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Shear-induced tilt in smectic-*A* elastomers

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Smectic-*A* elastomers combine the positional long-range order of mesogenic molecules in one dimension with the rubber elasticity of a polymer network. While the influence of uniaxial mechanical fields on the phase structure has been investigated intensively during recent years, the impact of shear forces on the orientation of mesogens remains unclear. We present x-ray experiments under shear strain, showing an induced macroscopic tilt depending on the applied shear angle and geometry of the setup.

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I. INTRODUCTION

The mechanical properties of smectic-*A* liquid single-crystal elastomers (S_A-LSCEs) have been investigated intensively during recent years [1–6]. A system that has been described both experimentally and theoretically was synthesized ten years ago by Nishikawa *et al.* by using end-on terminated mesogens, a bifunctional crosslinker, and a poly-(hydrogenmethylsiloxane) prepolymer in a Pt-catalyzed hydrosilylation reaction [1,2]. A permanently stable macroscopic orientation was obtained by the classical two-step process involving a second crosslinking under mechanical deformation [7]. The elastomer produced by this method shows a macroscopic in-plane fluidity and a modulus in the order of 10^7 N m^{-2} on deformation parallel to the layer normal (z direction), which might reflect the smectic layer compression modulus. After a threshold strain of about 3%, the modulus decreases significantly to 10^5 N m^{-2} and resembles the modulus in the isotropic state or in the direction perpendicular to the layer normal. The elastomer becomes turbid and a breakdown of the smectic-*A* monodomain structure is observed by small angle x-ray scattering (SAXS). The smectic layers reorient in stripe domains characterized by a splitting of the small-angle reflections, a loss of intensity and a decreased order parameter. Reorientation of layers is well known in low molecular weight (LMW) smectics as a mechanism to reduce effective strain in response to elongation imposed along the layer normal. Rotation takes an undulatory form to match boundary conditions at the clamping. In smectic-*A* elastomers, the threshold strain and angle dependence of this reorientation behavior and its undulation were described in continuum elasticity theory [8,9] and later the reorientation processes were described at high strains [10]. Recently, Stenull and Lubensky presented a more general description of smectic-*A* elastomers, according to which a small but nonzero tilt should be expected, upon deformation along the layer normal. Since smectic elastomers favor a constant layer spacing, a deformation along the layer normal will produce shear strains, which could unlock the layer normal and director above a critical threshold [11]. So far, a coupling of the director to a mechanical shear field has only been reported for smectic-*C* elastomers. Applying a shear force to a structure with a uniformly aligned director but with a conical distribution of the layer normals causes the director to rotate, yielding a macroscopically oriented network [12–14]. In smectic-*A* elastomers, one could expect the observation of a shear induced tilt analogue to the electroclinic effect of chiral smectic-*A** phases in electrical fields [15]. In order to check this assumption, we present x-ray measurements of Nishikawa's networks under shear strain, using different shear geometries. The experiments clearly support the theoretical predictions by Stenull, Lubensky, Adams, and Warner [16].

II. EXPERIMENTAL PART

For the experiments, we used the well-known side-chain networks, which show a broad smectic-*A* phase and a high-temperature nematic phase, as described in the literature a couple of years ago [1]. The sample was sheared at room temperature perpendicular to the layer normal k (z direction) in steps of approximately five degrees and allowed to relax for one hour. The applied shear angle was measured by a digital camera. The sample size was 7.4 mm $\times$ 5.0 mm $\times$ 0.45 mm. We used three different shear geometries. By using an apparatus presented in Fig. 1(a) or Fig. 1(b), the applied shear is accompanied by a compression, while the slider shown in Fig. 1(c) provides simple shear. X-ray diffraction measurements were performed with a rotating anode system and a graphite monochromator (*Stoe*), using Cu $K\alpha$ radiation with $\lambda = 1.5418$ Å. The scattered intensity was detected by a two-dimensional image-plate system (700 $\times$ 700 pixels, 250 μm, Schneider). The accuracy of the measured angle between small- and wide-angle reflections was estimated as $\pm 1°$.

III. RESULTS

Shearing a smectic-*A* elastomer is more difficult than for smectic-*C* networks. Applying a shear strain with the same setup used to induce a macroscopic orientation in smectic-*C* elastomers [Fig. 1(a)] [12,14] causes a smectic-*A* sample to buckle strongly. Even if the shear were applied stepwise with a relaxation time of one hour, no homogeneous deformation could be achieved. These experimental problems may be connected with the special shear geometry. Especially at

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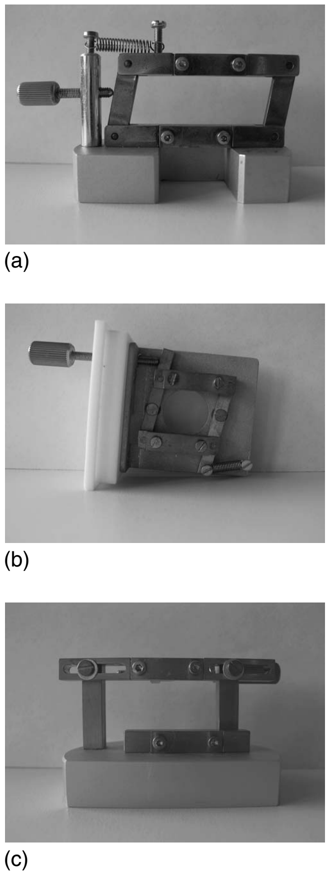

FIG. 1. Overview of different shear geometries: (a) shear with compression, (b) shear with compression but smaller translation (the screws in the middle fix the apparatus to a back plate), (c) simple shear.

higher angles, an additional compression of the sample occurs. Figure 1(b) shows a slightly improved apparatus. It still produces shear accompanied by a compression, but the translation is smaller. The buckling is weaker and the sample can be sheared up to angles of $\phi=13°$ before it ruptures. However, the measured tilt angle between small-angle and wide-angle reflections is $\theta=2°$ and therefore near the experimental error. In Fig. 1(c), a third apparatus is shown, which produces simple shear and shows the best experimental performance. There is no significant buckling and the sample can be sheared more than $\phi=20°$. The corresponding x-ray patterns show a small induced tilt for high shear angles (Figs. 2 and 3). The experimental results are summarized in Table I. The director follows the applied shear field, while the orientation of the smectic layers is uninfluenced. The resulting tilt

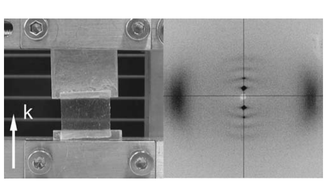

FIG. 2. Experimental setup using the apparatus shown in Fig. 1(c) and corresponding x-ray pattern without deformation; k represents the layer normal.

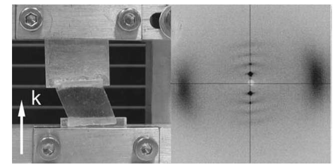

FIG. 3. Experimental setup using the apparatus shown in Fig. 1(c) and corresponding x-ray pattern at a shear angle of $\phi=21°$; k represents the layer normal.

increases continuously up to $\theta=6°$. This is clarified by the azimuthal intensity distributions of the wide-angle and small-angle reflections (Figs. 4 and 5, respectively). While the position of the wide-angle reflections changes with increasing shear angle, the position of the layer reflections remains constant. In particular, no layer rotation is observed. Also the orientational order parameter S remains unchanged under shear. With increasing tilt, a decreasing layer spacing should be expected. However, the changes are smaller than the detection limit of the used x-ray setup.

IV. DISCUSSION

For an induced macroscopic tilt of the mesogenic units, a decrease in the layer spacing should be expected and the unconstrained elastomer should shrink in its dimension parallel to the layer normal. At this point, the difference in the shear geometries becomes evident. If the shear is accompanied by a compression, a shrinkage of the elastomer is possible and the number of smectic layers remains unchanged. However, for simple shear the length of the sample in the direction of the layer normal (z direction) is fixed. If we assume a decreasing layer spacing as a consequence of an induced tilt, an increasing number of smectic layers should result. As observed experimentally, the response of the phase structure differs for the two shear geometries. For simple shear, the sample can be sheared to higher angles and the effect of an induced tilt is much more pronounced. Obviously the applied strain component leads to a more effective coupling of the director.

V. CONCLUSION

X-ray experiments under shear strain of a macroscopically oriented smectic-A elastomer are presented. With an increasing shear angle, a small tilt of the molecular axis is observed. Upon a maximum applied shear angle of $\phi=21°$, the induced tilt is $\theta=6°$ and thus in the range of the electroclinic effect in chiral smectic-A^* phases. This result provides

TABLE I. Results of the x-ray experiment under shear strain, using the experimental setup shown in Fig. 1(c).

Shear angle ϕ (deg)	Tilt angle θ (deg)	S	d (Å)
0	0	0.81 ± 0.03	29.3 ± 0.5
11 ± 1	3 ± 1	0.81 ± 0.03	29.2 ± 0.5
21 ± 1	6 ± 1	0.82 ± 0.03	29.5 ± 0.5

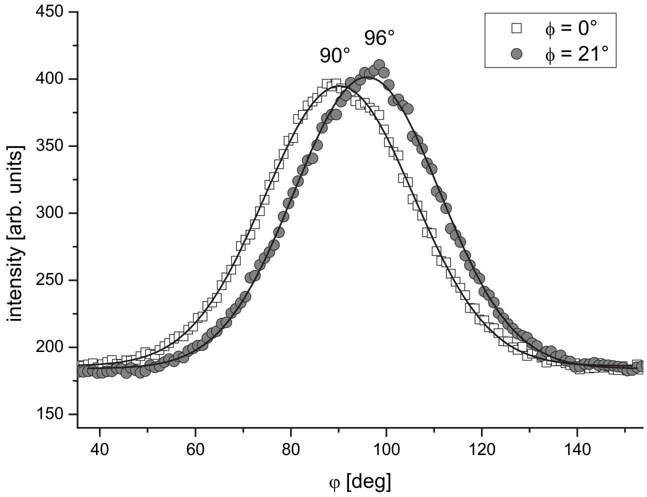

FIG. 4. Azimuthal intensity distributions of the wide-angle reflections and Gaussian fits in dependence of the applied shear angle ϕ.

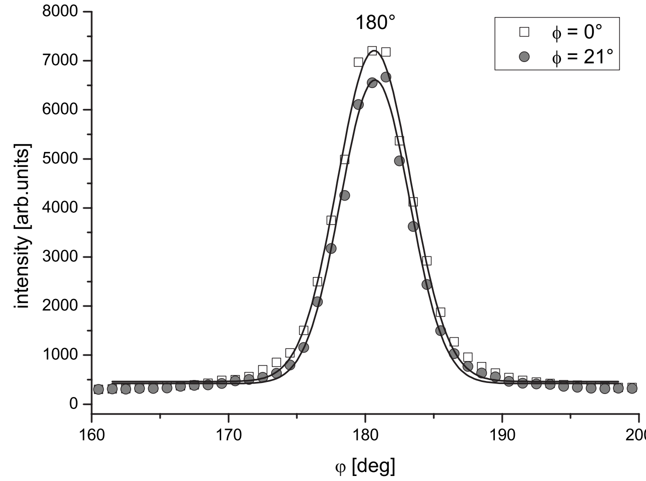

FIG. 5. Azimuthal intensity distributions of the small-angle reflections and Gaussian fits in dependence of the applied shear angle ϕ.

evidence to unlock the director and the smectic layer normal, as theoretically predicted by Stenull and Lubensky [11]. In chiral smectics, the effect induced by an electric field is particularly pronounced near the smectic-*A**-to-*C** transition. It would be interesting if an analogy exists for the mechanical effect, making even larger tilt angles possible. In the future, high-resolution x-ray measurements have to be performed to reveal more detailed information.

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