

Ultrahydrophobic Textile Surface via Decorating Fibers with Monolayer of Reactive Nanoparticles and Non-fluorinated Polymer

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Supplementary Information for general experimental details:

Fluorescence Labeling of the PGMA:

Poly (glycidyl methacrylate) (PGMA, $M_n = 382000$ g/mol, PDI = 2.5) was synthesized by free radical polymerization of glycidyl methacrylate in methyl ethyl ketone (MEK, Mallinckrodt Chemicals) and purified by multiple precipitations from MEK solution using diethyl ether (VWR International). The polymer was then fluorescence labeled

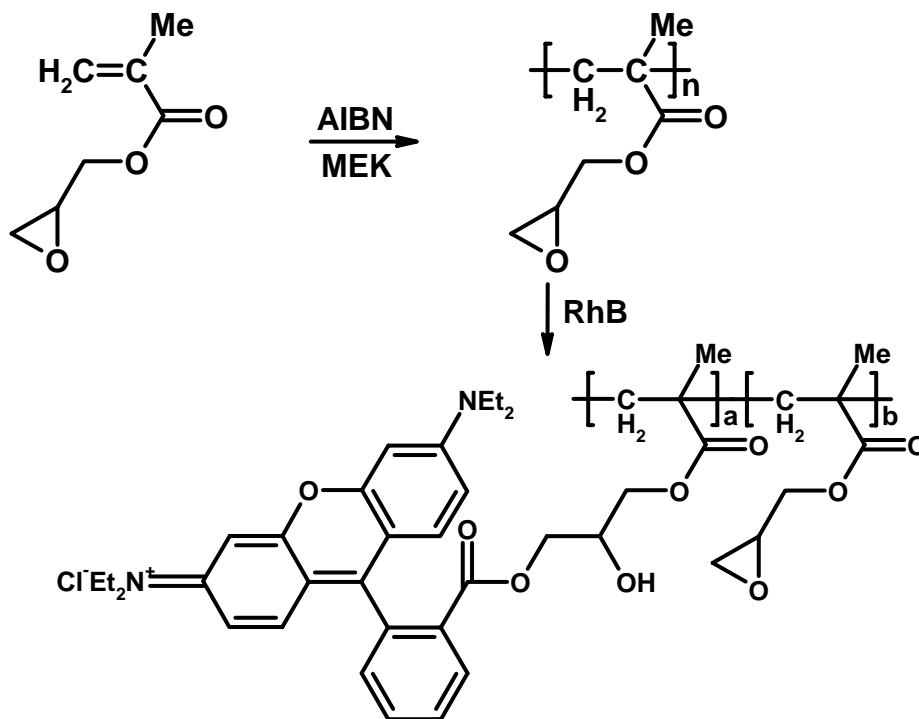


Figure 1S. Synthesis and fluorescent labeling of the PGMA macromolecular layer

with Rhodamine B (RhB, Alfa Aesar) in MEK solution (17: 1 RhB to PGMA molar ratio). The reaction was allowed to proceed for 24 hours at 70 °C. The polymer was then purified again by multiple precipitations from MEK solution using diethyl ether. The attachment of the RhB to the PGMA is expected to occur due to the reaction between the carboxyl groups present in the RhB to the available epoxy groups of the PGMA (**Figure 1S**).

Elemental analysis (Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer) demonstrated that about one of every 300 monomeric units in the PGMA chain reacted with 1 molecule of the rhodamine dye. The molecular weight of the labeled polymer was measured using Gel Permeation Chromatography (PGMA-RhB, $M_n = 402000$ g/mol, PDI = 2.2).

Functionalization of silica nanoparticles:

Bare silica particles in the form of nonporous, spherical beads with hydroxyl surface (diameter = 150 ± 30 nm, density = 1.96 g/cm³) were purchased from Polysciences, Inc. as aqueous suspension. Functionalization of the silica nanoparticles was performed using

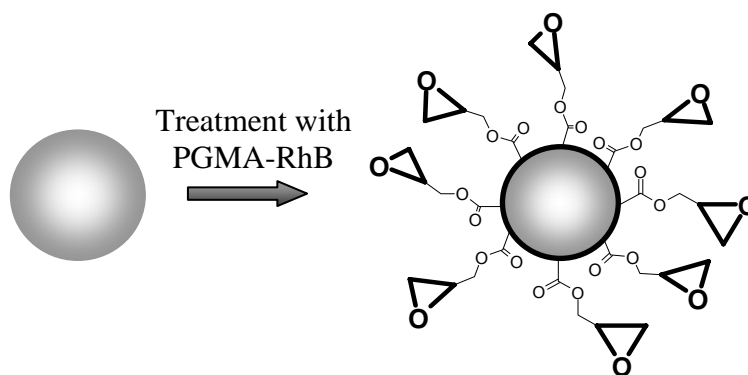


Figure 2S. Functionalization of the silica nanoparticles by treating the bare silica nanoparticles of 150 nm diameter with fluorescent labeled PGMA to create epoxidized silica nanoparticle.

5.2 wt. % (initial concentration) of silica particles in water (as received). Bare silica particles were dispersed in tetrahydrofuran (THF) by adding the aqueous suspension of the nanoparticles drop-wise into the THF solution under constant ultrasonication. Water was completely removed by several centrifuge precipitation and re-dispersing of the silica nanoparticle in THF. Thus a stable colloidal suspension of the particles in THF

(about 1 wt. %) was obtained and used for the further modification. The THF suspension containing the bare particles was injected drop-wise into 24ml of 3 wt. % PGMA-RhB solution in THF under ultrasonication. The mixture was sonicated for 1 hour and then the solvent was rotary-evaporated under a nitrogen steam. The residual was annealed in vacuum/nitrogen condition in oil bath preheated to 60 °C for 15 min. The particles were then re-dispersed in THF and purified. The purification process was repeated approximately four times to remove any ungrafted polymer from the nanoparticle (process employs a centrifugation step for the isolation of nanoparticles and ultrasound for re-dispersing in the THF solution).

The thickness of the PGMA-RhB grafted layer on the silica nanoparticle was measured using the atomic force microscopy (AFM) by depositing a diluted concentration of the functionalized nanoparticle on a clean silicon wafer (**Figure 3S**). The average diameter was found to be 157 nm (average deviation 11.0). From this the thickness of the PGMA-RhB layer was calculated to be approximately 4 nm. The thickness of PGMA-RhB layer was also verified using thermogravimetric analysis (TGA) and elemental analysis (EA). The results obtained from TGA and EA were found to be consistent with the AFM results.

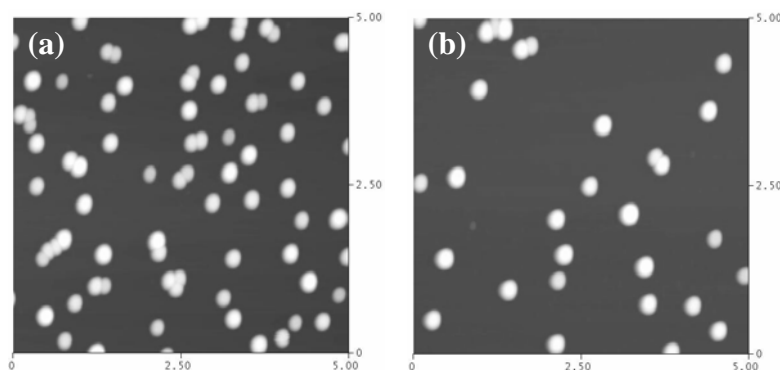


Figure 3S. AFM analysis of the bare silica nanoparticles (a) and PGMA-RhB covered silica nanoparticles(b). Vertical distance is 400 nm.

The surface coverage Γ , the PGMA-RhB chain density Σ and the surface concentration of the epoxy groups present in the functionalized silica nanoparticle (epoxy groups/nm² = ΣN , where N is the degree of polymerization) were also calculated as described by Iyer et al¹. Assuming the density of PGMA to be 1.08 gm/ cm³, the

corresponding values of Γ , Σ and the surface concentration of epoxy groups were calculated to be 4.32 mg/m², 0.006 chain/nm² and 18 epoxy groups per nm² respectively.

SEBS grafting to PGMA coated on Silicon Wafer:

The thickness of the PGMA layer on the silicon wafer was measured to be 3 ± 0.1 nm. Assuming the density of PGMA to be 1.08 gm/ cm³, the corresponding values of Γ , Σ and the surface concentration of epoxy groups were calculated to be 3.24 mg/m², 0.0067 chain/nm² and 14 epoxy groups per nm², respectively.

The PGMA covered silicon wafer was then dip coated to 1% SEBS solution prepared in toluene. After the dip coating, the wafer was annealed at 150 °C for 4 hours and later followed by several rinses of the wafer in toluene to remove any ungrafted polymer from the surface. The thickness of the SEBS layer was measured to be 10 ± 1.6 nm. Assuming the density of SEBS to be 0.905 gm/ cm³ (provided by the supplier), the corresponding values of Γ and Σ were calculated to be 9.05 mg/m² and 0.13 chain/nm² respectively. The contact angle after the SEBS grafting was measured to be $100 \pm 2^\circ$.

SEBS grafting to Polyester Film coated on Silicon Wafer:

A cleaned silicon wafer was dipcoated to 1.5 % polyester solution prepared from 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP). The polyester film (PET) was annealed at 140 °C for 2 hours and the thickness of the polyester film was measured to be 53 ± 0.5 nm. The PET film was then subjected to an alkali treatment (40 % NaOH for 2 minutes at room temperature) to generate hydroxyl and carboxylate end groups. The thickness of the PET film after the alkali treatment was found to 52 ± 0.2 nm suggesting a decrease in thickness of about less than 1 nm as compared to the PET film before the alkali treatment. The PET film coated on the silicon wafer was then dipcoated to 1% SEBS solution prepared from toluene. After the dip coating, the wafer was annealed at 150 °C for 4 hours and later followed by several rinses of the wafer in toluene to remove any ungrafted polymer from the surface. The thickness of the SEBS layer was measured to be 12 ± 4 nm. Assuming the density of SEBS to be 0.905 gm/ cm³ (provided by the supplier), the corresponding values of Γ and Σ were calculated to be 10.86 mg/m² and

0.16 chain/nm² respectively. The contact angle after the SEBS grafting was measured to be $99 \pm 5^\circ$.

In a parallel experiment the SEBS layer deposited on PET film was not annealed at 150 °C. In this case, where the reaction between maleic anhydride and hydroxyl groups on the polyester surface did not occur, the SEBS layer was removed from the substrate by the treatment with toluene.

References

¹ Iyer, K.S.; Luzinov, I.; *Macromolecules*, **2004**, *37*, 9538-9545.