

Acute Degradation of Surface-Bound Unsaturated Polyolefins in Common Solvents under Ambient Conditions

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Experimental

General. Silicon wafers were obtained from International Wafer Service (100 orientation, P/B doped, resistivity 1-10 Ωcm , thickness 450-575 μm). 5-Hexenyldimethylchlorosilane (95%, Gelest) was transferred to a custom-built Schlenk flask and stored under nitrogen. Grubbs catalysts 1st generation {benzylidene-bis(tricyclohexylphosphine)dichlororuthenium} and 2nd generation {1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene-dichloro(phenylmethylene)-(tricyclohexylphosphine)ruthenium}, 9-borabicyclo[3.3.1]nonane (9-BBN) dimer (crystalline, 98%), calcium hydride, ethyl vinyl ether, redistilled cyclooctadiene (COD), norbornene, and polybutadiene ($M_n = 1,530\text{-}2,070$ and $M_w = 420,000$ g/mol) were obtained from Sigma-Aldrich. Perchloric acid and *meta*-chloroperoxybenzoic acid (MCPBA) were purchased from Acros. Hydrogen peroxide (30%) and concentrated sulfuric acid were received from Fisher. All reagents were used as received unless specified otherwise. Dichloromethane, toluene, and tetrahydrofuran (HPLC grade, Fisher Scientific) were dried through a solvent purification system (Pure Solv, Innovative Technology, Inc.), and deoxygenated further by bubbling nitrogen gas for one hour. House-purified water (reverse osmosis) was further purified using a Millipore Milli-Q system that involves reverse osmosis, ion-exchange, and filtration steps (18.2 $M\Omega\text{cm}$).

Instrumentation. Thickness measurements were carried out using an LSE Stokes Ellipsometer. The light source is a He-Ne laser with wavelength of 632.8 nm and angle of incidence of 70° (from the normal to the plane). Thickness was calculated using the following parameters: air, $n_o = 1$; silicon oxide, silane- and polymer-derived layers, $n_o = 1.46$; silicon substrate, $n_s = 3.85$ and $k_s = -0.02$. The reported thicknesses were averages of three to five measurements taken on different areas of each sample. Contact angles were measured with a Rame-Hart telescope goniometer with a Gilmont syringe and a 24-gauge flat-tipped needle, and Milli-Q water as the probe fluid. The dynamic advancing (θ_A) and receding (θ_R) angles were recorded while the probe fluid was being added to and withdrawn from the drop, respectively. The reported contact angles were averages of three to five measurements on each sample. The contact angle measurements on all surfaces were within $\pm 2^\circ$ of the averages. Atomic force microscopy images were taken using a Veeco Metrology Dimension 3100 scanning force microscope with a silicon tip operated in tapping mode (scan rate of 0.1 Hz). Nanoscope software was used to analyze surface roughness and cross-sections. Gel permeation chromatography was carried out in tetrahydrofuran at 40 °C with a flow rate of 1 mL/min (Polymer Laboratories columns and refractive index detector, K-2301). Poly(methyl methacrylate) standards were used for molecular weight standards.

Immobilization of a Silane Monolayer. Silicon wafers were cut into 1.3 x 1.5 cm pieces and cleaned by submerging in a freshly prepared piranha solution (volume ratio of H_2SO_4 to H_2O_2 is 7:3) for 1 h. **Caution: Piranha solution reacts violently with organic matter.** The wafers were then rinsed thoroughly with water and dried in an oven at 110 °C for 30 min. Upon cooling, clean wafers were immediately placed in a custom-designed glass holder, which was transferred to a clean Schlenk flask. 25 mL of anhydrous toluene and 0.5 mL of 5-

hexenyldimethylchlorosilane were introduced to the Schlenk flask under nitrogen. Silanization was carried out at 70 °C for 16 h. The wafers were then rinsed individually with toluene (2x), ethanol, and water, and dried under reduced pressure for 1 h. Silanized silicon wafers were used within 24 h of storage in a nitrogen-filled glove box.

Attachment of Initiators and SiROMP in the Vapor Phase. In the glove box (Innovative Technology, Inc), 10 mL of COD, 0.2 g of 9-BBN and 0.25 g of CaH_2 were allowed to stir overnight in a flask before 3 mL of the mixture was transferred to a 250 mL jar. In the case of norbornene, 0.3 g of neat solid was used. Silane-functionalized silicon wafers were immersed in a solution of 1.0 mM Grubbs catalyst in dichloromethane for 20 min in the glove box; both the first and second generation catalysts were used for norbornene but only the second generation worked well for COD. The substrates were thoroughly rinsed with dichloromethane before being placed in the jar where they were suspended on a stainless steel wire mesh; there was no contact between the substrates and monomers. The jar was sealed during the polymerization reaction for a desired amount of time at room temperature. Polymerization was terminated by immersing the samples in 10 mL of dichloromethane containing 1 mL of ethyl vinyl ether for 5 min. The samples were individually rinsed with dichloromethane multiple times, either in the glove box or in a fume hood, to remove extractable oligomers and polymers.

Epoxidation of Grafted Polymers. MCPBA (0.25 g) was dissolved in anhydrous tetrahydrofuran (25 mL) in a flask. Substrates with grafted polymer were submerged in the MCPBA solution for 72 h under ambient condition or inert atmosphere before they were rinsed with tetrahydrofuran (2x) and water (3x).

Hydrolysis of Epoxidized Polymers. Following the epoxidation reaction, wafers were submerged in dilute perchloric acid solution (0.7 mL of concentrated perchloric acid in 15 mL of water) for 24 h at room temperature. The samples were then extensively rinsed with water and dried in a dessicator for 2 h.