

## Nanostructures from POSS-Grafted Block Copolymer Precursors

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### ABSTRACT

A new method to prepare novel nanocomposites has been studied in which a polyhedral oligomeric silsesquioxane (POSS) monomer is grafted to a polyisoprene-*block*-polystyrene copolymer to yield an inorganic-organic hybrid copolymer (POSS-*g*-PI-*block*-PS). PS-*block*-PI copolymers (SI) were synthesized via anionic polymerization in tetrahydrofuran (THF) as solvent. The polyisoprene block of the SI diblock copolymers in this study featured a very high vinyl group fraction (65 mole % of 3,4-addition and 35 mole % of 1,2-addition) available to react with hydride-substituted POSS (isobutyldimethyl silane-POSS) to form a grafted block copolymer. Due to the immiscibility between POSS-grafted PI block and PS block, the grafted block copolymer developed a microdomain structure. The volume fraction of PS block in the grafted block copolymer was varied in the range of 0.45 to 0.37 in order to yield cylindrical PS microdomains in the matrix of POSS-grafted PI. After exposure to an oxygen plasma, it is expected that preferential erosion of the grafted block copolymer will occur for the organic portion (PS microdomains) thus leaving a well-defined nanoporous surface structure for nonlithographic functionalization of coated substrates.

### INTRODUCTION

Block copolymers consist of two or more different polymer blocks that are covalently bonded. Immiscibility between blocks gives rise to microphase separation where the microdomains have the dimension on the scale 10-100 nm. The shape of microdomains that form depends upon the volume fraction and the Flory-Huggins interaction parameter ( $\chi$ ) whereas their size is a function of the molecular weight of each block. Very recently, several reports have appeared that focus on surface patterning using block copolymer self-assembly behavior. [1-3] For example, polystyrene-*b*-polyethylene (SE) diblock copolymers and polypropylene-*b*-polyethylene-*b*-polypropylene (PEP) triblock copolymers were utilized to form a well-ordered surface pattern on a benzoic acid surface. [1,2] Also, polystyrene-*b*-polymethylmethacrylate (PS-*b*-PMMA) diblock copolymers have been ordered on self-assembled monolayers surfaces exposed to an intense and patterned x-ray flux. [3] Our present goal is to obtain organic/inorganic hybrid block copolymers and to prepare thin coatings that have well-ordered surface patterns. Such surface-patterned thin films will enable numerous practical applications after selective oxygen plasma etching of organic microdomains or matrix, especially patterned sensors from silicon substrates.

Previously we have studied nanostructures formed from polyhedral oligomeric silsesquioxane polynorbornene (POSS-PN) block copolymers as another example of a hybrid organic/inorganic block copolymer.[4] In particular, POSS-polynorbornene-*b*-

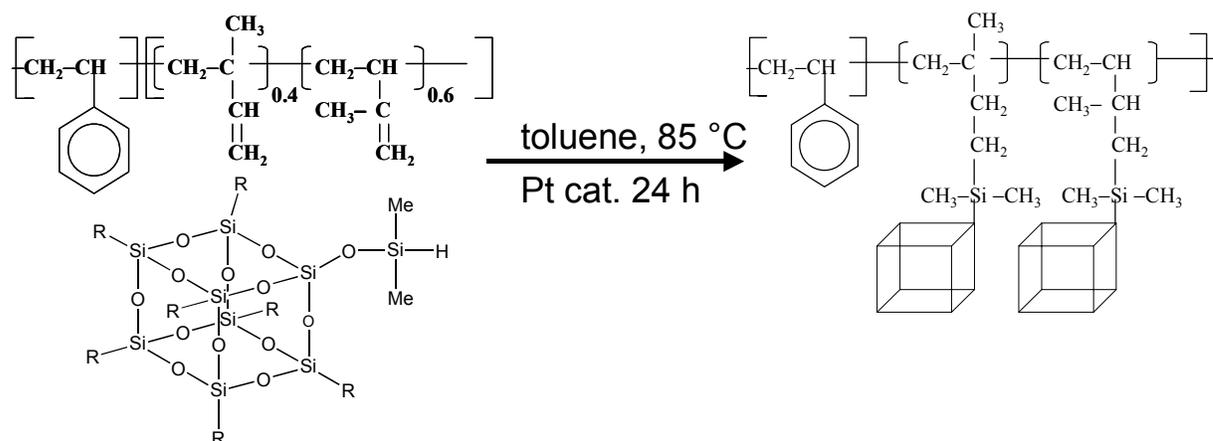
polynorbornene (POSS-PN-*b*-PN) block copolymers were synthesized via ring opening metathesis polymerization (ROMP) of a novel norbornenyl-POSS monomer. It was found that the nanostructures were very sensitive to monomer composition; however, it was not easy to prevent the formation of PN homopolymer during ROM polymerization which caused broad molecular weight distribution and complex morphologies. In the present study, we have used a different method to obtain hybrid organic/inorganic block copolymers by synthesizing styrene-*b*-isoprene block copolymer precursors with a narrow molecular weight distribution (via anionic polymerization) and then grafting a POSS-silane monomer to the isoprene block via hydrosilation reaction. We note that a similar approach to hybrid diblocks has been reported previously in which a different silane was employed.[5]

## EXPERIMENTAL

Polystyrene-*b*-polyisoprene (SI) block copolymer was synthesized via anionic polymerization. In order to yield PI-blocks with a high pendant vinyl group fraction, tetrahydrofuran (THF) was used as a solvent. At first, purified styrene monomer in THF was polymerized in a round bottom flask under vacuum using *sec*-butyl lithium as an initiator. During the polymerization the reaction solution featured a red color. After completion of PS polymerization, purified isoprene monomer was vacuum-transferred to the flask. Then, the color of the reaction solution changed from red to yellow. Dry methanol was injected into the flask to terminate the polymerization and the block copolymer was precipitated in an excess of methanol. This product was dried in a vacuum oven at 50 °C for 24 h. From gel permeation chromatography (GPC) analysis, the diblock copolymer featured a weight average molecular weight,  $\overline{M}_w$ , (relative to polystyrene standards) of 47300 g/mol and polydispersity index of 1.09.

POSS-grafted PS-*b*-PI copolymer was synthesized via hydrosilation reaction between dimethyl silane-POSS and PI block in SI diblock copolymer [5]. A schematic of the grafting reaction is shown in Scheme 1. Isobutyldimethyl silane-POSS (SH1305) was supplied by Hybrid Plastics and used as received. In order to determine the optimum reaction conditions, model hydrosilation reactions were carried out in which SH1305 was reacted with 1-heptene in dry toluene using platinum divinyltetramethyldisiloxane complex as a catalyst under various conditions of time and temperature, with  $T = 85$  °C for 24 h ultimately being found to be the optimum conditions. From  $^1\text{H-NMR}$ , in this case, it was observed that the silane proton peak of SH1305 at ca. 4.7 ppm disappeared, while several heptyl group proton peaks appeared between 0.5 and 1.3 ppm after hydrosilation reaction. Similarly, SH1305 the as-synthesized SI diblock copolymer were reacted under the same conditions as the optimized model hydrosilation. In this case, we monitored the hydrosilation reaction using FT-IR, with a small amount of reactant being extracted from the reactor after selected times had transpired. The POSS-grafted SI block copolymer was precipitated in methanol twice. From GPC, the POSS-grafted diblock copolymer was shown to have  $\overline{M}_w = 57400$  g/mol and to have a polydispersity index of 1.35.

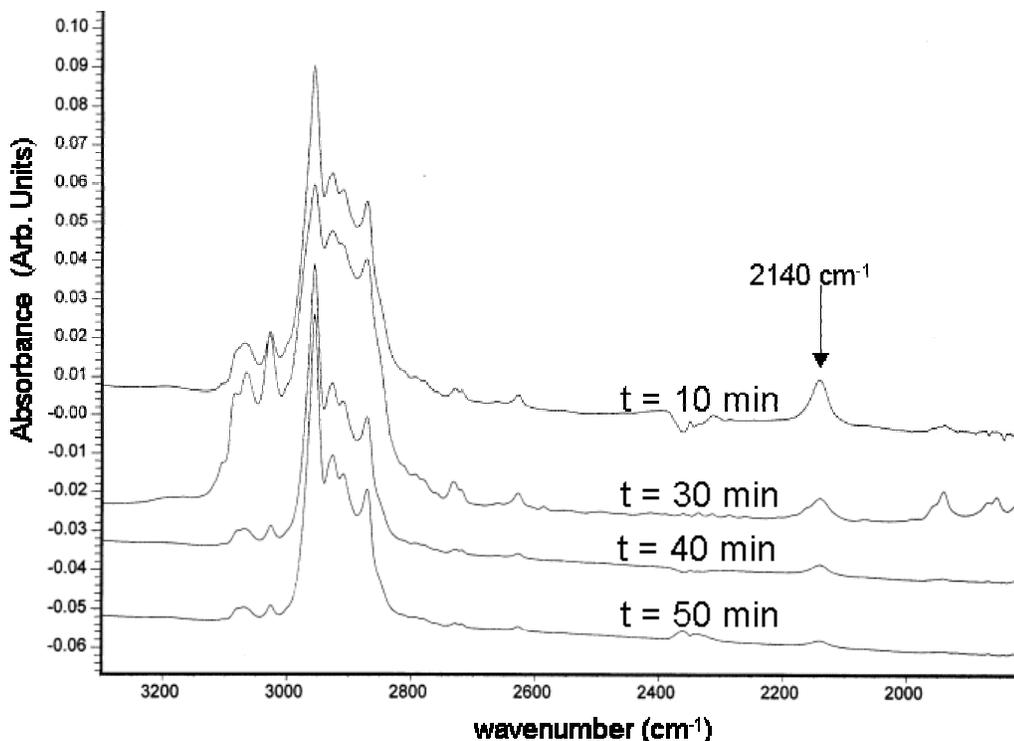
The weight-averaged molecular weight ( $\overline{M}_w$ ) and polydispersity index (PDI) were measured using gel permeation chromatography (GPC) using THF as a mobile phase and PS standards.  $^1\text{H-NMR}$  spectra, from  $\text{CDCl}_3$  solution, were obtained using the Bruker DMX-500. Glass transition temperature ( $T_g$ ) was measured with TA Instruments differential scanning calorimeter (DSC) at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ .



**Scheme 1.** Grafting of POSS-silane to polystyrene-*block*-polyisoprene copolymer. See text for details.

## RESULTS

**Reaction Monitoring:** For model hydrosilation reaction of SH1305 with 1-heptene,  $^1\text{H-NMR}$  was a good tool for monitoring the reaction since one can focus on Si-H peak at ca. 4.7 ppm after evaporative removal of the solvent, toluene, and any unreacted 1-heptene. However, in the case of the grafting reaction of SH1305 onto the SI diblock copolymer,  $^1\text{H-NMR}$  cannot easily reveal the silane proton (ca. 4.7 ppm) from the adjacent unreacted vinyl protons of the PI block (4.5 to 5 ppm). Thus, in order to monitor the hydrosilation reaction of SH1305 with SI block copolymer, FT-IR was used. In this case, one or two drops of the reactant sample was extracted from the reactor using a syringe and needle during hydrosilation reaction, placed on KBr plate, and dried to form a film on it. Figure 1 shows a time sequence of FT-IR spectra thus collected for different stages of the hydrosilation grafting reaction. It can be clearly seen that the silane (Si-H) peak is located at wavenumber  $2140\text{ cm}^{-1}$ . From Figure 1 and additional, longer time data, we can conclude that the hydrosilation grafting of the POSS-silane to PI block proceeds within 1 h.



**Figure 1.** Hydrosilation reaction monitoring using FT-IR spectra of (POSS-g-PI)-*b*-PS block copolymer.

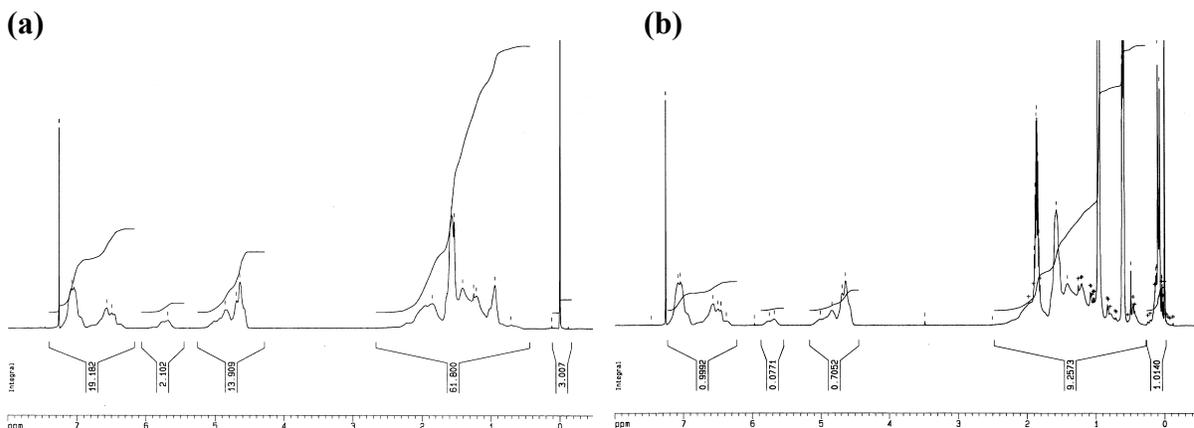
Polymer Characterization: Figure 2(a) shows  $^1\text{H-NMR}$  spectrum of PS-*b*-PI block copolymer. Due to the use of THF as the reaction solvent, we observe that the PI block has a very high vinyl group fraction. Based on Figure 2(a), in particular, one can conclude that PI block has 40 mole % of 1,2 addition and 60 mole % of 3,4-addition, and that the PS-*b*-PI block copolymer has 35 mole % of PS block and 65 mole % of PI block. The block copolymer thus has volume fraction of PI block equaling 0.55. Though it is difficult to predict without morphological evidence whether or not the block copolymer is microphase-separated, we hypothesize that this block copolymer has a lamellar structure because of the volume fraction, molecular weight, and immiscibility between PS and PI blocks which can be expressed by the Flory-Huggins interaction parameter,  $\alpha$ , which has the unit of mole/cm<sup>3</sup> [6], that is,

$$\alpha_{\text{PS/PI}} = -0.3188 \times 10^{-2} + 1.6585/T - 0.02018\phi_{\text{PS/PI}}/T. \quad (1)$$

We are presently conducting transmission electron microscopy (TEM) observations to test this hypothesis.

Figure 2(b) shows the  $^1\text{H-NMR}$  spectrum of (POSS-*graft*-PI)-*block*-PS block copolymer. Compared to Figure 2(a), it is observed that the area of vinyl proton peaks is slightly reduced and that several new peaks have appeared in the range of 0 to 2 ppm, representative of the isobutyl and methyl group protons in POSS. Based on the area ratio of phenyl proton to vinyl proton, one can estimate that 6 mole % of vinyl groups participated in the hydrosilation reaction. Combining the previously cited GPC data with

this  $^1\text{H-NMR}$  analysis, it is concluded that the volume fraction of PS block is reduced from 0.45 to 0.37 after hydrosilation reaction. The expected morphology of (POSS-*g*-PI)-*b*-PS is thus PS cylindrical microdomains in the matrix of POSS-*g*-PI block. Again, we are testing this expectation presently using TEM.



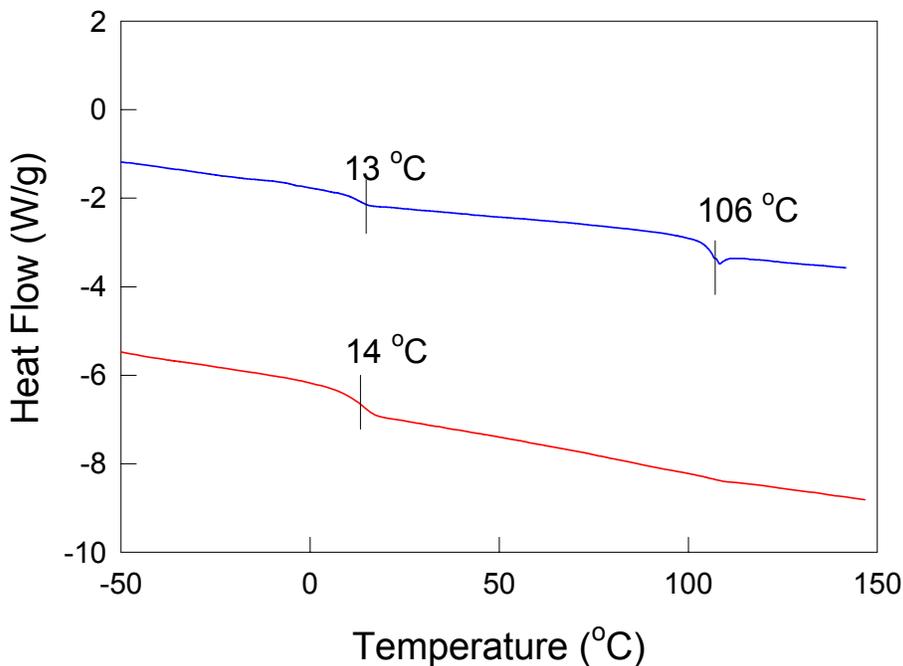
**Figure 2.** (a)  $^1\text{H-NMR}$  spectra of PS-*block*-PI diblock copolymer, and (b) (POSS-*graft*-PI)-*block*-PS diblock copolymer.

Figure 3 shows the thermal behavior of PS-*b*-PI (top) and (POSS-*g*-PI)-*b*-PS (bottom) block copolymers as detected using DSC. We observe that the PS-*b*-PI features two glass transitions,  $T_g$ 's, that appear at  $T = 13\text{ }^\circ\text{C}$  (attributed to the PI block) and at  $T = 106\text{ }^\circ\text{C}$  (attributed to the PS block). This observations substantiates our hypothesis that this block copolymer is microphased separated. We note that it is well known that the  $T_g$  of “high vinyl” PI is much higher than that of 1,4-PI (ca.  $-70\text{ }^\circ\text{C}$ ). It is quite surprising, though very reproducible, that the (POSS-*g*-PI)-*b*-PS block copolymer show only one  $T_g$  at  $14\text{ }^\circ\text{C}$  (lower trace) and that the  $T_g$  of the PS block could not detected below  $T = 150\text{ }^\circ\text{C}$ .

## CONCLUSIONS

A new route to develop nanostructured materials using organic/inorganic hybrid block copolymer was introduced. PS-*b*-PI diblock copolymers were synthesized via anionic polymerization and (POSS-*g*-PI)-*b*-PS block copolymers were subsequently prepared via hydrosilation reaction. It was observed that hydrosilation reaction of POSS silane with vinyl groups of PI block proceeds within 1 h. From  $^1\text{H-NMR}$ , we measured the grafting efficiency to be relatively low. In particular, 6 mole % of vinyl groups of PI block were found to react with the POSS silane. The thermal properties of PS-*b*-PI and (POSS-*g*-PI)-*b*-PS block copolymers were compared using DSC. For future studies, the morphology of the two block copolymers will be observed via transmission electron

microscopy (TEM) and surface patterning of our novel polymer thin films will be pursued by following examples from the Thomas [1,2] and Nealey [3] groups.



**Figure 3.** DSC traces for PS-*b*-PI diblock copolymer (top) and (POSS-*g*-PI)-*b*-PS diblock copolymer (bottom).

#### ACKNOWLEDGEMENTS

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