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Two symmetric triblock polystyrene-butadiene-polystyrene (SBS) copolymers with different styrene content were grafted with varying amounts of isobutyl-substituted polyhedral oligomeric silsesquioxane (POSS) molecules. The POSS octamers, $R'R_7Si_8O_{12}$ were designed to contain a single silane functional group, R', which was used to graft onto the dangling 1,2 butadienes in the polybutadiene block and seven identical organic groups, R=isobutyl (iBu). Morphology and phase transitions of these iBu-POSS modified SBS were investigated using small angle X-ray scattering and rheological methods. It was observed that POSS with isobutyl moiety, when grafted to the polybutadiene (PB), appears to show a high affinity to stay within the PB domain; effectively, they enhance the segregation between butadiene and styrene domains. This causes a shift in the phase diagram to lower styrene content. From the rheology, we observed that values of storage modulus, G', at temperatures below the order-disorder transition increase due to the grafting of iBu-POSS. These observations lead us to conclude that the local order morphology between styrene and butadiene domains was better preserved due to the enhanced segregation forced by iBu-POSS.

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Morphology and Phase Transitions in Styrene-Butadiene-Styrene Triblock Copolymer Grafted with Isobutyl Substituted Polyhedral Oligomeric Silsesquioxanes (Preprint)

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ABSTRACT

Two symmetric triblock polystyrene-butadiene-polystyrene (SBS) copolymers with different styrene content were grafted with varying amounts of isobutyl-substituted polyhedral oligomeric silsesquioxane (POSS) molecules. The POSS octamers, $R'R_7Si_8O_{12}$ were designed to contain a single silane functional group, R', which was used to graft onto the dangling 1,2 butadienes in the polybutadiene block and seven identical organic groups, R=isobutyl (iBu). Morphology and phase transitions of these iBu-POSS modified SBS were investigated using small angle X-ray scattering and rheological methods. It was observed that POSS with isobutyl moiety, when grafted to the polybutadiene (PB), appears to show a high affinity to stay within the PB domain; effectively, they enhance the segregation between butadiene and styrene domains. This causes a shift in the phase diagram to lower styrene content. From the rheology, we observed that values of storage modulus, G', at temperatures below the order-disorder transition increase due to the grafting of iBu-POSS. These observations lead us to conclude that the local order morphology between styrene and butadiene domains was better preserved due to the enhanced segregation forced by iBu-POSS.

Keywords: isobutyl-POSS, block copolymer, SAXS, phase transition behavior.

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INTRODUCTION

Block copolymers have been widely used as engineering materials since the early 1960s, and more recently they received interest for uses in nanotechnology. The main focus of their nanotechnology application is rooted in the ability to form self-assembled microstructure on the nanometer scale, which has lead to applications in membranes, templates for nanoparticle synthesis, photonic crystals, high-density information storage media, and beyond.[1, 2] More recently, block copolymers have been used in conjunction with nanoparticles, and the self-assembled copolymer microstructure has been exploited to control nanoparticle ordering within a particular phase or at the phase interface of the block copolymer matrix.[3, 4] Hence, it is critical to gain better understanding on how the surface chemistry of nanoparticles can influence the morphology of block copolymers. To eliminate complications of mixing interactions between particles and others, the problem may be simplified by confining the nanostructures to a particular domain of the block copolymer by grafting nanostructured chemicals to specific monomeric species.[5, 6] We have recently reported that the surface chemistry of the grafted nanostructures has profound effects on the host block copolymer morphology.[5] More specifically, polyhedral oligomeric silsesquioxane (POSS) was used as a model nanostructured chemical and was grafted to the polybutadiene midblock of a symmetric polystyrene-*block*-polybutadiene-*block*-polystyrene copolymer (SBS). Different chemical substituents of POSS (i.e., cyclopentyl (Cp), cyclohexyl (Cy), cyclohexenyl (Cye), and phenyl (Ph)) were studied because of their similar stereochemistry, similar molecular weight, and contrasting electronic properties. It was shown that the morphology of host SBS copolymer became more disrupted with an increasing amount of grafting, which was supported by a two-fold increase in primary scattering peak width and the disappearance of high order scattering peaks. Based on these

observations and the fact that the POSS were grafted to the butadiene, it was concluded that those POSS investigated favor polystyrene more than polybutadiene. This affinity to the styrene phase leads to a change from a lamellar to a perforated layer morphology as the amount of POSS grafting increases, and the level of perforation and stability of this morphology depends on the POSS moiety. These results although interesting, led us to investigate how SBS morphology will be affected if the grafted POSS has an organic moiety that favors polybutadiene.

In the following sections, we present results for the morphological changes in SBS grafted with isobutyl-POSS (iBu) to the butadiene domain. The iBu-POSS was grafted to SBS in the amounts of 5, 10, and 20 weight percent, and two SBS of similar overall degree of polymerization but with different styrene content were used. The morphology of the host SBS was either cylindrical or lamellar depending on the styrene content. Small angle x-ray scattering (SAXS) was used to quantify the morphological changes in SBS modified by different amounts of grafted iBu-POSS. Additionally, in combination with rheological measurements, we also report morphological transitions and their transition temperatures as a function of POSS content.

EXPERIMENTAL

The host polymers for this study were obtained from Dexco Polymers: Vector[®] 8508 and Vector[®] 6241. Both are symmetric SBS triblock copolymers and similar in their overall degree of polymerization, but due to their styrene content they have different morphologies at temperatures far below the order-disorder transition temperature, T_{ODT}. To avoid continually referencing the abstract material numbers, Vector[®] 8508 will be referred to as the C-series polymer because it has a cylindrical morphology at temperatures far below T_{ODT}. For similar

reasons, Vector® 6241 will be referred to as the L-series polymer because it has a lamellar morphology. A more detailed comparison of the two materials is available in Table I.

Table I. Comparison of Host SBS[a]

Material	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	PDI	Polystyrene Content	Self-Assembled Morphology	Series Name
Vector® 8508	62	59	1.05	29 wt.%	Cylindrical	C-series
Vector® 6241	72	71	1.02	43 wt.%	lamellar	L-series

[a] M_n and M_w (determined by GPC) are number-average and weight-average molecular weights, respectively. PDI is the polydispersity index (M_w/M_n). Weight percent of polystyrene is listed by the manufacturer and verified by integration of NMR signals. Self-assembled morphology is determined by small-angle x-ray scattering at room temperature.

POSS grafting was accomplished via a hydrosilation reaction in toluene. The procedures used to synthesized the iBu-POSS hydride and the conditions used for grafting to 1,2-butadiene were identical to our previously reported work.[5] iBu-POSS was grafted to each type of SBS in amounts of 5, 10, and 20 weight percent. Samples were prepared in the form of solvent cast films of approximately 0.3 mm thickness. The copolymer samples were dissolved in a toluene, a neutral solvent, in a 3.0 wt% concentration. Approximately 0.1 wt% Irganox® 1010 antioxidant (relative to the polymer) was also added to the solution to reduce degradation at high temperatures. The solvent was then allowed to evaporate slowly on glass at 20°C over a period of three days. The films were removed from the glass and were then annealed under vacuum at 60°C for seven days.

Small angle X-ray scattering (SAXS) was used to quantify the morphology changes, since it is capable of examining a large volume of material in the bulk state. The SAXS experiments were performed at beamline 15ID (ChemMatCARS) in the Advanced Photon Source (APS) at Argonne National Laboratory. The energy of radiation used for the experiments

was 8.27 keV ($\Delta E/E \approx 10^{-4}$), which corresponds to an x-ray wavelength of 1.50 Å. SAXS patterns were collected using a two-dimensional Bruker 6000 CCD X-ray detector with a 1024 x 1024 pixel array with a 92 x 92 μm pixel size. The camera length was 1.915 meters and was calibrated using silver behenate. The SAXS experiments were performed in order to observe the equilibrium morphologies and to verify thermally induced phase transitions. Isothermal experiments were sufficient to observe these phenomena. The protocol implemented for the isothermal experiments included a 10 minutes annealing time at the required temperature followed by a two-dimensional raster of 1 second exposures covering a 3 x 3 mm area of the film over a 5 minute time period. There are several purposes for performing the raster: it minimizes possible beam damage to the sample, it allows for greater statistical sampling, and it ensures that the sample has reached equilibrium.

Small-strain amplitude oscillatory shear experiments were used to measure T_{OOT} and T_{ODT}. Experiments were performed using a TA Instruments AR2000 rheometer with 25 mm parallel plate geometry equipped with an electric heating chamber. Samples were annealed at 150°C for 5 min then subjected to a temperature ramp with a heating rate of 2°C/min. To minimize sample degradation, a dry N_2 purge of 12 ml/min was implemented. The instrument software was used to determine the dynamic storage modulus $G'(\omega)$ as a function of temperature at a fixed strain amplitude of 2% and oscillatory frequency of 1 rad/s. The onset of each $G'(\omega)$ versus temperature discontinuity was used to determine the T_{OOT} and T_{ODT}. In practice, T_{OOT} and T_{ODT} are a function of both frequency and temperature ramp rate, so the listed value does not coincide precisely with the equilibrium transition temperature. However, this calculation is consistently applied throughout the unmodified SBS and POSS-SBS grafted series, and thus the effects of POSS attachments on the transition temperatures are comparable.

Results and Discussion

Figures 1 and 2 show the one-dimensional scattering profiles for all POSS-SBS copolymers investigated as measured by SAXS at 130°C. The C-series, which has a cylindrical morphology for the ungrafted SBS, is shown in Figure 1. The scattering patterns of the grafted C-series show little difference from the unmodified SBS. The peak positions are consistent with the structure factor for a hexagonally packed cylindrical morphology ($1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}\ldots$). Grafting up to 20 weight percent iBu-POSS to the host cylindrical morphology has little effect on relative peak position, primary scattering intensity, and even the intensities of the high order $\sqrt{7}$ and $\sqrt{9}$ peaks. All of these indicate that the cylindrical morphology is well-preserved after grafting. There is, however, a change in the relative intensity for the 3rd diffraction peak, which will be discussed in more detail later in this section.
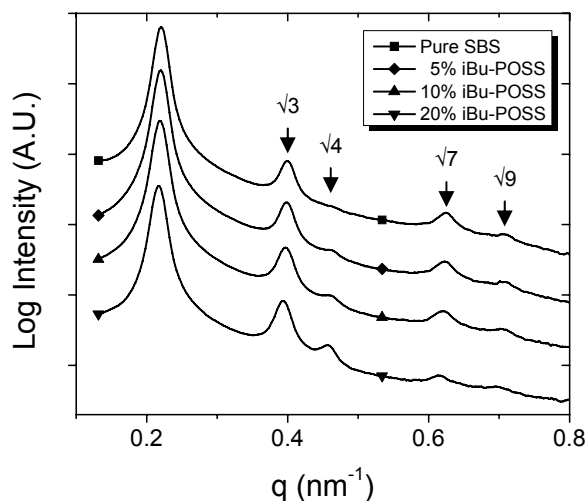

Figure 1. Integrated SAXS intensity vs. scattering vector, *q*, for SBS, Vector® 8508, triblock copolymers grafted with isobutyl-POSS at 130°C. The unmodified Vector® 8508 is of cylindrical morphology (C-series). Data are shifted along the log intensity axis to increase clarity.

Scattering profiles of the L-series, which have varying amounts of iBu-POSS grafted on Vector® 6241, are shown in Figure 2. The relative peak positions for the pure, 5%, and 10% are consistent with the structure factor for a lamellar morphology (1:2:3:4…). However, when grafted with 20 wt% iBu-POSS, the observed morphology changes to that of hexagonally packed cylinders. We note here that although only the 130°C SAXS data was shown, the cylindrical morphology was observed for all temperatures below the T_{ODT} investigated. This change in morphology can be attributed simply to changes in the overall polystyrene content of the Vector® 6241 upon grafting. By grafting 20 wt.% iBu-POSS, the weight fraction of polystyrene is reduced from 43 wt.% for the unmodified Vector 6241® to 34 wt.% in 20% iBu-POSS grafted Vector® 6241 (39 to 34 vol.%). This reduction in polystyrene content is large enough to change from lamellar to cylindrical morphology. An underlying assumption in this reasoning is that the grafting of iBu-POSS to the polybutadiene does not affect the degree of segregation between the butadiene and styrene domains. Thus, the morphology of modified SBS only depends on the overall volume fraction of a particular block. The argument is in parallel to those studies on highly selective solvent swelling of block copolymers.[7-9] In this case, the iBu-POSS is akin to the solvent molecules that are selective only to the polybutadiene domain. This is a reasonable assumption because the iBu-POSS are chemically grafted to polybutadiene, and thus they are confined within the butadiene domain. As a result, when iBu-POSS is grafted with polybutadiene, the modified POSS-SBS copolymer can be characterized by a resulting shift in composition of the host polymer system along the χN vs. f phase diagram, where χ is the Flory-Huggins parameter, N is the effective degree of polymerization, and f is the volume fraction of a particular block copolymer component.[8, 9]
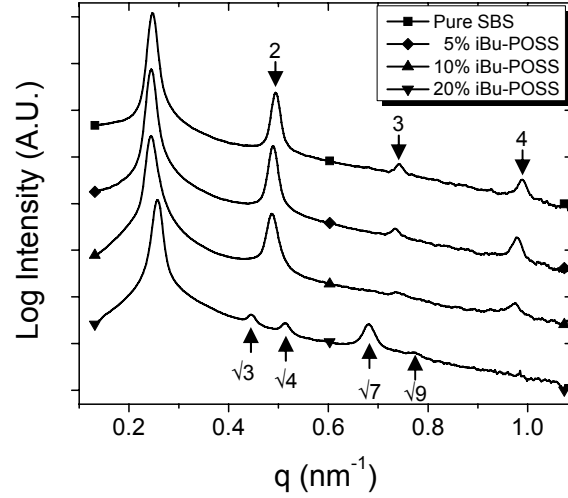
Figure 2. Integrated SAXS intensity vs. scattering vector, q, for SBS, Vector® 6241, triblock copolymers grafted with isobutyl-POSS at 130°C. The unmodified Vector® 6241 is of lamellar morphology (L-series). Data are shifted along the log intensity axis to increase clarity.

The argument of selective swelling of polybutadiene domain causing a phase shift can be further supported by revisiting the data from C-series in Figure 1. As mentioned previously, there is a change in the relative intensity for the 3rd relative-diffraction peak at position $\sqrt{4}q^*$, where q^* is the peak position of the primary diffraction. This peak is nearly unnoticeable in the unmodified SBS but steadily grows with increased iBu-POSS grafting. This change in relative intensity can be explained by a shift in the scattering form factor, which is related to the size of the polystyrene cylinders. With increased grafting, the volume or weight fraction of polystyrene is reduced, thus the form factor minimum is shifted to higher q. This gives rise a higher relative intensity for the $\sqrt{3}q^*$ and the $\sqrt{4}q^*$ peaks. In Figure 2 (L-series), one observes a similar shift in the form factor. Here, the $3q^*$ peak decreases in relative intensity for the 5 wt.% and is nearly indistinguishable for the 10 wt.%, while the $4q^*$ peak is still present for both systems. The missing $3q^*$ peak corresponds to a polystyrene layer thickness that is one third that of the entire

repeat unit. This coincides with the changes in volume fraction polystyrene from 39% for the unmodified SBS to the lower volume fractions in the 5 and 10 wt.% iBu-POSS (See Appendix for volume fraction calculations).

The d-spacing calculated from the primary diffraction peak position[10] for both series of iBu-POSS grafted SBS are shown in Figure 3. For comparison, we normalized measured d-spacing values of POSS-SBS to the unmodified SBS. For the C-series, a small, but measurable, amount of systematic increase in d-spacing was observed as the amount of grafted POSS increases. This increase in the length of periodicity was expected and is consistent with the interaction argument. When iBu-POSS is chemically grafted to polybutadiene, they are confined within the butadiene domain and do not interact with the styrene domain. For the C-series of POSS-SBS, the butadiene domain is a continuous phase. Hence, the addition of dimensionally well-defined nano-structured chemicals such as POSS to the continuous phase is expected to push apart the discrete phase, thus causing the d-spacing of periodic styrene domains to increase. For the L-series polymers, the analysis of d-spacing as affected by grafting iBu-POSS is somewhat more complicated due to the fact that there is a change in the morphology from lamellar to cylindrical morphology as we increase the amount of grafting per chain. The d-spacing calculated based on the primary peak position of Vector[®] 6241 grafted with 20 wt.% iBu-POSS must be multiplied by $\sqrt{(4/3)}$ to correspond to the nearest neighbor distance (D_{100}), so it can be consistent with the other calculated d-spacings in the L-series that have a lamellar morphology. As seen in Figure 3, there was an increase of about 10% in the d-spacing for Vector[®] 6241 grafted with 20 wt.% of iBu-POSS. This relatively large increase may, in part, be due to the comparison between the cylindrical and lamellar morphologies. However, it is more likely due to the greater volumetric grafting density for the L-series. At the same weight fraction

of grafting, both L-series and C-series have nearly equal overall volume fractions of POSS; however, the C-series has more polybutadiene by volume resulting in a 20% greater volume fraction of POSS within the polybutadiene domain of the corresponding L-series grafting. The consequential confinement of POSS for the L-series may introduce a noticeable POSS-POSS effect that contributes to a larger R_g for the SBS polymer chain or a greater segregation between the polybutadiene and polystyrene monomers. The increase in d-spacing observed for the iBu-POSS contrasts to our previous study where value d-spacing decreases for Vector® 6241 grafted with Cy, Cye, and Ph-POSS.

Figure 3. The d-spacing normalized to the unmodified SBS for the C-series and L-series at 130°C. For the L-series, there is a change in morphology from lamellar (0-10%) to hexagonally packed cylinders (20%). D_{100} for the cylindrical morphology corresponds to the nearest neighbor cylinder spacing which is consistent with the lamellar d-spacing. Error bars are on the order of the symbol size and were removed for clarity. The d-spacing for unmodified C-series and L-series SBS are 25.71nm and 25.41nm respectively.

Another quantitative measure of morphology is the full width at one half of the maximum intensity for the primary peak, Γ. Primary scattering peak width is correlated to the local order of the morphology. Factors that contribute to a broadening of peak width include: an increased

variance in domain thickness, a limited grain size, defects at grain boundaries, a reduced

monomeric segregation at the polystyrene-polybutadiene interface, etc. In Figure 4, the peak

width is normalized to unmodified SBS and plotted vs. the weight percent of grafted iBu-POSS

for both SBS series. Figure 4 shows that the peak width increases with increase in weight

percent of POSS grafting. The increase in relative peak width is likely due to an introduced

polydispersity during the grafting process. Because the POSS attachment is random during the

grafting reaction, one can expect a nearly binomial distribution of POSS per chain. This added

variation in molecular weight for the grafted systems is a likely contribution to the increase in

peak width. We must note here that the overall peak broadening for both series grafted up to 20

wt.% of iBu-POSS is much smaller (on the order of 10%) as compared with the same host SBS

block copolymer grafted with Cp, Cy, Cye, and Ph moiety of POSS (on the order of 100%) from

the previous study.[5] This observation once again confirms the non-interacting nature of iBu-

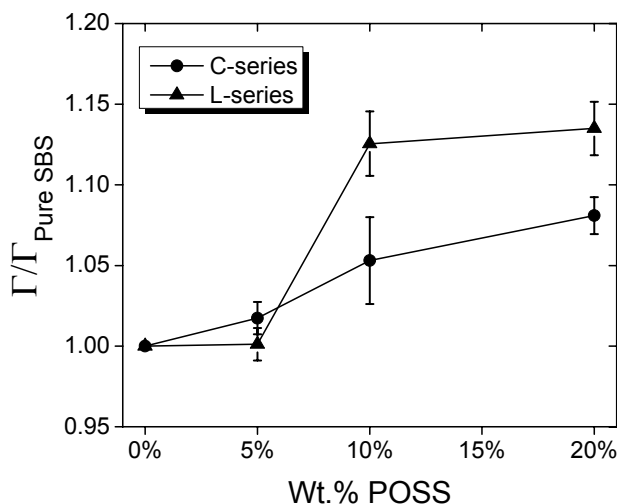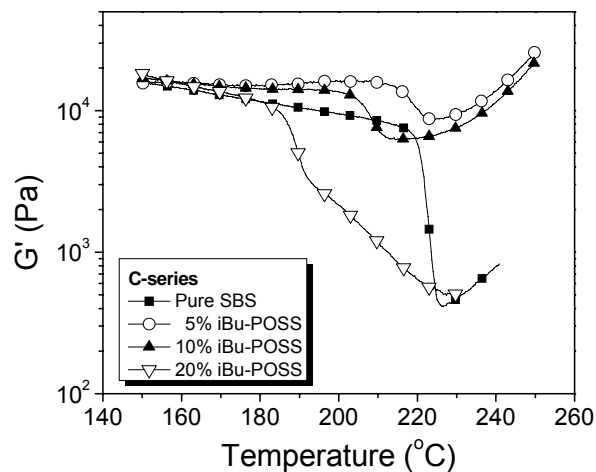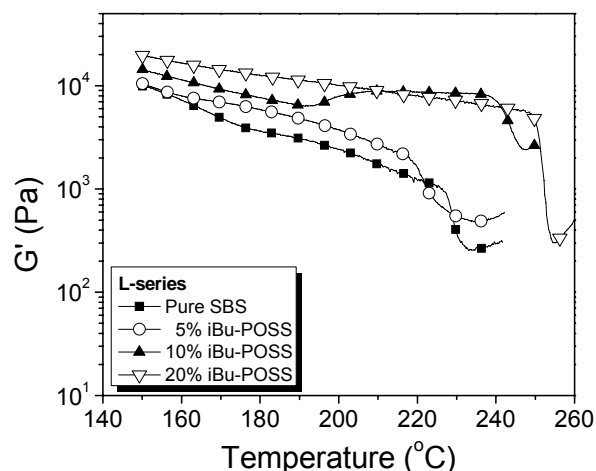POSS to the styrene domain and its affinity to stay within the butadiene domain.

Figure 4. Primary scattering peak width, Γ, is normalized to unmodified SBS for the C-series and L-series at 130°C. Peak width is measured as the full width at half the maximum peak height. Peak width for unmodified C-series and L-series SBS are 0.0168nm^{-1} and 0.0129nm^{-1} respectively.

The morphology phase behavior as a function of temperature can best be observed by examining the order-disorder and order-order transition temperatures. These transition temperatures were obtained from abrupt changes in the storage modulus, G'. The onset temperature of the G' change is referred to as the T_{OOT} or T_{ODT}.

Traces of storage modulus, G', versus temperature for C-series and L-series of iBu-POSS modified block copolymers are shown in Figure 5(a) and 5(b), respectively. It is interesting to point out here that in the ordered phase (i.e. $T < T_{ODT}$) values of G' are higher than the unmodified SBS for all iBu-POSS grafted SBS triblock copolymers. When grafted with small amounts of iBu-POSS (5 wt.%), we observed that the magnitude of G' drop at the order-disorder transition decreases for both host SBS block copolymers. These rheological observations reinforce the argument that segregation forces between polybutadiene and polystyrene are strengthened by grafting iBu-POSS to polybutadiene. This is in agreement with discussions of SAXS data, where suggestion that the local order morphology of the host SBS block copolymer are better preserved by grafting iBu-POSS to polybutadiene.

(a)

(b)

Figure 5. Storage modulus, G′, versus temperature for SBS triblock copolymers grafted with varying amounts of isobutyl-POSS (iBu-POSS) as indicated: (a) the cylindrical host morphology of C-series/Vector[®] 8508 and (b) the lamellar host morphology of L-series/Vector[®] 6241. G′ was obtained using small-strain oscillatory shear with strain amplitude of 2% and oscillatory frequency of 1 rad/sec. The temperature ramp rate was 2°C/min. The rheological experiments were done in a dry nitrogen environment to reduce thermal degradation.

In Figure 6(a), the T_{OOT} and T_{ODT} are plotted versus weight percent of iBu-POSS grafted for both series. The entire C-series maintains a cylindrical morphology at all temperatures below

T_{ODT}, and there is a continual decrease in the T_{ODT} with increased POSS grafting for this series. The L-series phase behavior is more complex. At all temperatures below T_{ODT}, the unmodified and 5 wt.% POSS have a lamellar morphology. The L-series 10 wt.% iBu-POSS undergoes an order-order transition between a lamellar and a cylindrical morphology, and it undergoes an order-disorder transition at a higher temperature. The 20 wt.% L-series material has a cylindrical morphology for all temperature below T_{ODT}.
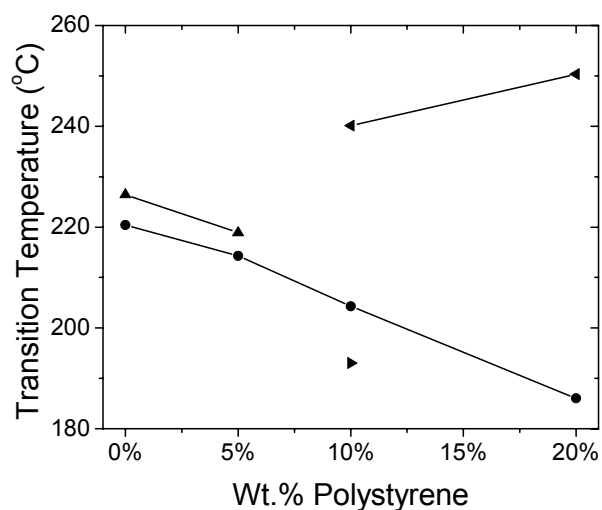

Figure 6. The T_{OOT} and T_{ODT} are plotted for both the C-series and L-series. There is an order-order transition in the L-series for the 10 wt.% iBu-POSS. All transitions were verified by SAXS. For the C-series, the ● symbol represents the cylindrical-disorder transition. For the L-series, ▲ represents the lamellar-disorder transition, ▶ represents the lamellar-cylindrical transition, and ◀ represents the cylindrical-disorder transition.

To put the T_{OOT} and T_{ODT} data in the context of the phase shift ideas discussed earlier, the transition temperatures are plotted in terms of χN vs. f_{PS} (volme percent of polystyrene) in Figure 7. In actuality, we have a ternary system of polystyrene, polybutadiene, and iBu-POSS. However, based on the phase shift arguments mentioned earlier, we plot the data assuming that iBu-POSS grafting only affects the fraction of polystyrene and has little effect on monomer segregation between polystyrene and polybutadiene. It is also assumed that N, the effective

degree of polymerization, has not been affected after grafting. The purpose of this plot is not to precisely define the phase space of the POSS-SBS grafts, but to put the T_{ODT} changes in the context of the reduction of polystyrene content by grafting which was discussed earlier. The values for χ were calculated using the fitted parameters obtained by Owens et al.[11] N was calculated using the average monomer density from the calculations in the Appendix. The transition temperature data are plotted as χN vs. f_{PS} polystyrene show consistency with other styrene-rubber phase diagrams.[8, 9, 12-14] Lines are added to guide the eye and separate the observed morphologies. The plot explains the T_{ODT} drop for the C-series in the context of a shift in composition, it clarifies the T_{ODT} increase for the 10 and 20 wt.% L-series data, and it relates the phase behavior between the two SBS polymer series. It is important to note that no complex phases like the bicontinuous gyroid or the hexagonally perforated lamellae morphologies were observed. It is possible that these phases exist, but they may not have been observable because of their narrow range of stability and the few grafting fractions implemented.

Figure 7 was plotted with three central assumptions: (1) grafting affects the fraction of polystyrene (f_{PS}), (2) grafting iBu-POSS does not affect the monomeric segregation between polystyrene and polybutadiene (χ), and (3) the effective degree of polymerization is not affected by grafting (N). The assumptions are reasonable within the context of the phase shift argument, but it is important to comment on how deviations from these assumptions will affect Figure 7. The fraction of polystyrene is a straightforward calculation, but it does not take into account the changes due to thermal expansion differences between the polystyrene, polybutadiene, and iBu-POSS. This is change is small when compared to the uncertainty in the density estimation of POSS which is on the order of $\pm 10\%$. This uncertainty will only contribute to a f_{PS} difference of approximately 0.005 for the 20 wt.% iBu-POSS grafts. Grafting does not affect the overall

effective degree of polymerization, N, but it may contribute to a small increase in the chain size, R_g, as mentioned in the d-spacing discussion. For grafting fractions of 20 wt.% iBu-POSS, this may be a more important factor. The consequence on this is a vertical shift on the χN axis at the T_{ODT}. The χ-parameter also caries a degree of uncertainty. χ has been calculated for SB diblocks and triblocks with and without symmetry considerations, but its precise value can vary on the order of a few percent.[11, 15, 16] The fitted χ that was used in Figure 7 was from Owens et al. because the polymer was well-characterized and had similar polydispersity. It is likely that iBu-POSS contributes to changes within the polybutadiene block, and further studies will be performed. However, it appears that grafting iBu-POSS to the butadiene block of SBS has little effect on the monomeric segregation between the polybutadiene and polystyrene blocks based on what we have seen in the preserved morphology, little changes in d-spacing and peak width, and the T_{OOT} and T_{ODT} behavior.
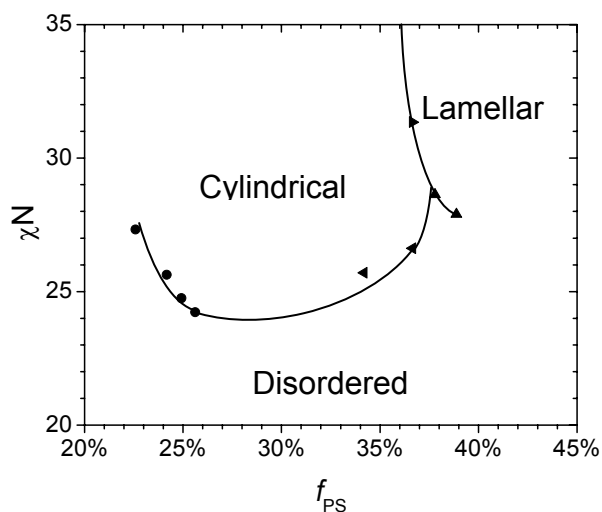

Figure 7. (b) The transition temperatures are plotted in terms of χN vs. the volume fraction of polystyrene, f_{PS}, for both SBS series. Unmodified C-series and L-series polymers have 0.26 and 0.39 f_{PS}, respectively. Lines are added to guide the eye and separate the observed morphologies. For the C-series, the ● symbol represents the cylindrical-disorder transition. For the L-series, ▲ represents the lamellar-disorder transition, ▶ represents the lamellar-cylindrical transition, and ◀ represents the cylindrical-disorder transition.

Conclusions

In this work, we investigated the phase behavior and morphology changes of SBS grafted with iBu-POSS. Two host SBS morphologies were examined at 0, 5, 10, and 20 wt.% grafting. The morphology and phase behavior observed for both systems is consistent with that of a shift in polystyrene content with little change in χ, which is similar to observations of selective swelling. The local and long-ranged order of the morphology is preserved for all SBS grafted with iBu-POSS copolymers investigated. There is little change in the d-spacing for both the cylindrical and lamellar morphologies. The 20 wt.% L-series has the largest d-spacing change, which may result from the higher volumetric grafting density compared to the other SBS grafted with iBu-POSS copolymers or from comparing cylindrical to lamellar morphologies. The selective swelling/phase shift behavior is again illustrated in the order-order and order-disorder morphology transitions. The transition temperatures are highly correlated to the polystyrene content, and the phase behavior is comparable to other styrene-rubber phase diagrams.

Appendix

Calculation for volume fraction of polystyrene. The volume percent polystyrene, f_{PS}, was calculated using bulk densities of 1.05 and 0.887 g/cm³ for polystyrene and polybutadiene respectively. The bulk density of the iBu-POSS hydride was estimated to be 1.73 g/cm³ based on solution scattering and weighing in water based on the Arrhenius method (±10% error).

$$f_{PS} = \frac{\rho_g}{\rho_{PS}} W_{PS}$$

$$\rho_g = \frac{1}{W_{PS}/\rho_{PS} + W_{PB}/\rho_{PB} + W_{POSS}/\rho_{POSS}}$$

$$\rho_g = \frac{1}{(1-W_{POSS})(W_{PSo}/\rho_{PS} + (1-W_{PSo})/\rho_{PB}) + W_{POSS}/\rho_{POSS}}$$

$$V_{PS} = \frac{W_{PSo}(1-W_{POSS})/\rho_{PS}}{(1-W_{POSS})(W_{PSo}/\rho_{PS} + (1-W_{PSo})/\rho_{PB}) + W_{POSS}/\rho_{POSS}}$$

where ρ_{PS}, ρ_{PB}, ρ_{POSS}, and ρ_g are the densities for polystyrene, polybutadiene, iBu-POSS hydride, and the POSS-SBS grafted system, respectively. W_{PS}, W_{PB}, and W_{POSS} are the weight fractions for polystyrene, polybutadiene, and iBu-POSS hydride for a particular POSS-SBS grafted system. The expression can be made more general by using the densities and the polystyrene weight fraction of the original SBS, W_{PSo}, and the weight fraction of POSS grafted, W_{POSS}. It is important to note that the above calculations assume no change in volume upon mixing and do not take into account differences in thermal expansion.

Wt.% POSS	Vector® 8508 C-series	Vector® 6241 L-series
0%	25.6%	38.9%
5%	24.9%	37.8%
10%	24.2%	36.6%
20%	22.6%	34.2%

Calculation for N. The parameters and notation used in the calculation of N are the same as those used by Owens et al.[11] N was normalized to constant monomer volume according to the geometric average by the following relations:

$$\rho^* = \left(\prod_{i=1}^{n} \rho_i \right)^{1/n}$$

$$b_i^* = b_i \sqrt{\rho_i / \rho^*}$$

$$N_i^* = N_i \left(b_i / b_i^* \right)^2$$

where ρ_i is the monomeric density of the ith component, ρ^* is the average monomer density, b is the statistical segment length, and N is the degree of polymerization. The monomeric density for polystyrene and polybutadiene used in the calculations are based on bulk densities of 1.05 and 0.887 g/cm^3 respectively (to achieve 10,100 and 16,400 mol/m^3 respectively).

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