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Electronic Supplementary Information (ESI)

Preparation of chemically recyclable bio-based semi-aromatic polyamides using continuous flow technology in mild condition

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Materials

Dimethyl furan-2,5-dicarboxylate (DMFDCA, 99.92%), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, 97%), 1,8-octanediamine (1,8-ODA, 99.75%) are purchased from Bidepharm. 1,5-pentanediamine (1,5-PDA, 97%) is purchased from Energy chemical. 1,10-decanediamine (99%) is purchased from Meryer. N-Methylpyrrolidone (NMP, 99.5%) and N,N-Diethylformamide (DEF, 99%) are purchased from Macklin. Dimethyl sulfoxide (DMSO, 99%) and tetramethylene sulfone (TMS, 99%) are obtained from Sigma-Aldrich. Solvents for NMR spectroscopy are used as received from Adamas-beta. Sodium trifluoroacetate (Na-TFA, 98 %) is acquired from Sigma-Aldrich. 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 99 %) and 1,8,9-anthracenetriol (dithranol, 98%) are purchased from Aladdin and Meryer, respectively. Both 1,8-diazabicycloundec-7-ene (DBU, 98%) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 98%) are obtained from Meryer. Titanium(IV) isopropoxide (TIPT, 95%) is purchased from Aladdin. All chemical compounds are used without further purification.

Polyamide synthesis

In the precursor formulation module, DMFDCA, PDA and TBD catalyst are first fully dissolved in solvents. Then this fluid is fed to the microreactor using syringe pumps (Leadfluid, TYD01-01-CE). The residence time (τ) in the microreactor is varied by adjusting the flowrate. The fluidic connection is enabled using IDEX 1/4″-28 fittings with fluorinated ethylene propylene (FEP) tubing of 1/16″ inner diameter (I.D.) and 1/8″ outer diameter (O.D.). Subsequently, the synthesis of PA5F is operated through the following two flow procedures (labeled as *Flow_1* and *Flow_2*). In *Flow_1*, FEP tubing of 5 m length is used. In *Flow_2*, two similar tubings are connected in series, as is shown in Figure S1, in which one is placed in a low temperature thermostatic bath, and the other is placed at an elevated temperature bath. The temperature of the oil in the bath is controlled by Hot Plate & Stirrer Accessories (Heidolph). After reaction finished, the polymer solution is collected for post-processing.

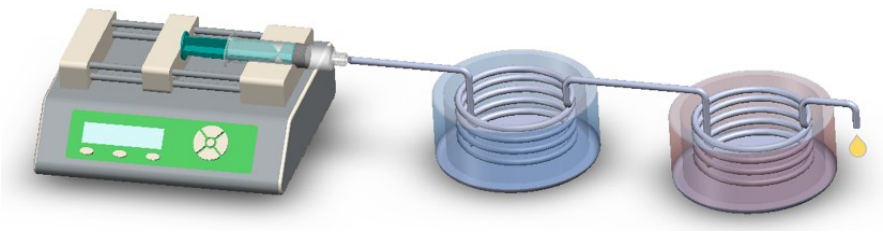


Figure S1. Continuous flow platform of *Flow_2* for polyamide synthesis

Characterization methods

^{1}H and ^{13}C NMR spectra are recorded on a Bruker Ascend (III) spectrometer at 400 MHz and 100 MHz with DMSO-d_6 or TFA-d_1 as the solvent. The chemical shifts are referenced relative to the tetramethylsilane. Fourier transform infrared spectra (FT-IR) tests are performed on a BRUKER TENSOR 27 Fourier infrared spectrometer. X-ray powder diffraction (XRD) tests are performed on a Bruker D8 Advance X-ray diffractometer.

Differential scanning calorimetry (DSC) analyses are conducted using a TA-instrument Discovery 250 system with a flow N_2 rate of 50 mL/min. The measurement is carried out according to the following process: sample is heated to 250 °C at a rate of 20 °C/min and held at this temperature for 3 min, then it is cooled down to 30 °C at a rate of -20 °C/min and subsequently heated to 250 °C again at a rate of 20 °C/min. Glass transition temperature (Tg) is recorded on the second heating scan.

Thermogravimetric analysis (TGA) is performed on a TGA550 thermal gravimetric analyzer. The results are recorded from 30 to 600 ℃ with rate of 10 ℃/min under a constant flow of nitrogen.

Gel permeation chromatography (GPC) is performed on on an Agilent Technologies 1260 Infinity II instrument with 14.5 mM LiBr in N,N-dimethylformamide as the mobile phase at 50 ℃ and a flow rate of 0.7 mL/min. Samples are prepared by dissolving 2 mg polymer in 1 mL mobile phase and filtered with a 0.2 μm nylon syringe filter before injection into the GPC. Polystyrene is used as standard sample to determine the molecular weight and dispersity.

Matrix-assisted laser desorption/ionization time of flight (MALDI-ToF) mass

spectrometry is performed using a Bruker Autoflex Speed instrument in linear positive mode. The polymer sample (10 mg/mL), matrix 1,8,9-anthracenetriol (dithranol) (10 mg/mL) and Na-TFA (0.1 M), all in HFIP solvent, are combined in the ratio 20:50:2 µL respectively. The solution is then centrifuged and 0.5 µL of the solution is dropped onto the MALDI plate and allowed to dry under ambient conditions. The remaining mass of different end-groups is calculated using following equation:

$$M_{eg} = M_{ps} - \{(M_{ru} \times n) + M_{cation}\}$$

where M_{eg} is the mass of end-group, M_{ps} is the mass of polymer species, M_{ru} is the mass of repeating unit, n is number of repeat units in the polymer species and M_{cation} is the mass of cation.

Chemical structure characterization of furan-based polyamides

ATR-FTIR (ν, cm^{-1}): 3301 (N–H stretching vibrations); 3116 (=C–H stretching vibrations of the furan ring); 2930, 2861 (asymmetric and symmetric C–H stretching vibrations); 1652 (C=O stretching vibrations); 1578 (aromatic C=C bending vibrations); 1533 (N–H bending vibrations); 1490-1434 (C–H deformation and wagging vibrations); 1360 (C–H rocking vibrations); 1290 (C–N stretching vibrations); 1162–1014 (=C–O–C= ring vibrations, furan ring); 957-759 (=C–H out-of-plane deformation vibrations, furan ring); 714 (–$(CH_2)_n$–, rocking vibrations).

Poly(pentamethylene furanamide) (PA5F)(^{1}H NMR, 400 MHz, DMSO-d6, δ ppm, 298 K): 8.48 (2H, -N**H**-CO-), 7.09 (2H, =C**H**- of furan), 3.25 (4H, -NH-C**H**$_2$-$(CH_2)_3$-C**H**$_2$-NH-), 1.53 (4H, -NH-CH_2-C**H**$_2$-CH_2-C**H**$_2$-CH_2-NH-), 1.33 (4H, -NH-$(CH_2)_2$-C**H**$_2$-$(CH_2)_2$-NH-). ^{13}C NMR (75 MHz, DMSO-d_6, δ ppm): 157.61 (–**C**O–NH–, from DMFDCA), 148.65 (–NH–CO–**C**(O)=CH–, furan), 114.68 (=**C**H–, furan), 38.88 (–CO–NH–**C**H_2–), 29.48 (–CO–NH–CH_2–**C**H_2–), 26.36 (–CO–NH–CH_2–CH_2–**C**H_2–).

Poly(octamethylene furanamide) (PA8F)(^{1}H NMR, 400 MHz, DMSO-d6, δ ppm, 298 K): 8.43 (2H, –N**H**-CO-furan-CO-N**H**-), 7.09 (2H, =C**H**– of furan ring), 3.22 (4H, –NH-C**H**$_2$-$(CH_2)_6$-C**H**$_2$-NH-), 1.49 (4H, –NH-CH_2-C**H**$_2$-$(CH_2)_4$-C**H**$_2$-CH_2-NH-), 1.26 (8H,–NH-$(CH_2)_2$-(C**H**$_2$)$_4$-$(CH_2)_2$-NH).

Poly(decamethylene furanamide) (PA10F)(^{1}H NMR, 400 MHz, DMSO-d_6, δ ppm, 298 K): 8.43 (2H, –N**H**-CO-furan-CO-N**H**-), 7.08 (2H, =C**H**– of furan ring), 3.22 (4H, –NH-C**H**$_2$-(CH$_2$)$_8$-C**H**$_2$-NH-), 1.47 (4H, –NH-CH$_2$-C**H**$_2$-(CH$_2$)$_6$-C**H**$_2$-CH$_2$-NH-), 1.26 (12H,–NH-(CH$_2$)$_2$-(C**H**$_2$)$_6$-(CH$_2$)$_2$-NH-).

Catalyst screening for polyamide synthesis

Catalytic performances are explored in the presence of 1,8-diazabicycloundec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and Titanium(IV) isopropoxide (TIPT), as shown in Figure S2. Notably, with DBU and DBN as catalysts, there are no polyamides precipitated when the reactor effluents are added dropwise into an excess amount of water, which indicates their low catalytic efficiency. The hydrogen bonding site and nucleophilic site of guanidine functionality in TBD plays an important role to accelerate the polymerization of DMFDCA and PDA, which other catalysts, DBU and DBN, do not possess. Compared to the polymerization catalyzed by TIPT catalyst, PA5F with higher isolated yield and T_g is obtained in the presence of TBD catalyst. Thus, TBD is selected as the preferred catalyst in this work.

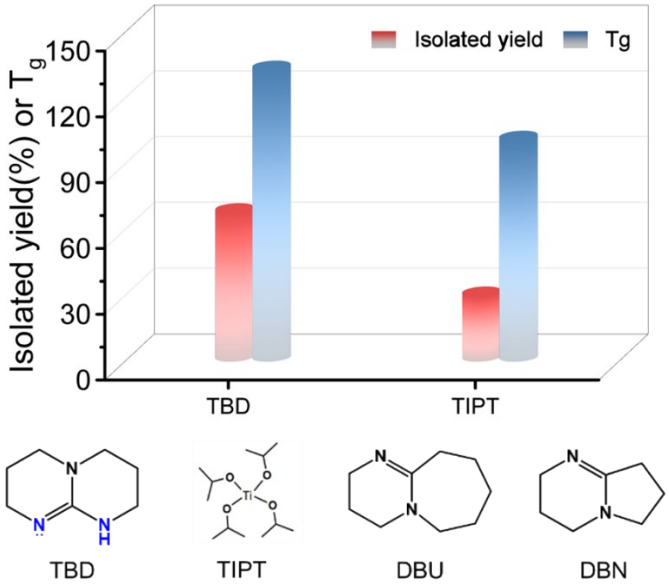


Figure S2. The isolated yield and T_g of PA5F in the presence of different catalysts, reaction conditions: T_R=90 °C, time=1h, catalyst loading=10 mol%, PDA/DMFDCA=1.

Effect of reaction time and temperature on molecular weight

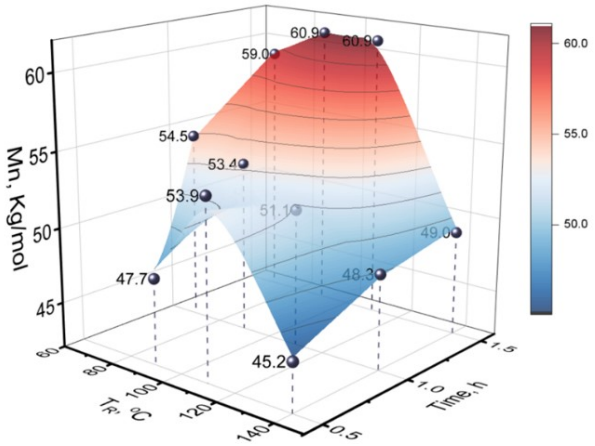


Figure S3. The effect of reaction time and temperature on molecular weight, reaction conditions: [DMFDCA]=0.92 mol/L, PDA/ DMFDCA=1, TBD=6 mol%.

Properties comparison of furan-based polyamides

Table 1 The properties comparison of furan polyamides

Entry	Polyamides	Monomers	Synthesis technique	Catalyst	Mn (kg/mol)	PDI	Tg (°C)	Tmax (°C)	Ref.
1	PA5F	FDCA, PDA	Ammonium salt route	-	10.46	2.64	86.0	420.5	[1]
2	PA10F	FDCA, DDA	Ammonium salt route	-	10.26	2.62	34.7	440.8	[1]
3	PA4F	DMFDCA BDA	Two-step melt polycondensation	TIPT	10	2.33	140	424	[2]
4	PA6F	DMFDCA HMDA	Two-step melt polycondensation	TIPT	11	2.91	127	434	[2]
5	PA8F	DMFDCA ODA	Two-step melt polycondensation	TIPT	10	2.99	129	442	[2]
6	PA10F	DMFDCA DDA	Two-step melt polycondensation	TIPT	11	3.30	96	446	[2]
7	PA6MF	DMFDCA MPDA	Two-step melt polycondensation	TIPT	8	2.40	136	429	[2]
8	PA10F	DMFDCA DDA	Bulk polymerization	TBD	27.7	2.25	103	454	[3]
9	PA10F	DMFDCA DDA	Two-step solid-state polymerization	SHP	6.3	3.67	97.6	445.6	[4]
10	PA8F	DMFDCA ODA	Enzymatic polymerization	N435	11.1	4.86	125	461	[5]

MP = Melt polymerization, ASR = Ammonium salt route, EP = Enzymatic polymerization, IP = Interfacial polymerization, BDA =1,4-butanediamine, PDA=1,5-pentanediamine, HMDA=1,6-hexanediamine, ODA=1,8-octanediamine, DDA=1,10-decanediamine, MPDA=2-methyl-1,5-pentanediamine, TIPT = titanium (IV) iso-propoxide, TBD = 1,5,7-triazabicyclo[4.4.0]dec-5-ene, SHP = sodium hypophosphite, N435 = Novozym 435

Extent of N-methylation

The residual TFA signal is set at 11.500 ppm. The integral value of the furan signal at 7.41 ppm is set to 2.000, all other signals are then integrated. The relative concentration of different functional groups is estimated following the ^{1}H NMR chemical shifts using following equations.

$$\%\ N-methylation = \frac{(integra\ at\ 3.00\ ppm + integral\ at\ 3.09\ ppm + integral\ at\ 3.18\ ppm)}{3} \times 100\%$$

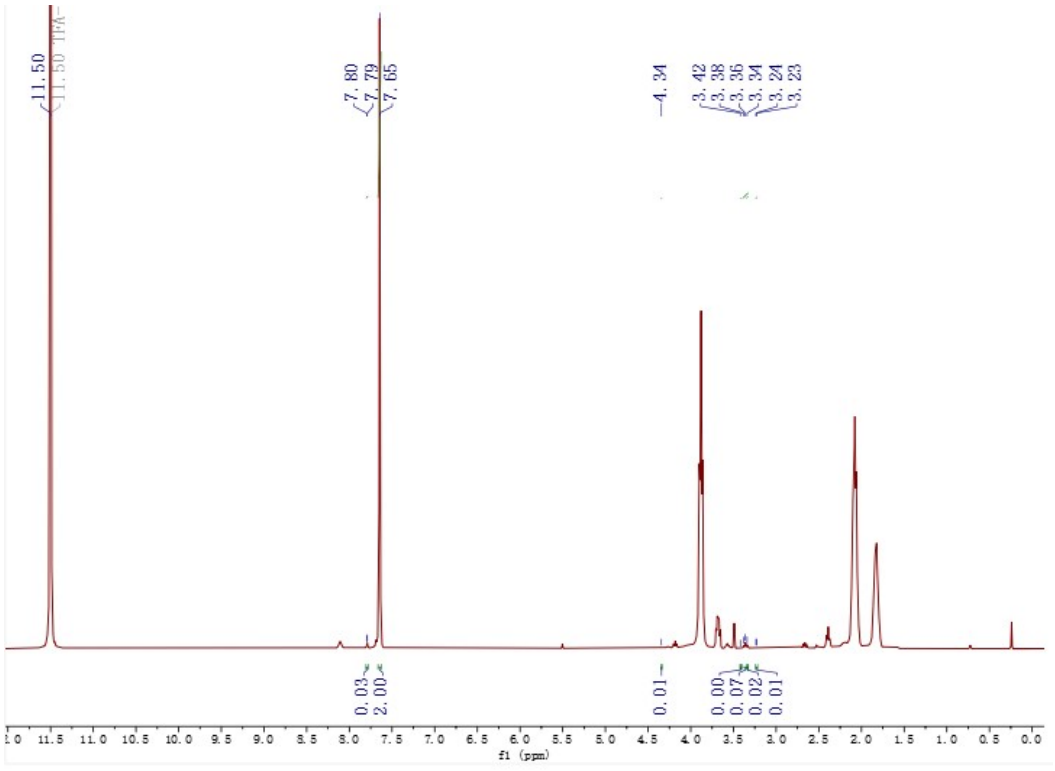
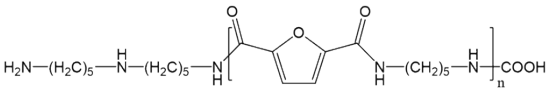
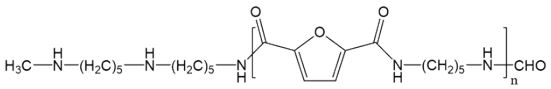
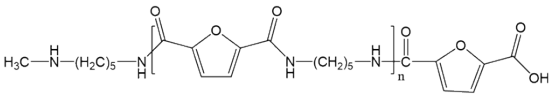
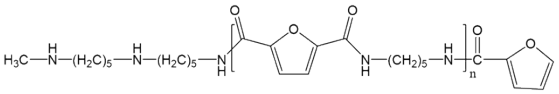
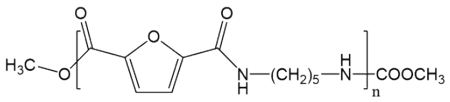
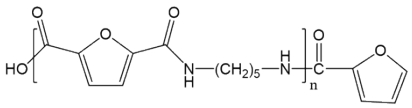
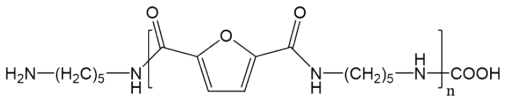
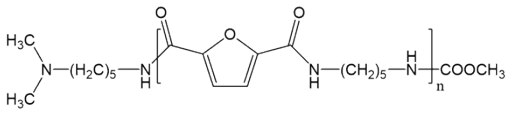


Figure S4. ^{1}H NMR spectrum of PA5F synthesized with temperature-varied two-step synthesis procedure recorded in *TFA-d_1*.

Table 2. MALDI-TOF MS analysis: end groups assignments of polyamides

Series	m/z (n)	Proposed end-groups	M_{EG} (cation) Assign.	M_{EG} (cation) Obs.
A	901.8 (3)		232.7 (H^+)	231.1 (H^+)
B	919.6 (3)		228.5 (Na^+)	229.1 (Na^+)
C	943.0 (3)		252.2 (Na^+)	254.3 (Na^+)
D	962.4 (3)		293.3 (H^+)	295.2 (H^+)
E	978.9 (4)		88.1 (H^+)	90.0 (H^+)
F	1004.2 (4)		112.4 (H^+)	112.1 (H^+)
G	1059.5 (4)		145.7 (Na^+)	146.2 (Na^+)
H	1102.9 (4)		189.1 (Na^+)	188.3 (Na^+)

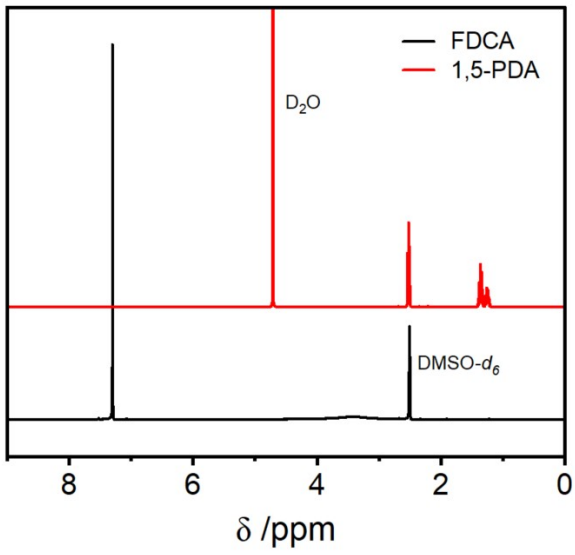


Figure S5. ^{1}H NMR spectrum of FDCA and 1,5-pentanediamine

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