Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Platinum Free Thermally Curable Siloxanes for Optoelectronic Application – Synthesis and Properties

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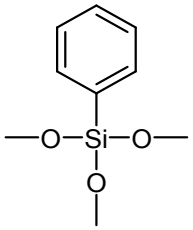
NMR spectroscopy

Phenyltrimethoxysilane



δ_H (400 MHz, $CDCl_3$): 7.71 – 7.34 (5 H, m, Si-Ph), 3.64 (9 H, s, Si-OCH_3)

δ_{Si} (80 MHz, $CDCl_3$): -54.49

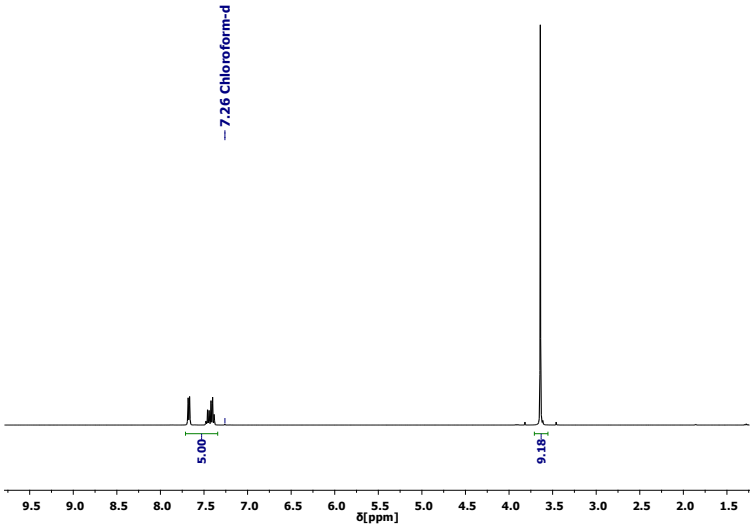


Figure ESI 1. ^{1}H NMR spectrum of phenyltrimethoxysilane monomer.

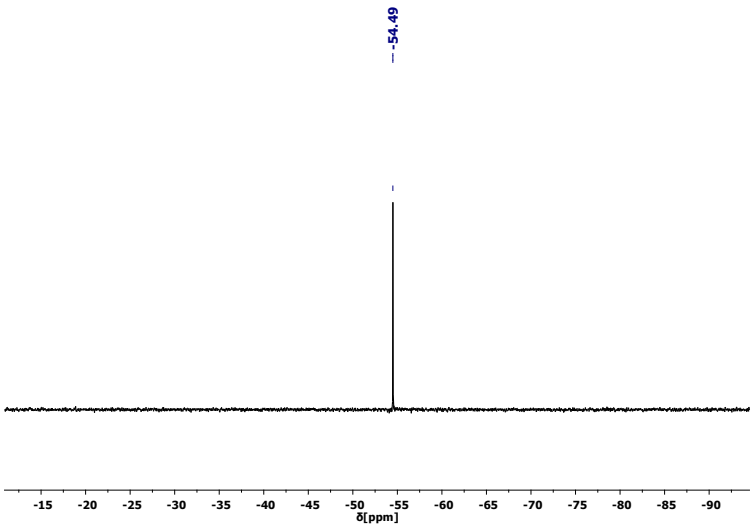
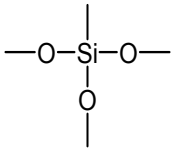


Figure ESI 2. ^{29}Si NMR spectrum of phenyltrimethoxysilane monomer.

Methyltrimethoxysilane



δ_H (300 MHz, $CDCl_3$): 3.50 (9 H, s, Si-OCH_3), 0.06 (3 H, s, Si-CH_3)

δ_{Si} (60 MHz, $CDCl_3$): -39.17

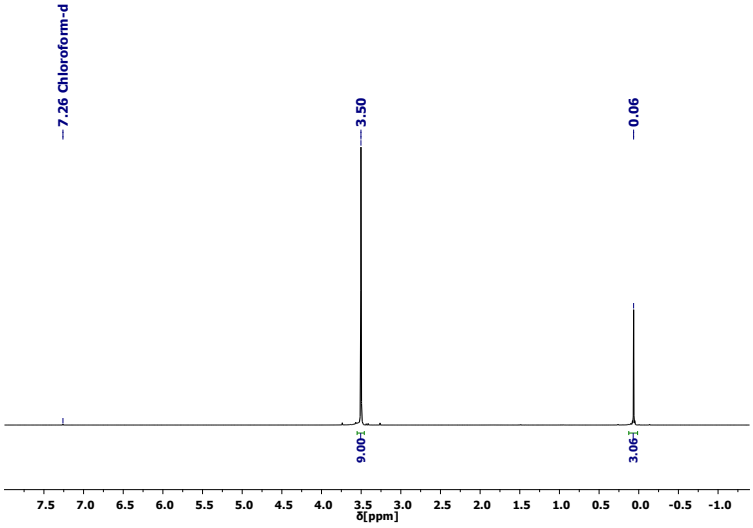


Figure ESI 3. ^{1}H NMR spectrum of methyltrimethoxysilane monomer.

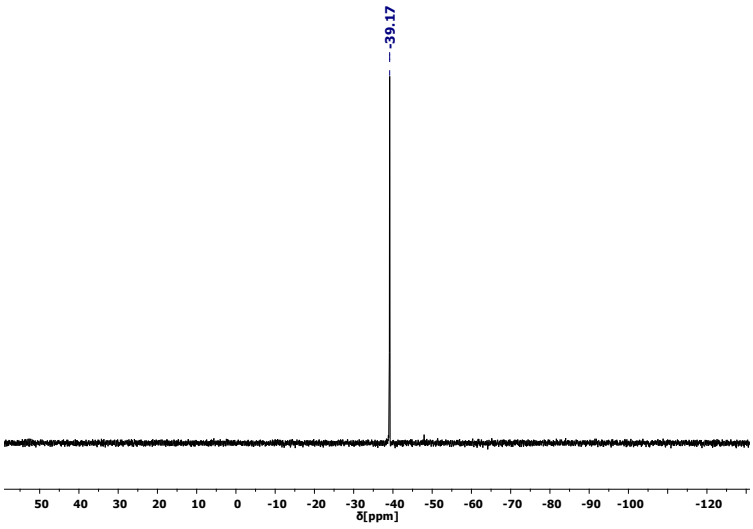
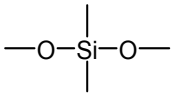


Figure ESI 4. ^{29}Si NMR spectrum of methyltrimethoxysilane monomer.

Dimethyldimethoxysilane



δ_H (400 MHz, $CDCl_3$): 3.39 (6 H, s, Si-OCH_3), 0.00 (6 H, s, Si-CH_3)

δ_{Si} (60 MHz, $CDCl_3$): -0.31

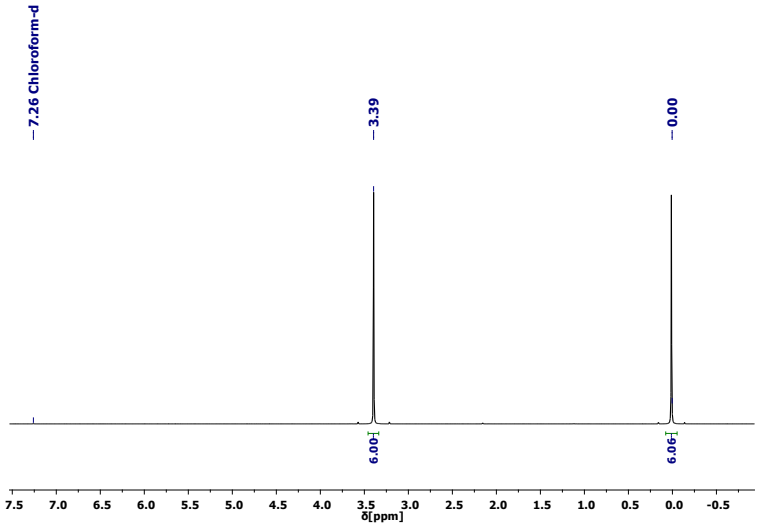


Figure ESI 5. ^{1}H NMR spectrum of dimethyldimethoxysilane monomer.

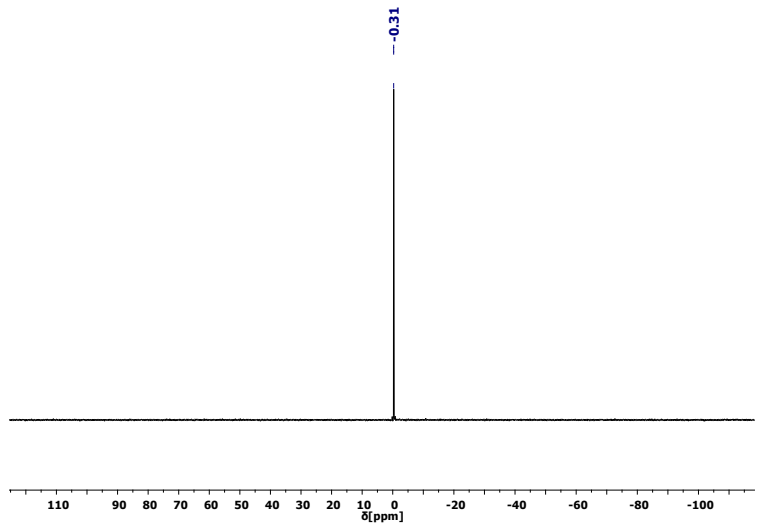
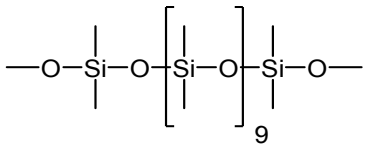


Figure ESI 6. ^{29}Si NMR spectrum of dimethyldimethoxysilane monomer.

Methoxy terminated Polydimethylsiloxane



δ_H (300 MHz, $CDCl_3$): 3.45 (6 H, s, Si-OCH_3), 0.20 – -0.01 (65 H, m, Si-CH_3)

δ_{Si} (60 MHz, $CDCl_3$): -10.18 – -11.31 (m), -20.76 – -22.21 (m)

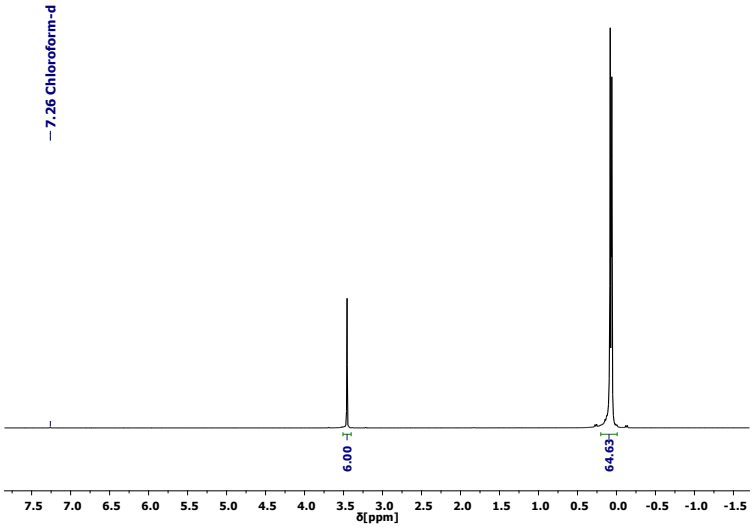


Figure ESI 7. ^{1}H NMR spectrum of methoxy-terminated polydimethylsiloxane oligomer.

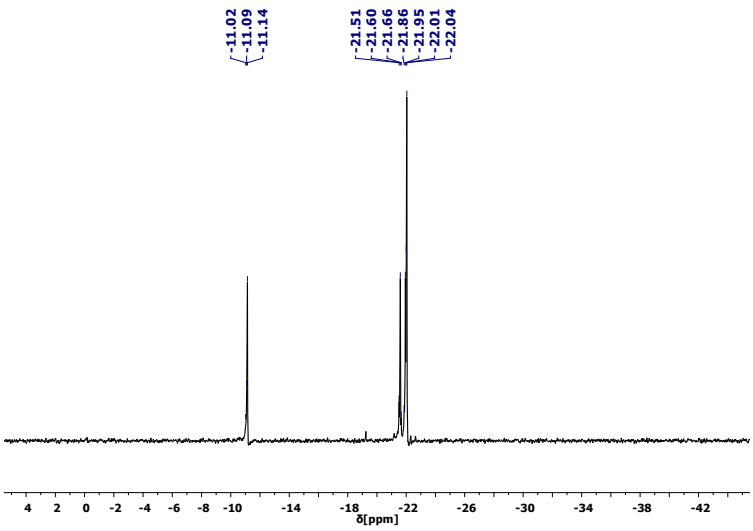


Figure ESI 8. ^{29}Si NMR spectrum of methoxy-terminated polydimethylsiloxane oligomer.

Sample 1 – after 3h of condensation

δ_H (300 MHz, $CDCl_3$): 8.08 – 6.88 (5 H, m, Si-Ph), 5.16 – 4.66 (m, $MeOD_4/H_2O$[39]), 3.80 – 2.93 (m, Si-OMe, MeOH, $MeOD_4$), 1.18 (t, *J* 7.0, EtOH[39]), 0.51 – -0.30 (m, Si-Me).

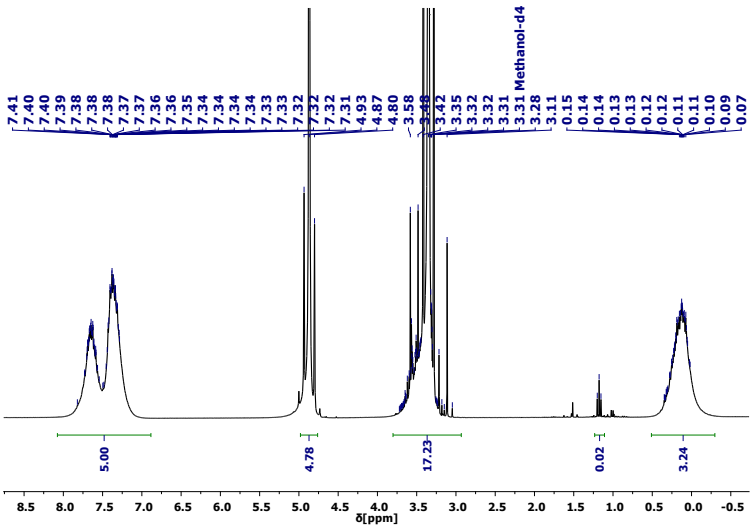


Figure ESI 9. [1]H NMR spectrum of the reaction mixture of sample 1 after 3 h of condensation reaction before methoxy-terminated polydimethylsiloxane was added.

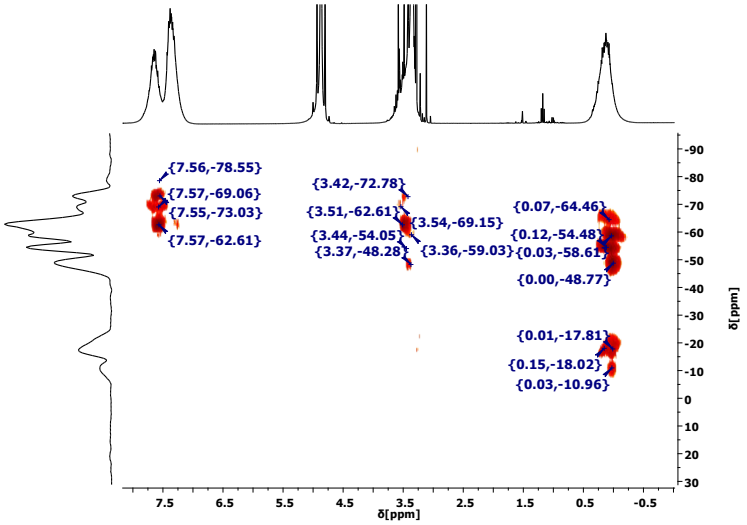


*Figure ESI 10. [29]Si-[1]H HMBC 2D NMR spectrum of the reaction mixture of sample **1** after 3 h of condensation reaction before methoxy-terminated polydimethylsiloxane was added.*

Sample 1 – unconsolidated Gel

δ_H (300 MHz, $CDCl_3$): 8.08 – 6.88 (m, Si-Ph), 5.16 – 4.66 (m, $MeOD_4/H_2O$[39]), 3.80 – 2.93 (m, Si-OMe, MeOH, $MeOD_4$), 2.14 (s, Acetone[39]), 1.18 (t, *J* 7.0, EtOH[39]), 0.51 – -0.30 (m, Si-Me).

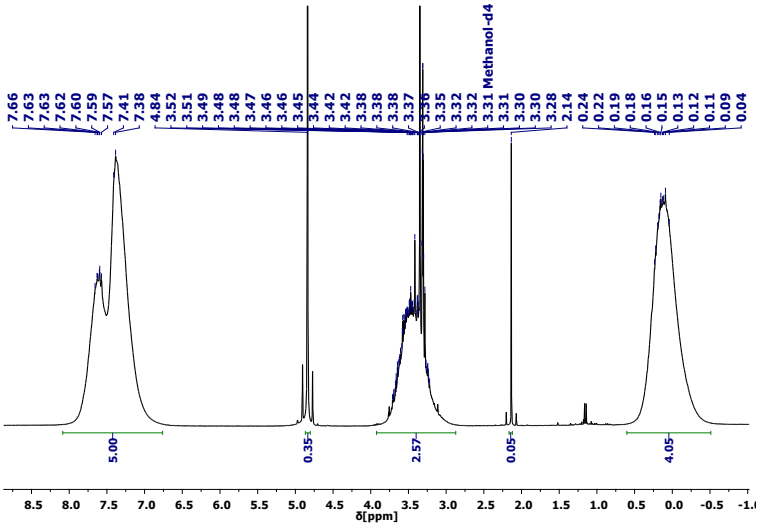


*Figure ESI 11. ^{1}H NMR spectrum of the unconsolidated gel like sample **1**.*

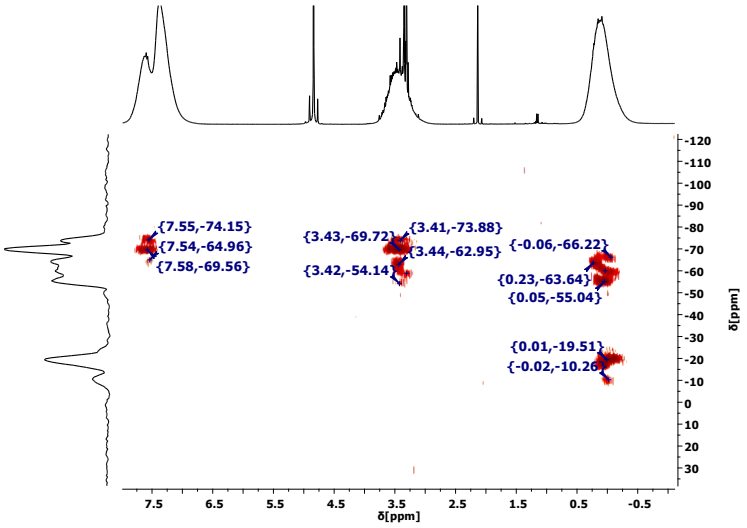


*Figure ESI 12. ^{29}Si-^{1}H HMBC 2D NMR spectrum of the unconsolidated gel like sample **1**.*

Sample 2 – after 3h of condensation

δ_H (300 MHz, $CDCl_3$): 8.03 – 7.02 (m, Si-Ph), 5.12 – 4.68 (m, $MeOD_4/H_2O$[39]), 3.78 – 2.95 (m, Si-OMe, MeOH, $MeOD_4$), 1.18 (t, *J* 7.0, EtOH[39]), 0.48 – -0.30 (m, Si-Me).

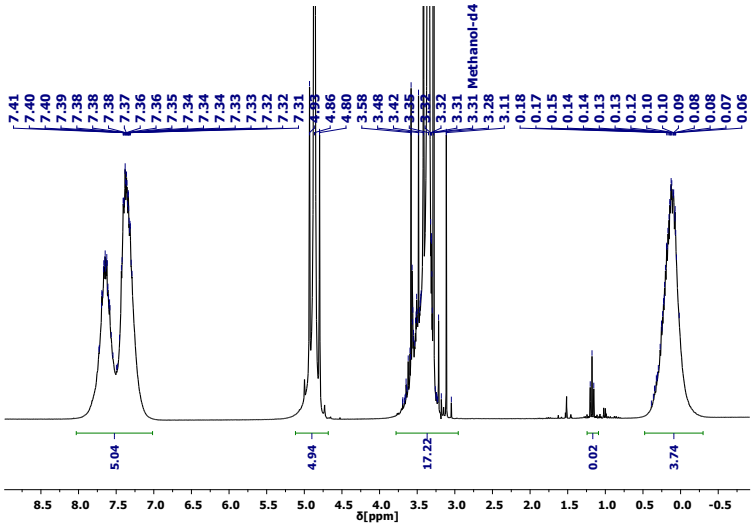


*Figure ESI 13. [1]H NMR spectrum of the reaction mixture of sample **2** after 3 h of condensation reaction before methoxy-terminated polydimethylsiloxane was added.*

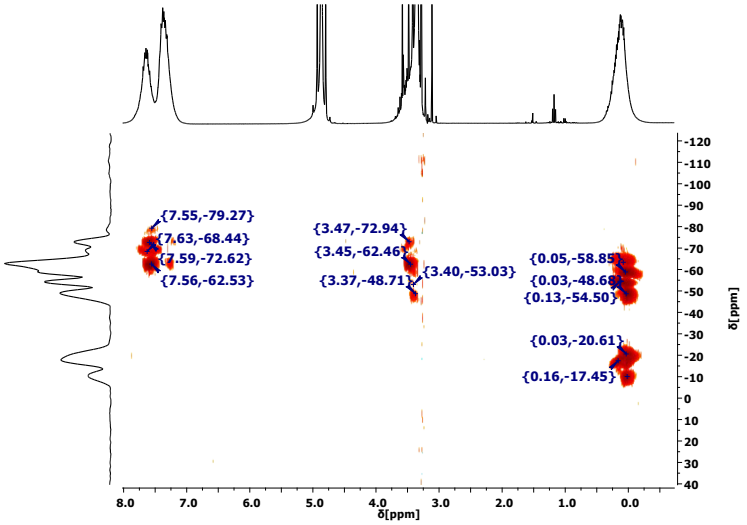


*Figure ESI 14. [29]Si-[1]H HMBC 2D NMR spectrum of the reaction mixture of sample **2** after 3 h of condensation reaction before methoxy-terminated polydimethylsiloxane was added.*

Sample 2 – unconsolidated gel

δ_H (300 MHz, $CDCl_3$): 8.02 – 6.82 (m, Si-Ph), 5.12 – 4.68 (m, $MeOD_4/H_2O$[39]), 3.87 – 2.95 (m, Si-OMe, MeOH, $MeOD_4$), 2.13 (s, Acetone[39]), 0.52 – -0.47 (m, Si-Me).

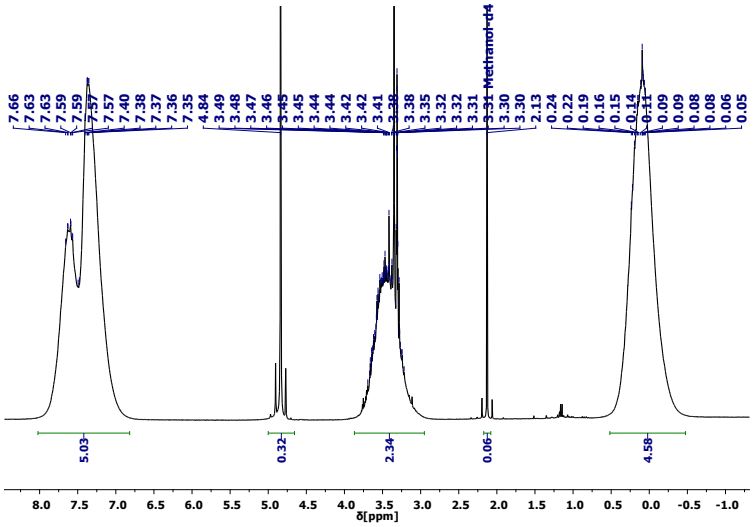


*Figure ESI 15. ^{1}H NMR spectrum of the unconsolidated gel like sample **2**.*

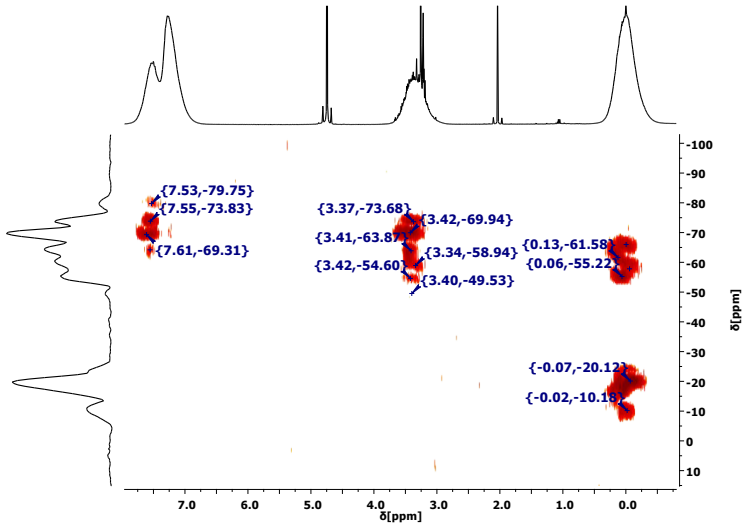


*Figure ESI 16. ^{29}Si-^{1}H HMBC 2D NMR spectrum of the unconsolidated gel like sample **2**.*

Sample 3 – after 3h of condensation

δ_H (300 MHz, $CDCl_3$): 7.95 – 7.01 (m, Si-Ph), 5.13 – 4.67 (m, $MeOD_4/H_2O$[39]), 3.75 – 2.96 (m, Si-OMe, MeOH, $MeOD_4$), 1.18 (t, *J* 7.0, EtOH[39]), 0.49 – -0.34 (m, Si-Me).

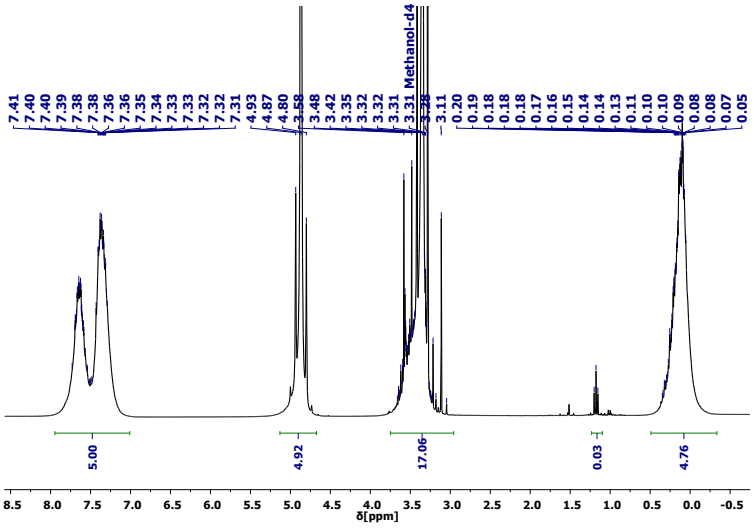


*Figure ESI 17. [1]H NMR spectrum of the reaction mixture of sample **3** after 3 h of condensation reaction before methoxy-terminated polydimethylsiloxane was added.*

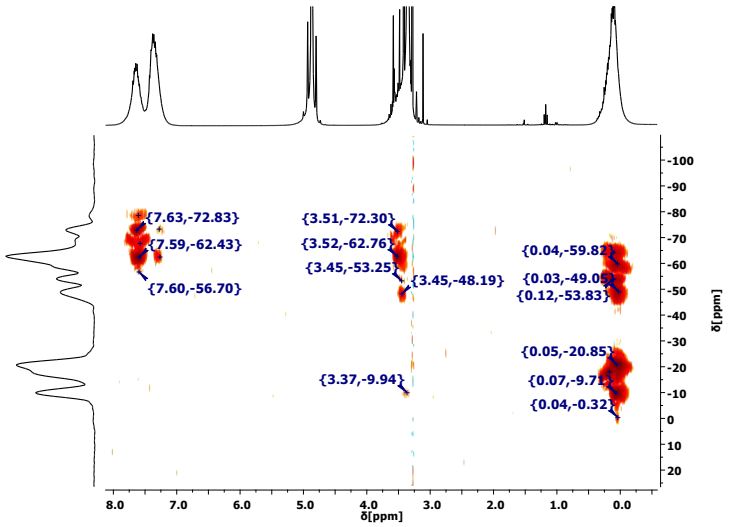


*Figure ESI 18. [29]Si-[1]H HMBC 2D NMR spectrum of the reaction mixture of sample **3** after 3 h of condensation reaction before methoxy-terminated polydimethylsiloxane was added.*

Sample 3 – unconsolidated gel

δ_H (300 MHz, $CDCl_3$): 8.07 – 6.87 (m, Si-Ph), 5.12 – 4.68 (m, $MeOD_4/H_2O$[39]), 3.87 – 3.01 (m, Si-OMe, MeOH, $MeOD_4$), 2.13 (s, Acetone[39]), 0.47 – -0.43 (m, Si-Me).

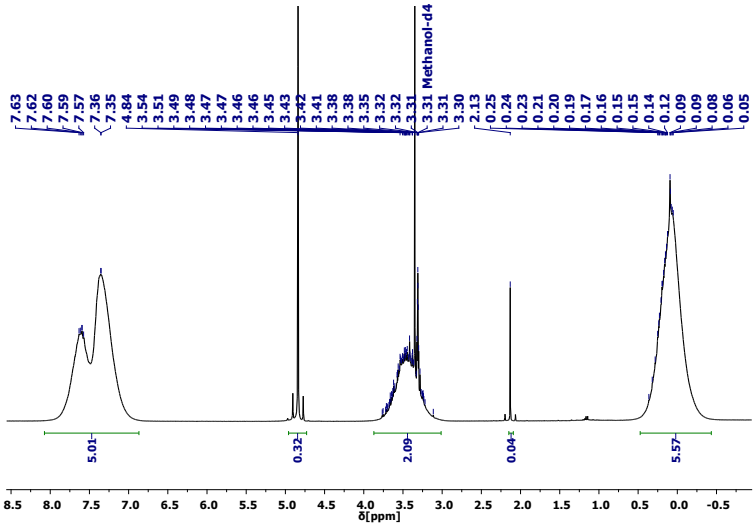


*Figure ESI 19. ^{1}H NMR spectrum of the unconsolidated gel like sample **3**.*

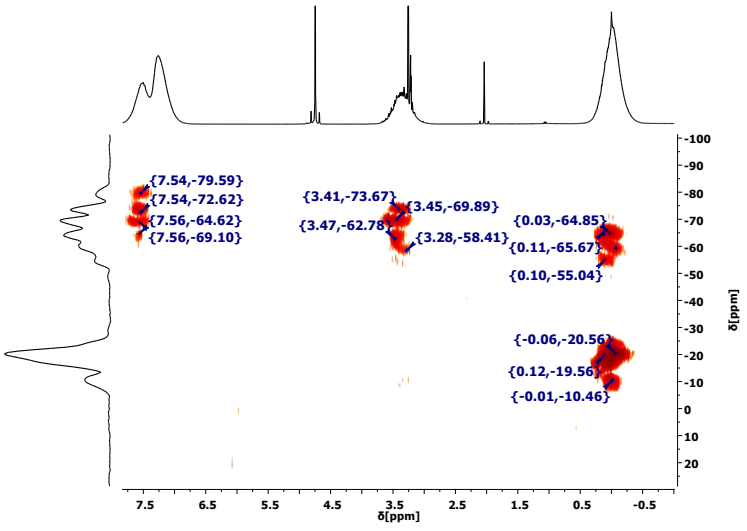


*Figure ESI 20. ^{29}Si-^{1}H HMBC 2D NMR spectrum of the unconsolidated gel like sample **3**.*

Sample 4 – unconsolidated gel

δ_H (300 MHz, $CDCl_3$): 7.95 – 6.83 (m, Si-Ph), 5.12 – 4.68 (m, $MeOD_4/H_2O$[39]), 3.83 – 2.94 (m, Si-OMe, MeOH, $MeOD_4$), 1.89 – 1.82 (m, unspecific impurity), 0.55 – -0.43 (m, Si-Me).

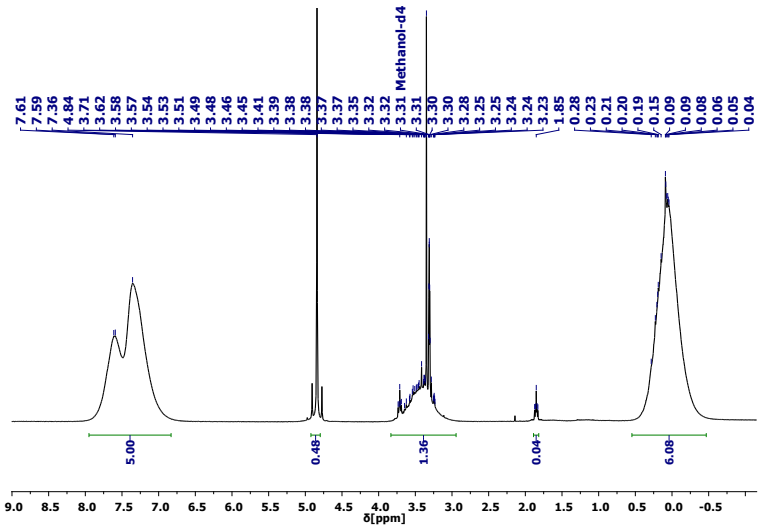


*Figure ESI 21. ^{1}H NMR spectrum of the unconsolidated gel like sample **4**.*

Sample 5 – unconsolidated gel

δ_H (300 MHz, $CDCl_3$): 8.08 – 6.80 (m, Si-Ph), 5.12 – 4.68 (m, $MeOD_4/H_2O$[39]), 3.79 – 2.99 (m, Si-OMe, MeOH, $MeOD_4$), 0.63 – -0.52 (m, Si-Me).

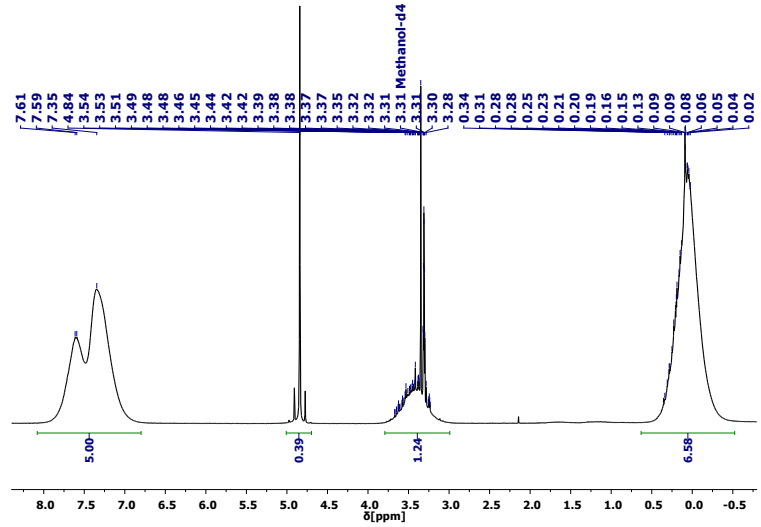


*Figure ESI 22. ^{1}H NMR spectrum of the unconsolidated gel like sample **5**.*

Sample 6 – unconsolidated gel

δ_H (300 MHz, $CDCl_3$): 7.99 – 6.78 (m, Si-Ph), 5.12 – 4.68 (m, $MeOD_4/H_2O$[39]), 3.80 – 3.06 (m, Si-OMe, MeOH, $MeOD_4$), 0.53 – -0.46 (m, Si-Me).

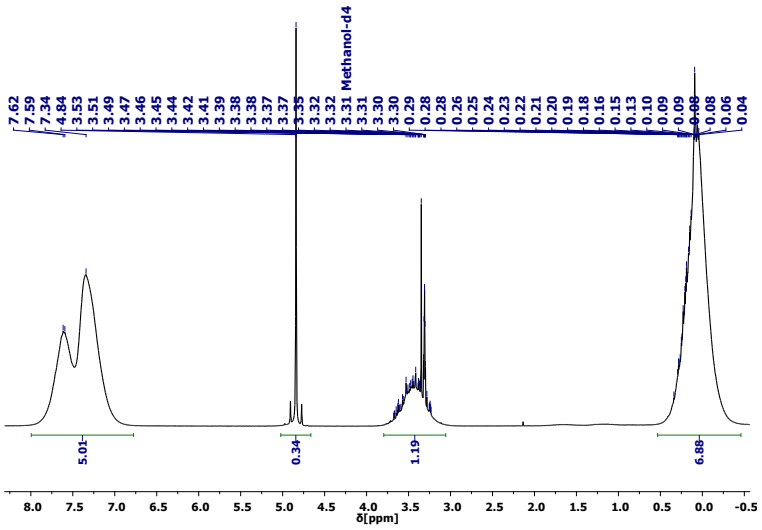


*Figure ESI 23. ^1H NMR spectrum of the unconsolidated gel like sample **6**.*

Sample 7 – unconsolidated gel

δ_H (300 MHz, $CDCl_3$): 8.02 – 6.82 (m, Si-Ph), 5.12 – 4.68 (m, $MeOD_4/H_2O$[39]), (m, Si-OMe, MeOH, $MeOD_4$), 0.57 – -0.45 (m, Si-Me).

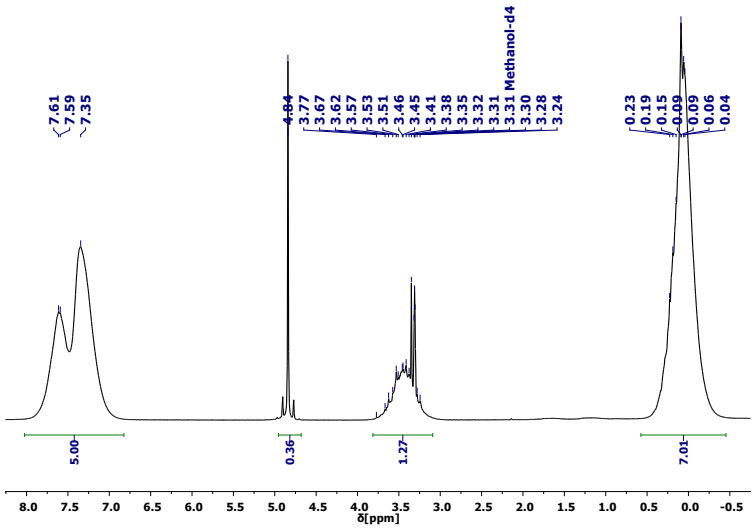


*Figure ESI 24. ^1H NMR spectrum of the unconsolidated gel like sample **7**.*

Sample 8 – after 3h of condensation

δ_H (300 MHz, $CDCl_3$): 7.85 – 7.13 (m, Si-Ph), 5.10 – 4.65 (m, $MeOD_4/H_2O$[39]), 3.83 – 2.89 (m, Si-OMe, MeOH, $MeOD_4$), 1.18 (t, *J* 7.0, EtOH[39]), 0.43 – -0.20 (m, Si-Me).

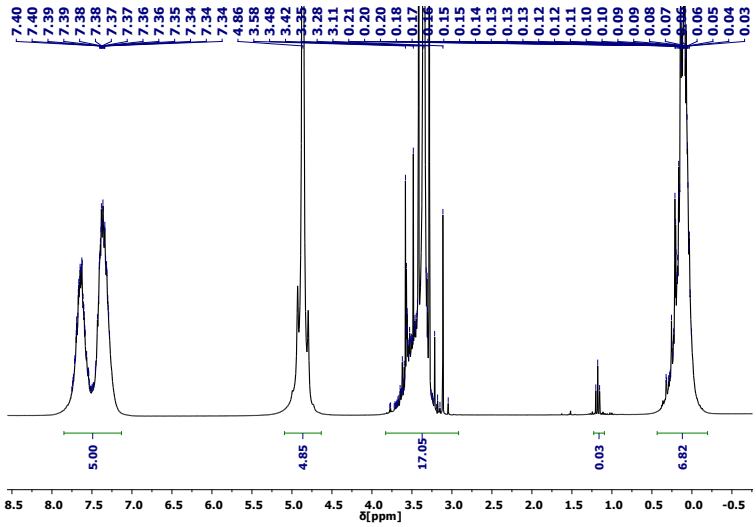


*Figure ESI 25. [1]H NMR spectrum of the reaction mixture of sample **8** after 3 h of condensation reaction before methoxy-terminated polydimethylsiloxane was added.*

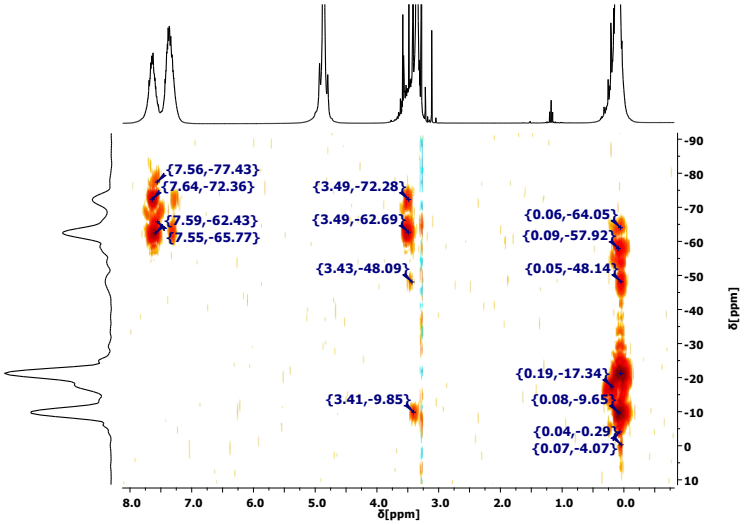


*Figure ESI 26. [29]Si-[1]H HMBC 2D NMR spectrum of the reaction mixture of sample **8** after 3 h of condensation reaction before methoxy-terminated polydimethylsiloxane was added.*

Sample 8 – unconsolidated gel

δ_H (300 MHz, $CDCl_3$): 8.09 – 6.85 (m, Si-Ph), 5.12 – 4.68 (m, $MeOD_4/H_2O$[39]), 3.87 – 3.11 (m, Si-OMe, MeOH, $MeOD_4$), 2.10 (s, Acetone[39]), 0.62 – -0.38 (m, Si-Me).

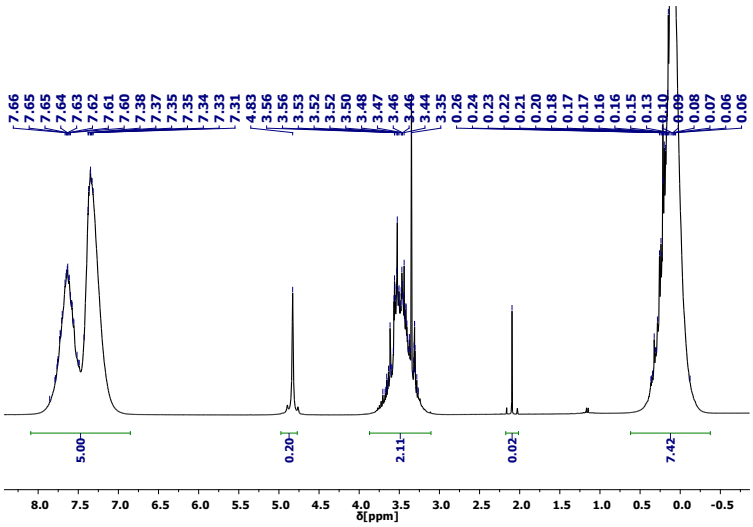


*Figure ESI 27. ^1H NMR spectrum of the unconsolidated gel like sample **8**.*

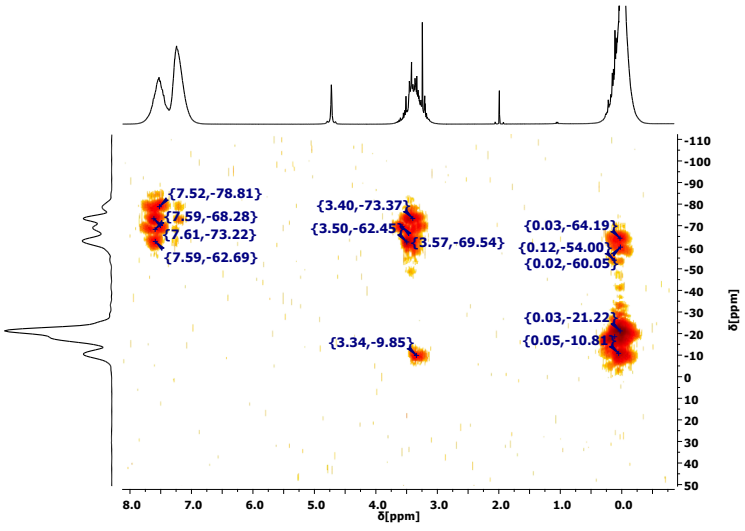


*Figure ESI 28. ^{29}Si-^1H HMBC 2D NMR spectrum of the unconsolidated gel like sample **8**.*

FTIR spectroscopy

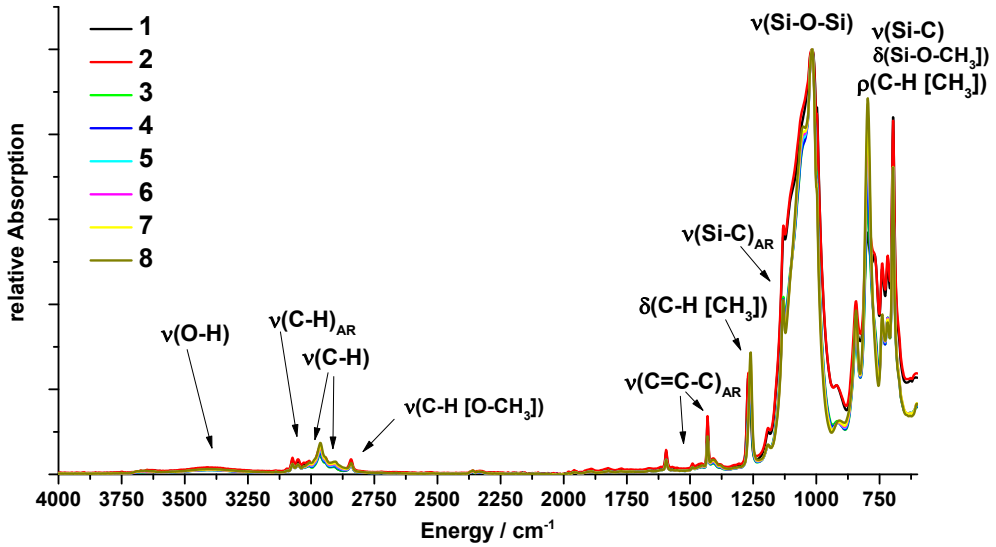


*Figure ESI 29. FTIR spectra of sample **1** – **8** with the main vibration bands noted.*

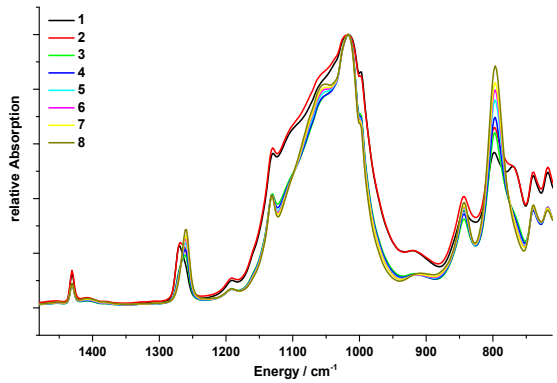


*Figure ESI 30. Enlarged segment of the FTIR spectra of sample **1** – **8**, illustrating the differences in shape of the Si-O-Si vibration bands at 1052 and 1016 cm^{-1} of the unconsolidated gels.*

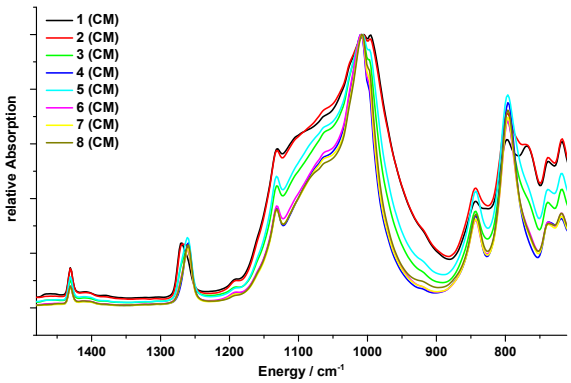


*Figure ESI 31. Enlarged segment of the FTIR spectra of sample **1** – **8**, illustrating the differences in shape of the Si-O-Si vibration bands at 1052 and 1016 cm^{-1} of the consolidated materials.*

Aging Experiments

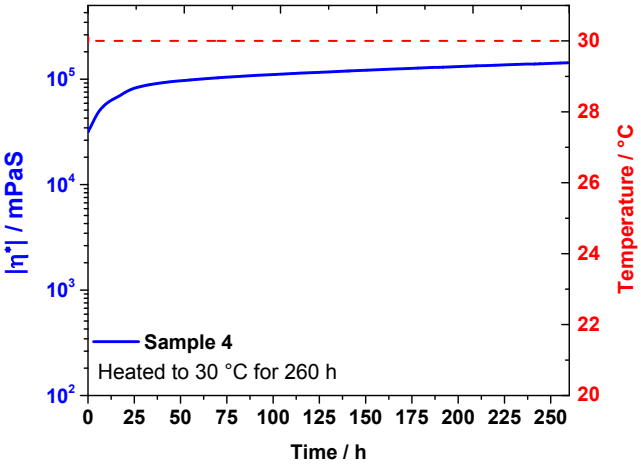


*Figure ESI 32. Absolute value of viscosity of sample **4** measured isothermally at 30 °C for 260h with an amplitude of 5%, a frequency of 1 Hz and a normal force value of 0.*

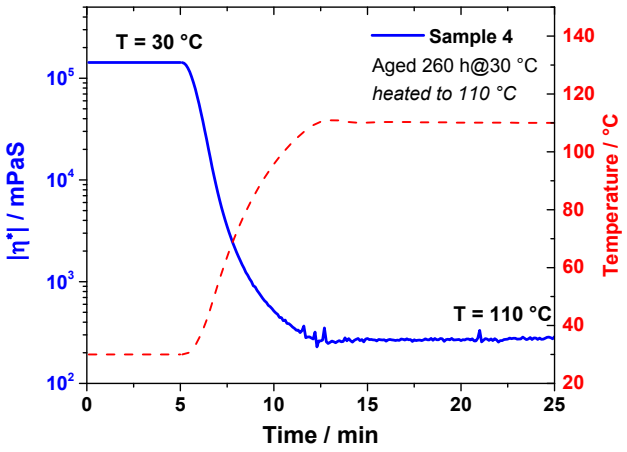


*Figure ESI 33. Absolute value of viscosity of sample **4** at 110 °C after heating it isothermally at 30 °C for 260h. Measured with an amplitude of 5%, a frequency of 1 Hz and a normal force value of 0.*

^{13}C CP-MAS-NMR

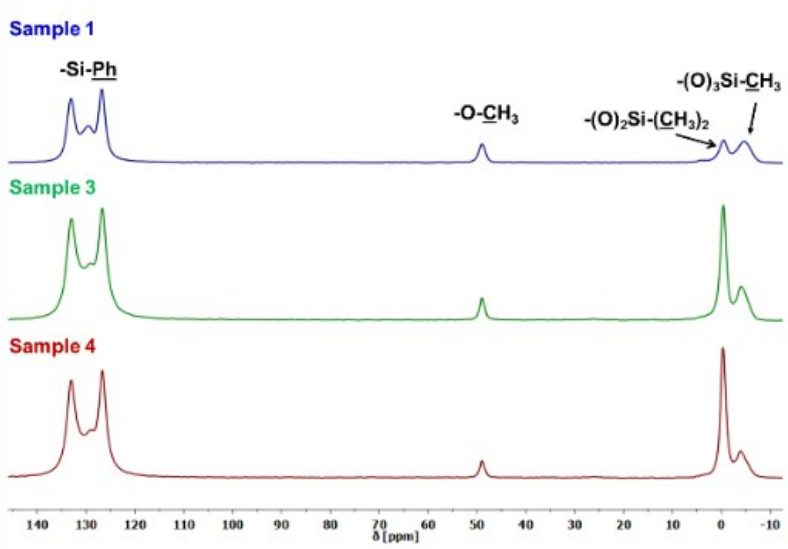


*Figure ESI 34. ^{13}C CP-MAS-NMR spectra of the cured samples **1, 3** and **5**.*

Thermogravimetric studies

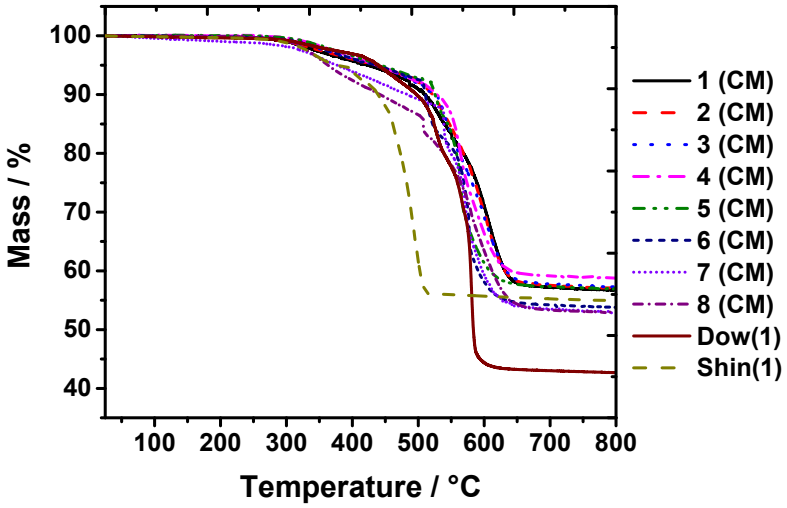


*Figure ESI 35. Thermogravimetric mass loss curve of sample **1** – **8** and the two reference encapsulation silicones Dow Corning OE6630 [Dow(1] and ShinEtsu KJR9022E [Shin(1)].*

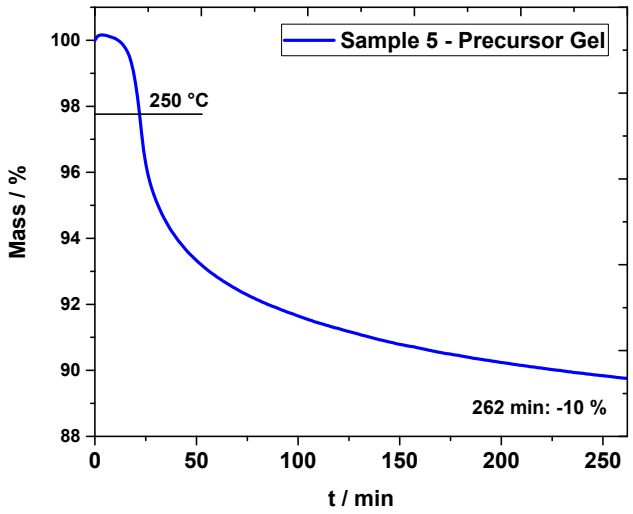


*Figure ESI 36. Thermogravimetric mass loss curve of sample **5** at isothermally 250 °C for 250 min. A mass loss of -10% was detected.*

DSC measurments

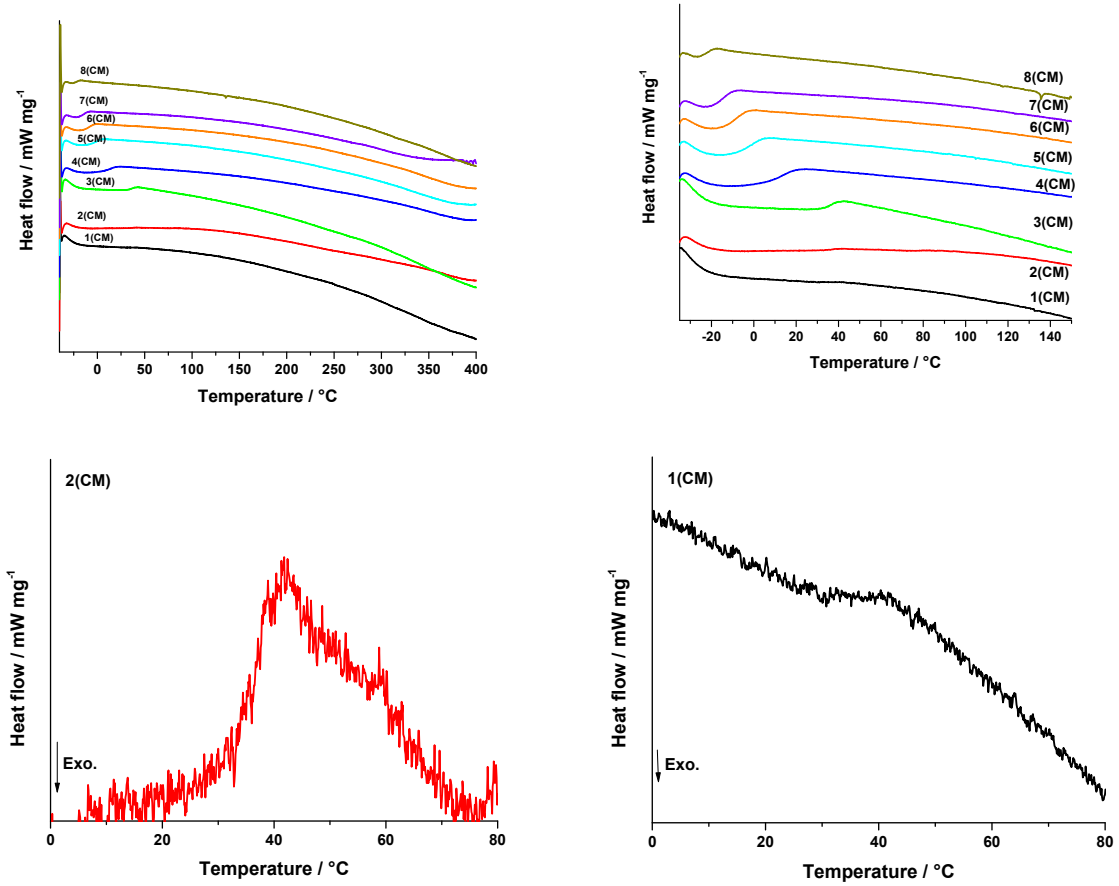


*Figure ESI 37. DSC measurements of the consolidated samples **3 – 8** measured from -40 to 400 °C with 5K/min under N_2 atmosphere (100 ml/min). The T_g value indicated by an inflection of the DSC curve increases with the hardness of the sample caused by a higher cross-linked structure. Enlarged curves of samples **1 and 2** show decrease in signal intensity.*

Transmission spectroscopy

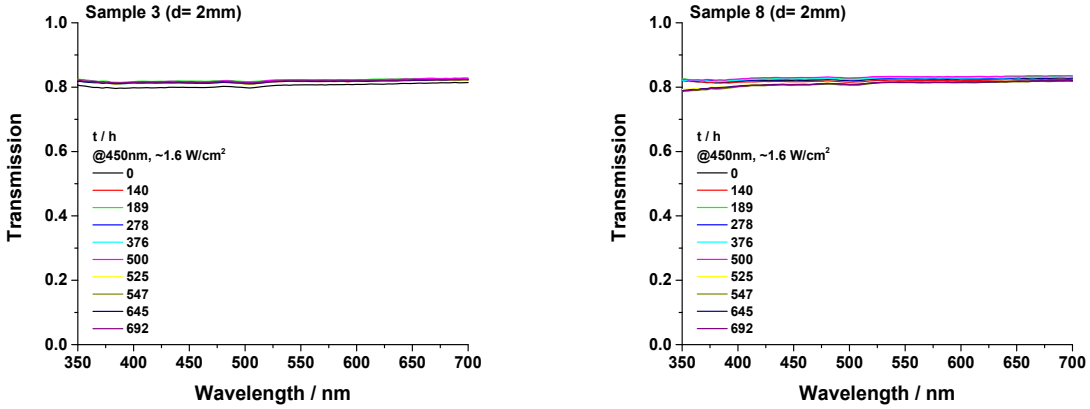


*Figure ESI 38. Transmission spectra of the consolidated samples **3** and **8** after the given time of irradiation at 450 nm with ~1600 mW/cm² and 60°C. There are no systematic changes detectable*

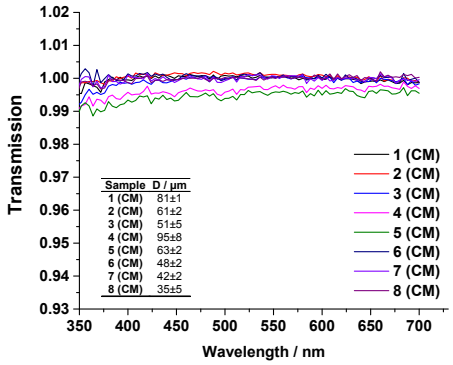


*Figure ESI 39. Transmission and thickness of films of sample **1** – **8** after consolidation at 200 °C for 1170 h. All samples show a minimum transmission of 0.98 in the measured wavelength range.*

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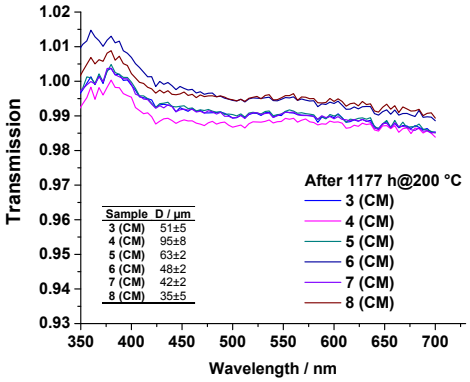

*Figure ESI 40. Transmission and thickness of films of sample **1** – **8** after a heat treatment at 200 °C for 1177 h.*

LED packaging demonstration

Packaging materials for optoelectronic devices needs to be castable, curable and sealed. The subsequently consolidated matrix needs to be crack and bubble free as well as elastic. To demonstrate the processability of the precursor polysiloxanes a polyphtalamide LED lead frame (1.4 x 0.7 x 0.4 mm) was casted with sample **4** and **6** by hand. The filled lead frames were heat treated to cure the polymers (160 °C, 20 h).

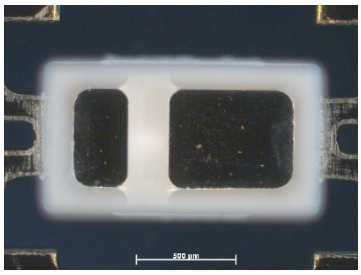

Figure ESI 41. Empty lead frame. Picture focused on the frames metal base.

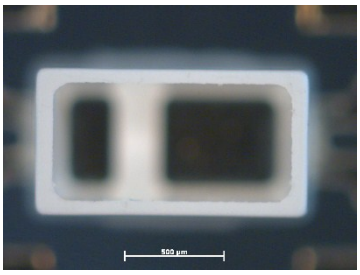

Figure ESI 42. Empty lead frame. Picture focused on the upper edge of the frame.

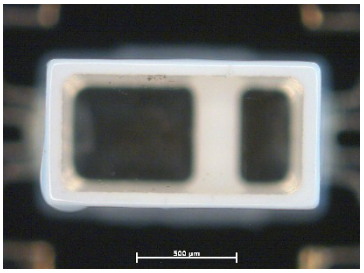

*Figure ESI 43. Lead frame filled with a smooth and transparent cast of sample **4**. Color impression is caused by the metallic base plate.*

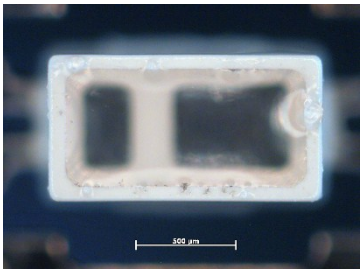

*Figure ESI 44. Lead frame with consolidated sample **4**. Color impression is caused by the metallic base plate.*

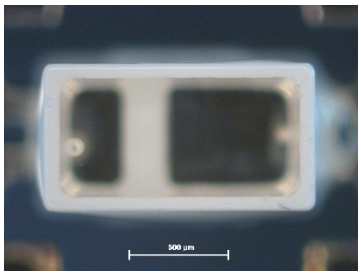

*Figure ESI 45. Lead frame filled with a smooth and transparent cast of sample **6**. Bubbles caused by the injection disappear after curing. Color impression is caused by the metallic base plate.*

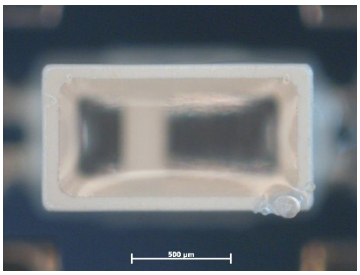

*Figure ESI 46. Lead frame with consolidated sample **6**. Color impression is caused by the metallic base plate*

Due to the difficult microscope supported injection by hand, the quality of the cast is not as good as automated industrial castings, indicated by overtopping and the small bumps of the consolidated gel on the lead frames edges. Both casted gel materials showed a very good processability. After the consolidation no bubbles or cracks inside the material can be detected. Shrinkage of the material is indicated by the convergence on the lead frames flanks. In summary, the materials are suitable as packaging material for LED applications.