

Supplementary Material for:

The Mechanism of Dielectric Constant Variation of POSS-based Organic-Inorganic Molecular Hybrids

*Chao Zhang,¹ Shanyi Guang,¹ Xiaobo Zhu,¹ Hongyao Xu,^{*1,2} Xiangyang Liu,³ Minhua Jiang²*

¹College of Material Science and Engineering & State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China.

² State Key laboratory of Crystal Materials, Shandong University, Jinan 250100, China.

³Department of Chemistry, National University of Singapore, 117542, Singapore.

Materials

Isobutylstyryl polyhedral oligosilsesquioxane (IBS-POSS-POSS) was purchased from the Hybrid plastic Co. Inc., octavinyl-polyhedral oligomeric silsesquioxane (OV-POSS) was purchased from Aldrich. Acetoxystyrene was purchased from Aldrich, distilled from calcium hydride under reduced pressure, and stored in sealed ampules in a refrigerator. Azobis-(isobutyronitrile) (AIBN) was refined in heated ethanol and kept in a dried box. Spectroscopy-grade THF and 1,4-dioxane were dried over 4 Å molecular sieves and distilled from sodium benzophenone ketyl immediately prior to use. All other solvents were used without further purification.

Preparation of POSS-based Hybrids

The hybrids were prepared using one-step free radical polymerization technique reported by our

group.¹⁻⁴ The typical examples of experimental procedure for PAS-POSS_{pendt} and PAS-POSS_{star} are given below, respectively. For PAS-POSS_{pendt3.14}, 4.568 g of acetoxystyrene (28.2 mmol) and 1.610 g of isobutylstyryl polyhedral oligomeric silsesquioxane (1.8 mmol) monomers in 40 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. For PAS-POSS_{star3.72}, 4.568 g of acetoxystyrene (28.2 mmol) and 1.140 g of octavinyl-polyhedral oligomeric silsesquioxane (1.8 mmol) monomers in 40 mL of dried 1,4-dioxane were polymerized using the AIBN initiator (1 wt % based on monomer) at 70 °C under a nitrogen atmosphere for 8 h. The product then was poured into excessive cyclohexane under vigorously agitation to dissolve the unreacted monomers and precipitate the hybrids. The 15.6 and 50.2 wt % yields of PAS-POSS_{pendt3.14} and PAS-POSS_{star3.72} were obtained through this procedure. The crude product was redissolved in THF to form a homogeneous and transparent solution. This solution was then added dropwisely into cyclohexane. This purification procedure was repeated twice to ensure that the POSS and organic monomers were removed thoroughly. For comparison, the homopoly(acetoxystyrene) (PAS) was prepared by the same polymerization method.

Chemical structure characterization

All the purified polymerization products were determined by the FTIR, ¹H NMR and ²⁹Si NMR spectra, and the satisfactory spectroscopic data corresponding to their expected molecular structures were given.

PAS: White powder. $M_w = 40600$, PDI, 1.41, (GPC, polystyrene). Yield: 67.2%. IR (KBr), ν (cm⁻¹): 1216 (Ar-O), 1763 (C=O), 1490, 910, 848 (C=C of Ar ring), 2940, 2870 (CH-CH₂). ¹H NMR (500

MHz, CDCl_3), δ (TMS, ppm): 1.35 (CH-CH_2), 1.74 (CH-CH_2), 2.24 ($-\text{COCH}_3$), 7.13~6.18 (Ar-H).

PS: White powder. $M_w = 32700$, PDI, 1.83, (GPC, polystyrene). Yield: 46.4%. IR (KBr), ν (cm^{-1}): 699, 753 (Ar-C), 1460, 1500, 1600 ($\text{C}=\text{C}$ of Ar ring), 2940, 2870 (CH-CH_2). ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 1.43 (CH-CH_2), 1.86 (CH-CH_2), 7.26~6.32 (Ar-H).

PMMA: White powder. $M_w = 31100$, PDI, 2.21, (GPC, polystyrene). Yield: 68.6%. IR (KBr), ν (cm^{-1}): 1148 (C-O-C), 1730 (C=O), 2940, 2870 (CH-CH_2). ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 1.54 ($\text{CH}_3\text{COOCH}_3$), 1.83 (C-CH_2), 3.6 (COOCH_3).

PAS-POSS_{pendt0.65}: White powder. $M_w = 30700$, PDI, 1.82, (GPC, polystyrene). Yield: 43.5%. IR (KBr), ν (cm^{-1}): 1210 (Ar-O), 1370 (O-C=O), 1760 (C=O), 1490, 910, 848 ($\text{C}=\text{C}$ of Ar ring), 2940, 2870 (CH-CH_2), 1109 (Si-O-Si). ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 0.62 ($\text{CH}_2\text{-CH}(\text{CH}_3)_2$), 0.94 ($-\text{CH}_2\text{-CH}(\text{CH}_3)_2$), 1.35 (CH-CH_2), 1.74 (CH-CH_2), 2.24 ($-\text{COCH}_3$), 7.13~6.18 (Ar-H). ^{29}Si NMR (79.49 MHz; solid), δ (ppm): -68 (Si-C), -80 (Si-Ar).

PAS-POSS_{pendt1.36}: White powder. $M_w = 26600$, PDI, 1.69, (GPC, polystyrene). Yield: 21.1%. IR (KBr), ν (cm^{-1}): 1210 (Ar-O), 1370 (O-C=O), 1760 (C=O), 1490, 910, 848 ($\text{C}=\text{C}$ of Ar ring), 2940, 2870 (CH-CH_2), 1109 (Si-O-Si). ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 0.62 ($\text{CH}_2\text{-CH}(\text{CH}_3)_2$), 0.94 ($-\text{CH}_2\text{-CH}(\text{CH}_3)_2$), 1.35 (CH-CH_2), 1.74 (CH-CH_2), 2.24 ($-\text{COCH}_3$), 7.13~6.18 (Ar-H). ^{29}Si NMR (79.49 MHz; solid), δ (ppm): -68 (Si-C), -80 (Si-Ar).

PAS-POSS_{pendt1.62}: White powder. $M_w = 23800$, PDI, 1.78, (GPC, polystyrene). Yield: 19.4%. IR (KBr), ν (cm^{-1}): 1210 (Ar-O), 1370 (O-C=O), 1760 (C=O), 1490, 910, 848 ($\text{C}=\text{C}$ of Ar ring), 2940, 2870 (CH-CH_2), 1109 (Si-O-Si). ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 0.62 ($\text{CH}_2\text{-CH}(\text{CH}_3)_2$), 0.94 ($-\text{CH}_2\text{-CH}(\text{CH}_3)_2$), 1.35 (CH-CH_2), 1.74 (CH-CH_2), 2.24 ($-\text{COCH}_3$), 7.13~6.18 (Ar-H). ^{29}Si NMR (79.49 MHz; solid), δ (ppm): -68 (Si-C), -80 (Si-Ar).

PAS-POSS_{pendt3.14}: White powder. $M_w = 18700$, PDI, 1.53, (GPC, polystyrene). Yield: 15.6%. IR (KBr), ν (cm^{-1}): 1210 (Ar-O), 1370 (O-C=O), 1760 (C=O), 1490, 910, 848 (C=C of Ar ring), 2940, 2870 (CH-CH₂), 1109 (Si-O-Si). ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 0.62 (CH₂-CH(CH₃)₂), 0.94 (-CH₂-CH-(CH₃)₂), 1.35 (CH-CH₂), 1.74 (CH-CH₂), 2.24 (-COCH₃), 7.13~6.18 (Ar-H). ²⁹Si NMR (79.49 MHz; solid), δ (ppm): -68 (Si-C), -80 (Si-Ar).

PAS-POSS_{star0.36}: White powder. $M_w = 43600$, PDI, 1.76, (GPC, polystyrene). Yield: 62.7%. IR (KBr), ν (cm^{-1}): 1216 (Ar-O), 1760 (C=O), 1460, 1500, 1600 (Ar), 2940, 2870 (CH-CH₂), 1109 (Si-O-Si). ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 1.38 (CH-CH₂), 1.77 (CH-CH₂), 2.25 (-COCH₃), 5.71~6.20 (Si-CH=CH₂), 7.01~6.32 (Ar-H). ²⁹Si NMR (79.49 MHz; solid), δ (ppm): -66 (Si-CHCH₂), -79 (Si-CH=CH₂).

PAS-POSS_{star1.37}: White powder. $M_w = 37500$, PDI, 1.64, (GPC, polystyrene). Yield: 58.3%. IR (KBr), ν (cm^{-1}): 1216 (Ar-O), 1760 (C=O), 1460, 1500, 1600 (Ar), 2940, 2870 (CH-CH₂), 1109 (Si-O-Si). ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 1.38 (CH-CH₂), 1.77 (CH-CH₂), 2.25 (-COCH₃), 5.71~6.20 (Si-CH=CH₂), 7.01~6.32 (Ar-H). ²⁹Si NMR (79.49 MHz; solid), δ (ppm): -66 (Si-CHCH₂), -79 (Si-CH=CH₂).

PAS-POSS_{star2.06}: White powder. $M_w = 33800$, PDI, 1.83, (GPC, polystyrene). Yield: 54.2%. IR (KBr), ν (cm^{-1}): 1216 (Ar-O), 1760 (C=O), 1460, 1500, 1600 (Ar), 2940, 2870 (CH-CH₂), 1109 (Si-O-Si). ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 1.38 (CH-CH₂), 1.77 (CH-CH₂), 2.25 (-COCH₃), 5.71~6.20 (Si-CH=CH₂), 7.01~6.32 (br, Ar-H). ²⁹Si NMR (79.49 MHz; solid), δ (ppm): -66 (Si-CHCH₂), -79 (Si-CH=CH₂).

PAS-POSS_{star3.72}: White powder. $M_w = 24700$, PDI, 1.65, (GPC, polystyrene). Yield: 50.2%. IR (KBr), ν (cm^{-1}): 1216 (Ar-O), 1760 (C=O), 1460, 1500, 1600 (Ar), 2940, 2870 (CH-CH₂), 1109 (Si-O-Si). ¹H

NMR (500 MHz, CDCl_3), δ (TMS, ppm): 1.38 (CH-CH_2), 1.77 (CH-CH_2), 2.25 ($-\text{COCH}_3$), 5.71~6.20 (Si-CH=CH_2), 7.01~6.32(Ar-H). ^{29}Si NMR (79.49 MHz; solid), δ (ppm): -66 (Si-CHCH_2), -79 (Si-CH=CH_2).

PS-POSS_{1.35}: $M_w = 28900$, PDI, 1.57, (GPC, polystyrene). Yield: 39.6%. IR (KBr), ν (cm^{-1}): 699,753 (Ar-C), 1109 (Si-O-Si), 1460,1500,1600 (C=C of Ar ring), 2940, 2870 (CH-CH_2). ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 1.43 (CH-CH_2), 1.86 (CH-CH_2), ~6 (Si-CH=CH_2), 7.26~6.32 (Ar-H). ^{29}Si NMR (79.49 MHz; solid), δ (ppm): -65.5 (s, Si-CHCH_2), -79.8 (s, Si-CH=CH_2).

PMMA-POSS_{1.36}: White powder. $M_w = 29300$, PDI, 1.72, (GPC, polystyrene). Yield: 53.1%. IR (KBr), ν (cm^{-1}): 1109 (Si-O-Si), 1148 (C-O-C), 1730 (C=O), 2940, 2870 (CH-CH_2). ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 0.83 (Si-CHCH_2), 1.01(Si-CHCH_2), 1.54 ($\text{CH}_3\text{COOCH}_3$), 1.83 (C-CH_2), 3.6 (COOCH_3), ~6 (Si-CH=CH_2). ^{29}Si NMR (79.49 MHz; solid), δ (ppm): -65.3 (s, Si-CHCH_2), -79.2 (s, Si-CH=CH_2).

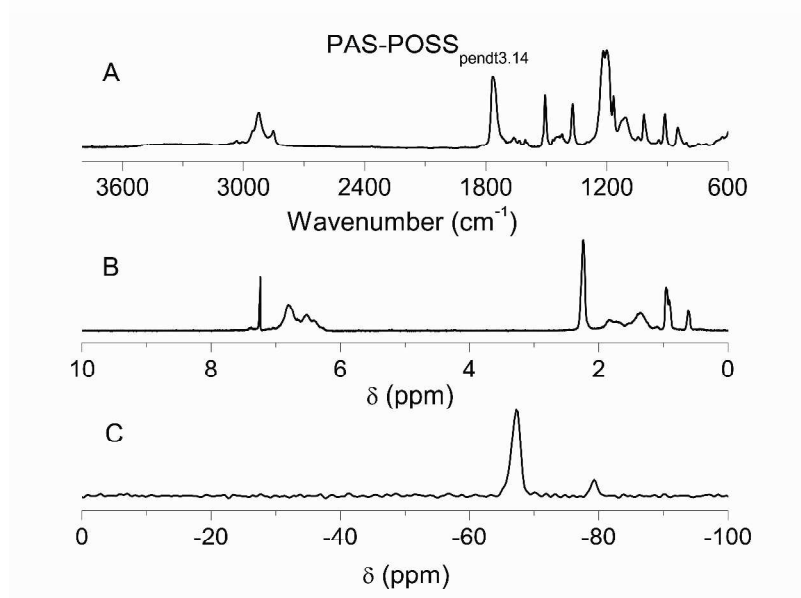


Figure 1. (A) FTIR, (B) ^1H NMR and (C) ^{29}Si NMR spectra of PAS-POSS_{pendt3.14} hybrids

Pendent-type inorganic-organic hybrid nanocomposites. All the FTIR spectra of PAS-POSS_{pendt}

show two characteristic absorptions of carbonyl stretching vibration and strong Ph-O stretching vibration absorption (1763 and 1216 cm^{-1}) as seen in Fig. 1, and a strong absorption peak centered at 1109 cm^{-1} from the siloxane stretching vibration, revealing that the isobutylstyryl-POSS moiety is incorporated into PAS molecular chains. Simultaneously, their ^1H NMR spectra exhibit proton resonance peaks at $\delta 7.13\sim 6.18$, 2.24 , 1.74 , 1.35 , 0.94 , and 0.62 ppm, including the resonance peaks of the isobutyl group (0.94 ppm, $-\text{CH}_2-\text{CH}-(\text{CH}_3)_2$; 0.62 ppm, $\text{CH}_2-\text{CH}(\text{CH}_3)_2$) and the carbonyl substituted methyl proton peak (2.24 ppm, $-\text{COCH}_3$), further confirming that isobutylstyryl-POSS was incorporated into the PAS. Otherwise, their ^{29}Si NMR spectra display two characteristic silica resonance bands at -67.8 and -80.0 ppm, corresponding to the substitution of silica in the POSS core by isobutyl and styryl group, respectively, providing additional evidences that the POSS moiety is attached to the PAS.

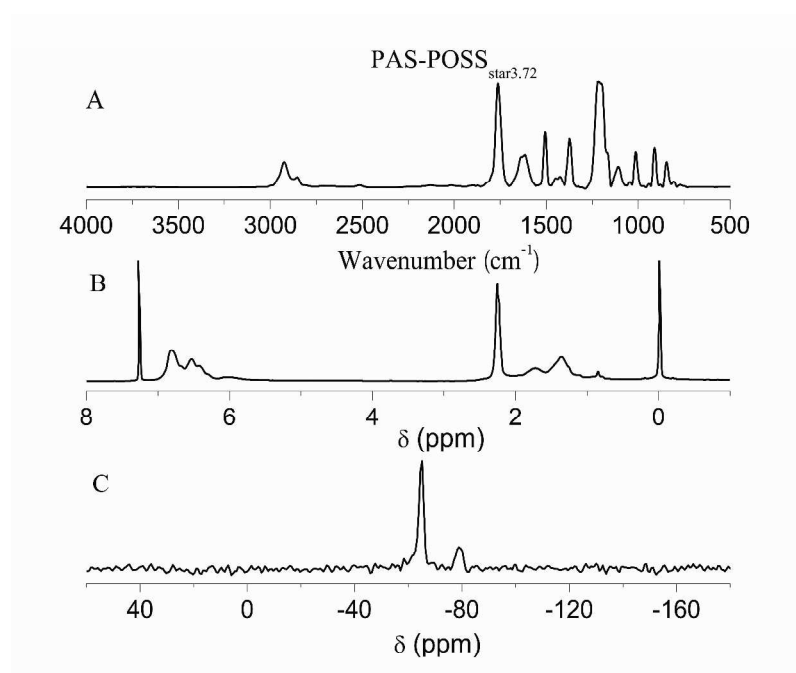


Figure 2. (A) FTIR, (B) ^1H NMR and (C) ^{29}Si NMR spectra of PAS-POSS_{star3.72} hybrids.

Star-type inorganic-organic hybrid nanocomposites. All the FTIR spectra of PAS-POSS_{star} show two characteristic absorptions of carbonyl stretching vibration and strong Ph-O stretching vibration absorption (1760 and 1216 cm^{-1}) and a strong symmetric absorption peak of the characteristic Si-O-Si

stretching of silsesquioxane cages (1109 cm^{-1}) (Fig. 2), indicating that the POSS cages are incorporated into the polymeric chains. The ^1H NMR spectra exhibit resonance peaks from 0.7 to 2.0 ppm of methine and methylene protons from the reacted vinyl groups of POSS and PAS backbones. Besides, there is a wide resonance band at nearby 6.0 ppm belonging to the unreacted vinyl protons of POSS molecules, indicating that not all the vinyl groups of POSS have participated in the copolymerization. Their ^{29}Si NMR spectra shows two resonance bands of the silicon atoms connected to the reacted and unreacted vinyl groups on the POSS cages at -66 and -79 ppm, respectively. The peak area at -66 ppm is much bigger than that at -79 ppm, indicating most vinyl groups of each POSS molecule have participated in the copolymerization to form hybrids. By calculating the peak area ratio, an average 5.3~7.6 of vinyl groups per POSS molecule have been copolymerized with acetoxystyrene, proving that the resultant hybrid is not linear molecules. In order to determine the structure of these hybrids, we also test its solubility in various solvents such as THF, CHCl_3 , dioxane, toluene, and so on. It is found that the hybrid can dissolve in almost all above common solvents, demonstrating that the resultant hybrids are mainly star-type rather than network structure since network hybrids are virtually insoluble in any solvent.

References

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