

Responsive Polymer Photonics**

Jelle E. Stumpel*[a]

Awarding Institute: Eindhoven University of Technology, Eindhoven (The Netherlands)**Date Awarded:** November 6, 2014**Supervisors:** Prof. Dr. Albertus P. H. J. Schenning, Eindhoven University of Technology, Eindhoven (The Netherlands); Prof. Dr. Dirk J. Broer, Eindhoven University of Technology, Eindhoven (The Netherlands)

Polymer coatings are of major importance in everyday life. Most of the surfaces that we use daily have been modified with a protective or aesthetic coating. However, the majority of these coatings are static. In other words, they are not responsive to external influences such as light or humidity. It is expected that responsive coatings will play an important role in meeting social challenges in the fields of sustainable energy, health care, and food safety. These functional properties are often determined by the surface topography and/or wettability. Recently, the development of stimulus-responsive polymer coatings that have dynamic rather than static properties has been the focus of considerable attention. For these so-called smart coatings, the properties change in response to an external stimulus. The functional properties can be adjusted autonomously depending on user needs or upon environmental changes. Such coatings hold great promise in a variety of fields including optical sensors, reflecting devices, as well as easy-to-clean materials and robotics (responsive topographies).

The research described in this thesis focuses on the development of responsive materials that operate in a reversible way. Photoresponsive and stimulus-responsive photonic coatings were prepared. The first type of coating undergoes photoinduced topographical alterations; coatings in the second category change colour upon exposure to a specific stimulus. Both types are based on liquid crystal or hydrogel-based materials and, in both cases, the response is a dimensional alteration that leads to changes in the initial surface topography and/or colour. The first chapter gives an overview of the stimuli-responsive photonic coatings that have been produced in the past.

The following two chapters describe the use of light-induced topographical changes in a crosslinked poly(*N*-isopropylacrylamide)-spiropyran hydrogel coating. When this coating is placed in an acidic environment, the colourless spiropyran derivative (Sp) spontaneously changes into its protonated strongly coloured merocyanine isomer (MCH⁺), as depicted in Figure 1. Exposure to visible light then results in back-isomerisation into the Sp form. The protonated MCH⁺ species is hydrophilic and its Sp isomer is hydrophobic. Spiropyran-based polyNIPAAAM (*N*-isopropylacrylamide) hydrogels therefore undergo a light-induced hydrophilicity change, resulting in an alteration in the dimensions of the hydrogel,

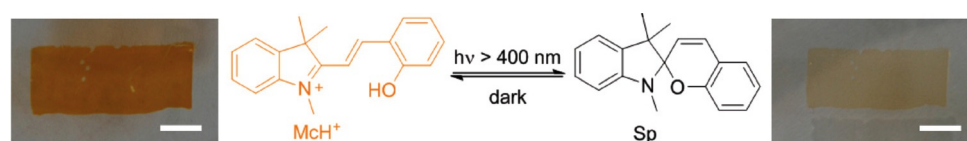


Figure 1. Isomerisation behaviour of protonated merocyanine (MCH⁺) into spiropyran (Sp) upon visible light exposure at pH 2.7. The left photograph displays a fully swollen hydrogel; the right photograph is the same hydrogel after photo-exposure (the scale bar represents 1 cm). Reproduced with permission from Ref. [6]. Copyright 2013, John Wiley and Sons.

[a] Dr. J. E. Stumpel

Laboratory of Functional Organic Materials & Devices (SFD), Department of Chemical Engineering & Chemistry
Eindhoven University of Technology, Building 14—Helix, De Rondom 70, 5612 AP Eindhoven (The Netherlands)
E-mail: j.e.stumpel@alumnus.tue.nl

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which can be visually observed (Figure 1). The degree of swelling and shrinkage in the hydrogel depends on the crosslink density of the material. Polymerisation-induced diffusion was used to control the spatial crosslink density in a hydrogel coating. This resulted in a corrugated structure after the material was swelled in a slightly acidic aqueous solution. Photo-exposure resulted in a reversible reduction of the height of this surface topography.

Further development of this material resulted in photoresponsive hydrogels that operate at neutral pH. In these hydrogels, acrylic acid acts as an internal proton source, resulting in a hydrogel coating that is photoresponsive in a neutral environment. After being placed in demineralised water, the slightly off-colour hydrogel film changed to a more intense orange colour, which indicates that the protonated merocyanine isomer formed spontaneously in water because of the carboxylic acid that is incorporated in the polymer backbone. Polymerisation-induced diffusion was used to obtain responsive surface topographies of the kind described above. Moreover, asymmetric ratchet-like structures were prepared using a prestructured substrate (Figure 2). In this system, the asymmetric change of the surface topography is a result of variation in the thickness of the hydrogel. The extent of the photoinduced alteration of the coating can be controlled by adjusting the crosslink density of the hydrogel.

The succeeding chapters report on responsive photonic coatings based on cholesteric liquid crystals (CLCs). In this liquid crystalline phase, an alternating refractive index change through the material results in the partial reflection of the incident light. CLC coatings which alter their colour upon water uptake have been prepared. Furthermore, water-responsive surface topographies were prepared in which the hydrogen-bonded supramolecular polymer coating had alternating regions with a CLC or an isotropic alignment. Treatment with an alkaline solution led to the disruption of the hydrogen bonds and the formation of carboxylates. Due to the hygroscopic nature of these moieties, the materials swelled when placed in water. Interestingly, the isotropic areas swelled uniformly, while the CLC areas mostly swelled unidirectionally. The structure of the surface topography was therefore accentuated after placement in water. A change in the helical pitch of the CLC region also led to a different reflected colour, while the isotropic areas are colourless in both the dry and the swollen state. Additionally, coatings were prepared that underwent dual-coloured patterned changes when placed in water.

A novel approach was used to produce the humidity-responsive optical sensors with a broad operational range. An interpenetrating polymer network (IPN) which combines CLC-based materials with hydrogels was used for this coating. A cholesteric polymer network was swollen with an acrylic acid-based mixture which was subsequently photopolymerised. The activation of this coating with an alkaline solution led to the formation of a hygroscopic potassium polyacrylate network in the CLC scaffold. Humidity-dependent volumetric changes in this IPN network led to a relative large colour change. Moreover, an IPN with a responsive surface topography was prepared. This coating consisted of regions containing both responsive potassium polyacrylate areas and static polystyrene areas. Depending on the pH or relative humidity, the surface became flat or structured (Figure 3).

Lastly, the fabrication of a hydrogen-bonded CLC coating which responds to gaseous trimethylamine (TMA), a substance produced by decay in fish is presented. Like the alkaline treatment, TMA deprotonates the carboxylic acids in the material and carboxylate salts are formed. Under anhydrous conditions, this salt formation causes a decrease in the molecular order that results in a colour loss. However, the hygroscopic coating swells under humid conditions, resulting in a clearly visible colour shift

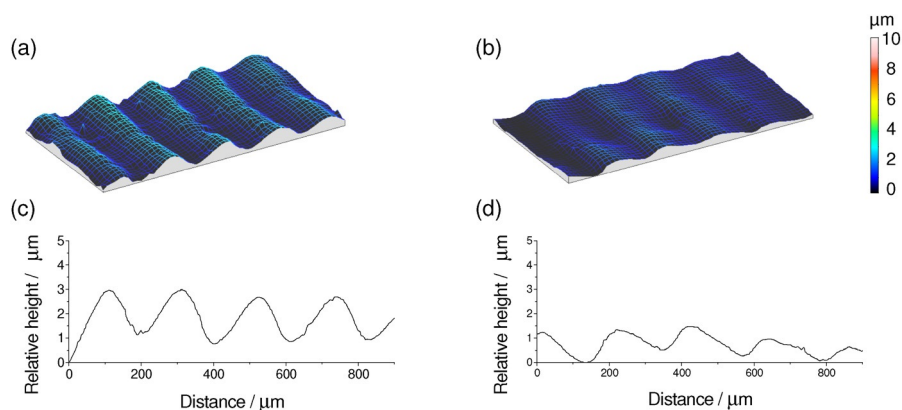


Figure 2. 3D height profiles of a hydrogel ratchet before (a) and after (b) light exposure and c,d) corresponding cross-sections of the surface topography, as observed by interferometry (dimensions of the surface are $505 \times 946 \mu\text{m}^2$).

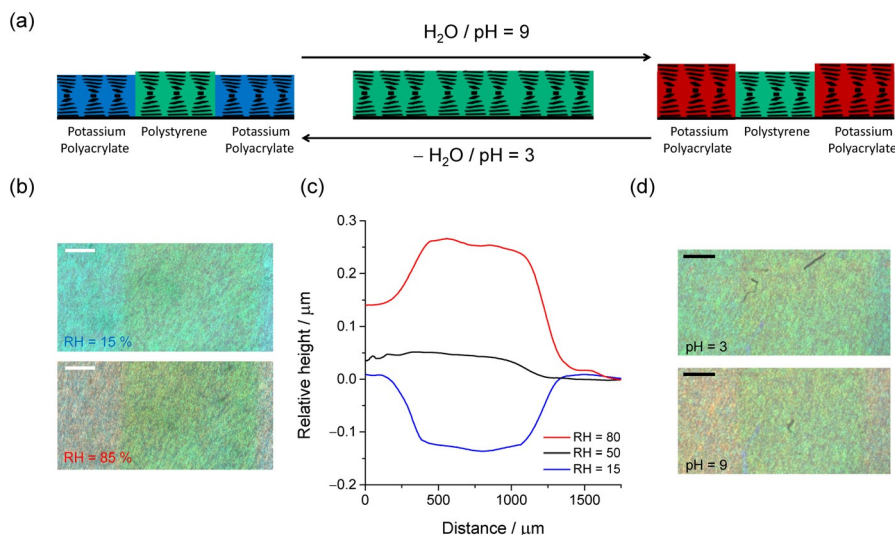


Figure 3. a) Schematic representation of the working mechanism of the patterned polystyrene poly(acrylic acid)-responsive IPN polymer film. b) Optical micrographs of a patterned IPN coating at a relative humidity (RH) of 15% and 85%. The colour change in the polyacrylate areas is clearly visible. c) Surface topography of the patterned humidity-responsive IPN coating at RH of 15%, 50%, and 80% ($T = 20^\circ\text{C}$), as observed by interferometry. d) Optical micrographs of the patterned IPN polymer film at a pH 3 and 9. The scale bar represents 250 μm . The mask used has alternating dark and transparent areas of 1 mm. Reproduced with permission from Ref. [1]. Copyright 2015, John Wiley and Sons.

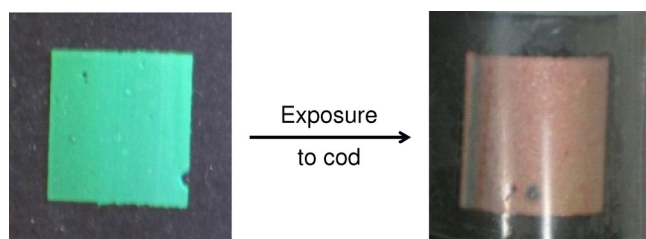


Figure 4. Photographs of the green-reflecting CLC film before and after exposure to spoiling cod. Reproduced with permission from Ref. [5]. Copyright 2014, John Wiley and Sons.

from green to red. This type of colour-changing CLC coatings can be used as optical sensors for the real-time detection of various analytes. In a proof-of-principle experiment, it was shown that these CLC films can be used as optical sensors to detect volatile amines that are produced by decaying fish (Figure 4).

Overall, this thesis shows that responsive photonic coatings that are of interest for a range of applications can be produced. The technology assessment discusses some of these applications in greater detail. The development of photo-responsive coatings has considerable potential for applications ranging from microfluidic devices to cell culturing. Turning to the use of responsive photonic coatings as sensors, preliminary results are presented which are expected to improve the selectivity of the sensor. Finally, the photochromic behaviour of spiropyran is discussed as a way of preparing smart windows and writable optical materials.

Keywords: cholesteric liquid crystals · hydrogels · optical sensors · polymer coatings · responsive materials

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