Supporting Information

MALDI-TOF analysis: additional end groups of the obtained FDCA-based heteroatom polyamides, ^{13}C NMR spectra of FDCA-based heteroatom polyamides produced via enzymatic polymerization in bulk, SEC elution curves of the obtained FDCA-based heteroatom polyamides, MALDI-ToF MS spectra of the obtained FDCA-based heteroatom polyamides with detailed peak interpretation.

Enzymatic Polymerization of Dimethyl 2,5-Furandicarboxylate and Heteroatom Diamines

*Dina Maniar[1], Katharina F. Hohmann[2], Yi Jiang[1], Albert J.J. Woortman[1], Jur van Dijken[1] and Katja Loos[1]**

[1]Macromolecular Chemistry & New Polymeric Materials, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen

[2]Institute for Organic Chemistry and Chemical Biology, Johann Wolfgang Goethe-University, Max-von-Laue-Straße 7, D-60438 Frankfurt am Main

Table S1. MALDI-ToF MS Analysis: additional end groups of the obtained PA DODAF

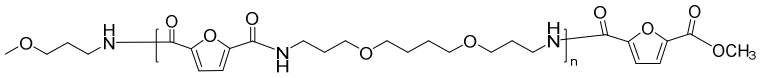
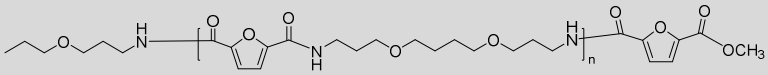
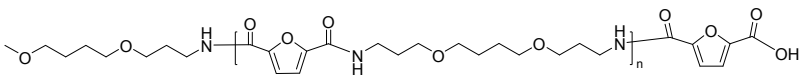
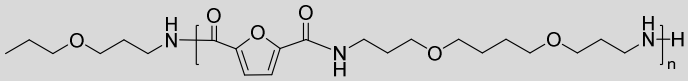
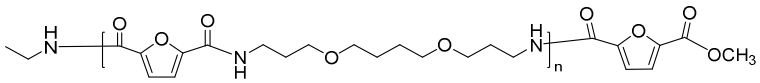
Entry	Polymer species	Remaining mass (amu)
I		241.1
J		269.13
K		299.13
L		117.12
M		197.07

Table S2. MALDI-ToF MS Analysis: additional end groups of the obtained PA DETAF

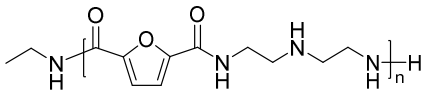
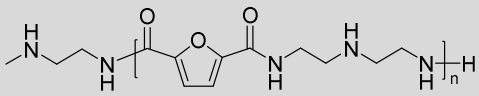
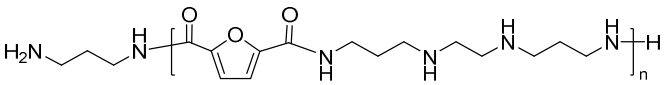
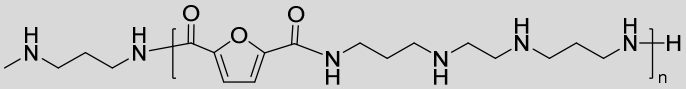
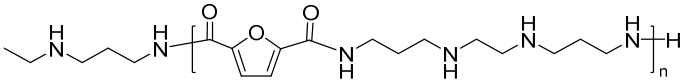
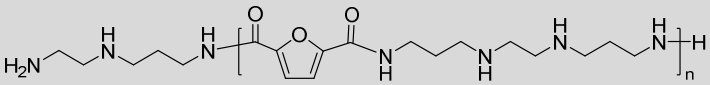
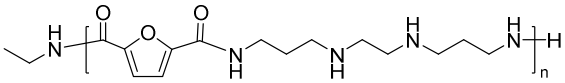
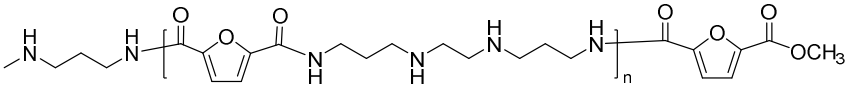
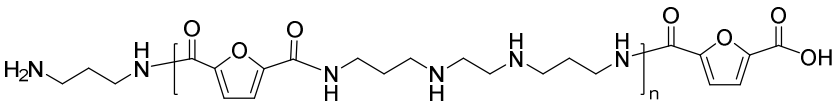
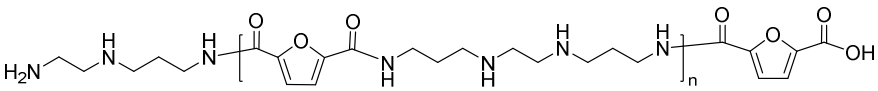
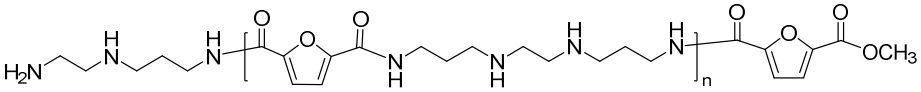
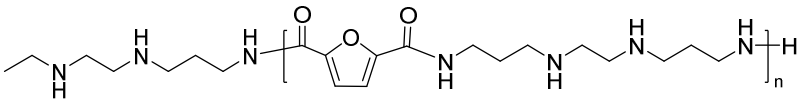
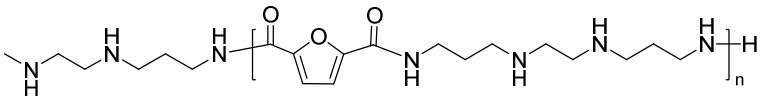
Entry	Polymer species	Remaining mass (amu)
I		45.06
J		74.09

Table S3. MALDI-ToF MS Analysis: additional end groups of the obtained PA EDDAF

Entry	Polymer species	Remaining mass

		(amu)
I		74.09
J		88.1
K		102.12
L		117.13
M		45.06
N		240.11
O		212.08
P		255.12
Q		269.14
S		145.16
T		131.14

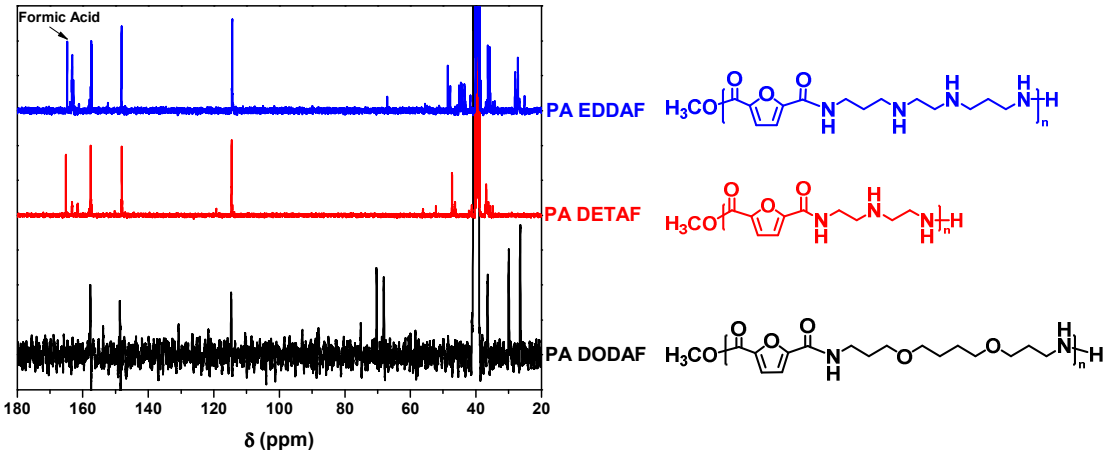


Figure S1. ^{13}C NMR spectra of FDCA-based heteroatom polyamides produced via enzymatic polymerization in bulk.

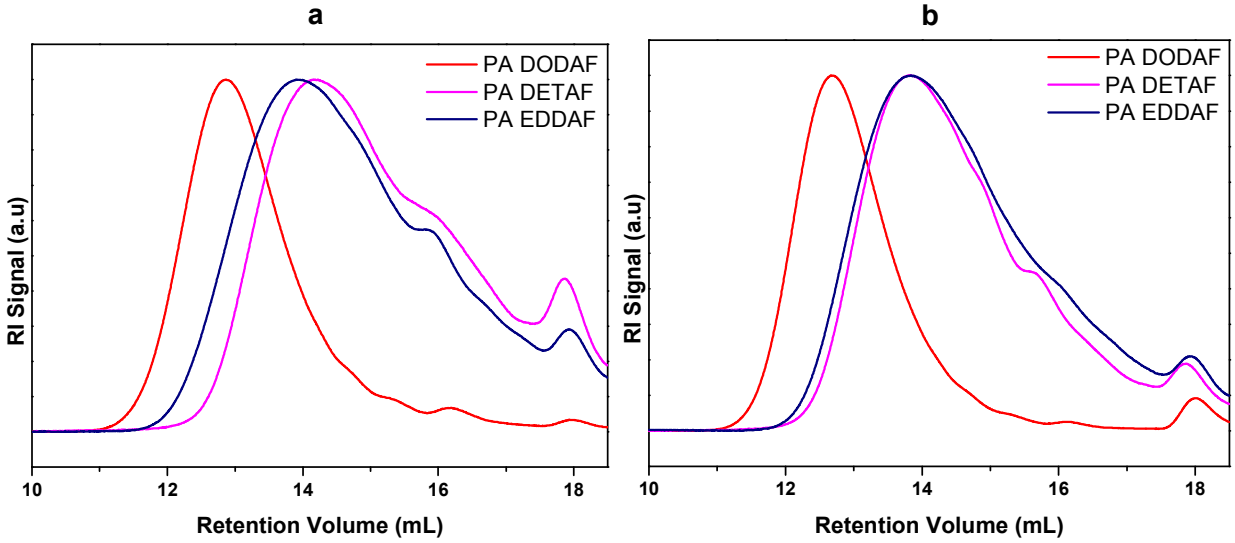


Figure S2. SEC elution curves of the obtained FDCA-based heteroatom polyamides: (a) enzymatic polymerization in solution; and (b) in bulk. The eluent was DMF with LiBr.

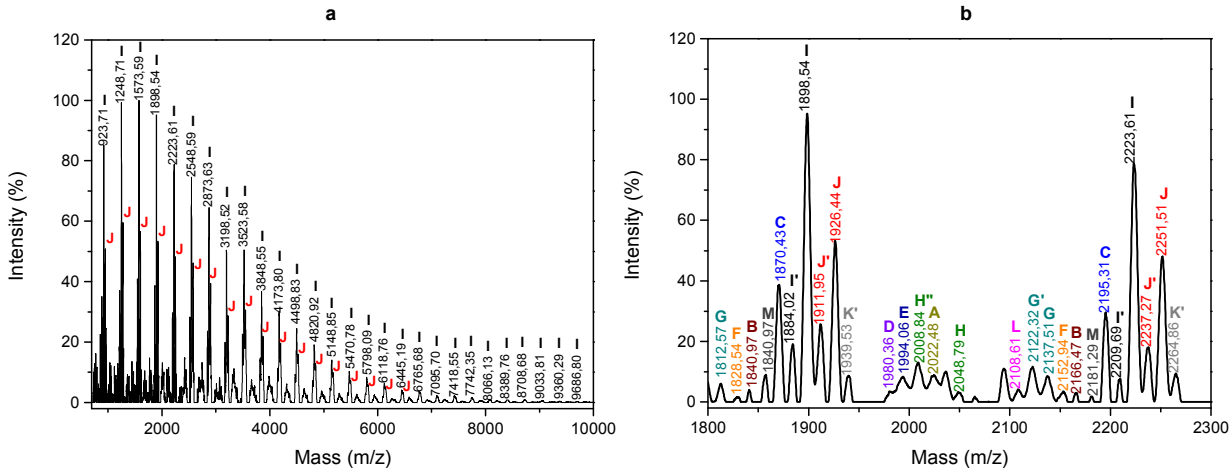


Figure S3. (a) MALDI-ToF MS spectrum of the obtained PA DODAF and (b) magnified part with detailed peak interpretation. A-H represent eight polyamide species ionized by K^+. G' represents the polyamides having the acid/acid end groups that are ionized by Na^+. H" represents the polyamide having ester/amide end groups that are ionized by H^+. I-M represent five polyamide species fragment due to the fragmentation in the heteroatom bond. I'-K' represent the polyamide species fragment that are ionized by Na^+. PA DODAF was produced via enzymatic polymerization in solution.

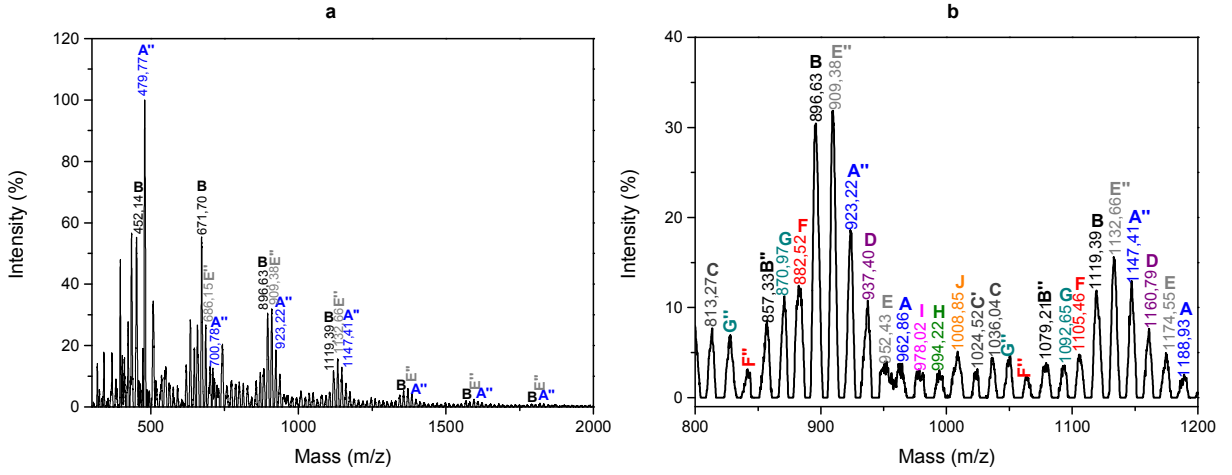


Figure S4. (a) MALDI-ToF MS spectrum of the obtained PA DETAF and (b) magnified part with detailed peak interpretation. A-H represent eight polyamide species ionized by K^+. C' represents the polyamides having the amine/amine end groups that are ionized by Na^+. A", B"

and E" represent the polyamide having ester/amine, ester/ester and acid/amine end groups that are ionized by H^+. I and J represent two polyamide species fragment due to the fragmentation in the heteroatom bond. PA DETAF was produced via enzymatic polymerization in solution.

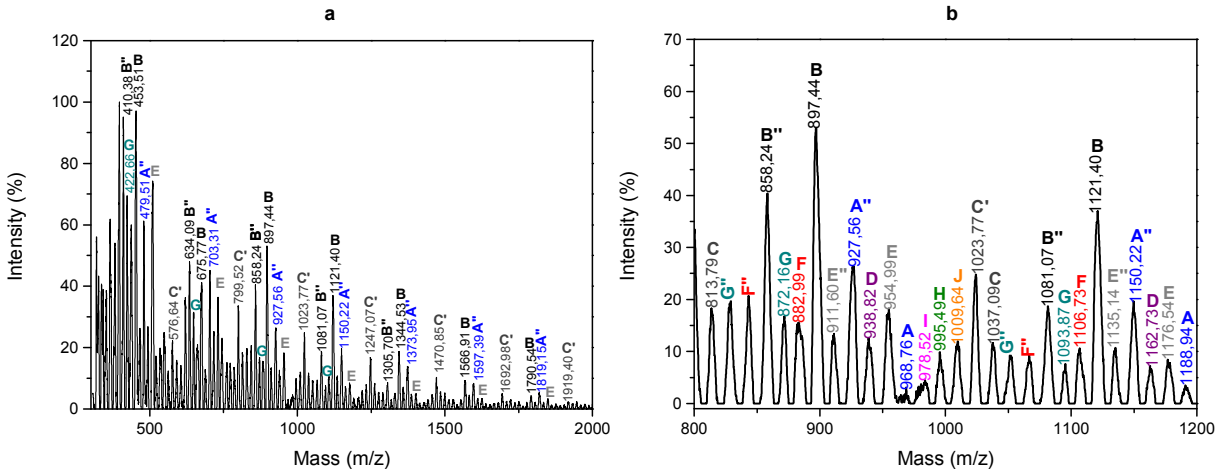


Figure S5. (a) MALDI-ToF MS spectrum of the obtained PA DETAF and (b) magnified part with detailed peak interpretation. A-H represent eight polyamide species ionized by K^+. C' represents the polyamides having the amine/amine end groups that are ionized by Na^+. A", B" and E" represents the polyamide having ester/amine, ester/ester and acid/amine end groups that are ionized by H^+. I and J represent two polyamide species fragment due to the fragmentation in the heteroatom bond. PA DETAF was produced via enzymatic polymerization in bulk.

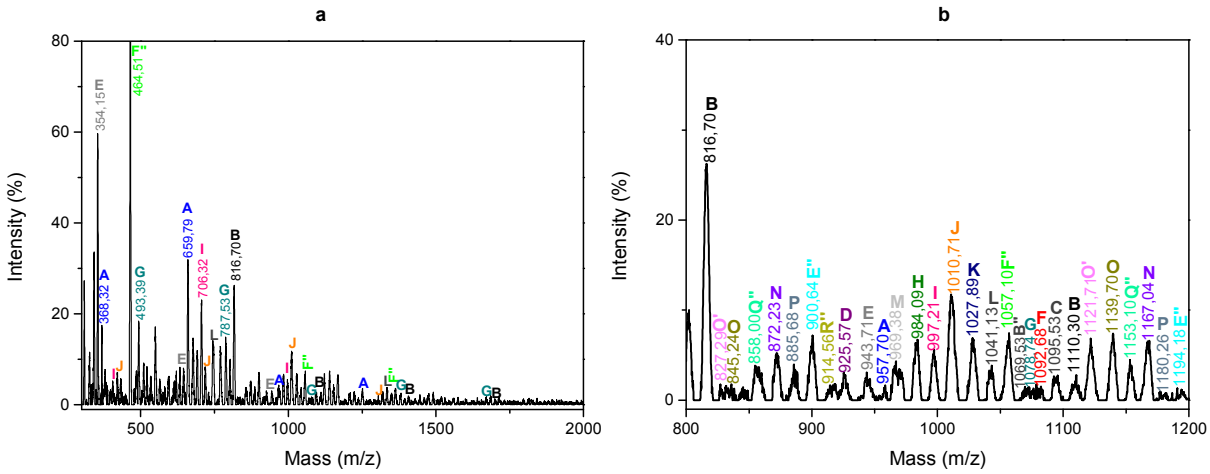


Figure S6. (a) MALDI-ToF MS spectrum of the obtained PA EDDAF and (b) magnified part with detailed peak interpretation. A-H represent eight polyamide species ionized by K^+. B", E" and F" represents the polyamide having ester/ester, acid/amine, and ester/acid end groups that are ionized by H^+. I-P represent eight polyamide species fragment due to the fragmentation in the heteroatom bond. O' represent the polyamide species fragment that are ionized by Na^+. Q" and R" the polyamide species fragment that are ionized by H^+. PA EDDAF was produced via enzymatic polymerization in solution.

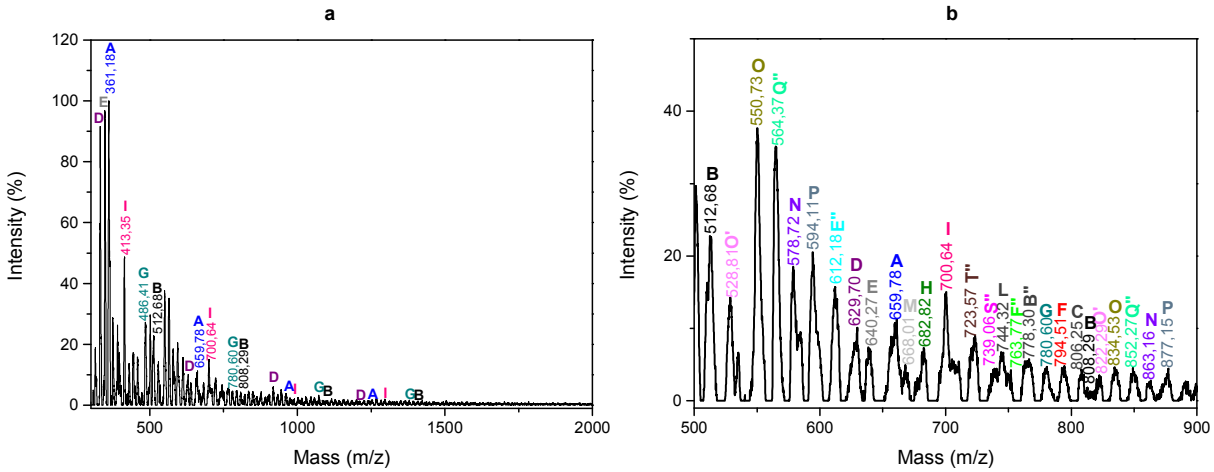


Figure S7. (a) MALDI-ToF MS spectrum of the obtained PA EDDAF and (b) magnified part with detailed peak interpretation. A-H represent eight polyamide species ionized by K^+. B", E" and F" represents the polyamide having ester/ester, acid/amine, and ester/acid end groups that are ionized by H^+. I, L-P represent six polyamide species fragment due to the fragmentation in the heteroatom bond. O' represent the polyamide species fragment that are ionized by Na^+. Q", S" and T" the polyamide species fragment that are ionized by H^+. PA EDDAF was produced via enzymatic polymerization in bulk.

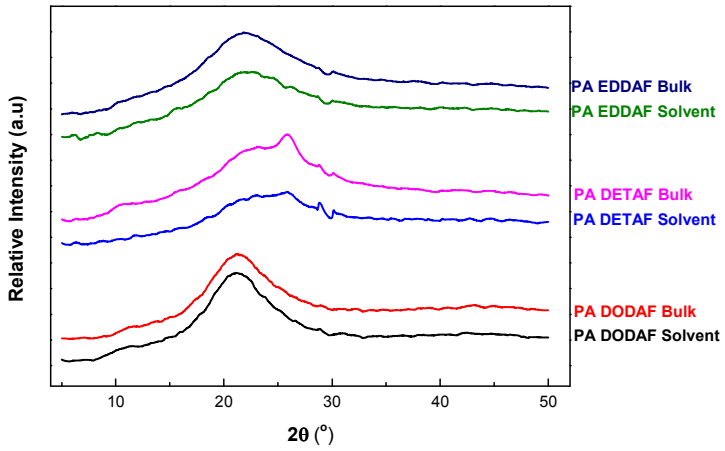


Figure S8. Wide-Angle X-Ray Diffraction (WAXD) spectra of the obtained FDCA-based heteroatom polyamides.