Articles

Smectic LC-Elastomers with NO Shape Change at the Phase Transition

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Liquid crystalline (LC) elastomers are well known for their reversible shape variation at the phase transition from the LC to the isotropic phase. We managed to prepare an oriented smectic monodomain of a crosslinked LC-polysiloxane which showed – contrary to the expectations – NO shape variation at all. This observation is in agreement with mechanical measurements on small LC-elastomer balloons made from the same materials. It is completely unknown why this type of "diluted" LC-polysiloxane (only about 25% of the repeating units are functionalized with mesogens) behaves like this.

1 Introduction

Liquid crystalline elastomers (LC-elastomers) combine LC-phases and the resulting anisotropic properties with the mechanical properties of a soft rubbery solid. [6,11,12,34] As a consequence, the conformation of the polymer chains is influenced by the liquid crystalline director field. This couples the shape of the LC-elastomer to the liquid crystalline order. They are presently finding an increasing interest as actuators. [9,23] Generally, size changes are found at phase transition temperatures, especially at the transition from the ordered liquid crystalline phase (e.g. smectic or nematic) to the disordered isotropic phase. [18] Figure 1 depicts the LC phase behavior of thermotropic calamitic (rod-like) liquid crystalline molecules.
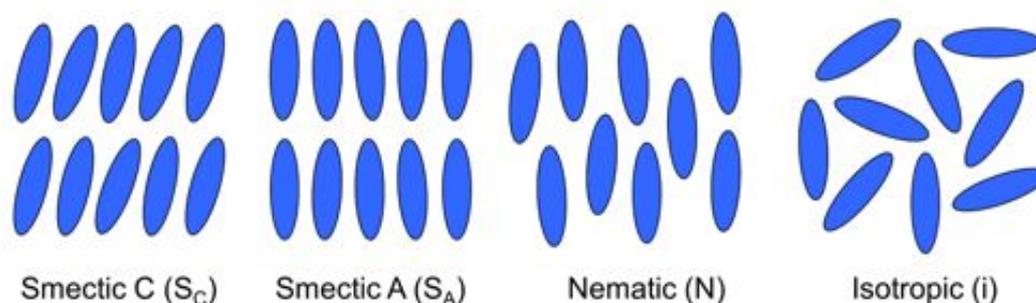
Figure 1: Mesomorphism in thermotropic calamitic mesogens. The molecular order decreases with increasing temperature. All long-range order is lost in the isotropic melt.

To improve the properties of an LC-elastomer, two aspects have to be optimized:

1. The anisotropy of the radius of gyration of the polymer chains in the LC-phase, which is the precondition for the size change at the phase transition, should be as large as possible. In this respect, smectic phases are attractive because they usually possess a larger order parameter compared to nematic phases. [21] Smectic LC-polymers are, however, more difficult to orient uniformly (monodomain) than nematics which is a precondition for a macroscopic shape change at the phase transition.

2. An isothermal shift of the phase transition temperature by an external stimulus is more desirable than a

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temperature variation. In this respect, photochromic dyes, which destabilize the LC-phase during isomerization, are attractive. Azo dyes are especially attractive in this context because they can be used to shift phase transition temperatures reversibly.[10,31,33] Photochromic dyes have been incorporated into LC-elastomers. It had, however, never been possible to prepare/crosslink these LC-elastomers by photocrosslinking, as the dye absorbs most of the photons.

As starting point for this work, we had succeeded in the synthesis of azo containing smectic LC-polymers which could be photocrosslinked – for the first time – into smectic elastomers due to an improved orientation technique.[4] Thereafter, we wanted to study their shape variation at the transition from the smectic A to the isotropic phase.

2 Results and Discussion

A smectic polysiloxane **P1** was synthesized by a hydrosilylation reaction (see Figure 2a). It was modified with azo-mesogens and acrylate terminated mesogens to yield polymers **P1a** and **P1b** (see Tab. 1). The details of their synthesis and characterization is described in Ref. 12. These smectic LC-polymers belong to a series of LC-polysiloxanes, in which only 1 out of 3 repeating units are functionalized with mesogen like groups.[7,8,14,16,22,26] The phase transition temperatures of the polysiloxanes **P1a-b** were characterized by DSC and polarizing microscopy. They are compiled in Tab. 1. All polymers exhibit the phase sequence S_X-S_C^*-S_A-i.

Table 1: Composition and phase sequences the LC-polymer series **P1-P1b**.

	x	y	z	w	Phase sequence
P1	1	0	0	2.9	S_X 29 °C S_C^* 61 °C S_A 89 °C i
P1a	0.8	0.08	0.12	2.9	S_X 36 °C S_C^* 67 °C S_A 86 °C i
P1b	0.8	0.14	0.06	2.9	S_X 30 °C S_C* 57 °C S_A 85 °C i

As the *cis*-form of the azobenzene side group destabilizes the LC-phase, it is possible to shift the phase transition temperature by photo-isomerization (Figure 2b).[4,22] This effect could be detected both for uncrosslinked polymers **P1a-b** and for crosslinked samples made from **P1a** and **P1b** at the clearing temperature (S_A-i) by polarizing microscopy. For **P1a** e.g. an isothermal shift of the S_A-i transition of more than 10 °C could be observed.[22]

These photoswitchable polymers could be photocrosslinked into oriented LC-elastomers or "single crystal LC-elastomers (SCLCE)" in the nomenclature of Finkelmann[20] by using the dichroism of the azo-chromophore in perfectly aligned samples to eliminate the absorption by the azo-chromophores parallel to the director.[4] Perfectly homeotropic aligned samples can be obtained by spin-coating and annealing thin films on substrates[15] (film

thickness 1-2 μm) because of the smectic layer structure which wants to orient parallel to the substrate. They look completely black if viewed between crossed polarizers which proves the homeotropic orientation. X-ray and TEM measurements prove their smectic phase and their orientation.[26,32] To crosslink polymers **P1a** and **P1b** they were mixed with Lucirin TPO as photoinitiator and irradiated with UV-light (about 360 nm) perpendicular to the surface of the substrate which is parallel to the director and perpendicular to the transition dipole moment of the azo-mesogens.
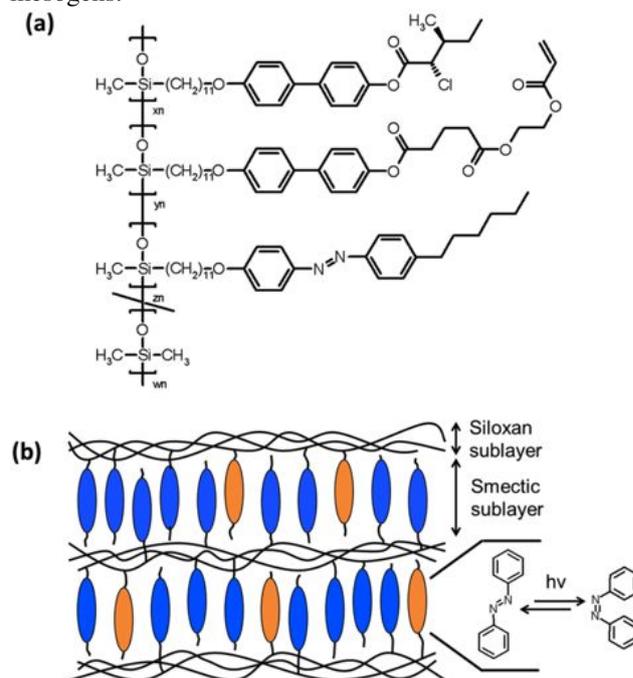
Figure 2: (a) Molecular structure of LC-polymers **P1**-**P1b**. (b) The *trans-cis* isomerization in oriented LC elastomers destabilizes the LC-phase and lowers the phase transition temperature, allowing an isothermal phase transition.

To demonstrate the influence of crosslinking, Fig. 3a shows a POM-image of a patterned partially crosslinked film of polymer **P1a** at room temperature. This polymer had been irradiated through a mask (left side covered, right side exposed) so that only the right part gets crosslinked. Then, it was heated into the isotropic phase and quickly cooled back to the LC-phase. After this process (rapid cooling), the covered part of the film (left side, uncrosslinked) turns birefringent because of the unoriented LC-phase. The crosslinked part (right side) shows, however, still the homeotropic orientation (black) because the network retains the memory of the homeotropic orientation. The irradiated part of the film swells – as expected – in good solvents but does not dissolve. This proves the crosslinking and the fact that an elastomer has been made.

Free-standing thin elastomer films can be prepared with this method by spincasting the LC-polymer onto NaCl pellets. After dissolution of the substrate with water, one obtains unsoluble and homeotropically oriented LC-elastomers with photo-addressable azo-chromophors (see

Fig. 3b). As expected, photocrosslinking is also possible in free standing films obtained by drawing of the uncrosslinked polymer over a hole. [29]
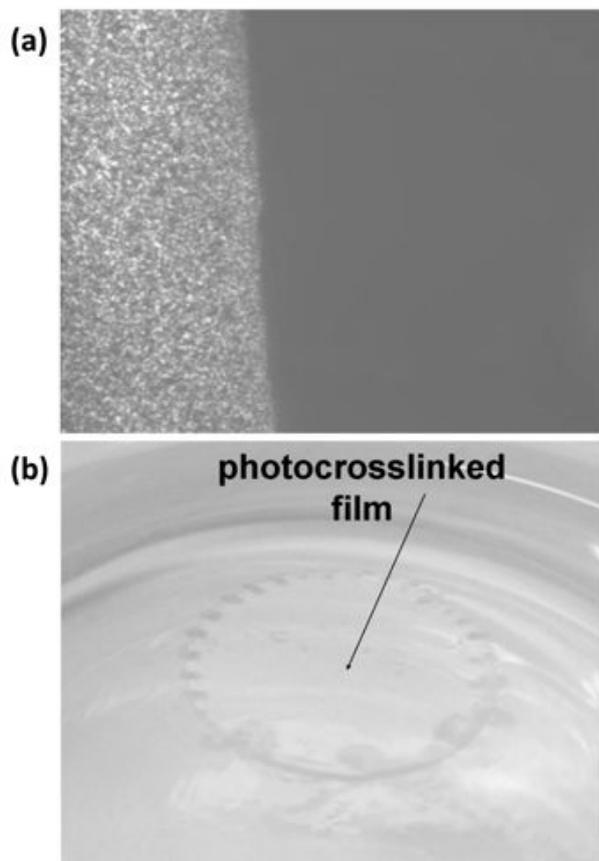
Figure 3: (a) Polarizing microscopy image of a partly crosslinked film (left: uncrosslinked, right: crosslinked) of **P1a** on a substrate; picture taken at room temperature after crosslinking the right side in the S_X-phase, heating to the isotropic phase and quick cooling to room temperature. (b) Free floating photocrosslinked film of **P1b** after dissolution of the substrate. The outer circle of the film is thicker and better visible. Pictures taken from Ref. 12.

As a result, we had obtained perfectly oriented smectic elastomers which are photo switchable because of the azochromophores. This allows an isothermal phase shift. Such monodomains of photoswitchable smectic LC-elastomers should open the possibility to induce shape changes either isothermally by irradiation (loss of the LC-phase due to isomerization) or by temperature changes (heating above the phase transition to the isotropic phase).

In the following, we tried very hard to observe these expected shape changes. At first, by irradiation and then, simply by heating the sample into the isotropic phase (see Tab. 1 for the corresponding phase sequence). To prevent sticking to the substrate, we used freely floating samples on silicone oil. To improve our resolution, we used a microscope to look at the samples (in size similar to Figure 3a, 1 cm diameter). But we never observed any shape change

at all. With our microscopical set-up, we are able to observe shape changes of the order of several micrometers. Given the size of the sample (cm), this would correspond to a relative shape change of less than 0.1%. Usually 20 to 100% of length changes are reported. [2,3,24]

The question to solve is then, why did we not observe any reasonable shape change in our system. At first, it should be noted that most of the experiments on LC-elastomers were made with nematic phases and only very few on elastomers with smectic phases. If smectic phases were investigated, the interest focused on the transition from the tilted smectic C to the orthogonal smectic A phase. [17] Thus, there are very few data available for comparison. Usually it is believed that smectics should show a larger shape change as the liquid crystalline order is larger in smectics than in nematics. [21,23,27] For shape variation, we have to consider, however, the anisotropy of the polymer chains in the smectic phase. And no systematic study exists on this topic.

Reports about shape variations during the transition from a smectic phase to the isotropic phase give rather different values. For some LC-main chain elastomers, rather large shape variations are observed [1,5,27] which are larger than that of comparable elastomers at the nematic-isotropic transition; for others (both of the LC-main chain- or LC-side chain type), a rather small shape change is observed which is smaller than that of comparable nematic systems. [3,19] However, it is difficult to relate the order parameter of the mesogens in the LC-phase to the chain anisotropy. This is evident e.g. from the fact that in side chain systems the polymer chain can adopt a prolate, an oblate or an isotropic confirmation (i.e., no preferred orientation at all). [23] Chain anisotropy has been explained for some very special cases but there is no way to predict it in a general way from the molecular structure. For smectics, the following argument can apply, too. If chain extends parallel to director (prolate configuration) in the nematic phase, they might get confined to the smectic layers. In this case, the overall anisotropy gets reduced. In addition, little is known for most of the systems about the quality of the smectic order. I.e., the correlation length of the smectic layers may be long range – as in classical smectics – or rather short range. [13]

There is another difference between the LC-elastomers studied here and the "usual" systems and this is based on the molecular structure. Most of the work done on LC-elastomers has been made with polysiloxane-elastomers, in which each dimethysiloxane repeating unit carries mesogens (so called LC-homopolysiloxanes). We work here with systems, in which only some repeating units carry mesogens while the other repeating units consist of unsubstituted dimethysiloxane units [14] (so called "diluted" LC-copolysiloxanes = diluted with dimethysiloxane units). These "diluted" LC-copolysiloxanes show a nanophase separation into mesogen rich and polymer rich sublayers, as proven by X-ray scattering [14,25] and as visualized by TEM measurements on LC-colloids. [32] Based on these facts, the polysiloxane chains in our elastomer have to be restricted – in the smectic phase – to the polysiloxane sublayer and adopt a 2D conformation. Thus, it should be highly

anisotropic and the loss of this anisotropy should lead to an especially large shape variation at the phase transition to the isotropic phase. However, no shape variation is observed at all! On the other side, the classical siloxane elastomers of Finkelmann belong nearly exclusively to the homopolymer type. For them, the shape change is well established.[21,24] So, obviously homo- and copolymers show very different mechanical properties. However, a different response to mechanical deformation has also been clearly identified for the "diluted copolymers" by work on thin films (free standing films or balloons). Small balloons made from smectic polysiloxanes have been used extensively to characterize their elastic property in detail.[28,30] They showed also no sign of a change of the sample dimensions at the transition from the smectic to the isotropic phase. In fact, the smectic elastomers from "diluted" LC-copolysiloxanes are rather soft solids, in which even the thickness of the smectic layers can be changed by stretching.[29]

After all these considerations, it remains still completely unclear why we are not able to observe any shape variations for the LC-elastomers made from "diluted copolysiloxanes" with smectic phases. Taking all available information together, the shape change at the transition to the isotropic melt might be small but some shape variation should be observable. Especially since the polymer main chain is restricted within the smectic phase to a 2D-like smectic sublayer.[14,25,32]

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