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Supporting Information

Can Poly(ε-Caprolactone) crystals nucleate glassy Polylactide?

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Synthesis of PLA-*b*-PC copolymer

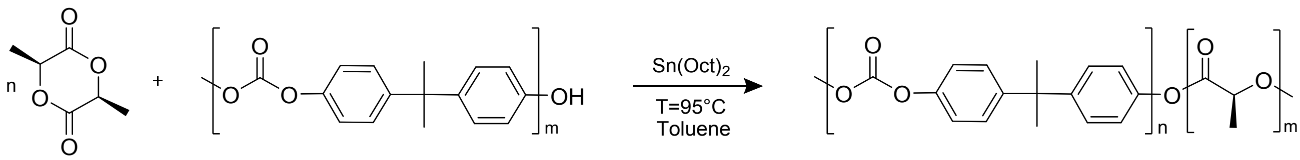


Figure S1. Synthesis of PLA-*b*-PC copolymer, from L-Lactide and polycarbonate olygomers

Materials. All chemicals were purchased from Sigma-Aldrich. L-Lactide was recrystallized from ethyl acetate and dried overnight under vacuum before use. Solvents and stannous 2-ethylhexanoate were used as received. Polycarbonate oligomers were prepared according to literature procedures[1](M_n=2600 g/mol) and purified by by precipitation into a 10-fold excess of methanol.

Synthesis of PLA-*b*-PC. In a typical experiment, L-Lactide and Polycarbonate were charged to a three-neck flask equipped with a condenser under nitrogen atmosphere (by following the composition of the copolymer and at total amount of 1g) containing Stannous 2-ethylhexanoate (0.1% mol/mol with respect to L-Lactide amount) and toluene (10 ml). The reaction was carried out at 95 °C for 24 hours under nitrogen and stopped by quenching it in an ice bath. The crude product was dissolved in a minimum volume of dichloromethane, followed by precipitation into a 10-fold excess of methanol. The copolymers were recovered by filtration and after drying under vacuum. ^{1}H NMR (400 MHz, CDCl3). δ 5.15 (br, 1H, Lactide-unit), 1.68 (br, 3H, Lactide-unit), 7.25 (br, 2H, Carbonate-unit), 7.17 (br, 2H, Carbonate-unit) and 1.66 (br, 6H, Carbonate-unit) ppm.

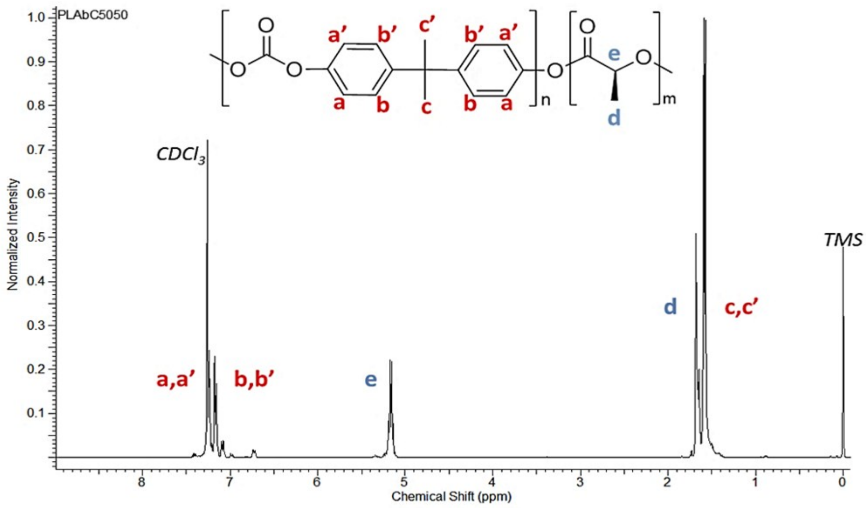
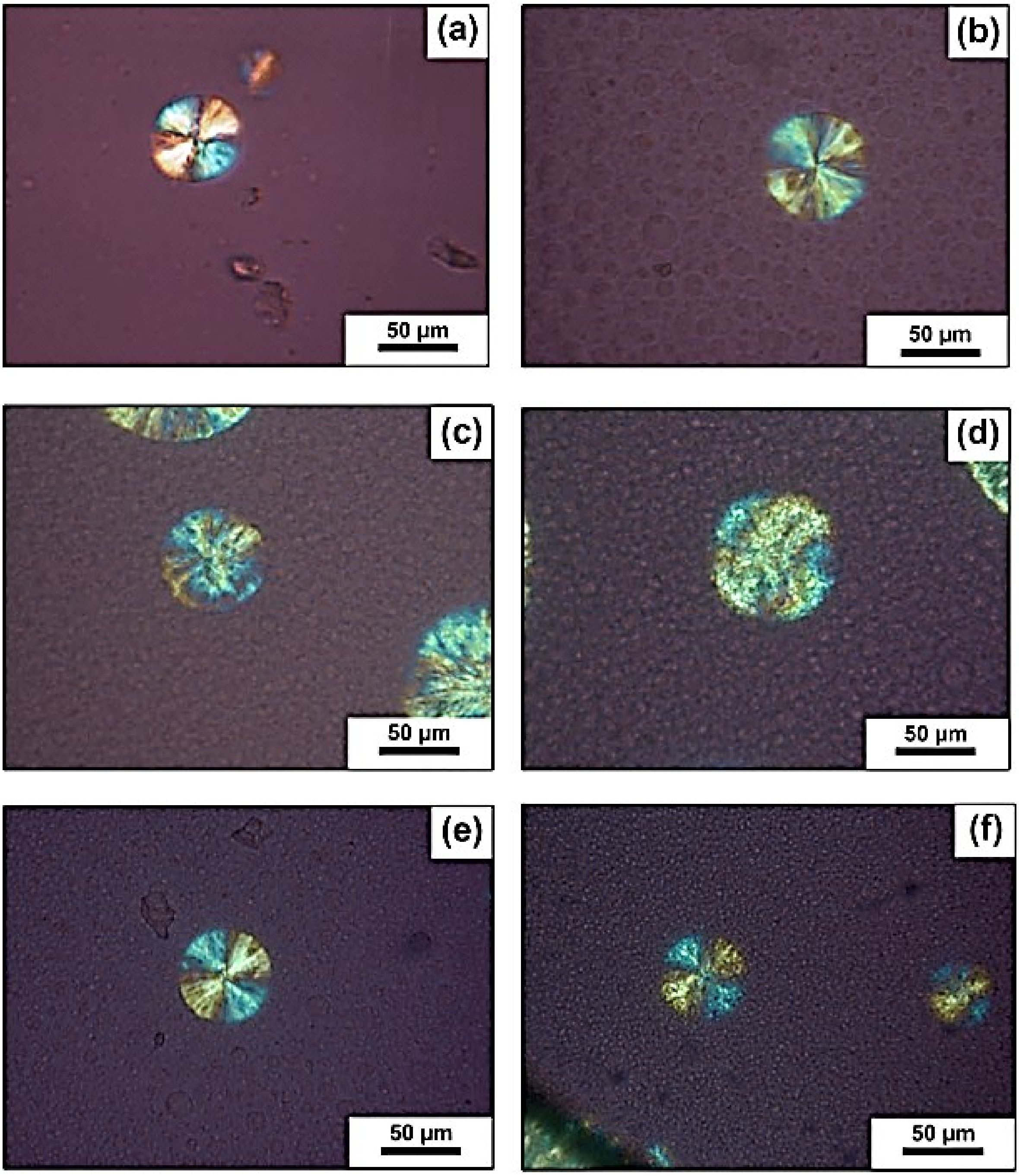


Figure S2. ^{1}H-NMR spectrum(400 MHz, CDCl3) and chemical structure of PLA-*b*-PC50-50

PLOM micrographs of the blends



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igure S3. PLOM micrographs of (a) PLA (b) PLA/PCL (c) PLA/PCL/PLA-b-PC80-20 (d) PLA/PCL/PLA-b-PC50-50 (e) PLA/PCL/PLA-b-PC15-85 (f) PLA/PCL/PC recorded at 128 °C and after 5 minutes from the begin of the crystallization from the melt state.

Avrami Fit

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 (Figure S4). 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 Eq. S1, whereas V_c range is selected from 0.03 to 0.20 in order to obtain the best fit within the primary crystallization range.

$$Vc = \frac{Wc}{Wc + \frac{\rho_c}{\rho_a}(1 - Wc)} \qquad \text{Eq. (S1)}$$

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:

$$Wc = \frac{\Delta H_{(t)}}{\Delta H_{TOT}} \qquad \text{Eq. (S2)}$$

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:

$$\log\left[-\ln\left[1 - V_c(t - t_0)\right]\right] = \log(K) + n\log(t - t_0) \qquad \text{Eq. (S3)}$$

Where *n* is the Avrami index and *K* is the overall crystallization rate constant. The experimental and predicted half–crystallization $\tau_{50\%}$ can be also determined by Origin® plugin developed by Lorenzo *et al*[2]. According to the Avrami equation, $\tau_{50\%}$ is:

$$\tau_{50\%} = \left[-\frac{\ln\left[1 - V_c\right]}{K}\right]^{1/n} \qquad \text{Eq. (S4)}$$

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.

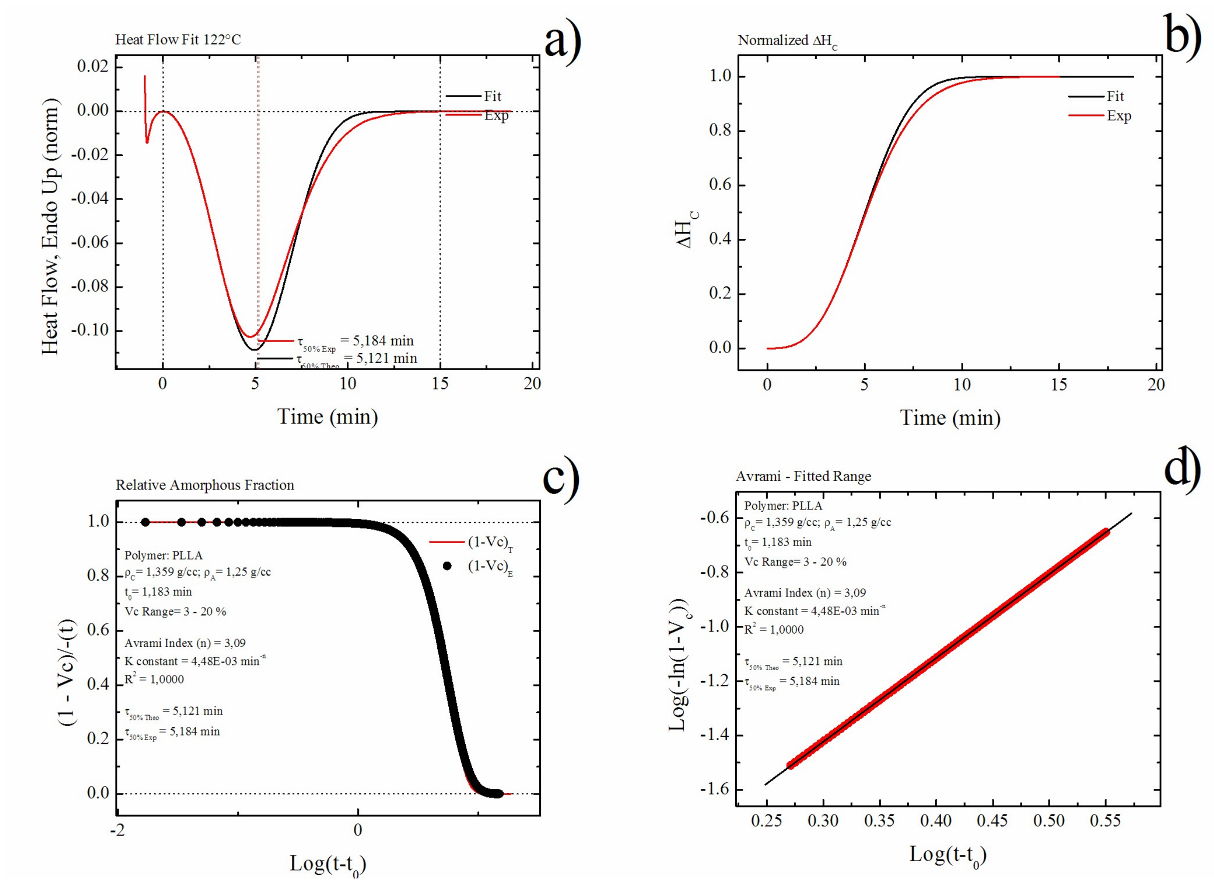

Figure S4. Table of Avrami plots obtained by the Origin® plugin developed by Lorenzo *et al*[2]. (a) Experimental DSC crystallization isotherm of PLA/PCL 122°C and its fitting with the Avrami equation. The experimental crystallization half–time is indicated. (b) Relative enthalpy of crystallization as 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

Table S1. Data obtained by the Avrami model

PLA/PCL

T(°C)	R^2	K	n	τ_{THEO} (min)	τ_{EXP} (min)
144	0.9999	0.185	1.3	2.759	2.482
140	1.0000	0.282	1.33	1.965	1.797
136	0.9999	0.579	1.39	1.139	1.140
132	1.0000	0.772	1.49	0.930	0.896
128	0.9999	1.040	1.58	0.776	0.749
124	1.0000	1.100	1.64	0.753	0.722
120	0.9998	1.080	1.81	0.785	0.763
116	0.9997	1.050	1.94	0.807	0.784
112	0.9997	0.891	2.13	0.889	0.865
108	0.9993	0.524	2.37	1.125	1.080
104	0.9991	0.310	2.64	1.355	1.290
100	1.0000	0.308	2.26	1.432	1.419
96	1.0000	0.208	2.14	1.755	1.735

PLA

T(°C)	R^2	K	n	τ_{THEO} (min)	τ_{EXP} (min)
140	0.9996	0.003	2.76	7.023	6.875
136	0.9999	0.007	2.63	5.811	5.703
132	1.0000	0.018	2.31	4.882	4.845
128	0.9997	0.020	2.31	4.686	4.542
124	1.0000	0.033	2.23	3.923	3.867
122	1.0000	0.027	2.35	3.870	3.872
120	0.9994	0.024	2.32	4.273	4.002
116	0.9992	0.024	2.29	4.317	4.025
118	1.0000	0.030	2.26	4.008	3.872
112	0.9998	0.029	2.19	4.255	4.050
108	1.0000	0.027	2.1	4.716	4.604
104	0.9978	0.273	2.43	1.468	1.346
100	1.0000	0.033	2.03	4.462	4.368

PLA/PCL/PLA-*b*-PC80-20

T(°C)	R^2	K	n	τ_{THEO} (min)	τ_{EXP} (min)
148	0.9984	0.864	1.31	0.845	0.975
144	0.9986	1.170	1.38	0.682	0.787
140	0.9986	0.653	1.3	1.047	1.174
136	0.9989	0.789	1.35	0.909	1.000
132	0.9994	0.878	1.4	0.844	0.893
128	0.9996	1.790	1.56	0.545	0.575
124	0.9999	1.780	1.62	0.559	0.568
120	0.9996	2.830	1.69	0.436	0.490
116	1.0000	3.180	1.81	0.430	0.435
112	0.9999	2.660	1.94	0.500	0.490
108	0.9998	0.767	1.95	0.949	1.082
104	0.9996	0.473	2.14	1.196	1.338
100	0.9996	0.273	2.09	1.561	1.508
96	0.9985	0.260	2.4	1.503	1.458
92	0.9999	0.174	2.76	1.648	1.657
88	0.9999	0.141	2.4	1.944	1.941
84	0.9999	0.076	2.29	2.633	2.607
80	1.0000	0.049	2.07	3.604	3.575

PLA/PCL/PLA-*b*-PC50-50

T(°C)	R^2	K	n	τ_{THEO} (min)	τ_{EXP} (min)
148	0.9997	0.255	1.36	2.087	1.860
144	0.9995	0.650	1.35	1.049	1.063
140	0.9993	1.330	1.46	0.642	0.685
136	0.9992	2.300	1.59	0.469	0.517
132	0.9999	0.705	1.6	0.990	0.923
128	0.9999	0.890	1.64	0.856	0.812
124	0.9999	1.150	1.71	0.744	0.710
120	0.9995	1.150	1.93	0.771	0.730
116	0.9996	1.320	2	0.725	0.695
112	0.9996	1.330	2.07	0.729	0.707
108	1.0000	0.340	2.19	1.386	1.398
104	1.0000	0.318	2.11	0.446	1.457
100	1.0000	0.240	2.12	1.649	1.680
96	1.0000	0.346	2.41	1.335	1.33
92	1.0000	0.226	2.39	1.598	1.585
88	1.0000	0.076	2	3.034	3.1

PLA/PCL/PLA-*b*-PC15-85

T(°C)	R^2	K	n	τ_{THEO} (min)	τ_{EXP} (min)
144	1.0000	0.070	1.94	3.272	3.215
140	1.0000	0.103	1.93	2.696	2.726
136	0.9994	0.107	2.2	2.337	2.144
132	1.0000	0.227	2.23	1.651	1.707
128	1.0000	0.396	2.13	1.301	1.349
124	1.0000	0.371	2.16	1.336	1.415
120	0.9999	0.181	2.11	1.890	1.922
116	1.0000	0.184	2.18	1.838	1.912
112	1.0000	0.183	2.13	1.871	1.933
108	1.0000	0.158	2.29	1.906	1.965
104	1.0000	0.194	2.11	1.830	1.862
100	1.0000	0.171	2.07	1.963	1.993

PLA/PCL/PC

T(°C)	R^2	K	n	τ_{THEO} (min)	τ_{EXP} (min)
144	0.9950	1.450	1.1	0.513	0.490
140	0.9961	2.560	1.22	0.343	0.393
136	0.9958	7.410	1.46	0.197	0.240
132	0.9988	2.320	1.3	0.393	0.337
120	1.0000	5.110	1.8	0.330	0.324
116	0.9999	5.350	1.89	0.339	0.327
112	0.9997	4.470	2.01	0.396	0.372
108	0.9992	1.760	2.21	0.656	0.610
104	0.9989	1.040	2.25	0.836	0.768
100	0.9990	0.635	2.33	1.038	0.967
96	0.9989	0.281	2.48	1.439	1.347
92	0.9992	0.11	2.67	1.992	1.882

References

1 M. R. Korn, in *Advances in Polycarbonates*, pp. 39–57.

2 A. T. Lorenzo, M. L. Arnal, J. Albuerne and A. J. Müller, *Polym. Test.*, 2007, **26**, 222–231.