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14. ABSTRACT The linear viscoelastic behavior of thermoplastic hybrid inorganic-organic polymers synthesized through radical copolymerization of styrene and styryl-based polyhedral oligosilsesquioxane (POSS), R7(Si8O12) (C6H4CH=CH2), with R = isobutyl (iBu), cyclopentyl (Cp) and cyclohexyl (Cy) were studied to reveal significant influence of the vertex group, R. The glass transition temperatures were found to feature a strong and complex POSS vertex group dependence, with iBu playing a plasticizer-like role and Cp & Cy enhancing the glass transition. Rheological measurements showed that all of the copolymers with lower weight fractions of POSS (0, 6 and 15 wt-%) followed the time-temperature superposition (tTS) principle. The rubbery plateau modulus (oNG) was found to decrease with increasing POSS content and showed a strong dependence on vertex group, with the ordering iBuPOSS > CpPOSS > CyPOSS, indicating increasing entanglement dilution with POSS size. At low deformation frequencies, a terminal zone was observed for the iBuPOSS-based copolymers, like pure PS; however, CpPOSS and CyPOSS copolymers lead to low frequency elasticity for higher POSS contents, suggesting a weak physical network, with a particular CpPOSS copolymer revealing critical gel behavior. We ascribe the observed rheological data to two distinct effects of POSS incorporation: (i) the effect of POSS grafting on microscopic topology of polymer chains, and (ii) intermolecular interaction between POSS and PS chain segments. From Vogel-Tanmmman-Fulcher plots of the terminal relaxation time, the apparent activation energy values for each copolymer series were found to monotonically increase with POSS content, indicating that POSS decreases rheological temperature sensitivity, consistent with tTS analysis for free volume thermal expansivity.						
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Vertex-Group Effects in Entangled Polystyrene-Polyhedral Oligosilsesquioxane (POSS) Copolymers

(PREPRINT)

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Abstract: The linear viscoelastic behavior of thermoplastic hybrid inorganic-organic polymers synthesized through radical co-polymerization of styrene and styryl-based polyhedral oligosilsesquioxane (POSS), $R_7(\text{Si}_8\text{O}_{12})$ ($\text{C}_6\text{H}_4\text{CH}=\text{CH}_2$), with R = isobutyl (ⁱBu), cyclopentyl (Cp) and cyclohexyl (Cy) were studied to reveal significant influence of the vertex group, R. The glass transition temperatures were found to feature a strong and complex POSS vertex group dependence, with ⁱBu playing a plasticizer-like role and Cp & Cy enhancing the glass transition. Rheological measurements showed that all of the copolymers with lower weight fractions of POSS (0, 6 and 15 wt-%) followed the time-temperature superposition (tTS) principle. The rubbery plateau modulus (G_N^o) was found to decrease with increasing POSS content and showed a strong dependence on vertex group, with the ordering ⁱBuPOSS > CpPOSS > CyPOSS, indicating increasing entanglement dilution with POSS size. At low deformation frequencies, a terminal zone was observed for the ⁱBuPOSS-based copolymers, like pure PS; however, CpPOSS and CyPOSS copolymers lead to low frequency elasticity for higher POSS contents, suggesting a weak physical network, with a particular CpPOSS copolymer revealing critical gel behavior. We ascribe the observed rheological data to two distinct effects of POSS incorporation: (i) the effect of POSS grafting on microscopic topology of polymer chains, and (ii) intermolecular

interaction between POSS and PS chain segments. From Vogel-Tanmman-Fulcher plots of the terminal relaxation time, the apparent activation energy values for each copolymer series were found to monotonically increase with POSS content, indicating that POSS decreases rheological temperature sensitivity, consistent with tTS analysis for free volume thermal expansivity.

INTRODUCTION

Polymer scientists actively seek to develop and understand hybrid nanomaterials – composites with a reinforcing phase that have at least one characteristic dimension in the range 1-100 nm – in order to realize materials that combine the processibility and property-tuning of polymers with outstanding stiffness and stability (thermal and chemical) of a reinforcing phase.¹⁻³ To date, an emphasis has been placed on the top-down approach of dispersing nanoscopic fillers within a polymer host with either melt mixing or solvent-assisted processing, the former being much more desirable for scaling to industrial processes. The most studied reinforcing fillers have been clay (aluminosilicates), graphite, silica, and carbon nanotubes. While few detailed rheological studies have been undertaken, it appears common that the rheological characteristics of the nanocomposite polymer host is adversely affected – from a processing perspective – through significant increases in melt viscosity and the creation of an elastic network with finite yield stress. Another, bottom-up, approach to hybrid nanocomposites involves the co-polymerization of a nanoscopic hybrid monomer, POSSTM, where POSS is a well defined, chemically functionalized spherosilicate termed polyhedral oligosilsesquioxane. POSS can be incorporated into polymers through chain-growth polymerizations with the use of vinyl- or vinylidene-functionalized POSS (e.g., styryl-POSS^{4, 5} or methacryl POSS⁶), step-growth polymerizations of POSS diols,⁷ or simple end-capping with mono-functional POSS.⁸ In contrast with the previously described dispersion route to hybrid nanocomposites, where nanoscale morphology is determined primarily by mixing and dispersion, the bottom-up approach leads more naturally to good dispersion (molecular- to nano-scale) that is determined primarily at the polymer synthesis stage and thermodynamically controlled self-assembly of the POSS moieties.⁹ However, similar to the dispersion-route, rheological

properties of POSS-based nanocomposites can be quite distinct from their homopolymer counterparts. Successful processing of POSS-based polymers requires an understanding of such rheological modifications and this is the subject of our present investigation.

In our previous paper,⁵ we demonstrated the essential role of the characteristic nanoscopic size of POSS moieties in determining the rheological properties of PS-based random copolymers incorporating isobutyl-functionalized POSS macromers (ⁱBuPOSS). The incorporation of ⁱBuPOSS significantly changed the polymer chain topology and introduced additional free volume, resulting in a decrease of glass transition temperature and rubbery plateau modulus, but increase in flow activation energy. Considering its nanoscopic character, POSS macromers feature one functional group and seven inert organic groups (so-called “R-groups”), all at the silicon-oxygen polyhedron vertex positions. Here, we will use the terminology “vertex group” and “pendant group” interchangeably. On a volumetric basis, and recognizing molecular motion, vertex groups may occupy as much as 80% of the molecular volume¹⁰ and this volume mediates interaction with other POSS groups and with non-POSS polymeric segments.

Thus far, some published research works have revealed that the pendant vertex group is one of the key factors to control POSS dispersion and the resulting rheological properties. Romo-Uribe et al.⁴ reported the linear viscoelastic properties of unentangled random copolymers from 4-methylstyrene and its POSS derivatives with R = cyclopentyl (Cp) and cyclohexyl (Cy). It was found that with increasing POSS content, the pendant CpPOSS and CyPOSS macromers tended to aggregate and form nanocrystals in the polymer matrix. Consequently, the corresponding rheological properties were profoundly altered with the increasing POSS incorporation level. Above a critical mole fraction of 8 mol-% CyPOSS, a secondary rubbery plateau appears with a magnitude $\sim 10^3$ Pa and in the frequency range where traditional terminal zone behavior occurs for the non-POSS analog. By comparison, CpPOSS-incorporating copolymers featured a higher critical mole fraction of approximately 16 mol-% for the onset of low-frequency solid-like response. They attributed this phenomenon to the intermolecular interaction due to the presence of POSS and can be described by the “sticky reptation” model developed

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by Leibler et al.,¹¹ which was conceived to describe the dynamics of hydrogen-bonded elastomers.^{12, 13} Unfortunately, because of the limited polymerization degree, findings on the narrow rubbery plateau (and the corresponding entanglement molecular weight) were a result of both molecular weight variation and POSS content, thus making it impossible to clarify an isolated POSS effect.

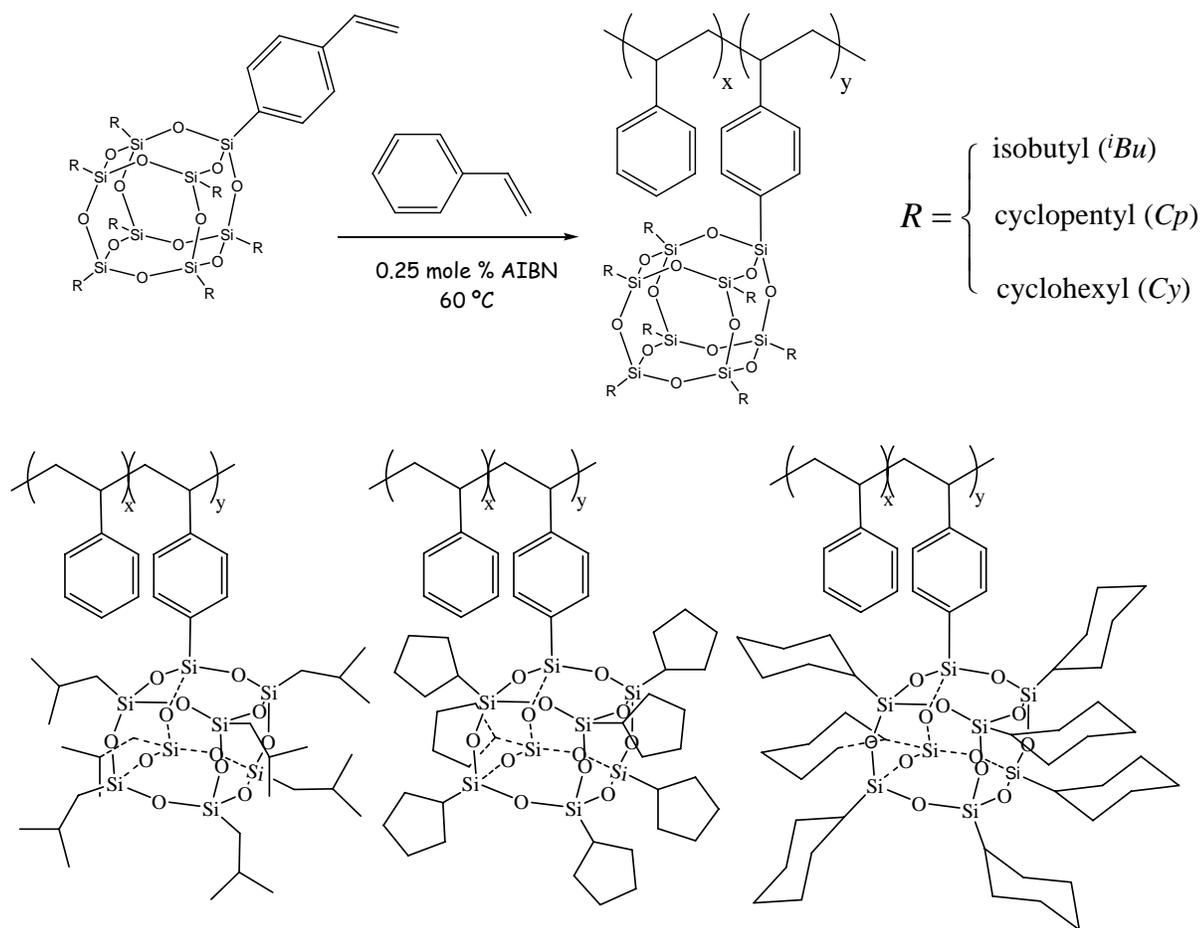
Kopesky et al.⁶ reported the linear viscoelastic properties of poly(methyl methacrylate) (PMMA) tethered and un-tethered by POSS. They found that the introduction of isobutyl-POSS (ⁱBuPOSS) led to an apparent increase of entanglement molecular weight. Meanwhile, at the same POSS loading (25 wt-%), the copolymer with CyPOSS featured a higher plateau modulus than the analogous ⁱBuPOSS copolymer. To be contrasted with the random copolymers incorporating ⁱBuPOSS, the terminal behavior of those tethered by CyPOSS showed significant rheological deviation from the expected terminal zone frequency dependence of storage and loss modulus: $G' \sim \omega^2$ and $G'' \sim \omega^1$, where G' and G'' are the shear storage and loss modulus, respectively.¹⁴

Clearly, POSS vertex group offers a compositional means to control the rheological behavior of polymers incorporating POSS. However, only few papers (those discussed above) have reported the rheological behavior of POSS-based polymeric nanocomposites as a function of vertex group in detail. Therefore, we were compelled to systematically explore the vertex group dependence of linear viscoelastic properties in the POSS-tethered polymers. In this paper, we seek to quantitatively reveal the role of vertex group composition in determining the linear viscoelastic properties of polymeric nanocomposites bearing POSS, using polystyrene (PS) as the model polymeric “host” copolymerized to yield POSS-pendant polymers with a variety of vertex-groups: isobutyl (ⁱBu), cyclopentyl (Cp) and cyclohexyl (Cy).

EXPERIMENTAL SECTION

Materials. In order to quantitatively elucidate vertex group dependence of the linear viscoelastic properties of polymeric nanocomposites bearing POSS moieties, we synthesized a series of PS-based

random copolymers in the range of 0 ~ 50 wt-% POSS macromer loading and with distinct vertex groups, specifically isobutyl (ⁱBu), cyclopentyl (Cp) and cyclohexyl (Cy). As shown in Scheme 1, the random copolymers were synthesized through free radical copolymerization using methods previously described.^{5, 15} Briefly, a 10.0 molal monomer solution in toluene containing a total of 3 grams of monomers was initiated using 0.25 mole-% azobis(isobutyronitrile) (AIBN). One representative synthesis to yield 6 wt-% POSS (designated hereafter as PS₉₄CyPOSS₆) follows: Under a nitrogen atmosphere, a dry O₂-free solution of toluene (2.73 mL), [(C₈H₇)Cy₇(Si₈O₁₂)] (180 mg, 0.196 mmole), styrene (2820 mg, 27.08 mmole) and AIBN (11.2 mg, 0.068 mmole) was heated to 60 °C for 2 days. This was then diluted with 15 mL CHCl₃ and precipitated into 100 mL of methanol. After stirring for 1 h, the copolymer was isolated on fritted glassware and air-dried overnight. ¹H-NMR spectroscopy (400 MHz) showed no unreacted monomers and confirmed that the product contained 0.70 mol-% or 6 wt-% POSS. The isolated yield of dry copolymer was 80% of the theoretical value. Other PS-POSS copolymers were polymerized in an identical fashion and isolated in yields ranging from 76 to 98%. We have adopted a nomenclature to immediately distinguish samples by composition: PS_XRPOSS_Y, where X is the wt-% of styryl comonomer, R is the POSS vertex group, and Y is the wt-% of POSS comonomer. As one example, PS₈₅ⁱBuPOSS₁₅ is a random copolymer containing 85 wt-% PS and 15 wt-% ⁱBuPOSS.



Scheme 1. Synthetic scheme for the preparation of random copolymers yielded from styrene and styryl-POSS through radical co-polymerization initiated by AIBN at 60 °C. POSS vertex group varies with isobutyl (ⁱBu), cyclopentyl(Cp) and cyclohexyl(Cy), drawn left to right on the bottom of the scheme.

We observed that the solubility of the random copolymers prepared from styrene and styryl-POSS depended strongly on the vertex group. The random copolymers incorporating ⁱBuPOSS (up to 50 wt-% ⁱBuPOSS content) readily dissolve in tetrahydrofuran (THF); however, the random copolymers incorporating CpPOSS and CyPOSS can't dissolve completely in organic solvents (such as THF, toluene and CHCl₃) and can only be swollen when POSS loading is beyond 15 wt-% CpPOSS and 30 wt-% CyPOSS, respectively. This solubility difference is apparently due to the formation of physical network by a multitude of POSS-POSS associations; cyclopentyl and cyclohexyl POSS have a much stronger degree of affinity than isobutylPOSS. This effect is not realized in unentangled low degree of polymerization copolymers. Due to this limitation of solubility, we only choose the random copolymers

with POSS loading up to 15 wt-% to compare the effect of vertex group on the rheological properties of random copolymers bearing POSS. 5 wt-% polymer solutions in THF were cast into TeflonTM casting dishes and dried at room temperature for four days. Next, the free-standing cast films were dried in vacuum at 50~60 °C for two days and then 80~90 °C for two days. In order to remove any residual solvent (THF), the films were finally dried above T_g (~ 120 °C) for 12 h further. The cast films dried in this manner had thicknesses of approximately 1.0 mm and were employed for further micro-structural and physical characterizations.

Characterization.

Wide-angle X-ray Scattering (WAXS). In order to assess the microstructures of the random copolymers, Wide Angle X-ray Scattering (WAXS) experiments were conducted at room temperature on the samples using a BRUKER D5005 X-ray diffractometer with rotating anode source operated at 40 kV and 40 mA. Nickel-filtered Cu K_α radiation with wavelength, $\lambda=1.5418\text{\AA}$, was used as the source. The scattering angle, 2θ , was scanned from 5° to 40° at a rate of 1.0 degree/min.

Thermal Analysis. The thermal transitions of the random copolymers were characterized using differential scanning calorimetry (DSC), employing a TA Instruments DSC-2920 equipped with a mechanical intercooler (cooling capability to $T = -60$ °C) under a continuous nitrogen purge (50 mL/min). Both calibrations of heat flow and temperature were based on a run in which one standard sample (indium) is heated through its melting point. The samples were sealed in aluminum pans with mass in the range of 5~10 mg. All measurements were conducted at a scan rate of 10 °C/min following a heat-cool-heat procedure from 0 °C to 250 °C. Glass transition temperatures (T_g) were determined by the midpoint of heat flow step-up (heat capacity step down) during second heating. In order to further assess the vertex group influence on the compatibility of POSS in PS host, samples with 50 wt-% POSS loading, though insoluble, were annealed at 150 °C for 12 hours. After annealing, the samples were

quenched to 0 °C and heated up to 250 °C with ramping rate of 10 °C/min in order to investigate their glass transition temperature and melting behavior.

Rheological Measurements. Linear viscoelastic properties were measured using an ARES rheometer (TA Instruments, Inc.). It was equipped with two torque transducers distinguished by their torque capacity: 200 g-cm and 2000 g-cm. The existence and extent of the linear viscoelastic regime was determined by measurements of the dynamic storage and loss moduli, $G'(\omega)$ and $G''(\omega)$ as functions of strain (0.1~10 %) at an angular frequency with 10 rad/s. All of the measurements were carried out within the linear viscoelastic range, where $G'(\omega)$ and $G''(\omega)$ were independent of strain. The dynamic moduli were measured as a function of frequency over the range $0.01 < \omega < 100$ rad/s at various temperatures above T_g in the range $120 < T < 180$ °C and under nitrogen atmosphere. All of the rheological characterizations are performed using the parallel plates with 8 mm diameter and with the gap between two plates being about 1.0 mm and known within 1 μ m resolution.

RESULTS

Synthesis and characterization of PS-POSS Copolymers. A series of PS-based random copolymers bearing POSS moieties with varying vertex group composition were synthesized by free radical polymerization in the presence of azobis(isobutyronitrile) (AIBN) as a radical initiator. GPC results revealed that all of the polymers synthesized were characterized by high molecular weight ($M_w > 1.5 \times 10^5$ g/mol) and correspondingly high number-average polymerization degree ($DP > 1000$). Their polydispersity indices (PDI) were typical of free radical polymerization, e.g. $PDI > 1.4$, and showed notable vertex dependence. Specifically, at high POSS loading, the copolymers bearing ¹BuPOSS feature lower PDI values than the counterparts bearing CpPOSS and CyPOSS. Furthermore, PDI values of the latter copolymers increased with increasing CpPOSS and CyPOSS loading, which could be due to their decreasing solubility with increasing CpPOSS and CyPOSS incorporation in the reaction media, toluene. ¹H-NMR characterization revealed that the actual POSS incorporation ratio in copolymers is

very close to the feeding ratio and independent of vertex group. These observations indicate that styryl-POSS macromer has very similar reactivity to that of styrene monomer and that the pendant POSS group does not influence the reactivity of the covalently attached styryl for free radical polymerization. The molecular characteristics of the copolymers were detailed in Table 1.

Table 1. Summary of Molecular Characteristics of Polystyrene-POSS Copolymers^{a,b}

Compound	$M_w \cdot 10^3$ (g/mol)	M_w/M_n	DP	wt%POSS	mol%POSS	# POSS _{chain}
PS ₁₀₀	161	1.43	1080	0.0	0.0	0
PS ₉₄ ⁱ BuPOSS ₆	186	1.46	1165	5.9	0.70	8
PS ₈₅ ⁱ BuPOSS ₁₅	195	1.40	1158	15.4	2.02	23
PS ₆₇ ⁱ BuPOSS ₃₃	300	1.52	1390	33.2	5.34	64
PS ₄₈ ⁱ BuPOSS ₅₂	419	1.65	1358	52.1	10.95	138
PS ₉₄ CpPOSS ₆	235	1.70	1248	6.1	0.66	8
PS ₈₅ CpPOSS ₁₅	436	2.53	1410	15.3	1.80	25
PS ₇₀ CpPOSS ₃₀	insoluble	-----	-----	-----	-----	-----
PS ₅₀ CpPOSS ₅₀	insoluble	-----	-----	-----	-----	-----
PS ₉₄ CyPOSS ₆	191	1.77	982	6.1	0.60	6
PS ₈₅ CyPOSS ₁₅	294	2.07	1180	15.2	1.64	19
PS ₇₀ CyPOSS ₃₀	635	2.81	1582	30.4	3.89	62
PS ₅₀ CyPOSS ₅₀	insoluble	-----	-----	-----	-----	-----

^a Molecular weight and Molecular weight distribution were determined by gel permeation chromatography (GPC) in CHCl₃, calibrated by polystyrene(PS) standards.

^b DP's are calculated from M_n and wt% POSS is derived from mol% POSS, which is directly measured from ¹H NMR spectroscopy.¹⁶

Microstructure. Figure 1 shows the wide-angle X-ray diffraction (WAXD) patterns of the three styryl-POSS macromers and PS-based random copolymers incorporating POSS moieties with three kinds of vertex group (ⁱBu, Cp and Cy), respectively, all taken at room temperature. As shown in Figure 1(a), all three styryl-POSS macromers feature the very intense and sharp diffraction peaks associated with the macromer crystalline structures. The single strongest characteristic diffraction peaks

of POSS macromers with isobutyl (ⁱBu), cyclopentyl (Cp) and cyclohexyl (Cy) are centered at *d*-spacing of 11.0Å, 10.8Å and 11.2Å, respectively. The WAXS pattern of pure PS is characterized by two amorphous halos: one is centered at a *d*-spacing of 4.5Å, ascribed to the correlation length between benzene rings along the chains¹⁷ and the other is centered at 8.3Å, attributed to the inter-chain correlation distance.¹⁸ WAXS patterns of the copolymers bearing POSS were found to be quite similar to each other, despite their differing vertex groups. All of them lack crystalline diffraction peaks of the POSS macromer crystals and, instead, indicate very similar structure to amorphous PS. In particular, for all of the copolymers studied, two characteristic amorphous halos appear, representing the inter-chain correlations at lower 2θ angle and the correlation distance between side groups along the chains at higher 2θ angle, respectively.

At the lower POSS loading level (≤ 30 wt-%), WAXS patterns of copolymers feature similar trends with increasing of POSS content among the different POSS vertex groups: the amorphous halo at the *d*-spacing = 8.3 Å shifts to lower scattering angles and the corresponding peak is slightly narrowed. Meanwhile, the amorphous halo at the *d*-spacing = 4.5 Å becomes a little broadened and also shifts to lower scattering angles. That the characteristic scattering peaks shift to larger *d*-spacing means that the incorporation of POSS moieties enlarges the inter-chain correlation distance and inter-side group correlation.⁵ Furthermore, in contrast with the styryl-POSS macromers, these two peaks are quite distinct from any crystalline reflections of the corresponding styryl-POSS macromers. In particular, the strongest ⁱBuPOSS macromer reflections appear at *d*-spacings of 11.0Å and 8.1Å; however, these regions of the copolymer WAXD patterns are devoid of any features. Thus, it is clear that copolymerization effectively prevents crystallization (or even aggregation) of POSS units, at least for low POSS contents (≤ 30 wt-%). That said, WAXS data alone can't distinguish the existence of small POSS clusters (2-3 molecules) or not.

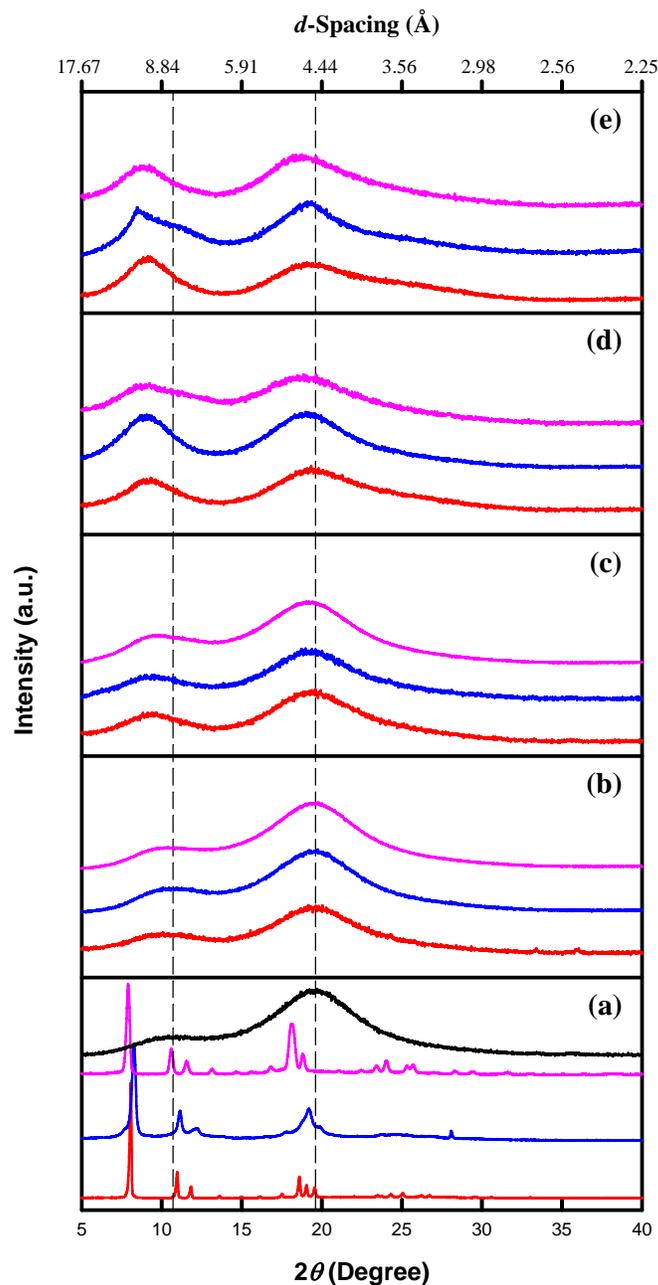


Figure 1. WAXS Patterns of PS-based random copolymers with varying POSS R-groups and POSS loading level. (a) pure POSS macromers and neat PS. red, blue and pink solid lines represent iBuPOSS, CpPOSS and CyPOSS macromers, respectively; Black solid line stands for pure PS. The weight percentage of POSS loading level varies with: (b) 6, (c) 15, (d) 30 and (e) 50 wt-%POSS. Red, blue and pink solid lines represent iBuPOSS, CpPOSS and CyPOSS-based random copolymers, respectively. The two black dash reference lines represent the characteristic scattering peak of pure PS centered at d -spacing of 4.5\AA and 8.3\AA , respectively.

Compared with the samples containing 30 wt-% POSS, the copolymer incorporating 50 wt-% CpPOSS (PS₅₀CpPOSS₅₀) exhibits a sharp peak centered at d -spacing = 10.5Å, which is very close to the strongest diffraction peak of styryl-CpPOSS macromer. Further, copolymers incorporating 50 wt-% ⁱBuPOSS (PS₅₀ⁱBuPOSS₅₀) and 50 wt-% CyPOSS (PS₅₀CyPOSS₅₀) exhibit only further narrowing of the diffuse scattering peak at higher d -spacing (lower 2θ) – remaining diffuse – and shifting of the smaller d -spacing halo (interchain spacing) to larger d -spacings. This stands in contrast to PS₅₀CpPOSS₅₀, which exhibited a crystalline diffraction peak at low angle. These distinct features at higher d -spacing provide evidence that the compatibility between POSS moiety and PS host has a vertex group dependence: CpPOSS is less compatible with PS host than ⁱBuPOSS and CyPOSS. The lack of microscopic ⁱBuPOSS and CyPOSS aggregation in PS host may be due to the favorable interaction between those POSS moieties and the PS segments, at least in comparison to POSS-POSS and PS-PS segmental interactions.

Indeed, prior research has indicated preferential interactions of POSS with polymer segments. Zhang *et al.*¹⁹ studied the effect of random copolymers of PMMA-POSS on the phase segregation of the typical immiscible polymer blend PMMA and PS prepared from spinning coating of toluene solution. They found that the CpPOSS moieties pendent to PMMA compatibilized polymer blends of PMMA and PS, indicated by profound interfacial tension reduction and interfacial fracture toughness increase. The authors attributed their observations to a favorable interaction between CpPOSS and PS homopolymer, combined with POSS attachment to a PMMA backbone that maintained the copolymers at the PS/PMMA interface. In the present study, comparison of CpPOSS, ⁱBuPOSS, and CyPOSS systems using WAXS analysis revealed that isobutyl-POSS (ⁱBuPOSS) and cyclohexyl-POSS (CyPOSS) featured a stronger favorable interaction with the PS host than CpPOSS, which aggregates to form nano-crystals in PS host beyond a critical concentration.

We must emphasize that at the lower POSS contents used in rheological investigations, in particular ≤ 15 wt-%, the vertex group dependency of the apparent compatibility between POSS and PS

host does not significantly influence the microstructure of the copolymers as revealed in WAXS pattern similarity. Regardless of vertex group, the pendent POSS groups are dispersed in the PS matrix nearly at a molecular level for these cases. Despite the microstructural similarity observed with WAXS, we anticipated vertex group specificity in physical property determination, given prior findings⁴ and POSS/styrene-segment interaction differences implied by WAXS at higher loadings. As such, the corresponding thermal and rheological properties are discussed in the following several sections.

Thermal Transitions. The effects of POSS vertex group and their level of incorporation on glass transition temperatures (T_g 's) of the PS-based random copolymers were measured using differential scanning calorimetry (DSC). The glass transition temperatures determined from the midpoint of enthalpy change are shown in Figure 2 (DSC curves are supplied in Supplementary Materials, Supplementary Figure 1). As can be observed, the glass transition temperature of the random copolymers depends in a complex way on POSS loading level and vertex group. First, let's take a look at the effect of POSS content. For ⁱBuPOSS-containing copolymers, the glass transition monotonically decreases with the increase of POSS loading, while the random copolymers bearing CpPOSS show the *opposite* trend: T_g increases with increasing CpPOSS content. CyPOSS-containing copolymers show intermediate behavior with non-monotonic composition dependence, in particular a minimum value of glass transition between 0 wt-% and 15 wt-% POSS loading. Thus, the glass transition temperature of pure PS is higher than that of copolymer incorporating 6 wt-% CyPOSS but lower than that of the one incorporating 15 wt-% CyPOSS. Beyond 6 wt-%, the glass transition temperature of CyPOSS copolymers increases significantly with CyPOSS loading such that, above 30 wt-%, T_g is greater for CyPOSS copolymers than for CpPOSS copolymers.

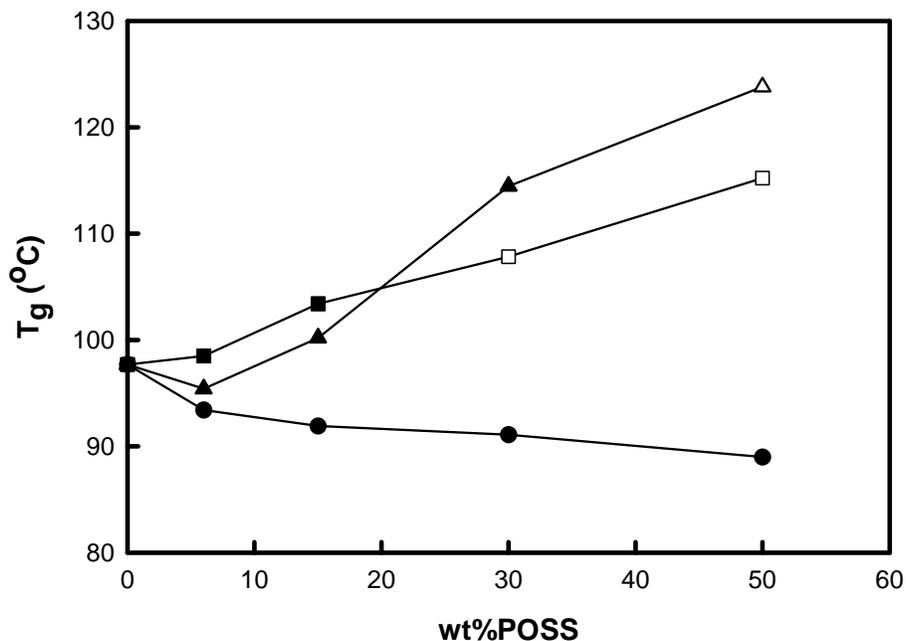


Figure 2. The variation of glass transition temperature (T_g) for as-cast PS-based copolymers films as the function of POSS content. T_g is determined from the midpoint of enthalpy change in the DSC trace curves. POSS vertex group varies with: (●) i BuPOSS, (■) CpPOSS, (▲) CyPOSS. The open symbols represent the samples insoluble.

To understand the observed T_g trends, consider that the presence of side groups is known to influence a particular polymer's T_g by an amount (and in a direction) that depends on the flexibility and bulk of the side group. Usually, rigid side chains and/or pendant groups decrease the flexibility of the backbone chain and lead to an increase in glass transition temperature. In principle, the glass transition of carbon-backbone polymers reflects the rotational energy barriers about σ bonds of the backbone chain, lower glass transition temperatures resulting from lower energy barriers. While rigid side groups may restrict torsion about σ bonds in the backbone chain, increasing T_g , the dominating effect of flexible side groups is to increase free volume, lowering T_g . For example, the glass transition temperatures for the poly(n -alkyl methacrylate) family²⁰ monotonically decrease with the $-(CH_2)_n-CH_3$ side chain length. In the case of pendent POSS moieties, the combined influence of these competing factors leads to complex T_g dependence on composition.

While POSS cages are undoubtedly rigid and their significant volume can induce a steric barrier that would increase T_g , the high density of chain ends from each dynamic vertex group of POSS is expected to increase free volume, potentially lowering T_g by internal plasticization. Because the size of POSS units (see Figure 1) and overall side-group flexibility are quite similar among the vertex groups (ⁱBu, Cy and Cp), we can't attribute the dramatic and complex vertex group dependence of T_g on only these two competing effects.

Strong specific intermolecular interactions (also called supplementary valences), such as hydrogen bonding, ion-ion interaction, acid-base interaction, among others, can restrict polymer chain motion and results in enhancement of T_g . In our case, the intermolecular interaction between POSS-POSS and POSS-polymer matrix is mainly through Van der Waals attraction, which is much weaker than those supplementary valences listed above. However, on a volumetric basis, seven inert vertex groups may contribute 80% of the POSS volume, which mediates interaction between POSS group and non-POSS polymeric segments. Undoubtedly, this kind of Van der Waals interaction can be tuned by varying the type of vertex group. In one report, Xu et al.^{21, 22} found that the presence of styryl-isobutylPOSS made the glass transition of the poly(acetoxystyrene) (PAS) and poly(vinylpyrrolidone) (PVP) dramatically decrease. Once the hydroxyl-styrene repeat unit was introduced to these two polymer chains, the glass transition temperatures dramatically increased because of the formation of hydrogen bonds between phenol group and POSS cage oxygens as well as between phenol group and pyrrolidone group. Conversely, for POSS functionalized with cyclopentyl (Cp) and cyclohexyl (Cy) vertex groups, the increase of glass transitions was extensively observed in the random copolymers, such as poly(4-methylstyrene-POSS),^{23, 24} poly(norbornyl-POSS),²⁵ poly(methacrylate-POSS),²⁶ Poly(siloxane-POSS),²⁷ among others. Typically, this takes place when the POSS content is a high weight % and is a measure of the interference of a POSS-based physical network with chain motion.

In total, the variation of glass transition temperature in the random copolymers is the net result of several effects: free volume fraction, steric barrier, and POSS—polymeric segment interactions. For ⁱBuPOSS copolymers, we observed monotonic T_g decrease within increasing loading (Figure 2) and

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thus infer that POSS-segment interactions are dominated by the internal plasticization of local free volume addition. In contrast, it is apparent from Figure 2 that intermolecular POSS- PS segment interactions are important in determining T_g of the CpPOSS and CyPOSS copolymers, with competition between free volume and intermolecular interactions evident in the latter case. Additional evidence for non-covalent intermolecular interactions will be found in the rheological behavior above T_g for the same materials, discussed later.

In last section, we reported on a relatively sharp peak that appeared in the WAXS pattern of PS₅₀CpPOSS₅₀, which is close to the characteristic diffraction peak of styryl CpPOSS macromer. In order to further confirm the presence of nanocrystals formed by POSS aggregation, we annealed the copolymers with 50 wt-% POSS at 150 °C for 12 h. The DSC heating curves (see Supplementary Figure 1) showed that only the PS₅₀CpPOSS₅₀ sample featured any evidence of a weak melting peak, which further proves that the tethered CpPOSS moieties can aggregate to form nanocrystals in PS host. Meanwhile, neither PS₅₀ⁱBuPOSS₅₀ nor PS₅₀CyPOSS₅₀ showed any evidence for POSS crystallization either by WAXS or DSC analysis. Thus, we are confident that CpPOSS features less compatibility than ⁱBuPOSS and CyPOSS in the PS host. Although CpPOSS shows phase-separation at the nano-scale while CyPOSS does not, it is interesting that the latter features the larger T_g increment than the former. We suggest that the interaction between CyPOSS and PS segments is stronger than that between CpPOSS and PS host and/or even than between CpPOSS and CpPOSS.

Rheological Behavior.

Time Temperature Superposition. To examine the effect of POSS and vertex group on the linear viscoelastic properties of PS random copolymers, isothermal frequency sweep tests were conducted within the temperature range 120 °C < T < 180 °C. This limited temperature span was chosen to avoid significant thermal degradation and side reactions, yet feature samples compliant enough (as 8 mm disks) to not over-torque the instrument. The principle of time-temperature superposition (tTS) was applied to obtain linear viscoelastic master curves. Frequency sweep data for a range of temperatures

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were shifted to a common reference temperature of 120 °C, using temperature-dependant frequency shift factors (a_T). The modulus shift factor (b_T) usually is close to unity and was not required here for good superposition. The data in the master curves were ensured to be in the linear regime by obtaining the strain-independent viscoelastic properties as revealed by strain sweep tests (not shown).

The master curves of random copolymers with 6 wt-% and 15 wt-% POSS varying with vertex group are compared in Figures 3 and 4, respectively, wherein the data extend over approximately 8 decades of reduced frequency. Like pure amorphous PS, all of the random copolymers were found to be thermorheologically “simple”, allowing time-temperature-superposition (tTS) to function within the temperature range, and exhibited glass-rubber transition, a rubbery plateau, and rubber-liquid transition and terminal zone regimes with the decrease of reduced frequency. Thus, it is confirmed that all samples studied are entangled as anticipated based on the molecular weight detailed in Table 1.

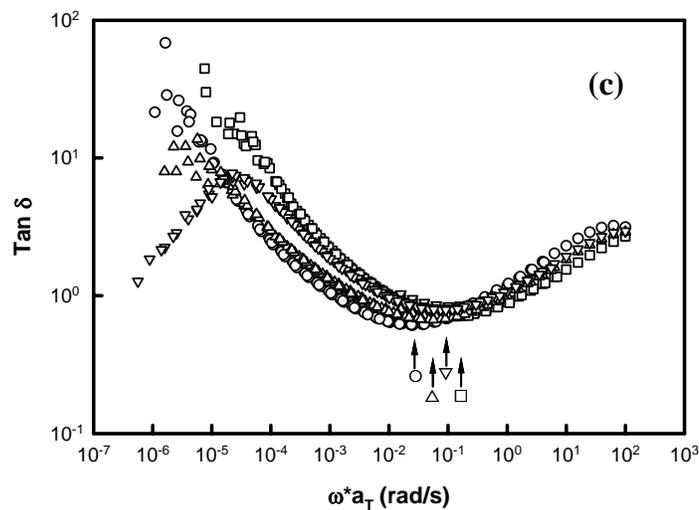
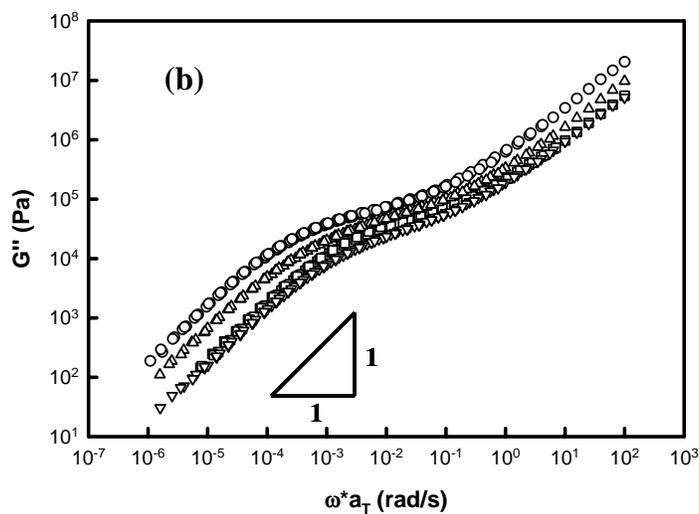
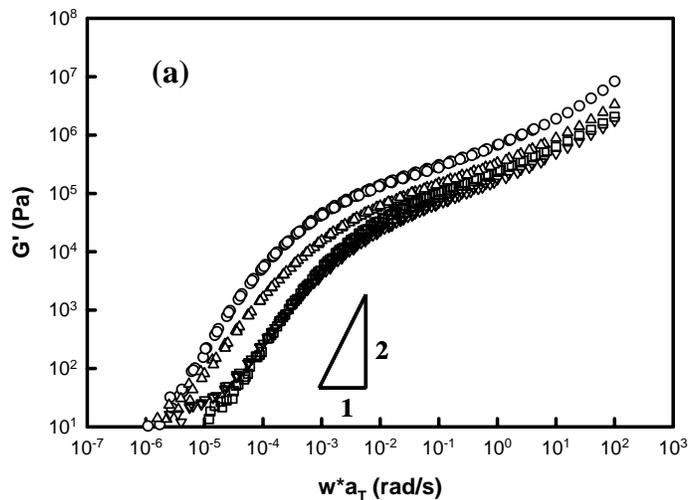


Figure 3. Master Curve of the copolymers incorporating 6wt-% POSS varying with vertex group: (○) PS, (□) *i*BuPOSS, (△) CpPOSS, (▽) CyPOSS, with reference temperature 120°C: (a) G' ; (b) G'' and (c) $\text{Tan } \delta$. The arrows in (c) indicate the minimum values of $\text{tan } \delta$ for each sample.

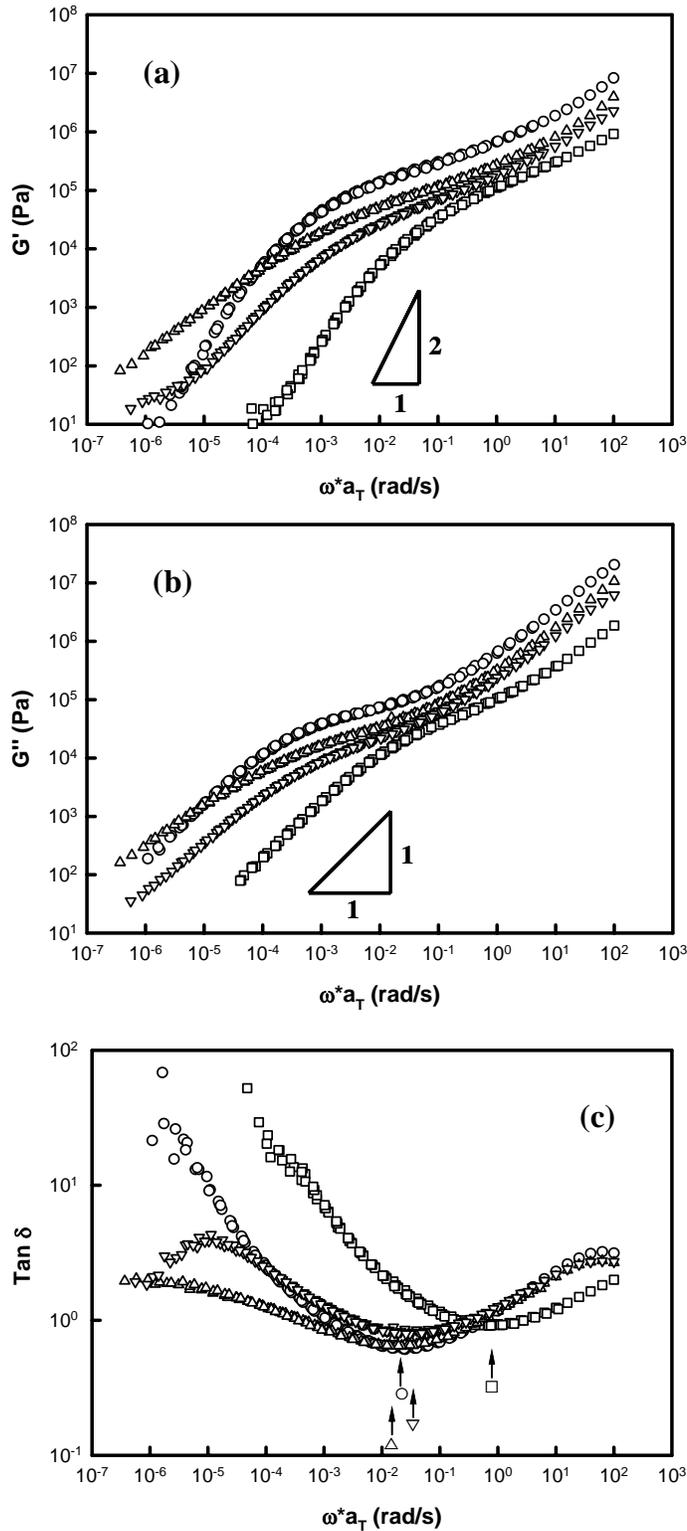


Figure 4. Master Curve of the copolymers incorporating 15wt-% POSS varying with vertex group: (○) PS, (□) *i*BuPOSS, (△) CpPOSS, (▽) CyPOSS, with reference temperature 120°C: (a) G' ; (b) G'' and (c) $\tan\delta$. The arrows in (c) indicate the minimum values of $\tan\delta$ for each sample.

The time-temperature-superposition (tTS) shift factor, $a_T(T)$, can be described by WLF-equation,

$$\log a_T = \frac{-C_1^g(T - T_g)}{C_2^g + (T - T_g)} \quad (1)$$

Here, $C_1^g = B/2.303f_g$ and $C_2^g = f_g/\alpha_f$, where f_g is fractional free volume at T_g , and α_f is the thermal expansion coefficient of fractional free volume.²⁸ Conventionally, the value of B is a constant and assumed to be 1. If the reference temperature, T_r , is different from glass transition temperature, WLF equation is rewritten as:

$$\log a_T = \frac{-C_1^r(T - T_r)}{C_2^r + (T - T_r)} \quad (2)$$

where $C_1^r = B/2.303f_r$, $C_2^r = f_r/\alpha_f$, and f_r is the fractional free volume at the reference temperature T_r . Furthermore, plots of $1/\log(a_T)$ versus $1/(T - T_r)$ should be linear if the WLF equation is a good representation of the temperature-dependent viscoelastic properties. In such cases, the WLF parameters can be determined from the slopes and intercepts of the plots. The relationship between C_1^r , C_2^r , f_r , and C_1^g , C_2^g , f_g can be expressed as follows,²⁸ noting that such calculations yield material properties that are independent of the arbitrarily selected $T_r=120$ °C value:

$$C_1^g = \frac{C_1^r C_2^r}{C_2^r + T_g - T_r} \quad (3)$$

$$C_2^g = C_2^r + T_g - T_r \quad (4)$$

$$f_g = \frac{B(C_2^r + T_g - T_r)}{2.303C_1^r C_2^r} \quad (5)$$

From these parameters, it is possible for us to evaluate the effect of POSS introduction on the free volume fraction and its temperature dependence.

Figures 5(a) and 5(b) show WLF plots of random copolymers with 6 wt-% and 15 wt-% POSS, respectively, revealing linearity, and thus WLF-applicability, for all vertex groups at these loadings. From the slope and intercept, we evaluated the C_1^r , C_2^r , f_r , whose values at the glass transition

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temperature can be calculated using Eqn. (3)-(5), as described above. The calculated values of free volume parameters of random copolymers with different POSS content and vertex group are tabulated in Table 2. While a clear trend in fractional free volume with POSS is absent for a fixed reference temperature of 120 °C, employing T_g as the reference temperature reveals an intriguing trend that the reference fractional free volume (f_g) monotonically *increases* with POSS content, regardless of vertex group. (Gratifyingly, the value of f_g for PS (0.0283) is nearly identical to the value reported in the literature.²⁹) These results imply that the presence of POSS molecules tends to create void volume in the glassy and melt states, which may increase segmental mobility. Meanwhile, the increase in f_g/B (free volume at T_g) also has a strong dependence on vertex group following the sequence: ${}^i\text{BuPOSS} < \text{CyPOSS} < \text{CpPOSS}$. Considering the glass transition behavior discussed previously (Figure 2), it is quite surprising that T_g follows the same trend as f_g/B (at least for low POSS contents), so that the polymer with highest T_g also has highest f_g/B .

Table 2. Summary of Viscoelastic Characteristics of Polystyrene-POSS Copolymers with various vertex group at reference temperature 120 °C.

Compound	C_1^r	$C_2^r(\text{K})$	f_r/B	f_g/B	$\alpha_f (\text{K}^{-1})$
PS ₁₀₀	8.18	47.84	0.0531	0.0283	11.09×10 ⁻⁴
PS ₉₄ ⁱ BuPOSS ₆	8.05	60.10	0.0540	0.0298	8.98×10 ⁻⁴
PS ₉₄ CpPOSS ₆	8.47	57.93	0.0513	0.0323	8.85×10 ⁻⁴
PS ₉₄ CyPOSS ₆	8.51	58.31	0.0510	0.0297	8.75×10 ⁻⁴
PS ₈₅ ⁱ BuPOSS ₁₅	9.15	85.55	0.0475	0.0319	5.55×10 ⁻⁴
PS ₈₅ CpPOSS ₁₅	10.06	81.31	0.0432	0.0342	5.31×10 ⁻⁴
PS ₈₅ CyPOSS ₁₅	10.72	96.96	0.0405	0.0323	4.18×10 ⁻⁴

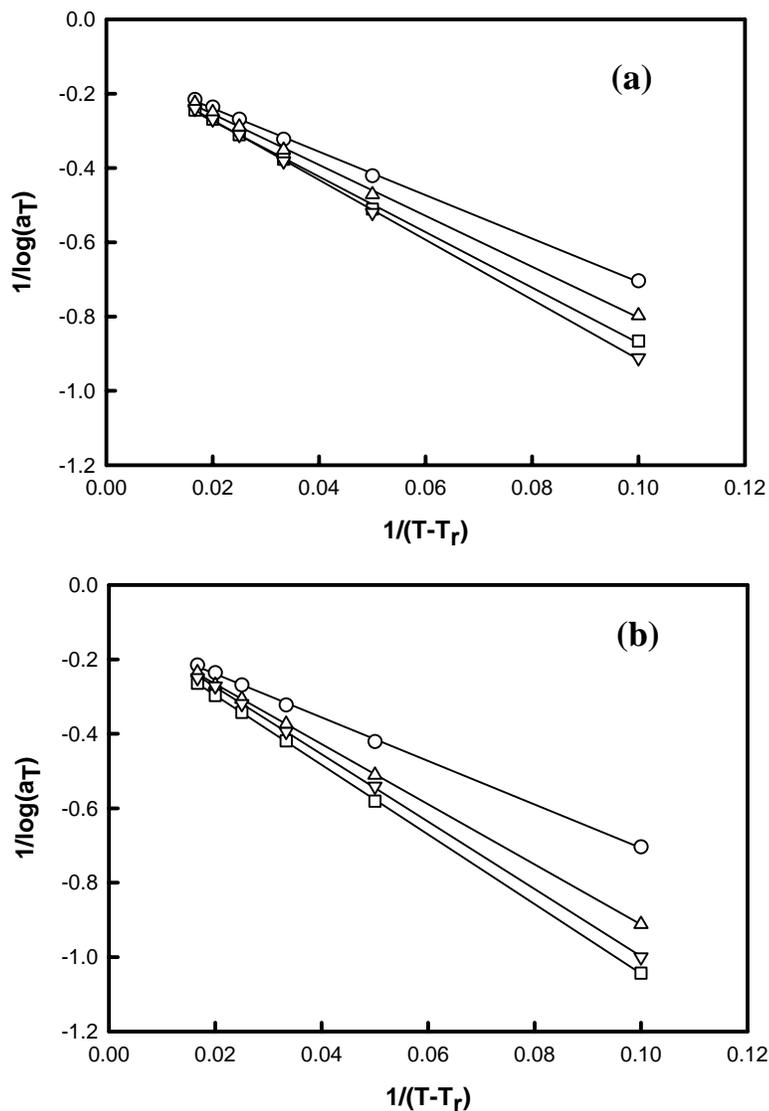


Figure 5. The WLF Function Plot of shift factor for as-cast films of the random copolymers as a function of vertex group with (a) 6wt% and (b) 15wt% POSS: (○) PS; (□) ⁱBuPOSS, (△) CpPOSS and (▽) CyPOSS with reference temperature 120 °C.

Like f_g , α_f also features a strong dependence of POSS loading level and vertex group composition. Regardless of vertex group, the values of α_f decrease with increasing POSS content, indicating that the presence of POSS reduces the temperature-dependence of fractional free volume. The vertex group dependence of α_f follows the sequence: CyPOSS < CpPOSS < ⁱBuPOSS, or inversely with POSS volume.^{30, 31} Above T_g , fractional free volume f follows the temperature-dependence:

$$f(T) = f_g + \alpha_f (T - T_g) \quad T \geq T_g \quad (6)$$

Based on our shift-factor measurements (Table 2), pure PS features much larger $f(T)$ values within the regime of rheological characterization ($120 \text{ }^\circ\text{C} < T < 180 \text{ }^\circ\text{C}$) than random copolymers incorporating POSS due to its largest α_f value (see Supplementary Figure 2), although it shows the lowest free

volume fraction at T_g . The observed differences suggest that POSS copolymers may exhibit quite low thermal expansion coefficients in the melt, and thus precision moldings of amorphous plastics with low residual stress, with CyPOSS-containing systems being the lowest. However, such experiments have not yet been pursued to our knowledge.

Rubbery Plateau. Rheologically, the so-called rubbery plateau appears above the glass transition temperature²⁹ and is characterized by the plateau modulus, G_N^o that is inversely proportional to the average molecular weight between two entanglements (temporary cross-links), termed the entanglement molecular weight, M_e . For polydisperse systems, the plateau modulus can best be determined by applying “tan δ minimum criterion”: G_N^o is equal to the storage modulus G' at the frequency where loss tangent, tan δ , is minimum in the plateau zone,^{32,33}

$$G_N^o = |G'|_{\tan \delta \rightarrow \min} \quad (7)$$

Indeed, both Figure 3(c) and Figure 4(c) revealed that a minimum in tan δ was well-defined for all samples, thus enabling application of this method to the present polydisperse copolymers. Figure 6 shows the plateau modulus of the random copolymers varying with POSS loading and vertex group, revealing monotonic decrease with POSS incorporation level for all POSS types. The G_N^o ($\approx 2.0 \times 10^5$ Pa) of PS we determined in this manner is quite close to the value of plateau modulus obtained by integrating the area under the terminal loss peak of mono-dispersed entangled PS (1.99×10^5 Pa).²⁹ Meanwhile, G_N^o is also sensitive to vertex group: the random copolymers incorporating ⁱBuPOSS show the largest plateau modulus among the various materials, and those with CyPOSS feature the lowest G_N^o values.

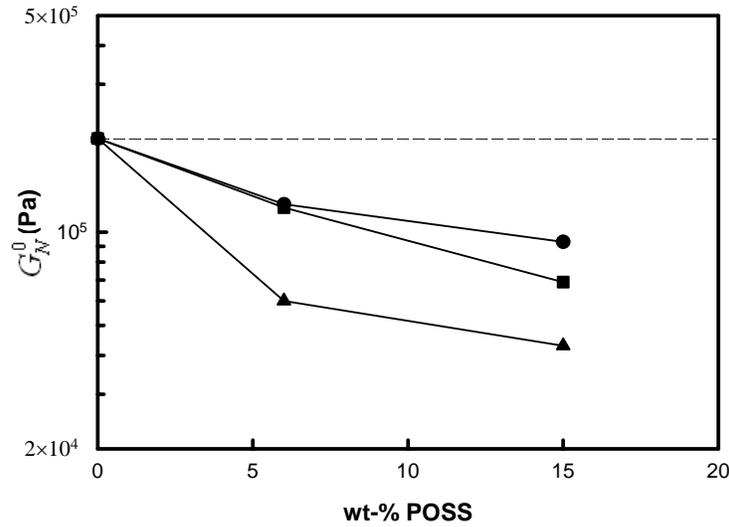


Figure 6. Rubbery Plateau Modulus (G_N^0) for as-cast films of the random copolymers varying with weight percentage of POSS as a function of vertex group: (●) i BuPOSS, (■) CpPOSS, (▲) CyPOSS. G_N^0 is determined by G' at minimum $\tan\delta$. The dash reference line is plateau modulus of PS reported by Onogi *et al.*, *Macromolecules*, **1970**, 3, 109-116.

The relationship between the characteristic value of G_N^0 and M_e can be expressed as follows:

$$G_N^0 = \frac{K\rho RT}{M_e} \quad (8)$$

where R is the universal gas constant, ρ is density, and T is the absolute temperature. K is a constant defined to be $4/5^{28, 34, 35}$ and the density of PS at room temperature is 1.05 g/cm^3 . Barry³⁶ and Larsson^{37, 38} reported crystal densities of POSS-related molecules with different R-groups from CH_3 - (1.51 g/cm^3) to $n\text{-C}_4\text{H}_9$ - (1.14 g/cm^3) to 1-naphthyl- (1.24 g/cm^3). All of them have densities higher than PS at room temperature. Qualitatively, it is reasonable to predict that the densities of POSS copolymers are higher than pure PS, though such data is absent from the literature. Therefore, in employing Eqn. (8), we approximated the copolymer density values by utilizing the PS temperature-dependent density, known³⁸ to follow form: ³⁹

$$\rho(\text{g/cm}^3) = 1.0865 - 6.19 \times 10^{-4}T + 0.136 \times 10^{-6}T^2; T(^{\circ}\text{C}) \quad (9)$$

for the the temperature range $100^{\circ}\text{C} < T < 220^{\circ}\text{C}$. Using this expression, it is apparent that the density of pure PS decreases slightly from 1.01 g/cm^3 to 0.979 g/cm^3 as the temperature increases from 120°C

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to 180 °C. Moreover, melt densities are not expected to increase more than several percent between samples, while G_N^o values were observed to change nearly an order of magnitude. Thus, dramatic reduction in G_N^o upon POSS copolymerization implies with certainty significant increase in M_e , increasingly so with increasing POSS volume as shown by the ordering in Figure 6.

Behavior in the Terminal Zone. Within the terminal zone, linear polymer chains fully relax stress by molecular diffusion and this leads to the following the characteristic power laws: $G' \sim \omega^2$ and $G'' \sim \omega^1$.^{14, 28} For the PS-POSS copolymers under study, as shown in Figures 3 and 4, we found the terminal frequency dependence of G'' to feature an exponent close to 1 for all samples, while the frequency dependence of G' at low frequencies revealed a power-law exponent that deviated from 2 significantly and further featured strong vertex group dependence. For random copolymers incorporating ⁱBuPOSS, the terminal slope of G' (Figure 3(a) and 4(a)) is slightly smaller than 2. In contrast, CpPOSS and CyPOSS copolymers featured dramatically altered frequency dependences of storage modulus (G') and loss tangent ($\tan\delta$) relative to PS and ⁱBuPOSS-PS in the terminal regime. For low CpPOSS incorporation level, PS₉₄CpPOSS₆, the terminal behavior is very close to pure PS and the random copolymers incorporating ⁱBuPOSS. When the CpPOSS content is increased to 15 wt-%, however, the slope of the resulting loss tangent, $\tan\delta$, becomes nearly frequency-independent at a value of ~ 2 (Figure 4(c); triangles), indicating that G' becomes parallel to G'' for reduced frequencies lower than the crossover of G' and G'' . This rheological phenomenon usually appears at the critical condition from liquid-like to solid-like behavior, or so-called “gel point,” first described in detail by Winter et al.^{40, 41} Critical gel behavior for PS₈₅CpPOSS₁₅ – while surprising – will be further substantiated by relaxation modulus measurements, reported below.

Random copolymers incorporating 6 wt-% and 15 wt-% CyPOSS also featured non-terminal rheological behavior: at frequencies lower than the crossover of G' and G'' , the G' slope decreases with decreasing reduced frequency (showing upward curvature) and tends toward frequency-independence. This results in a clear $\tan\delta$ peak and a secondary G' plateau, as shown in Figures 4(c) and 4(a),

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respectively, each at low frequencies. With increasing CyPOSS loading level, this secondary G' plateau increases. It is evident that no real terminal zone is exhibited in the random copolymers incorporating CyPOSS. By comparison, as discussed above, PS₈₅CpPOSS₁₅ showed critical gelation behavior, a regime perfectly intermediate between liquid to solid, while 6 wt-% CpPOSS was fluid-like at low frequencies. Considered together with the T_g behavior discussed in reference to Figure 2, we postulate that observed non-terminal behavior for CpPOSS and CyPOSS copolymers is due to intermolecular POSS-PS segment interactions, following the sequence of increasing strength: ⁱBuPOSS < CpPOSS < CyPOSS.

In order to further understand the effect of vertex group on the terminal behavior, we conducted the stress relaxation experiments, where shear stress is monitored following application of a small (linear) and near-instantaneous shear strain, γ_0 , to yield $G(t) = \sigma(t)/\gamma_0$. Figure 7 shows the stress relaxation curves of random copolymers with 15 wt-% POSS loading and different vertex group at 170 °C. The random copolymer with 15 wt-% ⁱBuPOSS has stress relaxation behavior quite similar to pure PS, while CpPOSS and CyPOSS copolymers feature quite unique behavior. Consistent with our assertion of critical gel behavior on the basis of dynamic oscillation data, PS₈₅CpPOSS₁₅ reveals a relaxation modulus following power law decay. This relaxation behavior is unique to “gel point” with self-similar structures.

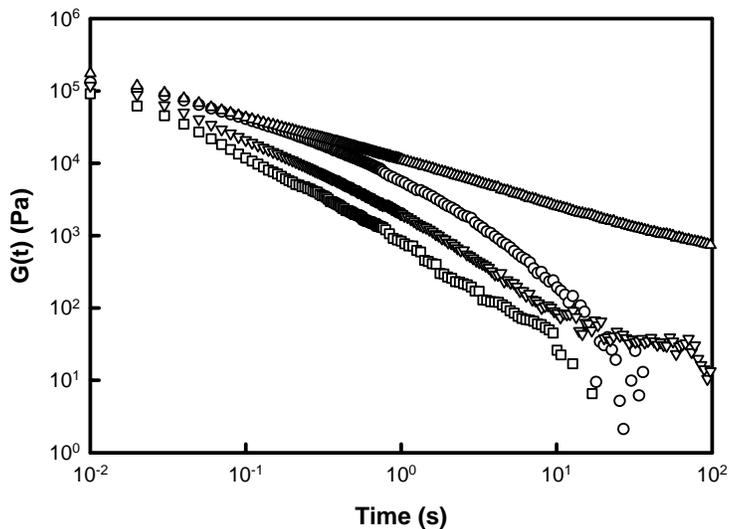


Figure 7. Shear relaxation modulus, $G(t)$, for as-cast films of the random copolymers with 15wt% POSS as a function of vertex group: (○) PS; (□) ⁱBuPOSS, (△) CpPOSS and (▽) CyPOSS with step shear strain of 5% at 170 °C.

Winter et al⁴⁰ suggested at the critical condition from melt-like to solid-like, the relaxation modulus could be expressed as follows:

$$G(t) = S_c t^{-n_c} \quad \text{for } t > \lambda_0 \quad (12)$$

where S_c is the gel stiffness, n_c is the critical relaxation exponent and λ_0 is the relaxation time denoting the crossover to some faster dynamics, such as segmental dynamics. For the PS₈₅CpPOSS₁₅, the gel stiffness, S_c , and the critical relaxation exponent, n_c , were measured to be 10⁴ Pa and 0.61, respectively. By comparison, the analogous CyPOSS copolymer, PS₈₅CyPOSS₁₅, displayed complex behavior, the relaxation first hesitating after ca. 10 s at a stress plateau of 60 Pa, followed by continued relaxation (as a fluid) after a total delay of around 80 s. The intermediate plateau observed is consistent with that seen in oscillatory shear, shown in Figure 4. Additionally, its shear modulus begins relaxing after a characteristic time of about 80 s with a slope close to 2, although the data is too noisy to accurately measure the slope within the limited data at long times.

Finally, we were interested in comparing the effect of vertex group on terminal relaxation behavior. Experimentally, there are several methods to obtain terminal relaxation time for linear polymers. In the framework of the tube model the relaxation of polymer chains in the terminal zone follows the configurational rearrangement accomplished by reptation-like diffusion along its contour with a random choice of new paths. The resulting terminal relaxation time predicted by this model can be expressed as:³⁴

$$\tau \equiv \eta_0 \cdot J_e^0 = \frac{12\eta_0}{\pi^2 G_N^0} \quad (13)$$

For the present study, however, we were unable to obtain zero shear viscosity values due to the lack of a clear terminal zone, discussed above, particularly for random copolymers of incorporating CyPOSS and CpPOSS. To proceed, we employed the reciprocal crossover frequency (ω_c) (where $G_c(\omega_c) = G'(\omega_c) = G''(\omega_c)$) in approximating the terminal relaxation time using the expression, $\tau_{app} \cong \omega_c^{-1}$. Further complicating matters, τ_{app} is a function of molecular weight, not held constant in our study due to

utilization of free radical polymerization. As such, the terminal relaxation time data exhibit complex dependence on POSS content, vertex group and polymerization degree, as shown in Figure 8 (a) and (b).

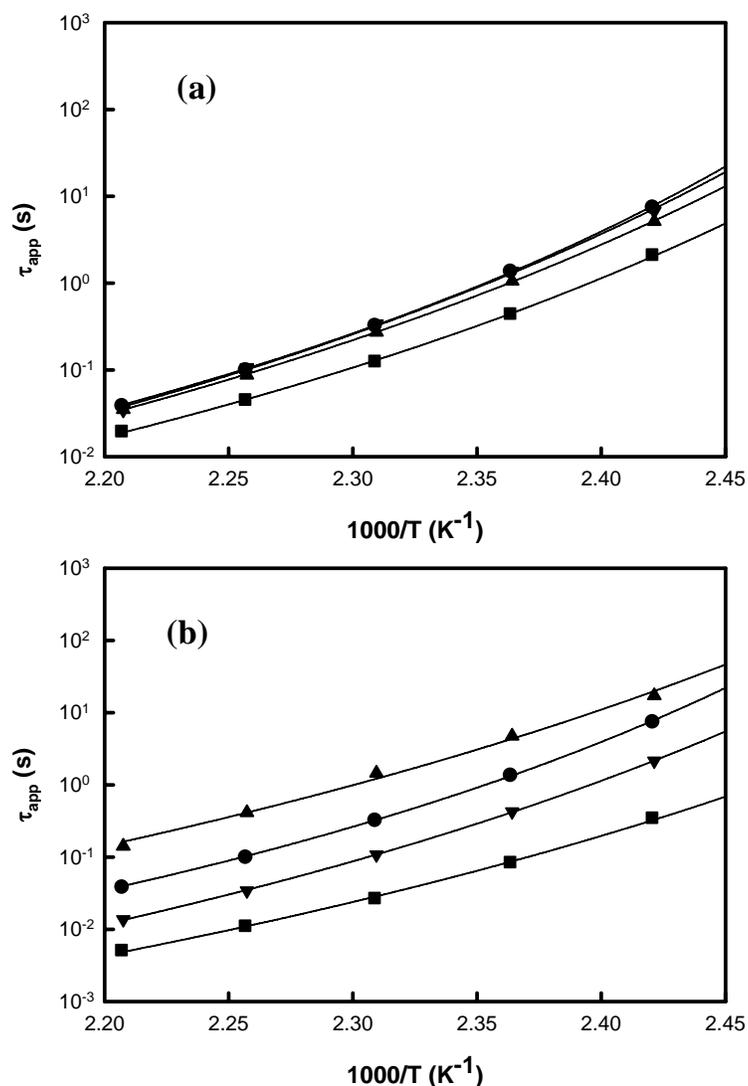


Figure 8. Temperature dependence of apparent terminal relaxation time (τ) for as-cast films of random copolymers as a function of vertex group with (a) 6wt% and (b) 15wt% POSS: (●) PS; (■) ⁱBuPOSS, (▲) CpPOSS and (▼) CyPOSS. The solid lines represent the best-fit VFTH curves for the copolymers and PS homopolymer.

Despite this complexity, we can rationally extract the impact of POSS on terminal relaxation behavior by focusing on its temperature dependence. Generally, the temperature dependence of terminal relaxation time within the range of $T_g < T < T_g + 100K$ can be well-described by the Vogel-Fulcher-Tamman-Hesse (VFTH) equation:⁴²⁻⁴⁴

$$\tau_{app} = A \exp\left(\frac{B}{T - T_0}\right) \quad (14)$$

where A is a pre-exponential factor with unit of time, T_0 is the so-called “ideal glass transition temperature” and B is referred to as the “apparent activation energy”, physically representing an Arrhenius-like temperature activation energy (though with units of temperature). Figure 8(a) and (b) show the temperature dependence of terminal relaxation time of random copolymers incorporating 6 wt-% and 15 wt-% POSS, together with the best-fit VTFH curves. As shown in Figure 9, the apparent activation energy, B , increases with increasing POSS content, regardless of vertex group. The copolymerization with POSS groups makes the temperature dependence of polymer chain relaxation less. Meanwhile, the apparent activation energy also features strong vertex group dependence: $i\text{BuPOSS} < \text{CpPOSS} < \text{CyPOSS}$. Thus, we observed the lowering of the temperature-sensitivity for apparent terminal relaxation time due to POSS incorporation and additional sensitivity to vertex group composition, consistent with α_f measurements within the WLF model, discussed earlier.

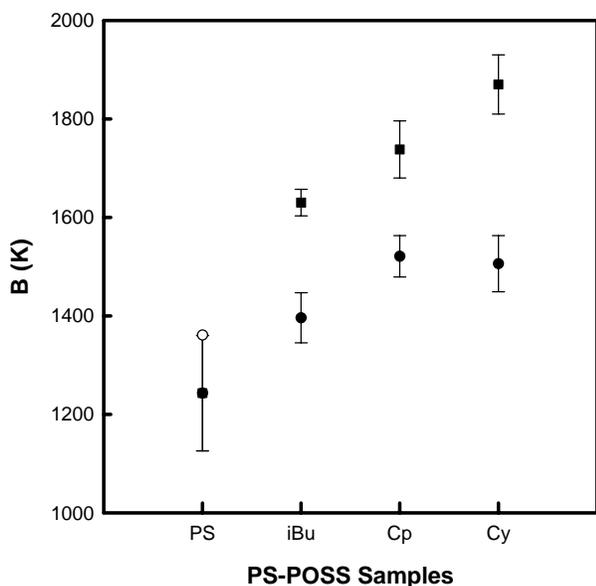


Figure 9. Best-fit apparent activation energy, B , of VTFH curves for PS-based random copolymers incorporating POSS moieties with different POSS vertex groups: (●) 6wt% and (■) 15wt% POSS. The open circle stands for the value reported previously⁴⁵.

DISCUSSION

Architecturally, POSS groups grafted on the PS chain can be considered compact, short-chain branches that alter the chain topology and introduce additional free volume.⁵ Additionally, if we regard the POSS molecule as a functional group, the presence of POSS results in additional intermolecular interactions between POSS-POSS and/or POSS-PS matrix. The analysis of WLF equation and the

terminal rheological behavior of the random copolymers confirmed these two categories of effects, respectively.

The rubbery plateau modulus is also related to the effect of POSS group on the microscopic topology of polymer chain and intermolecular interaction. It was argued, within the framework of the reptation tube theory, that the presence of POSS molecule significantly changes the microscopic topology of the random copolymer chains and leads to an increase in the effective tube diameter.⁵ It could be the origin of POSS-based dilution of entanglement density and the decrease of the resulting rubbery plateau modulus. If there is the strong intermolecular interaction, the plateau modulus will be enhanced and there will be two characteristic relaxation times above glass transition temperature (T_g): one for disentanglement and the other for disassociation of specific intermolecular interactions. This mechanism can be described by “sticky reptation” and appears in a model developed by Liebler et al.¹¹ for hydrogen-bonded elastomers. In this study, we observed that the rubbery plateau moduli for CpPOSS and CyPOSS copolymers *decreased* with the increasing POSS loading, while DSC data showed evidence for significant intermolecular interaction. Furthermore, the vertex group dependence of rubbery plateau modulus follows the sequence: CyPOSS < CpPOSS < ⁱBuPOSS. This trend is opposite expectations based on intermolecular interactions between POSS and PS host, suggesting that microscopic topology of polymer chains plays the dominant role in the rubbery plateau modulus when POSS loading is ≤ 15 wt-%.

Since their size is comparable to a polymeric coil, POSS groups grafted on the PS chain play the same role as branches. There are a few studies on the melt rheology reported for branched polystyrene.⁴⁵⁻⁴⁸ Ferri et al.⁴⁵ prepare the randomly branched polystyrene by copolymerization of styrene (St) and divinylbenzene (DVB) and studied the melt rheology of linear and randomly branched polystyrene (LPS and RBPS). They found that the shift factors (a_T) of LPS are not very different from those of RBPS. Meanwhile the activation energy was observed to slightly increase with the branching degree, demonstrating a weaker temperature dependence of terminal relaxation for RBPS than for LPS.

Our results revealed increasing activation energy with POSS incorporation (POSS branching) consistent

with the results observed in the randomly branched polystyrene.⁴⁵ There are several theoretical models to explain the effects of branches on the temperature dependence of terminal relaxation time, including coupling model,⁴⁹⁻⁵¹ and the reptation theory.⁵² Their predictions are consistent with our observations in the random copolymers from styrene and styryl-POSS, although they are applicable to the polymers with polymeric coil branches. This consistency may stem from the nature of the POSS branches, well-defined nano-scale cage, pendant to the polymer main chain.

Additionally, Romo-Urbe et al.⁴ noticed a ten-fold linear density (mass/backbone length) difference between styryl-POSS and 4-methyl styrene. The massive POSS elements, like non-diffusive “anchors”, were suggested to play a large inertial effect and dramatically alter dynamics of the whole polymer chain, speculation later substantiated by molecular dynamics (MD) simulations of Bharadwaj et al.¹⁰ on POSS-polynorbornene (PN) random copolymers. Moreover, MD simulations indicated that CpPOSS and CyPOSS-PN copolymers showed weaker temperature dependence of elastic moduli than pure PN, in accordance with the present report. Still further, the same authors reported volumetric thermal expansion coefficients for PN-POSS copolymer melts with 10 wt-% loading: PN₉₀CpPOSS₁₀ ($6.49 \times 10^{-4} \text{ K}^{-1}$) > PN₉₀CyPOSS₁₀ ($5.20 \times 10^{-4} \text{ K}^{-1}$). This vertex group dependence is in accordance with our observations in tTS analysis although they did not provide the corresponding value of iBuPOSS counterpart.

CONCLUSIONS

We investigated the thermal and linear rheological behavior of polystyrene (PS)-based random copolymers incorporating POSS with three kinds of vertex groups: isobutyl (iBu), cyclopentyl (Cp) and cyclohexyl (Cy). WAXS patterns showed a lack of POSS aggregation or crystallization at lower POSS loading levels, indicating that POSS disperses in the PS matrix nearly at a molecular level. For higher loadings (i.e. 50 wt-%), the compatibility between POSS and PS segments featured strong vertex group dependence: CpPOSS tended to aggregate into nano-crystals, confirmed by DSC experiments, while

ⁱBuPOSS and CyPOSS didn't. The glass transition temperature of the copolymers features complicated vertex group dependence with the T_g monotonically decreasing with increasing ⁱBuPOSS content and CpPOSS and CyPOSS featuring glass transition enhancement, though with complex dependence in the CyPOSS case. We assert that the vertex group dependence of the glass transition of the copolymers results from competing effects of free volume addition and intermolecular interactions.

Rheological characterization showed that time-temperature superposition (tTS) works well over the range of temperatures and POSS contents explored. The well-fitted WLF equation revealed vertex group dependence of the free volume fraction at glass transition, following the sequence: ⁱBuPOSS < CyPOSS < CpPOSS. Meanwhile, vertex group dependence of the corresponding thermal expansivity of free volume (α_f) follows the sequence: CyPOSS < CpPOSS < ⁱBuPOSS and the values of α_f decrease with the increasing POSS content. Regardless of vertex group, the rubbery plateau modulus decreased with increasing POSS content. It was argued, within the framework of the reptation tube theory, that the presence of a POSS moiety significantly changes the microscopic topology of the random copolymer chains and leads to an increase in the effective tube diameter and that this could be the origin of POSS-based dilution of entanglement density. More specifically, the rubbery plateau modulus was decreased in proportion to POSS size, following the sequence: ⁱBuPOSS > CpPOSS > CyPOSS.

Introduction of CpPOSS and CyPOSS comonomers dramatically altered terminal zone response, while ⁱBuPOSS copolymers were similar to PS homopolymer in this regard. In particular, ⁱBuPOSS copolymers featured a monotonic increase of $\tan\delta$ with the decreasing reduced frequency, while with the 15 wt-% CpPOSS copolymer revealed near frequency-independence $\tan\delta$, characteristic of a "critical gel." The loss tangent, $\tan\delta$, master curves of random copolymer with 6 wt-% and 15 wt-% CyPOSS featured an additional relaxation peak at the terminal zone, attributed to intermolecular interactions between POSS and PS matrix. The apparent terminal relaxation time, estimated by the crossover frequency, were found to be less sensitive to the temperature change for POSS copolymers than for the pure linear PS. Regardless of vertex group, the apparent activation energy the POSS copolymers

increased with the increasing POSS loading. Meanwhile, it also features strong vertex group dependence: ⁱBuPOSS < CpPOSS < CyPOSS.

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