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Supporting Information

Furan-Based Copolyesters from Renewable Resources: Enzymatic Synthesis and Properties

Dina Maniar, Yi Jiang, Albert J. J. Woortman, Jur van Dijken, and Katja Loos*[a]

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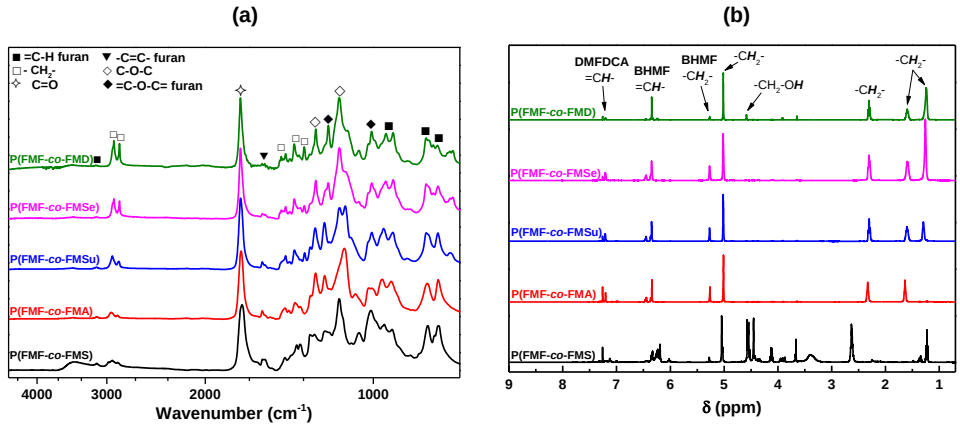

Figure S1. (a) ATR-FTIR, and (b) 1H-NMR spectra of the obtained furan-based copolyesters from DMFDCA, BHMF, and diacid ethyl esters.

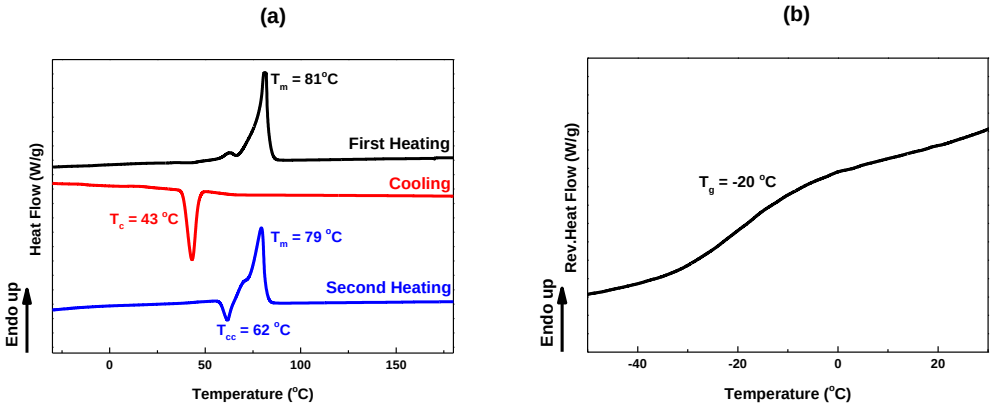

Figure S2. (a) DSC curves and (b) temperature modulated DSC (TMDSC) curves of P(FMF-co-FMD) from 12.5% DMFDCA, 50% BHMF and 37.5% diethyl dodecanedioate feed ratio.

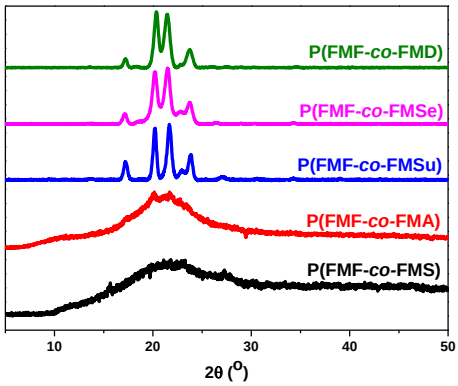

Figure S3. Wide-Angle X-Ray Diffraction (WAXD) spectra of the obtained furan-based copolyester from DMFDCA, BHMF and the diacid ethyl esters with feed ratio 12.5%: 50% : 37.5%, respectively.

Table S1. Molecular weights, degree of polymerization, and yield summary of the furan-based copolyesters obtained from different feed compositions of BHMF, DMFDCA, and aliphatic diols**.**

Polyester	Molar composition [%]						Molecular Weight[c]			$\overline{DP_n}$[d]	$\overline{DP_w}$[e]	Yield[f] [%]
	Feed[a]			Co-polyester[b]			$\overline{M_n}$ [g mol^{-1}]	$\overline{M_w}$ [g mol^{-1}]	Đ ($\overline{M_w}/\overline{M_n}$)			
	F_D	F_B	F_{AD}	X_D	X_B	X_{AD}						
P(FMF-*co*-BF)	50	12.5	37.5	49	8	43	1975	2820	1.43	18	26	61
	50	25	25	49	4	47	1400	1500	1.07	13	13	22
P(FMF-*co*-HF)	50	12.5	37.5	47	12	41	5600	18000	3.21	46	149	79
	50	25	25	53	7	40	1620	2110	1.30	13	17	50
P(FMF-*co*-OF)	50	12.5	37.5	46	12	42	16050	35350	2.20	122	269	86
	50	25	25	47	23	30	3100	5650	1.82	24	43	40
P(FMF-*co*-DF)	50	12.5	37.5	46	12	42	13900	28650	2.06	97	201	84
	50	25	25	55	8	37	1500	1600	1.07	10	11	14
P(FMF-*co*-DOF)	50	12.5	37.5	46	12	42	13150	24500	1.86	86	160	96
	50	25	25	54	6	40	1860	2300	1.21	11	14	39

[a] F_D, F_B, F_{AD} represent the molar feed ratio of DMFDCA, BHMF, and aliphatic diols, respectively. [b] X_D, X_B, X_{AD} represent the molar percentage of DMFDCA, BHMF, and aliphatic diol segment in the obtained furan-based copolyester, determined from ^{1}H-NMR. [c]The number average molecular weight ($\overline{M_n}$), weight average molecular weight ($\overline{M_w}$), and dispersity (Đ, $\overline{M_w}/\overline{M_n}$) were determined by SEC using $CHCl_3$ as the eluent. [d] $\overline{DP_n}$ (number-average degree of polymerization) = $2 \times [(\overline{M_n} - 62.06) / ((X_{FMF} \times M_{Repeating\ unit\ FMF}) + (X_{XF} \times M_{Repeating\ unit\ XF}))]$. [e] $\overline{DP_w}$ (weight-average degree of polymerization) = $2 \times [(\overline{M_w} - 62.06) / ((X_{FMF} \times M_{Repeating\ unit\ FMF}) + (X_{XF} \times M_{Repeating\ unit\ XF}))]$. [f] Isolated yield.

Table S2. Molecular weights, degree of polymerization, and yield summary of the furan-based copolyesters obtained from different feed compositions of BHMF, DMFDCA and diacid ethyl ester.

Polyester	Molar composition [%]						Molecular Weight[c]					
	Feed[a]			Co-polyester[b]			$\overline{M_n}$ [g mol^{-1}]	$\overline{M_w}$ [g mol^{-1}]	$Đ$ ($\overline{M_w}/\overline{M_n}$)	$\overline{DP_n}$[d]	$\overline{DP_w}$[e]	Yield[f][%]
	F_B	F_D	F_{DE}	X_B	X_D	X_{DE}						
P(FMF-*co*-FMS)	50	12.5	37.5	68	14	18	600	800	1.33	5	7	39
	50	25	25	46	37	17	700	1300	1.85	5	10	21
P(FMF-*co*-FMA)	50	12.5	37.5	50	12	38	8900	16850	1.89	73	137	47
	50	25	25	-[g]	-[g]	-[g]	1800	4100	2.27	-[g]	-[g]	6
P(FMF-*co*-FMSu)	50	12.5	37.5	49	13	38	5400	9300	1.72	41	71	56
	50	25	25	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	3
P(FMF-*co*-FMSe)	50	12.5	37.5	50	12	38	6350	11650	1.83	44	82	29
	50	25	25	48	34	18	-[g]	-[g]	-[g]	-[g]	-[g]	2
P(FMF-*co*-FMD)	50	12.5	37.5	51	7	42	2500	3450	1.38	16	22	35
	50	25	25	36	50	14	670	1800	2.68	5	13	6

[a]F_B, F_D, F_{DE} represent the molar feed ratio of BHMF, DMFDCA and diacid ethyl esters, respectively. [b]X_B, X_D, X_{DE} represent the molar percentage of BHMF, DMFDCA and diacid ethyl ester segment of the obtained furan-based copolyester, determined from ^{1}H-NMR. [c]The number average molecular weight ($\overline{M_n}$), weight average molecular weight ($\overline{M_w}$), and dispersity ($Đ$, $\overline{M_w}/\overline{M_n}$) were determined by SEC using $CHCl_3$ as the eluent. [d] $\overline{DP_n}$ (number-average degree of polymerization) = $2 \times [(\overline{M_n} - 62.06) / ((X_{FMF} \times M_{Repeating\ unit\ FMF}) + (X_{FMX} \times M_{Repeating\ unit\ FMX}))]$. [e] $\overline{DP_w}$ (weight-average degree of polymerization) = $2 \times [(\overline{M_w} - 62.06) / ((X_{FMF} \times M_{Repeating\ unit\ FMF}) + (X_{FMX} \times M_{Repeating\ unit\ FMX}))]$. [f]Isolated yield. [g]Cannot be determined.

Table S3. Thermal properties of the obtained furan-based copolyester

Polyester	DSC[b]				TGA[c]	
	T_g [ºC]	T_m [ºC]	T_c [ºC]	T_{cc} [ºC]	$T_{d\text{-}10\%}$ [ºC]	$T_{d\text{-}max}$ [ºC]
P(FMF-*co*-BF)[a]	-[d]	118	84	-[d]	220	370
P(FMF-*co*-HF)[a]	-0.7	108	60	60	230	380
P(FMF-*co*-OF)[a]	7	88[e]	-[d]	-[d]	230	390
P(FMF-*co*-DF)[a]	-[d]	92	68	-[d]	230	390
P(FMF-*co*-DOF)[a]	-[d]	84	61	-[d]	230	390

[a]Furan-based copolyester from DMFDCA, BHMF and aliphatic diol with feed ratio 50 %: 25 % : 25 %, respectively. [b]T_g = glass transition temperature measured from the modulated DSC heating scan, T_m = melting temperature measured from the second DSC heating scan, T_c = crystallization temperature upon cooling, T_{cc} = cold crystallization temperature from the second DSC heating scan. [c]$T_{d\text{-}10\%}$ = decomposition temperature at 10 % weight loss, $T_{d\text{-}max}$ = temperature at maximum rate of decomposition. [d]not detected at the tested temperature range. [e]Measured from the first DSC heating scan.