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ADHESION ENHANCEMENT OF POLYMERIC FILMS ON GLASS SURFACES BY A SILANE DERIVATIVE OF AZOBISISOBUTYRONITRILE (AIBN)

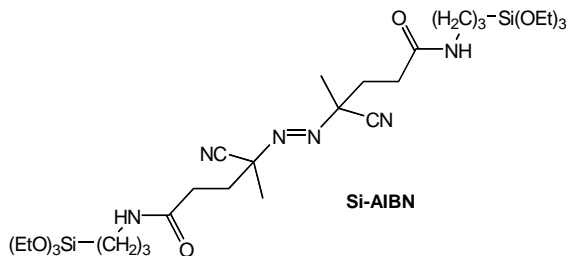
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Introduction

Adhesion of polymeric films on surfaces can be due to a combination of van der Waals, electrostatic or covalent interactions between the two materials. The interfacial adhesion between a polymer film and glass or metal can be improved by using a broad class of silane coupling agents.^{1,2} Typically, silane coupling compounds used for adhesion improvement have structure similar to (R'O)₃-Si-R, where R'O- is an alkoxy group and -R is an organofunctional group. Under appropriate reaction conditions alkoxy groups condense with hydroxyl groups available on the surface, resulting in surfaces decorated with organofunctional -R groups, which promote formation of covalent bonding of the coupling agent with polymeric networks.³ Alkoxy silanes with amino and vinyl organofunctional groups are common silane coupling agents and their adhesion-promoting abilities with polymeric films have been well-documented.⁴

In analogy to our previous work of forming conformal polymer coatings on three dimensional assemblies of silica nanoparticles (aerogels) via surface initiated polymerization (SIP), here we expand the scope of that work demonstrating the application of a new bidentate free radical initiator (Si-AIBN) as coupling agent that enhances adhesion of polystyrene (PS) and polymethylmethacrylate (PMMA).⁵ Si-AIBN was synthesized via a condensation reaction between 3-aminopropyltriethoxysilane (APTES) and azobiscyanovaleric acid. Si-AIBN is attached to the surface of glass by hydrolysis of the ethoxy groups and reaction with the hydroxyl groups of the surface. On supply of thermal energy those glass surfaces act like a macro initiator generating surface-bound radicals. In the presence of olefin monomers, surface-bound initiator starts formation of polymeric chains in analogy to a "grafting from" approach.⁶



Since each polymer chain is terminated by a molecule of the initiator, which is surface-bound, the adhesion of the resulting polymeric films on the substrate is promoted not only by mechanical interlocking of the polymeric chains but also by covalent bonding with the glass surface.

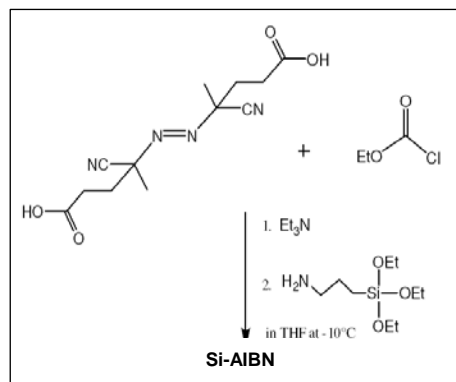
Experimental

Materials: All reagents and solvents were used as received unless otherwise noted. Azobiscyanovaleric acid (ABCA), ethylchloroformate, 3-aminopropyl triethoxy silane (APTES), tetramethoxysilane (TMOS), and ammonium hydroxide were purchased from Aldrich Chemical Co. Triethylamine was from Acros Chemicals and was further purified by distillation from calcium hydride. Anhydrous tetrahydrofuran (THF) was made by drying over lithium aluminum hydride. Styrene and methyl methacrylate (MMA) were from Aldrich Chemical Co. and were washed with 5% sodium hydroxide solution to remove the inhibitor, and purified by distillation at reduced pressure. Si-AIBN radical initiator was synthesized as reported before (Scheme 1).³

Preparation of polymeric films on glass surface: Glass slides (2''x2'') were cleaned by boiling for 2 min in Micro™ solution, washing with copious amounts of D.I. water and then boiling again in water for 2 min. Slides were

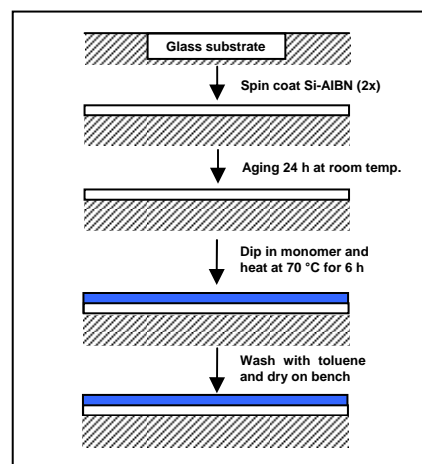
bench-dried for 24 h. A THF solution (0.1122 M) of Si-AIBN initiator was applied two times on these slides by spin coating (30 sec, 1500 rpm) followed by aging in the dark at room temperature for 24 h. The glass plates with radical initiator on the surface were processed in two different ways:

Scheme 1. Synthesis of Si-AIBN.



(a) By heating Si-AIBN modified glass in monomer (Scheme 2): Initiator-coated glass slides were dipped in 50 mL of neat monomer (MMA or styrene) in a 500 mL airtight container at 70 °C for 12 h. At the end of the period, the glass plates with the polymer films on them were washed with toluene and dried on the bench. Those dried films were tested for adhesion and their thickness was measured using Dektak II profilometry. Controls were prepared by heating glass plates in monomer without application of Si-AIBN initiator on their surface.

Scheme 2. Preparation of polymer films from monomers.



(b) By spin-coating Si-AIBN modified glass with a viscous polymer (Scheme 3): Inhibitor-free methyl methacrylate and styrene were heated separately at 130 °C for 6 h in closed containers to carry out partial thermal polymerizations into viscous pre-polymers. Such freshly prepared viscous pre-polymers were applied on Si-AIBN modified glass surfaces, and the glass plates were spun for 30 sec at 1500 rpm. Subsequently, films were cured for 6 h at 70 °C.

Results and Discussion

All PMMA and PS films formed on glass surfaces look uniform and show superior adhesion. The thickness of the initiator layer formed by spin coating the solution of Si-AIBN in THF was found by profilometry to be ~300 nm (Figure 1A). That layer was sufficient in order to carry out polymerization when heated together with monomer or pre-polymer (see Experimental), causing formation of PMMA or PS films covalently bonded to the surface.

The film thickness was measured again using profilometry and it as found in the range of 450 nm for films prepared from monomer (Figure 1B), and in the range of 1800-2000 nm for films prepared from pre-polymer.

Visibly smooth PMMA films formed by heating Si-AIBN modified glass plates with MMA do not appear as smooth under the electron microscope (Figure 2), but the average thickness of the polymer film observed by the microscope is similar to the thickness obtained by profilometry. Also the control carried out by heating glass plate without any modification with silane does not show any polymer film growth visually as well as microscopically.

Scheme 3. Preparation of polymer films from partially polymerized monomers.

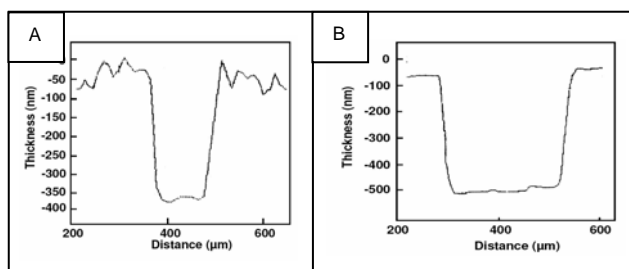
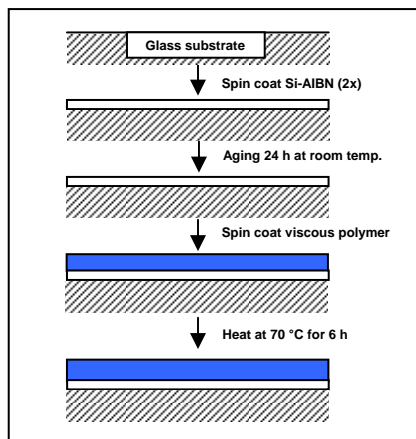


Figure 1. A. Profilometry of a Si-AIBN film spin-coated on a glass surface (300 nm). B. Profilometry of a PMMA film formed on glass surface from MMA (450 nm).

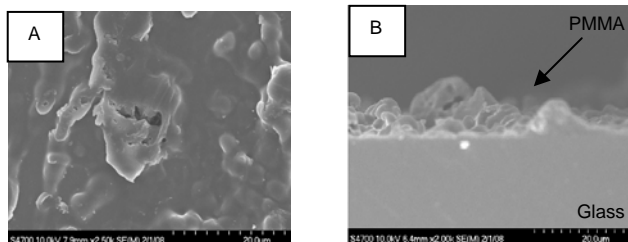


Figure 2. A. SEM of a PMMA film on a glass surface. B) SEM of a cross-section of a PMMA film on a glass surface.

The presence and identity of the polymer film on the surface of glass was confirmed by infrared (IR) spectroscopy. Figure 3 shows the IR spectra of PMMA and polystyrene grown on glass surface from the monomers. The spectra exhibit the features corresponding to commercially available bulk polymers and the peaks corresponding to silica are not prominent.

Polymer films prepared on glass surfaces by spin-coating viscous pre-polymers (see Experimental) show relatively higher thicknesses (1800-2000 nm) as compared to polymer films grown from incubation with the monomers.

In addition, when the viscous pre-polymer was spin-coated on glass surfaces modified with the silane derivative of the free radical initiator (Si-AIBN), the resulting films exhibited increased adhesion when compared with similar films deposited on glass surfaces without any modification. Adhesion testing (ASTM-D3359) was carried out on both PMMA and polystyrene films. Films grown according to Schemes 1 and 2 show good adhesion (5 B), while PMMA and PS films formed by spin-coating the pre-polymer on glass surfaces without any silane modification, followed by heating (to complete polymerization), resulted in very poor adhesion (0 B). Delamination of the polymer films from the glass surface is easy, which is the result of a physical only interaction of the polymer films with the glass surface.

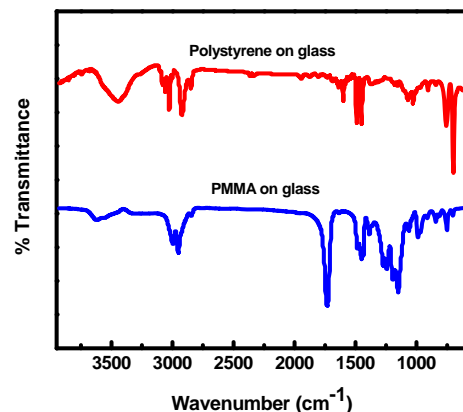


Figure 3. FTIR spectra of PMMA and polystyrene grown on silane modified glass surface.

Conclusions

Native Si-AIBN films formed on glass surfaces by spin-coating are essentially xerogels with moderately high surface areas. Surface initiated polymerization of olefins like styrene or MMA by surface-bound Si-AIBN results in polymer coatings with excellent adhesion, which is attributed to covalent bonding of the polymer with the glass surface through the free radical initiator.

Acknowledgements

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