Supporting information

Surface modification of polyester films with polyfunctional amines: effect on bacterial biofilm formation

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Table S1: FTIR ratio between the intensity (A_{1640}/A_{1180}) and the area ($Area_{1640}/Area_{1180}$) of the adsorption at 1640 cm^{-1} (stretching CO-NH) and the adsorption at 1180 cm^{-1} (stretching C-O-C) (A_{1640}/A_{1180}) for PLA aminolyzed with HDA at different reaction conditions. ND = Not determinable.

SAMPLE NAME	A_{1640}/A_{1180}	$Area_{1640}/Area_{1180}$
PLA	0.036	0
PLA_HDA_5 50°C EtOH	0.157	0.158
PLA_HDA_15 50°C EtOH	0.358	0.251
PLA_HDA_5 rt EtOH	ND	ND
PLA_HDA_5 rt MeOH	0.025	0.022
PLA_HDA_15 rt EtOH	0.045	0.032
PLA_HDA_15 rt MeOH	0.18	0.22

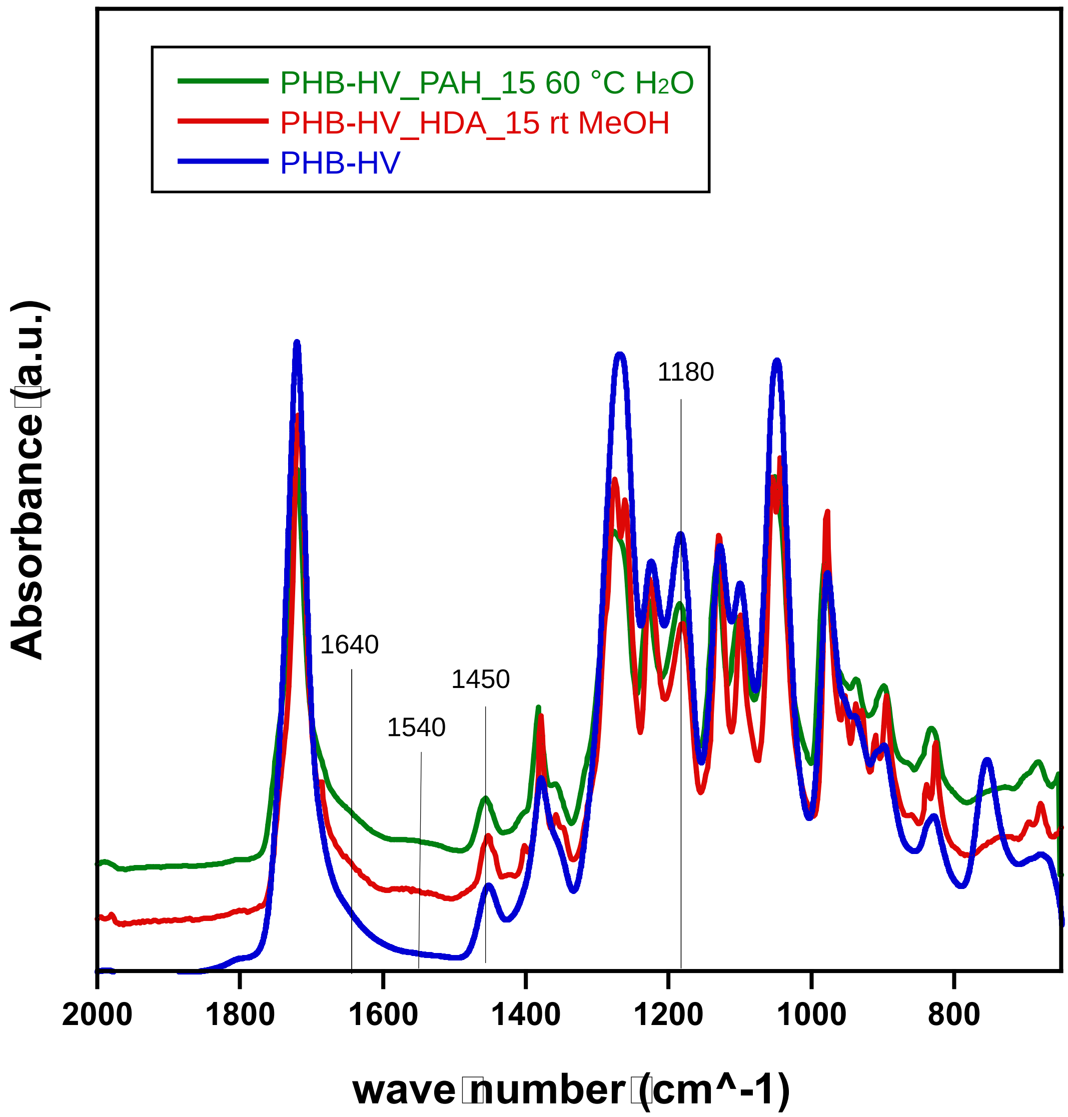

Figure S1. ATR-FTIR spectra of PHB-HV films aminolyzed with HAD and PAH. Surface aminolysis is confirmed by the presence of the absorption bands at 1640 cm^{-1} and 1540 cm^{-1} due to the introduced CO-NH amide groups. The bands at 1450 cm^{-1} and 1180 cm^{-1} are reference bands.

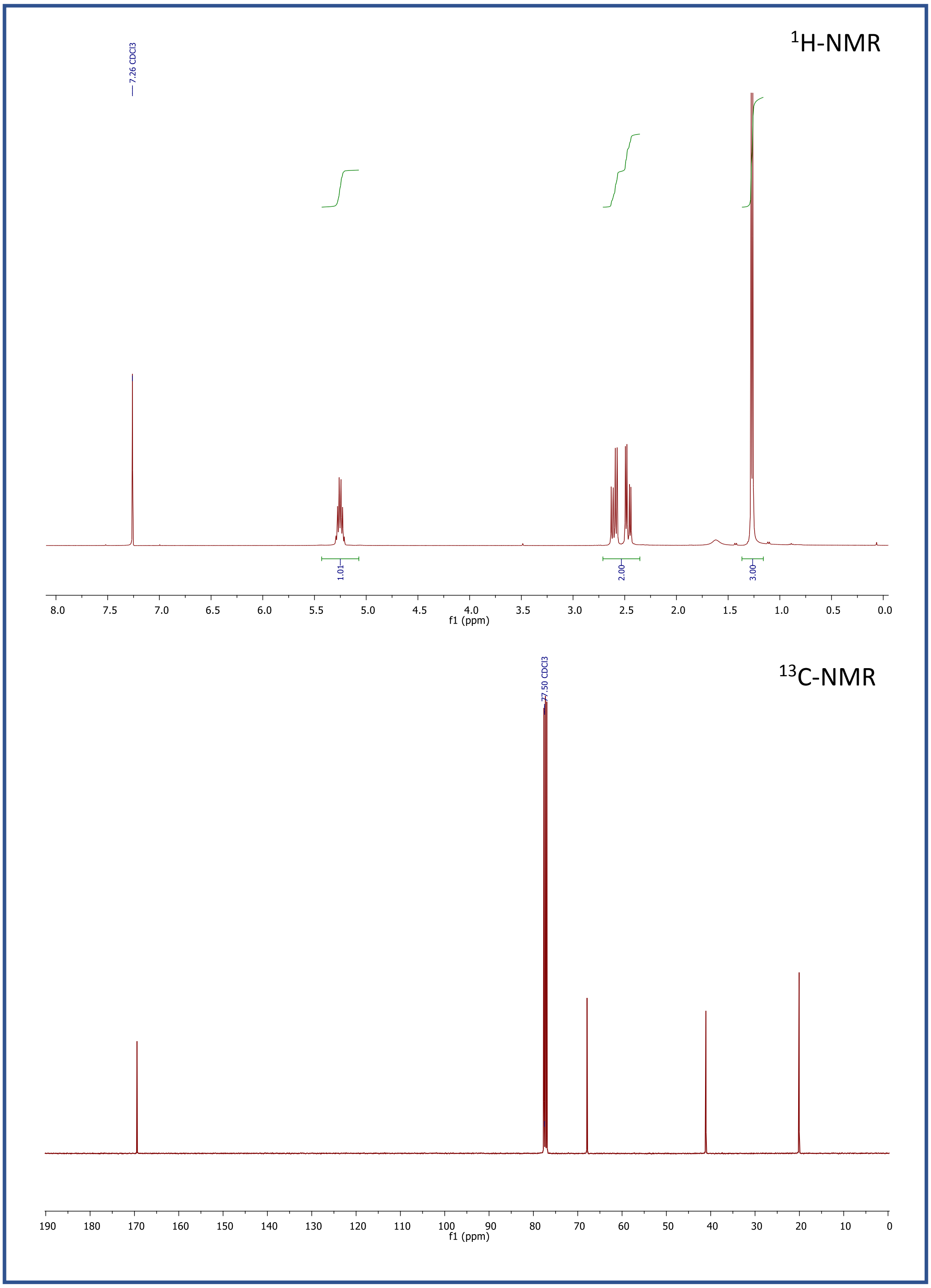

Figure S2. ^{1}H-NMR and ^{13}C-NMR spectra of pure PHB-HV (no aminolysis).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 – 5.01 (sext, 1H, β-CH), 2.71 – 2.31 (2xdd, 2H, α-CH_2), 1.27 (d, 3H, γ-CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.59 (C=O), 67.90 (β-CH), 41.08 (α-CH_2), 20.05 (γ-CH_3).

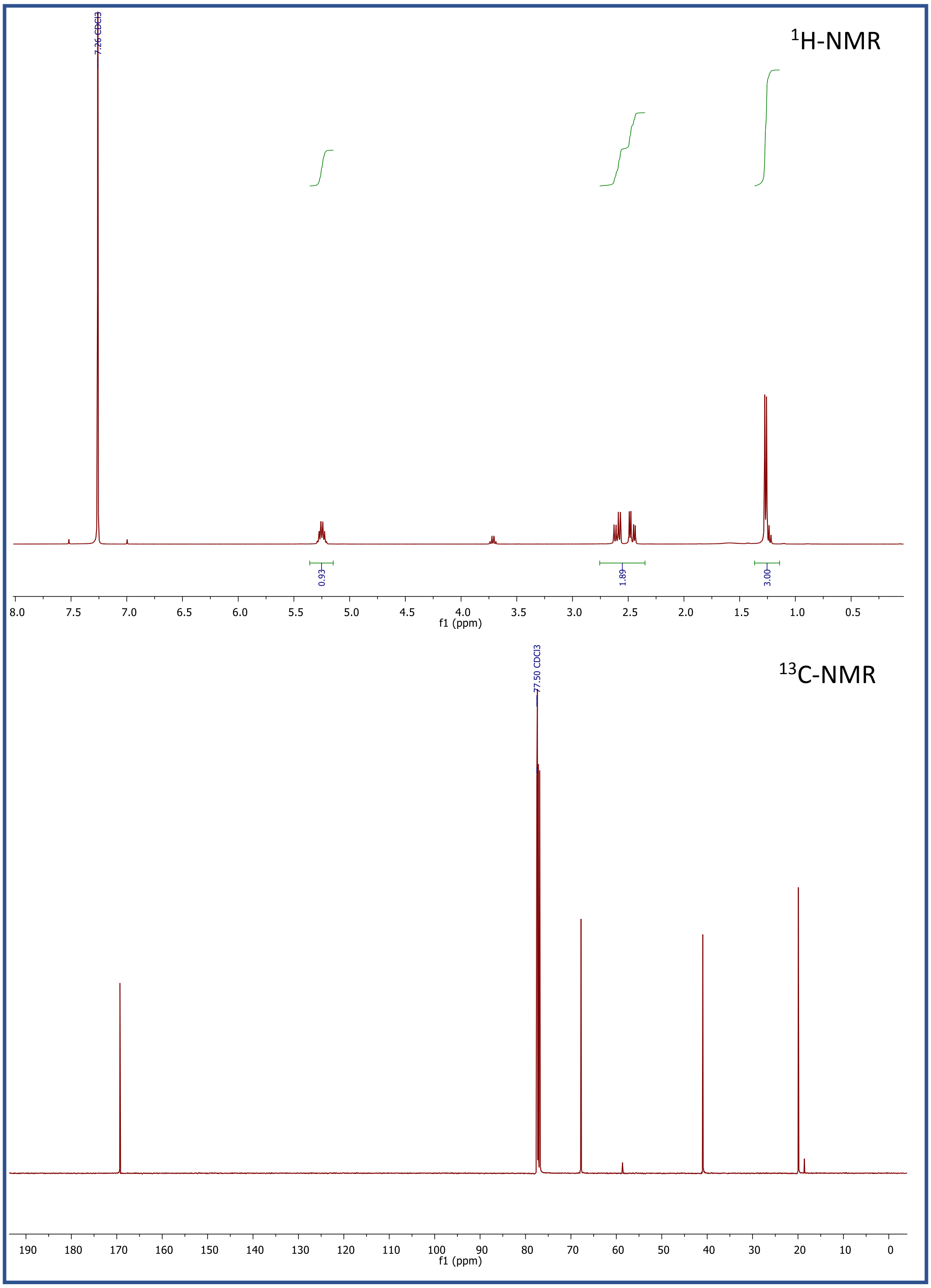

Figure S3. ^{1}H-NMR and ^{13}C-NMR spectra of the aminolyzed film PHB-HV_HDA_15

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 – 5.14 (sext, 1H, β-CH), 2.69 – 2.33 (2xdd,2H, α-CH_2), 1.25 (d, 3H, γ-CH_3) (EtOH traces at ca. 3.7 and 1.2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.29 (), 67.77, 40.95 , 19.93. (EtOH traces).

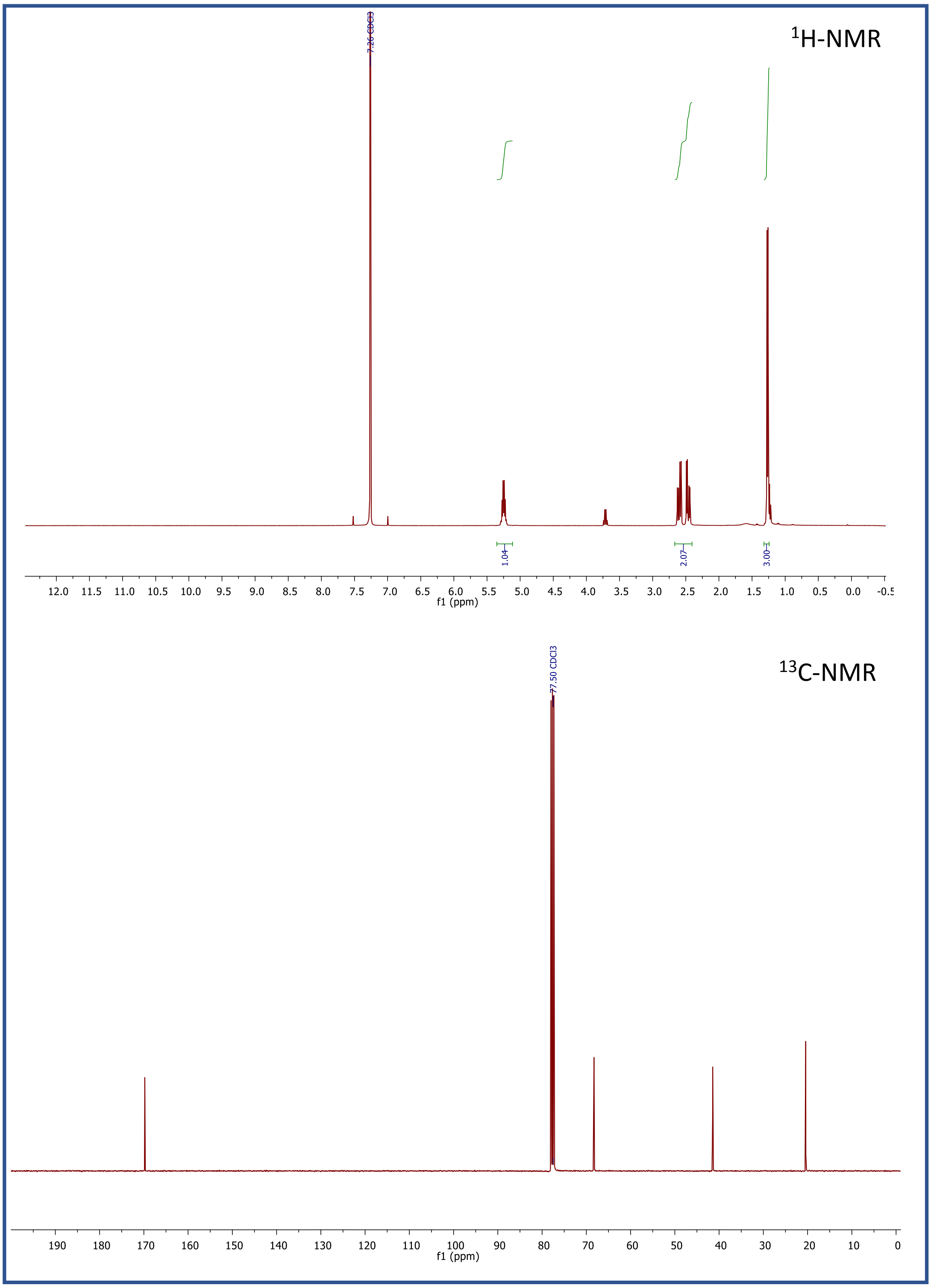

Figure S4. ^{1}H-NMR and ^{13}C-NMR spectra of the aminolyzed film PHB-HV_PAH_15

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 – 5.07 (sext, 1H), 2.78 – 2.36 (2xdd, 2H), 1.27 (d, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.78 , 68.26 , 41.45 , 20.42.

Table S2: Density of surface amino groups for the aminolyzed polymers, as determined with the ninhydrin colorimetric test, and element composition.

Sample	μmol NH_2/g	μmol /mm^2	C (%)	H (%)	O (%)	N (%)	Ratio N/C (%)
PLA	-	-	45.99	5.24	48.77	0	-
PLA_HDA_5	39.0	0.009	42.45	5.19	52.36	0.056	0.13
PLA_TEPA_5	13.9	0.004	44.51	5.42	50.07	0	-
PLA_PALA_5	20.0	0.006	44.37	5.45	50.18	0	-
PLA_HDA_15	51.1	0.010	47.44	5.72	46.65	0.19	0.40
PLA_TEPA_15	22.1	0.005	48.10	5.62	47,66	0	-
PLA_PALA_15	52.4	0.011	50.09	6.91	42.98	0.06	0.12
PHB	-	-	54.12	6.88	39.00	0	-
PHB_HDA_15	46.25	0.005	53.73	6.85	39.12	0.30	0.55
PHB_TEPA_15	55.53	0.013	54.41	7.12	38.11	0.36	0.66
PHB_PALA_15	66.82	0.013	44.68	5.47	49,83	0.02	0.04
PHB-HV	-	-	54.70	7.20	38.10	0	-
PHB-HV_HDA_15	85.71	0.0061	54.86	7.46	37.12	0.56	1.02
PHB-HV_TEPA_15	61.72	0.018	53.87	7.35	37.26	1.52	2.82
PHB-HV_PALA_15	200.51	0.024	51.28	7.07	41,61	0.04	0.08

The most reactive amine seems to be HDA as evidenced by the high density of surface amino groups at 5% amine concentration. When a higher amine concentration was used (15%), the sample PLA_PAH15 showed the highest N/C ratio, this finding being presumably related to the polymeric nature of this amine rather than to a higher degree of aminolysis.

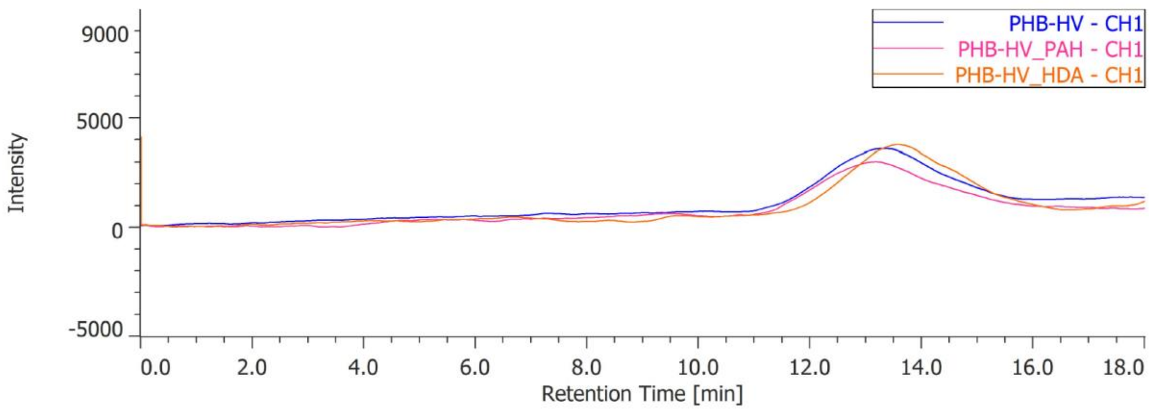

Figure S5: GPC chromatograms of pure PHB-HV and amminolyzed with HDA or PAH 15% amine concentration.