Small-scale screening of novel biobased monomers: the curious case of 1,3-cyclopentanediol

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**Reactor block design**

The temperature consistency in the reactor was tested by measuring the temperature on 3 different points in the reactor: temperature sensor in the bottom part, in the side part, and inside in oil in a HPLC vial. There was consistently a small deviation in temperature inside the reactor as compared to the set & bottom temperature, which is caused by heat loss of the reactor itself to the surrounding environment. This temperature-loss was compensated for in the settings: *i.e.* for a desired polycondensation temperature of 220 °C, the temperature was set to 228 °C.

| Set temp (°C) | Control bottom | Control side | Oil in vials |
|--------------|----------------|--------------|--------------|
| 100 °C       | 98 °C          | 92 °C        | 92 °C        |
| 150 °C       | 148 °C         | 140 °C       | 142 °C       |
| 200 °C       | 198 °C         | 186 °C       | 188 °C       |
| 250 °C       | 246 °C         | 230 °C       | 237 °C       |

The reactor was validated for polycondensation experiments by the polymerization of a known polymer: poly(ethylene terephthalate). First a consistency check was performed by polymerizing batches of 10 mg over 3 runs (Table 3), and secondly the effect of loading on the polycondensation was checked (Table 4). Overall, the polycondensation is considered to perform consistently well in order to perform polycondensation reactions on the novel polyesters described in this work.
**GC data**

Chiral GC data for cis/trans ratio determination of 1,3-cyclopentanediol.

**Figure 1.** Chiral GC chromatogram on the commercial batch of 1,3-cyclopentanediol.

| Peak | Fill | Peak Name | t_R | t_D | t_S | H (V) | H_{norm} | A (V.s) | A_{norm} | W_0.1 | Asym | Effic | Res |
|------|------|-----------|-----|-----|-----|-------|----------|---------|----------|-------|------|-------|-----|
| 1    |      | 29.14     | 29.06| 29.33|    | 0.01  | 14.55   | 0.04    | 12.12    | 0.12  | 1.75 | 1137189|
| 2    |      | 29.97     | 29.93| 30.02| 0.03 | 46.61 | 0.11    | 37.81   |          |       |      |       |     |
| 3    |      | 30.05     | 30.02| 30.48| 0.02 | 37.45 | 0.14    | 47.77   |          |       |      |       |     |
| 4    |      | 32.97     | 32.78| 33.18| 0.00 | 1.39  | 0.01    | 2.30    | 0.26     | 1.11  | 292616|

**Figure 2.** Chiral GC data on the commercial batch of 1,3-cyclopentanediol, with 12.12% cis, and 85.58% trans.
Detailed synthesis of trimers

A generally applicable synthesis method for the preparation of trimer pre-polymers has been developed based on previously reported synthesis method. The syntheses were performed in anhydrous conditions. A molar ratio of 3:1 diol:di-acid was used. A typical reaction is described: A solution of 9 mmol diol, 7 mmol pyridine, and catalytic amount of DMAP in 5 mL anhydrous THF was stirred in an ice bath in a 25 mL 2-neck round-bottom flask equipped with a condenser. At 0 °C, under N2-flow, a solution of 3 mmol di-acid chloride in 3 mL anhydrous THF was added dropwise. After stirring the reaction mixture overnight, the THF was removed in vacuo. The product was isolated by dissolving the mix in CHCl3.

Trimer 1,3-ethyleneglycol-terephthalate

The product was obtained as white solids (0.9 gr, 72% yield). 1H NMR (CDCl3, 300 MHz): δ 8.11 (bs, 4H), 4.95 (m, 0.93H), 4.69 (m, 2.11H), 4.31 (m, 1.80H), 3.70 (m, 1.81H). 13C NMR (CDCl3, 300 MHz): δ 165.5 (C=O), 134.4 & 133.79 (O=C-C), 130.1 & 130.0 (C=C), 67.5 (HO-CH2-CH2-O-C), 63.7 (C-O-CH2-CH2-O-C), 59.4 (HO-CH2-CH2-O-C).

Trimer 1,3-cyclopentanediol-terephthalate

The product was obtained as white solids (5.05 gr, 76% yield). 1H NMR (CDCl3, 300 MHz): δ 8.04 (s, 4H), 5.52 (bs, 0.28H), 5.39 (bs, 1.59H), 5.23 (bs, 0.23 H), 4.67 (bs, 1.77 H), 2.8 (m, 2.49H), 1.95 (m, 5.43H), 1.72 (m, 2.23H), 1.55 (m, 1.73H). 13C NMR (CDCl3, 300 MHz): δ 165.2 (C=O), 77.2 (CH-OR ring) 70.8 (CH-OH ring), 42.4 (OH2 ring), 33.6 (CH2 ring), 30.5 (CH2 ring).

Trimer 1,3-cyclopentanediol-furanoate

The product was obtained as white solids (1.99 gr, 62% yield). 1H NMR (CDCl3, 300 MHz): δ 7.16 (m, 2H), 5.53 (m, 1.90H), 5.39 (m, 0.16 H), 4.55 (m, 1.30H), 4.40 (m, 0.16H), 2.32 (m, 2.59H), 2.13 (m, 6.32H), 1.87 (m, 2.27H), 1.70 (m, 1.36H). 13C NMR (CDCl3, 300 MHz): δ 157.7 (C=O), 146.7 (C-O, furan ring) 118.2 (C-C, furan ring) 77.4 (CH-OR ring) 72.1 (CH-OH ring), 42.2 (CH2 ring), 33.5 (CH2 ring), 30.3 (OH2 ring).

Trimer 1,3-cyclopentanediol-furanoate, -8% cis

The product was obtained as white solids (1.12 gr, 67% yield). After drying at 110 °C discoloration occurred, the product was isolated by dissolving the mix in CHCl3, filter out the brown solids, and reduce the CHCl3 in vacuo, to re-obtain the product as white solids (0.64 gr, 38% yield). 1H NMR (CDCl3, 300 MHz): δ 7.12 (m, 2H), 5.46 (m, 2.27H), 4.60 (m, 1.74H), 4.51 (m, 0.16H), 2.22 (m, 2.53H), 2.12 (m, 5.91H), 1.85 (m, 2.56H), 1.73 (m, 1.82H). 13C NMR (CDCl3, 300 MHz): δ 158.4 (C=O), 146.8 (C-O, furan ring) 118.7 (C-C, furan ring) 79.7 (CH-OR ring) 73.2 (CH-OH ring), 41.6 (CH2 ring), 32.8 (CH2 ring), 30.3 (OH2 ring).

Trimer 1,3-cyclopentanediol-furanoate, -20% cis

The product was obtained as off-white solids (1.34 gr, 80% yield). After drying at 110 °C discoloration occurred, the product was isolated by dissolving the mix in CHCl3, filter out the brown solids, and reduce the CHCl3 in vacuo, to re-obtain the product as off-white solids (0.88 gr, 52% yield). 1H NMR (CDCl3, 300 MHz): δ
7.12 (m, 2H), 5.46 (m, 2.27H), 4.60 (m, 1.74H), 4.51 (m, 0.16H), 2.22 (m, 2.53H), 2.12 (m, 5.91H), 1.85 (m, 2.56H), 1.73 (m, 1.82H). \(^{13}\)C NMR (CDCl\(_3\), 300 MHz): \(\delta\) 158.4 (C=O), 146.8 (C-O, furan ring) 118.7 (C-C, furan ring) 79.7 (CH-OR) 73.2 (CH-OH ring), 41.6 (CH\(_2\) ring), 32.8 (CH\(_2\) ring), 30.3 (CH\(_2\) ring).

**Trimer 1,3-cyclopentanediol-furanoate, -30% cis**

The product was obtained as light brown solids (1.37 gr, 82% yield). After drying at 110 °C discoloration occurred, the product was isolated by dissolving the mix in CHCl\(_3\), filter out the brown solids, and reduce the CHCl\(_3\) in vacuo, to re-obtain the product as light brown solids (0.91 gr, 54% yield).

\(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.12 (m, 2H), 5.46 (m, 2.27H), 4.60 (m, 1.74H), 4.51 (m, 0.16H), 2.22 (m, 2.53H), 2.12 (m, 5.91H), 1.85 (m, 2.56H), 1.73 (m, 1.82H). \(^{13}\)C NMR (CDCl\(_3\), 300 MHz): \(\delta\) 158.4 (C=O), 146.8 (C-O, furan ring) 118.7 (C-C, furan ring) 79.7 (CH-OR) 73.2 (CH-OH ring), 41.6 (CH\(_2\) ring), 32.8 (CH\(_2\) ring), 30.3 (CH\(_2\) ring).

**Trimer 1,3-cyclopentanediol-furanoate, -40% cis**

The product was obtained as yellow oil (0.98 gr, 87% yield). After drying at 110 °C discoloration occurred, the product was isolated by dissolving the mix in CHCl\(_3\), filter out the brown solids, and reduce the CHCl\(_3\) in vacuo, to re-obtain the product as light brown solids (0.48 gr, 43% yield). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.12 (m, 2H), 5.46 (m, 2.27H), 4.60 (m, 1.74H), 4.51 (m, 0.16H), 2.22 (m, 2.53H), 2.12 (m, 5.91H), 1.85 (m, 2.56H), 1.73 (m, 1.82H). \(^{13}\)C NMR (CDCl\(_3\), 300 MHz): \(\delta\) 158.4 (C=O), 146.8 (C-O, furan ring) 118.7 (C-C, furan ring) 79.7 (CH-OR) 73.2 (CH-OH ring), 41.6 (CH\(_2\) ring), 32.8 (CH\(_2\) ring), 30.3 (CH\(_2\) ring).

**Trimer 1,3-cyclopentanediol-adipate**

The product was obtained as orange oil (5.31 gr, 86% yield). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 5.27 (m, 2.20H), 5.17 (m, 0.32H), 4.47 (m, 1.75H), 4.33 (m, 0.25H), 2.27 (m, 7.73H), 1.97 (m, 10.88H), 1.63 (m, 9.52H). \(^{13}\)C NMR (CDCl\(_3\), 300 MHz): \(\delta\) 173.1 (C=O), 75.5 (CH-OR ring) 72.3 (CH-OH ring), 42.4 & 33.6 & 30.5 (CH\(_2\) ring), 34.1 & 24.4 (CH\(_2\) adipate).

**Trimer 1,3-cyclopentanediol-sebacate**

The product was obtained light orange oil (6.42 gr, 88% yield). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 5.28 (m, 2.44H), 5.16 (m, 0.31H), 4.47 (m, 1.78H), 4.32 (m, 0.22H), 2.24 (m, 10.89H), 1.96 (m, 8.12H), 1.59 (m, 10.97H), 1.29 (bs, 11.89H). \(^{13}\)C NMR (CDCl\(_3\), 300 MHz): \(\delta\) 173.6 (C=O), 75.4 (CH-OR ring) 72.3 (CH-OH ring), 42.4 & 33.6 & 30.4 (CH\(_2\) ring), 34.5 & 29.0 & 24.9 (CH\(_2\) sebacate).

**Trimer 1,4-cyclohexanediol-terephthalate**

The product was obtained as white solids (0.89 gr, 50% yield). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 8.09 (m, 4H), 5.17 (bs, 1.24 H), 5.04 (bs, 0.76 H), 3.83 (m, 1.56 H), 2.05 (m, 6.09 H), 1.71 (m, 10.28H). \(^{13}\)C NMR (CDCl\(_3\), 300 MHz): \(\delta\) 165.2 (C=O), 129.5 (C=C terephthalic ring), 72.7 (cis-CH-OR), 70.8 (trans-CH-OR), 68.7 & 67.8 (CH-CH), 32.0 & 30.5 & 28.3 & 27.5 (CH\(_2\) cyclohexane).

**Trimer 1,4-cyclohexanediol-adipate**

The product was obtained as a yellow oil (1.78 gr, 95% yield). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 4.74 (ds, 2.92H), 3.74 (ds, 2.0H), 2.31 (s, 6.0H), 1.65 (m, 28.8H). \(^{13}\)C NMR (CDCl\(_3\), 300 MHz): \(\delta\) 172.9 (C=O), 71.6 & 69.7 (CH-OR), 68.8 & 67.8 (CH-CH), 34.1 & 24.3 (CH\(_2\) adipate), 32.1 & 30.5 & 28.6 & 27.4 (CH\(_2\) cyclohexane).
Trimer 1,4-cyclohexanediol-sebacate
The product was obtained as white waxy solids (1.64 gr, 98% yield). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 4.87 (ds, 2.5H), 3.77 (ds, 2.0H), 2.29 (m, 7.75H), 1.62 (m, 34.3H). $^{13}$C NMR (CDCl$_3$, 300 MHz): $\delta$ 173.4 (C=O), 71.4 & 69.4 (CH-OR), 68.9 & 67.9 (CH-OH), 34.7 & 25.0 (CH$_2$ adipate), 32.2 & 30.5 & 29.0 & 27.4 (CH$_2$ cyclohexane).

Trimer 1,4-cyclohexanediol-terephthalate
The product was obtained as white solids (1.36 gr, 66% yield). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.10 (bs, 6.06H), 4.29 (ds, 2.07H), 4.19 (ds, 3.70H), 3.56 (ds, 1.35 H), 3.50 (ds, 2.64H), 1.90 (m, 21.6H), 1.11 (m, 6.65H). $^{13}$C NMR (CDCl$_3$, 300 MHz): $\delta$ 165.9 (C=O), 134.2 (O=C-C, terephthalic ring), 129.5 (C=C terephthalic ring), 70.3 & 68.0 (CH$_2$-OR), 68.4 & 66.1 (CH$_2$-OH), 40.4 + 37.4 (CH-OH), 37.4 & 34.6 (CH-OR), 29.1 & 28.7 & 25.6 & 25.1 (CH$_2$ cyclohexane ring).

Trimer 1,4-cyclohexanedimethanol-adipate
The product was obtained light yellow oil (1.94 gr, 89% yield). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 3.93 (ds, 1.22H), 3.84 (ds, 2.49H), 3.48 (ds, 0.65H), 3.40 (ds, 1.35H), 2.26 (bs, 3.75H), 1.60 (m, 15.85H), 0.93 (m, 3.93H). $^{13}$C NMR (CDCl$_3$, 300 MHz): $\delta$ 173.4 (C=O), 69.3 & 67.1 (CH$_2$-OR), 68.4 & 66.0 (CH$_2$-OH), 40.3 + 37.3 (CH-OH), 37.3 & 34.5 (CH-OR), 33.9 & 24.4 (CH$_2$, adipate), 29.0 & 28.8 & 28.7 & 25.5 & 25.3 & 25.1 (CH$_2$ cyclohexane ring).

Trimer 1,4-cyclohexanedimethanol-sebacate
The product was obtained colorless oil (1.74 gr, 91% yield). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 3.98 (ds, 1.86H), 3.90 (ds, 3.96H), 2.90 (2.53H), 2.29 (m, 6.78H), 1.82 (bs, 7.95H), 1.43 (m, 31.10H), 1.00 (m, 6.81H). $^{13}$C NMR (CDCl$_3$, 300 MHz): $\delta$ 174.0 (C=O), 69.3 & 67.0 (CH$_2$-OR), 68.4 & 66.1 (CH$_2$-OH), 40.4 + 37.3 (CH-OH), 37.3 & 34.3 (CH-OR), 34.3 & 25.1 (CH$_2$, sebacate), 29.0 & 28.7 & 25.5 (CH$_2$ cyclohexane ring).
LC-MS data

The trimers of 1,3-CP-F with various cis content were dried at 110 °C, after which significant discoloration was visible (Figure 3). The obtained trimers were analyzed via LC-MS (Figure 4) to assess the degradation products (Table 2) prior to a second purification step.

![Obtained trimers of 1,3-CP-F, with varying cis content (8%, 20%, 30%, 40%, left to right), after drying at 110 °C, showing various stages of discoloration.](image)

**Figure 3.** Obtained trimers of 1,3-CP-F, with varying cis content (8%, 20%, 30%, 40%, left to right), after drying at 110 °C, showing various stages of discoloration.

![LC-MS data on partially degraded CP-F trimers after drying at 110 °C.](image)

**Figure 4.** LC-MS data on partially degraded CP-F trimers after drying at 110 °C.

**Table 2.** List of masses found for partially degraded 1,3-CP-F trimers in LC-MS, supporting Figure 4.

|                  | n=1         | n=2       | n=3       |
|------------------|-------------|-----------|-----------|
| Calculated mass  | 324.3       | 546.5     | 768.7     |
| (OH)             | 528.5       | 750.7     |
| (CPol)           | 462.4       | 684.6     |
| Peak 1           | 342 (H$_3$O$^+$ adduct) |            |           |
| Peak 2           | 463, 529, 547 |          |           |
| Peak 3           | 547, 564 (H$_3$O$^+$ adduct) |        |           |
| Peak 4           |             |           | 685, 751, 769 |
| Peak 5           |             |           | 769, 786 (H$_3$O$^+$ adduct) |
NMR data trimers

NMR analysis of trimer 1,2-ethyleneglycol-terephthalate

Figure 5. $^1$H-NMR analysis of trimer 1,2-ethyleneglycol-terephthalate.

Figure 6. COSY ($^1$H-$^1$H) NMR analysis of trimer 1,2-ethyleneglycol-terephthalate.
NMR analysis of trimer 1,3-cyclopentanediol-terephthalate

Figure 7. HSQC (1H-DEPT) NMR analysis of trimer 1,2-ethyleneglycol-terephthalate.

Figure 8. 1H-NMR analysis of trimer 1,3-cyclopentanediol-terephthalate.
Figure 9. COSY ($^1$H-$^1$H) NMR analysis of trimer 1,3-cyclopentanediol-terephthalate.

Figure 10. HSQC ($^1$H-APT) NMR analysis of trimer 1,3-cyclopentanediol-terephthalate.
NMR analysis of trimer 1,3-cyclopentanediol-furanoate – 8% cis

Figure 11. $^1$H-NMR analysis of trimer 1,3-cyclopentanediol-furanoate – 8% cis.

NMR analysis of trimer 1,3-cyclopentanediol-furanoate – 20% cis

Figure 12. $^1$H-NMR analysis of trimer 1,3-cyclopentanediol-furanoate – 20% cis.
NMR analysis of trimer 1,3-cyclopentanediol-furanoate – 30% cis

Figure 13. $^1$H-NMR analysis of trimer 1,3-cyclopentanediol-furanoate – 30% cis.

Figure 14. COSY ($^1$H-$^1$H) NMR analysis of trimer 1,3-cyclopentanediol-furanoate – 30% cis.
Figure 15. HSQC (\(^1\)H-DEPT) NMR analysis of trimer 1,3-cyclopentanediol-furanoate – 30% cis.

NMR analysis of trimer 1,3-cyclopentanediol-furanoate – 40% cis

Figure 16. \(^1\)H-NMR analysis of trimer 1,3-cyclopentanediol-furanoate – 40% cis.
NMR analysis of trimer 1,3-cyclopentanediol-adipate

Figure 17. $^1$H-NMR analysis of trimer 1,3-cyclopentanediol-adipate.

Figure 18. $^{13}$C-NMR analysis of trimer 1,3-cyclopentanediol-adipate.
NMR analysis of trimer 1,3-cyclopentanediol-sebacate

Figure 19. $^1$H-NMR analysis of trimer 1,3-cyclopentanediol-sebacate.

Figure 20. $^{13}$C-NMR analysis of trimer 1,3-cyclopentanediol-sebacate.
Figure 21. $^1$H-NMR analysis of trimer 1,4-cyclohexanediol-terephthalate.

Figure 22. $^{13}$C-NMR analysis of trimer 1,4-cyclohexanediol-terephthalate.
Figure 23. COSY (1H-1H) NMR analysis of trimer 1,4-cyclohexanediol-terephthalate.

Figure 24. HSQC (1H-DEPT) NMR analysis of trimer 1,4-cyclohexanediol-terephthalate.
NMR analysis of trimer 1,4-cyclohexanediol-adipate

Figure 25. $^1$H-NMR analysis of trimer 1,4-cyclohexanediol-adipate.

Figure 26. $^{13}$C-NMR analysis of trimer 1,4-cyclohexanediol-adipate.
NMR analysis of trimer 1,4-cyclohexanediol-sebacate

Figure 27. $^1$H-NMR analysis of trimer 1,4-cyclohexanediol-sebacate.

Figure 28. $^{13}$C-NMR analysis of trimer 1,4-cyclohexanediol-sebacate.
NMR analysis of trimer 1,4-cyclohexanediol-terephthalate

Figure 29. $^1$H-NMR analysis of trimer 1,4-cyclohexanediol-terephthalate.

Figure 30. $^{13}$C-NMR analysis of trimer 1,4-cyclohexanediol-terephthalate.
Figure 31. COSY ($^1$H-$^1$H) NMR analysis of trimer 1,4-cyclohexanedicarboximethanol-terephthalate.

Figure 32. HSQC ($^1$H-DEPT) NMR analysis of trimer 1,4-cyclohexanecarboximethanol-terephthalate.
NMR analysis of trimer 1,4-cyclohexanedimethanol-adipate

Figure 33. $^1$H-NMR analysis of trimer 1,4-cyclohexanedimethanol-adipate.

Figure 34. $^{13}$C-NMR analysis of trimer 1,4-cyclohexanedimethanol-adipate.
NMR analysis of trimer 1,4-cyclohexanedicarboxylic acid sebacate

Figure 35. $^1$H-NMR analysis of trimer 1,4-cyclohexanedicarboxylic acid sebacate.

Figure 36. $^{13}$C-NMR analysis of trimer 1,4-cyclohexanedicarboxylic acid sebacate.
Detailed polymerization of small-scale screening

Table 3. Details of polymerization of trimer ethylene glycol-terephthalate for validation of consistency of small-scale reactor.

| Monomer | run | Cat | Cat (mol%) | Weight input | Weight after rxn | weight loss % | theoretical | color | $M_n$ | $M_w$ | $\bar{D}$ |
|---------|-----|-----|------------|--------------|------------------|---------------|--------------|-------|-------|-------|--------|
| E-T     | 1   | Ti(IV)butoxide | 1.0% | 10.0       | 8.0             | 20%           | 24%          | white | 17340 | 77780 | 4.49   |
| E-T     | 1   | Ti(IV)butoxide | 1.0% | 9.0        | 6.0             | 33%           | 24%          | white | 19590 | 95900 | 4.90   |
| E-T     | 1   | Ti(IV)butoxide | 1.0% | 10.0       | 7.0             | 30%           | 24%          | white | 17710 | 74210 | 4.19   |
| E-T     | 1   | Ti(IV)butoxide | 1.0% | 8.0        | 6.0             | 25%           | 24%          | white | 18790 | 82990 | 4.42   |
| E-T     | 1   | Ti(IV)butoxide | 1.0% | 10.0       | 8.0             | 20%           | 24%          | white | 19120 | 85210 | 4.46   |
| E-T     | 1   | Ti(IV)butoxide | 1.0% | 13.0       | 11.0            | 15%           | 24%          | white | 15550 | 81800 | 5.26   |
| E-T     | 1   | Ti(IV)butoxide | 1.0% | 12.0       | 10.0            | 17%           | 24%          | white | 15830 | 78690 | 4.97   |
| E-T     | 1   | Ti(IV)butoxide | 1.0% | 11.0       | 8.0             | 27%           | 24%          | white | 17140 | 85710 | 5.00   |
| E-T     | 2   | Ti(IV)butoxide | 1.0% | 10.4       | 7.7             | 26%           | 24%          | white | 12900 | 34970 | 2.71   |
| E-T     | 2   | Ti(IV)butoxide | 1.0% | 9.8        | 6.9             | 30%           | 24%          | white | 16160 | 46640 | 2.89   |
| E-T     | 2   | Ti(IV)butoxide | 1.0% | 11.0       | 9.0             | 18%           | 24%          | white | 18730 | 72100 | 3.85   |
Table 4. Details of polymerization of trimer ethyleneglycol-terephthalate for study of effect on monomer loading in small-scale reactor.

| Monomer | Cat (mol%)  | Weight input | Weight after rxn | weight loss % | theoretical | color | $M_n$ | $M_w$ | $Đ$ |
|---------|-------------|--------------|------------------|---------------|-------------|-------|-------|-------|-----|
| E-T     | Ti(IV)butoxide | 1.0%   | 1.2             | 0.5           | 58%         | 24%   | white | 24990  | 74310 | 2.97 |
| E-T     | Ti(IV)butoxide | 1.0%   | 1.1             | 0.5           | 55%         | 24%   | white | 26830  | 72680 | 2.71 |
| E-T     | Ti(IV)butoxide | 1.0%   | 2.2             | 1.4           | 33%         | 24%   | white | 23040  | 80450 | 3.49 |
| E-T     | Ti(IV)butoxide | 1.0%   | 3.0             | 2.0           | 33%         | 24%   | white | 19980  | 63270 | 3.17 |
| E-T     | Ti(IV)butoxide | 1.0%   | 4.2             | 2.7           | 36%         | 24%   | white | 19740  | 64850 | 3.29 |
| E-T     | Ti(IV)butoxide | 1.0%   | 4.0             | 2.6           | 35%         | 24%   | white | 24860  | 71210 | 2.87 |
| E-T     | Ti(IV)butoxide | 1.0%   | 5.0             | 3.3           | 34%         | 24%   | white | 18590  | 54270 | 2.92 |
| E-T     | Ti(IV)butoxide | 1.0%   | 6.0             | 3.9           | 35%         | 24%   | white | 18370  | 58470 | 3.18 |
| E-T     | Ti(IV)butoxide | 1.0%   | 5.9             | 4.3           | 27%         | 24%   | white | 21420  | 63600 | 2.97 |
| E-T     | Ti(IV)butoxide | 1.0%   | 7.0             | 5.2           | 26%         | 24%   | white | 15760  | 47750 | 3.03 |
| E-T     | Ti(IV)butoxide | 1.0%   | 6.8             | 4.6           | 32%         | 24%   | white | 20360  | 55260 | 2.71 |
| E-T     | Ti(IV)butoxide | 1.0%   | 8.4             | 5.9           | 30%         | 24%   | white | 13090  | 38110 | 2.91 |
| E-T     | Ti(IV)butoxide | 1.0%   | 8.1             | 6.0           | 26%         | 24%   | white | 17200  | 44460 | 2.59 |
| E-T     | Ti(IV)butoxide | 1.0%   | 8.9             | 6.7           | 25%         | 24%   | white | 14820  | 42080 | 2.84 |
| E-T     | Ti(IV)butoxide | 1.0%   | 9.2             | 7.0           | 24%         | 24%   | white | 15360  | 46910 | 3.05 |
| E-T     | Ti(IV)butoxide | 1.0%   | 10.4            | 7.7           | 26%         | 24%   | white | 12900  | 34970 | 2.71 |
| E-T     | Ti(IV)butoxide | 1.0%   | 9.8             | 6.9           | 30%         | 24%   | white | 16160  | 46640 | 2.89 |
| E-T     | Ti(IV)butoxide | 1.0%   | 11.0            | 9.0           | 18%         | 24%   | white | 18730  | 72100 | 3.85 |
| E-T     | Ti(IV)butoxide | 1.0%   | 19.0            | 16.0          | 16%         | 24%   | white | 9669   | 38660 | 4.00 |
| E-T     | Ti(IV)butoxide | 1.0%   | 50.0            | 40.0          | 20%         | 24%   | white | 3695   | 12260 | 3.32 |
| E-T     | Ti(IV)butoxide | 1.0%   | 101.0           | 81.0          | 20%         | 24%   | white | 1613   | 4527  | 2.81 |
Table 5. Details of polymerization with 1,3-cyclopentanediol in the small-scale reactor.

| monomer       | Cat                  | cat (mol%) | Weight input | Weight after rxn | weight loss % | theoretical weight loss | color   | $M_n$ | $M_w$ | $D$  | $T_g$ (°C) | $T_m$ (°C) | $T_c$ (°C) |
|---------------|----------------------|------------|--------------|-------------------|---------------|-------------------------|---------|-------|-------|-----|------------|------------|------------|
| CPdiol-T      | -                    | 9.2        | 3.6          | 61%               | 31%           | opaque                  | 1035    | 1266  | 1.22 |
| CPdiol-T      | -                    | 9.8        | 4.7          | 52%               | 31%           | opaque                  | 1033    | 1259  | 1.22 |
| CPdiol-T      | -                    | 10.0       | 5.0          | 50%               | 31%           | opaque                  | n.o.    |       |      |
| CPdiol-T      | Ti(IV)butoxide 1.0%  | 9.7        | 7.8          | 20%               | 31%           | white                   | 5234    | 10812 | 2.07 |
| CPdiol-T      | Ti(IV)butoxide 1.0%  | 10.9       | 8.9          | 18%               | 31%           | white                   | 5341    | 10849 | 2.03 |
| CPdiol-T      | Ti(IV)butoxide 1.0%  | 9.5        | 7.6          | 20%               | 31%           | white                   | n.o.    |       |      |
| CPdiol-T      | Sn(II)Octanoate 1.0% | 9.8        | 7.4          | 24%               | 31%           | white                   | 3803    | 6711  | 1.76 |
| CPdiol-T      | Sn(II)Octanoate 1.0% | 9.6        | 7.0          | 27%               | 31%           | white                   | 3553    | 6358  | 1.79 |
| CPdiol-T      | Sn(II)Octanoate 1.0% | 10.0       | 7.6          | 24%               | 31%           | white                   | n.o.    |       |      |
| CPdiol-A      | -                    | 11.8       | 6.8          | 42%               | 32%           | clear light brown       | 1244    | 1697  | 1.36 |
| CPdiol-A      | -                    | 10.6       | 6.1          | 42%               | 32%           | clear light brown       | 1276    | 1792  | 1.40 |
| CPdiol-A      | -                    | 10.8       | 6.2          | 43%               | 32%           | clear light brown       | n.o.    |       |      |
| CPdiol-A      | Ti(IV)butoxide 1.0%  | 10.4       | 8.3          | 20%               | 32%           | opaque yellow           | 16183   | 55419 | 3.42 |
| CPdiol-A      | Ti(IV)butoxide 1.0%  | 11.0       | 8.5          | 23%               | 32%           | opaque yellow           | 17389   | 58078 | 3.34 |
| CPdiol-A      | Ti(IV)butoxide 1.0%  | 10.2       | 7.9          | 23%               | 32%           | opaque yellow           | -30.05  | n.o.  |      |
| CPdiol-A      | Sn(II)Octanoate 1.0% | 10.3       | 7.6          | 26%               | 32%           | opaque yellow           | 15667   | 39365 | 2.51 |
| CPdiol-A      | Sn(II)Octanoate 1.0% | 10.0       | 7.3          | 27%               | 32%           | opaque yellow           | 15737   | 45620 | 2.90 |
| CPdiol-A      | Sn(II)Octanoate 1.0% | 9.6        | 7.1          | 26%               | 32%           | opaque yellow           | -23.62  | n.o.  |      |
| CPdiol-S      | -                    | 11.6       | 6.4          | 45%               | 28%           | opaque                  | 1377    | 1911  | 1.39 |
| CPdiol-S      | -                    | 10.5       | 5.5          | 48%               | 28%           | opaque                  | 1400    | 1940  | 1.39 |
| CPdiol-S      | -                    | 10.4       | 5.7          | 45%               | 28%           | opaque                  | n.o.    |       |      |
| CPdiol-S      | Ti(IV)butoxide 1.0%  | 10.8       | 9.2          | 15%               | 28%           | white                   | 25167   | 93115 | 3.70 |
| CPdiol-S      | Ti(IV)butoxide 1.0%  | 10.6       | 8.6          | 19%               | 28%           | white                   | 24709   | 91541 | 3.70 |
| CPdiol-S      | Ti(IV)butoxide 1.0%  | 9.9        | 8.2          | 17%               | 28%           | white                   | -37.93  | 44.2  | 2.1  |
| CPdiol-S      | Sn(II)Octanoate 1.0% | 10.4       | 8.0          | 23%               | 28%           | white                   | 14333   | 34792 | 2.43 |
| CPdiol-S      | Sn(II)Octanoate 1.0% | 10.4       | 8.2          | 21%               | 28%           | white                   | 14669   | 35596 | 2.43 |
| CPdiol-S      | Sn(II)Octanoate 1.0% | 10.0       | 7.8          | 22%               | 28%           | white                   | -39.19  | 43.84 | 4.42 |
Table 6. Details of polymerization with 1,4-cyclohexanediol in the small-scale reactor.

| monomer        | Cat                        | cat (mol%) | Weight input | Weight after rxn | weight loss % | theoretical weight loss | color            | $M_n$ | $M_w$ | D   | $T_g$ (°C) | $T_m$ (°C) | $T_c$ (°C) | $T_{cc}$ (°C) |
|----------------|----------------------------|------------|--------------|------------------|---------------|-------------------------|------------------|-------|-------|-----|----------|----------|----------|---------------|
| CHdiol-T       | -                          | 10.0       | 10.0         | 0%               | 32%           | white powder            | 1055             | 1248  | 1.18  |     |          |          |          |                |
| CHdiol-T       | -                          | 10.2       | 10.2         | 0%               | 32%           | white powder            | 1056             | 1246  | 1.18  |     |          |          |          |                |
| CHdiol-T       | -                          | 10.1       | 9.8          | 3%               | 32%           | white powder            | n.o.             | n.o.  | n.o.  |     |          |          |          |                |
| CHdiol-T       | Ti(IV)butoxide 1.0%        | 9.7        | 9.7          | 0%               | 32%           | white powder            | 1100             | 1380  | 1.25  |     |          |          |          |                |
| CHdiol-T       | Ti(IV)butoxide 1.0%        | 10.4       | 10.3         | 1%               | 32%           | white powder            | 1098             | 1352  | 1.23  |     |          |          |          |                |
| CHdiol-T       | Ti(IV)butoxide 1.0%        | 10.6       | 10.4         | 2%               | 32%           | white powder            | n.o.             | n.o.  | n.o.  |     |          |          |          |                |
| CHdiol-T       | Sn(II)Octanoate 1.0%       | 9.8        | 9.8          | 0%               | 32%           | white powder            | 1128             | 1430  | 1.27  |     |          |          |          |                |
| CHdiol-T       | Sn(II)Octanoate 1.0%       | 10.6       | 10.6         | 0%               | 32%           | white powder            | 1140             | 1464  | 1.28  |     |          |          |          |                |
| CHdiol-T       | Sn(II)Octanoate 1.0%       | 9.9        | 9.9          | 0%               | 32%           | white powder            | n.o.             | n.o.  | n.o.  |     |          |          |          |                |
| CHdiol-A       | -                          | 10.4       | 5.7          | 45%              | 34%           | light brown             | 1147             | 1457  | 1.27  |     |          |          |          |                |
| CHdiol-A       | -                          | 10.3       | 5.8          | 44%              | 34%           | light brown             | 1147             | 1442  | 1.26  |     |          |          |          |                |
| CHdiol-A       | -                          | 10.6       | 6.0          | 43%              | 34%           | light brown             | n.o.             | n.o.  | 72.19 |     |          |          |          |                |
| CHdiol-A       | Ti(IV)butoxide 1.0%        | 9.5        | 7.4          | 22%              | 34%           | clear yellow            | 10542            | 28049 | 2.66  |     |          |          |          |                |
| CHdiol-A       | Ti(IV)butoxide 1.0%        | 10.0       | 7.3          | 27%              | 34%           | clear yellow            | 15957            | 45639 | 2.86  |     |          |          |          |                |
| CHdiol-A       | Ti(IV)butoxide 1.0%        | 9.8        | 7.3          | 26%              | 34%           | clear yellow            | 4.61             | 116.81 | 61.63 |     |          |          |          |                |
| CHdiol-A       | Sn(II)Octanoate 1.0%       | 9.7        | 6.8          | 30%              | 34%           | clear                   | 7654             | 17998 | 2.35  |     |          |          |          |                |
| CHdiol-A       | Sn(II)Octanoate 1.0%       | 9.6        | 7.0          | 27%              | 34%           | clear                   | 8101             | 19015 | 2.35  |     |          |          |          |                |
| CHdiol-A       | Sn(II)Octanoate 1.0%       | 10.1       | 7.6          | 25%              | 34%           | clear                   | 4.98             | 117.85 | 79.25 |     |          |          |          |                |
| CHdiol-S       | -                          | 9.8        | 5.9          | 40%              | 29%           | opaque                  | 1138             | 1439  | 1.26  |     |          |          |          |                |
| CHdiol-S       | -                          | 10.3       | 6.2          | 40%              | 29%           | opaque                  | 1124             | 1433  | 1.27  |     |          |          |          |                |
| CHdiol-S       | -                          | 10.4       | 6.1          | 41%              | 29%           | opaque                  | -38.03           | 37.54  | 27.83 |     |          |          |          |                |
| CHdiol-S       | Ti(IV)butoxide 1.0%        | 10.2       | 7.6          | 25%              | 29%           | clear                   | 15232            | 46792 | 3.07  |     |          |          |          |                |
| CHdiol-S       | Ti(IV)butoxide 1.0%        | 10.5       | 8.1          | 23%              | 29%           | clear                   | 16651            | 44504 | 2.67  |     |          |          |          |                |
| CHdiol-S       | Ti(IV)butoxide 1.0%        | 10.2       | 8.1          | 21%              | 29%           | clear                   | -22.05           | 75.04  | 8.21  |     |          |          |          |                |
| CHdiol-S       | Sn(II)Octanoate 1.0%       | 10.5       | 7.6          | 28%              | 29%           | opaque                  | 4937             | 10392 | 2.10  |     |          |          |          |                |
| CHdiol-S       | Sn(II)Octanoate 1.0%       | 9.8        | 7.4          | 24%              | 29%           | opaque                  | 5740             | 11025 | 1.92  |     |          |          |          |                |
| CHdiol-S       | Sn(II)Octanoate 1.0%       | 10.1       | 7.9          | 22%              | 29%           | opaque                  | -24.24           | 81.63  | 30.18 | 1.46 |          |          |          |                |
Table 7. Details of polymerization with 1,4-cyclohexanediol in the small-scale reactor.

| monomer          | Cat                  | Cat (mol%) | Weight input | Weight after rxn | weight loss % | theoretical weight loss | color                  | $M_n$ | $M_w$ | $D$ | $T_g$ (°C) | $T_m$ (°C) | $T_c$ (°C) | $T_{cc}$ (°C) |
|------------------|----------------------|------------|--------------|------------------|---------------|-------------------------|------------------------|-------|-------|-----|-------------|-------------|------------|---------------|
| CHdimeoh-T       | -                    | 10.0       | 9.1          | 9%               | 34%           | white, part melted      | 1072                   | 1572  | 1.47  |    |             |             |            |               |
| CHdimeoh-T       | -                    | 10.0       | 9.0          | 10%              | 34%           | white, part melted      | 1069                   | 1557  | 1.46  |    |             |             |            |               |
| CHdimeoh-T       | Ti(IV)butoxide 1.0%  | 9.8        | 8.0          | 18%              | 34%           | white, part melted      | 3814                   | 6615  | 1.73  |    |             |             |            |               |
| CHdimeoh-T       | Ti(IV)butoxide 1.0%  | 10.2       | 8.4          | 18%              | 34%           | white, part melted      | 3812                   | 6644  | 1.74  |    |             |             |            |               |
| CHdimeoh-T       | Ti(IV)butoxide 1.0%  | 9.6        | 7.9          | 18%              | 34%           | white, part melted      | n.o.                   | n.o.   | n.o.  |    |             |             |            |               |
| CHdimeoh-T       | Sn(II)Octanoate 1.0% | 10.4       | 8.3          | 20%              | 34%           | white, part melted      | 4084                   | 7181  | 1.76  |    |             |             |            |               |
| CHdimeoh-T       | Sn(II)Octanoate 1.0% | 10.4       | 8.4          | 19%              | 34%           | white, part melted      | 4065                   | 7083  | 1.74  |    |             |             |            |               |
| CHdimeoh-T       | Sn(II)Octanoate 1.0% | 10.0       | 8.3          | 17%              | 34%           | white, part melted      | n.o.                   | 98.03 | 47.48 |    |             |             |            |               |
| CHdimeoh-A       | -                    | 9.2        | 7.4          | 20%              | 36%           | opaque                  | 1736                   | 2655  | 1.53  |    |             |             |            |               |
| CHdimeoh-A       | -                    | 10.5       | 8.3          | 21%              | 36%           | opaque                  | 1720                   | 2587  | 1.50  |    |             |             |            |               |
| CHdimeoh-A       | -                    | 10.2       | 8.3          | 19%              | 36%           | opaque                  | n.o.                   | 81.82 | 30.23 |    |             |             |            |               |
| CHdimeoh-A       | Ti(IV)butoxide 1.0%  | 10.0       | 7.7          | 23%              | 36%           | yellow                  | 11597                  | 28016 | 2.42  |    |             |             |            |               |
| CHdimeoh-A       | Ti(IV)butoxide 1.0%  | 10.0       | 7.6          | 24%              | 36%           | yellow                  | 12018                  | 27542 | 2.29  |    |             |             |            |               |
| CHdimeoh-A       | Ti(IV)butoxide 1.0%  | 9.8        | 7.6          | 22%              | 36%           | yellow                  | n.o.                   | 98.03 | 47.96 |    |             |             |            |               |
| CHdimeoh-A       | Sn(II)Octanoate 1.0% | 10.5       | 8.3          | 21%              | 36%           | opaque                  | 12039                  | 26910 | 2.24  |    |             |             |            |               |
| CHdimeoh-A       | Sn(II)Octanoate 1.0% | 9.4        | 7.4          | 21%              | 36%           | opaque                  | 11897                  | 27617 | 2.32  |    |             |             |            |               |
| CHdimeoh-A       | Sn(II)Octanoate 1.0% | 10.2       | 8.1          | 21%              | 36%           | opaque                  | n.o.                   | 92.47 | 31.58 |    |             |             |            |               |
| CHdimeoh-S       | -                    | 10.3       | 8.7          | 16%              | 32%           | opaque                  | 2444                   | 4077  | 1.67  |    |             |             |            |               |
| CHdimeoh-S       | -                    | 10.3       | 8.6          | 17%              | 32%           | opaque                  | 2419                   | 4008  | 1.66  |    |             |             |            |               |
| CHdimeoh-S       | -                    | 9.4        | 8.0          | 15%              | 32%           | opaque                  | n.o.                   | 41.66 | 13.83 |    |             |             |            |               |
| CHdimeoh-S       | Ti(IV)butoxide 1.0%  | 9.3        | 6.8          | 27%              | 32%           | opaque                  | 13533                  | 34679 | 2.56  |    |             |             |            |               |
| CHdimeoh-S       | Ti(IV)butoxide 1.0%  | 10.2       | 7.5          | 26%              | 32%           | opaque                  | 24481                  | 59284 | 2.42  |    |             |             |            |               |
| CHdimeoh-S       | Ti(IV)butoxide 1.0%  | 9.8        | 7.1          | 28%              | 32%           | opaque                  | n.o.                   | 48.35 | -2.12 |    |             |             |            |               |
| CHdimeoh-S       | Sn(II)Octanoate 1.0% | 10.2       | 8.7          | 15%              | 32%           | opaque                  | 11587                  | 26096 | 2.25  |    |             |             |            |               |
| CHdimeoh-S       | Sn(II)Octanoate 1.0% | 9.8        | 8.2          | 16%              | 32%           | opaque                  | 12446                  | 26426 | 2.12  |    |             |             |            |               |
| CHdimeoh-S       | Sn(II)Octanoate 1.0% | 9.7        | 8.0          | 18%              | 32%           | opaque                  | -38.21                  | 44.08 | -13.51 |    |             |             |            |               |
MALDI-ToF-MS

MALDI-ToF-MS expected linear chains

The expected linear distributions for poly(1,3-CP-F) are cyclics (not shown) and linear diol terminated chains [SI_01] (Figure 37). Thermal dehydration leads to loss of hydroxyl groups [SI_02, and SI_03]. Further degradation can lead to loss of CPol group [SI_04], combined with dehydration [SI_05], eventually leading to diacid terminated chains [SI_06].

![Chemical structures](image)

**Figure 37.** Expected linear distributions of poly(1,3-CP-F): cyclic (not shown), linear diol ([SI_01]), dehydrated ([SI_02, SI_03]), loss of CPol and dehydrated ([SI_04, SI_05, SI_06]).

**Table 8.** Calculated m/z of linear chains depicted in Figure 37, with the weight of a potassium ion.

| #    | m/z n=1 + K⁺ | m/z n=2 + K⁺ | m/z n=3 + K⁺ | m/z n=4 + K⁺ |
|------|--------------|--------------|--------------|--------------|
| cyclic | 482.49       | 704.69       | 926.89       | 1149.09      |
| SI_01 | 584.62       | 806.82       | 1029.02      | 1251.22      |
| SI_02 | 566.60       | 788.80       | 1011.00      | 1233.20      |
| SI_03 | 548.59       | 770.79       | 992.99       | 1215.19      |
| SI_04 | 500.50       | 722.70       | 944.90       | 1167.10      |
| SI_05 | 482.49       | 704.69       | 926.89       | 1149.09      |
| SI_06 | 416.38       | 638.58       | 860.78       | 1082.98      |
MALDI-ToF-MS - side reactions with cyclopentene group

One expected side reaction is the reaction between two cyclopentene groups, which are generated by the thermal dehydration of pendant cyclopentanol groups. These double bonds can undergo (thermal) radical addition reactions, forming a Cp-Cp bond (Figure 38). The expected structures are diol terminated (SI_07), and dehydrated (SI_08, SI_09). Further degradation can lead to loss of CPol group (SI_10), combined with dehydration (SI_11), eventually leading to di-acid terminated chains (SI_12).

Figure 38. Expected linear distributions after CPene-CPene addition reaction.

| #     | m/z n=1 + K⁺ | m/z n=2 + K⁺ | m/z n=3 + K⁺ | m/z n=4 + K⁺ |
|-------|--------------|--------------|--------------|--------------|
| SI_07 | 650,72       | 872,92       | 1095,12      | 1317,32      |
| SI_08 | 632,7        | 854,90       | 1077,10      | 1299,3       |
| SI_09 | 614,69       | 836,89       | 1058,09      | 1281,29      |
| SI_10 | 566,60       | 788,80       | 1011,0       | 1233,20      |
| SI_11 | 548,59       | 770,79       | 992,99       | 1215,19      |
| SI_12 | 482,48       | 704,68       | 926,88       | 1149,08      |

Table 9. Calculated m/z of linear chains after Cp-Cp addition reaction depicted in Figure 38, with the weight of a potassium ion.
MALDI-ToF-MS - other possible side reactions

Two possible Diels-Alders 2+4 cycloaddition reactions are possible between the furan-group and the generated cyclopentene group. The first one (Figure 39, top) is the reaction of cyclopentene with a normal furan group of FDCA. The second one (Figure 39, bottom) is the reaction of cyclopentene with a decarboxylated furan group. The decarboxylation of FDCA is a well-known side reaction, and free acid groups on the furan ring are generated by the degradation mechanism described in this work. Furthermore, Diels-Alder reactions are also known to occur with these furan groups. A trace of SI_15 has been found in the samples with 30% cis 1,3-CPdiol in the polymer.

![Figure 39. Possible occurring Diels-Alder side reaction between the furan group and the cyclopentene group.](image)

Table 10. Calculated m/z of linear chains after Cp-Cp addition reaction depicted in Figure 39, with the weight of a potassium ion.

|   | m/z n=0 + K⁺ | m/z n=1 + K⁺ | m/z n=2 + K⁺ |
|---|-------------|-------------|-------------|
| SI_13 | 668,73      | 890,83      | 1113,13     |
| SI_14 | 650,73      | 872,93      | 1095,13     |
| SI_15 | 540,61      | 762,81      | 985,01      |
| SI_16 | 522,59      | 744,79      | 966,99      |
Obtained MALDI-ToF-MS spectra 8% cis

In the following MALDI-ToF-MS spectra, and the text, the distributions are numbered in accordance to the structures in Figure 37 and Figure 38, e.g. linear diol-terminated chains SI_01, is denoted as 1. The major ticks are aligned to the $M_0$ of the repeat unit CP-F (m/z 222.1), ranging from n=2 to n=6 of the linear diol-terminated chains 1.

MALDI-ToF-MS spectra obtained for poly(CP-F) with 8% cis, after thermal stability experiments at 180 °C, 200 °C and 220 °C (Figure 40). For the sample at 180 °C only one distribution of linear diol terminated chains (1) are obtained. At 200 °C more distributions appear: dehydrated linear chains 2, Cp-Cp addition 7, and linear ene-acid 5. At 220 °C distribution further linear dehydrated 3 appears, distribution 5 disappears, and 7 is dehydrated to 8.

Figure 40. Obtained MALDI-ToF-MS spectra for poly(1,3-CP-F) with 8% cis, after thermal stability experiments at 180 °C (blue, top), 200 °C (red, middle), and 220 °C (black, bottom).
Obtained MALDI-ToF-MS spectra 20% cis

MALDI-TOF-MS spectra obtained for poly(1,3-CP-F) with 20% cis, after thermal stability experiments at 180 °C, 200 °C and 220 °C (Figure 41). For the sample at 180 °C two distributions are found equally present: 1 linear diol terminated chains 1, and linear di-acid terminated chains 6. The third distribution is linear ene-acid terminated chains 5. At 200 °C mostly linear diol terminated chains 1 are present, together with dehydrated linear chain 2, and linear di-acid terminated chain 6. At 220 °C, linear diol terminated chains 1 disappears, with the appearance of dehydrated linear chains 2, and 3. Linear di-acid terminated chain 6 is almost gone, and Cp-Cp addition chains 7, and the dehydration 8 and 9 are appearing. Please note that 6 and 8 are close, but have a mass-difference of 4 dalton.

Figure 41. Obtained MALDI-ToF-MS spectra for poly(1,3-CP-F) with 20% cis, after thermal stability experiments at 180 °C (blue, top), 200 °C (red, middle), and 220 °C (black, bottom).
Obtained MALDI-ToF-MS spectra 30% cis

MALDI-ToF-MS spectra obtained for poly(1,3-CP-F) with 30% cis, after thermal stability experiments at 180 °C, 200 °C and 220 °C (Figure 42). For the sample at 180 °C two main distributions are found: linear diol terminated chains 1, and linear di-acid terminated chains 6. The third distribution is linear ene-acid terminated chains 5. At 200 °C the linear di-acid terminated chain 6 is most abundant, together with linear diol terminated chains 1, and dehydrated linear chain 2. The fourth distribution is linear ene-acid terminated chains 5. At 220 °C, linear diol terminated chains 1 disappears, with the appearance of dehydrated linear chains 2, and 3. Linear di-acid terminated chain 6 is almost gone, but Cp-Cp addition chains 7, and the dehydration 8 and 9 are appearing.

![MALDI-ToF-MS spectra](image)

**Figure 42.** Obtained MALDI-ToF-MS spectra for poly(1,3-CP-F) with 30% cis, after thermal stability experiments at 180 °C (blue, top), 200 °C (red, middle), and 220 °C (black, bottom).
Obtained MALDI-ToF-MS spectra 40% cis

MALDI-ToF-MS spectra obtained for poly(CP-F) with 40% cis, after thermal stability experiments at 180 ºC, 200 ºC and 220 ºC (Figure 43). For the sample at 180 ºC two distributions are found: linear diol terminated chains 1, and linear di-acid terminated chains 6. At 200 ºC the linear di-acid terminated chain 6 is most abundant, together with linear diol terminated chains 1, and dehydrated linear chain 2. The fourth distribution is linear ene-acid terminated chains 5. At 220 ºC, linear dehydrated chains 3 are most abundant. Dehydrated Cp-Cp adducts 8 and 9 have appeared alongside linear ene-acid terminated chains 5.

Figure 43. Obtained MALDI-ToF-MS spectra for poly(1,3-CP-F) with 40% cis, after thermal stability experiments at 180 ºC (blue, top), 200 ºC (red, middle), and 220 ºC (black, bottom).