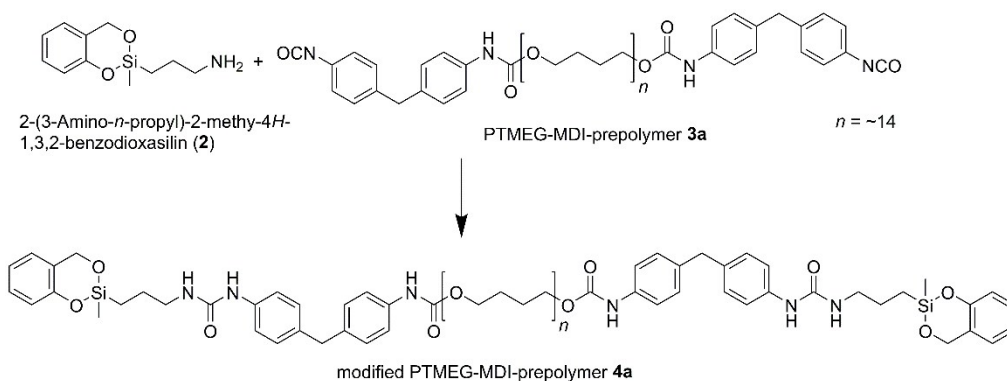# Design of nanostructured hybrid materials: twin polymerization of urethane-based twin prepolymer

D. Uhlig[a], S. Spange [a], A. Seifert[a], K. Nagel[a], S. Anders[b], L. Kroll[b], R. Stoll[c], F. Thielbeer[d], P. Müller[d] and K. Schreiter*[a]

**Supporting information**

Preparation of polyurethane twin-prepolymer **4a**:



**Scheme S1**: General reaction scheme for the preparation of twin prepolymer **4a** by end-capping of the isocyanate containing prepolymer **3a**. The reaction can be performed in solution or in situ directly after the preparation of **3a**.

In a three-necked flask with dropping funnel, internal thermometer and mechanical stirrer, 10.02 g (40.0 mmol) diphenylmethan-4,4′-diisocyanate (MDI) are placed and tempered at 50 °C. 18.0 g (18.0 mmol) polytetramethylene ether glycol (PTMEG; average molecular weight 1000 g/mol) were added to the molten MDI within 15 minutes. The reaction mixture was heated to 98 °C for 2 h. The dropping funnel was replaced by a septum. 9.88 g 2-(3-Amino-n-propyl)-2-methy-4H-1,3,2-benzodioxasilin (**2**) were slowly added through the septum to the prepolymer at 70 °C. The temperature was kept under 100 °C during the addition. Under minimized stirring rate the reaction mixture was stirred for 30 minutes at 70 °C.
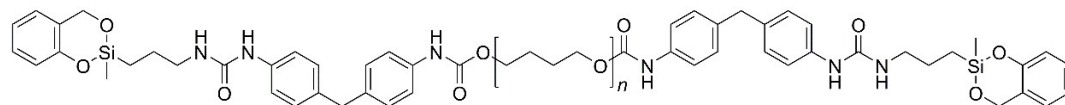


**$^1$H NMR (CDCl$_3$)**: $\delta$ [ppm] = 0.23 (s, 6H, Si-C$\underline{H}_3$), 0.70 (m, 4H, Si-C$\underline{H}_2$-), 1.46–1.73 (m (broad), O-CH$_2$-C$\underline{H}_2$- C$\underline{H}_2$-CH$_2$-O- (polymer); Si-CH$_2$-C$\underline{H}_2$-), 3.10 (m, 4H, C$\underline{H}_2$-NHCONH), 3.39 (s (broad), O-C$\underline{H}_2$-CH$_2$- CH$_2$-C$\underline{H}_2$-O- (polymer)), 3.85 (s, 4H, Ph-C$\underline{H}_2$-Ph), 4.14 (m, 4H, NHCO-O-C$\underline{H}_2$-), 4.87 (m, 4H, C$\underline{H}_2$-O-Si-), 6.80 (m, Ar-$\underline{H}$). **$^{13}$C {$^1$H} NMR (CDCl$_3$)**: $\delta$ [ppm] = −2.7 (Si-$\underline{C}$H$_3$), 12.6 ($\underline{C}$H$_2$-Si), 23.2 ($\underline{C}$H$_2$-CH$_2$-Si), 26.0/26.3/26.6 (-O-CH$_2$-$\underline{C}$H$_2$- $\underline{C}$H$_2$-CH$_2$-O- (polymer)), 40.0 (Ph-$\underline{C}$H$_2$-Ph), 42.2 (-NHCONH-$\underline{C}$H$_2$-), 63.8 ($\underline{C}$H$_2$-O-Si), 64.9 (NHCO-O-$\underline{C}$H$_2$-), 70.5 (-O-$\underline{C}$H$_2$-CH$_2$- CH$_2$-$\underline{C}$H$_2$-O- (polymer)), 119.3 (Ar-$\underline{C}$), 120.0 (Ar-$\underline{C}$), 121.2 (Ar-$\underline{C}$), 126.3 (Ar-$\underline{C}$), 127.0 (Ar-$\underline{C}$), 127.9 (Ar-$\underline{C}$), 129.1 (Ar-$\underline{C}$), 129.5 (Ar-$\underline{C}$), 129.7 (Ar-$\underline{C}$), 136.2 (Ar-$\underline{C}$), 153.1 (CH-$\underline{C}$-O-Si), 154.0 (NH$\underline{C}$O-O-), 156.4 (-NH$\underline{C}$ONH-). **$^{29}$Si NMR (CDCl$_3$)**: $\delta$ [ppm] = 3.05 (D$_0$).

Preparation of polyurethane twin prepolymer **4b**:

The procedure described above was applied for the preparation and modification of **3b**. Following quantities were used:

- 10.46 g MDI (41.8 mmol)
- 19.0 g polypropylene ether glycol (PPG; average molecular weight 1000 g/mol)
- 9.65 g **2**
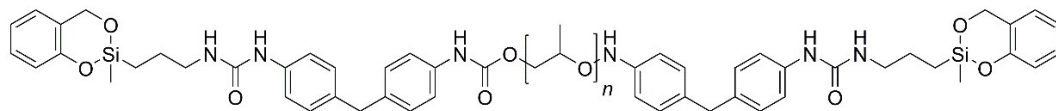


**¹H NMR (CDCl₃)**: $\delta$ [ppm] = 0.24 (s, 6H, Si-C$\underline{H}_3$), 0.71 (m, 4H, Si-C$\underline{H}_2$-), 1.11 (s, O-CH$_2$-CH(C$\underline{H}_3$)-O-, polyol), 1.55 (m, 4H, Si-CH$_2$-C$\underline{H}_2$-), 3.11 (m, 4H, C$\underline{H}_2$-NHCONH-), 3.38–3.53 (O-C$\underline{H}_2$-C$\underline{H}$(CH$_3$)-O-, polyol), 4.85 (m, 4H, C$\underline{H}_2$-O-Si-), 6.83–7.38 (Ar-$\underline{H}$). **¹³C {¹H} NMR (CDCl₃)**: $\delta$ [ppm] = −3.0 (Si-$\underline{C}$H$_3$), 12.42 ($\underline{C}$H$_2$-Si), 17.2 (-CH-$\underline{C}$H$_3$), 23.1 ($\underline{C}$H$_2$-CH$_2$-Si), 40.5 (Ph-$\underline{C}$H$_2$-Ph), 42.1 (-NHCONH-$\underline{C}$H$_2$-), 63.8 ($\underline{C}$H$_2$-O-Si), 64.0 (NHCO-O-$\underline{C}$H$_2$-), 71.7–75.5 (-O-$\underline{C}$H(CH$_3$)-$\underline{C}$H$_2$-O-), 119.1 (Ar-$\underline{C}$), 119.9 (Ar-$\underline{C}$), 120.9 (Ar-$\underline{C}$), 126.1 (Ar-$\underline{C}$), 126.9 (Ar-$\underline{C}$), 128.8 (Ar-$\underline{C}$), 129.2, 135.4, 136.1, 137.2, 153.0/153.4 (NH$\underline{C}$O-O-), 156.4/156.5 (-NH$\underline{C}$ONH-)**²⁹Si NMR (CDCl₃)**: $\delta$ [ppm] = 2.97 (D$_0$).

Preparation of polyurethane twin-prepolymer **4c**:

In a three-necked flask with dropping funnel, internal thermometer and mechanical stirrer, 4.94 g (22.23 mmol) isophoronediisocyanate (IPDI) are placed and tempered at 50 °C. 10.71 g (10.71 mmol) PTMEG were added to the diisocyanate within 5 minutes. After complete addition of the polyol, 0.01 mL dibutyltin dilaurate (Merck) was added to the reaction mixture and a slight temperature increase was observed (65 °C). After the reaction mixture cooled down to 50 °C, the reaction mixture was heated to 98 °C for 2 h. The dropping funnel was replaced by a septum. 5.14 g (23.05 mmol) **2** were slowly added with a syringe through the septum to the prepolymer at 70 °C. The temperature was kept under 100 °C during the addition. Under minimized stirring rate the reaction mixture was stirred for 30 minutes at 70 °C.
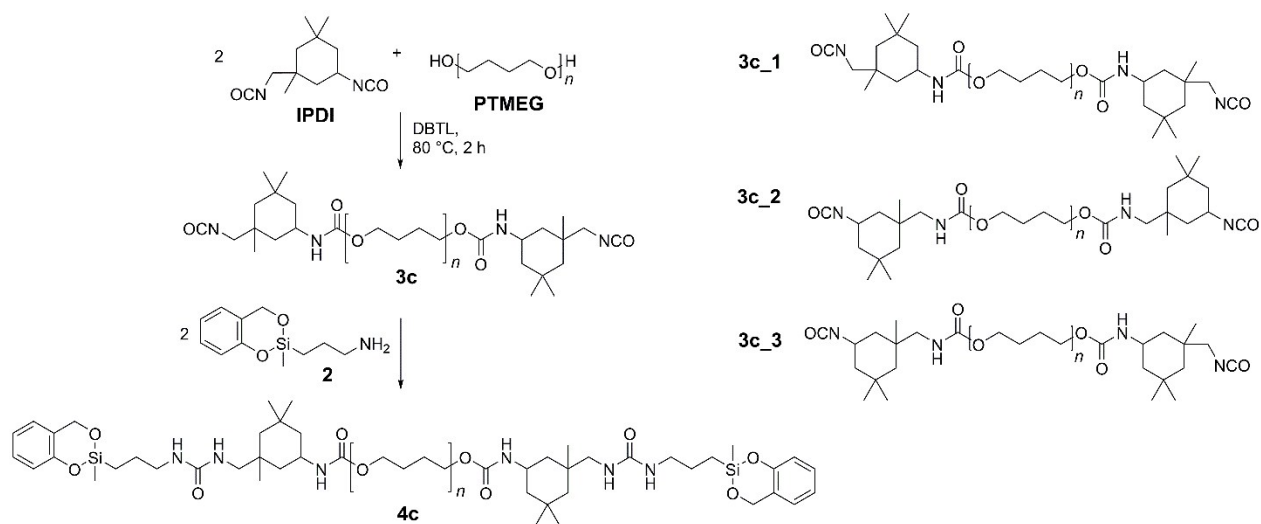


**Scheme S2**: Simplified reaction scheme for the preparation of the prepolymer **4c**. The prepolymer **3c**, and thus the prepolymer **4c** principally consists of different possible constitutional isomers (illustrated in structures **3c_1 – 3c_3**). The different *cis-* and *trans-* isomers of the cyclohexyl-increments are not considered in this scheme.
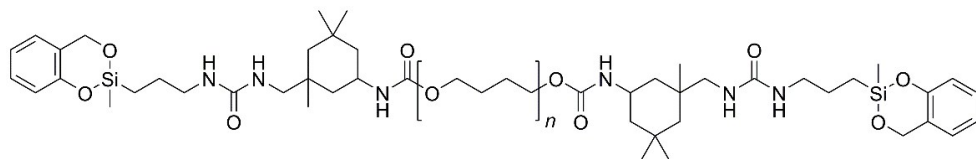
**¹H NMR (CDCl₃)**: δ [ppm] = 0.23 (s, 6H, Si-C$\underline{H}_3$), 0.70 (m, 4H, Si-C$\underline{H}_2$-),0.84 (C$\underline{H}_3$ IPDI), 0.95/0.97 (C$\underline{H}_3$ IPDI) 1.56 (m (broad), O-CH₂-C$\underline{H}_2$- C$\underline{H}_2$-CH₂-O- (polymer); Si-CH₂-C$\underline{H}_2$-), 2.82 (2H, -C$\underline{H}$NH-), 3.07 (m, 4H, C$\underline{H}_2$-NHCONH), 3.35 (s (broad), O-C$\underline{H}_2$-CH₂- CH₂-CH₂-O-(polymer)), 3.97 (m, 4H, NHCO-O-C$\underline{H}_2$-), 4.84 (m, 4H, C$\underline{H}_2$-O-Si-), 6.82 (m, Ar-$\underline{H}$), 7.08 (m, Ar-$\underline{H}$). **¹³C {¹H} NMR (CDCl₃)**: δ [ppm] = −3.2 (Si-$\underline{C}$H₃), 12.0 ($\underline{C}$H₂-Si), 23.2 ($\underline{C}$H₂-CH₂-Si), 26.1 (-O-CH₂-$\underline{C}$H₂- CH₂-CH₂-O- (polymer)), 42.1 (-NHCONH-$\underline{C}$H₂-), 53.6, 63.4 ($\underline{C}$H₂-O-Si), 64.0 (NHCO-O-$\underline{C}$H₂-), 70.1 (-O-$\underline{C}$H₂-CH₂- CH₂-$\underline{C}$H₂-O- (polymer)), 119.0 (Ar-$\underline{C}$), 118.3 (Ar-$\underline{C}$), 120.8 (Ar-$\underline{C}$), 125.9 (Ar-$\underline{C}$), 126.7 (Ar-$\underline{C}$), 128.7 (Ar-$\underline{C}$), 152.9/156.0 (NH$\underline{C}$O-O-), 158.9 (-NH$\underline{C}$ONH-). **²⁹Si NMR (CDCl₃)**: δ [ppm] = 2.89 (D₀).
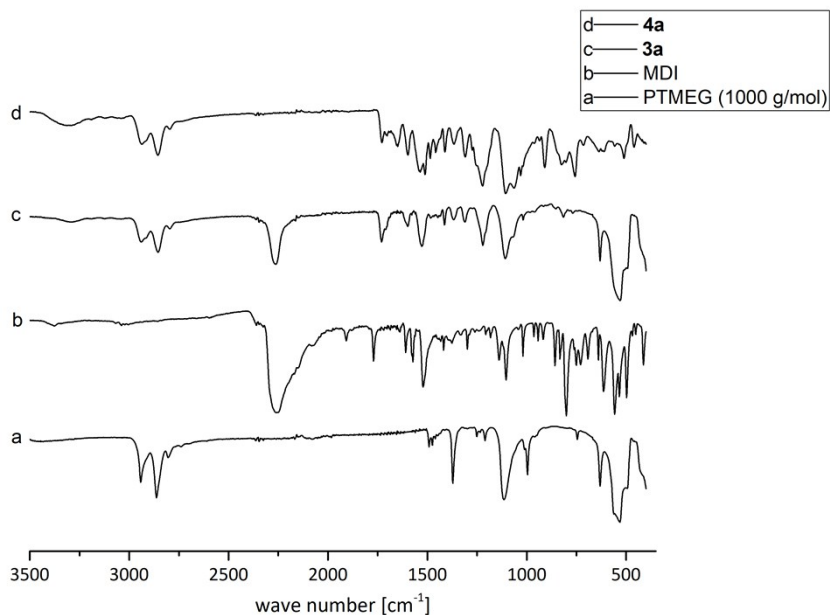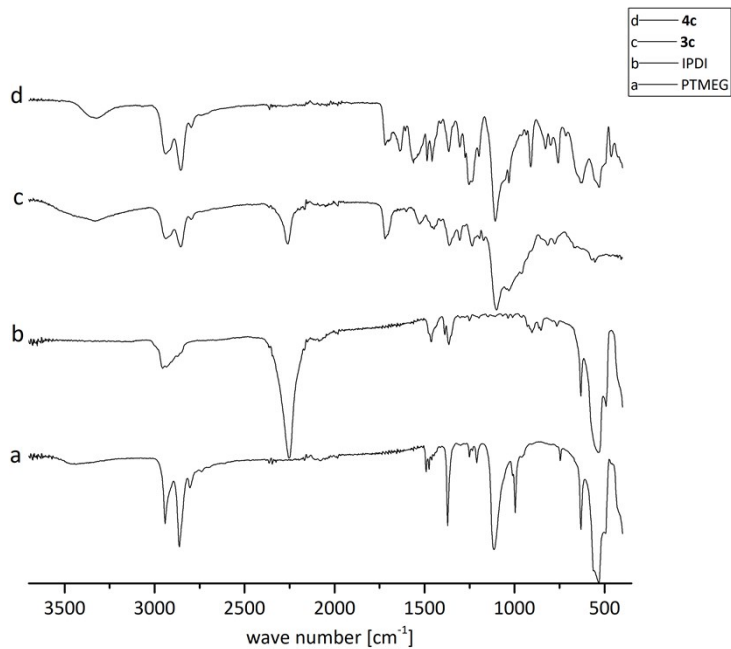
**Figure S1**: ATR-FTIR-spectra of the components for the prepolymer preparation (**a**: PTMEG; **b**: MDI), the resulting prepolymer (**3a**) and the product **4a**. The characteristic signal of the asymmetric NCO-stretching vibration at around 2300 cm$^{-1}$ vanishes due to the complete reaction with **2** between spectrum **c** and **d**.
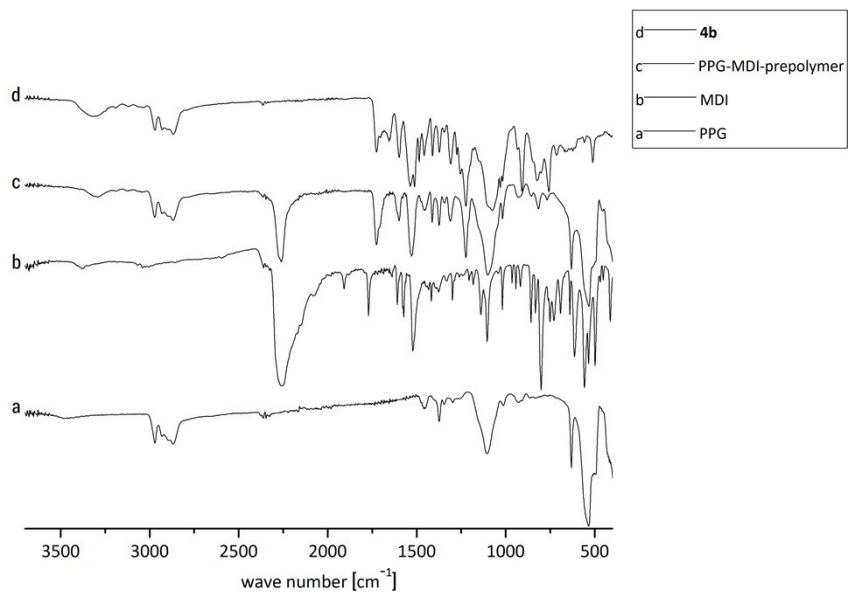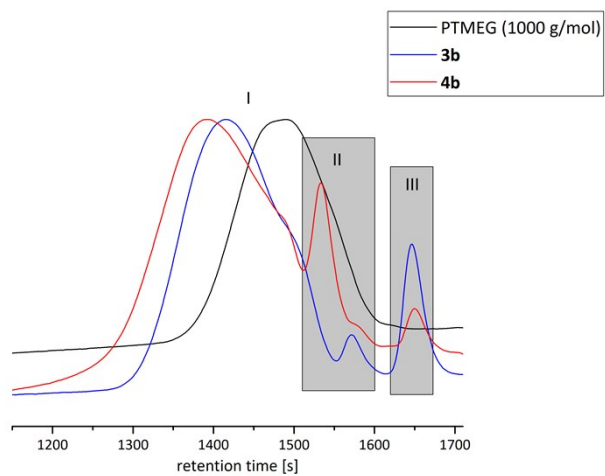


**Figure S2**: ATR-FTIR-spectra of the corresponding educts, as well as a sample of the reaction mixture (PPG-MDI-prepolymer **3b**) and the resulting twin prepolymer **4b**.

**Figure S3**: ATR-FTIR-spectra of the corresponding educts, as well as a sample of the reaction mixture (IPDI-PTMEG-prepolymer **3c**) and the resulting twin prepolymer **4c**.

SEC-measurements of **4a** and **4b**:

Prepolymer **4a**:



**Figure S4**: SEC-traces of the different stages of the in situ-preparation of twin prepolymer **4a**. The increase of the mass can be detected. Low molecular by-products are present due to the required excess of diisocyanate for the formation of the prepolymer.

**Table S1**: SEC-values of the different samples at the in situ preparation of **4a**.

| Sample | Signal | $M_n$ | PDI |
|---|---|---|---|
| PTMEG (1000 g/mol) | I | 1550 | 1.6 |
| **3a** | I | 3370 | 1.7 |
| | II | 530 | 1.03 |
| | III | 184 | 1.03 |
| **4a** | I | 4710 | 1.9 |
| | II | 860 | 1.06 |
| | III | 180 | 1.02 |

Signal III is assigned as MDI (MW 250.26 g/mol). Signal II can be interpreted as MDI-dimer which formed through hydrolysis of MDI and subsequent reaction with MDI. Signal II can be interpreted as adduct of **2** and MDI (2n **2** and n MDI 695.28 g/mol). Signal III can be assigned as unreacted MDI or **2**. The SEC-trace does not give information about the quantitative amount of those by-products. As no free isocyanate can be detected by ATR-FTIR-measurement, the amount of unreacted MDI is comparatively low (less than 1%).

Prepolymer **4b**:
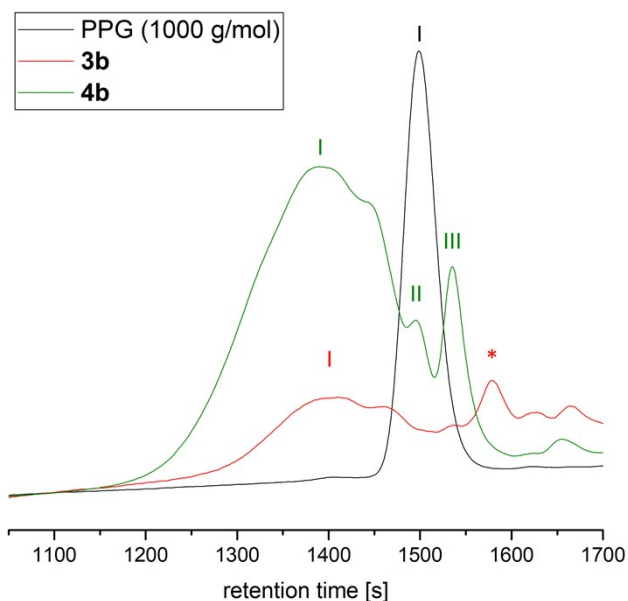


**Figure S5**: SEC-traces of PPG, PPG-MDI-prepolymer **3b** and **4b**.

Table S2: Determined SEC-values of PPG, PPG-MDI-prepolymer **3b** and **4b**.

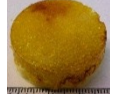| Sample | Signal | $M_n$ | PDI |
|---|---|---|---|
| PPG (1000 g/mol) | I | 1480 | 1.06 |
| **3b** | I | 5310 | 1.52 |
| | * | Outside the calibration range | |
| **4b** | I | 5160 | 2.26 |
| | II | 1590 | 1.01 |
| | III | 880 | 1.04 |

Polymerizations:

STP of **4a** with **1**:

Thermal induced STP of modified prepolymer **4a** with 2,2`-spirobi[4H-1,3,2-benzodioxasilin] (**1**):

Example with a molar ratio of **4a** : **1** of **85** : **15**. The reaction temperature was determined by DSC-measurement, whereas attempts with different reaction temperatures were also made.

In a 10 mL PTFE-wide-neck-flask with screw-cap and magnetic stirrer 1.14 g (0.58 mmol) of **4a** and 0.028 g (0.10 mmol) **1** are placed under argon. Under stirring, the flask was heated to 125 °C for 0.5 h. The magnetic stirrer was removed out of the slightly yellow reaction mixture. The reaction-flask was heated to 170 °C for 2 h. The obtained material were cut into small pieces with a scalpel for purification by extraction with dichloromethane for 48 h. The extracted material was dried in a vacuum oven at 40 °C to a constant mass.
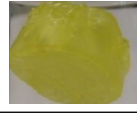
**Table S3**: Parameters for the polymerization of mixtures consisting of equimolar amounts **1** and **4a** at different reaction temperatures. Every sample was polymerized for 2 h. The calculated amount of silica for the equimolar mixture is 8.1 wt%.

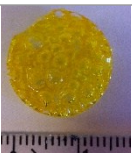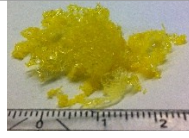| Sample | T [°C] | t [h] | extr. content [wt%] | silica content [wt%] (TGA) | |
|---|---|---|---|---|---|
| **HM5a_170** | 170 | 2 | 47 | 11 | |
| **HM5a_190** | 190 | 2 | 47 | 11 | |
| **HM5a_210** | 210 | 2 | 35 | 9 | |
| **HM5a_230** | 230 | 2 | 36 | 11 | |

STP of **4a** with **1** (varying monomer amounts):

**Table S4**: Monomer amounts, extractable contents, silica content (TGA) and images of the corresponding hybrid materials.

| Ratio 1 – 4a | | Name | Extractable content [wt%] | Silica [wt%] (TGA, extracted material) | Silica [wt%] (calculated) | |
|---|---|---|---|---|---|---|
| 95 | 5 | **HM5a_05** | 21 | 21 | 18 | |

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| | | | | | | |
|---|---|---|---|---|---|---|
| 85 | 15 | HM5a_15 | 33 | 19 | 13 |  |
| 50 | 50 | HM5a_50 | 47 | 11 | 8 |  |
| 15 | 85 | HM5a_85 | 25 | 6 | 7 |  |
| 0 | 100 | HM5a_100 | 14 | 6 | 6 |  |

**Table S5**: Polymerization of mixtures consisting of equimolar amounts **1** and **4b** at different temperatures for a time of 2 h.

| Name | T [°C] | extr. content [wt%] | silica content [wt%] (TGA) | |
|---|---|---|---|---|
| HM5b_170 | 170 | 84 | — |  |
| HM5b_190 | 190 | 49 | 11 |  |
| HM5b_210 | 210 | 33 | 12 |  |
| HM5b_230 | 230 | 45 | 9 |  |

**Table S6**: Extractable content for the samples with different monomer amounts of **1** and **4b** prepared at 190 °C for 2 h. The calculated silica content is 8.1 wt%. **4b** didn´t show s notable polymerization behavior at those conditions (sample **HM5b_100**). Therefore, **4b** was polymerized at 200 °C for 2 h (Sample **HM5b_100_200**).

| Ratio 1 : 4b | | Name | Extractable content [wt%] | Silica (TGA, extracted material) [wt%] | Silica (calculated) [wt%] | |
|---|---|---|---|---|---|---|
| 85 | 15 | HM5b_15 | 31 | 18 | 13 |  |
| 50 | 50 | HM5b_50 | 49 | 11 | 8 |  |
| 15 | 85 | HM5b_85 | 41 | 6 | 7 |  |
| 0 | 100 | HM5b_100 | 85 | 4 | 6 |  |
| 0 | 100 | HM5b_100_200 | 52 | 5 | 6 |  |

Polymerization of **4c**:

The procedure for the polymerization were kept consistent to the attempts described above. **4c** was polymerized alone at 170 °C for 2 h.

Solid-state-NMR investigations of the obtained, extracted hybrid materials:
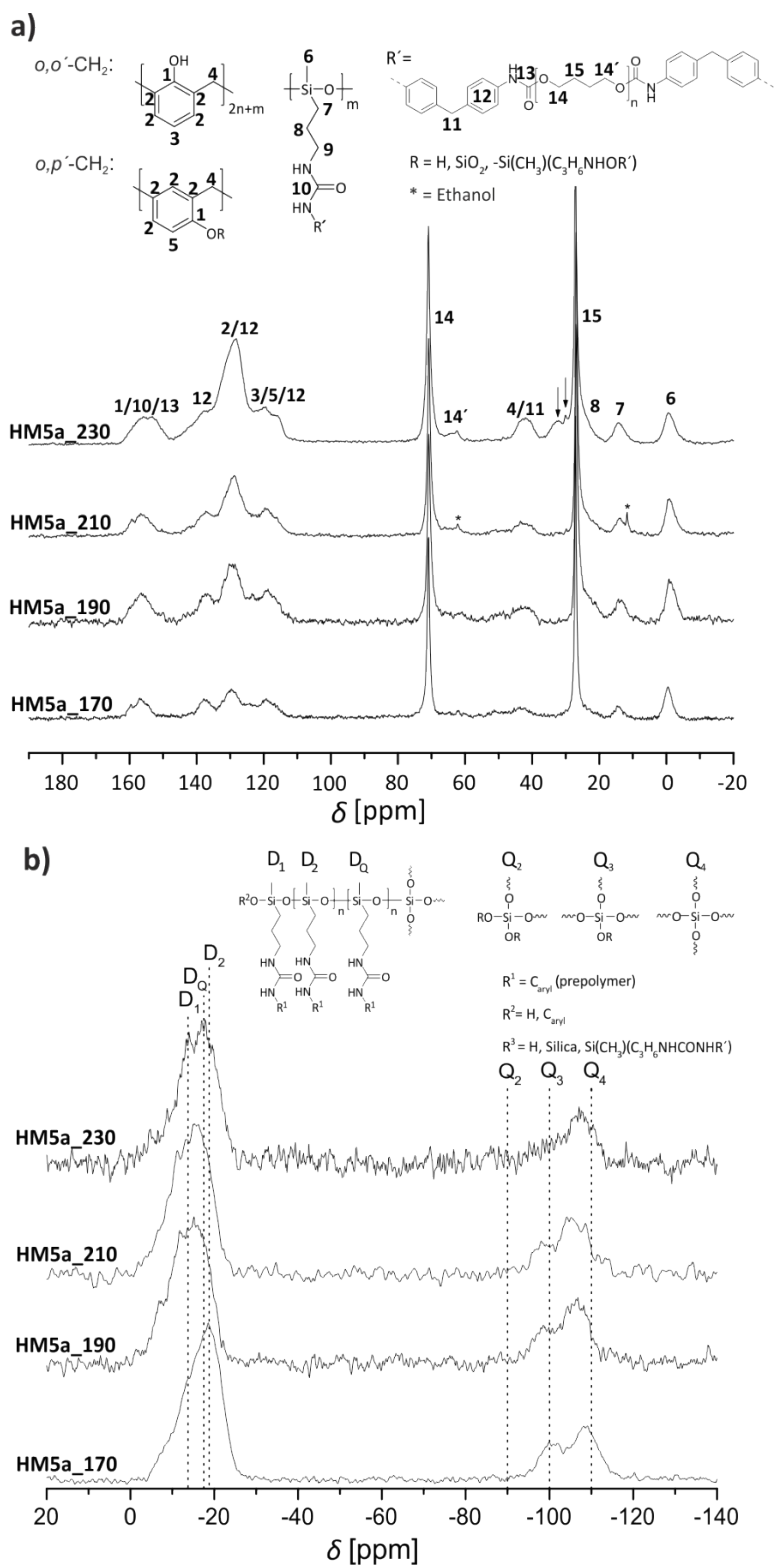


**Figure S6**: Solid-state-NMR spectra of the samples prepared with equimolar monomer amounts (prepolymer **4a** with **1**) at varied reaction conditions: (**a**) $^{13}$C-{$^1$H}-CP-MAS (Number of scans: **HM5a_170** 14077; **HM5a_190** 3799; **HM5a_210** 15568; **HM5a_230** 25700). (**b**) $^{29}$Si-{$^1$H}-CP-MAS-NMR (Number of scans: **HM5a_170** 62126; **HM5a_190** 10054; **HM5a_210** 11505; **HM5a_230** 9174).

Investigation of the extracts:

SEC:
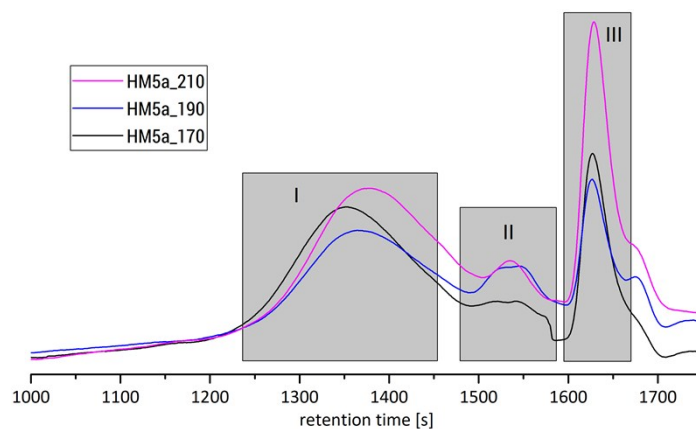


**Figure S7**: SEC-traces of the THF-soluble part of the extracts obtained by extraction with dichloromethane for 48 h of the samples **HM5a_170–190**.

**Table S7**: SEC-values of the THF-soluble parts of the extracts obtained by extraction with dichloromethane for 48 h.

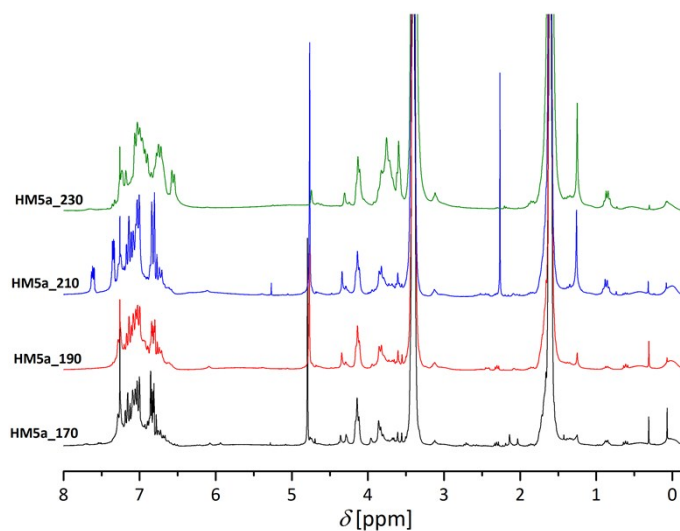| Sample | Signal | $M_n$ | PDI |
|---|---|---|---|
| HM5a_170 | I | 9500 | 1.7 |
| | II | 810 | 1.09 |
| | III | 218 | 1.06 |
| HM5a_190 | I | 8400 | 1.6 |
| | II | 900 | 1.06 |
| | III | 230 | 1.03 |
| HM5a_210 | I | 7300 | 1.6 |
| | II | 880 | 1.04 |
| | III | 210 | 1.09 |
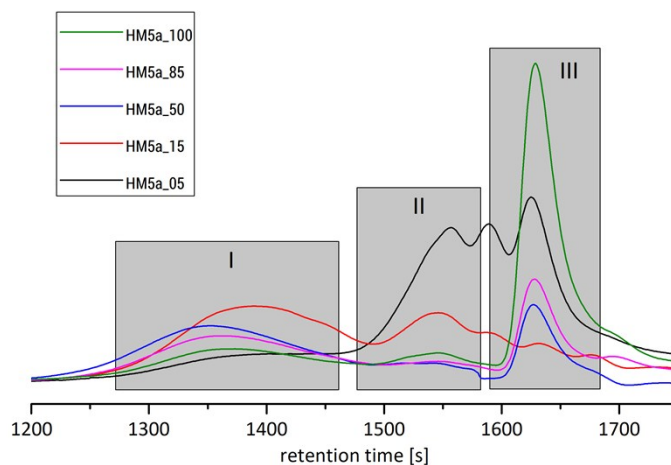


**Figure S8**: SEC-traces of the extractable parts of the samples prepared with different monomer ratios.

**Table S8**: Determined SEC-values.

| Sample | Signal | $M_n$ | PDI |
|---|---|---|---|
| HM5a_100 | I | 9300 | 1.32 |

| | | | | |
|---|---|---|---|---|
| | II | 830 | 1.08 |
| | III | 198 | 1.11 |
| **HM5a_85** | I | 8400 | 1.63 |
| | II | 790 | 1.06 |
| | III | 220 | 1.06 |
| **HM5a_50** | I | 9500 | 1.7 |
| | II | 810 | 1.09 |
| | III | 218 | 1.08 |
| **HM5a_15** | I | 6900 | 1.47 |
| | II | 860 | 1.05 |
| | III | 237 | 1.0 |
| **HM5a_05** | I | 8800 | 1.30 |
| | II | 420 | 1.01 |
| | III | 245 | 1.03 |

<u>$^1$H-NMR:</u>



**Figure S9**: $^1$H-NMR spectra of the extracts of the samples prepared at different conditions. Characteristic signals due to the polyether polyol-component (around 1.6 ppm and 3.4 ppm) and salicylic alcohol (CH$_2$-group at 4.8 ppm) identifiable. The extract of the sample prepared at 230 °C showed no signal due to salicylic alcohol at 4.8 ppm.
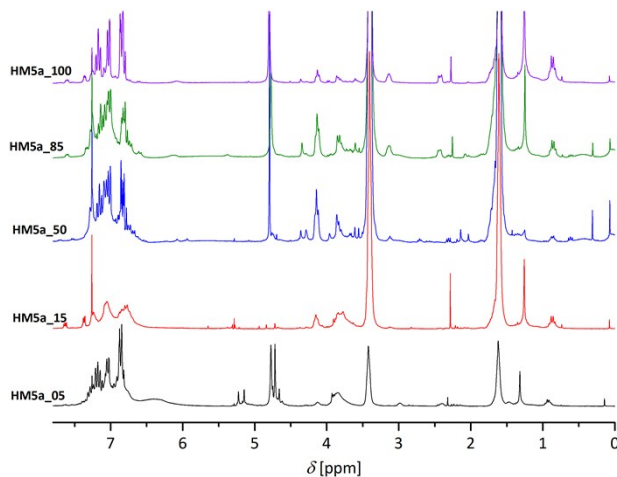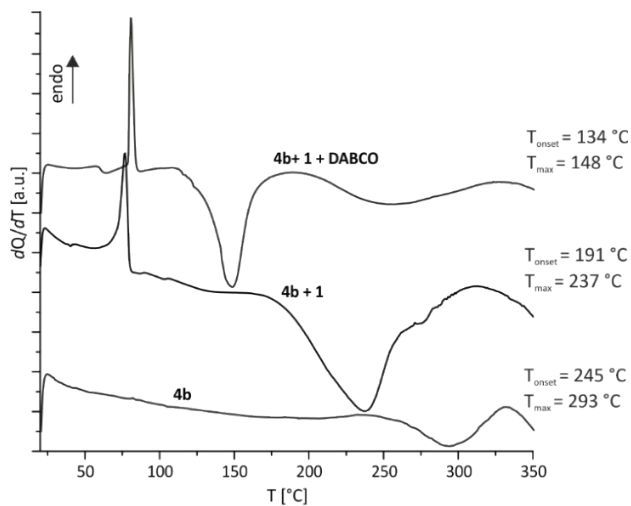
**Figure S10**: ${}^{1}$H-NMR spectra of the extracts of the samples prepared at different monomer amounts. Characteristic signals due to the polyether polyol-component (around 1.6 ppm and 3.4 ppm) and salicylic alcohol (CH$_2$-group at 4.8 ppm) are identifiable.
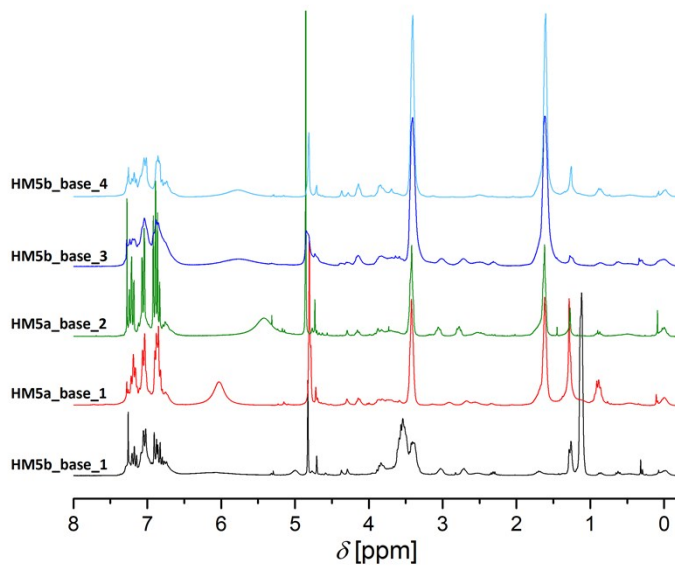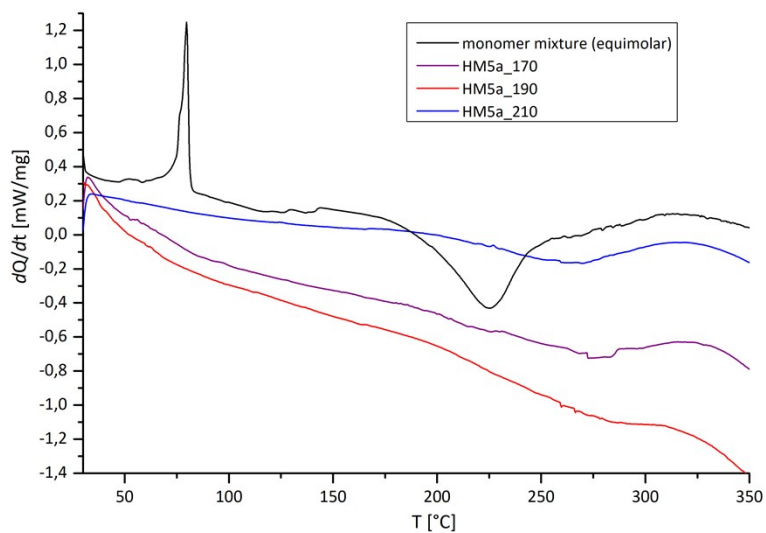


**Figure S11**: ${}^{1}$H-NMR spectra of the extracts of the materials prepared by base catalyzed STP.

## DSC-measurements:



**Figure S12**: DSC-curves of **4b**, the equimolar mixture of **4b** and **1** and the equimolar mixture with 1.0 wt% DABCO. The onset of the exothermic heat flow indicates the beginning of the polymerization.
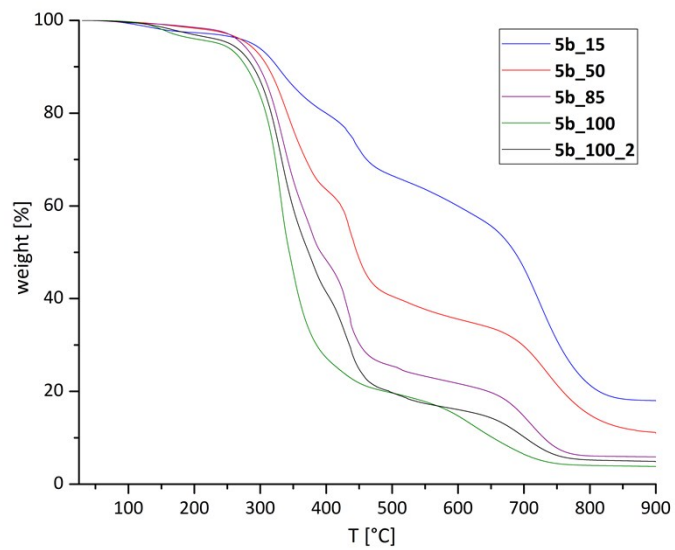
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**Figure S13**: DSC-curves of the unextracted samples with equimolar monomer amounts (**4a** and **1**) prepared at different conditions in comparison with the unpolymerized mixture.
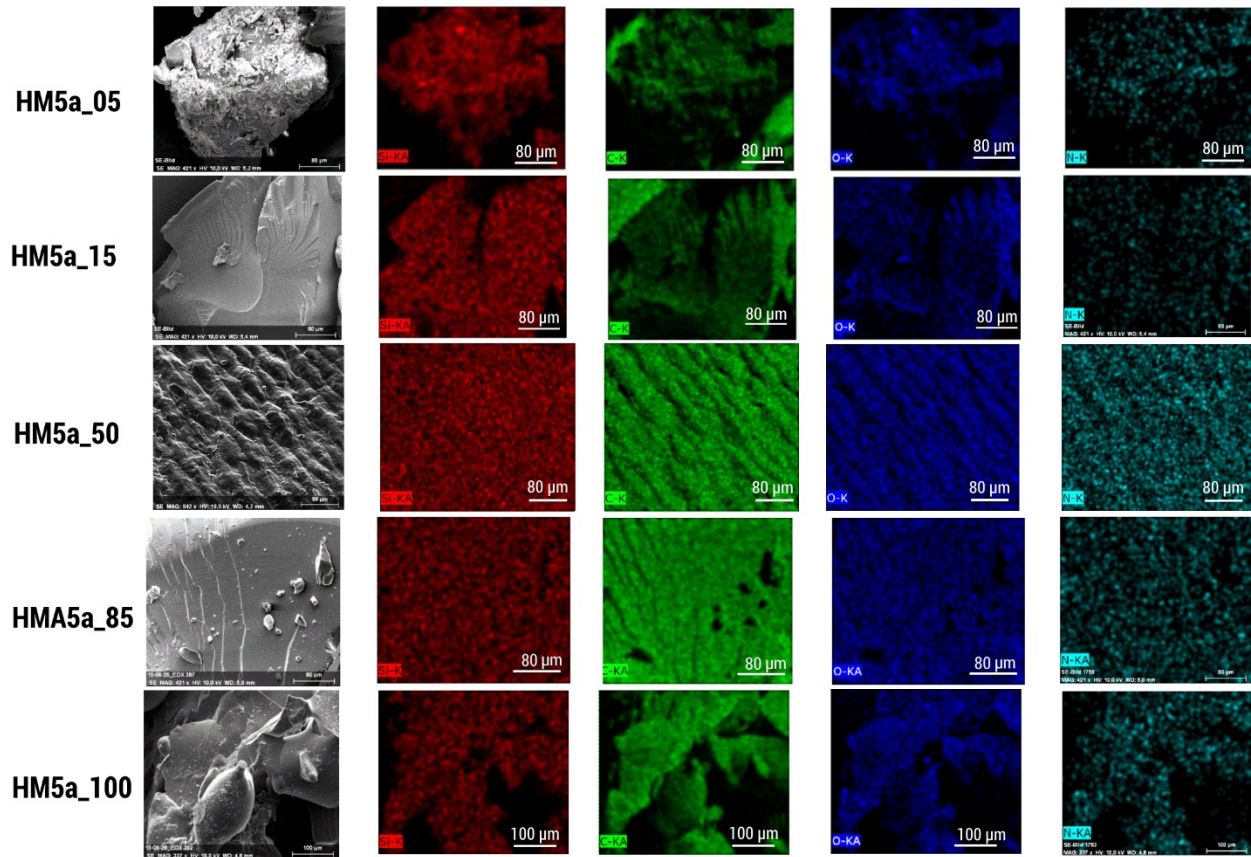
## TGA-measurements:
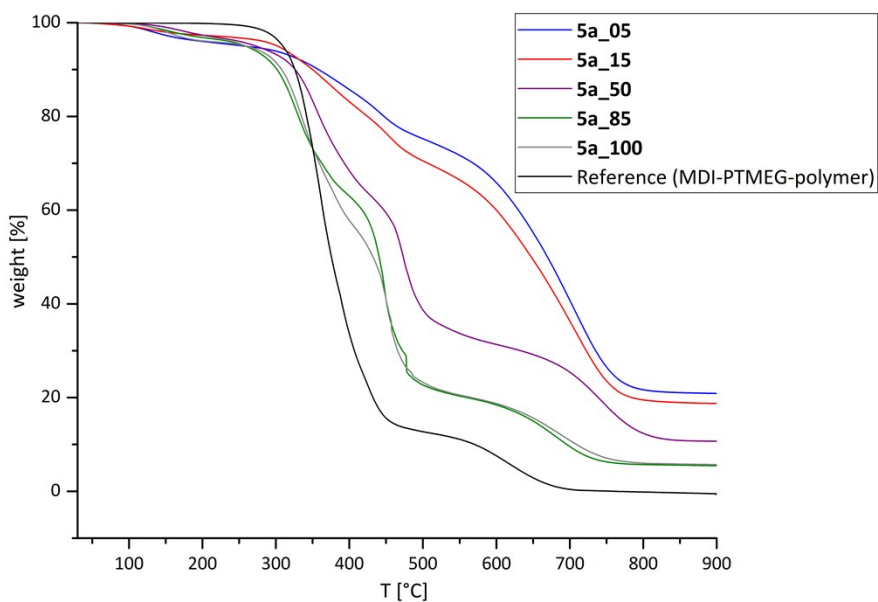


**Figure S14**: TGA-traces of the samples with different monomer amounts polymerized at 170 °C for 2 h.

**Figure 15**: TGA-traces of the samples with different monomer amounts (**4b** and **1**) polymerized at 190 °C for 2 h (except **5b_100_2** at 200 °C for 2 h).

SEM/EDX-measurement:



**Figure S16**: SEM- and EDX-images of the samples prepared with different monomer amounts. Explanation of the EDX-coloration: Si-red; Carbon-green; Oxygen-blue; Nitrogen-cyan.


Elemental analysis:

**Table 9**: Elemental analysis of the extracted hybrid materials prepared from **4a** and **1**.

| Sample | C [%] | H [%] | N [%] | C/N |
|--------|-------|-------|-------|-----|
| HM5a_05 | 58.14 | 5.63 | 1.40 | 41.52 |
| HM5a_15 | 59.56 | 6.30 | 2.63 | 22.69 |
| HM5a_50 | 61.78 | 8.00 | 4.45 | 13.88 |
| HM5a_85 | 64.03 | 8.59 | 4.56 | 14.04 |
| HM5a_100 | 64.10 | 8.60 | 4.20 | 15.24 |


**Table 10**: Elemental analysis of the extracted hybrid materials prepared from **4b** and **1**.

| Sample | C [%] | H [%] | N [%] | C/N |
|--------|-------|-------|-------|-----|
| HM5b_15 | 57.62 | 6.30 | 3.13 | 18.41 |
| HM5b_50 | 61.42 | 7.16 | 4.64 | 13.24 |
| HM5b_85 | 62.36 | 7.75 | 5.19 | 12.00 |
| HM5b_100 | 63.47 | 7.64 | 6.11 | 10.38 |
| HM5b_100_2 | 62.10 | 7.97 | 5.17 | 12.01 |

TG-MS-measurement of an equimolar mixture of **4a** and **1**:
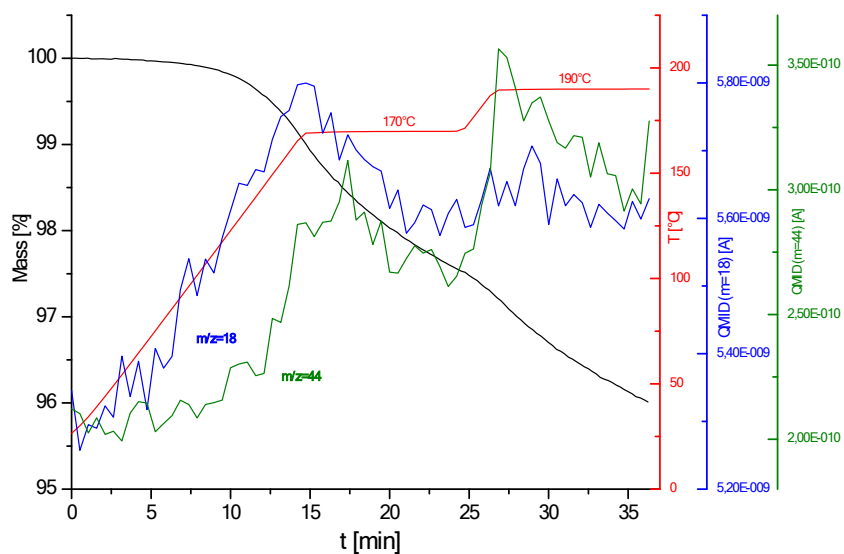


**Figure S17**: TG-MS measurement of the equimolar reaction mixture shows the release of water (m/z=18; blue line) with subsequent carbon dioxide release (m/z=44, green line). This result explains the slight foaming of the reaction mixture at the polymerization process.

## IR-measurement of different HMs (5a) and their corresponding educts
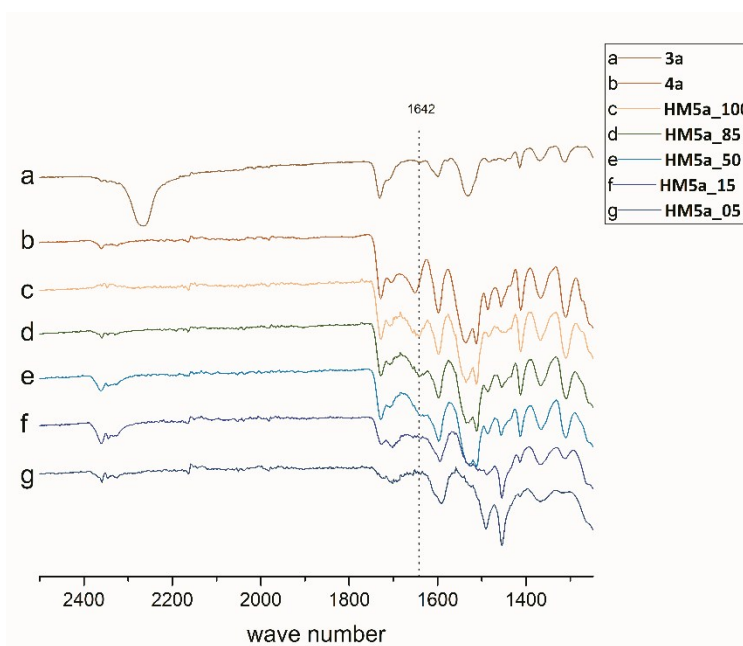


**Figure S18**: IR-spectra of the HMs derived from **4a** with different monomer amounts as well as their corresponding educts **3a** and **4a**.