

SUPPLEMENTARY MATERIAL

A straightforward methodology for the synthesis of α , ω -telechelic poly(dimethylsiloxane)s

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Estructural characterization

Vapor pressure osmometry: PDMS-DGE molecular weight estimation

The number- average molecular weight of PDMS-DGE was estimated by vapor pressure osmometry. Tests were carried on a Wescan Model 233 Molecular Weight Apparatus, at 50 °C, using toluene as solvent. Calibration was performed using sucrose octaacetate (SOA, M: 678.59 g/mol).

Vapour pressure osmometry is based on the difference in vapour pressure caused by the addition of a small amount of solute to a pure solvent. In the vapour pressure osmometer, a droplet of pure solvent and a droplet of solvent-solute are placed on separate thermistors surrounded by pure solvent vapour. The difference in vapour pressure between the two droplets results in a difference in temperature at each thermistor, which finally causes a voltage difference ΔV . The ΔV value is related to the molar mass M of the solute through **Equation S1**^[1,2],

$$\frac{\Delta V}{C} = K \left(\frac{1}{M} + A_1 C + A_2 C^2 \dots \right) \quad \text{Eq. S1}$$

Being C the concentration of the solute, K is the calibration constant, and A_i represents the coefficients.

The higher order terms arise from non-ideal solution behaviour. To calibrate the instrument, solutes that form nearly ideal mixtures with the solvent at low concentrations are chosen. Most of the higher order terms become negligible, and **Equation S1** reduces to:

$$\frac{\Delta V}{C} = \frac{K}{M} + K A_1 C \quad \text{Eq. S2}$$

Using SOA, the calibration constant K was determined from the intercept of the plot of $\Delta V/C$ versus C as in **Figure S1 (a)**. In the same way, from the intercept of **Figure S1 (b)** and coming backward into equation 2 the molar mass of PDMS-DGE was estimated, values are presented in **Table S1**.

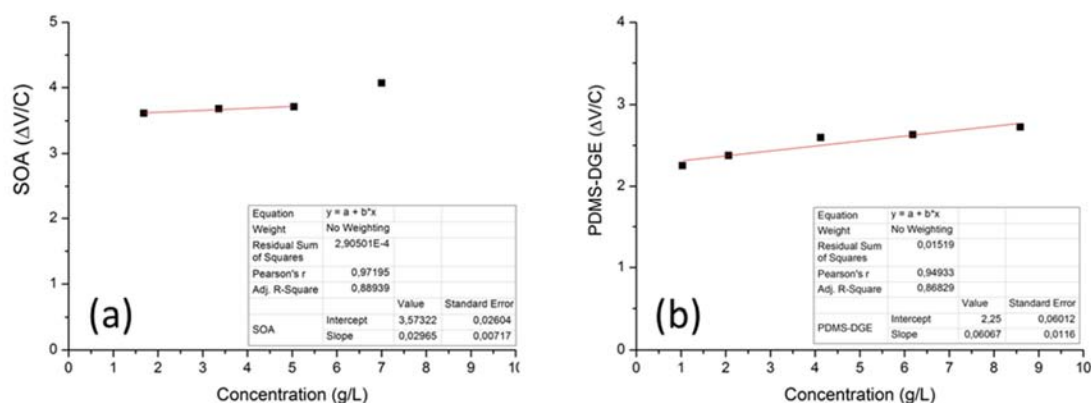


Fig. S1. Vapour pressure osmometry data obtained for SOA (a) and for PDMS-DGE (b).

Table S1. Vapour pressure osmometry data.

SAO	PDMS-DGE
M = 678.59 g/mol	K = 2424.7 μV
K/M = 3.5732 μV.mol/g	K/M = 2.25 μV.mol/g
K = 2424.7 μV	M = 1077.6 g/mol

¹H-NMR spectroscopy

Figures S1-S3 display ¹H-NMR spectra obtained from B2-OH, B2-SiH and B2-GMA, respectively together with integration areas values. At first, focusing in i, j, k & f and b signals, a good agreement was achieved regarding the ratio 10:1 that comes from the molecular structure; ratio values obtained for B2-OH, B2-SiH and B2-GMA are 10:1.22; 10:0.99 and 10:1.26 respectively. From the integration ratio between i, j, k & f, b ¹H signals and those from the specific functional group (Si-OH, Si-H and GMA), a quantitative relationship can be estimated for end-capping. In this sense, the resulting end-capping percentages are 95% for B2-OH, 85% for B2-SiH and 25% for B2-GMA. The deviation from 100 % end-capping efficiency was already discussed in the manuscript (siliconization procedure of fractionation ampoules in the case of chlorosilanes; reaction conditions and

multiple target groups in the case of glycidilmethacrylate). At this point it is worth to mention that integration area values from phenyl rings should consider solvent (deuterated chloroform), which might also contribute to its final value.

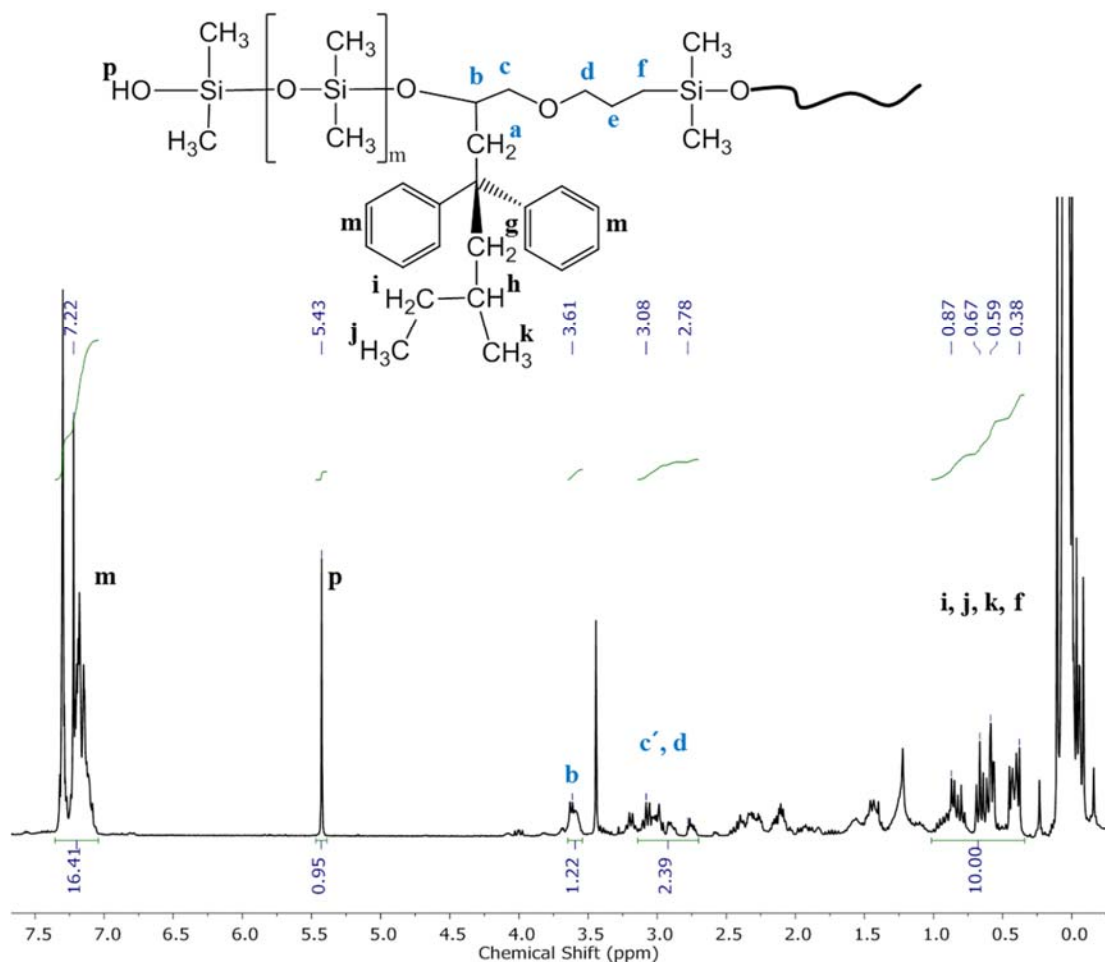


Figure S2. B2-OH ^1H -NMR spectrum.

B2-OH: ^1H -NMR (400 MHz, CDCl_3), 1.07-0.35 ppm (**i, j, k&f**, 10, **10H**); 5.43 ppm (**p**, 0.95, **1H**); 7.40-7.10 ppm (**m**, 16.41, **10H**), 3.26-2.75 ppm (**c'&d**, 2.39, **3H**); and 3.61 ppm (**b**, 1.22, **1H**).

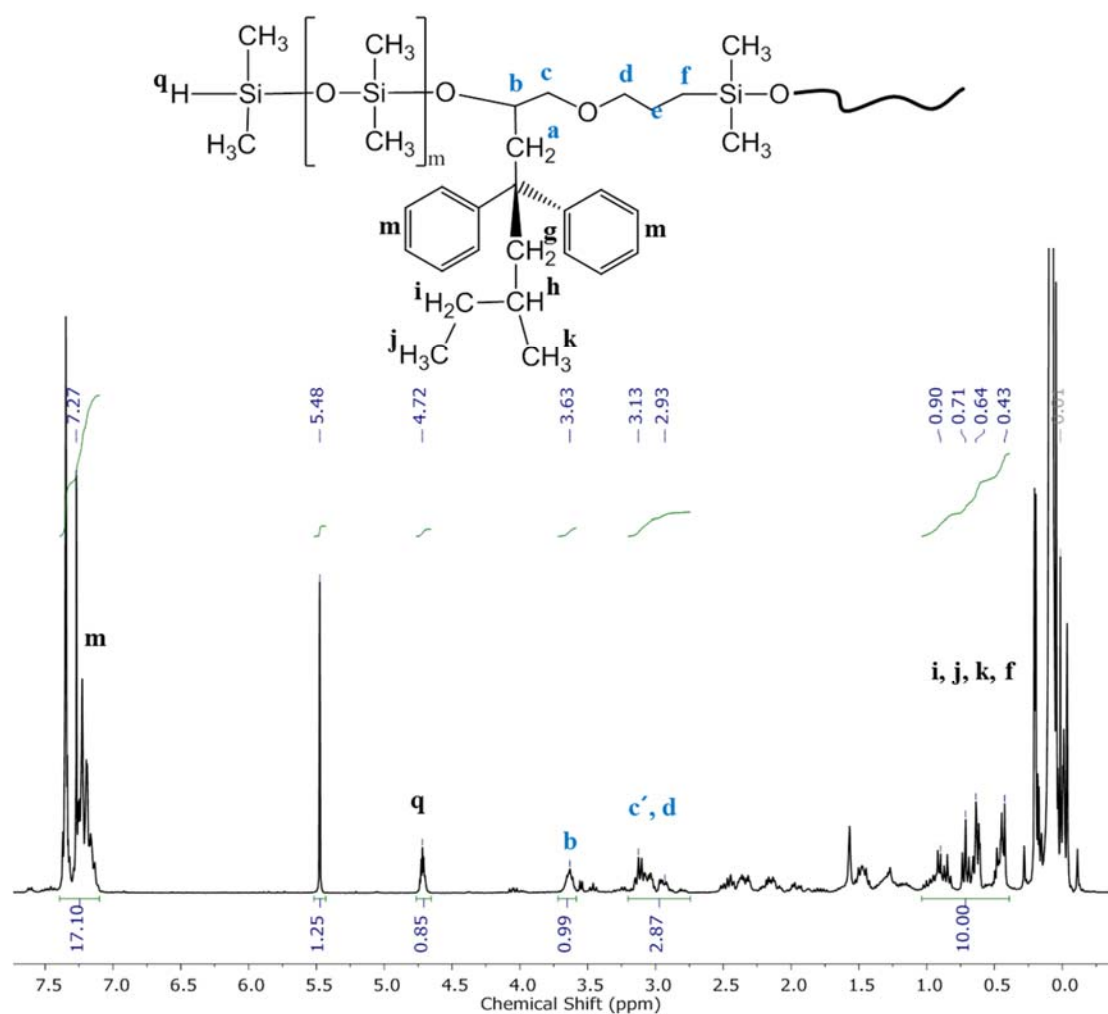


Figure S3. B2-SiH ^1H -NMR spectrum.

B2-SiH: ^1H -NMR (400 MHz, CDCl₃), 1.07-0.40 ppm (i, j, k&f, 10, **10H**); 4.72 ppm (q, 0.85, **1H**); 7.40-7.10 ppm (m, 17.10, **10H**), 3.26-2.75 ppm (c'&d, 2.87, **3H**); and 3.63 ppm (b, 0.99, **1H**).

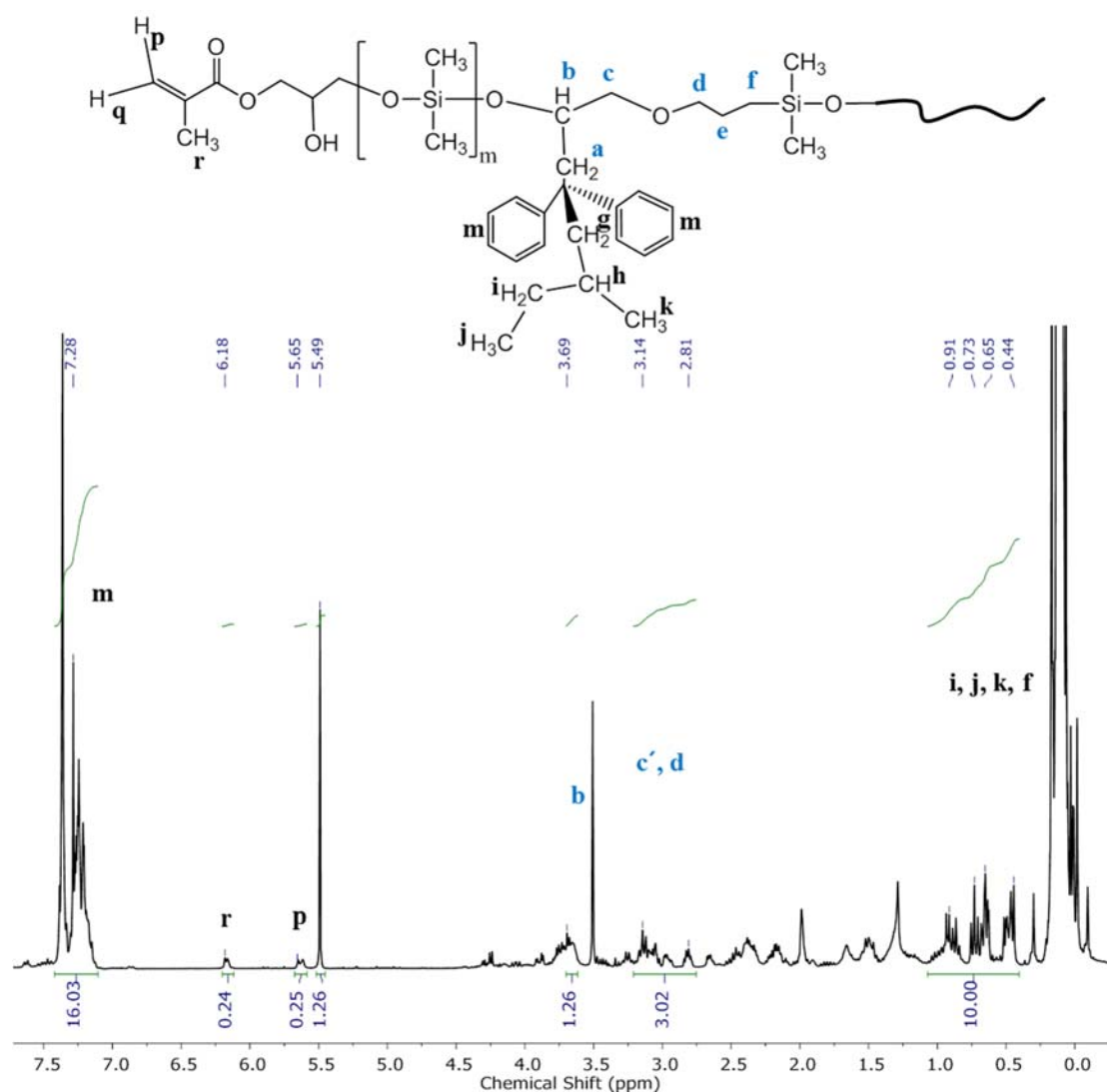


Figure S4. B2-GMA ^1H -NMR spectrum.

B2-GMA: ^1H -NMR (400 MHz, CDCl_3), 1.07-0.35 ppm (**i, j, k&f**, 10, **10H**); 6.18 ppm (**r**, 0.24, **1H**); 5.65 ppm (**p**, 0.25, **1H**); 7.40-7.10 ppm (**m**, 16.03, **10H**), 3.26-2.75 ppm (**c' & d**, 3.02, **3H**); and 3.61 ppm (**b**, 1.26, **1H**).

For B2-GMA, the Si-OH signal is predominant when comparing to those from vinyl hydrogens. This fact is in concordance with the low amount of GMA attached at the end of polymer chains.

Synthesis of vinyl terminated α,ω -PDMS after careful siliconization process

To verify if siliconization process was the clue of silanol's signal appearance, another synthesis was scheduled by employing a fresh chloro(dimethyl)vinylsilane ampoule as terminating agent obtained after a careful siliconization of the fractionation apparatus. To achieve this, the fractionation apparatus was filled with calcium hydride (1.5 g) and attached to the vacuum line. After 5 minutes, the apparatus was isolated from vacuum (by closing the corresponding stopcock) and 5 mL of chlorotrimethylsilane (Adrich) were injected via septum. By using external cotton pieces submerged in liquid nitrogen, the chlorotrimethylsilane inside was condensed over the inner glass surface. This procedure was repeated many times to ensure a fully contact of the chlorosilane with the glass surface. After this, the stopcock was opened and the remaining chlorotrimethylsilane inside was removed by exhaustive vacuum pumping (4 h), by condensing it into the corresponding vacuum trap. Once it was removed, the corresponding stopcock was closed; chlorodimethylvinylsilane (5 mL) was injected via septum, and stirred over calcium hydride during 30 minutes. Then, it was condensed in the siliconized ampoule by distilling under vacuum and employing external cotton pieces submerged in liquid nitrogen. Ampoule was detached from the fractionation apparatus by using a flame torch.

The synthesis of the corresponding vinyl terminated α,ω -PDMS was performed by employing the experimental procedure already described in the main text of the manuscript. Briefly, DPE ampoule (1 mL, 5.66 mmol) was broken and its content poured inside the reactor. After mixing with the solvent, *sec*-Bu⁻Li⁺ ampoule (9.7 mL, 2.72 mmol) was broken. A bright-red solution was immediately observed. After 3 h, the PDMS-DGE ampoule (1.1 mL, 1.36 mmol) was broken, and its content was poured inside the reactor. A light-green solution was

observed. The reaction between PDMS-DGE and *sec*-Bu⁻Li⁺/DPE adduct was left to proceed during 24 h, at room temperature. Then, the D₃ ampoule (26.1 g, 117.3 mmol) was broken, and a bright-yellow solution was immediately observed. This solution was left in equilibrium, at room temperature, for one day in order to obtain dimethylsiloxanylithium anions. Subsequently, THF ampoule (15 mL, 185 mmol) was broken in order to promote monomer polymerization. After 24 h of reaction at room temperature, the break seal of chloro(dimethyl)vinylsilane ampoule used as terminating agent (which was in a molar excess regarding initial PDMS-DGE ampoule) was broken. The reaction was left to proceed during 1 day and the resulting product was poured into a sodium bicarbonate aqueous solution. An organic/aqueous extraction step (three times, 20/80 v/v, hexane/10 wt% of sodium hydrogen carbonate solution) before methanol precipitation was employed. This procedure is necessary in order to avoid the presence of hydrochloric acid residues in the resulting polymer.

The resulting sample, labelled as B2Vi-20kDa, was characterized by size exclusion chromatography (SEC). SEC chromatogram is shown in **Figure S4**, and the corresponding SEC analysis is presented in **Table S2**. A narrow molar mass distribution, and $M_w/M_n = 1.15$ were obtained for the resulting polymer. In addition, as it is presented in the main text of the manuscript, ¹H-NMR analysis shows no evidence of silanol moieties.

Table S2. B2Vi-20kDa SEC data.

Sample	Mn _{teor} [*]	Mn [#]	M _w	M _w /M _n
B2Vi-20kDa	20,000	19,600	22,600	1.15

^{*}Expected Mn according to stoichiometry. [#]Obtained Mn according to SEC analysis.

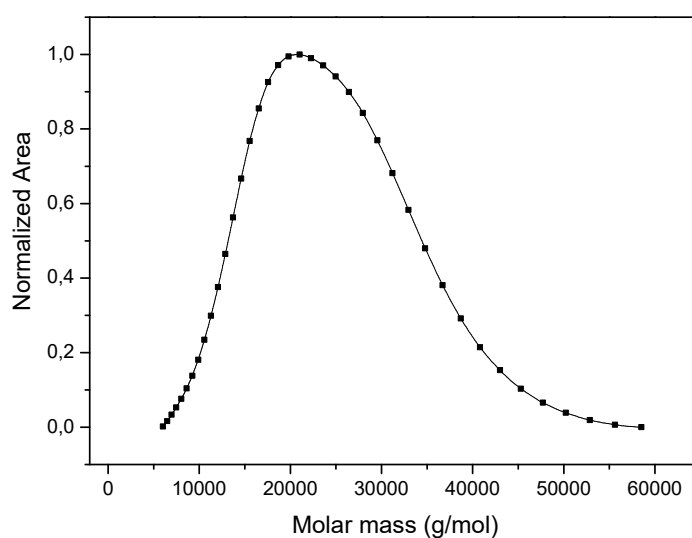


Figure S5. B2Vi-20kDa SEC chromatogram.

References

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