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Biobased poly(ester-co-glycoside) from reactive Natural Brønsted Acidic Deep Eutectic Solvent Analogue

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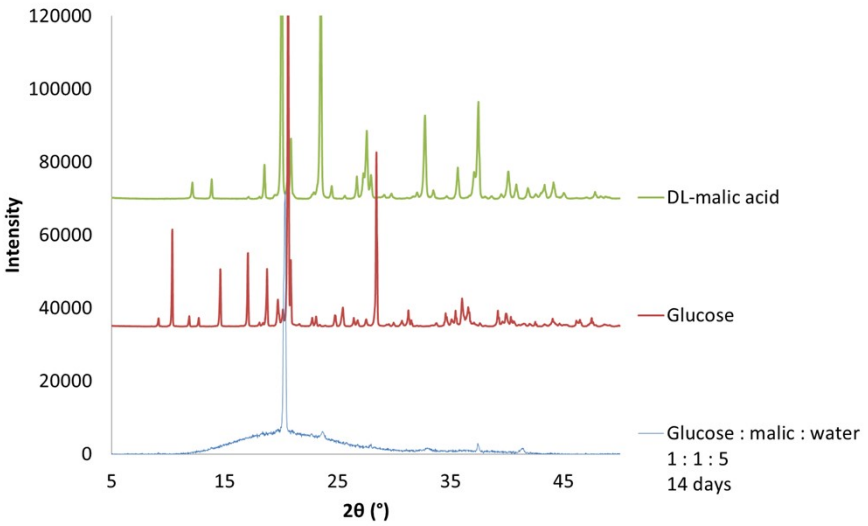

Fig.S1: XRD diffractogram of malic acid, glucose and the mixture {glucose : malic : water} (1 : 1 : 5 molar) after 14 days at 25 °C

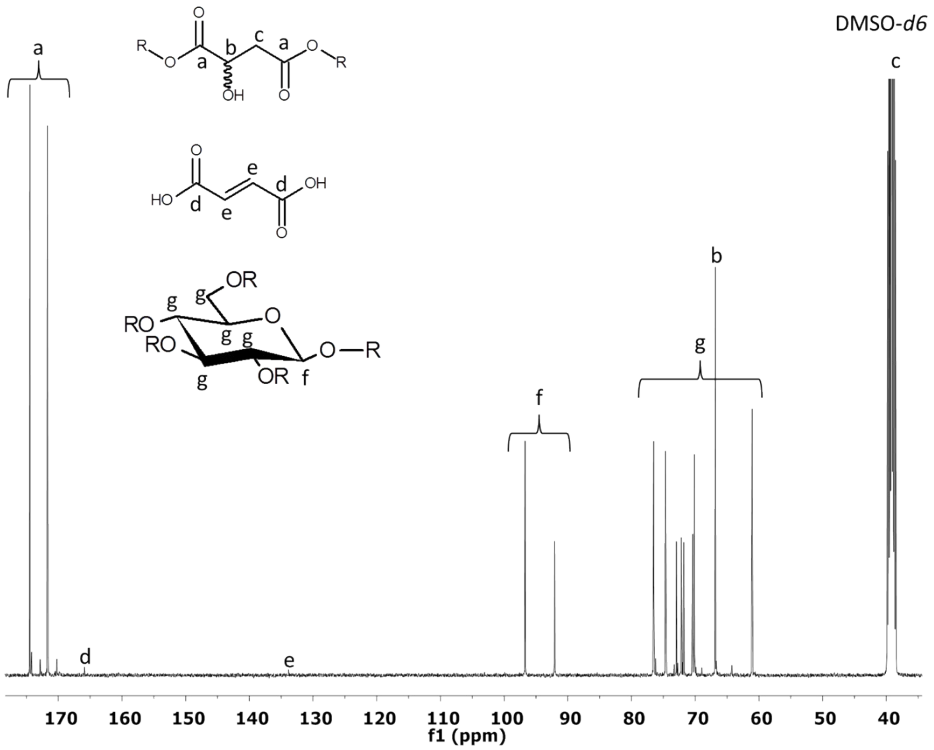

Fig.S2: ^{13}C NMR spectrum of {glucose : malic : water} (1 : 1 : 5 molar) after 2 months at 25 °C (signals are d and e are ascribed to fumaric acid, an impurity of malic acid) (DMSO-d6)

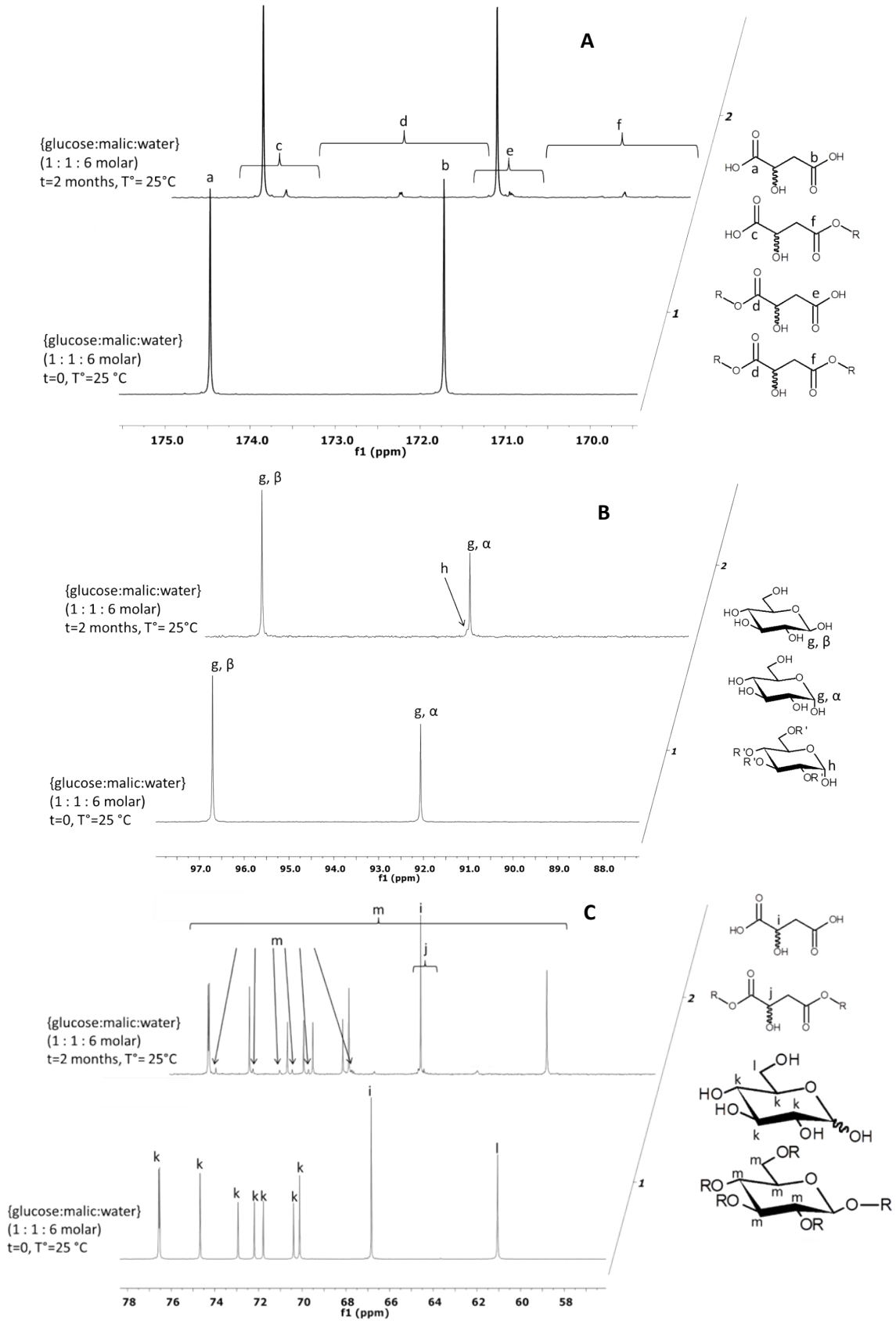

Fig.S3 :Zoom on the ^{13}C-NMR spectrum of the carbonyl region (A), the anomeric carbon of glucose unit (B) and the C-O links region (C) for a {glucose:malic acid:water}(1:1:6 molar) LTTM initially and after 2 months at 25 °C (DMSO-d6). In zone A, peaks c, d, e and f attest the presence of ester functions. In zone B, no peak related to converted anomeric carbon was detected. In zone C, peaks m attest that many OH have reacted to form esters, confirming that glucose is multifunctional with respect to esterification (see text for discussion).

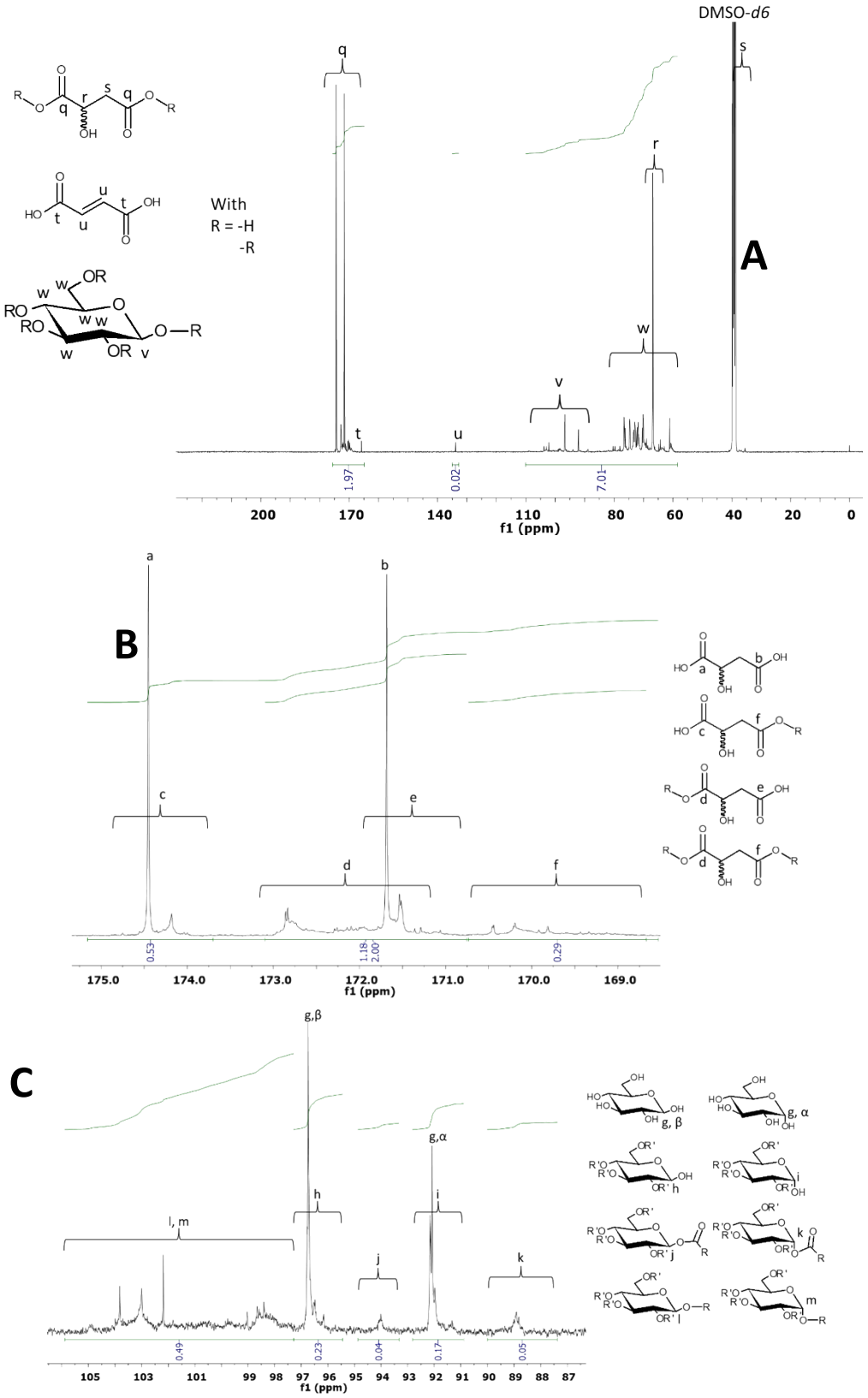

Fig.S4 : Zoom of ^{13}C-NMR spectrum of all regions (A), the carbonyl region (B) and the anomeric carbon of glucose unit (C) of the polymer obtained after 1 h 30 at 130 °C under argon for a {glucose: malic acid:water}(1 : 1 : 4 molar) LTTM (DMSO-d6). In part B, peaks c, d, e and f attest the presence of ester functions. In part C, peaks (j) and (k) on the one hand, and (l) and (m) on the other hand, attest that anomeric Cs have reacted according to an ester and glycosidic bond formation, respectively.

Calculation of esterification rate and glycosidic bond formation

Fig. S4.A shows the 13C NMR spectrum of a {glucose:malic:water} mixture after 1.5 h of polymerization under argon at 130 °C. The integration of peaks in the carbonyl region and C-O bonds account for 1.97 and 7.01, respectively. This integration is consistent with a quantitative ^{13}C NMR spectrum as both regions effectively count for 9 carbon atoms. It is therefore possible to compare the peaks with each other to make ratio calculations by integration.

To calculate the rate of COOH functions participating in the formation of ester bonds, we need to set the value of integration of the C=O region at 2. Figure S5.B shows that j and n represent an integration of 0.53 and 0.29 respectively. The average rate of esterification of COOH functions is given by the formulas below:

$$\int (a,b,c,d,e,f) = \int (a+c) + \int (b+e) + \int d + \int f = 2$$

$$\int (a+c) + \int d = \int (b+e) + \int f = 1$$

$$\%COOR = \frac{\int d + \int f}{\int (a,b,c,d,e,f)} \times 100 = \frac{\left(1 - \int (a+c)\right) + \int f}{\int (a,b,c,d,e,f)} \times 100$$

$$\%COOR_{1h30,130°C} = \frac{(1 - 0.53) + 0.29}{2} \times 100 \approx 38\%$$

Moreover, it is possible to obtain the rate of anomeric carbons involved in glycosidic bonds by observing the region of anomeric carbons between 87 and 105 ppm.

$$\%_{glycosidic\ bond} = \frac{\int l,m}{\int g,h,i,j,k,l,m} \times 100$$

In the case of Figure S4.C (1h30,130°C,Ar) :

$$\%_{glycosidic\ bond} = \frac{0.49}{0.49 + 0.23 + 0.04 + 0.17 + 0.05} \times 100 \approx 50\%$$

Name	Anomer	^{13}C NMR position (ppm)								
		1	2 or 3 or 4 or 5				6	O-C*H_3	O-(C*=O)-CH_3	O-(C=O)-C*H_3
Glucopyranose	α	92.05	72.18	72.92	70.39	71.77	61.05			
	β	96.7	76.53	76.56	70.11	74.65	63.66			
Levoglucosan		102.22	73.64	76.44	71.86	71.64	64.86			
Fructopyranose	α	63.12	97.15 #	67.92	71.35	63.63	58.72			
	β	64.23	97.9 #	67.66	69.05	69.05	63.58			
Fructofuranose	α	62.91	101.8 #	75.55	75.17	81.73	62.79			
	β	63.6	104 #	82.76	75.66	80.75	60.93			
Methylglucose	α	99.52	72.45	73.25	70.19	71.84	60.83	54.16		
	β	103.74	76.48	76.64	69.9	73.23	60.93	55.84		
Glucose pentaacetate	α	88.19	69.13	69.14	67.34	68.66	61.21		168.9 to 169.9	20.18 to 20.54
	β	90.74	69.97	71.67	67.58	71.3	61.37		168.7 to 169.9	20.17 to 20.38
D-(+)-Maltose α-Glucose-(1.4)-glucose	α-glucose(1-> α	100.59	72.69	73.26	70.09	73.16	60.53			
	α-glucose(1-> β	100.59	72.3	73.26	69.7	73.16	60.53			
	->4)-α-glucose	91.94	71.71	73.46	80.24	70.09	60.63			
	->4)-β-glucose	96.62	74.17	76.26	79.68	74.87	60.63			
D-(+)-Tréhalose α-Glucose-(1.1)-α-glucose	Symmetry	92.91	72.28	72.71	69.94	71.42	60.6			
D-(+)-Cellobiose β-Glucose-(1.4)-glucose	β-glucose(1->	102.99	73.15	76.3	69.87	76.6	60.86			
	->4)-α-glucose	91.87	71.26	71.91	80.82	69.67	60.33			
	->4)-β-glucose	96.48	74.33	74.56	80.57	74.89	60.39			
D-(+)-Gentiobiose β-Glucose-(1.6)-glucose	α-glucose(1->	103.01	73.38	76.73	69.83	76.7	60.85			
	->6)-α-glucose	92.05	72.88	73.35	69.86	70.36	68.94			
	->6)-β-glucose	96.66	74.61	76.46	70.03	75.01	68.73			
Sucrose	α-glucose(1->	91.59	71.47	72.73	69.69	72.66	60.35			
	->2) β-fructofuranose	61.91	103.86	76.88	74.13	82.38	61.97			
Saccharose octoacetate	α-glucose(1->	89.51	69.37	75.15	67.8	67.99	62.63		169.64 to 170	20.12 to 20.45
	->2) β-fructofuranose	61.72	103.12	68.95	74.13	77.89	63.54		169.2 to 169.54	20.12 to 20.45

Table S.1 : Table of assignment in ^{13}C NMR of the peaks of some molecules of interest in DMSO-*d6* at 298 K.

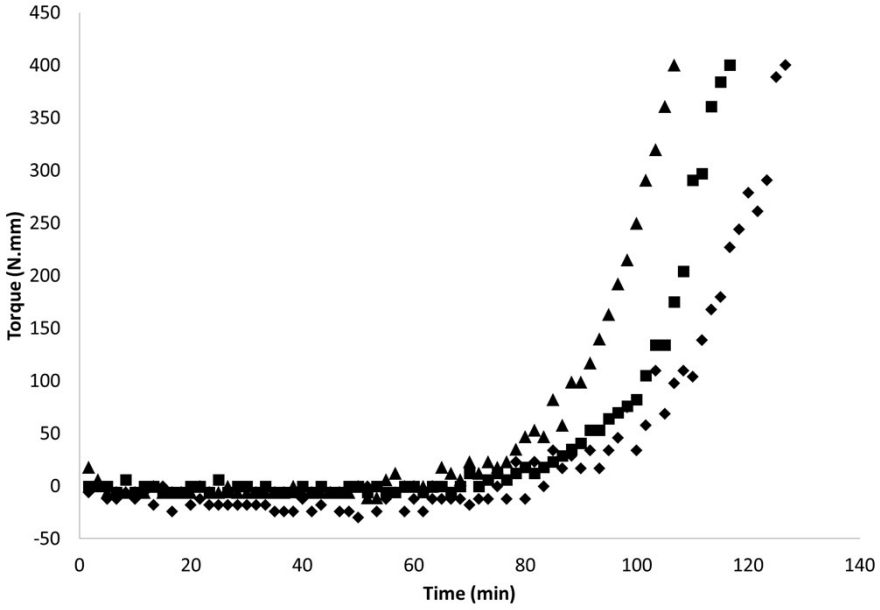

Fig.S5 : Torque monitoring during the reaction at 130 °C under argon of three mixtures {glucose : malic : water}(1 : 1 : x molar). Legend : Triangle : x = 1.9, square : x = 4.6 and lozenge : x = 6.

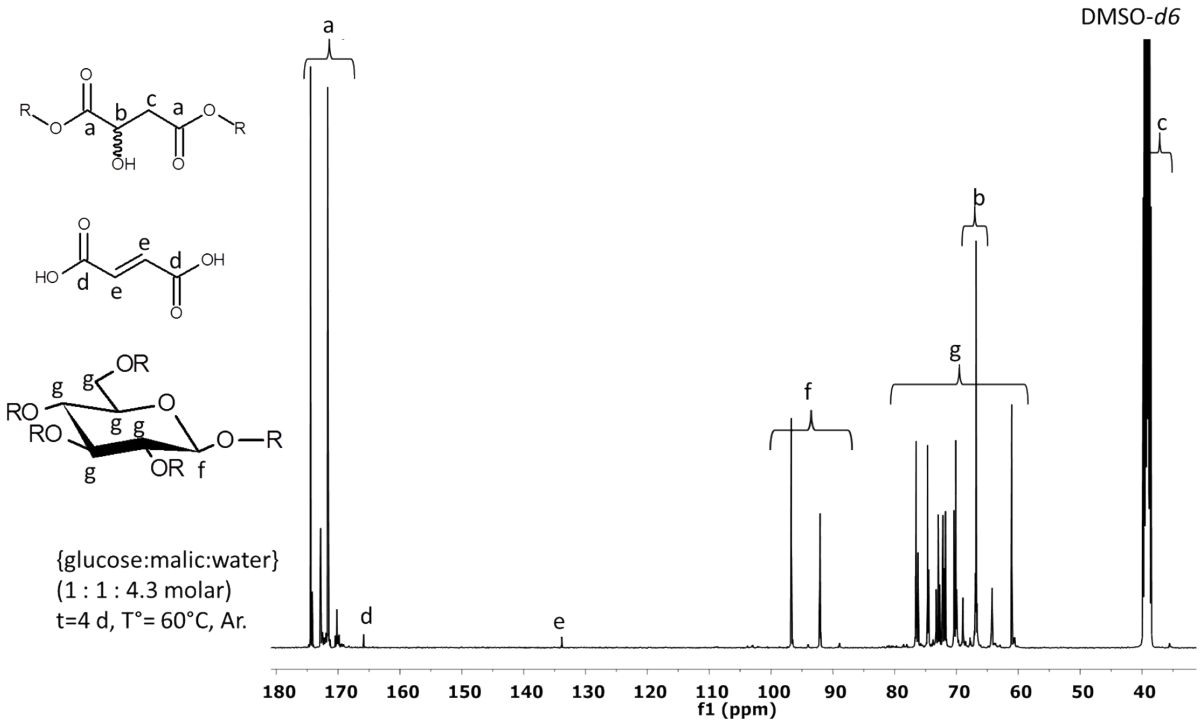

Fig.S6 : ^{13}C-NMR spectrum after 4 days at 60 °C for a {glucose: malic acid:water} (1:1:4 molar) NaLTTM (DMSO-d6). Many peaks visible in the carbonyl domain attests that ester groups were formed. Small bumps discernible around 105 ppm, characteristic of anomeric carbon involved in glycosidic bond, suggest that the corresponding reaction has started to occur.

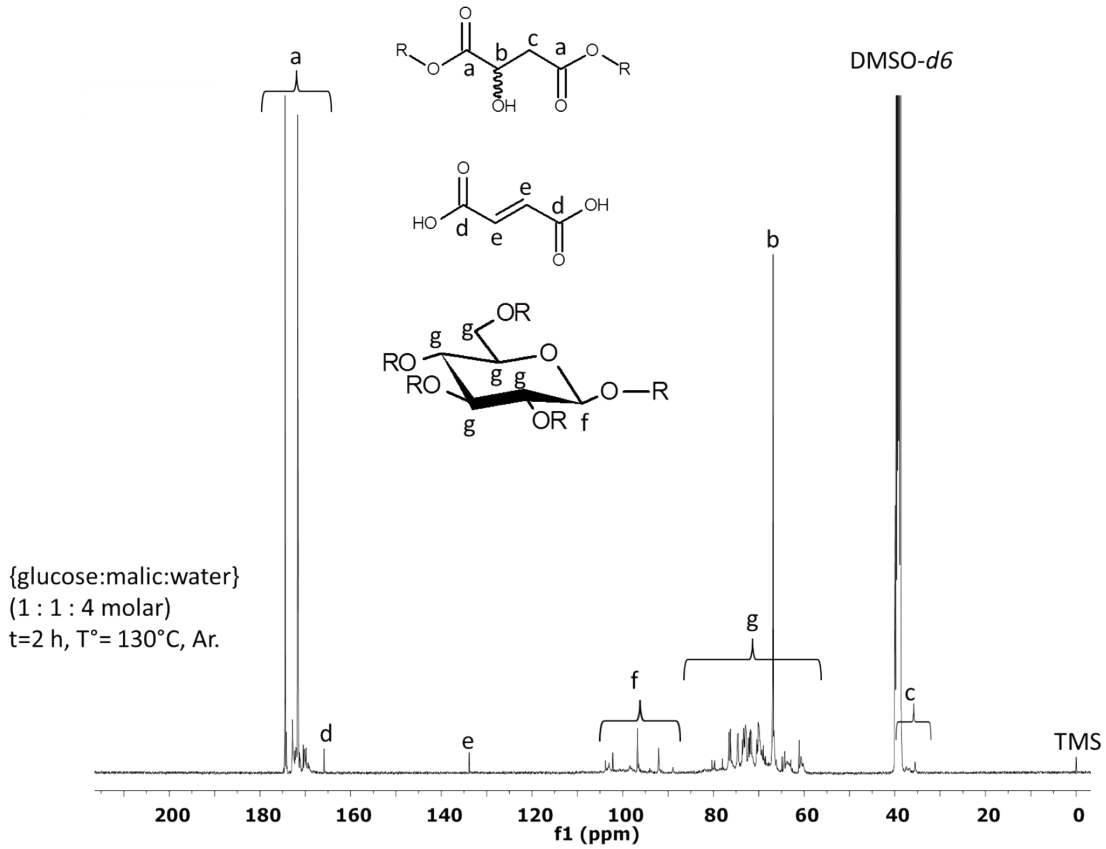

Fig.S7 : ^{13}C NMR spectrum of {glucose:malic:water} (1:1:4 molar) after 2 h at 130 °C

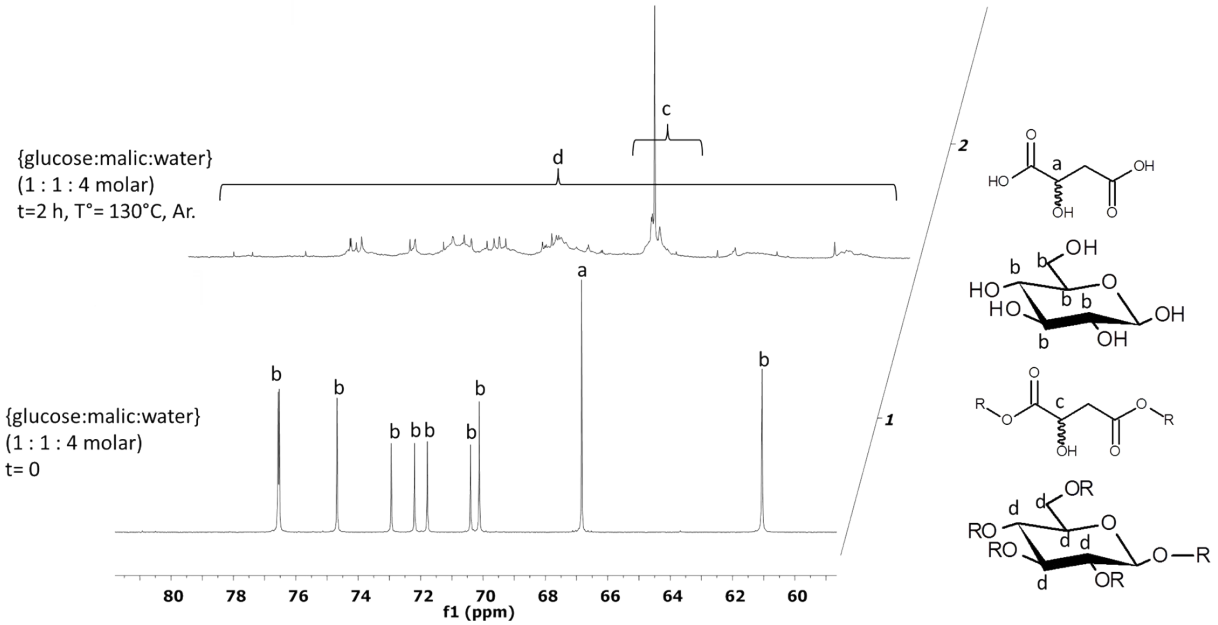

Fig.S8 : Zoom of the ^{13}C NMR spectrum of {glucose:malic:water} (1:1:4 molar) NaLTTM initially and after 2 h at 130 °C (DMSO-d6). Presence of peak {c} confirms that malic acid has reacted to form ester bonds; multiple peaks {d} confirms that OH functions have reacted (either through ester or glycosidic bond formation)

{Glucose : malic : water} (1:1:4 molar), 2 h, 130 °C, Argon A = Glucose unit, B = Malic unit, -H_2O = Dehydrated unit							
A	B	- H_2O	mass m/z + Na^+	A	B	- H_2O	mass m/z + Na^+
1	1		319	4	3	1	1018,8
2		1	347	4	3		1036,8
2			365	5	2	1	1064,8
1	2	1	417,1	5	2		1082,8
1	2		435	6	1		1128,8
2	1	1	463,1	4	4	1	1134,7
2	1		481	4	4		1152,7
3			527	5	3	1	1180,7
1	3	1	533,1	5	3		1198,7
1	3		551	6	2	1	1226,8
2	2	1	579	6	2		1244,8
2	2		597	7	1		1290,7
3	1	1	625	5	4		1314,7
3	1		643	6	3	1	1342,7
4			689	6	3		1360,7
2	3		712,9	7	2		1406,6
3	2	1	740,9	5	5		1430,5
3	2		758,9	8	1		1453,4
4	1	1	787	6	4		1476,6
4	1		805	7	3		1522,5
2	4		828,9	6	5		1569,5
5			851	9	1		1614,6
3	3	1	856,9	7	4		1638,5
3	3		874,9	8	3		1684,5
4	2	1	902,9	7	5		1754,5
4	2		920,9	8	4		1800,4
5	1		966,9	up to ≈ 2000 m/z			
3	4		990,8				

Table S. 2 : Result table of MALDI-ToF MS measurements on a {Glucose: malic: water} sample (1:1:4 molar) treated for 2 h at 130 °C under argon.

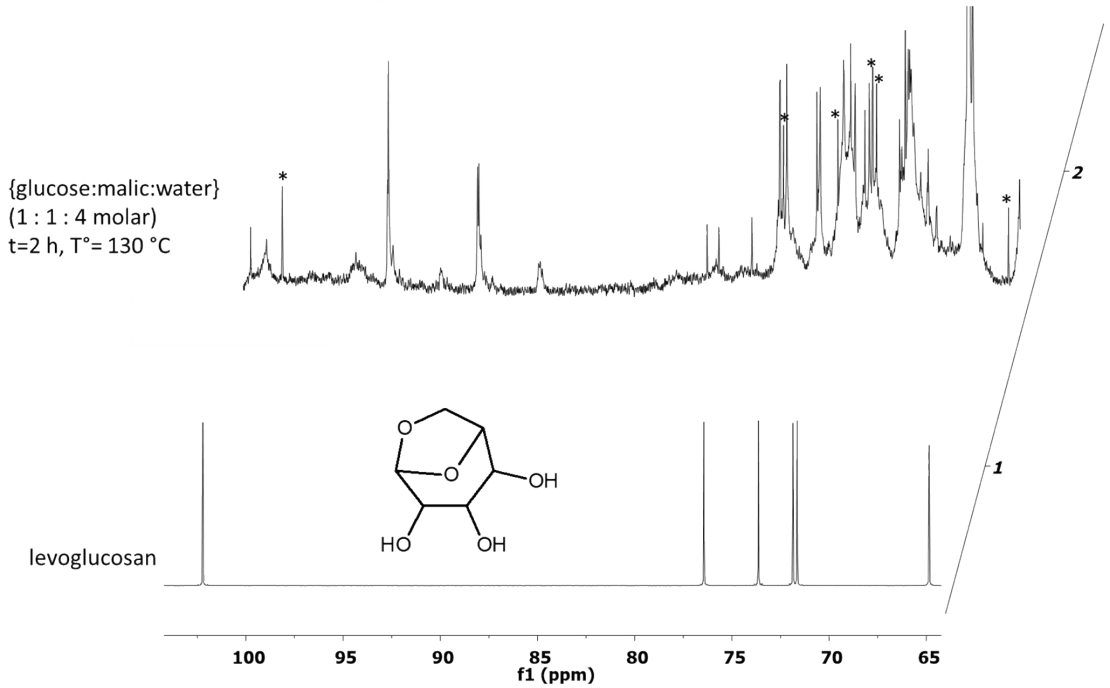

Fig.S9 : ^{13}C NMR spectrum of {glucose:malic:water} (1:1:4 molar) NaLTTM after 2 h at 130 °C in comparison with the spectrum of levoglucosan (DMSO-d6). * represents the characteristic peaks of levoglucosan.