«Supporting Information»

Quantitative Structural Study of cold crystallized PEKK

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Details on the calculation of Φ_I from the WAXS spectra

Schematics of the two crystal cells are reported in Figure S1.



Figure S1 Schematic of the Form I and II crystal cells (inspired from ref [1]) with visualization of the main inter-planar distances.

To obtain a reliable calculation of Φ_I from the WAXS spectra, the existence of all the calculated diffraction lines reported in the Table 1 was taken into account. Thanks to the WAXS experiments on pure form I and form II samples (Figure 2-d and b respectively) and to indications on intensity ratios from the literature [1] [2] some constraints on parameters were imposed during the Fityk [3] refinement. For example, in form II, the width of line (110) is always broader than that of the line (020). The intensity ratio I_{020}/I_{110} is around 0.5-0.7 for form II, and the ratio I_{200}/I_{110} is around 1 for form I. With these constraints, reliable fittings of WAXS experimental spectra, that respect the relative intensities and width of Bragg peaks usually observed for pure forms I and II, were obtained.

The amorphous contribution is modeled with the superposition of three broad peaks (Figure 2-c). This model calculated from the amorphous film is adjusted for the semi-crystalline samples. For the semi-crystalline samples, small deviations from the initial model are allowed in order to improve the global refinement of the spectra. These deviations are considered to be valid because the amorphous phase constrained between crystalline lamellae is not necessarily the same as the amorphous phase free from crystalline constraints.

Corrections of WAXS spectra and calculation of the normalized intensity in absolute units

To apply the absolute method, WAXS spectra intensity, $I_{Raw}(s)$, was first corrected from absorption (f_{abs}), polarization (f_{pol}) and Lorentz factor ($f_{Lorentz}$) using XSACT software [4]. These three contributions lead to a corrected factor f_{corr} . [4]

$$I_{corr} = I_{Raw} / f_{corr}$$
 with $f_{corr} = f_{abs} \times f_{pol} \times f_{Lorentz}$

$$f_{abs} = \frac{\ln T_r \times \left(\frac{1}{\cos 2\theta} - 1\right)}{e^{\ln T_r \times \left(\frac{1}{\cos 2\theta} - 1\right)} - 1}$$

with T_r , the sample transmission: $T_r = e^{-\mu L}$, μ : the linear absorption coefficient, and L: the thickness of the sample.

$$f_{pol} = 0.5 \times (1 + \cos^2 2\theta)$$
$$f_{Lorentz} = \frac{1}{4\cos\theta\sin^2\theta}$$

These corrections are implemented in the XSACT software [4], which are applied to the experimental spectra $I_{Raw}(s)$ or $I_{Raw}(2\theta)$. I_{corr} is thus obtained.

 I_{corr} is normalized using the fact that the scattered intensity integrated in all the reciprocal space is a constant. Using the formalism described by Vonk, $T(s_p)$ can be calculated [5].

$$T(s_p) = \frac{\int_0^{s_p} (\bar{f}^2 + \bar{f}) \cdot s^2 \cdot ds}{\int_0^{s_p} I_{corr} \cdot s^2 \cdot ds}$$

 $\overline{f^2(s)}$, the weighted mean-square atomic scattering factor, defined in the main article, is calculated for the chemical composition of PEKK (C₂₀H₁₂O₃) and using the tabulated values [6]. s² $\overline{f^2(s)}$ represents the coherent intensity, I_{cohe}, while the incoherent intensity, I_{incoh} = s². \overline{J} , where \overline{J} , the average of the incoherent intensities, in electron units, is calculated for the PEKK using an analytical expression [7]. The intensities calculated, (I_{cohe}+ I_{incoh}) and I_{incoh} are plotted Figure S2-a. Due to the reduced angular range used in this study, the normalization coefficient α (inset in Figure S2-a) is measured at s_p = 0.65 Å⁻¹, which is a reasonable estimation [5]. The normalized intensity in absolute units is deduced and the incoherent contribution is subtracted. Corresponding spectra I_{norm} and (I_{norm} – I_{incoh}) are reported Figure S2-a.

Absolute crystallinity calculated from the Ruland method

The separation of the crystalline peaks from the background of amorphous scattering was done using a similar procedure to the one already used and published [5] [8] [9]. The crystalline intensity, I_{cryst} is plotted in Figure S2-b.

The two methods presented in the main part of this article for the calculation of couples (X_c^{abs} , k) are applied to I_{cryst}. For the two methods, the lower and the upper limits of s were set at s₀ = 0.1 Å⁻¹ and s_p = 0.65 Å⁻¹, respectively. The graphical method [5], 1/R(s_p) versus s_p^2 , is illustrated Figure S2-c for the sample CC230. $X_c^{abs} = 0.18$ and k = 3.8 were calculated.



Figure S2 (a) Illustration of the normalization method, using the calculation of I_{cohe} and I_{incoh} , (b) separation of I_{cryst} from the amorphous background and (c) graphical method [5] for the determination of X_c^{abs} and k. Inset in (a) shows the evolution of T(s).

Results of calculation of

$$X_c^{abs} = R \times K = \frac{\int_0^\infty s^2 I_c(s) ds}{\int_0^\infty s^2 I(s) ds} \times \frac{\int_0^\infty s^2 \overline{f^2(s)} ds}{\int_0^\infty s^2 \overline{f^2(s)} D(s) ds}$$

for various [s₀, s_p] ranges and various k values are reported in Table S1 for sample CC230. The smallest standard deviation is observed for k = 2.7. For this k value, $X_c^{abs} = 0.17$ was calculated.

$[s_0, s_p]$	k = 0	k = 1	k = 2	k = 2,7	k = 3	k = 4
[0.1, 0.3]	0,152	0,160	0,169	0,175	0,178	0,188
[0.1, 0.4]	0,133	0,146	0,159	0,169	0,174	0,189
[0.1, 0.55]	0,114	0,132	0,153	0,169	0,176	0,202
[0.1, 0.67]	0,103	0,127	0,154	0,175	0,184	0,218
Mean X_c^{abs}	0,125	0,141	0,159	0,172	0,178	0,199
$\sigma(X_c^{abs})$	0,022	0,015	0,007	0,003	0,005	0,014

Table S1: Crystallinity of sample CC230 as a function of k and the integration interval $[s_0, s_p]$

Details on the crystallinity calculation from the WAXS peak-fitting method.

The WAXS spectra used is $I_{Raw}(2\theta)$ (see Experimental part). Before refinement and decomposition in amorphous and crystalline peaks, a linear background was determined, based on the intensity level at small and large angles [10] [11] [12]. The background was subtracted from the diffraction spectra. The weight crystallinity, χ_c^w is then calculated using the following equation:

$$\chi_{\rm c}^{\rm w} = \frac{\rm A_{\rm c}}{\rm A_{\rm c} + \rm A_{\rm a}}$$

in which Ac and Aa are the areas under fitted crystalline peaks and amorphous halos, respectively. Figure S3 shows a comparison of the crystallinities calculated with the three methods.



Figure S3: Comparison of the weight crystallinities deduced from the peak-fitting method, the Ruland method, and the Vonk-Ruland method.

With the peak-fitting method, as the normalization in absolute intensity and the subtraction of the incoherent intensity were not performed, a baseline must be subtracted. The choice of the angular domain is then critical because it defines the base line intensity to subtract to the amorphous contribution.

If the refinement was performed in a wide 2 θ range, from 5 to 60°, the background is estimated at 5° and 60°, a value of χ_c^w : 18.5% was calculated. For WAXS spectra recorded in smaller 2 θ range, it is not easy to evaluate the «correct» background, i.e. without suppression of significant intensity. This point is illustrated in Figure S4. When the background was evaluated at the limits of each 2 θ range, two values of $\chi_c^w = 18.5\%$ and 27% were calculated for the two respective angular domains: [5°, 60°], used in this study, and [10°, 35°], the angular range most frequently encountered in the literature. The crystal ratio can largely be overestimated due to an underestimation of the amorphous contribution for the smaller angular range.



Figure S4: Influence of the angular 2θ range on the weight crystallinity evaluation. In these cases, the background is defined in (a) and (b) at the boundaries of each 2θ range.

Influence on the heating rate from 20°C to the crystallization temperature

DSC traces of amorphous PEKK recorded during heating at 10, 20 and 50 °C/min were presented in Figure S5. Crystallization during heating at 10 and 20 °C/min were actually observed. Significant crystallization, above 225 °C, can be observed during heating at low heating rates, 10 and 20 °C/min. No crystallization was observed below 225 °C.



Figure S5: DSC traces of amorphous PEKK (T/I = 60/40) films during the first heating at various heating rates: 10, 20, and 50 °C/min

Crystallized films were taken out of the DSC pan and analyzed by WAXS to quantify the amounts of forms I and II. Results are reported in Figure S6.



Figure S6: Fraction of form I in PEKK 6002 cold crystallized during 4h00 at 280 °C and at 230 °C after heating ramp at various heating rates. The dotted lines are guides to the eye. The red arrows indicate the estimation of the heating rate for the sample crystallized inside the ventilated oven at 280 °C (form I fraction 46%).

The crystallization at 230 °C was not significantly affected by the heating rate to reach the crystallization temperature. Contrariwise, it is not the case for the crystallization at 280°C. The significant amount of form

II obtained after the crystallization at 280 °C for heating rate lower than 50 °C/min is due to the high rate of crystallization of the form II at around 240 °C for cold crystallization [13].



Complementary DSC experiments for a better understanding of the multiple melting endotherm.

Figure S7: Heating traces at various heating rates of PEKK cold crystallized at 200 °C.



Figure S8: Dependence of the (a) low and (b) high melting temperatures on heating rate for PEKK cold crystallized at $T_c = 200$ °C, and (c) evolution of the low endotherm peak temperature with crystallization time for PEKK cold crystallized at $T_c = 180$, 200, and 230°C.



Figure S9: Heating traces of PEKK crystallized in form I and form II.

Correlation between melting enthalpy from DSC and crystallinity from WAXS.



Figure S10: Melting enthalpy deduced from DSC measurements versus weight crystallinity from WAXS experiments.

- Ho, R.-M; Cheng, S. Z. D.; Hsiao, B. S.; Gardner, K. H. Crystal Morphology and Phase Identifications in Poly(aryl ether ketone)s and Their Copolymers. 1. Polymorphism in PEKK. *Macromolecules*, 1994, 27, 2136-2140.
- [2] Gardner, K. H.; Hsiao, B. S.; Matheson, R. R.; Wood, B. A. Structure, crystallization and morphology of poly (aryl ether ketone ketone). *Polymer*, 1992,33, 2483-2495.

- [3] Wojdyr, M. Fityk: a general-purpose peak fitting program. *Journal of Applied Crystallography*, 2010, 43, 1126-1128.
- [4] "XSACT: X-ray Scattering Analysis and Calculation Tool. SAXS &WAXS Data Analysis Software-Available online : http://www.xenocs.com/products/software," [Online].
- [5] Vonk, C. G. Computerization of Ruland's X-ray Method for Determination of the Crystallinity in Polymers. *Journal of Applied Crystallography*, 1973, 6, 148-152.
- [6] Alexander, L. E. X-ray Diffraction Methods in Polymer Science, New York: John Wiley & Sons, Inc, 1969.
- [7] Vedene, H.; Smith, J. R.; Ajitj, T.; Douglas, C. C. A new analytic approximation to atomic incoherent X-ray scattering intensities. *Acta Cryst.*, 1975,A31, 391-392.
- [8] Ruland, W. X-ray Determination of Crystallinity and Diffuse Disorder Scattering. *Acta Cryst.*, 1961, 14, 1180-1185.
- [9] Balko, J.; Lohwasser, R. H.; Sommer, M.; Thelakkat, M.; Thurn-Albrecht, T. Determination of the Crystallinity of Semicrystalline Poly(3-hexylthiophene) by Means of Wide-Angle X-ray Scattering. *Macromolecules*, 2013, 46, 9642-9651.
- [10] Murthy, N. S.; Minor, H. General procedure for evaluating amorphous scattering and crystallinity from X-ray diffraction scans of semicrystalline polymers. *Polymer*, 1990, 31, 996-1002.
- [11] Monar, K.; Habenschuss, A. Modeling the Principal Amorphous Halo in Quiescent Melts of Polyethylene and Ethylene Copolymers Using Wide-Angle X-ray Scattering and Its Implications. *Journal of Polymer Science: Part B: Polymer Physics*, 1999, 37, 3401-3410.
- [12] Rabiej, S. ; Ostrowska-Gumkowska, B.; Wlochowicz, A. Investigations of the Crystallinity of PA-6/SPS Blends by X-RAY Diffraction and DSC Methods. *European Polymer Journal*, 1997, 33, 1031-1039.
- [13] Choupin, T.; Fayolle, B.; Régnier, G.; Paris, C.; Cinquin, J.; Brulé, B. Isothermal crystallization kinetic modeling of poly(etherketoneketone) (PEKK) copolymer. *Polymer*, 2017, 111, 73-82.