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Stimulus–Responsive Nematic Gels

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Summary: Nematic elastomers exhibit a rich variety of stimulus–response behaviors owing to their hybrid characters of liquid crystals and elastomers. The nematic elastomers swollen by low molecular mass liquid crystals show anisotropic swelling, and their volume and shape significantly depend on temperature. The swollen nematic elastomers exhibit macroscopic deformation together with a large change in optical birefringence in fast response to electric fields (electro–opto–mechanical effect). The mechanical stretching of the nematic elastomers normal to the initial director drives the director realignment along the elongation axis.

Keywords: elastomers; gels; liquid-crystalline polymers; transition

Introduction

Liquid crystal elastomers (LCEs) represent a cross of liquid crystals and elastomers. The concept of LCEs was firstly proposed by de Gennes about thirty years ago.[1] They are crosslinked rubbery polymer networks with a sufficient amount of rigid mesogenic groups exhibiting liquid crystallinity. The materials along this concept were first synthesized by Kupfer and Finkelmann.[2] The unique characteristic of LCEs is the strong correlations of their macroscopic shape (deformation) and the molecular alignment of constituent mesogens.[3] A direct evidence of the presence of such coupling is the thermally induced deformation of LCEs in their dry (neat) state: The materials spontaneously elongate along the director when they undergo the transition from the randomly oriented (high-temperature isotropic) state to the globally aligned (low-temperature nematic) state. Many researchers studied the deformation of LCEs driven by the mesogen reorientation using various external fields such as temperature and light.[3] Most of the eariler studies examined the properties of LCEs in the dry (neat) states.

We demonstrate that LCEs swollen by nematic solvents (nematic gels) exhibit interesting responses to temperature variation and electric fields.[4] We also show that the imposed stretching normal to the initial director induces the director rotation towards the stretching axis accompanying the characteristic stress-strain behavior and dimensional variation.

Materials

The side chain LCEs were prepared by the method described elsewhere.[5] The chemical structures of reactive mesogenic monomer and crosslinker are given in Figure 1. The photocrosslinking was conducted in the globally aligned state of the mesogens in the glass cells coated with uniaxially rubbed polyimide layers. The resultant LCEs have a global uniaxial orientation of mesogens along the rubbing direction, i.e., monodomain structure.

Temperature Responsive Volume and Shape

The equilibrium anisotropic swelling of the LCEs in isotropic (non-nematogenic) and nematic solvents was investigated as a function of temperature (T).[5,6] Figure 2

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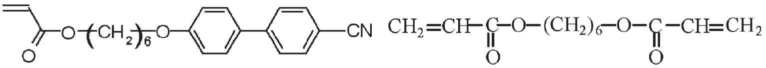

$CH_2{=}CH{-}C(=O){-}O{-}(CH_2)_6{-}O{-}C(=O){-}CH{=}CH_2$

Figure 1.
Chemical structures of reactive mesogenic monomer (left) and crosslinker (right).

displays the equilibrium principal ratios ($\lambda_{||}$ and $\lambda_{\perp}$) and degree of swelling (Q: $Q=\lambda_{||}\lambda_{\perp}^2$) in an isotropic solvent.[5] The subscripts $||$ and $\perp$ denote the directions along and normal to the director, respectively, and the reference state for λ is taken in the dry and isotropic state. The swollen LCE undergoes the nematic-isotropic transition at T_{NI}^G which is by far below the transition temperature in its dry (neat) state owing to the dilution effect of the non-nematogenic solvent on the nematicity of the LCE. In the high-temperature isotropic state of $T > T_{NI}^G$, the LCE is highly swollen without shape anisotropy. The nematic ordering at T_{NI}^G results in a volume reduction accompanying an elongation along the nematic director. In the low-temperature nematic state of $T < T_{NI}^G$, the gel is shrunken but the elongation increases with decreasing in T (i.e., increasing in nematic order). The volume transition driven by nematic ordering was firstly observed for a polydomain LCE without global director in isotropic and nematic solvents: The polydomain LCEs exhibit discontinuous volume change at T_{NI}^G but without anisotropic shape variation.[7–9]

Figure 3 illustrates the anisotropic swelling behavior of the LCE in a low molecular mass LC (5CB).[6] The system has two independent T_{NI}, i.e., T_{NI}^S and T_{NI}^G: The former is for the pure solvent outside the LCE, and the latter is for the swollen LCE. In the totally isotropic state of $T > T_{NI}^G$, the LCE swells largely without shape anisotropy. When cooled to T_{NI}^G, the nematic ordering inside the gel drives a volume reduction together with a stretching along the director similarly to the isotropic solvent systems in Figure 2. In the region of $T_{NI}^S < T < T_{NI}^G$, the cooling causes reswelling with further growth of shape anisotropy. In the totally nematic state of $T < T_{NI}^S$, the gel volume is almost the same as that in the totally isotropic state but they are elongated along the director. No thermal hysteresis effect on the swelling behavior was observed for the isotropic and nematic solvent systems. The features of the T dependencies of volume and shape in Figures 2 and 3 are universal, because the

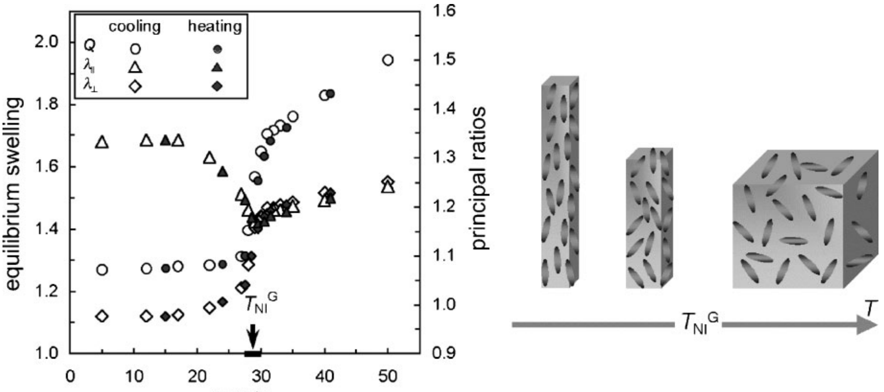

Figure 2.
Equilibrium degree of swelling (Q) and principal ratios ($\lambda_{||}$ and $\lambda_{\perp}$) along and normal to the nematic director for the nematic elastomer in di-*n*-butyl phthalate.

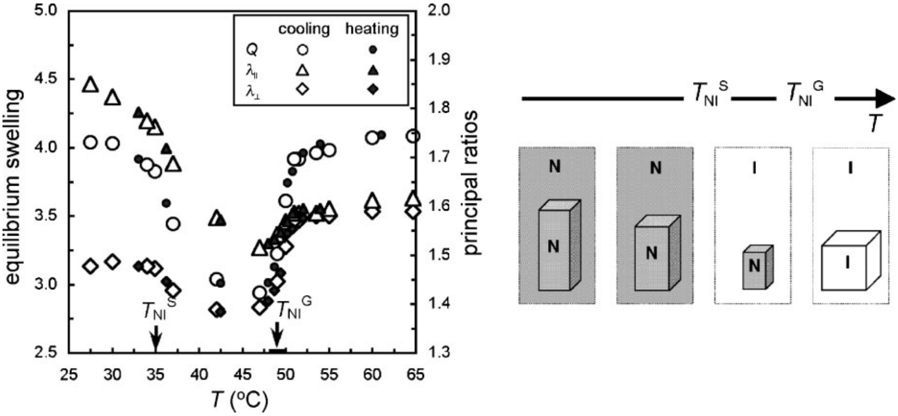

Figure 3.
Equilibrium degree of swelling (Q) and principal ratios ($\lambda_{||}$ and $\lambda_{\perp}$) along and normal to the nematic director for the nematic elastomer in the nematic solvent 5CB.

similar behavior was observed for other combinations of LCEs and solvents with different chemical structures. As is evident from Figures 2 and 3, the volume and shape of the swollen LCEs strongly depends on the nematic order of the constituent molecules. More quantitative themodynamical description is given by a mean field theory.[10–13] The theoretical predictions catch the trend of the observations,[5,6] and they show that the nematic order plays a major role in the swelling of LCEs. The swelling governed by nematic order also exhibits the interesting dynamics such as the dimensional overshoot or undershoot during swelling or shrinking.[14,15]

Electrically Driven Optical and Mechanical Effects

Sufficiently high electric field induces the rotation of director in swollen LCEs along the field axis, and it simultaneously drives macroscopic deformation owing to the strong coupling of orientational order and macroscopic shape. Figure 4 shows the pictures of the swollen LCE (by a nematic solvent) under electric fields (z-direction) normal to the initial director (x-direction).[16] The appearance of the gel under cross–polarized condition becomes dark under electric fields as a result of director reorientation along the field axis. Simultaneously, the dimension

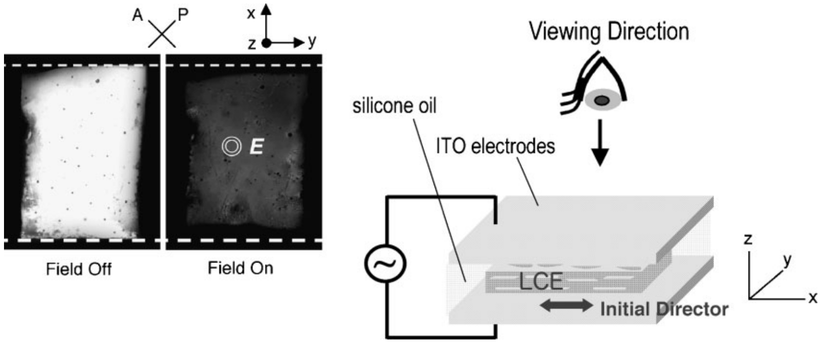

Figure 4.
The cross-polarized images of the swollen nematic elastomers under the AC electric field (amplitude: 750 V; frequency: 1 kHz). The cell gap and film thickness are 40 and 34 mm, respectively. The crosslinker concentration is 7 mol%, and the solvent (5CB) content is 76 vol%.

along the initial director decreases whereas there is no dimensional change in the y-direction (i.e., director rotation axis). The dimension along the field axis increases due to volume constancy. The stretching direction is identical with the direction of mesogen reorientation under electric fields. The dielectrically positive nematic gels are stretched along the field axis, while the dielectrically negative ones are elongated normally to the field direction.[17,18] The stretching direction depending on dielectric anisotropy clearly indicates that the electrical deformation mainly originates from the mesogen realignment. The coupled optical and mechanical effect in Figure 4 was firstly demonstrated in our study,[16] although either optical or mechanical effect was solely observed in some studies.[19–23] The key factors for the coupled effect are "mono-domain" structure of the LCEs and the mechanically unconstrained geometry where the specimens are not effectively sandwiched by rigid electrodes. The constrained geometry (where the specimens are firmly fixed by rigid electrodes) significantly suppresses the director realignment.[24]

Figure 5 illustrates the effective optical birefringence in the xy plane and macroscopic strains in the x– and y–directions as a function of imposed voltage amplitude.[24] At sufficiently high fields, the birefringence becomes less than 5% of the initial value. This indicates that the almost full (90°) rotation of director is achieved. An increase in voltage amplitude leads to an increase in the compressive strain in the x–direction but almost no dimensional change in the y–direction. A reduction in crosslink density results in an increase in mechanical effect: The maximum strain reaches almost 20% when the crosslinker concentration is 3 mol%.[24]

The rotation angle of director (θ) at a given voltage amplitude is estimated from the birefringence data using some valid approximations. The strain in the x–direction is linearly proportional to $\sin^2\theta$, which is observed for different samples with various crosslinking densities.[24] This characteristic θ-dependence of strain is similar to the theoretical picture of soft deformation specific to LCEs,[25,26] and it provides an important basis to understand the coupling of the director rotation and macroscopic strain.

The response times to "field-on" and "field-off" were also studied as a function of voltage. The rise times for optical and mechanical effects become smaller in proportion to the inverse square of voltage. The decay times for both effects are independent of voltage. These voltage dependencies are similar to that of the electro-optical effect of low molecular mass LCs. The optical rise and decay times of

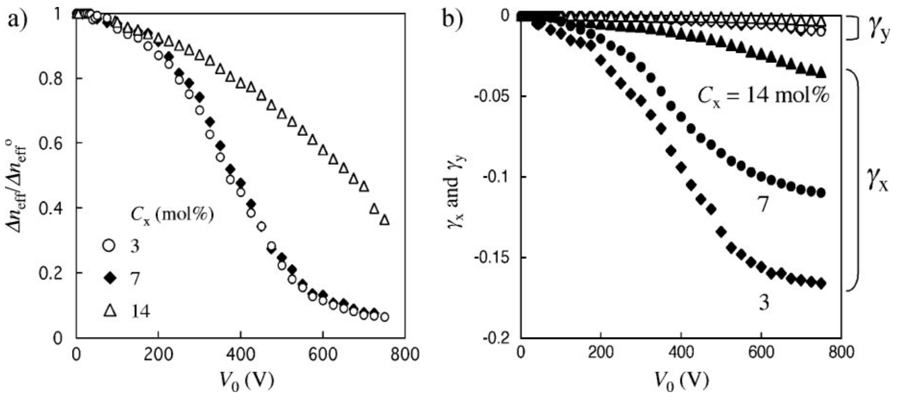

Figure 5.
Optical birefringence in the xy plane and macroscopic strains (γ_x and γ_y) as a function of applied voltage amplitude for the swollen LCEs with various crosslinker concentrations (C_x). The solvent contents for the swollen LCEs with $C_x = 3$, 7, 14 mol% are 82, 76 and 50 vol%, respectively.

swollen LCEs lie in order of 10^{-3} s but the response times of the mechanical effects are one order of magnitude larger than those of the optical effects. The physical origin of such large difference in response times between optical and mechanical effects remains unclear. It should be emphasized that the optical decay times of the swollen LCEs are three orders of magnitude smaller than those of the nematic solvent confined in the cell with the same thickness. This fast recovery of the swollen LCEs indicates that the recovery force (memory effect of initial director) is by far stronger than that (Frank elasticity) of the nematic solvent. It also suggests that the nematic solvent inside the gel moves fast together with the network mesogens.

Mechanically Driven Director Rotation

The mechanical stress imposed normally to the initial director can rotate the director of LCEs.[3] This issue has been studied for thin LCE films with planar alignment (the mesogen alignment parallel to the film surface).[3] We have investigated this issue using the thin LCE films with homeotropic alignment (the mesogen alignment normal to the film surface).[30] The homeotropic LCE films have the following merits relative to the planar ones: The dimensional variation along the axis of director rotation during stretching is directly observable; the complicated effect of clamps at the edges on the mesogen reorientation is avoidable.

Figure 6 displays the nominal stress (σ_z) and true strain (ε_y) in the y–direction (the axis of director rotation) as a function of true strain (ε_z) in the stretching (z–) direction.[27] It should be noted that the gradient for the ε_y–ε_z curve corresponds to the Poisson's ratio μ_{yz}. At the small strains of $\varepsilon_z < 0.15$, σ_z linearly increases with ε_z, and μ_{yz} is close to 0.5 which is the same as that of conventional isotropic elastomers. At the middle strain regions of $0.15 < \varepsilon_z < 0.35$, σ_z is almost constant and the ε_z dependence of ε_y becomes significantly small ($\mu_{yz} \approx 0.17$). At the high strains of $\varepsilon_z > 0.35$, σ_z increases again and μ_{yz} recovers to 0.5. The initial mesogen orientation recovers when the stress is released even after high stretching of $\varepsilon_z > 0.35$. The separately conducted FT–IR measurements reveal that the director rotation dominantly proceeds in the middle strain region while no further director realignment occurs at the high strains.[27] The stretching driven director rotation is characterized by a plateau stress and almost no dimensional change along the axis of director rotation. It should be emphasized that such deformation mode ($\mu_{yz} \approx 0$) was also observed in the deformation driven by director rotation under electric fields (Figure 5). This indicates that this is the characteristic deformation mode regarding the director rotation.

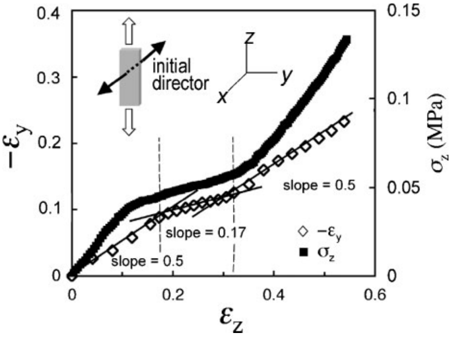

Figure 6.
Nominal stress σ_z and true strain in the y-direction as a function of tensile true strain ε_z for a thin nematic elastomer film with homeotropic alignment.

Conclusion

The monodomain LCEs with global director in solvents exhibit volume transition accompanied by shape variation at the nematic-isotropic transition inside the gels. In the isotropic state, the LCEs are highly swollen without shape anisotropy, while they become shrunken with an elongated shape along the director in the nematic state.

The swollen LCEs show a pronounced optical and mechanical effect in fast response to electric fields. The sufficiently high fields achieve almost full rotation of the director along the field axis and drive a large strain of more than 10%. The optical response times to the field imposition and removal are in the order of 10^{-3} s.

The uniaxial stretching of the homeotropic LCEs normally to their initial director induces the director rotation along the stretching axis. In the director rotation process, the stress becomes plateau and the deformation mode is close to pure-shear (no dimensional change along the director rotation axis). Such pure-shear like deformation is commonly observed for the director rotation processes under electric and mechanical fields.

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