ALIGNMENT OF NEMATIC LIQUID CRYSTALS CONTROLLED BY THE PHOTOCHROMIC REACTION OF AGGREGATED SURFACE AZOBENZENES.

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The alignment and the texture of a nematic liquid crystalline phase were regulated by the surface photochromic reactions of azobenzene (Az) pendent polymer films. On the poly(4-n-hexyl-4'-(11-methacryloyloxy-n-undecyl)-oxyazobenzene) film, the nematic phase exhibited three characteristic textures: marbled, homeotropic and schlieren textures, and each one of which was alternatively obtained by controlling photoexposure. Disappearance of the parallel domains and appearance of the homeotropic phase along with UV exposure corresponded to deformation of an oriented structure of *trans*-Az in the polymer.

1. INTRODUCTION

It is well known that the alignment of the liquid crystalline (LC) phase is strongly affected by the surface to which LC is attached[1]. For instance, a clean mica surface and a rubbed glass surface tend to induce the perpendicular alignment and the parallel alignment of the nematic LC phase, respectively. Such the surface-assisted LC alignment should be understood in terms of molecular interaction at the boundary. However, few experiments have been carried out from the above point of view. We have recently

† Reversible alignment change of liquid crystals induced by photochromic molecular films, part 9.

demonstrated that the reversible *trans-cis* photoisomerization of surface azobenzene (Az) chromophores induces the LC alignment change between the perpendicular state and the parallel state[2-7]. This clearly indicates high effectiveness of the boundary-molecules to the LC alignment. Such the photoinduced LC alignment change is applicable for the erasable direct read and write photomemory system.

Our preliminary results show new characteristics of the LC alignment change, which is regulated by the photochromic reaction of an oriented Az polymer film[7]. The LC phase alternatively displays one of following textures: schlieren, homeotropic or marbled texture. In the present article, the origin of the texture change is studied by means of UV-VIS spectroscopy and contact-angle measurement on Az polymer surfaces.

2. EXPERIMENTAL

2.1 Materials

Chemicals used in this study are shown in Figure 1. Nematic mixtures DON103 (RODIC Co.) and dichroic dye LCD118 (Nippon Kayaku Co.) were used as supplied. The synthesis of partially Az substituted polyvinylalcohol: P(C₆AzOC₁)VA, was reported previously[3]. Poly(4-n-hexyl-4'-(11-methacryloyloxy-n-undecyl)-oxyazobenzene): P(C₆AzOC₁₁O)MA, and other Az intermediates were prepared as follows.

Figure 1.
Chemical structures of and abbreviations
for Az polymers, nematic DON103 and
dichroic LCD118.

4-n-Hexyl-4'-(11-hydroxy-n-undecyl)oxyazobenzene (II)

4-n-Hexyl-4'-hydroxyazobenzene (I) was prepared by the conventional diazo coupling reaction between p-n-hexylaniline and phenol. The solution of 4.0g of (I) (14mmol), 4.3g of 11-bromoundecanol (1.2eq), 3.0g of potassium carbonate and 0.5g of 18-crown-6 in 30ml of acetone was refluxed for 17hrs. 100ml of acetone was added to the solution, and the excess salt was removed by filtration. The filtrate was then concentrated to precipitate crude material of (II). Recrystallization from ethanol gave 4.3g of the pure product (Yield; 82% from (I)).

4-n-Hexyl-4'-methacryloyloxy-n-undecyloxyazobenzene (III)

Into the ice-cooled solution of 5.0g of (II) (11mmol) and 3.1ml of triethylamine in 80ml of diethylether, the solution of 1.4g of methacryloylchloride (1.1eq) in 20ml of diethylether was added dropwise. The solution was stirred 4hrs at room temperature and refluxed for another 30min. Triethylaminehydrochloride was removed by filtration, and the filtrate was concentrated to dryness. (III) was recrystallized from hot ethanol (Yield; 75% from (II)).

Radical polymerization of (III)

The solution of 500mg of monomer (III) in 5.0ml of dry benzene containing 0.1wt% of azobisisobutyronitrile was heated for 36hrs at 60°C after several freeze-pump-thaw cycles to remove oxygen. The solution was then poured into a large amount of methanol to precipitate the crude polymer. Repeated precipitation from methanol gave pure homopolymer P(C₆AzOC₁₁O)MA (IV) (Yield; 36% from (III)).

2.2 Measurement

Polymer films were formed on quartz plates by spin-coating from the 1.0 wt% polymer solution: P(C₆AzOC₁₁O)MA in dry dioxane and P(C₆AzOC₁)VA in chloroform, and baked at 130°C for 1hr. The nematic DON103 was placed between a pair of the film-casted quartz plates with 8μm spacers.

The LC cell was exposed alternately to UV(365nm) and VIS(440nm) light from a 500W high pressure mercury lamp. Induced LC texture change was observed by Leitz Orthoplan-Pol polarizing microscope. Transmittance of the cell was monitored at 633nm with using a He-Ne laser under the cross-polar

condition. UV-VIS absorption spectra were collected by Yokogawa-Hewlett-Packard HP8452 diode-array spectrophotometer or by Shimadzu UV-160A spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Photoinduced LC Alignment Change by P(C₆AzOC₁₁O)MA Surface

P(C₆AzOC₁)VA film showed typical LC photoregulation as already found in many Az systems[2-7]. The LC alignment was changed between homeotropic and parallel by alternating the *trans*-Az surface and the *cis*-Az surface, respectively.

However, LC photoregulation by the P(C₆AzOC₁₁O)MA film was unusual and complicated. Figure 2 shows polarizing micrographs of LC textures. The initial alignment of the LC phase was parallel, and the texture was marbled (A-state). The texture consisted of many domains, each with its own homogeneous axis and tilting angle. The texture of the LC phase was changed from the marbled into the homeotropic (B-state) at first, then into the schlieren (C-state) by UV exposure. The change was reversible and successive VIS exposure gave the reverse process. The homeotropic B-state, which appeared between two different parallel states, was stable unless the cell was overexposed. The alignment change was accompanied by a large birefringence change as shown in Figure 3.

Figure 2.
Polarizing micrographs of the photoresponsive LC cell, P(C₆AzOC₁₁O)MA - DON103 system. The bar represents 100 μ m.
(A) The marbled texture observed before exposure or after sufficient VIS exposure.
(B) The transient homeotropic texture obtained during UV exposure.
(C) The schlieren texture obtained after sufficient UV exposure.

Figure 3.
The polarizing transmittance change of the photoresponsive LC cell, P(C6AzOC110)MA - DON103 system, at 633nm upon alternate exposure to UV and VIS light.

Figure 4.
Absorption spectra of the guest-host LC cell upon alternate exposure to UV and VIS light; at the marbled texture (A), at the homeotropic texture (B), and at the schlieren texture (C).
The cell consists of P(C6AzOC110)MA and DON103 containing 1.0 wt% of the dichroic dye LCD118.

When the LC cell contains dichroic dye LCD118, the alignment change can be monitored as the change in optical density (OD) of the cell. OD was changed in the order of schlieren C-state > marbled A-state > homeotropic B-state (Figure 4). Both A-state and C-state are in the parallel alignment, but difference arises in OD. The tilting angle in C-state should be larger than that in A-state, because the *cis*-Az surface has a higher surface energy than the *trans*-Az surface (See 3.3).

3.2 Photochromic Reactions of Az Polymer Films

Unbaked P(C₆AzOC₁)VA film exhibited an absorption band of *trans*-Az located at 342nm and a reversible spectral change due to *trans* - *cis* isomerization upon photoexposure[3]. Baking brought about blue-shift in the absorption of *trans*-Az ($\lambda_{\max}$ = 322nm) and irreversible nature into the first photochromic cycle. In the second photochromic cycle, however, the baked polymer exhibited a reversible spectral change. Formation of *trans*-Az

aggregates in the baking process and dissociation of the aggregates through *trans-cis* isomerization explained discrepancy between the first and the second photochromic cycles.

Similarly to P(C₆AzOC₁)VA, baked P(C₆AzOC₁₁O)MA film initially exhibited a narrow absorption band located at 324nm probably due to aggregation of *trans*-Az units (Figure 5). The absorption became broader and shifted to longer wavelength ($\lambda_{\text{max}}=330\text{nm}$) after one photochromic cycle, suggesting reduction of the amount of *trans*-Az aggregates. However, λ_{max} of *trans*-Az was still located at shorter wavelength than that of monomeric *trans*-Az. Besides, reversibility of spectral change in subsequent photochromic cycles was quite low and no clear isosbestic points was observed. The results indicate that Az-aggregates of P(C₆AzOC₁₁O)MA is easily formed at r.t. and a considerable amount of aggregates is existing even after several photochromic cycles. Since the spacer between Az unit and polymer backbone in P(C₆AzOC₁₁O)MA polymer is much longer than that in P(C₆AzOC₁)VA polymer, Az units in the former polymer can move more freely than in the latter polymer so that aggregation should take place efficiently.

Figure 5.
Photochromic spectral changes of the baked P(C₆AzOC₁₁O)MA film.
Forward process upon UV exposure (A1, 2, 3) and backward process upon VIS exposure (B1, 2). Arrows represent the direction of temporal spectra changes.

3.3 Contact Angles of Az Polymer Films

Contact angles (θ) of polymer surfaces to water and DON103 were measured (Figure 6). The P(C₆AzOC₁)VA films showed comparable changes in θ regardless of films' heat history except in the first photochromic cycle involving *trans*-Az aggregates. On the other hand, θ of the P(C₆AzOC₁₁O)MA film depends extremely on heat history of polymer, and large difference between the baked film and the unbaked film is existing even after several photochromic cycles. Since the difference is rather constricted when Az is *trans*, the surface energy of the P(C₆AzOC₁₁O)MA film is governed by the polymer bulk structure. The baking process was carried out probably above the glass transition temperature of P(C₆AzOC₁₁O)MA so that the structure of polymer backbone should be affected by orientation of Az side chains. Baked P(C₆AzOC₁₁O)MA should possess a backbone structure to form *trans*-Az aggregate preferably.

Figure 6.

Contact angle (θ) changes of Az polymer films upon photoexposure.

Left figure shows θ of the P(C₆AzOC₁)VA surface to water (upper) and DON103 (lower), respectively.

Right figure shows θ of the P(C₆AzOC₁₁O)MA surface to water (upper) and DON103 (lower), respectively.

3.4 Origin of the Multifarious LC Textures

Photochromic reaction of P(C₆AzOC₁₁O)MA can be divided into three periods: (i) the beginning of *trans*→*cis* (end of *cis*→*trans*) isomerization involving high concentration of oriented Az units, (ii) the intermediate period of isomerization after deformation of oriented Az units, and (iii) the end of *trans*→*cis* (beginning of *cis*→*trans*) isomerization.

In each reaction period, the surface has specific interaction with

LC molecules to display an individual LC texture. When Az units form ordered structures like aggregates or crystals, LC molecules may not interact with Az units effectively so that their alignment should be affected by other factors or interactive sites of the polymer surface (A-state). Similar effect was found in other Az polymers with short spacers between Az units and polymer backbone: the LC alignment was parallel initially due to low compatibility at the boundary, while it became homeotropic and photoresponsive after the systems were heated to allow effective interaction[6]. After UV exposure, liberated *trans*-Az units begin to interact with LC molecules to establish homeotropic alignment (B-state). Prolonged UV photoexposure increases *cis*-Az concentration in the polymer surface, and finally, the random schlieren texture of the LC phase is induced (C-state). All the textures originate from two factors: the surface energy and the surface structure.

4. CONCLUSION

Regulation of multifarious LC textures was demonstrated by the aggregated P(C₆AzOC₁₁O)MA polymer film. Each one of three distinctive textures: marbled, homeotropic and schlieren, was selectively obtained by controlling the amount of liberated *trans*-Az and *cis*-Az in the polymer film. The LC alignment change should be driven by at least two factors: the surface structure and the surface energy.

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