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Metastable Untwisted States in Cholesteric Elastomers

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Polymeric side chain liquid crystals consist of a polymer backbone and mesogenic side groups, chemically attached to the main chain by flexible spacer chains. Light cross-linking of the backbone leads to liquid crystalline elastomers.[1] In general, the interaction of nematic side groups with the main chain segments causes anisotropic main chain conformations, called prolate in the case of preferred parallel orientation of the segments with respect to the director and oblate in the case of preferred perpendicular orientation. The extent of the conformation anisotropy can be specified as the ratio r of the average step lengths of the main chain segment's random walk parallel and perpendicular to the director. As long as $r \neq 1$, the director field can be affected by mechanical deformation due to the interaction of side groups and main chain. In the case of prolate conformations ($r > 1$), the director tends to orient parallel to the direction of tensile stress and perpendicular in the case of oblate conformations ($r < 1$). When the nematic side groups (at least partially) are chiral, a helically twisted nematic director field (the so-called cholesteric structure) is obtained, which can be distorted by mechanical deformation. A unique feature of cholesteric liquid crystals is the selective reflection of circularly polarized light with the same handedness as the helix in a narrow range around a center wavelength $\Lambda_{R,0}$.[2] The transmission of oppositely polarized light is not affected significantly. The spectra are very sensitive to helix distortions.

For tensile stress applied perpendicular to the helix axis of cholesteric elastomer films and a deformation exceeding a critical value, untwisted states were predicted theoretically,[3,4] where the director only shows oscillations (see Figure 1). However, experimental studies[5] showed serious deviations from the theoretical expectations. The transmission of polarized light indicated a helix distortion much weaker than predicted. In particular, no clear indications for the existence of untwisted states were found.

Later, the contribution of the Frank elasticity (the elastic response to the distortion of a liquid crystal's director field) to the free energy density, previously neglected in comparison to the network elasticity, was studied theoretically.[6] It was found that a distorted director field with a director still showing complete rotations can exist as a metastable state even above the critical deformation. Here an untwisted state with an only oscillating director is stable. On the other hand, at deformations below the critical value, where a director field with a rotating director represents the stable state, a metastable untwisted state with an only oscillating director can exist. The critical deformation is then defined as that of equal free energies for structures with rotating and oscillating directors. A similar study was performed for so-called "imprinted" cholesteric elastomers, where a chiral solvent is removed after cross-linking.[7] There very high energy barriers for the nucleation of disclinations, necessary for direct transitions between states with rotating and oscillating directors, were estimated. The same should apply for cholesteric elastomers with chemically fixed chiral components. The energy barrier can be assumed to prevent effectively the transition from a metastable rotating to the stable oscillating state at deformations above the critical value λ_c.

The relative size of the Frank elasticity contribution can be denoted by introducing a reduced wavenumber $q_r = q_0(K_2/G)^{1/2}$, relating the helix wavenumber q_0 to the twist elastic constant K_2 and the rubber shear modulus G.[6] With reasonable values of $K_2 \approx 10^{-11}$ N, $G \approx 10^6$ N m^{-2}, and a helix pitch $p_0 = 2\pi/q_0 \approx 0.4 \times 10^{-6}$ m, one obtains $q_r \approx 0.05$. The distorted helix structures with rotating and only oscillating directors, according to (local) minima of the free energy, can be calculated numerically in dependence of q_r and the mechanical deformation λ_{xx} perpendicular to the helix axis. The corresponding reflection and transmission spectra for polarized light propagating parallel to the helix axis can be calculated using the fast version[8] of the Berreman 4 × 4 matrix algorithm.[9]

In Figure 2, the calculated transmission spectra of an elastomer film with rotating and oscillating directors at the critical deformation $\lambda_c = 1.091$ (resulting for $r = 1.3$ and $|q_r| = 0.05$) are shown. Refractive index values $n_e = 1.6543$ and $n_o = 1.5226$ of the quasi-nematic layers as obtained from measurements with an Abbe refractometer[10] were used. The refractive index of the surrounding medium was set to $n = 1$. The cholesteric elastomer film was assumed to have 50 director turns of a left-handed helix along its normal, corresponding well to the experiments, where the helical pitch was ≈0.4 μm at a film thickness of 20 μm (see below). The orientation of the director in the surface plane plays some minor role; here it was set to be parallel to the direction of strain. Whereas all spectra of the structure with only oscillating director correspond to a transmission gap nearly independent of the polarization of the incident light, the polarization still plays a large role for the spectra when the director shows complete rotations: Beside a common narrow central transmission gap, slightly blue-shifted according to a helix pitch decreasing affinely with the film thickness, symmetric sidebands appear in the spectra for circularly polarized light with the same handedness as the helix, and asymmetric sidebands appear for linearly polarized light. These significant changes allow to distinguish between structures with rotating and oscillating directors at deformations close to the critical value. However, in spectra of real cholesteric elastomers, imperfections show up even when advanced methods of film preparation are applied, possibly due to some remaining distribution of pitches and helical axes.[5]

In the present study it was attempted to force the formation of untwisted states by cooling strained elastomer samples from a temperature above the cholesteric−isotropic phase transition down to the cholesteric state, hence avoiding the high energy barrier connected with a direct transition from twisted to untwisted states. Siloxane-based elastomer films of 20 μm thickness (with a prolate conformation anisotropy corresponding to an odd number of atoms in the spacer chain of the side groups, a left-handed helix, and a cholesteric−isotropic phase transition at

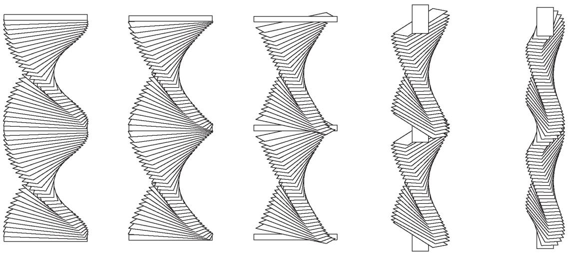

Figure 1. Deformation of the helix structure by tensile stress increasing from left to right. For the two rightmost structures, the deformations exceed a critical value, resulting in only oscillating directors, no longer showing complete rotations.

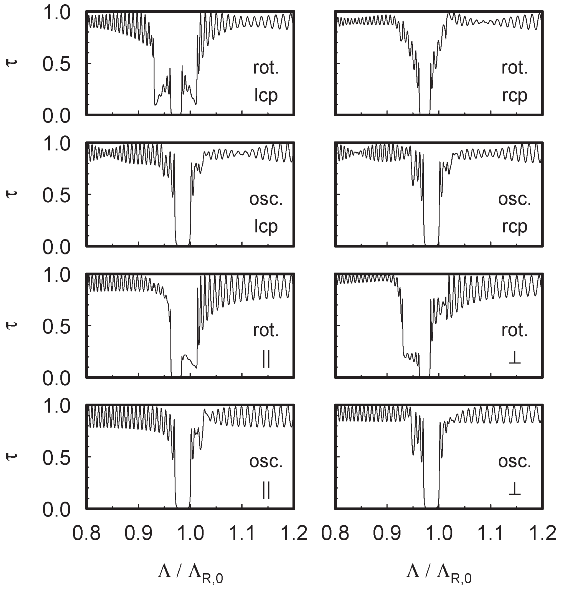

Figure 2. Calculated transmission τ for polarized incident light of an elastomer film with a prolate conformation anisotropy $r = 1.3$ and a reduced wavenumber $q_r = -0.05$ (negative sign corresponding to a left-handed helix) as a function of the reduced wavelength $\Lambda/\Lambda_{R,0}$ at the critical deformation λ_c, for states with rotating (rot.) and oscillating (osc.) directors as indicated. Polarizations: left (lcp) and right (rcp) circular, parallel (||) and perpendicular (⊥) linear with respect to the direction of strain.

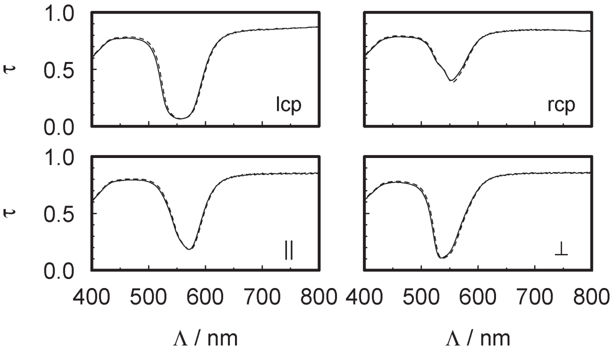

Figure 3. Transmission of an elastomer film at 40 °C and a deformation $\lambda_{xx} = 1.21$, cooled from isotropic to cholesteric state at $\lambda_{xx} = 1$ (full line) and at $\lambda_{xx} = 1.21$ (dashed line).

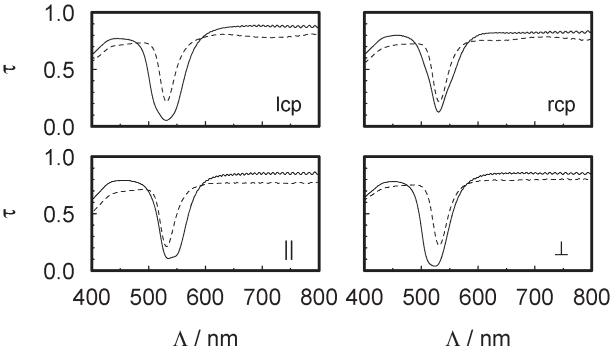

Figure 4. Transmission of an elastomer film at 40 °C and a deformation $\lambda_{xx} = 1.29$, cooled from isotropic to cholesteric state at $\lambda_{xx} = 1$ (full line) and at $\lambda_{xx} = 1.29$ (dashed line).

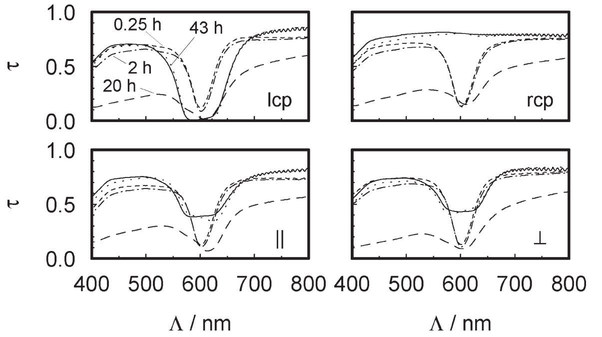

Figure 5. Transmission of an elastomer film, all recorded at 40 °C and a deformation $\lambda_{xx} = 1$. The full line spectra were obtained after cooling from the isotropic to the cholesteric state at $\lambda_{xx} = 1$. The broken line spectra were obtained after cooling from the isotropic to the cholesteric state at $\lambda_{xx} = 1.36$, followed by releasing the strain to $\lambda_{xx} = 1$ (recorded after different times after releasing of the strain as indicated). After 43 h, the spectra nearly coincide with the full line spectra.

$T_{ci} = 97$ °C) were used. The preparation of the films and the experimental setup, completed by a temperature-controlled sample chamber, were described previously.[5] The transmission spectra for polarized light, recorded after cooling, were then compared with those obtained for elastomers cooled unstrained.

At low deformations present at the phase transition, the transmission spectra do not show significant changes (see Figure 3). When the deformation during cooling exceeds a certain value, the spectra show strong changes and are found to be nearly independent of the polarization of the incident light (see Figure 4), in accordance with the spectra calculated for the theoretically expected director fields of states with only oscillating director. Obviously the critical strain (at the condition of formation of the cholesteric state) is within the range of the strains of Figures 3 and 4: $1.21 \le \lambda_c \le 1.29$. Similar spectra are obtained even after completely released strain; then the untwisted structures remain as metastable states.

Depending on temperature, these metastable untwisted states are found to persist for several hours. Then, passing intermediate states showing strong scattering of light, conversion to the stable twisted states is observed (see Figure 5). The opposite conversion, however, i.e., the conversion of a metastable state with rotating director to the stable state with oscillating director at strains above the critical value, is not observed even after several days.

The transition from a metastable to a stable state in general is considered to be prevented by a large energy barrier due to the nucleation of disclinations. The observed finite lifetime for the transition from metastable untwisted states to stable states with rotating director, however, may be caused by inhomogeneous deformation, in particular in vicinity of the clamps. There the local deformation can be assumed to be lower than the critical value, and therefore cooling leads to regions of twisted states, which will grow when the global deformation is reduced.

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