

# A one pot one step combined radical and ring-opening route for the dual functionalization of starch in aqueous medium

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Starch based materials are attractive bio-based alternative to fully synthetic polymers. Native starch has however limited thermoprocessability and properties and must be modified. In order to improve the properties of starch-graft-poly(butyl-acrylate-*co*-styrene) copolymers via a process as green as possible, we report herein a new method for the dual functionalization of the polysaccharide via a one pot one step reaction in aqueous medium combining free radical polymerizations and ring-opening chemistry. Poly(butyl acrylate) / poly(butyl acrylate-*co*-styrene) (ca. 60 000 g/mol) and oligo( $\epsilon$ -caprolactone) were grafted on starch with a grafting percentage up to 75 %. The copolymers show two glass transition temperatures: one around 55-60°C related to starch and a second attributed to the grafted vinyl polymers, from -46°C to 20°C depending on butyl acrylate/styrene ratio). The resulting dual functionalized materials exhibit excellent mechanical properties, with elongation at break in the range 20-210 %, while single functionalized starch shows less than 5 %.

**Keywords:** starch, graft copolymerization, structural / thermomechanical properties.

## 1. Introduction

Research towards biobased and biodegradable polymers has received much attention this last decade, due notably to environmental concerns and the depletion of oil resources (Chen, Kamitakahara & Edgar, 2020; Imre, García, Puglia & Vilaplana, 2019). In this context, starch is a promising starting material due to its availability and low cost that has been the subject of numerous studies (Chen et al., 2015; Fan & Picchioni, 2020). However, starch has limited thermoprocessability along with a strong hydrophilic character and poor mechanical properties as compared to conventional synthetic polymers (Averous & Halley, 2009). Starch can be plasticized with external plasticizers such as polyols (Lourdin, Coignard, Bizot & Colonna, 1997), urea/formamide combinations (Xiaofei, Jiugao & Jin, 2004) notably. However, some shortcomings, as plasticizer migration, induce an evolution of its properties over time and thus limit its applications.

To overcome some of these drawbacks, the polysaccharide can be blended with synthetic polymers (Wang, Yang & Wang, 2003), functionalized to yield starch esters and ethers (Aburto, Alric & Borredon, 1999; Shogren, 2003) or grafted with a polymer (Meimoun et al., 2018; Cazotti et al., 2020; Haq et al., 2020). Graft copolymerization is a very versatile way of functionalization allowing access to materials displaying a combination of the properties of the synthetic polymer and of the starch (Jyothi,

2010). In particular, the radical graft copolymerization can lead to starch-based materials with interesting properties. In this frame, the synthesis of starch/starch-*graft*-poly(butyl acrylate-*co*-styrene) copolymers by free-radical graft polymerization was conducted on native (Meshram, Patil, Mhaske & Thorat, 2009), acetylated (Mou, Li, Wang, Fei & Liu, 2012) starch and dextrin (David et al., 2019). Starch can also be modified by grafting polyesters on its backbone by ring-opening polymerization (ROP) in organic solvents (Chen et al., 2005; Rutot-Houzé et al., 2004) and in water (Choi, Kim & Park, 1999), a tin based catalyst being used for this purpose.

The combination of the two processes, *i.e.* radical and ring-opening grafting onto polysaccharides can give access to advanced materials with applications such as drug, fragrance containers or stimuli responsive materials (Chang, Yamabuki, Onimura & Oishi, 2008; Liu, Huang, Pang, Han & Ji, 2015; Yan et al., 2009). Diblock copolymers were grafted onto cellulose by combining in a sequential way ROP and Atom Transfer Radical Polymerization (ATRP), involving the use of copper halide, amine ligands and, in the examples reported herein, 2-bromopropionyl bromide (Berthier, Herrmann & Ouali, 2011; Östmark, Nyström & Malmström, 2008). In these studies, polyester is grafted as the first block by ROP of a cyclic ester, eventually after a first protection step of a part of the hydroxyl groups. The polymer chain end is further derivatized to yield an initiator for the controlled radical polymerization of a second monomer, leading to the second block.

The dual functionalization, *i.e.* the grafting of two different oligo/polymers was reported onto cellulose powder and cellulose derivatives such as hydroxyethylcellulose or diacetate cellulose by a multistep procedure involving the grafting of the controlled radical polymerization initiator (Chang, et al., 2008; Liu et al., 2015; Vlček et al., 2008). As a representative example, the radical macroinitiator is formed at the first step by the reaction of hydroxyl groups with 2-bromopropionyl bromide in a mixture of tetrahydrofuran (THF) and trimethylamine. The tin catalyzed ring-opening polymerization of  $\epsilon$ -caprolactone initiated by the remaining hydroxyl groups is then realized in xylene, followed by the ATRP of *N,N*-dimethylaminoethyl methacrylate in THF in the presence of *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) and CuBr (Yan et al., 2009).

The combination of radical and ROP processes was, as far we know, reported onto cellulose and never onto starch. The synthetic strategies reported in the literature involved multistep procedures, the use of organic solvents (*e.g.* THF, xylene), harmful compounds for the initiation of the controlled radical polymerization (*e.g.* copper halide, brominated derivatives) and tin catalyzed ring-opening polymerizations. In order to improve the properties of starch-*graft*-poly(butyl acrylate-*co*-styrene) copolymers, we developed in this contribution a greener process for the dual functionalization of polysaccharide via free-radical graft polymerization and ring-opening functionalization, using phosphoric acid as organocatalyst for the latter, and a one pot one step process in aqueous medium. The new bi-functionalized materials developed herein exhibit remarkable elongations at break, highlighting promising potentialities for stretchable films. The microstructure of copolymers is studied by Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared Spectroscopy (FT-IR), Size Exclusion Chromatography (SEC), Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA).

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## 85           2. Experimental

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87 The Materials and Characterization procedures are presented in the Appendix A.

88

89 Grafting reactions

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91 For all reactions, dry starch (30 g) was gelatinized in 120 mL water by heating at 95 °C for 30 minutes. 92 The temperature was then decreased to 85 °C. This leads to the disappearance of the granular structure 93 of starch. The chains are then more accessible for the grafting.

94       - *Free radical grafting*

95 Sodium peroxydisulfate (1 mol % *vs.* starch) previously dissolved in 10 mL of water, butyl acrylate 96 (BA) and/or styrene (St) (70-75 wt % *vs.* starch) were added dropwise for 1 h. The grafting

97 polymerization was carried out for 30 additional minutes. A few experiments carried out under inert  
98 atmosphere to avoid oxygen led to similar grafting ratio and microstructures than those conducted under  
99 air. The latter experimental conditions were thus chosen for the work.

100 - *Ring-opening grafting*

101 Phosphoric acid (1 mol % vs.  $\epsilon$ -caprolactone),  $\epsilon$ -caprolactone (CL) (25 wt % vs. starch) were  
102 added dropwise for 1h. The grafting polymerization was carried out for an additional 4 h.

103 - *One pot one step free radical and ring-opening grafting*

104 Sodium peroxydisulfate (1 mol % vs. starch) and phosphoric acid (1 mol % vs.  $\epsilon$ -caprolactone)  
105 previously dissolved in 10 mL of water were added dropwise for 1h via dropping funnel. At the same  
106 time, monomers: butyl acrylate and/or styrene (70-75 wt % vs. starch) and  $\epsilon$ -caprolactone (25-30 wt %  
107 vs. starch) were added dropwise for 1 h via second dropping funnel. The grafting polymerization was  
108 carried out for an additional 4 h.

109 - *Sequential free radical and ring-opening grafting*

110 Sodium peroxydisulfate (1 mol % vs. starch) previously dissolved in 10 mL of water, butyl  
111 acrylate and/or styrene (70-75 wt % vs. starch) were added dropwise for 1 h. The grafting polymerization  
112 was carried out for an additional 30 minutes. Then, phosphoric acid (1 mol % vs.  $\epsilon$ -caprolactone),  $\epsilon$ -  
113 caprolactone (25-30 wt % vs. starch) were then added dropwise for 1h. The grafting polymerization was  
114 carried out for an additional 4 h.

115 At the end of the reaction, for each process, the solution was poured in acetone and left during 24 h  
116 under magnetic stirring to remove the ungrafted polymer. The product was filtered and dried overnight.  
117 The procedure of purification was validated on a few samples by Soxhlet extraction in chloroform during  
118 24 h that led to the same ratio.

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120 The weight grafting percentage (GP) was determined by gravimetry as following:

$$121 \text{ GP} = [(\text{weight copolymer} - \text{weight of starch}) / \text{weight of starch}] \times 100$$
$$122 = [\text{weight of grafted polymer} / \text{weight of starch}] \times 100$$

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### 125 3. Results and discussion

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#### 127 3.1. Grafting reaction

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129 3.1.1 Syntheses of starch-*graft*-poly(butyl acrylate) and starch-*graft*-oligo( $\epsilon$ -caprolactone): single  
130 starch functionalization

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132 Entries representative of the grafting reactions starting from butyl acrylate and  $\epsilon$ -caprolactone  
133 on the starch via the different routes are presented in Table 1. Brønsted acid catalysis using phosphoric  
134 acid was chosen for the ring-opening since the molecule is harmless at low concentration (it is found in  
135 sodas) and it was already used successfully by some of us to graft oligo( $\epsilon$ -caprolactone) on dextran and  
136 methylated cellulose in aqueous medium (Stanley et al., 2014). Radical and ring-opening  
137 functionalizations were first assessed separately. The free radical graft copolymerization of butyl  
138 acrylate in water (entry 1) leads to an almost quantitative efficiency, as reported previously (David,  
139 2019). Rather long chains are grafted, with a number-average molecular weight of 80 300 g/mol, and a  
140 significant dispersity. The resulting degree of substitution (DS) is consequently low, around 0.0014.

141 Regarding the mechanism, the decomposition of potassium persulfate in aqueous medium  
142 containing an alcohol is described in the literature (Bartlett & Cotman, 1949). The formation of only  
143  $^{\circ}\text{CH}_2\text{OH}$  radicals in methanol has been confirmed by Electron Spin Resonance (Norman, Storey & West,  
144 1970). Indeed, radicals are more likely located on the carbon in  $\alpha$  position of the oxygen rather

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**Table 1** Dual functionalization of starch in aqueous medium: initial assessment <sup>a</sup>

Entry	Route <sup>b</sup> (time)	BA/CL <sup>c</sup> (% wt)	GP <sup>d</sup> (%)	GP <sub>BA</sub> <sup>e</sup> (%)	GP <sub>CL</sub> <sup>e</sup> (%)	DS <sub>1</sub> <sup>f</sup>	DS <sub>2</sub> <sup>f</sup>	M <sub>n</sub> <sup>g</sup> (g/mol)	M <sub>n,corr</sub> <sup>g</sup> (g/mol)	$\mathcal{D}_M$ <sup>g</sup>	T <sub>g1</sub> <sup>h</sup> (°C)	T <sub>g2</sub> <sup>h</sup> (°C)	T <sub>deg 1</sub> <sup>i</sup>	T <sub>deg 2</sub> <sup>i</sup>	$\sigma^j$ (MPa)	$\epsilon^j$ (%)
1	Radical (1.5 h)	75/0	69	69	-	0.0014	-	154 000	80 300	6.3	-46	56	254	343	0.3 ± 0.1	1.6±0.4
2	ROP (5 h)	0/25	1.6	-	1.6	0.0223	-	116 <sup>k</sup>	-	-	-	61	-	-	-	-
3	Dual (5 h) <i>Simultaneous</i>	75/25	69	62.5	6.5	0.0953	0.0337	60 800	34 200	3.8	-46	55	250	345	0.9 ± 0.5	2 ± 0.3
4	Dual (1.5 + 5 h) <i>Sequential</i>	75/25	72	68.9	3.1	0.0484	0.0191	44 000	25 500	7.7	-45	59	249	345	0.5 ± 0.1	2 ± 0.5

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<sup>a</sup> The starch was heated at 95 °C for 30 min in water before the grafting reaction at 85 °C.

149 <sup>b</sup> Sodium peroxydisulfate (1 mol % *vs.* starch) and phosphoric acid (1 mol % *vs.* CL) as initiator and catalyst

150 <sup>c</sup> wt % monomer in the feed *vs.* starch

151 <sup>d</sup> Overall grafting percentage determined by gravimetry

152 <sup>e</sup> GP<sub>PBA</sub> (%) GP<sub>oligo(CL)</sub> (%) are the grafting percentage of poly(butyl acrylate) and poly( $\epsilon$ -caprolactone), respectively, determined by <sup>1</sup>H NMR analysis in DMSO-  
153 d<sub>6</sub>/CDCl<sub>3</sub> (50/50) (see Appendix B)

154 <sup>f</sup> Degree of substitution, see Appendix A.2. For entries 3 and 4, DS<sub>1</sub> and DS<sub>2</sub> (DS<sub>PBA</sub> + DS<sub>PCL</sub>) are determined with the hypothesis of DP<sub>n</sub> of 1 and 3, respectively,  
155 for oligo( $\epsilon$ -caprolactone) because when the grafting was conducted by ROP only, the grafted chains were composed on average of a single caproyl unit.

156 <sup>g</sup> Number-average molecular weight as measured M<sub>n</sub> and corrected using Mark-Houwink-Sakurada factors M<sub>n,corr</sub> and dispersity  $\mathcal{D}_M$  of the grafted poly(butyl  
157 acrylate) chains determined by SEC (40 °C, THF, polystyrene standards) after acid hydrolysis (Appendix A.2)

158 <sup>h</sup> Glass transition temperature (T<sub>g</sub>) determined by DSC

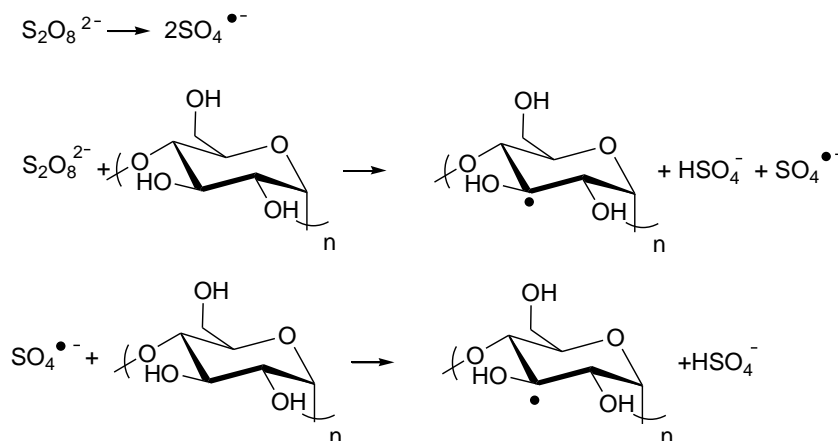
159 <sup>i</sup> Temperature of degradation determined by TGA (degradation 1: starch, 2: grafted chains)

160 <sup>j</sup> Maximum stress and elongation at break from tensile strength measurement

161 <sup>k</sup> M<sub>n</sub> determined by <sup>1</sup>H NMR analysis in DMSO-d<sub>6</sub> (DP<sub>n</sub> = 1.02, see Appendix D)

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164 than on the oxygen, and are more stable on more substituted carbons (Giese, 1986). Thus, it is likely that  
 165 the functionalization occurs preferentially on the carbons located on the sugar ring. Considering this, we  
 166 propose the initiation mechanism presented in Scheme 1 (the position 3 has been chosen arbitrarily).



182 **Scheme 1.** Proposed radical initiation mechanism in the presence of potassium persulfate in aqueous  
 183 medium

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186 The grafting conducted by ring-opening of the cyclic ester leads to a more modest grafting ratio  
 187 (entry 2).  $^1\text{H}$  NMR analysis shows that the grafted chains are composed on average of a single caproyl  
 188 unit (number-average degree of polymerization estimated at 1.02, Appendix D), providing a starch  
 189 hydroxyester compound. This result can be explained by the use of water as the solvent of the reaction,  
 190 which can either initiate the ROP of  $\epsilon$ -caprolactone or enable polycondensation via hydroxyacids  
 191 resulting from the hydrolysis of the lactone (Scullion & Zinck, 2012), both routes leading to the  
 192 formation of oligomers or polymers that are not grafted to the polysaccharide. To improve the yield and  
 193 DP, it would have been interesting to use less water or remove it during the reaction but in this case the  
 194 viscosity of the medium would be too important. It should be noted that the lactone conversion is  
 195 quantitative ( $^1\text{H}$  NMR analysis given in the Appendix E). The resulting DS is *ca.* 20 times higher than  
 196 the one obtained by the radical route, around 0.022 in these experimental conditions.

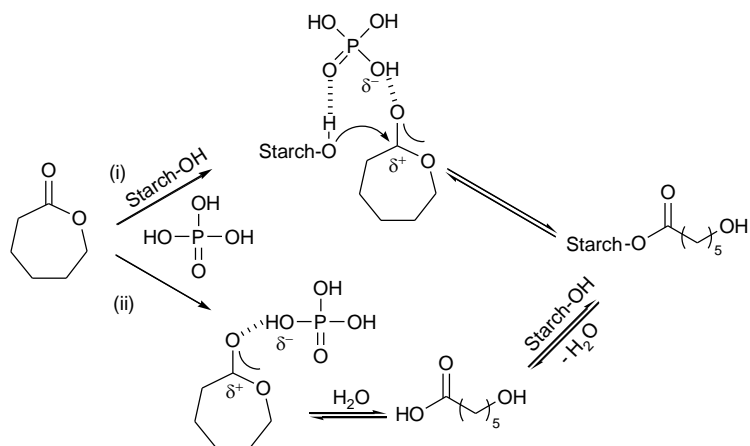
197 Regarding the grafting mechanism, one can either expect (i) a nucleophilic attack of the  
 198 carbohydrate hydroxyl on the lactone catalyzed by phosphoric acid, or (ii) the aforementioned  
 199 hydrolysis of the lactone followed by a condensation reaction between the so formed hydroxyacid and  
 200 the carbohydrate hydroxyl. This is represented in Scheme 2. Regarding the regioselectivity, we know  
 201 from our previous work (Miao et al., 2013) that both primary and secondary carbohydrate hydroxyls can  
 202 be engaged in a transesterification reaction with  $\epsilon$ -caprolactone in the presence of phosphoric acid  
 203 moieties. If the pathway (i) is the main mechanism, then we do not expect the reaction to be  
 204 regiospecific. For the condensation pathway (ii), primary alcohols are known to be more reactive in  
 205 esterification reactions than secondary alcohols. Thus, if this pathway (ii) is the main mechanism, it is  
 206 likely that primary alcohols are more involved than secondary alcohols.

### 207 208 3.1.2 Syntheses of starch-*graft*-[poly(butyl acrylate)/oligo( $\epsilon$ -caprolactone)]: dual fonctionnalization

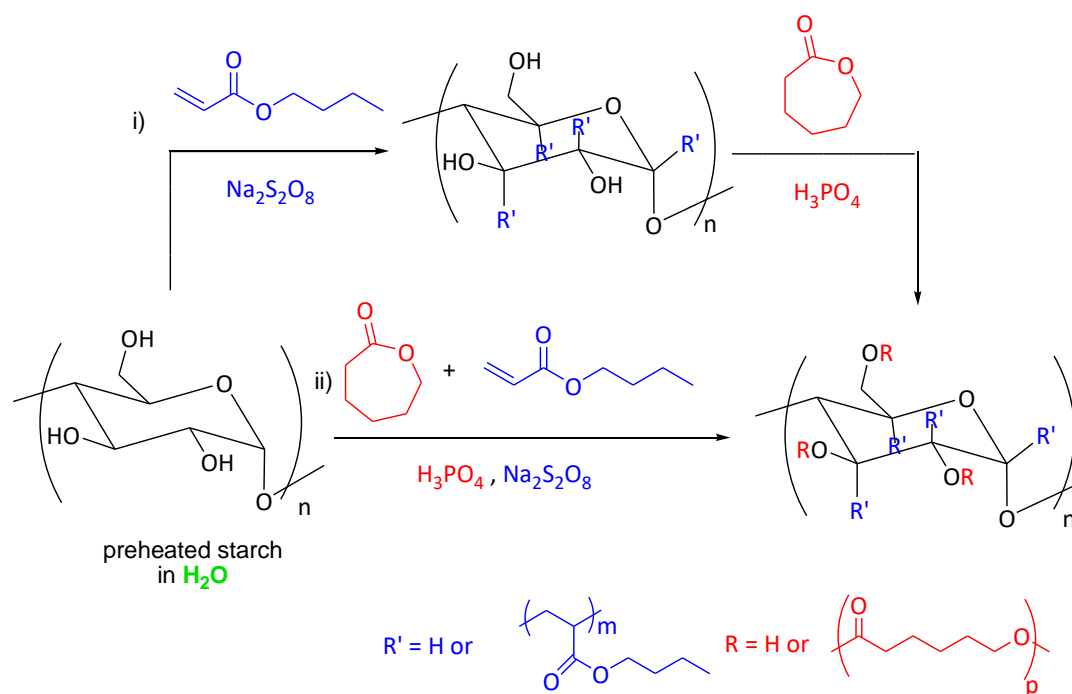
209

210 The one pot one step combination of the radical and the ring-opening routes in water  
 211 (represented in Scheme 3) is presented entry 3 and the resulting  $^1\text{H}$  NMR spectrum is shown Fig.1. The  
 212 assignments were made from the  $^1\text{H}$  NMR spectra of the starch and of poly(butyl acrylate) that are given  
 213 in the Appendix B.

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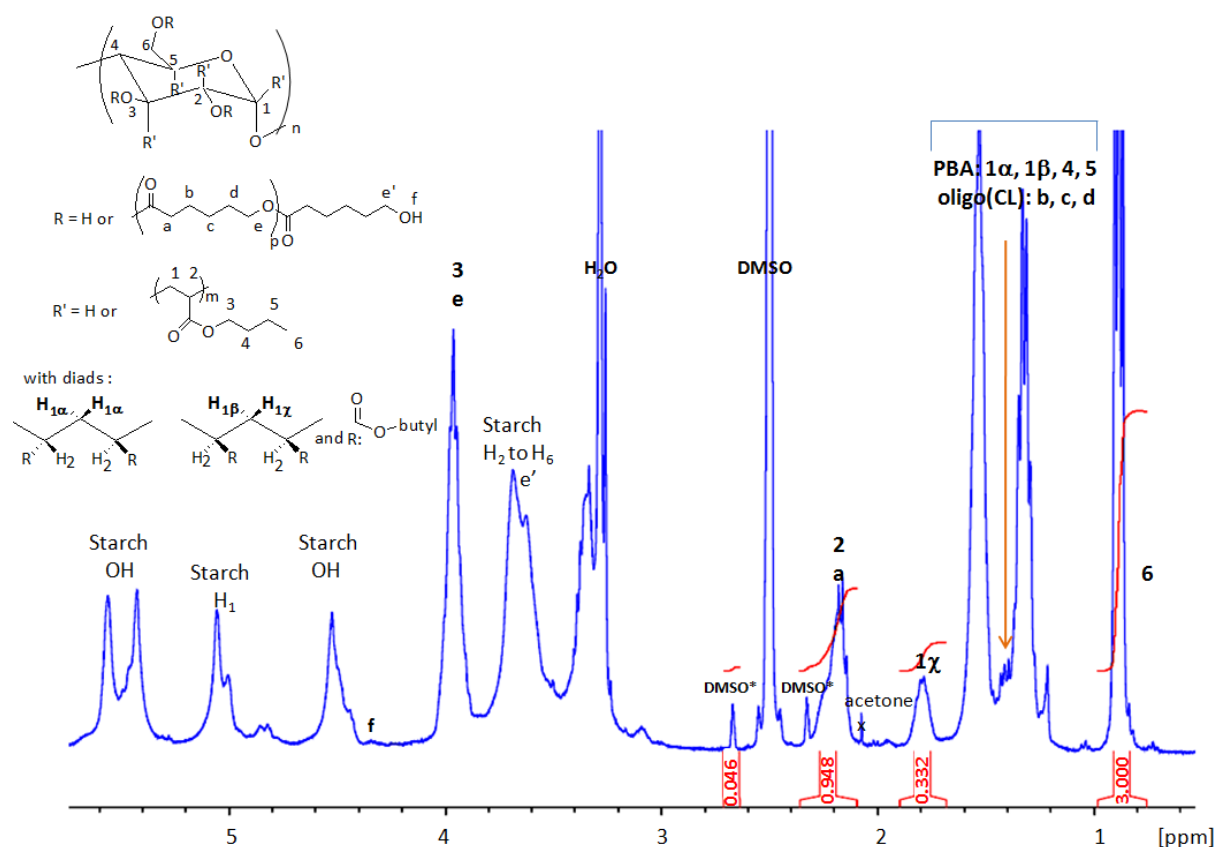


231 **Scheme 2.** Proposed ring-opening mechanism in the presence of  $\epsilon$ -caprolactone and phosphoric acid in  
232 aqueous medium.



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234 **Scheme 3.** One pot one step combined radical and ring-opening route for dual (i: sequential, ii:  
235 simultaneous) functionalization of starch in aqueous medium



239 **Fig. 1.**  $^1\text{H}$  NMR spectrum of the starch-graft-[poly(butyl acrylate)/oligo( $\epsilon$ -caprolactone)] obtained entry  
 240 3 in a mixture of  $\text{DMSO-}d_6/\text{CDCl}_3$  (50/50, 400 MHz)

241

242 In particular, the  $-\text{CH}_2$  signal of the poly(butyl acrylate) backbone is split into three due to the  
 243 presence of both *meso* and *racemic* diads (Brar, Kumar & Kaur, 2002). The caproyl and butyl acrylate  
 244 signals are overlapping due to the similarity of the molecules, even if a  $\text{CH}_2\text{-CH}_2\text{-CH}_2$  caproyl signal  
 245 can be evidenced around 1.4 ppm (shown by the arrow in Fig. 1). Signals representative of caproyl units  
 246 can also be seen on the  $^{13}\text{C}$  NMR spectra of the compounds given in Appendix C. Both butyl acrylate  
 247 and  $\epsilon$ -caprolactone are thus grafted, showing that the two reactions can occur simultaneously in water,  
 248 and validating the proof of our concept. If the overall grafting percentage is similar to entry 1, the  
 249 grafting ratio of the lactone is significantly improved, by a factor 4. Experiments conducted without the  
 250 starch (reported Appendix F) show that this increase of the grafting efficiency may neither be due to a  
 251 radical grafting of poly(butyl acrylate) on oligo( $\epsilon$ -caprolactone) nor to a transesterification between  
 252 acrylate and caproyl units. It may thus be attributed to the hydrophobic character of the PBA grafts  
 253 which could lead to an increase in the lactone and/or oligo( $\epsilon$ -caprolactone) concentration in the vicinity  
 254 of the polysaccharide. The combination of the two chemistries leads to PBA grafts that are significantly  
 255 shorter than those obtained by the single radical process. Regarding  $\epsilon$ -caprolactone, the hydrolyzed  
 256 grafts were found to be soluble in the aqueous phase containing the hydrolyzed starch chains and thus  
 257 could not be isolated. This is likely due to a very low number-average degree of polymerization, related  
 258 to the order of magnitude of 1 found by  $^1\text{H}$  NMR for a single ring-opening grafting (entry 2).

259 Experiments combining radical and ring-opening routes were also conducted consecutively, in  
 260 a two steps reaction, for the sake of comparison. One can start either by the radical route or by the ring-  
 261 opening one. We obtained significant grafting ratios for the consecutive process starting from the free  
 262 radical grafting reported entry 4. A slightly higher grafting ratio is obtained, with a lower amount of  
 263 cyclic ester, leading to a lower DS. The molecular weight of the graft is in the same order of magnitude,  
 264 yet slightly lower. The two steps consecutive reactions starting from ring-opening followed by radical  
 265 grafting led to poor results and will not be discussed here.

266 Even if the DS is low, the process can be considered viable as high GP and  $M_n$  grafted are obtained  
 267 for vinyl grafted. The grafting ratio of oligo( $\epsilon$ -caprolactone) is improved by 4 via the combination of  
 268 two routes of polymerization in aqueous medium compared to ROP alone.

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### 270 3.1.3 Syntheses of starch-*graft*-[poly(butyl acrylate-*co*-styrene)/oligo( $\epsilon$ -caprolactone)]

271 The combination of radical and ring-opening grafting was then realized using styrene as a  
 272 comonomer with butyl acrylate for the radical polymerization. The insertion of styrene into poly(butyl  
 273 acrylate) is expected to have an impact on the properties of the resulting materials, by *e.g.* modulating  
 274 the thermal and mechanical properties. Representative results are given entries 6 and 9 in Table 2  
 275 together with the reactions conducted in the sequential way (7 and 10) and via the single radical route  
 276 (5 and 8) for comparison.

277

278 **Table 2.** Dual functionalization of starch in aqueous medium with styrene and butyl acrylate as vinyl  
 279 comonomers<sup>a</sup>

Entry	Route (time) <sup>b</sup>	BA/St/CL <sup>c</sup> (%wt)	GP <sup>d</sup> (%)	BA/St <sup>d</sup> (%)	$M_n^e$ (g/mol)	$\mathcal{D}_M^e$	$T_{g1}^f$ (°C)	$T_{g2}^f$ (°C)	$T_{deg 1}^g$	$T_{deg 2}^g$
5	Radical (1.5 h)	50/25/0	64	62/38	91 300	4.4	4	59	250	356
6	Dual (5 h) <i>Simultaneous</i>	50/25/25	71	67/33	63 200	2.5	-1	56	252	351
7	Dual (1.5 + 5 h) <i>Sequential</i>	50/25/25	72	68/32	71 000	2.9	0	56	245	352
8	Radical (1.5 h)	35/35/0	65	47/53	85 900	2.8	20	57	253	357
9	Dual (5 h) <i>Simultaneous</i>	35/35/30	65	49/51	63 500	2.3	18	58	248	359
10	Dual (1.5 + 5 h) <i>Sequential</i>	35/35/30	75	48/52	59 000	2.8	18	58	249	359

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281 <sup>a</sup> The starch is heated at 95 °C for 30 min in water before the grafting reaction at 85 °C.

282 <sup>b</sup> Sodium peroxydisulfate (1 mol % *vs.* starch) and phosphoric acid (1 mol % *vs.* CL) as initiator and  
 283 catalyst

284 <sup>c</sup> wt % monomer in the feed *vs.* starch

285 <sup>d</sup> Overall grafting percentage determined by gravimetry, ratio of BA/St units in grafted chains was  
 286 determined by <sup>1</sup>H NMR analysis in DMSO-*d*<sub>6</sub>/CDCl<sub>3</sub> (50/50) (Appendix G)

287 <sup>e</sup> Number-average molecular weight  $M_n$  and dispersity  $\mathcal{D}_M$  of the grafted poly(butyl acrylate-*co*-styrene)  
 288 chains determined by SEC (40 °C, THF, polystyrene standards) after acid hydrolysis (Appendix A.2)

289 <sup>f</sup> Glass transition temperature determined by DSC

290 <sup>g</sup> Temperature of degradation determined by TGA (degradation 1: starch, 2: grafted chains)

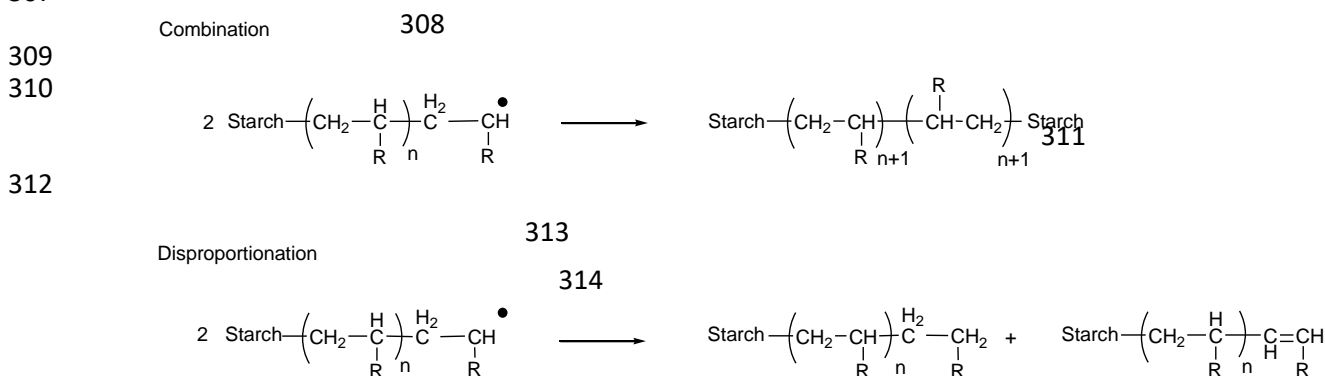
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293 The resulting grafting percentage is in the same order of magnitude than the one obtained using  
 294 only butyl acrylate in similar conditions (*e.g.* entries 5-6-7 *vs.* 1-3-4). The determination of the individual  
 295 grafting ratio, *i.e.* poly(butyl acrylate-*co*-styrene) *vs.* oligo( $\epsilon$ -caprolactone) is not possible by the <sup>1</sup>H  
 296 NMR method used previously due to signal overlapping, and we did not find any other suitable method  
 297 despite several trials. However, the ratio of butyl acrylate *vs.* styrene units in the grafted chains could  
 298 be determined by <sup>1</sup>H NMR analysis as reported in the Appendix G. It can be seen that the composition  
 299 of the poly(butyl acrylate-*co*-styrene) grafts follows the monomer feed. The molecular weights follow  
 300 the same trends as those observed while grafting PBA, *i.e.*  $M_n$  values lower than those obtained from the  
 301 radical process alone, the difference between the two processes being less important in the presence of  
 302 styrene. This could be explained by radical chains scissions. It is indeed known that acrylates favor the



303 occurrence of termination reaction by disproportionation while termination by combination is the main  
 304 process with styrene as the monomer (see Scheme 4) (Nakamura & Yamago, 2015). This may also  
 305 explain that the dispersities observed in the presence of the three monomers are lower than those  
 306 observed in the absence of styrene (2.5-4.4 vs. 3.8-7.7).  
 307



318 **Scheme 4.** Termination reactions by combination and disproportionation  
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321 The copolymers were analyzed by FT-IR (spectra in the Appendix H). The presence of the bands  
 322 at 1730 cm<sup>-1</sup> (ν(C=O)), at 1250 cm<sup>-1</sup> (ν(C-O)), and at 700 cm<sup>-1</sup> (deformation of aromatic function) are  
 323 characteristic of the butyl acrylate, caproyl and styrene groups respectively. The stretching frequencies  
 324 for ν<sub>as</sub>(CH<sub>3</sub>) and ν<sub>s</sub>(CH<sub>3</sub>) (corresponding to methyl of butyl chain) are observed at 2960 and 2872 cm<sup>-1</sup>,  
 325 respectively.  
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### 327 3.2 Thermal analyses

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 330 DSC analyses carried out on the grafted copolymers at 50 % relative humidity (thermograms in  
 331 the Appendix I) reveal two glass transition temperatures (T<sub>g</sub>) for all samples involving the radical  
 332 process, that are given in Table 1 and Table 2. The T<sub>g</sub> at -46 °C observed for entries 1; 3-4 corresponds  
 333 to the T<sub>g</sub> of poly(butyl acrylate). The second T<sub>g</sub> is found around 55 to 59 °C for all samples, whatever  
 334 the composition of the grafts, and is attributed to the glass transition of the starch backbone. The starch  
 335 alone has indeed a T<sub>g</sub> around 60 °C in similar conditions. When styrene is used as a comonomer for the  
 336 radical process, the low T<sub>g</sub> found around 2 °C (entries 5-7) and 19 °C (entries 8-10) increases with  
 337 increasing amount of styrene, the T<sub>g</sub> of polystyrene being around 100 °C. The presence of a single T<sub>g</sub>  
 338 for poly(butyl acrylate-*co*-styrene) grafted chains confirms a statistical microstructure which can be  
 339 expected from the reactivity ratios of the two monomers, r<sub>St</sub> 0.73-0.87 and r<sub>BA</sub> 0.17-0.30 (Fernández-  
 340 García et al., 2000). The thermograms did not show oligo(ε-caprolactone) glass transition or melting  
 341 temperatures, which can be ascribed to the low grafting ratio and the short size of the grafts. The  
 342 observation of two T<sub>g</sub> by DSC is an indication of a phase separation between starch and the grafted  
 343 polymer, which was already observed by us on starch-*graft*-poly(butyl acrylate) and starch-*graft*-  
 344 polystyrene copolymers in the form of two co-continuous phases (transmission electron microscopy  
 345 analyses, David et al., 2019).  
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347 TGA analyses were performed on the graft copolymers (Tables 1 and 2, curves in the Appendix  
 348 J). On all products, evaporation of water (contained in starch) below 100°C is observed. The unmodified  
 349 starch substrate degrades from 250 °C. Two main degradation stages are observed on the copolymers:  
 350 degradation of the starch part from 250 °C and degradation of grafted chains from 340 °C (entries 1-4)  
 351 or 350°C (entries 5-10). Adding styrene units on the copolymer increases the stability of the grafting  
 chains. The short grafts of oligo(ε-caprolactone) may degrade on the same stage as that of starch. Indeed,

352 for example starch acetates degrade in one stage of decomposition, the degradation being shifted towards  
353 higher temperatures with increasing DS (Wang et al., 2008).

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### 356 3.3 Mechanical behaviour

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358 Mechanical tests were then performed at 50 % relative humidity and room temperature. The  
359 results are presented in Table 1 (entries 1-4) and Figure 2A (entries 5-10). The temperature at which the  
360 mechanical tests were conducted is thus above the  $T_g$  of the grafted chains, which are as a consequence  
361 at the rubbery state, except for entries 8-10 where the  $T_g$  of the grafted chains is around 20 °C, and below  
362 the  $T_g$  of the starch. The copolymers obtained via single free-radical grafting copolymerization exhibit  
363 modest mechanical properties, with a stress at break around 0.3 MPa and an elongation at break close  
364 to 1.6 % (entry 1). The replacement of one third butyl acrylate by styrene in the feed allows to increase  
365 these properties to 8.7 MPa and 4.4 %, respectively, for the starch-*graft*-poly(acrylate-*co*-styrene)  
366 copolymer of entry 5. If the combination of the radical and ring-opening routes has a modest effect when  
367 butyl acrylate is used as a single radical monomer (entries 3 *vs.* 1), it leads to an impressive increase of  
368 the elongation at break when performed in the presence of 25% styrene (entries 6 *vs.* 5), by a factor as  
369 high as 17. When the radical grafting is performed with an equimolar amount of styrene and acrylate,  
370 the combination of the processes leads in turn to an increase of the stress at break from 6.6 to 7.4 MPa  
371 (entries 9 *vs.* 8), with a smooth increase of the elongation at break. The sequential route leads to similar  
372 results, with however a lower elongation at break (entry 7 *vs.* 6).

373 Both routes lead to similar performances in terms of GP, Mn, and thermal properties. The  
374 simultaneous route leads in turn to higher elongation at break. The promising results obtained in entry  
375 6 (BA/St/CL 50/25/25,  $\epsilon = 75$  %) prompted us to go further in this direction.

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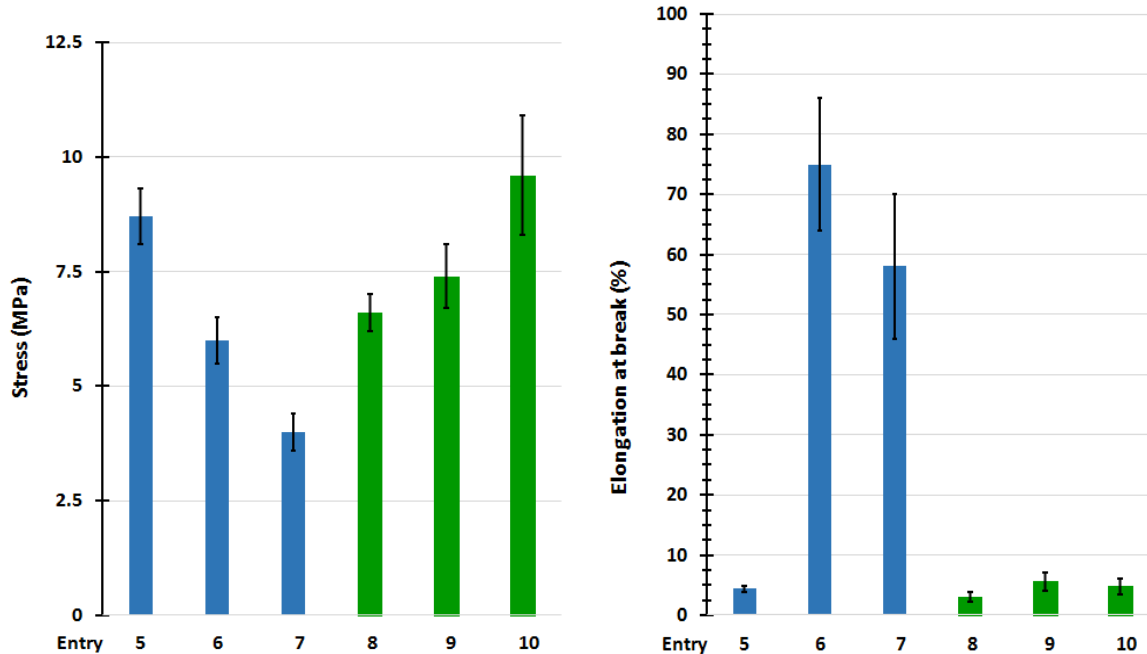
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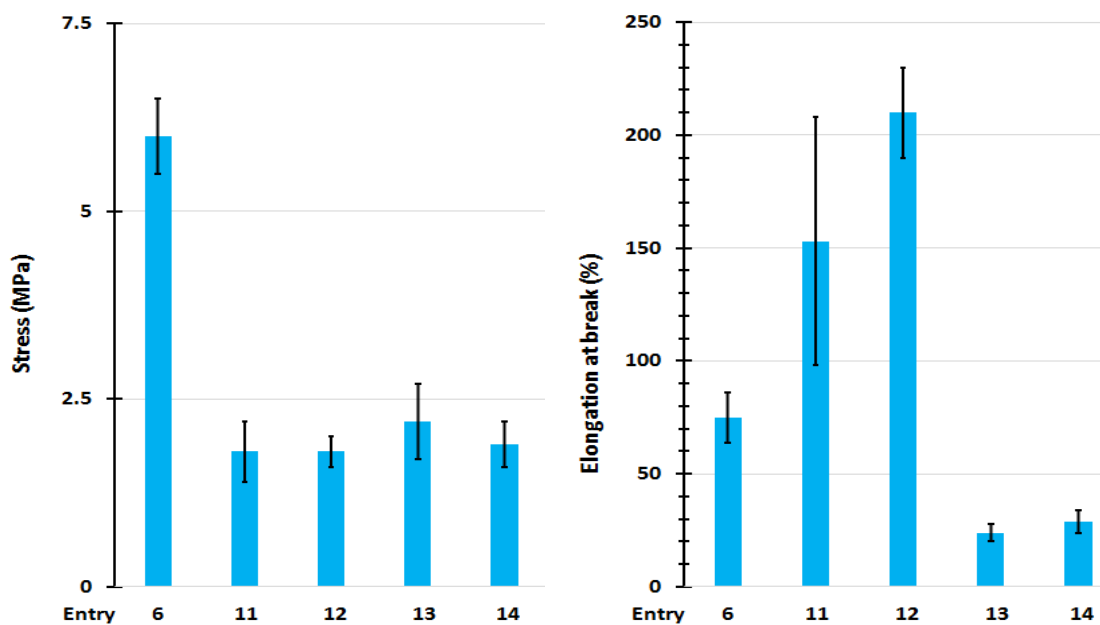
**A : Copolymers Entries 5-10 (Table 2)**



**5 : Radical (50%BA / 25%St)  
(35%BA / 35%St)**

**8 : Radical**

**B : Copolymers Entries 6, 11-14 (Table 3)**



**6 : 50%BA / 25%St / 25% CL**

**Dual Simultaneous**

**13 :**

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Fig 2 Stress and elongation at break of starch-graft-[poly(butyl acrylate-co-styrene) / oligo( $\epsilon$ -caprolactone)] at 20 °C, 50 % RH (numerical values Appendix K) in function of the monomers ratio (wt% vs. starch).

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### 3.5 Final adjustment of feed ratio: optimization of mechanical behaviour

A fine modification of the feed was realized in order to assess the effect of the composition on the mechanical properties in this range. The results are reported in Table 3 and Fig. 2B (the mechanical curves are presented in the Appendix K).

400 **Table 3** Simultaneous dual functionalization of starch in aqueous medium: optimization of the  
401 elongation at break<sup>a</sup>

Entry	BA/St/CL <sup>b</sup> (% wt)	GP <sup>c</sup> (%)	M <sub>n</sub> <sup>d</sup> (g/mol)	Đ <sub>M</sub> <sup>d</sup>	T <sub>g1</sub> <sup>e</sup> (°C)	T <sub>g2</sub> <sup>e</sup> (°C)
6	50/25/25	71	63 200	2.5	-1	56
11	50/20/30	69	62 000	2.8	-5	60
12	55/20/25	72	64 000	3.0	-10	59
13	55/15/30	68	66 000	2.6	-17	53
14	60/15/25	73	63 000	3.0	-21	57

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<sup>a</sup> The starch is heated at 95 °C for 30 min in water before the grafting reaction at 85 °C for 5 h. Sodium peroxydisulfate (1 mol % vs. starch) and phosphoric acid (1 mol % vs. CL) as initiator and catalyst.

<sup>b</sup> wt % monomer in the feed vs. starch

<sup>c</sup> Overall grafting percentage determined by gravimetry

<sup>d</sup> Number-average molecular weight M<sub>n</sub> and dispersity Đ<sub>M</sub> of the grafted poly(butyl acrylate-*co*-styrene) chains determined by SEC (40°C, THF, polystyrene standards) after acid hydrolysis (Appendix A.2)

<sup>e</sup> Glass transition temperature determined by DSC

411 The fine variation of the monomer ratios has neither a substantial influence on the grafting  
412 percentages (68-73 %), nor on the molecular weight distributions of the polyvinyl grafts (*M* values 62  
413 000 to 66 000 g/mol and dispersities 2.6 to 3). The T<sub>g</sub> of the grafted chains was found to be below 0 °C  
414 whatever the ratios. Mechanicals tests performed on these materials reveals elongations at break from  
415 *ca.* 20 % up to 207 % in this composition range (Fig. 2B.) The composition yielding to the higher  
416 elongation (BA/St 55/20) was assessed without the lactone, leading to a value of 14%. An increase factor  
417 of *ca.* 15 is thus confirmed while combining the two grafting processes for making the dual  
418 functionalized material. It is worth noting that the grafting of a small quantity of oligo(ε-caprolactone)  
419 allows to access to thermoplastic resins with interesting mechanical properties.

420 The visual observation of the specimen during the tensile test reported in Fig. 3 may bring some  
421 explanations of the phenomenon. Among the hypotheses able to explain the drop of elongation observed,  
422 a necking process during uniaxial tensile tests is clearly disregarded since there is no significant  
423 reduction in the section of the specimen located during the deformation. It can be seen that the specimens  
424 with high deformations whiten during tensile test. This bleaching is even more noticeable as the film is  
425 transparent before the test. It could be ascribed to the formation of cavities. In fact, cavitation is  
426 manifested by an increase in the inelastic volume and by a modification of the optical properties of the  
427 material (bleaching). The deformation profile, where a decrease in the maximum stress during the plastic  
428 deformation is observed, is also in agreement with cavitation phenomenons. The elongation at which  
429 the fracture occurs depends on the distribution of these cavities, *i.e* localized or in the whole material,  
430 and on the number of these cavities. The volume of deformation increases because of the creation of  
431 micro-voids while the shear operates without volume variation (Mikus et al., 2014). A more deep study  
432 is however necessary to confirm this hypothesis, and will be the subject of a forthcoming paper.

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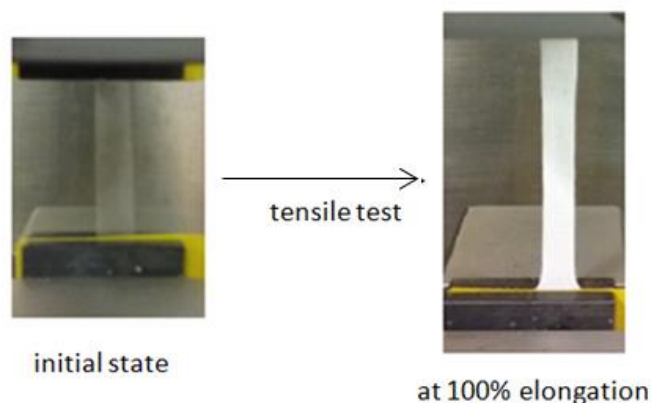
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447 **Fig. 3.** Evolution of the specimen during mechanical test of the starch-*graft*[poly (butyl acrylate-*co*-  
448 styrene acrylate) / oligo ( $\epsilon$ -caprolactone)] (55% BA / 20% St / 25% CL) obtained by "Radical + ROP"  
449 process  
450

#### 451 4. Conclusions

452 The dual functionalization of a starch is reported in a one pot one step route in aqueous medium,  
453 by combining free radical and ring-opening chemistries. Starch-*graft*-[poly(butyl acrylate)/oligo( $\epsilon$ -  
454 caprolactone)] and starch-*graft*-[poly(butyl acrylate-*co*-styrene)/oligo( $\epsilon$ -caprolactone)] copolymers  
455 were synthesized using sodium peroxydisulfate as radical initiator and phosphoric acid as  
456 organocatalyst. Compared to the single ring-opening process, an improvement in the grafting percentage  
457 of oligo( $\epsilon$ -caprolactone) is observed, by a factor of 2 to 4. The DSC analysis showed the presence of  
458 two glass transition temperatures, one related to the starch part and the other to the grafted vinyl  
459 polymers and being dependent on the butyl acrylate / styrene ratio. Interestingly, the resulting dual  
460 functionalized starches shows elongations at break as high as 210 % (BA/St/CL 55/20/25), a 15 fold  
461 increase when compared to the single free radical functionalization. The materials show thus promising  
462 potentialities in the field of stretchable films for light occulting applications.

463

#### 464 CRediT authorship contribution statement

465 Julie Meimoun: Conceptualization, Investigation, Methodology, Validation, Writing - original  
466 draft. Vincent Wiatz: Supervision, Validation. René Saint-Loup: Supervision, Validation, Writing –  
467 review. Julien Parcq: Supervision, Validation. Adéline David: Methodology. Grégory Stoclet:  
468 Methodology. Valérie Gaucher: Methodology. Audrey Favrelle-Huret: Conceptualization, Supervision,  
469 Validation, Writing – review. Fanny Bonnet: Conceptualization, Supervision, Validation, Writing –  
470 review. Philippe Zinck: Conceptualization, Methodology, Supervision, Validation, Writing - original  
471 draft, Writing – review.

472

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