

# **How composition determines the properties of isodimorphic poly(butylene succinate-*ran*-butylene azelate) random biobased copolymers: from single to double crystalline random copolymers**

*Idoia Arandia<sup>1</sup>, Agurtzane Mugica<sup>1</sup>, Manuela Zubitur<sup>2</sup>, Arantxa Arbe<sup>3</sup>,  
Guoming Liu<sup>4</sup>, Dujin Wang<sup>4</sup>, Rosica Mincheva<sup>5</sup>, Philippe Dubois<sup>5</sup>,  
Alejandro J. Müller<sup>1,6\*</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, 20018 Donostia-San Sebastián, Spain

<sup>2</sup>Chemical and Environmental Engineering Department, Polytechnic School, University of the Basque Country (UPV/EHU), 2008 Donostia-San Sebastián, Spain

<sup>3</sup>Materials Physics Center (CSIC-UPV/EHU), Paseo Manuel de Lardizabal 5, 20018 Donostia-San Sebastián, Spain

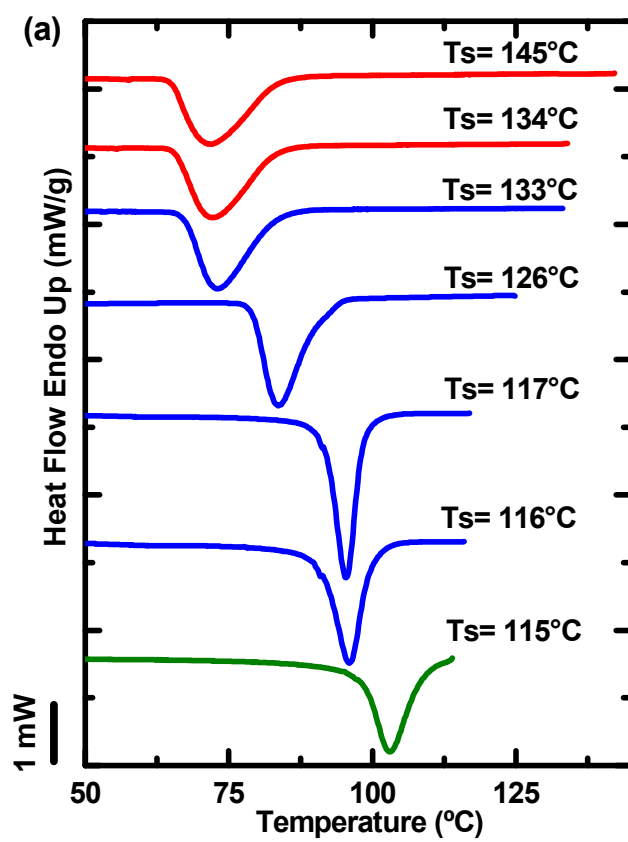
<sup>4</sup>Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China

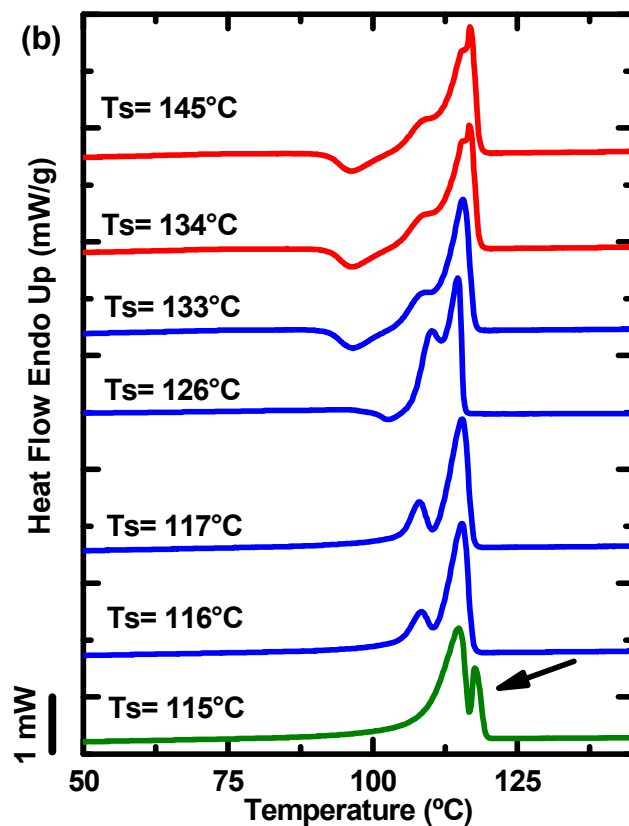
<sup>5</sup>Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons (UMONS), Place du Parc 20, 7000, Mons, Belgium

<sup>6</sup>IKERBASQUE, Basque Foundation for Science, Bilbao, Spain.

\*Corresponding author

## Supporting Information





**Figure S1.** Self-nucleation of PBS homopolymer: (a) DSC cooling scans from the indicated self-nucleation ( $T_s$ ) temperatures and (b) subsequent heating scans at  $10^\circ\text{C}/\text{min}$ .

Figure S1a shows cooling scans from selected  $T_s$  temperatures. At temperatures of  $134^\circ\text{C}$  and above, crystalline memory is completely erased and only high temperature resistant heterogeneities capable of nucleating the polymer during cooling remain. As a consequence, the peak crystallization temperature is constant in Figure S1 for these  $T_s$  temperatures and the melting traces are invariant upon subsequent heating, as seen in

Figure S1b. The described behavior occurs for  $T_s$  values equal or larger than 134°C, when the sample is within the complete melting domain (*Domain I*).

When  $T_s$  temperatures lower than 134°C (but higher than or equal to 116°C) are employed, PBS experiences only self-nucleation, and its crystallization temperature increases (Figure S1a). The corresponding maximum peak melting point in Figure S1b does not show signs of annealing. Therefore, the sample falls under the exclusive self-nucleation domain (*Domain II*). For higher  $T_s$  values within *Domain II*, like 133°C, the melting process of the sample upon subsequent heating (after the cooling from  $T_s$  shown in Figure S1a) does not change significantly, since cold crystallization is still observed in Figure S1b. However, at further decrease in  $T_s$  values within *Domain II*, cold crystallization disappears from the heating DSC trace and the double melting process is more pronounced (see for example the DSC traces corresponding to  $T_s=117$  or 116°C in Figure S1b). This is a consequence of an increase in the crystallization enthalpy produced during cooling from these lower  $T_s$  values as a result of the self-nucleation effect (compare the crystallization exotherms in Figure S1a for the samples cooled from  $T_s$  values 133°C and 117°C for example).

Finally when the  $T_s$  temperature is lower or equal to 115°C, partial melting occurs and the unmelted crystals experience annealing during the 5 min holding time at  $T_s$ , the sample is then in the self-nucleating and annealing domain (*Domain III*). This is easily distinguished by the appearance of a high temperature additional melting peak, signaled with an arrow in Figure S1b.