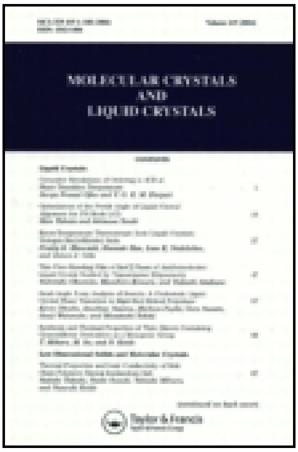

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Unusual Phase Separation Kinetics of Polyacrylate/E7 Blends

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The transmission versus time curves of in-situ UV-cured Tripropyleneglycoldiacrylate (TPGDA)/E7 films reveal three regions: A first domain corresponding to a transparent film of the initial TPGDA/E7 mixture before exposure to UV light. In the second time domain, the sample exhibits a fast relaxation process just after the beginning of the UV irradiation of the monomer/LC blend. A surprising third domain, characterised by an enhancement of the film transparency, is observed at longer relaxation times. This process, covering a period of time going from several milliseconds to minutes, depends on the conditions of sample preparation and film thickness.

Keywords Liquid crystal; monomer; phase separation kinetics; relaxation times; ultraviolet irradiation

1. Introduction

Polymer Dispersed Liquid Crystals (PDLCs), discovered some twenty five years ago by Fergason [1,2] and extensively studied by a large number of laboratories [3–14], represent great potential for a variety of electro-optical applications such as smart windows [3,4] and information displays. In their most common form, PDLC films are made of micron-sized liquid crystalline (LC) domains dispersed in a solid polymer matrix. The orientation of the LC molecules inside the domains change upon application of an electrical field and under certain conditions, the intensity of the transmitted light can be varied between an opaque off-state to a transparent on-state. These systems are generally prepared by a technique of phase separation induced by polymerization/crosslinking reactions (PIPS) of monomers under

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irradiation by UV light. The growth of the polymer network and the formation of LC domains lead to a drop of the optical transmission [5].

In this work, different processes were investigated during the preparation of PDLC films [10,15] by the phase separation method [15–17] under UV irradiation. Model mixtures were considered to understand the kinetics of polymerization and phase separation which show unusual relaxation phenomena [11,12]. During polymerization/crosslinking reactions the LC molecules become less miscible with the growing polymer. The length of polymer chains formed increases as polymerization proceeds; then the mixture will separate in two phases, one consisting of the isotropic chemically crosslinked polymeric network and the other consisting of isolated LC domains [6,7].

In this study of the kinetics of phase separation, the transmitted light was measured as function of time without applying an electric field, before, during and after the period of UV-light exposure. The optical transmission was measured until a constant value was reached indicating that the system was chemically and thermodynamically stable.

2. Experimental Part

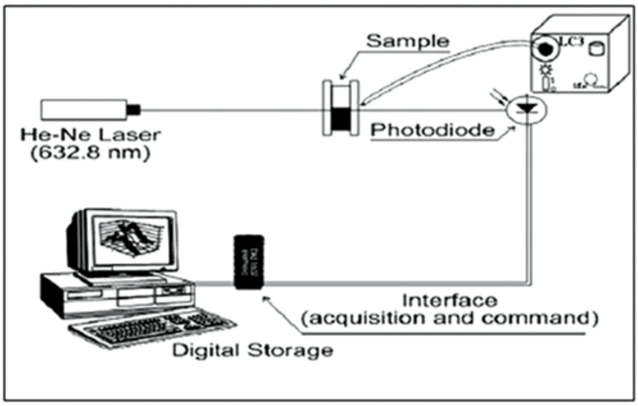
2.1. *Materials and Sample Preparation*

The commercial liquid crystal E7 was employed, provided by Merck KG (Darmstadt), which represents a mixture of four cyanobiphenylene derivatives. This LC mixture exhibits a nematic-isotropic transition temperature at $T = 60°C$ and presents a large nematic phase between −62°C and +60°C. Tripropyleneglycoldiacrylate (TPGDA), obtained by Cray Valley (France), was used as difunctional monomer.

Initial mixtures containing 30 weight-percent (wt.%) of monomer, 70 wt.% of E7, and 1 wt.% (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 standard glass plates. The film thickness of the polymer/LC films was measured by a micrometer calliper (Mitutoyo, uncertainty ± 1 μm).

2.2. *Experimental Methods*

The polymerization and crosslinking processes were induced by a LC–03 (Fig. 1) 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 distances of 3.5 cm and 1 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 10 s and 60 s by using an automatic shutter. In general, the same experiment was repeated six times to check for reproducibility of the results. No temperature control during the irradiation processes has been performed; the experiments were carried out at room temperature (293 K). 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 He-Ne laser light ($\lambda = 632.8$ nm) passing perpendicular through the monomer/LC film



(a)

(b)

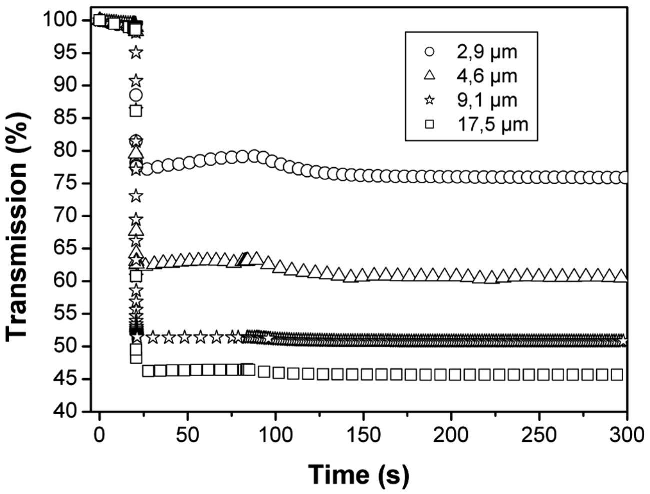
Figure 1. (a) Set-up for measuring optical transmission properties and UV exposure of monomer/LC films; (b) Source of Ultraviolet (UV) irradiation (Hamamatsu LC-3). (Figure appears in color online.)

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° (see Fig. 1).

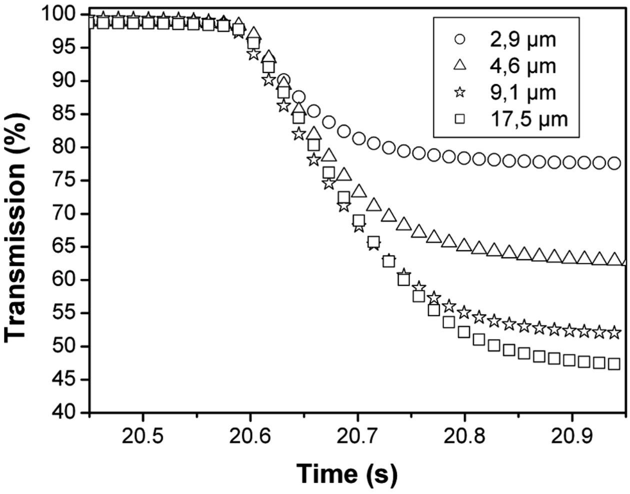
Measurements of the light transmitted by the films was made in the homogeneous state during 20 s, followed by data acquisition during 300 s covering the exposure time to UV light (10 s and 60 s) and the relaxation time after the end of sample illumination. Consecutive measurements of transmittance, in the absence of irradiation, were conducted during 30 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

Figures 2–5 show the kinetics of phase separation of the TPGDA/E7 system obtained by measuring the light transmission of samples which were exposed to



(a)



(b)

Figure 2. (a) Optical transmission of 30 wt.% TPGDA/70 wt.% E7 films exposed to UV-light. Exposure time = 60 s, the distance between the optical fiber and sample was 3.5 cm. (b) Zoom of Figure 2a between t = 20.45 s and t = 20.95 s.

UV light during 10 s (Figs. 3 and 5) and 60 s (Figs. 2 and 4). Two different distances between the end of the optical fiber and the sample, 3.5 cm (Figs. 2 and 3) and 1 cm (Figs. 4 and 5), were considered to vary kinetics of polymerization and phase separation. The fiber-sample distance of 3.5 cm was chosen as the lower limit to achieve a complete monomer/polymer conversion, whereas the fiber-sample distance of 1 cm corresponds to 100% monomer conversion and fast reaction kinetics.

The results indicate that the period of UV exposure of the sample has a significant effect on the evolution of film transmission. The transmission versus time curves of several samples reveal three distinguished domains: the first one, observed before the application of UV light, is characterized by high transmission values attesting

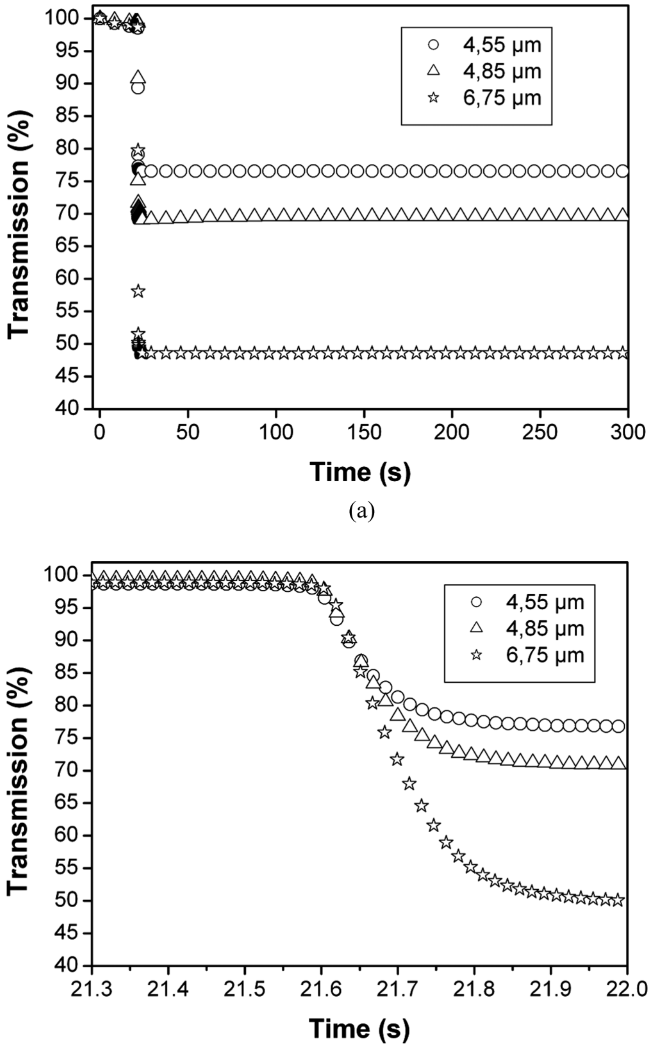
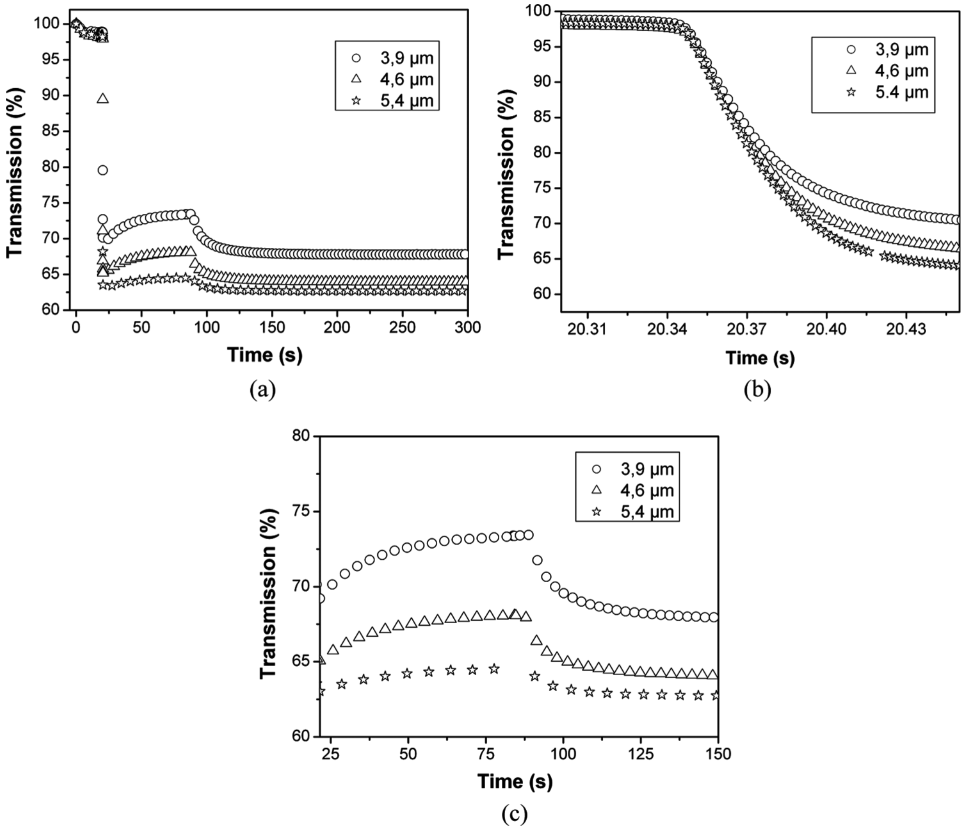


Figure 3. (a) Optical transmission of 30 wt.% TPGDA/70 wt.% E7 films exposed to UV-light. Exposure time = 10 s, the distance between the optical fiber and sample was 3.5 cm. (b) Zoom of Figure 3a between t = 21.30 s and t = 22.00 s.

that the films are optically homogenous. In the second domain, which begins just after the application of UV light, the sample exhibits a fast relaxation process. Since the polymerization rate under UV light is generally quite fast and the subsequent phase separation is also a rapid process, the initial growth of LC domains induces a strong light scattering and hence a sharp decrease of the transmission. A third time domain was also observed, characterized by an unusual enhancement of the film transparency, at longer relaxation times.

Figures 2 and 3, obtained at the same fiber-sample distance from two different UV-exposure periods, 60 s and 10 s, respectively, show that these relaxation



(a)

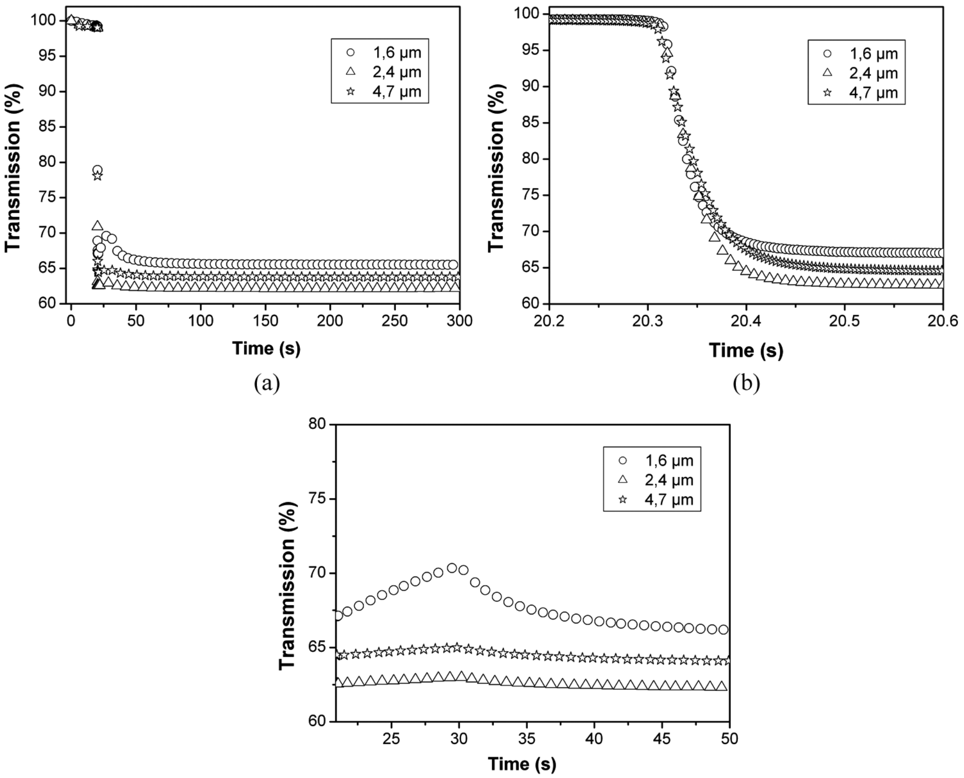
(b)

(c)

Figure 4. (a) Optical transmission of 30 wt.% TPGDA/70 wt.% E7 films exposed to UV-light. Exposure time = 60 s, the distance between the optical fiber and sample was 1 cm. (b) Zoom of Figure 4a between t = 20.30 s and t = 20.44 s. (c) Zoom of Figure 4a between t = 21.5 s and t = 150 s.

processes depend on the illumination time thus on the overall dose received by the films. As expected, the kinetics of phase separation became faster when the UV dose was increased, and the transmission values in the final OFF state decreased correspondingly, depending on the film thickness.

The re-enhancement of the transmission values occurring after the sharp decrease of the relaxation curves, as shown in Figures 2a, 4a/c, and 5a/c, reveal that an unusual effect took place. This increase of the transmission is probably due to a heating of the films induced by the infrared part of the spectrum of the UV source. In this case of prolonged irradiation time, temperature of samples may exceed the phase transition temperature to the isotropic phase, so that polymerization/crosslinking processes continue in the homogeneous one-phase region. The curves of all figures show that this thermal effect, observed at longer UV irradiation times, was more significant in the case of short optical fiber-sample distances. Such an effect is clearly observed in Figures 4a/c and 5a/c corresponding to the lower fiber-sample distance (1 cm). In Figures 2a and 4a/c, where the UV exposure time was kept constant at 60 s, the relaxation curves indicate that the unusual thermal effect was less significant



(a) (b)

(c)

Figure 5. (a) Optical transmission of 30 wt.% TPGDA/70 wt.% E7 films exposed to UV-light. Exposure time = 10 s, the distance between the optical fiber and sample was 1 cm. (b) Zoom of Figure 5a between t = 20.2 s and t = 20.6 s. (c) Zoom of Figure 5a between t = 20.9 s and t = 50 s.

in the case of large distances between the optical fiber and the film. Interestingly, the fast decrease of transmission, the enhancement effect, and the final transmittance values depend on the distance between the optical fiber and the sample.

4. Conclusions

PDLC films, prepared by in-situ UV-irradiation using a PIPS process, were investigated in order to understand the phenomena related to the kinetics of polymerization/crosslinking and polymer/LC phase separation. E7 as LC and TPGDA as prepolymer, were mixed together to form a homogeneous transparent system. A fast decrease of the transmission was observed when the films are exposed to UV-irradiation. Furthermore, the results show a significant re-enhancement of the transmission values probably due to an increase of the temperature of the samples by the infrared part of the spectrum of the powerful UV source. For high UV dose values, the temperature of the films can exceed the phase transition temperature from the nematic to the isotropic phase. This phenomenon strongly depends on the distance between the end of the optical fiber and the sample, the chosen monomer/LC system, film thickness, and the architecture of the polymeric system.

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