

SUPPORTING INFORMATION

Versatile and efficient functionalisation of multiallylic dendronised polymers: Can dense packing be reached?

Firmin Moingeon¹, Jérôme Roeser^{1,2}, Patrick Masson¹, Françoise Arnaud², Stéphane Méry^{1*}

¹*Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS-GMO).*

UMR 7504 CNRS-ULP. 23 rue du Loess, BP 43, 67034 Strasbourg Cedex 2, France

mery@ipcms.u-strasbg.fr

²*Laboratoire de Chimie-Physique, DSA, Institut Pluridisciplinaire Hubert Curien, ULP, CNRS,*

ECPM, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France

Materials and techniques.

All reagents were purchased from Aldrich, Acros Organic or Alfa Aesar, and were used as received, except for the following. 1,1,3,3,5,5,5-heptamethyltrisiloxane and Karstedt catalyst (platinum-divinyltetramethyldisiloxane complex: 3-3.5% Pt.) were purchased from Gelest. THF and toluene were dried over KOH and then distilled over sodium/benzophenone. 2-{2-(2-methoxyethoxy)ethoxy}ethanethiol was synthesised from 2-{2-(2-methoxyethoxy)ethoxy}ethanol, via the action of thiourea onto the tosylate intermediate, as described in refs [1]. AIBN was freshly recrystallised from MeOH before use.

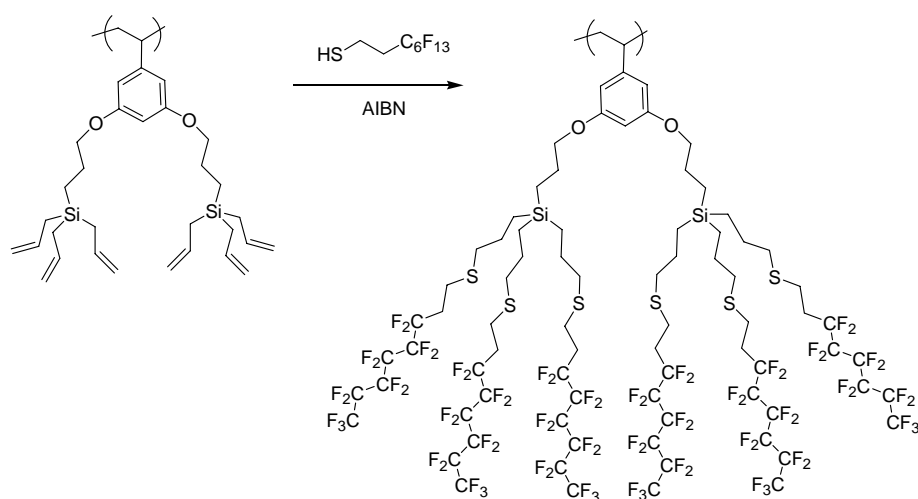
The SEC gel used to isolate the polymers from the reaction mixture was a SX1 Bio-Beads gel (Bio-Rad), given with a weight separation domain of 600-14000 Daltons. ¹H (300 MHz) and ¹³C (75 MHz) NMR spectra were measured using a Bruker AC300 spectrometer. Matrix Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) mass spectrometry analyses were performed on a Ultraflex Bruker Bremen apparatus at the Laboratory of Bio-Organic Mass Spectrometry (LSMBO) from the University Louis Pasteur in Strasbourg (Dr. J.M. Strub). Samples were prepared by mixing a dilute solution of 0.5 μ L of **poly(G1-F₆)** in CFC₁₂CF₂Cl with 0.5 μ L of a saturated solution of 1,8,9-trihydroxyanthracene (dithranol) in CH₂Cl₂. The analysis was performed using a (linear) negative mode with Bovin Serum Albumin calibration. Elemental analyses were carried out by the analytical department of the Institute Charles Sadron (ICS) in Strasbourg. Molecular weight determinations were

performed at ICS by size exclusion chromatography (SEC) in THF on a Waters chromatograph fitted with five PLGel 10 μm Mixed B columns and by using three detection modes: a differential refractometer detector (Shimadzu RID-10A) calibrated with polystyrene standards, a UV detector ($\lambda = 254$ and 280 nm) and a multi-angle laser light scattering (MALLS) detector (Wyatt DAWN DSP, $\lambda = 632.8$ nm). The reported \overline{M}_n (MALLS) values were calculated from \overline{M}_w (MALLS detection) and PDI values (refractometry detection). Infrared spectra were recorded on a computer-driven Digilab Excalibur 3000 FT-IR spectrometer equipped with a Pike Miracle diamond crystal Attenuated Total Reflection (ATR) accessory.

Starting multiallylic dendronized polymer.

The multiallylic polymers **poly(G1-allyl)** used for the functionalisation are prepared by anionic polymerisation technique, as described in ref. [2], and show the following characteristics: \overline{M}_w (MALLS detection) = 14650, PDI = 1.11.

Polyfluorinated polymer : poly(G1-F₆).

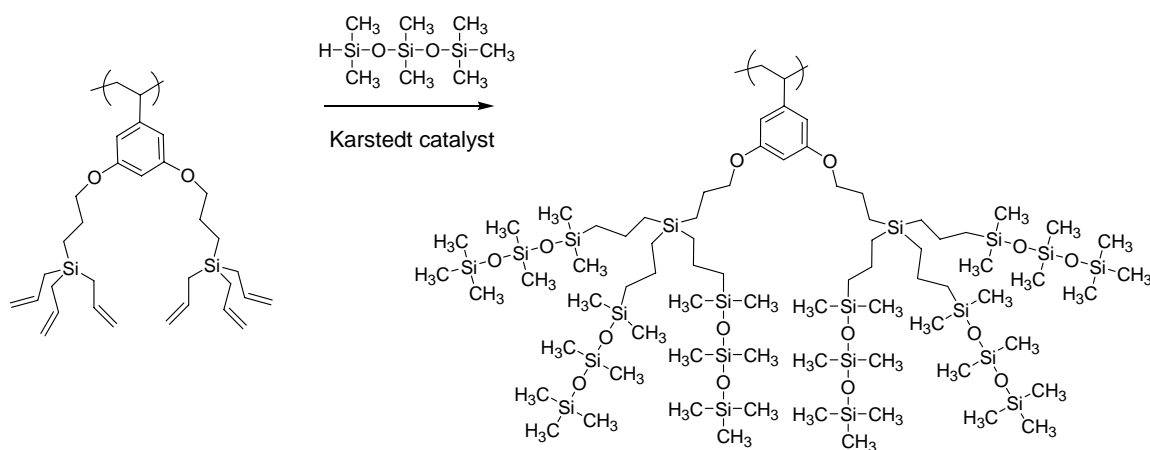


The radical addition of perfluorinated thiol onto the allylic groups of **poly(G1-allyl)** was performed using a modified known procedure (ref 3). A 25 mL two-necked flask was charged with 203 mg (2.33 mmol of allyle) of **poly(G1-allyl)**, 0.9 mL (3.8 mmol) of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanethiol and 0.4 mL of n-heptane as co-solvent.

The solution was degassed and placed under argon atmosphere. Then, AIBN (8 mg, 0.05 mmol) was introduced and the stirred solution was gradually heated at 50°C (1 hour), 60°C (1 hour) and at 70°C (18 hours). After cooling, the flask was charged again with 0.56 mL (2.36 mmol) of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanethiol and 8 mg of AIBN. The solution was once more degassed, placed under argon atmosphere and gradually heated from 50 to 70°C, then left at 80°C for 18 hours. Then, the solution was cooled down and poured into methanol. The resulting gummy precipitate was washed three times with boiling CHCl₃. It was then taken up with 1,1,2-trichloro-1,2,2-trifluoroethane and precipitated twice in methanol to give, after drying in vacuo, 670 mg (62%) of **poly(G1-F₆)** as a white sticky powder. Anal. Calcd (found) for (C₈₀H₇₈F₇₈O₂S₆Si₂)_n : C, 34.29 (34.55); H, 2.81 (2.76); F, 52.89 (51.82). ¹H and ¹³C NMR spectra are shown in figures **S1** and **S2**, respectively. FTIR spectrum is shown in figure **S9**.

Functionalisation ratio : $f \sim 100\%$ (from ¹H-NMR analysis and Maldi-TOF) and $f \sim 98\%$ (from fluor content analysis).

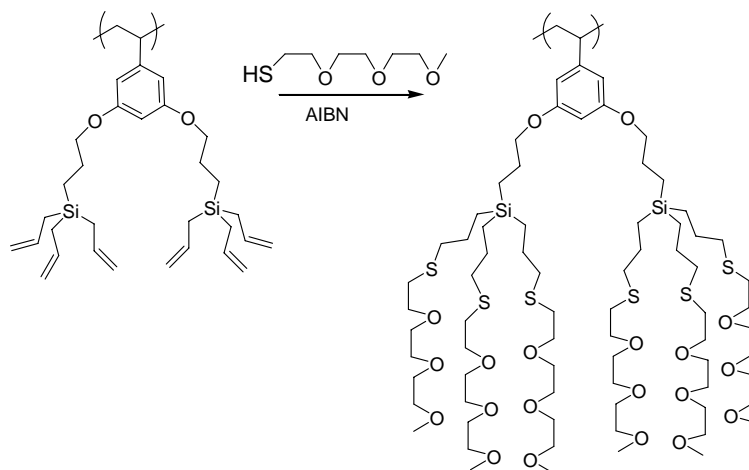
Polysilylated polymer : **poly(G1-Si₃)**.



A 25 mL two-necked flask was charged with 202 mg (2.32 mmol of allyle) of **poly(G1-allyl)**, 1.02 g (4.6 mmol) of 1,1,3,3,5,5,5-heptamethyltrisiloxane and 2 mL of toluene. Then, was introduced into the stirred solution 200 μ L (215 ppm) of a solution of Karstedt catalyst (2.5 mM in toluene, prepared from a commercial platinum-divinyltetramethyldisiloxane complex containing 3-3.5% of Pt). The mixture was bubbled with oxygen, placed under oxygen atmosphere and stirred for three days at room temperature (ref. 4) Another 200 μ L of the

Karstedt solution (215 ppm) was introduced and the solution was stirred for two more days at 45°C. The silylated polymer **poly(G1-Si₃)** was recovered from three precipitations into methanol from THF solution to give 465 mg (65% yield) of a white sticky gum. Anal. Calcd (found) for (C₇₄H₁₈₀O₁₄Si₂₀)_n : C, 47.89 (49.08), H, 9.78 (9.78), Si, 30.27 (28.88). ¹H and ¹³C NMR spectra are shown in figures **S3** and **S4**, respectively. FTIR spectrum is shown in figure **S9**. Functionalisation ratio : *f* ~ 85% (from ¹H-NMR analysis), *f* ~ 79% (from silicium content analysis).

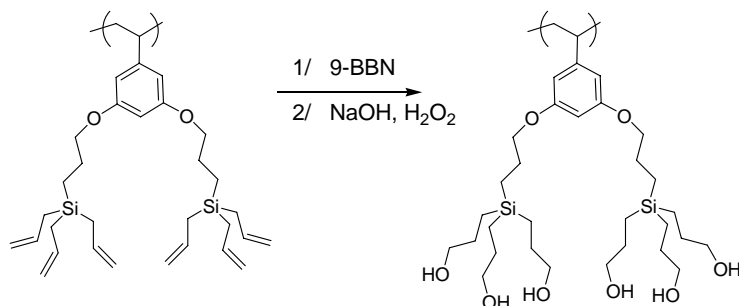
PEGylated polymer (Poly(G1-EG₃))



A carefully dried tube was charged with 190 mg (1.92 mmol of allyl) of **poly(G1-allyl)**, 0.5 mL toluene, 638 mg (3.54 mmol) of 2-{2-(2-methoxyethoxy)ethoxy}ethanethiol (prepared as in refs.1) and a solution of 7.9 mg (0.048 mmol) of AIBN in 0.7 mL toluene. After several freeze-pump-thaw cycles, the tube was sealed under vacuum and the mixture was heated to 50°C for four days under stirring. The reaction product was then evaporated to dryness. Isolation of the polymer from the unreacted mercaptan was performed by passing the crude polymerisation mixtures through a column filled with a SEC gel and eluted by THF by gravity flow. The product was then concentrated and dried under vacuum at 50°C overnight to give 466 mg (94% yield) of **poly(G1-EG₃)** as a transparent viscous oil. Anal. Calcd (found) for (C₇₄H₁₄₄O₂₀S₆Si₂)_n : C, 55.46 (54.65); H, 9.06 (9.01); S, 12.01 (11.63); Si, 3.51 (3.61). ¹H and ¹³C NMR spectra are shown in figures **S5** and **S6**, respectively. FTIR spectrum is shown in figure **S9**.

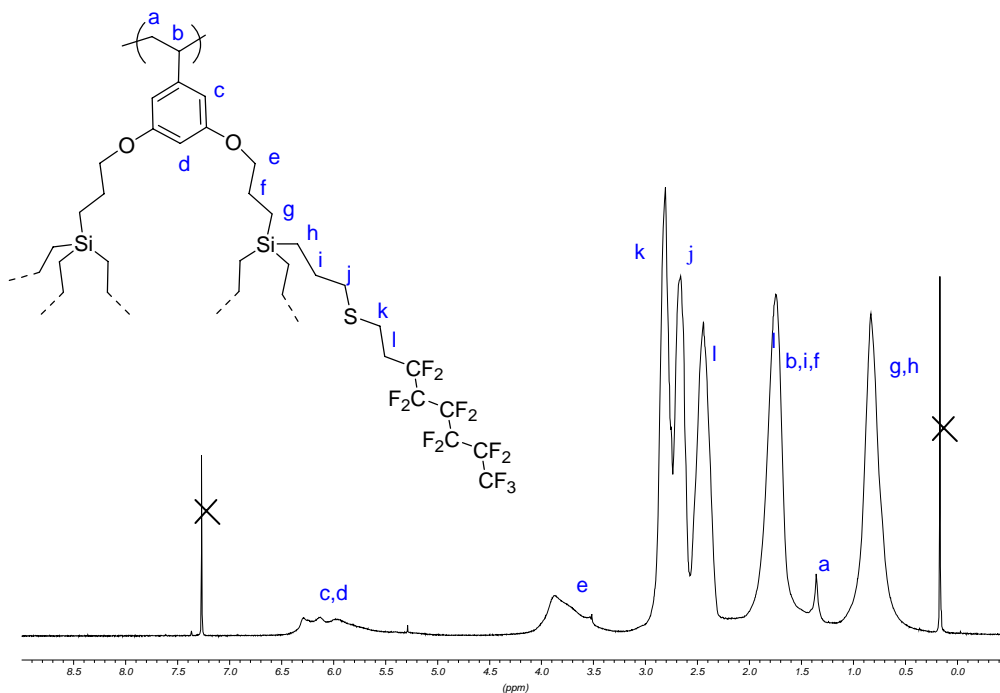
Functionalisation ratio : $f \sim 97\%$ from $^1\text{H-NMR}$ analysis and $f \sim 97\%$ from sulfur content analysis.

Polyhydroxylated polymer : poly(G1-OH).

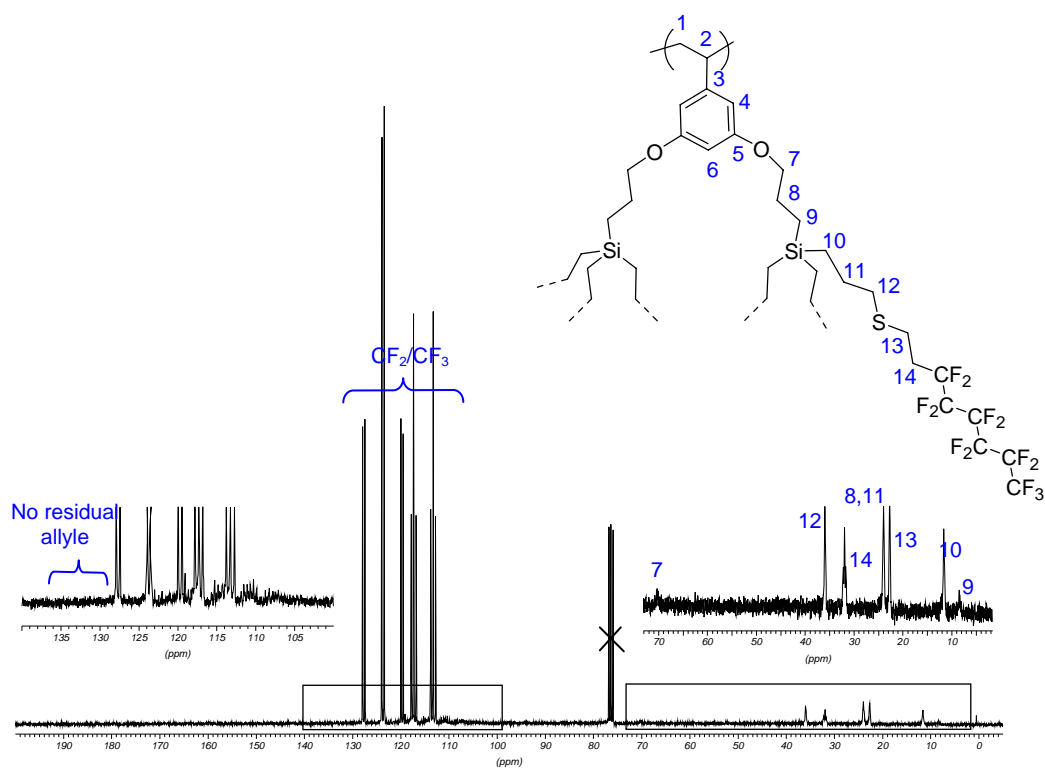


Perhydroxylation was performed by hydroboration/oxidation reaction sequence, using modified known procedures (refs 5) as follows. Into a degassed solution of 1.07 g (12.3 mmol of allyle) of **poly(G1-allyl)** in 50 mL of dry THF was added dropwise at room temperature and under argon atmosphere, 60 mL of a degassed THF solution of 9-BBN (0.5 M). The solution was allowed to be stirred for two days. After, 6 mL of aqueous solution of NaOH (6 M) was introduced. The solution was then cooled down by an ice/water bath and 12 mL of an aqueous solution of H₂O₂ (30%) were added dropwise. The stirring was continued for an additional 4 hours at room temperature. The white precipitate was filtered off and the filtrate was concentrated in vacuo. The residual boronic acid was then eliminated by refluxing with methanol, followed by a distillation. Finally, the hydroxylated polymer was isolated from the cyclooctanediol side-product by several precipitations from ethanol solution into cyclohexane and diethyl ether solvents. Recovered **poly(G1-OH)**: 200 mg, as a white product. Anal. Calcd (found) for (C₃₂H₆₀O₈Si₂)_n : C, 61.11 (61.45); H, 9.61 (9.53); Si, 8.93 (9.20). ^1H and ^{13}C NMR spectra are shown in figures **S7** and **S8**, respectively. The ^{13}C NMR spectrum reveals some traces of residual cyclooctanediol as well as traces of diethylether and ethanol solvent. FTIR spectrum is shown in figure **S9**. Polymer **poly(G1-OH)** is soluble only in alcohols and in DMSO, and thus could not be characterised by SEC.

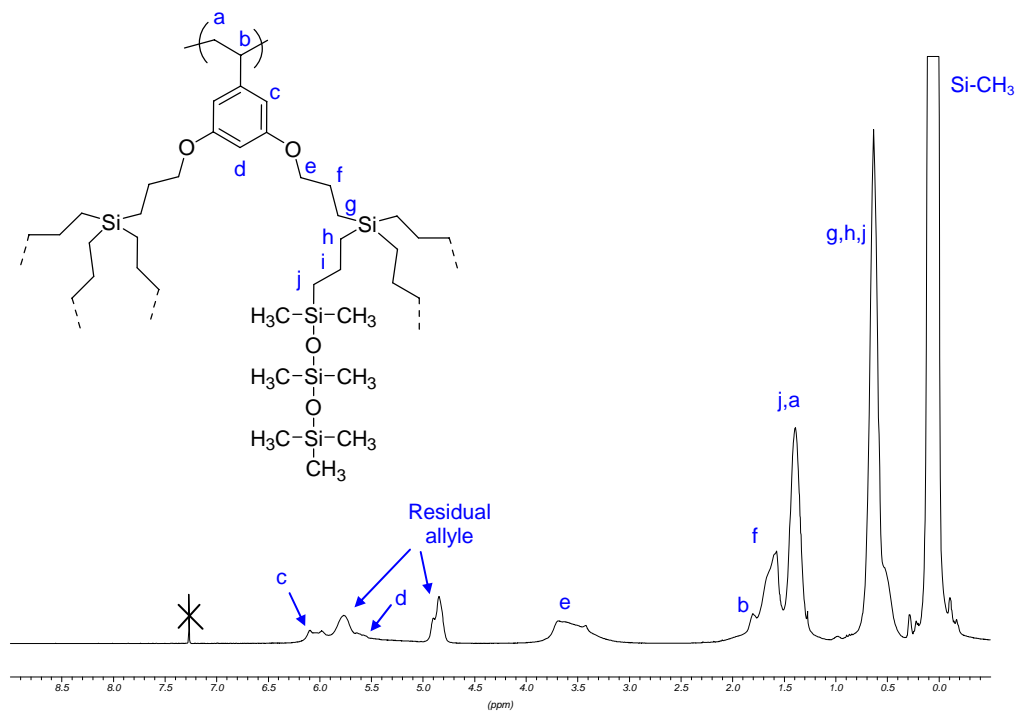
Functionalisation ratio f : $95\% < f < 99\%$ (from $^1\text{H-NMR}$ analysis) and $f \sim 97\%$ (from carbon content analysis).



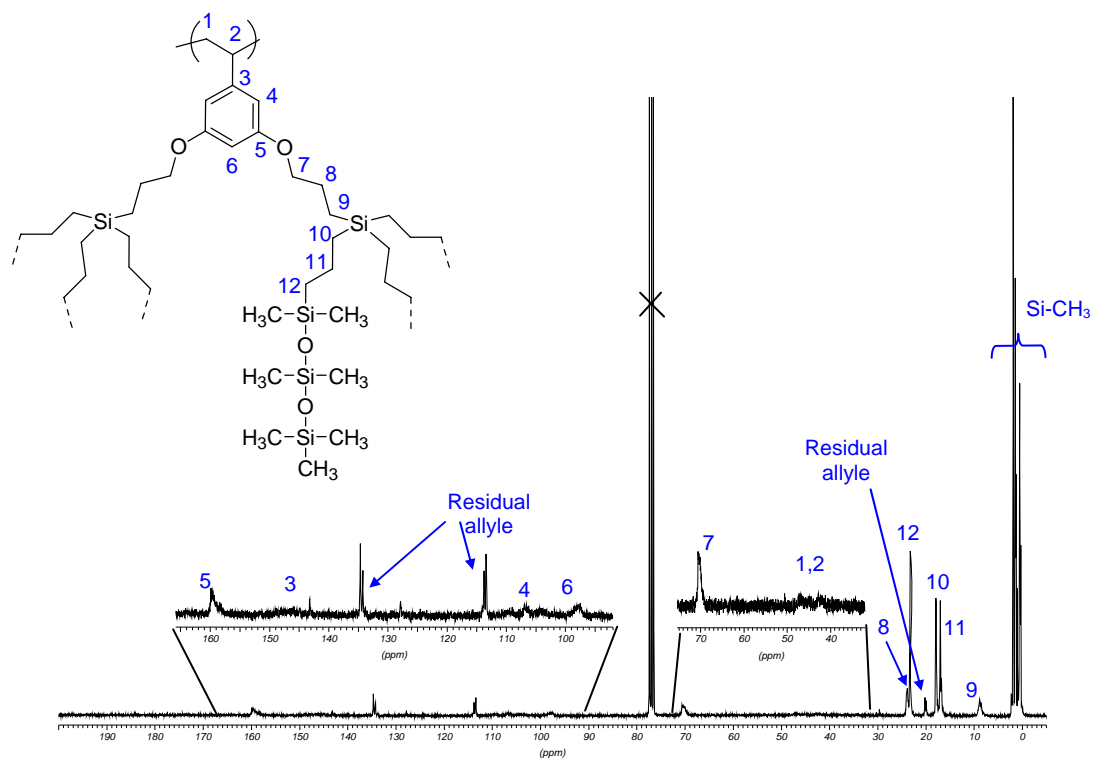
S1. ¹H-NMR spectrum of poly(G1-F6) in CDCl₃/CFCl₂CF₂Cl



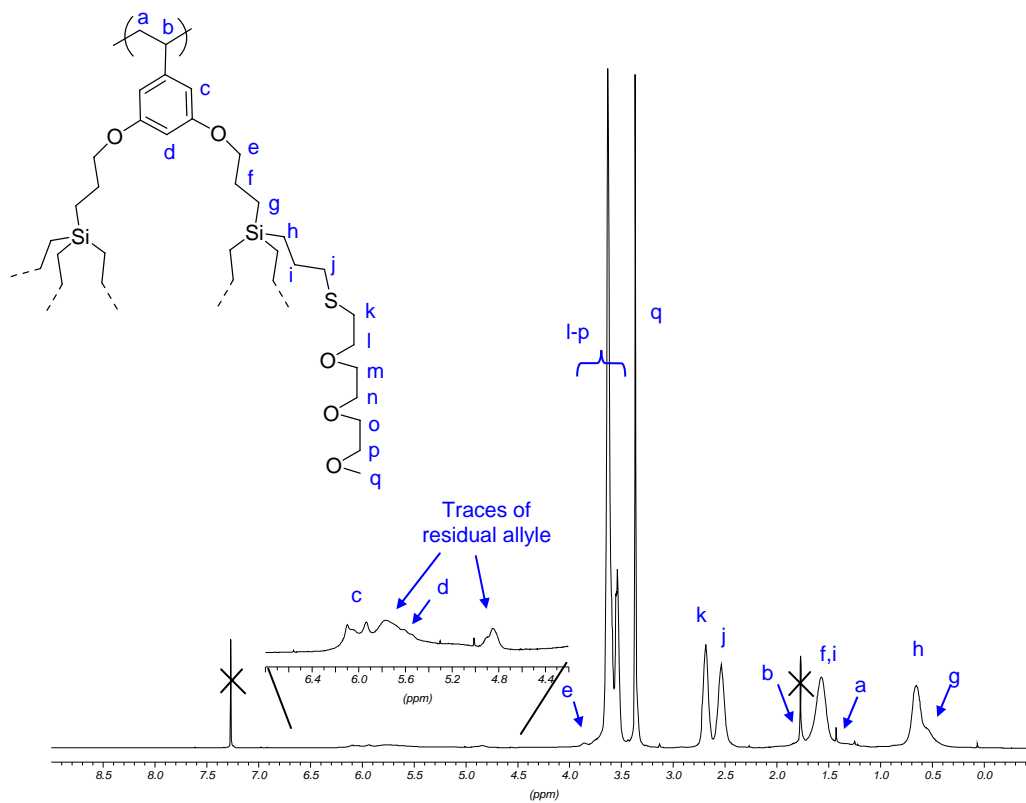
S2. ¹³C-NMR spectrum of poly(G1-F6) in CDCl₃/CFCl₂CF₂Cl



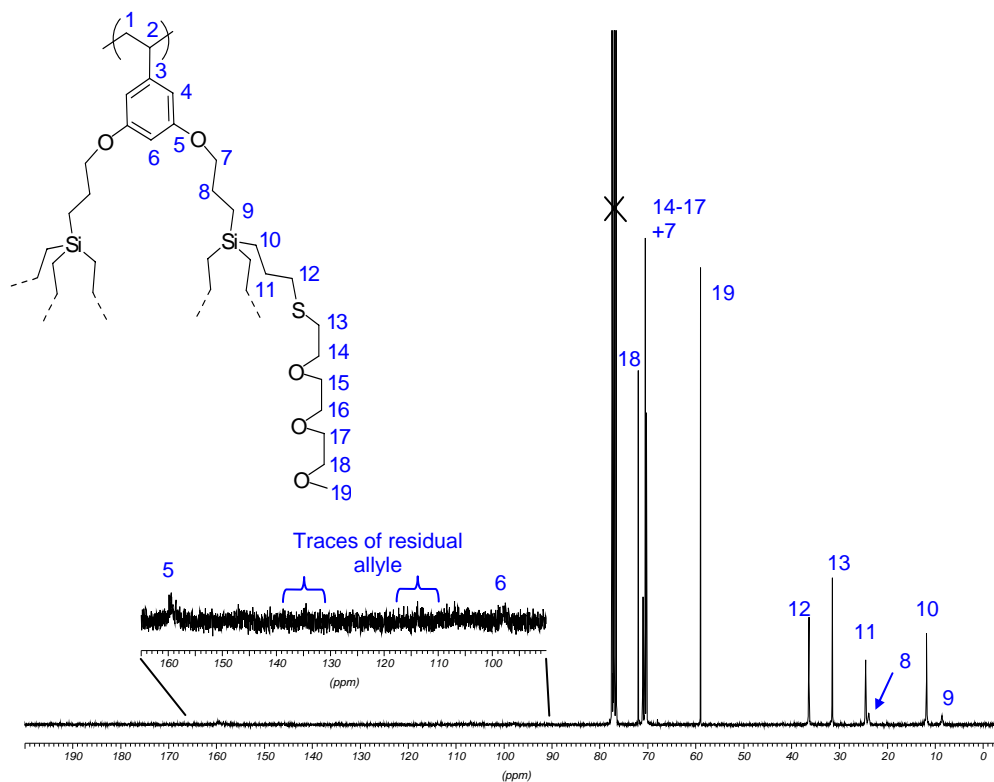
S3. ¹H-NMR spectrum of poly(G1-Si₃) in CDCl₃



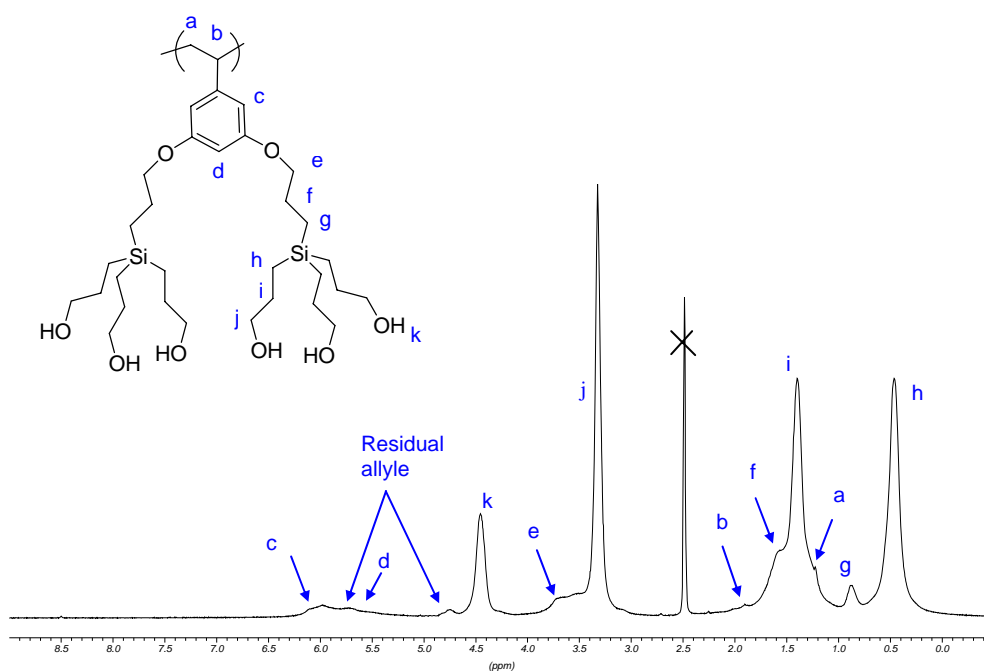
S4. ¹³C-NMR spectrum of poly(G1-Si₃) in CDCl₃



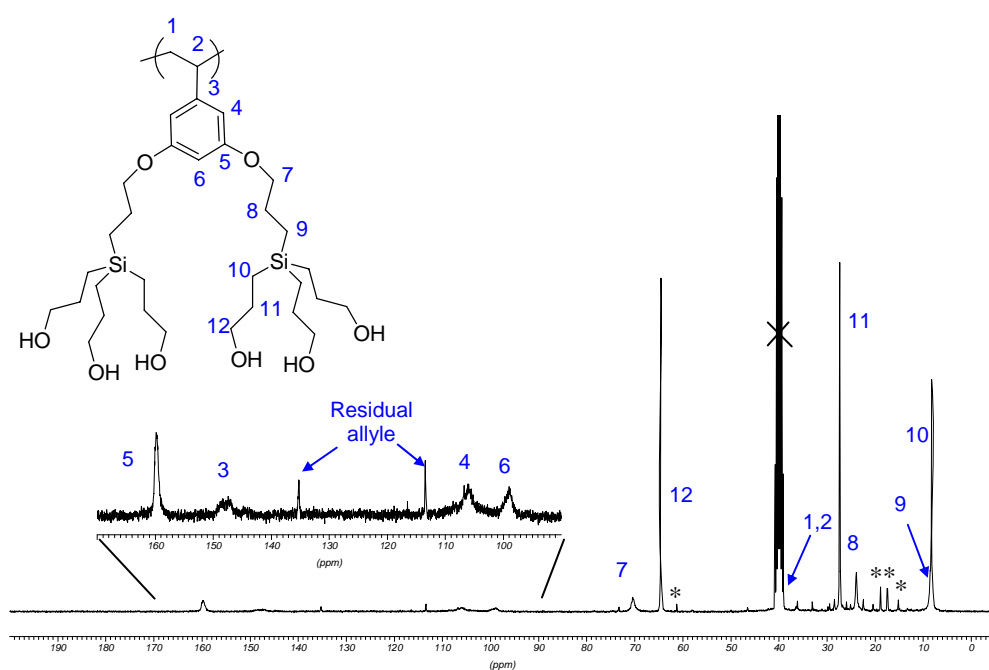
S5. ¹H-NMR spectrum of poly(G1-EG₃) in CDCl₃



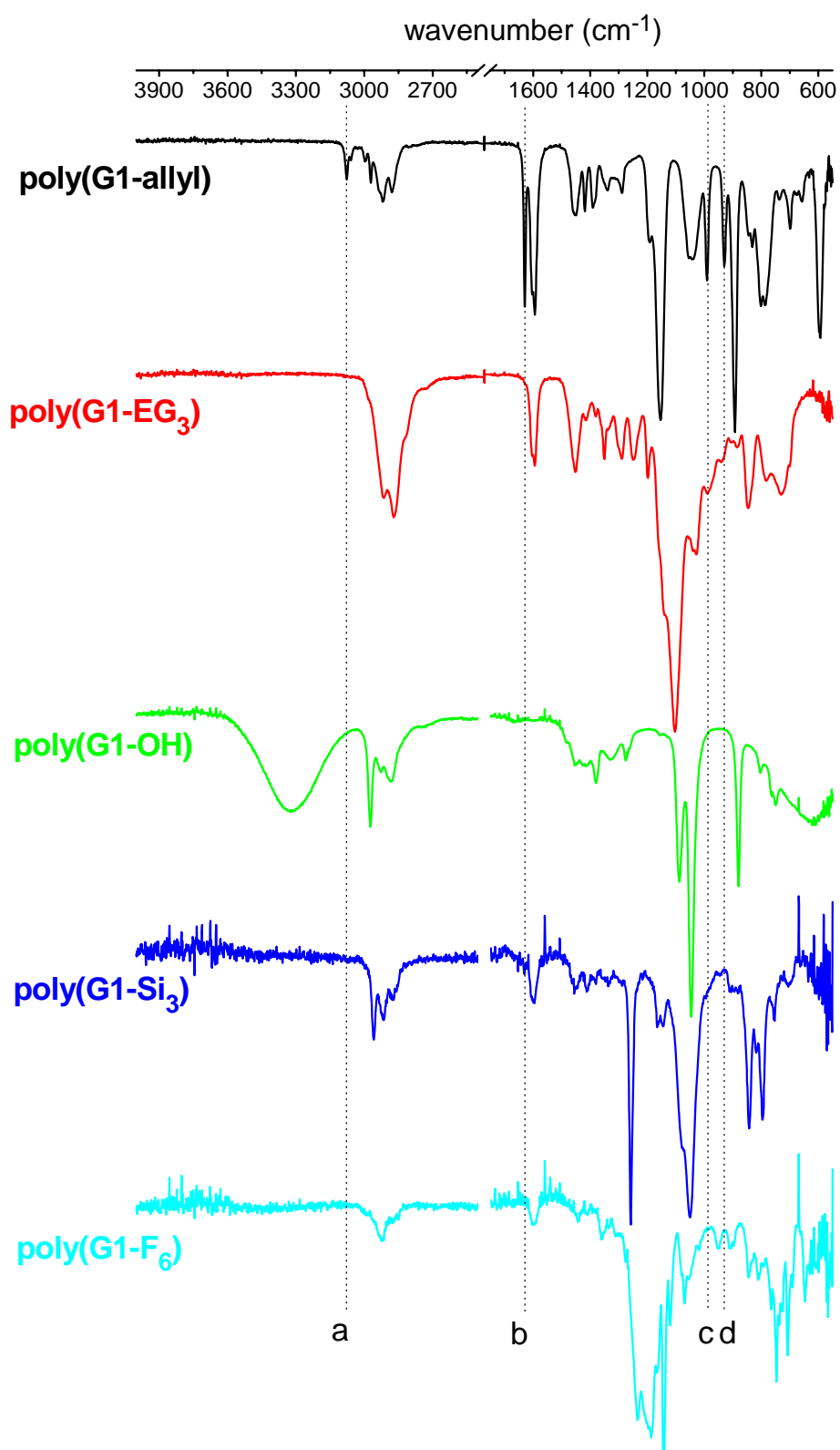
S6. ¹³C-NMR spectrum of poly(G1-EG₃) in CDCl₃



S7. ¹H-NMR spectrum of **poly(G1-OH)** in DMSO-*d*₆



S8. ¹³C-NMR spectrum of **poly(G1-OH)** in DMSO-*d*₆
(* indicate traces of residual cyclooctanediol, and diethylether and ethanol solvents)



S9. FTIR spectra of the starting multiallylic polymer **poly(G1-allyl)** and its functionalised homologues. Dotted lines indicate the position of the characteristic signals of the allyl groups (a: =CH₂ st; b: =CH δ oop; c and d: C=C st).

References:

- (1) (a) T. Nabeshima, T. Takahashi, T. Hanami, A. Kikuchi, T. Kawabe, Y. Yano, *J. Org. Chem.* **1998**, *63*, 3802-3803. (b) A. Snow, E. E. Foos, *Synthesis*, **2003**, 509-512.
- (2) F. Moingeon, P. Masson, S. Méry, *S. Macromolecules*, **2007**, *40*, 55-64.
- (3) K. Lorenz, H. Frey, B. Stühn, R. Mülhaupt, *Macromolecules* **1997**, *30*, 6860-6868.
- (4) J. Stein, L. N. Lewis, Y. Gao, R. A. Scott, *J. Am. Chem. Soc.* **1999**, *121*, 3693-3703
- (5) (a) T. C. Chung, M. Raate, E. Berluce, D. N. Schulz, *Macromolecules*, **1988**, *21*, 1903-1907. (b) K. Lorenz, R. Mülhaupt, H. Frey, U. Rapp, F. J. Mayer-Posner, *Macromolecules*, **1995**, *28*, 6657-6661