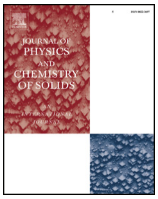
Journal of Physics and Chemistry of Solids 122 (2018) 36–40

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



Molecular alignment, large surface deformations and hysteresis effects in polydomain LC polymer films under an in-plane DC electric field

Laurens T. de Haan[a,b,*], Guofu Zhou[a,b,c,*]

[a] SCNU-TUE Joint Lab of Device Integrated Responsive Materials (DIRM), National Center for International Research on Green Optoelectronics, South China Normal University, Guangzhou, 510006, PR China
[b] Guangdong Provincial Key Laboratory of Optical Information Materials and Technology & Institute of Electronic Paper Displays, South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou, 510006, PR China
[c] Shenzhen Guohua Optoelectronics Tech. Co. Ltd., Shenzhen, 518110, PR China

ARTICLE INFO

Keywords:
Liquid crystals
Polymers
Surface deformation
In-plane switching

ABSTRACT

The response of multidomain liquid crystal polymer films to prolonged exposure to an in-plane DC electric field is investigated. Non-crosslinked polymers show a rotation of the mesogenic units along the field lines, but the rotation is asymmetric between the positive and negative electrodes. Crosslinked films respond by undergoing large surface deformations, with deformation profiles that correspond with the observed alignment profiles in non-crosslinked films, including asymmetry. Additionally, a strong hysteresis effect is observed, where subsequent exposures to the field lead to stronger and faster deformations.

1. Introduction

Stimuli-responsive polymer materials are an important subject in the field of materials science, and can lead to the development of new devices. Liquid crystals polymers are an interesting class of such materials, as they can undergo large, well-controlled shape deformations as a response to various stimuli. Examples of this are crosslinked liquid crystal polymer films that show bending [1,2], curling [3], and even complex shape deformations [4,5] and movement [6,7] when the stimulus is applied. In these examples, the deformation is usually caused by a decrease in order parameter, which causes a contraction along the alignment director and an expansion in all other directions. In addition to this change in dimensions, an increase in free volume can also be observed when the order parameter is decreased [8,9].

An interesting direction for liquid crystal polymers is towards stimuli-responsive structured surfaces [10]. The design of surface structures in other areas has already led to many applications, such as photonic surfaces [11,12], super hydrophobicity [13,14], antifouling [15,16], and the “gecko effect” [17], and the ability to make these structures change shape on command greatly expands their potential. Liquid crystal polymer networks have been used to achieve switchable surface structures [10]. These systems operate as arrays of microscopic actuators on the surface, where a decrease in order parameter is used to achieve the desired change in shape or increase in volume. Usually, the stimulus used to switch the surface structures is a temperature change [18,19], light [20,21], or a chemical stimulus [22], but from a device-making point of view it would be more useful to have a system that is triggered upon application of an electric field. Recently, a device was developed that uses in-plane AC electric fields between interdigitated electrodes to reduce the order parameter in an LC polymer film, to achieve localized free volume generation to reversibly generate surface structures [23].

Deformations under influence of an electric field can also be achieved in multidomain liquid crystal polymer films [24]. In this case, the driving mechanism for deformation is the rotation of the mesogenic units in the polymer networks, which increases the global order parameter. Of particular interest are so called isotropic genesis networks, which are polymerized in the isotropic phase and have a poorly defined multidomain nematic structure [25,26]. These materials are particularly susceptible to deformation in an electric field, with deformations up to 30% being observed in response to an AC electric field [24]. However, these materials were never used with in-plane electric fields to generate surface deformations, and the effect of long-term exposure to a DC field has also not been investigated.

This study reports the influence of the prolonged application of an in-plane DC electric field on a multidomain isotropic genesis liquid crystal polymer film. Initially, a non-crosslinked liquid crystal polymer film was subjected to an in-plane field and analysed with polarized

---

* Corresponding authors. SCNU-TUE Joint Lab of Device Integrated Responsive Materials (DIRM), National Center for International Research on Green Optoelectronics, South China Normal University, Guangzhou, 510006, PR China.
E-mail addresses: ldhaan@guohua-oet.com (L.T. de Haan), guofu.zhou@m.scnu.edu.cn (G. Zhou).

https://doi.org/10.1016/j.jpcs.2018.06.008
Received 7 February 2018; Received in revised form 28 April 2018; Accepted 5 June 2018

optical microscopy to demonstrate the rotation of the molecules along the field lines. Then, a crosslinked film was subjected to a similar field. It was found that a surface deformation appears, the profile of which corresponds well with the observed molecular rotations. Interestingly, a strong hysteresis effect was observed that resulted in increasingly larger deformations upon repeated and prolonged exposure to the electric field. Additionally, an asymmetry effect towards the positive electrode was observed which biases the molecular reorientation and corresponding deformation.

2. Experimental

2.1. Materials

The monoacrylate mesogen HCM020 and the diacrylate mesogen HCM009 were purchased from HCCH. The photoinitiator 1-hydroxycyclohexyl phenyl ketone was purchased from HEOWNS.

2.2. Equipment

Photopolymerization was carried out using an Omnicure 1500 UV lamp. The transition temperatures were determined using a Mettler Toledo DSC1. Polarized optical microscopy images were obtained using a Leica DM 2700P microscope. 3D surface profiles were obtained using a Fogal Nanotech Zoomsurf interferometer, while the samples were being heated using a Linkam hotstage.

2.3. Preparation of the non-crosslinked film

A mixture of HCM020 with 2% photoinitiator was prepared. The mixture was applied to a clean electrode slide at 90 °C. A cover slide was placed on top of the mixture and the plate was exposed to UV irradiation at 90 °C for 5 min.

2.4. Alignment analysis of the non-crosslinked film

Two electrical wires were attached to two adjacent electrodes of the electrode slide. The cell was then fixed on the hotstage using double-sided tape, which was brought to 90 °C. The cell was analysed using POM before, during, and after application of the DC electric field.

2.5. Preparation of the crosslinked film

A mixture of HCM020 with 2% HCM009 and 2% photoinitiator was prepared. The mixture was applied to a clean electrode slide at 90 °C. A cover slide was placed on top of the mixture and the plate was exposed to UV irradiation at 90 °C for 5 min. The cover slide was removed afterwards.

2.6. Alignment analysis of the crosslinked film

Two electrical wires were attached to two adjacent electrodes of the electrode slide. The plate bearing the crosslinked film was then fixed on the hotstage using double-sided tape, which was brought to 90 °C. The cell was analysed using 3D profilomery before, during, and after application of the DC electric field. The resulting profiles were leveled and smoothed. The total surface area of the profiles was calculated using Microsoft Excel.

3. Results and discussion

An isotropic-genesis polymer was fabricated by polymerizing a monoacrylate mesogen (Fig. 1a) at 90 °C in the isotropic state. To this monomer 2% of a photoinitiator was added to allow UV photopolymerization. This monomer was did not possess a liquid crystalline phase before polymerization, but became nematic after polymerization. When the formation of a polymer network was desired, 2% of a diacrylate crosslinker (Fig. 2b) was added. The glass transition temperature and the clearing point of the network were measured using DSC, and were found to be 38 °C and 132 °C, respectively. To be able to apply an in-plane electric field to the films, they were prepared on a glass plate bearing ITO electrodes with a 30 micron gap in between them (Fig. 1c). This slide was fitted with a top plate, and 15 μm spacers were used to create a gap with a controlled width, in which the monomer was polymerized. To apply an in-plane electric field to the film, two adjacent ITO electrodes were attached to a DC power source. The plate was placed on a hotstage to keep the material above the glass transition temperature and allow sufficient mobility of the molecules.

An experiment was performed in which a non-crosslinked polymer was subjected to an in-plane DC electric field to study the rotation of the molecules, which was studied using polarized optical microscopy. The hotstage was set to 90 °C. Initially, the polymer showed a multidomain nematic structure, in which the gap was visible due to a slight difference in alignment profile compared to the surroundings. When a 400 V electric field was applied, the molecules realigned in a few seconds. As expected, above the electrode gap the molecules adopted a planar alignment, which appeard brightly colored between crossed polarizers, while above the electrode a homeotropic alignment was formed which appeared dark. However, a distinct asymmetry could be observed, where the area over the positive electrode appeared darker compared to the area over the negative electrode. This implies a difference in alignment profile between these two areas. As the field was kept on for 23 min, slow darkening of some areas on the negative side took place, which showed that the alignment was still developing there. When the field was switched off, the alignment reverted back to multidomain, and the asymmetry in the alignment profile became even more pronounced. It is not clear why the response is asymmetric; however, it has been observed in other systems that liquid crystal polymers can contain ionic impurities which cause asymmetry in their response towards electric fields [27].

The deformation behavior of a crosslinked film was studied using optical profilometry. To do so, the top plate was removed after film preparation, and the glass plate bearing the electrodes and film was put onto a hotstage at 70 °C to control the temperature. The initially flat surface was monitored using the optical profiler, and a 400 V DC electric field was applied. A strong deformation of the surface was observed, consisting of a hill flanked by two valleys (Fig. 2a). A picture of the profile was taken periodically over a time span of 27 min to investigate the shape evolution over a prolonged time period (Fig. 2b). The deformation of the surface was relatively slow, and was still showing change after the 20 min mark. It was found that the shape evolution was asymmetric, with the valley forming on the positive side before forming on the negative side. This corresponds with the earlier observed asymmetry in the alignment profile of the non-crosslinked polymer. It can be assumed that the surface deformation is caused by the realignment of the molecules with corresponding expansion perpendicular to the alignment director and contraction parallel to it (Fig. 2c), as was shown in previous research [24].

The shape evolution over multiple cycles was also investigated. The voltage was switched off after 27 min, and then switched back on again. It was held at 400 V for 10.5 min, then switched off and on again, and held at 400 V for 6 min. Again, the profile of the surface was periodically measured while the voltage was applied. The cross-section of the profiles was plotted to gain insight into the change in morphology of the peak and valley at the end of each cycle (Fig. 3a). In addition, the total surface area of each profile was calculated, and the increase in surface area compared to the flat surface was plotted as a function of time for all three cycles (Fig. 3b). From these two figures, it became clear that during the second cycle, the surface deformation returned faster and with greater magnitude. In addition, the valley on the negative side returned immediately when the second cycle was started. On the third cycle, the deformation returned even faster, and while the