

# Orientation of a Chiral Smectic C Elastomer by Mechanical Fields

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## ABSTRACT

It is well known that, with respect to the director, nematic elastomers can be macroscopically aligned by uniaxial mechanical fields. Extending this method to a chiral smectic C elastomer, depending on the experimental set-up either smectic layer orientation or director orientation parallel to the stress axis occurs. In order to align the director and the smectic layers a biaxial mechanical field (e.g. shear field) consistent with the phase symmetry has to be used to achieve a macroscopically uniform orientation of the untwisted smectic C\* structure.

**KEYWORDS:** Chiral smectic C elastomer, Orientation, Mechanical fields

## INTRODUCTION

Since the description of the ferroelectric behavior of the chiral smectic C phase by Meyer *et al.* [1] this class of liquid crystals has attracted great industrial and scientific interest. But potential properties like ferroelectricity, piezoelectricity or second harmonic generation can only be obtained for well-oriented samples with an untwisted helicoidal structure. This orientation can be achieved for low molecular weight  $S_{C^*}$  systems by surface alignment, electric and magnetic field or by shear flow. But for liquid crystal (LC) polymers these techniques often fail owing to their high viscosity. However, using a mechanical field by drawing fibers from the melt offers the chance to obtain well-aligned samples.

LC elastomers that combine the mechanical properties of polymer networks with the anisotropic phase structure of liquid crystals are even better suited to obtain high orientation by mechanical fields. Detailed investigations were performed on

nematic elastomers applying a uniaxial mechanical field [2, 3]. Owing to the fact that the symmetry of a uniaxial mechanical field and the symmetry of the nematic phase are consistent well aligned samples can be realized where the nematic director (symmetry axis of the nematic phase) is oriented parallel to the mechanical field axis. Furthermore, from thermomechanical measurements we have learned that macroscopic dimensions of the elastomer scales linearly with the nematic order parameter [4].

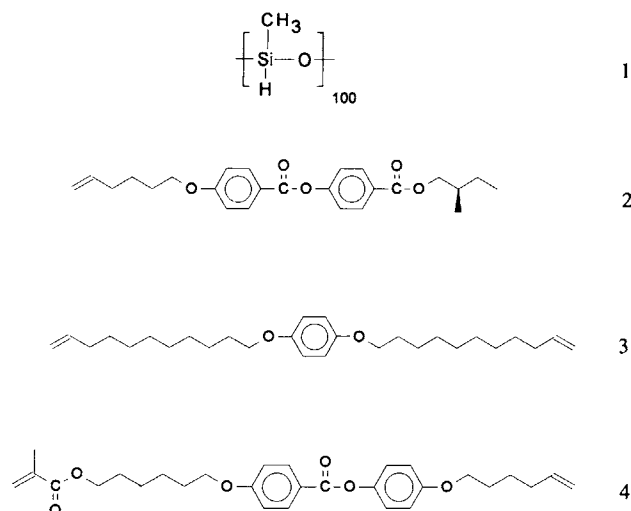
If we consider a uniaxial smectic A system, two different orientation processes can be observed [5]. Applying the uniaxial field in the smectic A phase causes a macroscopic orientation of the smectic layers parallel to the deformation axis. An orientation of the layers perpendicular to the mechanical field direction is observed when the system is deformed in a high-temperature nematic phase and subsequently cooled to the  $S_A$  state. From these observations it follows that uniaxial mechanical fields are sufficient to get a macroscopic alignment either of the director or of the smectic layers for the uniaxial  $S_A$  phase.

The question arises whether an elastomer exhibiting the biaxial smectic C phase or the helielectric chiral smectic C phase can also be uniformly aligned by a mechanical field. In this paper we present the synthesis and the orientation behavior of a chiral smectic C elastomer by mechanical field which yields macroscopically aligned systems.

## EXPERIMENTAL

### System

The elastomers are synthesized by an addition reaction of the polymethylhydrogensiloxane **1** with the mesogene **2** and the crosslinking components **3** and **4** [6] (Fig. 1).



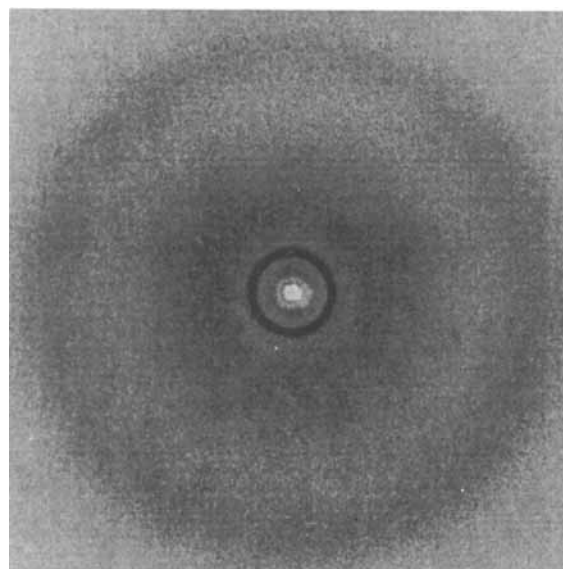
**FIGURE 1.** System under investigation.

The synthesis of the mesogenic unit is described in the literature [7]. In order to lock in the mechanically induced orientations, two crosslinking components **3** and **4** are used. Since the reaction of the vinyl group of **4** is faster by approximately two orders of magnitude than the reaction of the methacryloyl groups with the polymethylhydrogensiloxane monomer unit it can be assumed that the first crosslinking step is mainly performed by the divinyl compound **3**. After mechanical deformation of the elastomer, the crosslinking process is completed at elevated temperatures by the reaction of the methacryloyl groups of compound **4**.

The elastomer with 7% of **3** and 3% of the combined crosslinking agent **4** has a broad chiral smectic C phase in the temperature range from  $-17^{\circ}\text{C}$  ( $T_C$ ) to  $62^{\circ}\text{C}$  ( $T_C$ ) and is therefore suitable for orientation experiments at room temperature. The smectic structure is confirmed by the X-ray pattern of an elastomer (Fig. 2) which has not been mechanically loaded.

### Synthesis

The synthesis of liquid crystal elastomers follows the well-known procedure of hydrosilylation reactions with polysiloxanes [8]. The solution of 188 mg (3.00 mmol) of **1**, 984 mg (2.40 mmol) of **2**, 50 mg (0.12 mmol) of **3**, 86 mg (0.18 mmol) of **4** and 9  $\mu\text{l}$  of the Pt-catalyst SLM 86005 (Wacker Chemie, Burghausen) in 3 ml of absolute toluene is filtered using a 0.5  $\mu\text{m}$  Millipore filter into a centrifuge cell with a diameter of 5 cm and a height of 3 cm, excluding dust particles. To avoid tack, the inner wall of the cell is covered with PTFE film. The reaction is carried out under centrifugation (400 rpm) at  $60^{\circ}\text{C}$  for 70 min. Thereafter the whole cell is cooled to room temperature and the swollen elastomer is carefully removed from the cell. The swollen elastomer is fixed at one end with a clamp and the freely hanging film is dried for 24 hr at room temperature. During this time most of the toluene evaporates and the elastomer becomes liquid-crystalline. Simultaneously the elastomer becomes loaded with a



**FIGURE 2.** X-ray pattern of the chiral smectic C polydomain.

stress of  $3.2 \times 10^{-2} \text{ N/mm}^2$ . Thereafter the film is annealed for 48 hr at  $40^{\circ}\text{C}$  in a vacuum oven.

The polydomain sample is prepared as a reference under similar conditions; however, without load during the second crosslinking reaction.

### X-ray Measurements

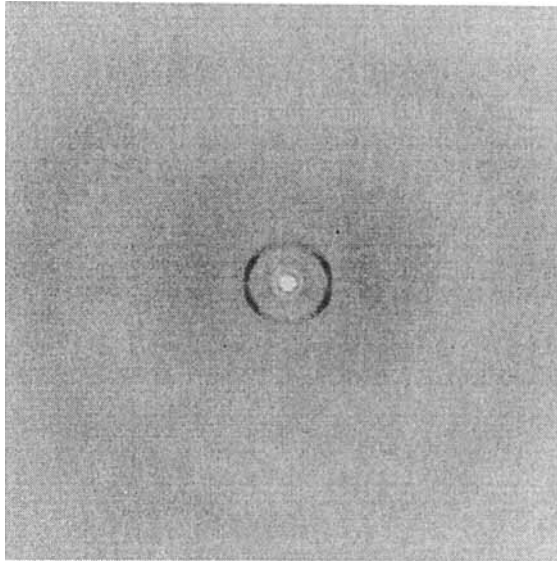
The X-ray measurements were performed using a Ni filtered  $\text{Cu-K}\alpha$  ( $\lambda = 15.4 \text{ nm}$ ) beam. A two-dimensional image plate system ( $512 \times 512$  pixels, 250  $\mu\text{m}$  resolution) was used as detector unit.

## RESULTS

### Uniaxial Deformation of the Elastomer

In order to investigate the influence of an uniaxial mechanical field a polydomain sample is synthesized without load during the complete addition reaction of the crosslinking components **3** and **4**. This elastomer is fixed in a stress apparatus and deformed up to  $\lambda = 1.6$  ( $\lambda = L/L_0$ ,  $L$  = sample length with load,  $L_0$  = sample length without load). After the deformation the elastomer remains for 12 hr in the stressed state and is finally investigated by X-ray measurements. For  $\lambda = 1.6$  a change in the distribution of the azimuthal intensity of the smectic small angle reflections ( $\sim 2.4 \text{ nm}$ ) can be observed (Fig. 3) compared with the unloaded elastomer. The greatest intensities of the small angle reflections are near the equator of the pattern, indicating that the smectic layers become aligned at an angle of  $\sim \pm 25^{\circ}$  perpendicular to the applied field. The wide angle pattern (0.4–0.5 nm) representing the mesogen–mesogen distance does not show a significant orientation. Owing to the mechanical properties of the elastomer, deformations above  $\lambda = 1.6$  causing better orientations are not feasible.

This result indicates similarities to the orientation mechanism of  $S_A$  polymer fibers as mentioned



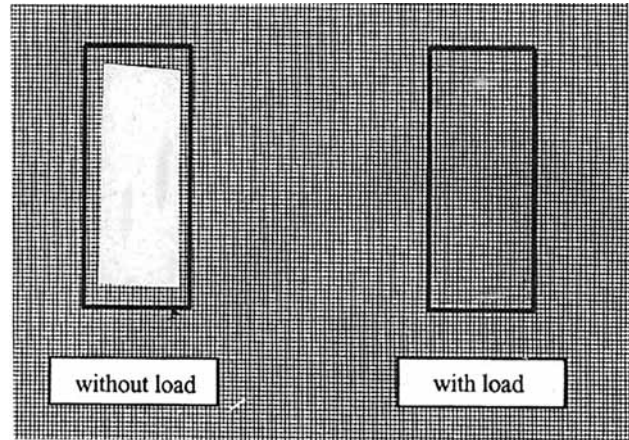
**FIGURE 3.** X-ray pattern after uniaxial deformation of the polydomain.

above. However, the quality of the orientation effect of the completely crosslinked system is very poor. If we consider the crosslinking units as immobile defects in the smectic structure, the poor orientation effect of the mechanical field might be explained. The units are fixed in the isotropic state of the elastomer and exhibit no order. In the smectic phase they essentially remain in the non-ordered state that is obviously not affected by the mechanical field. To avoid this problem we modified the experimental conditions that should yield ordered crosslinking molecules.

#### Uniaxial Deformation of the Swollen Elastomer

In the second orientation experiment the mechanical field is applied in the swollen state of the elastomer immediately after the first crosslinking step. The stress is applied on the isotropic sample still containing the solvent by carefully tensioning with weights. The sample remains loaded for 24 hr at room temperature and is finally dried in the vacuum at 40°C for two days. During this process the isotropic to smectic transformation is observed. Owing to the fact that the second crosslinking step takes place while the elastomer is deformed in the smectic state, the mechanically induced anisotropic network structure is chemically locked-in. Furthermore the mesogenic crosslinking component **4** which also adopts the smectic order reacts in the ordered state causing a topology of the crosslinking unit that is consistent with the LC phase structure. Actually, in contrast to the turbid polydomain sample the elastomer is highly transparent (Fig. 4), which indicates an orientation of the phase structure as known from the nematic elastomers. The orientation of the smectic phase is confirmed by X-ray measurement (Fig. 5) and reveals two important results:

1. The small angle reflections exhibit four distinct maxima indicating a layer orientation of the layer normal  $\pm 25^\circ$  to the stress axis.



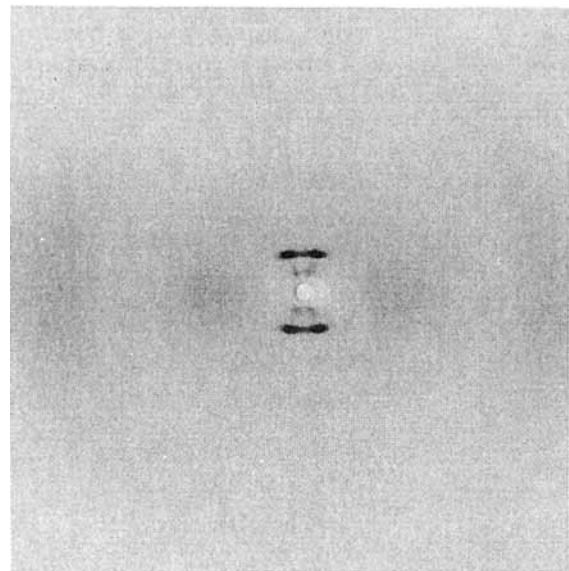
**FIGURE 4.** Chiral smectic C elastomer after second crosslinking step.

2. The azimuthal wide angle intensities exhibit clear horizontal maxima indicating an alignment of the director of the long molecular axis of the mesogenic units parallel to the stress axis.

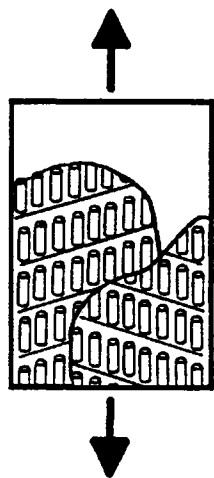
Under these experimental conditions the helicoidal structure is untwisted. Similar to nematic systems the mechanical field couples to the director orientation. A structure consistent with this result is schematically shown in Fig. 6. This is in contrast to the above-mentioned stress experiment in the smectic state, where the mechanical field couples to the layer orientation.

#### Shear Deformation of the Elastomer

The experiments clearly reveal that a uniaxial mechanical field is not suitable for obtaining a macroscopic uniform orientation of an  $S_C$  or untwisted  $S_C$  elastomer. Although the director concerning the long



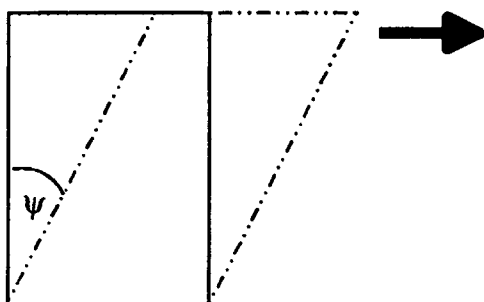
**FIGURE 5.** X-ray pattern after uniaxial deformation in the swollen state.



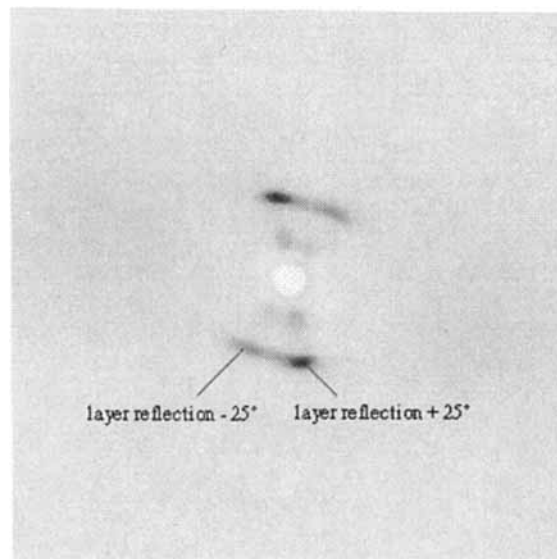
**FIGURE 6.** Orientation after uniaxial deformation in the swollen state.

molecular axis becomes uniaxially ordered, an equivalent orientation of the layer normal of  $\sim \pm 25^\circ$  remains with respect to the uniaxial stress axis. Considering the biaxial symmetry of the  $S_C$ -phase it is obvious that a mechanical field that is consistent with the LC phase symmetry must be applied. As we have learned from the strain experiment in the smectic phase, the mechanical field couples to the layer orientation. Consequently a suitable shear field (Fig. 7) should result in a uniform layer orientation of the elastomer aligned with respect to the director.

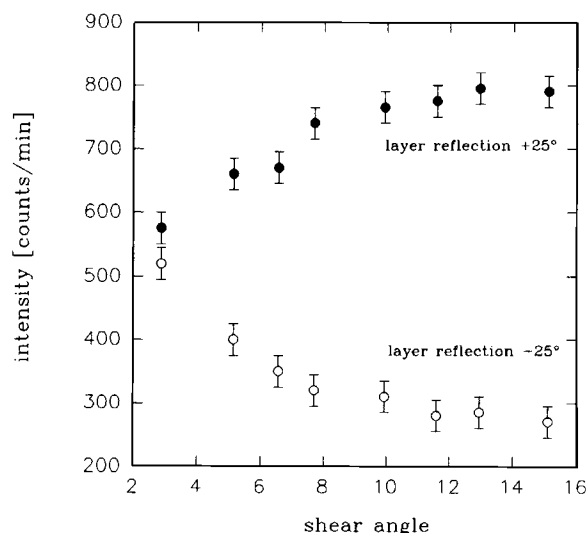
For the shear experiment we use the elastomer already aligned with respect to the director by the uniaxial field. The elastomer is gradually sheared with the angle  $\psi$  and analyzed by X-ray measurements after an annealing period of 12 hr at room temperature. The results are shown in Fig. 8(a) and (b). In Fig. 8(b) the change of the intensity of the small angle reflections is plotted versus the shear angle  $\psi$ . With the increasing  $\psi$  the intensity of the reflection corresponding to the  $+25^\circ$  increases while simultaneously the  $-25^\circ$  layer orientation becomes unfavorable. This result proves that a mechanical field consistent with the phase symmetry causes alignment of the smectic layers and the director towards a defect-free elastomer. A completely aligned sample is expected for the shear angle  $\psi = 25^\circ$ . However, for  $\psi > 16^\circ$  the elastomer under investigation starts buckling, providing no reproducible results. To obtain a better orientation effect



**FIGURE 7.** Shearing of the preoriented sample.

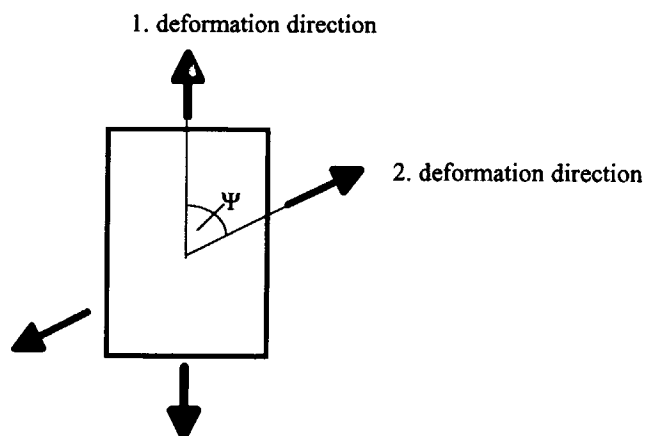


(a)

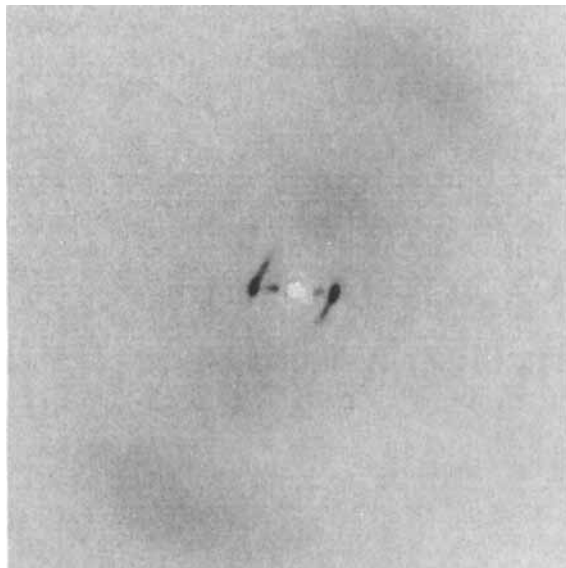


(b)

**FIGURE 8.** (a) Smectic layer reflections after shearing experiment ( $\psi = 16^\circ$ ). (b) Intensity of layer reflections plotted vs. shear angle.



**FIGURE 9.** Second deformation of the preoriented sample.



**FIGURE 10.** X-ray pattern after second uniaxial deformation.

an additional experiment is performed as schematically indicated in Fig. 9. The elastomer oriented with respect to the director by the first uniaxial deformation during the second crosslinking is uniaxially deformed by a second uniaxial stress experiment under the angle  $\psi = 65^\circ$  to the first deformation direction. Under these conditions for  $\lambda_2 \approx 1.5$  an excellent orientation of the sample results as indicated by the X-ray pattern shown in Fig. 10. The mechanical field now causes a layer orientation parallel to the mechanical field. The ratio of the intensities of the small angle reflections is 1:22 for the sample after the second deformation. This experiment clearly shows that a reorientation of the smectic layers can be achieved by uniaxial deformation in the smectic state. In combination with the director orientation in the swollen state or in a nematic phase

this technique yields macroscopically well-aligned samples.

## CONCLUSION

The experiments indicate that a biaxial  $S_C$  phase or an untwisted chiral  $S_C$  phase can be macroscopically uniformly aligned by a suitable mechanical field consistent with the LC phase symmetry. However, additional quantitative and systematic investigations are necessary to get a more detailed knowledge about the orientation mechanism concerning the interactions between layer and director alignment.

## ACKNOWLEDGMENTS

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