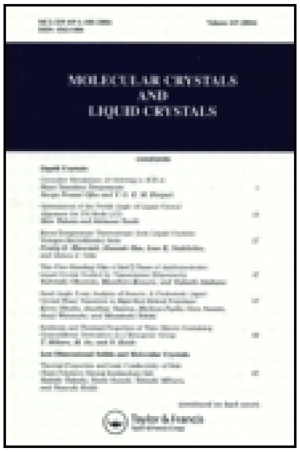

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Electro-Optical Effect Without Hysteresis for (Polymer/Liquid Crystal) Composite Films

Hirotsugu Kikuchi [a] , Hwan-Kyeong Jeong [a] & Tisato Kajiyama [a]

[a] Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka, 812, Japan

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Electro-Optical Effect Without Hysteresis for (Polymer/Liquid Crystal) Composite Films

HIROTSUGU KIKUCHI, HWAN-KYEONG JEONG and TISATO KAJIYAMA*
Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812, Japan

Phase-separation behavior of the composite films composed of polymer of a three dimensional network and low molecular weight liquid crystals (LCs) embedded in the network was studied on the basis of the evolution of optical heterogeneity in a casting solution during a film formation process and the morphology of the polymer networks. The electro-optical properties of the composite films based on electric field controlled light scattering were strongly dependent on the size of LC domains which was controlled by the solvent evaporation rate. When poly(diisopropyl fumarate), which is incompatible with the LC, was used as the matrix polymer, no electro-optical hysteresis was detected, while considerable electro-optical hysteresis was done for the composite film consisting of poly(methyl methacrylate), which is fairly compatible with the LC. However, when poly(methyl methacrylate) with high molecular weight (996k) was used as the matrix polymer, hysteresis decreased due to a decrease of compatibility.

Keywords: (polymer/liquid crystal) composite film; electro-optical effect; hysteresis; solvent evaporation rate; domain size

INTRODUCTION

A conception of the novel composite materials with the unconventional combination of a polymer and a low molecular weight liquid crystal (LC) burgeoned in the end of 1970s in order to apply unique characteristics of LC as a self-supported flexible film [1]. The preparation methods, aggregation structure and physical properties of the composite films consisting of various kinds of polymers and LCs have been extensively studied [2-9]. Recently, the composite films have attracted much attention because of their potentially promising applications, for example, large scale displays, switchable windows

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*Author to whom correspondence should be addressed and light shutters in projection systems [10-19]. The (polymer/LC) composite film can be switched between light scattering state and light transmitting one upon the removal and the application of an electric field, respectively, as schematically shown in Figure 1. The scattering and light transmitting states result from the macroscopically random orientation (Fig. 1(a)) and unidirectional one (Fig. 1(b)), respectively, of LC directors embedded in the three dimensional polymer networks. In the case that the LC possesses large birefringence, the spatial distortion of LC directors with the dimension of sub-μm induced by the complicated polymer network formations might be an important origin for the light scattering, in addition to the mismatch of refractive indices between polymer and LC [17]. It is apparent that the electro-optical characteristics of the (polymer/LC) composite film are strongly dependent on their aggregation states because the intensity of the light scattering is governed by the spatial heterogeneity [21]. In this paper, the electro-optical properties such as the response speeds, the driving voltage and the switching hysteresis have been investigated from the point of view of the aggregation states of the (polymer/LC) composite film such as the phase-separated state and the size of LC domain.

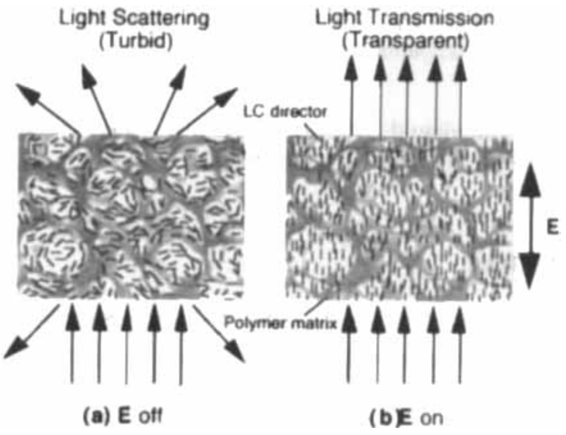

Figure 1. Schematic illustration of the light scattering-light transmission switching for (polymer/liquid crystal) composite film.

EXPERIMENTAL

Materials

Poly(diisopropyl fumarate) (Pdi-iPF) and poly(methyl methacrylate) (PMMA) shown in Figure 2 were used as matrix polymers. E8 (purchased from BDH Chemical Co. Ltd.) was used as an LC material. E8 is the nematic mixture consisting of several cyanophenyl type LCs.

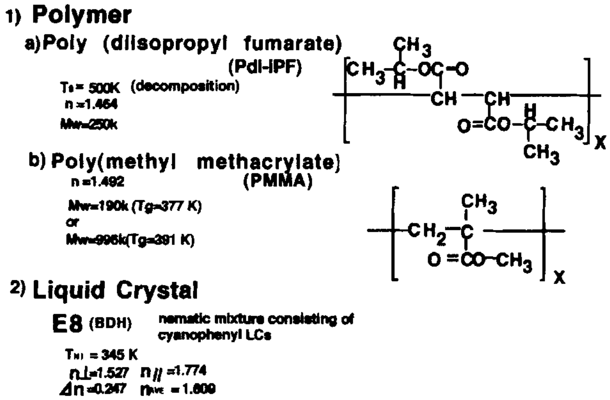

Figure 2. Chemical structures of the constituent polymers for the composite films

Preparation of the Composite Film

Composite films were cast from a chloroform solution of a mixture of polymer and LC materials under the condition of the constant temperature and the constant evaporation rate using an experimental arrangement shown in Figure 3. This setup also involves the measuring systems of a light scattering intensity and a weight change in a solution during the film formation process.

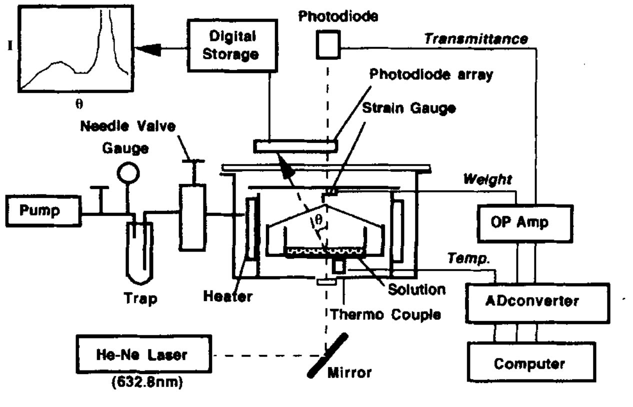

Figure 3. Measuring system of light scattering intensity profile and weight change in the (polymer/LC) solution during the film formation process.

The weight change was monitored using a semiconductor strain gauge. The time dependence of light scattering and light transmittance was evaluated using a He-Ne gas laser (wavelength of 632.8 nm, Uniphase) as an incident light beam. The transmitted light intensity was measured with a photodiode which was positioned at the direction of incident beam. The scattered intensity profile from the casting solution was detected with a photodiode array. The solvent evaporation rate was controlled by regulating the pressure in the solvent evaporation chamber with a needle valve and a vacuum pump. The weight ratio of (polymer/LC) was 40/60 and the initial concentration of the solution was 3-8 wt%. The thickness of the composite films finally obtained ranged 10-20 μm.

Scanning Electron Microscopy (SEM)

The aggregation state of the composite film was investigated by means of the scanning electron microscope (SEM, Hitachi S-430). The composite film was fractured in liquid nitrogen and then, the LC in the composite film was extracted with methanol (for Pdi-iPF) or n-hexane (for PMMA) at room temperature. The film and fracture surfaces were coated with gold for the SEM observation.

Electro-optical Measurement

In order to evaluate the electro-optical properties of the composite films, light transmittance changes upon the application of an a.c. electric field were studied by an experimental setup shown in Figure 4.

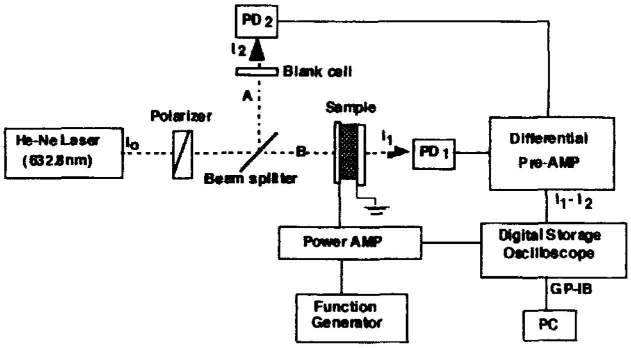

Figure 4. Schematic diagram of the measuring system of electro-optical properties of the composite film.

The composite films were sandwiched between two indium/tin oxide (ITO) coated glasses. A He-Ne laser was used as an incident light source. Measurement of the transmitted light intensity through the composite films without any polarizers was carried out with a photodiode under the modulation of an electric field. The transmitted light intensity through the sample cell was normalized by the magnitude of light intensity through a blank cell. The transient changes in the transmitted light intensity upon the application and the removal of an electric field were recorded with a digital storage oscilloscope.

RESULTS AND DISCUSSION

Formation Process of Phase-separated Structure of (Polymer/LC) Composite Film

The phase-separated structure of the (Pdi-iPF/E8) composite film was formed during the solvent evaporation from a uniform solution. In order to investigate the phase-separation process in the composite film, the light scattering characteristics during solvent evaporation were measured at 308 K. Though the weight of the solution decreased gradually with the process of solvent evaporation, the transmittance intensity dropped stepwise. The solvent evaporation process could be divided into the three stages based on the transmittance changes. In the 1st stage, the solution was almost clear and no change of the transmittance was observed. The transmittance of the solution decreased abruptly at the beginning of the 2nd stage and gradually approached to about 10 - 30 %. At the beginning of the 3rd stage, the transmittance decreased to nearly 0 % discontinuously. It is reasonable to consider that the reduction of the transmittance with time corresponded to the generation of light scattering in the solution due to the appearance of a phase-separated structure. In the 1st stage, the solution was optically homogeneous and did not exhibit light scattering except that due to density fluctuations. Since no optical anisotropy was observed and there remained much solvent at the beginning of the 2nd stage, it is obvious that optically isotropic phases were separated at the 2nd stage from the optically homogeneous solution. Then, an optical anisotropy was generated in the 3rd stage as concluded from the light transmittance observation under crossed nicols, resulting in the formation of the E8 LC phase. This clearly indicates that the appearance of the anisotropic E8 phase does not play an important role in the generation of the phase-separation, which occurs in an optically isotropic phases at the 2nd stage. Though chloroform, used as a casting solvent, is a good-solvent for both Pdi-iPF and E8, Pdi-iPF and E8 are not compatible each other without chloroform. Then, with the removal of solvent, the solution might be separated into a Pdi-iPF-rich phase and an E8-rich one because they prefer to be excluded each other. In other words, the E8-rich phase serves as a poor-solvent for Pdi-iPF. In the end of the 2nd stage, since the most of solvent evaporated, these phases might consist of solid-like Pdi-iPF and isotropic E8. After further solvent evaporation, the isotropic E8 phase transformed into the nematic phase, resulting in the generation of remarkably strong light scattering induced by the nematic directors in the 3rd stage.

Figure 5 shows the light scattering profiles in the 2nd stage as a function of the scattering vector $q=(4\pi/\lambda)\sin(\theta/2)$, where λ and θ are the wavelength and the scattering angle of the incident light, respectively. Since the light scattering profile exhibited the maximum in the 2nd stage. It is apparent that the periodic phase-separated structure of the Pdi-iPF-rich phase and the E8-rich one was formed in the solution in the 2nd stage. An increase in the scattering intensity maximum with the solvent evaporation time reflects an increase in the difference between refractive indices of the Pdi-iPF-rich phase and the E8-rich one. The plot of q at the maximum value of light scattering intensity, q_m, against time from the starting time of the 2nd stage is shown in Figure 6.

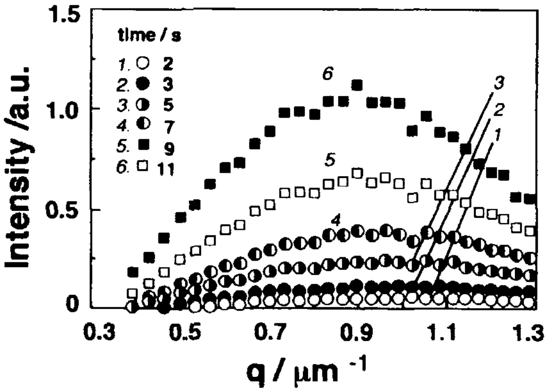

Figure 5. Scattering vector, q dependence of light scattering intensity as a function of the time of solvent evaporation for the (Pdi-iPF/E8:40/60) solution in the early period of the 2nd stage.

In the initial region in the 2nd stage, the magnitude of q_m showed almost the constant value though the scattering intensity increased as shown in Figure 5, and after 10 s, the magnitude of q_m started to decrease. The magnitude of q_m corresponds to the reciprocal of the periodicity of the phase-separated structure. Therefore, Figure 6 means that the periodicity of the phase-separated structure was almost constant at the early period in the 2nd stage and then, increased with the solvent evaporation time. It is well-known that there are two major mechanisms by which the two components in a mutual solution can phase-separate, (i) nucleation and growth and (ii) spinodal decomposition. In the case of the nucleation and growth mechanism, the domain sizes increases with time. On the other hand, in the case of the spinodal decomposition, the domains are of about the same size in the early stage of phase separation [22, 23]. Therefore, the light scattering behavior at the early period in the 2nd stage agrees with the kinetics of the spinodal decomposition. The strong and broad scattering due to multiple scattering from the anisotropic LC phase was observed in the 3rd stage. Though the intensity of light scattering remarkably increased in the 3rd stage, the scattering maximum disappeared because of the multiple scattering from the nematic phase. The light scattering data mentioned above indicates that the phase separation of the Pdi-iPF/E8 solution occurred at the beginning of the 2nd stage through the spinodal decomposition, and then, the domains might coalesce with each other, forming larger three dimensional spomgy structures with time.

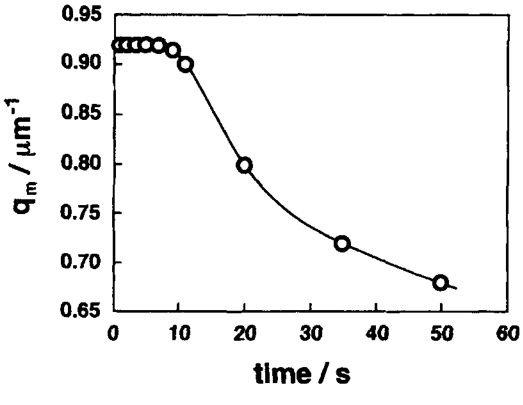

Figure 6. Time dependence of the maximum scattering vector, qm for the (Pdi-iPF/E8:40/60) solution in the 2nd stage.

The phase separation behavior of the (polymer/LC) composite during solvent evaporation can be explained from the phase diagram as schematically shown in Figure 7, which is a hypothetical phase diagram of the (Pdi-iPF/E8/chloroform) ternary system. The solid and broken curves in the phase diagram correspond to the binodal and spinodal lines, respectively. The binodal line separates the phase region into homogeneous and phase-separated regions. Also, the spinodal line separates the thermodynamically metastable and unstable regions. In the metastable region between spinodal and binodal lines, an initially homogeneous solution separates by a nucleation and growth mechanism. In the unstable region within the spinodal line, the phase separation proceeds via spinodal decomposition. During solvent evaporation, the concentration of the solution changes along the straight line in Figure 7.

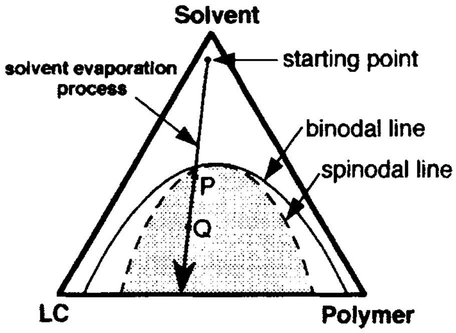

Figure 7. Hypothetical phase diagram of the (polymer/LC/solvent) ternary system. The arrow in the diagram shows a route of the solvent evaporation process.

The solution should pass the metastable region before it thrusts into the unstable region. Since the nucleation and growth process requires an activation energy, the phase separation rate is slow. On the other hand, the phase separation induced by the spinodal decomposition can proceed very fast because the energy barrier is negligible in the spinodal decomposition. Therefore, the solution should phase-separate preferentially via the spinodal decomposition. When the evaporation rate is fairly high, the phase-separation will not occur until the solution reaches a higher concentration region such as the point Q. Since the point Q is the further position from the spinodal line compared with the point P, the decomposition rate is much faster and the periodicity of the modulated structure is much shorter than those at the point P. Based on the spinodal decomposition mechanism, the resulting domain size will be larger when the solvent evaporating rate is slower. Figures 8 (a) and (b) show the SEM photographs of the matrix Pdi-iPFs after extraction of the E8 phase with ethanol from the (Pdi-iPF/E8:40/60 wt%) composite films, which were prepared at the solvent evaporation rates of 1.8 g h^{-1} and 7.0 g h^{-1}, respectively. It is clear from Figure 8 that the larger E8 domains were formed in the case of the slower solvent evaporation rate.

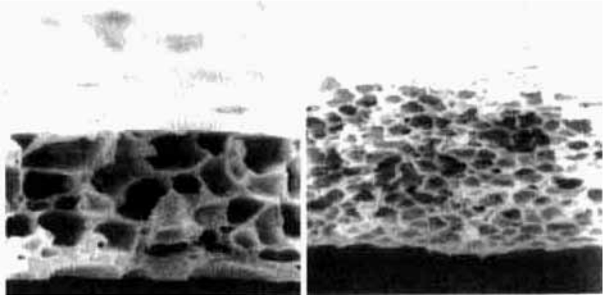

Figure 8. SEM photographs of the matrix Pdi-iPFs which were prepared at the solvent evaporation rates of (a) 1.8 g h^{-1} and (b) 7.0 g h^{-1}, respectively.

Electro-optical Switching of (Polymer/LC) Composite Film

The rise and the decay response curves of the electro-optical switching were measured for the (Pdi-iPF/E8:40/60 wt%) composite films prepared at the evaporation rates of 1.8 g h^{-1} and 7.0 g h^{-1}. The rise response times for the composite films prepared at the evaporation rate of 1.8 g h^{-1} and 7.0 g h^{-1} were about 1 ms and 5 ms, respectively. On the other hand, the decay response times for the composite films prepared at the evaporation rate of 1.8 g h^{-1} and 7.0 g h^{-1} were about 6 ms and 1 ms, respectively. When an electric field is applied to the liquid crystal surrounded by the polymer walls or the networks, three physical contributions with respect to (1) the elastic distortion energy of the deformed nematic, (2) the anchoring at the polymer/LC interface, and (3) the electric torque due to the dielectric anisotropy of the LC, should be exerted statically on the molecular alignment of LC. From the viewpoint of a dynamic process, (4) the viscosity for molecular reorientations of LC must be furthermore taken into consideration. Since the LC used in this study possesses a positive dielectric anisotropy, the LC molecules tend to align along the direction of an applied electric field. The viscosity opposes the molecular reorientation in both cases of the rise and decay processes. Though anchoring resists the molecular reorientation along the electric field in the rise process, it restores the macroscopically random orientation of LC directors in the decay process. Namely, the anchoring effect acts as opposing and restoring force for the rise and decay processes, respectively. The net anchoring strength is proportional to the area of the (polymer/LC) interface. The area of the interface in the composite film prepared at the evaporation rate of 7.0 g h^{-1} is much larger than that at 1.8 g h^{-1} because the size of LC domains shown in Figure 8(b) is smaller than that in Figure 8(a). Therefore, the anchoring effect in the composite film prepared at 7.0 g h^{-1} is much larger than that at 1.8 g h^{-1}. The difference in the response times for the composite films prepared at the evaporation rate of 1.8 g h^{-1} and 7.0 g h^{-1} clearly corresponds to the difference in the net strength of anchoring effects at the polymer/LC interface in the composite films.

Figures 9 (a) and (b) show the applied voltage dependence of the transmittance for the (Pdi-iPF/E8:40/60 wt%) composite films prepared at the evaporation rate of 1.8 g h^{-1} and 7.0 g h^{-1}, respectively. Two curves for reciprocating processes of increasing and decreasing voltage are given in each plot. The difference in the transmittance in the presence of an electric field for the composite films prepared at the evaporation rates of 1.8 and 7.0 g h^{-1} might be also explained by the difference in the anchoring effect. In general, the fraction of LC molecules strongly anchored by the polymer wall might be increased with decreasing the size of LC domains. As a result, the transmittance of the composite film prepared at 1.8 g h^{-1} was higher than that at 7.0 g h^{-1}. Also, the voltage required to attain a higher transmittance for the composite film prepared at 1.8 g h^{-1} was lower than that prepared at 7.0 g h^{-1}. This apparently corresponds to that the fraction of LC molecules strongly anchored by the polymer walls in the composite film might increase with decreasing the size of LC domains. Therefore, it can be concluded from Figure 9 that the size of LC domains in the composite film should be enlarged in order to realize a lower voltage drive.

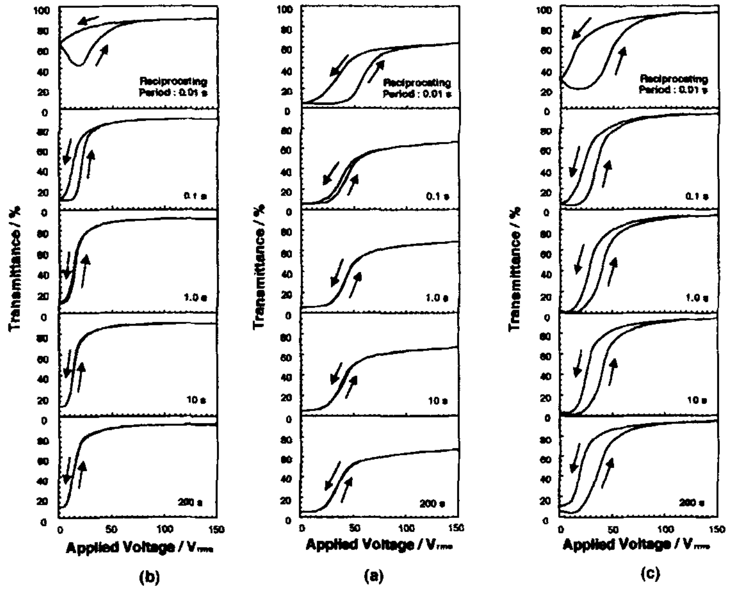

Figure 9. Applied voltage dependence of the transmittance for the (Pdi-iPF/E8:40/60 wt%) composite films prepared at the evaporation rate of (a) 1.8 g h^{-1} , (b) 7.0 g h^{-1} and (c) the (PMMA/E8:40/60 wt%) composite film.

The hysteresis of the electro-optical switching of the (polymer/LC) composite system has been a problem which must be solved for practical application as display materials. When the reciprocal period was longer than 1.0 s, the electro-optical hysteresis of the (Pdi-iPF/E8) composite film almost disappeared in the reciprocating process. However, the magnitude of the hysteresis increased with reducing the reciprocating period as shown in Figure 9. The hysteresis in the shorter range of reciprocating period may be attributed to the retardation of the LC molecular reorientation upon the amplitude modulation of an applied electric field. Since the decay time of the electro-optical switching is the order of ms, the time lag of the electro-optical response is not negligible in the range of the reciprocating period shorter than 0.1 s. Figure 9 (c) shows the applied voltage dependence of the transmittance for the (PMMA/E8:40/60 wt%) composite film when the weight-average molecular weight of PMMA is 190k. Large hystereses were observed in all cases of reprocating period from 0.01 s to 200 s for the (PMMA/E8) composite film. In the range shorter than 0.1 s, the hysteresis might result from the retardation of the LC molecular reorientation in a similar fashion to the (Pdi-iPF/E8) composite film. However, the hysteresis in the range longer than 1.0 s might be explained by another mechanism as follows. When an a.c. electric field is applied to the (polymer/LC) composite film, dielectric loss energy due to the interfacial polarization and/or the electric conduction is generated in the composite film. Then, dielectric loss energy would be converted into heat and/or an endothermic structural change in the composite film. If the matrix polymer is not compatible to LC, for example, the (Pdi-iPF/E8) composite, a large fraction of dielectric loss energy might be converted into just heat. However, on the other hand, in the case of the compatible mixture, such as PMMA to E8, it seems reasonable to consider that a part of dielectric loss energy would be converted into a structural change in the composite film and then, this enhances more the miscibility PMMA polymer and E8. An increase in phase-mixing between polymer and LC induces a decrease in the optical heterogeneity, that is, a decrease in the intensity of light scattering in the composite film. If the phase-separated structure is changed under the application of an electric field, the recovery to the original phase-separated structure after removing an electric field should take a longer time because it needs the molecular rearrangement. Then, it is reasonable to consider that the phase-separated structure in the increasing process of the applied electric voltage might be not same as that in the decreasing one, in the case that the degree of compatibility between polymer and LC increased fairly under the application of an electric field, for example, such as the case of the (PMMA/E8) system. That is to say, the light transmittance in the increasing process of the applied electric voltage is lower than that in the decreasing process, since the components of polymer and LC may be more phase-mixed in the latter process. On the other hand, if the components of polymer and LC are not compatible such as the case of the (Pdi-iPH/E8) system, an obvious electro-optical hysteresis in the range of reciprocating period longer than 1.0 s is not observed. A possible mechanism for the electro-optical hysteresis has been reported elsewhere[25].

The compatibility between polymer and LC in the composite film might be reduced with increasing molecular weight of the polymer. Therefore, it is expected that when a polymer with high molecular weight is used as a matrix polymer, the electro-optical hysteresis is remarkably reduced. Figure 10 shows the applied voltage dependence of the transmittance for the the (PMMA/E8:20/80 wt%) composite films composed of PMMA with the molecular weight of 996k. The composite film composed of PMMA with the molecular weight less than 190k exhibited a fairly large hysteresis as shown in Figure 9 (c), in comparison with a remakably reduced hysteresis for the composite film composed of PMMA with the molecular weight of 996k as shown in Figure 10. The comparison between Figures 9 and 10 supports our hypothesis that the compatibility at the interface between polymer and LC is one of the main origins for the electro-optical hysteresis in the composite film.

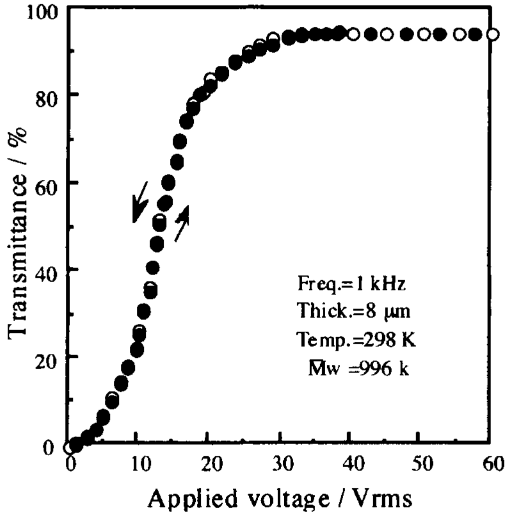

Figure 10. Applied voltage dependence of the transmittance for the (PMMA/E8:20/80 wt%) composite film consisting of PMMA with high molecular weight.

CONCLUSIONS

The phase separation behavior of the composite film during the solvent evaporation can be classified into 3 stages according to the experimental results of the light scattering properties of the solution. In the second stage, the spinodal decomposition occurred between polymer-rich phase and LC-rich phase which were still isotropic states. In the final stage, the anisotropic phase of LC was generated. The resultant size of the LC domain in the composite film was controlled by regulating the solvent evaporation rate. The electro-optical properties based on field controlled light scattering of the composite film were strongly dependent on the size of the LC domains and on the compatibility of the matrix polymer with the LC. Though the rise response time decreased, the decay response one increased with an increase in the size of LC domains in the composite film. Those electro-optical results could be explained by the effective anchoring strength at the interface of polymer and LC depending on the effective area fraction of the interface. When poly(diisopropyl fumarate), which was not compatible with the LC, was used as the matrix polymer, no electro-optical hysteresis was observed, while considerable electro-optical hysteresis was observed for the composite film consisting of poly(methyl methacrylate), which showed a certain compatibility with the LC. It is suggested that the phase-mixing at the interface induced during the application of an electric field is a possible mechanism affecting the electro-optical switching hysteresis.

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