

ANGULAR DEPENDENCE OF THE LIGHT SCATTERING OF
(POLYMER/LIQUID CRYSTAL) COMPOSITE FILMS

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ABSTRACT

A (polymer/Liquid-Crystal:LC) composite film exhibits reversible light scattering-light transmission switching upon electric field -OFF and -ON states, respectively. The incident angular dependence of the light scattering and the view angle for the (polymer/LC) composite films were investigated. Several polymers with different refractive indices and their blend polymer were used as a matrix polymer. The refractive index of the matrix polymer(n_p) was selected to match the ordinary refractive index(n_o) of nematic LC for an excellent transparent state of the composite film upon an electric field -ON state. The refractive index of a matrix polymer could be controlled by blending the other polymer which shows the optical miscibility to the matrix polymer. The light scattering properties of the (polymerA/polymerB/LC) ternary composite film depended on the ratio of polymerA/polymerB. The maximum transmission peak appeared at a normal incidence for the composite system with $n_p < n_o$. On the other hand, the maximum transmission peak moved at a certain angle away from normal incidence for the case of the composite system with $n_p > n_o$.

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INTRODUCTION

New types of LC displays which have LC channels[1] or domains[2,3] in a matrix polymer has been studied for possible application as a large-area and flexible display devices and light valve. A (polymer/LC) composite film which has continuous LC channels in a three dimensional spongy polymer network was developed first by Kajiyama et al. in 1979[4]. This composite film was named for "Self-supported Liquid Crystal Composite Film (SSLCF)" according to the aggregation structure of it. The matrix polymer in the biphasic composite film supports LC molecules in a continuous polymer channels and protects them from environment. This SSLCF composite film can be prepared by the water-casting[5] or doctor blade-casting method[1]. The first application for the electro-optical devices using the mismatch in the refractive indices of polymer matrix and nematic LC was attempted by Craighead and co-workers in 1982[6]. After that, many scientists published papers about electro-optical properties of the (polymer/LC) composite film using the mismatch in the refractive indices of polymer and LC[2,3].

We have reported the electro-optical properties and aggregation structure of the SSLCF composite film which exhibits reversible light scattering-light transmission switching upon electric field -OFF and -ON states, respectively[1]. The light scattering of the composite film upon electric field -OFF state is basically caused by the mismatch in the refractive indices of the polymer and LC and also, spatial distortion of nematic directors[5]. Since the spatial distortion of nematic directors in the composite film disappears upon an electric field -ON state, the degree of the light scattering of the composite film depends on the mismatch in the refractive indices of the polymer and LC. The advantages of the composite film for the display compared with the twisted nematic LC system[7] are (1) large-area and flexible display, such as potentially square several meters in size, or light valve (2) simple fabrication process of a large-area composite film and (3) its high contrast and wide view angle because it can be used without the polarizers. Pleochroic dyes (Guest-Host effect[8]) can be used for the composite film to give controllable light adsorption in addition to the light scattering upon an electric field -OFF state.

The research about the light scattering of the composite film provides us very useful knowledge about both polymer and LC. Analyzing the light scattering of the composite film requires various considerations for various parameters such as the birefringence of LC, the relative differences between

relationship of n_o and n_p , the shape or size of LC channels, thickness of the composite film and the miscibility between matrix polymer and LC and so on. The sizes of LC channels can be controlled by controlling the solvent evaporation velocity during the casting of the composite film[9].

The study on the incident angular dependence of the light scattering for the (polymer/LC) composite films is useful for the designing a broad viewing angular display and increasing a contrast ratio. The light transmission and the view angle of the composite film upon an electric field -ON state are strongly dependent on the mismatch of n_o and/or extraordinary refractive index(n_e) of LC and n_p . When the n_o is matched with n_p , the transmission intensity must be maximum at the normal incidence. It can be expected to control the refractive indices of the matrix polymer by blending the other polymer. The blend polymer should show optically miscibility to be used as a matrix polymer for the composite film. Therefore, it should be interested to investigate electro-optic response characteristics and light scattering properties for the (blend polymer/LC) composite system.

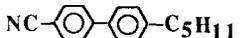
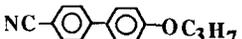
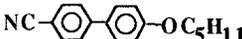
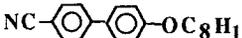
In this paper, the angular dependence of the light scattering properties of the binary composite films and the (polymerA/polymerB/LC) ternary composite films has been investigated.

EXPERIMENTAL SECTION

Fig.1 shows the chemical structures of the matrix polymer and LC materials for the composite films. All of the used matrix polymers showed very good transparency. The composite films were cast from a chloroform solution of a mixture of polymer and LC by drawing a doctor blade on the electrode surface (ITO glass). The weight ratio of (polymer/LC) was 40/60(w/w%) and the thickness of the composite films ranged 8-15mm. In order to evaluate the degree of light scattering and light transmission, the composite films were sandwiched between two ITO-coated glasses. The aggregation state of the composite film was investigated by scanning electron microscopic(SEM, Hitachi s-430) observation. The composite film was fractured in liquid nitrogen before the extraction of LC with n-hexane at room temperature for the SEM observation. The light scattering properties of the composite film was measured using the measuring system shown in Fig.2. The polarizations V and H are

perpendicular and parallel to the plane of incidence, respectively. The polarized direction of V is parallel to the axis of sample rotation. The composite sample could be rotated around the rotation axis with the incident angle, θ_i . The ϕ is the angle between light and photodiode. He-Ne laser (wavelength:632.8 nm) was used as a light source. The sample can be heated from room temperature to 473K. We measured the thermal properties, such as the glass temperature, T_g and the nematic-isotropic phase transition temperature, T_{NI} , were measured on the basis of the differential scanning calorimetry (DSC) analysis. A phasemicroscope was used to determine the miscibility of the components in the (polymer /E8) ternary composite film.

Liquid crystal: E8(Nematic mixture)

| Code | Chemical structure | Wt.(%) |
|------|---|--------|
| K-15 | NC-  -C ₅ H ₁₁ | 45% |
| M-9 | NC-  -OC ₃ H ₇ | 16% |
| M-15 | NC-  -OC ₅ H ₁₁ | 12% |
| M-24 | NC-  -OC ₈ H ₁₇ | 16% |
| T-15 | NC-  -C ₅ H ₁₁ | 11% |

$$T_{KN} = 261K \quad T_{NI} = 345K$$

$$n_{11} = 1.774 \quad n_e = 1.527$$

Polymer

1. Poly(diisopropyl fumarate) (Pdi-ipF) : $n=1.464$
2. Poly(methyl methacrylate) (PMMA) : $n=1.492$
3. Poly(diisopropyl fumarate-co-styrene) (PFU-co-ST) : 1.517
4. Poly(carbonate)(PC) : $n=1.586$
5. Poly(styrene)(PS) : $n=1.597$

Fig.1 Constituents for the composite film

RESULTS AND DISCUSSION

The view angle of the LC display is one of the most important key elements for the display technology. The fatal defects of the twisted nematic display system are the narrow view angle and the low contrast. The measuring system shown in Fig. 2 was used to measure the angular dependence of the transmittance of the composite films. Fig.3 shows the angular dependence of the relative transmittance of the H and V polarizations for the composite films upon an electric field -ON state. The maximum transmission peak of the V polarization appeared at the normal incidence, $\theta_i=0$ for any cases of the composite films. The maximum transmission peak of the H polarization appeared at the normal incidence, for the PMMA, Pdi-ipF, and PFU-co-ST composite systems with the condition of $n_o > n_p$. On the other hand, the

maximum peak of the H polarization moved at an angle away from the normal incidence in the case of the PC and PS composite systems with the condition of $n_o < n_p$. To understand the angular dependence of relative transmittance, the Fresnel reflection coefficients[10] and the angular dependence of the refractive index of the LC were taken into consideration.

Figs.4 and 5(a) shows the incident angular(θ_i) dependence of the effective refractive indices of the H and V polarizations for the aligned nematic liquid crystal. Also, Fig.5(b) shows the incident angular dependence of the

effective refractive indices(n_p) for matrix polymer and $n_H(\theta)$ of E8 in the case of an electric field -ON state. The magnitudes of the $n_V(\theta)$ and n_p are constant for the change of the incident angle of the V-polarized light in the case of an electric field -ON state. On the other hand, the effective refractive index of aligned LC for the H polarization, $n_H(\theta)$ is dependent on the incident angle of the H-polarized light. Therefore, in the case of $n_o < n_p < n_e$, $n_H(\theta)$ for E8 becomes the same magnitude as high as n_p at a certain incident angle.

The incident angle at the maximum H-transmittance peak can be calculated on the basis of the Fresnel coefficient and the angular dependence of refractive index of E8 as shown in Figures 5(a) and (b). Therefore, it is interesting to evaluate the incident angle at the maximum H-transmittance peak for the case of the composite system with the case of the $n_o < n_p < n_e$, because it appears at an angle away from the normal incidence, as shown in Fig.3. The incident angle at which n_p is equal to $n_H(\theta)$ as shown in Fig.5 is 62° and 66° for the PC and PS composite films, respectively. The incident angle of the maximum H-transmission peak should appear above the incident angle of 60° , when it is

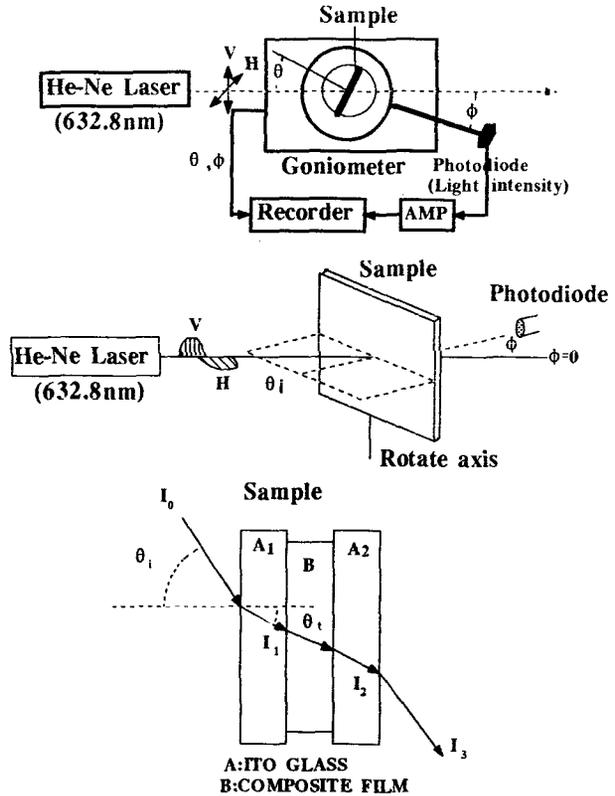


Fig.2 Experimental arrangement for light scattering measurement for the composite films

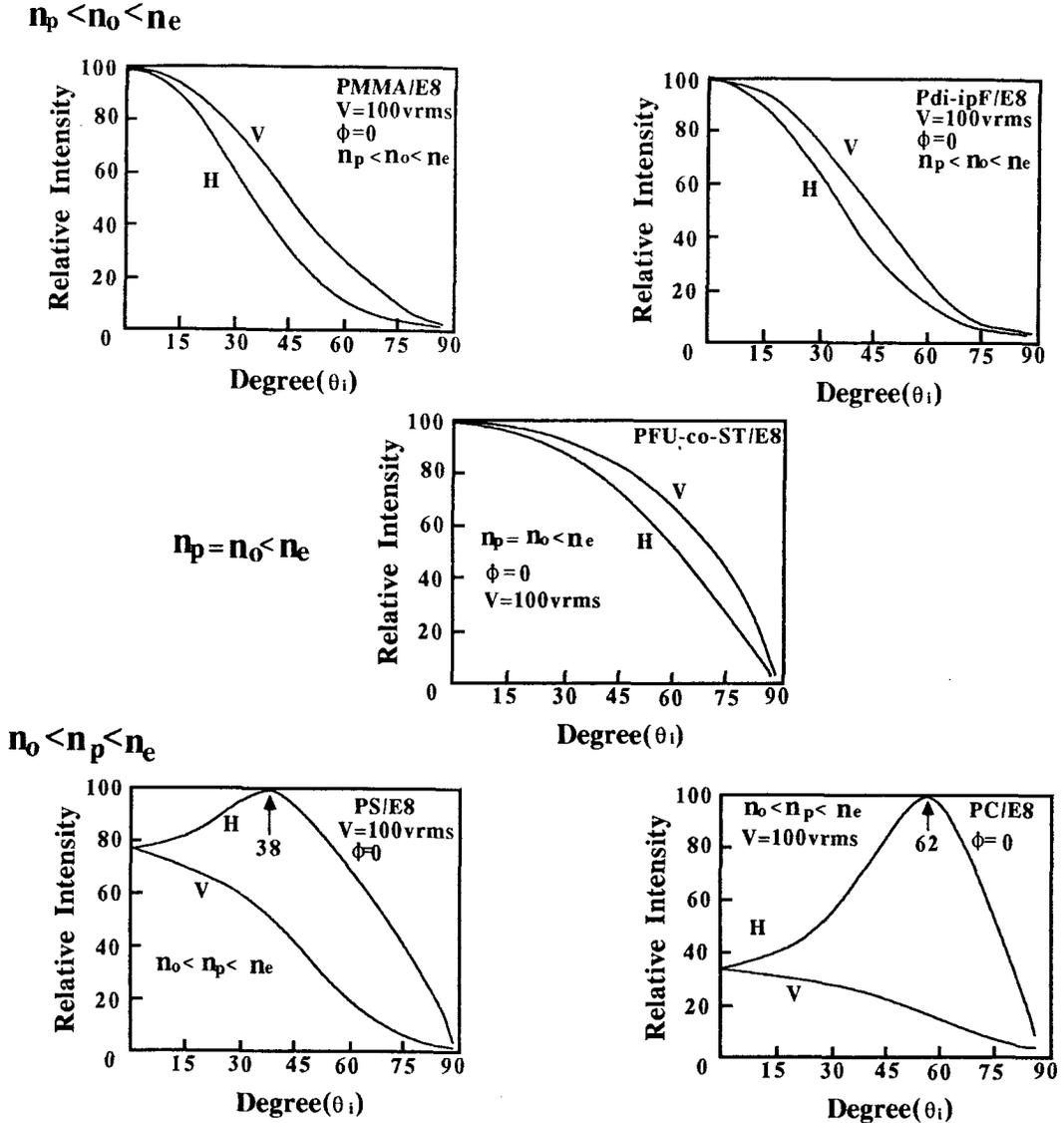
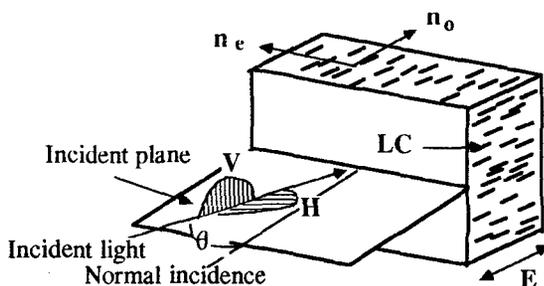


Fig.3 Angular dependence of the transmittance of H and V for composite film

calculated on the basis of the Franel coefficient and $n_H(\theta)$ of E8, for the PC and PS. However, the incident angle at the maximum H-transmission peak were experimentally observed at 38° and 60° for the PS and PC composite systems, respectively. Also, since the refractive index of PS is higher than that of PC as shown in Fig.5(b), the incident angle at the maximum H-transmission peak for the PS composite system should appear at the higher incident angle than that of the PC composite system. The difference between calculated results and the experimental data may be explained by the following aggregation states of the components in the composite film. Partial

dissolution of LC molecules in the polymer matrix at the interface makes an apparent magnitude of n_p decreased, because $n_H(\theta)$ of E8 is lower than lower than n_p in the lower θ range. This indicates that the maximum H-transmission peak should appear in alower range than the incident angle at $n_H(\theta)=n_p$.

The eutectic nematic mixture E8 is composed of about five kinds of cyanophenyl LCs in Fig.1. Fig.6 shows the DSC diagrams for E8, PMMA, PC, PS, and the composite films. The glass temperature, T_g of PMMA, PC and PS and isotropic temperature, TNI of E8 were changed in the composite films in comparison with those of the individual materials. T_g of the matrix polymer PMMA, PC and PS exists lower temperature than the TNI of E8 in the composite films. TNI of E8 in the (PMMA/E8) and (PC/E8) composite films decreased about 10K in comparison with that of E8 itself. These mean that the matrix polymer PMMA and PC, PS and E8 shows miscibility and and the E8 takes a role as a additive for the PC and PS. From these results mentioned above, it is aparent that the



$$n_v(\theta) = n_o \text{ (for V)}$$

$$n_H(\theta) = \frac{n_e n_o}{(n_o^2 \sin^2 \theta + n_e^2 \cos^2 \theta)^{1/2}} \text{ (for H)}$$

Fig. 4 Effective refractive indices for incident light upon an electric field -ON state

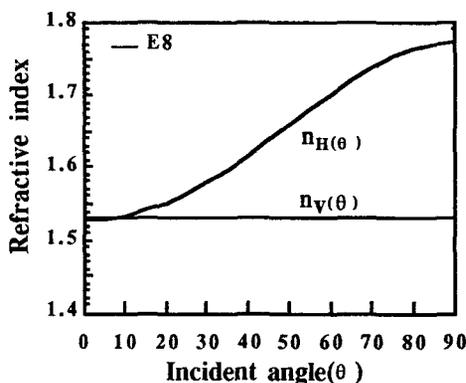


Fig. 5(a) Effective refractive indices of E8 and for H

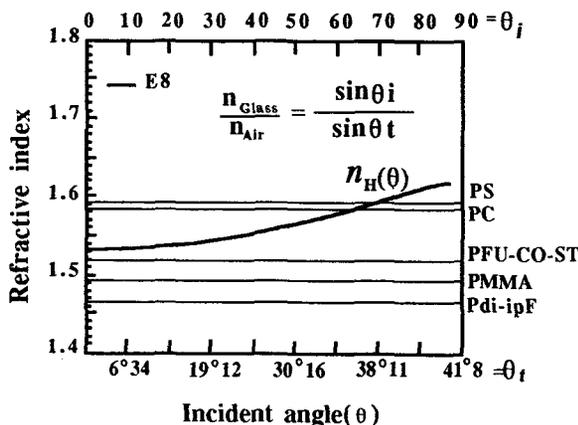


Fig. 5(b) Effective refractive indices of E8 in composite films for H

refractive index of the matrix polymer must be changed by dissolution of LC molecules into the matrix polymer. Even though the effect will not be so much, it is considerable that some component LCs do not infiltrate into the matrix polymer or the amount of the component LC molecules infiltrate into the matrix polymer is not equal. This can be a reason of the change of refractive index of the LC. The no of the E8 will be changed with the increase of amount of dissolved polymer PC and PS in the composite films.

Fig.7 shows the angular dependence of the of H- and V-transmittance for the (PMMA / PC/E8), and (PMMA/PS/E8), (20/20/60wt/wt%) composite films. In the case of the (PMMA/PC/E8) ternary composite film, the H and V- transmitted light intensity increase or decrease smoothly by the relationship of the refractive indices between LC

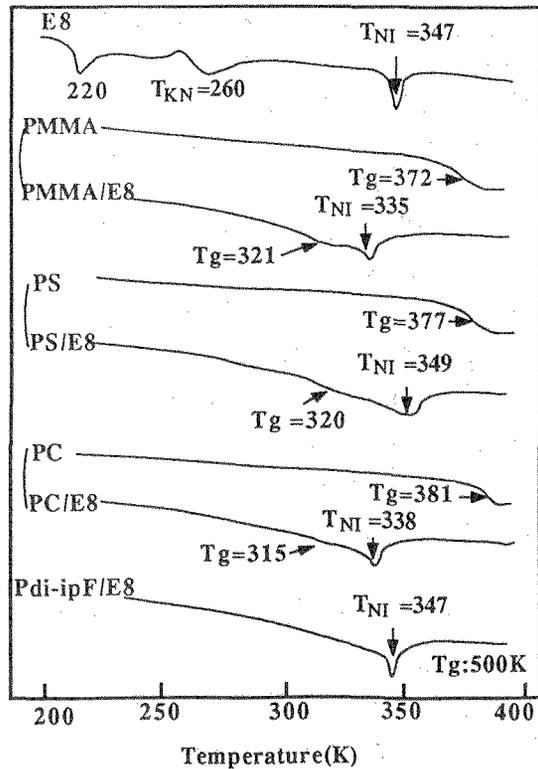


Fig. 6 DSC thermograms for the E8, matrix polymers and their composite films

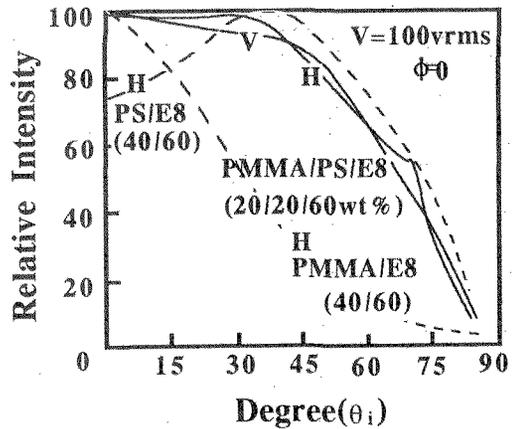
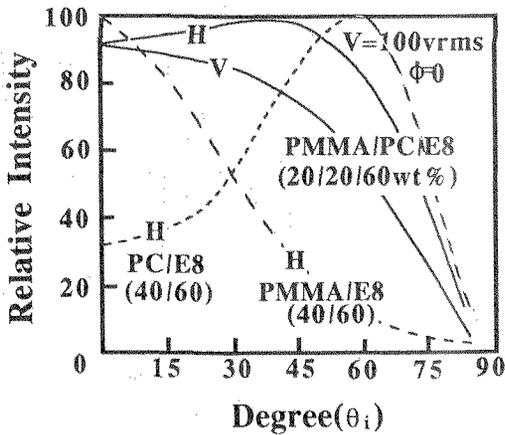


Fig.7 Angular dependence of the transmittance of (PMMA/ PC/E8) and (PMMA/PS/ E8) ternary composite films

and n_p with the change of incident angle, and the maximum H-transmission peak appeared at the incident angle of 32° . This indicates that the refractive index of the PMMA/PC blend matrix polymer is higher than that of no of E8, and is lower than that of PC in the (PC/E8) composite film. On the other hand, the H- and V-transmitted light intensity increase or decrease abruptly according to the change of incident angle for the (PMMA/PS/E8) ternary composite film. The difference of the angular dependence of the transmittance intensity for these two ternary composite systems may be explained on the basis of morphological observations as shown in Fig.8. Fig.8 shows the phase microscopic observation for the (PMMA /PC/E8) and (PMMA/PS/E8) ternary composite systems. Figure 8 shows that the PMMA/PC blend polymer is in the optical miscibility state and on the other hand, PMMA/PS blend polymer is in the phase separated state in the composite films. The angular dependence of the transmittance PMMA/PS/E8 ternary composite films changes whether the incident light proceeds in PMMA/E8 composite parts, PS/E8 composite parts or both of them.

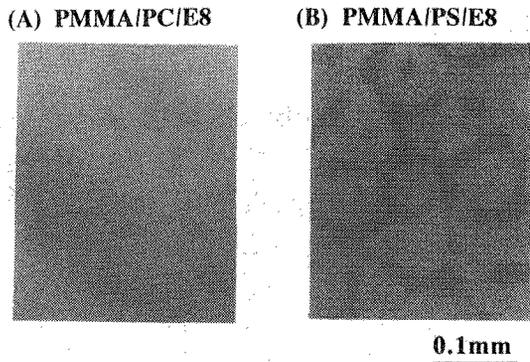


Fig. 8 Phase microscopic photographs for the (PMMA/PC/E8) and (PMMA/PS/E8) ternary composite films

Fig.9 shows the angular dependence of the of H-and V-transmittance for

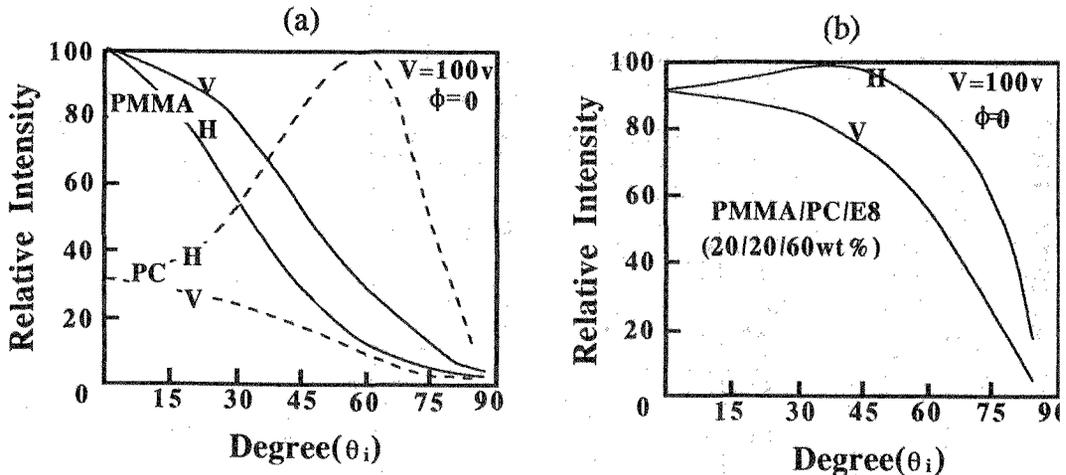


Fig.9 Angular dependence of the transmission of H and H for (PMMA/E8), (PC/E8) and (PMMA/PC/E8) composite films

the (PMMA/E8), (PC/E8) binary composite films and the (PMMA/PC/E8) ternary composite films. The angular dependence of the H- and V-transmittance intensity for the (PMMA/PC/E8) ternary composite film can be controlled freely by changing the ratio of the PMMA/PC. Of course, therefore, it is not difficult to obtain the PMMA/PC blend polymer as a matrix polymer of which the refractive index matches to n_o of LC in order to realize the maximum transmittance at the normal incidence.

CONCLUSIONS

In this paper, we investigated the angular dependence of the light scattering of the (polymer/LC) composite films. The angular dependence of the composite film depends on the relationships of refractive indices between polymer and n_e and n_o of LC. The refractive index of the matrix polymer can be controlled by using the blend polymer as a matrix which shows optical miscibility. And also, the angular dependence of the light scattering of the composite film depends on the miscibility between matrix polymer and LC.

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