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Influence of film thickness on the reorientation structure of photoalignable liquid crystalline polymer films

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ABSTRACT

Polarized UV absorption and near-edge X-ray absorption fine structure (NEXAFS) spectroscopies are used to investigate the influence of film thickness on the thermally stimulated photoinduced reorientation of a polymethacrylate film comprised of 4-methoxycinnnamoylbiphenyl (MCB) side groups connected with a decylene spacer (PMCB10M) in the bulk (>10 nm), at the inner-surface (~10 nm), and at the near-surface (<2 nm). Irradiation with linearly polarized (LP) UV light and subsequent annealing generate a biaxial molecular reorientation in the bulk of thick PMCB10M films, while the out-of-plane orientation is restricted in films less than 55-nm thick. In contrast, the in-plane reorientation is dominant at the near-surface regardless of the film thickness. Consequently, the roles of the rigid mesogenic MCB moieties and the flexible long decylene spacer depend on the film thickness.

1. Introduction

A polarization-axis-selective photoreaction of photosensitive polymeric films using linearly polarized (LP) light generates small optical and chemical anisotropies. These anisotropies can be used for photoalignment of low-molecular-weight liquid crystals (LCs) and functional materials [1–5], optical birefringent films [6,7], etc. When the anisotropic photoreaction is accompanied by the molecular reorientation, a large optical anisotropy is induced. Many types of LC polymeric films exhibit photoinduced molecular reorientation based on the self-organization characteristics of the LC materials [8–11]. In most cases, optical property of the film is investigated as the orientation structure in bulk, but the molecular orientation characteristics at the near-surface (<2 nm from the surface) as well as the three-dimensional (3D) orientation structure are important for LC alignment and birefringent device applications.

Previously, we investigated the thermally stimulated photoinduced reorientation of a polymethacrylate comprised of 4-methoxycinnamolybiphenyl (MCB) side groups connected via hexylene or decylene spacers (PMCB6M and PMCB10M, Fig. 1) in detail [12–15]. Irradiating with LPUV light and subsequent annealing in the LC temperature range of the material induces a significant uniaxial in-plane orientation of the MCB side groups of PMCB6M films in bulk [12], whereas an out-of-plane orientation is observed for PMCB10M films [13]. Furthermore, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy has clarified the significant uniaxial in-plane molecular orientation of PMCB6M at the near- and inner-surface (<10 nm) regardless of the film thickness, although the in-plane orientation characteristics in bulk decrease as the film thickness decreases below 90 nm [14].

In contrast, biaxial orientation has been achieved for 170-nm-thick PMCB10M films in the bulk, depending on the post-annealing temperature. However, the in-plane orientation is predominant at the near-surface regardless of the self-organization condition [15]. Compared to that of PMCB6M, the long decylene spacer plays an important role in the reorientation behavior.

The influence of film thickness on the reorientation structure of the mesogenic groups at the near-surface and in the bulk for the reorientation of PMCB10M films has yet to be investigated. For LC photoalignment applications, the dependence of the molecular orientation structure on film thickness should be clarified at the near-surface because the interaction between the near-surface of the photoalignment film and LC determines the LC alignment characteristics [16–18]. Additionally, the effect of film thickness on the 3D orientation structure is important for birefringent film

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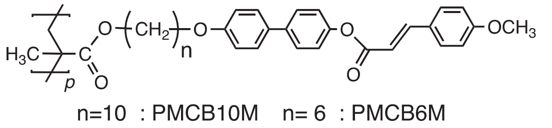

Fig. 1. Chemical structure of the liquid crystalline (co)polymers used in this study.

applications.

In this paper, we investigate the influence of film thickness on the thermally stimulated photoinduced molecular reorientation of PMCB10M films in the bulk (>10 nm), at the inner-surface (~10 nm), and at the near-surface (<2 nm). Polarized UV absorption spectroscopy is used to elucidate in the behavior in the bulk, while NEXAFS spectroscopy is used to analyze the orientation structures at the inner-surface and the near-surface [total electron yield (TEY) detection for <10 nm and auger electron yield (AEY) detection for <2 nm]. Irradiation with LPUV light and subsequent annealing generate biaxial molecular reorientation in the bulk of a thick (150 nm) PMCB10M film, while planar (in-plane) orientation is detected in the bulk and at the near-surface for films less than 55-nm thick. Additionally, the in-plane reorientation is dominant at the near-surface regardless of film thickness. The rigid MCB side groups tend to reorient planar at the near-surface, while the long alkylene spacers control the out-of-plane motion of the side groups for thick films.

2. Experimental

2.1. Materials

All starting materials were used as received from Tokyo Kasei Chemicals. PMCB10M, which exhibited a smectic phase between 116 and 291 °C (C 116 S_m 291 I), was synthesized according to the literature [13,15]. The number-average molecular weight and polydispersity were 46,400 and 1.80, respectively.

2.2. Photoreaction

Thin PMCB10M films (thicknesses: 15–210 nm) were prepared by spin-coating a methylene chloride solution of the polymers (0.1–2 w/w%) onto quartz or ITO/glass substrates. The photoreaction was performed using a high-pressure Hg lamp equipped with Glan–Taylor polarizing prisms and a cutoff filter (<300 nm) with a light intensity of 50 mW/cm^2 at 365 nm. After photoirradiation, the exposed films were annealed at elevated temperatures for 10 min to generate thermally stimulated molecular reorientation.

To conventionally evaluate the reorientation structure in the bulk, the polarized absorption UV–vis spectra were measured with a Hitachi U-3010 spectrometer equipped with Glan–Taylor polarization prisms. The reorientation characteristics in the bulk were evaluated using the in-plane dichroic ratio (*DR*) at 292 nm, which is expressed as Eq. (1).

$$DR = \frac{A_{||} - A_{\perp}}{A_{||} + A_{\perp}} \tag{1}$$

where $A_{||}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to the polarization (**E**) of LPUV light, respectively.

The 3D refractive indices (n_x, n_y, and n_z) of the film were evaluated using a polarimeter (Shintech OPTIPRO 11-200A) at 517 nm.

2.3. NEXAFS spectroscopy

The NEXAFS measurements were performed at the NewSUBARU Synchrotron Radiation Facility on beamline 7B (University of Hyogo), which delivers soft X-ray radiation undulator equipped with a plane grating monochrometer (slits: 150 μm). The radiation energy resolution was 300 meV at 280 eV based on a similar technique in the literature [19–21]. Two types of NEXAFS spectroscopies, TEY and AEY, were used to evaluate the orientation structure at the inner-surface (~10 nm), and at the near-surface (<2 nm), respectively. The detailed experimental geometry is illustrated in Fig. S1.

3. Results and discussion

3.1. Refractive indices of the as-coated films

Fig. 2 plots the refractive indices of the PMCB10M films as a function of film thickness. The refractive index in the planar direction (n_x, n_y) is smaller than that in the out-of-plane direction (n_z) for films thicker than 100 nm, indicating a partial out-of-plane orientation. In contrast, both n_x and n_y are larger in films less than 80-nm-thick (planar orientation). This tendency is confirmed by the angular dependence of the absorbance (Fig. 2, inset).

We previously detected the planar orientation for thick (>150 nm) as-coated PMCB6M films; the planar characteristics increase as the film thickness decreases [14]. On the other hand, the long decylene spacer in PMCB10M leads to the out-of-plane orientation of the side groups upon film formation when the film is sufficiently thick. The mesogenic MCB groups at the substrates and/or at the free-surface control the planar orientation because the MCB moiety itself tends to orient planar. Therefore, thin (<80 nm) PMCB10(6)M films have a planar orientation because the alkylene spacer does not affect the orientation.

3.2. Photoinduced orientation in the bulk

In case of the PMCB6M film, we have reported that a thermally stimulated photoinduced in-plane orientation (DR > 0.8, 150-nm-thick) is achieved when a film is exposed to LPUV light followed by annealing in the LC temperature range of the material. The generated in-plane order parameter decreases when the film thickness is below 90 nm [12,14]. In contrast, the PMCB10M film (170-nm-thick) shows a biaxial photoinduced reorientation, where the behavior depends on the post-annealing temperature [15].

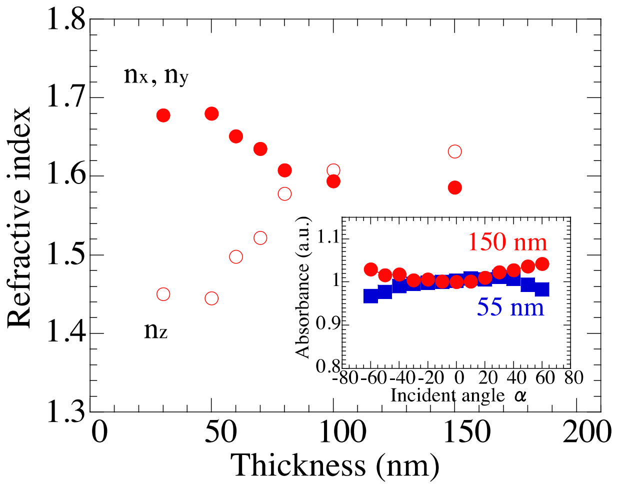

Fig. 2. Refractive indices of the as-coated PMCB10M film as a function of film thickness. Inset plots the angular dependence of the absorbance at 292 nm for 55- and 150-nm-thick films.