Supplemental Information: Mesoporous Organosilicate Films using Cross-Linked Micelle Pore Generators

Supplemental Figure 1. NMR of compound (1)
Supplemental Figure 2. NMR of compound (2)
Supplemental Figure 3. NMR of compound (3)
Supplemental Figure 4. NMR of compound (4)
Supplemental Figure 5. GPC plots of compounds (1), (2), (3), and (4)
Supplemental Figure 6. Calculated size distribution on uncross-linked block polymer (4) in methanol.
Supplemental Figure 7. Calculated size distribution of the cross-linked micelle in methanol initially after cross-linking and dialysis
Supplemental Figure 8. Calculated size distribution of the cross-linked micelle after 3 months in methanol
Supplemental Figure 9. a) AFM image of cross-linked micelles deposited on a silicon wafer at 0.01 mg/mL from methanol. b) Cross-sectional profile of a cross-linked micelle. The crosses on the AFM image Supplemental Figure 7a correspond to the dashed lines in Supplemental Figure 7b.
Nanoindentation protocol

Calibration:
Fused silica is used for calibration. The tip is a NorthStar cube corner probe. The probe had a radius of about 25nm when we began and is about 35nm now. The highest load is 10000uN and the smallest load is 60uN. These result in indentation depths of 500nm on the upper end and about 8nm on the low end. The probe is calibrated for the tip area function using C0, C1 and C2 coefficients for the zeroth, first and second order. Thus the tip shape will be described as a parabola. This is done for data which is fit for depth up-to 90nm. The fit is performed on the unload portion between 98% and 50% of the unload portion of the curve. The load function is 5-2-5 same as described below for your samples. The machine compliance was established with a berkovich probe and not a cube-corner probe. (mostly due to manufacturer's recommendations). The tool is Hysitron Triboindenter 950 system with a PerforMech controller.

Measurements:
With the same probe post calibration your samples are run. In general loads are 3uN, 5uN, 7.5uN, 10uN, 12.5uN, 15uN, 20uN, 25uN and 30uN. In our experience these loads are sufficient to evaluate samples with reduced modulii from 1.5GPa to 15GPa. Seven indents are performed separated by 10um each for every load, this absolutely ensure no cross-talk between measurements. The probe locates the surface with a set-point of 700nN. For each indent the probe and the sample equilibrate for a total of 2min. This is after the samples have thermally equilibrated for more than 8 hours. We also have a positive flow of nitrogen into the indenter enclosure so the samples are in a very dry environment for 8 hours at the minimum. We have not tried to quantify the level of moisture in the chamber but a sample of 'dri-rite' takes more than 15 days to change color. This is usually because while loading moisture gets into the chamber. The approximate drift into the sample at the set-point load varies from sample to sample with a minimum of 3nm and a maximum of about 15nm. This is a very complex number to predict as you would realize.

Once the drift rate is established usually less than 0.05nm/sec the indenter tip pulls 50nm away from the sample. Then it approaches the sample to perform the actual indent. The load function is set at 5-2-5, 5
load, 2 hold and 5 unload. Thus different loads end up with different loading rates. The probe then
withdraws and goes onto to perform the same load a different point or a different load. Then each of the
load vs. displacement curves is manually offset to determine the point for zero displacement for zero load.
This usually offsets the curves anywhere from 3nm to 15nm depending on the sample and pre-load. The fit
% is then decided for a family of curves at a particular load for the fit to ensure zero displacement at zero
load condition is satisfied. This is possible most of the time (>90%) but at times it is not possible. The
maximum fit region is 98% to 50% and 98% to 70% at a minimum. This data is fit to the parabolic area
function. For each load there are seven measurement. Many times the first measurement is the one most
affected by drift so needs to tossed out. So we have six measurements at-least at each load enough to define
a mean and a standard deviation. This is done for each load for a given sample. Thus we end-up having
about 50 independent measurements on each sample. Then we plot a graph of reduced modulus vs. contact
depth (not actual depth but both are correlated) and hardness vs. contact depth. For most materials we see a
classic soft sample on a hard substrate type effect where there is a small slope in the reduced modulus
curve. Then since we know during calibration what the approximate end radius of the probe is we choose
depths and modulus to get average reduced modulus. These usually end up being depths from 14nm to
22nm. Thus different materials have different loads which give such contact depths. In most of the cases
(>90%) we measure increasing modulii for higher contact depths and vice versa. This is expected due to
soft film on a harder substrate effect. The hardness is also averaged for the same contact depths. Thus the
reported avg. reduced modulus values are at least 20 independent data points averaged together. The graphs
are plotted with +/- one standard deviation on the values for each load. We have not had a sample where the
variation of the data on a sample for a load was more than 10% usually it is close to 5%. We have also done
repeated measurements on a sample which have been within 5% and batch to batch correlations which have
been similarly close.

The nanoindentation value listed in this manuscript is the intercept modulus. This is a Y-intercept of the
modulus data for zero displacement. In the absence of an ability to have a super-sharp probe and to do very
shallow indents this is a relatively good measure of the absolute minimum modulus for any given film. This
takes into account to the first order the soft film on a hard substrate effect. The hold portion of 2-seconds gives us a measure of creep-behavior of the film.

Once the measurements are over for one sample, the probe is 'cleaned' by doing 7 indents in quartz ranging with loads from 8000uN to 60uN. The process is then repeated for the next sample. The probe is re-calibrated every 1000 indents or so, thus about every 20-25 samples. Over the course of 1.5 years the probe end radius has changed from 25nm to 35nm. Thus there is probe-wear but not substantial. The samples themselves are glued with cyano-acrylate based super-glue onto a stainless steel puck. Extreme care is taken to ensure that the glue does not flow to the sides where the your material will absorb it. In case that happens the color change on the sides is very evident; the sample is discarded and a new sample prepared. The sample are held with a magnetic mount onto the base of the indenter. We had done tests with the manufacturer provided calibration quartz and super-glued quartz and found the machine compliance to be very similar thus the method of mounting samples with super-glue is reliable.