Supporting Information

Characterization Data for PEA and PEPA.

Side group ratios were calculated by ^{31}P NMR due to a large degree of signal overlap in the ^{1}H spectra, and an example is described for 2: Three peaks were present at δ= 25.4, -3.71 and -16.6 ppm. The chemical shift at δ=25.4 ppm represents the phosphoester group present on DPT, while the shifts at δ= -3.71 and -16.6 ppm represent polymer backbone phosphorus atoms bearing either (1) an amino acid ethyl ester and an oxygen linked DPT or ethyl ferulate or (2) two oxygen linked DPT or ethyl ferulate moieties, respectively.

PEA: Composition: 60% ethylferulate, 20% phosphoester, 20% alanine ethyl ester; ^{31}P (145 MHz, CDCl$_3$/MeOD (50:50)) δ (ppm): 25.5, -3.73, -15.7; ^{1}H (360 MHz, CDCl$_3$/MeOD (50:50)) δ (ppm): 7.33, 6.71, 6.13, 4.16, 4.04, 3.57, 4.44, 1.93, 1.65, 1.54, 1.43, 1.05; T$_g$: 79.9 °C; Total Yield: 57.9 %.

PEPA: Composition: 55% ethylferulate, 25% phosphoester, 20% phenylalanine ethyl ester; ^{31}P (145 MHz, CDCl$_3$/MeOD (50:50)) δ (ppm): 23.9, -6.11, -16.8; ^{1}H (360 MHz, CDCl$_3$/MeOD (50:50)) δ (ppm): 7.24, 6.86, 6.13, 4.13, 4.06, 3.48, 2.76, 1.91, 1.52, 1.22; T$_g$: 91.3 °C; Total Yield: 25.7 %. (Note: Molecular weights could not be determined due to the polymers insolubility in THF)
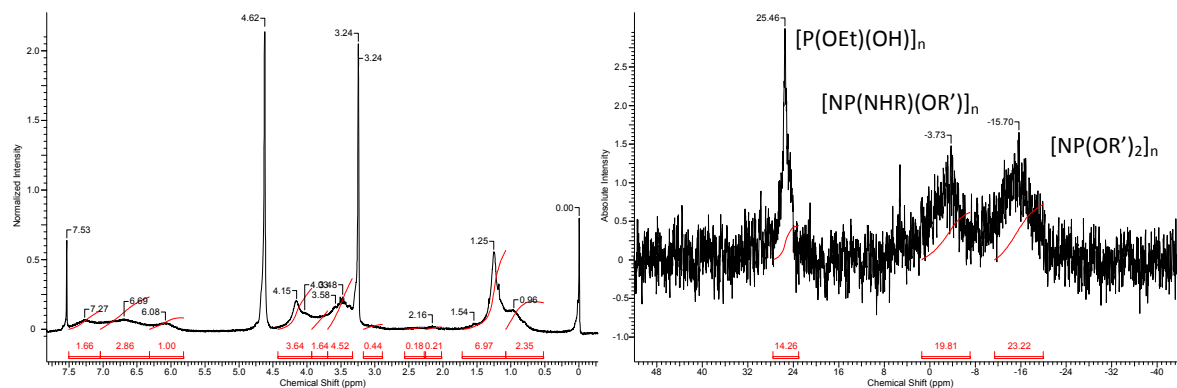

Figure: ^{1}H (left)/^{31}P (right) NMR spectra of **PEA**

Characterization Data for PAA and PAPA.

Side group ratios were calculated by ^{31}P NMR, and an example is described for polymer 5: Two peaks were present at δ 16.2 and -6.3 ppm. The chemical shift at δ 16.2 ppm represents the phosphonic acid group present on DPT, while the shift at δ -6.3 ppm represents the polymer backbone phosphorus atom bearing an amino acid ethyl ester and an oxygen linked DPT or tyramine.

PAA: Composition: 55% alanine ethyl ester,15% phosphonic acid, 30% tyramine ; [31]P (145 MHz, D_6-DMSO) δ (ppm): 18.8, 5.10, -15.9; [1]H (360 MHz, D_6-DMSO) δ (ppm): 9.47, 6.93, 3.90, 3.20, 3.17, 2.68, 2.51,1.05; T_g: 64.1°C; Total Yield: 38.0%.

PAPA: Composition: 45% tyramine, 15% phosphonic acid, 40% phenylalanine ethyl ester; [31]P (145 MHz, D_6-DMSO) δ (ppm): 16.2, -6.3; [1]H (360 MHz, D_6-DMSO) δ (ppm): 9.49, 7.10, 4.16, 3.67, 3.36, 2.68, 0.75; T_g: 58.2°C; Total Yield: 40.3 %. (Note: Molecular weights could not be determined due to the polymers insolubility in THF)
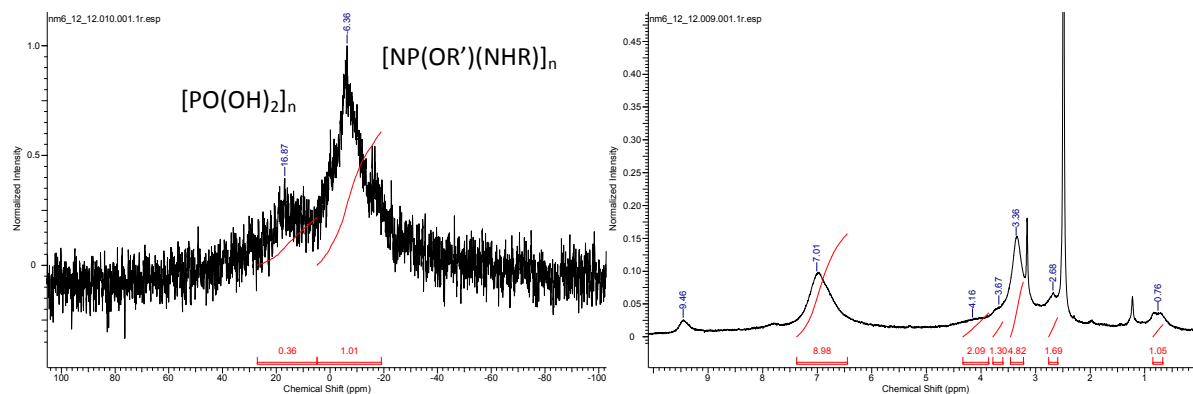

Figure: ^{1}H (left)/^{31}P (right) NMR spectra of **PAPA**

Hydrolysis Profiles of All Polymers Studied.

Hydrolysis was performed on 10 mg samples immersed in phosphate buffered saline at pH=7.4 and maintained at 37 °C, with samples taken out every week in triplicate and dried to determine

film mass loss. The order of increasing film mass loss after 4 weeks is: **PEPA** < **PAPA** < **PAA** < **PEA**.
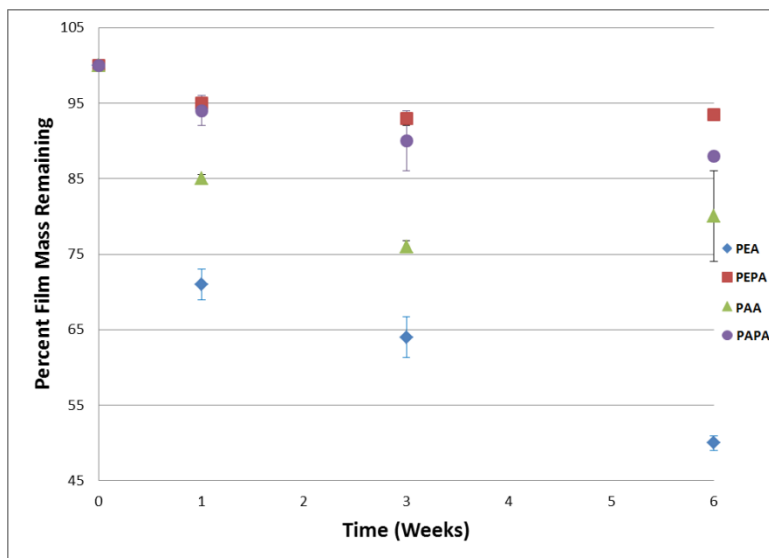

Figure: Hydrolysis data showing total films remaining (in percent of original mass) for all polymers studies as a function of time immersed in phosphate buffered saline.

Quantification of ion concentrations as a function of exposure time to SBF.

Relative signal intensities observed for polymers studied. Each set shows the same trend, of increasing signal intensity with increasing exposure time of each polymer to SBF. Similarly, the general trend of increasing signal intensity as a function of which polymer is observed follows **PAPA>PAA>PEA>PEPA**, which is in agreement with the observed mass gain data and ESEM observations.

Characterization of SIMS peaks for regions of interest.

Figure: The SIMS total ion image of **PAA** at week 3 with displayed regions of interest for open polymer areas (oval) and HAp features (rectangle). Individual mass spectra from each region of interest were summed and are compared to reference spectra.
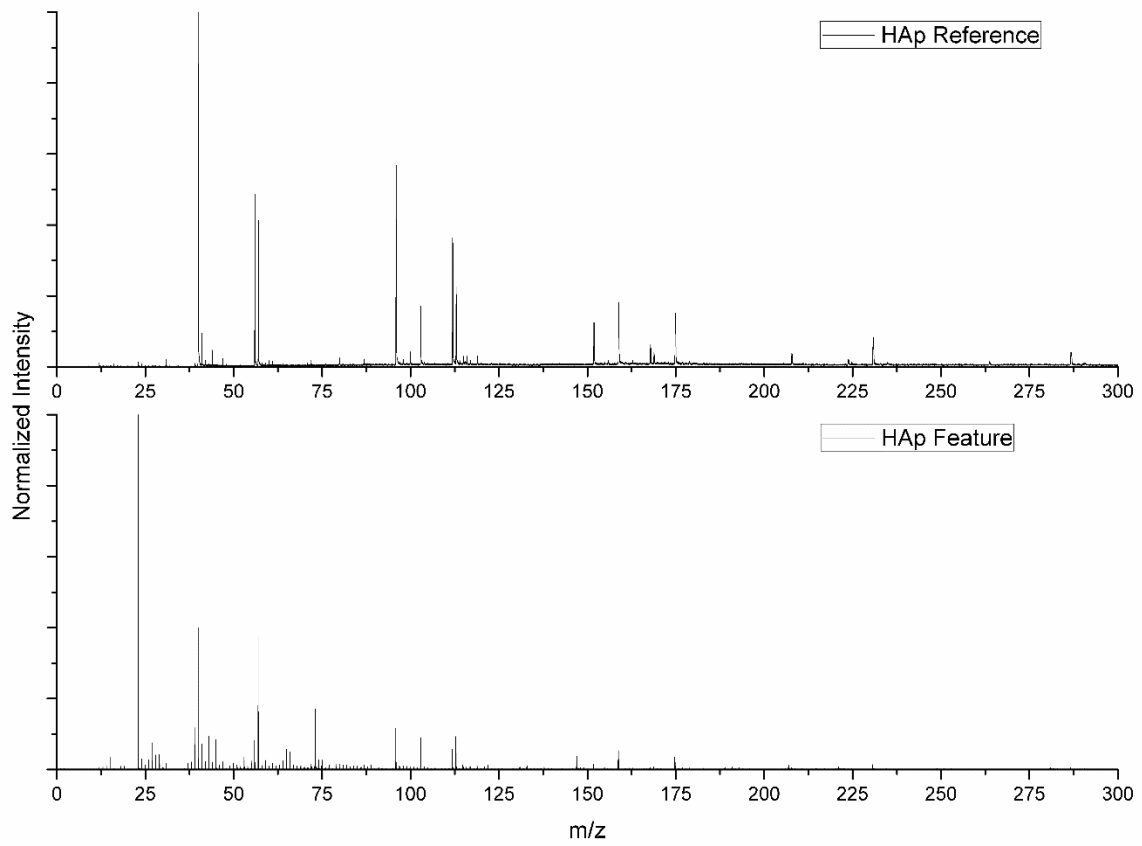
Figure: Mass spectra from the HAp feature of **PAA** week 3 are compared to HAp reference spectrum.
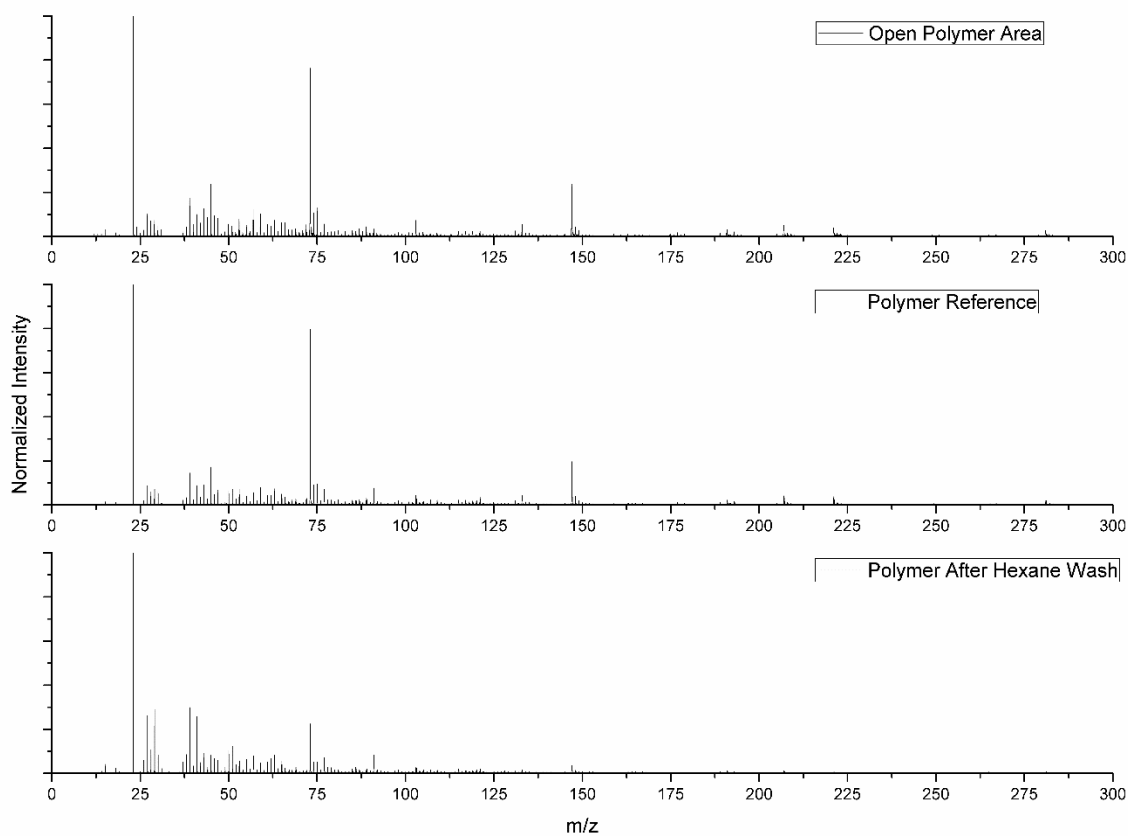
Figure: Mass spectra from the polymer region of **PAA** Week 3 are compared to a polymer reference spectrum and a polymer reference following triplicate washes in an excess of n-hexanes.