Influence of Substrate Wettability on the Morphology of Thin Polymer Films Spin Coated on Topographically Patterned Substrates

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Supporting Online Information

S1.0 Swelling of the Sylgard 184 (cross linked PDMS) Substrates during Spin Coating of Polystyrene films from Toluene

Typically, in standard spin coating, a substrate that is chemically inert to both the solvent and the solute (the polymer, in this case) is used. However, the substrates used here (cross linked Sylgard 184 substrates, type 1A) are themselves polymeric substrates and therefore may not be completely inert to the solvents during coating of the film on them, particularly as toluene is a good solvent for PDMS too. It may however be pointed out that there is an increasing trend of using polymeric substrates for casting thin films in various types of experiments.[1–8] For example, a cross linked PDMS substrate (similar to type 1A substrates used in the current study) has been used as a substrate on which direct spin coating has been performed from solvents like toluene, n-hexane, n-heptane etc. (each one is a good solvent for PDMS) in several recent articles on dewetting of thin polymer films on soft substrates,[1] dewetting of thin polymer films on topographically patterned substrates,[2-4] studies involving polymer bilayer and multilayers etc.[5–9]

Thus, the issue of spin coating on a substrate which shows limited interaction with the dispensed solution is no longer that unique. Actually, some of the papers cited above does include discussion on the possible interaction between the solvent and the polymeric substrates and show that swelling **does not** play a significant role during film coating, particularly when a cross linked PDMS substrate is used. This is attributed to a very low contact time between the solvent and the polymer substrate during spin coating.[5,8,9] The scenario is in clear contrast to other types of experimental arrangements like flow of solvent through a micro fluidic channels fabricated in cross linked PDMS matrix, where a large contact time results in significant (up to ~ 35 %) swelling.[10]

With the following set of experiments, we have also verified in course of this work that that swelling is NOT a major concern with the cross linked PDMS (type 1A) substrates used in our experiments (type 1 substrates).

For checking the swelling effects during spin coating on a patterned type 1A substrate, we dispensed a few drops of the solvent (toluene) only (without any polymer) on the substrate (figure S1A) and subsequently spun it (the solvent) on a spin coater. In this "solvent spinning" step, the solvent interaction time with the substrate PDMS layer is identical to that during actual spin coating of the film. However, as there is no polymer present in the dispensed drop, so whatever structural or morphological changes result to the substrate due to it's interaction with the dispensed solvent becomes evident after the "polymer free solvent" spinning step is complete. In order to ascertain if there is any damage or change to the substrate patterns due to solvent interaction, the substrate is scanned with an AFM before (figure S1A) and after (figure S1B) the "solvent spinning" step. It can be clearly seen, by comparing the two figures (S1A and S1B) and the cross sectional line scans provided as insets, that there is no change in the topography of the substrate, in terms of height or lateral dimension of the features due to the "polymer free solvent" spinning.
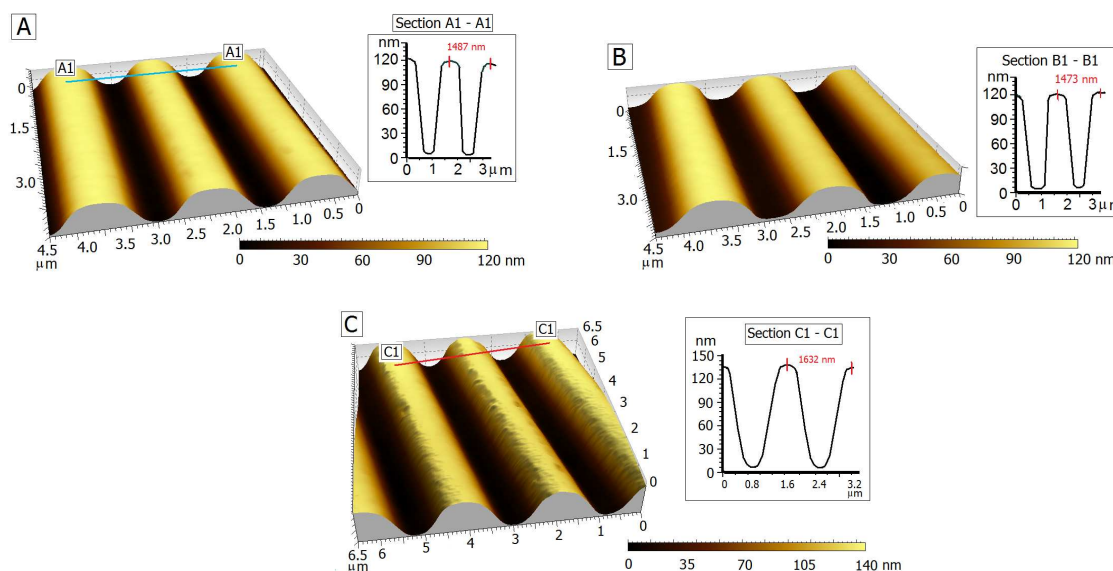

Figure S1: AFM image of a CD imprinted Sylgard 184 film (A) before and (B) after spinning for 1 minute with 200 µl of dispensed toluene. The cross sectional analysis shows no significant swelling or any other structural changes due to the interaction of the film with the solvent.(C) AFM scan of a type 1 substrate after immersion in toluene for 15 min.

While it might be tempting to conclude from the above observation that there is no solvent induced swelling during spinning, one may, at this stage, raise a valid question that whether such an approach (using an AFM) can at all be used for checking the swelling of a substrate.

To check the validity of this approach (if swelling of a structured PDMS substrate can at all be checked with an AFM or not!) a patterned cross linked PDMS (type 1A) substrate was kept immersed in toluene for 15 minutes (prolonged contact time, in comparison to spin coating). The sample, after withdrawing from the toluene bath was scanned with an AFM (figure S1C) where it can be seen that the stripe periodicity (λ_P), height (**h**) and width of the patterns (**l$_P$**) have all increased to ~ 1632 nm, ~ 137 nm and ~ 822 nm respectively, in contrast to their original values of λ_P ~ 1490 nm, **h** ~ 120 nm and **l$_P$**~ 755 nm (observed in figures S1A and S1B). It is obvious that this enhancement in feature dimensions is entirely attributed to swelling, which is further verified from the fact that the pattern dimensions are back almost to their original values after drying the sample used in figure S1C for 14 hours (and subsequently scanning it). It can also be seen in figure S1C that there is some degree of loss of fidelity of the patterns due to swelling. Further, the slight roughness seen on surface of the stripes in figure S1C (in comparison to smooth stripes in both S1A and S1B) probably indicate localized sticking of the AFM tip in contact with the softened and swelled PDMS substrate, due to prolonged immersion in toluene.

Thus, figure S1C firmly reiterates that AFM scan can indeed be used as a first approximation to check solvent induced swelling of a patterned polymeric substrate or film. Therefore from figure S1B one can convincingly argue that within the time frame of spin coating, there is virtually no effect of swelling on a plain patterned cross linked PDMS substrate.

Plazma oxidation of a Sylgard 184 film or layer results in a thin oxide crust layer which makes the layer completely wettable (CW) by toluene. In addition, it is also believed that this layer is impermeable and acts as a diffusion barrier, resisting any penetration of the solvent into the polymer matrix. This was convincingly verified by us, following the protocol described above, as we kept a plazma oxidized patterned Sylgard 184 substrate immersed into toluene for 15 minutes, and upon subsequent scanning it was found that there is no change in the lateral or vertical dimensions of the patterns. Thus, the silanized plazma oxidized substrates (type 3A substrates) used in some of our experiments are also completely swelling resistant.

S2: Morphological transition with increase in c_n on a patterned type 3A substrate (details of the substrate available in Table 1 of the main article)
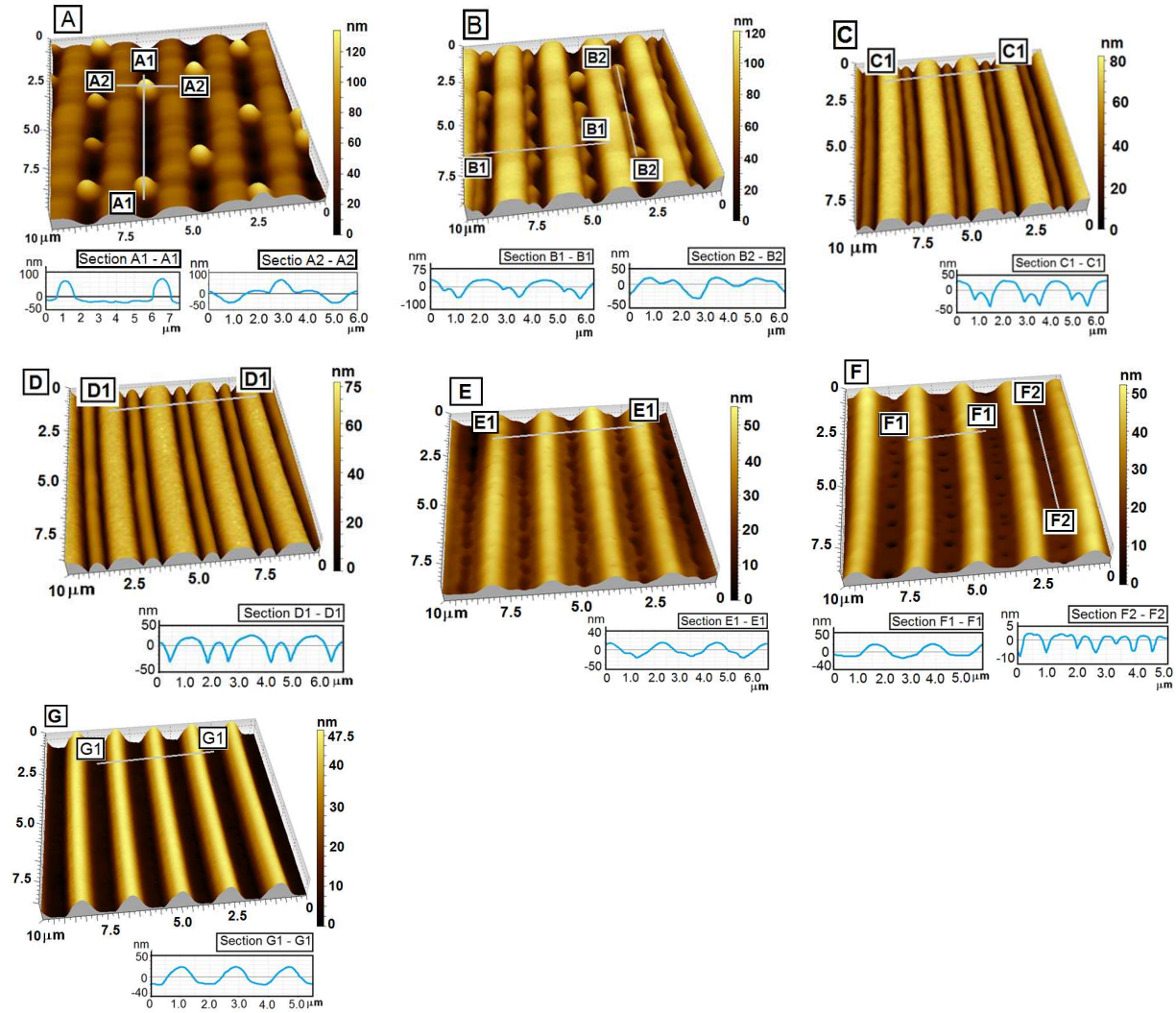

Figure S2: AFM images showing the morphological transition as a function of c_n obtained by direct spin coating of PS solution from toluene on a topographically patterned, type 3A PW substrate. (A) Array of droplets for $c_n \sim 0.15\%$; (B) Elongated droplets for $c_n \sim 0.25\%$; (C, D) thin polymer strips confined within the channels, for $c_n \sim 0.50\%$ and 1.00% respectively. (E) Signature of advancing meniscus of polymer for $c_n \sim 1.35\%$; (G) For $c_n \sim 1.50\%$, a film morphology where two ridges on the film surface are separated by a valley containing a well ordered array of nearly equal sized holes; (H) A continuous film covering the substrate fully with an undulating top surface for $c_n \sim 2.0\%$. Cross sectional line scans shown as insets to each frame.

S3: Morphological transition with increase in c_n on a patterned type 2A substrate (details of the substrate available in Table 1 of the main article)
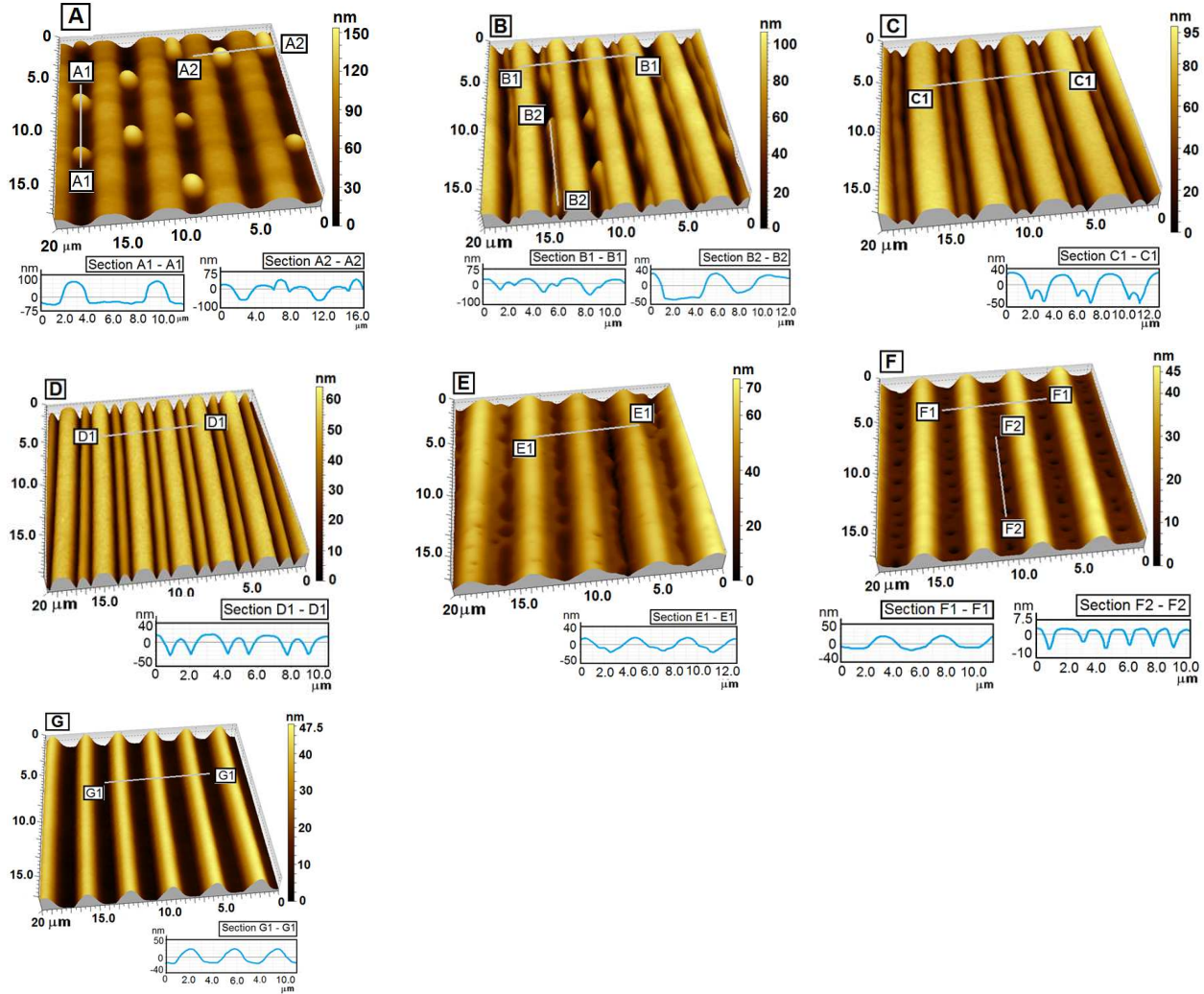

Figure S3: AFM images showing the morphological transition as a function of c_n obtained by direct spin coating of PS solution from toluene on a topographically patterned, **type 2A** PW substrate. (A) Array of droplets for $c_n \sim 0.25\%$; (B) Elongated droplets for $c_n \sim 0.4\%$; (C, D) thin polymer strips confined within the channels, for $c_n \sim 1.50\%$ and 2.50% respectively. (E) Signature of advancing meniscus of polymer for $c_n \sim 2.80\%$; (G) For $c_n \sim 3.0\%$, a film morphology where two ridges on the film surface are separated by a valley containing a well ordered array of nearly equal sized holes; (H) A continuous film covering the substrate fully with an undulating top surface for $c_n \sim 4.5\%$. Cross sectional line scans shown as insets to each frame.

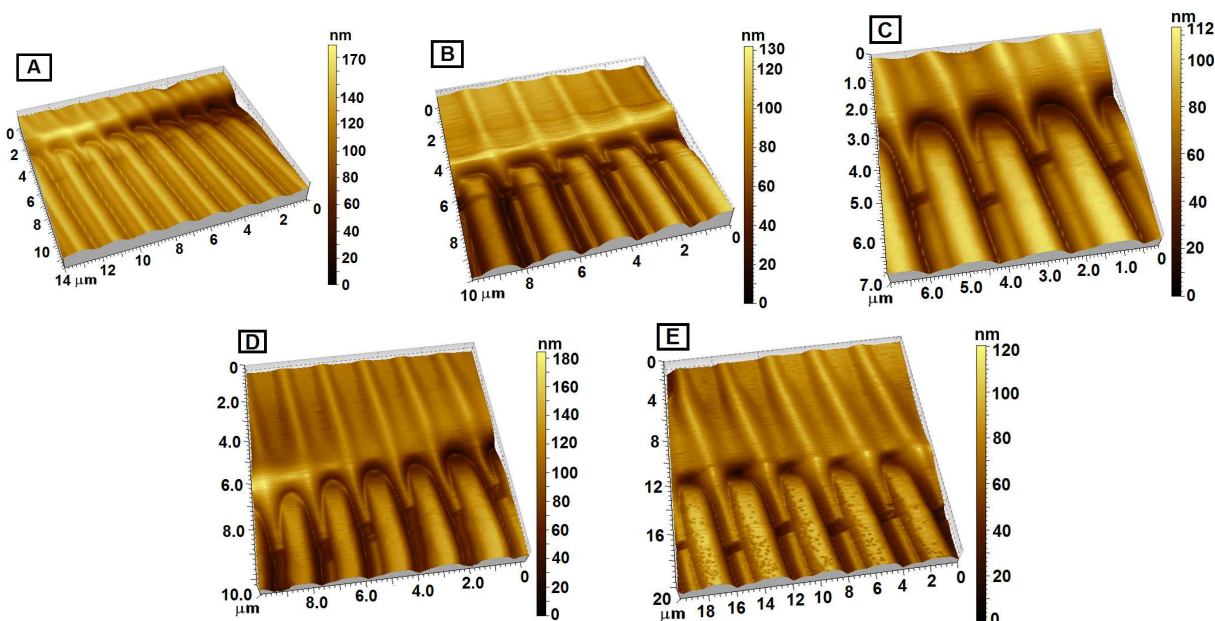**S4: Verification of out of phase pattern formation on patterned PW substrates in different experiments**

Figure S4: AFM images of areas where the film has been partially removed to uncover the underlying substrates, to verify the formation of 180° out of phase structures on PW substrates. (A) Substrate 1A, c_n ~ 3.0 %, polymer: **PS**; Solvent: **Toluene**; (B) Substrate 3A, c_n ~ 2.5 %, polymer: **PS**; Solvent: **Toluene** (C) Substrate 1A, c_n ~ 2.5 %, polymer: **PS**; Solvent MEK; (d) Substrate 3A, c_n ~ 2.5 %, polymer: **PMMA**; Solvent: **Toluene**; (E) Substrate 2A, c_n ~ 5.0 %, polymer: **PS**; Solvent: **Toluene.** In all cases, **200 µl** dispensed drop volume is used and RPM is 2500.

The above set of images shows that the out of phase pattern formation is a generic phenomenon, irrespective of the polymer and the solvent used, and depends only on the partial wettability of the substrate.

S5: Influence of Spin Speed on the morphology (on the PW substrates)

We performed some experiments in which the spin speed was varied. We observed that the morphological transition sequence as shown in figure 2 (and figures S2 and S3) remains nearly identical irrespective of the RPM. However, the transitions (from droplets to threads; from a discontinuous film to a continuous film etc.) occur at different concentrations with variation of RPM. For example, while we observe a morphology comprising array of isolated threads for c_n ~ 1.25 % at 2000 RPM, an array of isolated droplets is observed (similar to that shown in figure 2B, obtained for c_n ~ 0.1% for RPM of 2000) is obtained when RPM is 4000 and c_n ~ 1.25 %.

On the other hand a continuous film (similar to that shown in figure 2H, for $c_n \sim 1.75$ % at 2000 RPM) is obtained for $c_n \sim 1.25\%$ itself, at an RPM of 800.

The trend clearly shows that the nature of the morphological transformation remains same with change in RPM. However, one obtains a continuous at a higher concentration (c_t^*) at higher RPM and c_t^* is lower if RPM is low. We further checked that the continuous film on a PW patterned substrate is also out of phase, for different RPM.

Reference:

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