

Styrene–Butadiene–Styrene Triblock Copolymers Modified with Polyhedral Oligomeric Silsesquioxanes

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ABSTRACT: A novel hybrid organic/inorganic triblock copolymer of polystyrene–butadiene–polystyrene (SBS) containing grafted polyhedral oligomeric silsesquioxane (POSS) molecules was synthesized by a hydrosilation method. The POSS molecules were designed to contain a single silane functional group, which was used to graft onto the dangling 1,2-butadienes in the polybutadiene soft block. Unlike typical free radical copolymerizations commonly used for many other POSS incorporations investigated, this synthesis method allows us to make a series of polymers with varying amounts of POSS without any change to the overall degree of polymerization or structure of the main SBS backbone. This gives us a unique opportunity to study the POSS behavior in the matrix and know that all differences are solely due to the POSS grafted to the soft continuous butadiene phase. X-ray diffraction revealed that the grafted POSS are very well dispersed in the matrix of the hybrid polymer, which is compared to the strong phase segregation observed in a POSS physical blend. Small-angle X-ray scattering indicates that although the cylindrical morphology attributed to the styrene component was not altered by the presence of POSS, attachment of POSS to the continuous phase (polybutadiene block) causes the packing of discrete phase (polystyrene blocks) to lack long-range features. Results of dynamic mechanical analysis showed that the POSS has sterically hindered the motion of the polybutadiene blocks. More interestingly, the presence of POSS in the soft segments also resulted in a tapered $\tan \delta$ peak associated with the glass transition of polystyrene and a higher tensile strength when deformed at temperature near T_g of polystyrene without affecting the elongational behavior of SBS at temperatures above T_g of polybutadiene.

I. Introduction

ABA linear triblock copolymers, such as polystyrene–polybutadiene–polystyrene (SBS), are made of immiscible, but covalently bonded, linear blocks; they form phase-separated, self-organized domains on the scale of several tens of nanometers. At the usage temperature, the hard segments such as polystyrene are normally in the glassy state, while the soft segments such as polybutadiene are normally in the rubbery state. Depending on the relative composition ratio, block copolymers find industrial uses ranging from thermoplastic elastomers to impact-modified plastics. For the past several decades, much research has been conducted to investigate chain architectures and their relationships to the control of property, with a focus on controlling the domain morphology (e.g., spherical, cylindrical, lamellar, bicontinuous), order–order (OOT) and order–disorder (ODT) transitions, and deformations of the domain morphology.^{1–6}

Polymer nanocomposites are a new and active research area in the field of block copolymers. Block copolymers reinforced by various nanosized fillers have been prepared and studied; layered silicate-based nanocomposites have drawn the most attention thus far.^{7–9} Although domain morphology is not strongly influenced by the blending of layered silicates, these nanoreinforced block copolymers have shown promising property enhancements in various situations. A drawback for layered silicates as nanosized fillers is the difficulty to

achieve molecular-level dispersion, or “exfoliation” of these fillers even at low loadings, due to their incompatibility with the polymer matrix.

An alternative approach is to use polyhedral oligomeric silsesquioxanes (POSS); when POSS is covalently attached to the backbone of polymer chains, they can cause significant performance enhancements.^{10–15} However, most of this work is reported on POSS-containing hybrid polymers made from one-pot copolymerization method, where POSS monomers and organic monomers are mixed together prior to the polymerization process. It is known that the presence of POSS monomers can dramatically affect the rate of polymerization. Therefore, any changes in POSS monomer structure and/or initial feed ratios can result in different degrees of polymerization for each copolymer. Consequently, full analysis of the effect of POSS on a series of copolymers becomes difficult to quantify as each copolymer has variation in more than just POSS content.

In this paper, we synthesized and characterized a series of triblock SBS copolymers having POSS molecules selectively grafted to the soft butadiene segments. Unlike the previously mentioned one-pot copolymerization method, the molecular structure of the copolymer backbone, including molecular weight and polydispersity, was defined prior to attaching POSS to the butadiene block. The incorporation of POSS molecules does not change the sequence and the degree of polymerization. This gives us a unique opportunity to study the effect of POSS incorporation on polymer properties without introducing other effects that might arise from changes to the molecular structure of a host polymer. Presented below, we discuss the development of three POSS hydrides and their differences in reactivity rela-

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tive to the hydrosilation reaction used to covalently attach POSS to the backbone of a polymer chain. The morphology of SBS block copolymers with varying amounts of POSS attachment was investigated using small-angle X-ray scattering methods. Of current interest is the determination of POSS modification of solid-state properties such as glass transition temperatures, thermal-mechanical responses, and stress-strain behavior at usage temperatures.

II. Experimental Section

General Information in Synthesis. Toluene was dried by passage through activated alumina columns,¹⁶ 1,4-bis-(dimethylsilyl)benzene was distilled under dynamic vacuum prior to use, Karstedt catalyst (solution in xylenes) was purchased from Aldrich, Kraton D1102 (Shell) was dried at 60 °C overnight under vacuum, and POSS materials were obtained from Hybrid Plastics Inc. All NMR spectra were collected on either a Bruker 300 or 400 MHz instrument and obtained from CDCl₃ solutions. ¹H, ¹³C, and ²⁹Si NMR spectra (reported in ppm using the δ scale) were referenced to residual CHCl₃ at 7.26 ppm, to CDCl₃ at 77.0 ppm, and to external SiMe₄ at 0 ppm, respectively. HPLC were obtained on a HP 1090 liquid chromatograph by injecting 10 μ L of a 5 ppt sample onto a poly(vinyl alcohol)-silica gel column and eluting at 1 mL/min using a 5 vol % THF/95 vol % cyclohexane mobile phase and a Vorex MKIII evaporative light scattering detector. Molecular weights were determined using gel permeation chromatography and a combination of refractive index and multiangle laser light scattering measurements on a Wyatt Technology Corp. DAWN spectrometer.

Synthesis of POSS-Hydride 3, (c-C₅H₉)₇[Si₈O₁₂]-((CH₂)₃SiMe₂(C₆H₄)SiMe₂H). Under a dry nitrogen atmosphere, a toluene solution (50 mL) of POSS-allyl **4** (10.00 g, 10.62 mmol) was slowly added to a well-stirred 60 °C toluene solution (50 mL) of 1,4-bis(dimethylsilyl)benzene (21 g, 108 mmol) containing 90 μ L of 1.9% Pt Karstedt catalyst in xylene. After stirring overnight, silica was added to remove platinum, the solution was filtered, and the filtrate was precipitated into methanol (500 mL). The product was isolated by filtration and air-dried overnight to give a 72% yield (8.69 g, 7.65 mmol) of product. Hydride **3** has been fully characterized by HPLC, ¹H, ¹³C, and ²⁹Si NMR spectroscopy. ¹H NMR (δ , ppm, 400 MHz): 7.55 (mult, 2H, aromatic), 7.52 (mult, 2H, aromatic), 4.45 (sept, 1H, hydride, ¹J_{Si-H} = 3.6 Hz), 1.78 (mult, 14H, cyclopentyl CH₂), 1.54 (mult, 44H, cyclopentyl CH₂, propyl CH₂), 1.02 (mult, 7H, cyclopentyl CH), 0.88 (mult, 2H, propyl CH₂), 0.71 (mult, 2H, propyl CH₂), 0.37 (doublet, 6H, SiMe₂, ¹J_{Si-H} = 3.6 Hz), 0.27 (s, 6H, SiMe₂). ¹³C {¹H} NMR (δ , ppm, 100.6 MHz): 140.73, 137.75, 133.20, 132.93 (aromatic); 27.33, 27.30, 27.02, 26.98 (cyclopentyl CH₂); 22.25 (cyclopentyl CH); 19.10, 17.51, 16.31 (propyl CH₂); -3.14, -3.89 (SiMe₂). ²⁹Si {¹H} NMR (δ , ppm, 79.5 MHz): -3.40 (1Si, SiMe₂), -17.02 (1Si, SiMe₂H), -66.25 (4Si, SiCyclopentyl), -66.41 (3Si, SiCyclopentyl), -66.57 (1Si, Sipropyl). HPLC gave a single peak.

Example Grafting Reaction of 10 wt % POSS-Hydride 3 to SBS Polymer. Under a dry nitrogen atmosphere, a toluene solution (5 mL) containing 2 μ L of Karstedt catalyst and POSS-hydride **3** (0.23 g) was added to a well-stirred 60 °C solution of SBS (2.07 g) in dry toluene (20 mL). After stirring overnight, an aliquot was removed and checked by ¹H NMR to ensure complete consumption of the POSS-hydride. Platinum catalyst was removed by stirring with silica and activated charcoal followed by filtration. The filtrate was then added dropwise to a well-stirred hexane (50 mL)-methanol (100 mL) solution to precipitate the grafted polymer. Under these conditions, any ungrafted POSS remains in solution. A further purification was carried out by dissolving the polymer in chloroform and reprecipitated into methanol/hexane solution. The precipitated polymer was then dried in a vacuum oven at 50 °C overnight to yield 2.1 g of product. All the grafted polymers were prepared in this same manner.

Sample Preparation for Characterization. As-cast specimens were prepared by slowly evaporating the toluene from

2.5 wt % solutions at room temperature. Specimens were then kept in a vacuum oven at room temperature for approximately 2 days prior to the analysis.

Thermal-Mechanical Analysis. Dynamic mechanical analysis (DMA) was performed using the Rheometrics Scientific RSA-3 solid analyzer equipped with force-air oven operated in the tensile mode. The experiments were performed at 1 Hz with strain amplitude of 0.1% for temperatures ranging from -110 to -40 °C and 0.5% for temperatures ranging from 25 to about 100 °C. The heating rate used was 2 °C/min. The gauge length was set at 15 mm, and the width of tested specimens was 5 mm with approximately 0.5 mm thickness. The value of *T_g* reported in this paper is from the peaks of tan δ curves, which is not necessarily equal to the *T_g* obtained from the standard differential scanning calorimetry (DSC).

The RSA-3 solid analyzer was also used to examine stress-strain behavior of POSS-modified SBS block copolymers. Samples were first allowed to equilibrate at test temperature for 15 min prior to tensile stretching using a constant displacement rate. All samples were cut into strips of 4 mm in width with approximate thickness of 0.25 mm. The gauge length of 10 mm was used, and displacement rate used was 1 mm/min.

Wide-Angle X-ray Diffraction. The X-ray measurements were carried out on a Siemens Hi-Star unit with Cu K α radiation at a wavelength of 1.541 Å. Specimens were scanned from 5° to 30° with a scan speed of 0.2°/min.

Small-Angle X-ray Scattering (SAXS). SAXS measurements were carried out at the 15-ID-D (ChemMatCars), Advanced photon source (APS), Argonne National Laboratory (ANL). The wavelength used was 1.500 Å. A two-dimensional (2D) Bruker CCD X-ray detector was used to collect SAXS images of 1024 \times 1024 pixels with the resolution of 92 μ m per pixel. The sample-to-detector distance was 1902 mm. All SAXS images were normalized by the transmission intensity and air scattering. Silver behenate was used to calibrate SAXS measurements. A customized stretcher was used to collect SAXS images during the deformation of the samples. Typically specimens were cut into 4 mm width and 0.25 mm thickness, with gauge length of 10 mm. Unlike the mechanical stress-strain experiments, the specimens were allowed to rest for 5 min when they reached a specified stretching ratio in order to adjust the fixture to allow X-rays to pass the identical position at different stretching ratios.

III. Results and Discussion

Synthesis of a New POSS-Hydride 3: (c-C₅H₉)₇[Si₈O₁₂]-((CH₂)₃SiMe₂(C₆H₄)SiMe₂H). One of the simplest methods of modifying a polymer with a polyhedral oligomeric silsesquioxane (POSS) type molecule without changing the backbone degree of polymerization is to make use of a platinum-catalyzed hydrosilation reaction.¹⁷ The polymer must contain dangling olefins, and the POSS must have a reactive silane. To prevent cross-linking from occurring, the POSS macromer must contain just a single Si-H functionality. Three generations of such macromers are pictured in Figure 1. All three hydride types are derived from readily available POSS-trisilanols, R₇Si₇O₉(OH)₃, that provide a POSS skeleton with seven nonreactive "R groups" such as cyclohexyl, cyclopentyl, phenyl, or isobutyl.¹⁸

POSS-hydride **1** has been used to graft POSS onto short chain siloxanes.¹⁹ However, the hydride in this macromer is not as reactive as might be expected due to the presence of steric shielding from an organic pocket formed by the three large nearest-neighbor "R groups". The so-called "Schwab-hydride" **2** is a POSS-hydride synthon, created to make a more reactive graftable POSS.²⁰ The short siloxane tether places the hydride further away from the POSS cage such that the hydride functionality is not buried in the R-group pocket. However, this material can still suffer from some Pt-

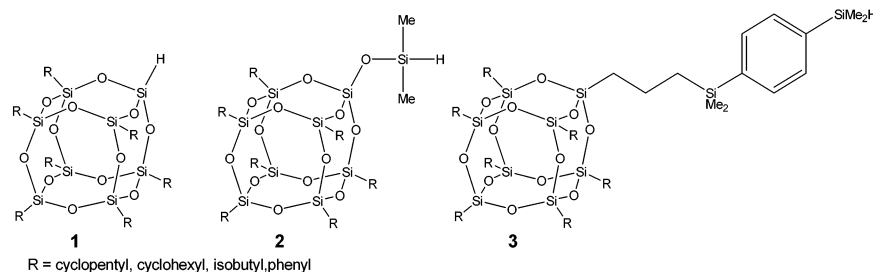


Figure 1. Three generations of POSS-hydrides derived from POSS-trisilanols.

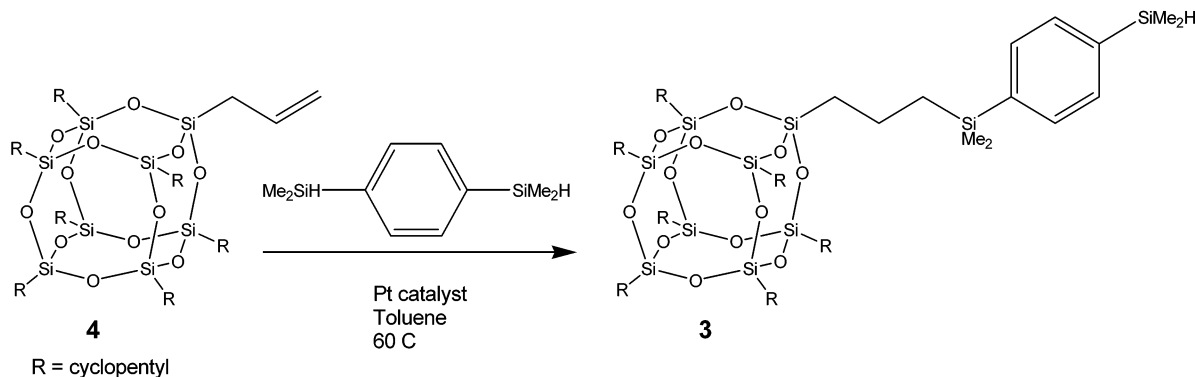


Figure 2. Synthesis of the more reactive cyclopentylPOSS-hydride.

catalyzed side reactions due to sterically slowed reactivity. We now report the first use of an even more reactive hydride-containing POSS **3**, where the hydride is connected to the POSS cage with a longer chain tether. This material grafts well even to high molecular weight butadiene-type polymers.

To obtain this new reactive POSS-hydride **3**, we carried out a hydrosilation reaction of a POSS-allyl with a 10-fold excess of 1,4-bis(dimethylsilyl)benzene in toluene solution at 60 °C (Figure 2). Detailed synthesis information is in the Experimental Section.

Synthesis of POSS-Grafted SBS Triblock Copolymers. The grafting of POSS-hydride **3** onto a styrene–butadiene–styrene triblock (SBS Kraton D1102) is illustrated in Figure 3. The SBS triblock polymer is a narrow disperse 72 000 g/mol ($M_w/M_n = 1.05$) material with a butadiene-to-styrene molar ratio of 5.3:1.0 containing approximately 92 styrene units on either end of a block of 975 butadiene units (16 mol % or 27 wt % polystyrene). ^1H NMR spectroscopy reveals that the polybutadiene block contains approximately 8.8 mol % 1,2-polymerized butadiene, and the remaining 91.2 mol % 1,4-polymerized butadiene contains unequal amounts of trans- and cis-olefins; there is significantly more trans than cis, but we did not quantify this difference because of inadequate resolution on a 400 MHz NMR instrument.²¹ We assume that there is a random distribution of these three units within the polybutadiene block. Only the dangling 1,2-polymerized butadiene is available for hydrosilation reactions. On average, each polymer chain contains 86 of these reactive dangling olefins. Theoretically, we could add between 1 and 86 POSS-hydrides to each chain; this is equivalent to a range from 2 to 58 wt % POSS. For this study, we grafted 5, 10, 15, and 20 wt % POSS to the base SBS triblock; this translates to an *average* of 3, 7, 11, or 15 POSS cages grafted to each chain. Of course, some chains will have less (or even no POSS) and some will have more than this average value.

The grafting of the POSS-hydride to the SBS polymer is conveniently followed by ^1H NMR spectroscopy. The $\text{Si}(\text{CH}_3)_2\text{H}$ unit has diagnostic resonances with a hydride septet at 4.45 ppm and a silylmethyl doublet at 0.37 ppm. As this moiety reacts with 1,2-polymerized butadiene (multiplets centered at 5.57 and 4.98 ppm), all these signals are reduced in intensity, and a new $\text{Si}(\text{CH}_3)_2$ signal grows in at 0.24 ppm.

Table 1 shows the GPC data obtained for the grafts. The addition of POSS increased the molecular weight and the polydispersity of the polymer. We interpret this result to be caused by the POSS units being unequally distributed to the polymer chains. For example, when 10 wt % POSS is grafted to the copolymer, each chain could graft 7 POSS units. However, a distribution is to be expected—some chains will have no POSS and some will have more than 7 POSS units—and because each POSS weighs approximately 1000 Da, this significantly impacts the GPC trace. Additionally, during our workup procedure, a partial fractionation occurs as some lower molecular weight polymers are removed by a hexane/methanol mixture.

It should also be pointed out that at approximately 15 wt % of POSS loading the surface area contributions of POSS is equivalent to that of the polymer chain itself. Therefore, at loadings of 15 wt % or greater, the POSS–POSS association may become more significant in the GPC and does not allow for separation of individual polymer chains.¹⁵ We propose that it is likely this POSS–POSS association that causes the observed step increase in molecular weight and polydispersity. In a future study we will investigate this effect selecting POSS with varying surrounding organic groups.

Wide-Angle X-ray Diffraction. By themselves, most POSS molecules are crystalline at room temperature; when simply blended into polymers, POSS molecules often remain in a crystalline form within the polymer matrix. Moreover, for some block copolymers, it was found by Fu and Hsiao²² that the POSS molecules form

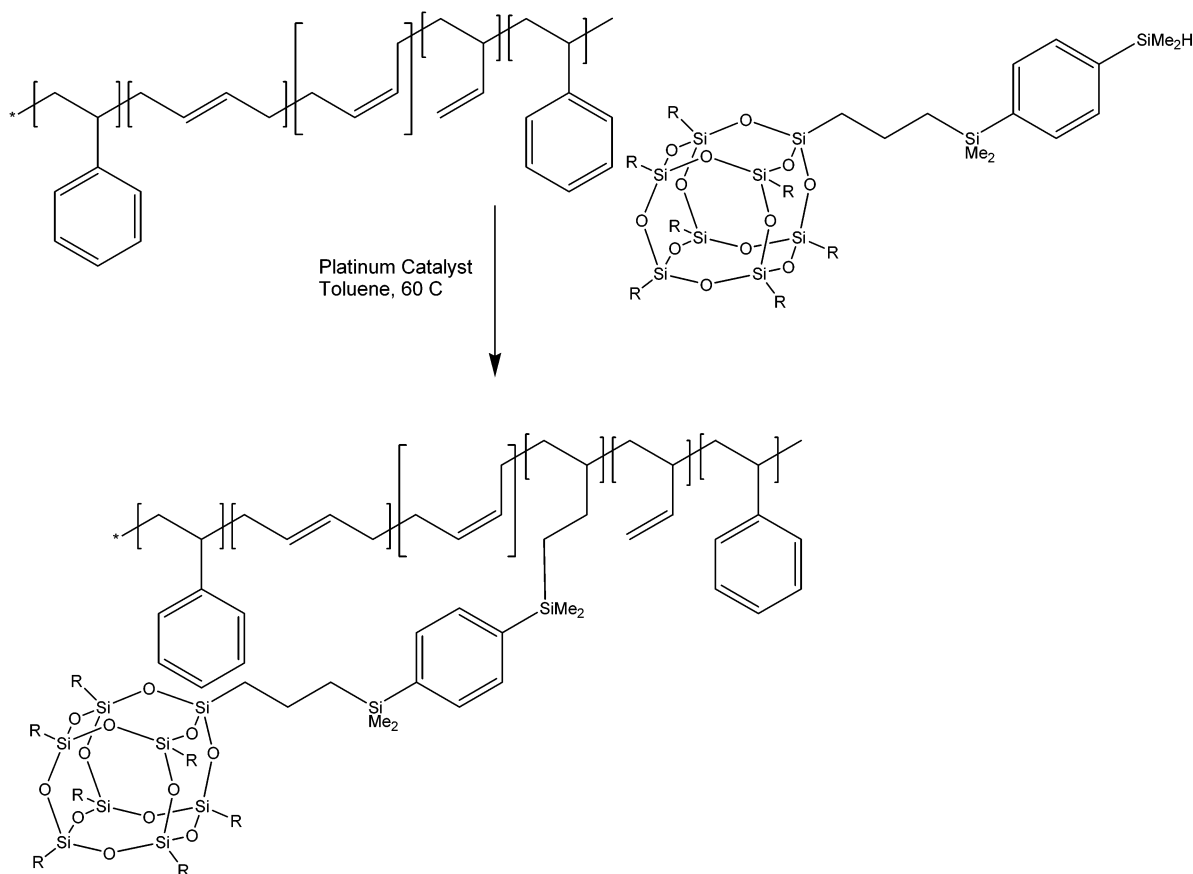


Figure 3. Grafting of the cyclopentyl POSS-hydride to Kraton D1102.

Table 1. Molecular Weight Data for the Various Polymers

wt % POSS	M_n	M_w	polydispersity
0	72 000	75 000	1.05
5	76 000	86 000	1.14
10	77 000	99 000	1.29
15	131 000	295 000	2.25
20	139 000	300 000	2.17
25	109 000	214 000	1.97
30	143 000	322 000	2.29

nanocrystals when chemically incorporated into the polyurethane hard domain. Pyun et al.²³ have also shown a strong POSS-related scattering peak for a triblock copolymer of *p*(MA-POSS)-*b*-*p*BA-*b*-*p*(MA-POSS), where the POSS molecules were attached to the hard methacrylate segment (MA). However, there is very little work reported on POSS grafted to the soft domain of block copolymers, where the soft segments of copolymers are in the rubbery state at room temperature (i.e., the T_g of the soft segments is usually around -100 to -60 °C). Since the POSS molecules may be more mobile when attached to the rubbery soft segment as compared to the glassy hard segment, one may presume that POSS molecules are easier to be dispersed in the block copolymer and will thus lose their crystallinity.

X-ray diffraction methods are commonly used to observe any evidence of POSS crystals in a polymer matrix. The X-ray diffraction patterns of SBS block copolymers containing POSS should exhibit crystal reflections of POSS if they are not fully dispersed at the molecular level, and the peak height of X-ray reflections may be used to estimate the degree of POSS dispersion. Figure 4 shows the X-ray diffraction profiles of various POSS-containing SBS block copolymers used in this study. The block copolymer itself (curve I) only has an

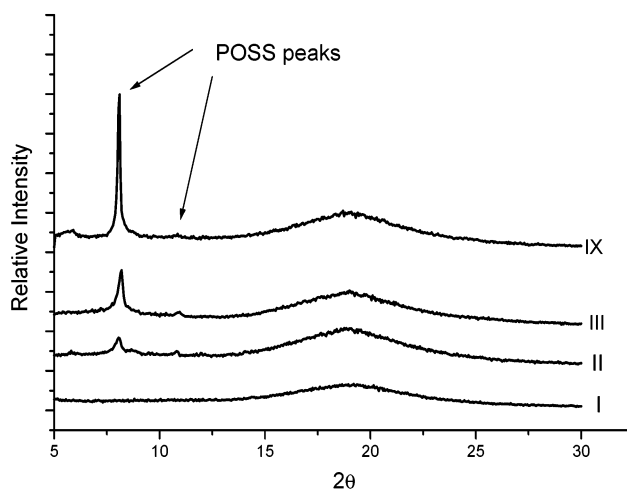


Figure 4. X-ray powder diffraction plots of (I) SBS control sample, (II) 10 wt % SBS-POSS copolymer, (III) 20 wt % SBS-POSS copolymer, and (IV) blend of SBS and POSS (10 wt %).

amorphous peak at $2\theta = 19^\circ$. The second sample we examined was 10 wt % POSS-hydride blended in SBS (curve IV), which was fabricated using the similar solution-casting method, where we simply blended the POSS-hydride with SBS copolymer in toluene and then evaporated the solvent to form a film. This film showed a distinct POSS peak ($2\theta = 8.1^\circ$), and a small diffraction peak at $2\theta = 10.1^\circ$ (marked by arrow), which indicates that the POSS hydride reprecipitated back into crystals in the SBS matrix upon solvent evaporation. Thus, SBS block copolymer blended with this POSS hydride is basically a phase-separated system, which should have similar morphology and properties to any particulate-

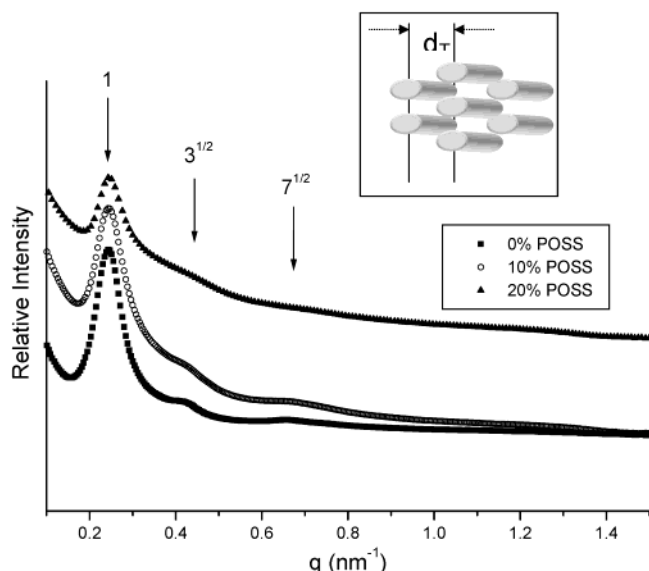


Figure 5. Small-angle X-ray scattering profiles for SBS-POSS copolymers in the through-view direction. The profiles were obtained by azimuthal scans from the raw image. The schematic drawing represents the morphology in through view and the d spacing (d_T) = $2\pi/q_{\max}$.

filled polymer. For the sample having exactly the same amount of POSS hydride (10 wt %), but now the POSS is chemically attached to the soft segments (curve II), there is only a barely observable POSS peak at $2\theta = 8.1^\circ$, indicating there is very little POSS crystallinity present. The POSS molecules are individually dispersed within the SBS matrix. For SBS grafted with 20 wt % of POSS hydride (curve III), more obvious POSS peaks at $2\theta = 8.1^\circ$ and 10.9° were observed. This observation suggests that there is some degree of crystallization and/or aggregation of POSS molecules, which can be attributed to the excessive POSS concentration such that crystallization is possible between closely located POSS molecules. However, these peaks are still much smaller than the SBS blended with 10 wt % POSS (curve IV), indicating that the ability for grafted POSS to form crystallites is still very small.

Small-Angle X-ray Scattering. The microstructure of SBS copolymer grafted with POSS was examined using small-angle X-ray scattering (SAXS). The volume fraction of polystyrene in the control SBS was calculated to be 23.4%, assuming the density of polystyrene and polybutadiene are 1.070 and 0.882 g/cm³, respectively. Figure 5 shows the SAXS profiles for the samples aligned with a through view (the incident beam was normal to the sample surface). The SAXS profiles were obtained by azimuthally scanning the images from the center point and then corrected for the air scattering and transmission intensity of the sample. As seen, the control SBS copolymer has three q_{\max} at $q = 0.243$, 0.421 , and 0.648 nm⁻¹ (marked by thick arrows). If we denote the peak position at $q_{\max} = 0.243$ nm⁻¹ to be q_1 , the other two successive peaks will have peak positions at $\sqrt{3}q_1$ and $\sqrt{7}q_1$, respectively. The Bragg peaks of such sequences are typical for hexagonally packed cylinders. However, the expected peak position at $\sqrt{4}$ was not observed in our experiment, which suggests that it might take an even longer time for the specimens to reach the equilibrium state than the 2 days of annealing time used in our study.

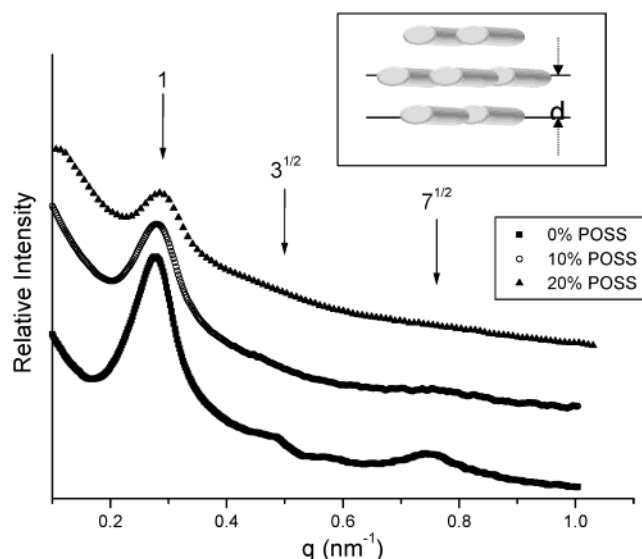


Figure 6. Small-angle X-ray scattering profiles for SBS-POSS copolymers in edge-view direction. The schematic drawing represents the morphology in edge-view, and the d spacing (d_E) = $2\pi/q_{\max}$.

In Figure 5, the control sample is also compared with SBS grafted with different weight fractions of POSS. All samples exhibit the same value of q_{\max} at $q = 0.243$ nm⁻¹. Since the d spacing is equal to $2\pi/q$, therefore all samples have approximately the same d spacing value of about 25.9 nm⁻¹ (shown as d_T in Figure 5). It is interesting to note that POSS grafted to the soft segments has no effect on the value of d spacing but does affect the intensity of the three d spacings. Considering that POSS molecules are "large" nanoparticles compared to the chain segment, they should occupy a significant volume fraction in the polymer matrix. The observed same d spacing indicates that the packing of the polystyrene cylinders has not been greatly altered by the POSS molecules. However, even though the presence of POSS (and thus higher volume fractions of the soft domain) did not seem to have direct impact to the morphology of polystyrene domain, it could still increase the degree of difficulty in achieving hexagonal-closed packing. This is observed and is shown in Figure 5, where the peak shape at $q = 0.421$ and 0.628 nm⁻¹ is gradually tapered with increase of POSS concentration. These two peaks were slightly tapered for SBS grafted with 10 wt % POSS, and for the sample grafted with 20 wt % POSS, these two peaks become more like shoulders, where the peak at $q = 0.243$ nm⁻¹ is barely observable. This indicates that attachment of POSS molecules to the continuous phase (polybutadiene block) causes the packing of discrete phase (polystyrene blocks) to lack long-range features. In other words, grafting of POSS to the continuous soft phase causes a gradual loss of long-range order of discrete hard phases with the increasing amount of POSS.

Figure 6 shows the SAXS profiles that are collected with an edge view. The q_{\max} of the first peak ($q = 0.277$ nm⁻¹) has shifted to a higher value as compared with the through view. This has been extensively explained in many references¹⁻⁵ and will be briefly discussed as follows. In the solution-cast films, polystyrene cylinders preferentially orient with their axes parallel to the surface (through-view surface). Volume contraction occurs when solvent evaporates, which causes the cylinders to become elliptical. Consequently, the hexagonal

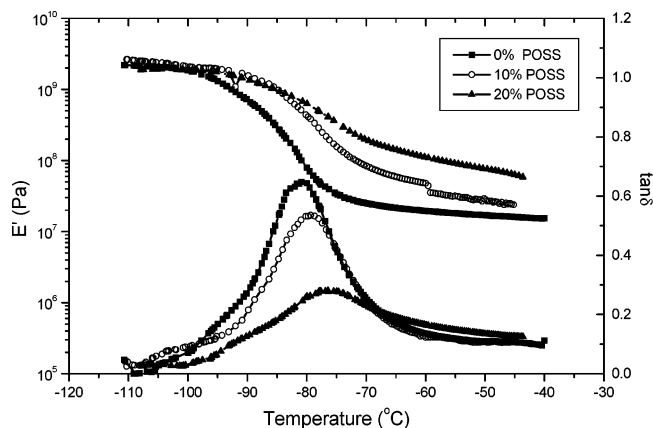


Figure 7. Dynamic mechanical analysis (DMA) for SBS-POSS copolymers in the glass transition regime of polybutadiene domains.

packing of the cylinders will be compressed in the planes that are parallel to the surface (through-view surface). In SAXS experiments, this compressed lattice will cause smaller d spacing (hence a larger q value). A schematic drawing of the edge-view morphology is shown in Figure 6, where the d spacing (denoted as d_E) is calculated to be 22.7 nm. As seen in Figure 6, we again observed that the control SBS sample exhibited a 1, $\sqrt{3}$, and $\sqrt{7}$ lattice sequence. Similar to the observation shown in Figure 5, after grafting of POSS to the SBS copolymer, the long-range ordering disappeared, and the q_{\max} peaks at 0.277 are broadened. Similar to the through-view data, the other two peaks have been tapered with increasing the amount of POSS molecules.

Dynamic Mechanical Analysis. Figure 7 shows DMA curves in the region of the glass transition temperature of the polybutadiene block. The 0, 10, and 20 wt % POSS grafted SBS samples had similar elastic storage moduli ($E' \sim 2.5$ GPa) at the starting temperature (-110 °C). As temperature gradually increased to -40 °C, we observed a significant drop in the storage modulus curve and the growth of a corresponding peak in $\tan \delta$ curve which indicates the glass transition of the polybutadiene block. Using the peak value from the $\tan \delta$ curve as the glass transition temperature, T_g , the control sample softens at -81 °C, which is expected for strongly segregated SBS systems. After attaching 10 and 20 wt % of POSS, the value of T_g is shifted to -79 and -76 °C, respectively. Interestingly, the value of the storage modulus at temperatures above T_g also increased with a higher fraction of POSS content. These observations suggest that when the flexible polybutadiene block is grafted with POSS, the chain's movement is hindered by the presence of POSS molecules and becomes less flexible. Another observation is that the peak height of the $\tan \delta$ peak decreases with increasing amounts of POSS incorporation. Since the amplitude of the $\tan \delta$ peak is associated with the change in the magnitude of movement as the polymer segments undergo the change from glassy state to rubbery state, the decrease in $\tan \delta$ peak height may be caused by more restricted dynamics in the rubbery state due to the grafting of POSS to butadiene block. All POSS samples showed a higher rubbery plateau modulus (from -60 to -40 °C) than the control, which is further evidence of POSS hindering flow in the polybutadiene block. The 20 wt % POSS sample was also found to have higher rubbery plateau modulus than the 10 wt % POSS sample.

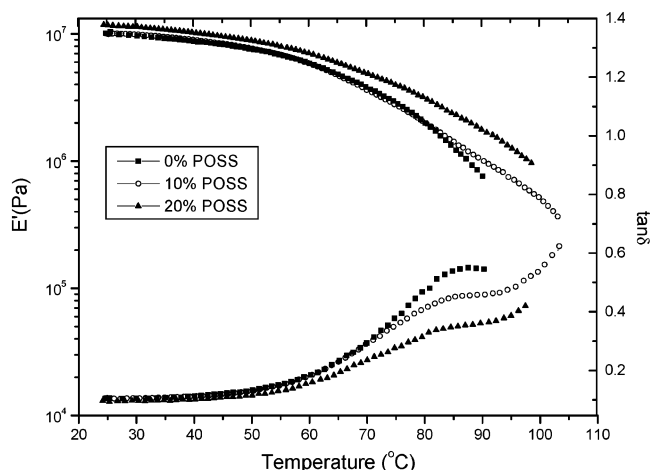


Figure 8. Dynamic mechanical analysis (DMA) for SBS-POSS copolymers in the glass transition regime of polystyrene domains.

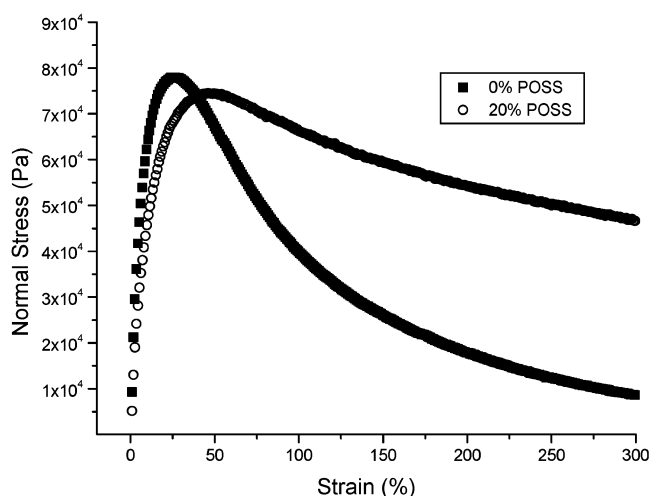


Figure 9. Representative stress-strain results for SBS-POSS copolymers compared to SBS control at 85 °C.

In Figure 8, we depict DMA curves from room temperature to the glass transition region of the polystyrene block. At room temperature, all samples show a similar storage elastic modulus (about 10 MPa). However, as temperatures increased, it was found that the POSS-grafted SBS copolymer exhibits a higher storage elastic modulus than the control. For example, as shown in Figure 8 at 90 °C, the value of E' for the control is around 0.73 MPa, while the value of E' for SBS grafted with 20 wt % POSS is around 1.7 MPa. At temperatures higher than 90 °C, the control sample could not be further tested to obtain accurate values in DMA because of its induced softness by the glass transition of polystyrene. Since the POSS molecules were grafted only to the butadiene block, we did not expect the $\tan \delta$ peak value (~ 85 °C) associated with the styrene block to be affected. However, it was found that SBS grafted with POSS showed a systematic decrease of this peak height with increasing amount of POSS. At this temperature, both butadiene and styrene blocks behave similarly and stress is loaded equally in both domains. Therefore, tapered $\tan \delta$ peaks for SBS-POSS copolymers should result from the POSS-reinforced soft domain. This phenomenon is consistent with other observations that were shown in the literature, where the POSS molecules are considered to be acting as "anchors"¹⁵ or "physical cross-linkers",²⁴ which limits

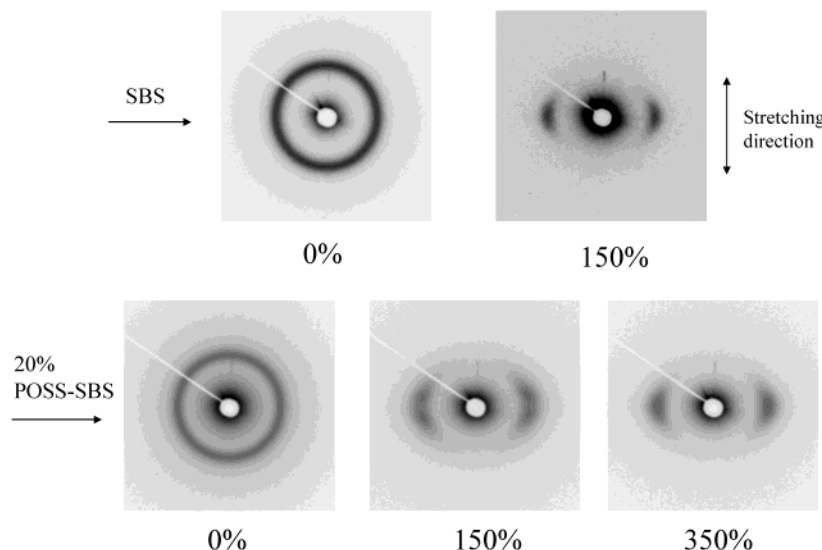


Figure 10. Examples of small-angle X-ray scattering patterns of SBS and SBS–POSS copolymer at different stretching ratios at 85 °C.

the mobility of the polybutadiene blocks and thus elongate the local relaxation time.

Deformation at Elevated Temperature. As discussed in the previous paragraph, it was suggested in this study and others that the POSS molecules can act like physical cross-linkers in the polymer matrix, especially at high temperatures (i.e., close or above the T_g of polystyrene component). In the linear viscoelastic regime, which was investigated using dynamic mechanical analysis, the SBS block copolymer grafted with POSS molecules showed a higher elastic modulus at elevated temperatures. For large deformations, topological constraints provided by the presence of POSS molecules will retard the deformation behavior of the polymers. In Figure 9, we depict the stress–strain curves of the control SBS sample and the 20 wt % POSS–SBS copolymers at 85 °C. As shown, the control sample yielded at around 40% strain. After that, the stress underwent a sharp decrease with continued deformation. At a strain of 150%, the stress is less than 40% of the yield stress. In contrast, the POSS–SBS copolymer showed a significantly better stress carrying capability than the control SBS sample. This result is consistent with our argument that the POSS are acting like physical cross-linkers in the polymer matrix. This topological constraint effect, which is largely associated with enhanced chain entanglements, is more obvious at high temperatures when the polymer chains are less restricted. The POSS molecules hinder the motion of polymer chains by providing multiple sites of physical constraint to oppose the viscous flow at high temperatures, and such resistance to flow is responsible for the improved load carrying capacity. To further investigate the structure changes during the stretching process at elevated temperatures, SAXS experiments were conducted. It is important to point out that the stretching process was not a continuous stretching process in SAXS. Rather, the sample was held at a certain stretching ratio for 5 min to complete the SAXS measurement. Using this experimental protocol, the control SBS film failed at strain of 150%. However, the SBS grafted with 20 wt % of POSS was able to be deformed to a strain of 350%. As shown in Figure 10, at 150% and 350% strain, both SBS and SBS grafted with POSS showed a SAXS pattern of elliptical peaks along the equator, which

suggests the reorientation of the cylindrical morphology to a high degree of orientation. Primitive analysis revealed that at 85 °C the SBS control undergoes a faster orientation process of the polystyrene domains than POSS–SBS. However, the detailed discussion of this orientation process is beyond the scope of this paper. A follow-up paper focusing on the structure changes as a function of deformation at various temperatures is currently under preparation.

IV. Conclusion

($c\text{-C}_5\text{H}_9$)₇[Si₈O₁₂][(CH₂)₃SiMe₂(C₆H₄)SiMe₂H), a new hydride derived from commercially available POSS-trisilanol, was synthesized and successfully grafted to a SBS triblock copolymer (Kraton D1120) using a hydrosilation method. These hybrid organic–inorganic copolymers preserved the molecular structures of the feedstock SBS, and thus the POSS influences can be compared in a precise manner with the same polymer backbones. X-ray diffraction reveals that the POSS can be molecularly dispersed in the polymer matrix by grafting. However, a minor amount of the POSS may form small aggregates due to geometric constraints. Because of this POSS dispersion at the molecular level, the SBS copolymer gradually loses its long-range ordering with increasing amounts of POSS molecules and causes the scattering of the cylindrical SBS structure to become diffuse in small-angle X-ray scattering observations. It was also observed that the incorporation of POSS did not provoke significant changes to the cylindrical structures, as evidenced by the identical intercylinder spacing in SAXS. The incorporation of POSS to the butadiene block enhanced the value of T_g for the polybutadiene block, and interestingly, we even observed an improved load carrying capability for the POSS modified SBS triblock copolymer at temperatures where the styrene block begins to soften.

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