Supporting Information (file 1 of 2)

# Wettability of Electrospun Films of Microphase-Separated Block Copolymers with 3,3,3-Trifluoropropyl Substituted Siloxane Segments

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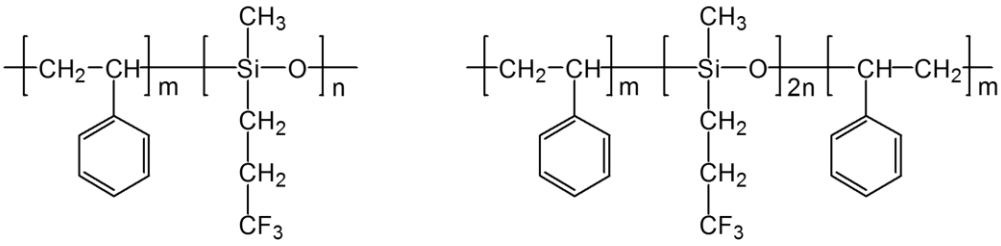


**Figure S1.** Chemical structures of PS-*b*-PMTFPS diblock copolymers and PS-*b*-PMTFPS-*b*-PS triblock copolymers.

**Table S1.** Glass transition temperature of PS precursors, PS-*b*-PMTFPS diblock copolymers and PS-*b*-PMTFPS-*b*-PS triblock copolymers.[a]

| Sample | $T_{g,\ homo\text{-}PS}$ (℃)[b] | $T_{g,\ PS}$ (℃)[c] | $T_{g,\ PMTFPS}$ (℃)[d] |
|---|---|---|---|
| $S_{198}FS_{26}$ | 104 | 98 | –[e] |
| $S_{106}FS_{54}$ | 99 | 97 | –66 |
| $S_{105}FS_{97}$ | 99 | 97 | –68 |
| $S_{100}FS_{191}$ | 99 | 98 | –69 |
| $S_{99}FS_{111}S_{99}$ | 98 | 96 | –67 |
| $S_{95}FS_{175}S_{95}$ | 98 | 96 | –68 |

[a] The glass transition temperature ($T_g$) was measured with a Q100 differential scanning calorimetry (DSC) (TA Instruments Inc.) calibrated with indium. After annealed at 150 ~ 160 °C, the samples were quenched down to –120°C at the maximum cooling rate of the instrument, and then scanned at a heating rate of 10°C /min from –120°C up to 150 °C.

[b] Glass transition temperature of PS precursors.

[c] Glass transition temperature of PS block in block copolymers.

[d] Glass transition temperature of PMTFPS block in block copolymers.

[e] The glass transition temperature of PMTFPS block was difficult to be clearly discerned due to a short length of PMTFPS block.

**Table S2.** Contact angles and roll-off angles of salad oil on the electrospun films.

| Sample [a] | salad oil [b] | | | |
|---|---|---|---|---|
| | static (°) | advancing (°) | receding (°) | roll-off (°) |
| $S_{198}FS_{26}$ | 131.7±1.4 | 135.9±0.4 | 127.0±1.9 | 8.9 |
| $S_{106}FS_{54}$ | 137.2±5.2 | 140.2±1.5 | 132.2±1.3 | 8.0 |
| $S_{105}FS_{97}$ | 143.6±1.6 | 145.7±1.2 | 140.0±1.8 | 5.7 |
| $S_{100}FS_{191}$ | 143.4±1.6 | 145.1±1.4 | 139.0±1.4 | 6.1 |
| $S_{99}FS_{111}S_{99}$ | 138.7±2.1 | 141.0±1.2 | 135.0±1.0 | 6.0 |
| $S_{95}FS_{175}S_{95}$ | 139.1±3.7 | 143.4±1.1 | 137.6±1.2 | 5.8 |

[a] The concentration of electrospinning solutions: (1) 15wt% in DMF: $S_{100}FS_{191}$; (2) 25wt% in DMF: $S_{198}FS_{26}$, $S_{105}FS_{97}$; (3) 25wt% in DMF and THF (1/1, v/v): $S_{99}FS_{111}S_{99}$, $S_{95}FS_{175}S_{95}$; (4) 30wt% in DMF and THF (1/1, v/v): $S_{106}FS_{54}$. Electrospinning conditions: tip-to-plate distance = 15 cm; humidity = 38%; flow rate = 0.6 mL/h; spinning voltage = 15 kV.

[b] Colored by Oil Red O (1-(2,5-Dimethyl-4-(2,5-dimethylphenylazo)phenylazo)-2-naphthol) with a concentration of 0.4mg/mL.

**Table S3.** Contact angles and roll-off angles of white mineral oil on the electrospun films.

| Sample [a] | white mineral oil [b] | | | |
|---|---|---|---|---|
| | static (°) | advancing (°) | receding (°) | roll-off (°) |
| $S_{198}FS_{26}$ | 126.6±2.5 | 131.4±1.1 | 120.6±0.9 | 10.8 |
| $S_{106}FS_{54}$ | 130.1±3.5 | 134.7±1.9 | 125.4±1.8 | 9.3 |
| $S_{105}FS_{97}$ | 140.7±2.9 | 143.7±1.2 | 137.0±1.1 | 6.7 |
| $S_{100}FS_{191}$ | 141.7±1.4 | 143.6±0.9 | 137.1±1.7 | 6.5 |
| $S_{99}FS_{111}S_{99}$ | 138.1±1.2 | 139.4±1.2 | 133.2±0.6 | 6.2 |
| $S_{95}FS_{175}S_{95}$ | 138.2±5.2 | 139.5±0.4 | 133.1±1.1 | 6.4 |

[a] The concentration of electrospinning solutions: (1) 15wt% in DMF: $S_{100}FS_{191}$; (2) 25wt% in DMF: $S_{198}FS_{26}$, $S_{105}FS_{97}$; (3) 25wt% in DMF and THF (1/1, v/v): $S_{99}FS_{111}S_{99}$, $S_{95}FS_{175}S_{95}$; (4) 30wt% in DMF and THF (1/1, v/v): $S_{106}FS_{54}$. Electrospinning conditions: tip-to-plate distance = 15 cm; humidity = 38%; flow rate = 0.6 mL/h; spinning voltage = 15 kV.

[b] Colored by Oil Red O (1-(2,5-Dimethyl-4-(2,5-dimethylphenylazo)phenylazo)-2-naphthol) with a concentration of 0.4mg/mL.

**Table S4.** Contact angles and roll-off angles of hexadecane on the electrospun films.

| Sample [a] | hexadecane [b] | | | |
|---|---|---|---|---|
| | static (°) | advancing (°) | receding (°) | roll-off (°) |
| $S_{198}FS_{26}$ | 116.6±1.7 | 119.8±0.9 | 105.9±1.4 | 13.9 |
| $S_{106}FS_{54}$ | 122.6±3.2 | 124.5±1.0 | 113.3±1.7 | 11.2 |
| $S_{105}FS_{97}$ | 134.2±4.1 | 135.3±1.4 | 126.2±0.7 | 9.1 |
| $S_{100}FS_{191}$ | 136.5±3.3 | 137.6±1.3 | 129.3±1.1 | 8.3 |
| $S_{99}FS_{111}S_{99}$ | 134.5±0.7 | 138.3±0.7 | 129.4±1.2 | 8.9 |
| $S_{95}FS_{175}S_{95}$ | 135.0±2.4 | 137.8±1.2 | 130.3±1.3 | 7.5 |

[a] The concentration of electrospinning solutions: (1) 15wt% in DMF: $S_{100}FS_{191}$; (2) 25wt% in DMF: $S_{198}FS_{26}$, $S_{105}FS_{97}$; (3) 25wt% in DMF and THF (1/1, v/v): $S_{99}FS_{111}S_{99}$, $S_{95}FS_{175}S_{95}$; (4) 30wt% in DMF and THF (1/1, v/v): $S_{106}FS_{54}$. Electrospinning conditions: tip-to-plate distance = 15 cm; humidity = 38%; flow rate = 0.6 mL/h; spinning voltage = 15 kV.

[b] Colored by Oil Red O (1-(2,5-Dimethyl-4-(2,5-dimethylphenylazo)phenylazo)-2-naphthol) with a concentration of 0.4mg/mL.

**Table S5. S**urface composition of the thin films of block copolymers determined by ARXPS at 30° and 60 °takeoff angle.

| Sample [a] | Si 2p (%) | | C 1s (%) | | O 1s (%) | | F 1s (%) | | *X* (%) [b] | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 60 ° | 30 ° | 60 ° | 30 ° | 60 ° | 30 ° | 60 ° | 30 ° | 60 ° | 30 ° |
| $S_{198}FS_{26}$ | 7.6 | 9.9 | 77.1 | 71.5 | 8.8 | 11.4 | 6.5 | 7.2 | 56.5 | 71.3 |
| $S_{106}FS_{54}$ | 10.1 | 12.9 | 61.5 | 56.2 | 10.1 | 12.4 | 18.3 | 18.6 | 79.2 | 95.5 |
| $S_{105}FS_{97}$ | 12.8 | 14.1 | 49.5 | 45.9 | 13.2 | 13.2 | 24.5 | 26.9 | 101.5 | 110.3 |
| $S_{100}FS_{191}$ | 11.1 | 12.7 | 53.2 | 49.9 | 11.6 | 11.9 | 24.1 | 25.5 | 90.9 | 100.8 |
| $S_{99}FS_{111}S_{99}$ | 9.7 | 10.2 | 57.4 | 53.1 | 10.5 | 12.1 | 22.3 | 24.6 | 80.9 | 86.7 |
| $S_{95}FS_{175}S_{95}$ | 12.3 | 12.7 | 50.3 | 46.9 | 11.9 | 14.0 | 25.5 | 26.4 | 98.9 | 104.1 |

[a] The thin films were prepared by spin coating on the aluminum foil (0.1 mm thick, 99.9% metals basis) from a concentration of 1.0 wt% in THF. The solvent was allowed to evaporate in air at room temperature, and then the films were further annealed at 120 °C under vacuum over 24 hours.

[b] *X* is the PMTFPS molar fraction at the surface, which is estimated by the carbon to silicon atomic ratios (C/Si) and given by the equation C/Si = [4*X* + 8 (1-*X*)]/*X*. It needs to be noted that some values of *X* are greater than 100%, which is likely caused by the interactions of fluorines with adjacent silicon atoms (Reference: Owen, M. J. Surface Tension of Polytrifluoropropylmethylsiloxane. *J. Appl. Polym. Sci.* **1988**, *35*, 895–901), and then more silicon atoms arrange at the outmost layer of block copolymer films.