Supporting Information

for

RNA-inspired intramolecular transesterification accelerates the hydrolysis of polyethylene-like polyphosphoesters

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Experimental Section

Materials.

All commercially available reagents and solvents were purchased from Sigma Aldrich, Alfa Aesar, and Fisher Chemical and were used without further purification. Deuterated chloroform was purchased from Sigma Aldrich. Dulbecco's phosphate-buffered saline (PBS) was purchased from Sigma Aldrich and a pH value of 7.4 was confirmed by a pH electrode. A 2 M NaOH solution was prepared by dissolving 7.97 g of NaOH was dissolved in 100 mL H_2O. To prepare 40 mL of pH 11 buffer, 3.7 mL 2 M NaOH was mixed with 20 mL 0.4 M $NaHCO_3$ solution (3.41 g in 100 mL H_2O) and 16.3 mL H_2O. The pH of the NaOH solution and the NaOH/$NaHCO_3$ buffer were determined by a pH electrode. For 1 L buffered artificial seawater, 34.0 g *Nano Reef Salt* (*Aqua Medic GmbH,* Germany) and 16.8 g $NaHCO_3$ has been filled to a total volume of 1 L with deionized water. The pH was determined with a pH electrode and adjusted to pH = 8.12 by adding 2 M NaOH stock solution (7 mL).

Methods.

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance 300, 500 and 700 spectrometers at 293 K and referenced to the residual solvent peak (^1H: $CDCl_3$: 7.26 ppm; ^{13}C: $CDCl_3$: 77.0 ppm) with chemical shifts (δ) given in ppm. The spectra were analyzed using MestreNova 14.1. For mass spectrometry, an Advion expression CMS-L mass spectrometer was used with atmospheric pressure chemical ionization (APCI). Size exclusion chromatography (SEC) measurements were performed with THF as the eluent on an Agilent Technologies 1260 instrument consisting of an autosampler, pump and column oven. The column set consists of 3 columns: SDV 10^6 Å , SDV 10^4 Å and SDV 500Å (PSS Standards Service GmbH, Mainz, Germany), all of 300 x 8 mm and 10µm average particle size. A flow rate of 1.0 mL/min and a column temperature of

30 °C was set and the injection volume was 100 μL. Detection was accomplished with a RI detector (Agilent Technologies). The data acquisition and evaluation was performed using PSS WINGPC UniChrom (PSS Polymer Standards Service GmbH, Mainz, Germany). Calibration was carried out by using polystyrene provided by PSS Polymer Standards Service GmbH (Mainz, Germany). To examine the thermal properties of the synthesized polymers by differential scanning calorimetry (DSC), a Mettler Toledo DSC 823 calorimeter was used. Three scanning cycles of heating/cooling were performed in a nitrogen atmosphere (30 mL/min) with a heating and cooling rate of 10 °C/min. Thermogravimetric analysis (TGA) was measured on a Mettler Toledo ThermoSTAR TGA/SDTA 851-Thermowaage in a nitrogen atmosphere. The heating rate was 10 °C/min in a range of temperature between 35 and 600−900 °C. For wide-angle X-ray scattering (WAXS) experiments were performed using a Philips PW1820 powder diffractometer with Cu radiation (wavelength 1.5418 Å). The crystal morphology was determined using a FEI Tecnai F20 transmission electron microscope operated at an acceleration voltage of 200 kV. Bright field (BF) and energy-filtered transmission electron microscopy (EFTEM) techniques were used for measurements. Solution-grown crystals of **poly-1H** were prepared from a 0.05% solution in ethyl acetate. The solution was heated to 70 °C in a temperature-controlled oil bath for 1 hour and slowly cooled down to room temperature. One drop of the resulting dispersion was drop-cast onto a carbon coated TEM grid, the excess liquid was blotted off with a filter paper, and the specimen was allowed to dry under ambient conditions.

Synthetic Procedures.

All reactions were performed under an Argon atmosphere otherwise stated.

Synthesis of 2-(benzyloxy)ethyl phosphorodichloridate (1a)

$POCl_3$ (37.0 g, 0.24 mol) was dissolved in 100 mL dry toluene and cooled to 0 °C. A solution of 2-(benzyloxy)ethanol (5.15 g, 33.8 mmol) and NEt_3 (3.79 g, 37.5 mmol) in 25 mL dry toluene was added dropwise within one hour. A white precipitate ($NEt_3 \cdot HCl$) formed during the reaction. The reaction mixture was left stirring overnight at room temperature. Filtration under an Argon atmosphere was performed and the residual $POCl_3$ and solvent were removed under reduced pressure. The obtained orange oil was used without further purification for the next step (82% yield, *note*: Figure S3 also shows di- and trifunctionalized impurities in 1a, which were not removed for the next reaction step).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.46 – 7.26 (m, 5H, aryl), 4.60 (s, 2H, Ph-C$\underline{H_2}$-O-), 4.47 (m, 2H, $POCl_2$-O-C$\underline{H_2}$-), 3.77 (m, 2H, $POCl_2$-O-CH_2-C$\underline{H_2}$-).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 128.51, 127.98, 127.75, 73.39, 70.72, 67.68

^{31}P NMR (121 MHz, $CDCl_3$) δ = 7.82.

Synthesis of 2-(benzyloxy)ethyl di(undec-10-en-1-yl) phosphate (1)

10-Undecen-1-ol (9.12 g, 53.6 mmol) and triethylamine (5.67 g, 56.0 mmol) were dissolved in 55 mL dry toluene and cooled to 0 °C. A solution of **1a** (7.6 g, 28.3 mmol) dissolved in 40 mL dry toluene was added dropwise within one hour. A white precipitate indicated the formation of $NEt_3 \cdot HCl$. After the addition was completed, the reaction mixture was further stirred at room temperature for 7 days. The ongoing reaction was monitored by ^{31}P NMR. The reaction mixture was filtered and washed with 0.1 M NaOH solution to remove any pyrophosphate side products.

The aqueous phase was extracted with petroleum ether several times before the organic phases were combined and washed with a slightly acidic HCl/NaCl solution. The organic phase then was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Column chromatography was performed with a Büchi Reverlis PREP system using petroleum ether and ethyl acetate as the eluent in alternating ratios ($R_f = 0.64$ in petroleum ether:ethyl acetate 2:1). The purified product was obtained as a viscous oil (8.2 g, 57% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.40 – 7.25 (m, 5H, aryl), 5.81 (m, 2H, -C$\underline{H}$=CH_2), 5.05 – 4.84 (m, 4H, -CH=C$\underline{H_2}$), 4.57 (s, 2H, Ph-C$\underline{H_2}$-O-), 4.25 – 4.14 (m, 2H, -O-PO_3-C$\underline{H_2}$-CH_2-OBn), 4.02 (q, J = 6.8 Hz, 4H, -O-PO_3-C$\underline{H_2}$-), 3.69 (t, J = 4.8 Hz, 4H, -CH_2-C$\underline{H_2}$-OBn), 2.03 (q, J = 7.0 Hz, 4H, -C$\underline{H_2}$-CH=), 1.64 (q, J = 6.8 Hz, 4H, -OPO_3-CH_2-C$\underline{H_2}$), 1.50 – 1.24 (m, 20H, alkyl).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 139.18, 137.89, 128.40, 127.71 (d, J = 3.6 Hz), 114.14, 73.21, 68.98 (d, J = 7.0 Hz), 67.85 (d, J = 5.9 Hz), 66.50 (d, J = 5.9 Hz), 33.80, 30.26 (d, J = 6.9 Hz), 29.91 – 28.48 (m), 25.43.

^{31}P NMR (121 MHz, $CDCl_3$) δ = -0.69.

APCI MS: m/z = 537.6 $[M+H]^+$

ADMET polymerization of 1

Monomer **1** (1.14 g, 2.1 mmol) was charged in a 25 mL Schlenk tube and degassed by three consecutive Argon/vacuum cycles. 17 mg of Grubbs catalyst 1st generation (0.1 mol%) were added under an Argon stream and the mixture was kept stirring for 5 min. The system was connected to a vacuum pump (4×10^{-1} mbar) and intensive bubbling indicated the start of the polymerization as ethylene gas evolved. After 5 min, the Schlenk tube was placed in an oil bath at 60 °C and was kept there overnight. The highly viscous mixture was allowed to cool down before a second portion of Grubbs catalyst 1st generation was added as well as 0.8 mL CH_2Cl_2 to dissolve the polymer. The polymerization was continued at 60 °C and 4 x 10^{-1} mbar for another 24 h. After cooling down, 5 mL CH_2Cl_2 and 150 µL ethyl vinyl ether were added to quench the catalyst. The color of the solution changed from purple to orange indicating the formation of the Fischer carbene complex of the Grubbs catalyst with ethyl vinyl ether. To remove this complex, the polymer was precipitated from methanol. After centrifugation, the product was isolated as a highly viscous, honey-like, dark brown oil in quantitative yield.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.38 – 7.27 (m, 5H, aryl), 5.36 (m, 2H, -C$\underline{H}$=C$\underline{H}$-), 4.57 (s, 2H, Ph-C$\underline{H_2}$-O-), 4.25 – 4.10 (m, 2H, -O-PO_3-C$\underline{H_2}$-CH_2-OBn), 4.01 (p, *J* = 6.8 Hz, 4H, q, *J* = 6.8 Hz, 4H, -O-PO_3-C$\underline{H_2}$-), 3.68 (t, *J* = 8.2, 6.6 Hz, 2H, -CH_2-C$\underline{H_2}$-OBn), 1.96 (m, 4H, -C$\underline{H_2}$-CH=), 1.64 (m, 4H, -OPO_3-CH_2-C$\underline{H_2}$), 1.28 (m, 20H, alkyl).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.89, 130.32, 129.86, 128.40, 127.70, 118.16, 73.20, 68.98 (d, *J* = 7.0 Hz), 67.85 (d, *J* = 6.2 Hz), 66.49 (d, *J* = 5.8 Hz), 32.63, 30.28 (d, *J* = 6.9 Hz), 29.77 – 28.83 (m), 27.24, 25.44.

^{31}P NMR (121 MHz, $CDCl_3$) δ = -0.70.

Hydrogenation of poly-1 to poly-1H

In a glass vessel equipped with a stirring bar, **poly-1** (1.97 g, 3.7 mmol) was dissolved in 90 mL THF. Residual oxygen was removed by bubbling Argon through the solution for 10 min. 1.45 g of 20 wt% $Pd(OH)_2/C$ were added and the glass vessel was placed in a ultra-sonication bath to achieve a better dispersion of the catalyst in the solution. Afterwards the glass vessel was charged in a 250 mL ROTH autoclave and the hydrogenation was performed at 80 bar H_2 at room temperature for

16 h. After filtration, the polymer was precipitated from methanol and isolated to obtain a solid, white polymer in quantitative yield.

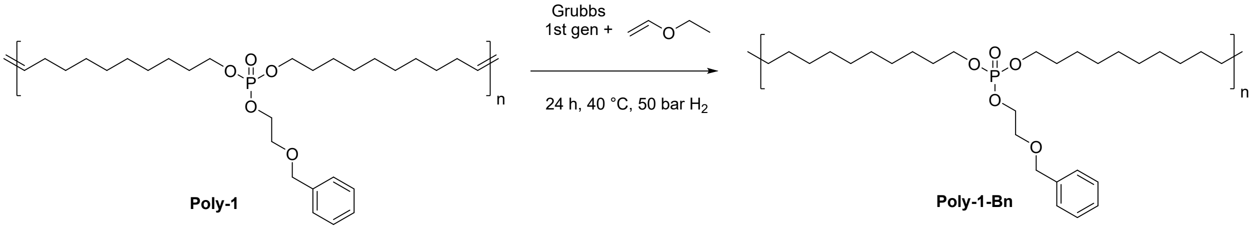
^{1}H NMR (300 MHz, CDCl$_3$) δ = 4.15 (dt, *J* = 9.3, 4.1 Hz, 2H, -O-PO$_3$-C$\underline{H_2}$-CH$_2$-OH), 4.06 (q, *J* = 6.8 Hz, 4H, -O-PO$_3$-C$\underline{H_2}$-), 3.82 (t, *J* = 4.3 Hz, 2H, -O-PO$_3$-CH$_2$-C$\underline{H_2}$-OH), 3.13 (b, -O$\underline{H}$) 1.68 (m, 4H, -OPO$_3$-CH$_2$-C$\underline{H_2}$), 1.25 (s, 32H, alkyl).

^{13}C NMR (75 MHz, CDCl$_3$) δ = 69.66, 68.21 (d, *J* = 6.1 Hz), 62.16, 30.27 (d, *J* = 7.0 Hz), 29.69 (d, *J* = 3.0 Hz), 29.56 (d, *J* = 4.7 Hz), 29.16, 25.44.

^{31}P NMR (121 MHz, CDCl$_3$) δ = 0.36.

Selective hydrogenation of poly-1 to poly-1Bn

Scheme S1: Synthesis of Poly-1-Bn.



The hydrogenation catalyst used for this reaction was obtained by the reaction of Grubbs catalyst 1st generation with ethyl vinyl ether according a literature procedure.[13] In a 250 mL glass vessel, 99 mg of **poly-1** was dissolved in 7.5 mL dry toluene. The solution was degassed by bubbling Argon through the solution for 5 minutes. 10 mg of the hydrogenation catalyst was added and the solution became orange. The glass vessel was charged into a ROTH autoclave and the system was flushed with H$_2$ twice before the hydrogenation was performed for 24 h at 40 °C at a pressure of 50 bar H$_2$. After cooling down, the now dark brown solution was concentrated at reduced pressure before precipitation from methanol. The product was isolated by centrifugation and dried under vacuum to give 80 mg of **poly-1Bn** (88% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.34 (m, 5H, aryl), 4.57 (s, 2H, Ph-C$\underline{H_2}$-O-), 4.19 (m, 2H, -O-PO_3-C$\underline{H_2}$-CH_2-OBn), 4.02 (q, 4H, -O-PO_3-C$\underline{H_2}$-), 3.69 (t, 2H, -CH_2-C$\underline{H_2}$-OBn), 1.65 (m, 4H, -OPO_3-CH_2-C$\underline{H_2}$), 1.25 (s, 32H, alkyl).

^{31}P NMR (121 MHz, $CDCl_3$) δ = -0.70.

Grafting-from polymerization of lactide with poly-1H macroinitiator

The macroinitiator **Poly-1H** (31 mg, 68.8 μmol) was weighed in a 25 mL Schlenk tube, dissolved in dry toluene and dried by lyophilization. Afterwards, the polymer was dissolved in 200 μL dichloromethane. Lactide was freshly recrystallized in ethyl acetate (3.3 g lactide in 2.2 mL solvent) and further dried by lyophilization from dry toluene. A solution of lactide in dry dichloromethane with a concentration of 1.5 mol L^{-1} was prepared and 550 μL of this solution (equals 117 mg / 0.81 mmol of lactide) were added to the macroinitiator. The polymerization was initiated by the quick addition of 600 μL of a 0.2 M DBU solution in dry dichloromethane (equals 18.3 mg / 0.12 mmol of DBU). After stirring at room temperature for 40 minutes, the polymerization was quenched by the addition of 2 mL of a formic acid solution in dichloromethane (20 mg mL^{-1}). The solution was kept stirring for 2 minutes, then the polymer was precipitated from ice-cold methanol. After centrifugation the product was isolated and dried under vacuum to give 78 mg of white, crystalline **poly-1H-*graft*-PLA**.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.17 (q, polylactide C$\underline{H}$), 4.35 (m, -O-PO_3-CH_2-C$\underline{H_2}$-OOC-), 4.20 (m, -O-PO_3-C$\underline{H_2}$-CH_2-OOC-), 4.02 (q, J = 7.0 Hz, -O-PO_3-C$\underline{H_2}$-), 1.74 – 1.62 (m, -OPO_3-CH_2-C$\underline{H_2}$), 1.63 – 1.50 (m, polylactide C$\underline{H_3}$), 1.25 (s, alkyl).

^{13}C NMR (176 MHz, $CDCl_3$) δ = 169.43, 69.05, 68.07, 66.72, 64.64, 63.98, 30.28, 29.64, 29.20, 25.44, 20.46, 16.74, 16.64.

^{31}P NMR (121 MHz, $CDCl_3$) δ = -0.86, -0.96.

Film degradation test

Hydrolytic Degradation of poly-1H at pH 11 and pH 13

Polymer films were prepared by drop-casting 200 µL of a **poly-1H** solution in $CHCl_3$ (120 mg mL^{-1}) onto square Microscope coverslips with a size of 22 x 22 mm. The samples were first dried at room temperature for 3 h and then under vacuum at 40 °C overnight. The weights of the films were about 21-23 mg. The polymer films with the coverslips were placed into well plates and 4 mL of either $NaHCO_3$/NaOH buffer (pH 11.1) or 2 N NaOH solution (pH 13.1) were added to each polymer sample. The degradation experiment was performed in double determination at 37 °C for time intervals of one, two and three weeks, respectively. The samples were not agitated during the experiment. After 13 days, 3 mL H_2O were added to each solution as large parts of water evaporated during the experiment. Another 3 mL H_2O each were added after 17 days. All polymers film were detached from the coverslips after all time intervals and the films were disintegrated into small fragments. The solutions were collected with plastic pipettes for latter surface tension measurements, while the remaining polymer film particles were washed twice with 4 mL H_2O each and then dried under vacuum at 35 °C overnight. Due to solubility restrictions, NMR and SEC measurements could only be performed with the samples immersed in $NaHCO_3$/NaOH buffer. Polymer samples immersed in 2 N NaOH solution remained insoluble in organic solvents after the degradation experiment.

Degradation of poly-1H in solution

15 mg of **poly-1H** were dissolved in 0.6 mL $CDCl_3$ in an NMR tube. 25 µL DBU were added and the degradation was monitored by NMR for 4 days.

Hydrolytic Degradation of poly-1H/poly-1Bn blend at pH 11

A 50/50 wt% polymer blend of **poly-1H** and **poly-1Bn** was prepared by mixing the two polymers and dissolving them in $CHCl_3$. Polymer films were prepared on glass coverslips analogue to the prior degradation test. In a well plate, films of **poly-1H**, **poly-1Bn** and **poly-1H/poly-1Bn** polymer blend were immersed each in 4 mL $NaHCO_3$/NaOH buffer (pH 11.1). The well plate was placed in an oven with a constant temperature of 37 °C. The polymer samples were not agitated during the degradation experiment. H_2O was added twice a week to compensate evaporated water. After 2 months, the degradation test was stopped and the sample isolation was performed analogue to the previous degradation test.

Hydrolytic Degradation in PBS buffer and artificial seawater

Polymer films were dropcast on glass coverslips. Then, the films were immersed each in 4 mL PBS buffer (pH 7.4) or artificial seawater (pH 8.1) in a well plate. The degradation experiments were performed in the dark at room temperature. The polymer samples were not agitated and 2 mL H_2O were added once a week to compensate evaporated water. After one, two, and four weeks, the polymer samples were isolated, washed with 4 mL H_2O and dried at 40 °C. All polymer samples remained completely soluble in $CDCl_3$ for NMR measurements and in THF for SEC measurements after the degradation experiments.

Quantum-mechanical calculations

Models of the structure presented in Scheme 1c have been built with the number of carbon atoms varying on each side from 2, 3, 4, 5, 6, 7, to 10. The activation Gibbs free energy of the cyclization step has been calculated for each of these models. It has been found that the value oscillates around 8.1 kcal/mol and thus for further studies the model with two carbon atoms on each side (7.8 kcal/mol) has been used and confirmed by comparison with the model comprising 4 carbon atoms on each side (8.7 kcal/mol). Geometries of these and all other considered structures have been first optimized at the DFT level of theory, using ωB97X-D functional[38] expressed in the def2-TZVP basis set[39] as implemented in the Gaussian16 program.[40] SMD continuum solvent model,[41] which uses bulk properties of the solvent to create a dielectric cavity in which the solute is immersed has been used with parameters corresponding to the aqueous solution. Vibrational analysis has been used to ensure that the optimized geometry corresponds to a stationary point representing a minimum on the potential energy surface (all normal modes being real) or a transition state (exactly one imaginary frequency).

^{1}H, ^{13}C, ^{31}P NMR spectra

Monomer NMR spectra

2-(benzyloxy)ethyl phosphorodichloridate (1)

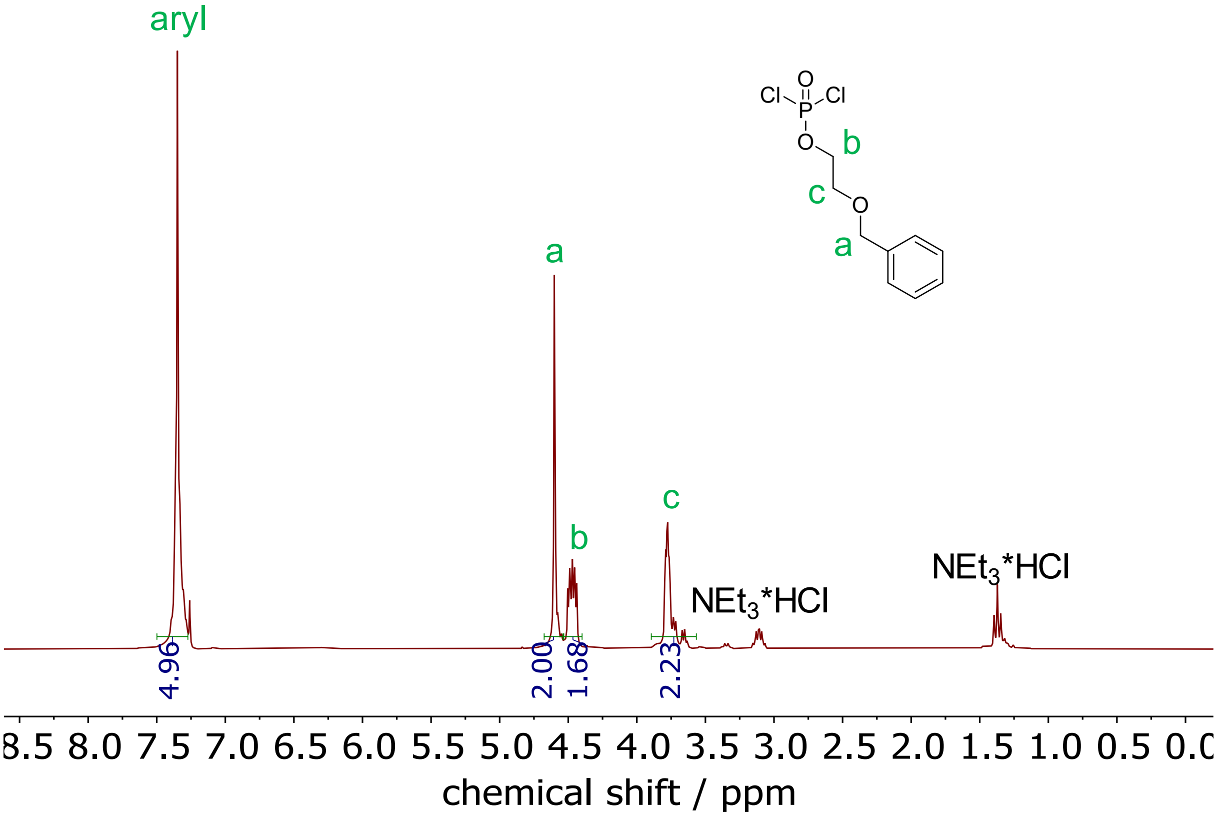


Figure S1: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) of **1**.

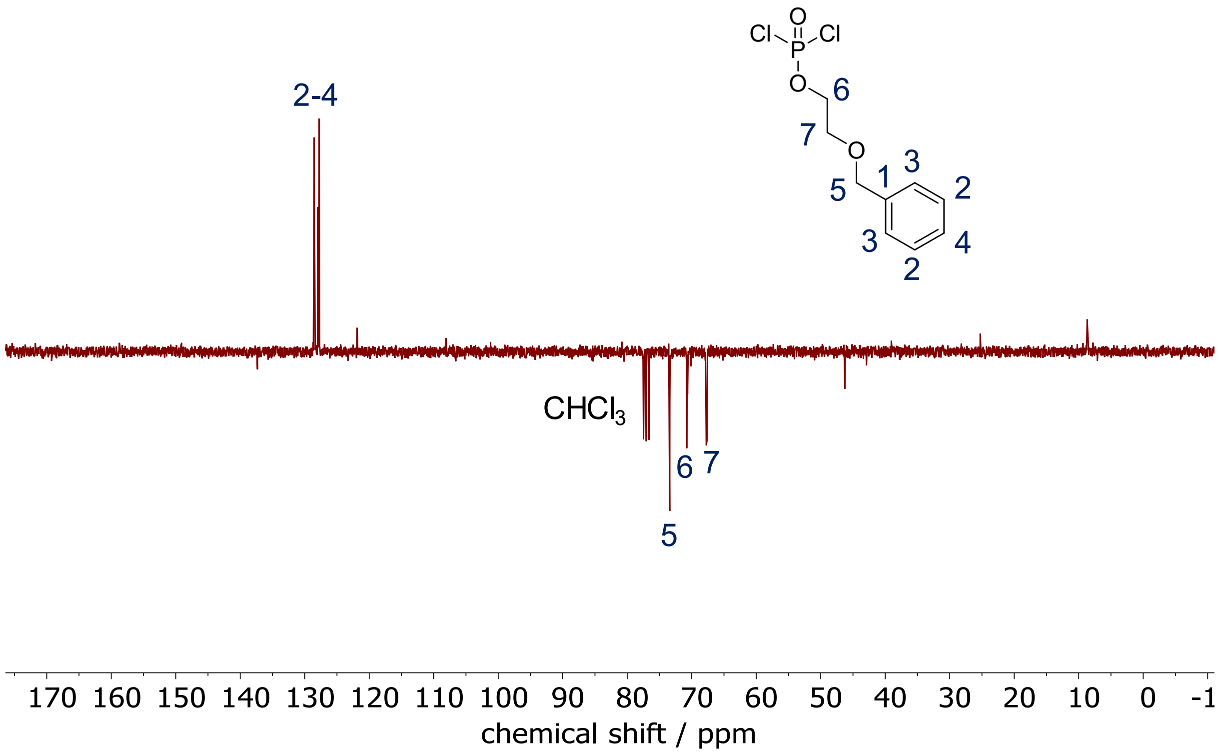


Figure S2: ^{13}C Distortionless Enhancement by Polarization Transfer (DEPT) NMR in $CDCl_3$ at 75 MHz at 298 K of **1**.

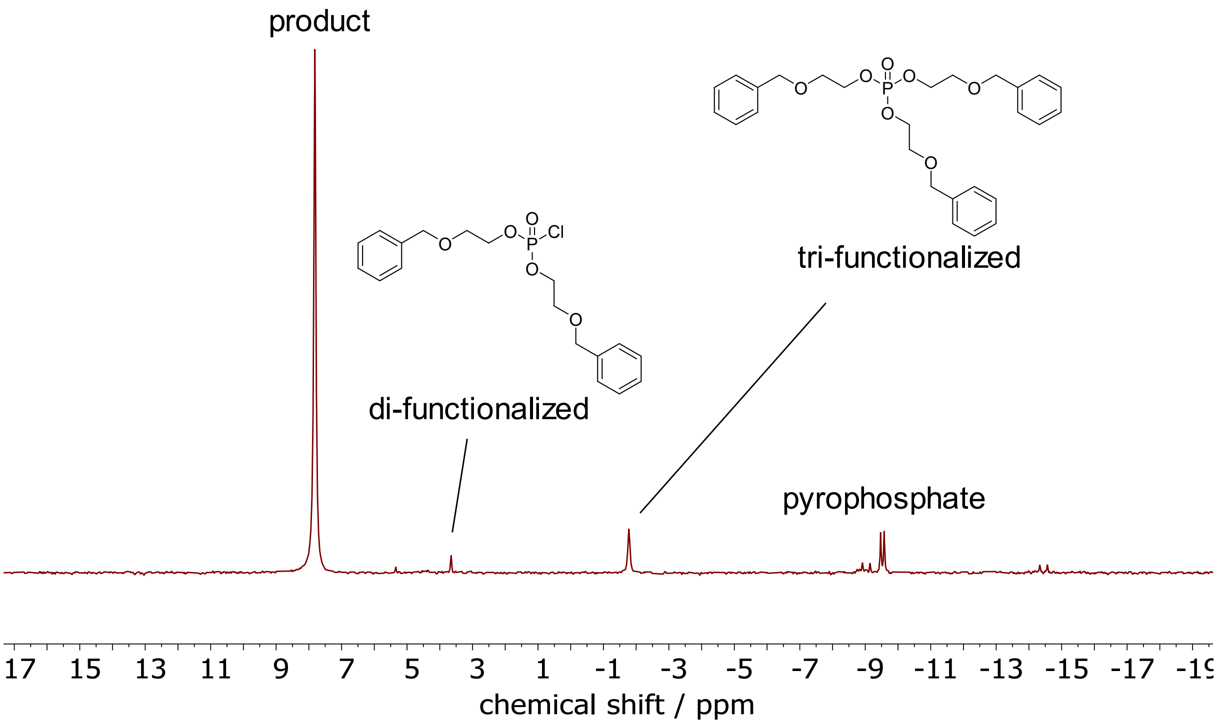


Figure S3: ^{31}P NMR in $CDCl_3$ at 121 MHz at 298 K of crude **1a**.

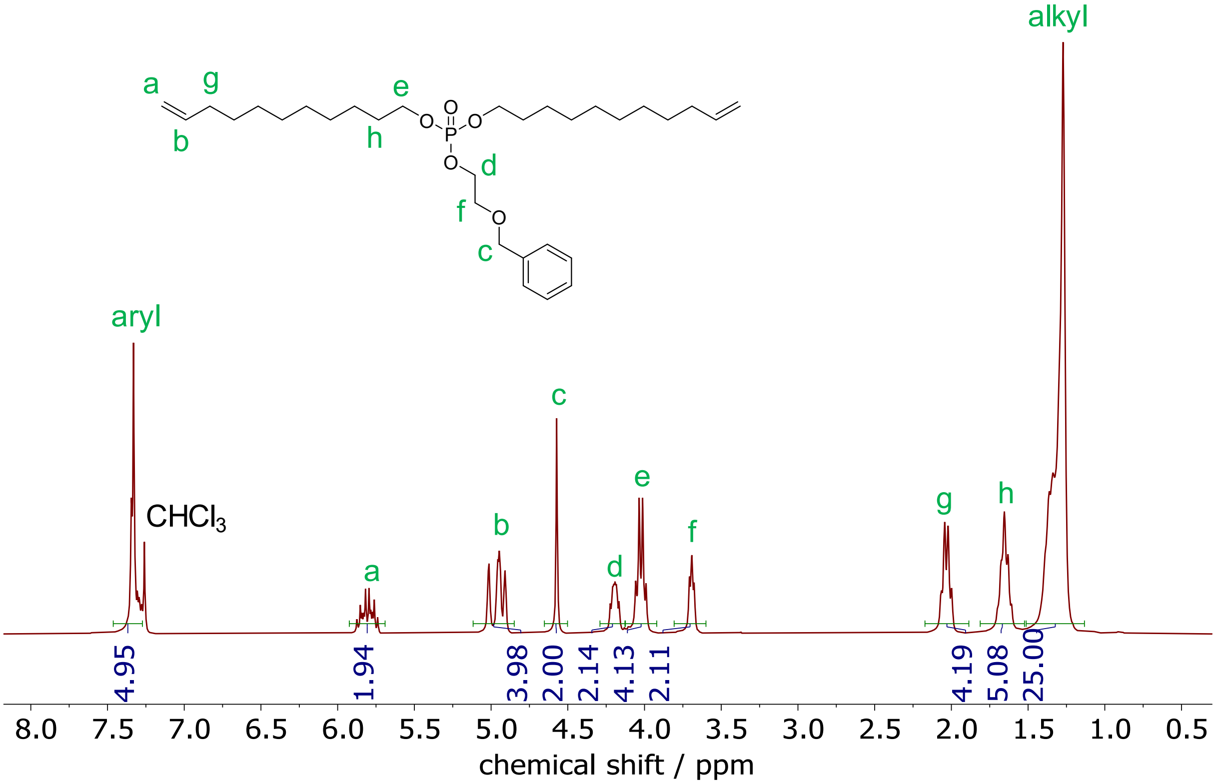


Figure S4: ^{1}H NMR in CDCl$_3$ at 300 MHz at 298 K of **1**.

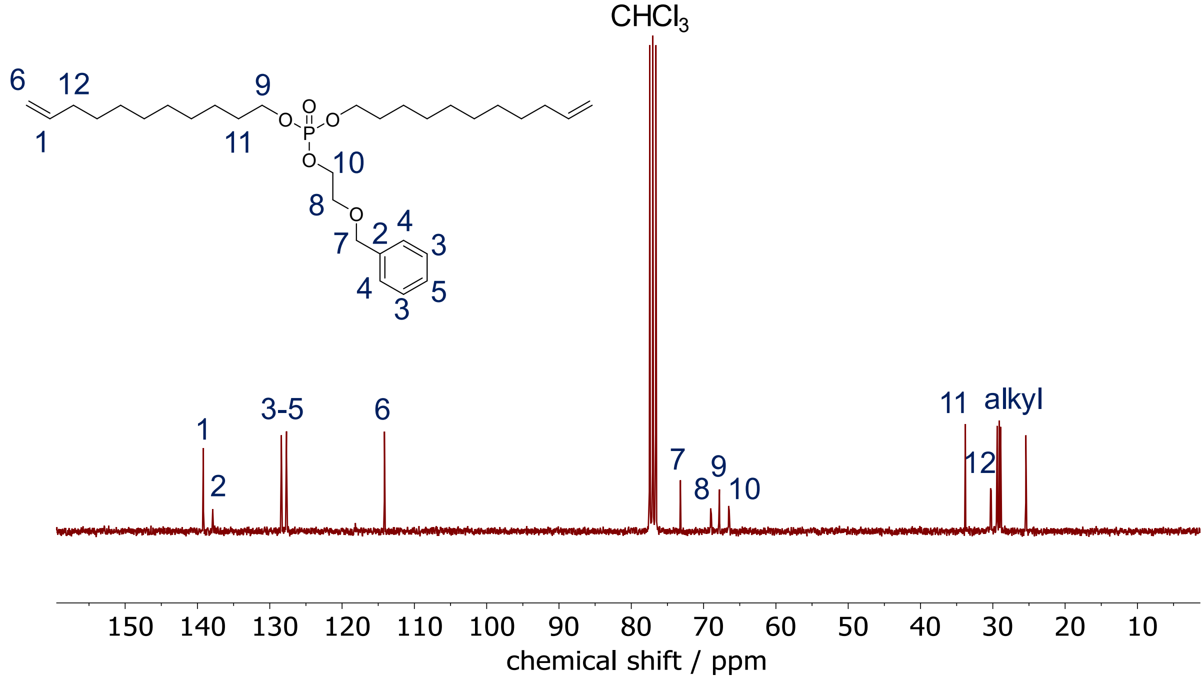


Figure S5: ^{13}C NMR in $CDCl_3$ at 75 MHz at 298 K of **1**.

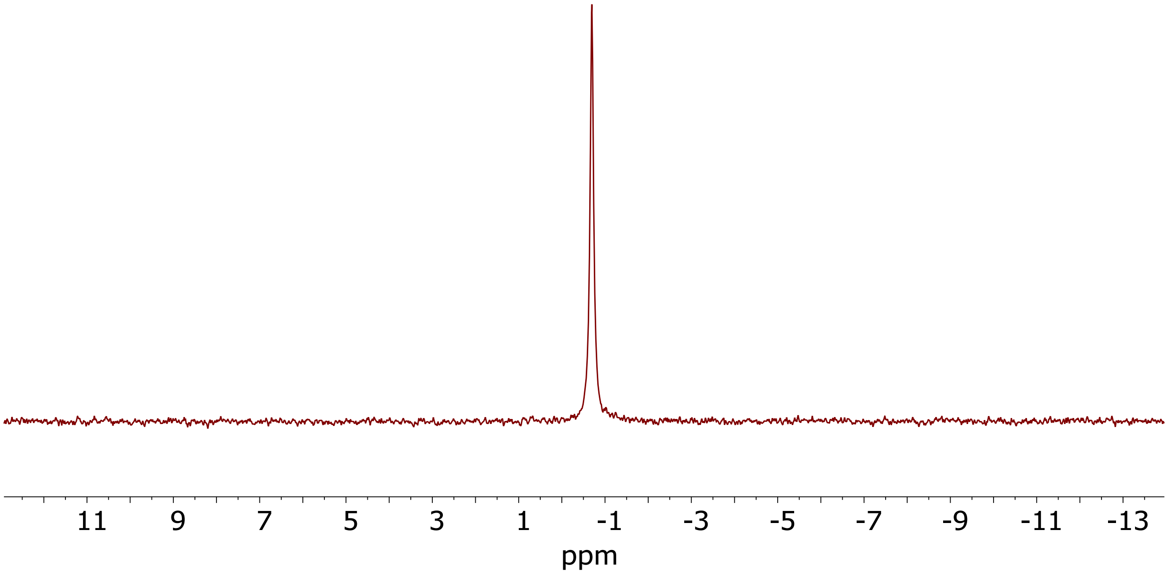


Figure S6: ^{31}P NMR in $CDCl_3$ at 121 MHz at 298 K of **1**.

Polymer NMR spectra

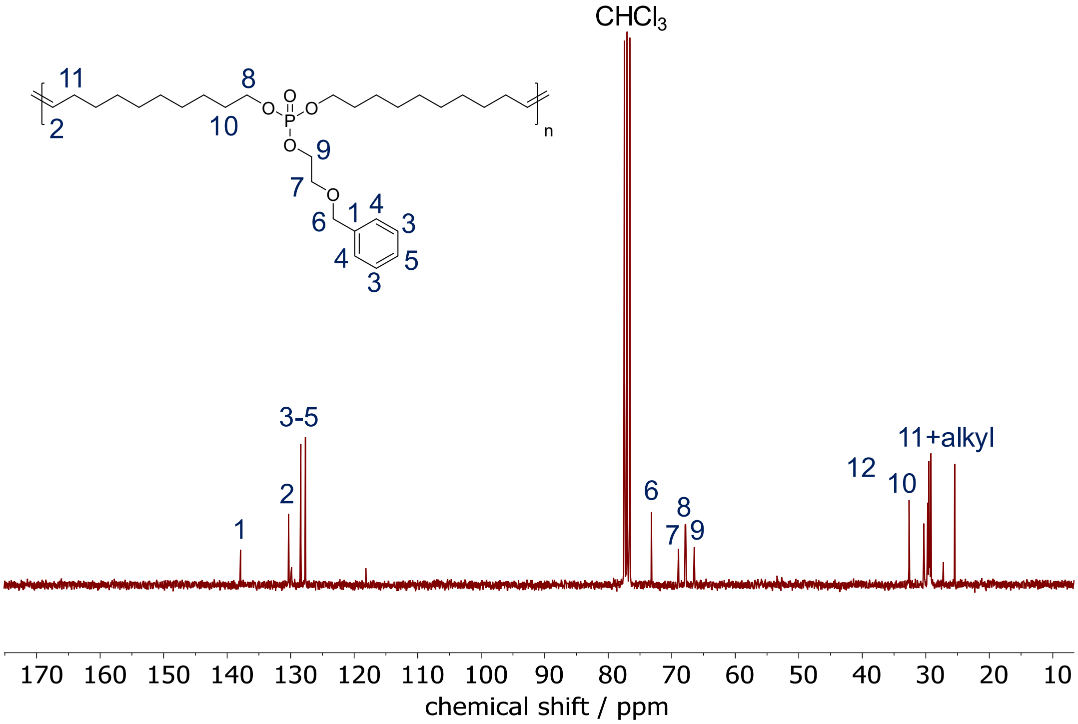


Figure S7: ^{13}C NMR in CDCl$_3$ at 75 MHz at 298 K of **poly-1**.

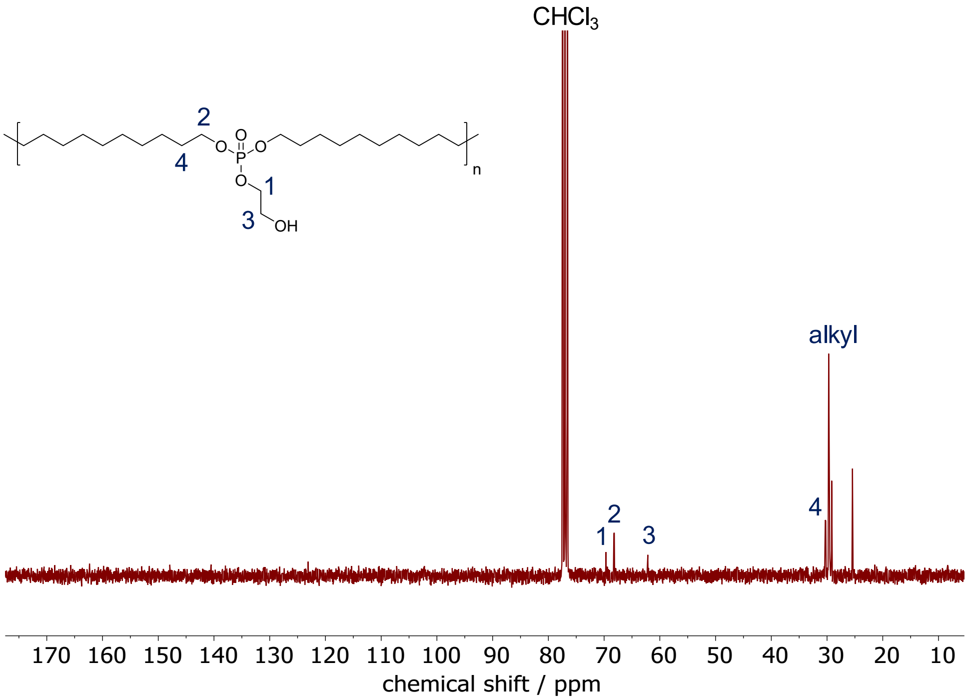


Figure S8: ^{13}C NMR in CDCl$_3$ at 75 MHz at 298 K of **poly-1H**.

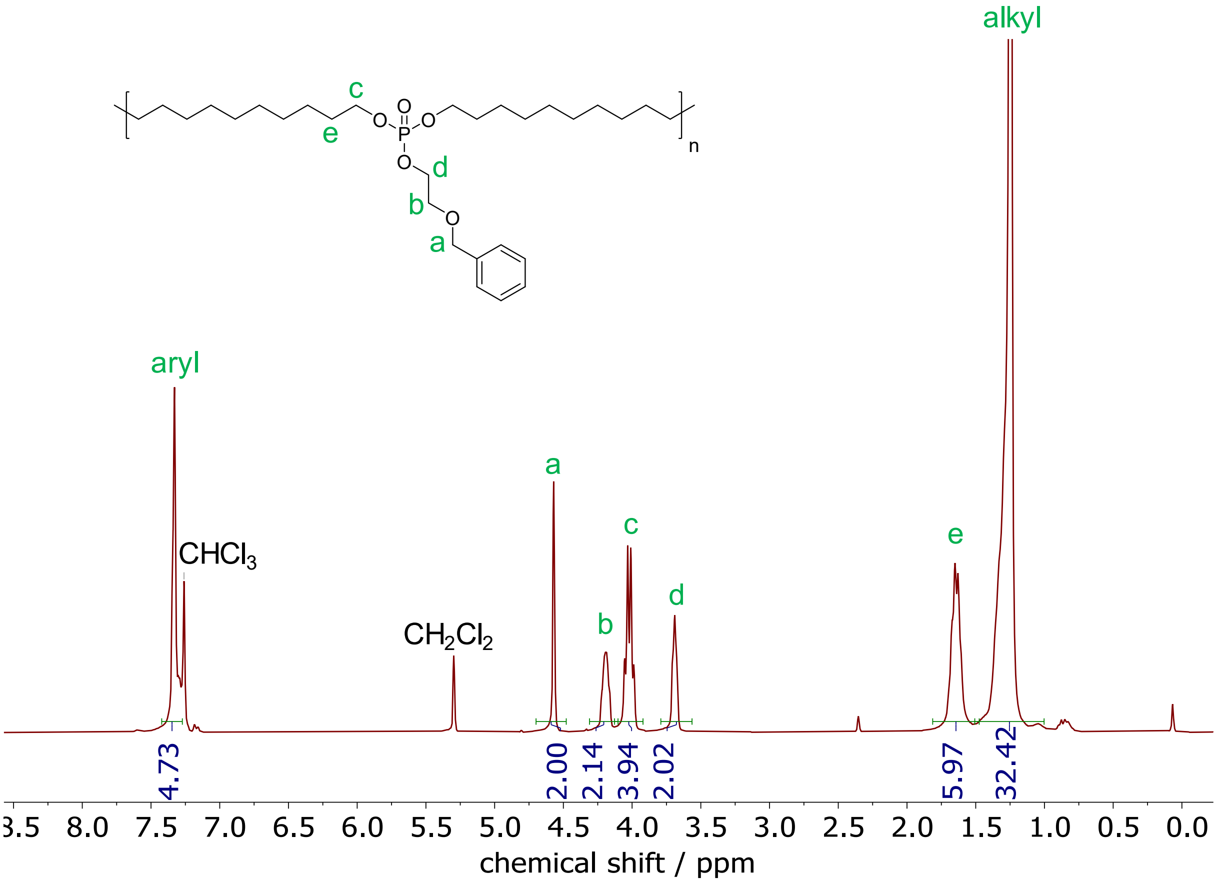


Figure S9: ^{1}H NMR in $CDCl_3$ at 300 MHz at 298 K of **poly-1Bn**.

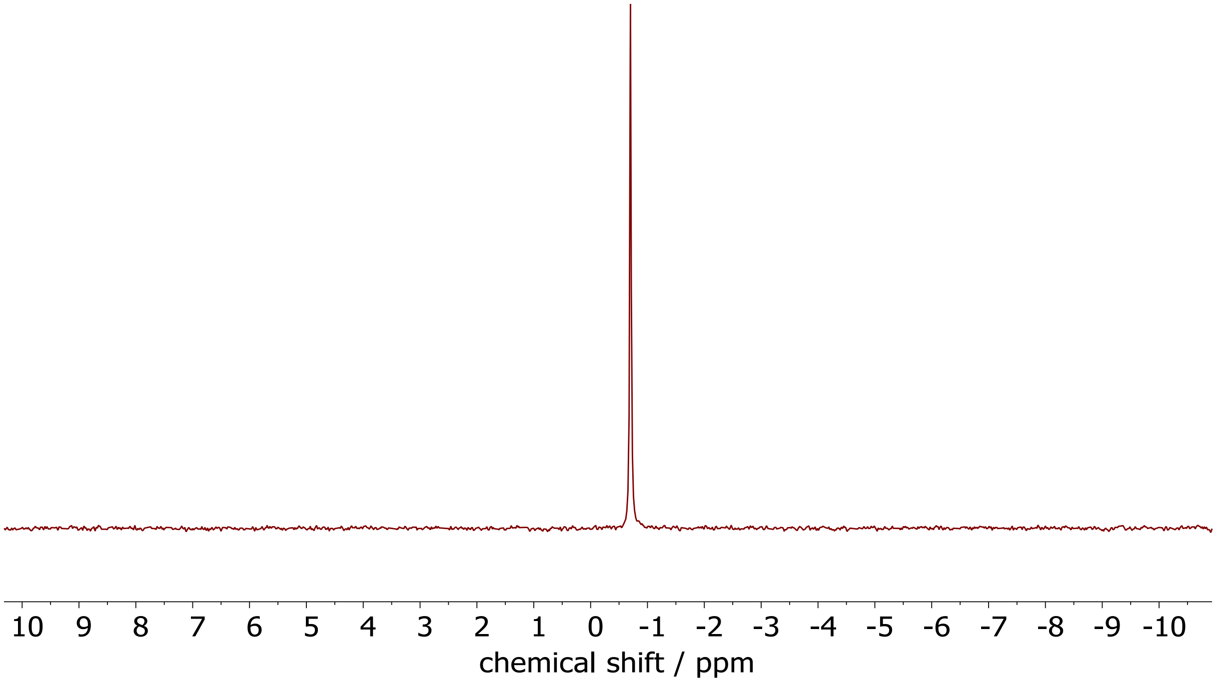


Figure S10: ^{31}P NMR in $CDCl_3$ at 121 MHz at 298 K of **poly-1Bn**.

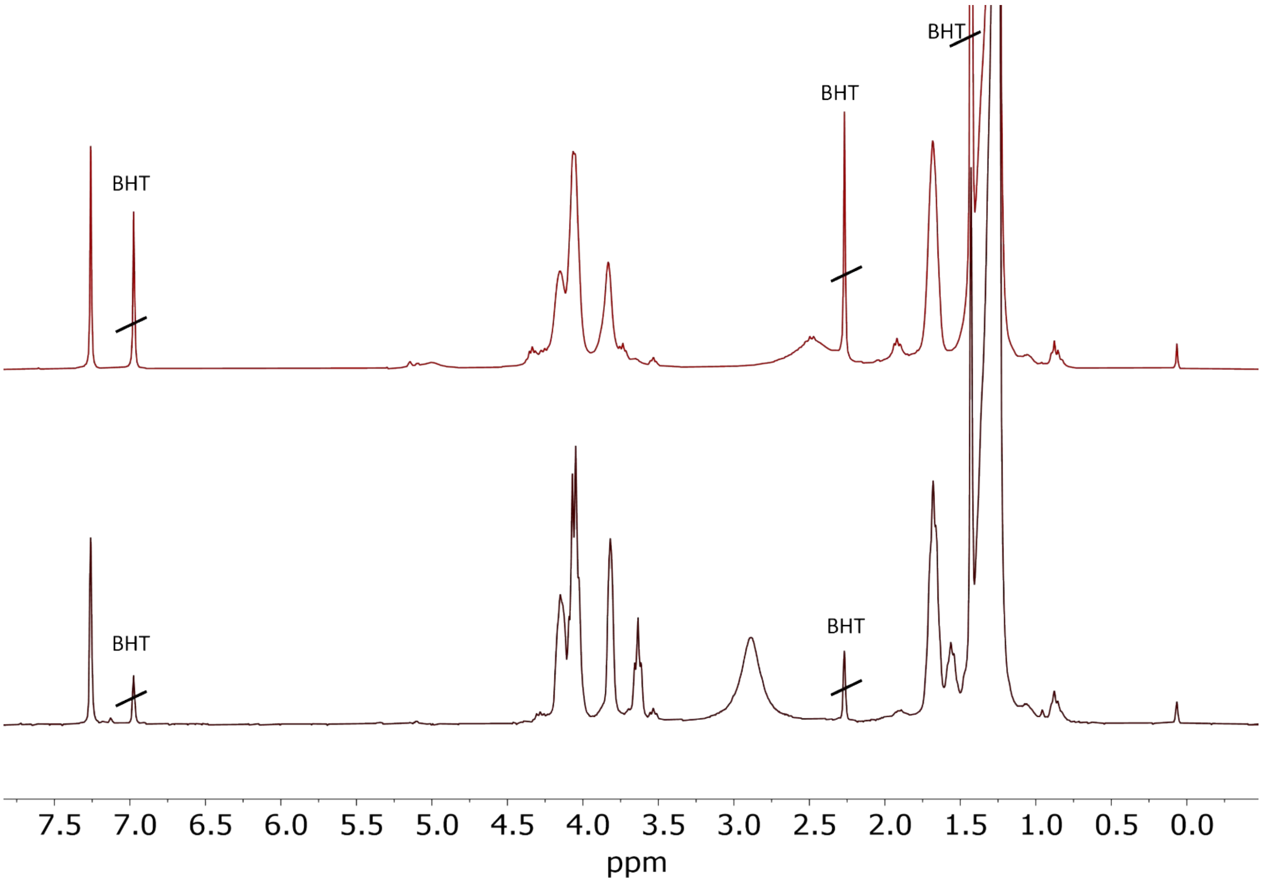


Figure S11: Overlay of ^{1}H NMR (in $CDCl_3$ at 300 MHz at 298 K) of **poly-1H** before (top) and after (bottom) storage at room temperature upon air for 2 months. Signals at 6.96, 2.26 and 1.40 ppm correspond to butylated hydroxytoluene (BHT), stabilizer.

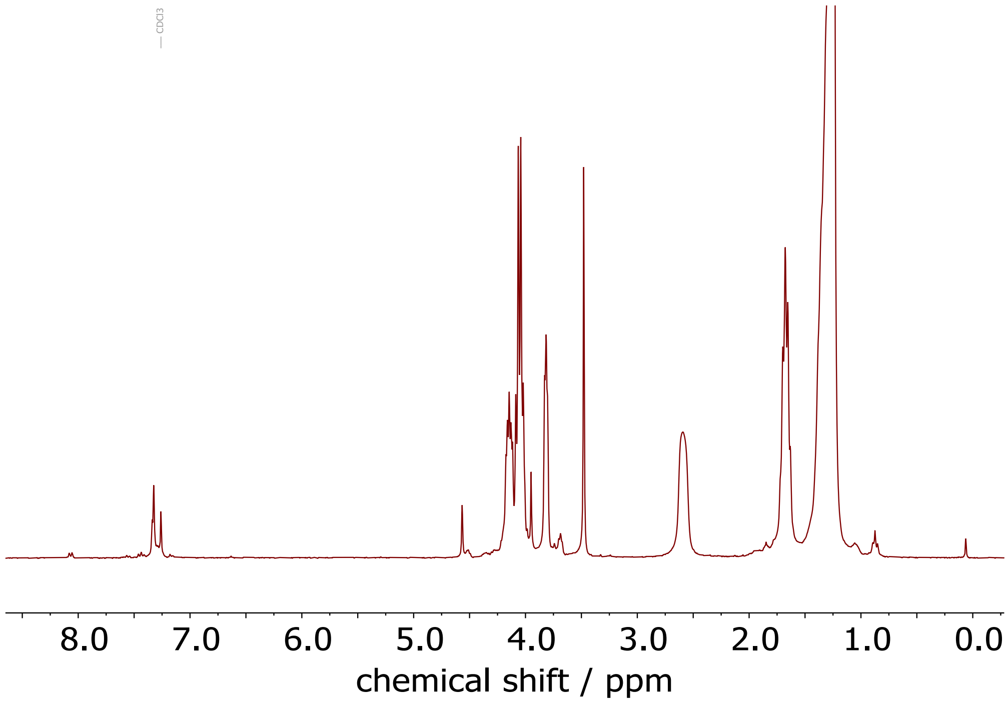


Figure S12: ^{1}H NMR in $CDCl_3$ at 300 MHz at 298 K of **poly-1H-*co*-poly-1Bn**.

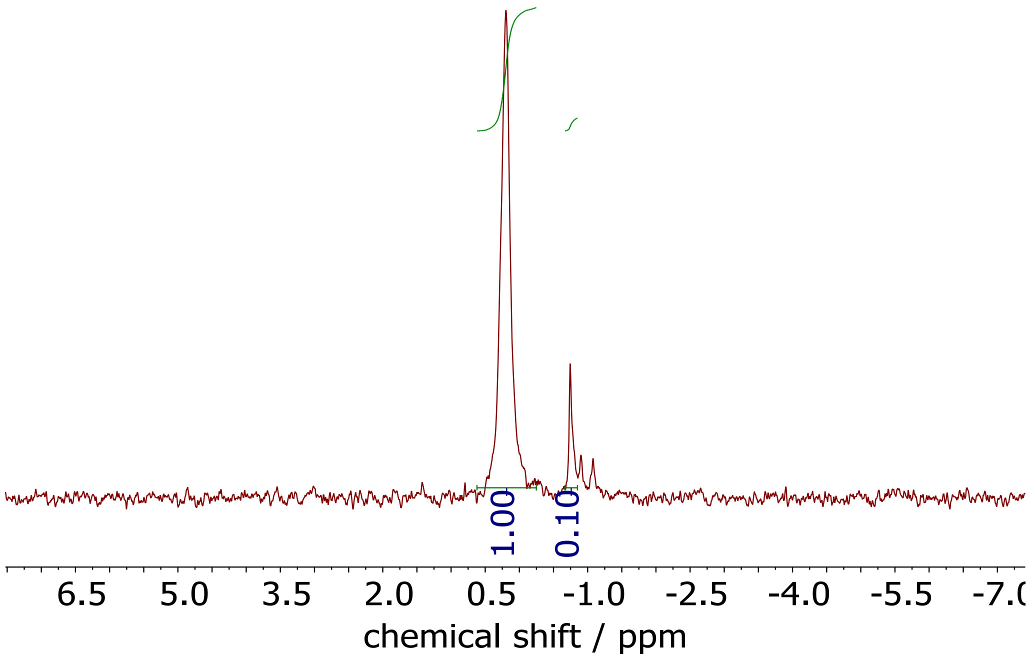


Figure S13: ^{31}P NMR in $CDCl_3$ at 121 MHz at 298 K of **poly-1H-*co*-poly-1Bn**.

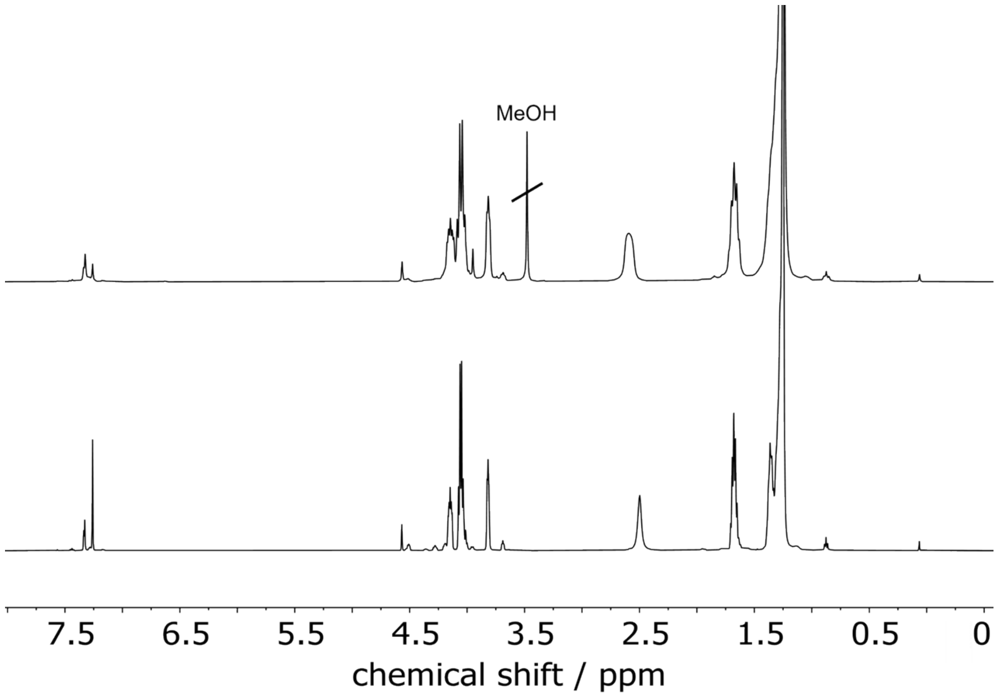


Figure S14: ^{1}H NMR spectra in $CDCl_3$ at 300 MHz at 298 K of **poly-1H-*co*-poly-1Bn** (table 1, entry 4) before (top) and after (bottom) being immersed in PBS buffer at pH 7.4 for four weeks.

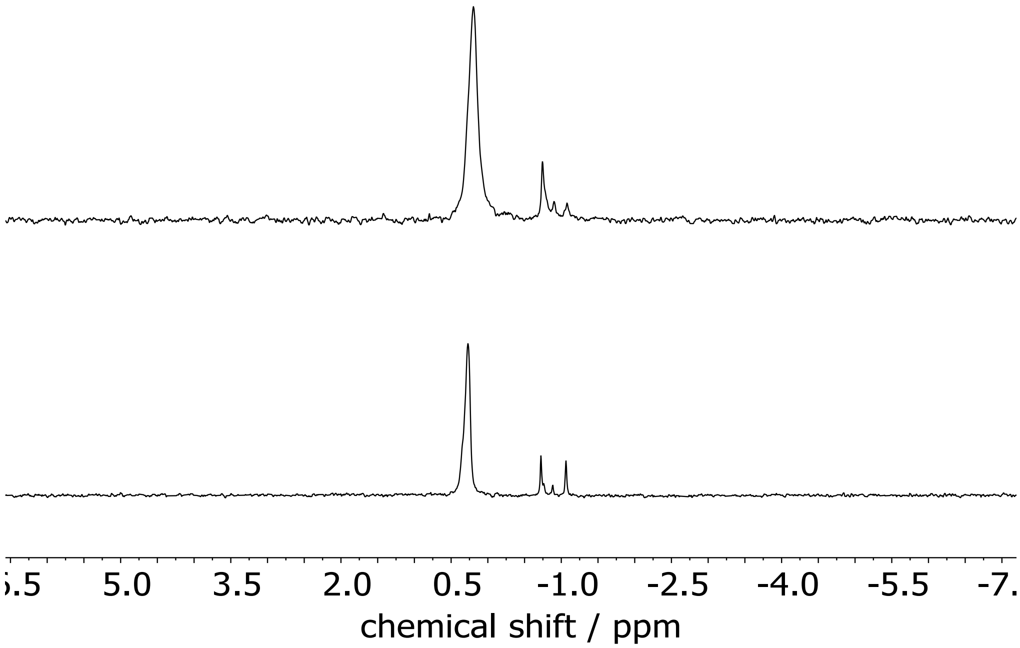


Figure S15: ^{31}P NMR spectra in $CDCl_3$ at 121 MHz at 298 K of **poly-1H-*co*-poly-1Bn** before (top) and after (bottom) being immersed in PBS buffer at pH 7.4 for four weeks.

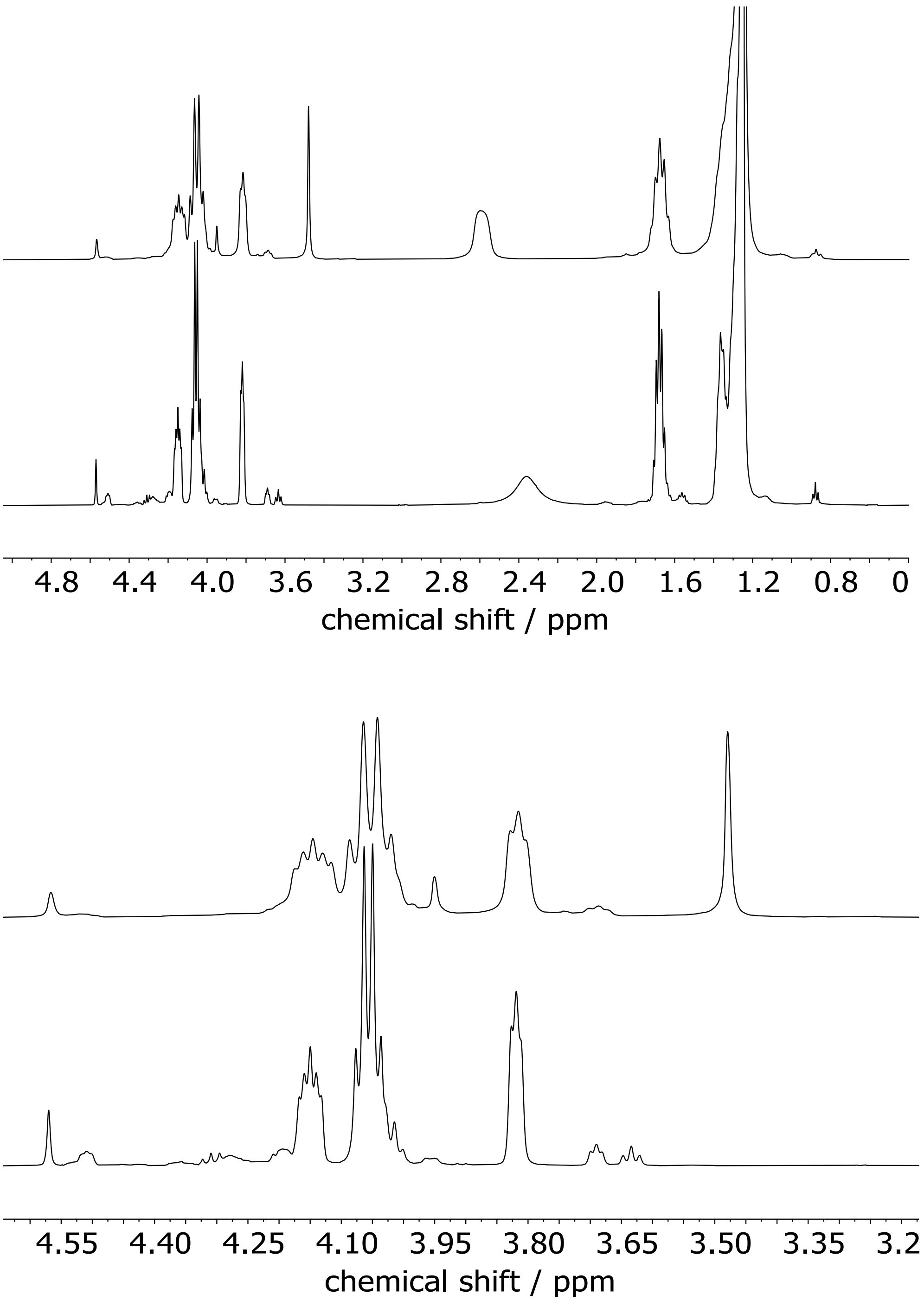


Figure S16: ^{1}H NMR spectra in $CDCl_3$ at 300 MHz at 298 K of **poly-1H-*co*-poly-1Bn** before (top line) and after (bottom line) being immersed in artificial seawater for four weeks. Bottom spectra: zoom on area between 4.6 and 3.2 ppm.

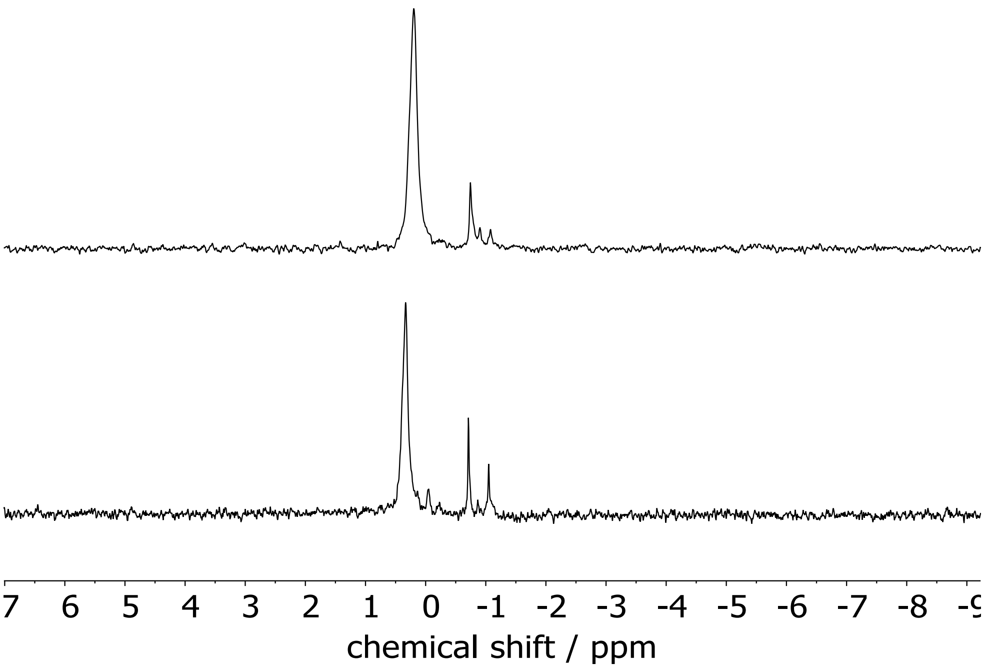


Figure S17: ^{31}P NMR spectra in $CDCl_3$ at 121 MHz at 298 K of **poly-1H-*co*-poly-1Bn** before (top) and after (bottom) being immersed in artificial seawater for four weeks.

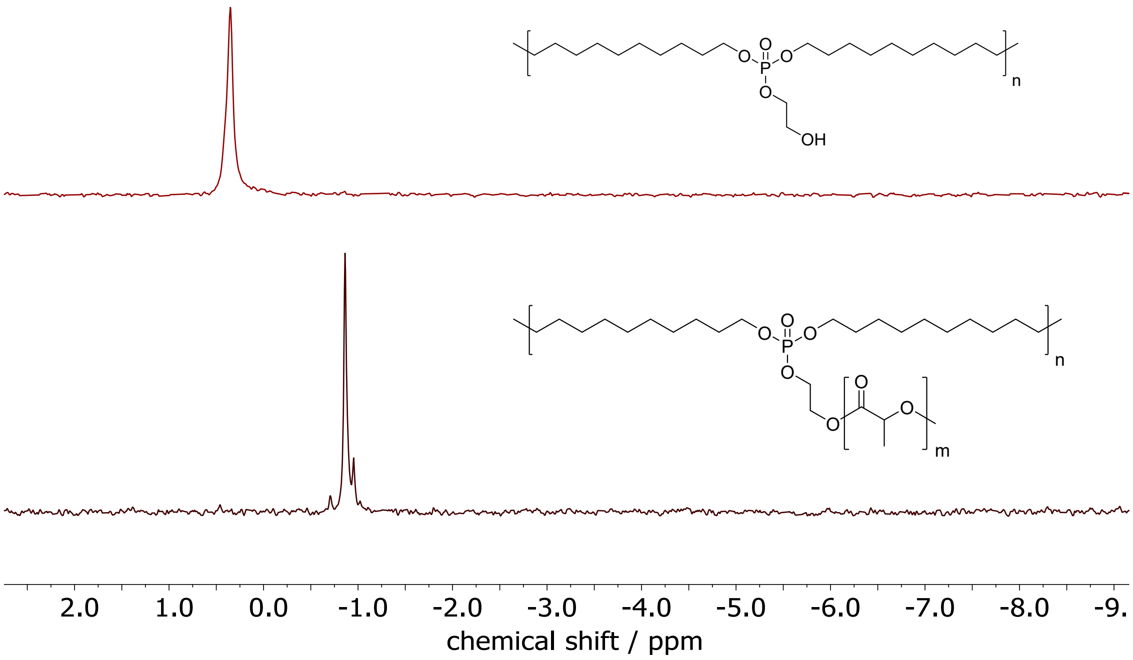


Figure S18: Overlay of ^{31}P NMR spectra of **poly-1H** (top) and **poly-1H-*graft*-PLA** in $CDCl_3$ at 121 MHz at 298 K.

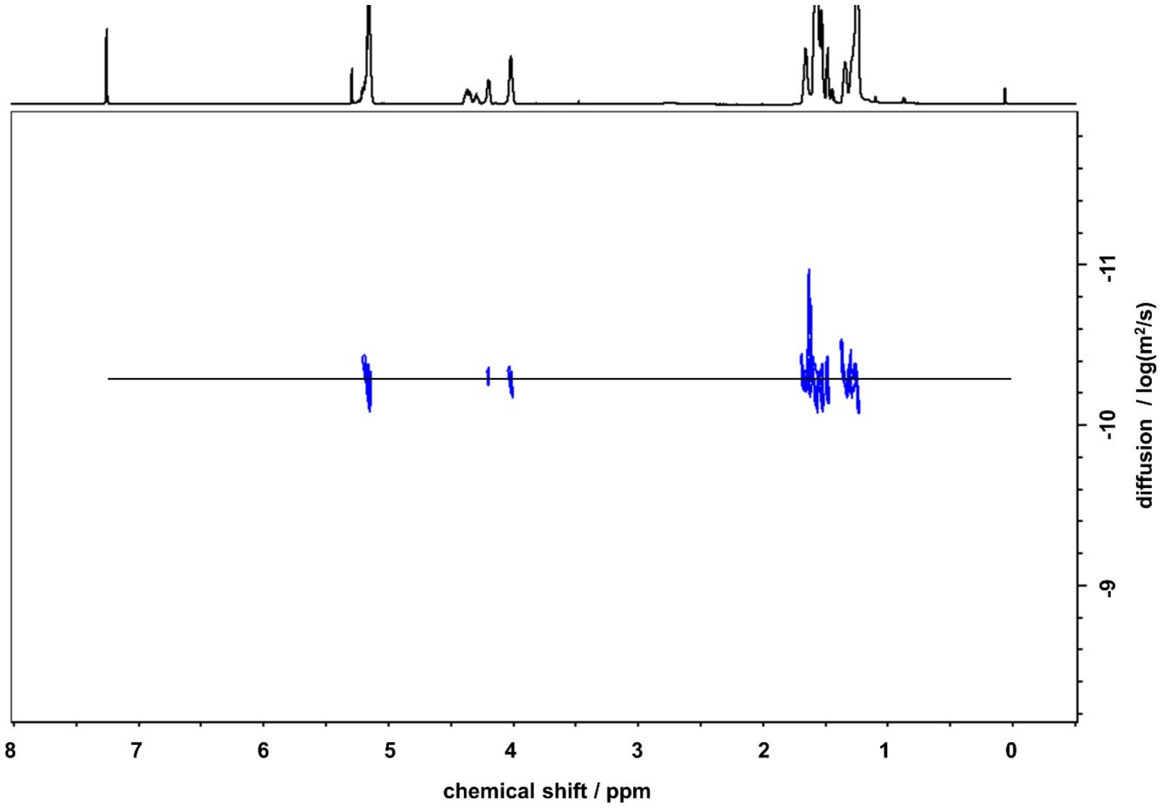


Figure S19: 2D-1H-DOSY NMR spectrum of **poly-1H-*graft*-PLA** in $CDCl_3$.

Size exclusion chromatography (SEC)

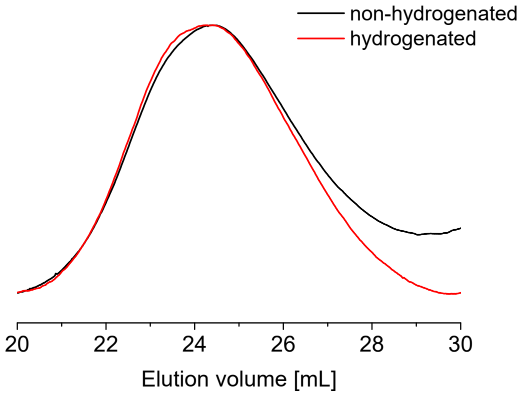


Figure S20: SEC elugrams of **poly-1** (black) and **poly-1H** (red) (entry 1).

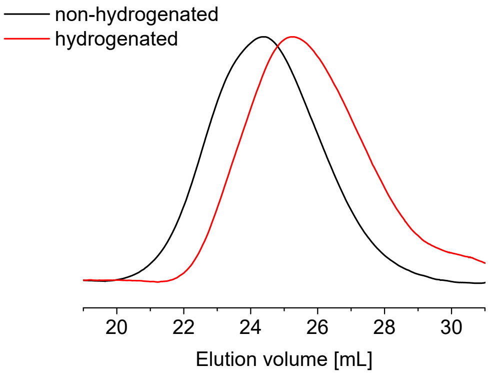


Figure S21: SEC elugrams of **poly-1** (black) and **poly-1H** (red) (entry 2).

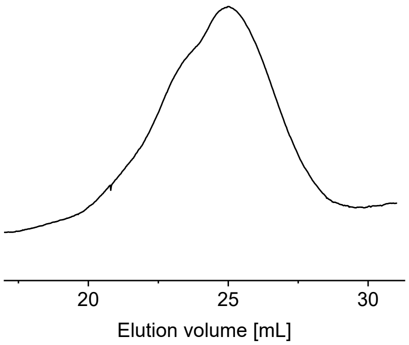


Figure S22: SEC elugram of **poly-1H-*co*-poly-1Bn** in THF.

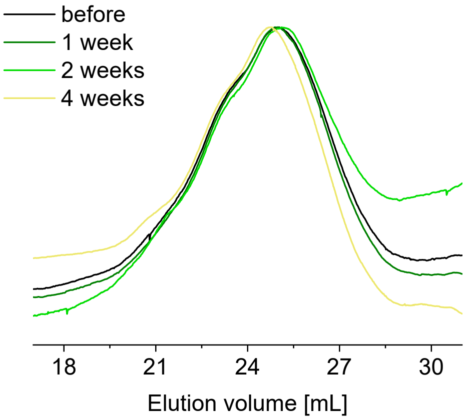


Figure S23: SEC elugrams in THF of **poly-1H-*co*-poly-1Bn** before (black) and after being immersed in PBS buffer for one week (dark green), two weeks (light green) and four weeks (yellow).

Thermal gravimetric analysis (TGA), Differential Scanning Calorimetry (DSC)

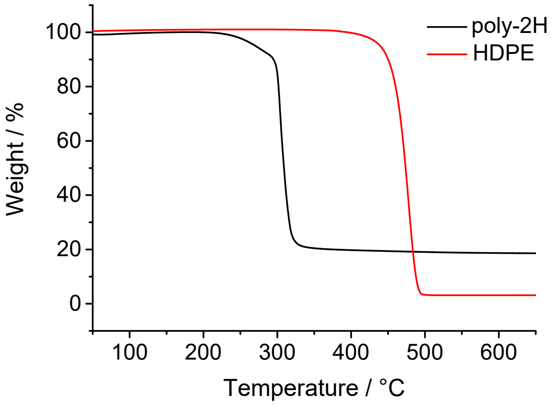


Figure S24: TGA thermogram of **poly-1H** (black) and HDPE (red).

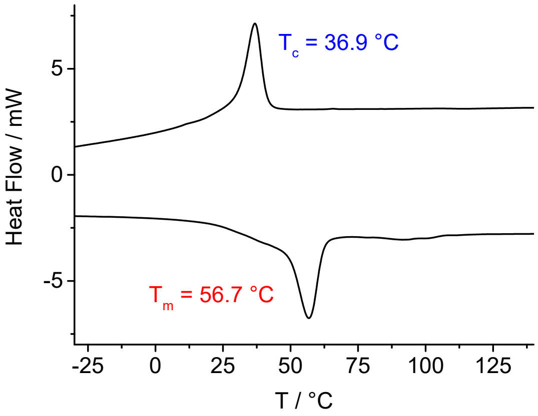


Figure S25: DSC thermogram of **poly-1H-*graft*-PLA**.

Mass spectrometry

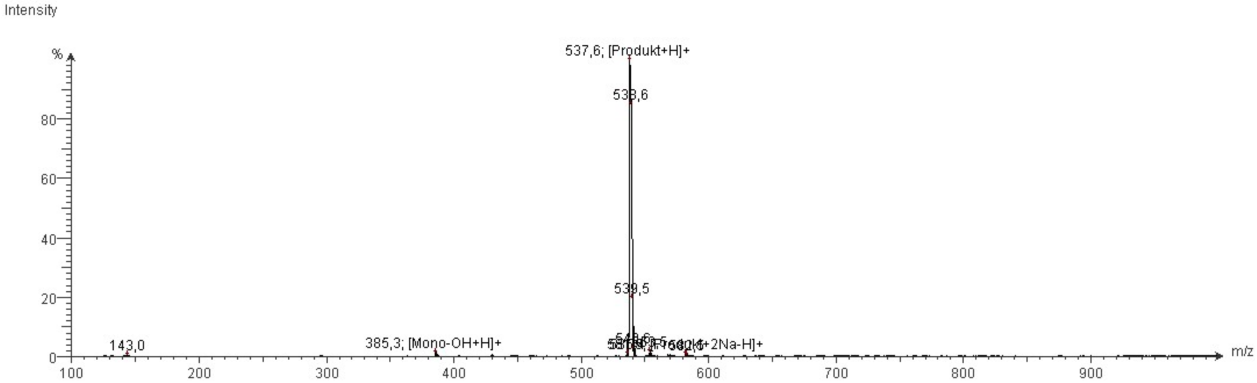


Figure S26: Mass spectrogram of **1** (atmospheric pressure ionization).

Film Degradation Test

Hydrolytic Degradation of poly-1H at pH 11 and pH 13

Table S1: Surface tension of different aqueous solutions before and after film degradation test of poly-1H. All values in mN m^{-1}.

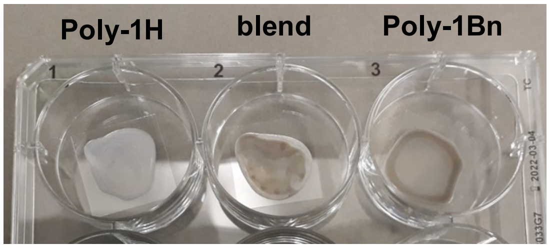
Time	NaOH/$NaHCO_3$ buffer		2 M NaOH	
Initial	59.7		75.6	
1 week	57.6	56.6	40.3	39.0
2 weeks	43.5	45.2	40.6	39.0
3 weeks	61.7	59.3	43.9	44.3

Table S2: pH values before and after film degradation test of poly-1H in different aqueous solutions.

Time	NaOH/$NaHCO_3$ buffer		2 M NaOH	
Initial	11.1		12.7	
1 week	10.6	10.5	12.7	12.7
2 weeks	10.7	10.7	12.8	12.8
3 weeks	10.5	10.6	12.9	12.7

Hydrolytic Degradation of poly-1H/poly-1Bn blend at pH 11

Before



After 2 months

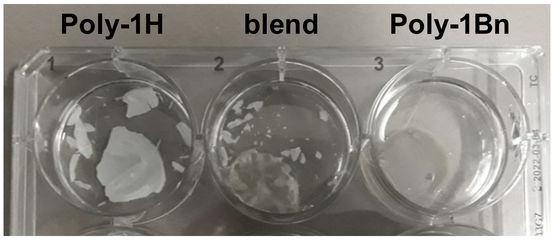


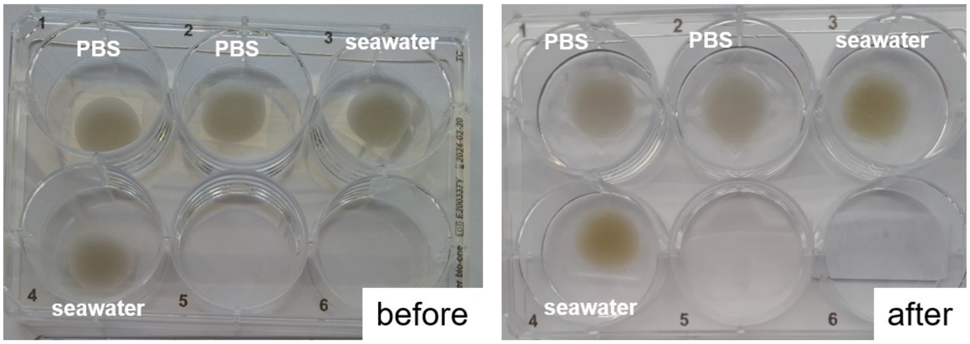
Figure S27: Films of **poly-1H**, **poly-1Bn** and a **poly-1H/poly-1Bn** polymer blend before and after 2 months immersing in aqueous $NaHCO_3$/NaOH buffer at pH 11.1 and 37 °C. Diameter of films is ca 2 cm.

Hydrolytic Degradation of poly-1H-co-poly-1Bn in PBS buffer solution and artificial seawater

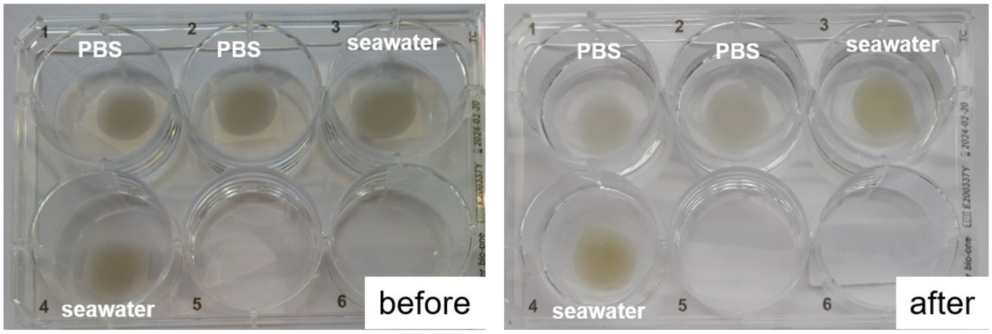
Table S3: pH values before and after film degradation test of poly-1H in different aqueous solutions.

Time	PBS buffer		artificial seawater	
Initial	7.4		8.1	
1 week	7.2	7.3	9.4	9.4
2 weeks	7.3	7.3	9.5	9.5
4 weeks	7.1	7.2	9.6	9.5

1 week



2 weeks



4 weeks

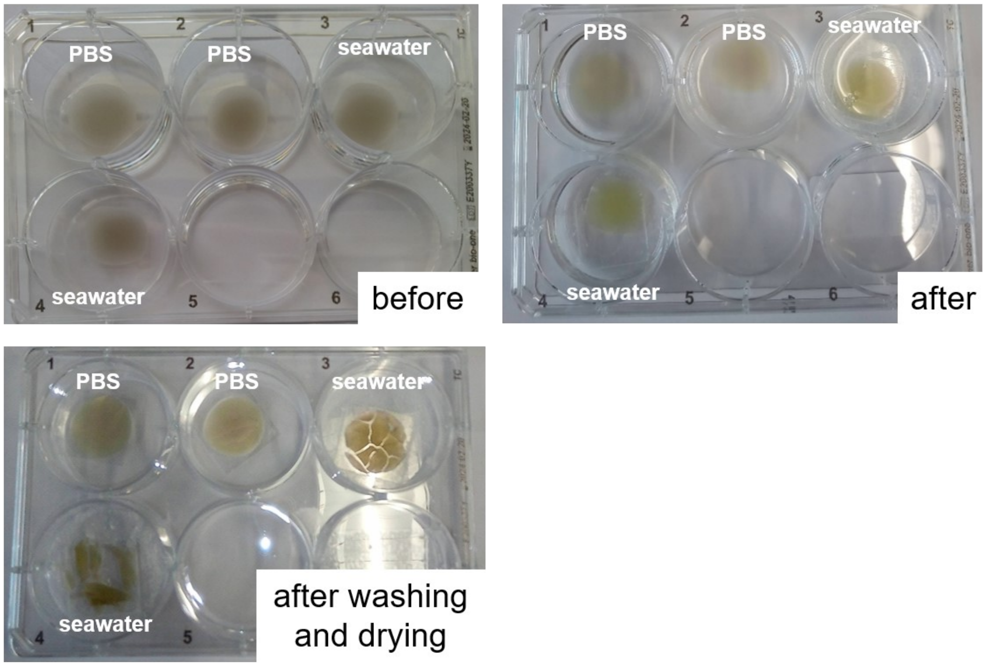


Figure S28: Films of **poly-1H-*co*-poly-1Bn** before and after being immersed in PBS buffer and artificial seawater for 1, 2 and 4 weeks. Diameter of films is ca 2 cm.