Selected Macroscopic Properties of Liquid Crystalline Elastomers

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In this short review we give an overview over selected macroscopic properties of sidechain liquid crystalline elastomers (LCEs) focusing on three closely related topics a) the influence of relative rotations between the director and the strain field on various reorientation instabilities, b) the nonlinear stress-strain curves for the polydomain - monodomain transition and for the reorientation transition in LCE monodomains and c) the shear mechanical response of LCEs in the linear regime. We consider only already existing real materials and do not discuss hypothetical "ideal" systems. We conclude that all observations reported to date can be accounted for without invoking the concept of soft elasticity, but instead relying on macroscopic dynamics in the linear and the nonlinear domain.

1 Introduction

Liquid crystalline elastomers (LCEs) are a new class of materials [1] (compare ref. [2] for a review of the early work up to about 1998), which combine the physical properties of two subsystems, namely of a network (like in an elastomer) [3] and of mesogenic units (liquid crystalline building blocks) used to form liquid crystalline phases in low molecular weight materials (LMWs) [4]. When the mesogenic units are incorporated into the polymer backbones, the materials are called main chain systems [5] (compare also ref. [6] for early work on main chain LCEs), while for the case of mesogenic units attached to the polymeric backbone via a flexible spacer, one speaks about sidechain materials. Sidechain liquid crystalline elastomers have been pioneered by Finkelmanns's group [1]. Originally only polydomain sidechain LCEs could be synthesized. Starting, however, with the work of Küpfer and Finkelmann [7, 8] it became possible to generate monodomains of a LCE, a liquid single crystal elastomer (LSCE) by using two cross-linking steps, where the first one is used to generate a weakly cross-linked network, which is then stretched to induce a monodomain, whose director orientation is then in turn 'imprinted' by the second cross-linking step [7, 8]. Depending on whether the cross-linking is done in the isotropic or the nematic phase a material with different properties results. When the cross-linking is done in the nematic phase, this information is fixed in the vicinity of the cross-linking points leading to an 'imprinted' order (also often called 'frozen-in' order) [9]. This is brought out very clearly when a sample thus prepared is exposed

to a mechanical stress applied perpendicular to the original direction of the monodomain. In this case the degree of order of the reoriented sample is reduced considerably when compared to the original sample [7, 8].

Over the last decade and a half different types of LCEs have been synthesized and characterized including nematic [1], cholesteric [1], smectic A [1, 10], smectic C* [11] and discotic LCEs [12]. The potential applications one has in mind for these systems span a range from soft contact lenses in ophthalmology to soft actuators and components of artificial muscles [13] along with potential use as nonlinear optical elements including second harmonic generation and a cholesteric laser [14].

So far one has studied the physical properties of this new class of materials mainly as a function of temperature, length of the spacer or variations of the chemistry for backbone, cross-linker and mesogenic units. It is clear, however, that for potential applications the most attractive option will be a substantial response to the application of low electric fields. This has led over the last couple of years to the most recently intensifying investigation of LCEs swollen with LMW nematic phases. In the course of these studies one has found large volume changes and volume transitions [15–17] as well as quite significant electro-mechanical effects in small to moderate electric fields [18–20].

One of the fundamentally interesting issues in the field of liquid crystalline elastomers is the question of the physical consequences of the coupling between the two 'subsystems', namely the mesogenic parts and the network. For weakly cross-linked liquid crystalline elastomers and gels, it turns out that relative rotations [21, 22] between the two subsystems play a crucial role in the understanding of the reaction of liquid crystalline sidechain elastomers to external electric, magnetic and mechanical fields. This topic will therefore be discussed in the next section. As the cross-linking density is increased, the average number of mesogenic sidechains between two cross-linking points decreases and eventually the system

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loses its genuine liquid crystalline properties [23]. In such densely crosslinked thermosets [24, 25] there is no longer a clearly defined dynamic degree of freedom related to nematic ordering nor are there relevant relative rotations.

Another rather prominent feature of liquid crystalline elastomers is the observation of a plateau region with almost zero or small slopes for intermediate values of the strain in the static stress-strain curves for two situations: i) for the polydomain - monodomain transition [26], and ii) for the director reorientation in monodomains under the influence of an external mechanical force applied perpendicularly to the original director orientation [7, 8, 27, 28]. This phenomenon has been interpreted in the neo-classical Gaussian chain model [29] (compare ref. [30] for a detailed exposition of this model) to reflect the property of 'soft' or 'semi-soft' behavior in the sense that one of the linear elastic coefficients vanishes provided the material has undergone a *spontaneous* shape change at a phase transition at higher temperature [31]. In sections 2 and 3 we will analyze in detail the linear and nonlinear aspects of the stress-strain relations observed for liquid crystalline elastomers and we will critically compare the phenomena found in LCEs with those observed in other systems, which show plateau regions when a specific thermodynamic force (such as the mechanical stress or the electric current) is plotted as a function of a related macroscopic variable (such as the strain, the strain rate or the electric field).

2 Linear elasticity

2.1 De Gennes' free energy

To be specific we discuss first how the macroscopic variables to describe the macroscopic behavior of a nematic sidechain elastomer are chosen. We focus here on weakly cross-linked nematic side-chain elastomers, where it is possible to define appropriate dynamic macroscopic variables. Furthermore, in nematic main-chain elastomers one cannot define the variables as simply as it is done here, since one cannot separate between elastic and nematic contributions as clearly.

The uniaxial symmetry of the nematic phase is described by a unit vector $\hat{\mathbf{n}}$, the so-called director, for which one cannot distinguish between head and tail. Under the conditions of weak cross-linking the suitable thermodynamic variables are the variations $\delta\mathbf{n}$ of the director $\hat{\mathbf{n}}$ with $\hat{\mathbf{n}} \cdot \delta\mathbf{n} = 0$ [22].

First we consider small deformations. In this case a description using linear elasticity is appropriate. For the description of elastic deformations we use the strain tensor $\boldsymbol{\varepsilon}$ with $\varepsilon_{ij} = \frac{1}{2}(\nabla_i u_j + \nabla_j u_i)$, which is well known from linear elastic theory; u_i are the components of the displacement vector $\mathbf{u}$.

Relative rotations describing rotations between the network and the director field, are macroscopic variables, which have been introduced to the macroscopic description of liquid crystalline elastomers by de Gennes [21].

These relative rotations exist as macroscopic variables neither for low molecular weight liquid crystalline materials nor for ordinary rubbers. Their influence on the macroscopic dynamics and under the action of external fields has been studied for nematic sidechain elastomers in ref. [22]. The influence of relative rotations has also been studied for cholesteric elastomers [32]. In this case relative rotations arise under the influence of an external electric field (rotato-electricity) and, very recently, for uniaxial magnetic gels [33], which are obtained when the gelation is performed under the influence of an external magnetic field [34].

We note that these relative rotations are very similar in spirit as macroscopic variables as the relative translations, which are common for incommensurate crystalline systems, for which one has two density waves coexisting in one or more direction(s) with incommensurate repeat distances. We refer to ref. [35] for a detailed discussion of the macroscopic dynamics of such a system.

Using linearized theory the rigid rotation of a solid body is characterized by $\omega_{ij} = \frac{1}{2}(\nabla_i u_j - \nabla_j u_i)$. In a uniaxial system this motion can be divided into a rotation around and two rotations orthogonal to the preferred direction. Rotations around the preferred direction are characterized by $\omega^{\parallel} = \frac{1}{2} n_i \epsilon_{ijk} \omega_{jk}$; for relative rotations, however, only the orthogonal rotations are relevant, namely $\omega_i^{\perp} = n_j \omega_{ij}$ with $n_i \omega_i^{\perp} = 0$. Since the rotation of the director is given by the variations δn_i, the relative rotations finally read $\tilde{\Omega}_i = \delta n_i - \omega_i^{\perp}$ [21, 22].

To simplify the following discussions, we present an expression for the energy density of the system containing the contributions we need below quite frequently. The distortion of a nematic phase is described by the Frank distortion energy [4]. Since we consider the components of $\boldsymbol{\varepsilon}$ and $\tilde{\boldsymbol{\Omega}}$ as small quantities one can expand their contributions to the energy density up to quadratic order. Collecting these terms, the energy density E reads

$$
\begin{aligned}
E = \ & \frac{1}{2}K_1 \left(\nabla \cdot \hat{\mathbf{n}}\right)^2 + \frac{1}{2}K_2 \left[\hat{\mathbf{n}} \cdot (\nabla \times \hat{\mathbf{n}})\right]^2 \\
& + \frac{1}{2}K_3 \left[\hat{\mathbf{n}} \times (\nabla \times \hat{\mathbf{n}})\right]^2 + \frac{1}{2}c_{ijkl}\varepsilon_{ij}\varepsilon_{kl} \\
& + \frac{1}{2}D_1 \tilde{\Omega}_i \tilde{\Omega}_i + D_2 \tilde{\Omega}_i \varepsilon_{jk} n_j \delta_{ik}^{\perp} + E_0
\end{aligned} \tag{1}
$$

with the Frank constants K_1, K_2, K_3, the coefficients D_1, D_2 and c_{ijkl}, which are of uniaxial symmetry. Summation over repeated indices is implied in Eq.(1) and in the following. $\delta_{ik}^{\perp} = \delta_{ik} - n_i n_k$ is the transversal Kronecker delta. E_0 contains all terms present in a simple liquid. The relative rotations contribute to a self energy term ($\propto D_1$) and a coupling term between the relative rotations and the strain tensor ($\propto D_2$).

2.2 Relative rotations and their influence on instabilities in LCEs

The first suggestion for detecting the influence of the consequences of D_2 was made in the same paper this quantity was introduced [21]. De Gennes showed that

the stress-optical coefficient (the ratio between the applicable dielectric constant in a specific geometry and the applied mechanical stress) could be substantially enhanced by the presence of D_2. So far there appears to be no experiment that has followed up on this prediction. In 1996 Weilepp and Brand [36] analyzed the onset of the stripe pattern observed for a nematic monodomain LCE under the influence of an external stress applied perpendicular to the original director orientation by Kundler and Finkelmann [27,28] in the framework of macroscopic dynamics. It was shown in ref. [36] that relative rotations play a crucial role in the understanding of the onset of this spatially heterogeneous reorientation pattern. It was found that macroscopically a vanishing value of D_2 would make the onset of this pattern-forming instability impossible.

More recently Müller and Brand [37] analyzed in a macroscopic description the analog of the Frederiks instability in a nematic elastomer [38] and its competition with the undulation instability using the approach of Refs. [21, 22]. Here one denotes by Frederiks instability the reorientational instability which can arise when an electric or magnetic field is applied to a nematic LMW monodomain in the planar or homeotropic geometry with the external field perpendicular to the director orientation [4]. They showed for the splay Fredericksz geometry that the size and sign of D_2 play a crucial role in determining whether the analogue of a classic Frederiks instability results or whether it is replaced by an undulation instability.

2.3 Shear mechanical response

To make contact with our results on piezorheometry and the associated discussion of soft elasticity [39–43], we use the notation of ref. [21] and write the relevant parts of the energy density (1) in the form $E - E_0 \equiv E_g = E_n + E_e + E_{en}$. Here E_e is the conventional elastic energy for a uniaxial solid

$$
\begin{aligned}
E_e &= \frac{c_{11}}{2}(\varepsilon_{xx}^2 + \varepsilon_{yy}^2) + c_{12}\varepsilon_{xx}\varepsilon_{yy} \\
&\quad + c_{13}\varepsilon_{zz}(\varepsilon_{xx} + \varepsilon_{yy}) + \frac{c_{33}}{2}\varepsilon_{zz}^2 \\
&\quad + 2c_{44}(\varepsilon_{yz}^2 + \varepsilon_{xz}^2) + 2(c_{11} - c_{12})\varepsilon_{xy}^2
\end{aligned}
\tag{2}
$$

where the c_{ij} are the elastic constants. E_n is the Frank elastic energy for the director

$$
\begin{aligned}
E_n &= \frac{K_1}{2}\left(\frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y}\right)^2 + \frac{K_2}{2}\left(\frac{\partial n_x}{\partial y} - \frac{\partial n_y}{\partial x}\right)^2 \\
&\quad + \frac{K_3}{2}\left[\left(\frac{\partial n_x}{\partial z}\right)^2 + \left(\frac{\partial n_y}{\partial z}\right)^2\right]
\end{aligned}
\tag{3}
$$

where K_1, K_2 and K_3 are the Frank elastic constants [4]. E_{en} is the coupling energy between the director and the network

$$
\begin{aligned}
E_{en} &= \frac{D_1}{2}\left[(\Omega_x - \omega_x)^2 + (\Omega_y - \omega_y)^2\right] \\
&\quad + D_2\left[(\Omega_y - \omega_y)\varepsilon_{xz} + (\Omega_x - \omega_x)\varepsilon_{yz}\right]
\end{aligned}
\tag{4}
$$

where D_1 is the stiffness modulus of the relative rotations and D_2 is the coupling constant between relative rotations and elastic deformations. In writing down these equations, we have introduced the linearized strain tensor

$$
\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_i}{\partial x_j}\right)
\tag{5}
$$

and the rotations

$$
\omega_i = \frac{1}{2}\epsilon_{ijk}\partial_j u_k
\tag{6}
$$

with the displacement field $\boldsymbol{u}$. Since we are interested in the linear response region, we can describe director rotations by $\boldsymbol{\Omega}$ with

$$
\delta\boldsymbol{n} = \boldsymbol{\Omega} \times \boldsymbol{n}
\tag{7}
$$

and thus relative rotations by $\boldsymbol{\Omega} - \boldsymbol{\omega}$. To be specific we have chosen the uniaxial direction to be the z direction. Next we discuss the two specific shear configurations of interest in analyzing the experimental results presented in ref. [39]. When a homogeneous shear is applied in the plane perpendicular to the director we have for the associated elastic energy, taking into account that only $\varepsilon_{xy} = \varepsilon_{yx} \neq 0$,

$$
E_g = 2(c_{11} - c_{12})\varepsilon_{xy}^2
\tag{8}
$$

and thus for the hydrodynamic value of $G'_\perp$

$$
G'_\perp = 4(c_{11} - c_{12})
\tag{9}
$$

This result shows that there is for the perpendicular geometry no coupling between the director and the network in the hydrodynamic limit.

For the parallel geometry for which the director lies in the shear plane, which we have chosen to be the $x - z$ plane, we have for the generalized energy E_g (with $\varepsilon_{zx} = \varepsilon_{xz} = 2\omega_y$)

$$
E_g = 2c_{44}\varepsilon_{xz}^2 + \frac{1}{2}D_1(\Omega_y - \omega_y)^2 + D_2(\Omega_y - \omega_y)\varepsilon_{xz}
\tag{10}
$$

Minimizing E_g with respect to $\Omega_y - \omega_y$ and inserting the result into E_g we have

$$
E_g = 2\left(c_{44} - \frac{D_2^2}{4D_1}\right)\varepsilon_{xz}^2
\tag{11}
$$

This result clearly shows that the effective elastic modulus for shear in the plane containing the director is reflecting the coupling of the network and the director rotations leading to a reduction of the shear modulus c_{44} by the amount $D_2^2/4D_1$. We have therefore for the macroscopic shear modulus $G'_\parallel$ in the hydrodynamic regime

$$
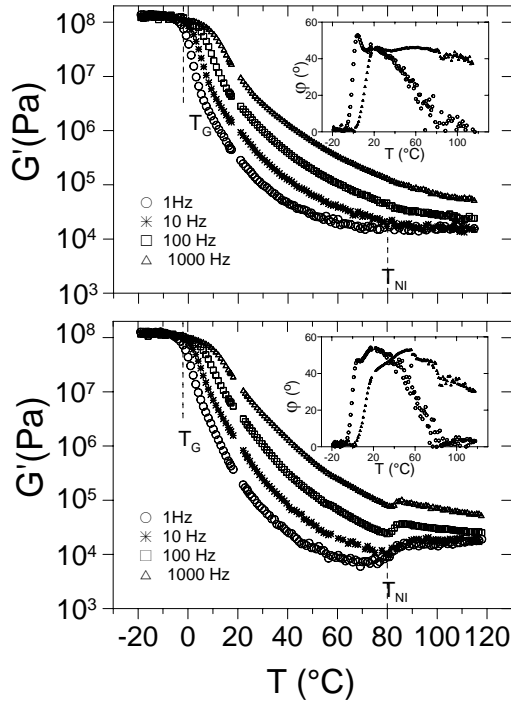G'_\parallel = 4\left(c_{44} - \frac{D_2^2}{4D_1}\right)
\tag{12}
$$

Fig. 1: Temperature dependence of the shear modulus $G'(T)$ and the phase shift $\varphi(T)$ for a monodomain sample. On the top the shear velocity $\mathbf{v}$ is perpendicular to the director and on the bottom the shear velocity is parallel to the director. In both cases one sees a dominant influence of the glass transition. For the parallel case there is also a slight reduction of G' in the vicinity of the extrapolated nematic - isotropic transition due to $\tilde{c}_{44} < c_{44}$. From ref. [39].

2.4 Soft elasticity

Using the neo-classical Gaussian chain model [30, 44, 45] it has been postulated that LCEs show 'soft elasticity', what corresponds to the requirement [44, 46]

$$\tilde{c}_{44} \equiv c_{44} - \frac{D_2^2}{4D_1} \equiv 0 \qquad (13)$$

where in the literature sometimes $\tilde{c}_{44}$ is called C_5. As we have seen above, this effective modulus is directly related to the shear modulus G of the LCE. Measurements of the shear rigidity modulus $G'_\parallel$ in the linear response regime are therefore a direct test of the soft elasticity concept. To rule out completely any role of soft elasticity for side-chain LCE, Martinoty's group has performed high precision experiments with a piezorheometer [39, 41, 43]. This is a technique designed to probe precisely the range of interest in the frequency domain, namely from ca. 10^{-2} to ca. 10^4 Hz. It has been successfully applied to study many aspects of liquid crystalline polymers and elastomers [47–52] as well as to the rheological behavior of polymers in samples of small thickness [53], to polyelectrolyte films [54], and to uniaxial magnetic gels [34]. In Fig.1 we have plotted the temperature dependence of the elastic modulus G' and of the phase shift φ between the elastic and viscous response, G'', for two geometries.
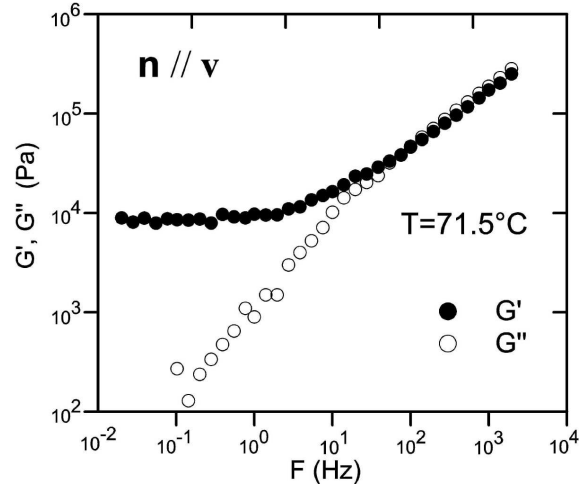

Fig. 2: G' and G'' for $\hat{\mathbf{n}} \parallel \mathbf{v}$ are shown for a frequency range down to frequencies of 0.02 Hz. From ref. [41].

The figure on the top shows the situation for which the director is perpendicular to the shear velocity $\mathbf{v}$, while the figure on the bottom shows the case $\mathbf{v} \parallel \hat{\mathbf{n}}$. While G' for the former geometry does not show any anomaly in the vicinity of the nematic - isotropic transition, it shows a dip for the latter geometry. This behavior can be easily accounted for [39] from the analysis of the macroscopic behavior of LCEs - compare also Eqs.(11) and (13) of the last section. Surely there is no indication whatsoever that G' would vanish anywhere.

To verify that the experiments were performed in the truly hydrodynamic regime, Fig.2 shows the behavior of G' and G'' in the frequency range down to 0.02 Hz. A clear-cut plateau value for G' is obtained, which confirms that the data displayed in Fig.1 do not show any low frequency anomaly down to the lowest experimentally accessible frequencies. For a more detailed discussion of dynamical aspects, cf. [42, 43].

Meanwhile the notion of 'soft elasticity' has been changed into 'semi-soft elasticity' meaning that $\tilde{c}_{44}$ is zero only in ideal systems, while in real systems it is finite, but small due to imperfections (for a list of those imperfections cf. [30]). Such a description would be reasonable, if the 'ideal' case would describe the basic features and the 'imperfections' would add some corrections. However, the measurements described above clearly show that $\tilde{c}_{44}$ is neither zero nor small, but of the order of the other elastic moduli, and therefore it is not appropriate to use it as a small perturbation. This conclusion does not come as a surprise, since recently Fried and Sellers [55, 56] have shown that the neo-classical Gaussian chain model [30, 44, 45] is incomplete and needs substantial modifications that render $\tilde{c}_{44}$ to be finite.

Some time ago it has been shown [31, 57] that isotropic solids that undergo a spontaneous change into an anisotropic state must have a zero shear modulus $\tilde{c}_{44}$ due to the Goldstone theorem. This symmetry argument,
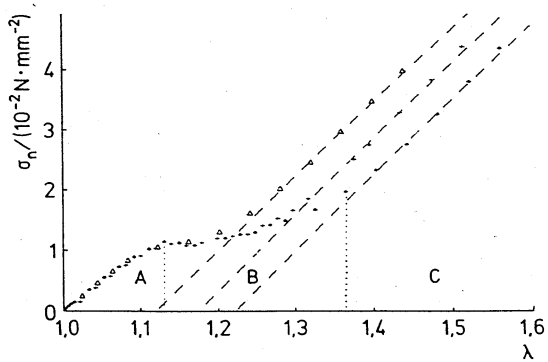
Fig. 3: The nominal stress σ_n is plotted as a function of the relative elongation λ $(= L/L_0)$ in the nematic phase for several reduced temperatures $T_{red} = T/T_c$: $(*) : 0.969$, $(+) : 0.991$, $\triangle : 0.996$. From ref. [26].

Fig. 4: The effective shear elastic modulus G'_{PL} of a poly-domain sample as a function of the relative elongation; the plateau of the stress-strain curve starts at $\lambda > 1.12$. From ref. [61].

however, is not applicable in the present case, since at the isotropic to nematic phase transition real side chain elastomers condense into a multi-domain structure without a shape change, if untreated. Only after stretching by an external force single domain elastomers are obtained. Then, of course, the shape anisotropy is not spontaneous, in particular for systems that are cross-linked for a second time in the stretched state. Like in ordinary anisotropic solids, there is no symmetry reason for $\tilde{c}_{44}$ to vanish.

3 Nonlinear stress-strain relations for LCEs

3.1 The polydomain to monodomain transition

The first observation of a plateau in a static stress-strain curve for liquid crystalline elastomers was described by Schätzle, Kaufhold and Finkelmann for a polydomain sample about 15 years ago [26]. They observed (see Fig.3) a linear relation between stress and strain for small (region A) as well as for large values of the strains (C). For intermediate values (B) a plateau region was found, the width of which diminishes when approaching the transition temperature T_c.

The behavior at small strains is the one familiar from almost all systems with a finite static shear modulus, which is in liquid crystalline elastomers due to the chemical cross-links. The plateau for intermediate values of the strain as well as the increase for even larger values of the strain can be understood in terms of the model put forward by Uchida [58,59], which takes into account elastic interactions [60] as well as random stresses. Uchida finds a plateau regime originating from a structural self-organization of domains due to the long range elastic interaction and emphasizes the role played by random internal stresses. Uchida demonstrates that the non-locality of the elastic interactions as well as the cross-linking conditions are crucial. He underlines the importance of both, the breaking of long range orientational
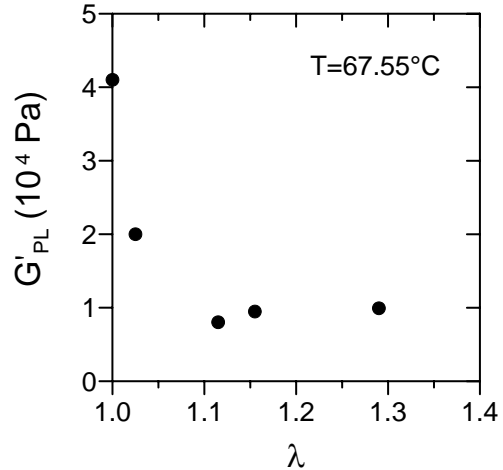
order by frozen internal stresses as well as the influence of quenched disorder on the mechanical response [59].

Clearly the plateau region is connected to the spatial heterogeneity associated with the transition from the polydomain to the monodomain structure. It is not related to a vanishing shear elastic modulus as has been verified directly by recent experiments of Collin et al. [61] shown in Fig.4. The effective modulus drops by a factor of 4, when stretched into the plateau, but is neither zero nor small. It should be noted that the waiting time between two shear measurements in Fig.4 is similar to that between two stress measurements in Fig.3 and, thus, both types of measurements correspond to the same 'equilibrium state'. Once the conversion from a polydomain to a monodomain has been achieved, an almost linear stress - strain behavior results at higher strains [58,59].

One does not expect the concept of soft elasticity to play any role for the plateau regime associated with the polydomain - monodomain transition, since for LCEs cross-linked in the isotropic phase no spontaneous overall preferred direction nor an accompanying shape change (but rather a randomly oriented domain texture) occurs when such a sample is cooled through the isotropic to nematic transition. Conversely, the plateau can be understood as due to the reorientation of the domains and does not require or imply a vanishing shear elastic modulus.

Thus we arrive at the conclusion that for the polydomain to monodomain transition the spatial heterogeneity caused by the many small domains plays the crucial role in the generation of the plateau in the static stress-strain curve.

3.2 The reorientation transition of LCE monodomains

Monodomains of LCEs were generated first by Küpfer and Finkelmann [7] using two cross-linking steps in the

nematic phase. In the first step a weakly cross-linked network was generated which was then stretched to allow for the second cross-linking step to take place on a time scale of about ten hours, fixing the information about the direction of the external mechanical stress within the network. That means that heating up such a LSCE into the (pseudo-) isotropic state and cooling down again into the nematic one, the former orientation is reobtained. This clearly shows [62] that nematic LSCEs are beyond the critical point, i.e. there is no true phase transition anymore and even in the (pseudo-) isotropic phase there is a small residual non-zero nematic order due to the imprinted directional information. Thus, the observed shape change at the isotropic to nematic transition is, although commonly called "spontaneous", not spontaneous in the sense of [31], but simply restores the state obtained by the second cross-linking step.

Later on it was argued [63] that a strong degree of spatial heterogeneity is responsible for the supercritical behavior, but very recently the group of Zalar [64] has shown that monodomains prepared according to the procedure of ref. [7] are beyond the critical point with a comparatively low degree of heterogeneity.

Already in this first report on such LSCEs, the authors also described an experiment, where an external mechanical stress was applied in a direction perpendicular to the fixed-in direction of the director. As a result, the static stress-strain curve had three regimes with a plateau-like regime at intermediate values of the strain – similar to the case of the polydomain - monodomain transition discussed in the last section – however with a much less well-defined plateau. This is shown in Fig.5 taken from ref. [7], which also shows the dichroic ratio indicating that above the intermediate plateau-like regime the director has rotated about 90°, and is parallel to the external stretch direction in the high strain regime. This reorientation was also monitored in the early experiments by x-ray diffraction [7, 8] and more recently by FTIR spectroscopy [65]. By the same experiments it became clear that the overall degree of nematic order was reduced after reorientation. The reorientation is reversible and after cessation of the external stress, the original perpendicular orientation is reobtained.

About a decade ago, Kundler and Finkelmann [27, 28] showed optically that the plateau in the stress-strain curve is closely related to the occurrence of a stripe pattern with domains of two different director orientations separated by domain walls. If the external stretching is not applied perpendicular to the director, but at an oblique angle, no stripe pattern has been observed [27]. Other biasing external fields, like magnetic fields or shear deformations, also prevent the evolution of clear stripe patterns [66]. No stress-strain measurements have been published for those cases. Clearly, the stripe texture is a spatially heterogeneous state. The occurrence of the plateau during the reorientation of LSCEs was interpreted as evidence for soft or semi-soft elasticity [29, 30]. However, as has been discussed above and shown in [43] there is no soft or semi-soft elasticity in
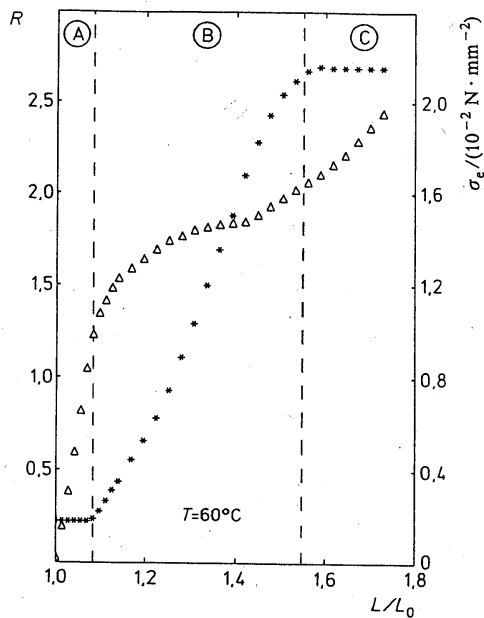

Fig. 5: The nominal external stress σ_e ($\triangle$) and the dichroic ratio R (*) are plotted as a function of the relative elongation L/L_0 of the nematic LSCE for $T = 60°C$. From ref. [7].

these LSCEs i.e. the shear elastic modulus is neither zero nor small. Indeed the initial slope of the stress vs. strain curve in Fig.5 gives a value of about 10^5 Pa for the elastic modulus demonstrating that there is no soft- or semi-softness involved. We do not believe that a theory, which is incapable of describing the linear elastic regime correctly, can be used to explain the physics of the nonlinear behavior. Instead, the key for understanding the plateau-like behavior very likely lies in the spatially heterogeneity of the system in this situation.

To support this hypothesis it helps to recall other systems for which one has observed experimentally, and analyzed theoretically, plateau regions when a thermodynamic force is plotted as a function of a thermodynamic variable. Typically, such a plateau region occurs for systems, which are no longer spatially homogeneous with respect to certain physically relevant quantities. Examples include the Gunn effect for which one observes charge domains with high and low carrier density in semiconductors [67–69] due to a negative differential resistance, the stress-strain curve in shape memory and martensitic alloys [70, 71] as well as in other alloys [72, 73] and the stress - strain-rate curves associated with shear-banding in metallic alloys [74] as well as in non-Newtonian fluids such as worm-like micelles [75, 76]. Finally the occurrence of a plateau region is commonly observed in the spatially inhomogeneous region of a system showing a two-phase region including the $p(V)$ (pressure vs. volume) diagram for van der Waals type behavior and the $p_a(A)$ (areal pressure vs. area) diagram for Langmuir-Blodgett films.

Of course, the physics of these systems is quite different from the LSCE case and they cannot be used as an immediate model, but in all these examples the plateau

is related to a 'two-phase' region of (either ordered or disordered) spatial inhomogeneities that occur to avoid thermodynamically forbidden negative slopes, e.g. a negative differential resistance for the Gunn effect, a negative compressibility in the van der Waals case, or a negative viscosity in shear banding. Quite similar, the plateau-like behavior in LSCEs during the director re-orientation appears to be due to the same type of mechanism, avoiding a negative elastic modulus in this case. This scenario has been corroborated by Conti et al. [77], who solved a model free energy of [29]. They found a plateau at intermediate strains, which is related to the occurrence of small-scale inhomogeneities due to director textures. Note that this model has a finite elastic shear modulus and can describe experiments only if for that modulus a nonzero value of the usual magnitude for polymeric networks is chosen. If the shear elastic modulus is put to zero, a 'plateau' of zero stress is trivially obtained and no initial regular elastic behavior with finite slope occurs in contrast to the experiments. Even for the LSCEs, whose second crosslinking step has been done in the isotropic phase, there is a finite plateau threshold (Fig.8 of [8]) in contradiction to soft elasticity. The finiteness of the plateau is not due to 'imperfections', but a necessary consequence of the production process of LSCEs, the second crosslinking step. Without it, there is never any monodomain material, but only polydomain samples, discussed in Sec.3.1.

Thus, soft elasticity does not correctly describe the physical origin of the plateau, i.e. the '2-phase behavior'. There is no reason that the description with a non-zero elastic modulus (that gets the physical picture right) is called 'semi-soft', since it is not just a small correction to the soft case, but is due to inherent properties of LSCEs.

4   Conclusions and perspective

In this short review we have summarized the current knowledge of two key issues concerning the physical properties of liquid crystalline side-chain elastomers, which are closely related: a) the role played by relative rotations between the network and the preferred direction characterizing broken rotational symmetry; and b) the physical picture and mechanisms behind the plateau region observed for the stress-strain curves for the poly-domain - monodomain transition as well as for the mon-odomains under an external mechanical stress applied perpendicularly to the 'imprinted' preferred direction.

For the future there are at least two outstanding challenges. First of all it will be important to calculate the stress-strain curve including the plateau from a fully nonlinear *macroscopic* theory incorporating both, the nonlinear Eulerian strain tensor as well as the complete nematic order parameter tensor, Q_{ij} [78–84]. We note, however, that this rather ambitious program has never been carried out in all detail for any of the systems showing plateau regions described in the last section. Therefore even the analysis of a model, which captures the essential ingredients and takes into account all the ap-propriate symmetry properties [85] would be a decisive step forward.

The other outstanding challenge is the issue whether soft LCEs in the spirit of Golubovic and Lubensky [31] exist. Certainly their theoretical description has led to many publications over the last few years [30, 57, 86–91]. The LCEs, which have been synthesized so far, however, do not satisfy the requirements of these theoretical models. The recent work of Fried and Sellers [55, 56] even suggests that it will be probably impossible to synthesize LCEs with the properties required in the theoretical work of Golubovic and Lubensky [31].

Another topic which will undoubtedly attract increasing attention in the near future are smectic A monodomain liquid crystalline elastomers. Their synthesis is fairly recent [92] and the analysis of their physical properties has just started [92,93]. For these materials one of the issues of interest in the framework of macroscopic dynamics is certainly the characterization of their nonlinear behavior including the questions whether relative rotations are as important as for nematic LCEs and whether there is also a plateau in the stress-strain curve for this class of materials. So far the nonlinear analysis was confined to a model based on Gaussian rubber elasticity [94]. In addition, it would be highly desirable from a modeling point of view to have quantitative data above, but close to the onset of the undulation instability [92, 93], since we have shown very recently [95], using the macroscopic approach, that the onset of the undulational instability in monodomain smectic A LCEs is associated with a forward bifurcation for all parameters investigated.

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