Nematic liquid single crystal elastomers

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1. Introduction

During recent years many applications of liquid-crystal (LC) side-chain polymers have been proposed, e. g. to use these materials for electro-optics (non-linear optics, NLO), integrated optics and storage devices. For all of these applications as well as for most quantitative measurements on LC polymers it is necessary to have samples with the optical axis of the LC polymer being macroscopically and uniformly aligned. Under these conditions where no defects of the LC structure are present, the LC polymers behave like single crystals with respect to their optical properties. However, the techniques commonly used to align liquid crystals, such as the application of electric, magnetic or surface forces, often fail for polymers. Only insufficiently aligned polymers are obtained which cannot be used for optical investigations and applications.

To overcome this problem, Broer et al. described a method starting from monomeric LC polymers which can be completely aligned by using conventional techniques[1]. By polymerizing these aligned multifunctional monomers, the uniform structure is fixed and highly crosslinked ordered polymers are obtained. In a completely different approach LC elastomers are used to get uniformly aligned LC structures[2]. Applying a mechanical field, excellently aligned samples are available. However, if the mechanical field is removed, the elastomers relax into the non-aligned state at temperatures above their glass transitions.

In this paper we describe a new approach which provides elastomers with permanent, macroscopically uniform alignment. These elastomers which are optically similar to organic or inorganic single crystals will be called Liquid Single Crystal Elastomers (LSCE).

2. Concept for LSCE

The analysis of the backbone conformation of an LC side-chain polymer yields a deviation from a statistical, spherical chain conformation[3-5]. Depending on the LC-phase structure and the linkage of the rigid LC moiety to the main chain, only a prolate or oblate chain conformation is consistent with the LC state. For the prolate (oblate) chain conformation the radius of gyration $R_{\parallel}$ parallel to the preferred orientation (director) of the mesogenic side groups is larger (smaller) than the radius $R_{\perp}$ perpendicular to the director (Fig. 1a, b). While for nematic polymers $R_{\parallel}/R_{\perp}$ is either $\approx 0,7$ or $\approx 1,3$, for smectic polymers the anisotropy of the radii of gyration is expected to exceed the nematic anisotropy towards a two-dimensional chain conformation with $R_{\parallel} \ll R_{\perp}$. The deviation from statistical spherical chain conformation costs

entropy which has to be compensated by the orientation energy of the side groups. While this holds without any external fields or surface effects on a local scale, on a macroscopic scale a compromise exists between a uniform director orientation and the corresponding uniformly anisotropic chain conformation by introducing local defects into the LC structure. On the macroscopic scale the material exhibits a director orientation close to an isotropic distribution which is most clearly demonstrated with smectic systems. Consequently, to obtain a macroscopic uniformly aligned system, the backbone conformation has to be consistent with the LC order over the whole sample dimensions.

From experiments with LC elastomers we learned that this uniform chain anisotropy can be easily realized by mechanical deformation[2]. Uniaxial elongation gives rise to a prolate, biaxial deformation to an oblate backbone coil, as schematically indicated in Fig. 1 (a), (b). Above a threshold deformation or threshold stress the network chains become sufficiently anisotropically ordered and give rise to a corresponding uniform orientation of the director. However, without mechanical field and above the glass transition temperature, these systems relax to the equilibrium state with an isotropic director orientation.
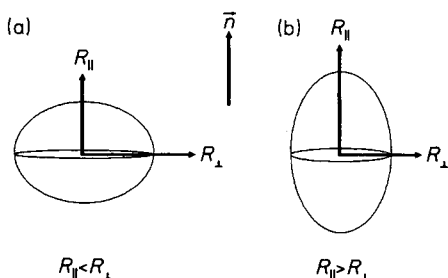

Fig. 1. Backbone conformation of LC polymers; (a) oblate with $R_\parallel < R_\perp$; (b) prolate with $R_\parallel > R_\perp$; $\vec{n}$ = director of the LC phase, $R_\parallel$ and $R_\perp$ being radii of gyration parallel and perpendicular with respect to the director

From these considerations and experiments the concept for LSCE is straightforward. A sufficient network anisotropy consistent with a macroscopically uniform director alignment has to be introduced into the elastomers by synthesis a priori. Under these conditions the LSCE will be stable without any external fields in the LC state and is formed reversibly at the isotropic-to-liquid-crystalline phase transformation. In the next section we will describe a synthesis route which follows this concept.

3. Synthesis and characterization of LSCE

For the synthesis of anisotropic networks the linear chains have to be ordered prior to the crosslinking reaction. This orientation can be achieved, e. g., in the melt under strain by simple extension[6]. To avoid experimental difficulties we decided to perform the crosslinking reaction in a two-step process, very similar to the procedure described by Greene et al.[7]. In the first step, a well defined weak network is synthesized. This network is deformed with a constant load to induce the network anisotropy. The load has to exceed the threshold load σ_{th}, which is necessary to obtain a uniform director orientation. In the second reaction step, a second crosslinking reaction locks-in the

network anisotropy. This two-step process benefits from the reproducibility of the induced network anisotropy before the final elastomer is obtained.

This concept has been realized by adding liquid-crystalline molecules and crosslinking components to poly(methylsiloxane)[a] (1) in a polymer-analogous reaction as shown in *Scheme 1*. In the first reaction step an equimolar concentration (with respect to the vinyl groups) of the liquid-crystalline monomer 2 and the two crosslinking components 3 and 4 is added to 1 in a solution of toluene.

Scheme 1:
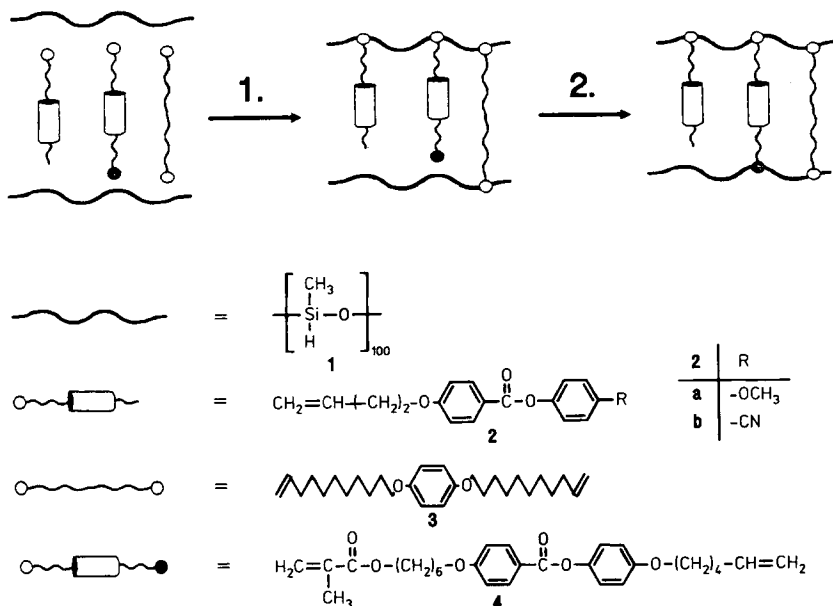
The key point of this reaction is the addition of the crosslinking component 4 with the functional vinyl- and methacryloyl groups. Detailed kinetic measurements of the addition reaction of vinyl- and methacryloyl-substituted derivatives to 1 have shown that under the experimental conditions the addition of the vinyl group is faster by approximately two orders of magnitude than the addition reaction of the methacryloyl groups[8]. Consequently in the first reaction step predominantly the crosslinking component 3 becomes active and forms an isotropic network in the solution. Thereafter the solvent is removed and the dry liquid-crystalline network is loaded above the threshold stress σ_{th} which causes the macroscopic director orientation. In the second reaction step at elevated temperature and under load the crosslinking process is completed via the methacryloyl groups. Finally the network is extracted with toluene to remove unreacted components and carefully dried.

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[a] Systematic IUPAC name: Poly[oxy(methylsilylene)].

The swelling process of the elastomers in toluene is highly anisotropic compared to a reference sample for which the second reaction step is performed without loading the elastomer. From swelling experiments together with the Flory-Huggins parameter calculated from the results of osmotic and light-scattering experiments the crosslinking density is estimated using the relation from Flory's swelling theory. The results are summarized in Tab. 1 and clearly prove that the reaction procedure enables the synthesis of highly anisotropic polymer networks which is reflected in the anisotropic swelling coefficient a. During the second crosslinking process the elastomer swells in the direction of stress by a factor of nearly 2 less (a_1) than perpendicular to the stress axis (a_2, a_3), whereas the reference sample with the isotropic network swells isotropically.

The elastomer exhibits a nematic phase. At the isotropic to nematic phase transformation a macroscopically uniformly ordered and completely transparent elastomer is formed reversibly without external field. The optical axis is oriented parallel to the axis of anisotropy of the network (stress axis during second crosslinking reaction). Optically the LSCE behaves like a single crystal of the same size.

Tab. 1. Swelling behaviour and average molar mass $\bar{M}_c$ of the strands of the networks of Liquid Single Crystal Elastomers (LSCE) (a_1 is parallel and a_2, a_3 perpendicular to the axis of applied stress during the second crosslinking process)

Sample	$a = \dfrac{L_{\text{swollen}}}{L_{\text{unswollen}}}$	$\bar{M}_c$ in g/mol from swelling experiment
LSCE	$a_1 = 1{,}1$	130 000
	$\left.\begin{array}{l} a_2 \\ a_3 \end{array}\right\} = 2{,}1$	
Reference sample	$\left.\begin{array}{l} a_1 \\ a_2 \\ a_3 \end{array}\right\} = 1{,}6$	93 000

X-ray measurements prove this structure and confirm the concept of LSCE. In Fig. 2 the LSCE is compared with the corresponding nematic liquid-crystal elastomer (LCE) with the isotropic network. The conventional elastomer is turbid and shows the small- and wide-angle halos typical for non-ordered nematics (Fig. 2(b)). The LSCE on the other hand is completely clear and translucent with an X-ray pattern characteristic for highly ordered nematics (Fig. 2(a)).

Simultaneously with the formation of the nematic phase at the isotropic-to-nematic phase transformation the LSCE macroscopically changes its shape by elongation of about 90% in the length parallel to the optical axis. This behaviour is similar to that of a conventional nematic elastomer with an isotropic network under constant *external* stress above the threshold stress for uniform orientation[2]. In this sense the LSCE possesses an *internal* mechanical field with the internal field strength σ_i tied up during the second crosslinking procedure. The internal field is also reflected in the nematic-to-isotropic phase transformation temperature, which is elevated by 2 K compared to
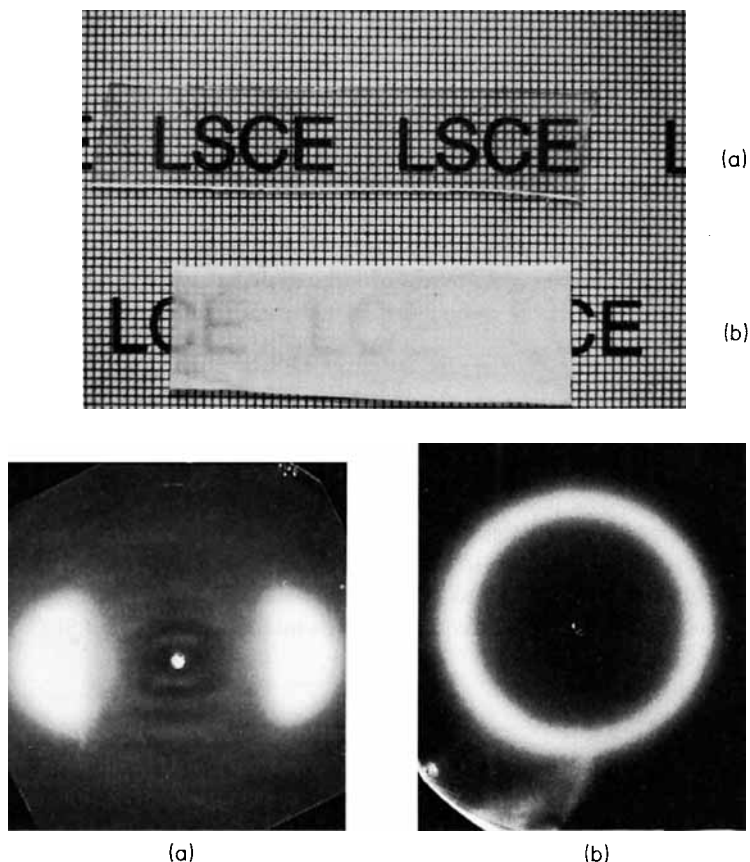
Fig. 2.   X-ray diagrams and photographs of (a) *Liquid Single Crystal Elastomers* (LSCE) and (b) the corresponding elastomer without load during the second crosslinking reaction

the corresponding reference sample with the isotropic network (see Tab. 2). The temperature shift towards higher temperature is consistent with previous experiments and theory[2, 9]. Finally it should be mentioned that at the glass transition the elastomer vitrifies to an anisotropic glass having the nematic structure.

Tab. 2.   Phase transition temperatures, nematic-to-isotropic phase transformation enthalpy $\Delta H_{n,i}$ and change of the isobaric specific heat ΔC_p at the glass transition of the *Liquid Single Crystal Elastomers* (LSCE). (The nematic-to-isotropic phase transformation temperature $T_{n,i}$ is determined by extrapolating the heating rate of the DSC-experiment to zero $K \cdot min^{-1}$)

	Phase transition temperature in K	$\dfrac{\Delta H_{n,i}}{J \cdot g^{-1}}$	$\dfrac{\Delta C_p}{J \cdot g^{-1} \cdot K^{-1}}$
LSCE	g 276 n 356	1,7	0,3
Reference sample	g 275 n 354	1,7	0,3

4. State of order and external mechanical field effect

Above the glass transition in the liquid-crystalline state the internal mechanical field (or tied-in network anisotropy) determines the orientation of the mesogenic side chain in the LSCE. Under the experimental conditions described above, the director is parallel to the stress axis applied during the second crosslinking process and parallel to the surface of the film. This allows the order parameter S of a free-standing film to be easily determined without any pretreatments. S is plotted in Fig. 3 versus the reduced temperature $T_{red} = T/T_{n,i}$ relative to the isotropic-to-nematic phase transformation temperature $T_{n,i}$. S has been determined by infrared dichroism measurements of the C≡N absorption band of the comonomer 2b using the simple relation for uniaxial phases

$$S = (A_\| - A_\perp)/(A_\| + 2A_\perp) \tag{1}$$

without corrections for the anisotropic inner field [10]. In this experiment the absorbances $A_\|$ and $A_\perp$ are determined from the integrated intensities of the CN absorption band with the incident light polarized parallel and perpendicularly to the director of the LSCE. The results are similar to nematic elastomers macroscopically ordered by an external field [2, 11]. It has to be noted that for $T > T_{n,i}$ in the pretransformation region a para-nematic order remains which is due to the internal field of the LSCE.
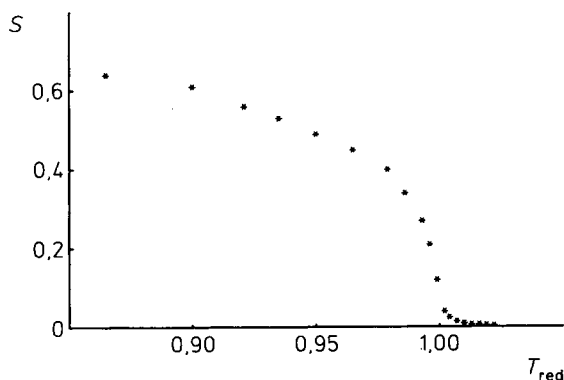

Fig. 3. Nematic order parameter S versus reduced temperature $T_{red} = T/T_{n,i}$ relative to the isotropic-to-nematic phase transformation temperature $T_{n,i}$ for Liquid Single Crystal Elastomers (LSCE)

Similar to reorientation effects of nematic systems in external fields, a director reorientation should be observed, if an external field is applied perpendicularly to the director of the LSCE and if the external field overcomes the internal field of the LSCE. This reorientation process is schematically presented in Fig. 4(a) – (c). In the beginning of the experiment (Fig. 4(a)) the director of the LSCE is located perpendicularly to the axis of the external mechanical field with the stress σ_e. For $\sigma_e < \sigma_i$ no reorientation occurs. If the external field equals the internal field with $\sigma_e \approx \sigma_i$ (Fig. 4(b)) three different arrangements of the director may occur, because this situation is similar to

a biaxial extension of the elastomer. As mentioned in Section 2 and Fig. 1, under these conditions an oblate backbone conformation exists.

Consequently:

i) if $\sigma_i = \sigma_e > \sigma_{th,b}$, where $\sigma_{th,b}$ denotes the biaxial threshold field, the director may become ordered perpendicularly to the internal and external stress axes. The elastomer is homeotropically aligned with respect to the surface of the film.

ii) if $\sigma_i = \sigma_e < \sigma_{th,b}$, the director may tend towards an isotropic orientation, i.e. the elastomer exhibits a "poly-domain" structure or

iii) the director is predominantly ordered within the $\sigma_i \sigma_e$ plane as schematically indicated with the upper scheme of Fig. 4(b).

If the external field overcomes the internal field with $\sigma_e > \sigma_i$ (Fig. 4(c)), the director should become ordered parallel to the external field being completely aligned for sufficient field strength σ_e.
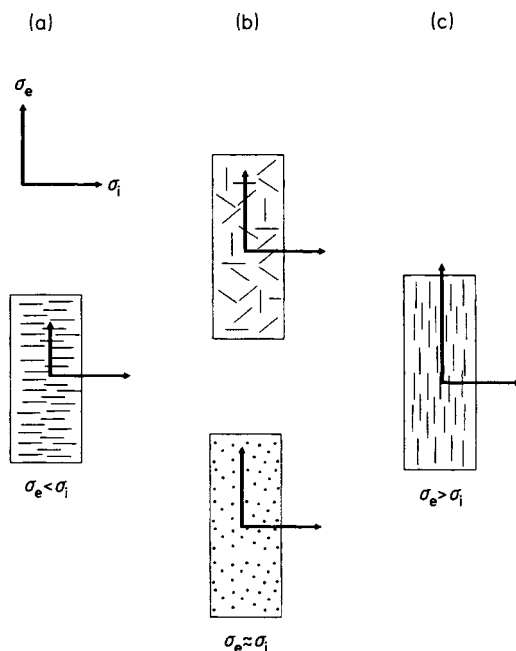

Fig. 4. Schematic representation of the director reorientation process with the external stress σ_e perpendicular to the internal stress σ_i. The bars indicate the director axis: (a) $\sigma_e < \sigma_i$; (b) $\sigma_e \approx \sigma_i$; (c) $\sigma_e > \sigma_i$

An isothermal experiment under equilibrium conditions confirming these considerations is shown in Fig. 5, where the dichroic ratio $R = A_\parallel / A_\perp$ of the CN-absorption band of **2b** and the external mechanical stress σ_e are plotted versus the elongation L/L_0 of the LSCE perpendicular to the director axis of the unstrained sample. In this experiment $A_\parallel$ and $A_\perp$ are related parallel and perpendicularly to the axis of the *external* stress σ_e (refer also to Fig. 4(a)−(c)). In Fig. 5 we can distinguish between three regions A, B, C with increasing stress σ_e.
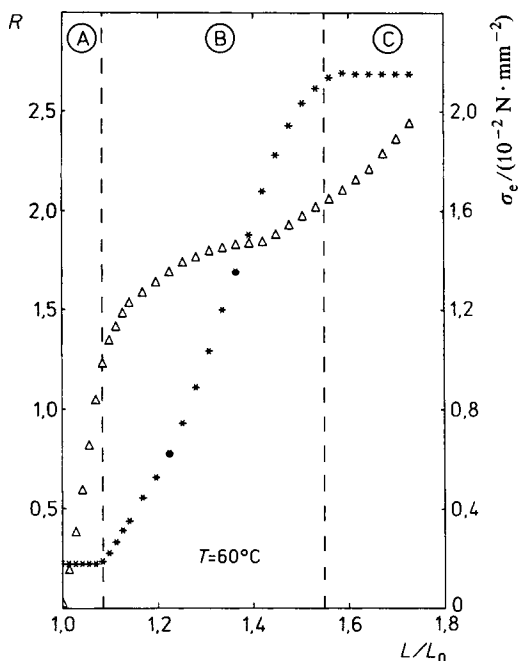
Fig. 5. Dichroic ratio R ($*$) and nominal external stress σ_e ($\triangle$) as function of the elongation L/L_0 of the nematic LSCE. The region A–C is described in the text. Temperature: 60 °C

In region A a linear stress-strain relation exists where the dichroic ratio R remains constant. According to Fig. 4(a) we can assume that in this region the director of the LSCE is perfectly aligned and with Eq. (1) the nematic order parameter $S = 0,53$. From the stress-strain relation Young's modulus perpendicular to the director axis of the LSCE is calculated to be $4,1 \cdot 10^{-2} \, N \cdot mm^{-2}$. The modulus differs considerably from the modulus parallel to the director axis which is $6,7 \cdot 10^{-2} \, N \cdot mm^{-2}$ as determined in a separate experiment. This also clearly proves the anisotropy of the LSCE.

In region B a nearly linear relation between R and strain exists while $\sigma(L/L_0)$ indicates a softening of the elastomer, since small changes of the stress cause large changes of the dimensions of the sample. If we assume that the nematic order parameter S is constant within this region, R reflects the director reorientation. This director reorientation is directly connected with the change of the sample dimensions displayed in the $\sigma(L/L_0)$ curve. Two facts have to be noted for region B:

i) the reorientation sets in at a distinct "threshold elongation" of $(L/L_0)_{th} = 1,1$ or corresponding "threshold stress". At this point the external mechanical field overcomes the orientation effect of the internal field of the LSCE.

ii) at $L/L_0 = 1,26$ the dichroic ratio R becomes one which indicates that $\sigma_i = \sigma_e$. According to Fig. 4(b) at this point either a "poly-domain" structure or a homeotropic orientation of the director exists. Actually under these conditions the sample strongly scatters light which is consistent with a polydomain structure rather than a homeotropic orientation. Therefore from this experiment we can conclude that the threshold stress $\sigma_{th,b}$ to obtain a homeotropic orientation by biaxial extension is larger than σ_e and σ_i at $R = 1$.

In the third region C, where R becomes independent of L/L_0 and σ_e, we can assume that the director is fully aligned parallel to σ_e with the nematic order parameter $S = 0,36$. This value is considerably below the value of S without external mechanical field in region A. Two arguments may explain this experimental result for region C:

i) the existing biaxial mechanical field due to σ_i and σ_e causes the effect and/or

ii) the LC crosslinking component 4 is not completely involved in the reorientation process and reduces the state of order. Consequently in region B the order parameter S is not constant as was assumed above but changes with σ_e. Only additional experiments with isotropic crosslinking agents can clarify this aspect.

5. Conclusion

The delicate interaction between backbone conformation and director orientation of the LC state enables the synthesis of exceptional systems which behave optically like single crystals having the same dimensions. However, numerous fundamental questions have to be quantified and solved with respect to network anisotropy or "internal mechanical field" and the interactions with the LC state. In this respect the liquid single crystal elastomers (LSCE) represent a new class of macromolecular systems distinguished by their macroscopically uniform anisotropy.

On the other hand, it is obvious to transfer the concept of LSCE to systems which are optimized in the LC moieties with respect to distinct physical properties such as non-linear susceptibilities [12], dichroic absorption, birefringence, dielectric anisotropy, etc. Furthermore it is straightforward to extend the concept to other synthesis routes and to duromers which are easily available by increasing the concentration of the crosslinking components. This will be described in a forthcoming paper. In this sense, the LSCE offer new interesting aspects for chemistry and applications.

6. Experimental part

Synthesis: The synthesis of liquid single crystal elastomers (LSCE) follows the well known procedure of hydrosilylation reactions with polysiloxanes [13]. The solution of 672 mg (2,25 mmol) of 2a, 45 mg (0,15 mmol) of 2b, 49,5 mg (0,12 mmol) of 3, 86,4 mg (0,18 mmol) of 4, and 9 μL of the Pt-catalyst SLM 86005 (Wacker Chemie, Burghausen) in 3 mL of absolute toluene is filtered using a 0,5 μm Millipore filter and filled 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 a Teflon® film. The reaction is carried out under centrifugation (4 000 r.p.m.) at 60 °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 30 min at room temperature. During this time most of the toluene evaporates and the elastomer becomes liquid-crystalline. Simultaneously the elastomer becomes carefully loaded with a stress of $2,4 \cdot 10^{-2}$ N · mm^{-2} which is above the threshold stress. Thereafter the film is annealed for 10 h at 30 °C and for 72 h at 60 °C to complete the crosslinking reaction. A second sample is prepared under similar conditions, however, without load during the second crosslinking reaction (poly-domain sample).

Swelling experiments: The crosslinking density was determined by swelling experiments in toluene. The average molar mass of the network chains, $\bar{M}_c$, was calculated according to Flory with $\bar{M}_c = \rho_e \cdot V_1 (0,5 - \chi)^{-1} \cdot q^{5/3}$ with ρ_e the density of the elastomer, V_1 the molar volume of the swelling liquid, q equilibrium volume ratio of the swollen and unswollen samples and χ the Flory-Huggins parameter. The χ parameter was calculated from the second virial coefficient

A_2 obtained from light scattering and osmotic measurements of a corresponding linear polymer with $\chi = 0.5 - A_2 \cdot \rho_p^2 \cdot V_1$. The results are summarized in Tab. 1 and have to be considered as relative values due to the imperfections of the theoretical approaches.

Differential scanning calorimetry and X-ray measurements: DSC measurements were performed with a Perking Elmer DSC-7. The X-ray diffractograms were obtained with a Philips PW 1730 and CuK_α radiation.

Mechanical and order-parameter measurements: The order parameter was determined by infrared-dichroism measurements of the $C\equiv N$ absorption band at $2229\ cm^{-1}$ in a Nicolet FTIR-spectrometer using linear polarizers. Simultaneously stress-strain measurements were performed in a home-constructed cell which is mounted within the spectrometer. Stress-, strain- and temperature were controlled via computer as described in detail previously[2, 14]. The experiments were carried out under equilibrium conditions.

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