

## SUPPORTING INFORMATION

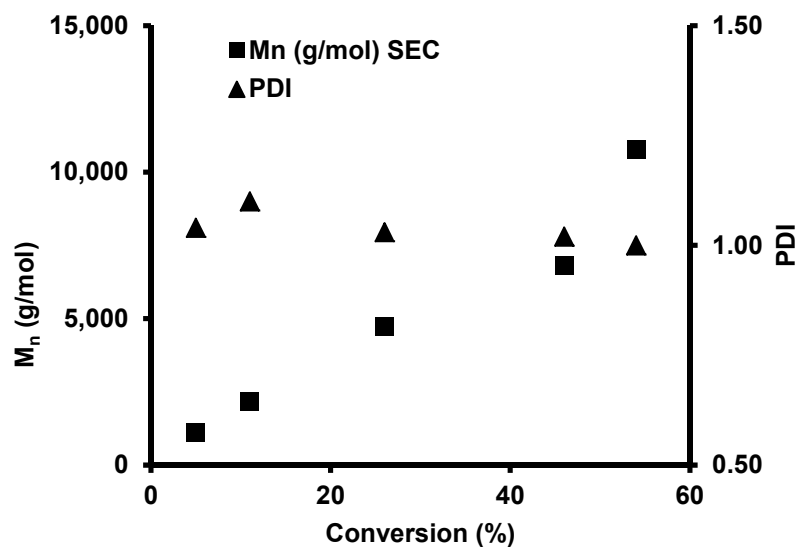
### Reversible Addition-Fragmentation Chain Transfer (RAFT) Copolymerization of Fluoroalkyl Polyhedral Oligomeric Silsesquioxane (F-POSS) Macromers

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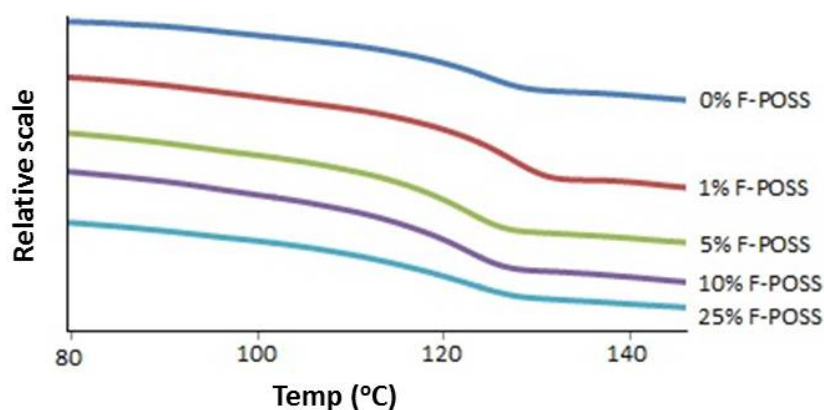
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**Figure S1.** Molecular weight/PDI vs. conversion for RAFT polymerizations of MMA in C<sub>6</sub>F<sub>6</sub>. SEC-MALLS measurements performed in THF.



**Figure S2.** Zoomed in DSC traces of F-POSS copolymers.  $T_g$  reported values are 127, 129, 124, 125, and 124°C for 0, 1, 5, 10, and 25 wt % F-POSS, respectively. 2<sup>nd</sup> heat cycle shown. Heating rate (10°C/min), exo up.

### S1. Methods and Experimental

*Materials.* F-POSS (**2**) was synthesized according to literature procedure. 3-methacryloxypropylmethyldichlorosilane (Gelest) was distilled prior to use. Hexafluorobenzene ( $C_6F_6$ , Synquest), Mixture of 1,3-dichloro-1,2,2,3,3-pentafluoropropanes (AK-225, AGC Chemicals Americas), and hexadecane (Aldrich) were used without further purification, unless otherwise stated. All reactions were performed under nitrogen.

*Characterization.*  $^1H$  and  $^{19}F$  NMR spectra were obtained on Bruker 300-MHz and 400-MHz spectrometers using 5 mm o.d. tubes. Surface roughness measurements and height images were taken on a Digital Instruments Nanoscope IV (AFM). AFM images were processed using Gwyddion software package. Differential scanning calorimetry (DSC) was measured on a TA Instruments DSC under  $N_2$  at a ramp rate of 10°C/min from 50 °C to 160 °C using a heat/cool/heat cycle. Glass transition temperatures ( $T_g$ ) were determined from the 2<sup>nd</sup> heat cycle.

*Size exclusion chromatography multiangle laser light scattering (SEC-MALLS).* SEC experiments were performed in asahiklin-225. Solvent was filtered through a 0.02  $\mu m$  filter to

remove any dust or particulates. Samples were analyzed at 1.0 mL/min flow rate through a PLgel 5  $\mu\text{m}$  mixed E column (Agilent) and PLgel 3  $\mu\text{m}$  mixed C column (Agilent) measuring at 25 °C. SEC-MALS instrumentation consisted of an Agilent 1260 Infinity HPLC quaternary pump, Agilent 1260 Infinity Autosampler, Wyatt DAWN<sup>®</sup> HELOS<sup>®</sup> MALS detector operating at 658 nm, and a Wyatt Optilab<sup>®</sup>rEX differential refractive index detector. The accuracy and reproducibility was confirmed with a polymethylmethacrylate (Aldrich) standard 40,000 g/mol. Absolute molecular weights were determined using the Wyatt Astra VI software package. The specific refractive index increment ( $dn/dc$ ) for copolymers was determined online using 100% mass recovery method in Astra VI software package. Polymer samples (0.80-1.50 mg/mL) were allowed to dissolve in solvent overnight and passed through a 0.2  $\mu\text{m}$  PTFE syringe filter before measurement.

*Surface Measurements.* Polymer films were prepared by spin casting copolymer solutions in asahiklin-225 (10 mg/mL) on oxygen plasma treated SiO<sub>2</sub> wafers at 900 rpm for 30 seconds. Films were subsequently dried under vacuum for 24 hours at 100 °C. Dynamic contact angles experiments were conducted on a dataphysics OCA20 goniometer. Experiments consisted of placing a 3  $\mu\text{L}$  drop of probing liquid onto a test substrate, adding an additional 2  $\mu\text{L}$  through a dispensing needle at a rate of 0.2  $\mu\text{L}/\text{sec}$ , and then removing 3  $\mu\text{L}$  at 0.2  $\mu\text{L}/\text{sec}$ . Consecutive frames (20-100) of experiment video during the addition and removal of probing liquid, where constant advancement or recession of the contact line was observed, were used to measure the advancing and receding contact angles, respectively. Measurements were made from a “tangent lean” fit using Dataphysics droplet fitting software.

*General copolymerization procedure:* In 5-mL reactor equipped with magnetic stirring bar methyl methacrylate (MMA, 2.00 g, 20 mmol), **2** (0.20 g, 0.048 mmol), 2-cyanopropan-2-yl

benzodithioate (8.80 mg, 0.04 mmol), azobisisobutyronitrile (AIBN, 1.30 mg, 0.008 mmol) were dissolved in a hexafluorobenzene. The resulting solution was added to a reaction vial and sealed with septa. The solution was deoxygenated via nitrogen purge for 15 minutes and immediately submerged in a 65°C oil bath for the preset reaction time. The polymerization was then quenched by cooling with ice water and the addition of hydroquinone (THF) solution (10 µl, 10 mg/mL). Polymer was precipitated in methanol, filtered, and dried under vacuum to yield a pink white solid (0.659 g). For  $M_w$  vs time polymerization procedure, after polymerizations were quenched, solvent and residual monomer were removed via evaporation.