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Polymerization-Induced Phase Separation in LC/Light-Curable Resin Mixture

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Polymerization-Induced Phase Separation in LC/Light-Curable Resin Mixture

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Nuclei generation and growth in initial photo-polymerization were investigated for a liquid crystal (LC) and light-curable resin mixture. The investigation showed that the dependence of nuclei density on the intensity was divided into three main regions: (1) the nuclei density had threshold exposure at low intensity, (2) the nuclei density was proportional to the intensity at middle intensity, (3) the nuclei density was saturated at high intensity. The nuclei growth also differs according to the initial nuclei density. We found that the nuclei grew large spheres at low nuclei density and the nuclei grew dendrites and eventually a polymer-network is formed at high nuclei density.

Keywords: photo-polymerization; phase separation

1.INTRODUCTION

Holograhic polymer dispersed liquid crystal (HPDLC) devices are promising

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for use in high-performance reflective displays because of their reflection capability and good color purity [1-2]. HPDLC devices are formed using holographic exposure and photo-polymerization-induced phase separation [3-4]. Phase separation of the LC and monomer mixture in conventional polymer dispersed liquid crystal is investigated using the miscibility gap under equilibrium. However, the photo-polymerization was far from the equilibrium. Therefore, it is important to investigate the initial photo-polymerization dynamics for the mixture. The nuclei generation and growth were investigated for an LC and light-curable resin mixture in the initial photo-polymerization.

2.EXPERIMENTAL

The LC and light-curable resin employed in the experiment were ZLI-4792 (Merck Japan, Japan) and LCR0208 (Toagosei Co, Japan), respectively. The latter was used to initiate polymerization to blue light (e.g., Ar ion laser at a wavelength, λ = 488 nm). LC was added to light-curable resin at an LC : light-curable resin = 50 : 50 weight ratio. The LC and light-curable resin were mixed together at room temperature until the mixture became homogeneous. This mixture was sandwiched between indium-tin-oxide (ITO) coated glass slides separated by a 10 μm thick spacer. The samples were exposed to an Ar ion laser beam with an irradiate of 10 – 100 mW/cm^2 for 2 seconds. The beam was unfocused, and had beam diameters of $\sim$ 10mm. Phase separation was photochemically induced by an Ar ion laser beam. In order to promote polymerization, the samples were kept in a dark place for 0-30 minutes. After that, one of the glass slides was removed and soaked in isopropyl alcohol for about 1 minute. The morphology of the samples was observed using a Nomarski differential interference microscope in the experiment of the nuclei generation and a scanning electron microscope (SEM) in the experiment of the nuclei growth.

3.RESULTS AND DISCUSSION

Our polymerization system and the nuclei generation rate

Our polymerization system consists of the nuclei generation process and the

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nuclei growth process. The nuclei generation process consists of two chemical reactions. The first reaction process is where the initiator is excited by an Ar ion laser and becomes the initiator radical. The second chemical reaction is where the initiator radical reacts with the monomer. This initiator radical compound is called a nucleus. After generation, nuclei react with the monomer again and again in rapid succession for a great many times. This process is called the nuclei growth process. However, the termination of polymerization is disregarded due to the initial photo-polymerization. That is, the nuclei are growing during this experiment.

In our polymerization system, the nuclei generation rate is shown as an equation (1). However, the concentration of the monomer is disregarded because it is higher than that of the initiator.

$$\frac{dn}{dt} = k[I][K] \tag{1}$$

where n is the nuclei density ($1/cm^2$), k is the reaction factor (1 / J), [I] is the intensity of Ar ion laser (W/cm^2), [K] is the concentration of the initiator, and t is the exposure time.

Dependence of nuclei density on exposure

In order to investigate the nuclei generation, the nuclei density was investigated as a function of the intensity in the initial photo-polymerization. In this experiment, nuclei were defined as compound that could be observed using the microscope.

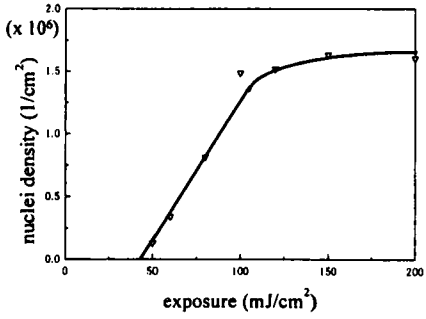

FIGURE 1 Nuclei density as a function of the exposure in a sample

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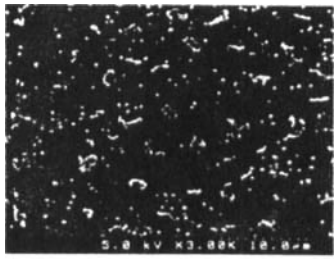
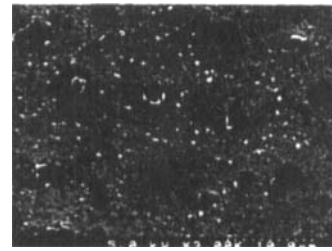
FIGURE 1 shows nuclei density as a function of exposure. From equation (1), the nuclei density could be considered to be directly proportional to the exposure. It can be seen from FIGURE 1 that the dependence of nuclei density on the exposure is divided into three main regions. In the first region ((1)< 40 mJ/cm^2), the nuclei density has threshold exposure because few initiators are excited by the exposure. In the second region (40 mJ/cm^2 < (2) < 100 mJ/cm^2), the nuclei density is proportional to the exposure. From the nuclei generation rate, we found a reaction factor of 1.50 x 10^{-14} (1/J) in this region. In the third region (100 mJ/cm^2 < (3)), the nuclei density is saturated because the initiator radicals recombine.

Nuclei growth according to initial nuclei density

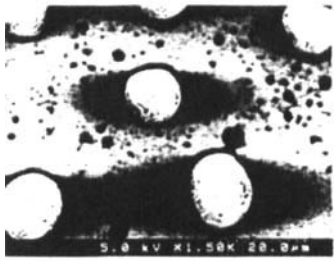
We investigated the nuclei growth for different densities by using two different Ar ion laser intensities, I_{ar} = 40 and 60 mW/cm^2. Immediately after irradiation, the initiator radical reacted with the monomer and nuclei were generated at both intensities (FIGURE.2(a) and 3(a)). We found that the density of nuclei at I_{ar} = 40 mW/cm^2 was lower than that at I_{ar} = 60 mW/cm^2. In the case of the intensity at 40 mW/cm^2, we found that these nuclei grew large spheres (FIGURE 2(b) and 2(c)). The diameter of these nuclei was about 12 μm after 30 minutes. The reason for the nuclei growth is as follows: FIGURE 2(a) shows that the distance between neighboring nuclei is long due to the low density of the nuclei. We assumed that the area around these nuclei is an effective area and that the monomer in this area can contribute to the polymerization. The probability of monomer supply from the effective area is isotropic. Therefore, the nuclei assume a spherical shape. The morphology of nuclei growth in FIGURE 3 is quite different. In this polymerization, a nucleus is joined to another nucleus (FIGURE 3(b)) and a polymer-network is formed after about 30 minutes(FIGURE 3(c)). The reason for the nuclei growth is as follows: FIGURE 3(a) showed that the distance between neighboring nuclei is short due to the high density of the nuclei. The effective area of the nuclei overlaps with that of neighboring nuclei. Since the probability of monomer supply is anisotropic, we obtain an anisotropic nuclei shape. As a result, the nuclei formed dendrites and eventually a polymer-network is formed.



(a)

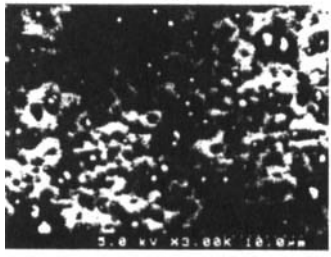


(b)

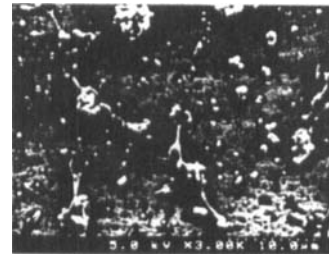


(c)

FIGURE 2 SEM photographs of an in-plane view of samples by exposure intensity (40 mW/cm^2) at various growth time: (a) 0 min., (b) 15 min., (c) 30min.



(a)



(b)

(c)

FIGURE 3 SEM photographs of an in-plane view of samples by exposure intensity (60 mW/cm^2) at various growth time: (a) 0 min., (b) 15 min., (c) 30min.

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4.CONCLUSIONS

Nuclei density in initial photo-polymerization was investigated as a function of Ar ion laser intensity. We found that the dependence of nuclei density on exposure was divided into three regions: (1) the low-intensity region, where the nuclei density had threshold exposure, (2) the middle-intensity region, where the nuclei density was proportional to the intensity, and (3) the high-intensity region, where the nuclei density was saturated. We also investigated nuclei growth for different densities using two different exposure intensities. We found that these nuclei form large spheres at low nuclei density. At high nuclei density, it was found that the nuclei form dendrites and eventually a polymer-network is formed.

Acknowledgement

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