



Supporting Information

for

Angew. Chem. Int. Ed. Z50930

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69451 Weinheim, Germany

Templation of Silsesquioxane Crosslinking Using Unimolecular Self Organizing Polymers

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Experimental Section.

General Methods. Commercial reagents were obtained from Aldrich and were used with out further purification. Bis(tricyclohexylphosphine)benzylidene ruthenium-(IV)-dichloride was purchased from Strem Chemicals and was used as received. THF and toluene were dried by refluxing over sodium, distilled and then degassed by three freeze-pump-thaw cycles prior to use. All manipulations were carried out using standard Schlenk or glovebox techniques under a nitrogen (N₂)

atmosphere. Deuterated chloroform was purchased from Cambridge Isotope Laboratories, Inc. Analytical TLC was performed on commercial Merck Plates coated with silica gel GF254 (0.24 mm thick). Silica Gel for flash chromatography was Merck Kieselgel 60 (230-400 mesh, ASTM). Nuclear Magnetic Resonance was performed on a Bruker AVANCE 400 FT NMR spectrometer which was used to record ^1H and ^{13}C NMR spectra unless otherwise stated. ^1H and ^{13}C NMR chemical shifts were referenced to TMS or the residual solvent peak. Gel Permeation Chromatography was performed in tetrahydrofuran (THF) on a Waters chromatograph equipped with four 5- μm Waters columns (300 mm X 7.7 mm) connected in series with increasing pore size (10, 100, 1000, 10^5 , 10^6 Å). A Waters 410 differential refractometer and a 996 photodiode array detector were employed. The molecular weights of the polynorbornenes were calculated relative to linear polystyrene standards. For TEM studies carbon-coated formvar grids (Ted Pella Inc.) were used as substrates. Field Emission Electron Microscopy (FESEM, Hitachi S-4700) was used to image the cross sectional morphology of the films. Silicon wafers were used as substrates for FESEM analysis. The dynamic mechanical analysis (DMA) measurements were done with a TA Instruments DMA 2980, under nitrogen atmosphere. The ramp rate was 5 degrees per minute. The modulated differential scanning calorimetry (MDSC) measurements were performed with the TA Instruments DSC 2920 and a ramp rate of 4 degrees per minute. The thermal gravimetric analysis measurements were done with

the TA Instruments Hi-Res TGA 2950, under nitrogen purge, and the ramp rate was 10 degrees per minute.

Preparation of unimolecular self assembling star polymer of number average radius (R_n) of 23.8 nm determined by Dynamic Light Scattering (DLS); sample B.

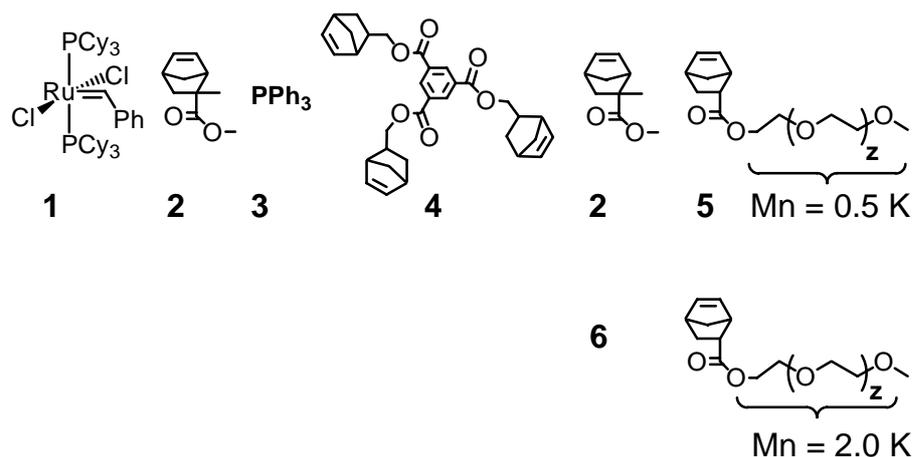


Figure 1. Numbering scheme for compounds.

The preparation of these star-shaped polymers was achieved by sequential addition of each block. Figure 1 (A) *Step 1, Preparation of Macroinitiator*: In a glove box 0.069 g (0.45 mmol) of the norbornene methyl ester **2** was added to a sample vial and dissolved in 1.4 g of toluene. Into another vial was weighed 0.0125 g (0.015 mmol) of bis(tricyclohexylphosphine)benzylidene ruthenium dichloride, catalyst **1** (Figure 1) which was dissolved in 2.4 g toluene. The norbornene methyl ester solution was added to the catalyst and the whole solution was transferred to a Schlenk flask fitted with a rubber septum. The flask was taken out of the

glovebox, connected to a vacuum line with argon as the inert gas and placed into a bath and warmed to 50 °C for 30 minutes. Sample analysis of the solution: Yield (^1H NMR) ~100%; GPC, M_n = 6000 g/mol (reference polystyrene), PDI (M_w/M_n) = 1.14. (B) *Step 2, Preparation of half star:* In the glove box, triphenylphosphine 0.0069 g (0.026 mmol) **3** was dissolved in toluene (2.14 g). This was taken out of the box and added to the reaction flask via a syringe. Into another vial was weighed the trifunctional norbornene monomer **4** (0.078 g, 0.14 mmol) which was dissolved in 7.5 g of toluene. This solution was taken up into a syringe fitted with a polytetrafluoroethylene canula. This was taken out of the box and the canula was fitted to the reaction flask containing the macroinitiator. Using a syringe pump, the crosslinker was added to the macroinitiator solution at a rate of 4 mL per hour and the reaction was allowed to stir for an additional 30 minutes. Sample analysis: Yield (^1H NMR) ~98%; GPC M_n = 85000 (reference polystyrene), PDI (M_w/M_n) = 1.18. R_h (DLS) = 8 nm. The molecular weight of the half-star determined by light scattering in THF was 158,000 (M_n). This puts an upper limit of 26 arms on this star polymer. (C) *Step 3, Growth from gel.* 0.43 g (2.5 mmol) of the norbornene methyl ester **2** was dissolved in 6 g of toluene. The solution was removed from the glove box in a syringe and added to the reaction flask. After 30 - 40 minutes, norbornene carboxylic acid ester with M_n 0.5 K PEO (0.13 g) **5** and norbornene carboxylic acid ester with M_n

2 K PEO (0.15 g) **6** was dissolved in 4.5 g of toluene and added to the reaction flask to give a gradient block copolymer shell of PEO. The reaction was allowed to stir for another 12 - 14 hours. The reaction was terminated by the addition of ethyl vinyl ether. 80% of monomer **5** was incorporated into the star as estimated from GPC intensities. Data on star **7**: $M_n = 360,000$ (reference polystyrene), PDI (M_w / M_n) = 1.3. R_h (DLS) = 25 nm.

(D) *Isolation*. The polymer could be isolated at this point, although it is susceptible to oxidative crosslinking. The solution was added to a flask and hexane was gradually added to the crude solution. The polymer formed a viscous oil at the bottom of the flask. Precipitation in this way removed any unreacted PEO monomer. The oil was dissolved and precipitated in the same fashion one additional time. To take out the residual ruthenium catalyst the oil was dissolved in THF and then passed through a plug of neutral alumina. The clear THF solution was then added directly to hexanes to precipitate the star-shaped polymer as a white fluffy solid. ^1H NMR (CDCl_3 , 400 MHz): δ 8.5 broad signal. 5.5-5.0 broad signal (peak maximum at 5.28), 4.2-3.6 broad signal (peak maxima at 4.16, 4.02), 3.58 sharp signal. 2.9-0.9 broad signals (peak maxima at 2.84, 2.53, 2.34, 2.21, 1.82, 1.31, 1.22, 1.04, 0.98) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 178.94, 177.42, 174.89, 135.47, 133.24, 131.00, 128.66, 71.71, 70.87, 69.53, 63.51, 59.39, broad signals 55-35 (peak maxima at 53.31, 51.99, 51.64, 50.51,

46.09, 44.67, 41.8, 6, 38.83), 25.11, 21.39 ppm. IR (KBr):
1748 cm^{-1} [$\nu(\text{C}(\text{O}))$].

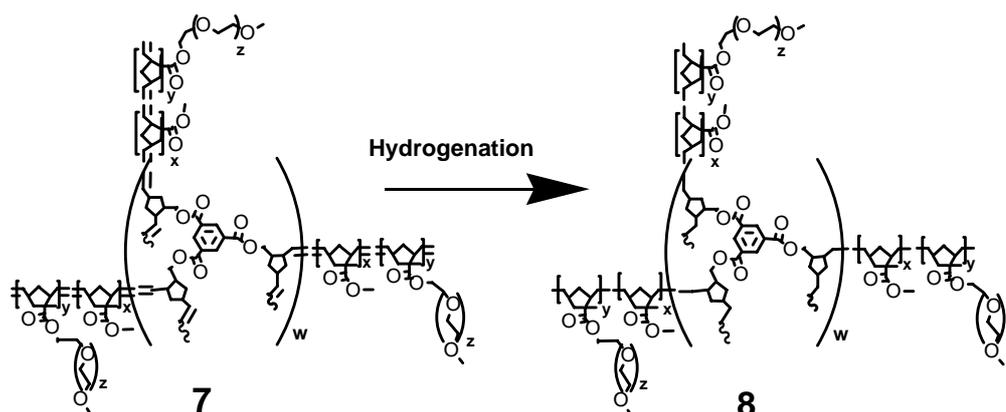


Figure 2.

(E) *Hydrogenation procedure.* Most often polymer **7** was not isolated, but was directly hydrogenated with para-toluensulfonhydrazid (1-2 g) for 24 hours in refluxing toluene (which was the original reaction solvent) under an inert atmosphere. Thinning the reaction solution with THF and then adding hexanes allowed isolation of the polymer. The material was precipitated several times to remove residual para-toluene sulfonhydrazid. The final precipitation was achieved by dissolving the polymer in a mixture of THF/ethanol and then adding the solution directly to hexanes to obtain **8** as a white fluffy solid, overall yield 0.59 g (70 %). ^1H NMR (CDCl_3 , 400

MHz): δ 3.64 sharp signal. 2.5-0.8 broad signals (peak maxima at 2.35, 2.17, 1.94, 1.88, 1.63, 1.27, 1.21, 1.17, 1.07, 0.86) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): 179.87, 178.49, 70.78, 52.18, 51.64, 50.65, 47.72, 46.45, 45.50, broad signal 39-38 (peak maximum 38.56), 36.17, 34.20, 29.69, 25.85, 20.72 ppm. (Note: For ^1H NMR, deuterated methanol or CF_3COOH , when added to the CDCl_3 was found to improve signal sharpness, consistent with the core corona characteristics of these polymers. This was not done for any of the data reported in this section).

Thermal analysis: Dynamic Mechanical Analysis: Broad $\tan \delta$ peak -25 to -15 $^\circ\text{C}$ with maximum at -20 $^\circ\text{C}$, (T_g PEO shell) broad $\tan \delta$ peak 50 to 100 $^\circ\text{C}$ with maximum at 70 $^\circ\text{C}$ (T_g norbornene core). Differential Scanning Calorimetry: T_m 45 $^\circ\text{C}$ PEO. IR (KBr): 1736 cm^{-1} [$\nu(\text{C}(\text{O}))$]

Preparation of unimolecular self-assembling star polymer with R_n 10.8 nm (DLS); sample A. The procedure for star polymer preparation was similar to that described above for the preparation of the half star. *Step 3, Growth from gel.* To the half star that had been prepared in a similar fashion to the star described above, was added 0.065 g (0.40 mmol) of the norbornene methyl ester in 2.83 g of toluene. After 30 minutes, a solution containing 0.15 g of the 0.5 K PEO norbornyl ester and 0.066 g of the norbornyl ester with a 2K PEO tail were dissolved in 4.0 g of toluene and added to the solution via syringe. The reaction was allowed to stir for

another 12 - 14 hours. 80% of monomer **5** was incorporated into the star as estimated from GPC intensities. Data on star **7**: M_n = 110,000 (reference polystyrene), PDI (M_w/M_n) = 1.2, R_h (DLS) = 11.3 nm. Isolated yield 0.30 g, 73%. The isolation procedure was similar to that described for sample B. ^1H NMR and ^{13}C NMR chemical shifts were similar to the larger star shaped polymer described above, although the signals were broadened.

Preparation of unimolecular self assembling star polymer of number average radius (R_h) of 25 nm containing contrast agent. Determined by Dynamic Light Scattering (DLS); Similar to sample B. The procedure for star polymer preparation was similar to that described above for the preparation of the half star. *Step 3a, Growth from gel, addition of contrast agent.* 0.075 g (0.2 mmol) of the norbornene methanol ferrocenyl ester **4b** was dissolved in 3 g of toluene. The solution was removed from the glove box in a syringe and added to the reaction flask containing the active half star (GPC: M_n 80,000 (reference polystyrene), PDI 1.20). The solution was allowed to stir for one hour before the next step (GPC: M_n 88,000 (reference polystyrene), PDI 1.21). *Step 3b, Growth from gel, addition of norbornene methyl ester.* 0.39 g (2.3 mmol) of the norbornene methyl ester **2** was dissolved in 3 g of toluene. The solution was removed from the glove box in a syringe and added to the reaction flask. After 30 - 40 minutes, norbornene carboxylic acid ester with M_n 0.5 K PEO

(0.13 g) **5** and norbornene carboxylic acid ester with Mn 2 K PEO (0.15 g) **6** was dissolved in 4.5 g of toluene and added to the reaction flask to give a gradient block copolymer shell of PEO. The reaction was allowed to stir for another 12 - 14 hours. The reaction was terminated by the addition of ethyl vinyl ether. 80% of monomer **5** was incorporated into the star as estimated from GPC intensities. Data on star: $M_n = 300,000$ (reference polystyrene), PDI (M_w / M_n) = 1.3. R_h (DLS) = 25 nm. ^1H NMR (CDCl_3 , 400 MHz): Similar to that described for sample B. Peaks corresponding to the ferrocenyl group was found at δ 4.19 and 4.38 ppm..

*Preparation of unimolecular self assembling star polymer of number average radius (R_h) of 11 nm containing contrast agent, determined by Dynamic Light Scattering (DLS); Similar to sample A. The procedure for star polymer preparation was similar to that described above for the preparation of the half star. Step 3a, Growth from gel, addition of contrast agent. 0.087 g (0.23 mmol) of the norbornene methanol ferrocenyl ester **4b** was dissolved in 3.5 g of toluene. The solution was removed from the glove box in a syringe and added to the reaction flask containing the active half star. The solution was allowed to stir for one hour before the next step (GPC: Mn 88,000 PDI 1.21). Step 3b, Growth from gel, addition of norbornene PEG shell. A solution containing 0.15 g of the 0.5 K PEO norbornyl ester and 0.066 g of the norbornyl ester*

with a 2K PEO tail were dissolved in 4.0 g of toluene and added to the solution via syringe. The reaction was allowed to stir for another 12 - 14 hours. Data on star: $M_n = 100,000$ (reference polystyrene), PDI (M_w / M_n) = 1.2 . R_h (DLS) = 11 nm. ^1H NMR (CDCl_3 , 400 MHz): Similar to that described for sample B containing contrast agent.

Preparation of porous films: Test structures for microscopic and dielectric characterization were prepared using standard on chip fabrication processing techniques. Copolymers of MSSQ and SiO_2 obtained from JSR Micro ($M_w = 4000$) and varying amounts (from 10 to 50 wt.%) of the star-shaped amphiphilic polymer with micellar characteristics were dissolved in a mutual solvent (e.g. 90% propylene glycol methyl ether, 10% ethylene glycol). The solutions were passed through a 1 μm Acrodisc® Glass Fiber filter and spin coated onto Si substrates. The substrate was spun at 2500 rpm for 30 seconds and placed on to a 50 °C hot plate under nitrogen to remove most of the solvent. Samples were then cured from 50 °C to 450 °C at a ramp rate of 5 °C/min and annealed at this temperature under a N_2 atmosphere for 1 hour before cooling

Thermal analysis of hybrid mixtures.

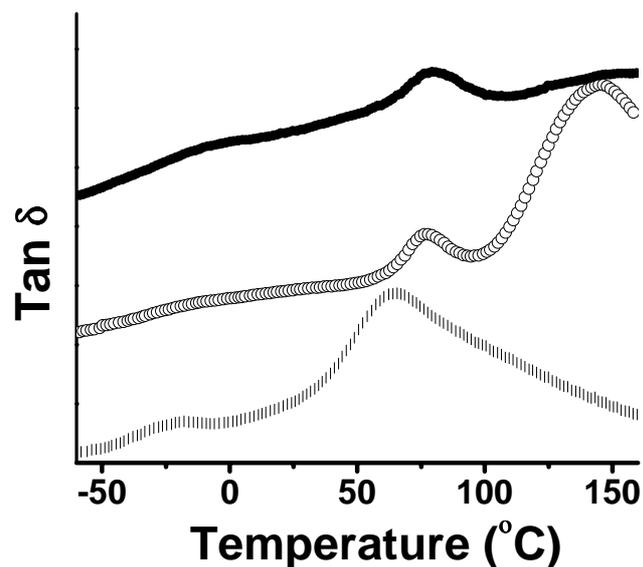


Figure 3. Tan δ curves from Dynamic Mechanical Analysis for (|) polynorbornene star-particle, (•••) Polynorbornene star in MSSQ resin after a soft cure to 150 °C and (★) after a cure to 200 °C.

Representative tan δ curves obtained from Dynamic Mechanical Analysis (DMA) for a norbornene star polymer (sample B, main text, Table 1) and the star polymer/MSSQ hybrid (20 wt.% porogen loading) after curing at different temperatures is presented (Figure 3).¹ Two Tg's were observed for the star-shaped polynorbornenes containing polyethylene oxide on the

¹ E. A. Turi, *Thermal Characterization of Polymeric Materials*, Academic Press, 1997, Vol.1.

periphery; a peak in the $\tan \delta$ at 70-75 °C corresponding to the polynorbornene backbone and an inflection point at -20 °C attributed to the amorphous portions of the polyethylene oxide segments. For the hybrid samples, the films were cured to both 150 °C and 200 °C and the DMA traces recorded. At 150 °C, partial curing of the MSSQ occurs, without decomposition of the polynorbornene. The $\tan \delta$ trace shows two maxima, one ~75 °C and another at 140 °C. The latter corresponds to the Tg of the partially cured MSSQ resin.² The other maximum in the $\tan \delta$ curve at 75-80 °C corresponds to the polynorbornene portion of the star dispersed in the MSSQ matrix. The PEO portion of the porogen (Tg -20 to -40 °C) is not detected by DMA, suggesting miscibility with the MSSQ prepolymer facilitating dispersion of the star-copolymer in the matrix. Since the MSSQ resin is only slightly crosslinked under these conditions and the Tg of the polynorbornene (Tg ~75 °C) is already evident, the core of the star-copolymer, exists as a separate, nanosized phase evenly distributed in the MSSQ resin. The porogen/MSSQ hybrid was then further cured to 200 °C. At this temperature crosslinking raises and broadens Tg of the MSSQ resin so that it is no longer separately observed in this trace. A broad maximum in the trace is still observed between 75-85 °C (Figure 3), consistent with a polynorbornene phase dispersed in the MSSQ resin. However, a distinct inflection point now appears

² Q. R. Huang, W. Volksen, E. Huang, M. Toney, C. W. Frank, R. D. Miller, *Chemistry of Materials*. **2002** 14, 3676.

at $-30\text{ }^{\circ}\text{C}$, suggesting the polyethylene oxide portion has now phase separated from the MSSQ. We anticipate that the compatibilizing PEO arms are expelled during the curing process by frustrated phase separation generating the final single polymer molecule templating morphology.

Low Frequency Dielectric Measurements.

Summary: The dielectric constants of porous MSSQ films obtained from 0, 20, 40 and 50 wt.% of star co-polymers (sample A) measured in Metal-Insulator-Semiconductor (MIS) configuration, yielded progressively decreasing values (100 KHz) of 2.8, 2.2, 1.8 and 1.7 with increasing porosity.

Procedure: A multiprobe capacitance analyzer was built to characterize the dielectric permittivity, in the frequency range 20 KHz to 1 MHz, in an array of identical MIS capacitors fabricated on a wafer. The setup has a nitrogen filled test chamber, a copper wafer holder, thermo-electric cooler, a temperature controlling unit and a multi probe station fixture to probe individual 16 MIS capacitors fabricated on a silicon wafer. A high precision LCR meter (HP4192a, from Hewlett Packard Inc.) is used to measure the capacitance of each MIS capacitor.

The dielectric constant of the porous thin films is calculated from the measured capacitance of a MIS capacitor. The dielectric layer is spin coated onto a p-doped silicon wafer

(3" X 375 mm, single side polished, boron, doped to a resistivity < 0.005 ohm-cm). The top aluminum metal contact is e-beam deposited using a shadow mask. A +1 Volt bias on the metal plate is applied to bias the MIS capacitor in the accumulation regime that avoids the influence of bias voltage and substrate type. Two calibration capacitors, built into multi-probe station, are used to measure the parasitic capacitance of the system associated with the multi-probe station probe and the LCR meter connection cables. From the thickness, measured independently, and capacitance measurement of each capacitor, the dielectric constant of thin film is calculated by averaging all these measured data to improve the measurement accuracy.