

THERMO-OPTICAL EFFECT AND HEAT-MODE LASER RECORDING  
PROPERTIES OF THE (POLYMER/LIQUID CRYSTAL) COMPOSITE  
FILMS

S. TANIOKA\*, H. KIKUCHI and T. KAJIYAMA

*Department of Chemical Science and Technology, Faculty of Engineering  
Kyushu University, 6-10-1 Hakozaki, Higashi-ku Fukuoka, 812 JAPAN*

*\*Chisso Corporation, Chiyoda-ku, Tokyo, 100 JAPAN*

ABSTRACT

(Polymer /liquid crystal:LC) composite films with electro-optical characteristics based on the light scattering were prepared by a coating method from a solution of poly(methyl methacrylate)(PMMA) and nematic mixture of LC(GR-63). The composite films were heated in a water bath up to 323-369 K and all the samples were cooled down in an ice water bath to 273 K. Upon heat treatment over the nematic-isotropic transition temperature,  $T_{NI}$ , the composite film was changed from an initial turbid state to a transparent state. When the composite film was heated above  $T_{NI}$ , the dispersed spherical LC droplets were formed in the matrix polymer and the size of LC droplets became smaller than the wavelength of visible light, resulting in a transparent state.

An organic dye of azo derivative(M-618) which exhibits a strong absorption at the wavelength in the vicinity of 530 nm was dissolved into the (PMMA/GR-63) composite film. A point of the ternary composite film was irradiated by the second harmonics of a pulsed Nd-YAG laser beam, 532 nm, through a photo mask. Since the laser absorbed in the composite film was converted into heat, the laser irradiated part was selectively changed to a transparent state. A heat mode laser recording was accomplished for the (polymer/LC) composite film for the first time.

---

\*To whom correspondent should be addressed.

## INTRODUCTION

Recently, functional characteristics of LC have been studied in many fields because of their unique orientational behaviors and hydrodynamic properties. The composite system of which LC phase is embedded in a three-dimensional polymer matrix can be self-supported LC (SSLC) film [1-10] in spite of the very low viscous character of LC. Therefore, functional characteristics of LC can be developed as a flexible SSLC film with ultrathin and large area. The SSLC film exhibits excellent characteristics of electro-optical effect based on the light scattering due to optical heterogeneity between the components and/or spatial distortion of nematic directors. Since the composite film has excellent characteristics of the electrically light switching between turbid and transparent states, the composite films have been expected as a large area, flexible electro-optical devices.

There have been current interests in the development of the laser recording system by using several light absorbents. Among possible recording materials, chalcogenide thin films [11-13] have been attracted a great deal of attention, but instability against humidity-induced oxidative degradation should have been concerned. Recently, organic-based systems [14-19] have been considered due to advantages in writing energy, fabrication cost, and stability. Among the organic-based systems, dyes [14-16], dye-loaded polymers [17-18] and metal-loaded polymers have been used as the promising materials.

Since, in the case of the (polymer/LC) composite system with an upper critical solution temperature (UCST) behavior, the polymer and LC are miscible above the critical temperature, the light scattering properties being induced from the optically heterogeneous aggregation state must be controllable upon heat treatment. Thus, the SSLC films are expected to be applicable as the heat-mode laser recording media.

In this study, thermo-optical effects of the (polymer/LC) composite films were initially investigated and then, its application as a novel type of the heat-mode recording system was discussed.

## EXPERIMENTAL SECTION

Figure 1 shows the chemical structure and physical properties of the matrix polymer, poly(methyl methacrylate) (PMMA) and nematic mixture GR-63, Chisso Co.). PMMA was used due to an optical isotropic state and an excellent

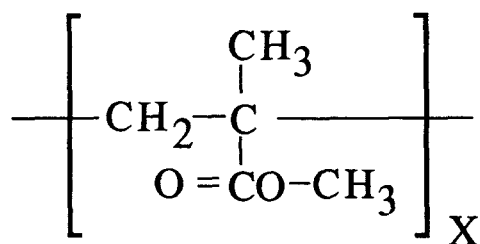
transparent characteristics. Its glass transition temperature,  $T_g$  is 375 K and its refractive index, 1.492 for the 589 nm at 293 K. The nematic-isotropic phase transition temperature of GR-63 was 337 K and its ordinary refractive index,  $n_o$  and extraordinary index,  $n_e$  is 1.552 and 1.774 for the conditions of 589 nm at 293 K, respectively.

The (PMMA/GR-63) composite films were prepared on a PET film by using a bar coating method at room temperature. Chloroform was used as a solvent and the concentration was 20 wt%. The weight fraction of GR-63 was changed from 0 to 0.7 at 0.1 intervals. In the case that the weight fraction of GR-63 was above 0.7, GR-63 could not be self supported in the composite film because of its high fluidity. The thickness of the composite film was 18  $\mu\text{m}$ . In order to avoid moisture upon the heat treatment in a water bath, the composite films were sandwiched between two PET films. Figure 2 shows the flow chart of the heat treatment. The composite films were initially heated for 10 sec in a water bath of 323-369 K. Then, all the samples were cooled for 60 sec in an ice water bath and taken out to an ambient air.

For the purpose of the heat-mode laser recording, the organic dye of azo derivative (M-615, Mitsui Touatsu Chem. INC.) which exhibits a strong absorption at the wavelength of the recording laser beam was dissolved into the composite films. A point of the ternary composite film was irradiated by the second harmonics of a pulse Nd-YAG laser beam (Continuum NY60-50), the wavelength of 532 nm, through a photo mask.

## 1. Polymer

## 2. Liquid Crystal



commercially available GR-63  
(nematic mixture with positive  
dielectric anisotropy)

PMMA : Poly(methyl methacrylate)

$$n=1.492 \quad T_g = 355 \text{ K}$$

$$M_n = 1.8 \sim 2.0 \times 10^5$$

$$T_{NI} = 336.5 \text{ K}$$

$$n_{//} = 1.744$$

$$n_{\perp} = 1.522$$

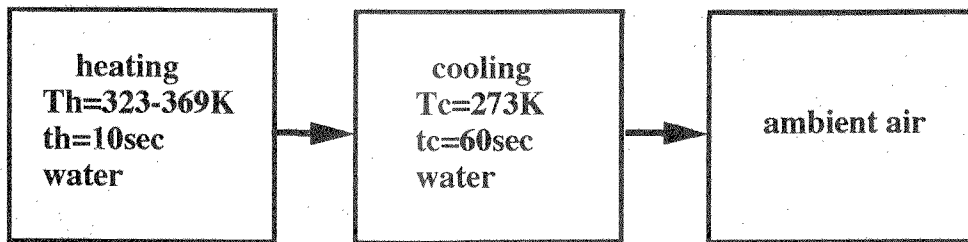
$$\Delta n = 0.222$$

Figure 1. Chemical structure and physical properties of the matrix polymer, poly (methyl methacrylate) (PMMA) and nematic liquid crystal mixture (GR-63)

The aggregation structure of the composite film was investigated by using a scanning microscopic(SEM, Hitachi S-430). For SEM observation, the composite film was fractured in liquid nitrogen after extraction of GR-63 with normal hexan at 300 K for 2 hours. The film and fractured surfaces were coated with gold.

To evaluate the light scattering properties, the transmittance was measured by using a He-Ne laser(wavelength, 632.8 nm) of which an incident light intensity through the composite film was detected with ohotodiode. The distance between the sample and the photodiode was 305 mm.

### heat treatment



Where  $T_h$  is the heating temperature,  $T_c$  is the cooling temperature,  $t_h$  is the heating time,  $t_c$  is the cooling time.

Figure 2. Flow chart of the heat treatment.

## RESULT AND DISCUSSION

### 3.1 Thermo-optical properties of the (PMMA/GR-63) composite films

The (PMMA/GR-63) composite films exhibit the strong light scattering and excellent electro-optical properties at room temperature. The thermo-optical properties of the composite films being induced by the heat treatment in a water bath were investigated. The heating temperature was controlled in a temperature range of 323-369 K and the cooling temperature was fixed at 273 K.

Figure 3 shows the heating temperature dependence of transmittance for the (PMMA/GR-63) composite films with the GR-63 weight fraction of 0.4-0.6. At around room temperature, the composite film was turbid due to its strong light scattering being caused by optical heterogeneity. However, the transmittance was abruptly enhanced above the neighborhood of the nematic-isotropic phase transition temperature,  $T_{NI}$  of GR-63. The contrast between an initial turbid state and a heat-treated transparent state is in a desired level as the thermal-recording system.

Figure 4 shows the SEM photographs for the (PMMA/GR-63) composite films with the GR-63 weight fraction of 0.6, (a) the as-cast sample from a chloroform solution and the heat-treated samples at (b) 333K, (c) 343K and (d) 369K. In the case of the as-cast sample and the heat-treated one below  $T_{NI}$ , the matrix polymer formed a three dimensional spongy matrix and the LC did a continuous phase in the polymer matrix. Upon heat treatment above  $T_{NI}$ , the LC formed the dispersed spherical droplets in the polymer matrix, and the higher temperature made the size of LC droplets smaller. Therefore, it is apparent that the miscible

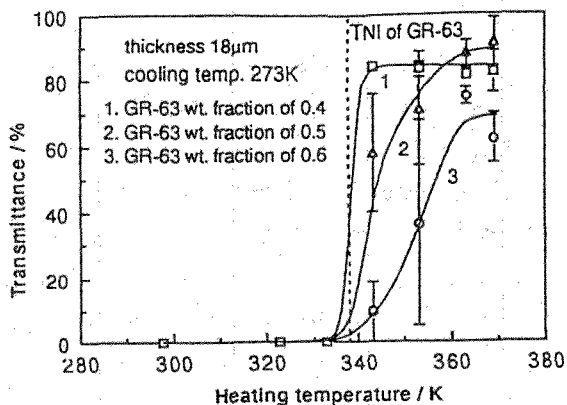


Figure 3. Heating temperature dependence of transmittance for (PMMA/GR-63) composite films.

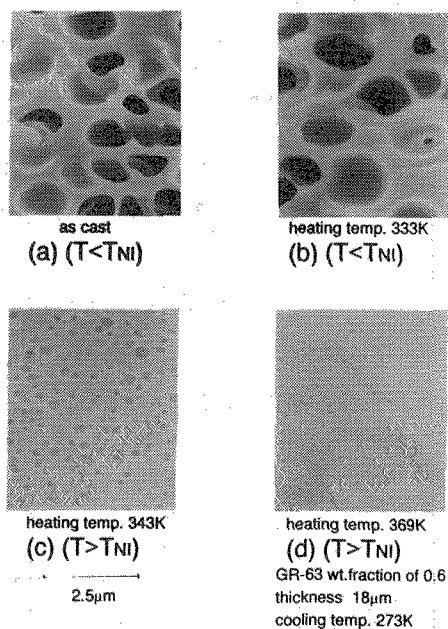


Figure 4. SEM photographs for the (PMMA/GR-63) composite films with GR-63 weight fraction of 0.6, (a) the as-cast sample from a chloroform solution and the heat treated samples at (b) 333K, (c) 343K and (d) 369K.

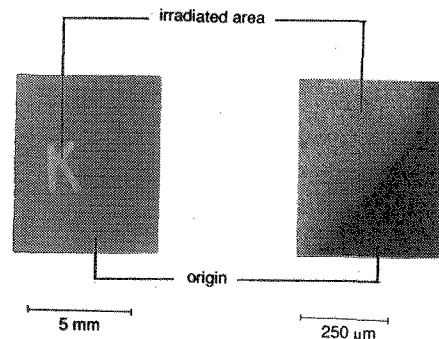
aggregation between PMMA and GR-63 on an optically phase-separated level is induced by the heat treatment above  $T_{NI}$  of GR-63. Since, in the course of cooling process, the partially compatible aggregation structure was quenched, the size of LC droplets became smaller than the wavelength of a measuring laser beam for transmitted light intensity. Thus, the optical heterogeneity was diminished, resulting in a remarkable increase in the transmittance. The result mentioned above indicates that the composite film can be a candidate for a novel type of thermal-recording system.

### 3.2 A heat-mode laser recording of the (PMMA/GR-63) composite films

For the purpose of the heat-mode laser recording on the basis of the transient heat effect being induced by a laser beam, an organic dye of azo derivative (M-618), which exhibits a strong absorption at the wavelength in the vicinity of 530 nm, was introduced into the (PMMA/GR-63) composite film, because the composite film itself can not absorb much energy. The organic dye was miscible in the composite film and exhibited thermal stability. A point of the ternary composite film was irradiated by the second harmonics of a Nd-YAG laser through a photo mask. A peak power of laser beam was 60 mJ.

Figure 5 shows the optical image of the heat-mode laser recording by using the (PMMA/GR-63/M-618=50/50/0 wt%) ternary composite film. Since the laser energy absorbed in the composite film was easily converted into heat, the sample temperature rose over  $T_{NI}$  and then, a laser irradiated part through a photo mask (K letter) was selectively changed to a transparent state.

The transparent state exhibited a long-term stability, at least for several years in a noncontrolled atmosphere. As the edge of laser irradiated part was sufficiently sharp, the heat-mode recording with a fairly high resolution is expected for this composite system. A heat-mode laser recording has been accompanied for the (PMMA /GR-63/M618) composite film for the first time.



sample  
PMMA/GR-63/M-618 = 50/50/1  
thickness 18 $\mu$ m  
recording laser beam  
pulse YAG laser (CONTINUUM NY60-50)  
wavelength 532nm  
single shot (recording power 60mJ) 10 times

Figure 5. Optical image of the heat-mode laser recording by using the (PMMA/GR-63/M-618) (50/50/1 w/w/w) ternary composite film.

## CONCLUSION

The thermo-optical properties of the (PMMA/GR-63) composite films were investigated over the heat treatment in a water bath. The composite film was changed from an initial turbid state to a transparent state upon heat treatment over  $T_{NI}$ . When the composite film was heated above  $T_{NI}$ , a bicontinuous phase composed of polymer and LC gradually transferred to a polymer-dispersed states. Therefore, the dispersed spherical LC droplets were formed in the polymer matrix and the size of LC droplets became smaller than the wavelength of visible light, resulting in an excellent transparent states. This indicates that the composite film can be a candidate for a novel type of thermal recording system.

In order to enhance the absorption of laser energy and construct the excellent heat-mode recording, an organic dye was introduced into the composite film. Heat-mode recording with high resolution was realized with Nd-YAG laser for the (PMMA/GR-63/M-618) composite film for the first time.

## REFERENCES

1. T. Kajiyama, Y. Nagata, E. Maemura and M. Takayanagi, Chem. Lett., **1979**, 679(1979).
2. T. Kajiyama, Y. Nagata, S. Washizu and M. Takayanagi, Chem. Lett., **1979**, 679(1979).
3. T. Kajiyama, S. Washizu and M. Takayanagi, J. Appl. Polym. Sci., **29**, 3955(1984).
4. T. Kajiyama, H. Kikuchi and S. Shinkai, J. Membrane Sci., **36**, 243(1988).
5. T. Kajiyama, H. Kikuchi, I. Terada, M. Katayose, A. Takahara and S. Shinkai, Current Topics in Polymer Science, **2**, 320(1987).
6. T. Kajiyama, J. Macromol. Sci.-Chem. **A25**, 583(1988).
7. T. Kajiyama, A. Takahara and H. Kikuchi, Polym. J., **23**, 347(1991).
8. T. Kajiyama, A. Miyamoto, H. Kikuchi and T. Kajiyama, New Polym. Mater., **2**, 27(1990).
10. T. Kajiyama, H. Kikuchi and A. Takahara, Proc. SPIE, **1665**, 20(1992).
11. D. Maydan, Bell Syst. Tech., **J. 50**, 1761(1979).
12. A. E. Bell and R. A. Bartolini, Appl. Phys. Lett., **34**, 275(1979).
13. M. Terao, K. Shigematsu, M. Ojima, T. Taniguchi, S. Horigome and S. Yonezawa, J. Appl. Phys., **50**, 6881(1979).

14. V. Novotny and L. Alexandra, J. Appl. Polm. Sci., **24**, 3212(1979).
15. A. E. Bell and F. W. Spong, IEEE J. Quantum Electron, **14**, 487(1978).
16. V. B. Jipson and C. R. Jones, J. Vac. Sci. Technol., **18**, 92(1981).
17. K. Y. Law et al, Appl. Phys. Lett., **36**, 884(1980).
18. D. G. Howe and J. J. Wrobel, J. Vac. Sci. Technol., **18**, 92(1981).
19. J. Drexler, J. Vac. Sci. Technol., **18**, 87(1981).