Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Plasticization and anti-plasticization effects caused by poly(lactide-*ran*-caprolactone) addition to double crystalline Poly(L-lactide)/Poly(ε-caprolactone) blends.

Matteo Rizzuto[a-c], Agurtzane Mugica[a], Manuela Zubitur[b], Daniele Caretti[c], Alejandro J. Müller*[a,d]

Synthesis of P(LA-*ran*-CL)LMw random copolymer.

P(LA-*ran*-CL)LMw was synthesized, according to the literature,[1] by ring opening polymerization (ROP) of e-caprolactone and D,L-lactide and tin(II) octaoate. The reaction was carried out overnight in an oil bath at 140 ºC and stopped by quenching it in an ice bath. The crude product was dissolved in a minimum volume of $CHCl_3$, followed by precipitation into a 10-fold excess of methanol. The copolymers were recovered by filtration and after drying under vacuum.

The analysis of the ^{1}H-NMR spectrum (Fig S.1) was performed using the work of Peponi *et al.*[2] as reference. The multiplet from 5.05 to 5.25 ppm is assigned to methane proton of polymerized lactide (f). The multiplet from 4.08 to 4.18 ppm is due to the CL proton (a) that linked to LA molecule, while the triplet at 4.05 ppm indicates that the CL proton a linked to another CL molecule.. The multiplet between 2.34 to 2.44 ppm is due to the CL proton (e) that linked to a LA molecule, while the triplet at 2.30 indicates that the CL proton e linked to another CL molecule. For the rest of the spectrum, multiplets at 1.66 ppm and 1.39 ppm are related to the CL protons (b), (d), and (c), respectively, and the multiplet at 1.56 ppm, to the LA methyl protons (g). So, the ratio of the LA signals to the CL signals results in a molar composition of the copolymers.

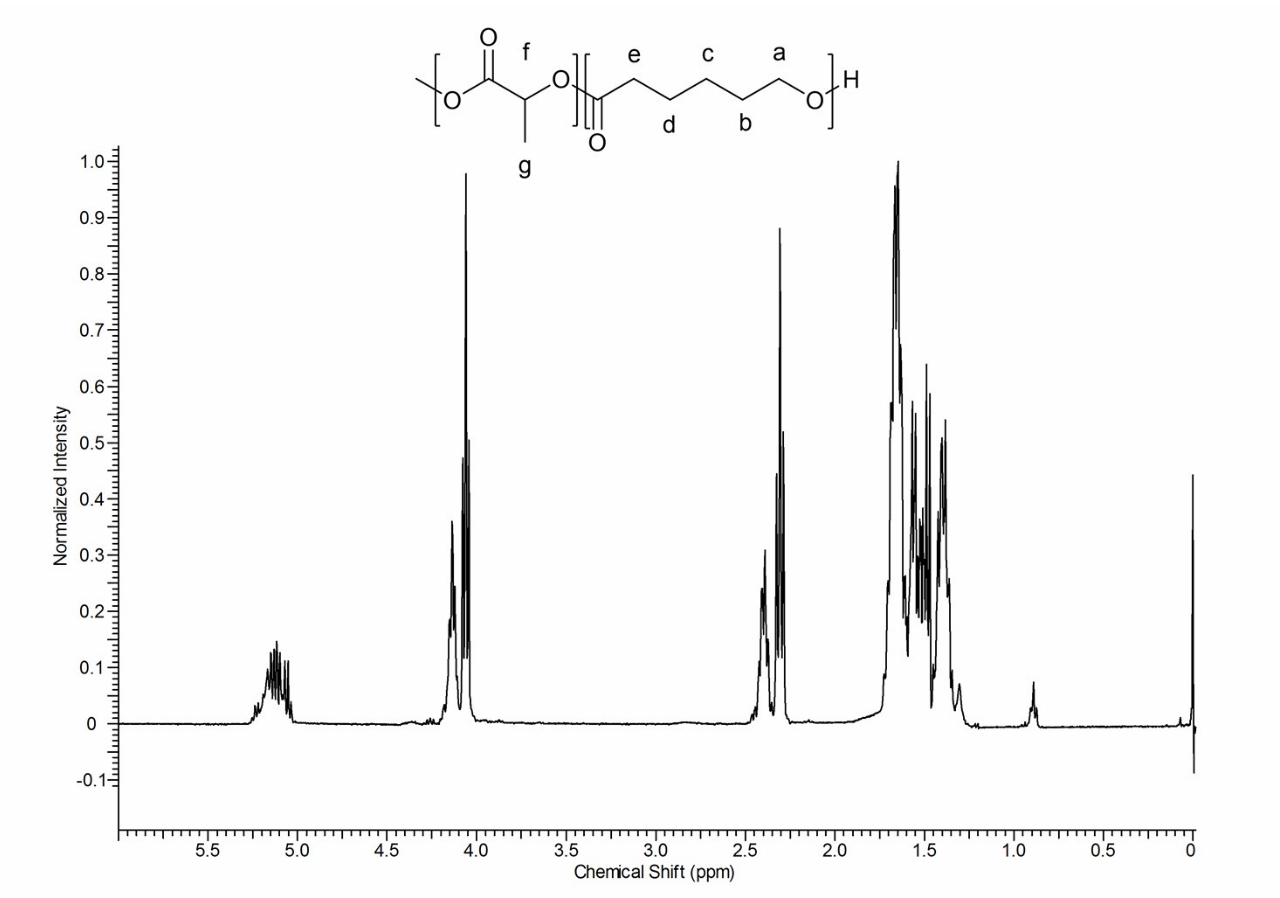

Fig. S.1 ^{1}H-NMR spectrum and chemical structure of the P(LA-*ran*-CL) random copolymer.

Avrami Fit

The Avrami Fit was performed using an Origin® software application called *Polymer Crystallization Plugin*. This Origin® plugin was developed by Lorenzo *et al.*[3] The Plugin is offered free upon request by Prof. A.J. Müller.

The data obtained by isothermal Differential Scanning Calorimetry (DSC) tests were used to perform the Avrami Fits and the graphical comparisons between the experimental data and the predictions of the theory. Firstly, it allows the baseline to be established and later calculate the integral of the calorimetric isothermal curve. Secondly, the linear fit according to the Avrami equation and fitting errors can be performed. V_c (relative volume fraction crystallinity) is calculated according to Ec. 1, whereas V_c range is selected from 0.03 to 0.20 in order to obtain the best fit within the primary crystallization range.

$$\boldsymbol{V_c} = \frac{\boldsymbol{W_c}}{\boldsymbol{W_c} + \frac{\boldsymbol{\rho_c}}{\boldsymbol{\rho_a}}(\boldsymbol{1} - \boldsymbol{W_c})} \tag{1}$$

Where ρ_c and ρ_a are the fully crystalline and fully amorphous polymer densities, respectively. For all calculations, ρ_a=1.25 g/cm^3 and ρ_c=1.359 g/cm^3 were used for PLA. The relative crystalline mass fraction W_c is calculated as:

$$W_c = \frac{\Delta H(t)}{\Delta H_{total}} \tag{2}$$

Where ΔH(t) and ΔH_{total} are the enthalpy as a function of crystallization time and the maximum enthalpy after completion of the crystallization process.
Finally, the Avrami equation is rearranged as follows:

$$\log\left[-\ln\left[1 - V_c(t - t_0)\right]\right] = \log(K) + n\log(t - t_0) \tag{3}$$

Where *n* is the Avrami index and *K* is the overall crystallization rate constant. The experimental and predicted half–crystallization time $\tau_{50\%}$ can be also determined by this Origin® plugin. According to the Avrami equation, $\tau_{50\%}$ is:

$$\tau_{50\%} = \left[-\frac{\ln\left[1 - V_c\right]}{K}\right]^{1/n} \tag{4}$$

Then, depending on the goodness of the fit (up to 50% conversion) there may be a difference between the experimental and predicted values of $\tau_{50\%}$. The parameters obtained by Avrami Fits are collected in Table S1 (sample of neat PLA), Table S2 (sample PLA/PCL), Table S3 (sample PLA/PCL/P(LA-*ran*-CL)LMw and Table S4 (sample PLA/PCL/P(LA-*ran*-CL)HMw.

Table S1 Parameters obtained by fitting the Avrami theory to PLA

T_c	$t_{50\% theo}$ (min)	$t_{50\% exp}$ (min)	n	K (min^{-n})	R^2	$1/t_{50 exp}$ (min^{-1})
130	29.029	28.384	3.28	1.10E-05	1.0000	0.0308
128	22.449	22.567	3.59	9.73E-06	1.0000	0.0402
126	21.191	21.234	3.3	2.94E-05	1.0000	0.0423
124	19.715	19.313	3.24	4.47E-05	0.9997	0.0454
122	18.052	17.686	3.23	6.01E-05	0.9993	0.0493
120	16.645	16.317	3.03	1.40E-04	0.9995	0.0535
118	15.856	15.567	3.12	1.26E-04	0.9998	0.0563
116	15.195	14.866	2.97	2.12E-04	1.0000	0.0580
114	15.125	14.717	2.84	3.06E-04	0.9999	0.0579
112	15.837	15.033	2.7	3.98E-04	1.0000	0.0550
110	15.816	15.317	2.68	4.21E-04	0.9998	0.0550
130	29.029	28.384	3.28	1.10E-05	0.9998	0.0308
128	22.449	22.567	3.59	9.73E-06	1.0000	0.0402
126	21.191	21.234	3.3	2.94E-05	0.9998	0.0423
124	19.715	19.313	3.24	4.47E-05	0.9997	0.0454

122	18.052	17.686	3.23	6.01E-05	0.9993	0.0493

Table S2 Parameters obtained by fitting the Avrami theory to PLA/PCL

T_c	$t_{50\%\ theo}$ (min)	$t_{50\%\ exp}$ (min)	n	K (min^{-n})	R^2	$1/t_{50\ exp}$ (min^{-1})
113	8.307	7.733	2.3	0.00503	0.9997	0.1293
110	6.415	5.933	2.36	0.00858	0.9993	0.1685
107	5.049	4.783	2.54	0.0114	0.9995	0.2091
104	3.756	3.684	2.97	0.0137	0.9998	0.2714
101	2.737	2.766	3.81	0.0149	1.0000	0.3615
98	2.271	2.283	3.58	0.0367	0.9999	0.4380
95	2.593	2.633	4.32	0.0113	1.0000	0.3798
92	2.843	2.85	3.8	0.0131	0.9998	0.3509
89	3.62	3.617	3.71	0.0059	0.9998	0.2765
86	5.587	5.633	4.04	0.00062	1.0000	0.1775
83	8.219	8.133	3.6	0.000352	0.9998	0.1230

Table S3 Parameters obtained by fitting the Avrami theory to PLA/PCL/P(LA-*ran*-CL)LMw

T_c	$t_{50\%\ theo}$ (min)	$t_{50\%\ exp}$ (min)	n	K (min^{-n})	R^2	$1/t_{50\ exp}$ (min^{-1})
134	7.864	8.133	3.1	0.00116	0.9999	0.1230
131	6.473	6.717	3	0.00257	1.0000	0.1489
129	5.932	6.117	2.84	0.00443	1.0000	0.1635
125	4.325	4.45	2.92	0.00962	1.0000	0.2247
122	3.874	3.934	2.63	0.0197	1.0000	0.2542
119	3.635	3.65	2.55	0.0257	0.9999	0.2740
116	3.836	3.867	2.65	0.0197	1.0000	0.2586
113	4.031	4.017	2.54	0.02	1.0000	0.2489
110	3.994	3.833	2.25	0.0306	0.9998	0.2609
107	4.008	3.9	2.3	0.0286	1.0000	0.2564
104	3.784	3.734	2.32	0.0315	1.0000	0.2678
101	3.883	3.75	2.4	0.0266	0.9999	0.2667
98	4.421	4.266	2.42	0.0191	0.9999	0.2344
95	4.942	4.8	2.56	0.0117	0.9998	0.2083
92	5.629	5.567	2.85	0.00553	0.9999	0.1796
89	6.607	6.617	2.99	0.00244	0.9998	0.1511

Table S4 Parameters obtained by fitting the Avrami theory to PLA/PCL/P(LA-*ran*-CL)HMw

T_c	$t_{50\%\ theo}$ (min)	$t_{50\%\ exp}$ (min)	n	K (min^{-n})	R^2	$1/t_{50\ exp}$ (min^{-1})
125	10,251	10,3	3,4	0,000253	1,0000	0,0971
122	5,121	5,184	3,09	0,00448	1,0000	0,1929
119	3,057	3,133	3,09	0,022	1,0000	0,3192
116	1,999	2,05	3,14	0,078	1,0000	0,4878
113	1,526	1,583	3,7	0,145	1,0000	0,6317
110	1,344	1,4	3,47	0,248	1,0000	0,7143
107	1,414	1,415	4,31	0,156	1,0000	0,7067
104	1,38	1,4	3,88	0,199	0,9998	0,7143
101	1,491	1,516	3,95	0,143	0,9999	0,6596
98	1,645	1,633	3,44	0,125	0,9996	0,6124
95	1,711	1,667	3,04	0,136	0,9996	0,5999
92	2,198	2,134	2,92	0,0695	0,9996	0,4686
89	3,121	3,017	2,89	0,00844	0,9996	0,3315

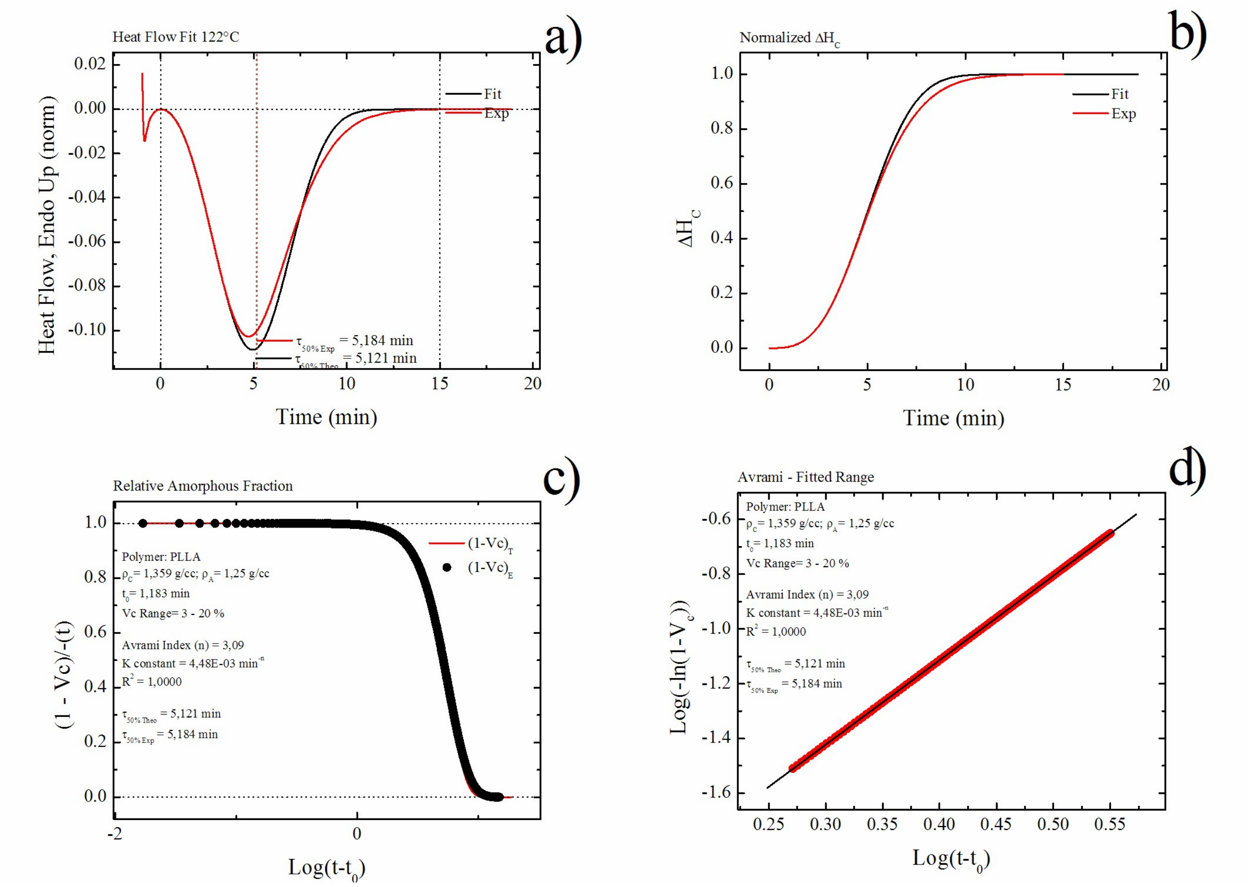

Fig. S2 Avrami plots obtained by the Origin® plugin developed by Lorenzo *et al.* (a) Experimental DSC crystallization isotherm of PLA/PCL/P(LA-*ran*-CL)HMw at 122°C and its fitting with the Avrami equation. The experimental crystallization half–time is indicated. (b) Relative enthalpy of crystallization (Ec. 2) as a function of time. (c) Evolution of the normalized volumetric fraction of the amorphous phase as a function of crystallization time. (d) Linear fitting of the Avrami equation in the primary crystallization range, where the slope indicates the Avrami index and the intercept the overall crystallization rate constant.

References

1. J. Odent, P. Leclère, J.-M. Raquez and P. Dubois, *European Polymer Journal*, 2013, 49, 914-922.
2. L. Peponi, A. Marcos-Fernández and J. M. Kenny, *Nanoscale Research Letters*, 2012, 7, 1-7.
3. A. T. Lorenzo, M. L. Arnal, J. Albuerne and A. J. Müller, *Polymer Testing*, 2007, 26, 222-231.