Polymer Bulletin 35, 365–370 (1995)

**Polymer Bulletin**

# Effects of molecular weight on morphology and electrooptical properties of polymethylmethacrylate/liquid crystal composites fabricated by a solvent-induced phase separation method

**Hiroshi Ono**[1,*], **Nobuhiro Kawatsuki**[2]

[1] Kuraray Co., Ltd., 1621 Sakazu Kurashiki, 710 Japan
[2] Department of Applied Chemistry, Himeji Institute of Technology, 2167 Shosha, Himeji, 671-22 Japan

Received: 1 February 1995/Revised version: 20 April 1995/Accepted: 25 April 1995

## Summary

The relationship between the electrooptical properties, morphology and molecular weight of polymethylmethacrylate (PMMA) in PMMA/liquid crystal composite films is clarified. The LC droplet size has decreased with increasing molecular weight of PMMA. The threshold voltage has increased with increasing molecular weight of PMMA in good agreement with a equation of Doane *et al*, qualitatively. Electrooptical response characteristics have included fast and slow mode. Thermal motion of PMMA at the interface between PMMA and LC seems to affect response time.

## Introduction

Polymer/low-molecular-weight liquid crystal (LC) composite films constitute a novel type of materials possessing exciting physical and chemical properties leading to wide varieties of applications, such as light shutters, flexible displays without polarizer, switchable windows, and other devices due to the possibility of electric-field-controlled light scattering.[1-7] Several methods to disperse LC droplets in a polymer matrix were reported with regard to methods of a solvent-induced phase separation (SIPS),[7] a photopolymerization-induced phase separation (PPIPS)[5,6] and an LC emulsion in aqueous polymer solution.[2,3]

Kajiyama *et al.* proposed the composite film consisting of polymethylmethacrylate (PMMA)/LC formed by the SIPS method and obtained the driving voltage of 40-120 $V_{rms}$.[7] One of the problems of the polymer/LC composite film is that the driving voltage is relatively higher than that of the conventional LC display which dose not contain a polymer matrix. Recently we have reported a new type of composite film prepared from two-step phase separation method composed of the SIPS method followed by the PPIPS method in order to fabricate a thin photocured polymer layer between the PMMA and the LC.[8,9] Electrooptical properties of the composite films had a low driving voltage of 18 $V_{rms}$. In order to apply the composite film to the devices, it is important to control the morphology and optical properties. However fabrication methods for controlled droplets sizes in PMMA/LC composite films have not been presented.

---

[*] Corresponding author

The purpose of the present study is to clarify the relationship between the electrooptical properties, morphology and molecular weight of PMMA.

## Experimental

Three kinds of PMMA with different molecular weight were used in the present study. PMMA with low molecular weight (Mw: 12,300, Mn: 5,920 (L-PMMA)) was obtained from Aldrich Co., Ltd., PMMA with middle molecular weight (Mw: 62,000, Mn: 31,500 (M-PMMA)) was synthesized by Kuraray Co. Ltd., and PMMA with high molecular weight (Mw: 313,000, Mn: 114,000 (H-PMMA)) was supplied from Kodak Co. Ltd. A nematic LC mixture with positive dielectric anisotropy (E7) was obtained from Merck Japan Ltd. The glass substrate with an ITO electrode was obtained from Matsunami Glass Company.

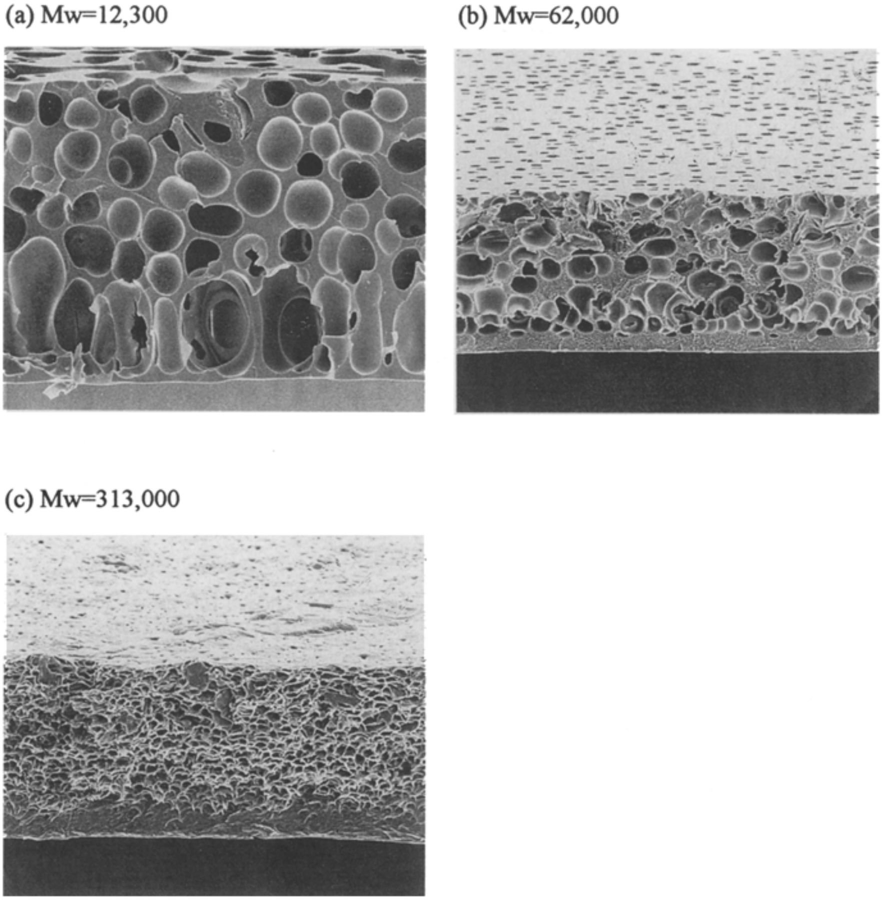
PMMA/LC composite films were prepared by a SIPS method. Four hundreds mg of PMMA and 600 mg of E7 were dissolved in 2 g of chloroform. The solution was spin-coated on an ITO-coated glass substrate. The composite films were then dried at 23 ℃. PMMA and E7 were phase separated and the composite films scattered light due to the difference between the refractive index of PMMA and that of E7. Film thickness of composite films was determined by a Rank-Tayler Hobson Talystep on the basis of a stylus contact method and were controlled at 15-17 μm.

Morphology of the composite films were observed by a scanning electron microscopy (SEM) and transmittance spectra. The samples for SEM observation were extracted with methanol at 23 ℃ for 60 s. Transmittance spectra of composite films were measured with a Hitachi U-4000 UV-VIS spectrometer.

Electrooptical measurements were carried out by measuring transmission of a He-Ne laser beam (632.8 nm) through a PMMA/LC composite film with increasing and decreasing the applied voltage between 0 and 80 $V_{rms}$ at a rate of 0.89 $V_{rms}$/s. Switching behavior of the film was also measured with an applied voltage 80 $V_{rms}$. Measurement system was described in detail previously.[10]

## Results and Discussion

SEM photographs of three PMMA/LC composite films with different molecular weight of PMMA are shown in Figs. 1(a)-1(c). LC droplet size in PMMA films decreased with increasing molecular weight of PMMA. LC droplet size in L-PMMA increased with closing to glass substrate, as shown in Fig. 1(a). This is primarily due to the higher solution viscosity of high $M_w$ polymer. Since the composite films were prepared from solvent, the LC droplet is formed in solvent removal, followed by agglomeration of small droplets to from large ones. The LC droplet agglomeration is more feasible in low $M_w$ polymer, clearly, consistent with the results.


(a) Mw=12,300

(b) Mw=62,000

(c) Mw=313,000

Fig. 1. SEM photographs of PMMA/LC composite films with different molecular weight.

LC droplet size might be small at the film surface since speed of solvent removal at the film surface was faster than that at the interface between the composite film and glass substrate. The LC droplet size can be observed by transmittance spectra on the basis of Rayleigh-Gans-Debye theory.[11] Figure 2 shows the transmittance spectra of three composite films with different molecular weight of PMMA. Slope of spectra increased with increasing molecular weight of PMMA. The color of transmitted light changed between white, red and yellow with increasing molecular weight of PMMA. The result suggests, from Rayleigh-Gans-Debye theory, that the LC droplet size decreased with increasing molecular weight of PMMA and was consistent with SEM photographs.

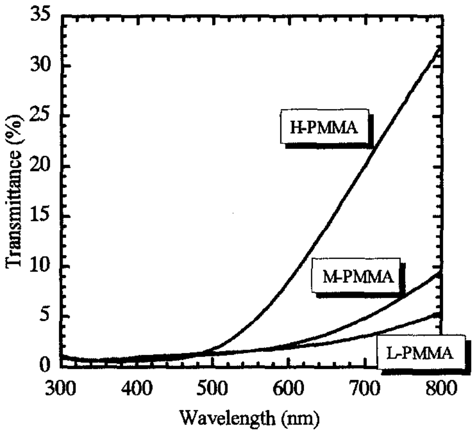


Fig. 2. Transmittance spectra of composite films with different molecular weight of PMMA.

The relation of applied voltage and transmittance is shown in Fig. 3. Threshold voltage ($V_{th}$) increased with increasing molecular weight of PMMA. In particular, H-PMMA/LC composite films could not be switched to transparent state even by the addition of 80 $V_{rms}$. The threshold voltage has been found to be dependent on the size of the LC droplets and should be a linear function of a reciprocal size of the droplets $R$ according to Eq. (1):[12]

$$V_{th} \cong \frac{d}{R}\left|\frac{K(l^2-1)}{\Delta\varepsilon}\right|^{1/2}, \qquad (1)$$

where $d$ is film thickness, $R$ is droplet radius, $K$ is effective elastic constant, $\Delta\varepsilon$ is dielectric anisotropy, and $l$ is aspect ratio of elongated droplet. From Eq. (1), threshold voltage decreases with the rise of the droplet size. As shown in Figs. 1(a)-1(c) and 3, threshold voltage increased with decreasing the LC droplet size and showed LC droplet size dependence in good agreement with Eq. (1), qualitatively. Since H-PMMA/LC composite films had small LC droplets and threshold voltage was higher than 80 $V_{rms}$, the composite films could not be switched to transparent state.

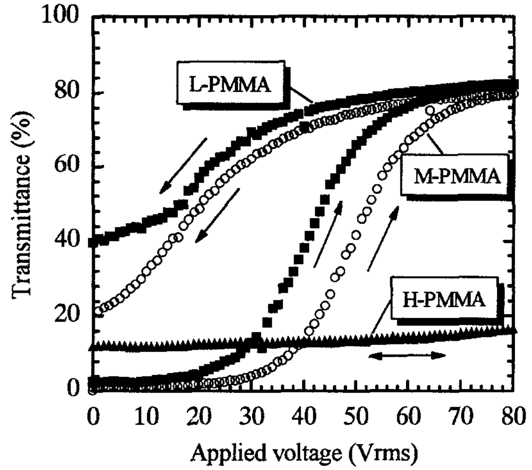


Fig. 3. Relation of applied voltage and transmittance in PMMA/LC composite films with different molecular weight of PMMA.

Maximum transmittance of both L-PMMA and M-PMMA was 82 % because the refractive index of PMMA was independent on molecular weight. Large hysteresis was observed in both L-PMMA/LC and M-PMMA composite films, as shown in Fig. 3. The hysteresis might have a relation to the switching behavior as described below. Electrooptical response characteristics of L-PMMA/LC and M-PMMA composite films are shown in Fig. 4. Slow component of decay time was observed. The thermal motion of PMMA could cause the hysteresis of the composite films. The slow component may be originated from thermal motion of PMMA at the interface between PMMA and LC.

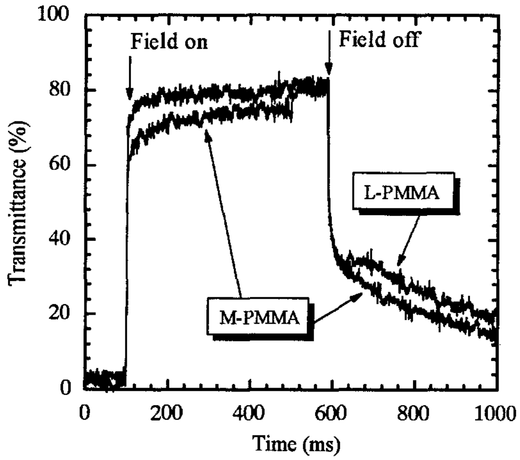


Fig. 4. Electric switching characteristics of L-PMMA/LC and M-PMMA/LC composite films.

## Conclusions

Morphology and electrooptical properties of PMMA/LC composite films with different molecular weight of PMMA were investigated. LC droplet size decreased with increasing molecular weight of PMMA. Threshold voltage increased with increasing molecular weight of PMMA because LC droplet size decreased. The result was consistent with a equation of Doane *et al*, qualitatively.

## References

1. H. G. Craighead, Julian Cheng and S. Hackwood (1982) Appl. Phys. Lett. 40: 22.
2. J. W. Doane, N. A. Vaz, B. G. Wu and S. Zumer (1986) Appl. Phys. Lett. 48: 269.
3. P. S. Drzaic (1986) J. Appl. Phys. 60: 2142.
5. H. Nomura, S. Suzuki and Y. Atarashi (1990) J. Appl. Phys. 68: 2922.
6. A. V. Koval, M. V. Kurik, O. D. Lavrentovich and V. V. Sergan (1990) Mol. Cryst. Liq. Cryst. 193: 217.
7. T. Kajiyama, H. Kikuchi and A. Takahara (1992) Proc. SPIE 1665: 20.
8. N. Kawatsuki and H. Ono, Chem. Lett., in press.
9. N. Kawatsuki and H. Ono (1995) J. Appl. Polym. Sci. 55: 911.
10. H. Ono and N. Kawatsuki (1994) Jpn. J. Appl. Phys. 33: 6268.
11. A. B. Loebe (1959) Off. Dig. 31: 200.
12. B. G. Wu, J. H. Erdmann and J. W. Doane (1989) Liq. Cryst. 5: 1453.