Supplementary Information

Enzymatic Polymerization of Furan-Based Polymers in Biobased Solvents

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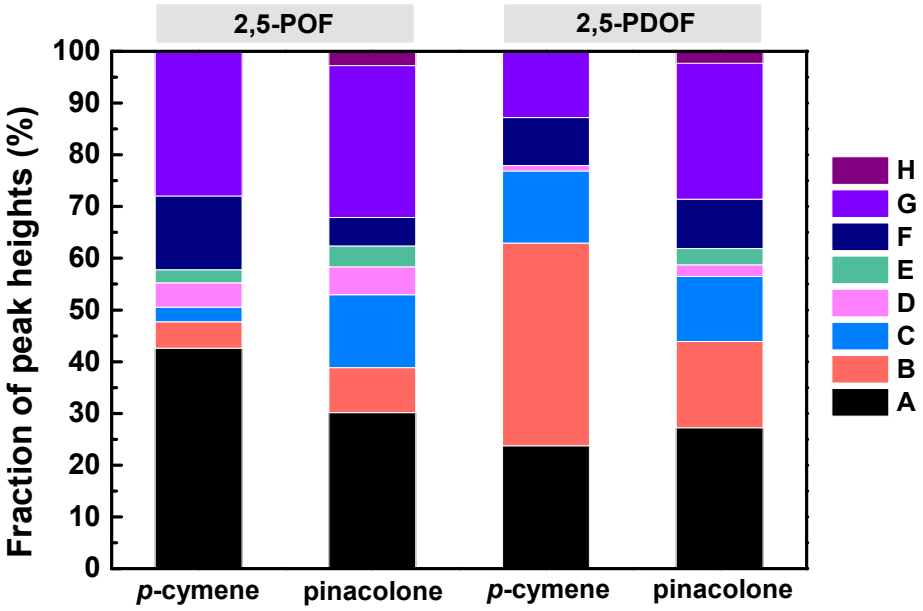

Figure S1. The Sum of peak height intensities of furan-based polyesters species from MALDI-ToF MS analysis and details of each species A to H are provided in Table 2.

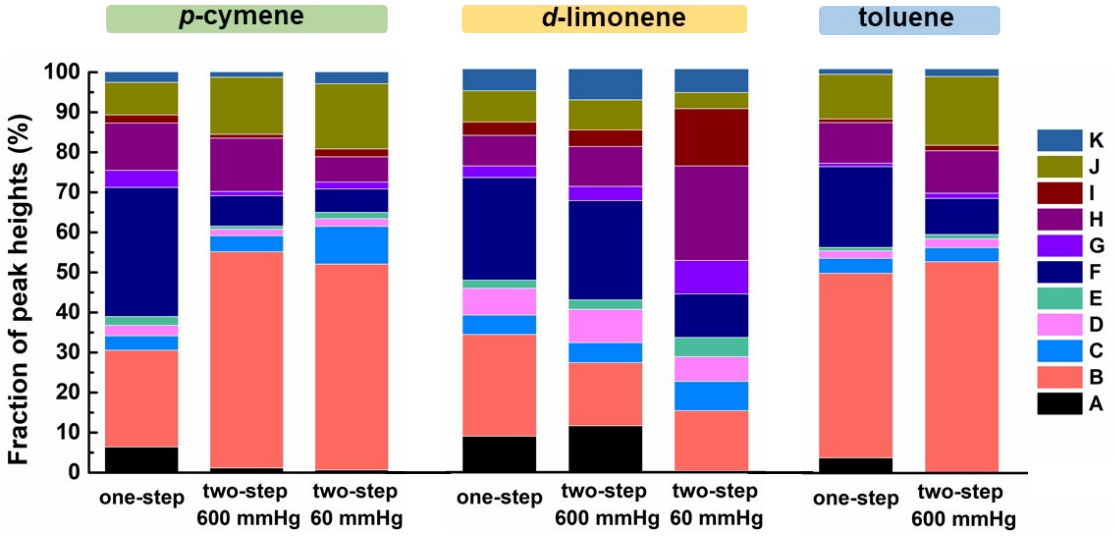

Figure S2. The Sum of peak height intensities of P(2,5-FMF-*co*-2,5-DF) species from MALDI-ToF MS analysis and details of each species A to K are provided in Table 3.

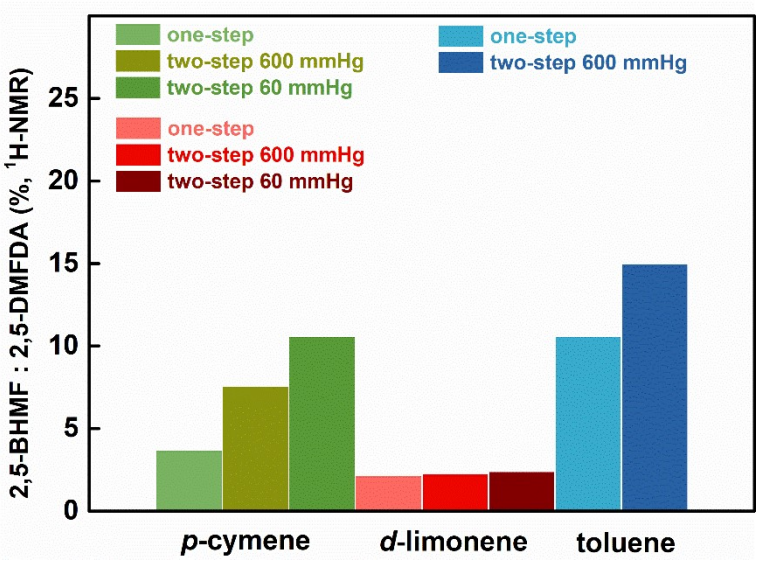

Figure S3. The molar fractions percentage of 2,5-BHMF comparison between P(2,5-FMF-*co*-2,5-DF) obtained in various method determined by ^{1}H-NMR spectroscopy

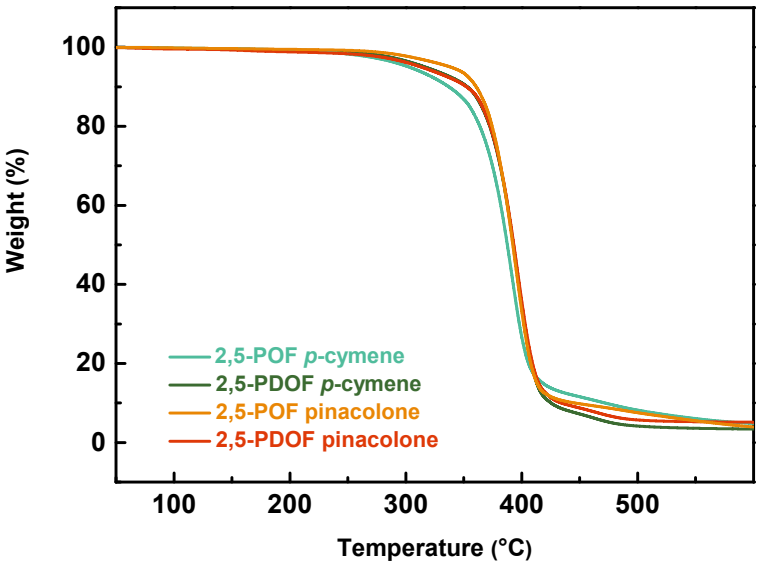

Figure S4. TGA curves of the obtained furan-based polyesters

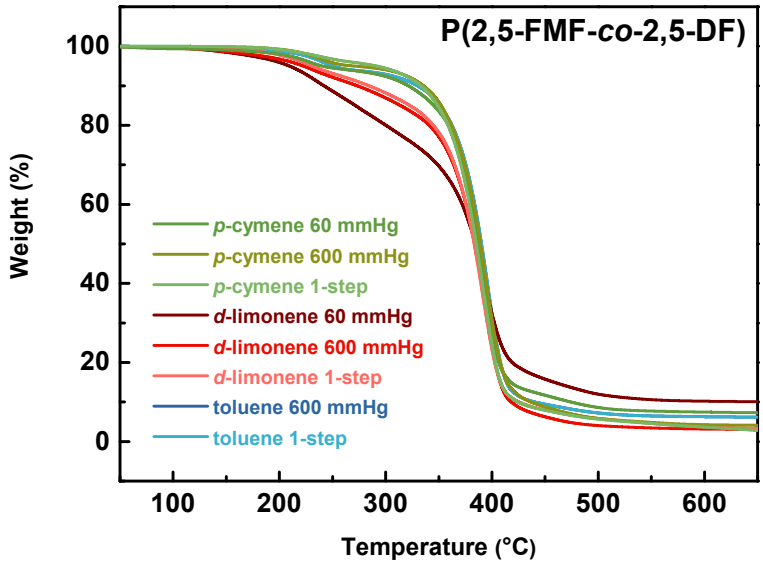

Figure S5. TGA curves of the obtained P(2,5-FMF-*co*-2,5-DF)

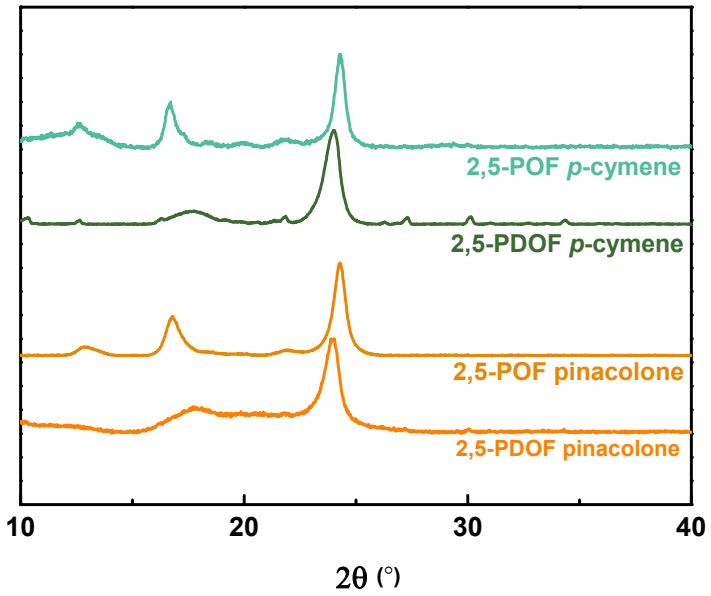

Figure S6. WAXD spectra of the obtained furan-based polyesters

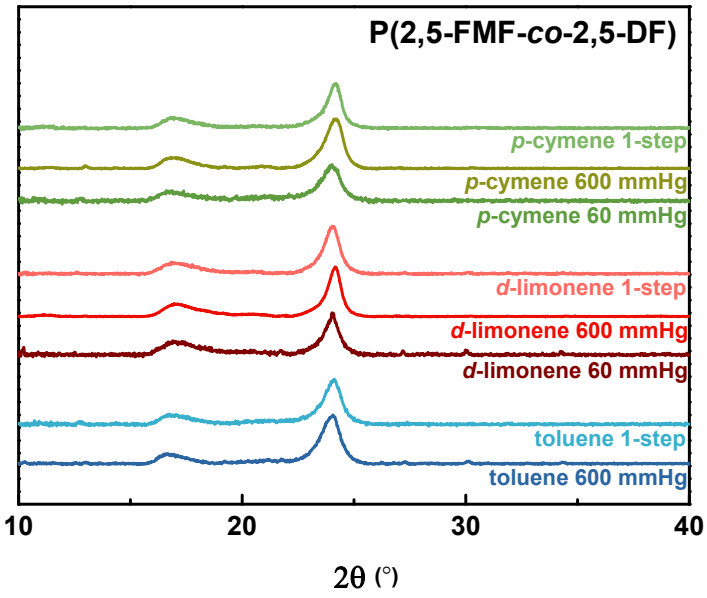

Figure S7. WAXD spectra of the obtained P(2,5-FMF-*co*-2,5-DF)

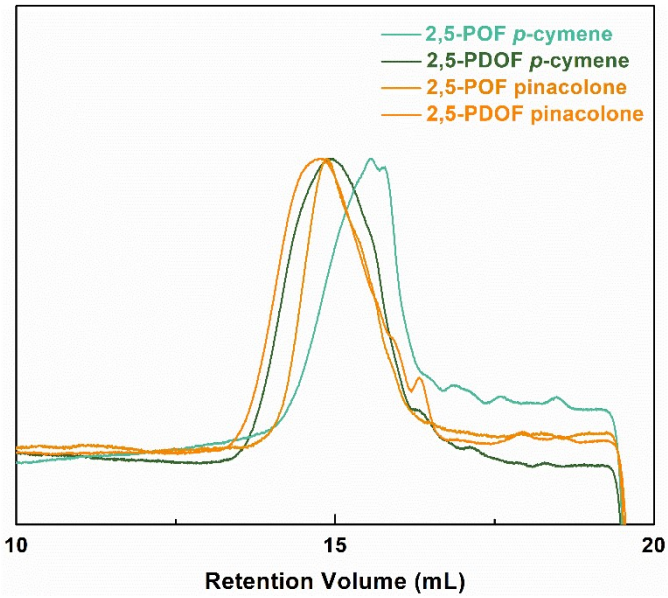

Figure S8. SEC elugrams of the obtained furan-based polyesters

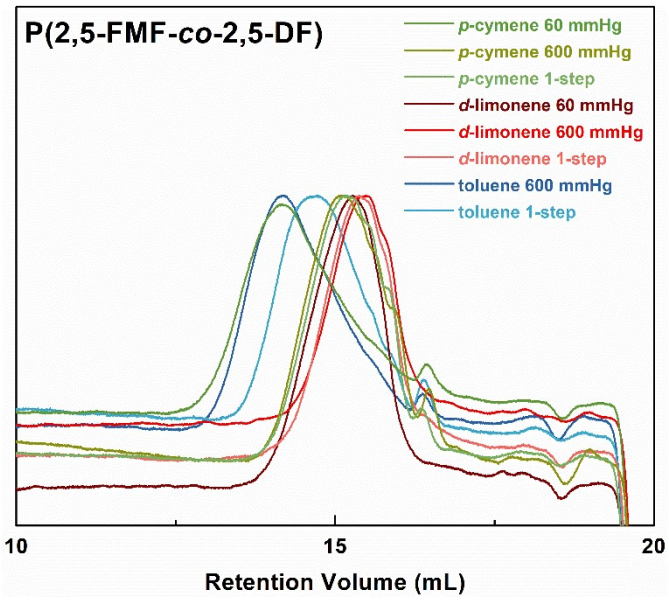

Figure S9. SEC elugrams of the obtained P(2,5-FMF-*co*-2,5-DF)

Table S1. Molecular weights and yields of the obtained furan-based polyesters in comparison with previous results.[14,39]

x[a]	Polymer	Solvent	$\bar{M}_{n^a}$ [g mol^{-1}]	$\bar{M}_{w^a}$ [g mol^{-1}]	Yield[b] [%]
8	2,5-POF	*p*-cymene	3350	5000	35
		Pinacolone	2400	4100	17
		Toluene	4450	8200	53
		$BMIMPF_6$	1550	2000	30
		U-ChCl	1800	2500	35
12	2,5-PDOF	*p*-cymene	4100	7000	63
		Pinacolone	3700	6200	48
		Toluene	5700	13300	60
		$BMIMPF_6$	2700	5400	56
		U-ChCl	1900	2700	41

[a] The number-average molecular weight ($\bar{M}_n$) and weight-average molecular weight ($\bar{M}_w$) were determined by SEC using $CHCl_3$ as the eluent; [b] isolated yield.

Table S2. Molecular weights and yields of the obtained P(2,5-FMF-*co*-2,5-DF)

Method	Solvent	$\bar{M}_{n^a}$ [g mol^{-1}]	$\bar{M}_{w^a}$ [g mol^{-1}]	Yield[b] [%]
One-step	*p*-cymene	3000	4400	42
	d-limonene	2400	3500	49
	Toluene	4300	7100	48
Two-step (600 mmHg)	*p*-cymene	3500	5900	47
	d-limonene	2300	3400	49
	Toluene	5800	11400	54
Two-step (60 mmHg)	*p*-cymene	5600	12800	61
	d-limonene	3000	4500	60

[a] The number-average molecular weight ($\bar{M}_n$) and weight-average molecular weight ($\bar{M}_w$) were determined by SEC using $CHCl_3$ as the eluent; [b] isolated yield.

Table S3. Properties of selected solvents

Solvent	Kamlet-Taft [a]		V_m [b] (mL/mol)	*Log P*	References
	β	π^*			
Toluene	0.12	0.50	107.10	2.58	Clark et al. [44]
p-cymene	0.13	0.39	156.06	3.47	Clark et al.[44]
Pinacolone	0.58	0.59	125.20	1.21	Byrne et al. [33]
d-limonene	0.00	0.16	162.17	4.57	Clark et al.[44]

[a] measured via UV spectroscopy taking the wavelength of maximum absorption, λ_{max}, in the relevant solvent, i.e., hydrogen bond accepting ability (β) using 4-nitroanisole, polarizability (π^*) using N,N-diethyl-4-aniline; [b] molar volume calculated as the ratio between molecular weight (M_w) and density (ρ) of the solvent

Table S4. Thermal and crystalline properties of the obtained furan-based polyesters

Polyester	Solvent	DSC				TGA	WAXD
		T_g [a] (°C)	T_m [b] (°C)	T_m [b] (°C)	T_c [c] (°C)	$T_{d\text{-}max}$ [d] (°C)	χ_c [e]
2,5-POF	*p*-cymene	10	138; 141	129; 138	118	394	56
	Pinacolone	5	121; 127	116; 126	104	390	51
2,5-PDOF	*p*-cymene	5	57; 102	94; 102	79	396	46
	Pinacolone	6	55; 100	91; 100	76	396	46

[a] T_g = glass transition temperature from the modulated DSC heating scan, [b] T_m = melting temperature from the second heating scan, [c] T_c = crystallization temperature from the cooling scan; [d] $T_{d\text{-}max}$ = temperature at the maximum rate of decomposition; [e] The degree of crystallinity (χ_c) was calculated from WAXD

Table S5. Thermal and crystalline properties of the obtained P(2,5-FMF-*co*-2,5-DF

Method	Solvent	DSC					TGA	WAXD
		T_g [a] (°C)	T_m [b] (°C)	T_m [c] (°C)	T_{cc} [c] (°C)	T_c [d] (°C)	$T_{d\text{-}max}$ [e] (°C)	χ_c [f]
One-step	*p*-cymene	-5	64; 99	80; 87; 98	- [g]	63; 73	238; 390	37
	(+)-limonene	-5	59; 73; 91	72; 81; 92	- [g]	50; 65	227; 390	35
	Toluene	-2	60; 101	84; 90; 101	- [g]	64; 70	239; 393	35
Two-step 600 mmHg	*p*-cymene	-1	60; 91; 101	87; 100	- [g]	69	238; 393	37
	(+)-limonene	-2	58; 73; 88	71; 89	25	46	232; 393	32
	Toluene	-3	55; 100	99	37	53	239; 393	35
Two-step 60 mmHg	*p*-cymene	-1	57; 99	87; 100	35	58	227; 391	37
	(+)-limonene	-3	69; 82	84	- [g]	9	237; 393	30

[a] T_g = glass transition temperature from the modulated DSC heating scan, [b] T_m = melting temperature from the first heating scan, [c] T_m = melting temperature and T_{cc} = cold crystallization temperature from the second heating scan, [d] T_c = crystallization temperature from the cooling scan; [e] $T_{d\text{-}max}$ = temperature at the maximum rate of decomposition; [f] The degree of crystallinity (χ_c) was calculated from WAXD; [g] not determined