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Thermal study of photopolymerization reaction in polyacrylate/liquid crystal blends

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ABSTRACT

PDLCs composite materials (Polymer Dispersed Liquid Crystal) were elaborated by polymerization induced phase separation under UV-light. Binary systems composed of Tripropyleneglycol diacrylate (TPGDA) monomer and a liquid crystal mixture (E7) were used as starting materials in the process of polymerization/crosslinking leading to a phase separation between polymer and liquid crystal. The time behaviour of the optical transmission of these films was experimentally studied during the period of exposure to UV-light in the absence of external applied fields. The transmission versus time curves of in-situ UV-cured 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, a second time domain where the sample exhibits a fast relaxation process just after the beginning of the UV irradiation of the monomer/LC blend and a unusual third domain, characterised by an enhancement of the film transparency at longer relaxation times. This process depends on the conditions of sample preparation and film thickness. In this study, a temperature of a sample has been controlled after, during and before the application of UV light. © 2020 The Authors. Published by Elsevier Ltd.

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1. Introduction

The mixtures of polymer and low-molecular-weight liquid crystal (LC) are of immense interest scientifically and technologically due to their potential applications in the domain of electrooptical devices and flat panel displays... [1,2]. In their most common form, PDLC films are made of micron-sized liquid crystalline (LC) domains dispersed in a solid polymer matrix [3,4]. 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 [4,5]. These systems are generally prepared by a technique of phase separation induced by polymerization/crosslinking reactions (PIPS) of monomers under irradiation by UV light. In this work, different processes were investigated that take place during the preparation of PDLC films by the phase separation method under UV irradiation. 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]. Model mixtures were considered to understand the kinetics of polymerization and phase separation which shows unusual relaxation phenomena [7]. In this study of phase separation kinetics, the transmitted light was measured as function of time without applying an electric field, before, during and after the period of UV-light exposure [7,8]. The kinetics of phase separation of the TPGDA/E7 system was obtained by measuring light transmission by the samples during the irradiation process. The temperature of the samples was controlled by an electronic thermal probe which the goal to check the cause of this new phenomenon.

2. Materials and methods

The liquid crystal used in this work was the LC E7 which represents a mixture of four cyanobiphenylene derivatives.

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Tripropyleneglycoldiacrylate (TPGDA) was used as difunctional monomer from Cray Valley-TOTAL Co., Corp. (France). Initial mixtures containing 30 wt-percent (wt.%) of monomer, 70 wt% of liquid crystal E7 (Merck KGaA, Germany), 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. A thermal probe fixed between two standard glass plates, is used for measurements of sample temperature. The film thickness of the polymer/LC films was measured by a micrometer calliper (Mitutoyo, uncertainty $\pm 1 \mu\text{m}$). A phase separation induced by polymerization/crosslinking processes, were induced by a LC3 irradiation source (from Hamamatsu) [7,8], equipped with a Xenon lamp and an optical fiber. The samples prepared, as mentioned above, were exposed to UV irradiation at distances of 3.5 cm, 2 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. The transmission of unpolarized He-Ne laser light ($\lambda = 632.8 \text{ nm}$) passing perpendicular through the monomer/LC film was measured as function of time without applying an electrical field.

3. Results and discussion

Fig. 1 show the kinetics of phase separation of the TPGDA/E7 system obtained by measuring the light transmission for samples which were exposed to UV light during 60 s (Fig. 1) and 10 s (Fig. 2). The distances D between the end of the optical fiber and the sample it was around 1 cm. 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 domains: a first one (from 0 s to 20 s), observed before the application of UV light, is characterized by high transmission values attesting that the films are homogeneous. The transmission measurement time in this domain was 20 s.

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 (a few ms), the initial growth of LC domains induces a strong light scattering and hence a sharp decrease in the transmission. A third time domain was also observed in the presence of UV radiation,

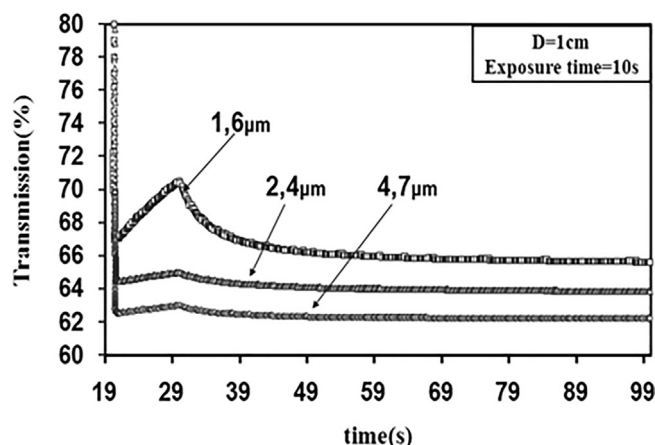


Fig. 2. Transmission of TPGDA/E7 films exposed to UV-light during 10 s for $D = 1 \text{ cm}$.

characterized by an unusual enhancement of the film transparency, at longer relaxation times. If the UV radiation is cut (after 60 s for Fig. 1 and 10 s for Fig. 2), the light transmitted decreases to low values corresponding to opaque PDLC films. The overall duration of our measure was 300 s. When the UV dose increases, the kinetics of phase separation become more fast, and a certain decrease of the transmission values in the final OFF states was observed, depending on film thickness. It is clear that for low-thickness samples ($3.9 \mu\text{m}$ in Fig. 1) the thermal effect observed in the third time is greater. The thinner the PDLC film is, the warmer it gets and it reaches higher temperatures. For the $5.4 \mu\text{m}$ thickness sample (Fig. 1), the thermal effect is less significant.

The re-enhancement of the transmission values occurring after the sharp decrease of the relaxation curves, as shown in Fig. 2, reveal that an unusual effect takes place. This increase in transmission (the third domain) is due probably to a heating of the films which is more important with increasing UV dose.

In this work, the temperature of sample has been controlled by a thermal probe after, during and before the application of UV light. The study of a temperature of sample TPGDA/E7 under UV light irradiation, from the thermal probe, was showed in Fig. 3. The temperature of the sample presents a peak value in the 10 first seconds.

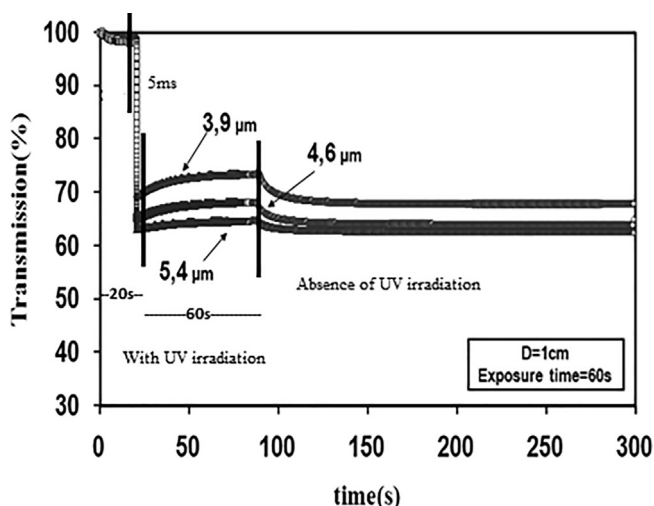


Fig. 1. Transmission TPGDA/E7 films exposed to UV-light during 60 s for $D = 1 \text{ cm}$.

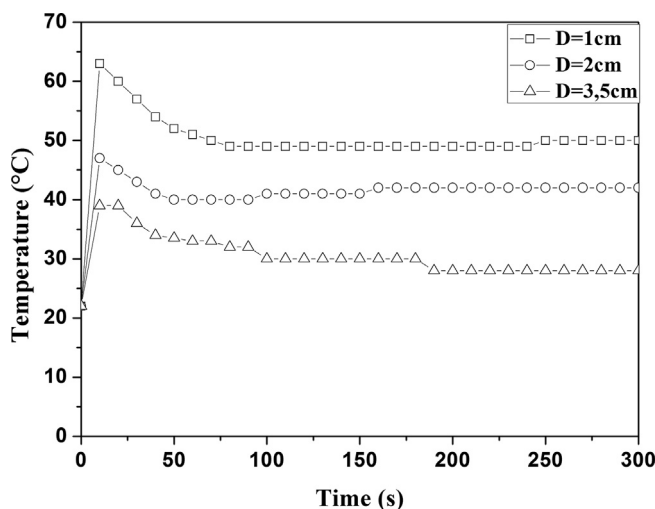


Fig. 3. Temperature of TPGDA/E7 films for three distances 1 cm, 2 cm and 3.5 cm.

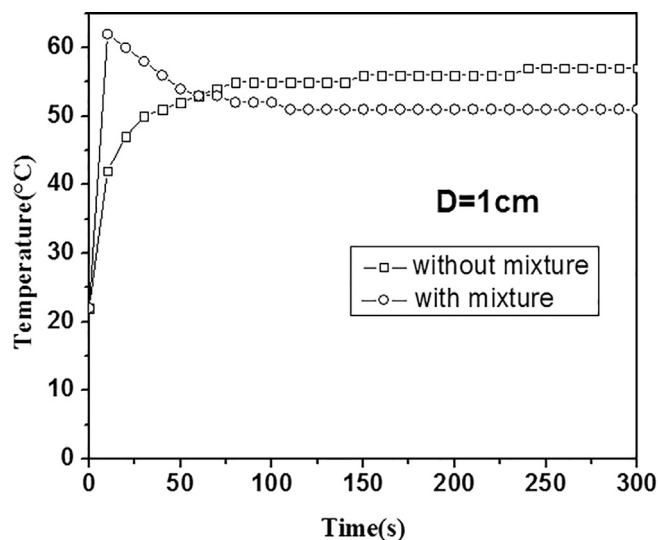


Fig. 4. Temperature of thermal probe with sample and without sample for three distances between optical fiber and the sample: 1 cm (a), 2 cm (b) and 3.5 cm (c).

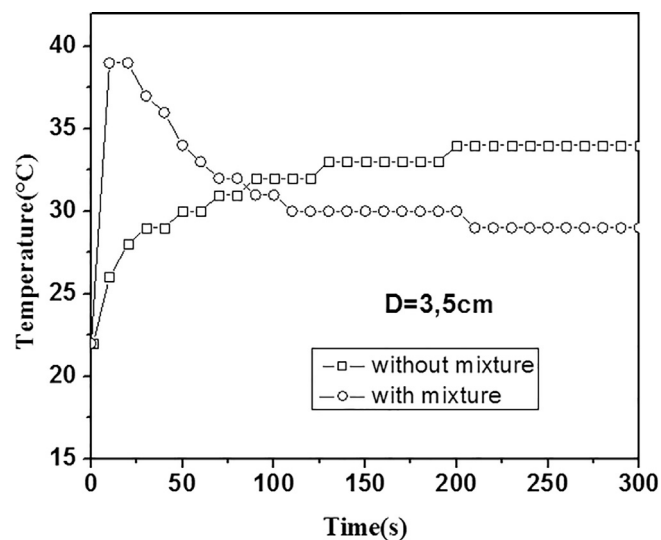


Fig. 4 (continued)

The figure clearly shows that, for the short distances between the optical fiber and the sample, the maximal temperature T_{\max} reach a value of 63 °C which is higher than the isotropic nematic temperature T_{NI} of LC E7. We also observed in Fig. 3 and Fig. 4, that the temperature of the sample decreases after this maximum value to have a stable state of a constant temperature from $t = 75$ s, although the lamp is always lit: this suggests that the new phenomenon observed in third time domain of transmission (see Figs. 1 and 2) is not due only to the IR part of the spectrum of UV light emitted by LC3 source, but it is also probably due to a thermal effect which is an accumulation of three effects: the effect of the exothermic reaction of polymerization which take place in the first millisecond when the UV irradiation is applied, and the effect of the thermal diffusivity of the mixture between the molecules of LC and the monomers as well as between the molecules of LC and the polymeric network.

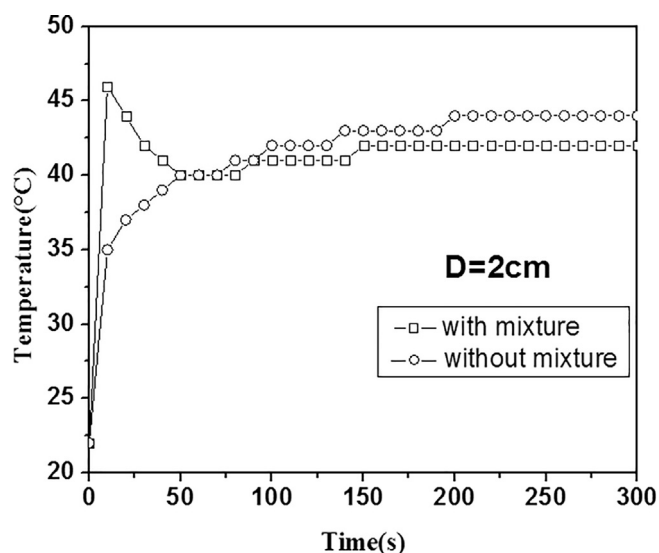


Fig. 4 (continued)

4. Conclusions

A rapid decrease in transmission was observed when the films are exposed to UV irradiation. Moreover, the results show a marked increase in light transmission that does not come simply from the thermal effect due to an increase in temperature of the sample by the infrared part of the spectrum of the UV source, but it probably also from the exothermic reaction of polymerization leading to the formation of polymer network and from a reaction between the diffusivity of monomer molecules and the liquid crystal molecules. This phenomenon strongly depends on the dose of UV light (the distance D) and the sample, the initial mixture chosen and the film thickness.

CRedit authorship contribution statement

Z. Hadjou Belaid: Conceptualization, Visualization, Supervision, Writing - original draft. **L. Benhabib:** Formal analysis, Data curation. **D. Beroguiiaa:** Investigation. **F.Z. Abdoune:** Validation, Supervision. **L. Méchernène:** Investigation, Writing - review & editing. **U. Maschke:** Resources, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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