

Supporting information

Synthesis, Characterization and Chondrocyte Culture of Polyhedral Oligomeric Silsesquioxane (POSS)-containing Hybrid Hydrogels

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Synthesis of octa-chlorine-functionalized POSS (OCPOSS)

OCPOSS was synthesized *via* the hydrolytic condensation of 3-chloropropyltrimethoxysilane as previously reported.¹ Briefly, 450 mL of methanol, 3-chloropropyltrimethoxysilane (19.88 g, 0.1 mol), and 22.5 mL of concentrated hydrochloric acid were mixed and stirred at room temperature for at least 5 weeks. OCPOSS was obtained as colorless crystals after filtrating, washing with methanol and deionized water, recrystallizing from acetone and drying in vacuo at 60 °C for 24 h (3.8 g, yield: 29.3%). ¹H NMR (400 MHz, CDCl₃, δ): 0.75-0.88 (t, 2H, Si-CH₂-), 1.80-1.96 (m, 2H, Si-CH₂CH₂-), 3.50-3.63 (t, 2H, Si-CH₂-CH₂-Cl).

Synthesis of octa-azido-functionalized POSS (OAPOSS)

OAPOSS was synthesized *via* the substitution reaction between OCPOSS and sodium azide.² OCPOSS (1.0 g, 0.9 mmol), NaN₃ (1.3 g, 20 mmol), and DMF (30 mL) were mixed and stirred at 50 °C in a 100 mL round-bottom flask for 24 h. OAPOSS was obtained as colorless viscous liquid after precipitating in a large amount of deionized water and drying in vacuo at 50 °C for 48 h (2.8 g, yield: 88.6%). ¹H NMR (400 MHz, CDCl₃, δ): 0.63-0.80 (t, 2H, Si-CH₂-), 1.55-1.82 (m, 2H, Si-CH₂CH₂-), 3.23-3.40 (t, 2H, Si-CH₂-CH₂-N₃).

Synthesis of alkyne-functionalized PEG

Alkyne-functionalized PEG was synthesized *via* the reaction between PEG and propargyl bromide.³ Briefly, sodium hydride (NaH) (0.2 g, 8 mmol) was

dissolved in 20 mL of anhydrous THF with vigorous stirring in a 250 mL round-bottom flask. PEG (1 mmol) in 50 mL THF solution was added dropwise to the flask with stirring at 0 °C. After stirring for 1 h, propargyl bromide (0.95 g, 8 mmol) diluted with 50 mL anhydrous THF was slowly dropped to the reaction mixture at 0 °C. The reaction was carried out for additional 24 h at room temperature. After reaction, the mixture was filtrated and thereafter the filtrate was extracted into dichloromethane to remove sodium bromide and excessive NaH. The organic layer was dried over MgSO₄, concentrated *via* rotary evaporation and precipitated in diethyl ether. The product was further dried in vacuum at 30 °C for 48 h (yield: 90.8%). In a typical case of alkyne-functionalized PEG (6k), ¹H NMR (400 MHz, CDCl₃, δ): 2.44 (s, 2H, HC≡C-), 4.22 (s, 4H, HC≡C-CH₂-), 3.45-3.85 (m, 545H, -CH₂CH₂-O-). FTIR (cm⁻¹, KBr): 3240 (≡C-H).

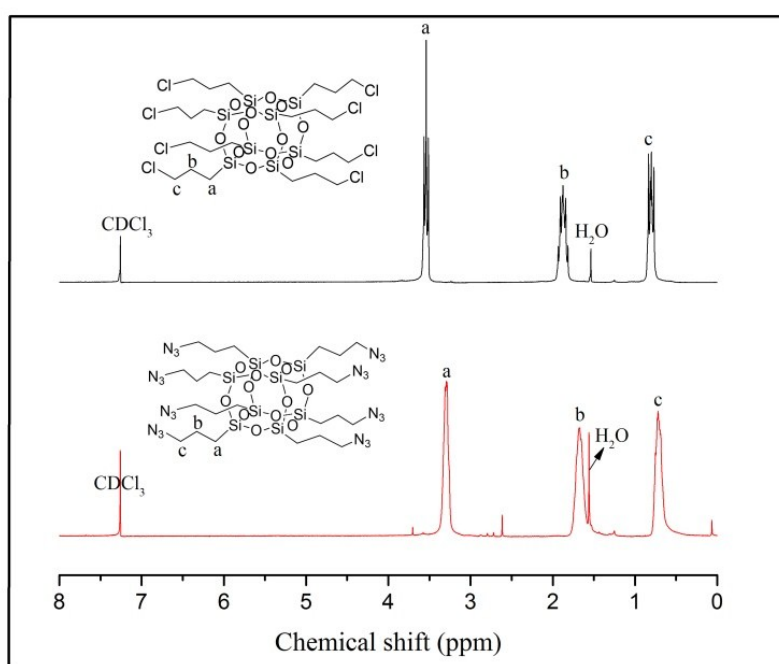


Fig. S1. ¹H-NMR spectra of OCPOSS and OAPOSS.

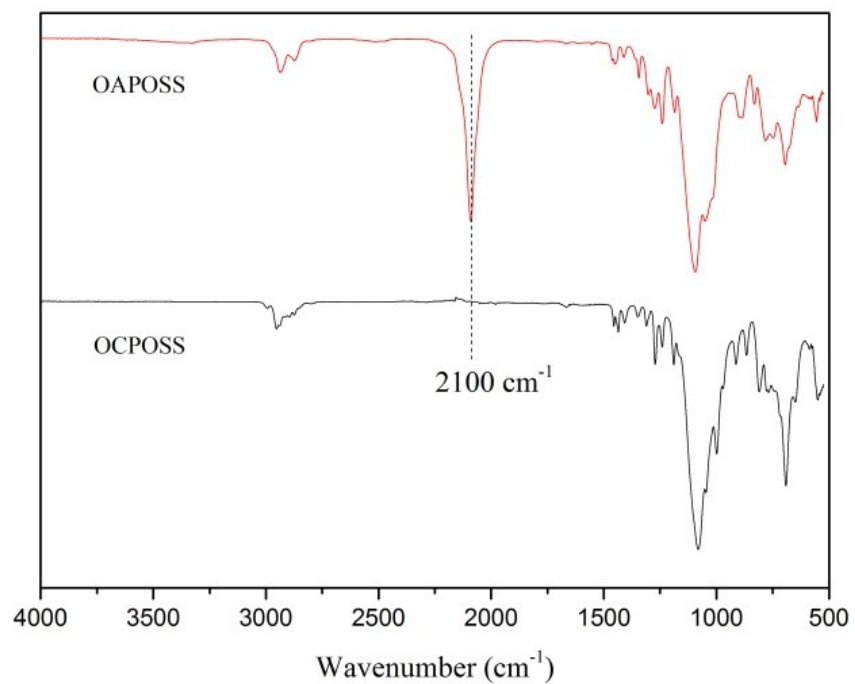


Fig. S2. FTIR spectra of OCPOSS and OAPOSS.

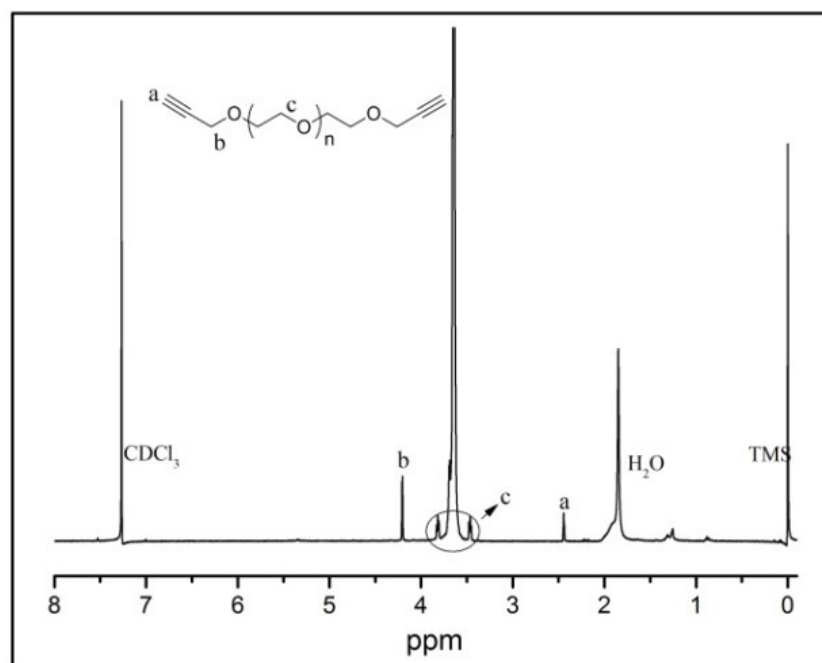


Fig. S3. ^1H -NMR spectrum of alkyne-functionalized PEG (6k).

References

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3. C.-C. Lin, *RSC Adv.*, 2015, **5**, 39844-39853.