Polyesters with bio-based ferulic acid units: crosslinking paves the way to property consolidation

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Electronic Supplementary Information (ESI)

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1. Considerations about the microstructure of the studied terpolymers

The studied terpolymers are prepared from a diacid (A_2 monomer; T or S), a diol (B_2 monomer; E, Pr, B), and from a ferulic acid derivative (F), an AB monomer with acid (A) and alcohol (B) functionality. The different reaction sites have to be considered for the non-symmetric BB' monomer iPr (BB' = -O-CH(CH_3)-CH_2-O- = $i\vec{P}r$; B'B = O-CH_2-CH(CH_3)-O- = $i\bar{P}r$) resulting in an increased number of microstructural units (right column).

Accordingly, the following DYADs can be formed:

AA-BB (example: *T-E*)	AA-BB‘ and AA-B'B (example: *T-* $i\vec{P}r$ *and T-*$i\bar{P}r$)
AA-BA (example: *T-F*)	AA-BA
BA-BB (example: *F-E*)	BA-BB' and BA-B'B (example: *F-* $i\vec{P}r$ *and F-*$i\bar{P}r$)
BA-BA (example: *T-F*)	BA-BA

In microstructure analysis the following TRIADs have to be considered:

AA-centred

BB-AA-BB (example: *E-T-E*)	BB'-AA-BB‘; BB'-AA-B'B, B'B-AA-BB' (example: $i\vec{P}r$*-T-*$i\vec{P}r$, $i\vec{P}r$*-T-*$i\bar{P}r$, $i\bar{P}r$*-T-*$i\vec{P}r$)
BB-AA-BA (example: *E-T-F*)	BB'-AA-BA; B'B-AA-BA (example: $i\vec{P}r$*-T-F,* $i\bar{P}r$*-T-F*)
AB-AA-BA (example: *F-T-F*)	AB-AA-BA

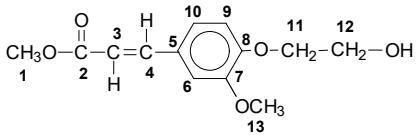
BB-centred	*BB'-centred*
AA-BB-AA (example: *T-E-T*)	AA-BB‘-AA (example: *T-iPr-T*)
AA-BB-AB (example: *T-E-F*)	AA-BB`-AB; AA-B'B-AB (example: *T-*$i\vec{P}r$*-F, T-*$i\bar{P}r$*-F*)
AB-BB-AB (example: *F-E-F*)	BA-BB'-AB (example: *F-iPr-F*)

AB-centred

BB-AB-AA (example: *E-F-T*)	BB‘-AB-AA; B'B-AB-AA (example: $i\vec{P}r$*-F-T,* $i\bar{P}r$*-F-T*)
BB-AB-AB (example: *E-F-F*)	BB‘-AB-AB; B'B-AB-AB (example: $i\vec{P}r$*-F-F,* $i\bar{P}r$*-F-F)*
AB-AB-AA (example: *F-F-T*)	AB-AB-AA
AB-AB-AB (example: *F-F-F*)	AB-AB-AB

2. NMR data and spectra

2.1 Methyl (E)-3-(4-(2-hydroxyethoxy)-3-methoxyphenyl)acrylate (F)



^{1}H NMR (DMSO-d_6), δ = 7.59 (d, 15.9 Hz, 1H; 4), 7.34 (d, 2.0 Hz, 1H; 6), 7.22 (dd, 8.4 Hz, 2.0 Hz, 1H; 10), 6.99 (d, 8.4 Hz, 1H; 9), 6.55 (d, 15.9 Hz, 1H; 3), 4.84 (t, 5.5 Hz, 1H; OH), 4.02 (t, 4.9 Hz, 2H; 11), 3.81 (s, 3H; 13), 3.72 (m, 2H; 12), 3.71 ppm (s, 3H; 1).

^{13}C NMR (DMSO-d_6), δ = 167.0 (2), 150.5 (8), 149.2 (7), 144.8 (4), 126.9 (5), 122.9 (9), 115.3 (3), 112.7 (10), 110.8 (6), 70.3 (11), 59.6 (12), 55.6 (13), 51.3 ppm (1).

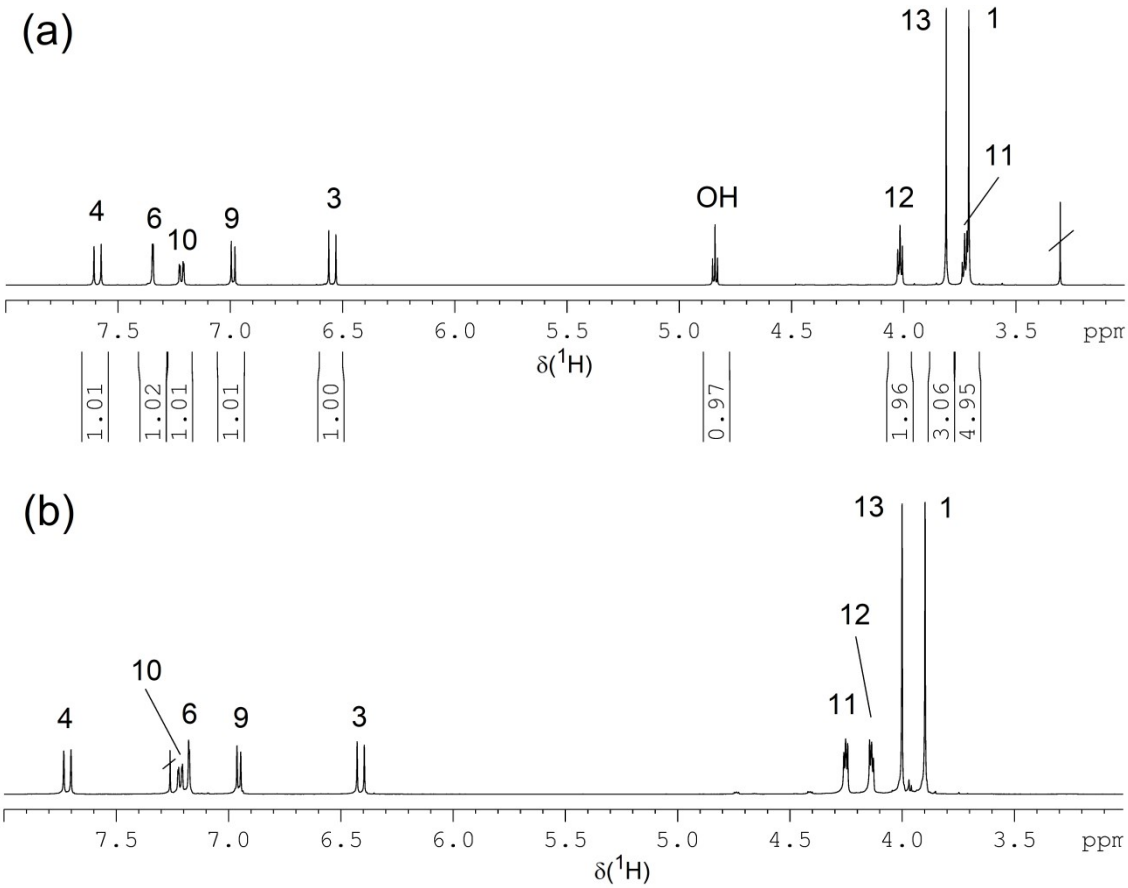


Figure ESI 1. ^{1}H NMR spectrum of monomer methyl (E)-3-(4-(2-hydroxyethoxy)-3-methoxyphenyl)acrylate (F) recorded (a) in DMSO-d_6 and (b) in $CDCl_3$/TFA-d (4:1 v/v) as solvent.

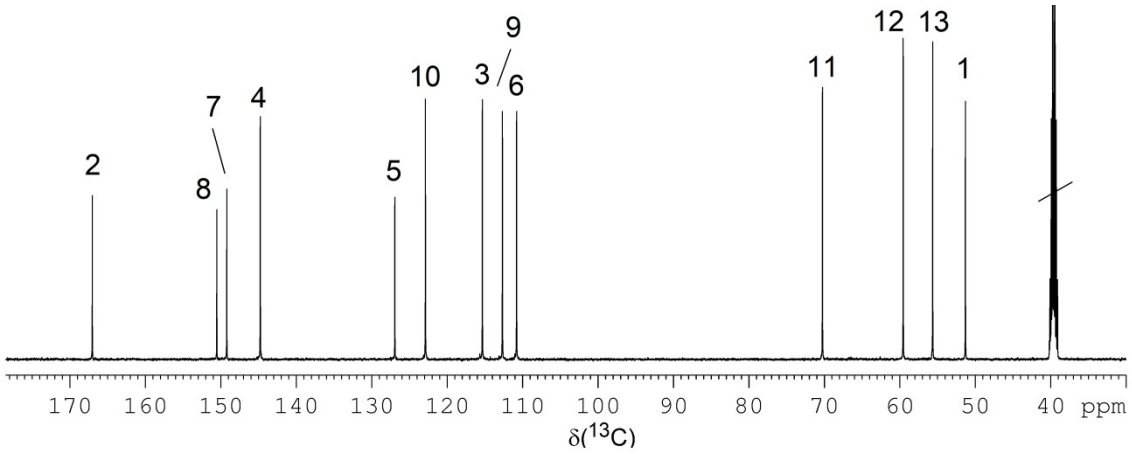
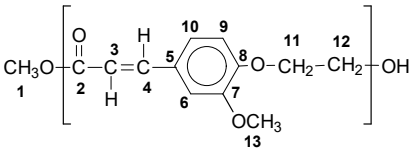


Figure ESI 2. ^{13}C NMR spectrum of monomer methyl (E)-3-(4-(2-hydroxyethoxy)-3-methoxyphenyl)acrylate (F) in DMSO-d_6.

2.2 Polymers

In general, the complexity of the spectra depends on the ratio of the three comonomers. The content of the different microstructural units (see ESI, section 1) depends on the comonomer ratio. The spectra show a larger number of intense signals for terpolymers with higher F content due to the higher content of F-containing dyads, triads etc. The reported chemical shift values are determined from the center of overlapping signals of an atom.

2.2.1 P(F)



^{1}H NMR ($CDCl_3$/TFA-d 4:1 v/v): δ 7.73 (4), 7.21 (10), 7.17 (6), 6.96 (9), 6.42 (3), 4.74 (12_{TFA}), 4.66 (12), 4.42 (11), 4.41 (11_{TFA}), 4.25 (11_{OH}), 4.14 (12_{OH}), 3.98 (13), 3.90 ppm (1).

^{13}C NMR ($CDCl_3$/TFA-d 4:1 v/v): δ 171.1 (2 next to CH_3O end group), 170.2 (2), 149.9 (8), 148.8 (7), 147.3 (4), 128.3 (5), 124.0 (10), 114.9 (3), 113.4 (9), 111.5 (6), 69.9 (11_{OH}), 67.1 (11), 66.4 (11_{TFA}), 65.9 (12_{TFA}), 63.8 (12), 61.1 (12_{OH}), 56.1 (13), 53.0 ppm (1).

There is a strong tendency of the hydroxyethyl end group (subscript $_{OH}$) to be esterified by the co-solvent TFA-d. This results in decreasing hydroxyethyl and increasing trifluoroacetoxyethyl signals during the measurement. Therefore, also the signals of the esterified hydroxyethyl end group (subscript $_{TFA}$) are included in the listing.

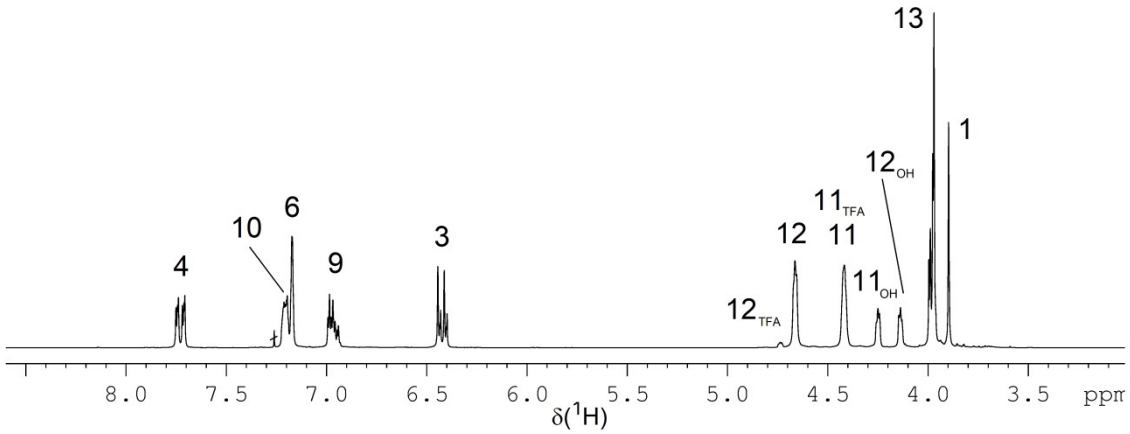


Figure ESI 3. ^{1}H NMR spectrum of oligomeric homopolyester P(F) in $CDCl_3$/TFA-d (4:1 v/v). Subscripts $_{OH}$ and $_{TFA}$ indicate signals from the OH and OC(O)CF_3 (after reaction with co-solvent TFA-d) end group, respectively.

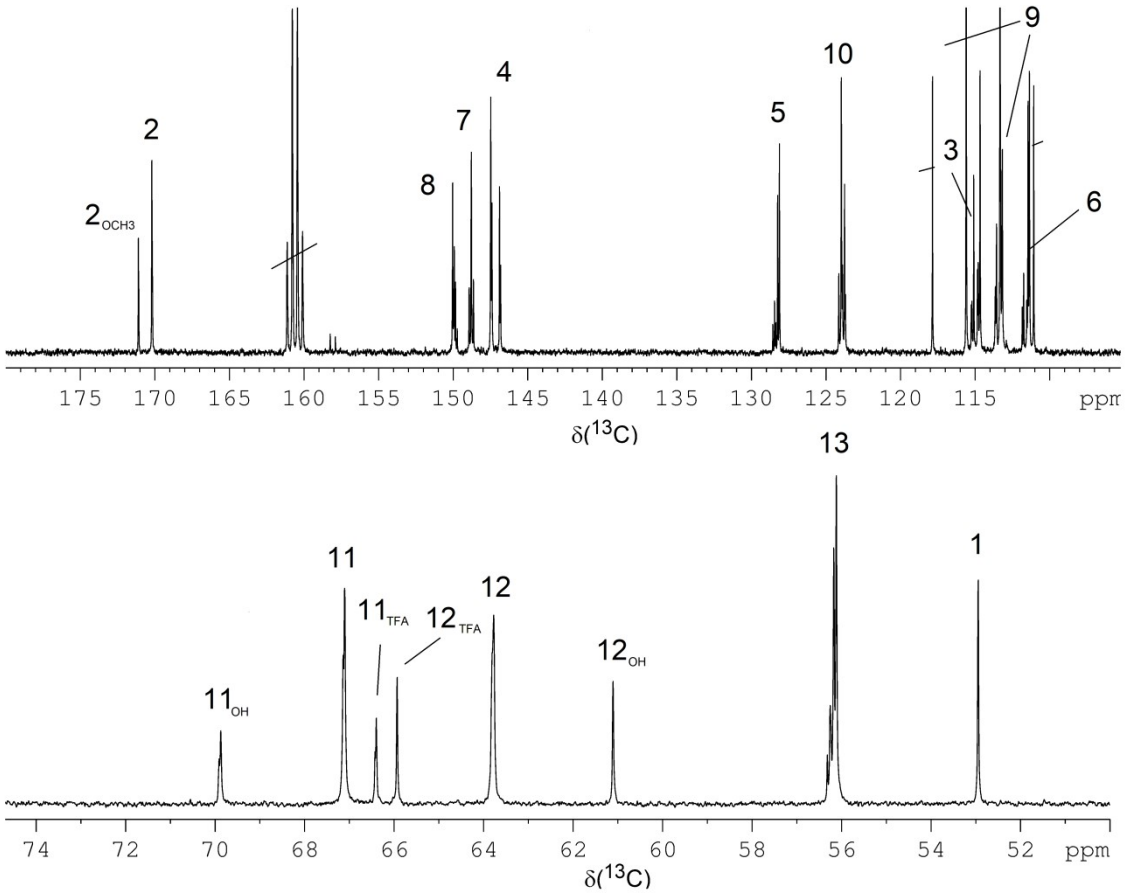


Figure ESI 4. ^{13}C NMR spectrum of oligomeric homopolyester P(F) in $CDCl_3$/TFA-d (4:1 v/v). Subscripts $_{OH}$ and $_{TFA}$ indicate signals from the OH and $OC(O)CF_3$ (after reaction with cosolvent TFA-d) end group, respectively. The content of esterified end groups is higher than in the ^1H NMR spectrum due to the longer measuring time.

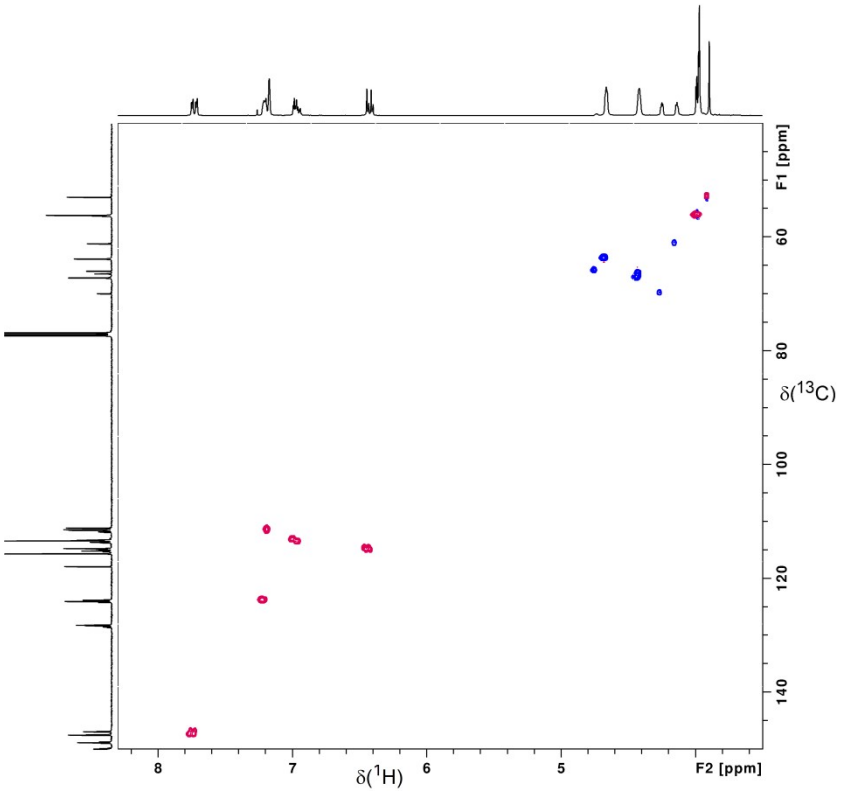
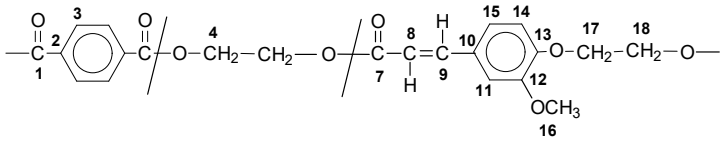


Figure ESI 5. Edited HSQC spectrum of P(F) in $CDCl_3$/TFA-d (4:1 v/v). CH, CH_3 – red; CH_2 – blue.

2.2.2 P(T-E-F)



^{1}H NMR (CDCl$_3$/TFA-d 4:1 v/v): δ 8.16 (3), 7.75 (9), 7.25 – 7.10 (11, 15), 7.00 (14), 6.45 (8), 4.85 – 4.60 (4, 18), 4.49 and 4.43 (17), 3.95 ppm (19).

^{13}C NMR (CDCl$_3$/TFA-d 4:1 v/v): δ 170.1 (7), 167.7 (1), 150.0 (13), 148.8 (12), 147.6 (9), 133.5 (2), 130.1 (3), 128.1 (10), 124.0 (15), 114.6 (8), 113.3 (14), 111.5 (11), 67.0 (17), 64.4 (18_{F-T}), 64.1–63.2 (4, 18_{F-F}), 56.2 ppm (16).

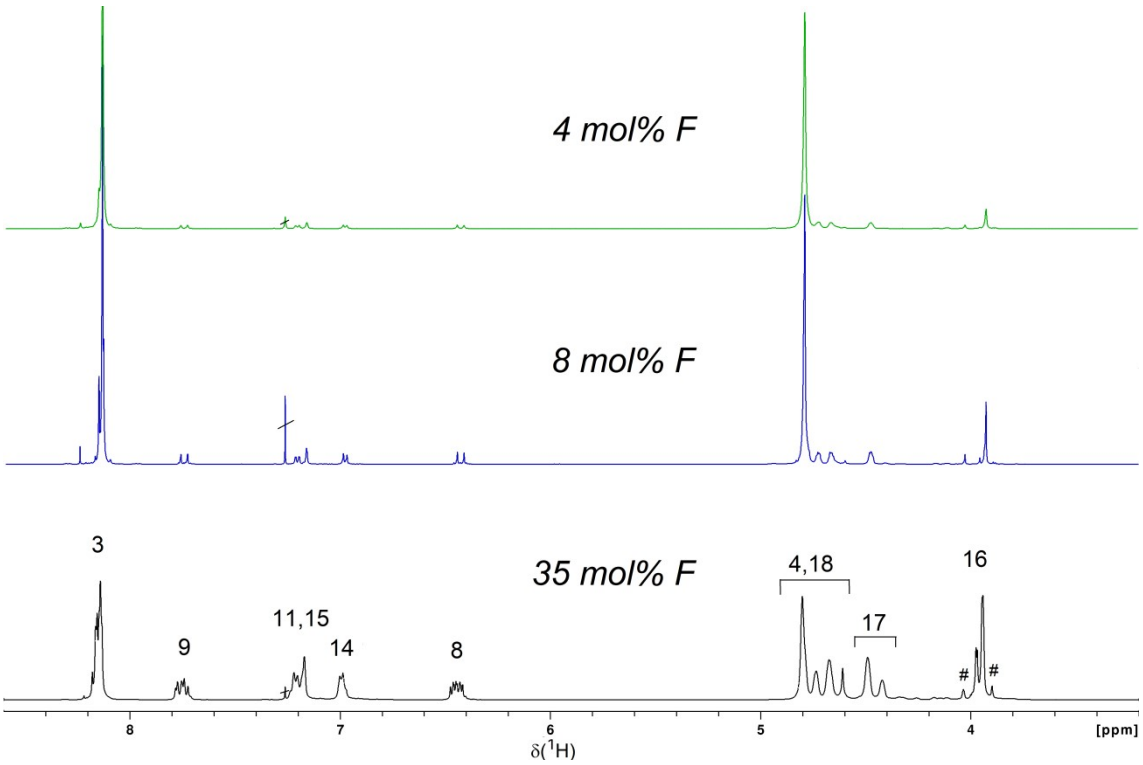


Figure ESI 6. ^{1}H NMR spectra of copolyesters of the P(T-E-F) series (CDCl$_3$/TFA-d 4:1 v/v). # marks signals of methyl ester end groups.

Calculation of terpolymer composition (in mol%)

from normalised signal intensities (I) of T (= I(H_2)/3), E (= [I(4.9 ppm to 4.3 ppm) - I(H_8+H_9)*2)]/4) and F (= I(H_9+H_8+H_{14})/3).

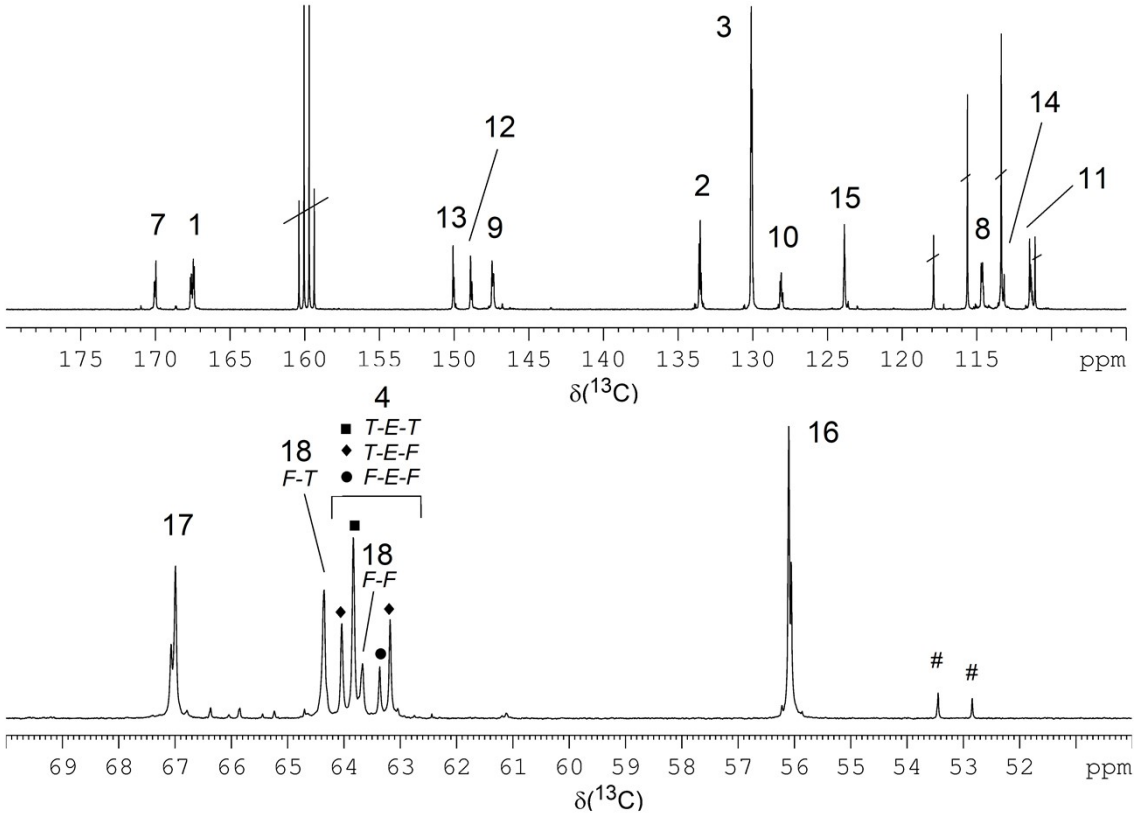


Figure ESI 7. ^{13}C NMR spectrum of P(T-E-F) with a F content of 35 mol% ($CDCl_3$/TFA-d 4:1 v/v). Triad signals are assigned for C_4 and dyad signals for C_{18}. # marks signals of methyl ester end groups.

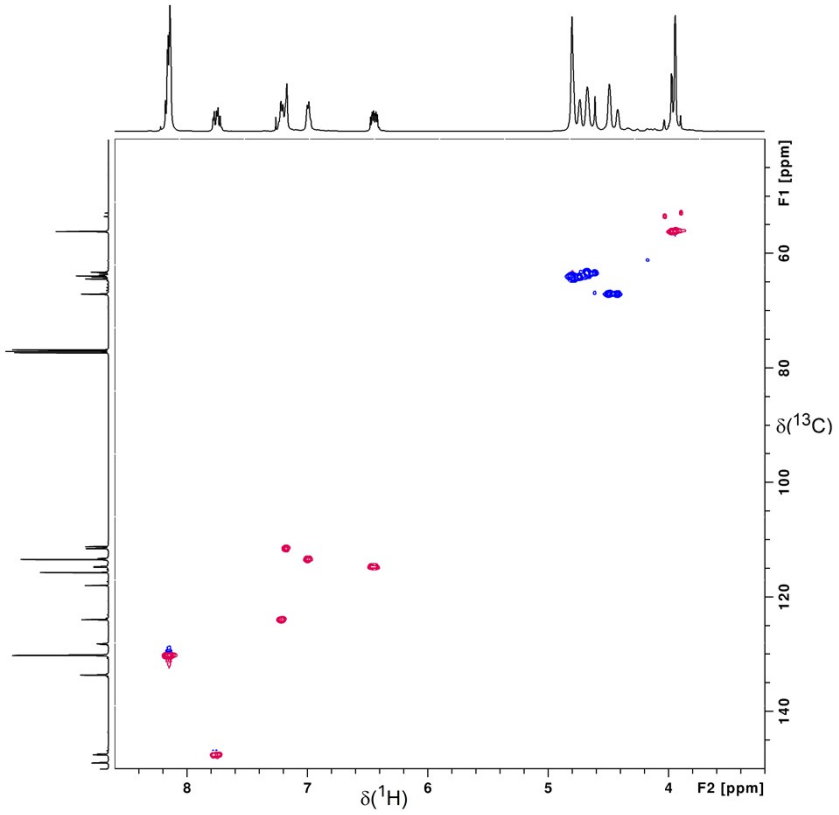
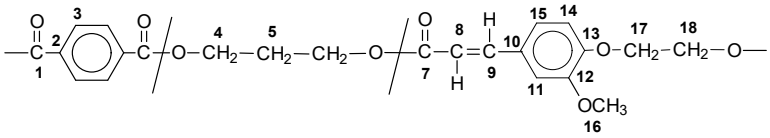


Figure ESI 8. Edited HSQC spectrum of P(T-E-F) with F content of 35 mol% ($CDCl_3$/TFA-d 4:1 v/v). CH, CH_3 – red; CH_2 – blue.

2.2.3 P(T-Pr-F)



^{1}H NMR ($CDCl_3$/TFA-d 4:1 v/v): δ 8.12 (3), 7.72 (9), 7.20 (15), 7.16 (11), 6.99 (14), 6.41 (8), 4.80 – 4.40 (4, 17, 18), 3.95 (19), 2.38 ($5_{T\text{-}Pr\text{-}T}$), 2.30 ($5_{T\text{-}Pr\text{-}F}$), 2.22 ppm ($5_{F\text{-}Pr\text{-}F}$).

^{13}C NMR ($CDCl_3$/TFA-d 4:1 v/v): δ 170.4 (7), 168.0 (1), 150.0 (13), 148.7 (12), 147.5 ($9_{F\text{-}F}$), 147.2 ($9_{F\text{-}P}$), 133.6 (2), 130.1 (3), 128.2 (10), 124.0 (15), 114.9 (8), 113.3 (14), 111.5 (11), 67.0 (17), 64.5 ($18_{F\text{-}T}$), 63.7 ($18_{F\text{-}F}$), 63.4 – 62.3 (4), 56.2 (16), 27.7 ppm (5).

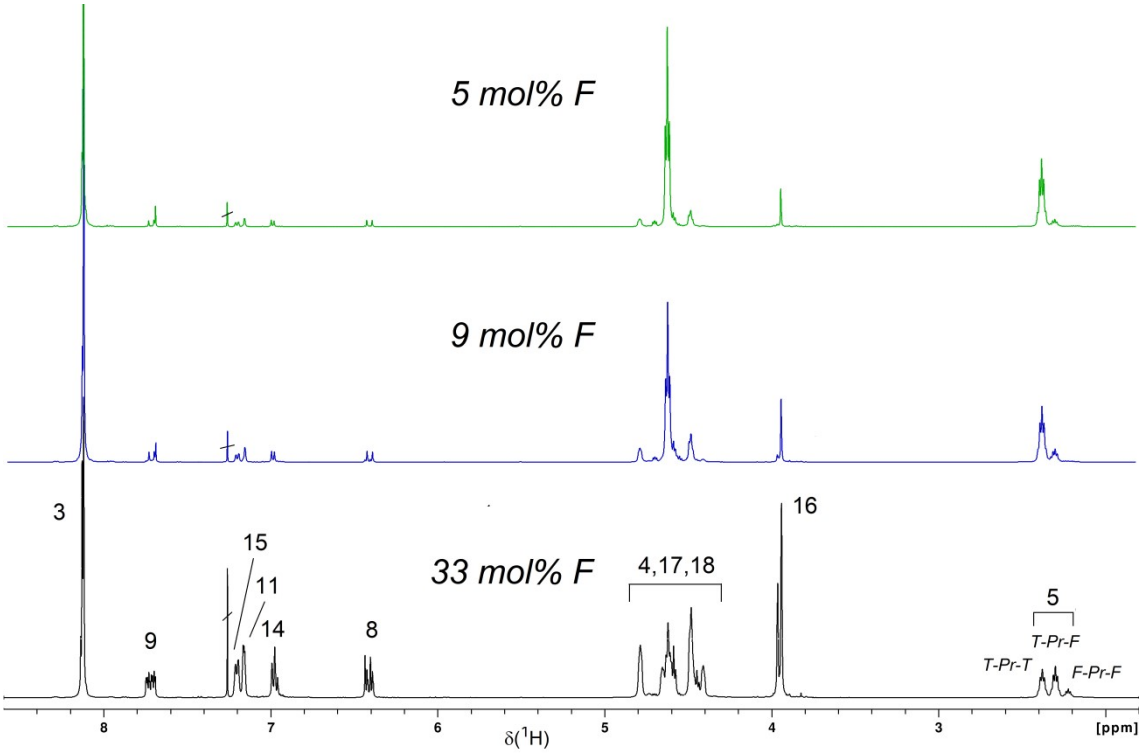


Figure ESI 9. ^{1}H NMR spectra of copolyesters of the P(T-Pr-F) series ($CDCl_3$/TFA-d 4:1 v/v). Triad signals are assigned for H_5.

Calculation of terpolymer composition (in mol%)

from normalised signal intensities (I) of T (= $I(H_3)/4$), Pr (= $I(H_5)/2$) and F (= $I(H_9+H_8+H_{14})/3$).

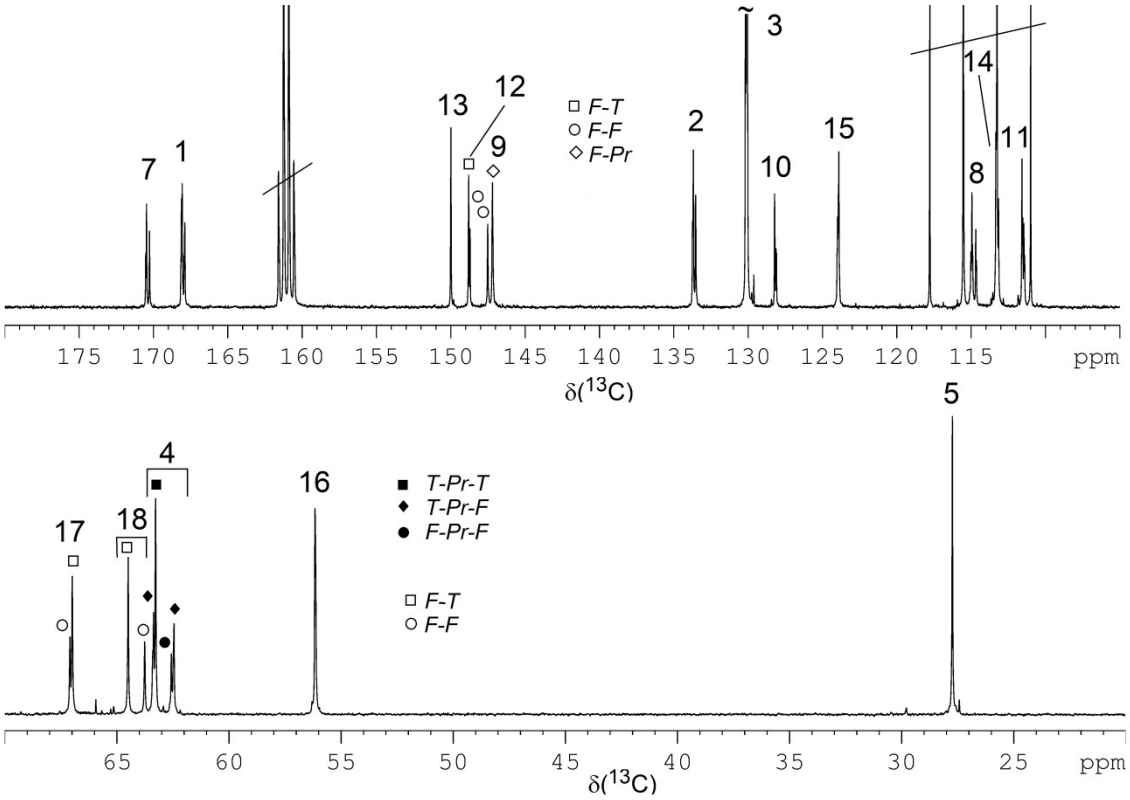


Figure ESI 10. ^{13}C NMR spectrum of P(T-Pr-F) with a F content of 33 mol% ($CDCl_3$/TFA-d 4:1 v/v). Triad signals are assigned for C_4 and dyad signals for C_{18}.

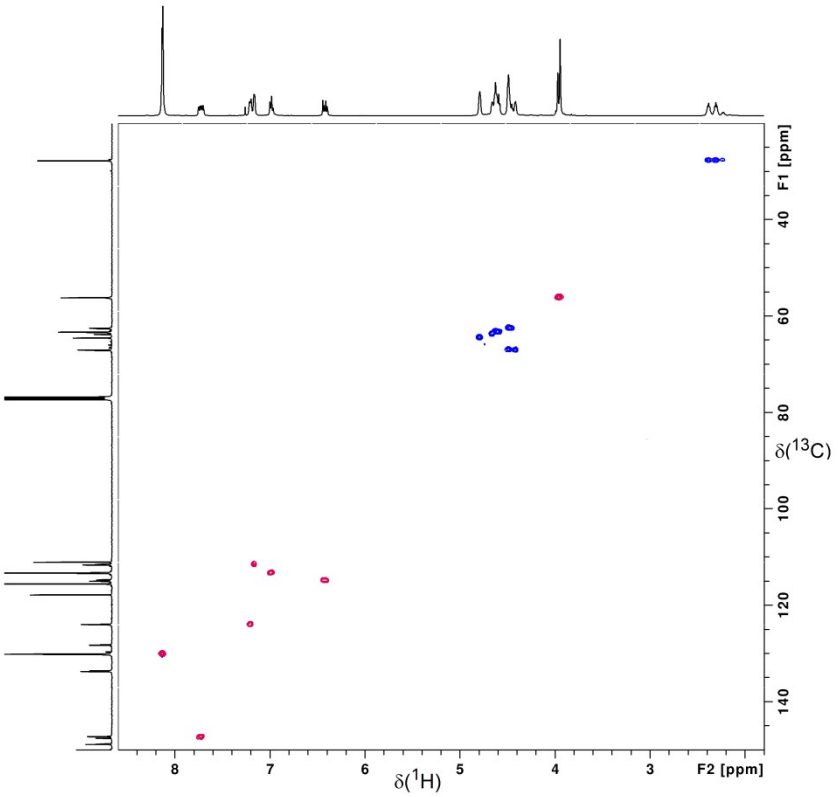
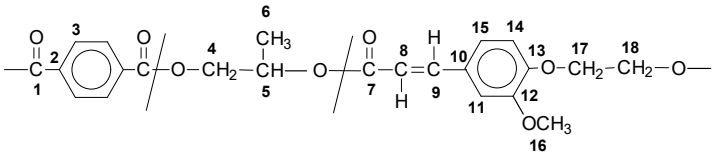


Figure ESI 11. Edited HSQC spectrum of P(T-Pr-F) with a F content of 33 mol% ($CDCl_3$/TFA-d 4:1 v/v). CH, CH_3 – red; CH_2 – blue.

2.2.4 P(T-iPr-F)



^{1}H NMR ($CDCl_3$/TFA-d 4:1 v/v): δ 8.10 (3), 7.71 (9), 7.25 – 7.1 (11, 15), 6.97 (14), 6.40 (8), 5.70 – 5.40 (5), 4.80 – 4.40 (4, 17, 18), 3.92 (16), 1.53 ppm (6).

^{13}C NMR ($CDCl_3$/TFA-d 4:1 v/v): δ 169.9 (7), 167.3 (1), 150.0 (13), 148.9 (12), 147.4 (9), 133.7 (2), 130.1 (3), 128.1 (10), 123.9 (15), 114.8 (8), 113.3 (14), 111.5 (11), 71.5 – 70.0 (5), 67.7 (4), 67.0 (17), 64.4 (18), 56.1 (16), 16.1 ppm (6).

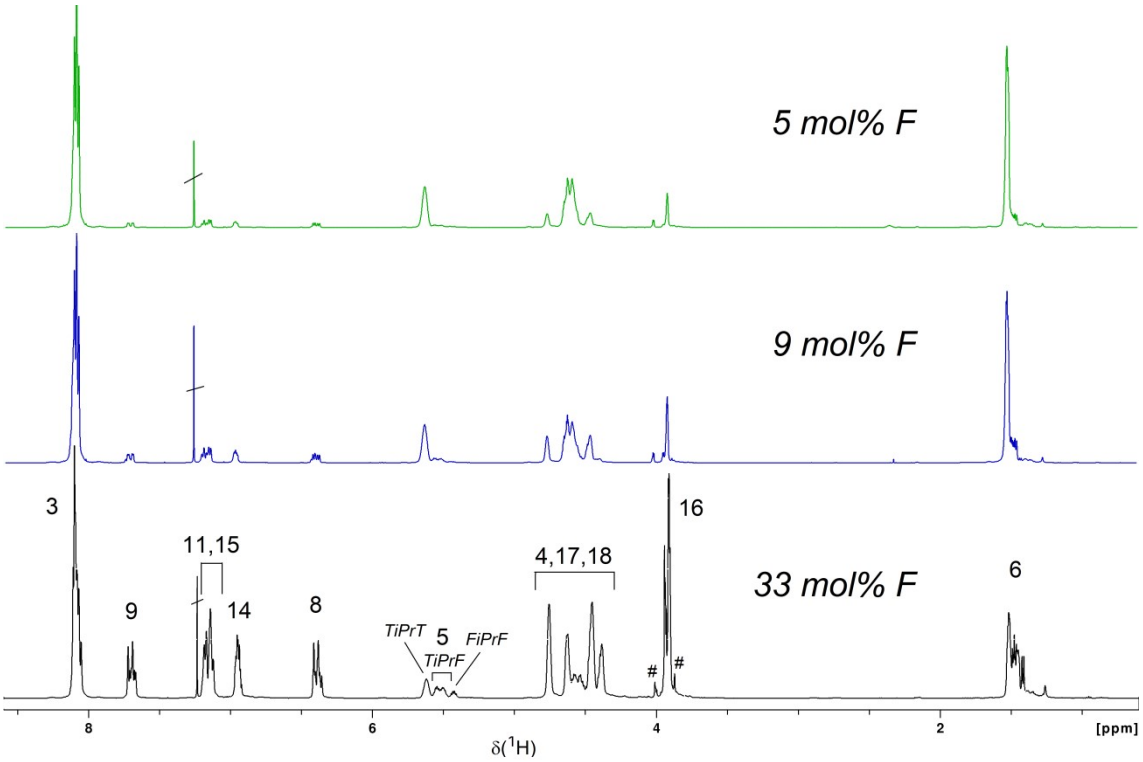


Figure ESI 12. ^{1}H NMR spectra of copolyesters of the P(T-iPr-F) series ($CDCl_3$/TFA-d 4:1 v/v). # marks signals of methyl ester end groups.

Calculation of terpolymer composition (in mol%)

from normalised signal intensities (I) of T (= $I(H_3)/4$), iPr (= $I(H_5 + H_6)/4$) and F (= $I(H_9+H_8+H_{14})/3$).

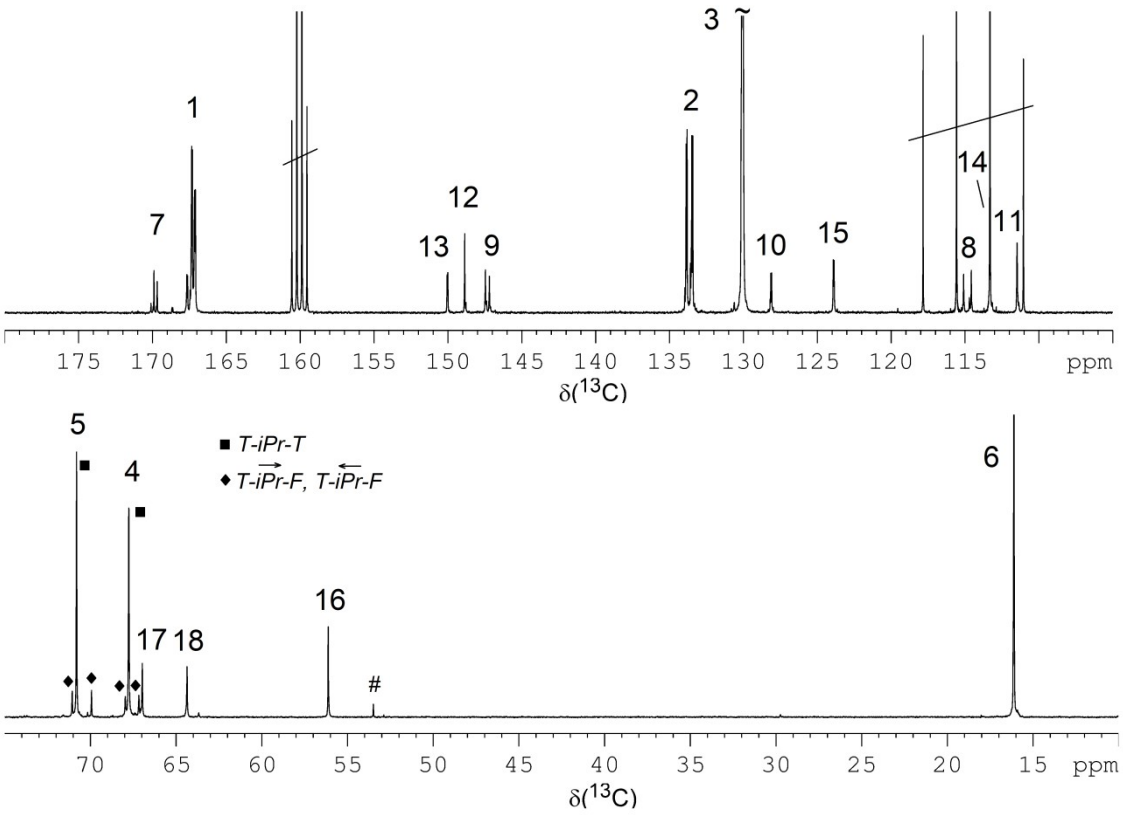


Figure ESI 13. ^{13}C NMR spectrum of P(T-iPr-F) with F content of 9 mol% ($CDCl_3$/TFA-d 4:1 v/v). Dyad signals are assigned for C_4 and C_5. The non-symmetric isopropyl unit leads to two T-iPr-F dyads, depending on whether the OCH is attached to T or F.

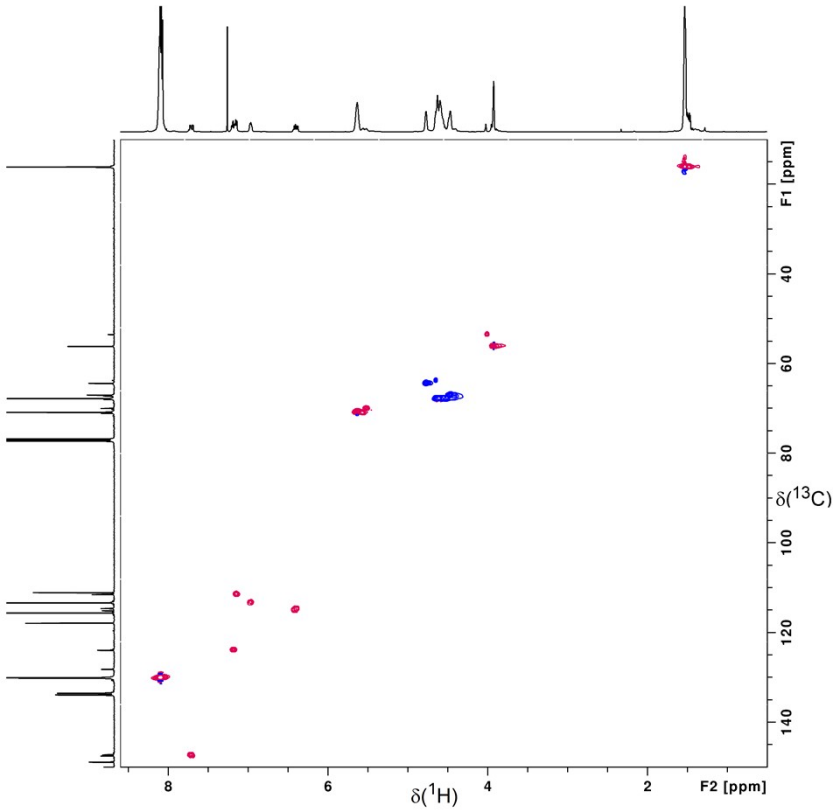
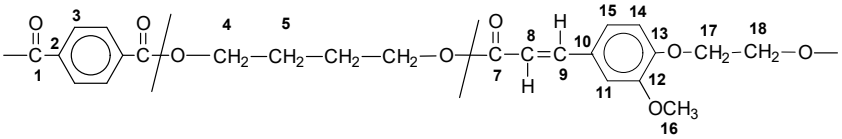


Figure ESI 14. Edited HSQC spectrum of P(T-iPr-F) with a F content of 9 mol% ($CDCl_3$/TFA-d 4:1 v/v). CH, CH_3 – red; CH_2 – blue.

2.2.5 P(T-B-F)



^{1}H NMR ($CDCl_3$/TFA-d 4:1 v/v): δ 8.13 (3), 7.72 (9), 7.21 (15), 7.12 (11), 6.98 (14), 6.42 (8), 4.79 ($18_{F\text{-}T}$), 4.66 ($18_{F\text{-}F}$), 4.60 – 4.30 (4, 17), 3.95 (16), 2.10 – 1.90 ppm (5).

^{13}C NMR ($CDCl_3$/TFA-d 4:1 v/v): δ 170.6 (7), 168.2 ($1_{T\text{-}B}$), 167.9 ($1_{T\text{-}F}$), 149.9 (13),148.8 (12), 146.9 (9), 133.8 (2), 130.0 (3), 128.3 (10), 123.8 (15), 115.2 (8), 113.4 (14), 111.6 (11), 67.0 (), 66.4 ($4_{B\text{-}T}$), 65.6 ($4_{B\text{-}F}$), 64.5 (18), 56.2 (16), 25.2 ppm (5).

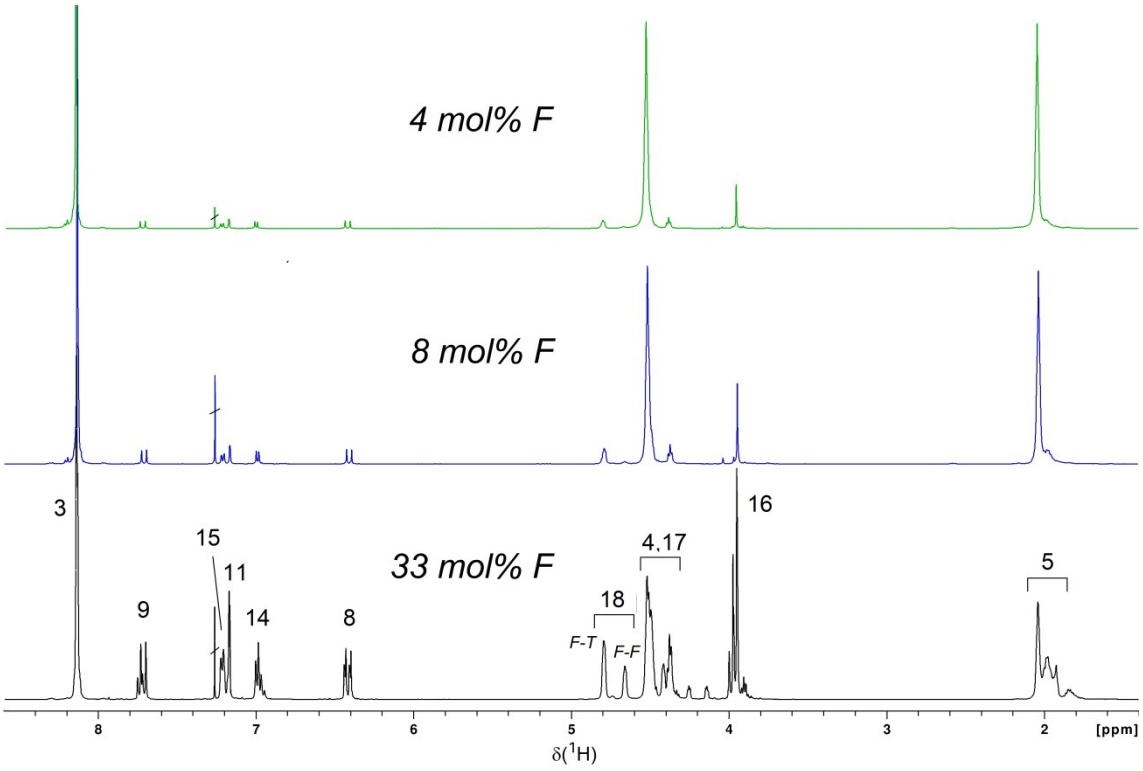


Figure ESI 15. ^{1}H NMR spectra of copolyesters of the P(T-B-F) series ($CDCl_3$/TFA-d 4:1 v/v). Dyad signals are assigned for H_{18}.

Calculation of terpolymer composition (in mol%)

from normalised signal intensities (I) of T (= $I(H_3)/4$), B (= $I(H_5)/4$) and F (= $I(H_9+H_8+H_{14})/3$).

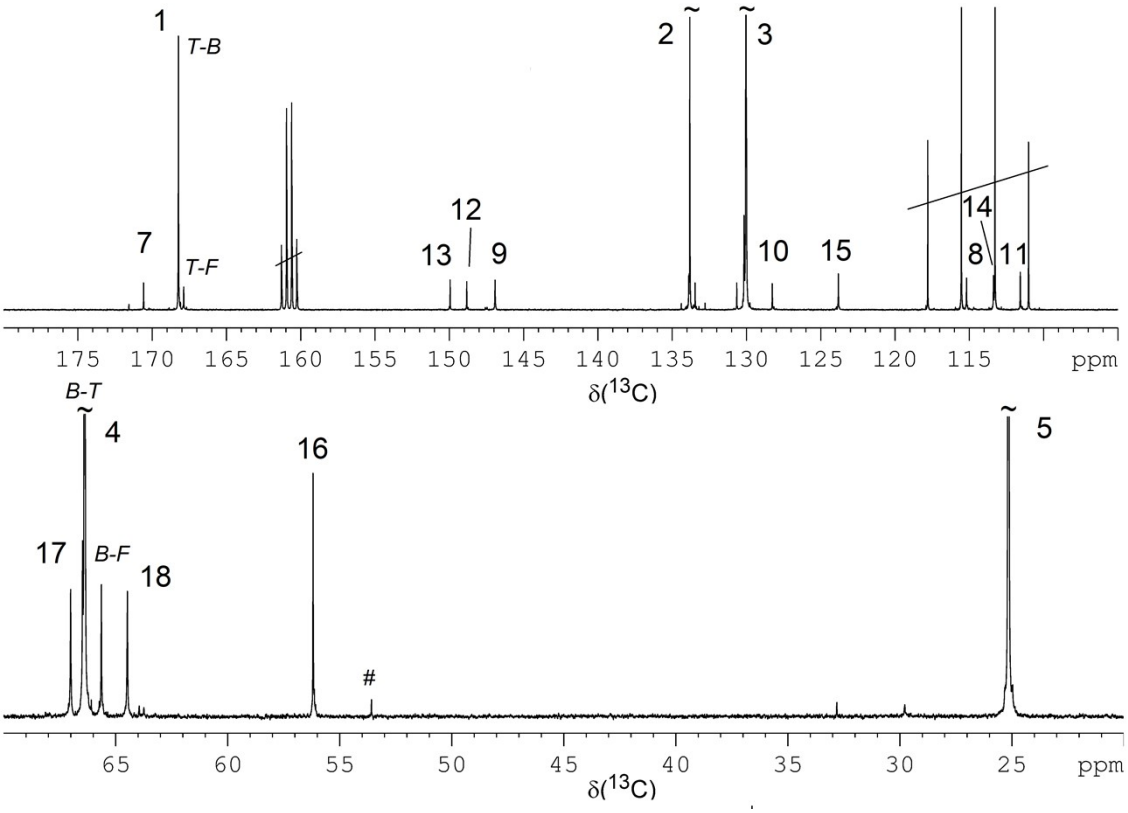


Figure ESI 16. ^{13}C NMR spectrum of P(T-B-F) with F content of 8 mol% ($CDCl_3$/TFA-d 4:1 v/v). Dyad signals are assigned for C_1 and C_4. # marks signal of methyl ester end group.

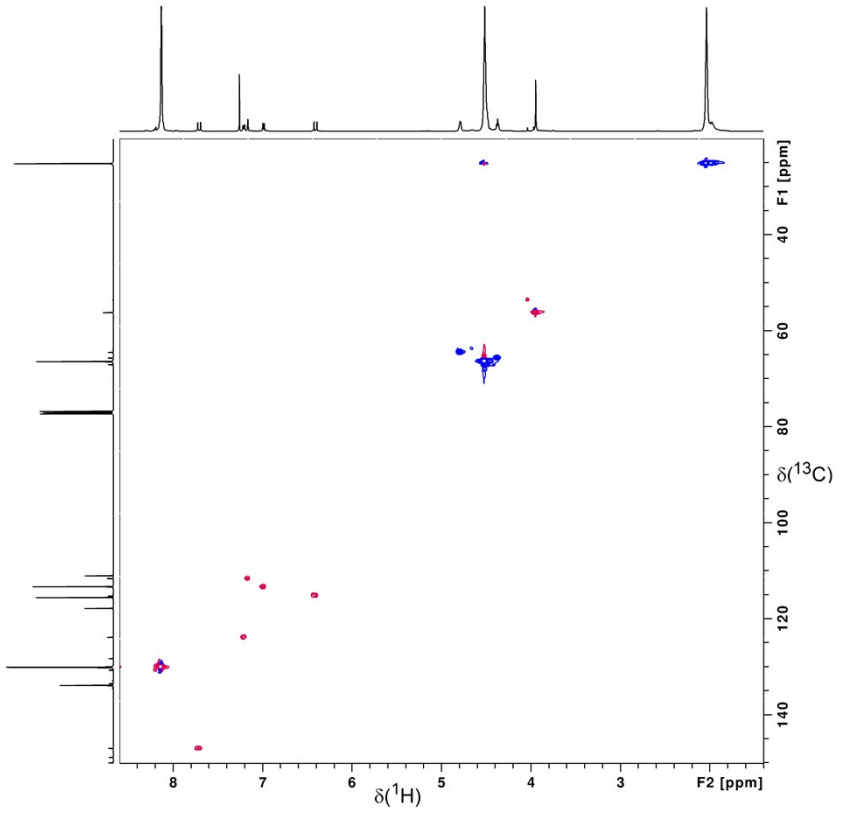
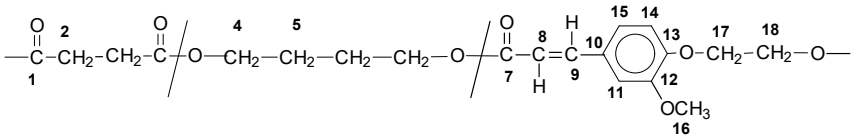


Figure ESI 17. Edited HSQC spectrum of P(T-B-F) with F content of 8 mol% ($CDCl_3$/TFA-d 4:1 v/v). CH, CH_3 – red; CH_2 – blue.

2.2.6 P(S-B-F)



^{1}H NMR (CDCl$_3$/TFA-d 4:1 v/v): δ 7.72 (9), 7.25 – 7.10 (11, 15), 6.94 (14), 6.41 (8), 4.66 (18$_{F\text{-}F}$), 4.54 (18$_{F\text{-}S}$), 4.45 – 4.15 (4, 17), 3.96 (16), 2.76 (2), 1.95 – 1.65 ppm (5).

^{13}C NMR (CDCl$_3$/TFA-d 4:1 v/v): δ 174.8 (1$_{S\text{-}B}$), 174.3 (1$_{S\text{-}F}$), 170.1 (7$_{F\text{-}B}$), 169.7 (7$_{F\text{-}F}$), 150.0 (13), 148.9 (12), 146.8 (9), 128.0 (10), 123.5 (15), 114.9 (8), 113.2 (14), 111.1 (11), 66.9 (17), 66. 0 – 65.2 (4), 63.7 (18), 56.0 (16), 29.0 (2), 24.8 ppm (5).

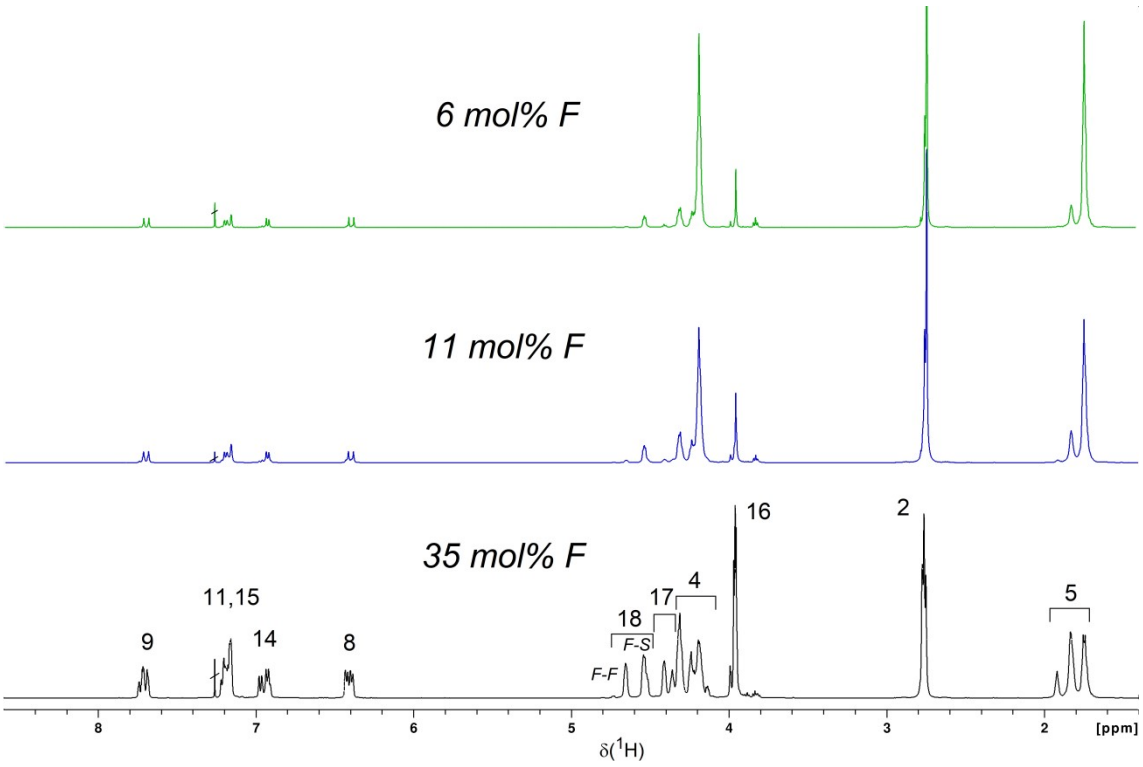


Figure ESI 18. ^{1}H NMR spectra of copolyesters of the P(S-B-F) series (CDCl$_3$/TFA-d 4:1 v/v). Dyad signals are assigned for H$_{18}$.

Calculation of terpolymer composition (in mol%)

from normalised signal intensities (I) of S (= I(H$_2$)/4), B (= I(H$_5$)/4) and F (= I(H$_9$+H$_8$+H$_{14}$)/3).

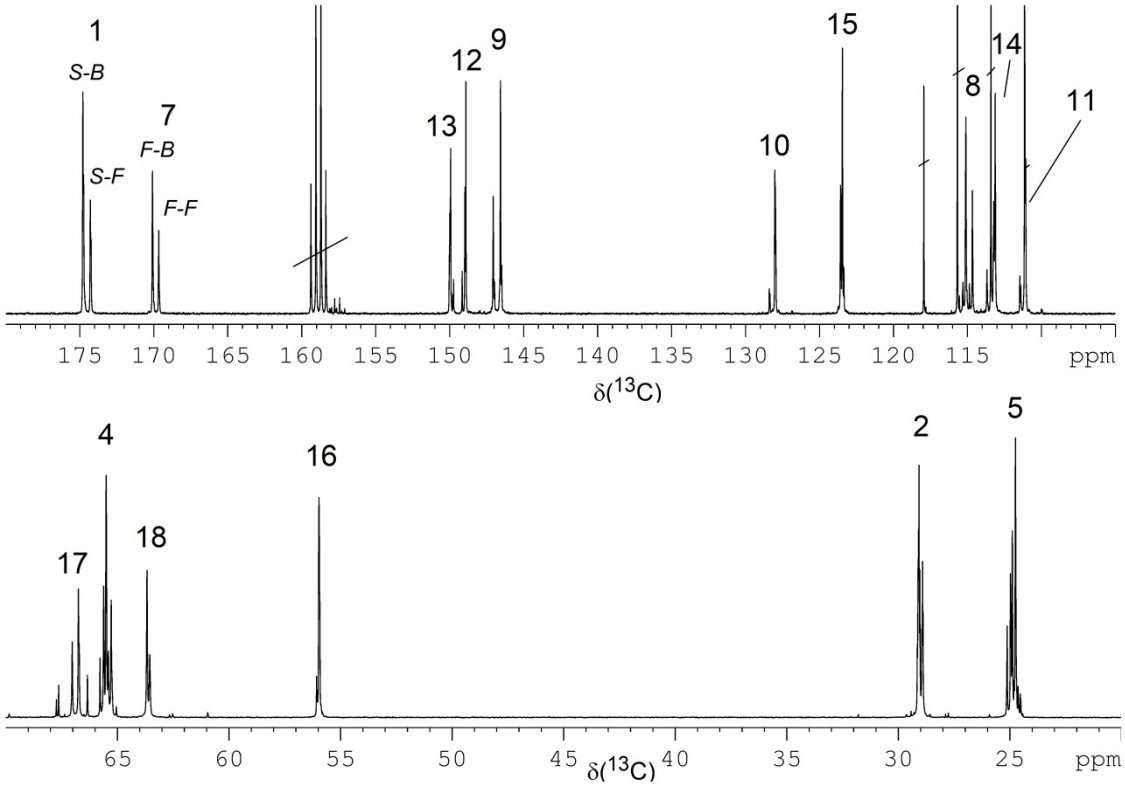


Figure ESI 19. ^{13}C NMR spectrum of P(S-B-F) with a F content of 35 mol% ($CDCl_3$/TFA-d 4:1 v/v). Dyad signals are assigned for C_1 and C_7.

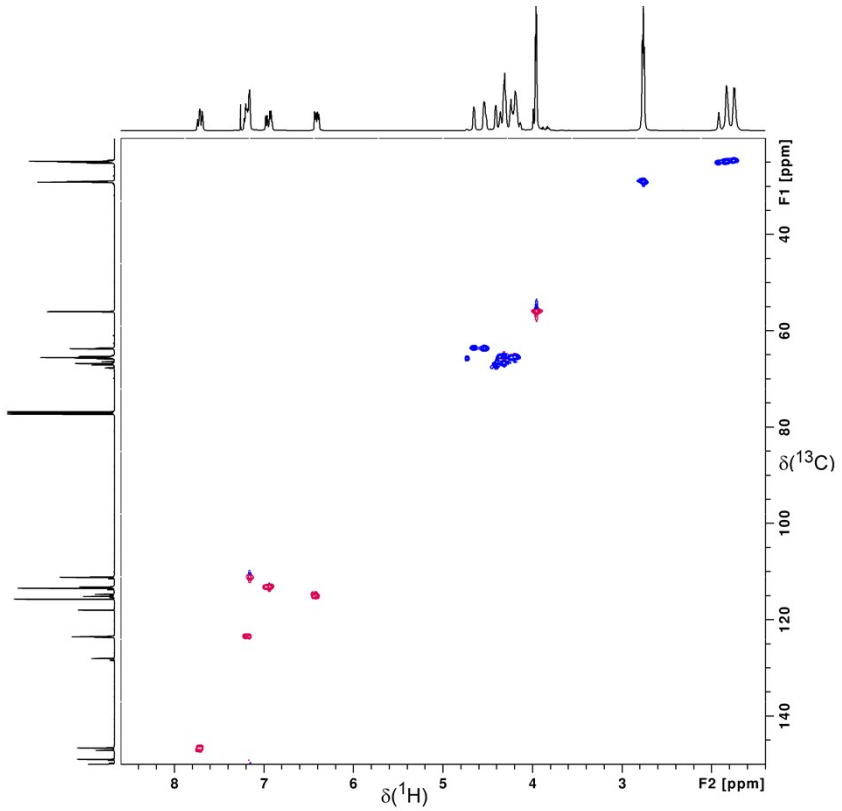


Figure ESI 20. Edited HSQC spectrum of P(S-B-F) with a F content of 35 mol% ($CDCl_3$/TFA-d 4:1 v/v). CH, CH_3 – red; CH_2 – blue.

3. SEC elution curves

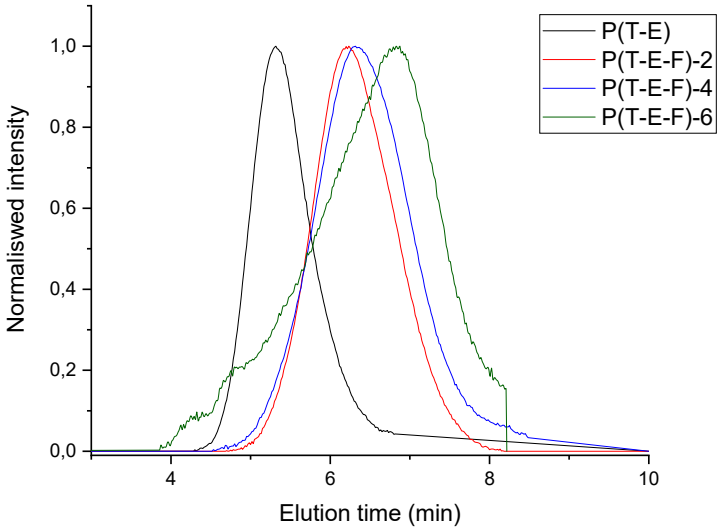


Figure ESI 21. SEC elution curves of the copolyesters of the P(T-E-F) series.

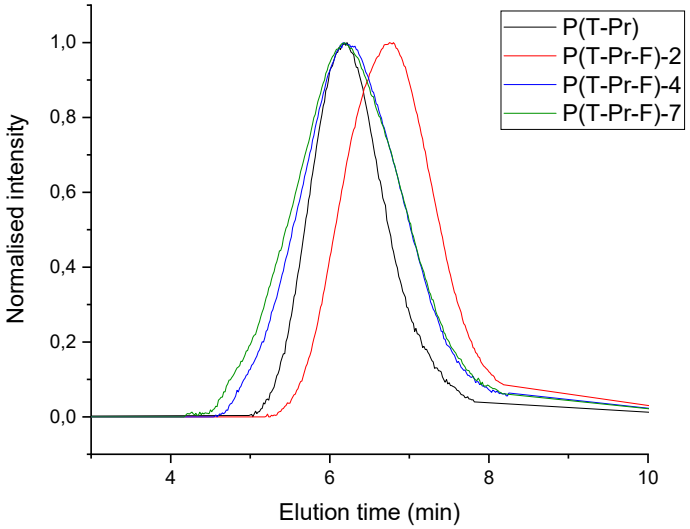


Figure ESI 22. SEC elution curves of the copolyesters of the P(T-Pr-F) series.

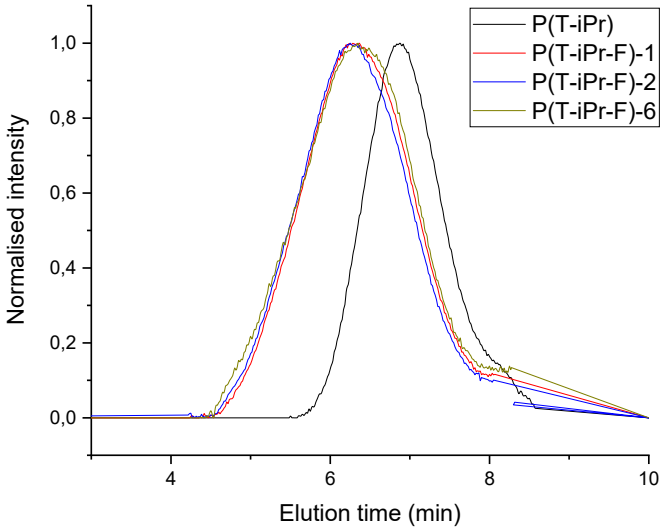


Figure ESI 23. SEC elution curves of the copolyesters of the P(T-iPr-F) series

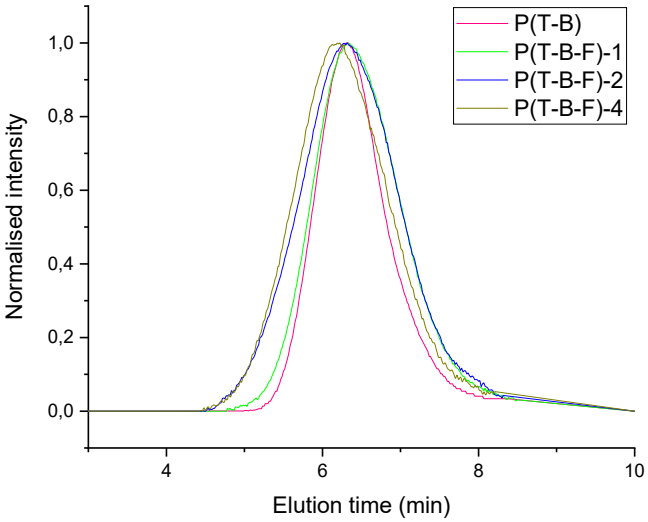


Figure ESI 24. SEC elution curves of the copolyesters of the P(T-B-F) series.

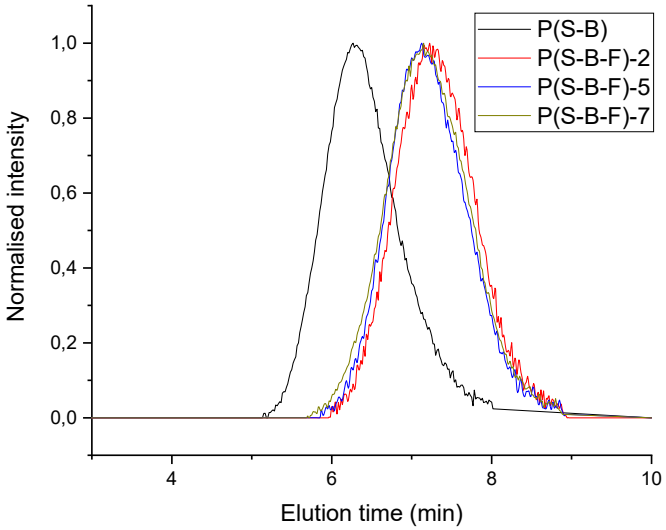


Figure ESI 25. SEC elution curves of the copolyesters of the P(S-B-F) series

4. Wide-angle X-ray scattering curves

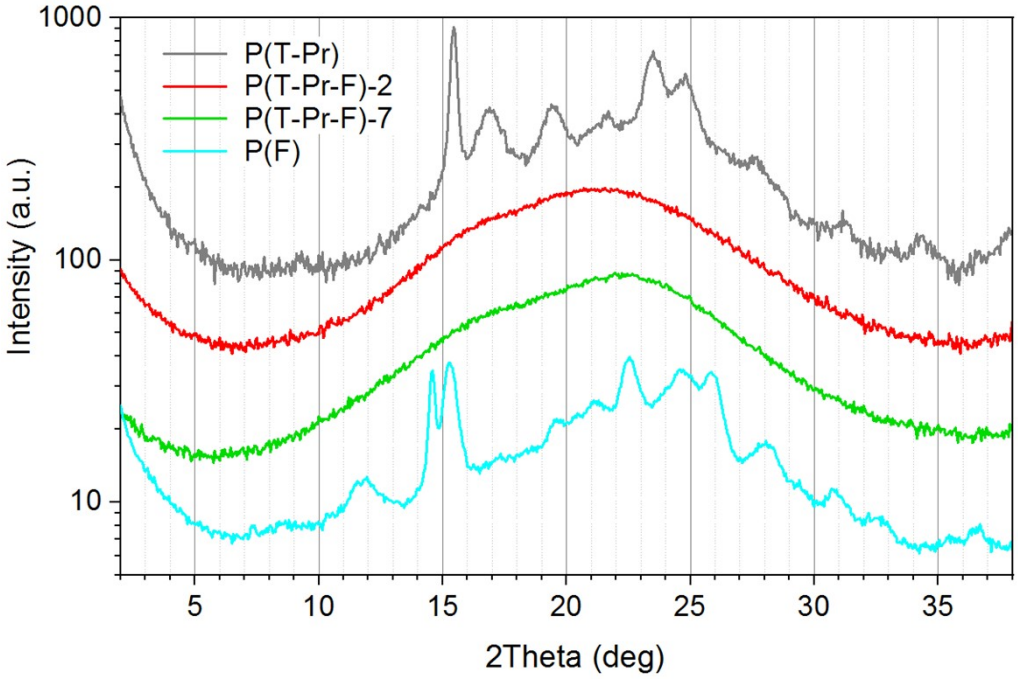


Figure ESI 26. WAXS curves of copolyesters of the P(T-Pr-F) series.

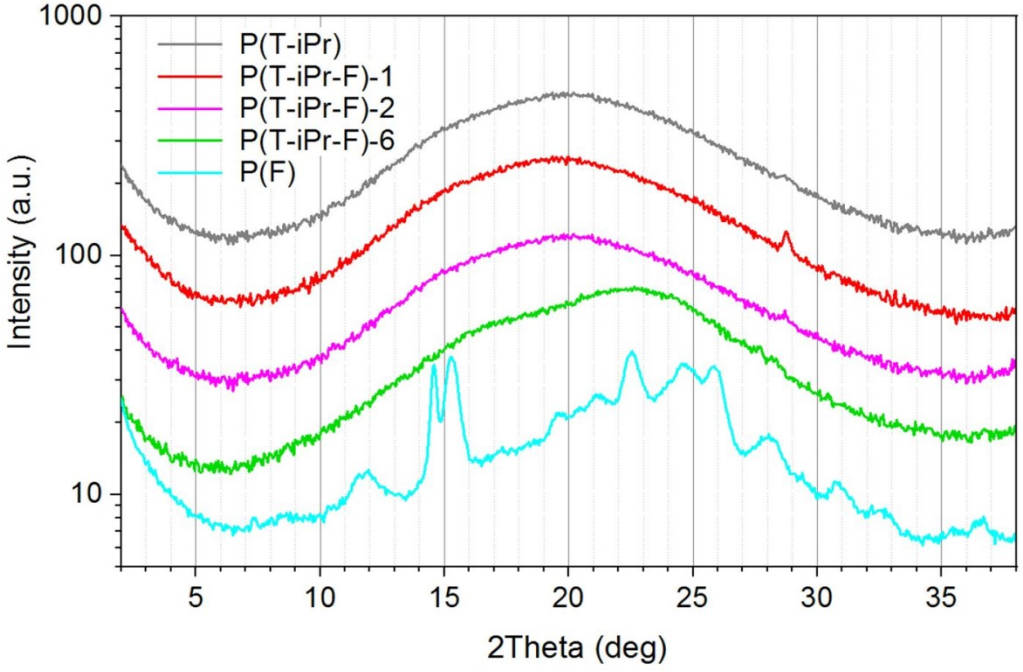


Figure ESI 27. WAXS curves of copolyesters of the series P(T-iPr-F).

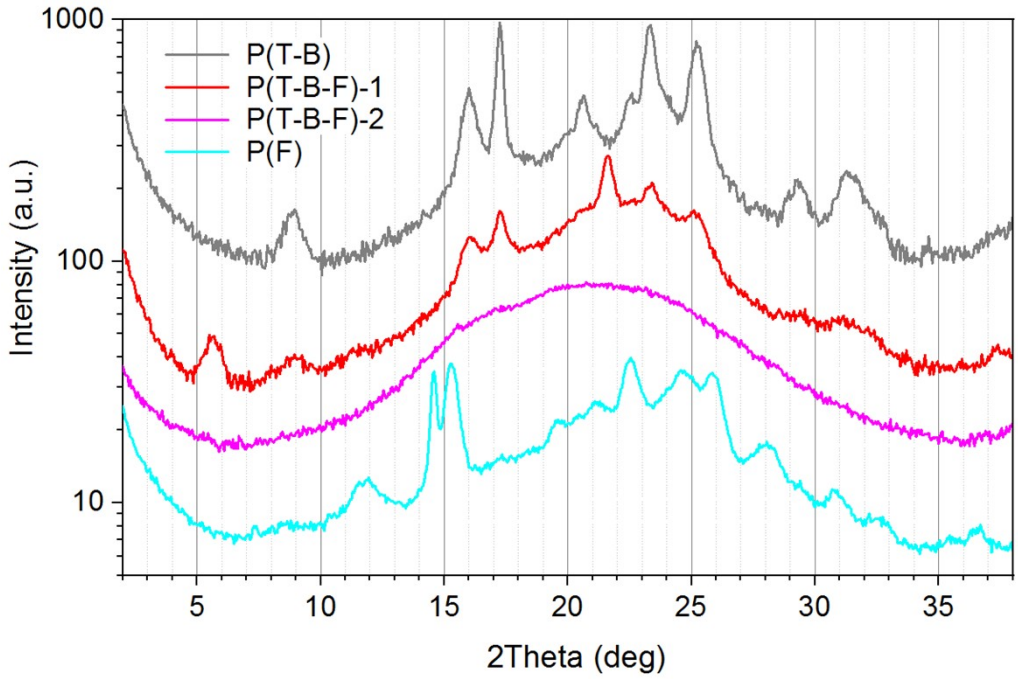


Figure ESI 28. WAXS curves of copolyesters of the series P(T-B-F).

5. DSC curves

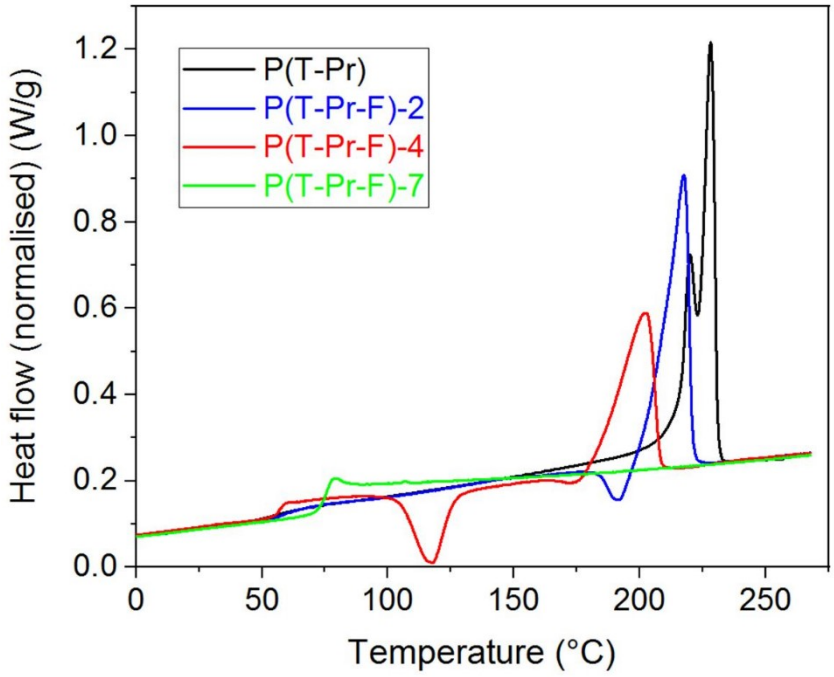


Figure ESI 29. DSC curves (2nd heating) of the terpolyesters of the P(T-Pr-F) series.

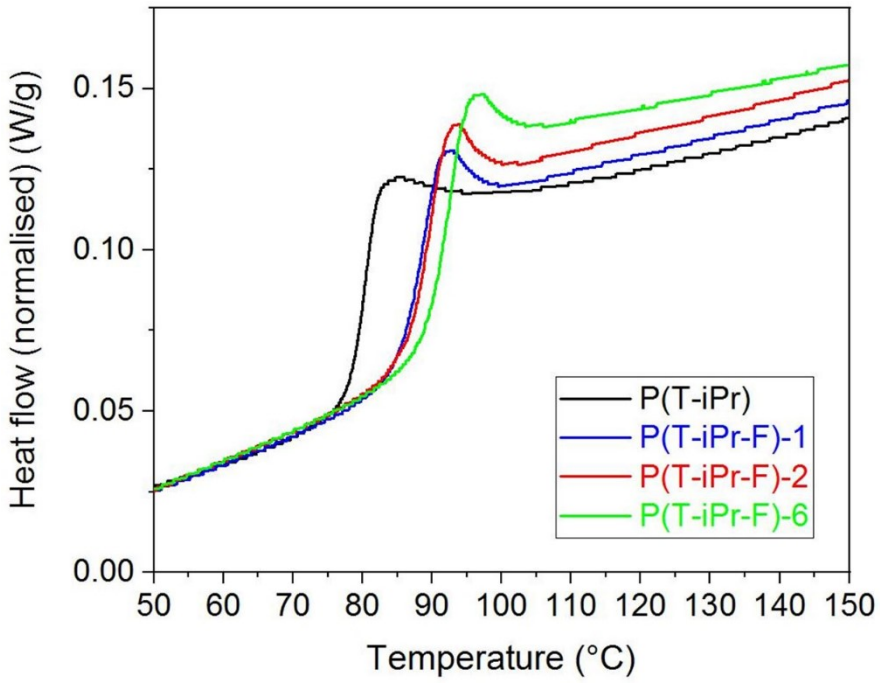


Figure ESI 30. DSC curves (2nd heating) of the terpolyesters of the P(T-iPr-F) series.

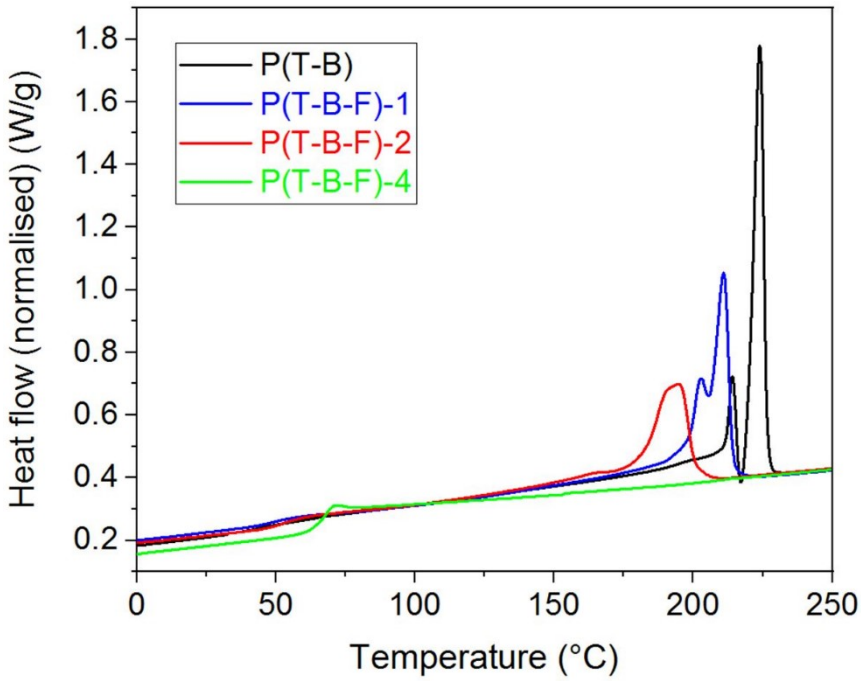


Figure ESI 31. DSC curves (2nd heating) of the terpolyesters of the P(T-B-F) series.

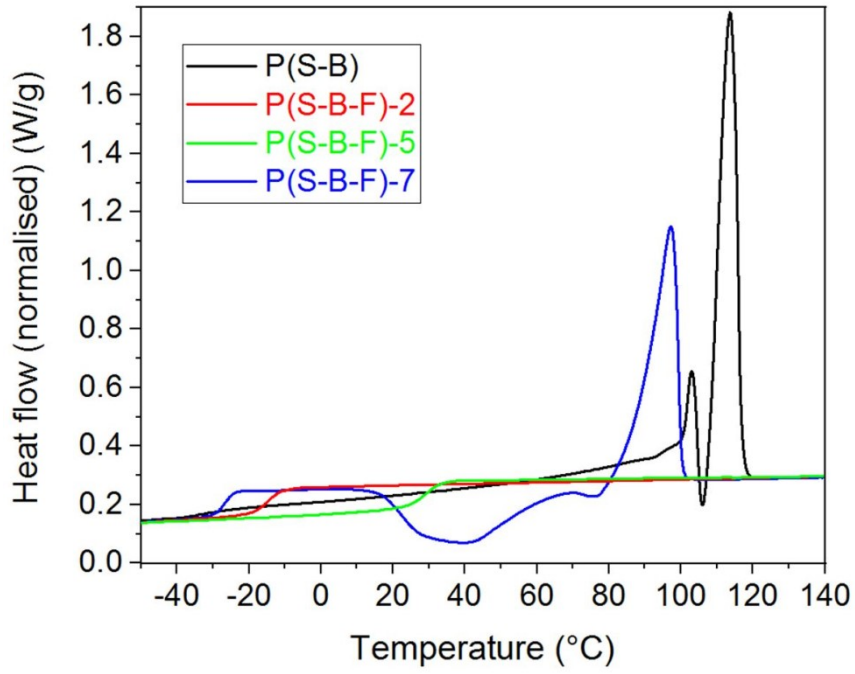


Figure ESI 32. DSC curves (2nd heating) of the terpolyesters of the P(S-B-F) series.

6. TGA data

Table ESI 1. TGA data (decomposition maximum T_{max} and residue at 800 °C) of the copolyesters studied.

Polymer	Molar content F (mol%)	$T_{max, TGA}$ (°C)	Residue at 800 °C (wt.-%))
P(T-E) [PET]	0	433	19.0
P(T-E-F)-2	4.3	434	18.0
P(T-E-F)-4	8.3	433	18.0
P(T-E-F)-6	34.6	425	18.0
P(T-Pr) [PTT]	0	400	8.0
P(T-Pr-F)-2	4.5	402	12.0
P(T-Pr-F)-4	8.9	404	15.5
P(T-Pr-F)-7	33.4	410	23.5
P(T-iPr)	0	373	6.0
P(T-iPr-F)-1	4.5	376	12.0
P(T-iPr-F)-2	9.1	377	14.0
P(T-iPr-F)-6	33.3	380/408	22.0
P(T-B) [PBT]	0	399	9.5
P(T-B-F)-1	4.3	399	12.5
P(T-B-F)-2	7.7	399	16.5
P(T-B-F)-4	32.7	409	~20
	S-diol/F		
P(S-B) [PBS]	0	403	1.3
P(S-B-F)-2	6.3	397	7.0
P(S-B-F)-5	11.3	399	9.0
P(S-B-F)-7	35.1	408	16.5
P(F)	100	235/385	31.0

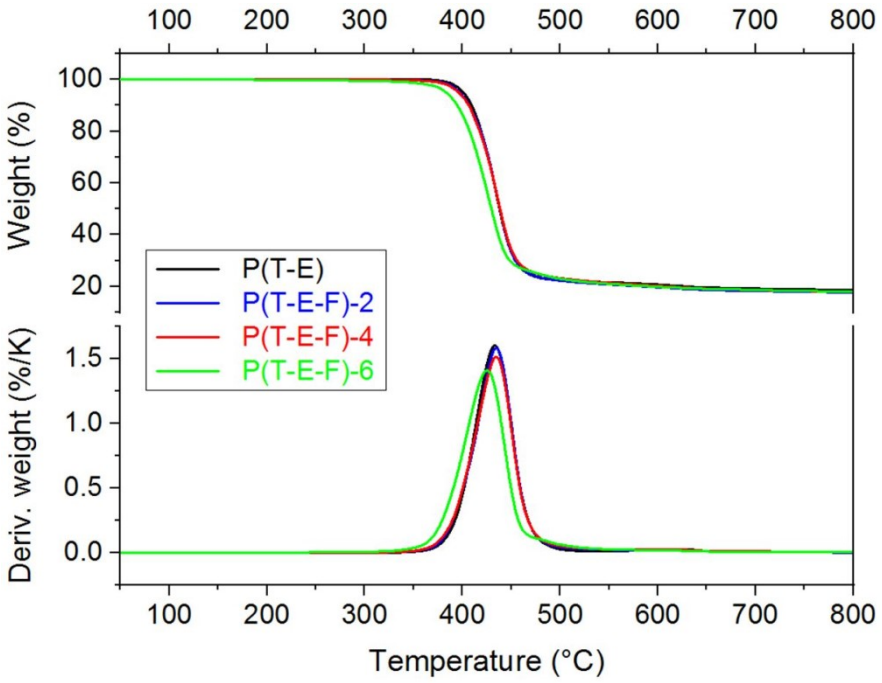


Figure ESI 33. TGA curves of the terpolyesters of series P(T-E-F).

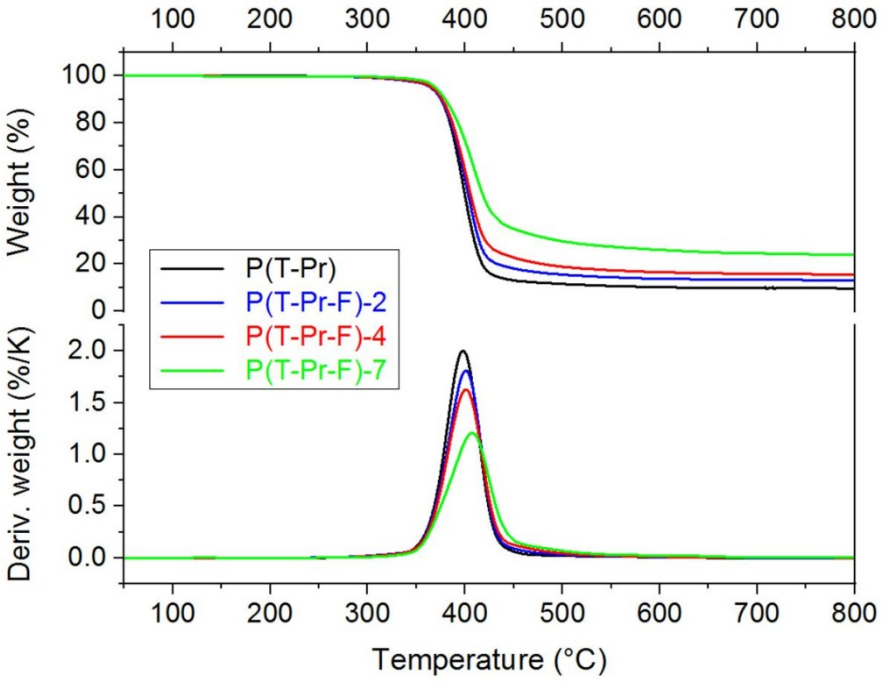


Figure ESI 34. TGA curves of the terpolyesters of series P(T-Pr-F).

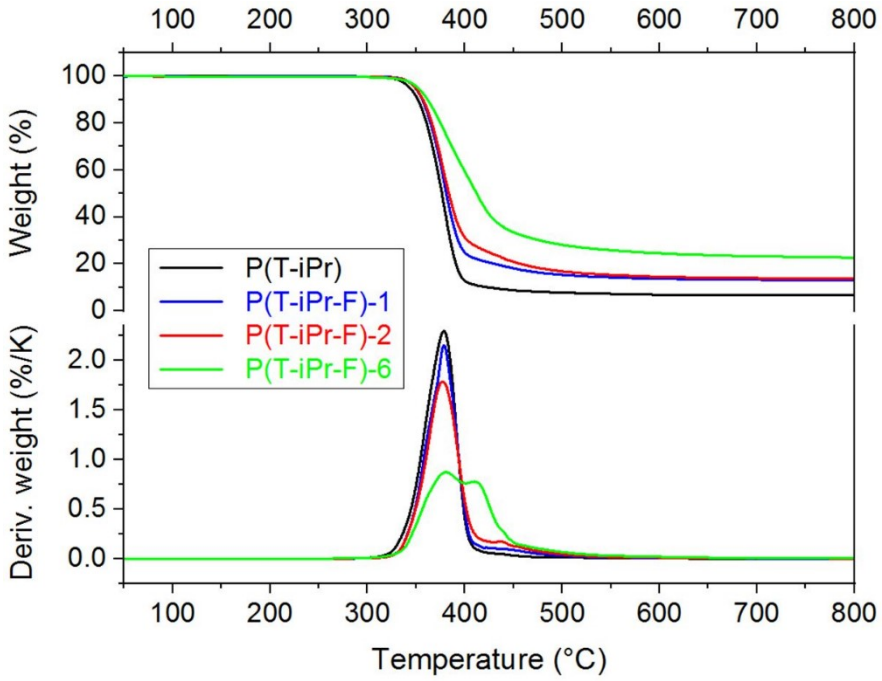


Figure ESI 35. TGA curves of the terpolyesters of series P(T-iPr-F).

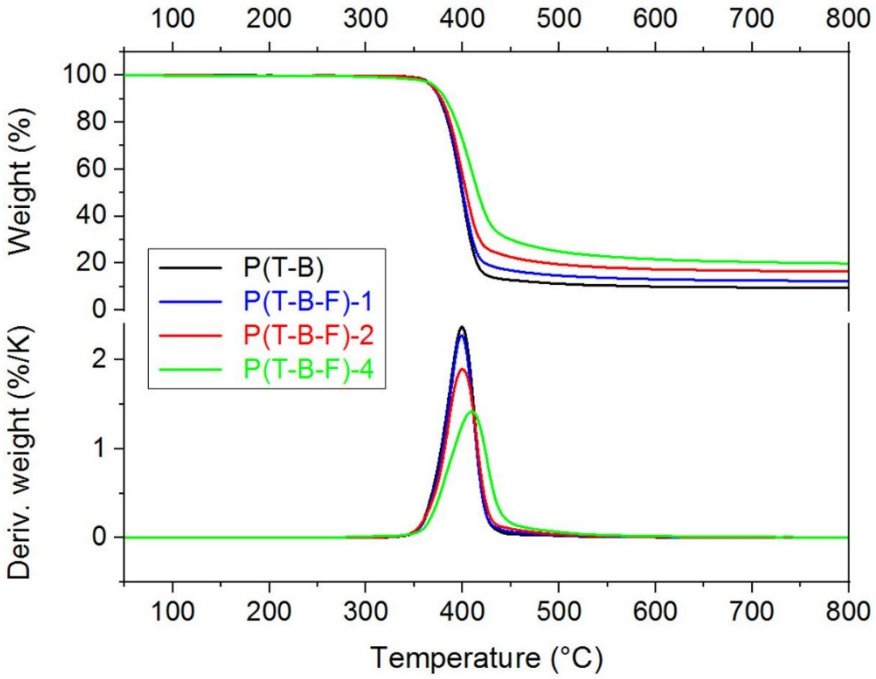


Figure ESI 36. TGA curves of the terpolyesters of series P(T-B-F).

7. Photographic images of copolyester films EB irradiated with different doses

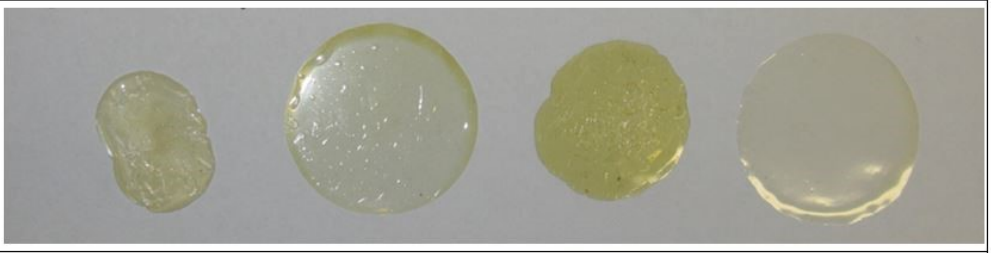
	Sample			
Dose (kGy)	P(T-E-F)-2	P(T-E-F)-4	P(T-E-F)-6	P(T-E)
0				
300				
400				
500				

Figure ESI 37. Photographic images of melt-pressed terpolyester films of series P(T-E-F) after EB treatment with different EB doses.

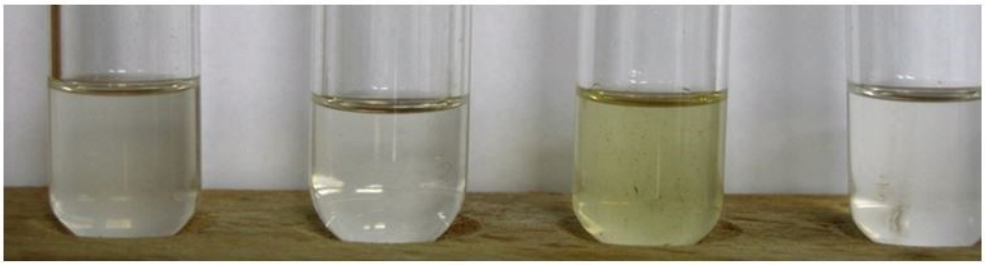
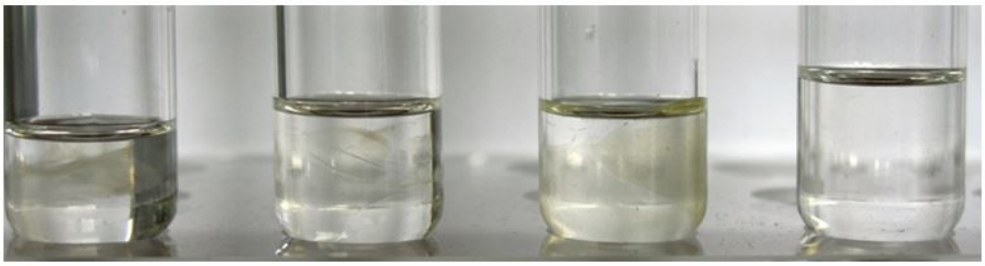
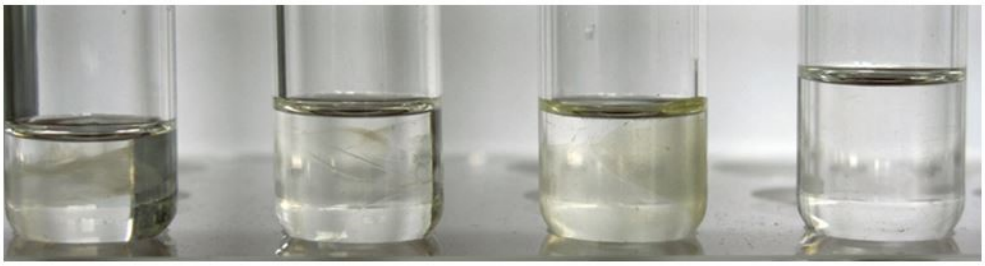
	Sample			
Dose (kGy)	P(T-E-F)-2	P(T-E-F)-4	P(T-E-F)-6	P(T-E)
0				
300				
400				
500				

Figure ESI 38. Photographic images of swelling experiments of EB treated terpolyesters in PFP/$CHCl_3$.

Figure ESI 39. Time dependent swelling behavior of P(T-B) and P(T-B-F)-1 after EB treatment with different doses in PFP/$CHCl_3$.

8. Raman spectra

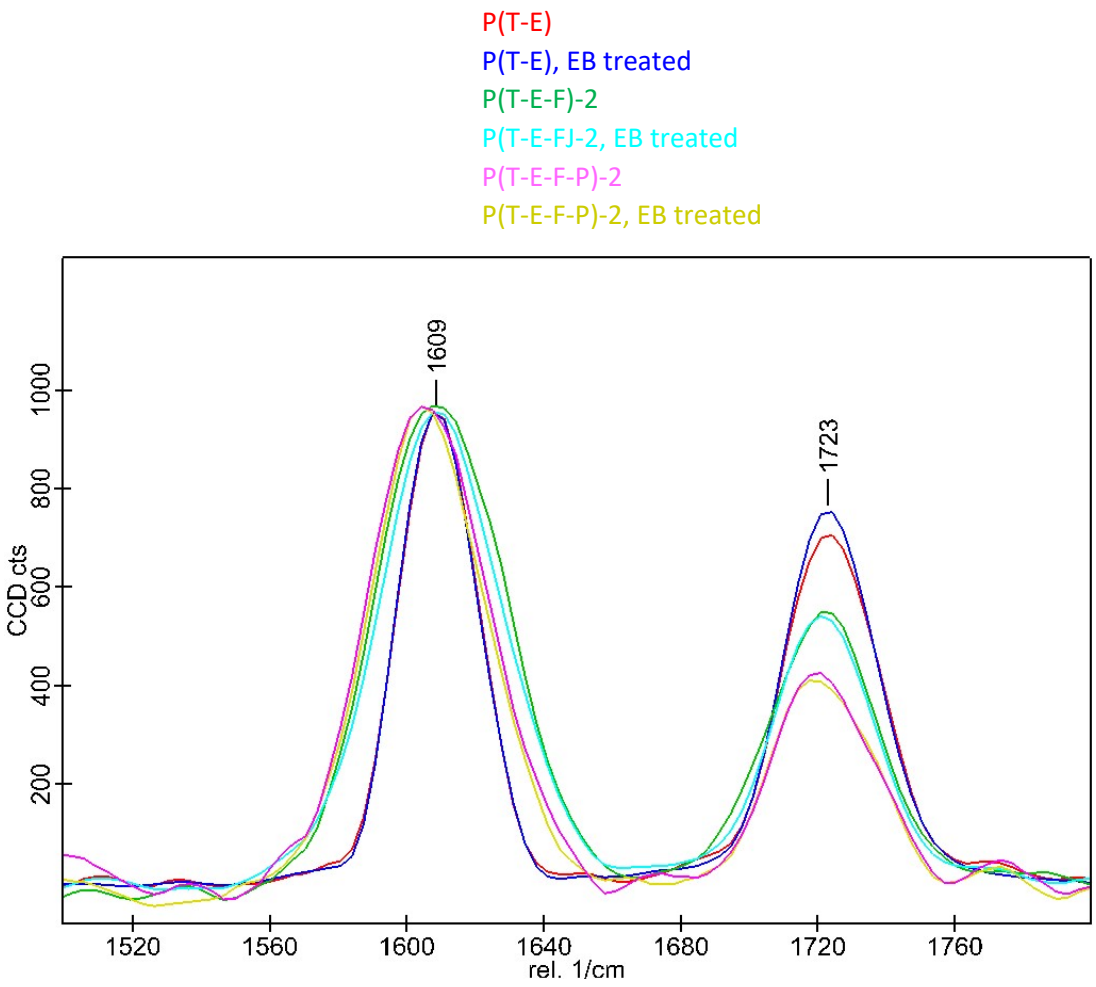


Figure ESI 40. Raman spectra (1500 – 1800 cm^{-1}) of terpolyesters of the P(T-E-F) series before and after EB treatment

10. Mechanical tests

Table ESI 2. Results of Shore D tests on melt-pressed terpolyester samples (average of 10 measurements).

Sample	Shore D	s
P(T-E) (PET)	80.39	1.03
P(T-E) (PET), 600 kGy	81.36	1.66
P(T-E-F)-2	80.73	0.84
P(T-E-F)-2, 600 kGy	80.71	1.35

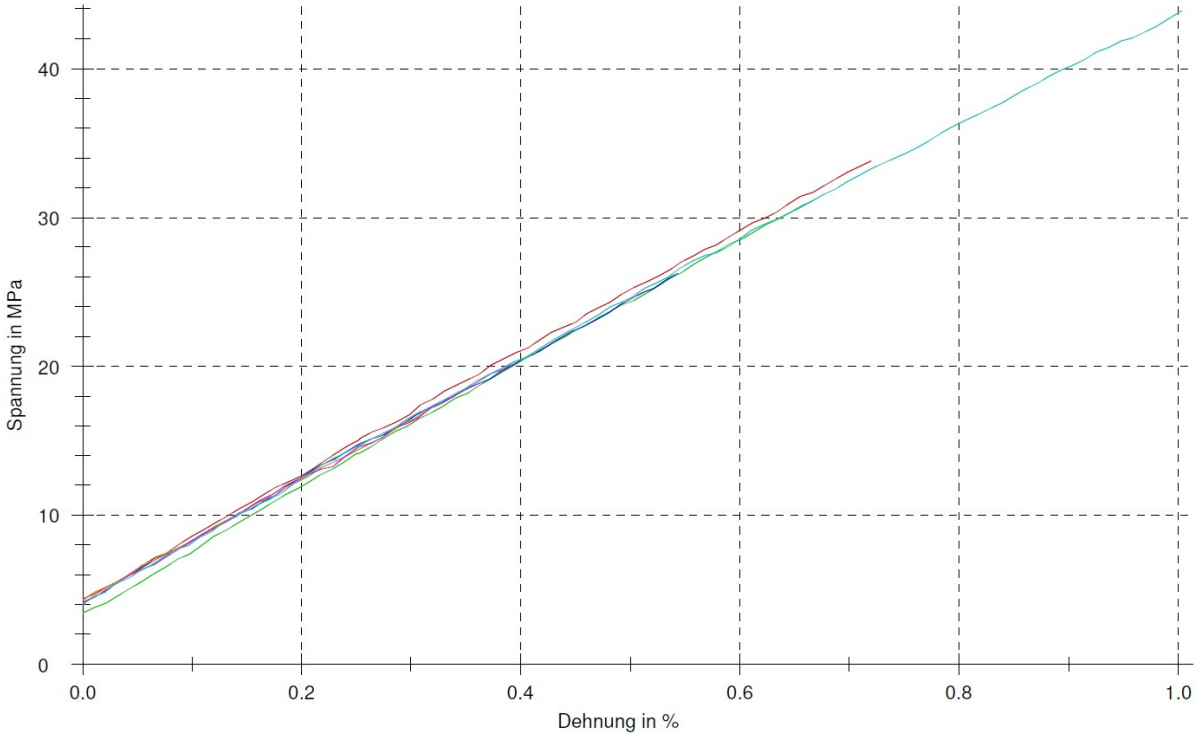


Figure ESI 41. Stress-strain curves of P(T-E-F)-2 fibres, as-spun.

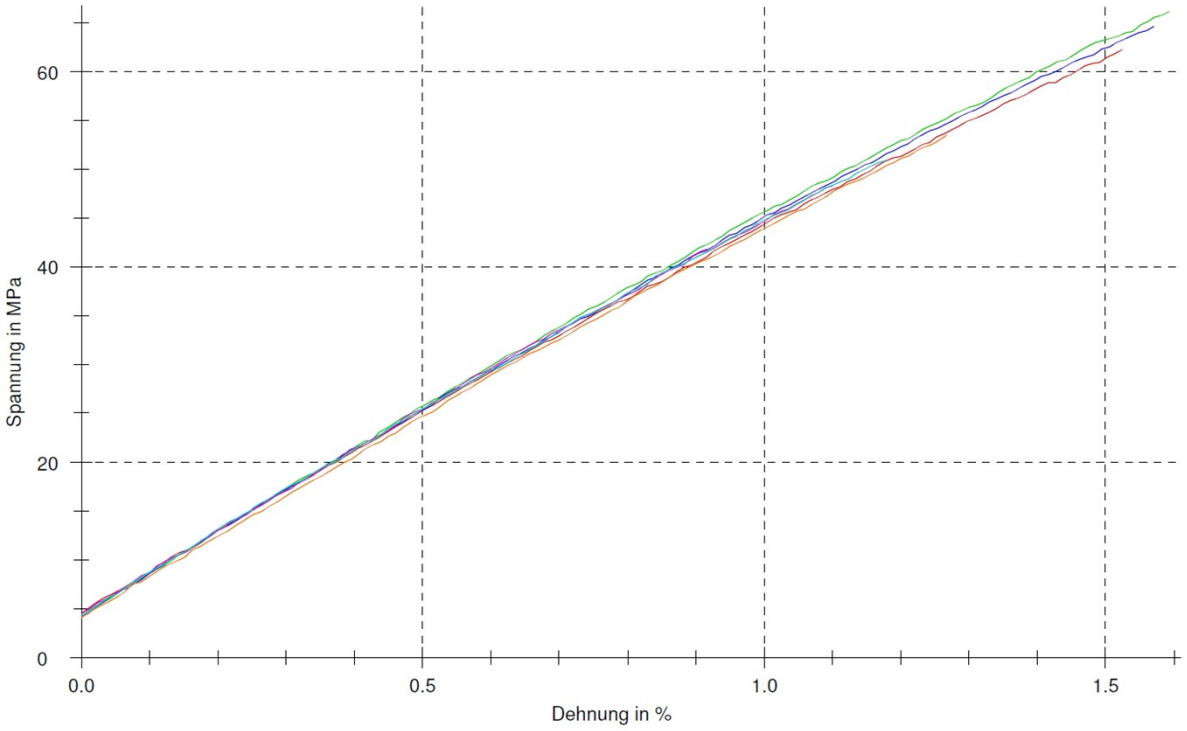


Figure ESI 42. Stress-strain curves of P(T-E-F)-2 fibres, EB treated (600 kGy).