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

Jing Bai\textsuperscript{a}, Zixing Shi\textsuperscript{a,*}, Jie Yin\textsuperscript{a} and Ming Tian\textsuperscript{b,*}

\textsuperscript{a} School of Chemistry & Chemical Engineering, State Key Laboratory of Metal Matrix Composite
Materials, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai, China.
Shanghai, 200240, China.
E-mail: zxshi@sjtu.edu.cn; Fax: + 86-21-54747445; Tel: + 86-21-54743268

\textsuperscript{b} State Key Lab of Organic-Inorganic Composites, Beijing University of Chemical Technology,
Beijing 100029, China
tianm@mail.buct.edu.cn

Fig. S1 (A) $^1$H NMR spectrum and (B) $^{29}$Si-NMR of POSS-SH in CDCl$_3$ (C) FTIR of POSS-SH

The structure of the (POSS-SH) was confirmed by spectral analyses including $^1$H 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 –CH$_2$ –, 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)