Supplementary Material (ESI) for Soft Matter

ELECTRONIC SUPPLEMENTARY INFORMATION

for

Cellulose-decorated cavities on ultrathin films of PMMA

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S1. Finding the TMSC/PMMA ratio for circular cavity formation

Laterally phase separated polymer blend films usually show patterns that are reminiscent of phase separation in spinodal decomposition. However, when the ratios become uneven, the minority phase tends to coalesce into droplets with roughly circular radial cross sections. The point in TMSC/PMMA weight ratios where the bicontinuous structures of the minority phase (TMSC and subsequently cellulose) start to arrange into droplet-like shape was determined experimentally. Figure S1 illustrates how the minimum TMSC/PMMA weight ratio for droplet formation was found.

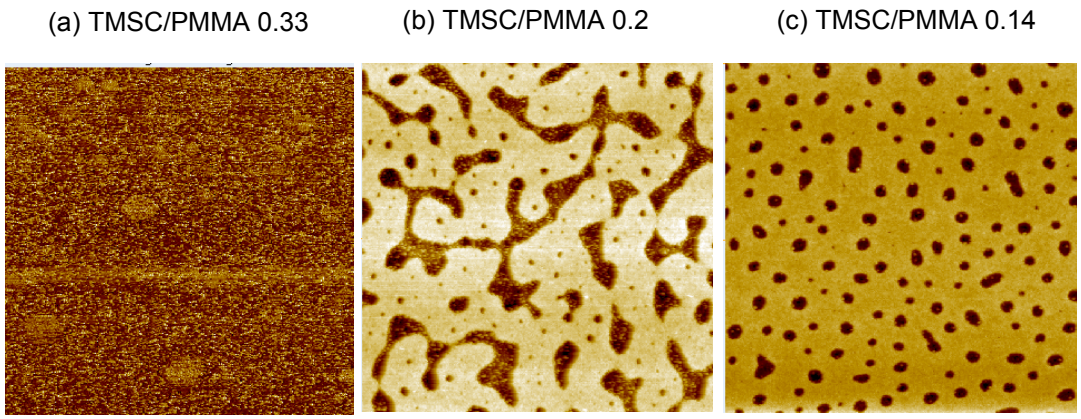

Figure S1. *5×5 μm^2 AFM height images of spin coated films of TMSC/PMMA blends where TMSC has been hydrolysed to cellulose after the film deposition. The initial TMSC/PMMA (w/w) ratios in the blends are (a) 0.33, (b) 0.20, (c) 0.14.*

S2. Image analysis of AFM data

AFM images from cellulose/PMMA films were subjected to image analysis by Scanning Probe Image Processor (SPIP, version 4.5.3) (Image Metrology, Lyngby, Denmark). Grain Analysis feature with Threshold algorithm was applied to measure the width, length and depth (z-range) of the cavities as well as their number and coverage. Threshold algorithm selects a certain plateau below which all the quantifiable features are regarded as cavities. Figure S2 demonstrates the image analysis of cellulose/PMMA film from a TMSC/PMMA ratio of 0.10. Three different samples were used of which three different (5×5 μm^2) images were scanned. In consequence, the AFM data in Figures 4 and 5 stems from 9 different images for each point in the graphs.

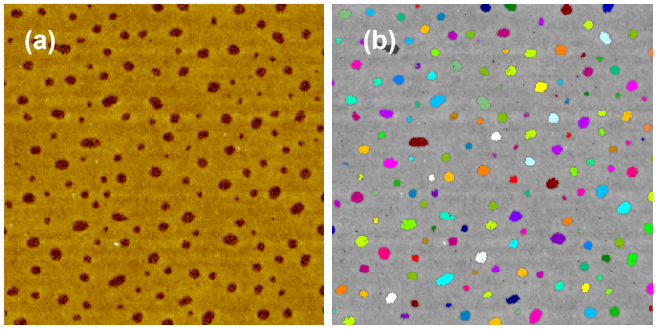

Figure S2. *5×5 μm^2 AFM height images of spin coated films of TMSC/PMMA 0.10 (w/w) ratio blends where TMSC has been hydrolysed to cellulose after the film deposition. (a) Normal height image, (b) height image where the analysed cavities are indicated by colours against the grey background (plateau).*

It is evident from Figure S2 that not all the cavities are circular in their radial cross section, especially with the higher TMSC/PMMA ratios (≥0.10). Since a common measure is desired for all the films, we opted for as assumption that all the cavities can be considered circular, *i.e.*, having a uniform diameter. This was achieved by adding together the width and the length of each cavity and dividing the sum by two. The average of these apparent diameters has been used in Figure 4.

S3. X-ray Photoelectron Spectroscopy (XPS)

X ray photoelectron spectroscopy (XPS) was used for surface chemical analysis, since AFM yields mainly morphological data. XPS measurements were performed with an AXIS 165 (Kratos Analytical, Manchester, UK) spectrometer using a monochromated Al Kα X-ray source at 100W under neutralisation. Samples were measured together with an *in-situ* reference after long pre-evacuation,[S1] in order to stabilise experimental conditions. Elemental surface compositions were determined from 1-1100 eV scans recorded with 80 eV pass energy and 1 eV step. Surface chemistry was monitored from high-resolution spectra of O 1s, C 1s and Si 2p regions, recorded with 20 eV pass energy at 0.1 eV step. Each specimen was measured at 2-5 different locations. No sample deterioration was detectable due to radiation or UHV exposure.

The high resolution XPS data confirmed that the surfaces consisted of PMMA and TMSC (in the case of TMSC/PMMA films) and PMMA and cellulose (in the case of cellulose/PMMA films). In wide scans we saw small contribution from the silicon substrate, too (see later). This complicated the analysis, as Si is the best indicator of the TMSC here. However, it was also an advantage, since this could be used as independent, alternative evaluation of the film, via elemental depth distributions, according to Tougaard.[S2,S3]

In order to visualize clear changes in the spectra, a wider range of polymer ratios was applied in the XPS analysis than in the main text (TMSC/PMMA ratio from 0.5 to 0.05 in contrast to 0.14 to 0.05 in the main text). With this setup, the change in the spectra due to decreasing TMSC/PMMA ratios was clear. In the wide spectra this showed up mainly in decreasing Si (Fig. S3). In the C 1s high-resolution spectra, the increase in the carbonate peak (indicative of PMMA) and a shift in non-resolvable first component (from C-Si of the TMSC towards the CC of the PMMA) were observed (Fig. S4).

XPS confrmed also that in desilylation the TMSC was transformed into cellulose without significant changes in the PMMA surface concentrations (see example in Fig. S5). Since there were no signs of the C-Si bond, the observed Si in these specimens must have originated from the substrate. The strong inelastic background tailing the Si peaks, indicative of a covered elemental distribution, confirmed this interpretation, too.

In the cellulose-PMMA films, the Si signal from the substrate was found to remain similar throughout the series, apart from the desilylated specimen with the highest TMSC-PMMA ratio (see Fig. S3, ratio 0.5, not reported elsewhere). However, this sample was found to form a double layer structure without indentations, so the substrate signal is expected to be subdued due to more uniform film covering it.

Furthermore, the Si background intensity in pairs of original-desilylated films was found to be similar, in spite of difference in the silicon peak intensities. This confirms that the surface coverage of the polymer film did not change significantly in desilylation. Thus, the substrate silicon should not contribute significantly to the changes observed in the TMSC-PMMA data in Fig. S3.

References

S1. L.-S. Johansson, J. Campbell, *Surf. Interface Anal.* 2004, **36,** 1018.

S2. S. Tougaard, A. Ignatiev, *Surface Sci*. 1983, **29**, 355.

S3. L.-S. Johansson, *Surf. Interface Anal*. 1991, **17**, 663.

S4. M. Holmberg, J. Berg, S. Stemme, L. Ödberg, J. Rasmusson, P. Claesson, *J. Colloid Interface Sci.* 1997, **186**, 369.

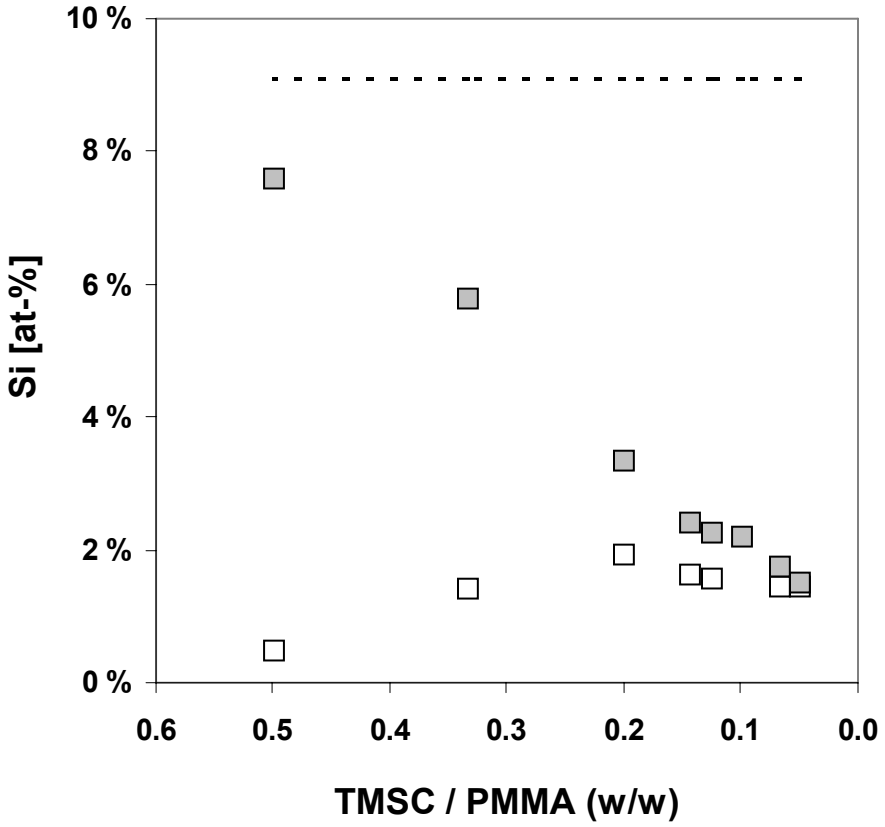

Figure S3. *Percentage of silicon, as determined by XPS from the TMSC/PMMA films (closed symbols), and from cellulose/PMMA (open symbols) films. The decrease in TMSC correlates with the decrease in apparent diameter (Figure 4) and coverage (Figure 5) determined from the AFM data. Note: broken line indicates XPS data for bulk TMSC film.*[S4]

S4. Spincoated TMSC/PMMA films before hydrolysis

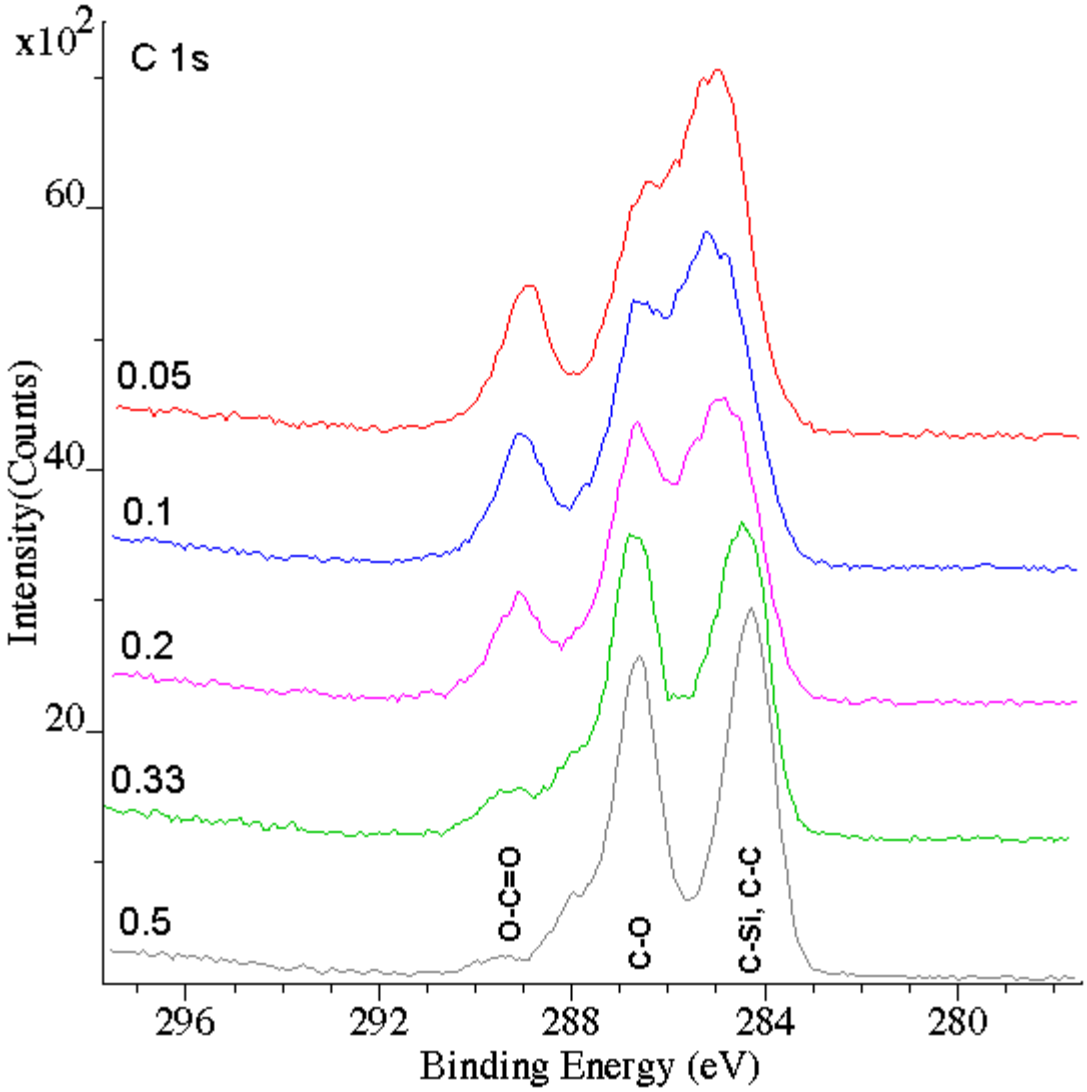

Figure S4. *C 1s high-resolution XPS spectra of five ultrathin spin coated films with varying TMSC-PMMA ratio.*

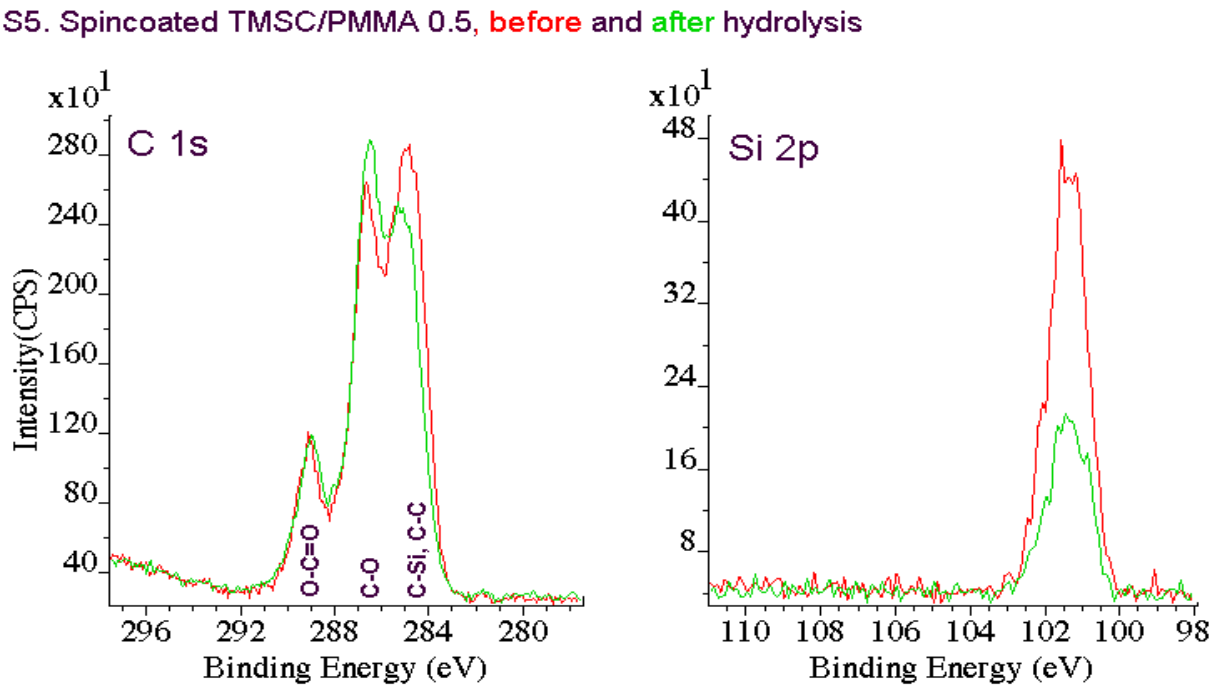

Figure S5. *C 1s and Si 2p high-resolution XPS spectra of spin coated ultrathin films with TMSC-PMMA ratio of 0.5, recorded before and after hydrolysis.*