

*Supporting Information*

# Controlling the Isothermal Crystallization of Isodimorphic PBS-*ran*-PCL Random Copolymers by Varying Composition and Supercooling

by Maryam Safari<sup>1</sup>, Agurtzane Mugica<sup>1</sup>, Manuela Zubitur<sup>2</sup>, Antxon Martínez de Ilarduya<sup>3</sup>, Sebastián Muñoz-Guerra<sup>3</sup>, Alejandro J. Müller \*<sup>1,4</sup>

<sup>1</sup> POLYMAT and Polymer Science and Technology Department, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel de Lardizabal 3, Donostia-San Sebastián, 20018, Spain.

<sup>2</sup> Chemical and Environmental Engineering Department, Polytechnic School, University of the Basque Country UPV/EHU, Plaza Europa 1, Donostia-San Sebastián, 20018, Spain.

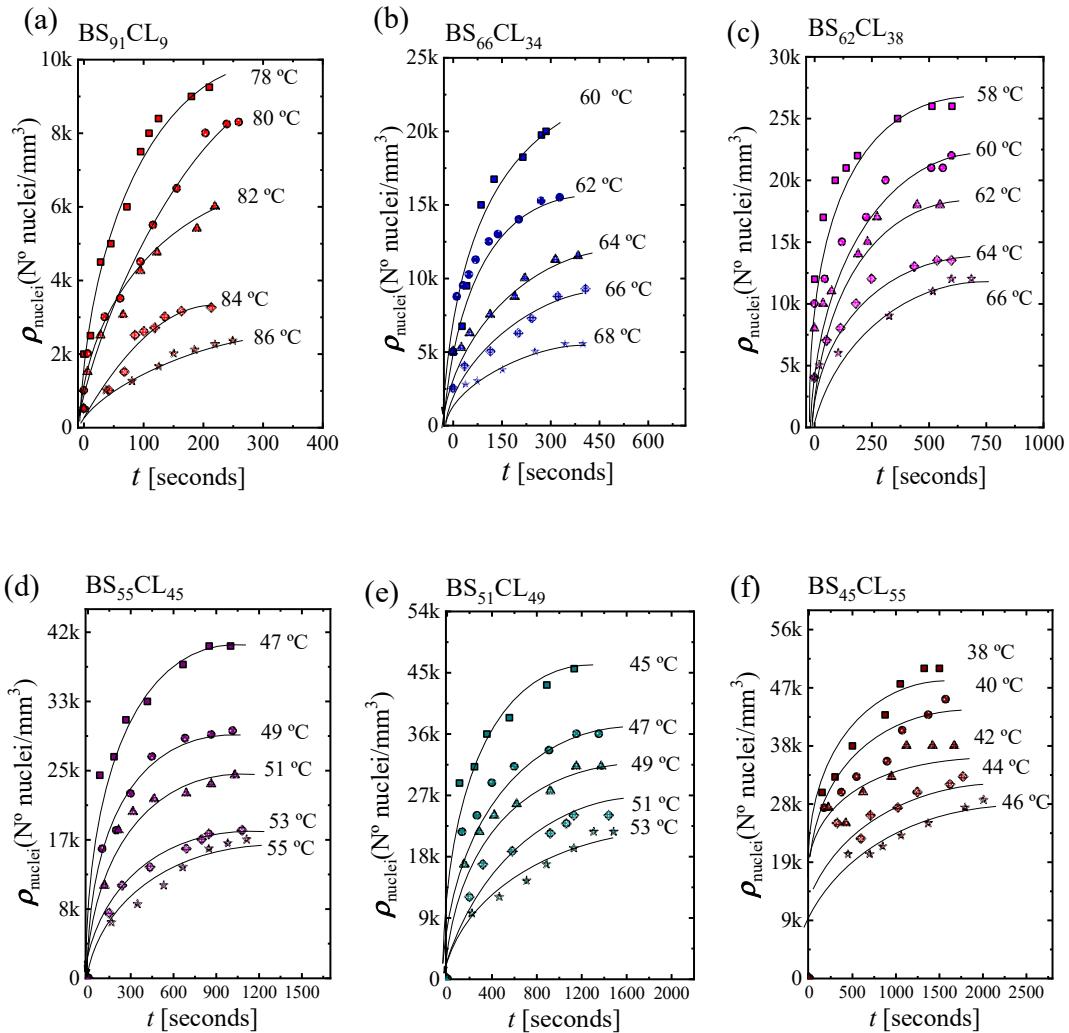
<sup>3</sup> Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, ETSEIB, Diagonal 647, Barcelona, 08028, Spain.

<sup>4</sup> IKERBASQUE, Basque Foundation for Science, María Díaz Haroko Kalea, 3, Bilbao, 48013, Spain.

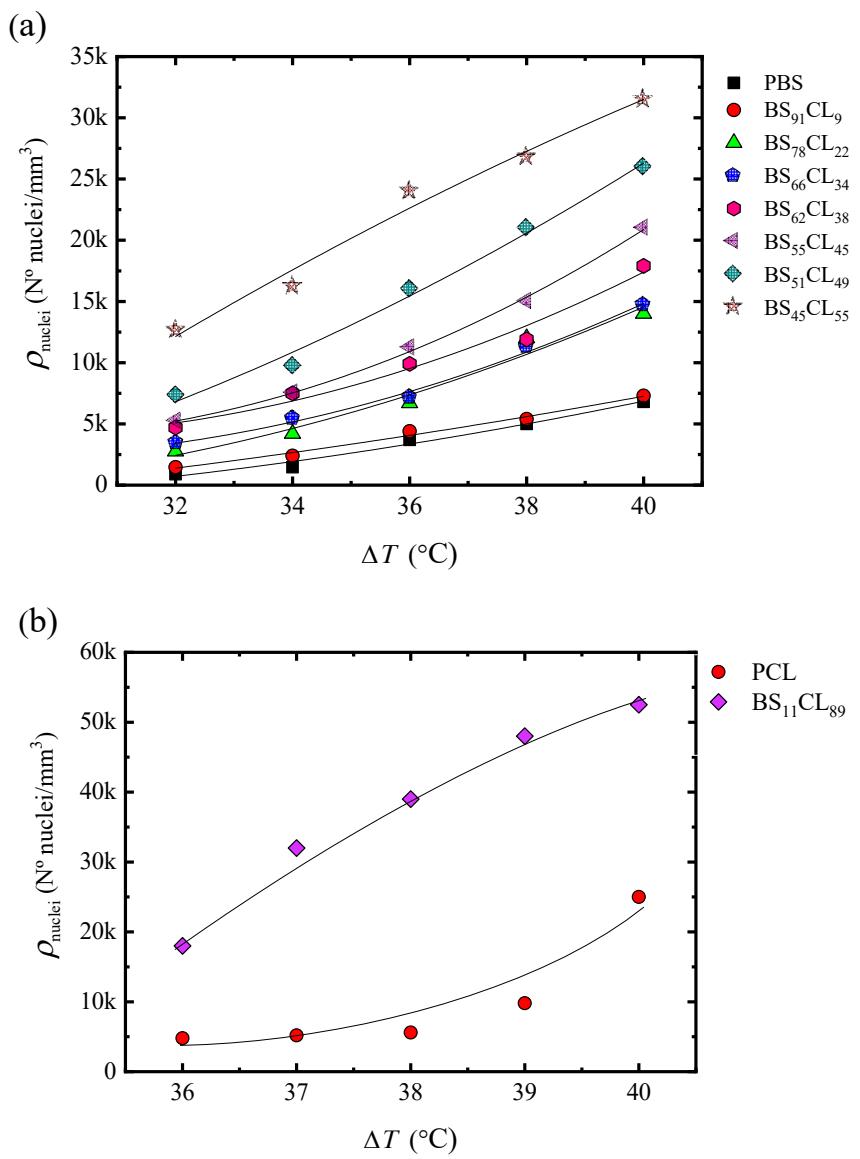
\* Correspondence: alejandrojesus.muller@ehu.es; Tel.: +34 943018191

**Table SI-1.** Equilibrium melting temperatures for CoP(BS<sub>x</sub>CL<sub>y</sub>) compositions and their corresponding homopolymers.

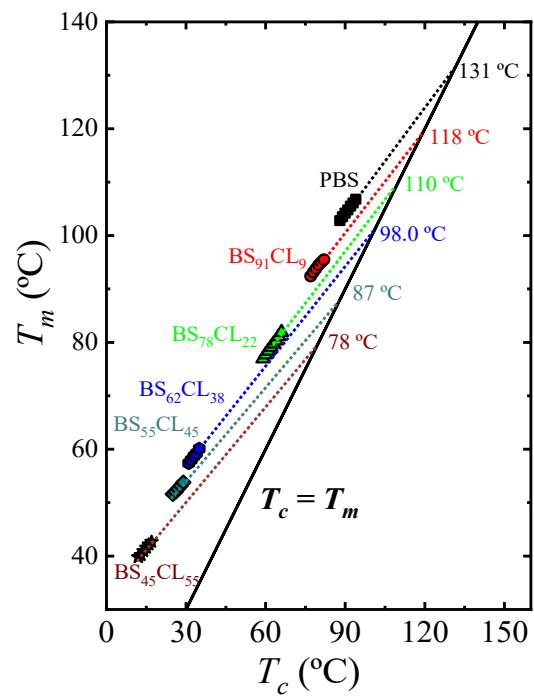
Copolyester	T <sub>m</sub> <sup>θ</sup> (°C)
<b>PBS</b>	131
<b>BS<sub>91</sub>CL<sub>9</sub></b>	118
<b>BS<sub>78</sub>CL<sub>22</sub></b>	110
<b>BS<sub>66</sub>CL<sub>34</sub></b>	100
<b>BS<sub>62</sub>CL<sub>38</sub></b>	98
<b>BS<sub>55</sub>CL<sub>45</sub></b>	87
<b>BS<sub>51</sub>CL<sub>49</sub></b>	85
<b>BS<sub>45</sub>CL<sub>55</sub>(BS-rich)</b>	78
<b>BS<sub>45</sub>CL<sub>55</sub>(CL-rich)</b>	35
<b>BS<sub>38</sub>CL<sub>62</sub></b>	38
<b>BS<sub>34</sub>CL<sub>66</sub></b>	42
<b>BS<sub>27</sub>CL<sub>73</sub></b>	47
<b>BS<sub>11</sub>CL<sub>89</sub></b>	63
<b>PCL</b>	88



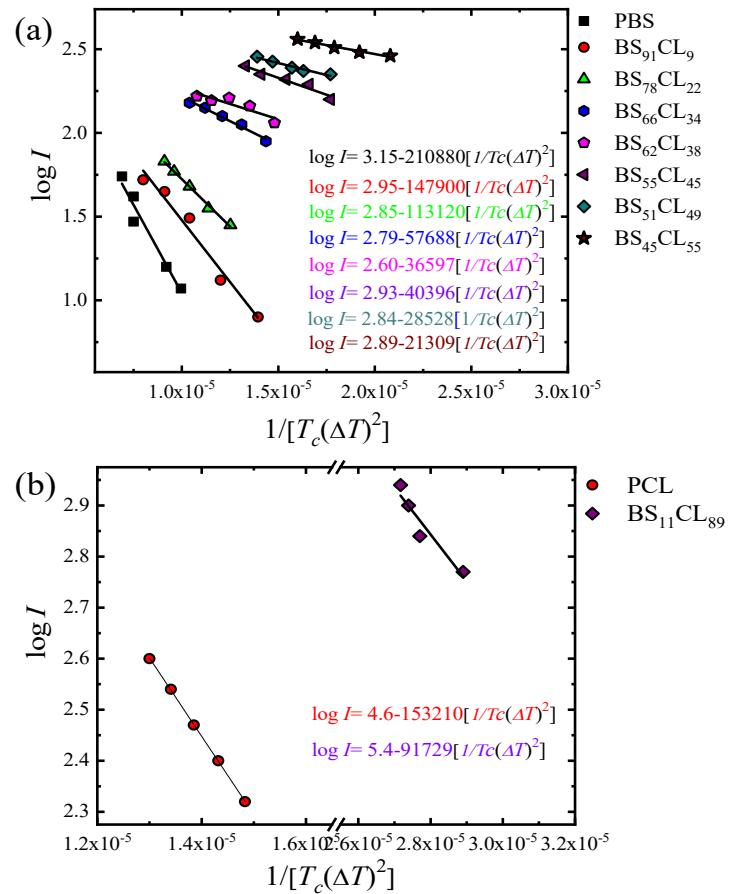
**Figure SI-1.** Nucleation kinetics studies by PLOM. Nuclei density as a function of time at different crystallization temperature for PBS-rich phase samples: (a) BS<sub>91</sub>CL<sub>9</sub>, (b) BS<sub>66</sub>CL<sub>34</sub>, (c) BS<sub>62</sub>CL<sub>38</sub>, (d) BS<sub>55</sub>CL<sub>45</sub>, (e) BS<sub>51</sub>CL<sub>49</sub>, and (f) BS<sub>45</sub>CL<sub>55</sub>.  $T_c$  employed are chosen so that  $\Delta T = 40, 38, 36, 34, 32 for all samples.$



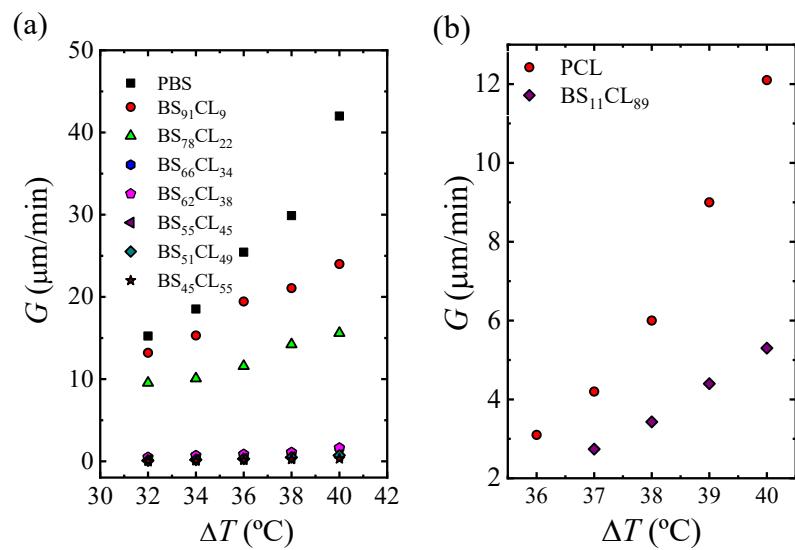
**Figure SI-2.** Nuclei density during isothermal crystallization as a function of  $\Delta T$  for PBS-rich (a) and for PCL-rich (b) copolymers.



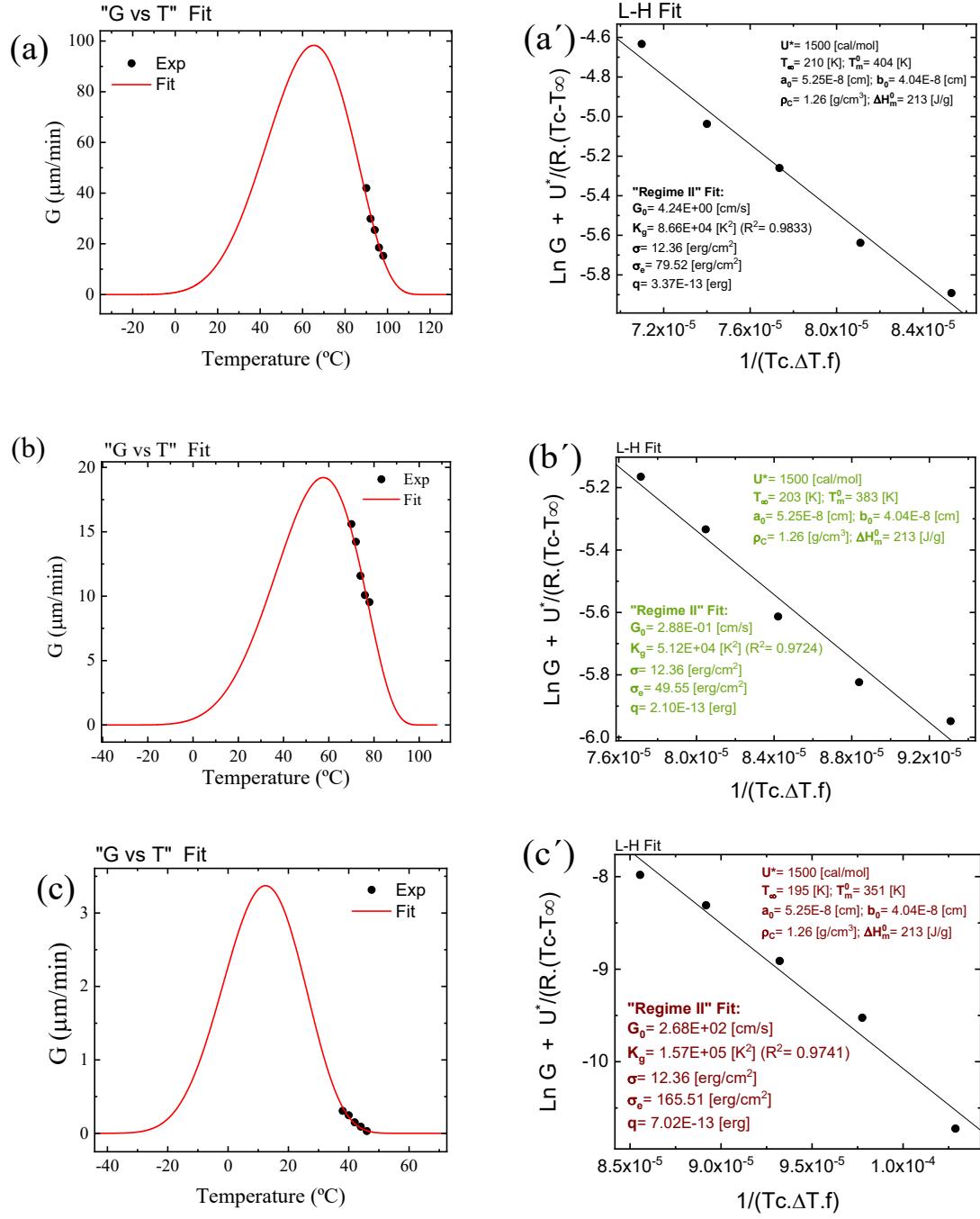
**Figure SI-3.** Hoffman-Weeks plots for PBS-*ran*-PCL compositions. The black solid line represents the thermodynamic equilibrium line  $T_m=T_c$ .



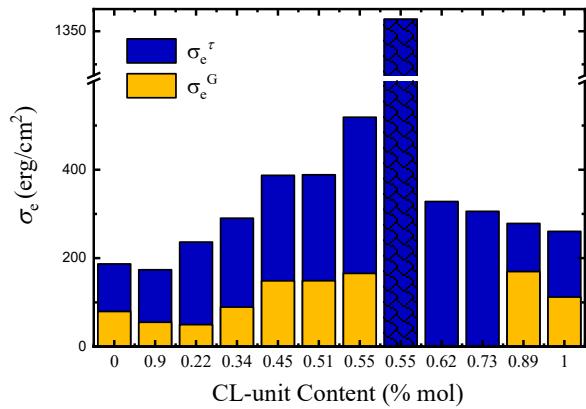
**Figure SI-4.** Plot of  $\log I$  versus  $1/T(\Delta T)^2$  and fitting to Turnbull–Fisher equation (Eq. 1) for PBS-rich (a) and PCL-rich (b) compositions.



**Figures SI-5.** Spherulitic growth rates  $G$  determined by PLOM for neat PBS and PBS-rich (a) and for neat PCL and PCL-rich (b) copolymers as a function of supercooling.



**Figure SI-6.** The fits to the Lauritzen-Hoffman equation using the free Origin plug-in developed by Lorenzo et al. [1] and the experimental data for the (a-a') PBS, (b-b') BS<sub>78</sub>CL<sub>22</sub>, and (c-c') BS<sub>45</sub>CL<sub>55</sub>.



**Figure SI-7.** The  $\sigma_e$  value versus CL-unit molar fraction that obtained for PLOM experiments ( $\sigma_e^G$ ) and DSC experiments ( $\sigma_e^\tau$ ).

## References

1. Lorenzo, A. T.; Arnal, M. L.; Albuerne, J.; Müller, A. J., DSC isothermal polymer crystallization kinetics measurements and the use of the Avrami equation to fit the data: Guidelines to avoid common problems. *Polymer testing* 2007, 26 (2), 222-231.