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High ON/OFF ratio photoswitchable viscoelasticity in an azo-based dimer with twist-bend nematic phase

Satoshi Aya^a, Antal Jákli^b, Corrie T. Imrie^c, Ágnes Buka^d, Fumito Araoka ^{*a}

^a RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan; ^b Chemical Physics Interdisciplinary Program and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA; ^c School of Engineering, University of Aberdeen, King's College, Aberdeen AB24 3UE, United Kingdom; ^d Institute for Solid State Physics and Optics, Wigner Research Center for Physics, Hungarian Academy of Sciences, P. O. Box 49, H-1525, Budapest, Hungary

ABSTRACT

In this paper, we present a new photoswitchable viscoelastic material with liquid crystalline natures, which exhibits two types of nematic liquid crystalline phases and a crystal phase beneath the isotropic liquid. We present its light-triggered phase behaviors and photoswitchability of the viscoelastic properties.

Keywords: Liquid Crystals, Nematic Liquid Crystals, Twist-Bend Nematic Phase, Azobenzene, Photoisomerization, Photoresponsive Materials

1. INTRODUCTION

In recent decades, photoswitchable materials have received tremendous attention, towards scientific understanding of molecular photomechanodynamics and practical application as light-driven mechanomaterials. Recently, the target of the research field has been shifting from exploring switchable elastic functions to exploring the viscoelastic ones. In such a new paradigm, liquid crystallinity plays a vital role due to the compresence of fluidity and structural ordering. There have been known a variety of liquid crystal phases, and each of them possesses a unique viscoelastic property characterized by its fluidity and ordering. Here, we demonstrate such a structure-photoresponsivity in a photoresponsive liquid crystalline azobenzene-based dimer molecules exhibiting the recently-found twist-bend nematic (N_{TB}) liquid crystal phase, by comparing the material performances in different phases.

2. EXPERIMENTAL RESULTS

2.1 Fundamental phase behaviors of liquid crystalline dimer

Recently, Paterson et al. developed a brand-new series of novel liquid crystalline oligomers,^{1,2} which inherently show the new liquid crystal phase, the so-called N_{TB} phase, in which liquid crystalline molecules are heliconically arranged along the nematic director as shown in Fig. 1(b). In this study, we use one of such dimeric liquid crystalline materials, (1-(4-butoxyazobenzene-4'-yloxy)-6-(4-cyanobiphenyl-4'yl)hexane, abbreviated as CB6OABOBu in the following (Fig. 1(a))¹. The specialty of CB6OABOBu lies in the photoresponsivity thanks to an azobenzene linkage introduced in one of the dimeric wings, which allows us to investigate the photoalteration of physical properties in the N_{TB} phase. The phase sequence of CB6OABOBu is: crystal (Cry) 104.7 °C N_{TB} 105.2 °C nematic (N) 151.7 °C isotropic liquids (I) upon heating and I 151.4 °C N 104.5 °C N_{TB} 83 °C Cry upon cooling. Figure 1 summarizes the key results reported in Ref. [1]:

*fumito.araoka@riken.jp; phone 81 48 462-1111; fax 81 48 467-9599; <https://www.cems.riken.jp/laboratory/psmru>

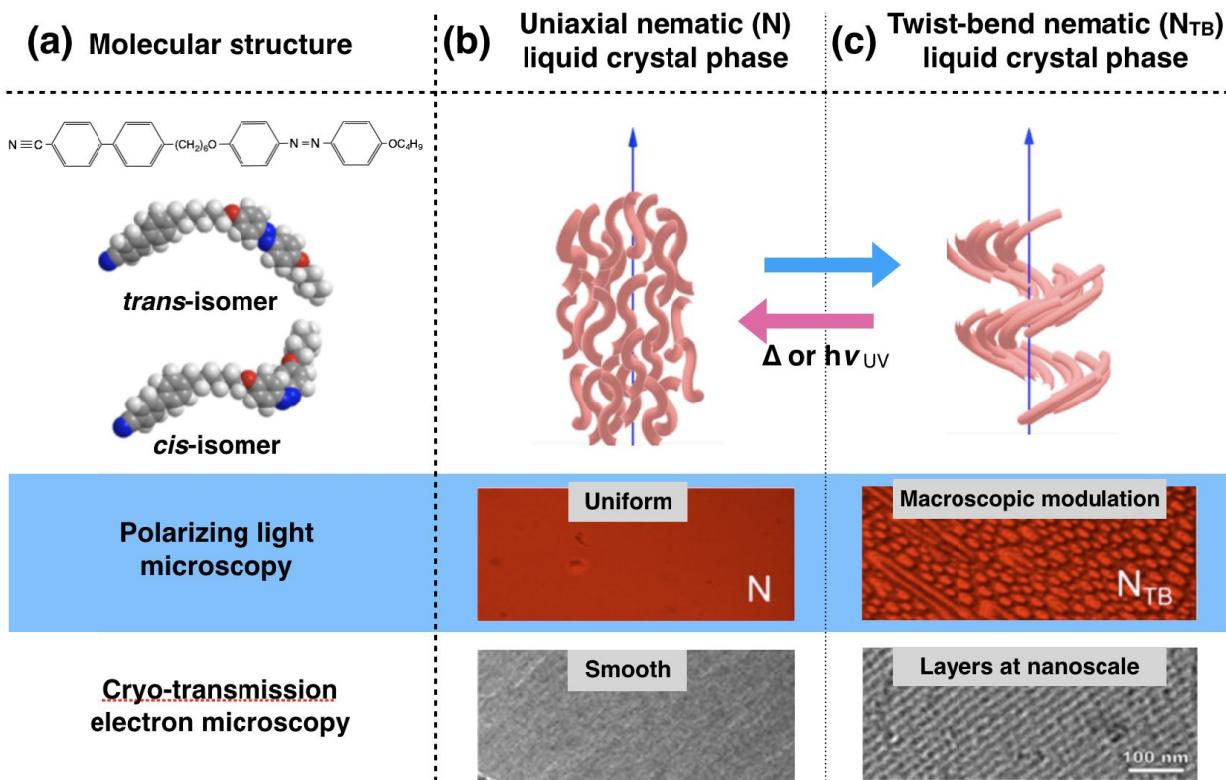


Figure 1. (a) Chemical structure and (b, c) structures of CB6OABOBu together with appearances on polarizing microscopy and transmission electron microscopy. Structural switching between the N_{TB} and N phases is also schematized. Adapted with permission from Ref. [1]. Copyright 2016 American Chemical Society.

(1) the heliconical molecular arrangement could reversibly be switched and erased by heat application or ultra-violet (UV) light irradiation; (2) as a result of (1), while polarizing light microscopy (POM) revealed a textural switching between a stripe-like modulated texture in the N_{TB} phase and an uniaxial aligned texture in the N phase, cryo-transmission electron microscopy (cryo-TEM) visualized the structural switching between pseudo-layering structure of the nano-pitched heliconical structure in the N_{TB} phase and the uniform state in the N phase. Since such a drastic structural alteration should modulate not only material's optical characteristics but also viscoelastic properties, we investigate viscoelastic properties of the material and focus on clarifying how the switching behavior in the N_{TB} phase differs from those in other phases. As a control material for light-driven viscoelastic switching experiment for the N_{TB} phase, a conventional calamitic liquid crystal, 1,7-bis-4-(4-cyanobiphenyl) heptane (CB7CB),^{3,4} was mixed with a liquid crystalline dye 4-butyl-4-methoxyazobenzene (BMAB, 1 wt%).^{5,6}

In order to clarify the thermodynamic information of CB6OABOBu, a home-made high-resolution differential scanning calorimetry (HR-DSC) was used.⁷ Figures 2 shows the heat flow profile as a function of temperature. In the displayed temperature range, the I-N and N-N_{TB} phase transitions can be clearly identified. Consistently to Ref. [1], the enthalpy variation at the N-N_{TB} phase transition is relatively smaller compared to that at the I-N transition. This difference could be the manifestation of a small difference in the energetic states, which probably means the structural (symmetry) difference between the N and N_{TB} phases, i.e., an additional local ordering of periodic heliconical twist rises up almost without changing the uniform mass density when going from the N phase to the N_{TB} phase, whereas positional ordering is kept absent for both phases.^{3,8}

The basic phase appearances and behaviors were investigated by using polarized light microscopy, as shown in Fig. 3. The material is introduced into a liquid crystal cell with planar anchoring condition but no rubbing treatment. We observed Schlieren texture in the N phase ($T > 105^\circ\text{C}$) and focal conics in the N_{TB} phase ($T < 105^\circ\text{C}$) on cooling process. By further cooling, crystallization occurs at about 83°C on cooling, which replaces the focal conics with highly-birefringent crystallites.

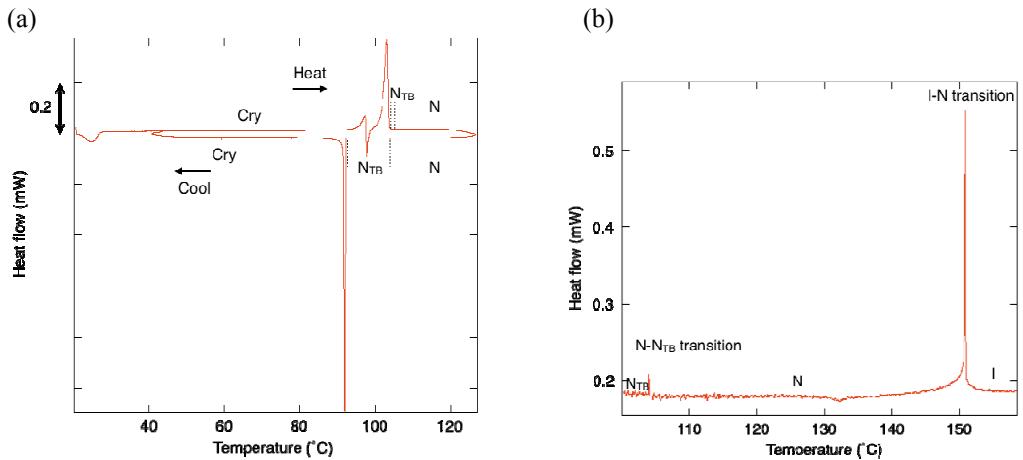


Figure 2. (a) Wide view of HR-DSC trace of CB6OABOBu at lower temperature during both heating and cooling the sample. (b) Magnified view of HR-DSC trace of CB6OABOBu during heating the sample.

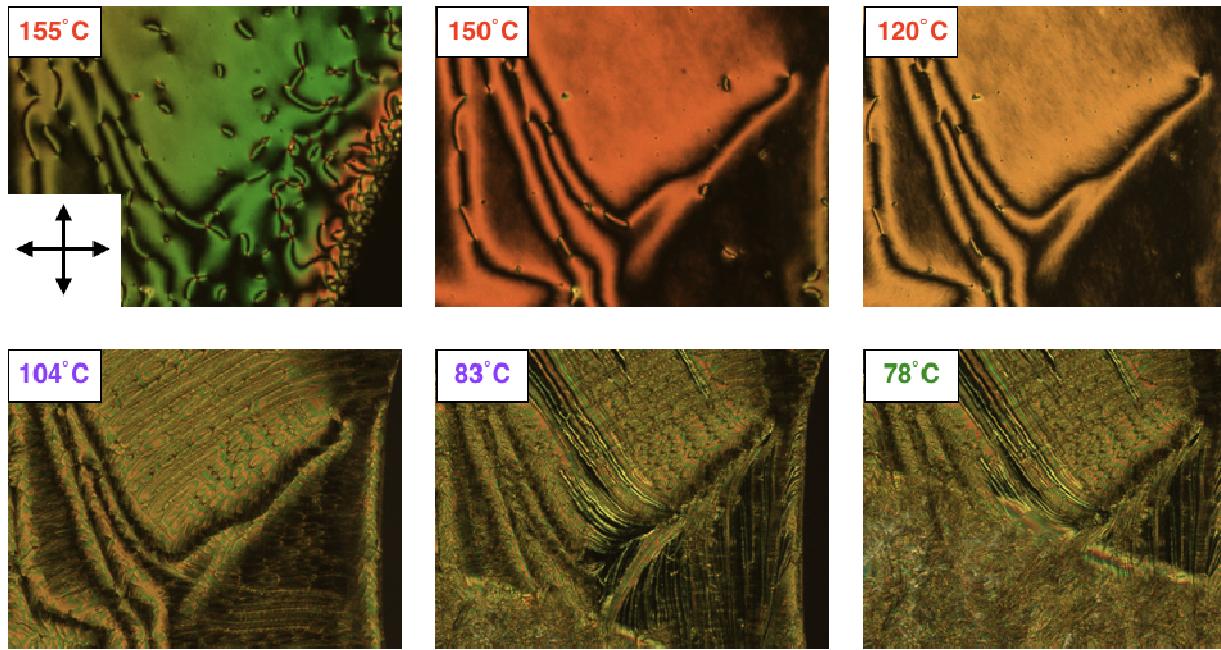


Figure 3. Texture observation in a planarly-treated cell without rubbing, taken at various temperatures under the polarizing light microscope. The colors of temperatures, red, purple, and green, indicate the N, N_{TB} and Cry phases, respectively.

In order to clarify the molecular orientation in the N_{TB} , the decrossing technique and non-analyzer texture observation were performed for a uniformly aligned liquid crystal cell with rubbing treatment. Figure 4(a) shows a stripe pattern, which is observed typically in the aligned N_{TB} phase, when the polarizers are slightly decrossed. These alternating colors of the stripes interchange when decrossing direction is reversed, such as shown between the leftmost and rightmost panels in Fig. 4(a). This means that the average orientations in the adjacent stripes are rotated about the axis parallel to the rubbing direction, i.e., the direction of the pseudo-layers of the heliconical structure. The orientational state in the stripe state can be considered as an analogue to the textures triggered by Helfrich-Hurault undulational instability often observed in many smectic phases.^{9,10} This suggests that the N_{TB} phase of CB6OABOBu has a compressive elasticity due to the heliconical pseudo-layer structure in the N_{TB} phase, in similar to the elastic properties in smectic phases. Indeed, as

visualized in Fig. 1, the nano-layering structure has been unambiguously confirmed by the cryo-TEM technique. Thus, the compressive elastic modulus can be estimated by considering the analogies between the N_{TB} phase and smectics. The detailed theoretical approach can be found in Ref. [11]. Therein, it is predicted that the compression modulus B can be expressed as:

$$B = 4K_2\theta_0^2q_0^2 \quad (1)$$

where K_2 , θ_0 and q_0 are the twist elastic constant, molecular tilting angle about the heliconical axis and wavenumber of the helix pitch. The typical value of B is found to be of the order of 10^4 - 10^5 Pa.

In addition, we examined the polarization dependence of visibility of the stripes using a green monochromatic filter ($\lambda=545$ nm) while the analyzer is removed throughout this observation. It turns out that the visibility of the stripes is the nicest when the input polarization is perpendicular to the rubbing direction, otherwise the visibility gets worse. This is attributed to the polarization dependence of light scattering through the stripes, meaning that the orientational modulation lies perpendicular to the rubbing direction, confirming the above-mentioned scenario of the Helfrich-Hurault undulational instability of the pseudo-layers of the N_{TB} phase.

In order to confirm the photoresponse of CB6OABOBu based on the photoisomerization of the azobenzene moiety, the UV-visible absorption spectrum was measured in a chloroform solution (Fig. 6) by using a UV-Vis spectrophotometer (V-650, JASCO). The absorption peaks corresponding to the $\pi-\pi^*$ transition of the *trans*-state and the *n*- π^* transition of the *cis*-state, respectively. Textural observation was made upon a UV illumination at a wavelength of 365 nm. When the UV illumination is made, the molecules are stimulated to undergo conformational variation from the *trans*-isomer to the *cis*-isomer (Fig. 1), which results in local geometrical frustrations, usually leading to a reduction of local ordering of the molecules. In the N phase, the UV illumination results in a light-induced phase transition to the I phase. In the N_{TB} phase, the neat texture shows stripes as shown in Fig. 7.¹ Moderate UV illumination switches the N_{TB} to the N phase. Interestingly,

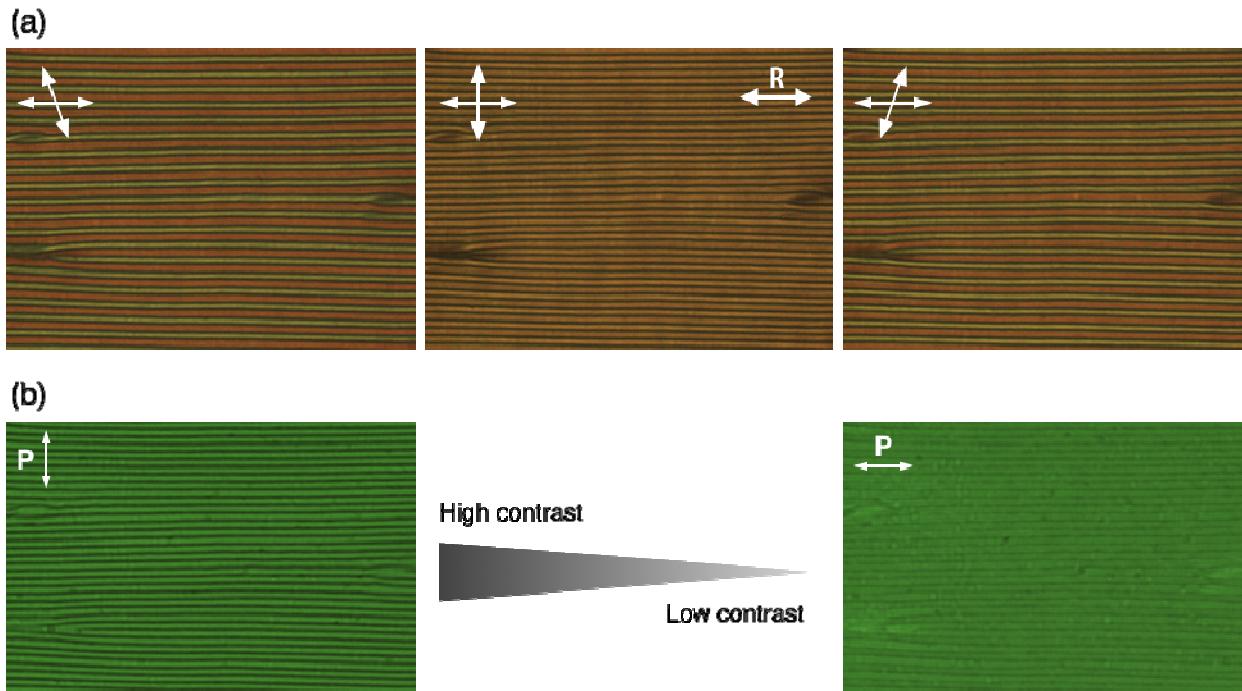


Figure 4. Texture observation in a rubbed cell. Rubbing treatment was made horizontally. (a) Polarizing light microscopy observed with cross-nicols polarization condition (center), and with slightly decrossing the analyzer to counterclockwise (leftmost) and clockwise (rightmost) directions. (b) Green monochromatric light (545 nm) observation without analyzer. The image contrast varies depending on the direction of the polarizer.

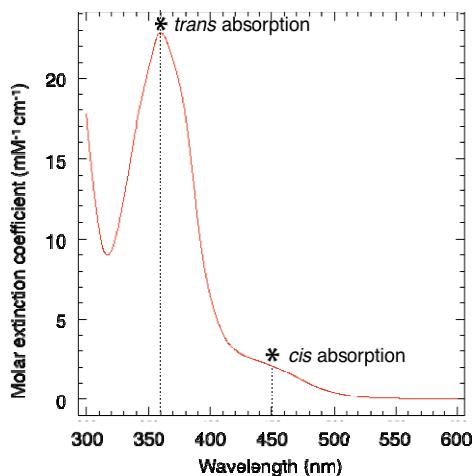


Figure 5. The UV-visible absorption spectrum of CB6OABOBu dissolved in chloroform. The sharp peak at 362 nm is corresponding to the $\pi-\pi^*$ transition of the *trans*-state and the shoulder at 451 nm to the $n-\pi^*$ transition of the *cis*-state, causing the photoisomerization to each other.

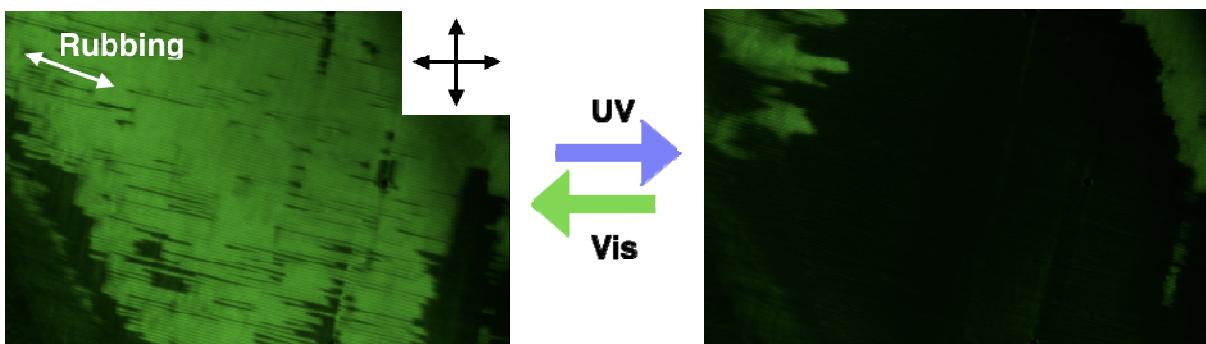


Figure 6. Reversible light-induced transition between the N_{TB} and N phases observed in a rubbed planar cell. The observation was made using the polarizing light microscope with the cross-nicols polarization condition and with the help of a green monochromatized color filter ($\lambda=545$ nm).

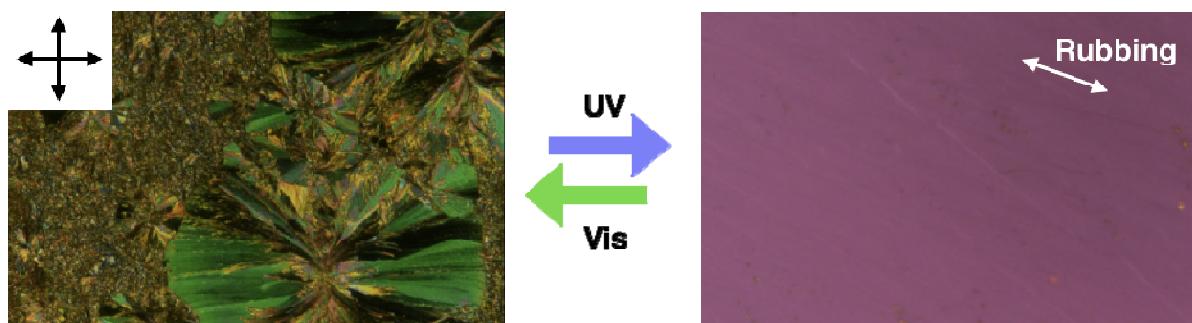


Figure 7. Reversible light-induced crystallizing and melting behaviors of CB6OABOBu in a rubbed planar cell observed under the polarizing light microscope with the cross-nicols polarization condition. A waveplate ($\delta\sim 550$ nm) was used for observation of the melted I phase to make sure of zero-birefringence.

during the stripes are vanishing, the stripes are shortened anisotropically, i.e., reducing the size along the rubbing direction. This indicates the nanometer-scale heliconical orientational state along the rubbing direction vanishes from the heads or the tails. The details of the dynamics should be further investigated in the near future. The recovery of the N_{TB} phase is relatively fast in 15 seconds. Detailed physical properties of each phase upon UV irradiation can be found in Ref. [1].

2.2 Dynamic viscoelastic properties

Further lowering temperature to the Cry phase results in a highly birefringent spherulite texture (Fig. 7). Illumination of UV light changes the Cry phase to a light-induced N phase (in several seconds) or I phase (in several tens of seconds). Considering light-triggered melting of crystalline solids is rarely seen except for several examples reported recently,¹²⁻¹⁵ the quick melting of the crystalline structures into the liquid crystalline state is a very unique phenomenon. Since usual crystals have large elasticity, whereas mesophases such as liquid crystals or soft-crystal states have relatively low elasticity and moderate viscosity, the switching between the Cry phase and a mesophase may serve as a mechanism for a high-contrast viscoelastic switchable material which is useful for mechanodynamic applications such as reversible adhesive, switchable fluid, molecular clutch, or so forth.

In order to probe the viscoelastic properties, rheological studies were made by using a commercial rheometer (MCR 502, Anton Paar) equipping with an optical elements to irradiate UV lights (Fig. 8(a)). A high-pressure mercury vapor short arc lamp (OmniCure S2000, Excelitas Technologies, filtered at $\lambda=365$ nm, maximum 70 mW/cm^2) was used as a light source. The UV light beam was illuminated onto the sample through a fiber light guide. Both of the bottom and top plates are customized to be made of glass for UV light transmission. The oscillatory mode was applied to extract dynamic restoring information of the material. The rheometer also equips temperature control so that the rheological behavior is examined in various thermotropic states. In our CB6OABOBu system, the viscoelastic properties differ significantly depending on the phases. For example, the storage modulus is of the order of 0.1 Pa, 1 Pa and 10^6 Pa in the I or N phase, and the N_{TB} and Cry phases, respectively. Since the contrast of switching is expected to be highest when melting from the Cry phase, we show a typical time dependence of the photoinduced viscoelastic switching at different UV irradiance in the Cry phase (Fig. 8(b)). It is obvious that the viscoelastic moduli can be tuned significantly by varying UV irradiance and the switching is reversible.

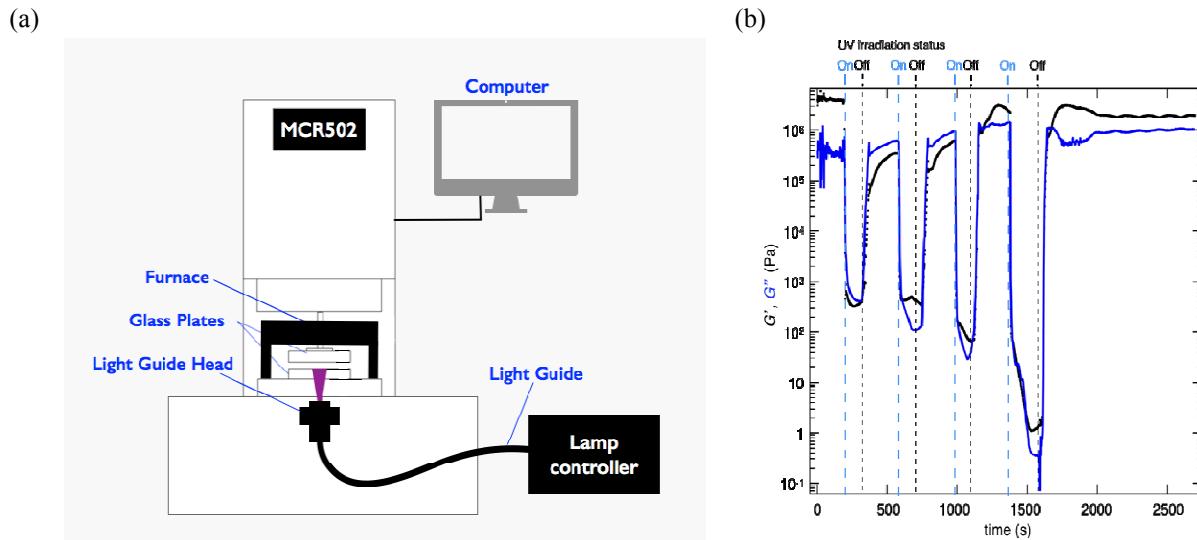


Figure 8. (a) Schematics of the rheological measurement setup for photo-induced viscoelastic switching. The UV light ($\lambda=365$ nm) from high-pressure mercury vapor short arc lamp is irradiated on the sample through the bottom plate made of glass. (b) Time-tracking of both storage (black line) and loss (blue line) moduli at different UV intensities. The UV intensity was increased with ON/OFF cycles; irradiance from left to right 13 mW/cm^2 , 22 mW/cm^2 , 31 mW/cm^2 , and 47 mW/cm^2 .

CONCLUDING REMARKS

In conclusion, we demonstrated the phase behaviors and rheological properties of an azobenzene-based liquid crystalline dimer, CB₆OABOBu, based on HR-DSC, POM, UV-Vis spectroscopy and rheological studies. The dimer exhibits a liquid phase, two liquid crystalline nematic phases and a crystalline phase. It was found that all of the phases can be molten to upper phases and be solidified back by irradiating and terminating UV light, thanks to the photoresponsivity due to the azobenzene moiety in the molecular core part. The high-contrast and high-speed switching behaviors should be addressed in more details, and the mechanism should be clarified in the future.

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