New Approach in the Synthesis of Hybrid Polymers Grafted with Polyhedral Oligomeric Silsesquioxane and Their Physical and Viscoelastic Properties

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ABSTRACT: Synthesis, chain characteristics, and time-dependent viscoelastic response of polyhedral oligomeric silsesquioxanes (POSS)-containing hybrid polymers were investigated. Unlike many other reported POSS hybrid copolymers works, the POSS-grafted copolymers used in this study, although having different amounts of POSS attachments, have the same degrees of polymerization and molecular weight distribution. This was accomplished by grafting different amounts of aluminosilsesquioxane onto a previously synthesized, random copolymer of styrene and vinyl-diphenylphosphine oxide, PSP. The coordination bonding between aluminum and phosphine oxide is quantitative, which enables the investigation of physical characteristics and viscoelastic response of polymers as influenced only by the POSS attachments. Similar to other hybrid polymers with covalently bonded POSS, we observed a systemic increase in the characteristic relaxation time of polymers at the terminal zone due to the POSS attachment. Linear viscoelastic response at different temperatures above $T_{\rm g}$ was studied using the small-strain amplitude oscillatory shear technique. It was found that these POSS-grafted copolymers obey the timetemperature superposition principle. In addition, for isothermal experiments, the linear viscoelastic response obtained for copolymer with varying amounts of POSS attachment were able to be superposed, thus demonstrating that these hybrid copolymers obey the time-POSS content superposition principle. We also examine the effect of POSS-POSS interactions on the long-term viscoelastic response of these copolymers. It was found that copolymers with high POSS attachments exhibit a slow gelation response when held isothermally at temperatures above $T_{\rm g}$ for extended periods of time, while copolymers with low POSS attachments remain unchanged for the same periods of time. Therefore, this observed gel-like behavior is due to the intrachain POSS-POSS interaction.

Introduction

Polyhedral oligomic silsesquioxanes (POSS) have attracted widespread interest as precursors to high-performance materials. Of particular interest have been POSS-containing inorganic-organic polymeric materials, which often exhibit enhanced performance characteristics versus stoichiometrically similar non-POSScontaining polymers.¹⁻³ Although it is generally recognized that POSS incorporation into organic polymers can have profound effects on polymer properties, relatively little is known with certainty about how the presence of POSS alters polymeric properties because it is difficult to prepare the necessary series of POSS-containing polymers that selectively isolate the POSS effects. Most of the work reported on POSS-containing copolymers has been one-pot syntheses, where POSS monomers and organic monomers were mixed together prior to the polymerization process.⁴⁻¹⁰ It is known that the presence of POSS monomers can have dramatic effects on the rates of polymerization.¹¹ Therefore, any changes in POSS monomer structure and/or initial feed ratios can lead to nonrandom and difficult-to-quantify changes in the resulting polymer. Hence, it is difficult to attribute the observed differences purely due to the addition of POSS.

In this paper we report a new approach to the synthesis of POSS-grafted copolymers and provide charac-

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terization results of these copolymers for the opportunity to develop structure-property relationships. These polymers are synthesized by grafting of Al-containing POSS cages onto a random copolymer of styrene and vinyl-diphenylphosphine oxide. Since the grafting of POSS cages occurs after polymerization, the effects of POSS incorporation can be investigated using polymers of common backbones. The physical characteristics of a single polymer chain as affected by the number of POSS attachments were studied using standard dilute solution techniques such as intrinsic viscosity and dynamic light scattering. In addition, the melt rheological behavior of these copolymers at different temperatures was investigated using the small-amplitude oscillatory shear method. Series of isothermal, frequency sweep experiments were used to examine the validity of the timetemperature superposition principle on these POSScontaining copolymers. We also examined time-temperature shift factors for these hybrid copolymers as affected by the amount of POSS attachments. Since there is only a limited miscibility between POSS molecules and the organic polymeric host, it was suggested that above a critical number of POSS attachments, a strong POSS-POSS interaction will influence the polymer dynamics. In this study we explore this interaction by examining the isothermal, viscoelastic response at different times at a temperature above the glasstransition temperature of the copolymers.

Experimental Section

Styrene (St, Aldrich) was washed three times with aqueous 1 M NaOH to remove inhibitors, then washed three times with

water, dried with anhydrous sodium sulfate overnight, distilled under nitrogen at reduced pressure, and kept refrigerated. Azobisisobutylnitrile (AIBN, Aldrich) was recrystallized from methanol before use. The solvents, toluene and dichloromethane, were water free and oxygen free. Ethanol was used as received. Vinyl-diphenylphosphine and Oxone (potassium peroxymonosulfate) were purchased from Aldrich Chemical Co. and used without further purification.

Dimerization of POSS Cages. Trisilanols with structure 1 are versatile precursors to POSS monomers. These trisilanols typically are reacted with trifunctional organosilicon reagents (e.g., $R'SiX_3$) to produce POSS monomers with the ubiquitous Si_8O_{12} framework.



The reaction chemistry of trisilanol 1a (R = c-C₆H₁₁) is especially well developed because it was the first POSS trisilanol available in synthetically useful quantities. In addition to "corner capping" reactions with RSiX₃, 1a reacts with a wide range of main-group, transition-metal, and lanthanide elements to afford fully condensed metal-silsesquioxanes. For example, the reaction of 1a with Me₃Al affords 2, which reacts quickly and quantitatively with phosphine oxides (e.g., Ph₃-PO) to produce cubeoctameric $AlSi_7O_{12}$ frameworks (e.g., 3a) that are isostructural with many common POSS monomers. The details of the chemistry for the synthesis of 2 and 3a have been described elsewhere.¹²



Here we extend the previous work with aluminum-containing silsesquioxanes to a polymer-bound phosphine oxide

prepared by copolymerization of styrene and vinyl-diphenylphosphine oxide. As described below, the reaction chemistry works equally well and provides a convenient method for preparing well-defined POSS-containing polymers for structural/ property studies.

Synthesis of Vinyl–Diphenylphosphine Oxide (VD-PhPO). In a 1 L one-necked flask, vinyl–diphenylphosphine (5.0 mL, 0.025 mol), Oxone (30.7 g, 0.050 mol), and dichloromethane (120 mL) were stirred at room temperature for 5 days. The solution was filtered to remove insoluble materials, and the filtrate was washed with water three times, dried over anhydrous sodium sulfate overnight, filtered, and evaporated to give a white solid. The white solid was purified by column chromatography (hexane/ether); the solvent was evaporated to give vinyl–diphenylphosphine oxide (VDPO, 3.3 g, yield 58%) as a white microcrystalline solid. ¹H NMR (CDCl₃): δ 6.22–6.40 (m, 2H), 6.61–6.75 (m, 1H), 7.44–7.51 (m, 4H), 7.51–7.58 (m, 2H), 7.67–7.74 (m, 4H). ³¹P NMR (CDCl₃, 85% H₃PO₄ as external standard): δ 24.83.



NMR Tube Reaction of 2 with VDPhPO: Synthesis of 3a. VDPhPO (10 mg, 0.04 mmol) and 2 (43.7 mg, 0.02 mmol) were dissolved in CDCl₃ (0.5 mL) in a 5 mm NMR tube. The formation of **3a** was quantitative within 5 min at room temperature. ¹H NMR (CDCl₃): δ 0.55-0.79 (m, 7H), 1.10-1.35 (m, 35H), 1.58-1.85 (m, 35H), 6.45-6.78 (m, 3H), 7.51-7.58 (m, 4H), 7.65-7.70 (m, 2H), 7.78-7.86 (m, 4H). ³¹P NMR (CDCl₃): δ 23.53, 23.77, 24.36, 26.70, 26.97, 27.07, 27.13, 27.22, 27.38, 27.54, 27.69, 27.75, 27.96, 124.95, 125.28, 125.78, 126.18, 129.12, 129.23, 131.95, 132.05, 133.89, 133.91, 139.79. ²⁹Si NMR (CDCl₃): δ -69.79, -68.67, -65.61 (3:1:3).



Synthesis of Styrene and VDPhPO Copolymers. In a 150 mL Schlenk flask, vinyl-diphenylphosphine oxides (1.9980 g), styrene (4.537 g), 2,2'-azobisisobutronitrile (AIBN, 0.3% of the total weight of monomers), and toluene (15.024 g) were added. The reactor was evacuated and backfilled with argon three times, and then it was tightly sealed and immersed in an oil bath at 60 °C. The solution was stirred for 3 days under argon. After cooling the solution was poured into a large excess of ethanol to precipitate the copolymer, which was collected by filtration. The polymer was then twice purified by dissolving in toluene, filtering, and then reprecipitating with ethanol. The resulting poly(styrene-co-vinyl diphenylphosphine oxide), PSP, was dried at 60 °C under vacuum to give a white powder (4.9 g, yield 75%); the composition was determined by ³¹P NMR spectroscopy using monomer VDPhPO as the reference; the ratio of integrated ³¹P NMR intensities for free VDPhPO and PSP copolymer was 1:1.6, which corresponds to a P content of 0.7 mmol of P per gram of copolymer. By changing the amount of AIBN used we were able to synthesize two different molecular weights of PSP; however, the molar ratio of dPhPO to styrene in the PSO copolymer is the same for both PSP.

Synthesis of POSS-Containing Polymers: Reactions of PSP with 2. Samples containing 0.1, 0.2, 0.5, and 0.9 Al per polymer-bound P=O were prepared. In a typical procedure PSP (ca. 1 g) and **2** were dissolved in dry CH₂Cl₂ in a 20 mL glass vial equipped with a small magnetic stirring bar. The total concentration of PSP and 2 in CH₂Cl₂ was 10 wt % for all reactions. Within 2 min of mixing the solution became clear and colorless; the reaction was continued for another 10 min. Evaporation of the solvent gave a white solid, which was dried overnight in a vacuum oven at 110 °C and 0.1 Torr. Provided that the number of P=O groups from PSP exceeds the number of Al sites provided by 2, the grafting reaction proceeds to completion with respect to 2 and the yield is quantitative. The mole fraction of POSS attached to P=O on the 1:1.6 VDPhPO/ PSP copolymer was confirmed by ¹H NMR spectroscopy in CDCl₃ using the total integrated intensities for all cyclohexyl groups on the POSS framework (δ 0.60–2.80 (m br)) and all aromatic protons (δ 5.90–7.90 (m br)). NMR spectral data for the copolymer containing 0.5 Al/P=O are as follows. ¹H NMR (CDCl₃): δ 0.60–2.80 (m br), 5.90–7.90 (m br). ³¹P NMR (CDCl₃, 85% H₃PO₄ as external standard): δ 32.8–34.0 (br), 35.0-38.1 (br) (free 'PO'), 49.0-50.1 (br), 50.5-53.2 (br) (coordinated 'PO'). ¹³C NMR (CDCl₃): δ 23.52 (br), 23.79 (br), 24.34 (br) 26.4-28.2 (m, br), 40.29 (br), 43.77 (br), 125.59 (br), 127.58 (br), 127.88 (br), 131.14 (br), 145.13 (br). ²⁹Si NMR $(CDCl_3) \delta$ 69.61 (br), -68.45 (br), -65.58 (br) (3:1:3).



Dynamic Light Scattering. A DynaPro Dynamic Light Scattering Instrument with Dynamic V6 (Protein Solution Inc.) software was used to determine the hydrodynamic radius of POSS-containing PSP in the diluted solution with a concentration of 12 mg/mL of anhydrous toluene. Anhydrous toluene was purchased from Aldrich and used as received. The instrument was equipped with a temperature-controlled microsampler (MSXTC-12), a host (DynaPro-99-E-6), and a temperature controller unit. The standard procedure is as follows: polymer was first dissolved in anhydrous toluene overnight with a concentration of 12 mg/mL, 80 μ L of the polymer solution was extracted using a microsyringe, and then injected into the microcell through a 0.45 μ m filter. The microcell was then inserted into the temperature-controlled microsampler, an elapsed time of 10 min was used for the temperature to equilibrate at 30 °C, and each measurement was then obtained using an acquisition time of 10 s with 80% laser power. The same sample solution was measured 30 times. The fluctuations in the intensity of the scattered light are related to the diffusion coefficient. The hydrodynamic radius, $R_{\rm H}$, is then calculated from the diffusion coefficient using the Stokes-Einstein relation of a spherical scatter.

Dilute Solution Viscometry. CANNON CT-1000 constant temperature bath and cannon-manning semi-micro viscometers with size 25 were used to measure the efflux time of copolymers at different concentrations. The measurements were taking at 30 \pm 0.01 °C. The initial concentration of samples was 75 mg/mL in anhydrous toluene. Anhydrous toluene was purchased from Aldrich and used as received. The filtration of polymer solution was carried out using a syringe with 0.2 μ m filters. The amount of polymer lost was assumed

Table 1.

low molecular weight samples 8.0 mol % dPhPO				high molecular weight samples 7.4 mol % dPhPO			
sample	$\substack{[\eta]\\(\mathrm{cm}^{3}\!/\mathrm{g})}$	K_{H}	$R_{ m H} \ (m nm)$	sample	$\substack{[\eta]\\(\mathrm{cm}^3\!/\mathrm{g})}$	K_{H}	$R_{ m H}$ (nm)
PSP 1-0 (0%) ^a PSP 1-1 (10%) PSP 1-2 (20%) PSP 1-3 (50%) PSP 1-4 (90%)	12.16 12.15 11.89 11.78	$0.51 \\ 0.48 \\ 0.42 \\ 0.38$	4.6 4.6 4.8 5.0	PSP 2-0 (0%) PSP 2-1 (10.9%) PSP 2-2 (21.7%) PSP 2-3 (54.5%)	$17.82 \\ 17.56 \\ 17.52 \\ 17.12$	$0.67 \\ 0.51 \\ 0.47 \\ 0.42$	5.7 5.8 6.1 6.5

 $^a\left(x\%\right)$ indicates the fraction dPhPO sites that is attached with POSS molecules.

to be negligible. Four different concentrations were used for each sample, and the average efflux time used to determine intrinsic viscosity was determined using average of 10 measurements with an error of 0.5%.

Rheological Experiments. All rheological experiments were performed using a Paar Physica rheometer, Universal Dynamical Spectrometer UDS200 operated with direct-strain control mode. The rheometer is equipped with a convectionheated air oven for temperature control within ± 0.1 °C of the set temperature. A parallel plate geometry with a diameter of 8 mm and a gap of 0.5 mm was used for all measurements obtained in this study. The fixture was preheated to the highest testing temperature, 200 °C, and lowered to obtain the zero-gap reference point. The molded disc-shaped specimen was then placed in the rheometer, and the top fixture was slowly lowered to the preset gap of 0.5 mm with minimal normal force. The sample was then subjected to a series of isothermal, small-strain oscillatory shear tests with oscillatory frequencies ranging from 20 to 0.01 rad/s and strain amplitude of 2%. To examine the validity of the time-temperature superposition principle and the effect of POSS addition on the values of the time-temperature shift factor, each sample was tested at temperatures ranging from 200 to 120 °C with a 10 °C interval. To examine the effect of long-term POSS-POSS interactions on the dynamics of polymer, the sample was first placed in the rheometer set at 210 °C and held isothermally for 15 min to equilibrate the sample temperature. The temperature of the testing chamber was then reduced to 170 °C while holding the gap constant. The sample was then subjected to a series of isothermal, small-strain oscillatory shear tests with oscillatory frequencies ranging from 20 to 0.01 rad/s and a strain amplitude of 2% for different elapsed times. The elapsed time begins when the sample first reaches 170 °C. Since only 5 min is needed for each frequency-sweep cycle, it is assumed that the linear viscoelastic experiment performed is a direct reflection of the state of polymer at the given elapsed time and the mechanical stimuli used to probe the state of polymer is too small to alter the molecular morphology of polymer melts.

Results and Discussion

Hydrodynamic Radius and Intrinsic Viscosity.

In Table 1 we depict the values intrinsic viscosity, $[\eta]$, and Huggins coefficient, $K_{\rm H}$, as obtained using the standard dilute solution capillary viscometry technique and hydrodynamic radius, $R_{\rm H}$, as obtained from the diffusion coefficient as measured by the dynamic light scattering measurement with spherical scatter assumption, respectively.

As observed, it is reasonable to suggest that as more POSS are attached to the host PSP polymer chain, the value of $R_{\rm H}$ for the corresponding copolymer was expected to increase. However, it is interesting to point out here that the value of the intrinsic viscosity, $[\eta]$, of the copolymer decreases with increasing amounts of POSS attachments. From the dilute solution theory it is suggested that the intrinsic viscosity relates to the Brownian dynamics of polymeric coils in solution. In the



Figure 1. Isothermal loss modulus, $G''(\omega)$, versus oscillatory angular frequency, ω , at different temperatures as indicated. The POSS-grafted copolymer used was a lower molecular weight copolymer of poly(styene-*co*-vinyl diphenylphosphine oxide), PSP, of 8 mol % diphenylphosphine oxide. A 50 mol % of diphenylphosphine oxide was attached with POSS.

dilute limit, for the hard spheres model and Rouse approximation, the value of $[\eta]$ can be expressed as^{13,14}

$$[\eta] = 2.5 \frac{\phi}{\rho} = 2.5 \frac{4}{3} \pi \frac{R^3}{M} \frac{N_A}{M}$$
(1)

where ϕ is the volume fraction occupied by the spheres in the solution and ρ is the density of spheres. With the hard-sphere assumption, $[\eta]$ is re-expressed with the hydrodynamics radius, $R_{\rm H}$, molecular weight of polymer, M, and $N_{\rm A}$ as Avogadro's number. If the increase in $R^{3}_{\rm H}$ is slower than the increase in the molar mass of the copolymer as the amount of POSS attachments increases, then it is reasonable for the value of $[\eta]$ to decrease as the number of POSS attachments per chain in the copolymer increases. Another interesting observation from the results of dilute solution viscometry is the changes of Huggin's coefficient with varying amounts of POSS per chain. From Table 1 it was observed that the value of the Huggin's coefficient, the slope of the specific viscosity versus concentration, decreases with an increasing number of POSS attachments per chain; the decrease in the Huggin's coefficient means that the specific viscosity of the copolymer is becoming less dependent on polymer concentration as more POSS are attached to the copolymer. In other words, as more POSS molecules are attached to the polymer chain, the interaction between the polymeric segment and solvent becomes weaker. Hence, the polarity and solubility of these POSS-containing copolymers in the solvent are changed with increasing number of POSS attachments per chain and thus affect the value of intrinsic viscosity for these hybrid copolymers.

Viscoelastic Response

Effect of Temperature and POSS Content.

The results of oscillatory experiments at different temperatures were obtained by plotting the storage modulus, $G'(\omega)$, and loss modulus, $G''(\omega)$, as a function of oscillatory frequency, ω . In Figure 1 we show the $G''(\omega)$ versus ω at temperatures ranging from 120 to 200 °C. Using a reference temperature of 160 °C we were able to shift the $G''(\omega)$ and $G'(\omega)$ curves obtained at different temperatures to form master curves of the



Figure 2. (a) Time-temperature loss modulus master curve, $G''(a_{T}\omega)$, versus reduced angular frequency, $a_{T}\omega$, of Figure 1. (b) Master curves of G' and G'' versus $a_{T}\omega$, shifted using the same time-temperature factor of the copolymer shown in Figure 2a. The reference temperature used for the master curve was 160 °C.

reduced $G'(\omega)$ and $G''(\omega)$ as shown in Figure 2a and b, thus validating the applicability of the time-temperature superposition principle for this POSS-containing copolymer. Examination of the applicability of timetemperature superposition was extended to all copolymers, regardless of the number of POSS attachments per chain. As shown in Figures 3a,b and 4 a,b, all POSSgrafted copolymers investigated in this study obey the time-temperature superposition principle.

In Figure 5 a and b we plotted the logarithm of the temperature shift factors of copolymers containing different amounts of POSS attachments versus temperature. From these figures it was observed that the amount of shift needed to form the master curve increases as the POSS content increases if one uses the same reference temperature for all copolymers tested. Since these copolymers have the same common backbone, this observation suggests that the POSS attachment delays the dynamics of the polymer chain in the melt state. This retardation of polymer dynamics is attributed to the nanoscopic size of the POSS cages attached to the host polymer chain. This may be related to the increase in the glass-transition temperature as the number of POSS attachments per chain increases. The uniqueness of our synthesis approach enables us to examine the effects of increasing numbers of POSS per chain without any influence from the change in the degree of polymerization and/or molecular weight distribution, since the same host polymer is used for this



Figure 3. (a) Time-temperature storage modulus master curves, $G'(a_T\omega)$, versus reduced angular frequency, $a_T\omega$, of POSS copolymers with different extent of POSS grafting on the high molecular weight copolymer of poly(styene-*co*-vinyl diphenylphosphine oxide), PSP, of 7.4 mol % diphenylphosphine oxide. (b) Time-temperature storage modulus master curves, $G'(a_T\omega)$, versus reduced angular frequency, $a_T\omega$, of POSS copolymers with different extent of POSS grafting on the low molecular weight copolymer of poly(styene-*co*-vinyl diphenylphosphine oxide), PSP, of 8 mol % diphenylphosphine oxide. The percent indicates the mole fraction of diphenylphosphine oxide sites with POSS attachment. The reference temperature used was 160 °C.

experiment. In Figure 6a we plotted loss modulus, G''-(ω), and complex viscosity, $\eta^*(\omega)$, versus angular frequency, ω , for copolymers grafted with different amounts of POSS at a given temperature, T = 170 °C. Using the superposition principle we are able to shift these curves to form master curves of reduced $G''(\omega)$ and $\eta^*(\omega)$, as shown in Figure 6b. Therefore, for a given temperature the linear viscoelastic response of POSS-grafted hybrid copolymers obeys the time-POSS content superposition principle. The validity of the time-POSS content superposition principle suggests that although the grafting of POSS molecules on the host polymer chain reduces the overall mobility of the polymer chain, the activation energy for motion of the polymer chain is not affected. In other words, although the POSS-POSS interaction in the polymer melts increases the characteristic relaxation time, the overall relaxation spectrum of the chain is not affected by the addition of POSS attachments.¹⁴⁻¹⁶

Effect of Time on POSS-POSS Interaction.

In Figure 7a we plotted the complex modulus, $G^{*}(\omega)$, versus angular frequency, ω , at different elapsed times



Figure 4. (a) Time-temperature loss modulus master curves, $G''(a_{T}\omega)$, versus reduced angular frequency, $a_{T}\omega$, of POSS copolymers with different extent of POSS grafting on the high molecular weight copolymer of poly(styene-co-vinyl diphenylphosphine oxide), PSP, of 7.4 mol % diphenylphosphine oxide. (b) Time-temperature loss modulus master curves, $G''-(a_{T}\omega)$, versus reduced angular frequency, $a_{T}\omega$, of POSS copolymers with different extent of POSS grafting on the low molecular weight copolymer of poly(styene-co-vinyl diphennylphosphine oxide), PSP, of 8 mol % diphenylphosphine oxide. The percent indicates the mole fraction of diphenylphosphine oxide sites with POSS attachment. The reference temperature used was 160 °C.

as indicated for the copolymer with the highest POSS content used in this study (about 7 mol % of polymer is grafted with POSS molecules). At a specified angular frequency the value of $G^*(\omega)$ increases as the elapsed time increases. This observation alone does not imply any morphological change in the polymer. We then plotted the damping factor, $\tan \delta = G''(\omega)/G'(\omega)$, versus ω , as depicted in Figure 7b. As the elapsed time increases, the values of tan δ become less dependent on the angular frequency. For the two longest elapsed times values of tan δ are almost independent of ω . This observation indicates that the viscoelastic response of this POSS-containing copolymer is changed from a liquidlike to gel-like behavior. The gel-like behavior may be due to a strong POSS-POSS interaction within the polymer chain, which acts like a physical cross-link and can have a significant effect on the mechanical properties of polymeric melts when annealed for extended periods of time at elevated temperatures. If the gel-like behavior is attributed to the intrachain POSS-POSS



Figure 5. (a) Time-temperature shift factor, a_T , versus temperature, T, of POSS copolymers with different extent of POSS grafting on the high molecular weight copolymer of poly-(styene-*co*-vinyl diphenylphosphine oxide), PSP, of 7.4 mol % diphenylphosphine oxide. (b) Time-temperature shift factor, a_T , versus temperature, T, of POSS copolymers with different extent of POSS grafting on the low molecular weight copolymer of poly(styene-*co*-vinyl diphenylphosphine oxide), PSP, of 8 mol % diphenylphosphine oxide. The percent indicates the mole fraction of diphenylphosphine oxide sites with POSS attachment. The reference temperature used was 200 °C.

interactions, then this transition of liquidlike to gel-like behavior requires that a sufficient amount of POSS is attached to the host polymer chain. To test this hypothesis the copolymer with the lowest POSS attachments per chain was used. In Figure 8 we plotted the complex modulus, $G^*(\omega)$, versus angular frequency, ω , at different elapsed times as indicated using the copolymer with the lowest POSS content in this study (about 0.8 mol % of polymer is grafted with POSS molecules). We observed no change of its viscoelastic responses for the entire duration of the experiment. We believe for copolymers with only a few POSS attachments, as in the case of one POSS attachment per 120 repeat units, the POSS molecule is surrounded mostly by other segments of the polymer chain, which will screen out the possibility of any POSS-POSS interaction. However, as in the case of a copolymer with an average of one POSS attachment per 14 repeat units, the length scale between successive POSS attachments is comparable to the length scale of a single POSS molecule. Therefore, strong POSS-POSS interactions were to be developed in time. The development of these POSS-POSS interactions is also supported by the observed



Figure 6. (a) Isothermal loss modulus, $G''(\omega)$, and complex viscosity, $\eta^*(\omega)$, versus angular frequency, ω , at 170 °C of POSS copolymers with different extent of POSS grafting on the high molecular weight copolymer of poly(styene-*co*-vinyl diphenylphosphine oxide), PSP, of 7.4 mol % diphenylphosphine oxide. (b) Master curves of $G''(a_p\omega)$ and $\eta^*(a_P\omega)$ versus reduced frequency $a_p\omega$. Solid symbols represent loss modulus, and empty symbols represent complex viscosity: (\bigcirc) no POSS attachment, (\square) 10.9 mol % of dPhPO sites was attached with POSS, (\diamondsuit) 21.7 mol % of dPhPO sites was attached with POSS, (\bigtriangledown) 54.5 mol % of dPhPO sites was attached with POSS).

decrease in the intrinsic viscosity and the Huggin's coefficient in the dilute solution viscosity measurements.

Conclusions

Two series of copolymers grafted with different amounts of POSS cages were synthesized. These POSS copolymers were synthesized by grafting Al-containing POSS cages onto a random copolymer of styrene and vinyl-diphenylphosphine oxide. By changing the concentration of initiator while maintaining identical molar ratios of styrene to vinyl-diphenylphosphine oxide we were able to synthesize different molecular weights of poly(styrene-diphenylphosphine oxide) with the same molar ratio of styrene and vinyl-diphenylphosphine for the host copolymers using free-radical polymerization. The Al-containing POSS is then attached to P=O via coordination bonding. Since grafting of POSS cages occurs after polymerization, this enables us to examine the effects of POSS incorporation in polymers of the same backbone.

Using dynamical light scattering of dilute solutions, the hydrodynamic radius of POSS-grafted copolymers



Figure 7. (a) Isothermal complex modulus, $G^{*}(\omega)$, versus angular frequency, ω , of the low molecular weight PSP (8 mol % dPhPO) with 90 mol % of dPhPO sites attached with POSS. (b) Isothermal damping factor, tan $\delta(\omega)$, versus angular frequency, ω , of low molecular weight PSP (8 mol % dPhPO) with 90 mol % of dPhPO sites was attached with POSS. The sample was annealed at 170 °C for amounts of time annealed prior to the small-strain oscillatory shear experiment.



Figure 8. Isothermal complex modulus, $G^*(\omega)$, versus angular frequency, ω , of the low molecular weight PSP (8 mol % dPhPO) with only 10 mol % of dPhPO sites attached with POSS. The sample was annealed at 170 °C for amounts of time annealed prior to the small-strain oscillatory shear experiment.

was determined. As expected, the hydrodynamic radius increases as the POSS content increases. However, more

details of the polymer chain structure in dilute solution were examined using dilute solution viscometry. To our surprise, the value of the intrinsic viscosity for POSSgrafted copolymers decreases with increasing POSS attachment per chain. Two possible explanations were suggested for this observation. On the basis of the hardsphere model, it is possible to reduce the value of the intrinsic viscosity if the increase in hydrodynamic volume is slower than the increase in molar mass of the copolymer as the amount of POSS attachments increases. However, coupled with the observed decrease in intrinsic viscosity is the decrease in the Huggin's coefficient, the slope of the specific viscosity versus concentration, as the POSS attachments per chain increases. The combination of these two observations suggests that the POSS-POSS interactions are stronger than POSS-monomer, POSS-solvent, monomer-monomer, and monomer-solvent interactions.

The melt rheology of POSS copolymers was examined using small-strain amplitude oscillatory shear with different angular frequencies. It was observed that the linear viscoelastic response of the POSS copolymers obeys the time-temperature superposition principle. In addition, for a given isothermal condition, we were able to demonstrate the applicability of a time-POSS content superposition principle to these POSS-containing copolymers provided the average length between successive POSS cages is long enough and it is freshly quenched to the testing temperature from a higher temperature. Otherwise, if the average length between successive POSS cages is comparable to the size of a POSS cage, the intrachain POSS-POSS interaction will gradually dominate the dynamics of POSS copolymer. The linear viscoelastic response of the POSS-grafted copolymers will then change from a viscoelastic liquidlike response to a viscoelastic gel-like behavior.

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