## Supporting Information for

# The synthesis and characterization of supramolecular elastomers based on linear carboxyl-terminated polydimethylsiloxane oligomers

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#### S-1: Synthesis of PDMS-COOH<sub>2</sub> oligomers

#### Preparation of PDMS-H<sub>2</sub> through cationic ring-opining polymerization of $D_4$

 $D_4$  and HMM were added in a thermo stated reactor fitted with a condensing tube, a stirring and a bottom valve. The reaction was conducted in the presence of an acid (3% by weight, 86 % H<sub>2</sub>SO<sub>4</sub>) for about 20 hours at room temperature. After then, acid was separated and the left system was neutralized with anhydrous NaHCO<sub>3</sub> through a stirring treatment at room temperature for another hour. The insoluble particles was filtered through a glass filter under reduced pressure and the volatile oligomers were removed by distillation under reduced pressure (< 15 mmHg) at 150 °C for no less than 3 hours. PDMS-H<sub>2</sub> containing different siloxane units (from n = 10 to 150) was prepared. The structure of PDMS-H<sub>2</sub> was confirmed using <sup>1</sup>H-NMR and FT-IR techniques.

FT-IR (KBr, cm<sup>-1</sup>): 2963 ( $v_{as CH_3}$ ), 2128 ( $v_{Si-H}$ ), 1262 ( $\delta_{s Si-CH_3}$ ), 1028-1092 ( $v_{Si-O}$ ), 866 ( $r_{Si-CH_3}$ ), 799 ( $v_{as Si-CH_3}$ ), 700 ( $v_{s Si-CH_3}$ ).

<sup>1</sup>H-NMR δ (CDCl<sub>3</sub>, ppm): 0.07 (s, Si-CH<sub>3</sub>), 0.19 (s, Si-CH<sub>3</sub> at chain ends), 4.71 (m, -Si-H).

#### Preparation of PDMS-tBMA<sub>2</sub> via hydrosilylation of PDMS-H<sub>2</sub> with tBMA monomer

PDMS-H<sub>2</sub> was first added in a thermostated reactor fitted with a condensing tube, a stirring system, rogen inlet and a bottom valve. After 5 minutes of nitrogen purge, 30ppm (compared to the molar quantity of Si-H) platinum catalyst (H<sub>2</sub>PtCl<sub>6</sub> in THF) was added, followed by heating the system to 80 °C. The monomer was then added into the system with a molar ratio of 1.1 : 1 compared to the molar content of Si-H. The reaction was left to proceed until no Si-H band (v = 2128cm<sup>-1</sup>) could be detected (5 hours at 80 °C under nitrogen). The resulting product was first purified by distillation under reduced pressure to remove the auto-polymer of tBMA.

FT-IR (KBr, cm<sup>-1</sup>): 2963 ( $v_{as CH3}$ ), 1732 ( $v_{C=0}$ ), 1460 ( $\delta_{as CH3}$ ), 1397, 1370 ( $\delta_{s CH3}$ ), 1262 ( $\delta_{s Si-CH3}$ ), 1024-1092 ( $v_{Si-O}$ ), 864 ( $r_{Si-CH3}$ ), 800 ( $v_{as Si-CH3}$ ), 703 ( $v_{s Si-CH3}$ ).

<sup>1</sup>H-NMR δ (CDCl<sub>3</sub>, ppm): 0.07-0.11 (m, Si-CH<sub>3</sub>), 0.70-1.00 (m, Si-CH<sub>2</sub>-), 1.16 (d,

-CH-CH<sub>3</sub>), 1.44 (s, -C(CH<sub>3</sub>)<sub>3</sub>), 2.46(m, -CH<sub>2</sub>-CH-).

#### Synthesis of PDMS-COOH<sub>2</sub> through acid hydrolysis of PDMS-tBMA<sub>2</sub>

PDMS-tBMA<sub>2</sub> was first added in a thermostated reactor fitted with a condensing tube, a stirring and a bottom valve. The acid catalyst (1% by weight, 98 %  $H_2SO_4$ ) was then added when temperature reached 85 °C to initiate the hydrolysis. The reaction was stopped after 3 hours of reaction at 85 °C. The crude products were first dissolved in chloroform and washed with distilled water for several times to remove the acid catalyst. Water phase was then separated and the left solution was treated with rotary evaporation and vacuum drying to obtain a purified product of PDMS-COOH<sub>2</sub>.

FT-IR (KBr, cm<sup>-1</sup>): 2500-3200 ( $v_{-OH}$ , dimer structures of PDMS-COOH<sub>2</sub>), 2963 ( $v_{as CH3}$ ), 1710 ( $v_{C=O}$ ), 1462 ( $\delta_{as CH3}$ ), 1262 ( $\delta_{s Si-CH3}$ ), 1022-1093 ( $v_{Si-O}$ ), 866 ( $r_{Si-CH3}$ ), 803 ( $v_{as Si-CH3}$ ), 698 ( $v_{s Si-CH3}$ ).

<sup>1</sup>H-NMR δ (CDCl<sub>3</sub>, ppm): 0.05-0.12 (m, Si-CH<sub>3</sub>), 0.75-1.05 (m, Si-CH<sub>2</sub>-), 1.24 (d,-CH-CH<sub>3</sub>), 2.61(m, -CH<sub>2</sub>-CH-).

Figure S1 showed the GPC trace of PDMS-H<sub>2</sub> (n = 13), PDMS-tBMA<sub>2</sub> (n = 13) and PDMS-COOH<sub>2</sub> (n = 13), which indicates the polydimethylsiloxanes chain keep stable during the hydrosilylation and acid hydrolysis processing.



**Figure S1.** GPC trace of PDMS-H<sub>2</sub>, PDMS-tBMA<sub>2</sub> and PDMS-COOH<sub>2</sub> (n = 13)

#### S-2: Synthesis of SESi materials

#### First step: reaction of PDMS-COOH<sub>2</sub> with DETA

 $PDMS-COOH_2$  and DETA were added at room temperature in a thermostated reactor fitted with a Dean-Stark trap, a stirring system, a nitrogen inlet and a bottom valve. In order to remove the water from the system as much as possible, a good heat preservation measurement was applied in the whole reaction process.

The mixture which is turbid at room temperature was heated to 120 °C under a 200 mL/min flow of nitrogen until a transparent mixture was obtained. It was then heated to 135 °C for 6 h under the same flow. The mixture was then cooled to room temperature and solubilized in chloroform and washed with water/methanol (weight ratio 5/2) mixture for no less than five times. The oligoamide was collected as a solution in chloroform.

FT-IR (KBr, cm<sup>-1</sup>): 3300 ( $v_{NH}$ ), 3072 ( $\delta_{NH}$ ), 2965 ( $v_{as CH3}$ ), 1650 ( $v_{C=O}$  amide), 1603 ( $v_{NC}$  imidazoline), 1549 ( $\delta_{NH}$ ), 1450 ( $\delta_{as CH3}$ ), 1262 ( $\delta_{s Si-CH3}$ ), 1020-1100 ( $v_{Si-O}$ ), 866 ( $r_{Si-CH3}$ ), 800 ( $v_{as Si-CH3}$ ), 699( $v_{s Si-CH3}$ ).

<sup>1</sup>H-NMR  $\delta$  (CDCl<sub>3</sub>, ppm): 0.05-0.15 (m, Si-CH<sub>3</sub>), 0.75-1.05 (m, Si-CH<sub>2</sub>-),1.20 (d, -CH-CH<sub>3</sub>), 2.38 (m, -CH<sub>2</sub>-CH-), 2.67 (t, NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>), 2.76 (t, C(O)NHCH<sub>2</sub>CH<sub>2</sub>NH), 2.80 (t, NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>), 2.86 (t, NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N-imidazoline), 3.15 (t, NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N-imidazoline), 3.33 (m, C(O)NHCH<sub>2</sub>CH<sub>2</sub>NH), 3.33 (m, C(O)NHCH<sub>2</sub>CH<sub>2</sub>NH), 3.68 (m, N(C)CH<sub>2</sub>CH<sub>2</sub>N-imidazoline).

#### Second step: reaction of urea with the oligoamidoamine

The chloroform solution was first distilled using a rotary evaporator to remove a majority of (no less than 70 % of the initial weight) the solvent. The left solution (after determination of the actual concentration) was then added in a thermostated reactor fitted with a stirring system and maintained at 80 °C overnight under 200 mL/min nitrogen flow to remove the remaining solvent. Solid urea was then added. The mixture was heated under a 200 mL/min nitrogen flow at 135 °C for 2 h, followed with a gradually increment of the reaction temperature to 160 °C by 5 °C every 60 min. During the heating process (around the temperature range from 150 to 160 °C), the mixture becomes viscoelastic and begins to rise

up the stirring stem. Once the whole content of the reactor had risen on the stirring stem, the stirring was stopped and the viscoelastic material was quickly removed from the stem using scissors while it was still hot and soft.

Once the material was cooled to room temperature, it became a stiff solid. Next, the material was granulated in the form of about 1mm thick fragments and washed in water at 50 °C for 72 h. After been dried in an oven at 120 °C for several hours, a transparent and yellowish final product was obtained.

FT-IR (KBr, cm<sup>-1</sup>): 3302 ( $v_{NH}$ ), 3069 ( $\delta_{NH}$ ), 2963 ( $v_{as CH3}$ ), 1655 ( $v_{C=O}$ ), 1603 ( $v_{NC}$ ), 1540 ( $\delta_{NH}$ ), 1451 ( $\delta_{as CH3}$ ), 1262 ( $\delta_{s Si-CH3}$ ), 1020-1100 ( $v_{Si-O}$ ), 866 ( $r_{Si-CH3}$ ), 802 ( $v_{as Si-CH3}$ ), 697( $v_{s Si-CH3}$ ).

<sup>1</sup>H-NMR  $\delta$  (CDCl<sub>3</sub>, ppm): 0.05-0.15 (m, Si-CH<sub>3</sub>), 0.75-1.00 (m, Si-CH<sub>2</sub>-),1.18 (d, -CH-CH<sub>3</sub>), 2.39 (m, -CH<sub>2</sub>-CH-), 3.20-3.50 (m, C(O)NHCH<sub>2</sub>CH<sub>2</sub>N-urea), 3.20-3.50 (m, -NCH<sub>2</sub>CH<sub>2</sub>NH-urea), 3.20-3.50 (m, CH<sub>2</sub>-NCH<sub>2</sub>CH<sub>2</sub>NHCO), 3.51 (m, C(O)NHCH<sub>2</sub>CH<sub>2</sub>N-imidazolidone), 3.85 (t, C(O)NHCH<sub>2</sub>CH<sub>2</sub>N-imidazolidone).

# S-3: <sup>1</sup>H-NMR analysis

In the second step, -NH<sub>2</sub> groups were first reacted with partial urea groups to form monoalkyl-urea derivatives (combined with a disappearance of the characteristic signals: -NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> at  $\delta = 2.67$  ppm and -NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> at  $\delta = 2.80$  ppm), –NH- groups were then reacted with the left urea to form 1, 1-dialkylurea derivatives (combined with a disappearance of the characteristic signal: -CONHCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub> at  $\delta = 2.76$  ppm), imidazolidone derivatives were also found to be formed for longer reaction times ( combined with a novel signal appeared at  $\delta = 3.85$  ppm belong to C(O)NHCH<sub>2</sub>CH<sub>2</sub>N-imidazolidone).



**Figure S2**. Evolutions of the reactions process in the second step monitored by <sup>1</sup>H-NMR spectra. The disappearance of amine methylene signals ( $\delta = 2.67$  and 2.80 ppm for primary amine methylene and  $\delta = 2.76$  ppm for secondary amine methylene) and appearance of imidazolidone signal ( $\delta = 3.85$  ppm, C(O)NHCH<sub>2</sub>CH<sub>2</sub>N-imidazolidone) can be followed.

## S-4: GPC results

In the two steps reaction process, a clear increase of the molecular weight was observed in the first step, whereas a slight change of the molecular weight was observed in the second step. For SESi samples prepared from low molecular weight PDMS-COOH<sub>2</sub>, increase of the carbon chain units during the reaction process may lead a huge change of the refractive index of oligomers, thus curves similar to Figure S3(A) may be obtained.



**Figure S3**. Molecular weight changes during the reaction process: (A) SESi<sub>1</sub>, (B) SESi<sub>2</sub> and (C) SESi<sub>3</sub>.

## S-5: Temperature-dependent infrared spectra

Once the temperature is increased to 200 °C, a clear shoulder at about 1710 cm<sup>-1</sup> was observed. In the cooling process, the absorption peak of  $v_{N-H}$  and  $v_{C=O}$  can't return to its original positions. Meanwhile, the shoulder at 1710 cm<sup>-1</sup> remains unchanged. Thus an irreversible process is conducted at higher temperature.



**Figure S4**. FT-TR spectra of SESi<sub>1</sub> (A) and changes of the peak positions of N-H stretching vibration ( $v_{N-H}$ ) and C=O stretching vibration ( $v_{C=O}$ ) (B) during the heating and cooling process around the temperature 40 °C – 220 °C.

## S-6: XRD curves at room temperature

No crystalline structure is detected above the room temperature according to the XRD tests. This indicates a poor stacking behavior of the hydrogen bonded groups in the SESi matrix, which may results from the diverse distribution of bonded groups and PDMS chain length.



Figure S5. XRD curves of: (A) SESi<sub>1</sub>, (B) SESi<sub>2</sub> and (C) SESi<sub>3</sub>.

#### S-7: Creep and stress relaxation curves

Figure S6 shows the results of creep experiments performed at 20 °C. When a stress of 5  $\times 10^4$  Pa is applied to SESi<sub>1</sub> for 1000 min, the strain is about 17 %. Once the applied stress is released, the sample completely recovers its dimensions in several minutes. For SESi<sub>2</sub> and SESi<sub>3</sub>, lower loads ( $2.5 \times 10^4$  and  $1.25 \times 10^4$  Pa respectively) are applied duo to their low mechanical strength compared with SESi<sub>1</sub>. Although the applied stress is lowered to  $1.25 \times 10^4$  Pa, strain of SESi<sub>3</sub> after 1000min is still as high as 154 %. However, after release of the stress, the sample is still able to recover its dimensions in nearly 24 hours. Therefore, we reasoned that interactions between the PDMS chains have afford SESi materials stable crosslinking structures, which is independent of PDMS chain length. The results of tensile stress relaxation tests at 20 °C have also testified our hypothesis (Figure S6). After maintaining the strain at 100% for 100 minutes, a stress equal to the equilibrium stress is reached for all the testing samples, which indicates the existence of stable crosslinks in the SESi materials.



**Figure S6**. Creep properties of different SESi specimens at 20 °C with the applied load of: (A)SESi<sub>1</sub>, 0.05MPa, (B) SESi<sub>2</sub>, 0.025MPa, (C)SESi<sub>3</sub>, 0.0125MPa.



**Figure S7**. Stress relaxation curves of SESi samples under a strain of 100% with an elongation rate of 500mm/min to approach the target strain: (A) SESi<sub>1</sub>, (B) SESi<sub>2</sub> and (C) SESi<sub>3</sub>.





**Figure S8.** Curves from cyclic tensile tests for different specimens at room temperature: (A) SESi<sub>1</sub>, (B) SESi<sub>2</sub>, (C) SESi<sub>3</sub>, (D) SR-1 (silicone rubber without filler) and (E) SR-2 (silicone rubber with 30 phr precipitated silica).

Sample ID	residual strain (%)	$\Delta W (J/m^3)$	$\sigma_0$ (MPa)	ε <sub>0</sub> (%)	tanδ
SESi <sub>1</sub>	11.0	1.791	0.178		0.162
SESi <sub>2</sub>	3.8	0.113	0.027		0.067
SESi <sub>3</sub>	3.8	0.025	0.006	20	0.066
$SR_1$	0.4	0.044	0.122		0.006
$SR_2$	2.1	1.474	0.491		0.048

**Table S1**. Internal frictions  $(tan \delta)$  of different testing specimens at room temperature

#### S-9: Tensile curves after different processing cycles

Rectangle specimens were obtained through a hot press molding method at 150 °C. SESi materials were first pre-heated at 150 °C for 5 minutes and immediately pressed with an applied load of 20MPa for 10 minutes, a cold pressing treatment was then applied to help maintain the size and shape of the specimens (**this is defined as one processing cycle**).

A good reprocessing ability of SESi materials has been confirmed through tensile tests of samples after different processing cycles. From Figure S4 we can also come to the conclusion that SESi materials are non-covalently cross-linked since no irreversible damage to the tensile properties is detected.



**Figure S9**. Comparison of the tensile curves (elongation rate, 500mm/min) of SESi materials after different processing cycles: one cycle (solid line), three cycles (dash line): (A) SESi<sub>1</sub>, (B) SESi<sub>2</sub> and (C) SESi<sub>3</sub>