

Electronic Supplementary Information (ESI):

Porous styryl-linked polyhedral oligomeric silsesquioxane (POSS) polymers used as support for platinum catalyst

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Supplementary Experimental Section

S1. Model Hydrosilylation Reaction. POSS-SiH (488 mg, 0.48 mmol), ethynylbenzene (392 mg, 3.84 mmol) and toluene (2.8 mL) were added into a pyrex tube. After the mixture was degassed through freeze-pump-thaw, Pt(dvs) (40 μ L) was added. Then mixture was degassed once again to seal pyrex tube under vacuum. The hydrosilylation polymerization reaction was carried out in oil bath at 80 °C for 12 h. After cooling to room temperature, solvent was removed, yielding oil product octastaryl POSS (PEB11). Similarly, the ethylbenzene amount was decreased to 196 mg (1.92 mmol) for synthesis of the crosslinked PEB21 gel. Another compound PSt (Figure S3) was prepared by replacing ethynylbenzene with styrene (400 mg, 3.84 mmol).

Supplementary Figures

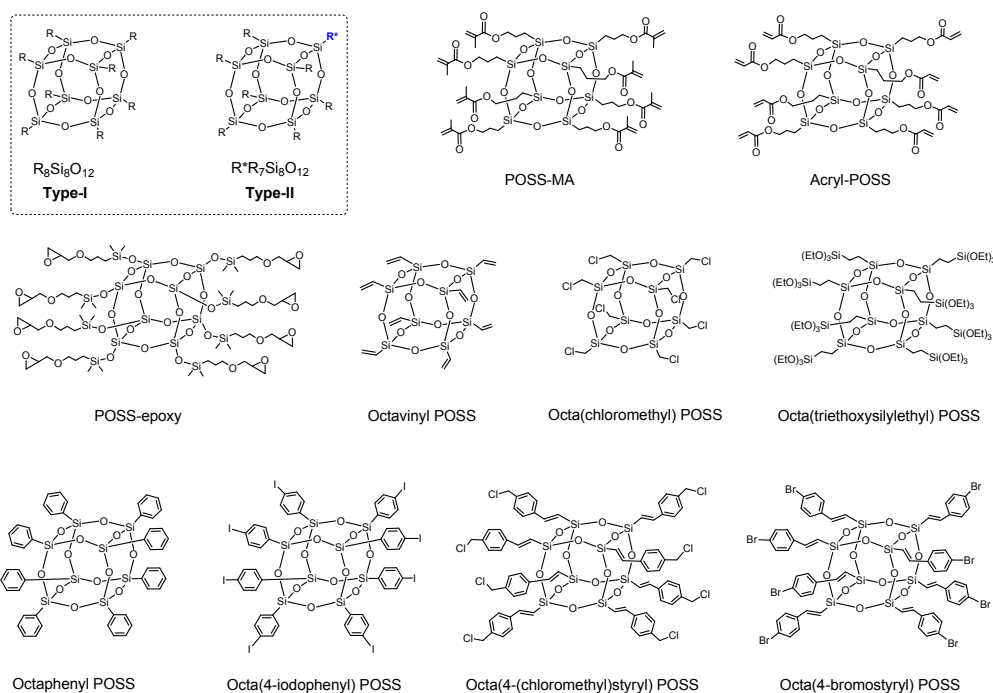


Fig. S1 Typical POSS reagents used to synthesize POSS-based polymers. POSS-MA,¹ acryl-POSS,² POSS-epoxy,³ octavinyl POSS,⁴⁻⁶ octa(chloromethyl) POSS,⁷ octa(triethoxysilyl) POSS,⁸⁻⁹ octaphenyl POSS,¹⁰⁻¹¹ octa(4-iodophenyl) POSS,¹² octa(4-(chloromethyl)styryl) POSS,¹³ and octa(4-bromostyryl) POSS.¹⁴⁻¹⁵ These POSSs reagents can be seen in following references.

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- 14 W. Chaikittisilp, A. Sugawara, A. Shimojima, T. Okubo, *Chem. —Eur. J.* 2010, **16**, 6006-6014.
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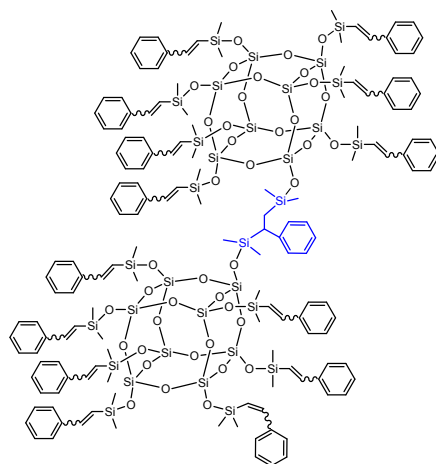


Fig. S2 Possible structure of a dimer generated from hydrosilylation reaction of POSS-SiH with EB. $M=3567.94$ and $[M+Na]^+=3590.94$ found in MALDI-TOF MS spectrum (Fig. 1d).

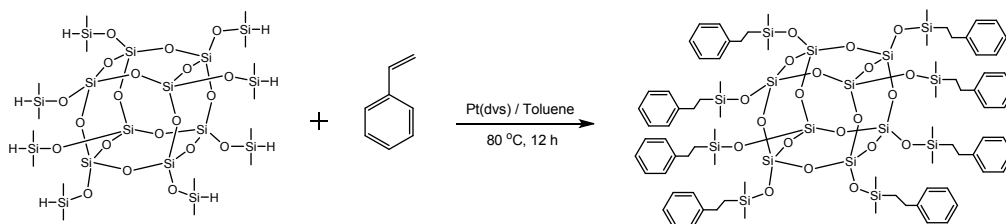


Fig. S3 Hydrosilylation reaction of POSS-SiH with styrene.

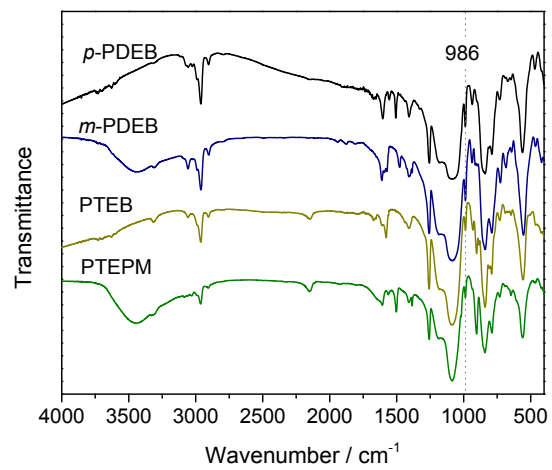


Fig. S4 FT-IR spectra of polymers prepared at equimolar ratio of [Si-H] to [C≡C].

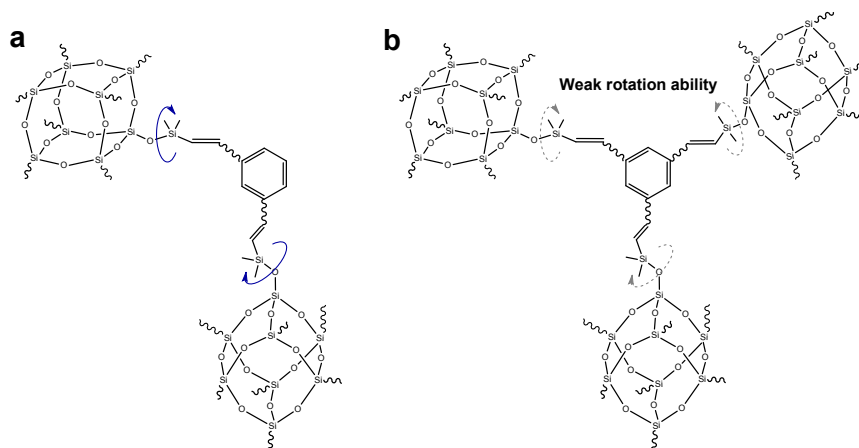


Fig. S5 Possible chemical structures of polymers (a) *m*-PDEB and (b) PTEB.

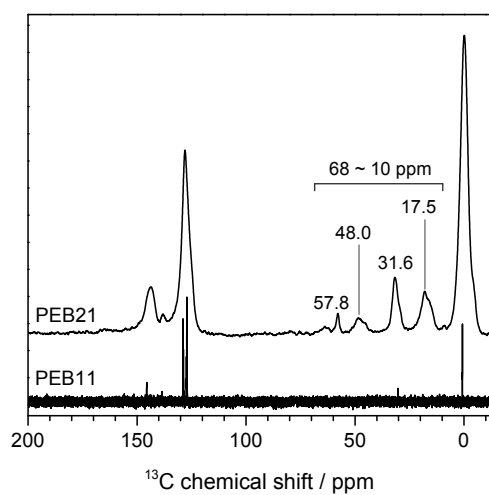


Fig. S6 Comparison of ^{13}C NMR spectra between PEB11 and PEB21.

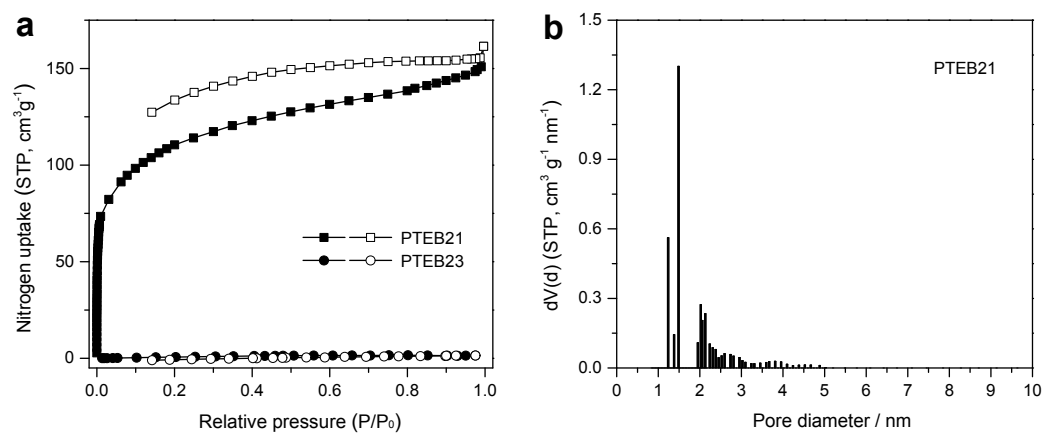


Fig. S7 (a) Nitrogen adsorption-desorption isotherms of polymers PTEB21 and PTEB23, and (b) pore diameter of PTEB21.

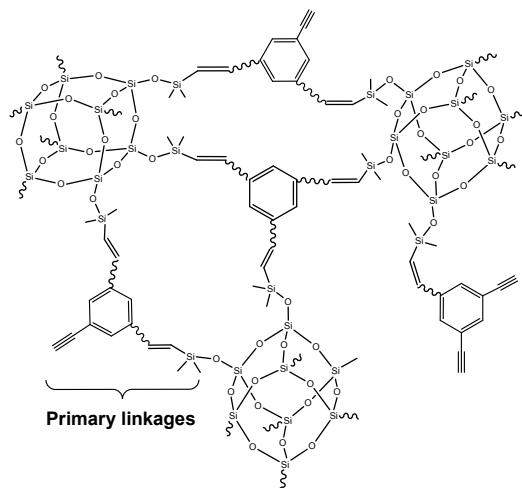


Fig. S8 Possible chemical structure of polymer PTEB23.

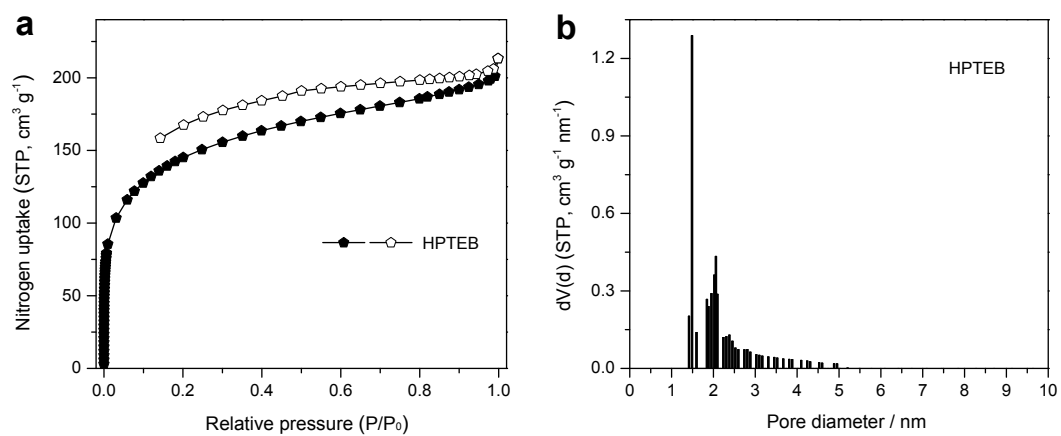


Fig. S9 (a) Nitrogen adsorption-desorption isotherms and (b) pore diameter distribution of HPTEB.

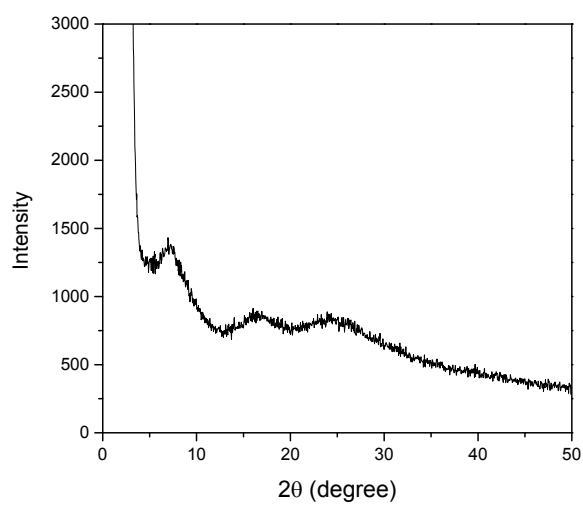


Fig. S10 PXRD pattern of Pt@HPTEB.

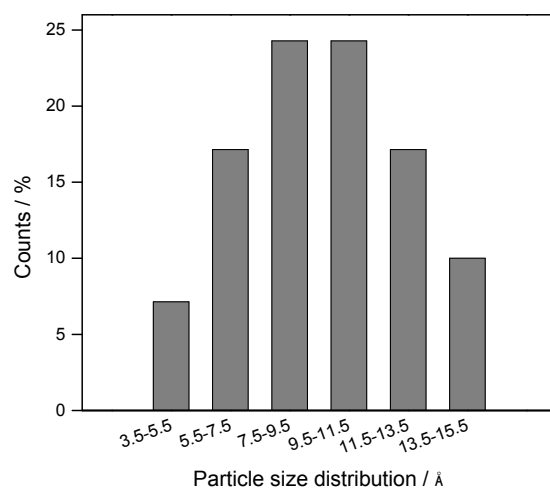


Fig. S11 Pt particle size distribution according to Fig. 7e. The particle size was counted using the Image J software

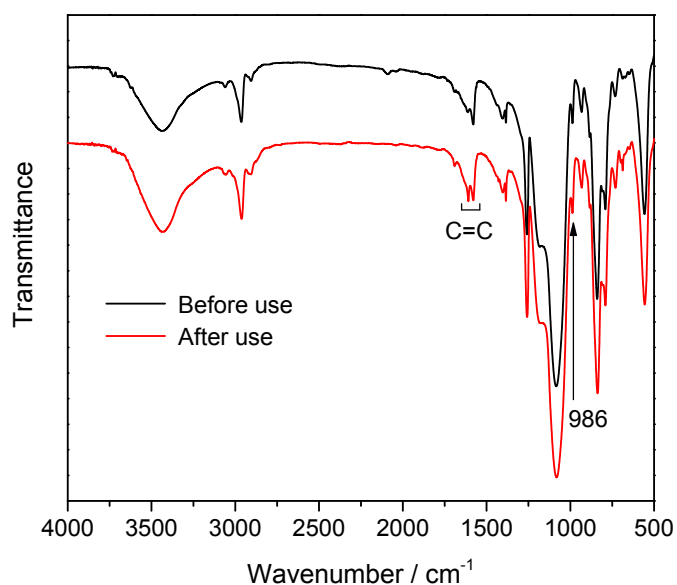


Fig. S12 FT-IR spectra of Pt@HPTEB before and after use. The peak at 1575-1610 cm^{-1} is derived from the stretching vibration of C=C bonds, while the peak at 986 cm^{-1} represents for β cis styryl linkage. The comparison of Pt@HPTEB before and after use indicated that vinyl groups were stable.