Thermal Behavior of Polystyrene-Silica Nanocomposites

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Abstract

The formation of covalently grafted polymer brushes on silica (SiO_2) nanoparticles was achieved by surface-initiated reversible addition-fragmentation chain transfer (si-RAFT) polymerization. RAFT initiator was first attached onto the surface of silica nanoparticles and then examined by ultraviolet-visible spectroscopy (UV-vis) analysis. From the resulting RAFT initiator-modified SiO_2 nanoparticles, polymer chains can be reliably grown from styrene derivatives having various halide groups (e.g., F, Cl, Br). These polymer chains were found to be narrowly dispersed by gel permeation chromatography (GPC). Differential scanning calorimetry (DSC) analysis of the polymer-SiO_2 nanocomposites showed a much higher glass transition temperature (T_g) than those of bulk polystyrene derivatives, consistent with previously observed data for polystyrene-SiO_2 nanocomposites. Within a reasonable range of molecular weight, it appears that polymer chains will gain thermal stabilities when being confined in nanoscale environments, such as being tethered to the surface of the SiO_2 nanoparticles.

Introduction

Well-defined polymer-inorganic nanocomposites with novel optical,[1,2] mechanical,[3] and thermal[4] properties can be used in many applications, including coatings, plastic reinforcement, diagnostics, and electronics.[5] These nanocomposites have been prepared either by physically mixing the two components together or by covalently linking them,[6,7] with the second strategy affording materials with a more stable interface (i.e., does not phase separate). Two main approaches have been reported to covalently attach polymers to a surface: the "grafting to" method, where premade polymers were covalently grafted to the surface of inorganic substrates via functional groups,[8] and the "grafting from" method, where polymer chains are grown in situ from the initiator-modified surface of the substrates.[9] The latter approach has been widely employed to grow high-density polymer layers with adjustable thickness, allowing for the tuning of properties and functions.[10] Thus, researchers have developed many reliable polymerization techniques for forming a wide range of polymer layers on solid substrates with precise molecular weights, compositions, and functionalities.

Among the known polymerization methodologies, living and/or controlled techniques, such as atom-transfer radical polymerization,[11] ring-opening metathesis polymerization[12], and reversible addition-fragmentation chain transfer (RAFT) polymerization,[2] are popular strategies for forming well-defined and uniform polymer layers on solid substrates.[13] Because the first two methods employ metal-based catalysts and could cause contamination, RAFT polymerization has been the most popular due to its organic nature and its high compatibility with a wide range of commercially available monomers.[2] In this research, the preparation of covalently attached polymer brushes of halogen-substituted styrene derivatives on SiO_2 nanoparticles using surface-initiated RAFT (si-RAFT) polymerization was outlined, and the T_gs of the resulting composite materials as a function of the halogen functionality on the styrene monomers was evaluated.

Background

In polymer nanocomposites, the thermal properties of the polymer component are often enhanced compared with those of the bulk polymers. For example, when a polystyrene outer layer is grown on monodispersed 20 nm silica nanoparticles, the polystyrene T_g increases to ~133° C in comparison with the 102° C T_g of bulk polystyrene.[14] This enhancement in thermal stability is attributed to a decrease in the mobility of the polymer chains, a result of the close interactions between the surface of the silica nanoparticles and the polymer.[14]

The mobility of polymer chains is also known to decrease as a function of monomer mass. For example, large halide substituents on styrene derivatives can greatly hinder the mobility of the polymer chains, resulting in a near-linear increase of T_gs in the order of increasing atomic weight, with T_g for poly(p-bromostyrene) being 30° C higher than that of polystyrene itself.[15]

Based on the aforementioned two studies, it was hypothesized that covalently linked composites between silica nanoparticles and halogenated polystyrene may possess much higher T_gs than either the parent polystyrene-SiO_2 nanocomposite or the bulk halogenated polystyrenes. Furthermore, beyond the simple additive of the two physical effects (mass and confinement), there could be additional chemical interactions between the halogen substituents and the surface hydroxyl groups (e.g., hydrogen bonding). By understanding the parameters that govern the changes in T_gs of the polymers, the physical and chemical interactions between the polymer components and the inorganic surface could be used to develop polymer-inorganic materials with enhanced thermal properties.

Approach

SiO_2 nanocomposites with various halogenated polystyrene derivatives were prepared and characterized in three steps: 1) functionalizing SiO_2 nanoparticles with RAFT initiator; 2) polymerizing para-halogenated styrene monomers from the surface of RAFT initiator-modified SiO_2 nanoparticles; and 3) characterizing the resulting polymer-SiO_2 nanocomposites.

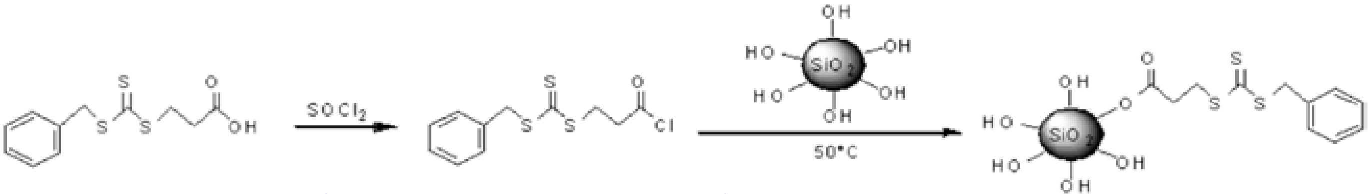

Figure 1. The attachment of RAFT initiator (3-benzylsulfanylthiocarbonylsufanylpropionic acid) on SiO_2 nanoparticle.

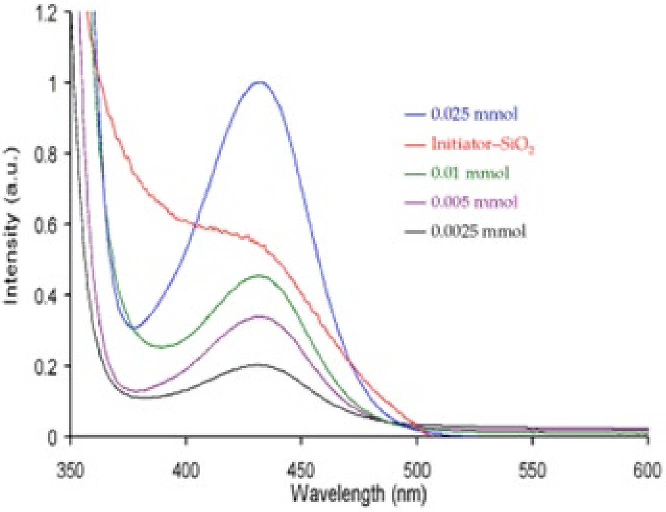

Figure 2. UV-vis spectra of known concentrations of free initiator and RAFT initiator grafted SiO_2 nanoparticles.

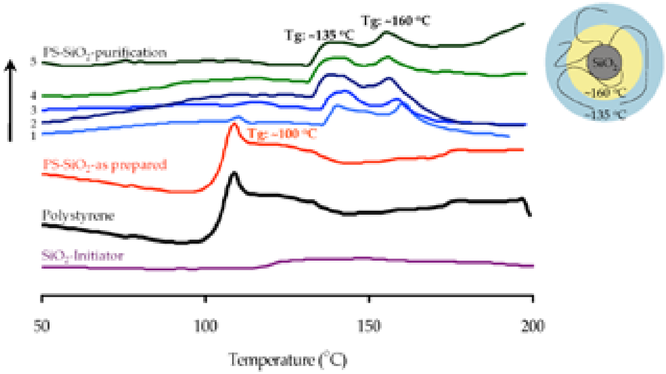

Figure 3. DSC curves of PS-SiO_2 nanocomposites showing the disappearance of the T_g peak of free PS after three centrifugation steps (left). Schematic illustration of the polymer domains that are potentially responsible for the two observed T_gs in pure PS-SiO_2 nanocomposites (right).

Functionalization of SiO_2 Nanoparticles with RAFT Initiator

The RAFT initiator 3-benzylsulfanylthiocarbonylsufanylpropionic acid was previously synthesized by Jun-Hyun Kim.[16] In a septum-capped round-bottom flask, this initiator acid (0.5 g) was first converted into its acid chloride derivative via treatment with excess thionyl chloride (4 mL) in anhydrous methylene chloride (4.7 mL).[2,13] After being heated for 2 hr at 50° C, the excess thionyl chloride and the solvent were removed using a Schlenk line. It is important to remove any excess thionyl chloride, as it can cause side reactions.

In a separate flask, a suspension of the silica nanoparticles (10–15 nm diameter, 33% by weight in MEK, ~ 5.0 g of SiO_2, obtained from the Nissan Chemical America Corporation, Texas) was reduced to a dry powder using a Schlenk line. This powder was then quickly added to the flask containing the RAFT initiator acid chloride derivative, and the whole assembly was purged with nitrogen for 15 min. Carbon tetrachloride (anhydrous grade, 13.34 mL) was then added to the flask, and the resulting mixture was stirred for an additional 20 hr at room temperature. During this time, the acid chloride group of the RAFT initiator reacted with the surface hydroxyl groups of the SiO_2 nanoparticles to form a surface-grafted RAFT initiator (Figure 1).[2] The final reaction mixture was concentrated to a minimum on a rotary evaporator to give a viscous brown liquid that was redispersed in MEK (70 mL) and equally divided into two 50 mL centrifugation tubes. To each tube was added a 1:1 v/v mixture of hexanes and THF (10 mL each). The resulting mixture was centrifugated (Eppendorf centrifuge 5804R, 15 amp version, 3500 rpm for 15 min) to remove unbound initiator and any impurities from the nanoparticles. After the mother liquor was decanted, the isolated solids were resuspended in a mixture of MEK (~35 mL) and hexanes (~10 mL) and sonicated (Fisher FS6 Ultrasonic Cleaner) for 5 min before being centrifugated again. The centrifugation and resuspension process were repeated a minimum of three times or until the supernatant layer was colorless. The pure RAFT agent-modified SiO_2 nanoparticles were finally resuspended in MEK (enough to make a suspension containing 0.33 g SiO_2 per mL of suspension) prior to use. Using UV-Vis, the number of RAFT initiator molecules on the SiO_2 nanoparticles was calculated by comparing the absorption of the RAFT initiator-modified SiO_2 against those of the free RAFT agent at known concentrations.

Si-RAFT Polymerization of PS Derivatives on SiO_2 Nanoparticles

Under nitrogen, styrene polymerization was initiated from the surface of the nanoparticles (1.5 mL of the suspension prepared above, 0.5 g of RAFT agent-modified SiO_2) in the presence of neat halogenated styrene monomers (5 mL) and the coinitiator AIBN (1.5×10^{-3} g).[2] After 4 hr at 60° C, the reaction flask was cooled to room temperature, and the polymerization was terminated by exposing the mixture to air. It is important to note that both the free polymer (formed via AIBN initiation) and the polymer grafted–SiO_2 nanoparticles were produced during the polymerization. These mixtures were simply separated by three centrifugation steps after suspending the mixtures in THF and hexanes (~1:1 v/v). The bottom layer containing polymer-SiO_2 nanocomposites was collected and air-dried overnight. The purity of the collected nanocomposites was subsequently confirmed by DSC analysis. The top layer was treated with excess methanol to precipitate the free polymers, which were collected via vacuum filtration and dried overnight.

Characterization of the Nanocomposites Formed between SiO_2 and Halogenated Polystyrene Derivatives

The purity and T_g of the polymer-SiO_2 nanocomposites were evaluated using differential scanning calorimetry (DSC). Each sample (5–10 mg) was loaded onto a DSC aluminum crucible cell (40 µL, Mettler Toledo International Inc.), heated under nitrogen at a constant heating rate of 10° C /min from 40° C up to 200° C, cooled back down to 40° C, and heated back up again to 200° C.[14] T_g values of all samples were chosen from the second heating cycle.

Gel permeation chromatography (GPC) was used to evaluate the molecular weight and the polydispersity index (PDI) of the free polymers as well as the polymer component in polymer-SiO_2 nanocomposites. All nanocomposites and free polymer samples were first treated with hydrofluoric acid (HF) overnight to dissolve any SiO_2 nanoparticles and impurities.[14] The samples were lyophilized and redissolved in HPLC-grade THF (1 mg/mL) for the analysis.

Results and Discussion

UV-vis analysis was employed to quantify the attachment of RAFT molecules on the surface of SiO_2 nanoparticles. Figure 2 shows the absorption spectra of solutions of initiator at known concentrations and of the initiator grafted on SiO_2 nanoparticles. The concentration of initiator grafted on SiO_2 nanoparticles was estimated to be 1.5 µmol/mL, equivalent to ~60 initiator molecules per nanoparticles.

DSC was used to examine the Tg of free polystyrene (PS) and as-prepared polystyrene-SiO_2 nanocomposites (Figure 3). Before purification, the mixture of PS and PS-SiO_2 exhibited a single T_g at ~103° C. After the free PS were removed by three centrifugation cycles, pure PS-SiO_2 nanocomposites were collected, which exhibited two distinctive T_gs at ~135° C and 160° C. These nanocomposites appear to be the first to show this behavior, with the 160-°C Tg being the highest ever observed. Previously, covalently grafted PS on SiO_2 nanoparticles was found to exhibit only a single T_g at 133° C, which was attributed to the decreased mobility of the polystyrene chains near the surface of the nanoparticles.[14] It was hypothesized that the high T_gs in this study's systems were caused by the different proximities of the polymer segments to the surface of the SiO_2 nanoparticle (Figure 3). Specifically, the PS segments that were closer to the SiO_2 surface were more constrained by the surface than remote segments, thus requiring more energy to pass from a glassy state to a rubbery state. Further examination is under way to verify this hypothesis.

The T_gs of free halogenated-styrene polymers and their corresponding composites with SiO_2 nanoparticles were also examined. DSC curves of the pure halogenated PS derivatives revealed increased T_gs in the order H < F < Cl < Br (Figure 4), in accord with previous research attributing decreased mobility of the polymer chains to increase in size of the halogen atom.[13] The T_gs of the nanocomposites between halogenated PS derivatives and SiO_2, except for the poly(bromostyrene)-SiO_2 sample, were slightly higher and broader than the corresponding free PS derivatives (Figure 5). In addition to the T_gs increases caused by the presence of halogen substituents in the free polymers, the increased T_gs in the nanocomposites were most likely the result of the aforementioned decreased mobility of polymer segments close to the SiO_2 surface.

Type of Styrene	Molecular Weight (M_n)	Degree of Polymerization (DP)	Polydispersity Index
Poly(bromostyrene)-SiO_2	196,000	1309	1.23
Poly(chlorostyrene)-SiO_2	181,000	1452	1.12
Poly(fluorostyrene)-SiO_2	122,000	1139	1.15
Polystyrene-SiO_2	69,000	755	1.14

Table 1. GPC data of polystyrene-SiO_2 nanocomposites.

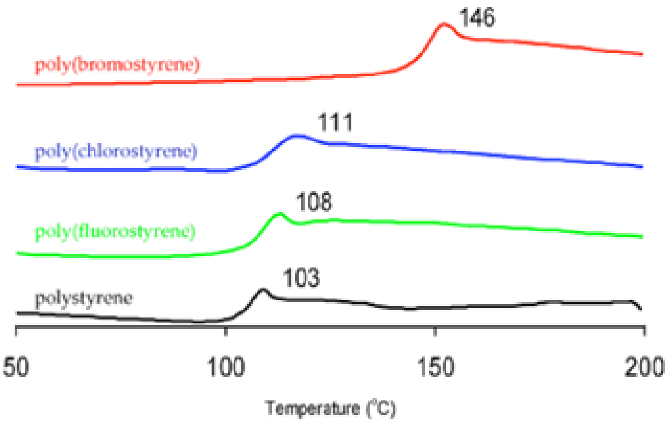

Figure 4. DSC curves of free poly(bromostyrene), poly(chlorostyrene), poly(fluorostyrene), and polystyrene.

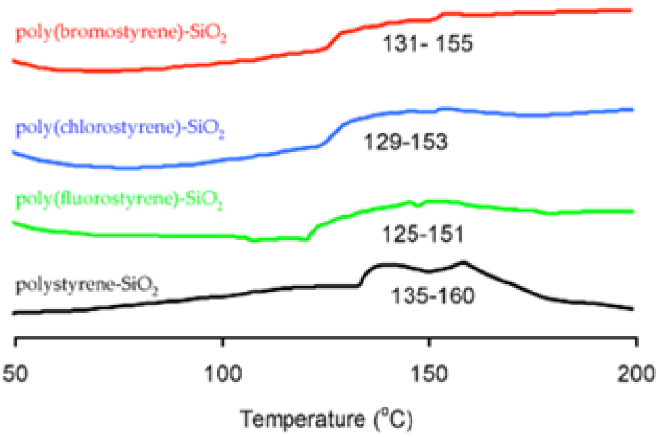

Figure 5. DSC curves of poly(bromostyrene)-SiO_2, poly(chlorostyrene)-SiO_2, poly(fluorostyrene)-SiO_2, and polystyrene-SiO_2 nanocomposites.

Table 1 shows the number/average molecular weight (M_n) of the halogenated PS derivatives after removal of the SiO_2 nanoparticles obtained from GPC measurements. All polymer samples prepared under the aforementioned reaction conditions had low polydispersity indexes (PDI), indicating a living polymerization. However, the average degree of polymerization (DP) for the halogenated polymers was much higher than that for the parent PS. This phenomenon has been attributed to the electron-withdrawing effect of the *p*-halide substituents,[13] which stabilized the free radical intermediate during the polymerization, leading to longer polymer chains for the halogenated PS derivatives in comparison with the parent PS.

It appears that shorter polymer segments on SiO_2 nanoparticles have more restricted mobility compared with longer chains. This decreased mobility accounts for the higher T_gs seen in the nanocomposites with shorter segments than those having longer chains. Because the current data set does not provide enough data to separate this effect compared with that of halogenation (i.e., How do different halogen substituents interacts with the surface?), future work will focus on the synthesis of different halogenated polystyrenes having the same DP. In this way, the ability of halogen substituents in polymers to interact with the surface of the nanoparticles can be properly examined.

Conclusion

In conclusion, it was shown that si-RAFT polymerization can be used to synthesize nanocomposites of SiO_2 nanoparticles with several halogenated PS derivatives. The resulting nanocomposites exhibited higher T_gs compared with those of the corresponding free PS. Research continues on the preparation of halogenated PS-SiO_2 nanocomposites where the chains of the polymer components are of similar length to examine the effect of halide groups on T_g changes. Understanding the relationships between the thermal stabilities of these nanocomposites and the functional groups in their polymer components can facilitate the development of polymer-inorganic materials with enhanced thermal properties.

This research was supported primarily by the Northwestern University Nanoscale Science and Engineering Research Experience for Undergraduates (REU) program under NSF award number ***EEC – 0647560****. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect those of the National Science Foundation.*

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