# Enzymatic synthesis of 2,5-furandicarboxylic acid-based semi-aromatic polyamides: enzymatic polymerization kinetics, effect of diamine chain length and thermal properties

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## Supporting Information

**Table S1.** Molecular weights and degrees of polymerization of the crude poly(octamethylene furanamide) (PA8F) from the one-stage enzymatic polymerization of DMFDCA (dimethyl 2,5-furandicarboxylate) and 1,8-ODA (1,8-octanediamine) at 90 °C in toluene

| Polymerization Time | $\bar{M}_n$ (g/mol) [a] | $\bar{M}_w$ (g/mol) [a] | $\bar{M}_p$ (g/mol) [a] | $\bar{DP}_n$ [b] | $\bar{DP}_w$ [b] | $\bar{DP}_p$ [b] |
|---|---|---|---|---|---|---|
| 2 h | 500 | 600 | 500 | 4 | 5 | 4 |
| 6 h | 600 | 900 | 600 | 5 | 7 | 5 |
| 9 h | 800 | 1700 | 1000 | 6 | 13 | 8 |
| 24 h | 1800 | 6400 | 5600 | 14 | 48 | 42 |
| 35 h | 1800 | 8600 | 5500 | 14 | 65 | 42 |
| 72 h | 2000 | 10700 | 6600 | 15 | 81 | 50 |

[a] $\bar{M}_n$ (number-average molecular weight), $\bar{M}_w$ (weight-average molecular weight) and $\bar{M}_p$ (peak molecular weight) were determined by SEC (conventional calibration), using LiBr/DMSO as the eluent; [b] $\bar{DP}_n$ (number-average degree of polymerization) $= 2 \times \bar{M}_n/M_{repeating\ unit}$, $\bar{DP}_w$ (weight-average degree of polymerization) $= 2 \times \bar{M}_w/M_{repeating\ unit}$, and $\bar{DP}_p$ (peak degree of polymerization, the major retention volume) $= 2 \times \bar{M}_p/M_{repeating\ unit}$, where $M_{repeating\ unit}$ is the molecular mass of the repeating units.

**Table S2.** Cumulative weight fractions of the crude PA8F from the one-stage enzymatic polymerization of DMFDCA and 1,8-ODA at 90 °C in toluene

| Retention Volume (mL) | Molecular Weight (g/mol) [a] | $\bar{D}P$ [b] | Cumulative Weight Fraction (%) [c] | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 2 h | 6 h | 9 h | 24 h | 35 h | 72 h |
| 33.2 – 34.2 | 200 - 500 | 2 - 4 | 37.9 | 28.1 | 16.0 | 5.2 | 4.8 | 5.1 |
| 32.5 - 33.2 | 500 - 800 | 4 - 6 | 54.2 | 50.7 | 24.3 | 7.1 | 6.7 | 6.5 |
| 31.1 – 32.5 | 800 - 2100 | 6 - 16 | 7.9 | 14.2 | 36.1 | 16.8 | 16.2 | 15.2 |
| 29.4 – 31.1 | 2100 - 5500 | 16 - 42 | 0.0 | 7.0 | 20.4 | 31.1 | 28.4 | 25.2 |
| 24.0 – 29.4 | 5500 – 67200 | 42 - 509 | 0.0 | 0.0 | 3.2 | 39.8 | 43.5 | 42.9 |
| 22.0 – 24.0 | 67200 - 178400 | 509 - 1350 | 0.0 | 0.0 | 0.0 | 0.0 | 0.4 | 5.1 |
| < 31.1 | < 2100 | < 16 | 100.0 | 93.2 | 76.5 | 29.3 | 27.8 | 26.8 |
| < 29.4 | < 5500 | < 42 | 100.0 | 100 | 96.8 | 60.2 | 56.1 | 52.0 |
| ≥ 29.4 | ≥ 5500 | ≥ 42 | 0.0 | 0.0 | 3.2 | 39.8 | 43.9 | 48.0 |

[a] Determined by the calibration curve generated by pullulan standards; [b] $\bar{D}P = 2 \times Molecular\ Weight/M_{repeating\ unit}$, where $M_{repeating\ unit}$ is the molecular mass of the repeating unit octamethylene furanamide; [c] Determined by SEC based on the refractive index signal.

**Table S3.** Results summary: N435-catalyzed polycondensation of DMFDCA and various aliphatic diamines using a one-stage method at 90 °C in toluene

| Polyamide | x [a] | NMR [b] | SEC [d] | | | | Isolation Yield (%) [g] |
|---|---|---|---|---|---|---|---|
| | | $\bar{M}_n$ (g/mol) | $\bar{M}_n$ (g/mol) | $\bar{M}_w$ (g/mol) | $D\bar{P}_w$ [f] | $Đ$ ($\bar{M}_w/\bar{M}_n$) | |
| PA4F | 4 | 3030 [c] | 12300 | 15800 | 152 | 1.30 | 7 |
| PA6F | 6 | 3316 | 13400 | 20600 | 174 | 1.50 | 23 |
| PA8F | 8 | 7800 | 13400 [e] | 48300 [e] | 365 [e] | 3.60 [e] | 53 |
| PA10F | 10 | 4209 | 13400 | 21200 | 145 | 1.60 | 35 |
| PA12F | 12 | 2062 | 9500 | 19900 | 124 | 2.10 | 16 |

[a] X is the number of the methylene units in the diamine segments, which defines the chain length of the tested aliphatic diamines; [b] $\bar{M}_n$ (number-average molecular weight) was determined by $^1$H NMR according to the method established in our previous report (see *Biomacromolecules* **2015,** 16, (11), 3674-3685); [c] $\bar{M}_n$ was calculated from $^1$H NMR with the assumption that all the obtained PA4F was terminated by amino groups at the one end and methoxyl groups at the other end; [d] $\bar{M}_n$, $\bar{M}_w$ (weight-average molecular weight), and $Đ$ (dispersity, $\bar{M}_w/\bar{M}_n$) were determined by SEC (conventional calibration) using LiBr/DMF (0.01M) as the eluent; [e] $\bar{M}_n$, $\bar{M}_w$ and $Đ$ of PA8F were determined by SEC (universal calibration) using LiBr/DMSO as the eluent; [f] $D\bar{P}_w = 2 \times \bar{M}_w/M_{repeating\ unit}$, where $M_{repeating\ unit}$ is the molecular mass of the repeating units; [g] Yield of purified products.

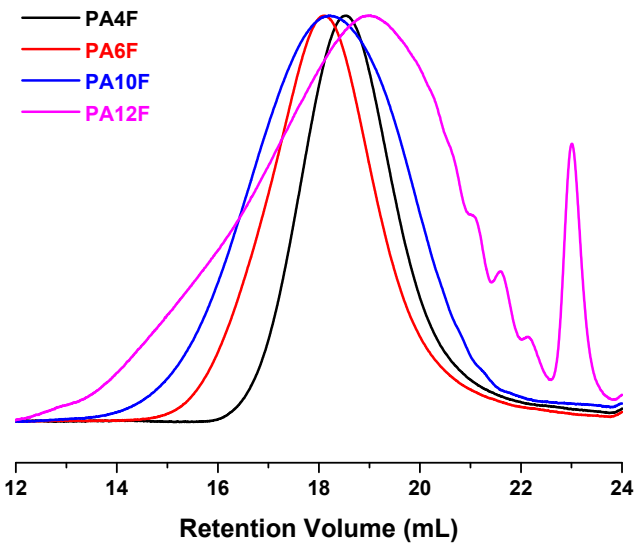

**Figure S1.** SEC elution curves of the obtained FDCA-based semi-aromatic polyamides (PAXF) produced via the one-stage enzymatic polymerization in toluene at 90 °C. The eluent was DMF with LiBr. X presents the methylene units in the diamine segments.

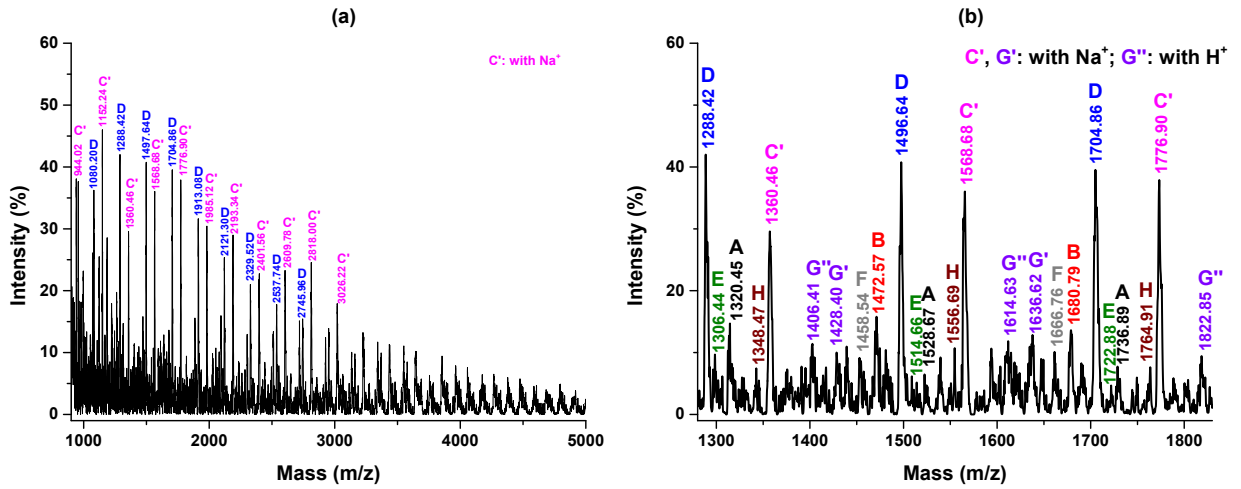


**Figure S2.** MALDI-ToF MS spectrum of the obtained poly(butylene furanamide) (PA4F) with detailed peak interpretation. PA4F was produced via the one-stage enzymatic polymerization of DMFDCA and 1,4-butanediamine (1,4-BDA) in toluene at 90 °C.

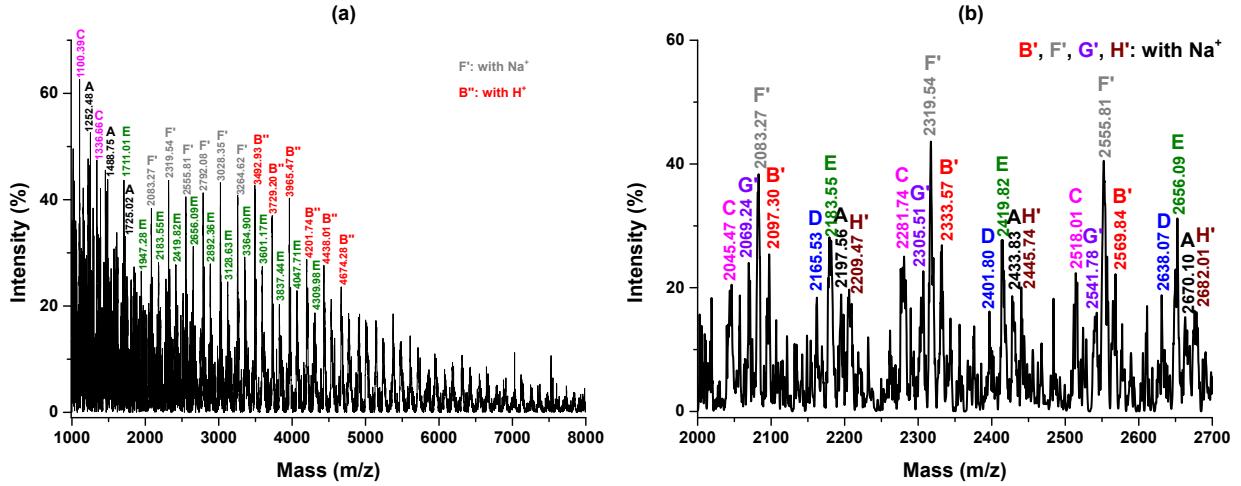

**Figure S3.** MALDI-ToF MS spectrum of the obtained poly(hexamethylene furanamide) (PA6F) with detailed peak interpretation. PA6F was produced via the one-stage enzymatic polymerization of DMFDCA and 1,6-hexanediamine (1,6-HDA) in toluene at 90 °C.

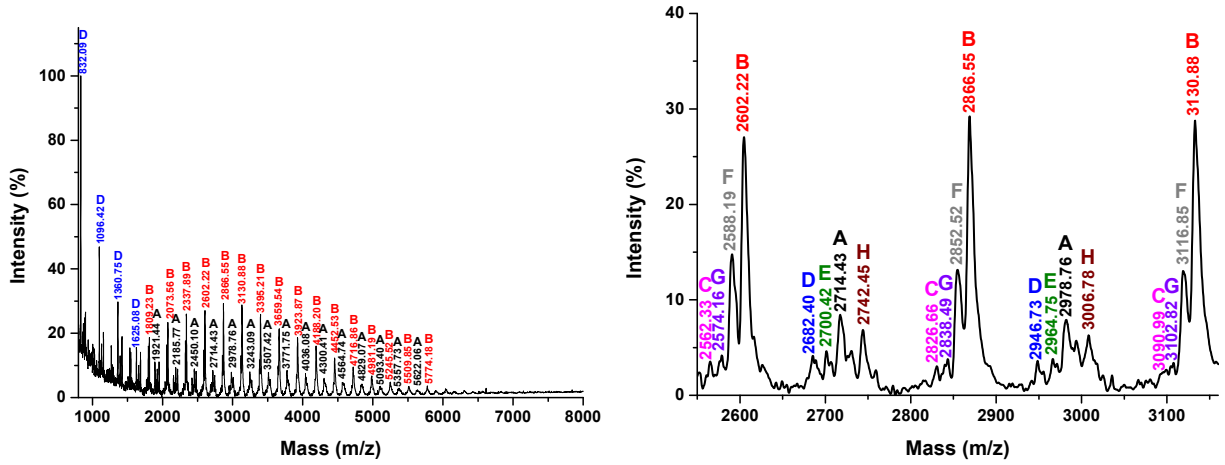


**Figure S4.** MALDI-ToF MS spectrum of poly(octamethylene furanamide) (PA8F) with detailed peak interpretation. PA8F was produced via the one-stage enzymatic polymerization of DMFDCA and 1,8-ODA in toluene at 90 °C.

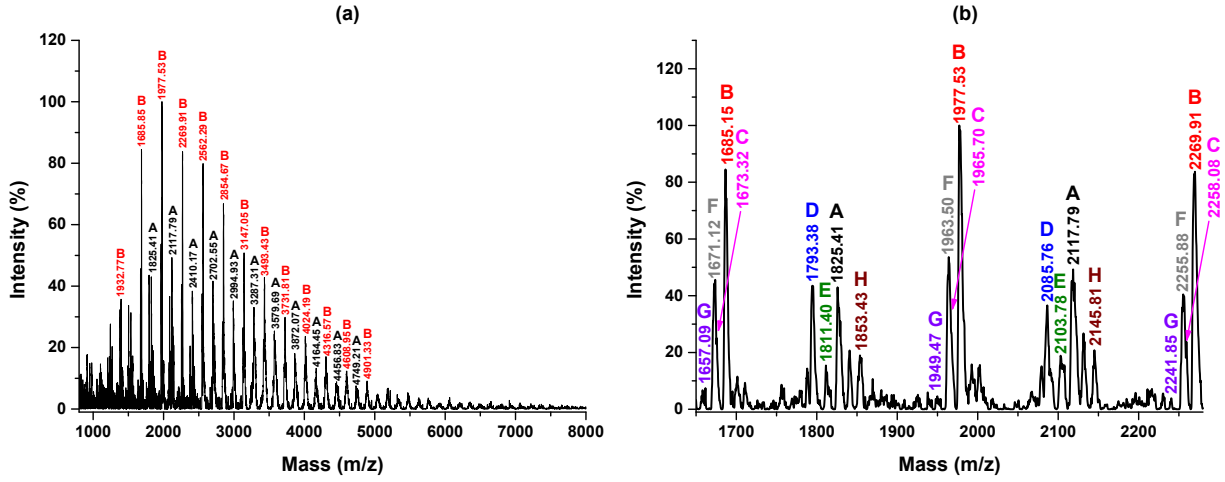


**Figure S5.** MALDI-ToF MS spectrum of the obtained poly(decamethylene furanamide) (PA10F) with detailed peak interpretation. PA10F was produced via the one-stage enzymatic polymerization of DMFDCA and 1,10-decanediamine (1,10-DDA) in toluene at 90 °C.

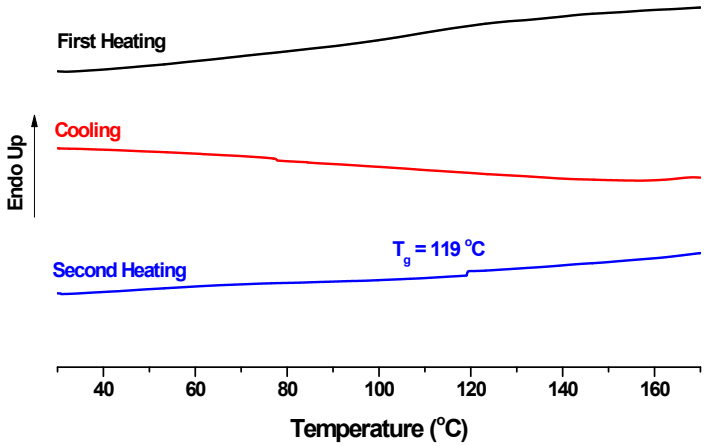


**Figure S6.** DSC curves of the obatined PA4F. PA4F ($\bar{M}_n$ = 12300 g/mol, $\bar{M}_w$ = 15800 g/mol) was produced via the one-stage enzymatic polymerization of DMFDCA and 1,4-BDA in toluene at 90 °C.

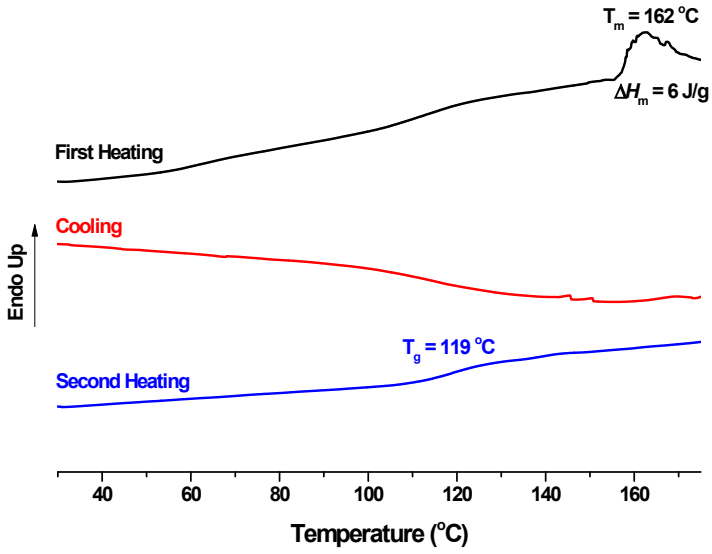


**Figure S7.** DSC curves of the obatined PA6F. PA6F ($\bar{M}_n$ = 13400 g/mol, $\bar{M}_w$ = 20600 g/mol) was produced via the one-stage enzymatic polymerization of DMFDCA and 1,6-HDA in toluene at 90 °C.

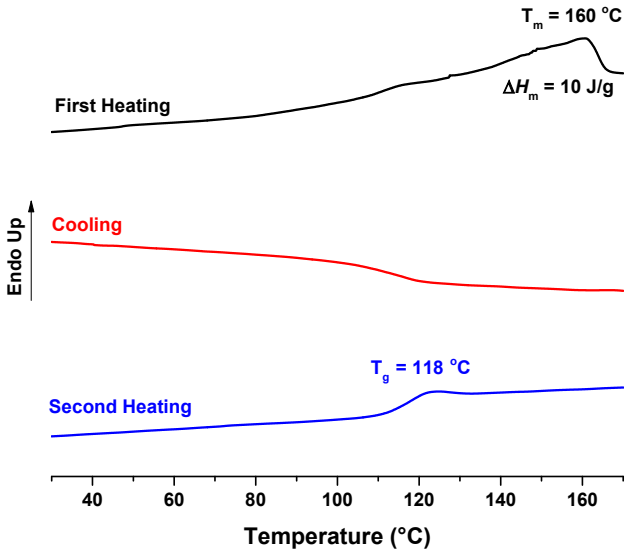


**Figure S8.** DSC curves of the obtained PA8F. PA8F ($\bar{M}_n$ = 13400 g/mol, $\bar{M}_w$ = 48300 g/mol) was produced via the one-stage enzymatic polymerization of DMFDCA and 1,8-ODA in toluene at 90 °C.

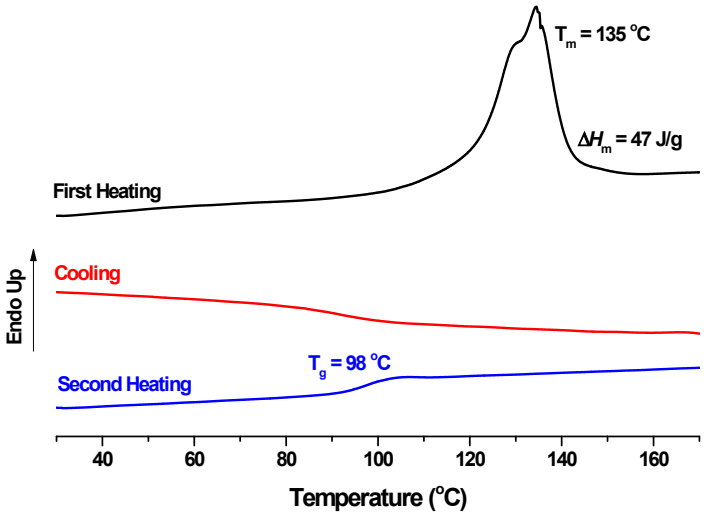


**Figure S9.** DSC curves of the obtained PA10F. PA10F ($\bar{M}_n$ = 13400 g/mol, $\bar{M}_w$ = 21200 g/mol) was produced via the one-stage enzymatic polymerization of DMFDCA and 1,10-DDA in toluene at 90 °C.