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ARTICLE TYPE

## A synthetic approach towards micron-sized smectic liquid crystal capsules *via* the diffusion controlled swelling method

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We demonstrate here a novel synthetic approach towards the micron-sized poly(methyl methacrylate) particles encapsulated with smectic liquid crystals (LC) *via* the emulsion polymerization using a diffusion-controlled swelling method. The effect of different emulsifier, seed particles, crosslinker content, LC content and polymerization temperatures on LC capsules' size and shape were studied to obtain the optimal condition. The results revealed polystyrene particles were better seed particles than poly(butyl acrylate) seed particles, yet they need more time to achieve the Ostwald ripening. By introducing a high amount of crosslinking agent, the LCs can be fully encapsulated without any leakage, while the capsules' shape changed from spheres to half-spheres when the LC loading in the starting material before polymerization is higher than 30%. The capsule size is about 2 to 10 microns with a broad distribution, as characterized by scanning electron microscopy and polarized optical microscopy. The LC capsules can be fractionated by centrifugation, and narrowly distributed capsules were obtained. The properties of the LC capsules were studied by differential scanning calorimetry, and it revealed that the LC content in the capsules was higher than the initial content in the emulsion.

### 20 Introduction

Recently, polymer dispersed liquid crystals (PDLC) for optical displays have attracted lots of interest, due to the advantages of being polarizer and alignment layer free, their simple preparation, and their potential application in flexible displays.<sup>1-30</sup> Among them, polymer sheets with micron-size distributed nematic liquid crystal systems were most extensively studied.<sup>1-16</sup> Switching between an opaque field-off state and a transparent field-on state is achieved by applying an electric field to adjust the refractive index of the liquid crystals to the polymer matrix. However, its application is limited due to the liquid crystal orientation defects around the surface of the dispersed liquid crystal and the polymer matrix. Recently, PDLC systems with smectic liquid crystals have been studied intensively due to their high contrast, energy saving, two stable states, and potential application in full colour displays.<sup>21-29</sup> Even when the power is off, they can be at an opaque reflecting planar texture or a transparent focal conic texture.<sup>28-31</sup> They do not need backlighting and thus have the advantages of being more energy efficient and having low manufacturing costs.

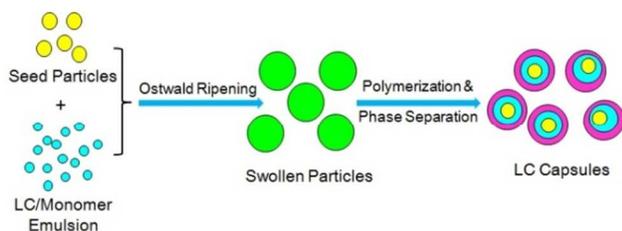
On the other hand, the PDLCs prepared by the general procedures of the phase separation-induced method or the encapsulation (emulsification)-induced method have a lot of problems in controlling the liquid crystal particle size and size distribution, and preventing clustering of the microdroplets. These issues are very important to electro-optical properties, such

as driving voltage and response time. It was determined that LC droplets with a size of several microns have the best electro-optical properties due to the balance between the transmittance and scattering of the incident light by the LC droplets.<sup>32-34</sup> Because the traditional processes have problems in producing PDLCs with uniform LC droplets, a new method, like encapsulating LCs in uniform, micron-sized polymer particles with controlled particle size and size distribution, seems promising, i.e., using the microencapsulation method to prepare PDLC capsules.<sup>35-38</sup> However, synthesizing LC capsules with a uniform particle size of several microns is very difficult because it is beyond the size of emulsion polymerization (usually a few hundred nanometers but up to ~2 microns in some extreme cases) and is still below the size of traditional mechanical processes (greater than several tens of microns). Besides, the high intrinsic viscosity of liquid crystals makes them hard to disperse, and they easily aggregate.

To overcome these problems, emulsion polymerization with a diffusion-controlled swelling method (DSM) based on Ostwald ripening, which has been recently used in the synthesis of uniform large polymer particles, was developed as an efficient microencapsulation method, as illustrated in Scheme 1.<sup>35,39-44</sup> During a traditional DSM process, seed particles were swollen by the monomer emulsion (swelling process) *via* Ostwald ripening. Then, polymerization occurred by UV light irradiation or heating. Suh et al.<sup>35</sup> used this method to synthesize nematic LC capsules and obtained a uniform particle size with low loading of liquid crystals (up to 30% of LC in weight). By the layer-by-layer

polymer-deposition technique, liquid crystal capsules<sup>36,45-47</sup> with a particle size of a few microns were synthesized. However, due to the thin polymer shell layer, the content can easily leak out from the capsules. The main drawback for the current reported works is the leakage of the encapsulated content from the capsules, which is useful for drug delivery applications, yet not suitable for the display purpose.

In this paper, we report the synthesis of smecticA liquid crystal capsules using the DSM. Polystyrene (PS) and poly(butyl acrylate) (PBA) particles were used as seed particles and their influence on the final capsules was studied. The LC capsules were examined by scanning electron microscopy (SEM) and polarized optical microscopy (POM), while the amount of LC in the capsules was determined by differential scanning calorimetry (DSC). Our purpose is to find an optimal way for the synthesis of LC capsules with high LC loading and without any leakage.



**Scheme 1** The synthetic route of LC capsules by diffusion-controlled swelling method.

## Experimental

### Materials

Methyl methacrylate (MMA, 99%, Acros) and styrene (99%, Acros) were washed with sodium hydroxide solution (10%) three times and then with deionized (DI) water until neutralization. After drying by sodium sulfate, monomer was distilled over calcium hydride (93%, Acros) under reduced pressure. Butyl acrylate (BA, 99%, Acros), ethylene dimethacrylate (EDMA, 98%, Acros), 1-hexanethiol (96%, Acros), 2-hydroxyethyl methacrylate (HEMA, 98%, Acros), polyvinylpyrrolidone (PVP, Sigma, Avg. Mol. Wt. 360K g/mol), potassium persulfate (99%, Acros), potassium carbonate (99%, Acros), and sodium dodecylbenzenesulfonate (SDBS, 88%, Acros) were used as received. Azobis(isobutyronitrile) (AIBN, 98%, Aldrich) was recrystallized 3 times by pouring its chloroform solution into methanol. The smectic liquid crystals, supplied by TechnoDisplay AS, were a mixture of 4-cyano-4'-alkylbiphenyls, which have a smecticA phase at room temperature and undergo a phase transition to the nematic phase at 72 °C. Their isotropization temperature is 78°C.

### Preparation of PBA seed particles

Details for the synthesis of PBA seed particles can be found elsewhere in the literature.<sup>48</sup> A two-step polymerization process was employed. In the first step, PBA pre-seed particles were synthesized under normal emulsion polymerization conditions with a particle size of about 200 nm. During the second step using butyl acrylate and styrene as monomer, the particles grew to 500 nm by DSM. The solution contained about 22 weight percent seeds.

### Preparation of PS seed particles

A slightly changed procedure from reference 49 was used here. 50 mg NaCl and 58 mg K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were dissolved in 90 g of water. After that, 10.5 g of styrene was added to the solution. The solution was stirred by a mechanical stirrer at a speed of ~ 400 rpm. It was then bubbled with N<sub>2</sub> for ~ 30 minutes and heated to 78°C to react for 36 h. The obtained PS particles had an average diameter of 1.5 μm.

### Encapsulation of LC in PMMA particles by DSM

MMA and EDMA were chosen as the monomer and crosslinker for encapsulation because they have a refractive index match with our LC material ( $n = 1.51$ ), thus the polymer shell will not diffuse the light in the liquid crystal transparent state if mixed together. Also, PMMA phase separates with our liquid crystal. Scheme 1 illustrates the LC capsule synthesis process based on DSM. Typically, a predetermined amount of LC, MMA, EDMA, AIBN and surfactant (10% SDBS solution or PVP360K or both) were mixed and homogenized (PowerGen 35, Fisher Scientific Co., speed: 25,000 rpm). For PBA seed particles, a small amount of PBA seeds was added to the solution and swollen for 6 hours. The solution was bubbled with nitrogen for 30 minutes, heated to 68°C, and polymerized for 1 day.

When using PS particles as seeds, the solution was swollen for 2 days and homogenized every 8 hours, with AIBN added 8 hours before polymerization. The solution was then diluted with water to 90 mL, bubbled with nitrogen for 30 minutes, heated to 68°C, and polymerized for 1 day.

### Methods

SEM was performed with a JEOL JSM 53101 scanning electron microscope operating at 30 kV. For LC capsules, the solution after polymerization was shaken well to disperse all the particles in the water. Then, a small portion of the solution was removed and diluted 10 times. One drop of the solution was placed on an aluminium foil surface and dried. Prior to measurement, the samples were coated for 30 s with silver using a Polaron E5400 sputter coater to improve electrical conductivity. The histogram of particles' size distribution is presented in Supplementary Information. Polarized optical microscopy (POM) observations were performed on an Olympus HB-2 microscope. DSC experiments were carried out in a Perkin-Elmer DSC-7 with a cooling refrigerator at 5 °C/min heating and cooling rates in the range of -5 °C to 150 °C.

### Results and discussion

PBA slightly crosslinked particles with a diameter of several hundred nanometers prepared by emulsion polymerization were widely used as seed particles due to their low glass transition temperature (below room temperature).<sup>39,48,50</sup> Thus, PBA particles were considered to be in the molten state and easily swollen by the loading material. The ratio of the added amount of monomers plus the loading material ( $m_m$ ) to seed amount ( $m_s$ ) determines the final particle size by the following equation<sup>51</sup>:

$$\left(\frac{D_f}{D_s}\right)^3 = \frac{V_m + V_s}{V_s} \approx \frac{m_m + m_s}{m_s} \quad (1)$$

Where  $D_f$ ,  $D_s$ ,  $V_m$ , and  $V_s$  are the diameter of the final

particles, the diameter of initial seed particles, the volume of the monomer plus loading material, and the initial seed particle volume, respectively. In this equation, we assume that all of the particles have the same density and that conversion from monomer to polymer is nearly 100%.

**Table 1.** Experimental recipe for emulsion polymerization using PBA emulsion as seed particles.

Ingredients	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
MMA (g)	15.0	26.0	5.0	2.5	5.0
EDMA (g)	0.2	0.2	0.15	0.5	2.0
HEMA (g)	-	4.0	-	-	-
LC (g)	-	-	3.0	3.0	3.0
AIBN (mg)	100	100	30	30	50
DI water (g)	100	120	90	90	90
10% SDBS (g)	0.40	0.20	0.40	0.30	0.30
PBA seed solution (g)	0.20	0.10	0.10	0.10	0.10

Table 1 lists some experimental conditions used to synthesize micron-sized particles. First, to test if DSM can be used in our case, we do trials without LC loading. Trial 1 is the typical optimized conditions using DSM to obtain micron-sized PMMA particles from PBA seed particles. Fig. 1a is the SEM image of the obtained PMMA particles. Most of the particles were around 2.2  $\mu\text{m}$  with some small particles near 1  $\mu\text{m}$ . The particle size was a little smaller than calculated from equation 1, which was 3.6  $\mu\text{m}$ . The

reason might be that some smaller PBA particles coexisted in the seed emulsion. These smaller particles are hard to be detected by LLS when there are large particles in the solution, thus making equation 1 slightly inaccurate. Another explanation may be a second nucleation occurred during our polymerization. Nevertheless, the obtained particle size distribution is quite narrow, and it has been shown that DSM works in our case.

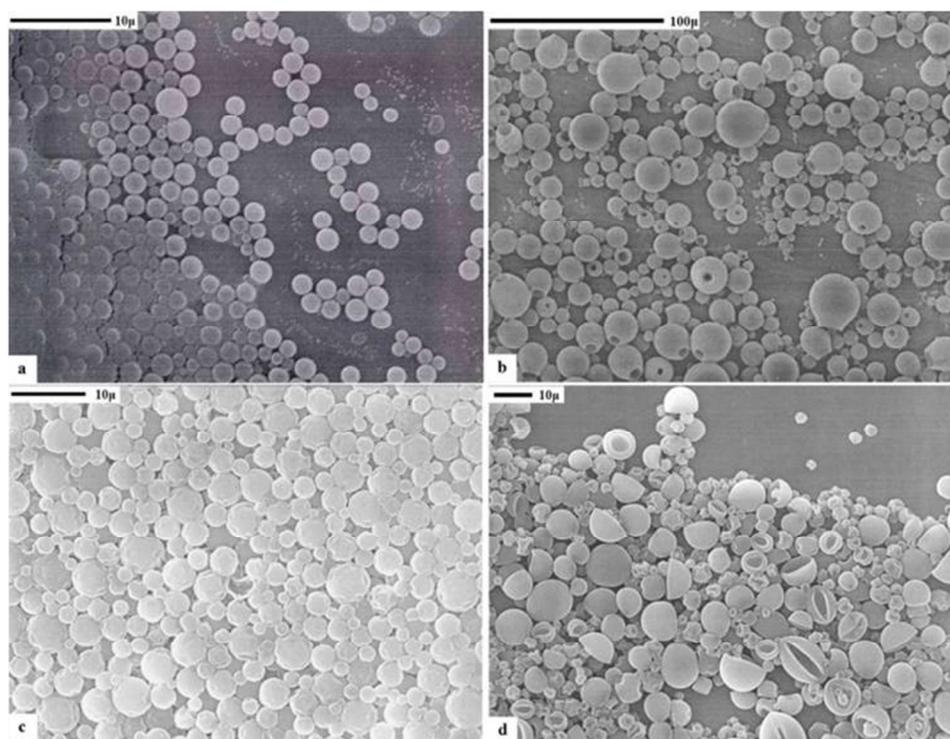


Fig. 1 SEM pictures of the PMMA emulsion particles from Trial 1 (a), Trial 2 (b), Trial 3 (c) and Trial 4 (d), with the average particle size of 1.9  $\mu\text{m}$ , 13.2  $\mu\text{m}$ , 3.2  $\mu\text{m}$ , and 7.2  $\mu\text{m}$ , respectively.

When the hydrophobic emulsion particles' size grows over microns, they will gradually precipitate from the solution, even with emulsifiers. Copolymerization of hydrophilic monomers will help the hydrophobic particles to be more stable in water, thus polymer particles with larger particle size can be obtained. In Trial 2, we added HEMA as the hydrophilic monomer to increase the stability of the polymer emulsion. The particle size does increase with a

broad particle distribution from 3  $\mu\text{m}$  to 30  $\mu\text{m}$  with the introduction of HEMA monomer, as shown in Fig. 1b. It is very interesting that the obtained particles have an open hole on the surface. This may due to the change of the surface interactions between the colloids, surfactant, and water, after HEMA introduced. When the PHEMA was surrounded by water, the PMMA tries to polymerize along the inverse direction, resulting in a hole in the particle. However, for the

desired application, the LC should not leak from the particles (to prevent the LC drops mixing in the pixels), so HEMA is

not suitable for this method.

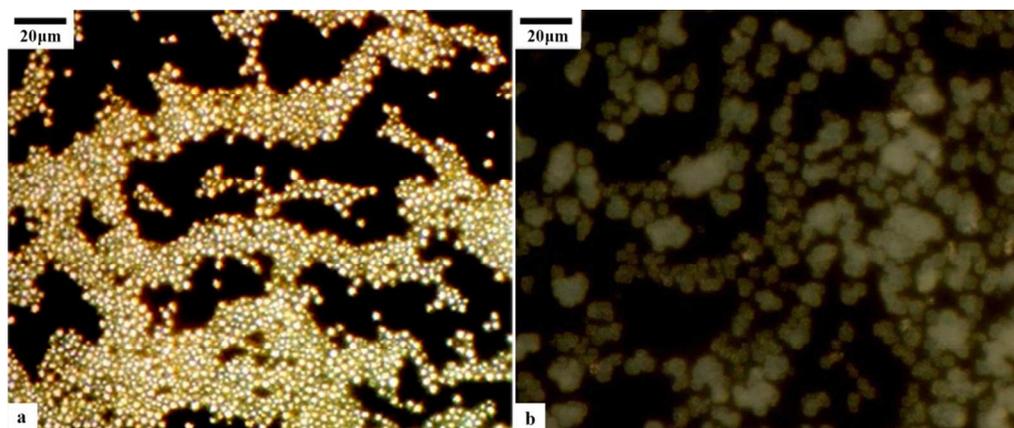


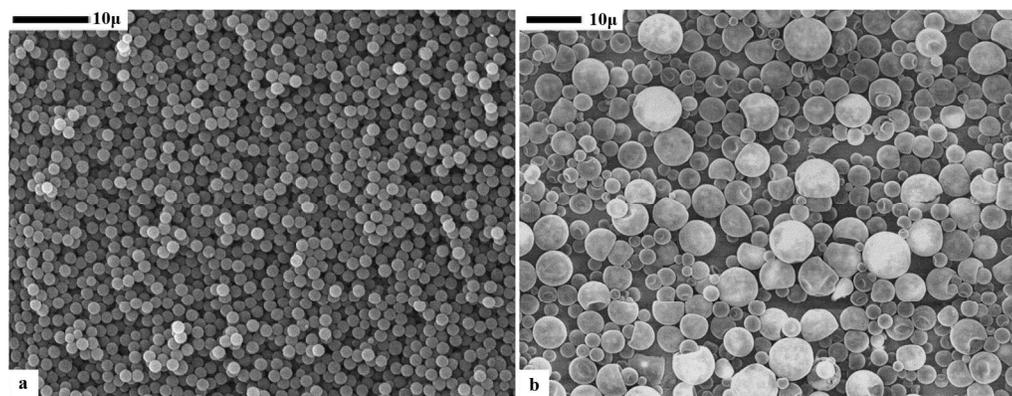
Fig. 2 Polarized optical microscopy pictures of emulsion particles from Trial 3, before methanol washing (a), and after methanol washing (b).

Trials 3, 4 and 5 are experimental recipes for the actual encapsulation of LCs into pure PMMA particles. The loading of the LC mixture was about 30% (Trial 5) to 50% (Trial 4). They all gave particles with a diameter of 2-10  $\mu\text{m}$  with a broad distribution. Fig. 1c is the SEM picture for the particles obtained from Trial 3, while Fig. 1d is from Trial 4. In Fig. 1c, the surface of the particles is not smooth with lots of wrinkles. The LCs were encapsulated into the PMMA particles since they have very strong birefringence under cross-polarized light in optical microscopy, as shown in Fig. 2a. The colloidal particles can be dispersed very well in water by shaking and slowly precipitated to the bottom. Once the water had dried, the particles coagulated and were very hard to be dispersed again. The coagulation of particles is due to the leakage of LCs from the capsules, which acted as glue due to high viscosity. This is proved by the methanol washing results, since LCs can be dissolved in methanol while PMMA can't. If LCs can leak from the capsules, birefringence should loss after methanol washing. Fig. 2b is the POM picture of particles after methanol washing. The birefringence of the particles was almost lost, indicating the LCs are not perfectly encapsulated.

High LC content in the particles is very important since this will increase the contrast and decrease the response time for colour displays. When loaded with 50% (weight) LCs and a high content of crosslinking agent (EDMA), the obtained particle shape changed from spheres to bowl-like half-spheres, as indicated in Fig. 1d. If we decreased the loading amount of LCs to 30%, as in Trial 5, the emulsion particle shape changed back to spheres, even after increased EDMA content. If no crosslinking agent was used in the system, the particles coagulated after polymerization with a spherical shape, mainly due to the coagulation of the LCs that remained on the particle surface. Thus, it is clear that the

bowl-like particles are a result of high LC loading with crosslinking agent. Since the LCs do not mix with PMMA and phase separation occurred somewhere during the polymerization period, the bowl-shaped particles plausibly formed during the phase separation process. As the density of the LC mixture ( $1.4 \text{ g/cm}^3$ ) is much higher than PMMA matrix ( $\sim 1.0 \text{ g/cm}^3$ ), phase separation of LC droplets makes the density in other volumes of the particle decrease significantly. At that time, the particle framework was nearly constructed because of the inclusion of crosslinking agent, and exclusion of water from the particles due to highly unfavorable interactions with PMMA. It follows that the particles shrink due to the intrinsic pressure. A similar phenomenon was observed in spherical polyelectrolyte microcapsules after the addition of polyelectrolyte in the outer medium.<sup>52,53</sup>

Even with highly-loaded crosslinking agent, about half of the LC capsules lost their birefringence after methanol washing. This might be due to the molten PBA seeds in the particle, as their  $T_g$  is below room temperature. A seed polymer with a  $T_g$  higher than room temperature should improve the encapsulation performance. The LCs may also stay inside the capsule if the polymer seed particle has some affinity for the LC mixture, which will promote the LC mixture to stay near the core part of polymer seeds. Using polystyrene (PS) latex as seed particles seems promising because they fulfil both of these requirements. However, since PS is in its glassy state at room temperature, research shows that DSM will not work if the PS particles are covered by emulsifiers, and thus, only surfactant-free PS particles can be swollen. Recent work in polymer colloid synthesis makes the synthesis of surfactant-free uniform PS latexes with a micron-sized diameter possible.<sup>49,54</sup>



**Fig.3** SEM picture of PS seed particles (a) and LC capsules from Trial 7 after methanol washing (b).

Fig. 3a is the SEM picture of the PS seeds synthesized by surfactant-free emulsion polymerization. The particles are very uniform with a particle size of  $1.66 \pm 0.03 \mu\text{m}$ . The size can be tuned by the feeding styrene concentration, ionic strength of the solution, polymerization temperature and the mechanical stirrer speed.<sup>49</sup> Unlike the PBA seed particle synthesis, we do not use any crosslinking agent here because the molecular weight of PS in the particle latex is very high, usually more than  $10^6 \text{ g/mol}$ . The dissociation of seed particles during the swelling process can't happen due to the physical entanglement of the PS chain. The solid content in the seed emulsion is  $\sim 10\%$ .

Trials 6-9 are experimental recipes, as shown in Table 2,

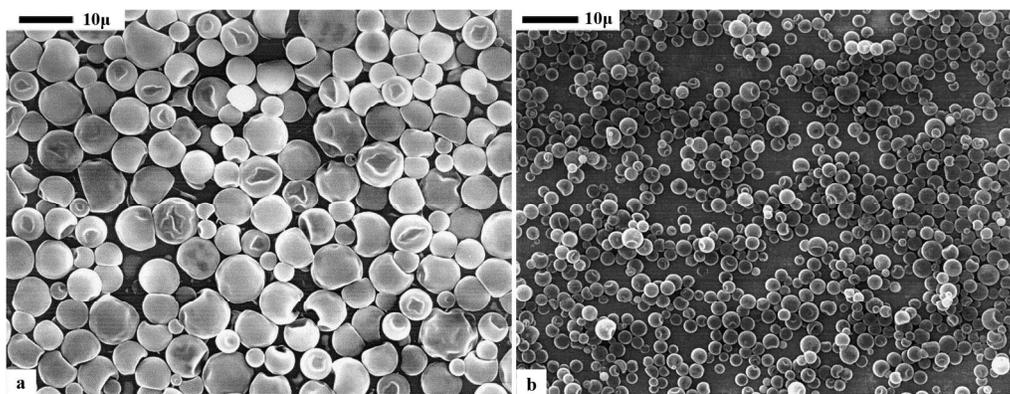
**Table 2.** Experimental recipe for emulsion polymerization using PS seed particles.

Ingredients	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10	Trial 11	Trial 12
MMA (g)	2.0	1.2	0.8	2.0	2.0	2.1	2.1
EDMA (g)	0.5	1.2	1.6	0.5	1.5	1.0	0.65
LC (g)	2.0	2.0	2.0	2.0	0.5	0.3	0.25
AIBN (mg)	30	30	30	30	30	30	15
DI water (g)	90	90	90	90	90	90	90
10% SDBS (g)	0.2	0.2	0.2	0.2	0.2	0.3	0.3
PS seed solution (g)	0.2	0.2	0.2	0.2	0.3	0.3	0.3
PVP360K (mg)	60	60	60	60	60	60	60
Temperature ( $^{\circ}\text{C}$ )	68	68	68	76	68	68	68
Particle Size ( $\mu\text{m}$ )	2~10	2~10	2~10	2~7	2~9	2~9	2~9

The crosslinking agent content increased from 20% in the monomer mixture in Trial 6 to 66% in Trial 8. All of these give LC bowl-like half-spherical capsules with a broad particle size distribution from 2~10  $\mu\text{m}$ . This is a consequence from equation 1 since in all these cases, the ratio of weight of monomers plus LC to PS seed particles is almost the same. The broad particle size distribution should be due to insufficient Ostwald ripening time due to the high

using the uniform PS particle solution as the seeds. All of these trials gave polydispersed particles with a diameter of 2 ~ 10  $\mu\text{m}$ . When observed under cross-polarized light, the particles obtained from Trials 6-8 have very strong birefringence even after methanol washing, indicating significant LC loading. Fig. 3b is the SEM picture of LC capsules obtained from Trial 7 after methanol washing. Clearly, the particles maintained their shape after washing, indicating that the LCs stayed inside the particle as was seen in POM. The capsules have the same bowl-like half-spherical shape as the LC capsules synthesized using PBA seeds with high LC loading and crosslinking agent.

$T_g$  of PS seeds. One can assume that the ripening time would be shorter at a higher temperature, and one would get more uniform particles. This is what we observed in Trial 9, where we increased the polymerization temperature to 76  $^{\circ}\text{C}$ . However, increasing the polymerization temperature introduced defects in the capsules, since most of the capsules' birefringence was lost after methanol washing.

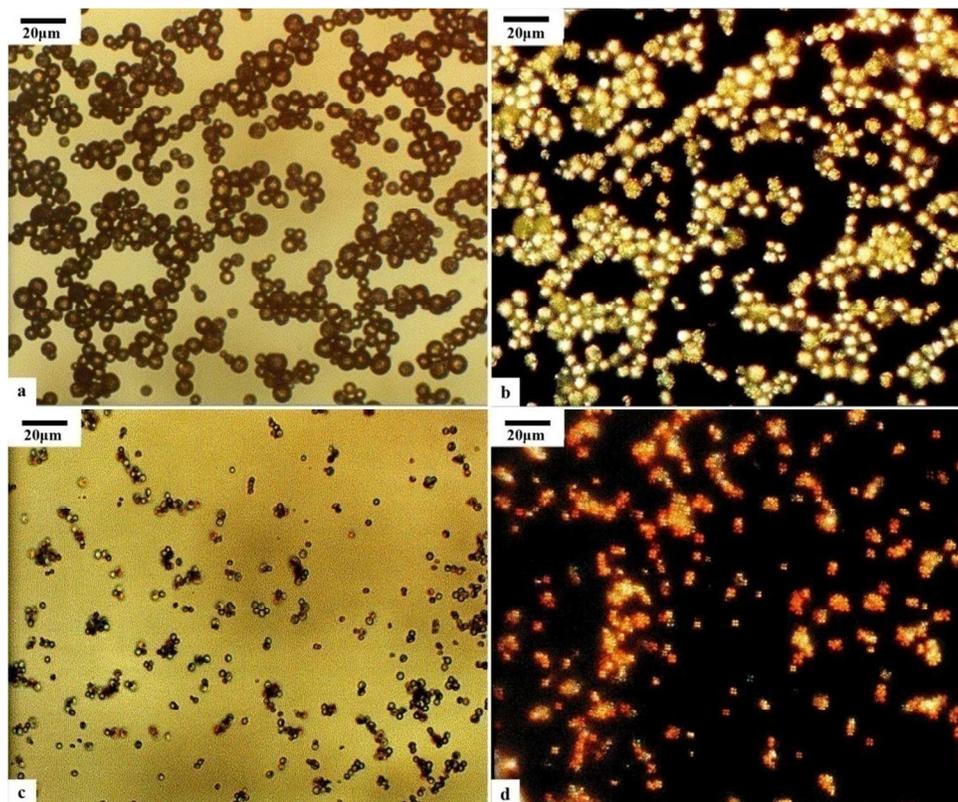


**Fig. 4** SEM picture of particles from sample 7A (a) and sample 7B (b). The particles show much narrower distributions compared to capsules without centrifuging (Fig. 3b).

We observed that if we characterize the capsules that precipitated first to the solution bottom without disturbing the solution, we will get very uniform particles, so centrifugation was used to fractionate the LC capsules from Trial 7. The capsules were well-dispersed in water by shaking. Then, the solution dispersion was centrifuged at 1000 rpm for 3 minutes. The precipitated particles at the tube bottom were redispersed in DI water, and the process was repeated 3 times. After the final centrifugation, the precipitated capsules at the bottom were subjected to SEM and POM observations. This method obtained the biggest capsules from the starting particles, indicated as sample 7A. The upper solution dispersion was removed and centrifuged at 1500 rpm for 5 minutes. The particles at the tube bottom from the upper dispersion were also observed under SEM

and POM. These are indicated as sample 7B. The particle size and shape can be seen in Fig. 4.

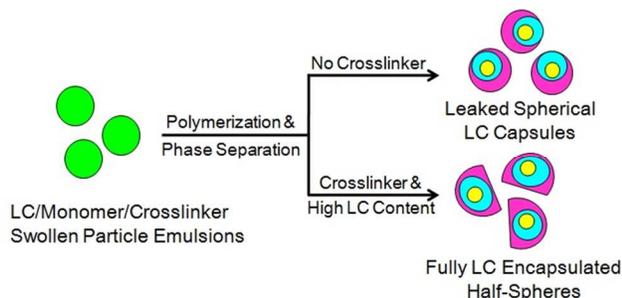
After fractionation, the particle size for sample 7A is  $6.1 \pm 2.1 \mu\text{m}$ , as indicated in Fig. 4a, and particle size for sample 7B is  $2.6 \pm 0.6 \mu\text{m}$ , as in Fig. 4b. The shape of the small capsules was more spherical than that of the large capsules and had a smaller dent on the surface. From the size of LC capsules versus the PS seed particles ( $1.66 \mu\text{m}$ ), the volume fraction of PS in the 7B capsules was about 20% (calculated from equation 1), while only 2% of the 7A capsules were PS, which can be neglected. This is further evidence to prove that a high loading ratio of the LCs plus monomer to PS seed will cause compressed, irregular shaped capsules.



**Fig.5** Optical microscopy (a, c) and polarized optical microscopy (b, d) pictures of sample 7A (a, b) and 7B (c, d).

Optical microscope and POM pictures of the LC capsules after fractionation are shown in Fig. 5. Fig. 5a is the optical microscopy picture of sample 7A in transmission mode. The particle size was about 6  $\mu\text{m}$  on average and agreed well with SEM observation. The bowl-like half-spherical shape was also observed. When observed by POM between cross-polarizers, the capsules showed very strong birefringence, as in Fig. 5b. Since every particle in Fig. 5a corresponded to have birefringence in Fig. 5b, we can conclude that among these obtained particles, the LC encapsulation was nearly 100%. The same phenomenon was observed for sample 7B. Every as-synthesized particle contained LCs inside. Similar images are shown in Fig. 5c and 5d. Surprisingly, in Fig. 5d, the focal conic texture of the particles was observed, which comes from the SmA LC mixture, yet it was not observed for the larger particle capsules (Fig. 5b). The reason may be due to the surface tension or irregular surface morphology of particle 7A since the geometric confinement will also affect the LC textures.<sup>24</sup> The uniform, large particle size of sample 7B, together with the fine liquid crystal textures, should make it proper for smectic LC displays.

The types of LC capsules synthesized *via* DSM are summarized and illustrated in Scheme 2. The highest level of LC loading in the initial material before polymerization for our system was about 70 (wt)%, while 80% LC loading resulted in a film on the emulsion surface and precipitates at the bottom. To our knowledge, this is the first reported preparation of LC capsules with high LC content and without any leakage. The narrowly distributed LC capsules obtained from centrifugation separation should be useful for displays.

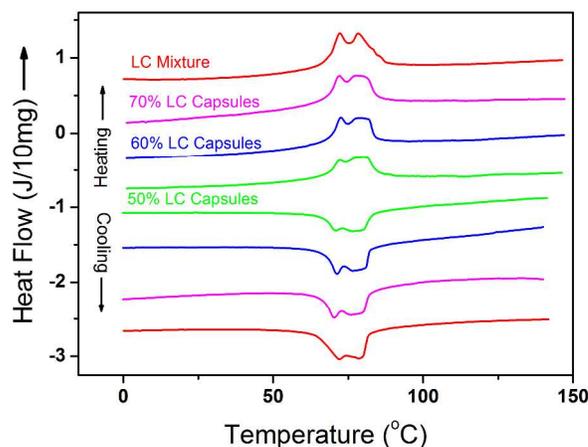


**Scheme 2** Summary of types of LC capsules synthesized at different conditions *via* diffusion-controlled swelling method.

Three kinds of capsules with LC initial loading of 50%, 60% and 70% were prepared (Trials 10-12), as indicated in Table 2. The capsules were separated from the emulsion by centrifugation at 1500 rpm for 10 minutes, followed by washing with excess methanol 3 times. The obtained white powder was then put into a vacuum oven and dried at room temperature for 1 day. TGA experiments revealed that there was no detectable water in the capsules as these three samples lost 1% weight at about 200  $^{\circ}\text{C}$ .

Fig. 6 is the first cooling and second heating DSC curves of the three capsule samples, together with the pure LC mixture as reference at a scanning rate of 5  $^{\circ}\text{C}/\text{min}$ . During heating, the first peak appeared at 72  $^{\circ}\text{C}$  corresponding to the smecticA to nematic phase transition. The second peak

corresponds to the nematic to isotropic phase transition. The first peak did not have any dependence on the LC content in LC capsules, while the second peak's shape and position changed slightly with LC content during the second heating process. Since in our case, the LC was encapsulated in the particle and the polymer network acts as confinement for the LC small droplets, this observation indicated that the confinement and/or surface anchoring did not affect the smecticA to nematic phase transition, but did affect the nematic to isotropic phase transition. Similar phenomena were observed during the cooling process.



**Fig. 6** Normalized DSC curves of the LC mixture (—), and LC capsules with different LC mixture start loading content of 50% (—), 60% (—), and 70% (—). Scanning rate: 5  $^{\circ}\text{C}/\text{min}$ .

Since PS and PMMA have glass transition temperatures at about 100  $^{\circ}\text{C}$ , the peak from 60  $^{\circ}\text{C}$  to 90  $^{\circ}\text{C}$  should be attributed only to the LC phase transitions. Thus, the actual amount of LC in the capsules can be determined by comparing the enthalpy of LC capsules ( $\Delta H_{\text{capsule}}$ ) to the pure LC mixture ( $\Delta H_{\text{LC}}$ ), using the following equation:

$$LC_{\text{capsule}} \% = \Delta H_{\text{capsule}} / \Delta H_{\text{LC}} \quad (2)$$

As the two peaks of smectic-to-nematic and nematic-to-isotropic state can't be separated, the total area of these two transitions was used to determine the LC content in the capsules.

The calculated value of LC content in capsules from DSC is 82%, 74%, and 60% for the initial LC loading of 70%, 60% and 50%, respectively. The value calculated from DSC is a little higher than the initial load. These are surprising since the LC capsules were washed with methanol (which dissolves the LCs) after being collected. One possible reason for this discrepancy might be that some monomer had not converted to polymer and was washed out by methanol. Application of these capsules in flexible displays is under current investigation.

## Conclusions

In this work, we reported the one pot synthesis of micron-sized smectic LC capsules by emulsion polymerization *via* a diffusion-controlled swelling method, using PS or PBA as seed particles

and MMA as monomer. It was found that PS particles are better seeds than PBA as they provided fully encapsulated LC capsules. The as-obtained LC capsules had a broad particle distribution with diameter from 2 to 10 microns, while narrowly distributed capsules can be obtained by centrifugation separation. High content of crosslinking agent in the monomer resulted in better encapsulated LCs, and half-spherical particles formed with high LC loading. The LC amount in the capsules was determined by DSC and was revealed to be higher than the initial loading amount. These are the first reported fully encapsulated smectic LC capsules with high LC content, and have potential applications in flexible displays and bistable displays.

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## Notes and references

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- <sup>30</sup> † Electronic Supplementary Information (ESI) available: the histogram of particles' size distribution from corresponding SEM images. See DOI: 10.1039/b000000x/
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**Table of contents entry for:****A synthetic approach towards micron-sized smectic liquid crystal capsules *via* the diffusion controlled swelling method**

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Micron-sized smectic liquid crystals encapsulated poly(methyl methacrylate) capsules were synthesized *via* the emulsion polymerization using a diffusion-controlled swelling method.

