

# Fabrication of Thermo-responsive Cotton Fabrics Using Poly(vinyl caprolactam-co-hydroxyethyl acrylamide) Copolymer

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## Abstract

A thermo-responsive polymer with hydrophilic to hydrophobic transition behavior, poly(vinyl caprolactam-co-hydroxyethyl acrylamide) (P(VCL-co-HEAA)), was prepared by copolymerization of vinyl caprolactam and N-hydroxyethyl acrylamide via free radical solution polymerization. The resulting copolymer was characterized by Fourier transform infrared spectroscopy (FTIR), <sup>1</sup>H nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The lower critical solution temperature (LCST) of P(VCL-co-HEAA) was determined at 34.5°C. This thermo-responsive polymer was then grafted onto cotton fabrics using 1,2,3,4-butanetetracarboxylic acid (BTCA) as crosslinker and sodium hypophosphite (SHP) as catalyst. FTIR and energy dispersive X-ray spectroscopy (EDS) studies confirmed the successful grafting reaction. The modified cotton fabric exhibited thermo-responsive behavior as evidenced by water vapor permeability measurement confirming decreased permeability at elevated temperature. This is the first demonstration that a PVCL based copolymer is grafted to cotton fabrics. This study provides a new thermo-responsive polymer for fabrication of smart cotton fabrics with thermally switchable hydrophilicity.

Keywords: thermo-responsive polymer, poly(vinyl caprolactam) (PVCL), LCST, water vapor permeability, smart cotton fabric

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## 35 **1. Introduction**

36 Cotton fabrics have many desirable properties, which include high absorbency, comfort,  
37 dyeability and low cost. Cotton consists of nearly 99% cellulose and the hydroxyl groups  
38 (-OH) available on the cellulose backbone have been used in variety of modification  
39 strategies to impart a new functionality to cotton fabric, such as wrinkle resistance and  
40 antimicrobial properties. In recent years, an emerging modification strategy has been  
41 centered on grafting stimuli-responsive polymer materials onto cellulose-based natural  
42 fibers to create materials that can respond to changes (temperature, pH or light) in the  
43 environment (Stuart et al., 2010; Yang, Esteves, Zhu, Wang, & Xin, 2012). A particular  
44 research interest is creation of thermo-responsive smart textiles with potential  
45 applications in skin care products, wound dressing products, smart permeability,  
46 deodorant fabrics, reversible wettability and physiological parameter monitoring (Hu,  
47 Meng, Li, & Ibekwe, 2012).

48 Thermo-responsive or temperature-sensitive polymers are a kind of smart materials that  
49 respond to changes in temperature and undergo a phase transition at the lower critical  
50 solution temperature (LCST) (De Las Heras Alarcón, Pennadam, & Alexander, 2005). At  
51 temperatures below LCST, these macromolecules are hydrophilic and soluble in water  
52 due to the dominant hydrogen bonding between hydrophilic segments of the polymer  
53 chain and water molecules. Alternatively, at temperatures above LCST, these  
54 macromolecules become hydrophobic and phase separate in water due to the strengthened  
55 hydrophobic interactions among hydrophobic segments (Ivan M Okhapkin, Irina R  
56 Nasimova, Elena E Makhaeva, & Alexei R Khokhlov, 2003; Qiu & Park, 2001). While  
57 most polymers increase their water solubility as the temperature increases, polymers with  
58 an LCST decrease their water solubility as the temperature increases.

59 Poly (N-isopropylacrylamide) (PNIPAm) and poly(vinyl caprolactam) (PVCL) are  
60 attractive thermoresponsive polymers with LCST in the range of physiological  
61 temperature, a property which makes them especially attractive for potential use in drug  
62 delivery, biochemistry, bioengineering or sensors (Bae, Okano, Hsu, & Kim, 1987;  
63 Schmaljohann, 2006). Although PNIPAm has been more widely studied, the use of PVCL

64 is a better alternative for bioapplications due to its higher biocompatibility (Cortez-Lemus  
65 & Licea-Claverie, 2016).  
66 Grafting of PNIPAAm to cotton fabrics has already been reported by a few authors (T.  
67 Chen, Fang, Zhong, Chen, & Wang, 2015; Wang et al., 2016). However, to our  
68 knowledge, this is the first demonstration that a PVCL based copolymer is used to  
69 manufacture smart fabrics. In this study, we synthesize and immobilize thermo-  
70 responsive copolymer poly(vinyl caprolactam-co-hydroxyethyl acrylamide), P(VCL-co-  
71 HEAA), onto cotton to obtain thermally switchable hydrophilicity. Hydroxyethyl  
72 acrylamide (HEAA) is used as co-monomer in order to add –OH functional groups to the  
73 copolymer. These –OH groups are able to graft the copolymer to cotton fabrics via a  
74 carboxylic acid-based crosslinker (BTCA). Furthermore, it should be noted that PHEAA  
75 is also biocompatible and has been widely used for biomedical applications (Zhang, Chu,  
76 Zheng, Kissel, & Agarwal, 2012). The properties of the copolymer are characterized by  
77 FTIR, <sup>1</sup>H NMR, GPC, DSC and TGA. The lower critical solution temperature (LCST) is  
78 also determined. FTIR and EDS studies are conducted to confirm the grafting reaction,  
79 and scanning electron microscopy (SEM) is used to study the surface morphology of  
80 modified cotton. Additionally, the thermo-responsive behavior of the resulting cotton  
81 fabric is investigated through water vapor permeability measurement.

82

## 83 **2. Experimental**

### 84 **2.1 Materials**

85 Standard desized, scoured, and bleached plain woven cotton fabrics (density 110 g/m<sup>2</sup>)  
86 were purchased from Testfabrics, Inc.. Vinyl caprolactam (VCL), 2,2'-azobis(2-methyl-  
87 propionitrile) (AIBN), dimethyl formamide (DMF), diethyl ether, 1,2,3,4-  
88 Butanetetracarboxylic acid (BTCA), and sodium hypophosphite monohydrate (SHP)  
89 were all purchased from Sigma Aldrich. N-(2-Hydroxyethyl) acrylamide (HEAA) was  
90 supplied by Santa Cruz Biotechnology. Deuterium oxide (D<sub>2</sub>O) was purchased from  
91 Cambridge Isotope Laboratories, Inc.. All chemicals were used as received without  
92 further purification.

## 93 **2.2 Synthesis of P(VCL-co-HEAA) copolymer**

94 P(VCL-co-HEAA) copolymer was synthesized by copolymerizing vinyl caprolactam  
95 (VCL) and hydroxyethyl acrylamide (HEAA) via free radical polymerization using AIBN  
96 as initiator and DMF as solvent. Reactions were performed in a three neck round bottom  
97 flask equipped with a reflux condenser and a N<sub>2</sub> inlet. The initial feed molar ratio of VCL  
98 to HEAA was 80:20. First, HEAA (16.10g, 140 mmol), VCL (77.84 g, 560 mmol) and  
99 DMF (345 mL) were added to the flask. The temperature was increased to 60 °C and the  
100 reaction mixture was stirred for 15 minutes under N<sub>2</sub> flow until all components were  
101 completely dissolved. Then, AIBN initiator (0.57 g, 3.5 mmol) was thoroughly dissolved  
102 in 5 mL of DMF and then injected into the flask to start the polymerization. The reactions  
103 were performed at 60°C for 16 hours under continuous N<sub>2</sub> flow. Polymerization was  
104 stopped by cooling down the reaction to room temperature. Afterwards, the polymer was  
105 precipitated in diethyl ether, filtered and dried in a vacuum oven at 50 °C overnight.

## 106 **2.3 Characterization of P(VCL-co-HEAA) copolymer**

### 107 2.3.1 <sup>1</sup>H Nuclear magnetic resonance (NMR)

108 The <sup>1</sup>H-NMR experiment of the copolymer was recorded at room temperature with an  
109 INOVA 400 spectrometer operating at 400 MHz and using D<sub>2</sub>O as solvent.

### 110 2.3.2 Gel permeation chromatography (GPC)

111 The molecular weight of the P(VCL-co-HEAA) copolymer was measured by a Waters  
112 ambient-temperature GPC equipped with a Waters 1515 isocratic HPLC pump and a  
113 Waters 2414 refractive index detector at 50°C. Dimethyl formamide (DMF) with 0.1%  
114 lithium bromide was used as mobile phase at a flow rate of 0.5 mL/min. The obtained  
115 molecular weight value was referred to polystyrene standards.

### 116 2.3.3 Thermogravimetric analysis (TGA)

117 Thermogravimetric analysis (TGA) of the P(VCL-co-HEAA) copolymer was performed  
118 from 30 to 800°C at a heating rate of 10°C /min using a nitrogen purge on TGA Q500,  
119 TA Instruments.

### 120 2.3.4 Differential scanning calorimetry (DSC)

121 Thermogram of the copolymer was acquired with a TA instruments DSC Q2000. The

122 procedure included a heat/cool/heat sequence at a rate of 10°C/min in the temperature  
123 between 0°C and 300°C to remove any effect of thermal history.

#### 124 2.3.5 Lowest critical solution temperature (LCST)

125 The lower critical solution temperature (LCST) of P(VCL-co-HEAA) in aqueous solution  
126 was measured on a Spectramax 384 spectrophotometer. Optical transmittance of 1 wt %  
127 polymer solution in water was measured at 500 nm as a function of temperature. The  
128 LCST value of the polymer was determined at the temperature showing an optical  
129 transmittance of 50%.

### 130 **2.4 Grafting of P(VCL-co-HEAA) to cotton fabrics**

131 Grafting of P(VCL-co-HEAA) to cotton fabrics was performed using BTCA as  
132 crosslinker and SHP as catalyst. A solution was prepared with 250g/L, 20g/L, and 30g/L  
133 concentrations of P(VCL-co-HEAA), BTCA, and SHP, respectively. Each cotton sample  
134 was soaked in the solution overnight at room temperature and then padded in a laboratory  
135 padder with two dips and two nips to reach a wet pickup of (120±5)%. The sample was  
136 dried at 85°C for 10 min and then cured in an oven at 160°C for 20 min. Finally, the  
137 sample was rinsed with deionized water and air-dried in a conditioning room  
138 (21.0±2.0°C, 65.0±4.0% relative humidity) for 24 h.

### 139 **2.5 Characterization of thermo-responsive cotton fabrics**

#### 140 2.5.1 Add-on

141 The weight of the conditioned cotton fabrics was recorded before and after the grafting  
142 process. The add-on of the thermo-responsive cotton fabrics was calculated as the relative  
143 weight increase of the fabric as shown in the following equation.

$$144 \text{ Add-on (\%)} = \left( \frac{m_f - m_0}{m_0} \right) \times 100 \quad (1)$$

145 where  $m_0$  is the initial weight of the fabric and  $m_f$  is the final weight of the fabric grafted  
146 with P(VCL-co-HEAA).

#### 147 2.5.2 FTIR

148 The Fourier transform infrared (FTIR) spectra of cotton fabrics were collected on a FTIR  
149 spectrometer (Magna 560, Nicolet Instrument Technologies, Fitchburg, WI, USA) using

150 a diamond attenuated total reflectance (ATR) accessory. The data were averaged over 64  
151 scans with a resolution of  $4\text{ cm}^{-1}$  in the range of  $4000$  to  $600\text{ cm}^{-1}$  for each sample.

#### 152 2.5.3 SEM-EDS studies

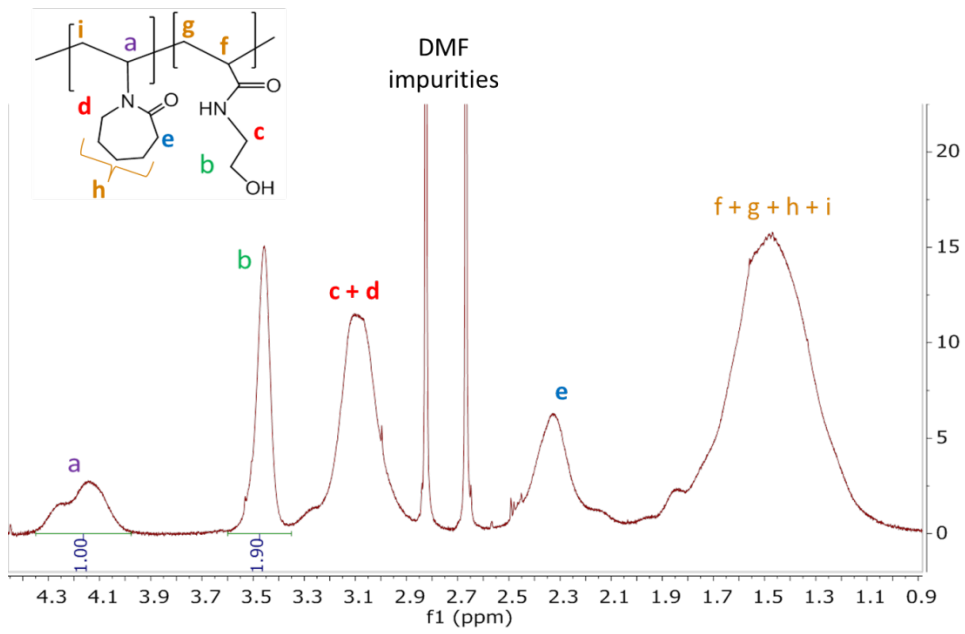
153 The surface morphology of cotton fabrics was examined on a field emission scanning  
154 electron microscope (LEO 1550 FESEM). The samples were mounted on aluminum stubs  
155 and sputter-coated with gold and scanned at 5 kV for SEM imaging. Energy dispersive  
156 X-ray spectroscopy (EDS) study was conducted to analyze the elemental compositions of  
157 cotton fabrics after grafting with P(VCL-co-HEAA) copolymer.

#### 158 2.5.4 Water vapor permeability (WVP) measurements

159 Water vapor permeability of the modified cotton fabrics was measured in accordance with  
160 BS 7209:1990 Test Method. Briefly, the test cotton fabric was sealed over the open mouth  
161 of a test dish which contains water, and the assembly placed in a controlled atmosphere.  
162 Over a period of time, successive weightings of the assembled dish were made and the  
163 rate of water vapor permeation through the test fabric was determined. Six test fabrics  
164 (three for treated samples and three for untreated samples) were tested in a similar manner  
165 and concurrently to determine WVP at room temperature ( $21^{\circ}\text{C}$ ) and also at  $50^{\circ}\text{C}$ .

### 166 **3. Results and discussion**

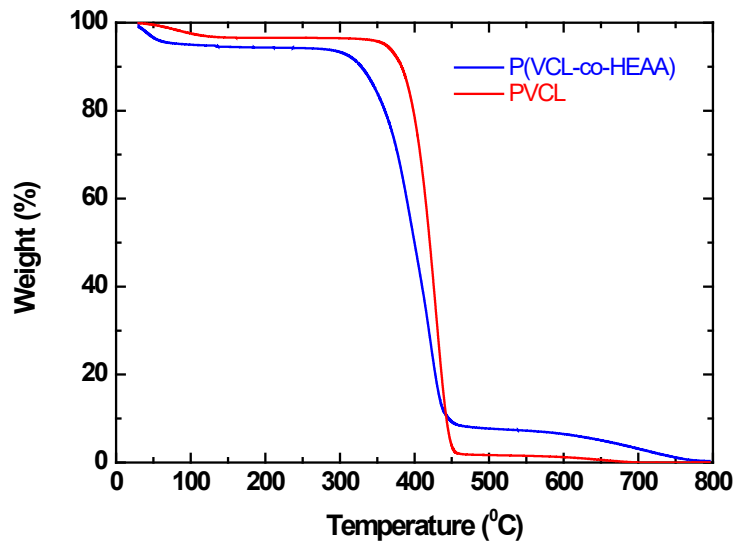
#### 167 **3.1 Synthesis and characterization of P(VCL-co-HEAA) copolymer**



168

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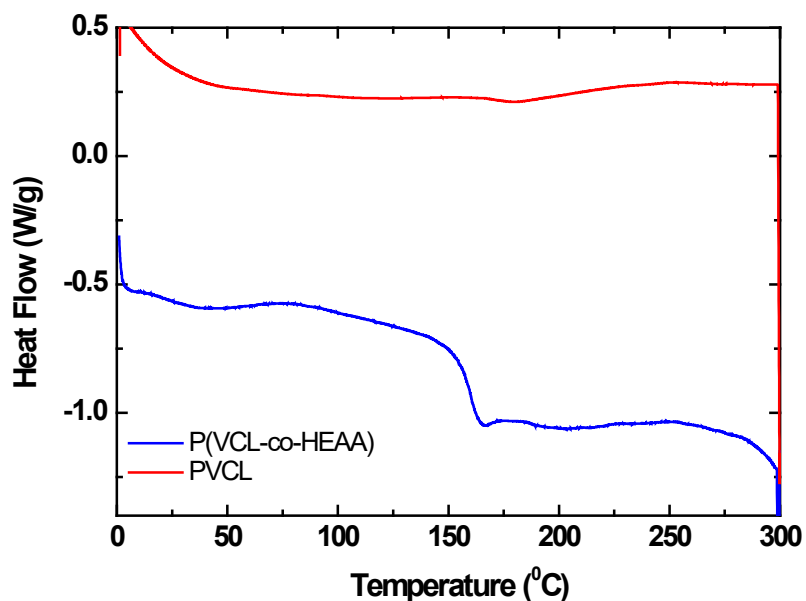
Figure 1.  $^1\text{H-NMR}$  of P(VCL-co-HEAA) copolymer



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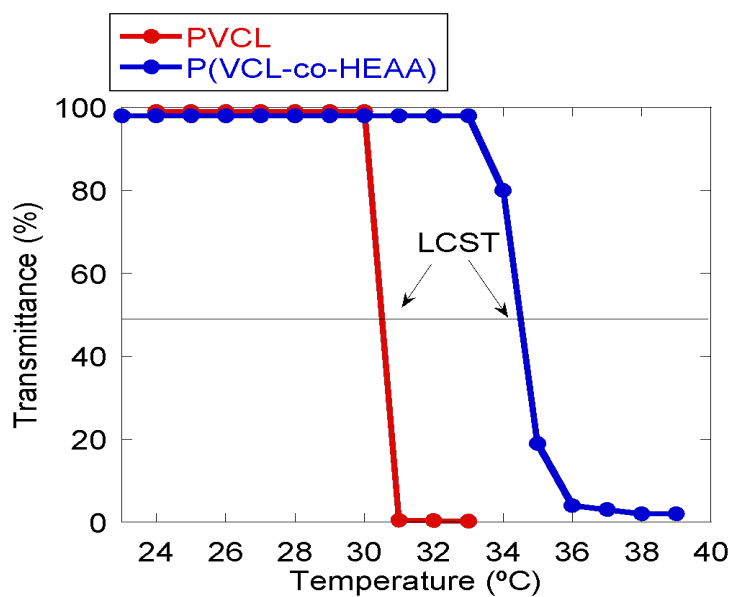
(a)



172

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(b)



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175

(c)

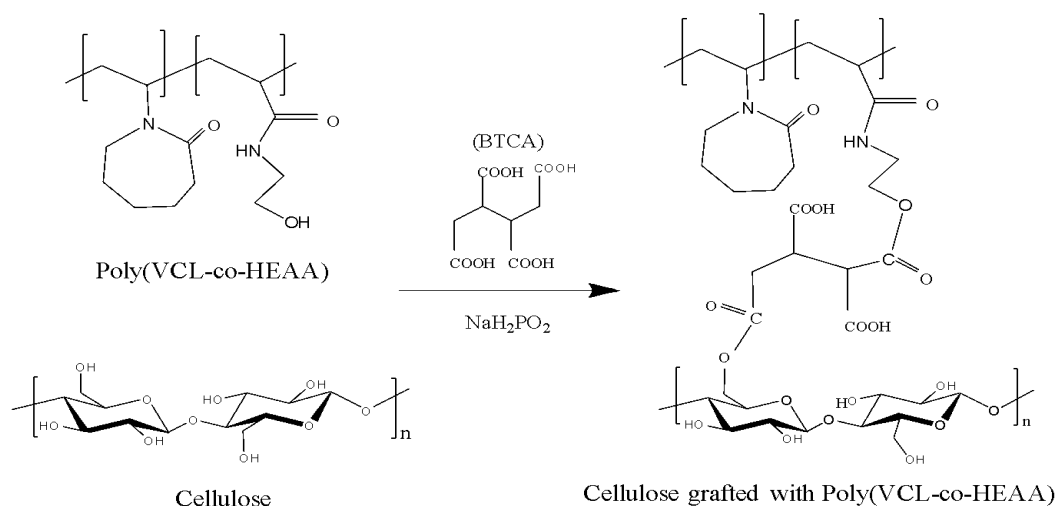
176 **Figure 2.** (a) TGA thermograms of PVCL and P(VCL-co-HEAA) copolymer; (b) DSC  
 177 thermograms of PVCL and P(VCL-co-HEAA) copolymer. The second heating cycle of a  
 178 heat/cool/heat sequence is shown; (c) Transmittance of PVCL and P(VCL-co-HEAA) copolymer in  
 179 an aqueous solution as a function of temperature.



180 Initial concentration of monomers and their reactivity ratios affect compositions of a  
181 copolymer. Figure 1 is  $^1\text{H-NMR}$  spectrum of P(VCL-co-HEAA) copolymer using  $\text{D}_2\text{O}$   
182 as the solvent. The molar composition of the copolymer was determined by integrating  
183 the peaks corresponding to VCL protons at 4.2 ppm (a) and HEAA protons at 3.5 ppm  
184 (b). A feed monomer ratio of 80/20 mol % VCL/HEAA yielded a 51/49 mol %  
185 VCL/HEAA in the final copolymer. This is attributed to the low reactivity ratio of PVCL  
186 as shown by other authors (Ivan M. Okhapkin, Irina R. Nasimova, Elena E. Makhaeva,  
187 & Alexei R. Khokhlov, 2003; Shah, Pal, Gude, & Devi, 2010). The more reactive HEAA  
188 monomer was preferentially incorporated into the copolymer even at a lower feeding ratio  
189 to VCL. The weight average molecular weight ( $M_w$ ) of P(VCL-co-HEAA) copolymer  
190 was determined by GPC to be 10,0551 g/mol with a polydispersity value of 1.9.  
191 The thermal properties of PVCL and P(VCL-co-HEAA) copolymer were analyzed by  
192 TGA studies, as shown in Figure 2(a). The initial weight loss was due to the liberation of  
193 absorbed moisture. The sharp weight decrease was associated with the thermal  
194 degradation of the polymer. The TGA thermograms showed that the synthesized  
195 copolymer had a decomposition temperature of up to  $420^\circ\text{C}$ . In contrast, PVCL  
196 decomposed at  $428^\circ\text{C}$ . This suggested that the addition of the hydrophilic comonomer  
197 HEAA did not affect the thermal stability of the copolymer remarkably. P(VCL-co-  
198 HEAA) is thermally stable for the subsequent pad-dry-cure finishing process where the  
199 grafting reaction with cellulose was achieved at  $160^\circ\text{C}$ .  
200 The glass-transition temperatures ( $T_g$ ) of PVCL and P(VCL-co-HEAA) copolymer were  
201 shown in Figure 2(b) and determined to  $190^\circ\text{C}$  and  $160^\circ\text{C}$  respectively. Introducing the  
202 hydrophilic comonomer HEAA into the copolymer led to a decrease in the  $T_g$ . This can  
203 enhance the crosslinking reaction between cellulose, the crosslinker and the copolymer  
204 in that the molecular chains of the copolymer starts to move at temperatures above  $T_g$ ,  
205 leading to an increased contact with cellulose and the crosslinker.  
206 Figure 2(c) shows the thermo-responsive behavior of PVCL and the copolymer. The  
207 LCST of the polymer was correlated with the temperature dependent phase separation of  
208 the polymer and determined by monitoring the optical transmittance change as a function

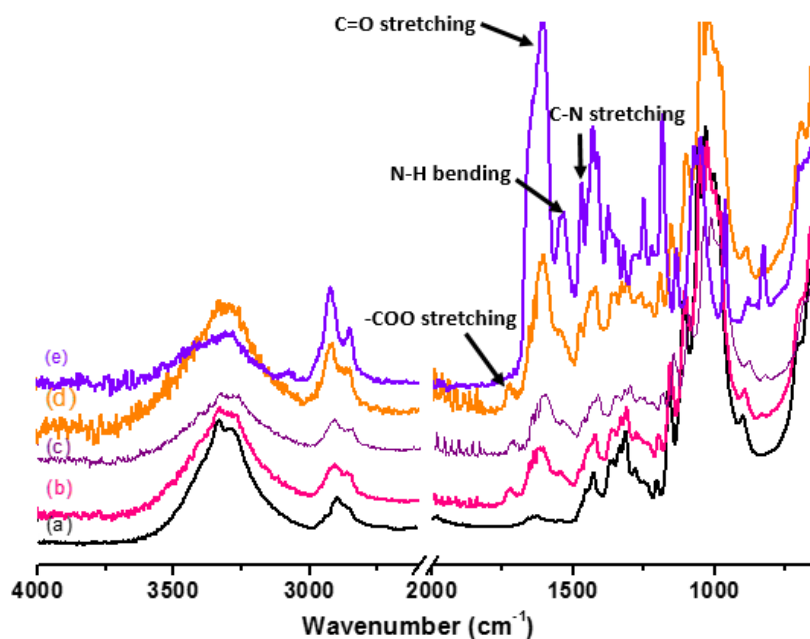
209 of temperature. PVCL has an LCST value at approximately 30.5°C. It is water soluble at  
 210 room temperature and precipitates at a temperature above 30.5°C. Introduction of a  
 211 hydrophilic comonomer, HEAA, shifted the LCST value of P(VCL-co-HEAA)  
 212 copolymer to 34.5°C. HEAA introduces additional hydrogen bonding in the copolymer,  
 213 thus hindering the transition from hydrophilic to hydrophobic and leading to an increase  
 214 in the LCST. An increase in the LCST of the PVCL based copolymer was also observed  
 215 when PVCL was copolymerized with hydrophilic hydroxymethyl acrylamide monomer  
 216 (González & Frey, 2017). It should be mentioned that HEAA has an –OH reactive  
 217 functional groups. Thus, the incorporation of HEAA into PVCL polymer chains can  
 218 facilitate the grafting reaction with cellulose while retaining the temperature sensitive  
 219 character.

### 220 3.2 Grafting of P(VCL-co-HEAA) to cotton fabrics



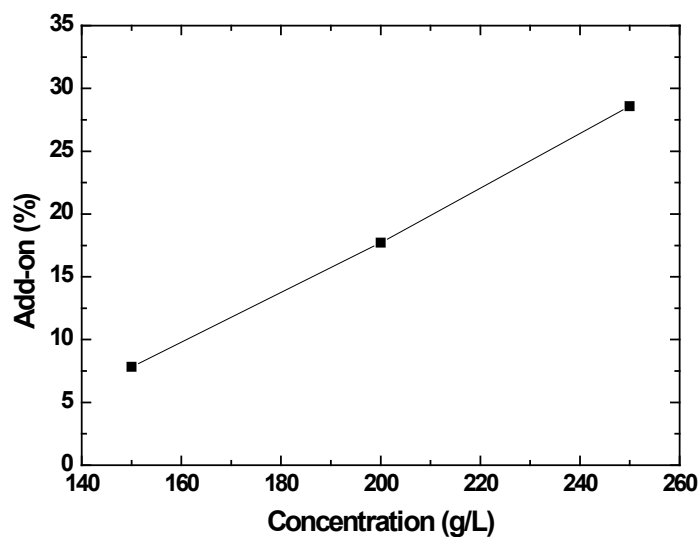
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222 **Scheme 1.** Crosslinking reaction between the crosslinker BTCA, cellulose and P(VCL-co-HEAA)  
 223 copolymer



224

225 **Figure 3.** FTIR spectra of (a) untreated cotton fabric; (b) cotton fabric treated with 150 g/L P(VCL-  
 226 co-HEAA); (c) cotton fabric treated with 200 g/L P(VCL-co-HEAA); (d) cotton fabric treated with  
 227 250 g/L P(VCL-co-HEAA); (e) P(VCL-co-HEAA) copolymer.



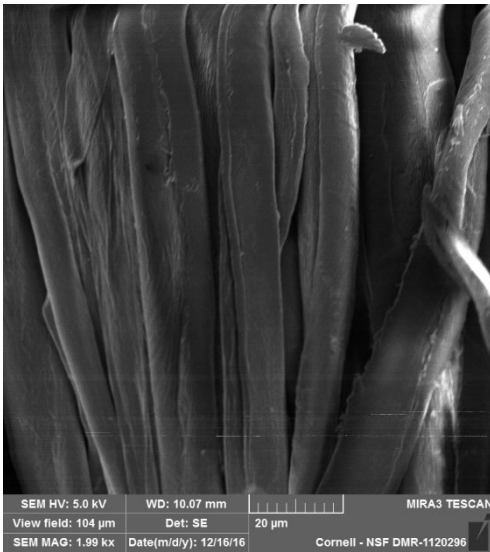
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229 **Figure 4.** The add-on of cotton fabric as a function of P(VCL-co-HEAA) concentration

230

231 FTIR was used to obtain information about the chemical structure of the thermo-  
232 responsive cotton after the grafting reaction. Figure 3 shows the FTIR spectra of P(VCL-  
233 co-HEAA) copolymer, untreated cotton fabric (control) and the fabrics treated with  
234 different concentrations of the copolymer. P(VCL-co-HEAA) copolymer contains amide  
235 groups that display a characteristic carbonyl absorption peak (C=O stretching, amide I  
236 band). The position of the amide I band is dependent on the degree of the hydrogen  
237 bonding and physical state of the compound (Kozanoğlu, Özdemir, & Usanmaz, 2011).  
238 In the FTIR spectra of P(VCL-co-HEAA) copolymer and the treated cotton fabrics, the  
239 peak for the C=O stretching vibration was observed at  $1615\text{ cm}^{-1}$ . With increasing the  
240 concentration of P(VCL-co-HEAA) copolymer from 150 g/L to 250 g/L, the intensity of  
241  $1615\text{ cm}^{-1}$  peak in the FTIR spectra of cotton fabrics also increased. Additionally, all  
242 treated cotton fabrics show a peak at  $1542\text{ cm}^{-1}$  assigned to N-H bending vibration (amide  
243 II) and a peak at  $1480\text{ cm}^{-1}$  associated with C-N stretching vibration (Zhao et al., 2012).  
244 This indicates that P(VCL-co-HEAA) copolymer has been successfully deposited onto  
245 cotton fabrics. The absorption peak at  $1723\text{ cm}^{-1}$  in Figure 3(b) to (d) is attributed to the  
246 ester linkage between -COOH of BTCA and -OH of cellulose and/or -OH of the  
247 copolymer as shown in scheme 1. Accordingly, this confirms the crosslinking reaction  
248 between the crosslinker BTCA, cellulose and the thermo-responsive copolymer.  
249 Figure 4 is the relationship between the amounts of P(VCL-co-HEAA) grafted to cotton  
250 as a function of the copolymer concentration. With more thermo-responsive copolymer  
251 incorporated in the finishing solution, the weight or add-on of the treated cotton increased  
252 accordingly, indicative of the successful immobilization of the copolymer. At a  
253 concentration of 250 g/L P(VCL-co-HEAA), the mass add-on of the cotton fabrics was  
254 as high as 30%.

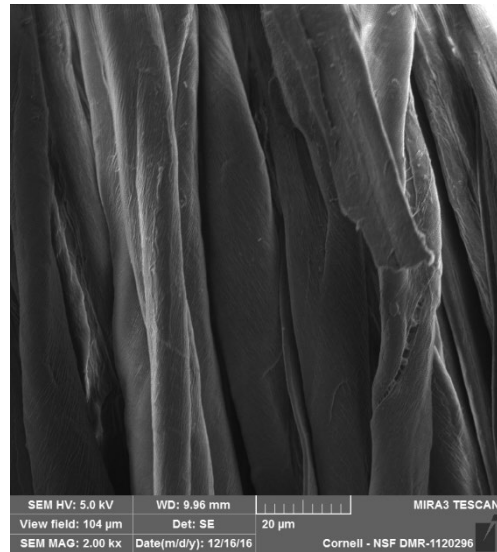
### 255 **3.3 Surface morphology and elemental compositions of cotton fabrics**



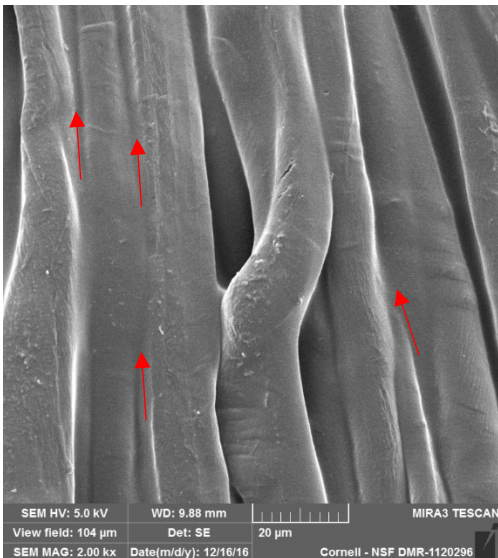
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(a)



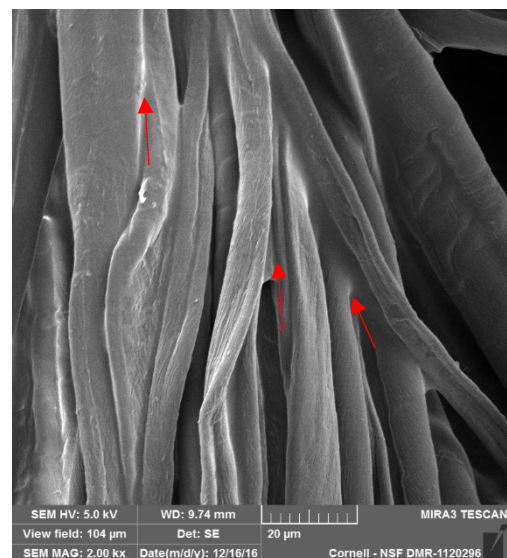
(b)



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(c)



(d)

260 **Figure 5.** SEM images of cotton fabrics (a) untreated cotton; (b) treated with 150 g/L copolymer; (c)  
261 treated with 200 g/L copolymer; (d) treated with 250 g/L copolymer.

262

263 Surface morphology and elemental compositions of the cotton fabrics grafted with  
264 P(VCL-co-HEAA) copolymer were obtained by using scanning electron microscopy  
265 (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). The SEM images are

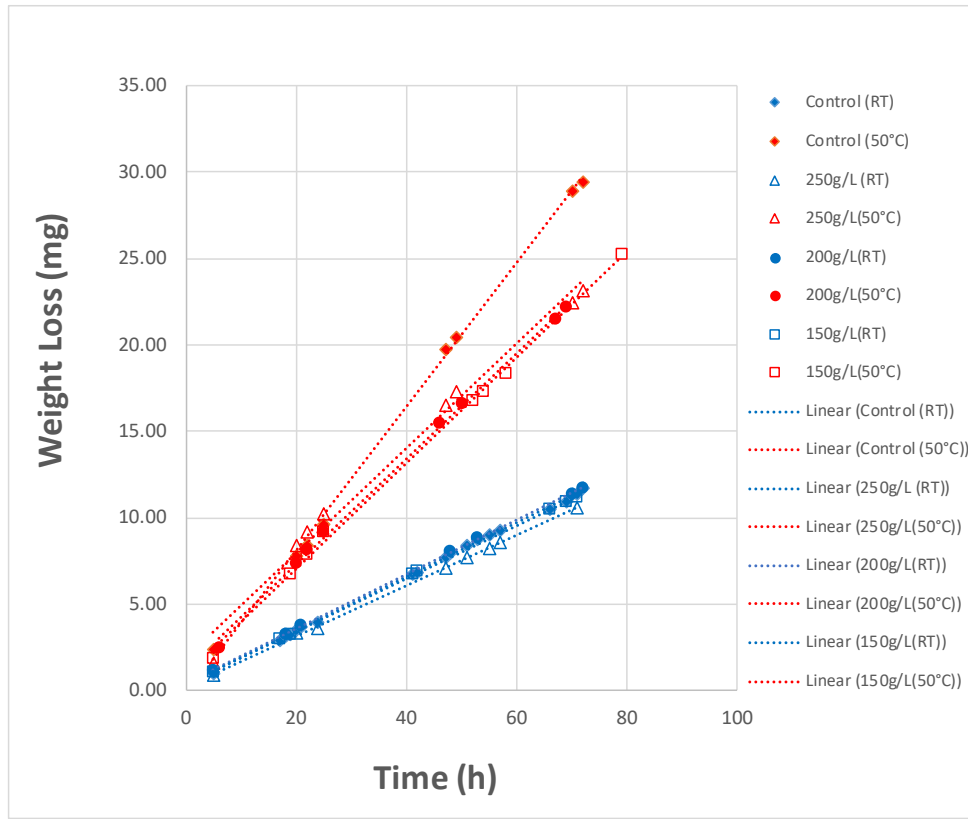
266 shown in Figure 5. Prior to the treatment, the cotton fibers appear to be individually  
 267 separated from each other. Once grafted with P(VCL-co-HEAA) copolymer, the fibers  
 268 tend to cohere with each other as shown by the arrows, indicating the deposition of the  
 269 copolymer on the surface. To ensure that the cotton surface is not covered by a film due  
 270 to the majority of BTCA reacting with poly(VCL-co-HEAA), a solubility test was  
 271 conducted by soaking the grafted cotton fabric in DMF on an armshaker for 24 h. We  
 272 observed that the fabric did not experience any weight loss in the solvent, indicating that  
 273 BTCA served as a bridge to crosslink with both poly(VCL-co-HEAA) and cellulose.  
 274 Elemental compositions (C, O, and N) of the treated cotton fabrics was analyzed by the  
 275 EDS studies and tabulated in Table 1. Each element produces characteristic X-rays that  
 276 are inherent to the atomic structure of the emitting element. The X-rays are displayed at  
 277 one or more specific energy levels in the EDS spectrum and give an indication of  
 278 elemental compositions (S.-C. Chen et al., 2004). Treated cotton comprises carbon,  
 279 nitrogen, and oxygen. While untreated cotton is composed of carbon and oxygen with a  
 280 trace amount of nitrogen from impurities or the ambient atmosphere. The increase in the  
 281 nitrogen content of cotton indicates that P(VCL-co-HEAA) copolymer was thoroughly  
 282 deposited onto cotton.

283 **Table 1. EDS analysis of the elemental compositions (C, O, and N) of cotton fabrics treated**  
 284 **with P(VCL-co-HEAA) copolymer**

Concentration	Weight percentage of the element (%)		
	C	O	N
0 (control)	66.86±6.91	32.66±4.86	0.48±0.19
150 g/L	63.55±6.27	32.74±4.54	3.71±0.62
200 g/L	67.70±7.07	28.52±4.37	3.78±0.76
250 g/L	73.87±7.76	19.57±3.14	6.55±1.15

285

286 **3.4 Thermo-responsive behavior of modified cotton fabrics**



287

288 **Figure 6.** Weight loss of unmodified (control) and modified cotton fabrics as a function of time at  
 289 room temperature (RT,21°C) and at 50°C.

290

291 The thermo-responsive behavior of the cotton fabrics grafted with P(VCL-co-HEAA)  
 292 copolymer was characterized by water vapor permeability (WVP) measurement.

293 The water vapor permeability (WVP, in g/m<sup>2</sup>/day) is given by the equation

$$294 \quad WVP = \frac{24M}{At} \quad (2)$$

295 where  $M$  is the loss in mass of the assembly over the time period  $t$  (in g);  $t$  is the time  
 296 between successive weighing of the assembly (in h);  $A$  is the area of the exposed test  
 297 fabric (equal to the internal area of the test dish) (in m<sup>2</sup>).

298  $A$  is given by the equation

$$299 \quad A = \left( \frac{\pi d^2}{4} \right) \times 10^{-6} \quad (3)$$

300 where  $d$  is the internal diameter of the test dish (in mm).

301 Figure 6 shows the weight loss of modified and unmodified cotton fabrics as a function  
 302 of time at room temperature (21°C) and also at 50°C. The weight loss value was the  
 303 average of three test fabrics with a standard deviation of less than 1mg. The slope of the  
 304 curve is the rate of water vapor permeation through the test fabric. Based on equations  
 305 (2) and (3), the WVP values were calculated and shown in Table 2. The correlation  
 306 coefficient ( $R^2$ ) are all greater than 0.999, indicating a good linear regression fitting. The  
 307 WVP studies demonstrated that at room temperature, P(VCL-co-HEAA) copolymer  
 308 exhibited hydrophilicity and the modified cotton fabrics behaved similarly to the  
 309 untreated cotton fabric with similar rate of water vapor permeation through the fabric and  
 310 therefore similar WVP. At 50°C, the copolymer underwent phase transition resulting from  
 311 aggregation of the chain molecules due to the intermolecular interactions between the  
 312 hydrophobic groups at elevated temperature. The grafted cotton fabrics switched from  
 313 hydrophilic to hydrophobic. Therefore, the treated cotton fabrics exhibited lower rate of  
 314 water vapor permeation and also WVP than the untreated cotton. It is also worthy to point  
 315 out that 6.7 wt% add-on of the fabric treated with 150g/L of the copolymer was sufficient  
 316 enough to achieve the same water vapor permeability with the fabric treated with 250g/L  
 317 of the copolymer. This thermally switchable hydrophilicity of cotton fabric makes it  
 318 applicable to protective clothing and other smart textiles.

319

320 **Table 2. Water vapor permeability of cotton fabrics treated with P(VCL-co-HEAA) copolymer**

Concentration	Water vapor permeability (g/m <sup>2</sup> /day)					
	Room Temperature			(50°C)		
	Slope (mg/h)	$R^2$	WVP	Slope (mg/h)	$R^2$	WVP
0 (control)	0.157	0.9991	695	0.417	0.9984	1849
150 g/L	0.151	0.9996	669	0.306	0.9983	1362
200 g/L	0.157	0.9998	697	0.306	0.9982	1359
250 g/L	0.146	0.9993	649	0.308	0.9915	1367

321

#### 322 4. Conclusions

323 A thermo-responsive copolymer P(VCL-co-HEAA) was synthesized by free radical  
 324 polymerization at 60°C. A feed monomer ratio of 80/20 mol %VCL/HEAA yielded a



325 51/49 mol % of ratio of VCL/HEAA in the copolymer due to a higher reactivity of HEAA.  
326 The copolymer had a glass transition temperature of 160°C and a decomposition  
327 temperature of up to 420°C as evidenced by DSC and TGA studies. The LCST value of  
328 the copolymer was 34.5°C. Thermo-responsive cotton fabrics were successfully  
329 fabricated by a grafting reaction using BTAC as crosslinker and SHP as catalyst. FTIR  
330 and EDS studies confirmed the deposition of P(VCL-co-HEAA) copolymer onto cotton.  
331 The modified fabrics exhibited temperature-responsive behavior in the water vapor  
332 permeability measurements. Compared to the unmodified cotton, 6.7 wt% add-on of the  
333 fabric grafted with the copolymer was sufficient enough to exhibit decreased water  
334 permeability at elevated temperature due to hydrophilic to hydrophobic transition. This  
335 study provides another alternative for fabrication of smart textiles and application in  
336 functional clothing.

337

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### 349 **References**

- 350 Bae, Y. H., Okano, T., Hsu, R., & Kim, S. W. (1987). Thermo - sensitive polymers as on - off  
351 switches for drug release. *Die Makromolekulare Chemie, Rapid Communications*, 8(10),  
352 481-485.
- 353 Chen, S.-C., Wu, Y.-C., Mi, F.-L., Lin, Y.-H., Yu, L.-C., & Sung, H.-W. (2004). A novel pH-sensitive  
354 hydrogel composed of N, O-carboxymethyl chitosan and alginate cross-linked by genipin

355 for protein drug delivery. *Journal of Controlled Release*, 96(2), 285-300.

356 Chen, T., Fang, Q., Zhong, Q., Chen, Y., & Wang, J. (2015). Synthesis and thermosensitive  
357 behavior of polyacrylamide copolymers and their applications in smart textiles.  
358 *Polymers*, 7(5), 909-920.

359 Cortez-Lemus, N. A., & Licea-Claverie, A. (2016). Poly (N-vinylcaprolactam), a comprehensive  
360 review on a thermoresponsive polymer becoming popular. *Progress in Polymer Science*,  
361 53, 1-51.

362 De Las Heras Alarcón, C., Pennadam, S., & Alexander, C. (2005). Stimuli responsive polymers for  
363 biomedical applications. *Chemical Society Reviews*, 34(3), 276-285.

364 González, E., & Frey, M. W. (2017). Synthesis, characterization and electrospinning of poly (vinyl  
365 caprolactam-co-hydroxymethyl acrylamide) to create stimuli-responsive nanofibers.  
366 *Polymer*, 108, 154-162.

367 Hu, J., Meng, H., Li, G., & Ibeke, S. I. (2012). A review of stimuli-responsive polymers for smart  
368 textile applications. *Smart Materials and Structures*, 21(5), 053001.

369 Kozanoğlu, S., Özdemir, T., & Usanmaz, A. (2011). Polymerization of N-vinylcaprolactam and  
370 characterization of poly (N-vinylcaprolactam). *Journal of Macromolecular Science, Part*  
371 *A*, 48(6), 467-477.

372 Okhapkin, I. M., Nasimova, I. R., Makhaeva, E. E., & Khokhlov, A. R. (2003). Effect of  
373 Complexation of Monomer Units on pH- and Temperature-Sensitive Properties of  
374 Poly(N-vinylcaprolactam-co-methacrylic acid). *Macromolecules*, 36(21), 8130-8138.

375 Okhapkin, I. M., Nasimova, I. R., Makhaeva, E. E., & Khokhlov, A. R. (2003). Effect of complexation  
376 of monomer units on pH-and temperature-sensitive properties of poly (N-  
377 vinylcaprolactam-co-methacrylic acid). *Macromolecules*, 36(21), 8130-8138.

378 Qiu, Y., & Park, K. (2001). Environment-sensitive hydrogels for drug delivery. *Advanced drug*  
379 *delivery reviews*, 53(3), 321-339.

380 Schmaljohann, D. (2006). Thermo-and pH-responsive polymers in drug delivery. *Advanced drug*  
381 *delivery reviews*, 58(15), 1655-1670.

382 Shah, S., Pal, A., Gude, R., & Devi, S. (2010). Synthesis and characterization of thermo-responsive  
383 copolymeric nanoparticles of poly (methyl methacrylate-co-N-vinylcaprolactam).  
384 *European Polymer Journal*, 46(5), 958-967.

385 Stuart, M. A. C., Huck, W. T., Genzer, J., Müller, M., Ober, C., Stamm, M., . . . Urban, M. (2010).  
386 Emerging applications of stimuli-responsive polymer materials. *Nature materials*, 9(2),  
387 101-113.

388 Wang, B., Wu, X., Li, J., Hao, X., Lin, J., Cheng, D., & Lu, Y. (2016). Thermosensitive Behavior and  
389 Antibacterial Activity of Cotton Fabric Modified with a Chitosan-poly (N-  
390 isopropylacrylamide) Interpenetrating Polymer Network Hydrogel. *Polymers*, 8(4), 110.

391 Yang, H., Esteves, A. C. C., Zhu, H., Wang, D., & Xin, J. H. (2012). In-situ study of the structure and  
392 dynamics of thermo-responsive PNIPAAm grafted on a cotton fabric. *Polymer*, 53(16),  
393 3577-3586.

394 Zhang, Y., Chu, D., Zheng, M., Kissel, T., & Agarwal, S. (2012). Biocompatible and degradable poly  
395 (2-hydroxyethyl methacrylate) based polymers for biomedical applications. *Polymer*  
396 *Chemistry*, 3(10), 2752-2759.

397 Zhao, C., Chen, Q., Patel, K., Li, L., Li, X., Wang, Q., . . . Zheng, J. (2012). Synthesis and  
398 characterization of pH-sensitive poly (N-2-hydroxyethyl acrylamide)-acrylic acid (poly  
399 (HEAA/AA)) nanogels with antifouling protection for controlled release. *Soft Matter*,

400 8(30), 7848-7857.

401