Photocontrol of Alignment of Liquid Crystals Using a Polymethacrylate bearing Azobenzene

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Films of poly[4-(2-methacryloylolethoxy)azobenzene] irradiated with linearly polarized light induced homogeneous alignment of liquid crystals (LC) like a rubbed polyimide film, because of surface anisotropy generated by photoreorientation of azobenzene moieties. Films annealed before irradiation needed more exposure energies of incident light to induce homogeneous LC alignment, than as-cast films. And also photo-rewriting from the initial LC alignment required a large energy to change, in the case of films contacting with LC layers. While a film without LC layers during irradiation caused photo-rewriting of LC alignment at an extraordinarily small energy (10 mJ cm^{-2}).

Keyword: azobenzene, liquid crystals, photoreorientation, polymer

1. Introduction

Liquid crystal (LC) alignment is strongly affected by the surface of substrates. For example, a rubbed thin film of a polyimide is generally used in LC display devices to give homogeneous LC alignment. The conventional LC displays employ the application of electric field to achieve the switching of alignment of bulk LC molecules. If the properties of a substrate surface are changed by the other external stimulation, LC alignment can be controlled without applying electric field. Photochromic reactions are available as a useful method for the reversible changes of surface nature to realize LC switching. This kind of phenomenon was first reported on a reversible change between homeotropic and planar (out-of-plane) alignment of nematic LC triggered by the trans-cis photoisomerization of azobenzene molecules which are introduced to a surface of silica substrate by silylation[1]. These surfaces have been called "Command Surfaces" because the surface molecular layer commands the alignment of a number of LC molecules. After that, spin-coated thin films of azobenzene-pendent polymers, LB films containing azobenzene derivatives and surface adsorbed azobenzene monolayer films

have been used also as command surfaces[1-4]. The results of these experiments revealed various factors affecting photoinduced alignment control.

The photocontrol of in-plane LC alignment has been reported by a few groups. Gibbons et al have employed an azobenzene derivative doped in a thin film of a polyimide. This surface induces a homogeneous alignment of nematic LC by irradiation with linearly polarized light (LPL), and the nematic director was controlled by adjusting the direction of polarization plane of actinic LPL. The author speculated that the alignment photocontrol is caused by the reorientation of azobenzenes in polymer matrices[5]. Our group investigated the in-plane photocontrol of LC alignment using various azobenzenes, which are linked covalently to glass surfaces or attached to polymer backbones[6-10]. It was found out that the molecular structure of azobenzenes influences the efficiency of the regulation of LC alignment and that the alignment direction of azobenzenes governs a nematic director. Interestingly, even though an LPL-induced optical anisotropy of azobenzene units in polymer films is very small, prominent homogeneous alignment is induced when a cell is fabricated using this kind of

azobenzene polymers covering a substrate surface. As the surface-assisted photocontrol of LC alignment is extremely sensitive to the surface nature, systematic investigation is very important. On the basis of such information, various factors such as molecular structures of commander molecules and the manner of the surface modification have to be optimized in order to obtain high-performance materials for the LC alignment photocontrol.

In this study, the photocontrol of LC alignment using spin-cast films of poly[4-(2-methacryloylolethoxy)azobenzene] (**pMAz2**) is dealt with to reveal the LC aligning performances. Spin-coated films of the azobenzene-pendent polymer are preferentially used because of the excellent optical quality of homogeneous LC alignment and the facility in sample preparation.

2. Experimental

2.1. Materials

A nematic LC, NPC-02, showing a T_{NI} at 35 °C and a dichroic dye of a diaminoanthraquinone, LCD118, were donated by Rodic and Nippon Kayaku Co., Ltd, respectively. The preparation of **pMAz2** has been reported[11]. The structures of these compounds are shown in Figure 1.

2.2. Physical measurements

A 3 wt% toluene solution of **pMAz2** was spin-coated on 1 x 3 cm² quartz plates to give thin

Figure 1 Structures of liquid crystals and dichroic dye and **pMAz2**

polymer films of 60-80 nm thickness which were measured with a Rank Taylor Hobson Talystep. Films were irradiated with 436 nm light from a Hg-Xe lamp (<1 J cm⁻²) or an ultra-high pressure Hg arc (>1 J cm⁻²) through a combination of Toshiba color filters, Y-43 + V-44. Linearly polarized light was obtained by passing through a polarizer. Irradiation energy was measured with an Advantest power meter TQ8210 equipped with a photosensor TQ82017. Photoisomerization and dichroism of azobenzene chromophores were followed by measuring normal and polarized absorption spectra with a Hitachi 320 spectrometer and a Hewlett-Packard diode array spectrometer 8452Ax. Static contact angles were measured using a Kyowa Interface Science Contact Angle meter CA-X.

2.3. Cell fabrication

A lecithin-treated glass plate bringing a homogeneous LC alignment was prepared by the method same as that described in the literature[12]. An LC cell was fabricated by putting the LC, which was doped with 1 wt % of the dichroic dye for the determination of an LC director, between a lecithin-treated glass plate and a glass plate spin-cast with the azobenzene polymer to give a hybrid-type guest-host (GH) LC cell. The LC doped with the dichroic dye was suspended with spherical glass beads of a 5 μm diameter for the adjustment of a cell gap. Cell fabrication was carried out at an ambient temperature.

2.4. Photoalignment determination

It has been confirmed that the transition moment of the dichroic dye at 632.8 nm coincides with the alignment director of LC. Therefore, the director can be determined from the anisotropic absorption of the dye.

3. Results

3.1 Dichroism

Films of **pMAz2** were irradiated with LPL, and subjected to polarized absorption spectrum measurement to evaluate the extent of dichroism. Polarized spectra of a **pMAz2** film irradiated with LPL are showed in Figure 2. The π - π^* absorption for the probe light with perpendicular polarization to the electric vector of the actinic light was slightly larger than that in parallel with it. This means that azobenzene chromophores reorient perpendicularly to the electric vector of actinic visible light in line with other systems consisting of polymer films incorporating azobenzene

Figure 2 Polarized absorption spectra of **pMAz2** for probe light perpendicular (solid line) to and parallel (dotted line) with the electric vector of 436 nm actinic light.

units[13,14]. As seen in the figure, the dichroism is not so outstanding. Such a small dichroism may be ascribed to the thermal randomization of photoinduced oriented state.

In order to obtain further information about LPL-induced photodichroism, dichroic ratios were measured as a function of exposure energy of LPL. A dichroic ratio (DR) is defined as follows:

$$DR = (A_{\perp} - A_{\parallel}) / (A_{\perp} + A_{\parallel}) \quad (1)$$

where $A_{\perp}$ and $A_{\parallel}$ denote absorbencies at 342 nm for a polarized probe light with electric vectors perpendicular to and in parallel with that of the actinic LPL, respectively. As shown in Figure 3, the dichroic ratio increases monotonously and levels off at an exposure energy of about 500 mJ cm⁻² or more upon.

3.1. Factors affecting photoalignment

Azimuthal LC alignment induced by the irradiation of a film of **pMAz2** with LPL was found to be much influenced by annealing conditions. When a spin-cast film was irradiated with 436 nm LPL, followed by cell fabrication, homogeneous alignment was induced. In order to determine the orientational direction of photoinduced alignment, the absorbencies of a

Figure 3 Exposure energy dependence of dichroic ratios (DR) of an **pMAz2** film irradiated with LPL

dichroic dye dissolved in LC were measured using a linearly polarized He-Ne laser beam (633 nm) as a function of the rotational angle of an LC cell. Figure 4a shows the results for the LC photoalignment after irradiation with LPL at 436 nm using an as-cast **pMAz2** film without any annealing treatment. Homogeneous alignment was induced by a dose of 10 mJ cm⁻². The fact that the absorbencies of the dye have maximum values at rotational angles at both 0° and 180° indicates unequivocally that the photoinduced LC alignment is just perpendicular to the electric vector of actinic LPL. As the photoaligned direction of LC is coincided with that of azobenzene residues in a **pMAz2** film upon LPL irradiation. LC molecules orientate parallel with the long axis of azobenzene moieties attached to polymer backbones. It is quite worthy to note that these exposure energies of 10 mJ cm⁻² for 436 nm light is extraordinarily small when it is compared with exposure energies for the photoreorientation of azobenzene..

The LC photoalignment triggered by a **pMAz2** film was drastically affected by annealing of the film. It should be stressed here that a homeotropic alignment is induced when a **pMAz2** film is heated at 100 °C above T_g of the polymer for 1 hr. As illustrated in Figure 4b, no photoinduced homogeneous alignment was generated even though a film was exposed to linearly polarized 436 nm light of an energy of 500 mJ cm⁻². Homogeneous alignment required an exposure energy of 3 J cm⁻². This value is 300 times of that for the photoalignment using a film without annealing.

Figure 4 Circular diagrams for the absorbance of a) GH cells with as-cast **pMAz2** films which were irradiated with 436 nm LPL of 0 (□), 5 (△) or 10 (○) mJ cm⁻², and b) those with annealed (100 °C, 1 h) **pMAz2** films which were irradiated with 436 nm LPL of 0 (□), 0.5 (△) or 3 (○) J cm⁻². The gray arrows represent the polarization of actinic LPL.

3.3. Reorientation of LC alignment

The photocontrol of LC alignment by command surfaces has been performed reversibly by alternate

irradiation with light with two different wavelength regions for the photochromic reaction of commander molecules, and thus photoimages in LC layers recorded in this way are rewritable[1-3]. This fact led the author to investigate the LPL-induced reorientation of LC using **pMAz2** films. For this purpose, the second LPL-irradiation of a **pMAz2** film for rewriting was carried out before and after cell assembly. These procedures are named procedure A and procedure B for second irradiation before and after cell assembly, respectively. Figure 5a shows the results for the rewritability for procedure A. **pMAz2** films were first irradiated with polarized 436 nm light of a 100 mJ cm^{-2} , followed by subsequent LPL-irradiation of variant exposure energies after the rotation of the polarization plane of LPL by 45° to be subjected to a cell assembly. Figure 5a displays that the orientational direction of LC changes gradually maintaining the dichroic character of the doped dye and that the photoreorientation of LC molecules is completed at exposure energy of 200 mJ cm^{-2} or less. Note here that this exposure energy brings about 75% of a saturated LPL-

Figure 5 Circular diagrams for the absorbance of GH cells with **pMAz2** films. The films were irradiated, before cell assembly, with LPL at an energy of 100 mJ cm^{-2} , and the polarization is represented by the gray arrows. a) procedure A: The second irradiation with LPL with the polarization as presented by the black arrow was made at energies of 0 ($\square$), 50 ($\triangle$) or 200 ($\circ$) mJ cm^{-2} before cell assembly. b) procedure B: The second irradiation with LPL with the polarization as presented by the black arrow, after cell assembly, was made at energies of 0 ($\square$), 0.5 ($\triangle$) or 2 ($\circ$) J cm^{-2} .

Figure 6 Reorientation angles of the LC director as a function of exposure energy of the second 436 nm LPL: procedure A ($\circ$) and B ($\triangle$).

induced dichroic ratio of azobenzenes in a **pMAz2** film. In other words, the photoreorientation of azobenzene moieties leads to the reorientation of LC molecules. In marked contrast to this, much exposure energy was needed to result in the photoreorientation of LC alignment for procedure B, as presented in Figure 5b. The LC alignment direction is altered gradually again without any deterioration of the dichroic ratio of the dye whereas much larger energies are required for the completion of the LPL-induced reorientation. These results are summarized in Figure 6 in which angles corresponding to the change in LC directors are plotted against the exposure energies of second polarized light.

4. Discussion

The effect of annealing of **pMAz2** films reflects the thermally induced alteration of their surface molecular structures. This was supported by the fact that an absorption spectrum of a film is modified after heat treatment at 100°C for 1 hr, as given in Figure 7; the absorbance at λ_{max} decreases slightly after annealing. It is very likely that the decrease is owing to molecular aggregation of azobenzenes or a conformational change of azobenzenes at an uppermost surface into the direction normal to a film surface. The former possibility is rather inappropriate since the spectral shapes is not affected by the heat treatment. An alternative evidence for the thermally induced reorientation of azobenzenes at a surface was obtained by the static contact angle measurement. As shown in Figure 8, contact angles for water droplets became larger after annealing. It has been known that contact angles for water on a polymer film increase often upon annealing as a result of a conformational change of polymer chains at a surface region in order to reduce a surface energy [15, 16]. The motions of polymer chains have been thought to be of two kinds; one

Figure 7 Absorption spectra of a **pMAz2** film before (solid line) and after (dotted line) annealing at 100°C for 1 h.

consists of a fast overturn of side chains while the another is a slow migration of main chains. It is reasonable to accept the idea that non-polar migrate to a topmost surface of a film via these motions during annealing to reduce a surface energy. On the other hand, it has been revealed that a polymer surface with a smaller surface energy tends toward the generation of homeotropic LC alignment[17]. This is in line with the assumption that the annealing triggers homeotropic alignment.

The homogeneous alignment was brought about at anomalously small energy when an as-cast film of **pMAz2** is illuminated with LPL before an cell-assembly (Figure 4a). A UV-visible absorption spectrum of a film of the polymer was essentially not altered after irradiation at such energy, indicating that an extent of the trans-to-cis photoisomerization is negligibly small even though LPL irradiation results in the reorientation of LC. These facts imply that the photochemistry at a topmost surface of the film proceeds faster than that in the bulk. This implication led the author to determine the rate of photoisomerization of ultrathin films of the polymer on a silica plate. The surface of the plate was modified with a dimethyl diethoxy silane reagent to make it so hydrophobic to minimize a direct interaction between a bare surface of a silica plate and polar residues of the polymer. Thus, it is reasonable to regard these ultrathin films as models of a surface layer of polymer films which are used for the photocontrol of LC alignment. The relation between constants of isomerization rates and concentrations of trans isomer during photoirradiation is given by the equation (2) when the rate constant is not change during the irradiation[18]

$$\ln([t]_0 - [t]_\infty) / ([t] - [t]_\infty) = [t]_0 / [t]_\infty (B + K)t \quad \text{--- (2)}$$

Figure 8 Time dependence of contact angles of a **pMAz2** films on heating at 100 °C.

where $[t]$, $[t]_0$ and $[t]_\infty$ are concentrations of trans isomer during, before and after UV-irradiation, respectively, and A, B and K are rate constants of trans-cis and cis-trans photoisomerization and cis-trans thermal isomerization, respectively. Figure 9 shows the first order plots for the trans-to-cis photoisomerization of **pMAz2** films of variant thickness. The results are noticeable in the following points. First, slopes in the first order plot increase with the reduction of film thickness; the faster photoisomerization is, the thinner the film is in the present thickness region. This suggests that the photoisomerization takes place anomalously faster at a topmost surface. Second, plots for a ultrathin film of 12 nm thickness demonstrates a linear relationship, indicating the photoisomerization obeys strictly the first order kinetics just as in solution photochemistry, whereas the plots deviate from the linearity for thicker films, for instance, of 50 nm or 100 nm thickness. It has been widely accepted that the photoisomerization of azobenzenes in polymer solids deviates from the first kinetics below T_g of polymers as a result of the distribution of a free volume and analyzed usually as a sum of more than two first order plots. In this context, it is worthy to note again the linear first order plots for a 12 nm film. These results show that the photoreactions of azobenzene units at a surface is faster than that in bulk. This is one of the reasons why LC molecules align uniaxially on a film irradiated with linearly polarized UV light at such a low dose. An alternative effect, as mentioned below, has to be taken into account. LC molecules orientate uniaxially on a polymer film even though an optical anisotropy of the film is quite low. In other words, LC molecules display a marked molecular amplification of a tiny extent of surface orientation.

Figure 9 The first order plots for trans-cis photoisomerization of the azobenzene unit in **pMAz2** films. The films are about 100 nm (○), 50 nm (△), 25 nm (□) and 12 nm (●) in thickness.

As seen in Figure 6, LC directors change upon the second LPL-irradiation with a polarization plane of 45° in respect to that of the first LPL irradiation. The director points at intermediate angles during the second LPL irradiation and finally at an angle approximately perpendicular to the polarization plane of actinic light. It is noteworthy that the reorientation angle levels off at 45° when LPL irradiation of a **pMAz2** film is performed before cell assembly whereas the director rotates up to 40° when LPL irradiation is made after LC cell assembly. The deviation of 5° suggests the hysteresis of LC alignment because no deviation is observed in the former experiment.

The photoreorientation of LC molecules proceeds much faster when LPL irradiation is carried out before cell assembly, as shown in 6. In other words, the presence of an LC layer suppresses the rate of LPL-induced rewriting. This suggests that LC molecules at a boundary region resist the photoinduced reorientation of azobenzenes at an uppermost surface probably owing to the formation of molecular aggregates consisting of LC molecules and surface residues. It has been reported previously in a series on the studies on command surfaces that marked temperature dependence of reorientation of LC emerges when azobenzenes are tethered from a silica surface through a siloxy bonding; faster reorientation was observed at higher temperatures, and the reorientation was drastically accelerated by heating above T_{NI} . This phenomenon has been interpreted in terms of the mobility of LC molecules at an interface due to the heating. In other word, a thermal energy is required for overcoming rotational strain in order to cause surface-assisted LC reorientation.

5. Conclusion

Heat treatment of a **pMAz2** film leads to the reduction of surface energy of the film and gives a homeotropic alignment of a nematic LC. The surface of the polymer was easy to be affected by environmental conditions. Studies on photoisomerization behavior of ultrathin films as a model of a surface layer of polymer films reveal that the trans-to-cis photoisomerization obeys the first order kinetics when a film is 12 nm in thickness. The surface-assisted photoregulation of LC alignment was achieved using **pMAz2** films.

The reorientation process of azobenzene units at a surface is resisted by the presence of LC layer owing the suppressive effect of LC molecules on the mobility of azobenzene. High photosensitivity for the LC reorientation is due to a rapid reorientation of azobenzene residues at an uppermost surface of a polymer film or a long range order effect of LC.

6. References

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