Electronic Supplementary Information for

Synthesis of diblock copolymers consistent of POSS-containing random methacrylate copolymers and polystyrene and their cross-linked microphase-separated structure via fluoride ion-mediated cage scrambling

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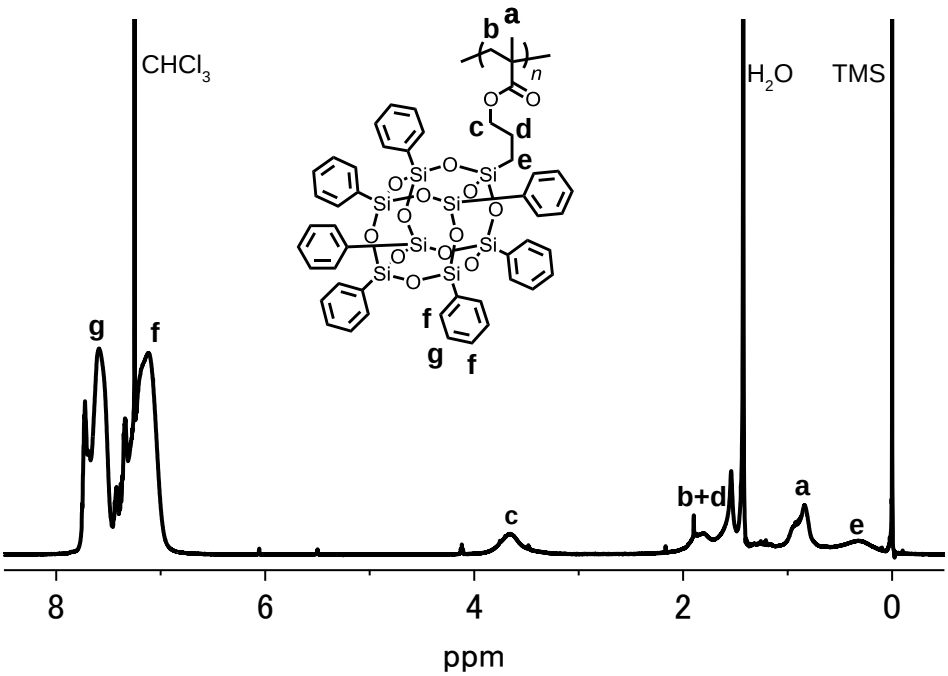

Fig. S1 ^{1}H NMR spectrum of PMAPhPOSS (**P1**) in $CDCl_3$.

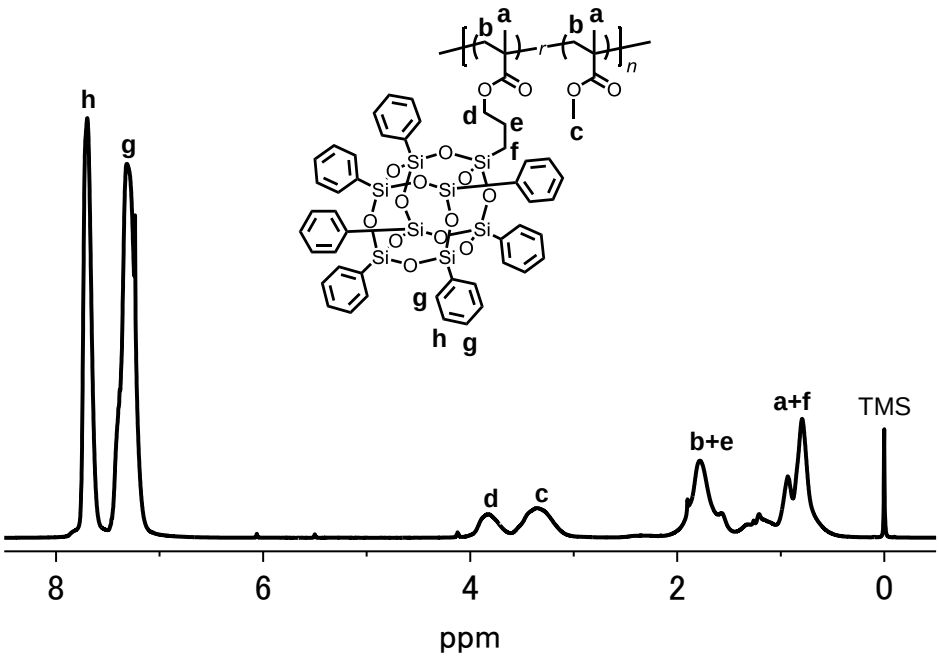

Fig. S2 ^{1}H NMR spectrum of P(MAPhPOSS-*r*-MMA) (**P2**) in $CDCl_3$.

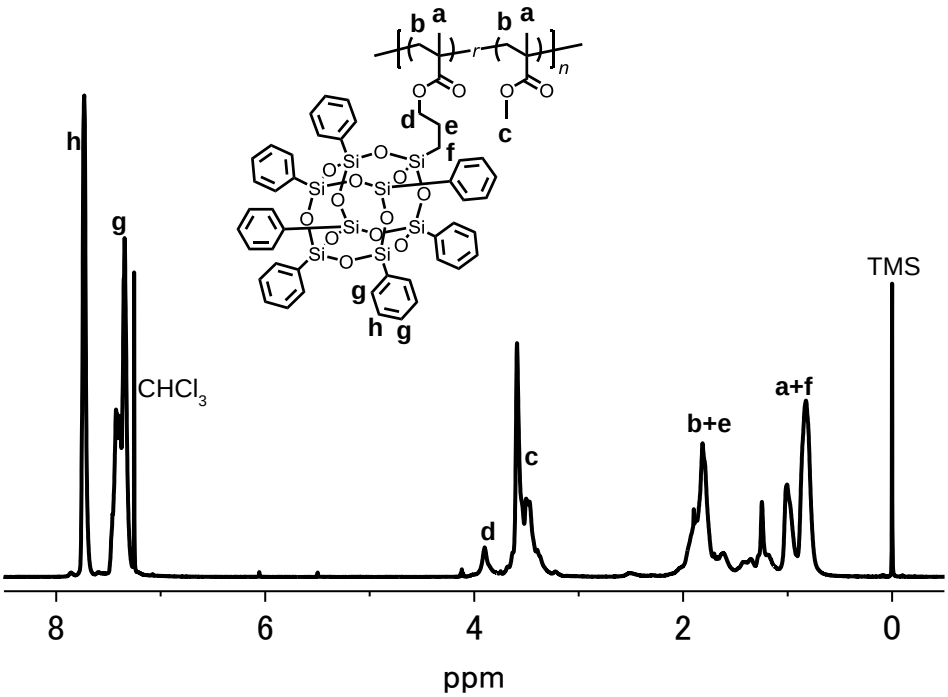

Fig. S3 ^{1}H NMR spectrum of P(MAPhPOSS-*r*-MMA) (**P4**) in $CDCl_3$.

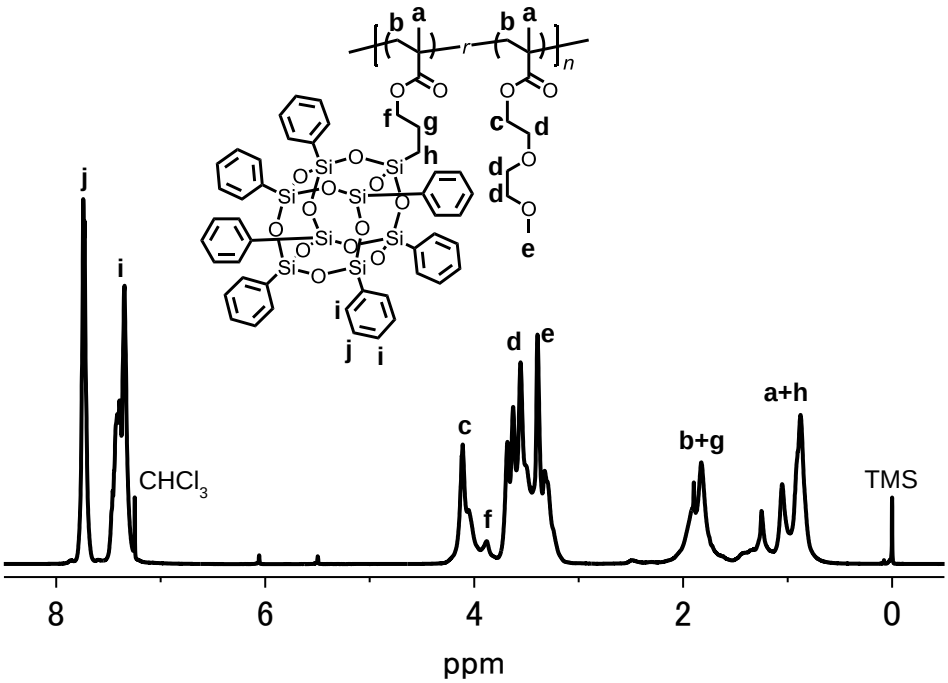

Fig. S4 ^{1}H NMR spectrum of P(MAPhPOSS-*r*-DEGMA) (**P5**) in $CDCl_3$.

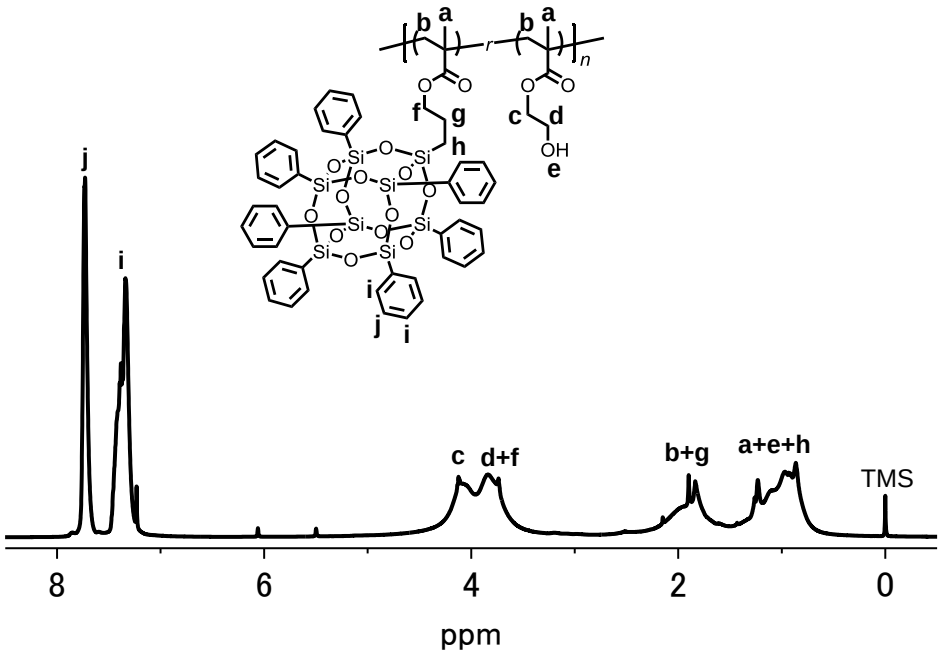

Fig. S5 ^{1}H NMR spectrum of P(MAPhPOSS-*r*-HEMA) (**P6**) in $CDCl_3$.

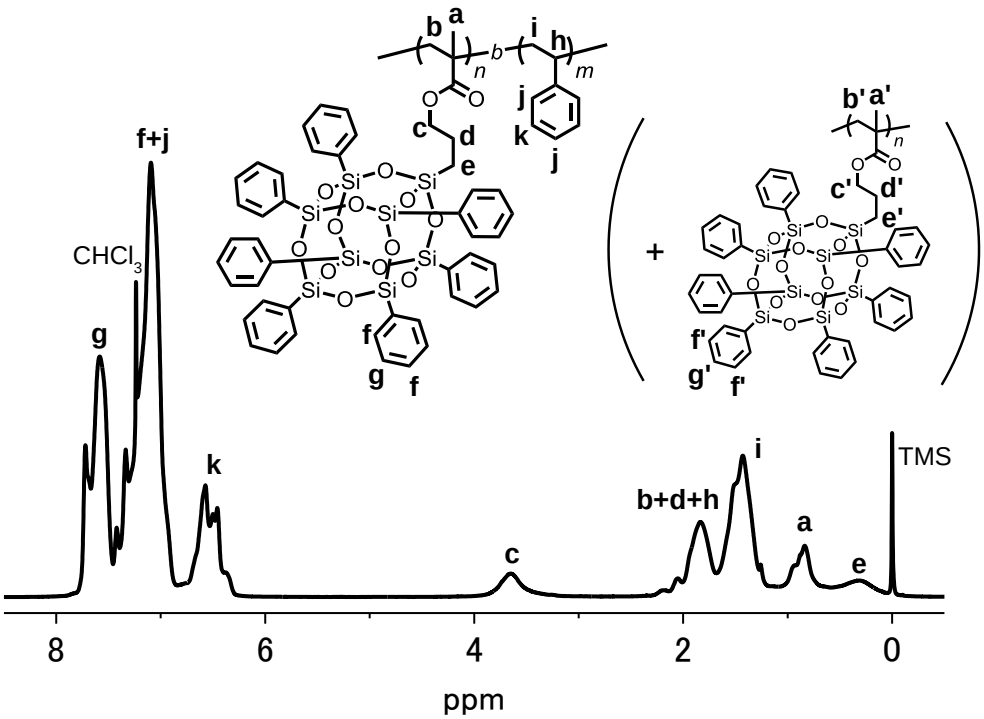

Fig. S6 ^{1}H NMR spectrum of PMAPhPOSS-*b*-PSt (**B1**) in $CDCl_3$.

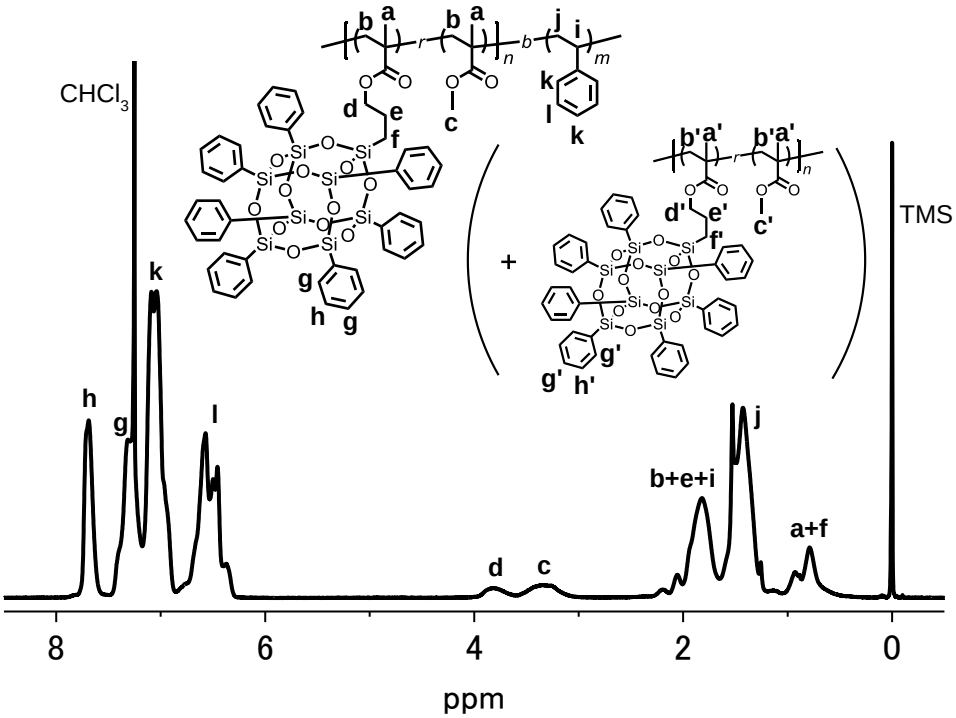

Fig. S7 ^{1}H NMR spectrum of P(MAPhPOSS-*r*-MMA)-*b*-PSt (**B2**) in $CDCl_3$.

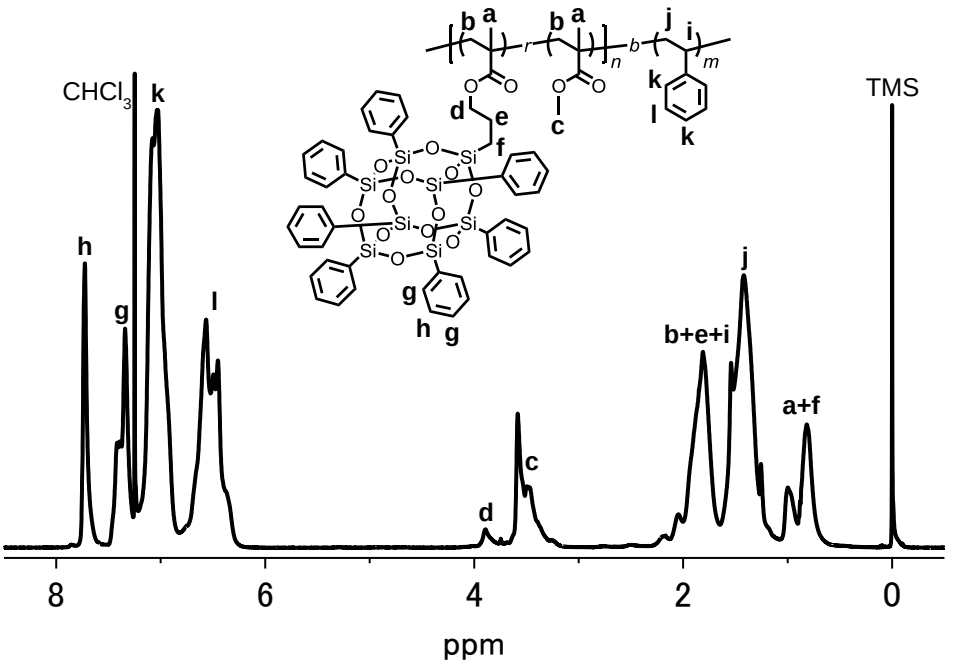

Fig. S8 ^{1}H NMR spectrum of P(MAPhPOSS-*r*-MMA)-*b*-PSt (**B4**) in $CDCl_3$.

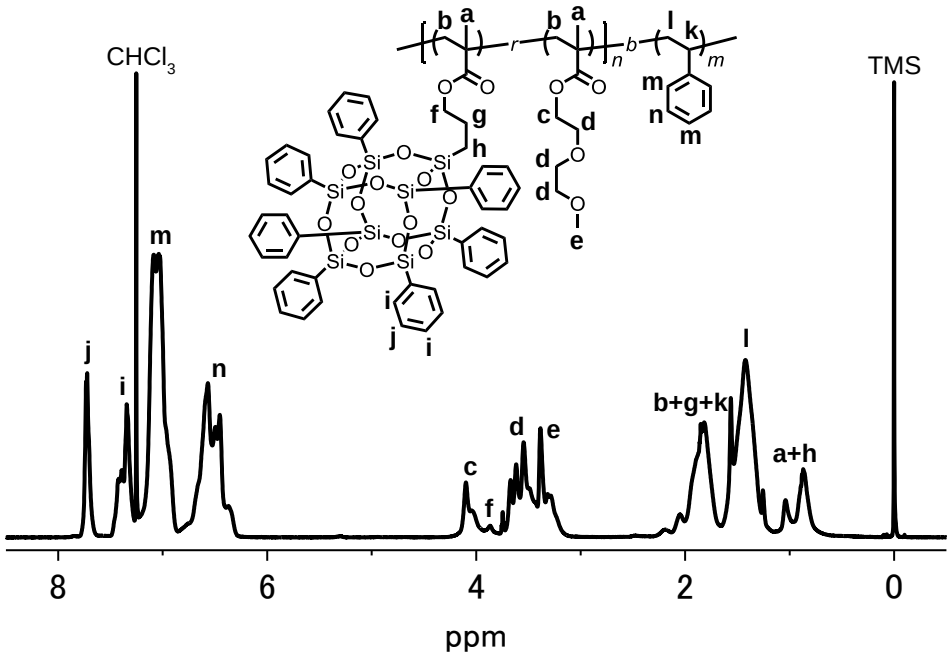

Fig. S9 ^{1}H NMR spectrum of P(MAPhPOSS-*r*-DEGMA)-*b*-PSt (**B5**) in $CDCl_3$.

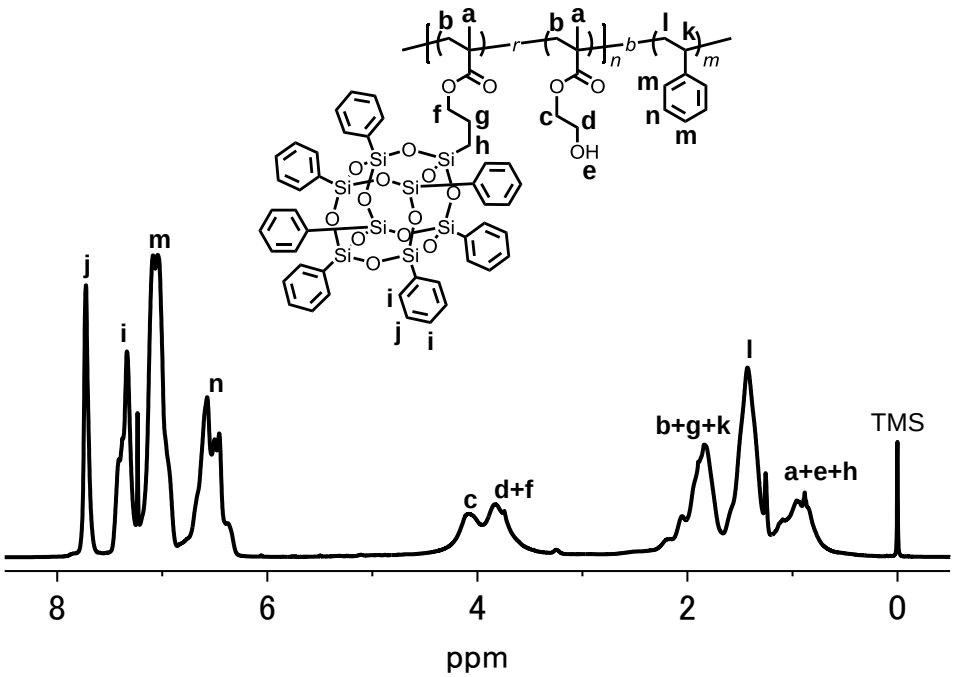

Fig. S10 ^{1}H NMR spectrum of P(MAPhPOSS-*r*-HEMA)-*b*-PSt (**B6**) in $CDCl_3$.

Fig. S11 Photo of the block copolymer (**B3**) gel swollen with THF. The gel was prepared by mixing **B3** with TBAF (1 equiv. to POSS unit) and BTSB (0.5 equiv. to POSS unit) in THF (10 wt%) followed by the evaporation of the solvent (Run 1 in Table 3). The gel was insoluble in any common solvent for more than 1 week.

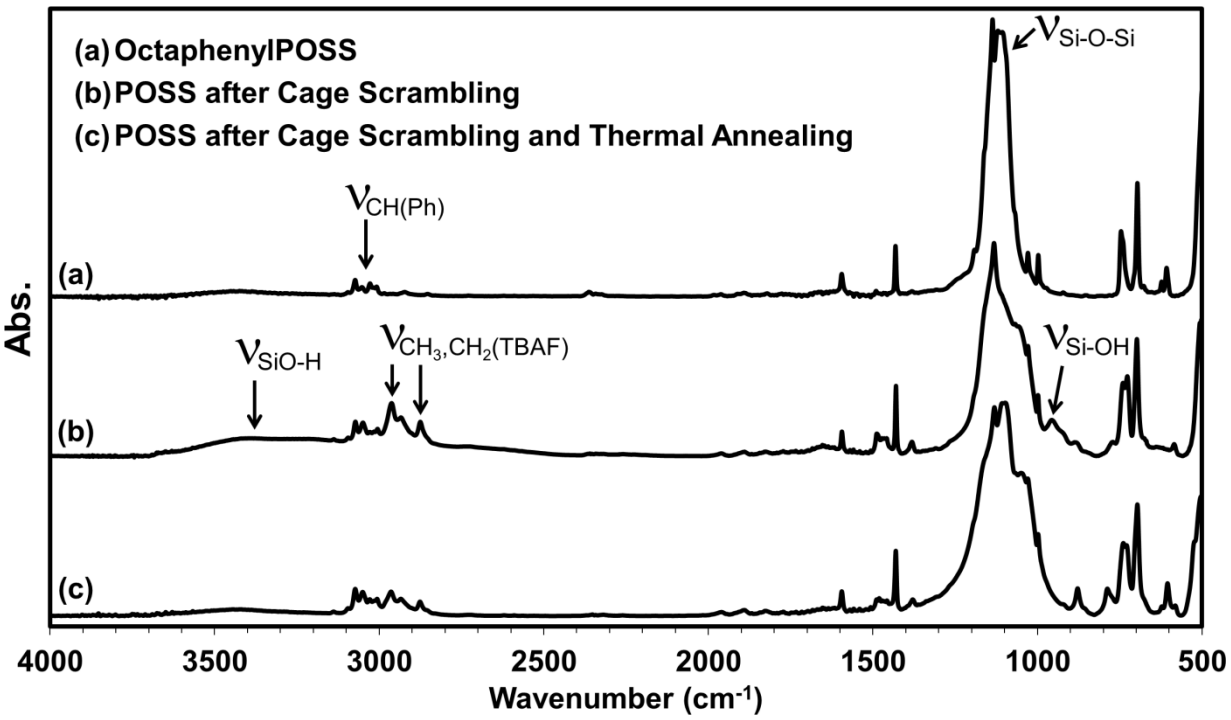

Fig. S12 FT-IR spectra of (a) OctaphenylPOSS, (b) OctaphenylPOSS after the reaction with TBAF (1 equiv. to POSS) in THF (10 wt%), and (c) OctaphenylPOSS after the reaction with TBAF and the subsequent thermal annealing. at 150 °C for 120 h.

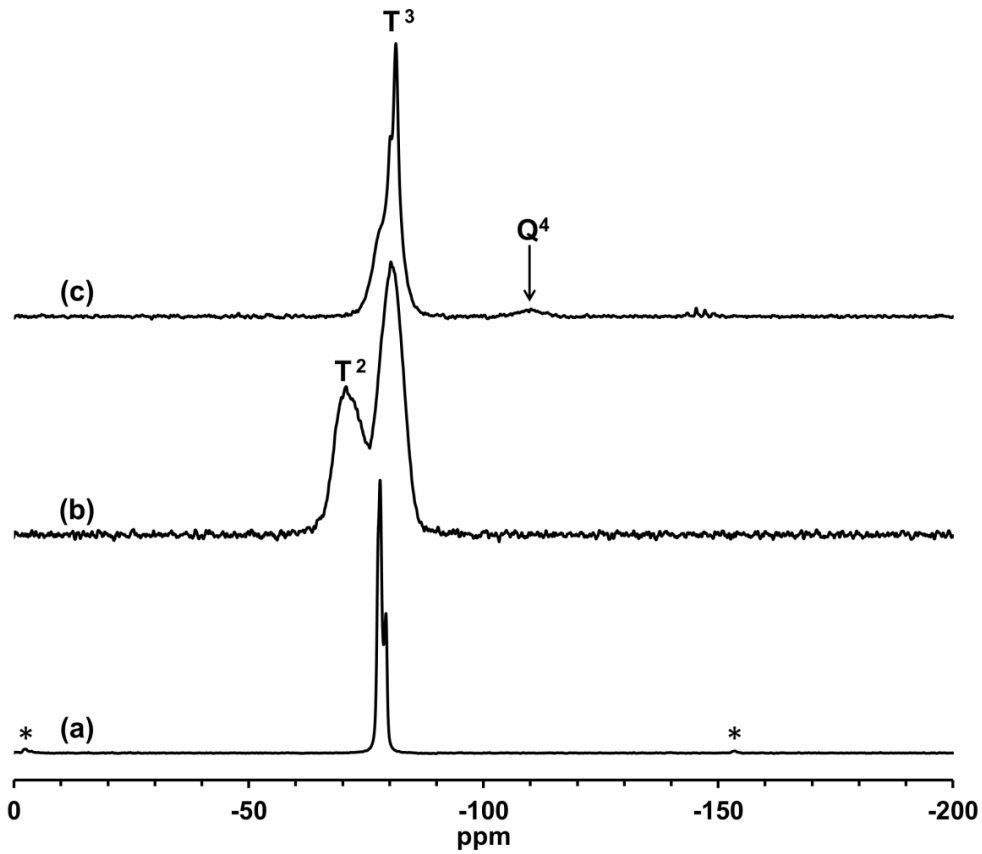

Fig. S13 ^{29}Si CP/MAS NMR spectra of (a) OctaphenylPOSS, (b) OctaphenylPOSS after the reaction with TBAF (1 equiv. to POSS) in THF (10 wt%), and (c) OctaphenylPOSS after the reaction with TBAF and the subsequent thermal annealing at 150 °C for 120 h. Peaks with * are the spinning side bands of the main peak (6 kHz).

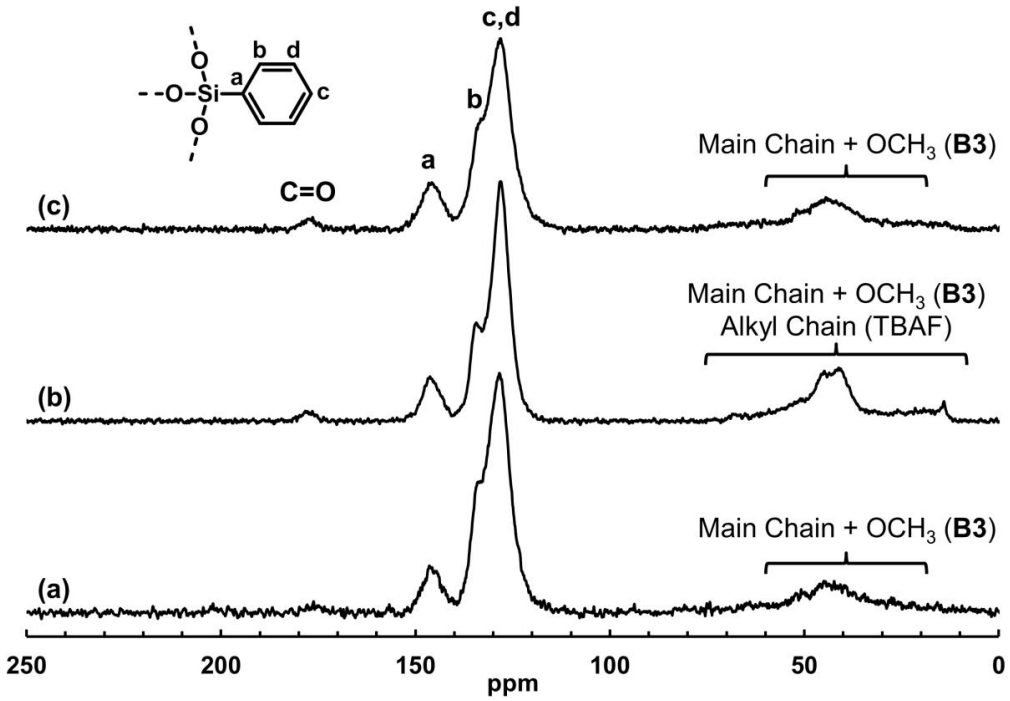

Fig. S14 ^{13}C CP/MAS NMR spectra of (a) **B3**, (b) **B3** after the cross-linking with TBAF (1 equiv. to POSS) and BTSB (0.5 equiv. to POSS unit) in THF (10 wt%), and (c) **B3** after the cross-linking and the subsequent thermal annealing. at 150 °C for 120 h.

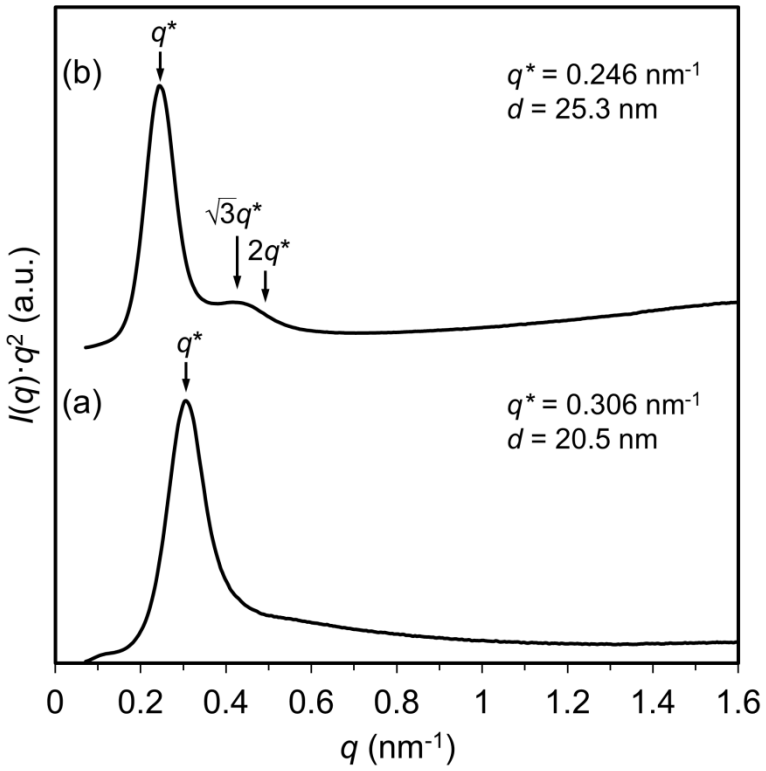

Fig. S15 Lorentz-corrected SAXS profiles of (a) P(MAPhPOSS-*r*-DEGMA)-*b*-PSt (**B5**) after the thermal annealing and (b) **B5** after the cross-linking by drying the THF solution (10 wt%) with TBAF (1 equiv. to POSS unit) and BTSB (0.5 equiv. to POSS unit) followed by the thermal annealing . The thermal annealing condition was at 150 °C for 120 h under N_2.