



An intensity superposition model to fit the small angle X-ray scattering of semicrystalline polymers and its application to the monitoring of non-isothermal crystallization



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ABSTRACT

Small angle X-ray scattering (SAXS) of Ethylene-1-Octene copolymer cooled from the melt at a constant rate is recorded and modeled. The theoretical SAXS curves based on the paracrystalline layer stacking model of Hermans cannot be well fitted to the experimental ones. Therefore it is assumed that lamellar stacks filling the copolymer volume may differ in their crystallinity and the curves are fitted by a model that combines intensities from all stacks under control of a crystallinity distribution function $P(\varphi)$. It is shown that a symmetric Gauss function is not suitable to approximate this distribution while the best fit is obtained for an asymmetric, positively skewed split Gauss function. The model provides good agreement of the morphological parameters of stacks with the values obtained from the one-dimensional correlation function. Additional determined parameters are: average crystallinity of the copolymer φ_s , invariant Q as well as standard deviation and skewness coefficient of $P(\varphi)$. During cooling the $P(\varphi)$ distribution becomes less asymmetric but simultaneously it clearly broadens. The skewness decreases first slowly but much faster for temperatures lower than 40 °C. Based on the transformations of the shape of $P(\varphi)$ distribution the changes in the structure of stacks and homogeneity of copolymer are discussed and related to the crystallization conditions.

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1. Introduction

Small Angle X-ray scattering (SAXS) is one of the most important tools for structural investigations of semi-crystalline polymers. As it is well documented by electron microscopic observations, from the point of view of SAXS technique, an isotropic polymer sample can be considered as an isotropic system of stacks composed of alternating crystalline lamellae and amorphous layers. Both the lateral size of stacks and their size along the lamellar normal are much bigger than the wavelength λ of X-rays and than the average periodicity within the stacks. As a result the experimental scattered intensity $I(s)$ is directly related to the one dimensional intensity function $I_1(s)$ which reflects the one dimensional order in stacks [1]

$$I_1(s) = 4\pi s^2 I(s) \quad (1)$$

where $s = 2\sin\theta/\lambda$ is the scattering vector. Having $I_1(s)$ one can determine the parameters of stacks in two ways. Very frequently, we use the so called one-dimensional correlation function $K(x)$ obtained by Fourier transformation of $I_1(s)$.

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Knowing the correlation function and applying the methods derived by Strobl & Schneider [2] and Vonk & Kortleve [3] one can determine the fundamental parameters of lamellar stacks *i.e.* average long period, thicknesses of crystalline lamellae and amorphous layers and volume crystallinity.

Alternatively, the structure of lamellar stacks can be determined by calculations consisting in the best fitting of a calculated, theoretical intensity function, related to an assumed model of lamellar stacks, to a given experimental SAXS curve.

In the literature one can find examples of application of various models. The simplest approach – a Single Stack Model, assumes that all stacks are statistically identical in respect of their internal structure. It means that all of them are characterized by the same average values of amorphous layer thickness A_o , average crystalline lamella thickness C_o and average long period L_o , where $L_o = A_o + C_o$. The thicknesses of crystals and amorphous layers fluctuate independently on one another and they are described by independent distribution functions $G_A(A)$ and $G_C(C)$ but in all stacks the distributions are the same. Theoretical intensity function for such a model is expressed by the relationships derived by Hermans [4] and discussed by Hosemann and Bagchi [5].

This so called general Hermans' paracrystalline stacking model has been used by several researchers who have assumed different types of distribution functions $G_A(A)$ and $G_C(C)$ (Gauss or others) and different numbers of layers in a stack (infinite or limited number) [6–12]. Unfortunately in many cases the theoretical curves described by the formulas of Hermans could not be well fitted to experimental SAXS curves. Somewhat better results were reported for a finite stack model. However in order to obtain some improvement in the quality of fit, the number N of lamellae in a stack had to be: $N \leq 2$ which is rather problematic value [9,12].

More complex models assume that the structure of all stacks is not the same [9,13–17]. It means that a polymer volume is inhomogeneous in terms of the structure of stacks. Some of the models [9,13,14] adopted an approach in which a polymer is considered as a system of stacks of different crystallinity. In such a case, according to the proposal of Blundell [9] the total scattered intensity per unit volume of a polymer can be presented as a superposition of intensities scattered by stacks of various crystallinity

$$I_1(s) = \int_0^1 I_1(s, \varphi) P(\varphi) d\varphi \quad (2)$$

where $I_1(s, \varphi)$ is a function which describes the intensity from a polymer in which all stacks have the same volume crystallinity φ and $P(\varphi)$ is a normalized distribution function giving the contribution of such stacks to the total intensity $I_1(s)$. It seems that a suitable name of such a model can be: an Intensity Superposition Model. This name will be used later on in this paper. The calculations based on such a model were performed by Blundell for low density polyethylenes with a Gaussian distribution as $P(\varphi)$ function. Obtained fits were better as compared with those reached with the Single Stack Model but still the progress was not satisfactory [9].

In our first paper dedicated to this subject [18] we analyzed the SAXS curves of isothermally crystallized, ethylene-1-octene (EO) copolymers. These copolymers were produced using a vanadium based catalysts and for this reason they were characterized by inter- and intramolecular homogeneity. The molecular weight distribution of such materials is relatively narrow, the comonomer content is constant and statistically the polymer chains do not differ from one another. Such well defined polymeric materials are very suitable for fundamental studies on the influence of the chain microstructure on melting/crystallization behavior, the resulting morphology and physical properties. Crystallization temperatures were chosen at the onset of crystallization as determined from independent heating-cooling DSC measurements. We showed that the Single Stack Model can be successfully used for these copolymers crystallized in such a way. The parameters obtained from model calculations agreed well with those determined from the correlation function [18]. However, our last studies on the same EO copolymers crystallized nonisothermally – during cooling from the melt at a constant rate, have revealed that the Single Stack Model is not suitable for them. It has turned out that it is impossible to fit the theoretical SAXS curves based on this model to the experimental ones. This fact have suggested that in the latter case, the fundamental assumption of the Hermans' model *i.e.* statistical identity of all stacks is not fulfilled. This is why in this work we have employed the Intensity Superposition Model. Investigations were performed for nonisothermally crystallized ethylene-1-octene copolymer with 5.2 mol% of 1-octene, one of those investigated in the paper mentioned above. At first we assumed that $P(\varphi)$ distribution is a Gauss function. We obtained better fits than in the case of the single stack model but still the improvement was small, particularly for the SAXS curves recorded at lower temperatures. Besides, it has turned out that the parameters of stacks determined from curve fitting method are clearly different than those ones obtained from one – dimensional correlation function. For this reason, we employed an asymmetric split Gauss function to describe $P(\varphi)$ instead of a symmetric Gauss distribution. Split Gauss function was constructed as a normalized combination of two “half Gauss” functions of different standard deviations on its left and right sides. The ratio n of this two standard deviations (asymmetry factor), similarly as other parameters of the theoretical curve, were optimized in the curve fitting procedure. Modeling was carried out for 32 curves recorded during cooling of the copolymer from the melt to room temperature. Performed calculations have shown that employing positively skewed $P(\varphi)$ functions we obtain a considerable progress in the quality of fitting of the theoretical curves to the experimental ones. It has also turned out, that the split Gauss function with an adjustable asymmetry factor can be successfully used to describe the distribution $P(\varphi)$ in the whole range of temperatures: from the early stages of crystallization up to the final solidification. For this reason it is more useful, than the Reinhold [19] function that we have used before in our first trials [20]. Obtained results confirm the hypothesis that in contrast to the isothermal crystallization,

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