Synthesis and Characterization of Hybrid Poly(phenylenemethylene) Having Functionalized Silsesquioxanes (POSS)

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New hybrid poly(phenylenemethylene) with functionalized polyhedral oligomeric silsesquioxanes (PPM-POSS) and poly(phenylenemethylene) with benzyl moieties (PPM-Benzyl) were prepared by the reaction of POSS-DMP or Benzyl-DMP and paraformaldehyde, respectively. The synthesized polymers could be well characterized by ¹H NMR, FT-IR, DSC, TGA, and EDS. This type of hybrid poly(phenylenemethylene) containing side-chain-tethered POSS pendant units consists of a linear rigid-rod poly(phenylenemethylene) in the main chain and POSS branches as inorganic parts attached to the main chain. This particular molecular architecture of hybrid PPM-POSS possesses the higher thermal decomposition and no glass transition temperatures relative to those of PPM-Benzyl with no POSS units. Furthermore, PPM-POSS shows very uniform distribution of spherical particles with a mean diameter 100 nm, while PPM-Benzyl shows uneven and large spherical particles with 1–5 μm size, as evidenced by scanning electron microscopy studies.

KEY WORDS: Silsesquioxane (POSS) / Poly(phenylenemethylene) / Thermal Decomposition Temperature / Glass Transition Temperature / Hybrid Polymer / Spherical Particles /

In recent years there has been considerable interest in organic-inorganic hybrid nanocomposites containing polyhedral oligomeric silsesquioxanes (POSS) because their use has resulted in unexpected improvement in physical and mechanical properties.^{1,2} The POSS molecules are octamers having the general formula (RSiO_{1.5})₈; they consist of a rigid, cubic silica core with nanoscale dimensions (0.3–0.4 nm) and multiple reactive functional groups.³ The POSS molecules are easily incorporated into some polymers such as acrylic,⁴ styryls,⁵ and epoxides⁶ by means of copolymerization or blending, requiring little or no alteration to existing synthetic processes because a variety of substituents attached to POSS enhances desirable solubility properties. POSS containing copolymers or blends have increased oxygen permeability, are thermoplastic or curable, have oxidation resistance, and higher thermal properties than those without the POSS moieties.

Previously, we have demonstrated various organic-inorganic hybrid nanocomposites based on POSS as inorganic precursors. Such examples are hybrid micelles,⁷ hybrid gels,⁸ hybrid liquid crystalline polymers,⁴ hydrophobic CaCO₃ composite particles,⁹ and homogeneously transparent polymer hybrid materials combined at the molecular level.^{10,11}

Phenolic resin is one of the widely used thermosetting resins because of its excellent ablative property, structural integrity, thermal stability, and solvent resistance.^{12,13} However, new functionalized phenolic polymers have remained relatively unexplored in the synthesis field of aromatic polymer. It is important to extend the chemistry of novolac for various electron-rich aromatic compounds, and create new functional materials based on the poly(phenylenemethylene) (PPM) backbone. Novolac-type phenolic/POSS nanocomposites with

high thermal stabilities and low surface energies were prepared by POSS containing eight phenol functional groups, phenol, and formaldehyde.¹⁴

Here, we report a new hybrid PPM presenting POSS units in their side chains. We incorporated the POSS units into PPM to improve its thermal stability and a uniform distribution of polymer particles. The bulky silsesquioxane groups were introduced to the main chain of PPM-POSS to inhibit intermolecular interactions between the resulting PPM-POSS. However, PPM-Benzyl with benzyl groups shows uneven larger aggregates of polymer particles caused by aromatic (π–π) interactions between phenyl groups of the resulting PPM-Benzyl. To the best of our knowledge, the introduction of POSS as inorganic groups into poly(phenylenemethylene) main chain has not yet been described. We believe that the fabrication of PPM containing side-chain-tethered POSS pendant units offers well-defined architectures and high thermal stability because of POSS units with a rigid, cubic silica core.

EXPERIMENTAL

General Procedure

¹H NMR spectra were obtained on a Bruker AVANCE400 400 MHz FT NMR spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Bio-Rad FTS-6000 infrared spectrometer. Differential scanning calorimetry (DSC) thermograms were obtained with a DSC2010, TA Instruments, Inc., at a heating rate of 10 °C/min under a nitrogen atmosphere. The thermal behavior was examined by thermogravimetric analysis (TGA) (TGA S-1000, Scinco) under nitrogen atmosphere. The

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crystallinity of PPM-POSS was determined by X-ray diffraction (XRD) (Rigaku Rint2000). The morphologies and structures of hybrid poly(phenylenemethylene) with POSS moieties were observed by scanning electron microscopy (SEM) (JEOL JSM-6700/LV) and energy dispersive spectrum (EDS), respectively. SEM and EDS samples were prepared by putting dried samples on the carbon tape attached to a SEM grid.

Materials

Cyclopentyltrichlorosilane (Aldrich), paraformaldehyde (Aldrich), benzyl bromide (Aldrich), trichloro[4-(chloromethyl)phenyl]silane (Lancaster), and 4-methyl-2,6-dimethoxyphenol (Aldrich) were used as received. Tetrahydrofuran (THF) and triethylamine (TEA) were distilled over sodium and calcium hydride, respectively. *N,N*-Dimethylacrylamide was distilled from calcium hydride under nitrogen. Other solvents and reagents were commercially supplied and used without further purification.

Synthesis of Chlorobenzylcyclopentyl-POSS (POSS-Cl)

Incompletely condensed trisilanol was prepared by the hydrolytic condensation reaction of cyclopentyltrichlorosilane in reflux aqueous acetone. POSS-Cl was prepared by corner-capping reaction of incompletely condensed trisilanol with a coupling reagent, trichloro[4-(chloromethyl)phenyl]silane, according to previously published procedures.^{15,16}

Synthesis of POSS-DMP

4-Methyl-2,6-dimethoxyphenol (0.16 g, 0.97 mmol) and potassium carbonate (0.13 g, 0.97 mmol) were mixed in DMF (10 mL), and the reaction mixture was heated at 60 °C under a nitrogen atmosphere for 1 h. POSS-Cl (1.00 g, 0.97 mmol) and potassium iodide (0.16 g, 0.97 mmol) were dissolved in dry THF (10.0 mL) and added dropwise over a period of 0.5 h to the mixture. The mixture was refluxed for 24 h, cooled to room temperature, diluted with water, and extracted with chloroform. The extracted organic layer was washed with water and concentrated in a vacuum to furnish POSS-DMP as a light yellow solid (0.50 g, 44%). ¹H NMR (CDCl₃, δ): δ 7.7 (d, 2H), 7.4 (d, 2H), 6.4 (s, 2H), 5.0 (s, 2H), 3.8 (s, 6H), 2.3 (s, 3H), 1.4–1.9 (m, 56H), 1.0 (m, 7H). ²⁹Si NMR (CDCl₃, δ): –66.5, –66.6.

Synthesis of Benzyl-DMP

4-Methyl-2,6-dimethoxyphenol (2.00 g, 0.01 mol) and potassium carbonate (1.62 g, 0.01 mol) were mixed in acetone (15 mL), and benzyl bromide (1.00 g, 0.01 mol) was added to the mixture slowly. The reaction mixture was refluxed for 24 h, cooled to room temperature, diluted with water, and extracted with chloroform. The extracted organic layer was washed with water and concentrated in a vacuum. The product was purified by flash column chromatography (hexane/ethyl acetate 10:90) to give a white powder (1.23 g, 47%). ¹H NMR (CDCl₃, δ): δ 7.5 (d, 2H), 7.3–7.2 (m, 3H), 6.4 (s, 2H), 5.0 (s, 2H), 3.8 (s, 6H), 2.3 (s, 3H).

Synthesis of PPM-POSS

POSS-DMP (0.50 g, 0.43 mmol) and paraformaldehyde (0.38 g, 0.01 mol) were mixed in acetic acid (15 mL), and sulfuric acid (3 mL) was added dropwise at 5 °C. The resulting mixture was stirred for 10 h at room temperature. The mixture was poured into methanol (150 mL) and a white precipitate was obtained. The white precipitate was collected by filtration and dried in a vacuum (0.33 g, 66%). *M*_n = 5,700, *M*_w = 10,300, *M*_w/*M*_n = 1.80, polystyrene standard; eluent, CHCl₃. ¹H NMR (CDCl₃, δ): δ 7.7–7.4 (m, 4H), 5.0 (m, 2H), 3.5–4.1 (m, 8H), 2.2 (m, 3H), 1.4–1.9 (m, 56H), 1.0 (m, 7H). ²⁹Si NMR (CDCl₃, δ): –66.4, –66.5.

PPM-Benzyl was prepared by the same procedures for PPM-POSS (0.42 g, 35%). *M*_n = 1,000, *M*_w = 2,900, *M*_w/*M*_n = 2.90, polystyrene standard; eluent, CHCl₃. ¹H NMR (CDCl₃, δ): δ 7.3–6.9 (m, 5H), 5.0 (m, 2H), 3.5–4.1 (m, 8H), 2.3 (m, 3H).

RESULTS AND DISCUSSION

The synthesis of poly(phenylenemethylene) containing the POSS groups (PPM-POSS) and benzyl groups (PPM-Benzyl) are presented in Scheme 1. PPM-Benzyl was prepared to investigate the effect of the POSS units on the thermal properties and molecular architecture of hybrid PPM-POSS. The hybrid PPM-POSS and PPM-Benzyl were prepared from POSS-DMP or Benzyl-DMP and paraformaldehyde under the acidic condition, respectively. The molecular weight of PPM-POSS is lower than expected, which can be attributed to steric hindrance caused by the bulky POSS units during the polymerization.

Figure 1 displays the ¹H NMR spectra of POSS-DMP, and PPM-POSS. For POSS-DMP, the CH₂ peak of POSS-Cl was shifted downfield to 5.0 ppm and three peaks at 2.3, 3.8, and 6.4 ppm derived from 4-methyl-2,6-dimethoxyphenol units appeared. The peak at 6.4 ppm is assigned as being a singlet due to the lack of coupling of the protons (of the two ring protons) in 4-methyl-2,6-dimethoxyphenol of POSS-DMP. In PPM-POSS, the peak at 6.4 ppm of POSS-DMP disappeared, whereas the new broad peaks of methylene groups attached to the backbone of PPM-POSS showed up at 3.5–4.1 ppm.

Figure 2 shows FT-IR spectra of PPM-Benzyl and PPM-POSS. The characteristic peaks for the POSS moieties (Si–O–Si) and double bond of PPM-POSS appear around 1100 and 1630 cm^{–1}, respectively. In case of PPM-Benzyl, there is no the broad Si–O–Si band derived from POSS units because PPM-Benzyl does not contain any silicon-containing groups.

Figure 3 displays the X-ray diffraction curves of POSS-Cl and PPM-POSS. We observed no X-ray diffraction peaks for PPM-benzyl. There are distinct diffraction peaks at 2θ = 8.3°, 11.2°, and 19.3° observed for POSS-Cl (Figure 3a). Three sharp diffraction patterns were observed at the same position in PPM-POSS (Figure 3b), which reflected that PPM-POSS had crystallinity derived from the rhombohedral crystal structure of POSS molecules.¹⁷ It is evident that the amorphous structure of PPM-Benzyl can easily make the intermolecular entanglement,

Scheme 1.

Figure 1. ^1H NMR spectra in CDCl_3 of (a) POSS-DMP and (b) PPM-POSS.

Figure 2. FT-IR spectra of (a) PPM-Benzyl and (b) PPM-POSS.

(a)

(b)

Figure 3. X-Ray diffraction curves of (a) POSS-Cl and (b) PPM-POSS.

Figure 4. SEM images of (a) PPM-Benzyl and (b) PPM-POSS.

which result in the larger aggregates compared to the PPM-POSS with the bulky POSS molecules.

Figure 4 presents the morphologies of PPM-Benzyl and PPM-POSS obtained by scanning electron microscopy (SEM). In case of PPM-Benzyl (Figure 4a), uneven PPM-Benzyl nanocomposites with 1–5 μm size are aggregated each other. For PPM-POSS, uniform nanocomposites with around 100 nm size are well formed, as shown in Figure 4b. This phenomenon is because of the absence of formation of large aggregates of PPM-POSS due to the intermolecular repulsion between bulky POSS groups. In other words, the lack of aromatic (π - π) interactions of benzyl ring in PPM-POSS due to the bulky POSS groups could be a reason for the formation of uniform 100 nm-sized particles. It is possible that the polymer chains of PPM-POSS, which have less mobility because of hard and bulky POSS groups, prevent any intermolecular entanglement thereby inhibiting the formation of larger aggregates. PPM-Benzyl without bulky POSS moieties shows uneven larger particles than PPM-POSS because of aggregations resulting from aromatic (π - π) interactions between phenyl segments in PPM-Benzyl.

The effectiveness of aromatic (π - π) interactions are supported by our previous results observed in the synthesis of poly(diallyl phthalate) hybrids prepared by utilizing sol-gel reaction of phenyltrimethoxysilane,¹⁸ the synthesis of polystyrene and silica gel polymer hybrids *via* π - π interactions,¹⁹ and the synthesis of polymer hybrids with ladderlike polyphenylsilsesquioxane as a template *via* the sol-gel reaction of phenyltrimethoxysilane.²⁰ We also confirmed that POSS units

Figure 5. EDS images of (a) PPM-Benzyl and (b) PPM-POSS.

Figure 6. DSC thermograms of (a) PPM-Benzyl and (b) PPM-POSS with a heating rate of 10 °C min⁻¹ under nitrogen.

were present and dispersed evenly in PPM-POSS by analyzing energy dispersive spectrum (EDS) (Figure 5). The appearance of Si atom's spectrum in EDS image showed that PPM-POSS was hybridized with inorganic multifunctional POSS pendant units.

Figure 6 represents DSC thermograms for PPM-Benzyl and PPM-POSS, respectively. PPM-Benzyl showed the glass transition temperature (T_g) at 100 °C, but PPM-POSS showed no T_g even by running the sample to a sufficiently high temperature to 300 °C. This result suggests that the tethered bulky POSS moieties not only reduce the aggregation of PPM-POSS but also retard the mobility of the polymer main chain.

Figure 7. TGA thermograms of (a) 4-methyl-2,6-dimethoxyphenol, (b) PPM-Benzyl, and (c) PPM-POSS.

Also, it is confirmed that POSS units are homogeneously dispersed in the PPM chains without any aggregation from the DSC data.

The highly enhanced thermal stability of PPM-POSS as compared to that of PPM-Benzyl was confirmed by TGA. The initiation of the weight loss of PPM-POSS was shifted to high temperature as compared to that of PPM-Benzyl (Figure 7). Especially, PPM-POSS showed high thermal stability at high temperature. These results indicate that the extremely high thermal stability of PPM-POSS is derived from the siliceous bulky POSS segments of PPM-POSS.

CONCLUSION

In summary, novel hybrid poly(phenylenemethylene) side-chain-tethered polyhedral oligomeric silsesquioxanes (PPM-POSS) and poly(phenylenemethylene) containing the benzyl groups (PPM-Benzyl) are synthesized, and their structures and thermal properties are characterized. The incorporation of the bulky POSS units into the PPM main chains results in the well-defined nanocomposites with around 100 nm size by reducing the degree of interchain aggregation. The aromatic (π - π) interactions of phenyl groups in PPM-Benzyl make uneven larger aggregates with 1–5 μ m size by increasing the degree of aggregation between the polymer chains. The POSS units incorporated into PPM-POSS are dispersed evenly in the

polymer matrix because of the low degree of aggregation from intermolecular repulsion between bulky POSS groups. The thermal stability of PPM-POSS is much higher than that of PPM-Benzyl due to inorganic POSS units of PPM-POSS.

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