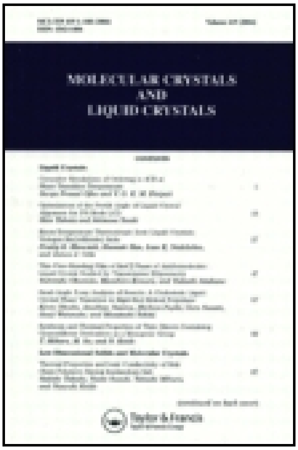

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Relaxation Behaviour of Monomer/Liquid Crystal Blends after Exposure to Ultraviolet Light

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Polymer Dispersed Liquid Crystal materials were elaborated by in situ polymerization induced phase separation under ultraviolet (UV) radiation. Binary model systems composed of a diacrylate monomer and a liquid crystal (LC), 4-cyano-4′-n-pentyl-biphenyl (5CB), were used as starting materials in the process of polymerization/crosslinking. The optical transmission of the monomer/LC films was monitored as function of time covering the period of exposure to UV-light and the following relaxation processes of the irradiated samples. The off-state transmission shows several characteristic processes, a short time relaxation process which decays within seconds, an unexpected intermediate period where transmission was found to enhance, followed by a long lasting relaxation process which takes tens of minutes to decay completely. A discussion of these processes in terms of the kinetics of phase separation is presented.

Keywords: liquid crystal; monomer; phase separation kinetics; polymer; relaxation process; ultraviolet irradiation

1. INTRODUCTION

A special class of polymer/liquid crystal (LC) composite materials, known as "Polymer Dispersed Liquid Crystals" (PDLCs), represent heterogeneous thin films consisting generally of micron-sized nematic liquid crystalline domains dispersed in a polymeric matrix [1,2]. These

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materials are particularly interesting for their electro-optical applications in the field of displays and privacy windows [3,4]. By applying an electrical field to the PDLC films, the direction of the LC molecules changes inside domains and, under certain conditions, the intensity of light transmitted by the film can vary between an opaque scattering off-state to a transparent on-state. These films are generally prepared by polymerization/crosslinking reactions of blends of LCs and low molecular weight monomeric species, under ultraviolet (UV) irradiation, leading to a phase separation between the growing polymer network and LC domains formed [5]. The electro-optical performances of these heterogeneous materials such as threshold and switching voltages, off- state and on-state transmissions, and response times depend, in a crucial way, on many parameters such as number density, size, and shape of LC domains [6,7]. These parameters are principally controlled by nature and conditions of the method of phase separation used.

In the present work, the kinetics of phase separation [8,9] was investigated during polymerization/crosslinking reactions, since these dynamic processes represent still an unresolved problem. The dynamics of the phase separation control to some extent the morphology of these PDLC systems [10–15]. In this communication, the dynamics of phase separation of selected well defined monomer/LC mixtures will be investigated to determine and to analyse the different processes of relaxations which accompany the preparation of PDLC systems during a polymerization induced phase separation method. During the polymerization/crosslinking processes, the LC molecules become less miscible with the formed polymer chains whose length increase as polymerization advances, and finally the mixture separates in two phases, an isotropic chemically crosslinked polymer network and domains of segregated LC.

To monitor the kinetics of phase separation, the optical transmittance of monomer/LC films will be measured without application of an electrical field, during the period of time of the UV-light exposure. It is important to follow the relaxation phenomena occuring after the irradiation period on a time scale allowing to obtain constant transmission values, indicating that the polymer/LC systems achieved a chemically and thermodynamically stable state.

A single compound, 4-cyano-4′-n-pentyl-biphenyl (5CB), was used as low molecular weight nematic LC. A series of three propyleneglycol-diacrylates, characterized by molecular weights of 300 g/mol, 540 g/mol and 900 g/mol, were employed as difunctional monomers, allowing to vary the crosslinking density of the obtained UV-cured polymer network under the same irradiation conditions.

2. EXPERIMENTAL PART

2.1. Materials and Sample Preparation

4-cyano-4′-n-pentyl-biphenyl (commercial designation 5CB) from Synthon Chemicals (Wolfen, Germany) was used as LC in this work. 5CB exhibits a nematic-isotropic transition temperature of $T_{NI} = 35.3^\circ C$ and a positive dielectric anisotropy. Three diacrylates with varying numbers of repeating propyleneglycol units between acrylic end groups were used as monomers. One of them was Tripropyleneglycoldiacrylate (TPGDA) from Cray Valley (France). Polypropyleneglycoldiacrylates (molecular weight in number: 540 g/mol and 900 g/mol) were obtained from Sigma-Aldrich (Germany). The monomers will be abbreviated hereafter as TPGDA, PPGDA540, and PPGDA900.

Initial mixtures containing 30 weight-percent (wt.%) of monomer, 70 wt.% of 5CB, and 1wt.% (of the weight of the monomer) of a photoinitiator (Lucirin TPO, from BASF) were mixed together for several hours until the mixture became homogeneous. For optical investigations, the initial reactive mixtures were sandwiched between two 0.7 mm thick standard glass plates before UV-light exposure. The film thickness of the polymer/LC films was measured by a micrometer calliper (Mitutoyo, uncertainty $\pm 1\,\mu m$).

2.2. Ultraviolet Curing and Optical Transmission Measurements

The polymerization and crosslinking processes were induced by a LC–03 irradiation source (from Hamamatsu), equipped with a Xenon lamp covering the spectrum between 250 and 800 nm, and an optical fiber. The samples prepared as mentioned above were exposed to UV irradiation at a distance of 3 cm from the end of the optical fiber. The light intensity was kept constant at its highest level, and the exposure time of the samples was varied between 9.75 s and 60.06 s by using an automatic shutter. In general, the same experiment was repeated five times to check the reproducibility of the results. No temperature control during the irradiation processes has been performed.

A standard set-up including a laser, a sample holder and a photodiode together with a computer controlled data acquisition was employed for studies of optical properties. The transmission of unpolarized HeNe laser light ($\lambda = 632.8$ nm) passing perpendicular through the monomer/LC film was measured as function of time without applying an electrical field. The distance between photodiode and sample was about 32 cm and the angle between the optical fiber and the axis Laser/sample/photodiode was 38° (Fig. 1).

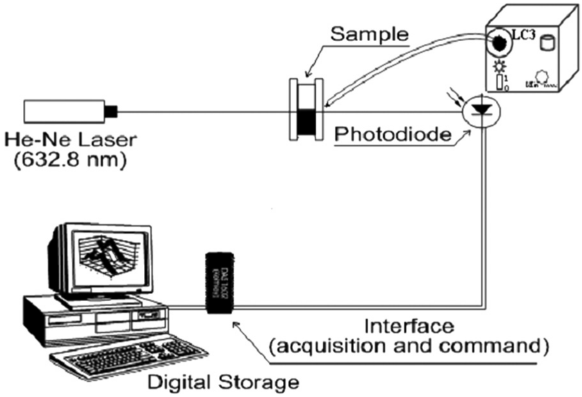


FIGURE 1 Set-up for measuring optical transmission and UV exposure of monomer/LC films. The LC–03 UV/visible lamp covers the spectrum from 250 nm to 800 nm.

Measurements of the light transmitted by the film was made in the homogeneous state during 20 s, followed by data acquisition during 100 s covering the exposure time to UV light (9.75 s–60.06 s) and the relaxation time after the end of sample illumination. Consecutive measurements of transmittance, in the absence of irradiation, were conducted during 20 s every 5 min, up to a total evaluation period of 30 min. The transmittance data were corrected using appropriate calibration standards.

3. RESULTS AND DISCUSSION

Polymer/LC films were prepared by polymerization induced phase separation of initially homogeneous monomer/LC solutions. In the absence of an electrical field applied to the films, the kinetics of phase separation was studied as function of applied UV dose for diacrylic monomers exhibiting the same chemical structure but different length between the two acrylic end groups. Samples were made from initial mixtures of composition 30 wt.% monomer and 70 wt.% LC prior to UV-curing. The intensity of transmitted light at right angle in the off-state was recorded as function of time.

Figure 2 shows the kinetics of phase separation of the TPGDA/5CB system upon UV irradiation, by measuring the transmittance as function of time for 6 representative samples which were exposed to UV-light during 9.75 s, 21.56 s, 32.68, 43.01 s, 56.08 s, and 60.06 s, respectively. The results clearly indicate that the period of

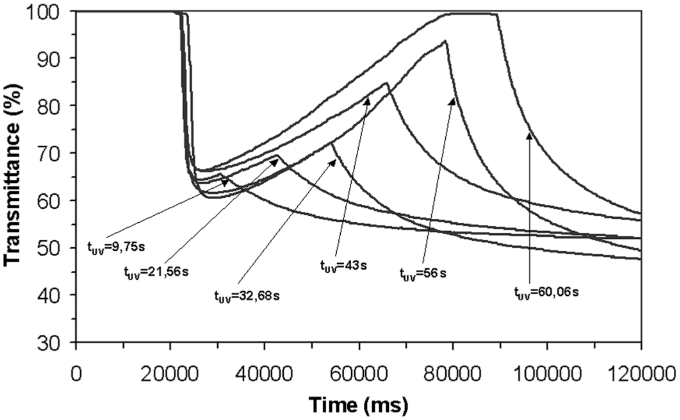
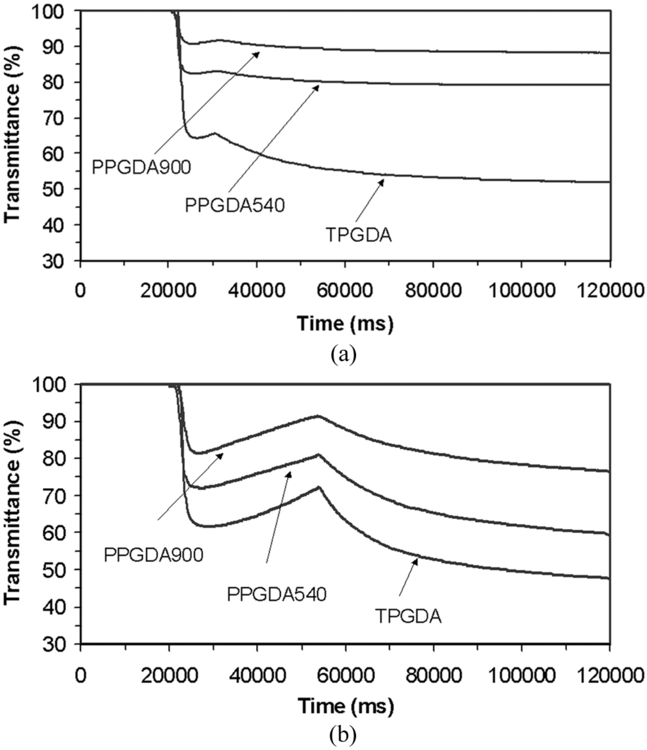


FIGURE 2 Transmission of 30 wt.% TPGDA/70 wt.% 5CB films exposed to different UV-light exposure times as indicated in the figure. Sample thicknesses were around 7 μm.

UV-exposure of the sample has a significant effect on the evolution of the film transmittance. In the first time domain spanning the range between $t = 0$ s and $t = 20$ s, the transmittance remains constant at 100%. The film texture is transparent meaning that the monomer/LC LC blends are homogeneous and no phase transition takes place. The time range starting from $t = 20$ s corresponds to the illumination period of the UV-light source. A fast relaxation process was observed whereby the film transmission undergoes a sharp drop. It can last only few seconds under certain conditions. In early stages of phase separation of LC domains, fluctuations grow fast inducing a rapid increase of the scattered light and a concomittent drop in the transmitted light. Since the rate of polymerization under a high UV intensity is fast, subsequently phase separation is equally rapid, and the initial growth of LC domains induces a strong scattering of light and a sharp decrease in the transmittance.

For times exceeding this first fast relaxation process, an unusual enhancement of the transmittance was observed. Depending on the UV-light exposure time, this process covers a period of time going from some seconds to several tens of seconds. Increasing UV-light exposure periods lead to increasing transmittance values. For example, for an exposure time of 9,75 s the maximum transmittance was $T_{\max} = 66\%$, whereas for an UV-light period of 60.06 s, a value of $T_{\max} = 100\%$ was achieved. It can be assumed that the UV-source used in our experiments not only emits in the range of UV- and visible wavelength, but also provides infrared radiation responsible for sample heating. Starting the irradiation process at room temperature, such a heating process usually takes place 2–3 s after illumination of the source, since the covering glass plate acts like a screen, thus delaying the increase of the sample temperature.

For times exceeding the maxima of transmission corresponding to the end of the irradiation period, Figure 2 shows decays of the transmittance due to the phase transition from an isotropic phase at higher temperatures to a nematic + isotropic phase at lower temperatures. The relaxation processes exhibit faster decays for films exposed to longer UV-light periods. Random orientation of nematic directors in the dispersed LC domains and the strong variation of refractive indices at the interface polymer/LC give rise to further enhancement of the scattering intensity.



(a)

(b)

FIGURE 3 Transmission versus time of 30 wt.% monomer/70 wt.% 5CB films exposed to two different UV-light exposure times (a) $t_{UV} = 9.75\,s$ and (b) $t_{UV} = 32.68\,s$.

The evolution of the kinetics of phase separation of the TPGDA/5CB mixture compared to PPGDA540 and PPGDA900 systems is shown in Figure 3, where the UV-light exposure period was chosen as a) $t_{UV} = 9.75$ s, and b) $t_{UV} = 32.68$ s, respectively. In the time domain between $t = 0$ s and $t = 20$ s, transmittance values of all homogeneous samples remain at 100%, as expected. The same fast relaxation process as shown in Figure 2 takes place for all monomer/LC systems when the films were illuminated by the UV-light source. Interestingly, the fast decrease of transmittance, the enhancement effect, and the final transmittance values depend on the molecular weight of the monomer. Transmittance values are decreasing in the following order PPGDA900, PPGDA540, TPGDA, thus inversely proportional to the chain length of the monomers.

In the case of PPGDA900, a loosely crosslinked polymer network will be formed by UV-curing, whereas a more dense network will be obtained for PPGDA540. TPGDA, possessing the shortest distance between the two reactive groups, gives the highest crosslinking density of the three monomers considered here. As a consequence, smaller segregated LC domains with dimensions close to the wavelength of visible light will be obtained by increasing the crosslinking density of the polymer network. The resulting polymerized TPGDA/LC films will, therefore, scatter visible light more strongly compared to PPGDA540- and PPGDA900-systems.

Comparison between Figures 3a and 3b shows that considerable lower transmittance values were obtained at $t = 120000$ s for all three monomers, if an UV-curing period of $t_{UV} = 32.68$ s was applied. It can be assumed that the irradiation time $t_{UV} = 9.75$ s, used for Figure 3a, does not lead to complete monomer conversion, so that the final transmittance values do not correspond to a stable thermodynamic state.

CONCLUSIONS

PDLC films prepared by in-situ UV irradiation using a polymerization induced phase separation process were investigated in order to understand the phenomena related to the kinetics of polymer/LC phase separation. A pronounced drop of the transmission was observed in all systems studied when the samples were initially exposed to the UV radiation. For irradiation times exceeding a few seconds, the results obtained from real time observations of the optical transmission indicate clearly an enhancement effect of the transmission due to a temperature increase of the samples by the infrared part of the spectrum of the UV source. In case of prolonged irradiation time, temperature of samples may exceed the phase transition temperature to the isotropic phase, so that the polymerization/crosslinking process continues in the one-phase region. Thermally controlled phase separation takes place on the cured films when the irradiation period ends.

These relaxation processes and the final off-state transmission depend on the polymer architecture i.e. the degree of crosslinking, which can be controlled by different chain length between the two reactive acrylic groups.

REFERENCES

[1] Fergason, J. L. (1984). US Patent, 4, 435, 047.
[2] Fergason, J. L. (1985). *SID Dig.*, *16*, 68.
[3] Gu, C., Xu, Y., Liu, Y., Pan, J. J., Zhou, F., & He, H. (2003). *Opt. Mater.*, *23*, 219.
[4] Lampert, C. M. (2004). Chromogenic smart materials. *Mater. Today*, *7*, 28–35.
[5] Doane, J. W., Golemme, A., West, J. L., Whitehead, J. B., & Wu, B. G. (1988). *Mol. Cryst. Liq. Cryst.*, *165*, 511.
[6] Carter, S. A., LeGrange, J. D., White, W., Boo, J., & Wiltzius, P. (1997). *J. Appl. Phys.*, *81*, 5992.
[7] Wang, M., Li, W., Zou, Y., & Pan, C. (1997). *J. Phys-D: Appl. Phys.*, *30*, 1815.
[8] Cahn, J. W. (1968). *Trans. Metall. Soc. AIME*, *242*, 166.
[9] Flory, P. J. (1953). *Principles of Polymer Chemistry*, Cornell University Press: Ithaca, New York.
[10] Nephew, J. B., Nihei, T. C., & Carter, S. A. (1998). *Phys. Rev. Lett.*, *80*, 3276.
[11] Xia, J., Wang, J., Lin, Z., Qiu, F., & Yang, Y. (2006). *Macromolecules*, *39*, 2247.
[12] Lin, Y.- H., Ren, H., Wu, Y. H., Liang, Y., & Wu, S. T. (2005). *Opt. Express*, *13*, 468.
[13] Qian, T., Kim, J. H., Kumar, S., & Taylor, P. L. (2000). *Phys. Rev. E*, *61*, 4007.
[14] Kim, J. Y. & Palffy-Muhoray, P. (1991). *Mol. Cryst. Liq. Cryst.*, *202–04*, 93.
[15] Zhang, W., Lin, J., Yu, T., Lin, S., & Yang, D. (2003). *Europ. Polym. J.*, *39*, 1635.