ELECTRONIC SUPPLEMENTARY INFORMATION

Sequential crystallization and morphology of triple crystalline biodegradable PEO-*b*-PCL-*b*-PLLA triblock terpolymers

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S1. Differential scanning calorimetry (DSC)

Several tests, at different cooling rates, were carried out to establish the ideal rate to achieve the crystallization of the blocks.

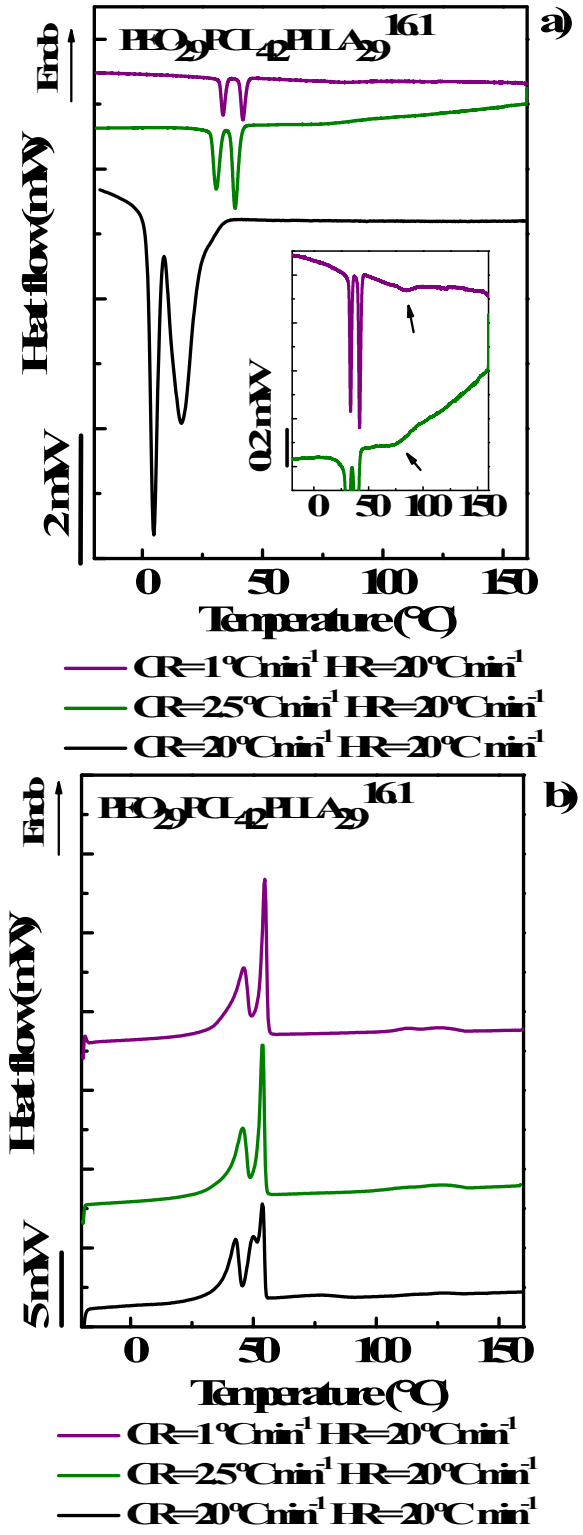

Figure SI.1. a) DSC cooling scans at several cooling rates (CR) after melting at 160 ºC for 3 min and b) Subsequent DSC heating scans at 20 ºC min^{-1} for $PEO_{29}PCL_{42}PLLA_{29}^{16.1}$.

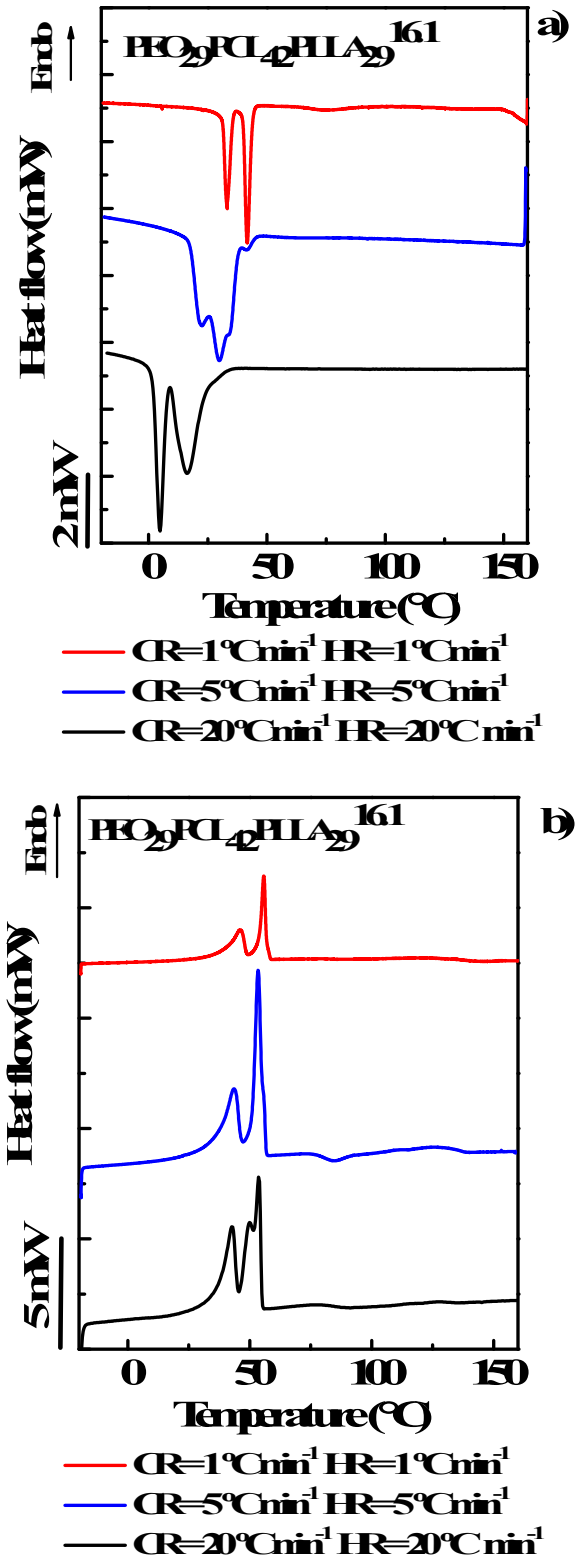

Figure SI.2. a) DSC cooling scans at several cooling rates (CR) after melting at 160 ºC for 3 min and b) Subsequent DSC heating scans at several heating rates (HR) for $PEO_{29}PCL_{42}PLLA_{29}^{16.1}$.

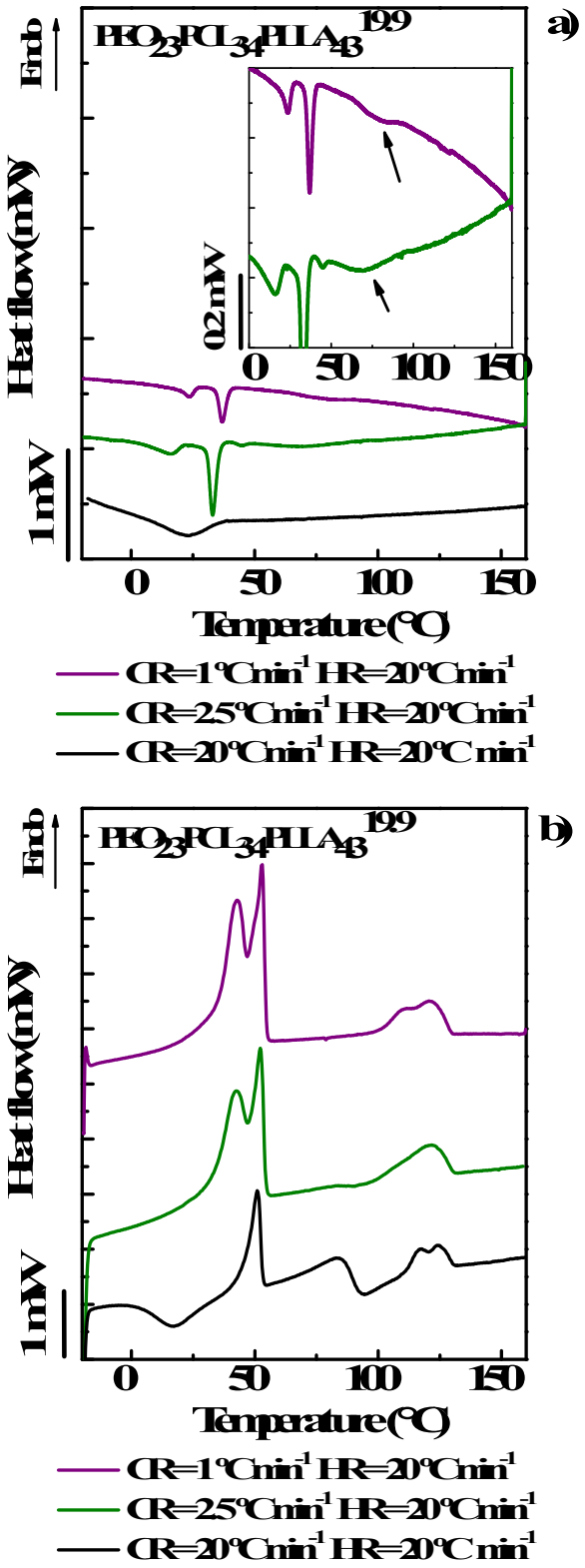

Figure SI.3. a) DSC cooling scans at several cooling rates (CR) after melting at 160 ºC for 3 min and b) Subsequent DSC heating scans at 20 ºC min^{-1} for $PEO_{23}PCL_{34}PLLA_{43}^{19.9}$.

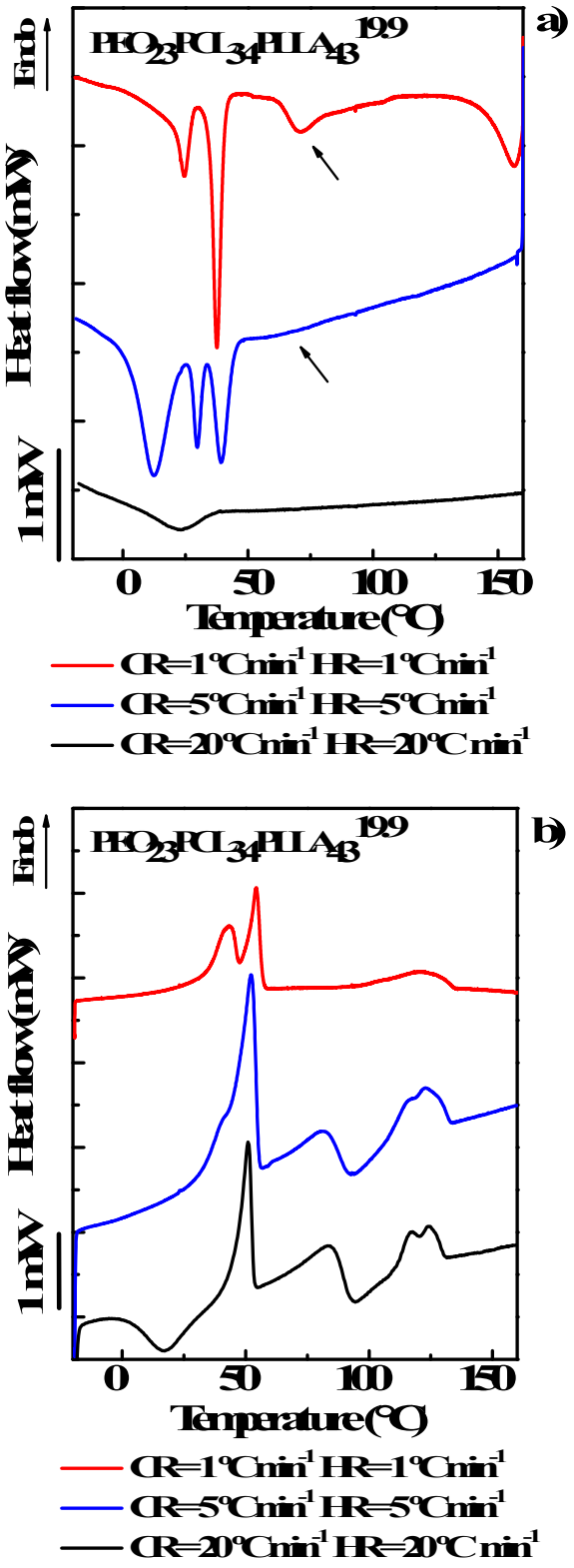

Figure SI.4. a) DSC cooling scans at several cooling rates (CR) after melting at 160 ºC for 3 min and b) Subsequent DSC heating scans at several heating rates (HR) for $PEO_{23}PCL_{34}PLLA_{43}^{19.9}$.

S2. DSC Thermal properties of the triblock terpolymers studied here and some diblock and triblock copolymers reported in the literature.

In Table S.1 are included the DSC thermal properties of the triblock terplymers and compared to relevant block copolymers previously reported.

Table S.1. Crystallization and melting temperatures of $PEO_{29}PCL_{42}PLLA_{29}^{16.1}$and $PEO_{23}PCL_{34}PLLA_{43}^{19.9}$ triblocks terpolymers compared to different linear diblock copolymers reported in the literature

Sample code	PLLA			PCL			PEO			Ref.
	Block M_w (kg mol^{-1})	T_c (ºC)	T_m (ºC)	Block M_w (kg mol^{-1})	T_c (ºC)	T_m (ºC)	Block M_w (kg mol^{-1})	T_c (ºC)	T_m (ºC)	
$PEO_{29}PCL_{42}PLLA_{29}^{16.1}$	**4.7**	**75.0**	**124.5**	**6.8**	**41.7**	**56.9**	**4.6**	**33.5**	**48.0**	**Samples**
$PEO_{23}PCL_{34}PLLA_{43}^{19.9}$	**8.5**	**72.3**	**121.8**	**6.8**	**36.7**	**54.2**	**4.6**	**22.1**	**45.0**	**reported here**
$L_{93}C_7^{18}$	15.7	102.6	171.7	1.7						
$L_{81}C_{19}^{21}$	16.7	102.8	170.5	3.9						
$L_{60}C_{40}^{21}$	12.4	102.8	168.9	8.5	0.5-11.3	54.4				Castillo, 2010[2]
$L_{55}C_{45}^{18}$	**9.5**	**98.3**	**166.9**	**8.1**	**20.8**	**55.0**				
$L_{44}C_{56}^{25}$	**11.1**	**91.8**	**166.5**	**14.2**	**23.2**	**56.5**				
$L_{32}C_{68}^{22}$	6.9	100.3	161.0	14.9	28.1	56.9				
$L_{10}C_{90}^{24}$	2.4	86.8	141.5	21.5	32.5	57.7				
PLLA2300*b*PEG5000	**2.3**	**93.0**	**140.1**				**5.0**	**34.1**	**54.7**	
PLLA6300*b*PEG5000	**6.3**	**105.2**	**153.8**				**5.0**	**34.6**	**42.2**	Sun, 2004[1]
PLLA12000*b*PEG5000	12.0	116.3	162.4				5.0	12.9	37.2	
PEO_5-*b*-$PLLA_{16}$	16.0	90.6	141.2				5.0		41.2	Huang,2008[3]
PEO_5-*b*-$PLLA_{30}$	30.0	100.0	142.1				5.0		39.7	
2LPCL_{50}-*b*-$PLLA_{43}$	12.45	102.4	151.7	11.33	12.6	51.2				Wang,2006[5]
PEOCL56				**6.24**	**30.4**	**55.4**	**5.0**	**30.4**	**55.4**	He, 2006[6]
PEOCL62				8.13	34.3	56.3	5.0	28.7	56.3	
PEG5000-PCL1000				1.0			5.0	34.7	59.8	
PEG5000-PCL2900				2.9			5.0	30.0	51.0/54.9	Sun, 2011[7]
PEG5000-PCL9200				9.2	34.6	56.7	5.0	29.3	44.6	
PCL_{13}-PEG_{45}-PCL_{13}				**3.0**	**16.5**	**51.7**	**2.0**	**12.2**	**41.2**	Wei, 2009[8]

References of supporting information

(1) Sun, J.; Hong, Z.; Yang, L.; Tang, Z.; Chen, X.; Jing, X. *Polymer* **2004,** *45*, 5969-5977.

(2) Castillo, R. V.; Müller, A. J.; Raquez, J. M.; Dubois, P. *Macromolecules* **2010,** *43*, 4149-4160.

(3) Huang, S.; Jiang, S.; An, L.; Chen, X. *J. Polym. Sci., Part B: Polym. Phys.* **2008,** *46*, 1400-1411.

(4) Muller, A. J.; Avila, M.; Saenz, G.; Salazar, J. In *Poly(Lactic Acid) Science and Technology: Processing, Properties, Additives and Applications*, Jimenez, A.,Peltzer, M.,Ruseckaite, R., Eds.; The Royal Society of Chemistry: Cambridge, 2015; Chapter 3, p 66.

(5) Wang, J. L.; Dong, C. M. *Macromol. Chem. Phys.* **2006,** *207*, 554-562.

(6) He, C.; Sun, J.; Ma, J.; Chen, X.; Jing, X. *Biomacromolecules* **2006,** *7*, 3482-3489.

(7) Sun, J.; He, C.; Zhuang, X.; Jing, X.; Chen, X. *J. Polym. Res.* **2011,** *18*, 2161-2168.

(8) Wei, Z.; Liu, L.; Yu, F.; Wang, P.; Qi, M. *J. Appl. Polym. Sci.* **2009,** *111*, 429-436."

S3. Polarized light optical microscopy (PLOM). Photographs videos

PLOM was performed on cooling from the melt in order to observe the sequential crystallization and superstructure formation of each block. Small videos made of PLOM photograps for each triblock terpolymer are presented.

TriblockTerpolymer 16.1.ppsx

TribloqueTerpolymer 16.1.ppsx

TriblockTerpolymer 19.9.ppsx

TriblockTerpolymer 19.9.ppsx