

1-1-2006

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Recommended Citation

M. B. Nair and F. D. Blum, "Synthesis and Thermal Behavior of Poly(Methyl Acrylate) Attached to Silica by Surface-Initiated ATRP," *Polymer Preprints*, American Chemical Society (ACS), Jan 2006.

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SYNTHESIS AND THERMAL BEHAVIOR OF POLY(METHYL ACRYLATE) ATTACHED TO SILICA BY SURFACE-INITIATED ATRP

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Introduction

The modification of the surface of an object dictates the response of the object to an external environment.¹ Surface-modified materials and nanoparticles have attracted immense interest due to the various desirable electronic, optical and magnetic properties they possess.² Silica is widely used as an inorganic filler. Surface modification of the silica, with a variety of organic moieties, facilitates the utilization of silica in conjunction with organic systems. The resulting organic/inorganic hybrid materials have significant potential applications.

This work reports the synthesis and characterization of modified silica, and poly(methyl acrylate) attached to the modified silica. An observation of the thermal behavior of poly(methyl acrylate) chains covalently attached to the silica-surface is reported.

Experimental

Synthesis of allyl 2-bromopropionate:³ In a round-bottomed flask equipped with a magnetic stir-bar, 200 mL of dry dichloromethane, 3.03 g of allyl alcohol and 5.30 g of triethylamine were added and the mixture was cooled to 0 °C in an ice-bath. Then 16.9 g of 2-bromopropionyl bromide was added dropwise, to the reaction mixture using an addition funnel, while the mixture was in the ice-bath. After complete addition, the mixture was brought to room temperature and was stirred for 18 h. The product was washed with 300 mL of distilled water, dried over anhydrous magnesium sulfate, and the solvent was evaporated to recover the allyl 2-bromopropionate. Figure 1 shows the reaction scheme.

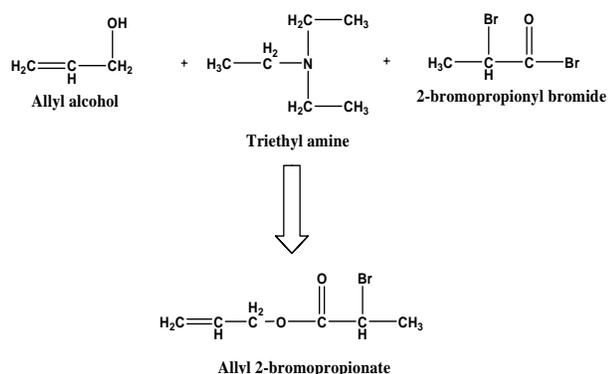


Figure 1. Synthesis of allyl 2-bromopropionate.

Hydrosilation.³ [Synthesis of (3-(2-bromopropionyl)propyl)dimethylethoxysilane (BPDS)]. In a round-bottomed flask equipped with a magnetic stir-bar, 8.43 g of allyl 2-bromopropionate was added. To this, the hydrosilation catalyst was added (containing 30 mg of hexachloroplatinic acid in 0.5 mL of diethylether/ethanol, 1/1 v/v). Then 5.92 g of dimethylethoxysilane was added dropwise to the flask, and the reaction mixture was heated at 80 °C. The progress of the reaction was monitored by checking the disappearance of the vinyl protons of allyl 2-bromopropionate. Figure 2 indicates the reaction scheme.

Surface modification of silica with BPDS.^{3,4,5} The silica used for this study was Cab-O-Sil, M5-P, (Cabot Corp, Tuscola, IL), with surface area 200 m²/g. In a round-bottomed flask equipped with a magnetic stir-bar, 2.5 g of silica and 50 mL of toluene were added. To this suspension of silica in toluene, 5 g of BPDS and 50 mL toluene were added and the mixture was heated to 85 °C and stirred for 12 h. The modified silica particles were isolated by centrifugation. The particles were washed with hexane to remove any adsorbed initiator (BPDS) molecules. The washing of the silica particles was carried out by subjecting the particles to 5 cycles of centrifugation,

resuspension in hexane, and finally the particles were dried in a vacuum oven overnight. Figure 3 indicates the reaction scheme.

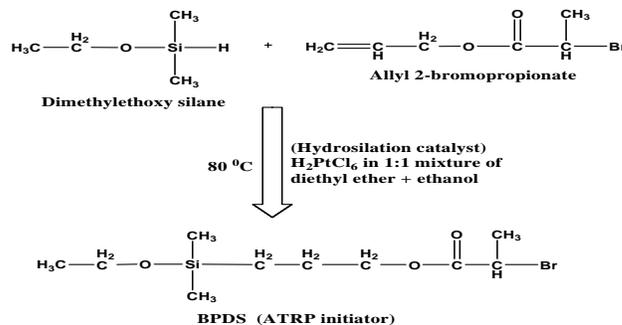


Figure 2. Synthesis of BPDS.

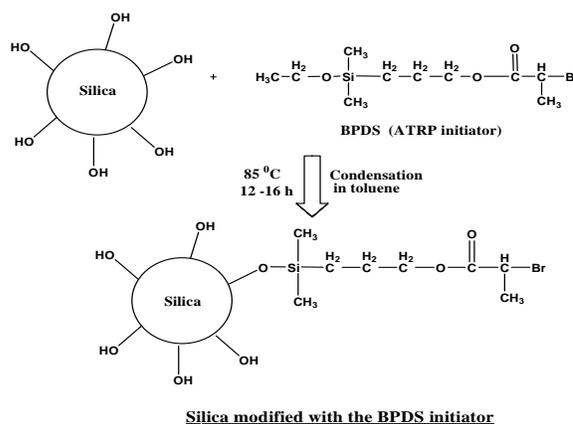


Figure 3. Surface modification of silica with BPDS.

Atom transfer radical polymerization (ATRP) of methyl acrylate was carried out using the BPDS modified silica particles as the initiator, CuBr as the catalyst, and pentamethyl diethylene triamine (PMDETA) as the ligand, to bond poly(methyl acrylate) chains covalently to the surface of silica particles. The PMA-silica composite, was isolated by centrifugation. The composite was washed with toluene several times (4 cycles of centrifugation and resuspension) to remove any adsorbed or unattached PMA chains that might be present. A final washing with hexane was carried out to remove the residual toluene, and the composite consisting of the PMA chains covalently attached to silica, was dried overnight in a vacuum oven. Figure 4 shows the polymerization scheme.

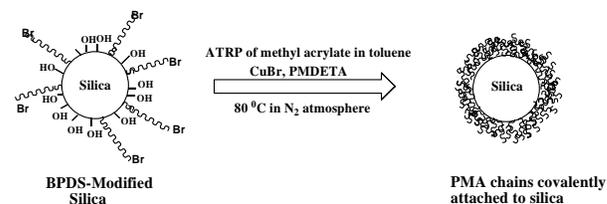


Figure 4. Surface initiated ATRP of methyl acrylate on silica by the "grafting from" method.

Results and Discussion

Characterization of the BPDS modified silica and the PMA-silica composite. Thermogravimetric analysis (TGA) was used to determine the grafting density of the BPDS on the modified silica, and to determine amount of polymer attached to the surface of silica. The modified silica samples and the PMA-silica composite samples were heated to 750 °C in the TGA and the weight loss obtained, was recorded as the amount of organic content present in the sample. Table 1 indicates the TGA results obtained.

The grafting density of BPDS on silica, calculated on the basis of the TGA results, was found to be 0.3 molecules of BPDS per nm² of silica. The TGA curves for the modified silica and the PMA-silica composite are shown in Figure 5. The weight loss for the BPDS modified silica was found to be 2.9% and that for the PMA-silica composite was found to be 7.1%.

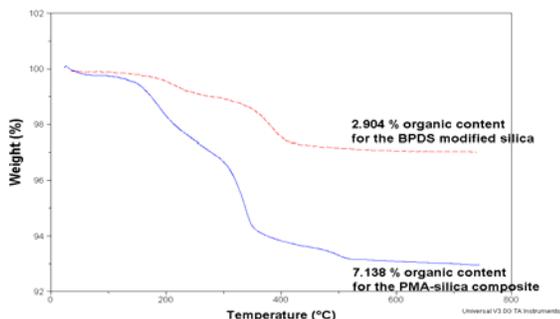


Figure 5. TGA curves for BPDS modified silica and PMA-silica composite.

Table 1. Weight Loss Data For The Modified Silica And The Composite.

Sample	Organic content (Weight %)
BPDS-modified silica	2.904
PMA-silica composite	7.138

From the TGA results it is clear that the PMA-silica composite has higher organic content relative to the BPDS modified silica. This suggests the attachment of the PMA chains onto the modified silica.

The FTIR spectra for the bulk silica, the BPDS modified silica, and the PMA silica composite, are shown in Figures 6 and 7. For both the modified silica and the PMA silica composite, a carbonyl stretch (C=O) was observed at around 1719 cm⁻¹ and C-H stretches were observed at around 2961 cm⁻¹ indicating evidence of the surface modification of silica. In the FTIR spectrum for the PMA-silica composite alone, the appearance of a peak at around 1470 cm⁻¹ (for the CH₃-O vibration in PMA) was observed which indicates the presence of poly(methyl acrylate) on the silica surface.

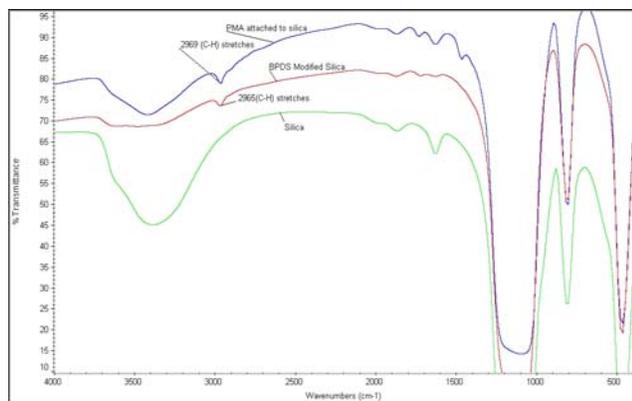


Figure 6. FTIR spectra of silica, BPDS modified silica, and the PMA attached to silica (PMA-silica composite).

Thermal behavior. The thermal behavior of the BPDS modified silica and the PMA-silica composite was studied with differential scanning calorimetry (DSC). The DSC curves are shown in Figure 8. The DSC curve for bulk PMA ($M_w = 28,670$ g/mole) is included for comparison. The glass transition observed for the bulk PMA sample is around 9 °C. For the BPDS modified silica, and the PMA-silica composite, a common transition is observed around 38 °C. This common transition is due to the BPDS attached onto the silica particles. The DSC curve for the PMA-silica composite also

shows another transition at a higher temperature of around 59 °C. This transition, due to the presence of the attached PMA chains on the modified silica, is consistent with PMA adsorbed on silica.⁶ The fact that this T_g for the bound material is much higher than that for the bulk, indicates that the mobility of the PMA chains are significantly restricted due to their covalent attachment onto the surface of silica.

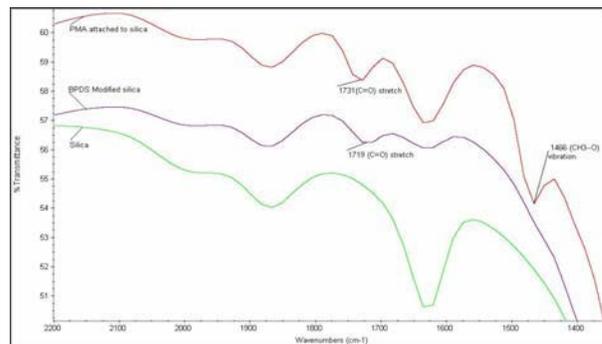


Figure 7. FTIR spectra (magnified) of silica, BPDS modified silica, and the PMA attached to silica (PMA-silica composite).

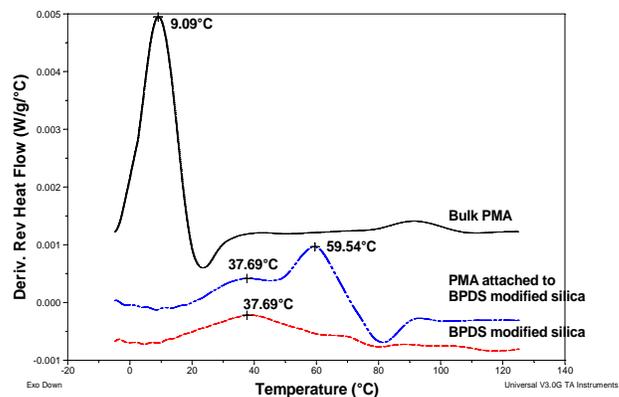


Figure 8. DSC results for the BPDS modified silica and the PMA-silica composite.

Conclusions

Silica was subjected to surface modification resulting in the covalent attachment of the ATRP-initiator (BPDS) on its surface. The modified silica was used as the initiator for ATRP of methyl acrylate to bond PMA chains covalently to silica. The characterization of the modified silica, as well as the PMA-silica composite, was carried out using TGA, FTIR, and DSC. The DSC result obtained for the PMA-silica composite, was consistent with PMA adsorbed on silica.⁶ It was observed that the covalent attachment of the PMA chains onto the silica surface, significantly restricts the mobility of the polymer chains and increases T_g .

Acknowledgements. We acknowledge the National Science Foundation (NSF) and the University of Missouri-Rolla for financial support of this research.

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