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An Optical Steam Sterilization Sensor Based On a Dual-Responsive Supramolecular Cross-Linked Photonic Polymer

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ABSTRACT: An optical time–temperature steam sensor is presented based on the loss of structural color in a supramolecularly cross-linked cholesteric liquid crystal photonic coating. A gradual decrease in the selective reflection band is observed upon exposure to temperatures above 105 °C related to the cholesteric to isotropic transition temperature. The linear polymers with carboxylic acid side chains provide physical cross-linking through hydrogen bonding that allows a time–temperature-dependent order loss through the dynamic equilibrium between supramolecular dimer and free monomer states. Steam is accelerating the color loss, and autoclave experiments show that the photonic supramolecular polymer is applicable as a steam sterilization sensor for medical applications.

KEYWORDS: steam sterilization, stimuli-responsive photonic polymers, cholesteric liquid crystal, optical sensors, supramolecular materials

1. INTRODUCTION

Steam sterilization is a standard method for sterilization of equipment in many dental practices, laboratories, and hospitals. Eliminating all microorganisms by steam sterilization requires exposure to an elevated temperature combined with saturated steam under pressure for an extensive amount of time. An autoclave is used to maintain a temperature of 121 °C (250 °F) for at least 20 min under saturated steam conditions. In many countries, it is legally obligated to validate the sterilization process. Typical methods use biological indicators or chemical indicators, which are placed inside an autoclave. Biological indicators require time to evaluate and have to be read under a microscope. Chemical indicators operate by heat-triggered coloration (autoclave tapes) or by heat/humidity-controlled diffusion of (toxic) ink. However, low-cost optical sensors easily applicable as labels are desired to verify whether the steam sterilization was performed properly on each item. Hence, the development of time–temperature steam sensors remains a challenge.

Over the last few decades, optical sensors based on photonic materials have been developed, which are able to respond to a broad range of analytes. These battery-free and easy-to-read sensors have recently gained industrial interest as the production process is scalable and the response can be tailored for different applications.

Time–temperature sensors have been reported by using shape-memory photonic materials.

Cholesteric liquid crystals (CLCs) are a class of photonic materials that reflect a certain wavelength of light as a result of the periodic helical ordering that is induced by a chiral dopant in the nematic liquid crystal mesophase. The spacing between the mesogens that corresponds to a molecular rotation of \(2\pi\) is called the cholesteric pitch and determines the position of the selective reflection band (SRB). The cholesteric structure can be fixed in a film through UV polymerization of reactive mesogens, yielding a polymer network.

Time–temperature sensors based on cholesteric liquid crystals have been demonstrated by compressing the cholesteric structure above the glass transition temperature \(T_g\). As such, the pitch is decreased, leading to a blueshift of the reflected light, which is fixed by cooling down below the \(T_g\). The original pitch is restored upon heating by making use of the shape memory, resulting in an irreversible sensor. Another type of optical time–temperature sensor was developed by imprinting a microstructure on the surface of a shape-memory CLC coating via stamping. The “programming” of a rough surface topography in the micrometer range causes light scattering, which conceals the reflected color instead of shifting it. A smooth surface is restored when exposed to temperatures above the \(T_g\), which reintroduces the initial color. Hitherto, a dual stimuli-responsive photonic coating, sensing temperature combined with humidity or steam in time, has never been reported.

In this work, a time–temperature steam-sensitive photonic coating is reported based on an irreversible shift from a color-reflective state to a light-scattering state by making use of the gradual cholesteric structure loss in a non-covalent, supramolecularly cross-linked coating that occurs in the isotropic phase. The presented method differentiates itself through the

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easy processability, as it does not require a programming step (compressing or surface stamping). The time-dependent sensitivity for both temperature and steam originates from the dynamic hydrogen bond sites of the carboxylic acid mesogens in the photonic material. When the coating is exposed to 121 °C for 20 min, the green color of the photonic coating disappears, offering the possibility to use the time−temperature steam polymer film as a validation sensor for steam sterilization.

2. RESULTS AND DISCUSSION

2.1. Fabrication and Thermal Characterization of a CLC Polymer Coating. In order to fabricate the photonic CLC polymer coating containing only hydrogen-bonded supramolecular cross-links, monoacrylate-based chiral dopant 1 with high helical twisting power was synthesized (for structural names and exact composition of the mixtures, see Figure S1 and Table S1). Chiral dopant (1) resembles a monoacrylate version of the commercially available chiral diacrylate derivative (6, Figure S1) with high helical twisting power and was synthesized from two earlier published precursors32,33 (7) and (8) (Figure 1a) by an esterification reaction. After crystallization, the monoacrylate-based chiral dopant 1 was obtained purely and fully characterized (see the Supporting Information). The monoacrylate chiral dopant has a high helical twisting power of 95 μm−1. The CLC mixture contains solely monoacrylate mesogens excluding covalent cross-linking. The liquid crystal monomer (2) is used to tune the crystalline−nematic transition, and the initiator Irgacure 369 (5) is added for initiating photopolymerization. By incorporating carboxylic acid-functionalized monoacrylate liquid crystal molecules (3) and (4) (∼53 wt %), supramolecular cross-linking proceeds through the hydrogen bonds between the benzoic acids (Figure 1b).

Photonic coatings are obtained by shearing the CLC mixture between two glass plates to induce cholesteric alignment planar to the substrate. The aligned mixture is polymerized at 40 °C with high intensity UV light (∼20 mW/cm²), yielding a green photonic polymer coating with an SRB around 530 nm (Figure 1c,d). In principle, every color can be obtained by adjusting the chiral dopant concentration. The periodic cholesteric structure is clearly illustrated by scanning electron microscopy (SEM) images (Figure 1e). The Fourier transform infrared spectroscopy (FT-IR) spectrum of the polymer coating showed an absence of the C=O acrylate stretching vibration peak at 1640 cm⁻¹, the CH₂ deformation vibration peak at 1410 cm⁻¹, and the C=O out-of-plane deformation vibration peak at 985 cm⁻¹, implying that polymerization has occurred. The carbonyl vibration peaks from 1680 to 1730 cm⁻¹ indicate the presence of hydrogen-bonded carboxylic acid dimers acting as supramolecular cross-links (Figure S4).34,35 Thermal characterization of the polymer coating by differential scanning calorimetry (DSC) shows a cholesteric to isotropic transition temperature (T_iso) at ∼105 °C (Figure S5).

2.2. Temperature Response of a CLC Polymer Coating. Upon heating the supramolecularly cross-linked photonic coating above T_iso to 120 °C, the coating becomes transparent due to the order loss of the photonic structure in the isotropic phase. Upon cooling below T_iso after exposing the coating to 120 °C for 20 min, a white scattering coating is obtained (Figure 2a); the transmission over the entire visible spectrum decreases due to scattering, which results in a decrease in the SRB (Figure 2b).

Figure 1. (a) Synthesis of the novel monoacrylate chiral dopant. (b) Chemical structures of the compounds used for the CLC polymer coating. (c) Photograph of a CLC polymer coating on a glass substrate with a black background. (d) UV−vis transmission spectrum displaying the SRB at ±530 nm. (e) SEM images of the CLC coating. Inset I shows the two-dimensional Fourier transformation of the area (inset II), illustrating the long-range cholesteric order.
The optical change and the decrease in the SRB through order loss in a polymer coating only occur when the coating is exposed to temperatures above the threshold $T_{iso}$. UV-vis spectra show tightening of the SRB at 100 °C ($<T_{iso}$) (Figure S6) caused by the reduction in birefringence near the phase transition temperature. Nevertheless, the exposure of the photonic polymer coating to temperatures below $T_{iso}$ does not change the SRB at room temperature. The exposure above $T_{iso}$ is time- and temperature-dependent; an exposure of 15 min above $T_{iso}$ at a temperature of 110 °C has no significant effect on the SRB of the coating at room temperature (Figure 3). However, 60 min of exposure to 110 °C (Figure 3) results in a decrease in the SRB. An SRB decrease after 60 min at 110 °C is comparable to a decrease after 20 min exposure to 120 °C (Figure 2). In other words, when the coating becomes transparent above $T_{iso}$, the exposure is actively recorded by the cholesteric order loss (vide infra) as a function of time and temperature, which is optically expressed as a decrease in SRB at room temperature.

The gradual permanent order loss is attributed to the hydrogen bond interactions, which provide supramolecular cross-linking. The hydrogen bonds manifest a temperature-dependent equilibrium between open or cyclic dimers and free carboxylic acid that allows the linear polymer chains to reorient. When a supramolecular cross-link becomes a free acid, the absence of a network allows reformation of a cyclic/open dimer in a different position. In the isotropic phase, the absence of order favors the chains to reorient into a disordered, unaligned structure over time, which is fixated in the nematic phase after cooling down below $T_{iso}$. Figure 4a displays the FT-IR absorption peak at 1680 cm$^{-1}$ to demonstrate that the relative population of hydrogen-bonded dimers decreases as a function of temperature. As such, the dimer-free acid equilibrium shifts toward free acid as a function of temperature, which generates the time–temperature dependency: a higher fraction of free acid means more freedom for the chains to reorient, resulting in faster loss of structure memory above the isotropic transition temperature threshold (Figure 4b).

Further proof that the time–temperature dependent functionality is induced by a dynamic hydrogen bond-based mechanism becomes evident when two additional polymer coatings are compared (compositions in Figure S1 and Table S1). A photonic coating without hydrogen bond-forming mesogens, i.e., containing only 1 and 2, demonstrates the absence of a time factor (Figure 5a): the coating immediately loses the cholesteric structure after exposure to a temperature above $T_{iso}$. Without supramolecular hydrogen bond cross-linking, no network-like forces are keeping the orientation preserved; as such, the cholesteric structure of the nematic phase is instantaneously lost when heated to the isotropic state. Contrarily, a coating with the covalent cross-linked chiral dopant (6, see Figure S1 and Table S1) shows that there is no structure loss possible through exposure to a temperature above $T_{iso}$ (Figure 5b). Due to the diacrylate chiral dopant, a network is formed with chemical cross-links. This will preserve the cholesteric structure in the nematic phase even after an extensive time in the isotropic phase.

2.3. Steam Sterilization Sensors. To study the potential application of the time–temperature sensitive photonic coating as an optical steam sterilization sensor, the effect of steam on the color change was studied (Figure 6). When the coating is placed inside an autoclave to apply typical conditions of a standardized method for sterilization, 20 min of exposure to saturated steam at 121 °C ensures a complete loss of the SRB (Figure 6b,c) instead of a decrease in SRB after exposure to 120 °C for 20 min (Figure 2b). The loss of cholesteric structure is also clearly shown in SEM images (Figure 6d). Water molecules can interact with the hydrogen bond sites of
the acid mesogens, which allows the cholesteric helices more freedom to reorient, accelerating the cholesteric order loss. After exposure to steam, the hydrogen bonds are restored in this disordered state (Figure S7). Furthermore, the water absorbed into the polymer causes surface roughening after drying (Figure 6a), resulting in a scattering surface structure. This surface scattering enhances the color loss effect and contributes to the elimination of any residual angular reflection that is observed when the coating is heated without steam (Figure S8). A modified autoclave program at a lower temperature (110 °C for 20 min) was tested to simulate an insufficient sterilization process, which did not result in a complete color loss of the CLC coating (Figure 7).

3. CONCLUSIONS

In this work, we have demonstrated a time−temperature steam photonic sensor based on a supramolecularly cross-linked CLC polymer coating. Due to the absence of covalent cross-linking, the exposure to a temperature above $T_{iso}$ can be tracked as a decrease in the SRB. The time−temperature dependence of coatings above $T_{iso}$ is recorded as a gradual structure loss of the cholesteric reflective system, which is fixated below $T_{iso}$. The structure loss is controlled by the dynamic hydrogen bond equilibrium allowing the time−temperature-dependent order loss, resulting in the loss of the reflection band. Additionally, the presence of saturated steam influences this equilibrium and accelerates the order loss; as such, time−temperature steam exposure can be recorded, which makes this particularly interesting for high-temperature humidity applications such as steam sterilization validation sensors. By changing the supramolecular cross-link density, it is possible to alter $T_{iso}$ in order to achieve total SRB loss exactly in the time frame necessary for the temperature and humidity conditions to guarantee sterilization (Figure S9). These coatings can be inkjet-printed as labels (Figure S10) and potentially form an alternative to current commercial sensors that are mainly based on the diffusion or solubility of inks.

4. EXPERIMENTAL SECTION

4.1. Materials. Cholesteric liquid crystal coatings were prepared by dissolving all components in tetrahydrofuran (THF) to ensure a homogeneous monomer mixture. For structural names and the exact composition of the mixture, see Figure S1 and Table S1. The concentration of the chiral dopant was chosen such that a coating with SRB in the visible spectrum was obtained. A monofunctional chiral dopant obtained from the synthesis was used to exclude any covalent cross-linking. Liquid crystal monomer helps to control the crystalline−nematic transition. By incorporating (∼53 wt %) carboxylic acid-functionalized monoacrylate liquid crystal molecules 3 and 4, supramolecular cross-linking proceeds through the hydrogen bond.
bonds between polymer strands. Initiator 5 (Irgacure 369) is used for initiating UV polymerization.

4.2. Glass Functionalization. Methacrylate-functionalized and perfluoro-coated glass slides were prepared as reported by Stumpel et al.45 Glass substrates were cleaned by sonication (ethanol, 15 min) followed by treatment in a UV ozone photoreactor (Ultra Violet Products, PR-100, 20 min) to activate the glass surface. The surface of the glass substrates was modified by spin-coating 3-(trimethoxysilyl)-propyl methacrylate solution (1 vol % solution in a 1:1 water−isopropanol mixture) or 1H,1H,2H,2H-perfluorodecylethoxysilane solution (1 vol % solution in ethanol) onto the activated glass substrate for 45 s at 3000 rpm followed by curing for 10 min at 100 °C.

4.3. Coating Fabrication. After evaporation of the solvent (THF) from the mixture, coatings were obtained by shearing the LC between two glass plates to induce cholesteric alignment planar to the substrate. The two glass plates create a cell that can easily be opened after polymerization: one methacrylate-functionalized glass plate covalently bonds with the coating and the other fluorinated alkylsilane-functionalized glass plate ensures detachment from the coating. The cell gap was chosen to be 18 μm by using a glue with 18 μm glass spacer beads. Photopolymerization was performed in the cholesteric phase at 40 °C for 5 min at ~20 mW/cm². After the cells were opened, the polymeric coatings remained on the acrylate-functionalized glass substrate.

4.4. Characterization Methods. Thermal transitions of the liquid crystalline coatings were analyzed by differential scanning calorimetry using a TA Instruments Q1000 calorimeter with constant heating and cooling rates of 10 °C/min. The reflection of the CLC coatings was measured through ultraviolet−visible spectroscopy by using a PerkinElmer LAMBDA 750 with a 150 mm integrating sphere over a range of 400−750 nm and equipped with a Linkam THMS600 heating stage to measure transmission spectra at specific temperatures. The temperature-dependent equilibrium of hydrogen bonding was monitored by infrared spectroscopy using a Varian FT-IR3100 equipped with a heatable Golden Gate ATR accessory in a range of 1800−1600 cm⁻¹ to focus on the cyclic/open dimer−monomer ratio of the liquid crystalline benzoic acids. Full polymerization was confirmed by comparing the spectrum of the polymer and monomer mixture in the range 1350−1800 cm⁻¹. The cholesteric structure was analyzed by scanning electron microscopy using a Quanta 3D FEG; the coating was cryogenically broken in liquid nitrogen to obtain a cross section and sputter-coated with gold at 60 mA over 30s. The setting for SEM analysis in secondary electron mode was an acceleration of 5 kV, working distance (WD) of 10 mm, and under high vacuum. Surface profile characterization was performed using a Bruker DektakXT, set to measurement range 65.5 μm and stylus force 3 mg.

4.5. Steam Sterilization Process. Steam sterilization is generally performed in an autoclave. The combination of steam and heat destroys microorganisms by the irreversible coagulation and denaturation of enzymes and structural proteins. Specific temperatures must be obtained to ensure microbial efficiency, which is

Figure 6. Influence of saturated steam on the photonic coating. (a) Surface roughness profile after exposure to heat compared to exposure in an autoclave. (b) Cholesteric coating at RT before and after exposure in an autoclave. (c) UV−vis absorption spectrum of the CLC coating before and after exposure in an autoclave. (d) SEM images of the CLC coating after exposure in an autoclave. Inset I shows a two-dimensional Fourier transformation of the area (II), illustrating a more complete loss of cholesteric order.

Figure 7. UV−vis transmission spectrum of the CLC coating before and after a modified autoclave program (20 min at 110 °C).
achieved with saturated steam under pressure at an elevated temperature. The steam sterilization method used a temperature of 121 °C for a period of 20 min at 2.1 bar, which are the recommended minimum exposure conditions for sterilization of wrapped health care supplies.1−3 To simulate a failed steam sterilization process, the temperature was changed to 110 °C (same period of 20 min at 2.1 bar).

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c00711.

Chemical structures and composition of the CLC mixtures, synthesis of chiral dopant (1), FT-IR analysis, DSC measurement, UV–vis spectrum of SRB thinning, angular dependent UV–vis spectra, and single substrate coating (PDF)

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**Author Contributions**
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**ABBREVIATIONS**

| CLC | cholesteric liquid crystal |
| SRB | selective reflection band |
| \( T_g \) | glass transition temperature |
| UV–vis | ultraviolet–visible |
| SEM | scanning electron microscopy |
| FT-IR | Fourier transformed infrared |
| DSC | differential scanning calorimetry |
| \( T_{\text{n/i}} \) | nematic–isotropic transition temperature |

**REFERENCES**


