Fluorinated Bottlebrush Polymers Based on Poly(trifluoroethyl methacrylate):
Synthesis and Characterizations
Supporting Information

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Materials.

2,2,2-trifluoroethyl methacrylate (Matrix Scientific) was passed through a Al2O3 column and distilled to remove the inhibitor. 5-norbornene-2-ol, mixture of endo and exo (Sigma-Aldrich), aluminum oxide (neutral, Fluka), α-bromoisobutyryl bromide (Sigma-Aldrich), cyclohexanone (Sigma-Aldrich), 2,2’-bipyridyl (Sigma-Aldrich), triethylamine (Fisher Scientific), Cl2(3-BrPy)2(H2IMes)RuCHPh (G3, Sigma-Aldrich) were used as received. Copper (I) chloride (Sigma-Aldrich) was recrystallized prior to use. HPLC grade THF (Sigma-Aldrich) was dried in a solvent purification system. HPLC grade ethyl acetate (Sigma-Aldrich) was used as received.
**Additional Instrumentation.**

GI-SAXS/WAXS measurements were carried out on an Anton Paar SAXSess mc² equipped with a multipurpose VarioStage. The scattered beam was recorded on an imaging plate (Multisensitive Storage Phosphor) and read using a Perkin Elmer cyclone 2D imaging plate reader. For the GI-SAXS/WAXS measurements, X-ray was generated at 40kV/50 mA and the X-ray beam wavelength was \( l = 1.541 \ \text{Å} \) (Cu Kα radiation). The incidence angle for the measurements was 0.2° and the distance between sample and imaging plate was 261 mm.

**Table S1.** Experimental Parameters for Rheology.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T ) (°C)</th>
<th>( \gamma_0 )</th>
<th>( \omega ) (rad/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFEMA_{22}</td>
<td>55 – 80</td>
<td>4% – 0.03%</td>
<td>100 – 0.1</td>
</tr>
<tr>
<td>PNB_{21-g-PTFEMA_{22}}</td>
<td>70 – 120</td>
<td>4% – 0.02%</td>
<td>100 – 0.1</td>
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<tr>
<td>PNB_{40-g-PTFEMA_{22}}</td>
<td>70 – 120</td>
<td>4% – 0.03%</td>
<td>100 – 0.1</td>
</tr>
<tr>
<td>PNB_{200-g-PTFEMA_{22}}</td>
<td>70 – 140</td>
<td>4% – 0.03%</td>
<td>100 – 0.1</td>
</tr>
</tbody>
</table>
Figure S1. $^{13}$C NMR of PTFEMA macromonomer 3. In CDCl$_3$, 125 MHz.
**Figure S2.** $^{19}$F NMR of PTFEMA macromonomer 3. In CDCl$_3$, 470 MHz.
Figure S3. $^{13}$C NMR of PNB-g-PTFEMA bottlebrush polymer 4. In CDCl$_3$, 125 MHz.
Figure S4. $^{19}$F NMR of PNB-g-PTFEMA bottlebrush polymer 4. In CDCl$_3$, 470 MHz.
Figure S5. Static water contact angle (a) on pure silicon wafer; (b) PTFEMA macromonomer 3; (c) PNB$_{21}$-g-TFEMA$_{22}$ bottlebrush polymer; (d) PNB$_{49}$-g-TFEMA$_{22}$ bottlebrush polymer; (e) PNB$_{200}$-g-TFEMA$_{22}$ bottlebrush polymer.
Figure S6. Linear viscoelastic spectra of the bottlebrush polymer PNB$_{21}$-g-PTFEMA$_{22}$ (blue), PNB$_{49}$-g-PTFEMA$_{22}$ (red), and PNB$_{200}$-g-PTFEMA$_{22}$ (orange).
Figure S7. GI-WAXS for polymer thin films. All samples show broad peak at $Q = \sim 12$ nm$^{-1}$ implying amorphous structure without crystalline order. The spacing of $L = 0.5$ nm corresponds to short distance correlation on the PTFEMA side chains.$^1$
Figure S8. GI-SAXS for polymer thin films.
Figure S9. TEM images of three bottlebrush polymers at low and high magnifications. PNB$_{22}$-g-PTFEMA$_{22}$ (left); PNB$_{49}$-g-PTFEMA$_{22}$ (middle); PNB$_{200}$-g-PTFEMA$_{22}$ (right).

Reference