Supporting Information for “Surface-Initiated Polymerization of Perfluoro-n-alkynorbornenes from Gold Substrates” by Faulkner et. al.

Polymerization Kinetics of pNBF8.
Films of pNBF8 were grown from gold surfaces by utilizing SI-ROMP. A HOC₄S/Au SAM was treated with trans-3,6-endo-methylene-1,2,3,6-tetrahydrophthaloyl chloride, a norbornene with pendant acid chlorides in the 4 and 5 positions, to produce an ester-linked norbornene group on the surface. The resulting surface was made catalytically active for ROMP by exposure to Grubbs 2nd generation catalyst. Subsequent exposure to 0.5 M NBF8 in dichloromethane (DCM) resulted in the growth of partially fluorinated polymer films from the surface in times ranging from 0 – 30 min. As depicted in Figure S1, the polymerization rate of NBF8 is fast resulting in thick films in as little as ~15 min. Polymerizations that exceeded 15 min did not result in thicker films as coupling and backbiting competes with metathesis and can actually result in decreased film thicknesses as observed by us and others.¹ ²

RAIRS of Drop-Cast pNBF10. A drop-cast film of pNBF10 was prepared utilizing ROMP in solution. Grubbs 2nd generation catalyst was added to 0.5 M NBF10 in dichloromethane at room temperature and polymerized for 30 min. The resulting polymer was cast onto a gold-coated silicon wafer and dried under vacuum for 24 h. RAIRS utilizes inherent
surface selection\textsuperscript{3} such that the intensity for a given mode in the IR spectrum is proportional to the square of the component of its dynamic dipole moment oriented along the surface normal. Due to the helical structure of fluoroalkyl chains, two types of CF\textsubscript{2} stretching peaks are expected in the IR: those lying along the helical axis ($\nu_{\text{ax}}$CF\textsubscript{2}, 1300-1400 cm\textsuperscript{-1}) and those perpendicular to the helical axis ($\nu_{\text{pd}}$CF\textsubscript{2}, 1100-1300 cm\textsuperscript{-1}).\textsuperscript{4-6} Figure S2 displays the RAIR spectrum for a drop cast film of pNBF10 where the absorbance of $\nu_{\text{pd}}$CF\textsubscript{2} to $\nu_{\text{ax}}$CF\textsubscript{2} is nearly equal. Thus, the orientation of fluorocarbon chains within polymer films grown from a surface can be determined if the ratios of $\nu_{\text{pd}}$CF\textsubscript{2} to $\nu_{\text{ax}}$CF\textsubscript{2} differs from 1. For films where $\nu_{\text{pd}}$CF\textsubscript{2} to $\nu_{\text{ax}}$CF\textsubscript{2} is $>>$ 1, the fluorocarbon chains are generally oriented parallel to the surface. However, if $\nu_{\text{pd}}$CF\textsubscript{2} to $\nu_{\text{ax}}$CF\textsubscript{2} is $<<$ 1, the fluorocarbon chains are primarily oriented normal to the surface.

**Solvent Effects on Film Growth.** To demonstrate the effect of solvent on SI-ROMP of NBF\textsubscript{n}, we grew pNBF4 and pNBF8 films in a variety of solvents and compared them to films grown in DCM. pNBF4 and pNBF8 films were prepared by exposure of Grubbs II-modified surfaces to 250 mM and 50 mM solutions, respectively, for 5 min. We observed little to no pNBF4 and pNBF8 film growth in chloroform or 1,2-dichloroethane, two halogenated solvents that are similar to DCM, although these solvents appear to solvate the monomers very well. However, pNBF4 films grown in 2,2,2-trifluoroethanol and 1,2,4-trichlorobenzene were
comparable to those grown in DCM. pNBF8 films grew only in 1,2,4-trichlorobenzene but were much thinner than pNBF8 films prepared in DCM. Others have also observed that ROMP performed in solvents with stronger polarity, such as DCM, are more effective and have faster turn-over rates than less polar solvents.\(^7\) For the SI-ROMP of pNBFn films, DCM appears to be an optimal solvent because of its significant polarity and capacity to solvate fluorinated species.

**Experimental Details.** Reflectance absorption infrared spectroscopy (RAIRS) was performed using a Varion Excalibur FTS-3100 infrared spectrometer. The p-polarized light was incident at 80° from the surface normal. The instrument was run in single reflection mode and equipped with a universal sampling accessory. A liquid-nitrogen-cooled, narrow-band MCT detector was used to detect reflected light. Spectral resolution was 2 cm\(^{-1}\) after triangular apodization. Each spectrum was accumulated over 400 scans using a deuterated octadecanethiol-\(d_{37}\) self-assembled monolayer on gold as the background.

Ellipsometric thicknesses were determined from a J.A. Woollam M-2000DI variable angle spectroscopic ellipsometer. Thicknesses and refractive indices were fit to data taken at 75° from the surface normal over wavelengths from 400 to 700 nm. Optical constants of the underlying gold used in the preparation of each sample were taken prior to polymer film deposition and used as a baseline for thickness measurements. Reported thickness values and errors represent the averages and standard deviations, respectively, from at least 3 different films. pNBFn film thicknesses greater than 100 nm were determined using a Veeco Dektak 150 surface profiler. Scanning electron micrographs were collected using a Raith eLINE electron beam lithography tool in image mode using an accelerating voltage of 10.0 kV, and a working distance of 10 mm.
References