Temperature-Responsive Photonic Devices Based on Cholesteric Liquid Crystals

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Cholesteric liquid crystals (CLCs) are a major class of photonic materials that display selective reflection properties arising from their helical ordering. The temperature response of CLCs, comprising dynamic reflection color changes upon variation of temperature, is exploited using material systems consisting of small mesogenic molecules, polymer-dispersed liquid crystals (PDLCs), polymer-stabilized liquid crystals (PSLCs), or liquid-crystalline polymers. Taking advantage of the easy processability and flexibility of the molecular design, these temperature-responsive CLCs are fabricated into different forms of photonic devices, including cells, coatings, free-standing films, and 3D objects. Temperature-responsive devices developed from CLCs are integrated for application in temperature sensors, energy-saving smart windows, smart labels, actuators, and adding aesthetically pleasing features to common objects. Herein, the device capabilities of the different material systems of temperature-responsive CLCs are summarized: small mesogenic molecules, PDLCs, PSLCs, and CLC polymers. For each system, examples of different device forms are presented, with their temperature responsiveness and the underlying mechanisms discussed. In addition, the potential of each material system for future device applications and product developments is envisioned.

1. General Introduction

1.1. Scope of the Article

Electromagnetic waves of different wavelengths are perceived by most eyes as different colors; this perception is ubiquitous to daily life as humans rely on light for visual recognition of objects, reception of signals, and appreciation of aesthetics. However, the visible spectrum makes up only a fraction of solar light: many wavelengths are invisible to the human eye but are still essential for life on Earth. Near-infrared (IR) light, for instance, is a major component of the Sun’s radiation reaching Earth, predominantly acting as a heating source. Photonic structures are composed of highly ordered stacks of alternating materials with differing refractive indices. This periodic modulation creates a “Bragg reflector” that selectively reflects light of wavelengths that fall in the forbidden bandgap of the structure, following Bragg’s law (Equation 1):

$$\lambda = 2dn_{\text{avg}} \cos \theta$$

where $\lambda$ denotes the bandgap’s central wavelength, $n_{\text{avg}}$ the average refractive index, $d$ the thickness of one periodic structure, and $\theta$ the angle of incident light. Common natural examples of static photonic structures include the alternating layers found in butterfly wings, the opal-like structures of bird feathers, and beetle carapaces. However, biology presents not only static but also dynamic color. Species such as sapphire-inid copepods, panther chameleons, and neon tetra fish can alter their skin colors for camouflage or communication purposes. These dynamic, vivid colors rely on dynamic photonic structures. Decades of biomimetic studies have been conducted to develop iridescent reflectors in the laboratory. Helicoid structures that act as Bragg reflectors can be built...
using self-assembled nanocrystals\cite{16-19} or blue-phase liquid crystals (LCs),\cite{20} but helicoid temperature-responsive devices are mostly realized using cholesteric liquid crystals (CLCs).\cite{21,22}

Typical thermotropic, calamitic LCs consist of rigid mesogenic groups and flexible spacers (Figure 2). The rigid mesogenic groups (cores) often include aromatic or hexagonal rings, providing crystalline order. The cores are linked to soft spacer units, usually aliphatic tails. The combination of cores and tails results in a system with crystalline order but liquid-like rheology due to the presence of both hard and soft moieties. By introducing

**Figure 1.** Photograph and SEM images of the photonic structure of a) a Morpho butterfly (Morpho didius, Reproduced under terms of the CC-BY license.\cite{2} Copyright 2015, The Authors, published by Springer Nature), b) a colored-feather bird (Cotinga maymana, Reproduced with permission.\cite{4} Copyright 2009, Royal Society of Chemistry), and c) a beetle (Chrysina gloriosa, Adapted with permission.\cite{6} Copyright 2009, The American Association for the Advancement of Science) showing the optical dependency of left (LCP)- and right (RCP)-handed circularly polarized light. d) Optical response of sapphirinid (Sapphirina metallina) males, showing color adaptivity to dark or light conditions. Reproduced with permission.\cite{9} Copyright 2016, John Wiley and Sons. e) Images of a chameleon, showing the changes of its skin color from a relaxed state to an excited state. Reproduced under terms of the CC-BY license.\cite{10} Copyright 2015, The Authors, published by Springer Nature. f) Images of a neon tetra fish and the color change of its lateral stripe during exposure to bright light. Reproduced with permission.\cite{11} Copyright 2015, John Wiley and Sons.

**Figure 2.** Schematic representation of the cholesteric phase with a demonstration of selective reflection. The central illustration demonstrates the general molecular structure of CLC systems. The chiral dopants have stereospecific centers that induce the helical twist in the host mesogens. A typical calamitic achiral LC molecule and a typical chiral dopant molecule are shown as an example (left), each with a rigid mesogenic group and flexible spacer unit(s). On the right is a schematic representation of the classical reflection band induced by planar-aligned CLCs, which is often characterized by transmission spectra. The notch in the transmission spectra represents the reflection center ($\lambda$). In some other works where reflection spectra were used, $\lambda$ is presented as the wavelength at the peak.
chiral molecules to the achiral nematic (N) phase, the mesogens self-assemble into the cholesteric (Ch) phase, also referred to as the chiral nematic (N*) phase. The cholesteric phase is similar to the achiral nematic phase but with a small rotational offset of the anisotropic mesogenic units from neighboring units, yielding a helicoidal structure, due to the presence of chiral dopants that induce the helical twist in either a right- or a left-handed manner, depending on the stereochemistry of the dopant’s chiral center. Incident circularly polarized light (CPL) of the same-handedness as the helix is reflected while the opposite handedness of CPL is transmitted. This means that for unpolarized incident light, a maximum of 50% of the incoming light can be reflected. The Bragg reflection wavelength ($\lambda$) of such helical structures is a function of the helical pitch ($p$) and $n_{avg}$ of the cholesteric phase, in which $p$ is equal to the $2\pi$ in Bragg’s law. When observed normal to the surface of the cholesteric ($\theta = 0^\circ$), the Bragg reflection equation can be simplified to Equation 2.

$$\lambda = p \times n_{avg}$$

where $p$ is defined as the distance over which $2\pi$ (full) rotations take place. The helical pitch of CLCs is determined by the helical twisting power (HTP, in $\mu m^{-1}$) of the chiral units, the measure of the capacity of compelling the planes of LCs to rotate through the depth of the layer in the case of planar CLC alignment, the concentration of chiral units in the system ($\epsilon$), and its enantiomeric excess (ee) (Equation 3). In most cases, ee is 1, as absolute stereospecific compounds are used. The sign of the HTP is defined as the handedness induced by the dopant, where a plus sign (+) stands for right-handedness and a minus sign (−) stands for left-handedness.

$$p = \frac{1}{HTP \times \epsilon \times ee}$$

A reflection band rather than a single reflection wavelength $\lambda$ is observed for CLCs, as shown in Figure 2. The width, $\Delta\lambda$, of the reflection band is related to $p$ and the birefringence $\Delta n$ induced by the ordinary $n_o$ and extraordinary $n_e$ refractive indices of the LC mesogens (Equation 4).

$$\Delta\lambda = \Delta n \times p = (n_e - n_o) \times p$$

Photonic structures must consist of highly ordered periodic microstructures for proper Bragg reflection. For CLCs, a planar monodomain alignment is required to present selective reflection properties without light scattering. The advantage of using CLCs lies in their ability to self-assemble into photonic structures. Compared with other forms of photonic crystal structures such as opals, block copolymers, and alternating refractive index layers, structural color from CLCs can be achieved without the presence of phase-separated materials. Furthermore, as a result of the liquid-like flow behavior, the alignment of CLCs can easily be realized by shear or capillary forces, or by use of alignment layers, enabling large-scale fabrication of CLCs into various device forms, including cells (material sandwiched between substrates), coatings (material on a single substrate), free-standing films, microcapsules, and even 3D objects.

Technologies based on stimuli-responsive CLC systems that alter their reflective color are rapidly developing. Light-responsive CLCs feature rapid and reversible color changes under light irradiation, promising for devices such as erasable displaying boards and sunlight-adaptive windows. Electrically responsive CLC devices change color and/or transparency under the influence of an electric field and are favorable for tunable light reflectors or privacy windows in which multiple optical modes can be altered dependent on the users’ preferences. Other CLC devices responsive to water chemicals, mechanical forces, and interfacing biomolecules demonstrated dynamic photonic properties and could be used as sensors and lasers, for instance. In particular, “smart” temperature-responsive CLCs have found their way into numerous applications as they can alter their pitch length, and thus their reflective color, autonomously with a change in temperature. Such autonomously responsive CLC systems are desirable as temperature indicators, interactive decorations, smart safety labels, and energy-regulating “smart” windows.

Responsive CLC materials can be divided into several categories based on their molecular structures. Classical CLC systems involve only small mesogenic molecules, where the mesogens have a high degree of freedom to rotate and displace. Reactive CLCs can be polymerized, creating linear polymers or crosslinked networks, although mesogens are prone to lose most of their temperature response when crosslinked. Hybrid systems between free mesogens (small molecules or oligomers) and crosslinked polymers are called polymer-stabilized liquid crystal (PSLC) systems, wherein the free mesogens are interpenetrated by the LC network. An alternative configuration is the polymer-dispersed liquid crystal (PDLC) system, in which the LC phase is encapsulated within a nonmesogenic polymer binder. Small mesogenic molecules, PSLCs, PDLCs, and polymers of CLC systems each have their own unique features related to working mechanisms and resulting temperature responses, suggesting different application suitability.

This Review presents an overview of recent developments in temperature-responsive CLC devices using small mesogenic molecules, PSLCs, PDLC, and polymeric CLC systems. We focus primarily on the temperature-responsive reflective color (TR-RC), in which changes in the reflected wavelength are visible while maintaining a planar monodomain cholesteric alignment, and discuss the potential of each material system for future device developments. Alternative systems with optical responses including complete loss of reflectivity and/or diffraction effects are outside the scope of this Review.

### 1.2. The TR-RC Mechanisms of CLCs

Introducing a variation in CLC reflective color with change in temperature can be achieved via different mechanisms, which are listed and briefly explained in the following subsections as they will appear throughout the text. All these TR-RC mechanisms rely on the change of essentially a single parameter, the pitch length $p$. 

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**Equation 2:**

$$\lambda = p \times n_{avg}$$

**Equation 3:**

$$p = \frac{1}{HTP \times \epsilon \times ee}$$

**Equation 4:**

$$\Delta\lambda = \Delta n \times p = (n_e - n_o) \times p$$
1.2.1. Isotropization

The most basic of all TR-RC behaviors occurs at the nematic-to-isotropic transition of CLCs, whereupon the structural color vanishes. Although this temperature response is outside the scope of this Review, it is important to address this essential concept here, as isotropization is present in almost every heated CLC system, unless it is highly crosslinked. Notably, some TR-RC systems that we introduce are reversible from the isotropic state or utilize isotropization to initiate the temperature response.

1.2.2. Heat-Responsive HTP of the Chiral dopant

The generation of a cholesteric phase requires the presence of a chiral center. This can either be achieved by adding a chiral dopant to achiral nematic LCs or using mesogens that themselves contain chiral centers (e.g., cholesterol-based derivatives). Individual chiral dopants have different HTP values, and often the HTP of chiral dopants is temperature dependent. The change of HTP upon heating/cooling results in a change of the CLC pitch via winding or unwinding of the helices (Figure 3a). This process does not require changes to the thickness of the sample but changes in the number of pitches through the layer thickness; these effects are always reversible.

1.2.3. Smectic–Cholesteric Transition (Sm–Ch)

In the smectic (Sm) phase, the LC mesogens adopt an ordered layered structure. Some CLCs have a smectic A (Sm) phase

Figure 3. Schematic representations of the different TR-RC mechanisms of CLCs: a) heat-responsive HTP; b) Sm–Ch transition; c) phase separation of nonmesogenic molecules; d) phase separation of mesogenic molecules; e) pitch increase due to anisotropic expansion upon heating; and f) shape memory mechanism.
transition at lower temperature, and passing through this phase transition can have a dramatic effect on the photonic structure. The pitch of the unwinding helices increases toward infinite with decreasing temperature, resulting in an exceptionally large reflection band shift over a relatively small temperature range. The Sm–Ch effect is understood as the gradual growth of Sm moieties out of the Ch phase that enlarges the pitch length (Figure 3b). Thus, the reflection band always red shifts with decreasing temperature, as the pitch is increased at lower temperatures. The closer to the Sm transition point, the sharper the variation of band shift, due to the pretransitional helix unwinding.

1.2.4. Phase Separation

This mechanism alters the helical pitch by the removal of incorporated substances (such as water or volatile organic solvents) from the cholesteric system. The substances may be removed by evaporation, precipitation, or by a phase separation between different LCs (Figure 3c,d). The removal of filler molecules such as water or achiral LCs leads to a reduction of the pitch, whereas removing chiral dopants leads to an increase in the pitch. The reversibility of these systems depends on whether the separated species can be reabsorbed by the LC matrix.

1.2.5. Thermal Expansion

Thermal deformation, usually manifested as an expansion with increasing temperature, is commonly seen in materials. For planar-aligned CLC polymers, anisotropic expansion occurs primarily along the director of the helix, leading to an expansion of pitch length and corresponding spectral red shift (Figure 3e). This process is usually reversible.

1.2.6. Shape Memory

Shape memory refers to the ability to deform the shape of a material into a temporary configuration and the recovery of the material back to its initial shape upon exposure to a stimulus. The shape memory mechanism of TR-RC CLCs utilizes the glass transition of a cholesteric polymer. In this process, the polymer chains are immobilized by maintaining the sample under its glass transition temperature ($T_g$), where the polymer has a higher modulus. Deformation in the CLC polymer above $T_g$ can be induced via applying a mechanical force (such as embossing or stretching), reducing the pitch length, and causing a blue shift in the reflection band, followed by cooling the sample to below $T_g$ to fix the temporary shape (Figure 3f). The blue-shifted reflection returns to its original value by heating the temporary shape above $T_g$, allowing the polymer to return to its initial shape as its elasticity recovers. This shape-memory recovery effect is irreversible without further modifications but the polymer may be subsequently reprogrammed.

2. Temperature-Responsive CLCs in Different Configurations

2.1. Small Mesogenic Molecules

Low-molecular-mass CLCs are the most extensively studied cholesteric systems. In early studies, CLC materials were primarily investigated by capillary filling of the material between two glass plates in the isotropic phase, followed by cooling until the cholesteric phase is reached; occasionally, the cells were directly filled in the Ch phase. The required planar Ch alignment sometimes forms spontaneously but is often aided by shearing the glass plates or using alignment layers coated on both substrates. Common materials serving as alignment layers are rubbed polyimide, polyvinyl alcohol, or photoalignment layers. The mechanisms of the TR-RC of CLC cells can include band shifting through heat-responsive HTP dopants, the Sm–Ch transition, and phase separation (vide supra).

A variety of temperature-sensitive dopants have been synthesized and investigated. The chemical nature of the chiral center is key to the variation of the HTP with temperature. The HTP variation stems from different interactions between the changing molecular conformations of the chiral dopant with the host. Typical chiral centers that exhibit thermal HTP sensitivity include, but are not limited to, carbohydrates, chiral 1,2-ethanediol esters, TADDOL derivatives, chiral amino anthraquinones, binaphthyl derivatives, and ephedrine/pseudoephedrines. Depending on the nature of the chiral dopant, the absolute HTP values can either increase or decrease with increasing temperature, leading to blue shifts or red shifts of the reflection band. In some cases, the sign of the HTP value can even convert upon temperature changes from “positive” (right-handed) to “negative” (left-handed) and vice versa, an event known as helix inversion. The helix inversion is a result from the competition of different chiral species or conformers of a compound that contribute to opposite handedness. In addition to the identity of the chiral core, features that determine the magnitude of HTP temperature sensitivity include the spacer length and side-group substituents. In contrast, the nature of the nematic LC host only plays a minor role in the temperature sensitivity of the CLC reflection band. A complete theory correlating the influence of the molecular structure on the HTP is not yet available. Table 1 shows the different TR-RC trends observed with HTP variation: a blue shift or red shift of the initial reflection band upon heating and the inversion of the HTP value during heating or cooling. In the example of helix inversion, the pitch length is reported rather than the wavelength, as the reflection band of this device is out of the normal visible detection range. Although few of these reported CLC systems resulted in actual demonstrators, it is expected that by selecting proper host/dopant molecules and tuning their ratios, different reflection wavelengths (pitch) regions could be accessible and the extent of their temperature responses could be optimized to suit the intended application.

Another frequently used method to establish TR-RC small-molecule CLC systems is based on the Sm–Ch phase transition. As an example, the reflection band shift in CLC systems can be
tuned using different ratios of the chiral dopant S811 in the nematic LC host E7 (Figure 4a) and a >450 nm shift of the reflection band is observed upon a temperature change of only 0.2 °C (Figure 4b). The combination of dopants and hosts is important in initiating this effect as the presence of a Sm–Ch phase transition is required. For instance, the chiral dopant S811 induces the Sm phase in the commercial hosts E7, ZLI-2806, and MLC-6608 but not in hosts such as MLC-0643 and ZLI-4608, which instead display normal shifts from changing the HTP with temperature. Maintaining planar helical alignment upon temperature variations in these systems is essential for transparent devices. In some cases, rather than shifting the reflection band, the sharp transition between the Sm and Ch phases can instead result in disruption of the planar helical alignment into a focal conic state, resulting in scattering. This misalignment can be corrected by annealing in the Ch temperature range with the assistance of an alignment layer. To minimize scattering, the rate of heating and cooling could be decreased.

In some CLC systems, the thermally driven pitch change is controlled by the solubility of the chiral dopants in the host (phase separation mechanism, vide supra), such as that observed with an oversaturation of the chiral dopant S811 (named as ZLI-811 in the article) in the LC host BL006 at lower temperatures (Figure 5a). Above 28 wt% of S811, the precipitation of dopant molecules as crystals could be observed at room temperature (Figure 5b). When the temperature increased, the solubility of the dopant increased, and the crystals gradually re-dissolved into the host, inducing a blue shift. This effect was reversible upon cooling. In comparison, no obvious over-saturation was seen when the chiral S811 content was 26 wt % or less (Figure 5c). Consequently, there was also little temperature response. A

![Table 1. Illustrative examples of TR-RC tendencies of HTP-changing chiral dopants in CLC cells.](image)

| TR-RC tendency       | Blue shift with heat<sup>a</sup> | Red shift with heat<sup>b</sup> | Helix inversion<sup>c</sup> |
|----------------------|---------------------------------|---------------------------------|-----------------------------|
| Chiral dopant structure | ![Structure](image) | ![Structure](image) | ![Structure](image) |
| Host<sup>a</sup>     | MLC-0643                        | SLC1717                        | SLC1717                     |
| Response<sup>b</sup> | ![Spectra](image)              | ![Spectra](image)              | ![Spectra](image)           |

<sup>a</sup>Commercial nematic LC mixtures; <sup>b</sup>Reflection spectra. Adapted under terms of the CC-BY license. Copyright 2014, OSA Publishing. Adapted with permission. Copyright 2014, Royal Society of Chemistry. Adapted with permission. Copyright 2009, Taylor & Francis.

![Figure 4. An example of the TR-RC behavior of a CLC system with Sm–Ch transition. a) CLC mixtures of E7 and S811 in cells showing a pitch–temperature relationship with different concentrations of the chiral dopant S811. b) Transmission spectra of the CLC cell with 21 wt% S811 indicating a significant blue shift upon heating. Reproduced with permission.](image)
similar effect has been reported in other CLC mixtures based on this phenomenon.\textsuperscript{[80,81]}

Indirect heating by applying an electric field can also be used to generate photonic bandgap tuning in CLC systems in a fashion similar to that described earlier.\textsuperscript{[76,82–85]}

Electrothermal color tuning is possible by applying an electric field between two conductive substrates\textsuperscript{[76,84,86]} or using only one conductive substrate with a specifically designed interdigitated electrode pattern.\textsuperscript{[85]}

Figure 5. Demonstration of a TR-RC CLC system (LC host: BL006, chiral dopant: ZLI-811, i.e., S811) based on the chiral dopant solubility. a) The reflection wavelength varies drastically above a critical chiral dopant concentration (26 wt%). The response becomes increasingly pronounced at higher doping concentrations. b) Microscopic images of the CLCs with 34 wt% chiral dopant ZLI-811 upon heating, showing a color shift and evidence of chiral dopant precipitation at room temperature. c) Microscopic images of the CLC mixture with 24 wt% chiral dopant ZLI-811 at 23 °C, showing the absence of oversaturation. Reproduced under terms of the CC-BY license.\textsuperscript{[53]} Copyright 2006, OSA Publishing.

Figure 6. Transmission spectra of a CLC mixture (MLC-2138:S811, 65:35 wt%) showing the induced bandgap shift upon applying a) a thermal and b) an electrothermal stimulus. c) Plot of the temperature increase and corresponding bandgap shift upon varying the applied voltage of a high-frequency in-plane electric field. Reproduced with permission.\textsuperscript{[85]} Copyright 2020, John Wiley and Sons. d) Frequency-induced heating at a constant applied voltage in a CLC cell. Reproduced under terms of the CC-BY license.\textsuperscript{[53]} Copyright 2018, OSA Publishing.
that generates an in-plane alternating current (AC) electric field. To give an example of electrothermally driven bandgap shifting, a CLC system consisting of a nematic LC mixture MLC-2138 and a chiral dopant S811 was used to fill a cell equipped with an interdigitated electrode pattern on top of a glass substrate. The system can operate autonomously by temperature changes [Figure 6a] or can be controlled manually by applying an AC electric field to the system [Figure 6b]. The electrothermal response can be controlled by tuning the applied voltage and/or frequency [Figure 6c,d]. In this case, the working principle is based on pseudodielectric relaxation effects that generate heat on demand within the system when a high-frequency AC electric field is applied, achieving spectral shifts. For example, a pixelated thermosensitive CLC device can be locally heated to any color by an electric field regardless of the ambient temperature.

A photothermal response can also be obtained upon incorporating a photo-absorbing dye in the TR-RC CLC system. By illuminating the sample with an appropriate light source, the dye absorbs the incoming light which is converted into heat; an IR dye could be added to a CLC mixture and cause significant heat generation upon illuminating the sample with IR light, for instance. The use of indirect stimuli to achieve a temperature increase allows for a broader application range of TR-RC CLC systems.

2.1.2. Coatings

Although small mesogenic molecules have been thoroughly studied in cells, recent advances in small-molecule systems have shifted the focus toward single-substrate devices, as coatings allow for easy scale-up production and could be introduced in a broader range of applications (e.g., flexible devices) compared with cell-based CLC systems. Small mesogenic molecular systems, however, suffer from poor performance stability over time due to their fluid-like behavior. Therefore, the CLC system must be confined to prevent LC leakage.

Confining a nonreactive CLC mixture with a hard polymer topcoat could improve the stability and toughness of the system. To prepare such coatings, a temperature-responsive CLC mixture is blended with UV-curable acrylate monomers and a UV absorber. After applying a layer of the unreacted mixture on top of a substrate, subsequent photopolymerization at a low intensity initiates a polymerization-induced phase separation [Figure 7a]. The UV absorber creates a steep light intensity

*Figure 7.* Demonstrations of photoinduced phase separation yielding a polymeric hard topcoat that protects the TR-RC CLC small mesogenic molecules underneath. a) Scheme of a one-step photopolymerization-induced phase separation. A homogeneous mixture containing CLCs and acrylate monomers is bar coated, followed by photopolymerization with low-intensity UV light. The mixture phase separates during polymerization causing the formation of a hard polymeric topcoat and a nonpolymerized CLC layer. b) The stratified coating shows a TR-RC change upon heating. c) Flexible devices were possible using a polycarbonate foil as a substrate. d) Leakage of the CLC layer can be prevented using a substrate with predesigned trays. e) A butterfly pattern was 3D printed from poly(lactic acid). After filling the trays with the CLC/monomer mixture and subsequent photoinduced phase separation, a reversible TR-RC behavior was observed upon heating and cooling. Reproduced with permission. Copyright 2019, Royal Society of Chemistry. f) Scheme of two-step photopolymerization-induced phase separation. (i) After coating the mixture, (ii) polymeric walls are formed using a mask during the first illumination step, (iii) phase separation was induced in the second photopolymerization step, and (iv) yielding a pixelated coating. g) The TR-RC response is not disturbed during bending and unbending due to the presence of the polymeric walls. Reproduced with permission. Copyright 2019, Royal Society of Chemistry.
gradient through the film thickness, causing the UV-curable monomers to rapidly polymerize near the top surface, promoting the diffusion of additional monomers to the film surface, thereby forming a hard polymeric topcoat. Thus, after photopolymerization, the CLC mixture is protected by a polymer layer and shows a reasonable degree of alignment. Upon heating, a blue shift was observed in a similar fashion, as has been reported for the cell-based CLC systems (Figure 7b), and the devices were flexible as a thin polycarbonate sheet was used as substrate (Figure 7c). In addition, substrates consisting of predesigned trays were fabricated to prevent LC leakage and enhance the structural integrity and robustness of the device (Figure 7d). Complex patterned substrates can be made in any arbitrary shape and pattern with a 3D printer, for example. Figure 7e shows an example of a phase-separated photopolymerized CLC coating on top of a printed substrate.

Coating robustness could be enhanced even further by introducing vertical polymer walls, which could directly be formed from the mixture. This is realized via a two-stage polymerization procedure using a mask at first to locally form vertical polymer walls out of the initial mixture during a first illumination step, followed by a low-intensity UV exposure as is described earlier (Figure 7f). The wall structures confine the CLCs in squared pixels, and this two-stage polymerization method makes the device less susceptible to damage upon bending. These devices can maintain their reflection colors without shifting, up to a 70 mm bending radius (Figure 7g).

2.2. Polymer-Dispersed Systems with Small Mesogenic Molecules

2.2.1. Microencapsulation of CLCs and Their PDLC Devices

Encapsulation of CLCs into uniform-sized shells resulted in the development of angular-independent TR-RC devices (Figure 8a–c). Using a microfluidic production method, TR-RC CLC material is confined in elastic shells of photocured silicone methacrylates. Remnant glycerol and polyvinyl alcohol from the emulsion solution at the shell interface provide a surface with planar anchoring conditions for the alignment, with the helical axis extending in the radial direction (Figure 8a). Due to the radial CLC configuration, the reflection color of the particles is independent of the viewing angle. The TR-RC was preserved in these capsules, which showed a red-to-green color shift between 18 °C and 34 °C (Figure 8d). A fluorescent dye was doped into the LC phase to allow for lasing. The radial alignment of the CLC leads to omnidirectional lasing, which can be used for imaging applications.

One can project that such microcapsules can be dispersed in a polymeric binder to establish cells or robust coatings. Such PDLC systems are often highly robust and can be produced without alignment layers, making them well suited for all manners of applications. However, the two-step protocol (microencapsulation and dispersion into the polymer matrix) can be time-consuming for device fabrication. One-step methods are more desirable for PDLC formation and are discussed below.

2.2.2. PDLC Coatings Fabricated via Emulsification

A route to attain PDLC systems without first creating the CLC capsules is to disperse the CLC material into an aqueous solution containing a polymer binder via an emulsification method. Upon emulsifying, the CLC material is dispersed as droplets due to the immiscibility between the aqueous solution and the CLC material. After coating the emulsion on top of a substrate, the system is left to dry. Deswelling of the deposited film, induced by water evaporation, promotes alignment into oblate spheroids due to the compression of the original CLC spheres (Figure 9). The planar helix orientation is thereby acquired due to the solidification of the polymer, which was present in the aqueous solution.

![Figure 8](https://www.advancedsciencenews.com)

**Figure 8.** a) Schematic of a photonic capsule composed of a CLC core with a dye dissolved into it, an inner alignment layer, and an outer elastic shell. b,c) Photograph and optical microscopy image of dried CLC capsules. The capsules maintain their spherical shape and radially aligned helical axes, which result in photonic crosscommunication. d) TR-RC demonstration of the CLC microcapsules observed using microscopy. Reproduced with permission. Copyright 2018, The American Association for the Advancement of Science.
The resulting reflective CLC coatings contain CLC droplets size dependent on the mixing rate during emulsification. A recent example of such emulsion-based PDLC coatings that exhibit a TR-RC response is based on CLCs having a Sm–Ch transition upon heating embedded in polyvinyl alcohol. Additional methods have been developed to achieve PDLC systems, but to our knowledge, the emulsion-based procedure is the most common method for rapidly obtaining thermosensitive reflective PDLC devices in a single production step. However, compared with the CLC capsules, the size distribution of the CLC droplets is broader, which induces light scattering that reduces the transparency of the PDLC films.

2.2.3. Commercial Applications Based on Thermosensitive Reflective PDLCs

Commercial products, such as Feverscan (LCR Hallcrest) and SFXC Liquid Crystal Sheets (SFXC), have been developed using microencapsulated TR-RC CLC inks. The formulations of these inks are confidential, but the product descriptions (e.g., the product sheets can be cut with scissors) strongly suggest that these formulations are based on one of the PDLC methods explained earlier. These flexible temperature-responsive sheets can be applied directly to a substrate as a label using an adhesive layer. These TR-RC inks can be bought separately and used to decorate a surface using spray coating and inkjet printing.

Despite these promising PDLC applications, some major challenges remain. The development of uniformly sized CLC capsules/droplets on large scales is challenging, and they can become inhomogeneously distributed after coating and drying. Due to the refractive index mismatch between the CLC spheres and the polymer binder, these films are prone to scattering, so this technique has not been used to develop transparent devices to date. To resolve this issue and enhance color contrast, a black background is typically used.

To the best of our knowledge, these PDLC systems are the only ones where a planar CLC alignment can be achieved without applying external stimuli (e.g., pressure and electricity) to the system. Other PDLC systems such as photopolymerization-induced PDLCs require an electric field to induce planar CLC alignment and have (to our knowledge) not been reported in combination with TR-RC CLCs. Most PDLC examples reported in the literature use an electric field to switch between opaque and transparent states, but these alternative PDLC systems are outside the scope of this Review.

2.3. Polymer-Stabilized Systems with Small Mesogenic Molecules

2.3.1. Cells

By stabilizing CLCs with a small amount of crosslinked LC network, the TR-RC functions of CLCs can be expanded. For instance, band broadening of the reflection was achieved using temperature-sensitive chiral dopants. These polymer-stabilized liquid crystal (PSLC) systems include 3.7–4.8 wt% of a crosslinked nematic network with the remainder of the mixture consisting of TR-RC, low-molecular-weight CLCs with temperature-sensitive chiral dopants. The loose network creates an “anchoring effect” for the small mesogenic molecules that generate band broadening (Figure 10a inset): nonreactive CLC molecules near the polymer network are physically constrained and are no longer able to respond to changing temperatures. In contrast, CLC molecules located further away from the polymer network have more freedom of motion, and their temperature response is unaffected by the network. As a result, the reflection band of the system is gradually broadened upon heating. Different combinations of chiral dopants were used to generate both blue- and red-shifted broadening with elevated temperatures. As an example, using a combination of thermosensitive chiral dopants polymerized at 0 °C, a sample device varied its reflective properties in the range of 860–2500 nm when heated from 0 to 34 °C (Figure 10a): red reflection was even visible at 34 °C as the reflection partially encroached the visible region (Figure 10b). This type of band-broadening CLC device is favored in the development of IR-rejecting “smart” windows, as the solar IR irradiation covers a wide wavelength range (between 800 and 2000 nm), requiring ultra-broadband reflection (normal cholesteric reflectors in the IR are generally restricted to ≈100 nm bandwidth). Other HTP-sensitive CLC systems were stabilized with crosslinked mesogenic networks and have led to similar band-broadening responses. Tuning of broadband PSLC systems can also be realized by introducing an inhomogeneous polymer network distribution through the thickness of the cell by creating a UV gradient during polymerization by adding a UV absorber.

More complex dynamic photonic properties and temperature responses can be achieved by engineering the polymer structures of PSLCs. In one example, a single-layered cell was developed that reflects both left- and right-handed CPL. After the fabrication of a non-responsive PSLC cell with a right-handed helix, the nonpolymerizable CLCs were removed. Although the network mesogens lack any chiral centers themselves, the scaffold
retains the right-handed helical structure (Figure 11a). After refilling the cell with left-handed temperature-sensitive HTP-changing CLCs, the cell reflects both left- and right-handed CPL, with static right circular polarized (RCP) light reflection (at ≈700 nm) and a responsive left circular polarized (LCP) light reflection (700–400 nm, from 165 to 190 °C), as shown by the transmission spectra (Figure 11b). The additive color benefited from both reflection bands can be seen as well, showing mixed colors with unpolarized light at 175 and 190 °C (Figure 11c).

Inducing temperature-responsive photonic effects is more difficult for PSLC systems composed of Sm–Ch–type CLCs. In one example of such an Sm–Ch PSLC system (SLC-1717/S811, host/dopant) with 4 wt% polymer network,[116] the cells did not display any band shift in response to temperature changes but rather turned opaque (scattering) after cooling to the smectic phase. Another example using an 8CB/S811 (LC host/dopant) system with 5 wt% polymer network shows a temperature-responsive band shift, though with a significantly reduced reflection bandwidth (750–950 nm, 200 nm range) in comparison with the same system without network stabilization (800–1300 nm, 500 nm range).[117] Compared with the rigid acrylate networks, elastomeric networks of polysiloxanes can support a larger Sm–Ch effect. For example, an LC system (8CB/12CB/SLC1717), which has a smectic–nematic phase transition, was blended with a
crosslinked polysiloxane elastomer that contained chiral mesogens for inducing the Ch phase, which resulted in a sharp Sm–Ch effect in the cell, even with 25 wt % elastomer fraction.\textsuperscript{[118]} The material shows a 1200 nm band shift over a temperature change of just 4.8°C. The assumption is that the elastomeric state of the network enables sufficient reorientation of the mesogens upon temperature variations to accommodate such an extreme transition.

The only reported case of band broadening when using PSLCs with an Sm–Ch phase transition is seen in a cell with an ultrathick (203 μm) LC layer containing 11 wt% acrylate network and 88 wt% of a nonreactive Sm–Ch phase transition CLC mixture.\textsuperscript{[119]} A small quantity of side-chain polysiloxane LC oligomer (about six mesogens per chain) was included in the mixture (5 wt%). The cell presents an extraordinarily large band broadening with decreasing temperature. At a polymerization temperature of 132°C, the reflection band was believed to be located below 300 nm. Driven by the Sm–Ch phase transition, the reflection band broadens as the cell cools. An ultra-broadband was presented (300–2500 nm) at room temperature, reaching the full range of the instrument limits. The authors assume that a very large nonuniform pitch distribution was induced during photo-polymerization, leading to this extraordinary effect. However, the contribution of the extreme layer thickness and side-chain oligomer to band broadening was not completely explained.

2.3.2. Coatings

Although PSLC systems utilize polymer networks, they primarily consist of small mesogenic molecules and are presumably not resistant enough to mechanical forces (e.g., touching) for use in coating applications. A rare example of a temperature-responsive PSLC applied as a coating is one using a 20 wt % polymer network that includes a chiral crosslinker species with a thermosensitive HTP.\textsuperscript{[120]} The PSLC was prepared via a cell-filling procedure, after which one glass plate was subsequently removed to obtain the coating. A red shift of color was observed after polymerization. The coating demonstrated a reversible color shift from green to red (575–650 nm) between 30 and 75°C (Figure 12a). To demonstrate the versatility of the film, a red pattern was drawn on the coating using a hot-pen. The color change was reversed upon cooling, whereupon the pattern disappeared (Figure 12b). However, the robustness of the coating surface when exposed to external stresses was not demonstrated.

2.4. Polymers

2.4.1. Cells

In contrast to small mesogenic molecules, the LC-to-crystal phase transition is normally suppressed in polymeric and oligomeric LCs, which instead display glass transitions. Noncrosslinked side-chain CLC polymers/oligomers have been synthesized and studied extensively in cells.\textsuperscript{[121,125]} The polymers/oligomers that show TR-RC properties usually have polysiloxane backbones and are driven by the Sm–Ch mechanism.\textsuperscript{[126,127]} The kinetics of the color shift are often slowed down as molecular weight is increased.\textsuperscript{[128]} It was found that apart from the types of mesogenic groups, the selection of spacer lengths and backbone chain lengths is also critical to the presence of a Sm–Ch transition.\textsuperscript{[129,130]}

CLC oligomers can be stabilized by a crosslinked network. TR-RC PSLC cells have been fabricated using a blend of partially crosslinked cyclic polysiloxane CLC oligomers and a helix-inversion compound 4-{[(S,S)-2,3-epoxyhexyloxy]phenyl} 4-(decyloxy)benzoate.\textsuperscript{[131,132]} The temperature at which the nematic phase (HTP = 0) was achieved (and helicity inversion occurs) was 83°C (Figure 13a). The mixture was polymerized at 97°C, where a right-handed helix with a reflection center at 2.7 μm was present. After polymerization and subsequent cooling to 74°C, the nonpolymerized helices inverted to left handed with a reflection center at 2.7 μm, resulting in a device reflecting both LCP and RCP light, therefore exceeding the 50% reflection limit usual for a single CLC layer (Figure 13b). By quenching the cell with liquid nitrogen, the responsive left-handed helix was vitrified; slowly warming the cell back to room temperature resulted in the fixation of the highly reflective state.\textsuperscript{[132]}

![Figure 12](https://www.advancedsciencenews.com/2100016)

**Figure 12.** a) Reflection spectra of the PSLC cell before/after polymerization at 30°C and upon heating to 75°C after polymerization. A red shift of reflection color upon heated is presented, as can be also seen in the photos. b) The PSLC coating was demonstrated by a pattern drawn in regions partially heated by a hot-pen. Upon cooling, the pattern disappeared. Reproduced with permission.\textsuperscript{[120]} Copyright 2010, Royal Society of Chemistry.
As might be expected, fully crosslinked CLC polymers impose even more restrictions on the mobility of the mesogens compared with the uncrosslinked CLCs or PSLCs. To give an example, a CLC polysiloxane elastomer was formed by reaction of a siloxane having initially a linear backbone, whereas the mesogenic group and crosslinker consisted of cholesterol and binaphthalene units, respectively. The spacer lengths of all monomers are three methylene groups in this study. Using 14 mol % crosslinker shows a reversible blue shift of the reflection band in the cell between 70 °C (near $T_g$) and 130 °C (near $T_i$). The thermal change of the HTP is attributed as the source of the responsivity. By maintaining the crosslinker ratio and increasing spacer lengths of the binaphthalene moiety, the elastomer still has TR-RC properties, through either a HTP changing (eight methylene groups) or Sm–Ch (ten methylene groups) mechanism. However, considering the short siloxane backbone used (four mesogens per chain on average), despite 14 mol% of the monomers being crosslinkers, it is...
Figure 15. a) Chemical structure of the side-chain siloxane oligomer. A reactive acrylate end-group on one of the side chains allows network formation during photopolymerization. b) Temperature-induced reflection band shift of the coating upon cooling to room temperature. The reported bandgap shift is reversible over several heating and cooling cycles due to the presence of the polymer network. Adapted under terms of the CC-BY license. Copyright 2020, The Authors, published by MDPI.

Figure 16. a) Chemical composition of the TR-RC coating based on phase separation: the LCE and 21 wt% of reactive chiral mesogens (RM-1 and RM-2) as the network after polymerization. b) Representation of the phase separation mechanism. Above $T_{Ch-I}$, diffusion of the LCE molecules toward the coating–air interface causes a contraction of the helical pitch corresponding to a blue shift of the reflection band. Cooling down below $T_{Ch-I}$ allowed the LCE molecules to diffuse back into the polymer network, and a corresponding red shift of the reflection band was observed over time. c) Photographs of the coating, showing the blue- and red shift during, respectively, heating above or cooling below $T_{Ch-I}$. Reproduced with permission. Copyright 2019, American Chemical Society.
estimated that the TR-RC elastomers have a low crosslink density. Upon tuning the elastomer composition with other spacer lengths or increasing crosslink densities, the TR-RC effect is lost, indicating that the responsivity is parameter sensitive.

Nonetheless, one example of the TR-RC cell with fully cross-linked acrylate networks is reported.\(^{[135]}\) The monomer mixture composition consists of 100% polymerizable units without any small mesogenic molecules. The chiral crosslinker PCHA (Figure 14a) displays a significant change of HTP with temperature due to the weakening of its hydrogen bond interactions. The polymerized cell containing PCHA produced a red shift from 570 to 611 nm when the temperature was increased from 60 to 200°C (Figure 14b). The authors argue that the remaining responsivity in the highly crosslinked system arises from the “free volume,” which can be understood as the freedom of mesogens reorientation of a few monomers that were unreacted during polymerization. In the following experiments, pH responsivity was found in this molecular system explored as a free-standing film, but the TR-RC property as a free-standing film was unfortunately not reported. Based on the proposed mechanism, one could assume that the TR-RC properties of this layer could be maintained or even increased as a free-standing film.

### 2.4.2. Coatings

TR-RC PSLC coatings with small mesogenic molecules have low durability due to LC leakage and susceptibility to physical damage, but by using oligomers in PSLCs, more robust coatings are possible. A Sm–Ch side-chain siloxane oligomer containing acrylate crosslinkers (Figure 15a) was synthesized, and photonic coatings were fabricated from this oligomer via bar coating with the aid of a nematic solvent, resulting in good planar cholesteric alignment.\(^{[136]}\) Polymerization of the acrylate network was conducted under UV light, followed by removal of the nematic solvent. As only a fraction of the oligomer is crosslinked (≈50% of all chains), the resulting coating contains both crosslinked networks and uncrosslinked oligomers and is therefore considered a PSLC system. Despite the significant crosslinking, this fully

![Figure 15. a) Chemical composition of the CLC mixture. Hydrogen bonding occurs between the chiral dopant (MAA) and the carboxylic end groups of the monoacrylate structures 6OBA and 6OBAM, resulting in a hydrogen-bonded CLC coating after photopolymerization. b) Upon heating to 160°C, a blue shift was observed, indicating the evaporation of the noncovalently bonded chiral dopant (MAA). c) 3D surface topography map of the CLC polymer coating that was locally heated with a laser beam, revealing a temperature-induced reduction in coating thickness. d) Local heat exposure allows for topographical changes and corresponding color patterns. Adapted with permission.\(^{[139]}\) Copyright 2016, Society of Photo-Optical Instrumentation Engineers (SPIE).](image-url)
polymerized and partially crosslinked polymer coating retained its temperature responsivity originating from the uncrosslinked fraction, resulting in a reversible ≈600 nm blue shift of the reflection center, from 1363 nm to 775 nm between 31 and 66 °C (Figure 15b). Below 31 °C, close to the Sm transition, the reflection band ceased to shift. It is believed that the rigid polymer chain prevents the smectic domains from growing further. The TR-RC performance of such coating is steady through multiple cycles, and through prolonged storage. In a later work, this molecular system is simplified using a crosslinked acrylate network with the noncrosslinkable oligosiloxane CLCs.\textsuperscript{[137]} Coatings were fabricated with different network ratios and their temperature responses were studied. An optimal network of 3 wt\% is found to retain a sufficient temperature response from blue to red, with full reversibility from the isotropic transition. Moreover, a commercial PDMS elastomer can be applied directly on top of the CLC layer to serve as a protective topcoat, protecting the coating from touching.

Another example of a PSLC coating with oligomers was obtained using a phase separation mechanism.\textsuperscript{[54]} The molecular system consists of an achiral siloxane oligomer that functions as a liquid crystal elastomer (LCE) and 21 wt % of reactive chiral mesogens (RM-1 and RM-2) that form a crosslinked network after photopolymerization (Figure 16a). The coating initially shows red color at room temperature (centered at 800 nm). Upon heating above the isotropic transition of the LCE, the coating reflection gradually blue shifts to 515 nm after 3.5 h as the LCE slowly diffuses towards the air interface (Figure 16b,c). A reversed shift is observed over a span of 3 weeks upon cooling below the isotropic temperature as the phase-separated LCE slowly mixes back into the PSLC, causing swelling and thus the reversal of the band shift.

Broadband CLC siloxane coatings could be developed by stacking narrowband CLC siloxane layers, each with different chiral dopant concentrations and thus different reflection bands on top of each other.\textsuperscript{[138]} Upon controlled thermal diffusion between the narrowband CLC layers, a broadband siloxane coating is formed with an effective pitch distribution throughout the film. Although no temperature response of the broadband CLC coating was reported, one could argue that a thermal response could be achieved using thermosensitive materials.

TR-RC coatings made of fully crosslinked CLC polymers are more often based on a change in layer thickness rather than on winding/unwinding of the helices (the HTP-changing and Sm–Ch mechanisms). By including volatile, noncovalently bonded substances in the crosslinked network, which may be removed by subsequent heating, the decreasing layer thickness results in a decrease in pitch length, and thus a blue shift of the reflection band. The association of carboxylic acid groups via hydrogen bonds was exploited in a crosslinked polymeric CLC film by incorporating a nonreactive dicarboxylic acid (R)-(+)-3-methyladipic acid (MAA) chiral dopant (Figure 17a).\textsuperscript{[139]} Increasing the temperature above 160 °C disrupts the hydrogen bonds between the carboxylic groups, leading to the evaporation of MAA and collapse of the film with concurrent blue shifts of reflection color irreversibly from orange to green (Figure 17b). Such collapse is visible by mapping surface topography (Figure 17c). The covalent crosslinking helps maintain the photonic structures during the collapse, allowing for color patterning upon local heat exposure using a laser beam as a “hot-pen” (Figure 17d). When only hydrogen bonds are used to supramolecularly crosslink the network, disassociation of the bonds leads to a loss of the mesogenic order due to the absence of a covalently crosslinked network, resulting in disappearance of the reflected color.\textsuperscript{[47]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure18.png}
\caption{a) Schematic presentation of the humidity-gated TR-RC coatings. The monomer mixture was bar coated on the substrated and was polymerized to form a polymer network. Subsequently, the cured coating was exposed to alkaline treatment to create the hygroscopic CLC coating that performs humidity-gated swelling and deswelling of the helices with temperature fluctuation. b) Temperature-induced bandgap shift of the CLC coating at a constant relative humidity of RH = 75%. The reflection band at ≈2000 nm is due to the absorbance of water. c) The coating can be modified to have a broadband reflection (≈400 nm bandwidth) using a UV absorber. The TR-RC property is retained (RH = 75%). d) SEM image of the cross section of the broadband CLC coating showing a pitch distribution along the coating thickness. Reproduced with permission.\textsuperscript{[140]} Copyright 2019, Royal Society of Chemistry.}
\end{figure}
Upon base treatment of this coating, the carboxylic acid groups (–COOH) are converted into carboxylate groups (–COO⁻), disrupting the hydrogen bonds. After drying, the coating becomes hygroscopic due to the presence of the ionic species. In this way, a humidity-gated, temperature-responsive CLC coating was developed. Under increased relative humidity (RH), the reflection band red shifts as the coating readily absorbs water from the environment. Subsequent temperature increase leads to deswelling via desorption of the water present in the coating, and the helical pitch decreases (Figure 18a). Experimental results show that when maintaining the RH at 75%, a band shift of 420 nm in the IR region is seen as the temperature is varied between 70 and −2 °C (Figure 18b). In contrast to the hydrogen-bonded coating using MAA, the color change of this coating is reversible by cooling if the RH is kept constant. Furthermore, by generating a chiral dopant concentration gradient using a UV-absorbing dye during photopolymerization, the reflection bandwidth can be broadened to ≈400 nm (Figure 18c–d). While the coatings were fabricated via bar coating, an inkjet printing technique was also applicable to such materials.

Introducing a shape memory effect causes TR-RC behavior in crosslinked CLCs. An example of a shape memory coating uses an acrylic CLC polymer where the polymer network is partially formed from hydrogen bonds to complement the covalent bonds, reducing the Tg of the system to around 60 °C. The coating is mechanically embodied above 60 °C to deform its helical structure. Upon cooling to room temperature (far below Tg), a temporary shape is obtained corresponding to a blue shift of the reflection band. The shape and color fully recover to their initial states when the coating is heated to 60 °C. This step cannot be reversed by subsequent cooling. To realize multiple stages of shape recovery, the initial crosslinked polymer coating (polymer network 1) was treated with an organic solvent to wash out the nonreactive mesogen (Figure 19a). The pores created during this step were filled with a mixture of photoinitiator and reactive monoacrylate. Upon photopolymerization, poly(benzyl acrylate) was formed (polymer network 2), creating a semi-interpenetrating CLC system that has a wide glass transition range between 10 and 54 °C and exhibits an initial orange reflectance (590 nm). Local embossing of the CLC coating by exerting a compression force results in blue reflection (435 nm) at 0 °C (Figure 19b). Upon heating to a temperature within the Tg range, different reflection colors are attained due to different stages of shape recovery (Figure 19c). A kinetic effect of shape recovery is observed, as the response rate accelerates when the recovery temperature is higher (Figure 19d). The complete red shift of color is only

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**Figure 19.** a) Chemical structures of the components used to develop a CLC coating having a semi-IPN network. During the first polymerization step, the monomers of polymer network 1 reacted to form a crosslinked CLC coating. After removal of the porogen, a mixture of benzyl acrylate and photoinitiator was allowed to infiltrate into the pores. During a second photopolymerization step, poly(benzyl acrylate) (polymer network 2) was formed to obtain a semi-interpenetrating network of a cholesteric polymer and poly(benzyl methacrylate). b) Procedure of mechanical embossing of the CLC coating, and the photographic presentation of the color recovery of the embossed coating at different temperature stages. c) Red shift of the embossed area upon heating from 0 to 75 °C. d) Recovery speed of the initial coating after embossing while heating at different temperatures over time (Δλ/Δλmax expresses the ratio of the measured red shift at a specific temperature to the red shift observed at 75 °C). Adapted with permission. Copyright 2017, American Chemical Society.
realized at 55 °C, indicating a recovery of the original state. These CLC polymer coatings can also be embossed with surface topographies to create additional optical effects: an arbitrary topography was used to emboss a CLC coating, having a low crosslinking density, achieving surface scattering which covers the original structural color of the CLC. The initial reflection could reappear upon heating the coating.[146]

Recently, CLC polymer-based particles were successfully synthesized[143] and used to fabricate paintable coatings. The planar-radial alignment of the Ch phase in these particles results in reflection colors independent of the viewing angle. Based on this work, CLC elastomer particles were developed that demonstrated shape memory effects via mechanical embossing.[144] These particles are embedded in a UV-curable acrylic binder for brush-paintable coatings (Figure 20a). The deformation of the CLC particles by embossing could be observed using scanning electron microscope (SEM) (Figure 20b,c). Interestingly, the binder material has shape memory properties as well. As a result, when embossed with micropatterns, the binder surface generates diffraction gratings (see step 2.2), making it a dual-temperature-responsive coating as the initial surface topography and the deformed CLC particles recover at different temperature stages (Figure 20d). It is worth noting that the TR-RC behavior of CLC polymer particles could perhaps be further explored: For instance, particle deformation that is triggered by isomerization of network substances has been demonstrated.[145]

### 2.4.3. Free-Standing Films/Objects

Obvious thermal expansion of the pitch has been demonstrated in highly crosslinked cholesteric liquid crystal elastomers (CLCEs), such as in the simple temperature-responsive photonic CLCE film using an acrylic network.[146] A monocacylate chiral dopant, a nonmesogenic crosslinker, and a non-crosslinkable nematic mesogen filled a cell and were polymerized. After opening the cell, the nematic solvent was removed, yielding cholesteric elastomer films which began red shifting above $T_g$ (59 °C), from green (centered 550 nm) to red (700 nm) near the isotropic transition point (110 °C) (Figure 21a). A physical thickening of the film was observed during this shift (Figure 21b, the “unconstrained” state). In contrast, no TR-RC was seen when the same molecular system was confined in a cell, where the film was unable to deform (see the “constrained” state). Similar effects are observed in another CLCE film consisting of crosslinked main-chain CLC oligomers[147] (Figure 21c), where the color of the material changes from blue to red when heated from 25 to 200 °C (Figure 21d). The magnitude of TR-RC can be controlled by the amount of chain extender (BDMT) added, which correlates with the crosslinking density of the material (Figure 21e,f). In another work using similar crosslinked main-chain CLC oligomers, where the chain extension reaction was conducted separately from photo-crosslinking, it is found that the chain extension reaction can red shift the

![Figure 20](image-url)

Figure 20. Schematic representation of the developed triple-shape memory photonic coatings. The photonic coating could be embossed twice as both the CLC particles and polymer binder have shape memory properties. The initial photonic coating could be reobtained by heating or localized illumination with blue light. SEM image of the cross-section of the photonic coating b) before embossing and c) after the first embossing step. d) Brush-painted multicolor coating showing the triple-shape memory effect upon dual-step embossing followed by heating or illumination with blue light. Reproduced with permission.[144] Copyright 2020, John Wiley and Sons.
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tion color as well. Patterns are created in the film by controlling the degree of chain extension in different regions. Although only disappearance of color is seen in these patterns upon heating, modifications on the chemistry should result in a TR-RC behavior as well.

Mechanically straining the CLCEs leads to compression of the helices, resulting in a blue shift of the reflection band, so the temperature response of the elastomer can be programmed with strain. In another crosslinked CLCE, chain-transfer groups are embedded in the network and are able to conduct addition/fragmentation chain transfer reactions (AFT) to reconfigure the network under UV irradiation (Figure 22a). When the AFT is conducted in a strained state at room temperature, the reconfigured network partially fixes both the strain and deformed helix (Figure 22b). Different degrees of reconfiguration can be controlled via exposure time, leading to different programmed colors upon release (Figure 22c). By heating the films above the isotropic transition, thermal expansion leads to a reversible reflection red shift. These programmed colors are erased by conducting the AFT again at the isotropic temperature.

TR-RC CLC polymer structures are also developed into 3D objects. A humidity-gated CLC polymer structure was successfully fabricated into micrometer-scale objects from monomers in cells using the two-photon polymerization direct laser writing (TPP-DLW) technique (Figure 23a). Like the coatings that this work is adapted from, these micro-objects present responsiveness in color to both temperature and humidity, which could be observed under a microscope (Figure 23b). Deformation of the thickness of the objects is observed with the response due to the working mechanism of absorption/desorption of water vapor (Figure 23c).

Finally, macroscale and reversible TR-RC objects from CLCEs were also successfully fabricated, realized via the shape memory effect. The starting material utilizes a tetrathiol that crosslinks the acrylic LC monomers via Michael addition when the mixture is aligned in a cell. After the thiol/acrylate crosslinking, the flat cholesteric film removed from the cell was deformed into the desired 3D shape, the helical pitch compressed under the stretching forces. The remaining acrylates were UV polymerized into a second network to fix the new shape (Figure 24a). The

Figure 21. a) Transmission spectra of an unconstrained CLCE film as a function of temperature for right-or left-handed CPL. b) Comparison of the central wavelength ($\lambda_R$) shift in an unconstrained and constrained film with a compressive strain $\epsilon_z = 0.15$. The constrained film showed no observable shift whereas the induced red shift in the unconstrained film was reversible upon cooling. Reproduced with permission. Copyright 2015, American Physical Society. c) Schematic representation of the chain extended and crosslinked CLCE polymer. The chemical structures of the components are simplified as symbols. d) Temperature-induced color changes observed in the CLCE film upon heating. e) The extent of the thermally induced red shift depends on the amount of chain extender (BDMT) added to the initial CLC mixture, affecting the wavelength range. Reproduced with permission. Copyright 2019, John Wiley and Sons.
Figure 22. a) Procedure to program the temperature response in CLCE films. Manual shearing was applied just below the isotropic phase transition to induce CLC alignment that was fixed by photopolymerization with visible light. Next, the films were stretched and the strain was fixed by irradiating the film with UV light (the AFT reaction). b) CLC alignment improves upon straining and leads to a decrease in haziness. A blue shift occurred due to the thickness decrease upon straining the film. c) The preprogrammed response of the CLCE films was demonstrated by heating and cooling. The bottom numbers indicate the duration of UV light irradiation during the AFT reactions. Reproduced with permission.\cite{154} Copyright 2020, John Wiley and Sons.

Figure 23. a) High-resolution 4D photonic microactuators can be created from a photoresist by selective TPP-DLW (step 1), which becomes responsive to humidity or temperature after cleaving the hydrogen bonds (step 2). b) Photonic response of the microactuators under influence of temperature or humidity, observed under the microscope with crossed polarizers. c) Direct (humidity response) or indirect (temperature response) actuation of the photonic microactuators is observed by monitoring dimensional changes of the actuator. Adapted with permission.\cite{155} Copyright 2020, American Chemical Society.
double network provides a reversible shape memory effect to the object. When heated to 197 °C, the object reverts to a flat film, but the deformed shape can be recovered by cooling (Figure 24b). A concurrent red shift of the reflection took place during this process due to the release of stress. In addition to the compression through the thickness, the initial stretching distorts the helices into an elliptical shape that reflects both left- and right-handed CPL, leading to 100% light reflection in the stretched state (Figure 24c). The reflection intensity reverts to 50% (single-handedness) upon heating. A beetle structure reflecting both left- and right-handed CPL was demonstrated, thereby outperforming beetles found in nature. The shape as well as the color of the beetle change with temperature. Adapted with permission. Copyright 2020, John Wiley and Sons.

3. Summary

TR-RC CLCs have been established ranging from simple low-molar-mass molecules and PDLC systems to polymers and complex PSLC systems. Coatings, films, and capsules have all been developed, so the material no longer must be confined to traditional glass alignment cells. This extends the diversity of applications that can be envisioned. In addition to the standard responses to changes of the surrounding temperature, indirect heating via electricity or light could lead to on-demand color tuning independent of environmental conditions, further broadening the scope of application. Table 2 shows the working mechanisms of small mesogenic molecules, PDLC, PSLC systems, and crosslinked polymers, depicting both their advantages and challenges. For the convenience of illustrating the device adaptation, the polymer class is subdivided into PSLCs with oligomers and fully crosslinked polymers. One or two representative device(s) are chosen to describe their wavelength range and temperature range of the response for a quantitative comparison.

Small-molecule CLCs have the greatest flexibility, and by taking advantage of temperature-sensitive HTP chiral dopants or the Sm–Ch transition, large, even near-infinite reflection, band shifts can be obtained by optimized selection of the LC host and chiral dopant. Due to their low viscosity, response speeds are rapid. Oligomeric CLCs share some of the mesogenic mobility of the small-molecule systems, so their optical responses are similar, albeit with slightly slower kinetics. However, the liquid-like state of such small molecules and oligomers restricts device versatility, as the CLC materials must be encapsulated to retain proper shape and alignment. Although attempts have been made to fabricate coatings using oligomeric CLCs with reversible responses, they have not yet proven themselves as robust and stable coatings. We believe that there are still many possibilities for new structures and device forms to be explored with CLC small molecules and oligomers.

PDLC coatings using TR-RC small-molecule CLCs trapped inside a polymer binder have been produced via one-step and two-step procedures. These PDLC configurations allow for more stable coatings and films, while maintaining many of the advantages of the small-molecule systems. Some commercially

Figure 24. a) Illustration of the shape memory CLCE film that is able to reflect both left- (L*) and right-handed (R*) CPL. The initial CLCE film reflects one-handedness of light. However, after stretching and subsequent curing, both left- and right-handed CPL are reflected. After programming the shape by curing, the elastomer is still able to reconfigure its shape during heating or cooling. b) Photographs of the CLCE film show color and dimensional changes upon heating. c) Transmission spectra of the CLCE film showing the TR-RC ability of the film. The reflection of unpolarized light can reach nearly 100% because both left- and right-handed CPL are reflected. d) Bioinspired CLCE beetle showing the reflection of both-handedness of CPL, thereby outperforming beetles found in nature. The shape as well as the color of the beetle change with temperature. Adapted with permission. Copyright 2020, John Wiley and Sons.

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Table 2. An overview of the TR-RC CLC systems presented in this Review. The different TR-RC mechanisms are summarized as well as the benefits and disadvantages of each system that have to be considered for possible device applications.

| TR-RC mechanism | References | Range of reflection | Temperature range of response | Merit for a device | Challenge for a device | Device form |
|-----------------|------------|---------------------|-------------------------------|--------------------|-------------------------|-------------|
| Small mesogenic molecules | HTP changing | Any possible range, dependent on the dopant and dosage | Between \( T_h \) and \( T_m \) usually \(< 150^\circ C\) | Fast response | Must be encapsulated | Cells |
| | [59–71, 88,90,92] | | | Large-range wavelength tuning possible, even inversion of helix | | Coatings |
| | Sm–Ch transition | From the lowest value below \( T_c \) until infinite at \( T_{sm-ch} \) | Between \( T_{sm-ch} \) and \( T_\beta \) usually \(< 150^\circ C\) | | | Microcapsules |
| | Over-saturation of chiral dopant | \( 450–1000 \text{ nm}^{[73]} \) | \( 23^\circ C – 45^\circ C^{[73]} \) | Fast response | | |
| PDLC with small mesogenic molecules | HTP changing | 400–700 nm\(^{[77]}\) | \( 25^\circ C – 35^\circ C^{[77]} \) | Fast response | Suffer from scattering | Cells |
| | Sm–Ch transition | | | Easy production | | Coatings |
| | [44,45,94,97] | | | Mechanically robust (commercial products available) | | Free-standing films |
| PSLC with small mesogenic molecules | HTP changing | 600–2500 nm, band broadening\(^{[119]}\) | 0–34 \(^{\circ} C^{[115]}\) | Complex optical response possible (e.g., band broadening, > 50 % reflection in a single layer) | | Cells |
| | [110–113,115,120] | | | Must be encapsulated | | |
| | Sm–Ch transition | 300–2500 nm, band broadening \(^{[119]}\) | 25–132 \(^{\circ} C^{[119]}\) | | | Cells |
| | [116–119] | | | Reduced wavelength tuning range | | |
| | PSLC with oligomers | HTP changing | \( \approx 2.3 \mu\text{m} – \text{infinite}^{[131,132]} \) | \( \approx 70–100 \text{C}^{[131,132]} \) | Complex optical responses possible | Limited examples | Cells |
| | Sm–Ch transition | 775–1363 nm\(^{[130]}\) | 31–66 \(^{\circ} C^{[130]}\) | Steady performance as coatings | Reduced wavelength tuning range | Coatings |
| | [136,137] | | | | Mechanically not robust\(^{[1]}\) | |
| | Network-oligomer separation | | 38–65 \(^{\circ} C\) (below/above \( T_c \) as a trigger)\(^{[14]}\) | Steady performance as coatings | Response speed slow (hours) | | Coatings |
| | [54] | 515–800 nm\(^{[14]}\) | | | Mechanically not robust\(^{[1]}\) | |
| Oligomers | Sm–Ch transition | 1250–2350 nm\(^{[128]}\) (oligomer and a dopant) | 16–61 \(^{\circ} C^{[128]}\) | Large-range wavelength tuning possible | Response kinetics slower than small molecules | Cells |
| | [121–127] | | | | Mechanically not robust\(^{[1]}\) | |
| Crosslinked polymers | HTP changing | \( \approx \text{from 600 to 500 nm (irreversible)}^{[139]} \) | \( > 160 \text{C (irreversible)}^{[139]} \) | Steady performance as coatings and objects | Must rely on solvents | Coatings |
| | Sm–Ch transition | \( \approx 750–1600 \text{nm (irreversible)}^{[140]} \) | \( > 2^\circ C \approx 70^\circ C^{(\text{irreversible})^{[140]} \) | | | 3D objects |
| | Absorption of substances | | | Mechanically robust | | |
| | [139–141,155] | | | | | |
| | Shape memory effect (irreversible) | \( \approx \text{from 435 to 590 nm}^{[42]} \) | 8–70 \(^{\circ} C^{[42]}\) | Steady performance as coatings | Irreversible response | Microcapsules |
| | [56,142,144] | | | Mechanically robust | | |
available PDLC devices have been realized based on this principle. However, one of the major shortcomings of PDLC systems is the intrinsically limited device transparency. Polymer-stabilized CLC systems contain a minor amount of crosslinked network (usually < 25 wt %). PSLCs with small mesogenic molecules can attain reflection band broadening upon heating via an anchoring effect, which makes them unique among the systems highlighted. These network structures can be engineered to achieve additional optical properties, such as both left- and right-handed helices in one layer. Further engineering of these structures may follow to adapt them for even more versatile TR-RC properties such as reflection of linearly polarized light. PSLCs with small mesogenic molecules have not been demonstrated as coatings or films to date, as the layers are still too vulnerable to mechanical forces. However, PSLCs incorporating siloxane oligomers have been successfully fabricated as stable coatings via methods such as bar coating. Mechanisms of HTP-changing chiral dopants or Sm—Ch transition can still be manifested in the presence of a network, although the color tuning range may be significantly reduced (down to a few hundred nm) by the restricted mobility of the mesogens. TR-RC coatings that apply network-oligomer separation mechanisms are also possible, but the response can take hours to complete due to the reliance on inherent diffusion mechanisms. As far as coating applications, PSLCs with oligomers appear optically reversible but are mechanically weak as improving the mechanical strength tends to come at a cost to the response freedom of the mesogens. This issue may be circumvented in the future by the application of a protective topcoat.

Crosslinked polymers have high mechanical stability, making them suitable for the fabrication of coatings, free-standing films, or even 3D objects. Absorption-based mechanisms are commonly applied in coatings, wherein the networks are chemically modified to allow swelling, resulting in extending the pitch. Irreversible TR-RC change is realized by the heat-driven release of volatile organic small molecules, which could make them useful as single-use temperature indicators. A reversible optical response is accomplished by controlling the absorption/desorption of water, allowing large TR-RC shifts of 500 nm, and even micron-scale 3D responsive objects were demonstrated from these humidity-gated CLC systems. Shape memory mechanisms in TR-RC CLC polymers are generally irreversible. The fabrication requires mechanical embossing to compress the pitch length, which may be subsequently released by heating. These systems are presented as prototype coatings for single-use indicator labels. A reversible, shape memory response in CLC polymers can be achieved by deforming the helices and then building in a second network. Thermal shape deformation accompanied by a color shift is realized in free-standing films and even 4D actuator objects. A reversible response can be also programmed by anisotropic thermal deformation mechanisms, with response over the full visible range and potential for more futuristic applications in robotics. However, challenges remain before implementing these techniques into daily life applications, as they currently require triggering temperatures that are too high (up to \( \approx 200 \) °C) and insufficient film production within cells. To address the latter challenge, the recently developed technique of 3D printing of LC polymers is promising for facilitating device fabrication with more freedom in the design of object shapes.

By selecting from a wide range of materials and mechanisms, the thermo-optical response of the devices can, in principle, be customized to any reflection color, wavelength tuning, and working temperature ranges, depending on the application. While prototype devices, including temperature indicators, IR-reflective smart windows, cold chain safety labels, actuators, and artistic decorations, have been described in this text, these materials have not yet been widely incorporated in commercial products. Fabrication processes and overall performance are the remaining keys to product development. Lab-based fabrication methods such as capillary cell filling is slow (window-sized devices could take hours) and may cause inhomogeneity issues when applied over larger areas. Paintable, photoinduced, and phase-separated coatings would therefore be of great interest. The PDLC systems already have shown promise for the development of commercial products, as CLC capsules can be blended into filler materials for easy processing as coatings and free-standing objects. However, they suffer from scattering and have therefore not proven themselves in transparent applications. Coatings and free-standing films face the challenge of balancing response and robustness.

Table 2. Continued.

| TR-RC mechanism | References | Range of reflection | Temperature range of response | Merit for a device | Challenge for a device | Device form |
|-----------------|------------|---------------------|-------------------------------|-------------------|-----------------------|-------------|
| Shape memory effect (reversible through modifications) | [154,156] | 500–670 nm$^{[156]}$ | 22–171 °C$^{[156]}$ | Steady performance as films and objects | Large operation temperature range required | Free-standing films 3D objects |
| Thermal shape deformation | [146–148] | \( \approx 500–700 \) nm$^{[147]}$ | 25–200 °C$^{[147]}$ | Steady performance as films and objects | Large operation temperature range required | Free-standing films |
|                |            |                     |                               | Mechanically robust | Complex optical responses possible | Cell process required |

$^{a}$Representative examples; $^{b}$Tc: crystallization temperature; T: isotropic transition temperature; Tm–Cs: smectic-to-cholesteric transition temperature; $^{c}$Mechanical robustness of these devices is not examined. The comments of “mechanically not robust” are inferred from the chemical compositions and the molecular mass of the systems.
Current coatings and free-standing objects are either very responsive but lack physical strength or are robust with only limited optical response. Nevertheless, the avenues for exploration of TR-RC CLC polymers are far from depleted, and attempts to find new materials and processing methods are ongoing. We are optimistic that a good balance will be met in the near future, which will allow more products to reach the market.

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Conflict of Interest

The authors declare no conflict of interest.

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