

Exotic Property of Azobenzenesulfonic Photoalignment Material Based on Relative Humidity

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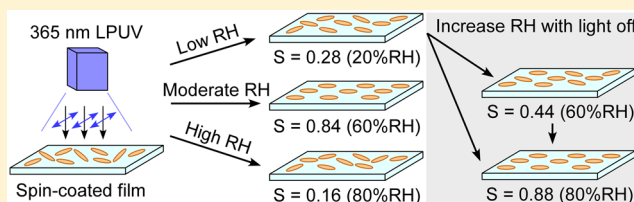
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Supporting Information

ABSTRACT: Azobenzene photoalignment materials are highly effective for liquid crystal alignment with high sensitivity and rewritability. A strong relationship between relative humidity and the alignment quality of a thin layer of azobenzenesulfonic dye has been investigated, where the photoinduced phase retardation, order parameter, and anchoring strength of the alignment layer are influenced dramatically by relative humidity. Our results provide fabrication guidance for the photoalignment process in both display and photonic applications. In addition, an exotic substantial ordering enhancement is observed by increasing the relative humidity without further light illumination, where the self-assembly of the photoaligned material incorporated with water molecules is the underlying reason for the enhanced high ordering ($S > 0.8$). Based on X-ray diffraction and depolarized optical microscopy observation, together with the photoalignment quality, a semicrystalline structure of the humidified azobenzenesulfonic material is proposed. The transition from amorphous solid at low relative humidity to semicrystal at high relative humidity provides a new perspective of understanding the hydrophilic photoalignment materials.



INTRODUCTION

The photoalignment technology, which has been rapidly developed since the first report in 1988, is a noncontact alignment approach for liquid crystal (LC) that could avoid contaminations and static charges caused by mechanical rubbing.^{1–4} The photoaligned materials can be easy-patterned to multidomains due to their rewritability and have the adaptability to sophisticated surfaces, and are therefore suitable for applications on different photonic devices, information storage, and processing and fabrication of various polarization-optical elements and devices.^{5–11} In particular, the photoalignment based on azobenzene materials is a reversible process where the alignment director is perpendicular to the polarization direction of the incident linearly polarized light of proper wavelength.^{11,12} The photoalignment layer could be obtained as spin-coated films,² Langmuir–Blodgett films,¹³ and self-assembled monolayers,^{1,14,15} and the order parameters of the photoaligned films have been reported on the order of 0.3–0.5.^{14,16} In our study, we found that the alignment quality of a thin layer of azobenzenesulfonic dye, i.e., the photoinduced phase retardation, order parameter, and the anchoring energy for LC, is influenced dramatically by relative humidity (RH),

and the order parameter of the alignment film could be tuned from 0.1 to above 0.8 by humidity under the same excitation dose. In addition, an exotic substantial ordering enhancement is observed by increasing the relative humidity without further light excitation, where the self-assembly of the photoaligned molecules with water molecules is the underlying reason for high ordering ($S > 0.8$). A semicrystalline structure is proposed for the humidified azobenzenesulfonic photoalignment material. The transition from amorphous solid at low relative humidity to semicrystal at high relative humidity provides a new perspective of understanding the photoalignment materials. This exotic property probably applies to many hydrophilic azobenzene photoalignment materials, such as brilliant yellow,¹⁷ CD1¹⁸ and so on, providing fabrication guidance for the photoalignment process in both display and photonic applications.

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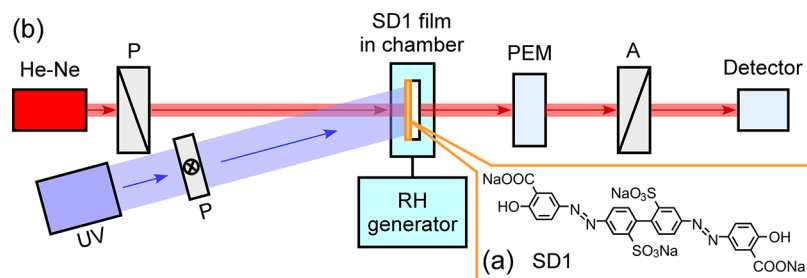


Figure 1. Schematic diagram of the experimental setup for *in situ* phase retardation measurement of the thin photoalignment film. (a) Chemical structure of SD1 molecule. (b) Experimental setup for *in situ* phase retardation measurement. The film-coated substrate is put in a sealed chamber, which is connected to a relative humidity (RH) generator. PEM is the photoelastic modulator. P and A are the polarizer and analyzer, respectively.

EXPERIMENTAL SECTION

The photoalignment material azobenzenesulfonic dye SD1 (Dainippon Ink and Chemicals, Inc. (DIC)) has been widely applied to various LC devices.^{9,10,19} It is hydrophilic with two sodium sulfonate groups in the middle and two hydroxyl and sodium carboxylate groups at the terminals (Figure 1a). To exclude water, the dried SD1 powder is stored in an argon-filled glovebox, which provides an inert environment, and the water vapor inside is controlled within 0.5 ppm. To get a thin homogeneous solid film, the SD1 powder is dissolved in *N,N*-dimethylformamide (DMF) at a concentration of 1 wt % and spin-coated on glass substrate at 3000 rpm for 30 s, which is then soft-baked at 100 °C for 15 min for solvent evaporation, giving an 11 nm-thick solid film (measured by Ellipsometer), where the film thickness is kept constant for the writing dynamics experiments throughout the paper. (The film thickness effect is small compared to humidity effect, and is discussed in Figure S1.) Then the film-coated substrate is put in a sealed chamber and taken out of the glovebox, which is then connected with a relative humidity generator (InstruQuest Inc.) to achieve a desired relative humidity at room temperature.

Upon exposure to 365 nm linearly polarized ultraviolet (LPUV) light, the randomly distributed azobenzene molecules tend to align perpendicularly to the light polarization. The small *in situ* phase retardation of the thin film is measured based on a photoelastic modulator (PEM) (Figure 1b), with an accuracy of ± 0.001 rad.²⁰ The probing He–Ne laser passes through crossed Glan-Thompson polarizers, with the photoalignment film and PEM in between, while the film is irradiated by LPUV from a mercury lamp incorporated with a 365 nm filter and a wire grid polarizer.

Before light exposure, the solid film is kept in the chamber with desired relative humidity for 5 min, which is long enough to reach equilibrium since no difference is observed by comparing the result with the one kept at that humidity for 1 h. To exclude the effect of other components in air, for example, nitrogen and oxygen, the writing dynamics has been measured under different gas environments at the same relative humidity. The humidity generator can be connected with different gas input, and therefore the output to the chamber is a mixture of that gas with water vapor. No difference is observed for nitrogen, oxygen, and argon at room temperature. Therefore, nitrogen and oxygen do not affect the photoalignment process of SD1, and all the measurements in this paper are done with nitrogen input.

For the azimuthal anchoring energy measurement, the LC cells are assembled with nematic LC placed in between two orthogonally photoaligned SD1 substrates at corresponding humidity environment, which is realized by a customized glovebox with nitrogen purging for humidity control. The actual twist angle ψ of LC is measured, and the azimuthal anchoring energy is calculated as $W_\phi = 2K_{22}\psi/d \sin 2\phi$,²¹ where ϕ is the deviation angle compared to the easy axis of the photoaligned film.

RESULTS AND DISCUSSION

Photoalignment Ordering at Different Relative Humidity. A strong dependence of the *in situ* phase retardation on

relative humidity is observed (Figure 2a). At low humidity, i.e., $\leq 30\%$ RH, the induced phase retardation saturates at low value

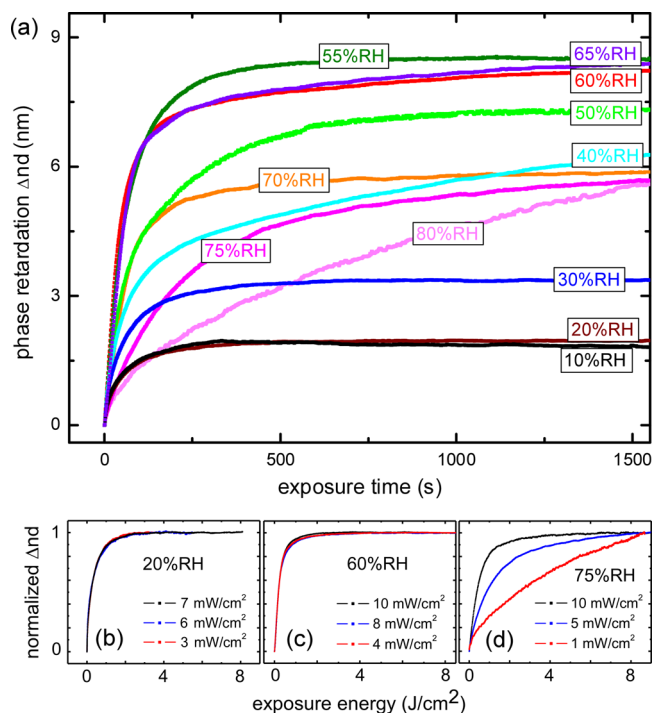


Figure 2. Writing dynamics of the photoalignment film under different relative humidity at room temperature. (a) The *in situ* phase retardation of the SD1 film induced by 365 nm LPUV at different relative humidity. The incident power is fixed at 5 mW/cm². (b–d) Comparison of normalized phase retardation induced by LPUV of different power at different relative humidity: (b) 20%RH, (c) 60%RH, and (d) 75%RH.

($\Delta nd \leq 3$ nm). As the relative humidity rises, the reorientation speed increases and the saturated phase retardation value gets much higher, which could go up to about 9 nm at around 60% RH. However, when the relative humidity is above 75%RH, the reorientation speed becomes much slower. It has been reported previously that the film alignment quality depends on exposure energy,¹⁹ i.e., the alignment ordering after LPUV exposure for a period at certain power is the same as the one with lower power but prolonged exposure time or higher power but shorten time correspondingly. In our study, we find that this situation is only valid for a certain humidity range (Figure 2b–d). For example, the normalized phase retardation curves overlap as a function of exposure energy with different pumping powers at 20%RH and 60%RH, respectively. However, they do not overlap anymore at

high humidity ($\geq 75\%RH$), indicating a nonlinear process different from the usual cases, which will be discussed later.

The induced film parameters at different relative humidity with the same exposure energy are provided in Figure 3. It has

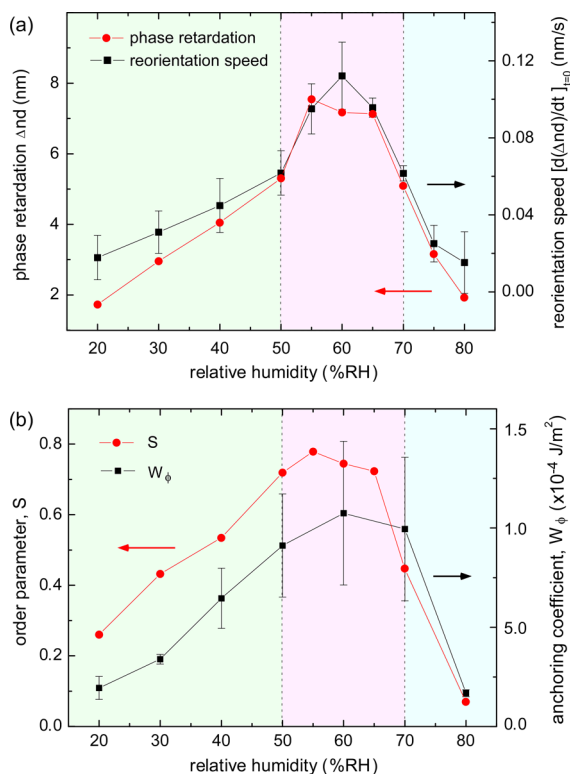


Figure 3. Ordering comparison of the photoalignment films induced by 1 J/cm^2 365 nm LPUV at different relative humidity. (a) Phase retardation (red circles) and reorientation speed (black squares). (b) Order parameter (red circles) and azimuthal anchoring coefficient (black squares). The LPUV power is 5 mW/cm^2 . Different background colors indicate different humidity regions for photoalignment: the green region indicates low humidity, which gives low ordering; the pink region indicates moderate humidity for best alignment quality; the blue region indicates high humidity which also gives low ordering. The detailed mechanism is discussed in the text.

been reported that 1 J/cm^2 LPUV exposure is enough for LC alignment,¹⁹ so all the parameters are measured with this excitation dose. After 3 J/cm^2 LPUV exposure, the induced anisotropy is saturated, and the corresponding parameters are also measured, which are shown in Figure S1. The induced phase retardation Δnd is obtained from Figure 2a, which shows that the film retardation increases with relative humidity until about 55%RH–60%RH and then decreases as the humidity further increases. The initial reorientation speed, which is the rate of phase retardation calculated from its derivatives, shows similar dependence (Figure 3a). The alignment quality could be checked directly by order parameter S . It is obtained through absorption spectrum measurements (Ocean Optics) and calculated as $S = A_{\parallel} - A_{\perp}/A_{\parallel} + 2A_{\perp}$, where the absorbance is measured parallelly (A_{\parallel}) and perpendicularly (A_{\perp}) to the molecular alignment direction at the peak value. It is impressive to find that the induced order parameter at 50%RH–65%RH could reach above 0.8 (at 3 J/cm^2 , Figure S1), giving excellent alignment film for various applications. The azimuthal anchoring energy for LC also depends on the relative humidity with the optimized case around 60%RH, consistent with the

other results (Figure 3b). According to our studies above, we find that the photoalignment quality of SD1 film depends strongly on the relative humidity. The alignment ordering is low at both low and high humidity environments, and the optimized relative humidity range is 50%RH–70%RH, which is recommended as the working window for the SD1 photoalignment film on applications of both LC display and photonic devices. For other hydrophilic azobenzene photoalignment materials, the relative humidity working window probably also exists, and the specific value may vary for different materials.

Ordering Enhancement with Light Off. It was reported that there was no relaxation of the photoaligned SD1 film after exposure,²⁰ which made it a good candidate for various applications.^{9,10,19} This phenomenon is rechecked at different relative humidities. No change is observed after long-time exposure at low humidity ($\leq 20\%RH$). However, starting from 30%RH, a phase retardation incensement is detected after the LPUV is switched off. At 30%RH the incensement is small, which is within 0.1 nm. Starting from 40%RH and above, a phase retardation raise of about 0.2 nm is observed. A comparison of the 20%RH and 60%RH cases is shown in Figure 4.

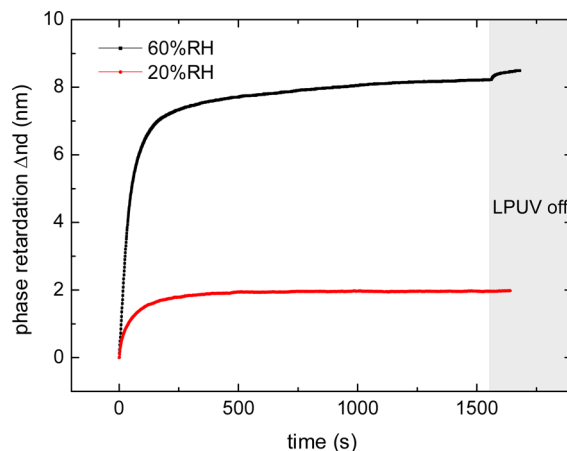


Figure 4. Writing and relaxation dynamics of SD1 film at different relative humidity. The gray area indicates where the LPUV is off. No change of phase retardation is observed at 20%RH, while there is a increment of 0.2 nm at 60%RH after LPUV is switched off.

Another interesting phenomenon is observed after excitation with humidity change, as shown in Figure 5. After excitation by 3 J/cm^2 LPUV at 20%RH, the phase retardation of SD1 film reaches its saturation value at about 2.2 nm, and the order parameter is measured to be 0.28. After the LPUV is switched off, the induced ordering remains constant at 20%RH as discussed above. However, after the relative humidity increases to 60%RH and is kept at 60%RH for 30 min without further excitation, the phase retardation of the prealigned film raises to 3.9 nm and order parameter to 0.44. If the relative humidity further increases to 80%RH and is kept at 80%RH for 30 min with LPUV off, the phase retardation rises dramatically to 9.6 nm, which is more than 4 times higher than its original value. Correspondingly, the order parameter increases substantially to 0.88, and the azimuthal anchoring strength also rises dramatically (Figure 5a). This unusual humidification-enhanced ordering property makes it applicable to data storage purposes, particularly in security technology. In contrast, lowering the relative humidity to the prealigned film brings a very small

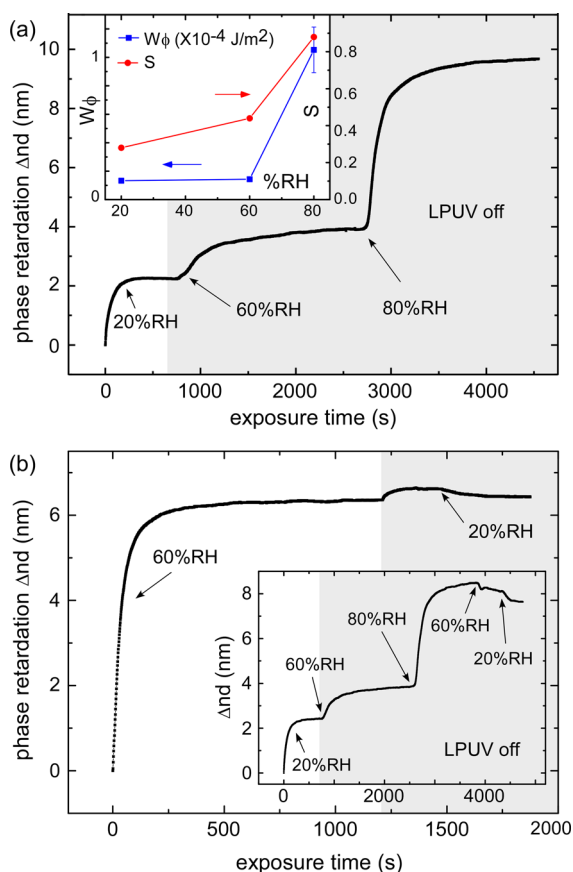


Figure 5. Film alignment before and after LPUV excitation with changing humidity. (a) The film alignment before and after LPUV excitation with increasing humidity. The film is written at 20%RH for 3 J/cm². After the LPUV is turned off, phase retardation does not change. After the relative humidity increases to 60%RH and then to 80%RH without light excitation, dramatic phase retardation increment is observed. The process where the relative humidity directly increases from 20%RH to 80%RH with light off is shown in Figure S2. Inset: order parameter, S , and azimuthal anchoring coefficient, W_{ϕ} , of the photoalignment film with changing humidity correspondingly. (b) The film alignment before and after LPUV excitation with decreasing humidity. The film is written at 60%RH. After the LPUV is turned off, phase retardation jumps up by about 0.2 nm. After the relative humidity decreases to 20%RH, very small decrease of phase retardation is observed. Inset: When the LPUV is turned off after the film is written at 20%RH, the relative humidity increases to 60% RH and then to 80%RH as in panel a. Then the relative humidity decreases to 60%RH and then to 20%RH. The gray areas indicate where the LPUV is off.

ordering change (Figure 5b), indicating that the bonding of water with SD1 molecule is strong and stable, which is hard to remove.

We need to notice that the humidification-enhanced ordering of this prealigned film is different from the one excited directly by LPUV at corresponding humidity. For example, the film after 3 J/cm² LPUV exposure at 80%RH yields an order parameter value of 0.16 (Figure 2 and S1), which is much smaller than the humidification-enhanced prealigned film ($S = 0.88$). The schematic illustration for the alignment process of the photoalignment films under the influence of different relative humidity at room temperature is shown in Figure 6, which is a summary of the discussed phenomena.

A similar ordering incensement after excitation (Figure 3) was observed in an azo-polymer at semicrystalline phase, which disappeared if it became amorphous with temperature change.²² Moreover, a film-ordering magnification phenomenon due to humidification was reported in a recent study on brilliant yellow dispersed in a triacetyle cellulose matrix, which is explained by its chromonic LC property,²³ and the quasicrystalline textures were also observed in the humidified brilliant yellow films.²⁴

To explore the property of the azobenzenesulfonic dye, X-ray diffraction (XRD) of the SD1 powder is performed. Although the relative humidity in the open air is around 60%RH, the powder may absorb more water during the material shipping and storage process, where obvious birefringence of the SD1 powder is observed under depolarized optical microscope. The powder XRD result shows some moderately sharp peaks in addition to the broad amorphous peak, as shown in Figure 7a. Several small peaks superimposed on the amorphous peak are detected between 20° and 30°, giving a spacing ranging from 3.3 to 4.0 Å. They are probably the distances of the aromatic rings between the molecules, corresponding to the stacking of chromonic columns.²⁵ The calculated d -spacings of other moderately sharp peaks can be assigned to the diffraction from a two-dimensional (2D) centered rectangular lattice, where the corresponding peaks are marked in Figure 7a. The peaks of 25.34 Å ($2\theta = 3.5^\circ$), 14.66 Å ($2\theta = 6.0^\circ$), and 9.01 Å ($2\theta = 9.8^\circ$) are the diffractions from (100), (010), and (110) planes of the 2D centered rectangular lattice, respectively, where the schematic structure of SD1 molecules with water are shown as the inset of Figure 7a. These values are reasonable compared to the size of SD1 molecule, which is 22.4 Å in length and 6.9 Å in width (calculated by the Molecular Mechanic Method), with water molecules (3.8 Å) in between. Based on the chemical structure of SD1 molecule (Figure 1a), this material is hydrophilic since there are two sodium sulfonate groups in the middle and two hydroxyl and sodium carboxylate groups at terminals. Hydration occurs site-selectively around these hydrophilic functionalities of SD1 stacks, indicated as the light blue regions in the inset of Figure 7a. The longer axes of the SD1 molecule stacks align along the [100] axis, and the shorter axes align along [010] axis, probably due to hydrogen bonding between these hydrophilic groups.

Typical nonamorphous textures are observed from super-hydrated SD1 films under depolarized optical microscopy as shown in Figure 7b-c. The films are obtained either by a solid SD1 film (spin-coated in DMF) exposed to saturated relative humidity (named as film i), or an SD1 film obtained directly from a water solution by spin-coating (named as film ii). The grazing incidence XRD (GI-XRD) results of these two films also show some moderately sharp peaks in addition to a broad amorphous peak (Figure 7a). For film i, a small peak appears at $2\theta = 11.14^\circ$, which may correspond to the loosely packed (020) planes. Film ii shows the (010) and (020) peaks as in the powder XRD, indicating that the preferential orientation growth of the film on glass substrate is in the (010) direction. Since the above hydrated SD1 film appears solid and the texture does not change after it is baked at 100 °C over half an hour (Figure 7b,c), we prefer not to define it as lyotropic LC. Together with the XRD result, which shows both a broad amorphous peak and some moderately sharp peaks, its semicrystalline property is therefore proposed.

However, this crystalline-like texture is not optically observed for the SD1 film under nonsaturated relative humidity

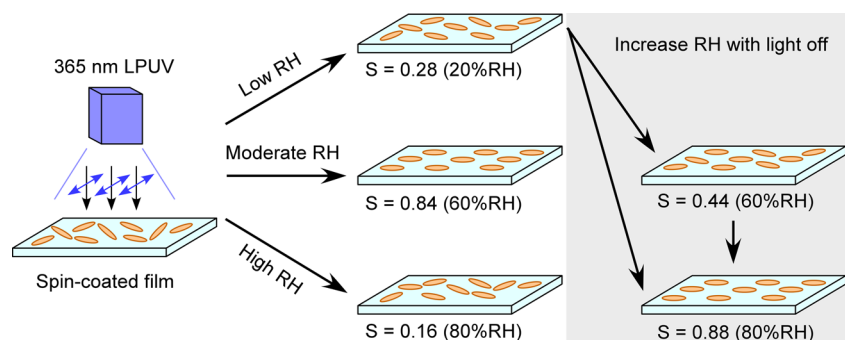


Figure 6. Schematic illustration for the photoalignment processes under the influence of different relative humidity at room temperature. The order parameter value (saturated value after 3 J/cm^2 LPUV excitation) is written as an example at corresponding humidity. The gray area indicates where the LPUV is off.

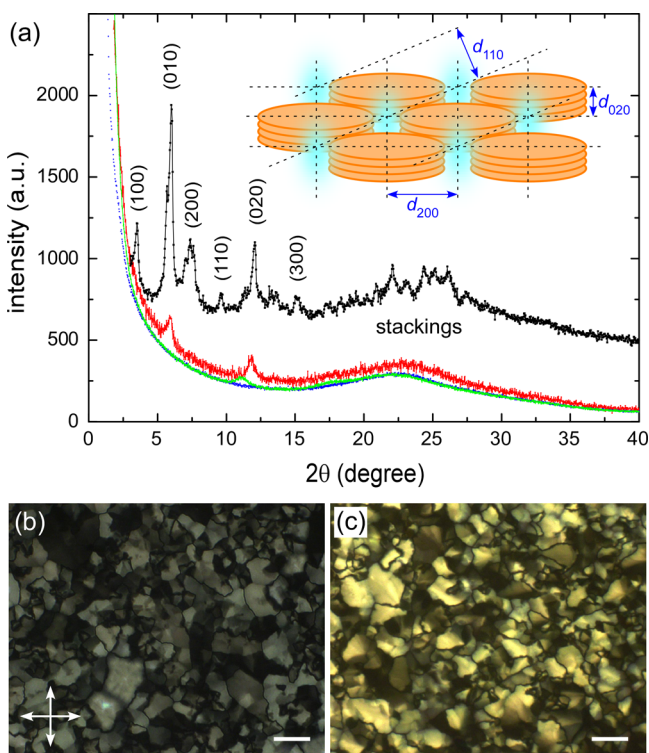


Figure 7. Semicrystalline structure of hydrated SD1 materials. (a) X-ray diffraction of SD1 powder (black) and films (blue, green, and red). The curves are rescaled or shifted for clarity. The powder XRD indicates a semicrystalline structure with 2D centered rectangular lattices for the assembled structure of the SD1 molecules (orange) with water molecules (light blue) in the inset. (b,c) The semicrystalline texture of hydrated SD1 film observed under depolarized optical microscope. The crossed arrows indicate crossed polarizers. The scale bars are $50 \mu\text{m}$. (b) A hydrated SD1 film (50 nm , spin-coated from DMF solution) after being exposed to saturated relative humidity. The GI-XRD signal is given as the green curve in panel a, while the blue curve is from the same film before exposure to the saturated relative humidity. (c) An SD1 film ($\sim 100 \text{ nm}$ thick) obtained by spin-coating a water-dissolved SD1 solution and then followed by soft baking at $100 \text{ }^\circ\text{C}$ for 15 min . The GI-XRD signal of this film is given as the red curve in panel a.

environment, where up to 95%RH has been tested. The film (50 nm) before LPUV exposure is isotropic, confirmed by depolarized optical microscopy observation. Also, no ordering change is detected based on phase retardation measurement as the relative humidity increases to high value ($<100\%RH$)

(detection area is around 1 mm^2). After it is aligned by LPUV, the film shows anisotropy and appears homogeneously bright when the alignment direction is 45° to the crossed polarizers (Figure S4). Therefore, the SD1 film under nonsaturated relative humidity environment has macroscopic amorphous appearance, and the crystalline interaction without condensed water is weak and only microscopic. This observation is consistent with the GI-XRD results of SD1 films under nonsaturated relative humidity environment (Figure 7a). It only shows the amorphous peak, where the microscopic crystalline signal may be too small to show up from the big amorphous signal.

For the photoalignment process, the solid film is amorphous at low relative humidity, and the alignment is controlled only by the actinic light. The aligned-film ordering is low probably since there is not enough free volume for reorientation.^{26,27} As humidity increasing, more water molecules insert and give more free volume to SD1 molecules. At 50%RH–65%RH, the induced order parameter could reach above 0.8. This value is exceptionally high compared to other reported value around 0.5, even for the azobenzene monolayer, where more volume is around each molecule.¹⁴ Therefore, in addition to more free volume, the intrinsic semicrystalline property of this material with the help of water must contribute to the high ordering although it is microscopic. The alignment of SD1 film is a result of the photoalignment and intrinsic semicrystalline property. When the relative humidity is between 30%RH and 70%RH, weak semicrystalline interaction is preferred, and the 365 nm LPUV light is stronger than this weak interaction. Thus, the 365 nm LPUV light could align SD1 molecules, and at the same time the semicrystalline property helps to form highly ordered structure spontaneously at the aligned direction. When the relative humidity is even higher ($\geq 75\%RH$), more water molecules are bounded to the hydrophilic functionalities of azobenzene molecules, and the semicrystalline interaction between the molecules becomes stronger. Since the azobenzene molecules have already bounded strongly to each other before LPUV exposure, a slower photoalignment process is observed and the breakage of their linkage depends on the LPUV power, giving a nonlinear process as shown in Figure 2d. When the SD1 film is exposed to a saturated relative humidity environment, the semicrystalline interaction becomes very strong and the semicrystalline structure becomes macroscopic, and, as a result, the film loses its photoalignment ability. Compared to brilliant yellow, whose crystalline structure appears when the relative humidity is above 50%RH,^{23,24} the macroscopic semicrystalline structure of the SD1 film appears

only when the relative humidity of the environment is above 100%RH, giving it a better photoalignment quality for practical application.

The free volume and the intrinsic semicrystalline property could also explain the phase retardation increment after the LPUV is switched off. When the relative humidity is above 30% RH, a small phase retardation increment is observed as shown in Figure 4, since the semicrystalline property prefers higher ordering.²² Moreover, if the SD1 molecules are prealigned at low humidity, the increment of relative humidity after irradiation results in a dramatic order enhancement (Figure 5a). The insertion of water molecules first adds more free volume to the azobenzene molecules. Second, a transition of amorphous solid to semicrystal is proposed with the help of water. The dominant prealigned molecules provide a torque to neighbors toward the alignment direction, and the film ends up with an enhanced ordering due to the semicrystalline property. The transition of amorphous solid to semicrystal is proposed with the insertion of water molecules, which helps lower the energy barrier toward crystallization²⁸ and provides a new perspective of understanding these kinds of photoalignment materials.

CONCLUSIONS

In summary, a strong dependence of photoalignment quality of the azobenzenesulfonic dye on relative humidity has been demonstrated. The photoinduced phase retardation, reorientation speed, order parameter of the alignment layer, and its alignment quality for LC under different relative humidities show dramatically different behaviors. At low humidity, the alignment ordering is low. As relative humidity increases, the film can be photoaligned better until about 60%RH, where the order parameter reaches above 0.8. As the humidity further increases, the alignment quality gets worse. According to our extensive study, the best relative humidity range for the SD1 photoalignment process is between 50%RH and 70%RH, which is recommended as a working window for the application of this photoalignment material for both photonic devices and displays. The humidity working window is also recommended for similar hydrophilic azobenzene photoalignment materials, where the specific value may vary according to different materials. Besides writing dynamics, the film alignment after excitation is also explored. A phase retardation increment after exposure has been observed at humidity above 30%RH. This increment is enhanced if the prealigned film gets more humidified after LPUV excitation: the film ordering increases substantially by about 4 times if the relative humidity changes from 20%RH to 80%RH, suggesting that a more ordered structure is preferred due to the insertion of water molecules. These phenomena are well explained by the semicrystalline property of the azobenzenesulfonic dye with water molecules, which is proposed based on XRD and depolarized optical microscope observations. The self-assembly of the photoaligned molecules with the insertion of water molecules contributes to the high ordering ($S > 0.8$). The transition from amorphous solid at low relative humidity to semicrystal at high relative humidity provides a new perspective of understanding the hydrophilic photoalignment materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b00417.

The writing dynamics of the photoalignment films with different thickness (Figure S1);²⁹ ordering comparison of the photoalignment films induced by 1 J/cm² and 3 J/cm² 365 nm LPUV at different relative humidities (Figure S2); film alignment before and after LPUV excitation with increasing humidity from 20%RH to 80% RH (Figure S3); aligned SD1 observed under depolarized optical microscope (Figure S4) (PDF)

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Notes

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