MISSOURI S&T

Missouri University of Science and Technology

Scholars' Mine

Chemistry Faculty Research & Creative Works

Chemistry

01 Jan 2008

Glass Transition Behavior of Poly(Methyl Acrylate) End-Grafted by ATRP to Amorphous Silica

Manikantan B. Nair
Missouri University of Science and Technology

Frank D. Blum
Missouri University of Science and Technology

Follow this and additional works at: https://scholarsmine.mst.edu/chem_facwork

Part of the Chemistry Commons, and the Materials Science and Engineering Commons

Recommended Citation

M. B. Nair and F. D. Blum, "Glass Transition Behavior of Poly(Methyl Acrylate) End-Grafted by ATRP to Amorphous Silica," *Polymer Preprints*, American Chemical Society (ACS), Jan 2008.

GLASS TRANSITION BEHAVIOR OF POLY(METHYL ACRYLATE) END-GRAFTED BY ATRP TO AMORPHOUS SILICA

Manikantan B. Nair and Frank D. Blum

Departments of Chemistry and Materials Science and Engineering and
Materials Research Center
Missouri University of Science and Technology
Rolla, MO 65409-0010

Introduction

Ultra-thin polymer films attached to solid substrates (supported films) have attracted significant interest in recent years. Supported films are used in the design of advanced materials like photoresists, lubricants and other electronic devices. Glass transition temperatures (T_gs) of supported polymer films have also been of significant interest. The T_g has been shown to depend on the thickness of the polymer film on the surface and the inherent nature of the surface. The effect of end-grafting of a polymer chain to a surface, on the T_g of the polymer has been studied previously.[1]

Reports on the study of glass transition behaviors of different types of supported polymer films on substrates of a varying nature exist. These studies include investigations of the dependence of T_g on various parameters like film thickness, nature of the substrate, molecular architecture, stereochemistry of the polymer and interfacial interaction effects.[10-15]

In this preprint, we report the study of the T_g behavior of poly(methyl acrylate) (PMA) chains covalently bonded to silica using a silane coupling agent. Several PMA-silica composite samples with different relative amounts (low, medium and high) of PMA attached to the silica were synthesized and the T_g of the attached PMA in each composite was determined using modulated differential scanning calorimetry (MDSC). The attached PMA, in the composite samples, exhibited interesting glass-transition behavior.

Experimental

Synthesis of the silane ATRP-initiator (Hydrosilylation):[2] The ATRP-initiators were synthesized using both mono and triethoxy silanes. Synthesis of (3-(2-bromopropionyl)propyl)triethoxysilane (BPTS) used the following procedure. To allyl-2-bromopropionate (0.026 mol) in a round-bottomed flask with a magnetic stir-bar, the hydrosilylation catalyst, hexachloroplatinic acid in isopropanol was added. Triethoxysilane (0.182 mol) was added dropwise to the reaction mixture using an addition funnel. The mixture was heated to reflux at 70-75 °C for about 3 h. The reaction was monitored with ^{1}H and ^{13}C NMR.

After completion of the hydrosilylation, as indicated by the complete disappearance of the allyl protons of allyl-2-bromopropionate, the reaction mixture was subjected to vacuum distillation to remove the unreacted triethoxysilane. Dry methylene chloride was added to the mixture and filtered over anhydrous magnesium sulfate to remove the Pt catalyst. The methylene chloride was evaporated under vacuum and the pure BPTS was recovered. The ATRP initiator, 3-(2-bromopropionyl)propyl)dimethylethoxysilane (BPDS) with the monoethoxy silane was synthesized similarly.

Surface modification of silica with BPTS:[3,4,5,6] Silica (Cab-O-Sil, M5P, Cabot Corp, Tuscola, IL, surface area = 200 m^2/g) was dried in a furnace at 500 °C overnight and cooled in a desiccator. The dried silica (2 g) was added to a round-bottomed flask containing a stir-bar and 200 mL of dry toluene was added and the flask was sonicated for 30 min, to thoroughly disperse the silica in the toluene. BPTS (0.3 g) was mixed with 75 mL of dry toluene and 0.05 g propylamine was added to the mixture. This BPTS/toluene/propylamine mixture was added dropwise with stirring, to the round bottomed flask containing the silica/toluene dispersion. The mixture was stirred at room temperature for 3 h. After the surface-modification reaction, the modified silica was separated by centrifugation. The product was washed with dry toluene, followed by five cycles of centrifugation and resuspension. The modified silica was then dried in a vacuum-oven overnight at 60 °C. Surface modification of the silica with BPDS was done similarly. The characterization of the modified silica was carried out using thermogravimetric analysis (TGA).

Synthesis of poly(methyl acrylate) end-grafted to silica by surface-initiated ATRP using the grafting-from approach: Synthesis was done by using the following procedure: The BPTS or BPDS modified silica, was placed in a round-bottomed flask and dry toluene was added. The mixture was sonicated for 15 min, to properly disperse the modified silica in the toluene. The catalyst, CuBr, was then added and the flask was sealed with a rubber septum. The flask was then flushed for 15-30 min with Ar gas to remove oxygen. Appropriate amounts of the monomer (methyl acrylate) and the ligand (PMDETA) were added as solutions in toluene, with a syringe flushed with N_2 gas, to maintain an inert atmosphere. The flask was then heated in an oil-bath at 75-80 °C for about 24 h. After the reaction, the PMA-silica composite, was separated by centrifugation. The product was washed with hexane followed by five cycles of centrifugation and resuspension, to remove the unreacted monomer. The composite was then dried in a vacuum-oven overnight at 60°C.

Results and Discussion

Our research group has previously studied the glass-transition behavior of PMA films physically adsorbed on silica. These films were physically adsorbed onto silica from solution. The most significant interfacial interactions between the PMA and the silica were the hydrogen bonding interactions. For these adsorbed PMA films on silica, it was observed that the segmental mobility of the polymer chains on the silica surface was restricted and, consequently, the T_g was higher, relative to the bulk T_g. For the adsorbed PMA films, the highest T_g observed, was on the order of about 20 °C, which was significantly higher than the bulk T_g (~ 10 °C) of PMA.[7,8,9]

Thermal characterization: The thermal behavior of the modified silica and the polymer composites, consisting of PMA chains covalently bonded to silica (PMA-silica composites), were characterized using thermogravimetric analysis (TGA) and modulated differential scanning calorimetry (MDSC). The attached amounts of PMA in the PMA-silica composites were determined using TGA and the results are tabulated in **Table 1**.

For the PMA-silica composites, the amounts of PMA attached to silica varied from 1.09 mg/m^2 to 5.80 mg/m^2 (**Table 1**). The MDSC results for the composite samples (composites A through F) exhibited two glass-transition temperatures (T_gs). **Figure 1** shows the thermograms of composites A and B, with relatively low attached amounts. For these composites, the components with lower T_gs (12 °C and 13 °C, respectively) were close to the bulk T_g of PMA. The higher T_g components were around 45 °C which was much higher than the bulk-T_g of PMA, or even the T_g of physically adsorbed PMA on silica.[7,9] **Figure 2** shows the thermograms of the composites C, D and E, with medium attached amounts. From the MDSC results, it is clear that for a given PMA-film on a silica surface, there exist differences between the segmental mobilities of the different PMA-segments on the surface. The lower-temperature T_g can be attributed to the more mobile PMA segments and the higher-temperature T_g can be attributed to the segments with restricted mobility, which are probably in close proximity to the surface. It is interesting to note that the restriction in segmental mobility is much more pronounced when the PMA chains are end-grafted to the silica surface, as opposed to when they are physically adsorbed.

The lower temperature transitions observed in samples C, D and E (23 °C, 9 °C and 19 °C respectively) represent the relatively more mobile PMA segments in the film. However, for samples C and E, the lower temperature component T_g (~20 °C) by itself, is substantially higher than the bulk T_g of PMA. This indicates that the covalent end-grafting at the surface has an effect on the PMA-segments located farther away from the surface. This interesting effect of end-grafting on the PMA segments located farther away from the silica surface, is also evident when a comparison is made between samples D and E. For these samples, the attached amounts are comparable (3.65 mg/m^2 and 3.82 mg/m^2 respectively), but the grafting densities are significantly different (0.45 and 1.41 molecules/nm^2, respectively), wherein sample E has about three times as many grafted polymer segments relative to sample D.

The higher temperature component transitions for samples C, D and E represent the less mobile PMA segments in the film. They were observed to be at much higher values (32 °C to 53 °C) because of arrested segmental mobility due to covalent bonding closer to the surface. **Figure 3** shows the thermograms of the composites F and G with relatively high attached amounts. The MDSC result for sample F indicates two transitions which can be explained as behaving similar to sample C. The MDSC result for sample G, with the highest amount (5.80 mg/m^2) attached, and a relatively high graft-density, exhibited a single broad transition at 31°C, which is significantly higher than the bulk-T_g of PMA or the T_g of physically adsorbed PMA on silica.

Table 1. Characterization Results From MDSC And TGA

PMA/Silica composite Sample	Attached amount (mg/m^2)[a]	T_g (°C)[b]	Graft-density (molecules/nm^2)[c]
Composite A	1.09	12 , 43	0.27
Composite B	1.61	13 , 45	0.27
Composite C	2.18	23 , 53	0.27
Composite D	3.65	9 , 32	0.45
Composite E	3.82	19 , 43	1.41
Composite F	4.53	25 , 51	0.45
Composite G	5.80	31	1.32

[a] From TGA, mg of PMA/ m^2 surface of silica
[b] From MDSC
[c] From TGA, molecules of initiator/nm^2 surface of silica
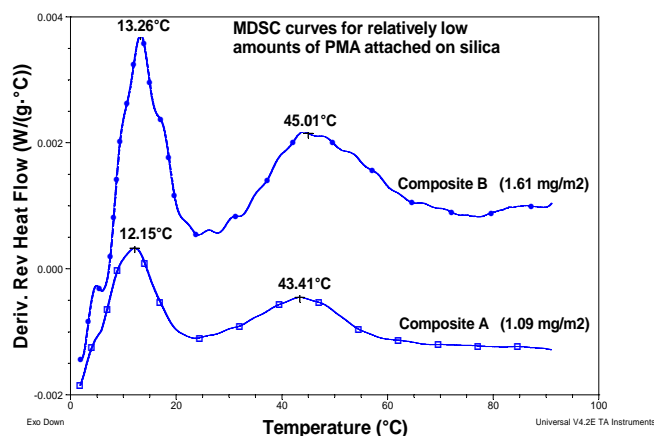
Figure 1. MDSC thermograms for low amounts of PMA attached on silica.

For sample G it appears that the glass-transition behaviors of the PMA segments throughout the film are uniform. For this sample, although, the covalent end-grafting significantly elevates the T_g of PMA beyond its bulk value, there does not appear to be a difference between the mobilities of the PMA segments in close proximity to the silica surface and the segmental mobilities away from the surface, given the amount attached and graft-density.
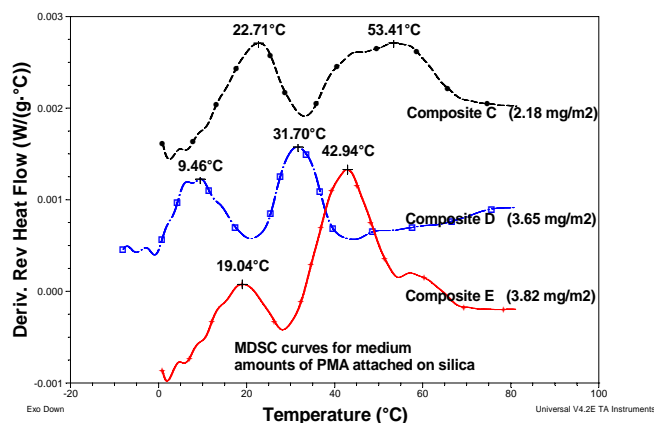
Figure 2. MDSC thermograms for medium amounts of PMA attached on silica.
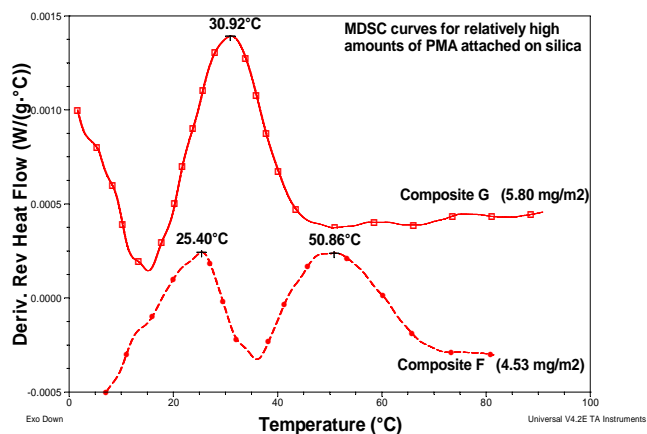
Figure 3. MDSC thermograms for high amounts of PMA attached on silica.

Conclusions

Non-porous amorphous silica was surface modified with monofunctional and trifunctional organosilane ATRP initiators, resulting in modified silica with initiators covalently bonded to the silica surface. The modified silica was used as a macroinitiator for the ATRP of methyl acrylate, resulting in PMA chains attached to the silica by a 'grafting-from' approach. It was observed that covalent end-grafting strongly influenced the T_g, resulting in a substantial elevation of the T_g of the PMA film. With T_g values on the order of 40 °C and above, this elevation was above and beyond the T_g of bulk PMA, as well as that of physically adsorbed PMA. These observations indicate that the mobilities of the PMA segments were significantly restricted due to the covalent bonding to the silica-surface. In addition, the complexity of the reactions and the varying products do not allow us to make more definitive statements about the effect of graft-density at this time.

References
(1) Yamamoto, S.; Tsujii, Y.; Fukuda, T. *Macromolecules,* **2002,** *35*, 6077.
(2) Marciniec B. Comprehensive Handbook on Hydrosilylation, Pergamon press, **1992,** 3.
(3) von Werne, T.; Patten, T. E. *J.Am. Chem. Soc.* **2001,** *123*, 7497.
(4) Prucker, O.; Ruhe, J. *Macromolecules,* **1998,** *31*, 592.
(5) Prucker, O.; Ruhe, J. *Macromolecules,* **1998,** *31*, 602.
(6) Nair, M. B.; Blum, F. D. *Polymer Preprints,* **2006,** 47(1), 315.
(7) Metin, B.; Blum, F. D. *Polymer Preprints,* **2005,** *46*, 437.
(8) Metin, B.; Blum, F. D. *J. Chem. Phys.* **2006,** *124*, 054908.
(9) Metin, B.; Blum, F. D. *J. Chem. Phys.* **2006,** *125*, 054707.
(10) Blum, F. D.; Young, E. N.; Smith, G.; Sitton, O. C. *Langmuir,* **2006,** *22*, 4741.
(11) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Faraday Discussions,* **1994,** *98*, 219.
(12) DeMaggio, G. B.; Frieze, W. E.; Gidley, D. W.; Zhu, M.; Hristov, H. A.; Yee, A. F. *Physical Review Letters,* **1997,** *78* (8), 1524.
(13) Fukao, K.; Miyamoto, Y. *Europhysics Letters,* **1999,** *46* (5), 649.
(14) Prucker, O.; Christian, S.; Bock, H.; Ruhe, J.; Frank, C. W.; Knoll, W. *Macromolecular Chemistry and Physics,* **1998,** *199*, 1435.
(15) See, Y-K.; Cha, J.; Chang, T.; Ree, M. *Langmuir,* **2000,** *16*, 2351.