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Stimuli-responsive photonic polymer coatings

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This feature article focuses on the highlights in the development of photonic polymer coatings that can change their volume or surface topology in a reversible, dynamic fashion when exposed to an external stimulus. Topographic response is established using hydrogels or liquid crystal polymer networks. By changing the surface corrugation in response to light various functional coating properties can be modulated, for instance wettability and/or mechanical friction. The same volume changes in photonic coatings caused by different stimuli lead to changes in light reflection.

Introduction

Polymer coatings play an important role in our society. They protect everyday objects from environmental influences. Coatings are also widely used for aesthetic purposes, adhesion-promotion/reduction, anti-reflection or anti-fouling. These functional properties are often determined by the surface topography. Recently, the development of stimulus-responsive polymer coatings which have dynamic rather than static properties has been a focus of considerable attention.^{1–6} In this category of coatings,

the properties change in response to an external stimulus. The functional properties can be adjusted autonomously depending on user needs or on environmental changes. It is expected that coatings of this type will play an important role in meeting social challenges in the fields of sustainable energy, health and food safety.

Using light to induce dimensional or structural changes is appealing since it can be done locally without contact and without changing the immediate chemical environment of the polymer coatings or the integration of electrodes. Photo-exposure can lead to the structural modification of a polymeric network, resulting in a change in the surface topography (Scheme 1). In particular, photo-induced alterations in the surface roughness or the hydrophilicity of materials are of interest since they cause changes in their wettability and/or changes in their adhesion properties.^{3,7,8} Coatings that respond

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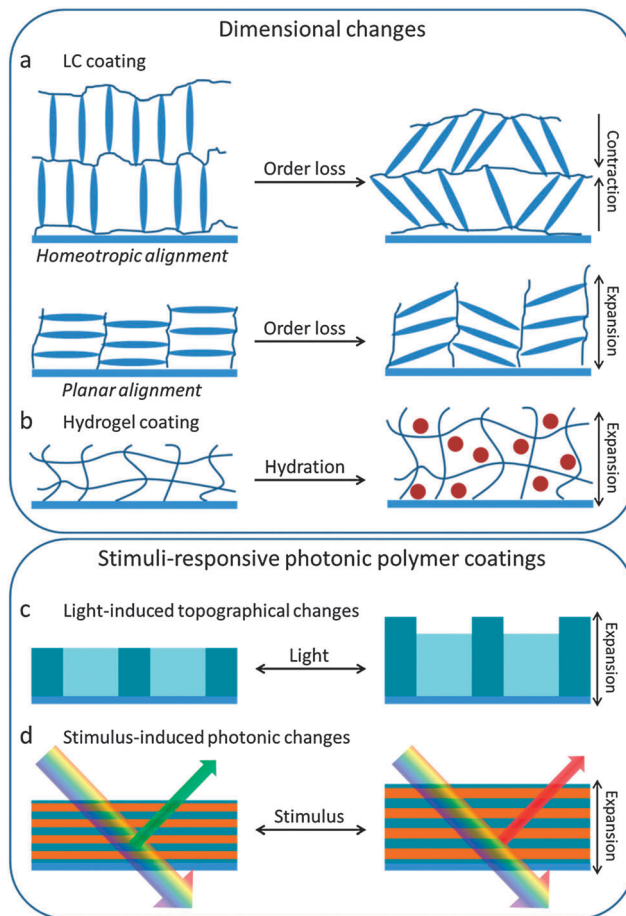


Dirk J. Broer

Dirk J. Broer is a polymer chemist and specialised in polymer structuring and self-organising polymer networks. In 1973, he joined Philips Research (Eindhoven, The Netherlands), where he worked on manifold research topics such as vapour-phase polymerisation, optical data storage, telecommunication fibres, and display optics. In 2010, he was appointed a fulltime professor at Eindhoven and University of Technology with a research emphasis on clean technologies in energy harvesting, water treatment, and healthcare. Prof. Broer is a member of the Royal Netherlands Academy of Arts and Sciences (KNAW). In total, he has around 240 publications in peer-reviewed journals and 120 U.S. patents.

to sunlight could be useful in the development of sun-tracking materials or materials with self-cleaning properties involving structural changes. A photochromic dye is usually incorporated in the coating to make a polymer photoresponsive.^{7,9,10} When exposed to light of a certain wavelength, this dye isomerises into a different form. The most commonly used dyes are azobenzene derivatives,^{11–13} which undergo *cis-trans* isomerisation, and hydrophobic spiropyran derivatives,^{14–16} which isomerise into the hydrophilic merocyanine form. Isomerisation of the photochromic dye leads to an alteration of the functional properties of the polymer coating as a result of topological changes. Usually, the materials for such coatings are based on liquid crystalline (LC) polymers or hydrogels and solvent gels (Scheme 1).^{17–19} Small changes in the molecular order of LC materials can lead to large dimensional changes (Scheme 1a).^{20,21} Volumetric and dimensional changes in gels are based on differences in swelling and shrinkage due to the adsorption or desorption of a solvent (Scheme 1b). By fabricating a patterned coating containing a different molecular orientation or having a difference in cross-link density, light responsive topographical changes be obtained (Scheme 1a–c).

In photonic coatings, a structural change may, for instance, lead to a colour change (Scheme 1d). Stimulus-responsive photonic coatings are interesting as optical sensing materials which change their colour autonomously in response to environmental changes and/or chemical stimuli. In photonic materials, shape and volumetric changes alter the optical properties.²² The advantages of polymeric sensors are their low cost, ease of fabrication and the fact that they can be operated battery-free. Most coatings with responsive optical properties are based on materials which operate as Bragg reflectors. Typical Bragg reflectors contain alternating layers of materials with high- and low-refractive indices that reflect light of a specific wavelength (Scheme 1d). Liquid crystals have been used for various kinds of optically responsive coatings.^{23,24} In the chiral nematic phase (or cholesteric liquid crystals, CLCs), the mesogens are aligned in a helical structure.



Scheme 1 Schematic representations of dimensional changes in polymer coatings. (a) Dimensional changes arise in a LC coating after loss of molecular order. Contraction and expansion is dependent on the molecular orientation. (b) Dimensional changes in a hydrogel coating as a result of hydration (water molecules, red spheres). (c) Topographical alterations of a photoresponsive polymer coating having patterned regions (dark and light blue regions) with a difference in molecular order (for example in LC systems) or crosslink density (for example hydrogels). (d) A stimuli-responsive photonic coating having alternating layers with high- and low-refractive indices leading to a change in the reflection of light upon expansion.



Albertus P. H. J. Schenning

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The anisotropy in the system leads to changes in the refractive index across the material, resulting in a one-dimensional photonic coating and causing the selective reflection of light.²⁵ Another way to prepare colour-reflecting materials involves using colloidal photonic crystals or inverse-opal structures in which spheres are periodically positioned in a hydrogel or an elastic matrix. This leads to the selective reflection of light that varies depending on differences in the properties of the spheres and the matrix. The positioning of the colloids alters when the material expands or contracts, resulting in a change in the reflection band.

In this feature article we report on responsive photonic coatings in which the response is a dimensional and/or volumetric change which can be observed as a variation in surface topography or an alteration in reflected colour (Scheme 1c and d). The first part of this feature article looks at coatings in which the volumetric and dimensional response is stimulated

by light. The second part will turn to photonic coatings in which exposure to a stimulus leads to an optical change in the polymer coating. Stimulus-responsive polymer materials such as freestanding films and shape-memory materials other than photonic coatings, and responsive coatings based on fluorescence or absorption processes, are outside the scope of this feature article.

Photoresponsive polymer coatings

Photoresponsive surface topographies

An interesting application for photoresponsive polymer coatings is an alterable surface topography. In some of these coatings, local photo-exposure leads to the expansion or compression of the exposed area of the surface topography. In other coatings, the pattern is imprinted in the polymer film and the response is non-uniform, leading to the formation or enlargement of protrusions.

Cholesteric liquid crystal (CLC) polymer coatings containing azobenzene moieties have been used to obtain photoswitchable surfaces (Fig. 1a).^{20,26,27} Due to the helical organisation of the molecular building blocks in the cholesteric material, expansion is usually in the direction perpendicular to the chiral nematic alignment (Fig. 1b). Protrusions are formed by exposing the polymer coating to light through a mask.²⁶ Depending on the polymer chain length, the protrusions can form reversibly (when the chain is long) or irreversibly (when the chain is short). Subsequent studies have been reported involving coatings in which the pattern is already present in the material before light exposure.²⁷ Films with alternating cholesteric and

homeotropically aligned regions have been prepared (Fig. 1b). Photo-exposure leads to the appearance of a relief structure since the expansion of the cholesteric areas is predominantly perpendicular to the plane of the film; the expansion of the homeotropic region is mostly parallel to the plane of the film (Fig. 1c). Recently, an even more straightforward, innovative approach has been reported.²⁸ It was shown that, when a cholesteric polymer network is applied to a homeotropic alignment layer, worm-like fingerprint textures are obtained without any photomask being required. When illuminated with UV light, these protrusions having sub micrometre dimensions are enhanced, leading to changes in the friction and adhesion properties of the material.

A popular monomer for the preparation of responsive polymer hydrogel networks is *N*-isopropylacrylamide (abbreviated as NIPAAM, Fig. 2a), which possesses well-studied thermoresponsive volumetrical changes.²⁹ When polyNIPAAM is above its lower critical solution temperature (LCST) of 30–35 °C, a macromolecular transition from a hydrophilic to a hydrophobic structure of the polymer chain takes place, causing a collapse due to the release of water. Hydrogel coatings have been prepared on a substrate with light-absorbing patterns which convert light into heat.³⁰ In these materials, photo-exposure leads to the partial shrinkage of the films and in turn to changes in the surface topography.

To make a hydrogel which is photoresponsive in itself, a photochromic dye can be incorporated in the polymer network. Early investigations of the incorporation of spiropyran in NIPAAM polymers in slightly acidic media have led to the development of photoresponsive hydrogel coatings.^{31,32} The working mechanism for the swelling and shrinkage observed in the hydrogel is shown schematically in Fig. 2b.³³ In an acidic environment, the hydrophobic spiropyran (Sp) spontaneously isomerises into hydrophilic protonated merocyanine (MCh). Exposure to visible light leads to the formation of Sp. When the irradiation is stopped, the more stable MCh is formed again. Upon incorporation in a linear NIPAAM polymer chain, Sp and MCh can induce the dehydration and hydration of the polymer chain because of the large difference in hydrophilicity between the two isomers. A crosslinker can be used to obtain polymer network coatings which operate as hydrogels (Fig. 2a). The light-induced hydration and dehydration mentioned here results in the reversible swelling or shrinkage of the entire hydrogel. In the dark, the gels are fully swollen; light exposure leads to the shrinkage of the gels. The photochromic behaviour of spiropyran can be fine-tuned by substituting electron-donating or electron-withdrawing groups on the benzene rings of the molecule or by making adjustments in the molecular composition of the hydrogels.^{33–35}

Sheet-like hydrogel coatings exposed locally to light to obtain restricted shrinkage have also been reported. This technique has been used to move objects over a hydrogel surface or to form microchannels or microvalves in microfluidic systems on demand (Fig. 3).^{33,36} Photoresponsive valves have been manufactured which can be opened or closed by local exposure to blue light.³⁷ Due to the thermoresponsive behaviour of pNIPAAM, it is also possible to control the valves using temperature changes.

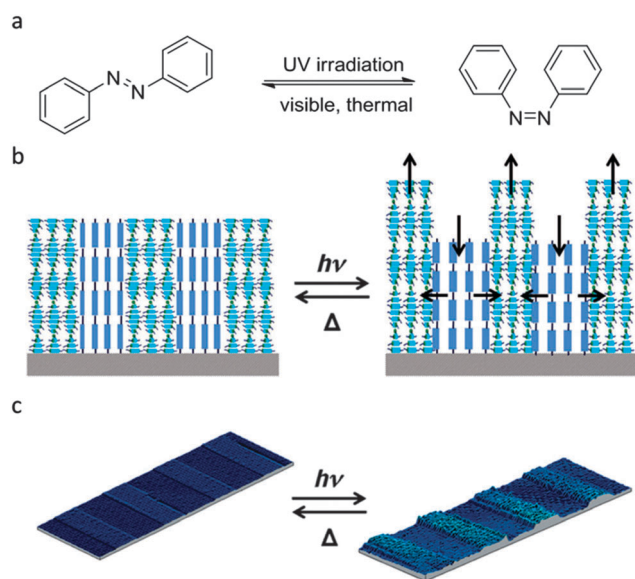


Fig. 1 (a) *Cis*–*trans* isomerisation of azobenzene derivatives upon exposure to light. (b) Schematic representation of an azobenzene-based liquid-crystal network containing striped patterns of alternating areas with chiral nematic order and homeotropic orientation. Upon exposure the chiral nematic areas expand perpendicularly to the plane of the film and the homeotropic areas contract in the perpendicular direction. (c) 3D images of surface topographies in the initial state and during illumination with UV light. Adapted from ref. 27 (Fig. 1b and c). Copyright © 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

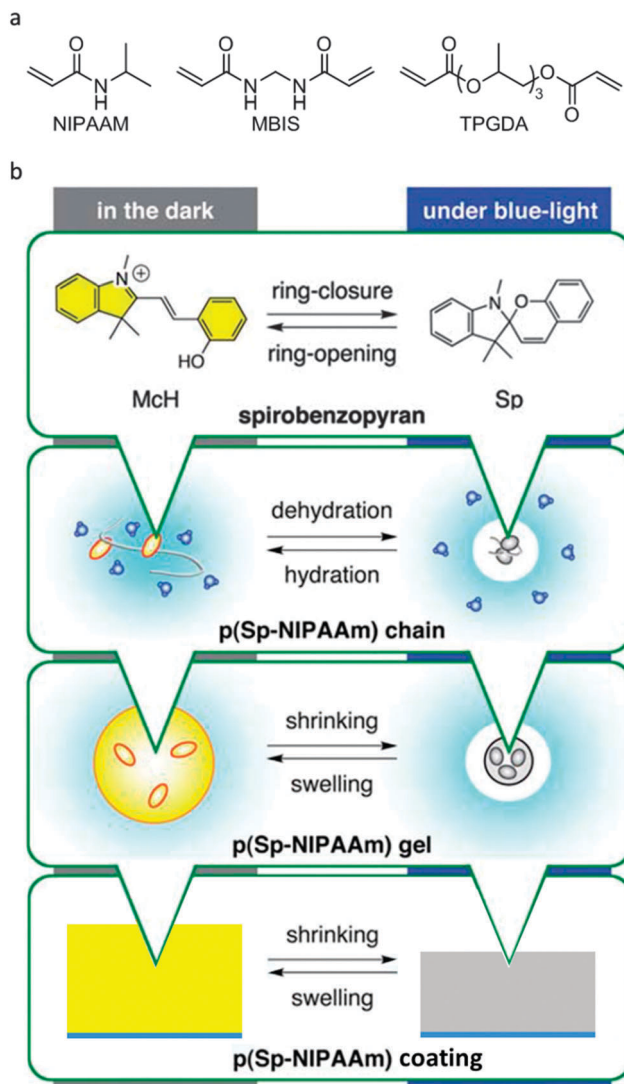


Fig. 2 (a) *N*-Isopropylacrylamide (NIPAAm) and two common crosslink agents: *N,N'*-methylenebis(acrylamide) (MBIS) and tri(propylene glycol) diacrylate (TPGDA). (b) Relations between the isomerisation of spiropyran into protonated merocyanine (top picture), the hydration behaviour of a p(Sp-NIPAAm) chain (next picture) and the volumetric change in a p(Sp-NIPAAm) gel in an acidic aqueous solution (next picture) and the response in an actual coating (bottom picture). Adapted from ref. 33 (Fig. 2b) with permission from The Royal Society of Chemistry.

Ionic liquids have been incorporated to prepare ionogel-based valves, which are more rigid.³⁴ Due to the low vapour pressure of ionic liquids and their thermal and chemical resistance, the resulting gels have semi-solid properties. Furthermore, it is possible to control the response time in these systems by varying the ionic liquid.

Another interesting application of spiropyran-based NIPAAm hydrogels are photoswitchable surface topographies.³⁸ Polymerisation-induced diffusion has been used as a tool to fabricate coatings with a difference in crosslink density throughout the film.^{39,40} Light exposure leads to shrinkage of the coating predominantly in the less crosslinked regions, and a decrease in the height difference of the relief structure is observed.

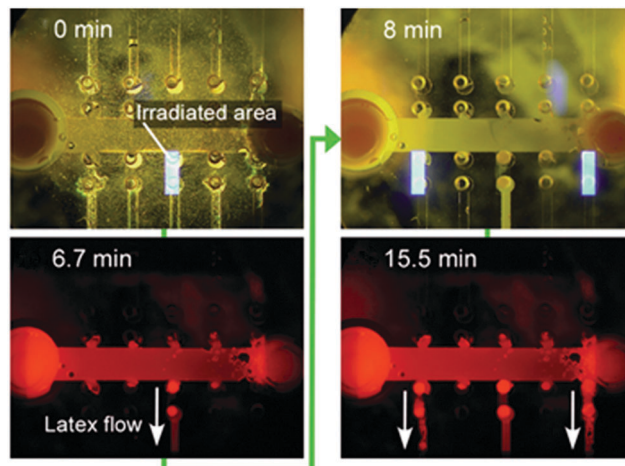


Fig. 3 Independent and parallel flow control in the PDMS microchannel network equipped with 10 photoresponsive microvalves created from a p(Sp-co-NIPAAm) hydrogel sheet. White arrows indicate the flow direction of the latex bead suspension. Independent control of a single microvalve was obtained by local light irradiation, as shown by the latex bead suspension flow after irradiation (dimensions of the images are $13.8 \times 10.6 \text{ mm}^2$). Adapted from ref. 36 with permission from The Royal Society of Chemistry.

Recently, spiropyran-NIPAAm-acrylic acid hydrogels which operate in a pH-neutral environment have been developed.⁴¹ In these systems, acrylic acid, which is copolymerised in the NIPAAm network, acts as an internal proton donor, leading to spontaneous formation of MCh. With the use of this approach, photoresponsive ratchet-like topographies have been developed.⁴² The coatings were prepared on pre-structured substrates. Depending on the crosslink density of the mixture used, ratchets which decrease their steepness or even form opposite ratchet structures after photo-exposure have been prepared (Fig. 4).

Photoresponsive wettability

When the structures of a surface topography are in the micro-metre size regime, they influence the wettability of the surface. When water fills the cavities, the wetting is in the Wenzel-type wetting regime. Depending on the topography, air pockets can also be formed, creating a more hydrophobic coating.^{43,44} Consequently, the surface roughness plays a decisive role in the wettability of the surface.^{45,46}

Most polymer coatings with photoresponsive wettability behaviour are based on rough surfaces which are modified to make them more hydrophilic or hydrophobic upon light exposure. Covalent attachment of azobenzene-functionalised poly(acrylamides) to a rough surface has led to extremely large contact angle (CA) differences ($\Delta\theta = 140^\circ$ in the advancing CA at the transition from Wenzel wetting to superwetting or more than 175° in the receding CA at the transition from superhydrophobic to Wenzel wetting).⁴⁷ The coated surfaces can be reversibly switched between different wetting regimes as a result of changes in surface energy induced by the isomerisation of azobenzene.

Another way of preparing surfaces with photoresponsive wettability is to coat a photoresponsive polymer on structured

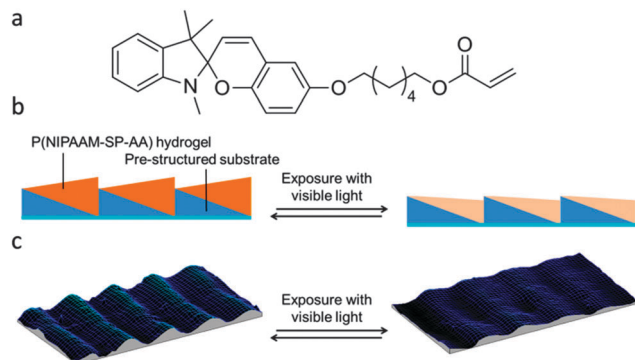


Fig. 4 (a) The molecular structure of the spiropyran (Sp) derivative that was used. (b) Schematic representation of the responsive of the p(NIPAAm-SP-AA) ratchet hydrogel and (c) 3D height profiles of the ratchet hydrogel before and after light exposure, as observed by interferometry (dimensions of the surface are $505 \times 946 \mu\text{m}^2$). Adapted with permission from *ACS Appl. Mater. Interfaces* 2014, **6**, 7268. Copyright (2014) American Chemical Society.

surfaces with micropillar arrays.^{48,49} After activation of a patterned silicon wafer, azobenzene-containing polymers can be spin or dip coated onto the surface. Isomerisation of *trans*-azobenzene into the *cis*-isomer leads to large changes in wettability, depending on the spacing of the pillars. The optimum for $10 \mu\text{m}$ square pillars is a spacing of $40 \mu\text{m}$, where a reversible photo-induced change in contact angle of 66° is observed, which is about 33 times larger than for the same coating on a flat substrate (Fig. 5).⁴⁸ Interestingly, if similar azobenzene-based polymers are coated on much smaller features, there is no hydrophobicity change observed after photo-exposure as the microstructure is dominating the superhydrophobicity of the system. However, photo-exposure leads to a change in adhesive force of these materials.⁴⁹ Water droplets can be pinned on the hydrophobic surface with the use of UV light illumination, whilst visible light exposure leads to a decrease in adhesion and the droplet rolls off the surface.

As stated before, spiropyran is a photochromic dye which undergoes a hydrophilicity change itself upon isomerisation (Fig. 2). This behaviour has also been used for photoresponsive wettability. Soft moulding lithography has been used to prepare a poly(ethyl methacrylate)-*co*-poly(methyl acrylate) film doped with nitrospiropyran.⁵⁰ Even though the spiropyran molecule is not incorporated in the polymer backbone, isomerisation leads to changes in the hydrophilicity of the flat surface. Due to the formation of air pockets and an increase in the hydrophobicity of the substrate, the photo-induced reversible changes in the contact angle of a spiropyran-dispersed polymer film surface can also be enlarged by a factor of 3 compared to a flat surface when the surface is micropatterned.

More recently, coatings based on hydrogels which can change between a superhydrophilic and moderate hydrophobic state have been developed. The hydrogels are prepared from crosslinked copolymer films made with spiropyran and NIPAAm.⁵¹ Photoisomerisation of MCH into Sp leads to dehydration and a hydrophilicity change in the hydrogel obtained (Fig. 2b). When these copolymers are grafted from a structured surface (nanorods), a light-induced change from 5° to 123° can be achieved in the static contact angle.

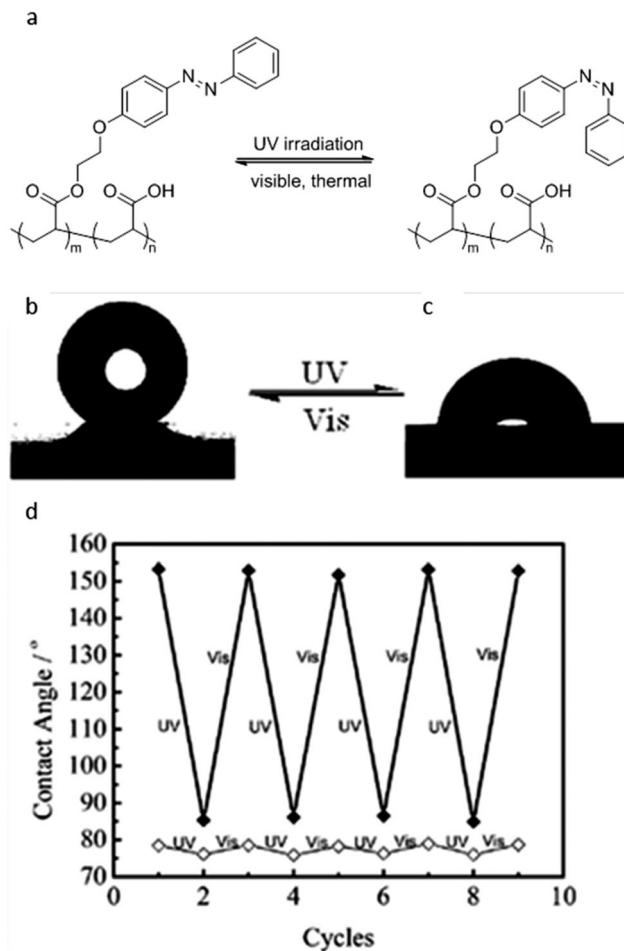


Fig. 5 (a) Chemical structure of the photochromic polymer. (b) Optical images of the shape of water drops on a substrate with $40 \mu\text{m}$ pillar spacing coated with azobenzene-containing polymer upon UV and Vis irradiation. (c) Reversible wettability behaviour by UV and Vis irradiation. (d) Reversible wettability behaviour by UV and Vis irradiation: \diamond represents CA on a flat silicon wafer; \blacklozenge represents CA on a patterned substrate with $40 \mu\text{m}$ pillar spacing. Adapted from ref. 48 (Fig. 5b and c) with permission from The Royal Society of Chemistry.

Photoresponsive cell adhesion

There is also interest in responsive materials for biomedical applications.^{4,9,52} Spiropyran-NIPAAm hydrogel coatings have been reported that can be used to control cell adhesion.⁵³ The spiropyran form is most stable at equilibrium in neutral pH conditions. UV exposure leads to the isomerisation of spiropyran into merocyanine. Micropatterned illumination results in a difference in cell adhesion in the different areas. After a subsequent washing step, the majority of the cells are left on the UV-exposed areas of the surface and the cell population is 20 times higher than in the non-exposed areas. This effect is most probably caused by the zwitterionic merocyanine causing more hydrophilic regions, which have a higher affinity for cells, although the exact mechanism is not yet fully understood. Cell adhesion properties can therefore be initialised by illumination with visible light while unwanted cells can be easily removed from their substrate with this technique.

Polymer coatings with responsive optical properties

Chemically responsive photonic polymers

The most simple material composition for polymeric photonic coatings is a 1D Bragg reflector consisting of alternating layers of high and low refractive index polymers. Block copolymers which form a lamellar gel have been used to produce polymers of this kind. An optical sensor for detecting various counterions has been developed.⁵⁴ The material acts as an ordinary Bragg reflector with alternating layers of polystyrene (PS) and 2-vinylpyridine (2-PVP). The response of the gel is due to the quaternisation of 2-PVP by bromoethane. Various kinds of anions have the ability to bind to the obtained pyridinium cations. Differences in the hydration energy of charged pyridine counterions lead to ion-specific swelling of the 2-PVP areas, whilst the PS remains unaffected. Initially the thickness of both layers was 24 nm and changed to 24 to 220 nm, depending on the coordinated counterion. This results in a change in the reflection band (Fig. 6 displays the mechanism and the colour change as a result of binding of various anions). An optical sensor for the detection of anions can be constructed in this way.

An exciting class of materials for responsive photonic properties consists of colloidal particles embedded in a responsive polymer network. The swelling of this type of coating in various liquids results in a spectral shift in the band gap. A colloid-based coating which can be used as photonic paper has been presented.^{55,56} Writing on the paper involves swelling the film locally with silicone liquids (Fig. 7). Interestingly, the degree of swelling (to which the colour change is related) is dependent on the molecular weight of the liquid. On an initial purple film, blue, green and red areas can be obtained by swelling using silicone liquids with a decreasing molecular weight.

Molecular imprinting has led to a colloidal crystal hydrogel sensor for bisphenol A.⁵⁷ The coating responds selectively to

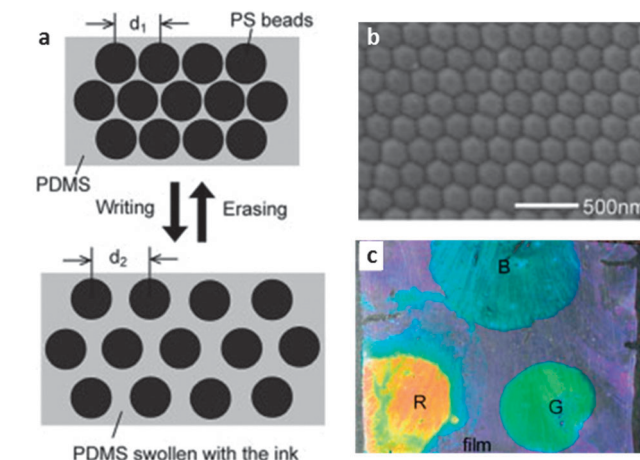


Fig. 7 (a) A schematic representation of the mechanism for a colloid-based material upon solvent uptake. (b) SEM image of the matrix. (c) Blue, red and green dots written on the same colloidal crystal using silicone liquids with molecular weights of 3780, 770 and 162 g mol⁻¹ respectively. Adapted from ref. 56. Copyright © 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

the target molecule through a loss in reflectance. In other words, there is a colourless shift. Interestingly, in control experiments where the sensor was exposed to reference compounds with chemical structure similar to bisphenol A, the initial reflection band remained unaltered. The production of a colloidal hydrogel in which boronic acid is incorporated in the polymer backbone leads to materials which can detect high glucose concentrations.⁵⁸ The system is not limited to the detection of organic analytes. For instance, the functionalisation of the system with 5-amino-8-hydroxyquinoline led to a similar sensor which can detect free Ni²⁺ concentration in the presence of human plasma.⁵⁹ Different colloidal crystal hydrogel ion-sensors based on crown ethers have also been reported.^{60,61} This system responds selectively to Pb²⁺ ions with a remarkably low detection limit (0.1 μM, 40 ppb). When a proper chelation agent is selected, this method can also be used for other ionic species.

Another type of band gap material that can be subjected to triggered metal-sensing is a CLC, which was mentioned above. This material self-organises in a periodic rotation of the predominant orientation of the molecules.⁶² The pitch determines the position of the band gap in the spectrum and therefore the colour of the material. When there is fixed alignment at the boundaries of the film, a change in volume normally results in a change of colour. Polymer-stabilised CLC metal sensors have been developed in which the incorporation of a crown ether in the polymer backbone leads to the ability to bind and detect metal ions.⁶³ Barium and potassium were detected successfully on the basis of a blue shift in the colour of the material (Fig. 8). The binding constant for bivalent barium was higher than for monovalent potassium ions. The exact mechanism underlying this shift is unclear. It is most probably caused by an increase in the isotropisation temperature. However, the blue shift could be the result of a focal conic deformation of the planar organisation or shrinkage due to interaction between charged crown ethers.

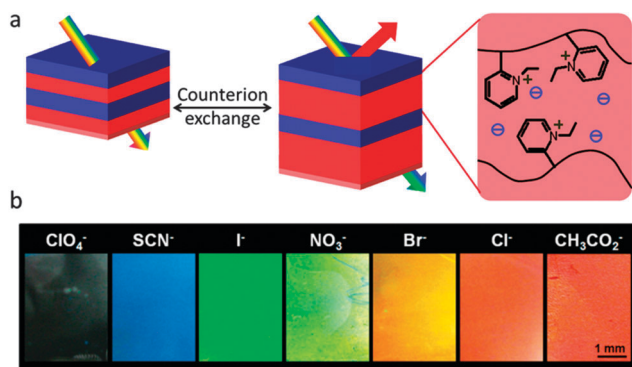


Fig. 6 (a) Schematic representation of the mechanism for the colour change in the PS-block-QP2VP photonic lamellar gels by counterion exchange. (b) Colour change of the photonic gel films quaternised for 36 hours with a direct exchange of counterions. The colour of the photonic gel films shifts from transparent to blue, green, and red as counterion hydration energy increases. The counterions were exchanged using a 10 mM solution of a variety of tetrabutylammonium salts. Adapted with permission from *ACS Nano* 2012, 6, 8933. Copyright (2012) American Chemical Society.

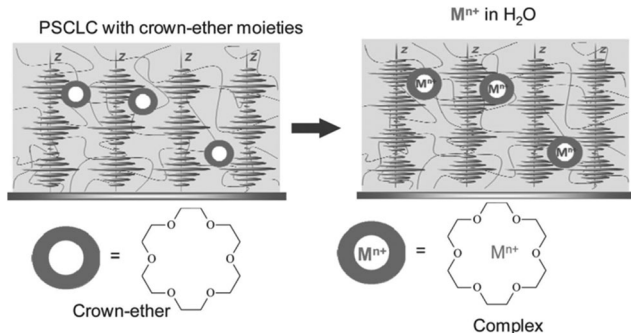


Fig. 8 The general working principle of PSCLC materials containing crown ether moieties for sensors for metal ions. Adapted from ref. 63. Copyright © 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

CLC polymer salt films have been used to discriminate between methanol and ethanol (Fig. 9).^{64,65} The porosity of the film allowed both solvents to penetrate into the material. Due to the difference in the molecular affinity of the film's interior with the solvent, it was possible to detect methanol in water. When the material comes into contact with an aqueous solution of ethanol, there is a larger red shift than when methanol is mixed in. This sensor is of interest for detecting trace amounts of methanol in wine or other alcoholic drinks. Hydrogen-bonded CLC materials have also been used for the detection of amino acids (Fig. 9).⁶⁶ Arginine, lysine and histidine in solution could be detected by a change in the reflected colour. Due to the alkaline nature of the amino acid (especially arginine, which has a basic guanidinium group), the hydrogen bonds are disrupted, leading to carboxylate moieties. These hygroscopic moieties absorb water from the solution, causing swelling and therefore a red shift in the reflection band of the film.

In addition to detection in solutions, the detection of gaseous compounds has also been reported.⁶⁷ An amine-responsive polymer-stabilised CLC mixture based on cholesteryl derivatives has been produced.⁶⁸ Due to the functionalisation of the cholesteryl unit with trifluoroacetyl groups which can form a hemiaminal, the coating is amine-responsive. The material is most sensitive to primary amines, such as 1-butylamine, since they are less sterically hindered than, for instance, secondary amines. More recently, a CLC coating has been used to detect gaseous trimethylamine (TMA).⁶⁹ The sensor works similar as

the CLC-based amino acid sensor (see above). TMA is absorbed by the carboxylic acid functionalised coating (Fig. 9). Presence of water at humid conditions results in swelling of the polymer film and a red shift of the reflection band. Such sensors are potentially interesting in the food industry, to detect volatile amines, that are produced by decaying fish.

Humidity-responsive photonic polymers

Materials which can autonomously detect differences in relative humidity (RH) have attracted a great deal of attention in applications in the medical and food industry.⁷⁰ A sensor based on hygroscopic CLC polymers, which can absorb water from the surroundings, has been reported (Fig. 9).⁷¹ Upon water uptake, the helical pitch increases and so light with a longer wavelength is reflected. The shift of 40 nm between a RH of 3% and 83% can be easily observed by the human eye. Small humidity changes are more challenging to observe. Another type of coating uses the holographic patterning of polymer-dispersed liquid crystals to form polymeric photonic crystals based on non-porous and nanoporous regions.⁷² This leads to rapidly-responding (1.5 second response time) humidity sensors. Upon water uptake by the nanoporous regions, their refractive index changes whilst the non-porous areas remain unchanged. The difference in refractive index between the different regions therefore decreases, leading to a red shift in the reflection band.

Nanoporous polymer humidity-responsive coatings with a colloid-like structure have also been made using silica nanoparticles dispersed in a photocurable poly(ethylene glycol diacrylate).⁷³ After polymerisation, the nanoparticles were removed in an etching procedure. Subsequent activation of the inverse-opal structures with O₂-plasma treatment led to an increase of the hydrophilicity of the coating. Humidity-dependent water uptake of the cavities led to a clearly visible colour shift. Other kinds of colloid-based sensors have been produced in which the colloids are still present in the responsive coating.^{74,75} The entire polymer matrix is made of hydrogel material, resulting in increased swelling with increasing humidity. The spacing between the 3D colloidal structure therefore increases and a red shift is seen. These systems are often based on inorganic colloidal particles such as Fe₃O₄ nanoparticles. But fully polymeric systems have also been reported in which the refractive index of the polymer particle is different enough from that of the polymer matrix to stimulate Bragg reflection. In these systems, colour changes up to 240 nm have been reported resulting from the concerted action of changes in index and periodicity as the matrix is taking up the water. (Fig. 10 shows the colour changes in such a system at a relative humidity between 20% and 100%).⁷⁴ The system consists of monodisperse latex spheres of poly(styrene-co-methyl methacrylate-co-acrylic acid) in a poly(acrylamide-bis(acrylamide)) matrix. A similar material was prepared by embedding a poly(styrene sulfonate-co-methylbutylene) copolymer, which forms a cylindrical morphology, in a poly(styrene sulfonate) (PSS) matrix in which the PSS areas expand under the influence of water.⁷⁰ The hexagonal organisation of the cylinders results in short diffusion pathways of water molecules, leading to a response time of just a few seconds.

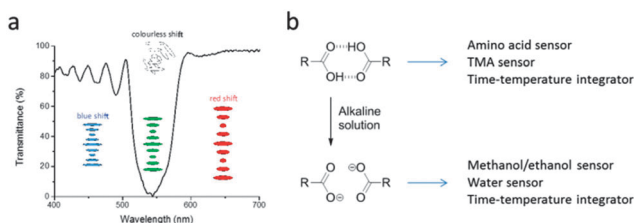


Fig. 9 (a) Schematic representation of the organisation of the mesogens in a CLC (b) the use of hydrogen-bonded CLC materials as amino acid and TMA sensor. The corresponding carboxylate salt can be used as methanol/ethanol and water sensor. Both polymer networks could be used as time-temperature integrator.

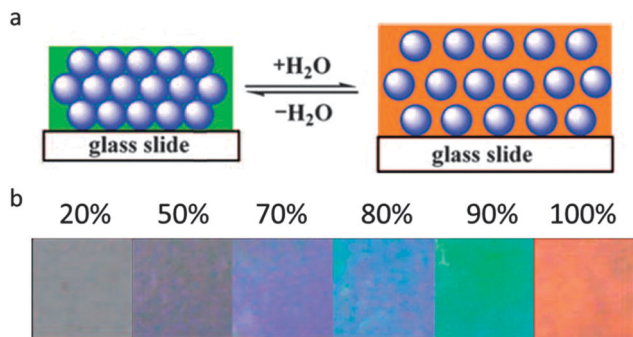


Fig. 10 (a) Schematic representation of a water-responsive colloid-based sensor. (b) Reversible changes of the colour of a photonic crystal hydrogel as a response to changes in the relative humidity. Photographs of the as-prepared photonic crystal hydrogel corresponding to a relative humidity of 20%, 50%, 70%, 80%, 90% and 100%, respectively. Adapted from ref. 74 with permission from The Royal Society of Chemistry.

pH-responsive photonic polymers

Photonic polymers can be used as optical pH sensors which react in a reversible way. Coatings in which the actual colour is pH-dependent have been reported. A polymerised crystalline colloidal array consisting of a poly(acrylamide) hydrogel with embedded polystyrene colloids and a colour shift of 300 nm has been reported.⁷⁶ The investigation of a similar system from which the colloidal particles had been removed resulted in an inverse-opal structure. This led to pH-sensitive materials in which the sensitivity depends on the amount of acrylic acid incorporated.⁷⁷ However, the response times of this system (~ 1200 seconds) need to be optimised for the development of real-time sensors. A different approach to preparing photonic pH sensors involves the use of carboxylic acid-based CLCs (Fig. 9).^{78,79} At a pH of 7, there is almost no response in the polymer film and a higher pH leads to the deprotonation of the carboxylic acid and therefore the formation of the carboxylate ions. The hygroscopic properties of this species lead to the absorption of water and a shift in the reflection band. The response becomes faster as the pH increases. Interestingly, the film can also be used to detect amino acids.^{66,79} Three thermoresponsive photonic polymers of which the intensity of the colour depends on the pH value are described in the next section.^{80–82}

Temperature-responsive photonic polymers

A well-studied stimulus for obtaining colour changes in polymeric coatings is temperature.⁸³ A Bragg-type reflector has been reported that covers the entire visible spectrum when the temperature is between 20 and 50 °C.⁸⁴ The coating was made by spin coating alternating layers of poly(methylstyrene-*co*-acrylamidobenzophenone) and poly(NIPAAM-*co*-acrylic acid-*co*-acrylamidobenzophenone). The system was crosslinked by UV exposure of the photosensitive benzophenone groups. When immersed in water, the volume of the layers containing NIPAAM changes in a temperature-dependent way while the other layers remain unaffected.

A mechanically embossed polymer-network CLC-based temperature sensor which returns non-reversibly to its original

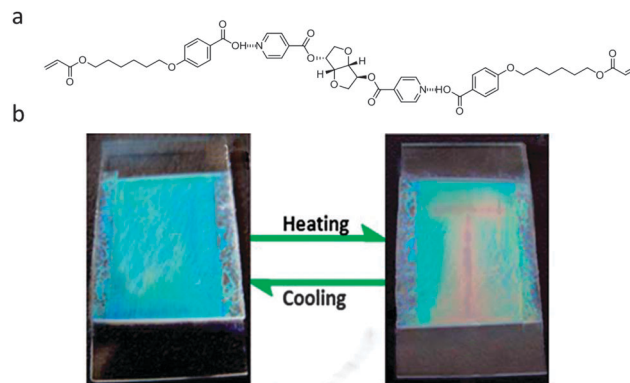


Fig. 11 (a) The hydrogen-bonded building block for a temperature-responsive coating and (b) photographs of the polymer stabilised cholesteric liquid crystal film after polymerisation and the letter “T” applied thermally to the film. Adapted from ref. 86 (Fig. 11b) with permission from The Royal Society of Chemistry.

state when heated above the glass transition temperature can be employed as a single use time-temperature integrator.⁸⁵ Self-assembled hydrogen-bonded CLC polymers result in coatings which respond to temperature changes⁸⁶ and can be used as thermally addressable reflective colour paper. An image (the letter “T”) can be written clearly using a hot pen (Fig. 11). The local increase in temperature leads to the disruption of the hydrogen bonds. After three hours, the image fades away as a result restoration of the H-bond interactions.

In addition to photonic coatings which respond solely to temperature, materials have been prepared with dual responses. The hydrogen-bonded system described above has been further improved to respond to pH as well.⁸² In this case, increasing pH leads to the formation of carboxylate groups and the subsequent swelling of the CLC network. When a proper polymer matrix is selected, more materials which are both temperature- and pH-responsive have been prepared.^{80,81,87} An inverse-opal gel consisting of 2-hydroxyethyl methacrylate, acrylic acid and

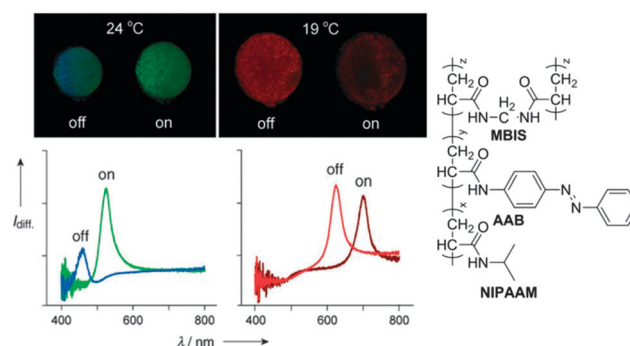


Fig. 12 Multicolour photochromic behaviour of a porous poly(NIPAAM-*co*-4-acryloylaminoazobenzene) gel in water at 19, 21, and 24 °C before UV irradiation and after the equilibrium degree of swelling had been reached in response to the UV irradiation (366 nm, 8.0 mW cm⁻²). The chemical structure of the material is depicted on the left (the ratio of monomers in the feed is $x : y : z = 95 : 3 : 2$). Adapted from ref. 88. Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

ethylene glycol dimethacrylate, and filled with thermosensitive gel particles, results in materials of this kind.⁸¹ The position of the reflection band of these coatings can be regulated thermally, whilst intensity depends on the pH of the surroundings. A similar copolymer network of NIPAAM, acrylic acid and a crosslinker has been developed.⁸⁰ A porous inverse-opal structure leads to comparable results. Another porous gel with azobenzene moieties incorporated in the polymer backbone with thermochromic properties has also been fabricated.⁸⁸ The material reflects light in the entire visible spectrum in a temperature-dependent way. Furthermore, due to the presence of the azobenzene derivatives, UV exposure leads to changes in the reflected colour when the temperature remains constant (Fig. 12).

Conclusions and perspectives

This feature article shows a diverse set of stimuli responsive, photonic, polymer coatings. The basic principle in all these coatings is the alternation of the volume or shape of the coating. Photoresponsive polymer coatings are mainly used to induce changes in the surface topography or roughness. Small structures can affect the wettability of a surface. Light-induced changes in these features lead to tremendous changes in wettability. The main purpose of responsive photonic materials is the development of optical sensors, based on Bragg reflectors, which can be analysed by the naked eye without any additional equipment.

Interestingly, both the photoresponsive coatings as well as the materials with an optical response usually consist of similar polymers, like liquid crystalline or hydrogel networks. These materials have the ability to translate small molecular changes in the polymer backbone into large deformations of the macroscopic polymer material. Particularly in hydrogels the properties of these types of materials can be easily altered as a result of subtle changes in the molecular composition. The response of hydrogels towards numerous kinds of stimuli leads to a change in the hydrophilicity of the material, *i.e.* the coating swells or shrinks. Due to the secondary structure of the hydrogels (like 3D colloidal or inverse opal structures), this volumetric change is transformed to reflection of a different wavelength. Similarly, CLC coatings with hydrogel-like properties are being used for sensing applications. The main advantage of the use of hydrogels is the large response which can be achieved towards different kinds of stimuli. However, hydrogels need to be operated in solution and therefore the coatings can be fragile.⁸⁹ Due to the high swelling in thick materials, hydrogel coatings tend to crease when being swelled. Furthermore, most of these materials are relatively soft, making them sensitive for various kinds of external influences. There is an increasing development in functional coatings based on more robust systems.⁹⁰ One method of reinforcing hydrogels is to use double networks or incorporate an ionic liquid, leading to an ionogel, which gives the hydrogel more toughness.³⁴ Furthermore, by using pre-structured surfaces, the amount of hydrogel material can be decreased.

Overall, the materials used for the development of photonic responsive coatings are rather limited and are still far from

being usable in daily life situations. There is a need to extend the toolbox of available molecules and polymers in order to produce photonic organic coatings with new and/or enhanced properties. Combining different triggers could also be interesting in this respect. For instance, materials which are both chemical as well as photo-responsive might be interesting for reusable sensors which can be cleaned by light. In case of optical sensors, often the selectivity, sensitivity, and signal changes are not optimal. Most sensors suffer from cross-selectivity. In this respect molecular imprinting could be appealing. Other important issues are the dimensions and structure of the responsive topographies. So far systematic studies that show the relation between dimension size and surface properties have not been reported. In addition, light responsive hierarchical double micro-nanostructured coatings have not been developed which could be interesting in the field of superhydrophobic and self-cleaning materials.

This feature article, however, shows that stimuli-responsive photonic coatings have many very appealing properties and have great promise in a variety of fields including optical sensors and responsive topographies with changeable functional properties.

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