Photoorientation of Liquid Crystalline Azo-Dendrimer by Nanosecond Pulsed Laser for Liquid Crystal Alignment

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ABSTRACT: Upon irradiation with nanosecond pulsed UV laser, surface periodic microstructure and photoorientation occurred simultaneously on the azobenzene functionalized liquid crystalline dendrimer films. The orientation of azo groups was perpendicular to the polarization of pulsed laser and dependent on the laser fluence. The in-plane orientation of azo groups presented parabola-shaped behavior with the increase of laser fluences. The out-of-plane reorientation of azo groups was closely related to thermal effect induced in the procedure of nanosecond pulsed irradiation, which led to the transformation of phase state of azo groups from smectic liquid crystal phase to isotropic phase. Annealing of irradiated film at its liquid crystalline temperature resulted in dramatic enhancement of in-plane orientation and out-of-plane redistribution of azo groups. Liquid crystal alignment on the irradiated film was controlled by a cooperative effect of surface topography and anisotropic molecular orientation simultaneously. Both factors can be modulated by annealing treatment. After annealing, the alignment of liquid crystal molecules can be changed from the direction of surface microgrooves to that of the molecular orientation.

1. Introduction

Great interests have been plunged into photoalignment of liquid crystal (LC) molecules, which is a promising candidate to replace conventional mechanical rubbing technology.[1,2] As a kind of alignment materials, polymers with photosensitive azo fragments localized in the main chain or graft chain were intensively investigated due to their high optical sensitivity.[3−6] Under actinic irradiation, azo groups display *E*/*Z* isomerization and induce LC alignment in the direction perpendicular to the polarization of light. However, the photoorientation of azo groups is generally limited to the rigidity of polymer chains and needs quite long time to achieve uniform alignment. Photosensitive polymers with optimizing properties are still the most attractive target for LC aligning materials.

Recently, synthesis and application of a new class of compound, azobenzene-functionalized dendrimer defined as azo-dendrimer, have drawn a great deal of interest due to the charming properties including high photosensitivity, low melt, and solution viscosity,[7−10] which manifests itself in a set of unique applications like holographic storage[7,11] and antenna for harvesting protons.[12] Several fascinating phenomena on dendrimers with photosensitive azo groups have been described related to their photophysical and photochemical behaviors.[13−17] For example, Bobrovsky et al. investigated the behavior of azo-terminated dendrimers under irradiation of actinic light and found that the photoorientation and photoisomerization of the *E*/*Z* transition did not occur simultaneously in some dendrimers.[16,17]

Thermal enhancement of orientation order in liquid crystalline polymers (LCP) is one of the most interesting properties of azo-polymer found in recent years.[18,19] In this case the initial orientation order generated in glassy state of LCP acts as a driving force for self-organization, resulting in a dramatic enhancement of the orientation order of LCP. Undoubtedly, study on photosensitive dendrimers with LC phase is of considerably scientific and practical importance because of their easy rearrangement and fast optical response. These aspects should be interesting for the development of new kind of alignment layer for LC molecules. Unfortunately, there are few reports on the LC alignment behavior on the liquid crystalline photosensitive dendrimers.

Another fascinating phenomenon that occurred on light irradiation of azo-polymer is the generation of periodic surface microstructure, which is also effective in controlling LC alignment.[20,21] Generally two methods are employed to fabricate surface microstructure. One is the irradiation of two-beam interference of continuous or nanosecond pulsed laser. Surface microstructure obtained by this method is named as surface relief grating (SRG), which has been intensively studied in the past decades.[22−25] The other way to fabricate surface microstructure is the irradiation of single-beam nanosecond pulsed laser.[26−29] The interference of incident laser and laser scattered by the film surface results in the periodic surface microstructure, which is namely laser-induced periodic surface structure (LIPSS). We previously investigated the fabrication of LIPSS on azo-functionalized poly(urethane-imide) and found that LIPSS was formed in a direction parallel to the polarization direction of incident pulsed laser. Orientation of azo moieties was also generated with the preferred direction perpendicular to LIPSS.[21] In comparison with SRG, LIPSS fabrication is easier, and this structure was found to be very effective in aligning LC molecules.

In this work, we investigated the photoorientation properties of liquid crystalline multiarm star-shaped azo-dendrimer films by pulsed irradiation. Pulsed irradiation led to the anisotropic orientation of azo groups, and the thermal effect accompanied by this procedure strongly affected the distribution of azo groups due to the change in aggregated state of azo groups. Furthermore, both the orientation of azo moieties and LIPSS showed a decisive effect on LC alignment. It is also found that the preferred direction of LC alignment can be altered via annealing.

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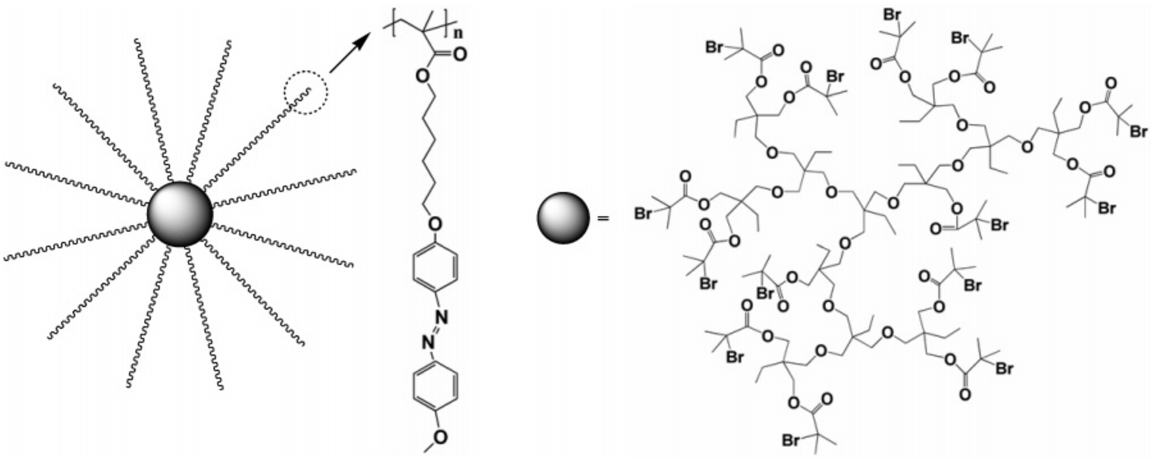

Figure 1. Schematic chemical structure of the multiarm star-shaped azo-dendrimer.

2. Experimental Section

The multiarm star-shaped azo-dendrimer, as shown in Figure 1, was synthesized via radical polymerization as described elsewhere.[30] The LCP films were prepared by spin-coating a THF solution (20 mg/mL) onto quartz plates. The thickness of the resultant film was about 160−190 nm measured by atomic force microscopy (AFM).

An s-polarized Nd:YAG laser (355 nm), with a pulse duration of 5 ns and repetition rate of 10 Hz, was used as light source. The spot of laser beams is 8 mm in diameter, and the intensity of the laser conforms to a Gauss distribution. Polymer films were fixed on an $X-Y$ platform, and moving speeds were 0.1 and 5 mm/s in X and Y directions, respectively. The incident angle was fixed at 15°.[29]

The surface morphologies of LCP films were investigated by AFM (Digital Instruments Inc., Nanoscope IIIa) in contact mode. Absorbance spectra of azo-dendrimer were recorded using a Perkin-Elmer lambda 20 UV−vis spectrophotometer. In order to characterize the influence of thermal treating temperature, the azo-dendrimer film was kept at 90 °C for 30 min and then cooled immediately. After measurement of UV−vis spectra, the same film was thermally treated at 140 °C for 30 min and applied to UV−vis spectroscopy again after cooling. The polarized UV−vis spectra were measured using the same device equipped with a Glan-Taylor prism. The in-plane order parameter, S, was calculated by[31,32]

$$S = \frac{A_{||} - A_{\perp}}{A_{\mathrm{large}} + 2A_{\mathrm{small}}} \tag{1}$$

$A_{||}$ and $A_{\perp}$ are the absorbance parallel and perpendicular to laser polarization direction (**E**), respectively. A_{large} and A_{small} refer to the larger and smaller absorbance of $A_{||}$ and $A_{\perp}$, respectively. The out-of-plane order parameter, S_h, was estimated by[31,32]

$$S_{\mathrm{h}} = 1 - \frac{A_{\mathrm{treated}}}{A_{\mathrm{initial}}} \tag{2}$$

A_{initial} is the absorbance of the as-coated azo-dendrimer film, and A_{treated} is the absorbance of the azo-dendrimer film after pulsed irradiation or thermal annealing. S and S_{h} were calculated by polarized UV−vis spectra at the wavelength of 355 nm.

A LC cell was fabricated by sandwiching nematic LC (5CB) between a dendrimer-coated substrate and a counter buffing polyimide (PI) substrate with the buffing direction perpendicular to the electric vector **E** of a polarized laser used to irradiate the dendrimer film. LC molecules can be homogeneously aligned along the buffing direction on the PI surface. Optical measurements were carried out by placing LC cells between crossed polarizers and measuring the transmittance from a He−Ne laser at 628 nm using a detector coupled to an oscillograph.

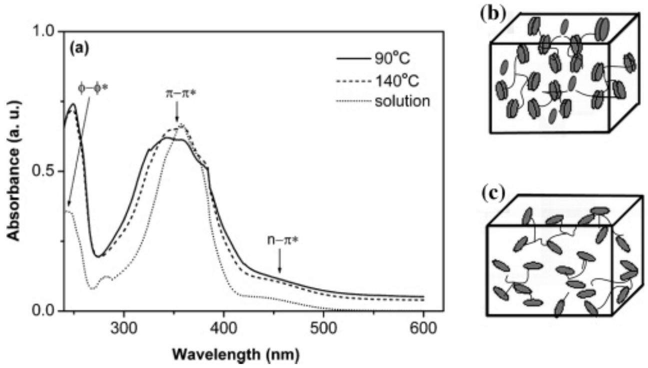

Figure 2. (a) Comparison of UV−vis spectra of azo-dendrimer annealed at 90 °C 140 °C and in THF solution. The annealing time is 10 min. Schematic illustration of azo groups in azo-dendrimer films thermally treated at (b) 90 and (c) 140 °C. The isolated and juxtaposed units represent nonaggregated and H-aggregated azo groups, respectively.

3. Results and Discussion

1. Phase Behavior. According to the results detected by polarized optical microscopy, DSC, and X-ray analysis, azo-dendrimer was characterized by the following phase behavior:[30]

G 74 SmA 92 N 132 I

where G, SmA, N, and I represent glass state, smectic LC phase, nematic LC phase, and isotropic phase, respectively. Figure 2a compares the UV−vis spectra of azo-dendrimer in different states. The peak at ∼240 nm is due to Φ−Φ* electronic transition of aromatic rings, the small shoulder at ∼460 nm is assigned to n−π* transition, and the maxima of the absorbance in the range of 340−360 nm corresponds to a strong $\pi-\pi$* electronic transition of the E-isomer. It is clear that the maximum absorbance (λ_{max}) of the azo-dendrimer in solution is the same as that of film treated at 140 °C, which is at the wavelength of 358 nm. For the film treated at 90 °C, an obvious blue shift of the λ_{max} from ∼358 to ∼343 nm occurred. The spectra showed a wider absorbance band and smaller absorbance in comparison with that of the film treated at 140 °C.

It was reported that azo groups in polymers with LC nature show a strong tendency to aggregate, and the aggregation is even more pronounced in the thin-film state.[33] The aggregation behavior is strongly influenced by packing consideration and phase transition. For the film treated at 90 °C, azo groups in the dendrimer film were assembled at smectic LC order, and their dipoles tended to redistribute in a form of parallel arrangement (H-aggregates), which led to the dramatic blue shift of maximum absorbance of azo groups. After fast cooling from 90 °C to room temperature, the distribution of azo groups at a smectic LC phase was frozen (Figure 2b). Correspondingly, the spectra showed a wider absorbance band, and a blue shift of the maximum absorbance occurred. However, for the film treated at 140 °C, the azo-dendrimer was in the isotropic state. The azo groups do not organize as H-aggregates due to high motional ability of molecules at this temperature. After cooling down immediately, the distribution of azo groups was kept in the film (Figure 2c). Therefore, the maximum absorbance of the film treated at 140 °C was at the same wavelength as that in solution. After thermal treatment at 140 °C, UV absorbance of the film treated at 140 °C increased compared to that treated at 90 °C, indicating that the homeotropic alignment in the film treated at 140 °C was destroyed and a part of azo groups tend to orientate in plane.[34] If we assumed the film treated at 140 °C to be the initial film, the out-of-plane orientation S_h of the film treated at 90 °C can be estimated according to formula 2, with the approximate value of 0.06.

2. LIPSS Formation on Azo-Dendrimer under Pulsed Irradiation. When a polymer film is exposed to single-beam pulsed laser, LIPSS can be formed only if the polymer has absorbance to the laser wavelength. AFM presented the formation of LIPSS on the dendrimer films after pulsed irradiation, as shown in Figure 3a. Figure 3b plots LIPSS amplitude as a function of laser fluences. It is demonstrated that LIPSS amplitude increased markedly with laser fluences followed by leveling off at a fluence of 4.0 mJ/cm^2 and then decreased when the laser fluence was higher than 8.4 mJ/cm^2.

The dependence was attributed to the mechanism of LIPSS formation, which was considered to be a result of thermally induced macroscopic mass movement procedure of surface molecules.[35] LIPSS formation mainly includes three stages: incubation, rapidly developing, and stable stage.[36] In the incubation period, incident laser interferes with laser beam scattered by the surface, which results in the periodic distribution of laser fluences. In bright regions the polymer surface receives high fluence and thus attains a higher temperature, while in dark regions the polymer surface remains unchanged. Polymer chains tend to flow from the region receiving higher fluence to the region receiving lower fluence by surface stress driving. However, no LIPSS can be formed on the polymer surface until the fluence reaches a critical value. The incubation is followed by a rapidly developing stage: LIPSS grows rapidly under laser irradiation and then enters in the stable stage in which more irradiation does not further increase the LIPSS amplitude, and the growth of LIPSS levels off owing to the limitation of penetration depth of laser. LIPSS amplitude starts to decrease if the laser fluence is up to the ablation threshold of the material.

3. Orientation of Azo Groups in Azo-Dendrimer under Pulsed Irradiation. It is well-known that the *E*/*Z* isomerization of azo groups occurs upon actinic irradiation, and the photochemical properties can be obviously changed in this procedure. However, compared to light or continued laser, irradiation by pulsed laser not only induces *E*/*Z* isomerization and photoorientation of azo groups in azo-dendrimer film but also involves the possibility of fast thermal heating,[37] which may alter phase behavior of azo-dendrimer films.

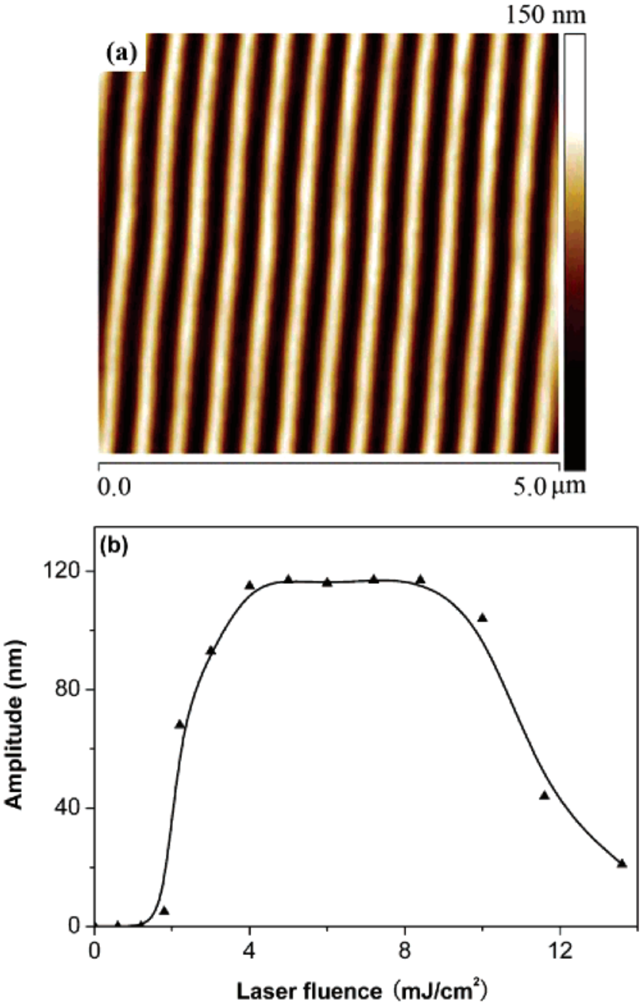

Figure 3. (a) Typical AFM image of LIPSS on the azo-dendrimer film irradiated with pulsed UV laser at a fluence of 3.0 mJ/cm^2. (b) Relationship between LIPSS amplitude and the fluences of pulsed UV laser.

Here we investigated the anisotropic orientation of azo groups as a function of laser fluences. The films used were annealed at 90 °C for 10 min. As shown in Figure 4a, azo groups exhibit anisotropic orientation with the preferred direction perpendicular to the pulsed polarization. Figure 4b shows the corresponding polarized UV−vis spectra of azo-dendrimer film after pulsed irradiation. The absorbance in the direction perpendicular to laser polarization, $A_\perp$, is larger than $A_{||}$, the absorbance parallel to laser polarization. Furthermore, the in-plane orientation order of azo groups increases with laser fluences (Figure 4c), and the maximal value of −0.084 is achieved at 4.0 mJ/cm^2. Then the orientation order begins to decrease with the increase of laser fluences. Here, the negative sign of in-plane orientation order means that the photoinduced orientation is perpendicular to the polarization of the pulsed UV laser.

In order to explain the above experimental results, we have to take into account the thermal effect induced by the nanosecond pulse. During nanosecond pulsed irradiation, azo groups with dipoles parallel to pump polarization are excited, leading to an anisotropic orientation of *E*-isomer and an instantaneous increase of the anisotropic orientation. Thus, orientation order increases with laser fluences. Meanwhile, the azo-dendrimer film underwent a high temperature of several hundred degrees due to the thermal effect of nanosecond pulse.[37,38] The strong thermal effect leads to local melting of the film surface, which makes the motion of surface molecules and subsequently the orientation

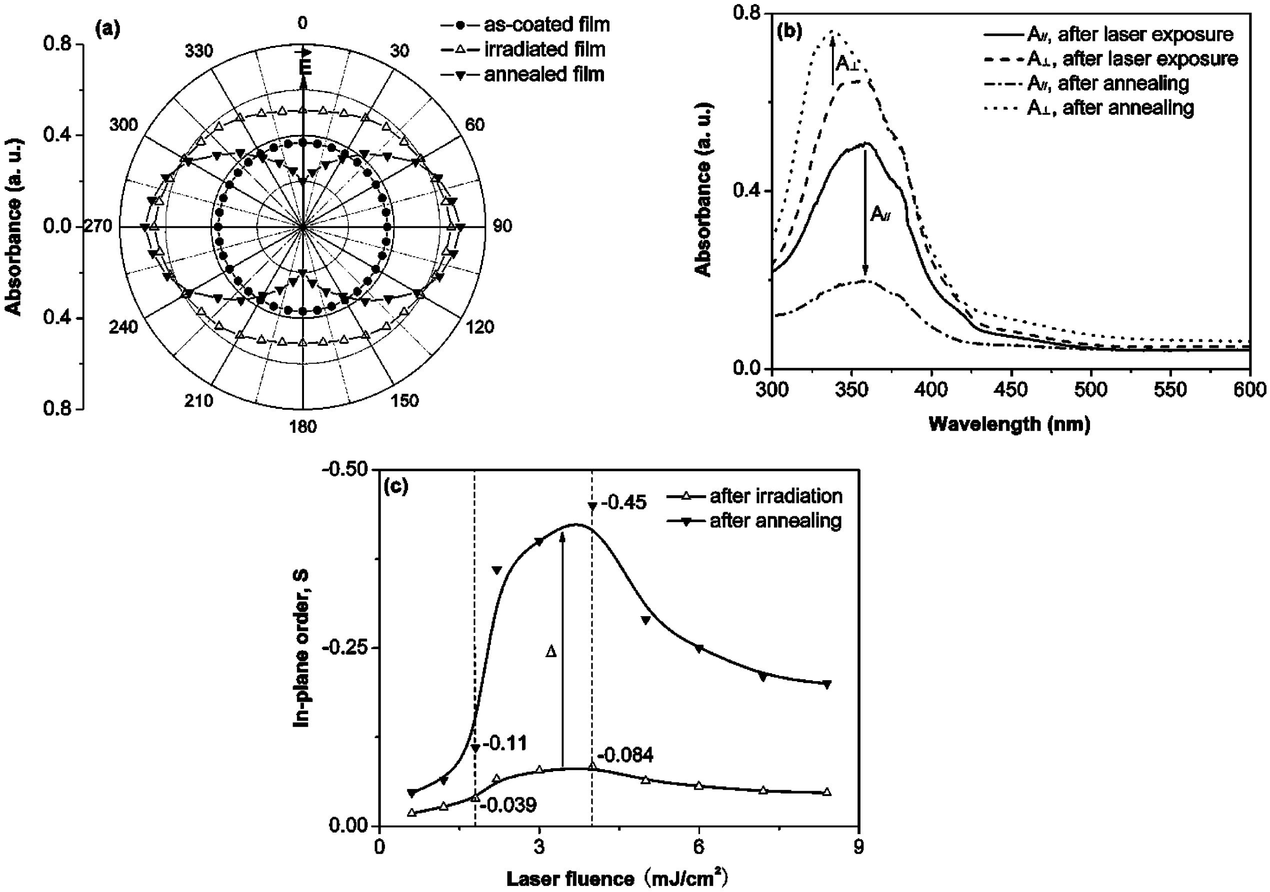

Figure 4. (a) Absorbance of azo-dendrimer films nonirradiated (●), pulsed irradiated at a laser fluence of 4.0 mJ/cm^2 (△), and after annealing at 90 °C for 10 min (▼) as a function of the angle between the electric vector of pulsed laser (**E**) and the polarization direction of UV spectra. (b) Polarized UV−vis spectra of the azo-dendrimer film after pulsed irradiation (4.0 mJ/cm^2) and after annealing (90 °C, 10 min). (c) The in-plane orientation order of azo-dendrimer films (calculated at 355 nm) as a function of laser fluence. The azo-dendrimer films were irradiated with pulsed UV laser (△) and subsequently annealed at 90 °C for 10 min (▼).

of azo groups easier.[29] On the other hand, the strong heating effect of pulsed laser irradiation also leads to the relaxation of oriented molecules and the decrease of laser-induced instantaneous anisotropic orientation. However, compared to the orientation of azo groups by pulsed laser irradiation, the molecular relaxation is a slower process.[39] At the end of each pulse, the polymer film is solidified and the remained orientation is frozen. That is to say, both laser intensity and surface temperature are the key factors in deciding the final anisotropic orientation of azo groups, and they show a contrary effect on the orientation order. At lower laser fluence, the thermal effect is rather weak, and the final orientation order increases with the increase of laser fluences. While at higher fluence, thermal effect becomes strong and leads to the relaxation of oriented molecules.[39] The contrary factors result in a parabola-shaped curve of the anisotropic orientation as a function of laser fluence.

Moreover, high temperature induced by the pulsed irradiation also provides the possibility of redistribution of azo groups, which is related to out-of-plane orientation of azo groups. It has been conformed by UV−vis spectra measurement of the irradiated azo-dendrimer films (Figure 5). After pulsed irradiation the absorbance increased compared to that of the as-coated film, which was independent of the level of laser fluences selected. The difference merely lies in that the degree of increase at higher fluence is larger than that at lower fluence, e.g., at 5.0 mJ/cm^2 (Figure 5b) and 1.8 mJ/cm^2 (Figure 5a). In addition, a red shift of maximum absorbance occurred after irradiation, and the shape of UV−vis spectra is similar to that of the film annealed at 140 °C.

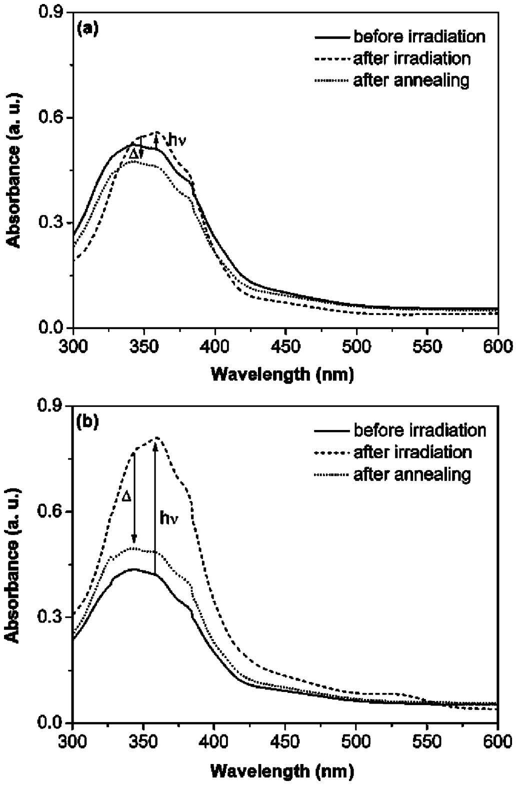

Figure 5. UV−vis spectra of azo-dendrimer films irradiated at a laser fluence of (a) 1.8 and (b) 5.0 mJ/cm^2.

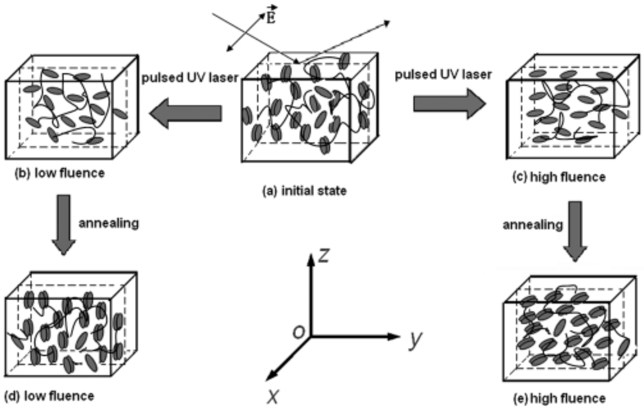

Figure 6. Illustrative presentation of molecular reorientation in the azo-dendrimer films induced by pulsed irradiation of Nd:YAG laser at 355 nm. The irradiated films were annealed at 90 °C for 10 min and then cooled immediately. The juxtaposition presents the H-aggregates of azo groups.

A reasonable explanation of this phenomenon may be that the laser-induced temperature on the azo-dendrimer surface exceeds 140 °C in the procedure of pulsed irradiation, even though at low laser fluence. In this case, H-aggregates of azo groups formed at 90 °C can be easily destroyed, leading to the transformation of phase state of azo-dendrimer from smectic to isotropic phase. In this case, UV−vis absorbance of the dendrimer film is similar to that of the film treated at 140 °C. Simultaneously, during pulsed irradiation, the *E*-isomer with a preferred homeotropic alignment tends to align in the direction perpendicular to pulsed polarization (in other words, the incident plane of laser), resulting in the redistribution of azo groups from originally homeotropic alignment to in-plane alignment. Therefore, UV−vis absorbance of azo groups increased (this process was presented in Figure 6).

4. Thermal Amplification of Photoorientation of Azo Groups. It was widely reported that thermal annealing at LC phase led to an enhancement of the orientation of LCP films.[18,19] The orientation existed in the initial LCP film was the driving force in this procedure. We tried to investigate whether thermal amplification is effective for the azo-dendrimer films. Here, annealing at 90 °C for 10 min was adopted as the thermal treating condition for the irradiated azo-dendrimer film. It is clearly demonstrated that the in-plane orientation underwent a remarkable enhancement after thermal annealing (Figure 4a,b). Figure 4c presents the changes in the in-plane orientation order of azo groups (filled curves in Figure 4c). After annealing, the in-plane orientation was dramatically amplified. It indicated that liquid crystalline dendrimers exhibit the self-amplification property, which is similar to that of comb-shaped LCP.[40,41] The amplified degree was closely related to laser fluences, for example 5.4 times from −0.084 to −0.45 at the fluence of 4.0 mJ/cm^2 and 2.8 times from −0.039 to −0.11 at the fluence of 1.8 mJ/cm^2. UV−vis spectra of the annealed films also revealed that most of azo groups appeared to turn toward out-of-plane and formed H-aggregates again during annealing, leading to the decrease of absorbance and blue shift of maximum absorbance of the *E*-isomer, as shown in Figure 5. The annealed azo-dendrimer showed smectic LC phase again. Moreover, the procedure of thermal enhancement was closely related to laser fluences. At the fluence of 1.8 mJ/cm^2, the absorbance of the annealed film is lower than that of the as-coated film, while the absorbance is larger than that of that of the as-coated film when the laser fluence is 5.0 mJ/cm^2.

To explain the above experimental results, the following model was proposed (Figure 6). The polarization of pulsed laser is along *X*: in the initial azo-dendrimer film azo groups are distributed in a preferred homeotropic alignment and form H-aggregates (Figure 6a). During pulsed irradiation, H-aggregates are destroyed, and the tendency of homeotropic alignment decreases as a result of the thermal effect of pulsed laser. Azo groups tend to reorient from out-of-plane to in-plane, closely to the *XOY* plane under high temperature. Irradiation with polarized laser also leads to the preferred orientation of *E*-isomer perpendicular to the pulsed polarization, in other words, in the *YOZ* plane, as shown in Figure 6b,c. During the nanosecond pulse, the surface temperature is higher than the transition temperature of isotropic phase whether the laser fluence is high or low. Under this condition, the azo-dendrimer film is isotropic and H-aggregates are destroyed. Simultaneously, azo groups tend to redistribute from out-of-plane to in-plane (closely to *XOY* plane). This redistribution is a thermodynamic process related to the film temperature. The deviating degree of molecules from the *Z* direction to the *XOY* plane is larger at high temperature than that at low temperature. As described in section 3.3, high laser fluence corresponds to high surface temperature. Thus, molecules at high fluence (Figure 6c) orient more closely to the *XOY* plane than that at low fluence (Figure 6b). After annealing at 90 °C, azo-dendrimer shows LC phase and azo groups form H-aggregates again. The photoorientation induced by pulsed irradiation can be amplified due to the LC nature of azo-dendrimer. In the annealing procedure, the molecules reorient from in-plane to out-of-plane. This process is also a thermodynamic process. For the film irradiated at low fluence, the deviation of molecules from the *Z* direction to in-plane is small during laser irradiation, so it is easy to reorient from in-plane to the *Z* direction during the annealing process, leading to the decrease of UV absorbance (Figures 5a and 6b−d). However, for the film irradiated at high fluence, the molecules orient more closely to the *XOY* plane. It needs larger energy and longer time to reorient from the *XOY* plane to the *Z* direction, in contrast to that irradiated at low fluence. So at the present condition the molecules still show a tendency of in-plane orientation though the deviational angle from the *Z* direction decreases after annealing (Figures 5b and 6c−e).

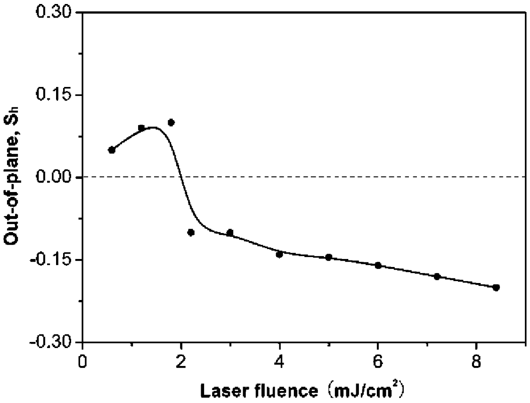

Figure 7. Out-of-plane orientation order of dendrimer films (calculated at 355 nm) as a function of laser fluences upon pulsed irradiation and subsequent annealing (90 °C, 10 min).

This character can also be conformed by the dependence of out-of-plane orientation of azo groups on laser fluences. Figure 7 presents the changes in the out-of-plane order S_h as a function of laser fluences. If laser fluences lower than 1.8 mJ/cm^2, the out-of-plane orientation order is positive and increases with laser fluences, indicating that azo groups tend to reorientation from in-plane to out-of-plane. If the laser fluence is above 1.8 mJ/cm^2, the out-of-plane order becomes negative and decreases with the increase of laser fluences, indicating that azo groups were redistributed from out-of-plane to in-plane.

5. LC Alignment on Liquid Crystalline Azo-Dendrimer. The alignment of LC molecules can be controlled by anisotropic surface of alignment layer, either by its topography or by oriented molecular chain, which was referred to as “command surfaces”.[3] In most cases, the two factors exist independently on the surface of alignment layer. For example, only anisotropy orientation of molecules occurred when photosensitive materials were exposed to polarized light,[42] and only periodic microgrooves were obtained when laser ablation technique was exploited to fabricate LC alignment layers.[43] Mechanical rubbing treatment induces both surface microgrooves and molecular orientation along the same direction. Both factors induce LC alignment along the rubbing trace.[44] However, in this work azo-dendrimer with LIPSS shows a unique property: the microgrooves of LIPSS are perpendicular to the photoinduced orientation of azo groups. That is to say, the two factors are competitive in deciding the direction of LC alignment. This property may show great potential in the development of a new kind of LC device.

To investigate the behavior of LC alignment on azo-dendrimer, a LC cell was then fabricated with the laser-irradiated dendrimer substrate and a buffing PI substrate with the buffing direction on the PI substrate perpendicular to laser electric vector **E** for the irradiated dendrimer film. Three laser fluences, 0.6, 2.2, and 3.0 mJ/cm^2, were chosen for pulsed irradiation. First we measured the transmittance of the He−Ne laser through LC cells. For a cell with uniform LC alignment between crossed polarizers, the transmittance changes with the rotation of LC cell with respect to the normal line of the substrate and can be calculated according to the following formula:

$$T = \sin^2(2\theta)\,\sin^2(\pi\Delta nd/\lambda)$$

where T is the transmittance of the light though the LC cell, θ is the rotation angle of LC cell, d is the thickness of the cell, Δn is the refractive index of the filled LC molecules, and λ is the wavelength of the detected laser. For a given cell, the terms except θ are fixed, and the transmittance is only related to the rotation angle θ. We considered the initial position of LC cell to be 0° when the buffing direction of the reference substrate was parallel to either polarization direction of the polarizers. Figure 8 presents the dependence of optical transmittance on the rotation angle of LC cell between crossed polarizers. The changes in the transmittance with a period of 90° demonstrated that homogeneous LC alignment was achieved on the azo-dendrimer films. However, for the cells with substrates irradiated at different laser fluences, the transmittance of LC cells exhibits obviously different behavior. In the case of 0.6 mJ/cm^2, the cell shows a minimum transmittance at the initial position as shown in Figure 8a, demonstrating that LC molecules are aligned in the same direction on both substrates (parallel-mode LC cell). Thus, it can be deduced that the LC molecules lie in the direction perpendicular to laser polarization on the azo-dendrimer-coated substrate. According to Figure 3b, no LIPSS was formed on the dendrimer film at this laser fluence, and LC alignment was controlled only by the molecular interaction effect. However, in the case of 3.0 mJ/cm^2, the LC cell exhibits maximum transmittance at the initial position, indicating that the direction of LC alignment on the two substrates was perpendicular to each other (twist nematic-mode LC cell). The result shows that LC molecules were mainly affected by topographic effect and aligned along the microgrooves of LIPSS. As for the azo-dendrimer film irradiated at an fluence of 2.2 mJ/cm^2, LIPSS with an amplitude of 68 nm was obtained on the dendrimer surface. In this case, the transmittance of LC cell lies in between the maximum and minimum value as shown in Figure 8a, indicating that LC molecules are aligned in a direction between LIPSS and the molecular orientation directions. Twist angle measurements proved that LC alignment was controlled by both intermolecular interaction effect and microgroove effect. Another attractive phenomenon about the LC alignment on the laser irradiated azo-dendrimer film is that the LC alignment direction can be changed from the microgroove direction to the molecular orientation direction after annealing of the azo-dendrimer film, as shown in Figure 8b. For the cell obtained using the azo-dendrimer film irradiated at 3.0 mJ/cm^2, LIPSS was completely erased after annealing, and simultaneously the degree of molecular orientation was dramatically amplified. As a consequence, the configuration of LC cell was changed from twist nematic mode to parallel mode and displayed dark field at the initial position after the thermal treatment. This property may have great potential in developing new kind of LC device.

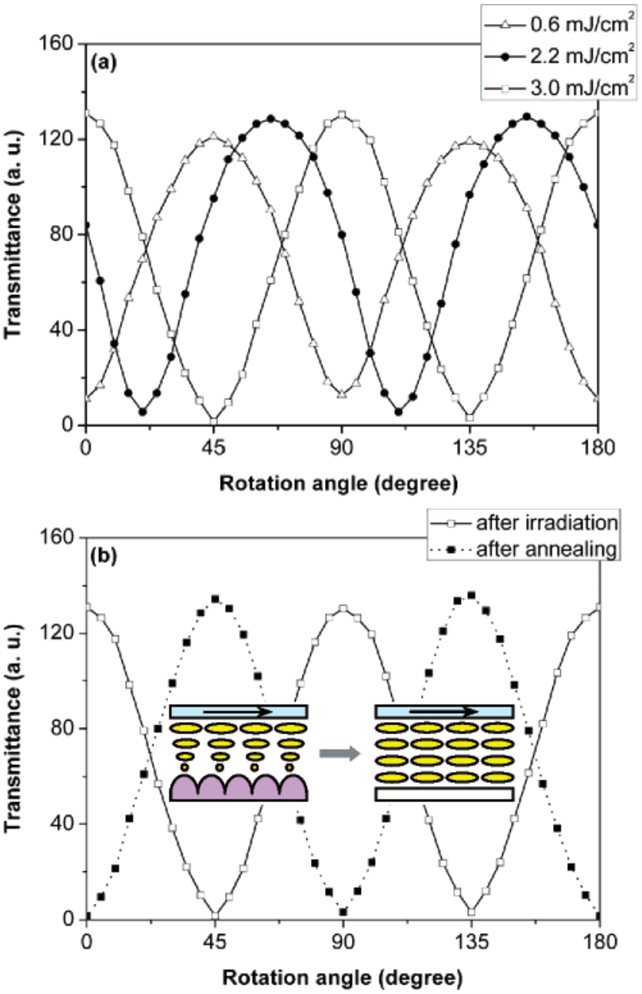

Figure 8. Optical transmittance of LC cells as a function of rotation angle of the cell between crossed polarizers. The LC cell was assembled by a counter buffing polyimide substrate and an azo-dendrimer substrate. (a) The dendrimer substrate was pulsed irradiated at a fluence of 0.6 (△), 2.2 (●), and 3.0 mJ/cm^2 (□). (b) The dendrimer substrate was irradiated at 3.0 mJ/cm^2 (solid line) and subsequently annealed at 90 °C for 10 min (dashed line). The inner image is a scheme of LC alignment in the cell before and after annealing. The arrow indicates the buffing direction on the counter polyimide substrate.

4. Conclusions

In summary, irradiation by nanosecond pulsed laser-induced LIPSS and photoorientation of azo groups in the liquid crystalline azo-dendrimer film simultaneously. The in-plane orientation of azo groups was perpendicular to the polarization of the pulsed laser and presented negative parabola-shaped behavior with the increase of laser fluences. The azo groups tended to form a structure with preferred in-plane orientation owing to thermal effect in the pulsed irradiation procedure. After annealing at the LC temperature, in-plane orientation order was enhanced and the maximum value was up to 0.45. H-aggregates of azo groups were formed again like the as-coated film and the out-of-plane reorientation in the annealing procedure was closely related to the laser fluence of previous process.

LC alignment on the pulsed irradiated azo-dendrimer films was controlled by both surface topography and anisotropic molecular orientation. The alignment direction of LC molecules can be shifted from the direction of surface microgrooves to the preferred direction of the molecular orientation after thermal treatment of the azo-containing dendrimer film. In addition, liquid crystalline azo-dendrimer exhibits controllable out-of-plane orientation, which possesses promising application in the pretilt angle of LC alignment.

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References and Notes

(1) Geary, J. M.; Goodbye, J. W.; Patel, J. S. *J. Appl. Phys.* **1987**, *62*, 4100–4108.

(2) Van Aerie, N. A. J. M.; Barmentio, M.; Hollering, R. W. J. *J. Appl. Phys.* **1993**, *74*, 3111–3120.

(3) Ichimura, K.; Suzuki, Y.; Seki, T.; Hosoki, A.; Aoki, K. *Langmuir* **1988**, *4*, 1214–1216.

(4) Gibbons, W. M.; Shannon, P. J.; Sun, S. T.; Swetlen, B. J. *Nature (London)* **1991**, *351*, 49–50.

(5) Shannon, P. J.; Gibbons, W. M.; Sun, S. T. *Nature (London)* **1994**, *368*, 532–533.

(6) Ichimura, K.; Kidowaki, M.; Akiyama, H.; Kudo, K.; Strehmel, V. *Macromol. Rapid Commun.* **1996**, *17*, 545–551.

(7) Archut, A.; Vögtle, F.; De Cola, L.; Azzellini, G. C.; Balzani, V.; Ramanujam, P. S.; Berg, R. H. *Chem.—Eur. J.* **1998**, *4*, 699–706.

(8) Sebastián, R. M.; Blais, J. C.; Caminade, A. M.; Majoral, J. P. *Chem.—Eur. J.* **2002**, *8*, 2172–2183.

(9) Gopalan, P.; Katz, H. E.; McGee, D. J.; Erben, C.; Zielinski, T.; Bousquet, D.; Muller, D.; Grazul, J.; Olsson, Y. *J. Am. Chem. Soc.* **2004**, *126*, 1741–1747.

(10) Ghosh, S.; Banthia, A. K.; Chen, Z. *Tetrahedron* **2005**, *61*, 2889–2896.

(11) Che, P. C.; He, Y. N.; Wang, X. G. *Macromolecules* **2005**, *38*, 8657–8663.

(12) Jiang, D. L.; Aida, T. *Nature (London)* **1997**, *388*, 454–456.

(13) McGrath, D. V.; Junge, D. M. *Chem. Commun.* **1997**, 857–858.

(14) Junge, D. M.; McGrath, D. V. *J. Am. Chem. Soc.* **1999**, *121*, 4912–4913.

(15) Weener, J. W.; Meijer, E. W. *Adv. Mater.* **2000**, *12*, 741–746.

(16) Bobrovsky, A. Y.; Pakhomov, A. A.; Zhu, X. M.; Boiko, N. I.; Shibaev, V. P.; Stumpe, J. *J. Phys. Chem. B* **2002**, *106*, 540–546.

(17) Bobrovsky, A.; Ponomarenko, S.; Boiko, N.; Shibaev, V.; Rebrov, E.; Muzafarov, A.; Stumpe, J. *Macromol. Chem. Phys.* **2002**, *203*, 1539–1546.

(18) Fischer, T.; Läsker, L.; Czapla, S.; Rübner, J.; Stumpe, J. *Mol. Cryst. Liq. Cryst.* **1997**, *297*, 489–496.

(19) Fischer, T.; Läsker, L.; Rutloh, M.; Czapla, S.; Stumpe, J. *Mol. Cryst. Liq. Cryst.* **1997**, *299*, 293–299.

(20) Ramanujam, P. S.; Pedersen, M.; Hvilsted, S. *Appl. Phys. Lett.* **1999**, *74*, 3227–3229.

(21) Lu, X. M.; Lu, Q. H.; Zhu, Z. K.; Yin, J.; Wang, Z. G. *Chem. Phys. Lett.* **2003**, *377*, 433–438.

(22) Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66*, 136–138.

(23) Kim, D. Y.; Tripathy, S. K.; Li, L.; Kumar, J. *Appl. Phys. Lett.* **1995**, *66*, 1166–1168.

(24) Ubukata, T.; Seki, T.; Ichimura, K. *Adv. Mater.* **2000**, *12*, 1675–1678.

(25) Bai, S.; Zhao, Y. *Macromolecules* **2002**, *35*, 9657–9664.

(26) Bolle, M.; Lazare, S. *J. Appl. Phys.* **1993**, *73*, 3516–3524.

(27) Hiraoka, H.; Sendova, M. *Appl. Phys. Lett.* **1994**, *64*, 563–565.

(28) Csete, M.; Marti, O.; Bor, Zs. *Appl. Phys. A: Mater. Sci. Process.* **2001**, *73*, 521–526.

(29) Lu, Q. H.; Wang, Z. G.; Yin, J.; Zhu, Z. K.; Hiraoka, H. *Appl. Phys. Lett.* **2000**, *76*, 1237–1239.

(30) He, X. H.; Yan, D. Y.; Mai, Y. Y. *Eur. Polym. J.* **2004**, *40*, 1759–1765.

(31) Meier, J. G.; Ruhmann, R.; Stumpe, J. *Macromolecules* **2000**, *33*, 843–850.

(32) Uchida, E.; Shiraku, T.; Ono, H.; Kawatsuki, N. *Macromolecules* **2004**, *37*, 5282–5291.

(33) Faul, C. F. J.; Antonietti, M. *Adv. Mater.* **2003**, *15*, 673–683.

(34) Yaroschuk, O.; Sergan, T.; Lindau, J.; Lee, S. N.; Kelly, J.; Chien, L. C. *J. Chem. Phys.* **2001**, *114*, 5330–5337.

(35) Sipe, J. E.; Young, J. F.; Preston, J. S.; van Driel, H. M. *Phys. Rev. B* **1983**, *27*, 1141–1154.

(36) Bolle, M.; Lazare, S. *Appl. Surf. Sci.* **1993**, *65–66*, 349–354.

(37) Evans, K. E. *J. Appl. Phys.* **1988**, *63*, 4946–4950.

(38) Bartholomeusz, B. J. *Appl. Opt.* **1992**, *31*, 909–918.

(39) Hildebrandt, R.; Hegelich, M.; Keller, H. M.; Marowsky, G.; Hvilsted, S.; Holme, N. C. R.; Ramanujam, P. S. *Phys. Rev. Lett.* **1998**, *81*, 5548–5551.

(40) Han, M.; Ichimura, K. *Macromolecules* **2001**, *34*, 90–98.

(41) Sapich, B.; Vix, A. B. E.; Rabe, J. P.; Stumpe, J. *Macromolecules* **2005**, *38*, 10480–10486.

(42) Kawanishi, Y.; Tamaki, T.; Sakuragi, M.; Seki, T.; Suzuki, Y.; Ichimura, K. *Langmuir* **1992**, *8*, 2601–2604.

(43) Behdani, M.; Keshmiri, S. H.; Soria, S.; Bader, M. A.; Ihlemann, J.; Marowsky, G.; Rasing, Th. *Appl. Phys. Lett.* **2003**, *82*, 2553–2555.

(44) Zhu, Y. M.; Wang, L.; Lu, Z. H.; Wei, Y.; Chen, X. X.; Tang, J. H. *Appl. Phys. Lett.* **1994**, *65*, 49–51.

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