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)₂(CH₂)₄, with R = isobutyl (iBu), cyclopentyl (Cp), and cyclohexyl (Cy), was studied to reveal a 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 and 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″) 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 BuPOSS-based copolymers, like pure PS; however, CyPOSS and CyPOSS copolymers lead to low-frequency elasticity for higher POSS contents, suggesting a weak physical network, with a particular CyPOSS 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−Tammann−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.
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 analogue. By comparison, CpPOSS-incorporating co-polymers featured a higher critical mole fraction of $\sim 16$ mol % for the onset of low-frequency solidlike 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 by Leibler et al., which was conceived to describe the dynamics of hydrogen-bonded elastomers. 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. reported the linear viscoelastic properties of poly(methyl methacrylate) (PMMA) tethered and untethered by POSS. They found that the introduction of isobutyl-POSS ('BuPOSS) 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 'BuPOSS copolymer. To be contrasted with the random copolymers incorporating 'BuPOSS, 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 $G'' \sim \omega^s$, where $G'$ and $G''$ are the shear storage and loss modulus, respectively.

Clearly, the POSS vertex group offers a compositional means to control the rheological behavior of polymers incorporating POSS. However, only a 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-pendent polymers with a variety of vertex groups: isobutyl ('Bu), 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 ('Bu), cyclopentyl (Cp), and cyclohexyl (Cy). As shown in Scheme 1, the random copolymers were synthesized through free radical copolymerization using methods previously described. Briefly, a 10.0 molal monomer solution in toluene containing a total of 3 g of monomers was initiated using 0.25 mol % azobisisobutyronitrile (AIBN). One representative synthesis to yield 6 wt % POSS (designated hereafter as PS$_6$CyPOSS$_{10}$) follows: Under a nitrogen atmosphere, a dry O$_2$-free solution of toluene (2.73 mL), [(C$_8$H$_7$)Cy$_7$(Si$_8$O$_{12}$)] (180 mg, 0.196 mmol), styrene (2820 mg, 27.08 mmol), and AIBN (11.2 mg, 0.068 mmol) was heated to 60 °C for 2 days. This was then diluted with 15 mL of CHCl$_3$ and precipitated into 100 mL of methanol. After stirring for 1 h, the copolymer was isolated on fritted glassware and air-dried.
overnight. 'H 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 styrly monomer, R is the POSS vertex group, and y is the wt % of POSS comonomer. As one example, PS_85BuPOSS_15 is a random copolymer containing 85 wt % PS and 15 wt % BuPOSS.

We observed that the solubility of the random copolymers prepared from styrene and styrly-POSS depended strongly on the compatiblity of POSS in PS host, samples with 50 wt % POSS were annealed at 150 °C for 4 days. Next, the free-standing cast films were dried at room temperature on the Teflon casting dishes, 10 cm in diameter, and dried at room atmosphere. All of the rheological characterizations were 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 μm resolution.

Table 1. Summary of Molecular Characteristics of Polystyrene—POSS Copolymers

| compound | M_n × 10^3 (g/mol) | M_n/M_w | wt % POSS | mol % POSS | no. POSS, a | viscoelastic regime were determined by measurements of the dynamic storage and loss moduli, G'(ω) and G''(ω), 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'(ω) and G''(ω) are independent of strain. The dynamic moduli were measured as a function of frequency over the range 0.01 rad/s < ω < 100 rad/s at various temperatures above T_g in the range 120 °C < T < 180 °C and under a nitrogen atmosphere. All of the rheological characterizations were 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 μm 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_n > 1.5 × 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 BuPOSS feature lower PDI values than the counterparts bearing CpPOSS and CyPOSS. Furthermore, PDI values of the latter copolymers increased with increasing CyPOSS and CyPOSS loading, which could be due to their decreasing solubility with increasing CyPOSS and CyPOSS incorporation in the reaction media, toluene. 'H NMR characterization revealed that the actual POSS incorporation ratio in copolymers was very close to the feeding ratio and independent of vertex group. These observations indicate that styrly-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 styrly for free radical polymerization. The molecular characteristics of the copolymers are detailed in Table 1.

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

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 radiation with wavelength λ = 1.5418 Å was used as the source. The scattering angle, 2θ, was scanned from 5° to 40° at a rate of 1.0 deg/min.

Nuclear Magnetic Resonance Spectroscopy (NMR). 'H NMR spectra were collected to assess monomer purity, monomer-free polymer, and to confirm the polymer backbone chemical structure. The spectra were obtained in CDCl3 solvent (~30 mg/mL) using either a Bruker 400 or 300 MHz instrument. Standard 1D proton spectra were obtained using a 30 s delay pulses to ensure complete relaxation and therefore accurate integral measurements.

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 5–10 mg. All measurements were conducted at a scan rate of 10 °C/min following a heat−cool−heat procedure from 0 to 250 °C. Glass transition temperatures (T_g) were determined by the midpoint of heat flow drop-step (heat capacity step up) 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 h. 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 and 2000 g·cm. The existence and extent of the linear
In particular, for all of the copolymers studied, two characteristic amorphous halos appear, representing the interchain correlations at lower 2θ angle and the correlation distance between side groups along the chains at higher 2θ angle.

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 interchain correlation distance and inter-side-group correlation. 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 11.0 and 8.1 Å; 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 cannot distinguish the existence of small POSS clusters (2–3 molecules) or not.

Compared with the samples containing 30 wt % POSS, the copolymer incorporating 50 wt % CpPOSS (PS50CpPOSS50) exhibits a sharp peak centered at d-spacing = 10.5 Å, 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-spacing. This stands in contrast to PS50iBuPOSS50, 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 the 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 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. studied the effect of random copolymers of PMMA−POSS on the phase segregation of the typical immiscible polymer blend of PMMA and PS prepared from spin-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 CyPOSS 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 CyPOSS, 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 CyPOSS, which aggregates to form nanocrystals in PS host when CyPOSS loading is 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 pendant POSS groups are dispersed in the PS matrix nearly at a molecular level for these
increasing may restrict torsion about temperature. In principle, the glass transition of carbon-backbone chain and lead to an increase in glass transition chains and/or pendent groups decrease the flexibility of the side group. Usually, rigid side groups may restrict torsion about \( \sigma \) 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) family decrease monotonically with the \( -(\text{CH}_2)_n-\text{CH}_3 \) side-chain length. In the case of pendant 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 (Bu, Cy, and Cp), we cannot attribute the dramatic and complex vertex group dependence of \( T_g \) only on these two competing effects.

Strong specific intermolecular interactions (also called supplementary valences), such as hydrogen bonding, ion–ion interactions, acid–base interactions, among others, can restrict polymer chain motion and result in enhancement of \( T_g \). In our case, the intermolecular interactions between POSS–POSS and POSS–polymer matrix are mainly through van der Waals attraction, which is much weaker than those 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 styrylisobutyl-POSS made the glass transition of the poly(acetoxy styrene) (PAS) and poly(vinylpyrrolidone) (PVP) decrease dramatically. Once the hydroxystyrene 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 pyrrolidine group. Conversely, for POSS functionalized with cyclopentyl (Cp) and cyclohexyl (Cy) vertex groups, the increase of glass transitions was observed extensively 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 with high wt % POSS 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–polymer segment interactions. For \( \text{BuPOSS} \) copolymers, we observed monotonous decrease in \( T_g \) with increasing loading (Figure 2) and thus deduce 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 Ps POSS and Cy POSS copolymers, with competition between free volume and intermolecular interactions evidenced in the latter case. Additional evidence for noncovalent intermolecular interactions will be found in the rheological behavior above \( T_g \) for the same materials, discussed later.

In the last section, we observed a relatively sharp peak in the WAXS pattern of PS\(_{50}\)CpPOSS\(_{50}\) close to the characteristic diffraction peak of styryl-CpPOSS macromer. 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 Supporting Information Figure 2) showed that only the PS\(_{50}\)CpPOSS\(_{50}\) sample featured any evidence of a weak melting peak (\( T_m \approx 183.8 \) °C), which further proves that the tethered CpPOSS moieties can aggregate to form nanocrystals in PS host. Meanwhile, neither PS\(_{50}\)BuPOSS\(_{50}\) nor PS\(_{50}\)CyPOSS\(_{50}\) showed any evidence for POSS crystallization either by WAXS or DSC analysis. Thus,
we are confident that CpPOSS features less compatibility than \( \text{‘BuPOSS} and CyPOSS in the PS host. Although CpPOSS shows phase separation at the nanoscale while CyPOSS does not, it is interesting that the latter features the larger \( T_g \) increment than the former. We suggest that the interactions between CyPOSS and PS segments are stronger than those between CpPOSS and the PS host and/or even than between CpPOSS and CpPOSS.

**Rheological Behavior.** Time—Temperature Superposition. To examine the effects of POSS moieties and their vertex groups on the linear viscoelastic properties of PS random copolymers, isothermal thermal sweep tests were conducted within the temperature range \( 120 \degree C < T < 180 \degree C \). This limited temperature span was chosen to avoid significant thermal degradation and side reactions, yet features samples compliant enough (as 8 mm disks) to not overtorque the instrument. The principle of 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, all samples studied are entangled as anticipated based on the molecular weight detailed in Table 1.

The time—temperature superposition (tTS) shift factor, \( a(T) \), can be described by the WLF equation

\[
\log a(T) = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)}
\]

where \( C_1 = B/2.303f_i \), \( C_2 = f_i\alpha_i \), and \( f_i \) is the fractional free volume at the reference temperature \( T_g \). Furthermore, plots of \( l(\log a(T)) \) vs \( 1/(T - T_g) \) 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.\(^5\)

WLF plots of random copolymers with 6 and 15 wt % POSS at reference temperature \( 120 \degree C \) (see Supporting Information Figures 3a,b) reveal the linearity, and thus WLF applicability, for all vertex groups at these loadings. From the slope and intercept, we evaluated the \( C_1, C_2, \) and \( f_i \), whose values at the glass transition temperature can be calculated as described previously.\(^5\) 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 \( 120 \degree C \), employing \( T_g \) as the reference temperature reveals an intriguing trend that the reference fractional free volume \( (f_i) \) monotonically increases with POSS content, regardless of vertex group. (Gratifyingly, the value of \( f_i \) for PS (0.0283) is nearly identical to the value reported in the literature.\(^28\)) 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 \( f_i/B \) (free volume at \( T_g \)) also has a strong dependence on vertex group following the sequence: \( \text{‘BuPOSS} < CyPOSS < \text{CpPOSS} \)

Considering the glass transition behavior discussed previously, it is quite surprising that \( T_g \) follows the same trend as \( f_i/B \) (at least for low POSS contents), so that the polymer with highest \( T_g \) also has highest \( f_i/B \).

Like the fractional free volume, \( f_i, \alpha_i \) also features a strong dependence of POSS loading level and vertex group composition. Regardless of vertex group, the values of \( \alpha_i \) decrease with increasing POSS content, indicating that the presence of POSS reduces the temperature dependence of fractional free volume. The vertex group dependence of \( \alpha_i \) follows the sequence \( \text{CyPOSS} < \text{CpPOSS} < \text{‘BuPOSS} or inversely with POSS.
volume. Above \( T_g \), fractional free volume \( f \) follows the temperature dependence

\[
f(T) = f_g + \alpha (T - T_g) \quad T \geq T_g
\]

Based on our shift-factor measurements (Table 2), pure PS features much larger \( f(T) \) values within the regime of rheological characterization (120 °C < \( T < 180 \) °C) than random copolymers incorporating POSS due to its largest \( \alpha \) value (see Supporting Information Figure 4), although it shows the lowest free volume fraction at \( T_g \). The observed differences suggest that POSS copolymers may exhibit quite lower thermal expansion coefficients than the homopolymer counterparts in the melt, and thus precision molding 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 temperature\(^{28} \) and is characterized by the plateau modulus, \( G_0 \), which 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 \( \delta \) minimum criterion”:

\[
G_0 = |G'|_{\tan \delta \text{ min}}
\]

Indeed, Figures 3c and 4c revealed a well-defined minimum in \( \tan \delta \) for all samples, thus enabling application of this method to the present polydisperse copolymers. Figure 5 shows the plateau moduli of the random copolymers varying with POSS loading and vertex group, revealing monotonic decreases with POSS incorporation levels for all POSS types. The \( G_0 \) 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 monodispersed entangled PS (1.99 × 10\(^5 \) Pa).\(^{28} \) Meanwhile, \( G_0 \) 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 \( G_0 \) values.

The relationship between the characteristic value of \( G_0 \) and \( M_e \) can be expressed as follows:

\[
G_0 = \frac{1}{K T^2}
\]

Table 2. Summary of Viscoelastic Characteristics of Polystyrene–POSS Copolymers with Various Vertex Group at Reference Temperature 120 °C

<table>
<thead>
<tr>
<th>compound</th>
<th>( C_1 )</th>
<th>( C_2 ) (K)</th>
<th>( f/B )</th>
<th>( f_g/B )</th>
<th>( \alpha ) (K(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS(_{100})</td>
<td>8.18</td>
<td>47.84</td>
<td>0.0531</td>
<td>0.0283</td>
<td>11.09 × 10(^{-4} )</td>
</tr>
<tr>
<td>PS(<em>{94})BuPOSS(</em>{6})</td>
<td>8.05</td>
<td>60.10</td>
<td>0.0540</td>
<td>0.0298</td>
<td>8.98 × 10(^{-4} )</td>
</tr>
<tr>
<td>PS(<em>{94})CpPOSS(</em>{6})</td>
<td>8.47</td>
<td>57.93</td>
<td>0.0513</td>
<td>0.0323</td>
<td>8.85 × 10(^{-4} )</td>
</tr>
<tr>
<td>PS(<em>{94})CyPOSS(</em>{6})</td>
<td>8.51</td>
<td>58.31</td>
<td>0.0510</td>
<td>0.0297</td>
<td>8.75 × 10(^{-4} )</td>
</tr>
<tr>
<td>PS(<em>{85})BuPOSS(</em>{15})</td>
<td>9.15</td>
<td>85.55</td>
<td>0.0475</td>
<td>0.0319</td>
<td>5.55 × 10(^{-4} )</td>
</tr>
<tr>
<td>PS(<em>{85})CpPOSS(</em>{15})</td>
<td>10.06</td>
<td>81.31</td>
<td>0.0342</td>
<td>0.0323</td>
<td>5.31 × 10(^{-4} )</td>
</tr>
<tr>
<td>PS(<em>{85})CyPOSS(</em>{15})</td>
<td>10.72</td>
<td>96.96</td>
<td>0.0405</td>
<td>0.0323</td>
<td>4.18 × 10(^{-4} )</td>
</tr>
</tbody>
</table>

Figure 4. Master curve of the copolymers incorporating 15 wt % POSS varying with vertex group: (○) PS, (□) 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.

Figure 5. Rubbery plateau modulus (\( G_0 \)) for as-cast films of the random copolymers varying with weight percentage of POSS as a function of vertex group: (●) BuPOSS, (■) CpPOSS, (▲) CyPOSS. \( G_0 \) 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].
where \( R \) is the universal gas constant, \( \rho \) is density, and \( T \) is the absolute temperature. \( K \) is a constant defined to be \( 4/5 \), and the density of PS at room temperature is 1.05 g/cm\(^3\). Barry and Larsson \(^{36,38} \) reported crystal densities of POSS-related molecules with different vertex groups from CH\(_2\) (1.51 g/cm\(^3\)) to \( n \)-C\(_9\)H\(_{18}\) (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 are absent from the literature. Therefore, in employing eq 4, we approximated the copolymer density values by utilizing the PS temperature-dependent density, known to follow

\[
\rho (\text{g/cm}^3) = 1.0865 - 6.19 \times 10^{-4}T + 0.136 \times 10^{-5}T^2; \quad T (\text{°C})
\]
Further complicating matters, the expression well-described by the Vogel–Fulcher–Tamman–Hesse (VFTH) equation:

$$\tau_{\text{app}} = \tau_\infty \exp \left( \frac{B}{T - T_0} \right)$$  \hspace{1cm} (8)$$

where $\tau_\infty$ is a short reference time scale (like a hopping 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). The ideal glass transition temperature, also known as the Vogel temperature, is less than the $T_g$ measured by DSC and can be computed as $T_0 = T_e - C_2 r$, with $T_e$ and $C_2$ defined earlier in the context of tTS. By best-fitting VFTH equation, with $T_0$ constrained by $C_2$ measurements and with the temperature dependence of terminal relaxation time of random copolymers incorporating 6 and 15 wt % POSS (Figure 7), we obtained the VFTH parameters as a function of POSS content and vertex group. Figure 8 shows the apparent activation energy, $B$, increases with increasing POSS content, regardless of vertex group. The copolymerization with POSS groups lowers the temperature dependence of polymer chain relaxation. Meanwhile, the apparent activation energy also features strong vertex group dependence: iBuPOSS < CpPOSS < CyPOSS, at least for the 15 wt % case. Thus, we observed the lowering of the temperature sensitivity for apparent terminal relaxation times due to POSS incorporation and additional sensitivity to vertex group composition, consistent with $\alpha_2$ measurements within the WLF model, discussed earlier.

**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. 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 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 molecules significantly changes the microscopic topology of the random copolymer chains and leads to an increase in the effective tube diameter. 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. In this study, we observed that the rubbery plateau moduli for CyPOSS and CyPOSS copolymers decreased with the increasing POSS loading, while their DSC data and terminal relaxation behaviors showed evidence for significant intermolecular interactions. 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 a dominant role in the rubbery plateau modulus when POSS loading is ≥15 wt %.

Since their sizes are comparable to a polymeric coil, pendent 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. Ferri et al. studied the melt rheology of linear and randomly branched polystyrene (LPS and RBPS). They found that the shift factors ($\alpha_i$) 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 those observed in the randomly branched polystyrene. There are several theoretical models to explain the effects of branches on the temperature dependence of terminal relaxation time, including coupling models and the reptation theory. Their predictions are consistent with our observations in the random copolymers of styrene with 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 nanoscale cage, pendant to the polymer main chain.

Additionally, Romo-Uribe et al. noticed a 10-fold linear density (mass/backbone length) difference between styryl-POSS and 4-methylstyrene. 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.

Conclusions

We investigated the thermal and linear rheological behavior of polystyrene (PS)-based random copolymers incorporating POSS with three kinds of vertex groups: isobutyl (Bu), cyclopentyl (Cp), and cyclohexyl (Cy). The weak iBuPOSS–PS segment interaction resulted in a glass transition temperature \( T_g \) that monotonically decreased with increasing iBuPOSS content. Conversely, the strong CpPOSS/CyPOSS–PS segment interaction resulted in 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.

Up to 15 wt % POSS loading, 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 the vertex group dependence of the corresponding thermal expansivity of free volume \( \alpha_L \) follows the sequence CyPOSS < CpPOSS < iBuPOSS, and the values of \( \alpha_L \) decrease with the increasing POSS contents. 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, which could be the origin of POSS-based dilution of entanglement density. The vertex group effect only plays a minor role in the rubbery plateau. More specifically, the rubbery plateau modulus decreased with increasing POSS content and in proportion to the POSS size, following the sequence iBuPOSS > CpPOSS > CyPOSS.

The strong interactions between CpPOSS/CyPOSS and PS matrix dramatically altered terminal zone response. In contrast, iBuPOSS copolymers and PS homopolymer featured a monotonically increasing \( \tan \delta \) with the decreasing reduced frequency; the 15 wt % CpPOSS copolymer revealed near frequency-independence \( \tan \delta \) at the terminal zone, characteristic of a “critical gel” formed by the strong interactions between CpPOSS–PS segments. The loss tangent, \( \tan \delta \), master curves of random copolymers with 6 and 15 wt % CyPOSS featured an additional relaxation peak at the terminal zone, also attributed to strong intermolecular interactions between CyPOSS and PS matrix. The apparent terminal relaxation times, 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 of the POSS copolymers increased with the increasing POSS loading. Meanwhile, it also features a strong vertex group dependence: iBuPOSS < CpPOSS < CyPOSS.

Supporting Information Available: Figures showing (1) \( ^1H \) NMR spectra of POSS–styrene monomer and PS\(_{90}\)CyPOSS\(_{10}\) copolymer, (2) raw differential scanning calorimetry (DSC) traces, (3) WLF function plots, (4) computed fractional free volume temperature dependences, and (5) Han plot of rheological data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

3. Huang, Z. M.; Zhang, Y. Z.; Kotaki, M.; Ramakrishna, S. Compos. Sci. Technol. 2003, 63, 2223–2253.