Supporting Information for

In-Chain Poly(phosphonate)s via Acyclic Diene Metathesis Polycondensation

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Tables

Table S1. Synthetic results for in-chain poly(phosphonate)s prepared by ADMET polymerization in solution using 1-chloronaphthalene as solvent or in bulk.

#	catalyst	Cat. / eq	$V_{solvent}$/mL	t / h	M_n /gmol^{-1}	M_w/M_n
Poly(1)-a	Grubbs 1st Gen.	0,06	-	4	-	-
Poly(1)-b	Grubbs 2nd Gen.	0,06	-	4	-	-
Poly(2)-a	Grubbs 1st Gen.	0,09	2	48	8700*	-
Poly(2)-b	Grubbs 1st Gen.	0,06	2	48	8000*	-
Poly(3)-a	Grubbs 1st Gen.	0,09	2	48	27900	1.67
Poly(3)-b	Grubbs 1st Gen.	0,06	2	48	20600	1.84
Poly(3)-c	Grubbs 1st Gen.	0,03	-	24	5030	1.41
Poly(4)-a	Grubbs 1st Gen.	0,09	2	48	27600	1.68
Poly(4)-b	Grubbs 1st Gen.	0,06	2	48	6700	2.49
Poly(4)-c	Grubbs 1st Gen.	0,03	-	24	3640	8.4

* determined by vapor pressure osmometry

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

Monomer Spectra:

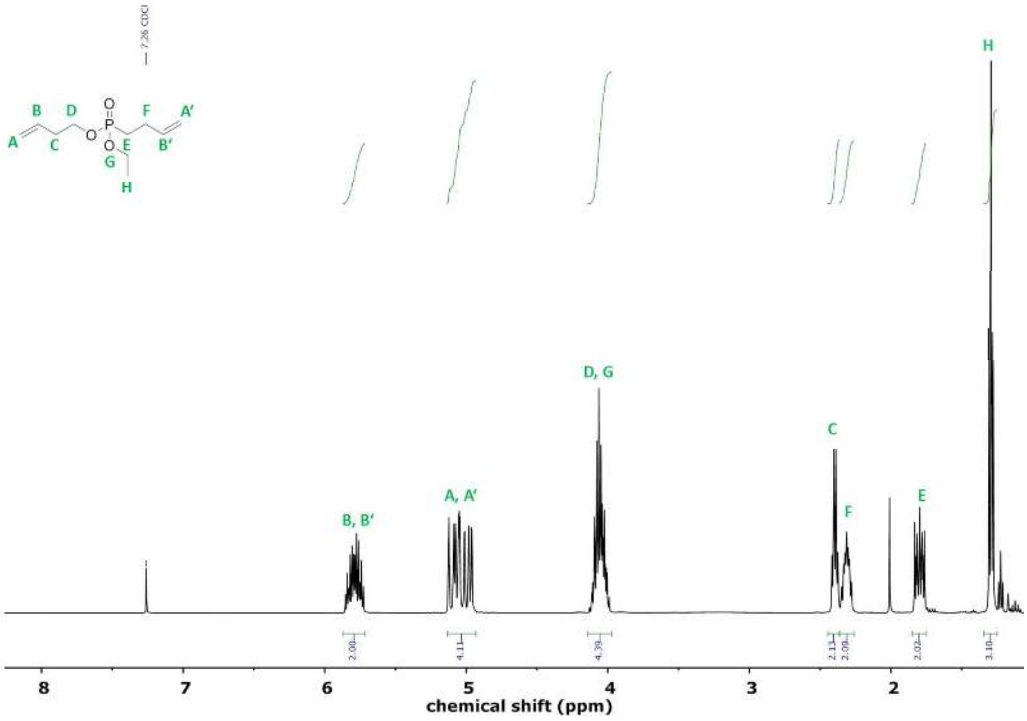


Figure S1. ^{1}H NMR of compound **1** at 500 MHz in $CDCl_3$ at 298 K.

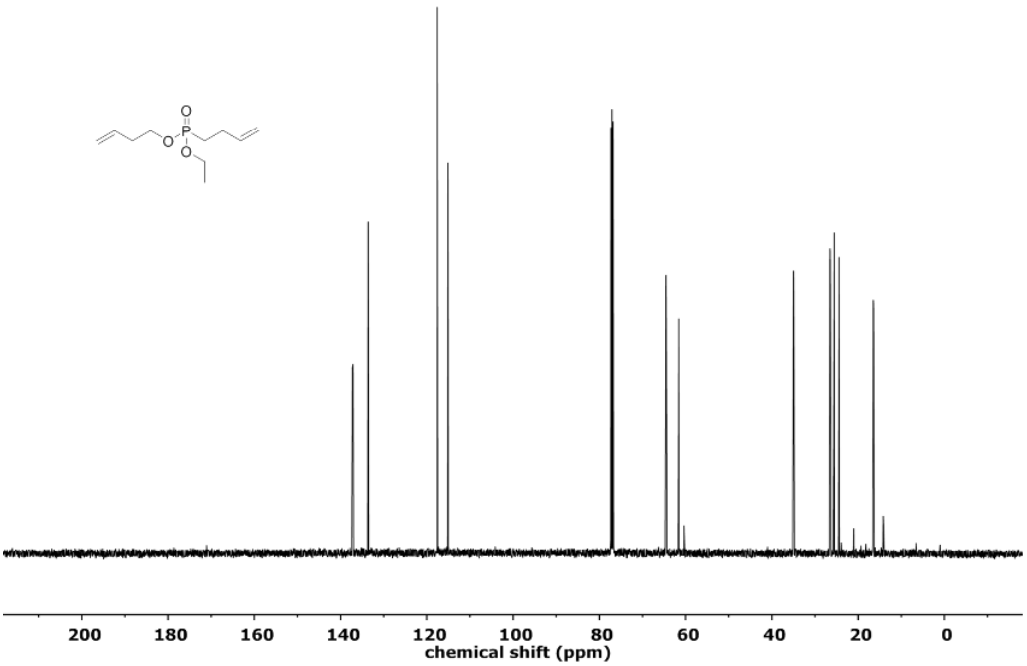


Figure S2. ^{13}C NMR of compound **1** at 126 MHz in $CDCl_3$ at 298 K.

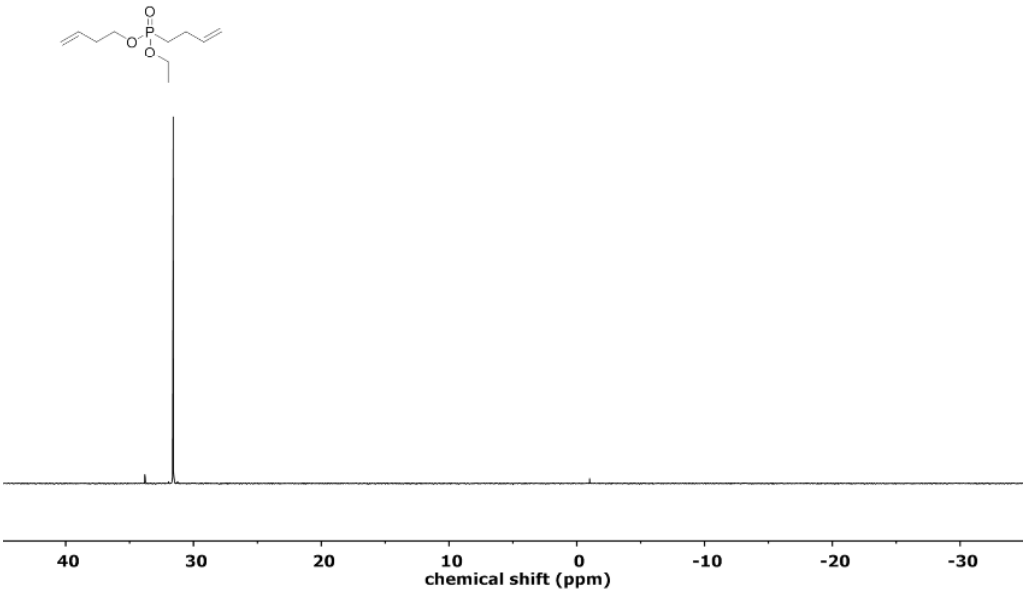


Figure S3. ^{31}P NMR of compound **1** at 202 MHz in $CDCl_3$ at 298 K.

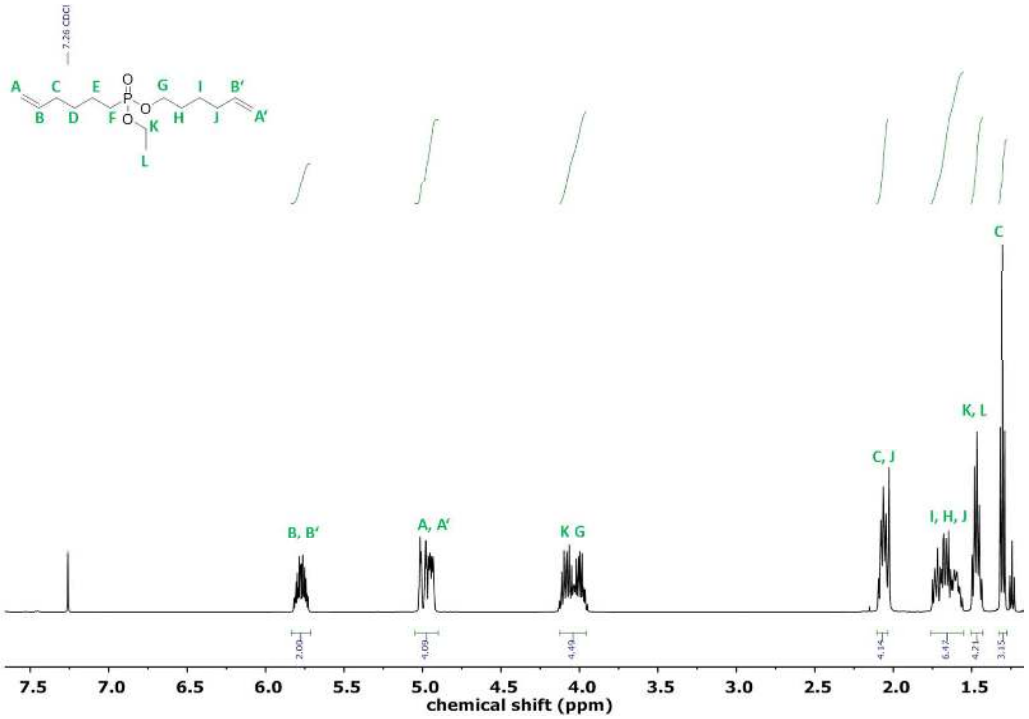


Figure S4.[1]H NMR of compound **2** at 500 MHz in $CDCl_3$ at 298 K.

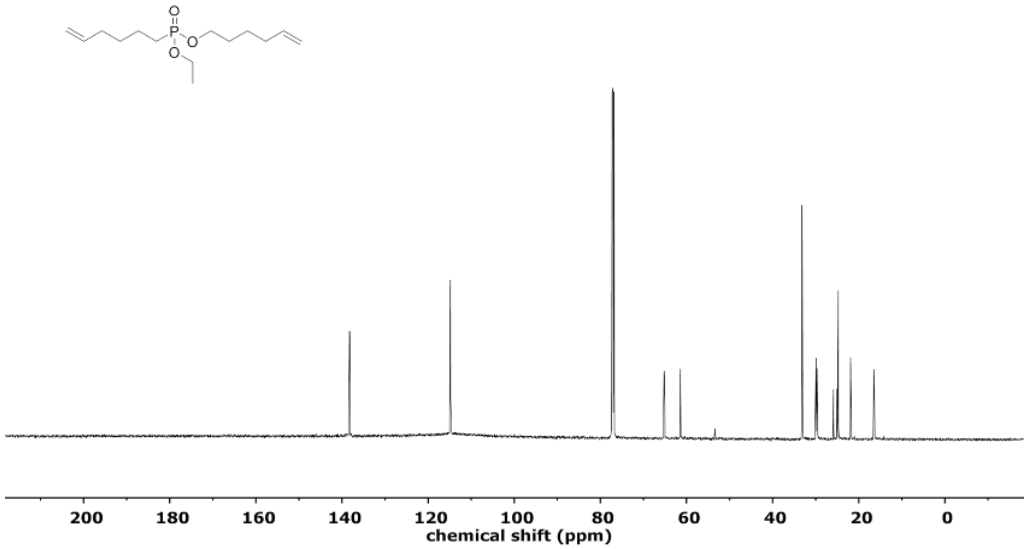


Figure S5.[13]CNMR of compound **2** at 176 MHz in $CDCl_3$ at 298 K.

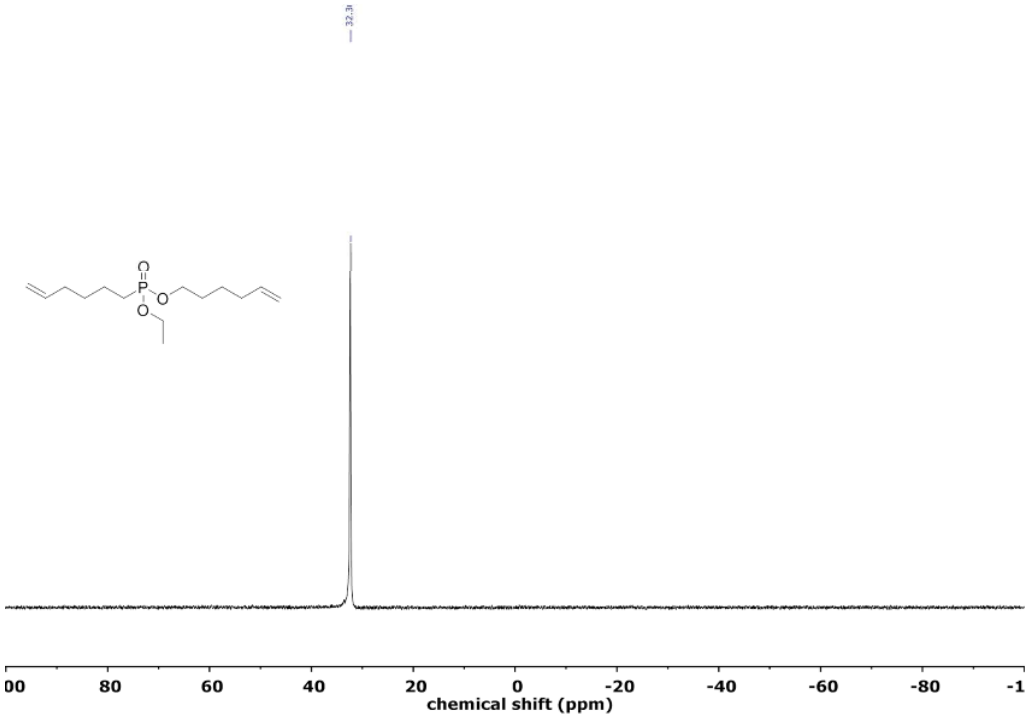


Figure S6. ^{31}P NMR of compound **2** at 283 MHz in $CDCl_3$ at 298 K.

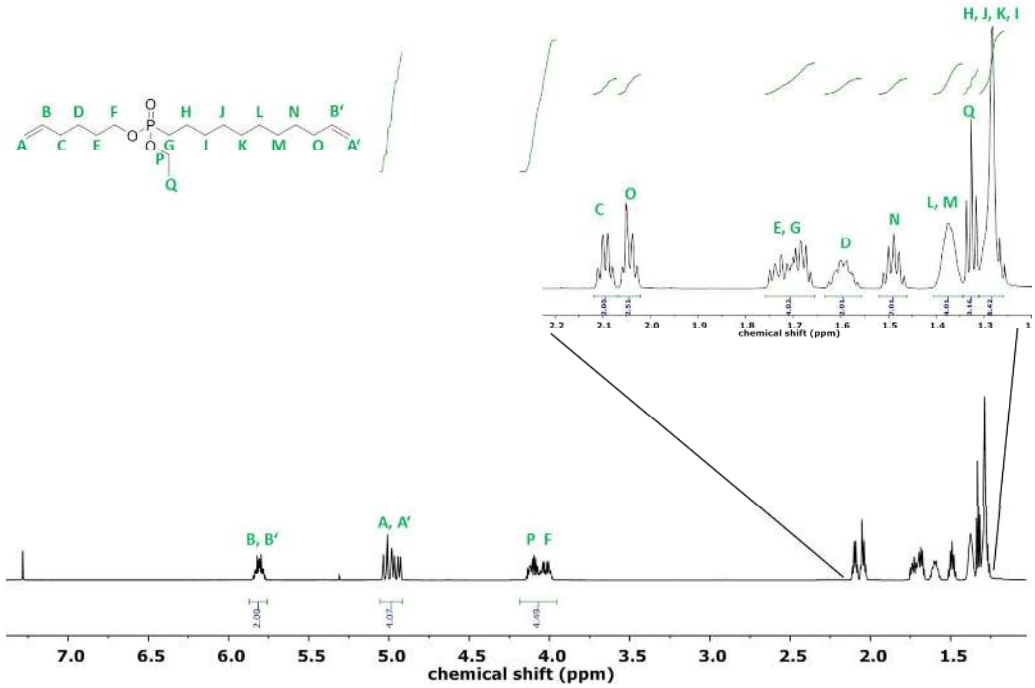


Figure S7. ^{1}H NMR of compound **4** at 700 MHz in $CDCl_3$ at 298 K.

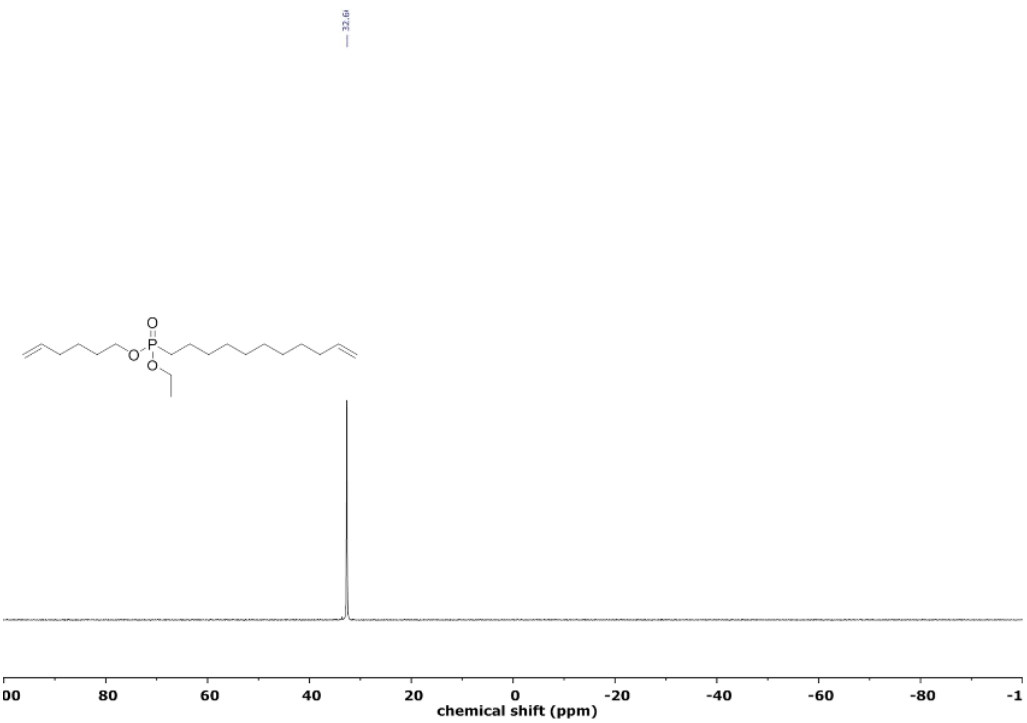


Figure S8. ^{31}P NMR of compound **4** at 283 MHz in $CDCl_3$ at 298 K.

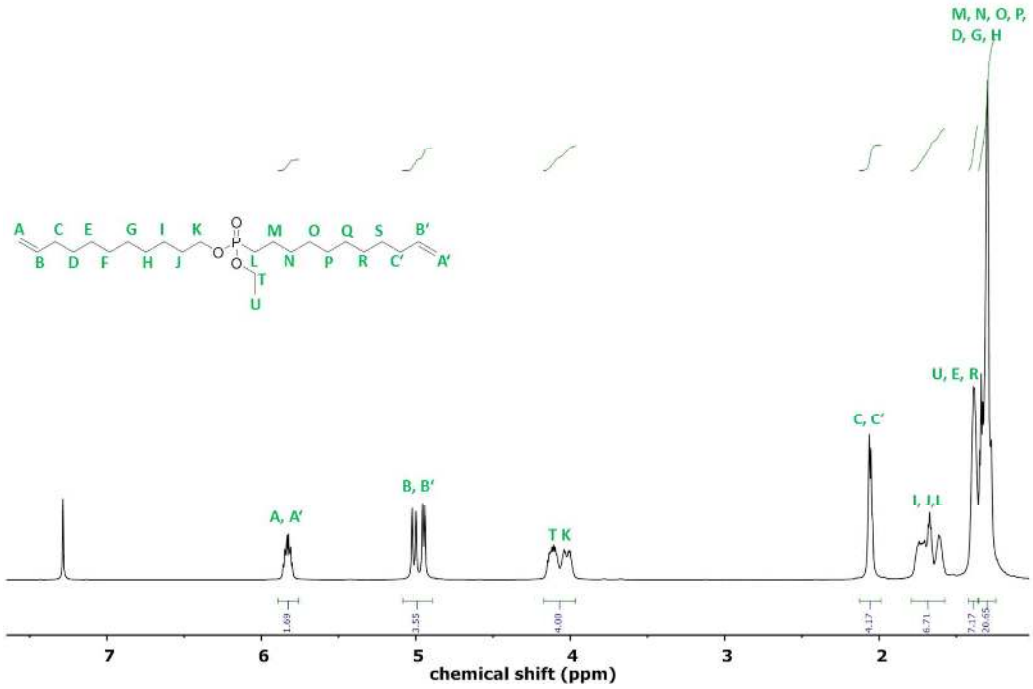


Figure S9. ^{1}H NMR of compound **3** at 700 MHz in $CDCl_3$.

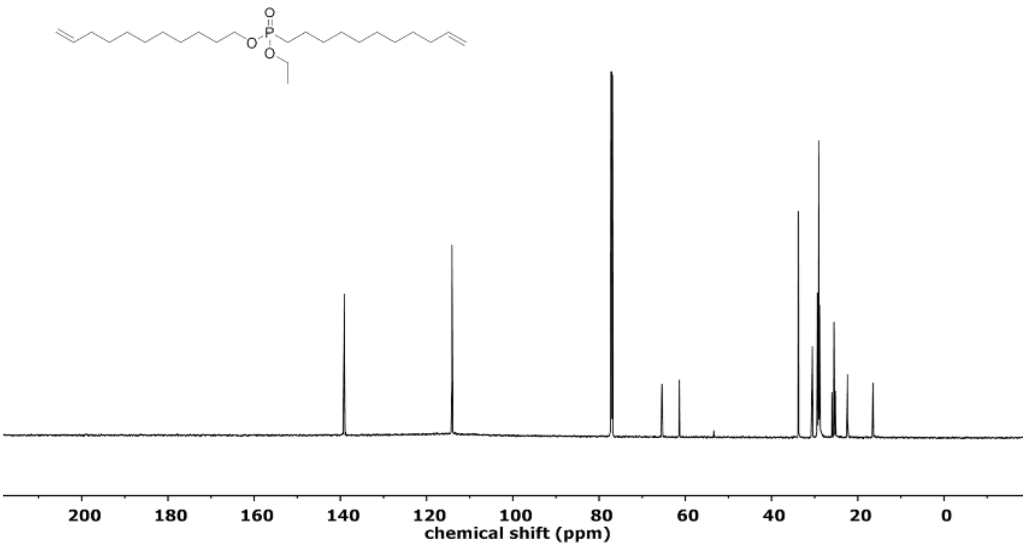


Figure S10. ^{13}C NMR of compound **3** at 176 MHz in $CDCl_3$ at 298 K.

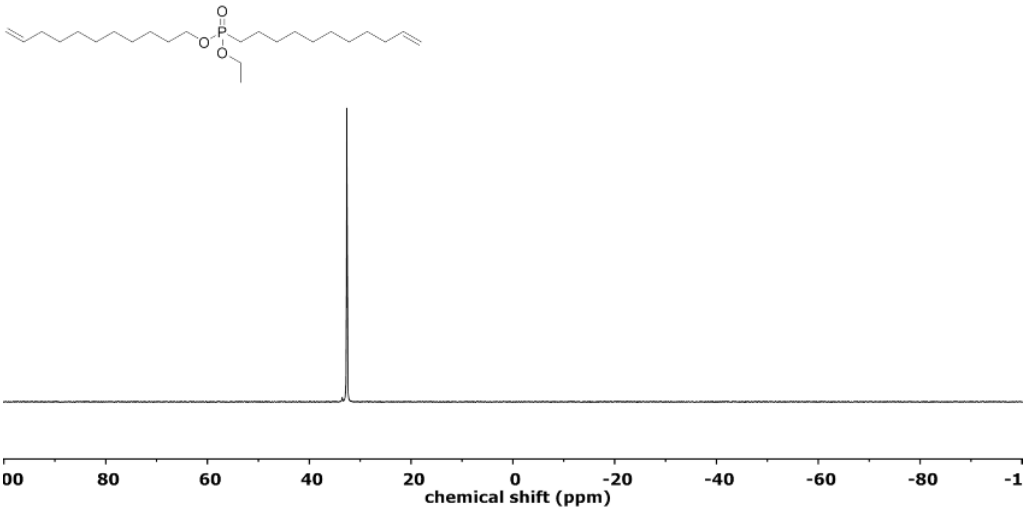


Figure S11. ^{31}P NMR of compound **3** at 283 MHz in $CDCl_3$ at 298 K.

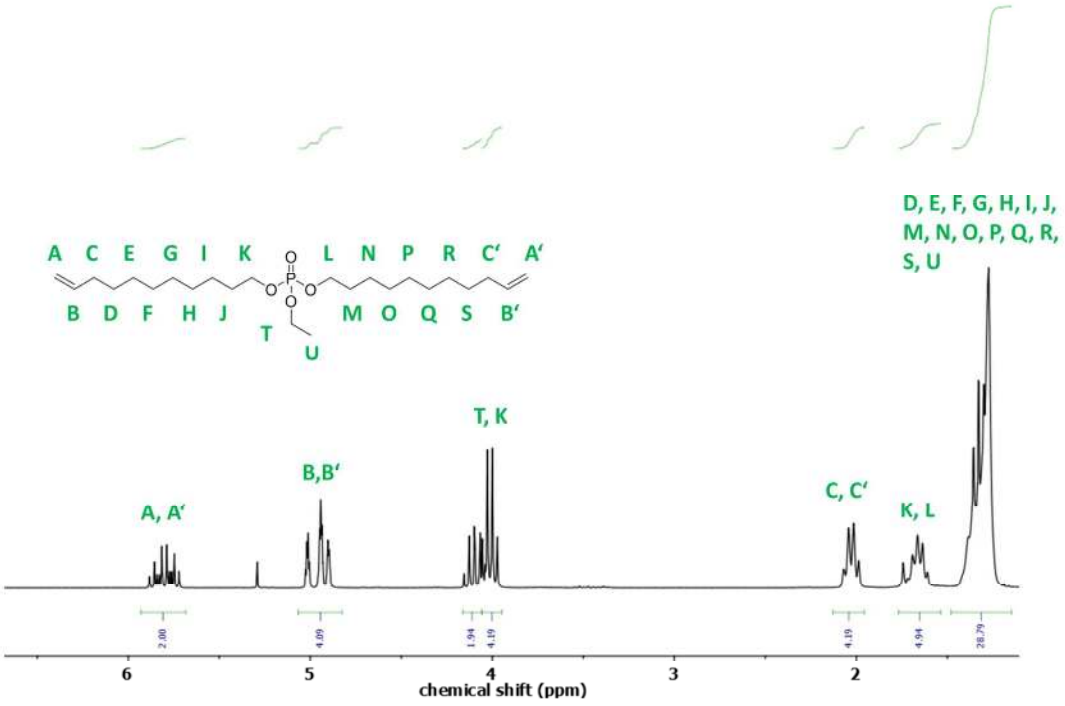
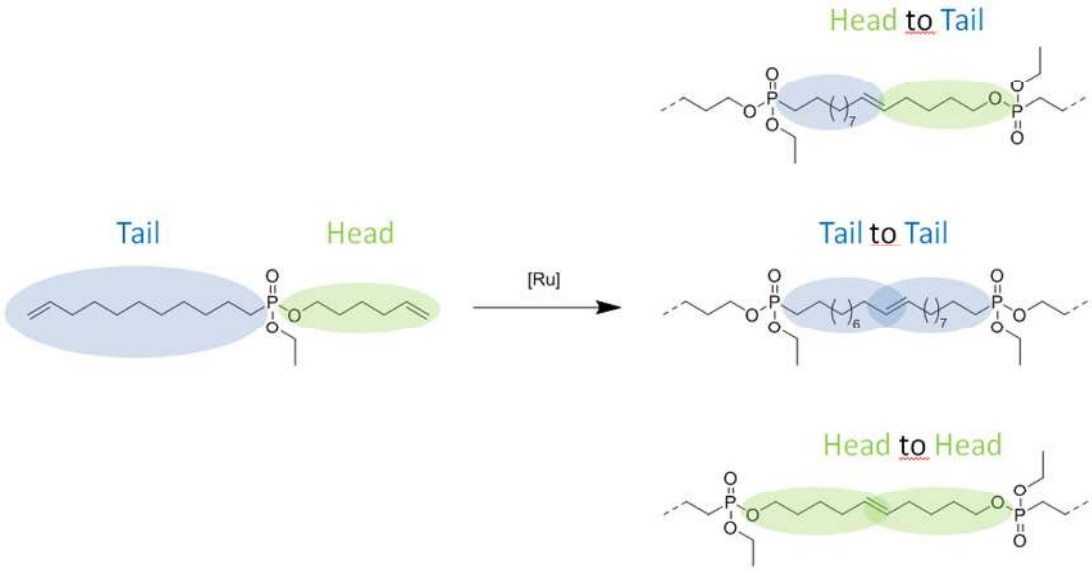


Figure S12. ^{1}H NMR of compound **5** at 300 MHz in $CDCl_3$.

Polymer NMR Spectra

The monomer architecture allows three different types of conjunction, i.e. head to tail, tail to tail and head to head (see **Scheme S1**), all contained in the obtained polymers. In the following, the polymer structures are presented in the simplified head to tail structure.



Scheme S1. Possible conjunctions within the polymer structure.

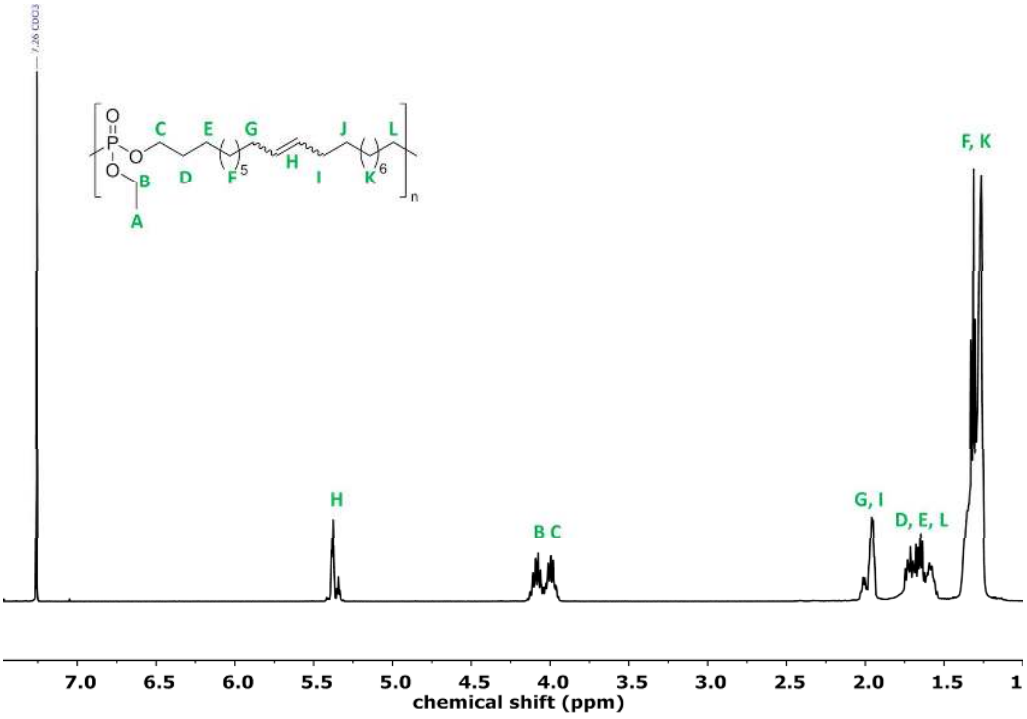


Figure S13. ^{1}H NMR of **poly(3)** at 500 MHz in $CDCl_3$.

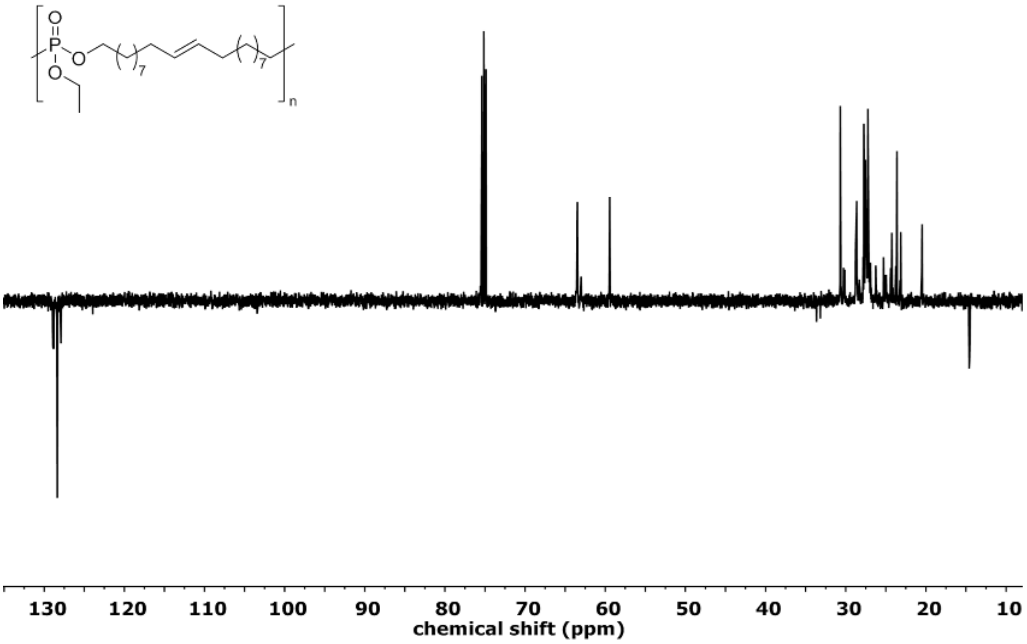


Figure S14. ^{13}C NMR of **poly(3)** at 126 MHz in $CDCl_3$ at 298 K.

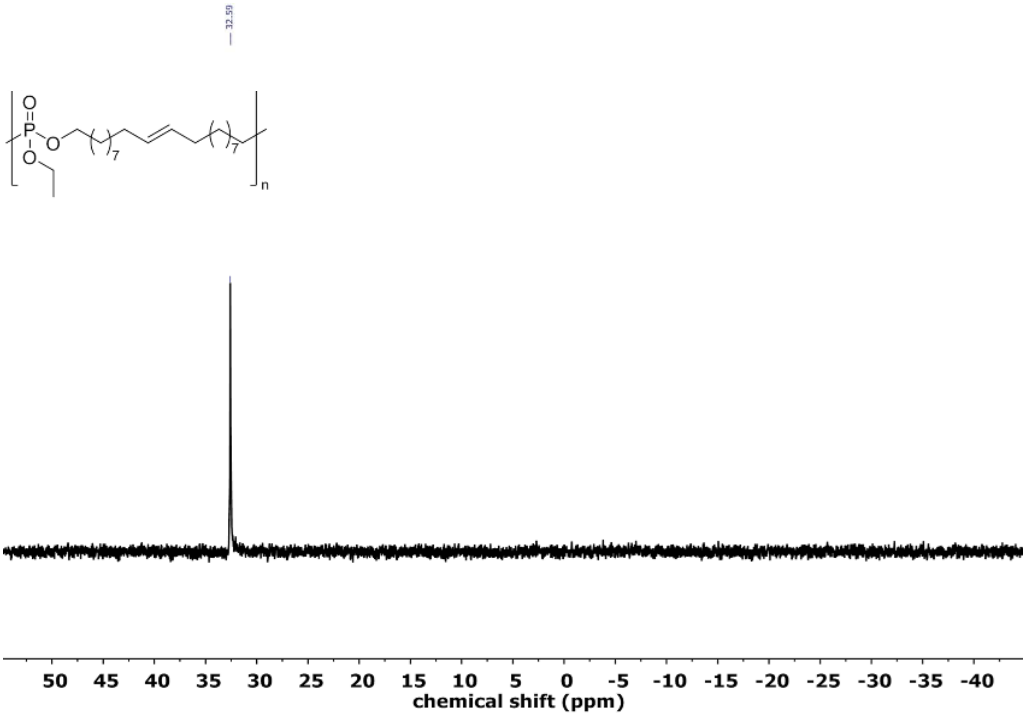


Figure S15. ^{31}P NMR of **poly(3)** at 202 MHz in $CDCl_3$.

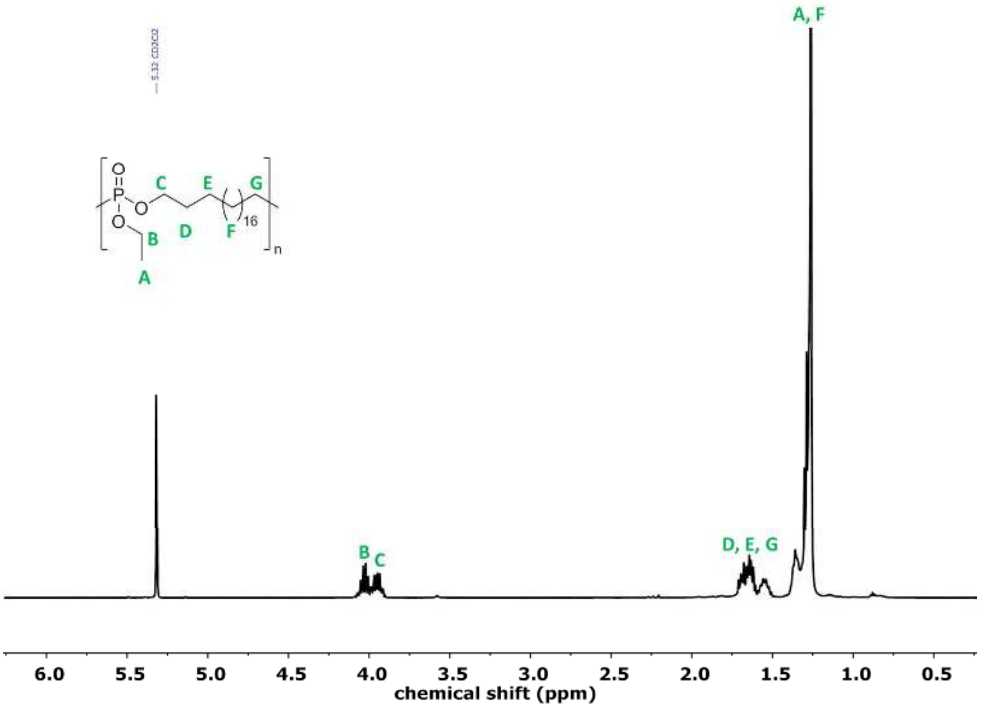


Figure S16. ^{1}H NMR of **poly(3)-H** at 500 MHz in CD_2Cl_2

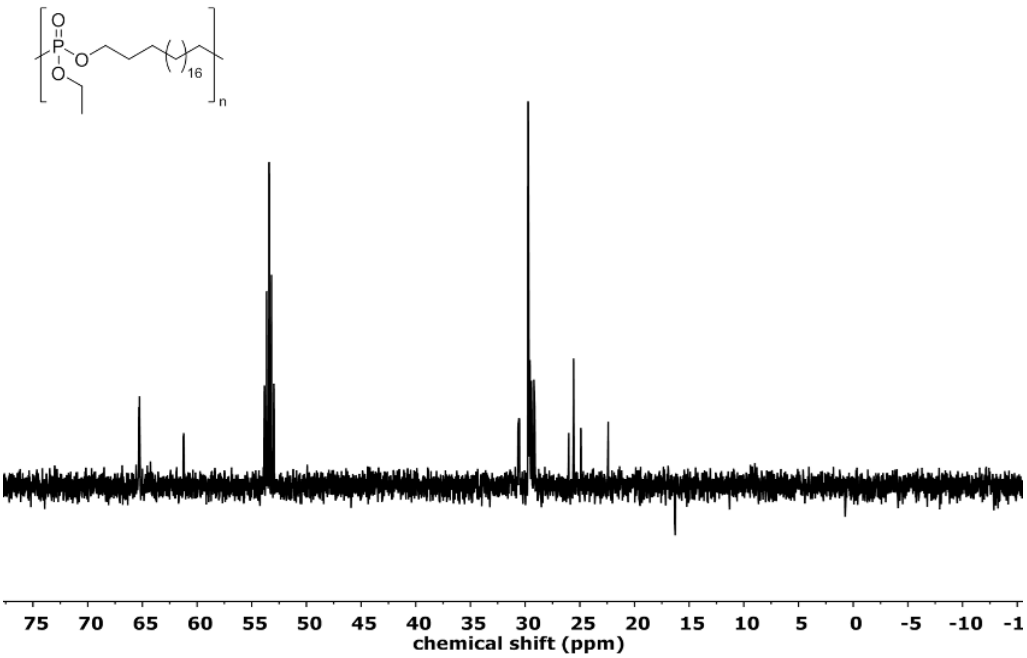


Figure S17. ^{13}C NMR of **poly(3)-H** at 126 MHz in CD_2Cl_2 at 298 K.

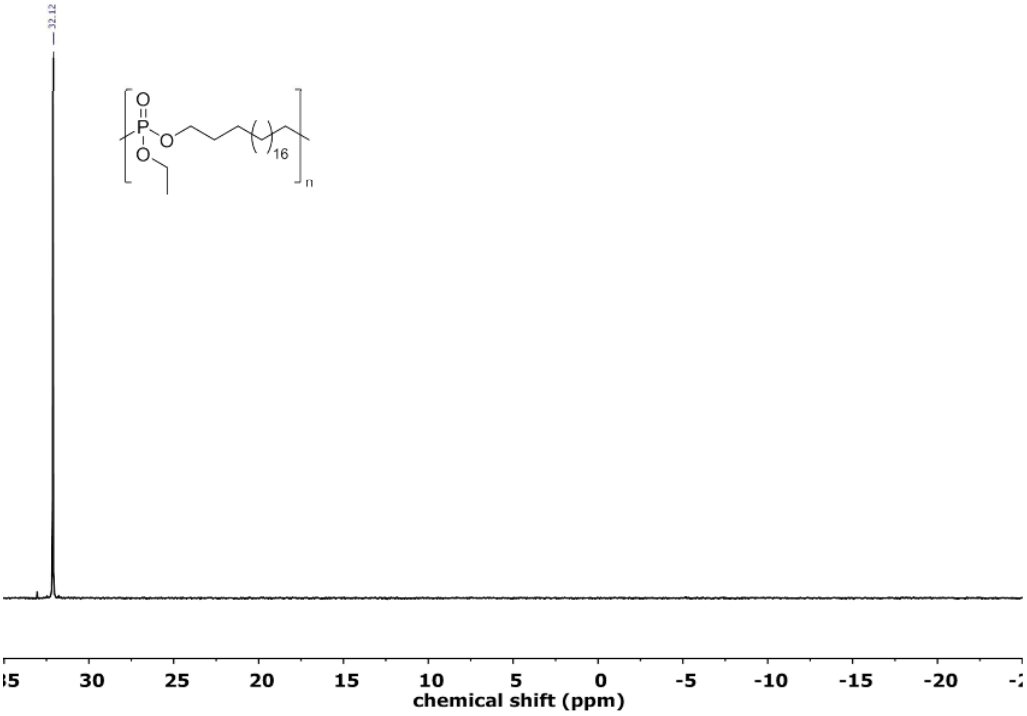
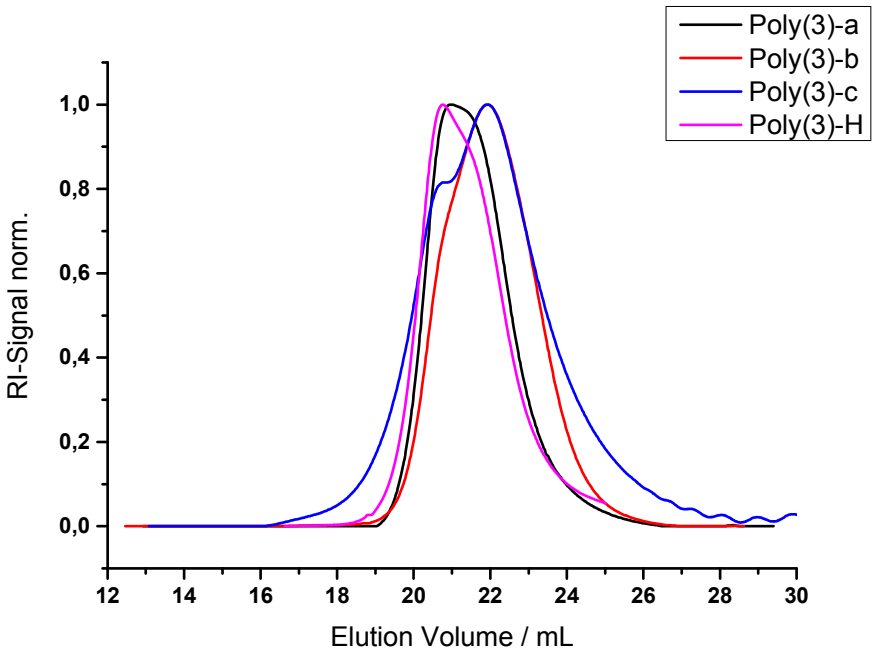


Figure S18. ^{31}P NMR of **poly(3)-H** at 202 MHz in CD_2Cl_2.

Size exclusion chromatography



Fiure S19. SEC elugrams of poly(**3**)s prepared ADMET polymerization.

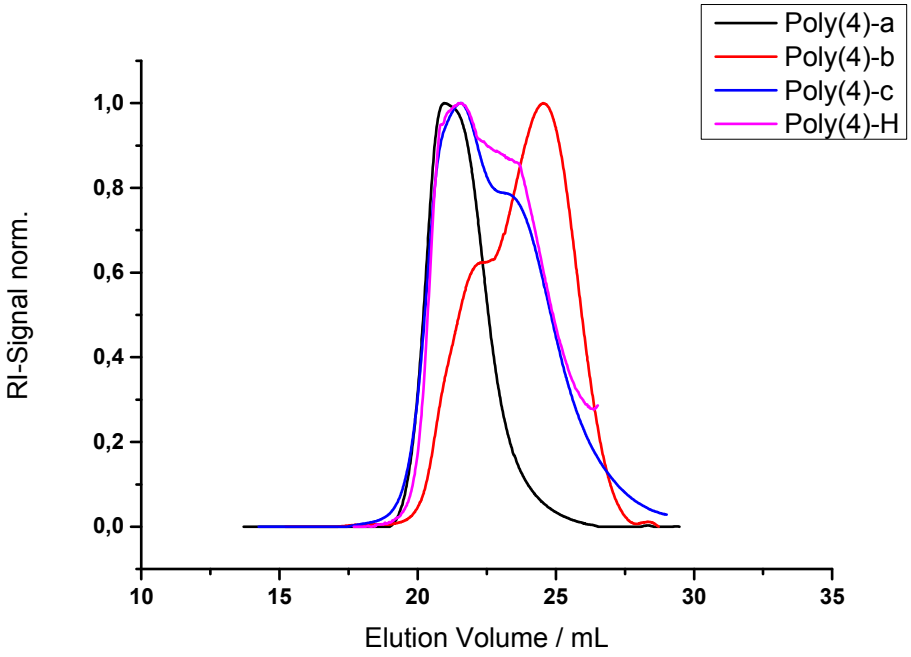


Figure S20. SEC elugrams of poly(**4**)s prepared ADMET polymerization.

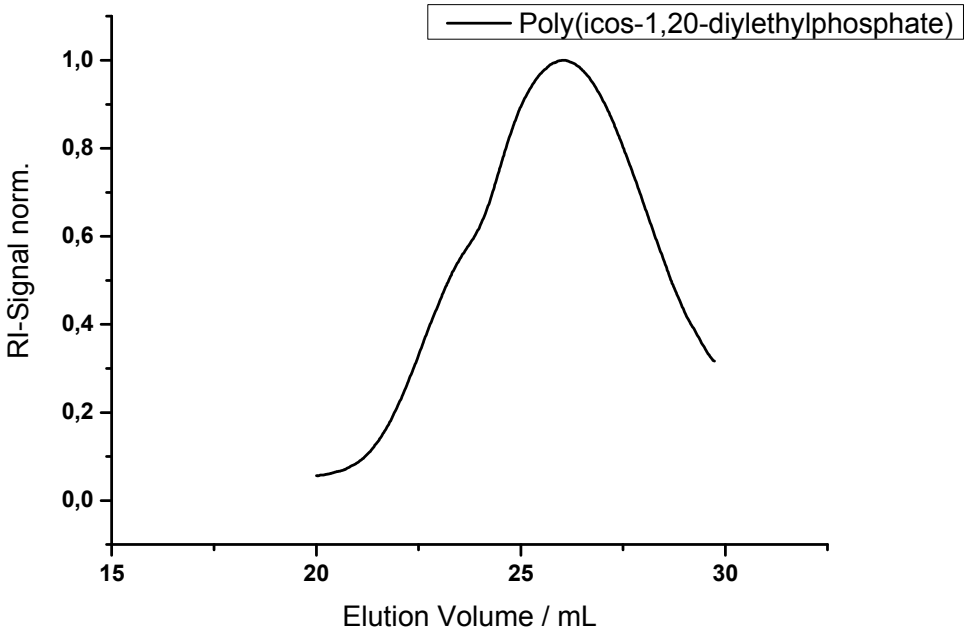


Figure S21. SEC elugrams of poly(**5**) prepared ADMET polymerization.

DSC, TGA

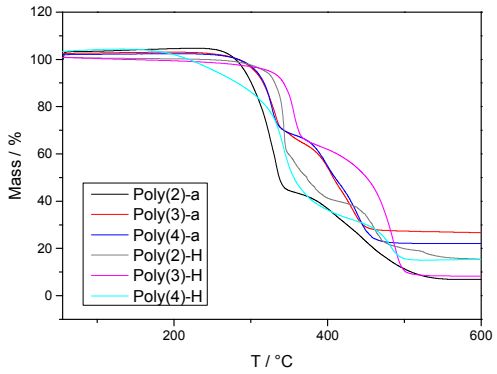


Figure S22. TGA thermogram of poly(4)-a and the corresponding hydrogenated polymer poly(4)-H.

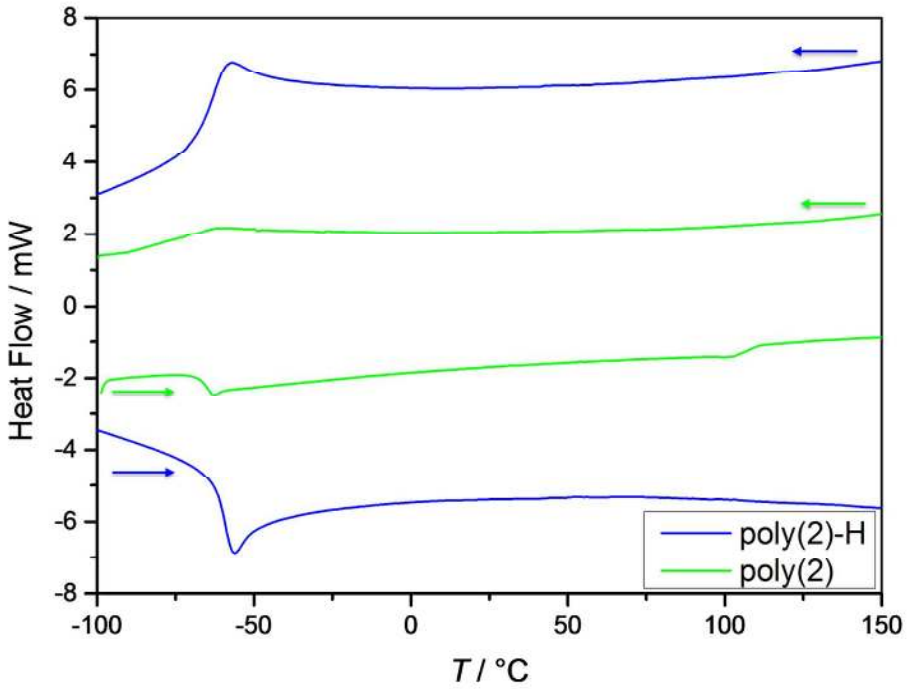


Figure S23. DSC thermogram of Poly(2)-a and the corresponding hydrogenated polymer Poly(2)-H.

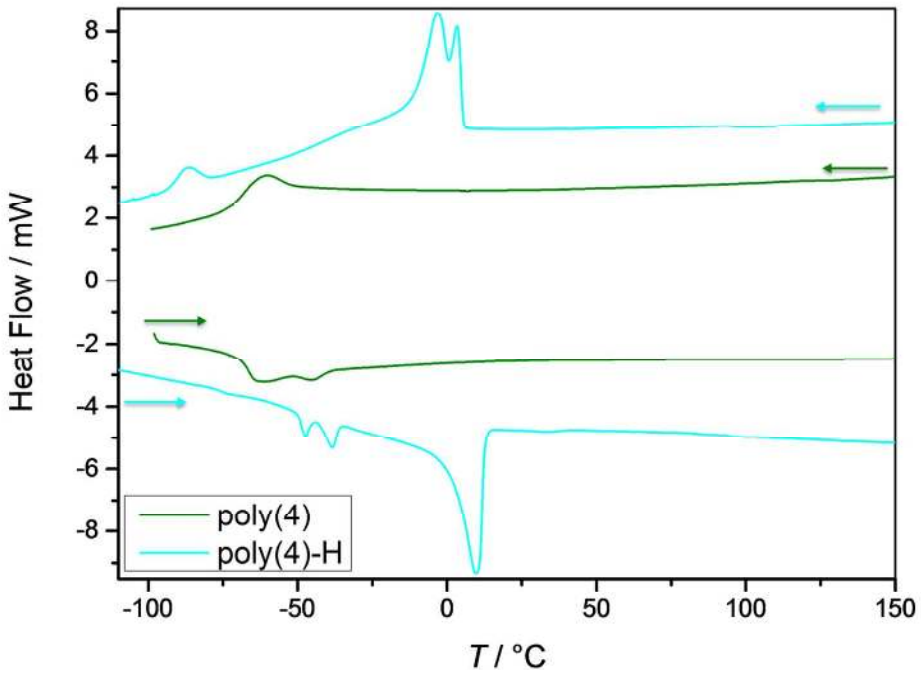


Figure S24. DSC thermogram of Poly(4)-a and the corresponding hydrogenated polymer Poly(4)-H.

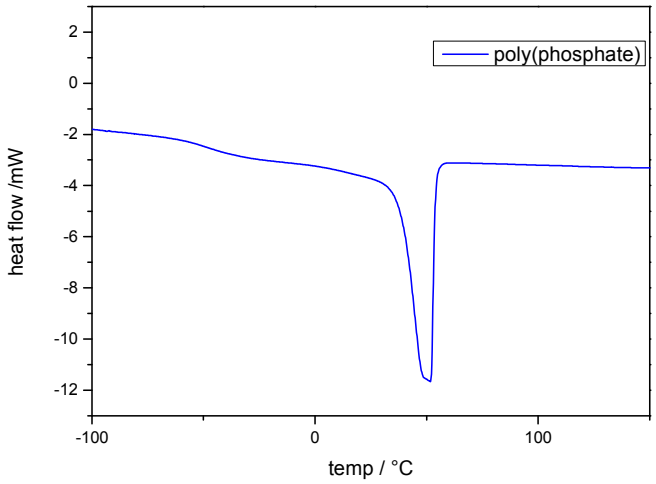


Figure S25. DSC thermogram (heating curve) of poly(5)-H .

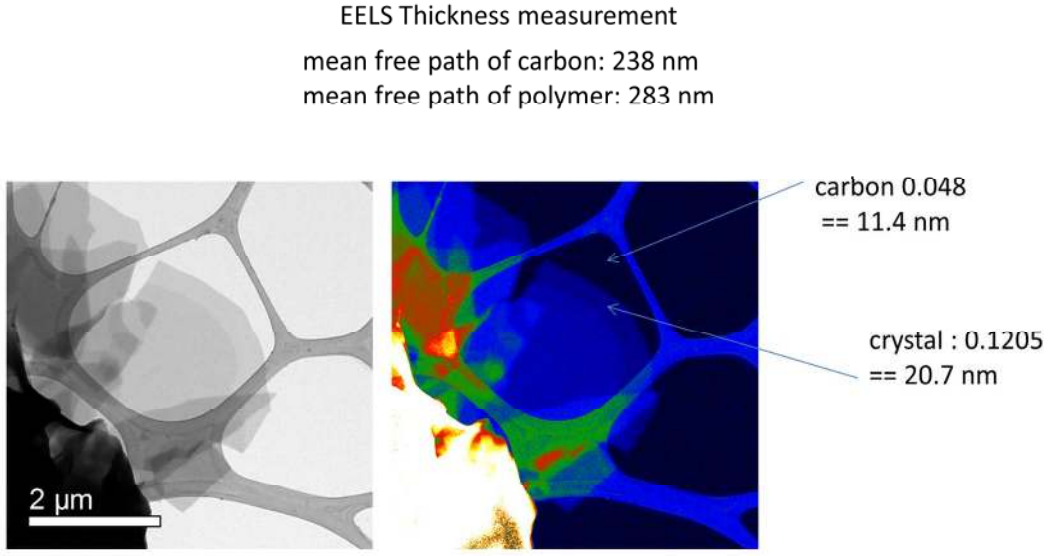


Figure S26. EELS thickness measurements for solution grown crystals of poly(3)-H.

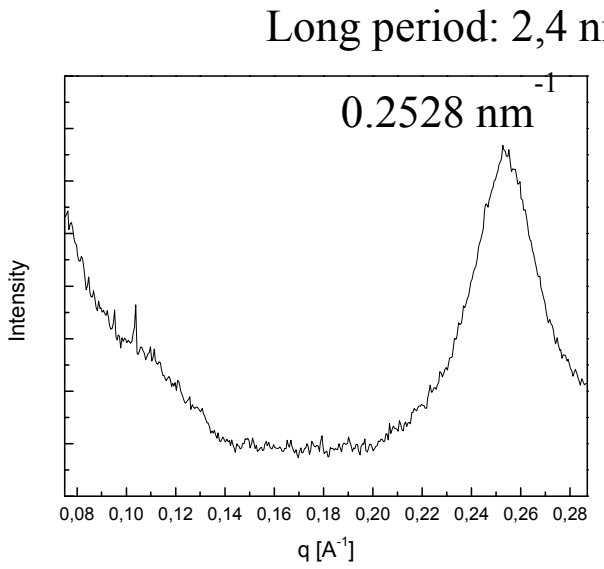


Figure S27. SAXS measurements of poly(3)-H.

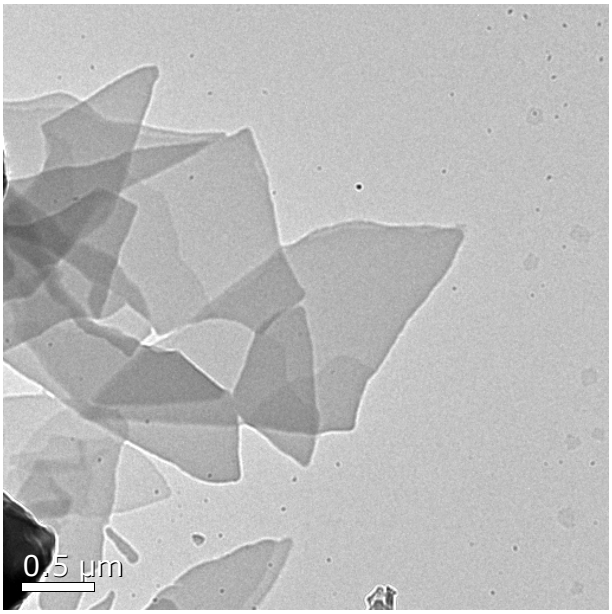


Figure S28. TEM BF micrograph of solution grown crystals of poly(3)-H from *n*-octane solution.

Additional References

1. Tannert, R., et al., *Synthesis and Structure−Activity Correlation of Natural-Product Inspired Cyclodepsipeptides Stabilizing F-Actin.* Journal of the American Chemical Society, 2010. **132**(9): p. 3063-3077.

2. Cho, J.-Y., et al., *Synthesis and Characterization of Polymerizable Phosphorescent Platinum(II) Complexes for Solution-Processible Organic Light-Emitting Diodes.* Organometallics, 2007. **26**(19): p. 4816-4829.
3. Yang, J., et al., *Activity-Based Probes Linked with Laser-Cleavable Mass Tags for Signal Amplification in Imaging Mass Spectrometry: Analysis of Serine Hydrolase Enzymes in Mammalian Tissue.* Analytical Chemistry, 2012. **84**(8): p. 3689-3695.