Electronic Supplementary Material (ESI) for Polymer Chemistry.


# Supporting Information

## Biocatalytic Approach towards Sustainable Furanic-Aliphatic Polyesters

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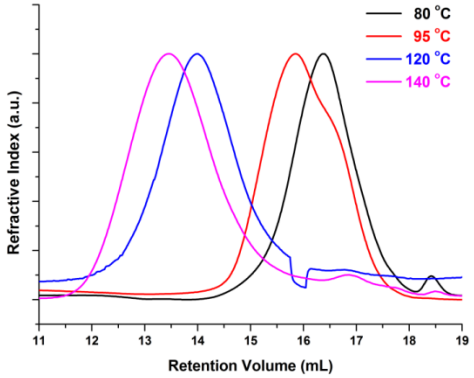



**Figure S1.** SEC retention curves of poly(hexamethylene furanoate) (PHF) from the temperature-varied two-stage enzymatic polymerizations. The temperature indicated here is the reaction temperature during the last 24 h reaction.

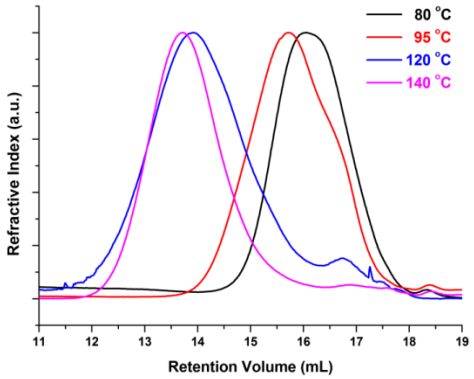



**Figure S2.** SEC retention curves of poly(octamethylene furanoate) (POF) from the temperature-varied two-stage enzymatic polymerizations. The temperature indicated here is the reaction temperature during the last 24 h reaction.

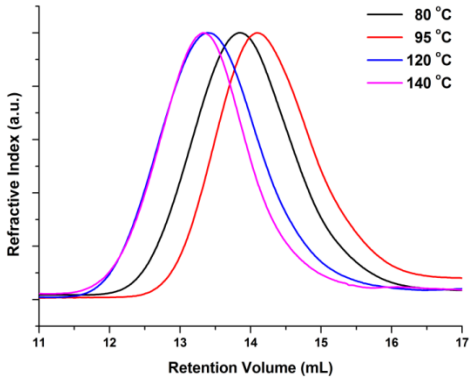



**Figure S3.** SEC retention curves of poly(decamethylene furanoate) (PDF) from the temperature-varied two-stage enzymatic polymerizations. The temperature indicated here is the reaction temperature during the last 24 h reaction.

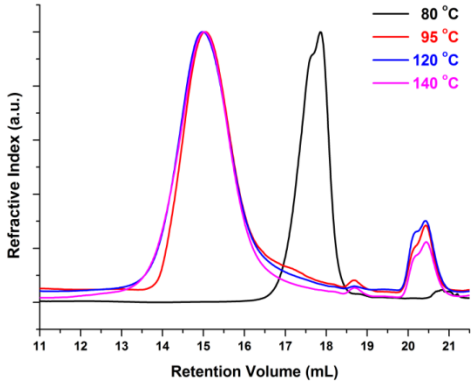



**Figure S4.** SEC retention curves of poly(diethylene glycol furanoate) (PDEGF) from the temperature-varied two-stage enzymatic polymerizations. The temperature indicated here is the reaction temperature during the last 24 h reaction.

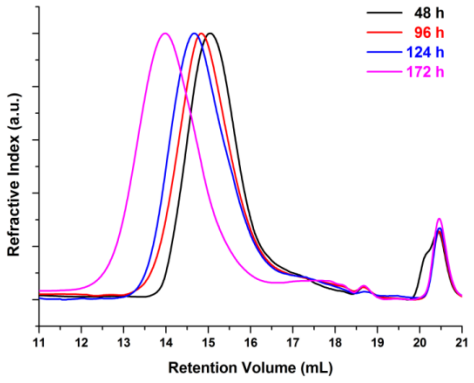



**Figure S5.** SEC retention curves of poly(diethylene glycol furanoate) (PDEGF) from the temperature-varied two-stage enzymatic polymerizations at 95 °C. The reaction time started to count after keeping the reaction at 80 °C for 26 h.

**Table S1.** Molecular weights of the obtained furanic-aliphatic polyesters from the CALB-catalyzed polymerizations of DMFDCA and various α,ω-aliphatic linear diols via the temperature-varied two-stage method

| | | | NMR [d] | SEC [e] | | | |
|---|---|---|---|---|---|---|---|
| Temperature (°C) [a] | Diol [b] | Polyester [c] | $\bar{M}_n$ (g/mol) | $\bar{M}_n$ (g/mol) | $\bar{M}_w$ (g/mol) | *Đ* ($\bar{M}_w/\bar{M}_n$) | Yield (%) [f] |
| 80 | 1,4-BDO | PBF | 1100 | 1200 | 1700 | 1.42 | 77 |
| 95 | 1,4-BDO | PBF | 1500 | 1400 | 2100 | 1.50 | 73 |
| 120 | 1,4-BDO | PBF | 2300 | 1500 | 3600 | 2.40 | 52 |
| 140 | 1,4-BDO | PBF | 2500 | 1600 | 5500 | 3.44 | 54 |
| 80 | 1,6-HDO | PHF | 2200 | 2500 | 3800 | 1.52 | 93 |
| 95 | 1,6-HDO | PHF | 3500 | 3800 | 5800 | 1.53 | 90 |
| 120 | 1,6-HDO | PHF | 11300 | 27500 | 70300 | 2.56 | 88 |
| 140 | 1,6-HDO | PHF | 15000 | 41100 | 106600 | 2.59 | 85 |
| 80 | 1,8-ODO | POF | 2400 | 3300 | 4800 | 1.45 | 88 |
| 95 | 1,8-ODO | POF | 4100 | 4600 | 7600 | 1.65 | 87 |
| 120 | 1,8-ODO | POF | 10700 | 29500 | 72500 | 2.46 | 88 |
| 140 | 1,8-ODO | POF | 11400 | 41000 | 87300 | 2.13 | 89 |
| 80 | 1,10-DDO | PDF | 10100 | 23700 | 48700 | 2.05 | 94 |
| 95 | 1,10-DDO | PDF | 9300 | 20000 | 37800 | 1.89 | 87 |
| 120 | 1,10-DDO | PDF | 16100 | 43000 | 90700 | 2.11 | 90 |
| 140 | 1,10-DDO | PDF | 16700 | 51600 | 104400 | 2.02 | 88 |
| 80 | DEG | PDEGF | 900 | 1000 | 1100 | 1.10 | 53 |
| 95 | DEG | PDEGF | 9900 | 9500 | 18300 | 1.93 | 73 |
| 120 | DEG | PDEGF | 10400 | 9800 | 20500 | 2.09 | 75 |
| 140 | DEG | PDEGF | 11400 | 10600 | 23300 | 2.20 | 95 |
| 95 | 2,3-BDO | P23BF | 900 | 900 | 1100 | 1.22 | 84 |

[a] The temperature is the reaction temperature during the last 24 h reaction; [b] 1,4-BOD = 1,4-butanediol, 1,6-HDO = 1,6-hexanediol, 1,8-ODO = 1,8-octanediol, 1,10-DDO = 1,10-decanediol, DEG = diethylene glycol, 2,3-BDO = 2,3-butanediol; [c] PBF = poly(butylene furanoate), PHF = poly(hexamethylene furanoate), POF = poly(octamethylene furanoate), PDF = poly(decamethylene furanoate), PDEGF = poly(diethylene glycol furanoate), P23BF = poly(2,3-butylene furanoate); [d] The number average molecular weight ($\bar{M}_n$) was calculated from the $^1$H-NMR spectra; [e] The number average molecular weight ($\bar{M}_n$), weight average molecular weight ($\bar{M}_w$), and dispersity (*Đ*, $\bar{M}_w/\bar{M}_n$) were determined by SEC in chloroform; [f] Isolation yield after purification in methanol except P23BF that was purified by hexane.

## Table S2. Cumulative weight fractions of poly(butylene furanoate) (PBF)

| Temperature (°C) [a] | High Molecular Weight ($\bar{M}_w$ > 1000 g/mol) | | Low Molecular Weight ($\bar{M}_w$ around 500 g/mol) | |
|---|---|---|---|---|
| | Retention Volume (mL) [b] | Cumulative Weight Fraction (%) [c] | Retention Volume (mL) [b] | Cumulative Weight Fraction (%) [c] |
| 80 | 14.32 - 18.38 | 97.7 | 18.38 - 19.25 | 2.3 |
| 95 | 15.18 - 18.30 | 96.5 | 18.30 - 19.25 | 3.5 |
| 120 | 14.10 - 18.28 | 91.5 | 18.28 - 19.25 | 8.5 |
| 140 | 13.36 - 18.25 | 90.0 | 18.25 - 19.25 | 10.0 |

[a] The temperature is the reaction temperature during the last 24 h reaction; [b] Retention volume was determined by SEC in chloroform; [c] Cumulative weight fraction was calculated from SEC using the universal calibration method.

## Table S3. Molecular weights of polycaprolactone (PCL) from control reactions

| Catalyst [a] | Solvent [b] | SEC [c] | | | Remark [g] |
|---|---|---|---|---|---|
| | | $\bar{M}_n$ (g/mol) | $\bar{M}_w$ (g/mol) | *Đ* ($\bar{M}_w/\bar{M}_n$) | |
| No CALB | Toluene | / [d] | / [d] | / [d] | / |
| Fresh CALB [a] | Toluene | 49400 [e] | 101100 [e] | 2.05 [e] | . |
| Recycled CALB-1 [a] | Toluene | 18700 [e] | 40000 [e] | 2.14 [e] | CALB was recycled from the temperature-varied two-stage enzymatic polymerization with DMFDCA in diphenyl ether using the following conditions: (1) 80 °C, 26 h; (2) 95 °C, 24 h; (3) 120 °C, 24h. [h] |
| Recycled CALB-2 [a] | Toluene | 21000 [e] | 51000 [e] | 2.43 [e] | CALB was recycled from the temperature-varied two-stage enzymatic polymerization with DMFDCA in diphenyl ether using the following conditions: (1) 80 °C, 26 h; (2) 95 °C, 24 h; (3) 140 °C, 24h. [h] |
| Used CALB | Diphenyl ether | 18900 [f] | 60500 [f] | 3.20 [f] | CALB and diphenyl ether were heated up at: (1) 80 °C for the first 26 h; (2) 95 °C for another 24 h; (3) 120 °C for the final 24 h. [i] |
| Used CALB | Diphenyl ether | 4100 [f] | 10700 [f] | 2.61 [f] | CALB and diphenyl ether were heated up at: (1) 80 °C for the first 26 h; (2) 95 °C for another 24 h; (3) 140 °C for the final 24h. [i] |

[a] The fresh and recycled CALB was dried overnight in the presence of $P_2O_5$ under high vacuum before use. [b] Solvent used for ring-opening polymerization of ε-caprolactone; [c] The number average molecular weight ($\bar{M}_n$), weight average molecular weight ($\bar{M}_w$), and dispersity (*Đ*, $\bar{M}_w/\bar{M}_n$) of polycaprolactone (PCL) from the ring-opening polymerization were determined by SEC; [d] No PCL was obtained; [e] Molecular weights were determined by SEC in THF; [f] Molecular weights were determined by SEC in

$CHCl_3$; [g] DMFDCA = dimethyl 2,5-furandicarboxylate; [h] The recycled CALB was washed respectively with chloroform, methanol and deionized water three times. Then it was stored in a refrigerator at 0 - 8 °C; [i] After thermal treatment, the used CALB with diphenyl ether were directly applied for the ring-opening polymerization of ε-caprolactone.

**Table S4.** MALDI-ToF MS analysis of the obtained furanic-aliphatic polyesters

| | | SEC [c] | | End groups [d] | | | | |
|---|---|---|---|---|---|---|---|---|
| **Temperature (°C) [a]** | **Polyester [b]** | $\bar{M}_n$ **(g/mol)** | $\bar{M}_w$ **(g/mol)** | **Ester/-OH** | **Ester/Ester** | **-OH/-OH** | **Cyclic** | **Ester/Aldehyde** |
| 80 | PBF | 1200 | 1700 | 1st | 2nd | 3rd | Trace | N.D. |
| 95 | PBF | 1400 | 2100 | 1st | 2nd | 3rd | 4th | Trace |
| 120 | PBF | 1500 | 3600 | 2nd | 1st | 4th | 3rd | Trace |
| 140 | PBF | 1600 | 5500 | 1st | 3rd | 4th | 2nd | N.D. |
| 80 | PHF | 2500 | 3800 | 1st | 2nd | 3rd | 4th | N.D. |
| 95 | PHF | 3800 | 5800 | 1st | 2nd | 4th | 3rd | Trace |
| 120 | PHF | 27500 | 70300 | N.D. | N.D. | N.D. | 1st | N.D. |
| 140 | PHF | 41100 | 106600 | N.D. | N.D. | N.D. | 1st | N.D. |
| 80 | POF | 3300 | 4800 | 1st | 3rd | 2nd | 4th | N.D. |
| 95 | POF | 4600 | 7600 | 1st | 2nd | 3rd | 4th | N.D. |
| 120 | POF | 29500 | 72500 | N.D. | N.D. | N.D. | 1st | N.D. |
| 140 | POF | 41000 | 87300 | N.D. | N.D. | N.D. | 1st | N.D. |
| 80 | PDF | 23700 | 48700 | N.D. | N.D. | 1st | 2nd | Trace |
| 95 [e] | PDF | 20000 | 37800 | Trace | Trace | Trace | 1st | Trace |
| 120 | PDF | 43000 | 90700 | Trace | N.D. | Trace | 1st | N.D. |
| 140 | PDF | 51600 | 104400 | N.D. | N.D. | N.D. | 1st | N.D. |
| 80 | PDEGF | 1000 | 1100 | 1st | 2nd | 3rd | 4th | N.D. |
| 95 | PDEGF | 9500 | 18300 | 3rd | 1st | Trace | 2nd | 4th |
| 120 | PDEGF | 9800 | 20500 | 4th | 1st | Trace | 2nd | 3rd |
| 140 | PDEGF | 10600 | 23300 | Trace | 2nd | N.D. | 1st | 3rd |
| 95 [f] | PDEGF | 10900 | 23800 | Trace | Trace | Trace | 1st | Trace |
| 95 [g] | PDEGF | 12300 | 27800 | Trace | Trace | N.D. | 1st | Trace |
| 95 [h] | PDEGF | 31400 | 69400 | N.D. | 2nd | N.D. | 1st | Trace |
| 95 | P23BF | 900 | 1100 | 2nd | 1st | Trace | Trace | 3rd |

[a] The temperature is the reaction temperature during the last 24 h reaction; [b] PBF = poly(butylene furanoate), PHF = poly(hexamethylene furanoate), POF = poly(octamethylene furanoate), PDF = poly(decamethylene furanoate), PDEGF = poly(diethylene glycol furanoate), P23BF = poly(2,3-butylene furanoate); [c] The number average molecular weight ($\bar{M}_n$) and weight average molecular weight ($\bar{M}_w$) were determined by SEC in $CHCl_3$; [d] The end groups were determined by MALDI-ToF MS. The marks, 1st, 2nd, 3rd, 4th, and Trace, represent the abundance sequence of the polymer species detected by MALDI-TOF MS from the most dominant (1st) to only detectable with trace amounts (Trace). N.D. = not detected; [e]

The polymerization was maintained at 95 °C for 48 h after reacted at 80 °C for 26 h; [f] The polymerization was maintained at 95 °C for 96 h after reacted at 80 °C for 26 h; [g] The polymerization was maintained at 95 °C for 124 h after reacted at 80 °C for 26 h; [h] The polymerization was maintained at 95 °C for 172 h after reacted at 80 °C for 26 h.

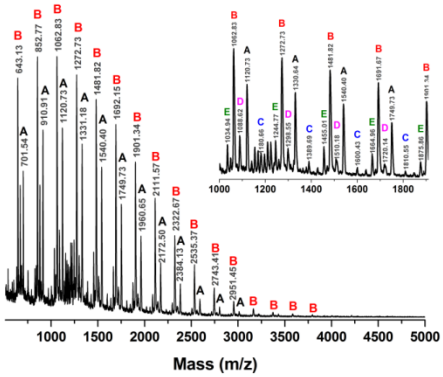



**Figure S6.** The MALDI-ToF MS spectrum of poly(2,3-butylene furanoate) (P23BF, $\bar{M}_w$ = 1100 g/mol) with peak interpretations. A, B, C, D, E represent the five polyester species ionized by $K^+$. They are terminated with ester/-OH, ester/ester, -OH/-OH, no end groups (cyclic), and ester/aldehyde groups, respectively. E' represents the polyesters with ester/aldehyde end groups that are ionized by $Na^+$.

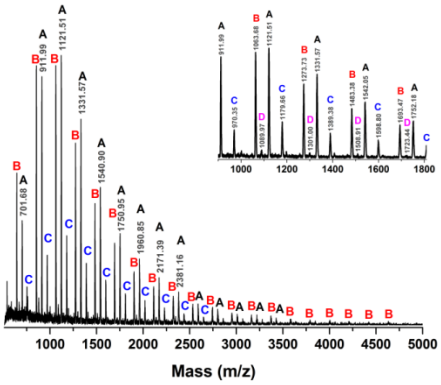



**Figure S7.** The MALDI-ToF MS spectrum of poly(butylene furanoate) (PBF, $\bar{M}_w$ = 1700 g/mol) with peak interpretations.

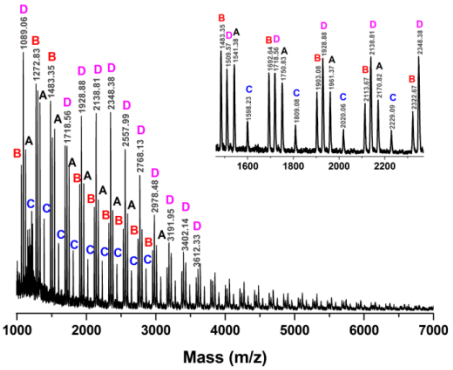



**Figure S8.** The MALDI-ToF MS spectrum of poly(butylene furanoate) (PBF, $\bar{M}_w$ = 5500 g/mol) with peak interpretations

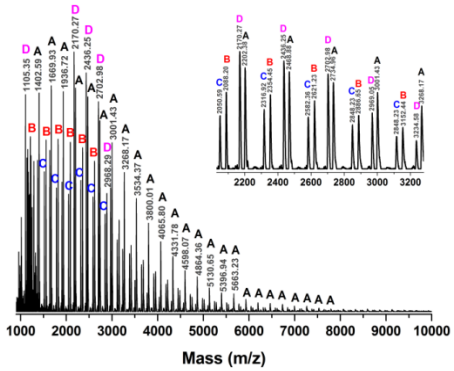



**Figure S9.** The MALDI-ToF MS spectrum of poly(octamethylene furanoate) (POF, $\bar{M}_w$ = 7600 g/mol) with peak interpretations

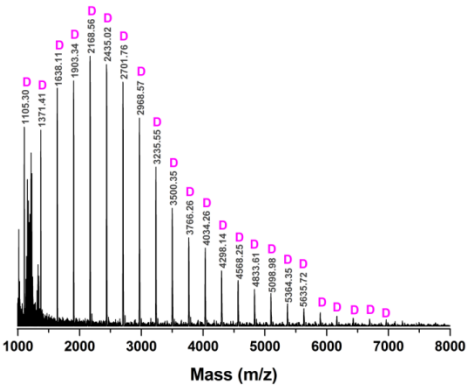



**Figure S10.** The MALDI-ToF MS spectrum of poly(octamethylene furanoate) (POF, $\bar{M}_w$ = 72500 g/mol) with peak interpretations

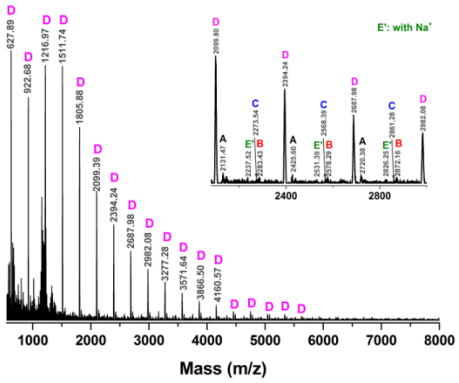



**Figure S11.** The MALDI-ToF MS spectrum of poly(decamethylene furanoate) (PDF, $\bar{M}_w$ = 37800 g/mol) with peak interpretations

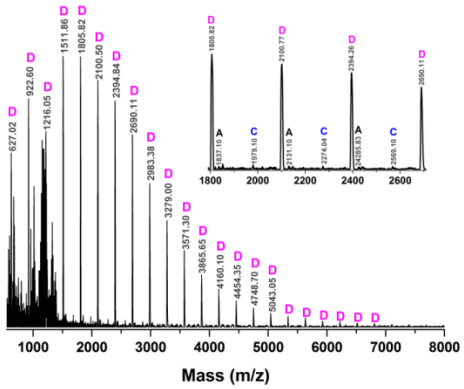



**Figure S12.** The MALDI-ToF MS spectrum of poly(decamethylene furanoate) (PDF, $\bar{M}_w$ = 90700 g/mol) with peak interpretations

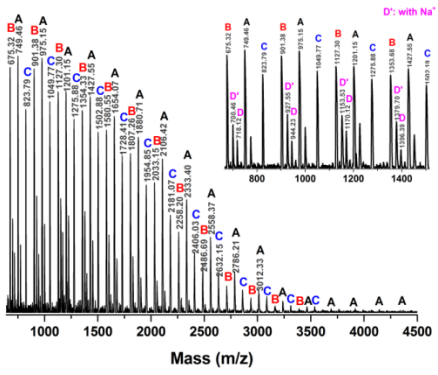



**Figure S13.** The MALDI-ToF MS spectrum of poly(diethylene glycol furanoate) (PDEGF, $\bar{M}_w$ = 1100 g/mol) with peak interpretations

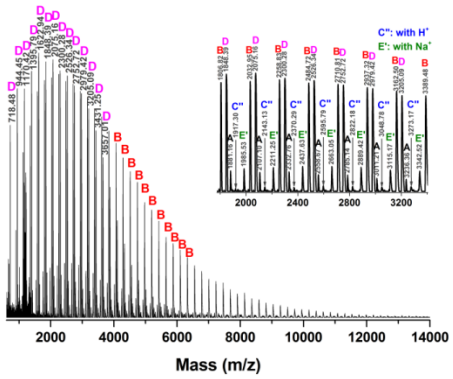



**Figure S14.** The MALDI-ToF MS spectrum of poly(diethylene glycol furanoate) (PDEGF, $\bar{M}_w$ = 20500 g/mol) with peak interpretations

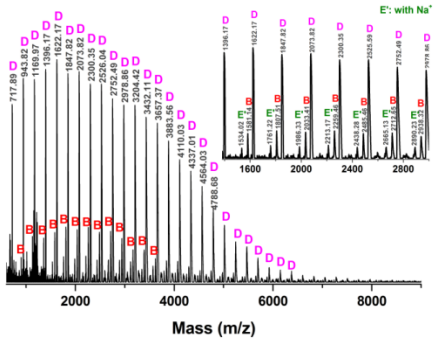



**Figure S15.** The MALDI-ToF MS spectrum of poly(diethylene glycol furanoate) (PDEGF, $\bar{M}_w$ = 69400 g/mol) with peak interpretations

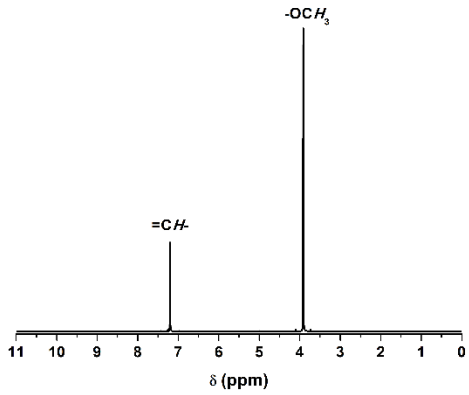



**Figure S16.** $^1$H-NMR spectrum of dimethyl 2,5-furandicarboxylate (DMFDCA) in $CDCl_3$-$d_1$

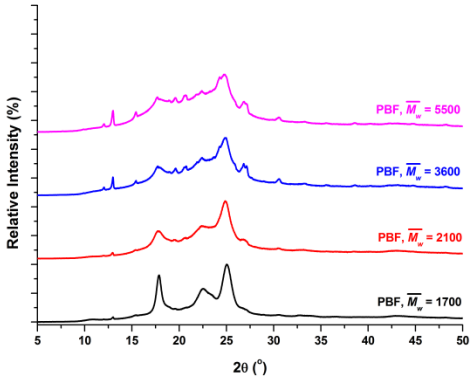



**Figure S17.** WAXD spectra of poly(butylene furanoate) (PBF)

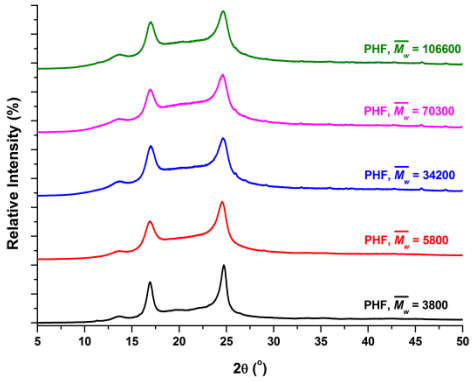



**Figure S18.** WAXD spectra of poly(hexamethylene furanoate) (PHF)

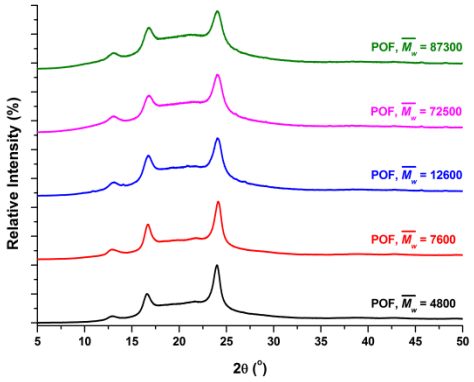



**Figure S19.** WAXD spectra of poly(octamethylene furanoate) (POF)

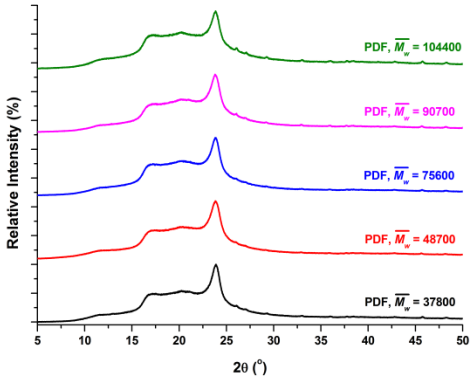



**Figure S20.** WAXD spectra of poly(decamethylene furanoate) (PDF)

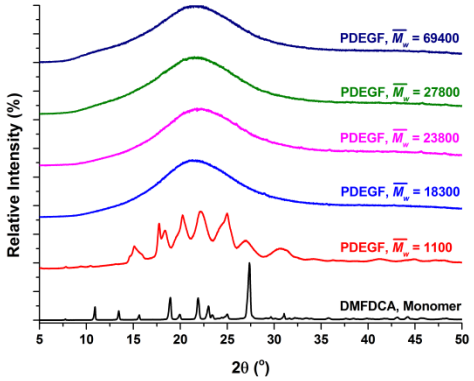



**Figure S21.** WAXD spectra of poly(diethylene glycol furanoate) (PDEGF) and the monomer dimethyl 2,5-furandicarboxylate (DMFDCA).

**Table S5**. Physical properties of the obtained furanic-aliphatic polyesters

| Polymer [a] | SEC [b] | | WAXD [c] | | DSC [d] | | | | | | | | | TGA [e] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 1st Heating | | Cooling | | 2nd Heating | | | TMDSC | | | | |
| | $\bar{M}_n$ (g/mol) | $\bar{M}_w$ (g/mol) | $\chi_c$ (%) | $T_m$ (°C) | $\Delta H_m$ (J/g) | $\Delta H_m^0$ (J/g) | $T_c$ (°C) | $\Delta H_m$ (J/g) | $T_g$ (°C) | $T_m$ (°C) | $\Delta H_m$ (J/g) | $T_g$ (°C) | $T_{d\text{-}5\%}$ (°C) | $T_{d\text{-}10\%}$ (°C) | $T_{d\text{-}max}$ (°C) |
| **PBF** | 1200 | 1700 | 56 | 145 | 70 | 123 | 112 | 54 | 25 | 147 | 65 | 26 | 311 | 334 | 393 |
| **PBF** | 1400 | 2100 | 52 | 156 | 66 | | 123 | 55 | 30 | 156 | 64 | 34 | 330 | 359 | 397 |
| **PBF** | 1500 | 3600 | 44 | 167 | 52 | | 132 | 47 | 31 | 167 | 48 | 31 | 347 | 365 | 398 |
| **PBF** | 1600 | 5500 | 42 | 168 | 49 | | 140 | 46 | 33 | 169 | 46 | 36 | 337 | 362 | 396 |
| **PHF** | 2500 | 3800 | 53 | 143 | 71 | 135 | 107 | 65 | 11 | 143 | 69 | 12 | 354 | 365 | 395 |
| **PHF** | 3800 | 5800 | 47 | 146 | 65 | | 112 | 61 | 14 | 146 | 57 | 13 | 363 | 373 | 397 |
| **PHF** | 16100 | 34200 | 36 | 147 | 52 | | 99 | 47 | 13 | 146 | 41 | 14 | 358 | 371 | 397 |
| **PHF** | 27500 | 70300 | 36 | 144 | 46 | | 90 | 38 | 15 | 143 | 34 | 15 | 362 | 372 | 398 |
| **PHF** | 41100 | 106600 | 37 | 140 | 47 | | 83 | 34 | 15 | 140 | 29 | 16 | 361 | 370 | 397 |
| **POF** | 3300 | 4800 | 39 | 145 | 72 | 180 | 117 | 67 | 9 | 144 | 60 | 13 | 355 | 368 | 399 |
| **POF** | 4600 | 7600 | 40 | 147 | 70 | | 116 | 63 | 9 | 146 | 57 | 12 | 363 | 373 | 399 |
| **POF** | 5800 | 12600 | 28 | 146 | 51 | | 111 | 49 | 7 | 146 | 43 | 9 | 365 | 375 | 403 |
| **POF** | 29500 | 72500 | 29 | 145 | 52 | | 105 | 44 | 6 | 144 | 37 | 6 | 371 | 380 | 404 |
| **POF** | 41000 | 87300 | 26 | 141 | 47 | | 99 | 39 | 6 | 141 | 34 | 6 | 360 | 372 | 399 |
| **PDF** | 20000 | 37800 | 24 | 111 | 48 | 198 | 66 | 42 | -8 | 111 | 37 | -8 | 367 | 377 | 403 |
| **PDF** | 23700 | 48700 | 25 | 111 | 47 | | 60 | 40 | -5 | 110 | 34 | -5 | 367 | 376 | 404 |
| **PDF** | 37000 | 75600 | 21 | 109 | 43 | | 65 | 35 | -7 | 108 | 29 | -6 | 363 | 374 | 402 |
| **PDF** | 43000 | 90700 | 21 | 110 | 44 | | 62 | 34 | -6 | 107 | 30 | -6 | 366 | 378 | 406 |
| **PDF** | 51600 | 104400 | 21 | 108 | 44 | | 66 | 31 | -5 | 106 | 25 | -5 | 369 | 378 | 402 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **PDEGF** | 1000 | 1100 | 55 | 55, 77 | 29 | 53 [f] | / [g] | / | 13 | / | / | 12 | 314 | 345 | 413 |
| **PDEGF** | 9500 | 18300 | 0 | / | / | / | / | / | 33 | / | / | 33 | 363 | 388 | 421 |
| **PDEGF** | 10900 | 23800 | 0 | / | / | / | / | / | 39 | / | / | 40 | 375 | 387 | 415 |
| **PDEGF** | 12300 | 27800 | 0 | / | / | / | / | / | 40 | / | / | 42 | 371 | 384 | 415 |
| **PDEGF** | 31400 | 69400 | 0 | / | / | / | / | / | 40 | / | / | 41 | 363 | 385 | 415 |
| **P23BF** | 900 | 1100 | 0 | / | / | / | / | / | 46 | / | / | 47 | 276 | 308 | 360 |

[a] PBF = poly(butylene furanoate), PHF = poly(hexamethylene furanoate), POF = poly(octamethylene furanoate), PDF = poly(decamethylene furanoate), PDEGF = poly(diethylene glycol furanoate), P23BF = poly(2,3-butylene furanoate); [b] The number average molecular weight ($\bar{M}_n$) and weight average molecular weight ($\bar{M}_w$) were determined by SEC in $CHCl_3$; [c] The degree of crystallinity ($\chi_c$) was calculated from the WAXD spectrum. [d] $T_m$ = melting temperature, $\Delta H_m$ = enthalpy of fusion, $\Delta H_m^0$ = enthalpy of fusion when $\chi_c$ = 100 %, $T_c$ = crystallization temperature, $T_g$ = glass transition temperature, TMDSC = Temperature Modulated Differential Scanning Calorimetry; [e] $T_{d\text{-}5\%}$ = decomposition temperature at 5 % weight loss, $T_{d\text{-}10\%}$ = decomposition temperature at 10 % weight loss, $T_{d\text{-}max}$ = temperature at maximum rate of decomposition; [f] Here $\Delta H_m^0 = 100 \times \Delta H_m \div \chi_c$ ; [g] / = not detected.

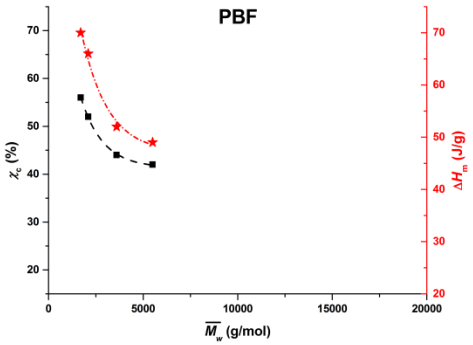



**Figure S22.** The degree of crystallinity ($\chi_c$) and the enthalpy of fusion ($\Delta H_m$, first heating scan) of poly(butylene furanoate) (PBF) as a function of the weight average molecular weight ($\bar{M}_w$)

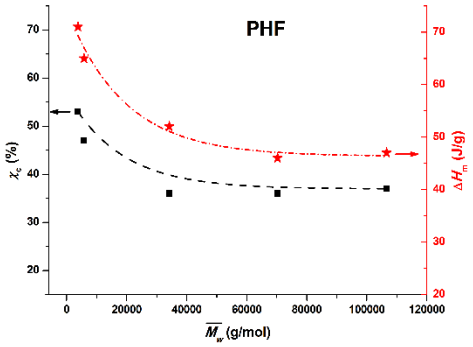



**Figure S23.** The degree of crystallinity ($\chi_c$) and the enthalpy of fusion ($\Delta H_m$, first heating scan) of poly(hexamethylene furanoate furanoate) (PHF) as a function of the weight average molecular weight ($\bar{M}_w$)

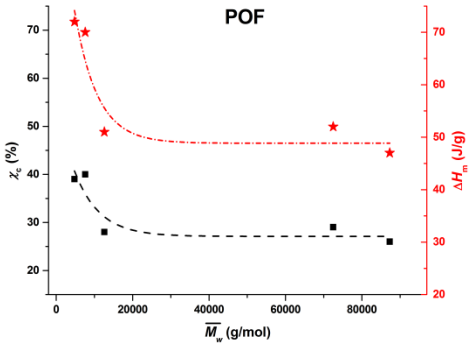



**Figure S24.** The degree of crystallinity ($\chi_c$) and the enthalpy of fusion ($^{\Delta H_m}$, first heating scan) of poly(octamethylene furanoate) (POF) as a function of the weight average molecular weight ($\bar{M}_w$)

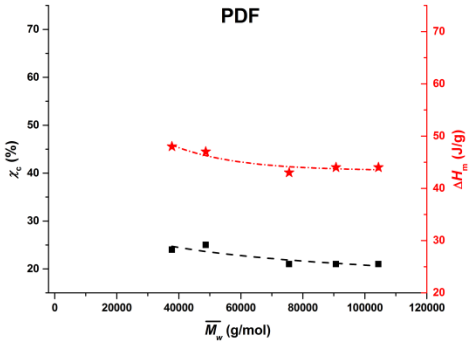



**Figure S25.** The degree of crystallinity ($\chi_c$) and the enthalpy of fusion ($^{\Delta H_m}$, first heating scan) of poly(decamethylene furanoate) (PDF) as a function of the weight-average molecular weight ($\bar{M}_w$)

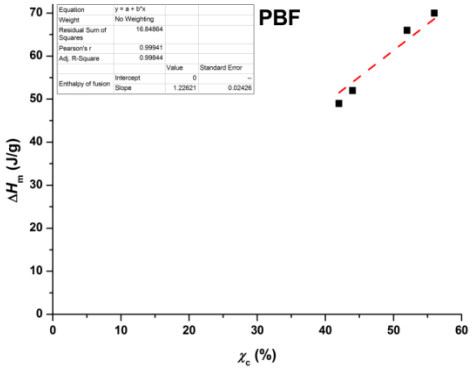



**Figure S26.** Linear fit of the enthalpy of fusion ($^{\Delta H_m}$) of poly(butylene furanoate) (PBF) as a function of the degree of crystallinity ($\chi_c$) using the equation: $^{\Delta H_m} = a + b \times \chi_c, where\ a = 0$.

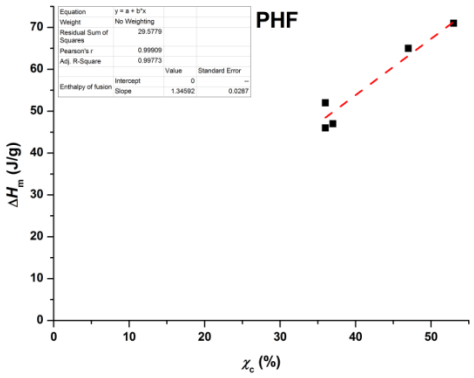



**Figure S27.** Linear fit of the enthalpy of fusion ($^{\Delta H_m}$) of poly(hexamethylene furanoate) (PHF) as a function of the degree of crystallinity ($\chi_c$) using the equation: $^{\Delta H_m} = a + b \times \chi_c, where\ a = 0$.

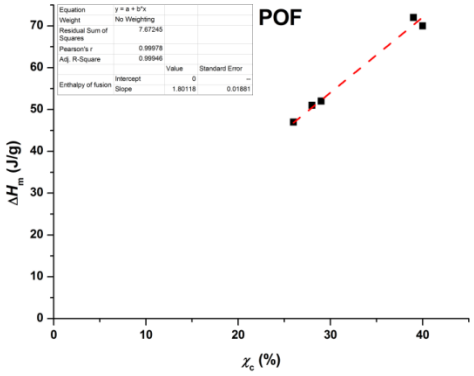



**Figure S28.** Linear fit of the enthalpy of fusion ($^{\Delta H_m}$) of poly(octamethylene furanoate) (POF) as a function of the degree of crystallinity ($\chi_c$) using the equation: $^{\Delta H_m} = a + b \times \chi_c, where\ a = 0$.

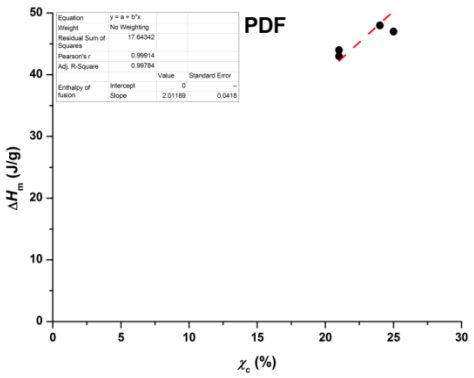



**Figure S29.** Linear fit of the enthalpy of fusion ($^{\Delta H_m}$) of poly(decamethylene furanoate) (PDF) as a function of the degree of crystallinity ($\chi_c$) using the equation: $^{\Delta H_m} = a + b \times \chi_c, where\ a = 0$.

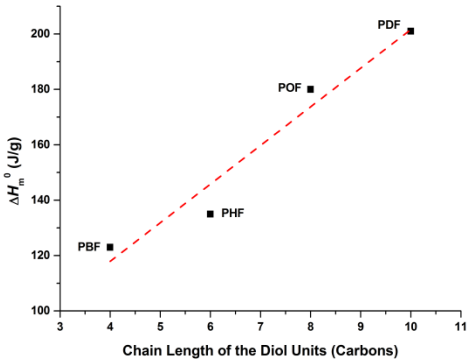



**Figure S30.** The enthalpy of fusion ($\Delta H_m^0$, 100 % degree of crystallization) of the furanic-aliphatic polyester as a function of the chain length of the diol units.

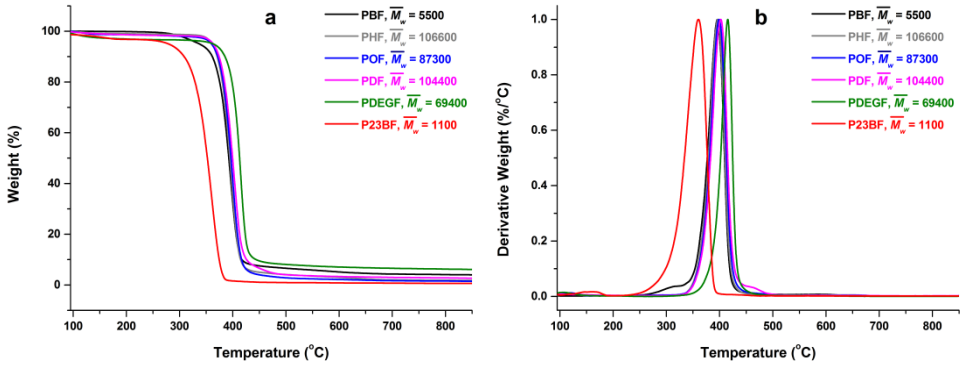
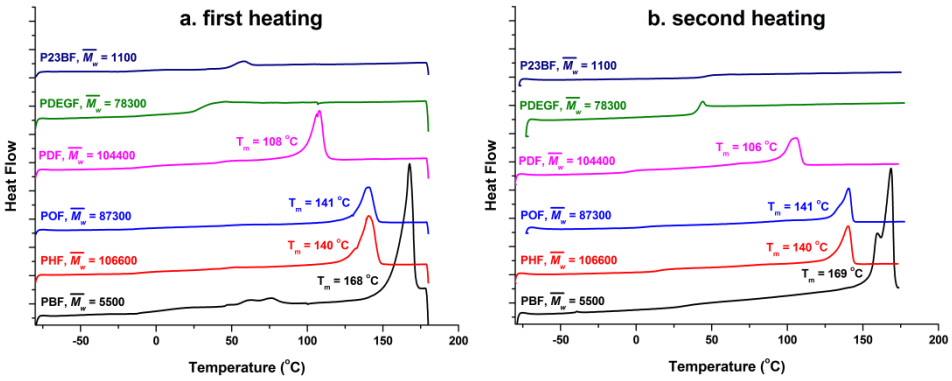



**Figure S31.** Representative TGA traces of the obtained furanic-aliphatic polyesters: (a) weight (%) as a function of temperature (°C); and (b) derivative weight (%/°C) versus temperature (°C).



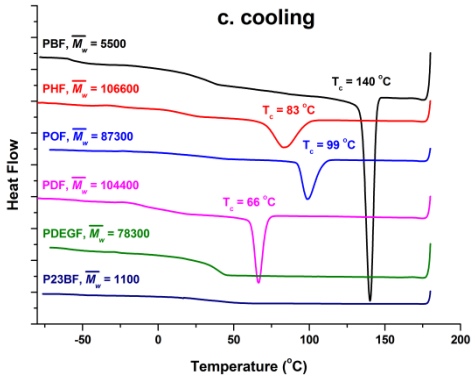



**Figure 32.** DSC curves of the obtained furanic-aliphatic polyesters. The heating and cooling rate were 10 °C/min.

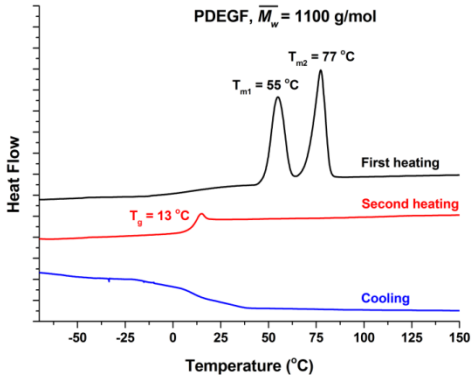



**Figure S33.** DSC curves of poly(diethylene glycol furanoate) (PDEGF, $\bar{M}_w$ = 1100 g/mol). The heating and cooling rate were 10 °C/min.

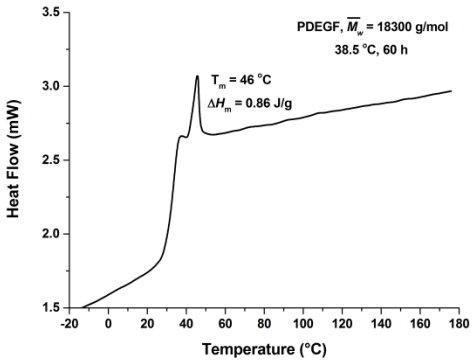



**Figure S34.** DSC heating curves of poly(diethylene glycol furanoate) (PDEGF, $\bar{M}_w$ = 18300 g/mol). The heating and cooling rate were 10 °C/min. After eliminated the thermal history, the sample was stored at 38.5 °C for 60 h before DSC measurement.

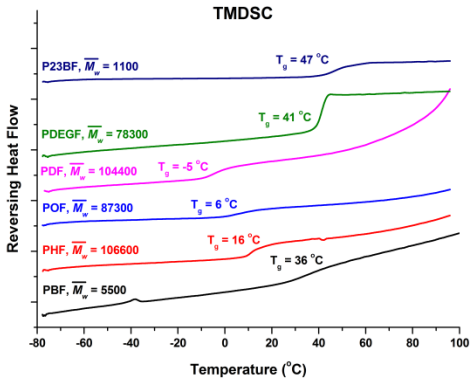



**Figure 35.** TMDSC (Temperature Modulated Differential Scanning Calorimetry) curves of furanic-aliphatic polyesters. The heating rate was 2 °C/min, with the temperature modulated at +/- 0.50 °C for every 60 seconds.