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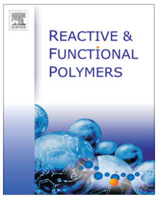

# Synthesis of high performance organic–inorganic composite via click coupling of block polymer and polyhedral oligomeric silsesquioxane[☆]

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## ABSTRACT

Novel hybrid systems based on poly(styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) and a polyhedral oligomeric silsesquioxane (POSS) have been synthesized via click chemistry. Different compositions of SEBS-functionalized POSS were obtained from the reaction of azide-functionalized styrene units of SEBS with alkyne-functionalized POSS molecules. Characterization of SEBS-functionalized POSS by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and nuclear magnetic resonance spectroscopy revealed that the POSS molecules were successfully attached to the phenyl group of the SEBS polymer chain following the click reaction. Homogeneous dispersion of POSS molecules in the polymer matrix was demonstrated by scanning electron microscopy. The POSS molecule showed excellent compatibility with polymer matrix, and as a consequence the remarkable enhancement of mechanical properties (breaking stress = 44%, modulus = 285%) and thermal stability for the resulting composite films was achieved. The reinforcing effect is ascribed to both the compatible homogeneous dispersion of POSS in the matrix and the covalent bond between SEBS and POSS molecules arising from the click coupling.

## 1. Introduction

Organic–inorganic hybrid materials have attracted immense interest with regard to their novelty and consequent potential applications [1,2]. These hybrid materials can be broadly described as multi-component systems where organic and inorganic components are combined to form a new nanomaterial exhibiting unique properties [3,4]. One crucial category of such hybrids involves silica or silsesquioxane as the inorganic component.

Polyhedral oligomeric silsesquioxane (POSS) is a type of inorganic three-dimensional nanostructured Si–O cage (formula $[RSiO_{1.5}]_n$, where $n = 8$, 10 and 12) with an overall diameter of 1–3 nm [5,6]. Incorporation of POSS into an organic–inorganic hybrid confers desirable properties upon the hybrid material, such as low flammability, oxidation resistance, lower density, increased mechanical, and thermal properties, and increased hardness [7,8]. The preparation of polymer–POSS systems, which has obvious economic appeal for the industrial development of POSS technology, has been explored using various techniques such as melt blending. Zhao et al. [9] reported differences in polymer–POSS compatibility, depending on the specific structure and substituents of the POSS. These results indicated that achieving a dispersion of POSS in organic polymers is not a straightforward process, and that the control of chemical and physical interactions between the organic matrix and nanofiller is crucial. POSS molecule contains Si–O cores which have the special cage structure and a good solubility; surrounded with tunable organic groups, which makes them an obvious choice for further functionalization to develop the nanohybrid material [10,11]. The POSS unit can be covalently incorporated into large molecules, by introducing one or more chemically reactive groups onto specific corners of the cage structure of Si–O cores, to provide sites for further chemical functionalization [12]. Previous researchers have outlined preparation methods and properties of POSS-containing hybrid polymers [13,14]. Strategies for the synthesis of covalently bonded POSS–polymer hybrids include, for example, the atom transfer radical polymerization method, which has been used to prepare hybrid polymers of varying topology such as star-shaped, block, and tadpole-shaped [15–17].

Polystyrene-block-poly(ethylene-co-1-butene)-block-polystyrene (SEBS), one of the earliest industrial and commercial thermoplastic

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elastomers, provides a remarkably broad platform for the development of multifunctional materials [18,19]. Modification of the PS block in SEBS block copolymers has received much attention as our requirement [20,21]. Considering the high reactivity of the phenyl ring of the PS block, the covalent functionalization of phenyl ring of the SEBS with POSS is an area of future research. The concept of "click chemistry," or the Cu (I)-catalyzed [3 + 2] Huisgen cycloaddition reaction of azides and alkynes, has emerged over the past few years as a promising synthesis approach from organic synthesis to materials chemistry [22,23]. POSS moieties have previously been used to modify polystyrene-block-polybutadiene-block-polystyrene triblock copolymers, whereupon the bulk morphology of the block copolymer was preserved [24].

The present study demonstrates the synthesis and characterization of the click-coupled POSS–SEBS hybrid material, which exhibits enhanced mechanical properties and thermal stability.

**Table 1**
Sample formulations of the hybrids.

| Run | $SnCl_4$ equivalent | Time (h) | Cl content (mol%) |
|---|---|---|---|
| SEBS–POSS-1 | 1.20 | 6 | 3.6 |
| SEBS–POSS-2 | 1.53 | 6 | 4.2 |
| SEBS–POSS-3 | 3.07 | 6 | 6.8 |
| SEBS–POSS-4 | 3.50 | 6 | 8.9 |

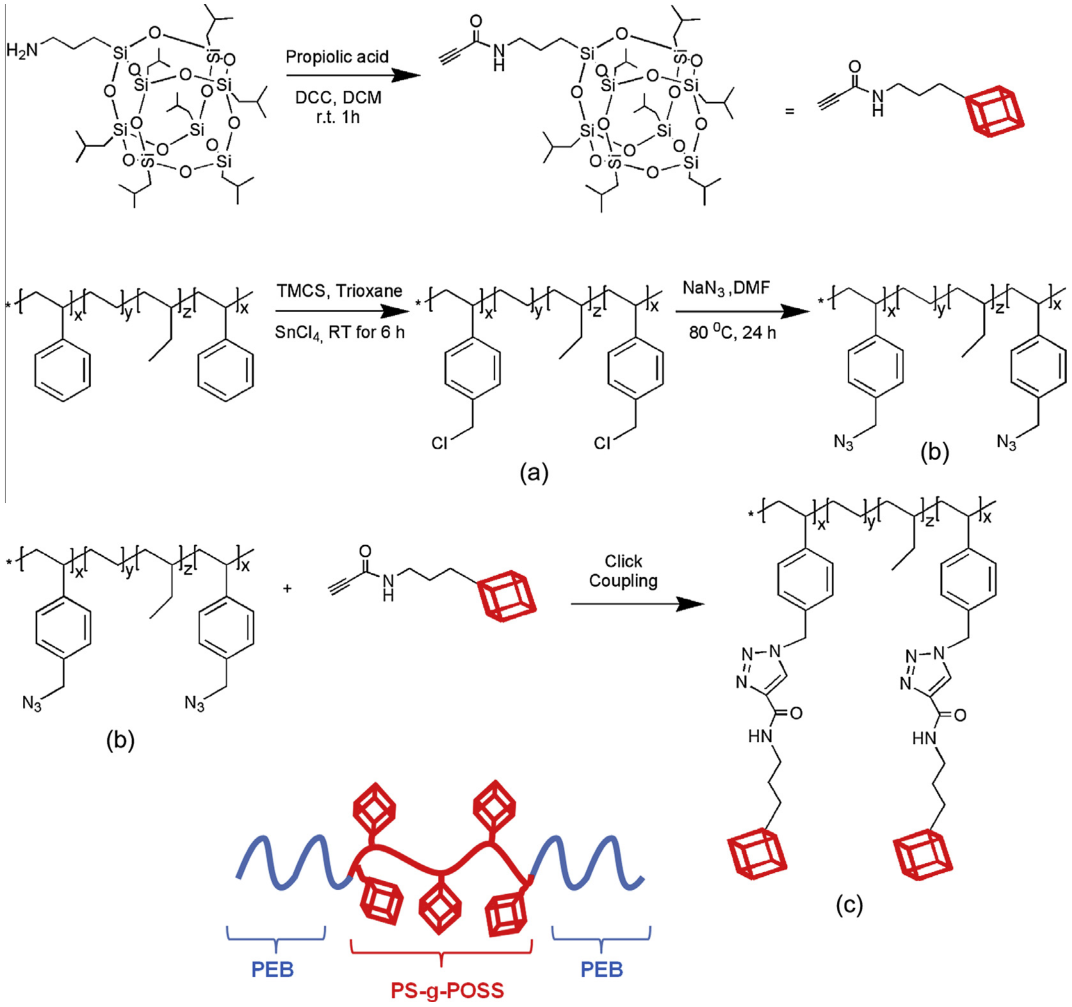
## 2. Experimental

### 2.1. Materials and reagents

SEBS block copolymer with 30 wt% polystyrene was provided by Kraton Polymers. Its polydispersity index and number average molecular weight (measured using gel permeation chromatography) were 1.2 and 68,000 g/mol, respectively. Aminopropylisobutyl POSS (AM0265) was purchased from Hybrid Plastic Co., and 1,3,5-trioxane (trioxane), chlorotrimethylsilane, tin (IV) chloride, propiolic acid, N,N′-dicyclohexylcarbodiimide (DCC), propargyl bromide, *p*-nitrophenol, tetrabutylammonium bromide, 3-methyl butyl nitrite, copper iodide, and 1,8-diazabicyclo[5,4,0]undecene-7-ene (DBU) were purchased from Sigma Aldrich; all were used as received.

### 2.2. Synthesis of azide-modified SEBS (SEBS–$CH_2N_3$)

SEBS–$CH_2N_3$ was synthesized by chloromethylation of SEBS and subsequent azidation of chloromethylated SEBS (SEBS–$CH_2$Cl), as reported elsewhere [25]. SEBS (7.5 g) and trioxane (8.1 g, 90 mmol) were dissolved with 375 mL of chloroform in a round-bottom flask, yielding a clear solution. The system was cooled to 0 °C, whereupon chlorotrimethysilane (34.2 mL and 270 mmol) and tin (IV) chloride (4.5 mL and 38.7 mmol) were added to the mixture.



**Scheme 1.** Alkylation of POSS (a), chloromethylation and azidation of SEBS (b), and click coupling between POSS-alkyne and SEBS–$N_3$ (c).