

Electro-optical Characterization of Transmission Holographic PDLC with Surfactant

Ju Yeon Woo, Eun Hee Kim, and Byung Kyu Kim

Dept. of Polymer Science & Engineering, Pusan National University, Busan 609-735, Korea

Phone : +82-51-510-2406 , E-mail : bkkim@pnu.edu

Abstract

The effects of surfactant on the electro-optic properties of holographic polymer dispersed liquid crystal (HPDLC) have been studied hoping to increase the diffraction efficiency and to reduce the anchoring energy at interfaces. Octanoic acid (OA) was used as surfactant. The 2,2,2 trifluoroethyl acrylate (TFEA) was added to the monomer mixture to enhance the phase separation and improve optical properties. The morphology of holographic gratings was examined using scanning electron microscopy (SEM). Addition of surfactant was likely to reduce the surface anchoring of the nematic droplet with the polymer surface which favors lowering of the switching field and to improve the optical qualities.

1. Introduction

Polymer dispersed liquid crystals (PDLCs) have been extensively studied for various electro-optical applications.¹ HPDLC gratings are formed in single step by exposing a homogeneous mixture of photo-reactive monomer and LC with an interference fringe pattern created by a holographic exposure apparatus.² In the hologram writing process, the photo-polymerization preferentially initiates at the high intensity regions. If monomer polymerizes on exposure to spatially modulated light, a concentration gradient of this monomer is produced because more monomers are consumed in the region of higher intensity of the sample. Then counter diffusion of monomer and LC occurs due to the concentration gradient formed by the polymerization. It should be emphasized that there is a distribution of droplet sizes within typical PDLC films which is related to the kinetics of the phase separation process.³

Recently the effects of prepolymer structure have been received considerable attention with regard to HPDLC. Sutherland et. al. reported the effects of varying monomer functionality on HPDLC grating.³ Crawford and his co-workers investigated the degree

of shrinkage according to urethane acrylate monomer functionality.⁴ Recently, Schulte and his co-workers⁵ used fluorine substituted acrylate monomers on the conventional formulation with LC (E7) to prepare HPDLC gratings with visible radiation. The motivation of using fluorinated monomers for the preparation of HPDLC was driven by the hypothesis that the chemical incompatibility between fluorinated compounds and LC may enhance the LC phase separation. Moreover, the presence of fluorine atoms at the LC/polymer interface of the HPDLC gratings may lower the LC anchoring strength thus lowering the switching voltage.

It should be noted that, in most visibly recorded HPDLCs to date, a number of additives typically are required.⁶ Because most of these systems have high switching voltages due to their very small-sized and irregular-shaped domains, surfactant is typically added to reduce the strong anchoring interactions of the droplet with the host polymer. Although this addition reduces the switching field substantially, it also leads to undesirable heating effects when an electric field is applied.⁷

This contribution describes the effect of surfactant on the morphological and electro-optical properties of HPDLC transmission gratings. Octanoic acid (OA) is used as surfactant. The contents of surfactant and LC have been systematically varied for HPDLC, and according to the content of surfactant, we obtained various electro-optical properties of the final films. Addition of surfactant was expected to lower anchoring energy at the interface of the LC and polymer by encapsulation and to increase the diffraction efficiency due to the reduction in droplet size. The morphology of holographic grating is examined using scanning electron microscopy (SEM). Real time measurements of grating formation have been obtained according to the content of surfactant and LC.

2. Experimental

To form a HPDLC device, a homogeneous mixture of a multi-functional monomer, a reactive diluent, a photoinitiator dye, a coinitiator, and a LC is prepared.

PUA is a segmented urethane oligomer tipped with acrylic functionality and it offer excellent toughness chemical resistance and adhesion to difficult substrates than any other class of radiation curable oligomer. Polypropylene glycol (PPG) with different molecular weights ($M_n=200, 400, 1000, 2000\text{g/mol}$) were reacted with molar excess of hexane diisocyanate (HDI) for over 1h at 80°C to obtain isocyanate (NCO) terminated polyurethane prepolymer. Then the reaction mixture was cooled down to 40°C and hydroxyl ethyl acrylate (HEA) was added to obtain HEA-capped urethane acrylate oligomers.^{8,9} This urethane acrylate oligomers are highly viscous and immiscible with LC. Mono-functional monomer helps to dissolve different compounds in the mixture and form homogeneous syrup. It is also essential to reduce the viscosity of an LC/monomer mixture. N-vinyl-pyrrolidone (NVP) has been used as mono-functional monomers. Multifunctional monomer viz Dipentaerythritol penta-/hexa-acrylate (DPHPA) has much higher reactivity and provide the polymer with extensive crosslinkings. The composition of oligomer / monofunctional / multifunctional diluents was 4 / 3 / 3 by weight. The small amount of Rose Bengal (RB) and N-phenylglycine (NPG) were added to sensitize for monomers for a visible cure.

Also, mono-functional fluorinated monomers (2,2,2-trifluoroethyl acrylate) were added to the monomer mixtures to enhance the phase separation and improve optical properties. And surfactant (octanoic acid) was added to the monomer mixtures ranging from 0 to 9 wt%.

The choice of the liquid crystal plays a very important role in the electro-optical performance and diffraction efficiency of the HPDLC. We have used E7 (BL001, Merck), an eutectic mixture of four cyanobiphenyl and a cyanoterphenyl mixture. The LC content was 30~45wt%.

The cell was constructed by sandwiching the prepolymer syrup/LC mixture between the two indium-tin-oxide (ITO) coated glass plates, with a gap of $10\mu\text{m}$, adjusted by a bead spacer. The prepolymer mixtures have been irradiated with an Ar-ion laser (514nm) of equal intensity with a total power of 100mW, with exposure times of typically 30s~180s.

The incident angles of the two beams outside the material are respectively 13° . For transmission gratings, the holographic fringes are normal to the sample substrate. Figure 1 shows the experimental setup we used to fabricate a transmission HPDLC.

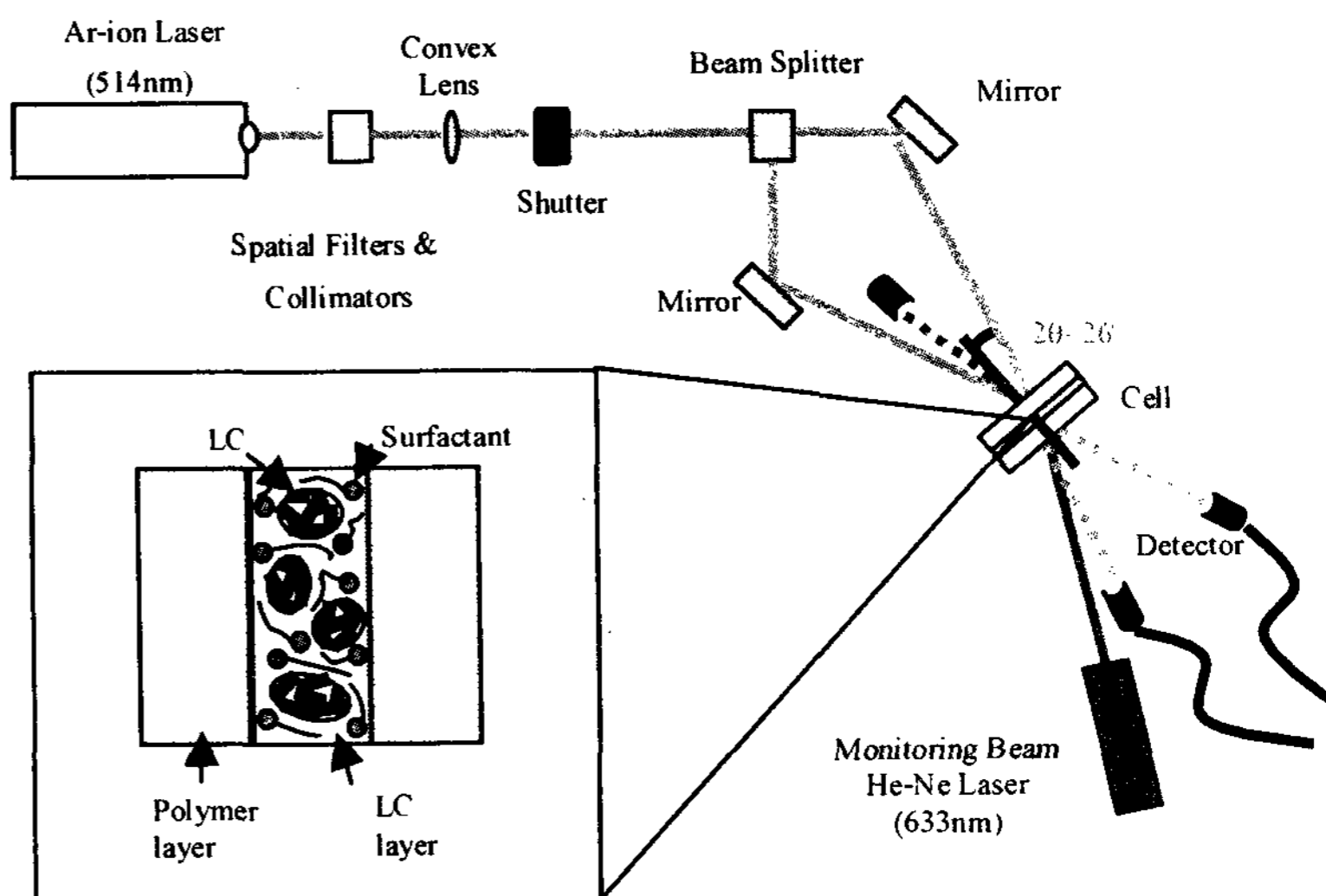


Figure 1. Experimental setup for measuring the electro-optical characteristics of the transmission gratings.

The diffraction efficiencies were measured with a photodiode using Ar-ion laser. Grating formation was monitored in real time using He-Ne laser at 633nm. Since the material is not sensitive to red light. For electrooptic measurements, a square wave voltage operating from 0 to 80V was applied across the HPDLC cell. The drive signal and the response of the photodiode were monitored with a digital storage oscilloscope. Grating morphology was identified by SEM (scanning electron microscopy). The samples were prepared by freezing and fracturing the HPDLC cells using liquid nitrogen, and extracting the LC molecular with methanol.

3. Results and discussion

Carre et al.¹⁰ have used real time diffraction from holographic gratings to study the mechanisms and kinetics of photopolymerization reactions. The diffraction efficiency as a function of curing time exhibits three main regions : 1) a short induction period during which on polymerization takes place ; 2) a period of rapid photoinitiator bleaching with concomitant fast free-radical polymerization and crosslinking indicated by a rapidly increasing diffraction efficiency ; 3) a plateau in the diffraction efficiency when most of the dye molecules are irreversibly bleached.

Figure 2 shows the measured curves of a real time study of grating formation in our system. A sample having an LC content of 35% shows the same general features described above both w/ surfactant and w/o surfactant. However, the induction period in this system is very short on the order of 100 μ s after start of exposure due to the high reactivity of the multifunctional monomers. The growth of the grating reaches a maximum around 50s. But, as the LC contents are increased up to 45% w/o surfactant, the curve is reduced sharply. This implies that fast LC dispersion of beginning stage, led to the droplet coalescence forms larger domains allowing scatterings. In case of w/ surfactant, the surfactant helps the droplet maintain the ideal size by protecting droplet coalescence at high fraction of LC, leading to high diffraction efficiency.

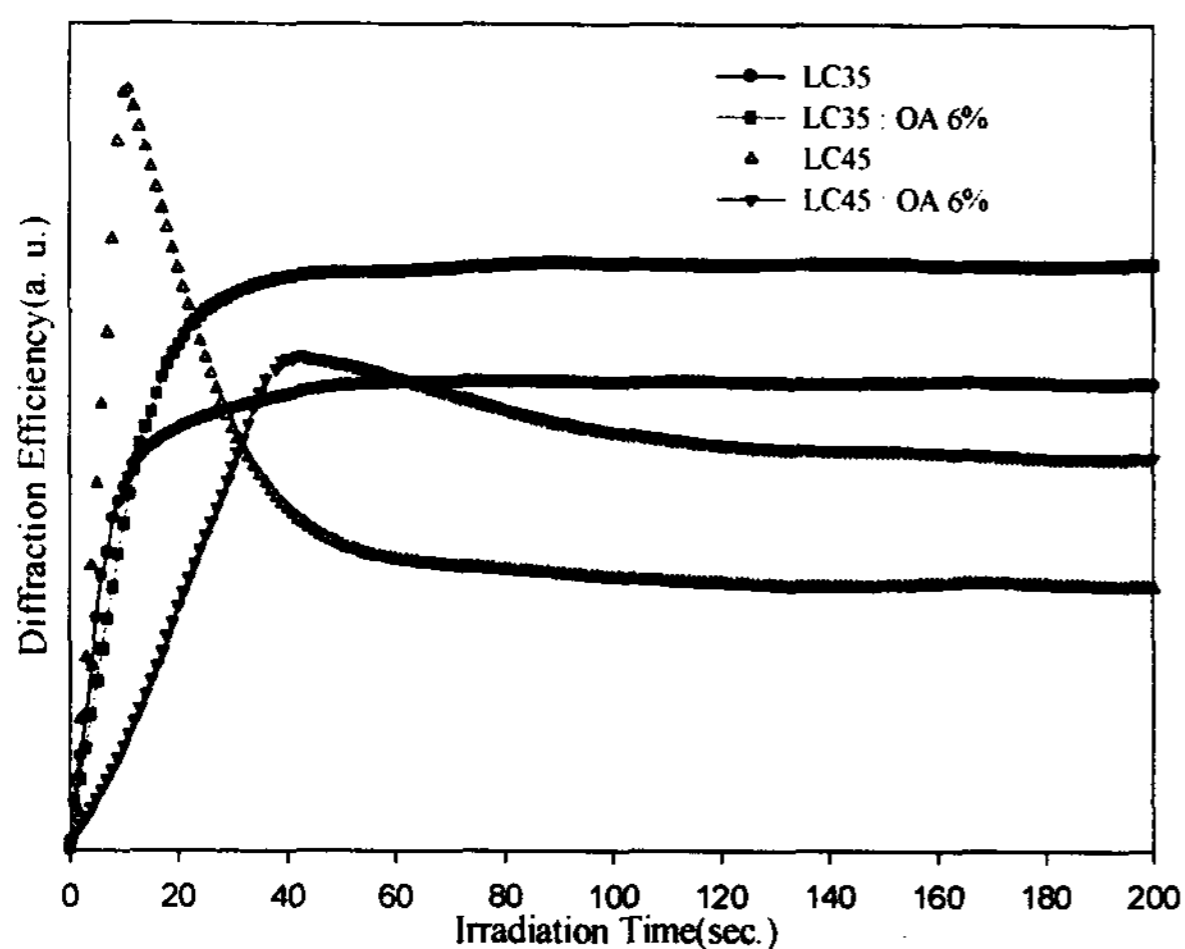


Figure 2. Diffraction efficiency as a function of time at 633nm in a HPDLC samples prepared without surfactant and with surfactant having 35 and 45 wt% LC (PPG400).

Figure 3 shows the SEM images of transmission grating. An SEM micrograph of HPDLC grating, prepared w/o surfactant is shown Figure in 3(a). Figure 3(b), 3(c) and 3(d) represent the SEM photographs of HPDLC gratings, each prepared by adding 3, 6, and 9% of surfactants, respectively. The darker regions of the micrographs are representative of the original location of the LC. Liquid crystal droplets are clearly evident and are regularly aligned along Bragg planes.

W/o surfactant, the morphology is a nearly bicontinuous phase of LC layer. The nearly spherical droplets are much larger and almost connected through a very tenuous polymer network. However, with surfactant the microstructures consist of spherical

LC domains well separated. The average size of LC domains found with surfactant is larger than that found w/o surfactant. Also, it is apparent from the SEM micrographs that with the increase in the content of surfactant, the LC domain size decreases in the transmission grating.

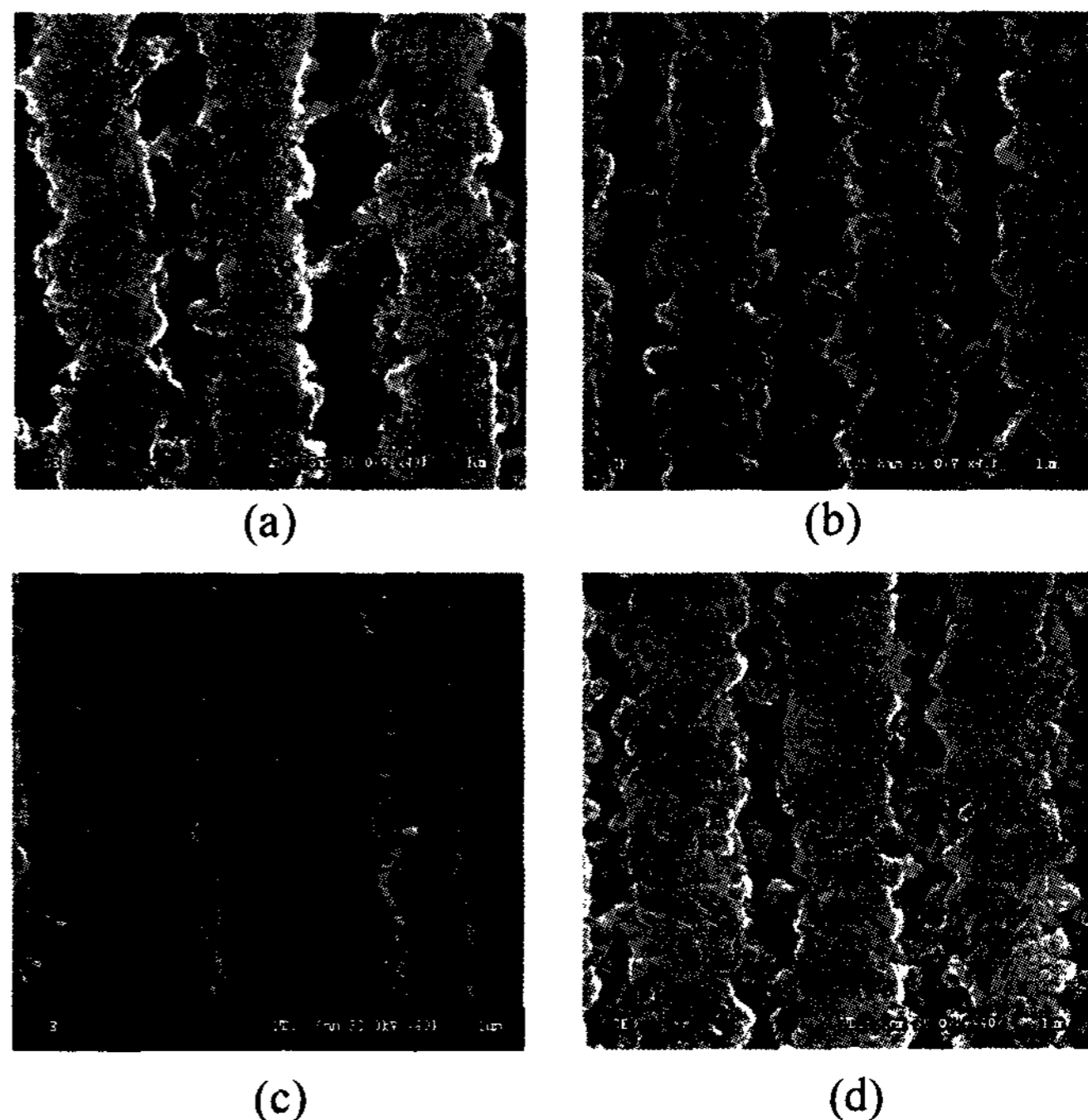


Figure 3. SEM morphology for transmission gratings prepared (a) without surfactant and substituting it with (b) 3% (c) 6% (d) 9% of surfactant (PPG400, LC35).

Diffraction efficiency- PPG molecular weight-content of surfactant relationship is plotted in Figure 4. As the PPG molecular weight increases, the rate of cure decreases because of the decreased number of reactive sites and the high viscosity of the reaction mixture. It is seen that the diffraction efficiency decreases with increasing PPG molecular weight, although a maximum is obtained for PPG400. In the case of PPG200, the rapid migration of LC molecules into the LC-rich phase will lead to extensive coalescence to form large LC droplets. This lowers droplet density and enlarge domain size leading to high scattering loss. Hence, the diffraction efficiency of the grating decreases. Also, diffraction efficiency monotonically increases with content of surfactant. The increase in diffraction efficiency with the increasing level of surfactant can be attributed to the significant decrease in the size and distribution of nematic domain.

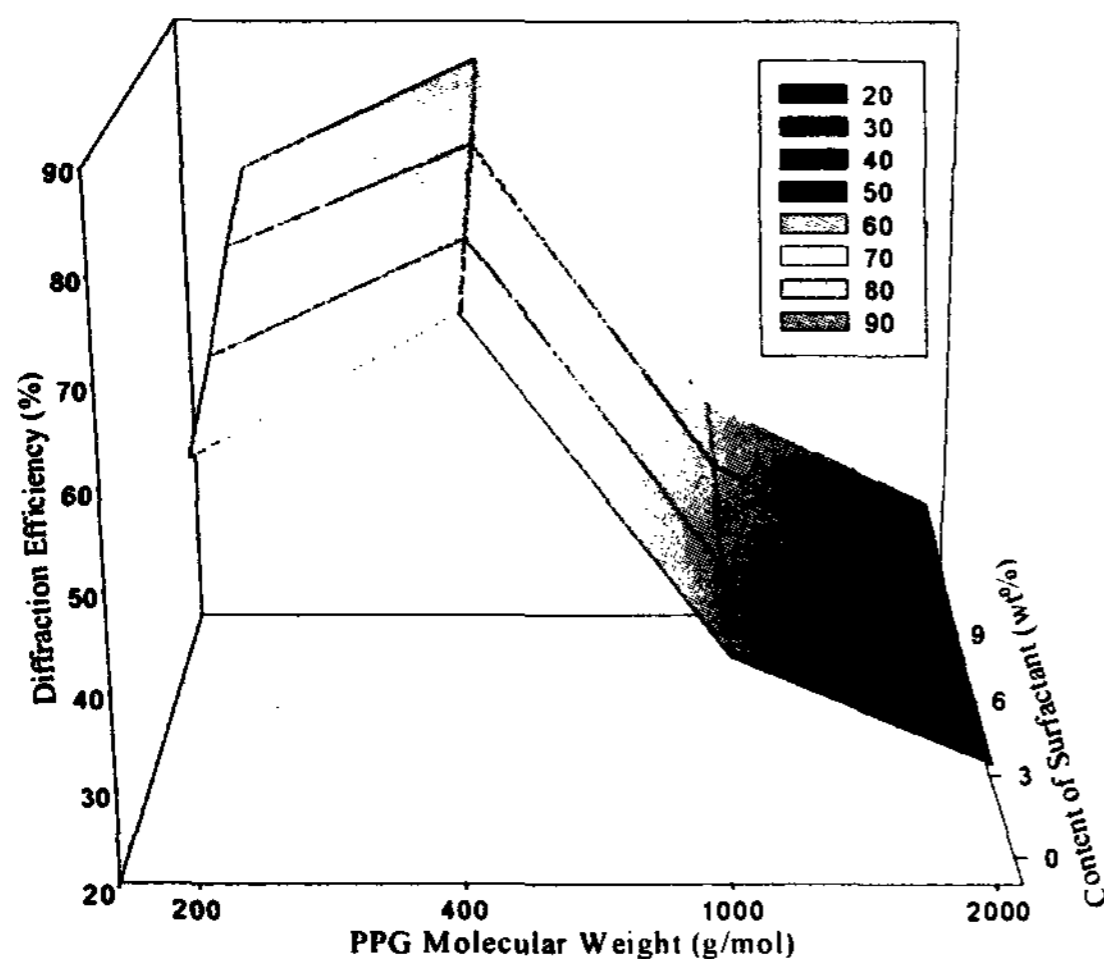


Figure 4. Diffraction efficiency-molecular weight-content of surfactant relationships of HPDLC films (LC35).

Figure 5 shows the applied voltage dependence of the diffraction efficiency of transmission HPDLC film. When a voltage is applied, diffraction efficiency decreases implying that LC molecules are oriented along the electric field direction. It has been observed that the HPDLC samples prepared w/ surfactant has lower switching voltages compared to the HPDLC samples prepared w/o surfactant. This implies that surfactants play an important role to lower anchoring energy at the interface of the LC and polymer by encapsulation. Also, it is seen that the switching voltages decreases with increasing amount of surfactant, but an optimum content of surfactant is 6wt%. Beyond 6% of surfactant loading, decreased LC droplet size leads to increase switching voltages.

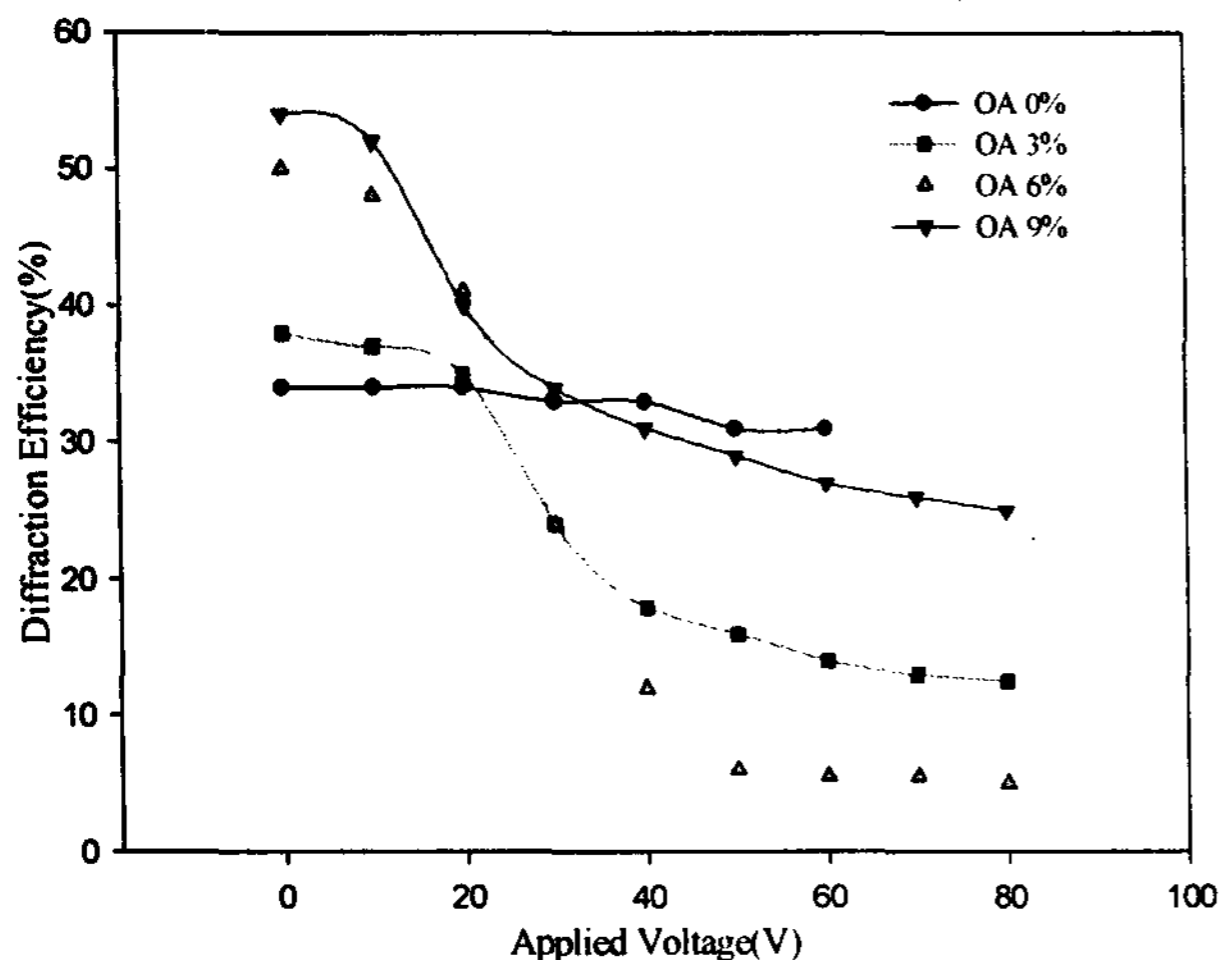


Figure 5. Diffraction efficiency of transmission gratings with applied electric voltage (PPG400, LC45).

4. Conclusion

The effects of the surfactant have been studied in terms of grating morphology, diffraction efficiency and electro-optic properties. Addition of surfactant was likely to favor lowering of the switching field. This implies that surfactant reduces anchoring energy at the interface of the LC and polymer by encapsulation. It is observed that as the content of surfactant increases LC droplets became small due to the protection LC droplet coalescence. Hence, an increased diffraction efficiency and a decrease in response time might result from a small droplet size. We found that an optimum content of surfactant (6%) exists.

5. Acknowledgements

The research has been supported by the Korean Ministry of Science and Technology(MOST) and Ministry of Information and Communication(MIC) via IMT2000

6. References

- [1] P. S. Drzaic, Liquid crystal dispersions, World Scientific, Singapore, 1995.
- [2] M. D. Sarkar, J. Qi, G. P. Crawford, Polymer, 43, 7335(2002).
- [3] R. T. Pogue, L. V. Natarajan, S. A. Siwecki, V. P. Tondiglia, R. L. Sutherland, T. J. Bunning, Polymer, 41, 733(2000).
- [4] G. Y. Warren, M. Desarker, J. Qi, G. P. Crawford, Proceedings of SID'01, 866(2001).
- [5] M. D. Schulte, S. J. Clarson, L. V. Natarajan, V. P. Tondiglia, D. W. Tomlin, T. J. Bunning, Abstr. Pap. Am. Chem. Soc., 2, 208(2000).
- [6] T. J. Bunning, L. V. Natarajan, V. P. Tondiglia, R. L. Sutherland, Annu. Rev. Mater. Sci., 30, 80(2000).
- [7] L. V. Natarajan, C. K. Shepherd, D. M. Brandelik, R. L. Sutherland, S. Chandra, V. P. Tondiglia, D. W. Tomlin, T. J. Bunning, Chem. Mater., 15, 2477(2003).
- [8] K. H. Lee, B. K. Kim, Polymer, 37, 2251(1996).
- [9] B. K. Kim, S. H. Kim, J. C. Song, Polymer, 39, 5949(1998).
- [10] C. Carre, D. J. Lougnot, J. P. Fouassier, Macromolecules, 22, 791(1989).