Supporting Information for

POSS Semitelechelic Aβ_{17-19} Peptide Initiated Helical Polypeptides and Their Structural Diversity in Aquaeous Medium

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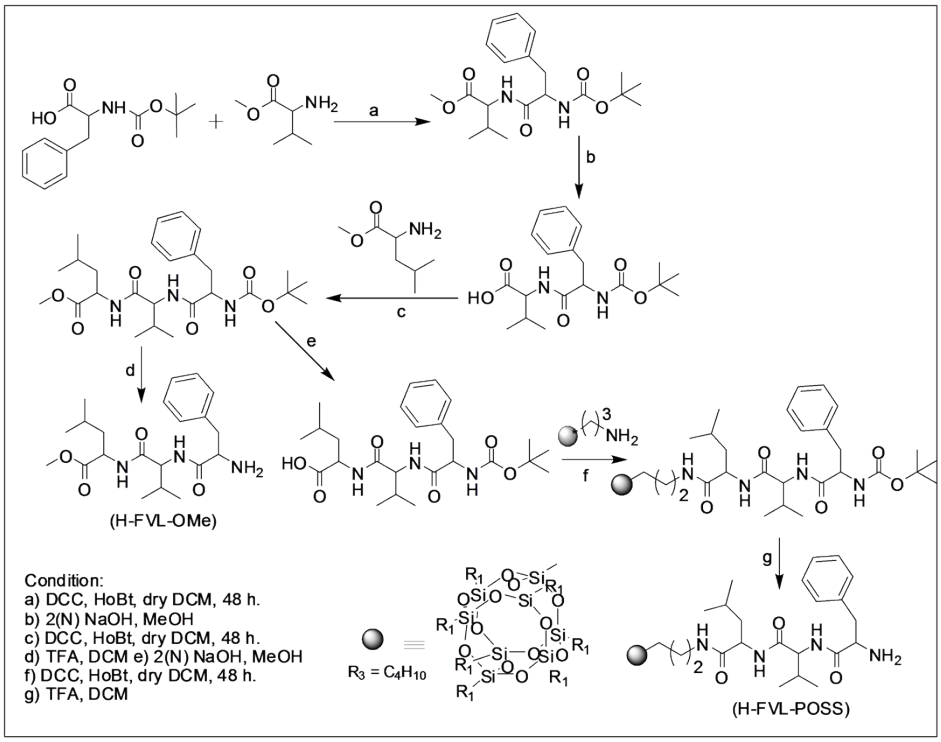
Synthesis of peptides: The two free *N*-terminal tripeptides namely, H-FVL-OMe and H-FVL-POSS were prepared through well conventional solution phase methodology *via* successive protection and deprotection approach. Note: *C*-terminus end group was protected by methyl ester group, while amine group was protected by Boc precursors. On the other hand methyl ester hydrolysis and Boc group deprotection were carried out by 1N NaOH and TFA treatment. All the intermediates were characterized by ^{1}H NMR spectroscopy and thin layer chromatography (TLC) on silica gel to reach the final initiators.

Synthesis of Boc-FVL-OH and Boc-FVL-OMe: The Boc-FVL-OH and Boc-FVL-OMe tripeptide were prepared according to our earlier reported procedure.[1]

Synthesis of H-FVL-OMe: For deprotection of Boc group, 3.0 mL TFA was added to Boc-FVL-OMe (1.43 g, 3.0 mmol) and the subsequent removal of the Boc group was monitored *via* TLC. After, 4 h of reaction, the TFA was removed by rotator evaporator. The resulting product was then dissolved in water (30 mL) and washed with ethyl acetate (2 × 30 mL). The pH of the aqueous solution was adjusted to 8-9 with sodium bicarbonate and the

peptide was extracted with ethyl acetate (3 × 20 mL). The organic extracts were collected, washed with saturated brine, dried over sodium sulphate, and evaporated under reduced pressure to obtain purified free amine terminated peptide. Yield = 1.10 g. ^{1}H NMR, ^{13}C NMR, FT-IR and ESI-MS are shown in Fig. S1, Fig. S2, Fig. S6 and Fig. S8, respectively.



Scheme S1 Synthesis of H-FVL-OMe and H-FVL-POSS *via* solution phase methodology.

Synthesis of H-FVL-POSS: POSS-NH_2 (3.0 g, 3.43 mmol) and Boc-FVL-OH (1.63 g, 3.43 mmol) were dissolved in dry DCM (40 mL) and the solution was purged with dry N_2. Then, a solution of DCC (0.71 g, 3.43 mmol) and HOBt (0.46 g, 3.43 mmol) in 10 mL of dry DCM was added drop-wise to the reaction mixture in an ice-water bath under stirring and was allowed to react at room temperature for 12 h. After removing insoluble DCU by suction filtration, the organic layer was further washed with 1N HCl, saturated $NaHCO_3$ and brine

solution and dried over Na_2SO_4. The organic solvent was removed by rotary evaporation and the crude product was purified by silica gel (100-200 mesh) column chromatography using 4% ethyl acetate as mobile phase, to get a white solid compound Boc-FVL-POSS, with a yield of 75%. In the next step, the Boc group was removed by TFA treatment followed by subsequent neutralization to get amine terminated peptide precursor. ^{1}H NMR, ^{29}Si NMR, ^{13}C NMR, FT-IR and ESI-MS are shown Fig. S3, Fig. S4, Fig. S5, Fig. S7 and Fig. S9, respectively.

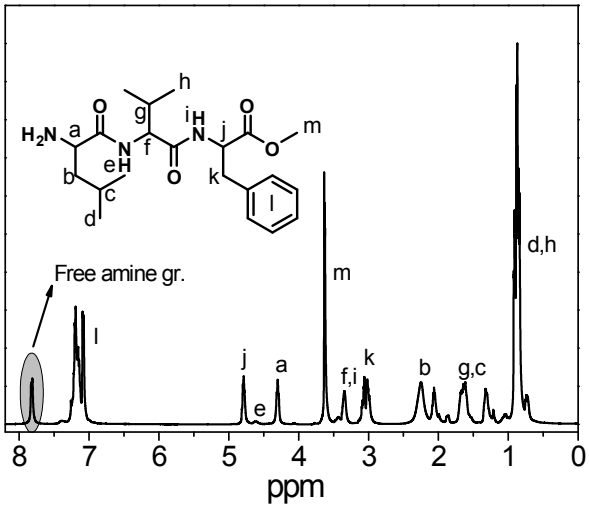


Fig. S1 ^{1}H NMR spectrum of H-FVL-OMe in $CDCl_3$.

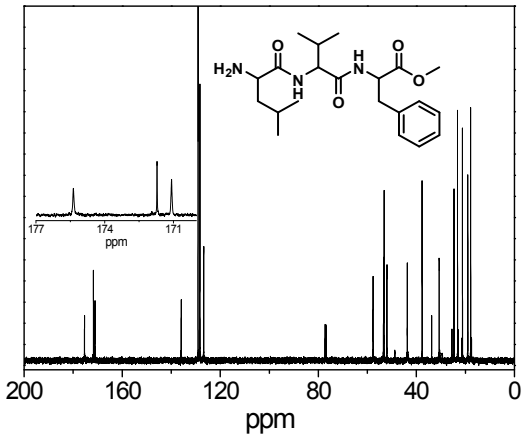


Fig. S2 ^{13}C NMR spectrum of H-FVL-OMe in $CDCl_3$.

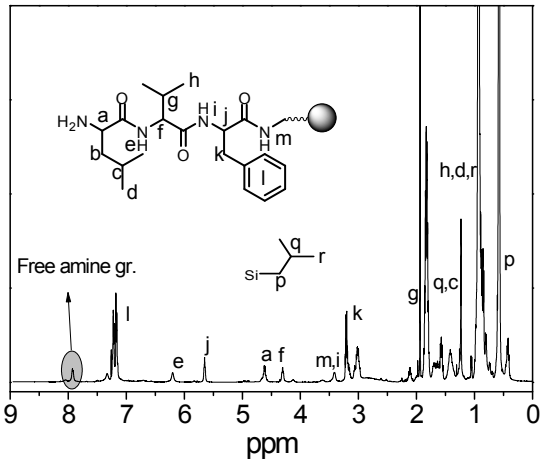


Fig. S3 ^{1}H NMR spectrum of H-FVL-POSS in $CDCl_3$.

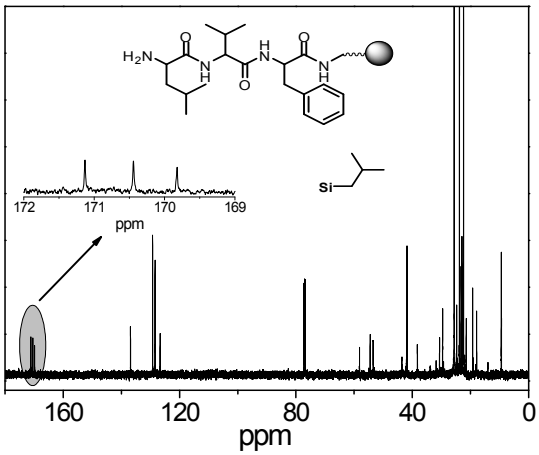


Fig. S4 ^{13}C NMR spectrum of H-FVL-POSS in $CDCl_3$.

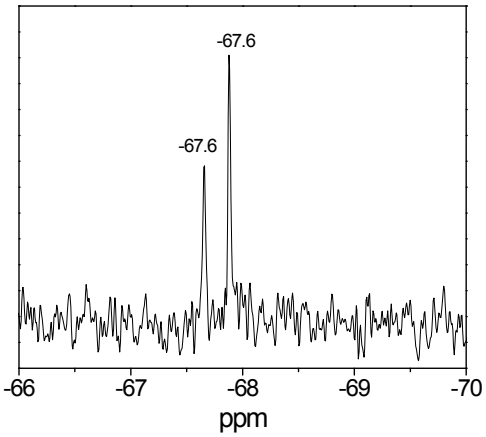


Fig. S5 ^{29}Si NMR spectrum of H-FVL-POSS in $CDCl_3$.

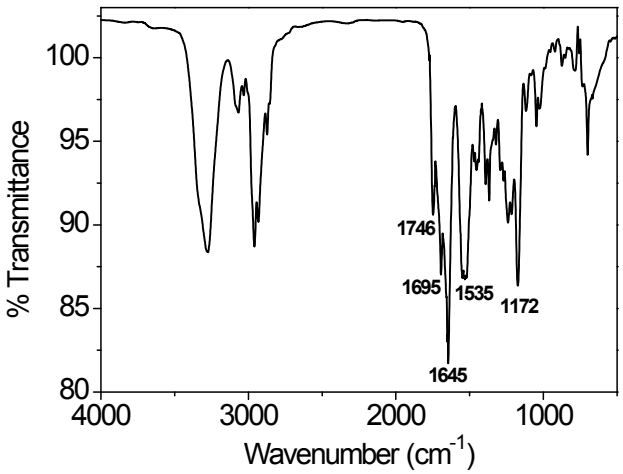


Fig. S6 Solid state FT-IR spectrum of H-FVL-OMe.

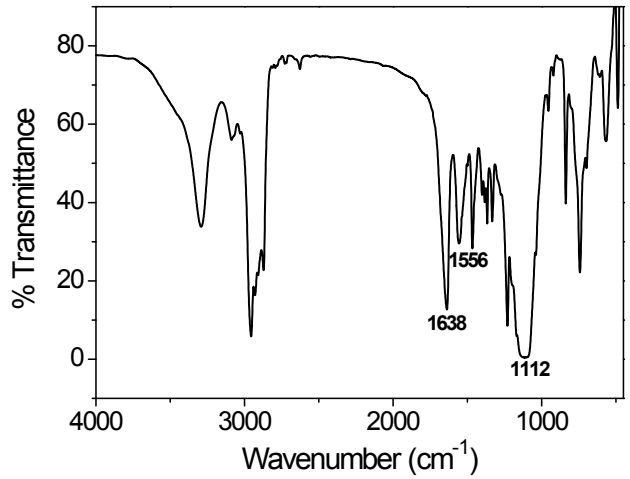


Fig. S7 Solid state FT-IR spectrum of H-FVL-POSS.

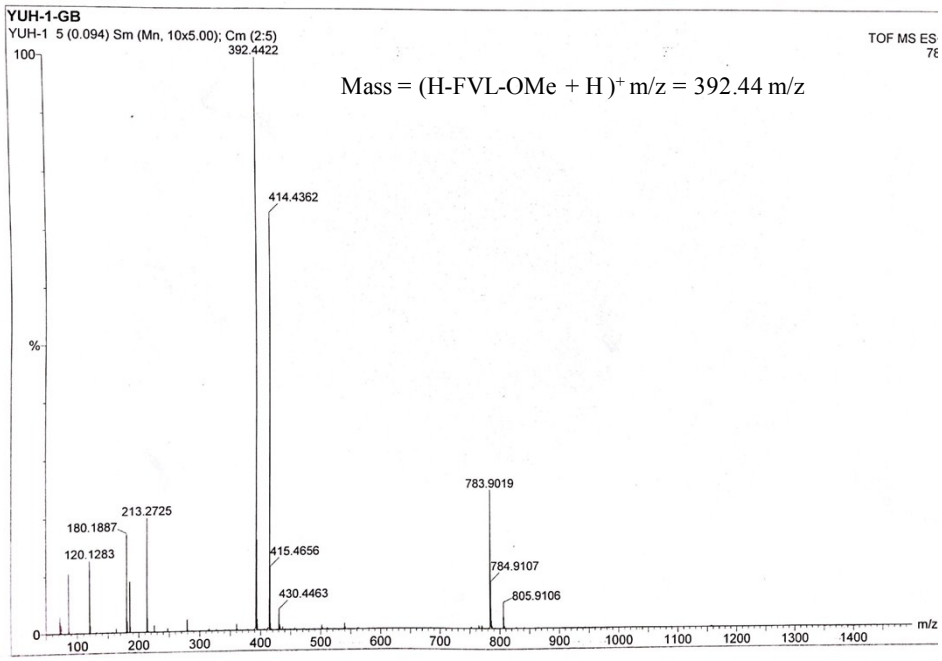


Fig. S8 ESI-MS spectrum of H-FVL-OMe.

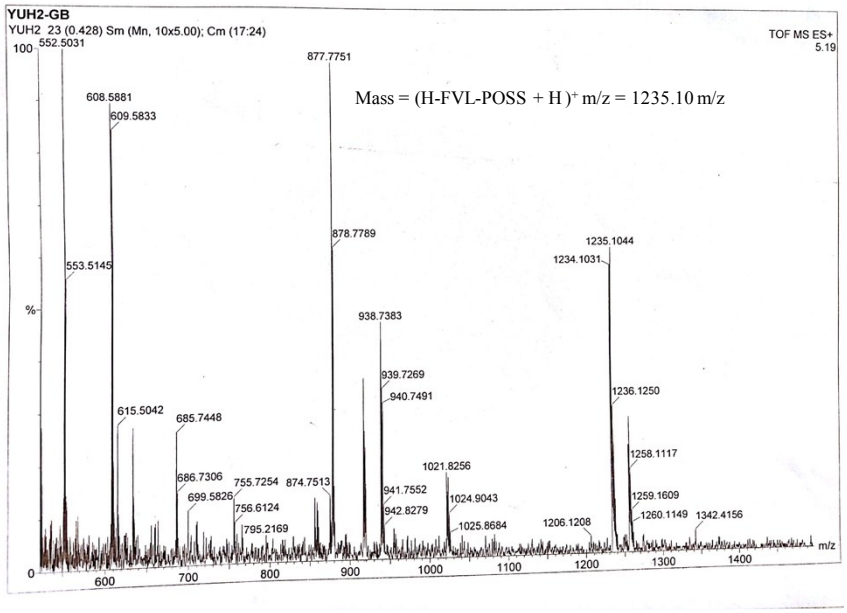


Fig. S9 ESI-MS spectrum of H-FVL-POSS.

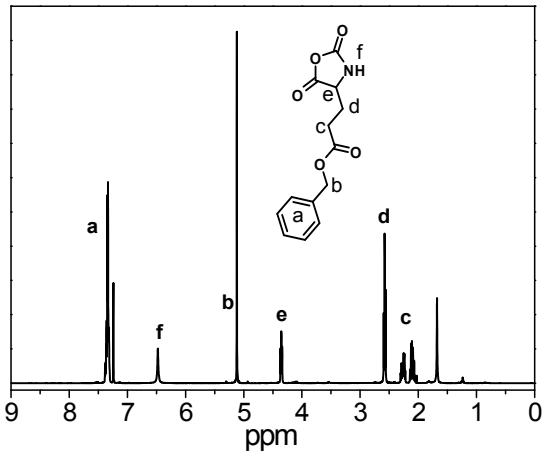


Fig. S10 ^{1}H NMR spectrum of BLG-NCA monomer in $CDCl_3$.

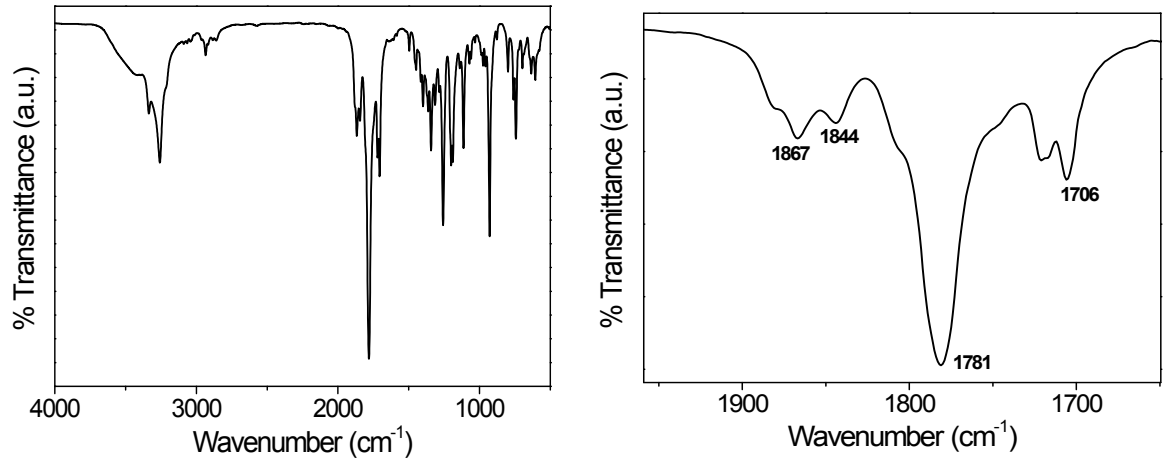


Fig. S11 FT-IR spectra of BLG-NCA monomer (A) full and (B) partial region.

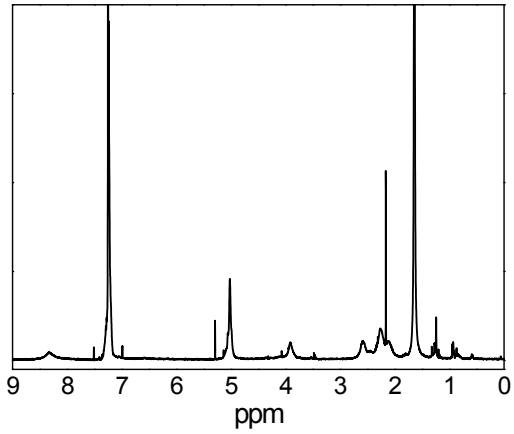


Fig. S12 ^{1}H NMR spectrum of **3a** in $CDCl_3$.

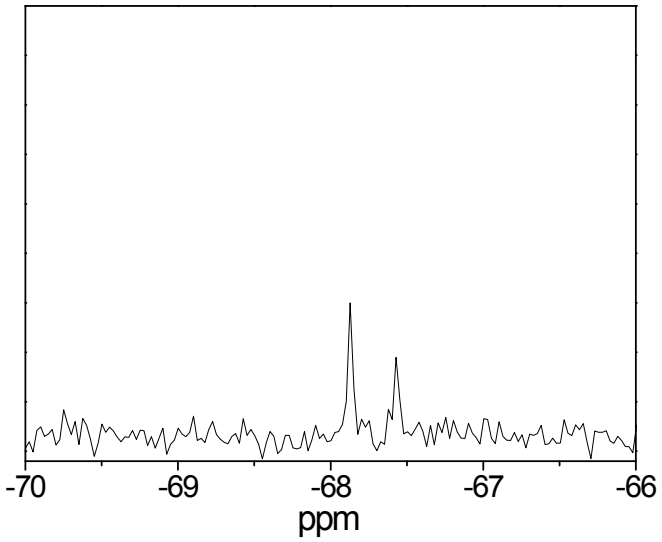


Fig. S13 The ^{29}Si NMR spectrum of **2a** in $CDCl_3$.

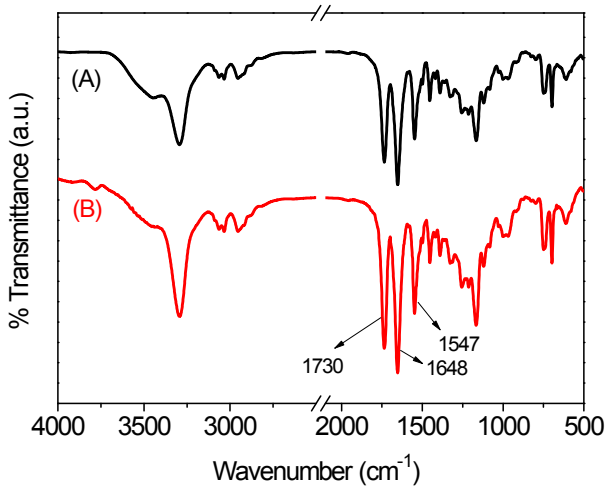


Fig. S14 Solution phase FT-IR spectra of (A) **1a** and (B) **2a** (recorded in $CHCl_3$).

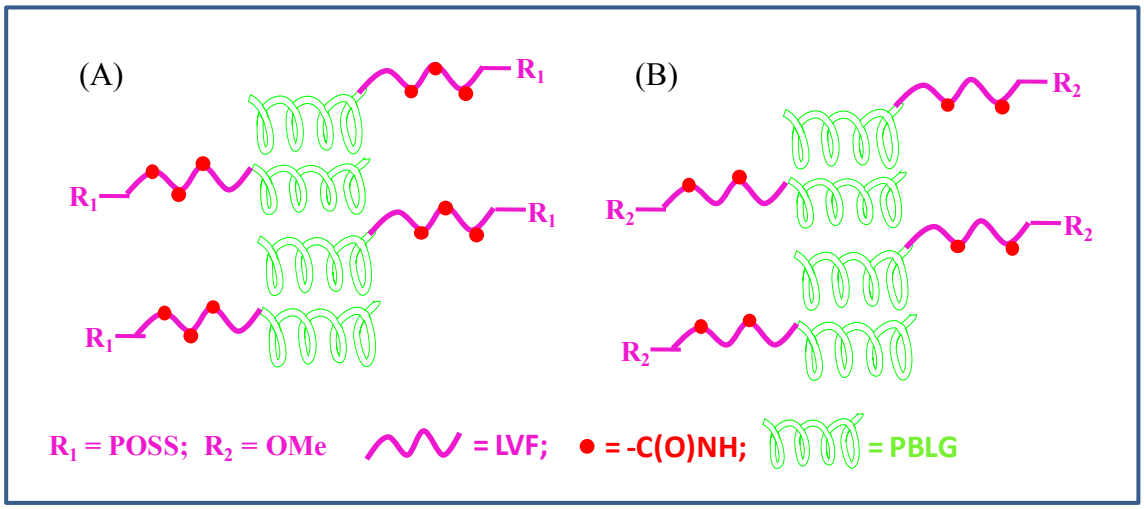


Fig. S15 Pictorial representation for the possible arrangements of (A) **2a** and (B) **1a**.

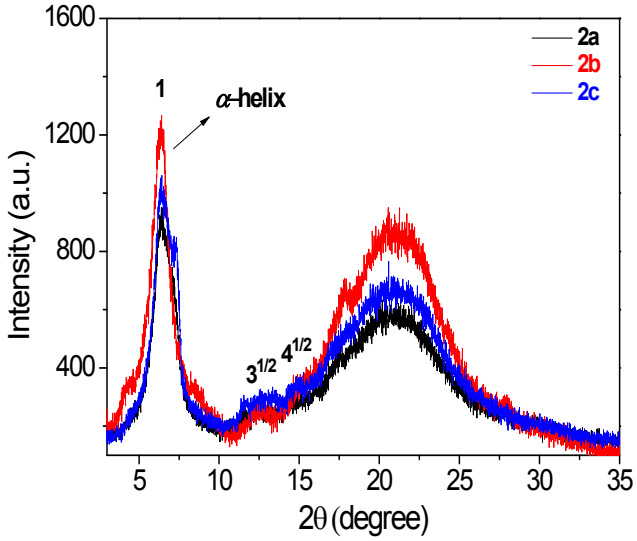


Fig. 16 PXRD spectra of **2a**, **2b** and **2c**.

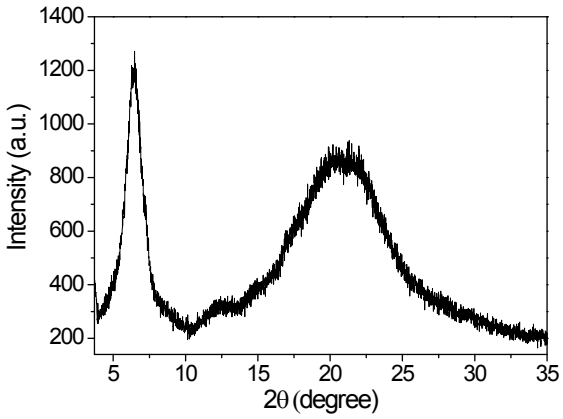


Fig. S17 PXRD spectrum of **3a**.

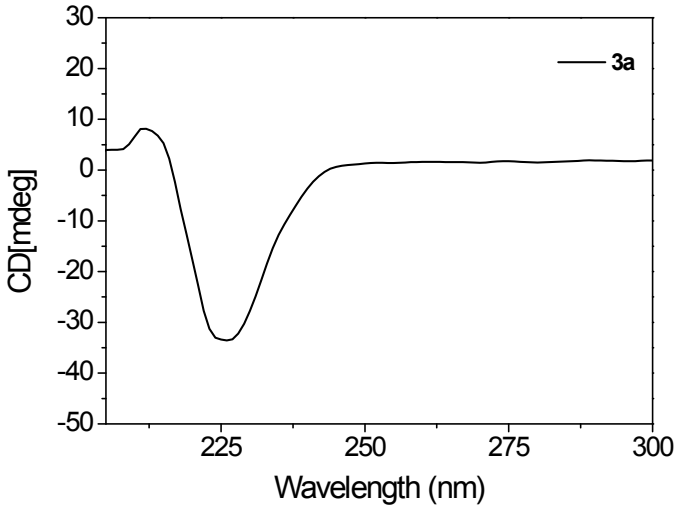


Fig. S18 CD spectrum of **3a**.

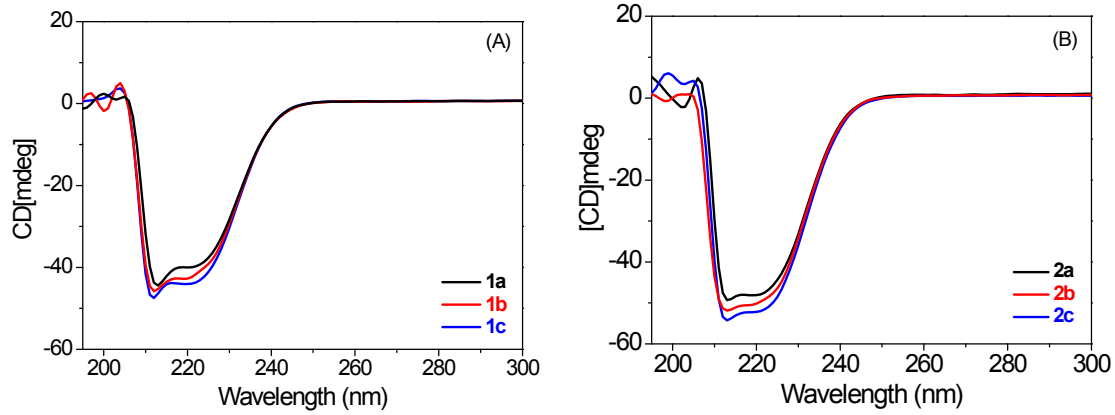


Fig. S19 CD spectra of (A) **1a**, **1b**, **1c**, and (B) **2a**, **2b**, **2c** in acetonitrile at 20 °C.

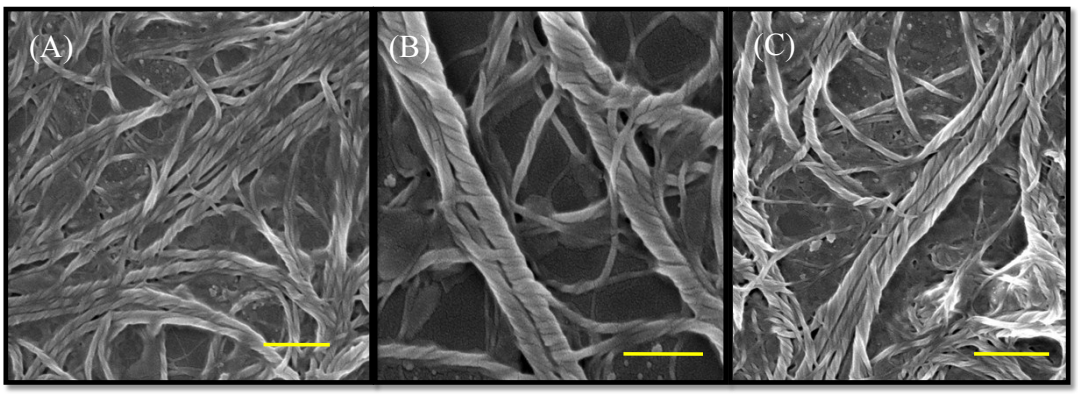


Fig. 20 FE-SEM images of (A) **1c**, (B) **2c** and (C) **3a**. Each scale bar indicates 200 nm. Sample concentration: 0.1 mg/mL.

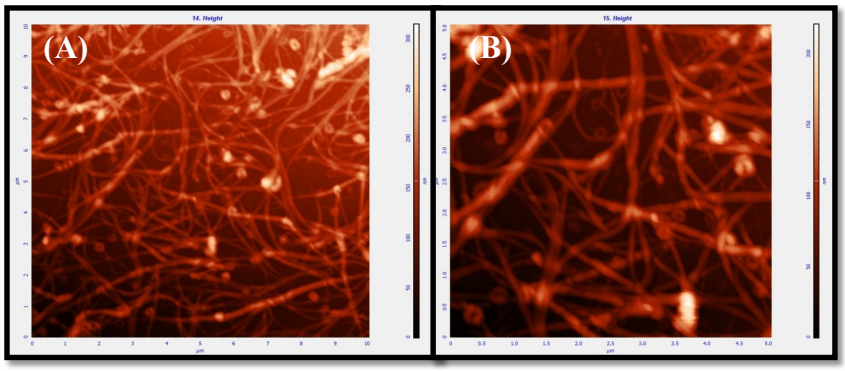


Fig. S21 Tapping mode AFM images of (A) **1c** and (B) **2c**. Sample concentration 0.01 mg/mL. Thickness of the AFM height image = 50 nm.

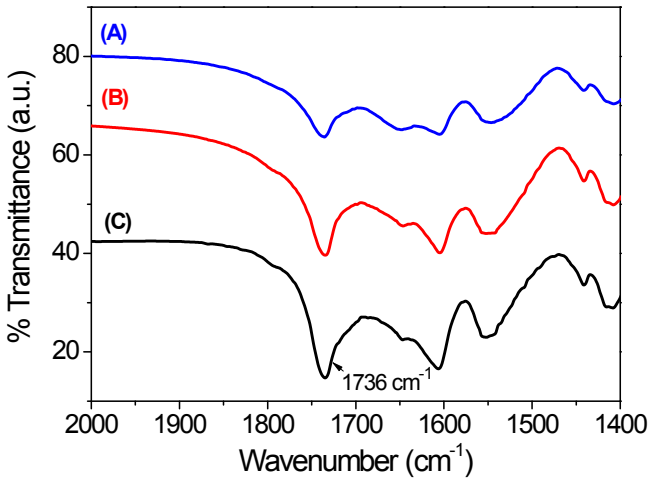


Fig. S22 FT-IR spectra of benzyl deprotected polymers: (A) **d1a**, (B) **d1b** and (C) **d3a**.

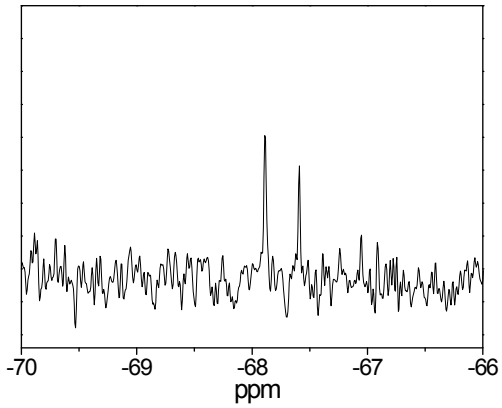


Fig. S23 ^{29}Si NMR spectrum of deprotected **d2a** in D_2O.

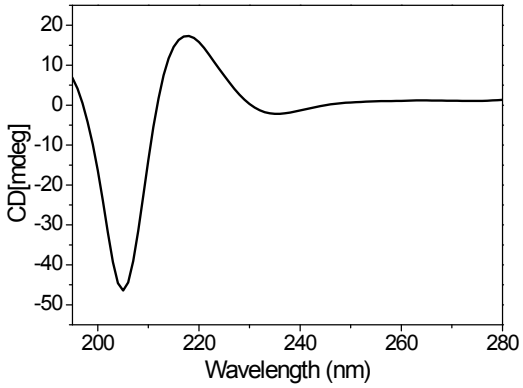


Fig. S24 CD spectrum of deprotected **d3a**.

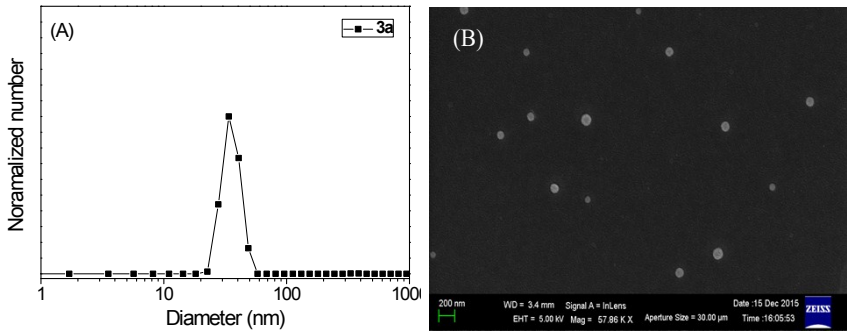


Fig. S25 DLS size distribution curve (A) and FE-SEM image (B) of **3a**.

References

1 S. Kumar, R. Acharya, U. Chatterji, P. De *Polym. Chem.*, 2014, **5**, 6039-6050.