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Elastic Properties of Liquid Crystal Elastomer Balloons

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We introduce a method to measure elastic properties of smectic liquid crystalline elastomers. Freely suspended smectic polymer films containing photoreactive groups are inflated to spherical bubbles and crosslinked by UV light irradiation. After crosslinking, the balloon volume is varied and elastic properties of the material are determined from the relation between radius and inner excess pressure. The influence of the network topology on the elastic behaviour is discussed.

Keywords: Smectic elastomers; elastic moduli

INTRODUCTION

Liquid crystal elastomers (LCE) combine in a unique way the rubber elasticity of polymer networks with anisotropic properties of liquid crystalline phases [1]. The formation of an elastic network leaves the phase sequences and many anisotropic properties nearly unaffected, but it introduces a coupling between the orientation of the mesogens and macroscopic elastic deformations of the network. Ferroelectric smectic phases, due to their strong interactions with electric fields, open the possibility to switch the mesogenic orientation even in presence of the network [2]. A typical ferroelectric hysteresis can be mea-

sured. It has been shown that the switching properties of ferroelectric LCE depend strongly on the network topology [2, 3]. The dynamics and mechanical properties of ferroelectric LCE have been investigated with various experimental methods, for example with dielectric spectroscopy [6] Michelson-interferometry [4], Fourier transform IR [5] and AFM [7]. For the determination of elastic moduli of smectic LCE, mechanical methods have been introduced [8]. It has been shown that the elastic response of smectic LCE can be strongly anisotropic, the modulus for deformations normal to the smectic layer can exceed the entropy elasticity of the network by orders of magnitude.

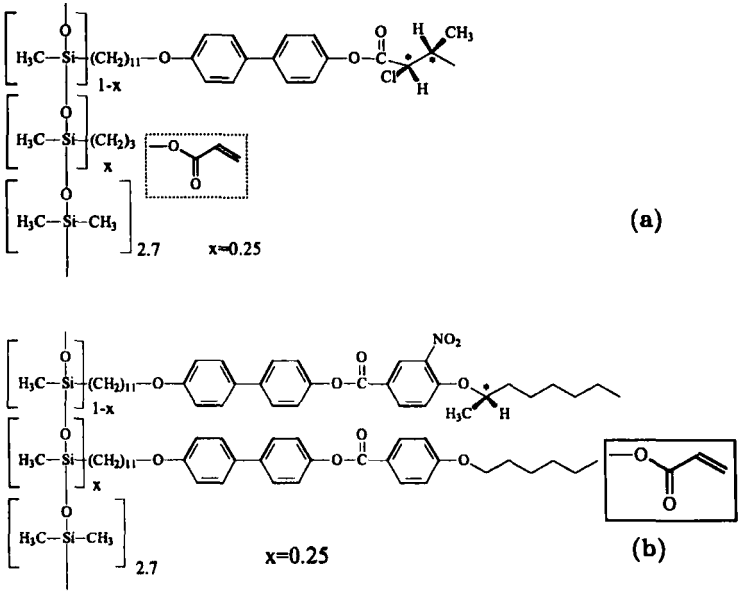

Figure 1: *Chemical composition of the polymers. (a) crosslinkable groups attached to the backbone by short spacers, (b) crosslinkable groups attached by spacers comparable to the mesogenic units,*

In this paper we present a method to determine elastic properties of smectic LCE from the inner pressure of LCE balloons. The technique is based on the preparation of smectic bubbles described earlier [9]. It allows the preparation of thin ordered membranes of FLCE and to study their viscous, elastic and plastic behaviour.

EXPERIMENT

The mesogenic materials are random side-chain copolymers containing mesogenic units and crosslinkable groups. The chemical compositions of the polymers are shown in Fig. 1. We compare two types of material here, one with the crosslinkable groups attached to the polymer backbone with short spacers. Here, crosslinking during UV irradiation will occur mainly within the smectic layers. Interlayer connections are formed only by the polymer backbone occasionally crossing the mesogen layers. The second type is built from polymers where crosslinkable groups are attached to spacers which are in length comparable to the mesogenic groups, and crosslinks will be created directly between different smectic layers. In the following, we will in short refer to the first material (Fig. 1a) as intralayer, to the second one (Fig. 1b) as interlayer elastomer. The phase sequences are *Cr 24° C SmC* 46-48° C SmA 67-69° C I* for the short spacer material (Fig.1a), and *Cr 52° C SmC* 89-90° C SmA 132° C I* for the long spacer material (Fig. 1b).

The experimental setup is basically equivalent to that described in [9, 10]. It consists of a copper thermobox with openings for optical observation and UV irradiation of the bubbles. A glass tube with its open end inside the thermobox is airtight connected to a pressure gauge and a syringe. A freely suspended film of the uncrosslinked polymer is drawn on the open capillary end and then inflated to a bubble by injecting air into the tube. After inflation, we irradiate the bubble with UV light, and the material is crosslinked, forming a thin smectic elastomer film. Film thicknesses are usually in the range of 1 to 5 micrometers. We determine the film thickness before crosslinking from optical transmission images of the bubbles [10]. When the material is completely crosslinked, the elasticity measurements are performed. The inner excess pressure and radius are recorded while the air volume in the balloon is varied. The relative uncertainty of the pressure measurements is better than 1 Pascal.

OBSERVATIONS

Before UV irradiation, the radius vs. pressure relation strictly follows the Laplace-Young equation $p = 4\sigma/R$, where R is the bubble radius and σ is the surface tension of the smectic material, p is the inner excess pressure. When the bubble is inflated, the radius of curvature of the membrane increases and the inner pressure consequently decreases.

Since the material is fluid and elastic forces in the smectic layer planes are absent, the bubbles have always exact spherical shape.

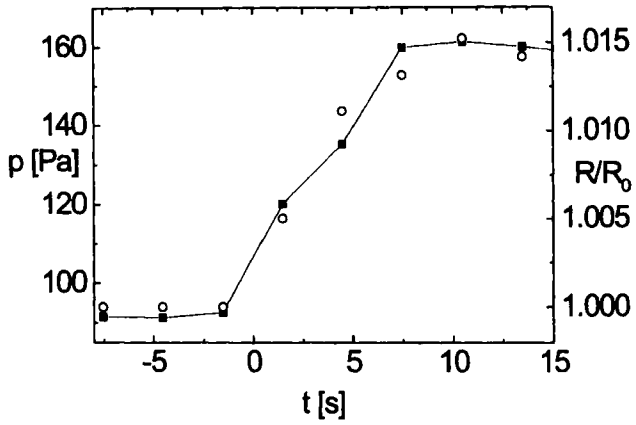

Figure 2: *Dynamic experiment with the interlayer elastomer at 139.1°C: comparison of the change of radius (open circles) and inner excess pressure (solid squares, line) after inflation of the balloon. R_0 denotes the radius at $p = 90Pa$. Within the experimental time resolution, equilibrium strain and pressure are established immediately.*

After the bubble has been irradiated with UV, the radius vs. pressure relation changes qualitatively and provides direct information about the state of crosslinking. Fig. 2 shows a typical characteristics of the inner pressure and respective balloon radius after air is pumped into the system. The elastic strain of the membrane after inflation leads to an increasing pressure in the balloon. The integration time of the pressure gauge limits the time resolution of pressure measurements to $\approx 1s$. Within this time resolution, the LCE material responds instantly. If the material were still fluid, one would expect a long term relaxation of the pressure accompanied by a slow expansion of the material. From long-term observations, we can exclude such effects for both investigated LCE. All elastic deformations of the balloons are completely reversible. When precautions are taken that the crosslinking is uniform everywhere on the membrane (uniform illumination, sufficiently homogeneous film thickness) the elastomer balloons retain

their shapes during inflation or deflation. Sometimes slight deviations from spherical shape are observed in the process of UV irradiation, such changes remain permanent when the network has finally formed.

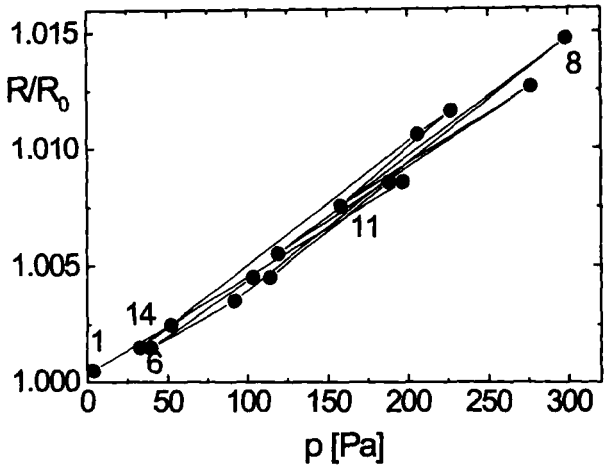

Figure 3: *Reversibility of the elastic deformations. The picture shows the radius expansion vs. pressure after a sequence of inflations and deflations of the material. Solid lines and numbers indicate in which sequence the experimental data have been obtained. The initial and final balloon radii at comparable pressures coincide within the experimental accuracy. Data shown for the intralayer material at 150.5°C.*

Figure 3 demonstrates the reversibility of the deformations. The sequence in which the data have been measured is indicated by the connecting straight line segments, some data points are labelled with the order of their appearance in the sequence. All data points can be fitted to a linear relation $R/R_0 \propto p$ where R_0 is the extrapolated balloon radius at zero excess pressure. The slope of this curve is a measure of the elastic modulus (see Discussion).

Figure 4 compares data for a balloon of the intralayer elastomer (solid squares) and one of the interlayer (open circles) elastomers. Both have comparable radii, the film thickness of the intralayer material is about 1.5 times larger that that of the interlayer balloon. It follows from the much larger slope for the interlayer material that its elastic

modulus must be considerably smaller than that of the intralayer elastomer, although the fraction of crosslinkable substituents is the same in the two basic polymers. We note in this context that the electrooptic properties of the two elastomers give (on first glance) a quite different picture of the influence of the network topology. The interlayer network has dramatic effects on the switching hysteresis of the SmC* phase in electric fields, in particular the switching times increase considerably. On the other hand, the intralayer network has only weak influences on both hysteresis curve and switching dynamics.

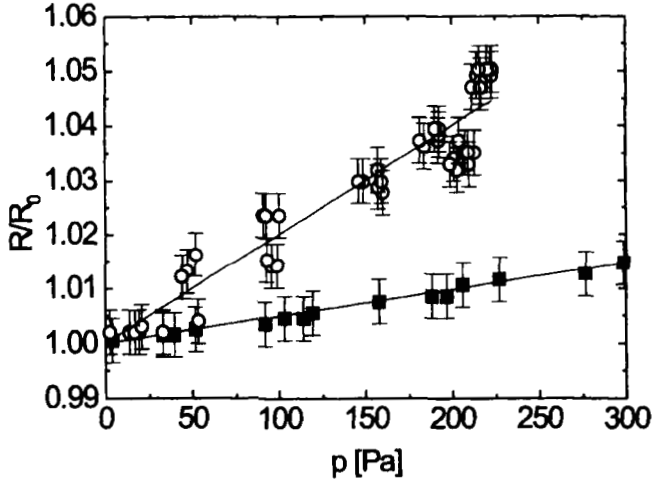

Figure 4: *Radius/pressure relation of the interlayer material (open symbols), balloon radius 2.57 mm and average film thickness 1.85 μm, T=139.1°C, and the intralayer elastomer (solid symbols), balloon radius 2.75 mm, average film thickness 2.7μm and T=150.5°C.*

DISCUSSION and SUMMARY

In order to establish a quantitative relation between the pressure, expansion and elastic moduli of the materials, the mechanisms for elastic behaviour have to be discussed. First, the network creates an entropy elasticity like in isotropic rubber. This elastic modulus should be observable in all phases of the material. It can be isotropic if the net-

work is non-oriented, but since the network topology seems to play an important role here one cannot exclude that the elastic modulus is different for strain in the smectic layer plane and normal to it. A theoretical treatment of the elastic properties of LCE including director effects in the mesogenic phases can be found, e.g. in a review article of Terentjev [11].

Second, one has to take into account that in the smectic mesophases an isotropic strain in the layer plane forces the material to reduce the film thickness, that is the spacing of smectic layers, to retain the volume. The compression of smectic layers is, however, penalized by a large layer compression modulus B. Another way to reduce the layer spacing in smectic phases could be the variation of molecular tilt in the smectic layers. In particular in the tilted smectic C phases, but also in the smectic A phase the material can achieve a reduction of the film thickness in case of isotropic in-plane stress by increasing the tilt angle, thus reducing the elastic term connected with the layer compression modulus. While these effects have to be considered in the smectic phases, only the entropy elasticity term remains in the isotropic phase. Therefore the curves presented in Fig. 4 have been measured at high temperatures where the uncrosslinked polymers both are in the isotropic phase. By polarizing microscopy we have made sure that the phase transitions are not significantly changed during crosslinking, therefore we can assume that the elastomers do not possess smectic order at these temperatures. For the discussion of the elasticity of the balloons it is therefore sufficient to consider entropy elasticity. A derivation of the relation between balloon pressure p, radius R and elastic modulus E for an isotropic material gives for small deformations

$$p \approx \frac{4D_0}{R_0} E \cdot \frac{R - R_0}{R_0}$$

where R_0 is the radius of the completely strain-free balloon, i.e. an extrapolation to $p = 0$, and D_0 is the corresponding film thickness. The elastic moduli extracted from the curves of Fig. 4 for the intralayer and interlayer material are 4.5 MPa and 1.65 MPa, resp.

It seems that the differences between the two network topologies in their electro-optic and elastic properties can be explained consistently: While the crosslinks in the interlayer material hinder the reorientation of the c-director dramatically, because they connect adjacent layers and fix the tilt azimuth of the mesogens, a stretching of the mate-

rial is easier than for the intralayer elastomer, because the crosslinks between the backbones are longer and thus much more flexible. In contrast, the quasi-2D crosslinking of the intralayer elastomer has weak influences on the switching behaviour since the coupling between adjacent layers remains weak. On the other hand the short crosslinks between the polymer backbones are much more rigid and therefore the rubber elastic modulus is noticeably higher.

A detailed investigation of the temperature dependence of the elastic properties and the variation of the portion of crosslinkable groups in the basic copolymers in forthcoming experiments will provide detailed information on the role of layer compression and induced tilt in the smectic mesophases.

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