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Dual temperature and light triggered water collection and release by cotton fibers

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Dual temperature and light triggered water collection and release by cotton fibers

Tom de Koning

Presentation letter

Deserts are known for their warm and dry landscape where fresh drinking water is not easily accessible. However wildlife has adapted; for instance the Namib Desert beetle can survive in the Namib Desert by collecting fog as drinking water. A material that collects this water out of the humid fogs would be highly desirable for many advanced applications or even drinking water.

Previously in Laboratory of Materials and Interface Chemistry (SMG), a temperature responsive hydrogel material, Poly(N-isopropylacrylamide) (PNIPAAm), was grafted from a cotton fiber by Activator Regenerated by Electron Transfer (ARGET) Atom Transfer Radical Polymerization (ATRP) by Zhang.[1] ARGET ATRP was preferred over regular ATRP, as it allowed easier practical conditions. PNIPAAm is a thermoresponsive polymer, which has a Lower Critical Solution Temperature (LCST) that can be used to collect water from the air. When it is below 32°C the PNIPAAm is hydrophilic and will absorb water. Above 32°C it is hydrophobic and will release the water, i.e. during the cold night and in the morning the material will collect the fog and during the warm day the water will be released.

The LCST can be controlled by adding more hydrophilic or hydrophobic groups into the polymer. When this is combined with a material which can switch between a hydrophilic and a hydrophobic state, the water collection can also be controlled. Functional Organic Materials and Devices (SFD) research group has been investigating light-responsive spiropyrans (SP). These molecules isomerize upon the irradiation of light between their hydrophilic and hydrophobic state due to ring opening, incorporating this in the polymer allows switching with light.

In this research a material that is both temperature and light responsive is investigated. Polymers of NIPAAm and a spiropyran were made. Polymers were made in solution as reference and grafted from a cotton fiber by ARGET ATRP to make a dual triggered light and temperature responsive water collection and release system. For the polymerization, free radical polymerization (FRP) was first tested. The results of this method proved that polymers of NIPAAm and spiropyran were not grafted from the surface of the cotton fiber without any further modifications of the cotton fiber.

Subsequently ARGET ATRP was used to start the polymerization from the cotton fiber, which was functionalized with an ATRP initiator to start the polymerization from the surface, and provide covalent bonds with the polymer.

ARGET ATRP of NIPAAm from the cotton fiber what was done before in a solvent with a MeOH/H_2O ratio of 1:1. Everything except the spiropyran can be dissolved in this solvent. Therefore a different ratio was used with a higher MeOH content. However with more MeOH the results of the ARGET ATRP were not as good with the MeOH/H_2O of 1:1. A solvent with MeOH/H_2O of 3:1 was used with half the spiropyran concentration.

The interaction of the water with the sample and the water uptake is tested with DSC, water uptake experiments, contact angle (CA) measurements and an optical microscope (OM) mounted with a Linkham cell. The most important samples which were tested are a sample with PNIPAAm with a weight increase of 158% and a sample with NIPAAm-Spiropyran-Acrylic Acid (NIPAAm-SP-AA) with a weight

increase of 60%. The DSC and CA results of the cotton fiber grafted with PNIPAAm showed similar results as Zhang[1] obtained. With DSC the LCST was found on at 32°C. With CA at 20°C the cotton absorbed the droplet completely. At 45°C and 65°C the cotton was first hydrophobic. After 30 second at 45°C the water was absorbed by the cotton. At 65°C the droplet stayed stable.

For the sample grafted with NIPAAm-Spiropyran-Acrylic Acid the LCST found with DSC was at 32°C. The CA result were the same as the sample with only PNIPAAm. Irradiation of light did not influence the CA which was expected.

The water uptake experiments show for NIPAAm and NIPAAm-SP-AA at 20°C a water uptake of 50% of its own weigt. This is lower as Yang[2] whom obtained 340% weight increase. The water uptake at 40°C is similar as Yang[2].

With the Linkham cell mounted on an OM the samples with NIPAAm and NIPAAm-SP-AA are tested. When started at 16°C the samples absorbed the condensed water and were swollen. The temperature was increased to see the deswelling of the sample with NIPAAm around 26°C. This is the same as the results of Zhang[1]. NIPAAm-SP-AA was also tested and showed a very small decrease in size. On these fiber less polymer was found so the decrease in size was smaller as for the sample with PNIPAAm.

Preface

This work represents the master graduation project of Tom de Koning, performed at the Eindhoven University of Technology (TU/e). The research is a collaboration between the two research groups Functional Organic Materials and Devices (SFD) and Laboratory of Materials and Interface Chemistry (SMG). It is performed under the supervision of Prof.dr. Albert Schenning (SFD), dr. Catarina Esteves (SMG) and Jeroen ter Schiphorst MSc (SFD).

In this report, the water uptake and release by a polymer grafted from cotton fiber, triggered by temperature and light is discussed. Grafting of PNIPAAm from cotton was previously published[1,2] as a temperature triggered water collection system. In this research, a spiropyran was incorporated in the PNIPAAm to make a material which is dually responsive to light and temperature.

The final presentation of this research will take place on the 08-05-2015, at 11:00, in room STO 0.88 at the TU/e.

Tom de Koning

May 1, 2015

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1   Introduction

Deserts are known for their harsh and warm climate and the resulting dry landscape. Therefore fresh drinking water is not easily accessible in poor desert-like areas. For many ecosystems the only accessibility of water is the high relative humidity during the morning, when dense fogs are formed. For instance, several plants and the Namib Desert beetle (Figure 1) rely on this fog to collect their drinking water.[3,4] A material that collects this water from the air during the night and releases this during the day would be highly desirable. An example of a machine capable of generating clean drinking water is the Water-Gen.[5] It condenses the water from the air by pumping it through the machine and cooling it. This machine can make 250 to 800 liter water per day depending on the temperature and humidity. However for the production of water electricity is needed, which may be not accessible in the desert.[5]
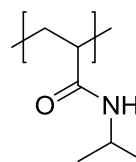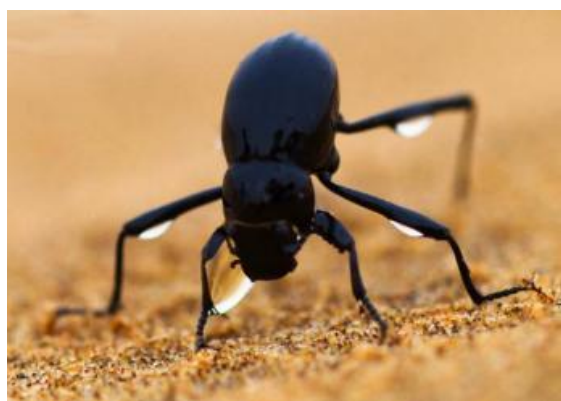
poly(N-isopropylacrylamide)

Figure 1 left) Namib desert beetle.[6] Right) molecular structure of poly(N-isopropylacrylamide)

Another example of a water collection and release system is the temperature triggered poly(N-isopropylacrylamide) (PNIPAAm)-cotton fibers from Yang et.al.[2,7] and Zhang.[1] When this polymer (Figure 1 right) is grafted from a cotton fiber, a sponge-like material is obtained, which is thermoresponsive and doesn't has the need of electricity to trigger the water collection or release. When the temperature is below the lower critical solution temperature (LCST), the water can be absorbed by the polymer. Above the LCST the polymer releases the previously absorbed water.[2,7] For PNIPAAm hydrogels this is around 32°C.[8–11] In the left part of Figure 2 a cotton fiber with PNIPAAm is schematically shown. The green part is below the LCST where the water is in between the PNIPAAm chains since the fiber is hydrophilic. In the red part of the figure the PNIPAAm repels the water because the cotton fiber became hydrophobic. The PNIPAAm was polymerized from the fibers by surface initiated Atom Transfer Radical Polymerization (ATRP) (further explained in 1.3.2) with a M_n of ≈ 30000 and polydispersity index (PDI) of 2,8. The cotton fibers which are made increased in weight by 460%. Water collect and release experiments showed that at 23°C a water-uptake of 340% of its own weight could be achieved. At 34°C it showed that the water-uptake was 24% of its own weight, making this material thermoresponsive. Zhang[1] also reported the water uptake and release of PNIPAAm-cotton fibers made by another ATRP method (ARGET). It was stable after several cycles in different humidities and different heating rates. This was investigated by measuring the thickness of the fibers in the swollen and shrunk state.
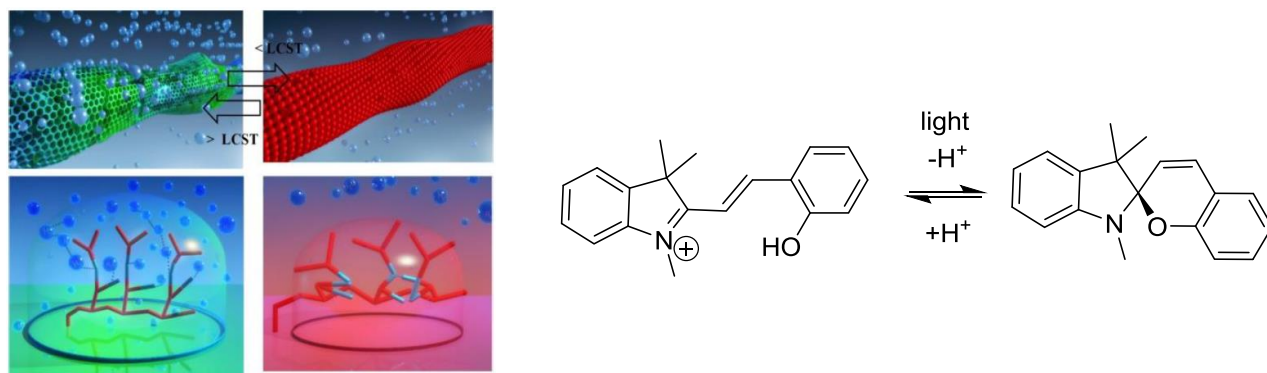
Another well-established hydrogel system is based on PNIPAAm-spiropyran material as reported by Ziółkowski et al.[12] and Stumpel et al.[13,14] The photochromic spiropyran (SP) can switch between a hydrophilic protonated merocyanine (MCH[+]) and a hydrophobic spiropyran state upon irradiation with light, resulting in a change in polarity.[15] This is shown in the right part in Figure 2. The polarity of the SP changes the hydrophilicity of the whole hydrogel. In the dark this hydrogel is in its swollen state, when irradiated with light it will shrink. Ziółkowski reported the self-protonation of PNIPAAm-spiropyran hydrogels.[12] In this system acrylic acid is copolymerized to protonate the merocyanine and form a more stable isomer. This is further explained in 1.2.

Water collection by cotton fiber can be achieved by grafting hydrogel based materials on the surface.[1,2,7,16] Cotton is a material found in nature and is commonly used in textile based materials.[17] The composition of cotton is based on 99% cellulose, which is composed of linear *D*-anhydroglucopyranose units (AGUs) that are linked by *β*-(1→4)-glycosidic bonds.[17,18] This is shown in Figure 3. An AGU has 3 alcohol groups that form inter and intra molecular hydrogen bonds. Because of these hydrogen bonds, cellulose has crystalline and amorphous domains, which makes it hardly soluble in common solvents.[17–19] The hydroxyl groups of the cellulose can be used for surface modifications.[17–21] When surface modification is used, a cotton fiber can get different functionalities e.g. better wettability, mechanical stability or adhesion.[2,22–24] Other research has been done in grafting stimuli responsive polymers that respond to temperature, light or pH.[2] When natural fibers are used in composite materials, a big concern is the water-uptake and release in different environments.[17,21] In the current research the water-uptake is desired and together with the high hydroxyl functionality the inexpensive cotton fiber can be transformed to a smart material.
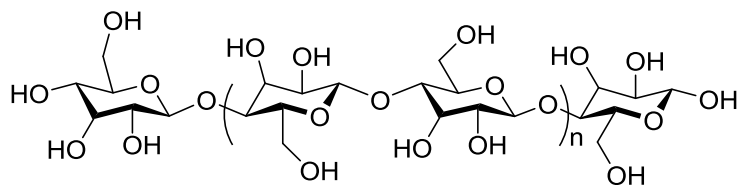

Figure 3 Molecular structure of Cellulose

1.1 Lower critical solution temperature (LCST) behavior

A water collection and release system based on cotton fibers coated with PNIPAAm uses the LCST to change the behavior of the system. The LCST is a phase behavior between two materials which is not comparable with the phase behavior of small molecules. The mixing small of molecules in solution is thermally induced, whereas polymer solutions can undergo thermally induced phase separation due to the LCST. The LCTS is a phase transition that changes the solubility of the polymer. This draws interest for smart polymers which can be used in for example sensors.[11,25] It is also believed that many functions of biopolymers are attributed to the phase transition at the LCST.[25,26]

To explain the LCST, PNIPAAm as polymer and water as solvent are used as example system. When the temperature is below the LCST, it is thermodynamically more favorable for the PNIPAAm to form hydrogen bonds with the water. When the temperature rises above the LCST, hydrogen bonds with the water are broken and inter- and intramolecular hydrogen bonds are formed within the polymer. Hydrogen bonding with water is translated to a hydrophilic polymer and inter- and intra-molecular hydrogen bonds translates to a hydrophobic polymer. This induces the phase separation of the PNIPAAm and for the PNIPAAm coated on the cotton fiber this translates to water collection and release.[2,9,27] Next to the LCST, it is also possible that molecules become insoluble at lower temperatures. This is called the upper critical solution temperature (UCST). In the left part of Figure 4 a temperature-composition phase diagram is shown of a weakly interacting polymer solution with a LCST and UCST. The axis of the graph show the temperature and the composition of the two components. PNIPAAm, used in this research only has a LCST. The LCST is the minima of the top curve and the UCST is the maxima of the bottom curve. In the spinodal area (dark grey) the polymer is not soluble and will precipitate. The binodal region (light grey) is a meta stable phase where the polymer will precipitate. Next to a phase diagram with a LCST, UCST or both such as in the left of Figure 4, it is possible for polymers to have variation with LCST or UCST as shown in the right of Figure 4. For example there are polymers with a LCST or UCST with multiple extrema, immiscibility loops and combinations of these. Examples of these possibilities are gives in the right parts of Figure 4.
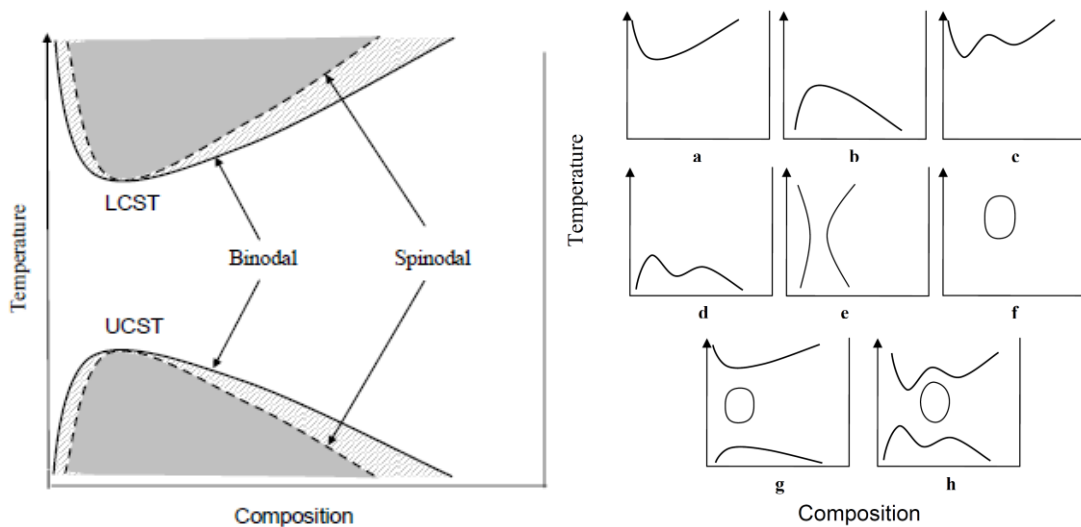
Figure 4 Left) Temperature-composition phase diagram of a weakly interaction polymer solution. The composition on the x-axis represents polymer:solution ratio. The LCST and UCST are respectively the extrema of the top curve and the bottom curve. At the top curve above and bottom curve beneath the binodal curve the polymer is not soluble and will precipitate. In the middle (white area) the polymer is soluble in the solvent. The grey area (binodal region) is a meta stable phase. In the dark region (spinodal region) the polymer is not soluble Right) Different possibilities for temperature-composition phase diagrams. a) LCTS, b) UCST, c)LCST with multiple extrema, d) UCST with multiple extrema, e) merged LCST and UCST, f) immiscibility loop, g) g, h) combinations of LCST, UCST and immiscibility loops[25]

The LCST depends on the polymer or the monomer compositions of the polymer what is used. In Figure 5 several structures of poly(N-substituted acrylamides) are shown which have a LCST between 25°C and 37°C.[25,26] These monomers have different hydrophilic and hydrophobic properties which influence the molecular interactions of the polymer. When hydrophilic molecules are copolymerized, the LCST rises, when hydrophobic molecules are copolymerized, the temperature drops.[8,10,13,25,26] Next to the composition, the LCST is also dependent on concentration, chain length and, for grafted polymers, the grafting density.[28] When molecules with switchable hydrophilic and hydrophobic properties, such as a spiropyran, are copolymerized in a polymer with a LCST, a material with switchable swelling and shrinking properties can be made. Next to spiropyran, acrylic acid is used in this research. Copolymerization of acrylic acid with NIPAAm has been reported by other researches,[8,10] which results in pH responsive swelling and a higher water uptake. It might also raise the LCST because of its hydrophilic properties.

Figure 5 chemical structure of poly(N-substituted acrylamide) with a LCST. a) poly(N-isopropylacrylamide) (PNIPAAm), b) poly(*N,N'*-diethylacrylamide) (PDEAAm, c) poly(2-carboxyisopropylacrylamide) (PCIPAAm), d) poly(*N*-(l)-(1-hydroxymethyl) propylmethacrylamide (P(l-HMPMAAm)), e) poly(*N*-acryloyl-*N'*-alkylpiperazine).[1,26]
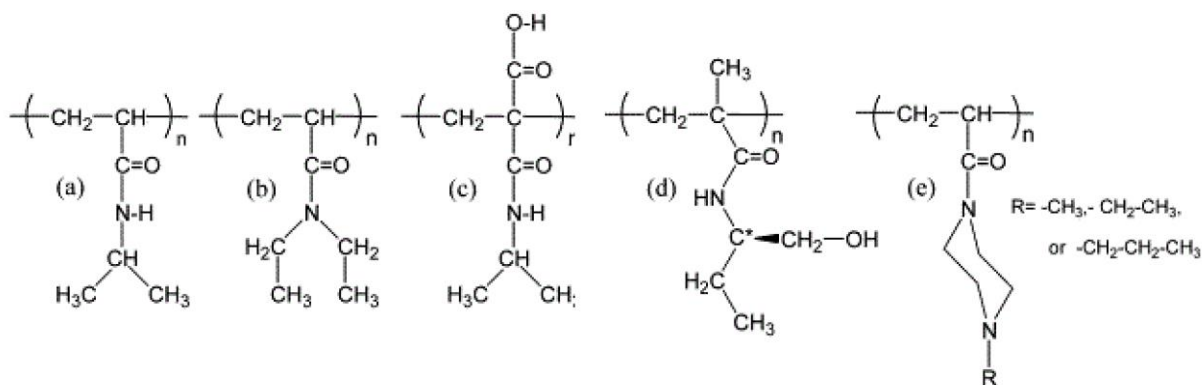
There are two different but related behaviors of the LCST. In a polymer solution with linear polymers and a high concentration, the LCST provides a phase separation on the macro scale (from a dissolved polymer in solution, to a precipitated polymer). In dilute systems, cross-linked and immobilized polymers which are constrained from phase transition, the LCST provides the swelling transition on the scale of the molecule or network.[9,25] This is schematically shown in Figure 6. This is also called the volume phase transition temperature (VPTT).[9,29,30] The water uptake of PNIPAAm grafted of the cotton is also related to the VPTT. The difference of the materials investigated here and the figure, is that the water is taken from the air and not from a solution.

a) **T < T**transition   b) **T > T**transition
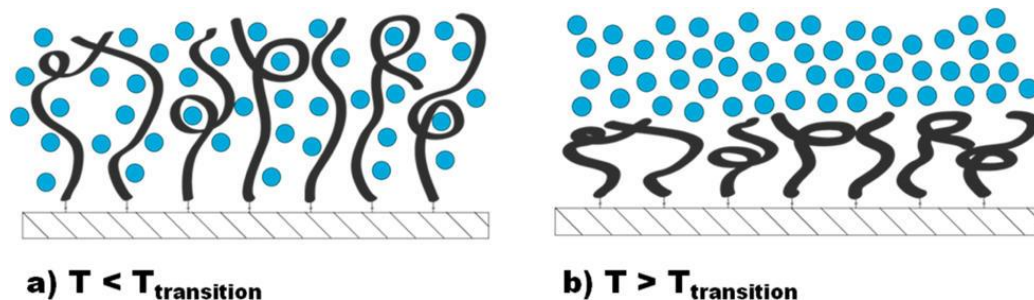
Figure 6 Schematic depiction of a swelled PNIPAAm polymer grafted of the substrate bellow the LCST (a) and of the collapsed polymer grafted of a substrate above the LCST (b)[9]

1.2 Spiropyran

To make the water collection and release light responsive, a spiropyran is used. In the past few years spiropyrans are increasingly used in dynamic materials. These molecules can undergo a reversible isomerization under influence of several stimuli. These stimuli are for example light[11,13–15,31–35], temperature[11,32,36], pH[11,15,32,36], metal ions[11,15,31,32,37] and mechanical stress.[15,31,38] The different isomers have different properties, such as structure[15,31,36], color[11,15,31,33,36], conductivity[15,31] and polarity.[13–15,31,33,34] The change in polarity is interesting for the water collection and release. In Figure 7 the spiropyran 6' hexa-acrylate (SP-A) that is used in this research and in the work of Stumpel[13,14] is shown. The molecule is buildup from an indoline and a chromene group that are connected perpendicular via a spiro junction. The molecule is copolymerized with NIPAAm through the hexa-acrylate on the 6' position on the ring.

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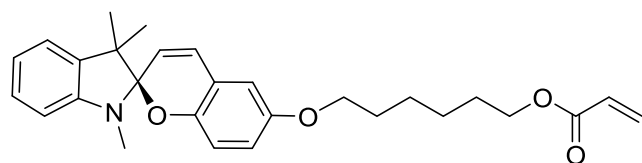
spiropyran 6' hexa-acrylate (SP-A)

Figure 7 Molecular structure of spiropyran 6' hexa-acrylate

1.2.1   Isomerization

The isomerization of SP is in most researches triggered by irradiation of light or protonation by an acid. In Figure 8 the SP (left) and the MCH[+] (bottom right) are shown. The isomerization from SP to MCH[+] and back is used in this research. The SP is hydrophobic and MCH[+] is, because of its charge, hydrophilic. In a dark and acid environment the MCH[+] will be present and will induce the water uptake of the polymer. When the polymer is irradiated with light, it will isomerize to the SP and induce the shrinking and thus water release of the system. Next to the MCH[+], also the merocyanine (MC) can be formed (top right Figure 8). This occurs when the SP is irradiated by UV light.

In this research an internal proton donor is used, reported earlier by Stumpel[13,14] and Ziółkowski.[12] This is done with acrylic acid which gave a local pH of 3. Because of this the use of an acidic solution, as described in other researches, to isomerize to the MCH[+] was not needed for the isomerization.[12–14,32] Next to that, the MCH[+] is more stable in the dark than the MC. To stabilize the MCH[+], a SP with the ether group on the 6' position is used. It is reported that an ether on the 6' position on the SP stabilizes the MCH[+] more than on other positions.[35] Other researchers report the use of a SP functionalized with a nitro compound at the 6' position.[15,31] The main difference between the nitro compound and the ether is the electron withdrawing and donating properties of the groups. The nitro compound is a deactivating group i.e. it withdraws the electron from the ring which makes it harder for the SP to isomerize to the MCH[+]. An ether acts as an activating group which donates electrons into the ring. Because of this the MCH[+] is easier formed and more stable.[35]
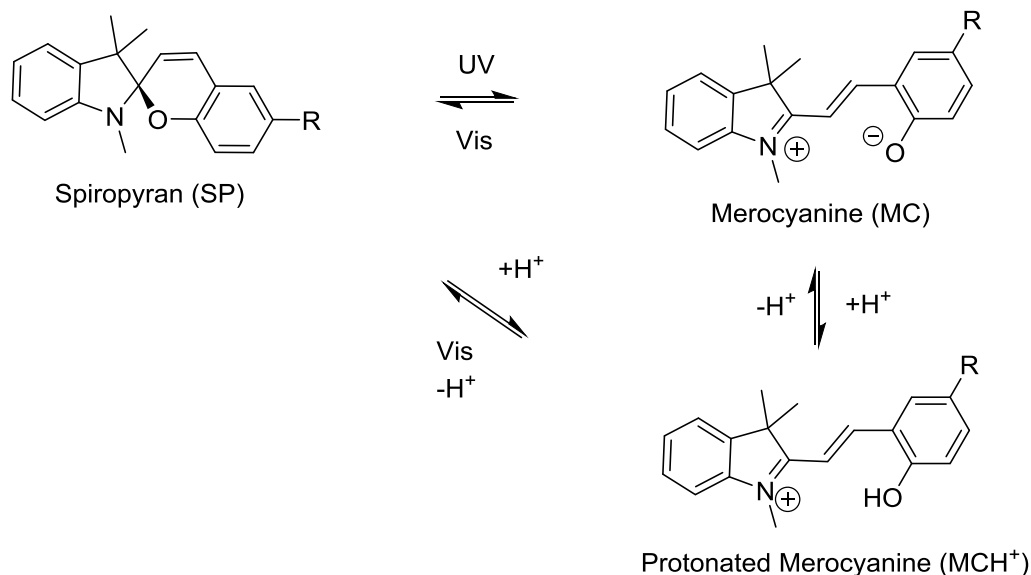
Figure 8 Isomerization of the spiropyran. SP can isomerize upon irradiation of UV light to the MC. When the MC is irradiated with visible light it goes back to the SP. When the SP or MC are exposed to an acid they isomerize to MCH⁺. The MCH⁺ can go back to the SP when it is irradiated with visible light but can also be deprotonated to form the MC.

1.2.1.1 *Optical properties*

The following examples for the absorption peaks are for a spiro with a nitro compound on the 6' position.[15] When the spiropyran is irradiated with visible light it will isomerize into its ring closed form. SP is colorless and absorbs UV light. This is typically at $\lambda \approx 280$ nm and at $\lambda \approx 335$ nm which is attributed respectively to the π-π bond in the indoline and the chromene part in the molecule. When the SP is irradiated with UV light, it undergoes isomerization to a ring opened MC. The MC absorbs mostly at 575 nm due to the π-conjugation which connects the indoline and chromene and gives the MC a blue color. When the MC gets protonated, the MCH⁺ forms. The MCH⁺ has a characteristic band at $\lambda \approx 420$ nm which gives the MCH⁺ a red color.

1.2.1.2 *Isomerization conditions*

There are different systems reported in literature where SP-A is used. For instance linear SP-A copolymerized with PNIPAAm in solution, PNIPAAm-SP grafted of a surface and PNIPAAm-SP hydrogels. Mostly the swelling and wettability are investigated, while the polymers were emerged in acidic solution and irradiated with blue light of a wavelength of 400-440nm. This showed a volume shrinkage upon the irradiation of light.[13,15,32,35,39] Wang et.al.[33] reported the switch of a PNIPAAm-SP system grafted from a silicon substrate. This system showed, upon irradiation of UV light (365 nm), a change in the contact angle (CA) of water from 43° to 139°. This change is from the isomerization of SP to MC. The CA changed back when the sample was exposed to visible light for 20 min. Stumpel[13,14] and Ziółkowski[40] reported the isomerization of SP to MCH⁺ in a neutral solution which is key for water absorption from air. This system release the water under irradiation of visible light.

1.2.2   Copolymerization of PNIPAAm and a spiropyran

The SP-A is covalently attached with the system by copolymerizing it with the NIPAAm and AA. This is important to induce the swelling and shrinking of the polymer by irradiation with light. Next to introducing these properties in the polymer, it will also make sure the SP does not leach out. When the SP is switched into the MCH$^+$, it will change its solvability, therefore non-covalent bond SP can phase separate which will be prevented when it's covalently bond. When the MCH$^+$ is formed there is also a chance that they will aggregate, which is also prevented when they are covalently bonded.[15] Next to these probably the most important benefit of the immobilization is the reduction of the photo degradation.[15] Although the photo isomerization of the SP is a reversible process, side reaction can occur that form molecules which don't have the same properties as the SP.[15]

1.3   Polymerization Techniques

1.3.1   Free radical polymerization (FRP)

Free radical polymerization (FRP) is a form of chain growth polymerization where long chains are obtained in three distinct steps: initiation, propagation and termination. The initiation start with the formation of a radical by the initiator which reacts with the first monomer. The propagation is the addition of more monomers to the chain until it meets another radical from a propagating chain or a chain stopper and it terminates.[41,42] FRP is the most used polymerization method used in the industry because it is one of the easiest methods to produce big volumes, which makes it economically feasible. A lot of different monomers and solvents can be used with no specific demand for high purity. A limitation of FRP is that it needs to be done in the absence of oxygen. When oxygen is present during the polymerization it will terminate the reaction by reacting with the radical. Other advantages of FRP is that it is possible to polymerize in bulk, solution, aqueous suspension emulsion, etc. At the start of the reaction immediately high molecular weight polymers are obtained. A drawback of free radical polymerization is the high concentration of radicals. Because of this, chain transfer and termination of the polymer chains are occurring often. These are undesirable events because they result in smaller polymer chains.

1.3.2   Atom-Transfer Radical-Polymerization (ATRP)

Atom-Transfer Radical-Polymerization (ATRP) is chain growth radical polymerization. It is a controlled polymerization technique, which makes use of the transfer of a halogen between an active and dormant chain (Figure 9).[43,44] In the active form the chain can propagate and in the dormant form the radical is dormant to be activated again. Termination and chain transfer are limited in ATRP but not totally prevented, therefore ATRP cannot be called a living polymerization, but it is a controlled radical polymerization technique.[45] The degree of polymerization (DP) depends on the consumed monomer, Δ[M], divided by consumed initiator, Δ[I]. By adjusting the monomer concentration and the initiator concentration the molecular weight can be controlled (i.e. DP is the amount of monomer per initiator).[44]

$$DP = \frac{\Delta[M]}{\Delta[I]} \tag{1}$$
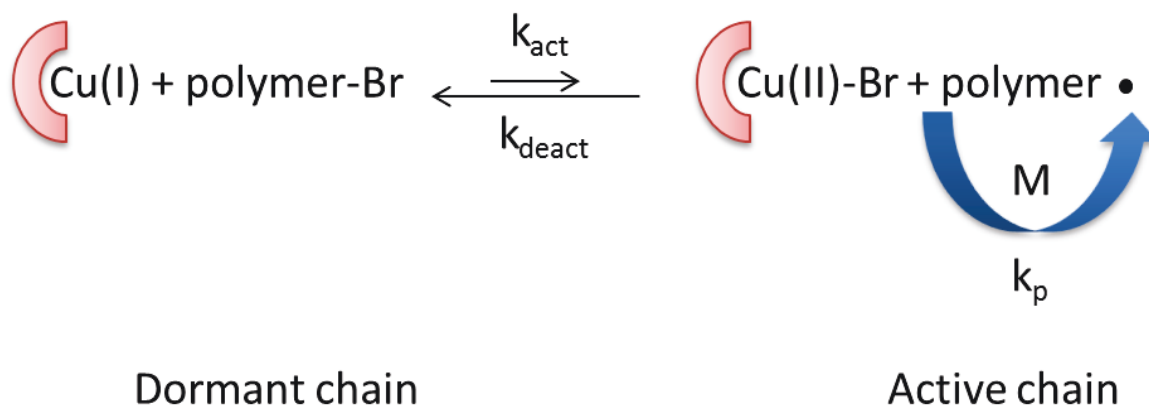
Figure 9 Mechanism of ATRP. On the left the copper(I), complex (half red ring) and dormant polymer chain are shown. The copper complex can get oxidized which forms a polymer with an active radical which can polymerize. The equilibrium is on the left side which prevents high radical concentration in the mixture.

The initiation of ATRP starts from an alkyl halide. When this alkyl halide is immobilized on a substrate a polymer can be grafted from it. The initiator can be covalently bound to a cotton fiber to start the polymerization from the surface. This is schematically shown in Figure 10.
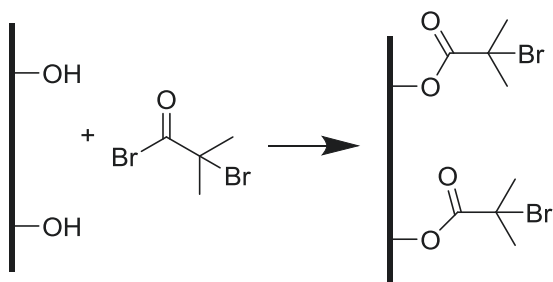
Figure 10 functionalization of the cotton fiber by an ATRP initiator (α-bromoisobutyryl bromide (BiB)). The dark line with OH groups represents the cotton. The BiB can react with the cotton to form a ester bond.

Several researchers used ATRP combination with a spiropyran functionalized acrylate. For example Ventura et.al[37] and Beiermann et.al.[38] functionalized a SP with respectively one and two ATRP initiators to make poly(methyl methacrylate). Wang et.al.[33] and Wagner et.al.[34] grafted a spiropyran functionalized acrylate from a silicon substrate. All these polymerizations were done with the SP isomer in a neutral solution. When in this research acrylic acid (or ascorbic acid what is used for ARGET ATRP) is added, the SP goes to its MCH$^+$ isomer. MCH$^+$ can form metal complexes, which might interfere with the copper complex from the ATRP.

1.3.2.1 *ATRP Mechanism and kinetics*

ATRP uses a transition metal complex, which is often copper, as shown in Figure 9. The ligand metal complex, $[(Lig)Cu^{1+}]$, is used as a mediator for the propagating radicals. In Figure 9 $[(Lig)Cu^{1+}]$ is oxidized to $[(Lig)Cu^{2+}Br]$ by an alkyl halide (P_n-Br) to form an active radical (P_n*). This is a reversible process, which equilibrium is strongly shifted to the dormant species. When oxygen is present during the reaction the Cu^{1+} will be oxidized to the more stable Cu^{2+} and not go back, which will terminate the reaction. Because

of the dormant species, the polymer chains can grow simultaneously and keep the concentration of radicals low, which prevents bimolecular termination. This result in good polymerization control. The control largely depends on the equilibrium between the activation, k_{act}, and the deactivation, k_{deact}, of the polymer chain ($k_{deact} > k_{act}$). K_{ATRP} is the ratio between the activation and deactivation constants and determines the number of radicals and so the rate of polymerization, termination and consequently the PDI. In the equation 2 the rate of polymerization is given.

$$R_p = k_p[P_n^*][M] = k_p K_{ATRP}[RBr]\frac{[(Lig)Cu^{1+}]}{[(Lig)Cu^{2+}Br]}[M] \tag{2}$$

Kinetics of ATRP resemble kinetics of FRP, because it is also depended on the radical concentration. Radical concentration is determined differently than in FRP. P_n^* is dependent on [(Lig)Cu^{1+}], [(Lig)Cu^{2+}Br], R-Br and K_{ATRP} where R-Br is the concentration of initiators. These concentrations also determine the PDI shown in equation 3.

$$PDI = \frac{M_w}{M_n} = 1 + \left(\frac{k_p[RX]_0}{k_{deact}[(Lig)Cu^{2+}Br]}\right)\left(\frac{2}{conv} - 1\right) \tag{3}$$

1.3.2.2 *ARGET ATRP*

A drawback of ATRP is the relatively large amount of metal catalyst, which remains in the polymer after the polymerization. Copper is mostly used as transition metal that gives the polymer a green color and toxicity. ATRP is just as FRP also intolerant for oxygen, which increases the complexity of the process. To overcome these problem activator regenerated electron transfer (ARGET) ATRP is used. Matyjazewski et.al.[44] first reported this variation on ATRP. This method uses less transition metal complex as regular ATRP, because the copper complex is regenerated in situ by the reducing agent. In ARGET ATRP the monomer, and the catalyst complex (in oxidized form) are added to a solvent. When the reducing agent is added, the complex will go to its reduced form (step 1 in Figure 11). Subsequently, the initiator can go to its activated form (step 2) where they can propagate (step 3) or terminate (step 4). When they terminate the catalyst complex can be reduced again by the reducing agent, this is step 5 from Cu(II)-Br to Cu(I). If the metal gets oxidized by oxygen, the reducing agent regenerates the complex to its reduced form (Figure 11 step 6). This is why an excess of reducing agent is needed and only a low amount of metal catalyst.
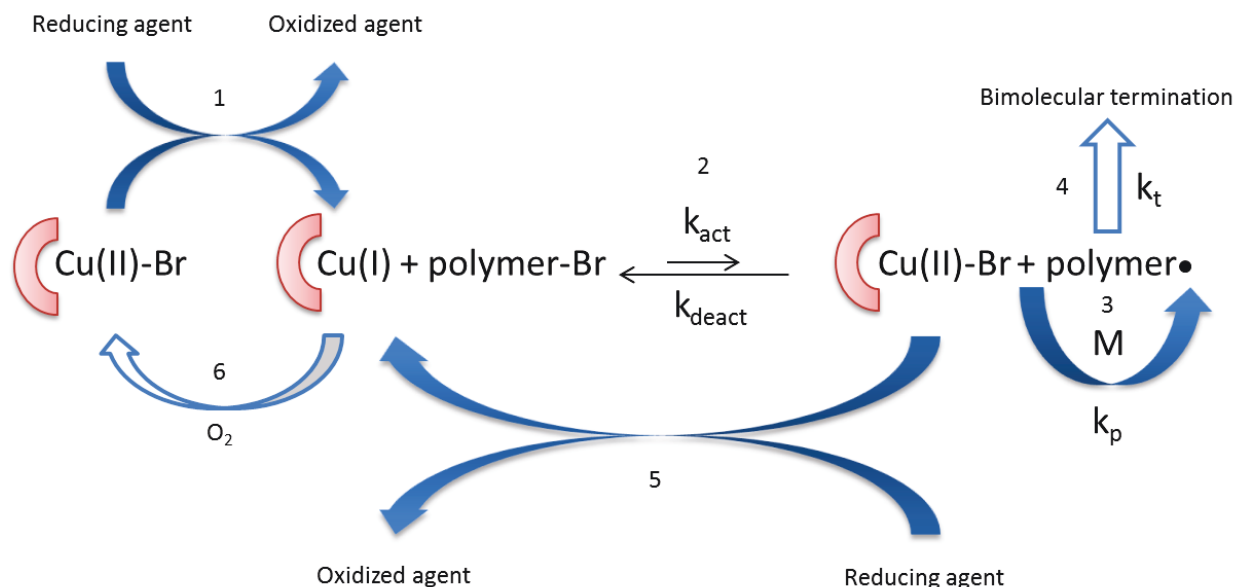
Figure 11 Mechanism of ARGET ATRP. To start the reaction Cu(II)-Br complex (half red ring) is reduced by the reducing agent to Cu(I) (step 1). The dormant polymer and the Cu(I) can go to their activated form to start the polymerization (step 2). Then it can go back to the dormant form to be activated again or it can get terminated (step 4). It can be reduced again by the reducing agent (step 5). Also when the Cu(I) get oxidized (step 6) by oxygen and is left in the oxidized Cu(II) form, the reducing agent can reduce the Cu(II) again to Cu(I) following step 1.

1.3.2.2.1 Reducing agent

In this research ascorbic acid is used as reducing agent because it has been used before with good results. When ascorbic acid oxidizes, to reduce the copper complex, it produces two protons. This is schematically shown in Figure 12 because the pH should be controlled in some of the experiments it should be noted that the pH will decrease during the experiment. Other reducing agent such as tin(II) 2-ethylhexyanoate are also used as reducing agent in ARGET ATRP.[44,46–49] When tin(II) 2-ethylhexyanoate is oxidized the pH remains constant.
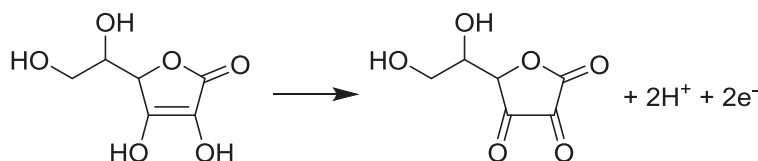
Figure 12 Oxidation of ascorbic acid. 2 protons and 2 e⁻ are produced.

1.3.2.3 *ARGET ATRP of Acrylic acid*

Acrylic acid gives problems when it is polymerized by ARGET ATRP. The carboxylic acid can form a complex with the catalyst which interferes with the polymerization.[50–54] Therefore a different method should be used. The carboxylic acid can be protected before polymerization and deprotected afterwards to obtain the acidic polymer. Two different possibilities to do this are polymerizing tert-butyl acrylate and the other possibility is polymerizing sodium acrylate. For tert-butyl acrylate, an ester is formed which cannot form a complex with the catalyst. A disadvantage of this method is that tert-butyl acrylate needs to be hydrolyzed by a strong acid to form the acrylic acid.[55,56] Because the initiator is also attached

to the cotton by an ester bond, it is possible that this bond will be hydrolyzed. The other option is the polymerization of sodium acrylate. With this method the proton is replaced by sodium by the addition of sodium hydroxide. The pH is lowered which deprotonates the acrylic acid and replaces it with the sodium. If the sodium is coordinated with the acrylic acid it can't coordinate with the catalyst complex. The deprotection of sodium acrylate can be done by washing with water which is less aggressive than the acid which is needed for the tert-butyl acrylate.[52–54,57,58] Another advantage of this method is that the SP remains in its closed form in this environment and also cannot form a complex with the copper complex.

1.3.3 Grafting

In this project ATRP is not only used because of the good polymerization control but also because it allows grafting. Grafting can be done in three different ways. Grafting through, grafting from and grafting to a substrate. Grafting from is when the polymer is polymerized from the substrate. Grafting to is when an end functionalized polymer chain is made and then attached to the substrate. Grafting through is done by polymerizing a macro monomer. A schematic representation of these grafting techniques is shown in Figure 13. The cotton fibers are previously prepared by grafting from the fiber by functionalizing the fiber with an ATRP initiator and then polymerizing the NIPAAm from the fiber.[2] This is called surface initiated (SI) ARGET ATRP.
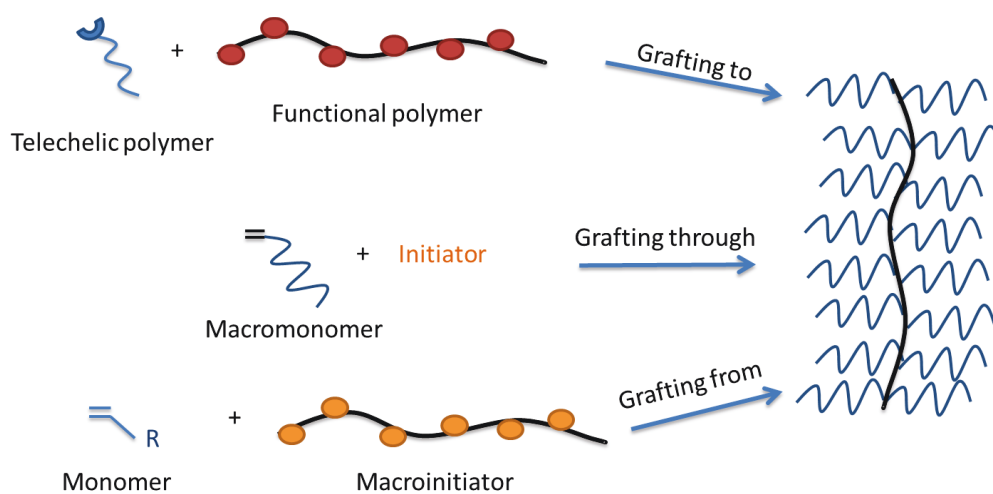
Figure 13 Different grafting methods. Grafting to is done by attaching a telechelic polymer to a polymer backbone. Grafting through is done by polymerizing a macromonomer. Grafting from is done by polymerizing a monomer from the backbone of a polymer.

Also different researchers have shown the functionalization of cellulose with an ATRP initiator,[1,2,17–19,43] while other have immobilized ATRP initiators on cardboard[20] and woodpulp,[59] which also has a high amount of cellulose. In all these researches α-bromoisobutyryl bromide (BiB) is used to functionalize the surface. Also in this project this ATRP initiator is used and attached to the cotton fiber so the PNIPAAm-SP-AA can be grafted from the fiber. Figure 10 already showed the reaction of BiB with the OH-groups of the cotton fiber.

2 Aim and Approach

For this research a material that allows water uptake and release in environments naturally present in for example deserts is investigated. Previously in SMG research group, PNIPAAm was grafted from a cotton fiber by ARGET ATRP to obtain a thermoresponsive water collection and release system. In SFD research group, research has been done with PNIPAAm-spiropyran hydrogels. Spiropyrans can isomerize upon the irradiation of light. In the dark this material is in its open form in which it is more polar than in its closed form. This will induce the swelling and shrinking of the polymer and will make the water collection responsive to light.

Inspired on work of Yang et.al.[2,7] (SMG) and Stumpel et al.[13,14] (SFD), an autonomous hybrid material is investigated that responds to temperature and light. Therefore N-Isopropylacrylamide (NIPAAm), acrylic acid (AA) and a spiropyran functionalized acrylate SP-A need to be polymerized and attached to a cotton fiber. First this was tried by FRP as this is easier from a practical point of view. Subsequently ARGET ATRP was used because this can be initiated from a surface. ARGET ATRP was started from a cotton fiber that is functionalized with an ATRP initiator.

Because SP-A and AA could interfere with the ARGET ATRP reactions, it was first tried to polymerize NIPAAm as Zhang[1] did. Later it was tried to copolymerize SP-A and AA. This way the effect of using different monomers for the polymerization can be investigated, as well as the influence in the water uptake for the different polymers can be obtained.

To investigate if the polymer was grafted from the cotton fibers, the weight of the fibers, before and after the polymerization was determined. Optical microscopy (OM) and scanning electron microscopy (SEM) were used to see if there were changes in the morphology of the surface of the cotton fibers. X-ray photoelectron spectroscopy (XPS) was used to see if the elemental composition on the fibers has changed.

To test the water uptake of the cotton fiber water-uptake experiments, contact angle with humidity chamber and temperature control. The OM was mounted with a Linkham cell. With the water uptake experiments it was tested how much water the cotton fibers can absorb from the air in different temperatures by measuring the weight of the fibers. The contact angle experiments were used to test the hydrophobicity in low and high temperatures in different humidities. With the Linkham cell OM set-up the swelling and deswelling of the fibers is investigated under influence of temperature. In these experiments the cotton fiber are also irradiated with light to investigate the isomerization of the MCH$^+$ to the SP.

3 Experimental

3.1 Chemicals

The cotton fabric was obtained from Textile Innovators Division of SDL ATLAS and pretreated as described in 3.4.1. *N*-isopropylacrylamide (NIPAAm, Aldrich 97%) was recrystallized in heptane (Biosolve). The following chemicals were used without further purification: Acrylic Acid (Aldrich 99%), 2,2'-Azobis(2-methylpropionitrile) (AIBN, Aldrich 98%), 4-(dimethylamino) pyridine (DMAP, Aldrich 99%), triethylamine (TEA, Aldrich 99%), 2-bromoisobutyryl bromide (BiB, Aldrich 98%), pentamethyldiethylenetriamine (PMDETA, Aldrich 99%), Copper(II)Bromide (Cu(II)Br, Aldrich 99%), ascorbic acid (Aldrich), methanol (MeOH, Biosolve), Tetrahydrofuran (THF, Biosolve), Diethylether (Biosolve), 6-((1',3',3'-trimethylspiro[chromene-2,2'-indolin]-6-yl)oxy)hexyl acrylate (SP-A) self-synthesized according the procedure described by Stumpel.[14]

3.2 Characterization

The scanning electron microscopy (SEM) images were recorded on a Phenom G1 or a JEOL JSM-5600 Scanning Electron Microscope. The cotton fiber was gold sputtered for imaging (1 min, 65 mA). The acceleration voltage was set to 5kV. The JEOL was used for the FRP samples and the Phenom for the ARGET ATRP samples.

^{1}H-NMR (400 MHz) spectra were recorded on a Varian spectrometer (Varian Mercury Vx 400). An average of 32 measurements was taken to obtain a better signal to noise ratio and long relaxation times are used. The polymers were dissolved in deuterated dimethylformamide (DMF). Splitting patterns are designated as s, singlet; d, doublet; dd, double doublet; t, triplet; quin, quintet; m, multiplet.

Gel permeation chromatography (GPC) was performed on a Varian PL-GPC50 Plus, with DMF as eluent. Polystyrene standards were used for calibration.

X-ray photoelectron spectroscopy (XPS) was measured on a Thermo Scientific K-Alpha instrument equipped with a monochromatic A1 Kα X-ray source operating at 200W. The base pressure was $1.6*10^{-8}$ Mbar. Wide energy survey scans were collected over the range of 0 to 1350 eV. The C1s, O1s, N1s, Br3p and Br3d signals were corrected for sensitivity[60] and the ratios between the elements were calculated from the areas of the peaks.

Optical microscopy (OM) analysis were performed with a Polyvar optical microscope with Reichurt Hung light source. Pictures were made with a Lumenara infinity 1 camera and infinity analyze software was used to analyze the images. The sample was prepared by pulling a single fiber out of the woven fabric. These fibers were stretched and taped on a glass slide. To investigate the swelling properties in water, some fibers were pre-wetted with a droplet of water.

The Linkham cell was used on the stage of the OM. Also with this characterization a single fiber was extracted from the cotton and stretched with double side tape without being in direct contact with the heating stage of the linkham cell. The temperature was controlled with a Linkham cell temperature controller and liquid nitrogen pump. The humidity was controlled by bubbling air through four flasks of demi water and then through the Linkham cell. The humidity was measured by a handheld humidity

sensor at the flow outlet of the cell. This is also done under the irradiation of light with a Zeiss Schott KL 1500 fiberoptic light source.

Static water contact angles (CA) were measured with an OCA30 from Data Physics. The HCG humidity generator was used to control the humidity in the cell were the measurement was done. The cell what was used was also equipped with a temperature controlling unit. A first 5µL water droplet was used to measure the static contact angle at 20°C after 20 minutes stabilizing in the humidity chamber. Then the temperature was raised to 45°C and 65°C to measure the contact angle with a different water droplets of the same volume also after 20 stabilizing inside the humidity chamber. This is also done under irradiation of light with same light source which is used for the Linkham cell.

To test the water-uptake by the polymer and the polymer coated cotton, the samples were placed in a humid environment. A schematic set-up is shown in Figure 14. The samples were placed in an open jar, which was placed in a closed jar, which was filled with water. This way a high humidity was reach within the chamber without direct contact of the samples with the water. The jars where kept at 20°C and 40°C temperature in the dark to reach an equilibrium. The samples were weight before and after to determine the water-uptake.
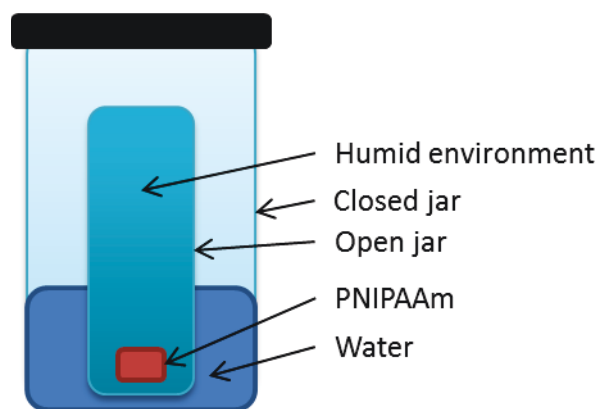
Figure 14 Experimental set-up for the water-uptake

Differential scanning calorimetry (DSC) measurements are performed on a Q2000 from TA instruments. Heating and cooling rates of 5°C/min were used in the temperature range from 20°C to 60°C. 5 mg of the polymer coated cotton fibers was pre-wet with 30 µl water and sealed in a T0-hermetic aluminum pan from TA instruments. 4 heating cycles per sample are used for these measurements.

3.3 Synthetic procedures

3.3.1 Free radical polymerization (FRP)
The NIPAAm, SP-A, AA and AIBN were dissolved in THF in a schlenk flask and degassed with freeze-pump-thaw cycles until no gas formation was visible. The reaction was done under an Argon atmosphere at reflux temperature (66°C) overnight. In the FRP reactions the ratio of [M]:[I] is 98:2. Two different experiments were performed, one with (FRP-2-C) and one without (FRP-1) the cotton fiber. In the experiment with the cotton fiber there was also 5% acrylic acid added, in the experiment without

cotton fiber, no acrylic acid was used. For the experiment without the cotton fiber the ratio of the monomer was NIPAAm:SP of 97:3. The reaction was done with the following amounts: NIPAAm (98,6mg 0,871 mmol), SP-A (11,9 mg, 0,027 mmol) and AIBN (3,0 mg, 0,018 mmol) , dissolved in 3 ml dry THF. For the experiment with the cotton fiber a ratio of NIPAAm:SP:AA of 94:1:5 was used. The following amounts were used: Cotton fiber (31,4 mg), NIPAAm (190,2 mg, 1,681 mmol), SP-A (7,9 mg, 0,018 mmol), AA (6,5 mg, 0,090 mmol) and AIBN (5,9 mg, 0,036 mmol), dissolved in 3 ml dry THF.

The polymers were analyzed by ^{1}H NMR. FRP-1 ^{1}H NMR spectra was as follows: ^{1}H NMR (400 MHz, DMF-d_7) δ 7.38 (br, 45H, NH), 7.13 (t, J = 7.4 Hz, 3H), 7.04 (d, J = 10.6 Hz, 2H), 6.79 (t, J = 7.4 Hz, 1H), 6.74 (d, J = 8.6 Hz, 2H), 6.64 (s, 1H), 6.57 (dd, J = 12.8, 8.4 Hz, 2H), 5.82 (d, J = 10.3 Hz, 1H), 3.95 (s, 53H), 3.62 (t, J = 6.6 Hz, 15H), 3.48 (s, 122H), 2.20 (d, J = 24.4 Hz, 56H), 1.86 − 1.34 (m, 122H), 1.12 (s, 301H). The ratio of NIPAAm:SP was calculated of 97,8:2,2. The ^{1}H NMR spectra of FRP-2 was: ^{1}H NMR (400 MHz, DMF-d_7) δ 12.35 (s, 5H), 7.44 (d, J = 44.0 Hz, 115H, NH), 7.13 (t, J = 7.1 Hz, 5H), 7.04 (d, J = 10.0 Hz, 2H), 6.79 (t, J = 7.3 Hz, 1H), 6.74 (d, J = 9.0 Hz, 1H), 6.64 (s, 1H), 6.57 (dd, J = 13.1, 8.2 Hz, 2H), 5.82 (d, J = 9.9 Hz, 1H), 3.95 (s, 125H), 3.62 (t, J = 6.6 Hz, 63H), 3.48 (s, 242H), 2.18 (s, 141H), 1.95 − 1.32 (m, 353H), 1.19 (d, J = 59.9 Hz, 760H). In this the ratio NIPAAm:SP:AA was 94,2:0,8:5

3.3.2 Functionalization of the cotton fiber with a bromide ATRP initiator
For this reaction typically the pre-treated cotton (31,4 mg), DMAP (catalytic amount) and TEA (0,203 ml, 0,0028 mmol) were added to a triple neck round-bottom flask with 15 ml dry THF. This mixture was flushed by a nitrogen flow to create a nitrogen atmosphere. BiB (0,17 ml, 0,0016 mmol) was added dropwise to start the reaction. This mixture was kept overnight at room temperature. The functionalized cotton was rinsed 3 times with THF, acetone, and water and dried overnight in a vacuum oven at 40°C.

3.3.3 Surface Initiated ARGET ATRP (SI-ARGET ATRP)
The SI ARGET ATRP reactions were done following the procedure described by Zhang[1] the best results for the polymerization of NIPAAm. For this research also SP-A and AA were polymerized. The ratios which were used are Monomer:Initiator:Cu(II):Lignad:Reducing agent ([M]:[I]:[Cu]:[L]:[R]) of 100:1:0,05:0,1:0,5 and a monomer concentration of 0,5 mol/L. For SP-A, 1 mol% and for AA, 5 mol% was used for the polymerization. NIPAAm was added to complete it to 100 mol%.

For a typical reaction of NIPAAm-SP-AA Copper(II)Bromide (1,15 mg, 0,005 mmol) and PMDETA (2,1 µL, 0,01 mmol) were added to a 20 ml MeOH/H_2O (1:1) solution. This was stirred till the copper was fully dissolved. Then NIPAAm (1,074 gr, 9,5 mmol), SP-A (44,5 mg, 0,10 mmol), AA (34 µL, 0,5 mmol) and pretreated cotton (31,4 mg) were added to the solution. The oxygen level was decreased by bubbling nitrogen through the solution for 1 hour. The reaction was started by the addition of ascorbic acid (8,8 mg, 0,05 mmol) dissolved in 2 ml MeOH/H_2O (1:1) solution. Through this solution also nitrogen was bubbled to decrease the oxygen level. The reaction was started by adding the ascorbic acid to the reaction mixture while it was stirring and in an ice bad. The reaction was done for 48 hours at room temperature. Afterwards the cotton was rinsed three times with water, methanol and ethanol to remove the residue monomer and catalyst. The fabric was dried overnight in a vacuum oven at 40°C.

3.3.3.1 *Deprotonation of Acrylic Acid*

Acrylic acid interacts with the ATRP catalyst and is therefore protected by converting it to sodium acrylate.[52–54] The acidic polymerization mixture was brought to pH 7 with a 0.5 M NaOH solution before the bubbling nitrogen trough the mixture. When the desired pH was reached the AA was flooded with Na^+ ions by the total addition of 18,2 mg NaCl. Since ascorbic acid produces H^+ during the reaction, the pH is measured during the reaction. This was done by taking samples which were measured by pH paper. To do this more controlled for AA-12 (sample with NIPAAm-SP-AA) the ascorbic acid solution was also neutralized to pH 7 before the reaction was started.

3.4 Purification

3.4.1 Washing of the Fiber

The bare-cotton fabric was washed in an aqueous solution containing a commercial soap-detergent and under magnetic stirring for 1 hour, at ~100°C. Subsequently the bare-cotton was thoroughly and consecutively rinsed with water, acetone and ethanol. Next, the bare cotton was immersed in distilled water and left in an ultrasonic bath for 5 min. This rinsing and sonification was repeated three times and after this the bare cotton was dried at 40°C under vacuum for 24 hours. The dried bare-cotton was then pre-treated with UV/Ozone irradiation for about 10 min on each side of the fabric prior to use.

3.4.2 Extracting polymer from the solution

To retrieve the product from the solution the polymer was precipitated with diethyl ether. The polymer was extracted with the use of a centrifuge, 10 minutes 8000 RPM.

3.4.3 Purifying the polymer-cotton fibers

The polymer-cotton fibers were soxhlet extracted with 200 ml methanol for 6 hour. This was done to remove the copper catalyst and residue monomer. The extracted solution was evaporated in a rotorvap for further characterization. The polymer-cotton fibers were dried at 40°C under vacuum for 24 hours.

4   Results and Discussion

In order to make the dual triggered water collection and release on cotton fiber, different polymers were made. FRP and ARGET ATRP in solution were done as reference experiment. First the FRP will be discussed and then surface initiated ARGET ATRP.

4.1   Free radical polymerization (FRP)

Two different polymers were made with FRP as described in 3.3.1. The first polymer (FRP-1) was made with a ratio of 97:3:0 and 2% initiator, which is the same as the polymer previously made by Stumpel et al.,[14] denoted as FRP-S (Table 1). The only difference was that 3 ml THF was used instead of 0,5 ml thus a lower concentration of the monomer and initiator was used. A second polymer (FRP-2-C) was made in the presence of a cotton fiber with a ratio of 94:1:5. A ratio of 94:1:5 was chosen because Ziółkowski et al.[12] showed 1% of spiropyran and 5% acrylic acid gave the best swelling properties. The reaction scheme is shown in Figure 15. After the reaction of FRP-1 and FRP-2-C, the polymer was precipitated from the solution and the cotton from FRP-2-C was purificated. The polymers were characterized by ^{1}H NMR, GPC and the cotton fiber was characterized by SEM. For the polymers containing spiropyrans, the reaction mixture was colored orange and after purification a white powder was obtained for FRP-1 and an orange powder for FRP-2-C. The orange color is the spiropyran what was isomerized to the MCH$^+$ by the acrylic acid.

Table 1 Experiments carried out with FRP

Sample	NIPAAm:SP:AA	[M]:[I]	Monomer Concentration (mol/L)	M_n (gr/mol)	M_w (gr/mol)	PDI	Weight increase cotton (mg)
FRP-1	97:3:0	98:2	0,3	2900	6400	2,2	N/A
FRP-2-C	94:1:5	98:2	0,6	2500	7500	3,0	0
FRP-S	97:3:0	98:2	1,8	6300	15000	2,4	N/A
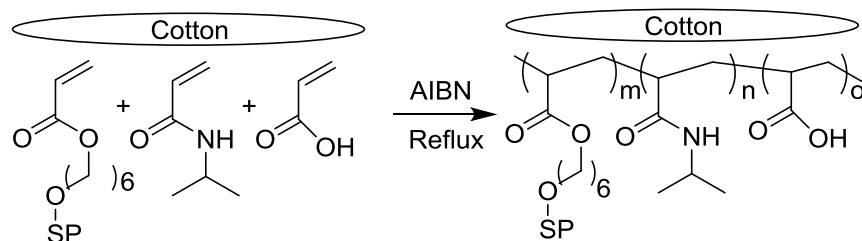
Figure 15 Free radical polymerization of NIPAAm, SP and AA in the presence of cotton (FRP-2).

The PDI, M_n and M_w of the polymers made with free radical polymerization were determined by GPC and shown in Table 1. FRP-S has more than double the M_n and M_w than FRP-1, which is probably due the lower monomer and initiator concentration in the mixture. This can be explained by the Mayo-Walling equation,[42] which shows that if the concentration of the monomers and initiators decreases, the M_n of the monomer will decrease. When comparing FRP-1 with FRP-2-C, the first has a slightly higher M_n. According the Mayo-Walling equation we would expect the opposite because FRP-2-C has double the

concentration of monomer and initiator in relation to FRP-1. This could be caused by the presence of the cotton in the polymerization mixture, which introduces hydroxyl groups of the cotton fibers or residual oxygen in the cotton fibers, which could have terminated the propagating chains. The PDI of FRP-2-C is higher than the PDI of FRP-1. This could also be under the influence of the cotton during the polymerization.

The cotton fiber from FRP-2-C had no weight increase (Table 1).In Figure 16 the SEM characterization of the FRP-2-C product is shown: in the left a bare cotton fiber as reference and in the right image the cotton fiber from FRP-2-C after extraction of the free polymer. There was no visible polymer attachment on the FRP-2-C and there was also no increase in the fiber diameter.
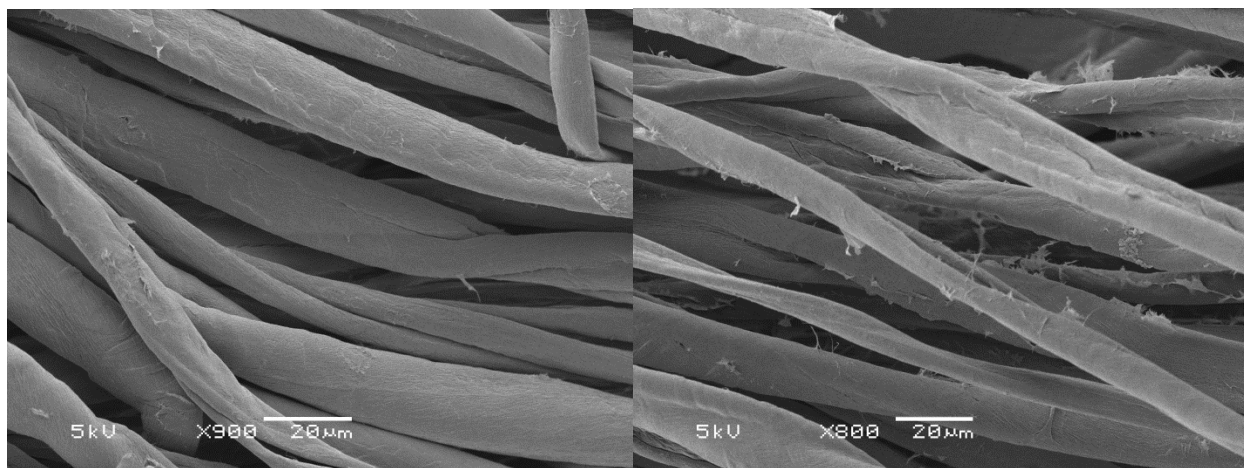
Figure 16 SEM image of a bare piece of cotton (left) and a piece of cotton, which was in presence of the free radical polymerization (FRP-2-C). On both, no polymer was observed.

This shows that with the FRP experiment the polymer did not get attached covalently to the surface of the cotton fiber. Therefore the surface should be functionalized with the initiator or a vinyl group to obtain random attachment points from which the polymer will be grafted. The next step was to try polymerizing from the surface so there is a covalent bond from the fiber to the polymer. This was done by surface initiated ARGET ATRP.

4.2 Surface Initiated ARGET ATRP

For the SI ARGET ATRP the method reported by Zhang[1] was used. In Figure 17 this method is schematically shown. First of all the cotton fiber was functionalized with BiB. In the second step of Figure 17 the ATRP initiator functionalized cotton is shown. From the ATRP initiator functionalized cotton the polymer was grafted. The ratios [Cu], [L] and [R] compared to the monomer concentration were kept the same in all reactions ([M]:[Cu]:[L]:[R] 100:0,05:0,1:0,5). The concentration of monomer was 0,5 mol/L for all reactions unless stated otherwise (Table 2).
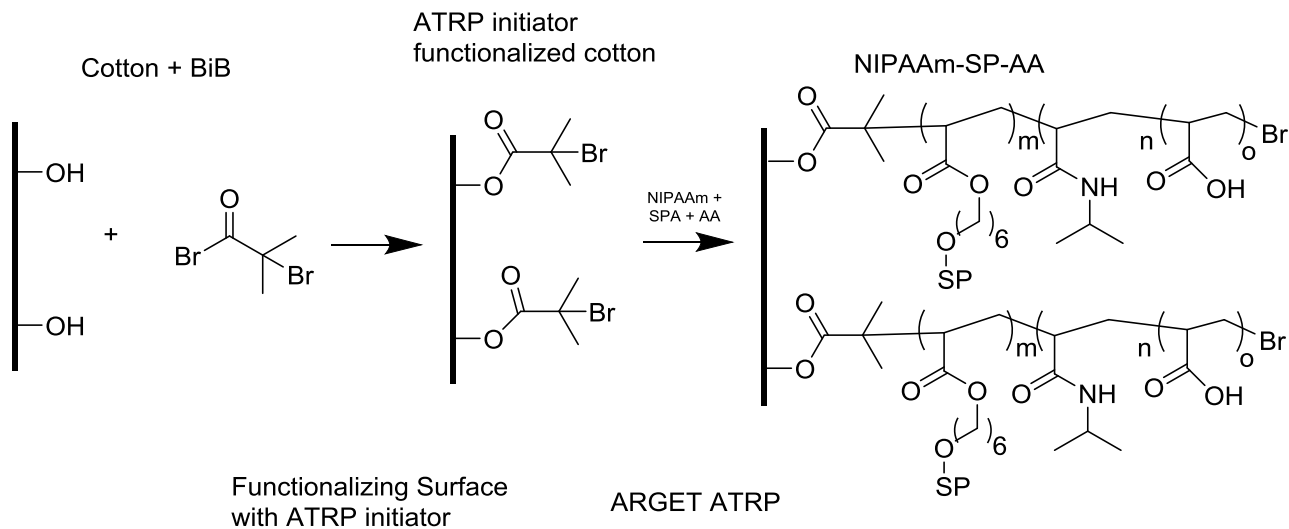
Figure 17 First step is the functionalization of the cotton fiber. Second step is the grafting of the copolymer from ATRP initiator functionalized cotton fiber.

First the cotton fiber was functionalized with BiB and characterized to see if the BiB was attached to the cotton. The result of this characterization are shown in paragraph 4.2.1.

Because the SP-A can have some interaction with the other components of the ARGET ATRP, it was investigated how the SP-A could be dissolved and what kind of colors this would give. Different solvents were tested to dissolve the SP-A and to estimate if could give a high polymer weight increase on the cotton fiber. Also different monomer concentrations were tested.

Then the interaction of AA with the ARGET ATRP was investigated. AA can make a complex with Cu^{2+} which when it is formed can't catalyze the reaction.[44,61] AA was sodium protected by neutralizing it with NaOH. Then NIPAAm, SP-A and sodium Acrylate were polymerized from the cotton fiber.

The reactions performed are shown in Table 2. These polymers are all made by SI ARGET ATRP from BiB-cotton. Different monomers and different solvents are used for the reactions. The weight increase was calculated as follows: $Weight\ increase = \frac{M_p - M_0}{M_0} * 100\%$ M_0 is the weight of the cotton fabric before the polymerization and M_p is the weight of the cotton after the polymerization.

Table 2 SI ARGET ATRP of NIPAAm, SP-A and AA

Sample	Solvent MeOH/H$_2$O	Monomer concentration (Mol/L)	Monomer	Weight increase	Remark
AA-1	1:1	0,5	NIPAAm-SP-AA	1%	SP 6', not dissolved
AA-2	1:0	0,5	NIPAAm	-	
AA-3	1:0	0,5	NIPAAm-AA	-	
AA-4	1:1	0,5	NIPAAm	158%	Method of Zhang[1]
AA-5	3:1	0,5	NIPAAm	36%	
AA-6	3:1	0,25	NIPAAm	1%	
AA-7	3:1	0,25	NIPAAm-SP	3%	SP 8'[1]
AA-8	3:1	0,25	NIPAAm-AA	10%	pH 7,
AA-9	3:1	0,25	NIPAAm-AA	2%	pH 10
AA-10	3:1	0,5	NIPAAm-AA	23%	pH 7
AA-11	1:1	0,5	NIPAAm-AA	127%	pH 7
AA-12	1:1	0,5	NIPAAm-SP-AA	60%	pH 9, SP 6'

[1] For AA-7 SP-8' was used instead of SP-6'.

The product of the reactions were characterized by OM, SEM and XPS. OM and SEM show a change in the surface morphology when the polymer is grafted from the cotton fiber. XPS shows a different composition of atoms on the fiber when the polymer is attached. To test the functionality of the cotton fiber functionalized with the polymers, CA, DSC, water uptake experiments and swelling experiments with a Linkham cell mounted on a OM were performed. These experiments show the interaction between the water and the fibers under the influence of light and/or temperature.

4.2.1 Functionalization of the cotton fibers with ATRP initiator

When the cotton is functionalized, a bromide containing moiety is introduced on the cotton fiber. With XPS the ATRP initiator functionalized cotton fibers were characterized to see if there is bromide from the initiator on the cotton fiber. In Figure 18 representative XPS spectra are shown. At 195 eV the Br 3p binding energies and at 70 eV the Br 3d binding energies are present. This is a qualitative indication that the ATRP initiator is attached on the cotton fiber. This characterization was done on every batch of ATRP initiator functionalized cotton.
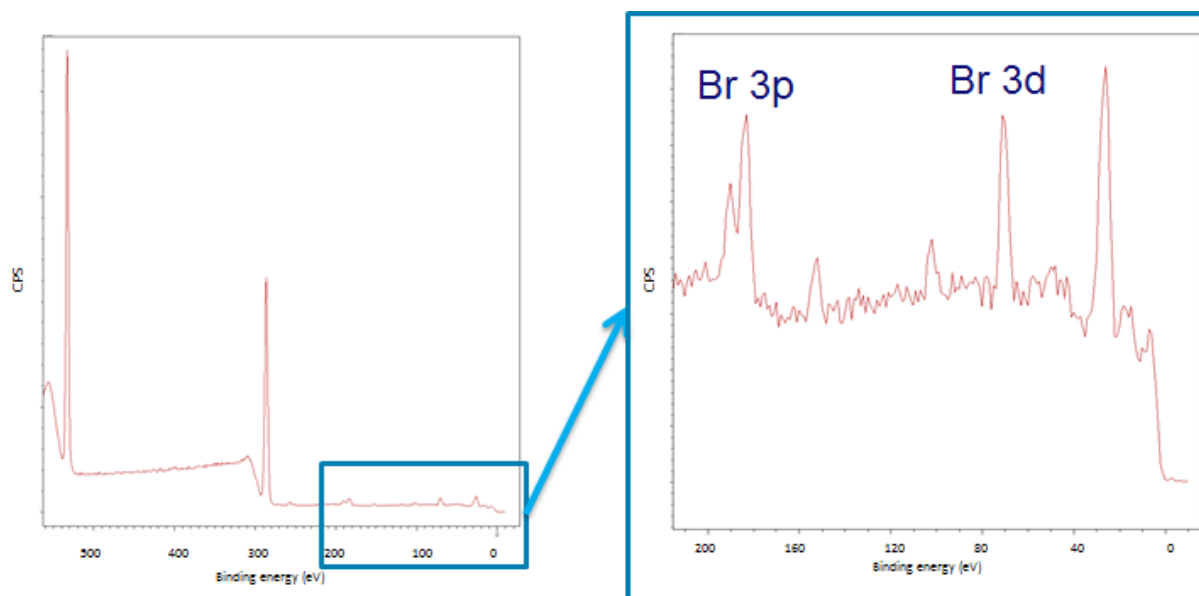
Figure 18 XPS spectra of the ATRP initiator functionalized cotton. Left) survey XPS spectra. Right) enlargement of the bromide binding energies.

4.2.2   Solubility

When it was tried to polymerize AA-1, which contained NIPAAm, SP-A and AA, not all components dissolved in the solvent (MeOH/H$_2$O 1:1) which was used by Zhang.[1] It was needed to dissolve 0,05 mol/L SP-A for the polymerization. Therefore solubility tests (Table 3) and compatibility and interaction tests (Table 4) were done with all components. In the previous work only NIPAAm was used as monomer which did not influence the color. SP-A and AA influence the color of the reaction mixture. Since the color of the reaction mixture is an important indication if the polymerization is still living, it is important to understand the colors when different components are added. Also the SP-A should be dissolved to participate in the reaction. First the solubility of SP-A in different MeOH/H$_2$O, H$_2$O and MeOH solvents was tested (Table 3). Only in a MeOH/H$_2$O mixture with a low amount of water SP-A could be dissolved. It also observed that every component is soluble in pure methanol. The SP-A did not dissolve in MeOH/H$_2$O 1:1 so this needed to be kept in mind for the experiments. Further solubility experiments of SP-A with different MeOH/H$_2$O ratios are discussed in 4.2.2.1.

Table 3 Solubility of ARGET ATRP components in a water/methanol mixture (v/v 1:1), water and methanol

	MeOH/H$_2$O 1:1	H$_2$O	MeOH
NIPAAm	y	Y	y
SP-A	n	n	y
AA	y	y	y
(Lig)Cu(II)	y	y	y
Ascorbic acid (R)	y	y	y

In Table 4 the results of a compatibility, interaction and solubility experiment of the SP-A are shown, in which different orders of addition were tried. The SP-A dissolved in methanol precipitated when the water was added. A white cloudy solution was obtained. When it was first tried to dissolve the SP-A in water, the SP-A did not dissolve and the solution stayed transparent (with white SP-A flakes). When the other components were added the experiment showed that the solution became orange when the AA was added. This confirms the presence of the MCH$^+$ (Figure 8).

Table 4 Experiements to investigate the compatibility, interaction of the SP-A. Different orders of addition were used to investigate if this improved the solubility of the SP-A.

Experiment	Observations	Orders of addition of components			
		1st	2nd	3th	4th
		H$_2$O	MeOH	Acrylic Acid	Cu complex
1	Dissolved	n	n	n	n
	Transparent	y	y	y	y
	Color	/	/	Orange	Orange
	Precipitate	Flakes	Flakes	Flakes	Flakes
		MeOH	H$_2$O	Acrylic Acid	Cu complex
2	Dissolved	y	n	n	n
	Transparent	y	n	n	n
	Color	Slightly bluish	White	Orange	Orange
	Precipitate	/	Cloudy	Cloudy	Cloudy
		MeOH	H$_2$O	Cu complex	Acrylic Acid
3	Dissolved	y	n	n	n
	Transparent	y	n	n	n
	Color	Slightly bluish	White	Blue	Green→yellow→orange
	Precipitate	/	Cloudy	Cloudy	Cloudy

When the NIPAAm, AA and copper complex are added to a MeOH/H$_2$O solution a Cu^{2+} complex is formed. When the reducing agent is added Cu^{2+} will be reduced to Cu^{1+}. The Cu^{1+} complex is colorless in a MeOH/H$_2$O solution and the Cu^{2+} is blue. This was confirmed by a reference experiment were the copper complex was dissolved in methanol with the addition of the reducing agent without the other components. This showed that in methanol, the copper complex becomes colorless to slightly green when it is oxidized. When acrylic acid is present this takes a couple minutes but without the acrylic acid this is instantaneous.

4.2.2.1   Solubility SP-A
With the first solubility tests, we have learned that the ratio of MeOH/H$_2$O needs to be adjusted to dissolve the SP-A. This was done by trying to dissolve the SP-A with different ratios of MeOH/H$_2$O solutions. SP-A dissolves well in MeOH and did not dissolve in H$_2$O. Water is needed for the polymerization to obtain good results (high polymer weight increase) for the SI ARGET ATRP (4.2.3).

When a monomer concentration of 0,5 Mol/L was used and 1% of this monomer is SP-A, 0,05 Mol/L SP-A needs to be dissolved. In Table 5 it is shown in what ratios and concentrations SP-A can be dissolved.

Table 5 Solubility of SP-A in different MeOH/H$_2$O ratios

Ratio MeOH/H$_2$O	Concentration (Mol/L)	Dissolved
4:1	0,05	Yes
3:1	0,05	No
$2\frac{1}{3}$:1	0,05	No
2:1	0,05	No
3:1	0,025	Yes
2:1	0,025	No

For these experiments SP-A was first dissolved in MeOH and then the water was added. The precipitation of the SP-A was very fast so, the water was added dropwise. It was only possible to dissolve SP-A for the MeOH/H$_2$O ratio of 4:1 with 0,05Mol/L. For the MeOH/H$_2$O ratio of 3:1, 0,025 Mol/L SP-A could be dissolved.

4.2.3 Solvent ratio

To polymerize SP-A by ARGET ATRP it needs to be dissolved in a solvent which also gives good polymerization results. For the AA-2, AA-4 and AA-5 reactions (Table 2), a MeOH/H$_2$O ratio of 1:0, 1:1 and 3:1 was used respectively. In what concerns the weight increase of the cotton fibers it was clear that water was needed for the polymerization. When no water was used the weight of the fiber did not increase, while with the ratio of 3:1 the weight of the fiber increased by 36%. With a 1:1 ratio the fiber increased in weight by 158% which is much higher than obtained by Zhang[1] (64,5%). From these results it can be concluded that water is needed for the polymerization. It is probably needed to maintain the ATRP complex. With less water the equilibrium of the reaction is probably shifted so no radicals at all are formed.

These fibers were characterized with OM and SEM to confirm the polymer was present on the fibers. When examined with the OM it was observed that several fibers AA-4 were coated with PNIPAAm. Figure 19 shows OM images of a coated fiber from AA-4. An increase in diameter of the fiber was observed after exposing it to water: from ≈46 µm to ≈58 µm. In Figure 20 images of AA-5 are shown. On these fibers less polymer was found. On the images it is seen that the fiber was not completely covered by the PNIPAAm. There were regions which were more covered and others not covered at all. Before the fibers were submerged in water the average diameter was ≈49 µm and increased to ≈53 µm when water was absorbed.
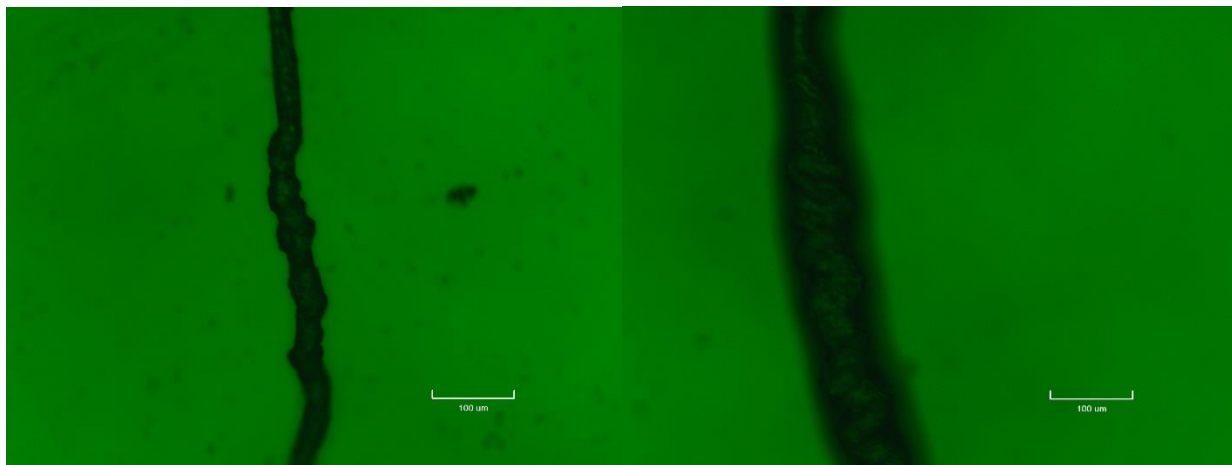
Figure 19 OM image of AA-4. In the left image it is in its dry state. The right image is after the fiber was submerged in water and removed afterwards.

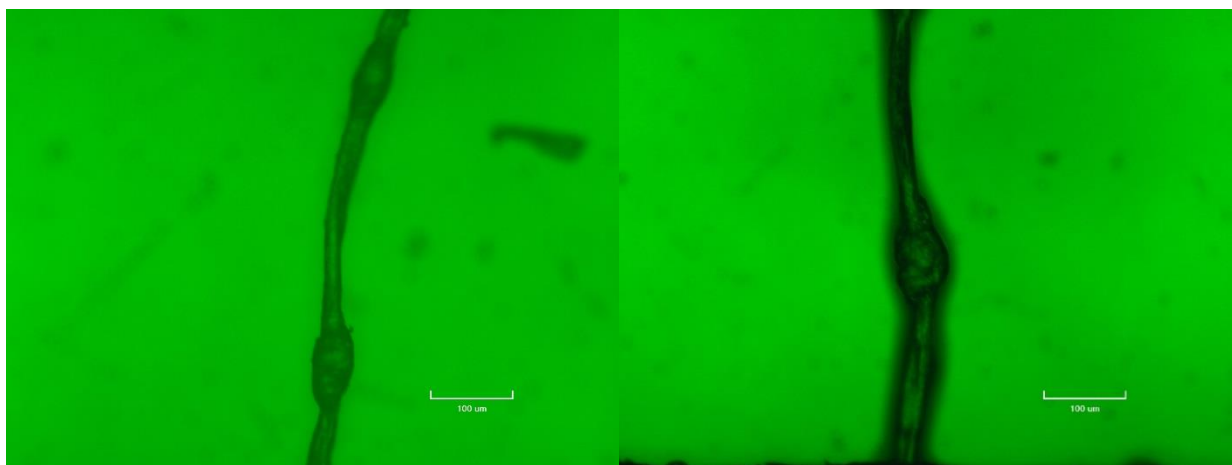**Figure 20 OM image of AA-5. In the left image it is in its dry state. The right image is after the fiber was submerged in water and removed afterwards.**

In Figure 21 SEM images of AA-4 (left) and AA-5 (right) are shown. They both have a rough polymer surface, AA-4 along the fiber and AA-5 only at the smaller coated regions. The surface structure observed was comparable with the surface structure obtained by Zhang.[1]
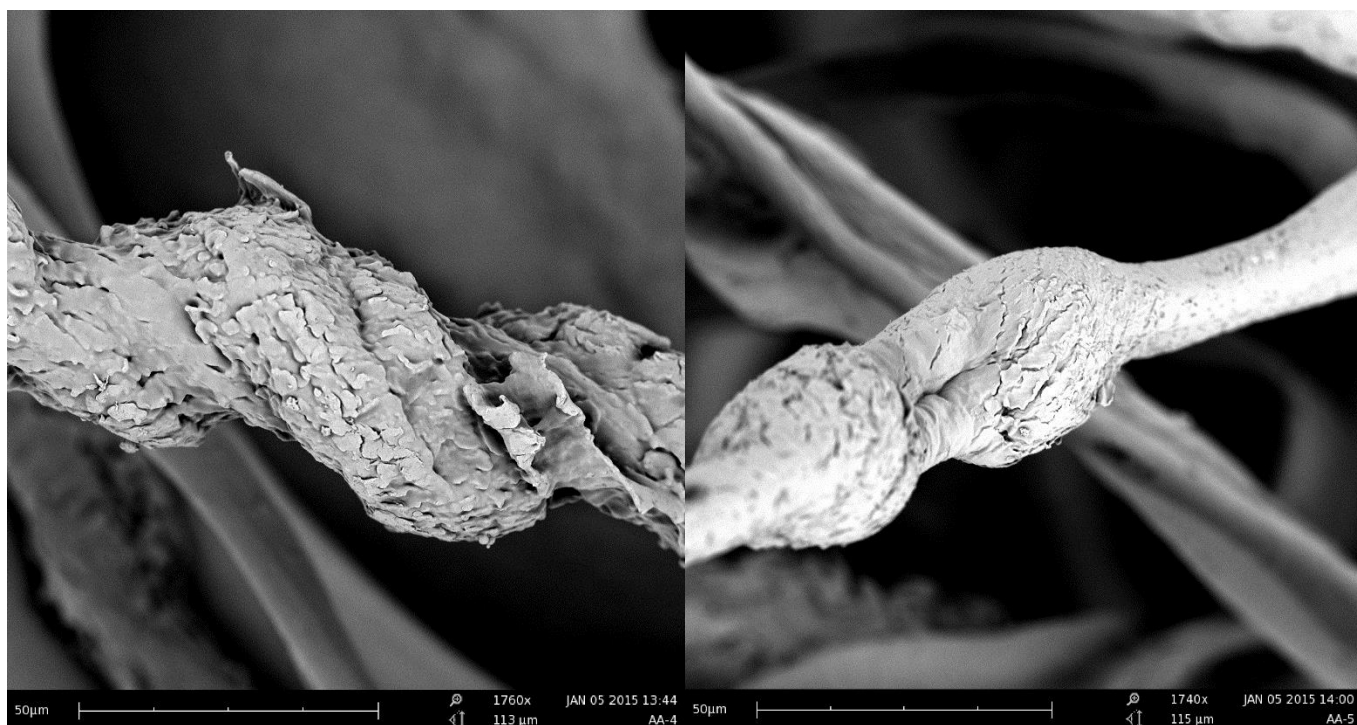
Figure 21 SEM images of AA-4 (left) and AA-5 (right).

4.2.4 ARGET ATRP of NIPAAm-SP

In the previous experiments it was shown that the polymerization of NIPAAm was possible in a MeOH/H$_2$O solution with a ratio of 3:1. In experiment AA-7 the monomer concentration is halved and a monomer ratio NIPAAm:SP-A of 99:1 is used. When the monomers were dissolved SP-A will gave the solution a darker blue color than without the SP-A. This indicates there could be some interaction with the copper in solution. When the ascorbic acid was added to the solution a red color appeared. This was probably due the isomerization of the SP-A to the MCH$^+$. As reference experiment AA-6 was also done without the SP-A (Table 2).

After the polymerization of AA-7 the cotton fibers with SP-A were colored orange. After purification by soxhlet this color was less but it remained orange. The fiber showed a weight increase of only 3%. The SEM images of the fibers showed some spots with polymer (Figure 22), which were identified before and after the soxhlet extraction. These spots are probably formed by solution polymerization. AA-6 also had a very low weight increase which indicates that there is hardly any polymer on the fiber.
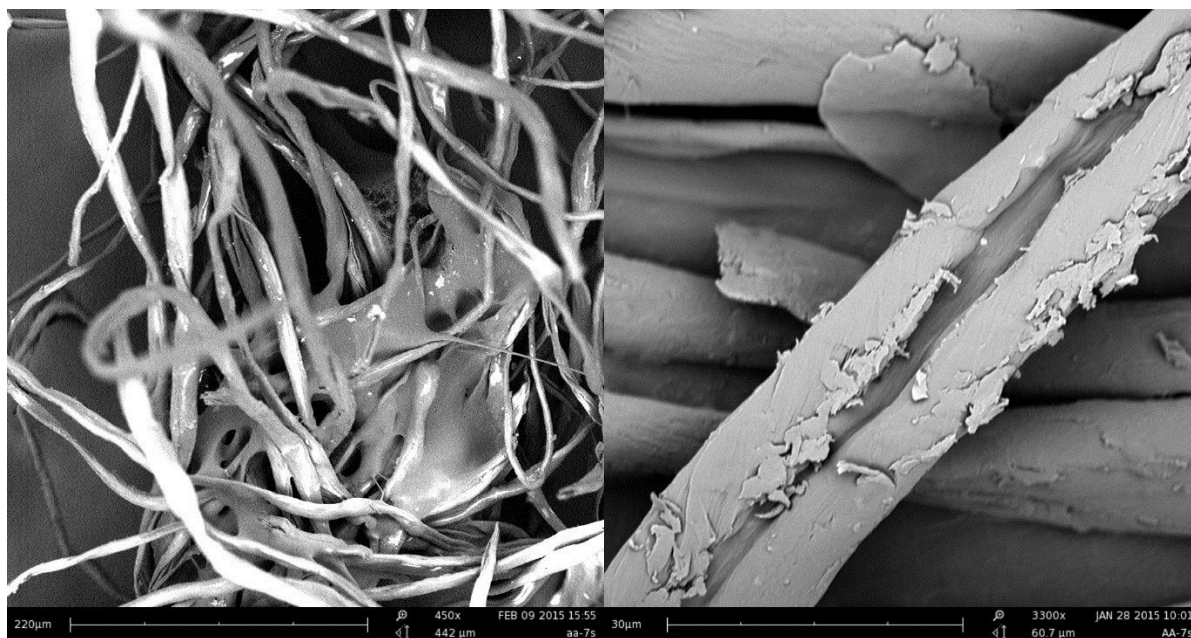
Figure 22 SEM image of AA-7.Left a lump of polymer is in between the fibers. This is probably solution polymerization. In the right image a cotton fiber with some grafted polymer is shown.

The XPS results of AA-6 and AA-7 showed similar O1s/C1s and N1s/C1S ratios (SI Table 4). Compared to bare cotton the O1s/C1s ratios decreased and the N1s/C1s ratios increased. The change in ratios show that the elemental composition on the surface of the fibers has changed. The small increase in weight is probably polymer.

4.2.5 ARGET ATRP of Sodium acrylate

In experiments AA-8 to AA-11 NIPAAm was copolymerized with protected AA. The reaction mixtures were neutralized by a 0,5 mol/L sodium hydroxide solution to deprotonate the AA. This was controlled by raising the pH above 7. Sodium chloride was also added to flood the AA with sodium ions. Apart from the addition of sodium hydroxide and sodium chloride, the reaction was carried out as previously described in paragraph 3.3.3.

AA-8 and AA-9 were performed with a 3:1 MeOH/H_2O solvent ratio and a 0,25 mol/L monomer concentration. AA-8 was done in pH 7 and AA-9 at slightly higher pH 10. After the reaction AA-8 and AA-9 had a weight increase of 10% and 2% respectively, the SEM images of AA-8 and AA-9 both showed fibers with smaller features as if they were damaged (Figure 23). It is not clear whether this was from polymer grafted from the surface or damages during the reaction (e.g. stirring), however, the fibers appear to be rougher than bare cotton fibers. Moreover ,although they are not completely covered, there are parts were polymer is definitely present.
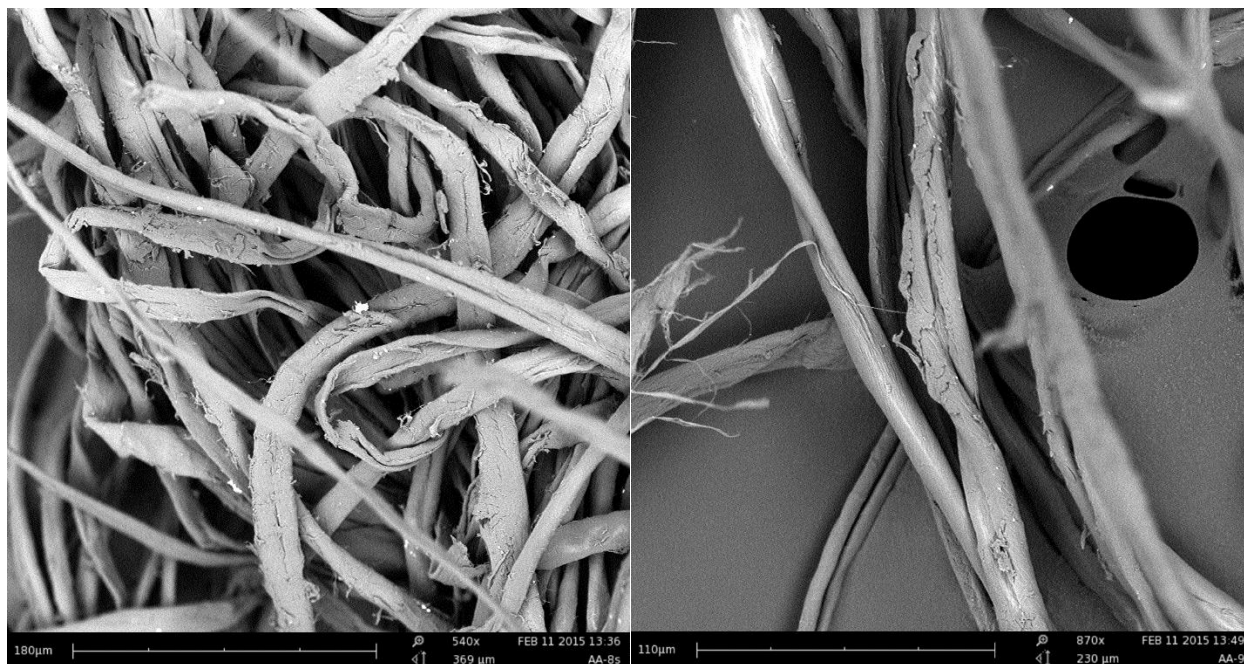
Figure 23 SEM images of AA-8 (right) and AA-9 (left). Both samples showed fibers covered with small strings as shown in the left. The right image shows some roughness what could be grafted polymer.

This was also shown by XPS (SI Table 4). The XPS spectra of the cotton fibers showed compared to bare cotton fibers a higher Ns1/Cs1 ratio but a lower Os1/Cs1 ratio which was as expected. There was also a trend for increasing weight increase because of the polymer, Os1/Cs1 decreases and Ns1/Cs1 increases. Compared to AA-4 were only NIPAAm was present, the spectra were comparable.

AA-10 and AA-11 were polymerized in a 3:1 and 1:1 MeOH/H_2O solvent respectively. Monomer concentration of 0,5 Mol/L was used. AA-10 has a weight increase of 23% and AA-11 of 126%. In Figure 24 two SEM images of AA-10 are shown and in Figure 25 two SEM images of AA-11 are shown. For both the left image is an overview and the right is enlarged on a fiber.
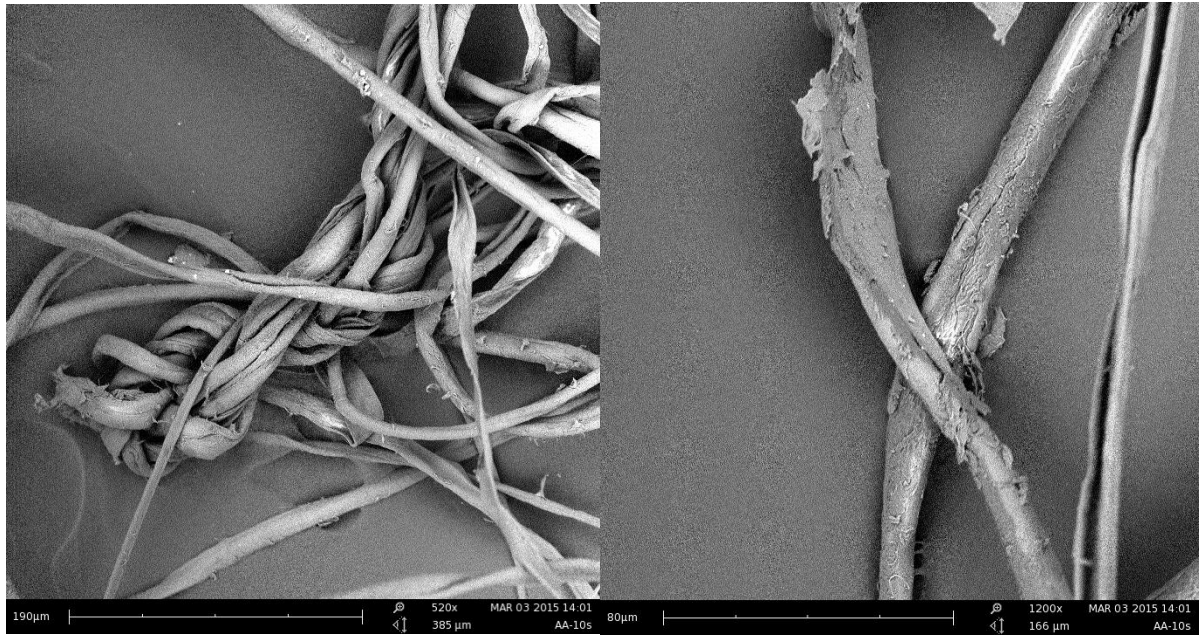
Figure 24 SEM images of AA-10. Left an overview and right is an enlarged fiber.
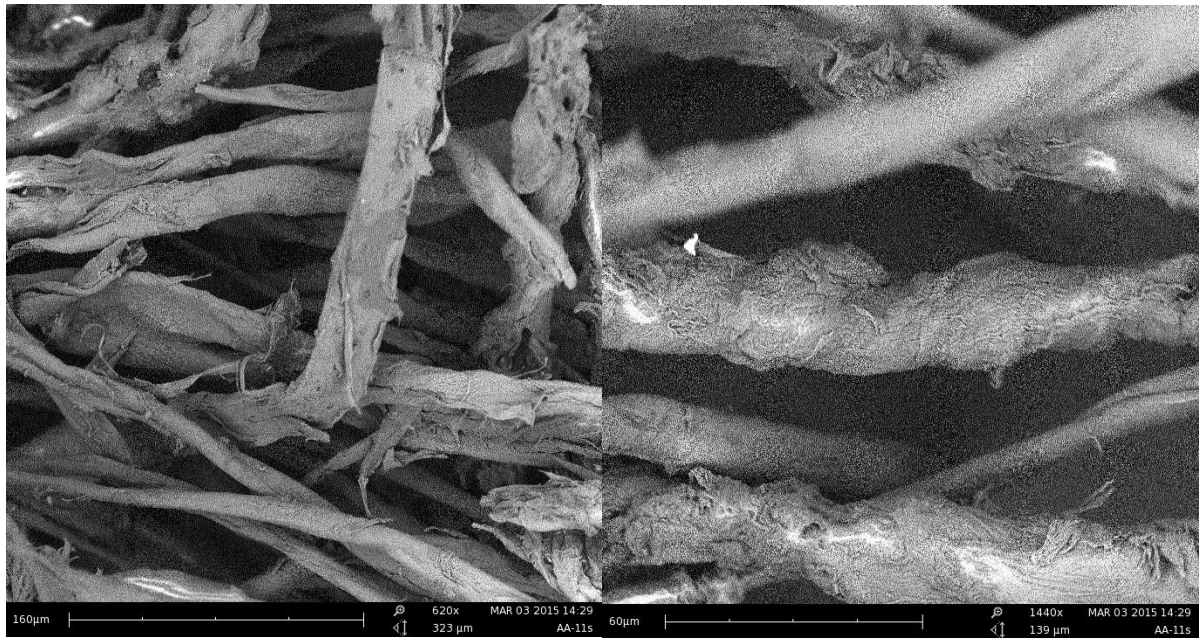

Figure 25 SEM images of AA-11. Left an overview and right is an enlarged fiber.

4.2.6 ARGET ATRP of NIPAAm-SP-Sodium acrylate

In the last AA-12 experiment NIPAAm was copolymerized with SP-A and sodium acrylate. Using the information obtained from previous reactions, a pH above 7, solvent ratio of 1:1 and a monomer concentration of 0,5 Mol/L was used (Table 2). Acrylic acid is in this environment deprotonated and protected by the sodium as described before. Hence, the SP-A is in its closed form. The solution was initially pH 5 and the red color of the MCH$^+$. When the pH was raised above 7, the color of the solution changed to blue. This is probably from the copper complex.

After the reaction the cotton obtained a blue color, which was probably due to the SP and copper on the cotton. After washing by soxhlet and water, the color of the cotton changed to orange. This indicates that the SP probably got protonated by the acrylic acid, as sodium was washed away.

Figure 26 shows the grafted polymer on the fiber. After extraction, a weight increase of 60% was obtained. AA-12 showed predominately fibers intermingled with polymer. The XPS experiments (SI Table 4) showed that the Os1/Cs1 and Ns1/Cs1 ratios were similar as the ratios of samples with NIPAAm-AA. This results show that there was polymer present on the fibers.
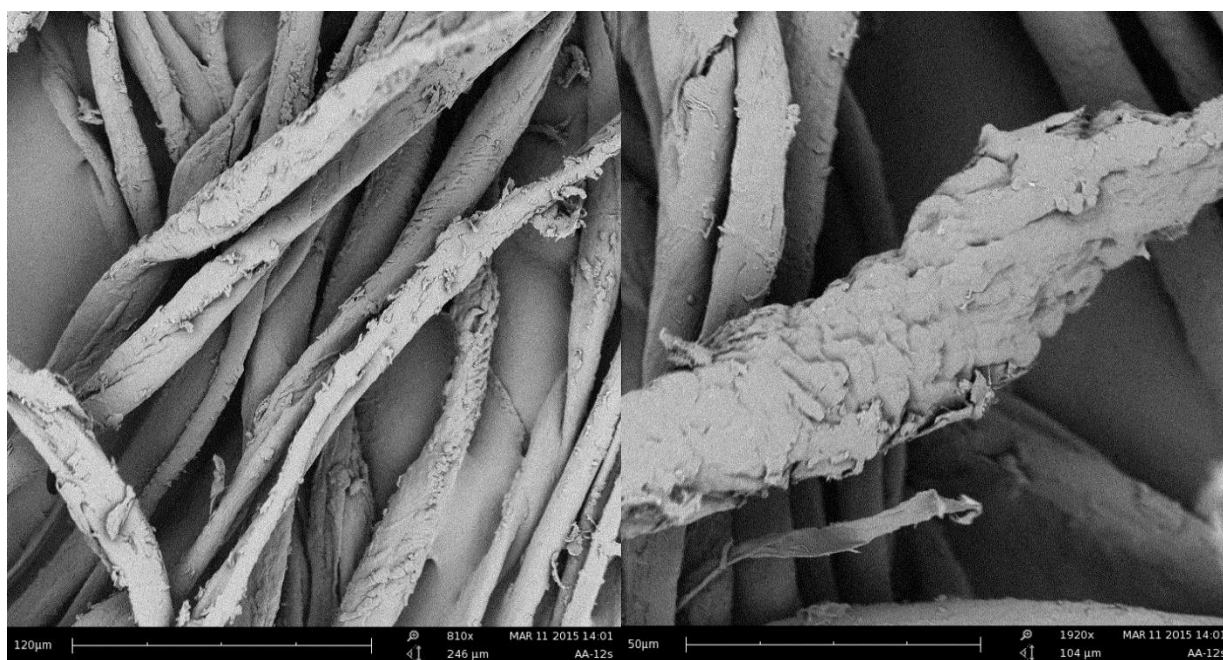

Figure 26 SEM images of AA-12. In the left image an overview is shown and in the right image the grafted polymer is visible in the fiber.

4.3 Water-uptake

To test the water uptake of the cotton fibers grafted with the polymers several experiments were done. These are described in the following sections. DSC was done to find the LCST. Water uptake experiments and the Linkham cell were used to see how much water could be absorbed and how much the fibers swell. With CA experiments the interaction between a water droplet and the fiber was examined.

4.3.1 DSC

To investigate were the critical transition temperature should be for the swelling and deswelling, DSC was done and the LCST was determined. Figure 27 shows the DSC graph of AA-4 were only PNIPAAm and the cotton are present. It shows an exothermic peak for the cooling cycle at 32°C, at this point hydrogen bonds with the water are broken and inter- and intra-molecular hydrogen bonds are formed. In the heating cycle an endothermic peak is found at 34°C, at this point the polymer breaks its inter- and intra-molecular hydrogen bonds and starts forming hydrogen bonds with the water. Similar LCST were also found by Yang[2] and Zhang[1].

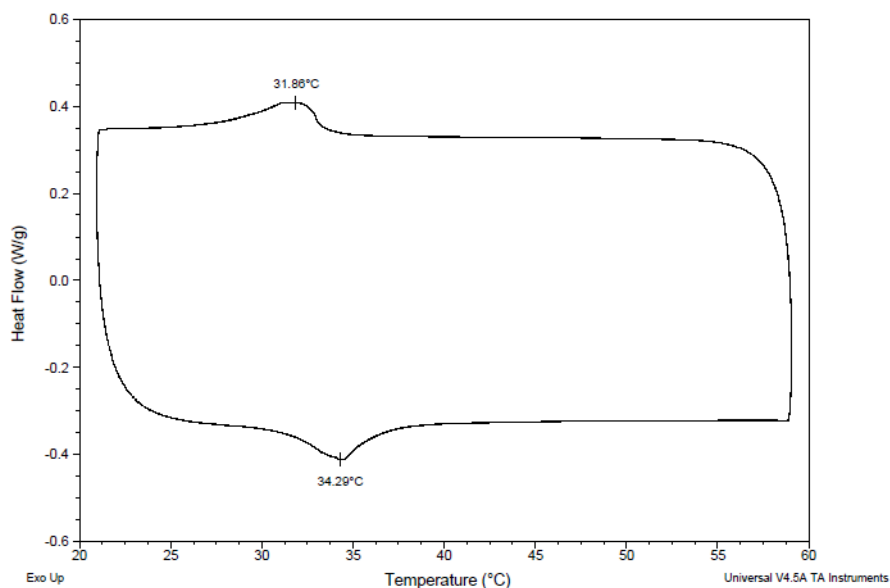**Figure 27 DSC result of AA-4**

AA-12 was also measured with DSC and shows similar result as AA-4. Its exothermic peak is found at 33°C and the endothermic peak is found at 34°C. In the dark DSC cup the MCH^+ and deprotonated AA might make the polymer more hydrophilic and could raise slightly the LCST. However the small increase in the temperature cannot be related to the increase in LCST temperature.
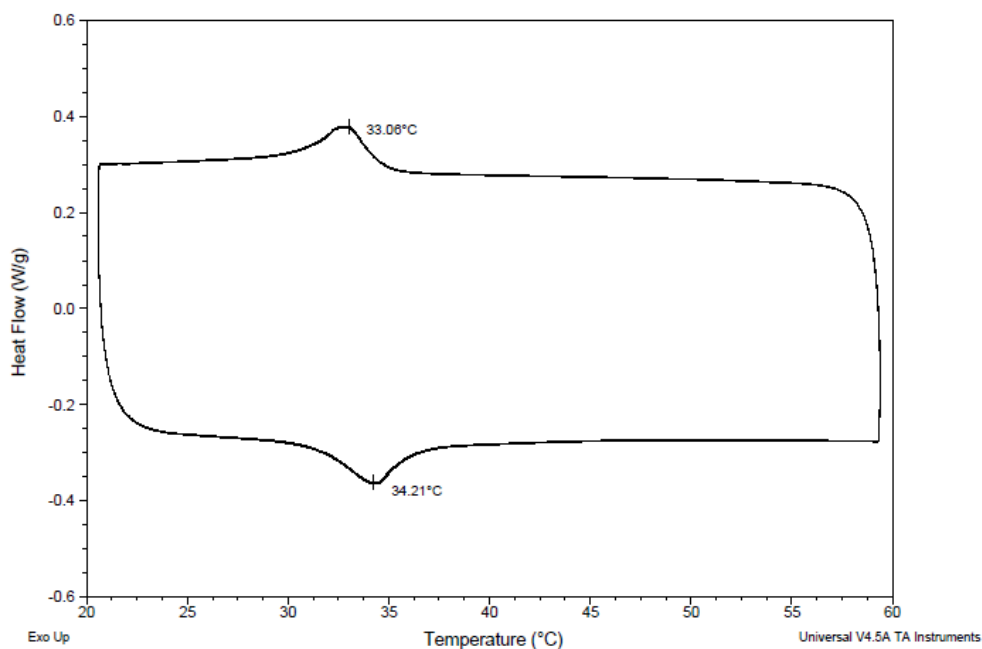
Figure 28 DSC results of AA-12

For AA-7 and AA-11, copolymerized with SP-A and AA respectively, the DSC graphs are shown in SI Figure 1 DSC results of AA-7 and SI Figure 2. The results show that AA-7 has no LCST. This is probably due to the low polymer content on the fibers. AA-11 showed only two small peaks, one exothermic peak at 32°C and an endothermic peak at 34°C. The AA should have raised the LCST a little because the polymer will become more hydrophilic. Just as in AA-12 this is not observed.

4.3.2 Weight increase

To investigate the water uptake of the polymers grafted from the cotton the weight increase was measured in different environments. The experimental set-up described in 3.2 is used to form a humid environment without direct water contact. With this method a relative humidity of 96% is reached,[2] and temperatures of 20°C and 40°C were used to test the temperature dependence of the polymer. The weight increase was determined by weighing the fiber before and after the water absorption. It was expected that the polymer would not absorb any water at temperature above the LCST. For the samples with the cotton, the cotton itself will absorb a percentage of water. Below the LCST the polymer and the cotton will both absorb water.

Polymer

In Table 6 the water uptake of the polymers prepared by ATRP is shown. Both polymers show a water uptake but at 20°C the FRP-2 has a higher water-uptake. At 40°C they both show a similar low water uptake.

Table 6 Water uptake of the polymers at 20C° and 40°C

Sample	20°C	40°C
FRP-1	20%	7%
FRP-2-C	25%	5%

4.3.2.1 *Cotton fiber*

The same experiment as above was also done with the samples from SI ARGET ATRP (Table 2). In Table 7 the results are shown. As reference a bare piece of cotton was also tested. In view of the long time needed for these experiments, only the most promising sample and the bare cotton were measured several times, the rest was only measured once. The water uptake of the bare cotton showed at 20°C an absorption of 30% of its own weight and at 40°C 15%. This implies that the cotton also released partially the water which was previously absorbed.

The samples with the highest weight increase (AA-4, AA-5, AA-11, and AA-12) show the highest water absorption at 20°C. The water uptake at 40°C is for these samples also a little higher as for the other samples. There is no significant difference between the different polymers which were grafted. The fibers grafted with NIPAAM, NIPAAm-AA and NIPAAm-SP-AA show a similar water uptake. This shows that the low amount of different monomer copolymerized do not influence significantly the amount of water that is absorbed or released.

There was a difference in weight increase observed between the samples made by FRP and SI ARGET ATRP. The polymers grafted of a surface had a higher weight increase at 20°C which could be due to the sponge-like structure what was observed by Yang.[2] At 40°C the sample prepared SI ARGET ATRP released less water. This is probably due to the water absorbed by the cotton fiber itself.

The samples previously made by Yang[2] increased in weight by 460% and collected 340%. It should be noted that these samples were prepared by ATRP (not ARGET ATRP). The reason for the lower water uptake by AA-4 is probably the lower polymer amount of polymer on the fibers. The water uptake above the LCST was 24% which is comparable with the polymers with the highest weight increase.

Table 7 Water uptake of the cotton fibers at 20C° and 40°C

Sample	20°C	40°C
AA-4	50%	24%
AA-5	40%	14%
AA-7	21%	11%
AA-8	23%	14%
AA-10	29%	13%
AA-11	44%	19%
AA-12	51% ±9%	15% ±9%
Bare cotton	30% ±7%	13% ±3%

4.3.3 Contact angle

Contact angle measurements were done on several samples. The samples with NIPAAm (AA-4), NIPAAm-SP (AA-7), NIPAAm-AA (AA-11) and NIPAAm-SP-AA (AA-12) are chosen. The experiments are performed in a humidity chamber with a temperature control unit. The experiments were done at 20°C and at 45°C in a relative humidity of 60%. The samples were also irradiated with light to investigate if the cotton would become more hydrophobic because of the isomerization from the MCH^+ to the SP. The contact angle of AA-12 was also measured at 65°C. For AA-12 the relative humidity was also varied to see if this would influence on the contact angle. The relative humidities used were 30% and 85%.

4.3.3.1 *Results CA*

The overall results of the CA measurements are shown in SI Table 1 and SI Table 2. AA-4 shows typical NIPAAm behavior. At 20°C the droplet gets absorbed by the cotton fiber. This changes when the temperature is increased above the LCST a CA of 115°. When AA-4 was irradiated with light, it did not change the hydrophobicity. The measurements of the CA for AA-11 were comparable with AA-4. In AA-11, AA is copolymerized which slightly lowers the CA of the sample because it is more hydrophilic.

AA-7 has SP copolymerized in the polymer. This changes the hydrophobicity of the fiber. At low and high temperatures the CA of water with this fiber was above 130°. The cotton fiber was much more hydrophobic than the other samples. This is probably due to the SP in the sample that is in its closed form. There is no acid to protonate to the MCH^+ form so in this polymer the SP is present. It is remarkable that despite the low polymer amount on the fiber, there is such a big influence in the contact angle. This fiber was also irradiated with visible light. This could only make the fiber more hydrophobic. It could be tried to irradiate this fiber with UV light so the SP will isomerize to the MC and will become more hydrophilic but this is out of the scope of this project.

AA-12 should be light and temperature responsive because NIPAAm, AA and SP-A are grafted from the cotton fiber. The CA measurements show similar result as found for AA-4. At 20°C the water got absorbed after several seconds and at 45°C stays for 30 seconds and then gets absorbed by the cotton fiber. These results are shown in Figure 29. There is no change observed after irradiation with light (Figure 30). At 65°C a contact angle over 100° is achieved in both light and dark conditions. This contact angle was stable over time. It could be that the polymer is not yet optimized for isomerization upon light. This is different as when it is in a hydrogel submerged in water. The MCH^+ which are present in the polymer might be isomerized to the SP but don't influence the polymer enough. Therefore different humidities were tested to see if this influenced the measurements. Relative humidities of 30% and 80% were tested but did not change the outcome of the measurements (SI Table 2), it was expected that light influenced the hydrophobicity of the fiber.

The CA was also tested on a pre-wet sample (SI Table 3). This was done by measuring right after another measurement. Because of the pre-wetting, fiber the new droplet was immediately absorbed by the cotton fibers, except at 65°C. These fibers did not absorb the water from the pre-wetting and always kept a stable and high CA.

The absorption of the water droplets after 30 seconds at 45°C is probably because the fibers are not completely covered by the polymer. Therefore there are spots were the fiber will be repelled (polymer), but after some time the bare cotton is reached and will absorb the water. At 65°C the water will be much less likely to be absorbed because the water will be evaporated quicker.
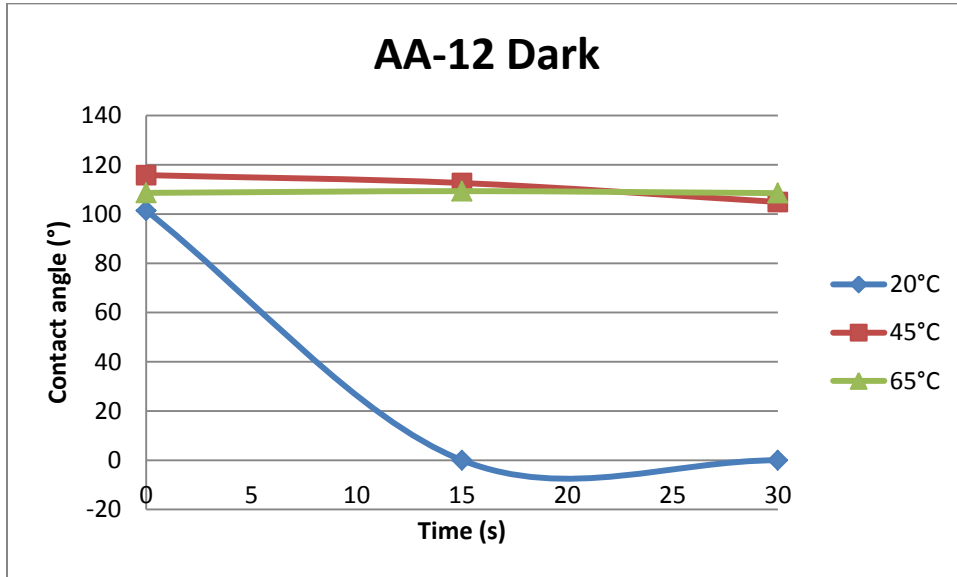

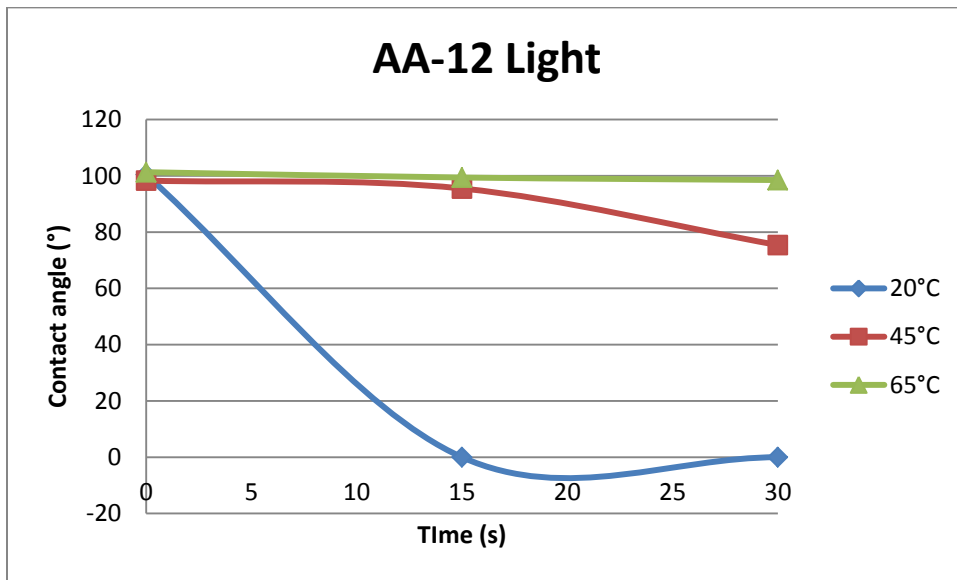**Figure 29 CA results of AA-12 in dark conditions and 60% RH.**

Figure 30 CA results of AA-12 in light conditions and 60% RH.

35

4.3.4 Linkham cell

To investigate the swelling and deswelling of the cotton fibers, fibers were observed by OM. Fibers were enclosed in a Linkam cell and submitted to different temperatures and humidity levels. First the temperature of the Linkham cell was lowered to 16°C to condense the water from the humid air onto the stage. The temperature was raised to 50°C with a rate of 1°C/min to let the fibers deswell. Zhang[1] showed that at low heating rates (2°C/min) the diameter of the fiber started decreasing at 21°C. 3 different spots were measured for AA-4 and AA-12 in dark and light conditions. It should be noted that also during the dark measurements the light from the microscope was used.

The thickest fiber of AA-4 was ≈140 μm when fully swollen at 16°C (fiber (1) in Figure 31). The graph shows the thickness measured on the 3 different spots. After the temperature reaches 24°C the fiber starts the Deswell. In Figure 31 the thickness of the fibers is plotted against the temperature. The fibers were also irradiated with light to see if this changed the deswelling. This shouldn't be because there is only PNIPAAm in this sample. In the graph of Figure 31 it is shown that the thickness and temperature when the fiber starts to deswell are the same.
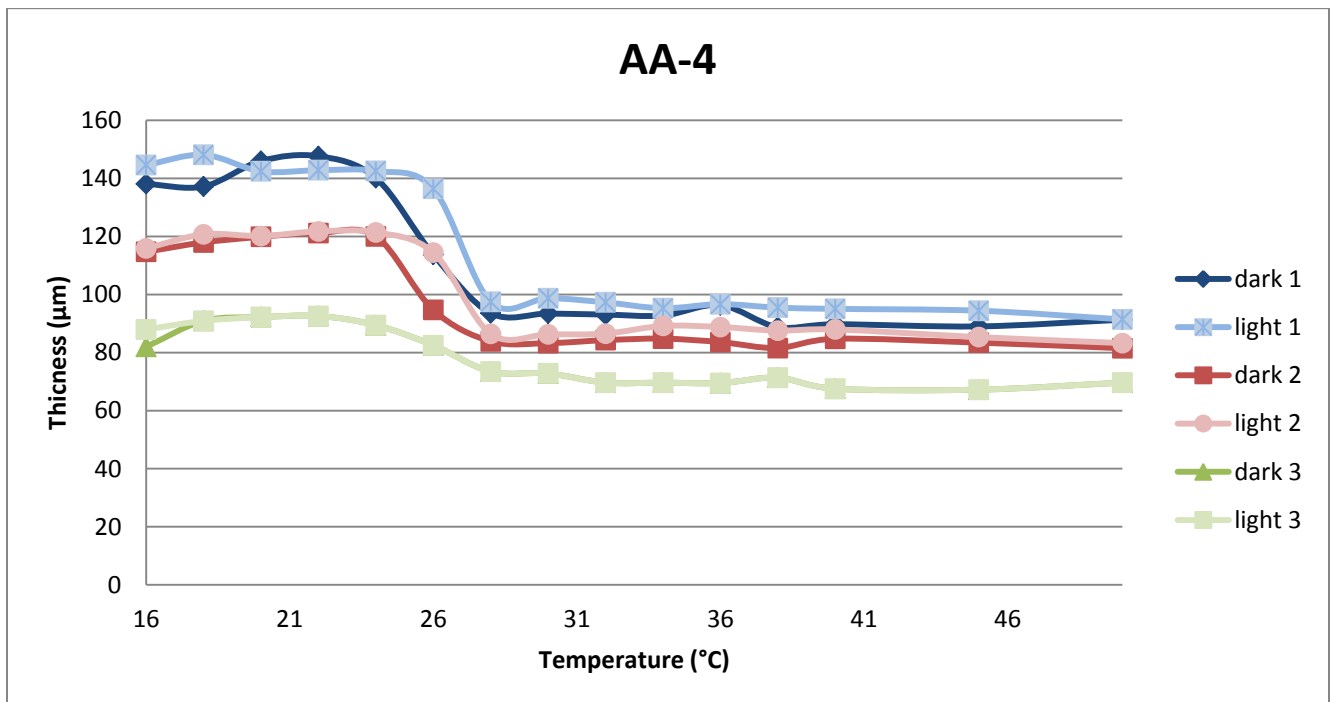

Figure 31 Results of AA-4 with the Linkham cell. The size of the fibers was investigated in a humid atmosphere under the influence of temperature and light.

These experiments were also performed for AA-12 of what the fiber are coated with PNIPAAm-SP-AA. The results of this experiment are shown in Figure 32. This fiber should show the same properties as AA-4 but it should release the water under influence of light. The fibers showed a small decrease in size when the temperature decreases but this is harder to distinct than for AA-4 because the sizes of the fibers are also much smaller. The thickest fiber (1) showed under radiation of light a small thickness as in the dark but for the other fibers this was not observed. This could be because of the change in thickness is too small because there is not enough polymer.
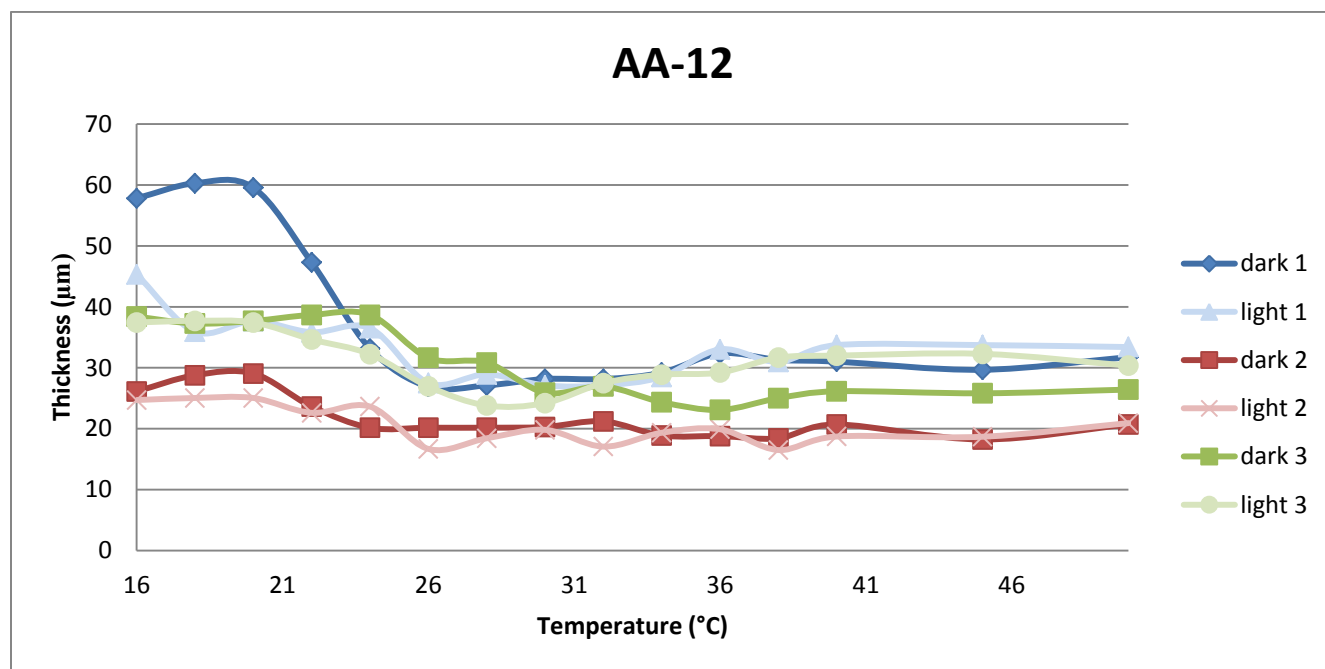

Figure 32 Results of AA-12 with the Linkham cell. The size of the fibers was investigated in a humid atmosphere under the influence of temperature and light.

5 Conclusion and future work

Polymers were made via FRP and ARGET ATRP. The FRP-2 showed no attachment on the cotton fiber. Both polymers made by FRP showed low water uptake at 20°C (25%) and released a big part of it at 40°C.

The polymerization of NIPAAm by ARGET ATRP was performed with no problems and done according the work of Zhang.[1] The polymerization of SP and AA by ARGET ATRP gave some troubles. SP did not dissolve in the solvent and AA poisons the catalyst. It is tried to find a solvent ratio with more MeOH, because SP does dissolve in solvents with a higher MeOH amount, but the weight increase was much lower. The polymers made by ARGET ATRP had the highest weight increase in a MeOH/H_2O solvent with a ratio of 1:1. AA was protected by NaOH to form sodium acrylate. This monomer is in a raised pH stable and won't poison the catalyst. This is combined with the polymerization of SP which is in its closed form when in a raised pH. This way the MCH$^+$ can't form a complex with the copper which is also an advantage. AA-12 which contained the monomers NIPAAm-SP-AA was made with this method with a weight increase of 60%. It was important for this reaction to control the pH. Over time the ascorbic acid formed protons during the reaction. But when it is kept above pH 7 the AA will be protected and the SP remains closed. OM and SEM showed that polymer was present on the fibers. The main difference between the two fibers was that AA-4 showed more self-standing fibers with polymer attached. With AA-12 these were less common and it was harder to extract a self-standing fiber with polymer because the woven fiber were intermingled with polymer.

The interaction of the water with the sample and the water uptake is tested with DSC, water uptake experiments, CA and Linkham cell. The DSC results from the AA-4 (NIPAAm) showed the same results as the DSC graphs from Yang[2] and Zhang.[1] The results of AA-12 (NIPAAm-SP-AA) showed similar results as AA-4. This means that the monomers which are copolymerized do not significantly change the LCST of the polymer. Also the graph of AA-11 (NIPAAm-AA) doesn't show an increase in the LCST temperature. Probably 5% AA does not introduce enough hydrophilic groups to increase the LSCT or to let it disappear.

The water uptake experiments show form AA-4 and AA-12 similar results. At 20°C 50% water uptake is obtained. This is lower as Yang[2] whom obtained 340% weight increase. The water uptake above the LCST is comparable with the water uptake of Yang[2]. Probably the lower polymer amount on the fiber is the reason for the lower water uptake of the fiber.

The CA measurements of AA-4 and AA-12 show similar results as the result form Zhang. At 20°C the water droplet is immediately absorbed by the cotton fibers. At 45°C first hydrophobic contact angles are obtained and after 30 second the droplet gets absorbed by the cotton fiber. This is probably because the cotton fiber is not completely covered by the polymer. After 30 seconds the water get absorbed by the bare cotton fiber. At 65°C a stable high contact angle was obtained for AA-12. This is probably because the cotton is water get repelled more by the sample.

With the Linkham cell AA-4 and AA-12 are tested. AA-4 shows a deswelling around 26°C the same as the sample of Zhang showed. No influence of light was observed with this measurement. AA-12 was also

tested and showed a very small decrease in size. AA-12. On these fiber less polymer was found on the fibers this can be concluded from the size from the swollen and deswollen fibers. To draw further conclusions fibers with more polymer are necessary to see the big size reduction of the fibers.

5.1 Recommendations on future work

The fiber which Yang obtained by regular ATRP had a higher weight increase by polymer than obtained in this research or by Zhang. Because of the higher polymer amount much more water was absorbed by Yang. To obtain an equal water uptake for the light and temperature responsive fiber this polymer amount should also be increased. Therefore it should investigated if it is possible for this system to obtain such high polymer content. Therefore the polymerization has to be optimized even more.

Also the composition of the monomers could be optimized for water absorption from the air. Ziółkowski[12] showed the best swelling properties for a hydrogel in water. This might not be optimal for swelling the polymer with water from the air.

To optimize the water uptake experiments the temperature need to be controlled better. For the CA experiments this could be done by using a temperature controlled chamber instead of a temperature controlled stage. The control of the humidity in the Linkham cell can also be optimized by measuring the humidity inside the chamber. When the temperature is measured outside the chamber in a different temperature, the measured humidity is not correct.

6 Acknowledgement

7 References

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Supporting Information
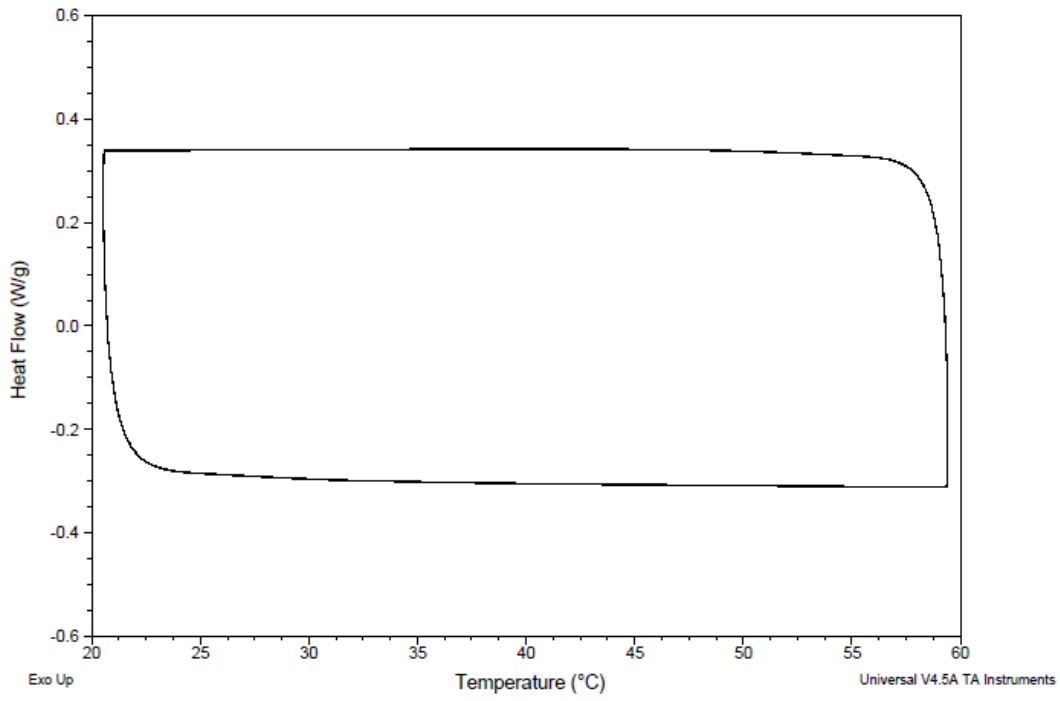
SI Figure 1 DSC results of AA-7
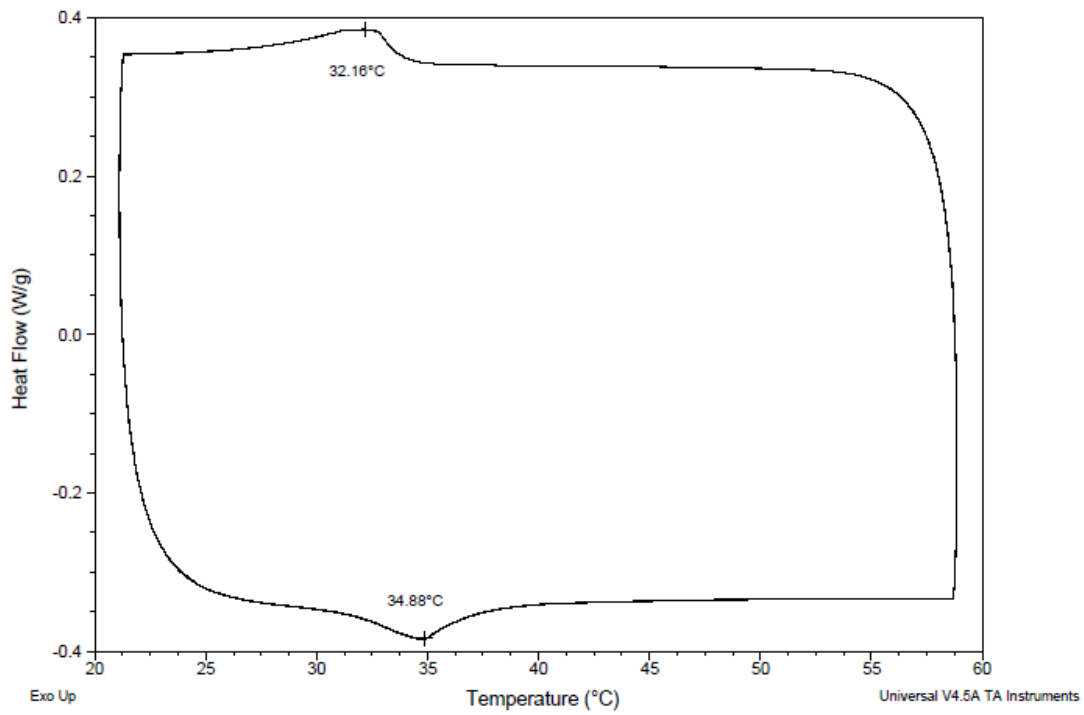
SI Figure 2 DSC results of AA-11

SI Table 1 Result CA of AA-4, AA-7 and AA-11

Sample	time (s)	20°C Dark	45°C Dark	20°C Light	45°C Light
AA-4	0	101,7	116,35	114,45	114,45
	15	30,3	114,4	114,1	114,1
	30	0	111,4	113,5	113,5
AA-7	0	132,9	132,7	133,55	133,55
	15	132,3	132,45	133,7	133,7
	30	132,1	132,25	133	133
AA-11	0	78,7	115	120,1	120,1
	15	42,1	112,75	116,95	116,95
	30	0	111	112,3	112,3

SI Table 2 Results CA of AA-12. CA measured at 20°C, 45°C and 65°C in a RH of 30% 60% and 80%

Sample	time (s)	20°C Dark	45°C Dark	65°C Dark	20°C Light	45°C Light	65°C Light
AA-12	0	0	114,6	113,95	41,1	79,25	120,05
RH 30	15	0	105,4	112,65	0	0	119
	30	0	0	111	0	0	114,75
AA-12	0	101,5	115,8	108,6	100,4	98,3	101,3
RH 60	15	0	112,6	109,3	0	95,5	99,4
	30	0	104,9	108,5	0	75,4	98,5
AA-12	0	106,1	108	106,9	121,45	0	123,55
RH 80	15	0	105,85	105,6	0	0	123,5
	30	0	101,75	104,8	0	0	123,25

SI Table 3 CA of AA-12 after pre-wetting.

Sample	time (s)	20°C Dark	45°C Dark	65°C Dark	20°C Light	45°C Light	65°C Light
AA-12	0	0	74,1	96,3	0	38,3	106,7
RH 60	15	0	0	94,95	0	0	110,05
	30	0	0	93,6	0	0	108,3

SI Table 4 The ratios of O1s/C1s and N1s/C1s obtained from XPS.

	Ratio Os1/Cs1	Ratio Ns1/Cs1
bib	0,611953	0,001925
bare	0,394051	0,022376
AA-4	0,160011	0,098869
AA-5	0,177519	0,13525
AA-6	0,222055	0,083257
AA-7	0,201231	0,064169
AA-8	0,338674	0,091516
AA-9	0,42772	0,083992
AA-10	0,220951	0,125286
AA-11	0,209507	0,121892
AA-12	0,217381	0,097099