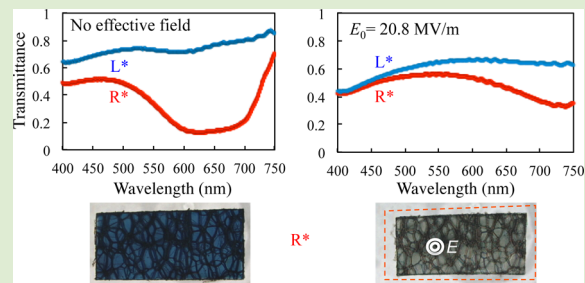


Electrical Actuation of Cholesteric Liquid Crystal Gels

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Supporting Information

ABSTRACT: We demonstrate that the cholesteric liquid crystal (CLC) gels with a global helical variation in their orientation exhibit the pronounced electro-optical and electromechanical effects under an unconstrained geometry. A sufficiently high electric field imposed along the helical axis drives a finite elongation exceeding 30% along the field axis, as well as a finite redshift of the selective reflection band which is opposite to the blueshift often observed for the conventional CLCs and the *in situ* polymer stabilized CLCs under an electric field.



Cholesteric liquid crystals (CLCs), which have a helical variation in their orientation, exhibit selective Bragg reflection at visible wavelengths when the helical pitch matches the wavelength of light.^{1,2} The selective Bragg reflection of CLCs has received considerable attention for applications in mirrorless lasers with low lasing thresholds and in display devices.^{3–5} The selective reflection bands of CLCs are switchable with changing temperature, light irradiation, and applied electric field.⁴ CLCs with switchable reflection colors are a promising material for reflection displays, color reflectors, and tunable lasers. In particular, electric field-induced color switching of CLCs is attractive because the electric field is capable of inducing fast reorientation of LC molecules. Considerable progress has been made in electric field-induced color switching of CLCs; in particular, the significance of *in situ* formed polymer networks in the stabilization of the cholesteric phase has been demonstrated in polymer-stabilized CLCs (PSCLCs). The introduction of polymer networks provides internal memory of the initial helical variation in the orientation, which enables the system to reorient itself quickly to the initial state upon the removal of the field.^{6–14}

Cholesteric liquid crystal elastomers are a rubbery polymer network containing mesogens with uniform orientation of the helical structure.^{15,16} CLC elastomers have the optical properties of CLC as well as the mechanical properties of rubber. CLC elastomers, which are a kind of cross-linked rubber, require no mechanical support for a stable orientation of the helical structure. The combination of rubber elasticity and liquid crystallinity results in a unique feature: the macroscopic shape and molecular orientation are strongly correlated with each other. On the basis of this feature, tunability of the selective reflection bands by mechanical tensile stress has been demonstrated for several CLC elastomers.^{17–20} The pronounced effects of an electric field on liquid crystal elastomers (LCEs) have been reported for polydomain nematic LCEs with isotropic genesis,²¹ ferroelectric smectic LCEs,^{22–25} and

nematic gels,^{26–32} i.e., nematic LCEs swollen by low-molecular-mass LCs. Several LCE materials exhibit finite macroscopic strain exceeding 10%, as well as a pronounced change in optical birefringence in quick response to an imposed electric field.^{21,33} The simultaneous electro-optical and electro-mechanical effects in LCE materials can potentially be used for soft actuators and sensors. The electric field-induced color change for PSCLCs was investigated in earlier studies, but macroscopic deformation was prohibited in this geometry. In PSCLCs, the polymer networks were made using *in situ* polymerization in the electro-optical cells, and the resulting gels were firmly sandwiched by rigid electrodes. Several studies have shown that such mechanical constraint considerably suppresses the electrical reorientation of the director in nematic gels and elastomers.^{34,35} In contrast, nematic gels under no mechanical constraint from the electrodes showed almost full rotation of the director in the field direction and simultaneously exhibited a finite macroscopic deformation, which is correlated with the degree of director rotation.^{33,35–37} CLC elastomers and gels are also expected to exhibit electromechanical and electro-optical effects specific to the cholesteric phase, but to the authors' knowledge, there has been no report that demonstrates experimentally the electric field effect on CLC elastomers and gels without mechanical constraint.

In the present study, we demonstrate that the electric field drives a macroscopic strain exceeding 30% as well as a significant variation in optical properties for CLC gels, which are CLC elastomers swollen by a low-molecular-mass LC, without mechanical constraint. Side-chain-type CLC elastomer films with global helical axes along the thickness direction were fabricated by the copolymerization of monoacrylate chiral mesogen and diacrylate cross-linker in the cholesteric phase

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with the corresponding alignment (Figure 1a). The elastomer films were allowed to swell in a low-molecular-mass LC, 5CB

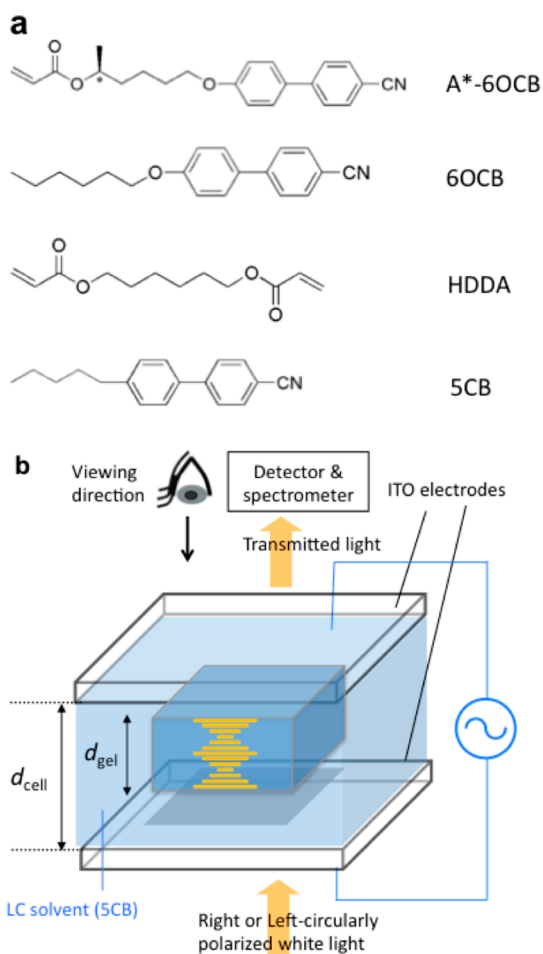


Figure 1. (a) Chemical structure of the materials used. (b) Schematic representation of the experimental setup for the measurements of the transmission spectra and macroscopic deformation under the electric field.

(Figure 1a), until the swelling reached equilibrium. The resulting CLC gel film, with a solvent content of ca. 68%, formed a single cholesteric phase which was characterized by a single cholesteric–isotropic transition temperature of 63 °C. The CLC gel was placed in an electro-optical cell whose gap (72 μm) was sufficiently larger than the film thickness (50 μm), so that the gel could have no mechanical constraint from the rigid electrodes. The cell was filled with the swelling solvent 5CB (Figure 1b). In this geometry, a square-wave AC electric field of 1 kHz with various apparent field strengths (E_0 : $E_0 = V_0/d_{\text{cell}}$, where V_0 and d_{cell} are the voltage amplitude and the gap between the electrodes, respectively) was imposed along the initial helical axis at 25 °C.

Figure 2 shows the transmission spectra and appearances of the CLC gel with respect to the normal incidence of white light with right- or left-circular polarization (designated as R* and L*, respectively) under various E_0 . In Figure 2a, a low electric field was applied to induce the uniform homeotropic alignment of the surrounding solvent to remove the turbidity resulting from its polydomain random texture, but this field strength was sufficiently low to cause no appreciable influence on the gel. Accordingly, the spectra and image in Figure 2a substantially

correspond to those of the gel in the relaxed state without an applied field. In the relaxed state, the transmittance for R* exhibits a considerable reduction in the wavelength (λ) range of 550 nm < λ < 750 nm, whereas that for L* does not. This feature results from the selective reflection of the gel for R* in the corresponding λ range. The dark blue color of the transmission image under R* is the complementary one, i.e., the results of the subtraction of the selective reflection from the white color. The gel exhibits an oily streak texture specific to CLCs with the helical axis parallel to the viewing direction.

Sufficiently high electric fields drive not only a pronounced change in transmission spectra but also a finite macroscopic deformation in the CLC gels, which is shown in Figures 2b–d. At the maximum field strength examined here (20.8 MV/m, Figure 2d), the gel shrinks equivalently in the two directions normal to the field axis by 13%, and the transmission image becomes almost colorless and transparent as a result of a shift of the center of the reflection notch to the upper end of the visible wavelengths. The CLC gels exhibit simultaneous electromechanical and electro-optical effects in fast response to the imposition of a field, and they quickly recover the initial state upon removal of the field. A video showing the response of the CLC gel to the imposition and removal of a strong electric field, i.e., $E_0 = 20.8$ MV/m, is available in the Supporting Information.

The contraction strain in the directions normal to the field and initial helical axes ($-\epsilon_{\perp}$), which is defined by $\epsilon_{\perp} = (l_{\perp} - l_{\perp 0})/l_{\perp 0}$ where l_{\perp} and $l_{\perp 0}$ are the dimensions in the deformed and undeformed states, respectively, increases with an increase in E_0 , when E_0 is higher than ca. 6 MV/m, which is a threshold for the onset of finite deformation (Figure 3a). Correspondingly, the dimensions along the field and initial helical axes increase due to volume conservation, i.e., $(1 + \epsilon_{\parallel})(1 + \epsilon_{\perp})^2 = 1$ (Figure 3b). At the maximum E_0 , the gel stretches along the field axis by 32%. This electrically stretching deformation along the field direction can be understood on the basis of the positive dielectric anisotropy of the constituent mesogen and 5CB. These mesogens tend to align in the direction parallel to the field axis, and the mesogen alignment induces stretching of the network backbone in the same direction. A similar type of electrical deformation was observed in the monodomain nematic gels with uniaxial planar alignment^{32,35} and polydomain nematic gels with the analogous mesogens.^{38,39} The uniaxial stretching along the helical axis was also observed by heating for the CLC elastomers,^{15,20} but this deformation originates from a change in the degree of alignment order, which is substantially different in origin from the electrical deformation driven by a change in director orientation. Note that the CLC gels preserve the oily streak texture even in the deformed state, and they recover the initial one upon the removal of the field. This result demonstrates the memory effect of the initial director configuration by cross-linking, which is generally observed in LCE materials.^{16,40} The effect of the oily streak texture on the electromechanical response observed here is unclear at present, although Ramos et al.⁴¹ pointed out a finite effect of the oily streak texture on the rheology of CLCs.

The electric field influences not only the location of the reflection notch but also the transmittance in the entire λ range examined here. Figure 3c illustrates the E_0 dependence of the characteristic wavelength of selective reflection (Λ_R), which was evaluated as the wavelength where the transmittance is a minimum in the notch. The E_0 dependence of the trans-

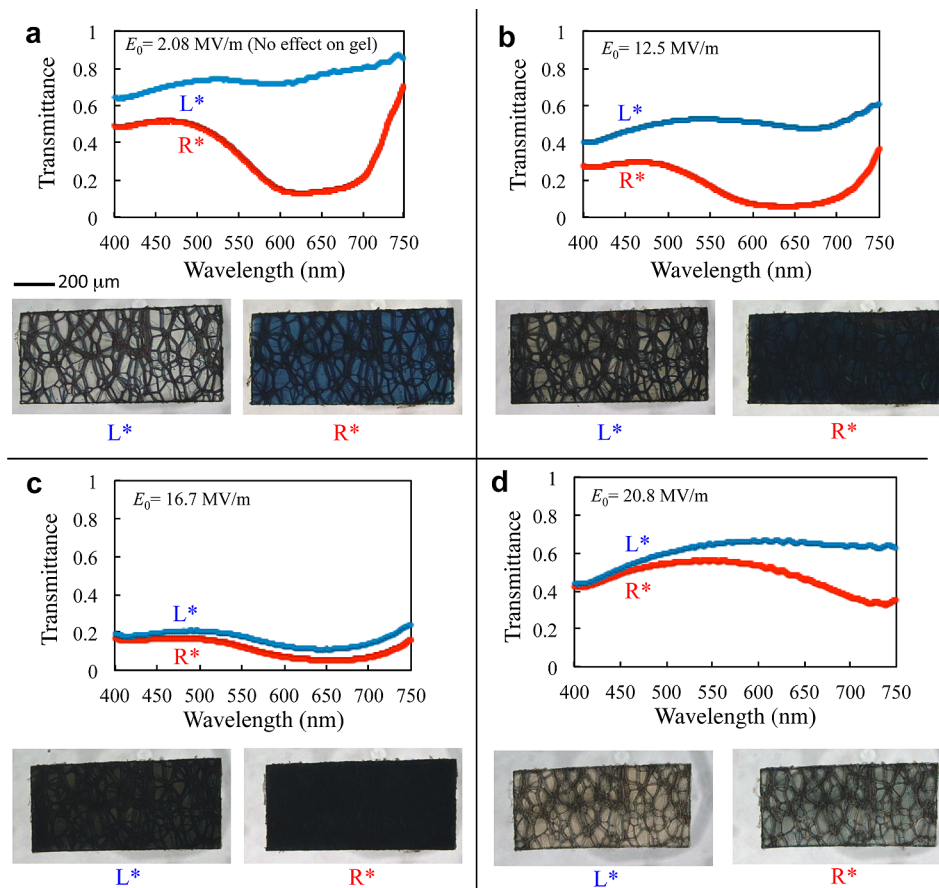


Figure 2. Transmission spectra and appearances of the CLC gels with normal incidence of white light with right- or left-circular polarization (designated as R* and L*, respectively) under various strengths of electric field. In (a), a small electric field is imposed to induce the uniform homeotropic alignment of the surrounding LC solvent to remove the turbidity from its random polydomain texture. Note that this field strength is sufficiently small to have no appreciable effect on the gel. The spectra and images substantially correspond to those of the gel in the relaxed state in the absence of a field. Under a moderate electric field [(b) and (c)], the gel becomes opaque and shrinks in the directions normal to the field and initial helical axes. (d) Under a sufficiently high electric field, the gel recovers transparency and shows a redshift of the reflection notch for R*. The gel also undergoes a finite contraction of 13% in the directions normal to the field and initial helical axes.

mittance at 450 nm (T_{450}) for L*, which has no relation to the selective reflection and can be a measure of the transparency, is also shown in the figure. At a low field strength of $E_0 < 6$ MV/m, neither Λ_R nor T_{450} is appreciably influenced by electric field. This threshold field strength is close to that for the onset of finite deformation (Figure 3a). At a moderate field strength of $E_0 > 6$ MV/m, an appreciable increase in Λ_R and a finite reduction in T_{450} with an increase in E_0 are observed. An increase in turbidity is also evident from the appearance of the gel (Figures 2b and 2c). At $E_0 \approx 17$ MV/m, the spectra for L* and R* are almost similar. Interestingly, at a sufficiently high E_0 of $E_0 > 20$ MV/m, the gel recovers the transparency, and a finite shift of the reflection band to longer wavelengths is clearly observed. The data of T_{450} in Figure 3c are not corrected for the change in thickness, but the large recovery in T_{450} at the high E_0 cannot be explained by a small reduction in thickness (ca. 8%) in the corresponding E_0 region. A decrease in transmittance with an increase in E_0 has also been observed in studies on PSCLCs,^{7,8,10} but the redshift of the reflection notch observed here is opposite to the blueshift reported in previous studies.^{6–10,12} These features will be discussed in detail later.

Figure 4a shows the correlation of the electrically driven changes in Λ_R and macroscopic film thickness. The quantity $\lambda_{||}$ in the figure is the ratio of the film thickness at E_0 to the initial

one (at $E_0 = 0$), and it is calculated from ε_{\perp} and the volume constancy using the relation $\lambda_{||} = (1 + \varepsilon_{\perp})^{-2}$. The quantity Λ_R in the vertical axis of the figure is reduced by Λ_R in the initial state (Λ_{R0}). The line with a slope of unity in the figure corresponds to the case of the affine variation of the helical pitch with film thickness. Obviously, the data considerably deviate downward from the line, and the increase in helical pitch is much smaller than that expected from the increase in film thickness on the basis of the affine variation. The data in the region of $E_0 < 20$ MV/m are well approximated by a straight line with a slope of 0.4. The data at $E_0 > 20$ MV/m deviate upward from this relation. Note that the value of E_0 for the onset of this deviation agrees with that for the onset of the substantial recovery of the transparency and the marked increase in Λ_R (Figure 3c). The imposed stretching of the CLC elastomers in the direction normal to the helical axis causes a blue shift of the reflection notch as a result of a dimensional reduction along the helical axis.^{17,19,20} The red shift driven by the electrical deformation is qualitatively similar in principle to the blue shift observed in these stretching experiments, in view of that Λ_R varies with the dimension along the helical axis.

Let us consider the effects of an electric field on the director configuration and macroscopic deformation in CLC gels. In the case of CLCs and PSCLCs under an electric field parallel to the

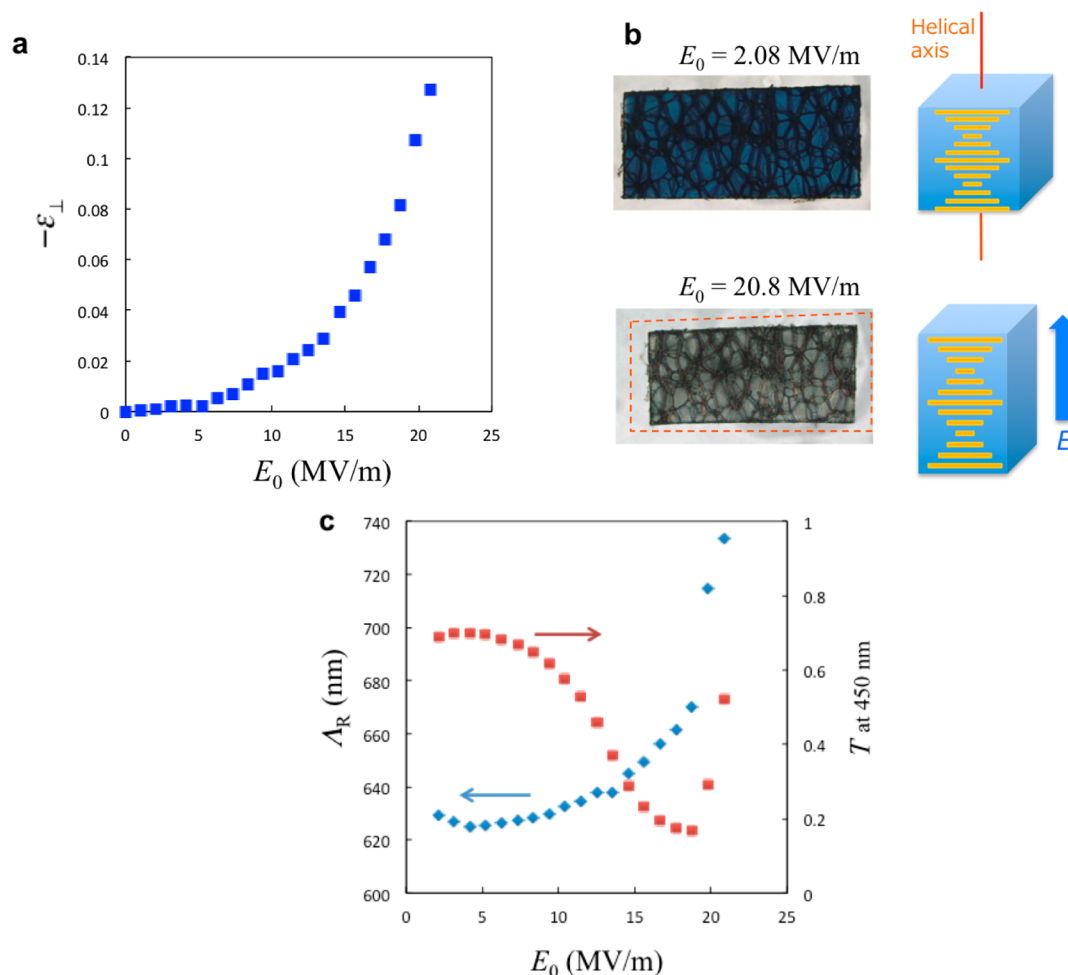


Figure 3. (a) Contractive strain in the directions normal to the field and initial helical axes as a function of apparent field strength. (b) Comparison of the appearances of the gel in the relaxed state and at a high electric field with maximum strength examined here. The high electric field drives a contractive strain of 13% in the direction normal to the field axis, resulting in the elongation of 32% in the field direction because of volume conservation. The corresponding video for the response of the gel to the imposition and removal of the electric field is available in the Supporting Information. (c) Characteristic wavelength of the selective reflection notch (λ_R) and the transmittance at 450 nm for L^* , which is not related to the selective reflection, as a function of apparent field strength.

initial helical axis, the main features of the variations in optical properties can be explained at least qualitatively on the basis of the undulating cholesteric texture called Helfrich deformation:^{7,42,43} The resulting pitch-inhomogeneity broadens the reflection notch and reduces the reflectance; the focal conic texture formed by Helfrich deformation increases the light scattering, which also decreases the reflectance; the local tilting of the helix results in shortening of the pitch observed from a normal axis, and thus the reflection notch shifts to a shorter wavelength, i.e., blueshift. The considerable reduction in reflectance under a moderate electric field in Figure 3c suggests that a finite degree of undulation of the cholesteric texture and the formation of the focal conic texture occur in the CLC gels (Figure 4b). The formation of a similar type of undulation was expected by a theoretical study⁴⁴ on CLC elastomers under a moderate electric field over a certain threshold field strength. A significant difference between the present system and PSCLCs is that the gels are allowed to undergo elongation along the initial helical axis, whereas no macroscopic deformation is allowed in the PSCLCs. A moderate degree of macroscopic elongation along the initial helical axis drives a redshift of the notch due to a widening of the helical pitch, whereas the

undulating cholesteric texture leads to a blueshift of the notch due to the local tilting of the helix. The experimental result (Figure 3c) means that the redshift caused by the pitch increase is larger than the blueshift effect driven by the undulation. Under a sufficiently high electric field, the CLC gels showed a considerable recovery of the reflectance and a significant degree of redshift of the reflection band. At high E_0 , the increase in film thickness exceeds 30%. This large degree of stretching along the initial helical axis results in a considerable widening of the helical pitch, i.e., redshift of the reflection notch. In addition, a large dimensional increase along the initial helical axis is expected to reduce the degree of undulation of the cholesteric texture because an origin of the undulation is the restriction of the macroscopic dimension along the initial helical axis. A reduction in the degree of undulation results in the recovery of the reflection. CLC gels at high E_0 still have a finite fluctuation of the helical axis because the selectivity is lower than that in the absence of a field. A higher electric field drives untwisting of the helical orientation toward uniform homeotropic alignment, but the full untwisting was not observed in the present study because such a high electric field experiment was precluded by the electric short circuit problem.

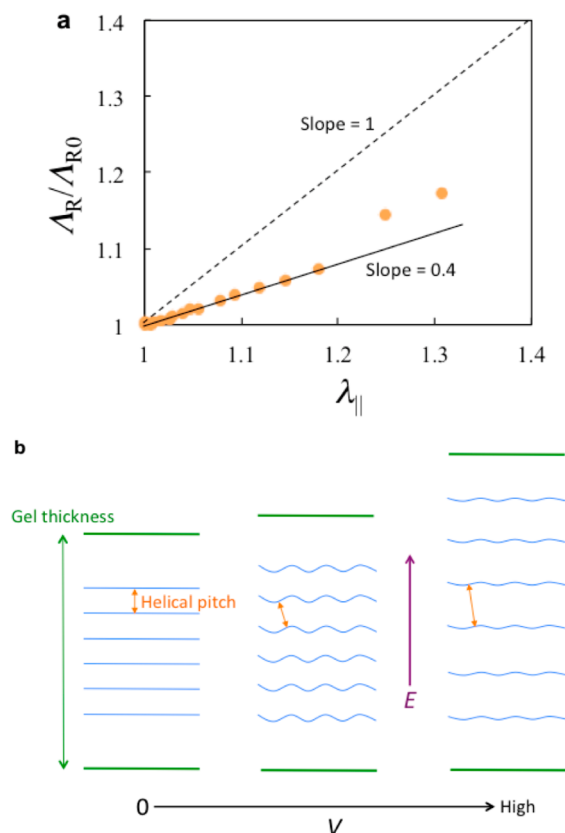


Figure 4. (a) Correlation of the changes in Λ_R and film thickness before and after the imposition of an electric field. The film thickness and Λ_R are reduced by the values in the relaxed state without a field. The line with a slope of unity corresponds to the case of affine variation of the helical pitch with film thickness. (b) Schematic representation of the conjectures for the effects of an electric field on the director configuration in the CLC gels.

In summary, we have demonstrated electrically driven deformation and variation in the optical properties of CLC gels, i.e., CLC elastomers swollen by low-molecular-mass LCs. A sufficiently high electric field induces a finite elongation exceeding 30% along the field axis, as well as a redshift of the selective reflection notch. The redshift of the reflection notch is opposite to the blueshift observed for PSCLCs where the macroscopic deformation is prohibited. The simultaneous electromechanical and electro-optical effects of free-standing CLC gels, which require no mechanical support for a stable orientation of the helical structure, not only increase the possibilities for their use in the design of soft actuators and sensors and LC device applications such as tunable lasers but also provide a challenging issue of the theoretical interpretation in the physics of soft matter.

EXPERIMENTAL METHODS

CLC elastomer films were prepared by radical photopolymerization of the reactive chiral LC monoacrylate (A*-6OCB; Figure 1a) and diacrylate cross-linker (HDDA; Figure 1a) in the presence of a nonreactive achiral LC solvent (6OCB; Figure 1a) using IRGACURE 784 as a photoinitiator. The molar ratio of A*-6OCB, 6OCB, and HDDA was 1:0.29:0.03. The reactant mixture was loaded in a glass cell with a gap of 35 μm . The surfaces of the glass substrates were coated with a rubbed polyimide layer, inducing planar orientation. The mixture was annealed for 3 days at 0 $^\circ\text{C}$, where it showed a monodomain Grandjean cholesteric texture; thereafter, the photo-

polymerization was performed at 0 $^\circ\text{C}$ by irradiation with light at a wavelength of 526 nm for 30 min. After the reaction, the glass substrates were removed from the cell, and the resultant gel films were left to swell in dichloromethane to wash away the unreacted materials and the nonreactive solvent (6OCB). The swollen gels were gradually deswollen by adding methanol to the swelling solvent, leading to fully dried CLC elastomer films. The CLC elastomer films were allowed to swell in a low-molecular-mass LC (5CB; Figure 1a) until the swelling equilibrium was achieved. 5CB was chosen as a swelling solvent instead of 6OCB because pure 6OCB is in the crystalline state at room temperature where the electric field experiment was conducted. In the fully swollen state, the 5CB content was 68%, and the film thickness was 50 μm . The ratio of A*-6OCB to 6OCB in the reactant mixture and the degree of swelling govern the helical pitch in the CLC gels. The A*-6OCB concentration was controlled so that the reflection notch could appear at visible wavelengths in the swollen state of the CLC elastomer films.

The swollen CLC elastomer films were placed between glass plates with indium tin oxide transparent electrodes (Figure 1b). A cell with a gap of 72 μm larger than the film thickness was filled with the swelling solvent (5CB). The spectral properties were obtained using a PMA-12 spectrometer (Hamamatsu Photonics) mounted on a microscope (Nikon LV100POL). A square-wave ac electric field of frequency 1 kHz with various amplitudes was imposed along the initial helical axis using a function generator (NF WF1943) and high-voltage amplifier (Matsusada Precision HEOPS-3B10). The dimensional change of the gels under the electric field was measured using the microscope equipped with a CCD video camera.

ASSOCIATED CONTENT

Supporting Information

Movie showing the simultaneous electromechanical and electro-optical effects of the CLC gel under a square-wave AC electric field of 1 kHz with $E_0 = 20.8$ MV/m. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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