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Electronic Supplementary Information for

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

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Fig. S1 ¹H NMR spectrum of PMAPhPOSS (P1) in CDCl₃.



Fig. S2 ¹H NMR spectrum of P(MAPhPOSS-*r*-MMA) (**P2**) in CDCl₃.



Fig. S3 ¹H NMR spectrum of P(MAPhPOSS-*r*-MMA) (**P4**) in CDCl₃.



Fig. S4 ¹H NMR spectrum of P(MAPhPOSS-*r*-DEGMA) (**P5**) in CDCl₃.



Fig. S5 ¹H NMR spectrum of P(MAPhPOSS-*r*-HEMA) (P6) in CDCl₃.



Fig. S6 ¹H NMR spectrum of PMAPhPOSS-*b*-PSt (B1) in CDCl₃.



Fig. S7 ¹H NMR spectrum of P(MAPhPOSS-*r*-MMA)-*b*-PSt (B2) in CDCl₃.



Fig. S8 ¹H NMR spectrum of P(MAPhPOSS-*r*-MMA)-*b*-PSt (B4) in CDCl₃.



Fig. S9 ¹H NMR spectrum of P(MAPhPOSS-*r*-DEGMA)-*b*-PSt (B5) in CDCl₃.



Fig. S10 ¹H NMR spectrum of P(MAPhPOSS-*r*-HEMA)-*b*-PSt (B6) in CDCl₃.



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 $^{\circ}$ C for 120 h.



Fig. S13 ²⁹Si 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 ¹³C 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 .