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The influence of nematic liquid crystal content on the electro-optical properties of a polymer dispersed liquid crystal prepared with monodisperse liquid crystal microcapsules

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Highly monodisperse poly(methylmethacrylate) (PMMA)/liquid crystal (LC) microcapsules were prepared by the solute codiffusion method (SCM). In SCM, the solvency of the dispersion medium and the swelling temperature were controlled to ensure complete swelling of the LC into the PMMA substrate particles. After the solvent evaporation procedure, mononuclear LC domains were formed in every particle, and overall the LC microcapsules maintained a spherical shape, monodispersity and smooth surface. PDLC cells prepared using the LC microcapsules exhibited an excellent contrast ratio and transmittance. By increasing the LC content in these LC microcapsules, the electro-optical properties of PDLC cells have been greatly improved.

1. Introduction

Polymer/liquid crystal (LC) composite systems are attractive for their potential application in fields such as light shutters, flexible displays and smart windows. Among these heterogeneous composites, polymer dispersed liquid crystals (PDLCs), consisting of micron-sized LC droplets embedded in a polymer matrix, have been investigated extensively for a wide range of electro-optic devices including information displays [1–6]. Unlike LCs in traditional displays, PDLCs are flexible and very easy to fabricate in large area displays since no orienting glass plates and therfore no complex surface treatments are required. Furthermore, their light transmittance is much higher than the common twisted- or supertwisted-nematic LC devices, owing to the absence of polarizers [7, 8].

The electro-optical response of PDLC films is based on electrically controlled light scattering by the LC molecules. In the absence of an electric field, the LC directors are arranged along the polymer surface causing light scattering and resulting in an opaque state. On the other hand, in the presence of an electric field of sufficient strength, the LC directors align parallel to the electric field and the film appears transparent [9]. The switching behaviour of PDLC films, resulting from the mismatching or matching of refractive index values between LC molecules and the polymer matrix, depends significantly upon the characteristics of the LC droplets in the polymer matrix such as shape, size, size distribution, and the amount of LC loaded. A wide size distribution of LC domains gives a broad transmittance change with an electric field and hysteresis [10]. An outstanding contrast ratio, low threshold and driving voltage for a PDLC can be achieved with higher content of LC in the polymer matrix due to the larger size and monodispersity of the LC droplets in LC microcapsules. However, conventional PDLC preparation methods utilizing phase separation such as polymerization-induced phase separation (PIPS), thermally-induced phase separation (TIPS), and solvent-induced phase separation (SIPS), lead to a broad size distribution of LC domains within the polymer matrix [11]. Also, it is difficult to control the size and size distributions of LC droplets and to obtain a high content of LC in the polymer matrix.

Recently, we have proposed a useful encapsulation method, called the solute codiffusion method (SCM) [12–15], to produce LC microcapsules. In the SCM, LC emulsions are swollen into monodisperse polymer particles, and subsequently LC droplets are created in a mononuclear form at each of the polymer particles by phase separation during solvent evaporation. By using the SCM, the size and size distribution of LC droplets can be tailored with ease, and it is possible to incorporate a large quantity of LC into the substrate particles. It has been confirmed that PDLCs using LC microcapsules show good electro-optical characteristics;

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for example, low driving voltages and high sharpness [14].

In the present research, in order to prepare a PDLC having good contrast ratio, lower threshold and driving voltages, the effects of LC content on the electro-optical characteristics of a PDLC formed using LC microcapsules were investigated. Phase separation during solvent extraction, and the morphology of the substrate particles and LC droplets were monitored through an optical and polarizing optical microscope (OM/POM) and a scanning electron microscope (SEM), respectively.

2. Experimental

2.1. *Materials*

Methyl methacrylate (MMA, Junsei Chemicals), poly(vinylpyrrolidone) (PVP, $M_w = 4.0 \times 10^4\,g\,mol^{-1}$, Aldrich Chemicals), 2,2′-azobis(isobutyronitrile) (AIBN, Junsei Chemicals) and aerosol-OT (AOT, Sigma Chemicals) were all reagent grade; polypropylene glycol diacrylate (PPGDA) was synthesized as a crosslinker [13, 16, 17]. Briefly, PPGDA is synthesized by the reaction of polypropylene glycol ($M_w = 2.0 \times 10^4\,g\,mol^{-1}$, Polyol) with acryloyl chloride (AC, Sigma) in tetrahydrofuran (THF, Mallinckrodt). Sodium dodecyl sulphate (SDS, Yakuri Chemicals), ethanol (J. T. Baker), methylene chloride (MC, J. T. Baker) and distilled deionized (DDI) water were used without further purification. The nematic liquid crystal (E7) is a eutectic commercial mixture of cyanobiphenyl derivatives purchased from E. Merck, UK. ($T_{NI} = 58°C$, $\Delta n = 0.22$, $\Delta\varepsilon = +13.8$).

2.2. *PMMA substrate particles by dispersion polymerization*

Highly monodisperse, crosslinked PMMA seed particles were produced by dispersion polymerization [13, 14]. PVP, AOT and methanol were weighed into a four-necked flask equipped with a reflux condenser, nitrogen inlet and mechanical stirrer. A MMA PPGDA AIBN mixture was then poured into the reactor and stirred vigorously to form a homogenous reaction mixture. The flask was submerged into a temperature-controlled water bath and polymerization allowed to proceed at 58°C for 24 h at 40 rpm. The PMMA particles were recovered after washing with water, centrifuging and drying at room temperature.

2.3. *PMMA/LC microcapsules by SCM*

PMMA substrate particles were redispersed in 0.25 wt % SDS ethanol/water (1/4, w/w) solution and swollen with a fine emulsion of LC and MC mixture utilizing an ultrasonic homogenizer until all emulsions disappeared completely. When more than 0.3 g of LC was used, the swelling temperature was raised to 38°C for complete swelling of LC emulsions into PMMA particles. The phase separation between LC and polymer occurred during MC evaporation at room temperature for 48 h and monodisperse PMMA/LC microcapsules containing a mononuclear LC domain were obtained. LC microcapsules were acquired by repeated precipitation and washing at room temperature. The standard method for the SCM process is given in table 1; a schematic of the SCM process has been shown previously [13–15].

Table 1. Standard method of SCM for preparation of LC microcapsules.

SCM step	Ingredient	Quantity/g
Seed dispersion	PMMA substrate	0.3
	SE solution[b]	40.0
SCM procedure[a]	LC	Variable[c]
	MC	2.7
	SE solution	15.0
Solvent evaporation[d]	—	—

[a]8 h, 100 rpm, 38°C.
[b]0.25 wt % SDS ethanol/water solution (1/4, w/w).
[c]0.3, 0.5, 0.7, 0.9 g of E7.
[d]At room temperature.

2.4. *Fabrication of PDLC cells*

PDLC cells were produced using LC microcapsules. LC microcapsules were mixed with a small amount of ethanol. The mixture was rubbed onto indium tin oxide (ITO) coated glass and sandwiched with another piece of ITO glass. Then, the PDLC cells were dried in a convection oven at 50°C, to evaporate the ethanol. The cell gap in the device was fixed to 25 μm using a PET film spacer. A schematic representation of the PDLC cells is shown in figure 1.

2.5. *Characterization*

The phase separation behavior and morphologies of the PMMA substrate particles and LC microcapsules were observed using an optical and polarizing optical microscope (OM/POM, Olympus BH-2) equipped with an image analyser and a scanning electron microscope (SEM, JSM-6300, Jeol). About one hundred individual particle diameters were measured from SEM

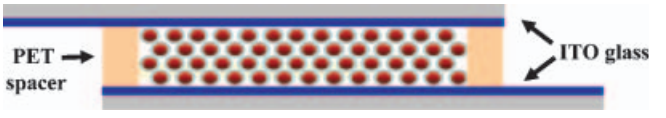

Figure 1. The PDLC cell fabricated using LC microcapsules.

photographs, the average was taken, and their polydispersity index (PDI) was determined. Electro-optical characteristics of PDLC cells were measured using a He-Ne laser (632.8 nm). All PDLC cells were tested three times to ensure repeatability of the measurement.

3. Results and discussion

3.1. *Monodisperse crosslinked PMMA substrate particles*

The monodispersity of the polymer particles is the key factor in the production of monodisperse microcapsules containing uniform LC droplets in each capsule. In our previous study [18], monodisperse PMMA particles were prepared successfully using dispersion polymerization. However, when the linear polymer particles were spread on to the PDLC substrates, leakage of LC molecules from the particles were found in the medium after the solvent evaporation step, even when the particles were highly monodisperse. To overcome this problem, 2 wt % of PPGDA, based on the monomer weight, was combined with MMA for the crosslinking of the particles. This macro-crosslinker, having a flexible backbone, would help to obtain a solvent-swellable substrate and prevent de-swelling of LC molecules after the solvent evaporation step. Non-spherical PMMA particles were obtained when PPGDA was greater than 2 wt %, and leakage of LC molecules was observed below 2 wt % of the crosslinker. In figure 2, an SEM photograph of the crosslinked PMMA particles is shown. These particles have high monodispersity and a smooth surface at 2 wt % of the crosslinker (2.7 μm, PDI = 1.01).

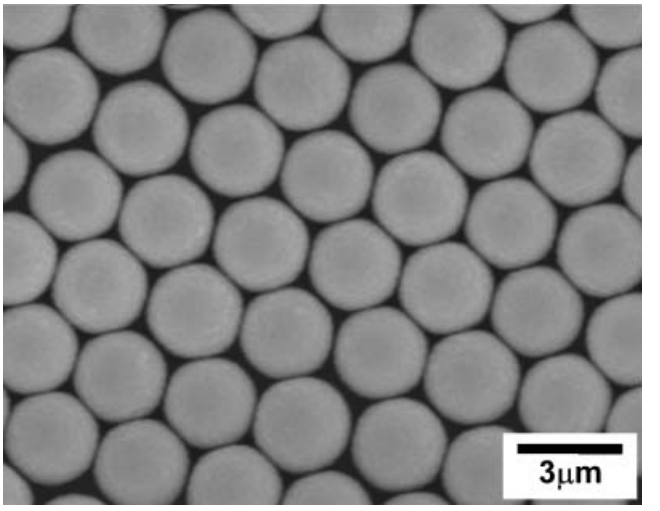

Figure 2. SEM photograph of the monodisperse and crosslinked PMMA seed particles.

3.2. *Preparation of LC microcapsules by SCM*

The basic concept of the SCM is that the fine solute/solvent emulsions are swollen efficiently into the micron-sized polymer particles by the process of Ostwald ripening [19–21]. In SCM, MC was employed as solvent for E7 because of its high solubility and low boiling point (40.1°C) [22]. By adjusting the solubilizing ability of the medium, swelling temperature, emulsion size or stirring speed, the swelling capacity of the polymer particles could be controlled easily. In our previous study [17], the ratio of ethanol/water of 1/4, and 0.25 wt % of SDS based on the medium were determined as optimum conditions for medium solvency when 0.3 g of substrate particles and 0.3 g of LC were used to produce LC microcapsules. However, when the LC content was greater than 0.3 g, a large amount of LC emulsion remained in the medium or at the interface of the substrate particles. To facilitate the migration of LC emulsion into the substrate, the swelling temperature was controlled in this work. The swelling temperature for complete swelling of LC above 0.3 g was achieved at 38°C. Over 38°C, incorporated MC was vapourized during the swelling step and the LC emulsion did not diffuse further toward the particles. At temperatures under 38°C, many emulsions remained in the medium even after swelling for several days. Despite the LC three times greater than seed weight (0.3 g seed, 0.9 g LC), a complete swelling of the LC emulsion toward PMMA particles was obtained, maintaining their spherical shape of microcapsules as shown in figure 3. Fine emulsion droplets were not detected in the medium, see figure 3 (*c*), and the size of particles was slightly increased indicating that the LC and MC mixture emulsion was completely swollen into the PMMA substrate particles. Finally the solvent was removed slowly at room temperature. During solvent evaporation, phase separation between polymer and LC became evident due to the difference in solubility.

3.3. *The morphology of LC microcapsules*

The shape of LC droplets in the polymer matrix depends on the LC content, and is an important factor in determining the optical density and contrast ratio of PDLCs [23, 24]. When a large content of LC was incorporated in the PDLC film via the conventional phase separation method, LC droplets did not maintain a spherical shape, or phase-inversion between the continuous polymer phase and the dispersed LC droplets occurred, which caused a poor contrast ratio. In addition, the electro-optical property of the PDLC was affected significantly by the LC droplet size in the polymer matrix [25]. However, as shown in figure 4, when LC microcapsules were prepared by SCM, the spherical and monodisperse shape of the

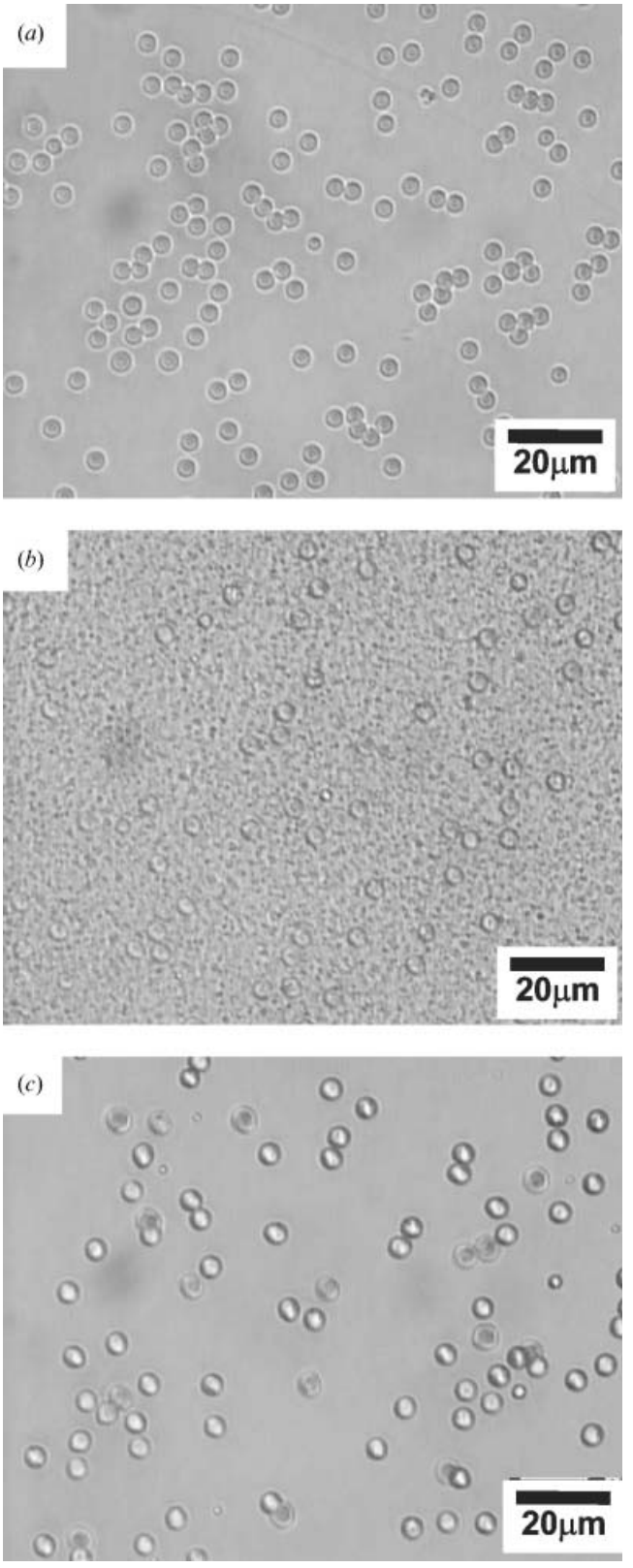

Figure 3. OM images of (*a*) PMMA substrate dispersion, (*b*) after adding LC/MC emulsion to medium, (*c*) after complete swelling of LC/MC emulsion into the seed particles, in a preparation of 3/9 microcapsules by SCM.

particles was observed through OM (left side) even though a large amount of LC was used. Also, uniform and clear LC domains were confirmed and the radial alignment of LC molecules was ascertained in each LC microcapsule by POM (right side). To confirm the loading state of LC in the microcapsules, SEM was used after the LC was extracted with heat and pressure. Figure 5 shows a round and single cavity in every microcapsule. From these results, it was concluded that phase separations between the polymer and LC occurred successfully after solvent extraction, and a mononuclear LC domain in the PMMA particles was then formed. A larger content of LC results in a corresponding increase in the size of LC microcapsules and hence the thickness of the PMMA wall gradually decreased. The average size of the PMMA/LC microcapsules was measured as 3.19, 3.60, 3.94 and 4.18 μm for 3/3, 3/5, 3/7 and 3/9, ratios of PMMA/LC, respectively.

3.4. *Electro-optical characteristics of PDLC cells*

PDLC cells fabricated from LC microcapsules placed on ITO glass slides (figure 1). The wall of a LC microcapsule was slightly melted by ethanol and formed as a polymer matrix during the drying procedure. However, this did not affect the shape of the LC domains in the PDLC cells. To obtain a good cell contrast ratio, multi-layers of LC microcapsules were employed by using a 25 μm PET spacer (more than five layers of capsules) to scatter the incident light sufficiently. Figure 6 shows the transmittance changes of PDLC cells relative to the applied voltage using capsules of varying PMMA/LC ratio. The driving voltages are summarized in table 2. Excessive leakage of LC molecules occurred in the 3/9 microcapsules after PDLC cell fabrication. It is assumed that the polymer matrix plasticized due to the large amount of LC. As shown in table 2, the PDLC cell, constructed using 3/3 microcapsules, have about half the threshold voltage and less than half the driving voltage value, in comparison with the PDLC cell using SIPS process. Interestingly, the threshold and driving voltages of PDLC incorporating 3/7 microcapsules were much lower than those of PDLCs from the SIPS process, even when a slightly thicker cell gap of 25 μm was employed. As shown in figure 6 and table 2, with increasing LC content in the microcapsules, lower threshold voltage and a sharper transmittance–voltage curve were obtained. The improvement of the electro-optical property in the PDLC cell resulted from the large size and monodispersity of the LC droplets in the LC microcapsules.

The sizes of LC droplets were estimated using the diameter of the LC microcapsules from figure 5. The same size of PMMA particles (2.7 μm) was used as a

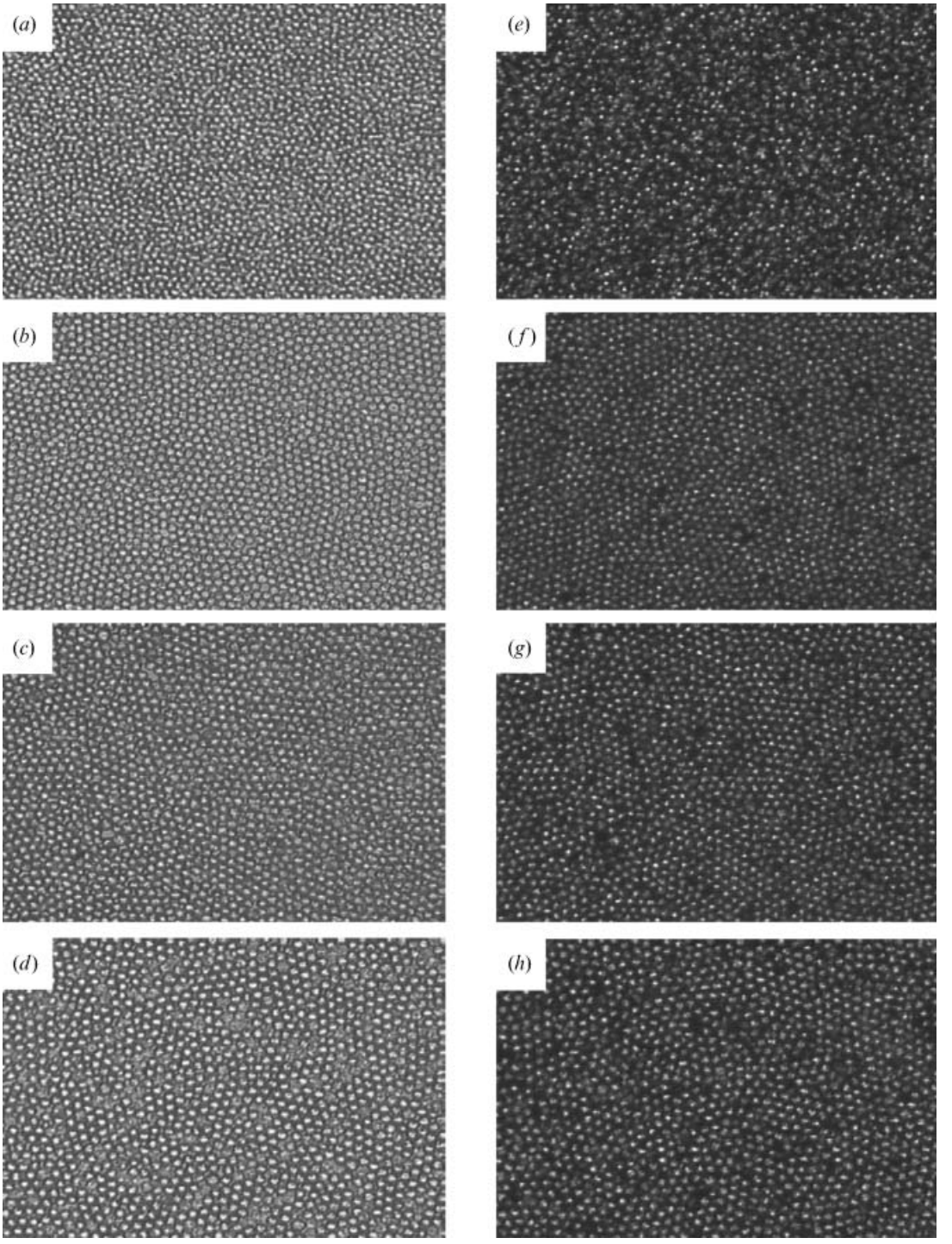

Figure 4. The optical (left side) and polarizing (right side) microscope images of PMMA/LC microcapsules: (*a*) and (*e*) of 3/3; (*b*) and (*f*) of 3/5; (*c*) and (*g*) of 3/7; (*d*) and (*h*) of 3/9.

substrate in the preparation of LC microcapsules and the diameters of microcapsule increased with the LC content. This means that the LC droplets in the microcapsules increased in size with the LC content. In addition, all samples showed a high contrast ratio and transmittance. PDLC cells using SCM microcapsules have excellent electro-optical characteristics and contrast ratios.

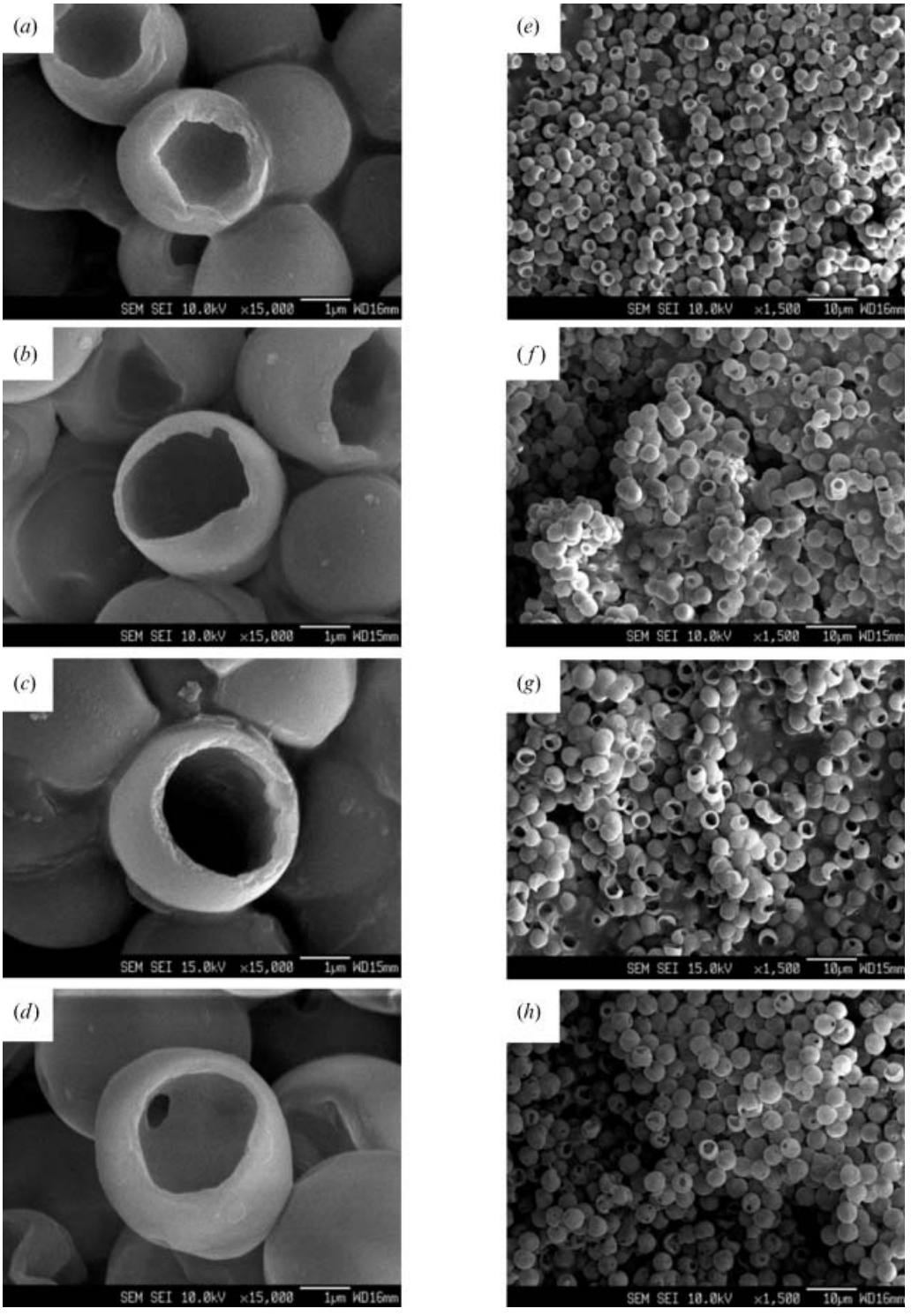

Figure 5. The morphological observation of extracted PMMA/LC microcapsules: (*a*) and (*e*) of 3/3; (*b*) and (*f*) of 3/5; (*c*) and (*g*) of 3/7; (*d*) and (*h*) of 3/9.

4. Conclusion

Monodisperse LC microcapsules obtained using monodisperse crosslinked PMMA particles were prepared and used as PDLCs. A large amount of LC was encapsulated completely as a core by controlling the medium solvency and swelling temperature during the SCM.

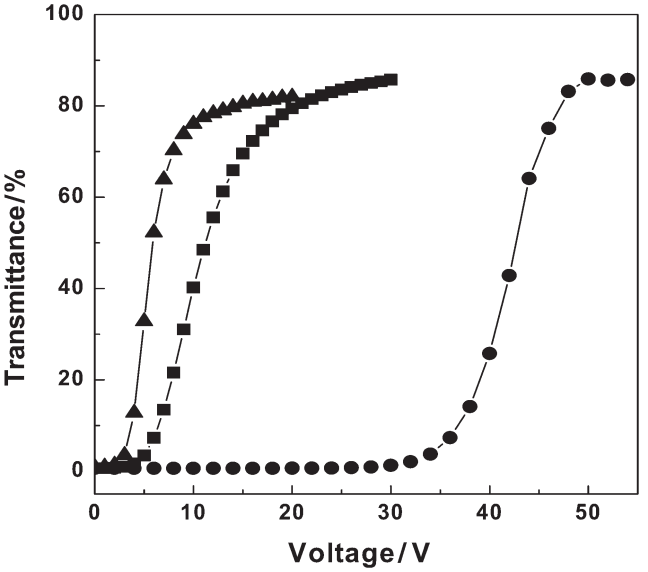

Figure 6. The electro-optical characteristics of PDLC cells using LC microcapsules: the ratio of PMMA/LC is 3/3 (-●-); 3/5(-■-); and 3/7 (-▲-).

During the solvent evaporation step, phase separation between polymer and LC occurred and a single domain was formed in every substrate particle. Microscope observations revealed the presence of spherical LC droplets, even when a large amount of LC was introduced. With increasing LC content, the electro-optical properties of the PDLC cell were greatly improved due to monodispersity of the LC domain and a large amount of pure LC molecules in a dispersed phase. Moreover, PDLC cells using PMMA/LC microcapsules also showed a high contrast ratio and transmittance. In conclusion, the amount of LC used in LC microcapsules significantly influences the electro-optical properties of PDLC cells.

Table 2. Electro-optical properties of PDLC cells fabricated from PMMA/LC microcapsules.

PMMA/LC ratio	Threshold voltage (V_{10})/V	Driving voltage (V_{90})/V
SIPS[a]	75	115
3/3	36	45
3/5	7	18
3/7	4	9
E7[b]	1.42	1.99

[a]PDLC film prepared by solvent-induced phase separation (SIPS), cell gap = 25 μm.
[b]Data from Merck Korea Ltd.

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