Light-induced disorder in liquid-crystalline elastomers for actuation

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ABSTRACT

Liquid-Crystalline Elastomers (LCEs) are materials which combine the entropic properties of a crosslinked polymer melt with the enthalpic properties of a liquid-crystalline state of order. LCEs show unique characteristics: visco-elasticity and order at the same time in one system. The elastic and the viscous properties come from the crosslinking and friction of the polymer chains, respectively, while the orientation comes from the mesophase which keeps the polymer backbone aligned. LCEs behave as normal polymer networks or rubbers when no energy-storing mesophase is present. This state of disorder can be induced by means of temperature or light. Thermally, the change in shape of LCEs can easily reach 300% when all the enthalpy stored by the mesophase is released and the crosslinked polymer chains are free to move and adopt a random coil conformation. The light-induced local disorder can be achieved when shape-changing molecules are incorporated in the LCE matrix. These compounds are able to absorb light, rearrange themselves in a new shape and subsequently disturbing the mesophase. This results in the molecules that are keeping the order no longer being able to sustain the retractive force of the polymer backbone, and the material contracts, exerting an actuating force. But how does a light sensitive side-chain LCE elastomer behave? And a main-chain LCE? What about nematics or smectics? Is a different kind of actuation, besides the common retractive force, possible? To answer these questions, new chemistry needs to be developed, together with new physics to understand the systems, and new applications need to be created.

Keywords: liquid-crystalline elastomer, nematic, smectic, photo-isomerization, mechanical actuation, azobenzene

1. INTRODUCTION

Liquid-crystalline elastomers (LCEs) combine the order characteristics of the liquid crystals and the physical properties of polymer networks.[1] When the domains of a LCE are oriented along one preferred direction (monodomain), the global order couples to the macroscopic dimensions of the system.[2] Thus, any induced local disorder can cause a drastic change in shape of a whole sample.

Side-chain liquid-crystalline elastomers (SCLCEs) consist of long chains of crosslinked polymers and small rod-like molecules with liquid-crystalline properties attached to the polymer backbone through a spacer.[3] Main-chain liquid-crystalline elastomers (MCLCEs) differ from the previous systems by their incorporation of the rod-like molecules to the polymer backbone,[4] and both the spacer and the rod belong to the chain.
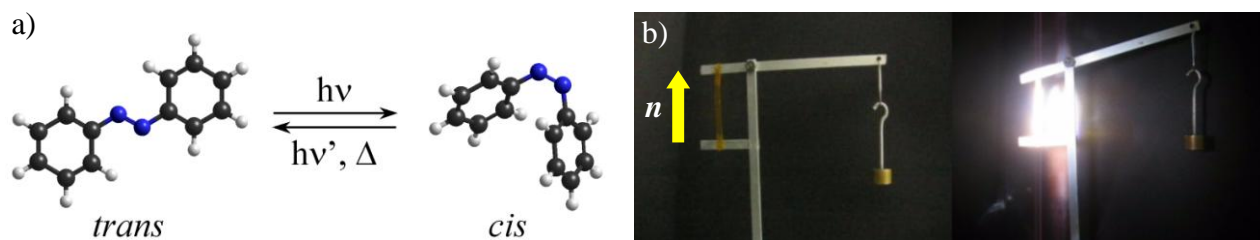

Figure 1. a) Azobenzene isomerization process: light induced *trans*-to-*cis* photo-isomerization (hν), and light or thermally induced *cis*-to-*trans* photo- (hν') or thermal-isomerization (Δ). b) Change in length of a liquid-crystalline elastomer containing photoactive azobenzene molecules after and before irradiation. (Note: movies and pictures can be downloaded from http://www.macromolchem.com)

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Light is a clean and non invasive way of transmitting energy. If some photoactive molecules are covalently bonded to the liquid-crystalline network and light falls on them, photons are absorbed by the dye molecule. Then, a photo-isomerization process takes place. Azobenzene molecules can undergo a transformation from their more stable *trans*-isomer to the *cis*-isomer (Figure 1a). This change in shape of the photoactive molecule induces disorder either by disturbing the liquid-crystalline phase[5-9] or by bringing closer the polymer backbones.[5,8,9] The result is the contraction of the extended polymer backbones of the photoactive LCE along the director *n* (Figure 1b).
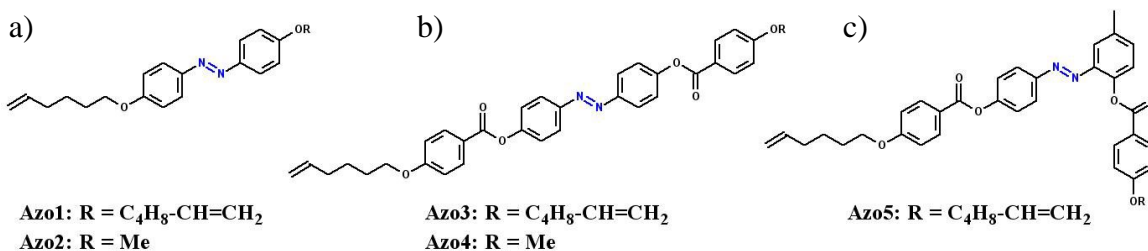
This work shows the opto-mechanical response of different LCEs that contain azobenzene molecules with different connectivity (pendant group, crosslinker or co-monomer) and architecture (length or symmetry), as well as their effect in different systems (side-chain or main-chain) and mesophases (nematic or smectic). By varying all these parameters, switchers and actuators can be designed and their properties tuned.

2. EXPERIMENTAL PART

2.1. Synthesis. The synthesis and characterization of all azobenzene derivates,[9,10] the isotropic crosslinker and all side-chain and main-chain mesogens are already described in the literature.[3,11-15]

Scheme 1 shows the chemical structures of the five azobenzene derivatives studied in this work. Three of them have two vinyl groups - Azo1, Azo3 and Azo5 -, which allow the use of the azoderivatives as crosslinkers in side-chain systems, or as co-monomers in main-chain networks. The other two azobenzene molecules contain only one terminal double bound - Azo2 and Azo4 -, and these compounds can only be used in side-chain elastomers as pendant groups.

Their architecture varies as follows: the azoderivates Azo1 and Azo2 are shorter (two aromatic rings) than the other three compounds Azo3, Azo4 and Azo5 (four aromatic rings). Finally, Azo5 is an asymmetric molecule, and this can induce opposite effects under irradiation with respect to the other four molecules when attached to the LCE.

a)
b)
c)

Azo1: R = C$_4$H$_8$-CH=CH$_2$
Azo2: R = Me

Azo3: R = C$_4$H$_8$-CH=CH$_2$
Azo4: R = Me

Azo5: R = C$_4$H$_8$-CH=CH$_2$

Scheme 1. Chemical structures of the azobenzene molecules: a) two aromatic rings molecule as a crosslinker (Azo1) or pendant group (Azo2), b) four aromatic rings molecule as a crosslinker (Azo3) or pendant group (Azo4), and four asymmetric aromatic rings molecule as a crosslinker (Azo5).

The synthesis of all LCEs was done by the two step crosslinking process developed by Finkelmann *et al.*[11,12] with minor modifications depending on whether a side- or main-chain system was obtained.[9,14,15] In a 5 mL flask, the corresponding mesogen and isotropic crosslinker, the azobenzene derivative (5 mol-%), and the reactive polymer backbone for SCLCEs or the chain extender for MCLCEs were placed. To this mixture, 1 mL of tiophene-free toluene and 20 μL of 1 %-Pt cyclooctadieneplatinum(II) chloride, Pt(COD)Cl$_2$, in dichloromethane were added. The mixture was placed in the spinning Teflon cell form which was spin casted and heated at 60 °C for 1 h 45 min (SCLCEs) or 4 h (MCLCEs) at 5000 rpm. Afterwards, the reactor was cooled and the elastomer was removed from the wall. Some loads were applied in order to align the elastomer and to obtain a monodomain sample during the deswelling process. In this first step the elastomer was not totally crosslinked. In order to fix this orientation, the crosslinking reaction was completed by leaving the elastomer in the oven under vacuum at 60 °C for 2 days. Figure 2 shows the chemical structures of all components for the obtaining of SCLCEs[9] and MCLCEs.[14,15]

In the synthesis of all SCLCEs, the concentration of the azoderivative (5.6 mol-%) and the total crosslinking density (11.1 mol-%) were kept constant. In this way, five nematic SCLCEs have been synthesized, where two of them have a short azoderivative (SCEAzo1 and SCEAzo2), two more have a long azobenzene compound (SCEAzo3 and SCEAzo4), and the last one has the asymmetric photoactive molecule (SCEAzo5). The samples SCEAzo2 and SCEAzo4 have the azo dye as a pendant group, while the rest of elastomers as a crosslinker.

In the synthesis of all MCLCEs, a flexible crosslinker with 5 reacting groups was used for preparing samples with 10, 5 and 2.5 mol-% of crosslinker. Then, for samples with 10, 5 and 2.5 mol-%, the number of mesogens on average in the polymer chains (degree of polymerization) would be 4, 8 and 16 respectively. The azoderivative and its concentration (5.0 mol-%) were the same for all the main-chain systems. Thus, three main-chain elastomers have been obtained where two of them are nematic (MCEAzo1-10 and MCEAzo1-2.5) and the other one smectic (MCEAzo1-5).
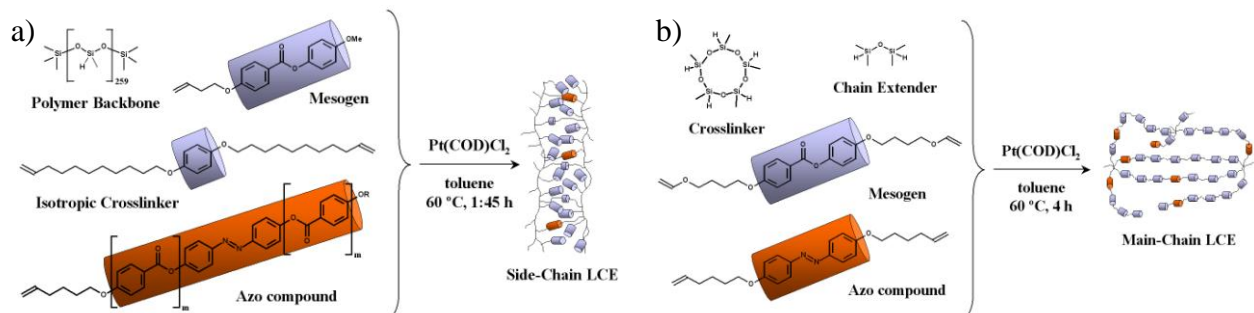
Scheme 2. a) Chemical structures of the isotropic crosslinker, polymer backbone, azobenzene molecule, and side chain mesogen for the obtaining of side-chain LCEs. b) Chemical structures of the flexible cyclic crosslinker, chain extender, azobenzene molecule, and main-chain mesogen for the obtaining of main-chain LCEs.

All the mesophases were determined by X-ray pattern, themoelastic behavior and differential scanning calorimetry experiments. Properties and characteristics of the eight LCEs are summarized in Table 1.

Table 1. Characteristics and properties for the SCLCEs and MCLCEs: mesophase, azobenzene type of molecule, irradiation wavelength (λ_{irr}), glass transition temperature (T_g), clearing temperature (T_c), and change in length (ΔL).

Sample	Mesophase	Azobenzene*	λ_{irr} (nm)	T_g (ºC)	T_c (ºC)	ΔL (%)
SCEAzo1	nematic	2R-S-C	380	-2	82	63
SCEAzo2	nematic	2R-S-P	380	-4	70	62
SCEAzo3	nematic	4R-S-C	360	8	107	58
SCEAzo4	nematic	4R-S-P	360	-2	82	67
SCEAzo5	nematic	4R-A-C	360	-3	80	17
MCEAzo1-10	nematic	2R-S-CM	380	-11	48	79
MCEAzo1-5	smectic	2R-S-CM	380	-7	51	227
MCEAzo1-2.5	nematic	2R-S-CM	380	-8	55	109

* 2R = two aromatic rings, 4R = four aromatic rings, S = symmetric, A = asymmetric, C = crosslinker, P = pendant, CM = co-monomer.

2.2. Measurements. Opto-mechanical measurements were performed with a self-constructed apparatus designed to measure the retroactive force as function of time under irradiation, or the relaxation process in the darkness. In a thermostated cell controlled by a Haake-F6 thermostat and a Pt100 thermoresistor, the sample was stretched by one Owis SM400 microstep motor and controlled by an Owis LSTEP-12 56.202.0000 microstep controller. The stress (σ) was measured by a Transducer Techniques GS0-10 transducer load cell (10 g) and analyzed by a Newport Electronics INFS-1001-DC7 high performance strain gage indicator. All relevant data such as temperature, time and stress (σ) were continuously logged and controlled by National Instrumets LabView 7.0 software. The sample was irradiated with UV-light using a Osram XBO150W/1 xenon arc lamp (150 W, 20 V, 7.5 A) that was in a Müller Elektronik-Optik LAX 1530 lamp housing connected to a Müller Elektronik-Optik SVX 1530 power source. To select the right wavelength, a Jobin Yvon H20 UV/Vis/NIR monochromator was used and a Ocean Optics USB2000 UV-Vis spectrophotometer (UV2/OFLV-4 detector, L2 lens, 5 µm slit, 200-850 nm) connected to the thermostated cell by a Ocean Optics P400-2-UV/VIS optical fiber (UV/Vis, 2 m, 400 µm) was attached to the back side of the cell. The temperature of the sample

was checked by using a Eurotherm Controls 2132 PID temperature controller with a 4-20 mA linear thermocouple type Pt100 attached to a parallel piece of the sample. The intensity of the radiation reaching the sample was 312 mW·cm^{-2}, measured by a calibrated Lot-Oriel Ophir-70260-2 radiant power meter with a Lot-Oriel Ophir-70282 Si-detector with PD300-UV head in the range from 250 to 1100 nm, and it was kept constant during the experiments.

3. RESULTS & DISCUSSION

The response of photoactive LCEs that contain azoderivatives as pendant co-monomers or crosslinkers for SCLCEs, and as co-monomers for MCLCEs was studied. An external field was applied in order to establish the effect of the azo dye architecture, its connectivity into the network, the degree of crosslinking of the elastomer and the kind of mesophase obtained. The change in shape of these azo compounds - from the *trans*-isomer (rod-like shape) to the *cis*-isomer (bended-like shape) - induces a local disorder in the domains, which couples to the change in the macroscopic dimensions of the LCE. Thus, the *cis*-isomer acts as an impurity in the liquid-crystalline surroundings. If the azobenzene molecule is a crosslinker (SCLCEs) or co-monomer (MCLCEs), then the photoactive molecule should generate an extra mechanical stress.

The common procedure for opto-mechanical experiments consists of fixing the sample (10 mm × 1 mm × 0.3 mm) at both extremities of the longest dimension along the director. One of the extremities of the sample is attached to the load cell, measuring the retractive force on irradiating, and the relaxation process when the irradiation was stopped. After reaching the set temperature, a pre-load (0.5 g, corresponding to a strain of $\lambda = 1.01$) was applied to the sample to get it well oriented and straight, and the irradiation process was started. Because the sample cannot shrink, a retractive force appears. Thus, every negative change in length when the elastomer is a free standing system should induce an increase in the stress when the sample is fixed from both extremes. This force was measured as function of time until the photo-stationary *cis-trans* equilibrium was reached. On arrival at the steady state, the sample was not irradiated anymore and a relaxation process started.

In this paper we show new opto-mechanical results of photoactive LCEs and the effect of the chemical constitution of the azoderivatives, together with their role in the elastomeric network: mechanical and/or disorder-induced effects. This chapter will describe the opto-mechanical experiments on i) nematic photoactive SCLCEs with symmetric azo compounds, ii) nematic photoactive SCLCEs with asymmetric azo compounds, iii) nematic photoactive MCLCEs, and iv) smectic photoactive MCLCEs.

3.1. Nematic Photoactive SCLCEs (short or long photoactive molecules as crosslinker or pendant group). The four nematic photoactive SCLCEs[9] (SCEAzo1, SCEAzo2, SCEAzo3 and SCEAzo4) containing symmetric azoderivatives (Azo1, Azo2, Azo3 and Azo4) show their corresponding opto-mechanical behavior of the stress ($\Delta\sigma$) as function of time (Figure 2). An exponential growth of the stress towards a photostationary equilibrium state was observed when the samples were irradiated with UV-light. The relaxation process occurred upon stopping the irradiation.
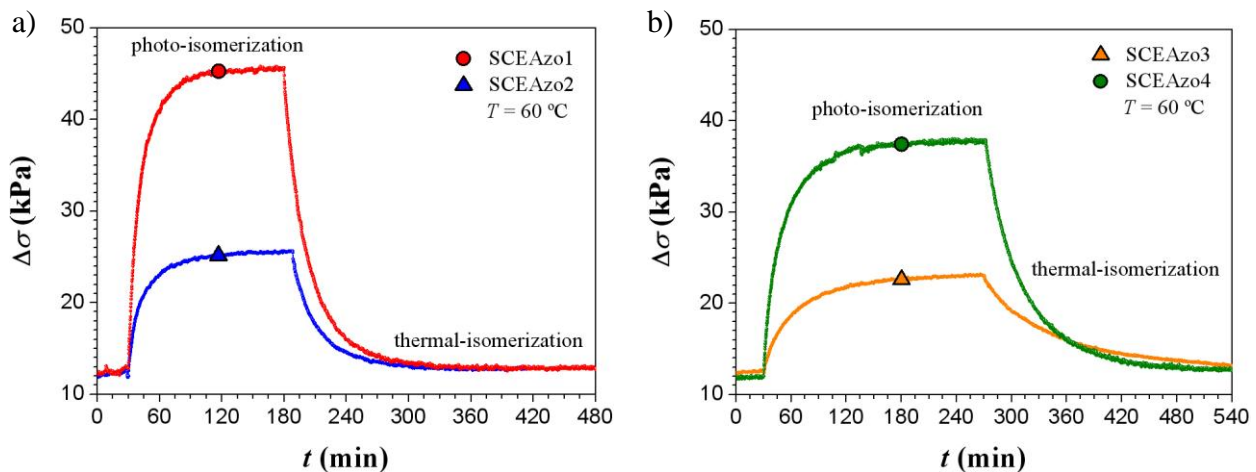

Figure 2. Opto-mechanical experiment on the nematic side-chain liquid-crystalline elastomers at 60 °C: a) SCEAzo1 and SCEAzo2 at $\lambda = 380$ nm, and b) SCEAzo2 and SCEAzo4 at $\lambda = 360$ nm.

Each first part of the curve contains the expression of the equilibrium between the photo- and thermal-isomerization processes, while the second part of the curve only contains the thermal-isomerization process. Two effects can be observed due to chemical constitution and connectivity of the azoderivatives: first, the azobenzene molecules as crosslinkers (Azo1 and Azo3) have a mechanical response of 2.4 to 2.3 times higher in average with respect to the corresponding pendant azobenzene groups (Azo2 and Azo4) at the same temperature. Their light induced stress is 58% due to the crosslinker nature, and 42% due to *cis*-isomer disorder induced shape; second, azobenzene molecules with two aromatic rings are more efficient (24% for pendant groups and 28% for crosslinkers) than four aromatic rings molecules in terms of mechanical response due to their rigidity.

The high mechanical efficiency of the azobenzene compound Azo1 is due to its more restricted movements, compared to the four aromatic rings azobenzene compound Azo3 (free movements from the two esters groups). The azobenzene crosslinkers are not only inducing disorder due to the changing in molecular shape from *trans* to *cis*. They create an extra mechanical response on bringing the polymer chains closer: the so-called cooperative effect.[9]

3.2. Nematic Photoactive SCLCEs (with long asymmetric photoactive molecules as crosslinker). The nematic photoactive SCLCE (Azo5) containing the asymmetric azoderivative (Azo5) shows its corresponding opto-mechanical behavior of the stress ($\Delta\sigma$) as function of time presented in Figure 3a. For this experiment, the sample was stretched after applying a pre-load of 1 g because a relaxation process was expected when irradiating the sample with UV-light. The chemical constitution of this asymmetric azo dye makes the *trans*-isomer as a bended-like shape molecule, and the *cis*-isomer as a rod-like molecule. Thus, the *trans*-isomer should behave as an impurity in this case, destabilizing the nematic phase – decreasing its clearing temperature. The *cis*-isomer is more compatible to the mesophase due to its shape and the clearing temperature should then be higher than when the *trans*-isomer is present.

The first part of the curve in Figure 3a is the equilibrium between both the photo- and thermal-isomerization processes; the second part of the curve is just the thermal-isomerization process. The first part of the opto-mechanical experiment already shows the decrease in the retractive force due to two effects: first, the formation of the *cis*-isomer during the photo-isomerization process leads to a more compatible structure with regards to the rod-like mesogens; second, the asymmetric azobenzene crosslinker expands and this expansion allows elongating the LCE. Both effects are the opposite version of the effects already explained in the previous chapter with the nematic photoactive SCLCEs containing symmetric azobenzene molecules into the network.[9]
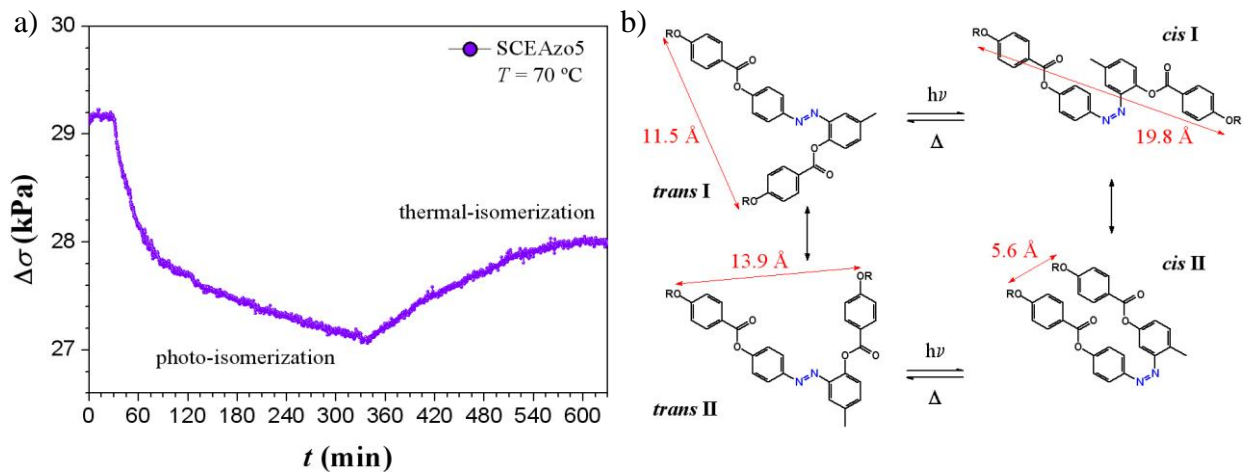

Figure 3. a) Opto-mechanical experiment on the nematic main-chain liquid-crystalline elastomer SCEAzo1 at 70 °C and $\lambda = 360$ nm. b) Chemical structures of the asymmetric azoderivative in the *trans* and *cis* state.

The second part of the opto-mechanical experiment shows an increase in the retractive force due to the re-formation of the *trans*-isomer state. The reason why the original stress value is recovered only by a 45% from the irradiation process might be explained by two factors: first, there are two stable conformations of the *trans*-isomer (*trans* I and *trans* II) with different distances between the extremes of the azobenzene (Figure 3b); second, when irradiating with UV-light the LCE is free to adopt whatever conformation with a more relaxed distribution of the crosslinkers and polymer backbones. Notice that the change in length of the monodomain of this sample is $\Delta L = 17\%$ (lower than the rest of SCLCEs), although its order parameter is $S = 0.61$. This is a clear indication of the effect of such an asymmetric crosslinker.

3.3. Nematic Photoactive MCLCEs. The two nematic photoactive MCLCEs[15] (MCEAzo1-10 and MCEAzo1-2.5) containing the symmetric azoderivative (Azo1) show their corresponding opto-mechanical behavior of the stress ($\Delta\sigma$) as function of time presented in Figure 4. The exponential growth and the exponential decay occurred upon turning on and off the UV-light, respectively.

The MCEAzo1-10 has crosslinking density of 10 mol-% and the MCEAzo1-2.5 of 2.5 mol-%. These crosslinking densities correspond to a degree of polymerization between crosslinking points of 4 and 16 repeating units, respectively. Thus, a strong mechanical actuation should be expected for the higher crosslinked sample.[15] Figure 4a shows this effect appearing due to the changes in the crosslinking density. The sample with 10 mol-% of crosslinking density is 6.35 times more mechanically-efficient than its corresponding 2.5 mol-% crosslinking density homologous, and 60% more efficient than the best performing of the nematic photoactive SCLCEs.
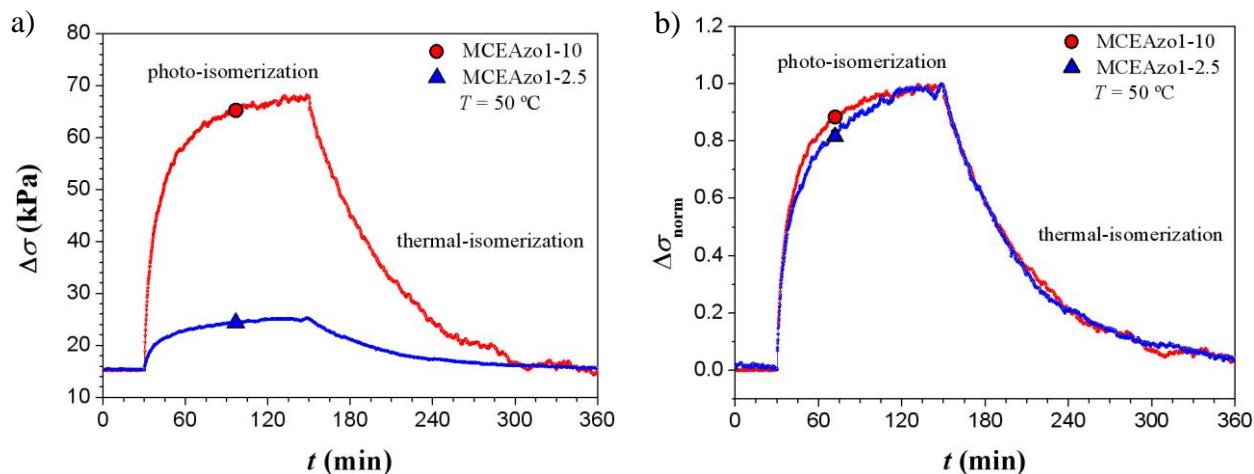

Figure 4. a) Opto-mechanical experiment on the nematic main-chain liquid-crystalline elastomers MCEAzo1-10 and MCEAzo1-2.5 at 50 °C and λ = 380 nm. b) Normalized curves during the photo- and thermal-isomerization processes for the two nematic photoactive MCLCEs.

This high mechanical efficiency for the more crosslinked MCLCE system is explained by the fact that all azobenzene molecules are part of the polymer backbone, and any conformational change or isomerization process couples to the macroscopic dimensions of the LCE. This effect is not that notable in SCLCEs because although a coupling is present between the mesogens and the polymer backbone until certain length of the spacer, there is still some freedom between both the molecules and the polymers.

In Figure 4b the normalized stress values are plotted together for both nematic photoactive MCLCEs. It seems that kinetics during the UV-light irradiation and relaxation processes differ a bit when the normalized curves are superimposed, showing a little bit faster photo- and thermal-isomerization processes in the sample with more crosslinking density. This effect might be explained by the fact that any change in the polymer conformation is transmitted more efficiently when the polymer chains are shorter or more nodes are present in the polymer network.

3.4. Smectic Photoactive MCLCE. The smectic photoactive MCLCE (MCEAzo1-5) containing the symmetric azoderivative (Azo1) shows its corresponding opto-mechanical behavior of the stress ($\Delta\sigma$) as function of time during three cycles in Figure 5. The exponential growths and the exponential decays happen during the illumination and the darkness, respectively.

The MCEAzo1-5 has a crosslinking density of 5 mol-% which is equivalent to 8 repeating units between crosslinking points. This LCE shows a smectic-C phase with a conical distribution of domains.[14] The presence of this smectic layering is the responsible for the higher young modulus with respect to nematic LCEs,[15] as well as for the shape memory effect already described in previous papers.[14-16] Figure 5a shows this effect during the first irradiation process with differences in the stress between the illumination and relaxation processes. The smectic photoactive MCLCE only recovers 55% of the maximum stress during the first thermal-isomerization process. This stress and the recovering are kept constant during the following irradiation and relaxation processes.

At the end of the first photo-isomerization process, the smectic layers are partially broken and the correlation is lost. At this stage, the smectic LCE would show an irreversible contraction if free: the shape memory effect. Since the sample is held from both extremities, a huge increase of the stress appears which is not recovered during the following relaxation process because of the shape memory effect. Then, the next cycles will start with an increased initial value of the stress (higher than the applied pre-load) corresponding to the final value reached at the end of the first cycle. The huge maximum stress value achieved during the irradiation processes - 6.20 times higher than that for the nematic photoactive MCEAzo1-10 - is achieved due to the energy required to slide the mesogens from one layer to the next.[15]
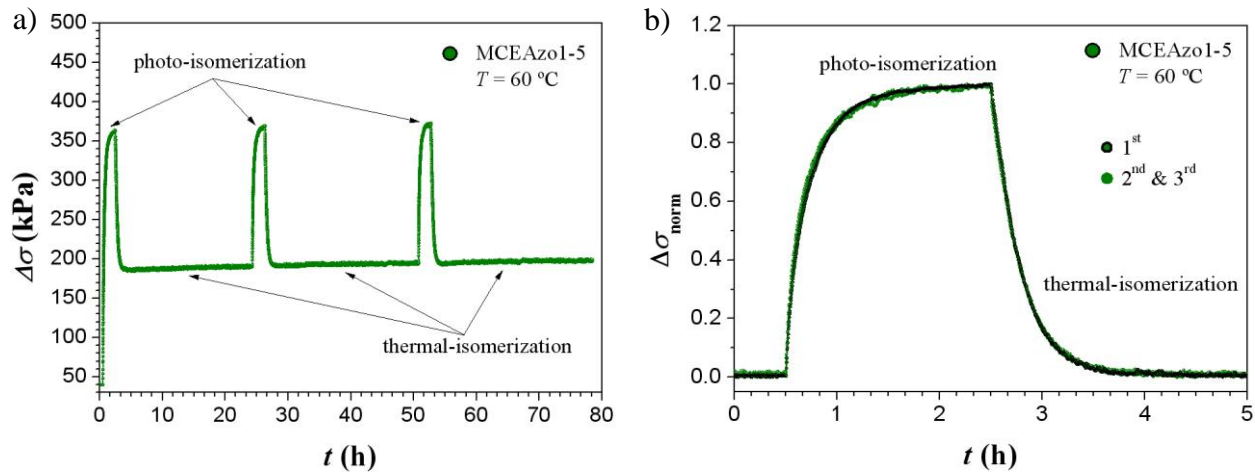

Figure 5. a) Opto-mechanical experiment on the smectic main-chain liquid-crystalline elastomer MCEAzo1-5 at 60 °C and λ = 380 nm. b) Normalized curves during the photo- and thermal-isomerization processes during the first, second and third cycles.

In order to evaluate the opto-mechanical evolution of the sample as function of time during both the UV-light irradiation relaxation processes, in Figure 5b the normalized stress values are plotted together. It seems that the kinetics of the two processes (photo- and thermal-isomerization) during all the cycles are the same when superimposing the normalized curves. Thus, the big difference between the first and second-third cycles – the residual stress from the first illumination curve – is caused by the shape memory effect mentioned above.

4. CONCLUSION

The opto-mechanical response of new photoactive LCEs has been studied using an opto-mechanical set-up that allows to study the pure photo-isomerization and thermal-isomerization processes at different temperatures, and to measure the maximum response of these systems. The change in architecture, connectivity and symmetry of the azobenzene molecules showed different behaviors of the LCE matrix.

For the nematic photoactive SCLCEs (SCEAzo1, SCEAzo2, SCEAzo3 and SCEAzo4), the two-ring azobenzene molecules have higher response than the corresponding four-ring molecules in SCLCEs, due to their rigidity. The azobenzene crosslinkers are more efficient than the common pendant molecules due to the so-called cooperative effect.

The nematic photoactive SCLCE (SCEAzo5) containing an asymmetric azobenzene crosslinker shows the reverse effect (compared to the symmetric azo dyes): a decrease in the opto-mechanical response during the photo-isomerization, and an increase during the relaxation process.

The nematic photoactive MCLCEs (MCEAzo1-10 and MCEAzo1-2.5) show a higher opto-mechanical response with respect to SCLCEs due to direct coupling of the azobenzene molecules to the polymer backbone. An increase in the efficiency has also been observed when the crosslinking density was increased.

Finally, the smectic photoactive MCLCE (MCEAzo1-5) has an opto-mechanical response higher than the corresponding nematic MCLCEs. The presence of the smectic layers increases this mechanical enhancement, and is the responsible for the shape memory effect which has been observed during the experiments.

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