Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

The effect of mono-sized liquid crystal domains on electro-optical properties in a polymer dispersed liquid crystal prepared by using monodisperse poly(methylmethacrylate)/liquid crystal microcapsules

Sung-Il Park; No-Hyung Park; Kyung-Do Suh

Online publication date: 11 November 2010

To cite this Article Park, Sung-Il , Park, No-Hyung and Suh, Kyung-Do(2002) 'The effect of mono-sized liquid crystal domains on electro-optical properties in a polymer dispersed liquid crystal prepared by using monodisperse poly(methylmethacrylate)/liquid crystal microcapsules', Liquid Crystals, 29: 6, 783 — 787
To link to this Article: DOI: 10.1080/02678290210136337
URL: http://dx.doi.org/10.1080/02678290210136337

LIQUID CRYSTALS, 2002, VOL. 29, NO. 6, 783–787

Taylor & Francis
Taylor & Francis Group

The effect of mono-sized liquid crystal domains on electro-optical properties in a polymer dispersed liquid crystal prepared by using monodisperse poly(methylmethacrylate)/liquid crystal microcapsules

SUNG-IL PARK, NO-HYUNG PARK and KYUNG-DO SUH*

Division of Chemical Engineering, College of Engineering, Hanyang University, Seoul, 133-791, Korea

(*Received 25 September 2001; in final form 21 January 2002; accepted 12 February 2002*)

Highly mono-sized poly(methyl methacrylate) (PMMA)/liquid crystal (LC) microcapsules having a mono-sized single LC domain were prepared by the solute codiffusion method and solvent evaporation. The size of the LC domain in the microcapsules could be controlled by the amount of LC introduced during the swelling stage. The electro-optical properties of the polymer dispersed liquid crystal (PDLC) prepared by using the microcapsules was highly improved. In particular, the threshold voltage was lowered and the switching behaviour with an applied electric field was sharpened drastically compared with PDLC prepared simply by solvent evaporation-induced phase separation.

1. Introduction

Polymer dispersed liquid crystals (PDLCs), which consist of micron-sized liquid crystal droplet dispersions in a continuous polymer matrix, have been intensively studied because of their great potential for applications in large display devices [1–8]. In PDLC, the characteristics of the LC droplets such as size and size distribution influence the electro-optical properties significantly. Generally, because a PDLC is prepared using phase separation methods, it has a broad size distribution of the LC droplets in the polymer matrix. Since a broad size distribution gives broadness of the transmittance change with an electric field and hysteresis [9], it has limited PDLC application only to the field of light shutters.

In our recent study, the solute codiffusion method (SCM) and solvent evaporation were studied for producing LC microcapsules, and were found to give effective control of the size and size distribution of LC droplets in PDLC. The concept of the SCM starts from the diffusion of a solute/solvent mixture into pre-existing polymer particles [10, 11] in an aqueous phase via Ostwald ripening [12–14]. In this method, the droplet size of the LC domain and the LC content in the microcapsules could be controlled without difficulty by the amount of LC/solvent mixture used in the swelling stage. These microcapsules could be applied to PDLC and expected to improve electro-optical properties significantly, due to the monodispersity of the LC domain size.

In the present study, PMMA/LC microcapsules were prepared by employing the SCM and solvent evaporation, and applied to PDLC cells. We investigated the electro-optical behaviour of PDLC prepared using the mono-sized PMMA/LC microcapsules and compared this with that of PDLC prepared using conventional methods.

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), aerosol-OT (AOT, Sigma Chemicals) and methanol (Mallinckrodt Co.) were all of reagent grade. Methylene chloride (MC, Aldrich Chemicals), sodium dodecylsulphate (SDS, Yakuri Pure Chemicals) and ethanol (Mallinckrodt Co.) were also used without further purification. Low molecular mass LC, MLC-6014 (MLC, $T_{NI} = 81°C$, $\Delta n = 0.13$, $\Delta\varepsilon = +18.0$) was purchased from E. Merck. To prepare a PDLC cell using the microcapsules, poly(vinylbutyral) (BL-S®, Sekisui Chemical Co.) was used as a binder.

*Author for correspondence; e-mail: kdsuh@hanyang.ac.kr

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2002 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290210136337

2.2. *Preparation of mono-sized PMMA substrate particles* [15, 16]

Highly mono-sized PMMA seed particles were produced by dispersion polymerization. AOT, PVP and methanol were weighed into a four-necked flask equipped with reflux condenser, nitrogen inlet apparatus and mechanical stirrer. Then, the MMA and AIBN solution was poured into the reactor and stirred vigorously to mix the reactants homogeneously. The mixture was then polymerized at 58°C for 24 h with 50 rpm stirring. PMMA seed particles were recovered after washing with water and centrifuging repeatedly and dried at room temperature.

2.3. *Microencapsulation of LC in PMMA seeds via the SCM*

The mono-sized PMMA particles were redispersed in 0.25 wt % SDS in a water/EtOH (4/1, g/g) solution for 30 min by sonication. They were swollen with an MLC/MC emulsion prepared by ultrasonic homogenization in a 0.25 wt % SDS solution in water/EtOH (4/1, g/g). The swelling was carried out with magnetic stirring at 10°C until the emulsion droplets disappeared completely. The MC in the swollen PMMA particles was evaporated slowly at room temperature for one day. Phase separation of the MLC occurred during solvent evaporation and mono-sized PMMA/MLC microcapsules each incorporating a mononuclear MLC domain could be obtained. Microcapsules were then washed with water repeatedly and dried at room temperature. A standard recipe and a schematic representation of the SCM and solvent evaporation are illustrated in the table and scheme, respectively.

2.4. *Preparation of PDLC cells*

PDLC cells were prepared using PMMA/LC microcapsules (PLC1 and PLC2) and poly(vinylbutyral) (PVB) as a binder. PDLCs prepared using PLC1 and PLC2 were denoted PLCF1 and PLCF2, respectively. Firstly, the PLC materials were mixed with a 10 wt % solution of BL-S® in ethanol in the weight ratio 1/1. The mixture was coated onto ITO glass and sandwiched with another ITO glass plate. The cell gap of PDLC was fixed using PET film as spacer (11 μm).

Table. The standard recipe for the SCM and solvent evaporation process (unit : g).

Stage	Ingredient	Microcapsules PLC1	Microcapsules PLC2
Seed dispersion	PMMA seed	0.3	0.2
	SE solution[a]	40	
MLC/MC emulsion[b]	MLC	0.3	
	MC	2.7	
	SE solution	15	
Solvent evaporation[c]	—	—	

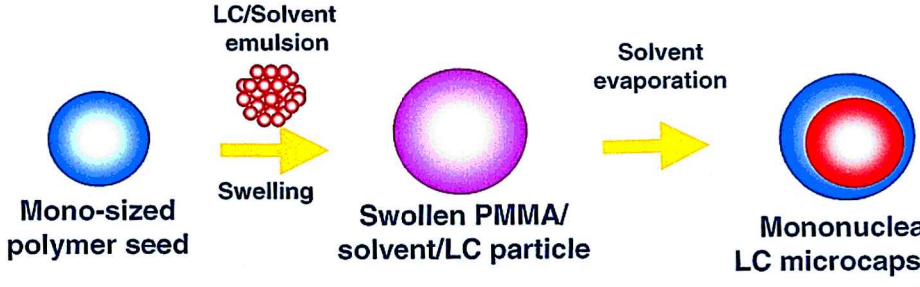
[a] 0.25 wt % SDS solution in aqueous ethanol = 4/1 (g/g).
[b] Preparation and swelling process carried out at room temperature.
[c] At room temperature, over 7 days.

2.5. *Measurements*

The morphologies of the PMMA seed particles and microcapsules were observed using optical microscopy (OM, Nikon Microphot Fax) and a scanning electron microscope (SEM, Hitachi model). The phase separation between PMMA and MLC in the microcapsules and the morphology of the dispersed LC domains in the PDLC cells were confirmed using a polarizing optical microscope (POM, Olympus BH-2) equipped with an image analyser. The electro-optical properties of the PDLC cells were measured using a He-Ne laser (632.8 nm).

3. Results and discussion

Substrate PMMA seed particles were manufactured by dispersion polymerization [10, 15, 17]; we could produce highly mono-sized PMMA/LC microcapsules using the solute co-diffusion method (SCM) [18–20] and solvent evaporation-induced phase separation (SIPS). In our previous papers [21–23], highly monodisperse



Scheme. The preparation procedure for LC microcapsules employing the solute codiffusion method (SCM) and solvent evaporation.

PMMA/LC microcapsules were prepared successfully by employing the diffusion-controlled polymerization method (DPM). However, the limit of LC content in the microcapsules could not be raised above 30 wt % based on the polymer particles, because large amounts of swollen components remained in the microcapsules after polymerization. Therefore, to increase the amount of LC incorporated in the microcapsules, we used an organic solvent which could be evaporated easily instead of employing a reactive monomer [24].

3.1. *Preparation of PMMA/MLC microcapsules by SCM and SIPS* [24]

The basic concept of the SCM is that dispersed polymer seed particles are swollen efficiently with a fine solute/solvent emulsion via Ostwald ripening [12–14]. The solubility of the disperse phase in the bulk phase is dependent upon the radius of curvature of a droplet. This results in smaller droplets dissolving into the bulk phase and then diffusing to and redepositing upon larger ones leading to an overall increase in average size of the emulsion; this is the process of Ostwald ripening. It is well known that this is caused by the chemical potential gradient between large and small particles and can be controlled by the solubility of the emulsion in the medium, the temperature, the stirring speed and the surfactant concentration etc. In the SCM process, MC having a relatively high dielectric constant ($\varepsilon = 9.1$) in a non-polar solvent was used as the solvent for the MLC. In this condition, PMMA seed particles were uniformly swollen and maintained their initial, spherical shape even after complete solvent evaporation.

3.2. *The morphology of PMMA/LC microcapsules in PDLC cells*

After the complete swelling of MLC/MC emulsions into polymer particles, the MC in the swollen PMMA seed particles was removed slowly at room temperature. LC domains are phase-separated during this SIPS process. The phase separation behaviour and morphology of the LC domain depend largely upon the solvent evaporation rate. As a result of the present study, the slow evaporation rate induced complete phase separation and a single LC domain formation in the microcapsules. This fact could be confirmed by observation by OM, POM and SEM.

Figure 1 shows SEM and POM photographs of the PMMA/LC microcapsules. As shown in figure 1 (*a*), the PMMA seed particles have a high monodispersity (polydispersity = 1.003) and their number average size is 5.97 μm. Even after the SCM and SIPS process, the PMMA/LC microcapsules maintain their spherical shape and monodispersity, figure 1 (*b*). The loading state

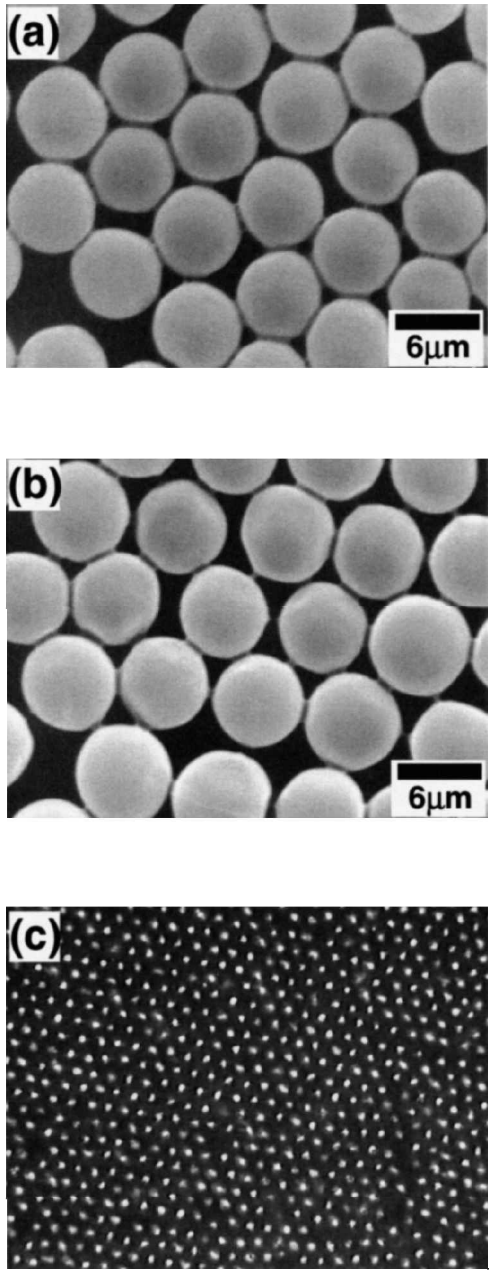


Figure 1. The morphological observation of PMMA/LC microcapsules using SEM (*a*, *b*) and POM (*c*): (*a*) PMMA seed particles; (*b*) PMMA/LC microcapsules; (*c*) PMMA/LC microcapsules.

of LC in the microcapsules was confirmed by POM. From figure 1 (*c*), we could verify that a single LC domain was formed in a microcapsule.

Figure 2 shows the images of PMMA/MLC microcapsules and PDLC cells obtained by POM using crossed polarizers. The PMMA/MLC microcapsules have a mono-sized LC domain which increases with increase in LC content. These results show that the LC droplet size can be controlled efficiently by the amount of LC

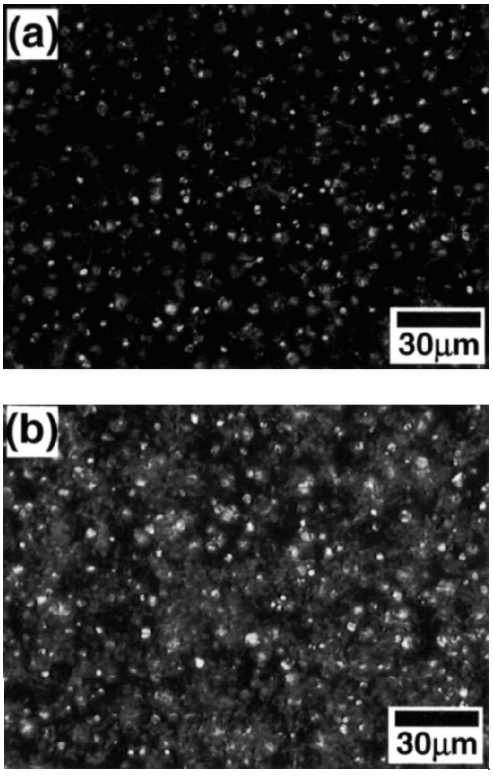


Figure 2. POM images of PMMA/MLC microcapsules in PDLC cells: (*a*) PLCF1; (*b*) PLCF2.

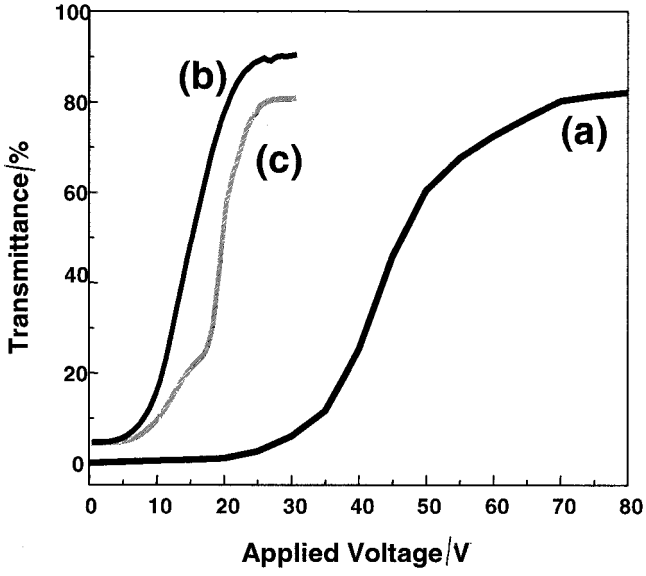


Figure 3. The electro-optical transmittance of PDLC cells as a function of applied voltage: (*a*) PDLC by SIPS process; (*b*) PLCF1; (*c*) PLCF2.

introduced. PLC1 in PLCF1 maintained a monodisperse LC domain. However, PLCF2 showed a broad size distribution of LC domains. This happened because a small amount of MLC in the microcapsules was squeezed out into the BL-S® matrix and formed other domains during PDLC cell preparation.

3.3. *The electro-optic measurements on PDLC cells* [25]

Figure 3 shows the transmittance change relative to applied voltage (*T–V* property). Curve (*a*) shows the *T–V* behaviour of a PDLC cell prepared using PMMA and MLC using the conventional SIPS method. This shows a threshold voltage around 40 V and a broad switching behaviour. Here, threshold voltage means the voltage at which the transmittance shows an enhancement of 10% based on the maximum transmittance. However, the *T–V* property of PLCF1 and PLCF2 showed a relatively low threshold voltage and narrow switching behaviour. Especially, curve (*b*) exhibits a high sharpness and a low threshold voltage. It is supposed that the monodispersity of the LC domains in the PDLC cells has sharpened the switching behaviour and that the small amount of surfactant existing at the interface of the LC domain and the PMMA in the microcapsules lowers the threshold voltage. On the contrary, curve (*c*) for PLCF2 shows that the threshold voltage has increased slightly in comparison with PLCF1, despite the large amount of LC incorporated, probably due to a size distribution of the LC domain. That is to say, a small amount of LC in the microcapsules has been squeezed out into the BL-S® matrix in the process of PDLC preparation and the excluded LC has formed other LC domains. This fact is confirmed in curve (*c*). The inflection in curve (*c*) is observed around 15 V, because of the difference in anchoring energy between polymer and MLC. That is, some LC domains are anchored by PMMA and others are by BL-S®. This causes the inflection, the broadness of switching behaviour and the increase in threshold voltage.

We conclude that PDLC cells prepared using mono-sized LC microcapsules show significant improvements in electro-optical property in comparison with PDLC cells prepared by the conventional SIPS method: (i) the threshold voltage decreases considerably; (ii) the transmittance behaviour with an applied electric field becomes much sharper.

4. Conclusion

In our studies, highly monodisperse PMMA/MLC microcapsules were produced by the SCM and SIPS. The slow evaporation rate of MC in swollen microcapsules led to formation of a single, uniform LC domain in the microcapsules. Phase separation patterns between polymer and LC during PDLC preparation may affect the electro-optical properties, due to the anchoring energy. It was found that the threshold voltage of PDLC cells prepared using microcapsules having a mono-sized LC

domain was much lower than that of cells prepared using simple SIPS. Also the monodispersity of the LC domains in the PDLC films enhanced the sharpness of switching behaviour remarkably.

This work was supported by the Brain Korea 21 Project.

References

[1] Craighead, H. G., Cheng, J., and Hackwood, S., 1982, *Appl. Phys. Lett.*, **40,** 22.
[2] Kawatsuki, N., and Ono, H., 1995, *J. appl. polym. Sci.*, **55,** 911.
[3] Shimada, E., and Uchida, T., 1992, *Jpn. J. appl. Phys.*, **31,** 352.
[4] Doane, J. W., Golemme, A., West, J. L., Whitehead, J. R., and Wu, B. G., 1988, *Mol. Cryst. liq. Cryst.*, **65,** 511.
[5] Pane, S., Caporusso, M., and Hakemi, H., 1997, *Liq. Cryst.*, **23,** 861.
[6] Chien, L. C., Lin, C., Fredley, D. S., and McCargar, J. W., 1992, *Macromolecules*, **25,** 133.
[7] Doane, J. W., Vaz, N. A., Wu, B. G., and Zumer, S., 1986, *Appl. Phys. Lett.*, **48,** 269.
[8] Zumer, S., and Doane, J. W., 1986, *Phys. Rev. A.*, **34,** 3373.
[9] Ono, H., and Kawatsuki, N., 1995, *Kobunshi Runbunshu*, **52,** 195.
[10] Kim, J. W., and Suh, K. D., 2000, *Polymer*, **41,** 6181.
[11] Kim, J. W., and Suh, K. D., *Macromol. Chem. Phys.* (in the press).
[12] Taylor, P., 1998, *Adv. Coll. Int. Sci.*, **75,** 107.
[13] Weiss, J., Hermann, N., and McClements, D. J., 1999, *Langmuir*, **15,** 6652.
[14] Binks, B. P., Clint, J. H., Fletcher, P. D. I., and Rippon, S., 1998, *Langmuir*, **14,** 5402.
[15] Kim, J. W., and Suh, K. D., 1999, *Colloid polym. Sci.*, **277,** 66.
[16] Shen, S., Sudol, E. D., and El-aasser, M. S., 1994, *J. polym Sci. A: polym. Chem.*, **32,** 1087.
[17] Li, K., and Stover, H. D. H., 1993, *J. polym Sci. A: polym. Chem.*, **31,** 2473.
[18] Higuchi, W. I., and Misra, J., 1962, *J. pharm. Sci.*, **51,** 459.
[19] Ugelstad, J., and Mork, P. C., 1980, *Adv. Coll. Int. Sci.*, **13,** 101.
[20] Ugelstad, J., 1978, *Makromol. Chem.*, **179,** 815.
[21] Park, J. G., Kim, J. W., and Suh, K. D., *Colloid & Surf. A* (in the press).
[22] Park, J. G., Kim, J. W., and Suh, K. D., 2001, *Colloid polym. Sci.*, **279,** 638.
[23] Park, N. H., Park, S. I., and Suh, K. D., 2001, *Colloid polym. Sci.*, **279,** 1082.
[24] Cho, S. A., Park, N. H., Kim, J. W., and Suh, K. D., 2002, *Colloid Surf. A.*, **196,** 217.
[25] Park, N. H., Cho, S. A., Kim, J. Y., and Suh, K. D., 2000, *J. appl. Polym. Sci.*, **77,** 3178.