

Electronic Supplementary Information

Sol Preparation

One pure silica sol was prepared using a single-step acid-catalysed hydrolysis of TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$) in ethanol ($\text{C}_2\text{H}_5\text{OH}$). Nitric acid (HNO_3) was chosen as catalyst. These reactants were mixed together with distilled water (H_2O), in the molar ratio $\text{TEOS} : \text{C}_2\text{H}_5\text{OH} : \text{HNO}_3 : \text{H}_2\text{O} = 1 : 3.8 : 0.085 : 6.5$. This mixture was refluxed for 3 hours at 60°C to yield the pure SiO_2 sol.

One methylated silica sol was prepared analogously to the silica sol. MTES ($\text{Si}(\text{OC}_2\text{H}_5)_3\text{CH}_3$) was used as a source for the methyl groups. A mixture with the same composition as above was refluxed for 2 hours and 45 minutes. At this stage MTES was added in the molar ratio $\text{MTES} : \text{TEOS} = 1 : 1$. The mixture thus obtained was further refluxed for another 15 minutes.

Several methylated silica sols with different methyl concentrations were prepared using a two-step process. A mixture with molar ratio $\text{TEOS} : \text{C}_2\text{H}_5\text{OH} : \text{HNO}_3 : \text{H}_2\text{O} = 1 : 3.8 : 0.0036 : 2.0$ was refluxed at 60°C for 90 minutes. At this stage MTES was added with a molar ratio $\text{TEOS} : \text{MTES} = 10 : 1, 10 : 3, 10 : 4, \text{ or } 10 : 6$, and the reflux was continued for another 30 minutes. This was followed by the addition of more nitric acid and water so that the final molar ratio was $\text{TEOS} : \text{C}_2\text{H}_5\text{OH} : \text{HNO}_3 : \text{H}_2\text{O} = 1 : 6.2 : 0.0108 : 6.0$ with variable MTES content. Finally, this was refluxed for 3 more hours, before it was diluted with ethanol. We were unable to prepare membranes for the sols with $\text{TEOS} : \text{MTES} = 10 : 4$ and $10 : 6$.

Gel Permeation Chromatography.

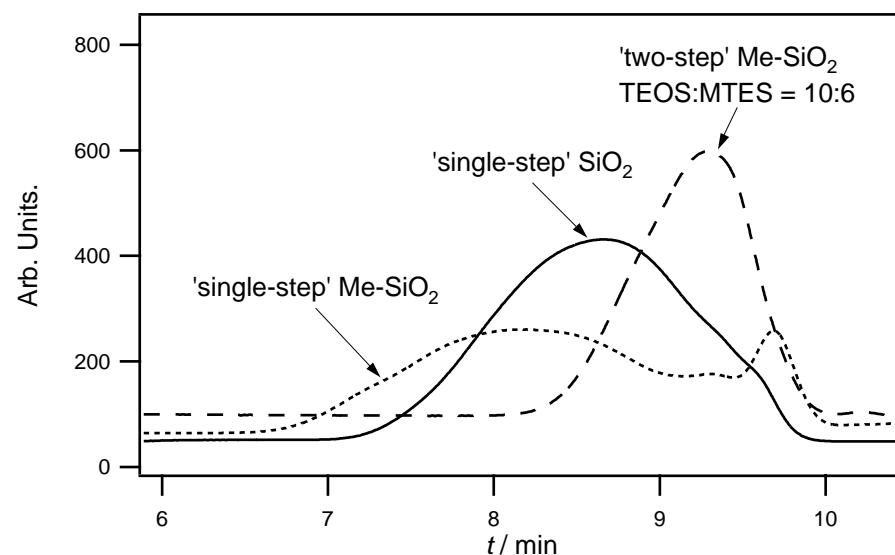


Figure 1S: Particle size distribution as a function of the elution time of the sols prepared with the 'single-step' procedure and the sol prepared with the 'two-step' procedure with $\text{TEOS}:\text{MTES} = 10:6$. We were unable to prepare a membrane from this last sol.

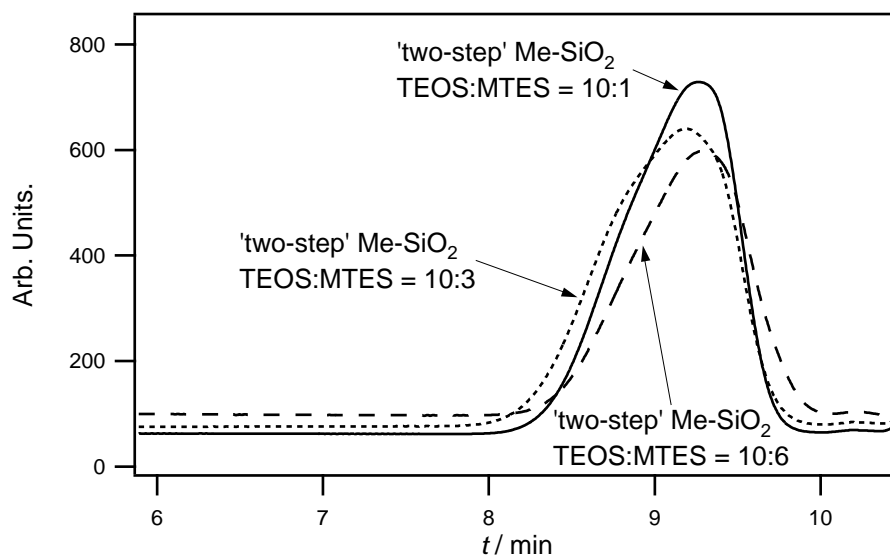


Figure 2S: Particle size distribution as a function of the elution time of the sols prepared with the 'two-step' procedure with TEOS:MTES = 10:1; 10:3, and 10:6. We were unable to prepare a membrane from this last sol.

The molar mass (M_w in kg/mol) can be calculated from the elution time (t , min) using $M_w = 10^{(-0.66t + 6.26)}$.

Nuclear Magnetic Resonance

Solid state ^{29}Si NMR spectra were collected on free-standing films prepared analogously to the membranes. The spectra were recorded on a Bruker MSL300 and Bruker MSL400, using a spinning rate of 4 kHz and one-pulse experiments with 90° pulses and 100 s recycle delay time. The number of acquisitions varies between 200 and 700, which corresponds to a measurement time of 5 to 19 hours. The summed concentration of T groups is equivalent to the methyl concentration.

Table 1S: The concentration of tetrafunctional (Q_i , from TEOS) and trifunctional (T_i , from MTES) units in free-standing films prepared from various sols.

TEOS : MTES	10 : 1	10 : 3	10 : 6	10 : 10
preparation route	two-step	two-step	two-step	single-step
CH_3/Si	0.09	0.23	0.37	0.50
T_{tot}	0.13	0.22	0.36	0.45
T_2	0.02	0.05	0.13	0.22
T_3	0.11	0.17	0.23	0.23
Q_{tot}	0.88	0.79	0.65	0.55
Q_2	0.04	0.05	0.05	0.02
Q_3	0.31	0.32	0.32	0.15
Q_4	0.52	0.42	0.28	0.38

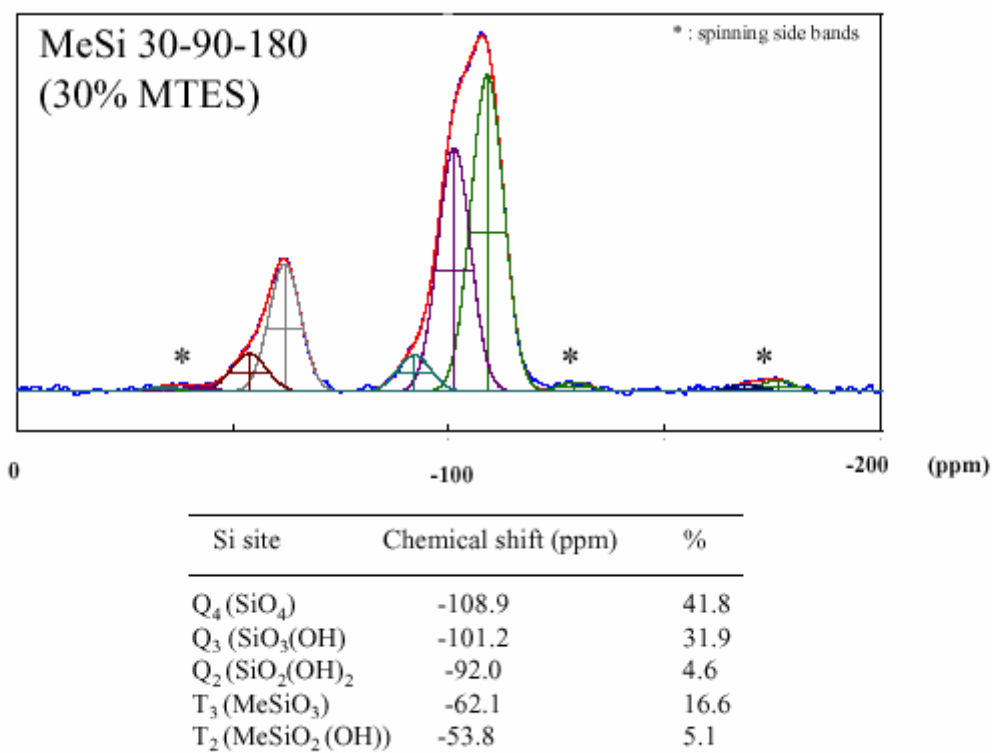
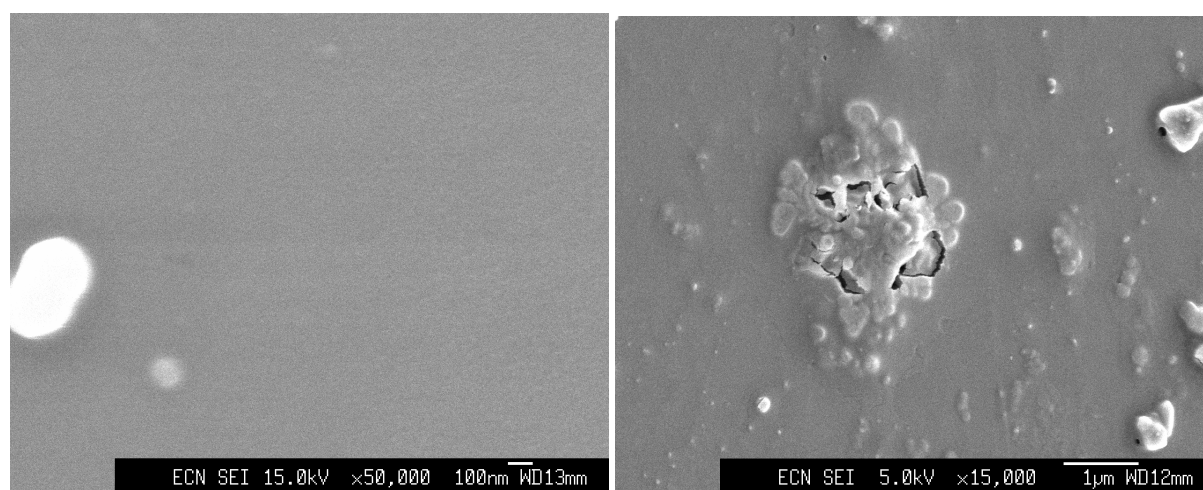


Figure 3S: Sample NMR spectrum including fit and numerical results for a methylated silica film prepared from a 'two-step' sol with initial TEOS : MTES ratio of 10 : 3.

Scanning Electron Microscopy



a) b)
Figure 4S: Two SEM micrographs showing typical surface appearance of a membrane before testing in pervaporation. The great majority of the membrane surface looks like the micrograph in a). Imperfections on the μm scale, as depicted in b), are present.