

Bending Behaviors of Azobenzene-containing Liquid Crystalline Polymers (AZ-LCP): Factors Influencing Bending Direction, Frequency and Degree

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Abstract. Liquid crystal polymers (LCP) containing azobenzene and its derivatives are fascinating and topics of intense scientific curiosities. As the addition of photo-responsive azobenzene, the LCP is exerted with the photochemical response, which shows fascinating and useful photo-induced motions and consequently enables a variety of applications in a lot of fields. In this review, we detail the macroscale mechanical motion of azobenzene containing liquid crystalline polymer (AZ-LCP) materials upon irradiation, with emphasis on the external and internal factors of bending behaviors of AZ-LCP, including bending direction, frequency and degree. We end with an outlook of challenging and competitive application as soft actuators.

1 Introduction

It is well known that both azobenzene and liquid crystal are particularly attractive and remain a topic of intense scientific curiosity. The self-assembly performance of liquid crystals and the photo-responsive properties brought by the addition of azobenzene group make AZ-LCP materials capable of the photoinduced motions, and allows precise and remote controls spatially by multiple adjustability such as polarization and intensity. Spurred by these soft materials light-controllable properties with chosen suitable light, the applications become fascinating in various fields, which include a lot of photo-driven devices [1] like the photomechanical energy harvesting [2], miniaturized transport, artificial flytrap [3] and now even extending into area of nanotemplates for nanoengineering and nanofabrication [4].

Photo-actuator of AZ-LCP has made progress within these fifteen years, starting with research on the conditional light-induced reversible volume changes only within thickness ranging from 250 to 1400 Å in 2005[5]. Then investigation gradually focus on the bending form, namely fast and large amplitude oscillation which is similar to hummingbird wingbeat and with little fatigue over cycles of AZ-LCP reported in 2008 [1]. In the following, the movement is converted and amplified into spring-like materials bending in twisting motions in 2014 [6], which displays a great qualitative improvement compared with the seemingly small motion than heretofore. Afterward, research in 2017 took advantage of fast cis-to-trans thermal relaxation to make the polymer films exhibit mechanical waves [2]. In the same year, Wani and his team designed a light-driven flytrap within the fiber-sized architecture [3]. In the previous reviews,

researchers concluded various applications of AZ-LCP materials such as the strategy and progress of designing the soft robotics [7], and some mainly focus on LC or LCP like various systems of liquid crystal containing materials [8], the historical development of liquid crystalline polymeric materials [9] and recent findings about photo-responsive liquid crystalline block copolymers (PLCBCs) [10]. However, no one has ever analyzed the influence factors of the photoinduced bending behavior of the AZ-LCP materials upon irradiation until now, and it is of great importance to help us to do further research. The following review might perfectly full the blank in this research area and enable us to design the new soft actuator with controllable bending direction, frequency and degree that perfectly match our needs and explore the potential application in the emerging industry like micromechanical industry and artificial industry [6].

In this review, we discuss the remarkable properties of the macroscale photomechanical behaviors of AZ-LCP materials upon irradiation, and focus specifically on the factors that influence its bending properties. We start by briefly introducing four factors of the bending direction, including phase-state of azobenzene [11, 12], initial alignment of mesogens [13], location of the azobenzene [14-17] and the polarization direction of light[18]. Then current reported materials on the affect of the oscillating frequency such as frequency of the laser blocking, cantilever thickness [1], materials, order parameter [19] and substituents to the azobenzene moiety are reviewed [15, 20-22]. After this, we discussed the important roles played by the thermomechanical properties, the temperature [23, 24] and the angle between molecules and long axis of ribben [6] in bending degree. Based on

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the existent analysis, our researchers can already manipulate ideal motion through designing novel molecular structures to achieve complex motion. For example, we can adjust its photomechanical performances like making the bending angle larger, the photo-responsive speed faster and fabrication process of AZ-LCP materials further improved. Last but not least, we close with a forward-looking overview of this materials about its area for applications.

2 Factors on bending directions

The phase-state of AZ-LCP may have an effect on the photomechanical behaviors. Ikeda and his co-workers had reported photoinduced bending towards the light source when liquid crystalline polymer was applied. Figure 1(a) gives out the possible mechanism based on two preconditions: (1) the film has a large molar extinction coefficient, the incident UV light could only penetrate the surface layer (<1 μ m) of the film; (2) the volume of aligned mesogens would contract upon UV irradiation. However, Barrett et. al demonstrated quite different photodeformation behaviors with amorphous azobenzene-containing polymers in which the azobenzene groups are disordered. As shown in figure 1(b), the film expanded upon the incident light, and could partially recover as the incident light was withdrawn. The surface expansion effect might cause the film bending away from the light source. In comparison, the reversed bending directions of azobenzene containing films might be attributed to whether the film is composed of liquid crystalline polymer or amorphous polymer.

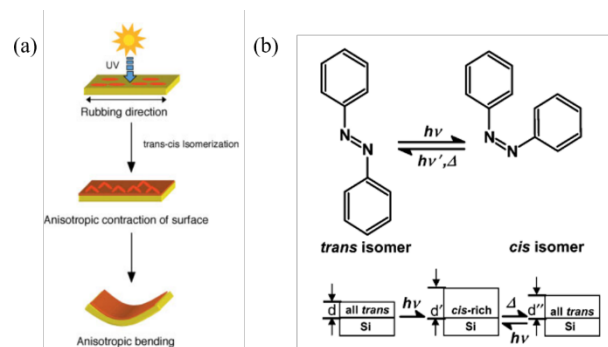


Fig. 1. (a) The mechanism of azobenzene-containing liquid crystalline polymer bending toward light source upon UV irradiation. Reproduced with permission from Ref.[2]; (b) Thickness change of amorphous azobenzene-containing polymer upon UV irradiation. Reproduced with permission from Ref. [3].

Mizuho Kondo and his team has discovered that photoinduced bending behavior of liquid-crystalline elastomer(LCE) was affected by initial alignment direction of mesogens within the film [13]. They investigated the bending behaviors of two alignment modes: homogeneous and homeotropic. Figure 2(a) and 2(b) show the performance of the films under the irradiation of unpolarized UV light, which indicates that (1) the homeotropic film bent away from the UV light (2) the homogeneous film bends toward the UV light along the alignment direction of mesogens. Figure 3(c) indicated the mechanism of corresponding bending behaviors enlarged from the the trans-cis photoisomerization behaviors of azobenzene mesogens. In the case of homogeneously aligned films, the irradiated mesogens on the surface contracts upon UV irradiation, resulting in the bending towards light source; while when the mesogens are homeotropically aligned, the surface conducted expansion and thus causing the film bend away from the light source.

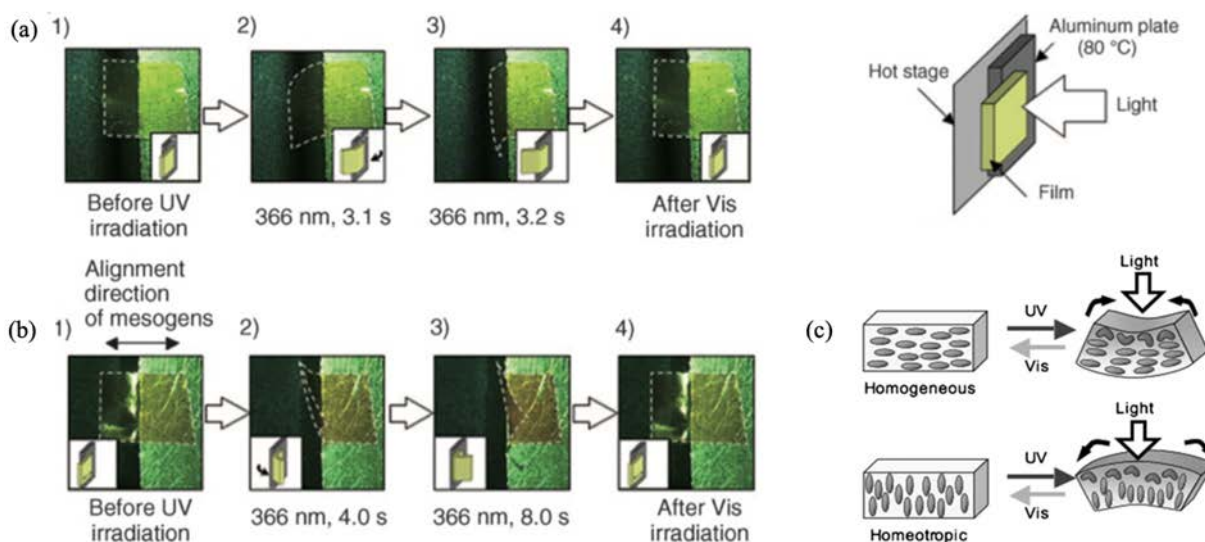


Fig. 2. (a) Bending behavior of the homogeneous film (b) and the homeotropic film. (c) Schematic illustration of the change. Reproduced with the permission from Ref. [11]

The position of photo-responsive mesogens in crosslinked AZ-CLCP also contributes to the reversible changes. According to the revealed photoinduced contraction or expansion behavior [14, 16, 17, 25], Yu and his team detected that the film containing homogeneously-aligned AZs in side chain bends away from the light source above a specific temperature [26]. They put the AZ-CLCP fibers on a hot state and irradiated with UV light(365 nm), and it was observed to

bend away from the light source when the temperature increased above 80 °C. Meanwhile, in previous work [8, 12, 13, 27-29], the overall photomechanical response has a common feature: the CLCP films or fibers, which bend toward light source, have photoactive AZ in the crosslinker. Therefore, they infer that whether AZ is located in the crosslinker or not plays an important role in deciding the bending direction of the CLCP material. Figure 3 displays the difference between them distinctly.

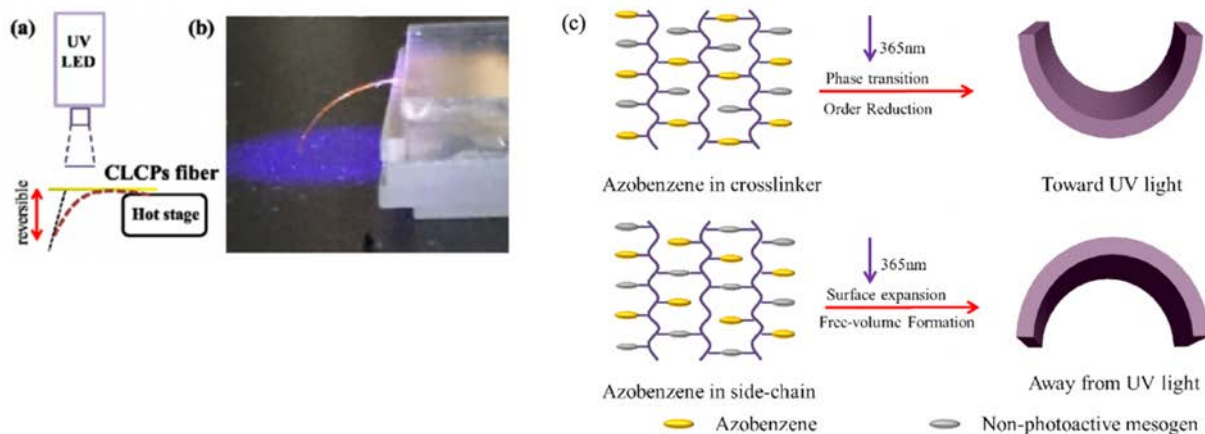


Fig. 3. (a) Experimental setup for photoinduced bending behavior of CLCP fibers upon irradiation with UV light. (b) significant bending of the fibers at temperature above 80°C (c) Schematic illustration of the different photoinduced deformation of AZ in crosslinker and side chain. Reproduced with the permission from Ref. [7]

The polarization direction of incident light also plays an important role in the photomechanical behaviors [18]. Yu and coworkers prepared the films by polymerizing a liquid-crystal monomer (molecule 1) and a diacrylate crosslinker (molecule 2) (9:1, mol/mol), both of which possess azobenzene moieties as shown in figure 4a [18]. After altering the polarization direction of light at 366 nm to 45°, 90° and 135° are shown in the fourth, sixth and eighth frames (figure 4b), respectively. It obviously indicates that the film is bent towards the incident light, and parallel to the polarization direction.

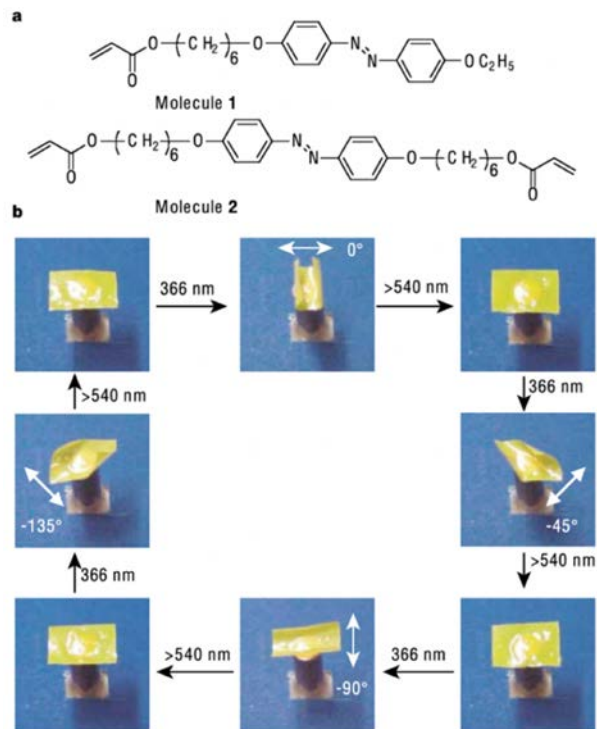


Fig. 4. (a) Chemical structure of the liquid-crystal monomer (molecule1) and crosslinker (molecule2). (b) The bending direction changes as the difference in angle of the linear polarized light. Reproduced with permission from Ref. [13]

3 Bending frequency

We summarized a variety of researches concentrated on the bending time and frequency of cantilever containing azo-LCN, and the related data of these materials is shown in Table 1.

Table 1. Oscillating Speed of Azobenzene liquid-crystalline polymers.

material	frequency (Hz) & bending time(s)	reference
azo-LCN	10Hz to almost 30Hz	[1]
PDLC	20-40s	[19]
PD-20CL-5	a few seconds to many minutes	[29]
A6M6	200-2000s	
AzoPy	60-2500s	
I	4-400s	[2]
II	3-40s	
DR1A	0.09-2s	

Timothy J. White and his team reported the oscillation of the azo-LCN cantilever when exposed to Ar⁺ laser beam. They discovered that the frequency of the oscillating depends on the frequency of the laser blocking and the cantilever thickness [1]. They discussed the oscillatory regularity of cantilevers with exposure to the laser beam. The optical setup displayed in figure 5a utilizes a spherical lens and a polarization rotator between the light source and azo-LCN cantilever to control the polarization direction of incident light. The rotation can be measured by the tip of cantilever with its displacement angle. When polarization parallel to the nematic director (long axis of the polymer cantilever), the cantilever bends from vertical (figure 5b-i) to 42° towards the laser source (figure 5b-ii). And then, when polarization perpendicular to n(E ⊥ n), the azo-LCN bends nearly 90° (figure 5b-iii). Once the cantilever is unexposed, it recover to vertical from either states (figure 5b-iv).

Besides, they tested the corresponding frequency of the oscillating azo-LCN cantilever through increasing the cantilever thickness. As figure 5c shows, when thickness of azo-LCN increase from 20 μm to 50 μm, the amplitude rises from 10Hz to almost 30Hz.

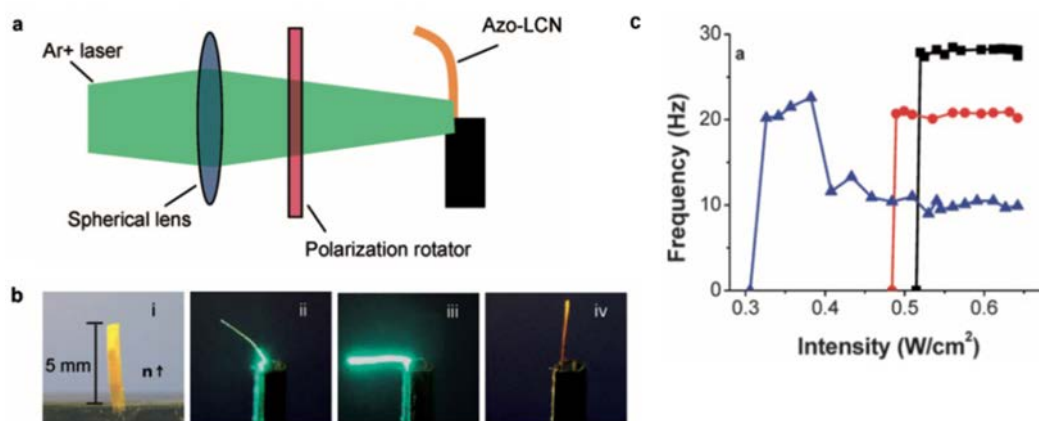


Fig. 5. (a) The setup made up of an Ar⁺ laser, a spherical lens, and a polarization rotator is utilized to make the azo-LCN cantilever photoactuated upon the laser. (b) The nematic director of the polymer is parallel to long axis of the polymer cantilever. In the beginning, the polymer cantilever is vertical (panel i). When polarization parallel to the long axis(E//n), the cantilever bends from vertical to 42°. towards the laser source (panel ii). After that, when polarization perpendicular to n(E ⊥ n), the azo-LCN bends nearly 90°. (panel iii), and without exposure, the cantilever recovers to vertical from either ii and iii states. (panel iv) (c) Frequency is faster with increased azo-LCNs thickness for 50 mm (■), 40 mm (●), and 20 mm (▲) Reproduced with permission from Ref. [14]

Yu and his team synthesized a polymer dispersed liquid crystalline (PDLC) material based on the light-responsive AZ mesogens and proved that both materials and order parameter play important roles in the bending frequency[19]. They made use of the phase reversion of PM6ABOC2 to obtain wrinkled LCP microparticles (LCPMs), and incorporate the microparticles into PVA solution (10 %) to fabricate the PDLC films. Furthermore,

they mechanically stretched the film at a specific elongation rate (the ratio of the stretched to original samples) to make the deformation from spheres to ellipsoids (figure 6a), which can be tested and proved through Polarized Optical Microscope (figure 6b). Upon irradiation, the bending time of the PDLC film(about 20-40s) is relatively longer than the film made of LCN reported in Ref.[1] (figure 6c), which means that LCPM

needs more time to recover to flat. Meanwhile, the bending time decreased with the increasing of elongation rate as demonstrated in figure 6c.

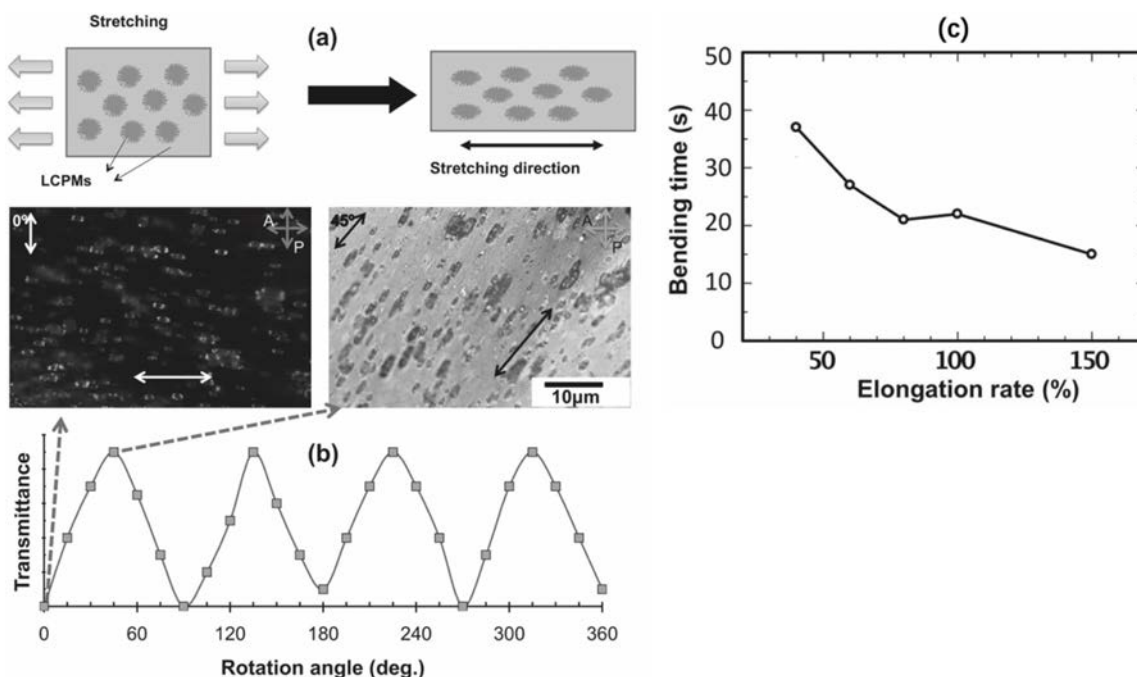


Fig. 6. (a) Schematic illustration of LCPM mechanical forming process and change of the LCPM photoinduced bending behaviors after mechanical stretching. a) Feasible scheme of LCPMs in the hybrid films. b) Polarized optical microscope images of hybrid LC films and transmittance of different rotation angle through two crossed polarizers (A, analyzer; P, polarizer). c) Relationship between elongation rate and bending time. Reproduced with permission from Ref. [15]

However, compared with the fast bending behaviors, it costs more time to regress after the photoisomerization. Anne Helene Gelebart and his teammates investigated the cis-trans relaxation time of several azobenzene derivatives with varied end groups [15, 20-22]. As figure

7 shows, the relaxation half-time of A6M6 is pretty long, meanwhile, azo-derivatives I and II shows faster relaxation. And the push-pull effect provided by hydrogen bond also play an important part in affecting the half-time [2].

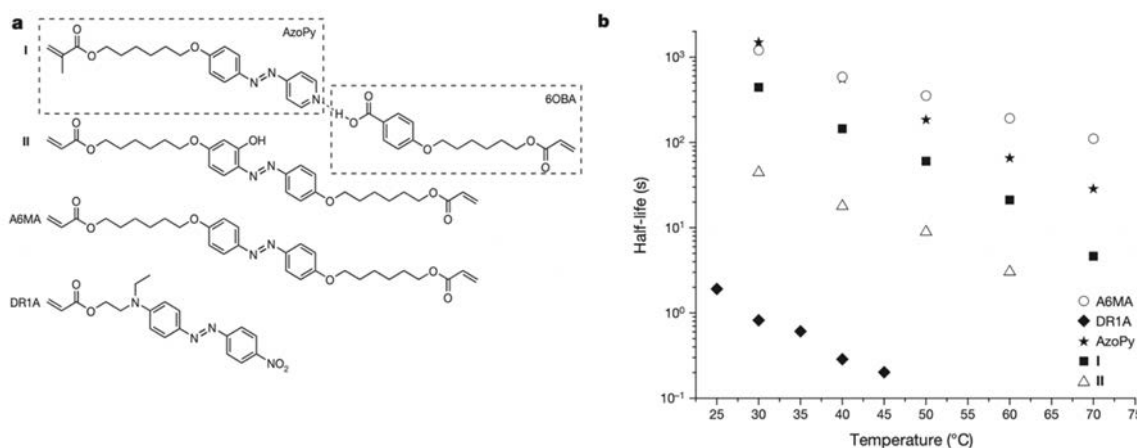


Fig. 7. Azo dyes and their cis-to-trans relaxation. a) Chemical structures of azo-derivatives. b) The half-lives of the azo-derivatives composed liquid-crystal cis-to-trans relaxation. Reproduced with permission from Ref. [20]

The experimental data explored by Lee and his team showed that the cantilever PD-20CL5 exist instantaneous and equilibrium bending at temperature above the T_g. Upon the UV irradiation, the cantilever would bend instantaneously in a larger degree and achieve equilibrium status after a few seconds [29]. The time to reach equilibrium is strongly related to temperature. As

the temperature goes up, the equilibrium time is longer; otherwise, the time needed to reach equilibrium state is shorter.

4 Bending angle

Kyung Min Lee and his team found out that the bending degree is largely dictated by the cross-link density. They tested thermomechanical property of different PD-20CL-xx samples (curing time presented as xx) like storage modulus (E'), loss modulus (E'') and glass transition temperature (T_g) and calculated the cross-linked density by eq : [23, 24] (shown in figure 8a).

$$\nu_e = E'_{\text{high}} / (3RT_{\text{high}})$$

As figure 8c reveals, the bending angles of azo-LCN cantilever composed by PD-20CL-5 and PD-20CL-60 are

(a)

sample code	T_g^a (°C)	T_{high}^b (K)	E'_{high}^c (MPa)	ν_e (mol/dm ³)
PD-20CL-1	44	367	23.08	2.09
PD-20CL-5	48	371	26.72	2.26
PD-20CL-15	61	384	31.5	3.29
PD-20CL-30	69	392	41.9	4.32
PD-20CL-60	80	403	73.9	7.25
PD-20CL-120	80	403	74.0	7.26

different within the same polarization angle (the test principle of bending is shown in figure 8b). In fact, the bending angle is reduced when the cross-link density becomes larger.

What's more, they found out that the instant bending degree of azo-LCN cantilever contained PD-20CL-5 is under the influence of temperature (when the temperature is higher than the T_g). When the temperature rose, the instant bending angle becomes larger accordingly.

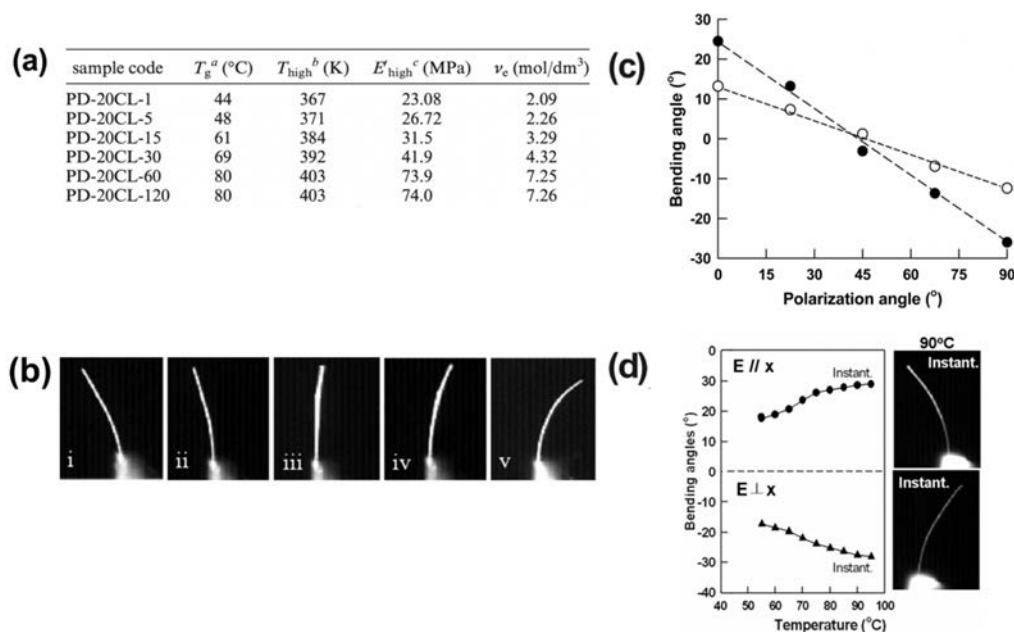


Fig. 8. a) The azo-LCN sample nomenclature of T_g , T_{high} , E'_{high} , and crosslink density. b) Photoinduced bending of azo-LCN cantilever (originally vertical) containing PD-20CL-5 under irradiation of 442nm laser light in different polarization angles. (i) 0°, (ii) 20°, (iii) 45°, (iv) 70°, and (v) 90° c) Summarization of accurate bending data through investigation on azo-LCN cantilever composed of PD-20CL-5 (○) and PD-20CL-60 (●) when exposed to 80mW/cm² of a 442nm laser. d) Instant bending angles of azo-LCN cantilever contained PD-20CL5 under polarized laser in $E \perp x$ and $E // x$ with various temperatures above T_g . Reproduced with permission from Ref. [12]

Iamsaard and his team detected that bending degree also influenced by the angle α between twist-nematic molecular orientation which in the identical direction with the molecules at mid-plane of the film and the long axis of the ribbon. They cut the liquid crystal film containing azo-LCN and chiral dopants S-811 and R-811 [6] from various directions, and got the ribbon bending in different directions with diverse angle α . To illustrate the

affected experimental law of α , figure 9a plots the photoacuation modes of azo-LCN cantilever doped with S-811 at different α . In the images shown in figure 9b, the direction of ribbon is from flat to left-hand spring, ring and right-hand spring at last, and bending degree here is like a spring which completely different from last mentioned ones.

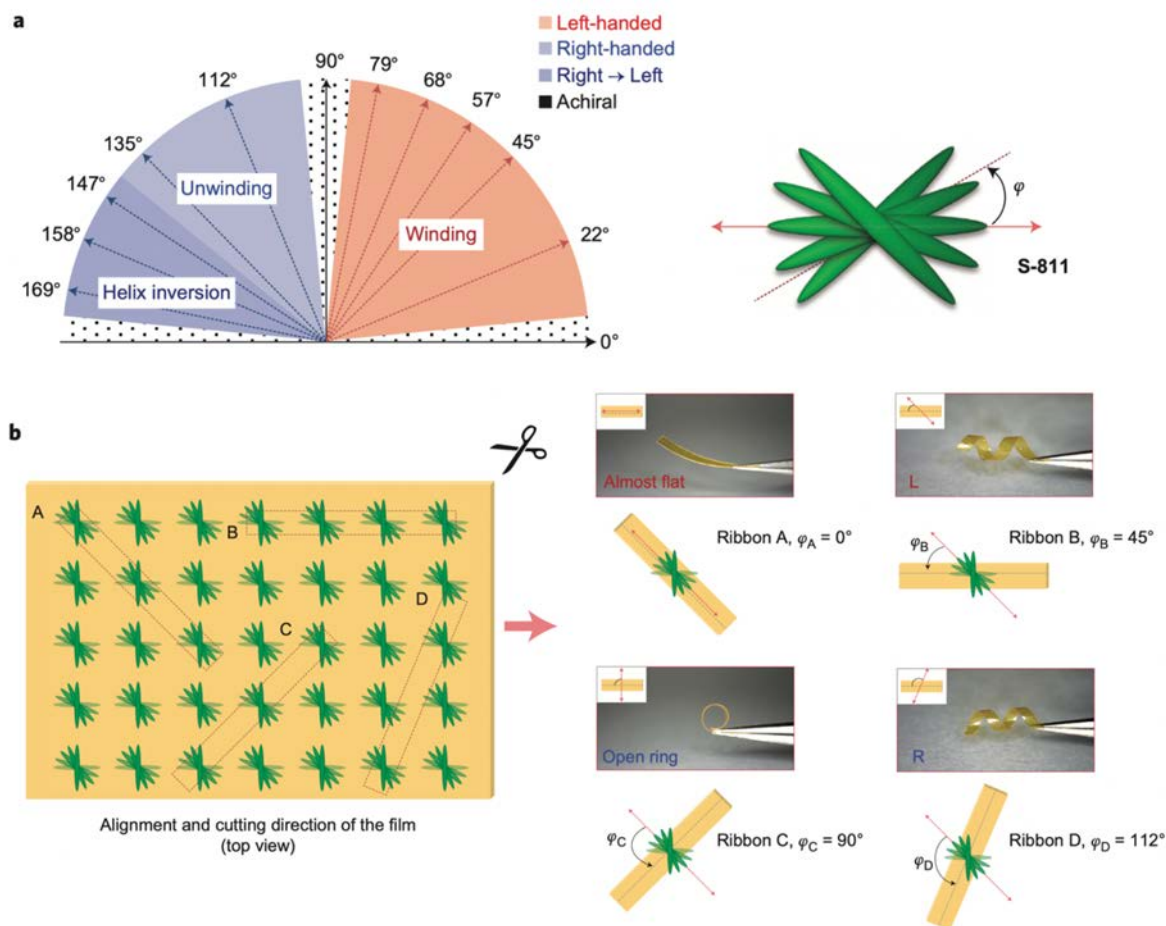


Fig. 9. a) Photoactuation modes of azo-LCN springs doped with S-811 twist left-hand directly. b) The ribbons bend in a variety of directions depend on the way they were cut.

5 Conclusion and outlook

Thereto, the photoinduced bending behaviors are usually described with properties such as bending direction, oscillating frequency and bending degree. Therefore, we summarized the influenced factors of the three increasingly interested properties. First, the phase-state of azobenzene, initial alignment of mesogens, the position of the crosslinked Azobenzene-containing liquid-crystalline polymers and polarization direction of light would affect the bending direction of AZ-LCP films. Then, we found out the factors contributing to oscillating frequency, including laser blocking frequency, cantilever thickness, materials, order parameter and substituents of azobenzene moiety. Later on, we pointed out the affecting factors of bending degree, including thermomechanical properties, temperature and the angle between molecules and long axis of ribbon.

Based on the operational analysis and detailed examination, the photo-responsive actuators have a lot of intriguing abilities, which includes no contact, remotely controlled and multiple adjustability. There are some research directions up to date with the rapid development of artificial intelligence (AI) such as highly integrated systems which can convert the external stimuli signal into

chemical or physical changes and an electric power-driven robot who can complete the expected missions. And there are also some processing problems, we can solve them by making the polymer actuators much softer or lighter, enabling them easily made into various shapes and have better mechanical performance with less fabrication process. The properties of AZ-containing LCP materials could also be further improved, we can boost the photo-responsive speed, increase the bending degree with versatile directionality control.

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