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Aggregation States and Electro-optical Properties Based on Light Scattering of Polymer/(Liquid Crystal) Composite Films

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Electro-optical properties based on light scattering controlled by a.c. electric field were investigated for polymer/(liquid crystal) composite films. Scanning electron microscopic observation for the matrix polymer after extraction of LC with methanol exhibited that LC molecules were continuously embedded in a three-dimensional spongy network of polymer matrix. Such a membrane system with many optical interfaces plays an important role on light scattering without an imposed electric field. A high contrast of light-switching was observed; 3% transmittance of the as-cast composite film changed to 81% with the response time of 0.3 ms in the case of an applied 250 Vp-p a.c. electric field of 10 kHz at 333 K.

Liquid crystalline (LC) materials for a display are utilized in a cell sandwiched between conducting glass plates because of a low viscous fluid nature. However, the geometrical shape of the device is fairly restricted in fabricating such a glass cell. Polymer/LC composite film, in which a continuous LC phase is embedded in a three dimensional network of polymer matrix, is a stable self-supported LC film in spite of its very low viscous character. Therefore, functional characteristics of LC can be developed as a self-supported flexible LC film with ultrathin and large area. The self-supported LC films were investigated as unique and novel permselective membranes for molecular filtration, oxygen enrichment, photoresponsible active and facilitated transport of metal cation and so on.$^{1-6)}$ The self-supported LC film can be expected to be useful as a very large area light-controllable film (light valve) or information display. In this study, the aggregation states and electro-optical properties of the polymer/LC composite films based on light scattering were investigated.

For electro-optic studies, several kinds of polymer/LC composite films were cast from appropriate solutions on a glass plate. A weight ratio of polymer/LC

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was 40/60 and the thickness of film was about 50 μm. Poly(methyl methacrylate) (PMMA), polystyrene(PSt), polycarbonate(PC), poly(vinyl chloride)(PVC) and several rubbers were used as matrix polymer components due to their optically isotropic and transparent characteristics. Cyanobiphenyl derivatives or these mixture in a nematic state were used as LC components. The aggregation states of the composite film were investigated by scanning electron microscopic (SEM) observation. In order to evaluate the electro-optical effect, the composite film was sandwiched between two ITO coated glass plates. A change of transmission light through the cell without any polarizers upon an imposed electric field (He-Ne laser, wave length of 632.8 nm) was measured by using a photodiode and recorded with a digital storage oscilloscope. A distance between the cell and the photodiode was 305 mm.

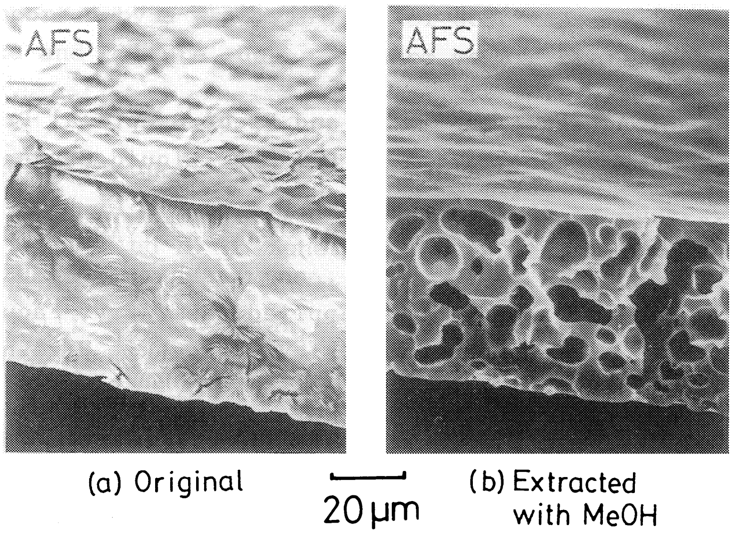


Fig. 1. Scanning electron microscopic photographs for the PMMA/E-44(40/60) composite film (a)as-cast from a chloroform solution, and (b)after extraction of E-44 with methanol at 300 K. The lower part is a fracture surface.

In a temperature range of an LC state, the polymer/LC composite film is milky and turbid in the case without an applied electric field because of its strong light scattering. Figure 1 shows the SEM photographs of the PMMA/E-44⁷⁾(nematic mixture) (=40/60) composite film before (a) and after (b) extracting E-44 with methanol at 300 K. From the results reported previously,²⁾ it is apparent that the matrix polymer formed a three-dimensional spongy network and the LC of E-44 formed a continuous phase in the polymer matrix. A degree of scattering, therefore, might be greatly dependent on the aggregation states of the composite film such as many optical interfaces. In addition, exuding of LC from the film surface could be prevented owing to formation of surface skin layer as clearly shown on an air facing surface (AFS) in Figure 1. A choice of polymer material and LC was an important factor to form the aggregation states of the composite film described above, in particular, the combination of PMMA and E-44 was one of the most suitable composite systems for electro-optical characteristics based on light scattering.

The electro-optical effect of the composite film based on light scattering was investigated under various conditions on the magnitude and the frequency of a.c. electric field. On- and off- electric fields make the composite film transparent and turbid reversibly. And also, the transmittance through the composite film could be continuously controlled by a strength of a.c. field. Figure 2 shows the applied voltage dependence of transmittance and the conventional rise time τ, as a function of measuring temperature. The magnitude of τ was defined as a time period to change from 10% to 90% of transmission light intensity. Remarkably rapid response of about 0.3 ms for light scattering of the composite film could be attained under the conditions of an imposed 10 kHz a.c. field of a few hundreds volt (Vp-p) at 333 K. A decay time which was defined as a time period to decay to 10% of transmission light intensity was typically within a few ms at 303 K. Further, the decay time increased with an increase in temperature, for example, it was about 50 ms at 333 K. On the other hand, the degree of transmittance remarkably increased with an increase in temperature in a lower voltage range (25 - 100 Vp-p). This indicates a considerable decrease in the magnitude of elasticity of LC and/or the strength of anchoring to orient LC molecules on the polymer surface over a temperature range here. Figure 3 shows the frequency dependence of the rise time τ and transmittance for the PMMA/E-44=40/60 composite film under the conditions of an applied 200 Vp-p a.c. electric field at 303 K. The rise time decreased and the degree of transmittance increased with an increase in frequency. In the case of measurements with low frequencies, a periodic flicker of transmittance was observed overlapping on an asymptotic increase of transmittance with an elapse of time. We also noticed that the weight ratio of polymer/LC=40/60 is optimum for the light control film from the point of view of both the light-intensity contrast and mechanical durability. Figure 4 shows the reversible turbid and transparent changes corresponding to off- (a) and on- (b) a.c. electric field, respectively, by using the composite film (PMMA/E-44=40/60) prepared by a bar-coating method. Since remarkable light intensity control of the polymer/LC composite film was observed, the self-supported LC film can be a candidate for a large area light valve or display device.

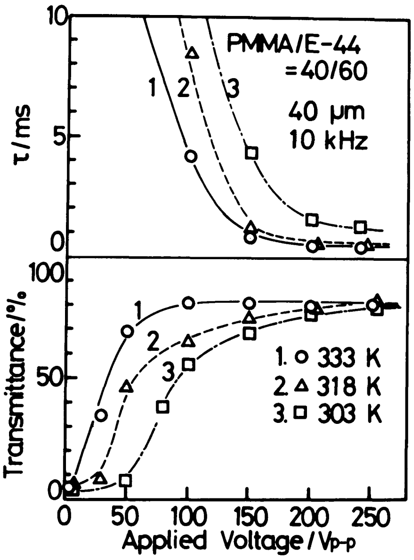


Fig. 2. Applied voltage dependence of transmittance and rise time τ at 10 kHz as a function of measuring temperature for the composite film.

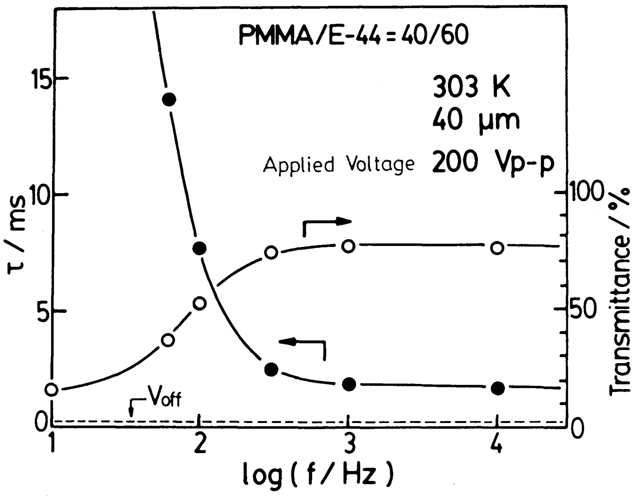
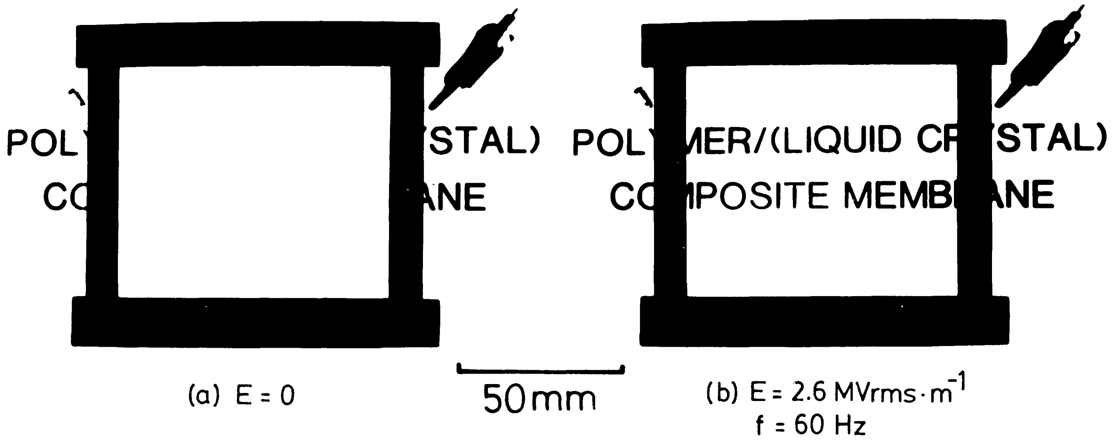


Fig. 3. Frequency dependence of transmittance and rise time τ under the conditions of 200 Vp-p and 303 K for the composite film.

With respect to light



(a) E = 0

(b) E = 2.6 MVrms·m^{-1}
f = 60 Hz

Fig. 4. Reversible turbid and transparent changes of the composite film upon off- (a) and on- (b) 60 Hz a.c. electric field with 130 Vrms. The thickness of the composite film was 50 μm.

scattering phenomena of the polymer/LC composite film, three origins may be proposed in the case of absence of an electric field; 1) a spatial distortion of nematic directors compulsorily induced by non-parallel matrix walls, 2) a discontinuous change of nematic directors among neighboring LC domains separated by thin polymer walls, and 3) an optical boundary between LC phase and matrix polymer. When an a.c. electric field is applied to the composite film, the directors reorient parallel to the direction of an applied field and then, the composite film becomes transparent owing to the following three possible reasons; 1) the spatial distortion of nematic directors in an LC domain vanishes, 2) the directors of LC domains separated by thin polymer walls align along the same direction, and 3) the refractive index of an LC phase is sufficiently close to that of a polymer matrix and then, their optical boundaries disappear. The possible mechanisms for reversible turbid and transparent changes of the composite film are still under investigation.

In conclusion, the polymer/LC composite film can be a novel and large area electro-optical material because of its controllable light intensity properties depending on the conditions of an applied a.c. electric field.

References

1)T.Kajiyama, Y.Nagata, E.Maemura, and M.Takayanagi, Chem. Lett., 1979, 679(1979).

2)T.Kajiyama, S.Washizu, and M.Takayanagi, J. Appl. Polym. Sci.,29, 3955(1984).

3)S.Washizu, I.Terada, T.Kajiyama, and M.Takayanagi, Polym. J.,16, 307(1984).

4)H.Kikuchi, M.Katayose, A.Takahara, S.Shinkai, and T.Kajiyama, Koubunshi Ronbunshu,43, 669(1986).

5)H.Kikuchi, M.Katayose, S.Shinkai, O.Manabe, and T.Kajiyama, Nippon Kagaku Kaishi, 1987, 423.

6)T.Kajiyama, H.Kikuchi, and S.Shinkai, J. Membr. Sci., 36, 243(1988).

7)purchased by BDH Ltd.(T_{KN}=267 K, T_{NI}=373 K, Δn=0.262).

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