on the diffusion and coalescence of LC molecules in polymer matrix. So it is expected that the hardening rate and the glass transition temperature of polymer matrix would be very important. Though polymer matrix having a low glass transition temperature has a low thermal stability, it has some advantages such as a well-defined PDLC morphology.

In our previous study, we proposed useful methods (diffusion-controlled polymerization method (DPM) and solute co-diffusion method (SCM)) for producing the mono-sized polymer/LC microcapsules [11, 12, 13] in which the size and size distribution of LC droplets can be easily controlled. These special types of polymer/LC microcapsules containing micron-sized LC domains could be applied to PDLC [13]. As a result, it is known that the electro-optical properties of PDLC are affected by the size and size distribution of LC droplets, the amount of LC, and the degree of phase separation of LC in PDLC.

In this work, in order to improve the phase separation of LC domain in polymer/LC microcapsules, monodispersed poly(methylmethacrylate-*co*-vinylacetate) particles were prepared and modified by hydrolysis and acetalization with butanal, hexanal, and octanal. All reactions were monitored by FT-IR and nuclear magnetic resonance (NMR). Then, the phase separation behaviors were evaluated by using a differential scanning calorimeter (DSC) and a polarized optical microscope (POM).

Experimental

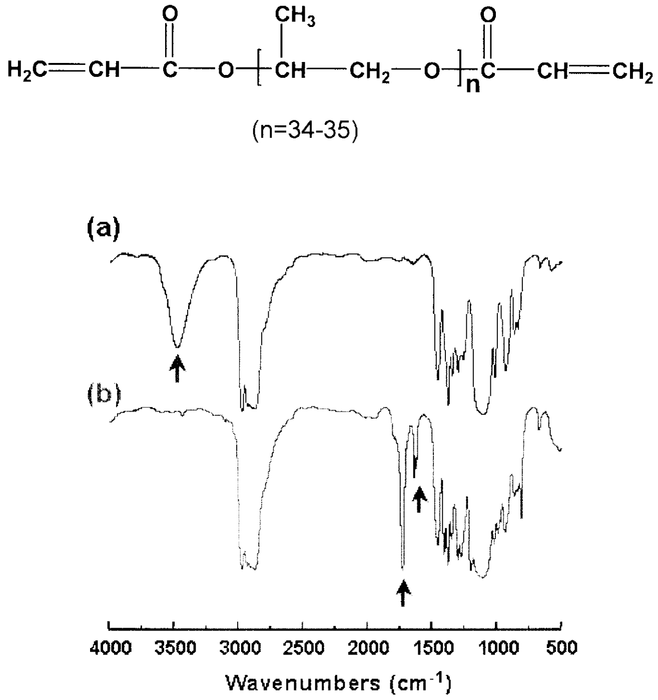
Materials

Methylmethacrylate (MMA, Junsei Chemical), vinyl acetate (VAc, Junsei Chemical), magnesium sulfate anhydrous ($MgSO_4$, Junsei Chemical), polyvinylpyrrolidone (PVP, $M_w = 4.0 \times 10^4\ gmol^{-1}$, Aldrich Chemical), 2,2'-azobis(isobutyronitrile) (AIBN, Junsei Chemical), aerosol-OT (AOT, Sigma Chemical), sodium hydroxide (NaOH, Junsei Chemical), sodium sulfate anhydrous (Na_2SO_4, Aldrich Chemical), sulfuric acid (samchun pure chemical), aldehydes (butyraldehyde (99%), hexanal (98%), and octyl aldehyde (99%), Aldrich Chemical), and methanol (Mallinckrodt) were all reagent grades. In the synthesis of crosslinker, polypropylene glycol (PPG, $M_w = 2000\ gmol^{-1}$, Polyol), acryloyl chloride (Sigma Chemical), and tetrahydrofuran (THF, Mallinckrodt) were used without further purification. Methylene chloride (MC, Aldrich Chemical), sodium dodecylsulfate (SDS, Wako Pure Chemical), ethanol (Mallinckrodt), and distilled deionized (DDI) water were also used without further purification. Low molecular weight LC, MLC-6014 (MLC, $T_{NI} = 81$ °C, $\Delta n = 0.13$, $\Delta\epsilon = +18.0$) was purchased from Merck.

Synthesis of PPG diacrylate as a crosslinker

To synthesize a crosslinker, the reaction of PPG and acryloyl chloride in THF was carried out at below 5 °C for 5 h and continued at 50 °C for 5 h. The product was extracted by adding water and chloroform. Organic layer was separated by using a separation funnel and dried with $MgSO_4$. Finally, chloroform was then evaporated with a rotary evaporator. Through this process, PPG diacrylate could be obtained. The molecular structure and FT-IR spectra of PPG diacrylate are illustrated in Fig. 1.

Figure 1a shows IR spectrum of PPG. The peak around 3500 cm^{-1} indicates the hydroxyl groups in PPG. After the 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 bond, respectively (Fig. 1b).



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

Fig. 1a, b. Molecular structure and FT-IR spectra of PPG based crosslinker. **a** PPG. **b** PPG diacrylate spectrum

Preparation of mono-sized poly (MMA-*co*-VAc) substrate particle

The mono-sized poly(MMA-*co*-VAc) particles were produced by dispersion polymerization. AOT, PVP, and methanol were weighed into the 250 ml four-necked round flask equipped with a reflux condenser, nitrogen inlet apparatus, and a mechanical stirrer. After mixing for 30 min at ambient temperature, MMA, VAc, AIBN, and PPG diacrylate homogeneous mixture were poured into the reactor and stirred vigorously to mix the reactants homogeneously at room temperature. The mixture was polymerized at 58 °C for 24 h with 50 rpm stirring. Poly(MMA-*co*-VAc) particles could be recovered by washing with water repeatedly and drying in air. A standard recipe is summarized in Table 1.

Table 1. Standard recipe for the dispersion polymerization of poly(MMA-*co*-VAc) substrate particles[a]

Ingredient	Weight (g)
MMA	13.2
Vinyl acetate[b]	1.5
PPG diacrylate	0.3
PVP K-30[c]	7
Aerosol-OT[d]	0.45
AIBN[e]	0.2
Methanol	82.85

[a] Polymerized at 58 °C for 24 h with 50 rpm stirring. Solid content was 14 wt%

[b] 10 wt% of vinylacetate (VA) based on MMA weight

[c] 6.6 wt% of PVP based on total weight

[d] Di-2 ethylhexyl ester of sodium sulfosuccinic acid

[e] 1.3 wt% of AIBN based on monomer weight

Hydrolysis of poly (MMA-*co*-VAc) substrate particles

Poly(MMA-*co*-VAc) substrate particles were redispersed in methanol with 40 wt% of NaOH aqueous solution. Hydrolysis was carried out at 55 °C for 24 h with magnetic stirring. Then, hydrolyzed poly(MMA-*co*-VAc) particles were washed with water repeatedly and dried in air. The reaction could be confirmed by using FT-IR. A standard recipe is summarized in Table 2.

Acetalization of hydrolyzed poly(MMA-*co*-VAc)

Hydrolyzed poly(MMA-*co*-VAc) substrate particles were dispersed in DDI water, Na_2SO_4, and 0.25 wt% SDS aqueous solution/EtOH (4/1, g/g). After aldehyde was dissolved in methanol with sulfuric acid, the mixture was poured into the reactor and stirred for 1 h at room temperature. Then, the reaction was carried out at 60 °C for 24 h. Acetalized particles were recovered by washing and drying in air. A standard recipe is summarized in Table 3.

Table 2. Standard recipe for hydrolysis of poly(MMA-*co*-VAc)[a]

Ingredient	Weight (g)
Poly(MMA-*co*-VAc)	5
Methanol	100
NaOH[b]	3

[a] 55 °C for 24 h
[b] 40 wt% of NaOH aqueous solution

Table 3. Recipe for acetalization of hydrolyzed poly(MMA-*co*-VAc)[a]

Ingredient		Weight (g)
Stage I	Hydrolyzed seed	1
	Sodium sulfate	1.5
	Sol.[b]	5
	DDI	30
Stage II	Aldehydes[c]	1
	Sulfuric acid	0.5
	Methanol	30

[a] 60 °C for 24 h
[b] 0.25 wt% SDS aqueous solution/EtOH (4/1, g/g)
[c] Butyraldehyde, hexanal, and octyl aldehyde

Table 4. Standard recipe for SCM and solvent evaporation process

Stage	Ingredient	Weight (g)
Seed dispersion	poly (MMA-*co*-VAc)	0.3
	Sol.[a]	40
MLC/MC emulsion[b]	MLC[c]	0.3
	Solvent[d]	2.7
	Sol.	15
Solvent evaporation[e]	–	–

[a] 0.25wt% SDS aqueous solution/ethanol (4/1, g/g)
[b] Preparation and swelling process is carried out at room temperature
[c] MLC-6014(Merck), $T_{NI} = 81$ °C, $\eta = 91$(at 0 °C)
[d] Methylene chloride, BP = 40 °C, $\epsilon = 9.1$
[e] At room temperature, over 7 days

Microencapsulation of LC in poly (MMA-*co*-VB) by using various aldehydes via SCM

Acetalized polymer substrate particles were redispersed in 0.25 wt% of SDS aqueous solution/ethanol (4/1, g/g). Dispersed substrate particles were swollen with MLC/MC fine emulsions at room temperature until all emulsion droplets disappeared completely. Then, MC in swollen microcapsules was evaporated slowly at room temperature. Mono-sized polymer/LC microcapsules incorporated a mononuclear LC domain could be obtained by the phase separation of MLC occurred during the solvent evaporation. A standard recipe and their schematic representation of SCM and the solvent evaporation are illustrated in Table 4 and Scheme 1, respectively.

Measurements

The synthesis of PPG diacrylate was monitored using a Fourier transform infrared spectroscope (FT-IR, Nicolet, Mahgna IR-550). The morphology of particles was observed using a scanning electron microscope (SEM, Hitachi model) and a polarized optical microscope (POM, Olympus BH-2) equipped with an image analyzer. The degree of phase separation between polymer and LC in microcapsules was estimated using a differential scanning calorimeter (DSC, Perkin-Elmer DSC-7 and TA instrument). All DSC measurement was carried out from 25 to 120 °C at 3 °C/min elevation temperature.

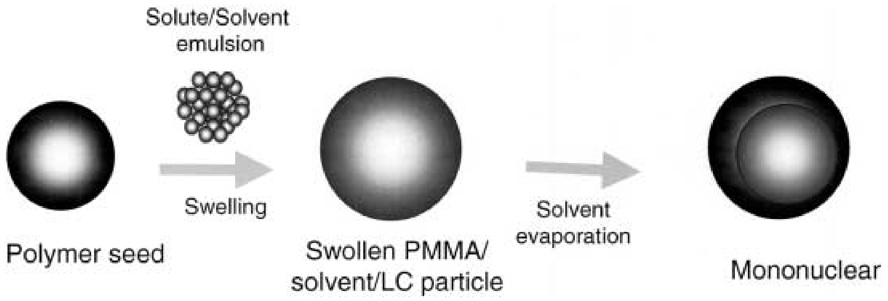
Results and discussion

Dispersion polymerization [14, 15, 16] is widely used to produce substrate polymer particles, due to the simple manufacturing of highly monodispersed micron-sized polymer particles. In our previous papers [11, 12, 13], highly monodispersed PMMA/LC microcapsules were prepared by employing the diffusion-controlled polymerization method (DPM) and the solute co-diffusion method (SCM) successfully.

Acetalization of hydrolyzed poly (MMA-*co*-VAc) by using aldehydes

Mono-sized poly(MMA-*co*-VAc) substrate particles were produced by dispersion polymerization. To maintain the monodispersity of polymer particles during hydrolysis and acetalization reaction, crosslinked polymer substrate particles were prepared by co-polymerizing with PPG diacrylate in dispersion polymerization. All the particles produced had a high monodispersity and a clear surface. Figure 2 shows the schematic representation of the proposed molecular structure and SEM image of poly (MMA-*co*-VAc) substrate particles.

Scheme 1. Preparation procedure for LC microcapsules by employing SCM



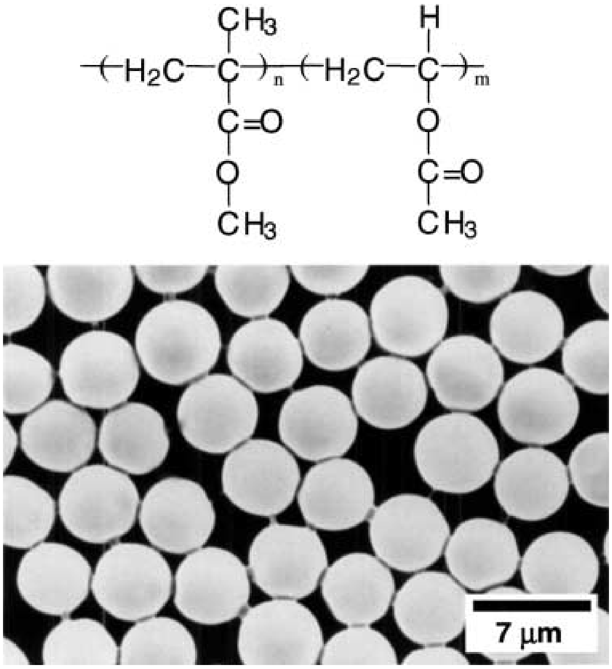


Fig. 2. Schematic molecular structure and SEM image of poly (MMA-*co*-VAc)

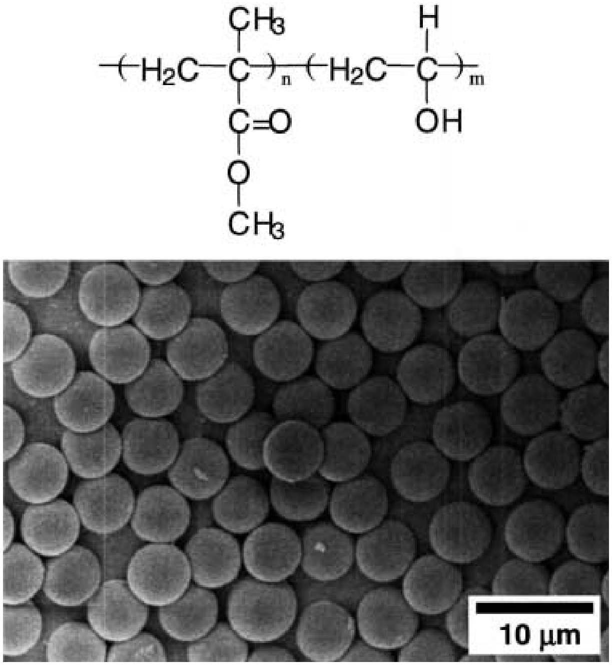
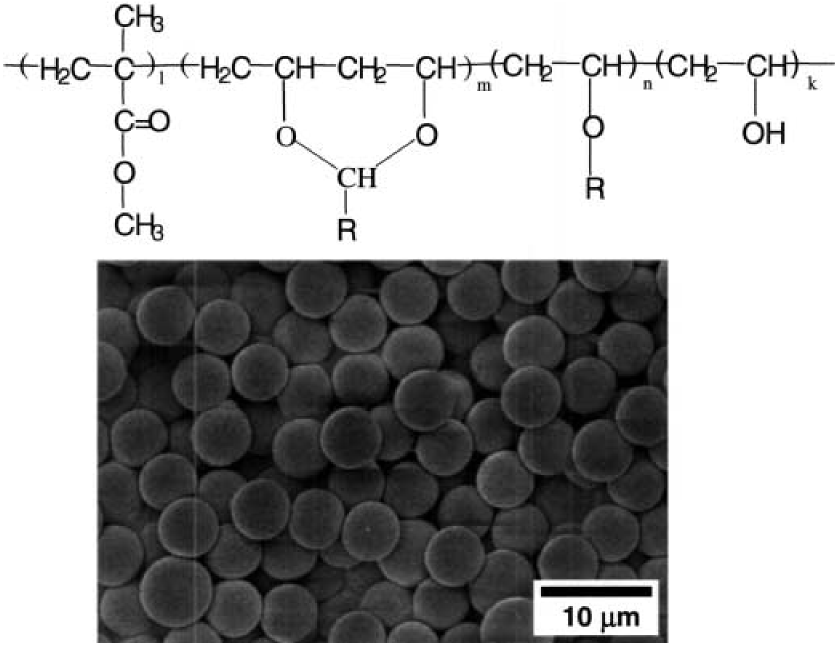


Fig. 3. Schematic molecular structure and SEM image of hydrolyzed poly(MMA-*co*-VAc)

The size and polydispersity (PDI) of poly(MMA-*co*-VAc) particle was 4.97 µm and 1.005, respectively. Substrate particles were hydrolyzed in basic condition to convert the acetate group to the hydroxyl group. The hydrolysis reaction was monitored by FT-IR and could be confirmed by appearance of the OH band around 3500 cm^{-1}. The size and shape of hydrolyzed poly (MMA-*co*-VAc) particles were maintained even after the hydrolysis reaction was completed as illustrated in Fig. 3.

Polar hydroxy groups obtained by the hydrolysis increase the interaction between polymer chains and we expect an increase of the glass transition temperature in comparison with poly(MMA-*co*-VAc).

Fig. 4. Schematic molecular structure and SEM image of poly (MMA-*co*-VB)



Acetalized polymer particles were manufactured by reacting hydrolyzed poly(MMA-*co*-VAc) particles with aldehydes. The molecular structure and SEM image of acetalized polymer particles are illustrated in Fig. 4.

The size and shape of particles were maintained even after acetalization. In general, it is well known that 100% acetalization cannot take place. Besides, the amount of hydroxyl group in particles is relatively small. Therefore, the probability of acetalization is expected to be below 10% based on the total weight. The glass transition temperature (T_g) of acetalized polymer particles is lowered with the higher the degree of acetalization.

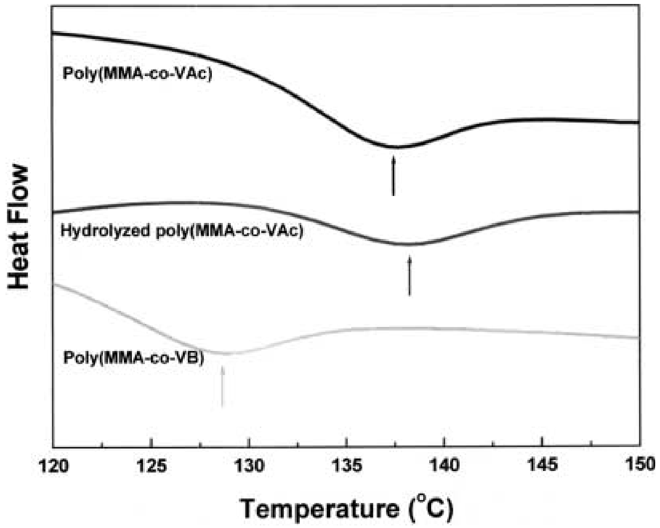


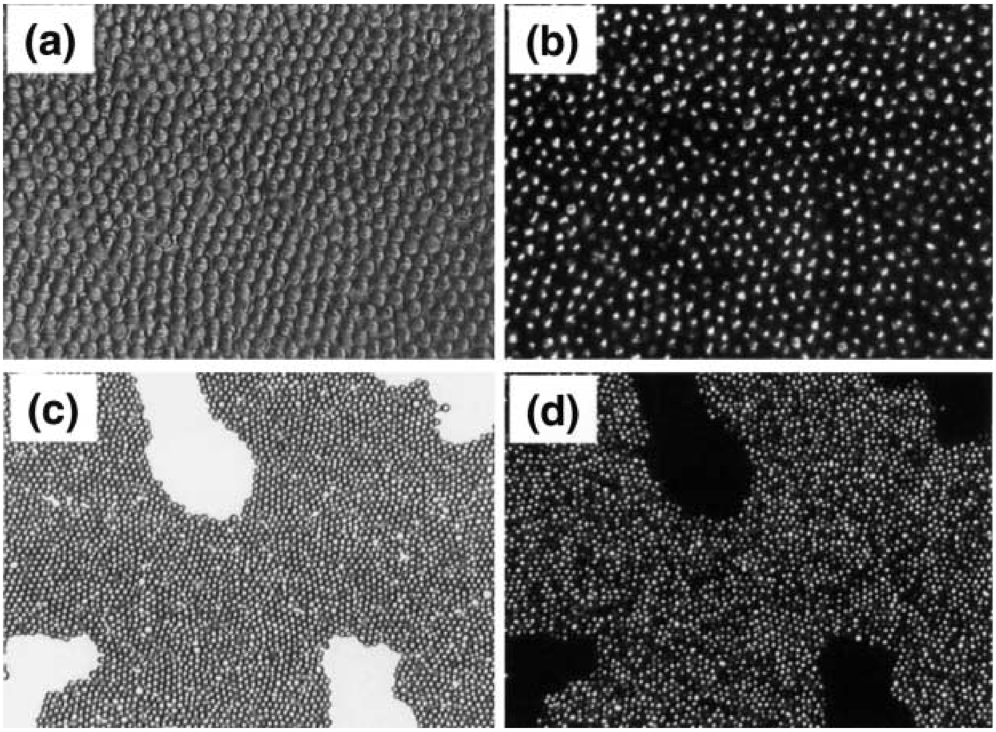
Fig. 5. DSC thermograms of substrate polymer

Figure 5 shows DSC thermograms of each of the substrate polymer particles. T_g of poly(MMA-*co*-VAc) is around 136 °C. T_g of hydrolyzed poly(MMA-*co*-VAc) is slightly higher than that of poly(MMA-*co*-VAc), due to the increase of interaction between chains (-OH formation). Because of the formation of cyclic acetal and rubbery property of poly(vinylbutyral), T_g of poly(MMA-*co*-VB) is lowered.

Microencapsulation of LC in acetalized substrate polymer by SCM

Mono-sized microcapsules were prepared by using the solute co-diffusion method (SCM). The SCM process starts with the diffusion of solute/solvent fine emulsions into the pre-existing monosized polymer particles via Ostwald ripening [17, 18, 19]. It is well known that Ostwald ripening caused by the chemical potential gradient between large and small particles can be controlled by the solubility of emulsion in the medium, temperature, stirring speed, and surfactant concentration etc. In our study, the swelling process was executed in 0.25 wt% SDS aqueous solution/ethanol = 4/1 at 25 °C with magnetic stirring. After complete swelling of LC/

Fig. 6a–d. OM (**a**, **c**) and POM (**b**, **d**) images for LC capsule-4: (**a**, **b** ×400) (**c**, **d** ×100)



MC emulsions, we could obtain uniformly swollen acetalized polymer particles. Then, MC in swollen particles was evaporated slowly at room temperature. In the process of evaporation, LC domains were phase-separated. The slow solvent evaporation led to the formation of a single and uniform LC domain in microcapsules and this could be confirmed by POM. The OM and POM photographs of capsule-4 are shown in Fig. 6.

Even after SCM, all the LC microcapsules maintained their initial spherical shape and monodispersity. In Fig. 6, we could verify that a single LC domain was formed in a microcapsule.

Figure 7 shows the POM photographs of capsule-6 and 8.

The phase separation of LC domain in capsule-4 (Fig. 6) was relatively clear in comparison with that in capsule-6 and 8. It is supposed that poly(vinylbutyral) moiety in polymer matrix caused the complete phase separation and a single LC domain formation. In capsule-6 and 8, on the contrary, the long side chains formed by the reaction of acetalization obstructed the alignment of low molecular weight liquid crystal.

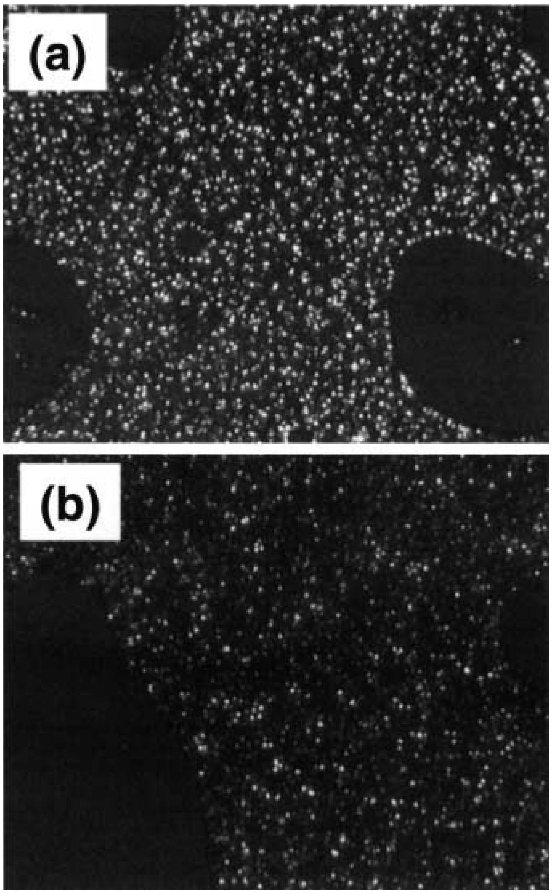


Fig. 7. POM photographs of LC capsule-6, 8 (**a**, **b**)

Phase separation behavior with DSC measurements

The degree of phase separation is one of the important factors in PDLC preparation because the LC dissolved in polymer matrix has a significant influence on electro-optical properties (the increase of threshold voltage, the increase of response time, and the decrease of contrast ratio etc.). Generally, the phase separation between LC and polymer was evaluated by DSC measurement [12]. T_{NI} of pure MLC-6014 is 81 °C and the enthalpy change at transition temperature was 2.789 J/g. However, MLC in microcapsules showed different results in comparison with pure MLC. The T_{NI} of MLC in microcapsules and the enthalpy change decreased because the anchoring of polymer/LC boundary enhances the transition of LC from nematic to isotropic phase. Generally, it is reported that the small amount of low molecular weight LC is dissolved in polymer matrix and that the LC dissolved in polymer matrix has an influence on the thermal properties and electro-optical properties of PDLC. So, the evaluation of phase separation of LC in polymer matrix is required and the criteria of this phenomenon can be evaluated by following equations [12, 20, 21]

$$\alpha = \frac{\Delta H_{NI(obs)}}{\phi \Delta H_{NI(LC)}} \tag{1}$$

$$\phi = \frac{m_p}{m_{LC} + m_p} \tag{2}$$

where, α is the amount of low molecular weight LC in LC droplet. $\Delta H_{NI(obs)}$ and $\Delta H_{NI(LC)}$ are the observed transition enthalpy and the transition enthalpy of pure LC, respectively. m_P, m_{LC}, and ϕ are the weight of polymer and LC in PDLC and the weight fraction of polymer matrix in PDLC, respectively. In this study, ϕ (= 0.5) is a

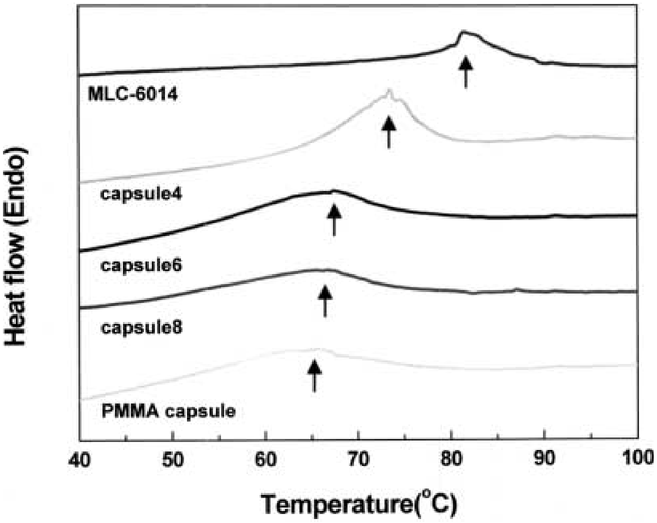


Fig. 8. DSC thermograms of LC microcapsules

Table 5. Degree of phase separation of LC microcapsules

	T_{NI} (°C)[a]	ΔH (J/g)	ϕ	α
MLC-6014	81.466	2.789	–	–
Capsule-4[b]	73.456	2.399	0.5	1.720
Capsule-6[c]	67.462	2.383	0.5	1.709
Capsule-8[d]	66.733	2.311	0.5	1.657
PMMA capsule	65.866	2.289	0.5	1.641

[a] T_{NI}: nematic-isotropic transition temp
[b] LC capsule-4: modified with butyral
[c] LC capsule-6: modified with hexanal
[d] LC capsule-8: modified with octanal

fixed value. The transition enthalpy was measured using DSC. DSC thermograms and the degree of phase separation (α) are shown in Fig. 8 and in Table 5.

The transition temperature and the enthalpy change by transition of LC microcapsules were relatively lowered in comparison with the pure MLC, indicating that the phase separation does not occur completely. However, capsule-4 was relatively well phase separated. This fact could be evaluated by looking at the α value. As the chain length of aldehydes lengthens, the degree of phase separation lowers because the long chain in polymer matrix obstructs the alignment of LC. In Table 5, the degree of phase separation and the observed transition enthalpy ($\Delta H_{NI(obs)}$) decreases due to the increase of dissolved LC in polymer matrix and disorder of LC molecules. It is suggested that the modified substrate polymer matrix enhances the transition of LC from nematic to isotropic phase and plays an important role in improving the phase separation.

Conclusions

Generally, phase separation patterns between polymer and LC during PDLC preparation affect the electro-optical properties due to anchoring energy and affinity. In order to improve the phase separation of LC in microcapsules, we modified the mono-sized poly (MMA-*co*-VAc) substrate particles using acetalization reaction with various aldehydes. Then, we produced highly mono-sized microcapsules using SCM. All the microcapsules maintained their initially spherical shape and monodispersity. The phase separation of LC in capsule-4 was relatively clear in comparison with that in capsule-6 and 8. It is supposed that poly(vinylbutyral) moiety in polymer matrix causes the complete phase separation and a single LC domain formation. On the contrary, the long alkyl chain formed by the acetalization reaction in capsule-6 and 8 obstructed the alignment of LC.

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