

Supporting Information

Robust procedure for large scale synthesis of a high molar mass, unsubstituted poly(*m,p*-phenylene)

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1. General

GC analyses were carried out on an Agilent 7820A GC equipped with an HP-5 MS column (30 m × 0.25 mm × 0.5 μm, 5% phenyl methyl-siloxane), FID detector, and helium as the carrier gas. All runs were performed with an initial temperature of 150°C and a gradient of 10°C/min after 8 minutes with a final temperature of 250°C.

Differential scanning calorimetry (DSC) measurements were carried out using a DSC Q1000 differential scanning calorimeter from TA Instruments in a temperature range of 25 to 250°C with a heating and cooling rate of 10°C/min. Samples of a total weight ranging between 1 and 2 mg were closed into aluminum pans of 40 μL, covered by a holed cap, and analysed under a nitrogen atmosphere.

¹³C CP/MAS spectra were recorded on a Bruker AVANCE 400 spectrometer operating at 100.5 MHz for ¹³C under MAS conditions with 2.5 mm rotors and a sample rotation frequency of 11 or 20 kHz and cross-polarization (CP) employing a contact time of 1 ms and ¹H high-power decoupling.

2. Synthesis of Pd[PPh₂C₆H₅COOH]₃ (Pd(L2)₃)

In a 50 mL Schlenk flask PdCl₂ (56 mg, 0.318 mmol) and 4-(Diphenylphosphino)benzoic acid (487 mg, 1.59 mmol) were dissolved in 2.8 mL DMSO. The suspension was degassed by 5 cycles of vacuum and nitrogen back-filling. During heating to 150 °C a red solution formed, which after 10 minutes at this temperature was allowed to cool down to 120 °C. After the addition of hydrazine hydrate (62 μL, 1.27 mmol) the mixture was allowed to cool to room temperature. Upon addition of 25 mL degassed THF, the catalyst precipitated as a yellow crystalline solid. The crystals were filtered through a Schlenk frit and washed twice with degassed THF. The catalyst was dried overnight and finally stored in a glovebox. ¹H NMR (300 MHz, DMSO, δ): 7.56 (d, 6H, *J*=7.9Hz), 7.22 (t, *J*=6.8Hz, 6H), 7.02-7.13 (m, 30H).

3. NMR Data

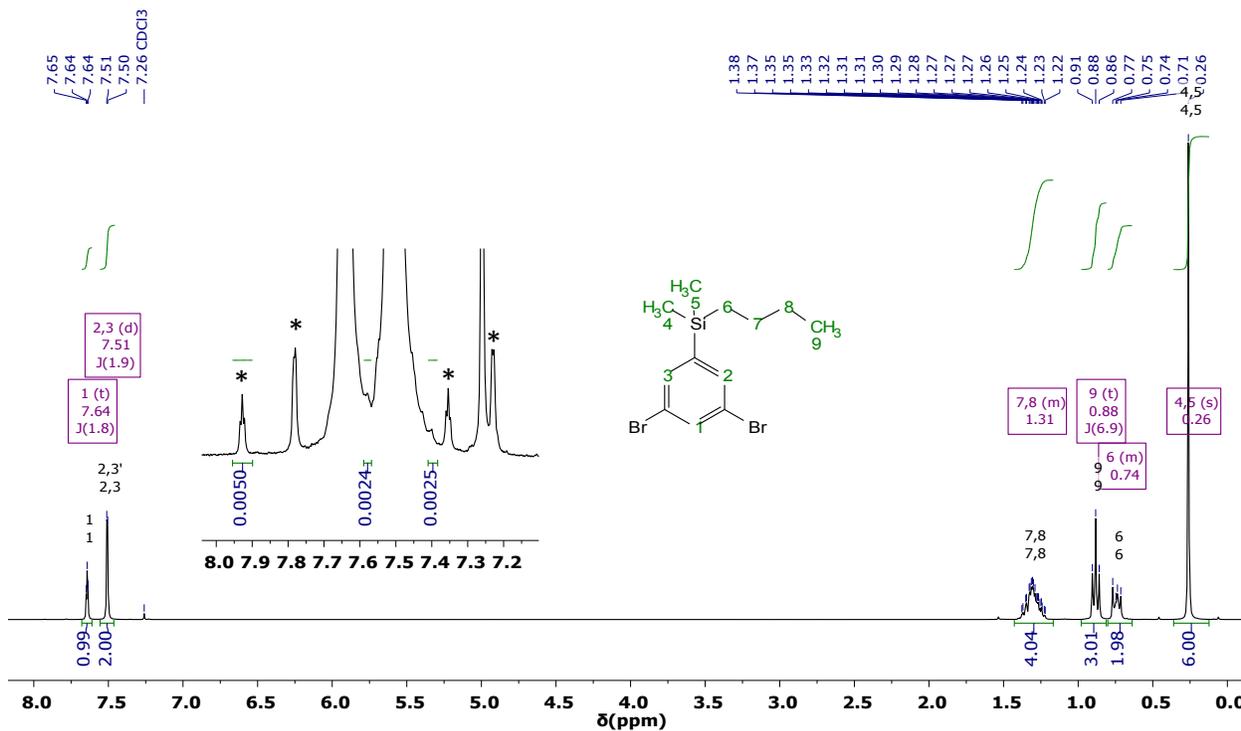


Figure S1 ¹H NMR spectrum of (3,5-dibromophenyl)butyl(dimethyl)silane in CDCl₃ at 25 °C with magnification in the aromatic region. ¹³C Satellites are marked with *. Some minor impurities in the size range of the ¹³C satellites are visible.

By comparing the integrals of the satellite signals with those of the impurities one can estimate the amount of purity to >99.5%. The estimation is based on the assumption that the impurity peaks also correspond to one proton, which would be the worst case.

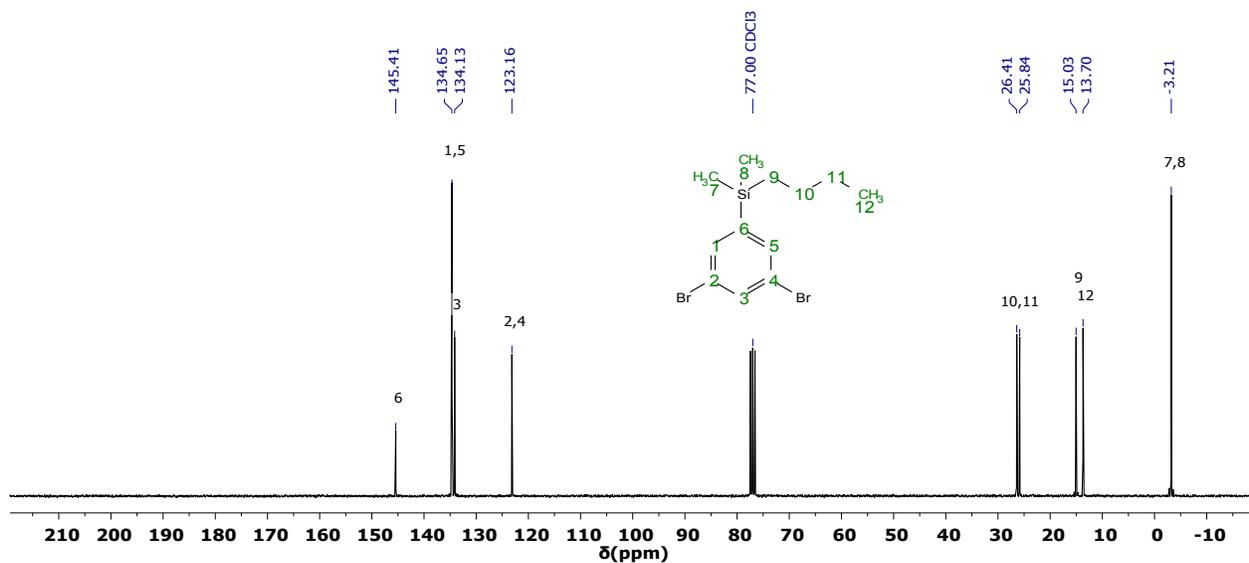


Figure S2 ^{13}C NMR spectrum of (3,5-dibromophenyl)butyl(dimethyl) silane in CDCl_3 at 25°C .

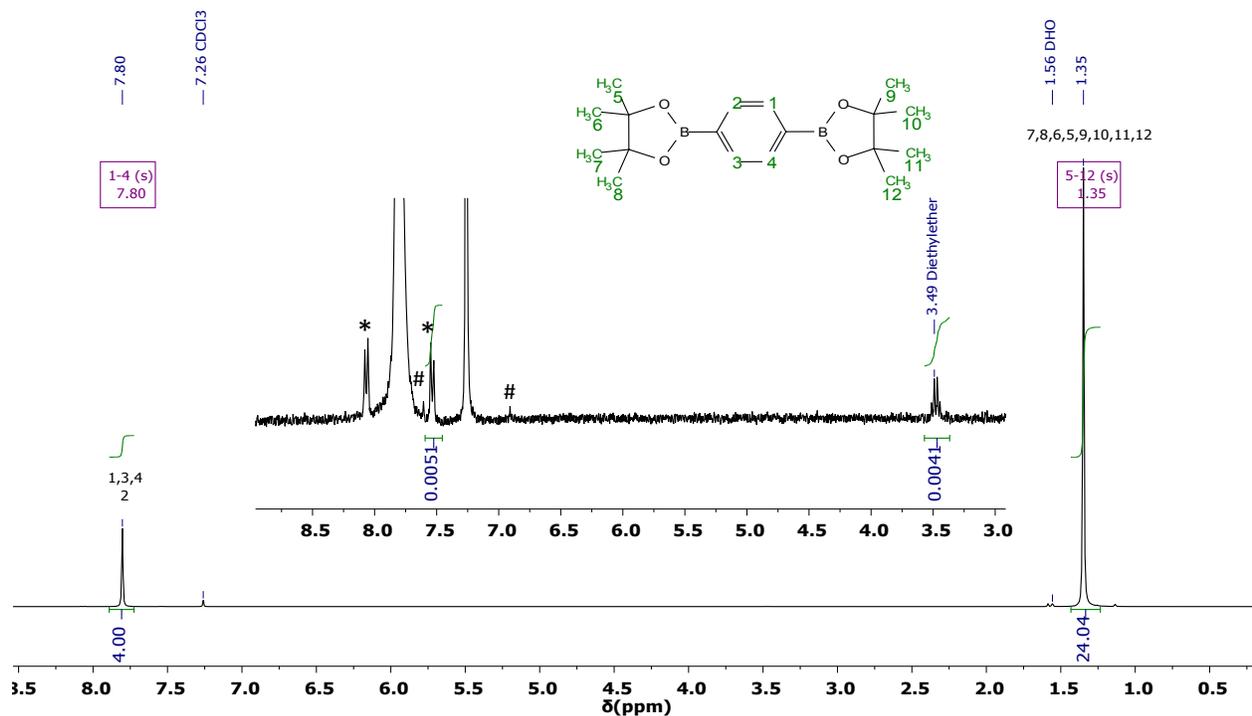


Figure S3 ^1H NMR spectrum of 1,4-benzenediboronic acid bis(pinacol) ester in CDCl_3 at 25°C with magnification. ^{13}C satellites of the compound and CDCl_3 are marked with * and # respectively. Some minor impurities, with a peak size of the ^{13}C satellites, can be seen.

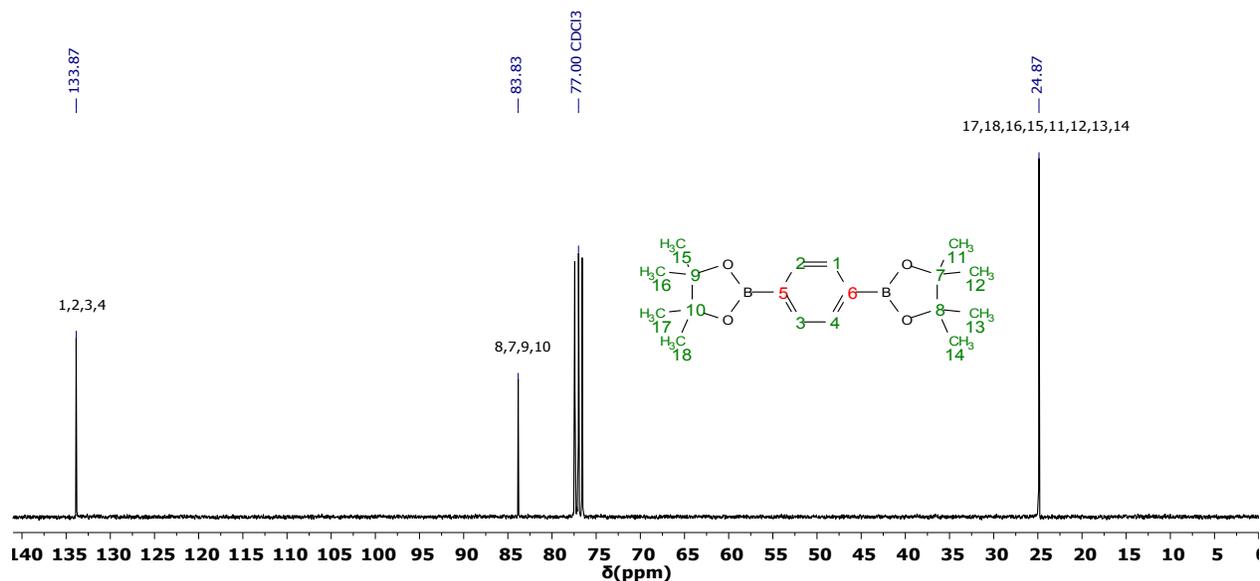


Figure S4 ^{13}C NMR spectra of 1,4-benzenediboronic acid bis(pinacol) ester in CDCl_3 at 25°C . The two carbons attached to the boron are not observed due to quadrupolar relaxations.

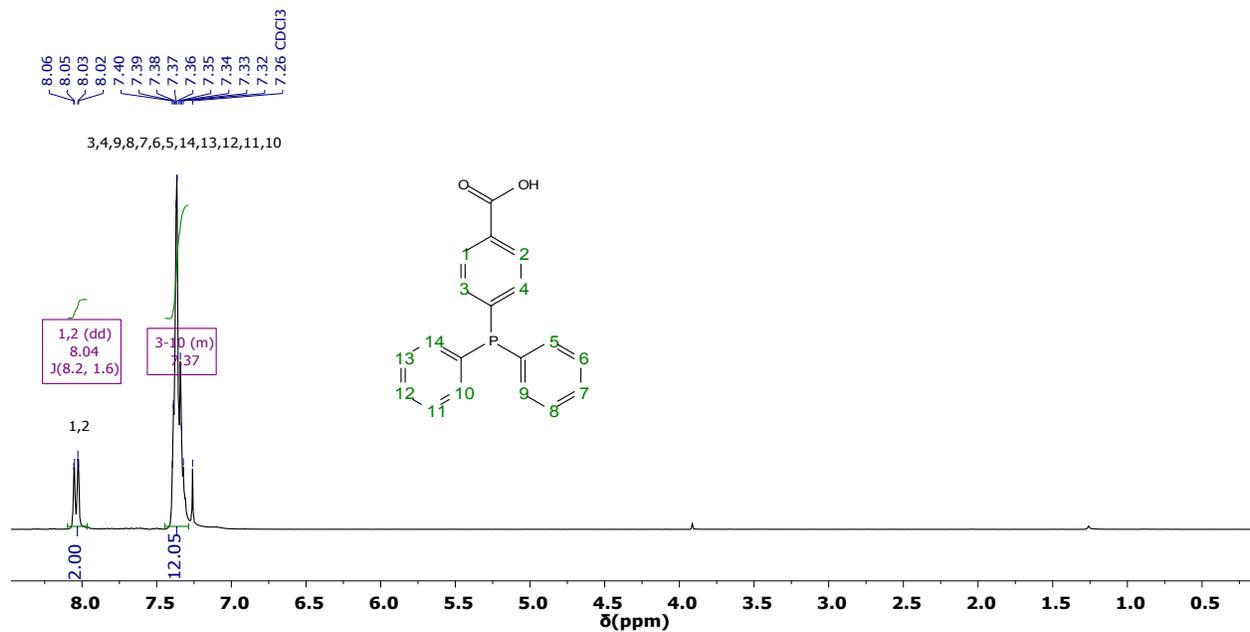


Figure S5 ^1H NMR spectrum of 4-(diphenylphosphino)benzoic acid in CDCl_3 at 25°C . The spectrum is in agreement with the literature¹

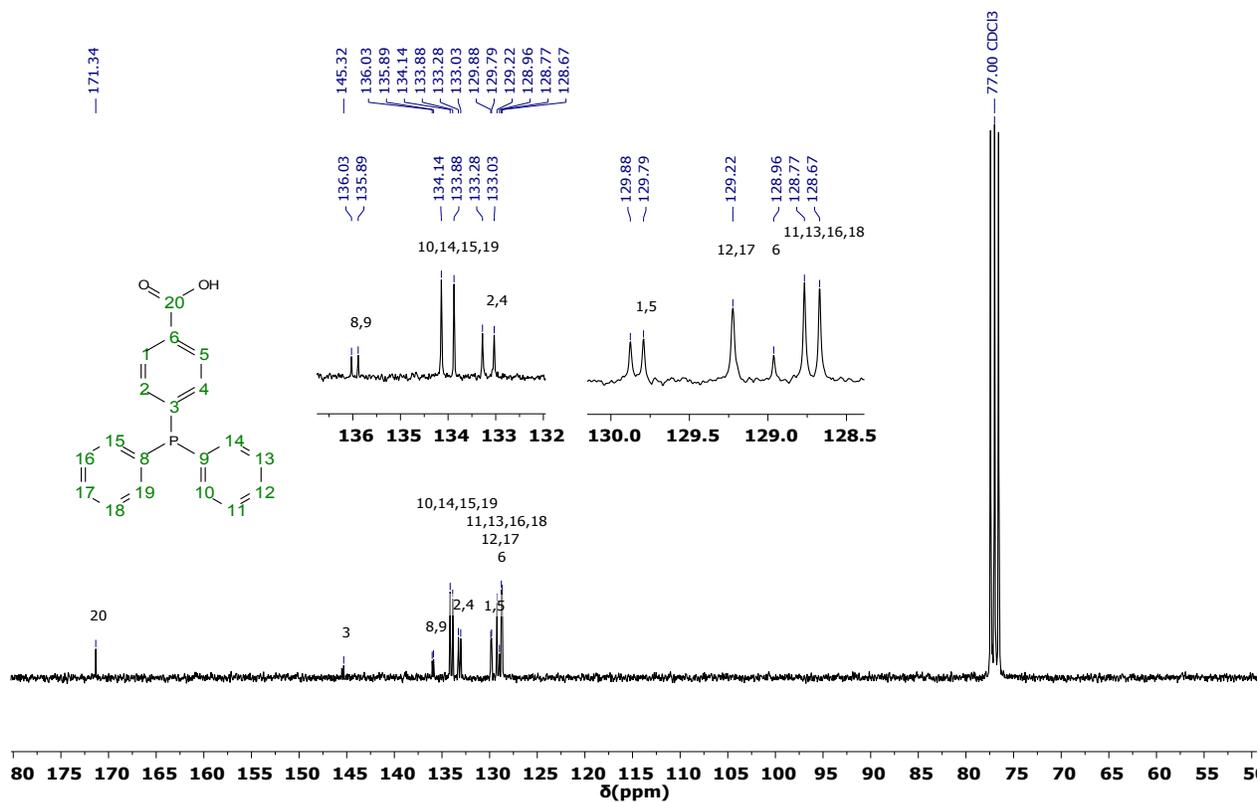


Figure S6 ^{13}C NMR spectrum of 4-(diphenylphosphino)benzoic acid in CDCl_3 at 25 °C with magnifications between 128 and 136 ppm. The doublet signals are due to the coupling with ^{31}P .

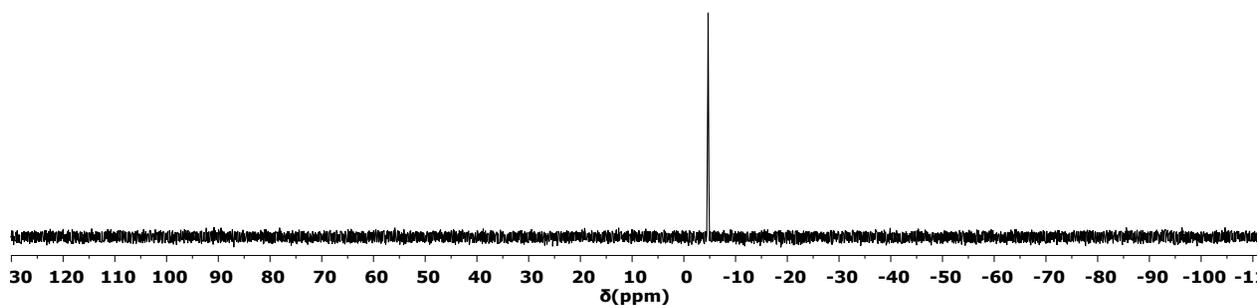


Figure S7 ^{31}P NMR spectrum of 4-(diphenylphosphino)benzoic acid in CDCl_3 at 25 °C. No standard was used as only one signal was expected.

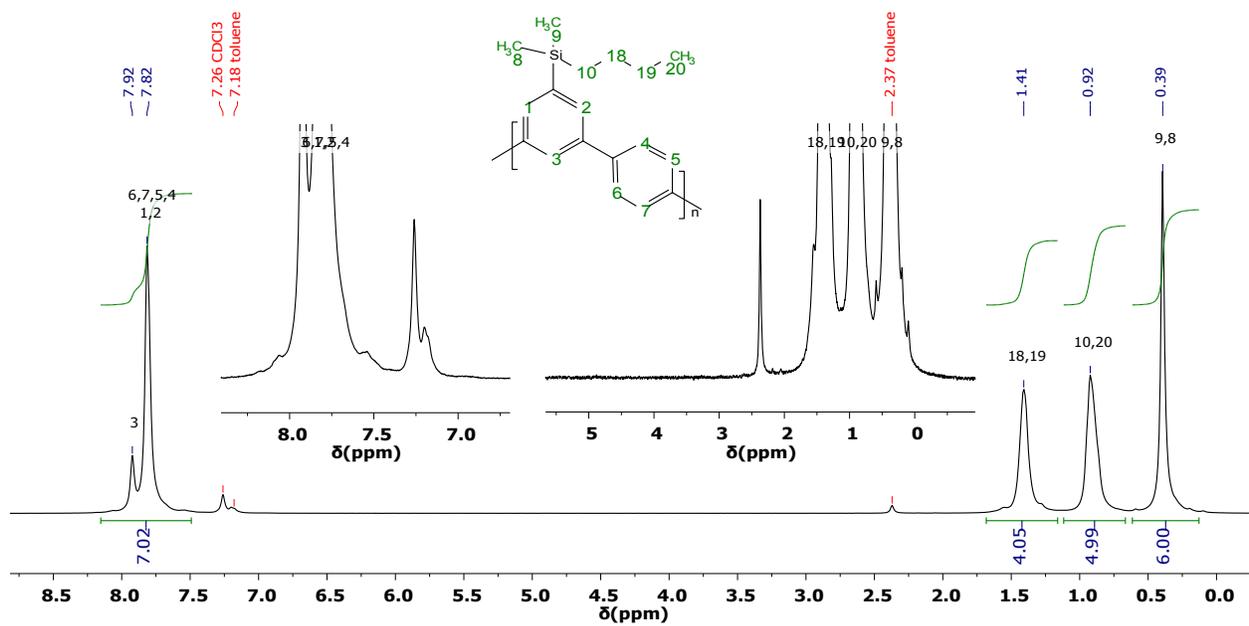


Figure S8 ^1H NMR spectrum of polymer **1c** in CDCl_3 at 25°C with magnification.

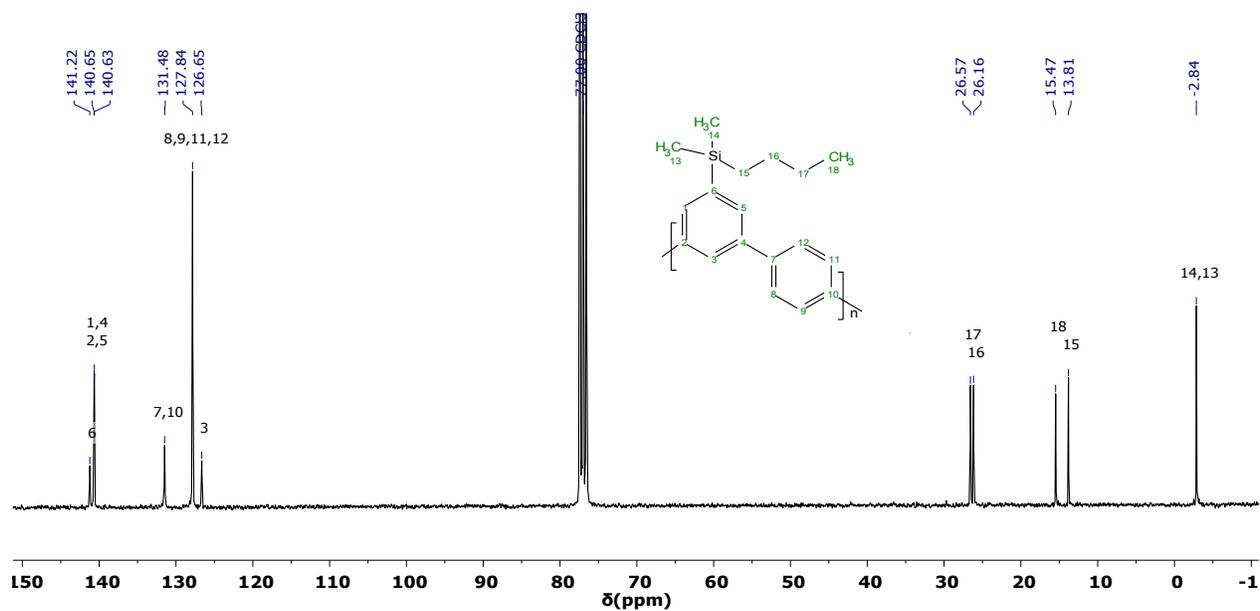


Figure S9 ^{13}C NMR spectrum of polymer **1c** in CDCl_3 at 25°C with magnification.

4. Gas chromatography

Figures S11-S13 show that at the given concentrations only a single signal appears besides the injection- and the solvent peak (THF). This already indicates a very high purity and allows the preparation of a calibration curve for the monomer. Finally the pure monomer **1d** was injected into the GC, which led to an oversaturation of the FID detector. This way a few minor impurities could be detected under strong magnification. By extrapolating the calibration curve to the concentration of the pure monomer, which was 3.90 M, the sum of the integrals of all impurities could be divided by the area extrapolated for the pure monomer. As a result a purity of 99.96% was calculated. This value is higher than the one determined by NMR. It should be mentioned that for the described method, we assumed the same extinction coefficient for the monomer and all impurities.

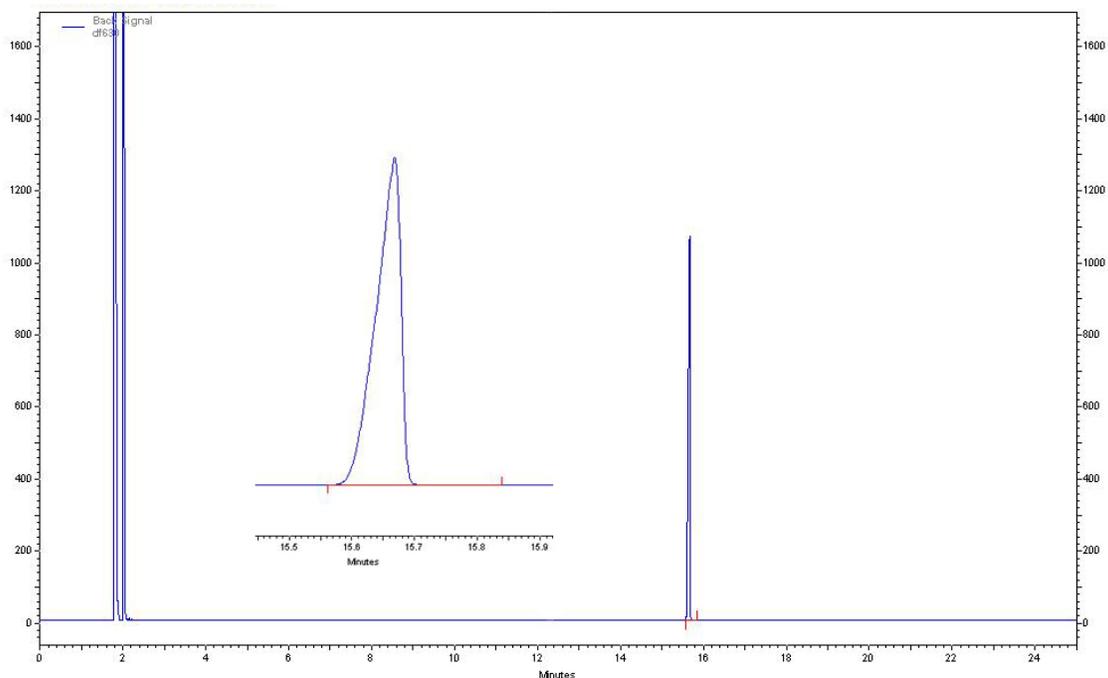


Figure S10 Gas chromatogram of a 0.156 M solution of monomer **2** in THF. The two peaks at around 2 minutes retention time correspond to the injection and solvent signal.

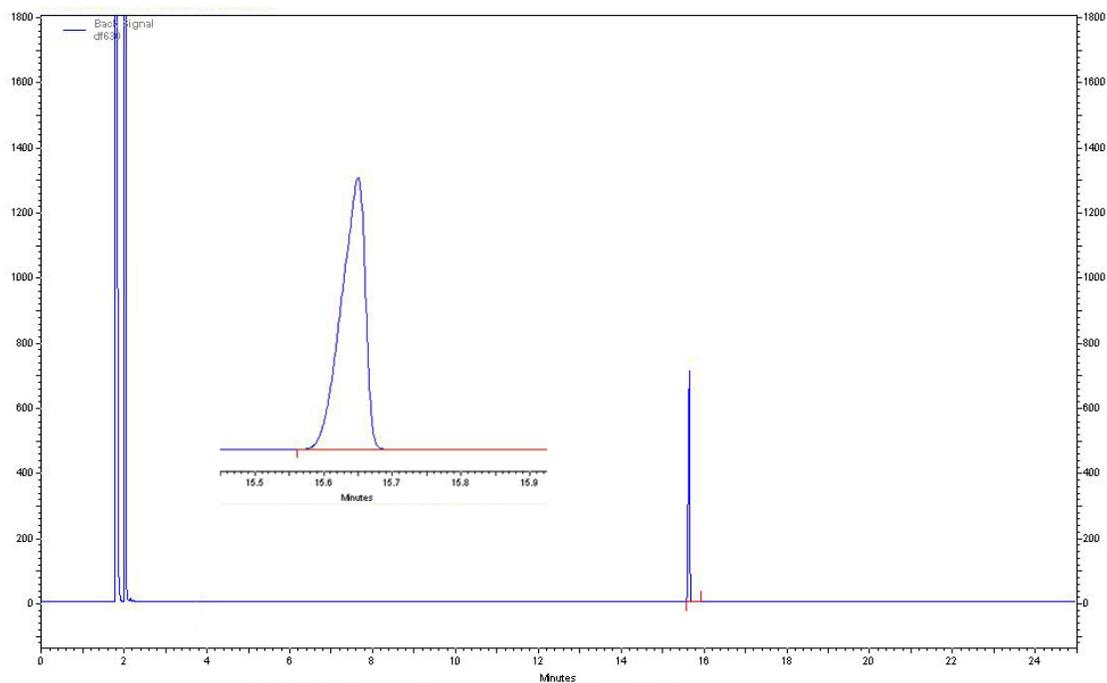


Figure S11 Gas chromatogram of a 78.0 mM solution of monomer **2** in THF. The two peaks at around 2 minutes retention time correspond to the injection and solvent signal.

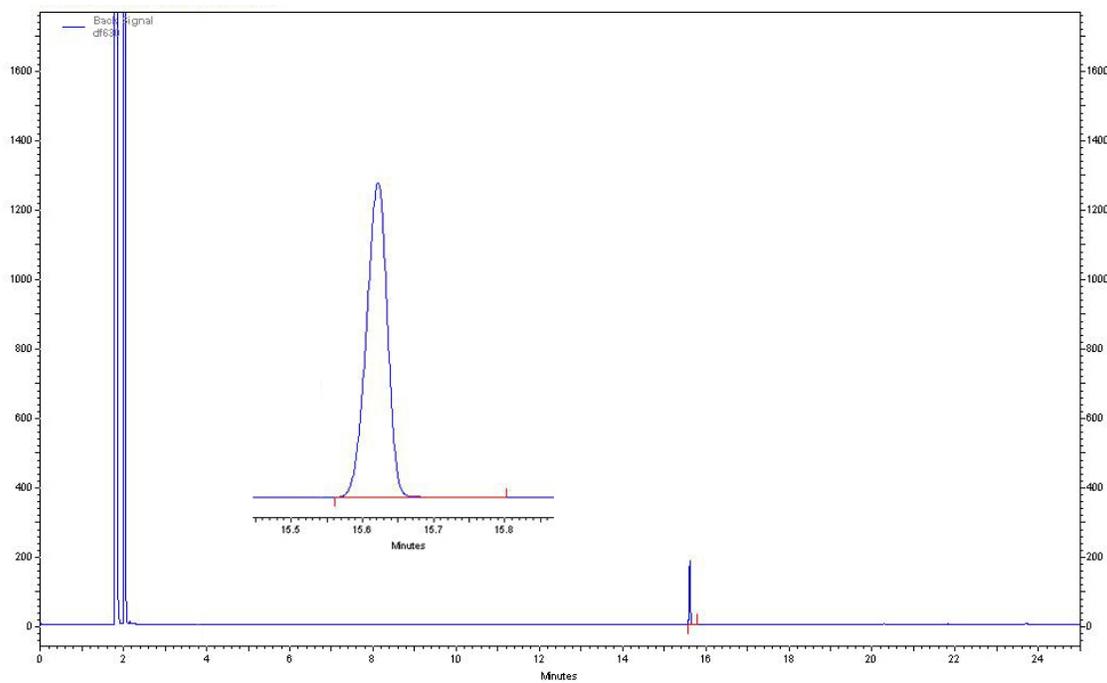


Figure S12 Gas chromatogram of a 15.6 mM solution of monomer **2** in THF. The two peaks around 2 minutes retention time correspond to the injection and solvent signal.

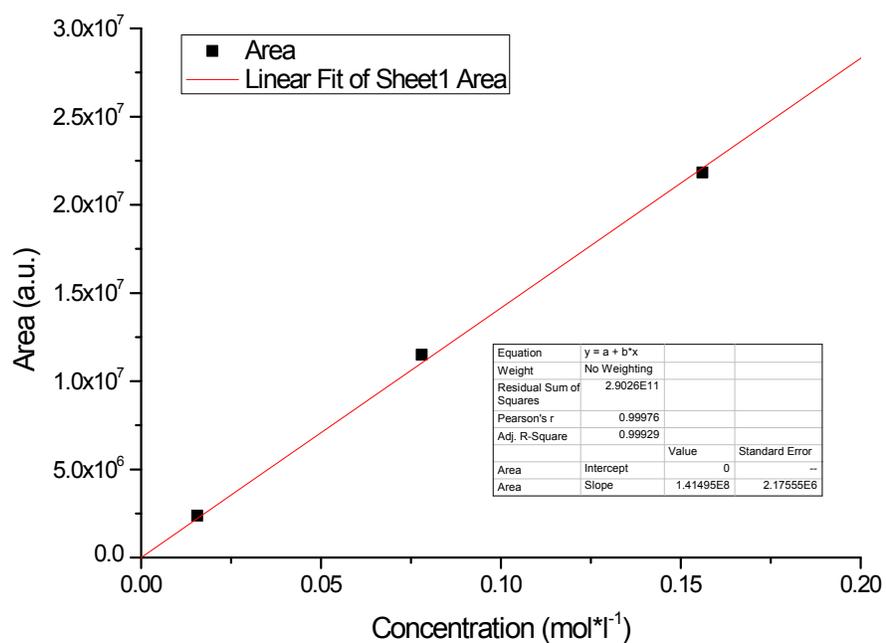


Figure S13 GC calibration curve for monomer **2**. The linear fit is used to determine the theoretical area of the non-diluted compound with a concentration of 3.90 M.

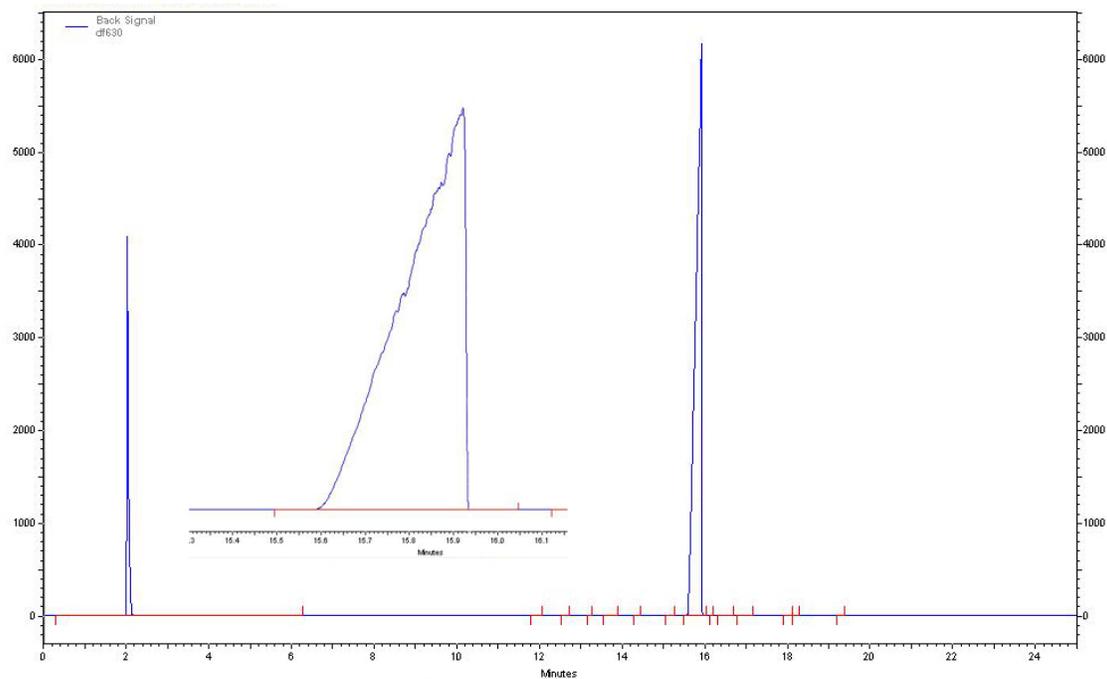


Figure S14 Gas chromatogram of non-diluted monomer **2**. The inset shows the oversaturated FID signal.

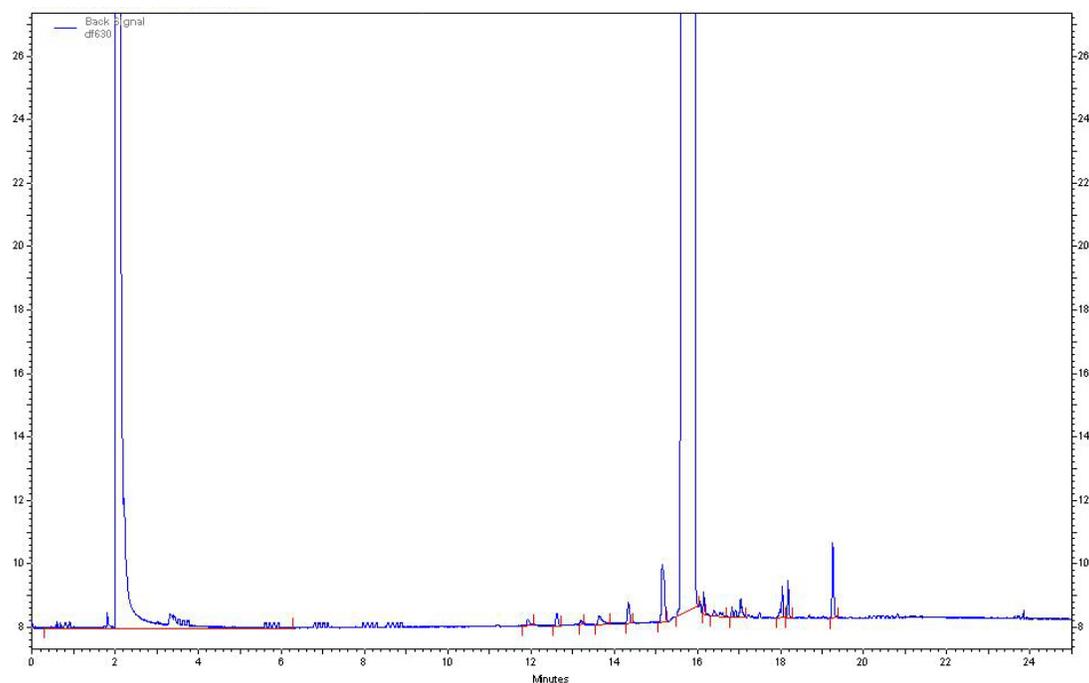


Figure S15 High magnification of figure S 14 reveals several minor impurities. By comparison of the impurities peaks areas with the theoretical value for the monomer peak area determined by the calibration curve in figure S13 a purity of 99.96 % was determined.

5. Comparison of catalytic activities

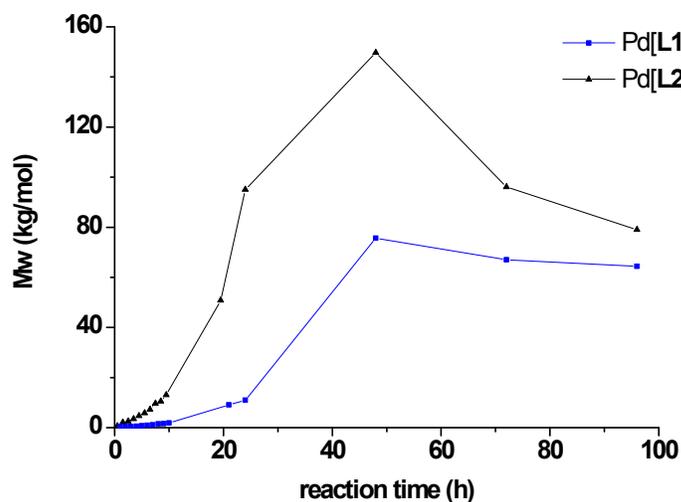


Figure S16 Comparison of the two catalysts. The displayed mass values are from GPC calibrated with PMMA standard, which leads to an even bigger overestimation than in the case of polystyrene calibration. The decrease towards the end of the reaction is due to the precipitation of high molecular weight material, which could not be collected by taking samples with a syringe.

6. Optimisation of the stoichiometric ratio

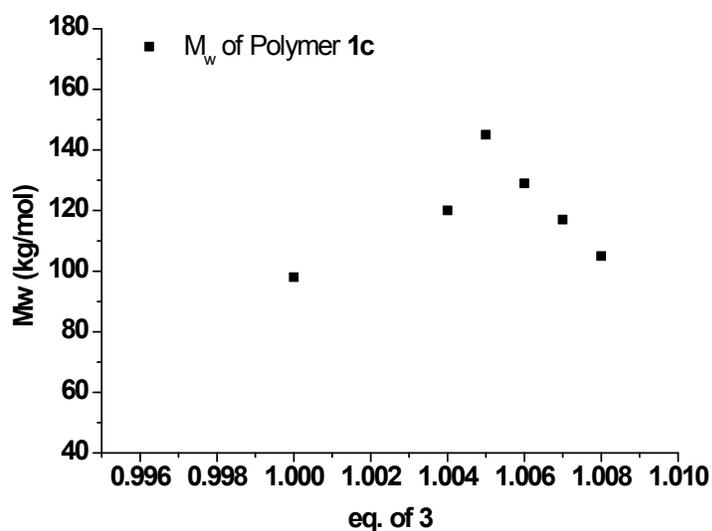


Figure S17 Determination of the perfect monomer ratio. The data point towards an optimal boron monomer excess of 1.005 eq. The experiments were performed on a 1 g scale. The molecular weights show that also in that scale a very high molecular weight can be reached when the stoichiometric ratio gets tuned very carefully.

Table S1 Results of polymerisations between monomer **2** and **3** in different stoichiometric ratios.

Entry	Equivalents of monomer 2	Equivalents of monomer 3	Mn [kg mol ⁻¹]	Mw [kg mol ⁻¹]	Yield [%]
1	1.000	1.000	7.3	98	93
2	1.000	1.004	11	120	n.d.
3	1.000	1.005	13	145	98
4	1.000	1.006	12	129	n.d.
5	1.000	1.007	7.8	117	91
6	1.000	1.008	10	105	96

7. TGA

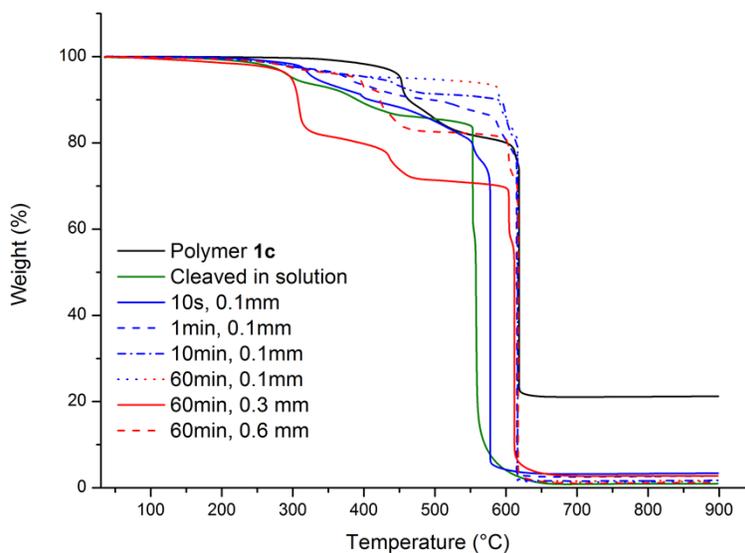


Figure S18 TGA curves of polymer **1c** before and after side chain removal at different acid exposure times. The time series with same film thicknesses is depicted in blue, while the thickness series is colored red. The degradation starts off at around 300 °C ending with a sharp drop at 600 °C. The differences are mainly due to the different sample appearances. We see a faster degradation when subjecting samples as fine powders compared to pieces of polymer films.



Figure S19 Picture of a 0.1 mm thick film of polymer **1c** (entry 9b Table 1) showing the possibility to produce transparent films of considerable size.

8. Solid State CP/MAS ^{13}C NMR

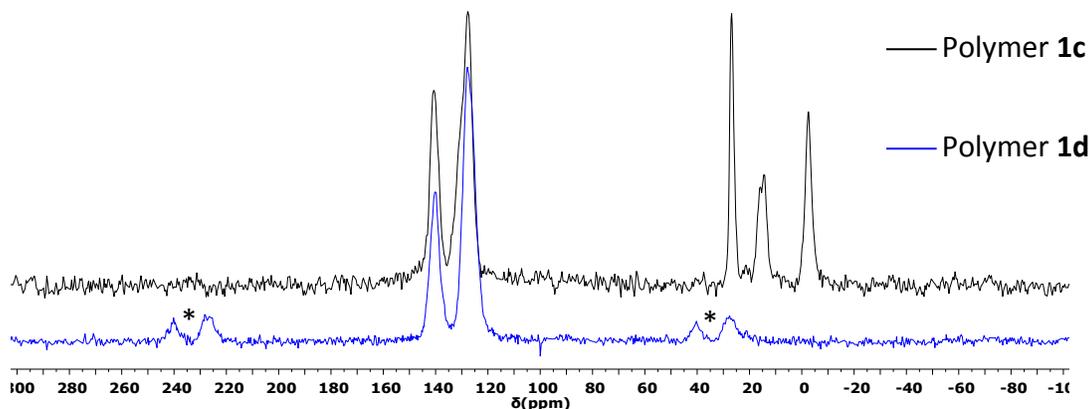


Figure S20 ^{13}C CP/MAS Solid State NMR of polymer **1c** at 25 °C with a spinning speed of 20 kHz (black) and of polymer **1d** at a spinning speed of 11 kHz (blue). The two spectra show the disappearance of the aliphatic signals upon acid treatment. The blue curve corresponds to a 0.1 mm thick film which was exposed to diluted TFOH for 60 minutes. The spinning side bands marked with * are not visible in the black spectrum because of the higher spinning speed.

9. IR Spectra

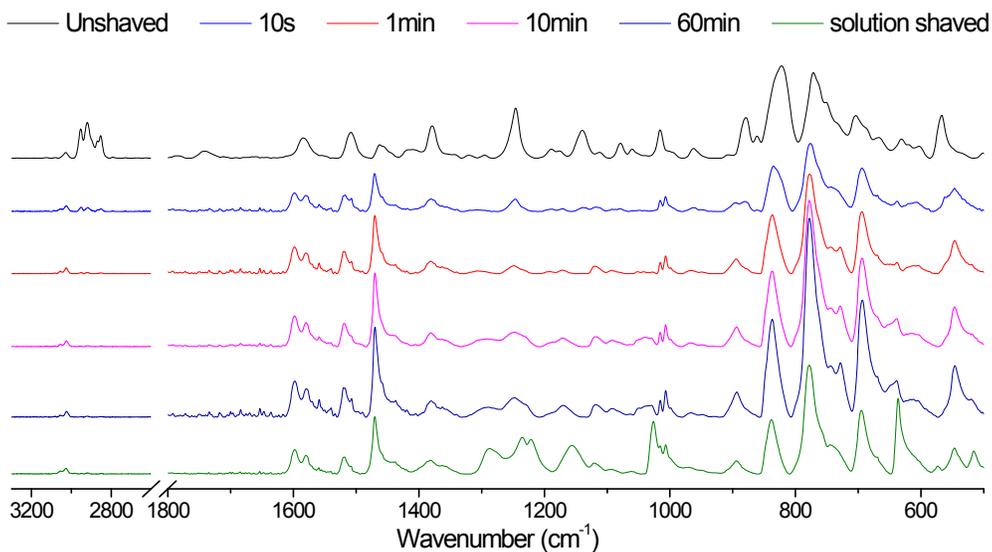


Figure S21 IR spectra of cleaved and uncleaved polymer. The acid exposure times correspond to the treatment with 10 wt.% TFOH in toluene. Besides the diminished aliphatic C-H stretching vibrations at $\approx 2900 \text{ cm}^{-1}$ also the characteristic deformation vibration for $\text{Si}(\text{CH}_3)_2$ at 1245 cm^{-1} diminishes until it overlaps with other signals.

10. DSC Curves

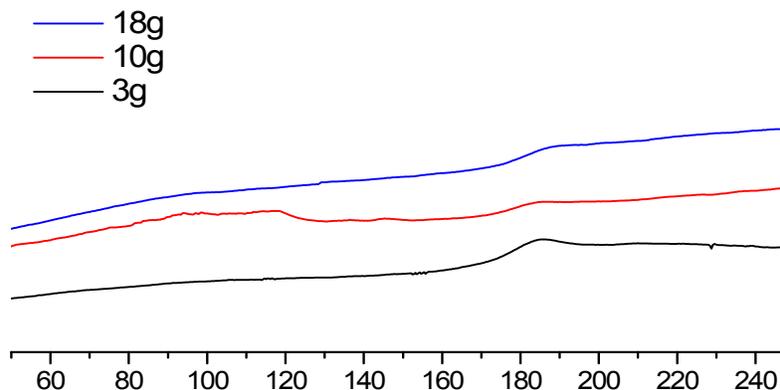


Figure S22 DSC curves of Polymer from Tabel1 entries 7a, 8b and 9b. The T_g is in a range between 173 °C and 183 °C.

11. MALDI-TOF of cyclic fraction

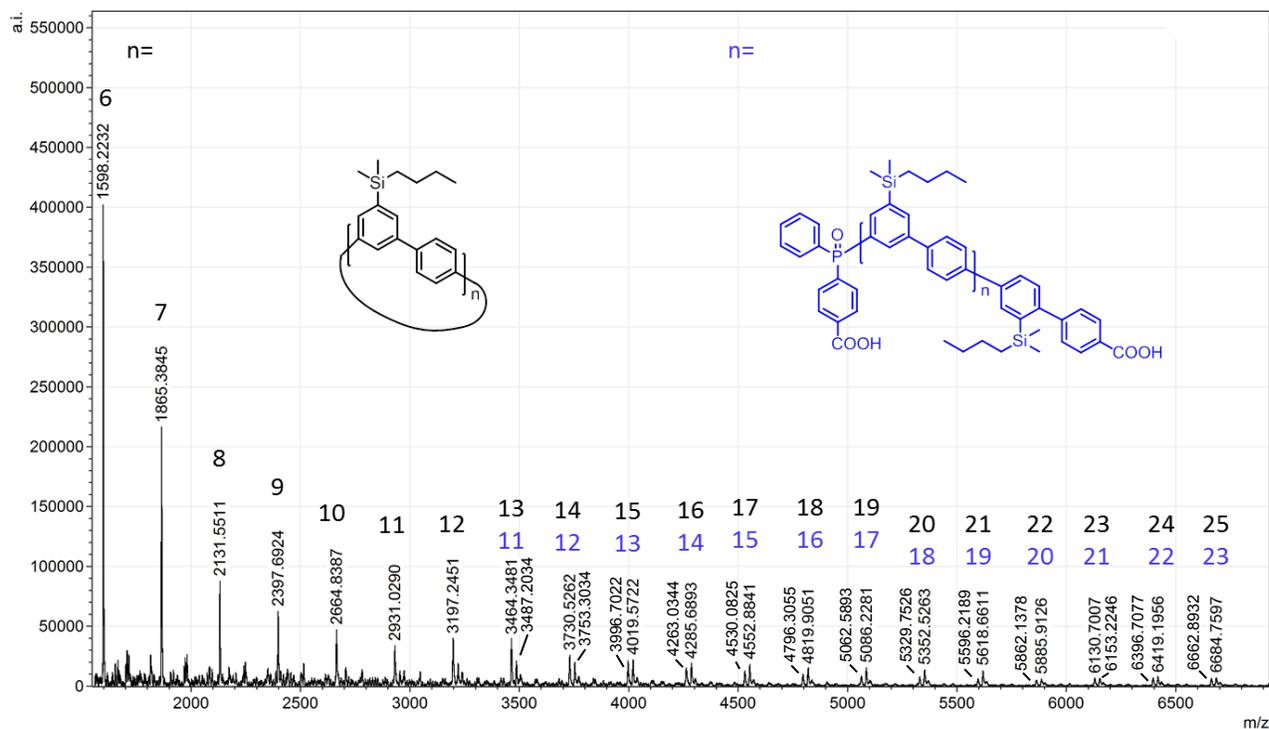


Figure S23 MALDI-TOF spectrum of the high retention Volume signal in GPC separated by Soxhlet extraction. The signals can be assigned to the macro cycle's mass ($266.4528n$) and a product of ligand scrambling ($266.4528n+556.6607$).

12. References

- 1 J. Li, H. Fu, P. Hu, Z. Zhang, X. Li and Y. Cheng, *Chemistry*, 2012, **18**, 13941–13944.