

An Efficient Approach to Surface-Initiated Ring-Opening Metathesis Polymerization of Cyclooctadiene

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Supporting Information

Experimental Section

Materials. Silicon wafers were obtained from International Wafer Service (100 orientation, P/B doped, resistivity 1-10 \square cm, thickness 450-575 \square m). Norbornenyltriethoxysilane (Gelest) was transferred to a custom-built Schlenk flask and stored under nitrogen. Hydrogen peroxide (30%) and concentrated sulfuric acid were used as received from Fisher. 1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylene-dichloro(phenylmethylene)-tricyclohexylphosphine)ruthenium (Grubbs catalyst - 2nd generation), 9-borabicyclo[3.3.1]nonane (9-BBN) dimer (crystalline, 98%), heptafluorobutyryl chloride (HFBC), redistilled cyclooctadiene (COD), and norbornene were obtained from Aldrich and used as received. Perchloric acid, bromine, carbon tetrachloride, and *meta*-chloroperoxybenzoic acid (MCPBA) were purchased from Acros and used as received. Dichloromethane and diethyl ether were dried and deoxygenated through a solvent purification system (Pure Solv, Innovative

technology Inc.). 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 Ω /cm).

Instrumentation. Water contact angles of the substrates were measured with a Rame-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Dynamic advancing (θ_A) and receding (θ_R) angles were recorded while the probe fluid was added to and withdrawn from the drop, respectively. The reported contact angle data were averages from at least three different areas of each sample. Thickness information was obtained using a Microphotronics EL X-01R Ellipsometer (Ellipsometerbau GmbH). The light source is a He-Ne laser with $\lambda = 632.8$ nm and the angle of incidence (from the normal) is 70°. The values reported are averages of three to five measurements made on different areas of each sample. X-ray photoelectron spectra (XPS) were recorded with a Physical Electronics Quantum 2000 ESCA Microprobe with Al K α excitation. Spectra were obtained at two take-off angles, 15° and 75° (between the plane of the surface and the entrance lens of the detector optics). Each reported XPS value is an average of at least three experimental data points. The topographic images of substrates were acquired with a Veeco Dimension 3100 Scanning Probe Microscope in tapping mode. A cantilever with a phosphorus (n) doped silicon tip purchased from Veeco was used. The images were collected with a scan rate of 0.1 Hz.

Cleaning of Silicon Substrates. Silicon wafers were cut into 1.3 x 1.5 cm pieces. Two different procedures were used to clean the substrates. Some substrates were dusted with compressed air, rinsed with reverse-osmosis water, and dried in a clean oven at 110 °C for 30 min. Others were submerged in a piranha solution (H₂SO₄:H₂O₂ = 7:3, **CAUTION: piranha reacts violently with organic matter**) for 1 h and thoroughly rinsed with Milli-Q water before the final drying step. Thickness of the native silicon dioxide is around 22 Å.

Attachment of Norbornenyl Groups. Norbornenyltriethoxysilane (~0.5 mL) was transferred to a clean and dry Schlenk flask under nitrogen. Clean silicon wafers were placed in a custom-designed glass holder and introduced to the Schlenk flask with no contact between the substrates and the silane. The flask was then closed and heated in an oil bath at 70 °C for 16 h. After silanization, wafers were rinsed with toluene thoroughly and dried under a gentle stream of nitrogen.

Immobilization of Initiators and SiROMP in the Vapor Phase. In a glove box, COD (8 mL), calcium hydride (1.0 g), and 9-BBN (0.4 g) were introduced to a flask and kept overnight before 1 mL of the mixture was transferred to a Schlenk flask. Meanwhile, a sample containing norbornenyl groups was immersed in a solution of Grubbs (II) (41 mg of Grubbs II catalyst in 1.0 mL of dichloromethane) for 20 min before the substrate was rinsed thoroughly with dry dichloromethane. This substrate was then placed in a glass holder and introduced to the Schlenk flask containing the COD mixture; there was no contact between the sample and the reaction mixture. The flask was sealed, removed from the glove box, and heated in an oil bath at 70 °C for a desired amount of time. The sample was then soaked in 4 mL of dichloromethane containing 0.2 mL of vinyl ether for 30 min before it was thoroughly rinsed with dichloromethane and dried under a gentle stream of nitrogen. The procedure used for polymerization of norbornene in the vapor phase was similar to that of COD except that 9-BBN and calcium hydride were not added to the monomer.

Labeling Double Bonds with Bromine. Silicon wafers grafted with polybutadiene films were immersed in a carbon tetrachloride solution of bromine (0.25 mL of Br₂ in 7.5 mL of CCl₄) in a Schlenk flask. The reaction was carried out at room temperature in the dark for 4 h before

the wafers were rinsed with dichloromethane and Milli-Q water and dried under a gentle stream of nitrogen.

Labeling Hydroxyl Groups with HFBC. Samples in a glass holder were suspended in a Schlenk flask containing HFBC (~0.3 mL) under nitrogen. The reaction was carried out at room temperature for 16 h. After reaction, the samples were thoroughly rinsed with toluene and dried under a gentle stream of nitrogen.

Epoxidation of Grafted Polybutadiene. MCPBA (0.15 g) was dissolved in diethyl ether (3 mL). Samples grafted with PBd films were maintained in the solution for 24 h at room temperature before they were removed and rinsed with copious amounts of diethyl ether and Milli-Q water.

Hydrolysis of Epoxidized Polybutadiene. After epoxidation, wafers were immersed in a perchloric acid aqueous solution (0.7 mL of concentrated perchloric acid in 15 mL of Milli-Q water) for 24 h at 90 °C. After the reaction, the samples were thoroughly rinsed with Milli-Q water and dried under a gentle stream of nitrogen.