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Electronic Supplementary Information

Main-chain liquid-crystal elastomers versus side-chain liquid-crystal elastomers: similarities and differences in their mechanical properties

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Uniaxial SCLCEs: methods of preparation and main characteristics of the resulting SCLCEs. The most used method, initiated by Finkelmann, is a method combining chemistry and mechanics, called the two-step cross-linking process. It consists to slightly cross-link a side-chain liquid-crystal polymer (SCLCP), then to stretch the obtained network to orient the mesogens, and finally to fully cross-link the network to chemically fix the orientation of the mesogens.[6,7] These uniaxial SCLCEs have a director oriented in the plane of the film along the stretching direction. They are characterized by strongly stretched chains leading to a mechanical anisotropy[16,17,21], a chain anisotropy[5], a non-Gaussian elasticity[14] and to a supercritical state for which the mechanical properties of these elastomers remain anisotropic in the high temperature range where the sample state is supposed to be isotropic (no nematic-isotropic transition).[16,17,21] The other methods are more traditional. They consists in cross-linking by UV irradiation a nematic SCLCP oriented either by an E-field or an H-field[8-11] or by a surface treatment of the sample-bearing glass slides.[12] However, obtaining a well oriented uniaxial SCLCE is limited to thicknesses smaller than 100 µm, due to the limited penetration of the UV irradiation. The orientation of the director can be parallel to the plane of the LCE film (planar geometry), as for the two-step cross-linking process, or normal to the surface of the LCE film (homeotropic geometry). These uniaxial SCLCEs are characterized by slightly stretched chains leading to a chain anisotropy[5], and a mechanical anisotropy[17] both smaller than those observed for the uniaxial SCLCEs prepared by the two-step cross-linking process, a Gaussian elasticity[14], and a subcritical state located between the nematic and isotropic states[17].

Uniaxial SCLCEs: subcritical and supercritical states. The critical mechanical point introduced by de Gennes[15] establishes that the nature of the nematic-isotropic (NI) transition depends on the value of the deformation σ applied to the liquid-crystal network for orienting the director, compared to that of the critical strain σ_c for which the NI transition is second-order. If $\sigma < \sigma_c$, the NI transition can be first order with the orientation order parameter S showing a discontinuity from a finite but small value in the nematic phase to a zero value in the isotropic phase. The transition can also be slightly first-order, with S different from zero in the isotropic phase but decreasing rapidly to zero when the temperature increases. In this case, the sequence of states as a function of the temperature increase is as follows: a uniaxial nematic state with high values of S (typically $S \geq 0.6$), then a semi-isotropic state but still uniaxial with an order parameter $S \neq 0$ because of the presence of oriented nematic domains - it is the sub-critical or para-nematic state - and finally a completely isotropic state with $S = 0$. For $\sigma > \sigma_c$, there is no longer NI transition. The nematic state remains nematic with $S \neq 0$, even at very high temperatures. The SCLCE is in the supercritical state. The SCLCEs prepared by the Finkelmann group by the two-step cross-linking process are supercritical[16-19,21] and those prepared by UV-irradiation are subcritical.[17] High resolution specific heat measurements associated with deuteron nuclear magnetic resonance measurements taken on SCLCEs prepared by the two-step crosslinking process confirm that these materials are supercritical and show that they have a low degree of heterogeneity[19], which excludes the possibility of supercriticality due to a high degree of spatial heterogeneity.[20]

Uniaxial SCLCEs: Gaussian and non-Gaussian elasticity. A question raised by the difference between the methods of preparation of SCLCEs is related to the Gaussian or non-Gaussian nature of their elasticity. Since Gaussian elasticity is characterized by a decrease in the storage shear modulus, G', when the sample is swollen[13], this question was answered by measuring the complex shear modulus G^* as a function of the swelling degree of the uniaxial SCLCEs. This study shows that the elasticity is non-Gaussian for the uniaxial SCLCEs prepared by the two-step cross-linking process, and Gaussian for the uniaxial SCLCEs prepared by UV-irradiation.[14] The Gaussian or non-Gaussian nature of the elasticity is therefore associated with the elongation of polymer chains. This also explains why the uniaxial SCLCEs prepared by the two-step cross-linking process are supercritical whereas those prepared with UV light are subcritical. As it will be seen below, the situation is different for the MCLCEs since their subcritical or supercritical states depends on the cross-linking density.

Uniaxial SCLCEs: shear mechanical properties. The shear experiments carried out on non-Gaussian[16,17,21] and Gaussian[14,17] uniaxial SCLCEs show that the frequency response is composed of two regimes: a low frequency regime, which corresponds to the hydrodynamic regime for which G' is independent of the frequency and $G'' \sim f$, and a regime occurring at higher frequencies characterized by a power law $G' \sim G'' \sim f^n$ with a value of the exponent n ($n \sim 0.5$) indicating that the response is Rouse-type. Both regimes are temperature dependent, as shown by their shift towards the high frequency range as the temperature is increased. The data also show that there is no separation between the time scales of the director and of the network[16,21], contrary to the theoretical prediction.[24]

In addition to the determination of the frequency regime, the shear experiments also make it possible to determine the mechanical anisotropy of the material. When the director is oriented in the plane of the film, as is the case for a uniaxial SCLCE prepared by the two-step cross-linking process, the shear applied in the directions parallel and perpendicular to the director gives access to the anisotropy of the shear modulus. For a shear applied in the direction parallel to the director, the shear modulus $G'_{\parallel}$ decreases due to the coupling between the shear and the director, as introduced by de Gennes.[1] In contrast, this coupling does not exist for a shear applied in a direction perpendicular to the director, and therefore $G'_{\perp}$ exhibits the conventional behavior of a rubber. This difference in behavior, which leads to the anisotropy in the shear modulus G' from the fact that one (C_5) of the five elastic constants of a uniaxial elastic medium is renormalized by the coupling between the strain and the director. This renormalized constant called $\tilde{C}_5$ (in literature this constant is sometimes called $\tilde{C}_{44}$), is smaller than C_5 and is directly measured by $G'_{\parallel}$. As a result, *G′* has an anisotropy governed by the value of the elastic constant $\tilde{C}_5$. A small anisotropy corresponds to a value of $\tilde{C}_5$ comparable to that of the other elastic constants, and a large anisotropy to a small value of $\tilde{C}_5$. The results show that the anisotropy corresponding to the hydrodynamic regime is small for all the SCLCEs prepared by the two-step cross-linking process.[16,17,21] A shear anisotropy, but still smaller, is also observed for the SCLCEs prepared by UV-irradiation.[17] The mechanical anisotropy of the network is therefore strongly influenced by the process of preparation used. The greater anisotropy of the uniaxial SCLCE prepared by the two-step cross-linking process can therefore be explain by the stiffness of the polymer chains resulting from their elongation associated with the stretching of the network used for orienting the director. Since the UV-preparation method also makes it possible to obtain a uniaxial SCLCE with a director aligned in a direction perpendicular to the plane of the film, the shear modulus G'_{normal} can be measured. The comparison between the G'_{normal} and $G'_{\parallel}$ behaviors shows that the relationship $G'_{\parallel} = G'_{normal}$ predicted by the theory[24] is verified in the hydrodynamic regime.[17] The results also show that the temperature range where the shear anisotropy persists above T_{DSC} is much smaller for the SCLCE prepared by UV-irradiation than for the SCLCE prepared by the two-step cross-linking process. Since the latter is supercritical[16,17,21] with highly stretched polymer chains, this observation suggests that the uniaxial SCLCEs oriented by the E- or H-fields are subcritical with polymer chains that are only slightly stretched. The difference in stiffness of the polymer chains contributes to the difference in shear anisotropy between the uniaxial SCLCE prepared by the two-step crosslinking process and the uniaxial SCLCE prepared by UV irradiation.

Uniaxial SCLCEs: anisotropy of polymer chains. The anisotropy of polymer chains can be determined from thermo-elastic measurements, which consist in measuring the spontaneous change in the length of the film in the direction parallel to the director, when the temperature is changed. The anisotropy is given by $r = (L/L_0)^3$ where the length L of the film is renormalized with respect to the length L_0 measured at high temperature.[23] The results[5] show that r is much smaller for the film prepared by UV-irradiation ($r < 2$) than for the film prepared by the two-step cross-linking process ($2 < r < 4$), as observed on a macroscopic scale for the shear mechanical anisotropy. Thus, the elasticity of the polymer chains contributes to the elasticity of the network. The more the polymer chains are stretched, the greater the anisotropy of the chains and the greater the shear mechanical anisotropy. However, the relationship between r and the spontaneous change in film length L is based on Gaussian elasticity. If the elasticity is non-Gaussian, as is the case for the film prepared with the two-step cross-linking process, the relation $r = (L/L_0)^3$ probably does not apply rigorously, but should describe qualitatively the thermal variation of r.

Uniaxial SCLCEs: soft and semi-soft elasticity. The elasticity of SCLCEs has given rise to a long debate about the applicability of the concept of soft elasticity to these materials.[30] Soft elasticity originates from the hypothetical spontaneous formation of an elastic solid with an internal degree of freedom emerging from an isotropic phase. This phase transition breaks the rotational symmetry of the isotropic phase and induces a Goldstone mode characterized by the vanishing of an elastic constant.[25] In the case of SCLCEs, the vanishing elastic constant is $\tilde{C}_5$.[26-28] However, laboratory-prepared uniaxial SLCEs do not spontaneously form from an isotropic phase, because their formation requires a certain alignment field. To take this fact into account, the zero value of $\tilde{C}_5$ has been replaced by a value that is non-zero but very small.[28,29] Thus, the uniaxial SCLCEs are said “soft” or “semi-soft” depending on whether $\tilde{C}_5$ is respectively zero or very small. The soft or semi-soft elasticity concept can be tested by shear experiments, since $G'_{\parallel}$ directly measures $\tilde{C}_5$ The results obtained in the hydrodynamic regime show that the value of $\tilde{C}_5$ is not small but similar to that of the other elastic constants, demonstrating that the soft or semi-soft elasticity concept does not apply to both the non-Gaussian[16,17,21] and Gaussian[17] uniaxial SCLCEs.

Semi-soft elasticity has also been extended to the dynamic case when SCLCEs are subjected to low-amplitude sinusoidal shear, assuming separation of time scales between the director and the network[24]. This theoretical extension predicts the existence of a semi-soft elastic plateau, which should appear at frequencies lower than those of the usual rubbery plateau. This low frequency elastic plateau is not observed, showing again that soft or semi-soft elasticity does not apply to uniaxial SCLCEs.[16,17,21]

Uniaxial SCLCEs: stress-strain experiments. The stress-strain experiments performed by stretching a SCLCE in a direction perpendicular to the initial orientation of the director (reorientation transition) revealed that the stress-strain curve has three distinct regimes corresponding to the small, intermediate and high strains induced by the increase of $\lambda = L/L_0$ where L and L_0 are the lengths in the stretched and the un-stretched state, respectively. The regime of small strains is characterized by an increase of the stress proportionally to the imposed strain λ , until a threshold strain λ_1. This is the classic rubbery response allowing the determination of the Young modulus E. Above λ_1, the stress increases more slowly or remains constant up to a threshold strain λ_2. This regime of the intermediate strains corresponds to the reorientation of the director. The region above λ_2 is the region of high strains for which the stress increases again with the strain, as for a conventional rubber. In this region, the director rotation is completed, and the director is parallel to the stretching direction. These stress-strain behaviors have been observed for samples prepared with the director oriented either by the mechanical stretching associated with the two-step cross-linking process[6,7,28,33], or by a magnetic or an electric field[8,11], or by a surface treatment of the sample-bearing glass slides.[12] Due to the Gaussian and non-Gaussian elasticity of the different SCLCEs, the neo-classical model[2,28,29,34-36] based on the Gaussian rubber elasticity theory well describes the stress-strain curves of Gaussian SCLCEs (i.e., those which are oriented before cross-linking with UV-irradiation)[17] and not the stress-strain curves of the non-Gaussian SCLCEs (i.e., those oriented mechanically).[17] Another question concerns the slope *p* of the flat (nearly flat) elastic plateau, which, according to the neo-classical model, is given by $p = \tilde{C}_5 \left[1 - {}^{1}\!/_{r\lambda_1^3}\right]$[17], and which has been interpreted as a consequence of soft (semi-soft) elasticity. [2,28,29] The quantitative check done with the E-field oriented Gaussian SCLCE, for which all the parameters are known ($\tilde{C}_5$ from the shear experiments performed in the hydrodynamic regime, λ_1 from the stress-strain curve, *r* from the thermo-elastic measurements) shows that the value of $\tilde{C}_5$ calculated from the slope *p* is not small and fully consistent with the measured value of $\tilde{C}_5$ ($\sim 4.7\ 10^4$ Pa), which shows that the elastic plateau is not due to soft (semi-soft) elasticity, as it was first believed.[2,28,29] It should be noted that in literature the elastic plateau is called the soft (or semi-soft) elastic plateau creating a lot of confusion in the scientific community since this plateau is not associated with the concept of soft (or semi-soft) elasticity. To avoid this confusion, soft (or semi-soft) elastic plateau should be replaced by flat (or semi-flat) elastic plateau. Such flat elastic plateaus have been observed in stress-strain curves of different types of systems that do not involve soft elasticity, such as elastic foams under compression[31], plastic foams under stretching, but in this latter case the elastic plateau is often truncated by the cell alignment[31], or even in a DNA molecule under streching[32].

Stress-strain experiments were also performed on poly-domain SCLCEs to obtain uniaxial SCLCEs.[7,40-43] The stress-strain curves are also characterized by an elastic plateau, theoretically attributed to soft elasticity (rotation of the director of the nematic domains with no energy cost)[44], or to a spatial heterogeneity change caused by the many small nematic domains.[45] Recent experiments on Gaussian SCLCEs show that the polydomain-monodomain transition depends on the genesis of the poly-domain sample with an applied strain that is smaller for a poly-domain sample prepared in the isotropic phase (isotropic genesis) than for a sample prepared in the nematic phase (nematic genesis).[46] This means that the constraint for rotation of the nematic domains is more robust for nematic genesis than for isotropic genesis, which leads to different nematic textures observed under an optical microscope.[47] The main features of the history of cross-linking are in qualitatively agreement with the results of the simulation work based on the spatial heterogeneities associated with the poly-domain - mono-domain transition .[45]

Uniaxial SCLCEs: shear measurements carried out during the reorientation transition of a uniaxial SCLCE. These experiments were carried out to check if the elastic constant $\tilde{C}_5$, which is different from zero for a relaxed sample, vanishes for the two thresholds λ_1 and λ_2 of the strain when the uniaxial SCLCE is stretched in a direction perpendicular to the initial orientation of the director. Such a behavior of $\tilde{C}_5$ predicted by the extension of the neo-classical model[37] and the biaxial model[38] can be observed only in the particular situation where the applied sinusoidal shear is parallel to the stretching direction and perpendicular to the initial orientation of the director. This behavior has been called semi-soft response, which still disorients the reader because it has nothing to do with the concept of soft (semi-soft) elasticity for which the small $\tilde{C}_5$ value represents an intrinsic property of the SCLCE network (see section: soft and semi-soft elasticity), but with tensile elasticity. In fact, this $\tilde{C}_5$ behavior can be seen as resulting from a soft mode associated with a second-order phase transition induced by the external stress λ, when λ tends to λ_1 or λ_2. A bifurcation-type model[39] based on non-linear relative rotations between the director and the network, and which therefore does not involve any notion of soft or semi-soft response, also leads to a similar conclusion, *i.e.*, the vanishing of an effective shear modulus at λ_1 and λ_2. The experiments were made on the Gaussian uniaxial SCLCE prepared by UV-irradiation of the nematic polymer oriented in homeotropic geometry. They show that the stretching of the sample does not significantly modify the *G*' value measured without stretching, and that the decrease in *G*' predicted when λ tends to λ_1 is not observed.

On the other hand, a dynamic light scattering study carried out on non-Gaussian uniaxial SCLCEs prepared with the two-step cross-linking process and tri-functional cross-linkers, revealed the existence of a dynamic soft optical mode when λ increases and tends to λ_1.[33] This result raises the question of whether this dynamic soft optical mode is coupled or not to the soft elastic mode characterized by the vanishing of the shear modulus $\tilde{C}_5$ at λ_1**.** Performing simultaneous mechanical and optical measurements on the same uniaxial SCLCE as a function of the stretch will solve this question.

Uniaxial MCLCEs: methods of preparation. Uniaxial MCLCEs are more difficult to synthesize than uniaxial SCLCEs because of the difficulty of obtaining a well-defined network with low soluble content.[47,48] The uniaxial MCLCEs prepared in the Finkelmann's group were synthesized in a one-step reaction by using a spin-casting technique in a centrifuge. The pioneering synthesis[49-52] was based on vinyl-terminated mesogens reacting under hydrosilylation conditions with a flexible crosslinker. In the subsequent syntheses, these mesogens have been replaced by vinyloxy-terminated mesogens in order to reduce the problems of impurities and side reactions during the hydrosilylation reaction and thus obtain well defined networks with low soluble content[47,48]. Using this new chemical approach, a series of uniaxial MCLCEs was prepared having either a nematic phase (N-MCLCE) or a smectic-C phase (SmC-MCLCE), according to the chemical structure of the mesogens and the degree of cross-linking.[47]

Uniaxial MCLCEs: stress-strain experiments. The stress-strain experiments were performed on uniaxial MCLCEs prepared with vinyloxy-terminated mesogens, which have either a nematic (N) or a smectic-C (SmC) mesophase depending on the chemical composition and structure of the mesogens as well as the degree of cross-linking.[47] The stress-strain curves obtained by stretching these uniaxial MCLCEs in a direction perpendicular to the initial orientation of the director (reorientation transition) lead to the following three observations: a) the stress-strain curves of both the N-MCLCE and SmC - MCLCE do not show the thresholds observed for the uniaxial SCLCEs around λ_1 but a soft variation, b) for the same density of crosslinking, the stress-strain curves of the N- and SmC-MCLCE are different, and c) for each uniaxial elastomer (N or SmC), the stress-strain curve strongly depends on the crosslinking density.[47] An additional stress-strain experiment performed on a poly-domain SmC-MCLCE shows that the orientational transition takes place continuously without threshold, as for the reorientation transition.[56] No stress-strain experiment was performed on polydomains N-MCLCE to date.

Uniaxial MCLCEs: Thermo-elastic experiments. These experiments were performed on the N-MCLCE and SmC-MCLCE samples studied by stress-strain experiments. They show that the thermo-elastic response depends on the nature of the MCLCE for a given cross-linking density (it is higher for the SmC-MCLCE than for the N-MCLCE), and the cross-linking density for a given MCLCE (N or SmC).[47]

Uniaxial MCLCEs: Critical behavior. The high-resolution ac calorimetry studies performed on the N-MCLCEs prepared with the vinyloxy-terminated mesogens show that the thermodynamic response of these systems is governed by the cross-linking density.[60] These systems exhibit indeed a subcritical (para-nematic) state for cross-linking densities between 2.5% and 8%, and a supercritical state for a cross-linking density of 12%. A similar high-resolution ac calorimetry study[61] performed on SmC-MCLCEs also prepared with the vinyloxy-terminated mesogens shows a very different thermodynamic response characterized by a strongly first-order SmC-I transition with a wide coexistence region regardless of the degree of cross-linking from 2.5 to 10 mol-%, which reflects the strong symmetry change at the transition.

Uniaxial MCLCEs: shear mechanical properties. This study[50], carried out on the uniaxial MCLCEs synthesized with vinyl-terminated mesogens (the pioneering synthesis), shows that this MCLCE exhibits a shear anisotropy in the nematic phase which disappears at temperatures located slightly above the N-I transition. Around the N-I transition, $G'_{\perp}$ exhibits a particular behavior that reflects the reorientation of the SmC domains as revealed by X-rays (all the N-MCLCEs synthesized so far have some smectic domains). Below the transition, in the nematic phase, there is no indication of soft or semi-soft elasticity, as for uniaxial SCLCEs. The time-temperature superposition method does not apply, because the structure of the polymeric chains is formed of two components (mesogens and flexible siloxane units), whose temperature dependence is different. The elastic response of the sample is highly dependent on the way experiments are conducted. If the sample is placed in the cell at a temperature below the transition region and the experiments are performed by increasing the temperature, the sample response is of the supercritical-type (no N-I phase transition), because the glass plates of the cell prevent the big increase in sample thickness around the transition region. A new sample must be used at each temperature of measurement for obtaining the true response of the system. The measurements taken on the uniaxial MCLCEs with vinyloxy-terminated mesogens, which will be described later, were carried out according to these two measurement methods.