

Preparations, Thermal Properties, and T_g Increase Mechanism of Inorganic/Organic Hybrid Polymers Based on Polyhedral Oligomeric Silsesquioxanes

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ABSTRACT: A series of novel hybrid poly(acetoxystyrene-*co*-isobutylstyryl-POSS)s (PAS-POSS) and poly(vinylpyrrolidone-*co*-isobutylstyryl-POSS)s (PVP-POSS) are synthesized and characterized. The POSS content in these hybrids can be controlled by varying the monomer feed ratio. The polyhedral oligosilsesquioxane (POSS) moiety can effectively increase the T_g of the resultant organic/inorganic hybrid polymer at a relatively high POSS content and produce the hybrid copolymer with narrower molecular weight distribution. The FTIR spectra are used to investigate the structure–property relationship of these hybrid polymers, and the T_g enhancement mechanism is discussed in detail.

Introduction

Polymeric hybrid materials have attracted great interest recently due to their advantageous performance relative to the nonhybrid counterparts. Typical hybrid materials may contain a cross-linked inorganic phase bonded (often covalently) with an organic phase.^{1,2} Recently, polyhedral oligosilsesquioxanes (POSS)-based hybrid polymers^{3–13} have received increasing attention among the academic community and industries because of the unique structure of the POSS macromer, which is a well-defined cluster with an inorganic silica-like core (Si_8O_{12}) surrounded by eight organic corner groups. This POSS macromer can be easily functionalized with a wide variety of organic groups that can be employed as monomer or comonomer in a typical polymerization. The preparation and properties of POSS-based hybrid polymers can be designed and controlled at the molecular level. Many POSS-based hybrid polymers have been prepared and possess a number of desirable properties.^{3–9} However, only a few papers have reported their T_g increase behavior.^{3–5} In the study, we will report the syntheses of a series of new POSS-based hybrid polymers and the structure–property relationship of these hybrid polymers.

Experimental Section

Materials. Isobutylstyryl polyhedral oligosilsesquioxane (POSS) was purchased from the Hybrid plastic Co. Inc., which was stored in a dried box before use. Vinylpyrrolidone and acetoxystyrene were purchased from Aldrich, distilled from calcium hydride under reduced pressure, and stored in sealed ampules in a refrigerator. High-purity azobis(isobutyronitrile) (AIBN) was kept in a dried box and used as received. Spectroscopic grade THF and toluene were predried over 4 Å molecular sieves and distilled from sodium benzophenone ketyl immediately prior to use. All other solvents were purchased from Aldrich and used without further purification.

Instrumentation. Thermal analyses were carried out on a DSC from DuPont (DSC-9000). The scan rate was 20 °C/

min within the temperature range 30–260 °C. The sample was quickly cooled to 0 °C from the melt for the first scan and then scanned from 20 to 280 °C at 20 °C/min. The glass transition temperature is obtained at the midpoint of the specific heat increment. FTIR spectra were measured with a spectral resolution of 1 cm^{-1} on a Nicolet Avatar 320 FT-IR spectrophotometer using KBr disks or pellets at room temperature. Weight- and number-average molecular weights (M_w and M_n) and polydispersity index (M_w/M_n) were determined by a Water 510 gel permeation chromatograph (GPC). ¹H NMR spectra were recorded on a Bruker ARX300 spectrometer using the chloroform-*d* solvent.

Polymerizations. All polymerization reactions were carried out under nitrogen using a vacuum-line system. Poly(vinylpyrrolidone-*co*-isobutylstyryl-POSS) (PVP-POSS) and poly(acetoxystyrene-*co*-isobutylstyryl-POSS) (PAS-POSS) were prepared by a conventional free radical polymerization technique. For comparison, the homopoly(vinylpyrrolidone) (PVP) and homopoly(acetoxystyrene) (PAS) were also synthesized as shown in Scheme 1. Typical experimental procedures for these polymers are given below. In a typical reaction, 9.8 mmol of vinylpyrrolidone (VP) and 0.22 mmol of POSS monomer in toluene (dried toluene, 7 mL) were polymerized using the AIBN initiator (1 wt % based on monomer) at 80 °C under a nitrogen atmosphere for 24 h. The product then was poured into excess cyclohexane under vigorously agitation to precipitate the copolymer, then purified in THF/cyclohexane, and dried in a vacuum oven. A 58.4 wt % yield was obtained through this procedure.

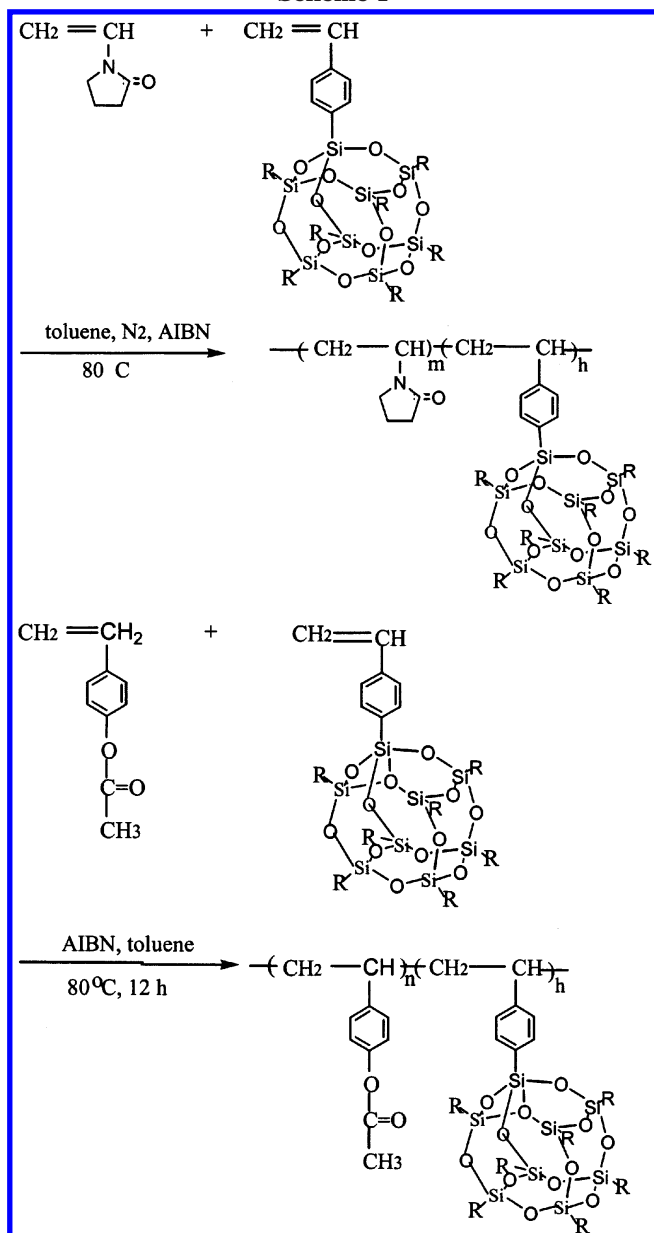
Determination of Component Contents.^{12,14} IR analysis was used to determine the respective component contents of these polymers. The pure poly(acetoxystyrene) (PAS), poly(vinylpyrrolidone) (PVP), and poly(isobutylstyryl polyhedral oligosilsesquioxane) (POSS) samples were prepared following similar procedures mentioned above. To establish a calibration curve, a series of POSS/PVP and POSS/PAS mixtures with known amounts of POSS were prepared. To ensure intimate mixing, PVP, PAS, and POSS were first dissolved in a solvent and then cast into a thin film. The carbonyl stretching vibration of the PVP is located at 1680 cm^{-1} . The POSS moiety exhibits a “robust” absorption centered at 1109 cm^{-1} . The carbonyl absorption band of the PAS is located at 1760 cm^{-1} . These carbonyl bands at 1680 and 1760 cm^{-1} were adopted as internal standards for POSS/PVP and POSS/PAS mixtures, respectively. The ratios of band areas, A_{1109}/A_{1680} and A_{1109}/A_{1760} , were plotted against the mole fraction of the POSS in the POSS/PVP and POSS/PAS mixtures, and the results are shown in Figure 1a,b. These plots gave a linear calibration

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Scheme 1



line between POSS mole fraction and respective band ratios. Therefore, the mole percent of the POSS in PVP-POSS (1) and POSS-PAS (2) copolymers can be calculated as follows:

$$Y_{\text{POSS}} = 0.082(I_{1109}/I_{1680}) + 0.0018 \quad (1)$$

$$Y'_{\text{POSS}} = 0.048(I_{1109}/I_{1760}) - 0.0012 \quad (2)$$

Results and Discussion

Polymerization. The polymerization of acetoxy-styrene is catalyzed by the AIBN initiator to obtain the poly(acetoxy-styrene) (PAS) polymer with a yield of 56 wt %. Figure 2 shows the IR spectra of the POSS-based PAS-POSS hybrid polymer, the pure POSS, and the parent PAS. The IR spectrum of the PAS-POSS hybrid polymer shows a new strong absorption peak centered at 1109 cm^{-1} from the siloxane stretching vibration, revealing that the POSS moiety is indeed incorporated into PAS molecular chains.

To further confirm that the POSS is indeed incorporated into the PAS rather than as a mixture, the

following procedures were carried out. The prepared PAS-POSS hybrid polymer is redissolved in THF to form a homogeneous and transparent solution. This solution was then added dropwise into cyclohexane, which is a nonsolvent for the PAS-POSS hybrid polymer but is a good solvent for the POSS. The precipitated product was collected by filtration to remove the unreacted POSS. Such redissolution and reprecipitation procedure were repeated more than three times, and the final product still displays the characteristic spectral peak in the region from 1150 to 1050 cm^{-1} with the same absorption intensity before and after purification. Similar redissolution and reprecipitation procedures were also carried out on a mixture of the POSS and the parent PAS; the finally obtained product does not give the siloxane characteristic peak (1150 – 1050 cm^{-1}), implying that the POSS macromer is indeed incorporated into the PAS polymer to produce the PAS-POSS copolymer. Essentially, all the POSS-based polymers prepared exhibit the characteristic absorption band at $\sim 1109 \text{ cm}^{-1}$, and the absorption intensity varies with POSS content in the reactant mixture. The pure PAS has an absorption band in the region of 1720 – 1800 cm^{-1} , where the POSS moiety does not have any absorption. This result implies that the band intensity at 1109 cm^{-1} can be further utilized to determine the POSS content of these copolymers by using the band area centered at $\sim 1760 \text{ cm}^{-1}$ as an internal reference. Using the strong absorption band of the carbonyl group in the PAS chain at 1760 cm^{-1} as an internal standard, we plot the I_{1109}/I_{1760} ratio against the POSS mole content, and a calibration line is obtained to give the eq 1 (e.g., Figure 1A). The POSS contents in these PAS-POSS copolymers thus determined are listed in Table 1. Table 1 clearly shows that the POSS content of the POSS-PAS copolymer increases with increasing the POSS feed ratio. Product molecular weight (M_w and M_n), polydispersities, and yield are also summarized in Table 1.

The molecular weights (M_w) of the parent poly(acetoxy-styrene) is 46.23×10^3 with a polydispersity of 2.61. When the polymer contains 0.35 mol % POSS, the M_w and polydispersity (PDI) decrease slightly at 40.06×10^3 and 2.13. With the increase of the POSS content, the M_w and PDI further decrease; for example, $M_w = 15.59 \times 10^3$ and PDI = 1.39 were obtained when the POSS content in the initial feed ratio is 8.10 mol %. The addition of POSS decreases the polymerization activity of the PAS and results in lower incorporated POSS based on the feed ratio possibly due to the steric bulkiness of the POSS macromer. A similar phenomenon was also observed in the copolymerization of POSS with ethylene.⁹

Polymerization of the vinylpyrrolidone catalyzed by AIBN results in $M_w = 599.8 \times 10^3$, PDI = 4.56, and a product yield of 62.3 wt %. When the POSS is added into the polymerization system, the product yield decreased only slightly, from 62.3 to 58.4 wt % with the POSS feed ratio of 2.25 mol %, while the polydispersity is drastically reduced from 4.56 to 1.20. The product polydispersity further decreases with the increase of the POSS feed ratio. The purified product clearly shows the characteristic IR absorption bands of the POSS moiety as shown in Figure 3.

Different from the copolymerization of AS and POSS, a higher molecular weight of the POSS-containing PVP-POSS copolymer can be produced in the high POSS feed

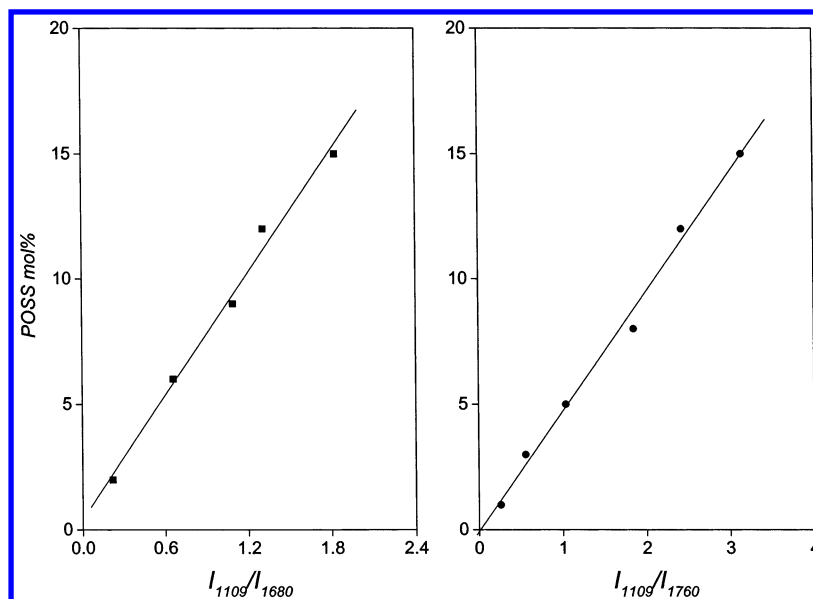


Figure 1. Calibration curve for determining component contents of POSS-based hybrid polymers using the area ratios of absorption bands of POSS at 1109 cm^{-1} , PAS at 1760 cm^{-1} , and PVP at 1680 cm^{-1} .

Table 1. Effect of POSS Feed Ratio on the Result of PAS-POSS

sample no.	feed mole ratio		product mole ratio			yield (wt %)	T_g^c ($^{\circ}\text{C}$)	M_w^d ($\times 10^3$ g/mol)	M_n ($\times 10^3$ g/mol)	PDI
	AS (mol %)	POSS (mol %)	PAS (mol %)	POSS ^a (mol %)	POSS ^b (mol %)					
1	100.00	0.00	100.00	0.00	0.00	56.2	122.1	46.23	17.71	2.61
2	99.65	0.35	99.02	0.98	0.41	40.0	113.6	40.06	18.84	2.13
3	98.60	1.40	98.73	1.27	1.38	19.1	105.8	16.40	9.34	1.76
4	97.42	2.58	98.53	1.47	2.66	19.5	104.7	22.75	13.03	1.74
5	93.79	6.21	96.77	3.23	4.18	14.5	103.2	14.86	10.34	1.44
6	91.90	8.10	95.97	4.03	5.43	9.2	107.8	15.59	11.21	1.39

^a Data were obtained based on the IR standard curve. ^b Determined by ^1H NMR. ^c Data were gathered on the second melt using a heating and cooling rate of 20 $^{\circ}\text{C}/\text{min}$. ^d Determined by GPC using the PS standard curve.

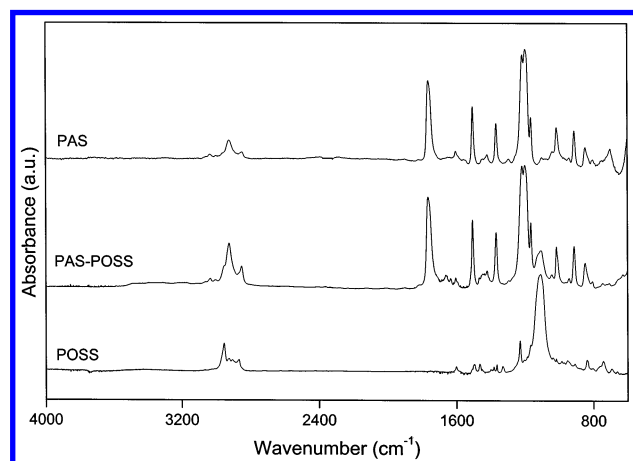


Figure 2. FT-IR spectra in the regions from 4000 to 600 cm^{-1} recorded at room temperature of pure POSS, parent PAS, and PAS-POSS.

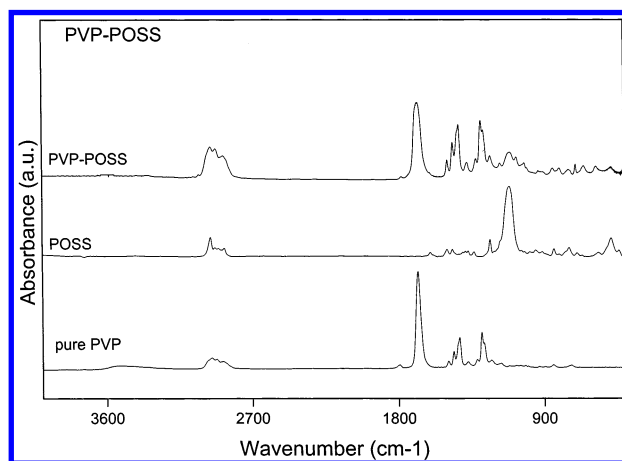


Figure 3. FT-IR spectra in the regions from 4000 to 600 cm^{-1} recorded at room temperature of pure POSS, parent PAS, and PAS-POSS.

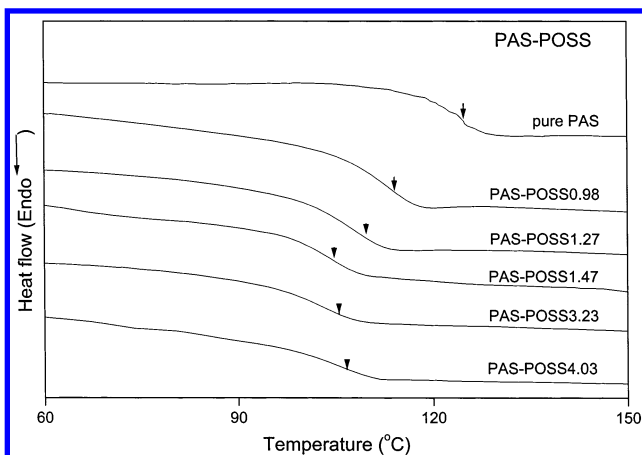
ratio (8.84 mol %), and a higher POSS incorporated copolymer can be produced by copolymerizing with vinylpyrrolidone possibly due to higher activity of the vinylpyrrolidone than the acetoxystyrene. When the POSS feed content is increased, the POSS content in the resulting hybrid also increased as shown in Table 2. Therefore, the POSS content of the hybrid can be effectively controlled by varying the POSS feed ratio. These polymer hybrids are completely soluble in common organic solvents such as THF, DMF, and chloroform. The excellent solubility of the POSS-containing

hybrid enables the characterization of their molecular structure by the solution spectroscopic method. The ^1H NMR spectra were obtained using a Bruker 300. The PAS-POSS (sample from Table 1, no. 5) exhibits proton resonance peaks at δ 7.13–6.18, 2.24, 2.01–1.58, 1.58–1.03, 0.94, and 0.62 ppm. The parent PAS does not possess any NMR resonance peak at less than δ 1.0 ppm. Therefore, the δ 0.94 ppm and δ 0.62 ppm resonance bands can be attributed to the isobutyl group (δ 0.94 ppm, $-\text{CH}_2-\text{CH}-(\text{CH}_3)_2$; δ 0.62 ppm, $\text{CH}_2-\text{CH}-(\text{CH}_3)_2$) of the POSS moiety. Similarly, the PVP-POSS

Table 2. Effect of POSS Feed Ratio on the Result of PVP-POSS

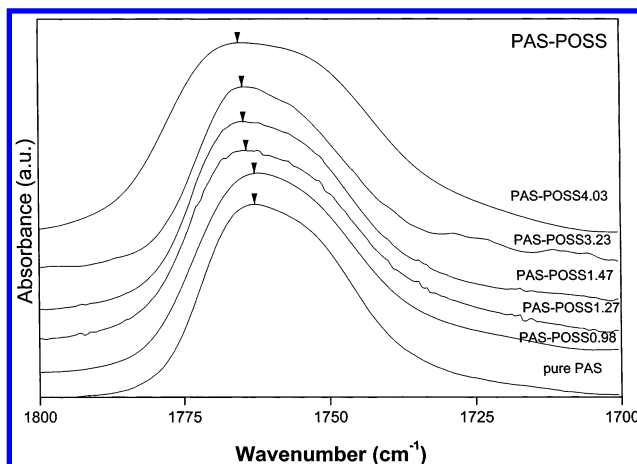
sample no.	feed mole ratio		product mole ratio			yield (wt %)	T_g^c (°C)	$M_w^d (\times 10^3)$ g/mol	$M_n (\times 10^3)$ g/mol	PDI
	VP (mol %)	POSS (mol %)	PVP (mol %)	POSS ^a (mol %)	POSS ^b (mol %)					
1	100.00	0.00	100.00	0.00	0.00	62.3	149.52	599.8	131.6	4.56
2	98.50	1.50	98.00	2.00	1.68	60.2	138.90	166.9	142.5	1.17
3	97.75	2.25	96.99	3.01	2.75	58.4	155.72	177.8	148.5	1.20
4	95.17	4.83	94.86	5.14	4.84	53.8	167.97	126.7	111.8	1.13
5	94.17	5.83	92.27	7.73	5.66	33.3	171.94	208.8	184.1	1.13
6	91.16	8.84	88.38	11.62	9.43	17.2	178.32	161.1	143.8	1.12

^a Data were obtained based on the IR standard curve. ^b Determined by ¹H NMR. ^c Data were gathered on the second melt using a heating and cooling rate of 20 °C/min. ^d Determined by GPC using the PS standard curve.

**Figure 4.** Differential scanning calorimetry thermograms of PAS and PAS-POSSs.

(sample from Table 2, no. 1) shows proton resonance peaks at δ 7.16–7.06 (w), 3.85, 3.70, 3.21, 2.02, 1.67, 0.94, and 0.61 ppm. Similar with the PAS-POSS, the resonance bands at δ 0.94 and δ 0.61 ppm are assigned to the isobutyl group (δ 0.94, $-\text{CH}_2-\text{CH}-(\text{CH}_3)_2$; δ 0.61, $\text{CH}_2-\text{CH}(\text{CH}_3)_2$) of the POSS moiety because the parent PVP does not possess the resonance spectra at this region. The chemical shift of δ 2.24 ppm in the PAS-POSS and the chemical shift at δ 3.22 in the PVP-POSS are attributed to the carbonyl-substituted methyl proton peak ($-\text{COCH}_3$) in the PAS species of PAS-POSS and the α -methylene proton relative to nitrogen in the pyrrolidonyl ring of PVP species, while the POSS moiety does not possess any resonance band in this region. Therefore, we can also estimate the POSS content in these hybrids based on the ¹H NMR spectra. The summarized results are listed in Tables 1 and 2.

Thermal Properties and T_g Increase Mechanism. Figure 4 shows the DSC thermograms of various PAS-POSS hybrids and the parent PAS. The PAS-POSS hybrid polymer with 0.98 mol % POSS has a T_g at 113.6 °C, which is even lower than the T_g of the non-POSS parent PAS (at 122.5 °C) by 8.9 °C. It appears that the presence of POSS moiety in the hybrid copolymers is unable to increase the T_g of the parent polymer. The presence of POSS at a relative smaller content actually reduces the dipole-dipole interaction of PAS molecules and plays an inert diluent role to decrease the self-association interaction of PAS molecules. The T_g of the PAS-POSS further decreases with the increase of the POSS content in the hybrid polymer and approaches a minimum at POSS = 3.23 mol % (Table 1). The lowest T_g of the PAS-POSS hybrid observed is at 103.1 °C. At a higher POSS content (4.03 mol %), the T_g of the PAS-POSS hybrid increases with the increase of the POSS content. Other than the diluent role to

**Figure 5.** Expanded FT-IR spectra in the regions from 1800 to 1700 cm^{-1} recorded at room temperature of parent PAS and PAS-POSSs.

decrease T_g of the PAS above-mentioned, the POSS moiety must play another role to increase the T_g which becomes dominant when its content is relatively higher (more than 4.03 mol %). To understand the T_g change mechanisms involved in these PAS-POSS hybrids, the characterization of infrared vibration spectra of these PAS-POSSs was carried out. Figure 5 shows the expanded FTIR spectra ranging from 1800 to 1700 cm^{-1} for the PAS and various PAS-POSSs. The PAS has a characteristic absorption band centered at 1760 cm^{-1} , which is attributed to the carbonyl vibration absorption of the PAS. This absorption maximum tends to shift toward higher frequency when the POSS is incorporated into the PAS. For instance, this PAS peak maximum at 1760 cm^{-1} decreases to 1762 cm^{-1} in the PAS-POSS1.27 (1.27 mol % POSS) but increases to 1765 cm^{-1} in the PAS-POSS4.03 (4.03 mol % POSS). In addition, the band is obviously widened at higher POSS content. Interestingly, a stronger shoulder peak at lower frequency (1750 cm^{-1}) is found in the PAS-POSS4.03. It appears that there is a new stronger dipole-dipole interaction existence between the POSS and the carbonyl of PAS species, which is probably responsible for the positive contribution to the T_g increase of the hybrid. However, the POSS itself does not cause T_g increase of the hybrid. The latter interaction (POSS-PAS) contribution is probably weaker than its diluent role of POSS to the self-association of PAS molecules in the PAS-POSS due to the relatively small content of the POSS cube. Figure 6 shows the expanded FTIR in the region from 1150 to 1050 cm^{-1} of various PAS-POSS's and the parent PAS. The POSS has a characteristic broad band centered at 1109 cm^{-1} , which is attributed to the siloxane vibration absorption within POSS molecules. Surprisingly, this siloxane characteristic band signifi-

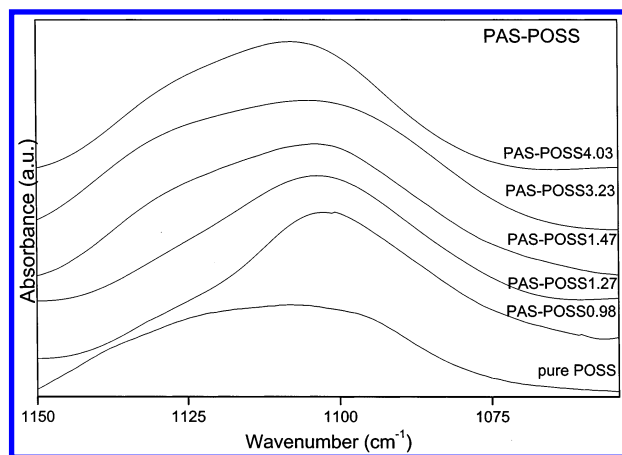


Figure 6. Expanded FT-IR spectra ranging from 1200 to 1050 cm^{-1} of POSS and PAS-POSSs recorded at room temperature.

cantly shifts to lower frequency with a small amount of the POSS within the PAS main chain. The absorption peak maximum is located at 1103 cm^{-1} with 0.98 mol % POSS. This result can be interpreted as the dipole-dipole interaction occurring between the POSS siloxane and the PAS carbonyl. When the POSS content is increased, the POSS-POSS interaction will increase as would be expected. This is why the siloxane vibration peak maximum shifts back toward the parent POSS absorption again at a higher POSS content. The nano-size POSS and the aggregated POSS cluster physically dominate local polymer chain motion which is able to provide another contribution to the T_g increase besides the POSS-PAS dipole interaction in the hybrid polymer when the POSS content is higher. Here, the POSS aggregation is mainly derived from the intramolecular or intermolecular POSS-POSS interaction, and the extent of such aggregation depends on the POSS content in the PAS-POSS copolymer. As mentioned above, the presence of POSS also plays the role of a diluent to reduce the extent of the PAS dipole-dipole interaction and thus decreases its T_g . It appears that these two adverse and competitive effects depend on the POSS content in the copolymer. At a relatively lower POSS content, the diluent role to depress T_g is dominant. At a higher POSS content, the POSS-POSS and POSS-PAS interaction becomes dominant. As a result, the observed T_g of the PAS-POSS hybrid decreases and then increases with the increase of the POSS content. A similar T_g increase was also found by Haddad³ and Mather.⁴ Haddad³ found that at a relatively higher POSS content (7.8 mol %) the MPS-POSS has a T_g at $98 \text{ }^\circ\text{C}$ higher than the parent poly(*p*-methylstyrene) at $93 \text{ }^\circ\text{C}$. Mather⁴ found that PN-POSS with 10 mol % of POSS also has a T_g higher than the parent poly(norbornene) by $10 \text{ }^\circ\text{C}$.

Figure 7 shows the DSC thermograms of various PVP-POSSs and the parent PVP. The PVP-POSS2.0 (2.0 mol %) shows a T_g at $138.9 \text{ }^\circ\text{C}$, which is less than that of parent PVP ($149.5 \text{ }^\circ\text{C}$) by about $10 \text{ }^\circ\text{C}$. However, the PVP-POSS3.01 (3.01 mol % POSS) has a T_g at $155.7 \text{ }^\circ\text{C}$, which is higher than that of the parent PVP ($149.52 \text{ }^\circ\text{C}$) by $6 \text{ }^\circ\text{C}$. Above 3 mol % POSS content, the T_g of the PVP-POSS increases with the increase of the POSS content. For instance, the PVP-POSS5.14 has a T_g at $167.97 \text{ }^\circ\text{C}$, which is higher than that of the parent PVP by $18 \text{ }^\circ\text{C}$. To clearly understand the T_g increase mechanism in the PVP-POSS hybrids, the FTIR characterization was carried out. Figure 8 shows the ex-

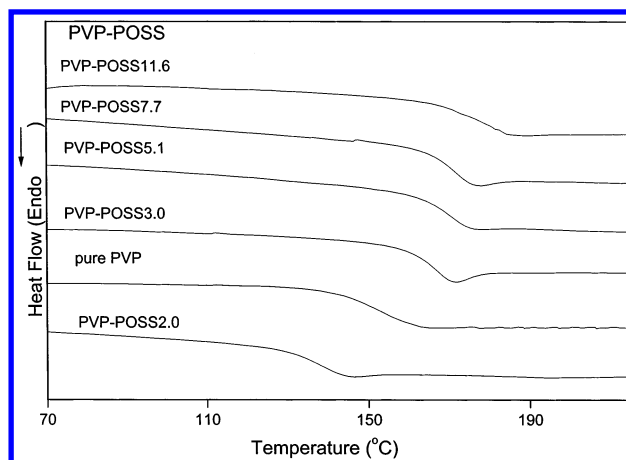


Figure 7. Differential scanning calorimetry thermograms of PVP and PVP-POSSs.

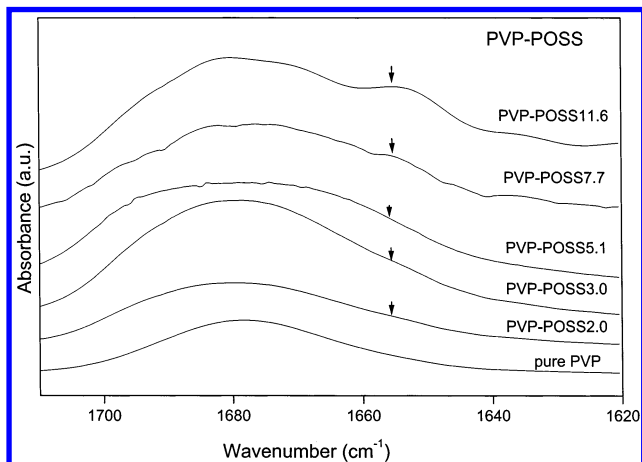


Figure 8. Expanded FT-IR spectra ranging from 17200 to 1600 cm^{-1} of parent PVP and PVP-POSSs recorded at room temperature.

panded FTIR spectra of various PVP-POSSs and the parent PVP ranging from 1720 to 1620 cm^{-1} . The parent PVP shows a characteristic carbonyl vibration band located at 1680 cm^{-1} . The absorption peak maximum slightly shifts toward higher frequency when the POSS moiety is incorporated into the PVP due to the inert diluent role of the POSS to the self-association interaction of the PVP molecules. Interestingly, the vibration band is obviously broadened asymmetrically on the low-frequency side, and a significant absorption shoulder appears at the lower wavenumber. This absorption shoulder increases with the increase of the POSS content. For instance, the PVP-POSS with 7.7 mol % POSS exhibits a significant strong shoulder peak centered at 1654 cm^{-1} , which can be assigned as the new dipole-dipole interaction between the POSS and PVP carbonyl. This result is also consistent with the result observed in carbonyl vibration spectra of PAS-POSS4.03, which is also in good agreement with the observed T_g enhancement of the PVP-POSS.

Figure 9 shows the expanded FTIR spectra of the pure POSS and various PVP-POSSs ranging from 1200 to 1040 cm^{-1} . The POSS has a characteristic vibration band located at 1109 cm^{-1} , while the PVP does not have any absorption in the same region. When the POSS moiety is incorporated into the PVP, the characteristic vibration band significantly shifts toward lower frequency and results in a broad absorption shoulder in lower wavenumber. This observation further confirms

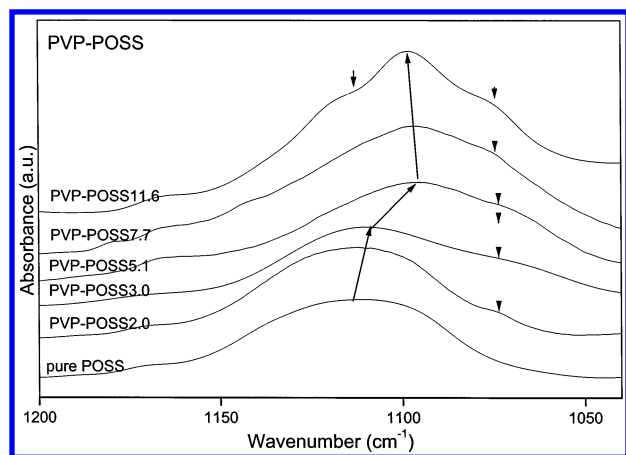


Figure 9. Expanded FT-IR spectra ranging from 1200 to 1050 cm^{-1} of pure POSS and PVP-POSSs recorded at room temperature.

that a stronger interaction occurs in the PVP-POSS hybrid polymer. The intensity of the shoulder also further increases with the increase of the POSS content (Figure 9). This observation is completely identical with the carbonyl vibration band change trend in the resulting polymer (Figure 8). In contrast between the PAS-POSS and the PVP-POSS hybrid polymer, the latter shows much stronger interaction than the former between POSS siloxane and carbonyl group. This is also consistent with their relative T_g changes, such as the PVP-POSS3.01 has a T_g increase while the PAS-POSS4.01 has a T_g decrease relative to their respective homopolymers.

Conclusions

In summary, a series of POSS-based hybrid polymer have been prepared, and their structure and thermal properties are characterized. The POSS content in the hybrid can effectively be controlled by varying the feed ratio. The POSS shows low activity in the copolymeri-

zation relative to other organic comonomers. However, the POSS-containing hybrid copolymer shows a significantly narrower molecular weight distribution (PDI). The T_g of hybrid polymer depends on three factors: (1) inert diluent role of POSS to reduce the self-association dipole-dipole interaction of parent polymer molecules (negative contribution), (2) the dipole-dipole interaction between POSS siloxane and the polar carbonyl of organic polymer species, and (3) the POSS-POSS inter- or/and intermolecular interaction. At a relative low POSS content, the dilute role plays the main role and results in T_g decrease. At a relative high POSS content, the POSS-PAS or POSS-PVP and POSS-POSS interactions play a dominant role and result in T_g increase.

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