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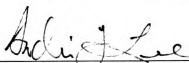
CHARACTERIZATION OF THE THERMODYNAMICS AND
DEFORMATION BEHAVIOR OF STYRENE-BUTADIENE-
STYRENE GRAFTED WITH POLYHEDRAL OLIGOMERIC
SILSESQUOXANES

presented by

Daniel B. Drazkowski

has been accepted towards fulfillment
of the requirements for the

Ph. D. degree in Materials Science



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CHARACTERIZATION OF THE THERMODYNAMICS AND DEFORMATION
BEHAVIOR OF STYRENE-BUTADIENE-STYRENE GRAFTED WITH
POLYHEDRAL OLIGOMERIC SILSESQUIOXANES

By

Daniel B. Drazkowski

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ABSTRACT

CHARACTERIZATION OF THE THERMODYNAMICS AND DEFORMATION BEHAVIOR OF STYRENE-BUTADIENE-STYRENE GRAFTED WITH POLYHEDRAL OLIGOMERIC SILSESQUIOXANES

By

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This research study uses a model nanostructure-copolymer system in order to develop a fundamental understanding of how polymers are affected by functionalized nanostructures. For this study, polyhedral oligomeric silsesquioxanes (POSS) was chosen as the model nanostructure and polystyrene-block-polybutadiene-block-polystyrene copolymer (SBS) as the model polymer host. The choice of materials and chemical reaction scheme for grafting the SBS-POSS copolymers allows for reproducible products with the opportunity for wide selection of nanostructure grafting fractions.

In order to examine the effects that the nanostructure's electronic properties have on the host polymer, the organic group of the POSS nanostructures was varied. To facilitate a rigorous comparison, four sterically similar, yet electronically different POSS derivatives were selected (cyclopentyl (Cp), cyclohexyl (Cy), cyclohexenyl (Cye), and phenyl (Ph)). Ph-POSS results in the greatest changes relative to the ungrafted SBS block copolymer because its chemistry has the largest contrast to the block in which it is grafted (polybutadiene) while simultaneously having the largest affinity toward the ungrafted block (polystyrene).

All four of the cyclic POSS were found to have some affinity toward the polystyrene phase, so iBu-POSS was investigated in order to observe the effects of incorporating a noninteracting nanostructure. Two host morphologies were examined in

order to compare noninteracting (iBu) and strongly interacting (Ph) POSS nanostructures. The morphology and phase behavior observed for noninteracting POSS is consistent with simply changing polystyrene content with no noticeable change in χ . Furthermore, local and long-ranged order of the morphology is well-preserved. The interacting nanostructures reduce χ substantially and disrupt the local order of the morphology, which is equivalent to a compatibilizing effect.

Deformation was studied to supplement the previous findings regarding the equilibrium morphology, and give further information on the nature of the interactions between POSS-polymer and POSS-POSS interactions. The mechanical properties for both the grafted copolymers inherently drop because nanostructure grafting reduces the polystyrene content. For the noninteracting iBu-POSS, the reduction in mechanical properties was consistent with the fraction of polystyrene because the nanostructures are noninteracting with the polystyrene block and do not qualitatively change the morphology. This was observed at both low (30°C) and high (70°C) temperatures. The interacting Ph-POSS behavior is more complex. With increasing Ph-POSS, the morphology becomes more disrupted which should result in an additional drop in mechanical properties. However, there is reinforcement at larger concentrations of Ph-POSS. The disrupted morphology of the 10% and 20% Ph-POSS results in a smaller grain size, which together with the presence of POSS crystallites reinforce, or network, the morphology. Low strain reinforcement is more prominent at lower temperatures. At high temperatures (but still below $T_{g,PS}$), the drop in mechanical properties from the disrupted morphology order outweighs the low strain reinforcement effects. Some reinforcement is still observed at these higher temperatures due to POSS-POSS effects.

To Jenni

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KEY TO SYMBOLS OR ABBREVIATIONS

2θ	scattering angle
a	cylinder-cylinder distance
b	statistical segment length of polymer specie
d	d-spacing
d^*	d-spacing of the primary scattering peak
d_{100}	cylinder-cylinder distance, lamellar repeat distance
d_{SD}	d-spacing in the stretching direction
f	Herman's orientation function
f_{PS}	volume fraction of polystyrene
iBu	isobutyl
kDa	kiloDaltons = 1000 Daltons = 1000 atomic mass units
q	scattering vector
q^*	position of the primary scattering peak
q_m	form factor is at a minimum
rad	radians
wt%	weight percent
x	unknown parameter
A.U.	arbitrary units
C	cylindrical morphology
Cp	cyclopentyl
Cy	cyclohexyl
Cye	cyclohexenyl
D	disordered morphology
$F(q)$	structure amplitude
G	gyroid morphology
G'	dynamic Storage Modulus
I	intensity
$I(\mu)$	angular dependence of the diffracted intensity
J_l	Bessel function of the first kind of order l
L	lamellar morphology
M_n	number average molecular weight
M_w	weight average molecular weight
N	degree of polymerization
$N(\mu)$	normalized orientation distribution function
PB	polybutadiene
PDI	polydispersity index = M_w/M_n
Ph	phenyl
PL	perforated layer morphology
POSS	polyhedral oligomeric silsesquioxane
PS	polystyrene
R	radius

R	organic group, molar gas constant
R'	reactive organic group
R_g	radius of gyration
S	spherical morphology
$S(q)$	structure factor
SAXS	small-angle X-ray scattering
SBS	styrene butadiene styrene triblock copolymer
S_i	i^{th} solution to $J_l(x) = 0$
T	thickness of the lamellae, temperature
T_g	glass transition temperature
$T_{g,PB}$	glass transition temperature of polybutadiene
$T_{g,PS}$	glass transition temperature of polystyrene
T_{ODT}	order-disorder transition temperature
T_{OOT}	order-order transition temperature
V^*	activation volume in which the polymer segment acts
W	weight fraction
WAXS	wide angle X-ray scattering
ϵ	strain
ϵ_E	engineering strain
$\epsilon_{Engineering}$	engineering strain
ϵ_H	Henky strain
ϵ_{Henky}	Henky strain
ϵ_{Local}	local strain of the morphology
$\dot{\epsilon}_y$	applied strain rate
θ	angle of diffraction, angular change in radians
λ	wavelength of radiation
μ	azimuthal angle
π	pi = 3.1415926535897932384626433832795...
ρ	density
σ	stress
σ_y	yield stress
χ	chi-parameter, Flory-Huggins parameter, monomeric segregation
ω	angular change in degrees
ΔH	energy barrier for jumping,
Γ	peak width
Γ_{SD}	peak width in the stretching direction
Γ_0	peak width at 0% strain, peak width for unmodified SBS
Δ	change
Π	product (mathematical calculation)
$^\circ$	degrees (angular or temperature)

CHAPTER 1.

INTRODUCTION

1.1. INTRODUCTION AND BACKGROUND

Over the last several decades, there has been a strong consumer demand to make current technologies operate on an ever smaller scale which has lead to increasing requirements on materials to bring these desires to practical application. Simultaneously, fundamental research in physics on quantum theory has opened the door for new technologies by pushing the materials scale even smaller – toward the atomic scale. This has spawned nanotechnology as a new field of research. Nanotechnology is the understanding and control of matter on the length scales of 1 to 100 nanometers. At this scale, matter functions differently from both the macroscopic level and scale of individual atoms which presents unique material properties available for research. These unique properties contribute to a breadth of nanotechnology application spanning from electronics to medicine.

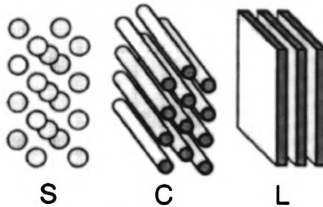
Block copolymers (BCPs) have received research interest over the past several decades because of their ability to form self-assembled microstructures¹⁻⁶, however they have been seriously considered for nanotechnology applications only in the last 15 years. Their renewed interest stems from the ability to manipulate the shape and size of their microdomains by controlling the properties of the polymer chain. In addition, BCPs offer a cost-effective way to obtain nanoscale order over relatively large distances. Some nanotechnology applications that block copolymers have been used in include: nanostructured membranes, templates for nanoparticle synthesis, photonic crystals, and high-density storage media⁶⁻⁸.

The attraction of block copolymers comes from the unique properties these materials possess compared to their homopolymer components. The dramatic change in properties is due to a self-assembled, ordered morphology that block copolymers are able to attain. These properties are strongly affected by the geometry and orientation of the morphology, so there have been many approaches to manipulate domain morphology over the past twenty years^{6, 9-11}.

The phase behavior of AB diblock and ABA triblock copolymers has been well-studied in bulk and solution both theoretically and experimentally^{1-5, 12-24}. The morphology of the block copolymer and its length scale depends on three critical factors: the product χN which quantifies the degree of segregation between the two blocks species, the volume fraction of each block, and the molecular architecture (i.e. diblock, triblock, star...) which includes copolymer asymmetry. N denotes the total degree of polymerization, and χ is the parameter which quantifies the chemical interaction between each block component. This parameter has both an enthalpic and entropic component and scales with temperature as roughly $A + B/T$ where A and B are constants and T is the absolute temperature. The degree of polymerization, volume fraction of each component, and molecular architecture are parameters that are controlled during material synthesis, however $\chi(T)$ is restricted to the choice of copolymer constituents.

At a sufficiently high degree of segregation, χN , block copolymer systems undergo microphase separation into self-assembled, ordered morphologies. Figure 1.1 shows the classical block copolymer morphologies in order of increasing volume fraction of minor component: spherical, cylindrical, and lamellar morphologies. The complex

Classical Morphologies



Complex Morphologies

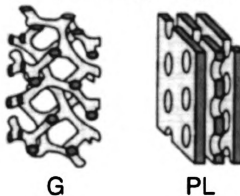


Figure 1.1. A schematic of the classical block copolymer morphologies of spherical (S), cylindrical (C), and lamellar (L) along with the complex gyroid (G) and perforated layer (PL) morphologies. This figure is after Matsen et al. *J. Chem. Phys.* **1999**, *111*, 7140.

gyroid and perforated lamellar morphologies may also exist in a narrow window of volume fractions between the cylindrical and lamellar morphologies^{1, 12, 25, 26}. The specific range of minor component volume fractions needed to obtain a particular morphology depends on the specific copolymer constituents and molecular architecture. Upon heating, the enthalpic difference between the monomeric species is abated, χ is reduced, and the morphology will eventually undergo a transition to a disordered state at the order-disorder transition temperature, T_{ODT} . It is also possible to have a thermally induced transition from one ordered morphology to another at an order-order transition temperature, T_{OOT} . Order-order transitions are only observed in small windows of volume fraction makeup for a particular block copolymer system. A phase diagram for a well studied diblock system can be seen in Figure 1.2. The phase diagram for a triblock system is fundamentally similar. In fact, the same equilibrium morphologies are present, but the position of the phase boundaries is shifted to higher χN due to the chain connectivity of the triblock.

In current bulk applications, block copolymers are often used as a component in a mixture of solvent or pure homopolymer. The addition of solvent or homopolymer to a block copolymer system can change the length scale or lattice spacing of the morphology, the T_{OOT} and T_{ODT} , and possibly the type of morphology^{17, 19, 20, 27}. Solvents can range from neutral to strongly selective depending on how it preferentially swells each microdomain of the copolymer morphology. Homopolymers that are of type A or B of the AB or ABA type copolymers have been shown to act as selective solvents in a block copolymer-homopolymer blend, but there are limits to solubility where phase separation

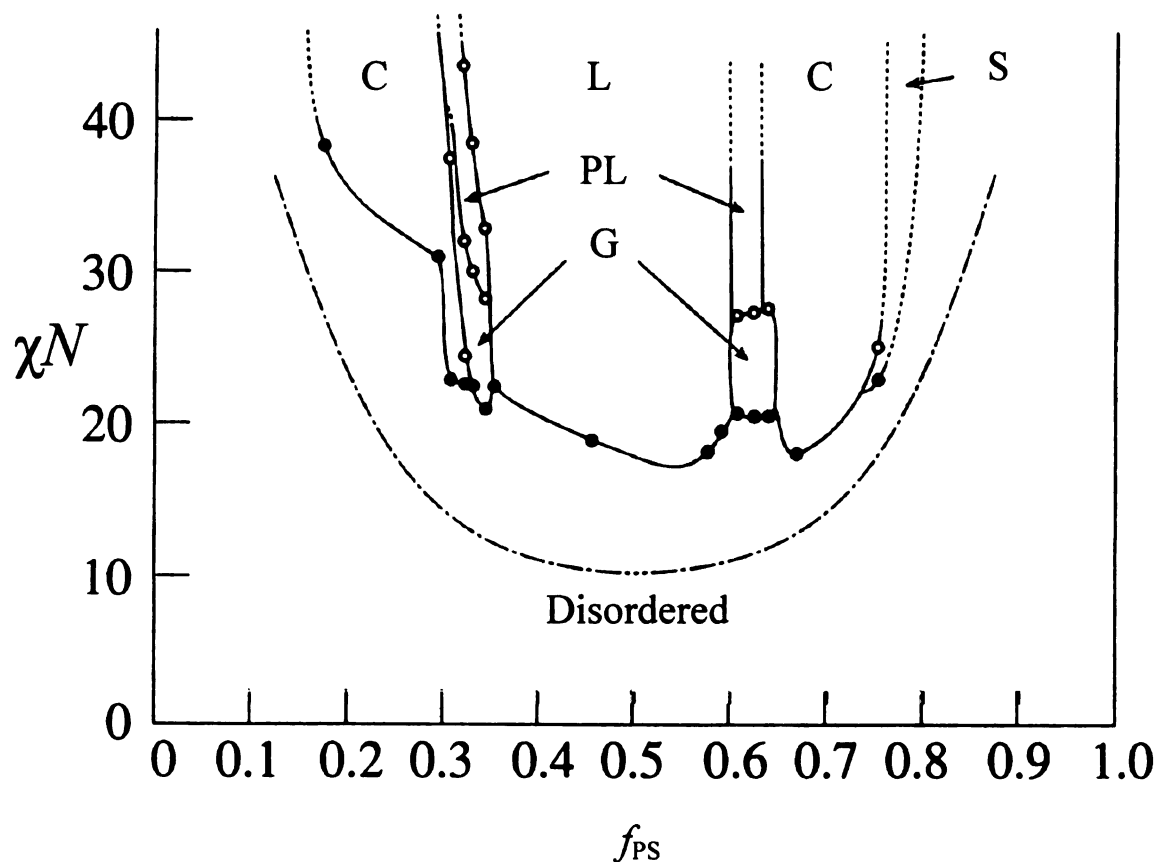


Figure 1.2. An experimentally determined phase diagram for polystyrene-polyisoprene diblock copolymers. The degree of segregation, χN , is plotted vs. the fraction of polystyrene, f_{PS} . The morphologies represented in the diagram include spherical (S), cylindrical (C), and lamellar (L) are displayed schematically along with the complex gyroid (G) and perforated layer (PL) morphologies. This figure is after Khandpur, A. K. et al., *Macromolecules* **1995**, 28, 8796.

takes place^{12, 14, 26}. Thus understanding how solvents of varying selectivity affect the copolymer morphology is important for block copolymer applications. The dependence of the T_{OOT} , T_{ODT} , and lattice spacing (d-spacing) of block copolymers in neutral and selective solvents, and the addition of homopolymer over a range of molecular weights have been performed and documented in previous studies^{12, 14, 19, 20, 26-30}.

Recent research interest has included the use of nanomaterials to further probe the property space of block copolymers^{6, 8, 18, 31-42}. Nanomaterials can be introduced into a polymer system by blending or chemical attachment. Blending is simple and can be done by a physical means, but there may be solubility limits resulting in phase separation. Attachment requires chemistry, but nanostructure solubility is generally not an issue. Chemical attachment can be performed during the initial polymerization reaction or by post-polymerization grafting. During the initial polymerization, the introduction of the nanostructure to the reactant mixture causes changes in the reaction chemistry^{18, 32-36}. Consequently, the reaction rates are dependent on the initial reactant and nanostructure composition. This can make it difficult to predict product molecular weight, molecular weight distribution, and the chemical distribution along the polymer chain. The absence of reproducibility is unfavorable for studies that hope to examine a wide range of well-characterized materials. Post polymerization grafting, on the other hand, allows one to use an initially well-characterized polymer system. Grafting can be performed by adding nanostructures to a specific location (e.g. the chain end for telechelic or hemi-telechelic) or by a random attachment to predetermined reaction sites along the polymer backbone. In any attachment scheme, the chemistry of the attachment limits the choice of both the host polymer and attached nanostructure.

In this study, the attachment approach is to graft a well-defined nano-structured chemical to a reactive segment of the copolymer³⁷⁻³⁹. If these nano-sized objects are on a similar length scale to the periodicity of the block copolymer, one expects the surface chemistry of the nano-structures to play a significant role in altering the thermodynamics and morphology of the copolymer matrix. A model group of nano-structured chemicals is polyhedral oligomeric silsesquioxanes (POSS). A fully condensed POSS molecule contains an inorganic Si-O core surrounded by organic groups. This gives the POSS a well-defined three dimensional structure, which is essential for performing a precise scientific study. These organic groups can be chosen to effectively tune the surface chemistry of the nanostructure and alter its interaction with the host copolymer blocks. In this study, POSS of the type $R'R_7Si_8O_{12}$ was chosen because they allow for a variety of choices for its organic constituents (R) and it offers a reactive group (R'). Polystyrene-block-polybutadiene-block-polystyrene copolymer (SBS) is the model polymer host because it offers a reaction site (1,2-butadiene segments), it is used as an engineering material, and it is commercially available in narrow molecular weight. A chemical reaction scheme for SBS-POSS copolymers is shown in Figure 1.3. In this reaction, the POSS nanostructures are attached randomly to the 1,2-butadiene segments of the SBS in prescribed amounts.

The choice of materials and chemical reaction scheme allow for flexible choices in nanostructure chemistry while maintaining precise host polymer properties (M_n , PDI,...). The products are reproducible because grafting is done on an already characterized polymer, so there are no confounding effects of M_n or PDI. Additionally,

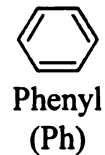
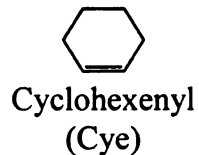
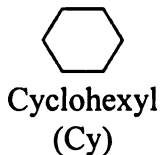
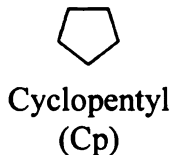
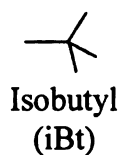
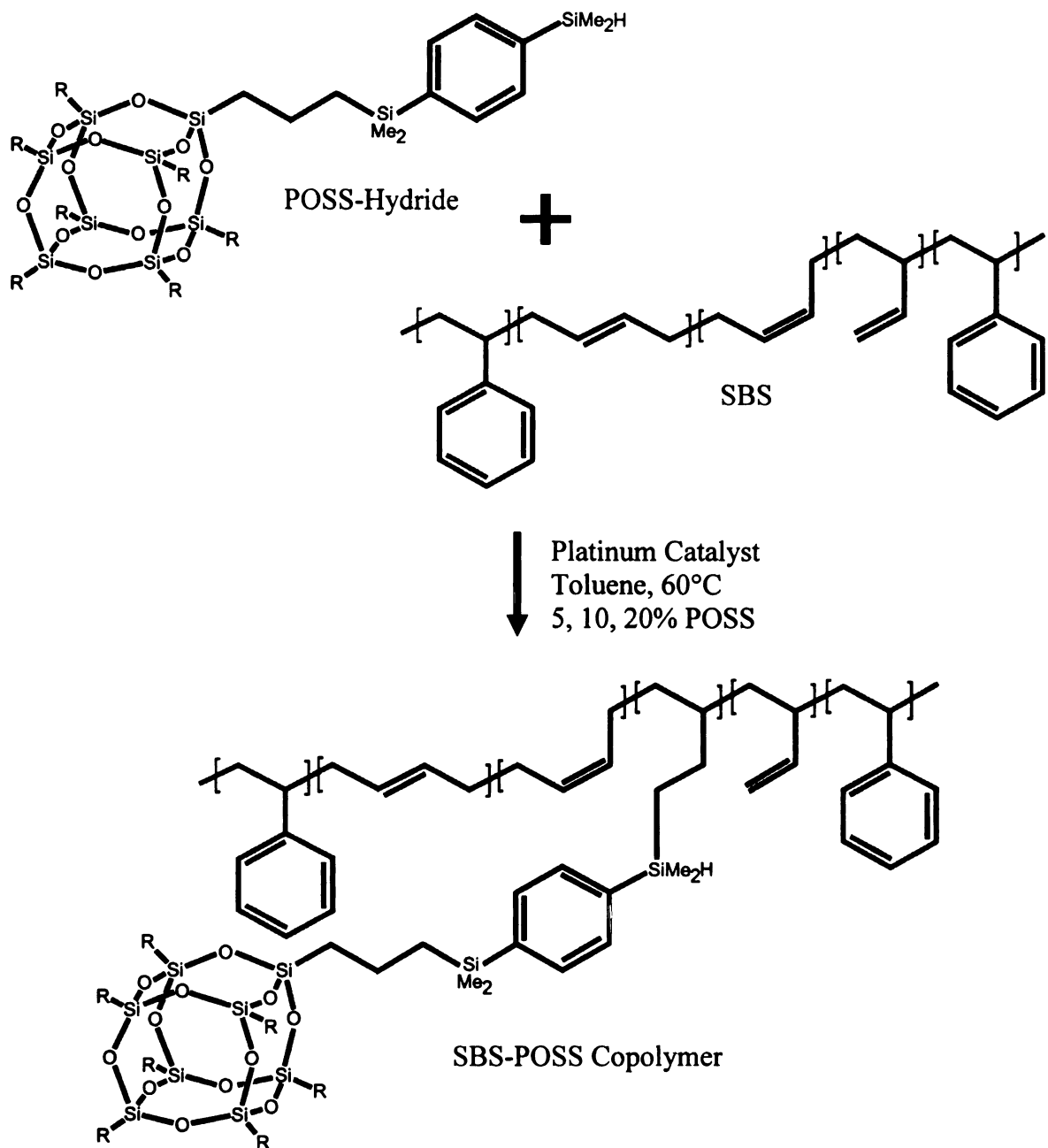


Figure 1.3. The reaction scheme for grafting of a POSS-hydride to the SBS triblock copolymer. The POSS nanostructure can be chosen to have a selected chemistry. Some potential chemical substituent groups are also listed.

creating products that vary in nanostructure content is as simple as measuring the amount to use as a reactant in the grafting reaction.

1.2. RESEARCH OBJECTIVES

The objective of this research is to develop a fundamental understanding of how block copolymers are affected by the attachment of functionalized nanostructures. To achieve this goal, the research will focus on two areas of study: thermodynamics and deformation studies. It is not only desirable to identify the effects of the nanostructures, but it is important to understand what factors are contributing to the observed changes. This knowledge will not only establish a foundation of knowledge for block copolymer systems incorporated with nanostructures, but the knowledge gained here can give insight into the current understanding of block copolymers, nanocomposites, other areas of nanotechnology, and the underdeveloped polymer-based quantum technology. The knowledge gained will also aid in the design of materials through better control of the microstructure, phase transition temperatures, and mechanical properties.

To understand thermodynamic influences on block copolymers one must examine their morphology. The equilibrium morphology represents the lowest energy state for the block copolymer. Changes in the morphology represent changes in the thermodynamics of the system. It will be important to understand not only how the equilibrium morphology is affected by nanostructure addition, but also what properties of the grafted nanostructure contribute to the changes in morphology.

The study of deformation on the system will probe the role of the nanostructures in the dynamics of the system. Because the mechanical properties are strongly related to the morphology, a thorough understanding of the morphology changes is necessary.

Next, it is important to identify whether the property changes are a result of the morphology or some other attribute of the nanostructure. Thus, one can uncover the contribution that the nanostructures have at the nanoscopic level in determining the mechanical properties.

CHAPTER 2.

THE SIGNIFICANCE OF NANOSTRUCTURE CHEMISTRY ON THE MORPHOLOGY AND TRANSITION TEMPERATURES IN POSS-GRAFTED SBS COPOLYMERS

2.1. INTRODUCTION

For a sufficiently high degree of segregation, block copolymers will undergo micro-phase separation into self-assembled ordered morphologies^{1-6, 13, 17, 19-21, 29, 43-50}. Various approaches to manipulate domain morphology have been explored by researchers over the past twenty^{5, 13, 17, 19-21, 29, 39, 43, 44, 47-51} and have led to an important class of engineering polymers often referred to as the thermoplastic elastomers. Hence, the recent interest in nano-reinforced polymers has included the use of “nanomaterials” to further explore the property space of block copolymers^{8, 39, 41, 42}. One such approach is to append the block copolymers using a well-defined nano-structured chemical to a given segment of the copolymer^{38, 39}. If these nano-sized objects are well dispersed on the length scale comparable to periodicity of block copolymer matrix, one expects the surface chemistry of the nano-structured chemicals and their interactions with different components of the block copolymer to play a significant role in altering the thermodynamics and morphology of the copolymer matrix. Polyhedral oligomeric silsesquioxanes (POSS) are a type of model nano-structured chemical. A fully condensed POSS contains an inorganic Si-O core surrounded with various organic groups useful for tuning the surface chemistry and interaction with the host copolymer matrix. POSS nanostructures can be either randomly blended or grafted to a particular phase of a

copolymer. This enables us to investigate the influence of nanomaterial chemistry on the thermodynamics and morphology of a block copolymer matrix.

The object of this chapter is to identify the significance of nanostructure chemistry on the thermodynamics of the host block copolymer. To accomplish this, we examine how the host copolymer morphology and its order-disorder transition temperature, T_{ODT} , are affected by the chemistry of grafted nano-structured chemicals. It is known that the addition of solvents or homopolymers to a block copolymer system can change the length scale or lattice spacing of the morphology, the T_{OOT} and T_{ODT} , and possibly the type of morphology. Solvents range from neutral to strongly selective depending on how they preferentially swell each microdomain of the copolymer morphology. Homopolymers that are of type A or B of the AB or ABA copolymers will also exhibit behavior like that of selective solvents in a block copolymer-homopolymer blend. Based on our previous work³⁹, polystyrene-block-polybutadiene-block-polystyrene (SBS) triblock copolymer was selected as the model copolymer matrix. SBS was chosen as a host polymer because it is commercially available in narrow molecular weight distributions, and it has been used in a wide range of applications. SBS also has the ability to form various self-assembled morphologies that allow for direct examination of how the insertion of a nano-structured chemical affects the morphology. The model POSS nanostructures used in this study are inorganic silicon-oxygen cages on the order of a nanometer in size with various organic moieties bonded to the silicon atoms^{31, 52-56}. Four POSS moieties used in this study for grafting to SBS triblocks are all of the formula $R'R_7Si_8O_{12}$. R' provides a single flexible Si-H linkage for grafting to polybutadiene while four different R groups, cyclopentyl (Cp), cyclohexyl (Cy), cyclohexenyl (Cye),

and phenyl (Ph), provide a range of sterically similar, yet electronically different organic moieties for investigating the tunability of the POSS nanostructures. Cp and Cy-POSS are saturated, Cy is unsaturated, and Ph is aromatic. Based on their electronic structure, it might be assumed that Cp and Cy-POSS will have a greater affinity for polybutadiene than polystyrene, whereas Ph-POSS will have a greater affinity toward polystyrene. Cy-POSS, having an electronic structure between Cy and Ph, will likely have relative compatibilities between the two as well. In addition, because the molecular weight and size of each POSS molecule are nearly identical, any differences found between POSS-grafted SBS copolymers will be directly attributable to R-group/SBS compatibility.

2.2. EXPERIMENTAL

2.2.1. *General information in synthesis*

The SBS used for this study of nanostructure chemistry was Vector[®] 6241 obtained from Dexco Polymers LP, a Dow/ExxonMobil Venture. According to the manufacturer, it is a pure, linear symmetric triblock copolymer containing less than 1% diblock with a polystyrene composition of 43 wt%. The number-average and weight-average molecular weights are 71 kDa and 72 kDa, respectively. This gives SBS respective degrees of polymerization of approximately 150-750-150. All initial POSS trisilanols were obtained from Hybrid Plastics Inc. Details covering the synthesis of each hydride reagent and the subsequent grafting reactions can be found in previously published work³⁸.

2.2.2. *Sample Preparation*

POSS-grafted SBS samples used for testing were prepared in the form of solvent cast films measuring approximately 0.3 mm in thickness. The copolymer samples were

dissolved in toluene, a neutral solvent, in a 3.0 wt% concentration. Approximately 0.5 wt% Irganox® 1010 antioxidant (relative to the polymer) was also added to the solution to reduce possible degradation at high temperatures. The solvent was then allowed to evaporate on glass at 20°C over a period of three days. The films were removed from the glass and annealed under vacuum at 60°C for seven days.

2.2.3. *Small-Angle X-ray Scattering (SAXS)*

SAXS measurements were performed at beamline 15ID-D (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 images were collected using a two-dimensional Bruker 6000 CCD x-ray detector with a 1024 x 1024 pixel array on a 94 x 94 mm area. The sample to detector distance was approximately 1900 mm and was calibrated using silver behenate.

Two types of SAXS experiments were performed: isothermal and temperature ramp. The isothermal experiments were used to examine how the equilibrium block copolymer morphology is affected by the type and amount of POSS grafted at selected temperatures. The samples were heated in an electric heating cell that consisted of a resistance heating element inside an enclosed 150 cubic centimeter volume. The heating cell had two Kapton® windows that allowed the x-ray beam to pass through the cell with little scattering and attenuation while containing the internal environment. A flow of nitrogen gas was used to both stabilize the temperature within the heating cell and reduce the degradation of the samples. All isothermal scans were performed after a five minute equilibration period. Data collection was performed over a period of several minutes by

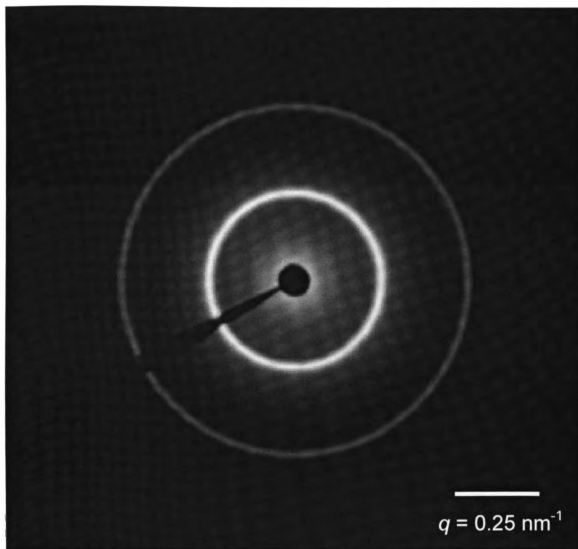
taking one second exposures at several points on a two dimensional raster covering a 3mm by 3mm area of the sample film. This was done to reduce the beam damage on the sample and to achieve better SAXS profile statistics by ensuring the sample morphology reached equilibrium and to examine errors due to possible temperature variations and morphological variations within the bulk material. Temperature ramp experiments were performed to examine the T_{ODT} of each block copolymer sample. Samples were heated to 150°C and held isothermally for 5 minutes before increasing temperature at a rate of 2°C/min. A flow of dry nitrogen gas was used to both stabilize the temperature within the heating cell and reduce sample degradation. T_{ODT} was calculated by examining the peak width as a function of temperature.

The 2-D SAXS images, like that in Figure 2.1, are through views of the cast films (i.e. the film surface is normal to the incident x-ray beam). The 2-D images show concentric, uniform intensity rings which indicate that the solvent casting process results in a random microdomain orientation analogous to a metallic polycrystal in the plane of the film surface. The 2-D SAXS images were integrated 360° azimuthally to give the SAXS profiles shown in Figure 2.2. The SAXS profiles show the intensity of scattered radiation versus the magnitude of the scattering vector, q .

$$q = \frac{4\pi \sin \theta}{\lambda} \quad (2.1)$$

where q is the magnitude of the scattering vector, 2θ is the scattering angle, and λ is the wavelength of radiation.

There are three features of these SAXS profiles that will be of interest in the results and discussion: the relative position and intensity of the higher order peaks that



Intensity (A.U.)

Figure 2.1. Two dimensional SAXS pattern of pure SBS at 130°C.

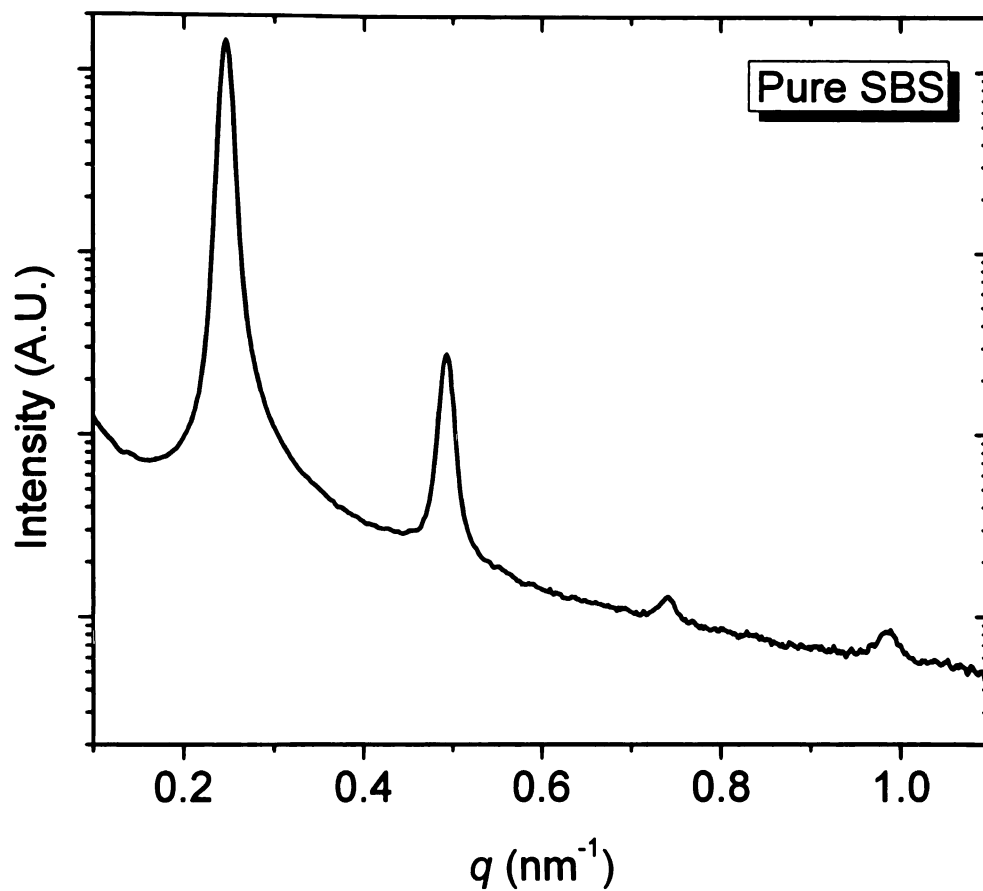


Figure 2.2. SAXS intensity versus scattering vector, q , based on 360° azimuthal integration of a 2-D image as depicted in Figure 2.1.

are defined by the type of morphology, the primary peak position that determines the lattice spacing (or d-spacing), and the primary peak width that is related to the local order of the morphology. In order to determine precise changes in peak position and intensity, peak statistics were calculated by fitting curves using nonlinear least squares regression analysis. The fitting function included a Gaussian peak of the form $A \exp[-(x - q^*)^2 / b]$ and a background of the form $A_1 x + A_0$ and/or a background of the form $\sum_{i=0}^4 A_i x^{-i}$ where $A_i > 0$. For the Gaussian peak, A is the amplitude of the peak, $\Gamma = 2\sqrt{b \ln 2}$ is the full width at half maximum of the peak, and q^* is the location of the peak maximum. One can obtain the relation between q^* and the lattice spacing by substituting Equation 2.1 into Bragg's law:

$$q^* = 2\pi / d \quad (2.2)$$

where d is the periodicity, lattice spacing, or d-spacing. A Gaussian peak was used for the fit because it well-represented the peak shape. There was an under estimation of the peak width/amplitude near the base of the peak, but this was small, symmetric, and did not affect the comparison of peak width statistics across a copolymer series. The linear and Ax^{-i} forms of the background fitting were used because of their excellent rate of convergence compared to exponentials and because they followed the monotonically decreasing background. The background ranged from 1% to 8% of the primary peak height on a linear scale, so both background forms have only a small effect on diffraction peak position and width. Calculated values for peak position and width for both forms of background were within the reproducibility of the experiment. The coefficient of

determination, R^2 , was on the order of 0.99 over the entire peak profile for a domain of 40 data points for many of the samples; this suggests a good fit to the data.

2.2.4. Rheological Characterization

Rheological testing was performed using a TA Instruments AR2000 rheometer with direct strain-control mode. The rheometer is equipped with an electric heater with a dry N_2 purge (purging rate used was 12 ml/minute); the temperature in the testing chamber is monitored with an embedded thermocouple within the bottom tool of the rheometer, which is in direct contact with the sample. Parallel plate geometry with diameter of 25 mm and gap of 0.2 mm was used for all measurements obtained in this study. The fixture was preheated to the initial testing temperature of 150°C, and lowered to obtain the zero-gap reference point. The disc-shaped specimen was then placed in the rheometer, and the top fixture was slowly lowered to the pre-set gap of 0.2 mm with minimal normal force. Samples were annealed at 150°C for five minutes prior to rheological testing. To determine order-disorder transition temperature, T_{ODT} , the samples were subjected to a fixed, small-strain oscillatory shear test with strain amplitude of 2% and oscillatory frequency of 1 radian/second at a heating rate of 2°C/minute. The strain amplitude of 2% is within the linear viscoelastic range at 1 rad/s for each material. Software provided by TA Instruments Inc. was used to determine the temperature-dependent storage modulus $G'(\omega)$ that was used for T_{ODT} analysis.

2.3. RESULTS AND DISCUSSION

2.3.1. Effect of POSS moieties on Morphology

The morphology of POSS-grafted SBS triblock copolymers was investigated using the small-angle X-ray scattering (SAXS) technique. SAXS offers not only a non-

destructive evaluation over a large volume of material but it also enables one to monitor changes in morphology as a function of temperature. Transmission Electron Microscopy (TEM) is another common technique used to investigate morphology of block copolymers⁵⁷. The main advantage of TEM is that it provides a real-space image of the material. However, there are several possible problems associated with this technique for SBS with nanoscopic inclusions. First, it is common practice to enhance absorption contrast by staining SBS with OsO₄ and thus better distinguish polybutadiene from polystyrene in the block copolymer. The chemical nature of POSS will undoubtedly affect the reaction between OsO₄ and butadiene, which may in turn alter the original morphology. Without staining, there will not be enough electronic contrast to investigate any morphology present. The POSS nanostructures in this study are principally organic in composition, so the volume fraction of POSS present in the butadiene segments will not provide enough contrast to reveal any useful morphological information. Another issue with TEM is that it examines only a small volume of the sample, so it will be uncertain as to whether the information gathered will be representative of the entire sample. In addition, sample preparation, which commonly includes lowering the temperature below the glass transition temperature of polybutadiene, will also alter the equilibrium morphology of these copolymers. TEM micrographs are not the best way to represent the bulk copolymer, especially when used to study the effect of POSS-grafted copolymers.

The 2-D SAXS profiles in Figures 2.3, 2.4, 2.5, and 2.6 show the integrated intensity as a function of scattering vector, q , for pure SBS along with 5, 10, and 20 wt%

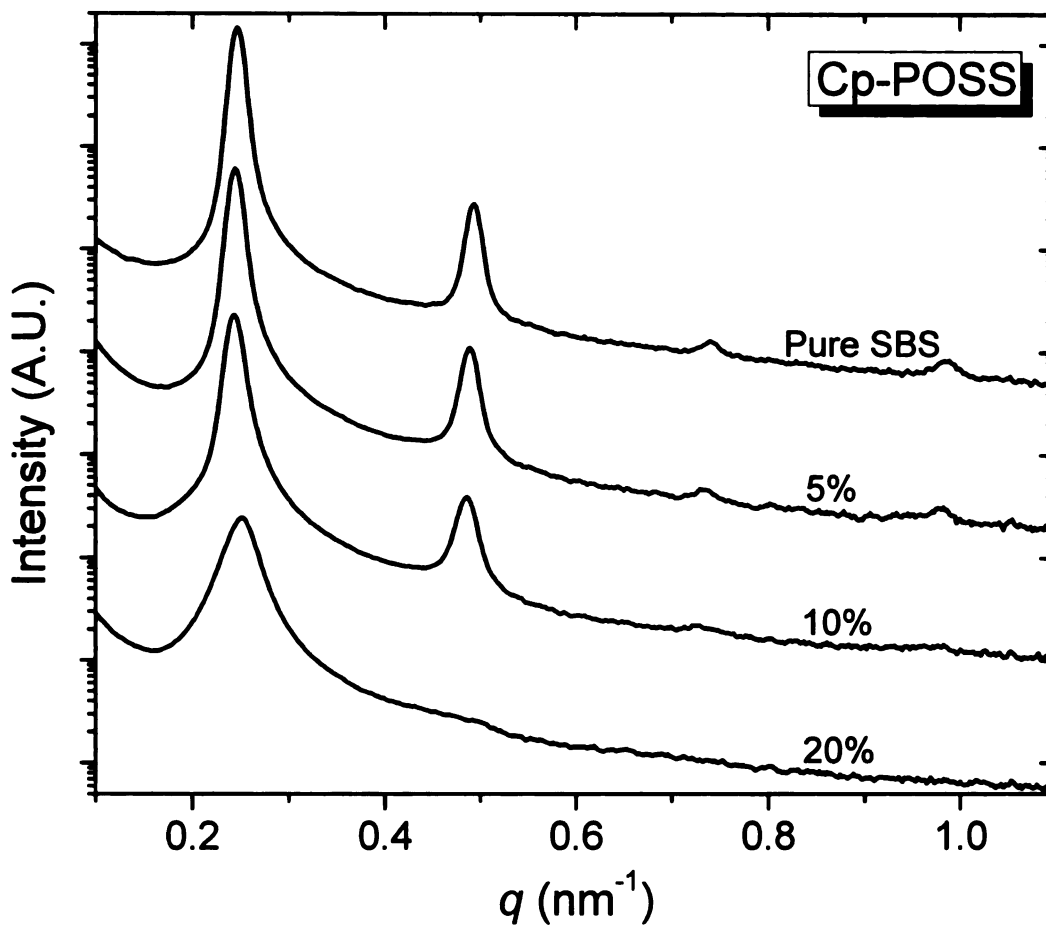


Figure 2.3. Integrated SAXS intensity versus scattering vector, q , for SBS triblock copolymers grafted with cyclopentyl-POSS (Cp) at 130°C: SBS control with no POSS, 5 wt% POSS, 10 wt% POSS, 20 wt% POSS.

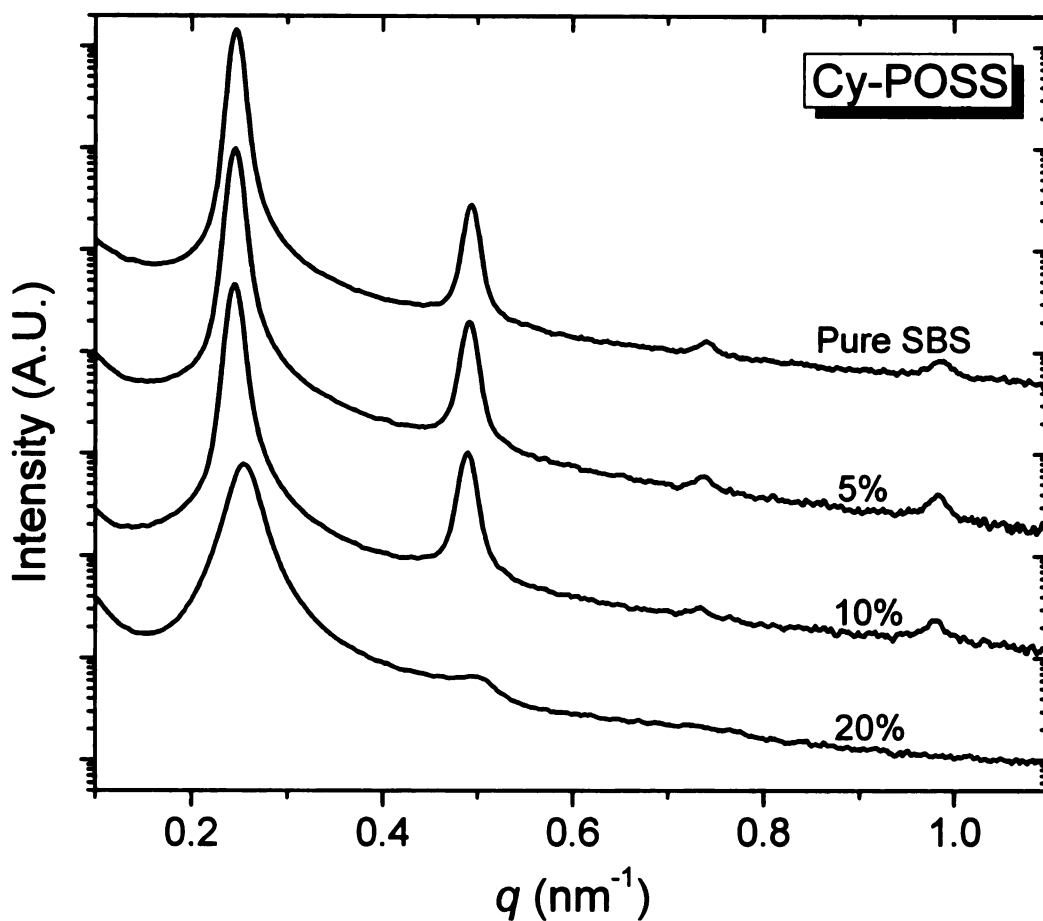


Figure 2.4. Integrated SAXS intensity versus scattering vector, q , for SBS triblock copolymers grafted with cyclohexyl-POSS (Cy) at 130°C: SBS control with no POSS, 5 wt% POSS, 10 wt% POSS, 20 wt% POSS.

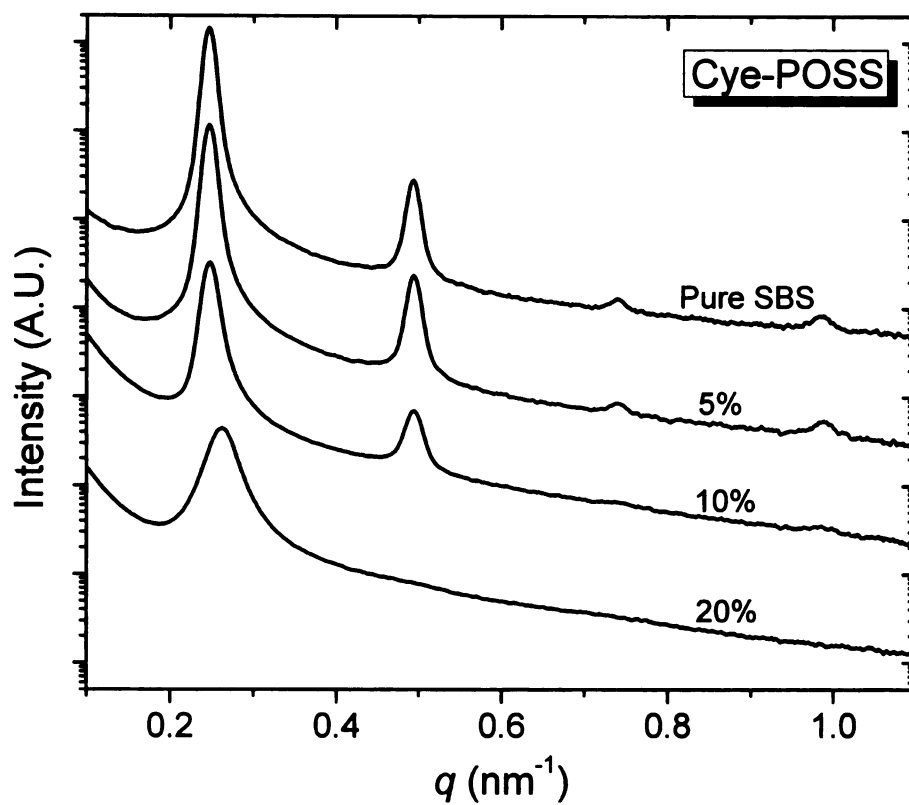


Figure 2.5. Integrated SAXS intensity versus scattering vector, q , for SBS triblock copolymers grafted with cyclohexenyl-POSS (Cye) at 130°C: SBS control with no POSS, 5 wt% POSS, 10 wt% POSS, 20 wt% POSS.

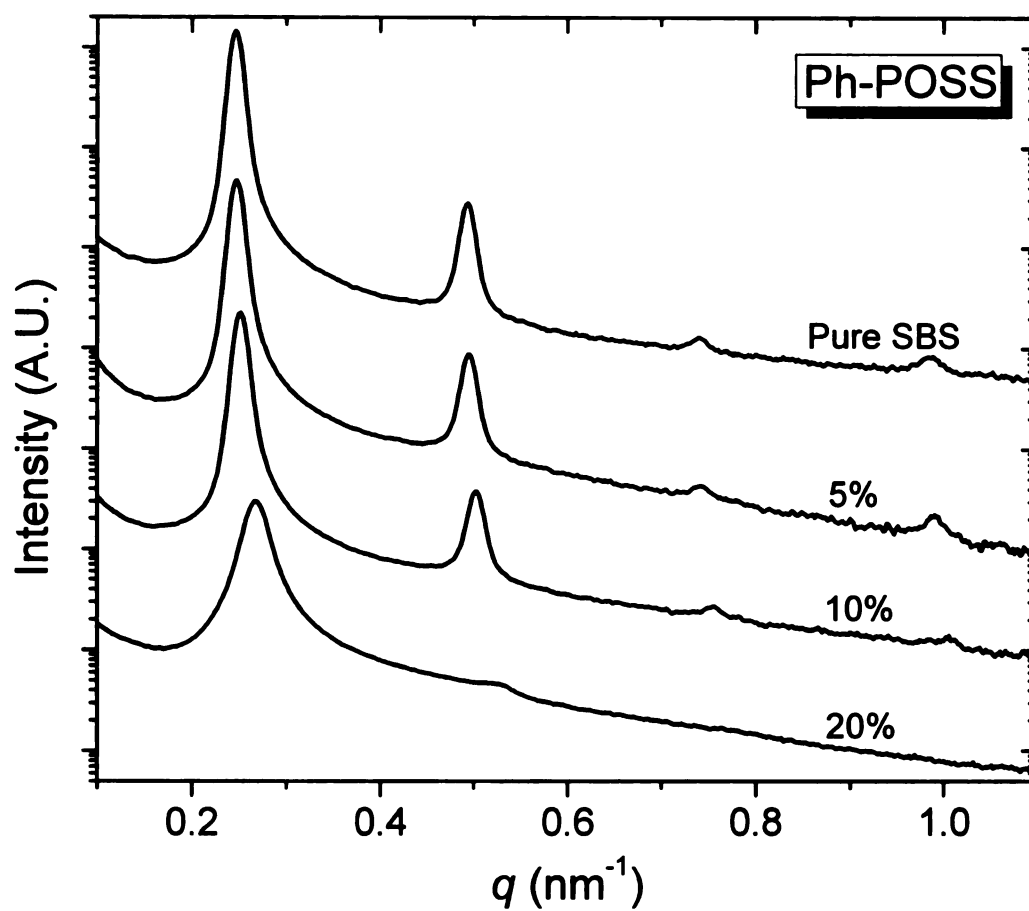


Figure 2.6. Integrated SAXS intensity versus scattering vector, q , for SBS triblock copolymers grafted with phenyl-POSS (Ph) at 130°C: SBS control with no POSS, 5 wt% POSS, 10 wt% POSS, 20 wt% POSS.

at 130°C for each POSS moiety used in this chapter. The relative locations of the peaks are determined by the morphology. The pure SBS has relative peak spacings of q^* , $2q^*$, $3q^*$, and $4q^*$, where q^* is the position of the first and most intense scattering peak, referred to as the primary diffraction peak. The observed integer spacing of the peaks is equivalent to the allowed intensities for the structure factor of a lamellar morphology which is anticipated for the 43 % polystyrene weight fraction based on other published works^{1, 5, 6, 14}. The 5% and 10 wt% POSS grafting of each moiety show little qualitative change from the pure SBS. The relative position and intensity of the higher order peaks do not change, which shows that the lamellar morphology is qualitatively unchanged. The presence and preserved intensity of the second, third, and fourth order peaks suggest that the long-range periodicity of the lamellae is maintained at these grafted POSS loadings. For samples with 20 wt% loadings the second order peak, though still present, has significantly diminished intensity, and there are no observed third or fourth order peaks. This suggests for Dexco 6241 SBS, when grafted with 20 wt% POSS of this chemistry, the basic form of the lamellar morphology exists on very short scales, but the longer range order of the lamellae has been disrupted. These changes in the SAXS profiles are similar to a perforated layer morphology^{12, 14, 26}. The addition of POSS to SBS alters the volume ratio of styrene and butadiene domains, and since the POSS is grafted to the butadiene block, POSS will act to swell the polybutadiene layers. However, the degree of selectivity may depend on the chemical substituent of POSS and its affinity toward polystyrene. Other than the order-disorder transition, no other morphological phase transitions were observed for any of the POSS-grafted SBS investigated.

The width of the primary peak for a copolymer specimen is affected by a number of factors. For undeformed materials, some of the factors that contribute to peak broadening in the lamellar morphology are: variance in lamellar thickness, a limited number of lamellae in the diffracting stacks (i.e. small domain or grain size), defects in the lamellae at the domain (grain) boundaries, curvature at the styrene-butadiene interface, and the distribution of monomeric species at the lamellae interface. Thus, the peak width can be used to quantify the relative local (or short range) order and/or defects of the morphology.

Figure 2.7 shows the peak width for each POSS moiety at 150°C as a function of POSS loading. The 5% and 10% grafted samples show only a small amount of broadening for all POSS moieties, but broadening becomes more significant when approaching 20%. At this high POSS loading, the noticeable increases in peak width can be associated with an increase in local disorder. These disrupted lamellar morphologies are similar to the qualities of a perforated layer morphology. The peak width data, coupled with the observation of high order diffraction peaks discussed earlier, suggests that grafting of up to 10 wt% of these types of POSS causes only negligible changes in the qualitative morphology as a whole. Both local ordering and long-range periodicity are maintained to a large degree. With the increased POSS grafting of 20 wt%, the morphology becomes considerably disturbed as noted by the significant peak broadening in conjunction with the reduced intensity and disappearance of higher order peaks.

Another possible factor which may contribute to the peak broadening is the alteration of the molecular weight distribution and polydispersity by grafting POSS

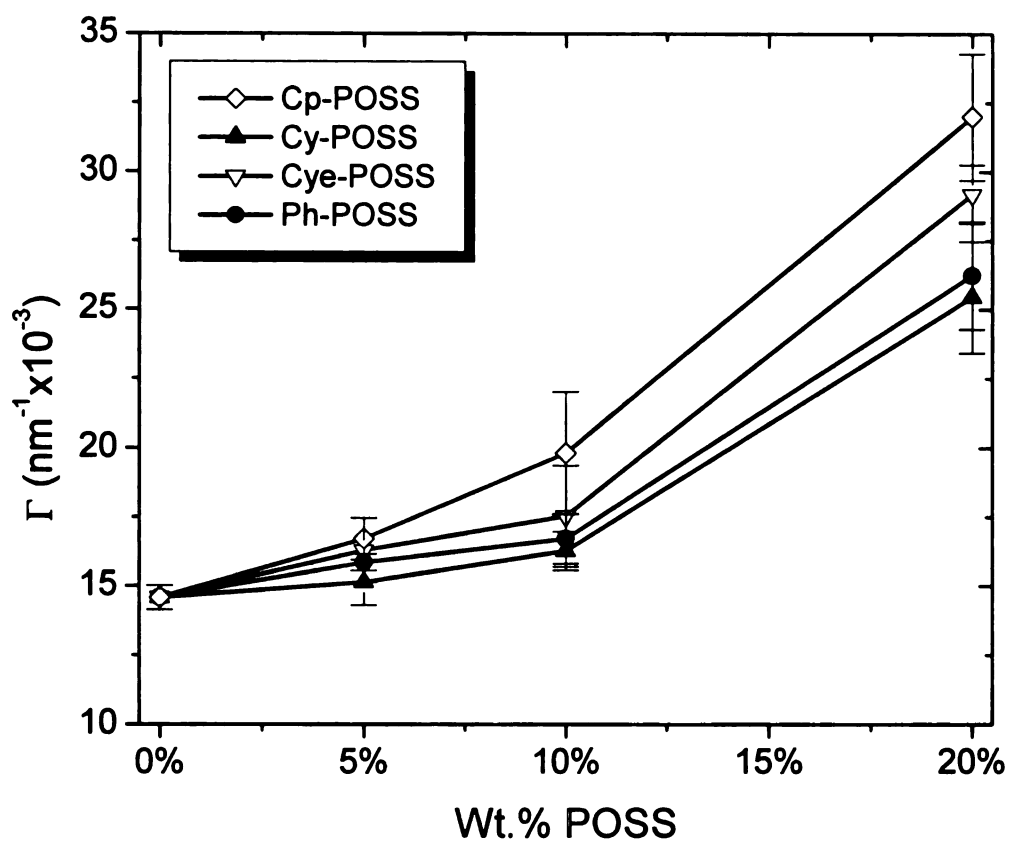


Figure 2.7. The first-order peak width at half maximum versus varying amount of POSS nanostructures with specified moiety of POSS as indicated ($\diamond$) cyclopentyl, Cp-POSS ($\blacktriangle$) cyclohexenyl, Cy-POSS (∇) cyclohexenyl, Cye-POSS ($\bullet$) phenyl, Ph-POSS.

nanostructures to a nearly monodisperse SBS triblock copolymer. Assuming the chemical attachment of POSS during the grafting reaction is random (i.e., each 1-2 polybutadiene reaction site is equally likely to undergo POSS attachment throughout the reaction), the distribution of POSS nanostructures per chain would be nearly binomial, which has a variance and thus will contribute to the overall polydispersity. This means one can expect that the grafted POSS-copolymer system will possess an increased variance and polydispersity.

To illustrate this effect, the molecular weight analyses of SBS grafted with varying amounts of phenyl-POSS (Ph) are listed in Table 2.1. The polydispersity due to the POSS attachment may account for some of the peak width and qualitative morphological changes, but it is unlikely that it accounts for the entire peak broadening. Compared to the overall SBS molecular weight, this variance is small, but nonetheless may still be a factor. One observation that supports this is the ability to form well-defined self-assembled morphologies at 10 wt% POSS grafting. In order to have this long range periodicity, the polymer must be sufficiently narrow in molecular weight. It is also assumed that Cp, Cy, Cye, and Ph-POSS are similarly affected.

The differences in peak width across POSS moiety at each grafting fraction are relatively small. In fact, other than the 20 wt% cyclopentyl (Cp) loading, all the data are within experimental error of each other. This suggests that the observed changes in the qualitative lamellar morphology may be similar for all of the POSS chemistries studied in this chapter. The small changes in peak width across POSS moiety match qualitatively with the SAXS profile comparison.

Table 2.1. GPC data for pure and Ph-POSS grafted SBS. M_w and M_n are weight average and number average molecular weights respectively (determined by GPC in units of kiloDaltons). PDI is the polydispersity index (M_w/M_n).

wt% POSS	M_w	M_n	PDI
0%	72	71	1.01
5%	76	74	1.03
10%	78	76	1.03
20%	100	93	1.08

The length of the lamellar period, the d-spacing, is inversely proportional to the position of the first order peak, q^* (Equation 2.2). Figures 2.8 and 2.9 show the d-spacing at 130°C and 150°C, respectively, for the lamellar morphology with the Cp, Cy, Cy, and Ph-POSS moieties. At both temperatures, significant POSS moiety and grafting fraction effects are observed. In general, a decrease in d-spacing with increasing amounts of POSS attachment was observed. The 5% data show the smallest decrease in d-spacing, where most of the differences are within experimental error. At 10%, the d-spacing decreases further for the Cy and Ph moieties while the Cp and Cy d-spacings remain virtually unchanged. At the highest loading of 20%, the d-spacing drop is significantly greater for all but the Cp POSS, which remains nearly unchanged. Similar analysis was performed at 150°C and the trend is similar, which is to be expected.

The d-spacing data shows the first observable differences between the types of POSS grafted. The extent of the d-spacing change is strongly influenced by the POSS substituent group chemistry. Cp-POSS has no statistical change at either temperature. Of the remaining moieties, Cy has the smallest change, Ph-POSS has the greatest change, while Cy-POSS lies in-between. In the case of the Cy, Cy, and Ph moieties, the d-spacing decreases, which results in an increased specific interfacial surface area for the morphology. This suggests a lesser degree of segregation between phase-separated domains, or decreases in the χ -parameter, for these grafted systems. The Cp-POSS samples show almost no change in d-spacing, so the specific interfacial area remains unchanged. This suggests that the Cp-POSS is strongly selective to polybutadiene in this temperature range and has little or no affinity toward the polystyrene block. For Cy-

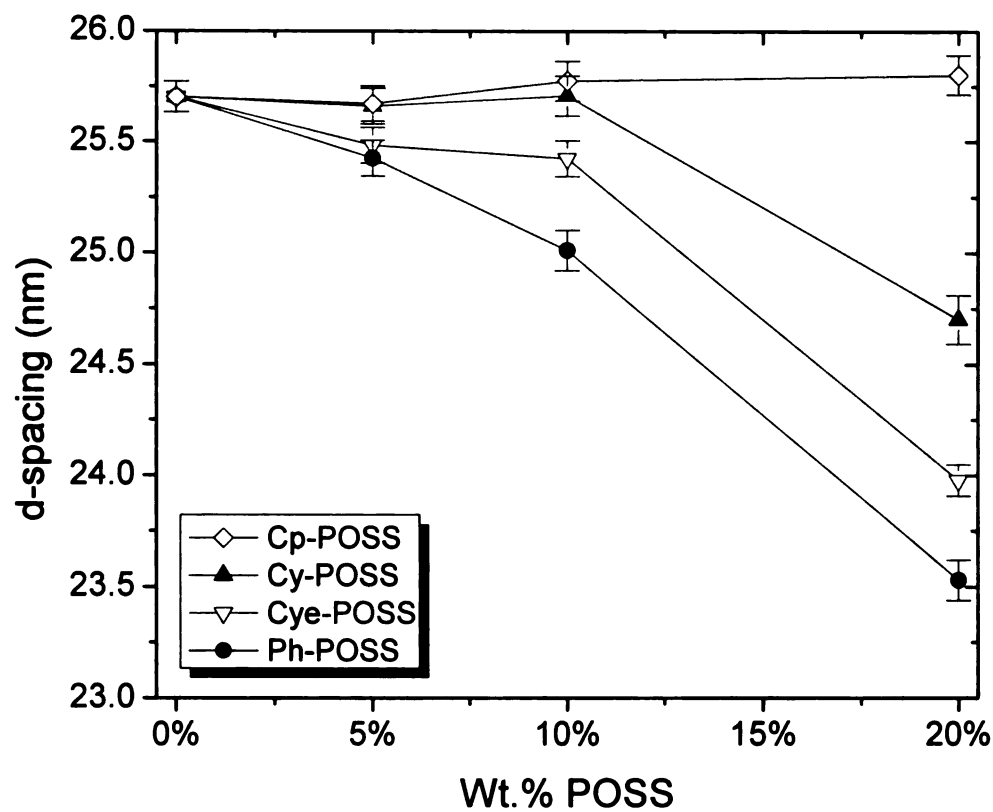


Figure 2.8. d-spacing of SBS triblock copolymer grafted with varying amounts of specified moiety of POSS at 130°C: ($\diamond$) cyclopentyl, Cp-POSS ($\blacktriangle$) cyclohexenyl, Cy-POSS (∇) cyclohexenyl, Cy-POSS ($\bullet$) phenyl, Ph-POSS.

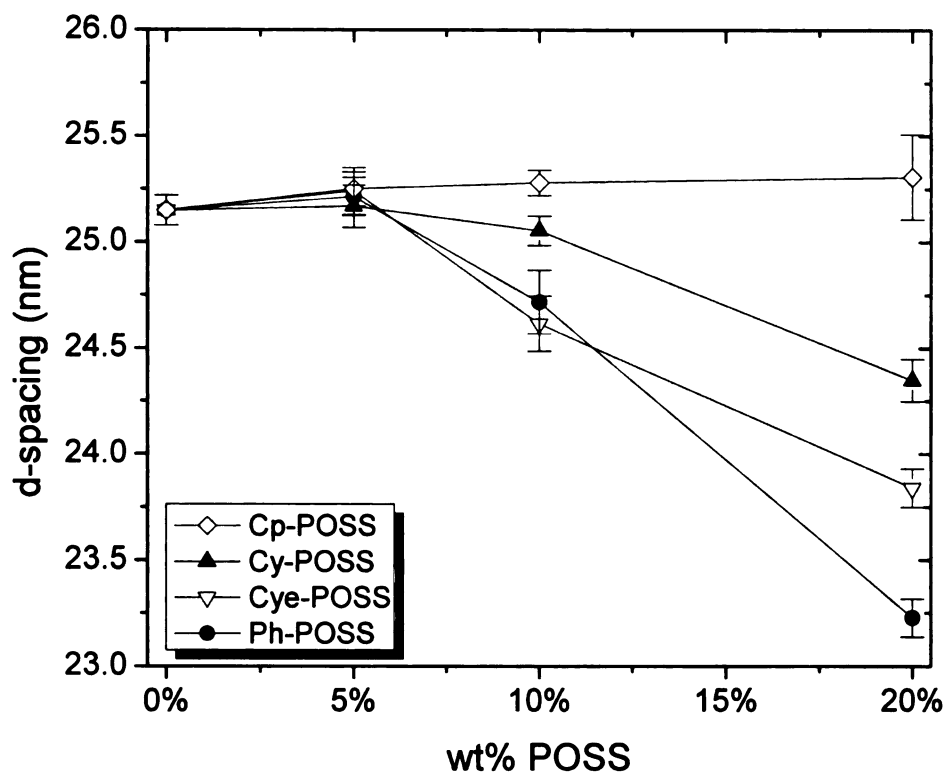


Figure 2.9. d-spacing of SBS triblock copolymer grafted with varying amounts of specified moiety of POSS at 150°C: ($\diamond$) cyclopentyl, Cp-POSS ($\blacktriangle$) cyclohexenyl, Cy-POSS (∇) cyclohexenyl, Cye-POSS ($\bullet$) phenyl, Ph-POSS.

POSS, minor changes in d-spacing are observed at 5% and 10% similar to the Cp data, but at higher loading of POSS there is a drop in d-spacing. This is attributed to a known compatibility difference between Cp-POSS and Cy-POSS with polystyrene³¹. The greater affinity of Cy-POSS toward polystyrene effectively reduces the χ -parameter, which subsequently causes a greater drop in d-spacing. For SBS grafted with Ph-POSS, the observed drop in d-spacing occurs at the lower POSS loadings. The Ph-POSS and the polystyrene repeat units of the block copolymer both possess aromatic moieties, while polybutadiene is aliphatic; this suggests that the Ph-POSS would have the greatest affinity to the polystyrene phase. The unsaturated Cy-POSS has more of a neutral chemistry, and its data lies between the Cy and Ph moieties as expected.

As stated earlier, high loading of POSS-grafted triblock copolymers have a disordered or disrupted morphology. This morphology results in a further decrease in d-spacing in addition to the compatibility argument alone. The extent of disruption is also likely affected by the chemical substituents of POSS examined.

2.3.2. Effect on the Order-Disorder Transition

Block copolymers have a limited temperature range of stability. Upon heating, entropic forces of mixing begin to overtake the entropic forces of segregation. The temperature that separates the ordered morphology from a disordered one is the order-disorder transition temperature, T_{ODT} . Figure 2.10 compares the behavior of pure SBS when it undergoes a transition from an ordered morphology to a disordered-state during heating as observed by means of both rheology and SAXS. The left axis shows the storage modulus, $G'(\omega)$, as determined from rheology and the right axis shows the peak

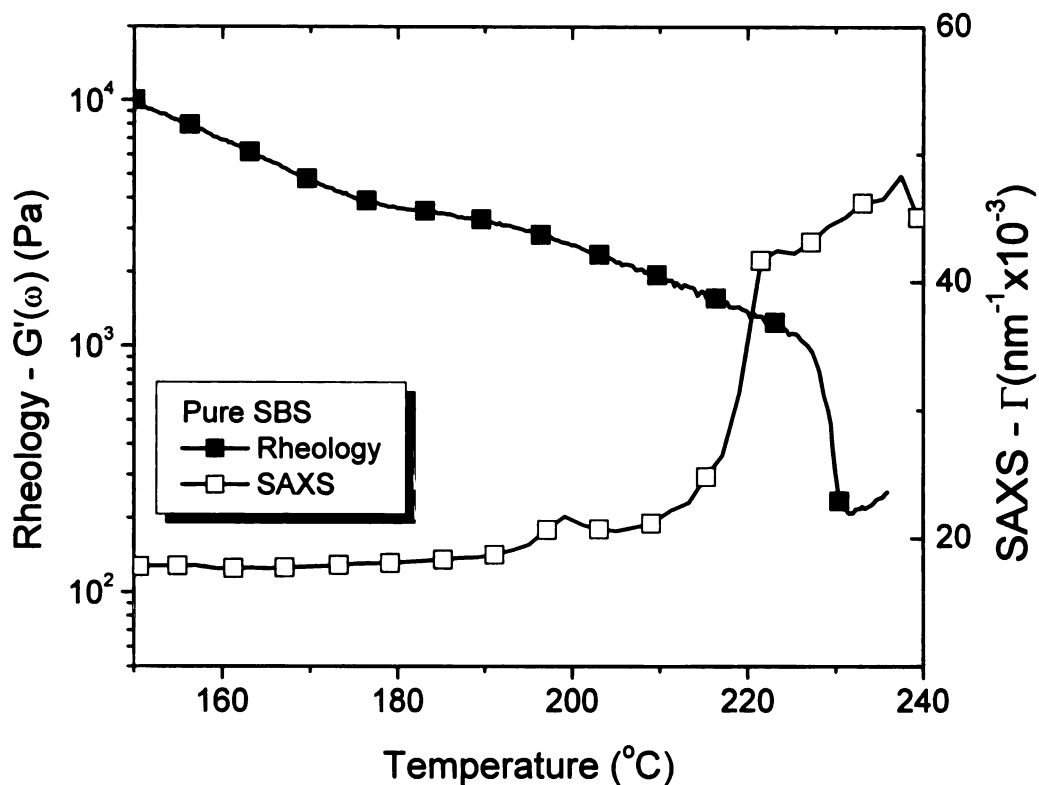


Figure 2.10. Rheological behavior as represented by the storage modulus, $G'(\omega)$ and SAXS profile as represented by the full-width at the half maximum of the first-order peak, Γ , at the order-disorder region for pure SBS.

width, Γ , as determined from SAXS; both are plotted over the same temperature range. During the rheological experiments, block copolymers exhibit a discontinuity in the plot of $\text{Log}[G'(\omega)]$ versus temperature. Here, the onset temperature of this discontinuity in $G'(\omega)$ is interpreted as T_{ODT} . In practice, T_{ODT} is a function of both frequency and temperature ramp rate, so the listed value does not coincide precisely with the equilibrium T_{ODT} ¹⁶. However, this interpretation is consistently applied throughout the pure and POSS grafted series and thus, the effect of POSS attachments on the value of T_{ODT} are all comparable. The onset point was calculated by determining the intersection of a line fitted in the ordered morphological state below the T_{ODT} , and a line fitted through the drop just after the T_{ODT} . The range of temperatures used for the fitting varied slightly based on the linearity of the two regions. The point of intersection for the two lines is largely influenced by the difference in slope of the fitted lines. Shallow or broad drops produce more uncertainty in the T_{ODT} determination. Sample-to-sample variation also contributes to T_{ODT} error and stems from morphological differences originating in sample preparation. Evaporation rates during the solvent casting process must be similar and annealing times must be long and of comparative duration to ensure reproducibility in copolymer morphology. If the solvent is evaporated too quickly or if the solvent is not completely removed during annealing, there will be noticeable changes in T_{ODT} . By performing multiple runs, sample variability was fractions of a degree for the casting/annealing scheme in place. Time sweeps were also performed at temperatures near T_{ODT} for some samples to ensure that confounding effects due to kinetics did not play a significant role in T_{ODT} determination.

In SAXS experiments concerning T_{ODT} , there are two common ways to measure T_{ODT} : the discontinuity in the plot of $1/\text{intensity}$ versus $1/T$ or the discontinuity in the plot of $1/\Gamma$ versus $1/T$ ^{1, 44, 49, 50}. For the purposes of this paper, plots of $1/\Gamma$ versus $1/T$ were used to determine the T_{ODT} from SAXS data because the discontinuities were more distinct than in plots of $1/\text{intensity}$. The T_{ODT} was interpreted as the midpoint of the $1/\Gamma$ discontinuity.

A comparison of measured T_{ODT} data for SBS grafted with varying amounts of Ph-POSS is shown in Figure 2.11. Although both rheological and SAXS measurements show the same trend of decreasing T_{ODT} with increasing POSS content, there is a disagreement in measured values. Another observation is that the rheological experiments showed less variation because they had sharper transitions and were more reproducible across multiple tests than the SAXS experiments.

Rheological determination of T_{ODT} for SBS grafted with different amounts of Cp, Cy, Cye, and Ph-POSS moieties are plotted in Figure 2.12. For all POSS loadings, there is a decrease in the T_{ODT} relative to pure SBS. At low weight fractions, the data trends are similar. At 5% grafting, there is a 4 to 7°C drop in T_{ODT} for all moieties. Increasing to 10% grafting results in a further drop in T_{ODT} for all moieties. At large weight fractions of grafted POSS, there is a change in T_{ODT} trend. The T_{ODT} for the Ph-POSS continues to decrease significantly but there is a divergence from this monotonic behavior for the Cp, Cy, and Cye moieties. This is attributed to the perforated layer-like morphology observed at high POSS loading. In this POSS-grafted SBS system, the perforated layer morphology is more thermally stable than the lamellar. Others have

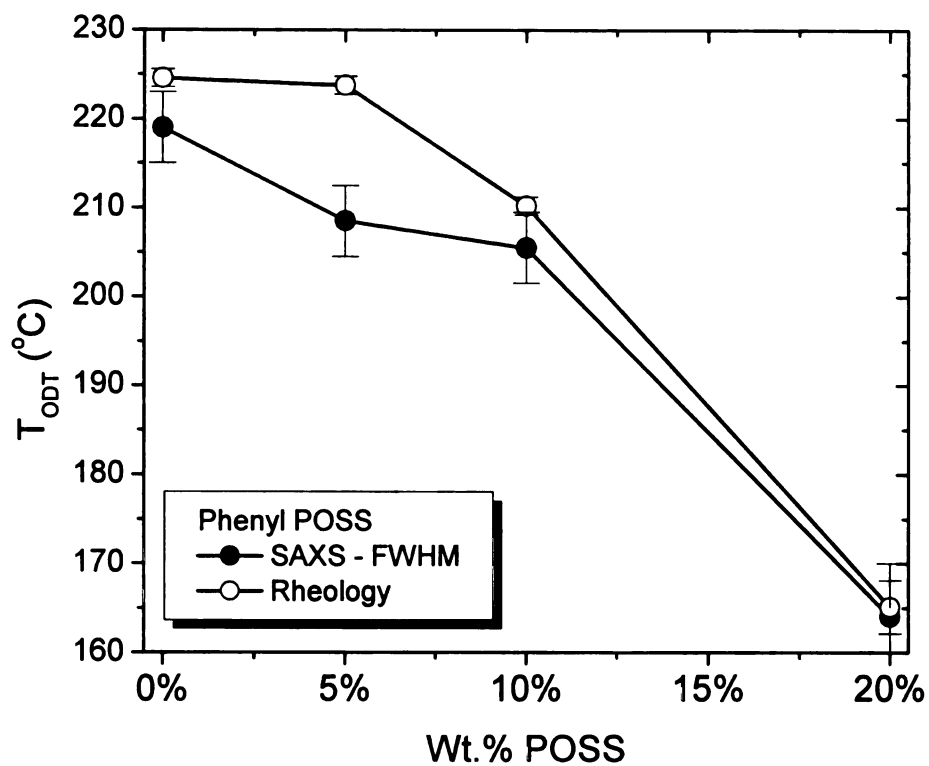


Figure 2.11. A comparison between T_{ODT} obtained from rheological and SAXS measurements for Ph moiety of POSS.

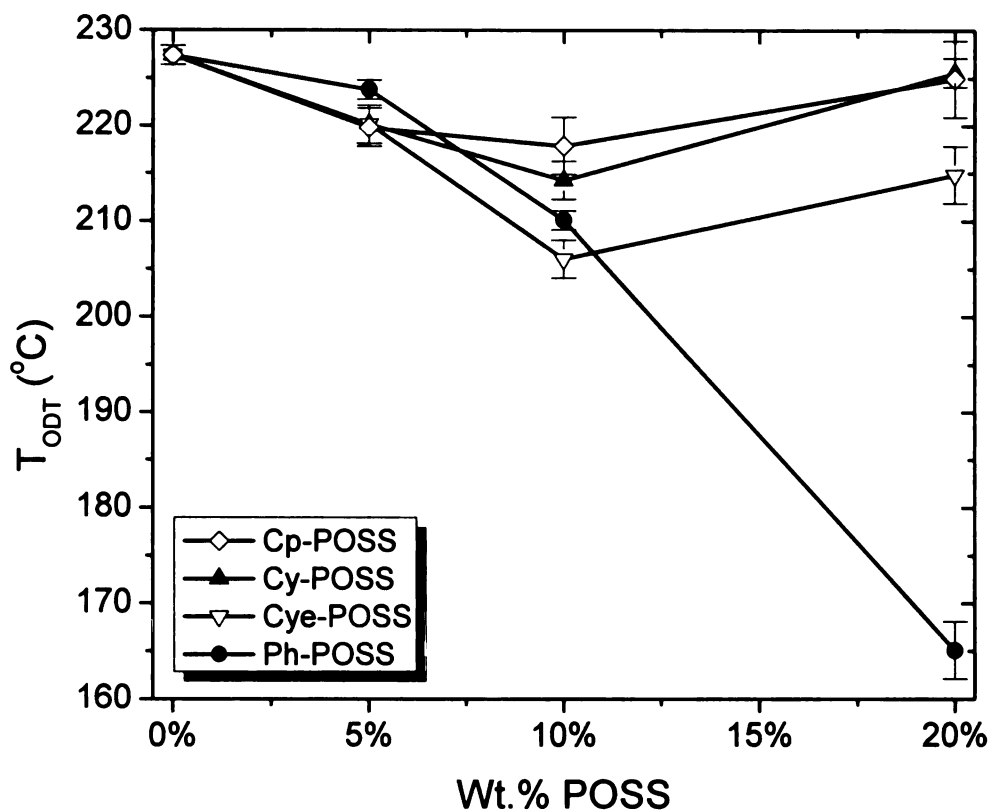


Figure 2.12. T_{ODT} of varying amounts of different moieties of POSS as determined using rheological measurement. ($\diamond$) cyclopentyl, Cp-POSS ($\blacktriangle$) cyclohexenyl, Cy-POSS (∇) cyclohexenyl, Cye-POSS ($\bullet$) phenyl, Ph-POSS.

made similar observations in different block copolymer systems where $T_{ODT, PL} > T_{ODT, L}$ ^{12, 14, 16, 26}. The T_{ODT} for Ph-POSS continues to decrease for 20 wt% grafting, contrasting the other types of POSS. Unlike the other moieties, the Ph-POSS has a much stronger affinity toward the styrene block. This was seen in the d-spacing of Figures 2.8 and 2.9, so it is likely to lead to different phase behavior than the other moieties. In another word, the decrease in χ -parameter overcomes the contribution attributed to the perforated layer morphology.

2.3.3. Effect on the Rheology

In the discussion of rheology to follow, a comparison is made for only Cy, Cye and Ph-POSS grafted SBS because they have the same number of carbon atoms in similar stereochemistry for each POSS attachment, which reduces confounding effects due to size and molecular weight. Thus, observed differences can generally be attributed to chemistry differences in the POSS nanostructures. Figure 2.13 shows the rheological data for the pure and 10% POSS grafted copolymers. For the temperature ranges examined, the Ph-POSS has nearly the same storage modulus as the pure SBS while the Cy and Cye moieties show a higher value for the temperature dependent storage modulus. The observed increase in storage modulus at low frequencies suggests that the POSS acts as reinforcement for the polybutadiene in the system. Exactly how the POSS nanostructures contribute is uncertain. For instance, there could be contributions to reinforcement deriving from POSS-polymer effects, POSS-POSS effects, or even from a change in morphology as a result of POSS grafting. The amplified modulus observed for the Cy and Cye moieties appears to be retained through the T_{ODT} explaining the

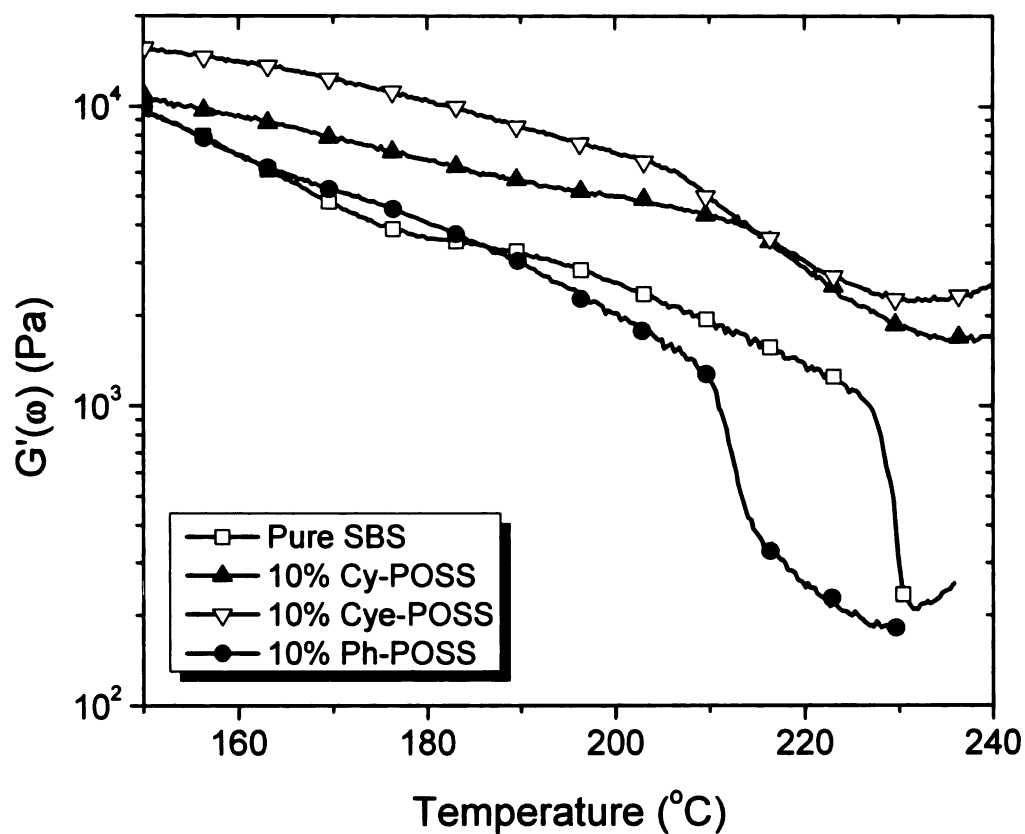


Figure 2.13. Storage modulus, $G'(\omega)$, as a function of temperature at 1 radian per second for pure and 10 wt% of POSS with specified moiety as indicated. ($\square$) pure SBS ($\blacktriangle$) cyclohexenyl, Cy, POSS (∇) cyclohexenyl, Cye, POSS ($\bullet$) phenyl, Ph, POSS.

diminished drop in modulus after the onset of order-disorder transition. The reinforced disordered state would hint that the reinforcement has less to do with the morphology and more to do with POSS-POSS effects. The relatively large POSS-POSS reinforcement may arise from the neutrality of the chemistry. Cy and Cye-POSS do not have an affinity toward either polybutadiene or polystyrene and may be more thermodynamically stable agglomerating or forming crystallites. Though no crystalline POSS was observed by x-ray diffraction at room temperature for these specimens, the behavior of POSS in the copolymers at high temperatures is uncertain. The 10% Ph-POSS does not show a modulus increase. This is almost certainly because the Ph moiety has a high affinity towards polystyrene segments, which in effect plasticizes the SBS copolymer.

The rheological data for the 20% SBS-POSS copolymers is shown in Figure 2.14. The T_{ODT} for the Cy and Cye moieties increases relative to the 10% due to the morphology change. Again, there is an observed increase in modulus for Cy and Cye that may be due to POSS reinforcement. Never the less, the reinforcement is greater and the drop in modulus is clearer. Both observations support a change to a perforated morphology. Other copolymers have noted an increase in the modulus on the order-order transition from a lamellar to a perforated layer morphology^{12, 14, 26}.

The T_{ODT} of the 20 wt% Ph-POSS does not increase like that of Cp, Cy, and Cye moieties, however the temperature range of the order-disorder transition as measured by rheology becomes broader. Figure 2.15 depicts the rheological and SAXS data for 20 wt% Ph-POSS through the order-disorder transition on the same plot. Though the rheological transition is broad (spanning nearly 50°C), the SAXS transition is narrower

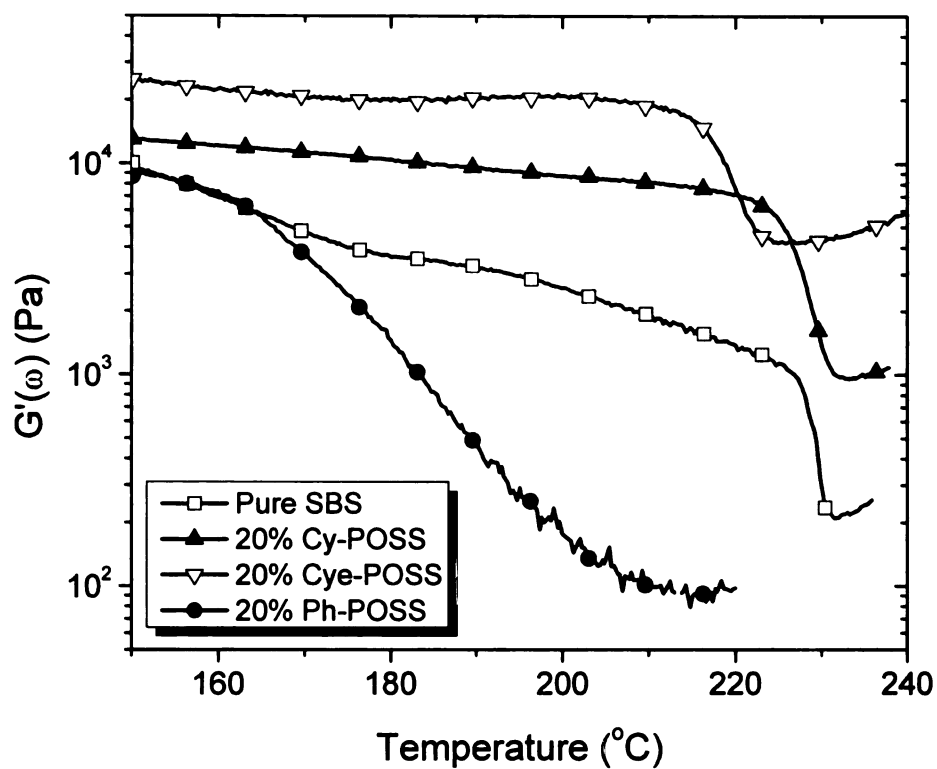


Figure 2.14. Storage modulus, $G'(\omega)$, as a function of temperature at 1 radian per second for pure and 20 wt% POSS with specified POSS moiety as indicated. ($\square$) pure SBS ($\blacktriangle$) cyclohexenyl, Cy, POSS (∇) cyclohexenyl, Cye, POSS ($\bullet$) phenyl, Ph, POSS.

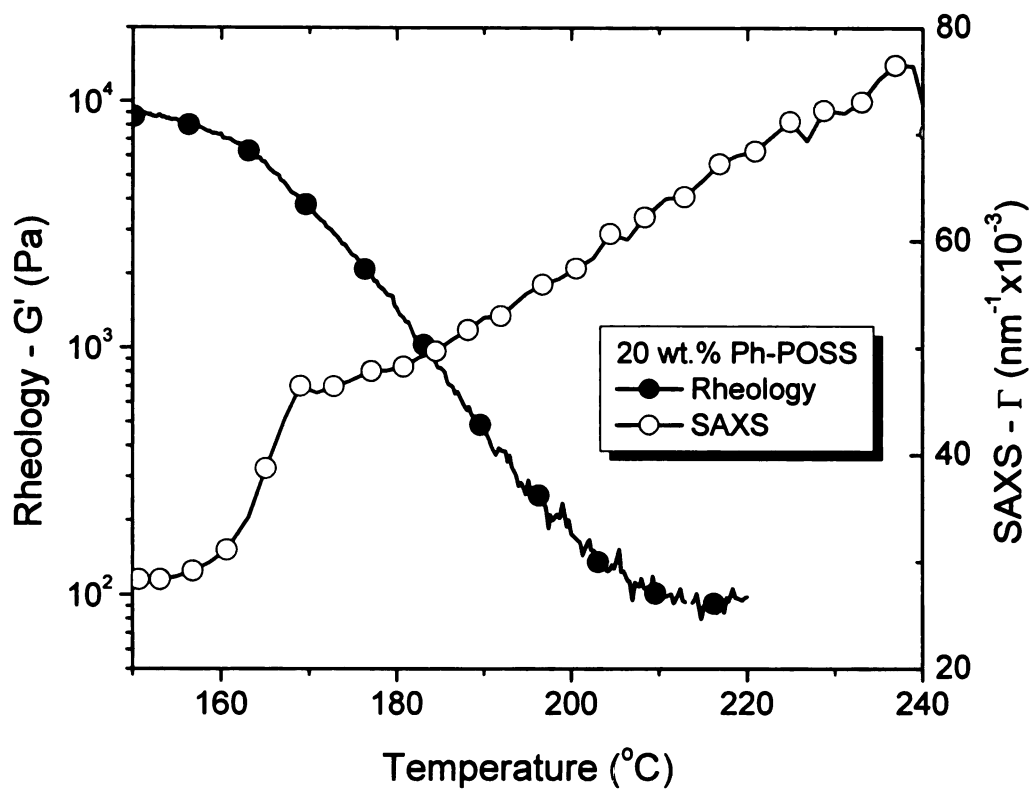


Figure 2.15. Data for computing rheological and SAXS T_{ODT} for 20 wt% Ph-POSS

(about 10°C). In each case, the respective transitions are broader than that of the pure SBS. This transition broadening, though magnified in this case, is observed in the other grafted systems. This broadening of the order-disorder transition may be due to some changes in the kinetics as affected by the POSS attachment, the change to perforated layer morphology, or there may be a variance to the SBS phases caused by an increase in polydispersity /complex phase behavior.

2.4. CONCLUSIONS

Using rheology and X-ray scattering, the effect of grafting four sterically similar, yet electronically different POSS derivatives onto the polybutadiene phase of a lamellar SBS triblock has been investigated. It is concluded that the POSS derivatives affect the SBS by changing the effective ratio of styrene to butadiene and by altering the styrene-butadiene segregation. Order-disorder transition temperature and d-spacing data show clear trends that follow POSS nanostructure chemistry: Ph > Cy_e > Cy > Cp. Here, grafting Ph-POSS results in greater changes when compared to the ungrafted SBS block copolymer. The reason being that the phenyl chemistry has the largest contrast to the block in which it is grafted (polybutadiene) while simultaneously having the largest affinity toward the ungrafted block (polystyrene). Cp-POSS has the smallest effect after grafting because it is most similar to the block in which it is grafted while simultaneously having the smallest affinity toward the ungrafted block.

All of the POSS grafted in this study resulted in a more disordered or disrupted morphology. This suggests that all of these POSS chemistries have at least some affinity toward the polystyrene phase. The POSS with phenyl moiety shows interesting behavior, as it is grafted to the polybutadiene phase and appears to be strongly interacting well with

the polystyrene phase. This causes a decrease in the lamellae d-spacing and also causes a drop in the order-disorder transition temperature due to an effect whereby the Ph-POSS is solvated by the polystyrene phase. The partly-unsaturated Cy-POSS shows a somewhat lessened attraction to the polystyrene phase, which in turn is greater than that exhibited by completely unsaturated Cy or Cp-POSS. At 20 wt% POSS grafting, SAXS and rheology have revealed that there is a change to a perforated layer morphology for the Cp, Cy, and Cy-POSS. For 20 wt% Ph-POSS, a perforated morphology is not present, but the lamellar morphology is disrupted. Complicated POSS-POSS effects convoluted with changes in morphology result in a greater dynamic storage modulus, G' , for these POSS.

CHAPTER 3.

PHASE BEHAVIOR OF POSS-GRADED SBS WITH NONINTERACTING OR INTERACTING POSS NANOSTRUCTURES

3.1. INTRODUCTION

Block copolymers have most recently received interest for uses in nanotechnology. The main focus of their nanotechnology application is rooted in the ability to form self-assembled microstructures on the nanometer scale, which has lead to applications in membranes, templates for nanoparticle synthesis, photonic crystals, high-density information storage media, and beyond.^{6, 7} 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.^{8, 41} Hence, it is critical to a gain better understanding of how the surface chemistry of nanoparticles can influence the morphology of block copolymers. To accomplish this, it is advantageous to eliminate complications of phase separation and mixing interactions between particles and polymer components. Thus, the task may be simplified by confining the nanostructures to a particular domain of the block copolymer by grafting nanostructured chemicals to a specific copolymer block^{38, 39}. The preceding chapter reported that the surface chemistry of the grafted nanostructures has profound effects on the host block copolymer morphology.³⁸ More specifically, polyhedral oligomeric silsesquioxane (POSS) was used as a model nanostructured chemical and was grafted to the polybutadiene midblock of a symmetric SBS copolymer. 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 the 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 nanostructures were grafted to the butadiene, it was concluded that those POSS moieties investigated favor polystyrene more than polybutadiene. This affinity to the styrene phase leads to a competition between entropic and enthalpic forces: the POSS enthalpically favors the polystyrene phase while disfavoring the polybutadiene phase in which it is grafted and the POSS entropically favors the polybutadiene phase. This results in a deterioration of the well-segregated interface which in turn affects the order of the morphology. With the addition of these *interacting* POSS nanostructures, there is a change from a lamellar to a perforated layer or disrupted morphology as the amount of POSS grafting increases and the level of perforation and stability of this morphology depends on the degree of POSS-polystyrene compatibility.

These results, although interesting, do not take full advantage of the self-assembled microstructure. The motivation for this next work is to create a model system in which nanostructures are confined and dispersed within a single domain of a block copolymer. This model system can then be utilized to explore particle-particle and particle-polymer interaction energies, and it can be extended to aid in the design of nanocomposite materials. In order to confine the nanostructures within the grafted domain and maintain a well-segregated morphology, it is necessary to remove the enthalpic interactions which lead to deterioration of the interface. To accomplish this, the

surface chemistry of the nanostructure must be selected so it is enthalpically favorable to the domain in which it is grafted and unfavorable to the other block. Isobutyl (iBu) was selected because it has an aliphatic chemistry similar to polybutadiene, which contrasts with the aromatic polystyrene. The new iBu-POSS copolymers will be contrasted with a new batch of Ph-POSS copolymers. The chemical reaction scheme was slightly altered from the previous batch to obtain a more random Ph-POSS attachment⁵⁸. This study also differs from the previous electronic effect study in that the iBu-POSS has does not have the same stereochemistry or molecular weight as the Ph-POSS, but the main focus is its noninteracting nature.

In the following sections, an attempt is made to probe the particle-polymer interaction energies and present results for the morphological changes in SBS grafted with iBu-POSS 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, morphological transitions and their transition temperatures as a function of POSS content is reported.

3.2. EXPERIMENTAL

3.2.1. Materials

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 3.1.

POSS grafting was accomplished via a hydrosilation reaction in toluene. The procedures used to synthesize the iBu-POSS hydride and the conditions used for grafting to 1,2-butadiene were identical to some of our published work.³⁸ 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.

3.2.2. X-ray Scattering

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

Table 3.1. Comparison of Host SBS. M_n and M_w are number-average and weight-average molecular weights, respectively (determined by GPC in units of kiloDaltons). 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.

Material	M_w	M_n	PDI	Polystyrene	Self-Assembled	Series Name
				Content	Morphology	
Vector [®] 8508	62	59	1.05	29 wt.%	cylindrical	C-series
Vector [®] 6241	72	71	1.02	43 wt.%	lamellar	L-series

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.

Wide-angle X-ray scattering (WAXS) was performed to observe whether there was any POSS crystal structure. To observe this crystal structure, a camera distance of 0.549 meters and a wavelength of 0.6199 Å were used to access a larger q -range. This allowed for investigation from 0.6nm^{-1} to 16.6nm^{-1} (0.38nm to 10.5nm d-spacing), which is within the diffraction range of POSS crystalline diffraction. Data was collected at 30°C using 5 second exposures for the undeformed specimens. Deformation was also performed at this camera length and temperature using 1 second exposures.

3.2.3. Rheology

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 N₂ 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 SBS-POSS grafted series, and thus the effects of POSS attachments on the transition temperatures are comparable.

3.3. RESULTS AND DISCUSSION

The first portion of this section will examine the effects of grafting iBu-POSS and Ph-POSS on the equilibrium morphology of SBS: the long-range and local order, and the d-spacing. Comparisons are in the melt state at 130°C to ensure equilibrium morphology and well below the T_{ODT} . The latter portion, the Morphology Transitions section, will focus the effects on T_{OOT} and T_{ODT} , which will tie in to theories presented in the Equilibrium Morphology section.

3.3.1. Equilibrium Morphology

Figures 3.1, 3.2, 3.3, and 3.4 show the one-dimensional scattering profiles for all SBS-POSS copolymers investigated as measured by SAXS at 130°C. Intensity is plotted

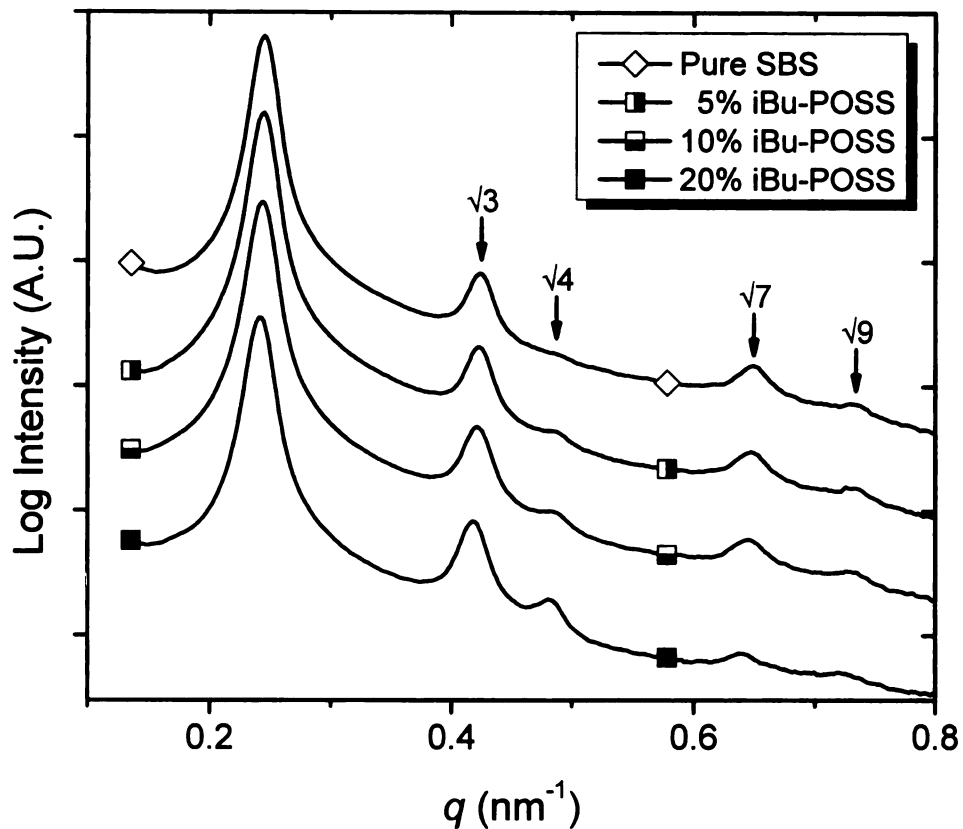


Figure 3.1. Intensity vs. scattering vector, q , at 130°C for C-series SBS (Vector[®] 8508) grafted with isobutyl-POSS (iBu). At this temperature, the pure C-series and iBu-POSS grafted copolymers have a cylindrical morphology. The 2-D SAXS images were integrated 360° azimuthally to obtain the profiles plotted in this figure, and the data are shifted along the log intensity axis to increase clarity (5% -0.7, 10% -1.4, 20% -2.1).

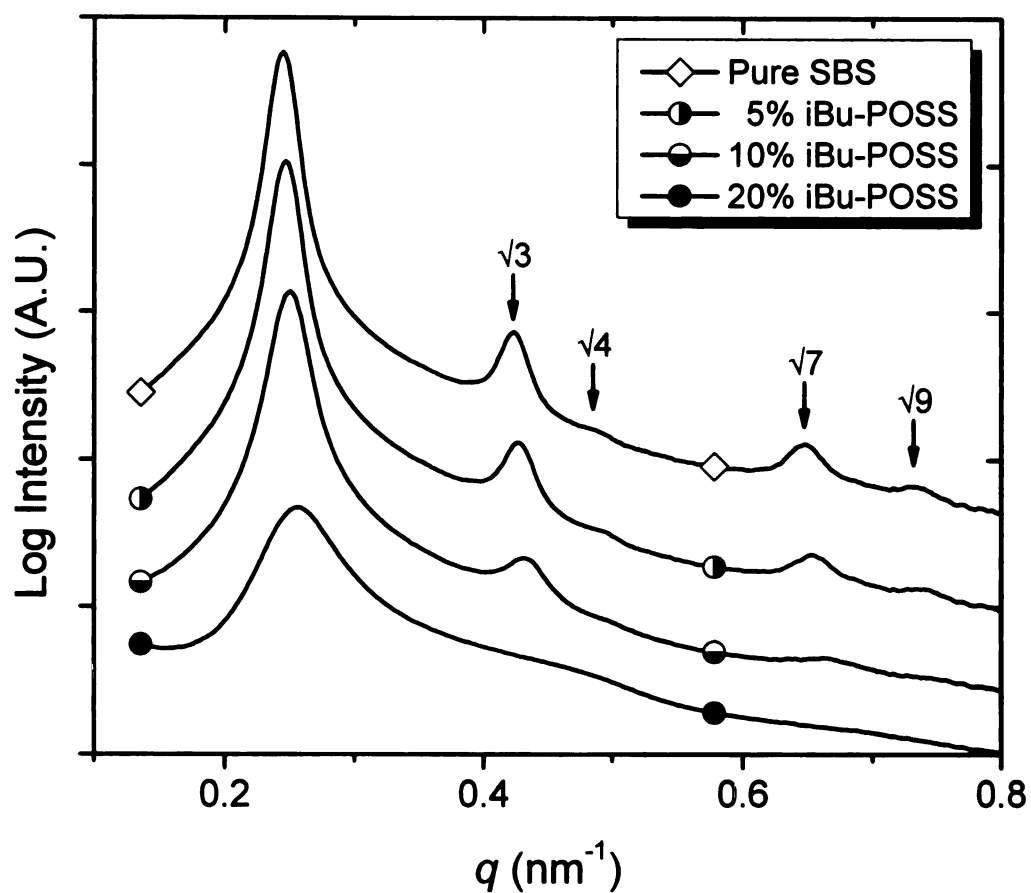


Figure 3.2. Intensity vs. scattering vector, q , at 130°C for C-series SBS (Vector® 8508) grafted with phenyl-POSS (Ph). At this temperature, the pure C-series and Ph-POSS grafted copolymers have a cylindrical morphology. The 2-D SAXS images were integrated 360° azimuthally to obtain the profiles plotted in this figure, and the data are shifted along the log intensity axis to increase clarity (5% -0.7, 10% -1.4, 20% -2.1).

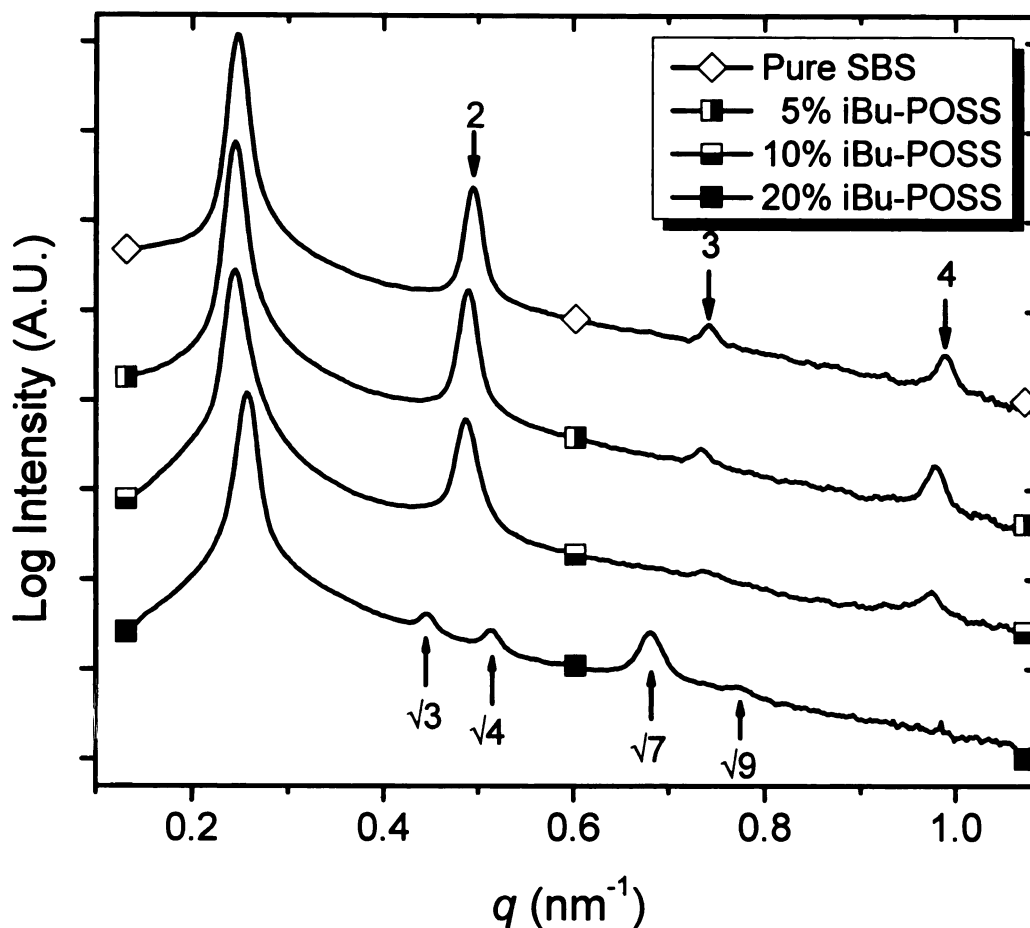


Figure 3.3. Intensity vs. scattering vector, q , at 130°C for L-series SBS (Vector® 6241) grafted with isobutyl-POSS (iBu). At this temperature, the pure L-series along with the 5% and 10% iBu-POSS grafted copolymers have a lamellar morphology, but the 20% iBu-POSS copolymer has a cylindrical morphology noted by the change in structure factor. The 2-D SAXS images were integrated 360° azimuthally to obtain the profiles plotted in this figure, and the data are shifted along the log intensity axis to increase clarity (5% -1.3, 10% -2.6, 20% -3.9).

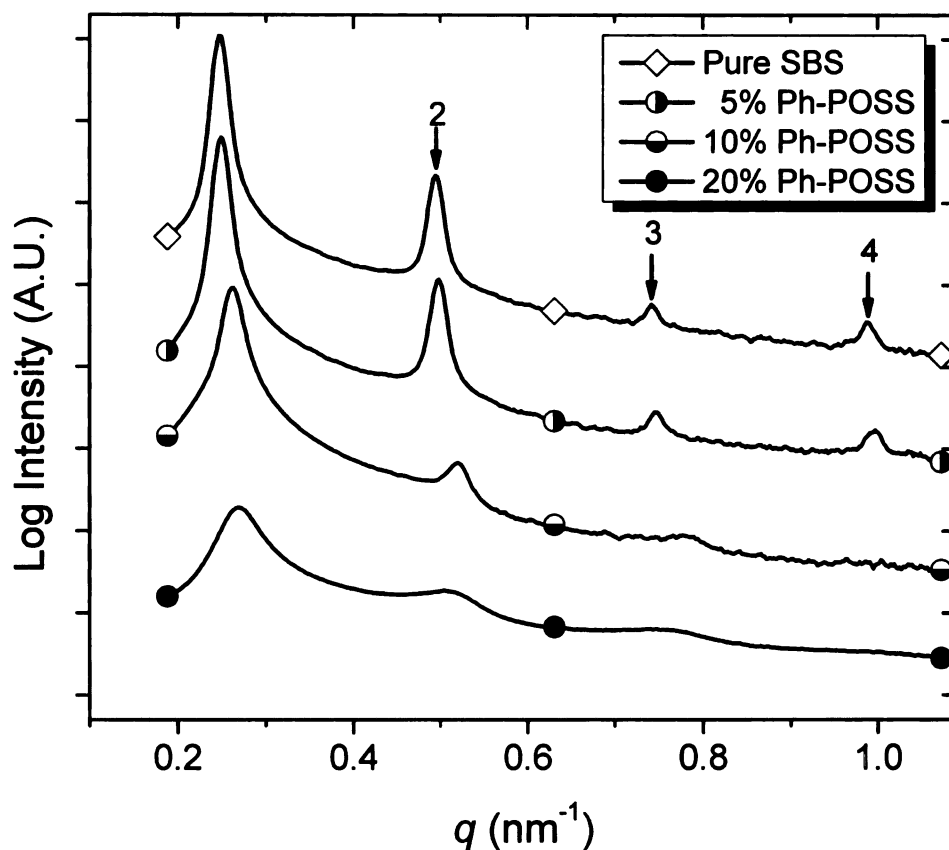


Figure 3.4. Intensity vs. scattering vector, q , at 130°C for L-series SBS (Vector[®] 6241) grafted with phenyl-POSS (Ph). At this temperature, the pure L-series and Ph-POSS grafted copolymers have a lamellar morphology. The 2-D SAXS images were integrated 360° azimuthally to obtain the profiles plotted in this figure, and the data are shifted along the log intensity axis to increase clarity (5% -1.3, 10% -2.6, 20% -4.6).

vs. the magnitude of the scattering vector q . The C-series, which has a cylindrical morphology for the ungrafted SBS, is shown in Figures 3.1 and 3.2 for iBu and Ph-POSS respectively. The scattering patterns of the C-series grafted with iBu-POSS show little difference from the unmodified SBS. The peak positions are consistent with the allowed intensities for the structure factor of a hexagonally packed cylindrical morphology ($1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}\dots$). 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.

The SAXS profiles in Figure 3.2 are for the C-series grafted with Ph-POSS series. Like the iBu-POSS grafts in Figure 3.1, the relative peak positions are consistent with the allowed intensities for the structure factor of a cylindrical morphology. Unlike the iBu-POSS, the cylindrical morphology becomes disrupted with increased Ph-POSS grafting. The difference in scattering profiles from the iBu-POSS shows that there is a difference in how the Ph-POSS interacts with the block components. The Ph-POSS series shows noticeable peak broadening and diminished diffraction intensity. The SAXS pattern for the 5% Ph-POSS graft shows little qualitative change from the pure SBS. The relative position and intensity of the higher order peaks do not change signifying the cylindrical morphology is well-preserved. For the 10% Ph-POSS, the diffraction intensity is relatively unchanged for the first diffraction peak, but the higher order diffraction peaks are visibly less than the pure and 5 wt%. The 20 wt% Ph-POSS grafted SBS shows a

sizeable decline in diffraction intensity along with substantial peak broadening. A cylindrical morphology is barely discernable and is qualitatively different than that observed in the pure SBS.

Scattering profiles of the L-series, which have varying amounts of iBu-POSS grafted on Vector[®] 6241, are shown in Figure 3.3. The relative peak positions for the pure, 5%, and 10% are consistent with the allowed intensities for the structure factor of 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. This change in Vector[®] 6241 morphology after grafting can be attributed simply to changes in the overall polystyrene content. 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. This reduction in polystyrene content is large enough to change the morphology from lamellar to cylindrical. 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.^{17, 19, 43} In this case, the iBu-POSS is akin to the solvent molecules that are selective only to the polybutadiene domain. This is a reasonable comparison 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 SBS-POSS 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.^{17, 19} This lyotropic phase transition does not occur for the C-series. The reason for this is because 43 wt% PS is closer to the lamellar-cylindrical boundary on the χN vs. f phase diagram than the 29 wt% PS is to the cylindrical-sphere boundary.

The SAXS profiles in Figure 3.4 are for the Ph-POSS series. The relative peak positions are consistent with the allowed intensities for the structure factor of a lamellar morphology. Unlike the iBu-POSS, the lamellar morphology is present for all the SBS-POSS copolymers. Again, this difference in phase behavior from the iBu-POSS shows that there is a difference in how the Ph-POSS interacts with the block components. Instead of a shift in phase behavior, the Ph-POSS series show noticeable peak broadening and diminished diffraction intensity. The SAXS pattern for the 5% Ph-POSS graft shows little qualitative change from the pure SBS. The relative position and intensity of the higher order peaks do not change signifying the lamellar morphology is well-preserved. For the 10% Ph-POSS, the diffraction intensity is visibly less than the pure and 5 wt%. The 20 wt% Ph-POSS grafted SBS shows a further decline in diffraction intensity along with substantial peak broadening; despite these observations, the 3rd and 4th order diffraction peaks are still discernible. Thus, a lamellar morphology is still present, but it is qualitatively different than that observed in the pure SBS.

The hypothesized noninteracting nature of iBu-POSS with the polystyrene domain can be further supported by revisiting the scattering data. The total scattering in Figures 3.1 and 3.2 has contributions from interparticle and intraparticle interferences, which are often referred to as lattice and particle scattering, respectively. Lattice

scattering determines the structure factor, while the particle scattering exhibits constructive and destructive interference depending on the size and shape of the particle. The diffraction peak disappears when its angular position coincides with that of the destructive interference of the particle scattering. Thus, some changes in relative diffraction intensity can be explained by a shift in the scattering form factor minimum, which again is related to the size of the particles contributing to scattering. In the case of the C-series, the polystyrene cylinders, or rods, contribute to the particle scattering. The particle dimension of interest is the cylinder radius^{59, 60}. The cylinder radius is related to the volume fraction of polystyrene, f_{PS} , which changes as a result of grafting as stated previously. For the L-series, the thickness of the polystyrene domains contributes to the particle scattering^{59, 61-63}. The relative thickness of the polystyrene layer thickness to that of the lamellae repeat distance is related to f_{PS} . The calculations used to derive f_{PS} and the form factor minima can be found in the Appendix, and the values of the first two form factor minima normalized to the primary scattering peak position are displayed in Table 3.2 for both the C-series and L-series. The form factor minimum, q_m , is divided by the primary scattering peak position, q^* , to obtain q_m/q^* so it can be related directly to the structure factor.

As mentioned previously for the C-series grafted with iBu-POSS in Figure 3.1, there is a change in the relative intensity for the 3rd relative-diffraction peak at position $\sqrt{4}q^*$, where q^* is the position of the primary diffraction peak. This peak is nearly unnoticeable in the unmodified SBS but steadily grows with increased iBu-POSS grafting. For the pure C-series SBS, the first form factor minimum, q_{m1} , is approximately

Table 3.2. Form Factor Minima for SBS-POSS Copolymers. The entire C-series and 20% L-series were calculated using the cylindrical form factor. The lamellar form factor was used for the 0%, 5%, and 10% L-series. q_{m1} and q_{m2} are the first and second form factor minima respectively. q^* is the position of the primary diffraction peak.

	wt% POSS	f_{PS}	q_{m1}/q^*	q_{m2}/q^*
Vector® 8508	0%	25.6%	1.99	3.64
C-series	5%	24.9%	2.02	3.69
	10%	24.2%	2.05	3.75
	20%	22.6%	2.12	3.88
Vector® 6241	0%	38.9%	2.57	5.14
L-series	5%	37.8%	2.65	5.29
	10%	36.6%	2.73	5.46
	20%	34.2%	1.72	3.15

1.99 and nearly coincides with the $\sqrt{4}q^*$ peak. This explains the nearly absent scattering peak. Grafting 5%, 10%, and 20% POSS reduces the volume fraction. Consequently, the form factor minimum is shifted to higher q , toward the value of 2.18 for 20% C-series, and away from the $\sqrt{4}q^*$ peak. The second form factor minimum, q_{m2} , is outside the range of interest for the C-series in this discussion.

By examining the L-series grafted with iBu-POSS in Figure 3.3, one observes a similar shift in the form factor. Here, the $3q^*$ peak decreases in relative intensity for the 5% and is nearly indistinguishable for the 10%, while the $4q^*$ peak is still present for both systems. The data in Table 3.2 show that the first form factor minimum increases from 2.57 for the unmodified SBS to 2.81 for the 10 wt% L-series. The diminishing $3q^*$ peak corresponds to a shift in form factor minimum toward $3q^*$. The 20% L-series grafted with iBu-POSS has a cylindrical morphology, so its form factor minima calculations show a discontinuity from the rest of the L-series. For this cylindrical morphology, the first minimum in the form factor is at $1.77 q/q^*$. This value is between the $\sqrt{3}q^*$ and $\sqrt{4}q^*$ peaks and clarifies the relative peak intensity difference when compared to the C-series. The second form factor minimum is at 3.24, near the $\sqrt{9}q^*$ peak, and can also be related to relative peak intensity differences compared to the C-series. The form factor observations are consistent with iBu-POSS confinement in the polybutadiene domain. This supports the theory that the iBu-POSS are confined within the polybutadiene domain and are not interacting with polystyrene.

The form factor minimum is derived from the volume fraction of polystyrene, so it should be the same for both iBu-POSS and Ph-POSS at each grafting fraction. However, the C-series Ph-POSS of Figure 3.3 do not follow the same form factor trends

of the iBu-POSS. This is because the Ph-POSS are interacting with the polystyrene phase. Instead of simply reducing the polystyrene content, Ph-POSS penetrate the polystyrene phase resulting in a reduced monomeric segregation at the polystyrene-polybutadiene interface. This will be discussed in further detail later. Thus, complete selectivity is lost and the phase shift theory does not apply. For the L-series grafted with Ph-POSS, as with the C-series, the morphology changes do not follow a simple shift in phase behavior.

The lattice spacing, or d-spacing, is calculated from the primary diffraction peak position (Equation 2.2) for both series of iBu-POSS grafted SBS are shown in Figure 3.5. In order to facilitate a comparison between morphologies, the measured d-spacing of SBS-POSS copolymers were normalized to the unmodified SBS. For iBu-POSS, the C-series shows a small, but measurable, amount of systematic increase in d-spacing was observed as the amount of grafted POSS increases. The d-spacing for block copolymers depends on a number of factors including the degree of polymerization, N , and monomeric segregation, χ . In this system of SBS grafted with POSS, the degree of polymerization does not change, but the overall molecular weight of the macromolecules does. The iBu-POSS is grafted to the polybutadiene block 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. This results in a more expanded chain conformation for the polybutadiene, 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 monomeric segregation can also affect d-spacing which may be altered by

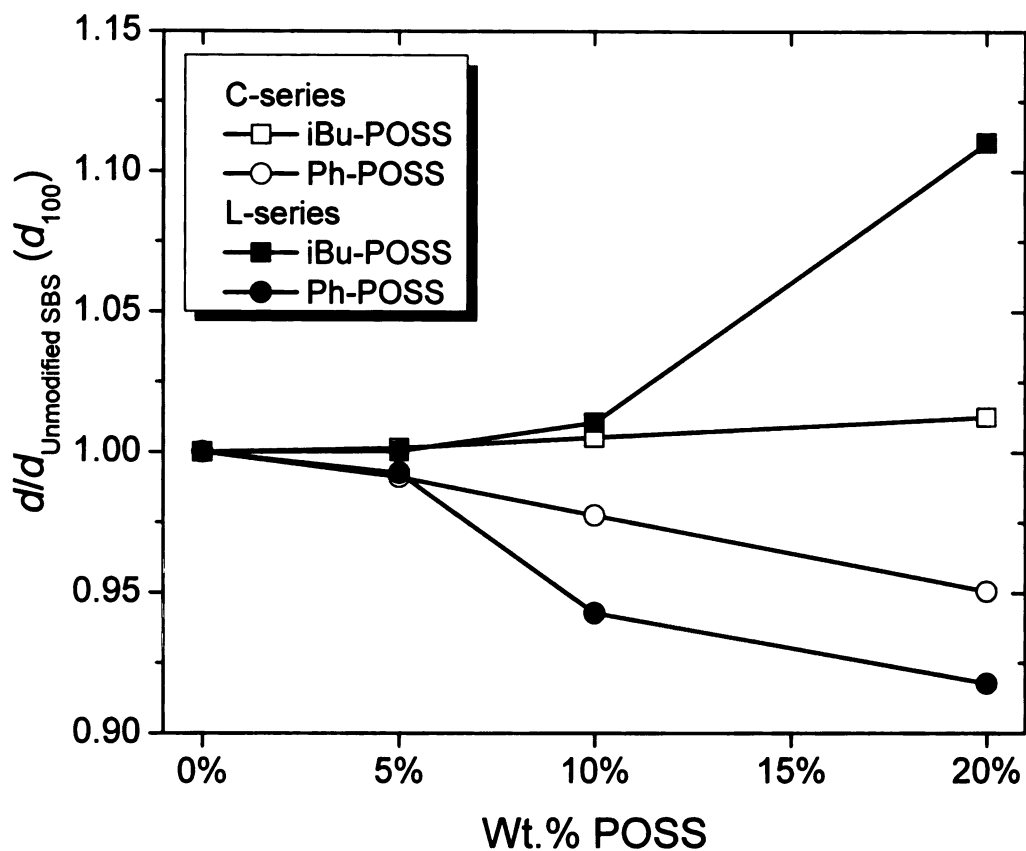


Figure 3.5. The d-spacing normalized to the unmodified SBS for the C-series and L-series at 130°C. For the L-series iBu-POSS (■), there is a change in morphology from lamellar (0 to 10 wt%) to hexagonally packed cylinders (20 wt%). d_{100} for the cylindrical morphology corresponds to the nearest neighbor 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.

grafting. The observed increase in d-spacing shown in Figure 3.5 along with the preceding R_g arguments implies that changes in χ after grafting iBu-POSS are small. It also confirms that the iBu-POSS does not have favorable compatibility with polystyrene which would reduce χ and subsequently the d-spacing.

For the L-series polymers grafted with iBu-POSS, 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 the amount of grafting per chain increases. The d-spacing for the 20 wt% iBu-POSS must be multiplied by $\sqrt[3]{4/3}$ 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 3.5, 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 the d-spacing decreases for Vector[®] 6241 grafted with Cy, Cy_e, and Ph-POSS.

The C-series and L-series SBS grafted with Ph-POSS again show different behavior than the iBu-POSS series. The Ph-POSS d-spacing decreases with larger grafting fractions; the L-series decreases more than the C-series. This drop in repeat distance can be explained by a concurrent drop in monomeric segregation, the χ -parameter. Unlike the iBu-POSS, which is non-interacting with polystyrene, the Ph-POSS have a greater affinity to the polystyrene block than the polybutadiene block because both polystyrene and Ph-POSS have a similar aromatic electronic structure. The enthalpic contribution to the monomeric segregation, χ , between the polystyrene and grafted polybutadiene will decrease when the Ph-POSS are situated near the block interface. Thus, a consequence of grafting Ph-POSS to the polybutadiene block is that the Ph-POSS modified polybutadiene block is more compatible with the polystyrene block. The reduced χ -parameter will result in a smaller d-spacing. With a larger fraction of Ph-POSS grafting, the modified polybutadiene block becomes more compatible with the polystyrene block and the d-spacing decreases further. Qualitatively, the Ph-POSS is acting as a compatibilizing agent for the two blocks. With higher concentrations of POSS, it is possible that an interphase region is created where polybutadiene and grafted Ph-POSS mingle with the polystyrene block. 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.

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, and a reduced monomeric segregation at the polystyrene-polybutadiene interface. All of these are associated with a disruption of the local lamellar order. In Figure 3.6, the peak width is plotted vs. the weight percent of grafted iBu-POSS and Ph-POSS for both SBS series. Analogous to the d-spacing data, Γ are normalized to unmodified SBS of each series to facilitate comparison between the two morphologies. Figure 3.6 shows that the peak width increases with a greater weight percent of POSS grafting, but the magnitude of change is different for each POSS type. One cause of peak broadening may originate from 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. At 5 wt% grafting, changes in Γ are minimal regardless of POSS type or morphology. When grafting 10%, there is a clear distinction drawn between the iBu and Ph-POSS. For the highest weight fractions, the overall peak broadening for iBu-POSS is much smaller (on the order of 10%) compared to the Ph-POSS (on the order of 200%). Both morphologies follow closely with one another based on the POSS type with the L-series having a slightly larger Γ . The large difference in peak width between the two POSS types clearly illustrates that there is an additional mechanism for peak broadening in the Ph-POSS series, and it must be related to the POSS chemistry. The reduced χ -parameter caused by Ph-POSS grafting leads to a larger interfacial thickness. More disorder or defects along the thickness of the lamellae should be accompanied by more disorder along its length, and a small domain size will contribute to peak broadening. Thus, it can also be deduced

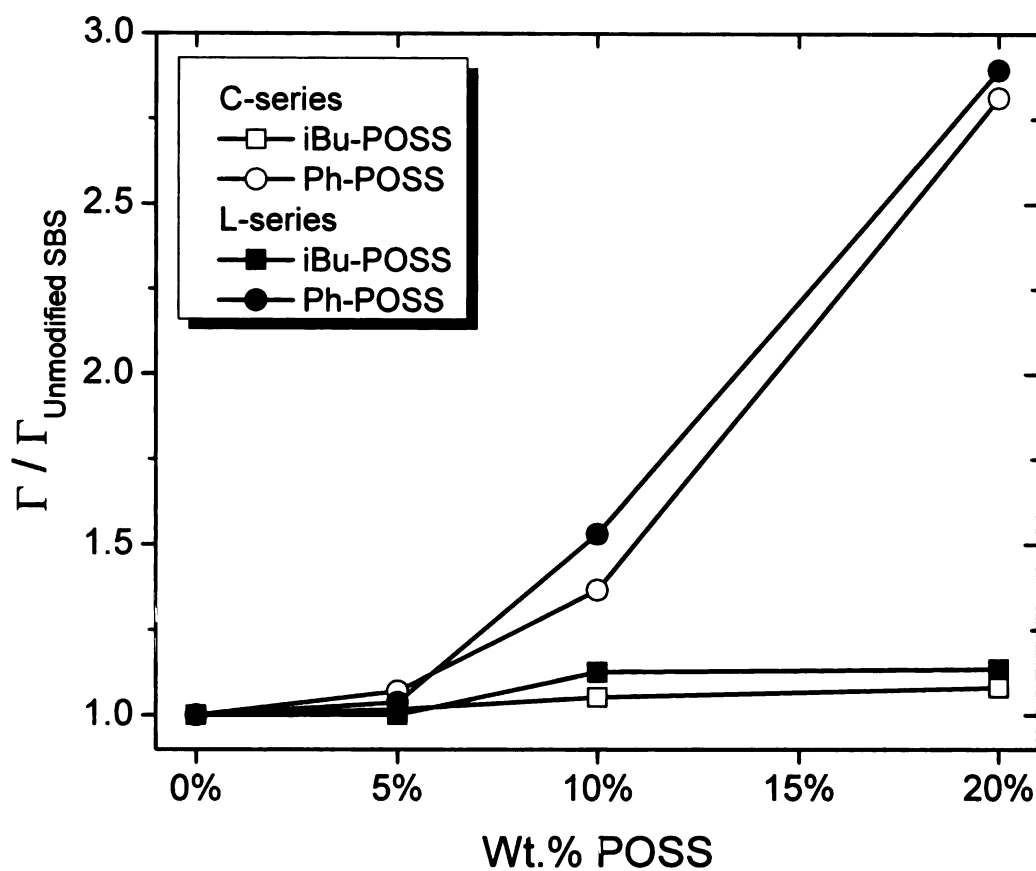


Figure 3.6. Primary scattering peak width, Γ , is normalized to unmodified SBS for the C-series and L-series SBS grafted with iBu and Ph-POSS at 130°C. Peak width is measured as the full width at half the maximum scattering peak height on a plot of intensity vs. q . Peak width for unmodified C-series and L-series SBS are approximately 0.0168nm^{-1} and 0.0129nm^{-1} respectively.

that the copolymers with larger peak widths will correlate to smaller domain (grain) size. The Γ increase is observed even for the 5 wt% Ph-POSS, but it becomes much more substantial in the 10 and 20 wt% Ph-POSS. The iBu-POSS is non-interacting with the polystyrene block, so the introduced polydispersity is likely the only significant contribution to peak broadening.

Wide-angle x-ray scattering, WAXS, was performed to probe the POSS length-scale. Figures 3.7 and 3.8 show the WAXS data for C-series and L-series SBS respectively. Data for pure SBS, 10%, and 20% POSS loadings are shown for each substituent group. It is nearly impossible to differentiate the high q -range data for the different SBS. This is because the high q -range examines small length scales; length scales on the order of POSS and polymer segments. The data for pure SBS shows scattering due to the morphology at the lowest q -range, a strong amorphous polymer peak near 14nm^{-1} , and a weaker amorphous shoulder at 7nm^{-1} . Upon grafting iBu-POSS, an amorphous peak appears near 6nm^{-1} for the 10% and grows more intense for the 20%. The amorphous scattering, as a result of POSS grafting, confirms that the iBu-POSS do not crystallize and are soluble in the polybutadiene phase. This again supports the noninteracting nature of the iBu-POSS leading to the preserved morphology order after grafting. The Ph-POSS copolymers show different behavior. There is a weak crystalline POSS diffraction peak at 5.87nm^{-1} ($d \sim 10.7\text{\AA}$) for the 10% Ph-POSS copolymer. For the 20% Ph-POSS, this peak is more intense and is accompanied by additional diffraction peaks.

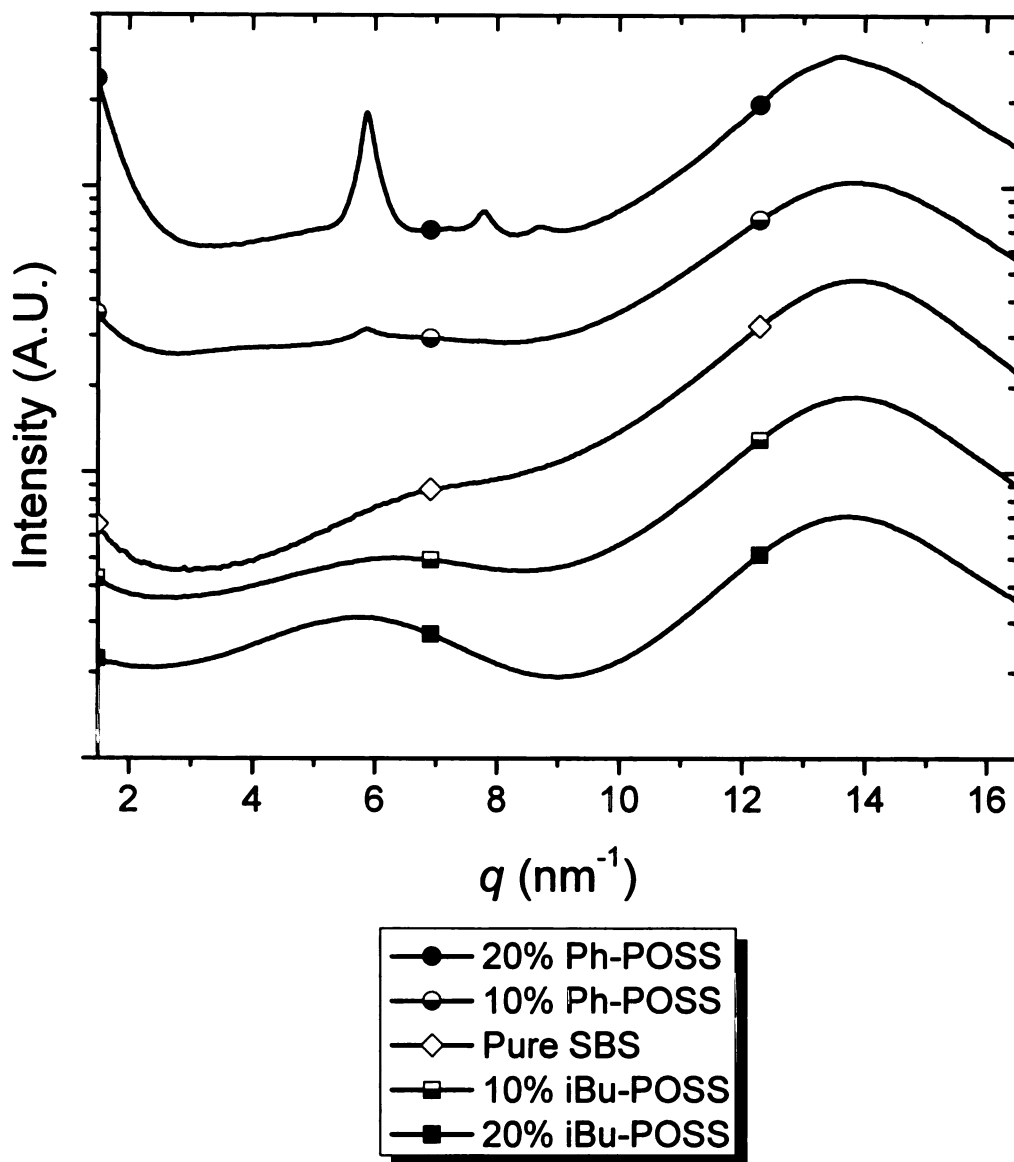


Figure 3.7. X-ray scattering data is plotted in the q -range for crystalline POSS for the C-series. The intensity is in arbitrary units and is normalized to constant incident and transmitted intensities. Crystalline POSS diffraction can be observed near $q \sim 5.87\text{nm}^{-1}$ ($d \sim 10.7\text{\AA}$), and amorphous polymer scattering at $q \sim 14\text{nm}^{-1}$ ($d \sim 4.5\text{\AA}$).

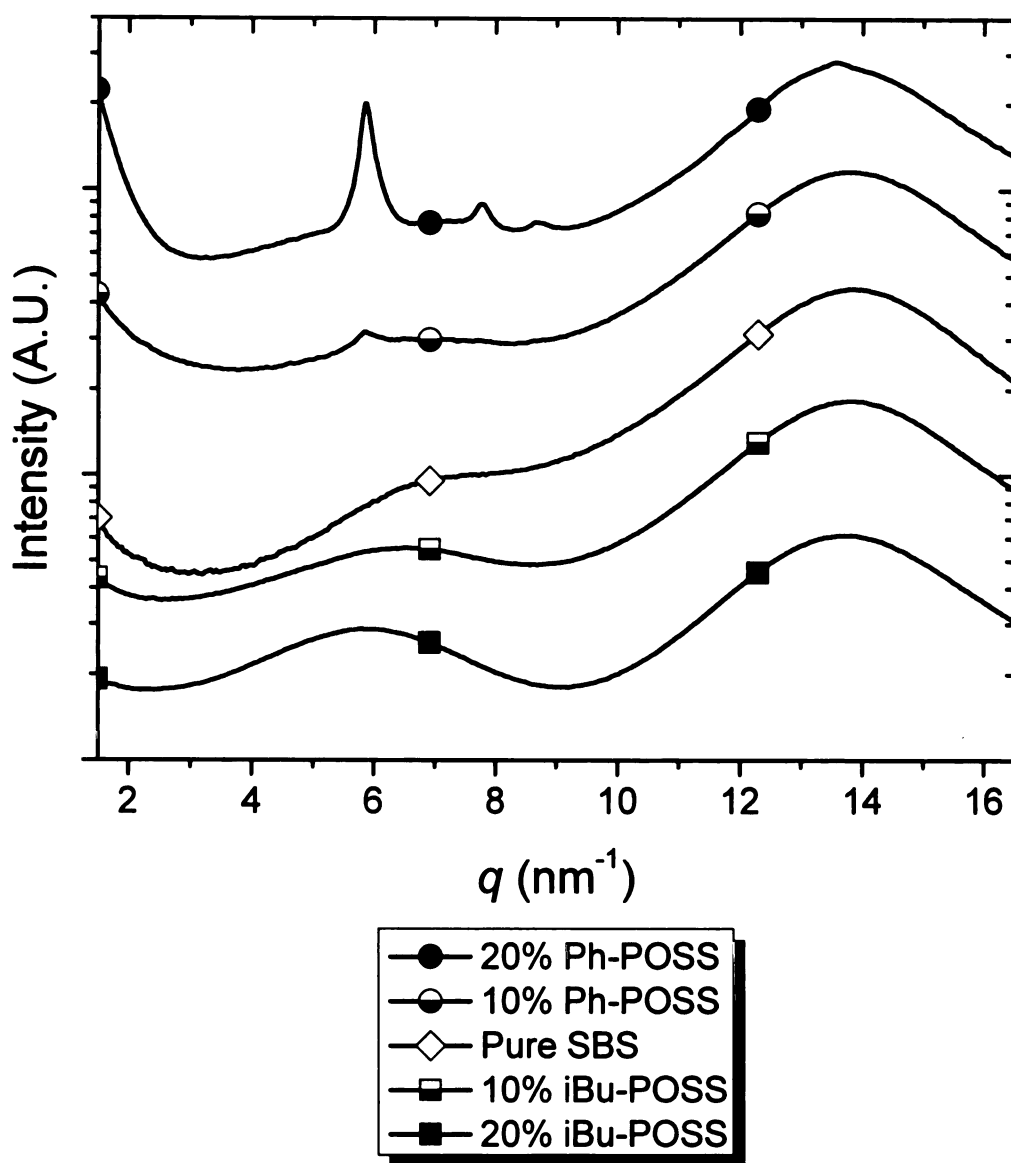


Figure 3.8. X-ray scattering data is plotted in the q -range for crystalline POSS for the L-series. The intensity is in arbitrary units and is normalized to constant incident and transmitted intensities. Crystalline POSS diffraction can be observed near $q \sim 5.87\text{nm}^{-1}$ ($d \sim 10.7\text{\AA}$), and amorphous polymer scattering at $q \sim 14\text{nm}^{-1}$ ($d \sim 4.5\text{\AA}$).

The presence of Ph-POSS crystallites is a consequence of poor Ph-POSS compatibility with polybutadiene. The chemical constraints of the grafting attachment do not allow the Ph-POSS to fully infiltrate the polystyrene phase and makes complete phase separation impossible. At sufficient concentration, the Ph-POSS agglomerate to form crystallites in order to mitigate the unfavorable enthalpic interactions within the polybutadiene domain. The crystallite size and uniformity is limited by the steric constraints of the polybutadiene polymer chain in which it is grafted to. It is also shown, by comparing the 10% and 20%, that greater Ph-POSS grafting leads to more and likely larger crystallites.

3.3.2. Morphology Transitions

The morphology phase behavior as a function of temperature can be examined by the order-disorder and order-order transition temperatures. These transition temperatures were obtained from rheology and determined by abrupt changes in the storage modulus, G' . For the order-disorder transition temperature, T_{ODT} , at low frequencies there is a precipitous drop in G' with increasing temperature, and the onset temperature of this drop is referred to as the T_{ODT} . Order-order transition temperature, T_{OOT} , may not always be as apparent as the T_{ODT} . Though there is often a discontinuity in G' , it may be a discontinuous increase or decrease. Additionally, SAXS measurements were performed near the T_{OOT} and T_{ODT} to insure the accurate designation of transition temperatures and morphologies. Traces of storage modulus, G' , versus temperature for C-series iBu and Ph-POSS grafted block copolymers are shown in Figures 3.9 and 3.10, respectively. L-series iBu and Ph-POSS grafted copolymers are shown in Figures 3.11 and 3.12, respectively.

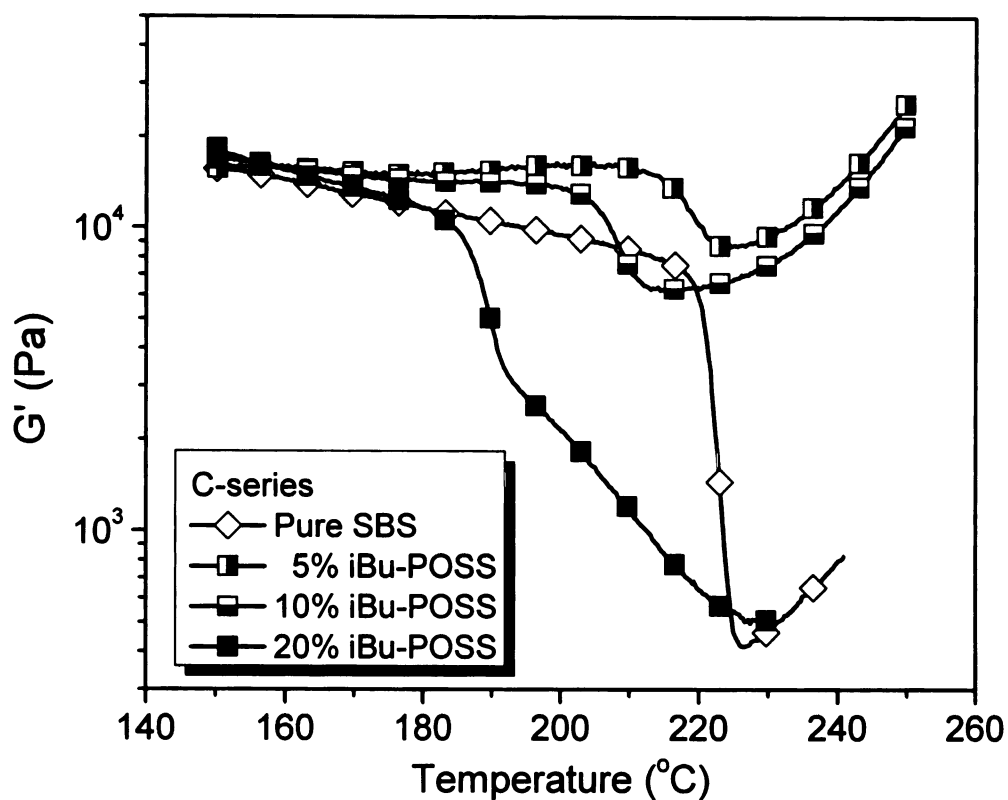


Figure 3.9. Storage modulus, G' , versus temperature for C-series (Vector® 8508) SBS grafted with varying amounts of isobutyl-POSS (iBu). G' was obtained using small-strain oscillatory shear with strain amplitude of 2% and oscillatory frequency of 1 radian/s. The temperature ramp rate was 2°C/min. The rheological experiments were done in a dry nitrogen environment to reduce thermal degradation. All four copolymers plotted undergo a cylindrical to disorder transition.

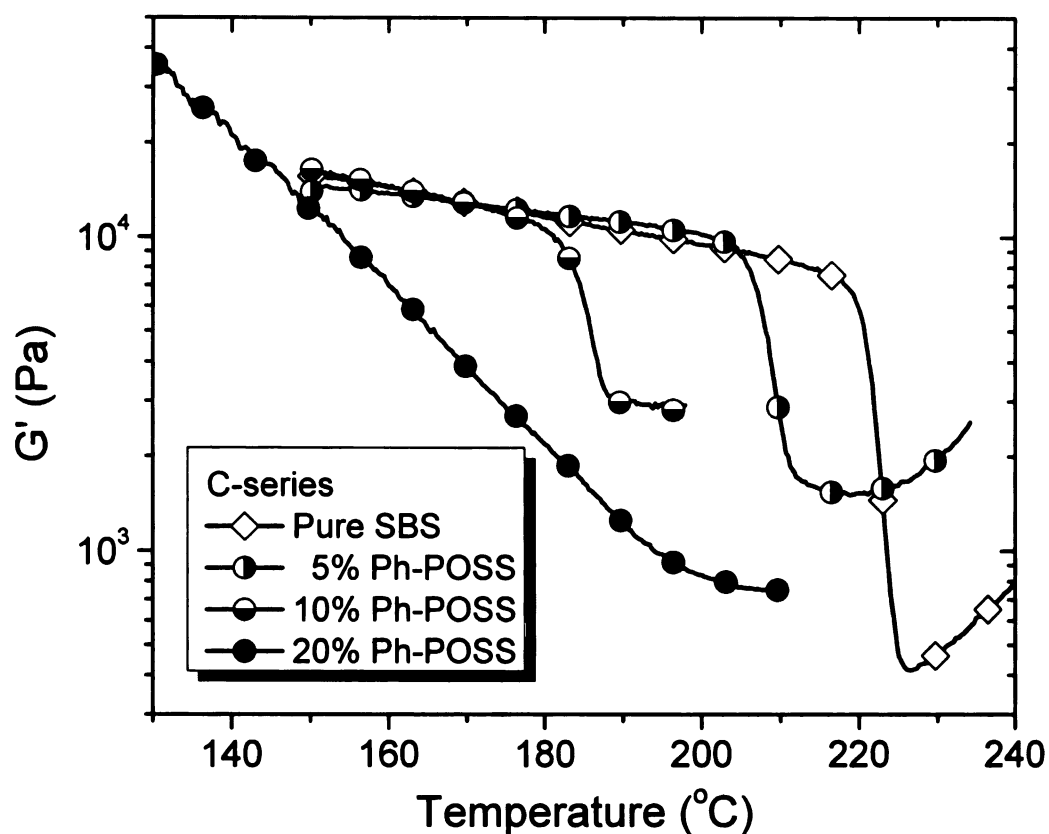


Figure 3.10. Storage modulus, G' , versus temperature for C-series (Vector[®] 8508) SBS grafted with varying amounts of phenyl-POSS (Ph). G' was obtained using small-strain oscillatory shear with strain amplitude of 2% and oscillatory frequency of 1 radian/s. The temperature ramp rate was 2°C/min. The rheological experiments were done in a dry nitrogen environment to reduce thermal degradation. All four copolymers plotted undergo a cylindrical to disorder transition.

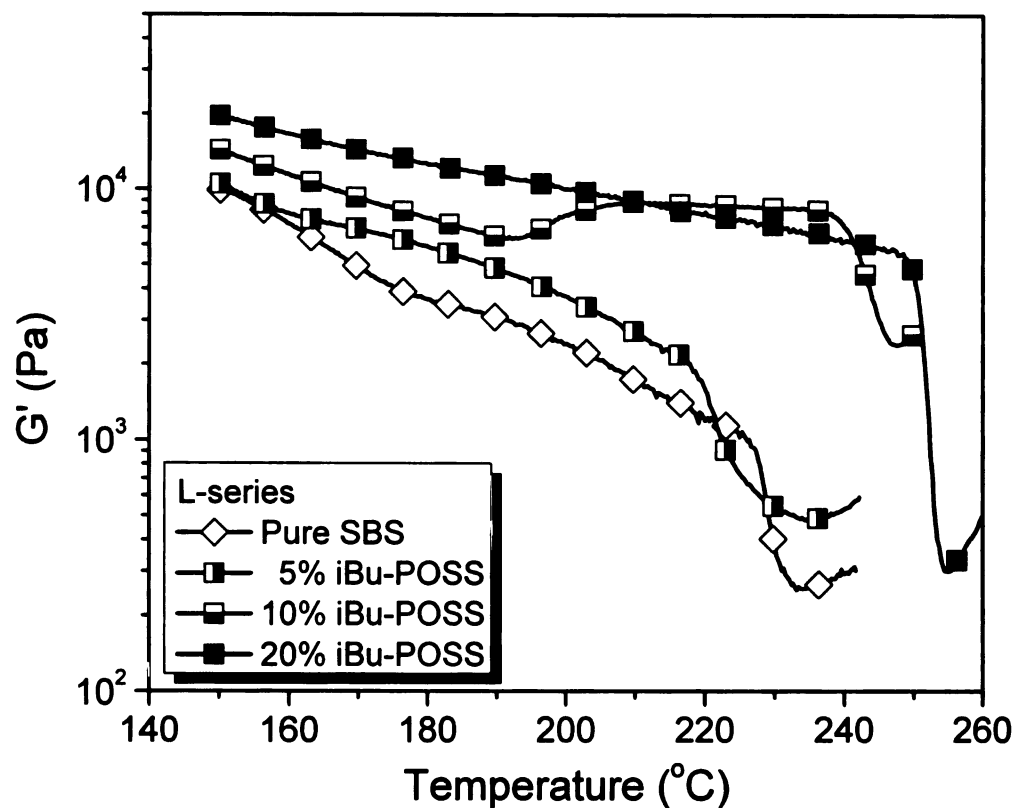


Figure 3.11. Storage modulus, G' , versus temperature for L-series (Vector® 6241) SBS grafted with varying amounts of isobutyl-POSS (iBu). G' was obtained using small-strain oscillatory shear with strain amplitude of 2% and oscillatory frequency of 1 radian/s. The temperature ramp rate was 2°C/min. The rheological experiments were done in a dry nitrogen environment to reduce thermal degradation. Pure SBS and 5% iBu-POSS undergo a lamellar to disorder transition, 10% undergoes a lamellar to cylindrical and cylindrical to disorder transitions, and 20% iBu-POSS undergoes a cylindrical to disorder transition.

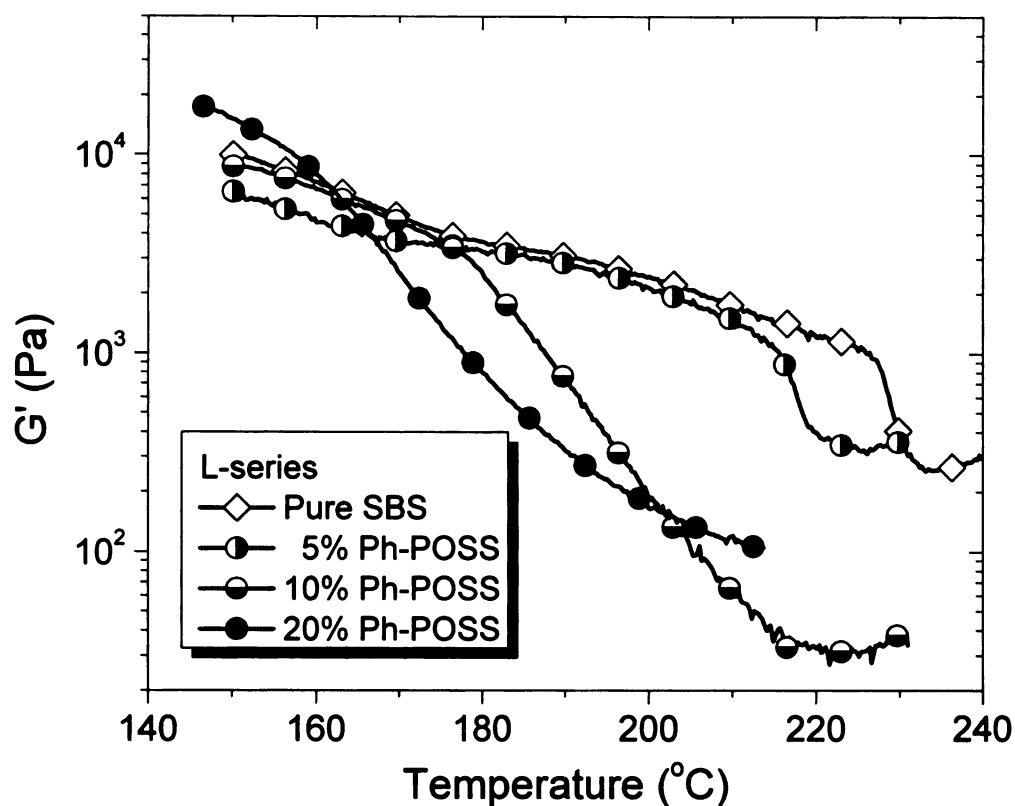


Figure 3.12. Storage modulus, G' , versus temperature for L-series (Vector[®] 6241) SBS grafted with varying amounts of phenyl-POSS (Ph). G' was obtained using small-strain oscillatory shear with strain amplitude of 2% and oscillatory frequency of 1 radian/s. The temperature ramp rate was 2 $^{\circ}\text{C}/\text{min}$. The rheological experiments were done in a dry nitrogen environment to reduce thermal degradation. All four copolymers plotted undergo a lamellar to disorder transition.

In Figure 3.13, the T_{ODT} are plotted versus weight percent of grafted POSS for the cylindrical morphology C-series. The trend is the same for both types of POSS. 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. However, there is a difference in magnitude. Ph-POSS has a larger drop in T_{ODT} than iBu-POSS. This is because of 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} . At 20 wt% Ph-POSS grafting, the initial morphology is so disturbed (and thus nearly disordered) that no order-disorder transition was observed.

The transition temperature data for the L-series grafted with iBu and Ph-POSS is displayed in Figure 3.14. The iBu-POSS copolymer phase behavior is relatively complex when compared to the Ph-POSS series. At all temperatures below T_{ODT} , the unmodified SBS and the entire Ph-POSS series have a lamellar morphology. The 5 wt% iBu-POSS also has a lamellar morphology below the T_{ODT} . However, the 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. Finally, the 20 wt% iBu-POSS 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 polystyrene content of the grafted material^{12, 17, 19, 20, 64}. The Ph-POSS series lacks any order-order transitions, so all of the Ph-POSS grafting yields a lamellar morphology for all temperatures below the T_{ODT} . T_{ODT} decreases with increasing grafting for the Ph-POSS series, which is related to a reduction in the χ -parameter, as stated

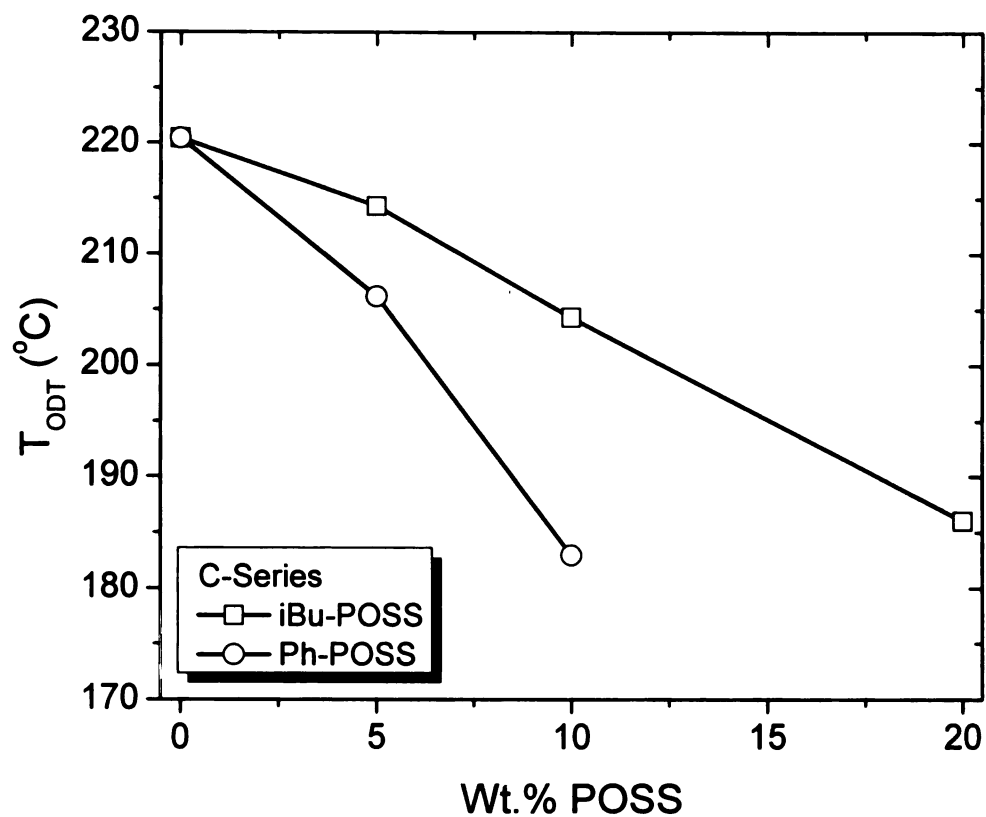


Figure 3.13. The order-disorder transition temperature, T_{ODT} , is plotted for C-series SBS grafted with iBu and Ph-POSS. Data points were calculated from rheological measurements, and all transitions were verified by SAXS.

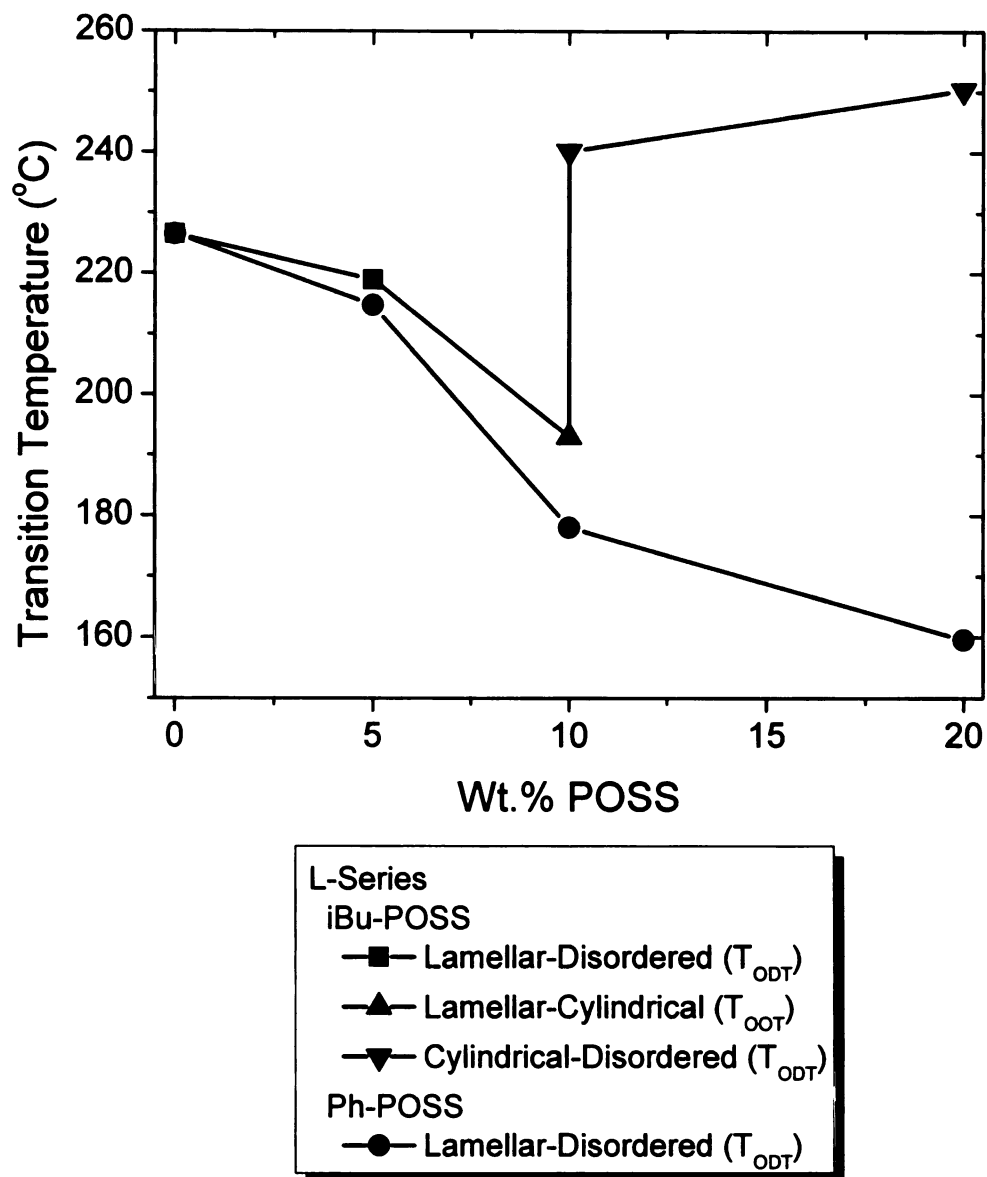


Figure 3.14. The T_{OOT} and T_{ODT} are plotted for L-series SBS grafted with iBu and Ph-POSS. There is an order-order transition for the 10 wt% iBu-POSS. For iBu-POSS, ■ represents the lamellar-disorder transition, ▲ represents the lamellar-cylindrical transition, and ▼ represents the cylindrical-disorder transition. For Ph-POSS, the ● symbol represents the cylindrical-disorder transition. Data points were calculated from rheological measurements, and all transitions were verified by SAXS.

earlier. With greater Ph-POSS grafting, the χ -parameter is reduced, which further reduces the T_{ODT} .

SAXS was performed to corroborate the phase changes observed in rheological experiments. Figure 3.15 shows the scattering patterns for 10 wt% iBu-POSS grafted to the L-series copolymer. This is the only grafted copolymer in this study that undergoes an order-order transition. At 130°C, a lamellar morphology is present. At 195°C, which is near the T_{OOT} , both lamellar (1, 2, 3) and cylindrical (1, 1.73, 2, 2.65) morphologies are present. Further heating past the T_{OOT} results in a cylindrical morphology.

To put the T_{OOT} and T_{ODT} data in the context of the noninteracting/phase shift ideas discussed earlier, the transition temperatures are plotted in terms of χN vs. f_{PS} (volume percent of polystyrene) in Figure 3.16. The solid lines are intended to connect the like transitions of each series, and the dashed lines are extrapolations outside the like transitions to illustrate a relation to the phase shift idea presented earlier in the discussion. The dashed line in the center of the figure relates the C-series and L-series cylindrical morphologies and separates the cylindrical and disordered morphologies. In actuality, there is a ternary system of polystyrene, polybutadiene, and iBu-POSS. However, based on the phase shift arguments mentioned earlier, the data is plotted assuming the iBu-POSS grafting only affects the weight fraction of polystyrene and has little effect on segregation between polystyrene and polybutadiene. It is also assumed that N , the effective degree of polymerization, has not been significantly affected after grafting. The purpose of this plot is not to precisely define the phase space of the SBS-POSS grafts, but to put the T_{ODT} changes in the context of the reduction of polystyrene content by grafting

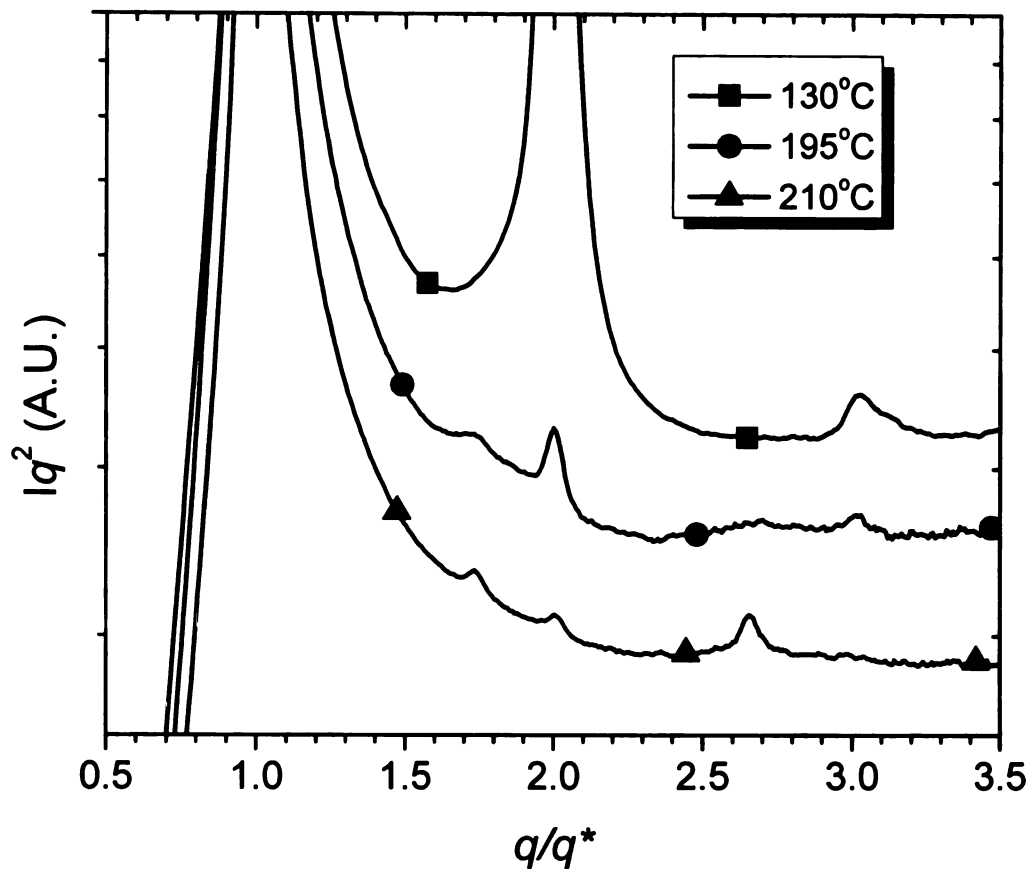


Figure 3.15. The figure shows Iq^2 plotted vs. q/q^* (where q^* is the q -position of the primary peak) for L-series 10% iBu-POSS at 130°C (■), 195°C (●), and 210°C (▲). The morphology is lamellar morphology at 130°C. Both lamellar and cylindrical morphologies are present near the T_{OOT} , 195°C. At 210°C only a cylindrical morphology is present.

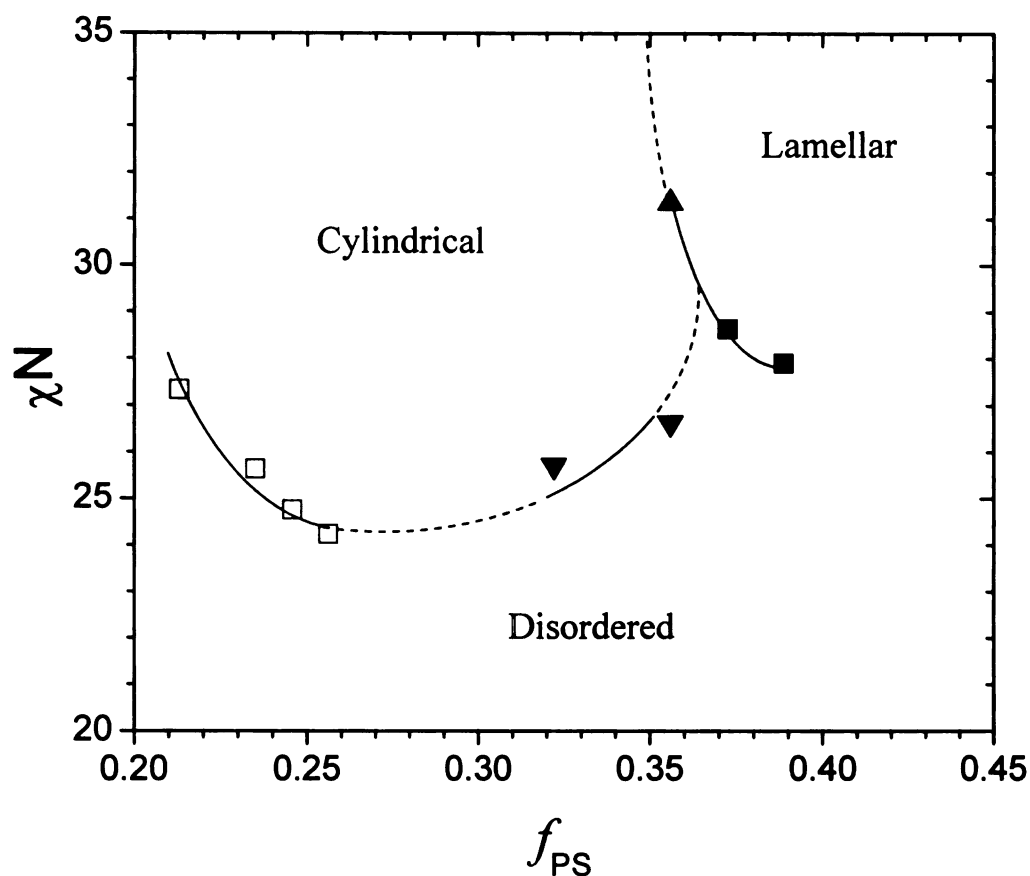


Figure 3.16. The transition temperatures are plotted in terms of χN vs. the volume fraction of polystyrene, f_{PS} , for both SBS series. Unmodified C-series and L-series polymers have 0.256 and 0.389 f_{PS} , respectively. Lines are added to guide the eye and separate the observed morphologies; solid lines connect similar morphology transitions and dashed lines are extrapolations. The $\square$ symbol represents the cylindrical-disorder transition for the C-series. For the L-series, $\blacksquare$ represents the lamellar-disorder transition, $\blacktriangle$ represents the lamellar-cylindrical transition, and $\blacktriangledown$ represents the cylindrical-disorder transition.

which was discussed earlier. The values for χ were calculated using the fitted parameters obtained by Owens et al.⁶⁵ 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.^{12, 17, 19, 20, 64} 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% L-series data, and it relates the phase behavior between the two SBS polymer series. It is important to note that no complex phases such as the bicontinuous gyroid or the hexagonally perforated lamellae morphologies were observed. It is possible that these phases exist, but they may not have been observed because of their narrow range of stability and the few grafting fractions implemented.

Figure 3.16 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). Support for these assumptions has been given in the preceding discussion and all are reasonable within the context of the phase shift argument. Nevertheless, it is important to comment on how deviations from these assumptions will affect Figure 3.16. 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 change is small and 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 deviation is expected to be only significant for the 20% L-series because it is the only grafted copolymer in this study to deviate more than 2% from the unmodified SBS d-spacings. If one was to adjust N for changes in R_g , it would result in a small vertical shift upward from the uncorrected point on the χN axis. The χ -parameter also contains 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.^{44, 65, 66} The fitted χ that was used in Figure 3.16 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 the observation of a preserved morphology, small increases in d-spacing and peak width, and the T_{OOT} and T_{ODT} behavior.

3.4. CONCLUSIONS

In this work, the phase behavior and morphology changes of SBS grafted with iBu and Ph-POSS have been investigated. Two host SBS morphologies were examined with POSS grafting at 0, 5, 10, and 20 wt% for noninteracting (iBu) and interacting (Ph) POSS. The morphology and phase behavior observed for iBu-POSS is consistent with that of a shift in polystyrene content with little change in χ . The local and long-ranged order of the morphology is preserved for all SBS grafted with iBu-POSS copolymers investigated. The Ph-POSS copolymers which interact with the polystyrene phase reduce

χ and disrupt the local order of the morphology. This is equivalent to a compatibilizing effect.

The information gathered in this study has yielded more information about how POSS affects the morphology of SBS. Figure 3.17 attempts to schematically represent and summarize the main findings. In this figure, a slice of the block copolymer structure is displayed stretching from the polystyrene phase (■) through the polybutadiene phase (□) and reaching to another polystyrene phase for 20% iBu-POSS grafted copolymer (top), pure SBS (middle), and 20% Ph-POSS. Polystyrene and polybutadiene polymer chains are represented by — and — colored lines respectively. For the 20% iBu-POSS copolymer (top), the iBu-POSS do not crystallize, and they are completely confined within the polybutadiene phase. The iBu-POSS do not crystallize because they have good compatibility with (or are soluble in) the polybutadiene block in which they are grafted. This, along with the fact that the iBu-POSS are noninteracting with polystyrene, accounts for the preserved polystyrene-polybutadiene interface. Another consequence of its noninteracting nature is the little or no change in d-spacing (except in the lamellar to cylindrical morphology change). Noninteracting means the monomeric segregation (χ -parameter) between polystyrene and polybutadiene is unchanged after grafting. The local and long range order of the morphology does not change (Γ remains constant). The most observable consequence of grafting iBu-POSS is the reduction of polystyrene content which shifts the phase behavior on the χN vs. f phase diagram. This would account for the changes in T_{ODT} , T_{OOT} , and the cylindrical morphology for 20% L-series grafted with iBu-POSS. It is important to remember here that these observations are within the

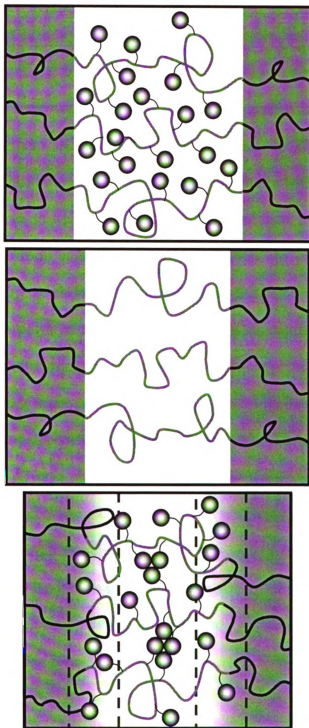


Figure 3.17. Schematic representation of the local morphology of 20% iBu-POSS grafted copolymer (top), pure SBS (middle), and 20% Ph-POSS. Polystyrene is represented by — (chain) and the color ■, polybutadiene is represented by — (chain) and the color white, and POSS is represented by ●. For 20% Ph-POSS (bottom), — — — distinguishes the interphase region.

context of the experiments. By increasing the grafting content to 30% or 40% may result in significant changes in morphology, transition temperature, and POSS-POSS crystal formation.

Although the same weight fraction of POSS is grafted in the 20% Ph-POSS copolymer (bottom), there are remarkable differences from its iBu-POSS counterpart. The Ph-POSS crystallize because they have poor compatibility with (or are insoluble in) the polybutadiene block in which they are grafted. To mitigate this enthalpic cost, the POSS agglomerate to form crystallites. These crystallites are small due to the steric restrictions imposed by the chemical grating to the polybutadiene chain. The Ph-POSS interact strongly with polystyrene phase which reduces the monomeric segregation (χ -parameter) between polystyrene and polybutadiene monomers; the Ph-POSS effectively act as a compatibilizing agent. This results in a smaller d-spacing, a lower T_{ODT} , a disrupted polystyrene-polybutadiene interface (Γ increases dramatically), and smaller domain (grain) size. At large grafting fractions, this disruption may be large enough to create an interphase region (denoted by ---) where polystyrene, Ph-POSS, and polybutadiene are present in significant amounts and is distinct from the polybutadiene and polystyrene phases. By increasing the grafting content, it may be possible to disrupt the morphology so much (and push the T_{ODT} below $T_{g,PS}$) that no thermodynamically stable, ordered morphology is possible.

CHAPTER 4.

DEFORMATION BEHAVIOR OF POSS-GRAFTED SBS: MECHANICAL PROPERTIES, MORPHOLOGY, AND POSS NANOSTRUCTURES

4.1. INTRODUCTION

The morphology of block copolymers plays a principal role in determining the mechanical properties of the material⁹⁻¹¹. The type of morphology and the orientation of this morphology are among these important factors. The ability to control the size and shape of the morphology is a valuable tool that allows for the precise design of materials. As mentioned earlier, SBS is a widely used thermoplastic elastomer. A general feature of thermoplastic elastomers is a hard block (crystalline or glassy) coupled to a rubbery soft block. These materials represent a class of multiphase polymers that contain a soft domain that is in close contact with a hard domain. The soft domain gives rise to elastomeric behavior of the material, while the hard domain increases the modulus and enhances the mechanical integrity of the material. In addition, some properties of thermoplastic elastomers can be tailored based on the ratio of hard to soft segments, but the range of this flexibility is limited by the constituent blocks. By incorporating nanostructures, it may be possible to push properties outside these limits.

For SBS, there are several length scales that influence the material properties. At the smallest scale are the individual monomers that make up the copolymer: polystyrene and polybutadiene. On a larger scale, near that of the polymer chain, is the self-assembled morphology. In the case of a lamellar morphology, the polymer chain is partitioned between the individual lamellae of polystyrene and polybutadiene. These

lamellae stack in alternating layers and extend laterally until they encounter another set of lamellae with a different orientation, and the boundaries between these regions of different orientation determine the domain or grain size of the morphology. Within a grain, the morphology has a fixed orientation. Typically, this grain size is on the order of one micron^{9, 10}.

The type of morphology plays a large role in the mechanical properties because each morphology has its own hard to soft segment ratio. The grain size and/or orientation also play a role¹¹ in some of the properties, especially when there are changes in continuity of each component (discontinuous A phase vs. continuous A phase).

The work discussed thus far has focused on the equilibrium morphology of this model polymer-nanostructure system. This has given tremendous insight as to the effects of nanostructure chemistry on the host polymer. However, outside of WAXS, little has been discussed about the nature of intra-nanostructure interactions (i.e. POSS-POSS interactions). The following work attempts to identify the effects of grafted nanostructure chemistry and content on the mechanical properties of our SBS model. Studying these effects in combination with the information gathered about the changes in morphology, it will be possible to reveal information relating to POSS-POSS interactions.

4.2. EXPERIMENTAL

4.2.1. Materials

The host polymer for this study was Vector® 6241 obtained from Dexco Polymers. According to the manufacturer, it is a pure, linear, symmetric triblock copolymer containing less than 1% diblock and has 43 wt% polystyrene. The number-

average and weight-average molecular weights are 71 kDa and 72 kDa respectively and were determined by GPC. This gives the SBS respective degrees of polymerization of approximately 150-750-150. POSS grafting was accomplished via a hydrosilation reaction in toluene. The procedures used to synthesize the POSS hydrides and the conditions used for grafting to 1,2-butadiene were identical to our previously reported work⁵⁸. Isobutyl-POSS (iBu) and Phenyl-POSS (Ph) were grafted to 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. To prepare the films, each SBS-POSS copolymer was 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 added to the solution to reduce polymer 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.

4.2.2. Mechanical Testing

Mechanical testing was performed on a Rheometric Scientific RSA-III solid analyzer with a 350 g transducer. SBS-POSS films were cut to a width of 3.75mm (0.3mm thickness), and a gauge length of 5mm was used. Samples were deformed at 30°C and 70°C at 0.001, 0.005, and 0.050s⁻¹ Henky strain rates.

4.2.3. X-ray scattering

X-ray scattering experiments were used to characterize multiple features of the SBS-POSS systems: equilibrium block copolymer morphology, possible POSS crystallite formation, and morphology changes during deformation. The experiments were performed at beamline 15ID-D (ChemMatCARS) in the Advanced Photon Source

(APS) at Argonne National Laboratory. Small-angle X-ray scattering (SAXS) patterns were collected using a Bruker 6000 CCD X-ray detector, which is a two-dimensional detector with a 1024 x 1024 pixel array covering an area 94mm x 94mm. The x-ray beam size was 0.5 x 0.5 mm in size; the wavelength and camera distance varied slightly for each experiment, as will be discussed. The x-ray radiation was monochromated using diamond (111) to achieve $\Delta E/E \approx 10^{-4}$.

Small angle x-ray scattering is ideal for examining the equilibrium morphology of the SBS-POSS copolymers because it is capable of measuring subtle changes in morphology by probing a large volume of material in the bulk state. By selecting the appropriate wavelength and camera distance, one can examine scattering at the length-scale associated with the block copolymer repeat distance, or d-spacing. For this set of experiments, the wavelength of x-ray radiation was selected to be 1.500 Å with a camera distance of 1.915 meters. The protocol implemented for the isothermal experiments included a 10 minute 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. The raster protocol was used because it minimizes possible beam damage to the sample, it allows for greater statistical sampling of the morphology, and it ensures that the sample has reached equilibrium.

In situ x-ray deformation experiments were also performed using the same x-ray wavelength and camera distance as the equilibrium morphology measurements because the same features were being investigated: the morphologies of the block copolymer. For these experiments, a specially designed tensile stretching device was constructed. The device had several attributes that were important for this set of experiments. First,

two co-rotating cylinders were driven by a stepper motor, which allowed for continuous stretching to an unbounded strain. In addition, the device had an enclosed environment with Kapton® windows and a forced-air convection heater that permitted deformation experiments at elevated temperatures. The SBS-POSS copolymers were cut to a width of 3.75mm (0.3mm thickness), and the gauge length in the stretching device is 25mm. For this set of experiments, a 0.005s^{-1} Henky strain rate was employed. Data was collected with 1 second exposures, but consecutive exposures were limited by the detector readout time of 8 second. Thus, data was collected at approximately 0.045 Henky strain. Deformation experiments for the lamellar morphology were carried out at 30°C and 70°C.

Wide-angle X-ray scattering (WAXS) was performed to observe whether any POSS crystal structure developed. In order to observe this crystal structure, a camera distance of 0.549 meters and a wavelength of $0.6199\text{\AA}$ were used to access a larger q -range. This allowed investigation from 0.6nm^{-1} to 16.6nm^{-1} (0.38nm to 10.5nm d-spacing), which is within the diffraction range of POSS crystals. Data was collected at 30°C using 5 second exposures for the undeformed specimens. Deformation was also performed at this camera length and temperature using 1 second exposures.

4.3. RESULTS AND DISCUSSION

4.3.1. Mechanical Testing

The mechanical properties of the SBS-POSS copolymers can supply further information about the nature of POSS in the block copolymer system. Uniaxial tensile deformation was performed on the SBS-POSS copolymers at 70°C and 0.005s^{-1} Henky

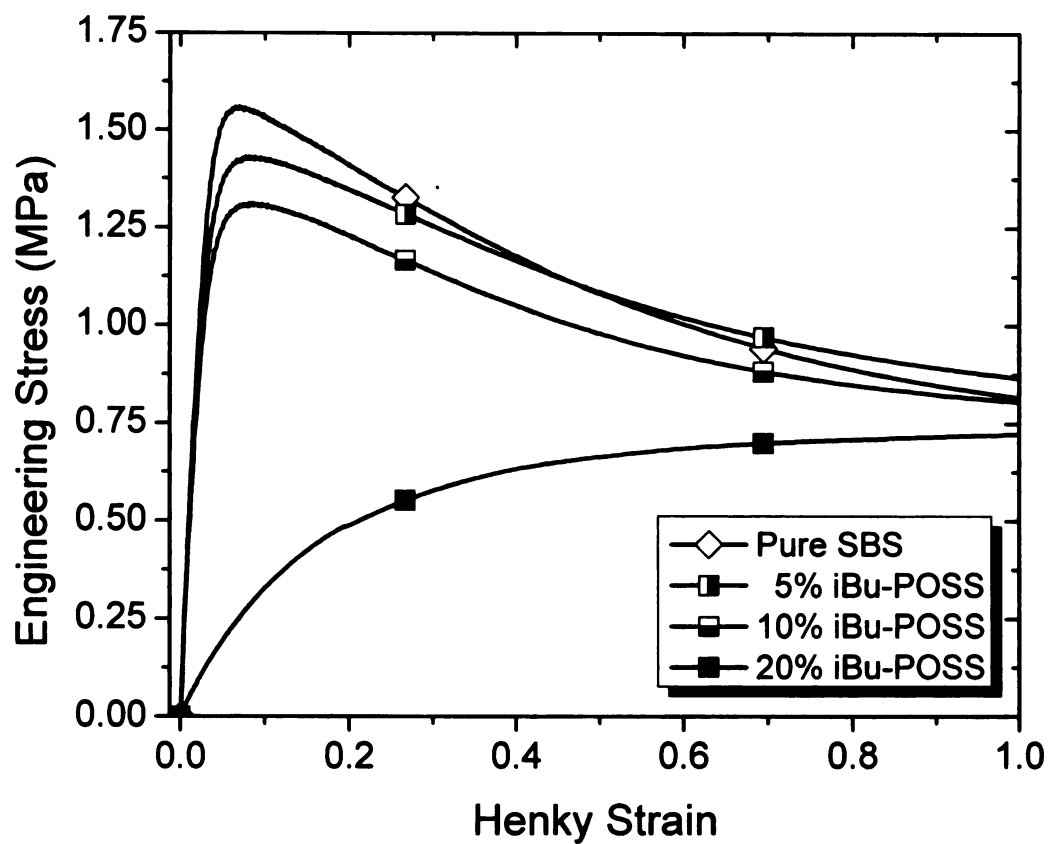


Figure 4.1. Stress-Strain data for isobutyl-POSS copolymers. Testing was performed at 70°C and using a Henky strain rate of 0.005s^{-1} under tensile deformation for SBS-POSS copolymers.

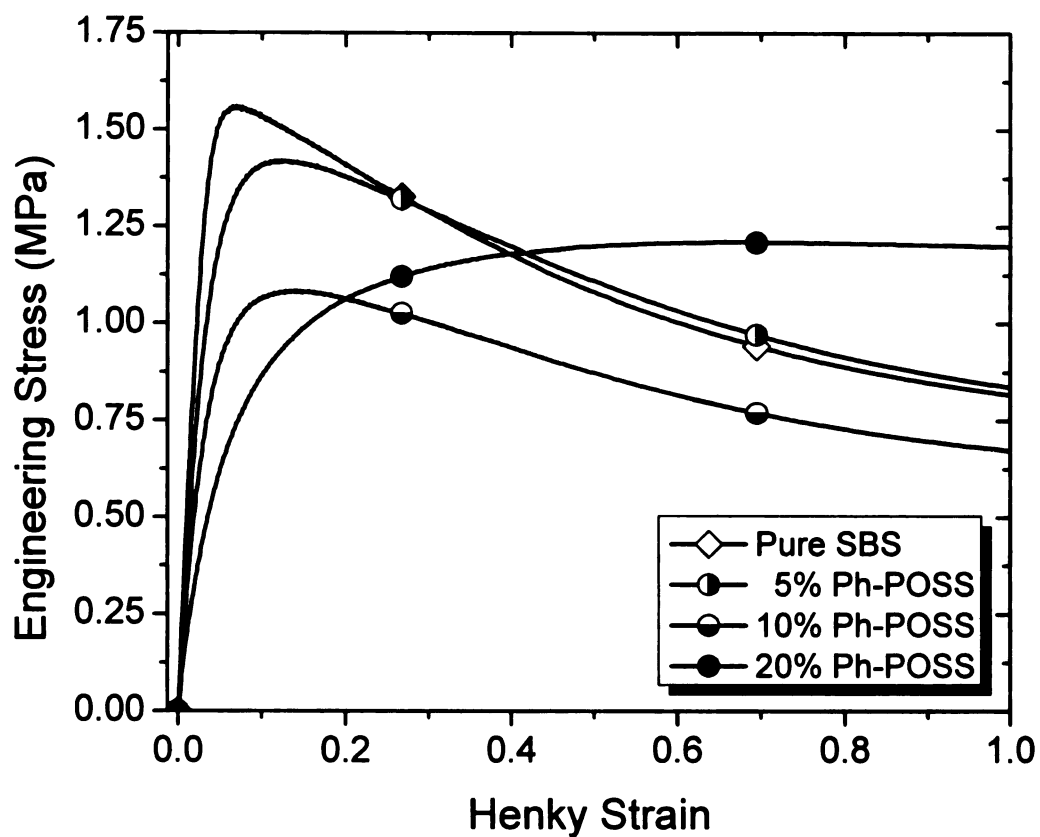


Figure 4.2. Stress-Strain data for phenyl-POSS copolymers. Testing was performed at 70°C and using a Henky strain rate of 0.005s^{-1} under tensile deformation for SBS-POSS copolymers.

strain rate. Figures 4.1 and 4.2 show the stress-strain curves for these iBu and Ph-POSS copolymers respectively. The pure SBS, having a lamellar morphology, exhibits an elastic response at strains below 0.03-0.04. It reaches a stress maximum near 0.07 strain, and the stress monotonically decreases at high strains until failure. For discussion purposes, the maximum supported stress will be noted as the yield stress, but this yield stress does not necessarily coincide with the onset of plastic deformation. The 5 and 10% SBS-POSS copolymers have a similar mechanical response, and the general shapes of the stress-strain curves are akin to the pure SBS. This is not a surprise since there is little change in the morphology of these systems as discussed previously. There are, however, trends following both the type and overall fraction of POSS grafted that will be discussed momentarily.

The mechanical behavior of the 20% POSS is more complicated. The 20% iBu-POSS has a substantial drop in mechanical response. The chief contributor to these reductions is the change in morphology from lamellar to cylindrical. The cylindrical morphology has a lower modulus and does not exhibit a yield stress because it has a continuous polybutadiene phase (soft/rubbery phase). Thus, the 20% iBu-POSS will be disregarded in the subsequent yield stress discussions. The 20% Ph-POSS also has an unusual shape with respect to the other copolymers. In particular it has a reaches its maximum supported stress at around 0.70 Henky strain or about 1.00 engineering strain; a nearly ten-fold increase compared to the other materials. The higher supported stress at high strains is observed on a smaller scale for the other POSS samples as well. Both 5% iBu and Ph-POSS have a slightly higher supported stress than pure SBS at high strains.

For the 10% POSS samples, the reduction in polystyrene outweighs possible POSS reinforcement.

It is important to note here that the 20% iBu-POSS has a monotonically increasing stress response in Figure 4.2. The pure C-series SBS of chapter 3, like the pure L-series Figure 4.1 has a monotonically decreasing stress after yield. The C-series copolymers have 29 wt% polystyrene, but it is likely that a cylindrical morphology with a weight fraction of polystyrene equivalent to the 20% iBu-POSS would also have a monotonically decreasing stress after yield. Thus, there may be a form of iBu-POSS reinforcement, but a rigorous comparison cannot be made to the 20% iBu-POSS because an equivalent unmodified system is not available.

The clearest distinction between the mechanical data for the pure SBS and the SBS-POSS copolymers is the maximum supported stress, or yield stress. Figure 4.3 shows the yield stress for the iBu and Ph-POSS copolymers. There is a trend of decreasing yield stress with increasing POSS grafting. This relates to a reduction in polystyrene content for the SBS-POSS copolymer systems; grafting 10 wt% POSS results in a 10% reduction of polystyrene by weight. Because $T_{g,PB} \ll 70^{\circ}\text{C} < T_{g,PS}$, the polystyrene has a significantly higher modulus than polybutadiene and consequently supports a greater load. The iBu-POSS follow a linear trend almost ideally matching the polystyrene content. The 5 wt% Ph-POSS yield stress follows the same trend as the iBu-POSS, almost matching the 5% iBu-POSS. However, there is an additional drop for the 10% Ph-POSS. As seen in other published work⁹⁻¹¹ and with the 20 wt% iBu-POSS, the morphology has a critical role in determining the mechanical properties of block copolymers. The additional yield stress drop is likely related to its slightly disrupted

lamellar morphology that was discussed previously in chapter 3. Another anomalous observation is the increased yield stress for the 20% Ph-POSS relative to the 10% Ph-POSS. The term yield stress is used rather loosely in reference to the 20% Ph-POSS. As one can see, the stress-strain curve in Figure 4.2 does not exhibit the same yielding behavior as the other SBS copolymers. Rather there is an extended region of strain with nearly constant supported stress, and the maximum of which is around 0.7 Henky strain or 1.0 engineering strain. The increased yield stress at this temperature is unlikely related to morphology changes because the 20% Ph-POSS has a more disrupted lamellar morphology than the 10%. The most likely cause for the increase is some sort of Ph-POSS reinforcement at higher strain, which will be discussed in more detail later. This reinforcement is significant enough to give the 20% Ph-POSS a higher supported stress than any of the other copolymers above 0.4 Henky strain.

The elastic modulus is plotted in Figure 4.4. Like the yield stress, the elastic modulus is strongly related to the polystyrene content and morphology of the block copolymer⁹⁻¹¹. As seen with the yield stress, there is a decreasing trend with increasing POSS grafting due to the change in polystyrene content. However, there are differences in relative magnitude between the POSS types. For the iBu-POSS, there is a linear trend for the 5% and 10% grafting, which nearly matches the relative magnitudes of the yield stress. This observation suggests that the change in polystyrene content is the major contributor to these mechanical response changes and supports the theory that the iBu-POSS are noninteracting with the polystyrene. The 20% iBu-POSS has a much lower modulus due to its cylindrical morphology. The Ph-POSS has a drop in modulus that is

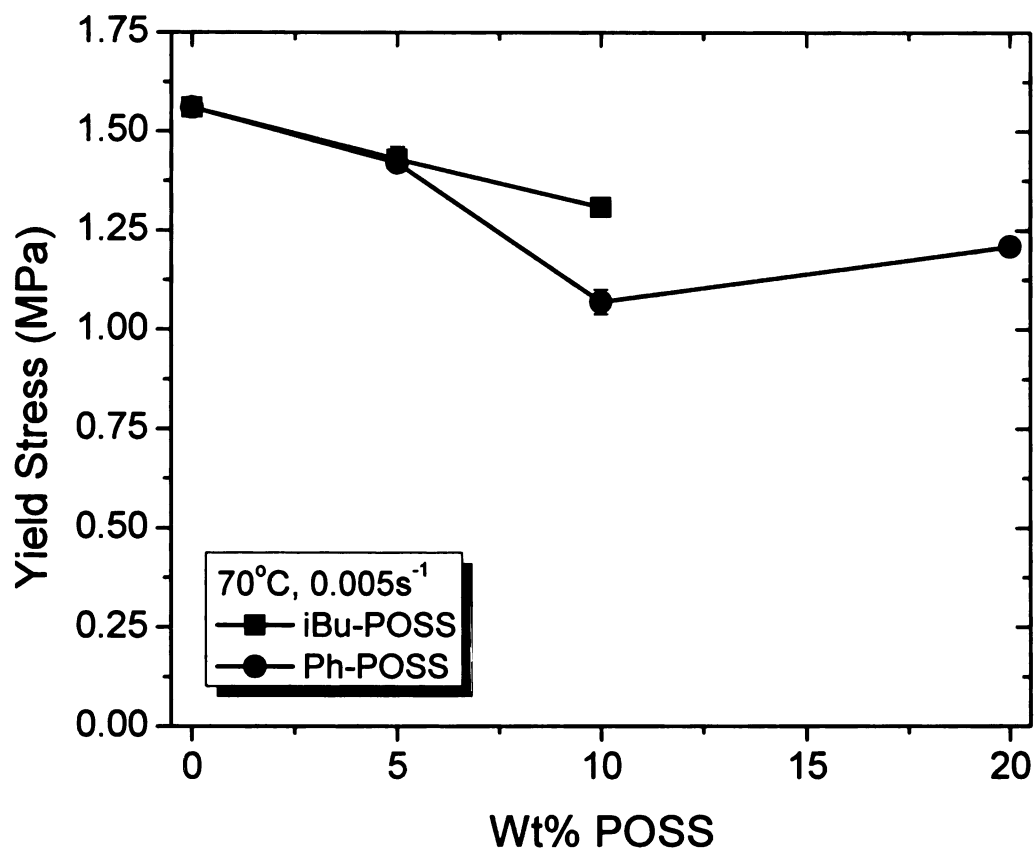


Figure 4.3. Yield stress for the SBS-POSS copolymers at 70°C using a Henky strain rate of 0.005s⁻¹.

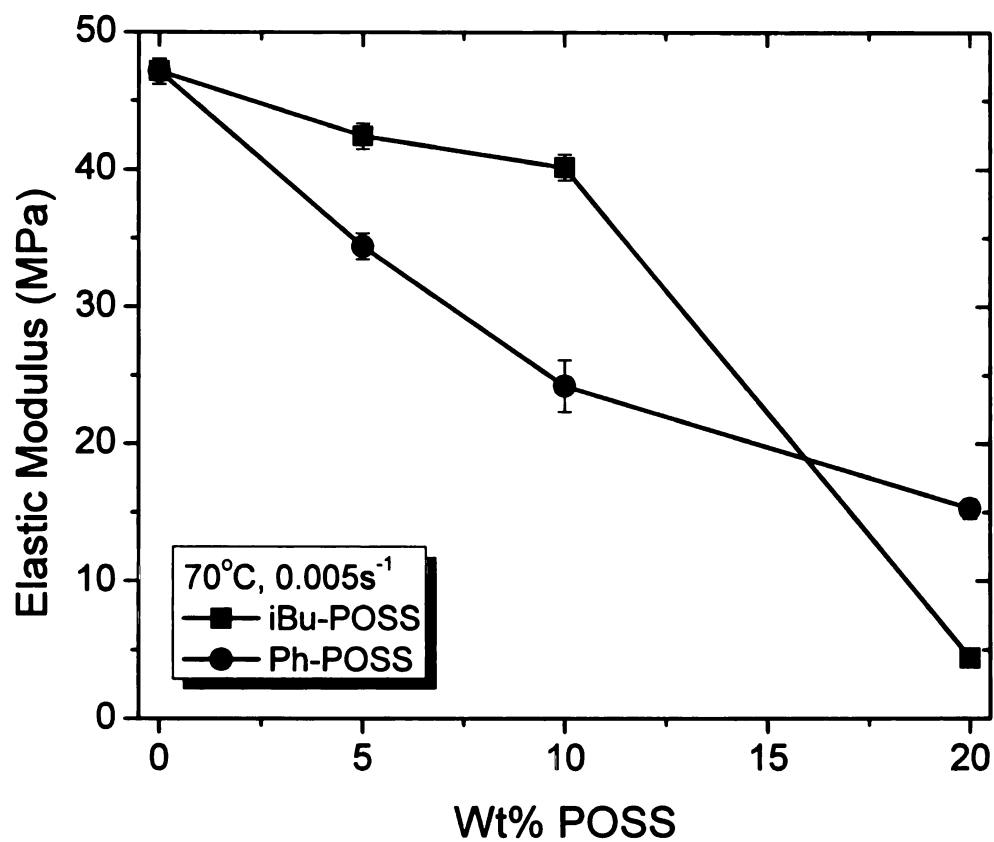


Figure 4.4. The elastic modulus (or Young's modulus) for the SBS-POSS copolymers at 70°C using a Henky strain rate of 0.005s^{-1} .

approximately three times greater than that observed for the iBu-POSS in the 5% to 10% range. There is also a further drop for the 20% Ph-POSS, which differs again from the yield stress data. The difference between nanostructure chemistry results in this disparity between POSS types. As discussed earlier, the iBu-POSS has little effect on the host SBS morphology other than changing the polystyrene content. The Ph-POSS, on the other hand, has a strong affinity toward the polystyrene domain, which effectively disrupts the host SBS morphology. The low strain properties that rely on precise morphological order are undeniably affected. The sharper drop in modulus for the Ph-POSS implies that the elastic modulus is more directly related to the initial morphology than is the yield stress, which is expected.

A more subtle difference between the POSS types is revealed in Figure 4.5. For both the 5% and 10% Ph-POSS, the stress strain curves have an additional drop in modulus compared to the iBu-POSS, which was shown quantitatively in Figure 4.3. At low strains, the lamellar morphology has a critical role in supporting the applied stress. At higher strains, the lamellae get pulled apart and shifted and a preferred orientation develops. In this higher strain range, the Ph-POSS have a relatively higher supported stress than the iBu-POSS. This is most easily observed in the 5 wt% copolymers because of their similar elastic moduli. The two stress-strain curves cross at 0.11 and again at around 0.70 strain. In this strain range, the Ph-POSS has a greater supported stress than the iBu-POSS copolymers despite its lower elastic modulus and equal polystyrene content. This hints that the Ph-POSS act as a greater reinforcement to the SBS, even at this low grafting fraction. Similar behavior is observed in the 10% systems, but there is a

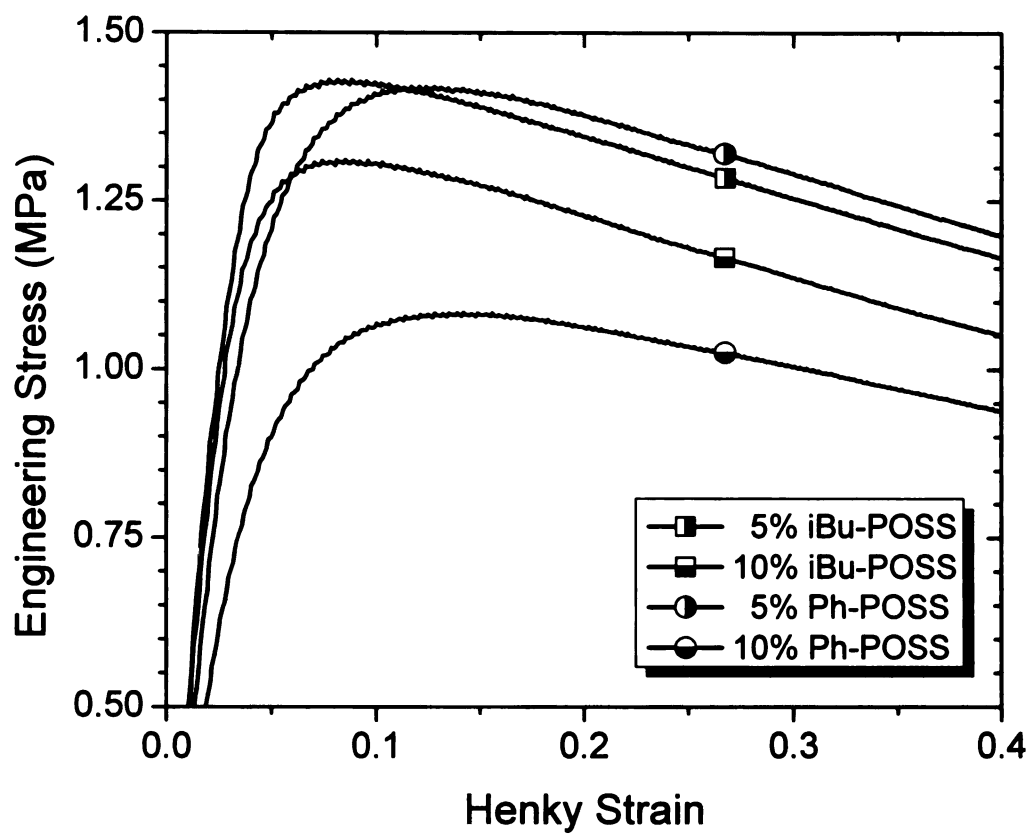


Figure 4.5. Stress-Strain data for 5 and 10 wt% SBS-POSS copolymers at 70°C and using a Henky strain rate of 0.005s^{-1} under tensile deformation for SBS-POSS copolymers.

larger difference in modulus and yield stress. Nevertheless, one can observe that the difference in supported stress between the two 10% copolymers decreases in this same strain range. In a parallel fashion, one can observe the yield strain for these copolymers. There is a higher yield strain for the Ph-POSS copolymers. Because of the lower elastic modulus, there is not significant POSS reinforcement contributing to the initial morphology. The higher yield strain and period of greater supported stress suggests that reinforcement is post-yielding at 70°C. This observed greater high-strain reinforcement for the Ph-POSS is exaggerated in the 20% sample, which hints at high strain reinforcement of the Ph-POSS.

The mechanical response for the SBS-POSS copolymers at 30°C can be observed in Figures 4.6 and 4.7. At 30°C and 0.005s⁻¹ Henky strain rate, the pure lamellar SBS has an elastic response at strains below 3%. It reaches a stress maximum near 6-7%, and again this stress will be noted as the yield stress. After yield, the stress supported by the copolymer decreases until 40% strain and begins to increase until failure. The lower temperature deformation results in a lower yield strain and increasing stress to failure when compared to 70°C. The mechanical responses for the iBu-POSS in Figure 4.6 show the same trends as 70°C. For 5% and 10%, there is little change in the shape of the curve, but instead there is a shift in magnitude that results from the reduced polystyrene content. At 20 wt% iBu-POSS, the morphology has changed from lamellar to cylindrical and there is a substantial drop in modulus and supported stress. Again, the 20% iBu-POSS does not have a yield stress, and will be disregarded in subsequent yield stress discussions. The Ph-POSS has obvious differences than the 70°C data and the 30°C iBu-

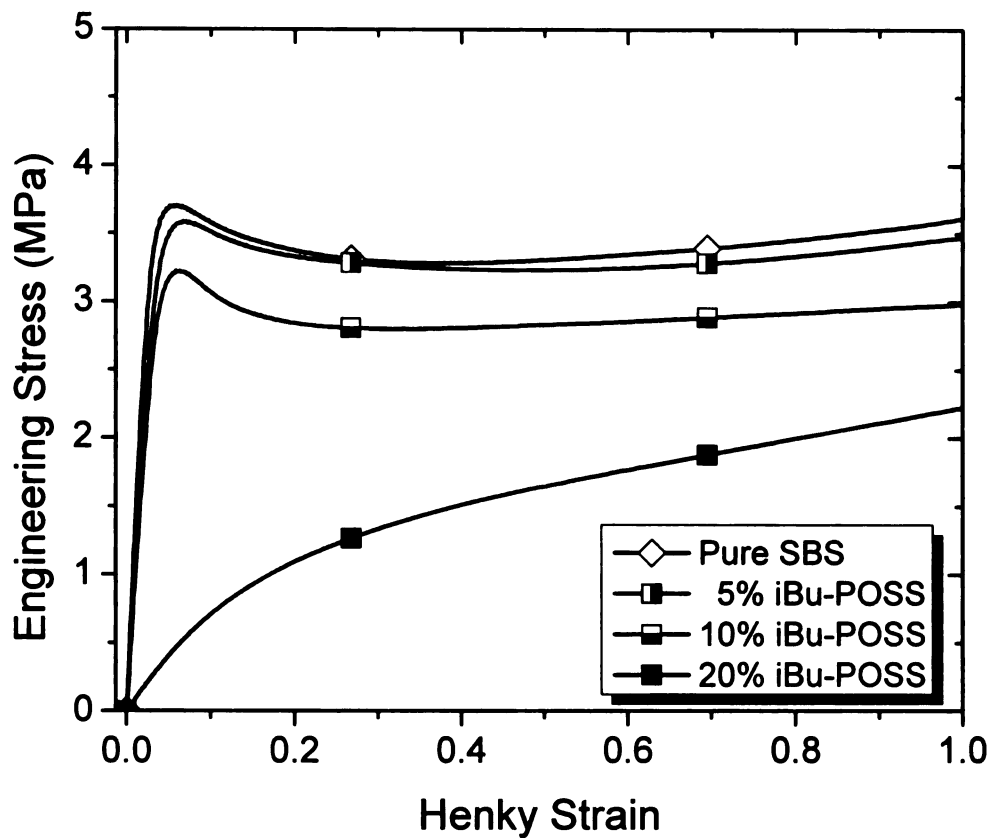


Figure 4.6. Stress-Strain data for isobutyl-POSS copolymers. Testing was performed at 30°C and using a Henky strain rate of 0.005s^{-1} under tensile deformation for SBS-POSS copolymers.

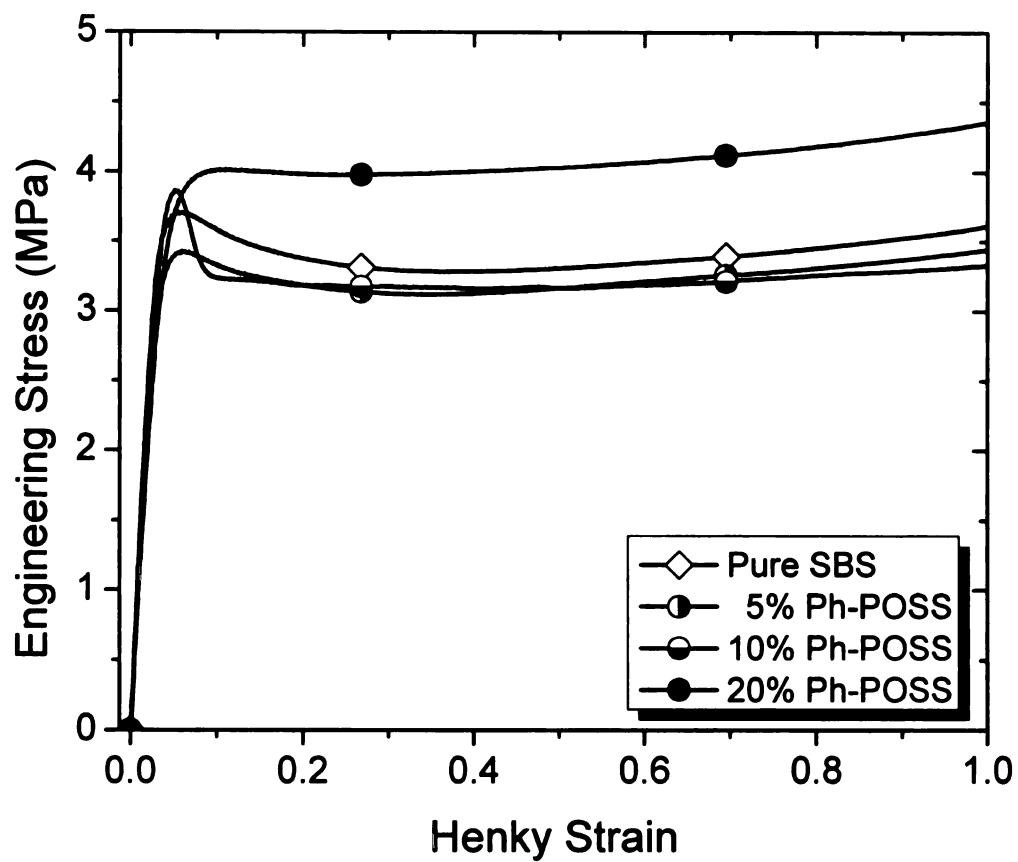


Figure 4.7. Stress-Strain data for phenyl-POSS copolymers. Testing was performed at 30°C and using a Henky strain rate of 0.005s^{-1} under tensile deformation for SBS-POSS copolymers.

POSS data as well. The most noticeable difference is the 10% Ph-POSS in Figure 4.7, which has a higher yield stress than pure SBS and a sizeable, abrupt drop in stress after yielding. The 20% Ph-POSS also has an increased yield stress than pure SBS; the highest yield stress of all SBS-POSS copolymer tested.

Figure 4.8 compares the stress-strain curves of the 5% and 10% SBS-POSS copolymers. The difference between the 5% iBu and 5% Ph-POSS is barely discernable outside of the change in magnitude. The 10% iBu-POSS has an additional drop in modulus and supported stress that is similar to what is observed at 70°C. The 10% Ph-POSS behavior differs significantly from what is seen at 70°C. At 30°C, it shows a large drop in stress after yielding and a relatively constant post-yield stress. This is consistent with stable neck formation during deformation. In polymer systems containing polystyrene, necking is often connected with the presence of a continuous polystyrene phase. Block copolymer illustrations of this include a parallel orientation of a single domain of lamellar morphology¹¹ and the gyroid phase⁶⁷. In the lamellar example, the single domain parallel orientation has polystyrene lamellae that extend the gage length of the specimen, but the unoriented gyroid morphology has a continuous polystyrene network created by the morphology.

It is possible that the Ph-POSS act to create a PS network that extends the length of the sample in the 10% Ph-POSS copolymer. The SAXS data show that a lamellar morphology is still present, but the Ph-POSS may act as a bridge between the lamellar polystyrene sheets. The polystyrene lamellae bridged by Ph-POSS may act together to complete a three-dimensional network. However, grafting 10 wt% means only about

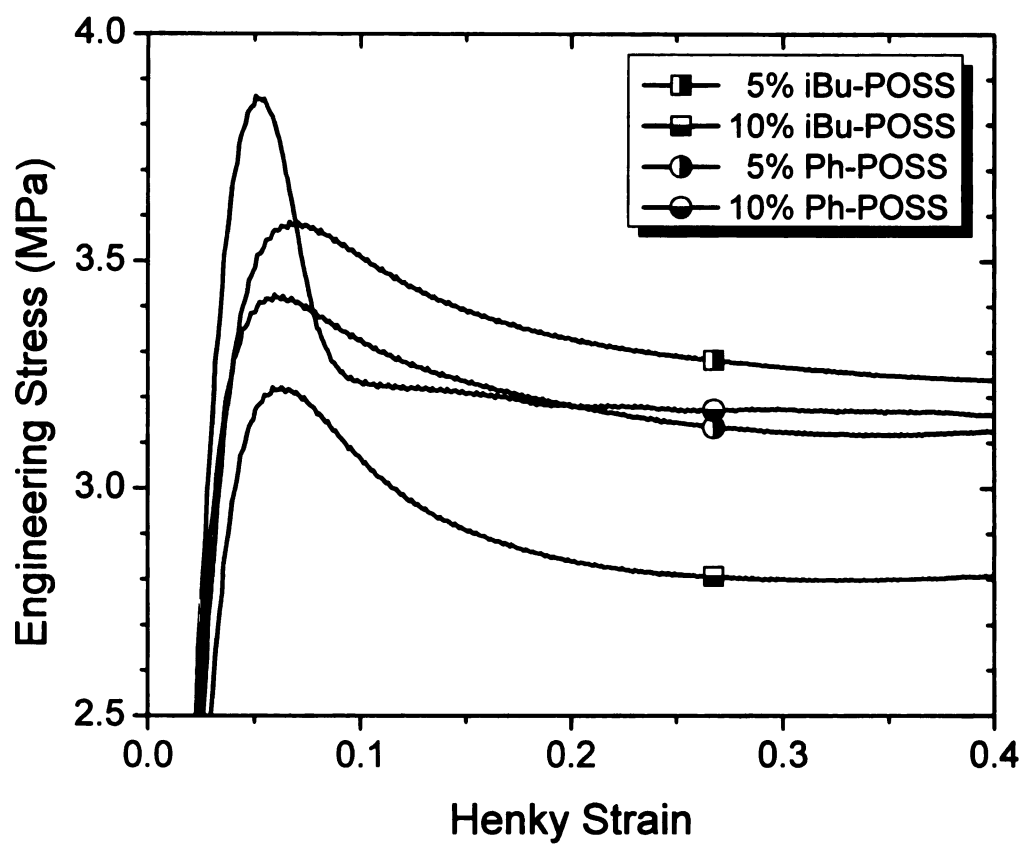


Figure 4.8. Stress-Strain data at 30°C and 0.005s⁻¹ Henky strain rate for 5 and 10 wt% SBS-POSS copolymers.

13% of the polybutadiene volume is occupied by POSS. It is unlikely that Ph-POSS bridges could span one entire polybutadiene layer let alone many layers. A three-dimensional polystyrene network may not necessarily extend via POSS from polystyrene lamella to lamella directly through the polybutadiene. Instead, it may be through the domain (grain) boundary. A reduced domain size is anticipated for the disrupted morphologies of 10% and 20%, and these domain boundaries can connect the polystyrene lamellae between domains. With the further addition of Ph-POSS to 20 wt%, the same stable necking does not occur. In this case, the lamellar morphology may be so disrupted that the polystyrene lamellae disintegrate at low strain. The Ph-POSS may still act to reinforce or bridge the surviving polystyrene fragments. In both the 10% and 20% Ph-POSS there would be an expected decrease in yield stress and modulus because of disturbed morphology, but the observed increase supports the theory of Ph-POSS contributing to mechanical reinforcement differently at the lower temperature.

The yield stress at 30°C and 0.005s⁻¹ Henky strain rate are shown in Figure 4.9. Again, the iBu-POSS copolymers show the same trend as 70°C. The 5% and 10% iBu-POSS are in the range of the ideal 95% and 90% of the pure SBS respectively. For Ph-POSS, 5% is again on the order of the 5% iBu-POSS; however, the 10% and 20% have increased in relation to the pure SBS and other copolymers at 70°C. At 70°C, they are less than pure SBS but are greater than pure SBS at 30°C.

The elastic moduli for the SBS-POSS copolymers, plotted in Figure 4.10, follow the yield stress trend but differ in magnitude. There is a decreasing trend with increasing POSS grafting due to the change in polystyrene content. For the iBu-POSS, there is a

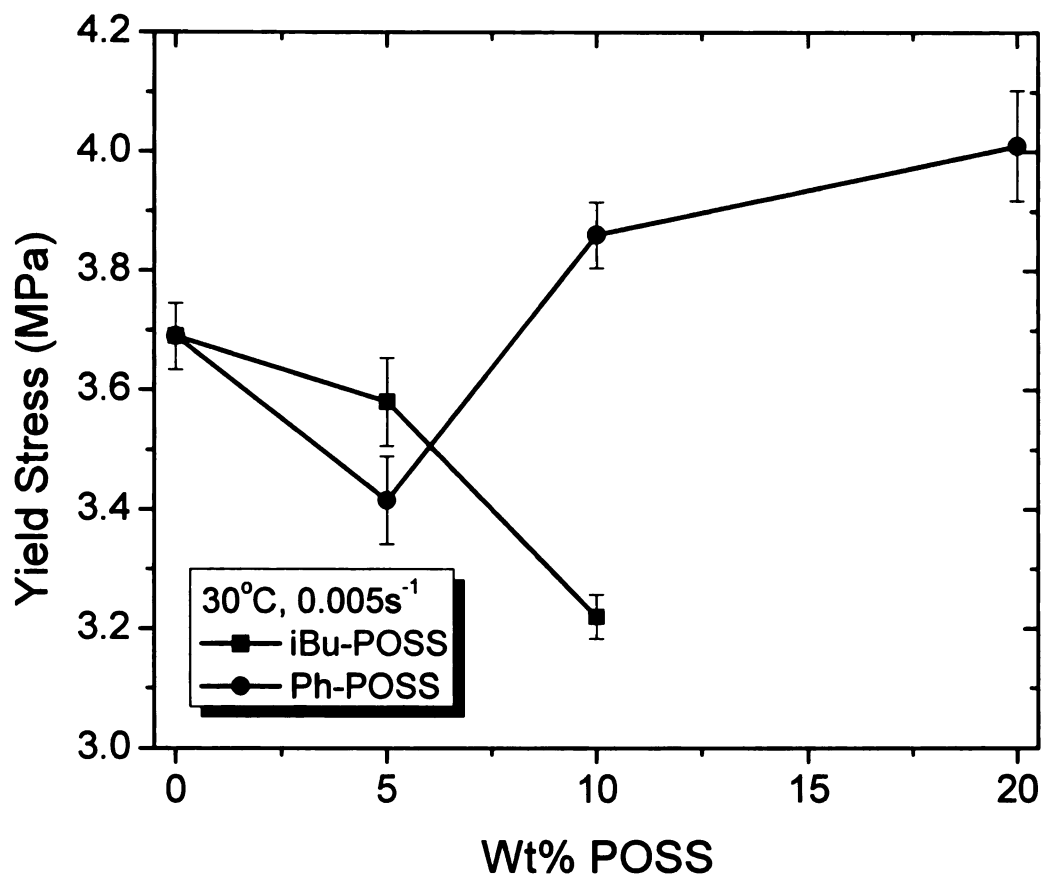


Figure 4.9. Yield stress for the SBS-POSS copolymers at 30°C using a Henky strain rate of 0.005s^{-1} .

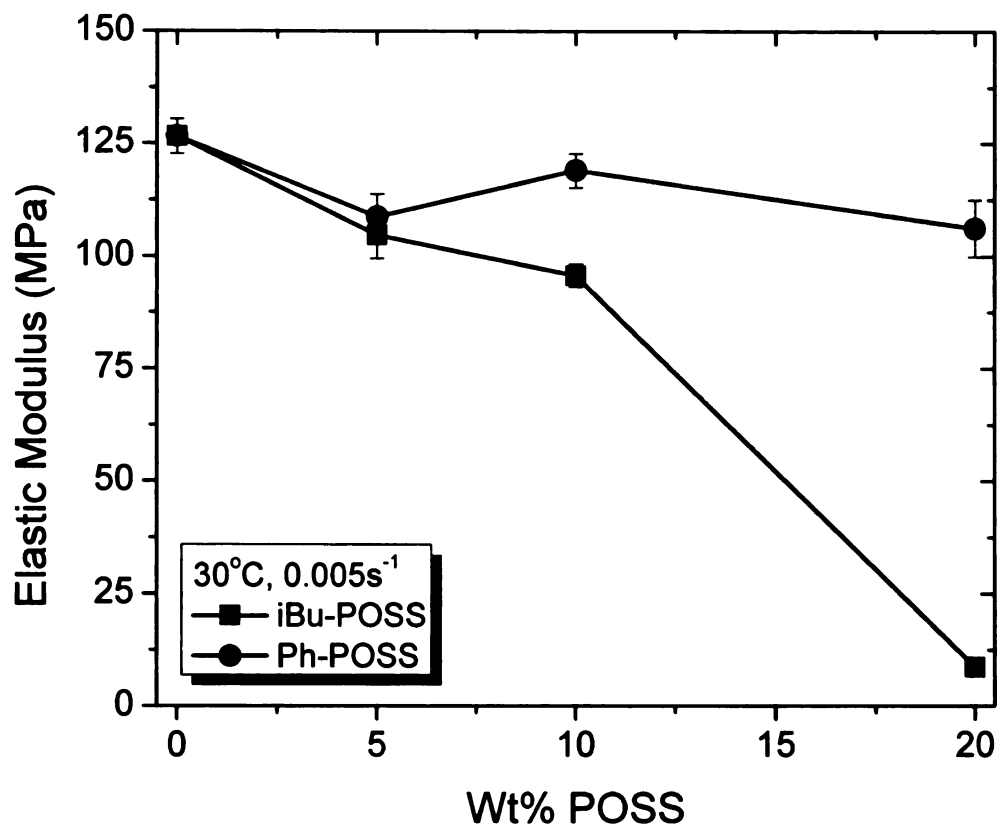


Figure 4.10. The elastic modulus (or Young's modulus) for the SBS-POSS copolymers at 30°C using a Henky strain rate of 0.005s^{-1} .

linear trend for the 5% and 10% grafting, and the 20% iBu-POSS has a much lower modulus. The difference in modulus trend from 70°C is that the Ph-POSS has a greater elastic modulus than the iBu-POSS at the lower temperature. The 5% Ph-POSS is greater than the 5% iBu-POSS, though its difference is on the order of experimental error. There is a relative jump in modulus for 10% Ph-POSS resembling the yield stress, but 20% drops to near the 5% Ph-POSS modulus. One would expect that the disrupted lamellar morphology of the 10% and 20% Ph-POSS would have a lower modulus than their respective iBu-POSS counterpart, but it is not the case. Again, reinforcement is present for the Ph-POSS copolymers. The morphology has a greater observable effect on the modulus, which accounts for the relatively lower 20% Ph-POSS modulus.

The influence of temperature on the yield stress and elastic modulus is shown in Figures 4.11 and 4.12, respectively. In Figure 4.11, temperature has the same effect on yield stress for pure SBS, 5% and 10% iBu-POSS, and 5% Ph-POSS. The 10% and 20% Ph-POSS copolymers show a significantly higher yield stress ratio, which means there is greater reinforcement for this property at lower temperatures relative to the pure SBS. The modulus data in Figure 4.12 show a slightly different trend. For the iBu-POSS there is a relatively small decrease in the elastic modulus ratio with increasing POSS showing little temperature effect. The Ph-POSS modulus, on the other hand, is strongly affected by temperature.

Both yield stress and elastic modulus data show that reinforcement effects for Ph-POSS are more significant at lower temperatures (if the reinforcement was equal at both temperatures, the data would match pure SBS). It is important to note that both yield

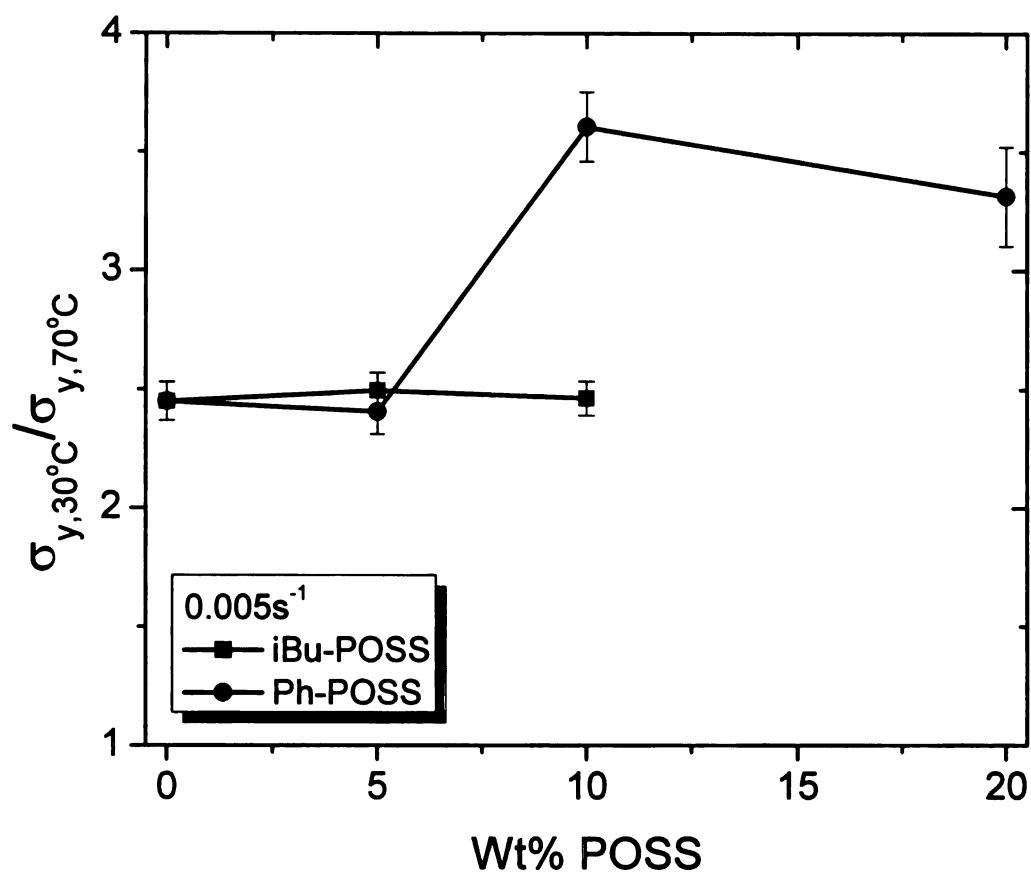


Figure 4.11. The ratio of the yield stress, σ_y , at 30°C to the yield stress at 70°C for a 0.005s^{-1} Henky strain rate.

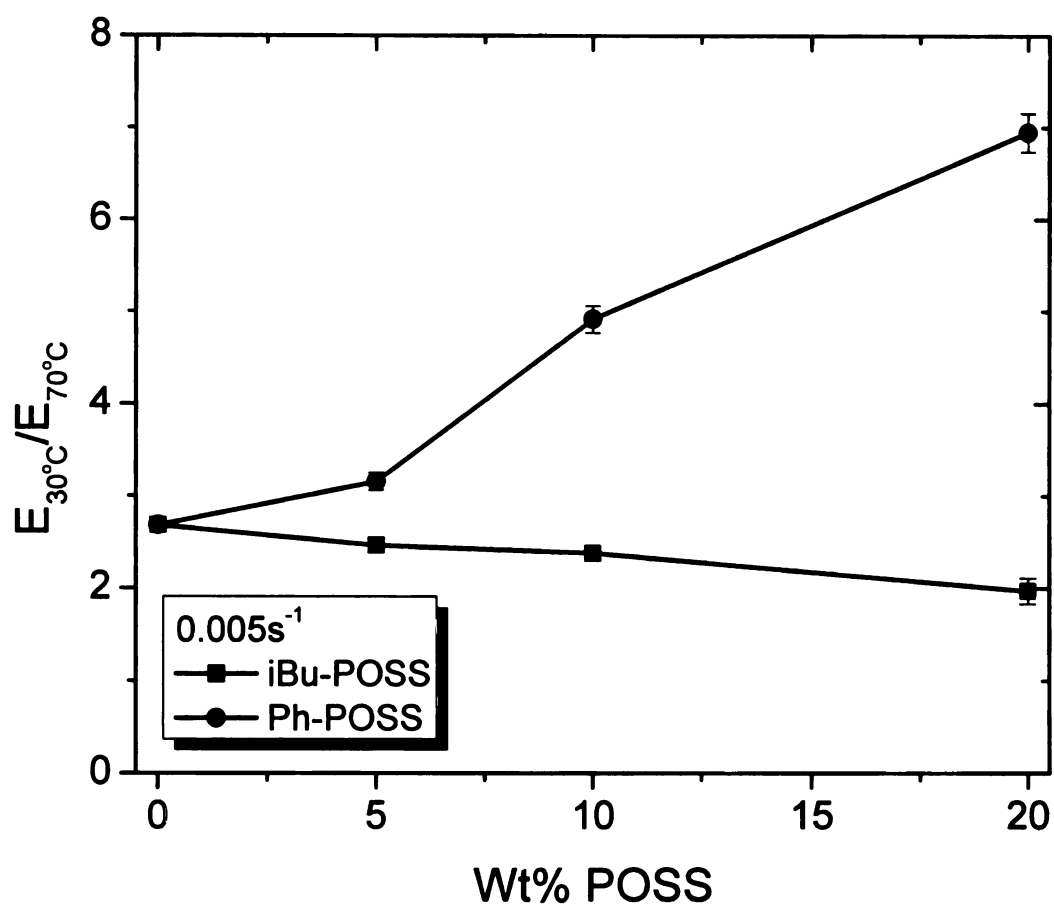


Figure 4.12. The ratio of the elastic modulus at 30°C to the elastic modulus at 70°C for a 0.005s^{-1} Henky strain rate.

stress and elastic modulus are low strain properties. The variation in trends between yield stress and modulus likely arises from the different strain ranges the two properties cover: elastic modulus $\lesssim 3\%$ and yield strain $\approx 7\%$. The elastic modulus, in the lowest strain range, is principally affected by the initial morphology of the copolymer. As strain increases to the yield strain, the morphology begins to deform, so larger effects of POSS reinforcement begin to emerge. Additional reinforcement is possible at higher strains as observed by the 20% Ph-POSS yield strain at 70°C, but it is difficult to find a comparable, quantitative material property at these high strains.

The effects of yield stress on strain rate at 30°C and 70°C are shown in Figure 4.13. The plot shows the yield stress, σ_y , normalized to temperature for pure SBS, 10% iBu and 10% Ph-POSS. Three strain rates of 0.001, 0.005, and 0.050s⁻¹ are plotted. The vertical shift between the temperatures shows that the yield stress is temperature dependent. The nonzero slope of the lines connecting each material indicates that the yield stress is also strain rate dependent. The slope for each line is approximately equal indicating that the strain rate dependence is the same for each material at both temperatures.

In order to correlate the effects of temperature and strain rate to the yield stress, one can use Eyring's model of the flow of solids⁶⁸. The model begins from a molecular foundation, where an atom, molecule, or polymer segment must pass over an energy barrier in moving from one position to another within the solid. Without an applied stress, this jumping is infrequent and random. Under an applied stress, the energy barrier for jumping decreases in the direction of applied stress. A consequence of this reduced

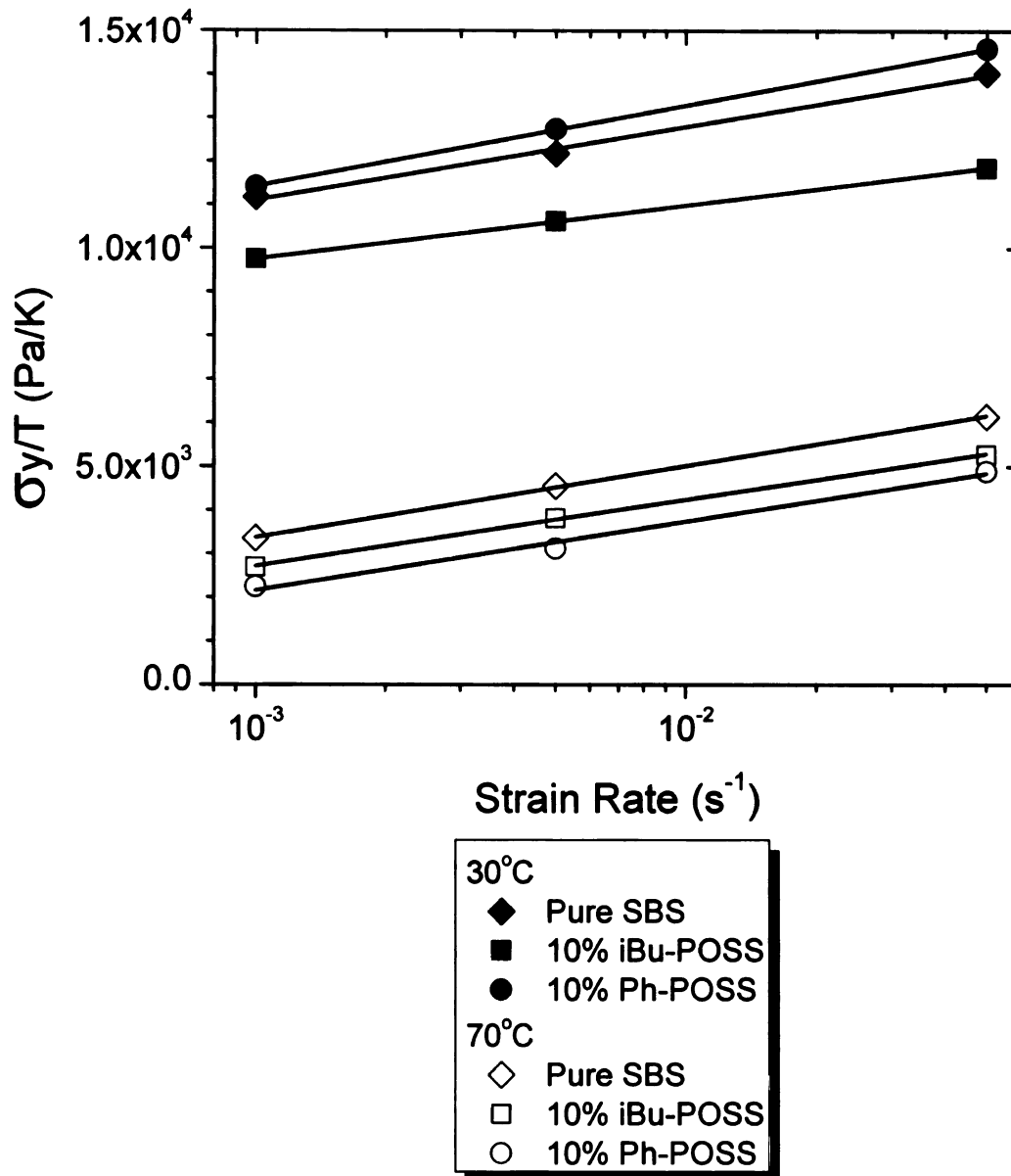


Figure 4.13. Yield stress data normalized to temperature (Kelvin) for three strain rates (0.001 , 0.005 , $0.050 s^{-1}$) and two temperatures ($30^\circ C$ and $70^\circ C$). Data is shown for pure SBS, 10 wt% iBu-POSS, and 10 wt% Ph-POSS.

energy barrier is a faster jumping rate in this direction resulting in an observable strain.

Eyring's equation is as follows:

$$\frac{\sigma_y}{T} = \frac{2}{V^*} \left(\frac{\Delta H}{T} + R \ln \left(\frac{\dot{\epsilon}_y}{\dot{\epsilon}_0} \right) \right) \quad (4.1)$$

where σ_y is the yield stress, T is the temperature, V^* is the activation volume in which the polymer segment (in this case) acts, ΔH is the energy barrier for jumping, R is the molar gas constant, $\dot{\epsilon}_y$ is the applied strain rate, and $\dot{\epsilon}_0$ is a constant. The slopes of the lines in Figure 4.13 are used to calculate V^* . ΔH can be calculated by comparing σ_y / T at constant $\dot{\epsilon}_y$ or by comparing $\dot{\epsilon}_y$ at constant σ_y / T .

Table 4.1 lists the calculated values for V^* and ΔH for the three materials in Figure 4.13. V^* is slightly greater for the 10% grafted systems, but the difference is on the order of experimental error. The interpretation of this in terms of the Eyring model is that the interaction volume for segmental jumping during deformation is increased after the grafting of POSS. An increase in V^* is reasonable considering that POSS are being added to the butadiene backbone in the grafting process. The difference in enthalpy barrier between the pure and POSS copolymers is on a comparably larger scale. The 10% iBu-POSS has a ΔH similar to the pure SBS, but the 10% Ph-POSS has a ΔH greater. From the viewpoint of the Eyring model, the increased ΔH signifies that the Ph-POSS grafting has created a greater energy barrier for segmental jumping. The electronic properties of the POSS nanostructures apparently have a greater role in determining the energy barrier rather than they do the interaction volume. Ph-POSS at or near the

Table 4.1. Values are calculated using Eyring's model on the flow of solids. V^* is based on the data at 70°C and ΔH is calculated using the data from the 0.005s⁻¹ Henky strain rate.

Material	V^* (m³/mol)	V^* error (m³/mol)	ΔH (kJ/mol)	ΔH error (kJ/mol)
Pure SBS	0.0233	± 0.0011	236.8	± 6.9
10 wt% iBu-POSS	0.0253	± 0.0017	231.8	± 11.3
10 wt% Ph-POSS	0.0243	± 0.0022	289.8	± 3.9

polystyrene-polybutadiene interface may be the cause for the greater ΔH . The presence of POSS crystallites, as observed by WAXS, may be another contributor for the higher ΔH . Analysis of the SBS-POSS copolymer microstructure can assist in the discernment of how Ph-POSS acts to reinforce the grafted copolymers.

4.3.2. *Small Angle X-ray Scattering*

During tensile deformation of block copolymers, changes in morphology can be observed using SAXS. Figure 4.14 shows a two-dimensional SAXS pattern at 70°C for pure SBS (a) before deformation and (b) at 0.3 Henky strain. Because the diffraction plane normal is coplanar with the incident and diffracted beam, the intensity of the diffraction pattern is a direct expression of the morphology in a given orientation. By qualitatively examining the diffraction pattern in Figure 4.14, one can see that the morphology is coupled to the strain field: dilating in the tensile direction (q^* decreases) and compressing in the transverse direction (q^* increases). There is also a change in the overall orientation of the morphology from random (isotropic intensity) to a preferred orientation (anisotropic intensity).

A more quantitative analysis of the morphology is preformed by examining slices of the diffraction pattern in directions of interest. For instance, integrating along the stretching direction $\pm 5^\circ$ can yield information about the morphology of lamellar sheets oriented orthogonal to the stretching direction (lamellae normal coincident with the stretching direction). Likewise, integrating perpendicular to the stretching direction can yield information about the morphology of lamellae oriented along the stretching direction. The hexagonally packed cylindrical structure has two-dimensional order, so

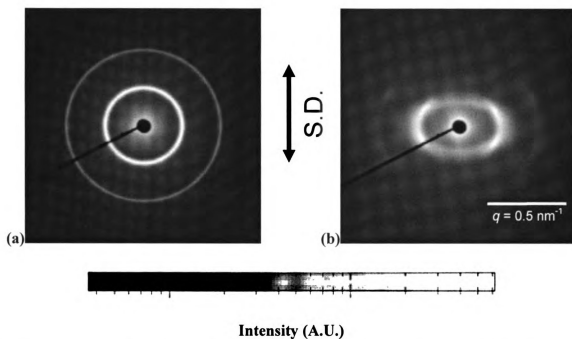


Figure 4.14. Two-dimensional SAXS patterns (through view) for (a) undeformed, pure SBS and (b) SBS deformed to a Henky strain of 0.3. Deformation was at a rate of 0.005s^{-1} in the stretching direction shown (S.D.) and at 70°C . Intensity is in arbitrary units.

there is not a one-to-one correspondence to the one-dimensional lamellar order. As a result, the 20% iBu-POSS will be omitted from the following analysis, so that only a comparison between lamellar morphologies is required.

The SAXS experiments for this study used an x-ray beam with a cross-section measuring 0.5mm x 0.5mm. This method gives diffraction data from a small fraction of the material gage length during deformation. Thickness variations along the length of the sample can lead to a difference between the macroscopic strain and local strain field. In order to insure proper interpretation of SAXS information, the data will be plotted vs. the local strain as measured by SAXS. The local Henky strain, ε_{local} , was calculated as:

$$\varepsilon_{local} = \ln \left(\frac{d_{SD}}{d_0} \right) \quad (4.2)$$

where d_{SD} is the d-spacing in the stretching direction measured by integrating $\pm 5^\circ$ from the stretching direction and d_0 is the undeformed d-spacing.

As mentioned earlier, peak width, Γ , is a quantitative measure of the morphology and is correlated to the local order of the morphology. Figure 4.15 plots Γ in the stretching direction (Γ_{SD}) normalized to the undeformed Γ for each SBS-POSS copolymer at 70°C and a rate of 0.005⁻¹. Because the q -range changes significantly during deformation, Γ was calculated in terms of real-space units instead of q -space. For pure SBS, Γ_{SD} increases during deformation. This corresponds to a decrease in the morphological order as the lamellae sheets are pulled apart. The iBu-POSS copolymers have nearly identical behavior to the pure SBS. This is because the iBu-POSS is noninteracting with polystyrene and merely changes the polystyrene content of the

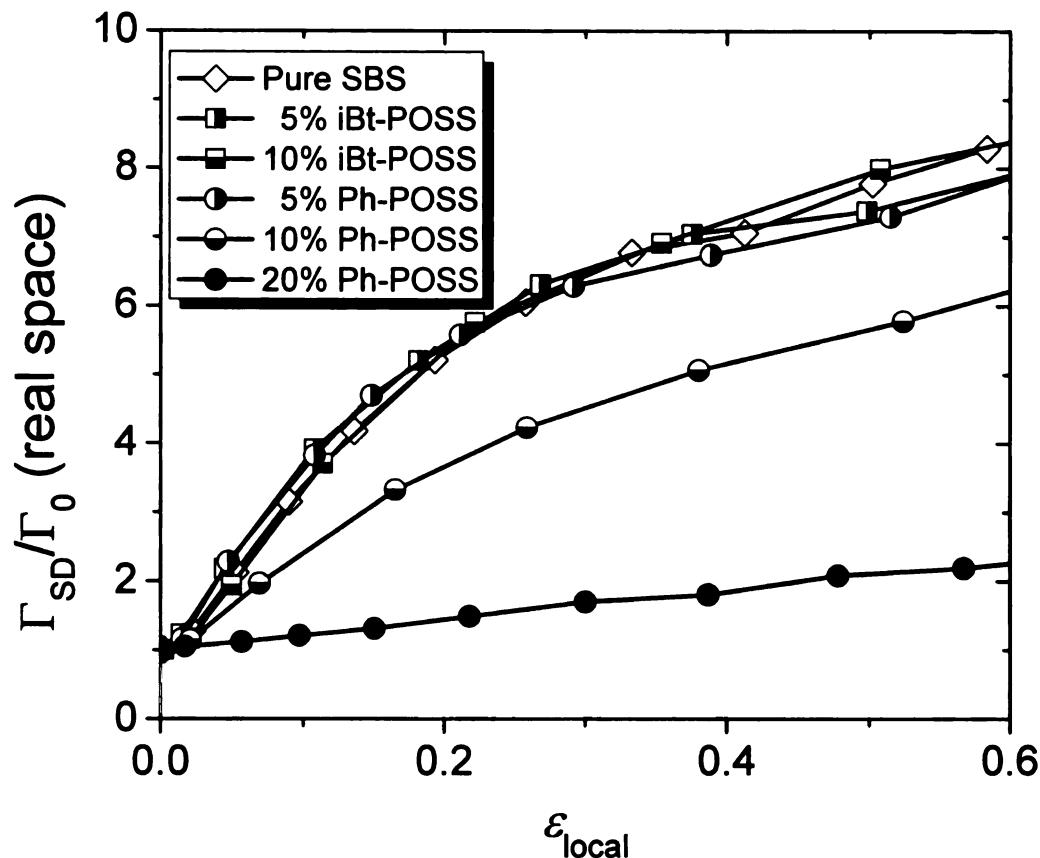


Figure 4.15. The normalized peak width in the stretching direction is plotted vs. the local strain, ϵ_{local} , for all lamellar morphology copolymers. Tensile deformation was performed at 70°C using a Henky strain rate of 0.005s⁻¹. To obtain the values of Γ_{SD} , the 2-D diffraction pattern is integrated $\pm 5^\circ$ along the stretching direction. From the subsequent plot of I vs. q , Γ is correlated to real-space measurements and is then normalized to the undeformed peak width for each individual copolymer.

copolymer. The Ph-POSS, on the other hand, has a more remarkable behavior during deformation. The 5% Ph-POSS has little apparent change from the pure SBS and iBu-POSS copolymers. The increased grafting of the 10% Ph-POSS shows a striking change compared to the unmodified systems. In the 10% Ph-POSS copolymer, the peak width has a smaller change during the deformation. The 20% Ph-POSS has an even more dramatic difference compared to the other systems. This implies that the 10% and 20% Ph-POSS copolymer morphologies are better preserved during the deformation process.

The preserved peak width and morphological order should not be confused with the overall morphological order because there is a large difference in peak width between the undeformed pure SBS and 20% Ph-POSS. Figure 12 shows that the Ph-POSS morphologies are better preserved relative to the undeformed morphology during deformation. Figure 13 shows the real-space peak width in the stretching direction for the pure SBS and Ph-POSS copolymers. The peak width for the Ph-POSS copolymers is initially greater than the pure SBS, which is indicative of the disrupted morphology. The copolymer morphologies are strained at an equivalent rate, but the pure SBS morphology becomes more disordered earlier than the Ph-POSS copolymers. At even a modest morphology strain of 0.15, the 20% Ph-POSS has a similar morphological order (as observed by peak width) to the pure SBS. Upon further deformation, the Ph-POSS peak width is narrower than pure SBS for all Ph-POSS grafting. The same analysis can be extended to primary peak intensity, and analogous conclusions are drawn. All three of the Ph-POSS copolymers collapse onto a similar peak width trend that is narrower than the pure SBS.

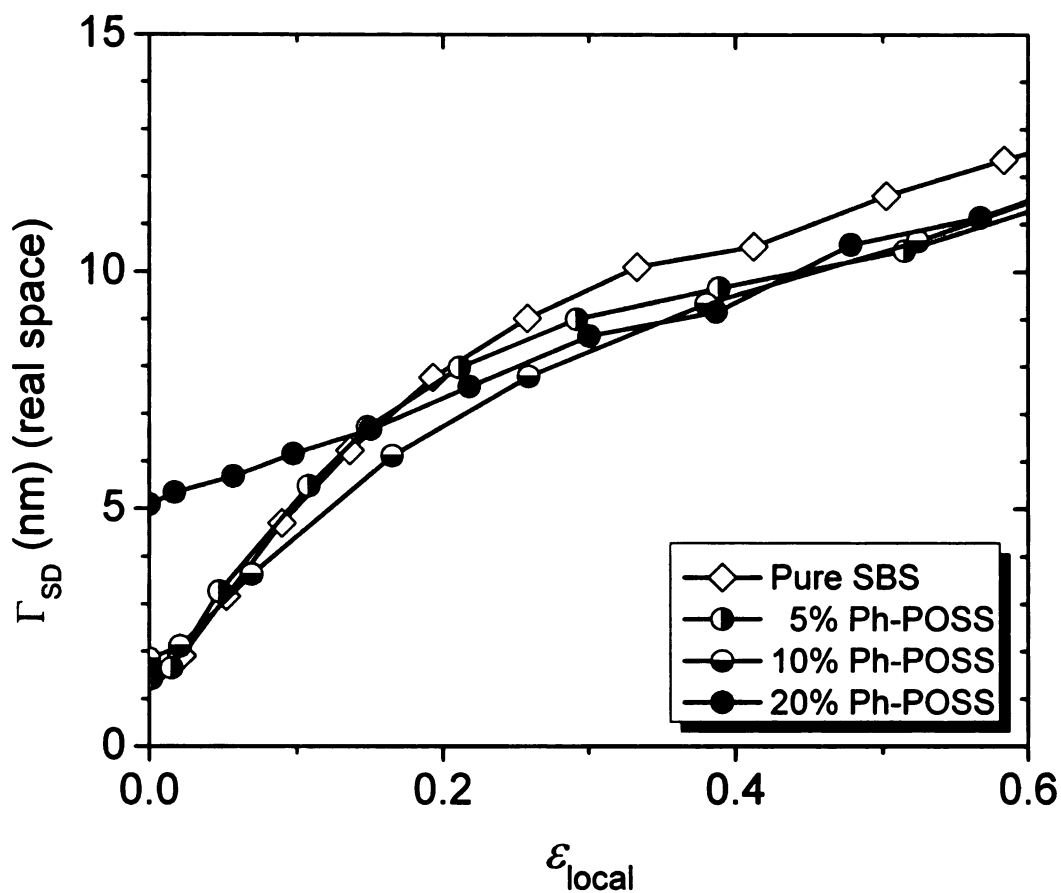


Figure 4.16. The real-space peak width in the stretching direction is plotted vs. the local strain, ϵ_{local} , for pure SBS and Ph-POSS copolymers. Tensile deformation was performed at 70°C using a Henky strain rate of 0.005 s^{-1} . To obtain the values of Γ_{SD} , the 2-D diffraction pattern is integrated $\pm 5^\circ$ along the stretching direction. From the subsequent plot of I vs. q , Γ is correlated to real-space measurements.

The peak width in Figures 4.15 and 4.16 are slices of the 2-D diffraction pattern that look at the lamellae whose normals coincide with the stretching direction. These figures are essentially a 1-D slice of a 3-D morphology structure. As seen in Figure 4.14, the SBS lamellae develop a preferred orientation during deformation. By quantitatively examining the preferred orientation of these patterns, one can gain a better understanding of the changes in the morphology in three dimensions. The overall orientation of the morphology is best represented by Herman's orientation function, f , given by Equation 4.3:

$$f = \left(3 \langle \cos^2 \mu \rangle - 1 \right) / 2 = \left(\frac{\int_0^{\pi/2} \int_0^{q_1} I(q, \mu) q^2 (\cos^2 \mu) dq d\mu}{\int_0^{\pi/2} \int_0^{q_1} I(q, \mu) q^2 (\sin \mu) dq d\mu} - \frac{1}{2} \right) \quad (4.3)$$

where $I(q, \mu)$ is the intensity of the two-dimensional diffraction pattern as a function of scattering vector q and azimuthal angle μ . The equation relates the diffraction intensity, which is assumed to be proportional to the number of diffracting planes, to the lamellae orientation, whose planes are normal to the direction of diffraction intensity. $f \rightarrow 0$ for a random orientation, $f \rightarrow 1$ for lamellae perfectly aligned in the stretching direction (lamellae normals orthogonal to the stretching direction), and $f \rightarrow -0.5$ when the lamellae are oriented orthogonal to the stretching direction (lamellae normals in the stretching direction). A more detailed discussion of Herman's orientation function can be found in the Appendix.

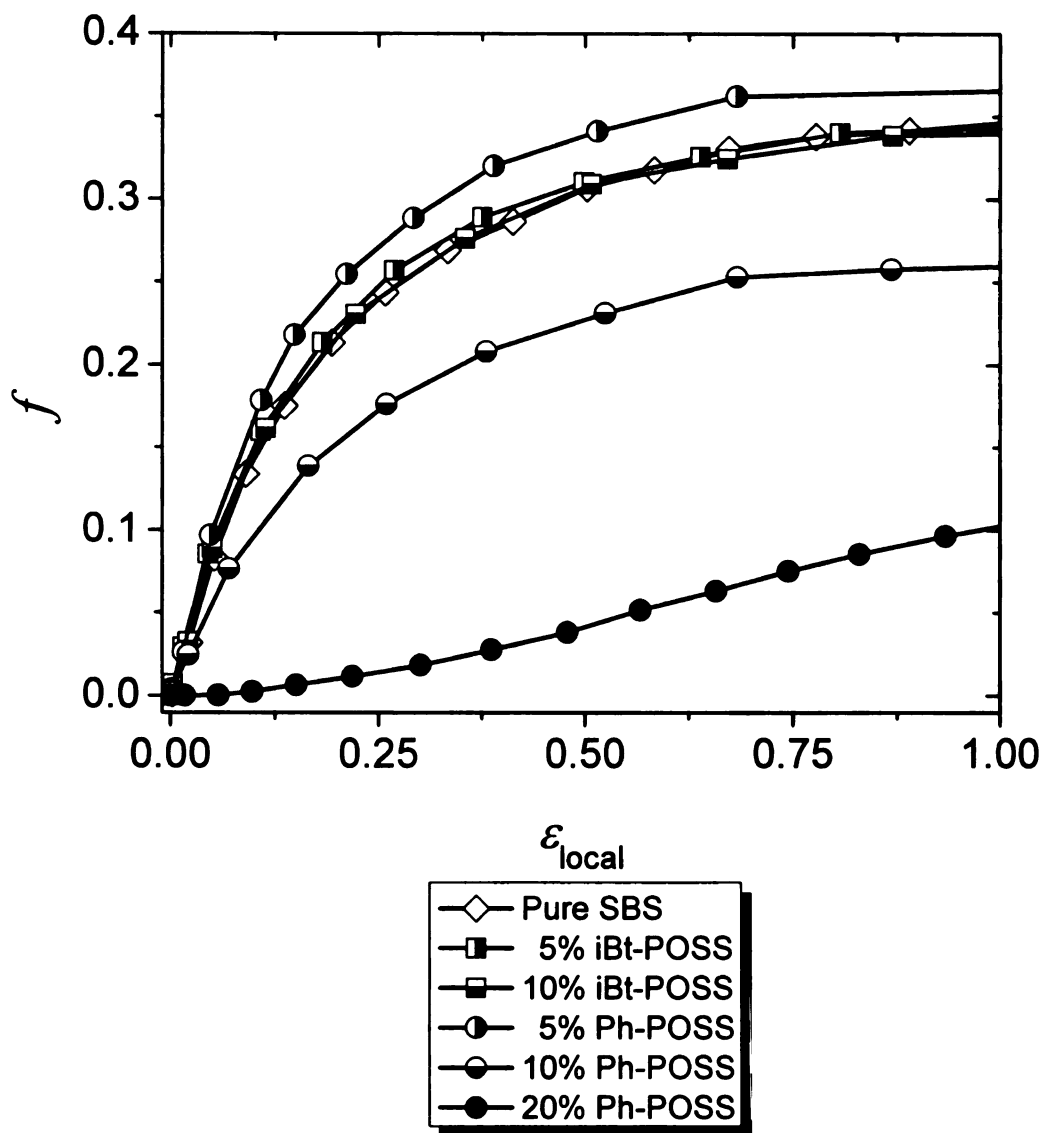


Figure 4.17. Herman's orientation function, f , is plotted vs. the local strain, ϵ_{local} , for the lamellar morphology SBS-POSS copolymers under tensile deformation at 70°C using a Henky strain rate of 0.005s⁻¹. The Herman's orientation function was calculated by integrating over the primary scattering peak q -range.

Herman's orientation function, f , is plotted vs. the local strain for the pure SBS and SBS-POSS copolymers at 70°C with a Henky strain rate of 0.005s⁻¹ in Figure 4.17. For unmodified SBS, the lamellae become oriented along the stretching direction as observed by an increase in f with strain. The rate of orientation change is greatest at low strains, levels off, and reaches a maximum lamellae alignment at higher strains. For the iBu-POSS copolymers, there is little difference from pure SBS. This can again be attributed to its noninteracting nature with the polystyrene phase, and in that sense is similar to the peak width data. The Ph-POSS again show behavior different than pure SBS. For the 5% Ph-POSS copolymer, there is a greater orientation change compared to the unmodified system. The 10% and 20% show a restricted orientation change. The restricted orientation change at high Ph-POSS loadings is similar to the peak width data in that there is a better preserved morphology during the deformation process, i.e. the strained morphology better resembles the undeformed morphology. In case of orientation change, it is more understandable that the Ph-POSS are acting to network the morphology. This network is possible because of the favorable enthalpic interaction of Ph-POSS with itself and the polystyrene domains. The Ph-POSS network bridges the polystyrene domains, and during deformation may act to preserve the order of the morphology and restrict orientation changes. The 5% Ph-POSS, at first glance, seems to deviate from this in Figure 4.17 by having greater orientation change.

There may be several contributing factors which stem from the fact that only a small fraction of Ph-POSS are grafted. First, unlike 10% and 20%, the 5% Ph-POSS has a better preserved morphology; the intensity and peak width are on the order of pure SBS and the iBu-POSS copolymers. The preserved morphology and lower fraction of POSS

suggest fewer POSS at the polystyrene-polybutadiene interface. As a result the POSS will play a slightly different role than in the 10% and 20% copolymers where these POSS disrupt the morphology and the polystyrene-polybutadiene interface. Another contributor to this anomalous behavior may be how f is defined in Equation 4.3. Intensity is assumed to be proportional to the number of diffraction planes. Intensity in particular directions (for instance the stretching direction) can decrease because the lamellae disintegrate and order is lost or because lamellae are tilted away from the diffraction condition (change orientation). Thus, reduced diffraction intensity in the transverse direction or preserved diffraction intensity in the stretching direction have the same effect on f . This would mean that the observed increase in f for the 5% Ph-POSS can be the result of preserved diffraction intensity from lamellae oriented along in the stretching direction, i.e. lamellae normals orthogonal to the stretching direction for 5%. To accompany these possible explanations, it has also been observed that lightly cross-linked SBS above $T_{g,PS}$ show a greater increase in f with deformation. The intensity observation and lightly cross-linked theories are supported by the previously stated hypothesis of a Ph-POSS network.

The peak width for the 30°C deformation data is shown in Figure 4.18. As in Figure 4.15, Γ in the stretching direction is normalized to the undeformed Γ for each SBS-POSS copolymer. Peak width increases faster at the lower temperature, so there is a lower strain at which the diffraction peaks are stretched beyond reliable fitting. For pure SBS, Γ_{SD} increases during deformation. The increase in Γ_{SD} is mild in the elastic range before reaching the yield stress. Above the yield stress, Γ_{SD} increases significantly. The iBu-POSS copolymers have nearly identical behavior to the pure SBS. This is similar to

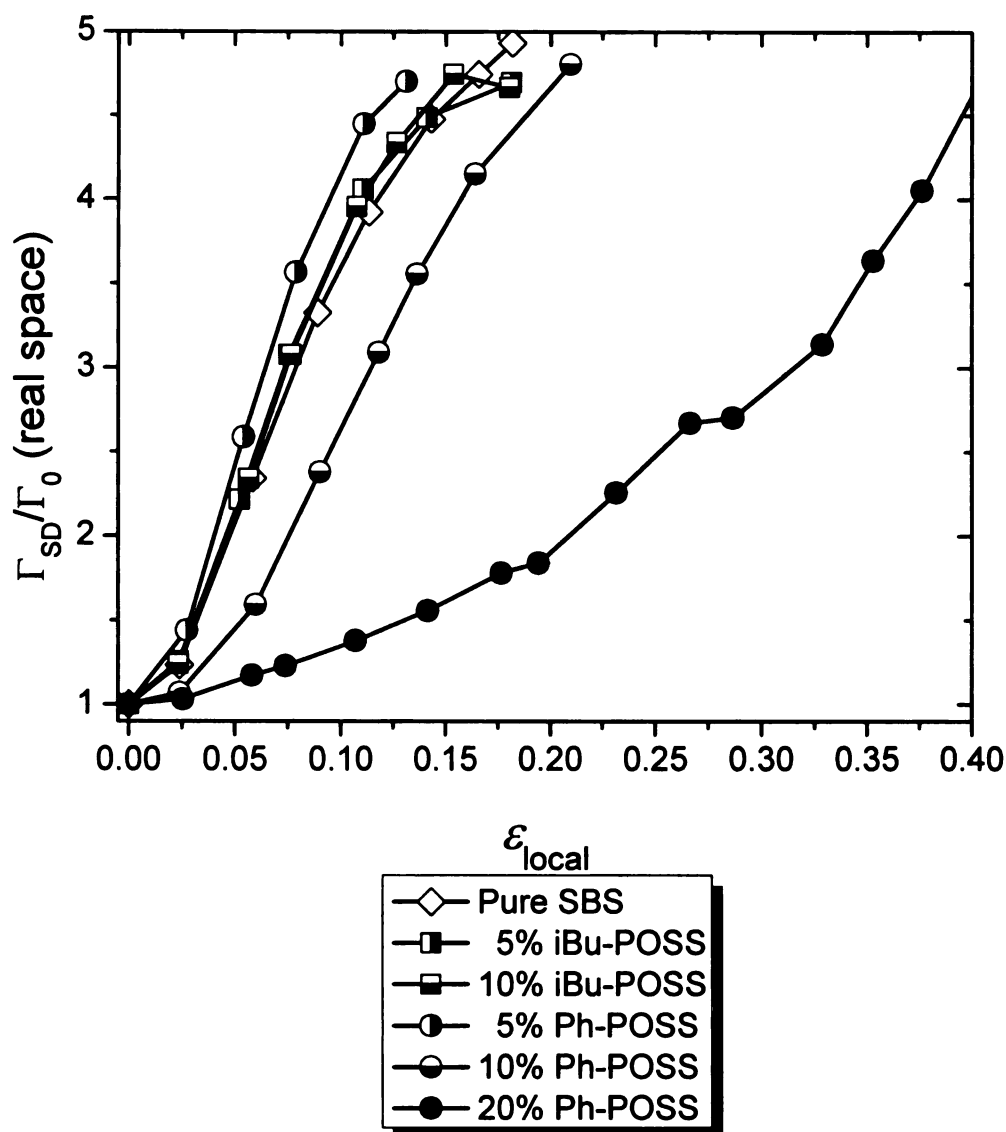


Figure 4.18. The normalized peak width in the stretching direction is plotted vs. the local strain, ϵ_{local} , for all lamellar morphology copolymers. Tensile deformation was performed at 30°C using a Henky strain rate of 0.005s⁻¹. To obtain the values of Γ_{SD} , the 2-D diffraction pattern is integrated $\pm 5^\circ$ along the stretching direction. From the subsequent plot of I vs. q , Γ is correlated to real-space measurements and is then normalized to the undeformed peak width for each individual copolymer.

the 70°C data because the iBu-POSS is noninteracting with polystyrene and merely changes the polystyrene content of the copolymer. The Ph-POSS again has a more remarkable behavior. The 5% Ph-POSS has a slightly higher relative peak width than pure SBS and iBu-POSS copolymers. The increased grafting of the 10% Ph-POSS shows a striking change compared to other copolymers. In the 10% Ph-POSS copolymer, the peak width has a smaller change during the deformation. The 20% Ph-POSS has an even more dramatic difference compared to the other systems. This implies that the 10% and 20% Ph-POSS copolymer morphologies are better preserved during the deformation process.

Figure 4.19 plots f vs. the local strain at 30°C with a Henky strain rate of 0.005s^{-1} . For unmodified SBS, the lamellae become oriented along the stretching direction as observed by an increase in f with strain. The rate of orientation change is greatest at low strains, and f reaches maximum lamellae alignment at higher strains. For the iBu-POSS copolymers, there is little difference from pure SBS. This can again be attributed to its noninteracting nature with the polystyrene phase, and in that sense is similar to the peak width data. The Ph-POSS again show behavior different than pure SBS. Like 70°C, the 5% Ph-POSS copolymer has a greater orientation change, and the 10% and 20% show a restricted orientation change compared to the unmodified system.

The magnitude of f has also changed; $f_{30^\circ\text{C}} < f_{70^\circ\text{C}}$. At temperatures farther below $T_{g,\text{PS}}$, the polystyrene lamellae are more brittle and tend to break up during deformation rather than shift orientation. This is evident in the lower strain to peak disappearance and lower f . 20% Ph-POSS has a negative f meaning little or no change in lamellae

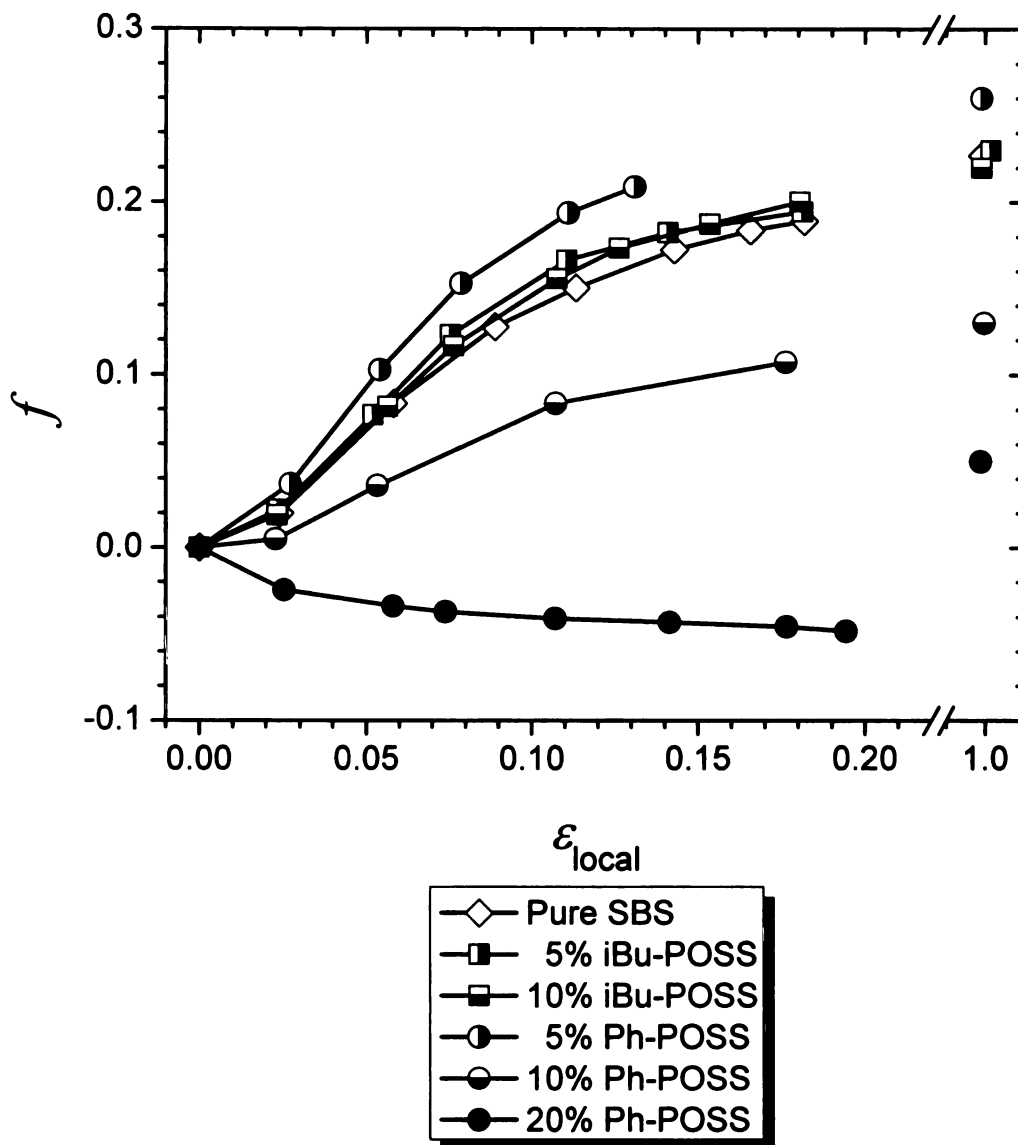


Figure 4.19. Herman's orientation function, f , is plotted vs. the local strain, ϵ_{local} , for the lamellar morphology SBS-POSS copolymers under tensile deformation at 30°C using a Henky strain rate of 0.005s⁻¹. The Herman's orientation function was calculated by integrating over the primary scattering peak q -range. f at 1.0 Henky strain is measured at the command strain.

orientation. The intensity of the 2-D diffraction pattern in the stretching direction is well-preserved showing almost no change, while the intensity in the normal direction diminishes. This is associated with lamellae that are stronger (i.e. retain their character more) when their normals are coincident with the stretching direction compared to when their normals are orthogonal to the stretching direction. To be certain of what exactly causes the negative f at 70°C, a detailed look at the deformation mechanisms of oriented copolymers is necessary. The f data also show the same temperature trends as the yield stress and modulus data where 10% and 20% Ph-POSS copolymers have more significant reinforcement (f is relatively lower) at 30°C compared to 70°C.

4.3.3. *Wide-angle X-ray Scattering (WAXS)*

The nature of the Ph-POSS crystallites during deformation was examined in further detail using deformation experiments. Figure 4.20 shows the Ph-POSS crystallite diffraction peaks in 20% Ph-POSS at selected strains during deformation. These deformation experiments were performed at a stretching rate of 0.005s^{-1} at 30°C. The intensities in Figure 4.20 are normalized to constant incident and transmitted intensities in order to compensate for differences in thickness, which decreases as the film is stretched. There are several features of the figure that are worthy of mention. The intensity of the diffraction peaks decrease with strain, and the width at half maximum increases concurrently. The intensities of the diffraction peaks are well-preserved in comparison to the morphology. The POSS crystallite diffraction intensity falls to 70% in the stretching direction at a Henky strain of 1.22, but the pure SBS morphology intensity falls to 70% at 0.04 at the same temperature. Crystalline diffraction peak broadening is

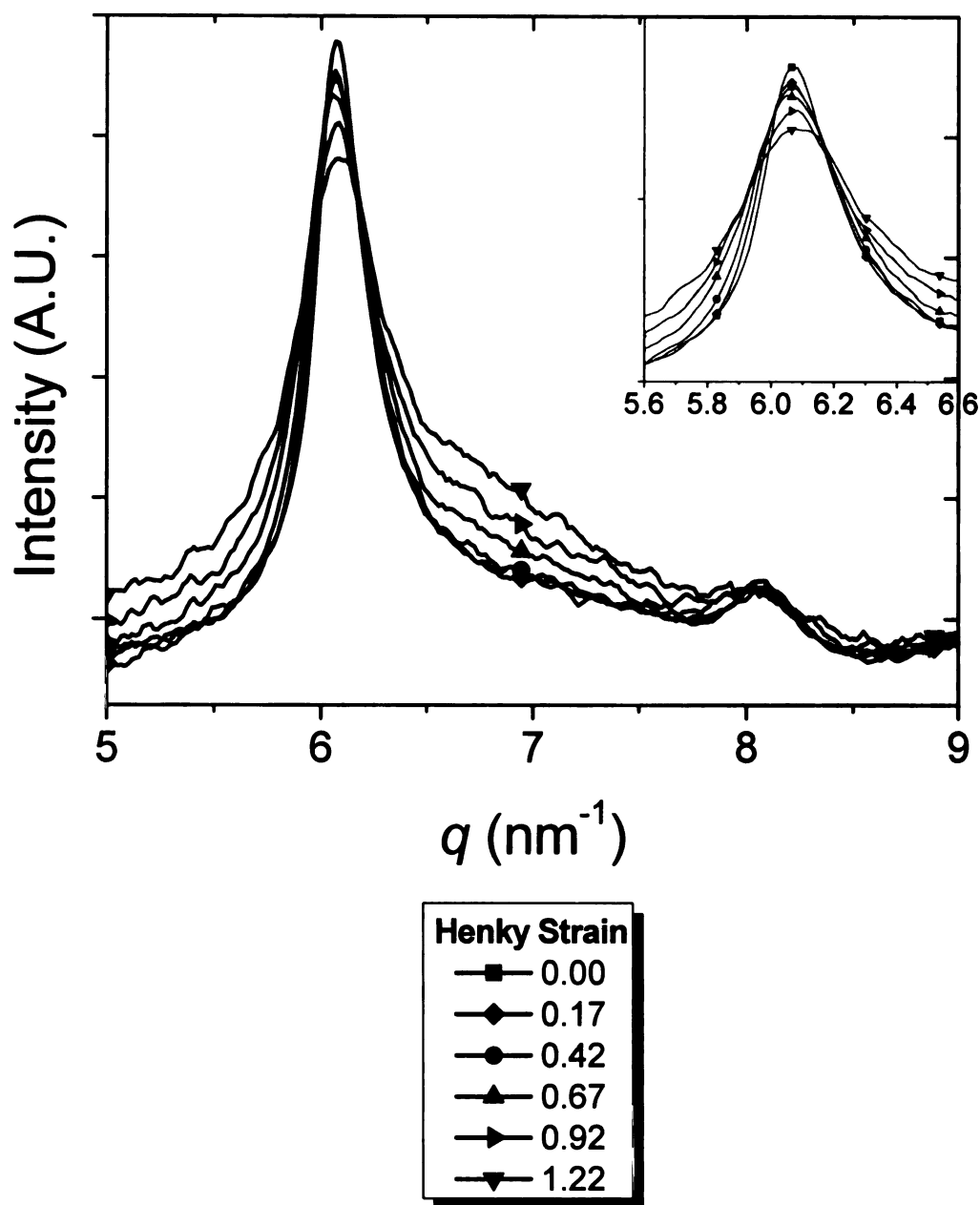


Figure 4.20. X-ray scattering data is plotted over a q -range of crystalline Ph-POSS during the deformation of 20% Ph-POSS. Intensity is in arbitrary units and is normalized to constant incident and transmitted intensities to compensate for thickness changes during deformation. Deformation was performed at 30°C using a Henky strain rate of 0.005s⁻¹. Data has been integrated 360° azimuthally.

generally caused by either a nonuniform strain or a decreasing crystallite size. By examining the diffracted intensity in the stretching and transverse directions, there is no observable change in d-spacing which if present would indicate strain. It is difficult to rule out nonuniform strain completely because there may be changes in strained crystallite orientation similar to that seen with the block copolymer morphology. It is likely that decreasing crystallite size is contributing to the peak width changes as well. As the SBS-POSS copolymer is deformed, crystallite structures may be pulled apart due to the chemical attachment of Ph-POSS to the polybutadiene block.

The differences between the diffraction data for the Ph-POSS crystallites and the block copolymer morphology during deformation generate information about the relative strength of POSS-POSS interactions and morphology stability. Figure 4.21 shows the local Henky strain for the morphology and crystallites of the 20% Ph-POSS copolymer along with the local morphology strain of pure SBS for comparison. The morphology strain is closely coupled to the command strain, as expected. The crystallites are strained to a maximum of 0.006. Figure 4.22 compares peak width in the stretching direction, Γ_{SD} , for the 20% Ph-POSS morphology and crystallites to the pure SBS morphology. Unlike the d-spacing, Γ_{SD} increases continuously, but its increase is at a much slower rate than the pure SBS and 20% morphologies.

The Ph-POSS crystallites have preserved intensity, minute d-spacing shift, and little broadening, all of which indicate that the crystallite POSS-POSS interaction is stronger than the SBS morphology. This is to be expected since the bond strength in crystals is often greater than in liquids or amorphous materials. The possibility of

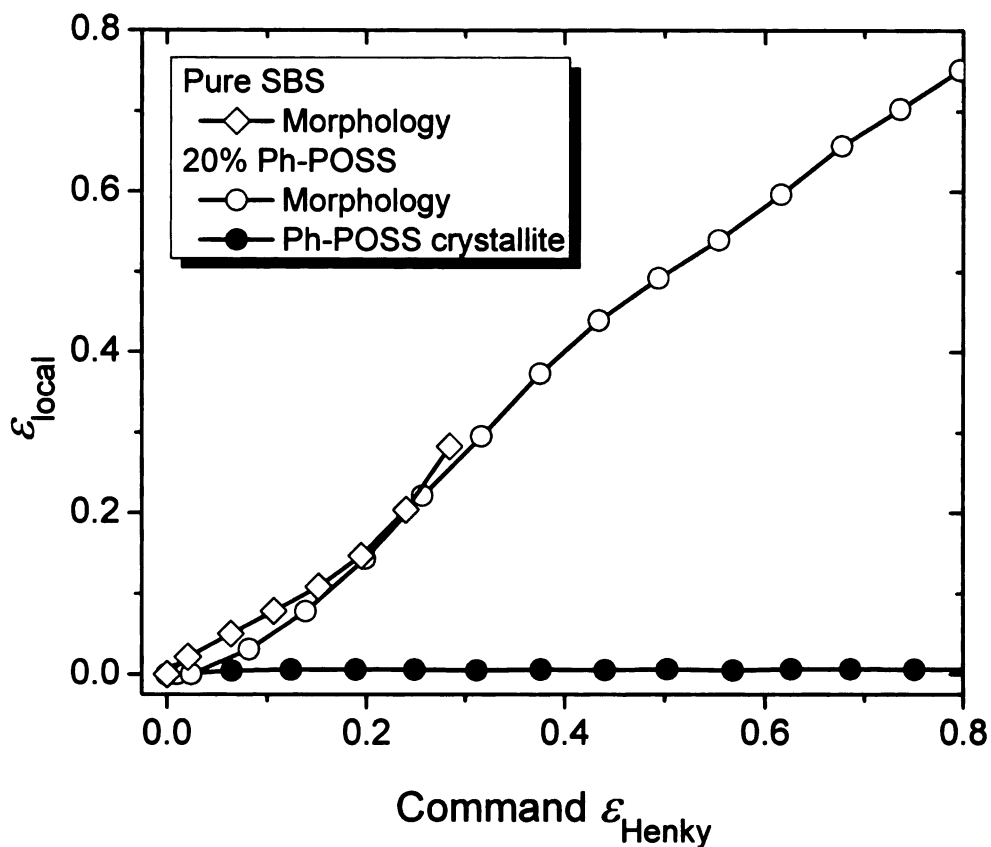


Figure 4.21. The local Henky strain of the morphology and Ph-POSS crystallites (as defined by Equation 4.2) is plotted vs. the command Henky strain. Data are plotted for the morphologies of pure SBS and 20% Ph-POSS along with crystallite data in the 20% Ph-POSS copolymer. Tensile deformation was performed at 30°C using a Henky strain rate of 0.005^{-1} .

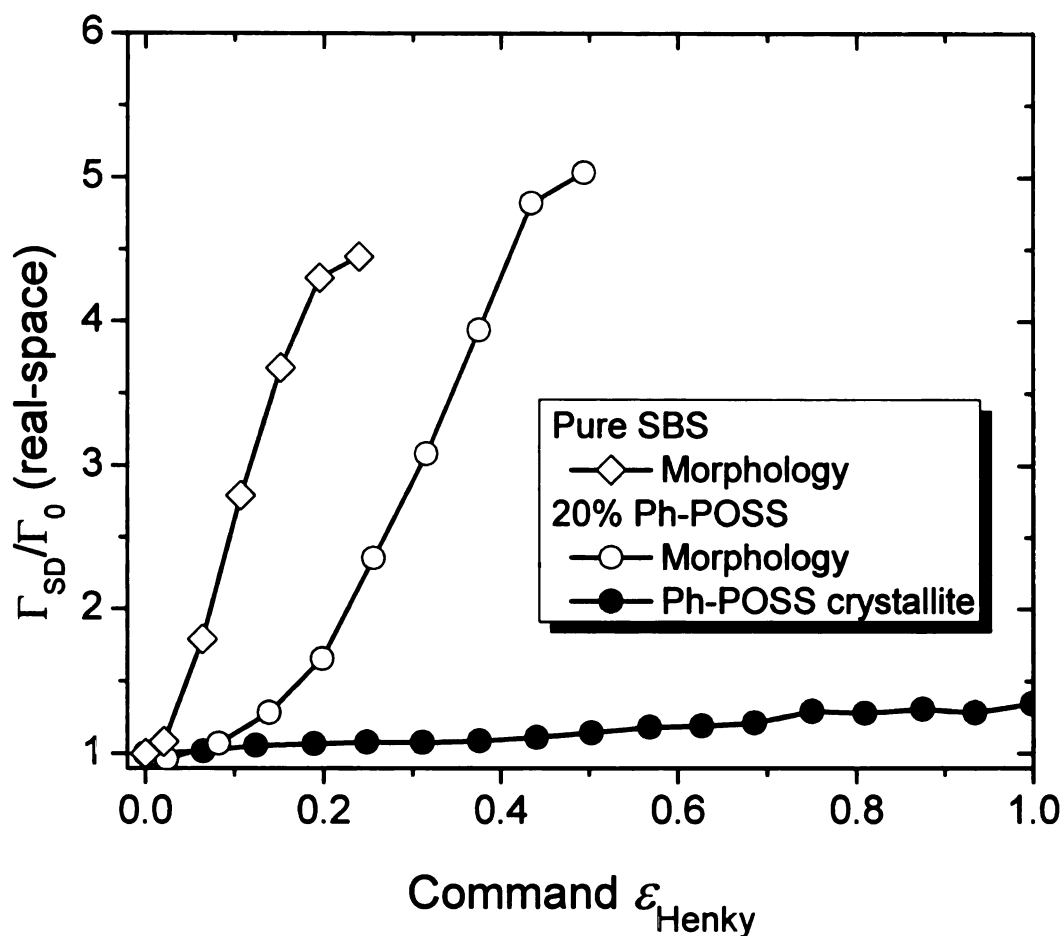


Figure 4.22. The normalized peak width in the stretching direction is plotted vs. the local strain for the morphologies of pure SBS and 20% Ph-POSS along with crystallite data in the 20% Ph-POSS copolymer. Tensile deformation was performed at 30°C using a Henky strain rate of 0.005s^{-1} . To obtain the values of Γ_{SD} , the 2-D diffraction pattern is integrated $\pm 5^\circ$ along the stretching direction. From the subsequent plot of I vs. q , Γ is correlated to real-space measurements and is then normalized to the undeformed peak width for each individual copolymer.

crystallite formation has two main criteria: ungrafted (and ultimately the grafted) POSS nanostructures must be able to crystallize and the POSS cannot be soluble in (or have favorable interactions with) the phase which it is grafted to. Both iBu-POSS and Ph-POSS have the ability to crystallize in their ungrafted form. However, the iBu-POSS is soluble within the polybutadiene phase and does not form crystallites. The Ph-POSS is insoluble in the polybutadiene phase and forms crystallites. Ph-POSS, as stated previously, has an affinity to and is soluble in the polystyrene domain, but complete phase separation is impossible because of the attachment to the polybutadiene block.

The presence of Ph-POSS crystallites is certainly a contributing factor to the reinforcement of the 20% Ph-POSS copolymer morphology. The relative strength and stability of these crystallites offer opportunity for reinforcement even at higher strains. Thus, these POSS-POSS connections are the main reinforcement mechanism for the high strain behavior of the 20% Ph-POSS in Figure 4.2. The Ph-POSS crystallites are similar to a crosslink junction for the polybutadiene. In the same way, POSS-POSS interactions are likely responsible for the reinforcement seen in the lower Ph-POSS loadings compared to the iBu-POSS in 4.5.

The contribution of possible POSS reinforcement mechanisms differ between 30°C and 70°C because of the glassy nature of the polystyrene at lower temperatures. This allows for a greater contribution from the small grain size reinforcement mechanism. At 30°C, polystyrene is stiffer, and in Figures 4.6 and 4.7 the high strain POSS crystallite reinforcement is not as noticeable; partly because when the morphology is broken apart at higher strains the residual polystyrene segments serve the same function as the crystallites.

4.4. CONCLUSIONS

The deformation studies supplement the previous findings regarding the equilibrium morphology, and they also give further information on the nature of POSS-polymer and POSS-POSS interactions. The grafting of POSS nanostructures causes a reduction in the polystyrene content. This inherently reduces the low strain mechanical properties of the copolymers. For iBu-POSS, the reduction in mechanical properties (elastic modulus and yield stress) was consistent with this simplistic model because the iBu-POSS are noninteracting with the polystyrene block. This was observed at both low (30°C) and high (70°C) temperatures. The Ph-POSS behavior is more complex. With increasing Ph-POSS, the morphology becomes more disrupted which causes an additional drop in mechanical properties (elastic modulus and yield stress). At larger concentrations of Ph-POSS, crystallites form which can act to reinforce the copolymers. The disrupted morphology of the 10% and 20% Ph-POSS results in a smaller domain (grain) size, which together with the POSS crystallites reinforce, or network, the morphology. The networked morphology has better preserved morphology order (Γ) and a reduced orientation change during deformation (f). At high temperatures (but still below $T_{g,PS}$), the drop in mechanical properties from the disrupted morphology order outweighs the low strain reinforcement effects. Some reinforcement is still observed at these higher temperatures due to POSS-POSS effects. There is a comparatively higher supported stress for the Ph-POSS copolymers. The 5% and 10% have subtle changes compared to their iBu-POSS counterparts. The 20% Ph-POSS shows the highest supported stress at strains above 0.40 Henky strain. In fact it has a yield strain of approximately 0.70 Henky strain.

CHAPTER 5.

CONCLUSIONS AND RECOMMENDATIONS

5.1. CONCLUSIONS

The objective of this research was to develop a fundamental understanding of how block copolymers are affected by the attachment of functionalized nanostructures. To accomplish this, a model nanostructure and copolymer were chosen. Polyhedral oligomeric silsesquioxanes (POSS) was chosen as the model nanostructure because it has a precise, well-defined structure and organic groups can be chosen to effectively tune its surface chemistry. Polystyrene-block-polybutadiene-block-polystyrene copolymer (SBS) is the model polymer host primarily because it offers a reaction site (1,2-butadiene segments), but also because it is available in narrow molecular weight. The chemical reaction scheme for grafting the SBS-POSS copolymers allows for reproducible grafting reactions that can be performed to produce a wide range of nanostructure grafting fractions.

The effect of grafting four sterically similar, yet electronically different POSS derivatives onto the polybutadiene phase of a lamellar SBS triblock was investigated in order to examine how nanostructure chemistry plays a role in a host copolymer. It is concluded that the POSS derivatives affect the SBS in two ways: by changing the overall content of the polystyrene and by altering the styrene-butadiene segregation. Order-disorder transition temperature and d-spacing data show clear trends that follow POSS nanostructure chemistry: $\text{Ph} > \text{Cye} > \text{Cy} > \text{Cp}$. Here, grafting Ph-POSS results in greater changes when compared to the ungrafted SBS block copolymer. The reason for this is that the phenyl chemistry has the largest contrast to the block in which it is grafted

(polybutadiene) while simultaneously having the largest affinity toward the ungrafted block (polystyrene). Cp-POSS has the smallest effect after grafting because it is most similar to the block in which it is grafted while simultaneously having the smallest affinity toward the ungrafted block. Nanostructure chemistry must be considered when they are to be incorporated into a homopolymer, polymer blend, or block copolymer.

iBu-POSS was investigated in order to observe the effects of incorporating a noninteracting nanostructure. Two host morphologies were examined with POSS grafting at 0, 5, 10, and 20 wt% to compare noninteracting (iBu) and strongly interacting (Ph) POSS nanostructures. The morphology and phase behavior observed for noninteracting POSS is consistent with simply changing polystyrene content with no noticeable change in χ . The local and long-ranged order of the morphology is well-preserved. The interacting nanostructures reduce χ and disrupt the local order of the morphology, which is equivalent to a compatibilizing effect. With this knowledge grafting can be used to shift the host block copolymer morphology to attain different morphologies.

The deformation studies supplement the previous findings regarding the equilibrium morphology, and they also give further information on the nature of the interactions between POSS nanostructures and the host polymer and interactions between the POSS nanostructures themselves. The mechanical properties (elastic modulus and yield stress) of the grafted copolymers inherently drop because nanostructure grafting reduces the polystyrene content. For the noninteracting iBu-POSS, the reduction in mechanical properties was consistent with this simplistic model because the nanostructures do not qualitatively change the morphology and are noninteracting with

the polystyrene block. This was observed at both low (30°C) and high (70°C) temperatures. The interacting Ph-POSS behavior is more complex. With increasing Ph-POSS, the morphology becomes more disrupted which causes an additional drop in mechanical properties (elastic modulus and yield stress). At larger concentrations of Ph-POSS, crystallites form which can act to reinforce the copolymers. The disrupted morphology of the 10% and 20% Ph-POSS results in a smaller domain (grain) size, which together with the POSS crystallites reinforce, or network, the morphology. The networked morphology has better preserved morphology order (smaller change in Γ during deformation) and a reduced orientation change during deformation (f is smaller). At high temperatures (but still below $T_{g,PS}$), the drop in mechanical properties from the disrupted morphology order outweighs the reinforcement effects. An exception to this can be made for the 20% Ph-POSS yield strain.

5.2. RECOMMENDATIONS

This work has established a base of knowledge in the area of grafted nanostructured materials. Based on the results of this work, there are several recommendations for future research that can advance this knowledgebase:

1. To develop a complete picture of the role that POSS nanostructures, it is necessary to examine the deformation mechanisms. The work would require the analysis of single grain copolymer samples in selected orientations. Supplemented with the unoriented deformation findings in chapter 4, valuable knowledge can be gained in role of POSS-POSS interactions and POSS in both the polybutadiene and polystyrene phases.

2. This study examined 5%, 10%, and 20% grafting by weight, but maximum possible grafting fractions can be pushed higher. Higher iBu-POSS grafting may lead to greater POSS-POSS effects due to the increased confinement. The L-series grafted with 20% iBu-POSS may be on the cusp of this threshold as seen in the d-spacing and deformation data.
3. It would be advantageous to graft to an SBS with a higher polystyrene content to widen the window of available POSS grafting fractions for the lamellar morphology. The 43 wt% polystyrene fraction was on the edge of the lamellar-cylindrical border in the morphology phase diagram. By selecting a polystyrene fraction > 50%, it may be possible to graft more than 20% iBu-POSS.
4. The temperature range investigated in this study is well above the glass transition temperature of polybutadiene. At temperatures near or below $T_{g,PB}$, the nanostructures may behave differently. In particular, the iBu-POSS may act as a reinforcement rather than maintain a noninteracting nature.
5. A complement study to the current polybutadiene grafted systems would be grafting POSS to polystyrene. Likewise, extending this scheme of grafting nanostructures to other polymer systems would also complement the current work.

APPENDIX

APPENDIX

Calculation for the 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 density of the iBu-POSS hydride was estimated to be 1.15 g/cm³ based on measurements of Larsson^{69, 70}.

$$f_{PS} = \frac{\rho_g}{\rho_{PS}} W_{PS} \quad (\text{A.1})$$

$$\rho_g = \frac{1}{W_{PS} / \rho_{PS} + W_{PB} / \rho_{PB} + W_{POSS} / \rho_{POSS}} \quad (\text{A.2})$$

$$\rho_g = \frac{1}{(1 - W_{POSS})(W_{PSo} / \rho_{PS} + (1 - W_{PSo}) / \rho_{PB}) + W_{POSS} / \rho_{POSS}} \quad (\text{A.3})$$

$$V_{PS} = \frac{W_{PSo}(1 - W_{POSS}) / \rho_{PS}}{(1 - W_{POSS})(W_{PSo} / \rho_{PS} + (1 - W_{PSo}) / \rho_{PB}) + W_{POSS} / \rho_{POSS}} \quad (\text{A.4})$$

where ρ_{PS} , ρ_{PB} , ρ_{POSS} , and ρ_g are the densities for polystyrene, polybutadiene, iBu-POSS hydride, and the SBS-POSS grafted system, respectively. W_{PS} , W_{PB} , and W_{POSS} are the weight fractions for polystyrene, polybutadiene, and iBu-POSS hydride for a particular SBS-POSS 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. Calculated f_{PS} for the C-series and L-series copolymers can be found in Table 3.2.

Calculations for N

The parameters and notation used in the calculation of N are the same as those used by Owens et al.⁶⁵ N was normalized to constant monomer volume according to the geometric average by the following relations:

$$\rho^* = \left(\prod_{i=1}^n \rho_i \right)^{1/n} \quad (\text{A.5})$$

$$b_i^* = b_i \sqrt{\rho_i / \rho^*} \quad (\text{A.6})$$

$$N_i^* = N_i \left(b_i / b_i^* \right)^2 \quad (\text{A.7})$$

where ρ_i is the monomeric density of the i^{th} 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/cm³ respectively (to achieve 10,100 and 16,400 mol/m³ respectively).

Calculations for the Form Factor Minima:

The cylindrical morphology of the C-series SBS is modeled as an arrangement of polystyrene cylinders aligned in a hexagonally packed manner. The hexagonal packing (interparticle order) yields the typical allowed intensities for the structure factor of a cylindrical morphology (1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, ...). The polystyrene cylinders themselves also contribute to the scattering profile through particle scattering or the form factor. The particle scattering for a cylindrical or rod-like particle, $F(q)$, where the length of the rod is much larger than the radius and in scattering directions orthogonal to the cylindrical axis scales by the relation^{59, 60}:

$$F(q) \sim \frac{J_1(qR)}{qR} \quad (\text{A.8})$$

where J_1 is the Bessel function of the first kind of order 1, q is the magnitude of the scattering vector, and R is the cylinder radius. In block copolymers, the cylinders have an interfacial thickness which contributes to an additional damping factor which does not contribute to the position of the scattering minima. Based on the Born approximation, observed scattering intensity scales as $F^2(q)S(q)$, where $F(q)$ is the form factor and $S(q)$ is the structure factor. The minimum intensity in this form factor can be found when $J_1(qR) = 0$ for values of $q > 0$. If we denote S_i as a solution to the equation $J_1(x) = 0$, then the q at which the form factor is at a minimum (denoted here as q_m) is related to the cylinder radius by:

$$q_m = \frac{S_i}{R} \quad (\text{A.9})$$

The volume fraction of polystyrene, f_{PS} , can be related to the cylinder radius, nearest neighbor cylinder distance ($a = d_{100}$), and the d-spacing of the primary scattering peak, d^* .

$$f_{PS} = \frac{2\pi}{\sqrt{3}} \frac{R^2}{a^2}; \quad d^* = \frac{\sqrt{3}}{2} a \quad (\text{A.10})$$

$$f_{PS} = \frac{\sqrt{3}\pi}{2} \frac{R^2}{d_*^2}; \quad R = \sqrt{\frac{2d_*^2 f_{PS}}{\sqrt{3}\pi}} \quad (\text{A.11})$$

The form factor minimum, q_m , is most easily compared to the morphology structure factor by the dimensionless ratio q_m/q^* .

$$q_m = S_i \sqrt{\frac{\sqrt{3}\pi}{2d_*^2 f_{PS}}}; \quad \frac{q_m}{q^*} = S_i \sqrt{\frac{\sqrt{3}}{8\pi f_{PS}}} \quad (\text{A.12})$$

The solutions, S_i , to $J_1(x) = 0$ are approximately 3.83171, 7.01559, 10.1735,... Values for the first two solutions of q_m/q^* can be found in Table 3.2.

In the case of the L-series, the structure amplitude for lamellae, or flat particles, whose in-plane dimensions are much greater than the thickness and spacing dimensions scales by^{59, 62}:

$$F(q) \sim \frac{\sin(qT/2)}{qT/2} \quad (\text{A.13})$$

where q is the magnitude of the scattering vector, T is the thickness of the lamellae. Observed scattering intensity scales as $F^2(q)$. The minimum in this form factor can be found when $\sin(qT/2) = 0$ for values of $q > 0$. The solution to this equation takes the form $qT/2 = \pi n$ where n is a positive integer (for $q > 0$). The relationships of q_m and q_m/q^* to f_{PS} are:

$$q_m = \frac{2\pi}{T} n = \frac{2\pi}{f_{PS} D} n; \quad \frac{q_m}{q^*} = \frac{1}{f_{PS}} n \quad (\text{A.14})$$

Values for the first two solutions of q_m/q^* can be found in Table 3.2, and a plot of the form factor for the pure C-series and L-series SBS is displayed in Figure A.1.

The calculations relating f_{PS} to the polystyrene cylinder radius and lamellae thickness assume that the entire volume of iBu-POSS is confined within the polybutadiene domain. In practice, the polystyrene cylinders and lamellae possess a size distribution, interfacial curvature, and interfacial thickness rather than existing as monodisperse hard particles. In addition, the orientation of the particles (cylinders and lamellae) is random in the plane of the film. Consequently, the form factor minima will not result in complete destructive interference, but it will result in reduced intensity for the allowed diffraction of the structure factor.

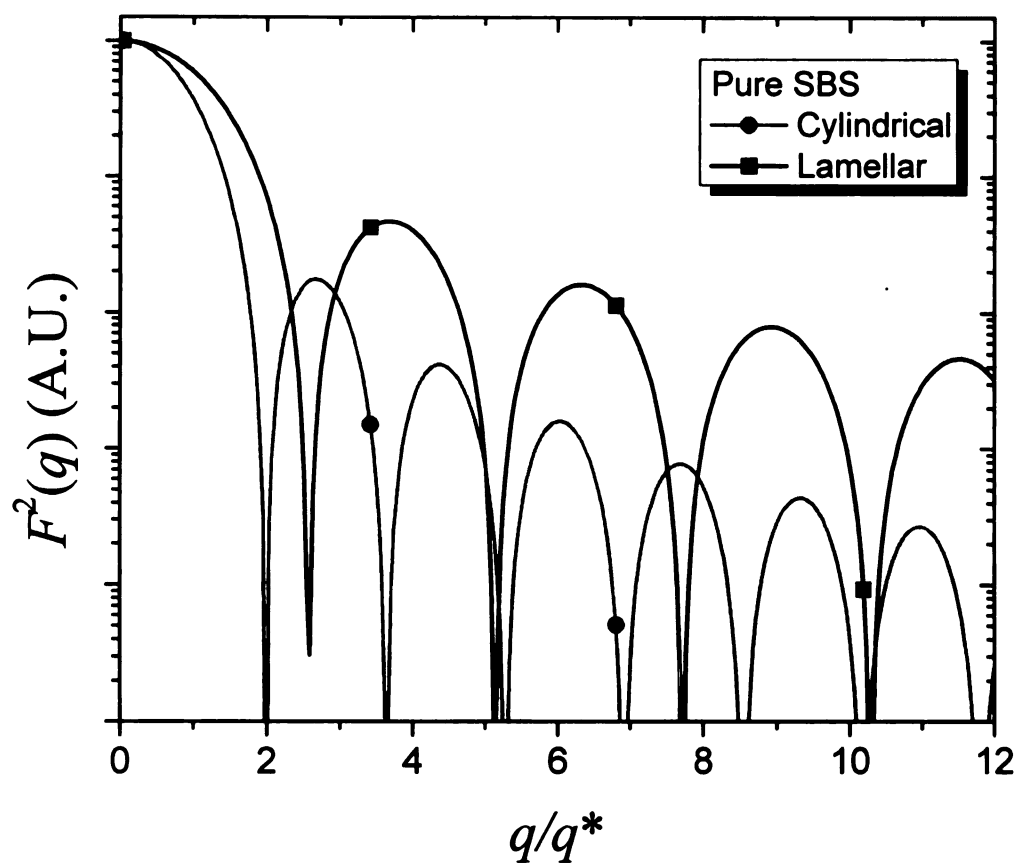


Figure A.1. Plot of the form factor for the pure C-series and L-series SBS.

Herman's Orientation Function

For a quantitative examination of how the orientation changes, one can observe the intensity as a function of azimuthal angle, μ , which is defined as the angle from the direction perpendicular to the stretching direction. The direction diffracted intensity is coplanar with the incident beam and diffraction plane normal. In addition, diffraction intensity is approximately proportional to the number of diffracting planes, so it is possible to correlate intensity in a particular direction and the number of diffraction plane normals oriented in that direction. Equation A.15 calculates the angular dependence of the diffracted intensity, $I(\mu)$ ⁷¹, and Equation A.16 represents the normalized orientation distribution function, $N(\mu)$. However, they require the assumption or limitation of a random texture or wire texture along the stretching direction.

$$I(\mu) = \int_{q_1}^{q_2} I(q, \mu) q^2 dq \quad (\text{A.15})$$

$$N(\mu) = I(\mu) / \int_0^{\pi} \int_{q_1}^{q_2} I(q, \mu) q^2 \sin \mu dq d\mu \quad (\text{A.16})$$

It is difficult to compare the $I(\mu, \varepsilon_H)$ quantitatively for various POSS-grafted systems. It is possible to summarize $I(\mu)$ as a scalar by calculating the average cosine squared of the diffracting intensity ($\langle \cos^2 \mu \rangle$) from the normalized orientation distribution function, $N(\mu)$. The degree of orientation can be more straightforwardly represented as a scalar by the Herman's orientation function or second-order orientation factor, f ⁷¹. f is related to the $N(\mu)$ through $\langle \cos^2 \mu \rangle$ by Equations A.17- A.19. For a random microdomain orientation represented by a uniform intensity ring, $f \rightarrow 0$. In the case of lamellae, $f \rightarrow 1$ for lamellae perfectly aligned in the stretching direction (lamellae normals orthogonal to

the stretching direction), and $f \rightarrow -0.5$ when the lamellae are oriented orthogonal to the stretching direction (lamellae normals in the stretching direction).

$$\langle \cos^2 \mu \rangle \equiv \int_0^\pi \cos^2 \mu N(\mu) \sin \mu d\mu \quad (\text{A.17})$$

$$f = \left(3 \langle \cos^2 \mu \rangle - 1 \right) / 2 = \frac{3}{2} \left(\int_0^\pi N(\mu) (\sin \mu) (\cos^2 \mu) d\mu - \frac{1}{3} \right) \quad (\text{A.18})$$

$$f = \left(3 \langle \cos^2 \mu \rangle - 1 \right) / 2 = \left(\frac{\frac{\pi q_2^2}{\int_0^{q_1} \int I(q, \mu) q^2 (\cos^2 \mu) (\sin \mu) dq d\mu}}{\frac{\pi q_2^2}{\int_0^{q_1} \int I(q, \mu) q^2 (\sin \mu) dq d\mu}} - \frac{1}{2} \right) \quad (\text{A.19})$$

The procedures for calculating f in this document begin with the 2D SAXS image. The diffraction pattern is integrated to get SAXS profiles of $I(q)$ for 91 angular slices (of 2° each) from -1° to 181° , where 90° coincides with the stretching direction (Figure A.2). Each angular slice represents a value of μ . Each of these patterns is subsequently integrated numerically in the form of Equation A.15 over a q -range of the primary diffraction peak to obtain $I(\mu)$ for 2° increments of μ . This data is then integrated with $\sin \mu$ to obtain the denominator in Equation A.16, and $N(\mu)$ is calculated. Another numeric integration is performed to obtain $\langle \cos^2 \mu \rangle$ and f is calculated arithmetically.

Tensile Device for In-Situ Deformation Experiments using SAXS

In-situ stretching was performed using two co-rotating cylinders driven by a stepper motor. A schematic of the setup is shown in Figure A.2. The setup allows for continuous stretching to an unbounded strain. The motor for the stretching device is

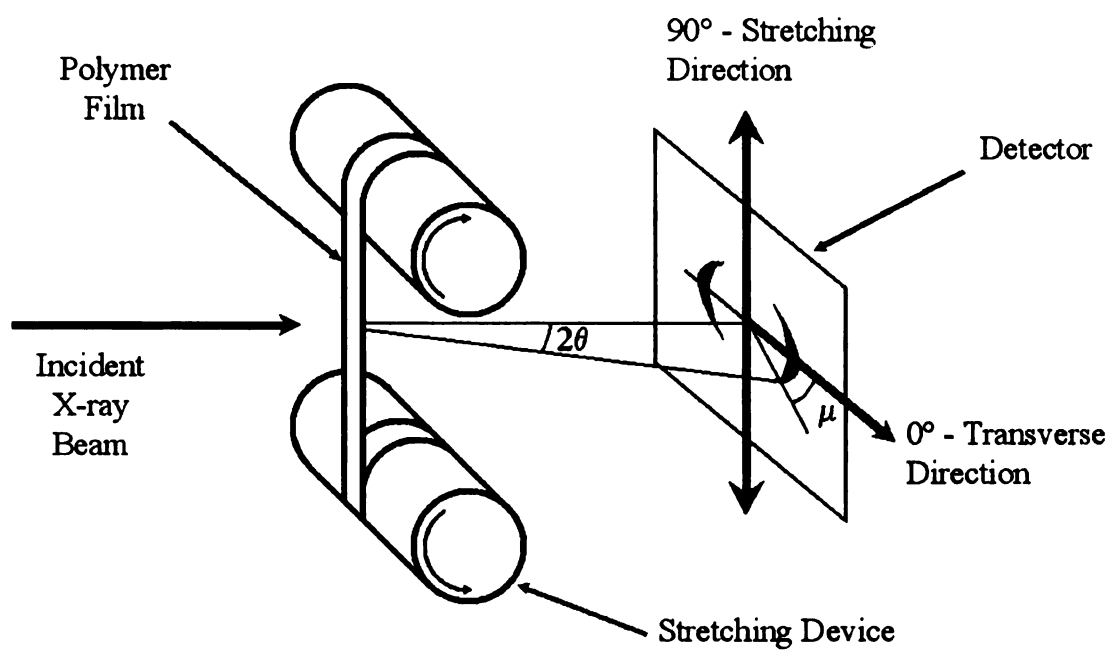


Figure A.2. A schematic of the experimental setup for in situ deformation experiments using small angle x-ray scattering.

directly connected to the bottom cylinder. The two cylinders are geared together so that they rotate in the opposite directions. When the motor is driven at a constant angular velocity, the polymer film experiences tensile deformation at a constant Henky strain rate. To facilitate an equal comparison, mechanical testing was also performed at a constant Henky strain rate.

Experimental Calculations for Stretching Device Strain

The calculations for strain are not straightforward because the film is no longer stretched when it is drawn up onto the cylinders, as seen in Figure A.3. If the entire length of the film was continuously stretched, the strain, ε (engineering), is

$$\varepsilon = \frac{\Delta L}{L_0} \quad (\text{A.20})$$

where ΔL is the change in length of the film and L_0 is the initial length of the film. ΔL can be related to the rotation of the co-rotating cylinders by:

$$\Delta L = 2R\theta \quad (\text{A.21})$$

where R is the cylinder radius and θ is the rotation of the cylinder in radians. A factor of 2 is needed because both cylinders rotate. Combining Equations A.20 and A.22:

$$\varepsilon = \frac{2R\theta}{L_0} \quad (\text{A.22})$$

To obtain the differential change in strain, $d\varepsilon$:

$$d\varepsilon = \frac{2R}{L_0} d\theta \quad (\text{A.23})$$

where $d\theta$ is the differential change in θ . Up to this point, the calculations are considered for when the entire length of the film was continuously stretched. Only the length

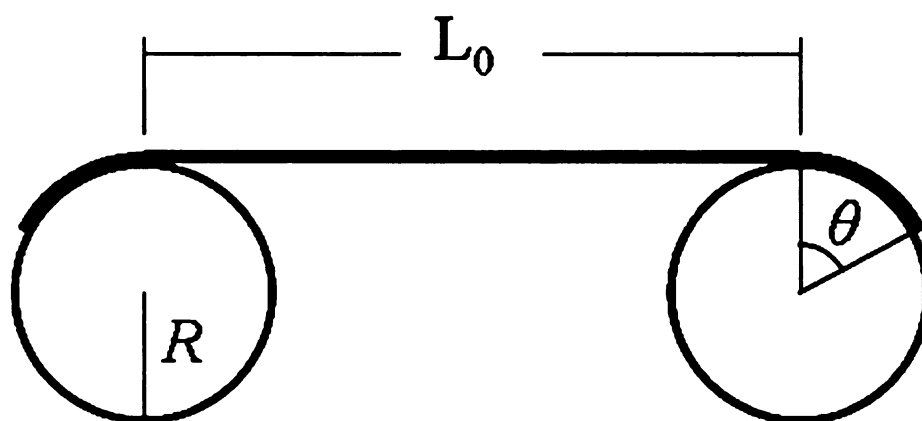


Figure A.3. A schematic of the mechanical portion of the stretching device.

between the cylinders, L_0 , is deformed in this setup. Thus, the actual strain will be larger than equation A.22 since the gauge length is a subsection of the total length. To account for the difference in strain, the effective length, L_{eff} , must be considered. L_{eff} is the length of the film if the entire film were deformed with the same strain that the center region of the film experiences. The effective strain, ε_{eff} , will represent the actual strain that the center region of the film experiences. Correcting the differential form of Equation A.23:

$$d\varepsilon_{eff} = \frac{L_{eff}}{L_0} \frac{2R}{L_0} d\theta \quad (A.24)$$

L_{eff} can be related to ε_{eff} , so Equation A.24 becomes:

$$d\varepsilon_{eff} = (1 + \varepsilon_{eff}) \frac{2R}{L_0} d\theta \quad (A.25)$$

Integrating Equation A.25 will result in the equation of the actual engineering strain, ε_E at rotation angle θ . The initial conditions are such that $\varepsilon_{eff} = 0$ at $\theta = 0$.

$$\int_0^{\varepsilon_E} \frac{d\varepsilon_{eff}}{(1 + \varepsilon_{eff})} = \int_0^{\theta} \frac{2R}{L_0} d\theta \quad (A.26)$$

$$\ln(1 + \varepsilon_E) = \frac{2R\theta}{L_0} \quad (A.27)$$

$$\varepsilon_E = \exp\left(\frac{2R\theta}{L_0}\right) - 1 \quad (A.28)$$

The equation for the actual strain can be simplified when expressed in terms of Henky strain, ε_H .

$$\varepsilon_E = \exp(\varepsilon_H) - 1; \quad \varepsilon_H = \ln(\varepsilon_E + 1) \quad (A.29)$$

$$\varepsilon_H = \frac{2R\theta}{L_0} \quad (A.30)$$

In terms of the actual stretching device, $R = 3/16$ inch and $L_0 = 1$ inch, then:

$$\varepsilon_H = \frac{3\theta}{8} = \frac{\pi\omega}{480} \quad (\text{A.31})$$

where ω is the angular change in degrees for the motor (or one of the cylinders since the motor is directly connected directly inline with one of the cylinders).

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