Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Info

Methods

Matrix-assisted laser desorption and ionization time-of-flight (MALDI-ToF) measurements were obtained with a Shimadzu Axima CFR MALDI-ToF mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. Dithranol (1,8,9-tris-hydroxy-anthracene) was used as a matrix. Samples were prepared by dissolving the polymer in $CHCl_3$ at a concentration of 10 g L^{-1}. A 10 mL aliquot of this solution was added to 10 mL of a 10 g L^{-1} matrix solution and 1 mL of a potassium trifluoroacetic acid (KTFA) solution (0.1 M in methanol as a cationization agent). A 1 mL aliquot of the resulting mixture was applied to a multistage target to evaporate $CHCl_3$ and create a thin matrix/analyte film. The samples were measured in positive-ion mode and in the linear mode of the spectrometer. Gel-permeation chromatography (GPC) measurements were carried out in THF, with samples at a concentration of 1 g L^{-1}. Sample injection was performed by a 717 plus auto sampler (Waters) at 30 °C (THF). Flow was 1 mL min^{-1}. In THF, three SDV columns (PSS) were employed with the dimensions 300 × 80 mm, 10 μm particle size and pore sizes of 106, 104 und 500 Å. Detection was accomplished with DRI Shodex RI-101 detector (ERC) and UV-Vis S-3702 detector (Soma). Calibration was carried out using polystyrene standards provided by Polymer Standards Service.

Table S1 ATMET polymerizations: reaction conditions and molecular weights

Monomer	Catalyst [a]	Polymer	Reaction time [hr]	Temperature [°C]	Ethylene removal	Mw [b]	Mn [b]	Mw/Mn [b]
1	2% G1	**P1**	1	80	Vacuum	3,000	1,600	2.5
1	2% G1	**P1**	12	80	Vacuum		gelation	
1	1.2% G1	**P1**	2	60	Vacuum		Oligomers	
1	1.2% G1	**No reaction**	2	r.t.	Vacuum			
1	0.5% G1	**P1**	0.5	80	Vacuum	2,500	1,000	2.5

[a] Grubbs catalyst 1st generation. [b] GPC in THF vs polystyrene standards

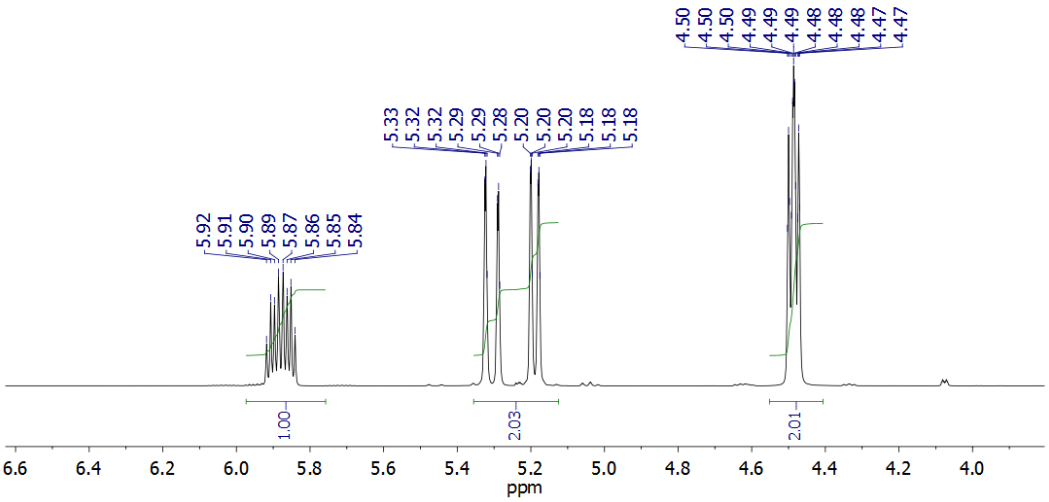

Fig. S1 ^{1}H NMR of triallyl-phosphate (500 MHz, 298 K, $CDCl_3$).

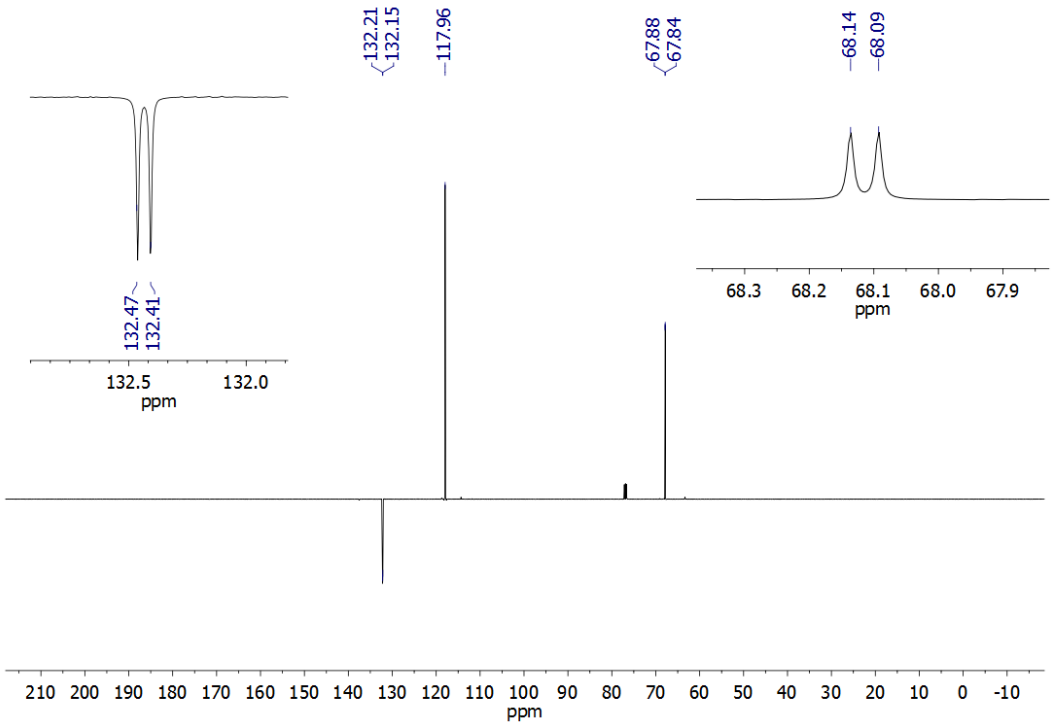

Fig. S2 ^{13}C NMR of triallyl-phosphate (126 MHz, 298 K, $CDCl_3$).

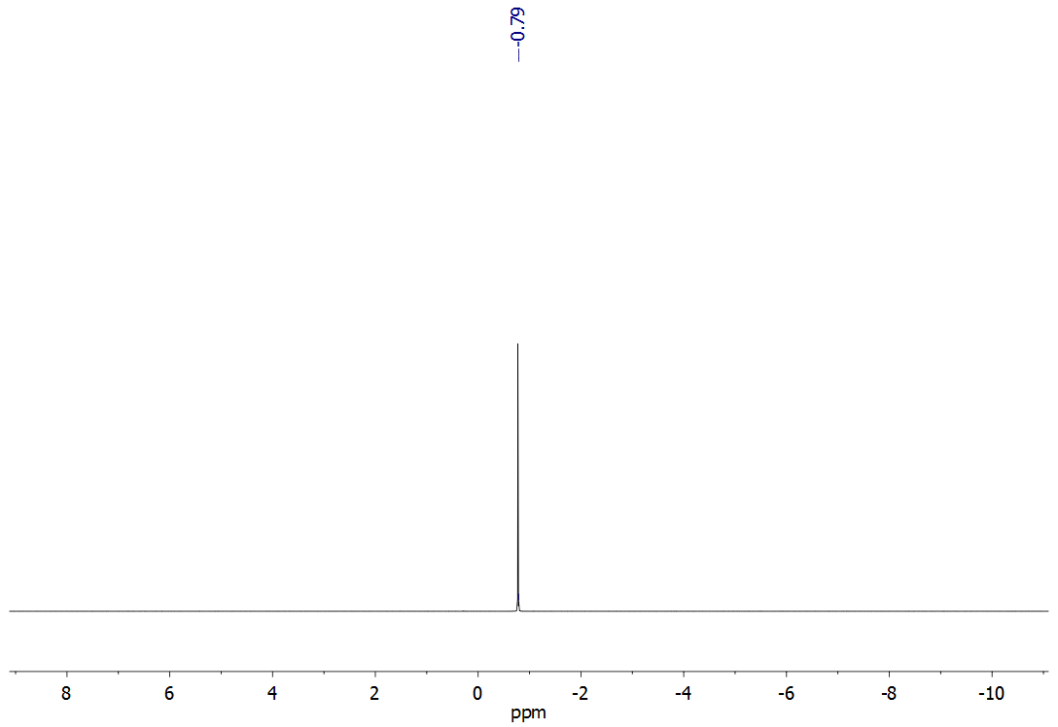

Fig. S3 ^{31}P NMR of triallyl-phosphate (202 MHz, 298 K, $CDCl_3$).

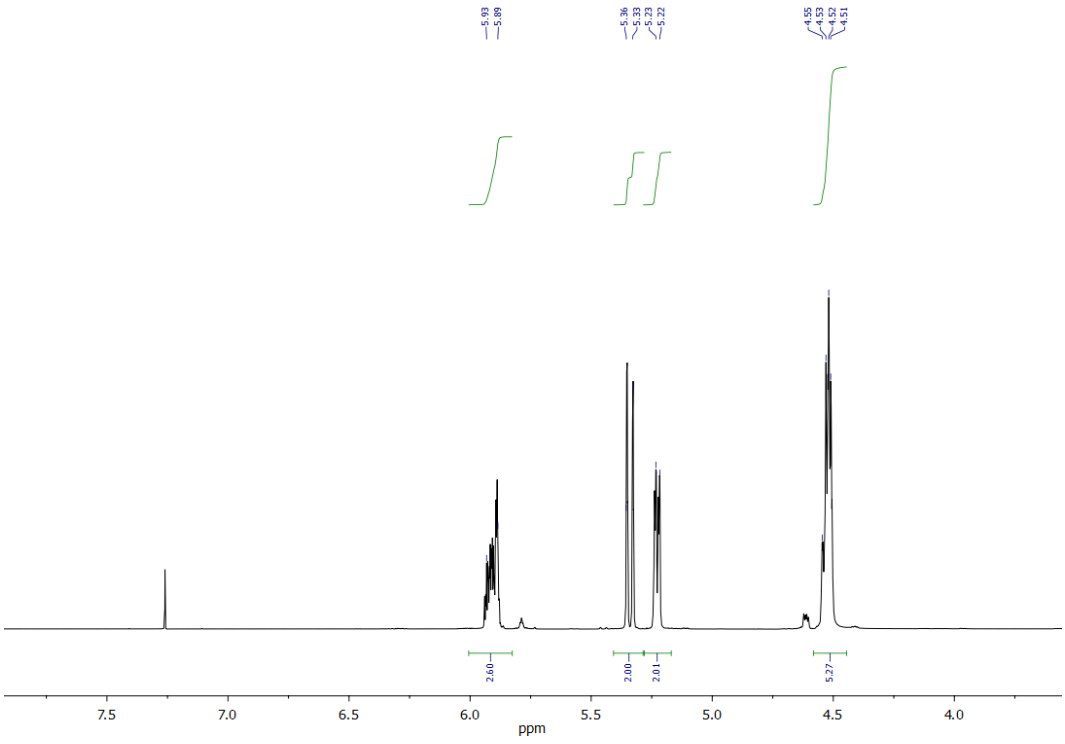

Fig. S4 ^{1}H NMR of **P1** (700 MHz, 298 K, $CDCl_3$).

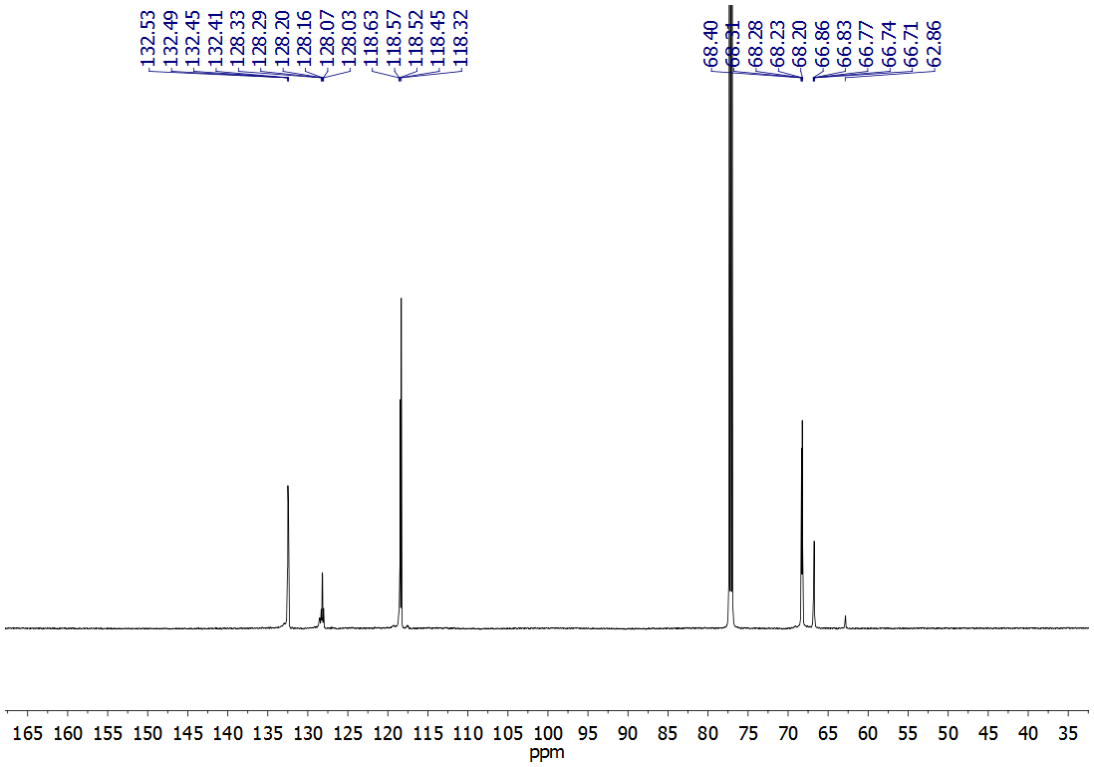

Fig. S5 ^{13}C NMR of **P1** (176 MHz, 298 K, $CDCl_3$).

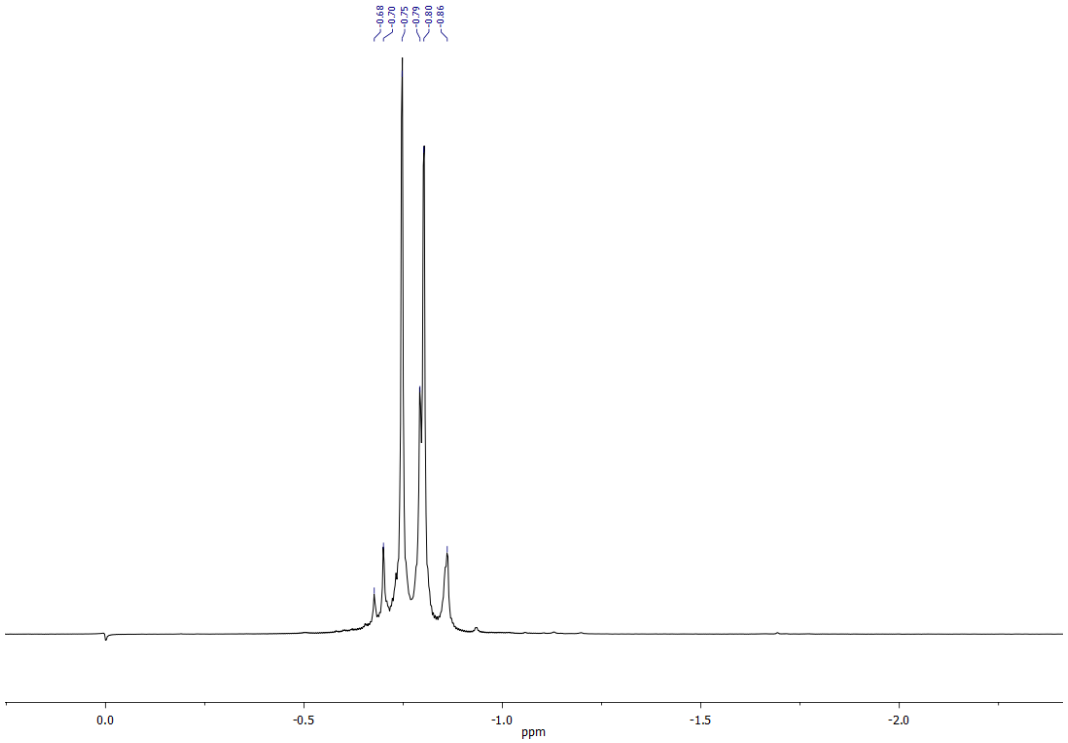

Fig. S6 ^{31}P NMR of **P1** (283 MHz, 298 K, $CDCl_3$).

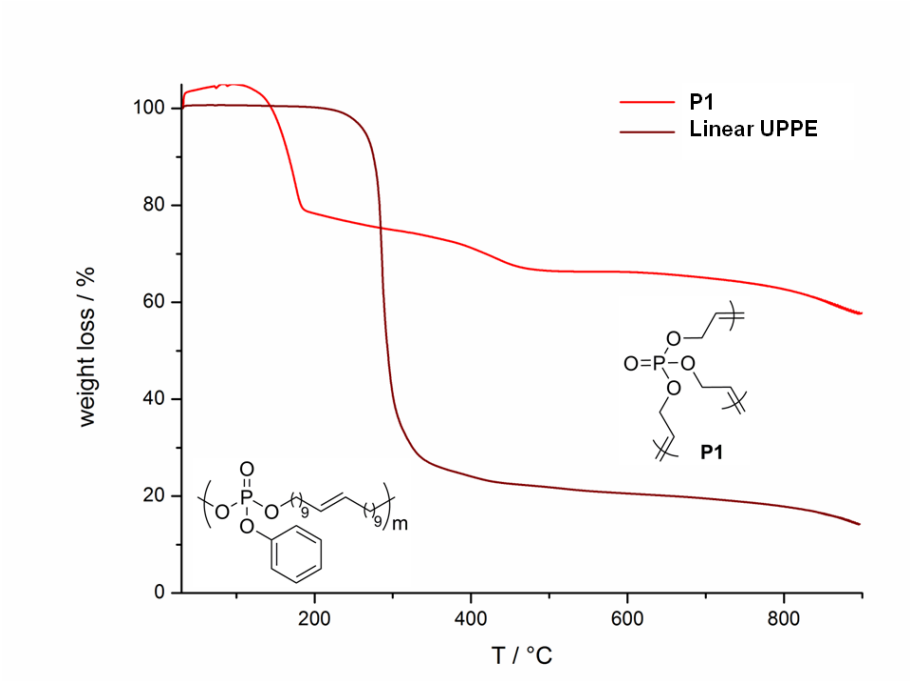

Fig. S7 TGA comparison between **P1** and a linear unsaturated polyphosphoester (UPPE).

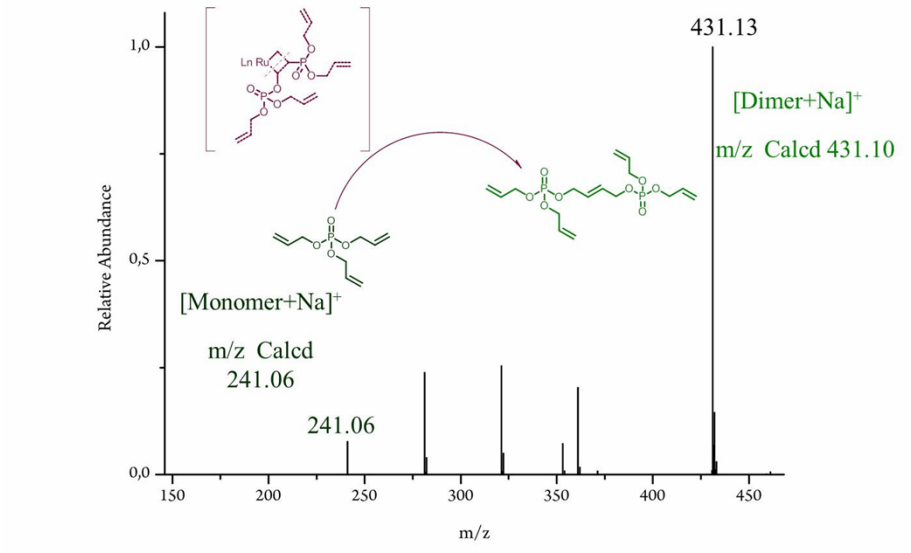

Fig. S8 Evidence of dimeric structure from ESI-MS: early metathesis step.

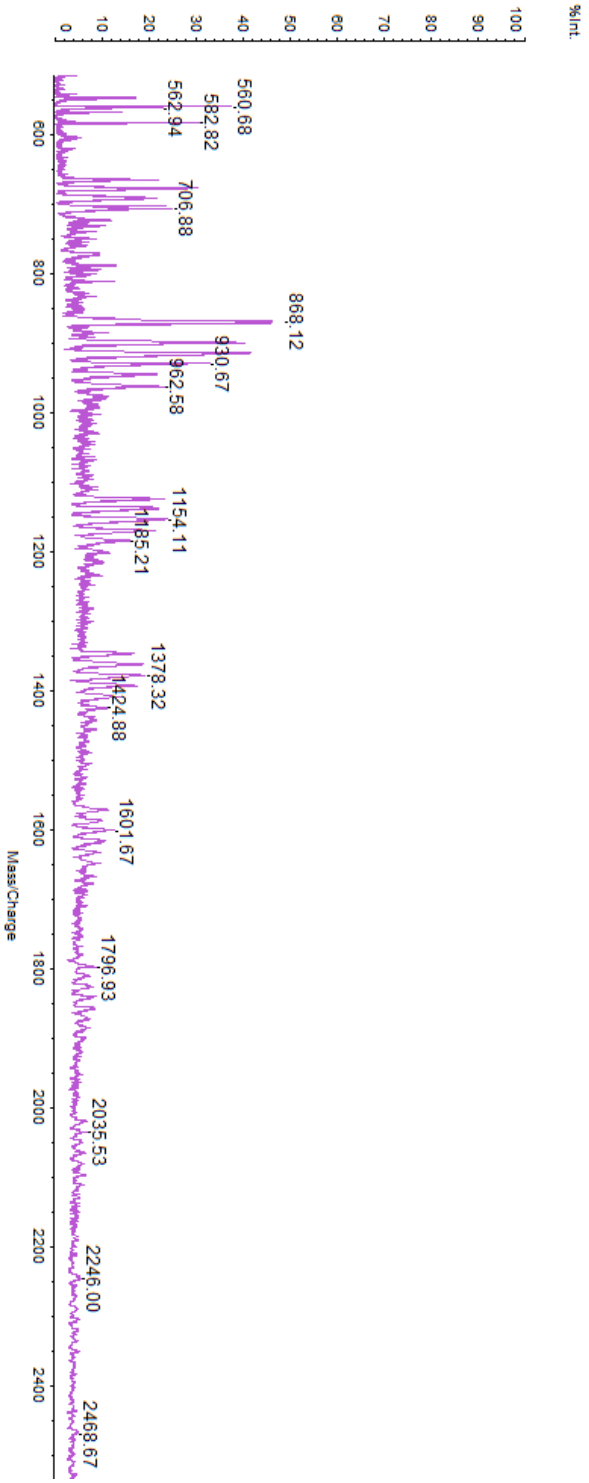

Fig. S9 MALDI spectrum of **P1.** (Dithranol was used as a matrix and potassium trifluoroacetic acid (KTFA) as a cationization agent)

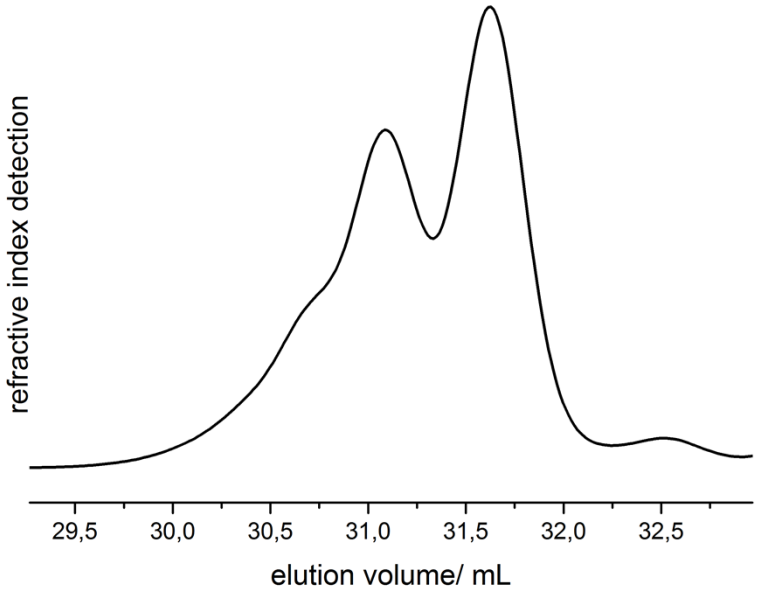

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Fig. S10 Representative GPC chromatogram of **P1** in THF.