SUPPORTING MATERIALS

Beyond 2,5-furandicarboxylic acid: status quo, environmental assessment, and blind spots of furanic monomers for bio-based polymers

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Abbreviations

1,2-DCE	1,2-Dichloroethane
1,2-DHA	1,2-Dihydroxyacetone
2,4-PEF	2,4-Polyethylene furanoate
2,5-PEF	Polyethylene Furanoate
2,5-PEF	2,5-Polyethylene furanoate
4-ClT	4-Chlorotoluene
4-HMF	4-(hydromethyl)fufural
5-HMF	5-(hydroxymethyl)furfural
AC	Acryloyl chloride
AcAc	Acetylacetonate
ACO	Acrylated castor oil
ADOD	Acrylated 7,10-dihydroxy-8(E)-octadecenoic acid
AESO	Acrylated epoxidized soybean oil
All_2C	Allyl carbonate
AMF	5-(aminomethyl)-2-furanmethanol
Ap	Apigenin
Ap-Fa-Bz	Benzoxazine
BAL	Benzaldehyde Lyase
BAMF	2,5-Bis(aminomethyl)furan
BDMF	3,3'-((furan-2,5-diylbis(methylene))bis(oxy))bis(propane-1,2-diol)
BHMF	2,5-Bis(hydromethyl)furan
BHMTHF	2,5-bis(hydromethyl) tetrahydrofuran
BOC_2O	di-tert-butyl dicarbonate
BOMF	2,5-bis((oxiran-2-ylmethoxy)methyl)furan
BPF	Bisphenol-furan
Bz	Benzaldehyde
CALB	Candida antarctica Lipase B
Cann.	Cannizaro reaction
CDI	Carbonyldiimidazole
ChCl	Choline chloride
Chromat.	Column chromatography
CHT	Metal catalysed hydrogen-transfer
CL	Caprolactone
CMF	5-(chloromethyl)furfural
***m*-CPBA**	*m*-Chloroperoxybenzoic Acid
CPO	Cyclopentanone
CPO	Conjugated Organic Polymer
CTF	Covalent triazine framework
DA	Diels Alder

DABA	2,5-diaminobenzenesulfonic acid
DAC	Dialkyl carbonate
DBTDL	Dibutyltin dilaurate.
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	Dichloromethane
DEC	Diethyl carbonate
DFF	2,5-diformylfuran
DGEBA	Bisphenol-A-diglycidylether
DHMF	4,4-di(hydroxymethyl)furoin
DHMFA	Di-5-hydroxymethylfurfural acetone
DHMFA-2	(1E,4E)-1,5-Bis((5-(hydroxymethyl)furan-2-yl)-2-methylpenta-1,4-dien-3-one
DHMFA-3	(2E,5E)-2,5-Bis(5-(hydroxymethyl)furan-2-yl)methylene)cyclopentan-1-one
DHMFA-4	(2E,6E)-2,6-Bis(5-(hydroxymethyl)furan-2-yl)methylene)cyclohexan-1-one
DIC	N,N'-diisopropylcarbodiimide
DIEA	N,N-Diisopropylethylamine
Dist.	Distillation
DLP	Digital light process
DMA	Dimethylacetamide
DMAP	N,N-dimethyl-4-aminopyridine
DMC	Dimethyl carbonate
DMSO	Dimethyl sulfoxide
DPC	Diphenyl carbonate
DPE	Diphenyl ether
DRS	Dielectric Relaxation Spectroscopy
DSC	Differential Scanning Calorimetry
ECH	Epichlorohydrin
ECHA	European Chemical Agency
EDG	Electron donating group
EF	E-factor
EG	Ethylene glycole
EGD	European Green Deal.
EPI	Diethyl toluene diamine
ER	Epoxy resin
ESOM	epoxidized soybean oil methacrylate
EUFU	Bis(4-allyl-2-methoxyphenyl) furan 2,5-dicarboxylate
EUFU-EP	Bis(2-methoxy-4-(oxiran-2-ylmethyl)phenyl)furan-2,5-dicarboxylate
EWG	Electron withdrawing group
Extr	Extraction
FA	Furfurylamine

FCA	Furoic Acid
FDBC	Furan-2,5-dibutylcarboxylate
FDBE	Furan-2,5-dicarboxylate butyl esters (mono- and diester)
FDCA	2,5-furandicarboxylic acid.
FDCDCl	Furan-2,5-dicarbonyl dichloride
FDCE	Bis(prop-2-enyl)furan-2,5-dicarboxylate
FDEC	Furan-2,5-diethylcarboxylate
FDM	2,5-Furandimethanol
FDME	Furan-2,5-dicarboxylate methyl esters (mono- and diester
FF	Furfural
FTIR	Fourier Transform Infrared Spectroscopy
FUROIN-4	5,5'-bihydromethyl furil
FUROIN-5	5,5'-bihydromethyl hydrofuroin.
G3P	Glyceraldehyde-3-phosphate
GABE	Dibutyl galactarate
GalA	Galactaric acid
GaME	Dimethyl galactarate
GHSV	Gas Hourly Space Velocity
GMA	Glycidyl methacrylate
GO	Graphen oxide
GPC	Gel permeation chromatography
GSC	Green and Sustainable Chemistry
GVL	γ-Valerolactone
HAP	hydroxyapatite
HDDA	1,6-hexanediol diacrylate
HDI	1,6-hexamethylene diisocyanate
HEFDC	Bis(2-hydroxyethyl)furan-2,5-dicarboxylate
HMFA	5-hydroxymethylfuranoic acid
HMZ	Hierarchical micro–mesoporous ZSM-5
HPA	Heteropolyacid
IPA	Isophthalic acid
IPDI	Isophorondiisocyante
ITQ-2	Two-dimensional delaminated zeolite
LDPE	Low density polyethylene
LHSV	Liquid Hourly Space Velocity
LUMO	Lowest Unoccupied Molecular Orbital
MA	Methyl acrylate
MAA	Methyacrylic anhydride
MAC	Methacrylic Acid
MCCh	Methacryloyl chloride
MCM-41	Mobil Company of Matter (Mesostructured Silica)
MDI	methylendi(phenylisocyanate)

MIBK	Methyl isobuthyl keton
MMA	Methyl methacrylate
MMT-[BHTM]	Montmorillonite-supported thiazolium ionic liquid
Mn	Number averaged of molecular weight
Mw	Molecular weight
NHC	N-heterocyclic carbene
NIPUs	Non-isocynate polyurethanes
NMP	N-methyl pyrrolidine
NMR	Nuclear Magnetic Resonance
NPs	Nanoparticles
OBMF	5,5-[oxybis(methylene)]bis-2-furfural
OBMF-H	5,5-oxybis(methylene)bis(furan-5,2-diyl)dimethanol
P(FS-co-BS)	Poly(2,5-furandimethylenesuccinate-co-butylene succinate
PA	Polyamides
PAA	Polyacrylate
PACM	4,4'-methylenebiscyclohexanamine
PBs	Polybenzoxazine
PC	Polycarbonate
PE	Polyester
PE-4	BHMF-based block copolymers
PES	Polyester
PET	Polyethylene terephthalate
PETg	Glycol-modified PET
PEUs	Poly(ester-urethane)s
PHU	Humin-like Resin
PLA	Poly(lactic acid)
PLA-b-PFS	Poly(lactic acid)-blockpoly(2,5-furandimethylene succinate)
PMI	Process Mass Intensity
POBC	Polyoxabicyclates
PSE	Poly(silyethers)
PTSA	*p*-toluene sulfonic acid
PU	Polyurethane
PVC	Poly (vinyl chloride)
Py	Pyridine
QDs	Quantum dots
r-DA	Retro Dleis-Alder reaction
ROMP	Ring-Opening Methatesis Polymerization
ROP	Ring-Opening Polymerization
SA	Succinic acid
Silica-g-[BI]	Silica-Grafted Azolium Salt
SLA	Stereolithography

TA	Terephtalic acid
TBAB	Tetrabutylammonium bromide
TBHS	Tetrabutylammonum hydrogen sulfate
TDI	2,4-toluenediisocyanate
TEA	Triethylamine
TEAB	Tetraethyl ammonium bromide
TEAC	Tetraethyl ammonium chloride
TFP	1,3,5-triformylphloroglucinol
TFT	Trifluorotoluene
Tg	Glass Transition Temperature
TGA	Thermogravimetric Analysis
ThDP	Thiamine-diphosphate dependent lyases
Tm	Melting Transition Temperature
TMP	2,2,6,6-tetramethylpiperidyl
TPT	1,3,4-triphenyl-4,5-dihydro1H-1,2,4-triazol-5-ylidene

Table S.1. Monomer thermal properties.

Compound	Functionality	Appearance	M. p. (°C)	B. p. (°C)	Degr. Temp. (°C)	Ref
HMF	**Aldehyde**	Solid	32 - 35	90 (0.03 mbar)	159	[1]
OBMF	**Aldehyde**	Solid	109	-	194	[1]
DFF	**Aldehyde**	Solid	108 - 110	-	-	[2]
BHMF	**Diol**	Solid	73	275	164	[1]
***cis*-BHMTHF**	**Diol**	Liquid	-	134-137 (8.00 mbar)	-	[3]
***trans*-BHMTHF**	**Diol**	Liquid	-	118-120 (6.70 mbar)	-	[3]
OBMF-H	**Diol**	Solid	82.5	-	214	[1]
Furoin-3	**Diol**	Solid	124	-	-	[4]
DHMFA	**Diol**	Semi-solid	-	-	-	[5]
Furfuryl amine	**Amine**	Liquid	-70	145	-	[6]
AMF	**Amine**	Liquid	118 - 121	-	-	[7]
BACMF (methyl)	**Carbonate**	Solid	71	-	185	[1]
OBMF-DC	**Carbonate**	Solid	62	-	187	[1]
2,4-FDCA	**Carboxylic acid**	Solid	280 - 284	-	-	[8]
FDCA (methyl)	**Ester**	Solid	109 - 111	140 - 145 (13.3 mbar)	-	[9]
FDCA (ethyl)	**Ester**	Solid	46 - 48	-	-	[9]
FDCA (butyl)	**Ester**	Solid	41 - 42	-	-	[10]
Adduct 11	**Diels-Alder**	Solid	112	-	-	[11]
Adduct 13	**Diels-Alder**	Solid	140 - 143			[12]
Furfuryl acrylate	**Acrylate**	Liquid	-	95 - 104 (23.9 mbar)	-	[13]

Table S.2. HMF synthesis that either miss data to allow metrics evaluation or have E-factor/PMI >100.[a]

#	Type[b]	Substrate (g/mmol)	Conc (M)	Catalyst (% mol/%wt)	Reaction conditions	Cat reuse	Yield (%)	E-f	PMI	Ref.
1[c]	A	D-fructose (40/222.2)	1.39	Purolite CT275DR (5% wt.)	DMC; 110 °C, 2 h	-	72[d]	27.7	7.8	[14]
2	A	D-fructose (10/55.6)	1.39	Purolite CT275DR (5% wt.)	DMC; 110 °C, 2 h	-	50	49.2	14.3	[14]
3	A	D-fructose (40/222.2)	1.39	Purolite CT275DR (5% wt.)	DMC; 110 °C, 2 h	-	47	48.2	17.4	[14]
4	B	D-fructose (20/111.1)	0.69	BF_3 OEt_2 (10% mol)	DMC/TEAB; 90 °C, 16 h	-	76	20.1	21.1	[15]
5	B	D-fructose (5/27.8)	0.35	[PPFPy][HSO_4] (7.5% mol)	MIBK/water; 100 °C, 0.75 h	-	83	36.0	37.0	[16]
6[e]	B	D-fructose (5/27.8)	0.35	[PPFPy][HSO_4] (7.5% mol)	DMSO; 100 °C, 0.5 h	10	84	91.0	57.3	[16]
7[f]	C	D-fructose (70/388.9)	0.06	WCl_6/HY (0.2% wt.)	[BMIM][Cl]/THF; 50 °C, 6 h	-	55	171.9	172.9	[17]
8	B	D-fructose (18/100.0)	0.44	BF_3 OEt_2 (0.13% wt.)	DMSO-toluene; reflux, 0.5 h	-	60	249.6	250.6	[18]
9	B	D-fructose (9/50)	0.33	Wet cation exchange resin Bayer OC1052 (444% wt.) Activated Carbon ROX (222% wt.)	H_2O;	-	48	331.7	332.7	[19]
10	B	D-fructose (0.1/0.6)	neat	NHC-$CrCl_2$ (54% wt.)	[BMIM][Cl]; 100 °C, 6 h	-	96	505.2	506.2	[20]
11[g]	B	D-fructose (1.5/8.3)	1.29	H_2SO_4 (2% mol.)	[BMIM][Cl]; 60-80 °C, 2.5 h	15	78	649.8	646.4	[21]
12[g]	B	D-fructose (18/100.0)	1.51	H_2SO_4 (2% mol.)	[BMIM][Cl]; 60-80 °C, 3.5 h	15	73	693.7	686.9	[21]

[a] The reported metrics do not consider the preparation of the catalyst. All yields are isolated, excepted where otherwise specified; [b] A = Autoclave, B = Batch, C = Continuous flow; [c] Excluding purification; [d] Yield refers to non-isolated HMF; [e] DMSO is partially recovered; [f] Reaction conducted in continuous biphasic system over a 42 h period where 7 cycles of 10.0 g each of D-fructose run at 6 h intervals were combined. The concentration and the Metrics refer to a single cycle; [g] Aqueous solution of NaCl/$NaHCO_3$ not included.

Table S.3. BHMF syntheses that either miss data to allow metrics evaluation or have E-factor/PMI >35. [a] *(1 of 2)*

#	Reaction type	Substrate (g/mmol)	Conc. (M)	Catalyst (% mol / %wt)	Reaction conditions	Cat. reuse	Yield (%)	E-f	PMI	Rif
1	**CTH**	HMF (0.13/1.00)	0.10	Hf-LS (77% wt)	*i*-PrOH; 100 °C, 2h	10	90	-	-	[22]
2	**CTH**	HMF (0.50/3.97)	0.13	MZH (80% wt)	2-BuOH; 150 °C, 5h	3	87	-	-	[23]
3	**CTH**	HMF -	-	Ru/Co_3O_4 (-)	1 bar; *i*-PrOH; 190 °C, 6h	-	83	-	-	[24]
4	**CTH**	HMF (0.13/1.00)	0.20	DUT-69(Zr) (80% wt.)	*i*-PrOH; 120 °C, 6 h	-	86	36.9	37.9	[25]
5	**CTH**	HMF (0.25/2.00)	0.20	UiO-66 (30% wt)	*i*-PrOH; 180 °C, 4h	5	82	38.2	38.8	[26]
6	**CTH**	HMF (0.25/2.00)	0.20 M	$Al_7Zr_3@Fe_3O_4$ (32% wt)	*i*-PrOH; 180 °C, 4h	5	71	44.2	44.8	[27]
7	**CTH**	HMF (1.00/7.93)	0.16 M	$ZrO(OH)_2$ (50% wt)	EtOH; 150 °C, 2h	1	83	47.8	47.6	[28]
8	**CTH**	HMF (0.50/3.97)	0.13 M	Zr-DTPA (60% wt)	*i*-PrOH; 140 °C, 4h	5	95	51.4	51.7	[29]
9	**CTH**	HMF (0.50/3.97)	0.13 M	MZCCP (50% wt)	2-BuOH; 140 °C, 5h	5	93	52.5	52.9	[30]
10	**CTH**	HMF (0.13/1.00)	0.10	Hf-H_3IDC-T (77% wt)	*i*-PrOH; 100 °C, 4h	-	92	67.8	68.0	[31]
11	**CTH**	HMF (0.12/0.95)	0.10	Hf-LigS catalyst (83% wt)	*i*-PrOH; 100 °C, 1h	10	90	69.6	69.8	[32]
12	**CTH**	HMF (0.13/1.00)	0.10	Zr-LS (77% wt)	*i*-PrOH; 100 °C, 2h	-	89	70.3	70.4	[33]
13	**CTH**	HMF (0.13/1.00)	0.10	NiO (60% wt)	*i*-PrOH; 180 °C, 6h	-	87	72.0	72.3	[34]
14	**CTH**	HMF (0.33/2.60)	0.08	M-Zr-MOF-808 (11% mol)	*i*-PrOH; 82 °C, 2h	5	96	77.1	77.8	[35]
15	**CTH**	HMF (0.06/0.50)	0.10	Mn-NCA-700 (92% wt)	*i*-PrOH; 160 °C, 1.5h	-	76	82.7	82.5	[36]
16	**CTH**	HMF (0.25/2.00)	0.20	NiO(P)-300 (24% wt)	*i*-PrOH; 150 °C, 4h	-	74	84.1	84.5	[37]
17	**CTH**	HMF (0.2/1.59)	0.06	ZrBa-SBA (50% wt)	*i*-PrOH; 150 °C, 2.5h	5	90	108.8	109.3	[38]
18	**CTH**	HMF (0.2/1.59)	0.06	ZrCa@CNS (500% wt)	*i*-PrOH; 190 °C, 10h	6	84	121.8	116.96	[39]
19	**CTH**	HMF (0.10/0.80)	0.05	$CuO\text{-}Fe_3O_4$/AC (100% wt)	N_2, 7 bar; EtOH; 150 °C, 5h	5	92	128.6	128.5	[40]
20	**CTH**	HMF (5.0/39.65)	0.13	Ru pincer complex (0.01% mol)	*i*-PrOH; *i*-PrONa; 82 °C, 10 min	-	90	170.7	171.7	[41]
21	**CTH**	HMF (0.1/0.67)	0.03	BZC (100% wt)	*i*-PrOH; 80 °C, 9h	-	98	189.3	189.1	[42]
22	**CTH**	HMF (0.15/1.21)	0.02	MgO (666% wt)	MeOH; 160 °C, 3h	-	99	261.4	259.1	[43]

[a] Isolated yield value or determined via GC-MS, HPLC or ^{1}H-NMR.

Table S.4. BHMF syntheses that either miss data to allow metrics evaluation or have E-factor/PMI >50. [a] *(2 of 2)*

#	Reaction type	Substrate (g/mmol)	Conc. (M)	Catalyst (% mol / %wt)	Reaction conditions	Cat. recycle	Yield (%)	E-f	PMI	Rif
23	**H**	HMF (-/-)	-	Cu/CeO_2-ZrO_2 (-)	H_2, 10 bar; EtOH; 170 °C, 2h	-	70	-	-	[44]
24	**H**	HMF (1.00/0.80)	0.08	Ru/MSN-Zr (5% wt)	H_2, 5 bar; H_2O; r.t., 4h	-	90	-	-	[45]
26	**H**	HMF (0.01/0.10)	0.05	Pt@Y (200% wt)	H_2, 20 bar; H_2O; 80 °C, 4h	-	99	-	-	[46]
27	**H**	HMF (-/-)	-	Pt/CeO_2-ZrO_2 (0.7% mol)	H_2, 1 bar; EtOH; r.t., 2h	-	95	-	-	[47]
28	**H**	HMF (-/-)	-	1.5K-Cu/Al_2O_3	H_2, 20 bar; 120 °C, WHSV = 1.0h^{-1}	-	99	-	-	[38]
28	**H**	HMF (0.06/0.50)	0.10	Cu@ZIF-8 (35% wt)	H_2, 20 bar; EtOH; 140 °C, 3h	-	99	-	-	[48]
30	**H**	HMF (0.50/4.00)	0.20	$Cu_{0.59}Mg_{2.34}Al_{1.00}$ (20% wt.)	H_2, 50 bar; EtOH; 100 °C, 3 h	-	99	32.2	33.2	[49]
31	**H**	HMF (0.50/4.00)	0.20	Ni_2Fe_1/CNTs (10% wt.)	H_2, 30 bar; BuOH; 110 °C, 18 h	-	96	32.9	33.9	[50]
32	**H**	HMF (1/7.93)	0.26	Cu-ZnO (30% wt.)	H_2, 30 bar; dioxane; 220 °C, 0.5 h	5	92	33.2	33.9	[51]
33	**H**	HMF (0.4/3.17)	0.13	Ru supported on Mg-Zr (50% wt)	H_2, 30 bar; H_2O/BuOH; 130 °C, 2h	-	94	63.8	64.8	[52]
34	**H**	HMF (0.03/0.20)	0.10	Au/Al_2O_3 (30% wt)	H_2, 65 bar; H_2O; 120 °C, 2h	-	96	74.3	75.3	[53]
35	**H**	HMF (0.25/2.00)	1.00	$Au/FeO_x/Al_2O_3$ (4% wt)	H_2, 30 bar; H_2O; 80 °C, 2h	-	96	81.7	82.7	[54]
36	**H**	HMF (0.03/0.25)	0.05	Cu/Al_2O_3 (50% wt)	H_2, 30 bar; MeOH; 130 °C, 1h	5	93	134.2	134.7	[55]
37	**H**	HMF (0.2/1.59)	0.08	Cu-Ni/γ-Al_2O_3 (250% wt)	H_2, 30 bar; THF; 130 °C, 6h	3	61	146.2	143.2	[56]

[a] Isolated yield value or determined via GC-MS, HPLC or ^{1}H-NMR.

Table S.5. BHMTHF syntheses that either miss data to allow metrics evaluation or have E-factor/PMI >50. [a]

#	Substrate (g/mmol)	Conc. (M)	Catalyst (% mol / %wt)	Reaction conditions	Cat. recycle	Yield (%)	E-f	PMI	Rif
1	HMF (0.50/3.97)	0.20	Pd/Al_2O_3 (20% wt)	H_2, 1 bar; EtOH 120 °C, 3h	-	99	-	-	[57]
2	HMF (0.15/1.20)	0.08	DTBM-SEGPHOS (5% mol) $Ru(methylallyl)_2COD$ (4.5% mol)	H_2, 10 bar; toluene; 120 °C, 16h	-	79	-	-	[58]
3	HMF (0.12/1.00)	-	Pd/C (5% wt)	H_2, 60 bar; [BMIm]Cl; 50 °C, 3h	-	89	-	-	[59]
4	HMF (0.10/0.79)	0.08	Ru/MSN-Zr-1 (3% mol)	H_2, 5 bar; H_2O; 25 °C, 4h	5	5	-	-	[60]
5	HMF (12.0/95.24)	0.79	Ni/SiO_2 (64 wt.%)	H_2, 69 bar; EtOH; 80 °C, 6h	-	-	-	-	[61]
6	HMF (0.15/1.19)	0.24	Pd/C (5% wt)	H_2, 50 bar; THF; 100 °C, 20h	-	34	-	-	[62]
7	HMF (-/-)	0.02 - 0.04	$Ni_{(1-x)}Al_x(OH)_2(CO_3)_{x/2}$*m H_2O (-)	H_2, 20 bar; H_2O; 80 °C, 6h	-	71	-	-	[63]
8	HMF (0.63/5.00)	0.50	Ru/TiO_2-lys-DP (0.18% mol – metal)	H_2, 40 bar; EtOH; 80 °C, 1.5h	-	99	-	-	[64]
9	HMF (1.31/10.40)	0.26	$Pd/La_2Ce_2O_7$ (-)	H_2, 40 bar; H_2O; 150 °C, 12h	-	88	-	-	[65]
10	HMF (-/-)	- 1% wt	Pd/SiO_2 (-)	H_2, 30 bar; THF; 100 °C, -	-	100	-	-	[66]
11	HMF (0.12/1.00)	0.13	Pd/MIL-101(Al)-NH_2 (16% wt)	H_2, 10 bar; H_2O; 30 °C, 12h	5	98	62.5	63.4	[67]
12	HMF (0.10/0.79)	0.08	Ni/CMo (10% wt)	H_2, 20 bar; H_2O; 140 °C, 2h	5	90	105.9	106.7	[68]
13	HMF (0.02/0.16)	0.08	NiRe (50% wt)	H_2, 50 bar; H_2O; 40 °C, 4h	-	77	126.3	127.3	[69]
14	HMF (0.06/0.50)	0.25	Pd/LDH-MgAl-NO_3 (16% wt)	H_2, 10 bar; H_2O; 30 °C; 3h	-	24	130.4	131.4	[70]
15	HMF (0.06/0.50)	0.10	Pd/C (10% mol)	H_2, 2 bar; CO_2, 2 bar; dioxane; 120 °C, 15h	-	57	155.2	156.2	[71]
16	HMF (0.12/1.00)	0.08	L-N20 (80% wt)	H_2, 50 bar; EtOH; 230 °C, 6h	-	42	175.8	175.0	[72]

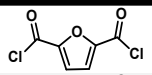
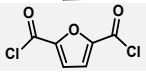
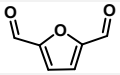
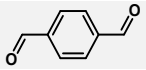
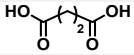
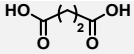
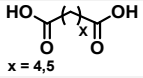
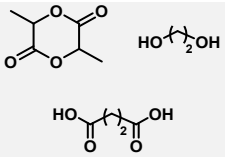
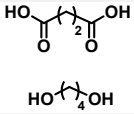
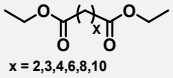
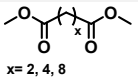
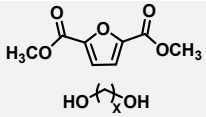
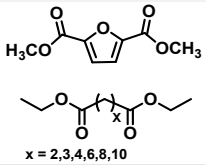
[a] Isolated yield value or determined via GC-MS, HPLC or ^{1}H-NMR.

Table S.6. DHMFA syntheses that either miss data to allow metrics evaluation or have E-factor/PMI >50. [a]

#	Substrate (g/mmol)	Conc.	Base	Reaction conditions	Yield (%)	E-f	PMI	Rif
1	HMF (0.21/1.65)	0.08 M	$NaOH_{(aq)}$	EtOH, acetone, 24 °C, 2h	60	-	-	[73]
2	HMF (2.00/15.87)	0.63 M	$NaOH_{(aq)}$	MeOH, acetone, -, -	-	-	-	[74]

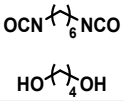
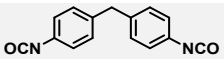
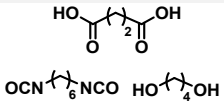
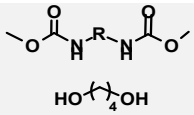
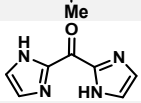
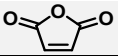
[a] Isolated yield value or determined via GC-MS, HPLC or ^{1}H-NMR.

Table S.7. BHMF-based polyesters.[a]

Polymer	Co-monomer	Catalyst /Base	Reaction conditions	M_n (g/mol)	M_w (g/mol)	T_g (°C)	T_d (°C)	Ref
PES-1		Et_3N	$CHCl_3$; 0 °C, overnight	-	-	-	200	[75]
PES-1		NaOH	TEAB; r.t.; 1 h	3.880	5.400	-	205	[76]
PES-1		DBU/Triazolium salt	THF, quinone; r.t., 16 h	7.800	-	-	< 200	[77]
PES-2		DBU/Triazolium salt	THF, quinone; r.t.,16 h	3.100	-	60	247	[77]
PES-3		DMAP/DIC	N_2, dichloroethane; r.t., 24 h, N_2	5.100 - 5.700	8.100-9.300	15	-	[78]
PES-3		DMAP/DIC	N_2, BuOH; r.t., 24 h,	2.700	4.000	15	-	[79]
PES-3	 x = 4,5	(TMP)MgCl·LiCl	Boc_2O, MeTHF; 60 °C, 24 h	6.400	16.000	-9	-	[80]
PES-4		DMAP/DIC	1) 120 °C, 24 h; 2) $CHCl_3$, N_2; r.t., 24 h	5.000 - 14.600	-	16 to 34	-	[81]
PES-5		DMAP/DIC	N_2, r.t., 24 h	4.300 - 7.200	-	-30 to 2	-	[82]
PES-3	 x = 2,3,4,6,8,10	CALB	DPE, 80 °C; 1) N_2, 2 h; 2) 0.5 bar, 4 h; 3) 2.6 mbar, 66 h	2.100-2.400	2.700-3.900	-38 to 4	250	[83]
PES-3	 x= 2, 4, 8	CALB	DPE, 85 °C; 1) 1 bar, 6 h; 2) 20 mbar 90h	2.800 - 3.100	-	-22 to 10	249-293	[84]
PES-6	 x = 4,6,8,10, 12	CALB	DPE, 80 °C; 1) N_2, 2 h; 2) 0.5 bar, 4 h; 3) 2.6 mbar, 66 h	1.400 - 16.000	1.500-35.000	-2 to 15	230-250	[85]
PES-7	 x = 2,3,4,6,8,10	CALB	DPE, 80 °C; 1) N_2, 2 h; 2) 0.5 bar, 4 h; 3) 2.6 mbar, 66 h	600 - 8.900	600-16.800	-19 to -6	- [b]	[85]

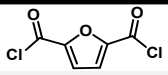
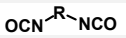
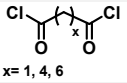
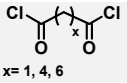
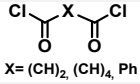
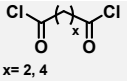
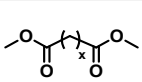
[a]Abbreviations: TEAB = Tetraethylammonium bromide; T_d = on-set thermal decomposition; DPE = Diphenyl ether; DMAP = N,N-dimethyl-4-aminopyridine; DIC = N,N'-diisopropylcarbodiimide; TMP = 2,2,6,6-tetramethylpiperidyl [b] Degradation of these PEs occurs in several stages and a significant weight loss was detected at temperatures around 220–280 °C.

Table S.8. Other BHMF-based polymers.[a]

Polymer	Co-monomer	Catalyst /Base	Reaction conditions	M_n (g/mol)	M_w (g/mol)	T_g (°C)	T_d (°C)	Ref
PU-1		$Zr(acac)_4$	N_2, DMA; 70 °C, overnight	13.000	-	-	-	86
PU-2		DBTDL	Ball milling (20 Hz); r.t., 1 h	-	163000	96	201	87
PU-3		1) DMAP, DIC; 2) $Ti(OBu)_4$ 3) none	1) N_2; r.t. 24 h 2) N_2, 140-220 °C, 2 h; 3) 130 °C, 1 h.	43.600 - 55.300	73000 - 140000	-25 to -3	266 - 275	88
PU-4		1) K_2CO_3; 2) K_2CO_3; 3) none	1) DMSO; 130 °C, 6 h; 2) 120 °C, 1.5 h 3) 150 °C; 3 h	200 - 3.000	-	-	214 - 224	89
PSE		Salen-Mn complex	Toluene; 130 °C, 40 h	11.000		15.6	453[b]	90
PSE		Iron β-Diketiminate	Benzene; 80 °C, 40 h	1.800	2.900	-	234	91
PC		CsF	EtOAc; 40 °C, 12 h	1.800 - 29.000	2800 - 59.400	15 to 35	150	92
PHU		none	Neat; 110 °C, 2 min	-	-	-	-	93

[a] Abbreviations: acac = acetylacetonate; DMA = Dimethyl acetamide; DBTDL = dibutyltin dilaurate; [b] Value referred to the 50% gravimetric loss ($T_{-50\%}$).

Table S.9. Other BHMF-based polymers.[a]

Polymer	Co-monomer	Catalyst /Base	Reaction conditions	M_n (g/mol)	T_g (°C)	T_d (°C)	Rif
BHMFTHF-PE		PbO	230 °C, 6 days	-	-	-	75
Furoin PU-1		DBTDL	THF; 30 °C,	4.300 - 39.800	62 to 140	216 - 234[b]	94
Furoin PU-3		DBTDL	45 °C, 48 h	17.600 - 23.900	78 to 87	204 - 216	95
Furoin PU-4		DBTDL	45 °C, 48 h	8.230 - 17.600	80 to 87	182 - 185	95
Furoin PE-1	 x= 1, 4, 6	Py	CH_3CN; 45 °C, 72 h	7.670 - 20.800	26 to 66	205 - 243	95
Furoin PE-2	 x= 1, 4, 6	Py	CH_3CN; 45 °C, 72 h	6.320 - 9.650	27 to 67	202 - 238	95
Furoin PE-3	 X= $(CH)_2$, $(CH)_4$, Ph	Py	THF; 25 °C, 24 h	3.200 - 7.800	27 to101	281 - 295	94
Furoin PE-4	 x= 2, 4	Py	THF; 25 °C, 24 h	-	52 to 89	188 - 215	94
Furoin PE-5		CALB	DPE, 1) 50 °C, 0.02 bar, 5 h; 2) 60 °C, 0.02 bar, 6 h; 3) 60 °C, 4 mbar, 10 h	1.150	-	-	96

[a] Abbreviations: DBTDL = dibutyltin dilaurate; Py = Pyridine; DPE = Diphenyl ether [b] Value referred to the 50% gravimetric loss ($T_{-50\%}$).

Table S.10. Some physical-chemical properties of furfurylamine.

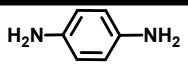
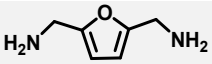
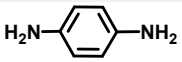
Appearance	colourless oil
Freezing point (°C, 1 atm)	-70
Boiling point (°C, at 1 atm)	144-145
Degradation temperature (°C, at 1 atm)	Not reported
Density (g/cm^3, at 20 °C)	1.1
Safety pictograms	flammable, corrosive, acute toxic, irritant

PubChem, Furfurylamine, https://pubchem.ncbi.nlm.nih.gov/compound/3438, (accessed March 23, 2023).

Table S.11. Additional procedure for the synthesis of furfurylamine.

#	Furfural (g/mmol)	Conc. (M)	Catalyst (% mol or % wt.)	Reaction conditions	Cat reuse	Yield (%)	E-f	PMI	Ref
1	0.5/5.2	2.60	Raney Co 50 mg	H_2, 10 bar; NH_3, 1 bar; MeOH, 120 °C, 2 h	10	98 (analytical)	84.3	85.1	[97]
2	0.05/0.5	0.10	Ru/Nb_2O_5 20 mg	H_2; 40 bar; NH_3, 10 bar MeOH, 90 °C, 2 h	3	94 (analytical)	88.5	89.0	[98]
3	0.05/0.5	0.13	12.5% Ru/MMT 30 mg	H_2, 10 bar; 25% aq. NH_3, 90 °C, 3 h	5	89 (analytical)	88.8	89.1	[99]
4	0.05/0.5	0.13	Ru-NP 0.2 mg in 1 mL MeOH	H_2, 20 bar; NH_3 in MeOH; 90 °C, 2 h	/	99 (analytical)	89.7	90.7	[100]
5	0.1/1.0	0.10	MC/Ni 20 mg	H_2, 1 bar; 36 wt% aq. NH_3, MeOH 80 °C, 12 h	/	88 (analytical)	95.6	96.6	[101]
6	0.1/1.0	0.10	Co@NC-800	H_2, 10 bar; 26.5 wt% aq NH_3, EtOH, 130 °C, 12 h	/	82 (analytical)	103.6	104.6	[102]
7	0.05/0.5	0.10	Co@C-600-EtOH (10 mg)	H_2, 20 bar; NH_3 7 M in MeOH, 90 °C, 4 h	8	87 (analytical)	89.6	90.3	[103]
8	0.05/0.5	0.08	Pt/CoFe-LDH	H_2, 20 bar; NH_3 26.5 wt.% in *i*-PrOH, 100 °C, 16 h	/	94 (analytical)	107.8	108.8	[103]
9	0.1/1.0	0.25	(ii) CuI (10% mol)	(i) NH_2NHTs, dioxane, 60 °C, 0.5 h (ii) Phthalimide, Cs_2CO_3, 110 °C, 2 h (iii) H_2NNH_2, H_2O, 110 °C, 2 h	/	78 (isol)	486.2	487.2	[104]
10	0.02/0.2	0.20	Pd(0)-AmP-MCF 13.4 mg	HCO_2NH_4, toluene 80 °C, 3 h	/	71 (isol)	1140.4	1141.4	[105]
11	0.005/0.05	0.005	Pd-NPs 2mg	H_2, 1 bar; aq. NH_3, H_2O; r.t., 3 h, pH 2	/	97% (analytical)	7856.7	7857.7	[106]
12	0.5/5	0.25	Ni/pNC 100 mg	H_2, 30 bar; NH_3, 4 bar, MeOH, 60 °C, 6 h	5	92 (analytical)	/	/	[107]
13	0.1/1	0.50	Ru/TiP-100 0.2 mol%	H_2, 17 bar; NH_3, 3 bar, MeOH, 30 °C, 24 h	/	91 (analytical)	?	?	[108]
14	0.2/2	0.67	Ni6AlOz 50 mg	H_2, 4 bar; 28% aq. NH_3 100 °C, 5 h	/	90 (analytical)	/	/	[109]

Table S.12. Bio-based polymers from aldehyde furanic monomers.

Monomer	Co-monomer	Reaction conditions	M_n (g/mo)l	M_w (g/mol)	T_g (°C)	T_d (°C)	Ref
DFF		EtOH or DMF, r.t., 1h	-	-	-	-	[110]
DFF		EtOH or DMF, r.t., 1h	-	-	-	-	[110]
OBMF		EtOH or DMF, r.t., 1h	-	-	-	-	[110]
BiFur	H_2N-$(CH_2)_n$-NH_2 n = 2-6	140 °C, 6 h, m-cresol[a]	3000 - 12000	-	40-90	263 - 339	[111]
DFF	Priamine	r.t. THF, 1 h	-	-	-10	300	[112]

[a] m-Cresol was not used in all the procedures.

Table S.13. Epoxides additional synthesis.

#	Substrate (g/mmol)	Conc M	Catalyst (% mol or % wt.)	Reaction conditions	Cat. reuse	Yield (%)	E-f	PMI	Ref
2	BHMF (50/0.4)	2.6	nd	Acetone nd	-	42	-	-	[113]
4	Bisphenol-HMF (0.4/1)	0.16	TBAB (36% wt.)	ECH, NaOH aq., H_2O; 60 °C, 6 h	-	33	51.1	52.1	[114]
5	BHMF (1.4/10.9)	1.1	TBAB (20.7% wt.)	ECH, NaOH aq., r.t., 4 h	-	61	72.4	73.4	[115]

Table S.14. Oxidative esterification of HMF to produce FDCA esters.[a]

#	Substrate (g/mmol)	Conc M	Catalyst (% mol or % wt.)	Reaction conditions	Cat. reuse	Yield (%)	E-f	PMI	Ref
1[b]	HMF (0.1/0.8)	-	Au/CeO_2 (1.3% mol), Na_2CO_3 (200% mol)	O_2 5 bar, MeOH; 130 °C, 15 h	-	FDMC 91	-	-	[116]
2[b]	HMF-PD (0.1/0.5)	-	Au/CeO_2 (2% mol), Na_2CO_3 (200% mol)	O_2, 5 bar, MeOH; 130 °C, 15 h	-	FDMC 92	-	-	[116]
3[b]	HMF-PD (0.1/0.5)	-	Au/CeO_2 (2% mol), Na_2CO_3 (200% mol)	O_2, 10 bar, EG, DMF; 110 °C, 24 h	-	HEFDC 91	-	-	[116]
4[b]	HMF (0.06/0.5)	0.10	Co_xO_y-N@C (1.5% mol), Ru@C (5% mol) K_2CO_3 (20% mol)	Air, MeOH; 50 °C, 18 h	-	FDMC 100	-	-	[117]
5[c,d]	HMF (0.03/0.25)	0.10	Co_xO_y-N + RuO_xN-@C-irregular (2000% wt.) K_2CO_3 (0.025 M)	O_2, 1.4 ml/min, MeOH; 62 °C, residence time 10 min	-	FDMC 56	-	-	[118]
6[d]	HMF (0.03/0.25)	0.08	Co_7Cu_3-NC	O_2, 2 bar, MeOH 80 °C, 4 h	-	FDMC 95	-	-	[119]
7[b]	HMF (0.06/0.5)	0.10	Co/Co-N/CN-700 (166% wt.)	O_2, 1 bar, MeOH; 80 °C, 5 h	-	FDMC 88	-	-	[120]
8[d]	HMF (0.04/0.3)	1.00	Co@NC Zn12-5	O_2, 1 bar, MeOH; 50 °C, 24 h	-	FDMC 95	-	-	[121]
9	HMF (2.14/17)	0.08	Co SAs-N@C	O_2, 100 ml/min, MeOH; 65 °C, 12 h	-	FDMC 83[f]	-	-	[122]
10	HMF (0.03/0.25)	0.08	Co_7Fe_3-NC	O_2, 2 bar; MeOH; 80 °C, 4 h	-	FDMC 93	-	-	[123]
11[c,e]	HMF	0.03	Co_7Fe_3-NC	O_2, 5 bar, 5.5 ml/min MeOH; 80 °C, GHSV 1320 h^{-1}, LHSV 0.6 h^{-1}	3 days	FDMC 91	-	-	[123]
12[b]	HMF (0.13/1.0)	0.05	$AuCu/Al_2O_3$ (79% wt.)	O_2,10 bar, MeOH; 105 C, 5 h	-	FDMC 98	-	-	[124]

[a] Isolated yield value or determined via GC-MS, HPLC or ^{1}H-NMR; [b] Volume of autoclave missing; [c] Continuous flow; [d] Amount of catalyst missing and/or unknown amount of O_2; [e] Catalyst was recycled.

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