

Supplemental Information

Side Chain Length Impacting Thermal Transitions and Water Uptake of Acrylate-Maleimide Copolymers with Pendent Catechols

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General Methods

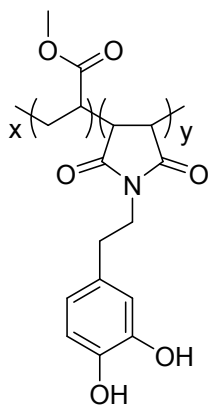
All ^1H NMR spectra were performed on a Bruker 400 MHz Avance III HD magnet. **PAMs-1-5** were referenced to acetone at 2.05 ppm, however monomer **1** was taken in CDCl_3 and referenced to tetramethylsilane at 0 ppm; ^{13}C NMR was referenced to chloroform at 77.23 ppm. Prior to use, azobisisobutyronitrile (AIBN) was recrystallized from methanol and all acrylates were sent through a basic alumina plug (58-60 Å mesh from Alfa Aesar) to remove their respective free radical inhibitor. DSC and TGA-MS experiments were performed using the Discovery-series systems from TA Instruments.

Gel Permeation Chromatography

Molecular weights of silyl protected **PAM-1-5** were determined on a Waters® system utilizing a refractive index detector and three 700 x 7.8 mm Phenogel® columns held at 40 °C: 10^5 Å, 10^3 Å and 100 Å. Mobile phase was unstabilized THF pumped at 1 mL / min. Samples (dissolved in THF at 1g / L) were injected into the system (50 µL) three times. Reported molecular weights are based on calibration curve from narrow molecular weight polystyrene standards (1000 kDa, 501.5 kDa, 97.2 kDa, 51 kDa, 10 kDa, 5.05 kDa, 1.7 kDa) injected intermittently with the samples.

General polymerization procedure

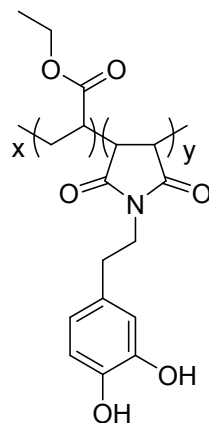
In a septa sealed vial, **1** (1 equiv) was mixed with its respective acrylate (1 equiv) and dissolved in 1,2-dichloroethane. A stock solution (15-30 mg / 1 mL) of AIBN in 1,2-dichloroethane was freshly prepared before each reaction and the proper amount (0.002 equiv) was introduced to the solution. The reaction was purged with nitrogen for 20-30 min and then heated to 85 °C overnight (12-18 h) under a positive nitrogen pressure. The polymerization was then quenched with cold methanol, shaken vigorously and decanted off (×3). The silyl protected polymer was then redissolved in minimal amounts of THF and 2 mL of conc. HCl (37%) was added dropwise and allowed to stir for 30 min. The mixture was precipitated into hexanes and decanted (×2). The polymer precipitate was redissolved in THF and was further precipitated into water (×3) to remove excess acid until the pH was at 6-7. The polymers were then dried under vacuum (0.17 Torr) for 4-5 hours to afford off white solids.



PAM-1

Poly(methacrylate)-*co*-1-[2-(3,4-dihydroxyphenyl)ethyl]-maleimide (PAM-1).

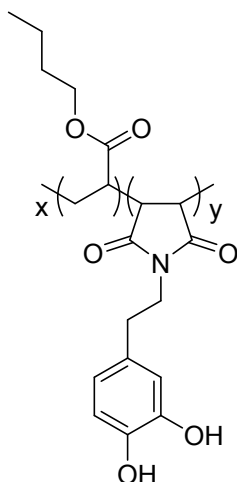
Compounds **1** (2.358 g, 5.107 mmol), AIBN (0.1303 M, 78.9 μ L, 0.01028 mmol), methyl acrylate (0.440 g, 5.107 mmol) were dissolved in 1,2-dichloroethane (1 mL) and subject to the general polymerization procedure. The product was isolated via precipitation to afford **PAM-1** (1.097 g) as an off white solid in 67 % yield ($x : y$, 53 : 47). $^1\text{H NMR}$ (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 7.80-7.65 (Ar-OH), 6.73 (Ar-H), 6.55 (Ar-H), 3.66 (-CH₃ and Ar-CH₂-CH₂-NR₂), 2.70 (Ar-CH₂-CH₂-NR₂). GPC (THF at 40 °C): $M_n = 114$ kDa, $M_w = 291$ kDa, PDI = 2.55.



PAM-2

Poly(ethylacrylate)-*co*-1-[2-(3,4-dihydroxyphenyl)ethyl]-maleimide (PAM-2).

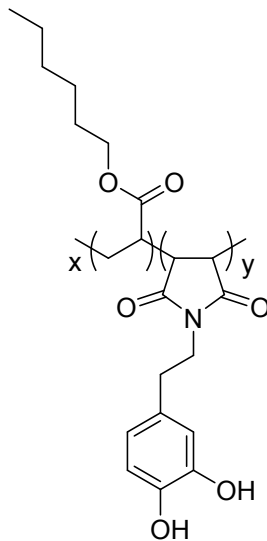
Compounds **1** (2.003 g, 4.338 mmol), AIBN (0.1365 M, 63.5 μ L, 0.008676 mmol), ethyl acrylate (0.434 g, 4.338 mmol) were dissolved in 1,2-dichloroethane (1 mL) degassed and subject to the general polymerization procedure. The product was isolated via precipitation to afford **PAM-2** (1.277 g) as an off white solid in 88% yield ($x : y$, 52 : 48). $^1\text{H NMR}$ (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 7.79-7.56 (Ar-OH), 6.73 (Ar-H), 6.56 (Ar-H), 4.15 (CO₂-CH₂-CH₃), 3.60 (Ar-CH₂-CH₂-NR₂), 2.70 (Ar-CH₂-CH₂-NR₂), 1.24 (-CH₃). GPC (THF at 40 °C): $M_n = 136$ kDa, $M_w = 513$ kDa, PDI = 3.81.



PAM-3

Poly(butylacrylate)-*co*-1-[2-(3,4-dihydroxyphenyl)ethyl]-maleimide (PAM-3).

Compounds **1** (2.177 g, 4.715 mmol), AIBN (0.1278 M, 73.8 μ L, 0.00943 mmol), butyl acrylate (0.535 g, 4.715 mmol) were dissolved in 1,2-dichloroethane (1 mL) degassed and subject to the general polymerization procedure. The product was isolated via precipitation to afford **PAM-3** (1.398 g) as an off white solid in 93% yield ($x : y$, 53 : 47). $^1\text{H NMR}$ (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 7.71 (Ar-OH), 6.74 (Ar-H), 6.56 (Ar-H), 4.11($\text{CO}_2\text{-CH}_2\text{-CH}_3$), 3.60 (Ar- $\text{CH}_2\text{-CH}_2\text{-NR}_2$), 2.70 (Ar- $\text{CH}_2\text{-CH}_2\text{-NR}_2$), 1.63 ($-\text{CH}_2-$), 1.40 ($-\text{CH}_2-$), 0.92 ($-\text{CH}_3$). GPC (THF at 40 $^\circ\text{C}$): $M_n = 134$ kDa, $M_w = 513$ kDa, PDI = 3.85.

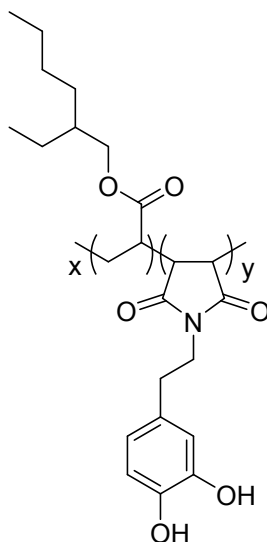


PAM-4

Poly(hexylacrylate)-*co*-1-[2-(3,4-dihydroxyphenyl)ethyl]-maleimide (PAM-4).

Compounds **1** (2.014 g, 4.362 mmol), AIBN (0.1241 M, 70.3 μ L, 0.008724 mmol), hexyl acrylate (0.681 g, 4.362 mmol) were dissolved in 1,2-dichloroethane (1 mL) degassed and subject to the general polymerization procedure. The product was isolated via precipitation to afford **PAM-4** (1.243 g) as an off white solid in 73% yield ($x : y$, 53 : 47). $^1\text{H NMR}$ (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 7.69 (Ar-OH), 6.74 (Ar-H), 6.56 (Ar-H), 4.10 ($\text{CO}_2\text{-CH}_2\text{-CH}_3$), 3.60 (Ar- $\text{CH}_2\text{-CH}_2\text{-NR}_2$), 2.71 (Ar-

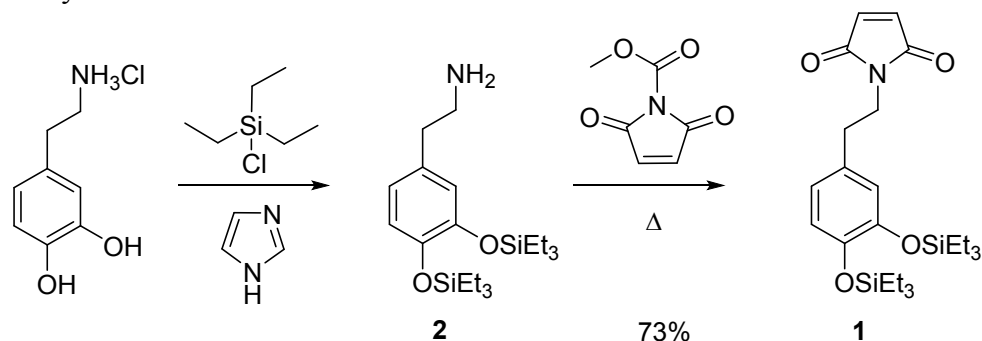
$CH_2-CH_2-NR_2$), 1.65 (-CH₂-), 1.31 ((-CH₂)₃-), 0.87 (-CH₃). GPC (THF at 40 °C): $M_n = 118$ kDa, $M_w = 384$ kDa, PDI = 3.27.



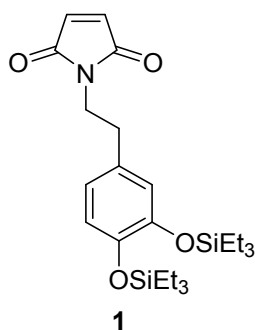
PAM-5

Poly(2-ethylhexylacrylate)-*co*-1-[2-(3,4-dihydroxyphenyl)ethyl]-maleimide (PAM-5). Compounds **1** (2.011 g, 4.355 mmol), AIBN (0.1179 M, 73.9 μ L, 0.00871 mmol), ethyl hexyl acrylate (0.803 g, 4.355 mmol) were dissolved in 1,2-dichloroethane (1 mL) degassed and subject to the general polymerization procedure. The product was isolated via precipitation to afford **PAM-5** (1.260 g) as an off white solid in 69 % yield ($x : y$, 52 : 48). ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.68 (Ar-OH), 6.74 (Ar-H), 6.56 (Ar-H), 4.05 (CO₂-CH₂-CH₃), 3.01 (Ar-CH₂-CH₂-NR₂), 2.71 (Ar-CH₂-CH₂-NR₂), 1.64 (-CH-), 1.32 (-CH₂-), 0.90 (-CH₃). GPC (THF at 40 °C): $M_n = 124$ kDa, $M_w = 278$ kDa, PDI = 2.24.

Scheme S1. Synthesis of monomer **1**.



Synthesis of monomer **1** was facile and robust. Following a similar procedure from Gademann and co workers¹, the catechol moiety of dopamine hydrochloride was protected via chlorotriethylsilane to afford 2-(3,4-bis((triethylsilyloxy)oxy)phenyl)ethanamine (**2**) in quantitative yield. In our hands, **2** discolored after a few hours so it was immediately coupled with N-methoxycarbonylmaleimide. N-methoxycarbonylmaleimide was prepared according to a previous literature procedure.²



1-(3,4-bis((triethylsilyloxy)oxy)phenethyl)-1H-pyrrole-2,5-dione (1**).** In a 500 mL round bottom flask open to the atmosphere, 2-(3,4-bis((triethylsilyloxy)oxy)phenyl)ethanamine (17.959 g, 47.049 mmol) was dissolved in CHCl₃ (300 mL) and stirred vigorously while N-methoxycarbonylmaleimide (8.028 g, 51.754 mmol) and trimethylamine (7.21 mL, 51.754 mmol) were added slowly. The reaction was allowed to stir for 30 min at room temperature and then refluxed overnight. The reaction was cooled to room temperature, quenched with water, and further extracted with chloroform (×3). The organic layer was dried with MgSO₄, filtered, and the solvent was removed via rotary evaporation to afford a red sludge. The crude mixture was then dried, packed with silica, and flushed through a silica plug with CHCl₃; the solvent was removed by rotary evaporation to afford **1** (15.860 g, 34.348 mmol) as pale yellow solid in 73% yield. ¹H NMR (400 MHz, CDCl₃) δ 6.72 (d, *J* = 8.7 Hz, 1 H), 6.62-6.59 (m, 4 H), 3.70 (t, *J* = 7.5 Hz, 2 H), 2.77 (t, *J* = 7.5 Hz, 2 H), 0.97 (dt, *J* = 7.7, 4.9 Hz, 18 H), 0.73 (dq, *J* = 7.8, 4.1 Hz, 12 H). ¹³C NMR (100 MHz, CDCl₃) 170.8, 146.9, 145.7, 134.2, 131.2, 121.9, 121.4, 120.7, 39.5, 33.9, 6.90, 6.88, 5.33, 5.29. IR (KBr, cm⁻¹): 2955, 2912, 2876, 1697, 1602, 1577, 1511, 1458, 1437, 1422, 1408, 1363, 1334, 1310, 1289, 1242, 1223, 1161, 1143, 1005. HRMS calcd for C₂₄H₃₉NO₄Si₂H⁺ [M + H]⁺, 462.2490; found, 462.2463.

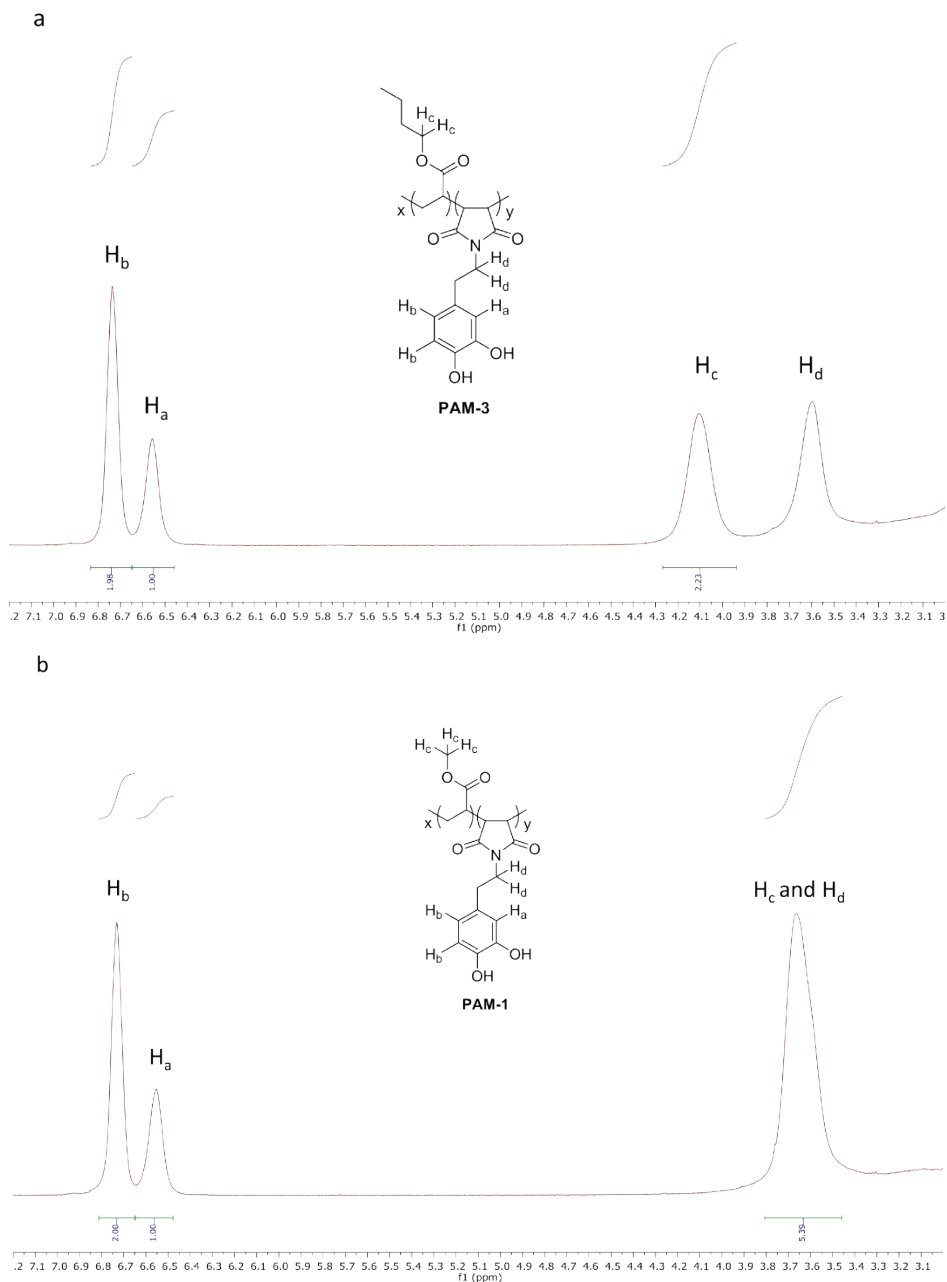


Figure S1. Determination of $x : y$ ratios for **PAMs** via ^1H NMR. (a) **PAM-3** is used as an example for **PAMs-2-5**. The acrylate (x) to maleimide (y) ratio was determined by comparing the ratio of the H_b aromatic protons to the methylene protons (H_c) alpha to the acetate as they both contain two protons. (b) The exception to this was **PAM-1** as the methyl protons from the acrylate overlap with the methylene protons from the maleimide. Hence, the sum of the aromatic protons (3.00) was compared to the difference (3.39) of H_c and H_d combined. H_a is arbitrarily set to 1 for all **PAM** integrations.

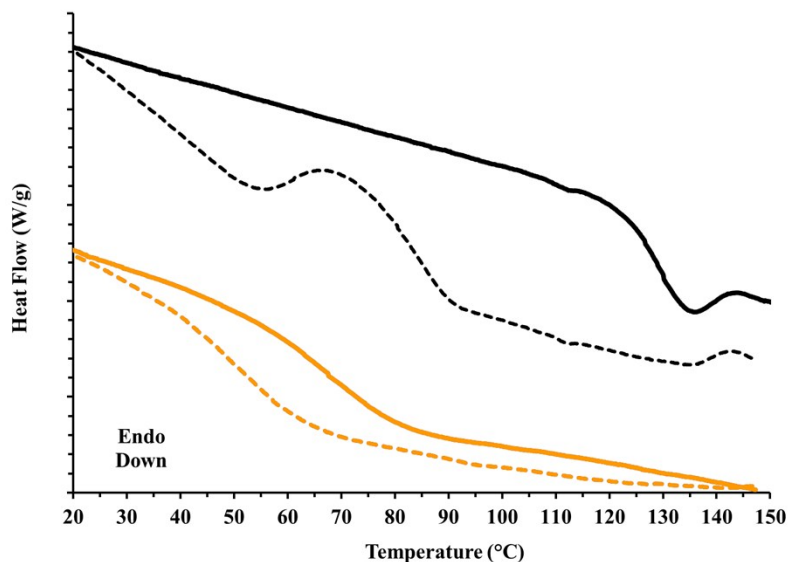


Figure S2. PAM-1 (black) and PAM-5 (yellow) DSC curves before oven (dashed lines) and after vacuum oven at 120 °C (solid lines). Exotherm at 70 °C in PAM-1 before oven (dashed line) is believed to be loosely bound water on the polymer. Shifts in T_g from wet to dry are proportional to polarity. Samples were ramped at 10 °C / min.

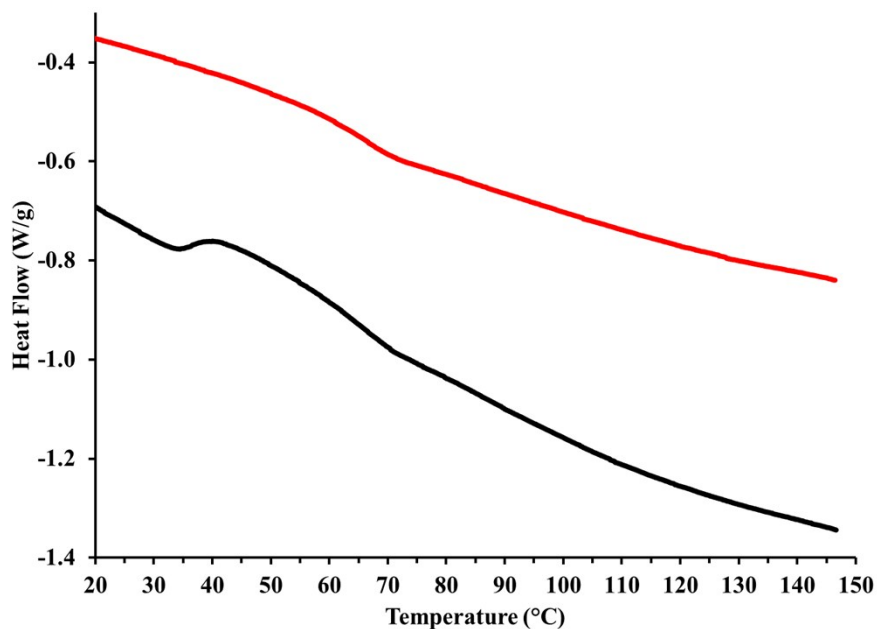
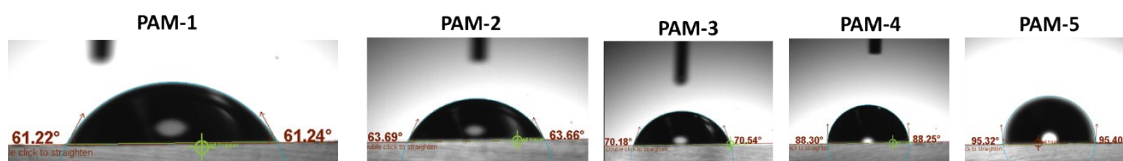


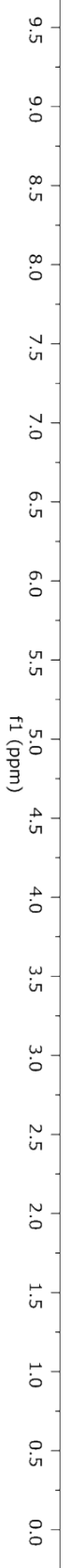
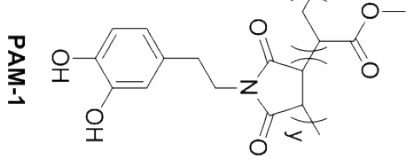
Figure S3. DSC of PAM-1 (black) and PAM-2 (red) second heat cycle after 10 days in ambient conditions. Samples were originally dried in the vacuum oven at 120 °C overnight to afford dry T_g . Samples were ramped at 10 °C / min.

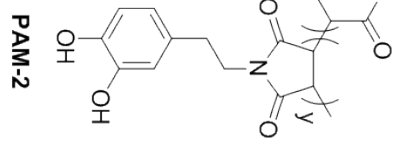
Table S1. Contact angle of **PAMs**

PAM	Contact Angle
1	60.2 ± 1.6
2	63.1 ± 1.7
3	70.8 ± 0.9
4	88.9 ± 2.1
5	93.8 ± 2.6

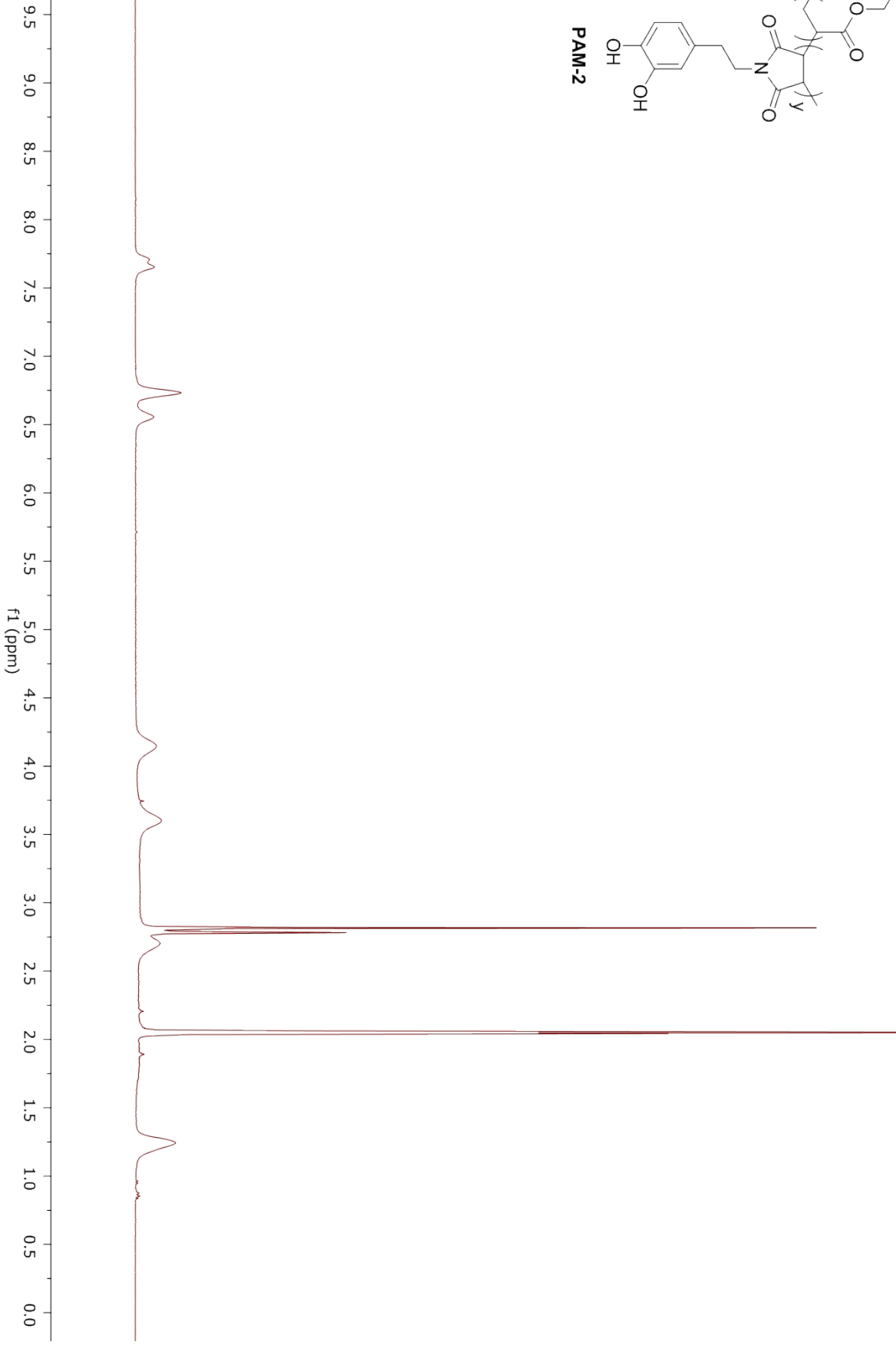


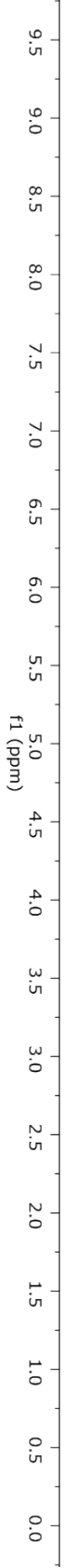
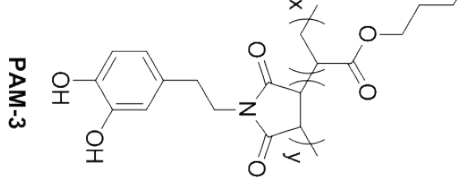
To prepare the films for contact angle measurements, ca. 50 mg of the respective **PAM** was dissolved in 1 mL of methyl ethyl ketone. Glass slides (ca. 1 x 1 in) were washed in methanol, annealed. Once the substrates were placed on the vacuum chuck 400 μ L was of the **PAM** solution was deposited down and spun at 800 rpm for 35 seconds and then ramped up to 1200 rpm for another 35 seconds. The substrates were then placed in an oven at 80 °C overnight under a nitrogen purge.

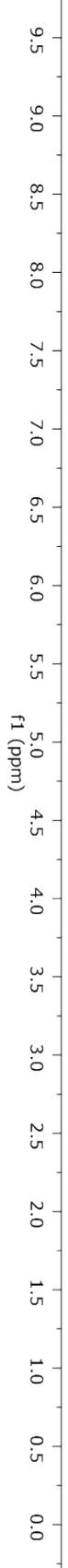
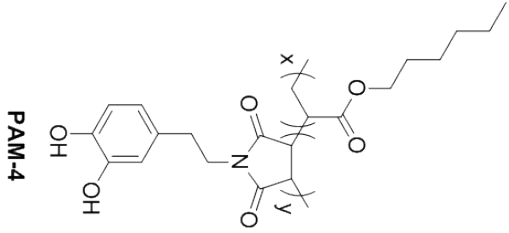


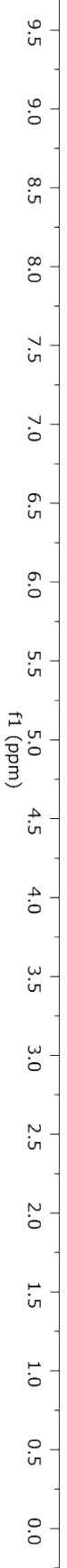
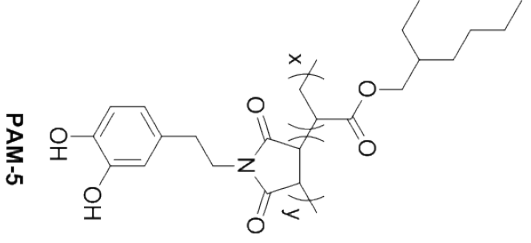


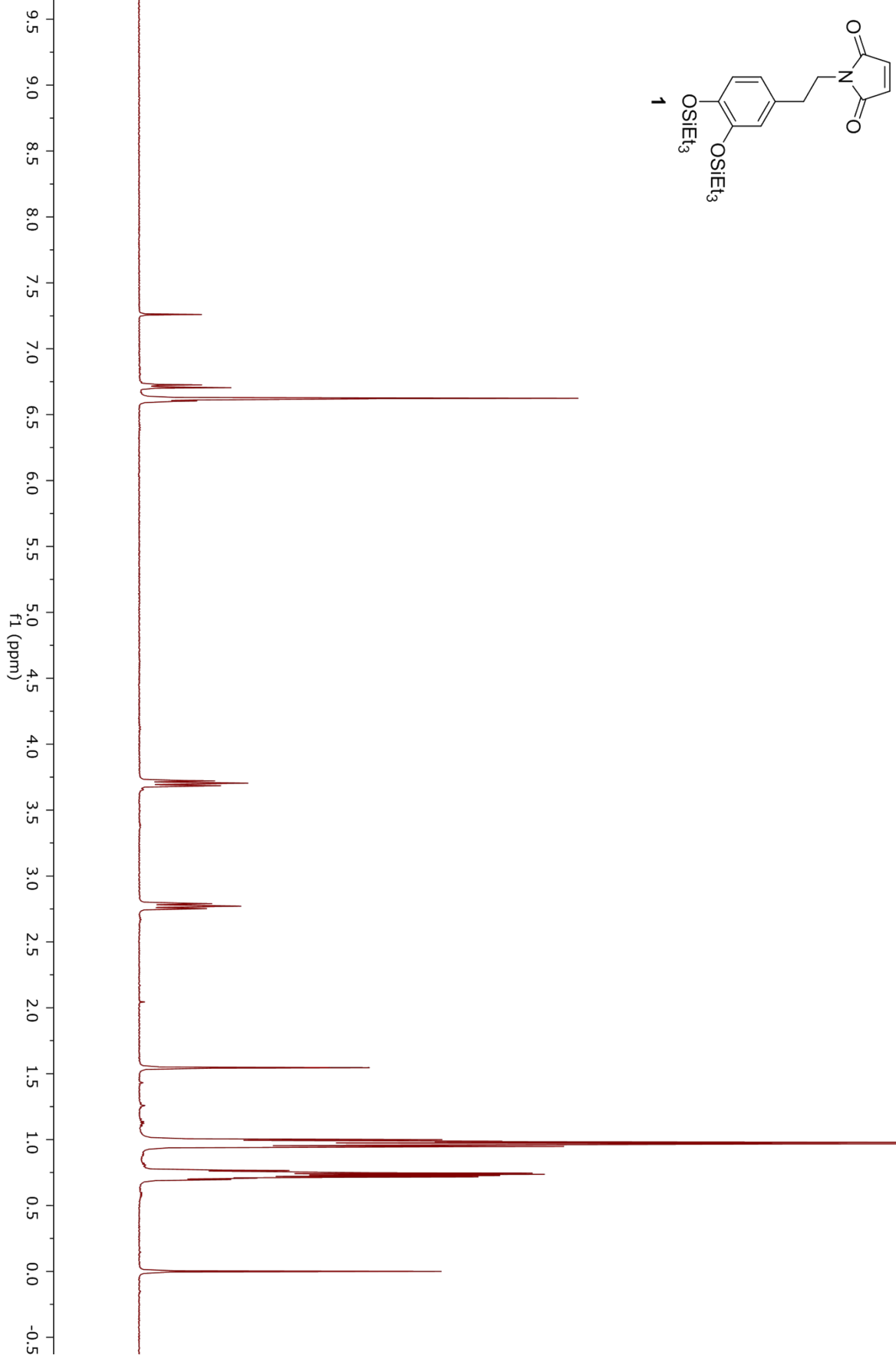
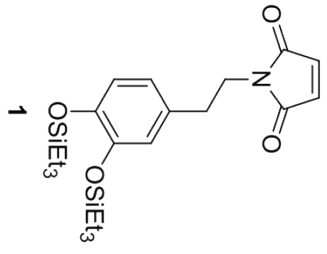
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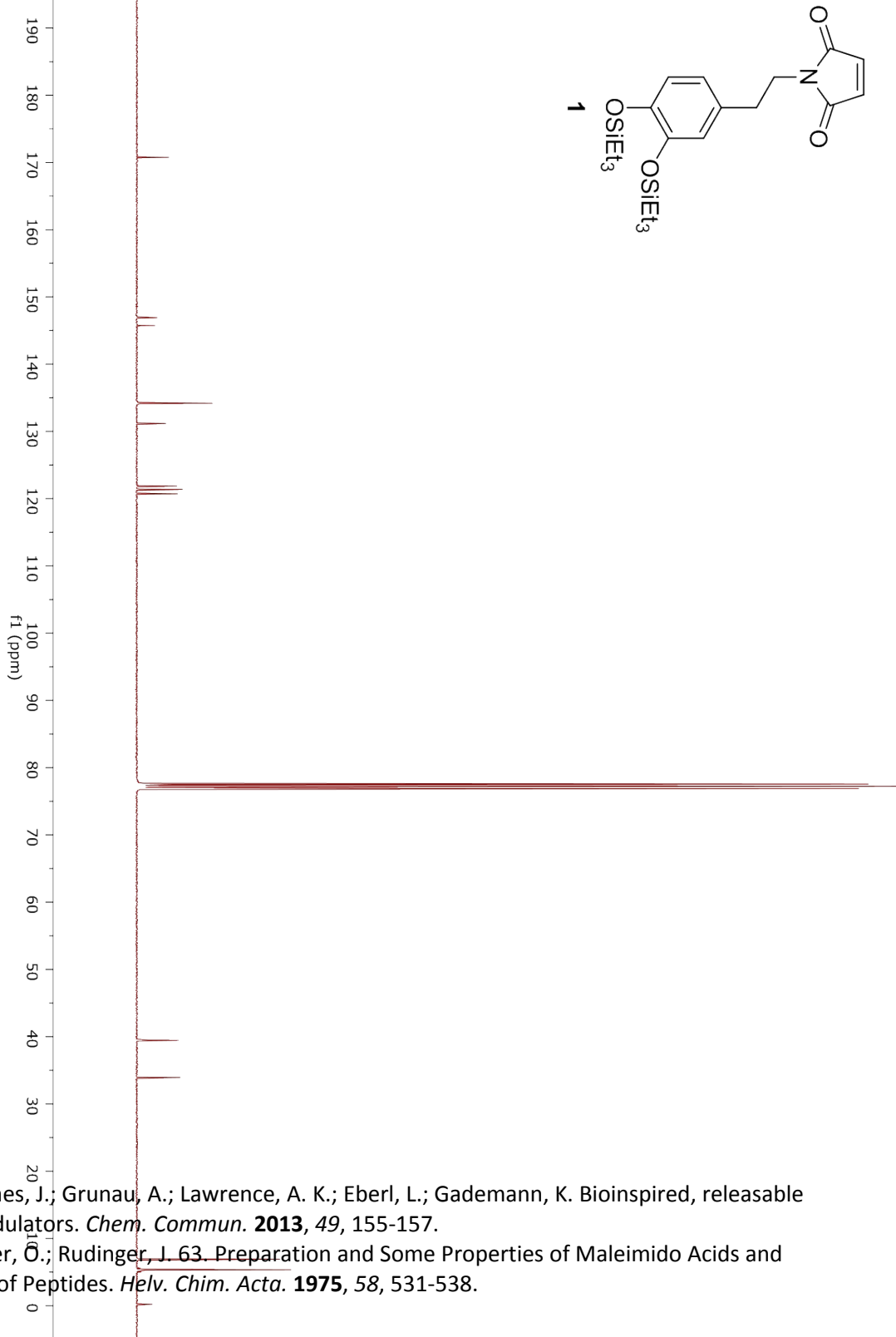
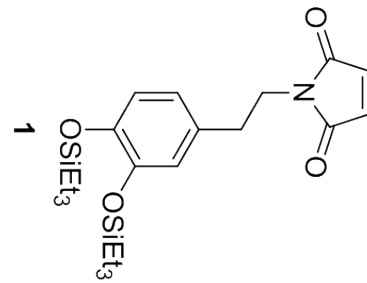












Referneces

- (1) Gomes, J.; Grunau, A.; Lawrence, A. K.; Eberl, L.; Gademann, K. Bioinspired, releasable quorum sensing modulators. *Chem. Commun.* **2013**, *49*, 155-157.
- (2) Keller, O.; Rudinger, J. 63. Preparation and Some Properties of Maleimido Acids and Maleoyl Derivatives of Peptides. *Helv. Chim. Acta.* **1975**, *58*, 531-538.