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 Al_2O_3 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), $Cl_2(3\text{-}BrPy)_2(H_2IMes)RuCHPh$ (**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 mc^2 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 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.

Sample	***T* (°C)**	**γ_0**	**ω (rad/s)**
$PTFEMA_{22}$	55 – 80	4% – 0.03%	100 – 0.1
PNB_{21}-*g*-$PTFEMA_{22}$	70 – 120	4% – 0.02%	100 – 0.1
PNB_{49}-*g*-$PTFEMA_{22}$	70 – 120	4% – 0.03%	100 – 0.1
PNB_{200}-*g*-$PTFEMA_{22}$	70 – 140	4% – 0.03%	100 – 0.1

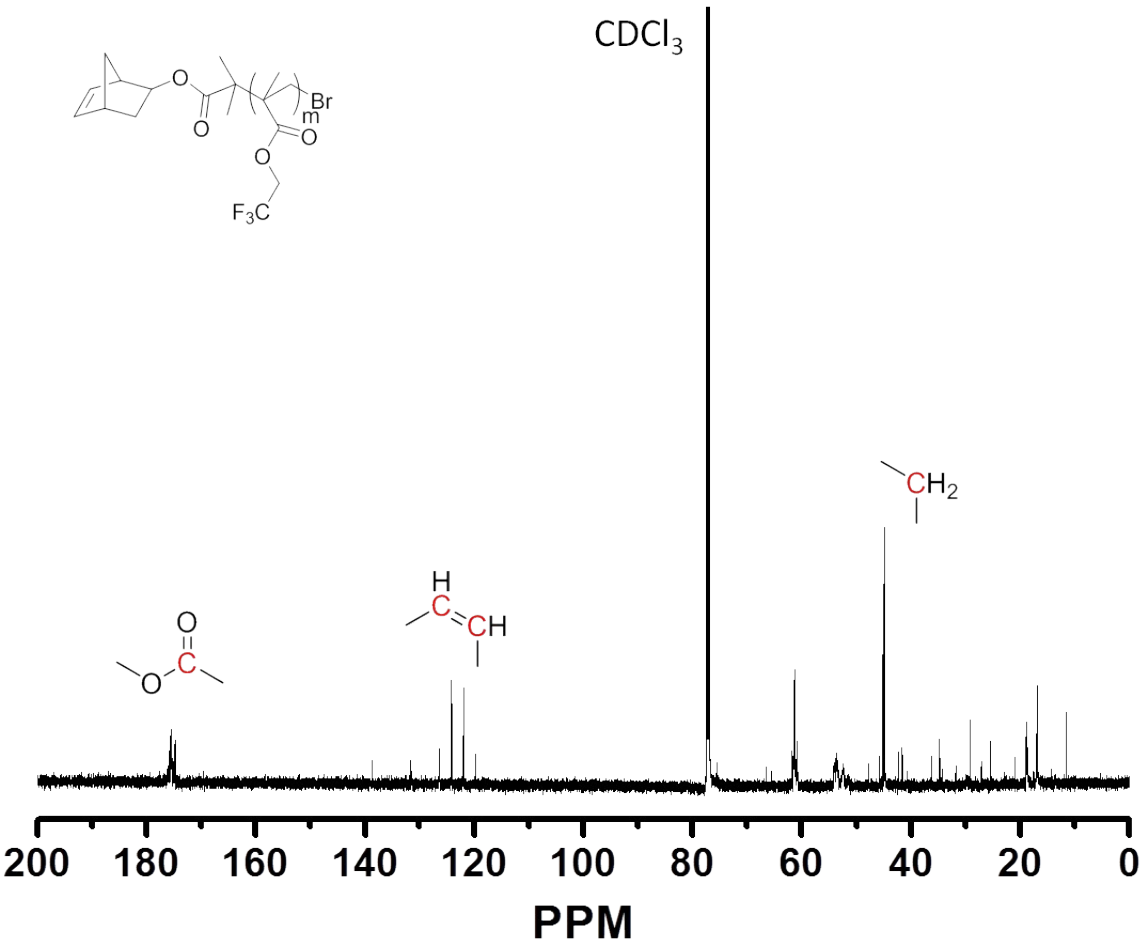

Figure S1. ^{13}C NMR of PTFEMA macromonomer **3**. In $CDCl_3$, 125 MHz.

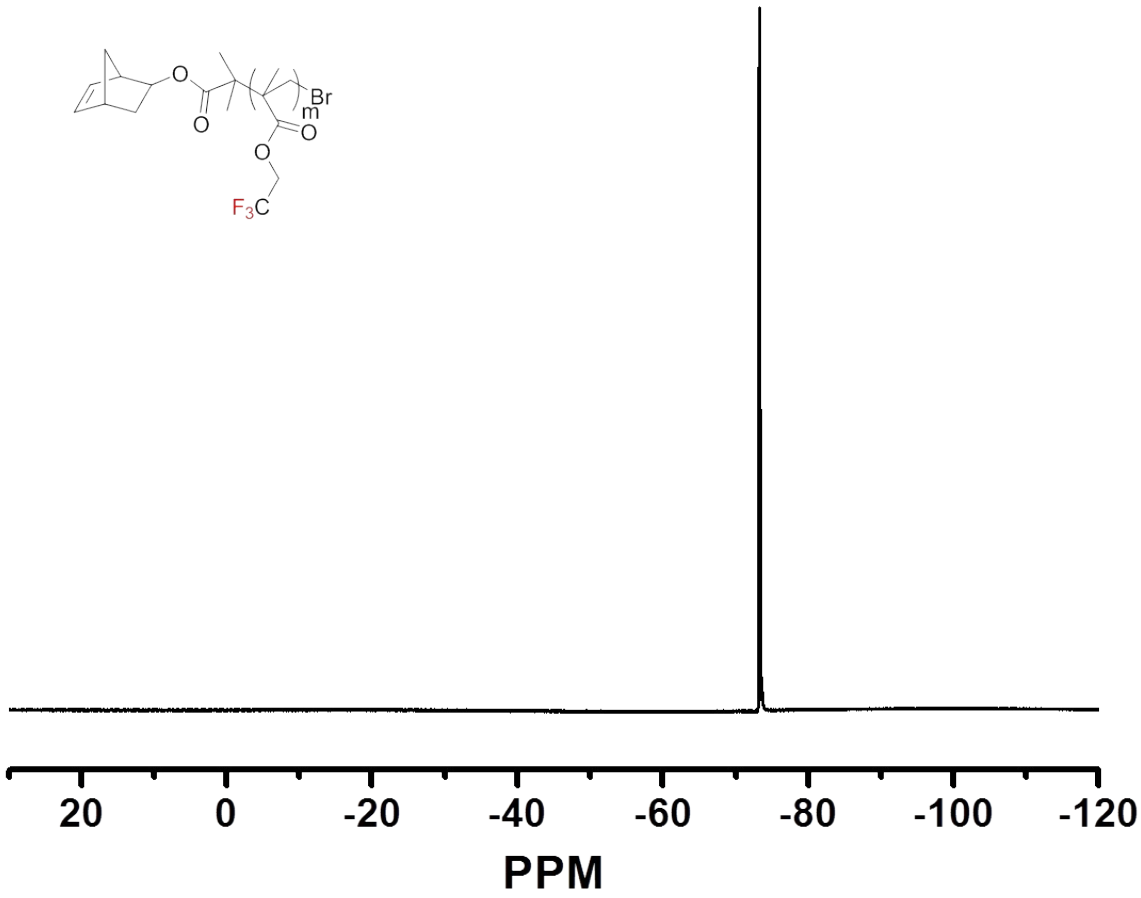

Figure S2. ^{19}F NMR of PTFEMA macromonomer **3**. In $CDCl_3$, 470 MHz.

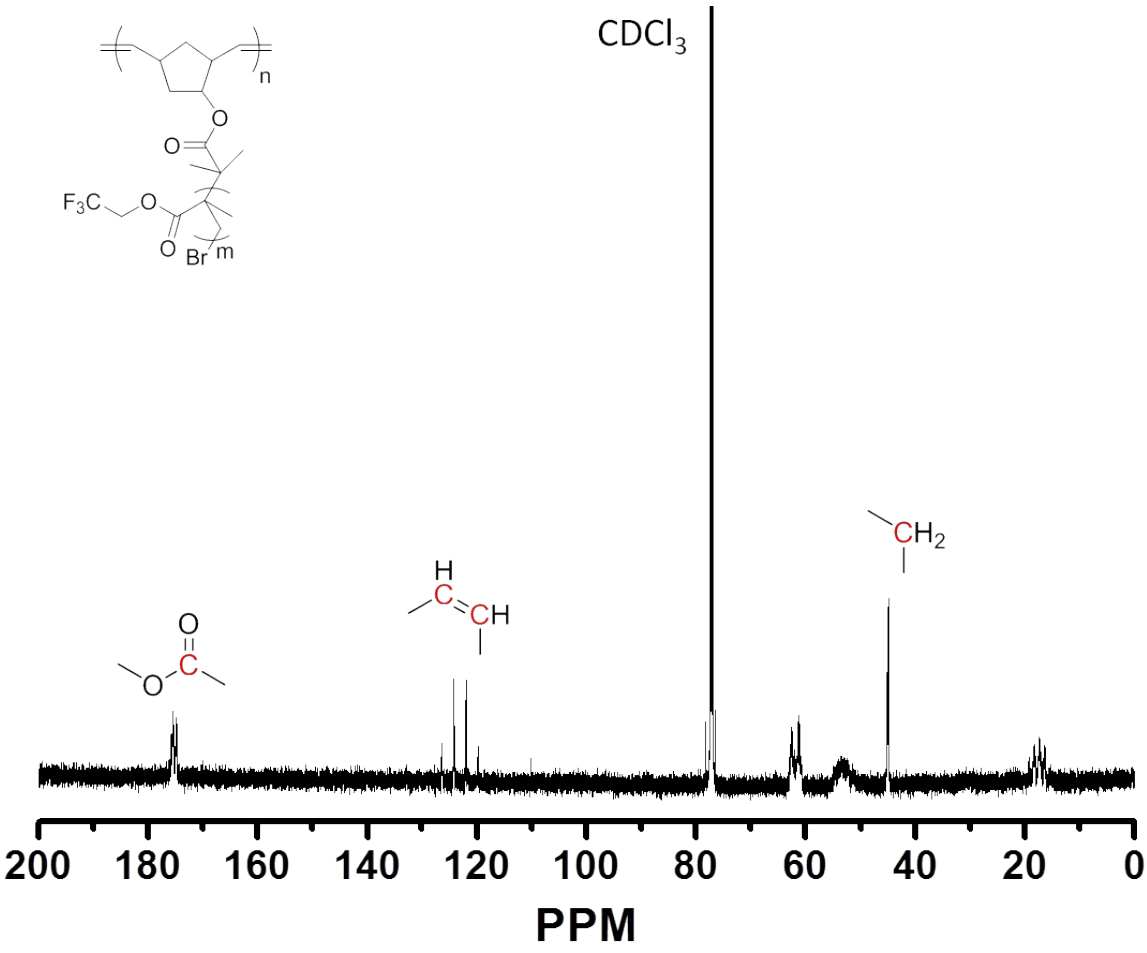

Figure S3. ^{13}C NMR of PNB-*g*-PTFEMA bottlebrush polymer **4**. In $CDCl_3$, 125 MHz.

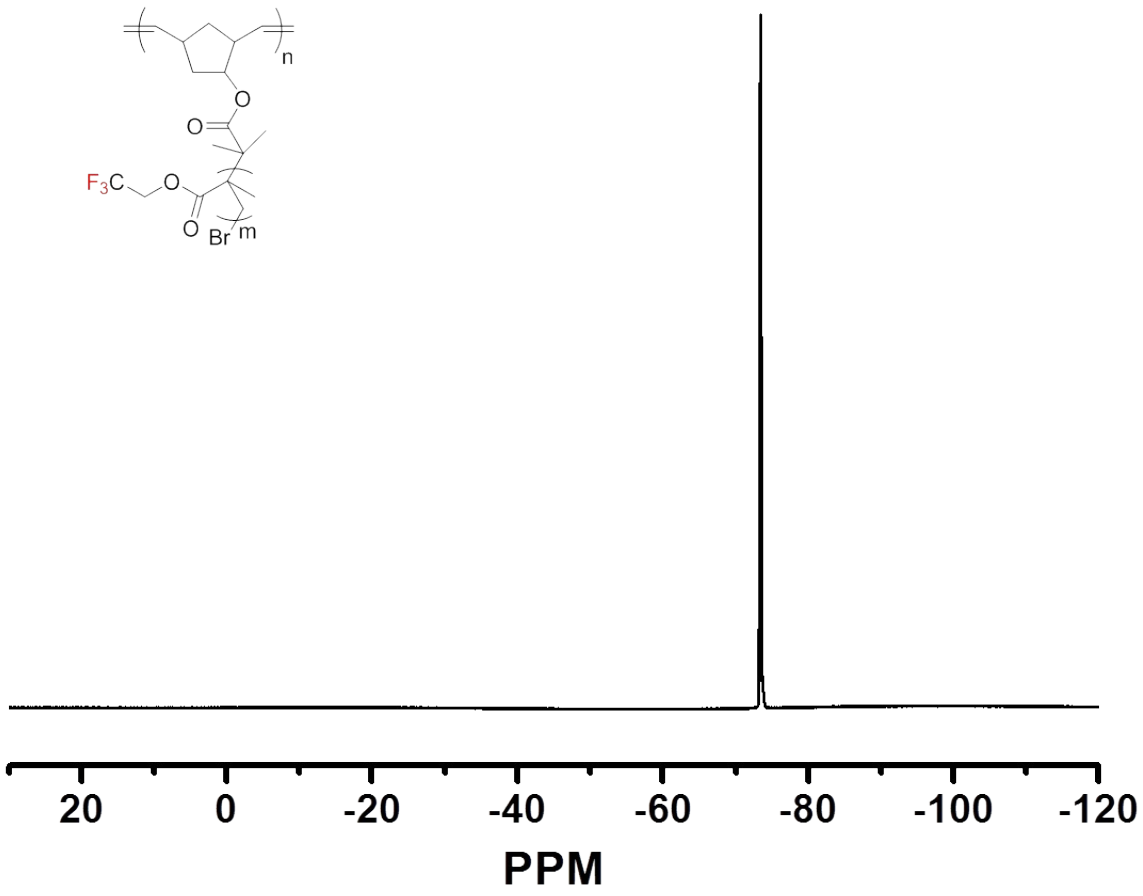

Figure S4. ^{19}F NMR of PNB-*g*-PTFEMA bottlebrush polymer **4**. In $CDCl_3$, 470 MHz.

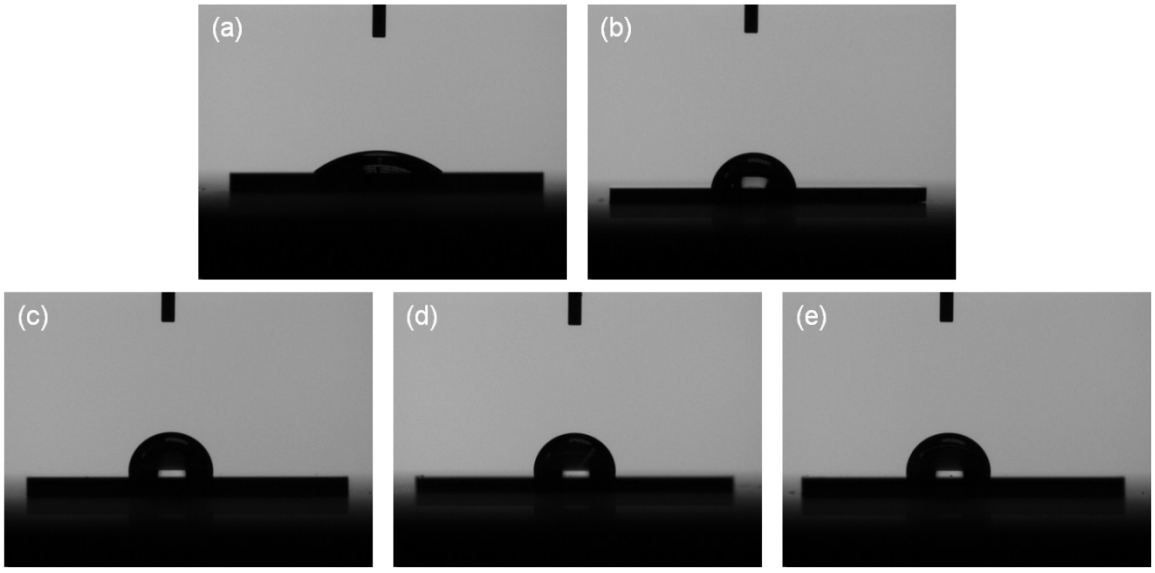

Figure S5. Static water contact angle (a) on pure silicon wafer; (b) PTFEMA macromonomer **3**; (c) PNB_{21}-g-$TFEMA_{22}$ bottlebrush polymer; (d) PNB_{49}-g-$TFEMA_{22}$ bottlebrush polymer; (e) PNB_{200}-g-$TFEMA_{22}$ bottlebrush polymer.

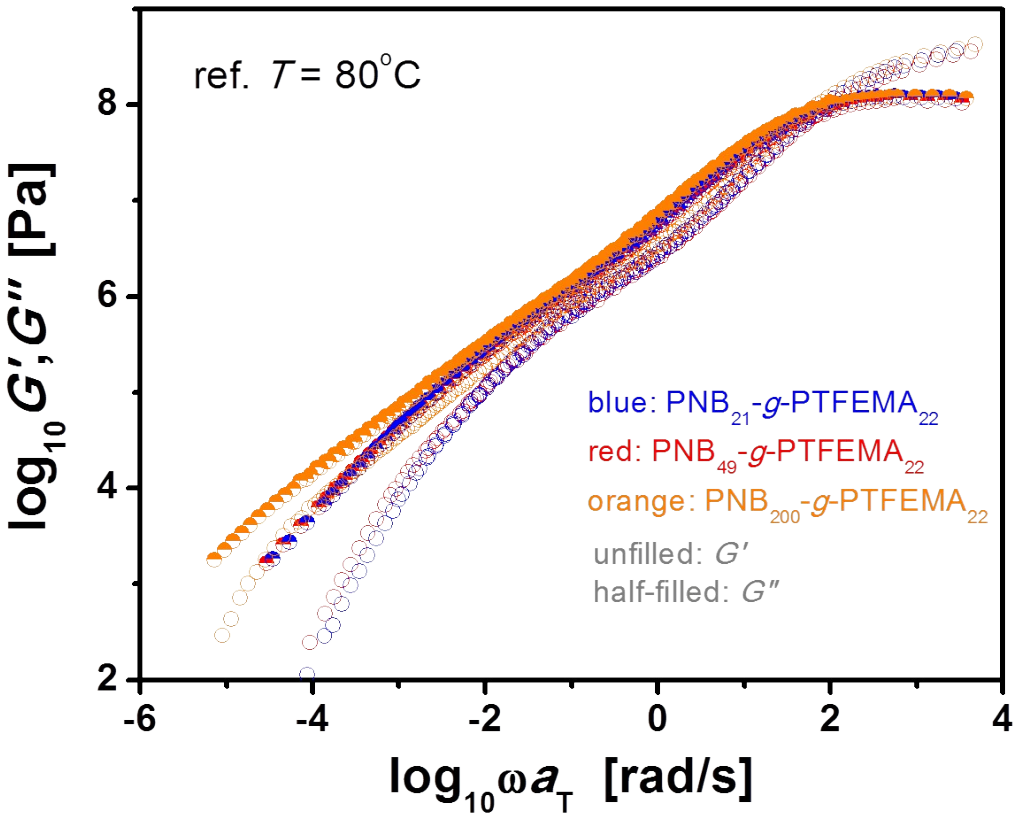

Figure S6. Linear viscoelastic spectra of the bottlebrush polymer PNB_{21}-*g*-$PTFEMA_{22}$ (blue), PNB_{49}-*g*-$PTFEMA_{22}$ (red), and PNB_{200}-*g*-$PTFEMA_{22}$ (orange).

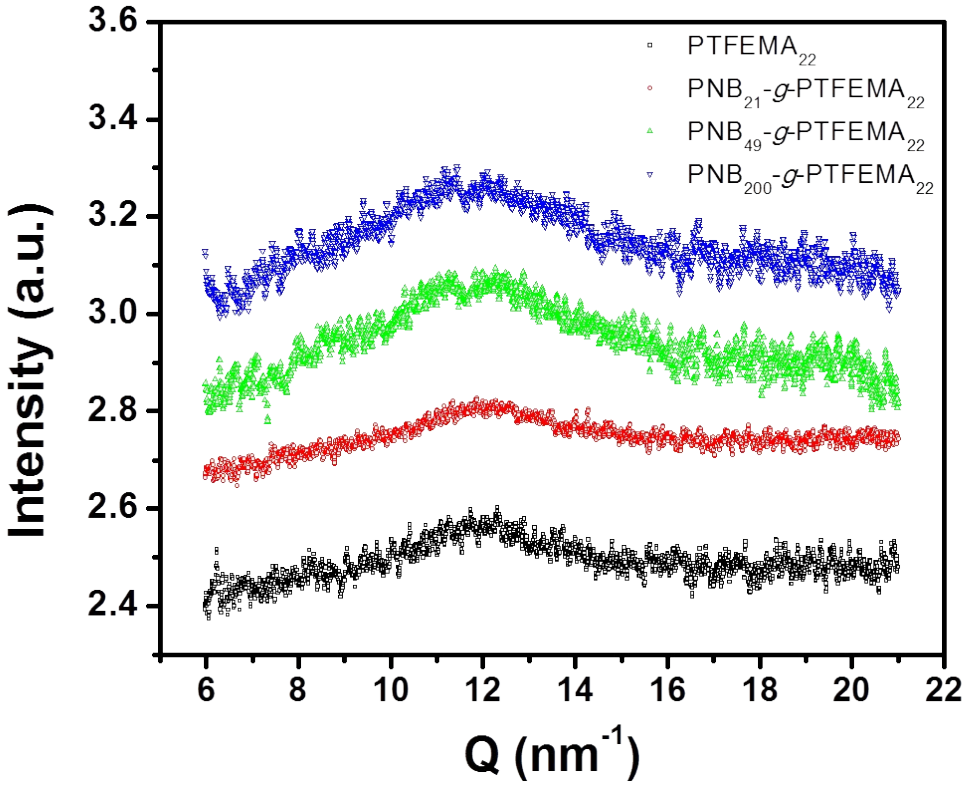

Figure S7. GI-WAXS for polymer thin films. All samples show broad peak at Q = ~ 12 nm^{-1} implying amorphous structure without crystalline order. The spacing of L = 0.5 nm corresponds to short distance correlation on the PTFEMA side chains.[1]

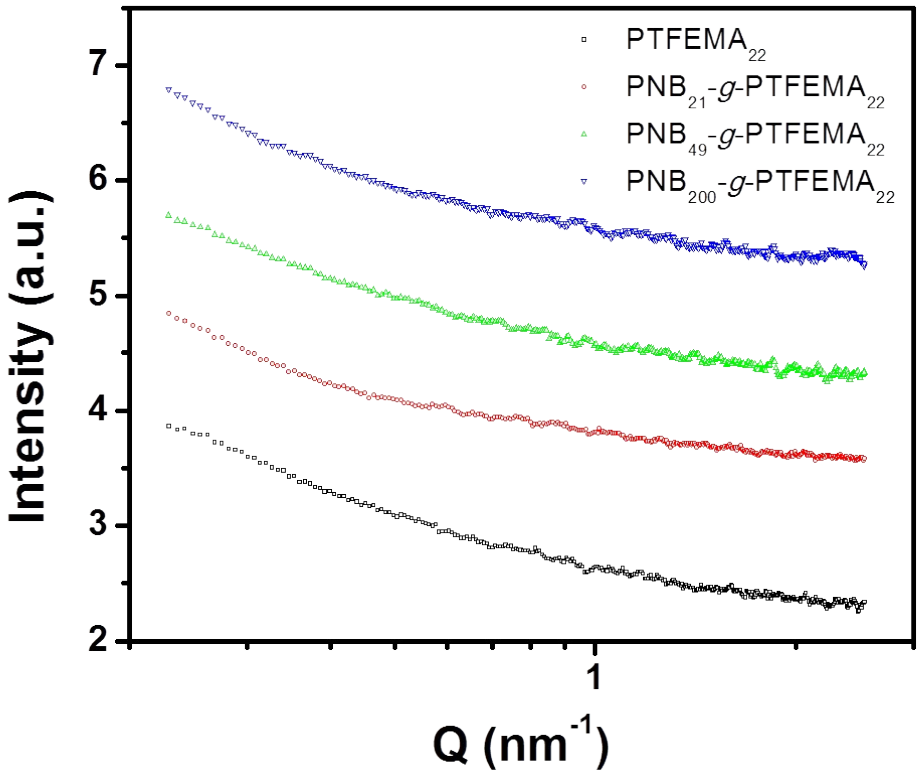

Figure S8. GI-SAXS for polymer thin films.

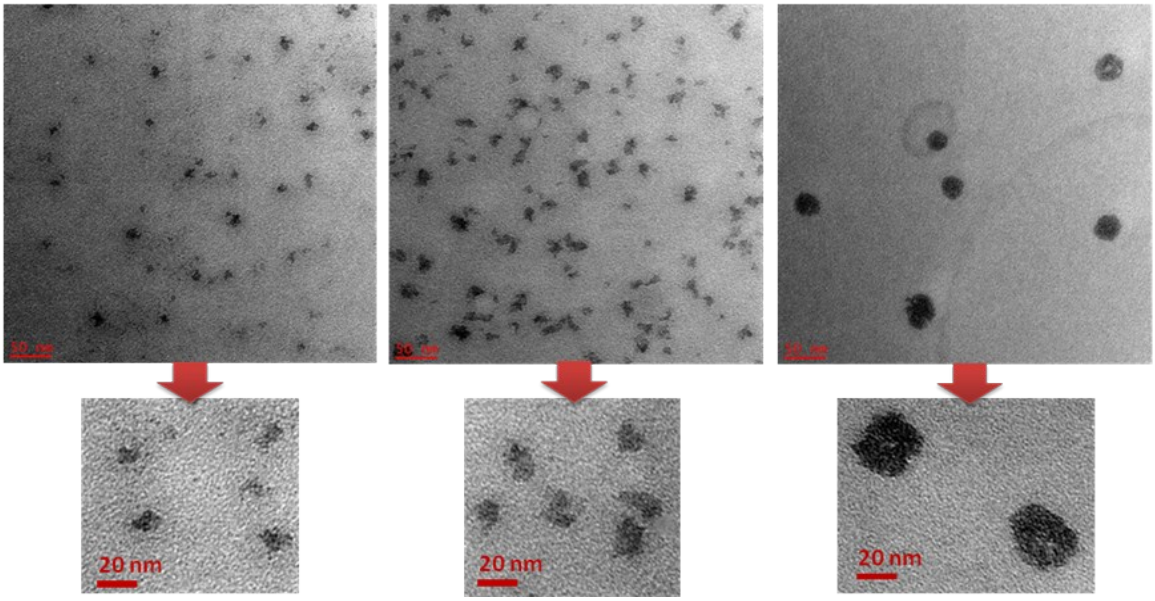

Figure S9. TEM images of three bottlebrush polymers at low and high magnifications. PNB_{22}-*g*-$PTFEMA_{22}$ (left); PNB_{49}-*g*-$PTFEMA_{22}$ (middle); PNB_{200}-*g*-$PTFEMA_{22}$ (right).

Reference

1 C. Grigoriadis, A. Nese, K. Matyjaszewski, T. Pakula, H. -J. Butt, G. Floudas, *Macromol. Chem. Phys*. 2012, **213**, 1311–1320.