Dual light and temperature responsive cotton fabric functionalized with a surface-grafted spiropyran-NIPAAm-hydrogel

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Highlighting work from the Eindhoven University of Technology.

Dual light and temperature responsive cotton fabric functionalized with a surface-grafted spiropyran–NIPAAm-hydrogel

A soaked cotton cloth can be manually wrung out to release water. This dual responsive hydrogel-coated cotton, which absorbs humidity from air, releases the absorbed water in response to a “molecular twist” triggered by sunlight and temperature. A PNIPAAm-based hydrogel covering the cotton fibers absorbs water from humid environments below LCST in the dark. A protonated merocyanine copolymerized with the PNIPAAm hydrogel can be photo-isomerized by light to the less polar spiropyran form, releasing the absorbed water with concomitant shrinkage of the fibers. The water can also be released by overcoming the hydrogel LCST in the dark.

Artwork designed by J. N. Murphy and ICMS Animation Studio.

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Dual light and temperature responsive cotton fabric functionalized with a surface-grafted spiropyran–NIPAAm-hydrogel†

J. ter Schiphorst,^a M. van den Broek,^{ab} T. de Koning,^{ab} J. N. Murphy,^a
A. P. H. J. Schenning^{*ac} and A. C. C. Esteves^{*bc}

A dual-responsive cotton fabric functionalized with a spiropyran–NIPAAm hydrogel, capable of dimensional changes upon irradiation with visible light or upon a temperature stimulus is reported. These volume changes are due to absorption and release of water, from and into the air, by increasing temperature above the LCST in the dark, and/or by irradiation with sunlight or white light from artificial sources. The material was obtained *via* grafting photo- and temperature-responsive monomers directly from the cotton fibers, using a facile controlled polymerization method, ARGET ATRP.

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Introduction

Smart polymeric materials that change their functional properties in response to changes in environmental variables, such as temperature,¹ humidity,² light,^{3,4} and pH,⁵ are currently the subject of widespread interest. Feedback from responsive polymers can take the form of changes in physical characteristics such as shape,⁶ reflectivity, colour,⁷ or porosity⁸ and are of great interest in the field of sustainable energy,⁹ water management,^{6,10} and personal comfort.¹¹ In particular, light as a stimulus is appealing, as light is easily accessible and non-invasive, *i.e.*, it does not require direct contact resulting in minimal impact on both material and surroundings.¹² Biologically-derived materials are interesting as substrates for these polymers, as they enable production from sustainable sources.^{9,13,14} When light triggering can be combined with bio-based fibers, responsive advanced materials become available that can, as an example, be applied in the textile industry.^{1,13,15,16} However, such materials have been scarcely explored to date. Only a few papers have reported light-responsive, cotton-based materials,^{17–21} none of which present reversible shape changes

based on interaction with humid air or water uptake and release, as we report here.

Recently, we developed a cotton fabric functionalized with a *N*-isopropylacrylamide (NIPAAm) hydrogel that was able to absorb a large amount of water from humid air, which could be subsequently released with a temperature trigger above the lower critical solution temperature (LCST) of the polymer.² This behaviour was repeatable for several cycles and was attributed to a combined effect of the intrinsic phase transition of PNIPAAm around the LCST and the change between extreme superhydrophilic/superhydrophobic morphologies of the hydrogel layer directly grafted on the cotton fibers. We have also fabricated light-responsive hydrogels using spiropyran-based derivatives.⁶ When copolymerized with a spiropyran–NIPAAm hydrogel, acrylic acid serves as an internal proton donor²² for the spiropyran isomerization to hydrophilic merocyanine-H⁺ (McH⁺), resulting in water uptake. The hydrophobic spiropyran (Sp) isomer can be reversibly formed upon illumination with white light, resulting in release of water.^{3,23}

In this work, we report a cotton-fabric functionalised with a dual-responsive hydrogel that changes thickness by absorbing and releasing water from humid air (Scheme 1) in the presence of a light or temperature stimulus. This dimensional change is reversible and repeatable and can be triggered by both stimuli.

To generate the functional textile, surface initiated activators regenerated by electron transfer atom transfer radical polymerisation (SI-ARGET-ATRP) was used. This method is particularly attractive for future up-scaling and industrial processing, since the synthetic conditions are quite accommodating, *i.e.*, it is tolerant to the presence of small amounts of oxygen; complex experimental apparatus are not required and minimal amounts of copper catalyst are used.^{24–26}

^aFunctional Organic Materials and Devices, Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, P.O. Box 513, 5600 MB Eindhoven, The Netherlands. E-mail: a.p.h.j.schenning@tue.nl

^bPhysical Chemistry, Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, P.O. Box 513, 5600 MB Eindhoven, The Netherlands. E-mail: a.c.c.esteves@tue.nl

^cInstitute for Complex Molecular Systems (ICMS), Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

† Electronic supplementary information (ESI) available: Materials and methods, SEM micrographs, IR spectra. See DOI: 10.1039/c6ta00161k

Scheme 1 Schematic representation of the polymer-grafted cotton fibers. A random distribution of the monomers in the polymer, with monomers incorporated in proportion of the feed ($x = 95$, $y = 5$, $z = 1$) is expected. The MCH^+ chromophore depicted in orange (left) results from the abstraction of a proton from the copolymerized acrylic acid units, isomerizing to a hydrophilic species, which triggers the uptake of water by the hydrogel. Subsequent illumination with white light isomerizes the chromophore back to the hydrophobic state (right), expelling the absorbed water.

Methods and materials

The cotton fabric obtained from Textile Innovators Division of SDL ATLAS was functionalized with an ATRP bromide initiator as previously reported.² The spiropyran based molecule was synthesized according to the procedure reported previously.²⁷ *N*-Isopropylacrylamide (NIPAAm, Aldrich 97%) was recrystallized in *n*-heptane and dried under vacuum at 40 °C for 24 hours. α -Bromoisobutyrylbromide (BiB, Aldrich 99%), triethylamine (TEA, Sigma Aldrich 99.5%), copper(II)bromide (CuBr_2 , Aldrich 99%), sodium acrylate (NaAc, Acros 97%), ascorbic acid (Aldrich), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), 4-(dimethylamino)-pyridine (DMAP, Aldrich, 99%), methanol (Biosolve) and dichloromethane (Biosolve) were used without further purification. Tetrahydrofuran was dried using a MB-SPS-800 drying system.

Typically, 30 mg of the initiator functionalised cotton fibers, 1 mL of copper-complex solution ($10.5 \mu\text{L mL}^{-1}$ PMDETA, 5.70 mg mL^{-1} copper(II)bromide (CuBr_2) solution in water), *N*-isopropylacrylamide (NIPAAm, 1.07 g, 9.50 mmol) and NaAc (47.5 mg, 0.50 mmol) were added to a round bottom flask. The flask was sealed with a rubber stopper and 8 mL distilled water was added. The spiropyran acrylate (SpA) derivative (44.5 mg, 0.10 mmol) was dissolved in 10 mL methanol and added to the mixture, which was then flushed with nitrogen for several hours. Ascorbic acid (44 mg, 0.25 mmol) was dissolved in 0.5 mL distilled water and added to 0.5 mL of a 0.1 M NaOH aqueous solution. The mixture was bubbled with argon for several hours.

To start the reaction, the ascorbic acid aqueous solution was added to the round bottom flask containing the mixture of all

the other reagents *via* a nitrogen purged syringe, through the rubber seal. The reaction took place at 0 °C for the first 2 hours and then for 24 hours at room temperature, after which the reaction was stopped by opening the round flask and exposing the mixture to air.

The cotton piece was removed from the flask and rinsed with methanol, ethanol, and water consecutively, for three times. Next it was Soxhlet extracted three times with 50 mL warm methanol for 1 hour. Subsequently, the material was dried in vacuum at 40 °C overnight.

For the reference experiments, where either sodium acrylate or spiropyran were absent in the copolymers, procedures similar to the ones described above were used. The amount relative to the monomers absent was replaced by similar molar additions of NIPAAm. Furthermore, the reaction with NIPAAm only and NIPAAm–NaAc only, were carried out with $2.1 \mu\text{L}$ PMDETA, 1.14 mg CuBr_2 and 8.8 mg ascorbic acid.

The full description of the equipments and procedures used for the characterization of the materials is available in the ESI.†

Results and discussion

Materials preparation

The fibers of a woven piece of cotton fabric were first functionalised with an ATRP initiator, by reacting the cellulose-hydroxyl functionalities with α -bromoisobutyrylbromide (BiB) (Scheme 2), according to procedures previously reported.² The presence of the initiator on the fiber surface was confirmed by X-ray photoelectron spectroscopy (XPS) with a characteristic signal of the bromine at 184 eV and 71 eV (Fig. SI-14†).

Subsequently, to introduce the light-responsive properties, NIPAAm, acrylic acid (in the sodium acrylate form) and an alkyl acrylate functionalised spiropyran monomers, were grafted from the cotton fibers by ARGET-ATRP (Scheme 2, (1) to (3)).

Scheme 2 Illustration of the functionalization of the cotton fiber. In the first step, the hydroxyl groups on the fibers are functionalized with an ATRP initiator. In the second step, (co) polymers are grafted from the surface of the cotton fiber using ARGET-ATRP, and the monomers (1) to (3).

The BiB-functionalised cotton was cut in small pieces of typically 30 mg and immersed in a 1 : 1 methanol : water mixture (20 mL), containing NIPAAm [N], sodium acrylate [P], spiropyran acrylate [S], copper bromide [Cu], ligand (PMDETA) [L] and ascorbic acid (reducing agent) [R] in a ratio of [N] : [P] : [S] : [Cu] : [L] : [R] = 95 : 5 : 1 : 0.25 : 0.5 : 2.5. The polymerisation under these conditions is particularly challenging, as deactivation of the copper catalyst might take place by the acrylic acid and merocyanine.²⁸ Therefore the reaction was carried out at pH = 9 and the sodium salt of the acrylic acid monomer was used.²⁹ A relatively high content of methanol was necessary to dissolve the spiropyran derivative. The total monomer concentration for all experiments was 0.5 mol L⁻¹. Furthermore for the ARGET ATRP, we used relatively higher concentrations of the copper catalyst and ascorbic acid, as compared to typical polymerizations by this technique,²⁸ to obtain higher grafting yields.

Materials analysis

Following the polymerisation, carried out at room temperature for 24 hours, the material was washed with warm methanol and water to extract non-reacted monomers and/or non-grafted polymers (see Materials section for details). Upon drying, the material became stiffer and faint yellow in colour. Gravimetric analysis revealed that the overall weight of the dried material increased considerably, up to 123% increase compared to the unmodified fabric (Table SI-1†), indicating the successful grafting of the copolymer and a dense coverage of the fibers surface, as compared to previous reports on cotton, modified by ARGET ATRP.²⁶

Scanning electron microscopy (SEM) analysis of the fibers extracted from the functionalized cotton fabric confirmed the large and near-complete coverage of the fibers with a polymer layer, showing a rough surface with small aggregates of the polymer (Fig. 1a–d and SI-1†). When compared with the bare cotton fibers, the surface was irregular and an increase in the diameter of roughly 7 μm was found. This is in agreement with the weight increase† and the morphology of the polymer layer is similar to what was previously reported for PNIPAAm-fibers functionalized by direct SI-ATRP.² The fibers were further characterized by infrared spectroscopy (Fig. 1e and SI-5† for overall spectra). The vibration peaks around 1733 cm⁻¹ and 1486 cm⁻¹, indicate the presence of the spiropyran moiety, while the peaks at 1639 cm⁻¹ and 1542 cm⁻¹, correspond to PNIPAAm, and the peak at 1386 corresponds to acrylic acid.⁵

When the hydrogel functionalized cotton fabric was immersed in water, it slowly turns yellow/orange, clearly revealing the presence of the hydrophilic McH⁺ isomer.⁶ It should be noted that a grafted cotton reference sample, lacking the acrylic acid moiety, exhibits barely any colour change.

Differential scanning calorimetry (DSC) confirms the presence of an LCST (~34 °C) (Fig. SI-3†), similar to PNIPAAm,

Fig. 1 SEM images of a cotton fiber with surface attached initiator before (a and c) and after ARGET-ATRP (b and d) of NIPAAm, sodium acrylate and spiropyran acrylate. ATR-IR spectra (e) of the cotton fibers without (blue) and with (black) hydrogel functionalisation. See also Fig. SI-6.†

although it widens and is not as clear as in the case of cotton fibers functionalized with PNIPAAm only.^{1,30–32} These results confirm the successful grafting of the acrylic acid, spiropyran and PNIPAAm monomers from the cotton fibers surface.

The monomer composition of the hydrogel polymer was, however, not possible to quantify in view of the difficulty to ungraft the polymers from the surface without decomposing or changing the properties of the initial materials.^{2,33} Furthermore, the low feed concentrations of both spiropyran acrylate and acrylic acid make analysis of the polymers by routine polymer characterization techniques very challenging. Nevertheless, based on earlier results, we expect that a random copolymer is formed.²⁷

In order to investigate the light responsive properties, the functionalized cotton fabric was immersed in water, upon which it turns yellow/orange, as it isomerises to the McH⁺ form. Further on, it is remarkable that within 1 minute of exposure to bright sunlight this material completely loses the yellow colour (Fig. 2 and SI-2†).

In a similar way, the yellow/orange-coloured cotton (Fig. 3a) was illuminated with a white lamp inside the laboratory, at 20 °C for 5 minutes. During exposure, the material turns completely white, indicating that the McH⁺ isomerises to the colourless spiropyran derivative (Fig. 3b).⁶ The material subsequently recovers its original yellow/orange colour when placed

† A factor of 2.2 to 3 was found assuming that the density of cotton is identical to that of hydrogel, which most likely is an overestimation, and that all fibers are coated similarly compared to the measured selection.

Fig. 2 The functionalised cotton in the laboratory (under fluorescent tube light) showing the yellow/orange colour (a) corresponding to protonated merocyanine formed after immersion in water. The cotton was placed in sunlight (b) (behind a glass window) and within 60 seconds the material completely lost its colour. See also Fig. SI-2.†

in the dark, as can be seen in Fig. 3c and d, where photographs were taken at 5 and 30 minutes after illumination, respectively.

After drying, the functionalized cotton fabric was placed in a highly humid environment ($\sim 97\%$ RH) and kept in the dark for several days at 20°C . The material weight was measured gravimetrically revealing an increase of approximately 50%, which indicates the ability to absorb a significant amount of water from a highly humid environment, with no direct contact

Fig. 3 Colour photographs of the functionalised cotton immersed in water: (a) before and (b) directly after exposure; (c) 5 minutes recovery and (d) 30 minutes recovery, after white light illumination. Optical micrographs of representative cotton fibers: (e) before and (f) after white light illumination. The scale bar represents $50\ \mu\text{m}$. Note: the green background is caused by a filter used in order to prevent isomerisation of the chromophore by the microscope white lamp. A series of these images was used to estimate average diameters, shown in the graph (g). The plot shows the fiber's average diameter in response to cycles of illumination (open squares), followed by recovery in the dark (closed circles).

with liquid water. Since the material is woven (*i.e.*, a piece of fabric is used) and contains only a surface-layer of hydrogel, no effect on the overall size of the cotton fabric was visually detected (with the naked eye) (Fig. 3a–d).

Light responsive behaviour

To analyse the volume changes in detail, cotton fibers were pulled at random from the woven material and placed in a high humidity environment ($\sim 97\%$ RH inside a chamber of a Linkam Cell) at 20°C , a temperature below the LCST of PNI-PAAm. For each measurement series, a common region of the fiber was isolated to ensure consistency, with measurements referenced to identical points along the length of the fiber. Analysis of images was carried out by aligning and thresholding each image, from which the centre line was determined by a force-directed fitting method. Edge-to-edge distances were determined at points spaced equidistantly along the centre line, along lines orthogonal to the centre line (Fig. SI-9†).§

In the absence of light, the yellow coloured fibers were swollen and had an average diameter of $\sim 40\ \mu\text{m}$ (Fig. 3e). Upon exposure to white light for 5 minutes, the fibers average diameter shrunk to $\sim 33\ \mu\text{m}$ (Fig. 3f). After switching off the light, the fibers re-swell to their original diameter. It should be noted that the large standard deviations result from the highly variable fiber widths; the standard deviation of the swelling/shrinking ratios, when comparing identical points along the length of the fiber, show no overlap (Fig. SI-8†). Distributions of both width and swelling/shrinking ratios, for all fibers (Fig. SI-10†), show that the width changes occur uniformly along the fiber, roughly in proportion to the diameter. Additionally, we note that the hydrogel is capable of bending the fiber, as revealed by detailed image analysis. At a position where the material bulges on one side, we observe a pivot point, likely resulting from imbalanced forces, where the fiber reversibly bends by $\sim 10^\circ$ (Fig. SI-11 and SI-12†).

Our results reveal that the fibres are capable of increasing $\sim 25\%$ in diameter, indicating a significant uptake of water from the air in the measured time frame of 5 minutes of recovery (Fig. 3g). These procedures were repeated for at least 5 consecutive cycles, resulting in a repeatable shrinking of the fibers diameter with irradiation, and consistent spontaneous swelling and recovery to the original diameter occurred each time the light was switched off (Fig. 3g).

These results clearly show that the cotton fibers are capable of absorbing and releasing a significant percentage of water in response to light, due to Sp-McH^+ isomerisation. It should also be noted that the reference cotton fibers functionalized without

§ For the image analysis procedure (Fig. SI-13†) Otsu Auto Local Threshold** in ImageJ^{††} was used to create binary images of the fibers. The fiber centre was found by taking the maximum along the x-axis of the binary image's distance map, then refining with force-directed graphing with edges exerting a force, $\propto d^{-2}$.⁴⁰ Widths are measured for fibers with length $>100\ \mu\text{m}$ (Table SI-2†), with points equidistantly spaced along the centre and the edges. The edge-to-edge distance was taken perpendicular to the centre line tangent.⁴¹ Fiber diameters tend to vary from sample to sample as can be seen in the SEM images, hence, identical sections of fibers were analysed for each measurement, with points indexed along the fiber length.

the acrylic acid moiety, *i.e.*, which cannot form the hydrophilic McH^+ derivative efficiently, only show very small volume changes (see Fig. SI-4†).

Temperature responsive behaviour

The temperature responsiveness of the functionalized hydrogel-cotton was also investigated (Fig. 4). By increasing the temperature above the LCST of PNIPAAm (up to 50 °C) in the absence of white light, the fiber diameter decreases, transitioning from an average of $\sim 42 \mu\text{m}$ at 15 °C to $\sim 31 \mu\text{m}$ at 50 °C, indicating the release of water (Fig. 4). This process was repeated for 5 cycles of 15–50 °C, illustrating the reversible

Fig. 4 Temperature-responsive behaviour of the functionalized cotton fiber through 5 consecutive temperature fluctuation cycles of 15 °C (closed circles) and 50 °C (open squares), in the dark (absence of white light, black curve) and under continuous white light irradiation (red curve).

Scheme 3 Schematic of the cotton material (gray) in response to the combination of light (left versus right) and temperature (top versus bottom) stimuli, depicting the dual responsiveness of the material. The extended brushes illustrate the material in the swollen state where the water molecules are between the brushes. Upon applying a stimulus, the material shrinks (contracted brushes) and the water is expelled.

water adsorption and release behaviour of the hydrogel functionalised fibers (Fig. 4).

Remarkably the temperature-induced response is similar to the light-induced switching behaviour, suggesting comparable changes of the NIPAAm hydrogel induced by both temperature and light. However, when the functionalized hydrogel-cotton is constantly illuminated with white light and similar temperature cycles are performed, the average diameter of the fiber is constant and consistent with the diameter of the material above PNIPAAm LCST (Fig. 4). This indicates that in the presence of light, the sole presence of the spiropyran in the closed hydrophobic form, seems to inhibit or drastically hinder the temperature-triggered transition of the PNIPAAm molecules towards a water-absorbing state.

Basically, for water uptake, this material effectively functions as an AND gate (Scheme 3 and Fig. SI-15†), in which humidity absorption only occurs when dark and low temperature (below LCST) conditions are combined. On the other hand, for water release, two situations are possible, either low temperature (below LCST) and irradiating with light, or remaining in the dark but increasing the temperature (above LCST).

Conclusions

A novel hydrogel functionalized cotton fabric can be dually triggered, by a light or temperature stimulus, to reversibly and repeatably change in volume and shape by absorbing and/or releasing water from humid environments. This was achieved with a facile and versatile surface-initiated controlled polymerization method, ARGET-ATRP,²⁴ used to graft monomers of NIPAAm, acrylic acid and a spiropyran-derivative directly from the surface of the cotton fibers.

This polymerization method may allow the functionalization of cotton or other natural and synthetic fibers with several other stimuli-responsive monomers,³⁴ so long as they are compatible with the experimental conditions, *e.g.*, being non-reactive towards the copper (or other metal) catalysts used. The reaction conditions are rather simple and easy to scale-up, making industrial application feasible.^{25,35,36}

This volume/shape changing hydrogel-cotton shows considerable potential for water extraction from air, which could have a high impact in areas where potable water sources are scarce,³⁷ *e.g.*, coastal deserts and foggy mountains. These responsive fibers may also find opportunities in other technological applications, such as breathable textiles and agricultural purposes. Furthermore, this dual-triggered material, actuated by temperature and light, has the particular advantage of functioning with AND-gate type logic, allowing orthogonal attenuation of the responsiveness. Finally, the faint but observable colour change during illumination, whether by fluorescent light or sunlight, provides a simple visual indicator of the optically-induced humidity absorption/release process.

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