

4-Miktoarm Star Architecture Induces PVDF β -phase formation in (PVDF)₂-b-(PEO)₂ Miktoarm Star Copolymers

Nicolás María[†], Jon Maiz^{†,‡,||*}, Valentin Rodionov[‡], Nikos Hadjichristidis[#], Alejandro J. Müller^{†,||*}

[†]POLYMAT and Polymer Science and Technology Department, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel Lardizábal 3, 20018, Donostia-San Sebastián, Spain

[‡]Centro de Física de Materiales (CFM) (CSIC–UPV/EHU) – Materials Physics Center (MPC), Paseo Manuel de Lardizabal 5, 20018 San Sebastián, Spain

^{||}IKERBASQUE - Basque Foundation for Science, María Díaz de Haro 3, 48013 Bilbao, Spain

[‡]Department of Macromolecular Science and Engineering Case Western Reserve University, 2100 Adelbert Rd, Cleveland, OH 44106, USA

[#]Polymer Synthesis Laboratory, KAUST Catalysis Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia.

***Corresponding authors:** jon.maizs@ehu.eus; alejandrojesus.muller@ehu.es

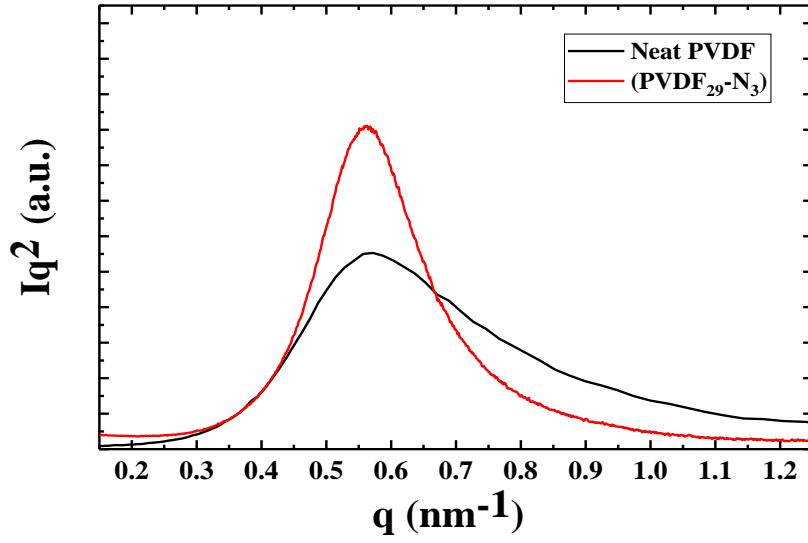


Figure S1. Lorentz-corrected SAXS patterns for neat PVDF and (PVDF₂₉-N₃)₂ sample.

The average lamellar thickness (l_c) can be estimated by SAXS, as follows:

$$l_c = d^* x_v \quad (\text{SI1})$$

In Eq. (SI1), x_v is the crystalline volume fraction, which can be calculated using the relevant densities. In our case, the densities are not available, so we made a rough approximation and employed the weight fraction directly (*i.e.*, X_c), obtained by DSC (see Table S1) according to:

$$l_c = d^* X_c \quad (\text{SI2})$$

The final values obtained for l_c from the SAXS patterns by Eq. (SI2) are listed in Table S1 for the neat PVDF and (PVDF₂₉-N₃)₂ sample.

Table S1: Comparison between DSC parameters related to the enthalpy (ΔH_m), crystallinity (X_c), and the SAXS parameters related to the long period (d^*) values and average lamellar thicknesses (l) obtained for the studied PVDF samples.

| | DSC | | SAXS | |
|--|--------------------|-----------|------------|----------|
| | ΔH_m (J/g) | X_c (%) | d^* (nm) | l (nm) |
| Neat PVDF | 42.5 | 39.9 | 11.2 | 4.5 |
| (PVDF ₂₉ -N ₃) ₂ | 56.8 | 53.3 | 11.2 | 6.0 |

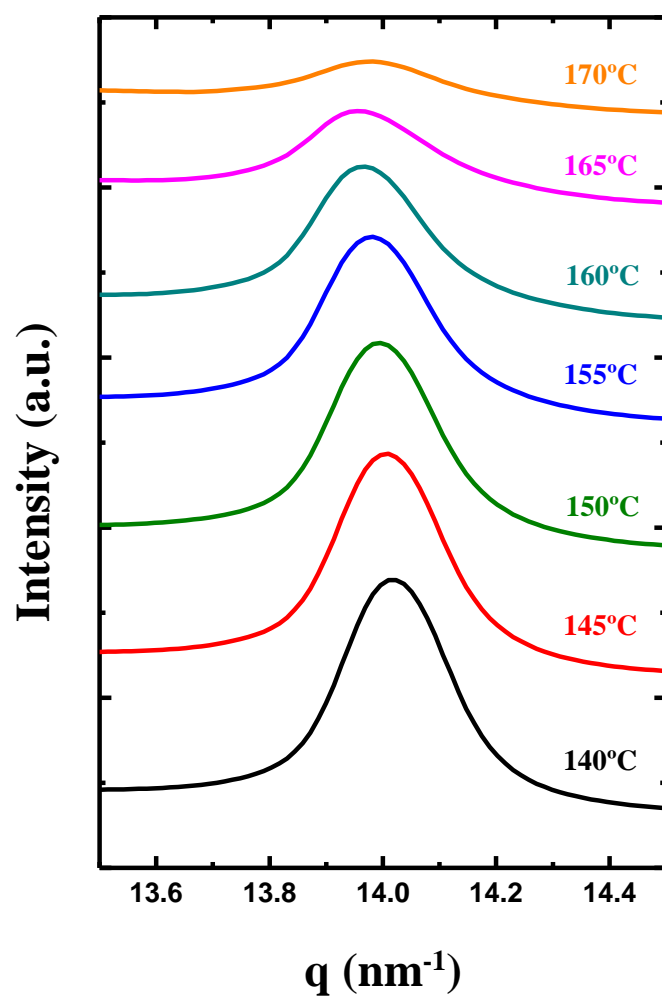


Figure S2. Evolution of the peak at 14.1 nm^{-1} , between 140-170°C, during the heating in WAXS diffraction of the (PVDF₂₉-N₃)₂ when the crystallization rate is 20°C/min.

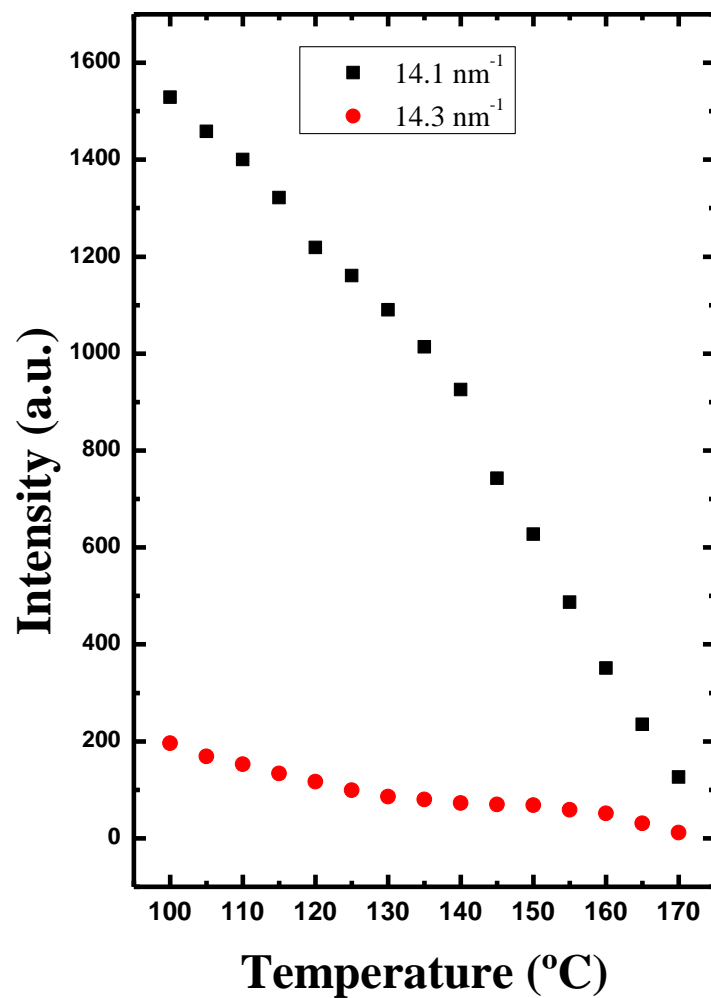


Figure S3. Evolution of the intensity of the peak at 14.1 nm^{-1} and the tail of this peak at 14.3 nm^{-1} during the heating in the WAXS analysis of the $(\text{PVDF}_{29}\text{-N}_3)_2$ when the sample is cooled down at $20^\circ\text{C}/\text{min}$.