## SUPPLEMENTARY INFORMATION

## Characterization of as cast B-5050 blends.

The B-50/50 blends investigated in this paper were obtained by casting from freely evaporating chloroform solutions. Completely transparent films were obtained in all cases. In addition their initial crystallinity was qualitatively assessed by means of FTIR spectroscopy using the skeletal bands located in the $900-1000 \mathrm{~cm}^{-1}$ spectral region (Macromolecules 2006, 39, 9291-9301).
Figure S1 compares the spectrum obtained for as cast B-5050 blends (light blue) with samples of different crystallinity degrees (all the spectra were recorded at room temperature). The green spectrum was obtained for a PDLLA film (PDLLA is the meso conformer of PLAs and is completely amorphous). It shows a band located at $955 \mathrm{~cm}^{-1}$ attributed to a skeletal vibration mode in amorphous PLAs. The spectrum of as cast PLLA (blue color) is very similar to that of PDLLA; but after isothermal crystallization from the melt at $160{ }^{\circ} \mathrm{C}$ for 5 h (see Macromolecules 2006, 39, 9291-9301), the cyan colored spectrum is obtained for PLLA. This spectrum shows a new band at about 920 $\mathrm{cm}^{-1}$, attributed to the crystalline skeletal mode. Moreover, when a PLLA/PDLA 50/50 is isothermally cold crystallized at $190^{\circ} \mathrm{C}$, the red colored spectrum is obtained, showing the crystalline band at about $908 \mathrm{~cm}^{-1}$.
As can be seen in the Figure S1, the spectrum obtained for the as cast B- 5050 blends nearly matches the one obtained for as cast PLLA; and both are very similar to the spectrum of PDLLA. In addition to the amorphous band located at $955 \mathrm{~cm}^{-1}$, both the as cast PLLA sample and the as cast B-5050 blends also show a very weak contribution in the $920 \mathrm{~cm}^{-1}$ region, indicating the presence of a minor amount of crystalline material. Since the spectrum of the as cast B-5050 blends is much closer to the one corresponding to the amorphous material than to the ones corresponding to the crystallized materials, the as cast samples are predominantly amorphous.


Fig. S1. FTIR spectra in the $900-1000 \mathrm{~cm}^{-1}$ region for: PDLLA (green); as cast PLLA (blue); as cast PLLA/PDLA 50/50 blend (light blue); PLLA isothermally crystallyzed from the melt at $160^{\circ} \mathrm{C}$ for 5h (cyan); PLLA/PDLA 50/50 blend isothermally cold crystallized at $190^{\circ} \mathrm{C}$ for 5 .

## Spherulite growth rates

The following plot shows the spherulite growth rates (obtained from the slope of the spherulite radius versus time plot) measured for the PLOM experiments in Figure 1 in the paper. As can be seen, all the isothermal crystallizations show linear trends up to $180^{\circ} \mathrm{C}$. However, in the experiment performed at $190^{\circ} \mathrm{C}$ a linear growth rate is only obtained during the first hour (approximately). Then growth rate begins to decay and crystal growth stops after about 4 hours. The table with the numeric values used to build Fig. S 2 is also added after the plot.


Fig. S2. Spherulite radius versus time obtained for the PLOM experiments in Fig. 1 (see paper)

| $\mathrm{Tc}=\mathbf{1 2 0}^{\circ} \mathrm{C}$ |  | $\mathrm{Tc}=130^{\circ} \mathrm{C}$ |  | $\mathrm{Tc}=140^{\circ} \mathrm{C}$ |  | $\mathrm{Tc}=\mathbf{1 5 0}^{\circ} \mathrm{C}$ |  | $\mathrm{Tc}=160^{\circ} \mathrm{C}$ |  | $\mathrm{Tc}=\mathbf{1 7 0}^{\circ} \mathrm{C}$ |  | $\mathrm{Tc}=180^{\circ} \mathrm{C}$ |  | $\mathrm{Tc}=190{ }^{\circ} \mathrm{C}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| t $($ min $)$ | radius <br> ( $\mu \mathrm{m}$ ) | $t$ $(\min )$ | radius <br> ( $\mu \mathrm{m}$ ) | $\begin{gathered} \mathrm{t} \\ (\mathrm{~min}) \end{gathered}$ | radius <br> ( $\mu \mathrm{m}$ ) | $\begin{gathered} t \\ (\min ) \end{gathered}$ | radius <br> ( $\mu \mathrm{m}$ ) | t $(\min )$ | radius <br> ( $\mu \mathrm{m}$ ) | $\begin{gathered} \mathrm{t} \\ (\mathrm{~min}) \end{gathered}$ | radius <br> ( $\mu \mathrm{m}$ ) | $\begin{gathered} \mathrm{t} \\ (\mathrm{~min}) \end{gathered}$ | radius <br> ( $\mu \mathrm{m}$ ) | t $($ min $)$ | radius <br> ( $\mu \mathrm{m}$ ) |
| 4 | 4.5 | 4 | 6.2 | 3 | 4.8 | 10 | 3.1 | 10 | 7.2 | 2 | 7.2 | 2 | 5.9 | 20 | 15.9 |
| 8 | 7.6 | 6 | 9.0 | 4 | 6.6 | 15 | 4.1 | 20 | 15.5 | 6 | 16.9 | 5 | 16.6 | 32 | 26.6 |
| 10 | 10.0 | 10 | 14.8 | 6 | 10.3 | 20 | 7.2 | 30 | 21.7 | 12 | 26.2 | 15 | 46.2 | 50 | 37.6 |
| 12 | 10.3 | 16 | 20.0 | 8 | 15.5 | 25 | 9.7 | 40 | 30.7 | 20 | 44.5 | 20 | 60.7 | 60 | 43.8 |
| 14 | 12.1 | 20 | 24.1 | 10 | 19.0 | 30 | 11.4 | 50 | 38.3 | 28 | 62.8 | 30 | 90.7 | 95 | 58.3 |
| 18 | 14.1 | -- | -- | 12 | 22.4 | 40 | 16.2 | 60 | 43.5 | 30 | 66.9 | 50 | 140.4 | 120 | 66.2 |
| 25 | 19.7 | -- | -- | 16 | 30.4 | 50 | 21.4 | -- | -- | 40 | 88.0 | -- | -- | 160 | 74.2 |
| -- |  | -- |  | -- |  | 60 | 25.2 | -- | -- | 50 | 98.7 | -- | -- | 180 | 76.6 |
| -- |  | -- |  | -- |  | 70 | 30.7 | -- | -- | -- | -- | -- | -- | 240 | 79.3 |
| -- |  | -- |  | -- |  | 90 | 39.7 | -- | -- | -- | -- | -- | -- | 300 | 80.0 |

