Supporting Information

for

Unlocking the potential of furan-based poly(ester amide)s: An investigation of crystallization, molecular dynamics and degradation kinetics of novel poly(ester amide)s based on renewable poly(propylene furanoate)

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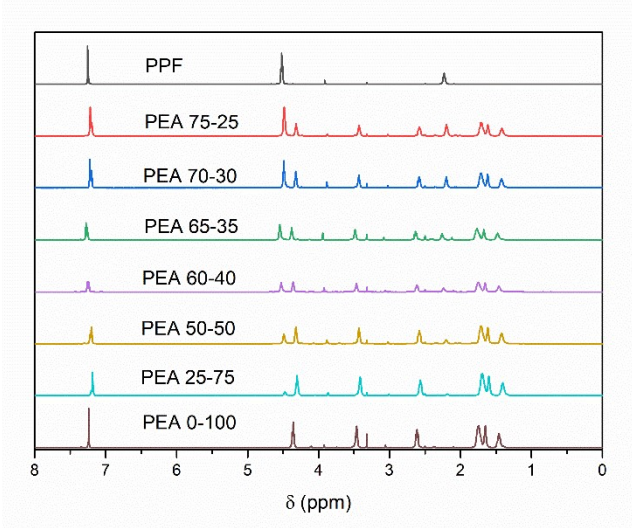
Synthesis of the amido diol

In brief, 1,4-diaminobutane was placed in a three-necked flask, equipped with a cooler and a mechanical stirrer, and dissolved in 2-propanol (200 mL mol^{-1}). Then, ε-caprolactone (2 equivalents) dissolved in 2-propanol (50 mL mol^{-1}) was slowly added to the diamine solution using a pump (0.6 mL/min). Stirring was continued overnight at room temperature. The resulting white pasty product was diluted with acetone and then washed several times with the same solvent to remove residual monomers and potentially formed oligomeric by-products by (homo)polymerization of the lactone. It was further purified by recrystallization from methanol and acetone and then dried under reduced pressure, whereby the respective product was obtained as a white powder.

Figure S1: ^{1}H spectra of all the synthesized copolymers, along with the homopolymers.



PPF

^{1}H NMR (500 MHz, DMSO-d^{6}/TFA) δ 7.25 (s, 2H), 4.52 (t, *J*=6.0 Hz, 4H), 2.23 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d^{6}/TFA) δ 159.9, 145.7, 119.1, 62.5, 26.2.

PEA 75-25

^{1}H NMR (500 MHz, DMSO-d^{6}/TFA) δ 7.22-7.20 (s, 2H), 4.48 (br, 2.8H), 4.32 (br, 1.2H), 3.43 (br, 1.2H), 2.58 (m, 1.2H), 2.20 (m, 1.4H), 1.71-1.61 (m, 3.6H), 1.42 (s, 1.2H). ^{13}C NMR (126 MHz, DMSO-d^{6}/TFA) δ 178.7, 160.2, 160.1, 159.9, 145.8, 145.7, 145.6, 145.5, 119.1, 118.9, 65.7, 62.5, 52.1, 40.7, 32.8, 26.4, 26.2, 24.2, 23.9, 23.8.

PEA 70-30

^{1}H NMR (500 MHz, DMSO-d^{6}/TFA) δ 7.22-7.20 (s, 2H), 4.49 (t, *J* = 5.6 Hz, 2.6H), 4.32 (t, *J* = 6.2 Hz, 1.4H), 3.43 (br, 1.4H), 2.58 (m, 1.4H), 2.20 (m, 1.3H), 1.71-1.61 (m, 4.3H), 1.43 (m, 1.4H). ^{13}C NMR (126 MHz, DMSO-d^{6}/TFA) δ 178.7, 160.2, 160.1, 159.9, 145.8, 145.7, 145.6, 145.5, 119.1, 118.9, 65.7, 62.5, 40.7, 32.8, 26.4, 26.2, 24.2, 23.9, 23.8.

PEA 65-35

^{1}H NMR (500 MHz, DMSO-d^{6}/TFA) δ 7.28-7.26 (s, 2H), 4.55 (t, *J* = 5.6 Hz, 2.3H), 4.38 (t, *J* = 6.1 Hz, 1.7H), 3.49 (br, 1.7H), 2.63 (m, 1.7H), 2.26 (m, 1.1H), 1.71-1.67 (m, 5.1H), 1.48 (m, 1.7H).

^{13}C NMR (126 MHz, DMSO-d^6/TFA) δ 178.7, 160.2, 160.1, 159.9, 145.8, 145.7, 145.6, 145.5, 119.1, 118.9, 65.7, 62.5, 40.7, 32.8, 26.4, 26.2, 24.2, 23.9, 23.8.

PEA 60-40

^{1}H NMR (500 MHz, DMSO-d^6/TFA) δ 7.26-7.24 (s, 2H), 4.49 (t, *J* = 5.2 Hz, 2.1H), 4.36 (t, *J* = 5.9 Hz, 1.9H), 3.47 (br, 1.9H), 2.62 (m, 1.9H), 2.24 (m, 1H), 1.75-1.65 (m, 5.7H), 1.46 (m, 1.9H). ^{13}C NMR (126 MHz, DMSO-d^6/TFA) δ 178.7, 160.1, 159.9, 145.8, 145.7, 145.6, 145.5, 119.1, 118.9, 65.7, 62.5, 40.7, 32.8, 26.4, 26.2, 24.2, 23.9, 23.8.

PEA 50-50

^{1}H NMR (500 MHz, DMSO-d^6/TFA) δ 7.22-7.20 (s, 2H), 4.49 (br, 1.7H), 4.32 (br, 2.3H), 3.43 (br, 2.3H), 2.58 (m, 2.3H), 2.20 (m, 0.8H), 1.72-1.62 (m, 6.9H), 1.42 (m, 2.3H). ^{13}C NMR (126 MHz, DMSO-d^6/TFA) δ 178.7, 160.2, 160.1, 160.0, 145.8, 145.7, 145.6, 145.5, 119.1, 118.9, 65.7, 62.5, 40.7, 32.8, 26.4, 26.2, 24.2, 23.9, 23.8.

PEA 25-75

^{1}H NMR (500 MHz, DMSO-d^6/TFA) δ 7.20-7.18 (s, 2H), 4.47 (br, 0.7H), 4.30 (br, 3.3H), 3.41 (br, 3.3H), 2.57 (m, 3.3H), 2.19 (m, 0.3H), 1.69-1.60 (m, 9.9H), 1.40 (m, 3.3H). ^{13}C NMR (126 MHz, DMSO-d^6/TFA) δ 178.7, 160.2, 145.7, 119.1, 118.9, 65.7, 62.5, 40.7, 32.8, 26.4, 24.2, 23.9, 23.8.

PEA 0-100

^{1}H NMR (500 MHz, DMSO-d^6/TFA) δ 7.24 (s, 2H), 4.36 (t, *J* = 6.2 Hz, 4H), 3.46 (br, 4H), 2.61 (m, 4H), 1.74-1.65 (m, 12H), 1.46 (m, 4H). ^{13}C NMR (126 MHz, DMSO-d^6/TFA) δ 178.8, 160.3, 145.8, 119.0, 65.8, 40.8, 32.9, 26.5, 24.3, 23.9, 23.8.

Figure S2: ^{13}C spectra of all the synthesized copolymers, along with the homopolymers. Quadruplet peaks centered at approximately 113.5 and 160.8 ppm are due to TFA-d_1.

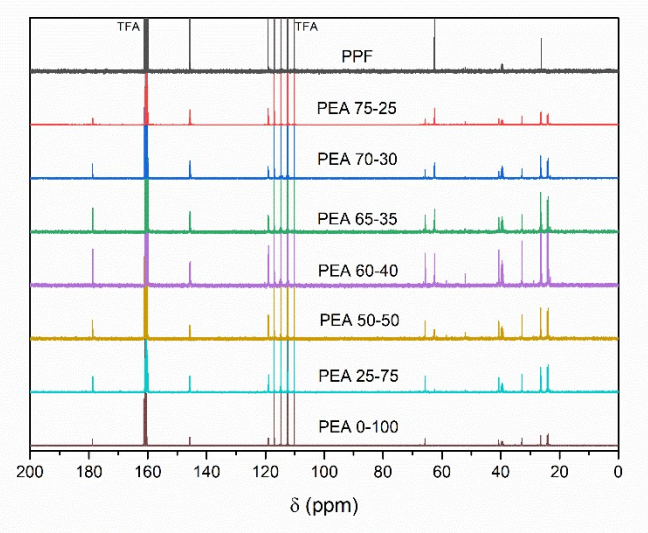


Figure S3: A) Magnified ^{13}C NMR spectra of the 60/40 P(PF-ADF) copolymer in the region 145.4-145.8 ppm. B) Possible triads in the synthesized poly(ester amides).

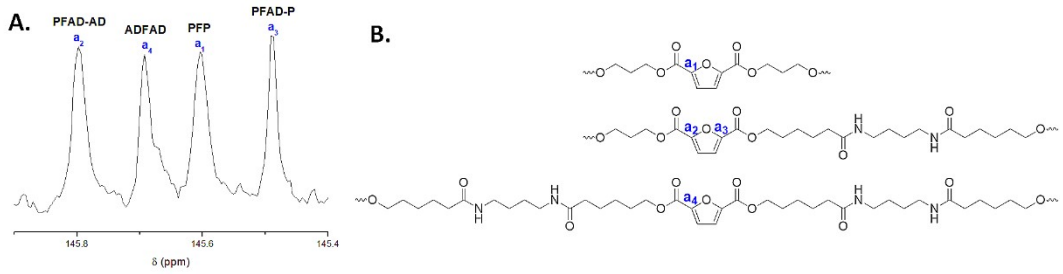


Figure S4: PLM photographs from cold crystallization of the materials

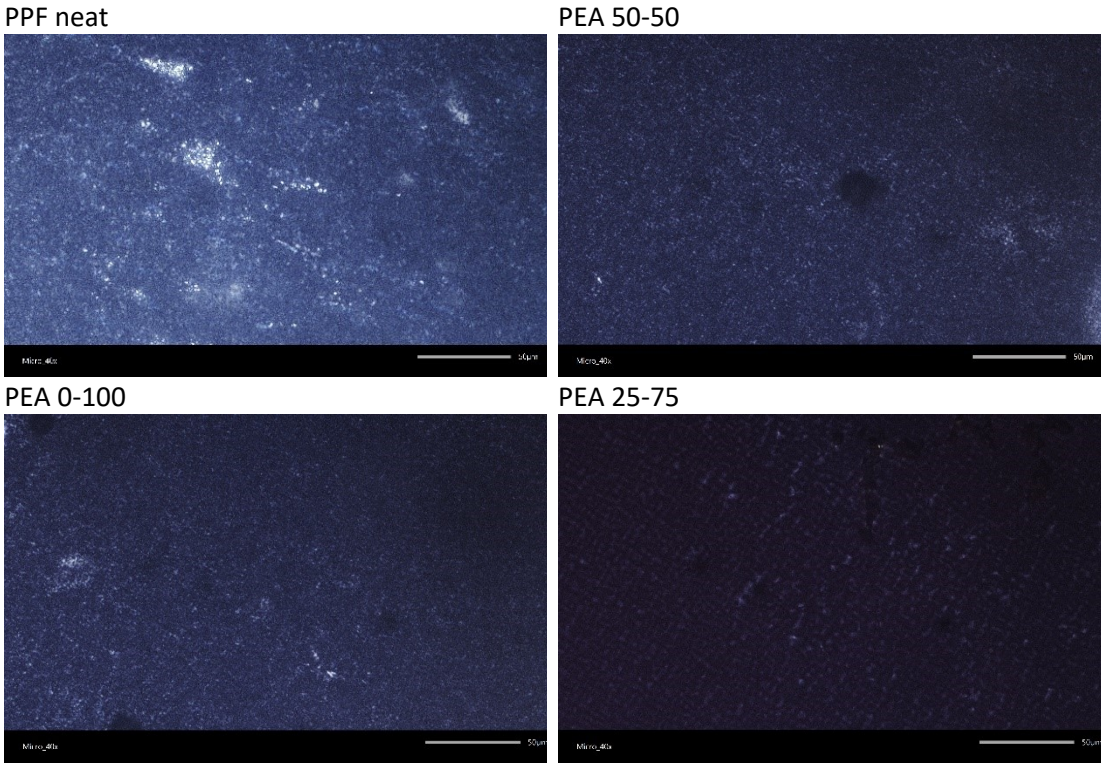


Table S1: Calculated values of the kinetic parameters of PPF, PEA 0-100 and PEA 50-50 copolymer, obtained from the model fitting kinetic analysis.

Sample	Activation energy (kJ/mol)	Pre-exponential factor (log A)	Reaction order (n)	log K_{cat}	Contribution	R^2
PPF						
1st reaction mechanism-reaction model **Cn Step A→B**	175.1	11.49	0.57	0.69	0.332	0.99997
2nd reaction mechanism-reaction	196.3	12.95	1.42	0.77	0.668	

model **Cn** **Step B→C**						
PEA 0-100						
1st reaction mechanism-reaction model **Cn** **Step A→B**	135.1	8.67	1.61	0.01	0.307	
2nd reaction mechanism-reaction model **Cn** **Step B→C**	182.8	12.42	1.52	0.23	0.43	0.99995
3rd reaction mechanism-reaction model **Cn** **Step D→E**	238.5	15.16	1.28	0.01	0.263	
PEA 50-50						
1st reaction mechanism-reaction model **Fn** **Step A→B**	128.6	9.81	2.33	-	0.091	
2nd reaction mechanism-reaction model **Cn** **Step B→C**	151.1	10.09	1.54	0.01	0.727	0.9999
3rd reaction mechanism-reaction model **Cn** **Step D→E**	231.7	14.83	1.58	0.01	0.182	

Figure S5: Total ion chromatographs

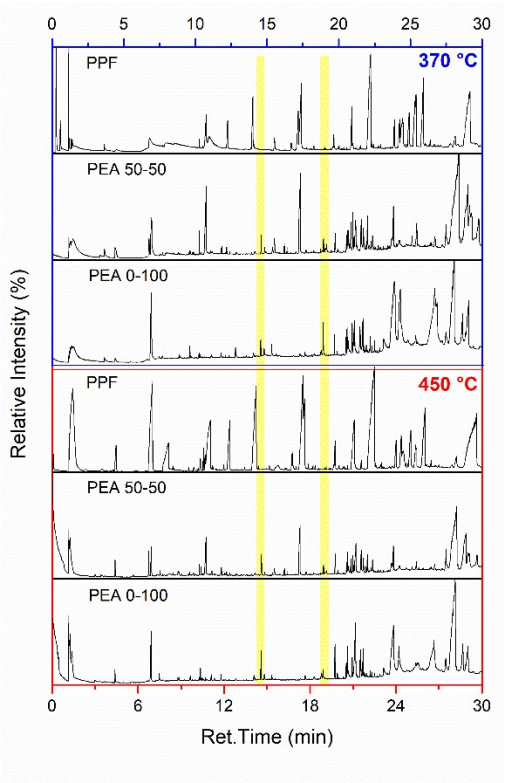


Figure S6: Comparative BDS isothermal plots of the imaginary part of ε'' versus frequency at −60 °C, showing effects on local mobility, i.e. on β_i, γ_i and δ_i processes recorded for *i*=PPF or PEA. The inset scheme described the origins of β_{PPF} process.

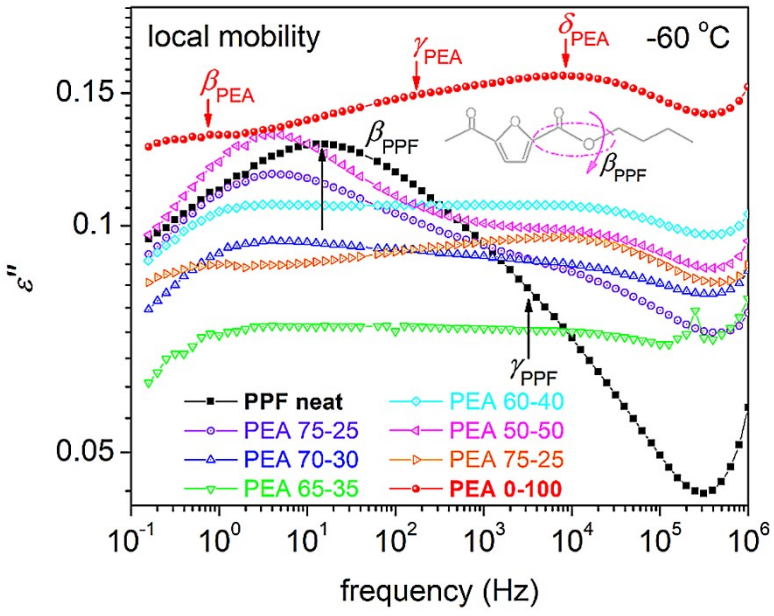
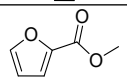
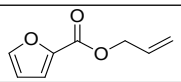
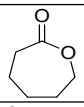
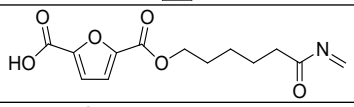
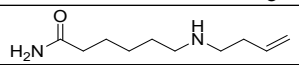
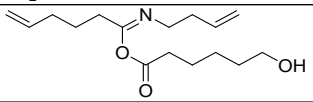
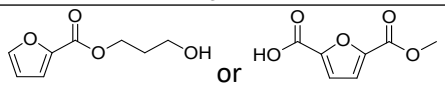
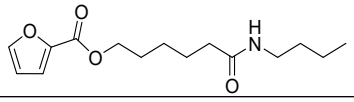
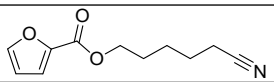
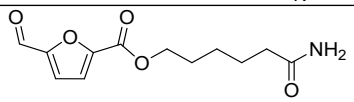
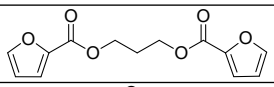
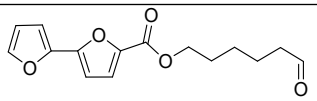
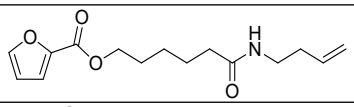
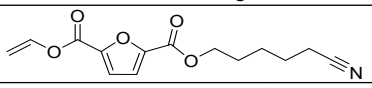
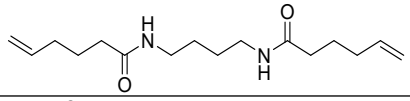
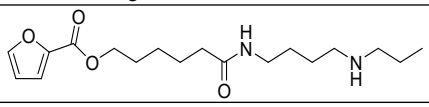
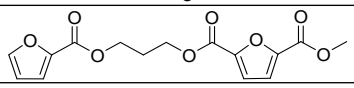
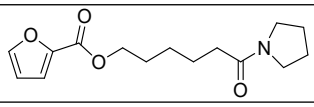


Table S2: Possible compounds resulting from the pyrolysis of the materials.

Poly(amido diol furanoate)	Poly(propylene diol amido diol furanoate) 50/50	M_w	Possible product

R_t (min)		R_t (min)			
370 °C	**450 °C**	**370 °C**	**450 °C**		
-	0.44	-	-	44	CO_2 or acetaldehyde
-	1.16	1.17	1.16	44	
-	1.24	-	1.23	58	acetone (??)
-	1.37	-	-	68	
-	4.39	-	4.40	126	
-	-	6.76	6.74	152	
6.93	6.92	6.94	6.94	114	
9.62	-	-	-	281	
-	-	10.28	10.28	184	
-	10.36	-	-	281	
-	-	10.75	10.74	170	 or
11.79	-	-	-	281	
12.78	-	-	-	207	Not identified
14.56	14.58	14.59	14.61	207	
14.79	-	-	-	253	
15.32	-	-	-	281	Not identified
-	-	17.32	17.31	264	
18.92	-	18.94	-	276	
19.71	19.74	19.76	19.78	279	
20.51	20.52	20.55	20.55	277	
20.59	20.60	20.61	20.62	280	
-	-	20.69	-	338	
-	-	20.87	20.85	322	

20.93	20.94	20.99	20.98	279	
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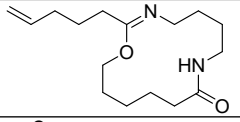
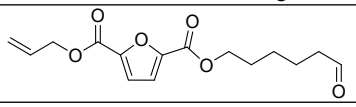
21.09	21.17	21.18	-	280	
-	-	-	21.19	294	
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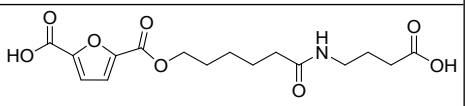
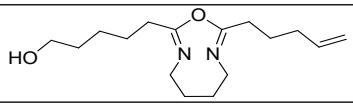
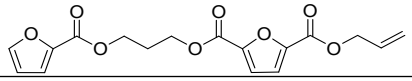
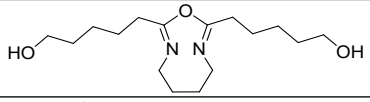
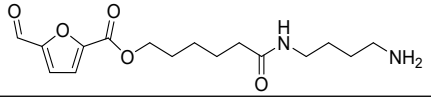
21.54	-	-	-	355	
21.68	21.70	21.73	21.72	280	
-	-	22.01	22.00	348	
22.20	-	-	-	298	
22.33	-	22.36	-	324	
-	-	-	22.37	444	Not identified
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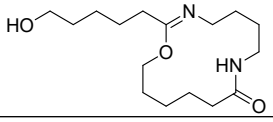
23.89	23.84	-	-	298	
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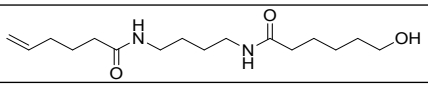
24.30	-	-	-	298	
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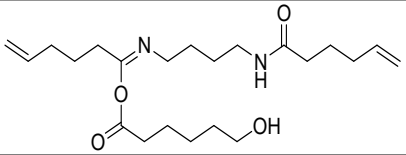
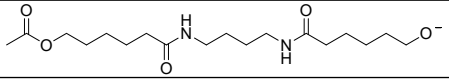
-	26.66	-	-	394	
26.70	-	-	-	357	
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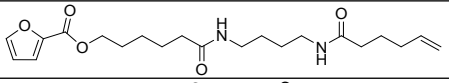
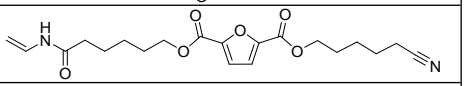
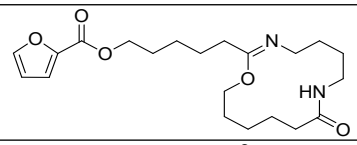
28.06	28.12	28.38	28.23	392	
28.65	-	29.02	28.87	390	
-	28.67	-	-	429	Not identified

29.07	29.01	29.15	-	392	
-	-	29.27	29.66	432