Supporting Information

Dynamically Tuning Transient Silicone Polymer Networks with Hydrogen Bonding

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1. Experimental

Chemicals and Characterization

The aminopropylsilicones DMS-A11 (**SAS9-0**, 850 - 900 g.mol^{-1}), DMS-A15 (**SAS38-0**, 3,000 g.mol^{-1}), DMS-A21 (**SAS65-0**, 5,000 g.mol^{-1}), DMS-A35 (**SAS673-0**, 50,000 g.mol^{-1}), and cyclopentasiloxane (D_5) were purchased from Gelest. D-Gluconolactone (97 %), cyrene, Amberlyst 25, and trifluoroacetic acid (99 %) were purchased from Sigma Aldrich. 2-Propanol and hydrogen peroxide (30 %) were purchased from Caledon. 2,3-O-Isopropylidene-D-4-ribonolactone (98 %) was purchased from Combi-Blocks.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 600 spectrometer. Differential scanning calorimetry was performed on a TA-instruments DSC Q200 calorimeter in a heat/cool/heat measurement. The sample and reference pans were heated from +20 °C to +140 °C with a heating ramp of 5 K.min^{-1}, kept for 1 min. at +140 °C, cooled to -88 °C with a cooling rate of 2 K.min^{-1}, kept at -88 °C for 2 min. and heated back to +140 °C with a heating rate of 5 K.min^{-1}. 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. Temperature dependent viscosity measurements were performed between 0 °C and +100 °C with a cooling rate of 15 K min^{-1} and a constant shear rate of 0.1 s^{-1}. Time-temperature superposition curves were calculated for 25 °C as the reference temperature from constant strain oscillatory frequency rheology measurements at different temperatures. The strain was set to 5 % (which is within the LVE region) and the angular frequency was continuously increased from 1 to 628 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 varied from -5 to +75 °C.

Synthesis of 5-Hydroxymethyl-2-oxotetrahydrofuran (Monolactone)

A mixture of cyrene (2 mL, 19.53 mmol) and Amberlyst 15 (0.82 g, 3.90 mmol, ion exchange capacity ≥4.7 equiv/kg) in water (3 mL) was cooled to 0 °C and treated by dropwise addition of 30 % H_2O_2 solution (2 mL, 20 mmol).[19] After the addition of H_2O_2 was complete, the reaction mixture was heated to 50 °C and stirred for 2 h. The reaction mixture was then cooled to RT. The residual peroxides, if present, were neutralized with Na_2SO_3. Amberlyst 15 resin was removed from the reaction mixture by filtration, washed with water, the filtrate was concentrated at reduced pressure, the residue was separated by chromatography on silica gel, using hexanes-EtOAc as eluent, gradient from 2:1 to 1:1 to afford 5-hydroxymethyl-2-oxotetrahydrofuran (1.7 g, 75 %).

^{1}H-NMR (600 MHz, chloroform-d, ppm) δ = 2.03-2.13 (m, 1H, CH_2), 2.17-2.26 (m, 1H, CH_2), 2.44-2.60 (m, 2H, CO-CH_2), 3.58 (dd, 1H, HO-CH_2, J = 11.9, 4.1 Hz), 3.78-3.85 (m, 1H, HO-CH_2), 4.54-4.68 (m, 1H, CH). ^{13}C-NMR (151 MHz, chloroform-d, ppm) δ = 177.9, 80.9, 64.1, 28.7, 23.2. IR (ATR-IR, cm^{-1}): 3424, 2941, 1758, 1460, 1419, 1352, 1291, 1270, 1182, 1153, 1096, 1059, 1019, 989, 934, 915, 886, 834, 803, 731, 700, 648.

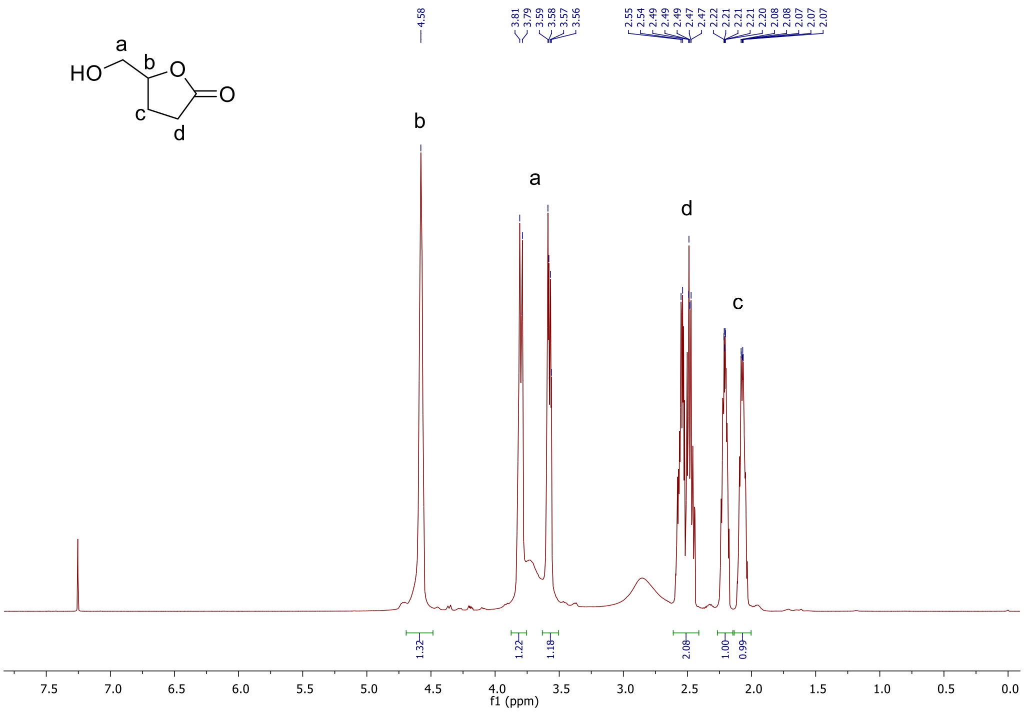


Figure S1. ^{1}H-NMR spectrum of 5-hydroxymethyl-2-oxotetrahydrofuran (monolactone) in chloroform-*d*.

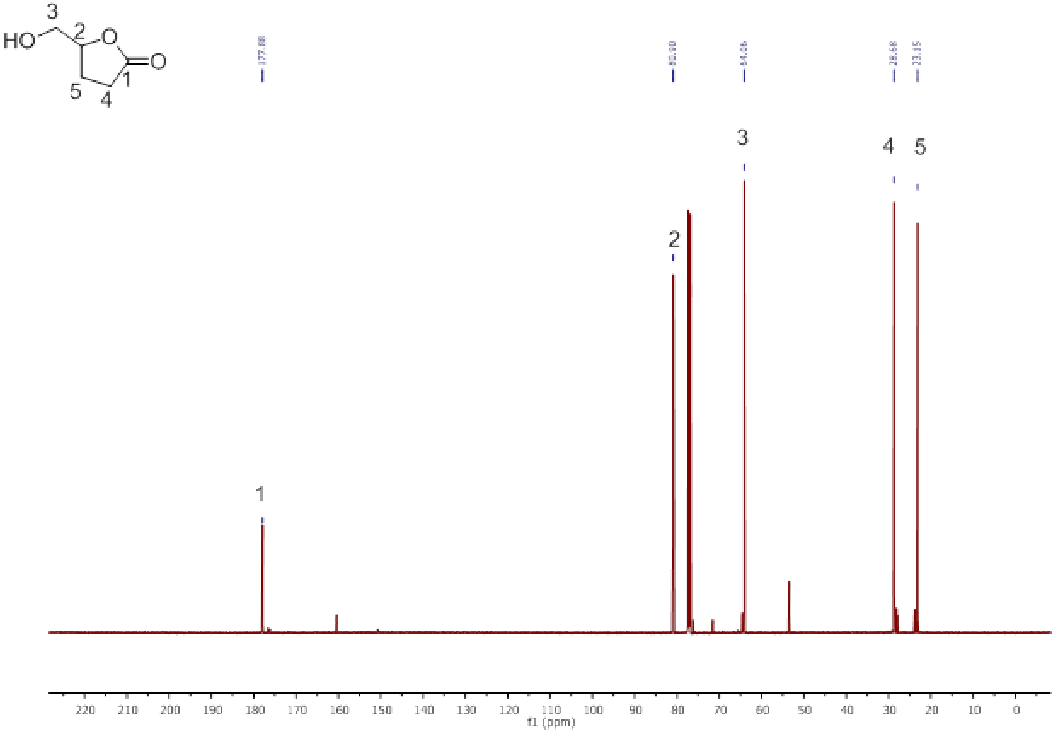


Figure S2. ^{13}C-NMR spectrum of 5-hydroxymethyl-2-oxotetrahydrofuran (monolactone) in chloroform-*d*.

Synthesis of Ribonolactone

To commercially available 2,3-acetal-protected ribonolactone (2.0 g, 10.63 mmol) was added dropwise at 0 °C a mixture of 1:1 TFA/H$_2$O (10 mL). The reaction was stirred for 12 h at RT and the solvents were evaporated to afford pure ribonolactone in quantitative yields.

^{1}H-NMR (600 MHz, deuterium oxide, ppm) δ = 3.87 (dd, 1H, HO-CH$_2$, J = 13.1, 4.1 Hz), 3.80 (dd, 2H, HO-CH$_2$, J = 13.1, 3.3 Hz), 4.38 (d, 1H, CH, J = 5.6 Hz), 4.58 (dd, 1H, CH, J = 3.6, 3.6 Hz), 4.74 (d, 1H, CO-CH, J = 5.6 Hz). ^{13}C-NMR (151 MHz, chloroform-d, ppm) δ = 178.5, 86.7, 69.5, 68.9, 60.5. IR (ATR-IR, cm^{-1}): 3345, 2962, 1762, 1673, 1397, 1259, 1224, 1179, 1135, 1078, 964, 897, 840, 799, 770, 608.

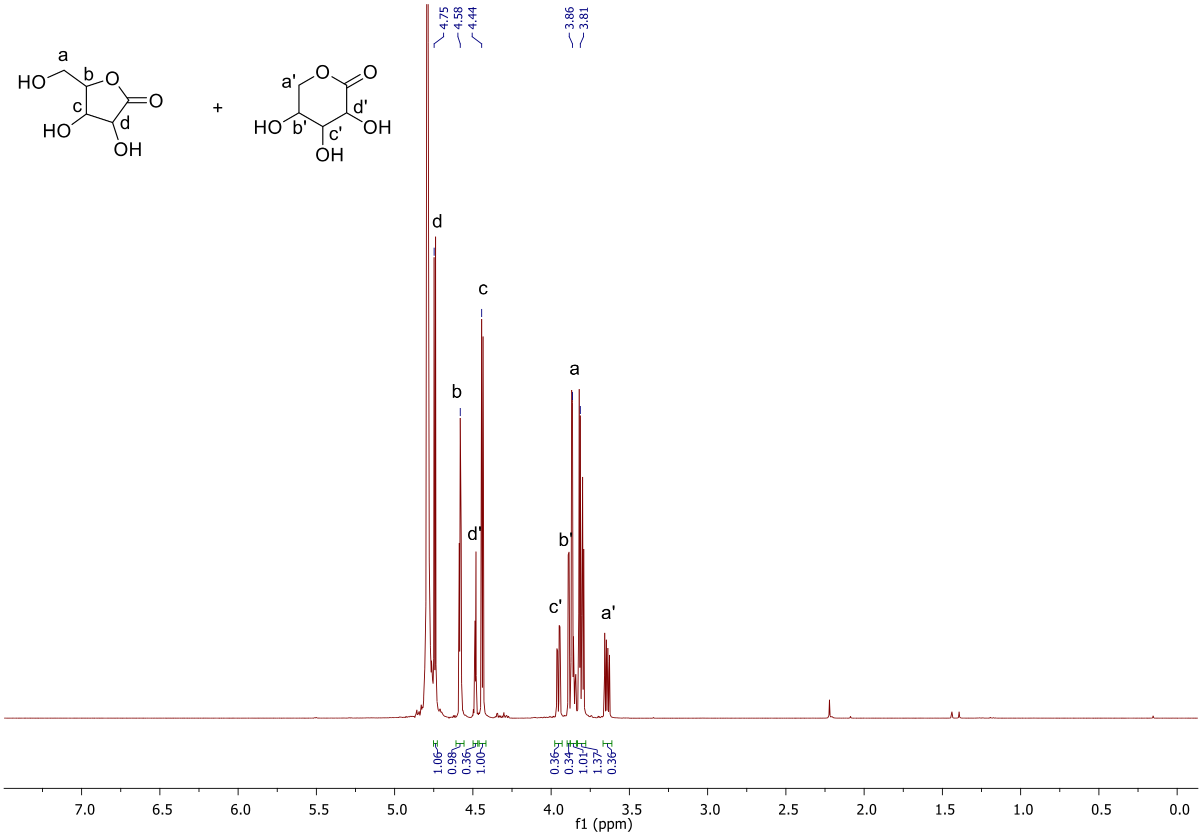


Figure S3. ^{1}H-NMR spectrum of ribonolactone in deuterium oxide.

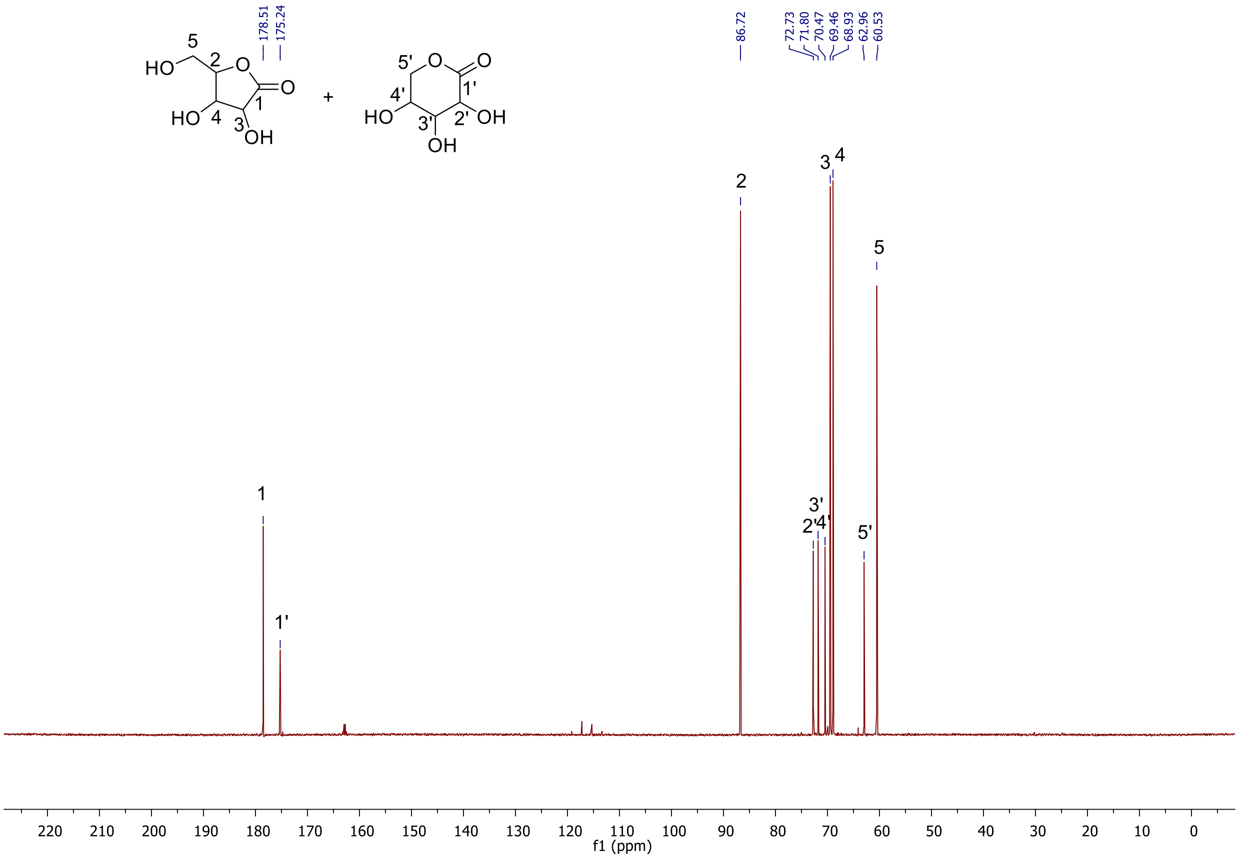


Figure S4. ^{13}C-NMR spectrum of ribonolactone in chloroform-*d*.

General Synthesis of Gluconamidosilicones

SASn-x, e.g., **SAS9-4** was prepared by dissolving telechelic aminopropylsilicone DMS-A11 (2 mmol, m = 1.80 g, MW ≈ 850 - 900 g.mol−1) in 2-propanol (4 mL) and combining the solution with 5-hydroxymethyl-2-oxotetrahydrofuran (4 mmol, m = 0.59 g) in a round-bottomed flask. The mixture was stirred at RT until reaction completion was confirmed by FT-IR and NMR spectroscopy. The solvent was removed under reduced pressure to give **SAS9-4** as a viscous fluid in quantitative yield. The reagent amounts required for each synthesis are given in Table S1. Note: all syntheses are essentially quantitative. Nonquantitative yields are only caused by incomplete removal from the reaction flask.

^{1}H-NMR (600 MHz, chloroform-*d*, ppm) δ = 0.05 (s, H, Si-CH_3), 0.51 (m, 2H, Si-CH_2), 1.49 (m, 2H, CH_2), 1.7 (m, 2H, CH_2), 2.35 (m, 1H, CH), 2.66 (m, 1H, CH), 3.16 (m, 2H, CH_2), 3.43 (m, 1H, CH), 3.55 (m, 1H, CH), 3.66 (m, 1H, CH). ^{13}C-NMR (151 MHz, chloroform-*d*, ppm) δ = 173.8, 71.8, 66.3, 42.8, 33.0, 28.9, 23.5, 15.3, 1.29, 1.14, 0.98. IR (ATR-IR, cm^{-1}): 3336, 2961, 2904, 1640, 1543, 1441, 1412, 1257, 1203, 1014, 861, 788, 702, 685.

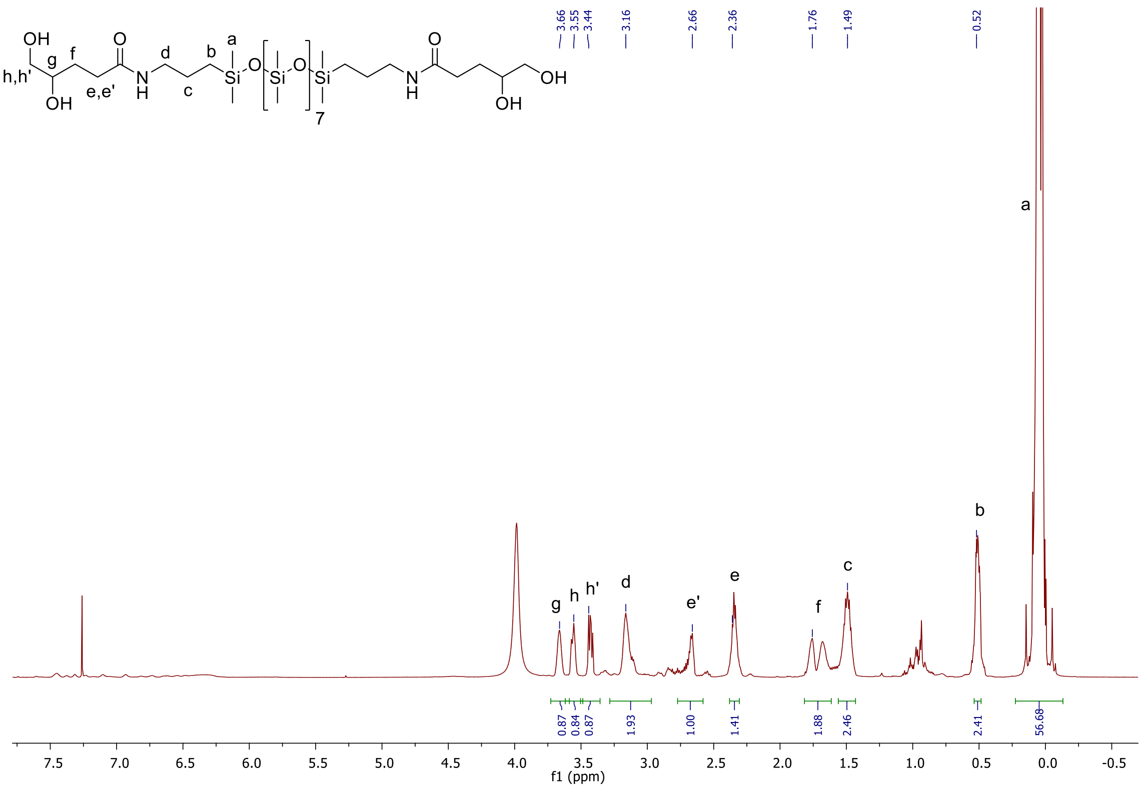


Figure S5. ^{1}H-NMR spectrum of gluconamidosilicone in chloroform-*d*.

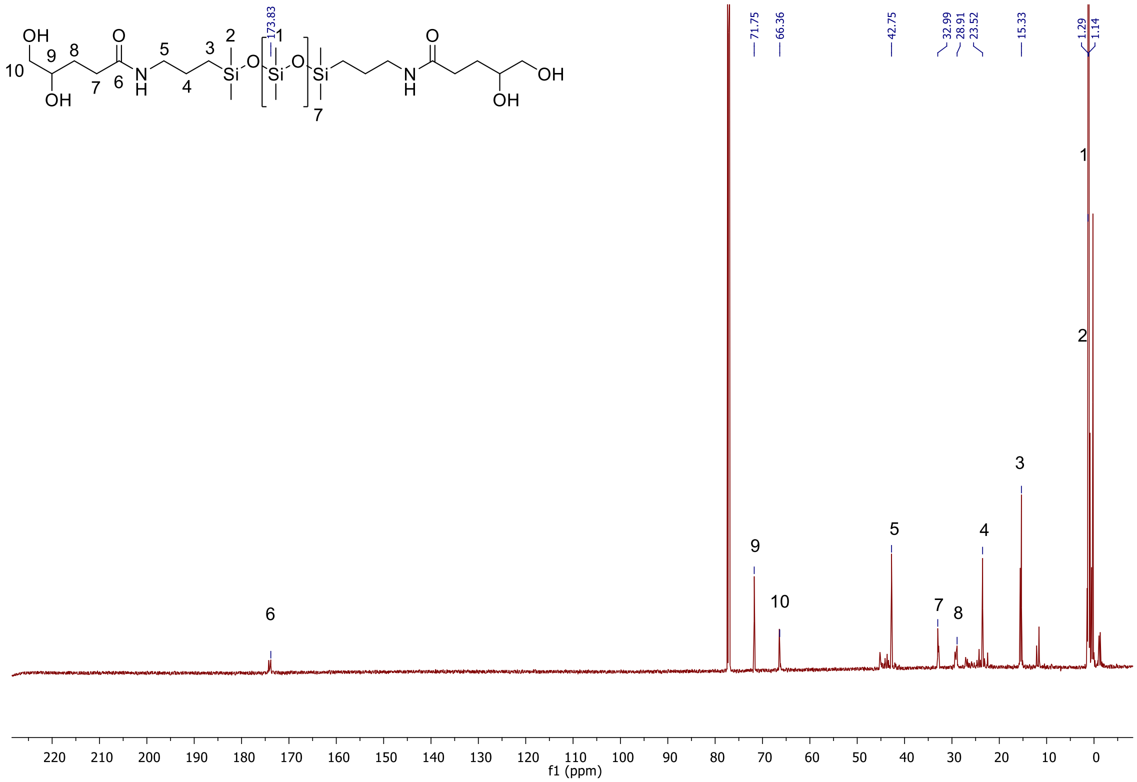


Figure S6. ^{13}C-NMR spectrum of gluconamidosilicone in chloroform-*d*.

Table 1. Formulations for the preparation of gluconamidosilicones based on the preparation method described for **SAS8-4**[a]

	SASn-0 (mmol)	**SASn-0 (g)**	**Monolactone (mmol)**	**Monolactone (g)**	**State at 25 °C**
SAS9-4	2.00	1.80	4.00	0.46	VL[b]
SAS38-4	"	6.01	"	"	VL[b]
SAS65-4	"	10.22	"	"	VL[b]
SAS673-4	0.20	10.14	0.40	0.05	VL[b]
	SASn-0 (mmol)	**SASn-0 (g)**	**Ribonolactone (mmol)**	**Ribonolactone (g)**	
SAS9-8	2.00	1.80	4.00	0.59	VL[b]
SAS38-8	"	6.01	"	"	TPN[b]
SAS65-8	"	10.22	"	"	TPN[b]
SAS673-8	0.20	10.14	0.40	0.06	TPN[b]
	SASn-0 (mmol)	**SASn-0 (g)**	**Gluconolactone (mmol)**	**Gluconolactone (g)**	
SAS9-10	2.00	1.80	4.00	0.71	S[b]
SAS38-10	"	6.01	"	"	S[b]
SAS65-10	"	10.22	"	"	S[b]
SAS673-10	0.20	10.14	0.40	0.07	TPN[b]

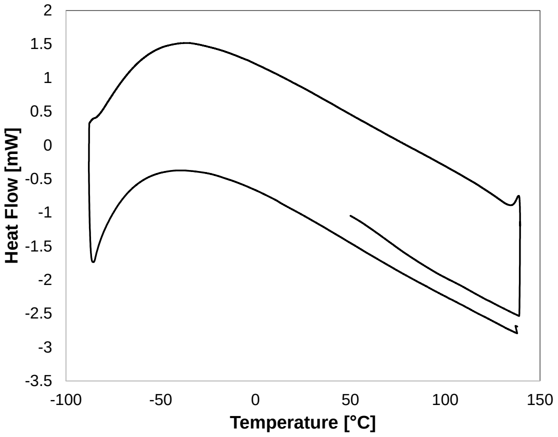
[a] The volume of 2-propanol used in all cases was 20 mL.

[b] VL: viscous liquid, TPN: able to form a transient polymer network, S: solid.

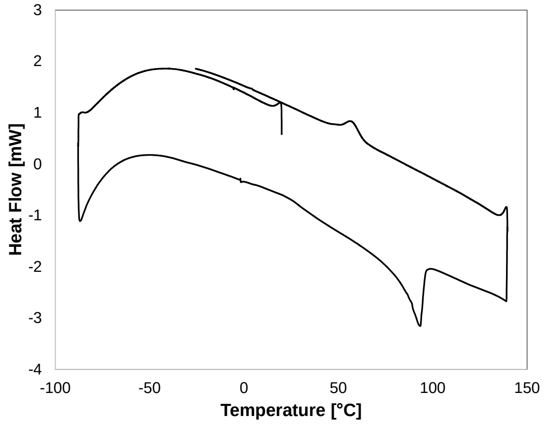
2. DSC

Silicones have a glass transition temperature lower than -120 °C and melt between -60 and -30 °C. Neither the starting materials **SASn-0** nor the silicones modified with OH groups exhibited glass transitions (down to -88 °C). The melting and crystallization temperatures, however, were increased after modification of the respective silicones with OH groups. The spectra prior and after modification with GDL are shown in Figure S7. **SAS9-10** for example melted at 93 °C, whereas no melting peak was observed for the starting material **SAS9-0** (down to -88 °C). A similar increase in the melting temperature was observed for **SAS38-0** after reaction with GDL. Whereas **SAS38-0** melted at -51 °C the GDL-modified analog showed a melting peak at 89 °C (**SAS38-10**). Two melting peaks (-45 °C and -36 °C) were detected for **SAS673-0** and one at -43 °C for the GDL-modified reaction product (**SAS673-10**). More details can be found in our previous publication.[21]

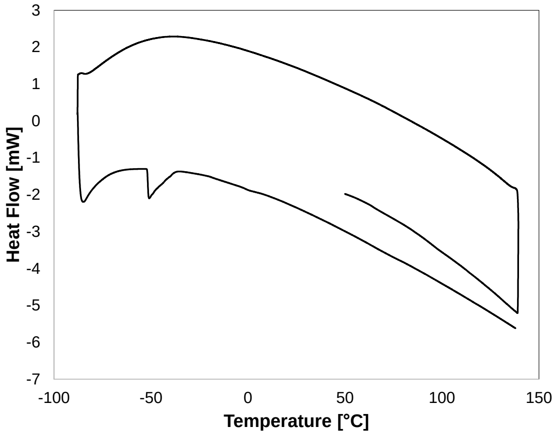
SAS9-0



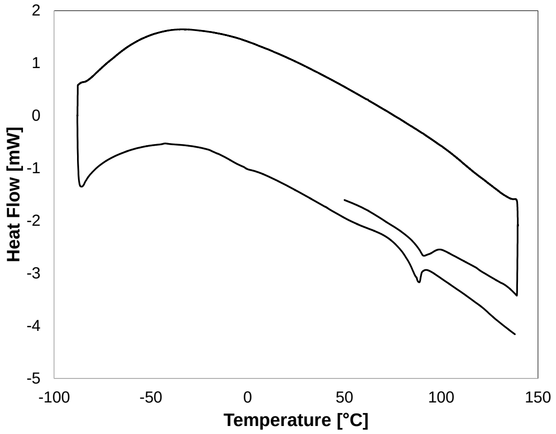
SAS9-10



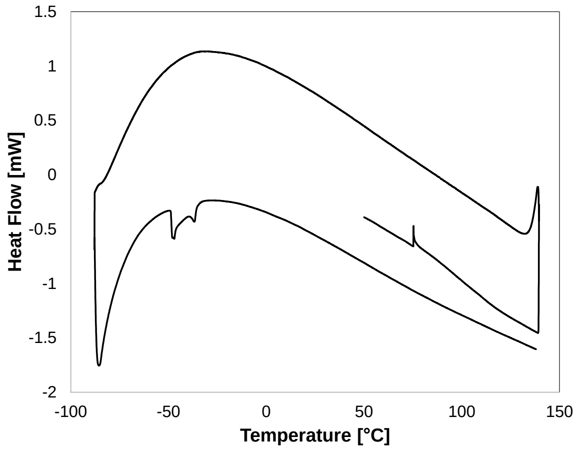
SAS38-0



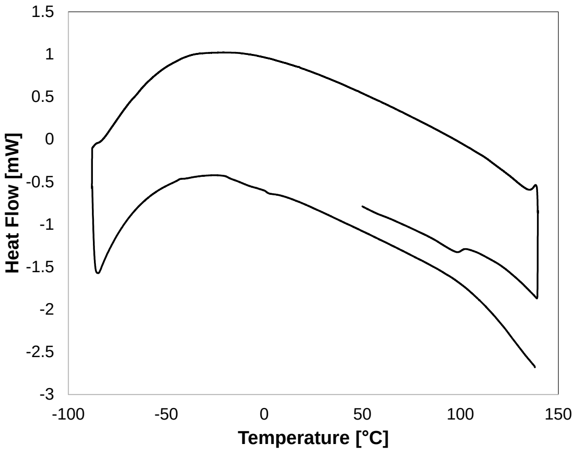
SAS38-10



SAS65-0



SAS65-10



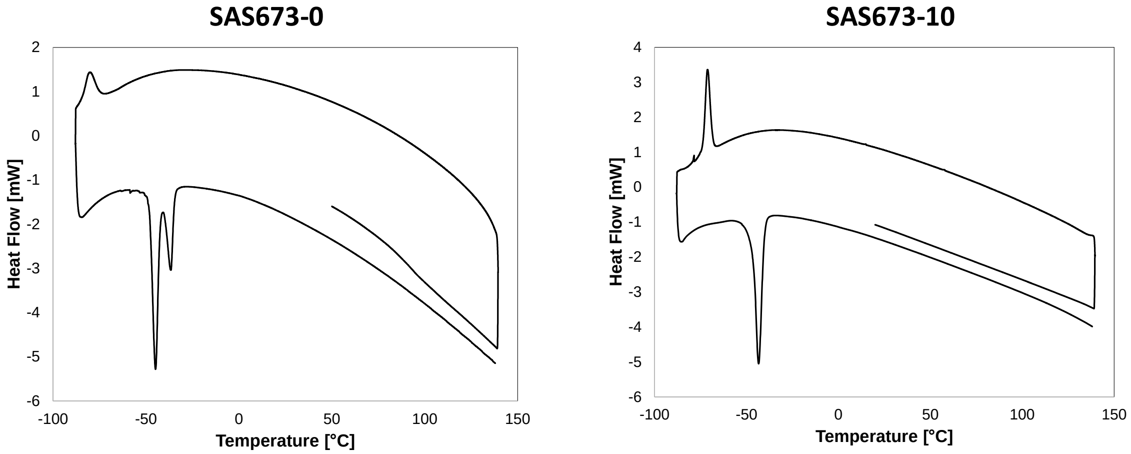


Figure S7. DSC spectra prior and after modification of telechelic aminopropylsilicones with GDL.

3. Rheology

Time Temperature Superposition Curves

The time temperature superposition curves of the samples **SAS9-4** and **SAS9-8** are shown in Figure S8. For the TTS curves of the samples **SAS38-x** see Figure S9. Note that the sample **SAS9-8** was too viscous to be measured at lower temperatures to give data at higher frequencies and that the sample **SAS9-10** was solid and could no be measured.

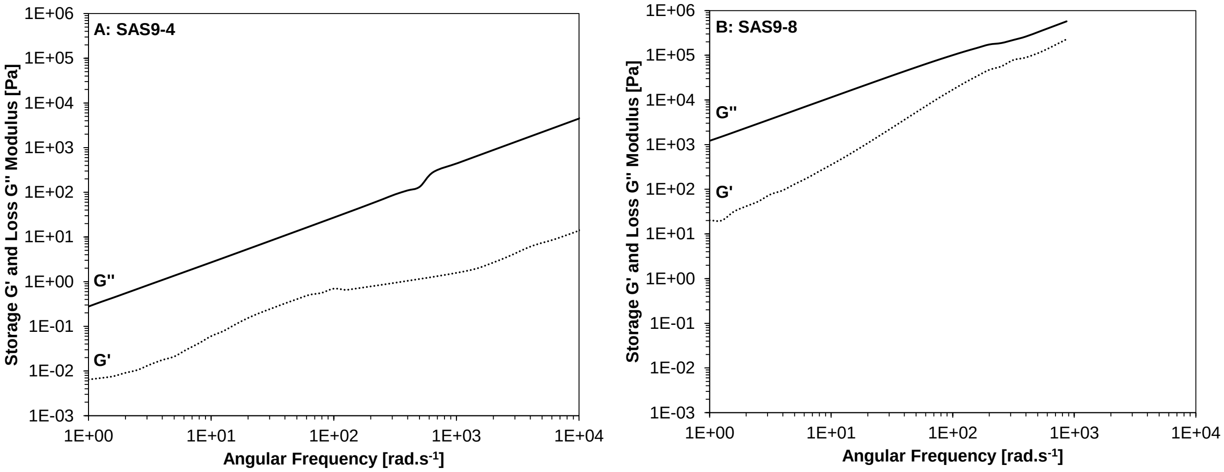


Figure S8. Time-temperature superposition curves of storage G' and loss G'' moduli of **SAS9-4** (A) and **SAS9-8** (B). TTS were calculated from constant strain oscillatory frequency rheology measurements for a reference temperature of 25 °C.

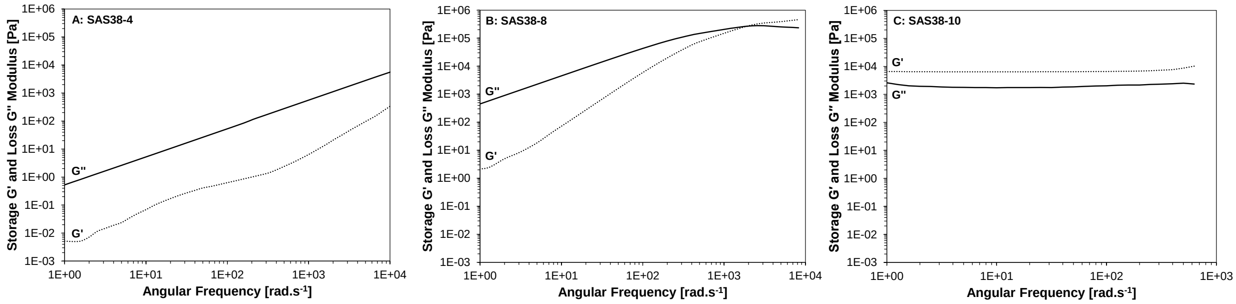


Figure S9. Time-temperature superposition curve of storage G' and loss G'' moduli of **SAS38-4** (A), **SAS38-8** (B), and **SAS38-10** (C).

Influence of Temperature

A TPN (Figure 5B) can transform into a viscous liquid (Figure 5A) and a dynamic solid (Figure 5C) into a TPN (Figure 5B) (and vice versa) by temperature changes. Figure S10 shows the TPN – viscous liquid transition of the sample **SAS673-10** and Figure S11 the dynamic solid – TPN transition of the sample **SAS65-10**.

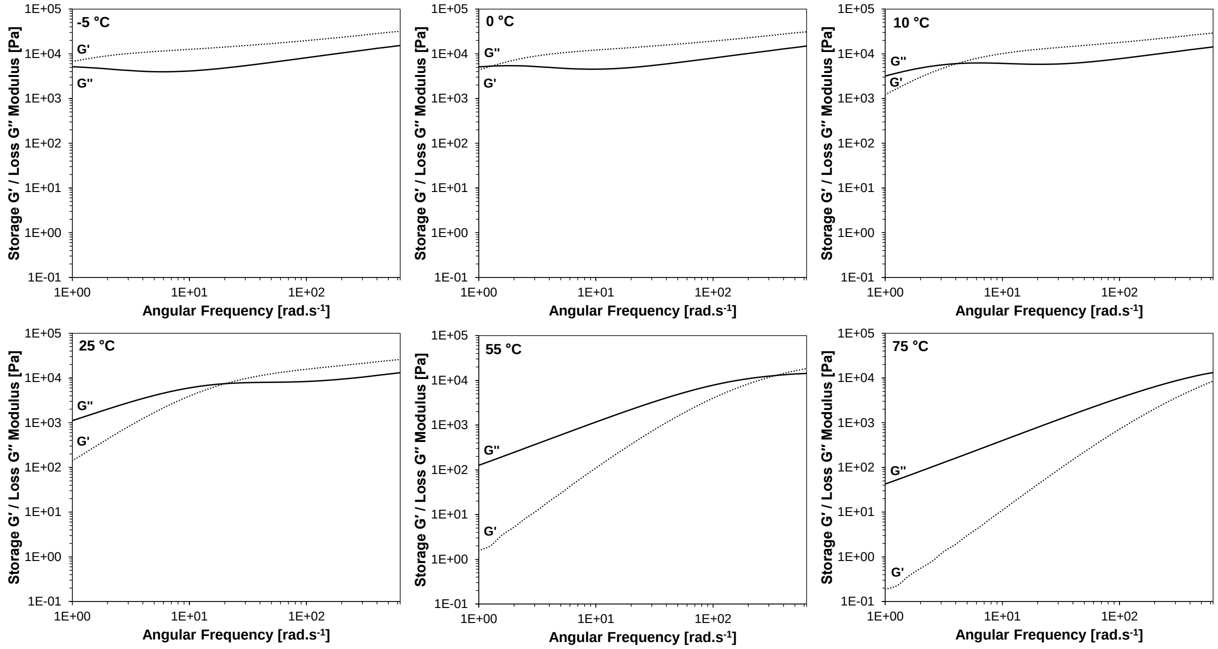


Figure S10. Constant strain oscillatory rheology measurement of **SAS673-10** at different temperatures.

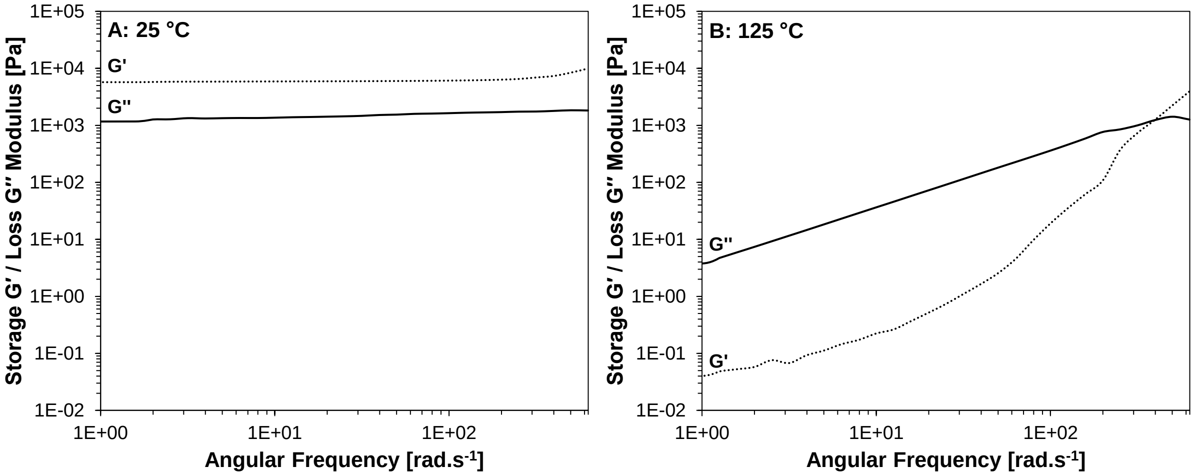


Figure S11. Constant strain oscillatory rheology measurement of **SAS65-10** at 25 °C (A) and 125 °C (B).

Addition of a Silicone Oil

A TPN can be generated by dilution of a dynamic solid with a silicone oil (decreasing the HO/D ratio) as shown in Figure S12 for the sample **SAS65-10**.

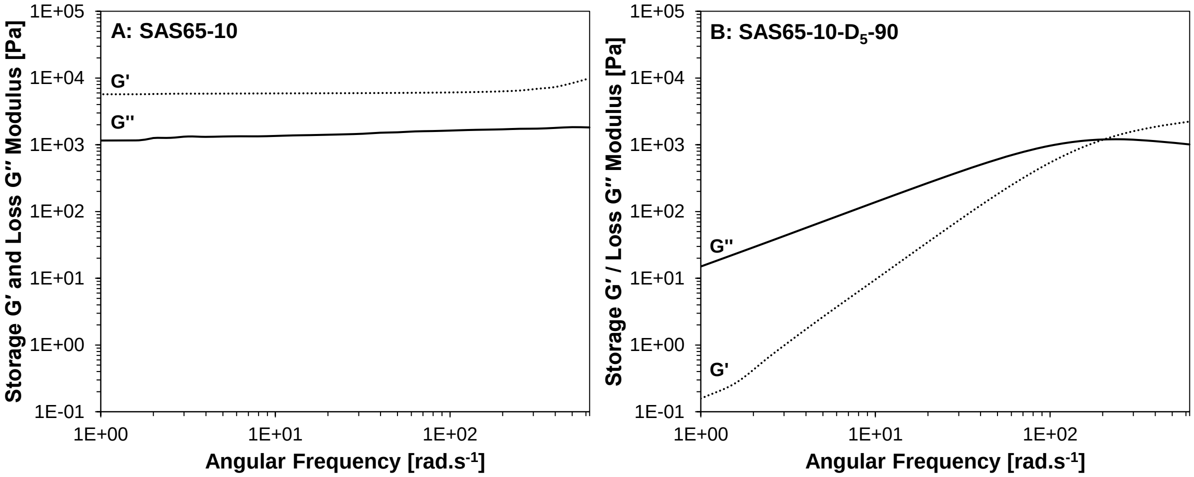


Figure S12. Constant strain oscillatory rheology measurement of **SAS65-10** prior (A) and after (B) the addition of D_5.

Addition of D_5, IPA, H_2O

Based on the amount of the sugaramidosilicone **SAS673-10**, 2 wt% and 5 wt% of 2-propanol, the low molecular weight silicone oil cyclopentasiloxane (D_5, $(Me_2SiO)_5$), or H_2O was added and the viscoelastic properties determined by constant strain oscillatory rheology measurements. The results are shown in Figure S13.

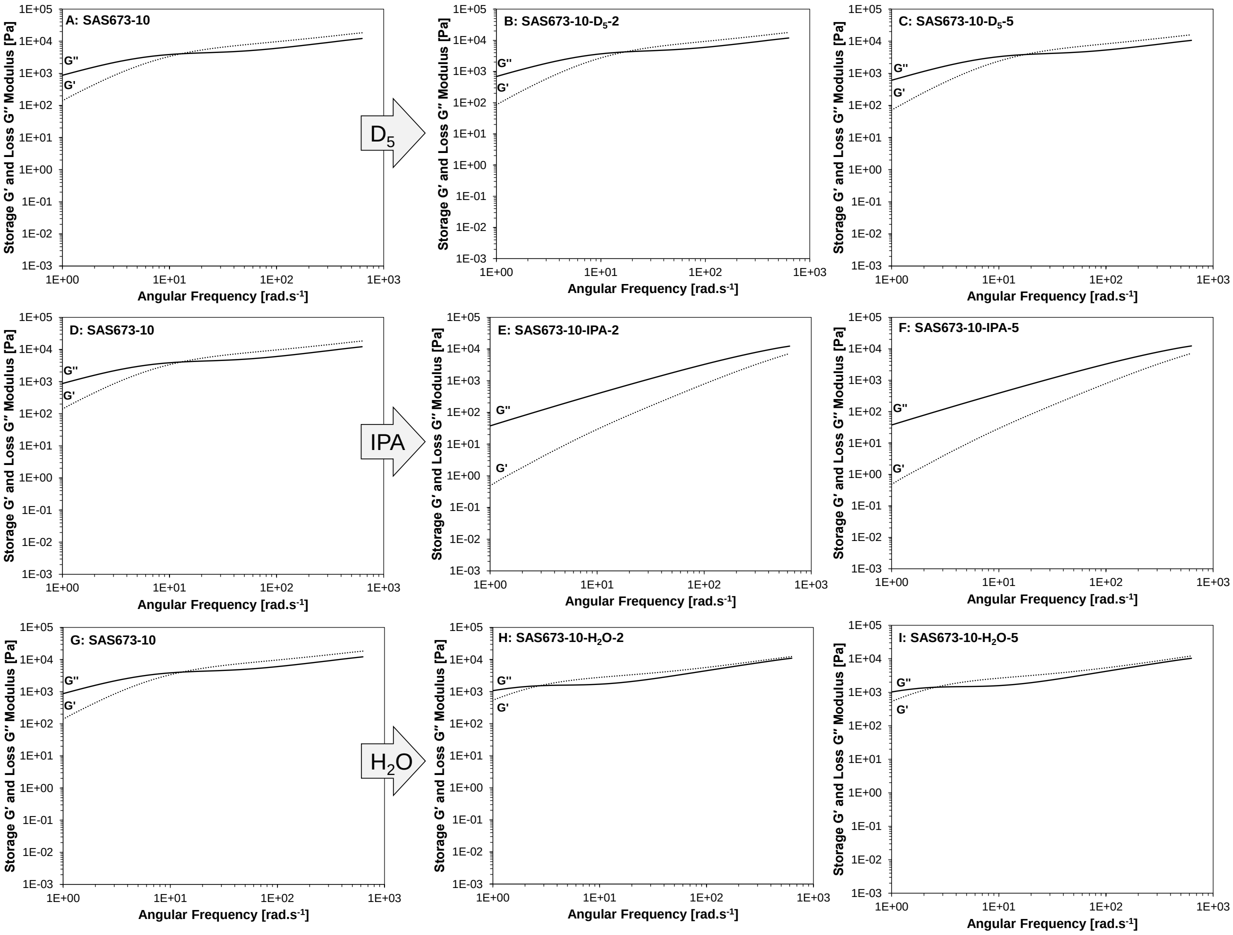


Figure S13. Constant strain oscillatory frequency rheology measurements of **SAS673-10** before (A, D and G), after the addition of 2 wt% D_5 (B), IPA (E), or H_2O (H), and after the addition of 5 wt% D_5(C), IPA (F), or H_2O (I).

Ball Dropping Experiments

To investigate the energy absorption properties, 2.5 g of the respective sample was placed into a 2.5 cm diameter FlackTek cup (sample height: 6 mm). A steel ball with a diameter of 12 mm (m = 6.95 g) was dropped from a height of 10 cm onto the sample and the penetration depth of the steel ball 0.5 s after the impact was measured.

Dilution of the samples:

To investigate the effect of different solvents on the energy damping properties of the sugaramidosilicone **SAS673-10**, the fluid was diluted with 10 wt% of the silicone oil cyclopentasiloxane (D_5) (**SAS673-10-D5-10**), 10 wt% tetrahydrofuran (**SAS673-10-THF-10**), or 10 wt% 2-propanol (**SAS673-10-IPA-10**).

Following videos are available showing the shock-absorption properties of **SAS673-x** with or without dilution with organic solvents by ball dropping experiments.

- **SAS673-10.mov** (slow motion)
- **SAS673-10-D5-10.mov** (slow motion)
- **SAS673-10-THF-10.mov** (slow motion)
- **SAS673-10-IPA-10.mov** (slow motion)