

# A quantitative analysis of small- and wide-angle X-ray diffraction curves of homogeneous ethylene-1-octene copolymers

Stanislaw Rabiej\* and Malgorzata Rabiej

University of Bielsko-Biala, Willowa 2, 43-309 Bielsko-Biala, Poland. Correspondence e-mail: stanislaw.rabiej@ath.bielsko.pl

Received 15 August 2006  
 Accepted 22 December 2006

© 2007 International Union of Crystallography  
 Printed in Singapore – all rights reserved

This paper presents a comparison of the results obtained with two methods employed in the analysis of small-angle X-ray scattering (SAXS) curves of isothermally crystallized homogeneous ethylene-1-octene copolymers: a method based on the calculation of the one-dimensional correlation function and a method based on model calculations and curve fitting. Data obtained from time-resolved SAXS investigations are supported by the results of simultaneous wide-angle X-ray diffraction (WAXD) measurements of crystallinity development during isothermal crystallization.

## 1. Introduction

In most cases, small-angle X-ray scattering (SAXS) patterns of semicrystalline polymers are analyzed using the related one-dimensional correlation function obtained by Fourier transformation of the experimental intensity distribution *versus* the scattering vector. Knowing the correlation function and employing the methods derived by Strobl & Schneider (1980), Vonk & Kortleve (1967) and Goderis *et al.* (1999), one can determine the fundamental parameters of lamellar stacks, *i.e.* the average long period and the thicknesses of the crystalline lamellae and amorphous layers. The parameters characterizing lamellar stacks can also be determined by modeling their structure and obtaining the best fit of a theoretical intensity distribution, calculated for the assumed model of stacks, to the experimental SAXS curve. The number of optimized parameters of the stacks depends on the complexity of the model. In this work, both methods of analysis were employed and the results obtained were compared. The measurements were performed for three homogeneous ethylene-1-octene copolymers of low crystallinity (less than 0.2). Generally, in the curve-fitting method, lamellar stacks are characterized by the long period, by the average thicknesses of the lamella and the amorphous layer, and by the independent distribution functions of the lamella and amorphous layer thicknesses. This paper shows that, in the case of the samples investigated, the model can be considerably simplified. Low crystallinity means that the average thickness of the crystalline lamellae is much smaller than the average thickness of the amorphous layers. For this reason, it was assumed that the standard deviation of the lamellar thickness distribution is negligible compared with the standard deviation of the amorphous layer thickness. The calculations performed showed quite good agreement between the parameters obtained from the curve-fitting method and from the correlation function. Additionally, it was shown that the mass fraction crystallinity calculated from the SAXS method is fully consistent with that determined from the wide-angle X-ray diffraction (WAXD) method. The results obtained indicate that the simplified model should be useful in the analysis of all semicrystalline lamellar systems in which one phase dominates considerably over the other.

## 2. Experimental

Measurements were carried out during isothermal crystallization of three homogeneous ethylene-1-octene copolymers of moderate 1-octene concentration: 4.34, 5.2 and 6.6 mol%, sample codes EO4, EO5 and EO7, respectively. The copolymers were synthesized at DSM Research (The Netherlands) using a metallocene catalyst system. Crystallization temperatures (366, 370 and 357 K) were determined from independent differential scanning calorimetry measurements. Before the measurements, the samples were melted at 453 K and cooled at the same rate of 10 K min<sup>-1</sup> to the crystallization temperature. Time-resolved synchrotron SAXS and WAXD investigations were performed using the X33 double focusing camera of the European Molecular Biology Laboratory (EMBL) at DESY, Hamburg. A standard acquisition system with two one-dimensional gas-filled delay line detectors was used. The wavelength of the X-rays was 1.5 Å. During isothermal crystallization, SAXS and WAXD curves were registered simultaneously every 6 s in the first stage of crystallization (0–15 min) and every 12 s in the second stage (15–30 min). SAXS curves were recorded in the range  $2.23 \times 10^{-3} \text{ \AA}^{-1} < s < 4.45 \times 10^{-2} \text{ \AA}^{-1}$  ( $s = 2 \sin \theta / \lambda$ ,  $2\theta$  is the scattering angle and  $\lambda$  is the wavelength of the radiation). WAXD patterns were recorded in the range  $11.17^\circ < 2\theta < 38^\circ$ . SAXS and WAXD data processing was preceded by their normalization to the intensity of the primary beam and correction for the detector response. In addition, in the case of the SAXS data, an averaged melt pattern of a given sample was subtracted from each curve to eliminate the background scattering from the sample holder and other possible sources.

## 3. SAXS data elaboration

The morphological parameters of the lamellar stacks in the investigated copolymers were determined from the linear correlation function  $K(x)$ , calculated by the cosine transformation (Strobl & Schneider, 1980) of the intensity distribution:

$$K(x) = \int_0^\infty I(s) s^2 \cos(2\pi s x) ds, \quad (1)$$

where  $I(s)$  is the scattering intensity and  $x$  is a distance in real space.

Prior to the calculation of the correlation functions, the experimental curves were smoothed using spline functions and extrapolated to low and high angles. At high angles, the experimental curve was fitted with a function given by Ruland (1971), assuming a pseudo two-phase structure with a transition layer between the amorphous and crystalline regions and a sigmoidal density gradient in this layer:

$$\lim_{s \rightarrow \infty} I(s) = B + \frac{P}{s^4} \exp(-4\pi^2 \sigma^2 s^2), \quad (2)$$

where  $B$  is a constant background scattering due to electron-density fluctuations within the phases,  $P$  is the Porod constant and  $\sigma$  is a parameter characterizing the thickness of the transition layer. These three parameters were found using the Marquand–Levenberg nonlinear least-squares fitting procedure. The experimental curve was extrapolated to zero angle by fitting of a second-order polynomial to the function  $I(s)s^2$  from equation (1). Finally, the constant background  $B$  was subtracted from the extrapolated curve and the cosine transformation was performed employing the computer program *OTOKO* (Boulin *et al.*, 1986). Using the correlation function, the long period ( $L$ ) and the volume fraction of the crystalline phase in the lamellar stacks ( $\phi_L$ ) were determined directly (Strobl & Schneider, 1980). The thicknesses of the crystalline ( $C$ ) and amorphous ( $A$ ) layers in the stacks were calculated as follows:

$$C = \phi_L L \quad (3)$$

and

$$A = (1 - \phi_L)L \quad (4)$$

Next, the fraction  $\alpha_s$  of the total volume of the sample occupied by stacks of lamellae was calculated using the method proposed by Goderis *et al.* (1999) and the total volume fraction crystallinity of the sample was determined as

$$x_v = \alpha_s \phi_L. \quad (5)$$

Finally, using the densities of amorphous and crystalline phases given by Swan (1960), the volume fraction crystallinity was transformed into mass fraction crystallinity  $x_M$

$$x_M = \left[ 1 + \frac{d_A}{d_C} \left( \frac{1 - x_v}{x_v} \right) \right]^{-1} \quad (6)$$

#### 4. WAXD data elaboration

WAXD curves were analyzed using *WAXSFIT*, a new version of the computer program *OptiFit* (Rabiej, 2003) prepared for the elaboration of large sets of data from real-time synchrotron experiments. After subtraction of a linear background, the normalized experimental diffraction curve  $I_E(2\theta)$  was resolved into crystalline peaks 110 and 200 and an amorphous halo by fitting of a theoretical curve  $I_T(2\theta)$  which was a sum of functions describing individual components. Both the crystalline peaks and the amorphous halo were represented by linear combinations of Gaussian and Lorentzian functions,

$$F_i(x) = f_i H_i \exp \left\{ -\ln 2 \left[ \frac{2(x - x_{oi})}{w_i} \right]^2 \right\} + \frac{(1 - f_i) H_i}{1 + [2(x - x_{oi})/w_i]^2}, \quad (7)$$

where  $x$  is the scattering angle  $2\theta$ , and  $H_i$ ,  $w_i$  and  $x_{oi}$  are, respectively, the peak height, the width at the half height and the center. The shape coefficient  $f_i$  is equal to 1 for the Gaussian profile and 0 for the Lorentzian one. In the program, the theoretical curve was fitted to the

experimental one using a multi-objective optimization procedure (simultaneous minimization of the sum of the squared deviations between experimental and theoretical curves and of the sum of the squared deviations between the experimental curve and the component function representing the amorphous halo) and a hybrid algorithm which combines a genetic algorithm with the classical optimization method of Powell. Crystallinity was calculated as the ratio of the integral intensity in the profiles of the crystalline peaks to the total scattering intensity. The calculations showed that, in the case of all samples investigated, the upper level of crystallinity reached at the end of isothermal crystallization was not higher than 0.2.

#### 5. Model calculations

In the model of Hosemann, a semicrystalline polymer is considered as a system of stacks of lamellar crystals separated by amorphous layers. The lamellae are assumed to be flat and of infinite lateral dimensions. All stacks are statistically identical and have the same characteristics. The parameters of such a model are the average thicknesses of the lamella ( $C_o$ ) and the amorphous layer ( $A_o$ ) and the average long period of the stack ( $L_o$ ). The height of the stacks is assumed to be much larger than the long period. The thicknesses of the crystalline lamellae and amorphous layers vary independently and are described by independent distribution functions  $H(C)$  and  $h(A)$ . The theoretical scattering intensity of such a one-dimensional system in the direction perpendicular to the lamellae is the sum of two components:

$$J_1(s) = J_B^o(s) + J_C(s), \quad (8)$$

where  $J_B(s)$  is determined by the electron-density distribution in a stack and  $J_C(s)$  represents the scattering intensity of a whole stack as an isolated object. According to Hosemann & Bagchi (1962):

$$J_B(s) = \frac{\Delta \rho^2}{4\pi^2 s^2 L_o} \frac{|1 - F_C|^2 (1 - |F_A|^2) + |1 - F_A|^2 (1 - F_C)^2}{|1 - F_C F_A|^2} \quad (9)$$

and

$$J_C(s) = \frac{\Delta \rho^2}{2\pi^2 s^2 N L_o} \text{Re} \left\{ \frac{F_A (1 - F_C)^2 (1 - F_A F_C)^N}{1 - F_A F_C} \right\}, \quad (10)$$

where  $\Delta \rho$  is the difference in electron density between crystalline and amorphous phases,  $N$  is the number of lamellae in a stack, and  $F_C$  and  $F_A$  are, respectively, the Fourier transforms of the distributions  $H(C)$  and  $h(A)$ . When the height of stacks is large compared with the wavelength ( $N L_o \gg \lambda$ ), the intensity  $J_C(s)$  can be neglected in the experimentally accessible region. Assuming that the thickness distributions  $H(C)$  and  $h(A)$  are described by Gaussian functions, the corresponding Fourier transforms are given by the following equations:

$$F_C = \exp(-2\pi^2 s^2 \sigma_C^2) \exp(2\pi s i C_o) \quad (11)$$

and

$$F_A = \exp(-2\pi^2 s^2 \sigma_A^2) \exp(2\pi s i A_o), \quad (12)$$

where  $\sigma_C$  and  $\sigma_A$  are the standard deviations of  $H(C)$  and  $h(A)$  distributions.

Substituting equations (11) and (12) into (9) we obtain:

$$J_B^o(s) = \frac{\Delta\rho^2}{4\pi^2s^2L_o} \times \frac{|1-|F_L|^2-|F_C|(1-|F_A|^2)\cos(2\pi sC_o)-|F_A|(1-|F_C|^2)\cos(2\pi sA_o)|}{|1-F_L|^2} \quad (13)$$

where

$$F_L = \exp(-2\pi^2s^2\sigma_L^2)\exp(2\pi siL_o), \sigma_L^2 = \sigma_C^2 + \sigma_A^2$$

and

$$|F_C| = \exp(-2\pi^2s^2\sigma_C^2)$$

$$|F_A| = \exp(-2\pi^2s^2\sigma_A^2)$$

$$|F_L| = \exp(-2\pi^2s^2\sigma_L^2),$$

where  $\sigma_L$  is a standard deviation of the long period  $L$  distribution.

In the case of polymers of low crystallinity considered in this work, the crystalline lamellae are considerably thinner than the amorphous layers. For this reason, one can suppose that a similar relation holds for the standard deviations (Blundell, 1970). One can assume that  $\sigma_A > \sigma_C$ , and finally  $\sigma_A^2 \gg \sigma_C^2 \simeq 0$ . In this way, equation (13) can be considerably simplified.

The final formula for the theoretical intensity profile  $J_1(s)$  used in this work is given by:

$$J_1(s) = Z \left\{ \frac{\sin^2(\pi s \phi L_o)}{(\pi s \phi L_o)^2} \right\} \times \left\{ \frac{[1 - \exp(-4\pi^2s^2g^2L_o^2)][\exp(-4\pi^2\sigma^2s^2)]}{1 - 2\exp(-2\pi^2s^2g^2L_o^2)\cos(2\pi sL_o) + \exp(-4\pi^2s^2g^2L_o^2)} \right\} \quad (14)$$

where  $Z$  is a constant,  $\phi = C_o/L_o$ , and  $g$  is a reduced standard deviation of the long period,  $g = \sigma_L/L_o$ . The second exponential term in the numerator accounts for the changes in the intensity distribution caused by a transition layer between crystalline and amorphous regions (Ruland, 1971) and  $\sigma$  is a parameter characterizing a sigmoidal electron-density profile in this layer.

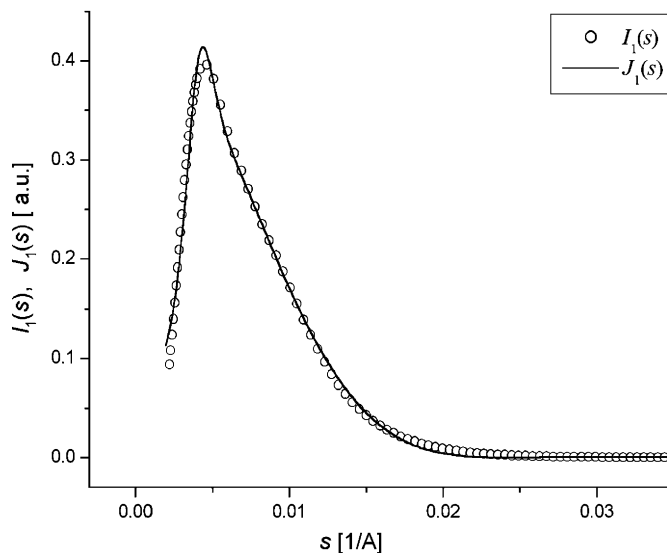
The parameters of the model employed were found by best fit of the theoretical intensity profile  $J_1(s)$  to the equivalent experimental one-dimensional scattering intensity  $I_1(s)$ . In order to obtain the latter, the experimental curve  $I(s)$  was multiplied by  $4\pi s^2$  (Crist & Morosoff, 1973).

## 6. Results and conclusions

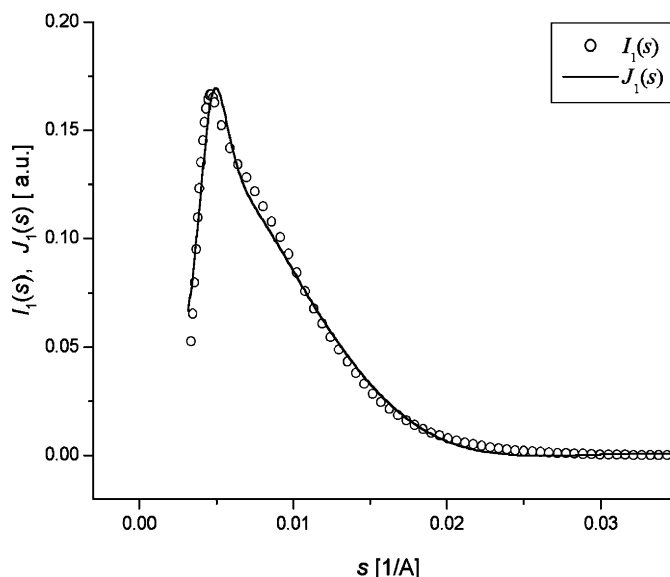
Theoretical functions  $J_1(s)$  were calculated and fitted to the experimental one-dimensional profiles  $I_1(s)$  by means of a computer program prepared for this purpose.

In the program, five independent parameters were optimized according to the best least-squares fit, using the classical method of Powell: the average long period  $L_o$ , the volume fraction crystallinity of stacks  $\phi = (C_o/L_o)$ , the reduced standard deviation of the long period  $g = (\sigma_L/L_o)$ ,  $\sigma$  characterizing the transition layer thickness, and a scaling constant  $Z$ . Before the fitting, a constant background  $B$  was subtracted from experimental curves  $I(s)$  using the method described above in the paragraph dedicated to SAXS data elaboration. A good fit of the theoretical profiles to experimental ones was obtained for all curves registered during isothermal crystallization. Examples, for samples EO4 and EO7, are shown in Figs. 1 and 2. The curves are well fitted over a broad range of scattering vector  $s$ .

Moreover, for all three investigated samples the parameters of the lamellar stacks determined from fitting of the curves agree very well

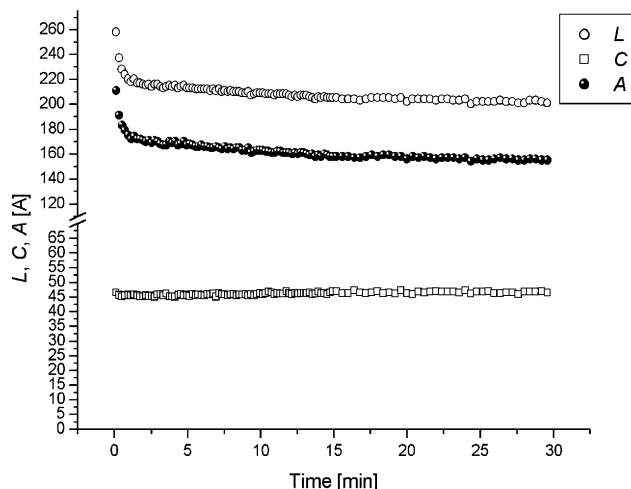


**Figure 1**  
Best fit between theoretical  $J_1(s)$  and experimental  $I_1(s)$  one-dimensional intensity profiles for sample EO4.

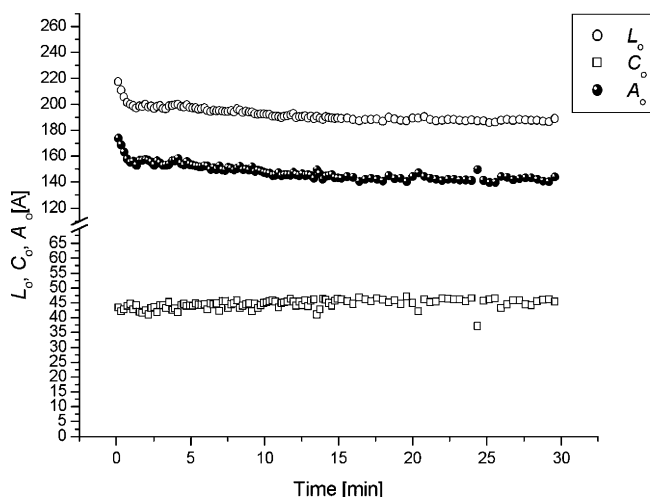


**Figure 2**  
Best fit between theoretical  $J_1(s)$  and experimental  $I_1(s)$  one-dimensional intensity profiles for sample EO7.

with those obtained with the method of Strobl & Schneider (1980), *i.e.* from the correlation function related to a given experimental curve. The parameters calculated with the two methods for sample EO4 can be compared in Figs. 3 and 4. Indeed, the values of  $L_o$  and  $A_o$  determined with the fitting method are about 10–13% lower than those determined from the correlation function, but this could be expected. In general, the long period calculated from the correlation function represents the most probable value and is higher than the mean value, particularly when considerable deviations from periodicity occur in the stacks (Crist, 2000). This was the case in the samples investigated, as the reduced standard deviation of the long period was found to be in the range 0.35–0.45. On the contrary, the thickness of the crystalline lamellae determined from the correlation function is related to the number average value (Crist, 2000). This is why the differences between the values of this parameter determined from curve fitting and from the correlation function are less than 5%.

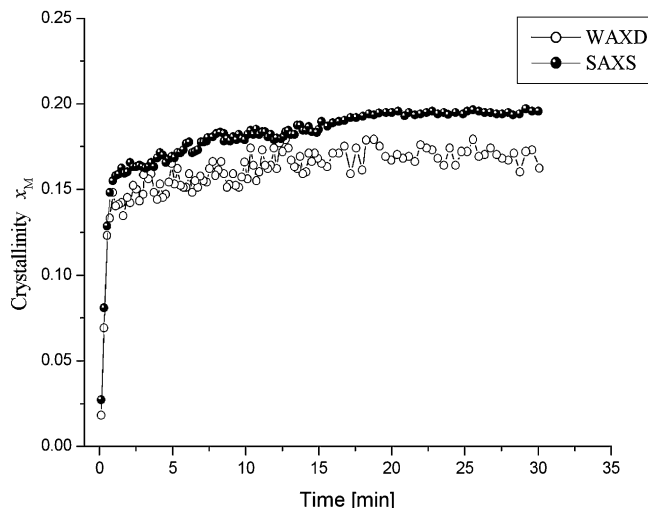


**Figure 3**  
The long period and the thicknesses of the crystalline lamellae and amorphous layers during isothermal crystallization of the sample EO4, determined from the correlation function.



**Figure 4**  
Average long period and average thicknesses of crystalline lamellae and amorphous layers during isothermal crystallization of the sample EO4, determined from curve fitting.

Using the method of Goderis *et al.* (1999) and Swan's (1960) relations for the densities of amorphous and crystalline phases, the volume fraction crystallinity values calculated from SAXS data (from the correlation function) were transformed into a mass fraction crystallinity and compared with the values obtained with WAXD. The plots of crystallinity *versus* time determined with the two methods are very close to one another and exhibit the same trends (Fig. 5). Similar plots



**Figure 5**  
Crystallinity of sample EO4 during isothermal crystallization at 366 K determined with SAXS and WAXD.

were obtained for the remaining two samples, EO5 and EO7. In general, the values found with SAXS are slightly higher than those obtained from WAXD, because part of the transition layer between the crystalline and amorphous phases is taken as crystalline in this method. The consistency of the results obtained confirms that the simplified model of lamellar stacks used in this work correctly describes the real structure of investigated copolymers of low crystallinity and can be successfully employed in the analysis of SAXS curves.

This work was financed by the Polish Committee for Scientific Research, grant No. 3 T08E 091 27.

## References

- Blundell, D. J. (1970). *Acta Cryst.* **A26**, 476–483.
- Boulin, C., Kempf, R., Koch, M.H.J. & Mc Laughlin, S.M. (1986). *Nucl. Instrum. Methods A*, **249**, 399–411.
- Crist, B. (2000). *J. Macromol. Sci. B*, **39**, 493–518.
- Crist, B. & Morosoff, N. (1973). *J. Polym. Sci.* **11**, 1023–1045.
- Goderis, B., Reynaers, H., Koch, M. H. J. & Mathot, V. B. F. (1999). *J. Polym. Sci. Part B*, **37**, 1715–1738.
- Hosemann, R. & Bagchi, S. N. (1962). *Direct Analysis of Diffraction by Matter*. Amsterdam: North Holland.
- Rabiej, M. (2003). *Fibres Text.* **11**, 83–87.
- Ruland, W. (1971). *J. Appl. Cryst.* **4**, 70–73.
- Strobl, G. R. & Schneider, M. (1980). *J. Polym. Sci. Polym. Phys. Ed.* **18**, 1343–1359.
- Swan, P. R. (1960). *J. Polym. Sci.* **42**, 525–534.
- Vonk, C. G. & Kortleve, G. (1967). *Kolloid Z. Polym.* **220**, 19–24.