

“Clicking” Fluorinated Polyhedral Oligomeric Silsesquioxane onto Polymers: A Modular Approach toward Shape Amphiphiles with Fluorous Molecular Clusters

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Supporting Information

Supplementary Chemical Synthesis.

Synthesis of chain transfer agent ETC: 1-Dodecanethiol (14.9 g, 0.074 mmol), acetone (42.8 g, 0.74 mol), and Aliquat 336 (1.20 g, 2.95mmol) were mixed in a 250 mL flask and then cooled to 10 °C. Sodium hydroxide aqueous solution (50 wt %) (6.13 g, 0.077 mol) was added dropwise. After stirred for 30 min, a mixture of carbon disulfide (5.6 g, 0.07 mol) and acetone (7.44 g, 0.13 mol) was added and stirred for another 10 min. Chloroform (13.12 g, 0.12 mol) was then added, followed by the addition of sodium hydroxide aqueous solution (29.5 g, 0.40 mol). The solution was stirred overnight. After pH being adjusted to about 2 by addition of HCl aqueous solution, the precipitated phase was collected by filtration and purified by recrystallization in hexanes to give yellow crystal solid (23.4 g). ¹H NMR (CDCl₃, 300MHz, ppm, δ): 3.3 (t, 2H, -CH₂S-), 1.75 (m, 6H, -C(CH₃)₂-COO-), 1.29 (t, 20H, -(CH₂)₁₀-), 0.9 (t, 3H, -CH₂CH₃).

TC (10 g, 27.5 mmol) and anhydrous ethanol (2.53 g, 55.0 mmol) was added to a 250 mL flask with 150 mL of anhydrous CH₂Cl₂. DMAP (0.34 g, 2.8 mmol) and DIPC (4.16 g, 33.0 mmol) was added. The solution was stirred at room temperature for 24 h. Oil-like crude product was obtained by removing solvent, which was further purified by column with CH₂Cl₂: hexanes = 1:1 as the eluting solvent. ¹H NMR (CDCl₃, 300MHz, ppm, δ): 4.13 (t, 2H, -CH₂OOC-), 3.3 (t, 2H, -CH₂S-), 1.75 (m, 6H, -C(CH₃)₂-COO-), 1.29 (m, 23H, -(CH₂)₁₀-; -OCH₂CH₃), 0.9 (t, -3H, CH₂CH₃).

Synthesis of 4-oxo-4-(prop-2-yn-1-yloxy) butanoic acid: Propargyl alcohol (2.00 g, 35.7 mmol) and oxolane-2, 5-dione (3.92 g, 39.2 mmol) were dissolved in a 100 mL round bottom

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flask. DMAP (0.44 g, 3.56 mmol) and triethyl amine (3.6 g, 35.7 mmol) were then added to the solution and stirred overnight. HCl (aq) was added dropwisely to adjust pH to about 2.0. The solution was washed with purified water twice, followed by drying with sodium sulfate. solid colorless product was obtained upon removal of solvent, which was further purified with flash column with chloroform as the eluting solvent. ^1H NMR (CDCl_3 , 300MHz, ppm, δ): 11.4 (m, 1H, $-\text{COOH}$), 4.7 (d, 2H, $-\text{CH}_2-\text{OOC}-$), 2.6 (t, 4H, $\text{HOOC}-\text{CH}_2\text{CH}_2-\text{OOC}-$), 2.5 (t, 1H, $-\text{CCH}$).

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Calculation of FPOSS functionality.

FPOSS-PS.

Degree of FPOSS functionality (f) can be calculated based on Eq. S1.

$$f = \frac{(S_{n+r} + S_{h+i} + S_s) / 46}{S_b / 2} \quad (\text{S1})$$

Where S_{n+r} , S_{h+i} , and S_s are the integration area of protons on the FPOSS moiety (see Figure 3 for detailed assignment); while S_b is the integration area of proton b on the initiator. The number of FPOSS per chain (N_{FPOSS}) is equal to f . Calculated results are listed in table 1.

PS/FPOSS.

Degree of polymerization of poly(vinyl benzyl chloride) segments (N_{PVBC}) and PS segments (N_{PS}), and overall molecular weight of PS/Cl can be calculated based on Eq. S2.

The number of FPOSS per PS/FPOSS chain (N_{FPOSS}) is equal to N_{PVBC} . Results are listed in table 1.

$$N_{PVBC} = \frac{S_B / 2}{S_A / 2}$$
$$N_{PS} = \left(\frac{S_C / 5}{S_A / 2} - \frac{S_B / 2}{S_A / 2} \right) \quad (\text{S2})$$
$$M_n^{overall} = N_{PVBC} * 152 + N_{PS} * 104$$

where S_A , S_B , and S_C are the integration area of proton a , proton b , and aromatic protons between 6.2 – 7.3 ppm, respectively (Figure 6a, 6b).

FPOSS-PS-*b*-PEO and PS-(FPOSS)-PEO.

Degree of FPOSS functionality (f) can be calculated based on Eq. S3

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$$f = \frac{(S_{n+r} + S_{h+i} + S_s) / 46}{S_b / \left(\frac{M_n^{PEO}}{44} * 4\right)} \quad (\text{S3})$$

where S_{n+r} , S_{h+i} , and S_s are the integration area of protons on the FPOSS moiety (see Figure 3 for detailed assignment); while S_b is the integration area of protons on PEO block. The number of FPOSS per chain (N_{FPOSS}) is equal to f . Calculated results are listed in table 1.

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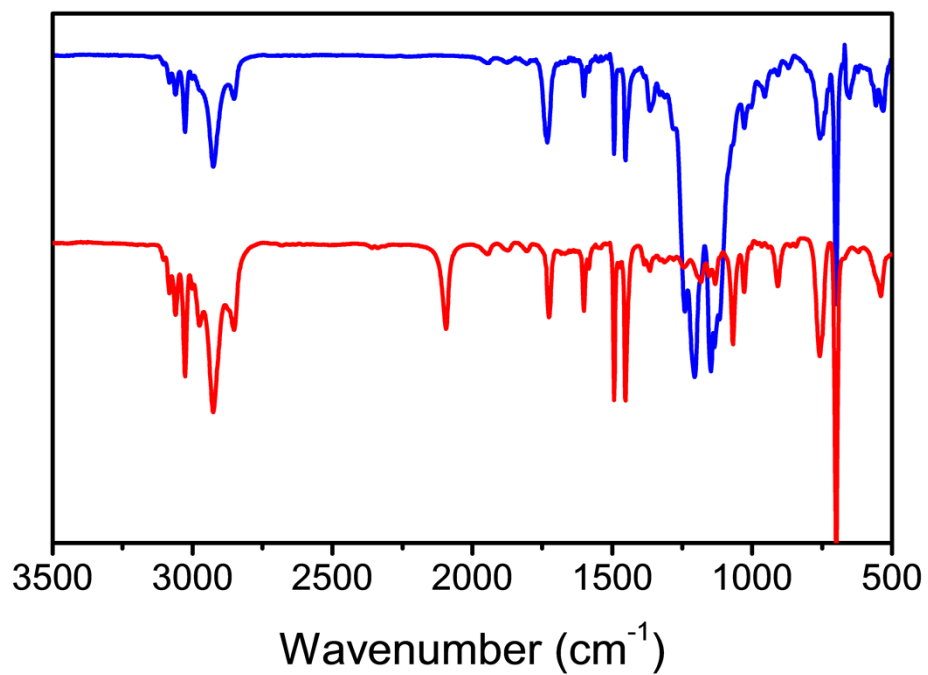
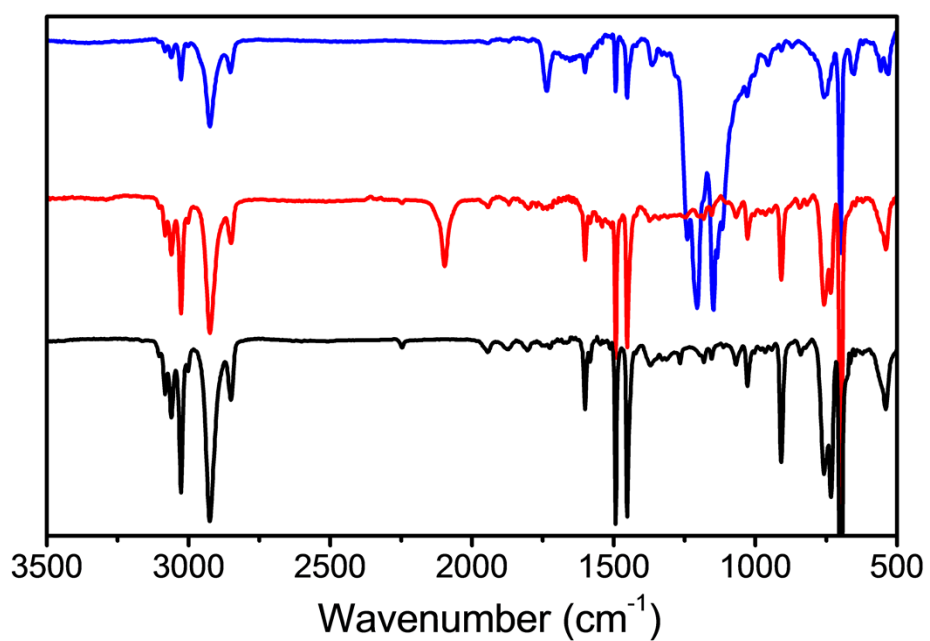


Figure S1. FI-IR spectra of PS-N₃ (red) and PS-FPOSS (blue). The results were based on the sample FPOSS-PS₂₄.



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Figure S2. FI-IR spectra of PS/Cl (black), PS/N₃ (red) and PS-FPOSS (blue). The results were based on the sample PS₂₃₀/FPOSS₁₀.

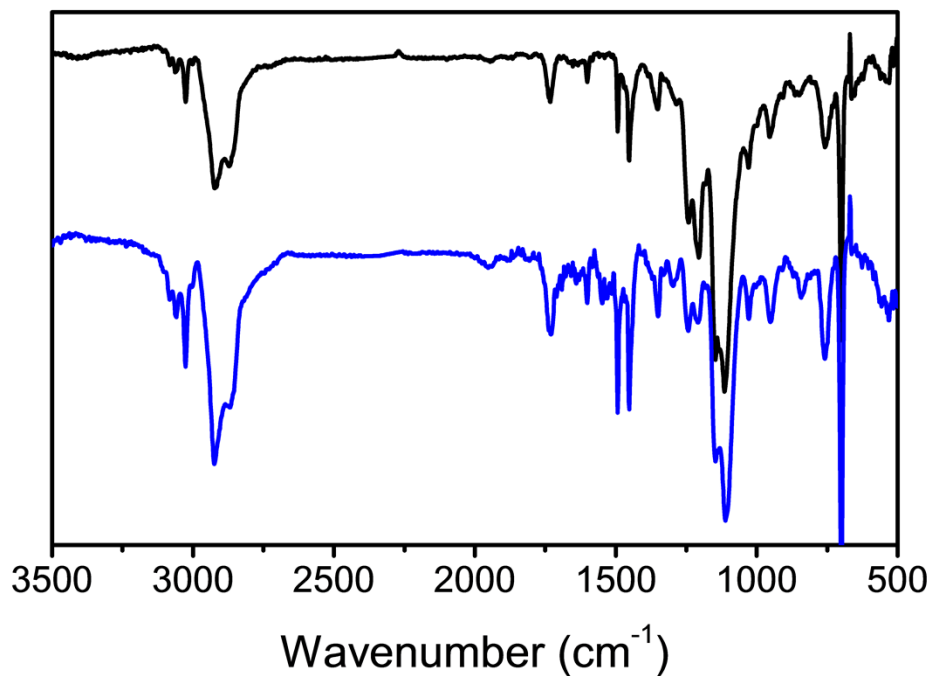


Figure S3. FT-IR spectra of fFPOSS-PS-*b*-PEO (blue), PS-FPOSS-PEO (black). The results were based on the sample FPOSS-PS₂₈-*b*-PEO₄₅ and PS₅₂-(FPOSS)-PEO₄₅, respectively.