



Influences of Ortho-Fluoroazobenzenes on Liquid Crystalline Phase Stability and 2D (Planar) Actuation Properties of Liquid Crystalline Elastomers

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In this article, the influences of ortho-fluoroazobenzenes (o-Fbs) on liquid crystalline (LC) phase stability and actuation properties of liquid crystalline elastomers (LCEs) are presented. Such o-Fbs find interest because they allow full photoswitching with visible light (no ultraviolet (UV) radiation). Novel o-Fb monomers and crosslinkers are synthesized and characterized. Different amounts of an LC mixture are replaced with synthesized o-Fbs successively and their influences on the LC phase stability in the *cis* and *trans* forms are observed through measuring the related clearing temperatures via polarized optical microscopy. LCE precursors containing 0, 1, 3, 5, 7, and 10 mol% o-Fb monomer or crosslinker are aligned in a magnetic field and polymerized as films in the LC phase. Thermal and visible light-controlled photochemical 2D (planar) actuation properties of LCE samples are investigated and compared to LCEs containing a liquid crystalline non-fluorinated azobenzene monomer as reference. It is shown that, while the favorable photochemistry is obtained, the integration of o-Fbs is less effective for photoswitching of the LC phase, because i) less o-Fbs can be integrated without destroying the LC phase and ii) the *trans*–*cis* isomerization is less effective in destroying the LC phase.

1. Introduction

Recently, environment-friendly technologies find great research interest. One of the main drivers for this might be the ongoing global warming. Consequently, devices using or propelled by solar, wind, or water power become more and more attractive.^[1–4] This trend can be observed up to the research field of soft actuators like liquid crystalline elastomers (LCEs). Here, progress was made to apply environment-friendly visible light or sunlight as actuation stimulus.^[5,6]

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In general, LCEs have gained great interest as stimuli-responsive and actuator materials in the last decades.^[7–16] They consist of shape anisotropic molecules (mesogens) that are incorporated in a weakly crosslinked polymeric network (an elastomer). Therefore, they show the entropy elasticity of elastomers as well as the anisotropic characteristics of liquid crystals. Mesogens are either incorporated into the polymer backbone (main-chain LCE) or linked to it via flexible spacers (side-chain LCE).^[17–20] They cause the molecular self-organization in liquid crystalline (LC) phases (mesophases). In nematic phases, for example, rod shaped mesogens align with their long axis roughly parallel to a common director and thus have directional but no positional order.^[21,22] Integrated in a polymeric network, they act as an anisotropic environment for the polymer chains and stretch them to some extent in the mesophase.^[7,13–16,23] On the other hand, in the isotropic state the order

is lost and polymers can adopt their favored isotropic coil conformation. Switching between these states results in a macroscopic shape change if the LC state is present as a monodomain within the LCE sample. Shrinkage parallel to the director and expansion in the perpendicular direction are observed while the volume is kept constant.^[13–16,24] These actuation properties had already been predicted by de Gennes in 1975.^[25,26] So far, actuations up to 400%^[27] could be observed for main-chain LCEs while side-chain LCEs could achieve actuations of up to 70%^[26,28] corresponding to the increase in length.^[7] To obtain a monodomain, LCE samples need to be pretreated to align mesogens before crosslinking. This is usually done in magnetic^[29,30] or electric fields,^[31] with the help of photoalignment layers^[32,33] or by mechanical stretching of prepolymerized samples.^[7,10] After alignment, crosslinking can occur via covalent or physical netpoints.^[7,8,34]

To investigate actuation properties of LCEs, it is necessary to switch between the liquid crystalline and the isotropic state. This requires an external stimulus. Such stimulus can be, for example, a change of temperature,^[35] irradiation with light,^[36,37] a pH change,^[38] or the use of electric or magnetic fields.^[39,40] Most attention has been paid to temperature changes. This often requires temperatures far beyond ambient temperature and mostly the whole actuator device has to be heated which results in high energy consumption. In contrast, light as a

remote-controlled stimulus can easily be focused on specific actuator areas. This has attracted attention to light-controlled LCEs in many research groups.^[41–43]

A plastic motor, that converts light energy to mechanical energy, was presented by Ikeda et al.^[44] With the same concept, a 3D robotic arm motion and an inchworm-like movement could be imitated.^[45] The group of Fisher developed light-controlled, self-propelled micro-swimmers.^[46] Broer et al. mimicked artificial cilia synthesized by inkjet printing which could be bent with light.^[47] Furthermore, a huge amount of light-actuating LCE particles or tubes could be synthesized with the help of a microfluidic set-up in our group.^[23,48]

A remark is necessary in this context: Elastomers are a subclass of crosslinked polymers with a low crosslinking density resulting in long polymer chains between the net-points. Thus, they can easily be deformed to high strains and swell strongly in good solvents. Typical elastic moduli (bulk state, above T_g) are in the range of MPa or below. Highly crosslinked systems, also called thermosets, are—on the contrary—hard materials with little deformability, which hardly swell. Their elastic moduli lie in the range of GPa. From LC polymers both types of networks can be made, depending on the amount of incorporated crosslinking agent.^[49] LCEs (low crosslinking density) show phase transitions (e.g., clearing points) and a temperature-dependent LC order parameter. In LC thermosets (high crosslinking density) the LC order is “frozen” and nearly temperature independent although photoisomerization can change the order slightly. Thus, bending actuations, as result of ultraviolet (UV) irradiation from one side, are often reported for LC networks with a high crosslinking density.^[49] However, here we want to concentrate on 2D deformations in the plane, which require large deformations and a low crosslinking density.

All light-controlled examples which have been mentioned before use azobenzene groups as chemical compound. In LCEs, they can cause phase transitions through light irradiation by switching between the trans and cis state.^[50,51] Whereas the trans form shows a rod-like state and can integrate well in the nematic LC phase, the cis form shows a bend-like structure. This structure disturbs the ordered LC phase so that the clearing temperature is decreased. Switching from trans (ground state) to cis state can be triggered (for conventional azochromophores) through irradiation with UV light. Back-isomerization can take place thermally in the dark or through irradiation with visible (vis) light (>450 nm).^[8,52–54]

Recently, it was argued, in relation to environmental concerns, that the requirement of high-energy UV light to induce trans $\rightarrow$ cis isomerizations is undesired.^[55] Moreover, the UV light might potentially limit the device lifetime by degrading the azobenzene or damaging its surroundings.^[5,55,56] These detriments might restrict their practical use in biological systems and material sciences.^[51] A possibility to circumvent UV radiation is the separation of the n $\rightarrow$ π^* azobenzene absorption bands of trans and cis forms in the visible range of spectrum. Since they mostly overlap, it is impossible to achieve sufficient isomerizations with visible light before.^[51]

This is why much effort has been made to separate these n $\rightarrow$ π^* bands, but also to boost visible light absorption and control cis lifetimes, through substitutions in the ortho- and

para-positions of azobenzene structures.^[51,56–59] The Hecht group developed and investigated ortho-fluoroazobenzenes (o-Fbs).^[51,56] The fluorine atoms in ortho-positions lower the energy of the n-orbital of the Z-isomer by reducing the electron density near the N=N bond and as a result, cause a separation of the n $\rightarrow$ π^* absorption band in the visible range of spectrum. Hereby, separations of up to 50 nm were achieved which allow a cis $\rightarrow$ trans and trans $\rightarrow$ cis isomerization with green and blue lights.^[51] A separation of n $\rightarrow$ π^* bands of even 100 nm was reported for a covalently ortho-ethylene bridged azobenzene. Here, the bridge causes a distortion of the trans isomer and affects the π and π^* molecular orbitals.^[60] Woolley et al. synthesized an azobenzene with four methoxy groups in the ortho-positions which results in a splitting of 36 nm. In this case, the energy levels of all orbitals are increased because of the repulsive interactions of azobenzene n-orbitals with the lone pair energy orbitals of the oxygen atoms.^[61] In both the last cases the splitting results from a dramatic distortion of the azobenzene groups.^[51]

In first experiments, n $\rightarrow$ π^* band separated azobenzene groups were already integrated in LCEs to trigger them with visible light. Here, the research focused on visible light-controlled bending motions. Yu et al. synthesized azotoluene containing LCEs which showed bending and unbending motions by irradiating them with light of 445 and 530 nm.^[6] In this case, the enlarged conjugation structure of the azobenzene units enable switching between cis and trans states triggered through visible light.^[62,63] In the groups of Schenning and Debije an o-Fb compound has been integrated into an LCE network to investigate the induction of bending of a statistical chaotic sunlight-driven actuator.^[5]

However, to the best of our knowledge no data from pure 2D shrinkage and elongation actuations (planar, no bending) of LCEs containing n $\rightarrow$ π^* band separated azobenzenes have been reported yet. Furthermore, no investigations of the influence of visible light controllable azobenzenes and especially ortho-fluorinated azobenzenes have been made concerning the LC phase stability.

We could already prove in our group that large 2D actuations of up to 40% are also possible with LCEs containing non-ortho-substituted azobenzenes. For this, irradiation with wavelengths on the edges of the $\pi \rightarrow \pi^*$ absorption band (400–450 nm) of the trans form, which are less absorbed, was used. This allowed light to penetrate the complete sample and caused homogeneous actuations.^[23,52]

In this work, we present the synthesis of a new o-Fb monomer and an o-Fb crosslinker. We integrate them in LCEs and investigate their influence on the stability of LC phases and their influence on 2D planar actuation properties of synthesized LCEs. Additionally, we will make comparisons to LCEs containing a liquid crystalline non-fluorinated azobenzene monomer, as described in the previous section, to get insights into the effectiveness of both systems.

2. Results and Discussion

2.1. Synthesis of Ortho-Fluorinated Azobenzene Crosslinker and Monomer

This paper aims at the preparation of LCEs which can be switched completely with visible light. For this purpose, an o-Fb

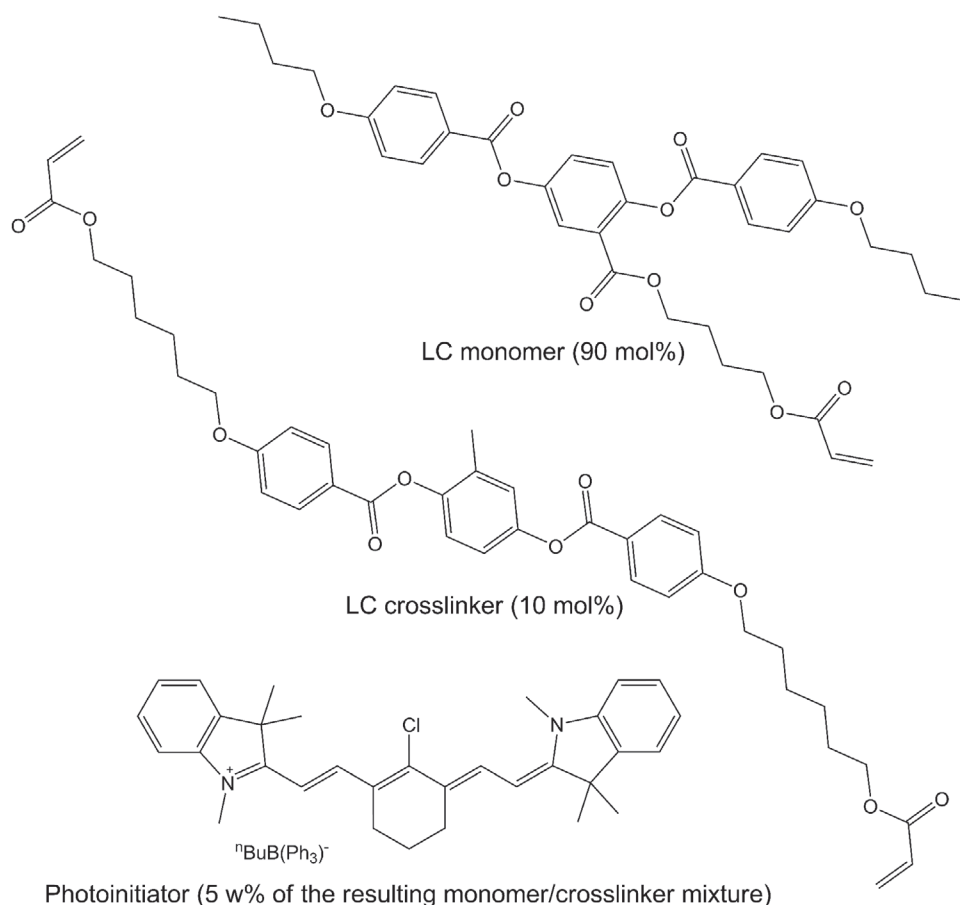


Figure 1. Chemical structures of the LCE precursor used to study the influence of o-Fb crosslinker and monomer on LC phase stability and LCE actuation properties. The precursor consists of an LC monomer (4'-acryloyloxybutyl 2,5-(4'-butyloxybenzoyloxy)benzoate), an LC crosslinker (2-methyl-1,4-phenylene bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate)) and a photoinitiator (1,3,3,1',3',3'-hexamethyl-11-chloro-10,12-propylene-tricarbocyanine triphenylbutyl borate or CBC).

monomer and crosslinker were synthesized to integrate them in LCE systems. For the understanding of their role during switching and to optimize the resulting LCEs, their influences on LC phase stability as well as LCE actuation properties should be investigated.

For this, an LCE precursor consisting of an LC monomer (4'-acryloyloxybutyl 2,5-(4'-butyloxybenzoyloxy)benzoate), an LC crosslinker (2-methyl-1,4-phenylene bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate)) and a photoinitiator (1,3,3,1',3',3'-hexamethyl-11-chloro-10,12-propylene-tricarbocyanine triphenylbutyl borate or CBC) was chosen to study the effects. Chemical structures are shown in **Figure 1**. LCEs consisting of the shown LC monomer (without the LC crosslinker) have been studied in detail elsewhere.^[24,26,30,35]

CBC as an infrared photoinitiator was taken because integration of o-Fbs will lead to strong UV light absorption and consequently make initiation with UV initiators difficult. To circumvent this problem, CBC—which has an absorption maximum at 780 nm—can be used which has been described first by Keller et al.^[23,64,65] Since the absorption of o-Fbs in this range of spectrum is much lower, the penetration of samples and thus initiator activation becomes easier.

Monomer and crosslinker were chosen because both are liquid crystalline and show nematic mesophases.^[18,28] In contrast to components which would show different LC behaviors, this allows better comparability when replacing each of them with corresponding o-Fbs.

Analogous to LC monomer and crosslinker, o-Fb monomer and crosslinker containing acrylate groups were synthesized since they should show similar polarities and a similar polymerization behavior. Thus, a statistical and homogeneous incorporation into resulting LCEs should be obtained. We furthermore paid attention to similar alkyl spacers between acrylate groups and the aromatic core (especially for the crosslinkers). Synthetic routes of both new azo-dyes (monomer **6** and crosslinker **5**) are shown in **Figure 2**.

Ethyl 3-amino-3,5-difluorobenzoate **1** was synthesized as described by Hecht et al.^[51] who also synthesized diethyl-4,4'-(2,2',6,6'-tetrafluoro)azobenzene dicarboxylate **2** through oxidative dimerization with potassium permanganate and iron(III) sulfate.^[51] Because of the very low yield of 23% that was achieved, we wanted to avoid this reaction. Instead, we followed a synthesis described by Minikata et al. who found an efficient and metal-free synthetic method for symmetric and unsymmetric

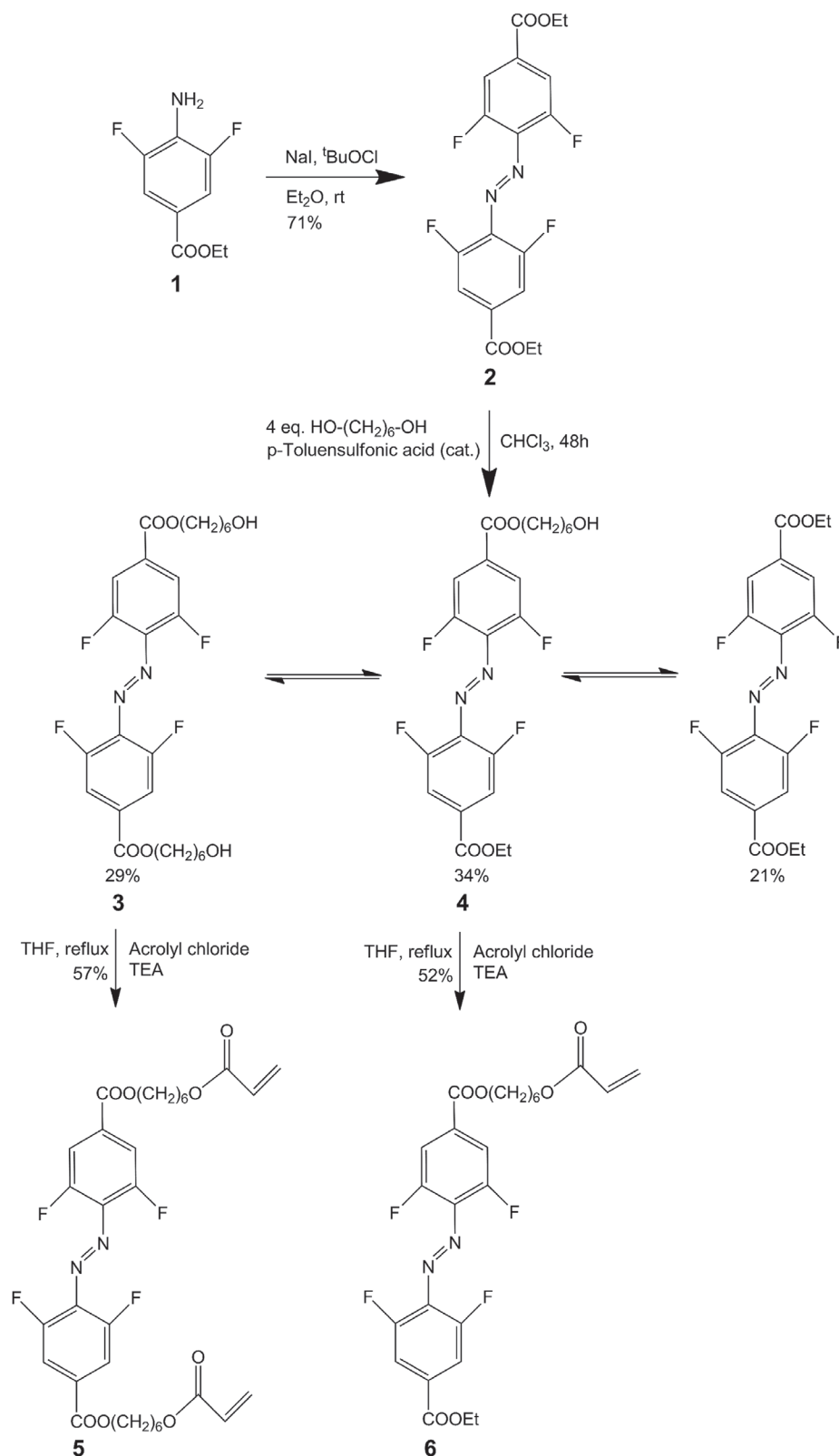


Figure 2. Synthetic route to synthesize o-Fb crosslinker **5** and monomer **6**. Diethyl-4,4'-(2,2',6,6'-tetrafluoro)azobenzene dicarboxylate **2** is obtained through oxidative dimerization of ethyl 3-amino-3,5-difluorobenzoate **1** with *t*BuOI. Mono- and disubstituted transesterification products (**3** and **4**) are synthesized with an acid transesterification reaction of **2** with four equivalents of 1,6-hexanediol. Basic reactions of **3** and **4** with acryloyl chloride lead to **5** and **6**.

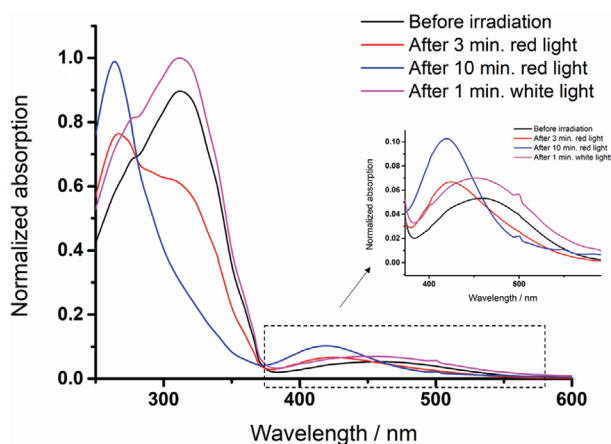


Figure 3. UV/vis spectra of o-Fb monomer **6** in chloroform before irradiation with any light source in its ground state, after irradiation with red light for 3 and 10 min and after irradiation with a cold white light source for 1 min.

aromatic azobenzene compounds using tBuOI. Hereby, the non-fluorinated sibling of **2** could be obtained with a yield of 95%.^[66] With this method we could obtain **2** with a yield of 71%.

An acid transesterification reaction with four equimolar amounts of 1,6-hexanediol and p-toluene sulfonic acid as catalyst led to a mixture of the two transesterification products (**3** and **4**) and the educt in chemical equilibrium. After purification, mono- and disubstituted transesterification products were converted with acryloyl chloride under basic conditions to synthesize o-Fb crosslinker **5** and monomer **6** with yields of overall 5% and 4%. ¹H-nuclear magnetic resonance (NMR) spectra of both are shown in Figures S1 and S2, Supporting Information.

2.2. Analysis of o-Fb Monomer and Crosslinker through UV/vis Spectroscopy

Switching between cis and trans states of o-Fb monomer and crosslinker were analyzed via UV/vis spectroscopy. Due to similar structures, their behavior under light irradiation with different wavelengths did not show any significant differences. UV/Vis spectra of a solution of the o-Fb monomer in chloroform before irradiation with any light source and after irradiation with red and white light are shown in **Figure 3**.

Before irradiation with any light source mainly the trans form is present as the most stable state. The $\pi \rightarrow \pi^*$ absorption band is found at 310 nm and the $n \rightarrow \pi^*$ absorption band at 460 nm. When irradiated with red light (>500 nm but mainly red light, in Figure S3, Supporting Information the absorption spectrum of the red light filter used for irradiation is presented) these bands decrease and $\pi \rightarrow \pi^*$ as well as $n \rightarrow \pi^*$ absorption bands of the cis form increase at 265 and 420 nm. This proves the separation of the $n \rightarrow \pi^*$ bands in the visible range of the spectrum as already described before for o-Fbs in the literature.^[51,56] Trans $\rightarrow$ cis isomerization occurs because $n \rightarrow \pi^*$ absorption takes place mainly from the trans form at wavelength higher than 500 nm. After irradiation with a cold white light source, bands corresponding to the trans isomer

appeared again (emission spectrum of the white light source is shown in Figure S4, Supporting Information). Here, the range of wavelengths can mainly be absorbed from the cis form.

2.3. Investigation of the Influences of o-Fb Monomer and Crosslinker on Liquid Crystalline Phase Stability

Starting with the mixture of LC monomer and crosslinker (see Figure 1, ratio 90:10), parts were exchanged for o-Fb monomer **6** and crosslinker **5**. Then the influences on the stability of the LC phase of resulting mixtures were observed via polarized optical microscopy. First of all, no birefringence of the pure o-Fbs could be observed indicating that both are not liquid crystalline at all.

Secondly, amounts of 1, 3, 5, 7, 10, 20, 30, and 50 mol% of the LC monomer and 1, 3, 5, 7, and 10 mol% of the LC crosslinker were successively replaced and the clearing temperatures of the resulting mixtures were investigated (Here, mol% is the amount of o-Fbs regarding the complete mixtures out of LC monomer and crosslinker. It is not related to the individual parts of monomer and crosslinker.) Amounts higher than 10 mol% regarding to the crosslinker were not investigated since it would lead to an increased crosslinking density of resulting LCE networks and thus probably have an effect on actuation properties which make comparisons impossible.

The LC monomer was also replaced with 4-butoxy-2'-(4-methacryloyloxybutoxy)-4'-(4-butoxybenzoyloxy)azobenzene **7** as another LC monomer containing a non-fluorinated azobenzene group to study an LC reference system for comparisons. Mixtures were investigated without initiator system. Chemical structures of the azobenzenes **5**, **6**, and **7** are shown in **Figure 4**.

Clearing temperatures of the mixtures shown in Figure 1 (without initiator) in dependence of their amount of integrated azobenzenes (**5**, **6** and **7**) are presented in **Figure 5**. The non-fluorinated azobenzene monomer **7** is liquid crystalline and shows a T_{NI} of 84 °C which is below the T_{NI} of 98 °C of the LC monomer used in the system.

Consequently, a decrease of the clearing temperature from 98 to 84 °C is expected through replacement of 0 to 50 and 90 mol%. However, slight differences of these temperatures are found since the 10 mol% LC crosslinker content (T_{NI} of 92 °C) has a small influence on the system.

On the other hand, with increasing amounts of o-Fb compounds clearing temperatures decreased drastically. This behavior was expected since the LC phase originating from the other components is disturbed through their non-liquid crystallinity. As a result, the LC order is decreased and thus the isotropic phase is reached earlier. A mixture containing 50 mol% o-Fb monomer did not show any birefringence down to room temperature what indicates a clearing temperature below. The influences of fluorinated monomer **6** and crosslinker **5** are almost the same. The crosslinker has a slightly greater effect which can be explained with its higher molecular mass. The presented clearing temperatures (Figure 5) decrease of about 10 °C when 5 wt% CBC initiator is added to the mixtures. This result shows directly a limitation of the new ortho-substituted azochromophores: they show a nice photochemistry, but are very limited in the amount, which can be added to the LC mixture.

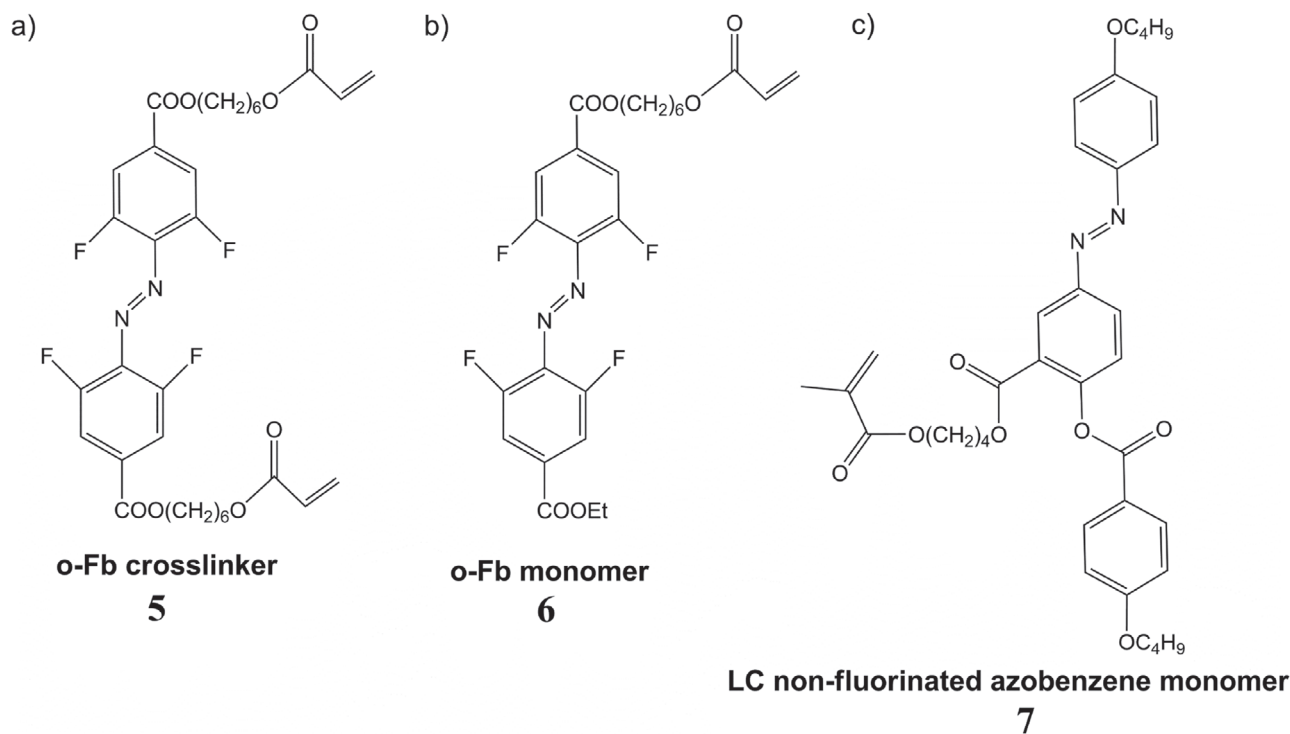


Figure 4. Chemical structures of a) o-Fb crosslinker **5**, b) o-Fb monomer **6**, and c) LC non-fluorinated azobenzene monomer **7** that were used to replace LC monomer or crosslinker of the mixture shown in Figure 1 to analyze clearing temperatures.

2.4. Decrease of Clearing Temperatures of o-Fb Monomer and Crosslinker Containing Liquid Crystalline Systems through Irradiation with Red Light

Liquid crystalline to isotropic phase transitions of described mixtures resulting from switching between trans and cis state were analyzed.

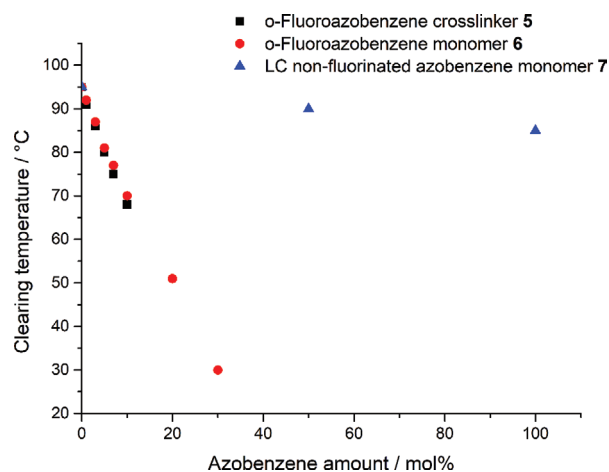


Figure 5. Clearing temperatures of mixtures containing the LC monomer (4'-acryloyloxybutyl 2,5-(4'-butyloxybenzoyloxy)benzoate) and the LC crosslinker (2-methyl-1,4-phenylene bis(4-((6-(acryloyloxy) hexyl)oxy) benzoate)) shown in Figure 1 in dependence of their amounts of o-Fb crosslinker **5**, o-Fb monomer **6**, or an LC non-fluorinated azobenzene monomer **7** (molar ratio of monomer/crosslinker is kept at 90/10).

Therefore, LCE formulations were heated slightly below their clearing temperatures (see Figure 5) and irradiated with red light to transform o-Fbs from their trans form to their cis form. A slow disappearance of the LC phases was observed within 8 min proving that phase transitions take place through visible light irradiation. When mixtures were left in the dark or irradiated with a cold white light source, thermal or light-induced reversion took place and thus a return of birefringence could be observed. An example of a mixture containing 5 mol% o-Fb monomer at 80 °C is shown in Figure 6.

The microscope pictures show that a decrease of clearing temperature takes place as a result of trans → cis isomerization. Thus, we analyzed the differences of clearing temperatures between trans and cis state of the o-Fbs **5** and **6** in dependence of their concentrations in the mixtures. Again, mixtures with LC non-fluorinated azobenzene monomer **7** were also analyzed as a reference system. Results are shown in Figure 7.

Since o-Fb monomer and crosslinker did not show any differences (up to 10 mol%) in this study, we just show the data of the o-Fb monomer. In general, increasing the amount of azobenzene compound results in a stronger decrease of clearing temperatures during trans → cis isomerization when irradiated with red light (for o-Fb monomer **6**) or UV light (for the non-fluorinated reference system **7**). This is due to the higher amount of azobenzene groups in their cis state which disturb the LC phase. Data for 30 mol% or higher o-Fb monomer concentrations could not be obtained since clearing temperatures of the mixtures in their cis states were already below room temperature.

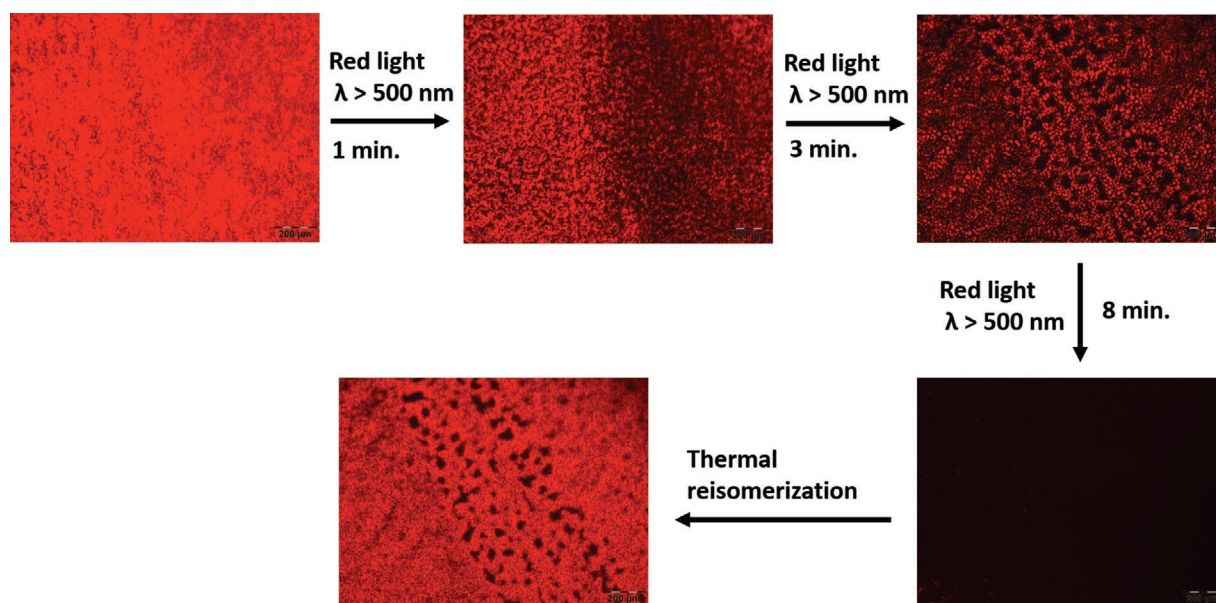


Figure 6. Polarized optical microscopy images of a mixture containing the LC monomer 4'-acryloyloxybutyl 2,5-(4'-butyloxybenzoyloxy)benzoate (85 mol%), the LC crosslinker 2-methyl-1,4-phenylene bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate) (10 mol%) and the o-Fb monomer **6** (5 mol%). The mixture was heated slightly below clearing temperature (80 °C) and was irradiated with red light. Within 8 min the LC phase disappeared completely. After leaving the mixture 40 min in the dark, thermal back-isomerization was observed (scale bar: 200 μ m).

Another effect which can be seen is that the decrease caused by o-Fb **6** is much lower in comparison to the non-fluorinated azobenzene monomer **7**. Additionally, the decrease of the clearing temperature is almost linear in all mixtures up to 20 mol%, except for an amount of 50 mol% for the reference system **7** where it gets lower.

We think that the reason for the different effects on clearing temperatures lies in the non-liquid crystallinity of o-Fb **6**. Compound **7** transforms during isomerization from a mesogenic

to a strongly non-mesogenic structure. On the contrary, o-Fb **6** disturbs the liquid crystalline phases anyhow, both in the trans and cis form. Thus, the effect of isomerization gets smaller. Since irradiation with white light caused a rapid reappearance of the LC phase of the samples containing o-Fbs (Figure 6) and since no decrease of birefringence could be observed, photo-thermal effects should be insignificant (see also LCE actuations below).

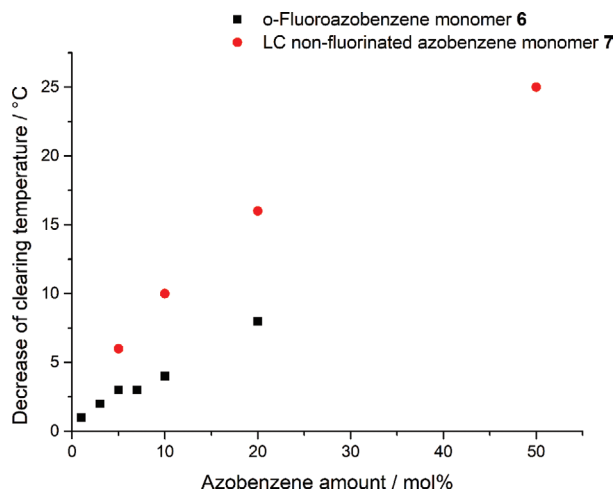


Figure 7. Decrease of clearing temperatures of mixtures containing the LC monomer 4'-acryloyloxybutyl 2,5-(4'-butyloxybenzoyloxy)benzoate and the LC crosslinker 2-methyl-1,4-phenylene bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate) shown in Figure 1 in dependence of their amounts of the o-Fb monomer **6** or the LC non-fluorinated azobenzene monomer **7** in mol% (molar ratio of monomer/crosslinker is kept at 90/10).

2.5. Synthesis of Azobenzene Containing LCEs

Formulations of LC monomer (Figure 1), LC crosslinker (Figure 1), and different amounts of o-Fbs **5** or **6** were mixed with 5 w% photoinitiator CBC which was synthesized in situ (see Section 4). The mixtures were heated to 110 °C into the isotropic phase between two glass plates separated with a 50 μ m spacer foil in a magnetic field and cooled down slowly to 55 °C into the nematic phase to align mesogens.^[30] Afterward, they were polymerized through light irradiation for 10 min on each side of the films.

LCEs containing the reference azobenzene monomer **7** were synthesized in every composition. On the other hand, LCE films containing more than 10 mol% o-Fb monomer **6** or crosslinker **5** were neglected due to the negative effect on alignment and thus actuation properties (see the next section). Since o-Fbs not only strongly absorb light in the UV region, but also in the visible range of spectrum—and thus slightly disturb initiation of CBC—polymerization and crosslinking times increased with increasing amount of o-Fbs. These longer reaction times in comparison with the LC non-fluorinated azobenzene monomer **7**, for which photoinitiation with CBC works well, made the synthesis of particles with our microfluidic setup impossible

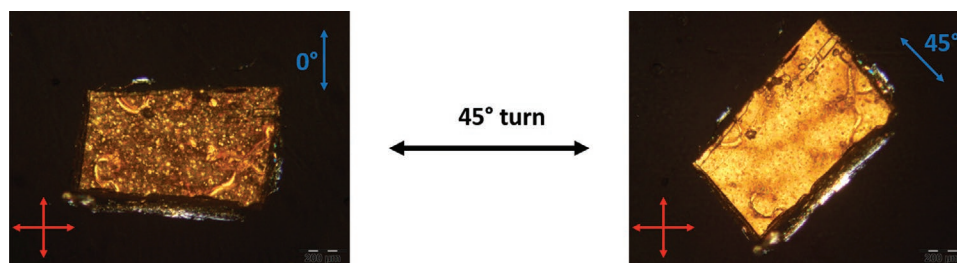


Figure 8. Polarized optical microscope images of an LCE containing o-Fb monomer **6** (5 mol%). The alignment is proven through turning the sample from 0 to 45° with regard to the crossed polarizers showing a dark and a bright state. The red arrows indicate the positions of the crossed polarizers and the blue arrows indicate the director's alignment (scale bar: 200 μ m).

since particles in microfluidic flow cannot be irradiated for 20 min. In contrast, the reference system just had very short reaction times and microfluidic particles could be synthesized without any problems as described previously.^[23,52] Alignment of the films was proven with polarized optical microscopy showing a dark and a bright state if the director lies parallel or at a 45° angle regarding to the crossed polarizers (**Figure 8**).

2.6. Investigation of Thermal and Photochemical Actuation Properties of LCEs Containing o-Fbs

Thermal and photochemical actuation properties of LCEs containing synthesized o-Fb monomer **6** and crosslinker **5** were investigated. To observe thermal actuations, films were heated from 30 to 130 °C and reversible actuations were measured optically (with a microscope) within 5 °C temperature intervals. In this way, the clearing temperatures were determined, for which the order parameter and thereby the length decreases strongest with increasing temperature. For photoactuations, all films were irradiated 5 °C below their clearing temperatures with red light (>500 nm but mainly red light, see absorption spectrum of the red light filter in Figure S3, Supporting Information) for 8 min to obtain maximal visible light actuations. Same was done with LCEs containing the non-fluorinated azobenzene reference monomer **7**, but using UV light. Values for o-Fb monomer **6** containing LCEs are shown in **Table 1**. Actuations are defined as the difference of the film length before and after actuation divided by the shorter length (always the dimension in which the film length decreases during heating or light irradiation has been regarded).

The thermal actuation of the LCE without azochromophore (first line of Table 1) is in the same range as observed for similar systems.^[26,30,33] The maximal thermal actuation decreases then, at first, slightly with increasing azobenzene component up to 5 mol%. When increasing the azobenzene content further to 7 and 10 mol% the thermal actuations decrease drastically. As mentioned above, the o-Fb monomer **6** is not liquid crystalline and disturbs the LC phase (lowers the clearing temperature). Since the polymerization was performed at 55 °C for all samples it gets thus very close to the clearing temperature of the samples with higher o-Fb **6** amount (about 60 °C with initiator). Thus, the order parameter and the backbone anisotropy of the polymer chains during crosslinking decrease and consequently the magnitude of actuation decreases with increasing o-Fb content.

Concerning photoactuation, the situation is more complex. At first, it increases up to a o-Fb monomer **6** content of 5 mol%. This is due to the stronger effect of the trans $\rightarrow$ cis isomerization on the LC order with increasing concentrations. However, it then decreases drastically for LCEs containing 7 and 10 mol% o-Fb monomer. This has presumably the same reasons as described for the thermal actuations. Overall, it should be mentioned that the extent of photoactuation is rather low compared to other azobenzene containing chromophores. This is a result of the combined effect of the i) limited amount of o-Fb, which can be incorporated due to the destruction of the LC phase and ii) smaller effect of photoisomerization of **5** and **6** on the clearing temperature (see Figure 7). As described in the previous section, the integration of a higher o-Fb amount would not be useful since further disturbance of alignment would result in further decrease of actuation properties.

Examples of thermal and photochemical actuations of a film containing 5 mol% o-Fb monomer are shown in **Figure 9**.

Photochemical actuation with red light is completed after 8 min. Thermal back-actuation in the dark lasts about 40 min and can be accelerated to 2 min through irradiation with a cold white light source that causes back-isomerization of o-Fbs to their trans form. It was shown that non-fluorinated azobenzene monomer **7** containing counterparts need about 16 min for back-isomerization. This might be because the cis state of o-Fbs is more stable as reported previously and thus needs more time for back-isomerization.^[23,57]

Table 1. Measured thermal actuations and photoactuations of LCE films consisting of an LC monomer (4'-acryloyloxybutyl 2,5-(4'-butyloxybenzoyloxy)benzoate), an LC crosslinker (2-methyl-1,4-phenylene bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate)), and a photoinitiator (CBC) in dependence of their amount of integrated fluorinated o-Fb monomer **6**. Temperatures of LCE films during light irradiation are shown in the right column.

Amount of o-Fb monomer [mol%]	Thermal actuation [%]	Photoactuation [%]	Temperature during photoactuation [°C]
0	34.6	0	115
1	32.0	3.2	115
3	28.9	5.8	105
5	28.0	13.2	95
7	11.0	3.7	85
10	7.5	2.4	75

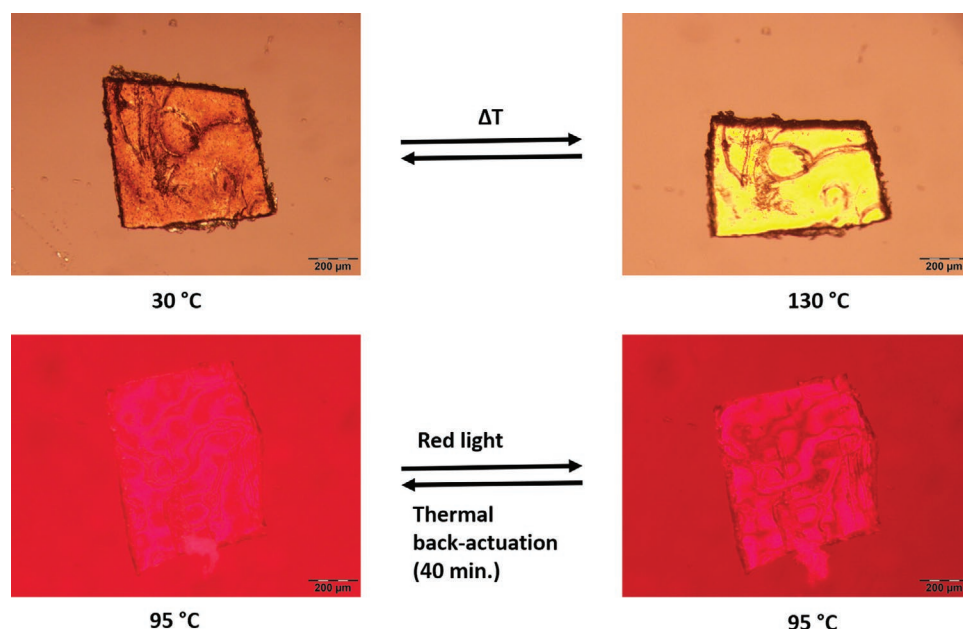


Figure 9. Reversible thermal actuation between 30 and 130 °C and photoactuation with red light as well as thermal back-actuation at 95 °C of a LCE film synthesized at 55 °C out of an LC monomer (4'-acryloyloxybutyl 2,5-(4'-butyloxybenzoyloxy)benzoate), an LC crosslinker (2-methyl-1,4-phenylene bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate)), and a photoinitiator (CBC) containing 5 mol% o-Fb monomer **6** (scale bar: 200 μm).

Data for LCEs containing the o-Fb crosslinker **5** are shown in **Table 2**.

The effect of the fluorinated o-Fb crosslinker **5** on LCE actuations (**Table 2**) is generally comparable to the effect of the fluorinated o-Fb monomer **6** (**Table 1**) with the difference that thermal actuation gets more strongly reduced already at low concentrations (3 and 5 mol%). The reason for this is not clear. It might be that the o-Fb crosslinker reduces the mobility of the system and thus the actuation at the phase transition to the isotropic phase. The lower photochemical actuation is then a natural consequence.

Maximum photoactuations are observed for LCEs containing 7 mol% o-Fb crosslinker. Again, the increase of photoactuation with higher concentrations in the beginning can be explained because the higher amount of fluorinated azobenzene groups

leads to a higher cis concentration after light irradiation which results in a stronger disturbance of the LC phase. The decrease at 10 mol% relates to the decrease of thermal actuation with increasing amount of azobenzene component.

Films containing different amounts of LC non-fluorinated azobenzene monomer **7** were synthesized for comparisons. In contrast to the o-Fb systems, they all showed thermal actuations between 35% and 40%. As shown before, the LC azobenzene reference monomer does not disturb the LC phase drastically. Reversible photoactuations through UV light increased from 0% to 30% with increasing azobenzene content (0–90 mol%) showing the increased influence of azobenzene cis concentrations on LC phase destruction.

To exclude the fact that photothermal effects caused by absorption and dissipation of light (i.e., temperature increase) contribute significantly to actuation, we irradiated the LCE films with and without the red light filter. That is, we applied the whole spectrum (broad band irradiation with “white” light, see Supporting Information; this irradiation induces a cis–trans isomerization.) or only the red part of it (it induces the trans–cis isomerization). The distance between the samples and the light source were kept constant. Regarding LCEs containing o-Fbs, the presented actuations were observed exclusively by irradiation with red light (>500 nm). However, no significant actuations were measured by irradiation with white light (no red light filter) although this light contains also the red part of the spectrum leading to, at least, the same amount of absorbed light. Thus irradiation with white light should lead to the same amount of dissipated light energy and the same temperature increase.

Additionally, complete photochemical back-actuations were realized using irradiation with white light. It would be incomplete in the case of significant photothermal effects. Thus,

Table 2. Measured thermal actuations and photoactuations of LCE films consisting of an LC monomer (4'-acryloyloxybutyl 2,5-(4'-butyloxybenzoyloxy)benzoate), an LC crosslinker (2-methyl-1,4-phenylene bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate)), and a photoinitiator (CBC) in dependence of their amount of integrated fluorinated o-Fb crosslinker **5**. Temperatures of LCE films during light irradiation are shown in the right column.

Amount of o-Fb monomer [mol%]	Thermal actuation [%]	Photoactuation [%]	Temperature during photoactuation [°C]
0	34.6	0.0	115
1	31.0	2.7	115
3	17.3	3.1	105
5	12.0	5.8	95
7	11.1	6.0	85
10	7.6	2.0	75

it can be concluded that there is no significant photothermal effect in the sample under the applied conditions (no lasers, but lower intensity LEDs as light source).

3. Conclusion

The results of our studies give new insights into the actuation properties of o-Fb containing LCEs and the effects of o-Fbs on LC phase stabilities.

We show synthetic routes to synthesize an o-Fb crosslinker and monomer with good yields that are integrated in LCEs up to 10 mol%.

Due to their non-liquid crystallinity, they disturb the stability of the liquid crystalline phases with increasing amount and thus lower their clearing temperatures. Therefore, they cannot be integrated at high concentration into LCEs to increase the magnitude of actuations with increasing amount.

The resulting LCEs show 2D (planar, no bending) photoactuations up to 13.2% triggered with visible light. This is to the best of our knowledge the only and highest pure 2D shrinkage and elongation photoactuation of visible light-triggered LCEs containing $n \rightarrow \pi^*$ band separated azobenzenes.

Maximum photoactuations are found for LCEs containing 5 mol% o-Fb monomer or 7 mol% o-Fb crosslinker. These LCEs show the best compromise between a maximum effect of lowering the LC order through trans $\rightarrow$ cis isomerization of o-Fbs through light irradiation and thus actuation and a decrease of order through non-liquid crystalline o-Fbs which hamper thermal and consequently photoactuations in general.

A "classical" (not ortho-disubstituted) LC azobenzene monomer is integrated in LCEs as a reference system to study the impact of liquid crystallinity. Here, of course, maximal actuation can be made much bigger by increasing the amount of azobenzene since it does not disturb the liquid crystalline order. Thus, it shows that, while the favorable photochemistry can be achieved in o-FBs, they are less effective for photoswitching of the LC phase, because i) less o-FBs can be integrated without destroying the LC phase and ii) the trans $\rightarrow$ cis isomerization is less effective in destroying the LC phase. We deduce that the choice of system depends on the application and how far near UV light (360 nm) has to be excluded.

Our LCEs containing o-Fbs are attractive for applications where 2D photoactuations by avoidance of UV light are desired. They enable and facilitate, for example, the practical use in biological systems and materials sciences where UV light potentially disturb the surroundings of actuators.

4. Experimental Section

Materials and Reagents: Ethyl 4-amino-3,5-difluorobenzoate,^[51] the liquid crystalline monomer 4'-acryloyloxybutyl-2,5-(4'-butoxybenzoyloxy) benzoate,^[35] the liquid crystalline azomonomer (4-butoxy-2'-(4-methacryloyloxybutoxy)-4'-(4-butoxybenzoyloxy) azobenzene),^[67] the liquid crystalline crosslinker 2-methyl-1,4-phenylene bis(4-((6-(acryloyloxy) hexyl)oxy)benzoate),^[68] the dye for the initiator (1,3,3',3'-hexamethyl-11-chloro-10,12-propylene-tricarbocyanine iodide),^[64] and tert-butyl hypochlorite^[69] were synthesized as described in the literature.

Butyryl choline butyltriphenylborate (Borat V) was purchased from Spectra group limited.

Sodium iodide was purchased from Alfa Aesar. Diethyl ether, chloroform, dichloromethane, cyclohexane, tetrahydrofuran, sodium sulfate, sodium thiosulfate, sodium bicarbonate, acryloyl chloride, and silicon oil (1000 cSt) were purchased from Sigma-Aldrich. 1,6-Hexanediol and p-toluenesulfonic acid (monohydrate) were purchased from Acros Organics. Triethylamine and sodium chloride were purchased from Merck.

Synthesis of Diethyl-4,4'-(2,2',6,6'-Tetrafluoro)Azobenzene Dicarboxylate (2): Ethyl 4-amino-3,5-difluorobenzoate (6.0 g, 30 mmol) and sodium iodide (9.2 g, 60 mmol) were dissolved in 200 mL diethyl ether. Tert-butyl hypochlorite (7 mL, 60 mmol) was added at room temperature under argon atmosphere. The mixture was stirred for 4 h, quenched with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (1 M, 600 mL) and extracted with dichloromethane (4 $\times$ 600 mL). Organic extracts were dried over sodium sulfate and removed under reduced pressure to yield the crude product that was purified by column chromatography (eluent: cyclohexane/diethyl acetate 9:1). The pure product was obtained as an orange solid (4.2 g, 11 mmol, 71%). ¹H-NMR (300 MHz, CDCl_3) (E-isomer/Z-isomer): δ 7.78/7.53 (m, 4H), δ 4.43/4.36 (q, 4H), δ 1.43/1.37 (t, 6H).

Synthesis of Mono- and Disubstituted Transesterification Products (3 and 4): Diethyl-4,4'-(2,2',6,6'-tetrafluoro)azobenzene dicarboxylate (0.73 g, 1.8 mmol), 1,6-hexanediol (0.85 g, 7.2 mmol) and p-toulene sulfonic acid monohydrate (0.80 g, 4.2 mmol) were dissolved in 20 mL chloroform and heated under reflux for 48 h. The solution was then cooled to room temperature, washed with water, saturated aqueous sodium bicarbonate, and water. Chloroform was removed and the mixture of products was purified by column chromatography (eluent: cyclohexane/ethyl acetate 1:1). Monosubstituted transesterification product 4 (0.29 g, 0.6 mmol, yield: 34%) and disubstituted transesterification product 3 (0.29 g, 0.5 mmol, yield: 29%) were obtained as orange/red solids. A part of diethyl-4,4'-(2,2',6,6'-tetrafluoro)azobenzene dicarboxylate (0.15 g, 0.4 mmol, yield: 21%) was reobtained as an orange solid. ¹H-NMR (disubstituted transesterification product 3) (300 MHz, CDCl_3): δ 7.75 (m, 4H), δ 4.37 (t, 4H), δ 3.67 (t, 4H), δ 1.93–1.67 (m, 4H), δ 1.67–1.31 (m, 12H); ¹H-NMR (monosubstituted transesterification product 4) (300 MHz, CDCl_3): δ 7.75 (m, 4H), δ 4.40 (m, 4H), δ 3.67 (t, 2H), δ 1.93–1.72 (m, 2H), δ 1.70–1.54 (m, 2H), δ 1.54–1.36 (m, 7H).

Synthesis of o-Fb Crosslinker (5): Disubstituted transesterification product 3 (0.25 g, 0.5 mmol) was dissolved in 5 mL dry THF in a Schlenk flask. An excess of triethylamine (0.45 mL, 3.3 mmol) was added and the mixture was stirred for 20 min at 0 °C. Afterward, acryloyl chloride (0.1 mL, 1.0 mmol) was added slowly and the solution was stirred at room temperature overnight. THF was evaporated and dichloromethane was added. The organic solution was washed with saturated sodium bicarbonate solution and sodium chloride solution three times each. The organic layer was dried over anhydrous sodium sulfate and dichloromethane was evaporated. The crude product was purified by column chromatography (eluent: cyclohexane/ethyl acetate 9:1) to obtain the product as an orange/red solid (0.17 g, 0.3 mmol, yield: 57%). ¹H-NMR (300 MHz, CDCl_3) (E-isomer/Z-isomer): δ 7.78–7.48 (m, 4H), δ 6.41 (m, 2H), δ 6.12 (m, 2H), δ 5.81 (m, 2H), δ 4.37 (t, 4H), δ 4.18 (t, 4H), δ 1.90–1.60 (m, 8H), δ 1.60–1.35 (m, 8H).

Synthesis of o-Fb Crosslinker (6): Disubstituted transesterification product 4 (0.25 g, 0.5 mmol) was dissolved in 5 mL dry THF in a Schlenk flask. An excess of triethylamine (0.45 mL, 3.3 mmol) was added and the mixture was stirred for 20 min at 0 °C. Afterward, acryloyl chloride (0.5 mL, 0.5 mmol) was added slowly and the solution was stirred at room temperature overnight. THF was evaporated and dichloromethane was added. The organic solution was washed with saturated sodium bicarbonate solution and sodium chloride solution three times each. The organic layer was dried over anhydrous sodium sulfate and dichloromethane was evaporated. The crude product was purified by column chromatography (eluent: cyclohexane/ethyl acetate 9:1) to obtain the product as an orange/red solid (0.14 g, 0.3 mmol, yield: 52%). ¹H-NMR (300 MHz, CDCl_3) (E-isomer/Z-isomer): δ 7.78–7.48 (m, 4H), δ 6.41 (m, 1H), δ 6.12 (m, 1H), δ 5.81 (m, 1H), δ 4.40 (m, 4H), δ 4.18 (t, 2H), δ 1.90–1.60 (m, 4H), δ 1.60–1.35 (m, 7H).

Analysis of the o-Fb Monomer and Crosslinker: Synthesized o-Fb monomer and crosslinker were analyzed in chloroform with UV/vis spectroscopy using a Jasco spectrophotometer V-630. The solutions were irradiated with light of different wavelengths for desired times before measurements took place. ¹H-NMRs were measured using a 300 MHz spectrometer (model: Avance III HD 300) from Bruker.

Preparation of Films: Desired amounts of liquid crystalline monomer (4'-acryloyloxybutyl 2,5-(4'-butyloxybenzoyloxy)benzoate), liquid crystalline crosslinker (2-methyl-1,4-phenylene bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate)) and the particular azobenzene compound were dissolved in tetrahydrofuran. A monomer amount of 90 mol% and a crosslinker amount of 10 mol% were kept constant. 1.6 w% 1,3,3',3'-hexamethyl-11-chloro-10,12-propylene-tricarbo-cyanine iodide and 3.4 w% Borate V (w% referred to the monomer/crosslinker mixture) were added to synthesize 1,3,3',3'-hexamethyl-11-chloro-10,12-propylene-tricarbo-cyanine triphenylbutyl borate in situ. The mixture was heated to 110 °C on a glass slide with a precision hot plate which was purchased from Harry Gerstig GmbH in a magnetic field (generated by a horse-shoe magnet, $B > 100$ mT). A second glass slide was placed on top of the first one whereas a spacer foil kept them separated. The mixture was cooled down to 55 °C within 40 min and irradiated with a red light HighPower LED (623 nm), which was purchased from Conrad for 10 min on each side. Afterward, photopolymerized and crosslinked LCE films were removed and cut into small stripes of a couple of hundred micrometers for analysis.

Analysis of LCE Film Actuations: Actuation properties were analyzed with a (polarized optical) microscope (microscope model: Olympus BX51 from Olympus).

To investigate the thermal behavior, LCE pieces were heated to the desired temperature with a microscope hot stage (model: Linkam TMS 94). Images were taken using a microscope camera (model: Olympus DP22) and lengths of films were measured using microscope imaging software (Olympus cellSens Standard).

Light-induced actuations were analyzed with the same equipment. Films were heated to the desired temperature and irradiated with the light beam of a cold white light source KL1600 from Schott (spectrum is shown in Figure S13, Supporting Information) without or in combination with a red light filter (OG 590 Schott, the absorption spectrum is shown in Figure S14, Supporting Information) which was held in the light beam. Back-actuations of o-Fb containing LCEs were achieved through irradiation with the same cold white light source but without using the filter or by leaving the films in the dark for 40 min.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

liquid crystalline elastomers, liquid crystalline phase stabilities, ortho-fluorinated azobenzenes, soft actuators, visible light-triggered actuations

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