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Supporting information for article:

Self-assembly of block copolymers under non-isothermal annealing conditions as revealed by grazing-incidence small-angle X-ray scattering

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S1. Evaluation of beam damage on Block copolymer samples

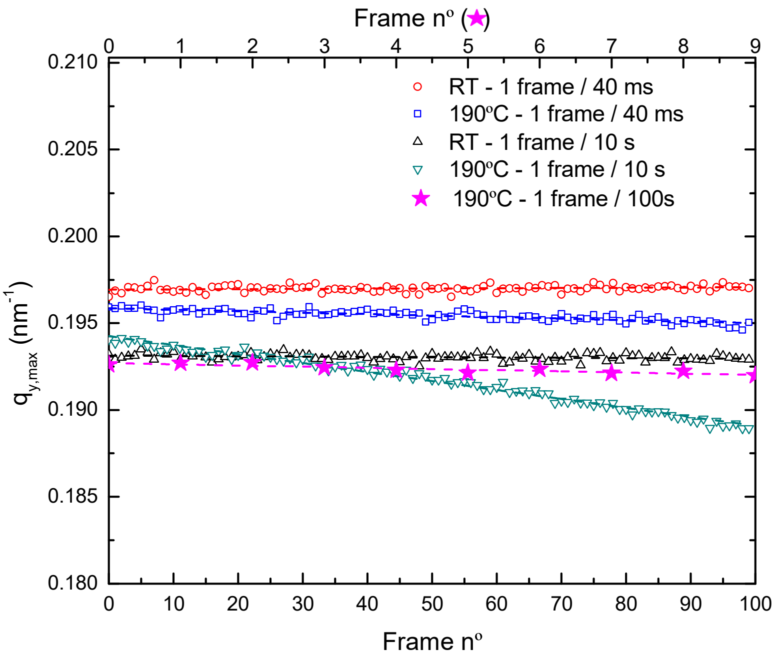

Figure S1 Effect of the GISAXS beam on the block copolymer sample at room temperature (RT) and at 190ºC. Evolution of Yoneda main peak position ($q_{y,\, max}$) at five different acquisition conditions. In the first fourth samples, 100 frames were taken using first 40 ms of exposure time (blue and red circles) and using 10s of exposure time (black and green triangles).As expected longer acquisition times and higher temperature caused more damage on the sample. In the last experiment, the sample was heated at 190ºC and 10 frames with an acquisition time and period of 1s and 100s were taken. The annealing time and temperature of this sample is similar than previous sample but the observed beam damage was minimal.

S2. Evolution of GISAXS patterns during isothermal annealing at different temperatures

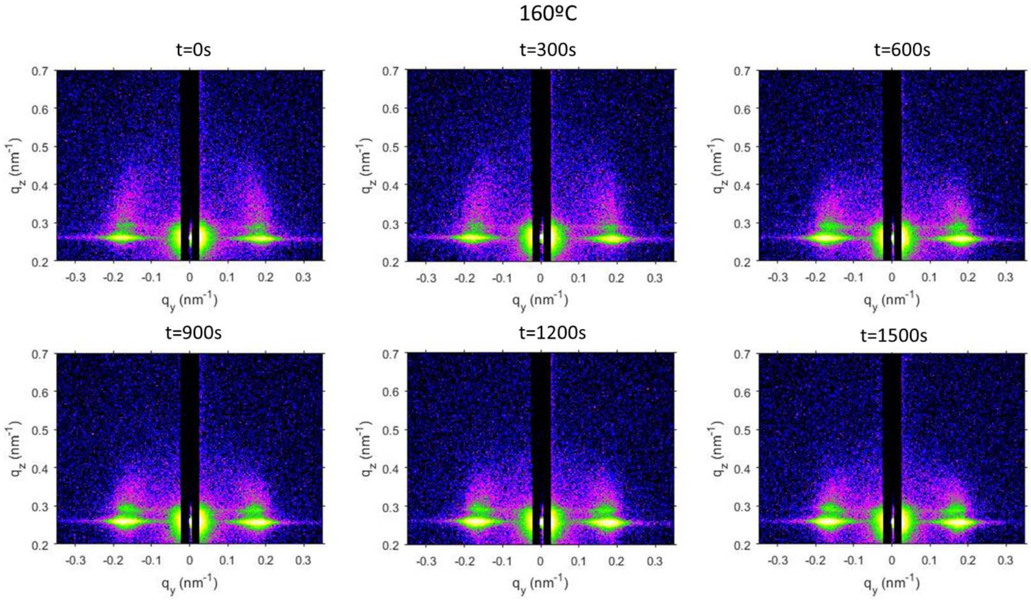

Figure S2 Selection of GISAXS patterns at different processing times during the thermal annealing at 160 ºC. After reaching 160 ºC (t = 0 s) with a ramp rate of 50 ºC/min, GISAXS patterns were collected with a frame rate of 1 frame of 0.037 s every 300s.

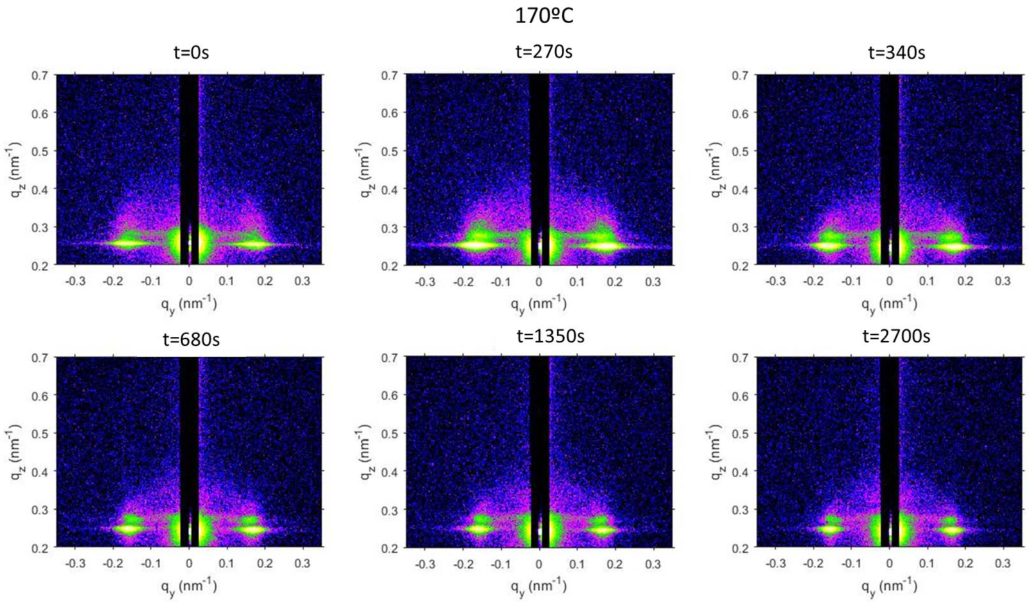

Figure S3 Selection of GISAXS patterns at different processing times during the thermal annealing at 170 ºC. After reaching 170 ºC (t = 0 s) with a ramp rate of 50 ºC/min, GISAXS patterns were collected with a frame rate of 1 frame of 0.037s every 135s.

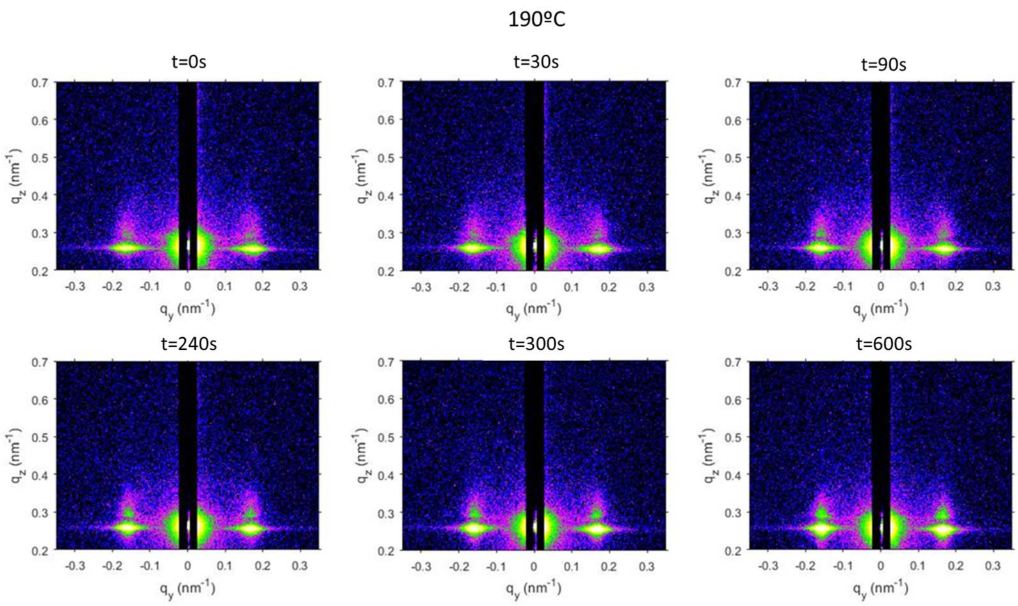

Figure S4 Selection of GISAXS patterns at different processing times during the thermal annealing at 190 ºC. After reaching 190 ºC (t = 0 s) with a ramp rate of 50 ºC/min, GISAXS patterns were collected with a frame rate of 1 frame of 0.037 s every 30s.

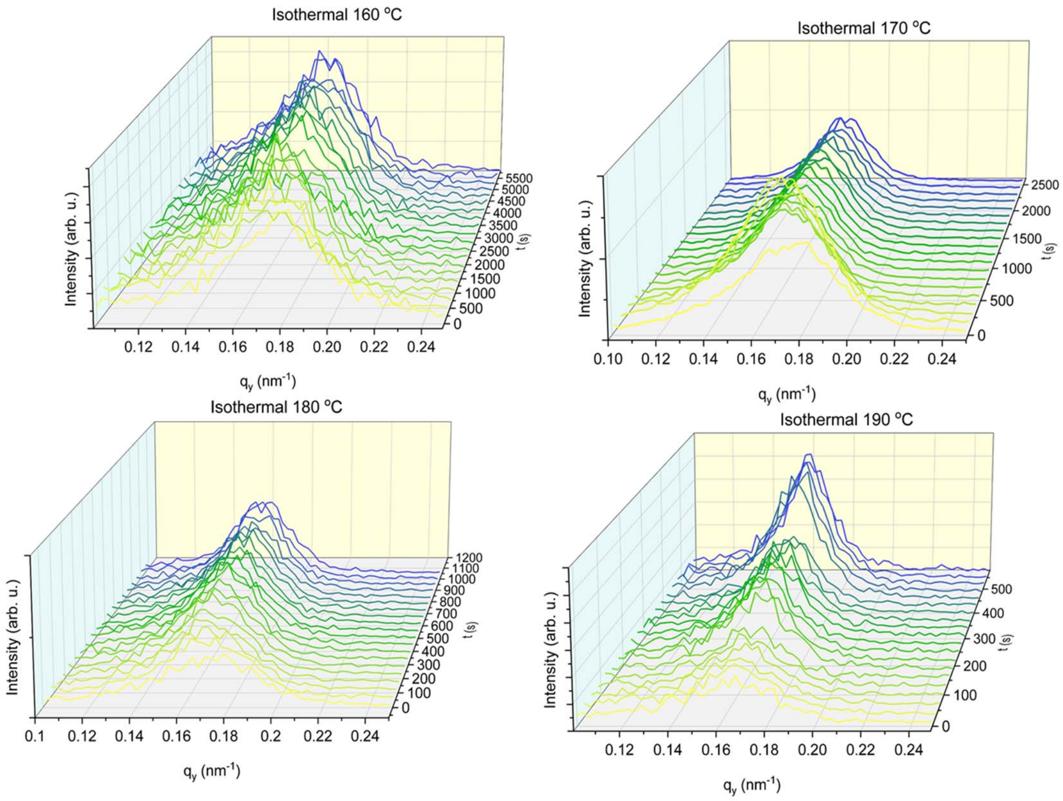

Figure S5 Detailed view of evolution with annealing time of the horizontal line cut at the first order scattering peak at Yoneda position. The profiles are extracted from the colour maps in Figure 4 (main text). The increase of the peak intensity and a reduction of the peak broadness during the thermal annealing arise from an increase of the long range order of the block copolymer pattern.

S3. Block copolymer evolution at low temperatures

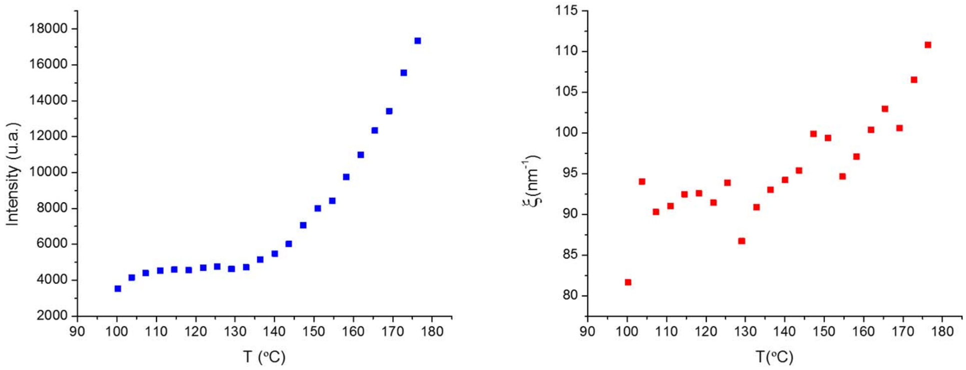

Figure S6 Intensity and correlation length of the first order peak at Yoneda band plotted as a function of the temperature. The experimental values were taken from GISAXS patterns during a heating ramp at 5ºC/min. At low temperatures, up to 145ºC, there is not evolution on the block copolymer film, both intensity and correlation length remain constant. The initial order at lower temperatures is attributed to solvent evaporation during the spin-coating and at the beginning of the annealing process.

S4. Power exponent calculated using classical approach vs new model

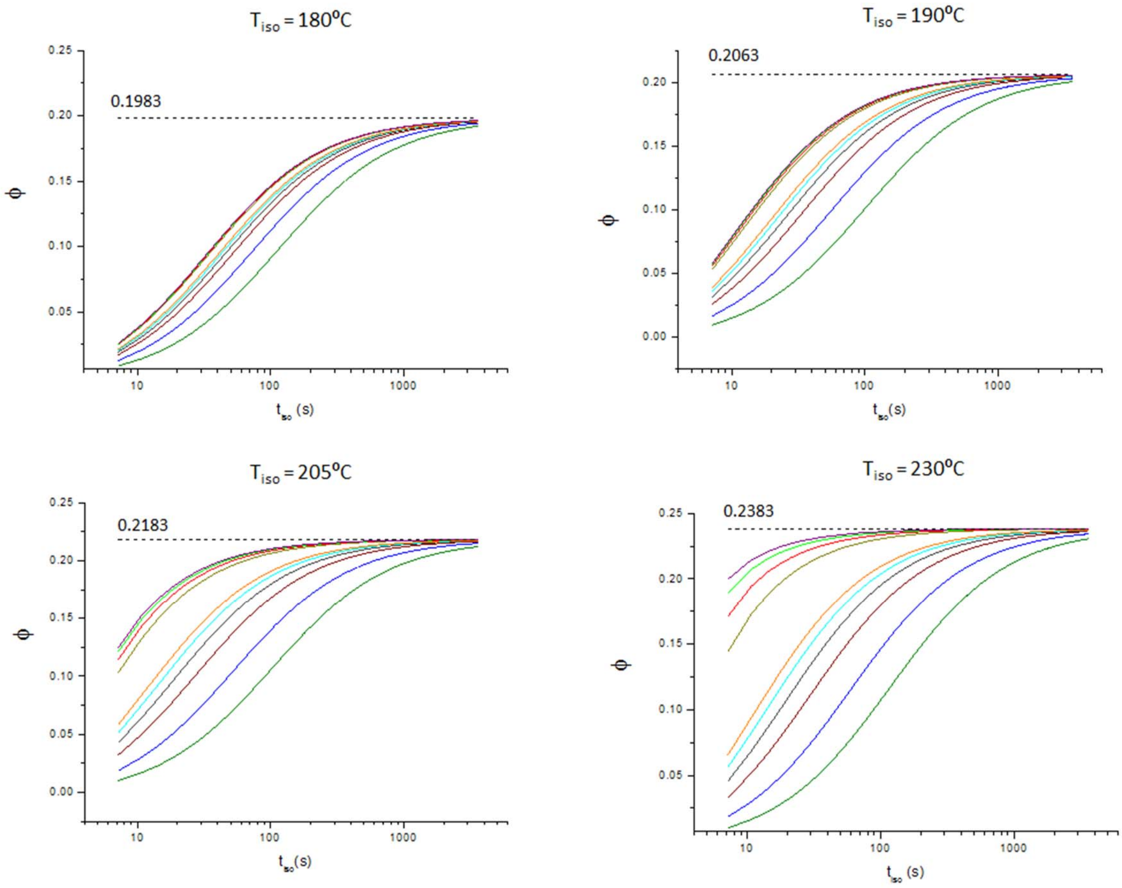

Figure S7 Power exponent, ϕ, at different temperatures calculated from simulated curves using the classical approach, $\xi = A_T t^{\phi}$, from the slop of the curve $\log \xi$ vs $\log t$. The value of the power exponent calculated taking into account the equivalent time, $\xi = A_T (t + t_{eq})^{\phi}$, is represented by a dashed line on each graph. Before isothermal annealing, the samples are annealed from 150ºC to the target temperature, T_{iso}, using a heating ramp of 1ºC/s and a starting correlation length of 90nm. This demonstrate that only at long annealing times, the classical approach can be used for the calculation of the power exponent.