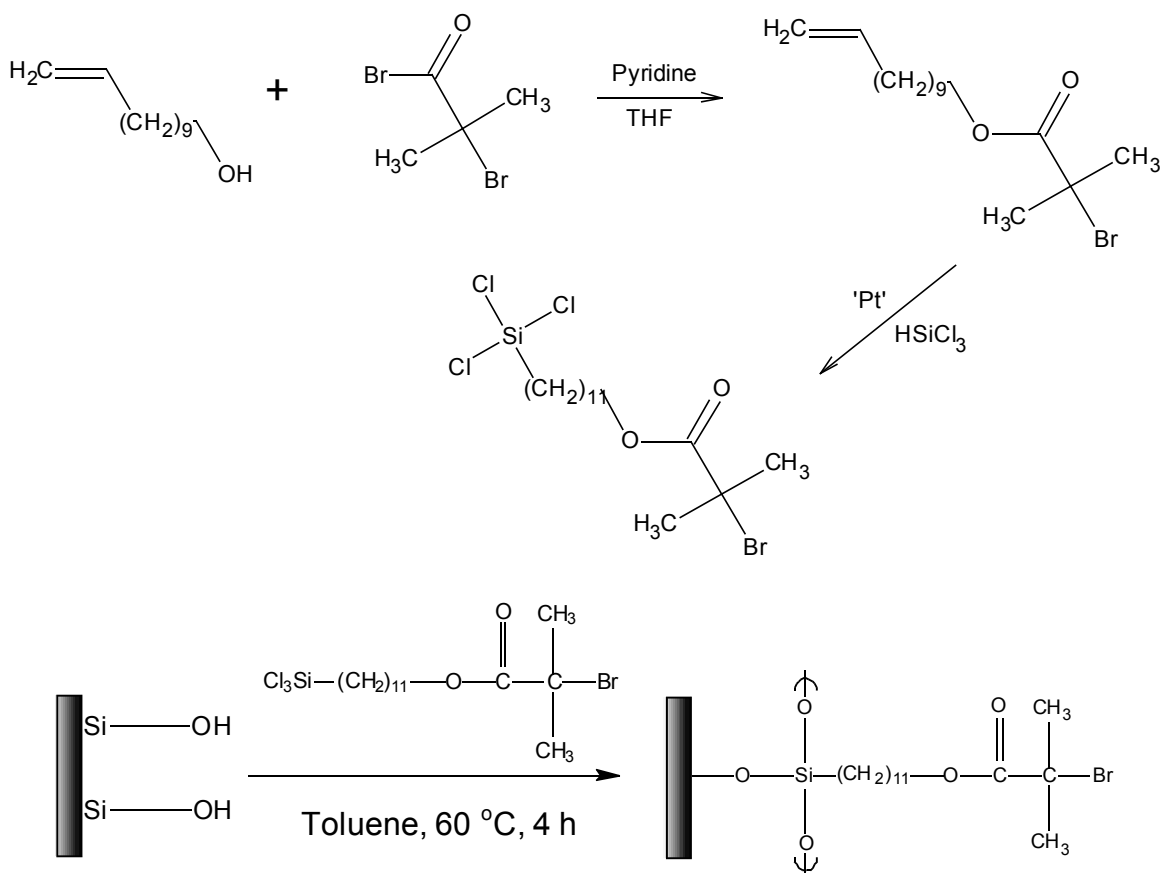


Synthesis and Deposition of (11-(2-Bromo-2-methyl)propionyloxy)undecyltrichlorosilane

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1. Procedure

a. 10-Unden-1-yl 2-Bromo-2-methylpropionate³

2-Bromoisobutyryl bromide (6.8 mL, 55 mmol) was added drop-wise to a stirred solution of ω -undecylenyl alcohol (10 mL, 53 mmol) and pyridine (4.8 mL, 59 mmol) in dry tetrahydrofuran (THF) (50 mL). The mixture was stirred at room temperature overnight (Note 1) followed by dilution with hexane (100 mL). The mixture was then washed once with 2 N HCl and twice with water. The organic phase was dried over anhydrous sodium sulfate for 6 h and filtered. The solvent was removed from the filtrate under reduced pressure and the residue was purified by flash column chromatography using silica gel as the stationary phase and hexane/ethyl acetate (25/1 v/v) as the eluent. The solvent was then removed *in vacuo* to give a yield of 12.87 g (77%) of 10-undecen-1-yl 2-bromo-2-methylpropionate as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ : 1.23-1.37 (br m, 12H); 1.63-1.70 (m, 2H); 1.93 (s, 6H); 2.03-2.07 (q, 2H); 4.14-4.18 (t, 2H); 4.91-5.02 (m, 2H); 5.78-5.86 (complex m, 1H) ppm.

*b. (11-(2-Bromo-2-methyl))propionyloxy)undecyltrichlorosilane*³

To a solution of 10-undecen-1-yl 2-bromo-2-methylpropionate (11.54 g, 36 mmol) in trichlorosilane (25 mL, 250 mmol) was added a 1:1 (v/v) ethanol/diethyl ether solution of chloroplatinic acid, H₂PtCl₆ (110 mg, 5 mL). The mixture was gently refluxed at 40°C for 4 h. Excess trichlorosilane was removed under reduced pressure followed by dilution with CH₂Cl₂ (Note 2). The solution was then filtered through a short column of anhydrous magnesium sulfate followed by removal of solvent under reduced pressure. The product, 13.73 g (84%), was then used without further purification. ¹H NMR (300 MHz, CDCl₃) δ: 1.28-1.44 (br m, 16H); 1.56-1.73 (m, 4H); 1.93 (s, 6H); 4.15-4.19 (t, 2H) ppm.

c. Deposition of (11-(2-Bromo-2-methyl))propionyloxy)undecyltrichlorosilane

Into a dried 20 mL round-bottom flask was placed a freshly cleaned silicon wafer and ATR crystal and the flask was sealed with a septum. Dry toluene (10 mL) and a 25wt-% solution of initiator in toluene (0.15 mL (Note 3)) were added to the flask via syringe and the flask was heated at 60°C for 4 h. The silicon wafer and ATR crystal were then removed and sequentially washed with toluene, CH₂Cl₂ and ethanol; and then dried in a stream of air. The ATR-FTIR spectrum of deposited (11-(2-bromo-2-methyl))propionyloxy)undecyltrichlorosilane is given in Figure 3. The peaks at 2853 and 2925 cm⁻¹ were assigned to the CH₂ stretching and C-H stretching vibration, respectively. The peak at 1736 cm⁻¹ was assigned to the carbonyl stretching vibration of the ester group. The contact angles, determined using high purity HPLC water, were $\theta_{\text{advancing}} = 87^\circ$ and $\theta_{\text{receding}} = 74^\circ$ (Note 4). The thickness of deposited (11-(2-bromo-2-methyl))propionyloxy)undecyltrichlorosilane was determined by ellipsometry and was typically 1.9 ± 0.3 nm (Note 5). [See Note 6 and Figure 4 for potential side reaction observation].

2. Characterization

ATR-FTIR spectra were recorded using a Nicolet System 730 spectrometer using a modified 4XF beam condenser (Harrick Scientific). Spectra were recorded at 2 cm⁻¹ resolution and 500 scans were collected. Contact angles were determined using a Ramé-Hart NRL-100 contact angle goniometer equipped with an environmental chamber and tilting base mounted on a vibrationless table (Newport Corp.). Advancing and receding values were determined using the tilting stage method at an angle of 35°. Drop volumes were 10 μ L. Ellipsometric measurements were performed on a Gaertner model L116C ellipsometer with He-Ne Laser ($\lambda = 632.8$ nm) and a fixed angle of incidence of 70°. For calculation of the layer thickness, refractive indices of $n = 1.455$ (for silicon oxide)⁴ and $n = 1.508$ (for the initiator layer) were used. ¹H NMR spectra (δ , ppm) were recorded on a Bruker AM-300 (300 MHz) spectrometer in CDCl₃.

3. Notes

1. The reaction flask was covered with aluminum foil to reduce the exposure to light.
2. A bulb-to-bulb distillation technique, with a slightly reduced pressure, was used due to the low boiling point of trichlorosilane ($\sim 37^\circ\text{C}$). CAUTION – The large excess of trichlorosilane may cause the solution to “bump” over into the collection flask. Be sure to include a stir bar in the solution to aid in the boiling of the trichlorosilane. Also, leaving the catalyst (which has a tendency to precipitate out), acts to aid in trichlorosilane removal.
3. Rather than storing raw trichlorosilane initiator, the initiator was diluted with distilled toluene to afford a 25% w/w solution. The solution was wrapped in aluminum foil to reduce light exposure, and stored in a chemical freezer.
4. Variation in contact angles is typically $\pm 2^\circ$ for $\theta_{\text{advancing}}$ and $\pm 3^\circ$ for θ_{receding} with hysteresis (the difference between the two measurements) of $12^\circ \pm 2^\circ$.
5. Theoretical thickness for initiator layer, assuming no vertical or horizontal crosslinking and a 10° tilt angle, was calculated to be 2.02 nm based on standard bond angles and lengths.
6. Occasionally, during the deposition of the initiator, a peak at 2250 cm^{-1} that varies in relative intensity appears (Figure 2). This has been attributed to the appearance of Si-H species. The appearance of this species tends to lower the overall initiator layer thickness and affects the initiating capability of the deposited initiator. Removing the excess trichlorosilane first and using repeated reduced-pressure distillations during the initiator synthesis can remove the Si-H peak entirely.

4. References

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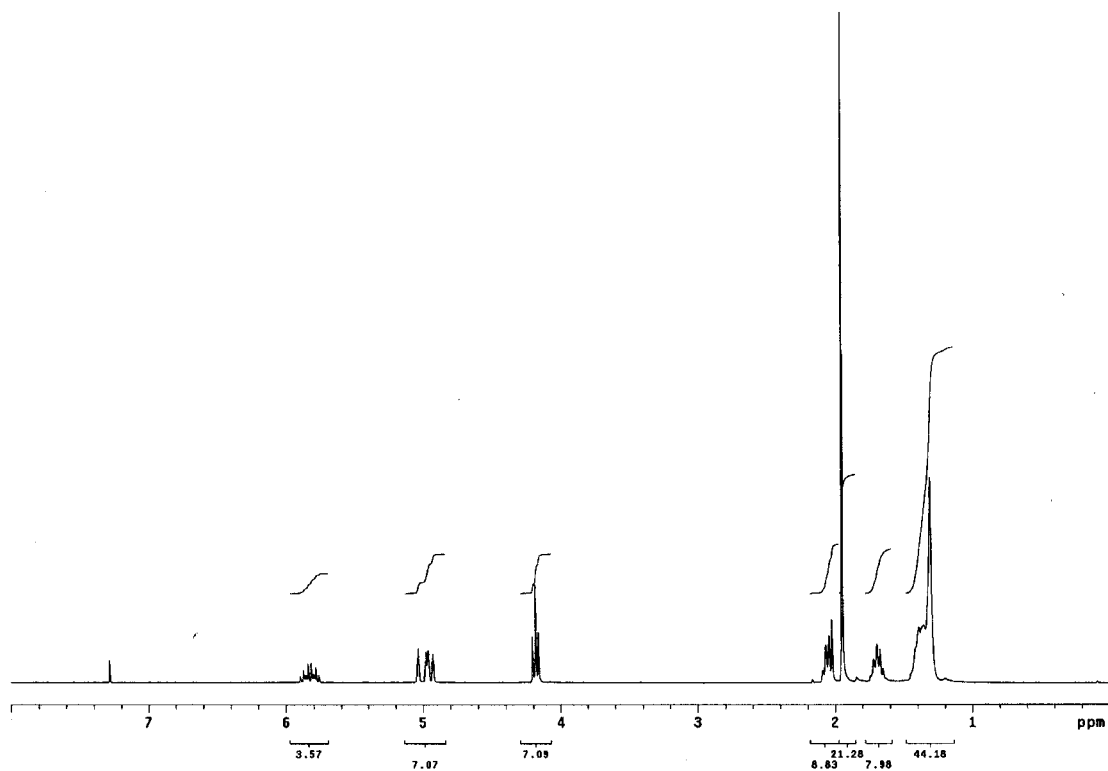


Figure 1. ¹H NMR spectrum of 10-unden-1-yl 2-bromo-2-methylpropionate

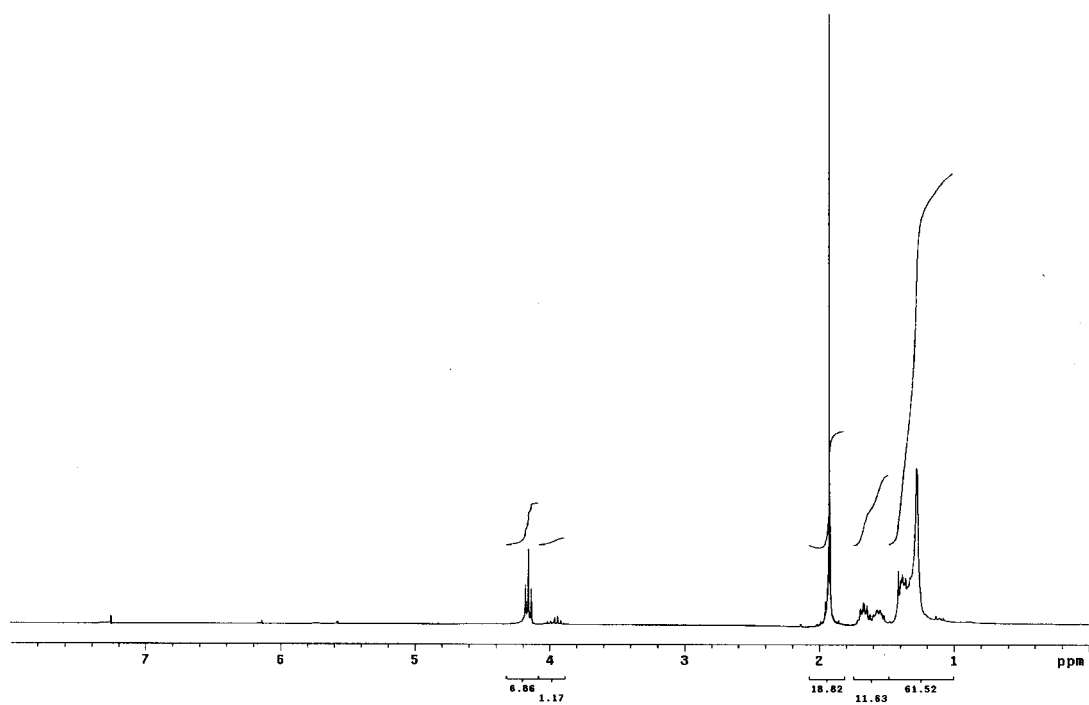


Figure 2. ¹H NMR spectrum of (11-(2-bromo-2-methyl)propionyloxy)undecyltrichlorosilane

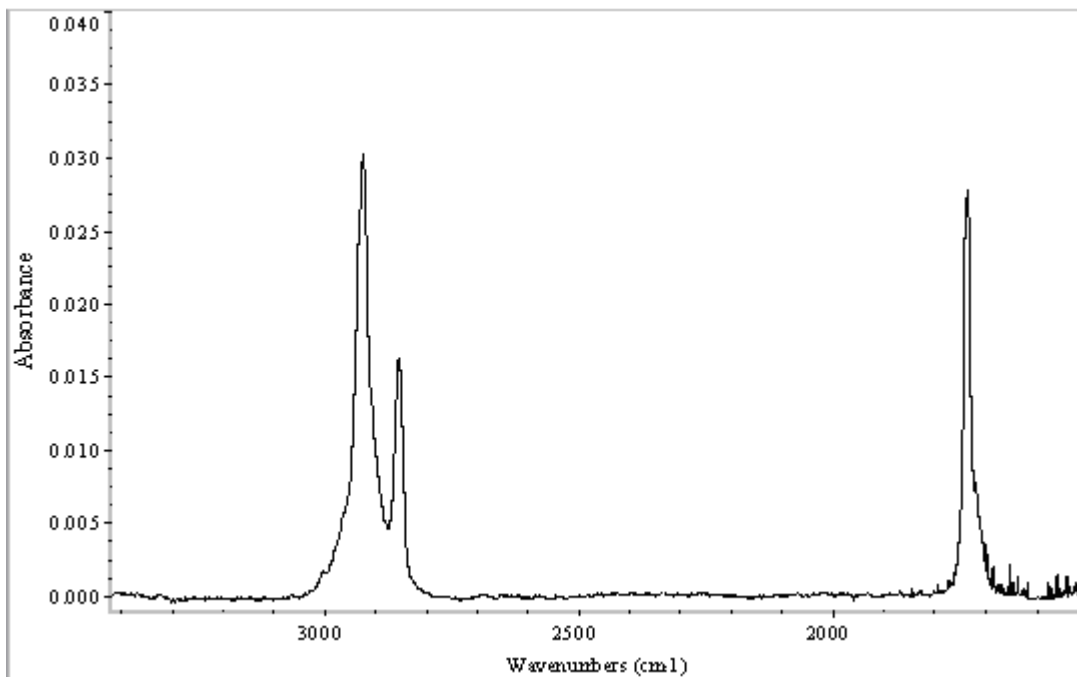


Figure 3: ATR-FTIR Spectrum of deposited (11-(2-bromo-2-methyl)propionyloxy)undecyltrichlorosilane

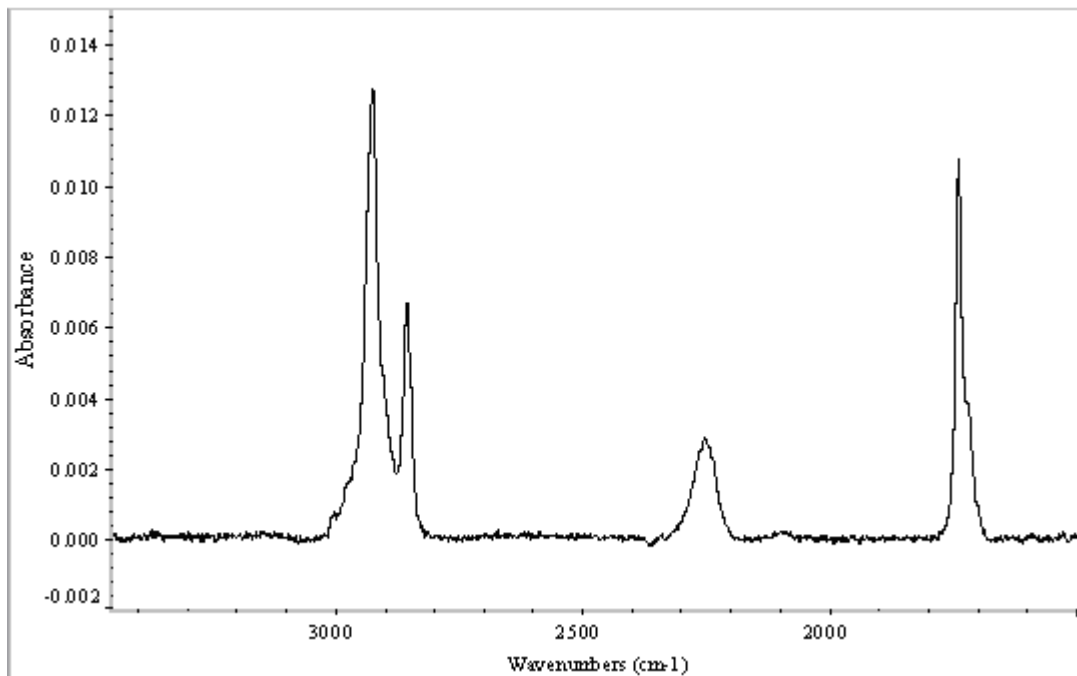


Figure 4: ATR-FTIR Spectrum of deposited (11-(2-Bromo-2-methyl)propionyloxy)undecyltrichlorosilane containing Si-H impurity