Time-Dependent Deformation of Structurally Chiral Polymer Networks in Stabilized Cholesteric Liquid Crystals

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ABSTRACT: Polymerization of crosslinkable liquid crystal monomers in chiral liquid crystalline media stabilizes the phase and enables distinct electro-optic properties relative to small-molecule analogs. Particularly interesting are cases where the polymerization forms a crosslinked polymer network that maintains a “structural” chirality. Recent reports have employed this methodology to realize a diverse set of electro-optic responses in polymer stabilized cholesteric liquid crystals (PSCLCs) including reflection bandwidth broadening, reflection wavelength tuning, and dynamic scattering modes. It has been proposed that the mechanism at the root of these electro-optic responses is an ion-mediated, electromechanical deformation of the stabilizing and structurally chiral polymer network. In an effort to better understand the nature of these deformations, here we have characterized the electro-optic response of PSCLCs with different polymer concentrations and crosslink densities. The dynamic response of PSCLCs to electric fields exhibits a time-dependent behavior reminiscent of the creep of polymeric materials to mechanical deformations. The electro-optic response can be described as the superposition of two contributions: the fast deformation of a relatively soft component of the polymer network (1–2 s) and the slower (10–20 s) deformation of a harder component.

INTRODUCTION Polymer-stabilized cholesteric liquid crystals (PSCLCs) are composite material systems in which a liquid crystalline monomer has been polymerized within a low-molecular-weight cholesteric liquid crystal (CLC) component, to form a polymer network that possesses the same orientation characteristic as the liquid crystal phase in which it was formed. Recently, we have reported the dynamic electro-optic responses of PSCLCs and shown that these PSCLCs can exhibit reflection band tuning1–4 bandwidth broadening5–8 and switching between scattering and reflection states.9–13 These effects are enabled by the presence of the polymer network, as the low molecular mass CLC component does not respond directly to an electric field in the geometry of interest, due to the sign of the dielectric anisotropy. An ion trapping, electromechanical mechanism6,7 has been proposed to explain the dynamic electro-optic responses of PSCLCs that are based on structural chirality. The current understanding is that ions initially present in the CLC mixture remain trapped in/on the polymer network during the fast photopolymerization process.14 When a DC bias is applied through the thickness of a polymerized sample, the electrostatic force acting on the ions leads to a distortion the polymer network.1,7 The deformation of the polymer network is toward the negative electrode. The small-molecule CLC components of the system follow the deformation of the polymer network, due to the anchoring to the stabilizing network, leading to a change in the position or bandwidth of the characteristic reflection mode relative to the unbiased sample. The density of the ions of the host media strongly influences the electro-optic response of the PSCLCs.15

The polymer network is viscoelastic and can exhibit time-dependent deformation to applied loads.16–18 The type and magnitude of the viscoelastic response of a polymer is affected by the molecular structure and morphology of the polymer, the temperature, and the magnitude and duration of applied external loads. The deformation under a constant load as a function of time is referred to as creep.16–21 In PSCLCs formulated with nematic liquid crystals with negative dielectric anisotropy, Δε < 0, the deformation of the stabilizing polymer network resulting from the application of a DC voltage through the device can be thought of as a form of electric-field induced creep. The magnitude and time

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evolution of this creep response is determined by the viscoelastic properties of polymer network and trapped ions. We have shown that the electro-optic response of PSCLCs depends on sample composition, curing conditions (UV intensity and curing time), polymer concentration, and type and concentration of photoinitiator. The viscoelastic properties of the polymer network can be influenced by many of these parameters.

In our previous study, we reported the ability to regulate the repeatable tuning behavior (from 100 to 400 nm range) and the effect of duration and magnitude of the applied field on the time dependent electro-optic response in PSCLCs formulated with nematic liquid crystals with $\Delta c < 0$. Tuning over broader ranges was observed for electric fields of larger amplitude and the response was found to be time dependent, leading to larger tuning range with time as the electric field was applied. Here, we investigate the time-dependent electro-optic response of PSCLC in detail, to elucidate the contribution of viscoelasticity to the manifestation of the electro-optic response. The effect of the polymer concentration in the PSCLCs and the magnitude of the applied DC voltage on creep evident in the electro-optic responses are discussed. Specifically, the electro-optic response to applied DC bias and the recovery after the field is switched off can each be described to a good approximation by a 4-parameter model, characterized by two response times. Two composition regimes are identified based on the electric field dependence and magnitude of the response times.

EXPERIMENTAL

Preparation of Negative Dielectric Anisotropy Polymer Stabilized Cholesteric Liquid Crystals ($\Delta c < 0$ PSCLCs)

Alignment cells were prepared from ITO-coated glass slides (Colorado Concepts). The glass slides were cleaned using an ultrasonic bath in methanol and acetone, followed by air plasma treatment. The cleaned glass slides were spin-coated with a polyimide alignment layer (PI 2555, Nissan Chemicals). The alignment layers were rubbed with a cloth, and the cell was constructed to ensure planar alignment conditions. The cell gap was controlled by mixing 15 μm thick glass rod spacers into an optical adhesive. Samples were prepared by mixing 0.4 wt % of a photoinitiator (Omnired 369, IGM Resins), two right-handed chiral dopants (R1011 and R811, Merck), 0–8 wt % of a chiral liquid crystal monomer (SL04151, AlphaMicron, Inc.), and a $\Delta c < 0$ achiral nematic liquid crystal (MLC 2079, Merck). SL04151 is right handed. The chemical structures are shown in Supporting Information, Figure S1. All materials were used as received. The compositions of the CLC mixtures, PSCLC-#, where # is the polymer content in wt %, are summarized in Supporting Information, Table S1. After filling the cells with the mixtures, the polymer networks within the CLCs were formed by photoinitiated polymerization of the chiral monomer by exposing the cells to 365 nm light (OmniCure 1000, Exfo) for 3 min. During the exposure, the cell was rotated at an angular velocity of 2 rev/s. The rotation axis was along the mid line of the cell, within the plane of the cell substrates, and perpendicular to the axis of the expanding UV beam. The UV light intensity was ~100 mW/cm$^2$.

Electro-Optic Measurements

The optical properties of the PSCLCs were characterized in transmission mode at normal incidence. The spectra were collected with a fiber optic spectrometer (USB4000 and NIR256, Ocean Optics). Right-handed circularly polarized light (RH CPL) was used as the probe beam. Transmission spectra were collected before, during, and after application of DC electric fields across the LC cells. The electro-optic responses of the samples were monitored while either increasing the DC bias at 1 V/s or applying the target bias in a step-wise manner and holding it for 30 s. The rise (fall) time is defined in this context as the interval during which the pitch position changes from 10% to 90% (from 90% to 10%) of its tuning range at a given DC field.

RESULTS AND DISCUSSION

Prior reports have detailed large shifts in the selective reflection exhibited by PSCLCs formulated with nematic liquid crystals with $\Delta c < 0$, induced by the application of a DC electric field across the sample. The electrical control of the selective reflection is illustrated in Figure 1(a) for PSCLC-5, containing 5 wt % of the chiral liquid crystal monomer SL04151. The magnitude of the shift observed for an applied field depends on the concentration of polymer in the sample. As shown in Figure 1(b), increasing the concentration of SL04151 increases the required DC bias to induce tuning of a given magnitude. The increase in the monomer concentration inherently results in an increase in crosslinking density of the polymer network. As in bulk polymeric materials, an increase in crosslink density in PSCLCs should increase the stiffness of the stabilizing network and accordingly, increase the magnitude of the force required to induce a given deformation in the material. Detailed in prior examinations, the electric field susceptibility of the polymer stabilizing network is associated with ion impurities trapped in and potentially onto the polymer network. Accordingly, the network should experience a force proportional to the electric field and to the local charge on it. Through anchoring interactions between the liquid crystal and the stabilizing polymer network, a field-induced deformation of the structurally chiral network (in the present case, an elongation in pitch length) is subsequently transferred to the small-molecule LC component in the PSCLCs, dictating a change in the CLC pitch (observed here as a red-shift in the position of the selective reflection). Notably the structural chirality overpowers the nascent chirality of the mixture, derived from the chiral transfer from the dopants and the nematic host. Critically, no shift in the reflection band is observed if the polymer network is not present [black circles in Fig. 1(b)], as $\Delta c < 0$ and the LC molecules are already oriented perpendicular to the electric field.

The change in reflection peak does not occur instantaneously when the field is applied and the observed wavelength can
depend on how the field is applied (e.g., as a step function, with a gradual ramp over time, etc.). To provide a better physical understanding of the deformation of the polymer network to electric fields, we studied the response of a series of samples with different polymer content as a function of time after a constant DC electric field was turned on. Figure 2 presents the electro-optic response of PSCLC-5.5. Its selective reflection is centered near 630 nm with no applied voltage [black trace in Fig. 2(a)]. A 83 V DC voltage was then applied continuously for more than 30 s. During this time the reflection band red-shifted by more than 300 nm to approximately 970 nm. As evident in Figure 2(b), this shift occurs progressively, with the center of the reflection band moving away from the initial position by increasingly larger amounts after the electric field is applied and approaching a plateau value at long times. Evident in both Figure 2(a,b), the reflection band slowly “creeps” over time toward the maximum range. The creep evident in the electro-optic response of the PSCLCs could be attributable to the viscoelastic properties of the crosslinked polymer network.

Similar measurements were conducted on samples as a function of polymer concentration and field strength. The optical properties of the samples were monitored over time when the field was turned on (typically for 30 s) and then turned off. The samples were allowed to relax completely before they were probed again (a minimum of 5 min). The electro-optic response of PSCLC-5 and PSCLC-6 is summarized in Figure 3. The electro-optic response of PSCLC-7 and -8 are included in the Supporting Information, Figure S2. Similar to the data in Figure 2(b), over the 30 s period during which the voltage is applied, the reflection peak of any given PSCLC sample shifts continuously to longer wavelength with time and approaches a plateau value that depends on the magnitude of the applied electric field, as can be seen in Figure 3(a) for PSCLC-5. The magnitude of the plateau of the peak red-shift becomes larger with increasing voltage for any given sample, as was the case when the voltage was increased progressively over time [see Supporting Information, Figure S3 for a comparison of plateau values with the peak positions from Fig. 1(b)]. When the DC bias is turned off, the reflection peak returns to the original wavelength position over the course of a few seconds. It can also be noticed from the data in Figure 3 that the time dependence of the response is not the same at all voltage values. For example, for PSCLC-5 the peak position reaches its plateau within a few seconds from turning the voltage on at 20 V and 30 V, but it is still shifting at 30 s when V = 80 V [Fig. 3(a)]. Differences among samples are also present, both regarding the magnitude of the plateau values at a given
voltage value (larger red-shifts are observed in PSCLC-5 relative to PSCLC-6) and the evolution over time of the peak position (the plateau is approached faster for PSCLC-6 than PSCLC-5).

Figure 4 presents the response times for PSCLC samples prepared with 5–8 wt % SL04151 as a function of applied voltage. The response times (rise and fall times) are obtained from the 10%–90% method (see Experimental Section). The PSCLC with 5% polymer concentration exhibits rise times of 4–5 s at low voltage (20–30 V) and 7–8 s at higher voltage. The fall times have the same trend, but are slightly shorter: ca. 3 s at low voltages (20–30 V) and 4–5 s for \( V > 40 \) V. The behavior is different for the sample with 6 wt % and higher polymer content in several respects. All the response times for these samples are shorter than for PSCLC-5, being in the range 1.5–3.5 s; the samples exhibit only a small increase in response time with increasing voltage; and the decay times are only slightly shorter than the rise times. In addition, there is a very weak dependence on polymer content in this range. Thus, the increase in polymer concentration from 5 to 6 wt % seems to be a transition point in the viscoelastic response of the polymer network in the CLC medium.

To further elucidate the time-dependent viscoelastic deformation of the polymer network, the electro-optic response of the PSCLCs was analyzed by fitting the experimental data to model equations. The experimentally measured optical response (tuning of the reflection notch position \( \Delta \lambda \)) can be used to quantify the mechanical deformation of the polymer network:

\[
\frac{\Delta \lambda_0}{\lambda} = \frac{(\lambda(t) - \lambda_0)}{\lambda_0} = \frac{(\bar{n} p(t) - \bar{n} p_0)}{\bar{n} p_0} = \Delta p / p_0 \tag{1}
\]

where \( \lambda(t) \) and \( \lambda_0 \) are the center wavelength of the reflection mode at a given time \( t \) after an electric field is applied or turned off and at equilibrium without field. \( p(t) \) and \( p_0 \) are the corresponding pitch values and \( \bar{n} \) is the average refractive index of the material, which is assumed to be constant. The normalized pitch change \( \Delta p / p_0 \) is a dimensionless quantity and is the equivalent to the normalized mechanical deformation of a material in the classical sense (strain \( \varepsilon_2(t) \)). The applied DC voltage or the electric field \( E = V / L \), in V/µm, where \( L \) is the sample thickness) is the external input stress.

Figure 5(a,b) shows the electric field induced pitch change \( \Delta p / p_0 \) by application of 40 V DC starting at time \( t = 0 \) s for a 30 s duration and the recovery after the voltage was switched off for sample PSCLC-5, respectively. Normalized pitch changes of all samples and voltages are shown in Supporting Information, Figure S4.

The electric field induced pitch changes were fitted with a 4-parameter model given by the sum of two monomolecular growth terms (when the field is applied) or exponential decay terms (during the recovery after the field is turned off):
Field on:

\[ E_p(t) = a \left( 1 - e^{-t/\tau_{1,on}} \right) + b \left( 1 - e^{-t/\tau_{2,on}} \right) \]  

Field off:

\[ E_p(t) = c e^{-t/\tau_{1,off}} + d e^{-t/\tau_{2,off}} \]

where \( \tau_{1,on} \) and \( \tau_{2,on} \) are the characteristic retardation times for the response with the field on, and \( \tau_{1,off} \) and \( \tau_{2,off} \) are the recovery times when the field is turned off. The fitting parameters \( a \) and \( b \) represent the amplitudes of the two contributions to the total deformation \( E_p \) when the field is on, and \( c \) and \( d \) are the corresponding amplitudes during the recovery. The fitting of the experimental data to the 4-parameter model in eqs 2 and 3 was reasonably good, with a coefficient of determination \( (R^2) \) exceeding 0.98 for all cases. The fitting results for the response of PSCLC-5 to 40 V are included in Figure 5 (lines). We also examined single growth and decay curves \( (b = 0 \text{ in eq 2 and } d = 0 \text{ in eq 3}) \) to model the experimental electro-optic data (one example for the PSCLC-5 sample is shown in Supporting Information, Fig. S5), but in general the quality of the fit was poor relative to the 4-parameter model.

The two retardation times \( (\tau_{1,on} \text{ and } \tau_{2,on}) \) for the electro-optic response of PSCLCs with 5–8 wt % polymer concentrations obtained for the fitting based on eq 2 are summarized in Figure 6. For the purpose of this discussion, \( \tau_{1,on} \) is the shorter of the two response times, describing the initial fast deformation of the polymer network, and \( \tau_{2,on} \) characterizes the slower deformation that follows. The PSCLC with 5 wt % polymer concentration shows overall slower responses \( (\tau_{1,on} = 0.5–2.5 \text{ s and } \tau_{2,on} = 6–23 \text{ s}) \) compared to the PSCLCs with 6–8 wt % polymer concentrations \( (\tau_{1,on} = 0.3–1 \text{ s and } \tau_{2,on} = 3–8 \text{ s}) \). The ratio between the two response times \( \tau_{1,on}/\tau_{2,on} \) are in the range 5–17 for these samples and voltage ranges.

For all samples, the response times increase with increasing voltage. This indicates that the polymer network behaves in a nonlinear manner. In the terminology of classical polymer mechanics, the system described by eq 2 is equivalent to two Kelvin models in series, where a Kelvin model\textsuperscript{18,19,22} is an idealized system composed by a linear spring and linear dashpot linked in parallel. Each Kelvin unit is characterized by a response time given by \( \tau = \eta/R \) (where \( \eta \) is the coefficient of viscosity of the dashpot and \( R \) is the elastic modulus of the spring) and is independent on the applied stress. The variability in the parameters \( \tau \) for the PSCLC samples obtained from the fitting (as well as the 10%-90% response
The relaxation times $\tau_{1,\text{off}}$ and $\tau_{2,\text{off}}$ for PSCLC-5 and PSCLC-6 show a similar trend to that of the retardation times (Supporting Information, Fig. S6). In particular, PSCLC-6 has a faster relaxation response than PSCLC-5. In both PSCLC-5 and PSCLC-6, the relaxation times increase with voltage. However, for a given sample and voltage, the values of $\tau_{1,\text{on}}$ and $\tau_{1,\text{off}}$ (or $\tau_{2,\text{on}}$ and $\tau_{2,\text{off}}$) are not always the same, which is another indication of the nonlinear nature of the viscoelastic response.

Figure 7 summarizes the values for the deformation amplitude parameters $a$ and $b$ obtained from the curve fitting of the experimental data using the 4-parameter model in eq 2. For all samples, the $a$ values are larger than the $b$ values, indicating that the fast component of the polymer network deformation provides the largest contribution to the electro-optic response of the PSCLCs. This also implies that the fast component is softer than the slow one for all voltage values.

The PSCLCs with 6–8 wt % polymer concentrations show very similar $b$ values. Comparatively, the $b$ values for these samples are small with respect to PSCLC-5. For PSCLC-5, the parameter $b$ increases approximately linearly with voltage and a straight line through the experimental data intersects the voltage axis around 7 V (Supporting Information, Fig. S7). This can be thought of as the minimum (threshold) voltage needed to activate the deformation of the slow component. The values of $b$ for the 6–8 wt % PSCLC samples also exhibit, to a first approximation, a linear increase with voltage. The results on amplitude $b$ suggest that the network component responsible for this response behaves approximately as a linear elastic medium.

The parameter $a$ decreases in magnitude with increasing polymer content at any given voltage, indicating that the polymer network becomes harder to deform at higher cross-linking densities. For all samples, the values of $a$ increase with increasing voltage and this increase is superlinear (upward curvature in the trend line). Thus, the fast component of the deformation of the polymer network is responsible for the nonlinear elastic behavior evident in the electro-optic data. This component becomes softer at higher strains and at lower polymer concentrations.

The components responsible for the fast (soft) and slow (stiff) electro-optic response may be attributable to heterogeneity in the polymer stabilizing network. For example, the polymer concentration could be distributed nonuniformly across the sample thickness or further, the large photoinitiator to monomer concentration could result in distributions of either crosslink density or ion sensitivity. Comparison of the results from samples with different thicknesses and polymerization rates (UV illumination intensities) may allow distinguishing among these possibilities. However, it is clear from this examination that the network component imparting the slow response seems to saturate at about 6 wt % polymer concentration and its contribution does not increase if the polymer content is increased.
CONCLUSIONS

The electromechanical deformation of a crosslinked, stabilizing polymer network on the electro-optic response of CLCs is examined. The temporal response of tuning of the selective reflection of the PSCLCs is creep-like. Informed by close examination of the response time of the PSCLC samples as a function of polymer concentration (i.e., crosslink density), the contribution of the viscoelasticity of the polymer stabilizing network is explored. Increasing the concentration of the polymer stabilizing network reduces the magnitude of creep, indicating that the stiffness of the network increases at higher crosslink densities. The polymer deformation can be described as the superposition of two components: a fast and soft component, and a slow and stiff component. Accordingly, the trend in response times and amplitudes are different for the two components and their relative contribution to the total deformation of the sample varies with polymer content. The viscoelastic properties of this class of materials are, in general, not linear, and thus the electro-optic response of a device may depend on the deformation history. This investigation provides insight on how macroscopic device characteristics, such as the wavelength of the Bragg reflection, can be used to build a physical model for the underlying polymer network, whose deformation drives the electro-optic response.

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REFERENCES AND NOTES


