

PREPARING ORGANIC-INORGANIC NANOCOMPOSITE VIA SELECTIVE DISPERSION OF PS-TETHERED SiO₂ PARTICLES IN POLYSTYRENE-BLOCK-POLYMETHYLMETHACRYLATE COPOLYMER

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Introduction

Block copolymers are known for their microdomain separation which attains various periodic nanostructures under proper compositions and conditions.¹⁻⁸ In recent years, nanotemplating studies involving the block copolymers have gained extensive interest. Nanowires such as Co, Ag, and Au or nanoparticles such as CdSe, Pd and TiO₂ have been reported either to grow in or to be blended into a specific microdomain.⁹⁻¹¹ The selective dispersion of nanoparticles in one of the microdomains has great potential in applications such as photonic crystals with enhanced refractive index contrast between microdomains,⁹⁻¹¹ and nanoporous hybrid membranes after etching one of the microdomains. The growth of nanoparticles in one of the microdomains of a diblock copolymer often requires the functionalization of that specific microdomain with precursor complexes followed by an in-situ reduction of that precursor complexes to form nanoparticles. On the other hand, the blending of nanoparticles into one of the microdomains requires the pretreatment of nanoparticles with various surfactants, such as ionic or nonionic types, or functioning agents containing functional groups compatible with the targeted microdomain.

Under proper conditions, homopolymer hA could be solubilized in the A block either locally or uniformly. These studies have prompted us to explore another approach to selectively disperse SiO₂ nanoparticles in a PS-*b*-PMMA diblock copolymer. Here in the current study, we have synthesized two PS-*b*-PMMA diblock copolymers with different ratios of PS to PMMA block lengths, having either an alternating lamellar layers or cylindrical microstructures, as well as a trimethoxysilane-terminated homopolystyrene (PS-silane). This PS-silane was thereafter tethered to SiO₂ nanoparticles to form PS-SiO₂ particles, and these PS-SiO₂ particles were then blended quantitatively with PS-*b*-PMMA to make an organic-inorganic nanocomposite material with a targeted PS/PMMA volume ratios. The nanosize and the uniform distribution of the PS microdomain in the PS-*b*-PMMA polymer thus enabled an uniform distribution of the inorganic SiO₂ particles in the organic polymeric matrix

Experimental

Materials

Styrene and methyl methacrylate (both with a purity of 99%) were acquired from Aldrich and predistilled with CaH₂ to remove the inhibitor before use. *n*-Butyllithium was obtained from Taiwan Synthetic Rubber Corp. 1,1-diphenylethylene purchased from Alfa Aesar had a purity of 98% and was diluted in toluene at a concentration of 0.6M before use. (3-Chloropropyl)trimethoxysilane was acquired from Aldrich at 97% purity. Colloidal nano-sized silica of a diameter of 10~20 nm was supplied by Echo Nano-bio Co., Ltd., Taiwan as a clear suspension in isopropanol with a solid content of 30%.

Measurements

The molecular structures of PS-*b*-PMMA samples were determined from ¹HNMR (Varian-Unity INOVA-500 MHz) spectra of samples in CDCl₃ at 30 °C. The functional groups of samples were analyzed with a Shimadzu SSU-8000 FTIR spectrophotometer. Scanning electron microscope (SEM) images were obtained on a Hitachi S4800 Type I SEM system for sample deposited onto a TEM grid (copper, 3.0 mm, 200 mesh, and coated with a Formvar film). The atomic force microscope (AFM) height-mode micrographs were obtained from the Quesant Universal SPM Instruments, using as the AFM tip a silicon nitride-based cantilever coated with a magnetic film.

Synthesis and Characterization of PS-*b*-PMMA

The synthesis of PS-*b*-PMMA was accomplished via a sequential anionic polymerization in toluene. The choice of toluene as the solvent was due to the need of a polar environment for the polymerization of MMA.

Synthesis and Characterization of PS-silane

Functionalization of SiO₂ by anchoring PS-silane onto nano silica via the sol-gel reaction to (making PS-SiO₂)

In this work, a total of 0.5 g of PS-silane was dissolved in 15 g of DCB followed by the addition of 10 g of isopropanol and 0.09 g of 30wt% SiO₂ in IPA solution. The mixture was agitated at 75°C for 3 mins and then 2 g of 0.1M HCl was added. The sol-gel reaction was allowed to take place for 2 hrs before the PS-SiO₂ was precipitated out in methanol.

Blending of PS-*b*-PMMA with PS-SiO₂ to make a hybrid film

Results and Discussion

Two PS-*b*-PMMA samples have been synthesized in this work and their molecular specs have been determined from GPC and ¹HNMR. Based on the determined molecular weights, the volume fraction of PS and PMMA blocks are calculated using the known densities, ρ_{PS} (=1.05 g/cm³) and ρ_{PMMA} (=1.19 g/cm³) of the corresponding homopolymers:

Table 1 Molecular characteristics of PS-*b*-PMMA samples

	Mol% of styrene	Mw _{absolute} of PS	Mw _{absolute} of PS- <i>b</i> -PMMA	Vol% of Styrene	PDI
Sample(1)	36.67	8655	23037	40.57	1.21
Sample(2)	25.53	17750	67535	28.79	1.26

The synthesized PS-silane has been verified by GPC and ¹HNMR to have a molecular weight of 2363 (PDI: 1.10) which comprises a PS chain length of 2200 and a terminal 3-CPTMOS (molecular weight : 163 after the elimination of chlorine atom).

The successful completion of the sol-gel reaction between PS-silane and SiO₂ has been verified by the disappearance of Si-O-C stretches and the generation of Si-O-Si stretches in the PS-SiO₂ spectrum (as shown in Fig. 1).

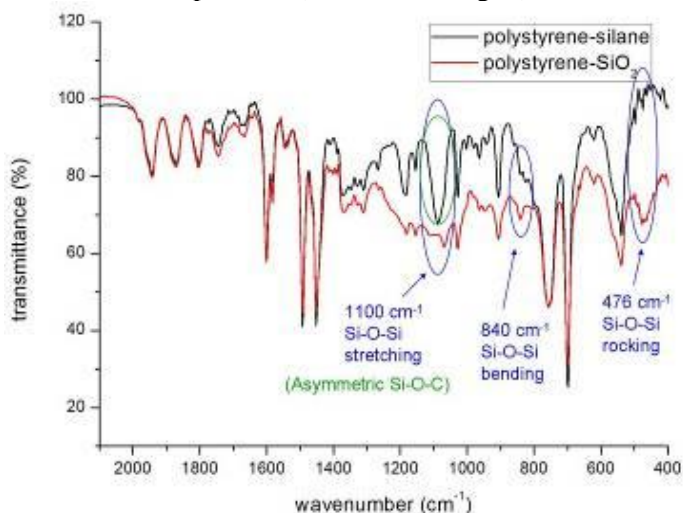


Fig. 1 FTIR spectra for PS-silane and PS-SiO₂

While the sol-gel reaction occurs between PS-silane and nano silica particle, sol-gel reaction also occurs between nano silica particles owing to the silanol groups on the surface of these particles. As a result, it is difficult either to analyze the number of PS-silane molecules bonded to each nano silica particle or to achieve a uniform size of the final PS-SiO₂ particles. Nevertheless, the observed particle size of PS-SiO₂ is within a narrow range of 15~40 nm.

Blending various amount of these PS-SiO₂ particles into the aforementioned PS-*b*-PMMA samples enables us to make composite materials with various PS to PMMA ratios, which indirectly affects the morphologies.

Owing to the indistinguishable electron densities of PS and PMMA, RuO₄ has been used for the dyeing of PS microdomain to facilitate the SEM analysis. It is clearly seen that all PS-SiO₂ particles are selectively residing in the islanded PS microdomains and the PS microdomains are enlarged by the incorporation of PS-SiO₂ particles. Furthermore, the incorporation of PS-SiO₂ particles also transforms the morphology from cylinders to islanded bicontinuous microstructures because of the inherent low surface energy of SiO₂.

Conclusion

With PS-tethering, SiO₂ nanoparticles have been dispersed selectively in the PS microdomain of PS-*b*-PMMA block copolymer. The incorporation of SiO₂ particles not only enlarges the PS microdomain but also reduces the surface energy of the PS microdomain and transforms the morphology from either lamellar layers or cylinders to islanded bicontinuous microstructures. An excessive amount of PS-SiO₂ would pose an extreme constraint on the molecular rearrangement and even make the microdomain separation unobservable. The nanosize and the uniform distribution of the PS microdomain in the PS-*b*-PMMA polymer thus enabled us to achieve a uniform distribution of the inorganic SiO₂ particles in the organic polymeric matrix.

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