Supporting Information

A Facile Route for the Synthesis of Sub-Micron Sized Hollow and Multiporous Organosilica Spheres

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1. Equipment

Figure S1 Equipment used in the synthesis of sub-micron sized hollow and multiporous organosilica spheres: IKA RCT basis magnetic stirrer / heater with thermostat, oil bath, 500 mL glass latex reactor equipped with condenser and IKA RW 20 DZM mechanic stirrer.

2. Emulsion Formation

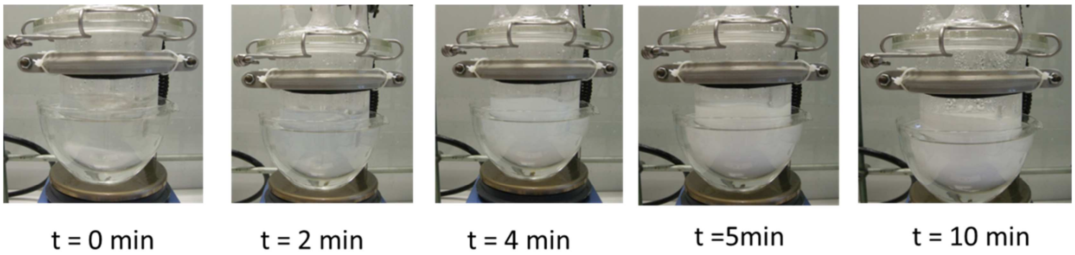

Figure S2 Emulsion formation in the synthesis of the sub-micron sized hollow organosilica spheres at p*H* 11 and at 60°C. Ph-TMS was added at t = 0.

3. Pendant drop experiments

Interfacial tension measurements were performed using a conventional pendant-drop technique set-up with a 1.8 mm needle, using the Krüss DSA 100 equipped with DSA software. Images of the drop were taken every 10 seconds until the drop fell off.

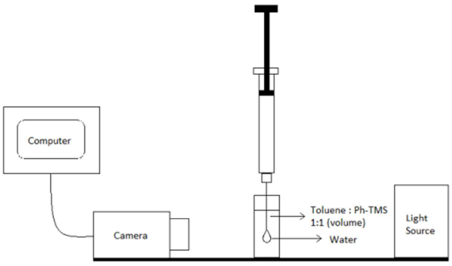

Figure S3 Schematic representation of the experimental setup for the pendant drop experiments.

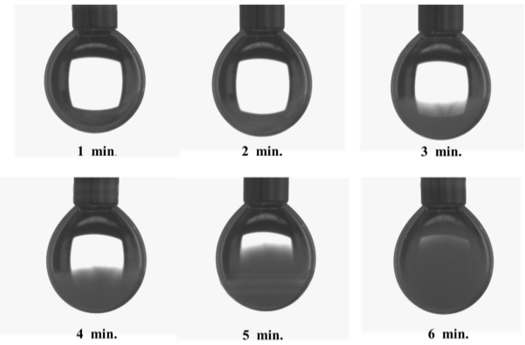

Figure S4 Shell formation observed in the pendant drop experiment.

4. Particles obtained through substitution of 10 vol-% Ph-TMS with TMOS or TEOS

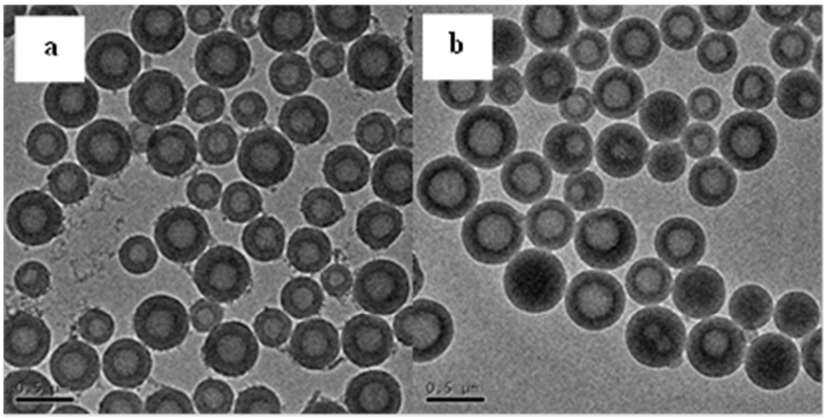

Figure S5 a) TEM image of phenyl siloxane spheres prepared from a Ph-TMS / TMOS mixture b) TEM image of phenyl siloxane spheres prepared from a Ph-TMS / TEOS mixture.

Table S1. Average particle size of particles obtained through substitution of 10 vol-% Ph-TMS with TMOS or TEOS

	Average Particle Size D_{av} and standard deviation σ [nm]	**Size Distribution σ/D_{av}**	**Average shell thickness t_{av} [nm]**
TEOS	427 (σ = 71)	0.17	96
TMOS	398 (σ = 75)	0.19	91

5. Particles obtained through addition of inert solvents to the oil phase

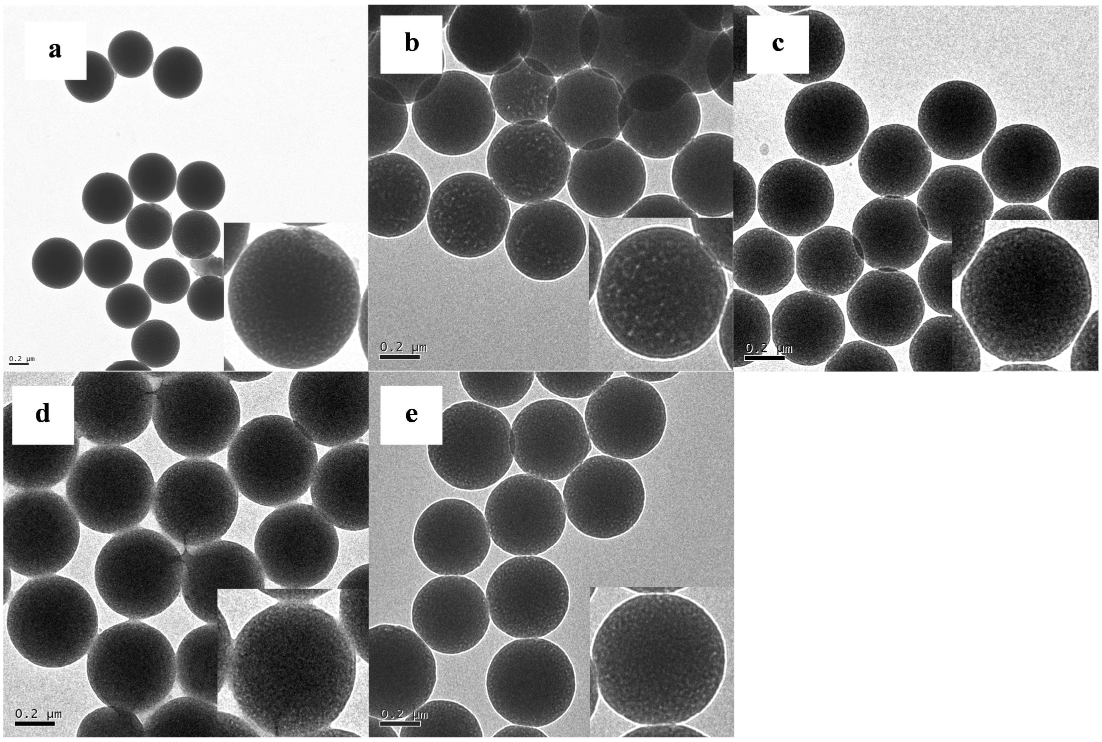

Figure S6 TEM images of a) phenyl siloxane spheres prepared through addition of toluene, b) phenyl siloxane spheres prepared through addition of cyclohexane, c) phenyl siloxane spheres prepared through addition of 1,2-dichlorobenzene, d) phenyl siloxane spheres prepared through addition of mesitylene, e) phenyl siloxane spheres prepared through addition of o-xylene.

Table S2. Average particle and pore size of particles obtained through addition of inert solvents to the oil phase

Solvent	Average Particle Size D_{av} and standard deviation σ [nm]	Size Distribution σ/D_{av}	Pore size [nm]
Toluene	493 (σ = 38)	0.077	5 - 10
Cyclohexane	391 (σ = 11)	0.028	10 - 30
1,2-Dichlorobenzene	359 (σ = 56)	0.16	5 - 10
Mesitylene	429 (σ = 23)	0.054	5 - 10
***o*-Xylene**	395 (σ = 28)	0.071	5 – 10

6. X-ray diffraction (XRD) analysis

XRD measurements were carried out on a Bruker Discover D8 using Cu Ka radiation, with Ni filter for CuKb filtering on primary side. Bragg-Brentano setup was used with fixed sample illumination of 10 mm, and 2.5 degree Soller slits. On secondary side Soller slits of 2.5 degree were used with a Lynxeye detector. Suppression of air scattering and direct beam detection was done by using a knife-edge at 4 mm above the sample.
Sample were prepared by drying an aqueous particle dispersion at 50°C onto a “low background” sample of silicon.

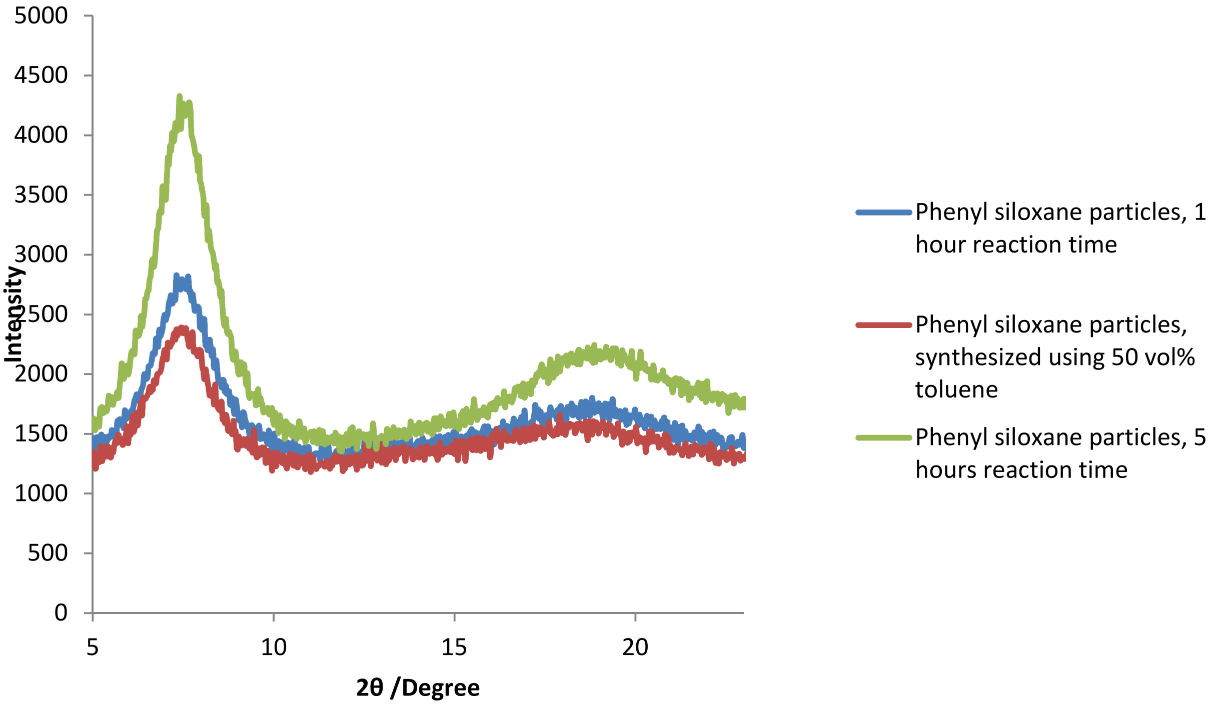

Figure S7 XRD patterns of the phenyl siloxane particles after 1 hour reaction time (blue), the phenyl siloxane particles after 5 hours reaction time (green) and the phenyl siloxane particles synthesized using 50 vol% toluene (red).

Table S3. Assignment of the XRD signals of phenyl siloxane particles

Sample	Peaks [˚]	Chain-to-chain distance [nm]	Intrachain distance [nm]
Phenyl siloxane particles, 1h	7.32; 18.24	1.21	0.49
Phenyl siloxane particles, 5h	7.41; 19.02	1.19	0.47
Phenyl siloxane particles, synthesized using 50 vol% toluene	7.32; 17.92	1.21	0.49

7. Brauner-Emmett-Teller (BET)-analysis

Nitrogen adsorption-desorption measurements were performed by Philips Inovation Services using a Gemini V (Micromeritics). Samples were heated to 600˚C for two hours, and subsequently dried at 200˚C for 12 hours under vacuum.

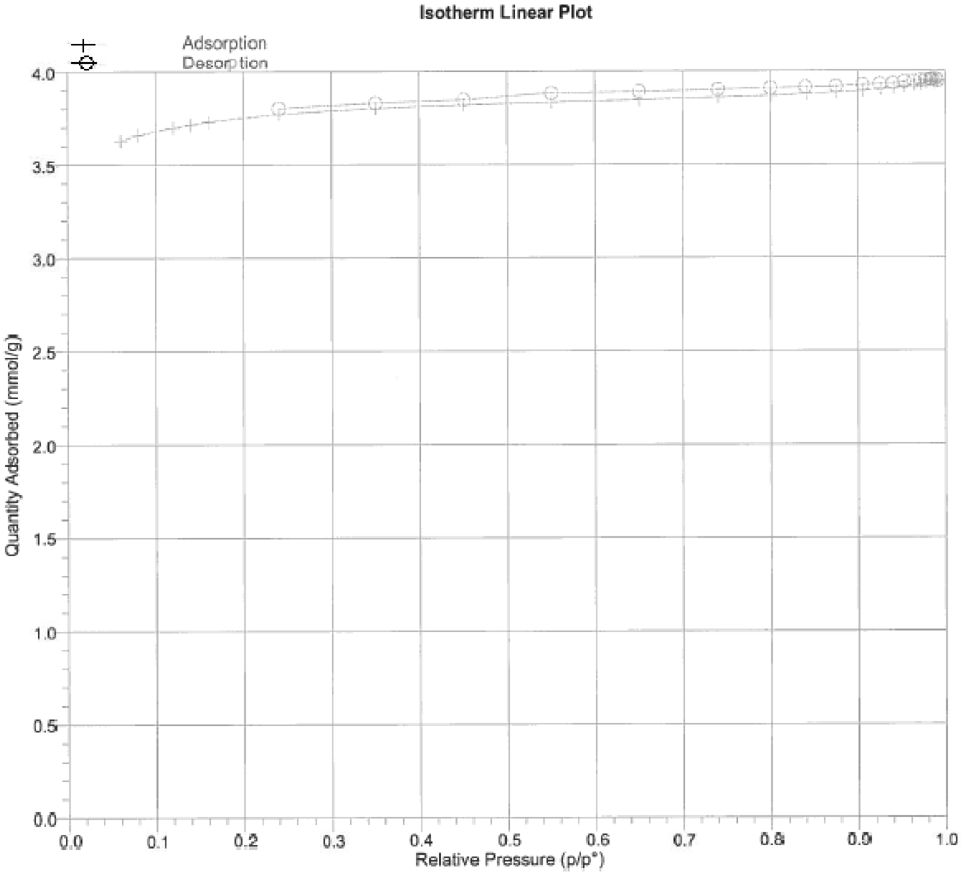

Figure S8 N_2 adsorption and desorption isotherm for phenyl siloxane particles, with a reaction time of 1 hour.

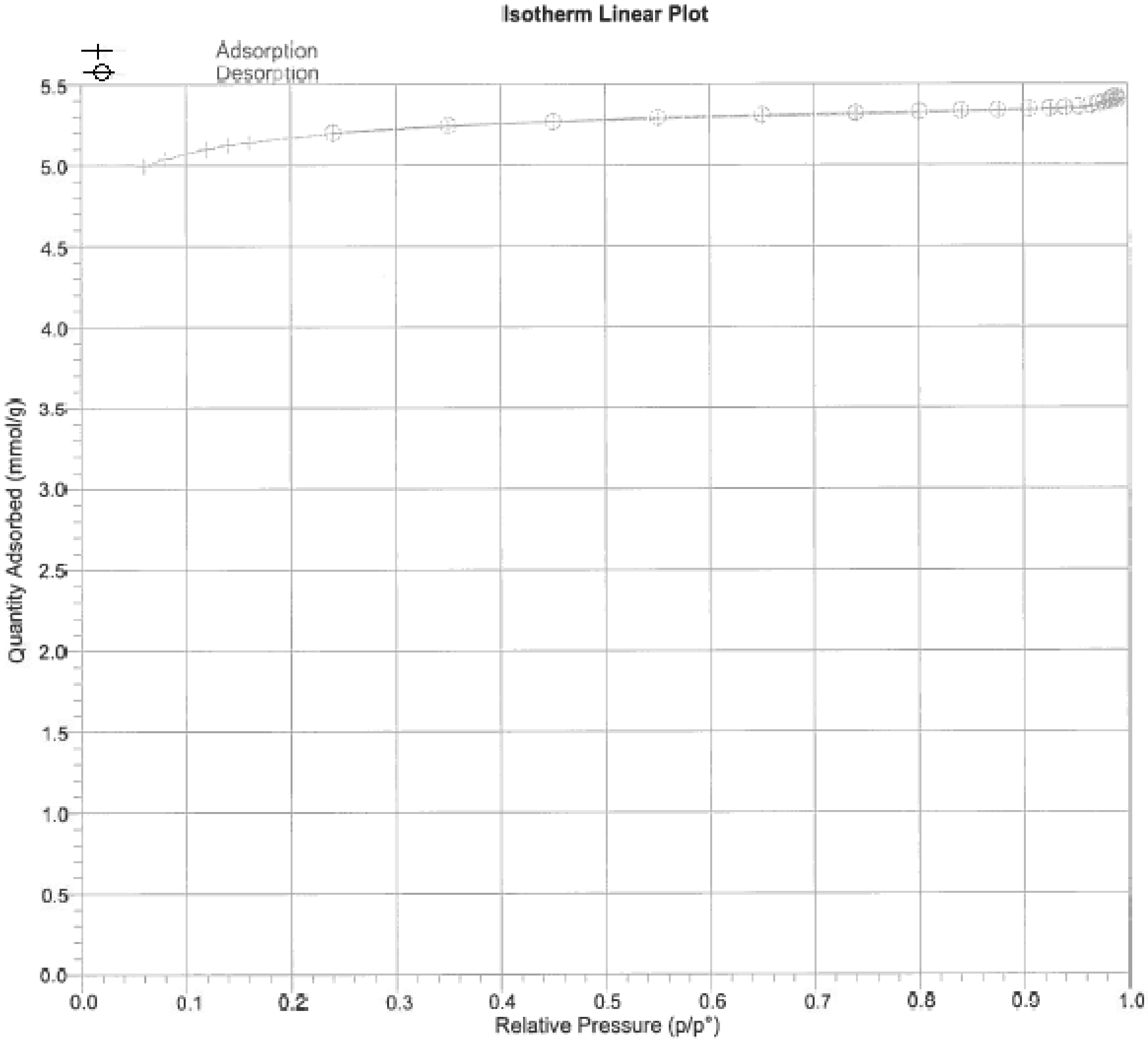

Figure S9 N_2 adsorption and desorption isotherm for phenyl siloxane particles, with a reaction time of 5 hours.

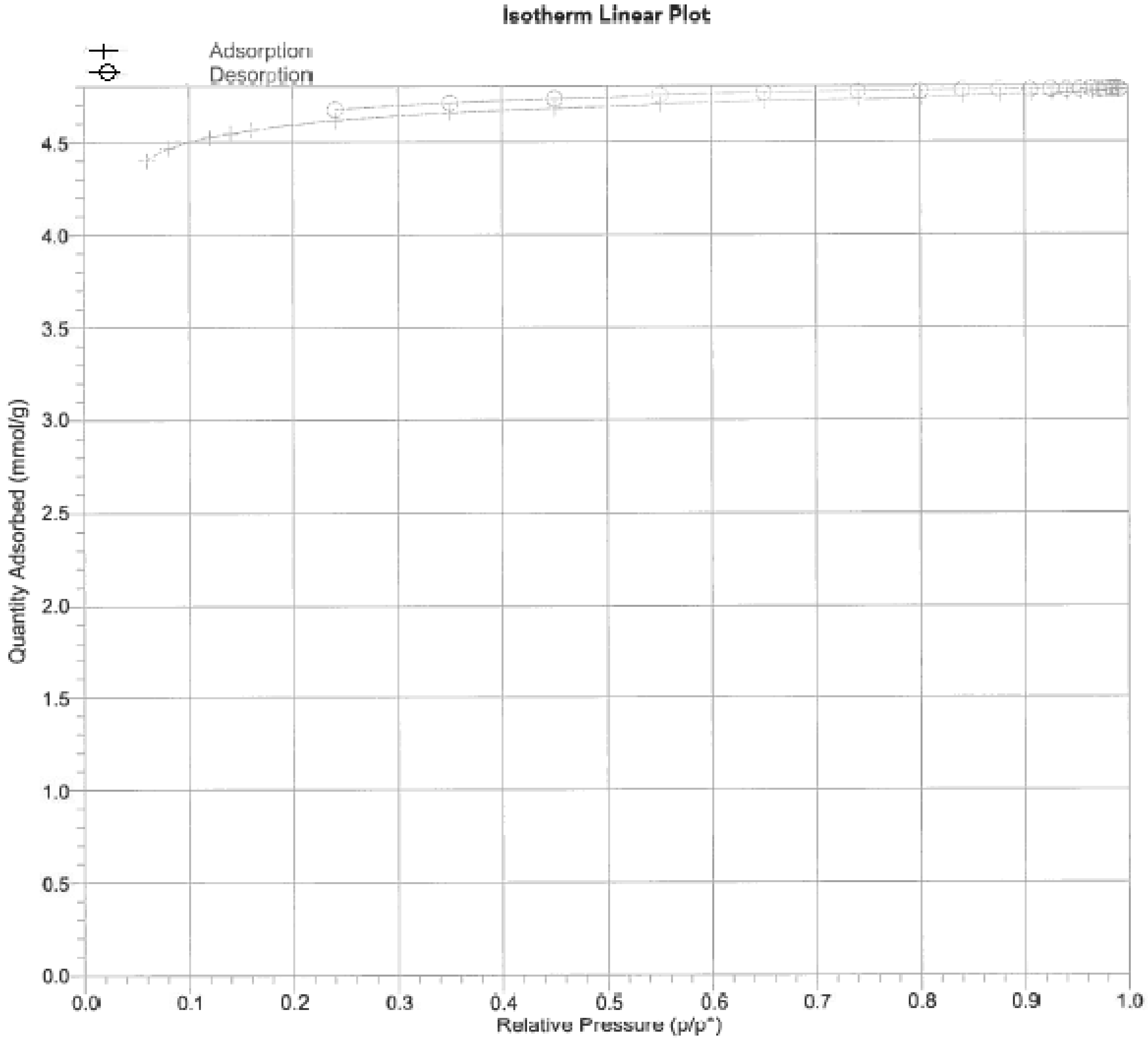

Figure S10 N_2 adsorption and desorption isotherm for phenyl siloxane particles, prepared using 50 vol% toluene.

Table S4. BET Data of phenyl siloxane particles

Sample	Isotherm type (according to IUPAC nomenclature)	BET surface [m^2/g]	Total pore volume [cm^3/g]	Micropore volume [cm^3/g]	Mesopore volume [cm^3/g]
Phenyl siloxane particles, 1h	type 1	250	0.137	0.114	0.023
Phenyl siloxane particles, 5h	type 1	380	0.187	0.156	0.031
Phenyl siloxane particles, synthesized using 50 vol% toluene	type 1	340	0.166	0.137	0.029

8. Infrared (IR) spectroscopy

IR spectra were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Scientific) in the ATR mode (diamond crystal).

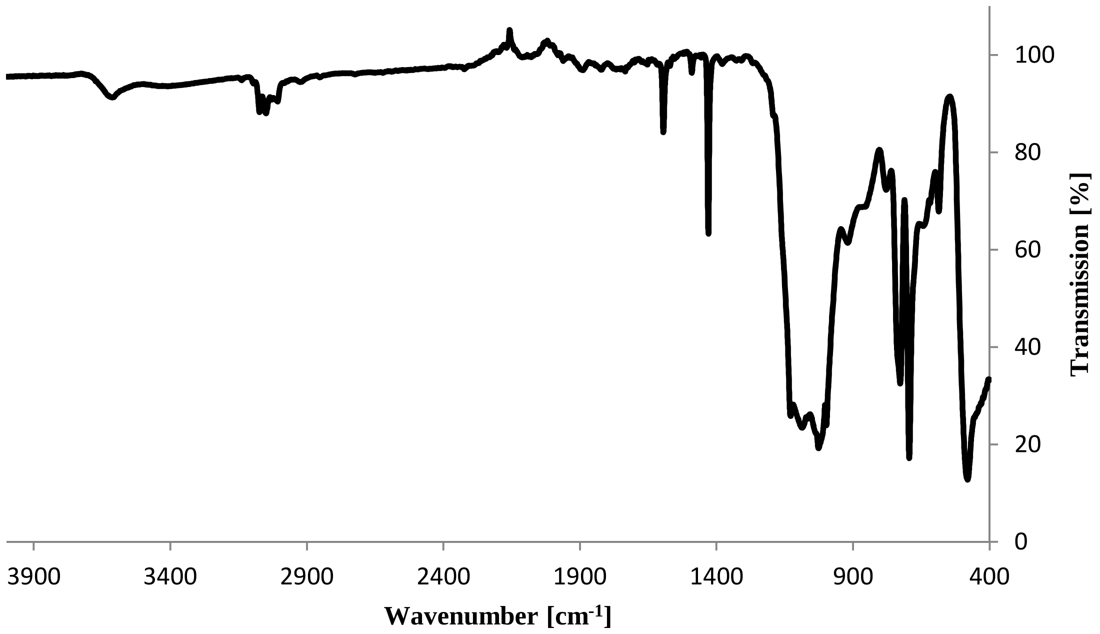

Figure S11 IR spectrum of phenyl siloxane particles, 1 hour reaction time.

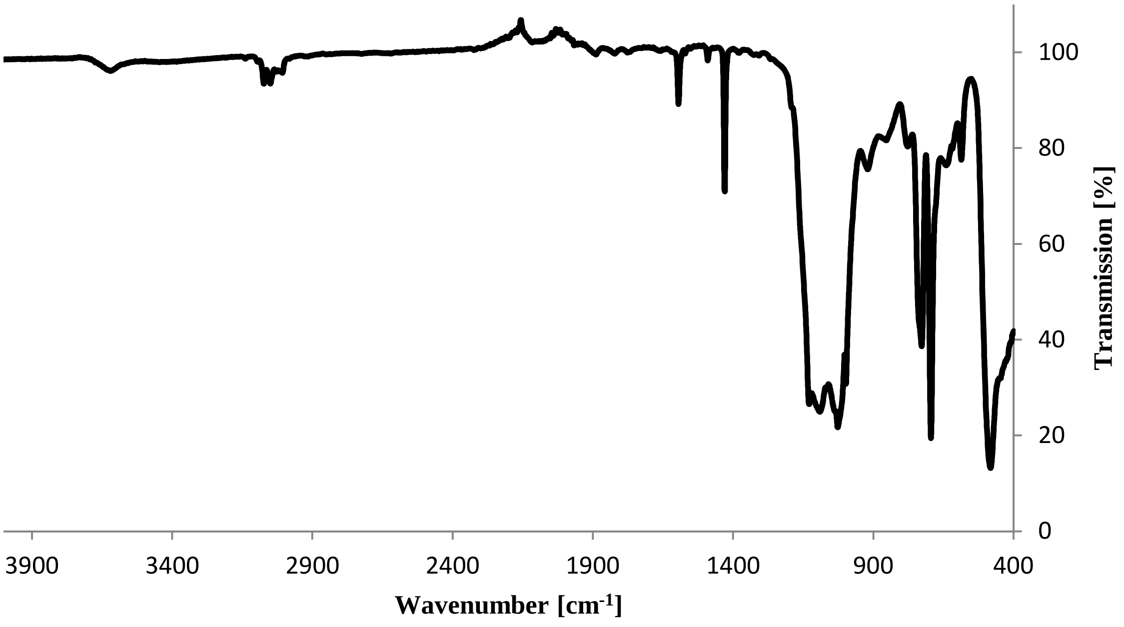

Figure S12 IR spectrum of phenyl siloxane particles, 5 hours reaction time.

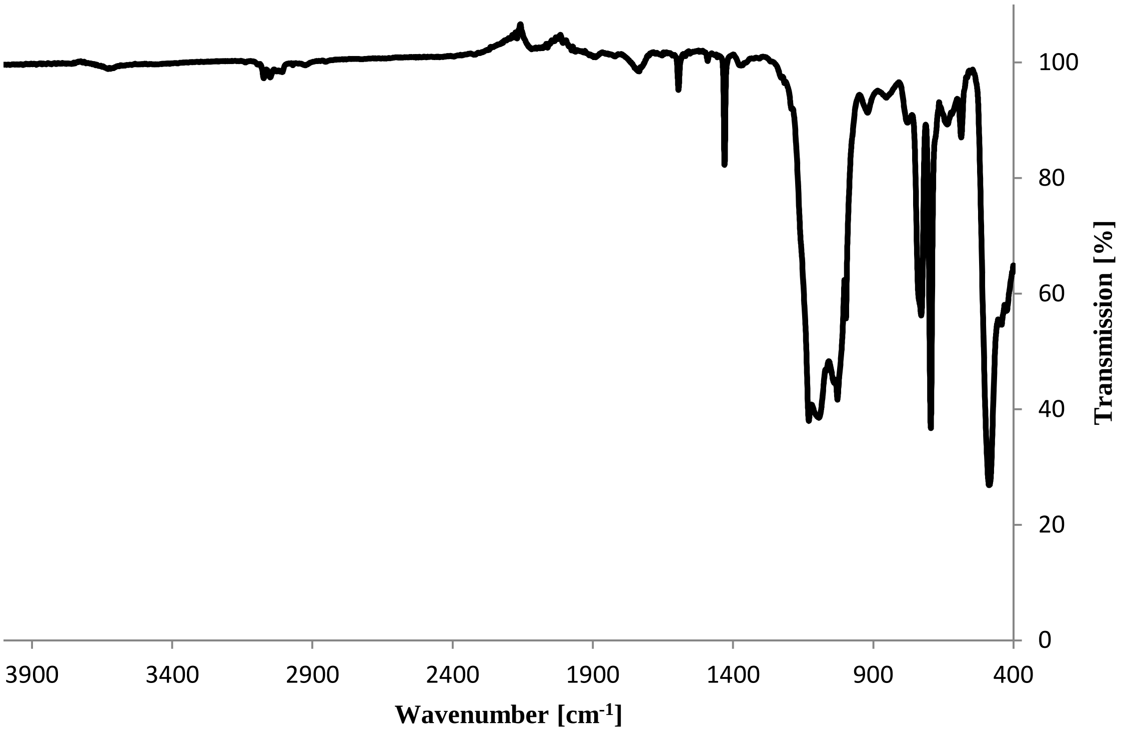

Figure S13 IR spectrum of phenyl siloxane particles synthesized using 50 vol% toluene.

Table S5. Main absorptions of the phenylsiloxaneparticles, 1 hour reaction time.

Wave Number [cm $^{-1}$]	Assignement	Notes
3618	ν (Si-O-H)	From free Si-O-H groups [1]
3075, 3053	ν (C-H)	Phenyl[1]
3006	ν (C-H)	Phenyl [2]
1961,1888, 1828, 1768, 1653	Harmonic and combination vibrations of aromats	Phenyl [2]
1595	ν (C-C)	Phenyl [1]
1429	δ (C-H)	Phenyl [1]
1128	ν (Si-O-Si)	Phenyl-SQ, T10 [1,3]
1088	ν (Si-O-Si)	Phenyl-SQ, Non-equilibrated [1,3]
1027	ν (Si-O-Si)	Unclear which type of SQ[4]
997	Breathing of phenyl ring	Phenyl [1]
727, 694	γ (C-H)	Phenyl [1]
480	γ (C-H)	Phenyl[1]

ν = stretching; δ = in-plane bending; γ = out-of-plane bending.

Table S6. Main absorptions of the phenylsiloxaneparticles, 5 hour reaction time.

Wave Number [cm $^{-1}$]	**Assignement**	**Notes**
3619	ν (Si-O-H)	From free Si-O-H groups [1]
3075, 3051	ν (C-H)	Phenyl[1]
3006	ν (C-H)	Phenyl [2]
1967,1888, 1823, 1776, 1658	Harmonic and combination vibrations of aromats	Phenyl [2]
1595	ν (C-C)	Phenyl [1]
1429	δ (C-H)	Phenyl [1]
1128	ν (Si-O-Si)	Phenyl-SQ, T10 [1,3]
1090	ν (Si-O-Si)	Phenyl-SQ, Non-equilibrated [1,3]
1028	ν (Si-O-Si)	Unclear which type of SQ[4]
997	Breathing of phenyl ring	Phenyl [1]
727, 694	γ (C-H)	Phenyl [1]
481	γ (C-H)	Phenyl[1]

ν = stretching; δ = in-plane bending; γ = out-of-plane bending.

Table S7. Main absorptions of the phenylsiloxaneparticles prepared using 50 vol% toluene.

Wave Number [cm $^{-1}$]	**Assignement**	**Notes**
3619	ν (Si-O-H)	From free Si-O-H groups [1]
3074, 3051	ν (C-H)	Phenyl[1]
3006	ν (C-H)	Phenyl [2]
1967,1890, 1820, 1736, 1653	Harmonic and combination vibrations of aromats	Phenyl [2]
1595	ν (C-C)	Phenyl [1]
1431	δ (C-H)	Phenyl [1]
1129	ν (Si-O-Si)	Phenyl-SQ, T10 [1,3]
1093	ν (Si-O-Si)	Phenyl-SQ, Non-equilibrated [1,4]
1028	ν (Si-O-Si)	Unclear which type of SQ[5]
997	Breathing of phenyl ring	Phenyl [1]
729, 694	γ (C-H)	Phenyl [1]
481	γ (C-H)	Phenyl[1]

ν = stretching; δ = in-plane bending; γ = out-of-plane bending.

(1) L. A. S. de A. Prado, E. Radovanovic, H. O. Pastore, I. V. P. Yoshida, I. L. Torriani, *J. Polym. Sci., Part A: Polym. Chem.* 2000, **38**, 1580.

(2) M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der organischen Chemie*, Thieme, Stuttgart, 2002.

(3) X. Wang, J. Li, L. Wu, *Polym. Adv. Technol.* 2011, **22**, 2151.

(4) J. F. Brown, Jr., L. H. Vogt, Jr., P. I. Prescott, *J. Am. Chem. Soc.* 1964, **86**, 1120.

(5) P. J. Launer, *Infrared analysis of organosilicon compounds: spectra-structure correlations*, Silicone Compounds Register and Review, 1987.

9. Thermogravimetric Analysis (TGA)

TGA spectra were recorded on a Discovery TGA (TA Instruments). Samples were loaded in platinum pans and ramped at 5 ˚C/min to 900 ˚C under dry air with a flow rate of 20 mL/min.

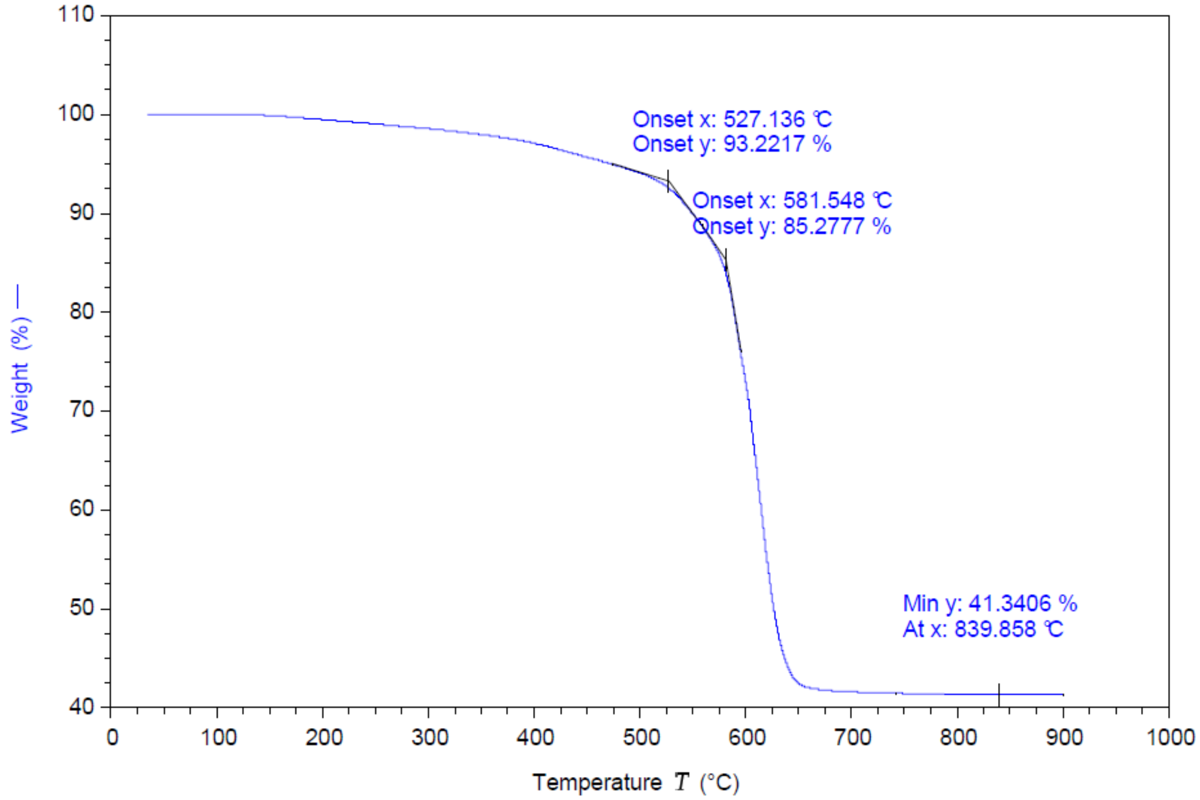

Figure S14 TGA data of the phenylsiloxaneparticles, 1 hour reaction time.

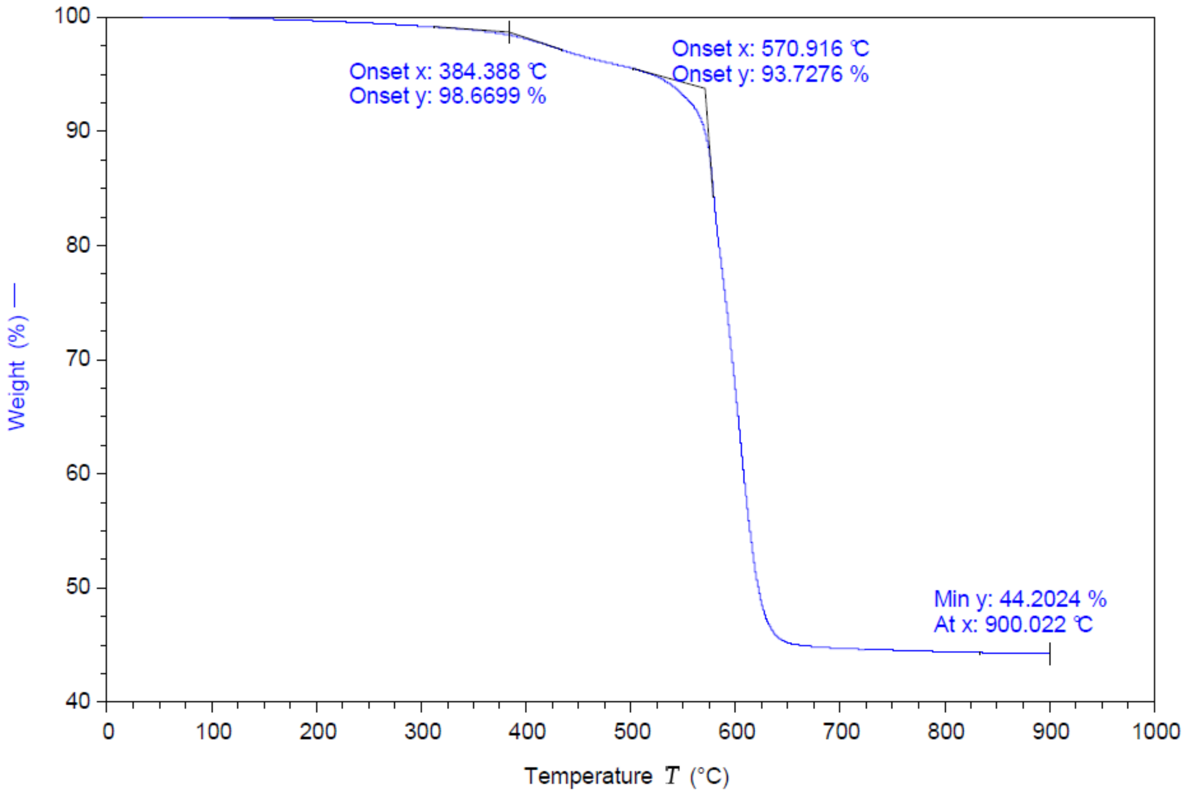

Figure S15 TGA data of the phenylsiloxaneparticles, 5 hours reaction time.

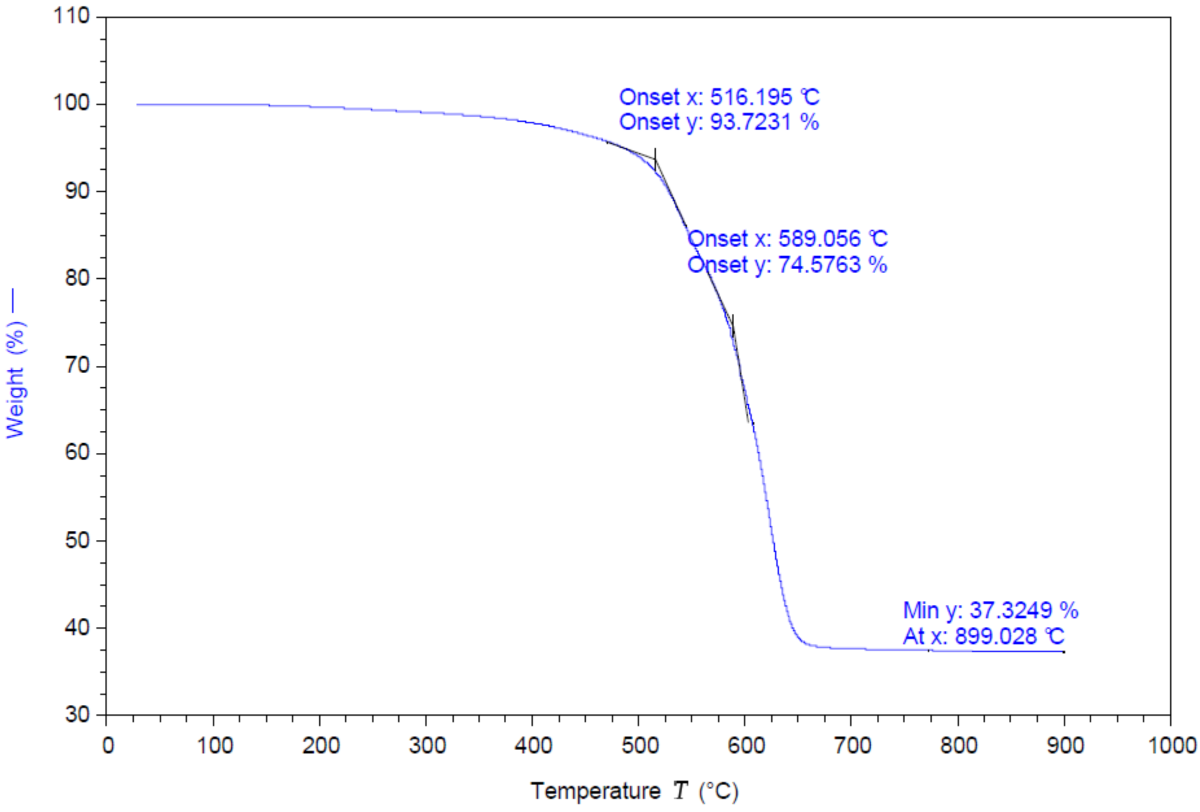

Figure S16 TGA data of the phenylsiloxaneparticles prepared using 50 vol% toluene.

10. Experimental

Materials: Phenyl trimethoxysilane (deposition grade, 98 %), ammonium hydroxide solution (30-33% solution), tetraethoxysilane (reagent grade, 98 %), tetramethoxysilane (reagent grade, 98 %), cyclohexane (ACS reagent, 99 %), 1,2-dichlorobenzene (99 %) and *o*-xylene (99 %) were ordered from Sigma-Aldrich. Mesitylene (99 %) wasordered at Fluka. Ethanol (absolute, analytical reagent, dehydrated) and toluene (analytical reagent) were ordered from Biosolve. All chemicals were used as received.

Phenyl siloxane nano spheres synthesis:
Demineralized water (300 mL) was heated to 60 ºC in a 500 mL reactor. Ammonium hydroxide solution (30-33%, 30 mL) was added in order to obtain a p*H* of 11. Phenyltrimethoxysilane (2.79 mL, 14,9 mmol) was added under mechanical stirring (250 rpm). Within approx. 3-6 minutes a milky emulsion formed. The reaction was stirred at 60 ºC for one hour. To stop the reaction, the reaction mixture was cooled on ice to room temperature. The reaction mixture was centrifuged at 3214 xG for 20 minutes after which the supernatant was removed and the pallet redispersed in ethanol. The pallet was redispersed using an ultrasound bath for 15 minutes. Afterwards the dispersion was, again, centrifuged at 3214 xG for 20 minutes after which the supernatant was removed and the pallet was redispersed in demineralized water.
When part of the phenyltrimethoxysilane in the above procedure is replaced with organic solvent, the organic solvent was added to the reaction before the phenyltrimethoxysilane is added.

11. Electron Microscopy

SEM: SEM measurements (Figure 5) were carried out using a FEI, quanta 600 microscope. Samples were prepared by drying a dispersion droplet on a cleaned microscope slide and were subsequently sputtered with a gold coating. The accelerating voltage used was 25 kV.
TEM: TEM measurements (Figure 1, 4 and 6a) were performed using a FEI Tecnai 20 (type Sphera) microscope operating with a 200 kV LaB6 filament and a bottom mounted 1024 x 1024 Gatan msc 794™ CCD camera. Samples were prepared by drying a dispersion droplet on a 200 mesh Cu grid with Quantifoil R 2/2 holey carbon film (Quantifoil Micro Tools GmbH). Cryo-TEM samples were studied on the TU/e cryoTITAN (FEI, www.cryotem.nl) operated at 300 kV, equipped with a field emission gun (FEG), a post-column Gatan Energy Filter (GIF) and a post-GIF 2k x 2k Gatan CCD camera. Sample preparation was performed using an automated vitrification robot (FEI Vitrobot Mark III) for plunging in liquid ethane (Figure 3). All TEM grids were surface plasma treated for 40 seconds using a Cressington 208 carbon coater prior to use.
STEM: STEM measurements (Figure 6b) were performed using a FEI NovaNano SEM 650 operated at high vacuum with a solid-state BSED (CBS). Beam deceleration (4 kV) is applied to reduce electron beam energy to a landing energy of 1 kV, improving resolution and contrast, providing more detailed information of the surface structure. The SEM was operated

at 5 kV, spotsize 2, a working distance of 5 mm and aperture used was 30 µm. The samples were prepared by drying a dispersion droplet on a 30 nm carbon film attached on a 300 Mesh copper grid.