Supporting Information

Capturing the Real Time Hydrolytic Degradation of a Library of Biomedical Polymers by Combining Traditional Assessment and Electrochemical Sensors

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Tables

Table S1. Molar mass (M_n) and dispersity ($Đ$) values of the evaluated polymers over the degradation time. T0-T4 are respectively 0, 5,10, 15 and 20 days for PLLA, PDLLA, PLTMC, PCLA, PCL; 0, 5, 7, 10, 15 days for PLGA and PCLDX and 0, 2, 5, 7 and10 days for PDLLGA. N=3 in all the cases.

Polymer	T0		T1		T2		T3		T4	
	M_n (kg mol^{-1})	$Đ$	M_n (kg mol^{-1})	$Đ$	M_n (kg mol^{-1})	$Đ$	M_n (kg mol^{-1})	$Đ$	M_n (kg mol^{-1})	$Đ$
PLLA	144.8	1.5	15.0 ± 3.0	2.2 ± 0.05	10.0 ± 1.5	2.4 ± 0.3	4.0 ± 0.1	4.4 ± 0.7	3.0 ± 0.1	4.2 ± 0.1
PLGA	142.1	1.5	1.4 ± 0.1	3.2 ± 0.5	1.0 ± 0.05	3.3 ± 0.2	0.5 ± 0.05	4.5 ± 0.5	0.3 ± 0.01	5.1 ± 0.2
PDLLA	136.6	1.6	65.8 ± 3.0	2.2 ± 0.1	7.4 ± 1.0	2.3 ± 0.4	0.9 ± 0.05	4.2 ± 0.5	0.2 ± 0.01	5.1 ± 0.2
PDLLGA	97.7	1.6	19.0 ± 1.9	3.0 ± 0.1	0.4 ± 0.1	4.2 ± 0.2	0.1 ± 0.1	3.9 ± 0.4	–	–
PCLA	114.7	1.6	33.1 ± 5.0	3.0 ± 0.1	13.6 ± 5.3	2.8 ± 0.5	2.9 ± 0.3	4.2 ± 0.1	1.5 ± 0.2	5.0 ± 0.6
PLTMC	134.2	1.6	133.5 ± 6.8	2.0 ± 0.1	127.3 ± 1.6	1.0 ± 0.0	108.7 ± 1.5	1.8 ± 0.0	92.1 ± 3.4	1.9 ± 0.1
PCL	114.7	1.8	87.3 ± 5.7	2.0 ± 0.1	70.8 ± 4.3	2.1 ± 0.0	44.8 ± 5.1	2.5 ± 0.1	38.4 ± 2.2	2.7 ± 0.4
PCLDX	78.3	1.8	20.6 ± 2.3	2.0 ± 0.0	16.8 ± 2.2	2.1 ± 0.3	8.6 ± 0.6	2.8 ± 0.2	4.6 ± 0.3	3.3 ± 0.2

Table S2. Apparent constants of hydrolysis rate extrapolated for the evaluated polymers.

Polymer	k (days^{-1})
PLLA	0.11
PLGA	0.17
PDLLA	0.40
PDLLGA	1.03
PCLA	0.22
PLTMC	0.02
PCL	0.07
PCLDX	0.15

Table S3. Mass loss (%) values of the evaluated polymers over the degradation time. T1-T4 are respectively 5,10, 15 and 20 days for PLLA, PDLLA, PLTMC, PCLA, PCL; 5, 7, 10, 15 days for PLGA and PCLDX and 2, 5, 7 and 10 days for PDLLGA. PDLLGA has an extra time point at 15 days: mass loss = 100 %. N=3 in all the cases.

Polymer	T1	T2	T3	T4
PLLA	6.8 ± 1.2	11.6 ± 1.1	16.7 ± 1.0	18.3 ± 4.1
PLGA	23.4 ± 0.9	37.7 ± 0.9	46.5 ± 1.0	52.3 ± 3.1
PDLLA	5.9 ± 1.4	18.3 ± 3.4	38.6 ± 4.4	77.0 ± 7.4
PDLLGA[b]	7.8 ± 0.1	47.2 ± 2.1	79.8 ± 0.5	95.2 ± 1.1
PLCA	1.6 ± 1.4	4.2 ± 2.5	15.8 ± 5.0	24.4 ± 2.2
PLTMC	4.3 ± 0.8	5.2 ± 0.4	4.8 ± 0.5	5.0 ± 0.2
PCL	0.6 ± 0.2	1.0 ± 0.5	1.3 ± 0.2	1.1 ± 0.4
PCLDX	8.5 ± 2.5	12.5 ± 1.4	20.1 ± 4.0	22.6 ± 4.1

Table S4. pH values of the incubation media for each of the evaluated polymers over the degradation time. T1-T4 are respectively 5,10, 15 and 20 days for PLLA, PDLLA, PLTMC, PCLA, PCL; 5, 7, 10, 15 days for PLGA and PCLDX and 2, 5, 7 and10 days for PDLLGA. PDLLGA has an extra time point at 15 days: pH = 3.3 ± 0.0. N=3 in all the cases.

Polymer	T1	T2	T3	T4
PLLA	7.4 ± 0.0	7.4 ± 0.0	7.2 ± 0.1	7.2 ± 0.0
PDLLA	7.6 ± 0.0	7.5 ± 0.0	6.2 ± 0.1	3.9 ± 0.1
PLGA	6.8 ± 0.0	5.8 ± 0.1	4.3 ± 0.1	3.8 ± 0.0
PDLLGA[b]	7.5 ± 0.01	5.5 ± 0.6	3.6 ± 0.0	3.3 ± 0.0
PLTMC	7.6 ± 0.0	7.6 ± 0.0	7.6 ± 0.0	7.5 ± 0.2
PLCA	7.5 ± 0.0	7.3 ± 0.1	7.0 ± 0.0	6.6 ± 0.1
PCL	7.5 ± 0.0	7.5 ± 0.0	7.6 ± 0.0	7.4 ± 0.1
PCLDX	7.4 ± 0.0	7.4 ± 0.0	7.3 ± 0.0	7.1 ± 0.2

Table S5. L-lactate concentration [μM] in the incubation media for each of the evaluated polymers containing L-lactide as monomeric unit over the degradation time. T1-T4 are respectively 5,10, 15 and 20 days for PLLA, PDLLA, PLTMC, PCLA, PCL; 5, 7, 10, 15 days for PLGA and PCLDX and 2, 5, 7 and10 days for PDLLGA. PDLLGA has an extra time point at 15 days. L-lactate concentration = 5175 ± 473 μM. N=3 in all the cases.

Polymer	T1	T2	T3	T4
PLLA	157 ± 82	197 ± 17	559 ± 90	855 ± 83
PLGA	753 ± 71	2743 ± 389	4000 ± 172	5249 ± 433
PDLLA	–	29 ± 20	1282 ± 72	3740 ± 162
PDLLGA[b]	78.1 ± 11.2	422 ± 22	2268 ± 149	4078 ± 231
PLCA	51 ± 13	253 ± 88	1217 ± 90	2286 ± 164
PLTMC	–	–	–	–

Table S6. Linear fitting of pH as function of the mass loss (Figure 6c).

Polymer	Linear fitting equation	R^2
PLLA	pH = -0.02 Mass loss + 7.6	0.84
PDLLA	pH = -0.05 Mass loss + 8.2	0.98
PLGA	pH = -0.10 Mass loss + 9.4	0.96
PDLLGA	pH = -0.05 Mass loss + 7.9	0.99
PCLA	pH = -0.04 Mass loss + 7.5	0.98

Table S7. Linear fitting of the L-Lactate released (%) as function of the mass loss (Figure 6d).

Polymer	Linear fitting equation	R^2
PLLA	L-Lactate = 0.72 Mass loss - 13.6	0.997
PDLLA	L-Lactate = 0.53 Mass loss - 9.9	0.999
PDLLGA	L-Lactate = 1.89 Mass loss - 118.7	0.95

Calculation for the L-lactate released %

Eq. S1.

$$L-lactate\ released\ \% = \frac{[L-lactate]_t}{[L-lactate]_{max}} \times 100$$

Where $[L-lactate]_t$ is the concentration measured at specific time in the incubation medium and the $[L-lactate]_{max}$ is the maximum concentration expected for a total degradation of each polymer and it is calculated based on the composition.

As an example, calculation for the $[L-lactate]_{max}$ of PLGA is reported.

Eq. S2.

$$\begin{cases} mol\%\ LA : mol\%\ GA = 82{:}18 \\ \left(mol\%\ LA\ \times 144.12\frac{g}{mol}\right) + \left(mol\%\ GA\ \times 116.07\frac{g}{mol}\right) = m(mg) \end{cases}$$

By solving the system of equation and knowing the mass (m) in mg of each film sample and that, the total volume of the incubation medium is 0.030 L:

Eq. S3.

$$[L-lactate]_{max}(\mu M) = \frac{\frac{m\ (mg)}{169.63\ \frac{g}{mol}} \times 2}{0.030\ L}$$