

Light-induced Phase Transition of Lyotropic Liquid Crystals and Motion Behavior of Micron Objects via Photochemical Azobenzene Molecules

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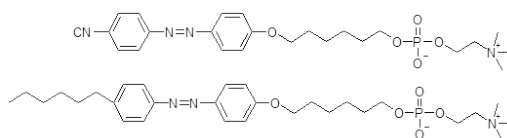
Abstract. Ternary lyotropic liquid crystal (LLC), was prepared by mixing tetradecyltrimethylammonium bromide (MTAB), water and azobenzene (Az). The phase transition of the LLC was induced from LC phase to isotropic (I) one upon Ar⁺ laser, which was owing to the trans-cis-trans photoisomerization cycle of Az during the irradiation. After that, the LC phase gradually recovered from I phase to nematic (N) phase when being exposed to dark condition. It was also suggested that the recovery time from I to N was different with the Az structures, temperature and ratio of MTAB/Az in the ternary system. Then, the effect of light irradiation on the motion behavior of micron objects dispersed in the ternary LLC film was studied. It was found that the micron objects which dispersed in the irradiated area moved toward the center of the irradiated area, while the micron objects which dispersed around the irradiated area moved away from the irradiated area.

Introduction

Az can exhibit trans-cis isomerization by UV and reversible one by visible (Vis) light. Owing to the photo-isomerization behavior, much effort has been focused on the Az compounds to control phase transition of LCs as well as alignment of LCs for applications on optical displays and assembly technology, which have been studied by various external stimuli, such as gravitational field, external electric, magnetic fields, thermo, and light [1-8].

Many works have recorded the application on assembly technology and manipulation of micron objects, and the driving force is ascribed to surface tension gradient or phase transition. As the paper reported by S.N. Varanakkottu, et al, the inward flow are induced when Az compound are dissolved in water and irradiated with UV light, which is supported by the gradient in surface tension between the difference of trans-form and cis-form Az [9]. Similarly, the gradient in surface tension can also be used to control the motion of glass rods in Az-doped polyethylene glycol films, as found by Su Ma et al [10]. However, Lohn, et al described the micron objects can be assembled by thermo-induced phase transition [2], whose driving force is also accorded with our previous work [6-7, 12].

In addition, LLC phases, as one type of LCs, are abundant in living systems. For example, many proteins and cell membranes are LLCs. Other well-known examples of LLCs are solutions of soap and various related detergents, as well as the tobacco mosaic virus [13-15]. So the LLC also plays an important role in our daily life, while there is little or no related study reported on the manipulation of micron objects on the surface of LLCs. Herein, we investigated the effect of hydrophilic Az compounds, A3 and HA3 (the molecular structures were shown in Scheme1), on the phase behavior of LLC and a manipulation of micron objects (glass rods) on Az-doped LLC films.



Scheme 1. Structures of Azobenzene-Containing compound A3 and HA3

Experiment

The photoisomerization behaviour of A3 and HA3, synthesized by literature methods [16], were examined in methanol solution by monitoring changes in the absorption spectra from a UV/Vis spectrometer at room temperature. Then, the samples of ternary LLCs, containing tetradecyltrimethylammonium bromide (MTAB, 39.6%), water (60.4%) and Az (A3/HA3), which was prepared according to the procedure described in reference [17], were prepared. To reduce water evaporation losses from the system, the Az-doped or together with micron objects-including LLC films were sealed up using UV-curable adhesive.

Results and Discussion

Photoisomerization Behavior. As shown in Fig. 1, for A3-methanol solution, the UV/Vis absorption spectra were characterized by a strong $\pi-\pi^*$ transition of trans-A3 moiety at about 360 nm and a weak absorption at about 440 nm, which originated from $n-\pi^*$ transition. The absorbance decreased at about 360 nm and increased at 440 nm when the solution was exposed to UV ($\lambda=365$ nm, 30 mW), indicating the photoisomerization from the trans-form to the cis-form occurred. Similarly, HA3 also exhibited the same photoisomerization behavior as A3 in methanol solution, whose typical trans-/cis-isomer was assigned to the peaks at 350 nm and 440 nm, as shown in Fig.1(c).

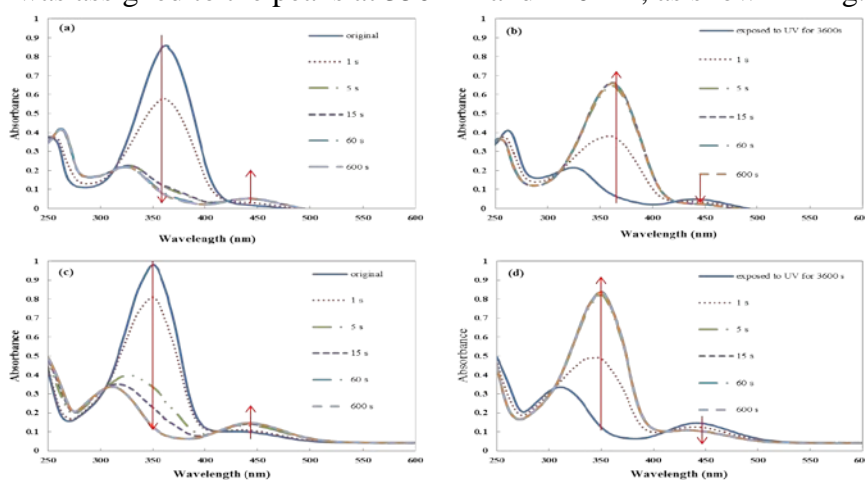


Fig. 1 Changes in absorption spectra of A3 (a) (b) and HA3(c) (d) in methanol solution by irradiation with UV (a) (c) and Vis light (b) (d) at room temperature

The photostationary state reached after 60 s for both of A3-methanol and HA3-methanol solution. In addition, Vis light ($\lambda=436$ nm, 130 mW) irradiation caused an increase and a decreased of the absorbance values at about 360 nm and 440 nm, indicating the back photoisomerization from cis to trans be induced upon Vis light. The trans-cis isomerization rate of A3 and HA3 was calculated as 92.0% and 87.2%, respectively when exposed to UV light for 600 s. The cis-trans isomerization rate was also different and gave a rate 48.1%, 37.7% within 1 s upon Vis light, which suggested that the cis-A3 was more easily to isomerize into trans form compared to the cis-HA3. This was maybe owing to that comparatively strong electron withdrawing substituents -CN in A3 decrease the barrier for isomerization, thus A3 underwent faster cis-trans isomerization compared to HA3 with electron donating substituent $-C_6H_{13}$ [18].

Phase Transition of LLC by Thermal Effect. To explain the phase transition behavior of the LLCs with different Az compounds and different ratio of MTAB/Az, POM and DSC was carried out, respectively. Fig.2 (a), (b) and (c) exhibited the typical N textures, which were associated with samples MTAB, MTAB: A3=95:5 and MTAB: A3=98:2. In addition, as shown in Fig.2 (d) (e) and (f), all the 3 samples showed one endothermic peak ranging from 20 °C to 50 °C. The results revealed that all samples, MTAB, MTAB: A3=95:5 and MTAB: A3=98:2, showed N as LC phase, and the phase transition temperature from N to I phase was almost same at about 36 °C, 36.5 °C and 37 °C, respectively, indicating the addition of A3 had almost no effect on the phase behaviour of MTAB molecules in water.

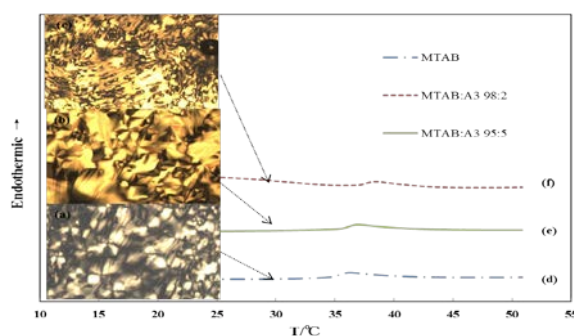


Fig. 2 Typical textures of MTAB-water LLCs and DSC heating thermograms of LLCs with different ratio of MTAB/Az (a) (d) MTAB; (b) (e) MTAB: A3=95:5; (c) (f) MTAB: A3=98:2 (molar ratio)

The MTAB molecules doped with different amount of HA3 (MTAB: HA3=95:5/98:2) also exhibited almost the same N-I phase transition. However, compared to A3-doped LLC, the HA3-doped-LLC exhibited much higher phase transition temperature. For examples, the phase transition of MTAB: A3= 95:5 from LC phase to I phase was about 37 °C, which was lower than that of 56 °C for the sample of HA3 doped one. It is considered to contribute the fact that the trans-form HA3, doped in LLC, has a well ordered molecular arrangement with MTAB.

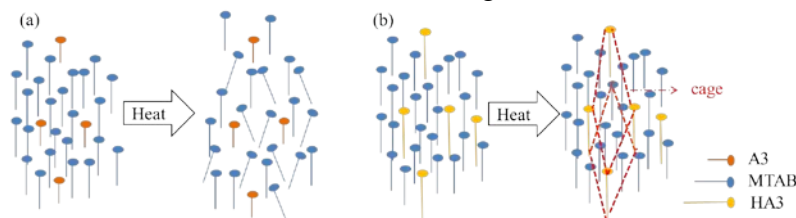


Fig. 3 Illustration of thermal-induced phase behavior for (a) A3-doped MTAB; (b) HA3-doped MAB

On the other hand, the molecular length of trans-HA3 is calculated as 21.1 Å and relatively longer than that of MTAB (19.0 Å), which also supports a “cage” or “frame” to keep the orientation of MTAB molecules in water. In contrast, trans-A3 (16.9 Å) is shorter than that of MTAB, the “cage” can hardly be formed or invalid to fix the MTAB molecules in a limited a region to keep its well-ordered arrangement at high temperature, as the illustration in Fig.3. Therefore, the MTAB doped with HA3 LLC exhibited a higher phase transition temperature than that of A3.

Phase Transition of LLC by Vis Light. In addition to the thermal-induced phase transition, an irradiation with Ar+ laser, as an external stimulus, was also carried out to study its effect on phase behavior. During all the irradiation process, a thermostat was used to keep the samples at 30 °C which was less than the phase transition temperature. As shown in Fig.4, the none-Az-doped MTAB sample always exhibited the N phase, even though the sample was exposed to Ar+ laser. The texture did not change at all, either. For the Az-doped samples, before irradiation, owing the molecules were arranged in order, all the two samples also showed the N phase. However, as shown in Fig.4 (b), when the Az-doped samples were irradiated with Ar+ laser, the samples lost their birefringence, so the phase transition from N to I state was induced.

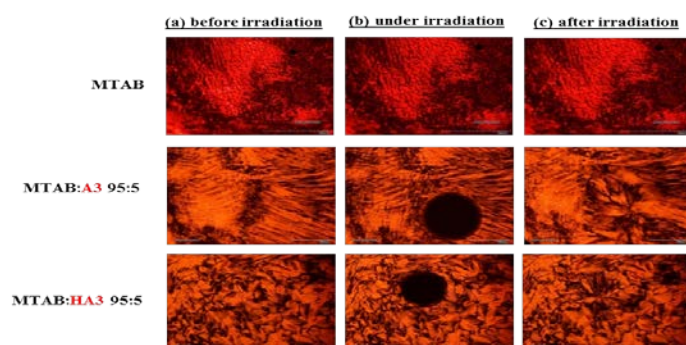


Fig. 4 Typical textures of MTAB-water LLC with different Az (MTAB/Az=95:5) (a) before; (b) under; (c) after irradiation using Ar⁺ laser (T=30 °C, light intensity=70 mW)

Similar experiment conducted in our previous work [6,7,12] explained the mechanism of phase transition by Ar⁺ laser irradiation in terms of order-disrupting molecules Az through conformational changes. That means the phase transition can be induced in an Az-doped-LLC system in which Ar⁺ laser exposure directly decreased the order of the mixture through trans-cis-trans cycle photoisomerization of Az moiety. In addition, this photo-induced I state returned to the N phase (Fig. 4 c) spontaneously within a certain period of time after removal of the Ar⁺ laser. The surface textures of the samples after Ar⁺ laser irradiated were a little bit different from the one before irradiation, which was because of the thermostability for the trans-form Az, thus the cis-trans isomerization occurred spontaneously along with the phase transition from I to N phase.

Effects of Az and Temperature on Recovery Time from I Phase to N Phase. Results from the photo-induced phase transition were suggested that trans-cis-trans cycle photoisomerization of A3 and HA3 was the driving force for the mechanism of phase transition behavior when being irradiated by Ar⁺ laser. The responsive time of the phase transition from N to I was almost same (immediate) for all the samples. However, the recovery time from I to N varied in structures of Az, temperatures and MTAB/Az ratios, as shown in Tab.1.

Tab.1 Effects of Az and temperature on recovery time (irradiated with Ar⁺ laser at 70 mW)

No.	Az	Molar ratio (MTAB/Az)	Phase transition	Irradiation time[s]	Recovery time[s]	Temperature [°C]
1	No		unavailable	84		30
2	A3	10:1	available	84	37	30
3	A3	95:5	available	84	107	30
4	A3	98:2	available	84	179	30
5	HA3	95:5	available	84	≈180	30
6	HA3	95:5	available	84	≈300	20
7	HA3	98:2	available	84	≈1080	30
8	HA3	98:2	available	84	≈1800	20

To illustrate the importance of chemical structures of Azs those doped in LLC films, A3 and HA3 were used, which had a strong withdrawing substituent –CN and electron donating substituent –C₆H₁₃, respectively. Moreover, the two Az compounds also had different rigidity for the hydrophobic chain. After continuous 84 s exposure to 488 nm laser following exposure to dark condition, the recovery time of A3-doped-LLC film (No.3) from I state to N phase was much shorter than that of HA3-doped-LLC film (No.5). The same experimental phenomena was also found when compared No.4 to No.7. It was suggested that recovery time was shorter for A3 with a strong withdrawing substituent. One of the reasons was owing to the faster cis-trans isomerization of A3 molecules as the explanation in Fig.1. The other reason was considered to be the possibility that the HA3 doped LLCs had a flexible hydrophobic chain, such flexible chain drove HA3 to be more hindered and difficult to be completely recover from cis to trans.

Additionally, it also can found out that with the ratio of the water-resolvable Az increased, the recovery time from I to N phase accelerated. The effect of temperature on recovery time was further illustrated between No.5 and No.6 in the table. The recovery time of HA3-doped-LLC film (No.5) which was exposed to 30 °C was much less than that to 20 °C (No.6). The same experimental phenomena was also found when compared No.7 to No.8, which was considered to be the thermal motion of LLC molecules.

Motion Behavior of Micron Objects in LLC Film. In our previous work [12], we have demonstrated that the phase transition can support a driving force for the motion of micron objects. The driving force makes all micron objects move as a track of circles in the four cross regions which are divided by rubbing direction of the substrate and perpendicular line. Herein, the different motion behaviors were observed for the micron glass rods (G.R.) in A3-LLC (98:2) films. As shown in Fig.5, the G.R. dispersed in the irradiated area moved toward the center of isotropic area when being irradiated by Ar+ laser, whose motion behavior was totally different from the G.R. dispersed around irradiated area. That means the G.R. marked in ellipse in Fig.5 would move away from the dark area upon Ar+ laser.

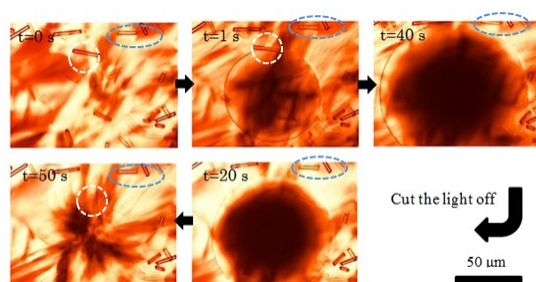


Fig.5 Optical micrographs of the G.R./A3/MTAB/H₂O (2:98) mixture irradiation with Ar+ laser (488 nm, 40 mW) at 25 °C in the glass cell (thickness: 200 μm). The term t in figures indicates the exposure time

In addition, the moved glass rods dispersed around the irradiated area could almost move back to the original position when being exposed to dark condition for some time, whose reversible motion behavior was not available for the glass rods dispersed in the irradiated area. According to our previous work [8, 9, 12], it was suggested that the phase transition supported the main driving force for the motion behavior of glass rods placed around the irradiated area.

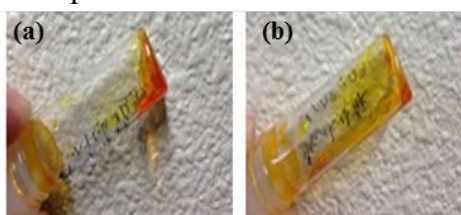


Fig. 6 Photographs of vials containing A3/MTAB/H₂O (2:98) LC molecules before (a) and after (b) irradiation with UV light for about 1min

Since monodirectional cis-trans isomerization can be induced by UV light, irradiation with UV light was carried out to investigate the viscosity changes. As shown in Fig.6 (a), before irradiation, the sample seemed to be a gel with high viscosity, while the sample turned into a state with low viscosity after irradiated by UV light as shown in Fig. 6 (b), because the sample flowed from the vial bottom to top. Thus, for the glass rods placed in the irradiated area, the surface tension gradient was considered to be the main driving force [9-10], when the LLC turned into a liquid state with low viscosity.

Summary

We have demonstrated that the HA3 molecules doped in LLCs are effective to preserve the molecular orientation of LLCs at relatively higher temperature, which means HA3 allows the thermally

induced a higher phase transition temperature from LC phase to I phase. It is also shown that the transition from LC phase to I one for the Az-doped LLCs films can also be induced by Vis light (Ar+ laser), the reversible phase transition of which can also be induced by exposure in dark condition. The recovery time of the reversible phase transition depends on the structure of Az molecule, temperature and ratio of MTAB/Az. The use of fixing Ar+ laser enables the control of micron glass rods in a way of moving toward and away the irradiation region for the ones dispersed in and around the irradiation region, whose driving force is due to the surface tension gradient and phase transition, respectively.

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