Sustainable polyvinyl acetals from bioaromatic aldehydes

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Electronic Supplementary Information (ESI)

Supplementary Information Available: Synthetic details and complete polymer characterization data.

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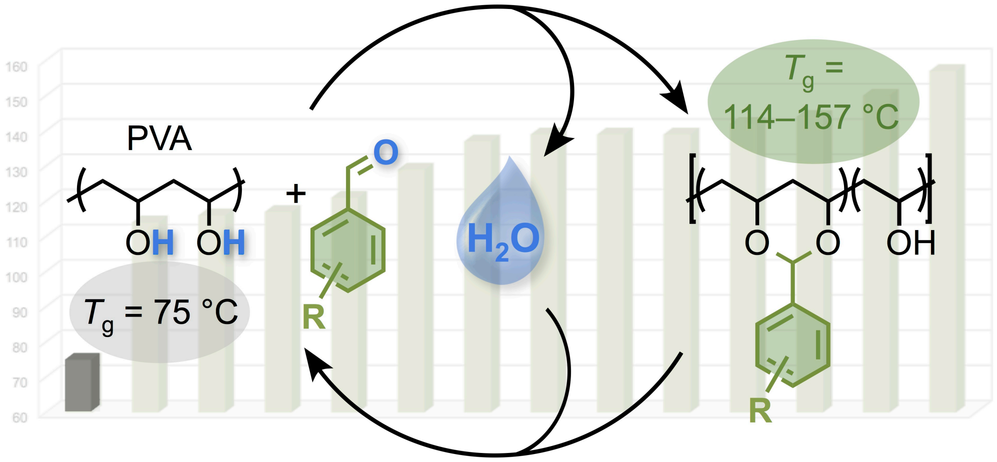
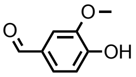
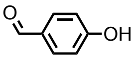
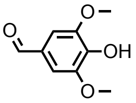
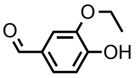
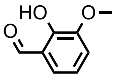
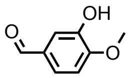
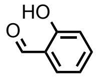
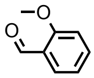
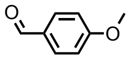
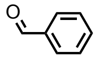
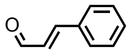
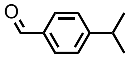
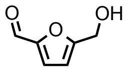
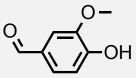


Summary of Polymerization Data

Table S1 Level of acetalization, thermal analysis, calculated molecular weight, and GPC molecular weight data for polyvinyl aromatic acetals[a]

Entry	Aldehyde	Yield (%)	Acetal. (%)	T_g (°C)[b]	T_{95} (°C)[c]	Calculated M_n (Da)[d]	GPC M_n (Da)[e]	GPC M_w (Da)[e]	PDI[e]
0 **PVA**	none	–	none	75	222		22,300	45,500	2.05
1 **PV-VV-A**		31.1	63.3	142	199	43,700	25,700	54,900	2.14
2 **PV-HB-A**		37.6	68.8	157	224	40,400	22,800	52,500	2.31
3 **PV-SY-A**		54.9	54.1	139	224	44,700	28,800	59,700	2.08
4 **PV-EV-A**		44.7	63.5	114	185	46,000	22,800	51,600	2.27
5 **PV-OV-A**		54.4	57.6	139	234	41,800	24,500	58,900	2.40
6 **PV-IV-A**		46.9	66.9	139	278	45,000	24,500	53,400	2.18
7 **PV-SA-A**		55.7	64.0	150	241	39,100	17,000	45,000	2.65
8 **PV-OA-A**		70.5	73.4	121	296	44,300	11,200	33,100	2.96
9 **PV-PA-A**		55.7	66.4	116	241	42,100	22,100	51,200	2.32
10 **PV-BZ-A**[f]		84.6	74.8	129	298	38,900	13,300	37,000	2.78
11 **PV-CI-A**		55.5	68.3	117	215	42,000	n/a	n/a	n/a
12 **PV-CU-A**		57.2	57.6	137	308	41,200	n/a	n/a	n/a
13 **PV-HMF-A**[f]		80.0	58.5	144	286	38,200	n/a	n/a	n/a
14 **PVA***	none	–	none	70	120	146,000–186,000[g]	n/a	n/a	n/a
15 **PV-VV-A***		64.4	73.8	145	235	310,000–395,000	n/a	n/a	n/a

[a] Reaction conducted in dimethyl sulfoxide at 60° C for two hours (except as noted) with 2 mol% *p*-TSA. Ratio of [aldehyde]/[1,3-diol] = 2.6. [b] Determined by DSC. [c] Temperature reported upon 5% mass loss by TGA. [d] *Calculated* number average molecular weight (M_n) from initial M_n = 22,300 Da of PVA (or 146,000–186,000 for entry 15) augmented by % acetalization as determined by ^{1}H NMR. [e] M_n, M_w, and PDI obtained by GPC in hexafluoroisopropanol (HFIP) at 40 °C versus PMMA standards. [f] Reaction conducted for 6 hours. [g] M_n range, as reported by the manufacturer.

Polymer Synthesis

Synthesis of polyvinyl vanillin acetal *PV-VV-A* (Table S1, entry 1)

On a Schlenk line, a 250 mL round bottom flask (Flask A) was charged with 1.00 g (22.50 mmol) polyvinyl alcohol and 0.077 g (0.45 mmol) *p*-TSA. This flask was fitted with a bump trap and attached to the Schlenk line and the other openings were sealed with rubber septa. The system was evacuated and backfilled with nitrogen before injection of 7.5 mL of DMSO via syringe. Full dissolution was accomplished by heating to 90 °C under nitrogen. A second 250 mL round bottom flask (Flask B) was charged with 4.45 g (29.25 mmol) vanillin. The flask was fitted with a bump trap and rubber septa were attached to the Schlenk line before evacuation and backfilling with nitrogen. Flask B was then injected with 5 mL of DMSO via syringe and stirring effected complete dissolution at room temperature. This vanillin solution was then transferred to Flask A via syringe. The reaction was heated under nitrogen at 60 °C for 2 hours. The crude product was precipitated by adding the cooled reaction to 350 mL aqueous sodium bicarbonate. The precipitate was isolated by decanting, washed twice with 150 mL deionized water, and air dried overnight. NMR analysis of the crude product (4.22 g) showed the presence of water and unreacted vanillin (2.50 grams theoretical yield). Purified product was obtained by dissolving 0.40 g of crude product in 15 mL of DMSO, stirring overnight, and reprecipitating in 350 mL of aqueous sodium bicarbonate. The precipitate was isolated by decanting, washed twice with 150 mL deionized water, and air dried overnight. The final product (0.08 g) was obtained as a white powder. The isolated yield is calculated as 31.1%. Note that purification was conducted on a fraction of the crude product; therefore isolated yield is based on extrapolated numbers. ^{1}H NMR (DMSO-d_6) δ ppm 1.1–1.8 (m, $-CH_2-$, 6.32 H), 3.26 (br, O*H*, 1.65 H), 3.69 (m, $-OCH_3$, 3 H), 3.90 (m, C*H*–OR, 3.36 H), 5.35, 5.56, 5.65 (m, –OCAr*H*O–, 1H), 6.68, 6.76, 6.87 (m, Ar-*H*, 3 H). The small peak in the region 1.8–2.0 ppm was ignored since it belongs to the non-hydrolyzed acetyl $-CH_3$ groups. ^{13}C NMR (DMSO-d_6) δ ppm 37.6, 38.3, 44.6, 44.9, 46.3, 46.7, 56.1, 63.3, 64.3, 73.1, 73.6, 100.5, 110.7, 115.3, 119.3, 130.9, 147.3, 147.5.

Synthesis of polyvinyl 4-hydroxybenzaldehyde acetal *PV-HB-A* (Table S1, entry 2)

This product was synthesized using the same procedure as for **PV-VV-A**. Flask A was charged with 1.00 g (22.50 mmol) polyvinyl alcohol, 0.077 g (0.45 mmol) *p*-TSA, and 7.5 mL DMSO. Flask B was charged with 3.58 g (29.25 mmol) 4–hydroxybenzaldehyde and 5 mL DMSO. The contents of flask B were transferred to flask A via syringe. The reaction was heated under nitrogen at 60 °C for 2 hours. NMR analysis of the crude product (3.59 g) showed the presence of water and unreacted 4-hydroxybenzaldehyde (2.19 grams theoretical yield). The purified product was obtained in a similar fashion to **PV-VV-A**; 0.40 g were utilized. The final product (0.09 g) was obtained as a white powder. The isolated yield is calculated as 37.6%. Note that purification was conducted on a fraction of the crude product; therefore isolated yield is based on extrapolated numbers. ^{1}H NMR (DMSO-d_6) δ ppm 1.1-1.8 (m, 5.81 H), 3.88, 3.99, 4.33 (m, 4.86 H), 5.40, 5.60, 5.68 (m, 1 H), 6.70 (s, 2 H), 7.19 (s, 2 H), 9.47 (br, s, 1 H), showing a degree of acetalization of 68.8%. ^{13}C NMR (DMSO-d_6) δ ppm 37.6, 38.4, 44.7, 45.0, 46.3, 46.7, 63.1, 64.3, 72.8, 73.4, 100.4, 115.0, 127.6, 130.4, 157.8.

Synthesis of polyvinyl syringaldehyde acetal *PV-SY-A* (Table S1, entry 3)

This product was synthesized using the same procedure as for **PV-VV-A**. Flask A was charged with 1.00 g (22.50 mmol) polyvinyl alcohol, 0.077 g (0.45 mmol) *p*-TSA, and 7.5 mL DMSO. Flask B was charged with 5.33 g (29.25 mmol) syringaldehyde and 5 mL DMSO. The contents of flask B were transferred to flask A via syringe. The reaction was heated under nitrogen at 60 °C for 2 hours. NMR analysis of the crude product (3.99 g) showed the presence of water and unreacted syringaldehyde (2.89 grams theoretical yield). The purified product was obtained in a similar fashion to **PV-VV-A**; 0.40 g were utilized. The final product (0.16 g) was obtained as a white powder. The isolated yield is calculated as 54.9%. Note that purification was conducted on a fraction of the crude product; therefore isolated yield is based on extrapolated numbers. ^{1}H NMR (DMSO-d_6) δ ppm 1.1-1.8 (m, 7.39 H), 3.27 (m, 2.63 H) 3.68 (m, 6 H), 3.92 (m, 4.35 H), 4.34 (m, 1H), 5.36, 5.62 (m, 1 H), 6.61 (s, 2 H), showing a degree of acetalization of 54.1%. ^{13}C NMR (DMSO-d_6) δ ppm 37.2, 37.9, 44.0, 44.5, 45.8, 46.3, 56.0, 62.9, 63.8, 72.8, 73.3, 100.2, 103.8, 129.5, 135.7, 147.6.

Synthesis of polyvinyl ethylvanillin acetal *PV-EV-A* (Table S1, entry 4)
This product was synthesized using the same procedure as for **PV-VV-A**. Flask A was charged with 1.00 g (22.50 mmol) polyvinyl alcohol, 0.077 g (0.45 mmol) *p*-TSA, and 7.5 mL DMSO. Flask B was charged with 4.87 g (29.25 mmol) ethylvanillin and 5 mL DMSO. The contents of flask B were transferred to flask A via syringe. The reaction was heated under nitrogen at 60 °C for 2 hours. NMR analysis of the crude product (5.64 g) showed the presence of water and unreacted ethylvanillin (2.70 grams theoretical yield).The purified product was obtained in a similar fashion to **PV-VV-A**; 0.40 g were utilized. The final product (0.09 g) was obtained as a white powder. The isolated yield is calculated as 44.7%. Note that purification was conducted on a fraction of the crude product; therefore isolated yield is based on extrapolated numbers.^{1}H NMR (DMSO-d_6) δ ppm 1.29 (s, 3 H), 1.1-1.8 (m, 6.30 H), 3.42 (m, 2.23 H), 3.90 (m, 2 H), 3.95 (m, 3.86 H), 5.36, 5.59, 5.65 (m, 1 H), 6.72, 6.79, 6.88 (m, 3H), showing a degree of acetalization of 63.4%. ^{13}C NMR (DMSO-d_6) δ ppm 14.8, 37.1, 37.8, 44.0, 44.6, 45.8, 46.2, 63.0, 63.9, 72.5, 73.1, 73.8, 100.0, 111.8, 115.0, 118.9, 130.0, 146.3, 147.5.

Synthesis of polyvinyl *ortho*-vanillin acetal *PV-OV-A* (Table S1, entry 5)
This product was synthesized using the same procedure as for **PV-VV-A**. Flask A was charged with 1.00 g (22.50 mmol) polyvinyl alcohol, 0.077 g (0.45 mmol) *p*-TSA, and 7.5 mL DMSO. Flask B was charged with 4.46 g (29.25 mmol) *ortho*-vanillin and 5 mL DMSO. The contents of flask B were transferred to flask A via syringe. The reaction was heated under nitrogen at 60 °C for 2 hours. NMR analysis of the crude product (5.82 g) showed the presence of water and unreacted *ortho*-vanillin (2.54 grams theoretical yield). The purified product was obtained in a similar fashion to **PV-VV-A**; 0.40 g were utilized. The final product (0.10 g) was obtained as a white powder. The isolated yield is calculated as 54.4%. Note that purification was conducted on a fraction of the crude product; therefore isolated yield is based on extrapolated numbers. ^{1}H NMR (DMSO-d_6) δ ppm 1.1-1.8 (m, 6.95 H), 3.77 (s, 3 H), 3.90-4.5 (m, 3.27 H), 5.74, 6.02 (m, 1 H), 6.73, 6.89, 6.97 (m, 3 H), 8.58 (br, s, 1 H)), showing a degree of acetalization of 57.6%. ^{13}C NMR (DMSO-d_6) δ ppm 36.4, 37.0, 42.4, 44.1, 44.6, 46.1, 55.9, 62.9, 63.7, 72.7, 73.4, 96.1, 111.7, 118.5, 119.1, 125.6, 143.7, 147.4.

Synthesis of polyvinyl isovanillin acetal *PV-IV-A* (Table S1, entry 6)
This product was synthesized using the same procedure as for **PV-VV-A**. Flask A was charged with 1.00 g (22.50 mmol) polyvinyl alcohol, 0.077 g (0.45 mmol) *p*-TSA, and 7.5 mL DMSO. Flask B was charged with 4.45 g (29.25 mmol) isovanillin and 5 mL DMSO. The contents of flask B were transferred to flask A via syringe. The reaction was heated under nitrogen at 60 °C for 2 hours. NMR analysis of the crude product (5.01 g) showed the presence of water and unreacted isovanillin (2.54 grams theoretical yield). The purified product was obtained in a similar fashion to **PV-VV-A**; 0.40 g were utilized. The final product (0.10 g) was obtained as a white powder. The isolated yield is calculated as 46.9%. Note that purification was conducted on a fraction of the crude product; therefore isolated yield is based on extrapolated numbers. ^{1}H NMR (DMSO-d_6) δ ppm 1.1-1.8 (m, 5.98 H), 3.73 (s, 3 H), 3.93 (m, 2.96 H), 4.42 (m, 1.42 H), 5.38, 5.56, 5.67 (m, 1 H), 6.82 (m, 3 H), 8.99 (br, s, 1 H), showing a degree of acetalization of 66.9%. ^{13}C NMR (DMSO-d_6) δ ppm 37.1, 37.8, 43.9, 44.6, 46.3, 46.9, 55.6, 62.7, 64.5, 72.3, 73.0, 99.8, 111.5, 113.5, 117.1, 131.9, 146.0, 147.7.

Synthesis of polyvinyl salicylaldehyde acetal *PV-SA-A* (Table S1, entry 7)
This product was synthesized using the same procedure as for **PV-VV-A**. Flask A was charged with 1.00 g (22.50 mmol) polyvinyl alcohol, 0.077 g (0.45 mmol) *p*-TSA, and 7.5 mL DMSO. Flask B was charged with 3.58 g (29.25 mmol) salicylaldehyde and 5 mL DMSO. The contents of flask B were transferred to flask A via syringe. The reaction was heated under nitrogen at 60 °C for 2 hours. NMR analysis of the crude product (5.29 g) showed the presence of water and unreacted salicylaldehyde (2.20 grams theoretical yield). The purified product was obtained in a similar fashion to **PV-VV-A**; 0.40 g were utilized. The final product (0.09 g) was obtained as a

white powder. The isolated yield is calculated as 55.7%. Note that purification was conducted on a fraction of the crude product; therefore isolated yield is based on extrapolated numbers. ^{1}H NMR (DMSO-d_6) δ ppm 1.1-1.8 (m, 6.25 H), 3.79, 3.96, 4.27, 4.42 (m, 4.24 H), 5.70, 5.98 (m, 1 H), 6.77 (m, 2 H), 7.10 (m, 1 H), 7.32 (m, 1 H), 9.32 (br. s, 1 H), showing a degree of acetalization of 64.0%. ^{13}C NMR (DMSO-d_6) δ ppm 37.1, 37.9, 44.2, 44.5, 45.8, 46.2, 62.8, 63.7, 72.6, 73.3, 96.0, 115.4, 118.6, 125.1, 127.3, 129.3, 154.4.

Synthesis of polyvinyl *ortho*-anisaldehyde acetal *PV-OA-A* (Table S1, entry 8)

This product was synthesized using the same procedure as for **PV-VV-A**. Flask A was charged with 1.00 g (22.50 mmol) polyvinyl alcohol, 0.077 g (0.45 mmol) *p*-TSA, and 7.5 mL DMSO. Flask B was charged with 3.98 g (29.25 mmol) *ortho*-anisaldehyde and 5 mL DMSO. The contents of flask B were transferred to flask A via syringe. The reaction was heated under nitrogen at 60 °C for 2 hours. NMR analysis of the crude product (3.60 g) showed the presence of water and unreacted *ortho*-anisaldehyde (2.35 grams theoretical yield). The purified product was obtained by dissolving 0.40 g of crude product in 15 mL of DMSO, stirring overnight and reprecipitating in 350 mL of methanol, and isolated by decanting and air drying overnight. The final product (0.24 g) was obtained as a white powder. The isolated yield is calculated as 70.5%. Note that purification was conducted on a fraction of the crude product; therefore isolated yield is based on extrapolated numbers. ^{1}H NMR (DMSO-d_6) δ ppm 1.1-1.8 (m, 5.45 H), 3.72 (s, 3 H), 3.93 (m, 1.72 H), 4.29 (m, 0.97 H), 5.70, 5.97 (m, 1 H), 6.93 (m, 2 H), 7.29 (m, 1 H), 7.43 (m, 1 H), showing a degree of acetalization of 73.7%. ^{13}C NMR (DMSO-d_6) δ ppm 36.3, 36.9, 42.0, 42.1, 43.8, 44.2, 55.5, 62.9, 68.4, 72.7, 73.4, 95.3, 111.1, 120.1, 126.9, 127.0, 129.7, 156.2.

Synthesis of polyvinyl *para*-anisaldehyde acetal *PV-PA-A* (Table S1, entry 9)

This product was synthesized using the same procedure as for **PV-VV-A**. Flask A was charged with 1.00 g (22.50 mmol) polyvinyl alcohol, 0.077 g (0.45 mmol) *p*-TSA, and 7.5 mL DMSO. Flask B was charged with 3.99 g (29.25 mmol) *para*-anisaldehyde and 5 mL DMSO. The contents of flask B were transferred to flask A via syringe. The reaction was heated under nitrogen at 60 °C for 2 hours. NMR analysis of the crude product (3.85 g) showed the presence of water and unreacted *para*-anisaldehyde (2.35 grams theoretical yield). The purified product was obtained in a similar fashion to **PV-VV-A**; 0.40 g were utilized. The final product (0.14 g) was obtained as a white powder. The isolated yield is calculated as 55.7%. Note that purification was conducted on a fraction of the crude product; therefore isolated yield is based on extrapolated numbers. ^{1}H NMR (DMSO-d_6) δ ppm 1.1-1.8 (m, 6.02 H), 3.74 (s, 3 H), 4.02 (m, 3.29 H), 4.43 (m, 1.02 H), 5.46, 5.64, 5.75 (m, 1 H), 6.88 (m, 2 H), 7.32 (m, 2 H), showing a degree of acetalization of 66.4%. ^{13}C NMR (DMSO-d_6) δ ppm 37.0, 37.7, 42.3, 44.5, 45.8, 46.2, 55.1, 62.8, 63.9, 72.4, 73.0, 99.7, 113.2, 127.4, 131.6, 159.2.

Synthesis of polyvinyl benzaldehyde acetal *PV-BZ-A* (Table S1, entry 10)

This product was synthesized using a similar procedure to **PV-VV-A**. Flask A was charged with 1.00 g (22.50 mmol) polyvinyl alcohol, 0.077 g (0.45 mmol) *p*-TSA, and 7.5 mL DMSO. Flask B was charged with 3.10 g (29.25 mmol) benzaldehyde and 5 mL DMSO. The contents of flask B were transferred to flask A via syringe. The reaction was heated under nitrogen at 60 °C for 6 hours. NMR analysis of the crude product (4.32 g) showed the presence of water and unreacted benzaldehyde (2.00 grams theoretical yield). The purified product was obtained in a similar fashion to **PV-VV-A**; 0.40 g were utilized. The final product (0.16 g) was obtained as a white powder. The isolated yield is calculated as 84.6%. Note that purification was conducted on a fraction of the crude product; therefore isolated yield is based on extrapolated numbers. ^{1}H NMR (DMSO-d_6) δ ppm 1.1-1.8 (m, 5.35 H), 4.06 (m, 2.61 H), 4.50 (m, 0.85 H), 5.50, 5.76 (m, 1 H), 7.37 (m, 5 H), showing a degree of acetalization of 74.8%. ^{13}C NMR (DMSO-d_6) δ ppm 37.0, 37.7, 42.2, 43.9, 44.3, 47.2, 62.3, 68.2, 72.5, 73.1, 99.6, 126.1, 127.9, 128.3, 139.1.

Synthesis of polyvinyl cinnamaldehyde acetal *PV-CI-A* (Table S1, entry 11)

This product was synthesized using the same procedure as for **PV-VV-A**. Flask A was charged with 1.00 g (22.50 mmol) polyvinyl alcohol, 0.077 g (0.45 mmol) *p*-TSA, and 7.5 mL DMSO. Flask B was charged with 3.86 g (29.25

mmol) cinnamaldehyde and 5 mL DMSO. The contents of flask B were transferred to flask A via syringe. The reaction was heated under nitrogen at 60 °C for 2 hours. NMR analysis of the crude product (5.52 g) showed the presence of water and unreacted cinnamaldehyde (2.30 grams theoretical yield). The purified product was obtained in a similar fashion to **PV-VV-A**; 0.40 g were utilized. The final product (0.09 g) was obtained as a white powder. The isolated yield is calculated as 55.5%. Note that purification was conducted on a fraction of the crude product; therefore isolated yield is based on extrapolated numbers. ^{1}H NMR (DMSO-d_6) δ ppm 1.1-1.8 (m, 5.86 H), 3.94 (m, 2.94 H), 4.44 (m, 1.30 H), 5.15, 5.43 (m, 1 H), 6.23 (m, 1 H), 6.68 (m, 1 H), 7.36 (m, 5 H), showing a degree of acetalization of 68.3%. ^{13}C NMR (DMSO-d_6) δ ppm 37.1, 37.9, 44.0, 44.5, 45.9, 46.2, 62.8, 63.9, 72.0, 72.8, 99.6, 126.6, 128.1, 128.65, 128.75, 132.2, 135.7.

Synthesis of polyvinyl cuminaldehyde acetal *PV-CU-A* (Table S1, entry 12)

This product was synthesized using the same procedure as for **PV-VV-A**. Flask A was charged with 1.00 g (22.50 mmol) polyvinyl alcohol, 0.077 g (0.45 mmol) *p*-TSA, and 7.5 mL DMSO. Flask B was charged with 4.33 g (29.25 mmol) cuminaldehyde and 5 mL DMSO. The contents of flask B were transferred to flask A via syringe. The reaction was heated under nitrogen at 60 °C for 2 hours. NMR analysis of the crude product (3.88 g) showed the presence of water and unreacted cuminaldehyde (2.49 grams theoretical yield). The purified product was obtained by dissolving 0.40 g of crude product in 15 mL of DMSO, stirring overnight and reprecipitating in 350 mL of deionized water. The precipitate was stirred with 15 mL ethanol overnight, isolated by decanting and air drying overnight. The final product (0.15 g) was obtained as a white powder. The isolated yield is calculated as 57.2%. Note that purification was conducted on a fraction of the crude product; therefore isolated yield is based on extrapolated numbers. ^{1}H NMR (DMSO-d_6) δ ppm 1.07, 1.16 (m, 6H), 1.1–1.8 (m, 6.94 H), 2.81 (m, 1 H), 3.93 (m, 3.20 H), 5.46, 5.65, 5.74 (m, 1 H), 7.26 (m, 4 H), showing a degree of acetalization of 57.6%. ^{13}C NMR (DMSO-d_6) δ ppm 23.8, 33.2, 37.6, 38.1, 41.5, 42.0, 43.5, 44.6, 62.7, 64.2, 73.0, 73.3, 99.9, 125.7, 126.1, 136.9, 148.6 (peaks at 18.6 and 56.0 derive from residual ethanol).

Synthesis of polyvinyl hydroxymethylfurfural acetal *PV-HMF-A* (Table S1, entry 13)

This product was synthesized using the same procedure as for **PV-VV-A**, except the reaction time was 6 hours. Flask A was charged with 1.00 g (22.50 mmol) polyvinyl alcohol, 0.077 g (0.45 mmol) *p*-TSA, and 7.5 mL DMSO. Flask B was charged with 4.33 g (29.25 mmol) hydroxymethylfurfural and 5 mL DMSO. The contents of flask B were transferred to flask A via syringe. The reaction was heated under nitrogen at 60 °C for 6 hours. NMR analysis of the crude product (2.24 g) showed the presence of water and unreacted hydroxymethylfurfural (1.95 grams theoretical yield). The purified product was obtained in a similar fashion to **PV-VV-A**; 0.40 g were utilized. The final product (0.29 g) was obtained as a white powder. The isolated yield is calculated as 80.0%. Note that purification was conducted on a fraction of the crude product; therefore isolated yield is based on extrapolated numbers. ^{1}H NMR (DMSO-d_6) δ ppm 1.1-1.8 (m, 6.84 H), 3.79 (m, 1.26 H), 3.97 (s, 2 H), 4.43 (m, 4.39 H), 5.24 (s, 1 H), 5.52, 5.77 (m, 1 H), 6.26 (m, 2 H), showing a degree of acetalization of 58.5%. ^{13}C NMR (DMSO-d_6) δ ppm 37.0, 37.9, 43.8, 44.1, 44.4, 46.3, 55.6, 61.5, 62.5, 72.4, 73.4, 94.8, 107.3, 108.2, 150.5, 155.0.

Synthesis of high molecular weight polyvinyl vanillin acetal *PV-VV-A** (Table 1, entry 15)

This product was synthesized using the same procedure as for **PV-VV-A**. Flask A was charged with 1.00 g (22.50 mmol) polyvinyl alcohol (MW 146,000-186,000 Da), 0.077 g (0.45 mmol) *p*-TSA, and 7.5 mL DMSO. Flask B was charged with 4.45 g (29.25 mmol) vanillin and 5 mL DMSO. The contents of flask B were transferred to flask A via syringe. The reaction was heated under nitrogen at 60 °C for 6 hours. NMR analysis of the crude product (4.88 g) showed the presence of water and unreacted vanillin (2.54 grams theoretical yield). The purified product was obtained in a similar fashion to **PV-VV-A**; 0.41 g were utilized. . The final product (0.16 g) was obtained as a white powder. The isolated yield is calculated as 64.4%. Note that purification was conducted on a fraction of the crude product; therefore isolated yield is based on extrapolated numbers. ^{1}H NMR (DMSO-d_6) δ ppm 1.1-1.8 (m, 5.42 H), 3.30 (m, 2.40 H), 3.72 (m, 3 H), 3.90 (m, 3.48 H), 5.38, 5.59, 5.66 (m, 1 H), 6.71, 6.78, 6.88 (m, 3 H), showing a degree of acetalization of 58.5%. ^{13}C NMR (DMSO-d_6) δ ppm 37.1, 38.7, 44.0, 44.4, 46.2, 46.8, 55.4, 62.7, 63.1, 72.5, 73.1, 100.2, 110.2, 115.0, 118.9, 129.5, 147.3, 147.7.

Methods for Optimization Studies

The following methods were used for the optimization studies summarized in Tables S2–S5.

Polyvinyl vanillin acetal, NMP series (Table S2)
A 50 mL round-bottom flask was charged with 1.00 g (22.50 mmol) polyvinyl alcohol and 20 mL of N-methyl pyrrolidone (NMP). The flask was then fitted with a reflux condenser and full dissolution was accomplished by heating to 90 °C under nitrogen. The system was then charged with 0.077 g (0.45 mmol) *p*-TSA and the corresponding mass of vanillin and heated under a nitrogen atmosphere for the time and at the temperature reported in each entry. The crude product was precipitated by adding the cooled reaction to 350 mL aqueous sodium bicarbonate. The precipitate was isolated by decanting, washed twice with 150 mL deionized water, and air dried overnight. The purified product was obtained in a similar fashion to **PV-VV-A**; 0.40 g were utilized. Note that purification was conducted on a fraction of the crude product; therefore isolated yield is based on extrapolated numbers.

Polyvinyl vanillin acetal, DMSO series (Table S3)
The procedure was the same as for the NMP series above, except that dimethyl sulfoxide (DMSO) was utilized as the reaction solvent.

Polyvinyl vanillin acetal, different acid catalysts (Table S4)
The procedure was the same as for the NMP series or DMSO series above (depending on the entry), except different acid catalysts, with the corresponding equivalents, were used instead of 2 mol% *p*-TSA.

Polyvinyl vanillin acetal, drying agents (Table S5)
The procedure was the same as for the NMP series above, with the addition of drying agents either inside the reaction flask (1 g of $MgSO_4$ or 2 g of 4Å molecular sieves), entries S38–S41, or of 500 mg $MgSO_4$ in a paper bag hanging above the reaction by a wire hook, entries S42 and S43.

Summary of Optimization Results and Kinetic Studies

Table S2 Optimization Study – Polyvinyl Vanillin Acetal NMP Series

Entry	Mol. eq. Vanillin	T (°C)	Time (h)	Yield (%)	T_g (°C)	Acetal. (%)
16	2.6	60	6	61	127	61.2
17	2.6	60	24	34	131	65.4
18	2.6	60	48	79	139	55.8
19	2.6	80	24	60	94	58.0
20	2.6	100	24	77	138	62.2
21	2	60	24	68	116	52.2
22	3	60	24	65	104	58.2

Table S3 Optimization Study – Polyvinyl Vanillin Acetal DMSO Series

Entry	Mol. eq. Vanillin	T (°C)	Time (h)	Yield (%)	T_g (°C)	Acetal. (%)
23	2.6	60	24	54	143	59.0
24	2.6	80	24	65	135	62.0
25	2.6	100	24	56	114	62.0
26	2.6	60	48	64	109	57.8
27	2.6	80	48	63	92	60.0

Table S4 Optimization Study – Polyvinyl Vanillin Acetal using various acid catalysts

Entry	Acid Catalyst	Mol. %	Solvent	Yield (%)	T_g (°C)	Acetal. (%)
28	HCl	43.3	NMP	0	-	-
29	AcOH	43.3	NMP	0	-	-
30	H_2SO_4	21.7	NMP	0	-	-
31	H_2SO_4	2	NMP	55	139	54.6
32	$MeSO_3H$	2	NMP	0	-	-
33	$MeSO_3H$	5	NMP	0	-	-
34	*p*-TSA	2	NMP	34	131	65.4
35	*p*-TSA	2	DMSO	54	143	59.0
36	H_2SO_4	2	DMSO	0	-	-
37	H_2SO_4	5	DMSO	0	-	-

Table S5 Optimization Study – Polyvinyl Vanillin Acetal using various drying agents

Entry	Drying Agents	Time (h)	Yield (%)	T_g (°C)	Acetal. (%)
38	4Å molecular sieves	6	31	109	50.8
39	$MgSO_4$ anhydrous	6	94	103	54.0
40	$MgSO_4$ anhydrous	24	70	104	60.0
41	$MgSO_4$ anhydrous	48	73	72	56.4
42	$MgSO_4$ anhydrous (bag)	24	85	93	52.6
43	Na_2SO_4 anhydrous (bag)	24	53	44	60.8
44	-	24	34	131	65.4

Table S6 Kinetic Study – Polyvinyl Vanillin Acetal – One Pot Reaction with Periodic Aliquot Removal

Entry	Time (h)	Yield (%)	T_g (°C)	Acetal. (%)
45	1	45	136	33.3
46	2	48	134	49.6
47	3	44	138	48.8
48	4	42	139	46.3
49	5	40	139	42.6
50	6	43	139	44.5
51	8	39	139	50.8
52	12	39	138	50.0
53	24	44	137	50.2
54	48	38	138	49.0

Thermogravimetric Analysis (TGA) Thermograms

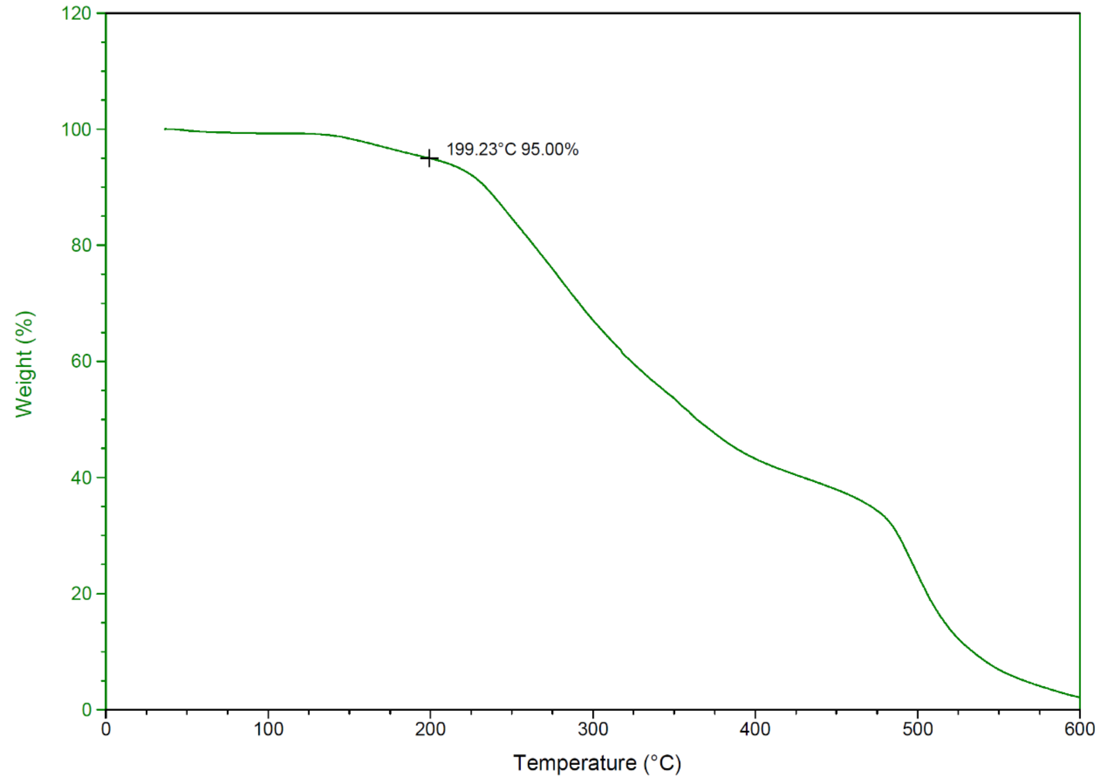


Figure S1. TGA Thermogram of **PV-VV-A** (Table S1, Entry 1).

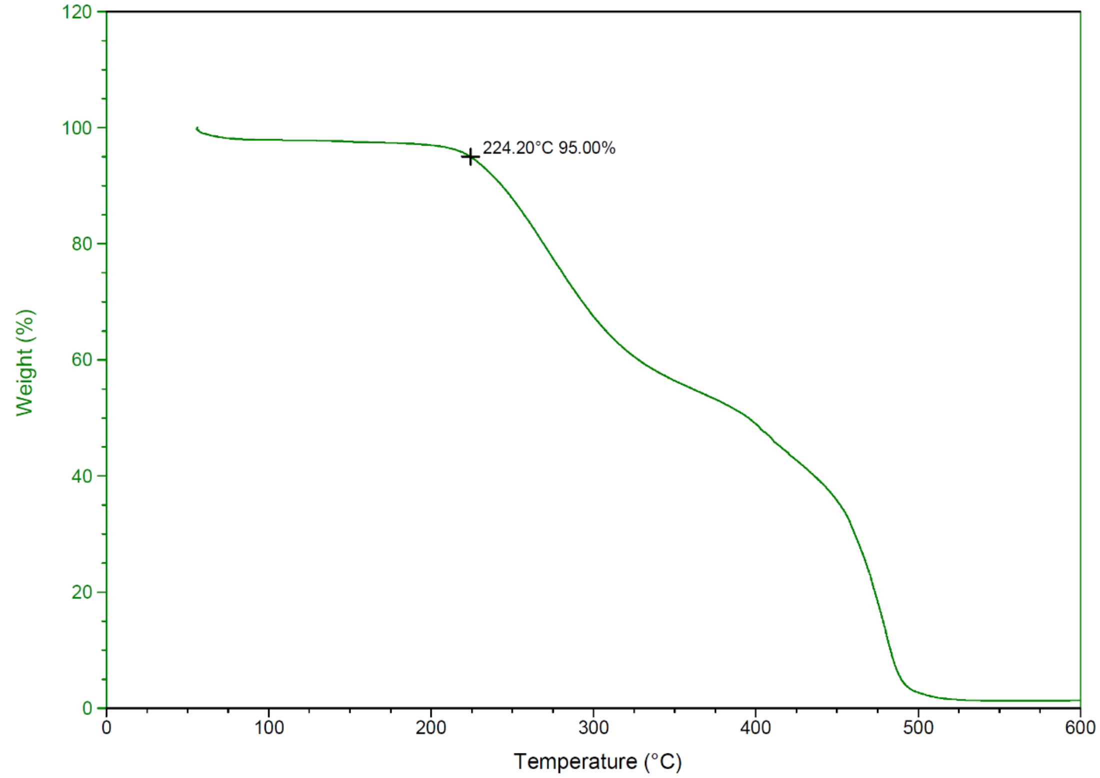


Figure S2. TGA Thermogram of **PV-HB-A** (Table S1, Entry 2).

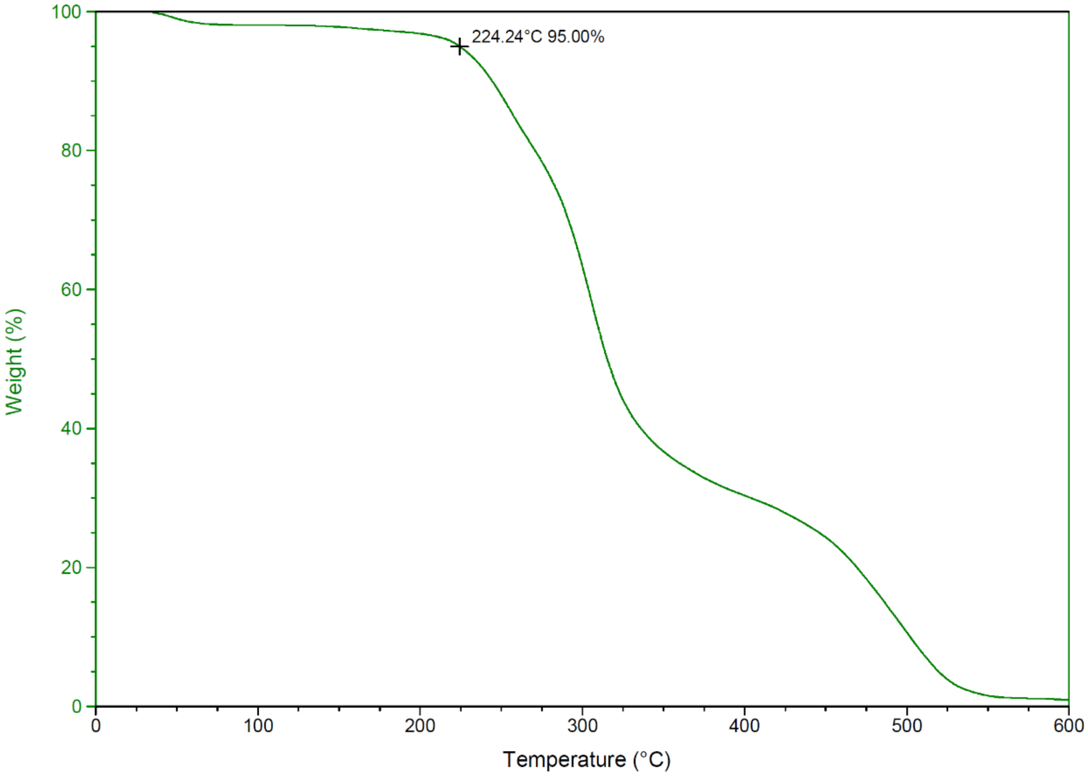


Figure S3. TGA Thermogram of **PV-SY-A** (Table S1, Entry 3).

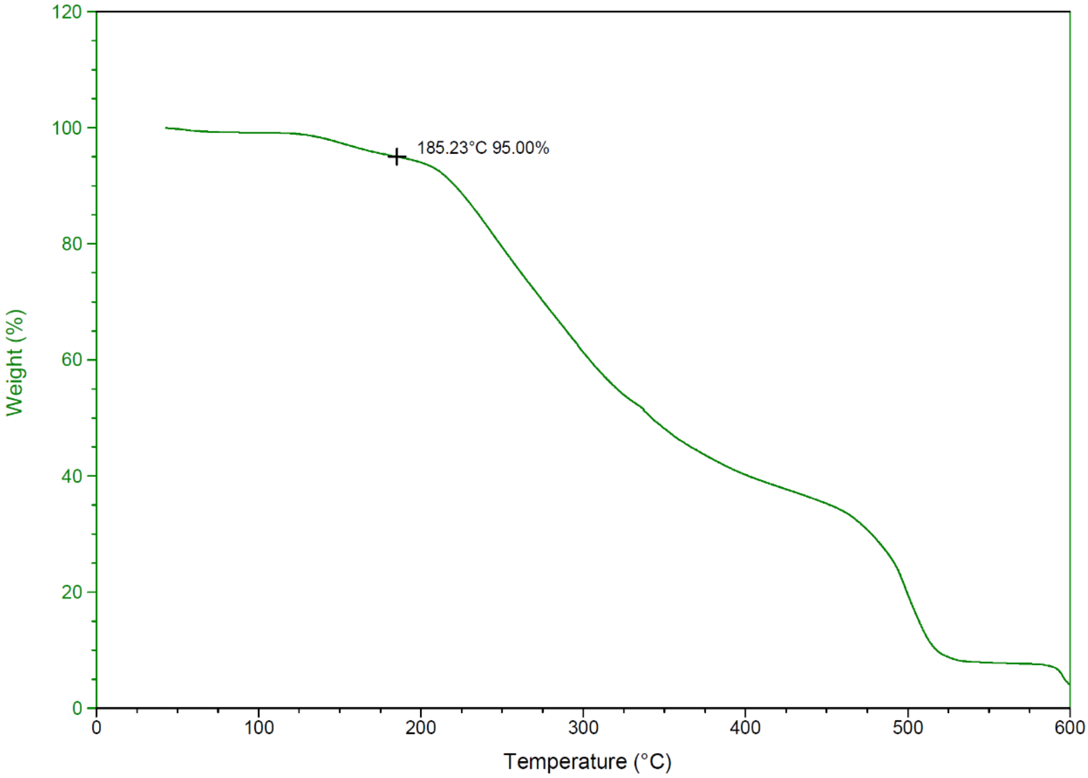


Figure S4. TGA Thermogram of **PV-EV-A** (Table S1, Entry 4).

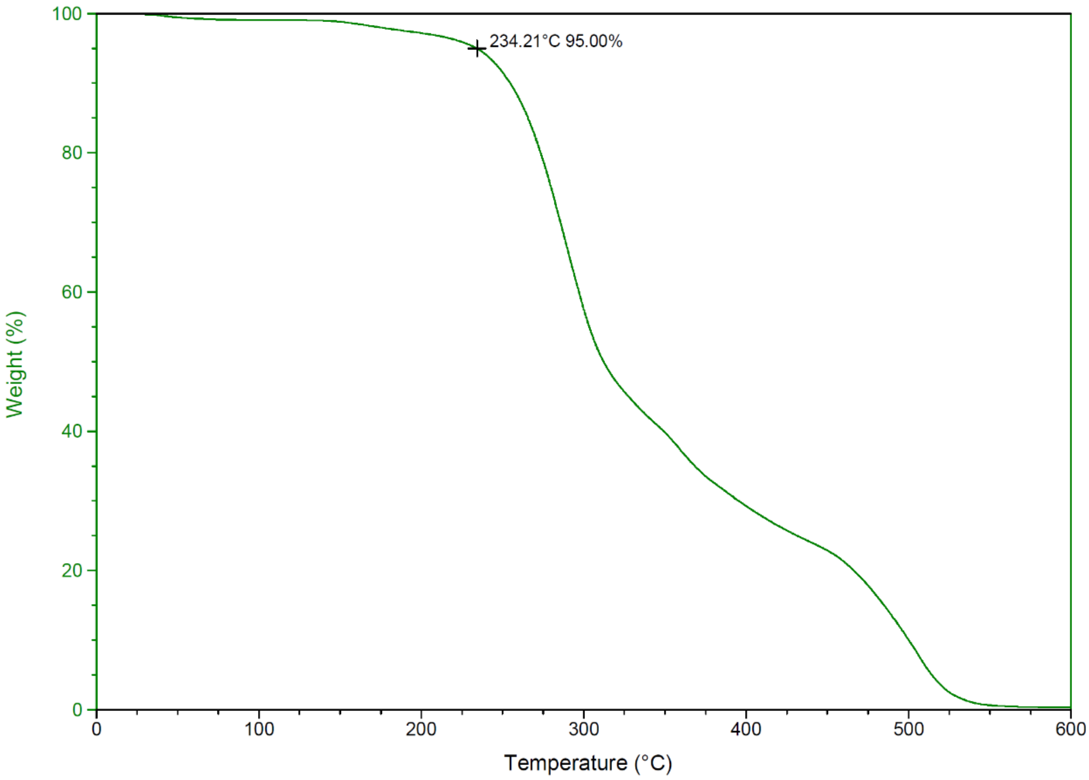


Figure S5. TGA Thermogram of **PV-OV-A** (Table S1, Entry 5).

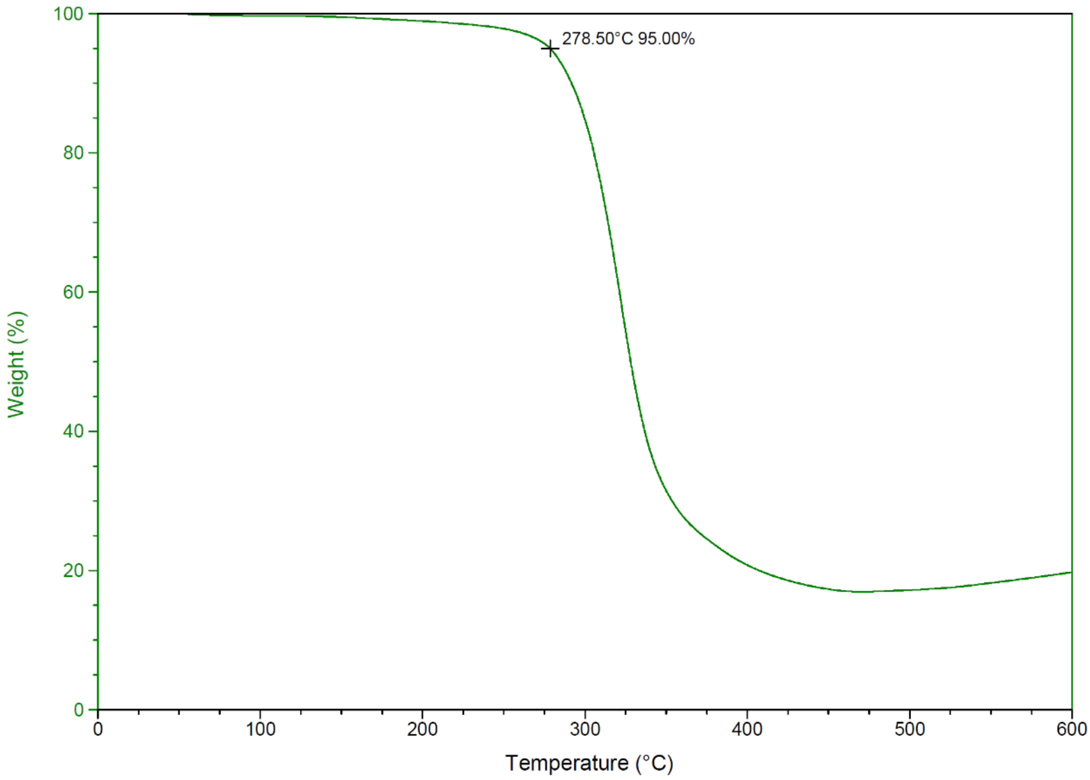


Figure S6. TGA Thermogram of **PV-IV-A** (Table S1, Entry 6).

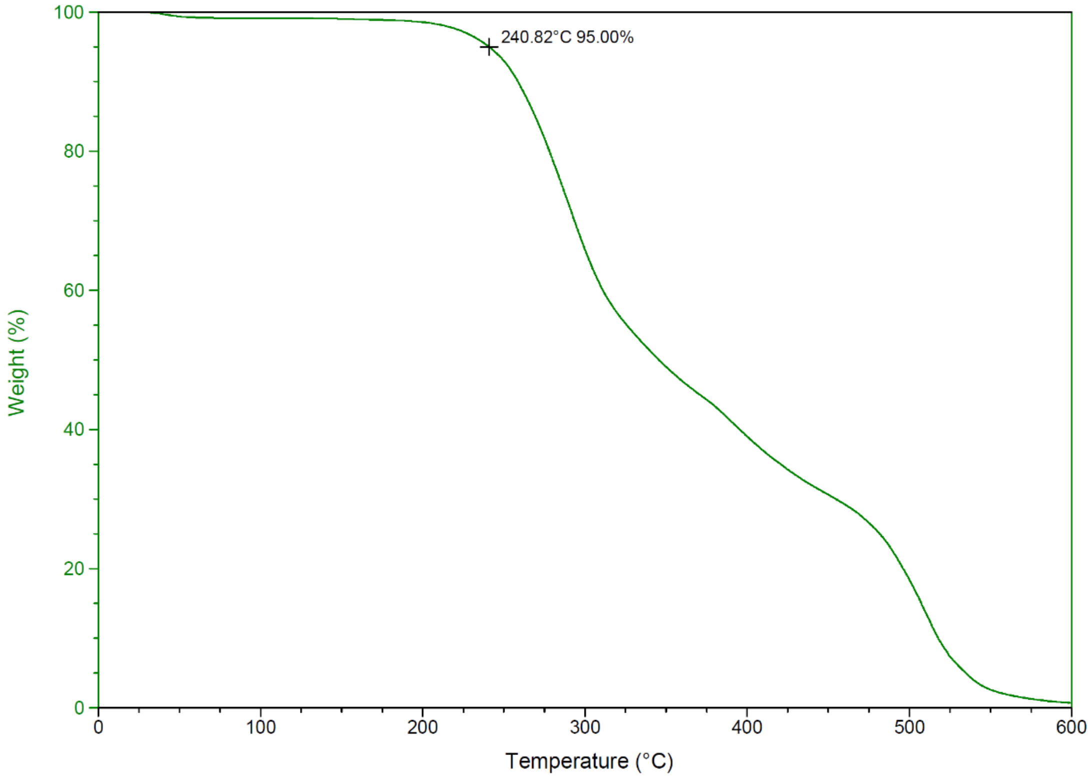


Figure S7. TGA Thermogram of **PV-SA-A** (Table S1, Entry 7).

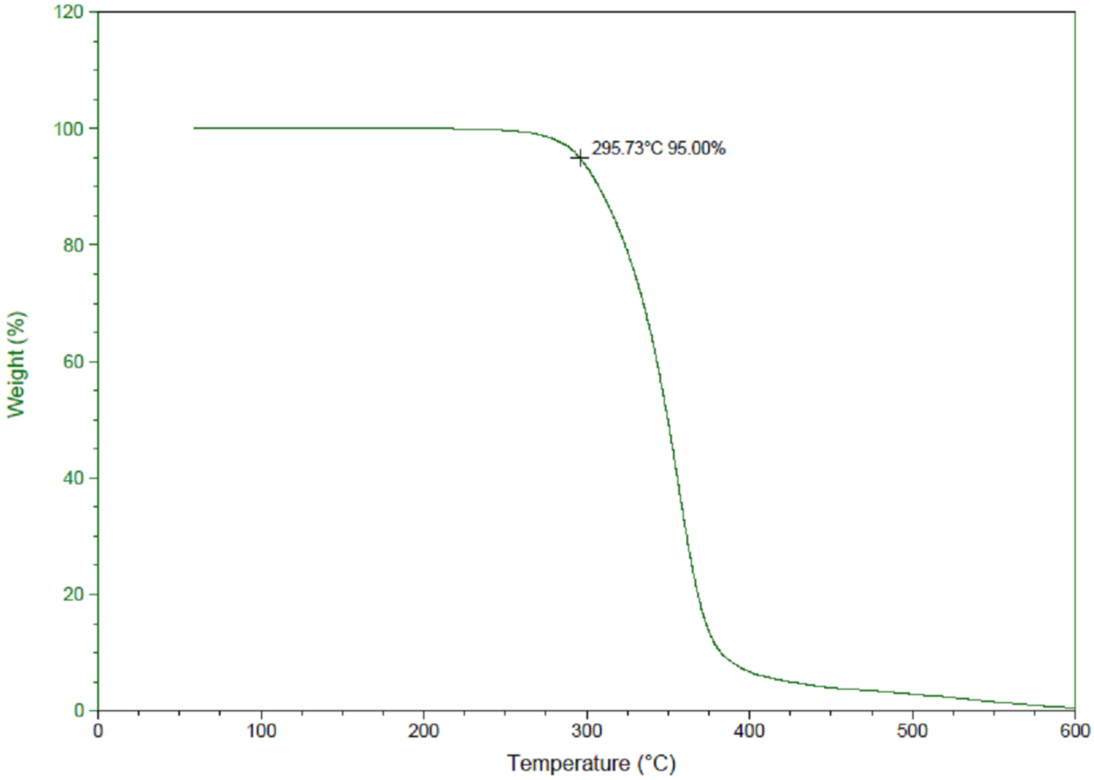


Figure S8. TGA Thermogram of **PV-OA-A** (Table S1, Entry 8).

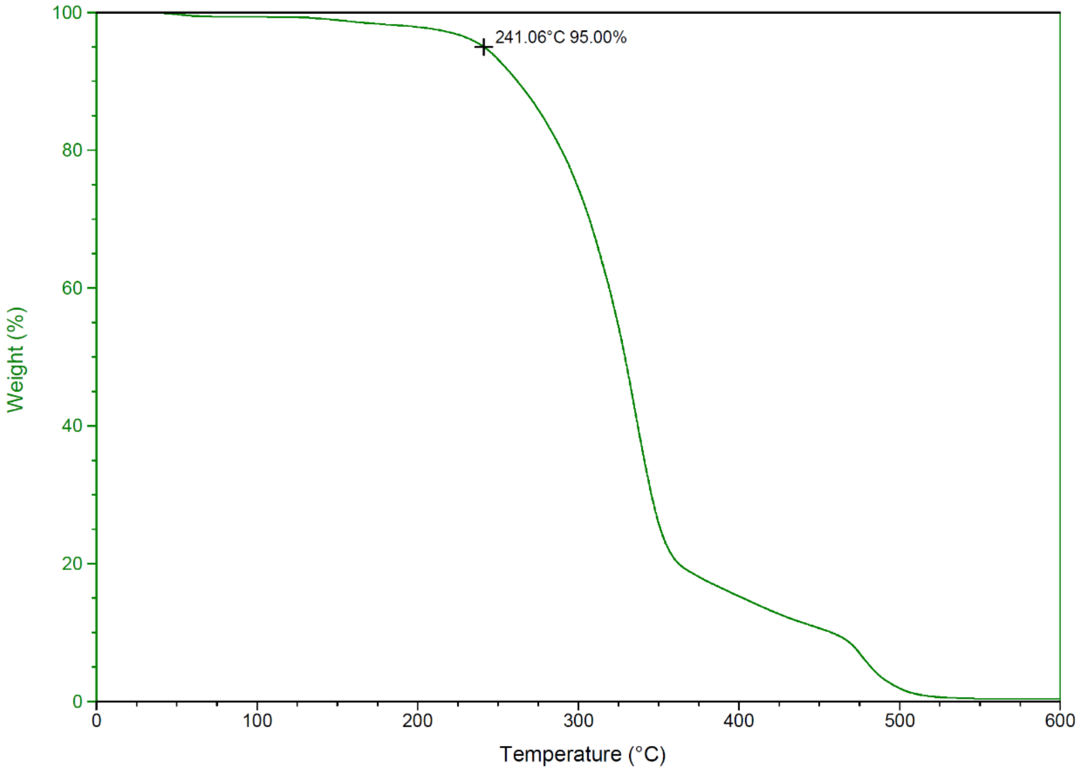


Figure S9. TGA Thermogram of **PV-PA-A** (Table S1, Entry 9).

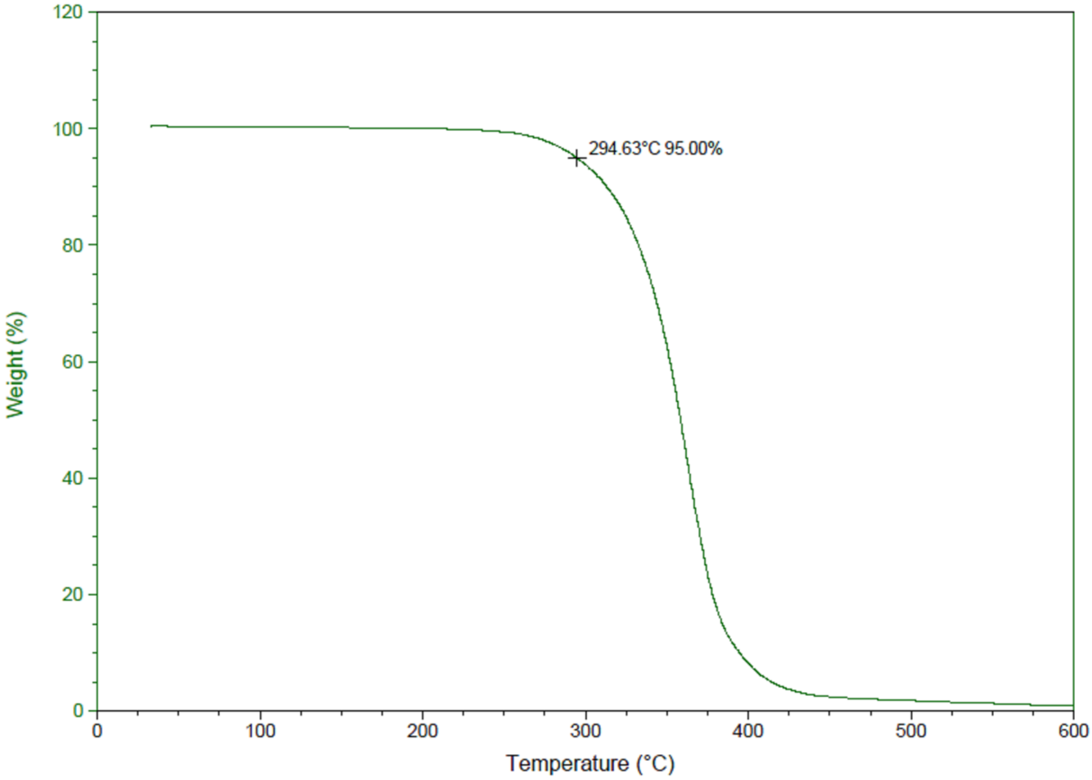


Figure S10. TGA Thermogram of **PV-BZ-A** (Table S1, Entry 10).

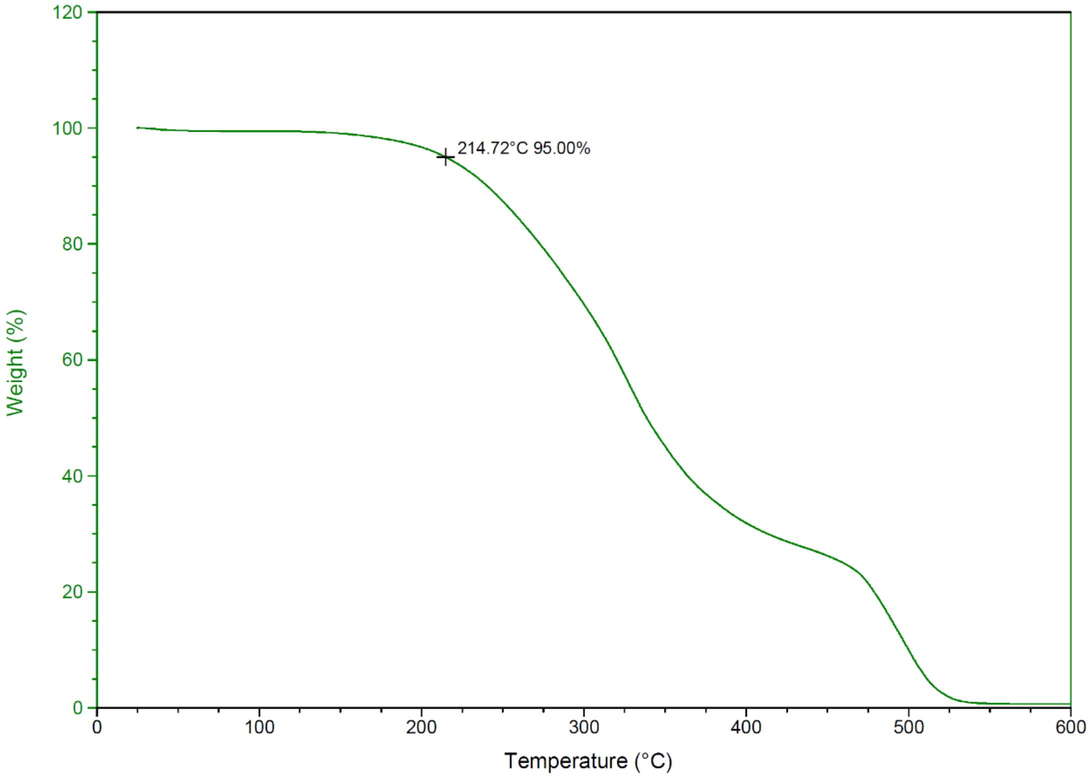


Figure S11. TGA Thermogram of **PV-CI-A** (Table S1, Entry 11).

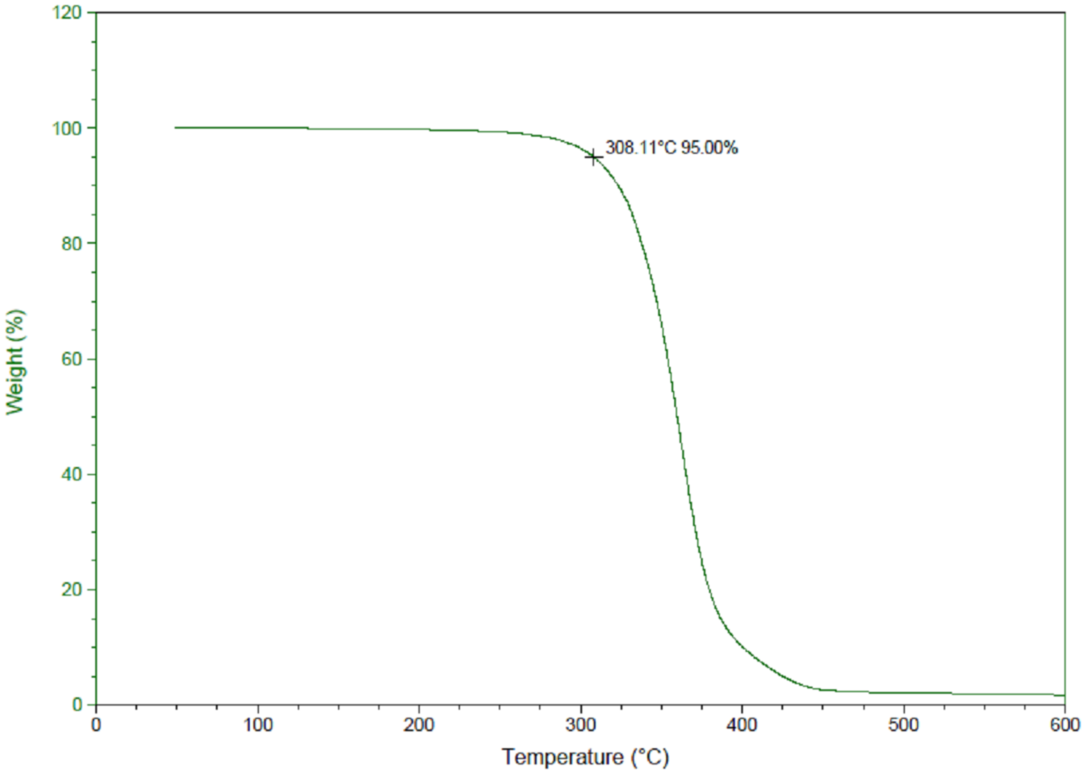


Figure S12. TGA Thermogram of **PV-CU-A** (Table S1, Entry 12).

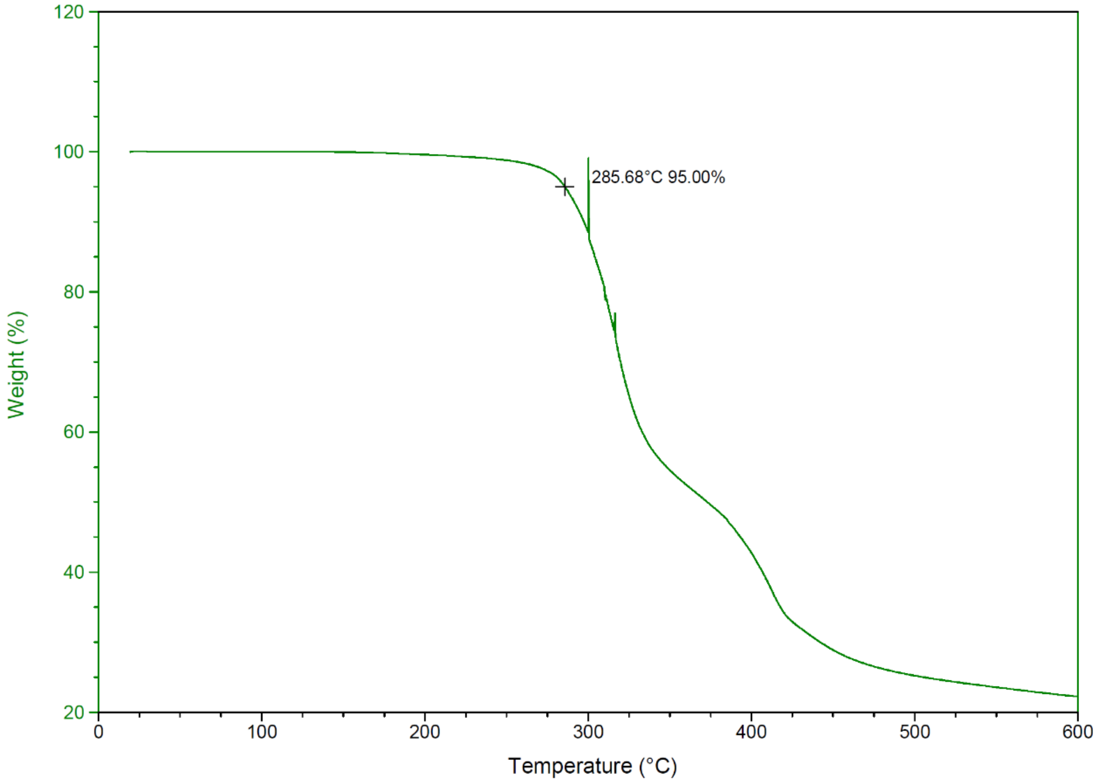


Figure S13. TGA Thermogram of **PV-HMF-A** (Table S1, Entry 13).

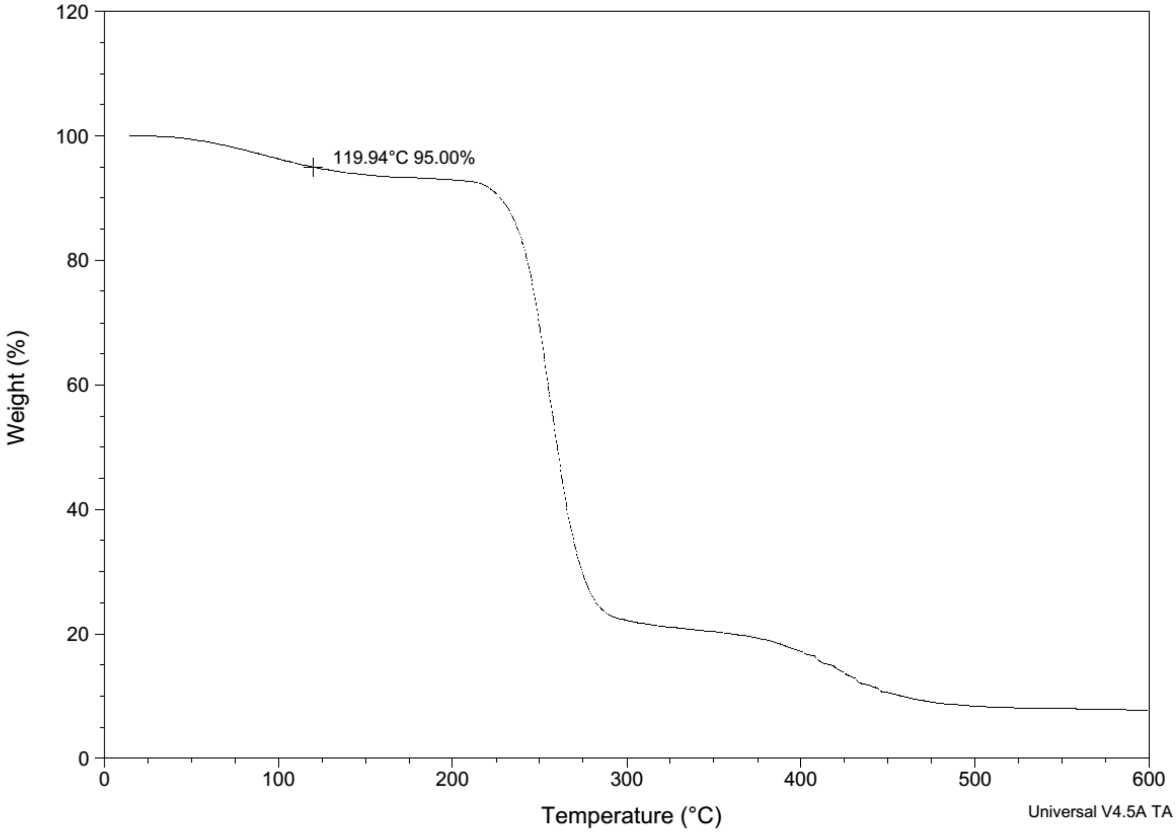


Figure S14. TGA Thermogram of **PVA*** (Table S1, Entry 14).

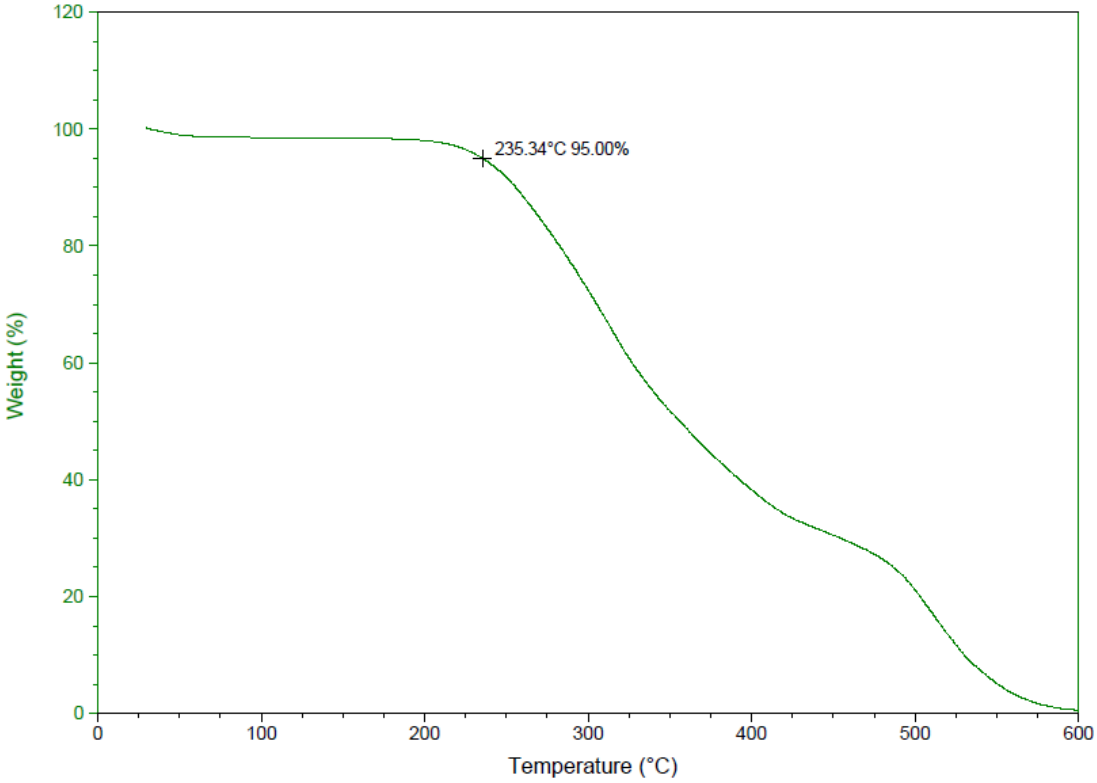


Figure S15. TGA Thermogram of **PV-VV-A*** (Table S1, Entry 15).

Differential Scanning Calorimetry (DSC) Thermograms

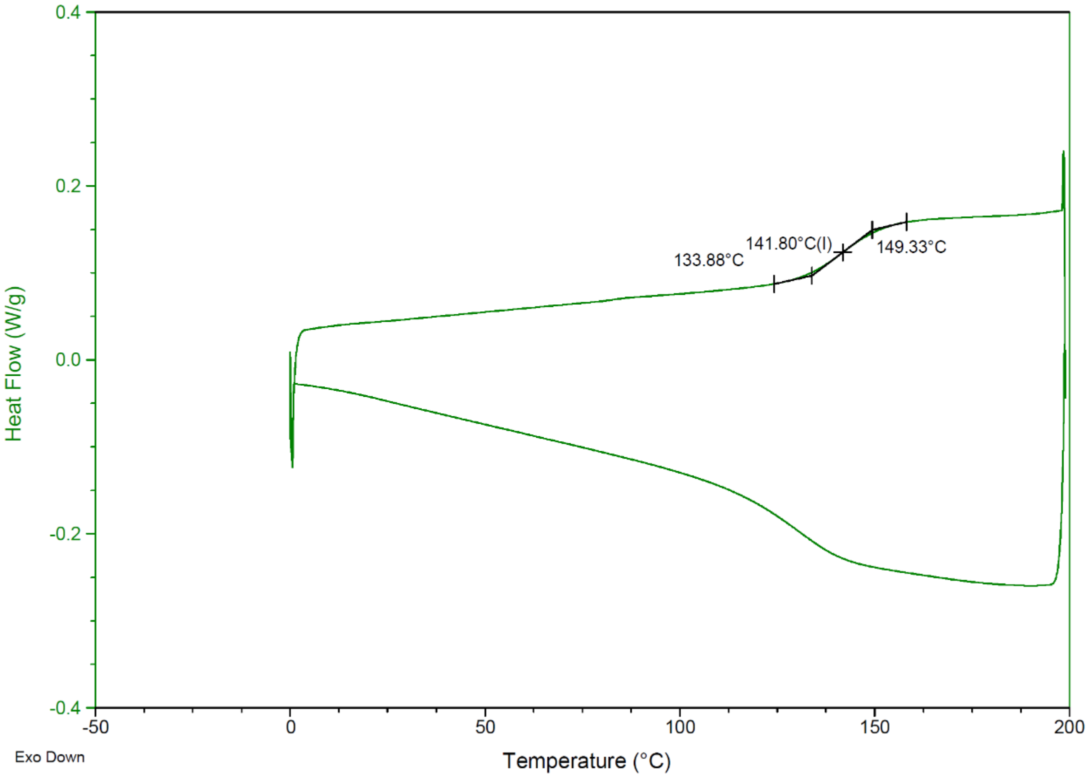


Figure S16. DSC Thermogram of **PV-VV-A** (Table S1, Entry 1).

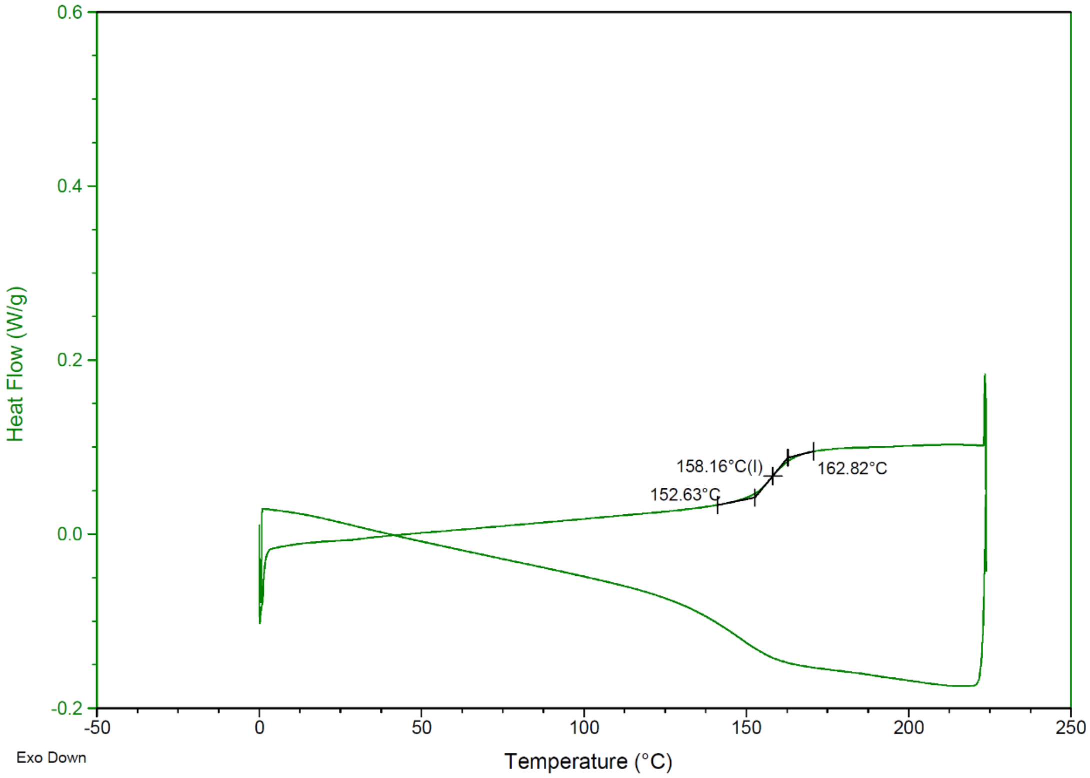


Figure S17. DSC Thermogram of **PV-HB-A** (Table S1, Entry 2).

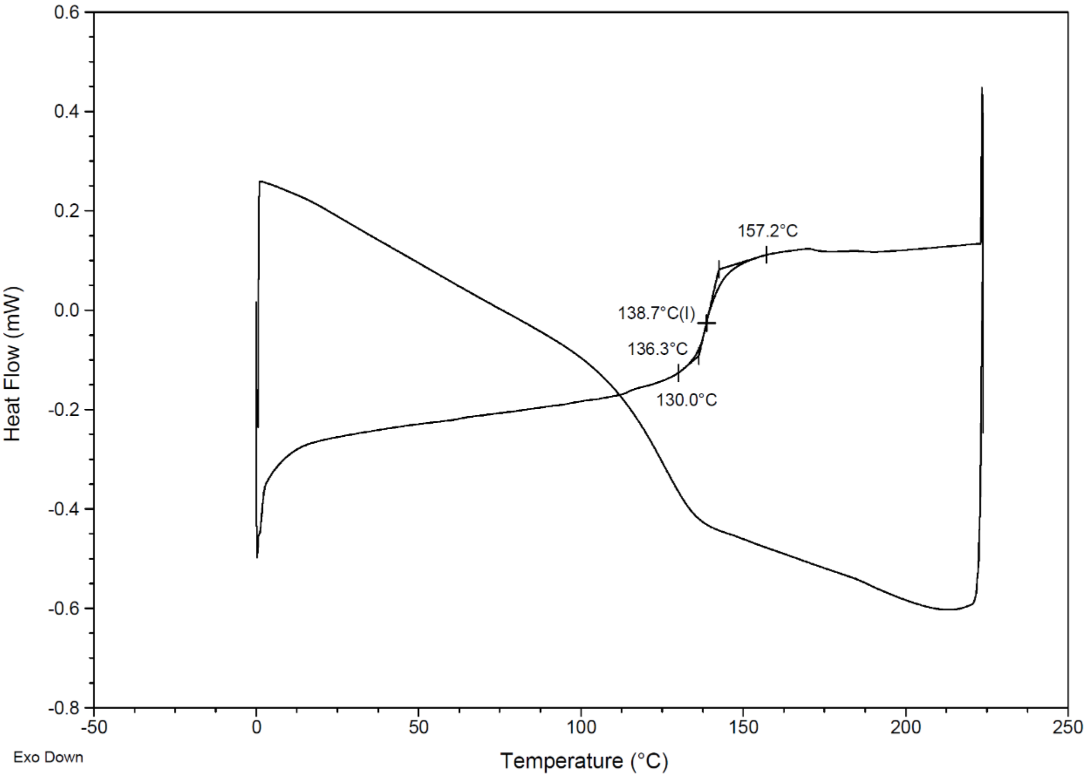


Figure S18. DSC Thermogram of **PV-SY-A** (Table S1, Entry 3).

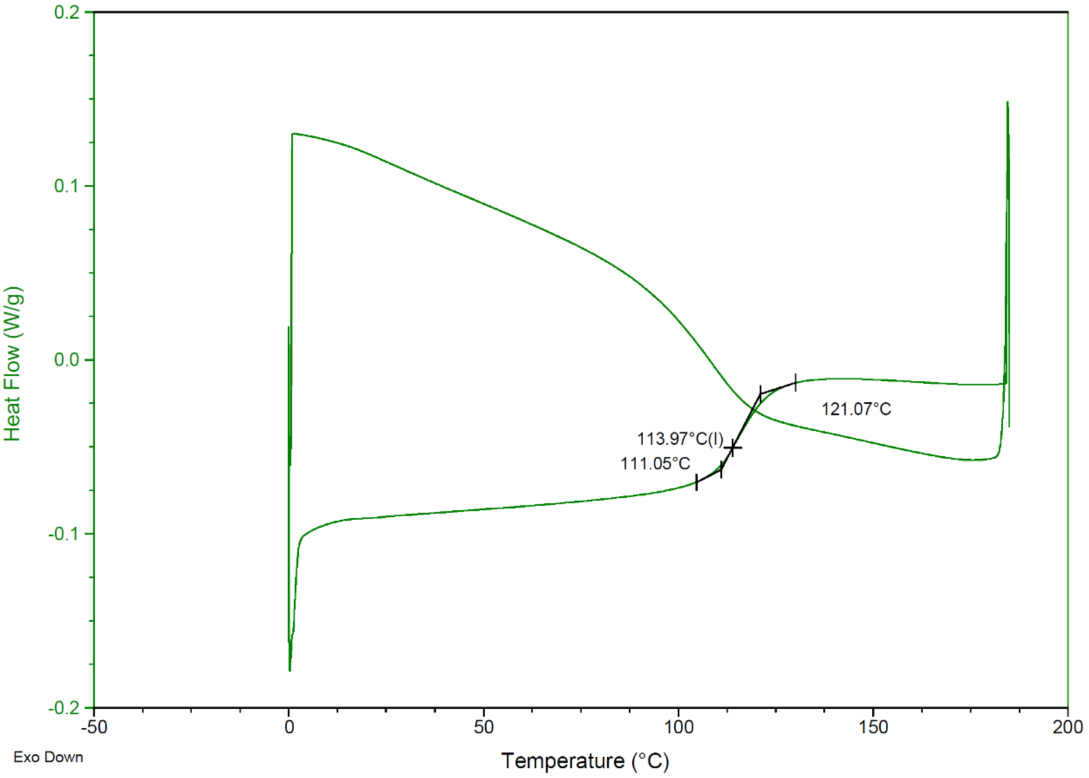


Figure S19. DSC Thermogram of **PV-EV-A** (Table S1, Entry 4).

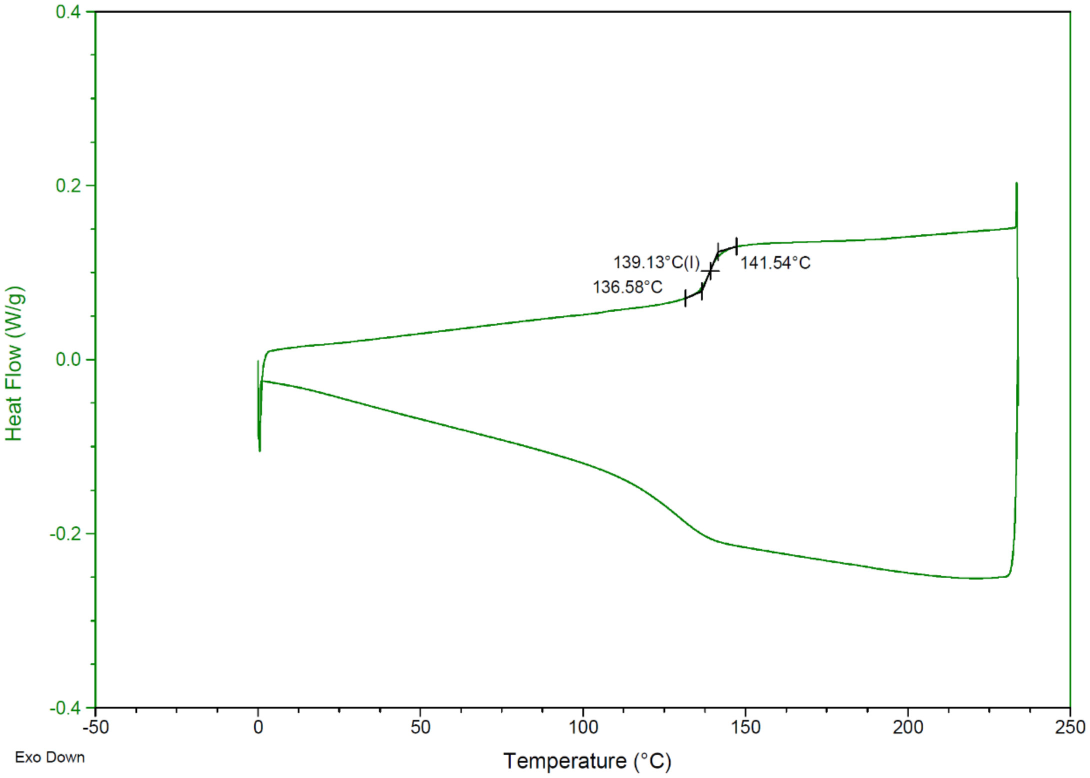


Figure S20. DSC Thermogram of **PV-OV-A** (Table S1, Entry 5).

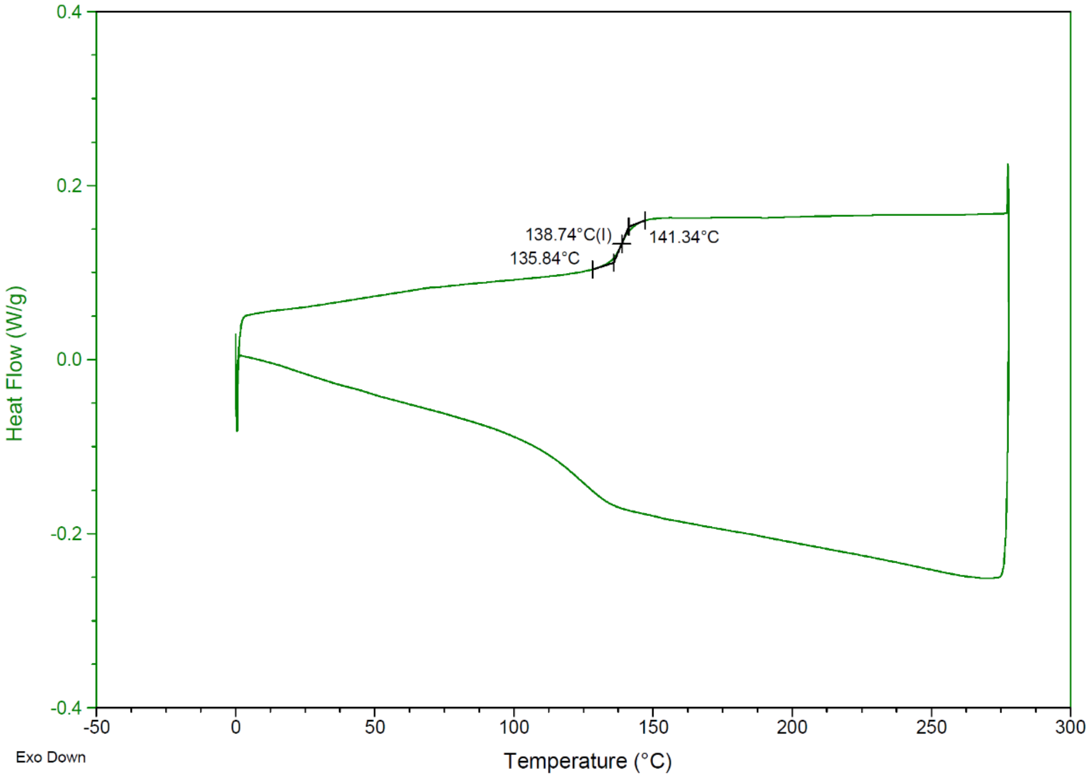


Figure S21. DSC Thermogram of **PV-IV-A** (Table S1, Entry 6).

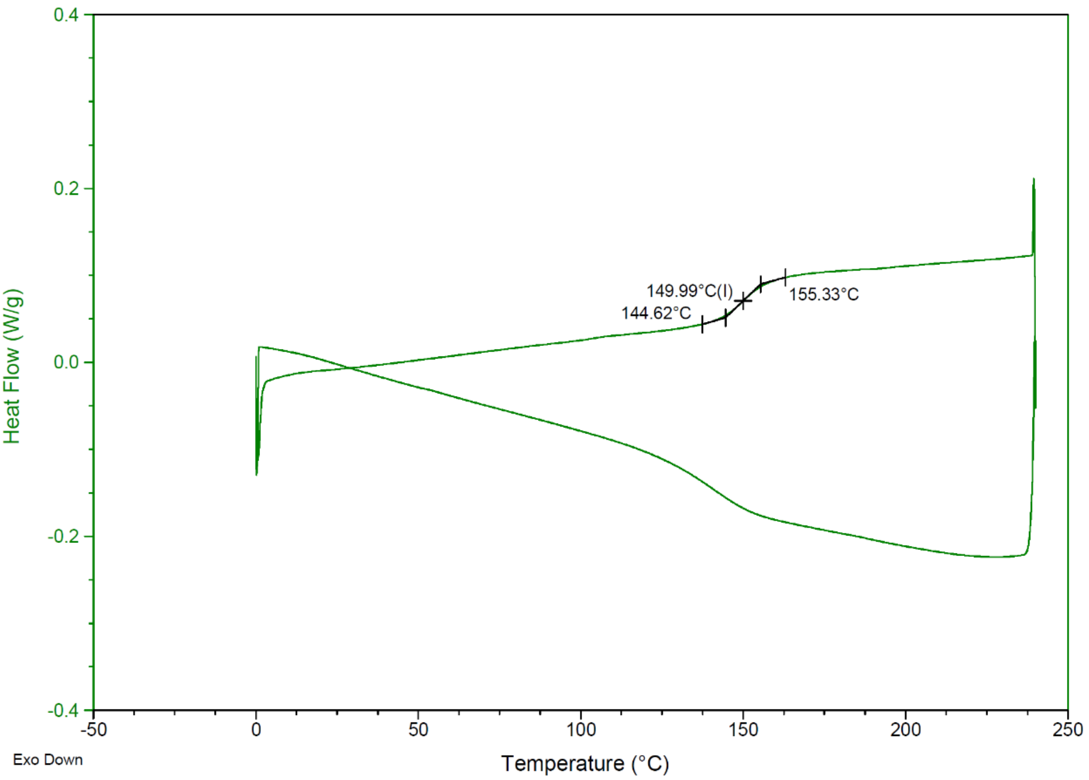


Figure S22. DSC Thermogram of **PV-SA-A** (Table S1, Entry 7).

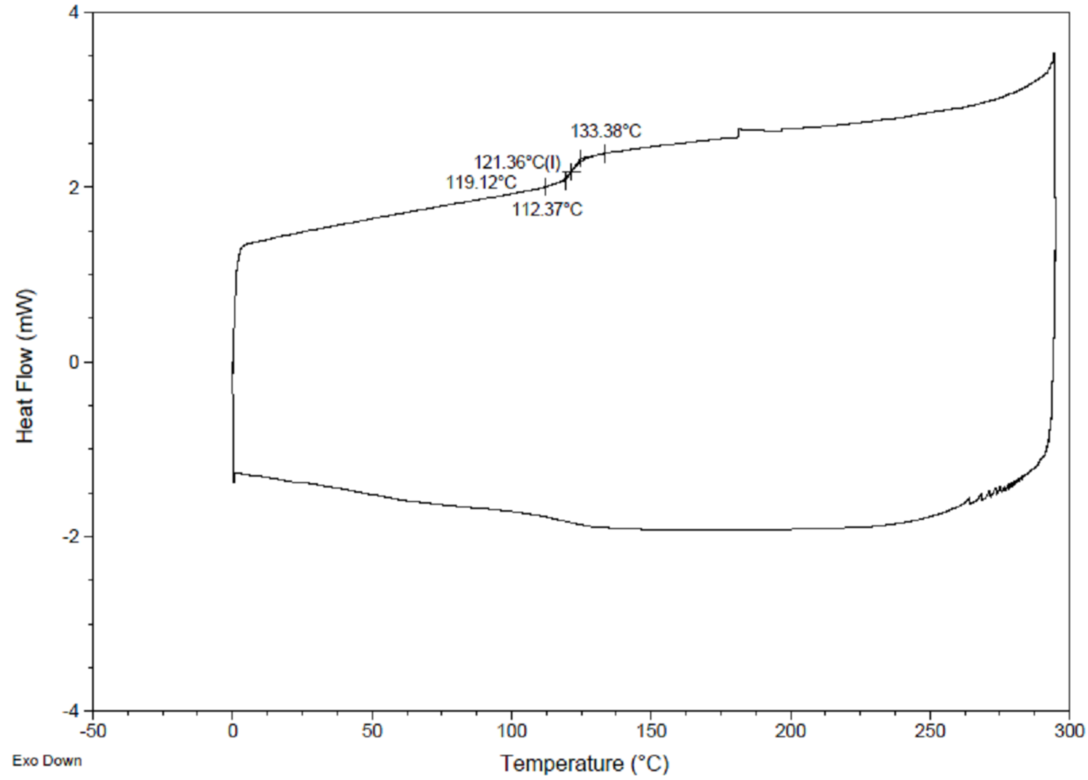


Figure S23. DSC Thermogram of **PV-OA-A** (Table S1, Entry 8).

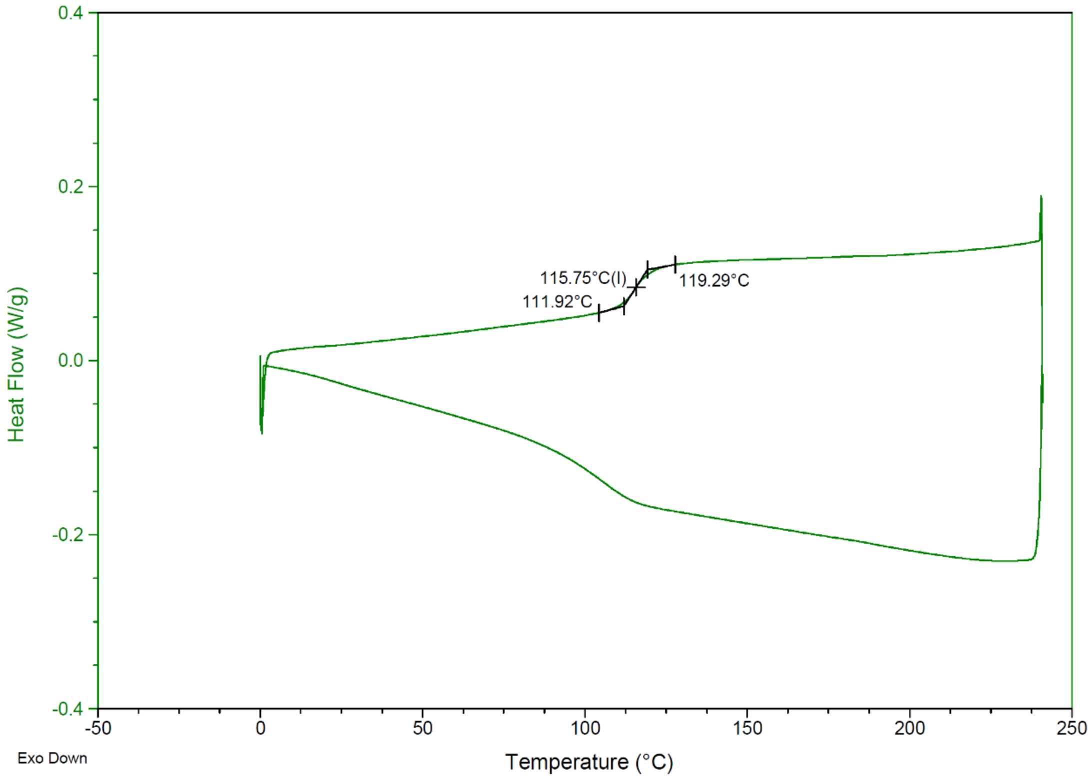


Figure S24. DSC Thermogram of **PV-PA-A** (Table S1, Entry 9).

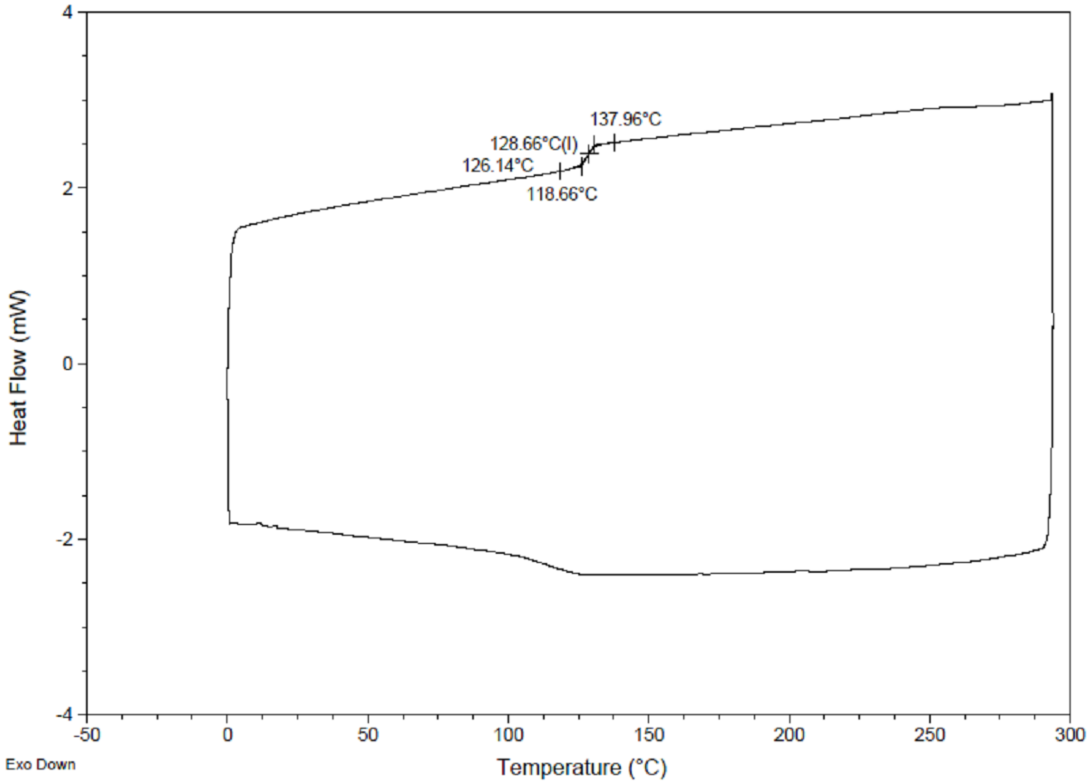


Figure S25. DSC Thermogram of **PV-BZ-A** (Table S1, Entry 10).

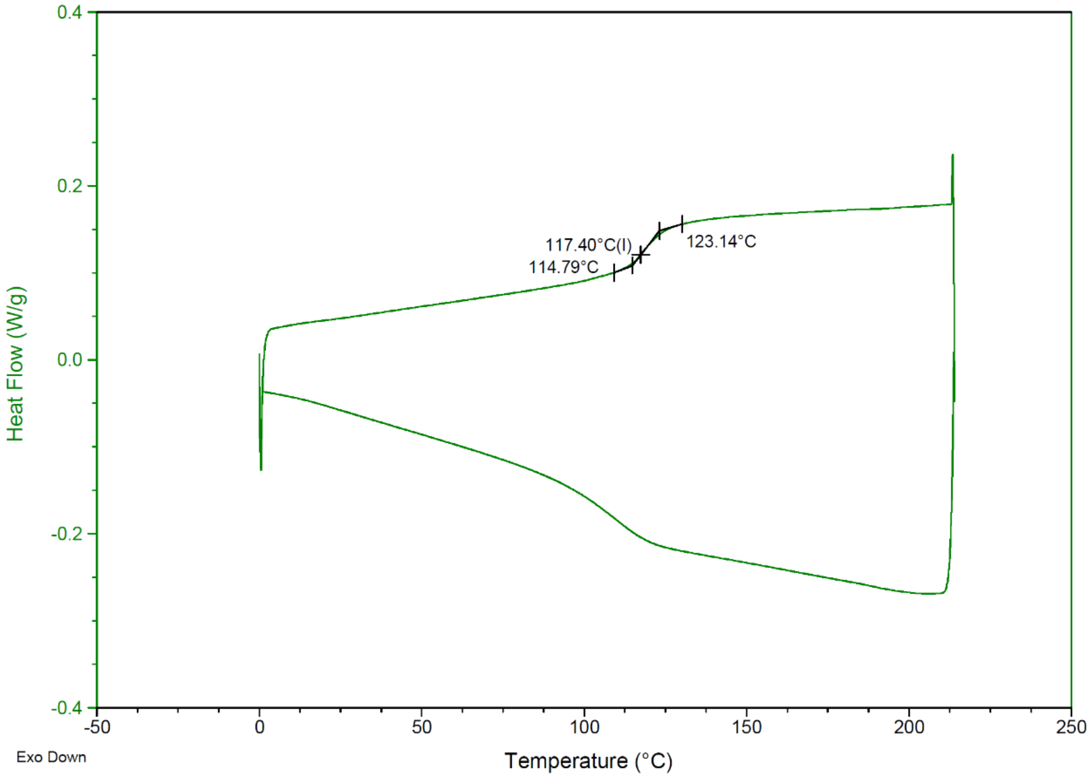


Figure S26. DSC Thermogram of **PV-CI-A** (Table S1, Entry 11).

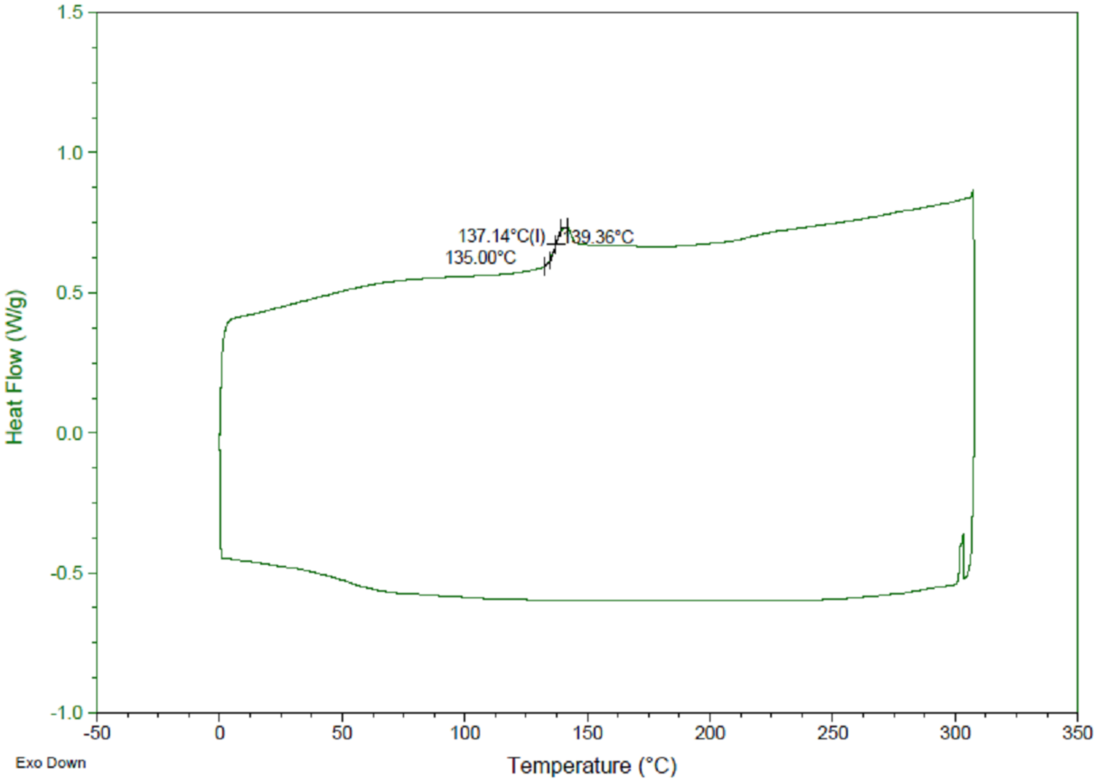


Figure S27. DSC Thermogram of **PV-CU-A** (Table S1, Entry 12).

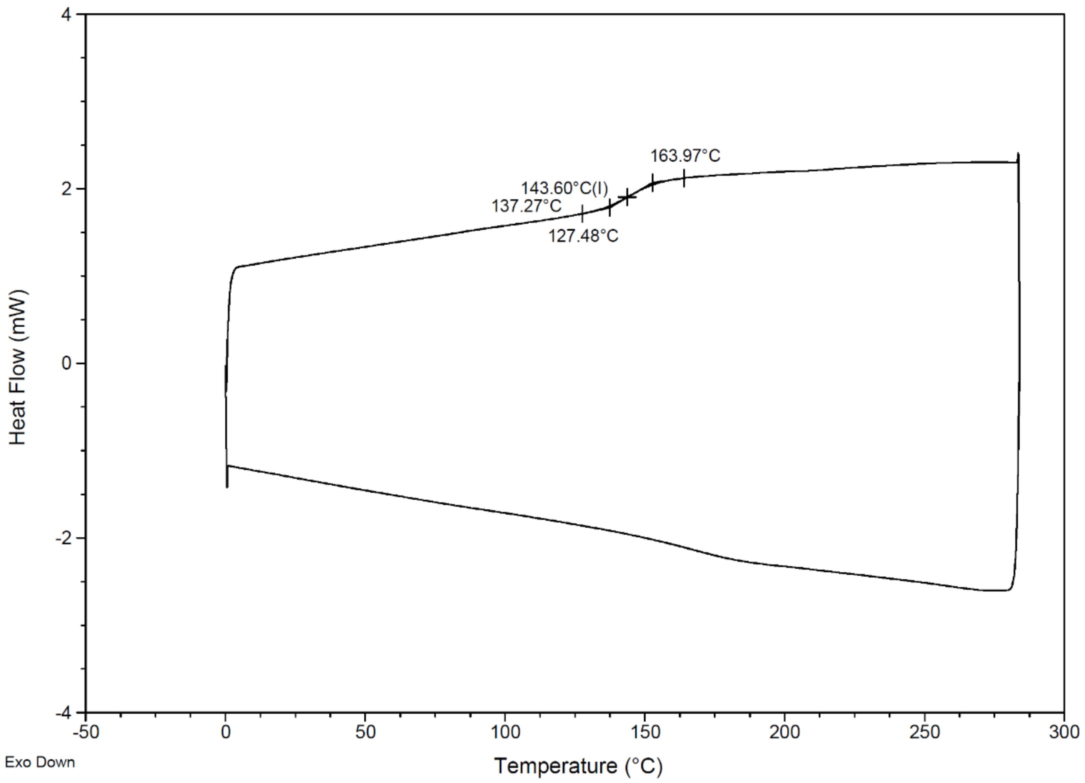


Figure S28. DSC Thermogram of **PV-HMF-A** (Table S1, Entry 13).

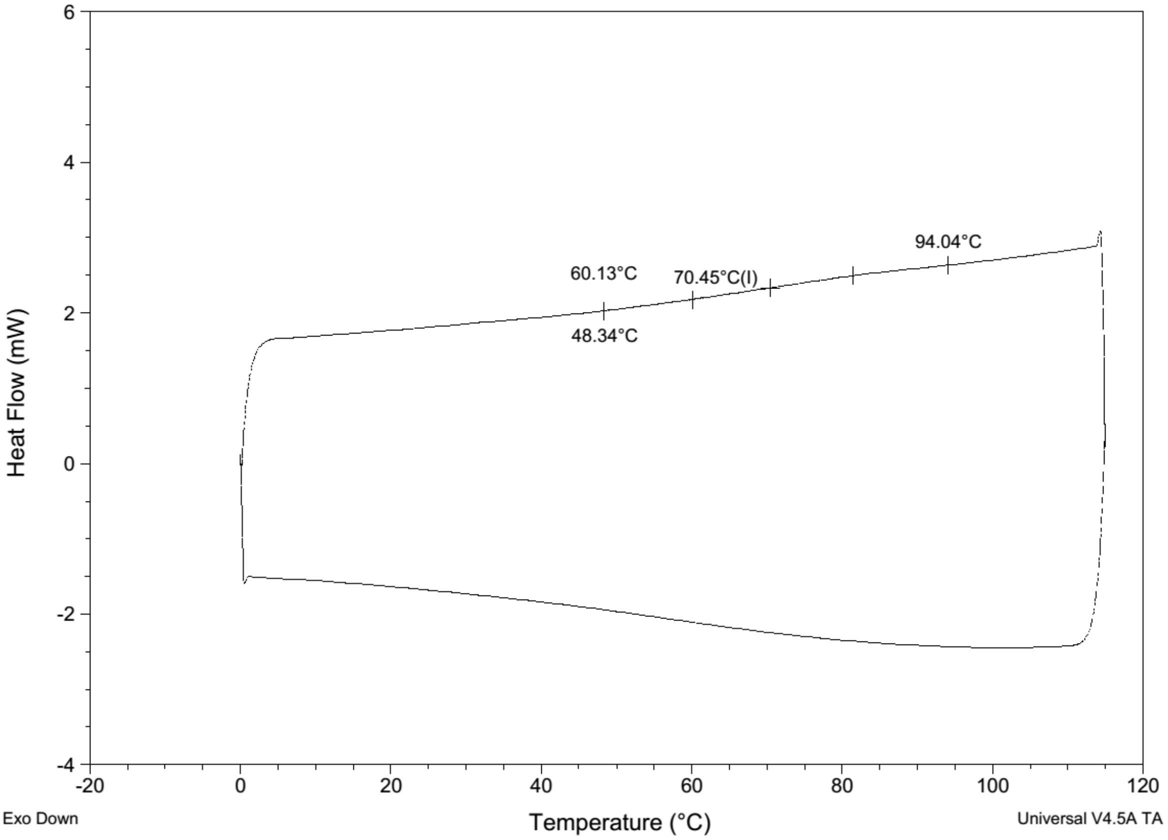


Figure S29. DSC Thermogram of **PVA*** (Table S1, Entry 14).

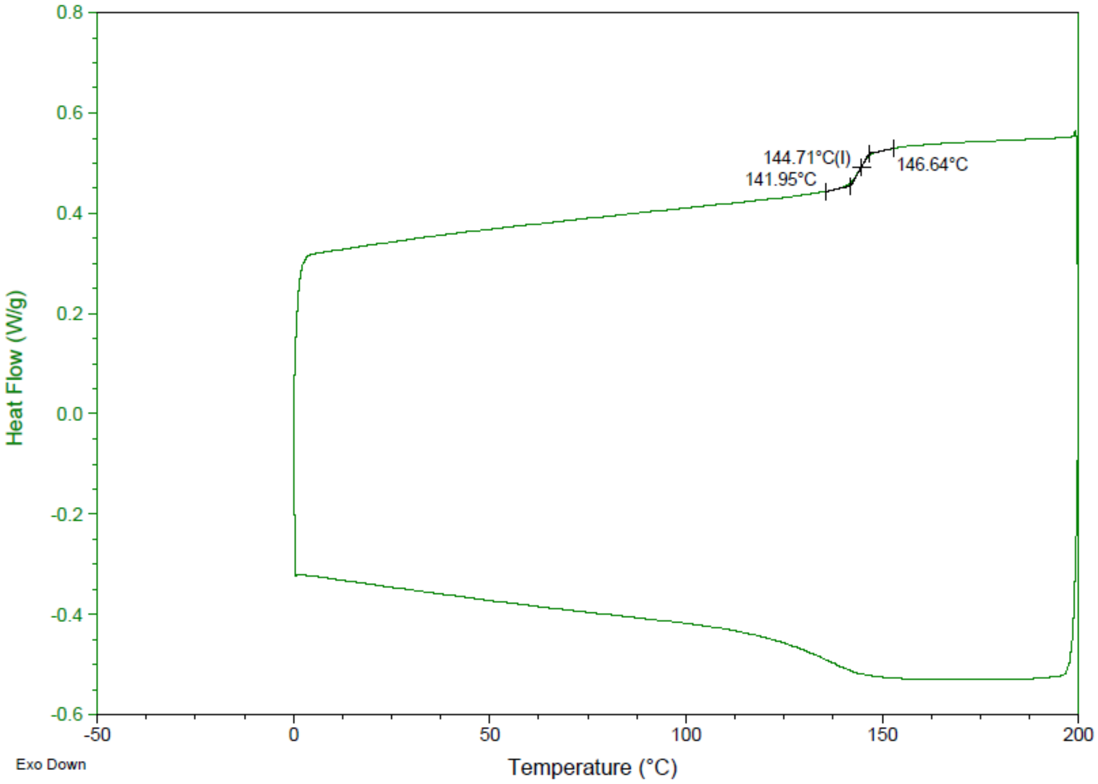


Figure S30. DSC Thermogram of **PV-VV-A*** (Table S1, Entry 15).

Gel Permeation Chromatography (GPC) Analysis

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	39963	22267	45529	70526	94466	67039	2.045

Peak information

	Start (mins)	End (mins)
Baseline region 1	11.02	11.58
Peak 1	14.17	20.87

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.39	10983729.932	58712.592

Chromatogram

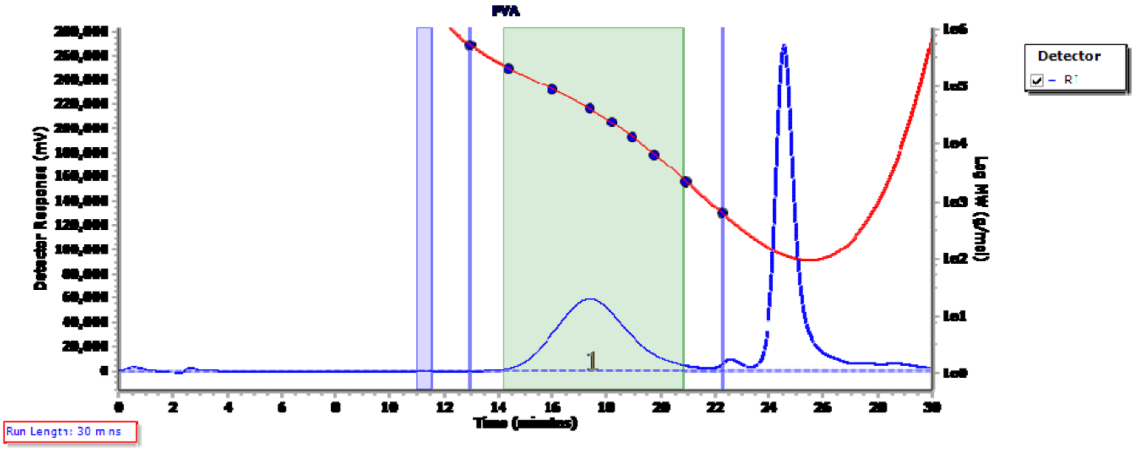


Figure S31. GPC Chromatogram of **PVA** (Table S1, Entry 0).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	42706	25695	54906	97254	165869	89815	2.137

Peak information

	Start (mins)	End (mins)
Baseline region 1	10.77	11.35
Peak 1	12.95	21.42

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.69	2221255.040	10983.992

Chromatogram

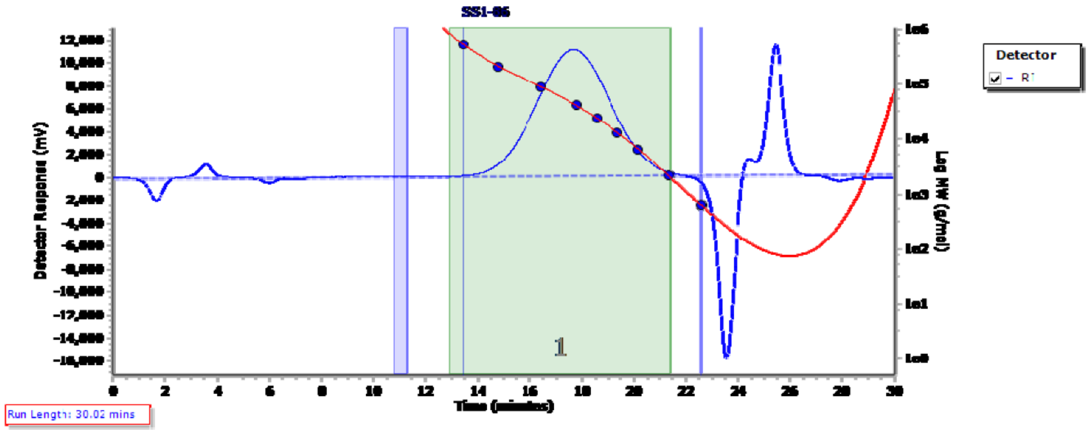


Figure S32. GPC Chromatogram of **PV-VV-A** (Table S1, Entry 1).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	37454	22764	52523	101861	171845	93284	2.307

Peak information

	Start (mins)	End (mins)
Baseline region 1	0.00	1.83
Baseline region 2	29.47	29.97
Peak 1	13.58	21.20

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.90	3019497.257	14503.716

Chromatogram

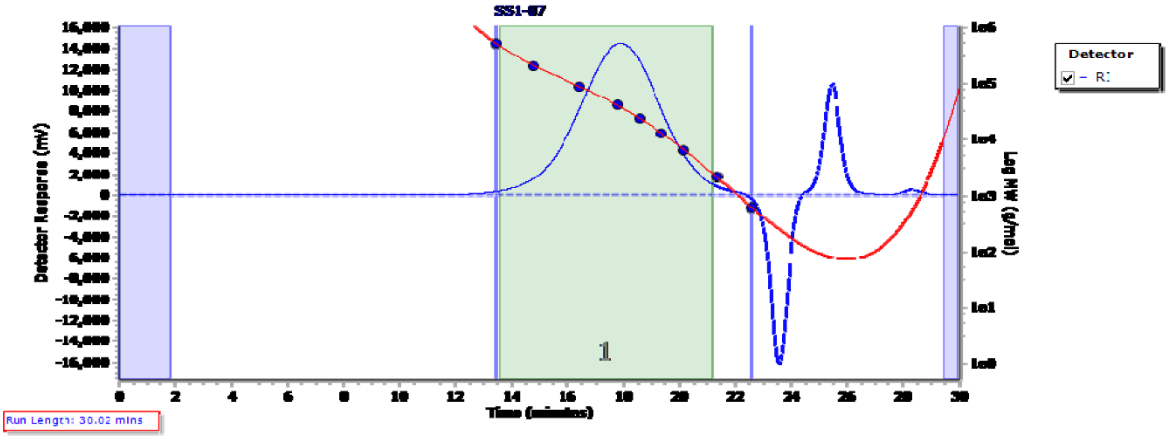


Figure S33. GPC Chromatogram of **PV-HB-A** (Table S1, Entry 2).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	46275	28750	59666	99618	145073	93440	2.075

Peak information

	Start (mins)	End (mins)
Baseline region 1	1.22	2.59
Baseline region 2	29.11	29.97
Peak 1	13.91	21.35

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.56	5697828.782	28234.645

Chromatogram

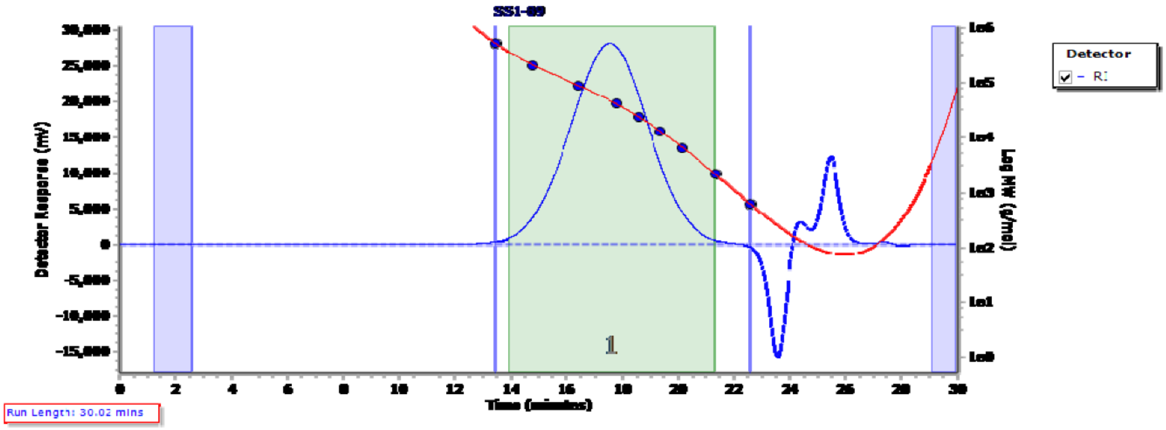


Figure S34. GPC Chromatogram of **PV-SY-A** (Table S1, Entry 3).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	41215	22766	51597	85951	121758	80909	2.266

Peak information

	Start (mins)	End (mins)
Baseline region 1	0.40	2.52
Baseline region 2	29.50	29.97
Peak 1	14.23	21.77

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.74	4544257.224	22335.468

Chromatogram

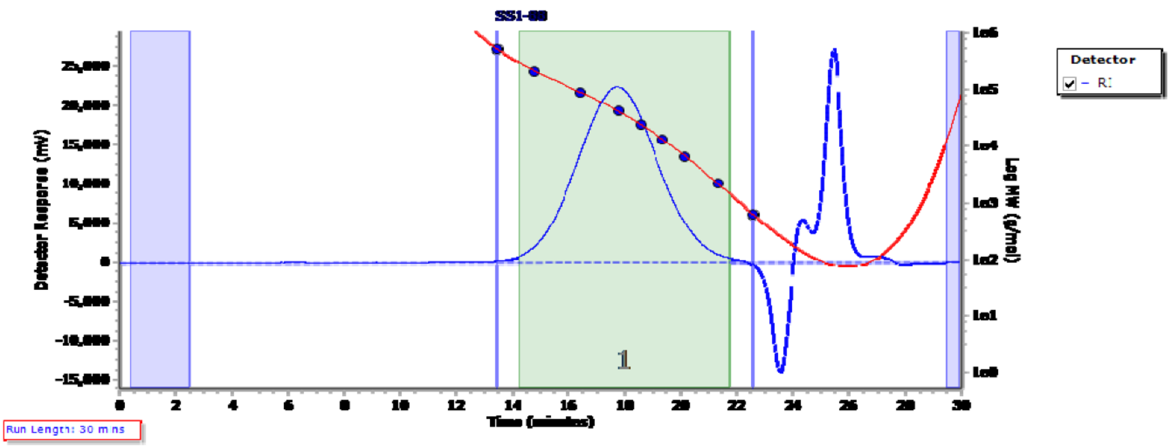


Figure S35. GPC Chromatogram of **PV-EV-A** (Table S1, Entry 4).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	47033	24520	58929	102439	156622	95511	2.403

Peak information

	Start (mins)	End (mins)
Baseline region 1	2.58	3.31
Baseline region 2	29.64	30.01
Peak 1	13.60	21.90

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.53	3335915.215	16069.401

Chromatogram

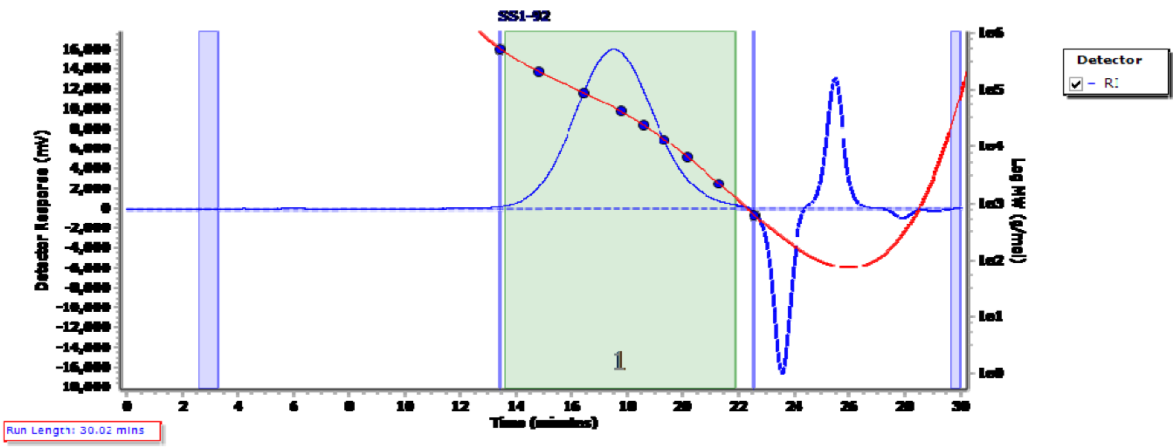


Figure S36. GPC Chromatogram of **PV-OV-A** (Table S1, Entry 5).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	42351	24529	53368	91660	139375	85566	2.176

Peak information

	Start (mins)	End (mins)
Baseline region 1	1.24	2.18
Baseline region 2	29.82	30.00
Peak 1	13.64	21.28

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.70	3833001.750	18872.962

Chromatogram

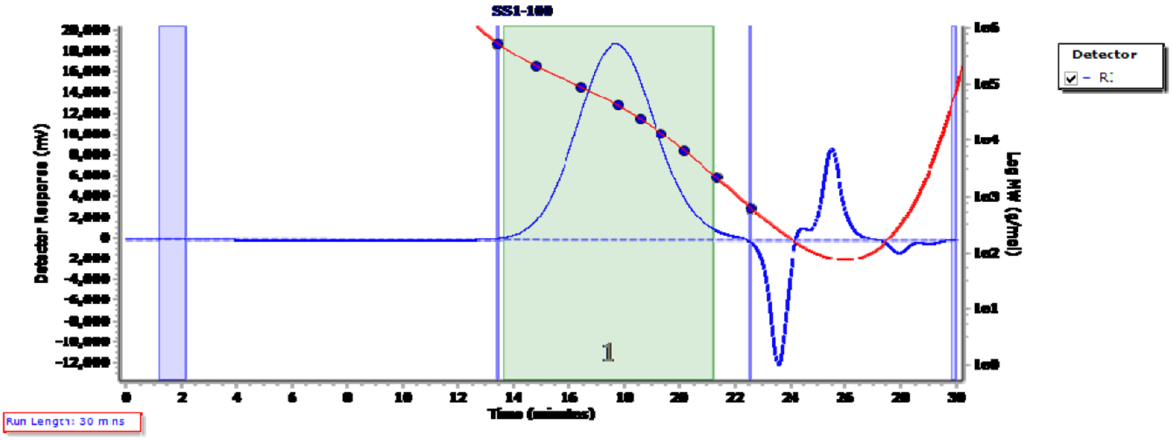


Figure S37. GPC Chromatogram of **PV-IV-A** (Table S1, Entry 6).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	33135	17009	45024	85599	136413	79126	2.647

Peak information

	Start (mins)	End (mins)
Baseline region 1	1.82	2.98
Baseline region 2	29.57	30.01
Peak 1	13.75	21.71

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	18.08	4058974.919	18722.163

Chromatogram

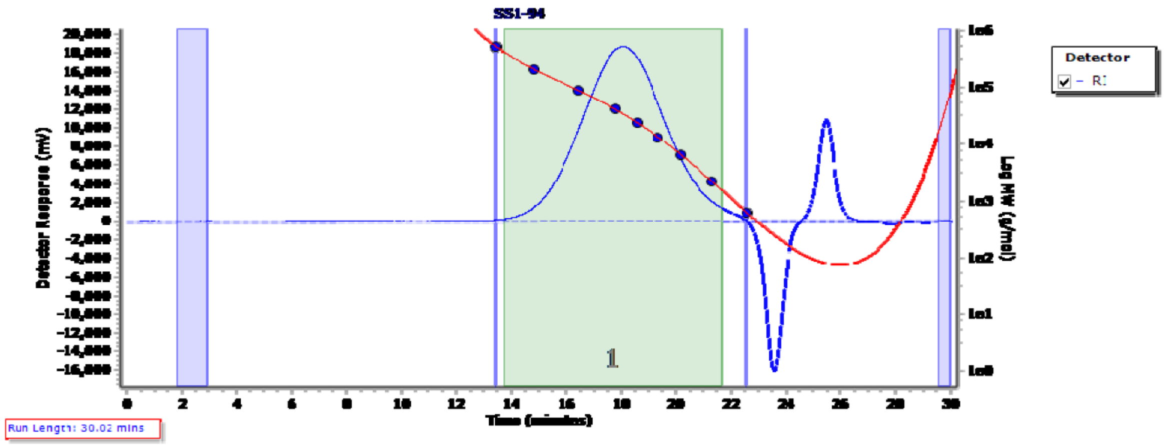


Figure S38. GPC Chromatogram of **PV-SA-A** (Table S1, Entry 7).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	26423	11175	33113	59131	82909	55604	2.963

Peak information

	Start (mins)	End (mins)
Baseline region 1	5.60	6.80
Baseline region 2	29.57	30.00
Peak 1	14.98	22.37

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	18.41	5310695.498	25066.822

Chromatogram

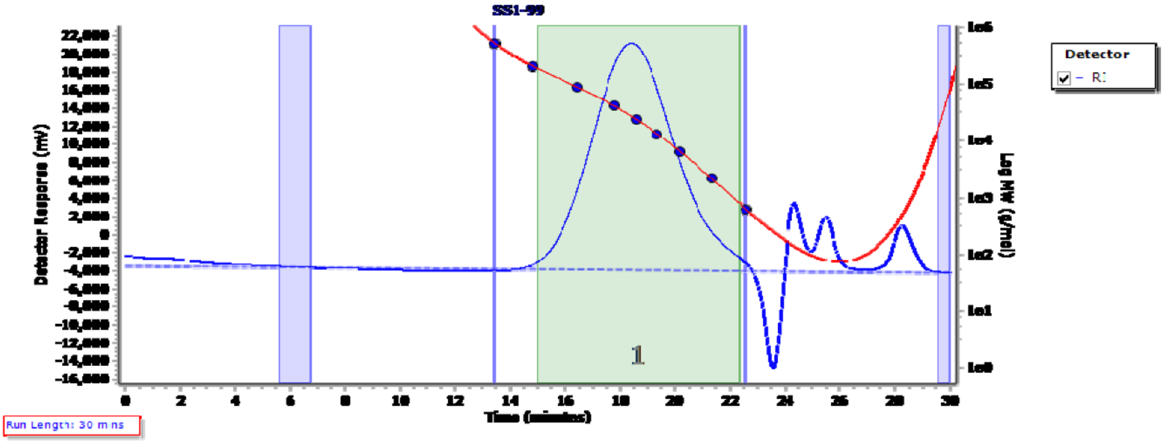


Figure S39. GPC Chromatogram of **PV-OA-A** (Table S1, Entry 8).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	41999	22055	51153	85925	123796	80741	2.319

Peak information

	Start (mins)	End (mins)
Baseline region 1	1.08	2.84
Baseline region 2	29.18	29.97
Peak 1	14.05	21.77

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.71	3943358.139	19349.050

Chromatogram

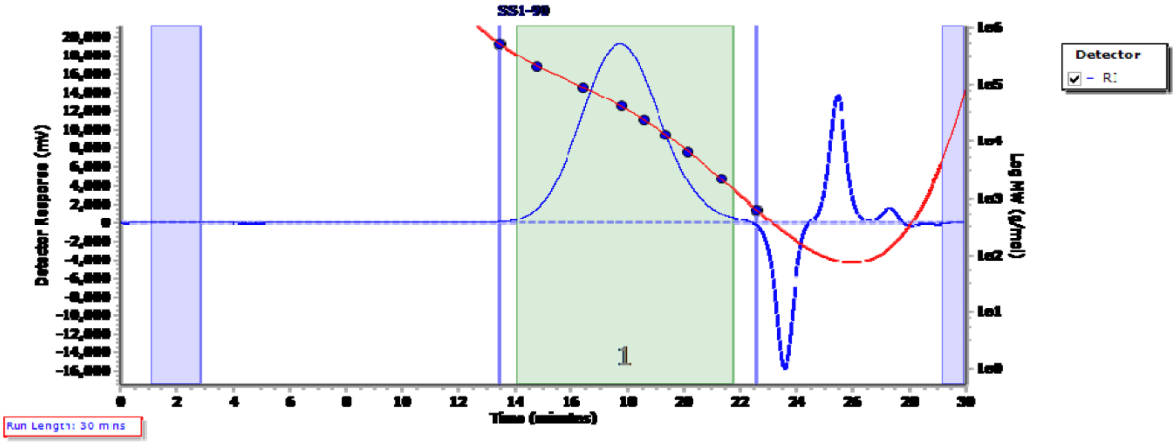


Figure S40. GPC Chromatogram of **PV-PA-A** (Table S1, Entry 9).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	29535	13305	37040	66949	100918	62461	2.784

Peak information

	Start (mins)	End (mins)
Baseline region 1	0.29	2.91
Baseline region 2	29.13	30.01
Peak 1	14.08	22.33

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	18.25	3337716.905	16158.357

Chromatogram

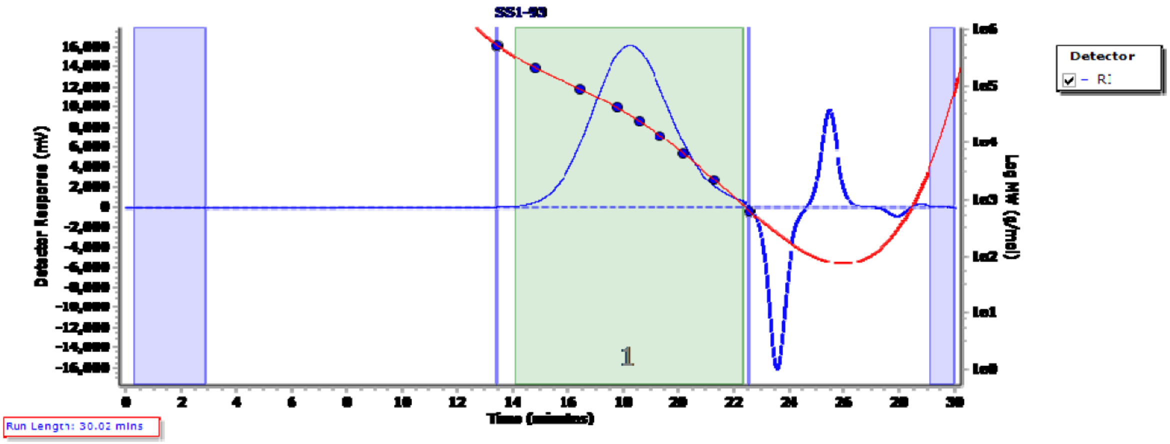
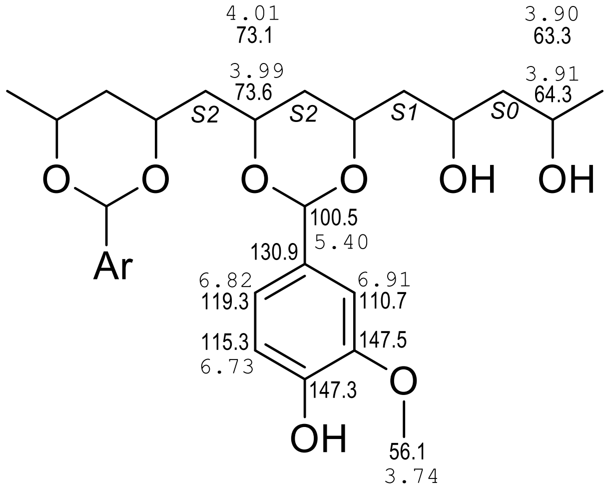


Figure S41. GPC Chromatogram of **PV-BZ-A** (Table S1, Entry 10).

2D NMR Spectra and Analysis

Through a complete NMR characterization of the sample **P-VV-VA**, it was possible to assign the peaks for both ^{1}H and ^{13}C in all the entries. Complete assignment for the **P-VV-VA** sample is included below as well as the spectra used for that assignment.



S2: 38.3 (1.28,1.58) 37.6 (1.26, 1.67)
S1: 44.9 (1.45,1.54) 44.6 (1.70)
S0: 46.7 (1.35) 46.3 (1.34, 1.37)

Figure S42. Full ^{1}H and ^{13}C NMR assignments for **PV-VV-A** (Table S1, Entry 1).

The ratio of the intensity of the acetal proton at 5.40 and the intensity of the methylene protons between 1.00 and 2.00 ppm affords the degree of acetalization of PVA by vanillin, around 60% (Figure S43).

Of the methine carbons in PVA, those at 73.6 and 73.1 couple in the gHMBC spectrum (Figure S44) with the acetal proton at 5.40, therefore the oxygen bound to them is in an acetal moiety. The methine carbons at 64.3, 63.3 carry OHs. The gHSQC spectrum displays distinct ranges for the protons of these two types of methine, around 4.00 for the ones in the acetal and around 3.90 for the ones carrying OHs (Figure S45). This allows the assignment of the methylene groups in PVA as *S2* – a methylene between two acetal oxygens, *S1* – a methylene between an acetal oxygen and an OH, and *S0* – a methylene between two OHs. In the gHSQCTOCSY spectrum, the *S2* carbons at 38.3 and 37.6 display cross-peaks with protons at 4.00 only and the *S0* carbons at 46.7 and 46.3 with protons at 3.90 only, while the *S1* carbons at 44.9 and 44.6 have cross-peaks with both of these types of methylene protons (Figure S46).

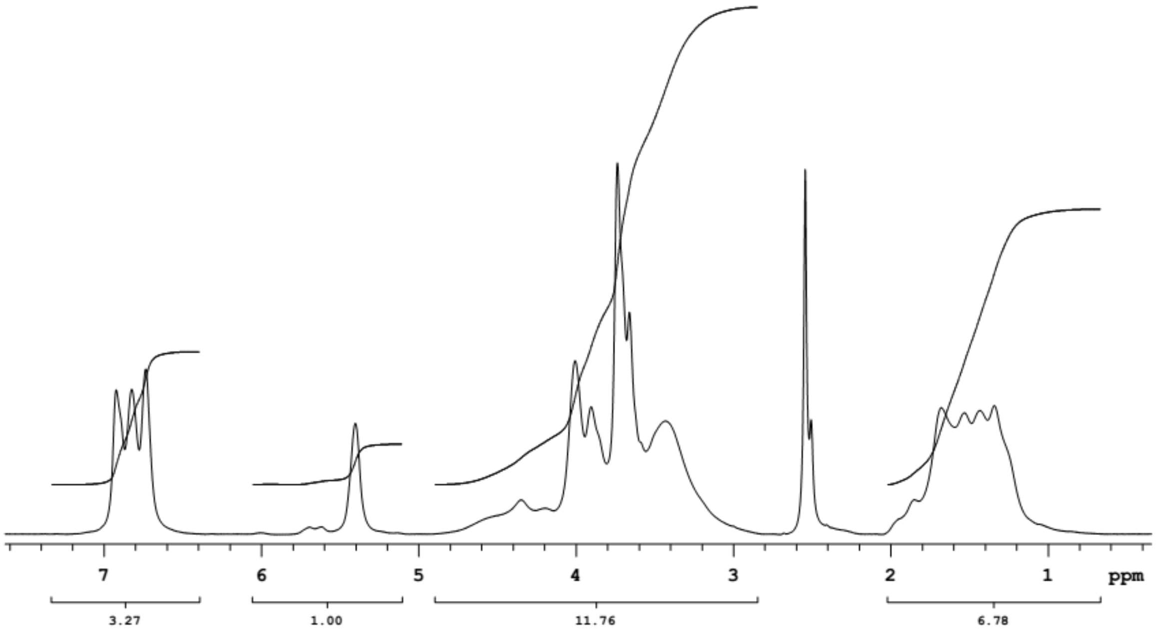


Figure S43. Zoomed area of ^{1}H NMR spectrum of **PV-VV-A**.

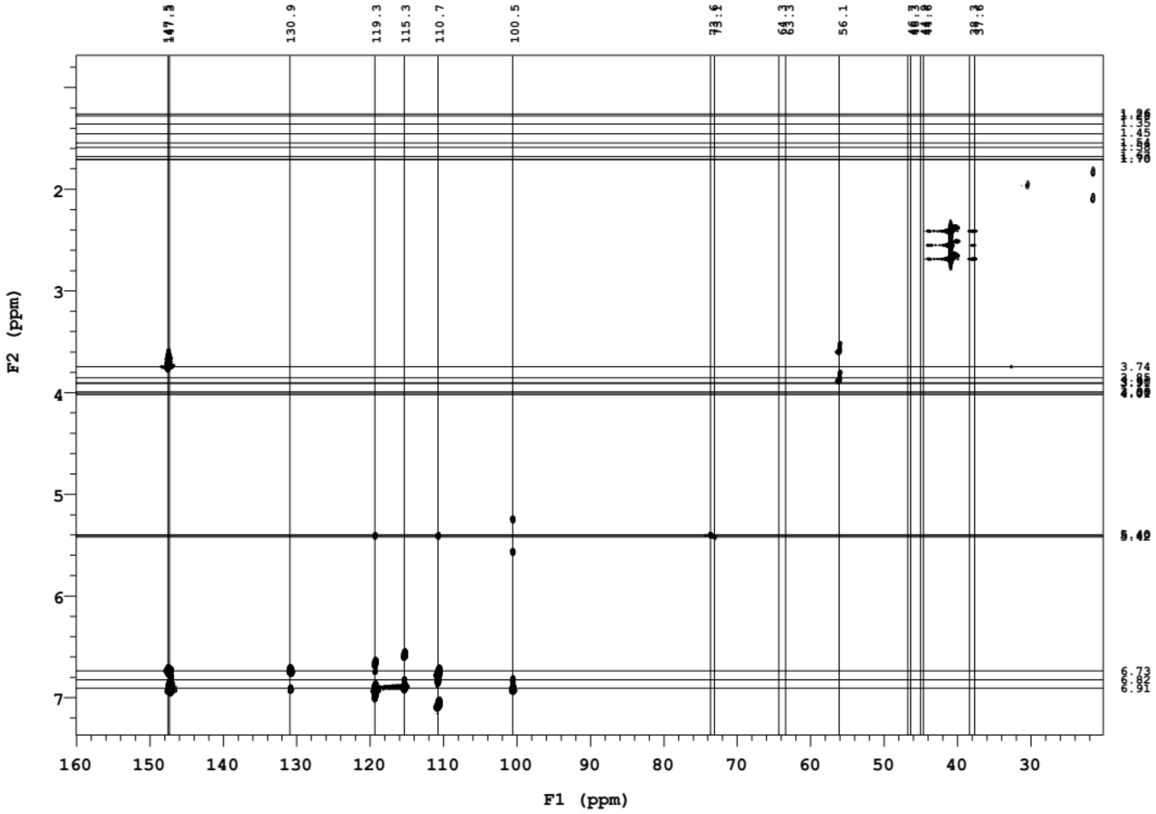


Figure S44. gHMBC spectrum of **PV-VV-A**.

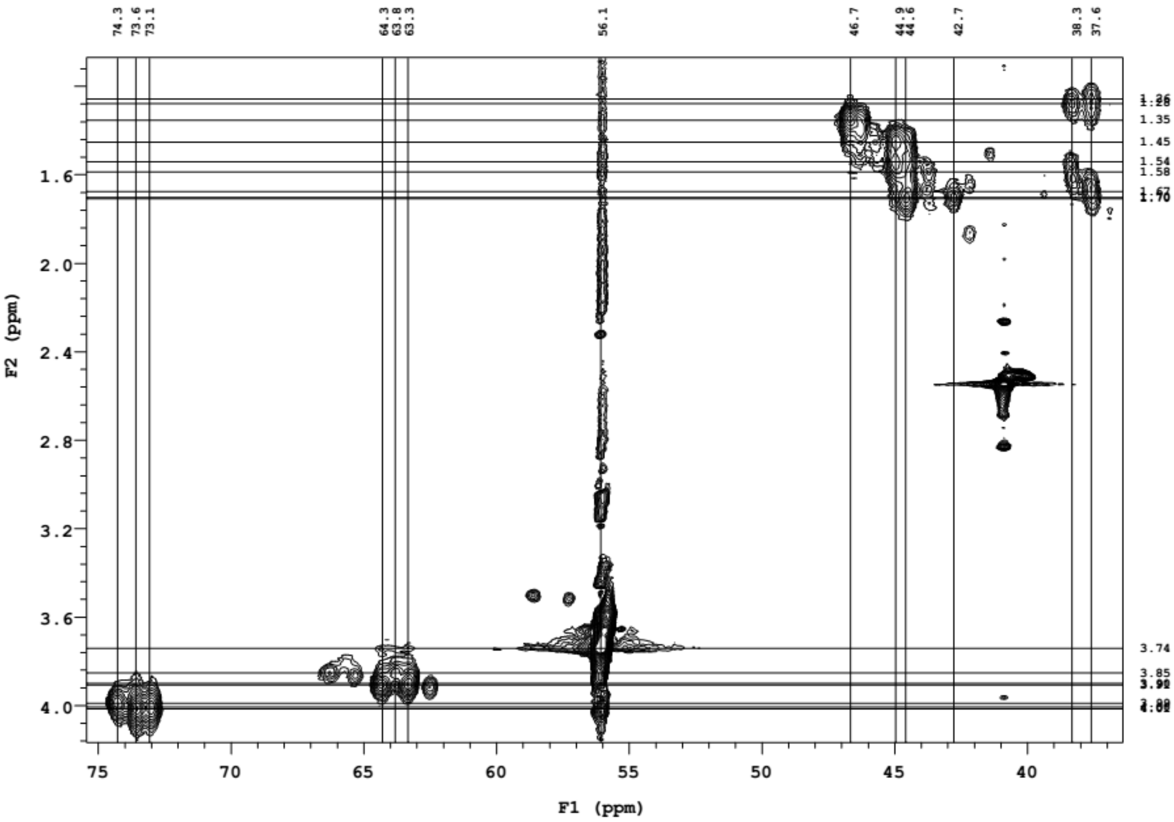


Figure S45. gHSQC spectrum of **PV-VV-A**.

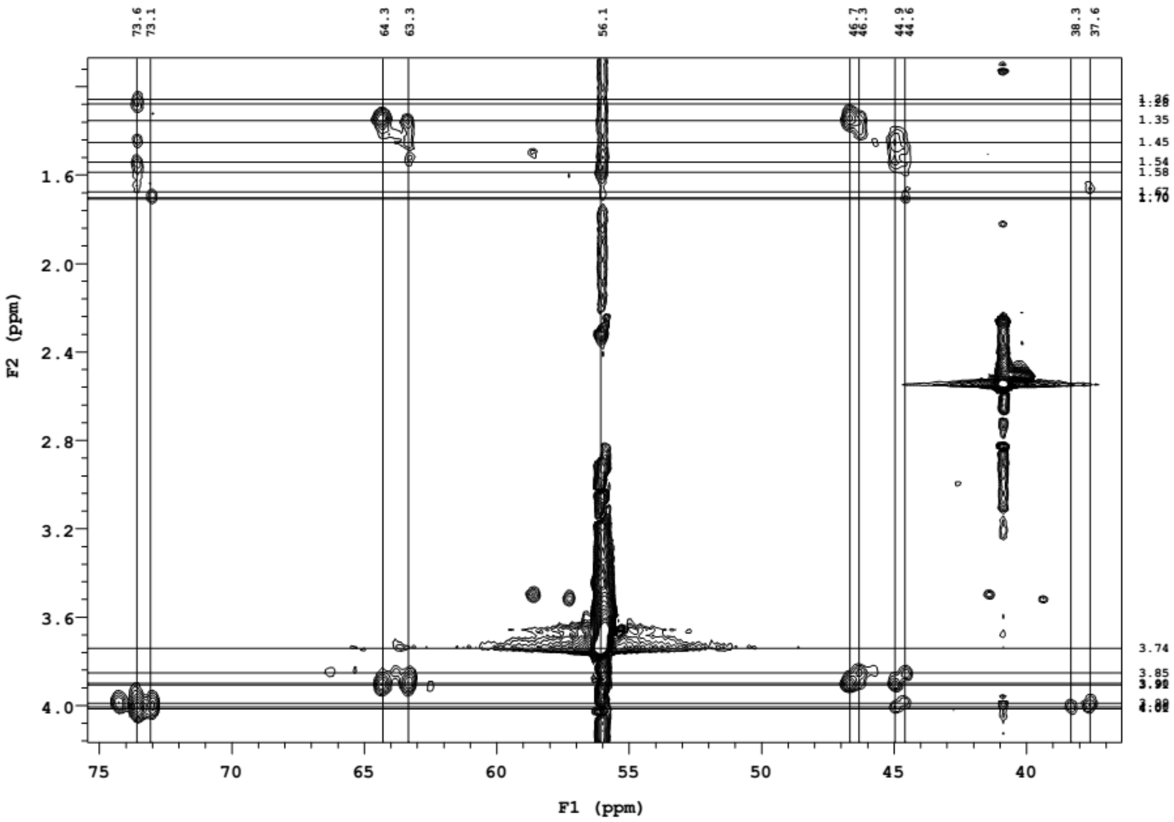


Figure S46. gHSQCTOCSY spectrum of **PV-VV-A**.

^{1}H NMR Spectra

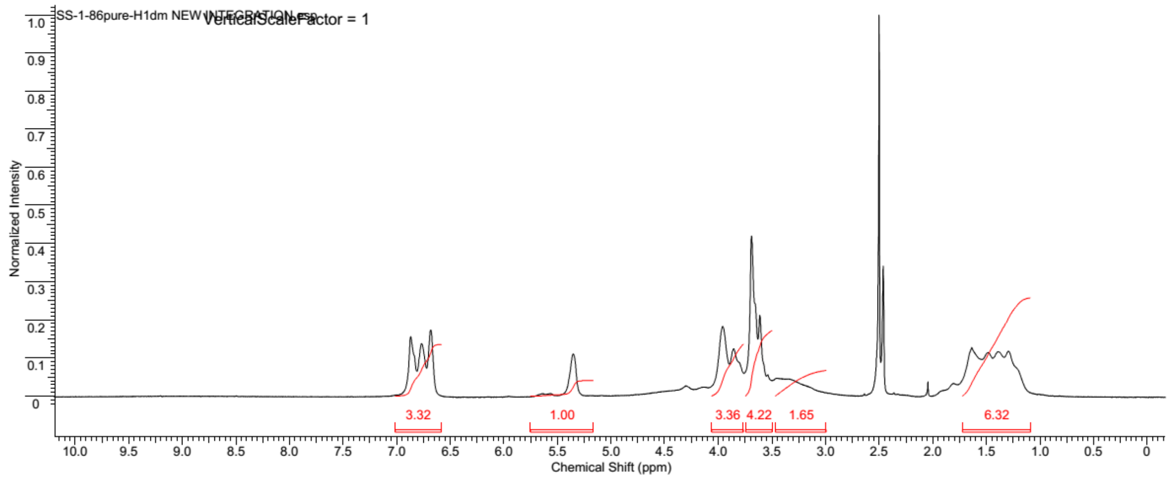


Figure S47. ^{1}H NMR Spectrum **PV-VV-A** (Table S1, Entry 1). % Acetalization = (4x1)/(6.32) = 63.3%

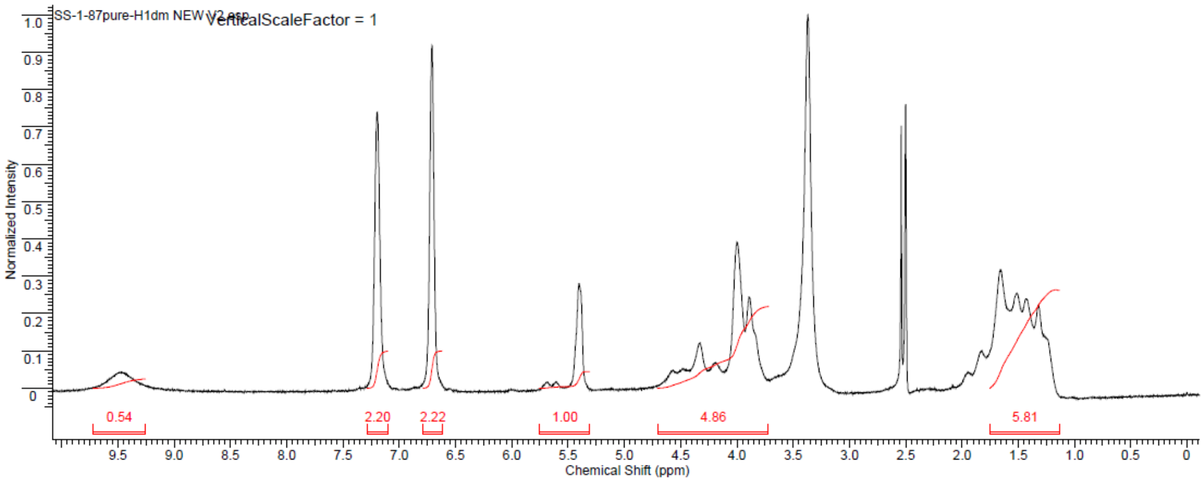


Figure S48. ^{1}H NMR Spectrum **PV-HB-A** (Table S1, Entry 2). % Acetalization = (4x1)/(5.81) = 68.8%

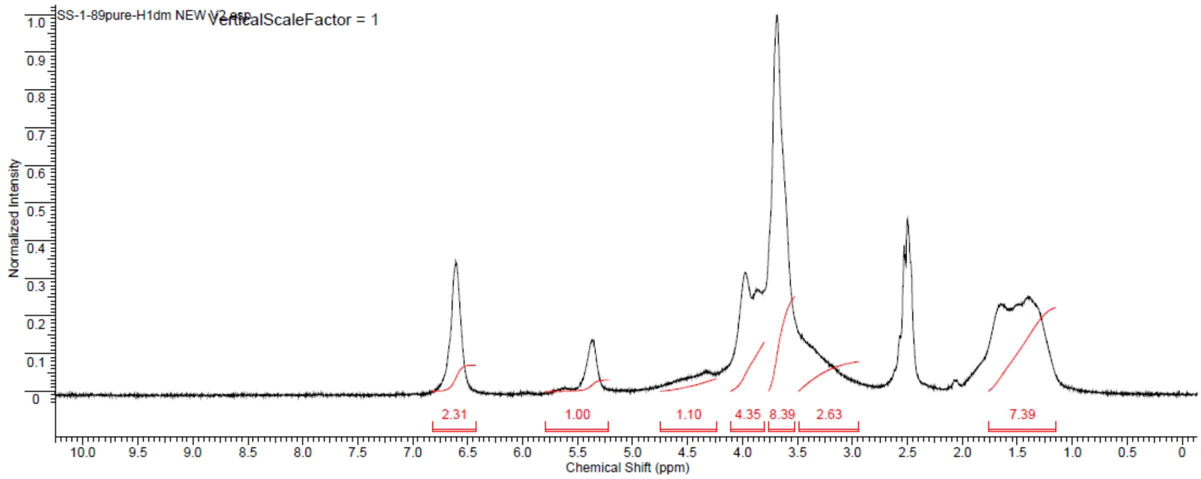


Figure S49. ^{1}H NMR Spectrum **PV-SY-A** (Table S1, Entry 3). % Acetalization = (4x1)/(7.39) = 54.1%

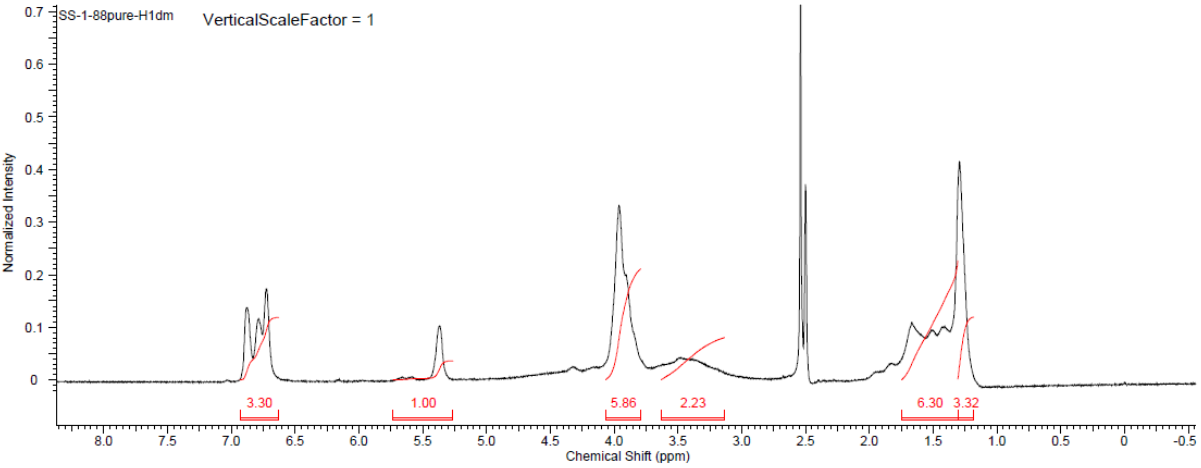


Figure S50. ^{1}H NMR Spectrum **PV-EV-A** (Table S1, Entry 4). % Acetalization = (4x1)/(6.30) = 63.5%

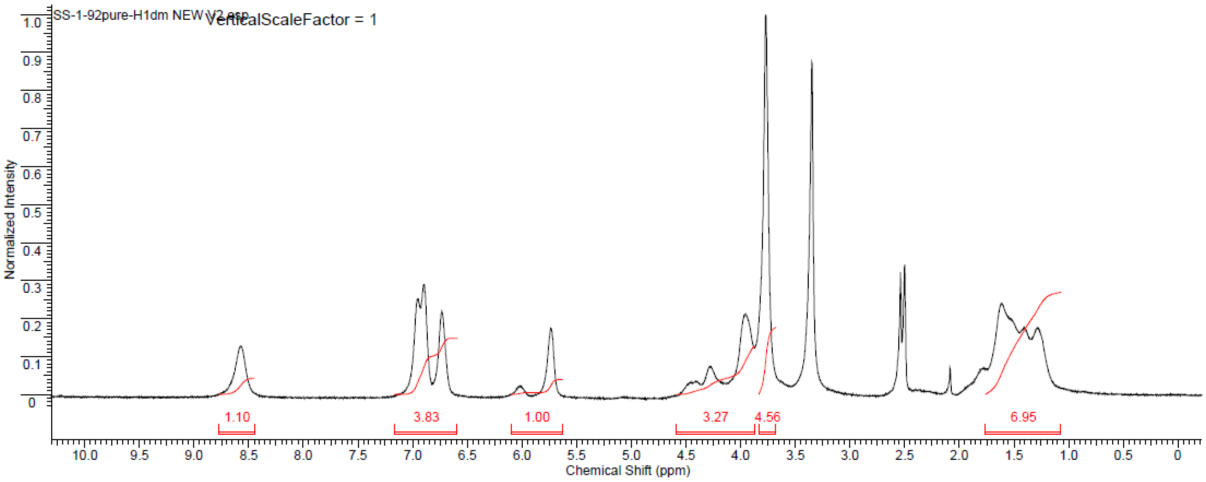


Figure S51. ^{1}H NMR Spectrum **PV-OV-A** (Table S1, Entry 5). % Acetalization = (4x1)/(6.95) = 57.6%

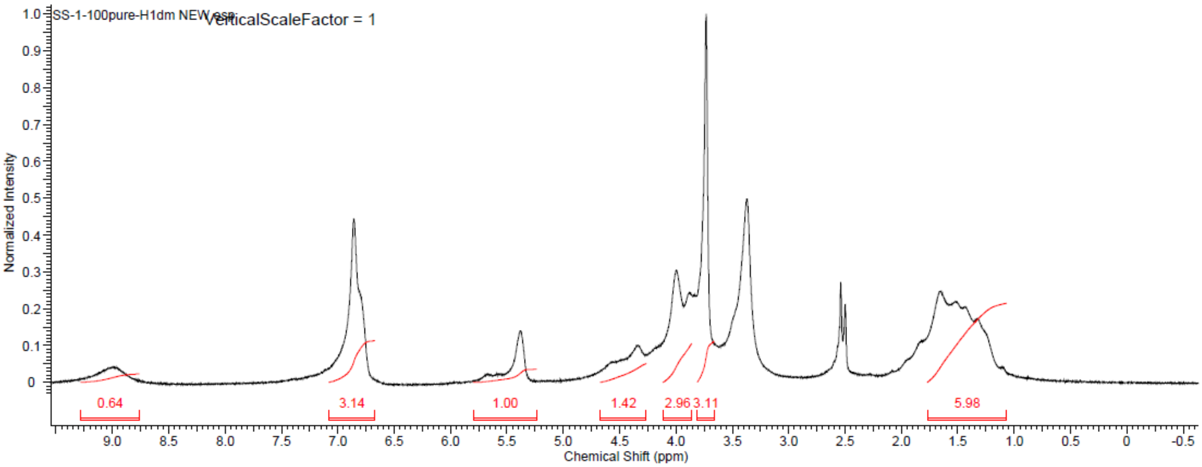


Figure S52. ^{1}H NMR Spectrum **PV-IV-A** (Table S1, Entry 6). % Acetalization = (4x1)/(5.98) = 66.9%

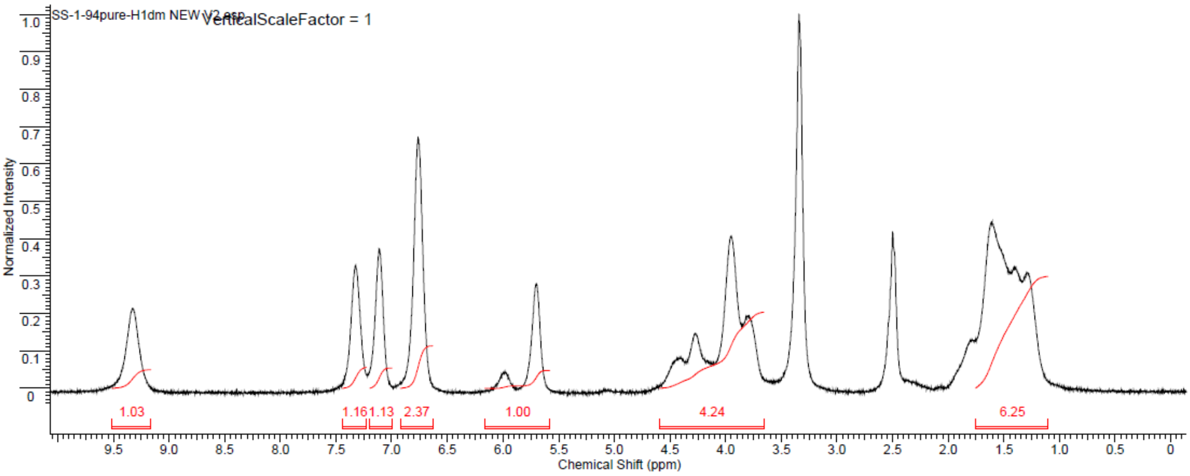


Figure S53. ^{1}H NMR Spectrum **PV-SA-A** (Table S1, Entry 7). % Acetalization = (4x1)/(6.25) = 64.0%

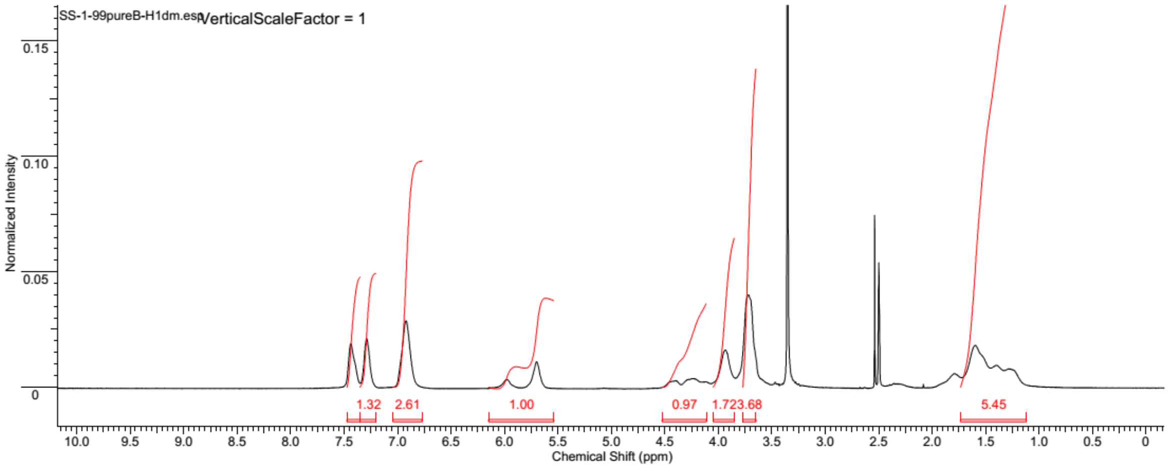


Figure S54. ^{1}H NMR Spectrum **PV-OA-A** (Table S1, Entry 8). % Acetalization = (4x1)/(5.45) = 73.4%

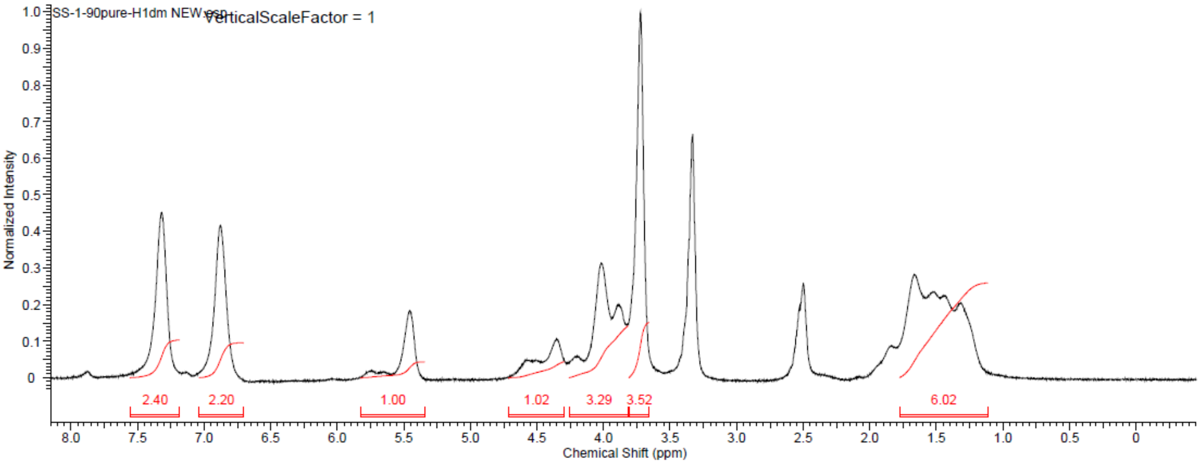


Figure S55. ^{1}H NMR Spectrum **PV-PA-A** (Table S1, Entry 9). % Acetalization = (4x1)/(6.02) = 66.4%

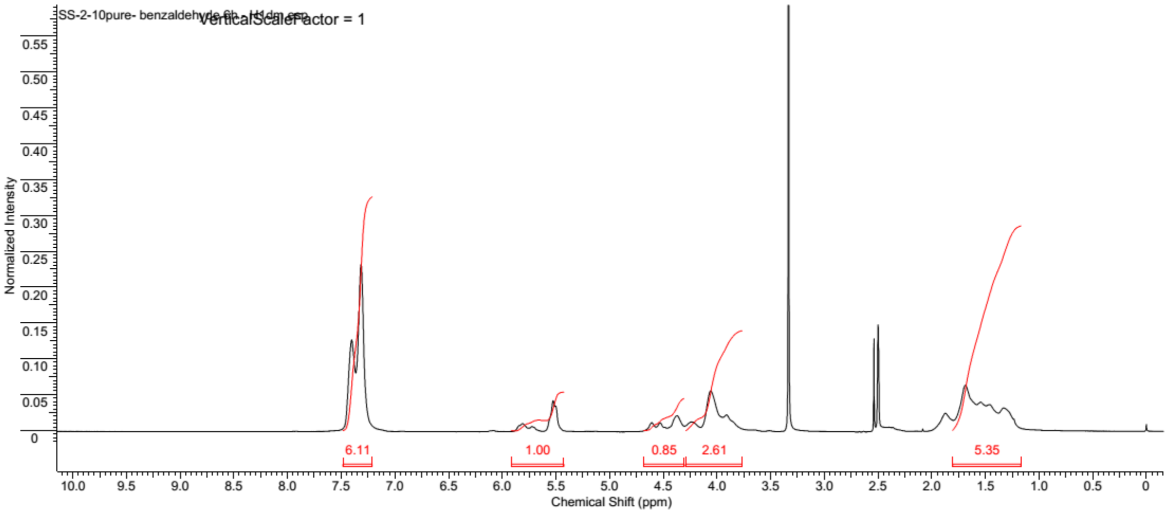


Figure S56. ^{1}H NMR Spectrum **PV-BZ-A** (Table S1, Entry 10). % Acetalization = (4x1)/(5.35) = 74.8%

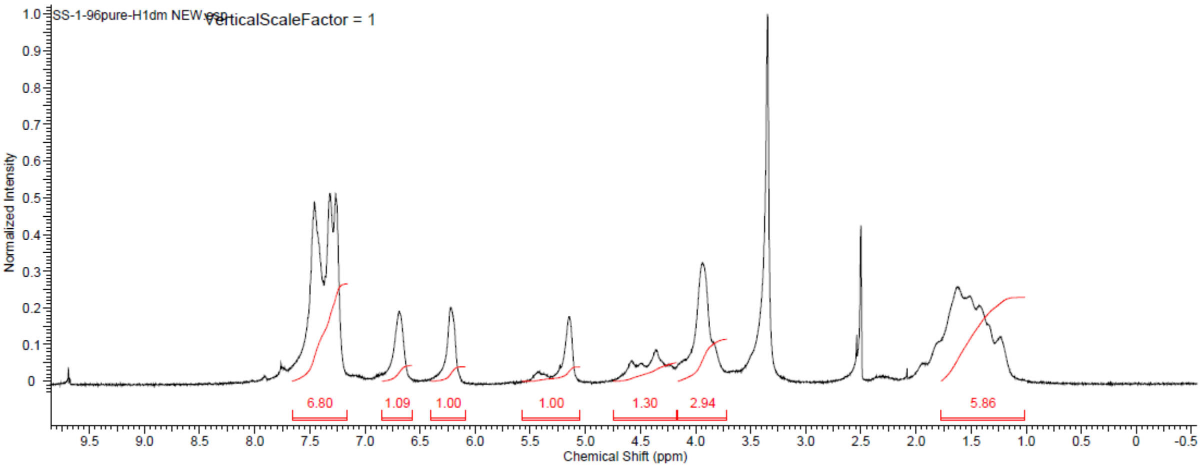


Figure S57. ^{1}H NMR Spectrum **PV-Cl-A** (Table S1, Entry 11). % Acetalization = (4x1)/(5.86) = 68.3%

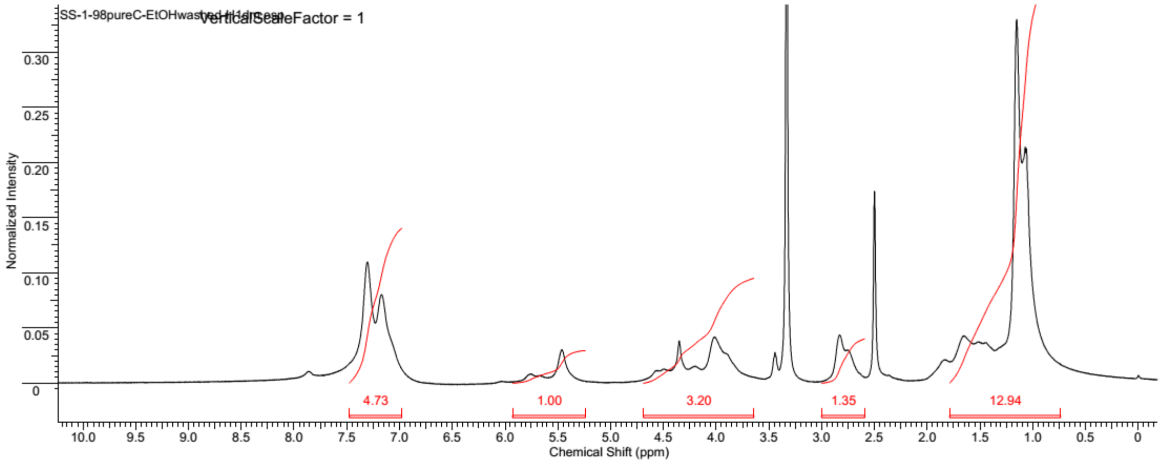


Figure S58. ^{1}H NMR Spectrum **PV-CU-A** (Table S1, Entry 12). % Acetalization = (4x1)/(12.94–6) = 57.6% (subtract 6 methyl-protons from 12.94)

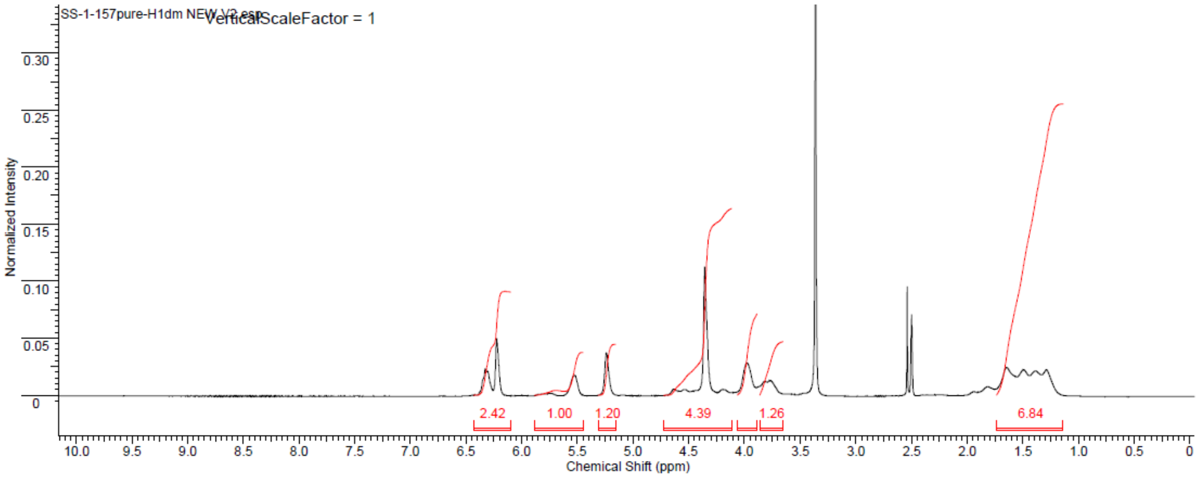


Figure S59. ^{1}H NMR Spectrum **PV-HMF-A** (Table S1, Entry 13). % Acetalization = (4x1)/(6.84) = 58.5%

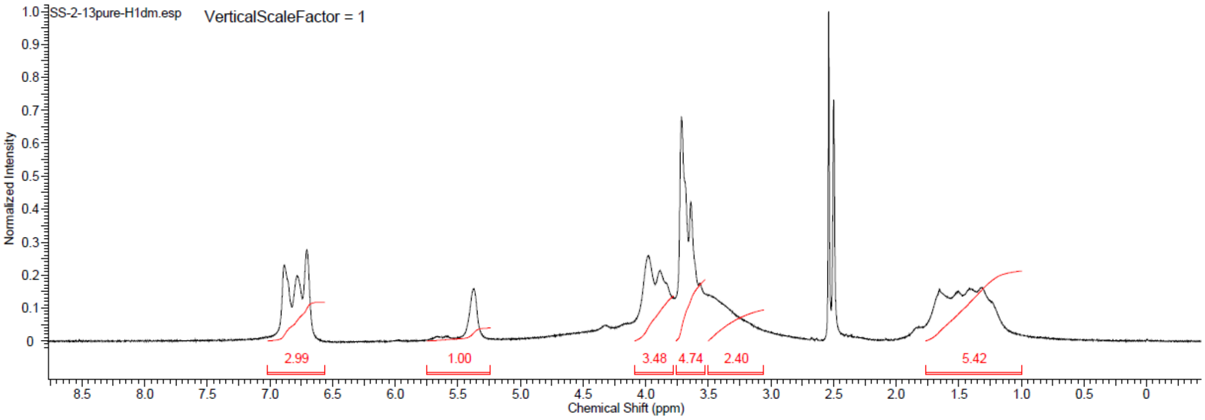


Figure S60. ^{1}H NMR Spectrum **PV-VV-A*** (Table S1, Entry 15). % Acetalization = (4x1)/(5.42) = 73.8%

^{13}C NMR Spectra

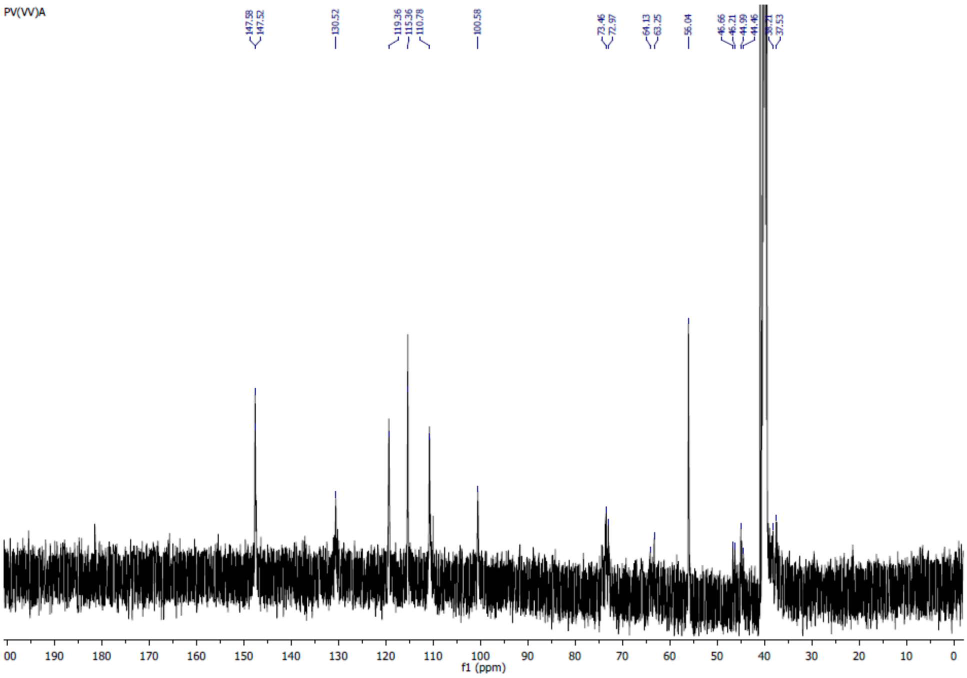


Figure S61. ^{13}C NMR Spectrum of **PV-VV-A** (Table S1, Entry 1).

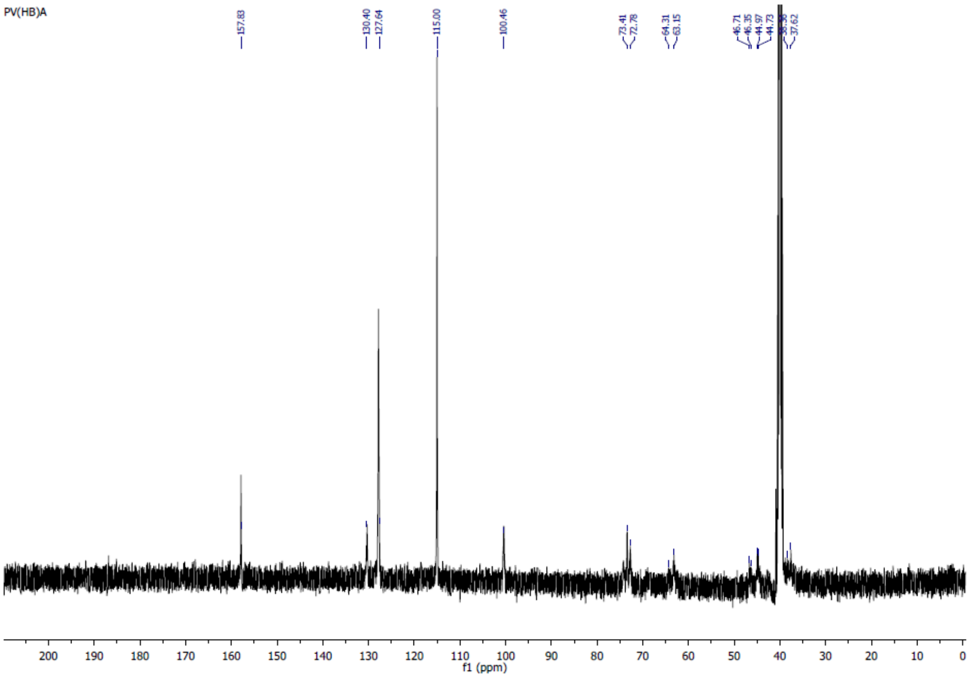


Figure S62. ^{13}C NMR Spectrum of **PV-HB-A** (Table S1, Entry 2).

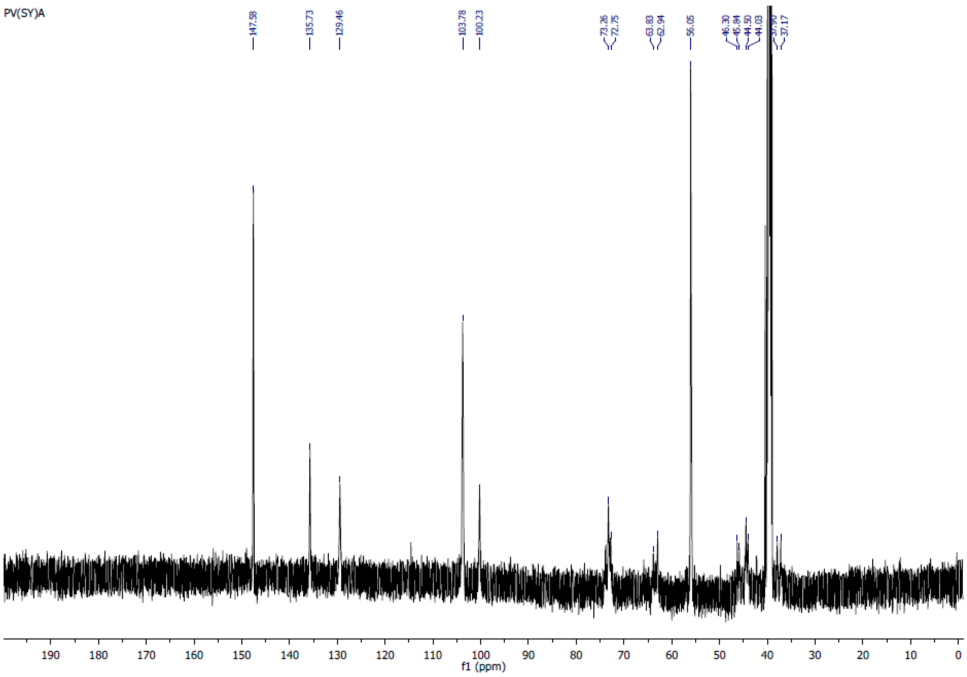


Figure S63. ^{13}C NMR Spectrum of **PV-SY-A** (Table S1, Entry 3).

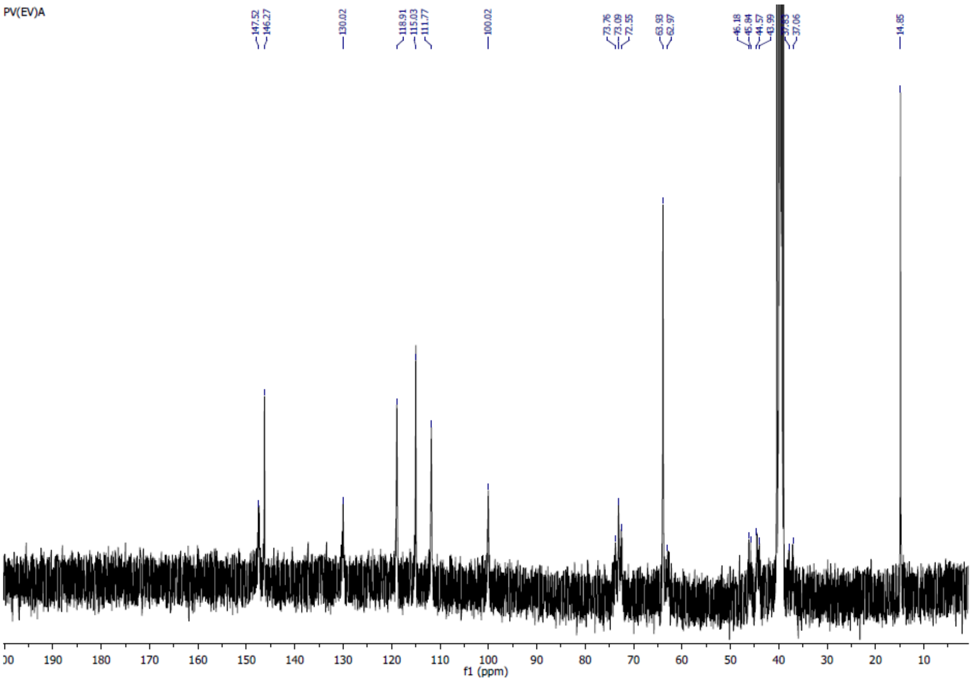


Figure S64. ^{13}C NMR Spectrum of **PV-EV-A** (Table S1, Entry 4).

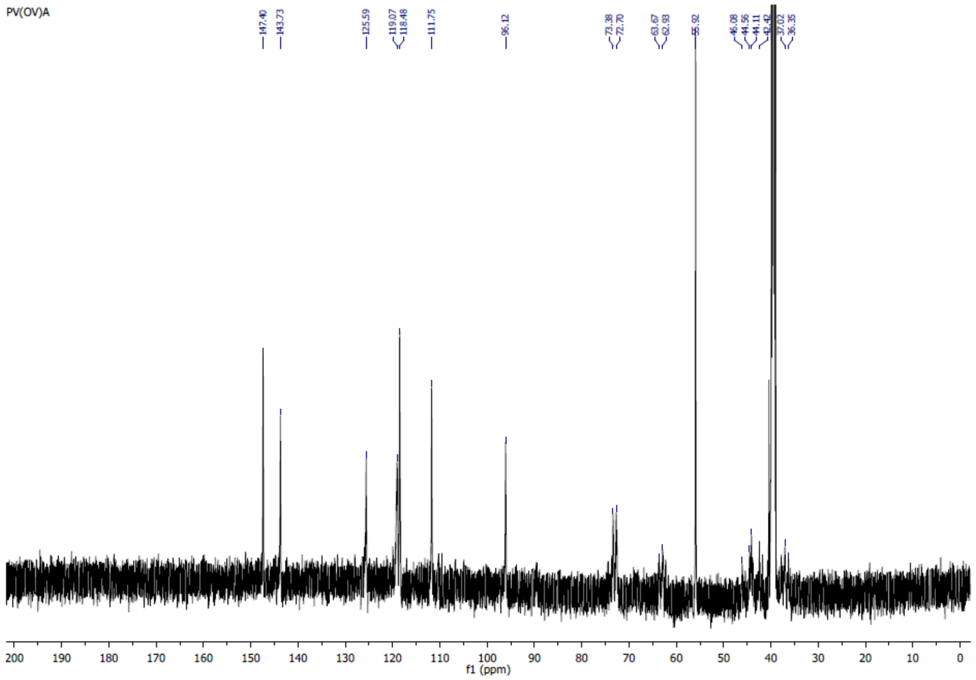


Figure S65. ^{13}C NMR Spectrum of **PV-OV-A** (Table S1, Entry 5).

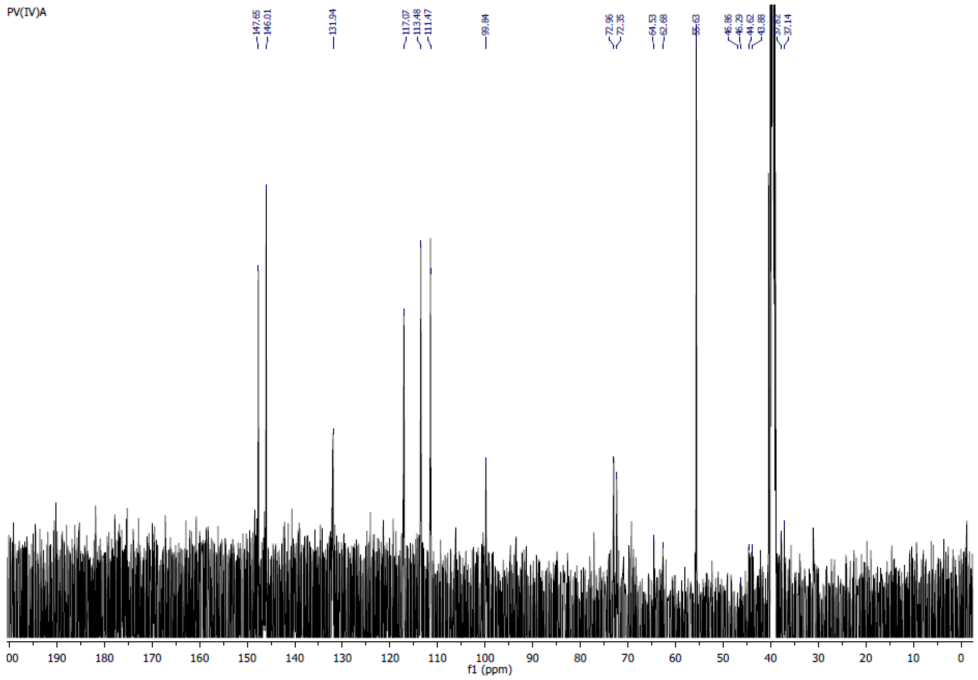


Figure S66. ^{13}C NMR Spectrum of **PV-IV-A** (Table S1, Entry 6).

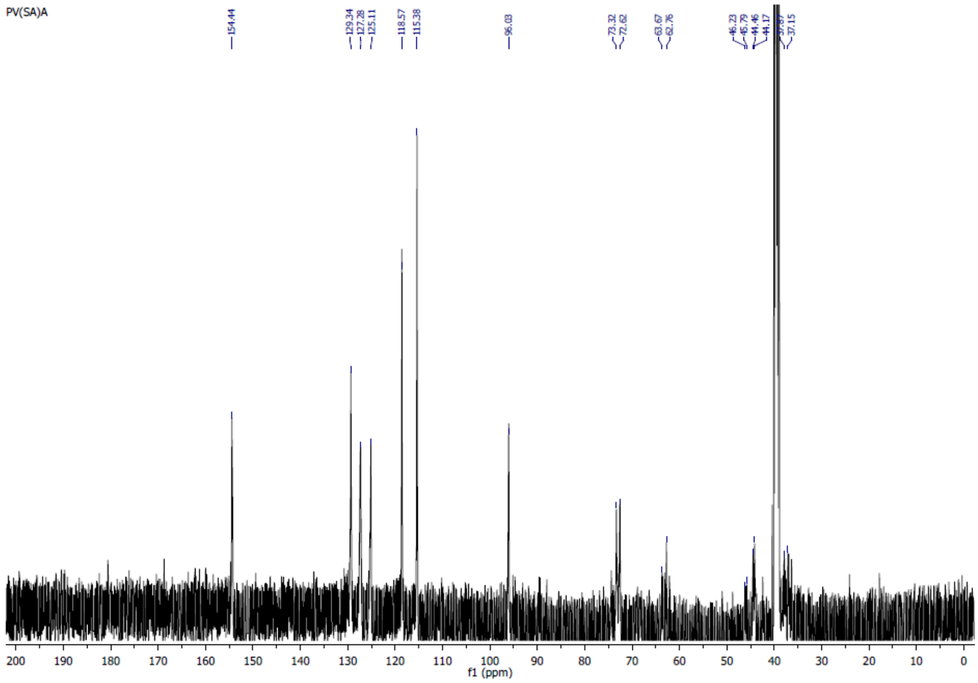


Figure S67. ^{13}C NMR Spectrum of **PV-SA-A** (Table S1, Entry 7).

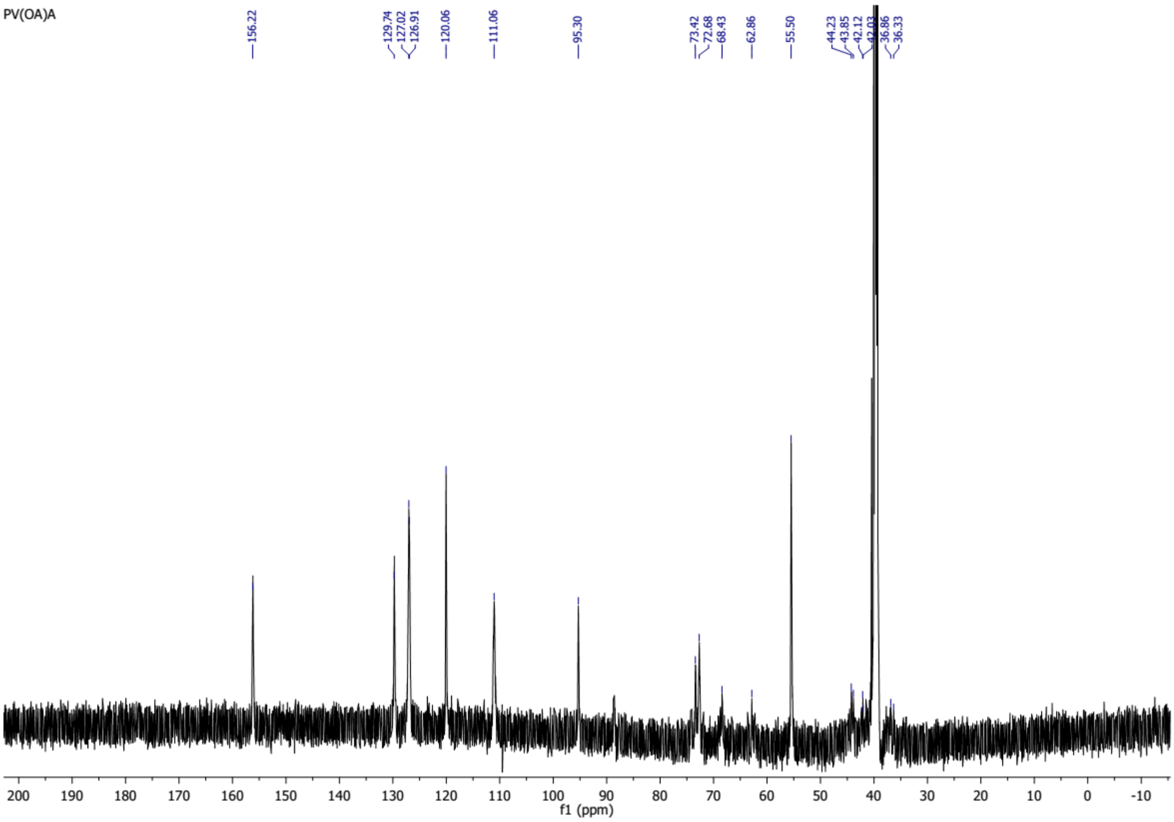


Figure S68. ^{13}C NMR Spectrum of **PV-OA-A** (Table S1, Entry 8).

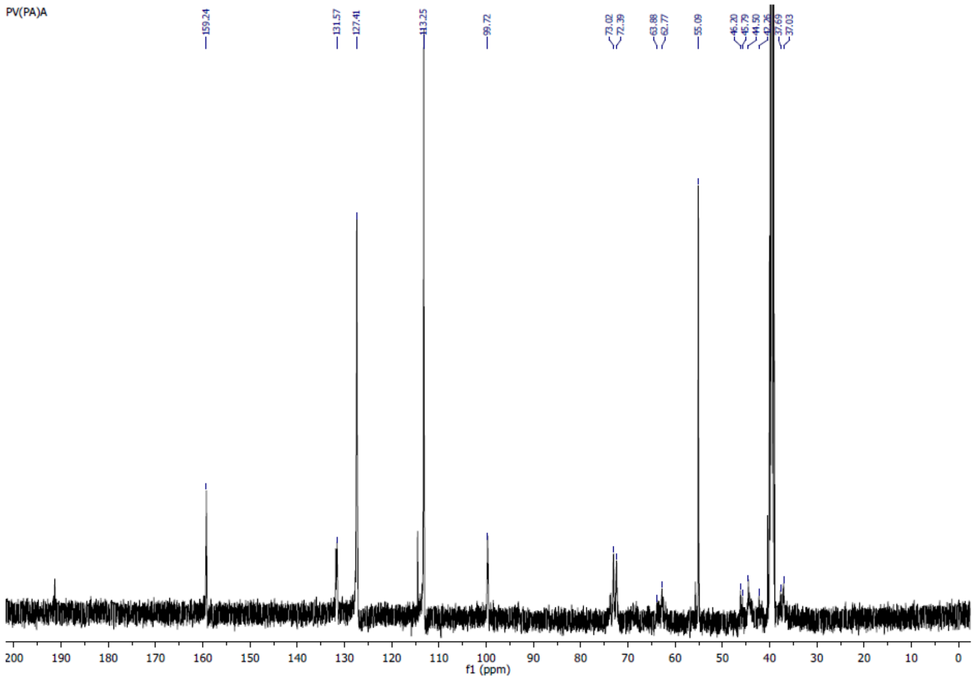


Figure S69. ^{13}C NMR Spectrum of **PV-PA-A** (Table S1, Entry 9).

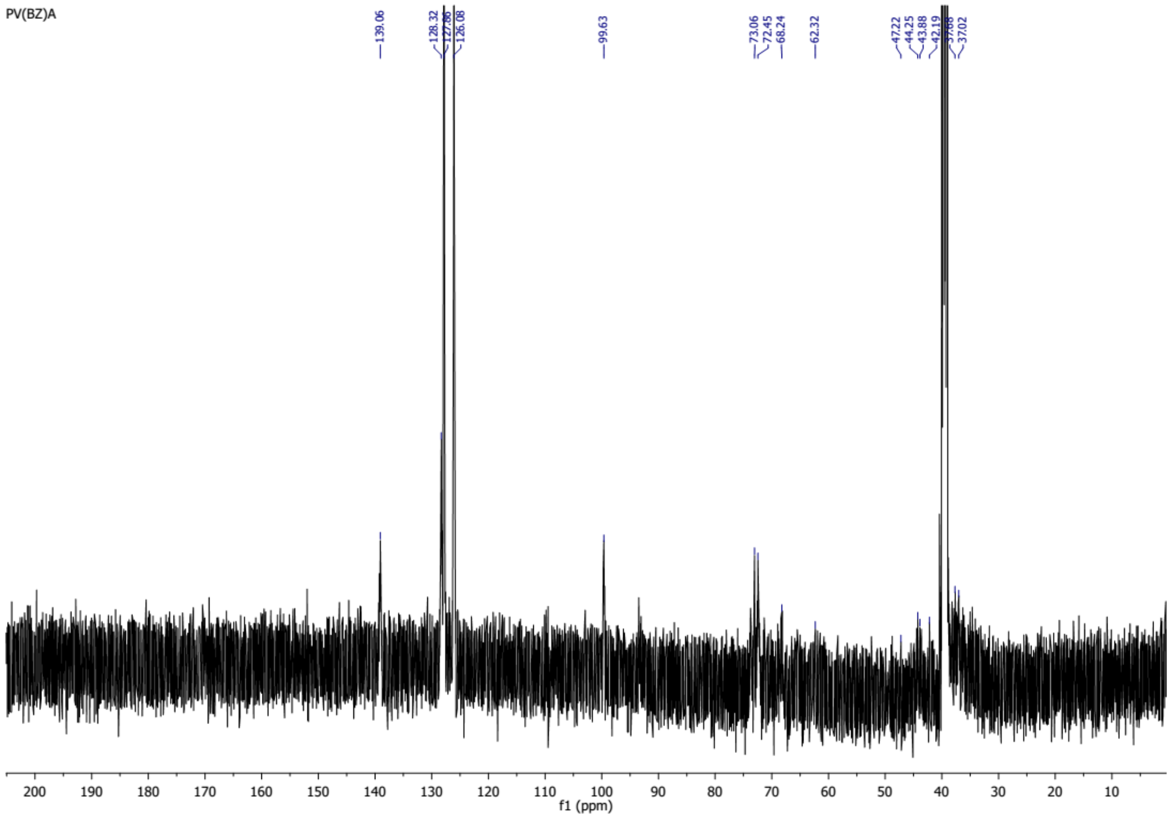


Figure S70. ^{13}C NMR Spectrum of **PV-BZ-A** (Table S1, Entry 10).

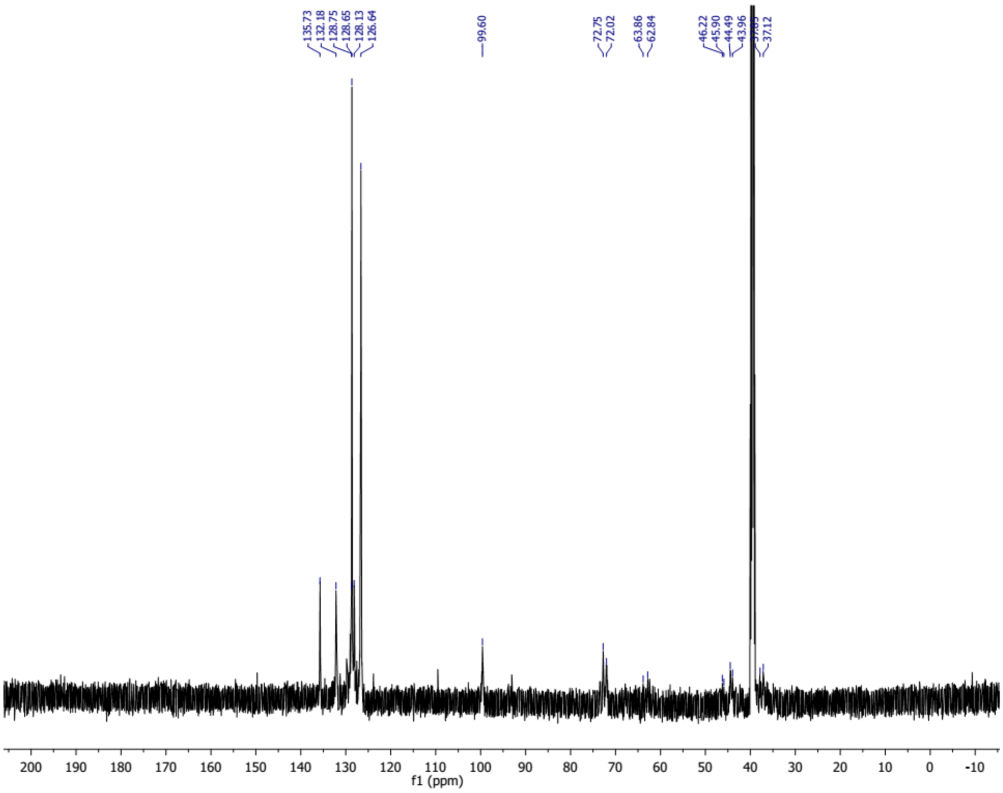


Figure S71. ^{13}C NMR Spectrum of **PV-Cl-A** (Table S1, Entry 11).

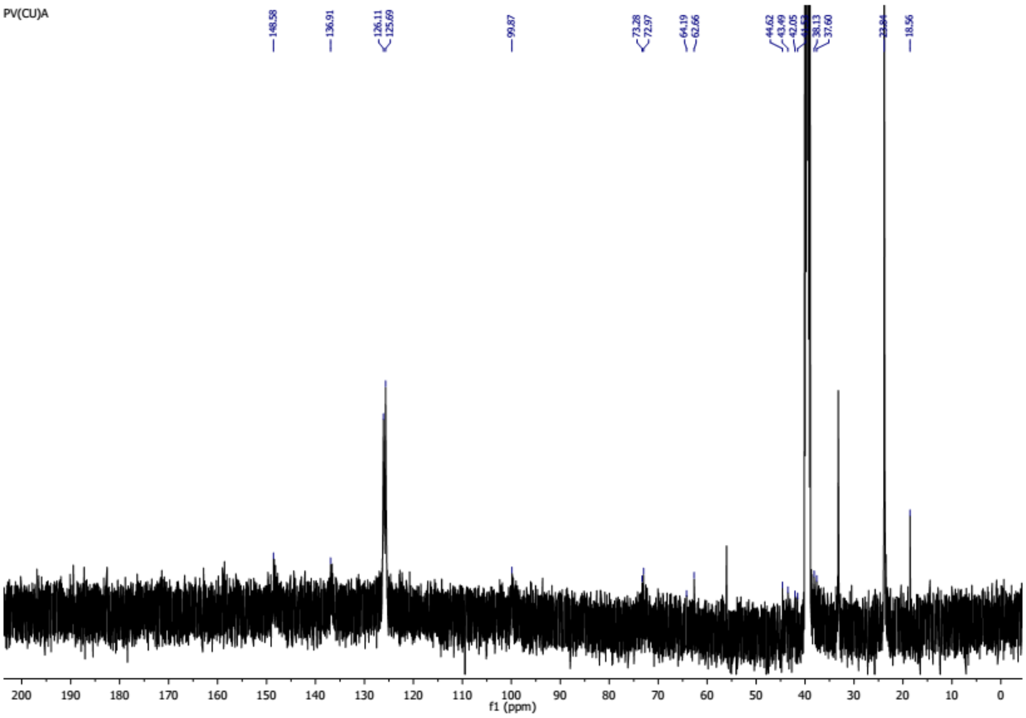


Figure S72. ^{13}C NMR Spectrum of **PV-CU-A** (Table S1, Entry 12).

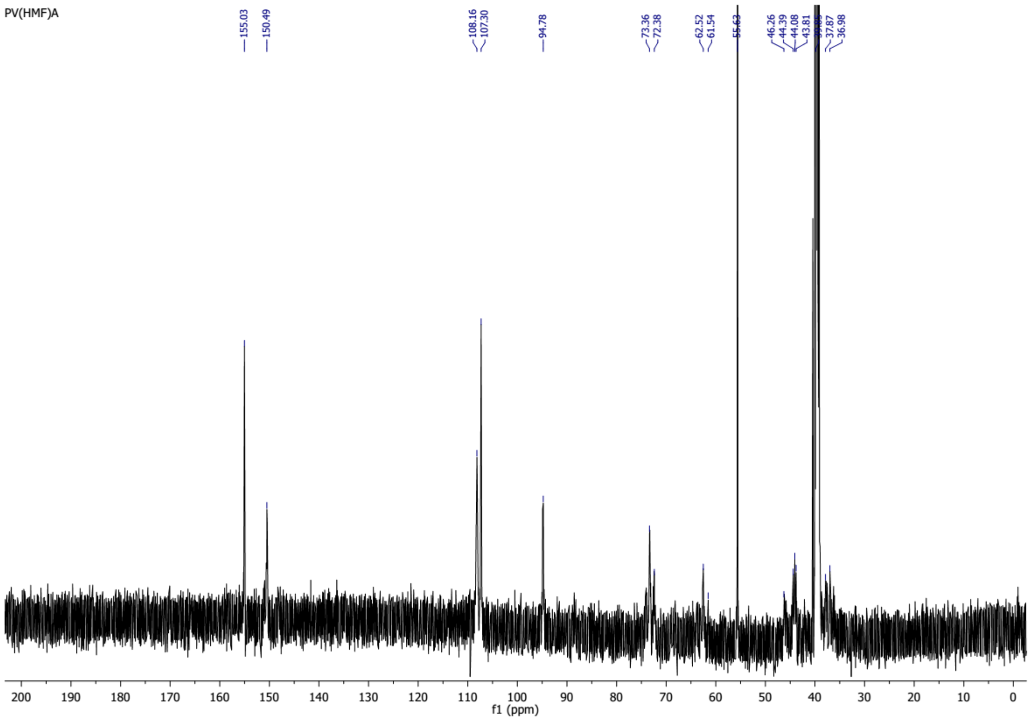


Figure S73. ^{13}C NMR Spectrum of **PV-HMF-A** (Table S1, Entry 13).

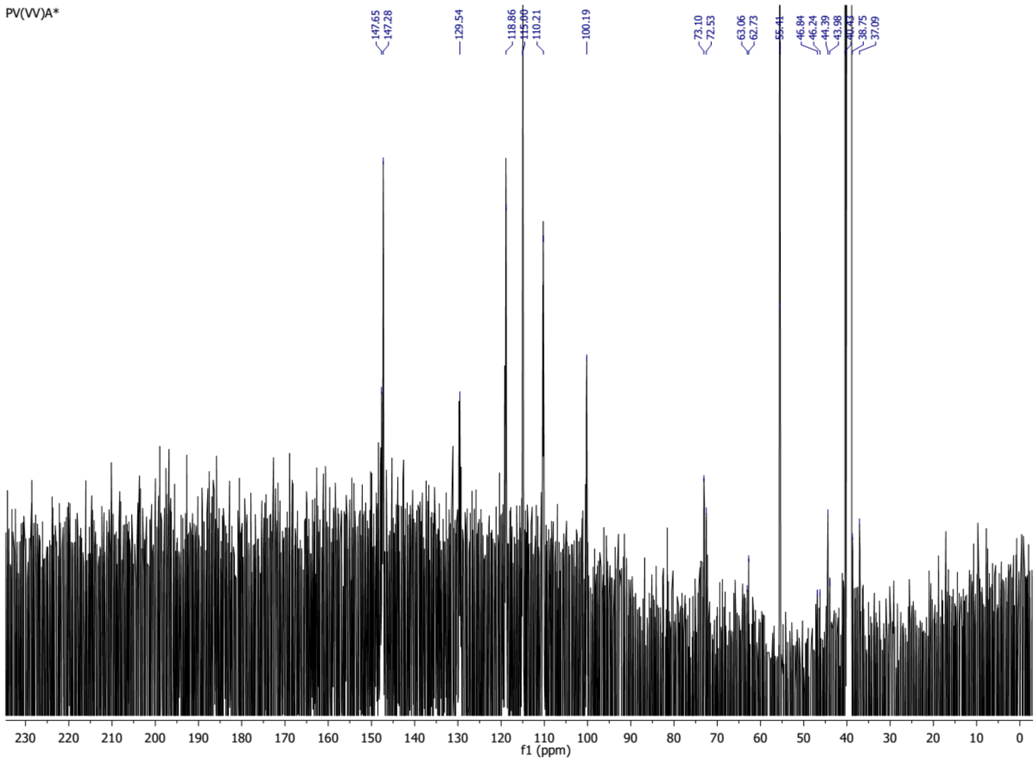


Figure S74. ^{13}C NMR Spectrum of **PV-VV-A*** (Table S1, Entry 15).

Degradation Study Photographs

Degradation studies were performed on **PV-VV-A** in the following aqueous media: pH 1, pH 2, pH 3, pH 5, deionized water (DIW), and seawater. Pictures were taken every hour for the first 9 hours, and then daily. Below are selected photographs from T = 0 hours, 3 hours, 24 hours, 48 hours, and 7 days.

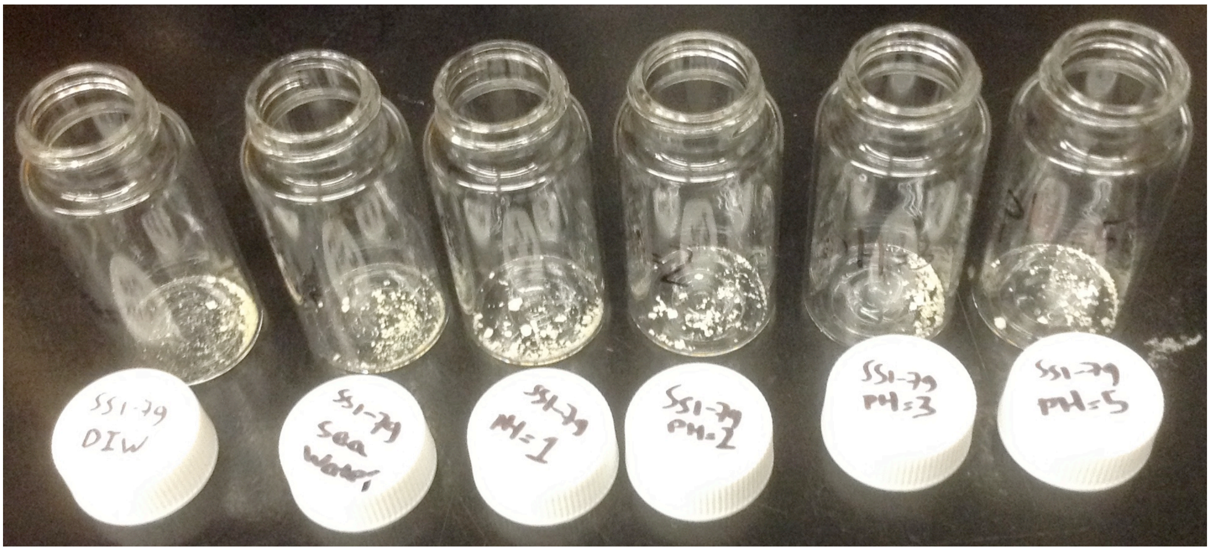


Figure S75. Initial photograph of **PV-VV-A** before addition of aqueous media.

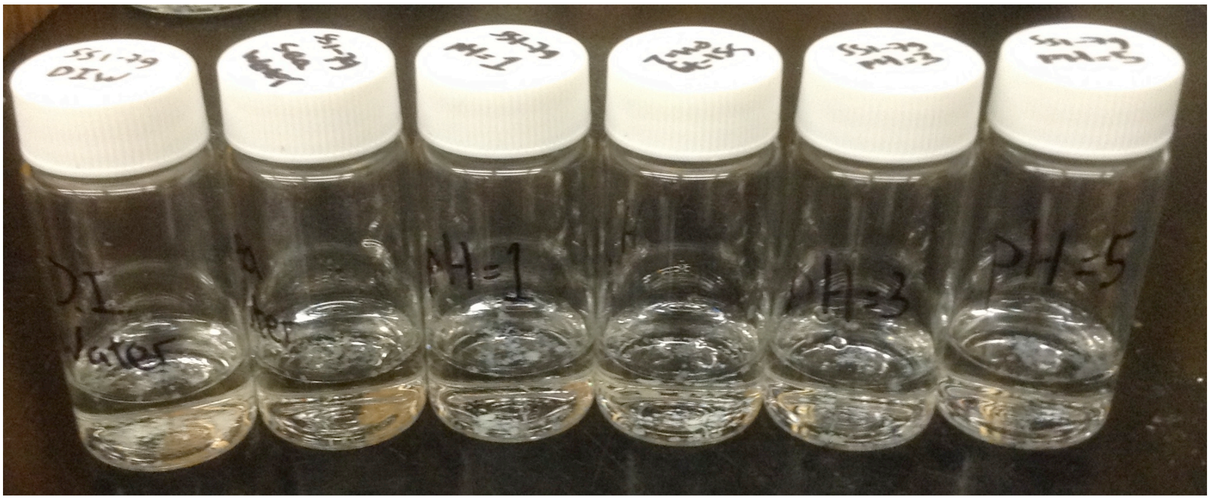


Figure S76. Initial photograph of **PV-VV-A** after addition of aqueous media.

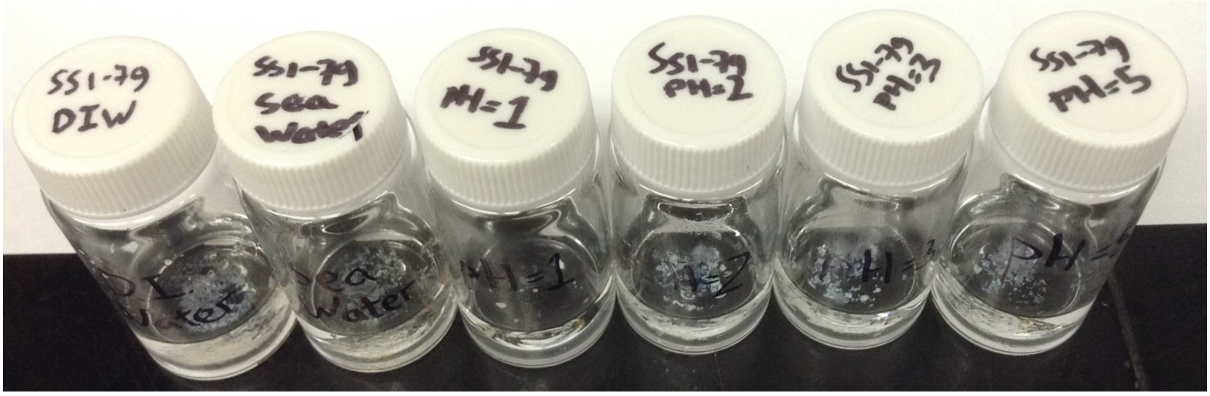


Figure S77. Photograph of **PV-VV-A** 3 hours after addition of aqueous media (note that sample at pH 1 has dissolved almost completely).

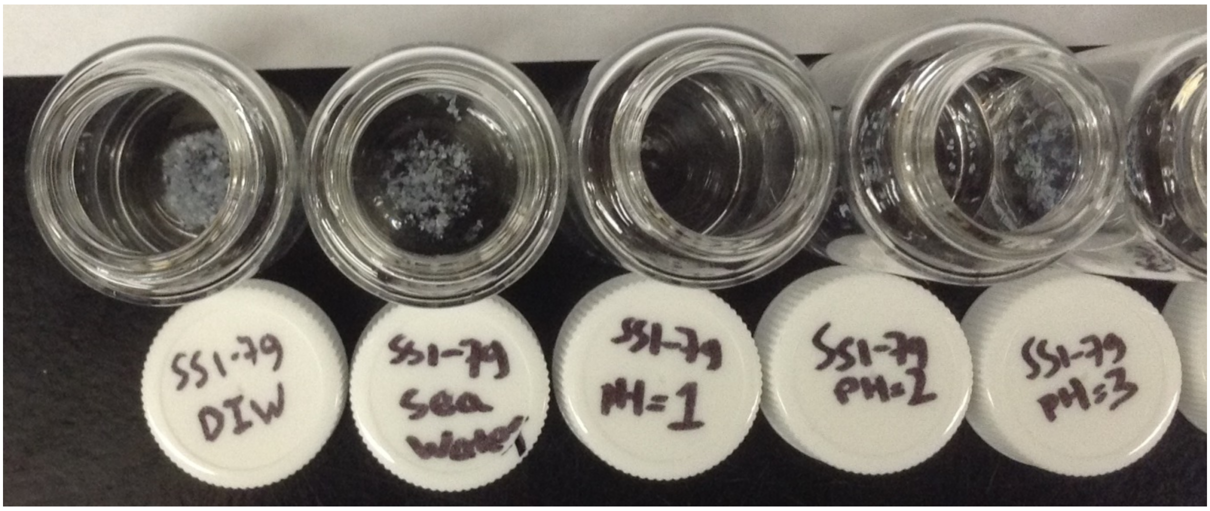


Figure S78. Zoomed photograph of **PV-VV-A** 3 hours after addition of aqueous media, for DIW, seawater, and pH 1. Note that the sample at pH 1 has dissolved almost completely.

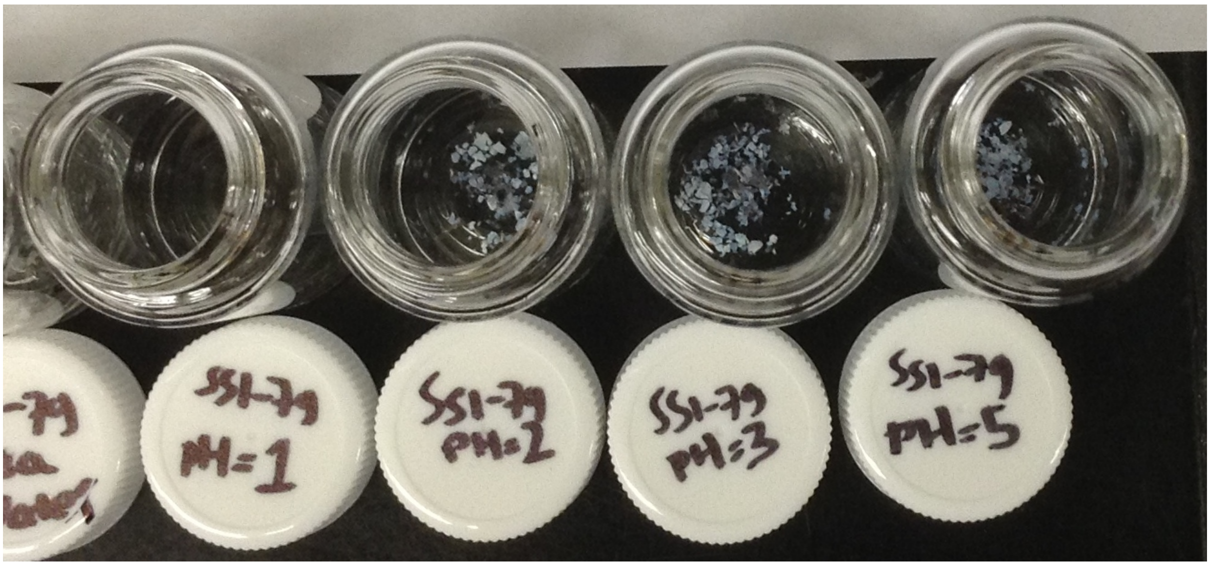


Figure S79. Zoomed photograph of **PV-VV-A** 3 hours after addition of aqueous media, for pH 2, pH 3 and pH 5.

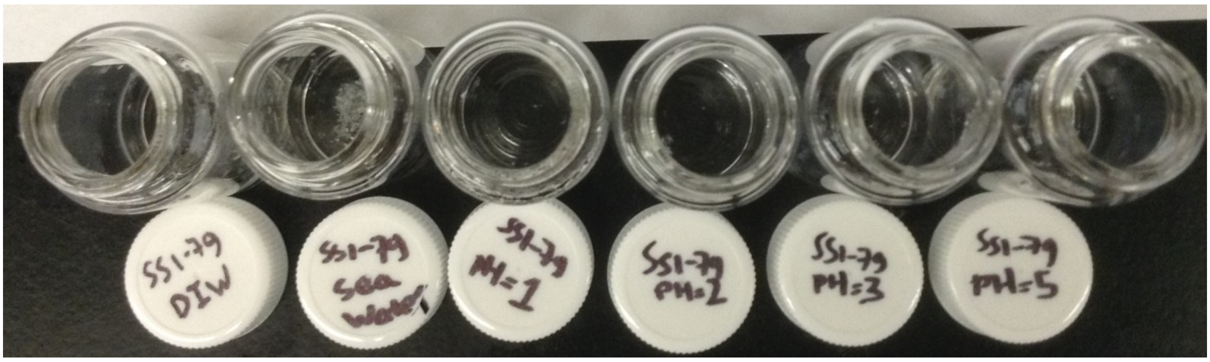


Figure S80. Photograph of **PV-VV-A** 24 hours after addition of aqueous media. Note that the samples at pH 1 and pH 2 have dissolved completely.

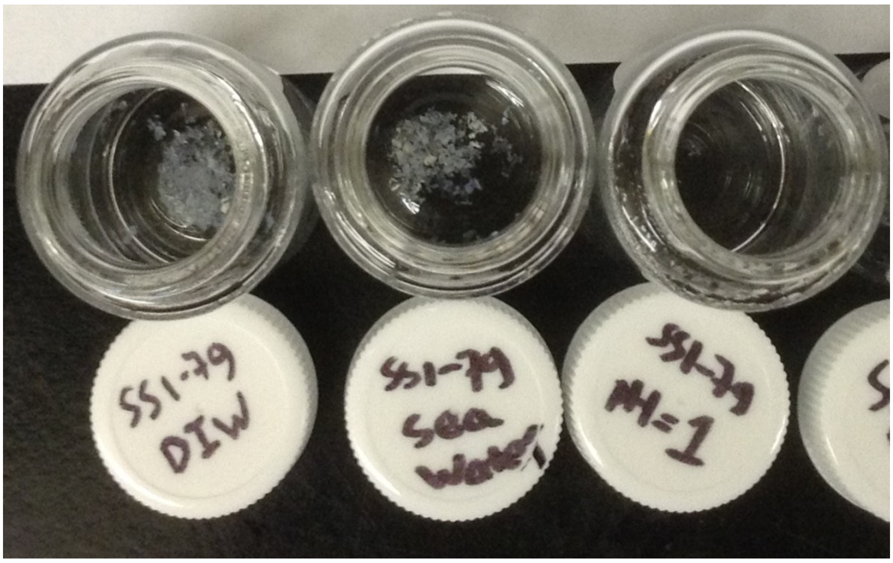


Figure S81. Zoomed photograph of **PV-VV-A** 24 hours after addition of aqueous media, for DIW, seawater and pH 1. Note the sample at pH 1 is completely dissolved.

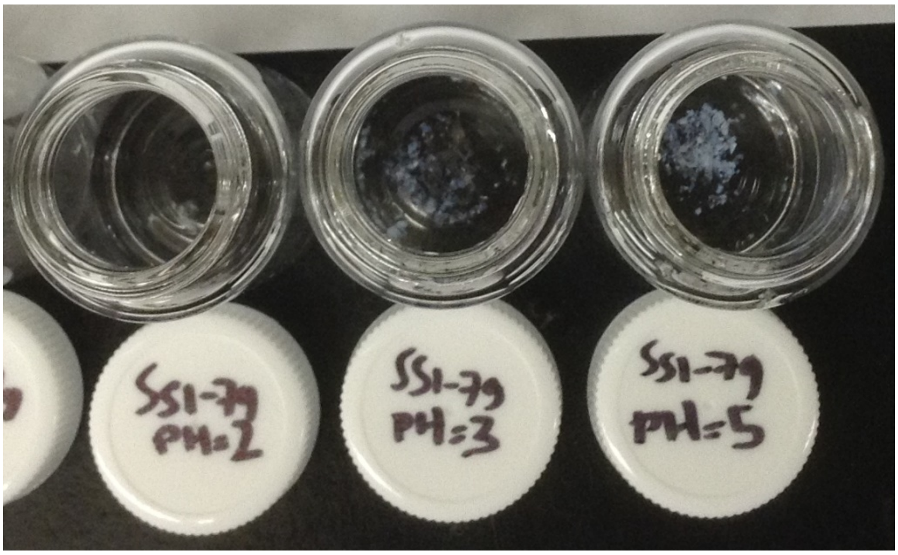


Figure S82. Zoomed photograph of **PV-VV-A** 24 hours after addition of aqueous media, for pH 2, pH 3, and pH 5. Note the sample at pH 2 is completely dissolved and the sample at pH 3 is partially dissolved.

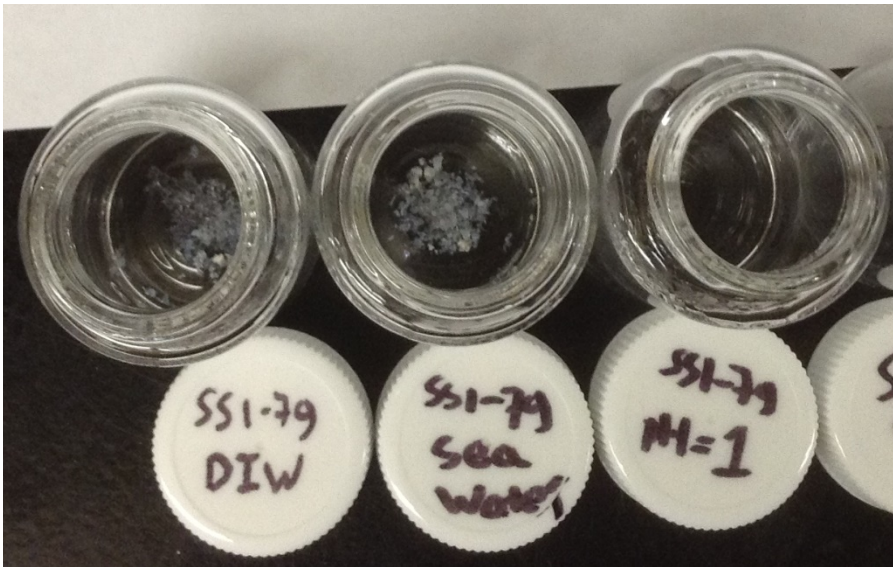


Figure S83. Zoomed photograph of **PV-VV-A** 48 hours after addition of aqueous media, for DIW, seawater and pH 1. Note the sample at pH 1 is completely dissolved.

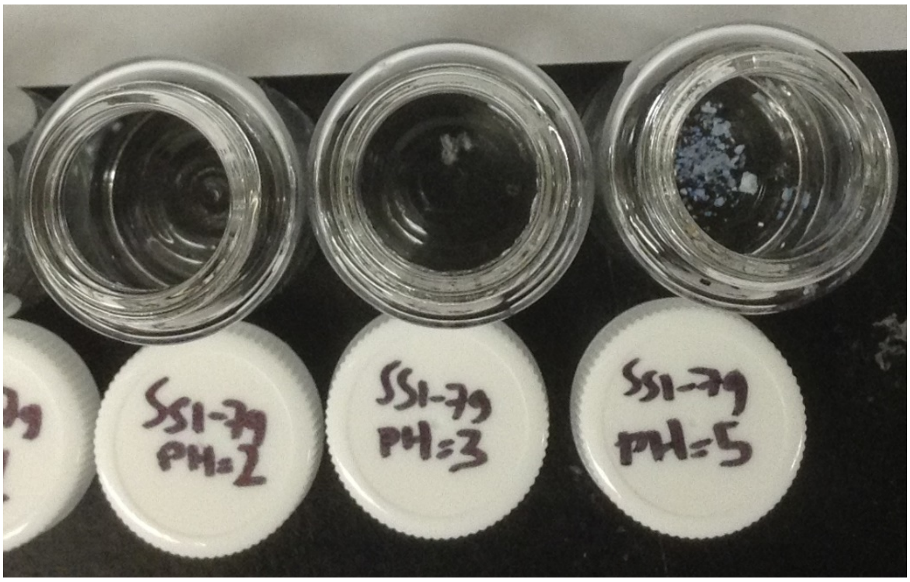


Figure S84. Zoomed photograph of **PV-VV-A** 48 hours after addition of aqueous media, for pH 2, pH 3, and pH 5. Note the samples at pH 2 and pH 3 are completely dissolved.

Figure S85. Photograph of **PV-VV-A** 7 days after addition of aqueous media. No further changes are observed after 48 hours.

Accelerated Hydrolysis ^{1}H NMR Spectra

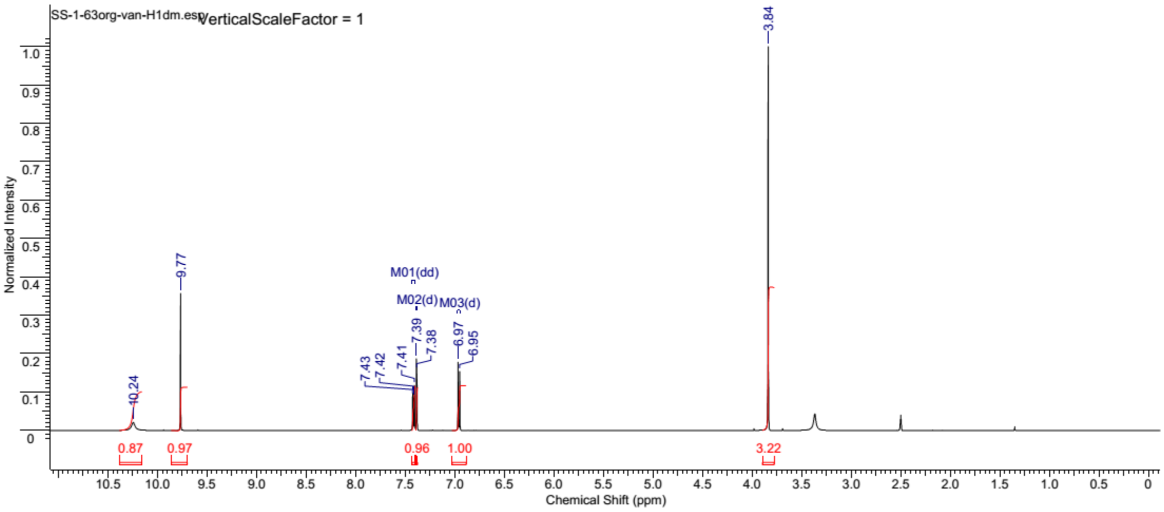


Figure S86. ^{1}H NMR spectrum of organic phase (vanillin) after extraction of hydrolysis product on **PV-VV-A** (Table S1, Entry 1). ^{1}H NMR: (500 MHz, DMSO-d_6) δ ppm 3.84 (s, 3 H), 6.96 (d, *J*=8 Hz, 1 H), 7.39 (d, *J*=2 Hz, 1 H), 7.42 (dd, *J*=8, 2 Hz, 1 H), 9.77 (s, 1 H), 10.24 (br. s, 1 H).

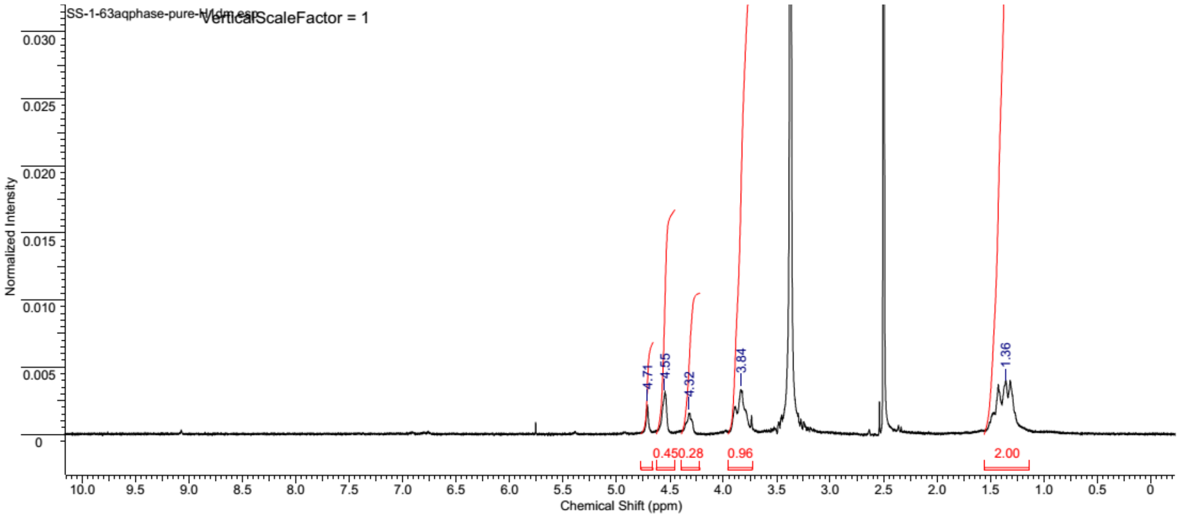


Figure S87. ^{1}H NMR spectrum of organic phase (PVA) after extraction of hydrolysis product on **PV-VV-A** (Table S1, Entry 1). ^{1}H NMR: (500 MHz, DMSO-d_6) δ ppm 1.36 (m, 2 H), 3.84 (m, 1 H) 4.32, 4.55, 4.71 (m, 1 H).

Kinetic Study Final ^{1}H NMR Spectrum

Taken after 1008 minutes (16.8 hours) in the NMR instrument.

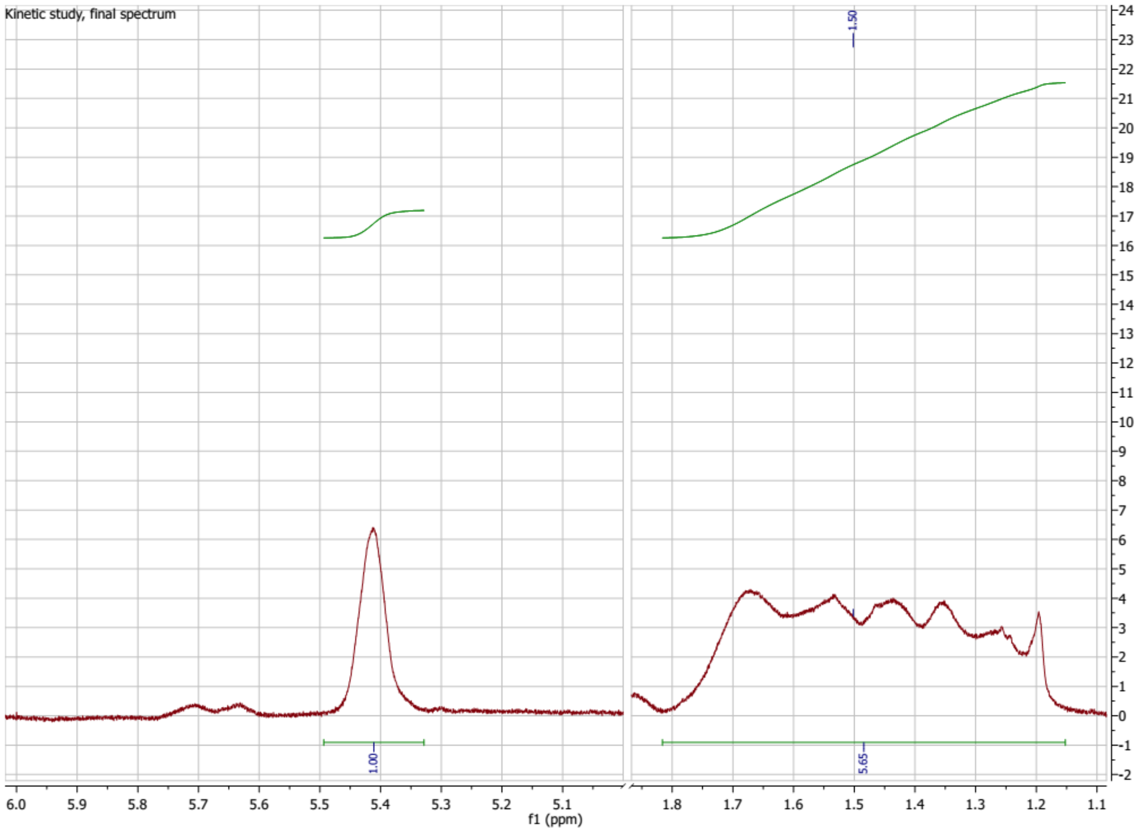


Figure S88. Zoomed ^{1}H NMR spectrum showing final NMR after 1008 minutes (16.8 hours) of reaction time. % Acetalization = (4x1)/(5.65) = 70.8%