

Significant glass transition temperature increase based on polyhedral oligomeric silsesquioxane (POSS) copolymer through hydrogen bonding

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Summary

A series of poly(vinylphenol-co-vinylpyrrolidone-co-isobutylstyryl polyhedral-oligosilsesquioxane (PVPh-co-PVP-co-POSS) copolymers were prepared by free radical copolymerization of acetoxystyrene, vinylpyrrolidone with POSS (PAS-co-PVP-co-POSS) following by selective removal of the acetyl protective group, and results in significant glass transition temperature increase. The thermal properties and hydrogen bonding of these copolymers were investigated by differential scanning calorimetry and fourier transfer infrared spectroscopy and good correlation between thermal behaviors and infrared spectroscopy results were observed.

Introduction

A polymer possessing high T_g is of great interest in polymer science and industry due to its potential application. In our previous studies [1], we have found that the T_gs of poly(vinylphenol) (PVPh)/poly(vinylpyrrolidone) (PVP) blends are significantly higher than the values predicted by the Fox rule. Furthermore, the T_gs of poly(vinylphenol-co-vinylpyrrolidone) (PVPh-co-PVP) copolymers are substantially greater than their corresponding PVPh/PVP blends at the same mole fractions of PVPh and PVP due to the composition heterogeneity in a hydrogen bonded polymer [2]. Here, a problem is raised, can we obtain further T_g increase in this PVPh-co-PVP copolymer matrix through incorporation of other materials? Recently, the polyhedral oligosilsesquioxane (POSS) hybrid polymer materials have attracted great attention because of their effectively reinforced thermal decomposition and antioxidation properties in polymer matrix [3-9]. Very few studies have been reported on T_g behavior and the reinforcement mechanism of the POSS hybrid polymer. Haddad et al. [3], reported that T_gs of polystyrene-co-POSS (PS-co-POSS) copolymers are lower than the pure PS when the POSS content is less than 7.8 mole% based on DSC and DMA analyses. Furthermore, the PS-co-POSS copolymer containing 16 mole% of POSS has a T_g which is 22°C higher than that of the pure PS. Mather et al [4] found that the T_g of the poly(norbornyl-POSS) copolymer is 28°C higher than the

pure poly(norbornene) when the POSS content is 7.7 mole%.

From our knowledge, no research concerning the POSS hybrid copolymer through hydrogen bonding has been reported. As a result, in this present study, a series of poly(vinylphenol-co-vinylpyrrolidone-co-POSS) (PVPh-co-PVP-co-POSS) copolymers were prepared to compare the glass transition temperature between PVPh-co-PVP-co-POSS and PVPh-co-PVP copolymers. In our previous study [10], we have found that the poly(vinylphenol) is difficult to be synthesized directly from the vinylphenol monomer because of chain transfer and other side reactions involved. Therefore, PVPh-co-PVP-co-POSS copolymers were prepared by free radical copolymerization of acetoxystyrene, vinylpyrrolidone and styrylisobutylPOSS, following by selective removal of the acetyl protective group. Fortunately, from this procedure, we can clearly distinguish the thermal properties between the non-hydrogen bonded and hydrogen bonded segments of the PVP and POSS.

Experimental section

General Procedure

Thermal properties were characterized under a nitrogen atmosphere on a DSC from Du-Pont (DSC-9000). FTIR (Infrared) spectra were measured with a spectral resolution 1 cm^{-1} on a Nicolet Avatar 320 FT-IR Spectrophotometer. M_w , M_n and polydispersity index (M_w / M_n) were estimated by a Water 510 gel permeation chromatograph (GPC).

Materials

Isobutylstyrylpolyhedral oligosilsesquioxane (POSS) was purchased from the Hybrid plastic Co. Inc. of U.S.A. Both vinylpyrrolidone and acetoxystyrene, purchased from the Aldrich, were distilled from calcium hydride under reduced pressure and stored in sealed ampuls in a refrigerator. The high purity azobisisobutyronitrile (AIBN) (Aldrich) was also kept in the dry box and used as received. Spectroscopic grade THF and toluene (Aldrich) 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.

Preparation of polymer hybrids

All polymerization reactions were carried out under nitrogen using a vacuum-line system. The poly(acetoxystyrene-co-vinylpyrrolidone-co-isobutylstyryl polyhedral oligomeric silsesquioxanes) (PAS-PVP-POSS) was prepared by a free radical polymerization method using the azobisisobutyronitrile (AIBN) initiator (1 wt% based on monomer) at $80\text{ }^\circ\text{C}$ under nitrogen atmosphere for 24 hours. The product then was poured into excess cyclohexane under vigorous agitation to precipitate the copolymer, then purified in THF/cyclohexane and dried in a vacuum oven. The synthesis of PHS-PVP-POSS copolymer was carried out by dispersing PAS-PVP-POSS copolymer in a mixture of aqueous sodium carbonate and dioxane for 2 hr at $40\text{ }^\circ\text{C}$ under nitrogen atmosphere. The product was then poured into an excess

hydrochloric acid solution under vigorous agitation to precipitate the copolymer, then rinsed with water, dried in a vacuum oven. The respective component content of these polymers were estimated by using FTIR analysis [11].

Results and Discussion

We chose the PHS-PVP copolymer with ~50 mol% of the PVP as the polymer matrix in the preparation of the POSS based hybrid polymers because this chosen copolymer composition possesses the highest T_g among other compositions due to the optimum balance in hydrogen bonding interaction between hydroxyl groups of PHS and carbonyl groups of PVP [2,10]. Figure 1 shows DSC thermograms of the PAS-co-PVP-co-POSS2.2 copolymer, PAS-co-PVP copolymer, pure PVP homopolymer, PVPh/PVP blend, PVPh-co-PVP copolymer, PVPh-co-PVP-co-POSS0.8 copolymer, PVPh-co-PVP-co-POSS2.2 copolymer and PVPh-co-PVP-co-POSS3.2 copolymer ranging from 60°C to 270°C. Clearly, the observed T_gs are in the order of PVPh-co-PVP-co-POSS3.2 > PVPh-co-PVP-co-POSS2.2 > PVPh-co-PVP-co-POSS 0.8 > PVPh-co-PVP copolymer > PVPh/PVP blend > pure PVP homopolymer > PAS-co-PVP copolymer > PAS-co-PVP-co-POSS2.2 copolymer and the results are summarized in Table 1. The observed T_g rise under almost same mole fraction of PVP and its T_g difference is very interesting. Certain specific interactions must exist in these polymer systems containing almost same mole fraction of PVP. Therefore, we turn our attention to the infrared spectra to investigate the specific interaction of these polymer systems

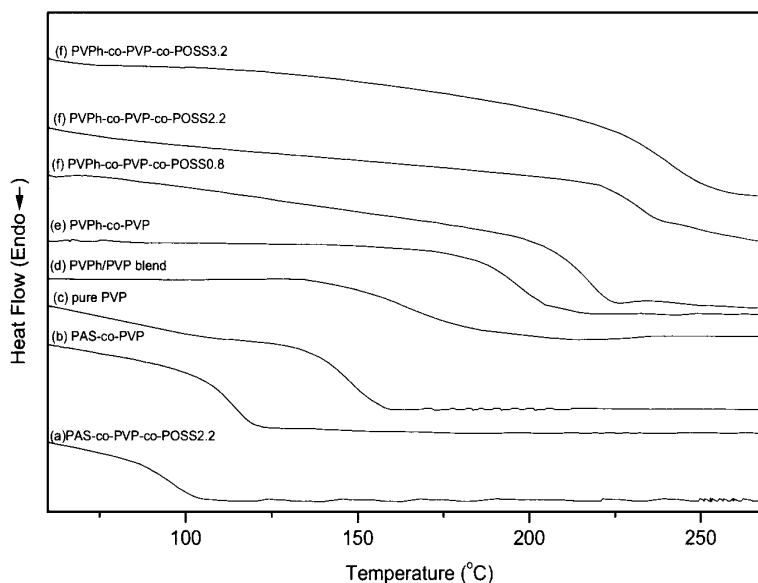


Figure 1. DSC thermograms of PAS-co-PVP-co-POSS, PAS-co-PVP, pure PVP, PVPh/PVP blend, PVPh-co-PVP and with different POSS contents of PVPh-co-PVP-co-POSS.

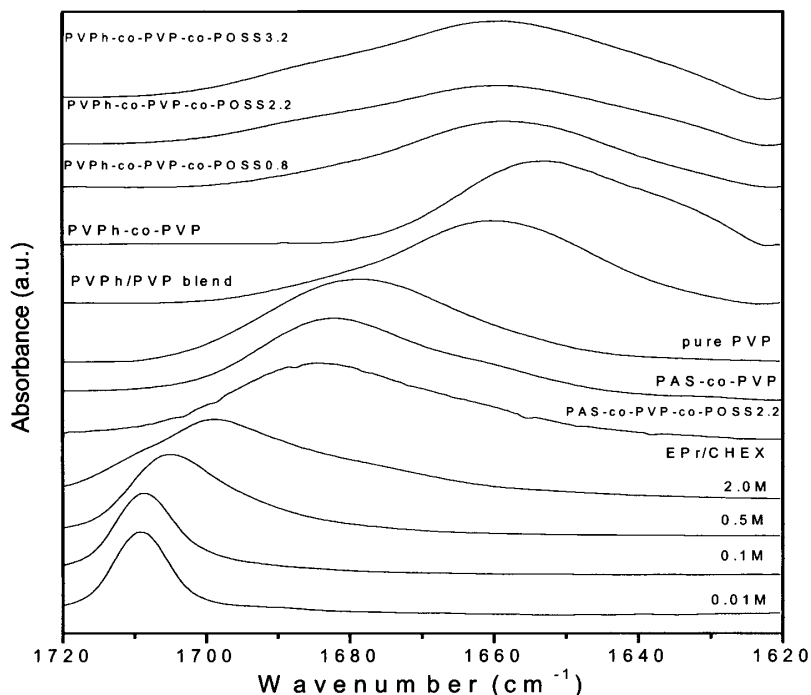


Figure 2. FTIR spectra recorded at room temperature in the region 1720 cm^{-1} - 1620 cm^{-1} for various EPr concentrations in cyclohexane, PAS-co-PVP-co-POSS, PAS-co-PVP, pure PVP, PVPh/PVP blend, PVPh-co-PVP and with different POSS contents of PVPh-co-PVP-co-POSS.

Figure 2 shows FTIR spectra of the carbonyl stretching recorded at room temperature ranging from 1620 cm^{-1} to 1720 cm^{-1} for different concentrations of the ethylpyrrolidone in cyclohexane (EPr is a model compound for the PVP), PAS-co-PVP-co-POSS2.2, PAS-co-PVP, pure PVP, PVPh/PVP blend, PVPh-co-PVP, PVPh-co-PVP-co-POSS0.8, PVPh-co-PVP-co-POSS2.2 and PVPh-co-PVP-co-POSS 3.2 copolymers. The carbonyl band of the ethylpyrrolidone/cyclohexane solution becomes broader and shifts to the lower wavenumber with increasing EPr concentration in cyclohexane because of higher probability of the pyrrolidone/pyrrolidone interaction. These results confirm that the wavenumber and half-width are both dependent upon their specific and dipole interactions between molecules or polymer chains. In addition, the pure PVP homopolymer possess lower wavenumber and broader half-width relative to the EPr solution in cyclohexane due to no inert diluent (non-polar group) present in the pure PVP homopolymer. Therefore, the probability of dipole-dipole interaction of the PVP is expected to be greater than that of the EPr/cyclohexane solution. However, by incorporation of acetoxystyrene monomer into the PVP chain, the half-width of the PVP carbonyl band at 1680 cm^{-1} is decreased and shifts to higher wavenumber at 1682 cm^{-1} . As a result, the T_g of the PAS-co-PVP is significantly depressed (26°C) due to lower dipole-dipole interaction of the pyrrolidone moieties in the polymer chain. The carbonyl band of the PAS-co-PVP at 1682 cm^{-1} shifts slightly higher at 1683 cm^{-1}

with the incorporation the POSS moiety into the PAS-co-PVP copolymer chain. It appears that the incorporation of the inert diluent group (POSS) into the polymer chain decreases its original dipole-dipole interaction. For this reason, the Tg of PAS-co-PVP-co-POSS2.2 is also significantly lower (24°C) than the PAS-co-PVP copolymer. This result provides evidence why most POSS hybrid polymer systems give a relative lower Tg than the original polymer matrix at a lower POSS content.

Table 1. Information of these polymers in this study.

No.	Aberration	Polymer Composition (mol%)			Mn	Tg (°C)
		PVP	PAS	POSS		
P1	PAS-co-PVP-co-POSS2.2	43.0	54.8	2.2	4300	98.5
P2	PAS-co-PVP	45.0	50.0	-	4800	122.4
P3	Pure PVP	100.0	-	-	52000	148.4
P4	Pure PAS	-	100.0	-	21500	122.3
		PVP	PVPh	POSS		
P5	Pure PVPh	-	100	-	11000	149.0
P6	PVPh/PVP blend	45.0	55.0	-	-	175.0
P7	PVPh-co-PVP	45.0	55.0	-	4800	194.9
P8	PVPh-co-PVP-co-POSS0.8	43.0	56.2	0.8	4700	205.8
P9	PVPh-co-PVP-co-POSS2.2	43.0	54.8	2.2	4300	212.2
P10	PVPh-co-PVP-co-POSS3.2	44.0	52.8	3.2	4200	245.3

Finally, we would like to turn our attention on this hydrogen bonded polymer system in this study. Figure 2 also shows that the carbonyl band shifts from 1682 cm⁻¹ to 1650 cm⁻¹ after deacetylation of the PAS-co-PVP into PVPh-co-PVP copolymer. This shift is attributed to the hydrogen bonding formation between vinylphenol and vinylpyrrolidone segments on the copolymer chain. Therefore, the Tg of the PVPh-co-PVP are approximately 72°C higher than that of the PAS-co-PVP by transforming a relatively weak dipole interaction of the PAS-co-PVP copolymer into a relatively stronger hydrogen bonding in the PVPh-co-PVP copolymer. Interestingly, the carbonyl stretching of the PVPh/PVP blend shifts only to 1660 cm⁻¹ due to the compositional heterogeneity in hydrogen bonded polymer system as mentioned previously [2], which is consistent with the observed glass transition temperature difference (20°C) between the PVPh-co-PVP copolymer and the miscible PVPh/PVP blend. However, the carbonyl band of the PVPh-co-PVP-POSS0.8 copolymer shifts to 1654cm⁻¹, revealing that portion of the hydroxyl group of PVPh forms hydrogen bonding with the siloxane of the POSS. Therefore, the carbonyl band of the PVPh-co-PVP-co-POSS shifts to higher wavenumber from 1650 to 1660cm⁻¹ and the free carbonyl group of the PVP is now appeared with increasing the POSS content. Indeed, this result indirectly provides the evidence that the hydrogen bonding exists between the hydroxyl group of the PVPh and the siloxane group of the POSS. As a result, the Tg increased with the increase of the POSS content in PVPh-co-PVP-co-POSS system because of multiple hydrogen bonding formation in this nano-scale of POSS-containing copolymer. Surprisingly, the Tg of the PVPh-co-PVP-co-POSS2.2 is drastically higher than the PAS-co-PVP-co-POSS2.2 by as much as 124°C after deacetylation. Similarly, this phenomenon is caused by transforming the relatively weak dipole-dipole interaction of the PAS-co-PVP-co-POSS copolymer into the strong hydrogen bonded nanocomposite of the PVPh-co-PVP-co-POSS copolymer.

Conclusions

It is worthy to point out here, both PVPh and pure PVP possess Tgs at about 150°C. Nonetheless, the incorporation of only 3.2 mole % of POSS into the PVPh-co-PVP copolymer chain results in drastic Tg increase to 245°C, higher than both homopolymers by about 95°C. We believe that this study provides an alternative novel approach to create a higher Tg through structural design based on the POSS moiety.

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