

## Supporting Information

### Reactive oligo(dimethylsiloxane) mesogens and their micropatterned nanostructured thin films

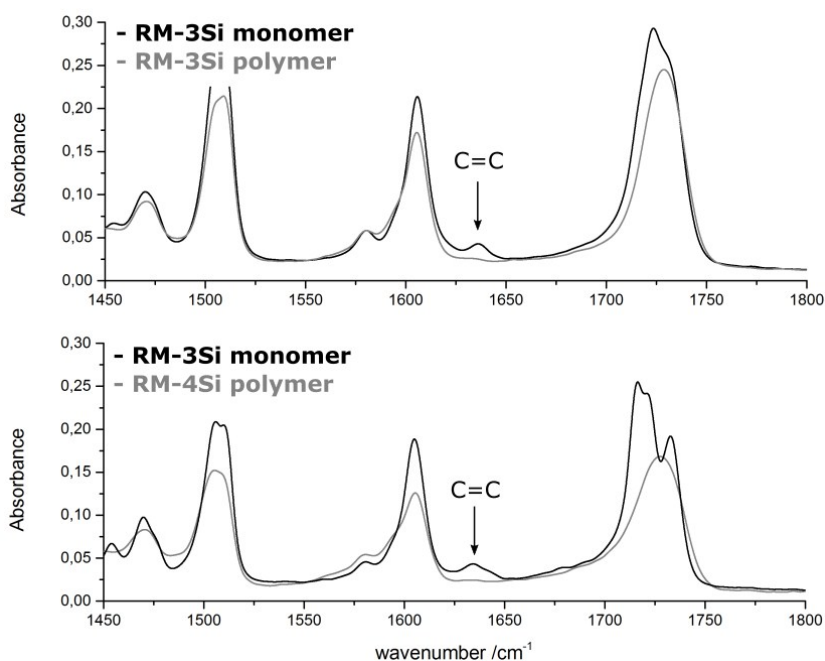
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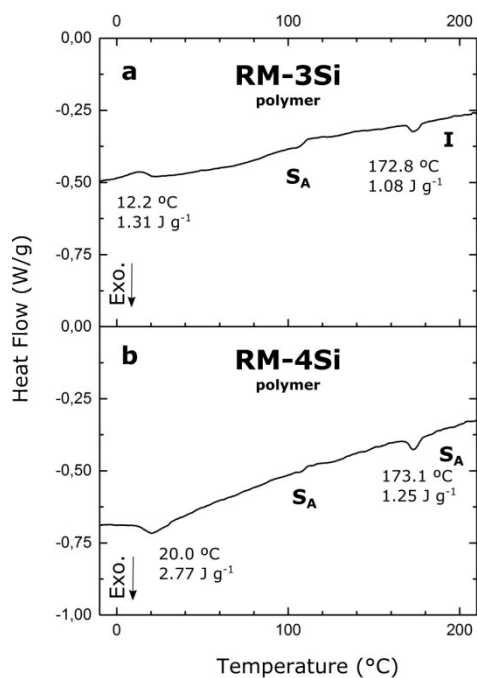
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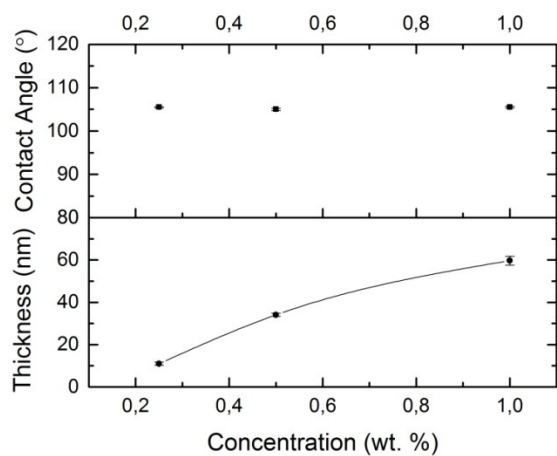
### Supporting Figures:



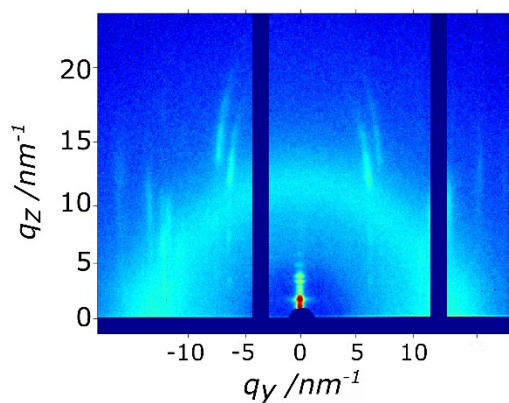
**Figure S1.** FTIR data for the reactive mesogens and corresponding polymers. Upon photopolymerization the C=C bond of the acrylate groups at 1635 cm<sup>-1</sup> disappears.



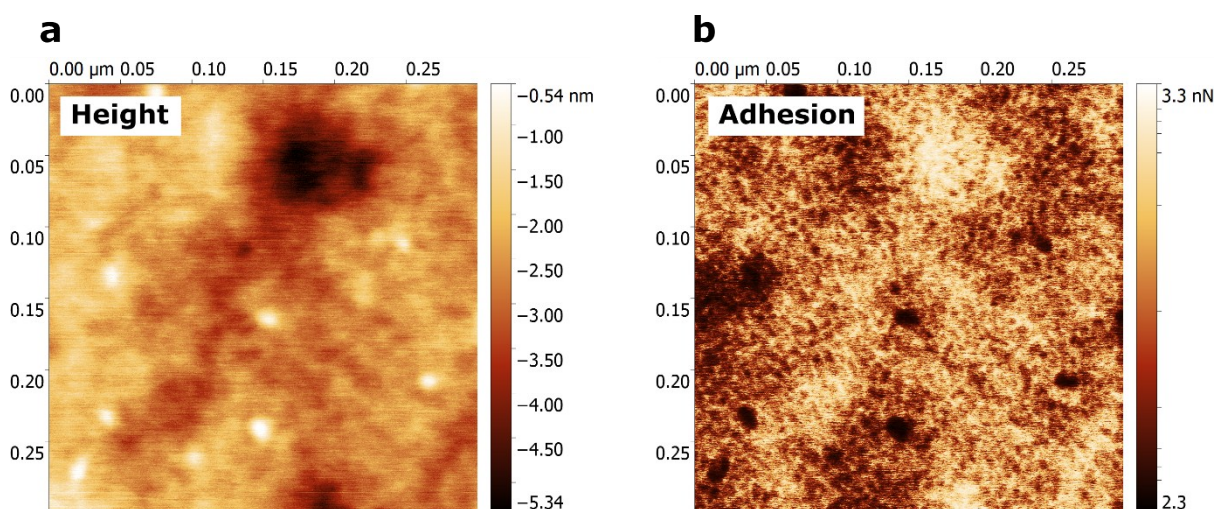
**Figure S2.** DSC thermographs of a) **RM-3Si**, and b) **RM-4Si**, after photopolymerization.



**Figure S3.** Film thickness profiles and static contact angle of polymerized **RM-4Si** thin films, as function of the spin-coating concentration (chloroform).



**Figure S4.** Wide-angle grazing-incidence x-ray diffraction (GIWAXS) data for a **RM-4Si** thin film of thickness 60 nm prior to photopolymerization. The data was obtained at room temperature and around the critical angle. Small-angle diffraction peaks are found at  $q = 1.84 \text{ nm}^{-1}$  and  $q = 3.66 \text{ nm}^{-1}$ , which correspond to a periodic layered structure with an interlayer distance of  $d = 3.4 \text{ nm}$ . Several reflections corresponding to crystallites are visible in the wide-angle region ( $q > 10 \text{ nm}^{-1}$ ), which were formed in the hours between the film preparation and measurement.



**Figure S5.** High-resolution Peakforce tapping AFM data, a) height, and b) adhesion, for a polymerized **RM-4Si** thin film of a thickness of 60 nm. Several areas are marked by a lower adhesion compared to the rest of the film, which suggests they consist of a different chemical composition.

## Synthetic procedures and characterization:

### 4-(allyloxy)phenyl acetate (**1**)

To 1.8 g (12 mmol) of 4-(allyloxy)phenol in 20 ml of dichloromethane was added 1.8 ml of triethylamine. The reaction mixture was stirred under nitrogen atmosphere. The solution was cooled in an ice-water bath. Subsequently 0.8 ml of acetyl chloride in 10 ml of dichloromethane were added dropwise and the reaction mixture was stirred for 10 minutes. The mixture was washed once with 30 ml of water and once with 30 ml of 2 N HCl solution and dried over MgSO<sub>4</sub>. The organic solution was filtered through celite and the solvent was evaporated to yield 2 g of 4-(allyloxy)phenyl acetate (**1**) as a yellow oil. Yield: 86.8%; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.00 – 6.89 (m, 4H); 6.09-5.96 (m, 1H); 5.41 (dq, 1H); 5.29 (dq, 1H); 4.51 (ddd, 2H); 2.27 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 169.82, 156.28, 144.33, 133.20, 122.32, 117.67, 115.33, 69.18, 21.04.

### 4-(3-(1,1,3,3,5,5,5-heptamethyltrisiloxanyl)propoxy)phenyl acetate (**2a**)

1.3g (6.76 mmol) of **1** and 1.5g of heptamethyltrisiloxane (6.74 mmol) were brought under Argon atmosphere and dissolved in 7 ml of dry toluene. To this 200 μL of a 1 mg/mL solution in dry DCM of dichloro(1,5-cyclooctadiene)platinum(II) catalyst was added. The mixture was heated to 60 °C and stirred overnight. After evaporation, the compound was purified by column chromatography on silica gel (n-hexane/ethyl acetate = 16:1 v/v) to yield 1.39 g (3.35 mmol) of the siloxane-acetate (**2a**) as an oil. Yield: 50%; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 6.95 – 6.81 (m, 4H); 3.85 (t, 2H); 2.27 (s, 3H); 1.76 (m, 2H); 0.61 (m, 2H); 0.09-0.05 (m, 21H).

### 4-(3-(1,1,3,3,5,5,5-heptamethyltrisiloxanyl)propoxy)phenol (**3a**)

1.05g (2.54 mmol) of **2a** was dissolved in 60 mL methanol. 3 mL of ammonium hydroxide (28%) in 10 mL water was added. The mixture was stirred under argon atmosphere overnight at room temperature. Roughly 50 ml of water and 100 ml of diethyl ether were added to the solution and the

organic phase was separated. The aqueous phase was extracted twice with roughly 50 mL diethyl ether. The organic fractions were combined and the solvent evaporated. Water remained present, and therefore the sample was extracted twice with 50 mL DCM. The sample was dried over magnesium sulfate and solvent removed in vacuo. Purification by column chromatography on silica gel (n-hexane/ethyl acetate = 7:1 v/v) gave 676.4 mg (1.81 mmol, 71%) **3a** as a clear viscous fluid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 6.80 – 6.74 (m, 4H); 3.87 (t, 2H); 1.79 (m, 2H); 0.64 (m, 2H); 0.09-0.05 (m, 21H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 153.18, 149.35, 116.02, 115.66, 71.30, 23.28, 14.15, 1.82, 1.28, 1.13.

**4-(3-(1,1,3,3,5,5,5-heptamethyltrisiloxanyl)propoxy)phenyl 4-(4-(acryloyloxy)butoxy)benzoate (RM-3Si)**

208 mg (0.56 mmol) of **3a** was added to 163 mg (0.56 mmol) 4-(6-acryloyloxyhexyloxy) benzoic acid (**6OBA**) and 1 mg of 4-dimethylaminopyridine (DMAP) in a few mL dry DCM. The solution was put under Argon gas and placed in an ice bath. After cooling for several minutes, 115.2 mg (0.56 mmol) of dicyclohexylcarbodiimide DCC dissolved in dry DCM was added to the solution. The reaction was kept for 5 hours, after which the solvent was removed. The crude product was purified on column chromatography on silica gel (n-hexane/ethyl acetate = 10:1 v/v), to yield 100 mg (0.155 mmol) **RM-3Si**. Yield: 28%; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 8.13 (d, 2H); δ 7.09 (d, 2H); δ 6.97 – 6.91 (m, 4H); δ 6.40 (d, 1H); δ 6.12 (m, 1H); δ 5.82 (d, 1H); δ 4.18 (t, 2H); δ 4.03 (t, 2H); δ 3.92 (t, 2H); δ 1.87 – 1.69 (m, 6H); δ 1.56 – 1.45 (m, 4H); δ 0.67 (m, 2H); 0.12-0.04 (m, 21H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 153.18, 149.35, 116.02, 115.66, 71.3, 23.28, 14.15, 1.82, 1.28, 1.13. MALDI-TOF ([M+Na]<sup>+</sup>: 669,23 g/mol). MALDI-TOF MS (m/z): [M+Na]<sup>+</sup> calcd for C<sub>32</sub>H<sub>50</sub>O<sub>8</sub>Si<sub>3</sub> 669.27, found 669.23.

**(((1,1,3,3,5,5,7,7-octamethyltetrasiloxane-1,7-diyl)bis(propane-3,1-diyl))bis(oxy))bis(4,1-phenylene) diacetate (2b)**

1.47 g (7.66 mmol) of **1** and 1.03 g (3.64 mmol) of 1,1,3,3,5,5,7,7-octamethyltetrasiloxane were dissolved in 5 ml of dry toluene. To this 500  $\mu$ L of a 1 mg/mL solution in dry DCM of dichloro(1,5-cyclooctadiene)platinum(II) catalyst was added. The mixture was heated at 60°C and stirred under argon atmosphere for 7h. Solvent was removed and the crude product was purified by column chromatography on silica gel (n-hexane/ethyl acetate = 5:1 v/v) to yield 1.62 g (2.43 mmol, 67%) **2b** as a viscous fluid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.99-6.82 (m, 8H); 3.89 (t, 4H); 2.27 (s, 6H); 1.82 (m, 4H); 0.66 (m, 4H); 0.13-0.08 (m, 24H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.39, 157.32, 144.51, 122.76, 71.34, 23.73, 14.69, 1.76, 0.70.

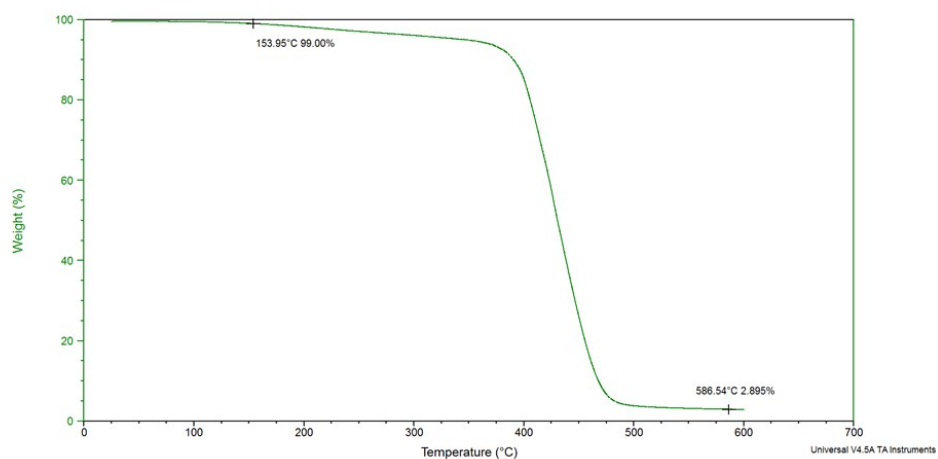
#### **4,4'-(((1,1,3,3,5,5,7,7-octamethyltetrasiloxane-1,7-diyl))bis(propane-3,1-diyl))bis(oxy))diphenol (**3b**)**

1.33 g (1.99 mmol) of **2b** was dissolved in 40mL methanol, and 3mL of ammonium hydroxide (28%) in 10 mL water was added. The mixture was stirred under argon atmosphere overnight at room temperature, after which 30 mL of water and 60 mL of diethyl ether were added. The organic phase was separated, dried, and removed in vacuo to yield 1.08 g (1.71 mmol, 85%) **3b** as a viscous fluid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.94 (br s, 2H); 6.79 (m, 8H); 3.89 (t, 4H); 1.83 (m, 4H); 0.68 (m, 4H); 0.18-0.10 (m, 24H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.85, 149.62, 116.16, 115.76, 71.41, 23.24, 14.12, 1.23, 0.16.

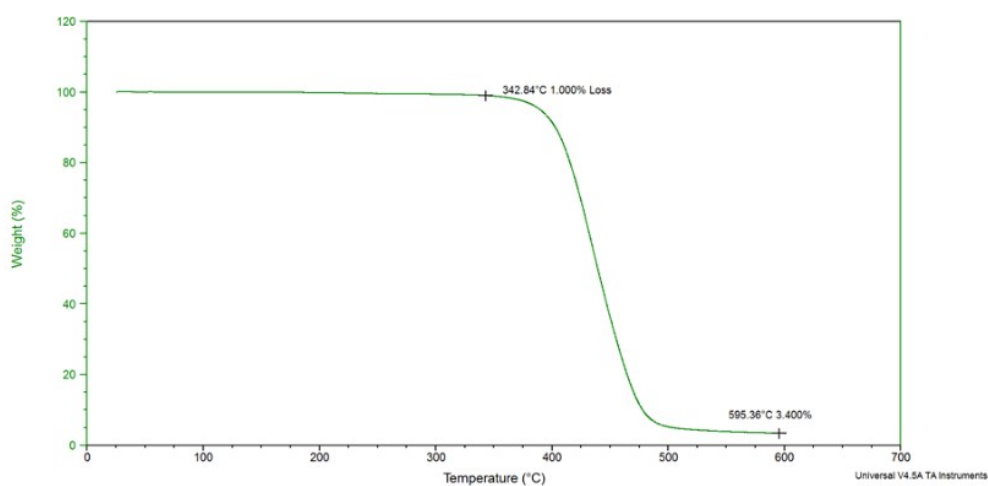
#### **(((1,1,3,3,5,5,7,7-octamethyltetrasiloxane-1,7-diyl))bis(propane-3,1-diyl))bis(oxy))bis(4,1-phenylene) bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate) (**RM-4Si**)**

522 mg (0.89 mmol) of **3b**, 525 mg (1.80 mmol) of 6OBA, 20 mg (0.16 mmol) 4-dimethylaminopyridine (DMAP), and 3 mg (0.01 mmol) butylated hydroxytoluene (BHT) were dissolved in dry DCM, brought under Ar atmosphere, and cooled in an ice bath. 370 mg (1.79 mmol) dicyclohexylcarbodiimide (DCC) was dissolved in dry DCM and slowly added to the reaction vessel and the reaction was left overnight. The solution was filtered, evaporated and purified through a silica column with hexane/ethyl acetate (50:50) as the eluent to yield 905 mg (0.80 mmol) **RM-4Si** as

a clear paste. Yield: 89%.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.13 (d, 4H);  $\delta$  7.08 (d, 4H);  $\delta$  6.97 – 6.89 (m, 8H);  $\delta$  6.24 (d, 2H);  $\delta$  6.13 (m, 2H);  $\delta$  5.82 (d, 2H);  $\delta$  4.19 (t, 4H);  $\delta$  4.02 (t, 4H);  $\delta$  3.92 (t, 4H);  $\delta$  1.86 – 1.68 (m, 12H);  $\delta$  1.53 – 1.43 (m, 8H);  $\delta$  0.71 (m, 4H); 0.13-0.08 (m, 24H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.27, 165.27, 163.30, 156.74, 144.32, 132.20, 130.56, 128.54, 122.44, 121.76, 115.02, 114.20, 70.87, 68.02, 64.45, 28.98, 28.54, 25.72, 23.22, 14.18, 1.84, 1.30. MALDI-TOF MS (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{58}\text{H}_{82}\text{O}_{15}\text{Si}_4$  1153.46, found 1153.47.



TGA data for RM-3Si



TGA data for RM-4Si