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Preliminary communication

Thermal stability of alignment of a nematic liquid crystal induced by polyimides exposed to linearly polarized light

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The thermal stability of alignment of a nematic liquid crystal (LC) on three polyimide (PI) films exposed to linearly polarized light at 366 nm was investigated. Polarizing optical microscopy analysis indicates that the thermal stability of the LC alignment on the PI film without significant structural change was higher than that with obvious structural change.

Rubbed polyimide (PI) films have commonly been used to induce the alignment of liquid crystals (LCs). However, the rubbing process causes dust particles and electrostatic damage. To overcome these shortcomings, several non-rubbing photoalignment techniques have been developed [1–4]. It has been reported that photoinduced isomerization of azochromophores [1], cross-linking of coumarin prepolymers [2], and degradation of PIs [3, 4] could be used to control LC alignment. Among these methods, photoinduced alignment using PIs is of great interest, because PI films have been widely used in practical LC devices. It is believed that the anisotropic photodegradation of the PI main chain causes the LC alignment [4, 5]. However, one does not know whether the photodegradation affects the thermal stability of the LC alignment. The induction of the alignment is important, but maintenance of the alignment may be more important for applications. Therefore, it is very necessary to investigate the thermal stability of the LC alignment on ultraviolet (UV) exposed PI films. To our knowledge, there have been no such systematic studies. In the present study, we have explored the relation between the thermal stability of the alignment of a nematic LC on PIs exposed to linearly polarized light at 366 nm and the photodegradation of the PIs.

Three types of PI film were used as alignment layers (the structures of the PIs are shown in figure 1). Glass substrates were spin-coated with 2.5 wt % poly(amic acid) solutions at 200 rpm for 5 s and at 2000 rpm for 15 s; the surface-treated substrates were then baked at 250°C for 2 h. The thickness of the PI films was about 50 nm, as measured with a Kosaka SE-3A Surfcorder. Linearly polarized UV light at 366 nm was obtained from a 500 W high pressure mercury lamp through a combination of glass filters (Toshiba; UV-D36C, UV-35, IRA-25S) and a Sigma Koki polarizer. With the polymer film facing the light source, the PI-coated substrates were irradiated with the linearly polarized light. The intensity of the

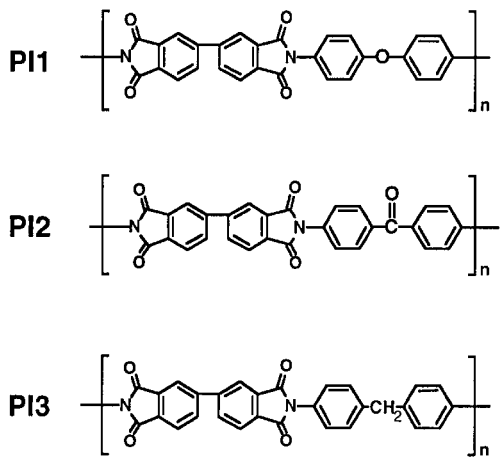

Figure 1. Chemical structures of polyimides PI1, PI2, and PI3 used in this study.

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linearly polarized light at the surface of the PI film was 4.0 mW cm^{-2}. LC cells with a gap of 5 μm were assembled with the PI-coated substrates which had been exposed to the linearly polarized light. 4′-Pentyl-4-cyanobiphenyl as a nematic LC was introduced into the cells at 80°C in the isotropic state, and the cells were gradually cooled to the nematic phase. The LC-filled cells were annealed for 0.5 h at a series of temperatures, and then cooled to the nematic phase again; the alignment behaviour of the LC molecules was now examined using an Olympus Model BH-2 polarizing microscope.

Figure 2 (*a*) shows photographs of three LC cells with PI films that were exposed to linearly polarized light at 26.5 J cm^{-2} (exposure time, 110 min); they are viewed between crossed polarizers before annealing treatment, and the circle-like areas in the centre of each cell are the exposed areas. When the direction of the polarization of the linearly polarized light was parallel to either of the polarizers, the exposed parts were dark. This fact indicates that the three types of PI exposed to the linearly polarized light generate alignment of the LC. Figure 2 (*b*) shows that after annealing, the LC alignment in the LC cell with alignment film PI1 remained almost unchanged. On the other hand, the alignment in the cells with alignment films PI2 and PI3 had deteriorated.

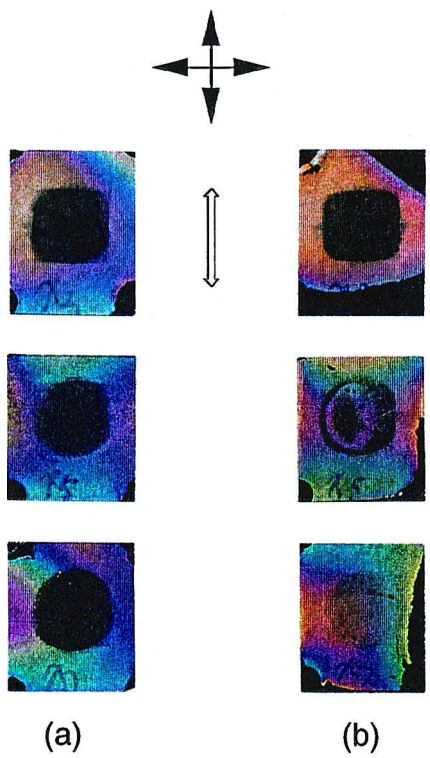

Figure 2. Photographs of exposed LC cells between crossed polarizers: (*a*) before annealing treatment; (*b*) after annealing treatment at 130°C. The black arrows indicate the direction of the optic axis of the polarizers; the white arrow indicates the direction of polarization of the linearly polarized light. Alignment layers, in order, from top to bottom were PI1, PI2, and PI3.

Figure 3 shows the effect of annealing temperature on the efficiency of alignment of the LC on the three types of PI film exposed to linearly polarized light at 26.5 J cm^{-2} (exposure time, 110 min). In figure 3, T_{max} and T_{min} stand for maximum and minimum of the transmittance of the light (wavelength > 540 nm) through the UV-exposed LC cells between crossed polarizers measured using the polarizing microscope equipped with a power meter. It was found that T_{max}/T_{min} could be used as a parameter to evaluate the photoinduced alignment behaviour of the LC [6]. The LC alignment on all the UV-exposed PI films can be maintained unchanged for over one and a half years at room temperature. However, as shown in figure 3, for the cells using UV-exposed PI2 as the alignment film, the LC alignment quality showed an appreciable decrease with annealing treatment above 60°C. A similar result appeared in the cells using exposed PI3 film above 75°C. On the other hand, for the cells with exposed PI1 film, the LC alignment changed little at annealing temperatures as high as 130°C.

In our previous study, we reported that photoinduced structural change for the film PI1 with a diphenyl ether moiety was much lower than that for PI2 with a benzophenone moiety and PI3 with a diphenyl methane moiety when uniform alignment of the LC was obtained [6, 7]. Figure 3 indicates that the LC alignment in the cell with UV-exposed PI1 films in which no significant structural change took place showed a higher thermal stability than that with exposed PI2 and PI3 films in which marked structural change occurred. These results suggest that the thermal stability of the LC alignment is strongly related to the degree of chemical reaction of the PI films upon UV exposure and that the serious

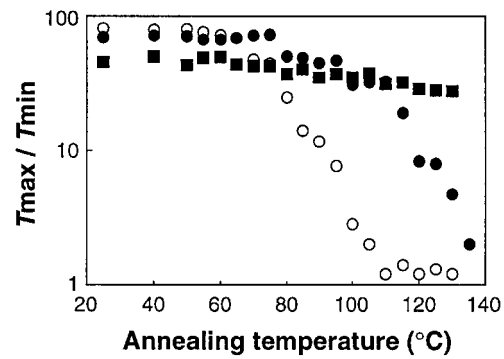

Figure 3. The alignment efficiency of the LC on various PI alignment films exposed to linearly polarized light at 26.5 J cm^{-2} (exposure time 110 min) as a function of annealing temperature: (■) PI1; (○) PI2; (●) PI3.

structural change occurring in the PI alignment films is unfavourable to the thermal stability of the LC alignment.

It was found that after PI2 and PI3 films were irradiated with the linearly polarized light in air, an anisotropic photo-oxidation process created an anisotropic force which dominated the LC alignment [8]. At room temperature, the oxidized groups produced by the UV light are stable. However, with increase in temperature, the activity of the oxidized groups is enhanced, and the groups react with the LC molecules or with each other [9]. Therefore, the photoinduced anisotropic force is weakened by the thermal treatment, which causes a decrease in LC alignment uniformity.

Additionally, the anisotropy in morphology of the film caused by the photochemical reaction is believed to be responsible for the LC alignment [10]. However, the thermal treatment of the LC-filled cells could modify the fine morphology of the PI surface, since the microscopic structure of a polymer surface is sensitive to heating [11], which also diminishes the LC alignment efficiency.

Chemical reaction induced by UV light could produce the driving force which causes the alignment of the LC molecules. However, it has been reported that photochemical reaction in PIs would produce charges that could induce noticeable image sticking and flicker [9, 12]. Our results indicate that serious photochemical reaction also leads to a remarkable reduction in the thermal stability of the LC alignment. Thus, one of our future projects is to develop a new type of PI film which can provide excellent and stable LC alignment.

In conclusion, we have studied the effect of temperature on the alignment efficiency of a LC on UV-exposed PI films. The results indicate that significant change in the PI structure caused by UV light results in a remarkable decrease in thermal stability of the LC alignment. The origin of the decrease is discussed.

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