

Printable Optical Sensors Based on H-Bonded Supramolecular Cholesteric Liquid Crystal Networks

Nicole Herzer,[†] Hilal Guneyusu,[†] Dylan J. D. Davies,[†] Derya Yildirim,[†] Antonio R. Vaccaro,[†] Dirk J. Broer,[†] Cees W. M. Bastiaansen,^{†,‡} and Albertus P. H. J. Schenning^{*,†}

[†]Functional Organic Materials & Devices, Eindhoven University of Technology, PO Box 513, Eindhoven, The Netherlands

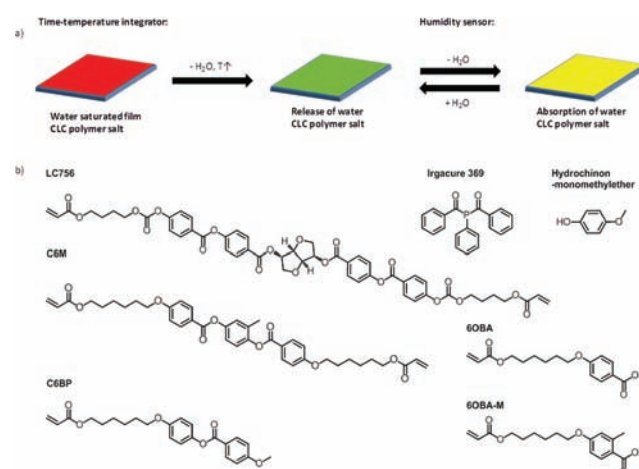
[‡]Department of Materials, Queen Mary University of London, Mile End Road, London E1 4NS, U.K.

Supporting Information

ABSTRACT: A printable H-bonded cholesteric liquid crystal (CLC) polymer film has been fabricated that, after conversion to a hygroscopic polymer salt film, responds to temperature and humidity by changing its reflection color. Fast-responding humidity sensors have been made in which the reflection color changes between green and yellow depending on the relative humidity. The change in reflection band is a result of a change in helix pitch in the film due to absorption and desorption of water, resulting in swelling/deswelling of the film material. When the polymer salt was saturated with water, a red-reflecting film was obtained that can potentially act as a time/temperature integrator. Finally, the films were printed on a foil, showing the potential application of supramolecular CLC materials as low-cost, printable, battery-free optical sensors.

Stimulus-responsive materials capable of dynamic color tuning or switching have received increased attention for applications as displays and reflectors.^{1–3} In recent years, cholesteric liquid crystals (CLCs) that reflect circular polarized light at a given wavelength as a result of the self-organizing molecular helices have also proven to be attractive to construct optical sensors that do not require batteries.^{4–12} In these sensors, a responsive molecular trigger provides specificity that, because it is embedded in the well-defined supramolecular helical structure, leads to an amplified material response, resulting in a change of the reflection band. For example, H-bonded units have been used as molecular triggers in CLC films to construct thermally switching reflective color films^{13–15} and optical sensors that change color upon exposure to changes in pH and even amino acids.^{16,17} However, these materials were prepared in cells, which hampers their application. We have shown that it is possible to print nematic liquid crystals that after polymerization could be used as cilia-inspired actuators.¹⁸ Furthermore, we have reported on humidity-responsive actuators based on H-bonded nematic LCs in which the H-bonds were first treated with base to make a hygroscopic polymer salt that can absorb water.¹⁹ We now report the fabrication of printable CLC sensors based on our H-bonded liquid-crystalline polymer salts that act as humidity sensors and potential temperature/time integrators at temperatures that are appealing for food packaging and pharmaceutical applications (Scheme 1a).

Scheme 1^a



^a(a) Schematic representation of the time/temperature integrator and humidity sensor. The water-saturated CLC polymer salt has a red color that, above a defined temperature, gives a green film. The resulting CLC polymer salt is highly responsive to humidity as a result of absorption/desorption of water. (b) Chemical composition of the CLC mixture (wt%): 6OBA, 21.9; 6OBA-M, 21.9; LC756, 4.5; C6BP, 38; C6M, 13; photoinitiator (Irgacure 369), 0.6; and inhibitor (Hydrochinon-monomethylether), 0.1.

We first constructed CLC films and investigated their humidity- and temperature-sensing properties. To prepare the H-bonded CLC films, a chiral liquid-crystalline mixture was used, based on our earlier work on actuators¹⁹ containing both chemically (polymerizable acrylate groups) and physically (carboxylic acid groups, which form H-bonded dimers) cross-linkable groups (Scheme 1b). The reactive mesogens C6M and LC756 act as chemical cross-linker and chiral dopant, respectively, while 6OBA and 6OBA-M are the H-bonding molecular triggers. C6BP is added to decrease the crystalline–nematic phase transition. Thin layers were deposited by dissolving the CLC mixture (Scheme 1b) in THF (1:1) and bar-coating onto a polyimide-coated rubbed glass substrate.

After photopolymerization at a temperature ($T_{\text{curing}} = 53\text{ }^{\circ}\text{C}$) within the chiral nematic phase, planar CLC films were fabricated with thicknesses of 5–7 μm . The concentration of

Received: February 24, 2012

Published: April 23, 2012

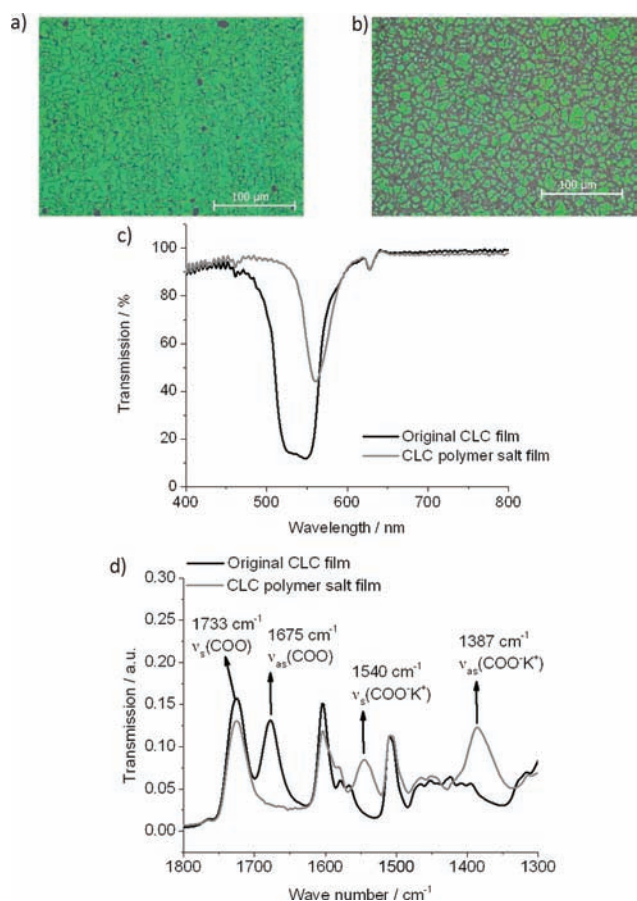


Figure 1. Microscope images without polarizers in reflection mode of (a) the original green-reflecting film showing the typical oily streak texture of the CLC film and (b) the formed polymer salt CLC film showing the green-reflecting color as well as more defects/inclination due to the activation process. (c) UV-vis transmission spectra taken with circular polarizers before (black solid line) and after (gray solid line) formation of a polymer salt. (d) FT-IR spectra of free-standing film (black solid line) and after formation of the polymer salt (gray solid line).

LC756 (HTP, $\beta_M \approx 76 \mu\text{m}^{-1}$)²⁰ was such that a green-selective reflection band (SRB) position was obtained. These CLC films show the typical oily streak texture of CLC films (Figure 1a) having a SRB at $\lambda = 540 \text{ nm}$ with an intensity of 90% using a circular polarizer (Figures 1c and S2, Supporting Information). FT-IR spectroscopy revealed small vibrations between 2800 and 2500 cm^{-1} and an asymmetric vibration at 1675 cm^{-1} pointing to H-bonded dimers formed by 6OBA and 6OBA-M (Figures 1d and S1).

For the humidity sensor, a hygroscopic CLC polymer salt was first formed. The CLC film on glass was deposited in a KOH (0.05 M) solution for 10 min. When the KOH solution penetrates into the film, the reflection color changes from green to red and finally to colorless. Subsequently, the film was dried in air, yielding again a green-reflecting film with its SRB red-shifted by $\sim 10 \text{ nm}$ ($\lambda = 550 \text{ nm}$) at ambient conditions (Figure 1b,c). The intensity of the SRB has decreased by 60% of its original intensity, indicating that not all cholesteric order is restored. The SRB is, however, narrower and still has enough intensity to see the green-reflecting color by eye. FT-IR spectroscopy (Figure 1d) of the dried polymer showed the disappearance of the vibration at 1675 cm^{-1} due to the H-

bonded dimer formation and manifestation of two new vibrations that emerge at $\nu_s = 1540 \text{ cm}^{-1}$ and $\nu_{as} = 1387 \text{ cm}^{-1}$, indicating the formation of a potassium carboxylate salt. Since the asymmetric carboxylic acid vibration at 1675 cm^{-1} completely vanished after the deposition in basic solution, it can be assumed that the conversion to the polymer salt is complete. Additionally, the small vibrations between 2800 and 2500 cm^{-1} disappear, which proves that the H bonds are broken. Moreover, a $\nu(\text{OH})$ vibration at 3370 cm^{-1} appears (Figure S3), which could be related to the presence of water in the film, explaining the 10 nm red shift in the UV/vis transmission spectrum (Figures 1c and S2) after activation (vide infra). These data reveal that a CLC polymer salt has been formed that still has a strong green-reflecting color.

We first investigated if a humidity sensor could be constructed from our films. The influence of humidity on the CLC polymer salt film was studied in a gas flow chamber equipped with a UV/vis spectrophotometer. The CLC polymer salt films were exposed to relative humidities (RHs) of 83, 70, 60, 40, and 3% (Figure 2). When the film was exposed to 83%

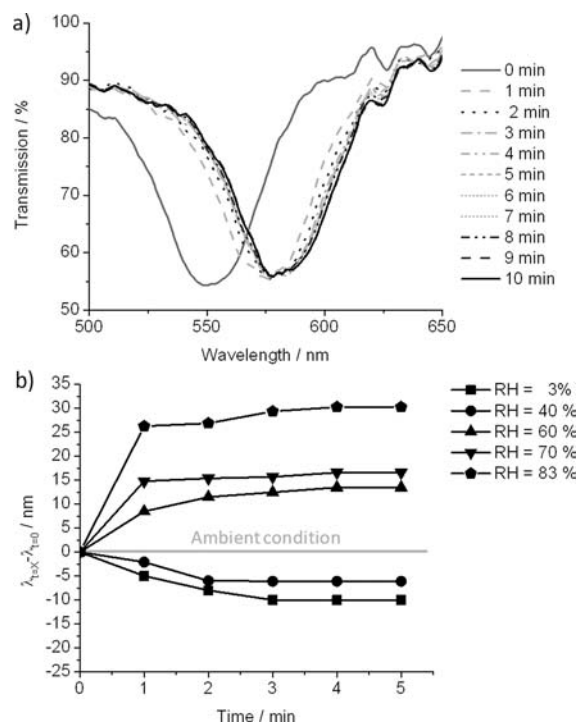


Figure 2. Humidity influence on SRB on the CLC polymer salt film. (a) UV/vis transmission spectra over time for exposure to 83% RH. (b) The relative shift of SRB to the original SRB (ambient condition) wavelength versus time is plotted for 3, 40, 60, 70, and 83% RH.

RH, the SRB (550 nm, green) shifted immediately to the red, reaching a value of $\lambda = 580 \text{ nm}$ (yellow reflection color) after 2 min (Figure 2a). Most likely if the humidity is high, the hygroscopic film absorbs water, leading to swelling of the polymer film. Since the number of helical turns through the thickness of the film is fixed because of the chemical cross-links, swelling leads to an increase of the helical pitch. A quick response of less than 2 min was observed for all tested RHs (Figure 2b), and the degree of the SRB shift depended on the RH. Interestingly, in the case of RH = 3%, the SRB shifted to the blue by about -10 nm . Since the polymer salts were prepared under ambient conditions, it is most likely that water

is released from the film, leading to shrinkage. Shrinkage of the films results in a decrease of the pitch, causing a blue shift of the reflection band.

The optical response of the film to different humidities is fully reversible. When the film was exposed successively for 5 min to RH = 10%, 5 min to RH = 80%, and again for 5 min to RH = 10%, a fast reversible optical response was observed (Figure S4). This behavior indicates that the CLC polymer salt film can quickly absorb and release water, showing that a real-time humidity sensor can be constructed that responds to RHs from 3 to 83% in a fast and reversible fashion, covering a color range from green to yellow.

The latter results motivated us to see if we could also use our CLC as a temperature sensor in which the release of water depends on the temperature. To have a maximal red-shifted reflection band, the CLC polymer salt film was placed in a water solution, showing immediately a color shift from green to red. When the film was taken out of the water and dried gently from the outside, the red color remained in this water-saturated film. UV/vis spectroscopy (Figure S5b) revealed a SRB at $\lambda = 710$ nm, with intensity $\sim 30\%$. FT-IR measurements (Figure S5a) showed that the $\nu(\text{OH})$ vibration at 3370 cm^{-1} is largely increased, revealing the uptake of water in the film.

To see if this film could be used as a temperature sensor, the film was stored at room temperature. Interestingly, after 10 min the red-reflecting colored film returned to its original green-reflecting color. UV/vis spectra monitored over time showed at first only a single SRB at ~ 680 nm (Figures 3a and S6).²¹ After 3 min, this SRB decreased its intensity, and a new SRB appeared at lower wavelength, $\lambda = 530$ nm, within 10 min (Figure S6). By monitoring the peak area of the $\nu(\text{OH})$ vibration at 3370 cm^{-1} , which is related to the amount of water

in the CLC film, the evaporation of water could be determined (Figure 3a). Remarkably, in the first 10 min, 40% of the water evaporated. The rate of the evaporation is faster in the beginning and slows to $\sim 20\%$ of the starting intensity. Comparing the FT-IR and UV/vis spectroscopy data suggests that only 40% of the water must evaporate to shift the SRB from red (683 nm) to green (530 nm) reflection color. However, it should be noted that FT-IR spectroscopy mainly probes the surface of the film, while UV/vis spectroscopy measures the reflection band of the entire film.

The operational temperature window of water-saturated CLC films as temperature sensors was investigated by monitoring the changes of the SRB of water-saturated CLC films at lower temperatures (Figure 3b). The films were kept at room temperature ($20\text{ }^\circ\text{C}$), in a refrigerator ($+4\text{ }^\circ\text{C}$), and in a freezer ($-25\text{ }^\circ\text{C}$). Interestingly, in the freezer, the red color of the film was still visible after a month. Monitoring the relative change of the SRB versus time (Figure 3b, black line) shows nearly no change in the reflection color after 18 days at $-25\text{ }^\circ\text{C}$. The small blue shift could be due to the fact that the SRB of the film had to be measured at room temperature, and therefore some water could have been released. At $+4\text{ }^\circ\text{C}$, the SRB returns to its original green color after 1 h (Figure 3b, light gray line), and at room temperature, the transformation process requires only 10 min (Figure 3b, gray line). These results suggest that the color changes are due to the rate of evaporation of water and motivated us to measure the responsiveness of the films around the melting point of water. Accordingly, an optical microscope was employed with a cooling unit, and optical monitoring experiments were performed at $+5$, $+1$, 0 , -1 , and $-5\text{ }^\circ\text{C}$. The images of the CLC film at the starting time, after 30 min, and after 60 min are shown in Figure 3c. The CLC film changes at $+5$ and $+1\text{ }^\circ\text{C}$ within 1 h from red-reflecting color to green-reflecting color, demonstrating time scales similar to those of the experiments observed at the refrigerator temperature, where at -5 , -1 , and $0\text{ }^\circ\text{C}$, no obvious changes in the reflecting color occurred. This result points toward the melting and subsequent volatilization of water as the trigger of the color change. At the moment it is, however, unclear if the water that is inside the material is frozen at $0\text{ }^\circ\text{C}$. It is well known that liquid water in nanopores can exist well below the freezing point of water.²² Since the color response occurs only above a certain temperature, our water-saturated films can be regarded as a time/temperature integrator that could be interesting for monitoring the temperature history of food and medical samples.²³ It should, however, be noted that for this application, contact of the polymer salt film with liquid water should be avoided since the color changes in the film are reversible, meaning that when the green-reflecting film is dipped in liquid water, the red color appears again.

To show the potential applications for smart packaging of food and medical samples, the CLC mixtures were used as ink to print the sensor on glass and on a foil substrate by using a Dimatix inkjet printer. A stable droplet THF solution of the CLC mix was found by adjusting the voltage, cartridge temperature, and waveform. The cartridge temperature was $55\text{ }^\circ\text{C}$, and the plate temperature was optimized for glass ($55\text{ }^\circ\text{C}$) and triacetyl cellulose (TAC) foil ($53\text{ }^\circ\text{C}$), which is suitable for roll-to-roll processing. To obtain a planar alignment, rubbed poly(imide)-coated glass and rubbed TAC foil were used. After printing, the films were moved to a hot plate at $80\text{ }^\circ\text{C}$ to evaporate the solvent. Subsequently, the films were placed on a

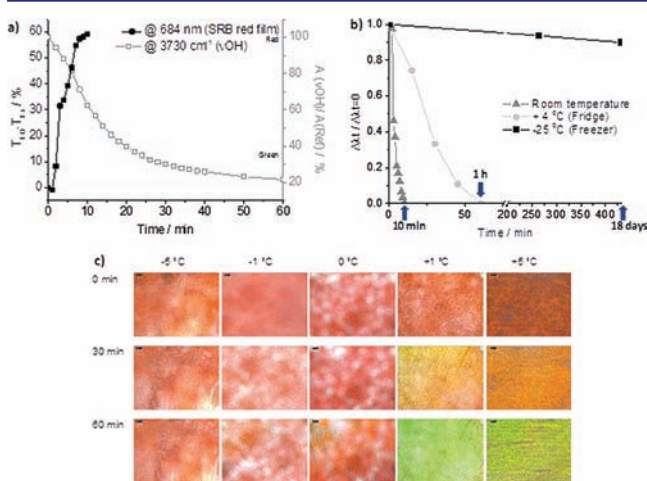


Figure 3. (a) Evaporation of water from the water-saturated polymer salt film at room temperature monitored by UV/vis spectroscopy (black axis), shown as a plot of transmission intensity at 684 nm at time 0 minus transmission intensity at time x versus time (black squares), and FT-IR spectroscopy (gray axis), shown as plot of peak area ($A(\nu\text{OH})$ at 3370 cm^{-1}) relative to the reference peak area at 1383 cm^{-1} as a function of time (gray hollow squares). (b) Time response of the water-saturated polymer salt film at room, refrigerator, and freezer temperatures: the y -axis signal $\Delta\lambda_t/\Delta\lambda_t = 0$ is used as measure for the response versus time at different temperatures. The lines are added as a guide to the eye. (c) Microscopy images in reflection mode without polarizers of the water-saturated polymer salt film at -5 , -1 , 0 , $+1$, and $+5\text{ }^\circ\text{C}$ after 0, 30, and 60 min.

hot plate at 53 °C under nitrogen atmosphere and photopolymerized for 5 min with UV light. The polymerization temperature is chosen to be just below the nematic-to-isotropic phase transition temperature, revealing the best CLC films. Strong green-reflecting films were obtained for the glass slide and on TAC foil samples (Figure 4a,b). Optical microscopy

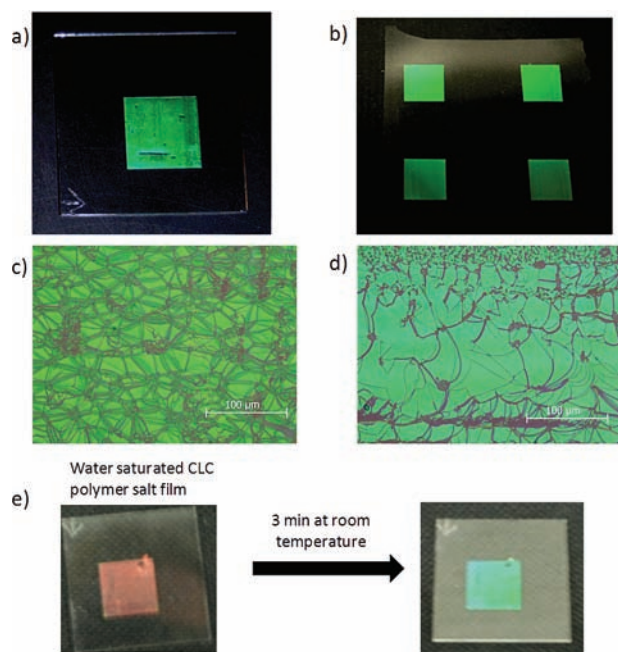


Figure 4. Photographs of CLC films inkjet-printed on (a) polyimide-coated glass and (b) TAC foil. Microscope images in reflection mode without polarizer of inkjet-printed films on (c) polyimide-coated glass and (d) TAC foil. (e) Photographs of inkjet-printed water-saturated CLC polymer salt film on polyimide-coated glass in water (left red film) and after 3 min at room temperature (right green film).

images show an oily streak texture and the green-reflecting color on the glass substrate (Figure 4c), while on TAC foil, the print line can be seen (Figure 4d). The inkjet-printed CLC films are characterized by a strong reflection band around $\lambda = 530$ nm (Figure S7).²¹

To see if the inkjet-printed films still act as sensors, the CLC film on glass was transformed to the polymer salt by treatment with KOH (0.05 M). Subsequently, the CLC polymer salt was saturated with water, yielding a red-reflecting film (Figure 4e). After the film was maintained for 3 min at room temperature, a green-reflecting film was obtained, showing that the printed films still act as sensors (Figures 4e and S8). The inkjet-printed film responds faster than the bar-coated samples, which might be due to larger defects present in the printed film (Figure 4c versus Figure 1a), leading to a faster release of water.²¹

In summary, printable optical sensors are made from H-bonded CLC materials, which act as battery-free humidity sensors that respond to relative humidities ranging from 3 to 83% in a fast and reversible manner. Furthermore, potential temperature/time integrators have been constructed that operate at temperatures that are interesting for the packaging industry and might find applications in the control of the cold chain of food and pharmaceuticals. We believe that fine-tuning of the performance of the films is possible by using different polymer salts and liquid-crystalline mixtures. Our results show

the great potential of supramolecular CLC materials as low-cost, printable, battery-free optical sensors.

■ ASSOCIATED CONTENT

Supporting Information

UV/vis and FT-IR measurements of the system and experimental information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

a.p.h.j.schenning@tue.nl

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partly supported by the Dutch Polymer Institute. We acknowledge Casper van Oosten for his initial work on polymer CLC sensors.

■ REFERENCES

- (1) Spruell, J. M.; Hawker, C. J. *Chem. Sci.* **2011**, *2*, 18. Wojtecki, R. J.; Meador, M. A.; Rowan, S. J. *Nat. Mater.* **2011**, *10*, 14.
- (2) Kato, T.; Mizoshita, N.; Kishimoto, L. *Angew. Chem., Int. Ed.* **2006**, *45*, 38. Sagara, Y.; Kato, T. *Nat. Chem.* **2009**, *1*, 605.
- (3) Broer, D. J., Crawford, G. P., Zumer, S., Eds. *Cross-linked Liquid Crystalline Systems*; CRC Press, Taylor and Francis Group: 2011.
- (4) Ohm, C.; Drehmer, M.; Zentel, R. *Adv. Mater.* **2010**, *22*, 3366.
- (5) White, T. J.; McConney, M. E.; Bunning, T. J. *J. Mater. Chem.* **2010**, *20*, 9832. McConney, M. E.; White, T. J.; Tondiglia, V. P.; Natarajan, L. V.; Yang, D.-K.; Bunning, T. J. *Soft Mater.* **2012**, *8*, 318.
- (6) Akagi, K. *Chem. Rev.* **2009**, *109*, 5354.
- (7) Hu, J.; Liu, S. *Macromolecules* **2010**, *43*, 8315.
- (8) Pieraccini, S.; Masiero, S.; Ferrarini, A.; Spada, G. P. *Chem. Soc. Rev.* **2011**, *40*, 258.
- (9) Sutarlie, L.; Qin, H.; Yang, K.-L. *Analyst* **2010**, *135*, 1691.
- (10) Mujahid, A.; Stathopoulos, H.; Lieberzeit, P. A.; Dickert, F. L. *Sensors* **2010**, *10*, 4887.
- (11) Han, Y.; Pacheco, K.; Bastiaansen, C. W. M.; Broer, D. J.; Sijbesma, R. P. *J. Am. Chem. Soc.* **2010**, *132*, 2961.
- (12) Sutarlie, L.; Lim, J. Y.; Yang, K.-L. *Anal. Chem.* **2011**, *83*, 5253.
- (13) Chen, F.; Guo, J.; Qu, Z.; Wei, J. *J. Mater. Chem.* **2011**, *21*, 8574.
- (14) Hu, W.; Cao, H.; Song, L.; Zhao, H. Y.; Li, S. J.; Yang, Z.; Yang, H. J. *J. Phys. Chem. B* **2009**, *113*, 13882.
- (15) Guo, J.; Chen, F.; Qu, Z.; Yang, H.; Wei, J. *J. Phys. Chem. B* **2011**, *115*, 861.
- (16) Shibaev, P. V.; Chiappetta, D.; Sanford, R. L.; Palffy-Muhoray, P.; Moreira, M.; Cao, W.; Green, M. M. *Macromolecules* **2006**, *39*, 3986.
- (17) Shibaev, P. V.; Sanford, R. L.; Chiappetta, D.; Rivera, P. *Mol. Cryst. Liq. Cryst.* **2007**, *479*, 161.
- (18) van Oosten, C. L.; Bastiaansen, C. W. M.; Broer, D. J. *Nat. Mater.* **2009**, *8*, 677.
- (19) Harris, K. D.; Bastiaansen, C. W. M.; Lub, J.; Broer, D. J. *Nano Lett.* **2005**, *8*, 1857.
- (20) Performance Chemicals: Paliocolor LC 242 and LC 756. <http://www.elecs-korea.com/board/file/1116949999.pdf>.
- (21) The SRB of the polymer salt and water-saturated CLC film depends on fabrication technique (printing versus bar-coating) and the salt content. We are investigating this behavior in more detail.
- (22) Findenegg, G. H.; Jaehnert, S.; Akcakayiran, D.; Schreiber, A. *Chem. Phys. Chem.* **2008**, *9*, 2651.
- (23) Time/temperature integrating frameworks based on discotic liquid crystals have been reported: Cavallini, M.; Calò, A.; Stoliar, P.; Kengne, J. C.; Martins, S.; Maticotta, F. C.; Quist, F.; Gbabode, G.; Dumont, N.; Geerts, Y. H.; Biscarini, F. *Adv. Mater.* **2009**, *21*, 4688.