Supplementary Information (SI) for ChemComm.

Tuning the Viscoelasticity of Sugar-Silicone Polymers Using Caramelization

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SUPPORTING INFORMATION

1. Materials and Methods

Materials

Telechelic 3-(aminopropyl)-terminated polydimethylsiloxanes DMS-A15 (3000 g mol-1), DMS-A21 (5000 g mol-1), DMS-A31 (25000 g mol-1) and DMS-A35 (50000 g mol-1) and pendant AMS-132 (2.5% aminopropyl monomers, 5250 g mol-1), AMS-162 (6.5% aminopropyl monomers, 4500 g mol-1) and AMS-191 (10% aminopropyl monomers, 2500 g mol-1) were purchased from Gelest. d-Gluconolactone, N-butyl gluconamide and isopropanol were purchased from Sigma-Aldrich. All compounds were used as received.

Methods

Rheology was studied on a TA Instruments HR-2 Rheometer equipped with a 40 mm 1.0° cone and a Peltier plate for controlled heating and cooling. The gap between the two plates was set to 200 µm for all experiments. For the viscosity measurements the strain was set to 5 % (which is within the LVE region) and the angular frequency was continuously increased from 0.1 to 1 rad.s-1. For constant strain oscillatory measurements the strain was set to 5 %, the angular frequency was increased from 1 to 628 rad.s-1, and the temperature was set to 25 °C.

Young's moduli were measured using a Biomomentum Mach-1 Mechanical Testing System. Mach-1 Motion software was used to control the machine with the following sequence of commands: Scan, Move Absolute, Zero Load, Find Contact, Stress Relaxation, Move Absolute, Wait. This sequence was repeated for each row of the 96-well plate (12 wells at a time). Each well was measured three times. The stress relaxation data was saved and analyzed using the Mach-1 Analysis software where Force (in the z direction) was plotted against Position (in the z direction). The radius of the probe on the Mach-1 instrument has a radius of 0.5mm. The sample thickness was measured for each sample and adjusted accordingly. The Poisson ratio was set to 0.3.

Dynamic scanning calorimetry (DSC) was measured on a TA-instruments DSC Q20 calorimeter with a heating ramp of 10 °C·min-1.

Thermogravimetric analysis (TGA) data were collected on Mettler Toledo TGA/DSC 3+ System under an argon gas environment according to the ASTM D 6370-99 (American Society for Testing and Analysis). The measurements were performed in alumina crucibles with a heating rate of 10 K.min^{-1}.

2. Nomenclature, Synthesis and Caramelization of Sugar-Silicones

Nomenclature

Telechelic and pendant aminopropylsilicone precursors are converted into telechelic **GT-x-Y** or pendant **GP-n+m-Y** sugar-modified silicones, where n and x represent the number of Me_2SiO monomers, m represents the number of $OMeSi(CH_2)_3NH_2$ monomers, and **Y** denotes the weight percent of $OSiMe(CH_2)_3N$-sugar monomers (~$(CH_2)_3NH$-$C_6H_{11}O_6$) formed upon reaction with gluconolactone.

Synthesis

GT-x-Y was prepared from telechelic aminopropylsilicone and *D*-gluconolactone (GDL) in IPA (20 mL) at room temperature. The mixture was stirred until the solution was homogeneous and no solid crystals of GDL remained (~48 hours on average). Reaction completion was confirmed by FT-IR spectroscopy and NMR. The same process was used for the synthesis of **GP-n+m-Y**, however these were prepared using pendant aminopropylsilicones. Reagent amounts required for each synthesis are given below.

Table S1. Recipes for **GT-x-Y**

Product	Starting Aminosilicone (g mol^{-1})	x	Amount of Aminosilicone	Moles of NH_2	Amount of GL	Moles of GL	Wt% sugar
GT-37-15	DMS-A15 (3000)	36	5.000 g	3.333 mmol	0.593 g	3.333 mmol	15
GT-334-2	DMS-A31 (25,000)	334	5.000 g	0.400 mmol	0.071 g	0.400 mmol	2
GT-672-1	DMS-A35 (50,000)	672	5.000 g	0.200 mmol	0.036 g	0.200 mmol	1

Table S2. Recipes for **GP-n+m-Y**

Product	Starting Aminosilicone (g mol^{-1})	n (m – NH_2)	Amount of Aminosilicone	% NH_2 X (%)	mmol NH_2	Amount of GL	mmol GL	
GP-68-8	AMS-132 (5250)	66 (1.7)	5.000 g	2.5	0.855	0.152 g	0.855	8
GP-56-28	AMS-162 (4500)	53 (3.7)	5.000 g	6.5	2.991	0.532 g	2.991	18
GP-30-37	AMS-191 (2500)	27 (3)	5.000 g	10	4.701	0.837 g	4.701	26

3. Caramelization of Sugar-Silicones

For each sugar-silicone, 0.300 g of the product was weighed into nine different neckless glass vials (35 mm height, 0.5 mm radius). The vials were left for 24 h to allow each sample to settle to the bottom. Each vial was then put into a 180 °C oven for different periods of time (5 min, 10 min, 15 min, 30 min, 60 min, 6 h, 24 h, 48 h, and 72 h). After heating for the set period of time, the sample was allowed to cool in the vial for 24 h, after which it was removed from the vial for further analysis (Tables S3 and S4).

Table S3. Changes in tan(δ) and *Shore OO* hardness after heating of telechelic polymers for different time periods at 180 °C.

Caramelization Time in minutes	**Phase[a] GT-37-15**	**Tan(δ)/Shore OO GT-37-15**	**Phase[a] GT-334-2**	**Tan(δ) /Shore OO GT-334-2**	**Phase[a] GT-672-1**	**Tan(δ) /Shore OO GT-672-1**
0	S	Brittle[a]	L	13.2/-	L	10.9/-
5	S	Brittle[a]	L	7.5/-	L	4.7/-
10	L	3.5 /-	L	5.3/-	L	4.6/-
15	L	3.4/-	L	3.4/-	L	3.4/-
30	L	2,3/-	L	1.4/-	L	1.5 /-
60	S	0,7/*29*	L	1.2/-	S	0.8/too soft[b]
360			S	0.24/*24*	S	*-/10*
1440[d]			S	*-/40*	S	*-/28*

[a] L (liquid), analyzed via rheology, S (solid), analyzed via Shore OO; data shown in italics.

[b] soft gel, too soft to be measured by Shore OO (note: Shore OO 10 ~ a soft gummy candy; 30 ~ a gel shoe insert; 60 ~ a rubber band).

Table S4. Changes in tan(δ) and *Shore OO* hardness after heating of pendant polymers for different time periods at 180 °C.

Caramelization Time in minutes	**Phase[a] GP-68-8**	**Tan(δ)/Shore OO GP-68-8**	**Phase[a] GP-56-28**	**Tan(δ)/Shore OO GP-56-18**	**Phase[a] GP-30-26**	**Tan(δ)/Shore OO GP-30-26**
0	L	176/-	L	16/-	L	4/-
5	L	61/-	L	2/-	L	2/-
10	L	46/-	S	0.9/43	S	*0.9/58*
15	L	28/-	S	0.6/49	S	*0.7/61*
30	L	9/-	S	N/A[d]		
60	L	1.4/-				
360	S	too soft[b]				
1440	S	too soft[b]				
2880	S	-/14				
4320	S	-/31				

[a] L (liquid), analyzed via rheology, S (solid), analyzed via Shore OO, data shown in italics.

[b] Soft gel, too soft to be measured by Shore OO. [d] N/A – not measured; too brittle.

4. Swelling Behavior

To investigate the swelling behavior of the samples, a defined mass (0.030 g) of GT37-15 after an extended caramelization time of 20 h was added to 1 mL of $CDCl_3$ and allowed to swell for 16 h, after which the mass was recorded. The samples were then dried in an oven at 60 °C for 16 h, cooled to room temperature, and the mass was measured again. The results are shown in Figure S1, and the corresponding masses are listed in Table S5. The data show that the sample swelled by a factor of 683, demonstrating that the solvent can penetrate the network and increase the distance between the polymer chains without dissolving the sample, indicating the presence of strong bonds between the polymer chains.

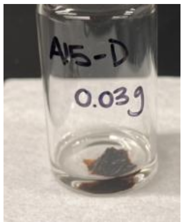
(A) Caramelized GT37-15 in $CDCl_3$	**(B) GT37-15 after removal of the solvent**
	

Figure S1: Images of GT37-15 during swelling in $CDCl_3$ for 16 h (A) and after evaporation of the solvent (B).

Table S5. Swelling of caramelized GT37-15 in $CDCl_3$

Original mass	**Mass after 16 h in $CDCl_3$**	**Swelling %**	**Mass after removal of the solvent**
0.030 g	0.206 g	683	0.032 g

5. Mobility of GT37-15

To test the mobility of GT37-15, the sample was filled into a glass vial, which was then placed on its side overnight. Afterward, the vial was returned to an upright position and allowed to stand for 2 days, after which the pictures shown in Figure S2 were taken. The images illustrate that, with increasing caramelization time, a solid-like material gradually transforms into a viscoelastic material with liquid-like properties, while further heating again results in solid-like materials without any observable flow behavior.

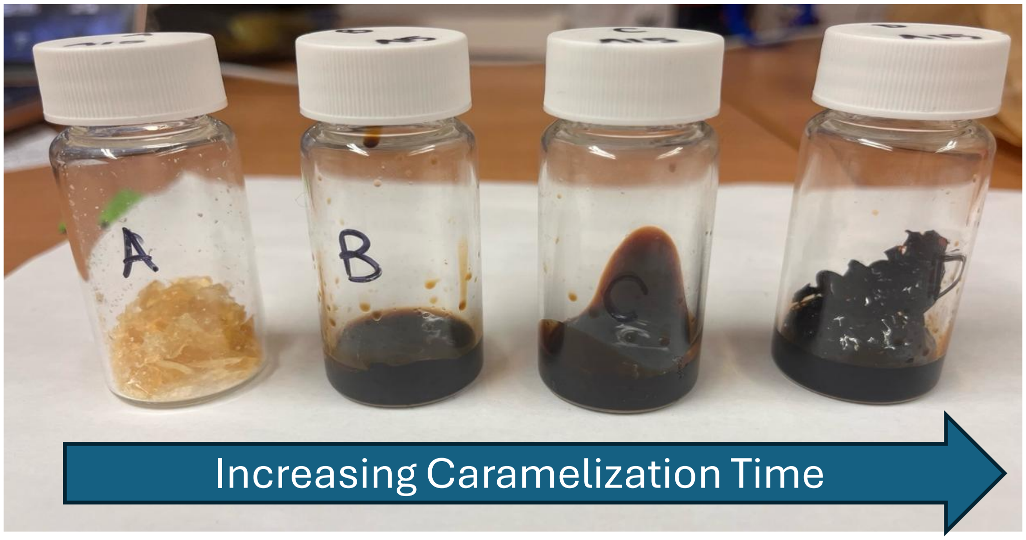


Figure S2: Mobility of GT37-15 during caramelization at 180°C. The sample was caramelized for a maximum of 20

Rheology Data

Oscillation sweeps were performed to measure the storage and the loss moduli of each sample (Table S6-S11). Tan(δ) values were calculated at an angular frequency of 1 rad.s^{-1} (Table S12, Table S13).

Table S6. Oscillation sweep of **GT-37-15** after 10- and 60-min heating at 180 °C (dotted line: storage modulus).

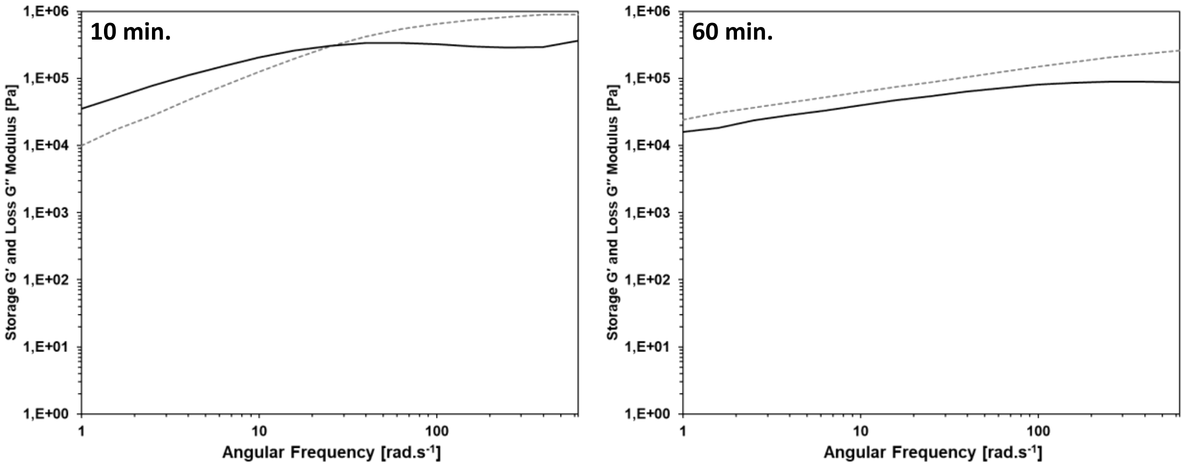


Table S7. Oscillation sweep of **GT-334-2** prior and after 60 min and 24 h heating at 180 °C (dotted line: storage modulus).

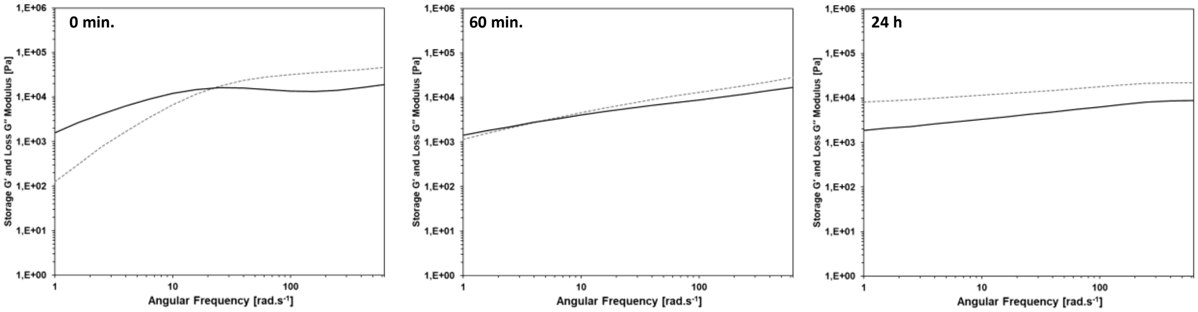


Table S8. Oscillation sweep of **GT-672-1** prior and after 30 and 60 min heating at 180 °C (dotted line: storage modulus).

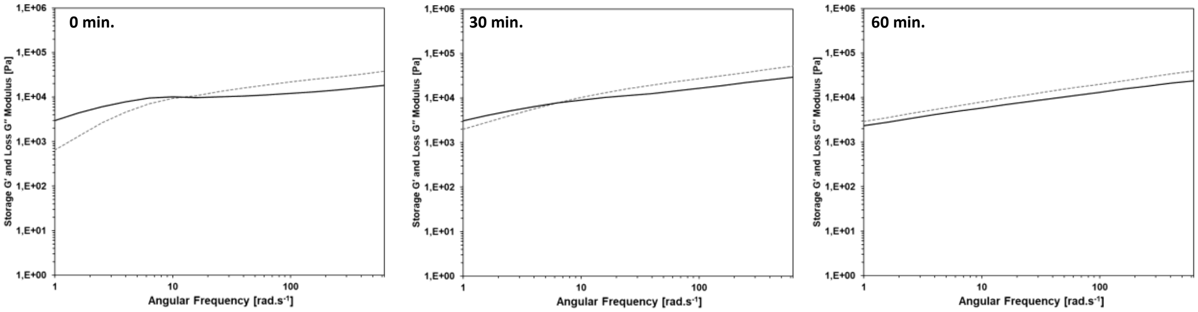


Table S9. Oscillation sweep of **GP-68-8** prior and after 60 min. and 24 h heating at 180 °C (dotted line: storage modulus).

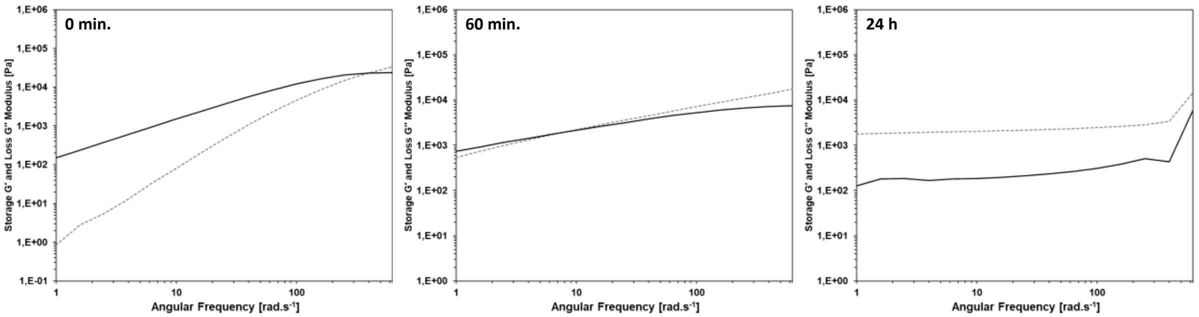


Table S10. Oscillation sweep of **GP-56-28** prior and after 5- and 15-min heating at 180 °C (dotted line: storage modulus).

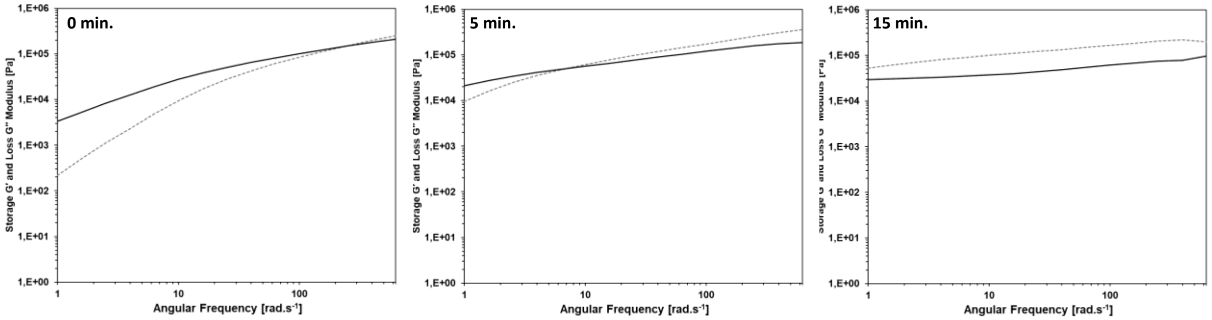


Table S11. Oscillation sweep of **GP-30-37** prior and after 5- and 15-min heating at 180 °C (dotted line: storage modulus).

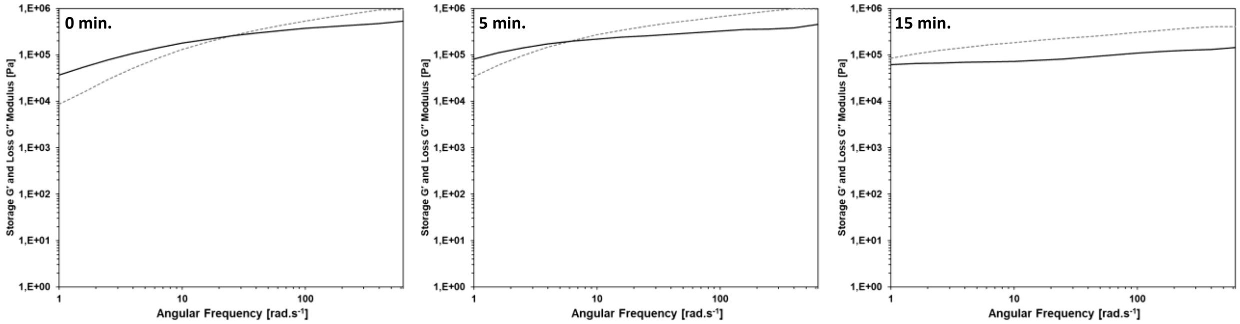


Table S12. Tan(δ) values of **GT-37-15**, **GT-334-2**, and **GT-672-1** prior and after caramelization at 180 °C.

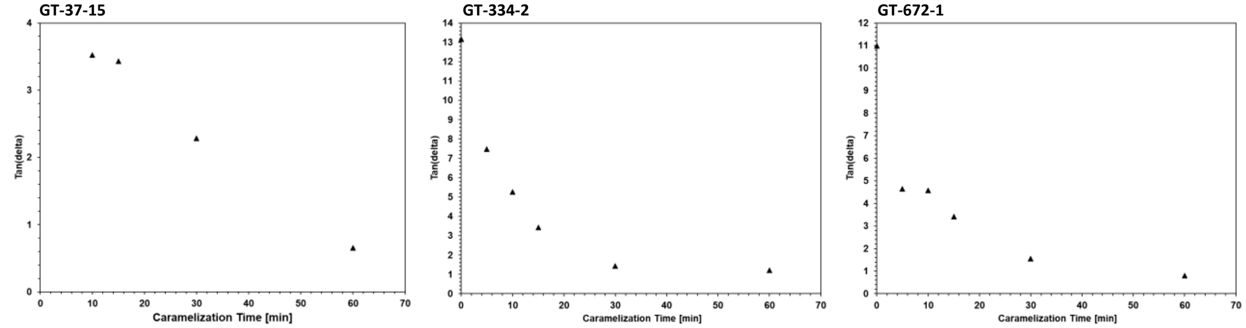


Table S13. Tan(δ) values of **GP-68-8**, **GP-56-28**, and **GP-30-37** prior and after caramelization at 180 °C.

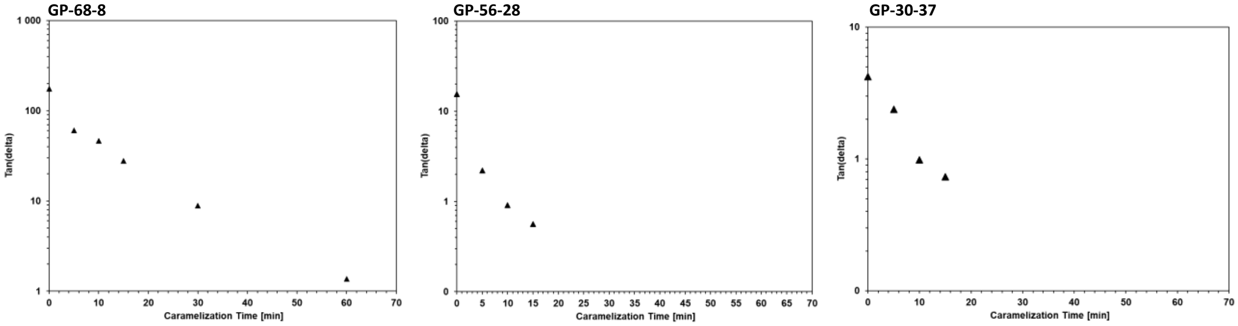
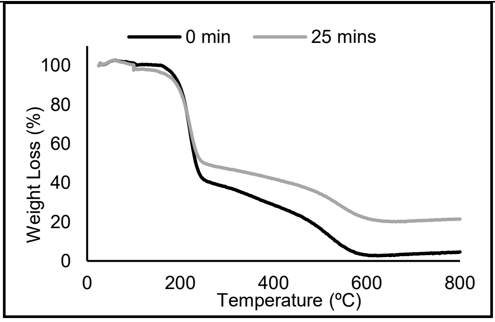
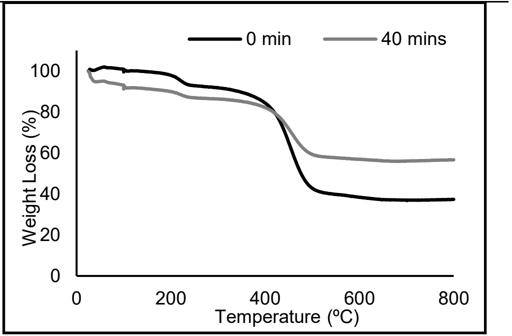
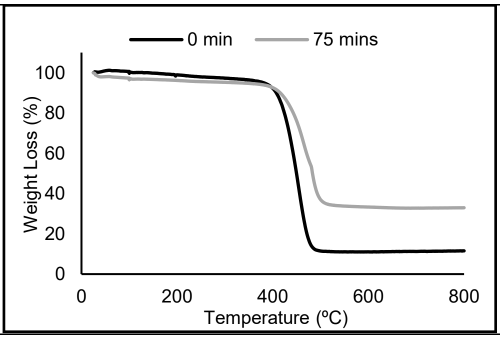
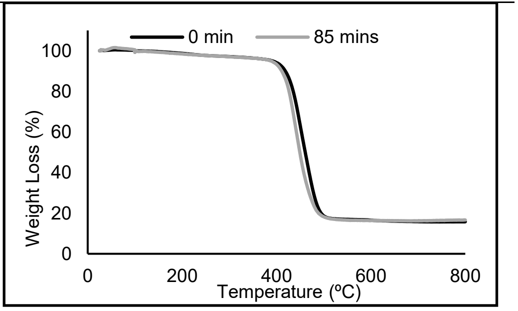


Table S14. TGA plots of the control sample **BG** and the samples **GT-37-15**, **GT-334-2**, and **GT-672-1** prior (black line) and after caramelization (grey line) at 180 °C.

	Prior to heating		After heating at 180 °C for t minutes
BG		**GT-37-15**	
GT-334-2		**GT-672-1**	

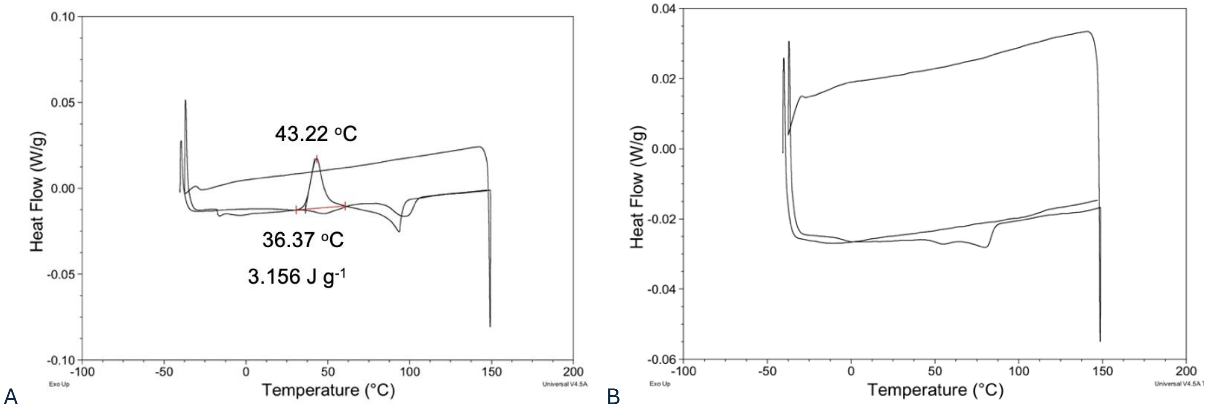


Figure S3. DSC plots for **GT-37-15** before (left) and after (right) caramelization. After heating at 180 °C for 20 min **GT-37-15** has no significant thermal transitions.