

Dynamic effects and adhesion of water droplet impacts on hydrophobic surfaces: bouncing or sticking

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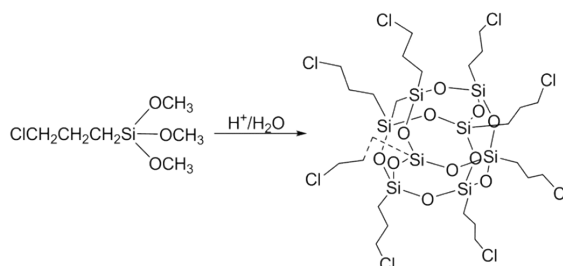
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Materials

Methyl methacrylate (MMA), Toluene and Alumina (Al₂O₃, 100-200 mesh) were obtained from Tianjin Fuyu Fine Chemicals Co Ltd. Cuprous chloride (CuCl) was obtained from Tianjin BASF Chemical Reagents Co Ltd. Pentamethyldiethylenetriamine (PMDETA) and trifluoroethyl methacrylate (TFEMA) were purchased from Aldrich. γ -Chloropropyl trimethoxysilane was obtained from Nanjing Xiangqian Chemical Reagents Co Ltd. The materials were purified according to previous study.¹ The other reagents were of chemically pure grade, and used without further purification.

Synthesis of the OCP-POSS initiator

Octa (γ -chloropropyl) silsesquioxane (OCP-POSS) was synthesized *via* the hydrolytic condensation according to the literature,^{2, 3} and the synthesis route was shown in Scheme S1. The hydrolysis of γ -chloropropyl trimethoxysilane (Cl(CH₂)₃Si(OCH₃)₃, 10 mL) was performed in methanol (200 mL) in the presence of concentrated hydrochloric acid (8 mL). After reacting for 5 days in a 65 °C oil bath under rapid stirring, a white solid was obtained. Then the product was washed with methanol for three times and dried under vacuum at 50 °C for 2 days.

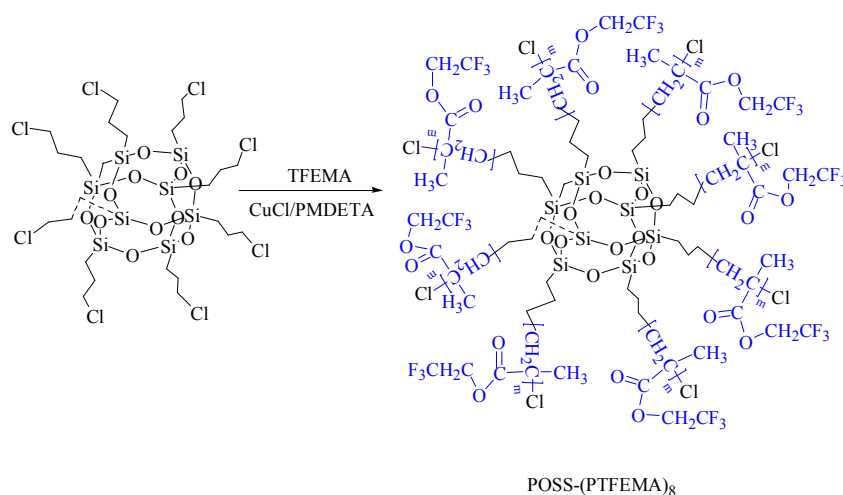


Scheme S1. Synthetic route of POSS-Cl₈

Synthesis of POSS-(PTFEMA)₈

The ATRP process was carried out using -CH₂CH₂CH₂Cl bonded on a POSS cage as the initiation

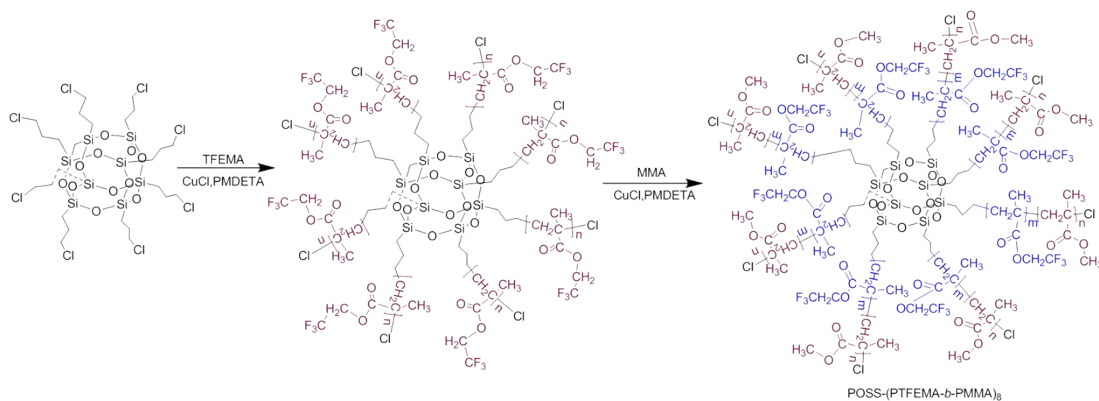
group and under a nitrogen environment (Scheme S2). In the nitrogen, the, OCP-POSS (0.1 mmol), PMDETA (0.3 mmol), toluene (10 mL), TFEMA (10 mL) and CuCl (0.1 mmol) were added into the flask equipped with a magnetic stir bar. The system was evacuated three times, filled with dry nitrogen, and placed in an oil bath warmed at 110 °C. After 24 h, the polymerization was terminated by cooling the flask in ice water. Then the mixture was diluted with tetrahydrofuran (THF), filtered over an alumina column to remove the catalyst, and poured into a tenfold methanol-water solution. The product was obtained after filtration and drying at 50 °C in a vacuum overnight.



Scheme S2 Synthetic route of POSS-(PTFEMA)₈

Synthesis of POSS-(PTFEMA-*b*-PMMA)₈

The process was obtained through a one-pot reaction (Scheme S3).



Scheme S3. Synthetic route of POSS-(PTFEMA-*b*-PMMA)₈

At first, a tailor-made flask in ice bath maintained an overpressure of dry nitrogen to remove oxygen totally. Then OCP-POSS (0.1 mmol), PMDETA (0.3 mmol), toluene (10 mL), TFEMA (10 mL) and CuCl (0.1 mmol) were added into the flask equipped with a magnetic stir bar. The system was evacuated three times, filled with dry nitrogen, and placed in an oil bath warmed at 110 °C. After 24 h,

the MMA (10 mL) was added into the system and reacted for 24 h. The polymerization was terminated by cooling the flask in ice water. Then the mixture was diluted with THF, filtered over an alumina column, and poured into tenfold methanol. The product was obtained after filtration and drying at 50 °C in a vacuum overnight.

Characterization

Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AVANCF-300 NMR spectrometer. Samples for ^{29}Si NMR and ^1H NMR were prepared in CDCl_3 , and tetramethylsilane (TMS) was used as an internal standard. Gel permeation chromatography (GPC) was used to determine the molecular weights, with Shodex OHpak SB-803 HQ (300×8 mm) as chromatographic columns. It was carried out at 298 K with THF as solvent (0.5 mL/min) and polystyrene as calibration.

Results

The NMR analysis of $\text{POSS}-(\text{Cl})_8$, $\text{POSS}-(\text{PTFEMA})_8$ and $\text{POSS}-(\text{PTFEMA}-b\text{-PMMA})_8$ were shown in Figure S1 to S3.

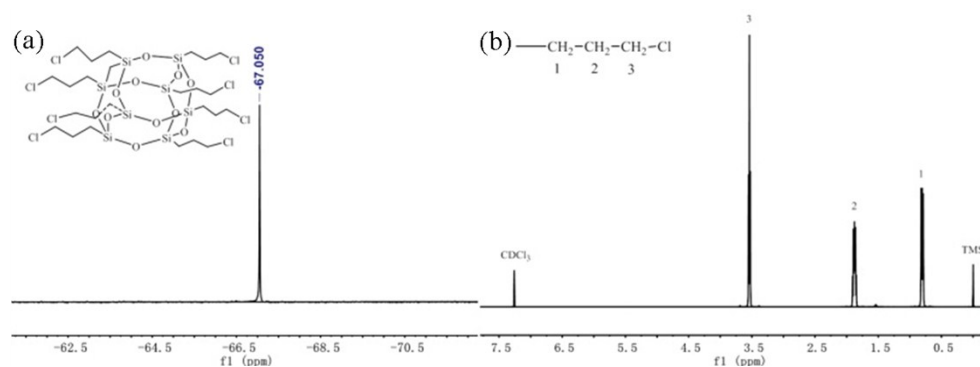


Figure S1 (a) ^{29}Si NMR, (b) ^1H NMR spectra of $\text{POSS}-(\text{Cl})_8$ in CDCl_3

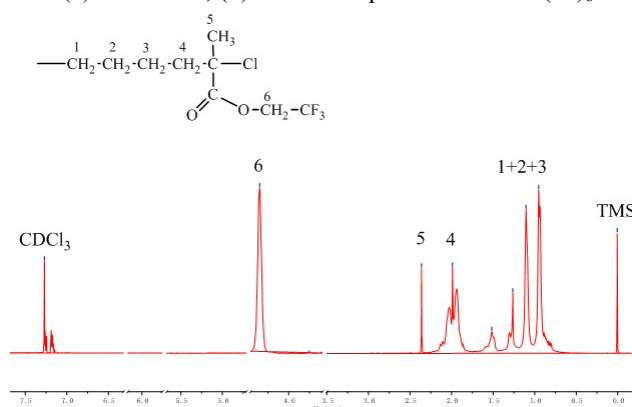


Figure S2 The ^1H NMR spectrum of $\text{POSS}-(\text{PTFEMA})_8$

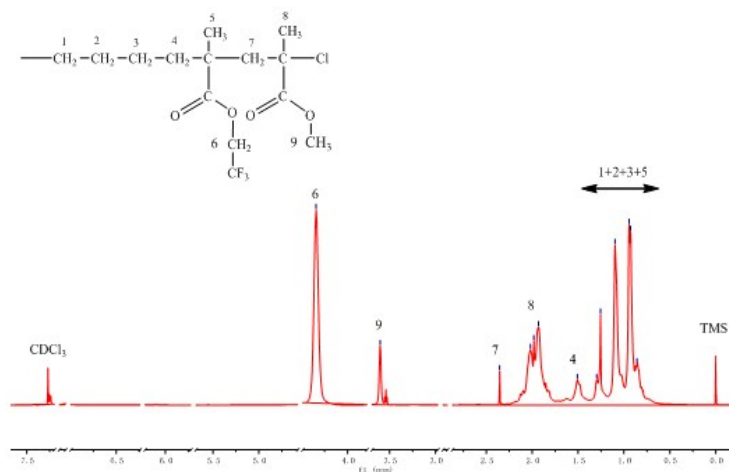


Figure S3 The ¹H NMR spectrum of POSS-(PTFEMA-*b*-PMMA)₈

Reference

1. X. Qiang, X. Ma, Z. Li and X. Hou, Synthesis of star-shaped polyhedral oligomeric silsesquioxane (POSS) fluorinated acrylates for hydrophobic honeycomb porous film application. *Colloid and Polymer Science*, 2014, **292**, 1531-1544.
2. Z. Ge, D. Wang, Y. Zhou, H. Liu and S. Liu, Synthesis of organic/inorganic hybrid quatrefoil-shaped star-cyclic polymer containing a polyhedral oligomeric silsesquioxane core. *Macromolecules*, 2009, **42**, 2903-2910.
3. Y. Liu, X. Yang, W. Zhang and S. Zheng, Star-shaped poly(ϵ -caprolactone) with polyhedral oligomeric silsesquioxane core. *Polymer*, 2006, **47**, 6814-6825.