# **Supporting Information**

# Transient block copolymer topologies for generating nanoporous polymer membranes

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# Volatility of the casting solvents

The vapor pressures at 20°C are given by  $p_{THF}^0 = 173$  mbar and  $p_{DMF}^0 = 3.8$  mbar, i.e. THF has a 48-fold vapor pressure compared to DMF (see Table S1). Assuming a similar diffusivity of the two solvents (similar values of  $\lambda$ ) we expect a similar ratio of 48:1 for the evaporation rates.

Evaporation rates were measured for the pure solvents. The data are displayed in Table S1

**Table S1.** Measured loss of weight for the pure solvents THF and DMF starting from 70  $\mu$ L and 50  $\mu$ L respectively.

THF (70 μL)		DMF (50 μL)	
Time [sec]	Mass [mg]	Time [sec]	Mass [mg]
0	61.2	0	48
5	54.2	5	43
15	48.5	10	42.2
25	43	20	42
35	37	30	41.9
45	32	40	41.7
55	27	50	41.4
65	22	60	41.1
75	17	70	40.8
85	13	80	40.5
95	8	90	40.4
105	5	100	39.9
115	2	110	39.8
125	1	120	39.4
135	0	130	39
-	-	140	37.8
-	-	150	38.4
-	-	160	38.2
-	-	170	37.6
-	-	180	37.6

The experiments confirmed the expectations and rendered a ratio 43:1 relative to equal volumes (10  $\mu$ L).

#### **Anisotropic PS-P4VP-scattering patterns**

Kinetic studies using *in-situ* synchrotron SAXS were also performed with PS-*b*-P4VP diblock copolymers. Evidence of the ordered cylindrical phase (OC) mentioned in the trajectories described in Figures 4 and 5 was obtained at higher evaporation times where anisotropic scattering patterns were found after 70 seconds.



**Figure S1.** Evolution of scattering patterns of an evaporating PS-*b*-P4VP ( $M_n$ =100k, f(4VP)=0.25) solution in DMF/THF: 7/3. The anisotropic scattering pattern appears after 70 seconds.

Anisotropic patterns were found for PS-P4VP block copolymers likely due to the better solubility of P4VP in DMF which results in a different swelling behavior and a more stable OC-phase than found for PS-P2VP.

More detailed ternary phase diagram (see Figure 4)



**Figure S2.** Detailed version of Fig. 4 displaying more AFM-images obtained along the evaporation trajectories. In Fig. 4 the number of images have been reduced to improve clarity.

# Enlarged AFM images of the ternary phase diagram (see Figure 4)

Series black: 15wt% SVP-1 in DMF



**Figure S3.** AFM height image of a polymer membrane cast from a solution of 15 wt% S2VP-1 in pure DMF after an evaporation time of 40 seconds.

#### 100.0 nm 100.0 nm 75.0 nm 0.0 3.0 µm 0.0 Height 3.0 µm 0.0 Height 3.0 µm Height 100.0 nm 200.0 nm 3.0 µm 0.0 Height 0.0 Height 3.0 µm

#### Series purple: 15wt% SVP-1 in DMF/THF: 70/30

**Figure S4.** AFM height image of a polymer membranes cast from a solution of 15 wt% S2VP-1 in DMF/THF: 70/30. The evaporation times are 0 sec, 15 sec, 30 sec, 40 sec and 60 sec respectively.

# Series yellow: 15wt% SVP-1 in DMF/THF: 50/50



**Figure S5.** AFM height image of a polymer membranes cast from a solution of 15 wt% S2VP-1 in DMF/THF: 50/50. The evaporation times are 0 sec and 15 sec respectively. Series green:

#### Series green: 15wt% SVP-1 in DMF/THF: 30/70



**Figure S6.** AFM height images of polymer membranes cast from a solution of 15 wt% S2VP-1 in DMF/THF: 30/70. The evaporation times are 0 sec, 15 sec, 30 sec, respectively.

### Series blue: 15wt% SVP-1 in pure THF



**Figure S7.** AFM height images of olymer membranes cast from a solution of 15 wt% S2VP-1 in pure THF. The evaporation times are 0 sec, 15 sec, 30 sec and 60 sec. The last image was taken from a completely dried membrane.

#### Series orange: 10 wt% SVP-1 in pure THF



**Figure S8.** AFM height image of a polymer membrane cast from a solution of 10 wt% S2VP-1 in pure THF.

Series red: 20 wt% SVP-1 in pure THF



Figure S9. AFM height images of polymer membranes cast from a solution of 20 wt% S2VP-

1 in pure THF.