

Supporting Information

**Simple Approach for Preparation of Polyhedral Oligomeric Silsesquioxanes crosslinked
Poly(styrene-*b*-butadiene-*b*-styrene) Elastomer with Unique Micro-morphology via UV-
Induced Thiol-Ene Reaction**

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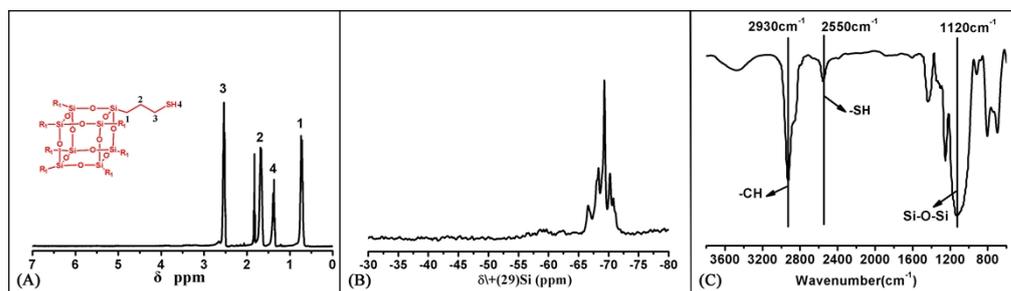


Fig. S1 (A) ¹H NMR spectrum and (B) ²⁹Si-NMR of POSS-SH in CDCl₃ (C) FTIR of POSS-SH

The structure of the (POSS-SH) was confirmed by spectral analyses including ¹H NMR and FTIR spectra (shown in Figure S1). As shown in Figure S1A, the ¹H NMR spectrum of the POSS-SH monomers exhibits the proton signals attributed to the three kind of methylene at 0.74, 1.69 and 2.54 ppm, respectively. And the peak at 1.37 ppm belongs to the -SH groups.

The structure of POSS-SH is also supported by FTIR spectra, and the attribution of each band is also signed in Figure S1(C), the absorption peak at 2930 cm⁻¹ belongs to alkyl -CH₂ -, and the band located at 2550 cm⁻¹ is assigned to S-H, indicating the existence of thiol groups, the signal of Si-O-Si asymmetric stretching appears at 1120 cm⁻¹.

The results of the spectral analyses confirm the successful synthesis of POSS-SH.

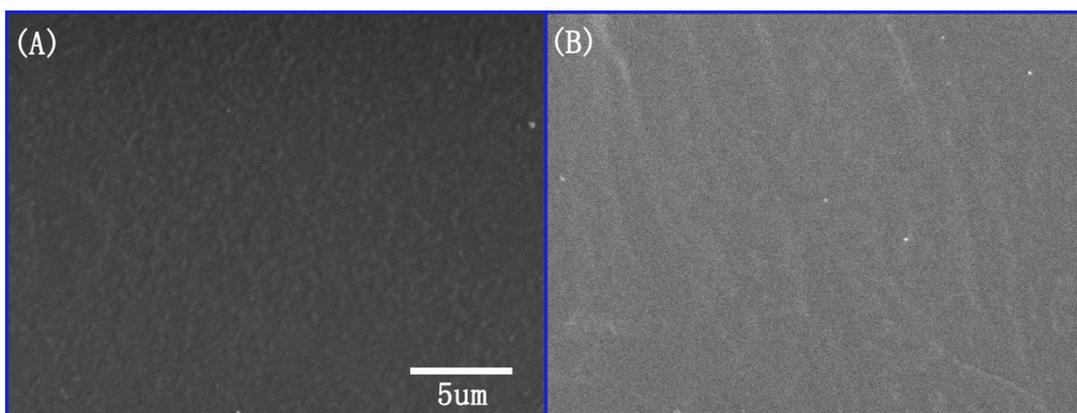


Fig.S2 SEM images: (A) SBS (B) SBS with 2wt% POSS

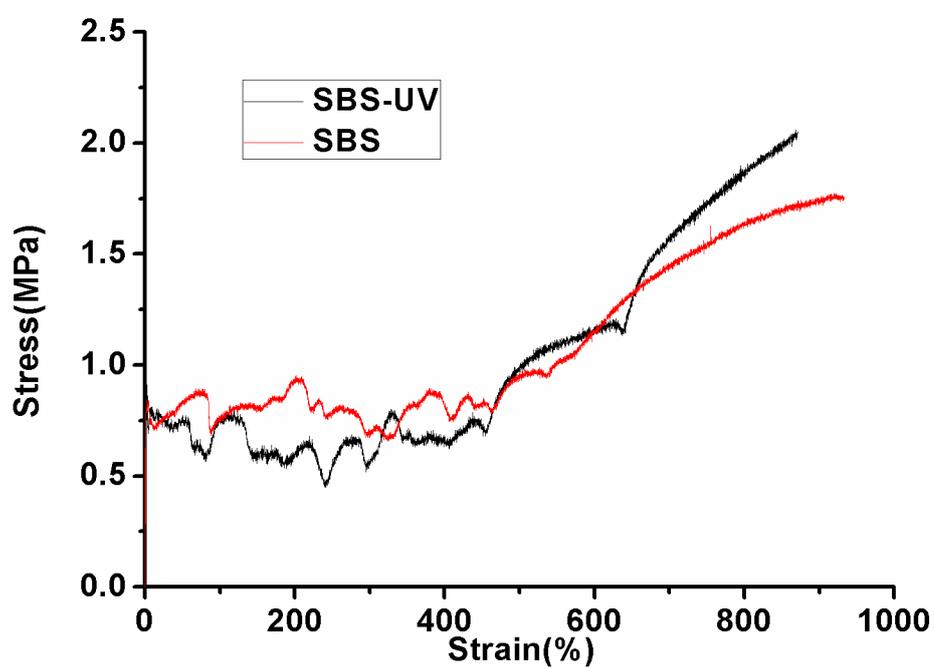
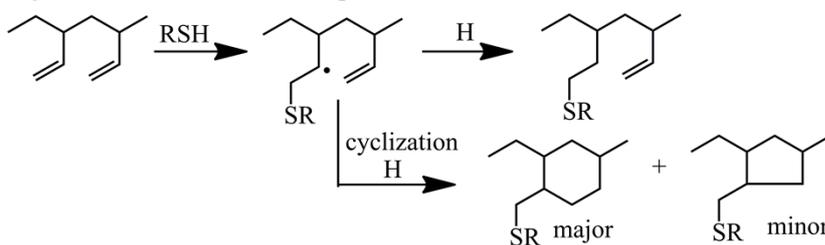


Fig.S3 stress-strain curves of pure SBS film before (SBS) and after (SBS-UV) UV- radiation



Scheme S1 possible pathway of the radical photoaddition of thiols on to the 1,2-PB

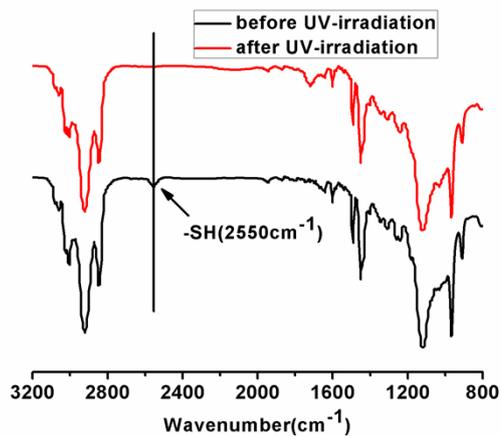


Fig.S4 FTIR of the film (SBS/POSS-2) before and after the UV-irradiation

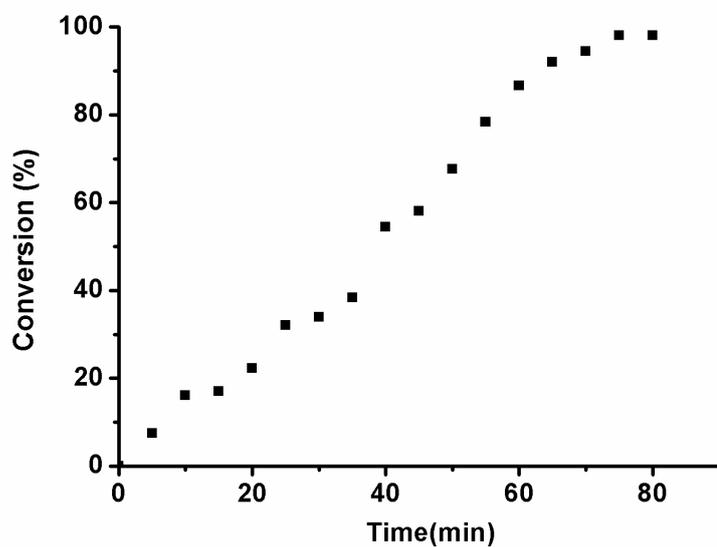


Fig. S5 Conversion of thiol groups according to the FTIR results every five minutes

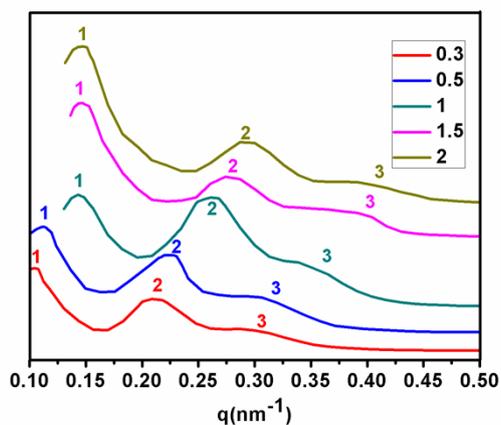


Fig. S6 SAXS profiles of SBS containing POSS-SH
SAXS Studies

SAXS studies for samples have been performed to examine the phase behavior of the

chemistry cross-linked triblock copolymers with POSS-SH. Shown in Fig.S6 are the SAXS profiles of the SBS containing 0.3, 0.5, 1, 1.5 and 2 wt% POSS-SH. The profiles of the SBS series samples exhibit multiple interaction peaks. According to the position of each first-order scattering peak, the Bragg's spacing d_m values are obtained to be 60.2, 55.9, 43.8, 42.8 and 42.6 nm for SBS with 0.3, 0.5, 1, 1.5 and 2 wt % of POSS-SH. It is found that the positions of the first-order scattering peaks slightly shift to the higher q values when the content of POSS-SH increases suggesting that the average distance between neighboring domains decreased with increasing the content of POSS-SH as shown on the AFM phase images. For the SBS containing 0.3 wt% (and/or higher except the sample with 1wt% POSS-SH) POSS-SH, the scattering peaks appear at the q values of 1, 2, and 3 relative to the first-order scattering peak positions (q_m), which implied that the nanodomains can be lamellar. For the sample with 1 wt% POSS-SH, the second and the third peak appear at less than 2, and 3 relative to the first-order scattering peak positions, which may be explained with the less well-ordered structure as shown on Fig.3D. Though the slight deviation exists, the sample with 1 wt% POSS-SH still shows the partial lamellar structure. The SAXS result is in a good agreement with that obtained on the way of AFM phase.

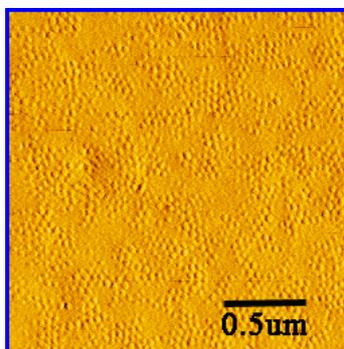


Fig.S7 AFM phase images of the sample SBS-UV(the pure SBS irradiated by UV-light)