Morphology and Phase Transitions in Styrene-Butadiene-Styrene Triblock Copolymer Grafted with Polyhedral Oligomeric Silsesquioxanes

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ABSTRACT

Symmetric triblock copolymer of styrene-butadiene-styrene (SBS) was grafted with varying amounts of polyhedral oligomeric silsesquioxane (POSS) with different organic moieties. The POSS, $R'R_7Si_8O_{12}$, was designed to contain a single silane functional group, R', which was used to graft onto the dangling 1,2 butadienes in the mid-butadiene block, while the other seven identical organic group, R_7, interact with styrene end-blocks at different level. Morphology and phase transitions of these POSS-modified SBS triblock copolymers were investigated using time-resolved small angle X-ray scattering and rheological methods. It was observed for isobutyl moiety POSS (iBu-POSS), appears to show a high affinity to stay in the butadiene domain. While phenyl moiety POSS (Ph-POSS), due to its preference with styrene blocks, the driving force to reduce enthalpy comes at expense of the entropy to remain in butadiene domain, leading to a qualitative change at the interface of phase separated domains.

Keywords: POSS, Block copolymers, SAXS, Order-Order transition, Order-disorder transition.

1. 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 a specific copolymer block.[5,6] Polyhedral oligomeric silsesquioxanes (POSS) are a type of model nano-structured chemical, it can be made to graft to a specific to a particular phase of a copolymer. This enables us to investigate the influence of nanochemicals on the thermodynamics and morphology of a block copolymer matrix.

In this paper, we report the effect of surface chemistry of the grafted nanostructures on the host block copolymer morphology. More specifically, polyhedral oligomeric silsesquioxane (POSS) was used as a model nanostructured chemical and was grafted to the polybutadiene midblock of a symmetric SBS triblock copolymer. Results from two different chemical substituents of POSS, i.e., phenyl (Ph) and isobutyl (iBu), were compared due to their contrasting differences when interact with the host polystyrene endblocks.

In the following sections, we probe the particle-polymer interaction energies and present results for the morphological changes in SBS grafted with either Ph-POSS or iBu-POSS to the butadiene domain. The amounts of POSS grafted to SBS were varied from 5 to 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 POSS. Additionally, in combination with rheological measurements, we also report morphological transitions and their transition temperatures as a function of POSS content.

2. EXPERIMENTAL

The host polymer for this study was obtained from Dexco Polymer: Vector® 6241. It is a symmetric SBS triblock copolymer. The unmodified Vector® 6241 exhibited a lamellar morphology from room temperature to its order-disorder temperature.

POSS grafting was accomplished via a hydrosilation reaction in toluene. The procedures used to synthesize the Ph-POSS and iBu-POSS hydrides were published in our previously reported work elsewhere. In addition, synthesis conditions used for grafting to POSS hydrides to 1,2-butadiene can also be found in those previously reported work.[5] 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 the order-order and order-disorder transition temperatures, T_{OOT} and T_{ODT} respectively. 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 radian/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.

3. RESLUTS

Small-angle x-ray scattering, SAXS, is a useful tool for examining the morphology of block copolymers because diffraction occurs on a length scale that is accessible by this technique.[7-9] Figure 1 shows the scattering profiles at 130°C for each POSS-SBS copolymer that was investigated earlier in our laboratory.
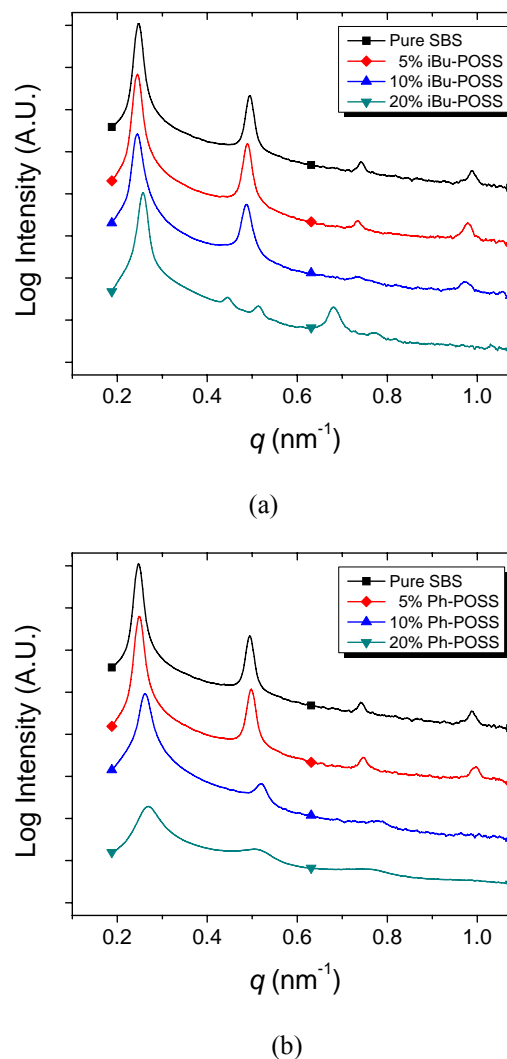

(a)

(b)

Figure 1. Integrated SAXS intensity vs. scattering vector, q, at 130°C for symmetric triblcok styrene-butadiene-styrene, SBS, Vector® 6241, copolymers grafted with (a) isobutyl-POSS and (b) phenyl-POSS. *Data are shifted along the log intensity axis to clarity. All copolymers have a lamellar morphology except the 20% iBu-POSS, which has a cylindrical morphology.

A block copolymer with varying amounts of isobutyl-POSS, iBu-POSS, grafted to the polybutadiene mid-block is shown in Figure 1 (a). 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 $(1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}\ldots)$. This change in morphology can be attributed simply to changes in the overall polystyrene content of the POSS-SBS copolymers after grafting. By grafting 20 wt% iBu-POSS, the weight fraction of polystyrene is reduced from 43 wt% for the unmodified SBS to 34 wt% in the 20% iBu-POSS grafted SBS (or 39 to 33 vol.%). This reduction in polystyrene content is large enough to cause a change in morphology from lamellar to cylindrical. An underlying premise for this reasoning is that grafting of iBu-POSS to the polybutadiene does not significantly 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. This can only occur if the iBu-POSS is confined within the polybutadiene block and is non-interacting with the polystyrene block. This argument parallels to those studies on highly selective solvent swelling of block copolymers, which is to be expected because the iBu-POSS are chemically grafted to polybutadiene, and thus are confined within the butadiene domain[10]. In addition, iBu-POSS is anticipated to unfavorably interact with the polystyrene block since the polystyrene is an aromatic polymer and the iBu-POSS has an aliphatic functionality. Accordingly, as iBu-POSS is grafted to the 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.

The SAXS profiles in Figure 1 (b) show the block copolymer with phenyl-POSS, Ph-POSS, grafted to the polybutadiene mid-block. Unlike the iBu-POSS, a lamellar morphology is present for all of the Ph-POSS-SBS copolymers investigated. The difference in phase behavior implies that there is a difference in how the Ph-POSS interacts with the block components. Instead of a shift in phase behavior or a straightforward reduction in polystyrene content like that of iBu-POSS grafted SBS, the Ph-POSS grafted SBS shows noticeable peak broadening and diminished diffraction intensity. The overall peak broadening for the 20% iBu-POSS is much smaller (on the order of 10%) compared to the 20% Ph-POSS (on the order of 200%). The large difference in peak width suggests that there is an additional mechanism for peak broadening for Ph-POSS grafted SBS which is related to the POSS chemistry. Although, Ph-POSS enthalpically prefers the polystyrene block, it is chemically attached (via grafting) to the polybutadiene block. The driving force to reduce enthalpy comes at the expense of the entropy for the remaining polybutadiene block, leading to a qualitative change at the polystyrene-polybutadiene interface. The resulting competition leads to a more disrupted interface and along with the reduced χ-parameter, leads to a larger

interfacial thickness. Thus, peak broadening is observed for as little as even 5 wt% Ph-POSS, becoming more substantial in the 10 and 20 wt% Ph-POSS.

The position of the primary diffraction peak is related to the thickness of one repeat distance, or d-spacing, of the block copolymer morphology. For the lamellar morphology, the d-spacing (denoted in Figure 2 as D_{100}) is the distance covering one polystyrene and polybutadiene layer, and can be calculated by the relation $d = 2\pi/q^*$, where q^* is the primary peak position. The primary peak position for the cylindrical morphology does not correspond to the nearest neighbor cylinder repeat distance (which is consistent with the lamellar d-spacing). Consequently, the d-spacing calculated based on the primary peak position of 20 wt% iBu-POSS must be multiplied by $\sqrt{(4/3)}$ to correspond to D_{100}, so it can be consistent with the other calculated d-spacing values.
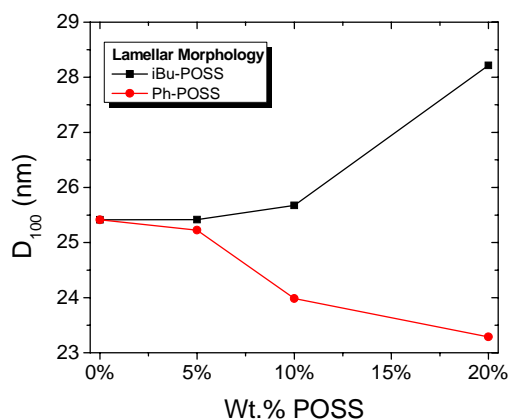

Figure 2. The D_{100} d-spacing plotted vs. the weight percent POSS grafting at 130°C. For the iBu-POSS series, there is a change in morphology from lamellar (0-10%) to hexagonally packed cylinders (20%). D_{100} for the cylindrical morphology corresponds to the nearest neighbor cylinder repeat distance which is consistent with the lamellar d-spacing.

The d-spacing for block copolymers depends on a number of factors including the degree of polymerization, N and monomeric segregation factor, χ. The d-spacing data are shown in Figure 2 for both POSS types. The data for the iBu-POSS series polymers show that the d-spacing increases as a result of grafting. The iBu-POSS is grafted to the polybutadiene and is subsequently confined there. The iBu-POSS occupies volume within the butadiene phase and may contribute to a greater self-avoiding polymer chain conformation, which leads to an increase in R_g for this block. The polystyrene block is unaffected, and the final result is an observed increase in d-spacing.

The differences in chemistry between Ph-POSS and iBu-POSS are again illustrated in Figure 2. For the Ph-POSS grafted SBS, value of d-spacing decreases with increased in the grafting content. This drop in repeat distance can be explained by the concomitant drop in the χ-

parameter. Unlike the iBu-POSS, the Ph-POSS have a greater affinity towards the polystyrene block than to the polybutadiene block because of its aromatic structure. The result of grafting Ph-POSS to the polybutadiene block is that the Ph-POSS modified polybutadiene block is more compatible with the polystyrene block. This reduces the monomeric segregation between the copolymer segments, subsequently reducing the d-spacing. With a larger fraction of Ph-POSS grafting, the modified polybutadiene block becomes more compatible with the polystyrene block and the value of d-spacing further decreases. Qualitatively, the Ph-POSS is acting as a compatibilizing agent for the two segregated blocks. This mechanism for d-spacing change contrasts greatly with the iBu-POSS series, where iBu-POSS is compatible with polybutadiene and non-interacting with the polystyrene block.

The morphology phase behavior as a function of temperature can best be observed by examining the order-order and order-disorder transition temperatures. In Figure 3, the T_{OOT} and T_{ODT} are plotted versus weight percent of grafted POSS. The phase behavior of the iBu-POSS grafted SBS is relatively complex when compared to the SBS grafted with Ph-POSS. At all temperatures below T_{ODT}, the unmodified SBS and the entire Ph-POSS series have a lamellar morphology. The 5 wt% iBu-POSS grafted SBS also has a lamellar morphology below the T_{ODT}. However, the 10 wt% iBu-POSS grafted SBS exhibits an order-order transition between a lamellar and a cylindrical morphology at around 195°C, and an order-disorder transition at a higher temperature. Finally, the 20 wt% iBu-POSS grafted SBS has a cylindrical morphology for all temperatures below T_{ODT}. Although the transition temperature behavior for the iBu-POSS series appears complicated, it is merely related to the overall polystyrene content and the thermal stability of the SBS with a particular degree of polymerization and fraction of polystyrene. T_{ODT} decreases with increasing grafting for the Ph-POSS series, which is related to a reduction in the χ-parameter, as stated earlier. With greater Ph-POSS grafting, the χ-parameter is reduced, which further reduces the T_{ODT}.
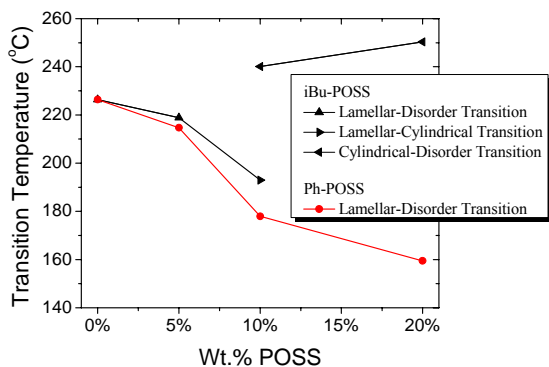

Figure 3. The T_{OOT} and T_{ODT} are plotted for both the iBu-POSS and Ph-POSS series. There is an order-order transition in the iBu-POSS series for the 10 wt%. All transitions were verified by SAXS. For the iBu-POSS, ▲ represents the lamellar-disorder transition, ► represents the lamellar-cylindrical transition, and ◄ represents the cylindrical-disorder transition. For the Ph-POSS, the ● symbol represents the lamellar-disorder transition.

4. CONCLUSIONS

We have observed that the chemistry of the grafted nanostructures has a profound effect on the morphology of the host block copolymer. More specifically, POSS was used as a model nano-structured chemical and was grafted to the polybutadiene midblock of a symmetric polystyrene-*block*-polybutadiene-*block*-polystyrene copolymer (SBS). Two different chemical substituents of POSS, i.e., isobutyl (iBu) and phenyl (Ph), were studied because of their contrasting interaction with respect to the polystyrene block. It was shown that the morphology of the host SBS copolymer was shifted to lower polystyrene contents with iBu-POSS, resulting in a cylindrical morphology at 20 wt% iBu-POSS grafting. The order of the morphology was preserved based on the observed presence of high-order diffraction peaks and negligible broadening of the primary peak. These observations reinforce the hypothesis that iBu-POSS does not interact with the polystyrene block. When Ph-POSS is grafted, the morphology becomes more disrupted with an increasing amount of grafting. This is supported by the disappearance of high-order diffraction peaks, a 200% increase in primary scattering peak width, and a persistent drop of the T_{ODT}.

5. REFERRENCES

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