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

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Photochromic characteristics of monodisperse microcapsules containing azobenzene derivative-doped nematic liquid crystals

NO-HYUNG PARK, SUNG-LL PARK and KYUNG-DO SUH*
Division of Chemical Engineering, College of Engineering, Hanyang University,
Seoul 133-791, Korea

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Highly mono-sized dye-doped liquid crystal (LC) microcapsules were prepared by the solute codiffusion method for application in photoswitchable devices. Azobenzene derivatives, which can be photoisomerized by irradiation with UV (366 nm) and visible (433 nm) light, were used as a photoresponsive dichroic dye. The microcapsules have a spherical shape and a single dye-doped LC domain. After UV light (366 nm) irradiation, PDLC films prepared using the microcapsules attained a photostationary state within 10 min and this state maintained stability. PDLC films made by employing a dichroic dye having electron donor and acceptor groups in the molecule showed especially good photoisomerization properties. The reversible *trans-cis*-photoisomerization occurred sharply by irradiating alternately with visible and UV light.

1. Introduction

Polymer/liquid crystal (LC) composites have been the focus of many investigations because of their potential applications. Recently, polymer dispersed LC (PDLC) [1–6] and polymer stabilized LC (PSLC) [7, 8] have been widely studied and applied intensively in the field of display devices due to such advantages as their polarizer-free and alignment layer-free nature, fast response times, simple preparation, etc. However, because of their low contrast ratio and broad switching behaviour, the use of PDLCs for display devices is limited and many studies have been carried out to overcome the problems. Generally, to improve the contrast ratio, the use of dichroic dye-doped LCs was proposed [9–11]. Almost all dichroic dyes show the attractive property of photoisomerization using light. As a result, investigation of this phenomenon has been focused on the manufacture of photocontrollable devices which have a high contrast ratio [12–15].

Generally, it is known that a change in the transmittance of a PDLC can be achieved by three approaches: (i) the changes result from occurrence of the LC to isotropic phase transition on applying heat [16, 17]; (ii) the changes occur by the reorientation of the LC on applying an electric fields [1–8]; (iii) the changes take place by the photochromic reaction of photochromic molecules such as azobenzene derivatives, stilbene derivatives, etc [9–11, 18]. The configuration of azobenzene derivatives can be transformed reversibly through the process of photoisomerization. *Cis*-azobenzene is formed using UV light around 366 nm, and transformed into the *trans*-azobenzene by visible light around 433 nm. When azobenzene derivatives exist in the LC, they affect the LC phase significantly. *Cis*-azobenzene destroys the LC phase but, on the contrary, *trans*-azobenzene is aligned with the LC molecules and enhances the LC phase. This means that the mesophase of an azobenzene-doped LC can be controlled by light irradiation.

In our study, in order to manufacture photocontrollable PDLC films having a sharp switching behaviour, monodisperse microcapsules containing azobenzene derivative-doped nematic LCs were prepared by employing the solute codiffusion method (SCM) [19, 20]. Then, the photochemical characteristics of PDLC films prepared using the microcapsules were investigated.

2. Experimental

2.1. *Materials*

To prepare the PMMA seed particles (see the scheme), methyl methacrylate (MMA, Junsei Chemicals), methanol (Mallinckrodt Co.), aerosol-OT (AOT, Sigma Chemicals), azobis(isobutyronitrile) (AIBN, Junsei Chemicals) and polyvinylpyrrolidone (PVP, $M_w = 40\,000$ g mol^{-1}, Sigma Chemicals) were used. In the SCM, sodium dodecylsulphate (SDS, Yakuri Chemicals), ethanol (99.95%, Baker Co.) methylene chloride (MC, Baker Co.) and distilled deionized (DDI) water were used without further purification. The low molecular mass LC (MLC-6014, $T_{NI} = 81$°C, $\Delta n = 0.13$, $\Delta\varepsilon = +18.0$) was purchased from E. Merck. 4-Dimethylamino-4′-nitroazobenzene

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

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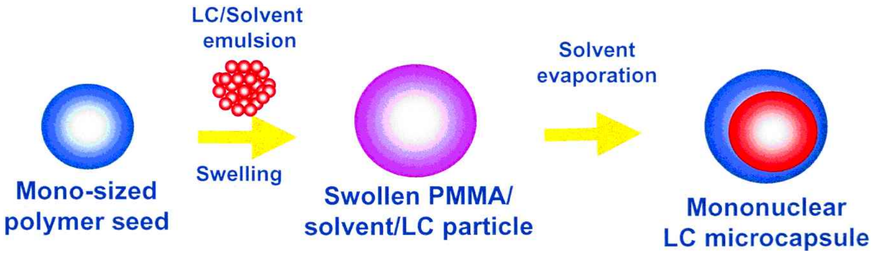

Scheme. Schematic representation of the SCM process.

(N-Az), 4-dimethylamino-4′-ethoxyazobenzene (E-Az) and 4-dimethylamino-4′-methoxyazobenzene (M-Az) were used as azobenzene-based dichroic dyes (Aldrich Chemicals). The chemical structures of the dichroic dyes used in our work and the configurational changes on irradiation with UV and visible light are shown in figure 1.

2.2. *Preparation of mono-sized PMMA substrate particles* [21, 22]

Highly mono-sized PMMA seed particles were produced by dispersion polymerization. AOT, PVP and methanol were weighed into a four-necked round-bottomed flask equipped with a reflux condenser, nitrogen inlet apparatus and mechanical stirrer. Then, MMA and AIBN solutions were poured into the reactor and stirred vigorously to make the reactants homogeneous. The mixture was then polymerized at 58°C for 24 h with stirring at 50 rpm. PMMA seed particles were recovered after washing with water, centrifuging repeatedly and drying at room temperature. A standard recipe for PMMA seed preparation is shown in table 1.

Table 1. Standard recipe for the preparation of PMMA seed particles[a].

Ingredients	Weight/g
MMA	10
PVP[b]	4
AOT	0.45
AIBN[c]	0.1
Methanol	85.45

[a] 58°C, 24 h; 10 wt % of monomer concentration based on total weight.
[b] 4 wt % of PVP (M_w = 40 000 g mol^{-1}) based on total weight.
[c] 1 wt % of AIBN based on monomer weight.

2.3. *Microencapsulation of LC in PMMA seeds via the SCM* [20]

PMMA seed particles were redispersed in 0.25 wt % aqueous SDS mixed with ethanol (SDS solution/ethanol = 4/1, g/g). The dispersed PMMA seed particles were swollen with a fine emulsion of the dye-doped LC/MC at room temperature until all the emulsion droplets disappeared completely. Then, the MC in the swollen microcapsules was evaporated off slowly at room temperature. Phase separation of the dye-doped LC phase occurred during solvent evaporation and mono-sized PMMA/dye-doped LC microcapsules incorporating a mononuclear dye-doped LC domain were obtained. A standard recipe for the SCM process is given in table 2. A schematic representation of microcapsule preparation is shown in the scheme.

Table 2. Recipe for the preparation of PMMA/LC microcapsules.

Ingredients[a]	Weights/g
Seed dispersion process	
PMMA seed	0.3
SE solution[b]	40

	N-0.1	N-0.3	E-0.1	E-0.3	M-0.1	M-0.3
SCM process						
LC	0.2997	0.2988	0.2997	0.2988	0.2997	0.2988
Dichroic dye[c]	0.0003	0.0012	0.0003	0.0012	0.0003	0.0012
MC	2.7					
SE solution	15					

[a] N, E and M are defined in figure 1.
[b] Ethanol: 0.25 wt % SDS solution = 1 : 4.
[c] Azobenzene derivatives.

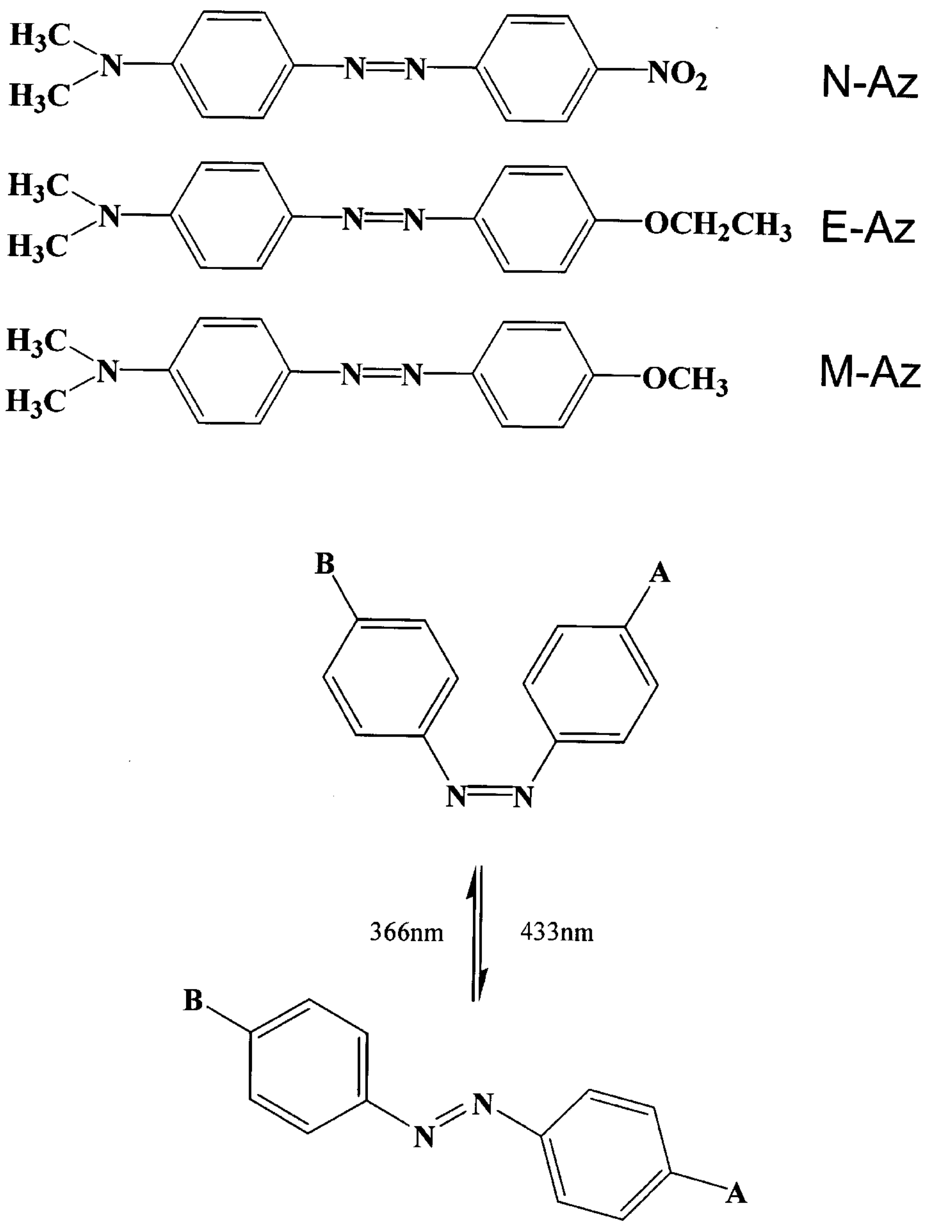

Figure 1. Chemical structures of the azobenzene derivatives used in this study and the isomerization of such molecules.

2.4. *Preparation of PDLC cells*

PDLC cells were prepared using the PMMA/dye-doped LC microcapsules. Firstly, the microcapsules were mixed with a 10 wt % solution of urethane acrylate (UA) in ethanol in the weight ratio 1/1. The mixture was coated onto ITO glass and sandwiched with another ITO glass plate. Then, UV curing of the UA was carried out for 5 min. The cell gap of the PDLC film was fixed at 11 μm using PET film spacer.

2.5. *Measurements*

The morphologies of the PMMA seed particles and microcapsules were observed using a scanning electron microscope (SEM, Hitachi model), optical microscopy (OM, Olympus BH-2) and polarizing optical microscopy (POM, Olympus BH-2) equipped with an image analyser. The optical properties on irradiation with light were measured using a UV/visible spectrophotometer (Shimadzu model UV-2101 PC).

3. Results and discussion

Substrate PMMA seed particles were manufactured by dispersion polymerization [21, 22], and we could produce mono-sized microcapsules using the solute codiffusion method (SCM) [20, 23, 24]. The basic concept of SCM is that dispersed polymer seed particles are swollen efficiently using a fine emulsion of solute/solvent via Ostwald ripening [25–27]. It is well known that

Ostwald ripening 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, stirring speed, surfactant concentration, etc. In this work, the SCM conditions are determined by controlling the solvent power of the medium and the surfactant concentration.

3.1. *The morphology of the dye-doped LC microcapsules*

The mono-sized PMMA substrate particles were produced by dispersion polymerization. All substrate particles show a high monodispersity and a clear surface (5.97 μm, polydispersity (PDI) = 1.003), and the monodispersity was maintained even after microcapsule formation. The morphology of the PMMA seed particles and the microcapsules was observed by SEM and the photographs are shown in figure 2.

After the complete swelling of the dye-doped LC/MC emulsions into polymer particles, the MC in the swollen PMMA seed particles was removed slowly at room temperature. Dye-doped LC domains phase separated during solvent evaporation. The slow evaporation rate induced complete phase separation and formation of a stable LC domain in the microcapsules. This fact could be confirmed by observation by OM and POM and the results are shown in figure 3.

As shown in figure 3 (*a*), the microcapsules have a spherical shape and are monodisperse. The domain morphology of the dye-doped LC in the microcapsules was confirmed by POM. From figures 3 (*b*) and 3 (*c*), we

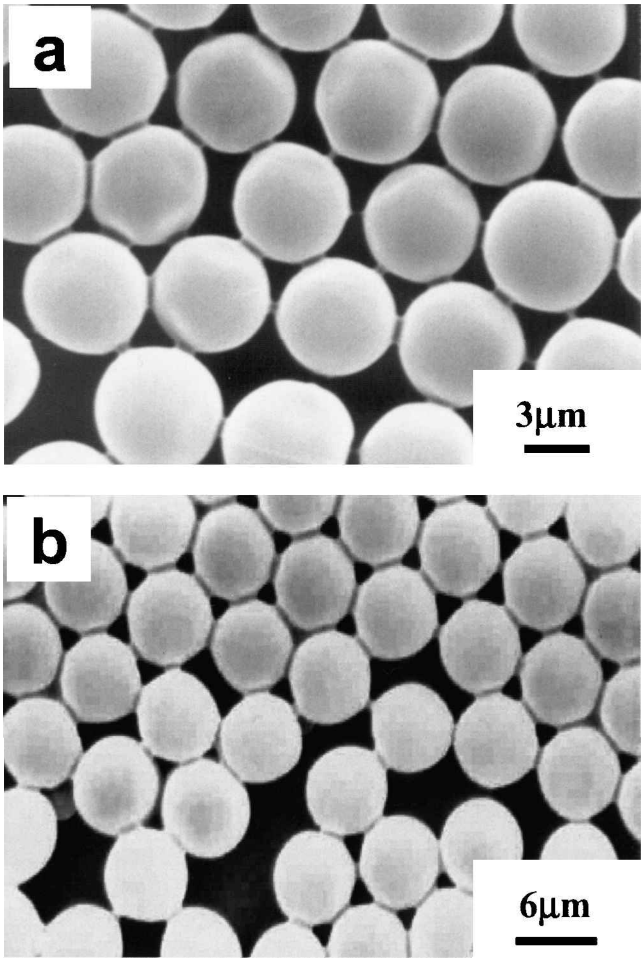

Figure 2. The morphology of microcapsules observed by SEM: (*a*) PMMA seed particles; (*b*) dye-doped LC microcapsules.

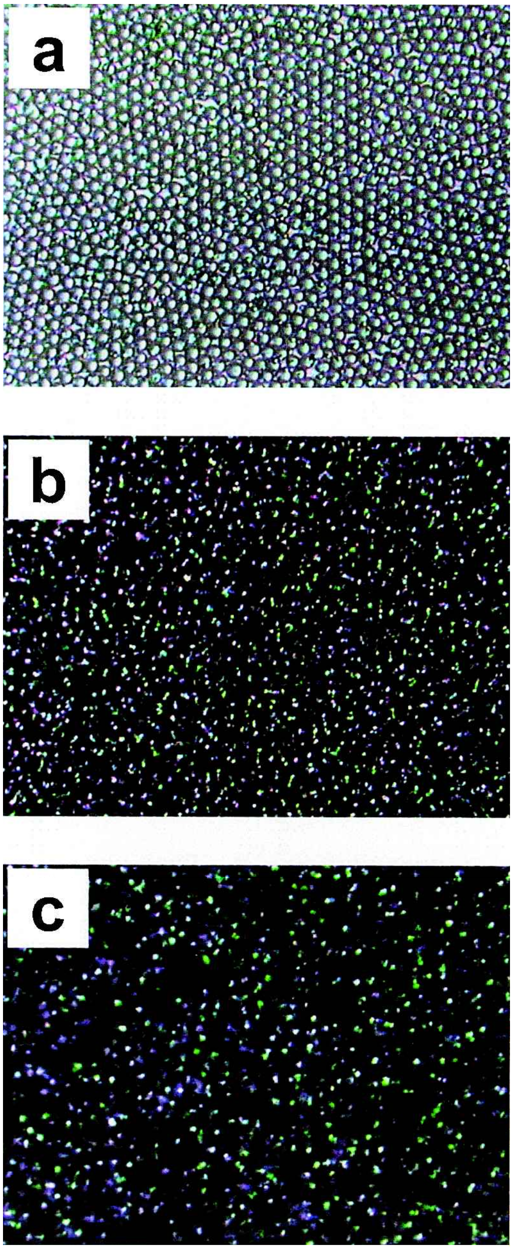

Figure 3. The morphology of microcapsules observed by OM and POM: (*a*) N-0.3 (measured by OM); (*b*) E-0.3 (measured by POM); (**c**) N-0.3 (measured by POM).

could observe yellowish and reddish single dye-doped LC domains in the microcapsules. The dye N-Az gave relatively large LC domains in the microcapsules due to the high degree of phase separation. It is assumed that N-Az, having electron donor and acceptor [28] groups in the molecule, is easy to align with the LC molecules, resulting in enhanced liquid crystallinity. However, dye M-Az gave films with no phase separated LC domains even after solvent evaporation.

3.2. *Photochemistry of PDLC films using dye-doped LC microcapsules*

The absorbance of the PDLC films under UV irradiation is shown in figure 4. The absorbance around 500 nm was measured using a UV/visible spectrophotometer and 366 nm irradiation.

PDLC film attained a photostationary state within 10 min after irradiating with UV light (366 nm). This means that the dye-doped LC molecules in the microcapsules are rearranged through the photoisomerization, the *trans*-form of the azobenzene derivative being transformed into the *cis*-form. After 10 min, almost all the *trans*-form is photoisomerized to the *cis*-form. In previous research [7, 8], polymers having the azobenzene moiety reached a photostationary state after about 30 min. These results show that the switching behaviour of PDLC films prepared using the microcapsules is much faster than that of conventional azobenzene-based polymer film, due to the low anchoring energy resulting from the presence of surfactant molecules at the interface between the LC domain and the PMMA shell, from the Ostwald ripening process and the monodispersity of the LC domains. Of course, the rate of photoisomerization of a dye-doped low molecular mass LC is faster than that of a polymer having an azobenzene-moiety. However, the microcapsule systems maintain the configuration even after irradiation is stopped, and the memorizing ability is similar to that of an azobenzene-based polymer. With M-Az and E-Az, the degree of absorbance change on UV irradiation is slight and smaller, respectively, and this fact is also confirmed by the following experimental results.

The *cis*-*trans* back-isomerization of the azobenzene derivatives is induced photochemically by visible light irradiation. That is, we can expect the nematic phase to recover quickly by irradiating with visible light. The PDLC films were irradiated at 366 and 433 nm alternately in a darkroom. The reversible photochemical reaction of the PDLC films is shown in figure 5.

Since the *cis*-*trans*-isomerization of dye-doped LC proceeds effectively by visible light irradiation, this results in a rapid increase in the light absorbance. Then, when UV light is irradiated, the *trans*-*cis*-isomerization occurs and the phase is changed from nematic to isotropic, which decreases the light absorbance. As shown in figure 5, the dichroic dye molecules in each LC domain

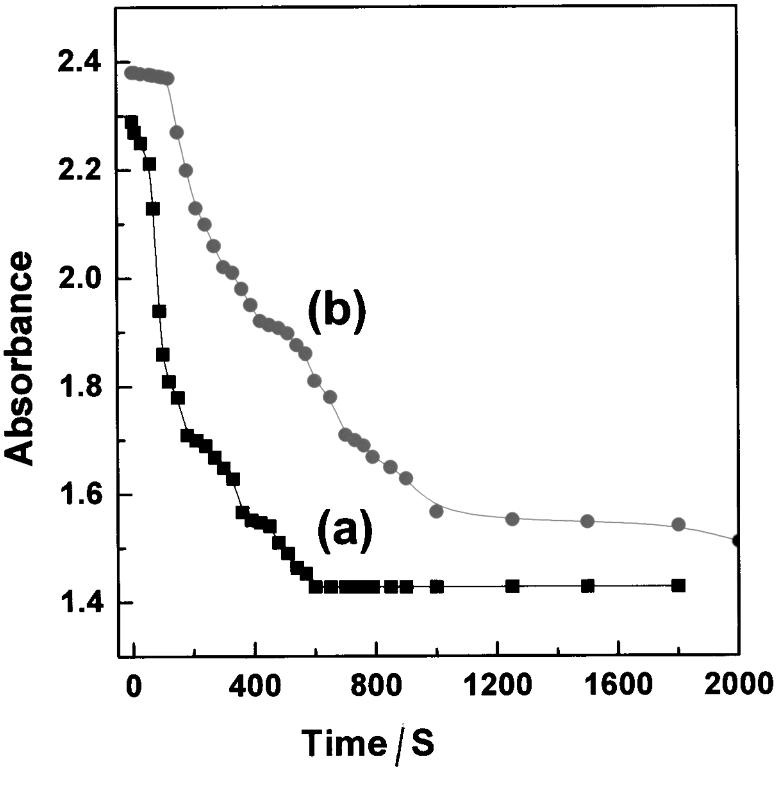

Figure 4. Absorbance change of PDLC films under UV irradiation: (*a*) PDLC using microcapsules; (*b*) PDLC made by a conventional SIPS method.

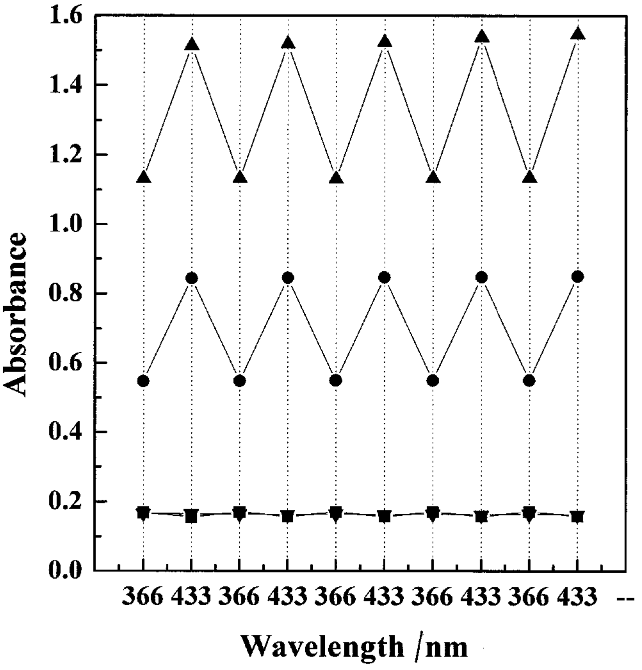

Figure 5. The reversible photochemical reaction of PDLC films (irradiation at 366 and 433 nm alternately) (▲: N-0.3; ●: E-0.3; ▼: N-0.1; ■: M-0.3).

change their configuration easily and align sharply, due to the monodispersity. Especially, film N-0.3 made from dye N-Az shows a good photoisomerization behaviour. This happens because the dichroic dye has electron donor and acceptor groups in the molecule and this enhances the electronic mobility.

4. Conclusions

In our studies, highly monodisperse dye-doped LC microcapsules were produced by dispersion polymerization and the SCM. The average particle size and PDI of the PMMA substrate particles were 5.97 µm and 1.003, respectively. The slow evaporation rate used induced complete phase separation and stable LC domain formation in the microcapsules. Especially, films of the N series show relatively well phase separated LC domains in the microcapsules. PDLC films prepared using the microcapsules reached a photostationary state within 10 min when irradiated with UV light. This indicates that the dye-doped LC molecules in a microcapsule are rearranged by the UV light. The reversible *trans-cis*-isomerization and the *cis-trans* back-isomerization occurred sharply on irradiating alternately with visible and UV light.

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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. poly. 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., 1998, *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] Rajaram, C. V., Hudson, S. D., and Chien, L. C., 1995, *Chem. Mater.*, **7**, 2300.
[8] Rajaram, C. V., Hudson, S. D., and Chien, L. C., 1996, *Chem. Mater.*, **8**, 2451.
[9] Lee, H. K., Kanazawa, A., Shiono, T., and Ikeda, T., 1998, *Chem. Mater.*, **10**, 1402.
[10] Zaplo, O., and Stumpe, J., 1992, *Mol. Cryst. liq. Cryst.*, **213**, 153.
[11] Kajiyama, T., KiKuchi, H., and Nakamura, K., 1993, *Proc. SPIE*, **1911**, 111.
[12] Palffy-Muhoray, P., Lee, M. A., and West, J. A., 1990, *Mol. Cryst. liq. Cryst.*, **179**, 445.
[13] Simoni, F., Cipparrone, G., Umeton, C., Arabia, G., and Chidichimo, G., 1989, *Appl. Phy. Lett.*, **54**, 896.
[14] Simoni, F., Cipparrone, G., and Umeton, C., 1990, *Appl. Phy. Lett.*, **57**, 1949.
[15] Simoni, F., Cipparrone, G., Duca, D., and Khoo, I. C., 1991, *Opt. Lett.*, **16**, 360.
[16] Cipparrone, G., Umeton, C., Arabia, G., Chidichimo, G., and Simoni, F., 1990, *Mol. Cryst. liq. Cryst.*, **179**, 269.
[17] Palffy-Muhoray, P., Frisken, B. J., Kelly, J., and Yuan, H. J., 1989, *Proc SPIE*, **1105**, 33.
[18] Kawanishi, Y., Tamaki, T., and Ichmura, K., 1991, *J. Phys. D: appl. Phys.*, **24**, 782.
[19] Park, N. H., Park, S. I., and Suh, K. D., 2001, *Colloid polym. Sci.*, **11**, 1082.
[20] Cho, S. A., Park, N. H., Kim, J. W., and Suh, K. D., 2002, *Colloid Surf. A*, **196**, 217.
[21] Kim, J. W., and Suh, K. D., 1999, *Colloid polym. Sci.*, **277**, 66.
[22] Shen, S., Sudol, E. D., and El-Aasser, M. S., 1994, *J. polym Sci. A: polym. Chem.*, **32**, 1087.
[23] Park, N. H., Park, S. I., and Suh, K. D., *Coll. polym. Sci.* (in the press).
[24] Park, S. I., Park, N. H., and Suh, K. D., *Liq. Cryst.* (in the press).
[25] Taylor, P., 1998, *Adv. Coll. Int. Sci.*, **75**, 107.
[26] Weiss, J., Hermann, N., and McClements, D. J., 1999, *Langmuir*, **15**, 6652.
[27] Binks, B. P., Clint, J. H., Fletcher, P. D. I., and Rippon, S., 1998, *Langmuir*, **14**, 5402.
[28] Hasegawa, M., Yamamoto, T., Kanazawa, A., Shiono, T., and Ikeda, T., 1999, *Adv. Mater.*, **11**, 675.