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Alignment and Optical Properties of LC Retarder Film Photo-Polymerized at Various Conditions

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Investigation of the properties of the liquid crystalline polymer (LCP) retarder films, formed by photo-polymerization of a reactive LC mixture at various conditions, has shown that the alignment, the birefringence and the thermal stability of the LCP film are governed by the conversion of photo-polymerization (CP) of reactive LCs. The CP of the LCP film photo-polymerized in air has increased with the intensity of irradiation light, which reduces both the degree of in-plane alignment of LCs and the birefringence but gives the better thermal stability of the film. The photo-polymerization in an inert environment has induced the higher CP and the better thermal stability of the LCP film than the in-air polymerization.

Keywords: alignment; birefringence; order parameter; photo-polymerization; reactive liquid crystal

INTRODUCTION

Liquid crystalline polymer (LCP) retardation films have been applied to various types of LCDs [1]. They are suitable for in-cell technology and flexible display technology as well as have the several advantages such as the thickness and weight reduction of the device and the improvement of the LCD's electro-optical properties [2–4]. The LCP film is typically made from photo-polymerization of a reactive LC monomer precursor and requires a specific (in-plane and out-of-the-plane) alignment of the constituent LC molecules

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for the desired optical performance [4–7]. Its optical properties are thus expected to depend on the LC alignment characteristics and the photo-polymerization conditions.

In this work, we have investigated how the alignment and optical properties of the LCP depend on the conditions for photo-polymerization of a reactive calamitic LC mixture, such as the irradiation intensity and the polymerization circumstances, and what is the key factor to affect the LCP properties.

EXPERIMENTAL

A reactive, calamitic LC monomer mixture (Merck RMS03-013C: LCM), which consists of LCs with one or two acrylate terminals and is designed for in-air polymerization, was spin-coated on a rubbed polyimide (Nissan Chemical SE-1691), followed by drying. The LC monomer film was then photo-polymerized, either in air or under nitrogen, by irradiation of an 1 kW high-pressure Hg lamp with varying the intensities. The optical properties of the polymerized LC film were measured using an evaluation equipment for optical films (RETS-100, Otsuka Electronics) and the degree of the in-plane alignment of LC molecules, i.e., the LC order parameter was determined by investigation of IR dichroism for the LCP film.

RESULTS AND DISCUSSION

The optical characteristics of LCP retarder films are likely to depend on the alignment of LC molecules. It is thus important to control the degree of the in-plane alignment. Figure 1 is the polarized IR spectra of the LCP fabricated on the rubbed polyimide, which show significant dichroism. The absorbance of 1605 cm^{-1} band ($A_{ll,1605}$), corresponding to C=C stretching of the phenyl groups in the LC's core, for IR polarization parallel to the rubbing direction is greater than the band absorbance ($A_{\perp,1605}$) for IR polarization perpendicular to the rubbing direction. It indicates that the LC molecules align preferentially along parallel to the rubbing direction. The value of S was here determined as follows: $S = (A_{ll,1605} - A_{\perp,1605})/(A_{ll,1605} + 2A_{\perp,1605})$.

The photo-polymerization of acrylated LCs in air can cause oxygen molecules in air to react with the radicals of the initiators, which affects the polymerization. The effects of intensity of irradiation light on the in-air photo-polymerization and the properties of the LCP film have been investigated. Table 1 shows that the conversion of polymerization (CP) of the LCP increases with the light intensity for a fixed UV dosage. For relatively lower intensities, the radicals of the

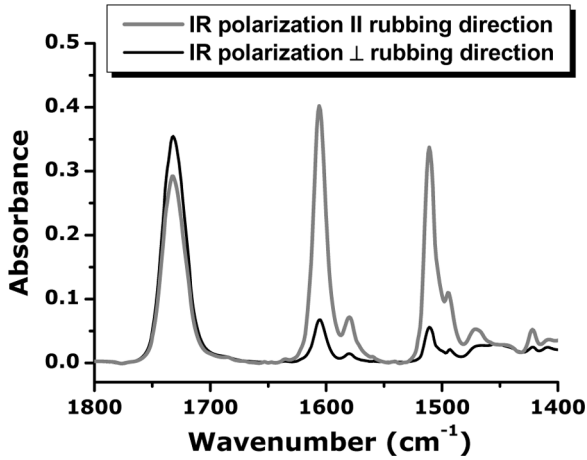

FIGURE 1 The polarized FTIR spectra for the aligned & photo-polymerized LCM.

photo – initiator are longer exposed to air and thus the more radicals react with oxygen, not with participating in polymerization, which results in a decrease in the CP. On the other hand, both the LC order parameter and the birefringence show the opposite trend; they decrease as the intensity increases (Table 1). A higher irradiation intensity induces a higher CP and also more rapid polymerization, which causes more (disturbance) of the aligned LC molecules and subsequently reduces the degree of in-plane alignment of LC molecules and the film's birefringence.

In case of photo-polymerization under nitrogen, the higher CPs were obtained than in the case of the in-air polymerization, as expected, due to no reaction of initiator radicals with oxygen. The order parameters and the birefringences of the LCP films polymerized

TABLE 1 The Conversion of Polymerization (CP), the Order Parameter (S) and the Birefringence (Δn) of LCM Photo-Polymerized at Various Conditions

Intensity of 365 nm light, exposure time	Polymerization in air			Polymerization under N_2		
	CP (%)	S	Δn	CP (%)	S	Δn
0.5 mW/cm^2, 16 s	60	0.63	0.24	82	0.58	0.17
1.0 mW/cm^2, 8 s	63	0.62	0.22	83	0.57	0.17
2.0 mW/cm^2, 4 s	68	0.61	0.20	85	0.58	0.18
4.0 mW/cm^2, 2 s	69	0.61	0.20	85	0.58	0.17
8.0 mW/cm^2, 1 s	73	0.60	0.19	86	0.58	0.17

TABLE 2 The Change in the Conversion of Polymerization of LCM, Photo-Polymerized at Various Conditions, with Thermal Annealing

Photo-polymerization conditions		30 min-annealing (%)				
		None	At 150°C	At 180°C	At 200°C	At 230°C
In air	1 mW/cm^2 for 8 s	63	66	76	85	93
	4 mW/cm^2 for 2 s	69	70	76	87	92
	8 mW/cm^2 for 1 s	73	74	81	89	93
Under N_2	1 mW/cm^2 for 8 s	83	84	89	90	95
	4 mW/cm^2 for 2 s	85	85	88	90	94
	8 me/cm^2 for 1 s	86	87	88	92	96

in inert circumstances show relatively smaller values than those done in air. However, the alignment and the optical properties of the LCP films polymerized under nitrogen have not shown the dependence on the intensity of irradiation light observed in the in-air polymerization.

In case that the LCP film is applied to LCD in-cell technology, in which the temperature goes over 200°C, the thermal stability of the film is a very important factor. The thermal stability of the LCP films polymerized at various UV irradiation conditions. Table 2 shows the CP of the LCP film keeps up increasing as thermal annealing becomes more severe. This result indicates the initiators are thermally decomposed and thus the reactive LC molecules remained on the film are again polymerized all around the film by thermal annealing. Figures 2 and 3 show the changes in the order parameter and the birefringence of the LCP film polymerized at various intensities of UV irradiation for a fixed dosage with thermal annealing, respectively. As shown in Table 2, thermal treatment of the LCP film causes

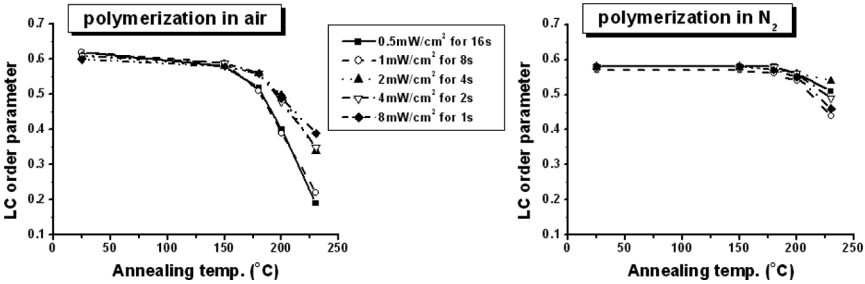

FIGURE 2 The change in the LC order parameter of LCM, photo-polymerized at various conditions, with thermal annealing.

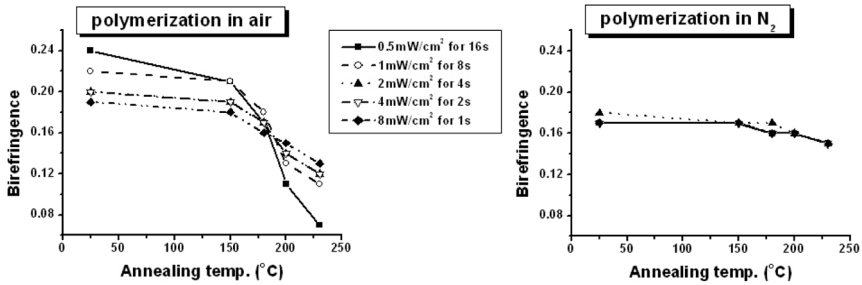

FIGURE 3 The change in the birefringence of LCM, photo-polymerized at various conditions, with thermal annealing.

the progress of additional polymerization of unreacted LC molecules for both the polymerizations in air and under nitrogen, but more in the former case. The aligned LC molecules in the LCP films are disturbed by this thermal polymerization, which reduces the degree of in-plane alignment of LCs and subsequently the birefringence of the film. The photo-polymerization in an inert environment has induced the more thermally stable LCP film than in-air polymerization and the film's thermal stability is not dependent on the light intensity. On the other hand, the thermal stability of the LCP film polymerized in air tends to increase with the irradiation intensity. The results in Figs. 2 and 3 and show that the stability of LCP film greatly depends on the CP, which is because the more photo-polymerization results in the more stable polymer network.

CONCLUSIONS

How the photo-polymerization conditions of reactive LCs affects the properties of the LCP film, such as the conversion of polymerization, the LC order parameter, the birefringence and thermal stability, has been investigated. In case of in-air polymerization, a higher intensity of UV irradiation has induced the higher conversion of polymerization, because of the effect of oxygen's reaction with initiator radicals, which reduces both the degree of in-plane alignment of LC molecules and the birefringence of the film but gives the more thermally stable film. The LCP films polymerized in inert circumstances, whose the properties are not dependent of the irradiation intensity, have shown the more progressed polymerization than those cured in air, resulting in the better thermal stability.

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