Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

First phosphorus AB_2 monomer for flame-retardant hyperbranched polyphosphoesters: AB_2 vs A_2+B_3

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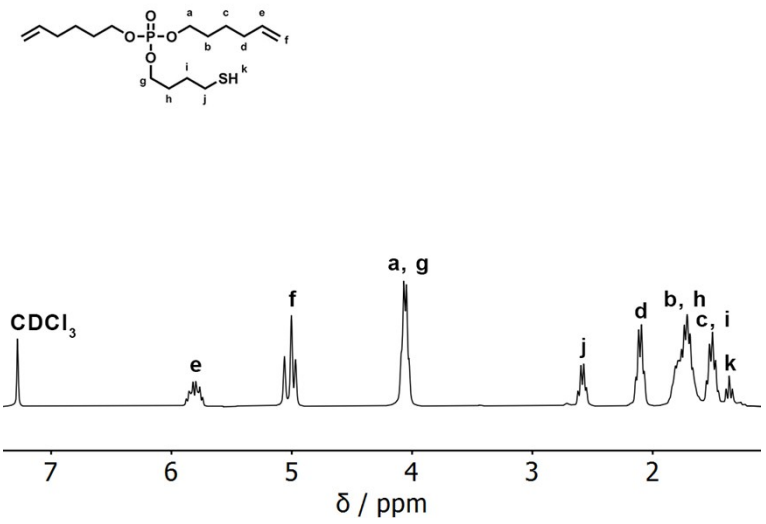


Figure S1. ^{1}H-NMR (300 MHz in $CDCl_3$ at 298 K) of **1**.

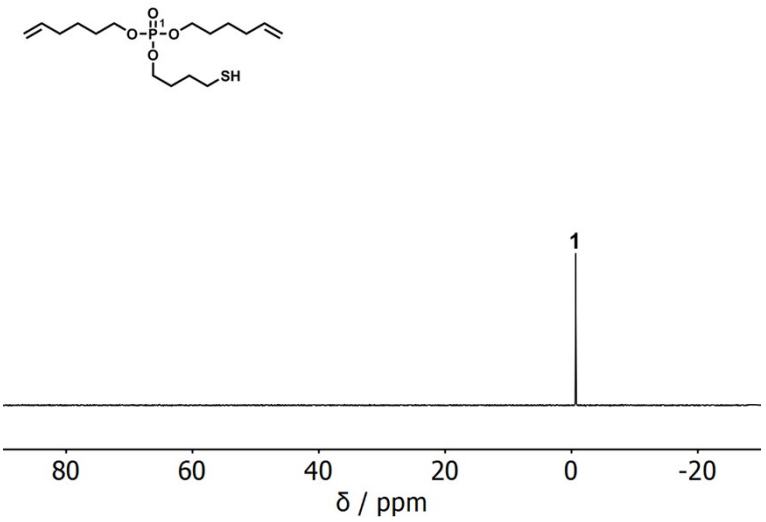


Figure S2. ^{31}P {H}-NMR (121 MHz in $CDCl_3$ at 298 K) of **1**.

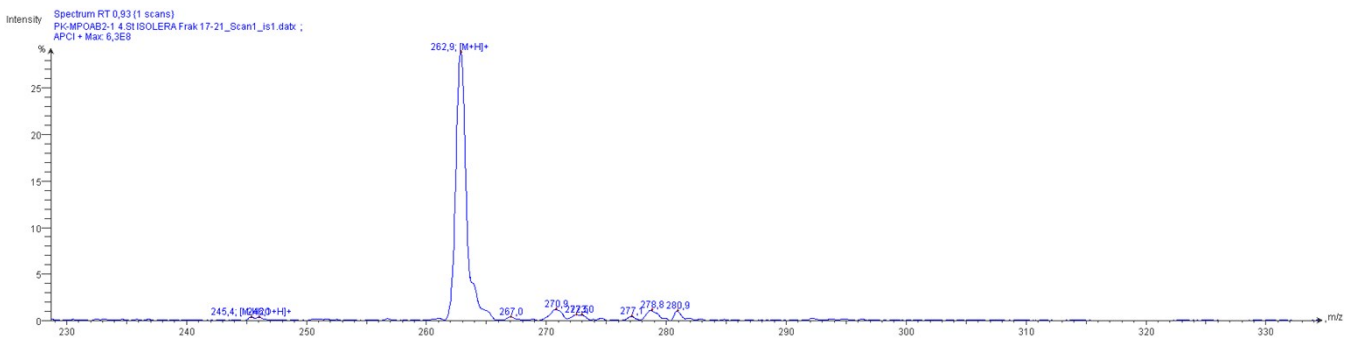


Figure S3. ASAP-MS of **1** $[M+H]^+$ 262.9 m/z.

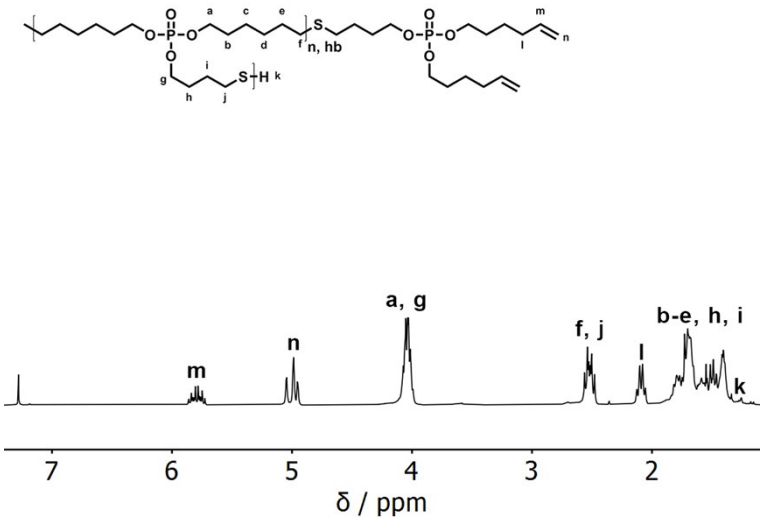


Figure S4. ^{1}H-NMR (300 MHz in $CDCl_3$ at 298 K) of **poly-1**.

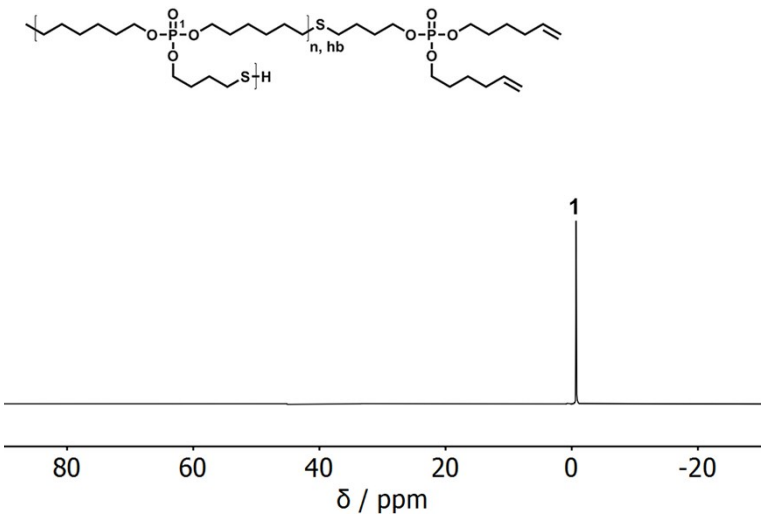


Figure S5. ^{31}P {H}-NMR (121 MHz in $CDCl_3$ at 298 K) of **poly-1**.

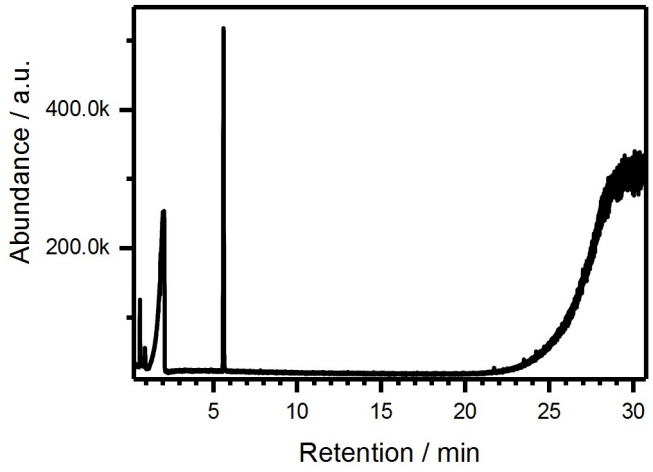


Figure S6. Total ion chromatogram of pyrolysis GC MS of **poly-1** measured at 250 °C (first decomposition step).

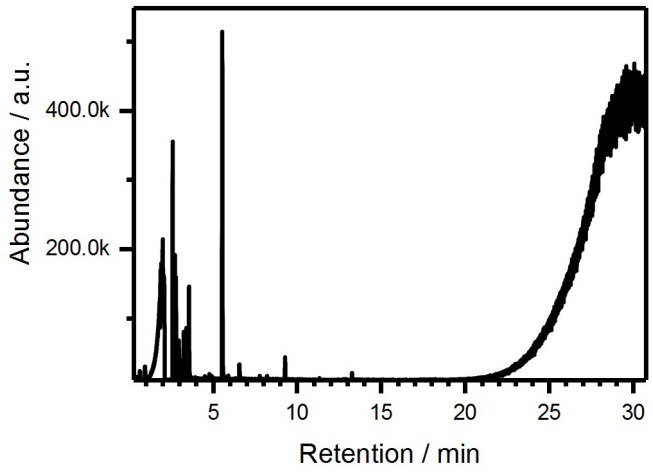


Figure S7. Total ion chromatogram of pyrolysis GC MS of **poly-1** measured at 500 °C (full decomposition).

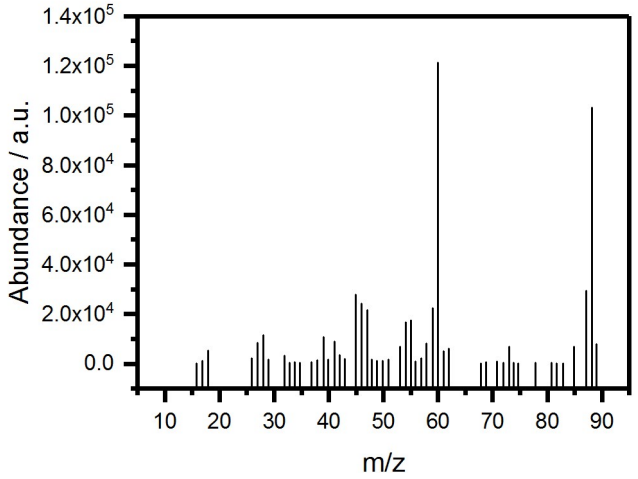


Figure S8. Mass spectrum at 5.62 min in the pyrolysis GC MS total ion chromatogram of **poly-1** at 250 °C, identified by NIST 14 library as tetrahydro thiophene.

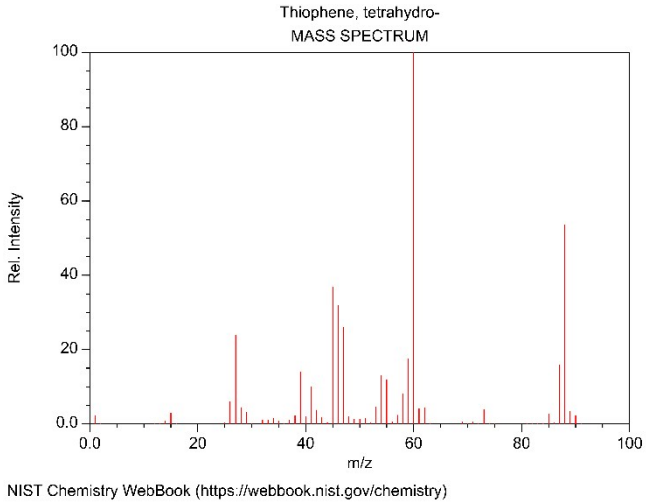


Figure S9. Comparative spectra of tetrahydro thiophene from NIST chemistry webbook.

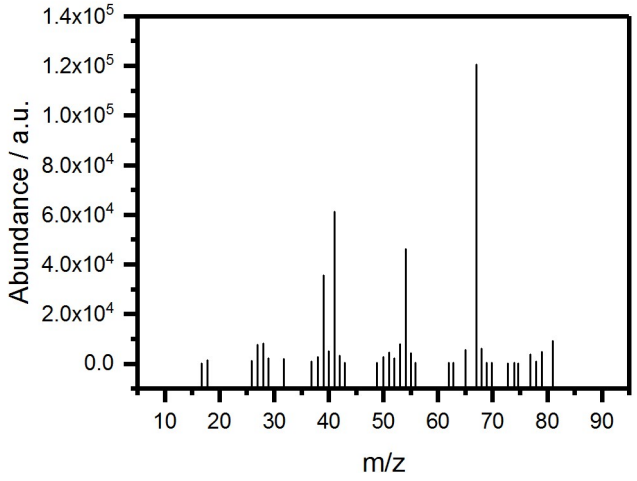


Figure S10. Mass spectrum at 2.60 min in the pyrolysis GC MS total ion chromatogram of **poly-1** at 500 °C, identified by NIST 14 library as 1,5-hexadiene.

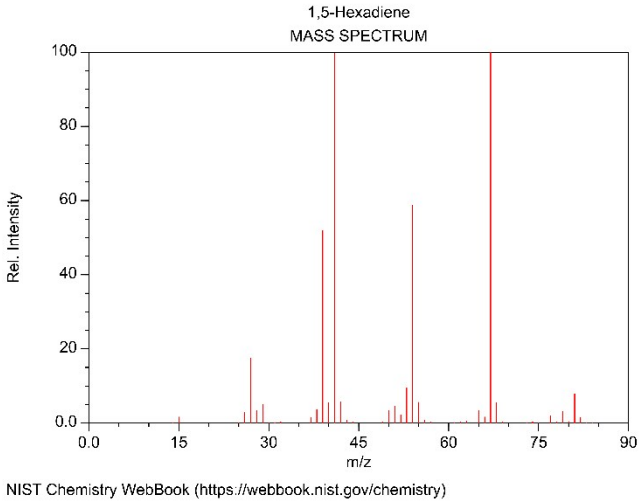


Figure S11. Comparative spectra of 1,5-hexadiene from NIST chemistry webbook.

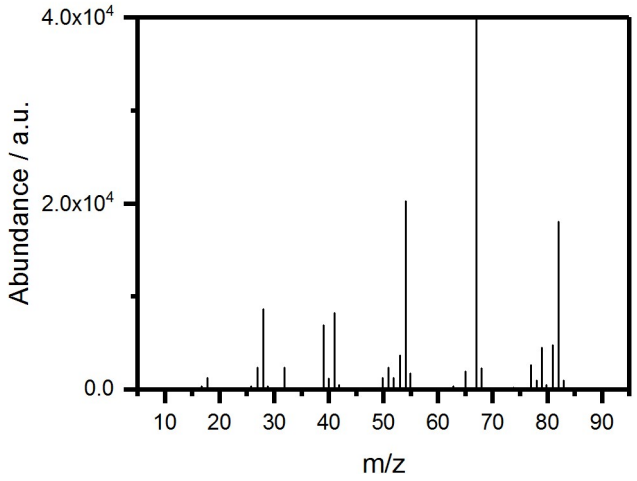


Figure S12. Mass spectrum at 3.56 min in the pyrolysis GC MS total ion chromatogram of **poly-1** at 550 °C, identified by NIST 14 library as cyclohexene.

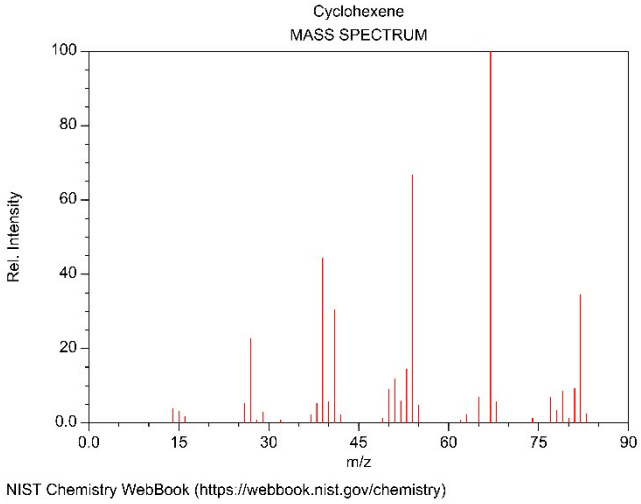


Figure S13. Comparative spectra of cyclohexene from NIST chemistry webbook.

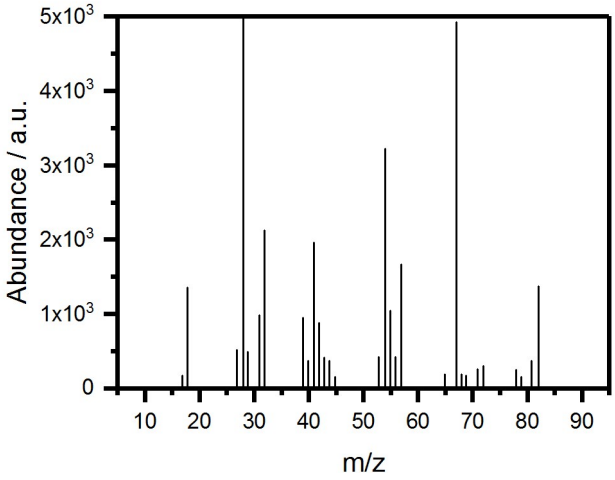


Figure S14. Mass spectrum at 6.57 min in the pyrolysis GC MS total ion chromatogram of **poly-1** at 500 °C, identified by NIST 14 library as 5-hexen-1-ol.

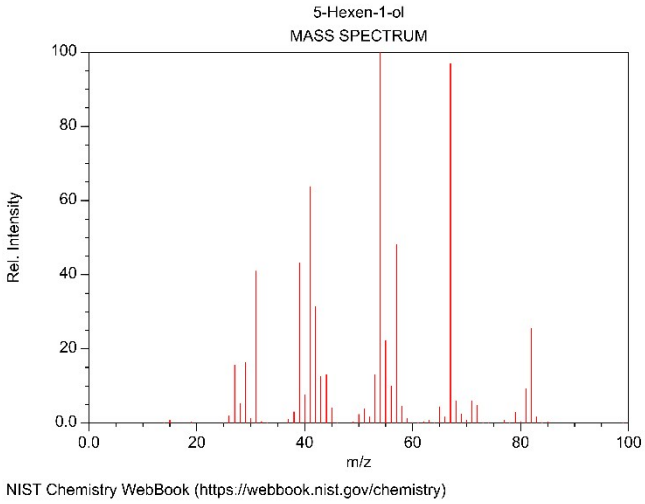


Figure S15. Comparative spectra of 5-hexen-1-ol from NIST chemistry webbook.

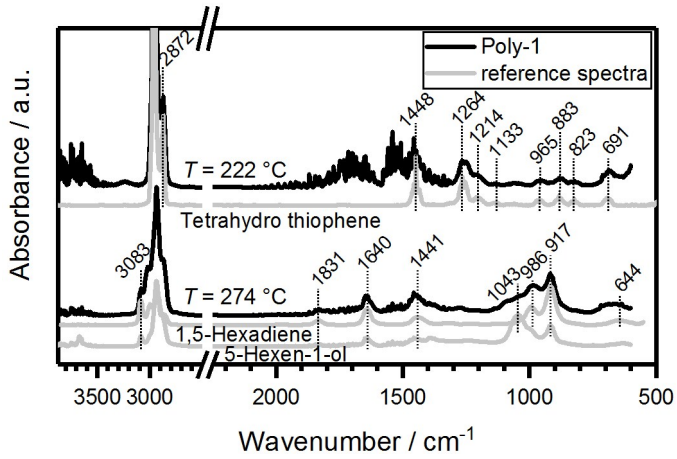


Figure S16. TGA-FTIR spectrum of **poly-1**, identifying the main decomposition products (tetrahydro thiophene; 1,5-hexadiene; 5-hexen-1-ol) at specific decomposition temperatures (222 °C, 274 °C) using references from NIST library.

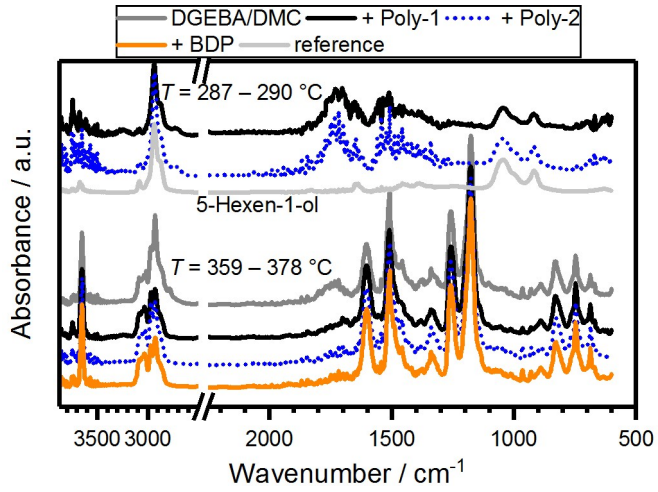


Figure S17. Evolved gas analysis of **EP-FRs** during pyrolysis via TGA coupled with FTIR (TG-FTIR), comparing the products at ca. 290 °C and ca. 360 – 380 °C.

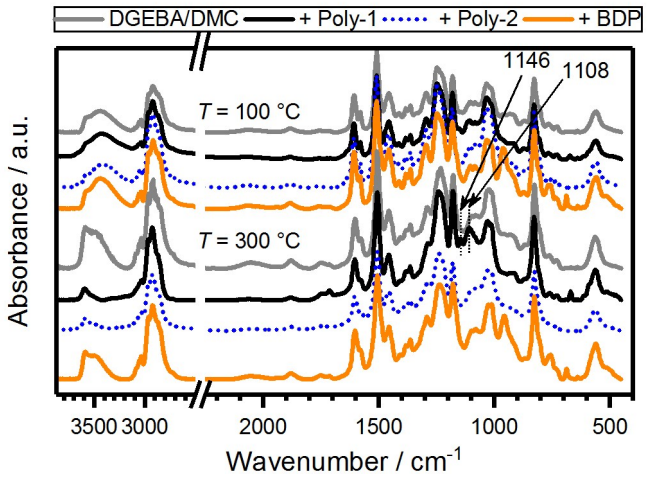


Figure S18. Results from hot-stage FTIR measurements, comparing the condensed phase spectra of **EP-FRs** at 100 °C and 300 °C.

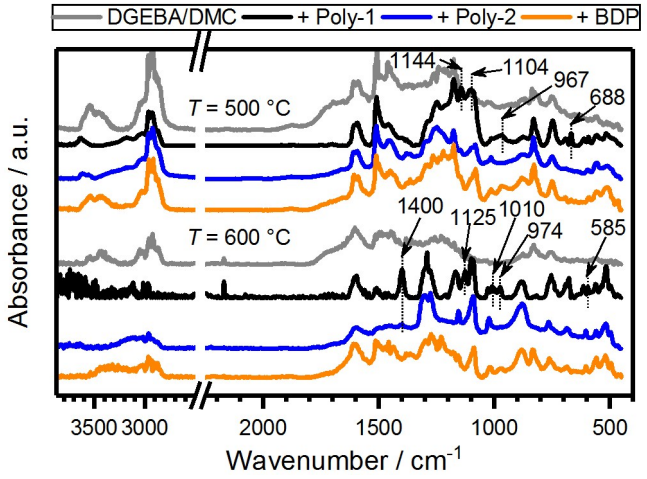


Figure S19. Results from hot-stage FTIR measurements, comparing the condensed phase spectra of **EP-FRs** at 500 °C and 600 °C.

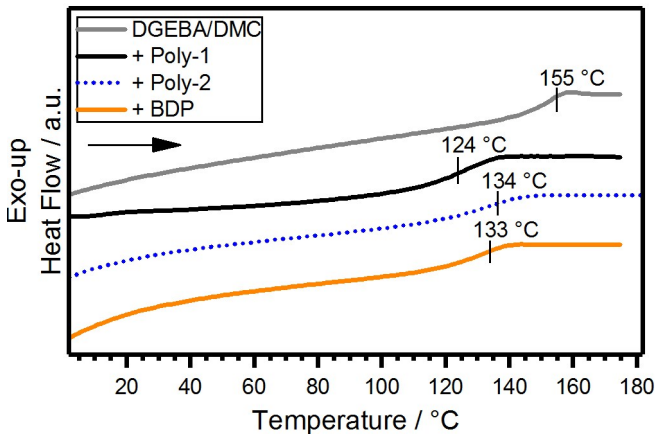


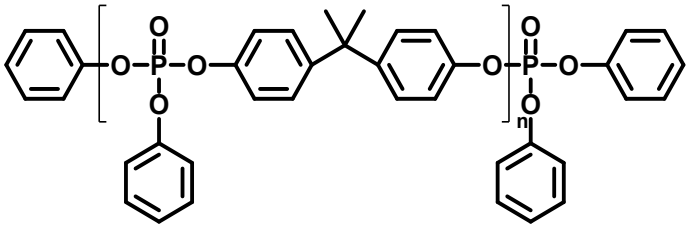
Figure S20. Results from DSC measurements, comparing glass-transition temperatures (T_g) of **EP** and EP-FRs.

Table S1. Results from cone calorimeter measurements of EP-FRs, comparing total heat evolved (THE; = total heat released at flame-out), peak of heat release rate (PHRR), time to ignition (t_{ig}), residue yield, and effective heat of combustion (EHC; = THE / total mass loss).

	EP	**EP-poly-1**	**EP-poly-2**	**EP-BDP**
THE / MJ m^{-2}	108.4 ± 2.6	85.9 ± 0.0	89.8 ± 3.0	87.4 ± 1.2
PHHR / kW m^{-2}	1696 ± 180	1170 ± 32	953 ± 41	1180 ± 41
t_{ig} / s	47 ± 1	39 ± 2	38 ± 3	42 ± 6
Residue / wt.-%	0.7 ± 0.1	11.5 ± 0.8	7.5 ± 0.6	3.1 ± 0.2
EHC / MJ kg^{-1}	26.9 ± 1.0	24.3 ± 0.2	24.3 ± 0.6	22.7 ± 0.2

Table S2. TGA results of **EP** and EP-FRs, comparing onset temperature ($T_{5\%}$), temperature of maximum mass loss rate (T_{max}), and residue at 700 °C.

	EP	**EP-poly-1**	**EP-poly-2**	**EP-BDP**
$T_{5\%}$ / °C	338 ± 1	268 ± 1	289 ± 1	304 ± 1
T_{max} / °C	372 ± 1	350 ± 0	351 ± 1	357 ± 0
Residue / wt.-%	4.5 ± 0.1	7.9 ± 0.3	7.7 ± 0.0	8.2 ± 0.1



Scheme S1. Chemical structure of bisphenol A bis(diphenyl phosphate) (**BDP**).

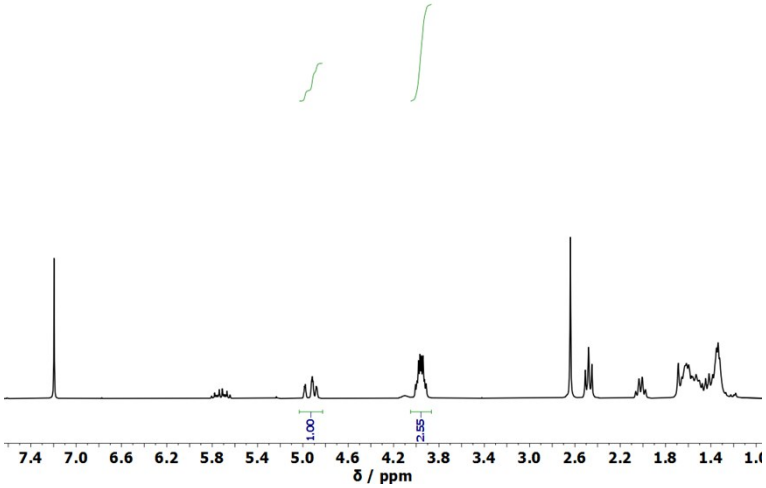


Figure S21. ^{1}H-NMR (300 MHz in $CDCl_3$ at 298 K) of **poly-2** showing a ratio of $n_{Double\text{-}bond}/n_{Ester}$ of 0.39.

Table S3. Elemental analysis of **poly-2**. %C, %H, %N and %S was measured, the other values were calculated as follows: %O&P = 100-(%C+%H+%N+%S); $\%P_{\%O\&P}$ = M(P)/(4*M(O) + M(P)) * 100%; %P = %O&P * $\%P_{\%O\&P}$ / 100%.

	%C	**%H**	**%N**	**%S**	**%O&P**	**$\%P_{\%O\&P}$**	**%P**
Poly-2	55.23	8.66	0	12.48	23.64	33	7.7