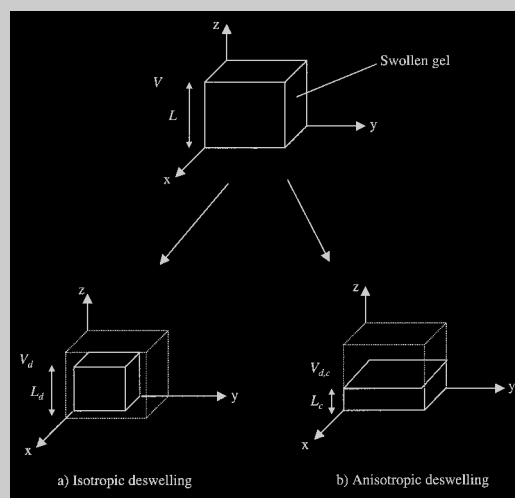


Communication: Cholesteric liquid single-crystal elastomers (LSCE) were obtained by an anisotropic deswelling method. The resulting network is investigated by means of optical microscopy and X-ray measurements, which reveals that this orientation method is suitable to obtain a highly ordered cholesteric LSCE with the helical axis being perpendicular to the biaxial extension axis.

Schematic representation of the isotropic and anisotropic deswelling process for LC networks.



Cholesteric Liquid Single-Crystal Elastomers (LSCE) Obtained by the Anisotropic Deswelling Method

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Introduction

The cholesteric or twisted nematic phase exhibits a helicoidal superstructure, characterized by pitch length p . If the cholesteric phase is uniformly ordered in the Grandjean texture in the direction of the pitch axis, circularly polarized light of the wavelength λ_R is reflected, where λ_R is directly proportional to p . Due to this exceptional optical property, cholesteric systems can be applied to reflective displays and optical filter systems.^[1]

The cholesteric state in polymer networks possesses additional properties due to the coupling between network and anisotropic phase structure. This allows mechanical fields to directly affect the liquid crystalline (LC) phase structure and state of order.^[2,3] Piezoelectricity and the variation of the helicoidal pitch emerge as mechanical field effects.^[4–7] To analyze these anisotropic mechanical effects, cholesteric liquid single-crystal elastomers (cholesteric LSCE) are necessary that are macroscopically uniformly ordered with respect to the cholesteric phase structure.

There exist essentially two synthetic approaches to obtain LSCE: i) A cholesteric monomer system or linear polymer is macroscopically ordered by an external electric/magnetic field or by surface alignment. Under these

conditions a crosslinking reaction is performed; ii) in a two-step crosslinking reaction, a network is synthesized. After gelation in the first step, a mechanical field is applied that causes a network conformation consistent with the uniformly ordered LC phase structure. Under these conditions, the crosslinking reaction is completed in the second step.

It is the advantage of the second approach to obtain samples that are not limited in their macroscopic dimensions. In this paper, we describe a new procedure to obtain cholesteric LSCE by an anisotropic deswelling method. This process causes a chain conformation of the networks that should be consistent with a uniformly ordered cholesteric phase, and we analyze whether the expected orientation of the helicoidal structure occurs.

Experimental Part

Synthesis

The synthesis of cholesteric elastomers follows the procedure of a hydrosilylation reaction (Figure 1) with poly[oxy-(methylsilylene)] (**1**). The solution consisting of 1 mmol of **1**, 0.9 mmol of achiral and chiral monomer (**2** and **3**), 0.033 mmol of **4**, and 5 μ l of the Pt-catalyst SLM86005

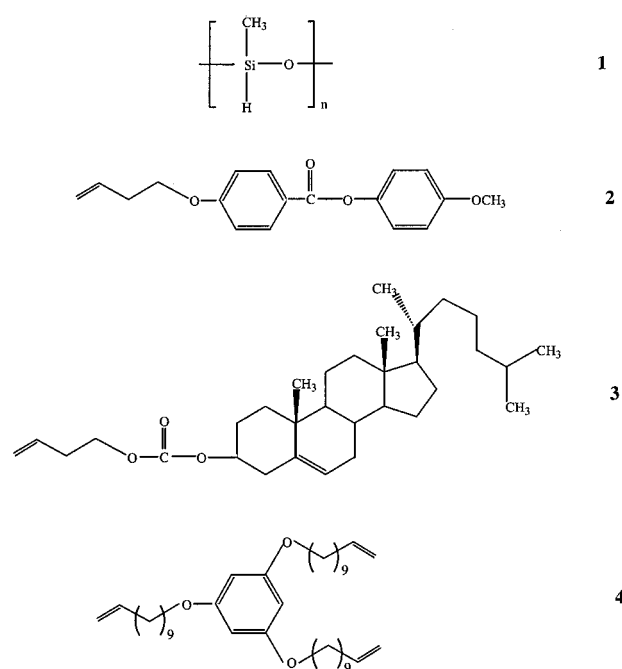


Figure 1. Chemical structure of the materials under investigation.

Table 1. Chemical composition and degree of swelling q of the elastomers.

Elastomer	Mole fraction of component				Degree of swelling q
	1	2	3	4	
ChoE 1	1	0.54	0.36	0.033	4.5 ± 0.1
ChoE 2	1	0.63	0.27	0.033	4.5 ± 0.1
ChoE 3	1	0.72	0.18	0.033	4.6 ± 0.1
ChoE 4	1	0.76	0.14	0.033	4.4 ± 0.1
ChoE 5	1	0.81	0.09	0.033	4.4 ± 0.1

(Wacker Chemie, Burghausen) in 1 ml toluene is filtered using a 0.05 μm Millipore® filter in a centrifuge cell with a diameter of 5 cm and a height of 1 cm, excluding dust particles. In order to avoid tack between elastomer and centrifuge cell, the inner wall of the cell is covered with a PTFE film. The hydrosilylation reaction is carried out under centrifugation (4500 r.p.m.) at 90 °C for 5 h. Thereafter, the solvent is allowed to evaporate slowly under centrifugation (4500 r.p.m.) at 90 °C over a period of 5 h. After removal of the elastomer from the PTFE support, the elastomer was additionally dried for 24 h at 60 °C in a vacuum oven. Typically, and depending on the dimension of the centrifuge cell, the dimensions of the network are $150 \times 10 \times 0.3 \text{ mm}^3$. The chemical composition of the synthesized elastomers is shown in Table 1.

Differential Scanning Calorimetry (DSC)

The elastomers were analyzed by means of differential scanning calorimetry (DSC-7, Perkin Elmer). Glass transition temperature T_g , cholesteric-to-isotropic phase transformation

Table 2. Glass transition temperature T_g (experimental error about ± 2 °C), cholesteric-to-isotropic transformation temperature $T_{n,i}$ and corresponding enthalpy changes $\Delta H_{n,i}$ of the elastomers.

Elastomers	$\frac{T_g}{^\circ\text{C}}$	$\frac{T_{n,i}}{^\circ\text{C}}$	$\frac{\Delta H_{n,i}}{\text{J} \cdot \text{g}^{-1}}$
ChoE 1	2	66 ± 1	0.8 ± 0.1
ChoE 2	3	67 ± 1	1.3 ± 0.1
ChoE 3	1	67 ± 1	1.4 ± 0.1
ChoE 4	1	67 ± 1	1.1 ± 0.1
ChoE 5	0	68 ± 1	1.1 ± 0.1

temperature $T_{n^*,i}$ and the corresponding enthalpy changes $\Delta H_{n^*,i}$ of the elastomers are shown in Table 2.

X-ray Diffraction Measurements

X-ray scattering measurements were performed with monochromatic CuK_α -radiation ($\lambda = 0.154184 \text{ nm}$) using a two-dimensional image plate system (700×700 pixels, 250 μm resolution). The incident beam was either in the x,y -direction or perpendicular to the film surface in z -direction (cf. Figure 2).

UV/VIS Spectrophotometer Measurements

The selective reflection wavelengths of the network were measured by means of UV/VIS spectroscopy at room temperature.

Refractive Index Measurements

The refractive indices of the network were measured with an Abbe refractometer at room temperature. Ordinary and extraordinary refractive indices n_o and n_e were determined by simply putting the LSCEs on the surface of the prism of the Abbe refractometer. For the nematic LSCE, the optical axis is parallel, for the cholesteric LSCE perpendicular to the surface of the prism. Under these conditions with linear polarized light, the ordinary and extraordinary refractive indices can be determined directly.

Swelling Experiments

To ensure that the crosslinking density of the networks is identical, the degree of swelling q was determined by swelling experiments in toluene at 25 °C. The sample dimensions in the swollen and unswollen state were obtained by means of optical microscopy. The values of q are shown in Table 1.

Results and Discussion

Concept

To obtain cholesteric networks with a monodomain structure, it is necessary to achieve a network conformation that is consistent with the helicoidal structure of the cholesteric phase. Since a cholesteric phase is a twisted nematic phase, the local director n is not constant in space

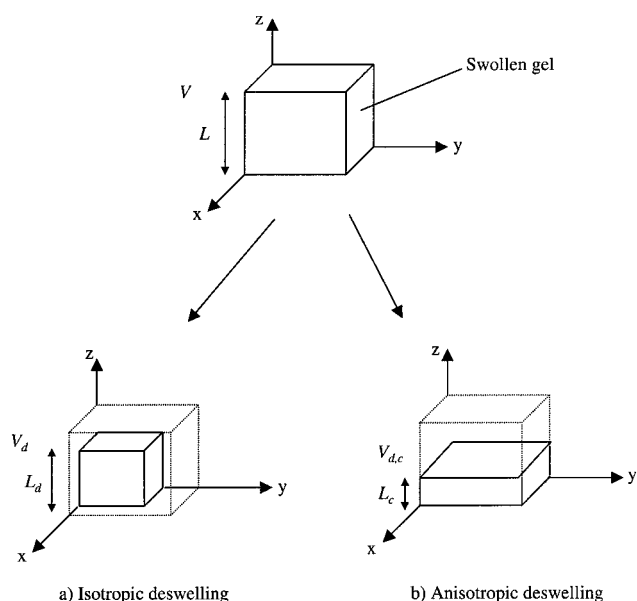


Figure 2. Schematic representation of the isotropic and anisotropic deswelling process for LC networks.

but helically arranged perpendicular to an axis that we call the z -axis. Because the local nematic chain conformation is prolate, the helicoidal arrangement of n in the z -direction will cause an overall oblate network conformation. This situation is very similar to a uniaxial compression of a nematic network in the z -direction that causes a planar orientation of the director with n perpendicular to the compression axis in the x,y -plane.^[8]

Unfortunately, a uniform uniaxial compression or biaxial mechanical deformation of a dry network or even of a swollen network causes experimental difficulties. To overcome these problems we make use of a deswelling process that is employed in the synthesis of the LC networks. Normally, a deswelling process is isotropic. The network deswells simultaneously in all dimensions and the spherical shape of the chain conformation of the network strands is not affected (Figure 2a). However, if the deswelling process is performed anisotropically, the chain conformation becomes modified. To obtain an oblate conformation that should cause a uniform orientation of the cholesteric structure, we applied an anisotropic deswelling process as indicated in Figure 2b. The process is accomplished in two steps to lock-in the network anisotropy.

In the first step, in a solution of the initial reactants, a weakly crosslinked gel is synthesized by a still incomplete crosslinking reaction. This isotropic gel exhibits a statistical, spherical network chain conformation.

The second step represents the key point of the orientation process. In contrast to the isotropic deswelling described in Figure 2a, the gel is allowed to deswell only in the z -direction while the dimensions in the x,y -plane stay constant (Figure 2b). During the deswelling process,

additionally the transformation of the isotropic gel into the cholesteric state takes place. Finally, under these conditions, the crosslinking reaction is completed.

The resulting network exhibits an overall oblate chain conformation that should cause a planar orientation of n in the x,y -plane. The basic question remains as to whether the spontaneous twist elasticity of the cholesteric phase is sufficient to realize a uniform Grandjean texture with the helix axis parallel to the z -direction.

Synthesis

For the synthesis of the cholesteric LSCEs, in the first step a partial addition reaction of poly(methylhydrogensiloxane) (**1**) with mesogens **2** and **3** and crosslinking component **4** is performed in the solvent toluene. The result of the first step is a weakly crosslinked gel with a statistical, spherical network chain conformation.

The second step is the deswelling process followed by the completion of the reaction. The crosslinked gel is allowed to deswell only in the z -direction while the dimensions in the x,y -plane stay constant (Figure 2b) by slow evaporation of the solvent toluene under centrifugation. During the deswelling process, the phase transformation to the cholesteric phase takes place.

The chemical composition and degree of swelling q of the synthesized elastomers are summarized in Table 1. As shown in Table 1, the composition of the mesogens is varied while the concentration of the crosslinking agent remains constant. Consequently, the crosslinking density of the networks should be identical, which can be identified by the swelling behavior of the networks. Assuming no variation of the solubility parameter by changing the ratio of the mesogenic side groups of the different networks, the swelling equilibrium and degree of swelling q should be identical. Actually, within the experimental error, q is the same for all elastomers. From these results it is confirmed that the synthesis of the elastomers is successful and reproducible. The cholesteric-to-isotropic phase transformation temperature $T_{n^*,i}$ is also not affected by the different compositions of the networks. DSC measurements reveal (Table 2) that $T_{n^*,i}$ stays constant within experimental error.

Structure of the Cholesteric Elastomers

The basic question, whether the anisotropic deswelling process yields a uniform alignment of the director in the x,y -plane and whether the spontaneous twist is sufficient to produce a Grandjean texture with the helical axis in z -direction, is already directly answered by visual inspection of the networks after the second crosslinking step. According to the concentration of chiral comonomer **3**, the networks reflect circularly polarized light of the wavelength λ_R .

This reflected light is analyzed by reflectivity measurements of λ_R at room temperature. The reciprocal reflec-

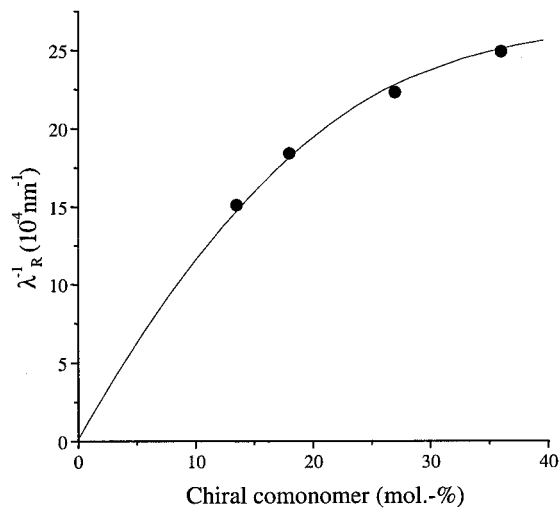


Figure 3. Reciprocal reflection wavelength vs the mole fraction of chiral comonomer at room temperature.

tion wavelength $1/\lambda_R$ as a function of chiral comonomer x_{ch} is shown in Figure 3. As expected, the reflection wavelength decreases as the chiral comonomer increases.

The refractive indices of pure nematic network and cholesteric networks were measured to obtain the helical twisting power (*htp*). The refractive indices n_o and n_e of pure nematic component in the cholesteric network can be obtained according to the following equations:

$$n_o = n_{e,\text{ch}}$$

$$n_e = (2n_{o,\text{ch}}^2 - n_{e,\text{ch}}^2)^{1/2}$$

$$n = (n_e + n_o)/2$$

Mean refractive index n as a function of chiral comonomer x_{ch} is shown in Figure 4. As expected, the refractive index decreases linearly as the chiral comonomer increases. From this, pitch p of the cholesteric networks can be obtained by $\lambda_R = np$.

The $1/p(x_{\text{ch}})$ relation can be fitted with a quadratic function^[9] and for $(dp^{-1}/dx_{\text{ch}})_{x_{\text{ch}} \rightarrow 0}$ we obtain a helical twisting power (*htp*) of $2.0 (10^{-2} \text{ nm}^{-1})$, which is similar to the *htp* of linear copolymers having the same chemical constitution.^[10]

To confirm the uniform alignment, additional X-ray diffraction measurements were performed. The diffraction pattern of elastomer ChoE2 at 23°C is shown in Figure 5a for the incident beam in the z -direction. A diffuse wide-angle halo with a uniform azimuthal intensity distribution is obtained, which confirms a planar oriented director. In Figure 5b, the incident beam is perpendicular to the z -direction, i.e. in the x,y -plane. The azimuthal maxima of the diffuse wide-angle reflection are located at $\varphi = 90^\circ$ and 270° indicating that the helical axis is

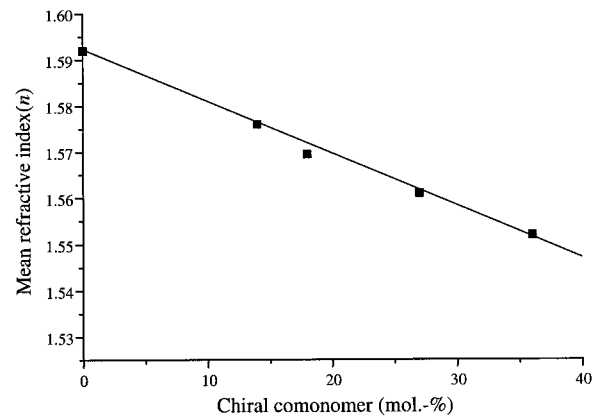


Figure 4. Mean refractive index vs the mole fraction of chiral comonomer at room temperature.

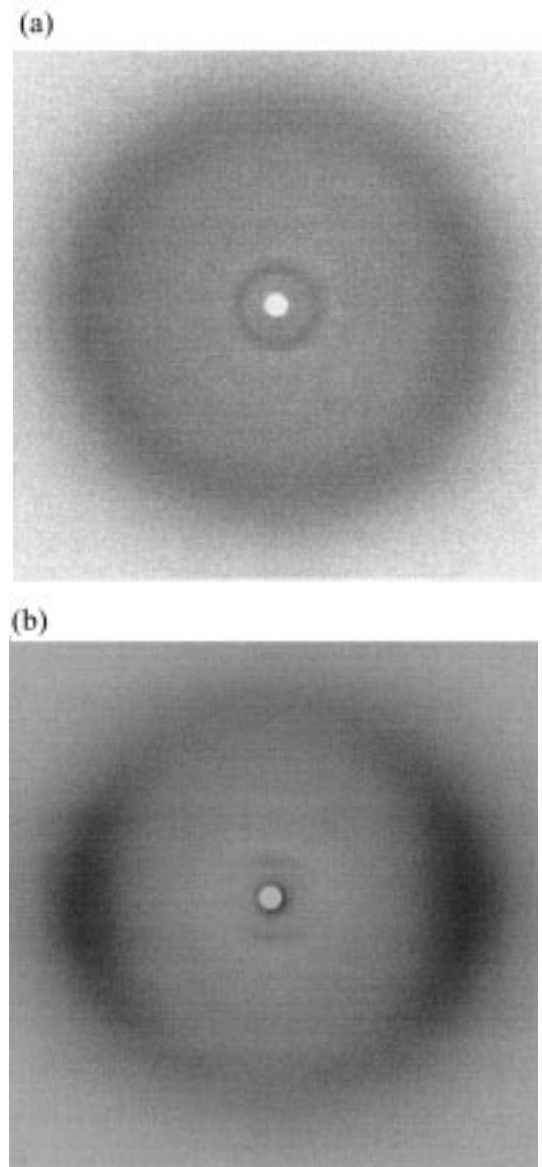


Figure 5. X-ray patterns of the cholesteric elastomer in (a) z -direction and (b) x,y -plane.

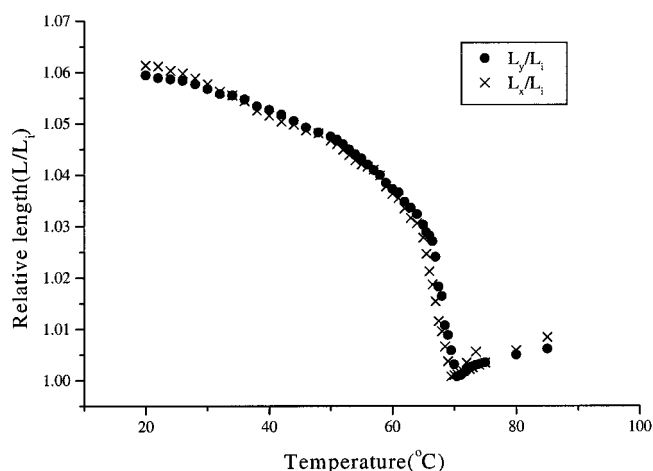


Figure 6. Dimensions of the network in x - and y -direction as a function of temperature.

oriented in the z -direction or perpendicular to the x,y -surface of the elastomer film. It should be mentioned that the diffuse halos at small angles are due to some smectic fluctuations in the cholesteric state. This behavior is quite common for binary systems, where one component exhibits a smectic phase (here the homopolymer with chiral monomer **3**).

From these results, it is verified that the synthesis procedure causes a highly ordered cholesteric elastomer, in which the helical axis is oriented in z -direction. Furthermore, the spontaneous twist elasticity of the cholesteric phase is sufficient to realize a uniform Grandjean texture. Obviously, the deswelling procedure causes an overall oblate conformation of the network strands, which is consistent with the cholesteric phase structure. To get a more quantitative insight into the efficiency of the deswelling process, the thermoelastic behavior of network ChoE2 is determined. The results are shown in Figure 6, where the dimensions of the network in the x - and y -directions are analyzed as a function of temperature. L_x and L_y are scaled to length L_i of the isotropic network at 67°C. At the isotropic-to-cholesteric phase transformation, the network spontaneously elongates equally in both directions. This spontaneous extension of the network in x,y plane causes the spontaneous compression in the z -direction, which is the direction of the helical axis. If we neglect the isobaric thermal expansion of the volume of the network, the spontaneous compression of the network at $T = 20^\circ\text{C}$ is about $\lambda = 0.88$ compared to the isotropic state.

It is interesting to compare this result with the deformation of the gel in the first synthesis step during the deswelling process. According to Figure 2, we have three different states: i) the swollen network with volume V , ii) the (macroscopically isotropic) dry network with V_d , and iii) the compressed network with $V_{d,c} = V_d$. If the com-

pression of the dry network followed the route from V_d via V to $V_{d,c}$, the compression would be $\lambda = L_c/L_d$ where L_c is the sample dimension in the direction of the compression axis. Because $L_c = LV_d/V$, the deformation becomes $\lambda = (V_d/V)^{2/3}$. For our networks, $V_d/V = 0.5$ and $\lambda = 0.63$. Under these conditions, the crosslinking reaction proceeds to completion. It has to be noted that the topology of the final network does definitely not correspond to a conventional dry network compressed with $\lambda = 0.63$.

Conclusion

Anisotropic deswelling of a partly crosslinked network causes an oblate network chain conformation that is sufficient to cause a macroscopic orientation of the cholesteric phase structure. This state of orientation is locked in by a proceeding crosslinking reaction. The overall oblate chain conformation of the final network is directly reflected in the spontaneous change of dimensions at the isotropic-to-cholesteric phase transformation. Already a simple visual inspection of the networks shows interesting opto-mechanical properties, which have to be analyzed in detail and compared to very recent theoretical predictions of mechanically induced director reorientation effects.^[11] This will be described in a forthcoming paper.

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