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# Location of the Azobenzene Moieties within the Cross-Linked Liquid-Crystalline Polymers Can Dictate the Direction of Photoinduced Bending

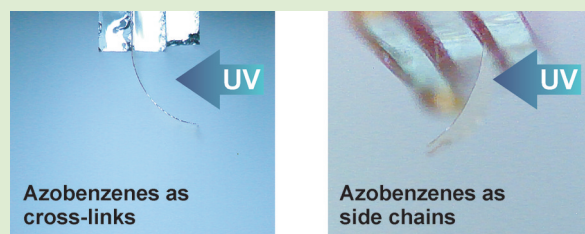
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## Supporting Information

**ABSTRACT:** We present a simple way to control the photoinduced bending direction of azobenzene-containing cross-linked liquid-crystalline polymers. By changing the location of the photoactive azobenzene moieties from cross-links to side-chains, the bending direction of the sample is reversed under identical irradiation conditions. In addition to providing a versatile route toward directionality control of the photoinduced macroscopic motions, this observation highlights the complicated nature of the photo-mechanical response of azobenzene-containing cross-linked liquid-crystalline polymers, showing that the photomobile behavior can be determined by seemingly small details on the materials design.



In an effort to develop light-driven actuators and functional materials that reversibly change their size and/or shape upon photoirradiation, photomechanical effects in material systems bearing photochromic moieties have created a great deal of research interest in recent years.<sup>1–6</sup> The photomechanical response has been investigated in, for example, organic crystals,<sup>6–8</sup> amorphous polymers and molecular glasses,<sup>9,10</sup> and liquid-crystalline (LC) polymers containing photoisomerizable molecules.<sup>11–13</sup> In particular, the photoinduced three-dimensional motions of azobenzene-containing cross-linked LC polymers have been actively studied.<sup>14–16</sup> Azobenzene is an ideal trigger for controlling the LC alignment: it can be mesogenic in the *trans*-conformation,<sup>17</sup> being therefore easily incorporated into the LC phase without destructuring the molecular alignment. In the *cis*-conformation, azobenzene efficiently destructs the LC alignment, for which reason even a small concentration of the azobenzene moieties can promote photochemical phase transition and induce significant photo-mechanical response into the material system.<sup>18</sup> In a properly designed LC polymer network, the light-generated force can be large enough to move relatively heavy macroscopic objects.<sup>19,20</sup>

The photoinduced bending in azobenzene-containing cross-linked LC polymers is initiated by photoisomerization-induced destruction in the initial LC alignment. In case of homogeneously aligned sample, UV irradiation results in asymmetric uniaxial contraction of the polymer network, which causes the film to bend toward the light source. Conversely, if the chromophores are homeotropically aligned, UV irradiation gives rise to photoexpansion of the surface layer, and the sample bends away from the light source.<sup>21</sup> Clearly, the

initial chromophore alignment plays an important role in dictating the bending behavior. On the other hand, in some material systems the bending direction can be controlled by the polarization direction of the excitation beam or by clever materials design, which has been attributed to optically induced reorientation of the azobenzene moieties perpendicular to the polarization of the irradiation beam<sup>22,23</sup> and to internal composition gradients within the LC polymer network, respectively.<sup>24</sup>

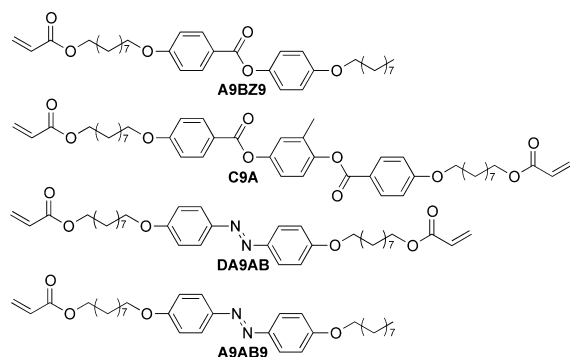
Here, we demonstrate that the bending direction of homogeneously aligned low-azobenzene-concentration cross-linked LC polymers can be controlled by the nature of binding between the azobenzene mesogens and the LC polymer network. Under similar irradiation conditions, a sample bearing the azobenzenes as cross-links bends toward the light source, whereas a sample containing the azobenzenes as side chains bends away from it. The significance of this observation is two-fold: on one hand, it provides a versatile route toward directionality control of the photoinduced bending motion. On the other hand, it serves to highlight the complicated nature of azobenzene-containing LC polymers, the overall photo-mechanical response of which is driven by delicate balance between several photoisomerization-induced effects.

This work is comprised of the preparation and photo-mechanical characterization of two azobenzene-containing cross-linked LC polymers, both of which bear equal overall

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cross-linker concentrations (20 mol %) and equal concentration of the azobenzene moieties (5 mol %) but differ in their nature of binding of the azobenzenes to the polymer network. A sample consisting of A9BZ9 (80 mol %), C9A (15 mol %), and DA9AB (5 mol %), denoted as cross-A5C20, contains the azobenzenes as cross-links. The other sample, side-A5C20 (75 mol % A9BZ9; 20 mol % C9A; 5 mol % A9AB9), contains only the nonphotoactive cross-linker C9A, and the azobenzenes are attached to the cross-linked polymer network as side chains. The constituent compounds were synthesized according to previously reported methods,<sup>25,26</sup> and their chemical structures are shown in Figure 1.



**Figure 1.** Chemical structures of the compounds used in this study.

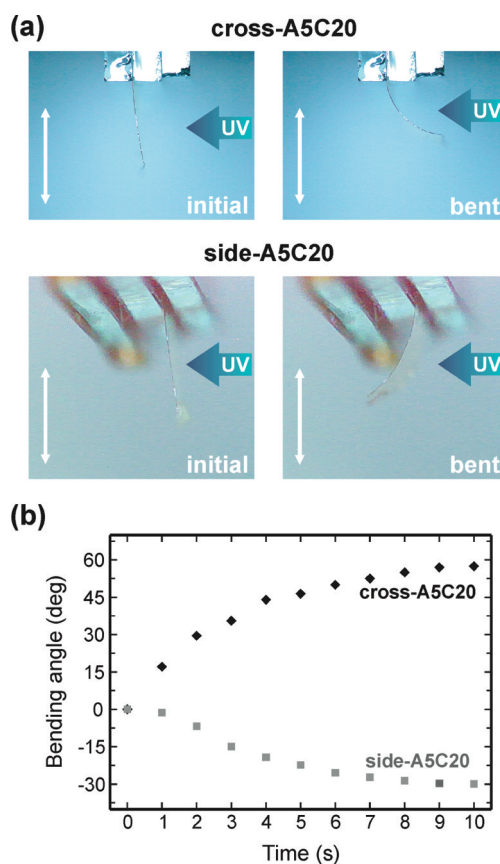
To investigate the relation between the location of the azobenzene moieties within the cross-linked polymer (i.e., side-chains vs cross-links) and the photomechanical response of the material system, it is important to keep other factors affecting the bending behavior (e.g., LC phase behavior, order parameter, film thickness, cross-linker concentration) similar. As shown in Table 1, both the order parameter of molecular

**Table 1. LC Phase Behavior and the Order Parameter of Molecular Alignment for Cross-A5C20 and Side-A5C20**

sample	phase transition temperatures (°C)	order parameter (UV-vis)
cross-A5C20	G 41 SmA 140 N	0.73
side-A5C20	G 48 SmA 140 N	0.76

alignment and the LC phase transition temperatures are essentially the same for cross-A5C20 and side-A5C20 (see the Supporting Information for UV-vis spectra, POM images, and DSC and XRD curves). Hence, we believe that the differences in their bending behavior arise solely from the difference in the location of the azobenzene moieties.

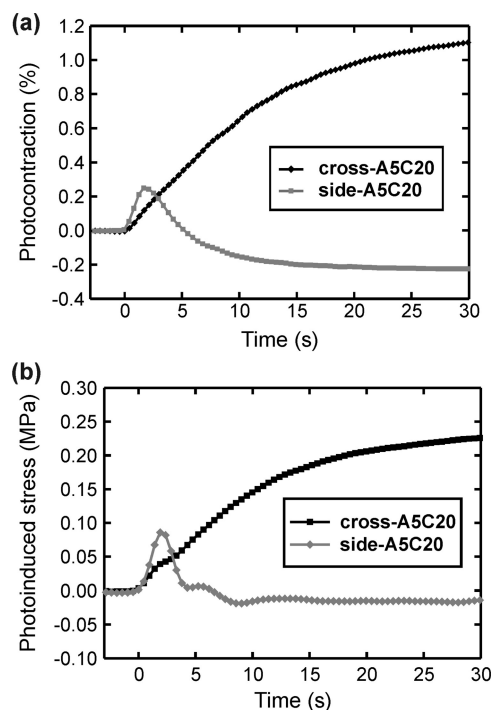
The photoinduced bending for cross-A5C20 and side-A5C20 is illustrated in Figure 2. Upon UV irradiation, cross-A5C20 bent rapidly toward the light source, as expected based on our earlier reports on photoinduced bending of related homogeneously aligned cross-linked azobenzene-containing polymers.<sup>27,28</sup> On the other hand, under identical irradiation conditions the bending direction for the side-A5C20 film was opposite, and rather unexpectedly the sample bent away from the light source. This behavior can be understood in view of the photocontraction/expansion curves shown in Figure 3a. The cross-A5C20 contracted upon UV irradiation, and due to the gradient in the *cis*-azobenzene concentration the contraction is asymmetric, causing the sample to bend toward the light



**Figure 2.** (a) Illustration of the opposite photoinduced bending behavior for cross-A5C20 (top) and side-A5C20 (bottom) upon UV irradiation. The arrow denotes the mesogen alignment direction. (b) The bending angle for cross-A5C20 and side-A5C20 upon UV irradiation as a function of time. We define bending toward the UV light source as the positive direction. The irradiation wavelength and intensity were 365 nm and 10 mW/cm<sup>2</sup>, respectively.

source. For side-A5C20, the film photocontracted rapidly and reached the maximum contraction of 0.25% after 1.5 s of irradiation (Figure 3a). This initial contraction relaxed subsequently, and in the photostationary state the sample *photoexpanded* by ca. 0.25%. As a consequence, the sample bent away from the light source, whereas the initial transient photocontraction showed up as a delay between starting the irradiation and the onset of bending (Figure 2b).

The results shown in Figures 2 and 3a demonstrate that in homogeneously aligned, highly ordered azo-polymer networks, the photoinduced length change and the bending behavior can be dictated by the location of the photoactive azobenzene moieties. Clearly the photoinduced macroscopic motions are driven by different photoisomerization-induced effects in the cross-A5C20 and side-A5C20. However, the overall photomechanical response of related material systems depends delicately on various factors: for instance if the concentration of the nonphotoactive C9A cross-linker is increased from 20 mol % to 60 mol %, the sample containing the azobenzenes in the cross-links still bends toward the light source (even if the bending is less efficient),<sup>28</sup> but the motion of the side-chain-functionalized sample is suppressed. By the same token, if the azobenzene concentration is increased to 20 mol % or higher, the samples bend toward the light source (at least under high-intensity irradiation) irrespective of the location of the azobenzene moieties.<sup>27</sup> Obviously, extensive studies on, for



**Figure 3.** (a) Photoinduced contraction/expansion and (b) photoinduced stress for cross-ASC20 and side-ASC20 upon UV irradiation (365 nm, 10 mW/cm<sup>2</sup>).

example, the azobenzene concentration and intensity dependence, are required to gain a more comprehensive understanding of the observed behavior. For now, this observation serves as an example of a versatile route toward directionality control of the photoinduced bending motion, without changing the initial mesogen alignment<sup>21</sup> or adjusting the parameters of the actinic light source.<sup>10,22</sup>

Lastly, we would like to consider the potential cause for the unconventional bending behavior of the side-ASC20 film. First, the UV irradiation can give rise to photothermal heating, which can potentially result in photoinduced actuation either through thermal expansion of the material system<sup>29</sup> or through thermally induced uniaxial contraction of the aligned polymer network.<sup>30</sup> These effects can be ruled out in the present case: the former does not explain the opposite bending behavior of cross-ASC20 and side-ASC20, which have equal absorption coefficients as well as order parameters and should therefore exhibit comparable thermal expansion in the mesogen alignment direction. The latter effect would result in bending toward the light source, not away from it as observed for side-ASC20. A more plausible explanation is provided by the photoisomerization reaction itself. It has been shown by Barrett et al. by ellipsometry and neutron reflectometry studies that in amorphous side-chain-functionalized polymers, azobenzene photoisomerization requires excess free volume to take place; hence *trans*–*cis* isomerization can give rise to expansion of polymer thin film upon photoirradiation.<sup>31,32</sup> We propose that the bending behavior of side-ASC20 is a consequence of such free volume effect. The azobenzene moieties efficiently isomerize even within the cross-linked material system (see Supporting Information, Figure S2), which leads to a decrease in the order parameter of molecular alignment: the birefringence of the homogeneously aligned side-ASC20 decreased by ca. 4.5% from 0.137 to 0.131 upon UV irradiation.

Due to the relatively high absorbance, the *cis*-concentration is highest at the film surface (the birefringence values given above are averaged over the whole sample), resulting in surface volume expansion and subsequent bending away from the light source. A similar free-volume effect is likely to be present also in cross-ASC20, but it is overshadowed by photocontraction of the polymer chains with azobenzene units as cross-links. The *trans*–*cis* photoisomerization in cross-links causes much more pronounced photomechanical effect into the material system. This is evidenced by photoinduced stress measurements: the stress is negligible for side-ASC20, but notable, 0.25 MPa, for cross-ASC20 in the photostationary state (see Figure 3b). Further evidence for the fact that competing photoisomerization-induced effects dictate the photoinduced bending behavior is provided by the initial transient photocontraction/photo-generated stress of side-ASC20 (Figure 3). At present we have no explanation for this behavior but propose that, as the azobenzene moieties have higher mobility in the side-chain functionalized system, the material rapidly relaxes to minimize the long-range uniaxial strain generated by photoisomerization. If the azobenzenes are located at the cross-links or if their concentration is high,<sup>27</sup> such relaxation cannot take place.

To conclude, this study demonstrates that the location of the photoactive azobenzene moieties within the homogeneously aligned cross-linked LC polymers can provide a facile method for directionality control of the photoinduced bending motion. If the azobenzenes are attached to the polymer as cross-links, the film photocontracts upon UV irradiation and bends toward the light source. Under similar irradiation conditions, a film containing the same concentration of the azobenzenes (5 mol %) as side-chains photoexpands and bends away from the excitation light source. We tentatively propose this discrepancy to originate from the competition between long-range uniaxial strain generated by the photoisomerization of the cross-linked azobenzene moieties (leading to photocontraction) and the higher free-volume requirement of the *cis*-azobenzenes as compared to *trans*-azobenzenes (leading to photoexpansion). This study demonstrates that by proper design of the material system either one of these effects can be made to dominate the overall photomechanical response, providing for facile directionality control of photoinduced bending.

## EXPERIMENTAL METHODS

The samples were prepared by *in situ* photopolymerization of the mixtures of the compounds, using 2 mol % of a photoinitiator (Ciba Specialty, Irgacure 784). The mixtures were melted at 110 °C and injected into 20  $\mu$ m thick glass cells, coated with rubbed polyimide to obtain homogeneous mesogen alignment. The mixtures were cooled down to 50 °C (at this temperature, both photopolymerizable mixtures exhibited a smectic A phase) at a cooling rate of 0.1 °C/min. The photopolymerization was carried out using a 500 W high-pressure mercury lamp (Ushio, UI-501HQ) equipped with glass filters (AGC techno glass, Y-52, and IRA-25S). The intensity was set to 2.0 mW/cm<sup>2</sup>, and the polymerization time was 2 h. The polymerized samples were removed from the glass cells, rinsed in ethyl acetate to remove any unreacted monomers, and dried overnight under reduced pressure.

The mesogen alignment at room temperature was evaluated by polarized optical microscopy (Olympus, BH-2) and polarized UV–vis spectroscopy (Jasco, V-650). The thermodynamic properties of the polymerizable mixtures and the final samples were evaluated with a differential scanning calorimeter (DSC Seiko Instruments, EX-TRAR6000, DSC6220G), at heating and cooling rates of 10 °C/min. At least three scans were performed to check the reproducibility. The phase behavior of the polymers was determined by simultaneous



measurement of X-ray diffraction patterns and DSC curves (Rigaku, Ultima IV).

Bending of the films was induced by irradiation with unpolarized light from a 365 nm UV-LED (Keyence, UV-400 with UV-50H and L-8) at room temperature. The bending behavior was monitored with a digital camera (Omron, VC-HRM20Z and VC1000). We used time dynamics of the bending angle (determined by drawing a line between the mounting point and the tip of the film and calculating the angle with respect to the vertical direction) to quantify the bending behavior. The photocontraction and photoinduced stress were measured with a thermomechanical analyzer (TMA, Shimadzu, TMA-60) by clamping the films at both ends and using an initial load of 10 mN in the mesogen alignment direction.

## ■ ASSOCIATED CONTENT

### Supporting Information

Polarized UV-vis spectra and polarized optical micrograph (POM) images of the photopolymerized samples, the changes in absorption spectra upon UV irradiation, DSC curves, and X-ray diffraction patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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