

Synthesis and Characterization of Novel Organic/Inorganic Hybrid Polymers Containing Polyhedral Oligosilsesquioxanes

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Abstract: Hybrid polymers, poly(vinyl pyrrolidone-*co*-isobutyl styryl polyhedral oligomeric silsesquioxanes)s (PVP-POSS) were synthesized by one step polymerization and characterized using GPC and DSC. Addition of POSS significantly increases the T_g of polyvinylpyrrolidone at a fair high POSS content and obtained high molecular weight polymers with very narrow molecular distribution. The POSS content in the resulted hybrids can be controlled by varying the POSS feed ratio.

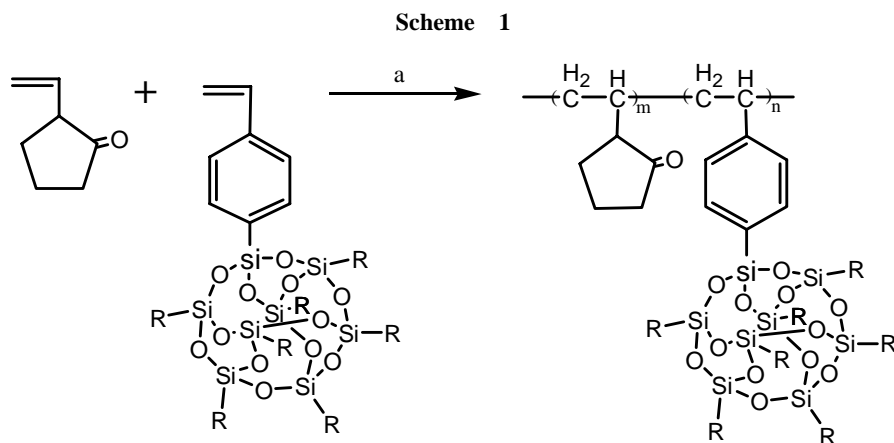
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Typical hybrid materials contain three-dimensional cross-linked sol-gel networks, in which an inorganic silica-like phase is dispersed into the polymer matrix. Recently, well-defined polyhedral oligomeric silsesquioxanes-based hybrid polymers have attracted increasing scientific interest¹. Several nanocomposite hybrid polymers have been prepared from polyhedral oligomeric silsesquioxanes (POSS)²⁻⁷ and exhibit increased T_g²⁻⁵, T_{dec}⁶, resistance to oxidation⁷, and miscibility as well as reduced flammability. The POSS is a cubic silica that is rigid and has completely defined dimension (0.53 nm) with eight organic groups (functional or inert) appended to the vertexes of the cube. The functional groups can be selectively varied to prepare various POSS-based hybrid polymers. It makes the hybrid polymer to be designed at molecular level. Herein, we wished to report the high molecular weight hybrid polymers with very narrow molecular distribution and enhanced T_g from vinyl pyrrolidone and isobutylstyryl polyhedral oligomeric silsesquioxanes (**Scheme 1**).

Experimental

The isobutyl styryl polyhedral oligosilsesquioxanes (POSS) was purchased from Hybrid plastic Co. Inc. of United States and kept in a dried box before use. Acetoxystyrene was purchased from Aldrich, distilled from calcium hydride under reduced pressure and stored in sealed ampuls in a refrigerator. High purity azobisisobutyronitrile (AIBN) also from

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Aldrich was kept in 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.

All polymerization reactions were carried out under nitrogen using a vacuum-line system. These poly (acetoxystyrene-*co*-isobutylstyryl POSS)s (PAS-POSS) copolymers were prepared by a free radical polymerization method. For comparison, a pure poly (acetoxystyrene) (PAS) was also synthesized. A typical example of experimental procedure for these polymers is given below. In a typical reaction, 810 mg of acetoxystyrene (AS, 5.00 mmol) and 161 mg of isobutylstyryl polyhedral oligosilsesquioxane (POSS, 0.18 mmol) monomers in 10 mL dried toluene were polymerized using the azobisisobutyronitrile (AIBN) initiator (1 wt% based on monomer) at 80°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. 40.0% yield was obtained through this procedure.

Results and Discussion

All polymerization reactions were carried out under nitrogen using a vacuum-line system. These poly(vinylpyrrolidone-*co*-isobutylstyryl POSS)s (PVP-POSS) copolymers were prepared by a free radical polymerization method. 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 spectroscopic method. The results are listed in **Table 1**.

It is seen in **Table 1**, that the molecular weight (MW) of the parent poly(vinyl pyrrolidone) is 599.8×10^3 with a polydispersity of 4.56 and 62.3% yield. When the POSS is added into the polymerization system, the product yield decreased only slightly, from 62.3 wt% 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. When the POSS feed ratio

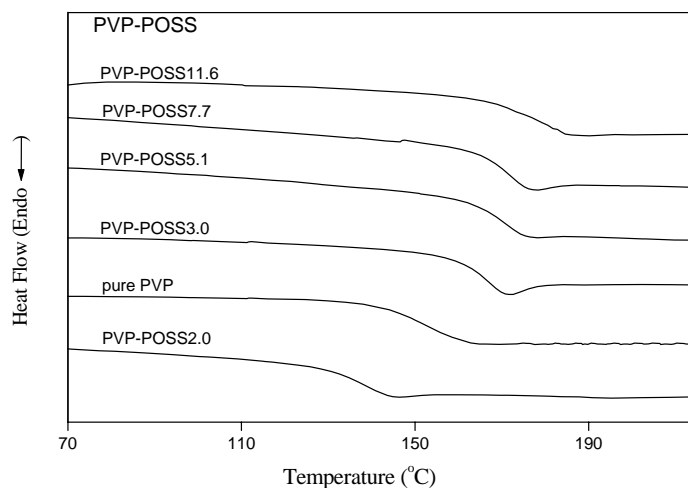
reaches 4.83 mol% with 4.84 mol% POSS content in the copolymer, the M_w and polydispersity (PDI) decrease slightly at 126.7×10^3 and 1.13, respectively. With the increase of the POSS content, PDI further decrease, for example, PDI = 1.12 is obtained when the POSS content was 11.62 mol% in the 8.84 mol% initial feed ratio. The average-molecular weight is lowered when the POSS is incorporated into the polyvinylpyrrolidone. It shows that the POSS decreases the polymerization activity of the vinylpyrrolidone possibly due to the steric bulkiness of the POSS macromer. Similar phenomenon was also observed in the copolymerization of POSS with ethylene⁸. Simultaneously, it was found that the PDI in all the POSS based hybrid PVPs are very low, showing that the POSS seems to play a role of the active reagent in the polymerization of vinylpyrrolidone. When the POSS feed content is increased, the POSS content in the resulted hybrid is also increased as shown in **Table 1**. Therefore, the POSS content of the hybrid can be effectively controlled by varying the POSS feed ratio.

Figure 1 shows the DSC thermograms of various PVP-POSSs and the parent PVP. The T_g of PVP-POSS 2.0 (2.0 mol %) is 138.9 °C, which is lower than that of parent PVP (149.5 °C) by about 10 °C. However, the PVP-POSS 3.01 (3.01 mol% POSS) has a T_g at 155.7 °C, which is higher than that of the parent PVP (149.52 °C) by 6 °C. The T_g of the PVP-POSS containing 3 mol% POSS increases with the increase of the POSS content. For instance, The PVP-POSS 11.62 has a T_g at 178.32°C, which is higher than that of the parent PVP by 29.8 °C. We think the presence of POSS may reduce the extent of the PVP carbonyl dipole-dipole interaction, thus, decreases its T_g when the POSS content is low. At a higher POSS content, the dipole interaction between the POSS siloxane and the PVP carbonyl, nanosize POSS and the aggregated POSS cluster physically dominates local polymer chain motion, which is able to provide another contribution to the T_g increase in the hybrid polymer. Further investigations of mechanism of the T_g increase are in progress.

Table 1 Effect of POSS feed ratio on the result of PVP-POSS

Sample No.	VP	POSS	PVP	POSS ^a	POSS ^b	Yield (wt %)	T_g^c (°C)	M_w^d ($\times 10^3$ g/mol)	M_n ($\times 10^3$ g/mol)	PDI
	(mol %)	(mol %)	(mol %)	(mol %)	(mol %)					
	Feed mole ratio		Product mole ratio							
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
2	97.75	2.25	96.99	3.01	2.75	58.4	155.72	177.8	148.5	1.20
3	95.17	4.83	94.86	5.14	4.84	53.8	167.97	126.7	111.8	1.13
4	94.17	5.83	92.27	7.73	5.66	33.3	171.94	208.8	184.1	1.13
5	91.16	8.84	88.38	11.62	9.43	17.2	178.32	161.1	143.8	1.12

^aData were obtained based on IR standard curve. ^bdetermined by ¹H NMR. ^cData were gathered on the second melt using a heating and cooling rate of 20 °C/min. ^ddetermined by GPC using PS standard curve.

Figure 1 The differential scanning calorimetry thermograms of PVP and PVP-POSSs

Acknowledgments

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