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Effect of Curing Process on the Dynamic Response of Polymer Dispersed Liquid Crystal Films

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Summary: The time relaxation of the optical transmission of polymer-dispersed liquid crystal films was investigated after application of an electric rectangular pulse. These films, consisting of liquid crystalline microdomains dispersed in a polymer matrix, were obtained by polymerization induced phase separation using ultraviolet and electron beam curing techniques. The effects of the curing procedure and film thickness on the transmission properties were investigated. The electro-optical response was expressed via a hierarchy of order parameters. A good agreement between the experimental data and calculated transmission values was found.

Keywords: liquid crystals; optical properties; phase separation; polymers; relaxation

Introduction

Polymer-dispersed liquid crystal (PDLC) materials, which appeared in the 1980 s, have been extensively studied for various electro-optical applications that are currently revolutionizing liquid-crystal display technology.[1–6] Under normal mode conditions, these materials appear in form of thin films consisting of micron-sized phase separated domains of low molecular weight nematic liquid crystal (LC), randomly dispersed in a polymer matrix. Since the LC molecules can change their orientation under the influence of an applied electrical field,[1] these films can switch between a highly scattering opaque state and a transparent state upon application of an external electric field with sufficient amplitude.[2–4] The applications of PDLC films, such as flexible display devices, optical shutters, and switchable windows,[5,6] are based on the electrically controllable light scattering properties of the LC domains.

Upon applying an electrical field, LC molecules near the center or the phase separated LC domains quickly orient along the field direction, giving a fast optical response. However, LC molecules at the surface layer of the domains rotate slowly, giving a slow optical response. Upon removal of the electric field, the center of the LC domains can quickly relax while the rest moves slowly because the LC molecules are anchored on the polymer surface, yielding optical memory effects.

In general, the electro-optical properties of PDLC materials depend on dimension, architecture, and morphology of LC domains, sample composition, kinetics of polymerization and phase separation, and other parameters. An increasing number of interesting computational and experimental studies were reported on this topic.[7–13] Deshmukh et al. investigated the effects of temperature and composition on the optical and electro-optical properties of a linear polymer/LC system.[8] The influence of the nature of monomers, crosslinking agents, and additives on sample morphology and electro-optical performances has been studied by White et al.,[9] Li et al.,[10] Kashima et al.,[11] He et al.,[12] and Wang et al..[13]

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These authors showed that it is possible to some extent to control LC domain sizes and to optimize the electro-optical properties of resulting PDLC films by adjusting the polymer chain length between two adjacant crosslinking points, the chemical structure of the monomer, the amount of crosslinking agent, reaction temperature, etc..

He et al. reported on the effect of polymer molecular weight on electro-optical properties of PDLC films prepared by addition fragmentation chain transfer polymerization: [14,15] Increasing the polymer molecular weight leads to higher saturation voltages and decreasing memory effects. The effect of droplet size on photorefractive properties of PDLC materials was also investigated.[16] Akbarzadeh et al simulated the behaviour of a single nematic bipolar droplet in a PDLC film, in order to obtain its optimal aspect and elastic constant ratios under the conditions of short relaxation and response times.[17]

Here, we consider the dynamics of selected PDLC films, consisting of a nematic LC dispersed into a polymer matrix, by monitoring their time evolution of the optical transmission undergoing a rectangular electric field pulse. Two modes of preparing PDLC materials were employed based on polymerization-induced phase separation mechanisms using either electron-beam (EB) or ultraviolet (UV) radiation curing processes. Other important parameters, such as film thickness and droplet morphology, were also considered to evaluate their impact on the relaxation behaviour.

Experimental Part

Materials

The eutectic mixture of cyanoparaphenylene derivatives known as E7 (Merck) was used in this work. It exhibit a positive dielectric anisotropy: $\Delta\varepsilon = 14\varepsilon_0$ (ε_0 is the dielectric permittivity of vacuum), a nematic-isotropic transition temperature $T_{NI} = 61°C$ and an optical birefringence $\Delta n = n_e - n_0 = 0.2195$.[18–20] Tripropyleneglycoldiacrylate (TPGDA) monomer was obtained from Cray Valley (France).

A precursor mixture containing 30 weight-percent (wt-%) of TPGDA and 70wt-% of E7 was cured using EB-radiation. 2wt-% (of the acrylate mixture) of a photoinitiator (Lucirin TPO, BASF) was included in the initial mixture in the case of UV-cured samples. These blends were mixed at room temperature for several hours until they became homogeneous. Samples prepared by introducing the initial reactive mixture between a glass plate (Balzers, Liechtenstein) and a Polyethyleneterephthalate (PET) sheet (Renker, Germany), both coated with a thin transparent layer of conducting indium/tin oxide. A 100 μm thick PET-sheet was used for the UV curing process and a 50 μm thick PET-sheet for employed for the EB curing process to allow a uniform penetration of the applied dose in the depth of the sample.

Crosslinking Polymerization

The EB generator used was an Electrocurtain Model CB 150 (Energy Sciences Inc.), delivering an operating high voltage of 175 kV. The samples prepared as mentioned above were placed on a tray which was passed under the irradiation source on a conveyor belt. They were exposed to a beam current of 7 mA and a constant conveyor speed of 0.19 m/s allowing to achieve a dose of 105 kGy (1 kGy = 1 J/g), which was choosen to allow complete conversion of the monomer to a chemically crosslinked polymer network.[21] Several duplicate samples were prepared to check the reliability of the results.

The UV irradiation source used in this study was a Minicure Model MC4-300 (Primarc UV Technology) equipped with a medium pressure mercury arc lamp rated 80 W per cm. The samples prepared as described above were placed on a conveyor belt; and the dose received by the sample was 150 mJ/cm^2.

The film thickness was measured by a micrometer calliper (Mitutoyo; uncertainty: ±1μm). No temperature control during the irradiation processes has been performed.

Optical Measurements

The optical measurements were made at room temperature by recording the transmission of unpolarized HeNe laser light ($\lambda = 632.8$ nm) at normal incidence to the film. The transmission measurements were corrected using appropriate calibration standards. Measurements of transmission were made as a function of time starting with 30s in the initial off-state T_{OFF} followed by a period of 60s in the on-state T_{ON} (transmission at its maximum). The counting relevant for this paper started at the time where the electric field rectangular pulse ceased and have been followed during 60s. This procedure was repeated for films of different thicknesses and cured under different conditions. The frequency of the applied signal was maintained at 145 Hz while its amplitude was changed in such a way that it corresponded to the maximum transmission (T_{ON} constant) for each film thickness. The experimental set-up is displayed in Figure 1.

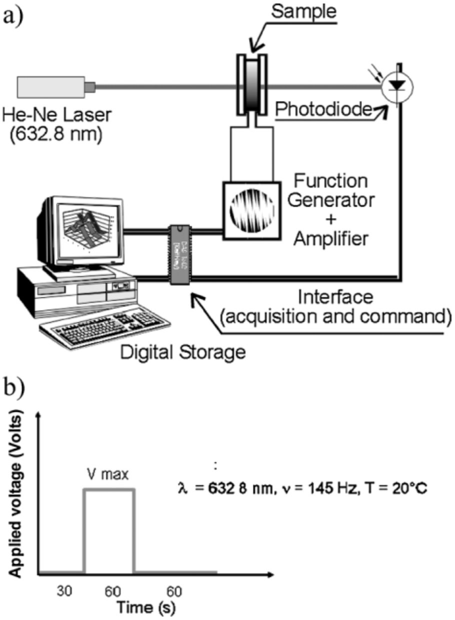

Figure 1.
(a) Experimental set-up used to measure the time relaxation of PDLC films; (b) Variation of the applied sinusoidal voltage as a function of time.

Results and Discussion

Experimental Results

Figure 2 shows the variation of the normalized transmission T/T_{on} versus time for UV-cured films of different thicknesses, starting at the time, where the electrical field was removed after applying the pulse. These samples were exposed to a dose of 150mJ/cm^2 to obtain a complete conversion of the monomer to a chemically crosslinked polymer network.[21] At short relaxation times, the curves do not show a clear tendancy in terms of the film thickness. As expected, light transmission decreases at longer relaxation times as the film becomes thicker thus enhancing the scattering of light. These relaxation curves exhibit at least two distinct relaxation processes, a fast process at short times followed by a slow process for longer times. This effect is more pronounced for thicker films. Figure 3 reveals that the initial decay of the transmission values cannot be fitted by a single exponential function since the variation of the corresponding logarithmic data with time do not show a linear behaviour.

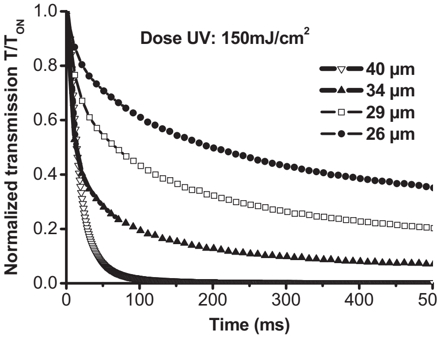

Figure 2.
T/T_{ON} versus time for UV cured TPGDA(30 wt-%) / E7(70 wt-%) films with different thicknesses (irradiation dose 150 mJ/cm^2). The electric field applied corresponds to a rectangular pulse lasting 60s at the voltage applied and the origin corresponds to the time when the field is removed.

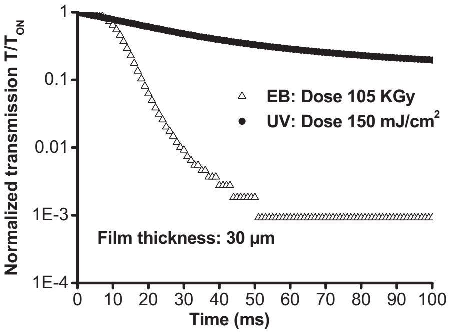

Figure 3.
T/T_{on} versus time for UV- and EB-cured TPGDA (30 wt-%) / E7 (70 wt-%) films.

In order to correlate the data obtained from UV-cured films to samples from EB processing, Figure 3 includes an example of the relaxation behaviour of a EB-cured film possessing the same thickness compared to the UV-sample. The irradiation dose of 105 kGy for EB irradiation corresponds to a maximum conversion of the acrylic double bonds with only a slight difference between the two cases. Figure 3 clearly shows that the relaxation time after application of an electric pulse is shorter for the EB-cured film, which can be explained by the more homogeneous dispersion of LC domain dimensions and shapes in the EB-case.[22]

Comparison of the Experimental Data with Theory

The optical response of PDLC films can be described by a simple model based on a minimization of the total electrical and elastical energy of the nematic LC droplets (domains) dispersed in the polymer matrix. This model is based on the assumption that the internal configuration of the LC droplets is not significantly altered under the application of an external electrical field, and that only the droplet director changes its direction with the applied field. Following this model, the optical response can be expressed by a hierarchy of order parameters to calculate light transmission of a PDLC sample. The anisotropic properties of nematic droplets depend on their nematic director fields which can be influenced by external electric or magnetic fields. It is assumed that in the electrical off-state the droplet axes are randomly oriented throughout the sample volume, and that the LC droplets exhibit an ellipsoidal shape. The importance of this model lies in its capacity to describe the phenomenon of the optical response.[23–24]

The dynamic response of a PDLC film can be obtained by considering the various torques acting on the LC contained within the droplets. Since the free energy of a droplet can be expressed in terms of the orientation of the droplet nematic director $\vec{N}_d$, the dynamic equation for the orientation of $\vec{N}_d$ is obtained by assuming that the two couples, elastic and induced by the electrical field, are balanced by viscous damping torque, then:

$$\Gamma\dot{\theta} = \frac{\partial}{\partial\theta}(F_{el} + F_E) \tag{1}$$

where θ is the angle between the droplet director and the direction of the applied field, Γ is a viscosity coefficient of the LC confined within the droplets, and F_E and F_{el} are the electric and elastic free energies, respectively. For a bipolar droplet one obtains:

$$\begin{aligned} \mathbf{F}_E &= -\frac{\mathbf{1}}{\mathbf{3}}\varepsilon_a E^{\mathbf{2}}_{App}\mathbf{S}\mathbf{S}_\mathbf{d}\mathbf{P}_\mathbf{2}\left(\overleftarrow{u}.\vec{\mathbf{N}}_\mathbf{d}\right); \\ \mathbf{F}_{el} &= -\frac{\mathbf{1}}{\mathbf{3}}\frac{\mathbf{K}}{\mathbf{R}^{\mathbf{2}}_{\mathbf{eff}}}\xi^{\mathbf{2}}\mathbf{S}\mathbf{S}_\mathbf{d}\mathbf{P}_\mathbf{2}\left(\vec{\mathbf{L}}.\vec{\mathbf{N}}_\mathbf{d}\right) \end{aligned} \tag{2}$$

ε_a represents the dielectric anisotropy of a LC molecule, E_{App} is the intensity of the applied field, S is the local order parameter, K is average elastic constant of the LC, R_{eff} is the effective radius of curvature, ξ is the eccentricity of the droplet, $\vec{\mathbf{L}}$ is the unit vector along the cavity symmetry axis, $\overleftarrow{u}$ is an unit vector along the direction of the applied field, and P_2 (x) is the second Legendre polynomial. We are interested here in the situation where the electric field is suddenly removed. Then the equation of motion becomes:

$$\dot{\theta} = \frac{1}{2\tau}\sin 2\gamma\left[\frac{\sin 2\theta}{\tan 2\alpha} - \cos 2\theta\right] \tag{3}$$

where

$$\sin 2\alpha = \frac{\sin 2\gamma}{\sqrt{\sin^2 2\gamma + (e^2 + \cos 2\gamma)^2}} \tag{4}$$

γ is the angle between the symmetry axis of the cavity and the direction of the applied field. τrepresents the caracteristic time of a droplet defined by:

$$\tau = \frac{R_{eff}^2}{K\varepsilon^2 S S_d}\Gamma \tag{5}$$

e is the reduced field defined by:

$$e = \frac{E_{App}R_{eff}}{\xi}\sqrt{\frac{\varepsilon_0\varepsilon_a}{K}} \tag{6}$$

where ε_0 is the dielectric permittivity of the vaccum, and $R_{eff}^2$is the mean squared curvature of the director field in the droplet.

The integration of equation (3) gives:

$$\omega = -\tan(\gamma)e^{-t/\tau} \tag{7}$$

with

$$\omega = \tan(\theta - \gamma) \tag{8}$$

The time dependance of the order parameter S_s(t), which is the second Legendre polynomial, can be easily obtained:

$$\mathbf{S}_s(t) = \frac{\mathbf{1}}{\mathbf{4}}\int_0^{\pi}\left(3\frac{(1-\omega\tan\alpha)^2}{(1+\omega^2)(1+\tan^2\alpha)} - 1\right)\sin\theta\, d\theta \tag{9}$$

and similary the average fourth Legendre polynomial can be written as:

$$P_{4S} = \frac{1}{2}\int\frac{1}{8}\left[\left(35\left(\frac{(1-\omega\tan\alpha)^2}{(1+\omega^2)(1+\tan^2\alpha)}\right)^2\right) - 30\left(\frac{(1-\omega\tan\alpha)2}{(1+\omega^2)(1+\tan^2\alpha)}\right) + 3\right]\sin\theta\, d\theta \tag{10}$$

In the absence of multiple scattering, the light intensity of the out-going light travelling perpendicular to a PDLC film can be described as follows:

$$I(z) = I_0 e^{-\rho_d\sigma_s z} \tag{11}$$

where I_0 represents the incoming light intensity, ρ_d is the number density of droplets, σ_s is the scattering cross section of the droplet, and z is the film thickness. The average scattering cross section of a droplet was obtained as a function of the two order parameters S_s (t) and P_{4s}(t).

In this work the scattering cross section can be calculated using two approaches: Rayleigh Gans Approximation (RGA) or Anomalous Diffraction Approach (ADA).[25–27] The ADA approximation will be used here, which is valid for larger droplets and which gives a better description for EB-cured films. In this approach, the scattering cross section is expressed as follows:

$$\sigma_s{}^{ADA} = \frac{1}{2}\sigma_0(kd)^2\left(\frac{\Delta n}{n_p}\right)^2\left[\left(\frac{\delta}{\Delta n}\right)^2 - \frac{2}{3}\frac{\delta}{\Delta n}(1+S_s) + \frac{4}{105}(7 - 10S_s + 3(P_{4s}))\right] \tag{12}$$

where σ_0 is the geometrical cross section:

$$\sigma_0 = \pi\frac{d^2}{4} \tag{13}$$

d is the mean droplet diameter, k is the wave number of the light, Δn is the birefringence of the LC molecule expressed by:

$$\delta = n_p - n_0 \tag{14}$$

where n_p is the refractive index of the polymer matrix and n_0 is the ordinary refractive index of the LC.

When the droplet size is much smaller than the wavelength of light, the RGA approximation can be used. Here the total scattering cross section for a droplet averaging over all droplet director orientations in the film can be written as:

$$\sigma_s{}^{RGA} = \sigma_0\frac{(kd)^4}{108}\left[(\xi - \eta S_d)^2 + \eta S_d(2\xi + \eta S_d)(1 + S_s)\right] \tag{15}$$

where

$$\xi = \frac{1}{3}Tr(\underline{\varepsilon}_r) - 1 \tag{16}$$

with

$$\underline{\varepsilon_r} = \frac{1}{\varepsilon_p}\begin{bmatrix} \varepsilon_\perp & 0 & 0 \\ 0 & \varepsilon_\perp & 0 \\ 0 & 0 & \varepsilon_{//} \end{bmatrix} \qquad (17)$$

ε_r is the relative dielectric permittivity tensor of the LC, and $\varepsilon_{//}$and $\varepsilon_\perp$are the parallel and perpendicular components of the dielectric constant of the LC molecule. $\varepsilon_p$is the dielectric permittivity of the polymer matrix.

$$\eta = \frac{\varepsilon_{//} - \varepsilon_\perp}{3\varepsilon_p} \qquad (18)$$

The ordinary and extraordinary indexes of refraction of E7 at a wavelength of 632.8 nm and at room temperature are $n_o = 1.5216$ and $n_e = 1.7378$, respectively. The only two parameters used for the fit of the dynamic response are the coefficient of viscosity Γ and the elastic constant K of the LC medium confined within the droplets. An average value of droplet radii equal to 150nm was considered, according to observations on the morphology of these systems obtained by scanning electron microscopy.[28] All other parameters (eccentricity of the droplet, effective radius of curvature, and the viscosity of the LC droplets) were kept constant during the calculations with the exception of the film thickness which is introduced individually. Finally the fitting procedure will be carried out in optimizing the parameters Γ and K.

Figure 4 and 5 represent the experimental data together with the theoretical results, using the two approaches described above, reflecting the relaxation of the normalized transmission with time. In general, the theory describes quite well the experimental relaxation behaviour. In particular, Figure 4 displays a comparison of theoretical and experimental results of relaxation of the transmission of PDLC samples prepared by EB-curing using the ADA approach. A good agreement was observed between experiment and theory for both thin and thick films. The theoretical calculations gave an elastic constant $K = 0.9.\ 10^{-13}$ N and a viscosity coefficient $\Gamma = 0.15$ P. This value of K obtained by the theory, using the approach of the ADA; is significantly different from the known value (in the order of 10^{-12} N). This result is not surprising since the relaxation of the optical transmission of these complex systems depends on many parameters, which are not well-known experimentally. K was chosen as the fit parameter because it represents the parameter that controls to a large extent the profile of the relaxation curve and seems to give the best adjustment in terms of relaxation times of these systems.

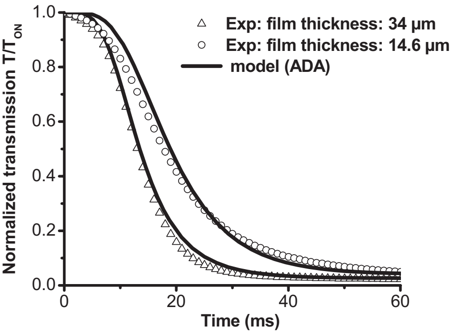

Figure 4.
Experimental (symbols) and theoretical (lines) dependencies of T/T_{on} on relaxation time of EB-cured TPGDA (30 wt-%) / E7 (70 wt-%) films with two different thicknesses calculated in the ADA approximation.

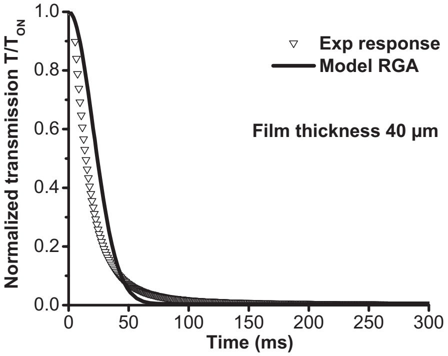

Figure 5.
Experimental (symbols) and theoretical (lines) dependencies of T/T_{on} on relaxation time of a UV-cured TPGDA (30 wt-%) / E7 (70 wt-%) sample calculated in the RGA approximation.

In the case of the film elaborated under UV irradiation, shown in Figure 5, only the

RGA theory allows to obtain a satisfactory description of the experimental results, which could still be improved. However, a good agreement between theory and experiment was observed particularly in the beginning of the first fast relaxation process. For longer relaxation times, the difference between theoretical and experimental findings became more significant. In the RGA approximation used here, the theoretical calculations yielded an elastic constant $K = 0.2.\ 10^{-13}$ N and a viscosity coefficient $\Gamma = 0.25$ P.

It should be pointed out that the chosen model is supposed to describe a homogeneous material including an uniform distribution of LC droplets of identical shapes and sizes. In real PDLC systems the situation is usually much more complicated since quite often, a large polydispersity in size and shape of the droplets is found, especially for the UV-cured samples.

The anchoring effects at the polymer/LC interface should also be taken into account, particularly for smaller domain sizes. Thus, the theoretical description of the dynamic response of UV-cured systems, which certainly present multiple relaxation modes, require a more sophisticated model to obtain a more reasonable fit of the experimental data.

Conclusion

In this work, the time decay of light transmission of EB- and UV-cured PDLC films was analyzed in terms of film thickness, after applying an electrical pulse. The experimental data were rationalized by using a dynamic model based on simple assumptions, yielding at least a qualitative description of the optical reponse of the complex PDLC materials. Analysis of sample morphologies reveal often polydisperse distributions of LC domain sizes and shapes, which cannot be taken into account by the model discussed here.

Comparison of experimental and theoretical results for EB- and UV –cured materials indicate the presence of at least two modes of relaxation, a fast relaxation process followed by a slow mode. The ADA model indeed describes well the relaxation behaviour of EB-cured films, whereas experimental results from UV-cured samples coincide better with the RGA model. For samples prepared by EB-curing, the shape of the experimental curves suggest the presence of a dominant single relaxation mode, which seems to be in good correlation with the morphological results revealing the presence of nearly monodisperse LC domains.

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