전기장하에서 액정이 배열된 구조를 가진 PDLC 필름의 온도에 따른 전기광학적 특성에 관한 연구

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Temperature Effect on Electro-Optic Responses of a PDLC Film with and without Pre-Aligned LC Droplets

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요 약: 용융 상태의 PMMA/E7 블랜드를 이용하여 전기장이 인가된 상태에서 상분리됨으로서 미리 배열된 액정 방울 구조를 가진 PDLC 필름과 그렇지 않은 것의 전기광학 특성을 온도의 변화에 따라 조사하였다. 필름의 동작 온도에 따른 응답 시간에 관한 연구로부터 상분리되어 있는 블랜드 내의 고분자 벽면과 액정 방울 간에는 어느 정도의 두께를 가진 유효 계면이 존재하고 또한 이 계면 내에서는 액정의 농도 경사가 있음이 도출되었으며 또한 이 계면의 두께는 온도에 따라 달라지는 것으로 생각되었다. 한편 이 유효 계면 내의 고분자들은 냉각시에 전기장에 의해 받은 응력 때문에 계면에서의 액정 온도에 영향을 미치는 것으로 생각되었으며 이러한 결과로서 전기장이 인가된 상태에서 만들어진 PDLC 필름은 인가된 전기장이 없어지면 곧 바로 일어나는 응력 해소 과정으로서 시간에 따라 필름의 투명도 변화를 나타내고 또한 이 과정은 처음의 fast relaxation에 계속된 slow relaxation의 두 가지의 연속된 서로 다른 메카니즘에 의해 진행되는 것으로 관찰되었다.

ABSTRACT: Temperature effects on the electro-optic properties for the PDLC films of PMMA/E7 blend prepared with and without pre-aligned LC droplets within the blends were investigated. The observations of the electro-optic response times with temperature for the films led to a result that there is an effective interfacial region between the polymer matrix and bulk LC-rich droplets, having a thickness with LC concentration gradient, i.e., from lower LC concentration of matrix-side to the higher one of LC droplet-side. It was also considered that the thickness of this interfacial region could be changed depending on temperature. In the effective interfacial region, moreover, the polymer chains of matrix-side can affect the LC relaxation motions of droplet-side, by relaxing their own stresses exerted by electric field on cooling the PDLC film with AC field, exhibiting two different relaxation processes of the film at a fixed temperature, i.e., the fast relaxation and the slow one.

Keywords: polymer/LC, PDLC, electro-optics, effective interface, relaxation.

INTRODUCTION

The principle of electro-optic responses of polymer-dispersed liquid crystal (PDLC) film, which are the heterogeneous systems composed of the low molecular weight liquid crystal (LC) droplets dispersed in various polymer matrices, is based on the refractive index matching between polymer matrix and LC. It is well known that these properties are severely affected by the various factors such as the chemical and physical properties of the LCs and polymers, droplet size, shape, densities, film thickness, and operation temperature.[1] Since Fergason[2] and Doane et al.[3] introduced the potential capabilities and the practical use of PDLC film, remarkable interests are focused on both applied and basic researches.[3-8]

Recent works on temperature effects on PDLC film composed of polyvinyl formal (PVFM) and E7 showed that the electro-optic properties such as driving voltage and turn-off time response changed drastically near the glass transition temperature of polymer matrix.[9-10] Authors of those researches reasoned that the surface anchoring force might play a major role for the change. Further research proved that surface anchoring force, especially azimuthal anchoring force, could be a main factor for the change.[11] Because surface anchoring force is originated from interfacial interaction between the polymer wall and LC molecules in the droplets, above mentioned results indicate that the change in the interfacial properties with temperature can lead to a severe change in the electro-optic (EO) response of PDLC film.

More recent work on the interface of PDLC film using electron paramagnetic resonance (EPR) showed that there was an interfacial region in PDLC film having a thickness, in which it appeared quite fluid and had little or no average order.[12] As authors mentioned, however, although EPR observation showed no order because it measured the average order of the region, there should be minimal LC orders at droplet surface that could control the droplet configuration and director orientation.

The interfacial morphologies as well as the droplet size and shape can be modified by several methods such as mechanical stretching or phase separation with an external field, resulting in even faster EO responses.[1,13] When the external electrical field above threshold is applied on a PDLC film while the phase separation occurs in the blend, LC molecules with positive dielectric anisotropy are forced to be aligned parallel with the applied field. The matrix polymer chains at the interface in droplets are also forced to be oriented by the LC aligning. When the film was cooled to room temperature that is below T_g of matrix, interfacial polymer chains may fix the LC molecules at surface as aligned state. The resulting PDLC film appears almost transparent. This pre-aligned PDLC film method can be used as a new technique to determine the matrix T_g of PDLC films. It is also expected that this can be used to understand the interfacial properties of PDLC film more deeply by observing temperature dependency of EO responses.

In the present work, we prepared several PDLC samples with different LC concentrations by the thermally induced phase separation (TIPS) with and without an external field.[14] As a PDLC forming material, we used a blend of the thermoplastic polymethylmethacrylate (PMMA) matrix and a low molecular weight LC, E7, which is known as a partially miscible system.[16] We focused our attention especially on the effect of temperature around T_g of polymer matrix on the EO responses of sample films. The results will show that there is an effective interfacial region between polymer

matrix and bulk LC-rich droplets, having an effective thickness with LC concentration gradient, i.e., from lower LC concentration of matrix-side to higher one of LC droplet-side. And a model for effective thickness of interfacial region in the droplets will be suggested to explain the observed EO properties change with temperature.

EXPERIMENTAL

A low molecular weight LC eutectic mixture, E7, from BDH Chemical Co., Ltd., and PMMA of medium molecular weight from Aldrich Chemicals Co., Inc., were used to form PDLC film. These materials were used as received without further purification. Pre-determined amounts of PMMA and E7 by weight were dissolved in methylene chloride. The solution was poured into a petridish and then the solvent was removed by putting the petridish on a hot plate at 60 ℃ for about 1 day. A 20 μm-thick PDLC film was made by sandwiching the cast sample between two transparent indium-tin-oxide (ITO)-coated conducting glass plates on the hot plate. The hot plate temperature was set at 130 ℃. Residual solvent in sample could be completely removed on the hot plate during sample fabrication process. A recent work reported that thermal history, strength of applied external field, and time period prior to measurement are three important factors to affect the EO properties of PDLC film.[11] To keep the sample film at uniform condition during all the measurement, therefore, phase separation of the sample film was induced by TIPS in Mettler FP 82 hot stage controlled by Mettler FP 80 central processor, cooling it from 120 to 20 ℃ with cooling rate of 5 ℃/min. For a pre-aligned sample film, an AC electric field of 100 V_{rms} was applied on the sample during cooling process. Two copper-leads using conducting silver paste were attached to each side of the ITO-glass plates of the sample film for

applying AC electric field. To measure EO properties of the sample film with temperature, the sample was placed in a specially designed aluminum oven of which temperature could be controlled to ±0.01 ℃ by Lake Shore DRC 93CA temperature controller. Actual temperature of the sample in the oven for both heating and cooling cycle with a fixed scan rate was precisely calibrated using known materials. Several low molecular weight LCs from BDH, Ltd. such as 5CB, 7CB, 8CB, E7, and E48, were used for the oven calibration. HP 8904A Function Generator in conjunction with KEPCO BOP 500M Amplifier was used to apply a field on the sample in the oven. A white-light source and a He-Ne laser light source in combination with a photo-sensor connected to Keithley 194A High Speed Voltmeter were used to measure the EO properties of the sample film with temperature. All devices were connected to and controlled by a IBM compatible personal computer via GPIB interface. A specially programmed software using LabWindow was used for the equipment control, data acquisition, and analysis. A schematic diagram of the measurement system is shown in Fig. 1.
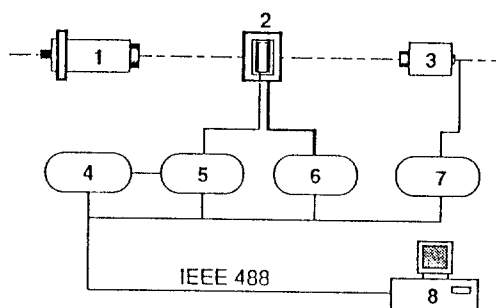
1. White/He-Ne Laser Light Source
2. Hot Stage with Sample Inside
3. Photo Detector
4. HP 8904A Function Generator
5. Kepco BOP 500M Power Supply/Amplifier
6. Lake Shore DRC 93CA Temperature Controller
7. Keithley 194A High Speed Voltmeter
8. IBM Compatible PC

Figure 1. Schematic diagram of the experimental set-up.

Phase separation behavior of the sample film was also observed using Leitz Laborlux 12 Pol polarizing microscope equipped with Mettler hot stage as mentioned above.

RESULTS AND DISCUSSION

Several recent studies have shown that the EO properties of PDLC films such as the on- and off-response times and the driving voltage change abruptly around the glass transition of polymer matrix.[9-11,15] Origin of these phenomena is understood as coming from the change of interfacial interaction in the films, i.e., interaction between the matrix polymer chains and LC molecules at interface. Because the interfacial interaction is responsible for surface anchoring energy, it is expected that the EO properties of PDLC film can also be altered by modifying the surface with an external field. Temperature dependent on-and off-response times of the 4/6 PMMA/E7 sample prepared with and without pre-aligned LC droplets are shown in Fig. 2. Both on-time (τ_{on}) and off-time (τ_{off}) responses are taken as the times for 90% of full on- and off-transmittance of the film, respectively. τ_{on}s of both pre- and un-aligned sample begin also to increase near T_g (Fig. 2A), ca. 36 ℃. Some fluctuation around 45 ℃ can be observed. This fluctuation around 45 ℃ above much higher temperature than T_g is considered due to the system instability, beginning to go through a homogenization process. The interface at this temperature seems to be so much mobile. It should be noted, however, because ton is caused by applying the external field, its time scale is much shorter than that of τ_{off}. There may be several factors for increase in τ_{on} near T_g. One is the thermal disturbance of LC molecules within droplets against the applied external field, the other is the increase in interfacial interaction between the LC molecules and the polymer chains which might be forced to align together with
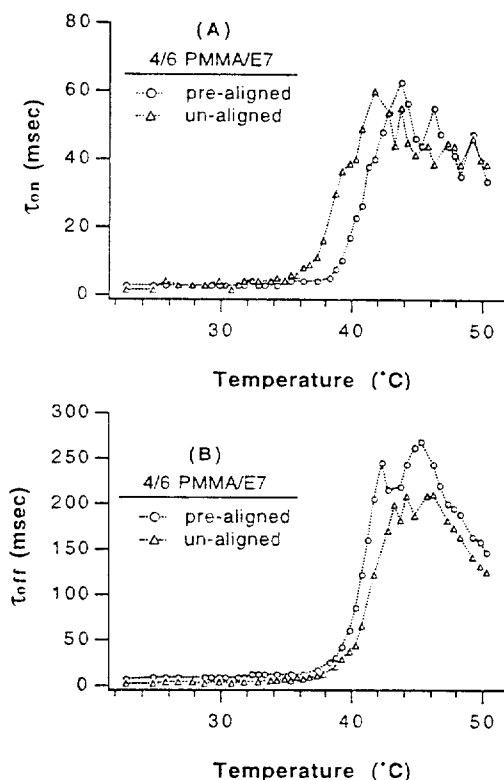

Figure 2. On- and off-time responses as a function of temperature for the 4/6 PMMA/E7 sample prepared with and without pre-aligned droplets. Heating rate was 0.2 ℃/min: (A) on-time responses and (B) off-time responses.

the LC molecules when the external field was applied, which resists against the LC molecules not to align together. Of the two, the latter is thought as more feasible when taking time scale of τ_{on} into consideration. It is worthy to note that, while τ_{on} of the un-aligned sample begins to change near 35 ℃, that of the pre-aligned sample can be still maintained as fast as that of the un-aligned sample until higher temperature, ca. 38 ℃, is reached. This phenomenon can be reasonably thought as, once the pre-aligned polymer chains, forced to align by the external field during sample preparation, begin to relax their stresses at increased temperature, the interactions between the polymer chains and the LC molecules in

the interface get started to be stronger to cause τ_{on} increase as is similar to the case of the un-aligned sample.

τ_{off} for the pre-aligned sample appears always a little longer than that of the un-aligned sample, which is reasonable when considering the aligning effect of the polymer chains and the LC molecules at interface induced by the electric field during sample preparation (Fig. 2B). As temperature increases near T_g of polymer matrix, τ_{off}s of both pre- and un-aligned sample begin to increase drastically at the same time. Fluctuation above much higher temperature than T_g can also be observed around 45 ℃, after then, τ_{off} decreases continuously as temperature increases.

It is important to know that how long the pre-aligned sample can maintain its original aligned state at a given temperature. When it is heated over the peak temperature, 45 ℃, as shown in Fig. 2, it is expected that all the original history can be lost, resulting that the sample comes back to the the same as the un-aligned one. For the un-aligned sample, though not shown in Fig. 2, it was found that temperature dependent τ_{on} and τ_{off} followed the same route for both heating and cooling cycle. To see the effect of the peak temperature on response times, it is necessary to measure the responses before and after heating around the peak temperature, 45 ℃. Fig. 3 shows that τ_{on} and τ_{off} responses of the pre-aligned 4/6 PMMA/E7 sample during one cycle of heating/cooling with a rate of 0.2 ℃/min to the temperature before and after the peak temperature, i.e., 40 (Fig. 3A) and 50 ℃ (Fig. 3B), respectively. In both cases, while some differences in τ_{on} could be detected around T_g, τ_{off} response below T_g was little changed, though it is somewhat shortened during cooling cycle compared with heating cycle. Because the pre-aligned polymer chains at interface changed to be more random at higher temperature, τ_{on} became more similar to the un-aligned sample resulting in similar pattern shown in Fig. 2A. τ_{off},
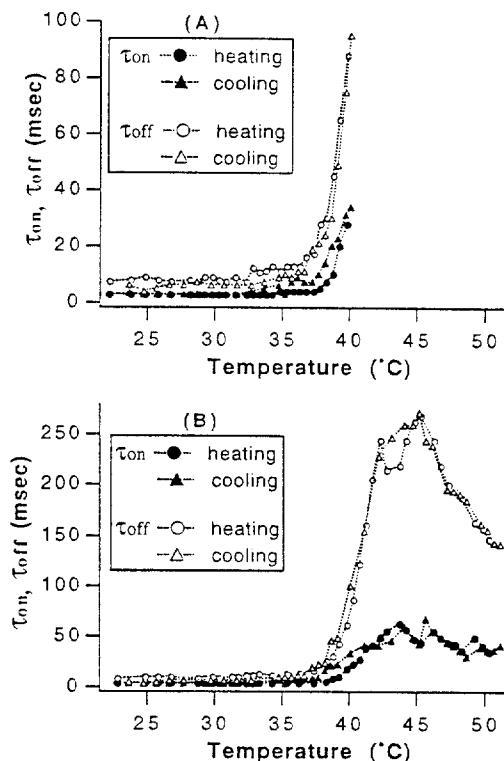

Figure 3. On- and off-time responses as a function of temperature for the pre-aligned 4/6 PMMA/E7 sample during one cycle of heating/cooling before and after the peak temperature: (A) responses during one cycle to temperature of 40 ℃ and (B) responses during one cycle to temperature of 50 ℃.

however, shows that it follows nearly the same process on both heating and cooling as shown in both Fig. 3A and 3B. Because τ_{off} is the relaxation process without an external field, the orientation of LC molecules is affected by interfacial state within the blend. It is considered, therefore, that long polymer chains, which is pre-aligned with LC molecules at interface exerted by an external field during sample preparation, seems to be able to be maintained during the experimental time scale although local segmental relaxation will severely affect τ_{on}. Considering all the results together obtained using the pre-aligned sample, it can be easily imagined that the EO properties of PDLC films is closely related to
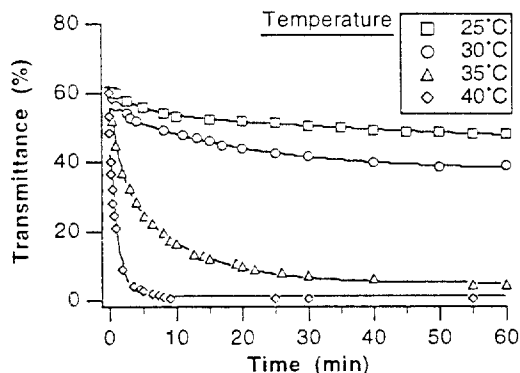
Figure 4. Time dependence of transmittance change of pre-aligned 4/6 PMMA/E7 sample at several fixed temperatures. Bold lines indicate curves fitted mathematically using a double exponential equation.

Table 1. Constants to Fit the Experimental Data in Fig. 4 Using Double Exponential Equation, $Y = K_0 + K_1{}^*\exp(-K_2{}^*x) + K_3{}^*\exp(-K_4{}^*x)$

temp.	K_0	K_1	K_2	K_3	K_4
25 ℃	42.8466	11.7436	0.0135	6.4250	0.2213
30 ℃	37.5911	17.4225	0.0489	5.1431	0.7231
35 ℃	4.9753	31.8923	0.0989	23.7160	0.7118
40 ℃	1.4976	45.9069	0.8843	12.4908	8.9701

interfacial properties and, moreover, polymer chains and LC molecules at the interface are easily movable with temperature change, which means that interface is not solid enough to fix LC molecules firmly, but comparatively flexible enough to let the LC molecules be mobile at surface. It is noteworthy that this concept of flexible interface can be applied to all the present PDLC systems because most polymer/LC blend systems are more or less partially miscible. In other words, there can be an interfacial region that has a thickness having LC concentration gradient.[12] It is, therefore, expected that the LC molecules just at surface of the polymer wall in the pre-aligned sample can relax their stress as soon as the external field is turned off. Fig. 4 shows the time dependent transmittance change of the pre-oriented 4/6 PMMA/E7 sample at several fixed temperatures around T_g. As shown clearly in the Figures, transmittances at all four temperatures begin to decrease with time as soon as the field is turned off. Although decreasing rates are different at each temperature, it is observed even at the temperature of 25 ℃. Another interesting point can be derived from this results. Data in the Figure can be mathematically well fitted using an equation including double-exponential terms. All the constants in the equa-

tion are shown in Table 1. As clearly shown in this Table, K_2 and K_4 represent two different relaxation rates, the slower and the faster one, respectively. This let us to think that the relaxation process occurring at interfacial region cannot be explained by a single relaxation mechanism, but should be explained by the composite mechanisms of two different relaxations, the faster relaxation just at the surface of droplet-side and the slower one affected by the polymer chains of matrix-side within the interfacial region. Ji and Kelly [11] explained that this process may be caused by the liquid crystal elastic deformation which can be a strong driving force to move the polymer chains on the surface. While the short time relaxation is from the elastic deformation of polymer chains, the long time one is from viscous deformation. From our study, another way to explain this phenomena is possible, i.e., the interfacial region has an effective thickness having a LC concentration gradient as mentioned above. According to this model, LC molecules of droplet-side on the surface of the interfacial region can move easily, showing the faster relaxation. They are, however, still affected by polymer chains of the inner region of matrix-side, exhibiting the slower relaxation.

CONCLUSIONS

The observations of response times and relaxation processes of a PDLC film with temperature led to a result that the interface between polymer matrix and bulk LC droplets has somewhat effec-

tive thickness having gradient of LC concentration. It was considered that this effective thickness of interfacial region was dependent on temperature. Polymer chains of matrix-side in the interfacial region can affect LC relaxation motions of droplet-side. This may be the origin of two different relaxation processes of PDLC film. Because the pre-aligned LC molecules of effective interfacial region of PDLC film can be easily disturbed by segmental motions of matrix polymer chains, exhibiting great change in transmittance, this technique presented in this paper can be usefully applied to determine the thermal properties of PDLC films such as T_g, T_{NI}, and T_{cl}.

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