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SANS study of the early stages of crystallization in polyethylene solutions

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Abstract

Crystallization of low molecular weight polyethylene from solution has been studied using small angle neutron scattering (SANS). The detection sensitivity of the volume fraction degree of crystallinity is estimated to be 10^{-5}, allowing for the measurement of the very early stages of crystal growth. SANS spectra for both the early and late stages of crystallization can be satisfactorily interpreted with a lamellar crystal model; there is no evidence of diverging or spinodal-decomposition-like density fluctuations during the early stage of crystallization in polyethylene solutions. A possible explanation of the dominant wavevector in small angle X-ray scattering that led to the proposal of 'spinodal decomposition' mechanism for early stage crystallization is suggested.

Keywords: Polyethylene; Crystallization; Neutron scattering

1. Introduction

The early stage crystallization in polymers has been a topic of interest since the beginning of the polymer science. After decades of intensive studies and spirited debates, a kinetic picture of nucleation and growth (NG) has generally been accepted [1–5]. In the classical view of the homogeneous nucleation, density fluctuations in supercooled liquids result in small clusters of ordered segments; those sub-critical-sized nuclei dissolve back into the liquid phase, whereas nuclei larger than the critical nucleus grow indefinitely. In recent years, there have been renewed interests in the mechanism of the structure development during the induction period of crystallization due to the proposal of a new mechanism with a rather different picture [7–10], in which supercooled melt undergoes 'spinodal decomposition' (SD) resulting in spatial separation of polymer chains into domains where chains have better conformational order and domains with chains like those in ordinary melts. This preordering process assists the initial nucleation of crystals from the melt. The SD proposal triggered more experimental and theoretical studies [11–18] as well as rethinking and discussions of the route toward polymer crystallization [19–22].

After more than two decades since the first notion of SD in polymer crystallization literatures [6] and one decade after the proposal of the SD mechanism for early stages of crystallization [7,8], new evidences are continually reported in recent years to support either SD [23–26] or NG [27–29] in polymer crystallization. Heeley et al. [23] gave detailed analysis of small angle X-ray scattering (SAXS) spectra on the early stage crystallization of isotactic polypropylene using Cahn–Hilliard theory and obtained a spinodal temperature, which is below the melting temperature. Ania et al. [24] revealed a characteristic wavelength of 14.7 nm of long-range density fluctuations growing with time during the induction period of polyamide 6, 6 crystallization using SAXS. Using optical microscopy, Nishida et al. [25] observed bicontinuous patterns, which were regarded as characteristic for SD, as PET melt was rapidly quenched below a stability limit. Zhang et al. [26] compared the differences between cold and melt crystallization in isotactic polystyrene and suggested that the melt crystallization process of polymer can be explained by the SD theory [12].

On the other hand, there are reports backing the classical NG picture. Chen et al. [27] studied the nucleation process of poly(ethylene oxide) (PEO) crystallization from both the isotropic and structured melt using simultaneous SAXS and wide angle X-ray diffraction (WAXD). They suggested the existence of primary nuclei in the melt due to localized large amplitude density fluctuation and calculated the size of nuclei

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as a function of time. Panine et al. [28] investigated the early stage of melt crystallization in low-density polyethylene using improved X-ray detection and found the behavior of SAXS data in the very early stages was not consistent with spinodal decomposition mechanism. Owen et al. [29] studied the room temperature crystallization of poly[(*R*)-3-hydroxybutyrate] using both ultra-small angle X-ray scattering (USAXS) and SAXS and found early development of structures was essentially lamellae with different forms of fractal aggregates.

It is clear that SAXS using synchrotron X-ray radiations has been playing an important role in the debate of the early stage crystallization mechanism. Much of the current controversies stemmed from different interpretations of SAXS signals prior to the appearance of the WAXD peaks. It is desirable that the same problem could be viewed from a different angle. Recent experiments show that small angle neutron scattering (SANS) using composition contrast is a useful tool complementing SAXS for studying polymer crystallization [30,31]. In this Letter, we report additional evidences of structural development during the early stages of crystallization in polymer solutions. While studies on oligomeric solutions do not directly address the controversies in mechanisms of melt crystallization, we hope to cast insights in this matter from the measurement point of view. Furthermore, the well-established optical microscopy observation of the spherulitic growth in polymer melts over length scales of many microns could not be satisfactorily accommodated in the SD mechanism, which involves density fluctuations of 10 nm. In this Letter, we point out an alternative picture to reconcile the scattering and morphology measurements.

2. Experiment

The polyethylene (PE) with $M_w = 2.1$ kg/mol and PDI ∼ 1.15 was obtained from the Pressure Chemical Co. PE solutions with volume fractions of $\phi_0 = 0.10$, 0.13 and 0.24 (in coil solutions) in deuterated *o*-xylene (>99 at.% deuterium, C/D/N Isotopes Inc.) were measured using the NG3 30m SANS instrument at the NIST Center for Neutron Research of the National Institute of Standards and Technology. Incident neutrons of wavelength $\lambda = 6$ Å and two sample-to-detector distances of 1.33 and 6.5 m yielded a range of scattering wavevectors, $0.006\ \text{Å}^{-1} < Q < 0.4\ \text{Å}^{-1}$. In the cooling study, the samples were first equilibrated at 120.0 °C then sequentially cooled to lower temperatures; SANS spectra were collected over a period of 27 min after the solution being isothermally stored at each temperature for ca. 170 min. The structure in solution could be considered arrested during the measurement. The temperature stability of the stage was within ±0.2 °C, and the temperature accuracy at the sample was ±0.5 °C. After the correction for background and detector efficiency, and the conversion to an absolute scale using the direct beam intensity, the 2D SANS intensity was circularly averaged to yield the total scattering cross section of the sample.

3. Results and discussion

Typical SANS spectra of the $\phi_0 = 0.24$ solution after cooling from 120.0 °C to various temperatures were shown in Fig. 1. The symbols are experimental data and the curves through symbols are the best model fitting. In the model as developed previously [30], lamellar crystals are assumed to coexist with coil chains; they contribute to scattering neutron independently. The low temperature (85.0, 90.0 and 95.0 °C) spectra show both the characteristic form and structure factors of stacked lamellae. The average long period and the lamellar crystal thickness at 85 °C obtained from model fitting are 230 and 180 Å, respectively, indicating extended-chain crystals. The degree of crystallinity, which is defined as volume fraction (ϕ_{cry}) in this manuscript, is estimated following a procedure described later.

A simplistic view of the scattering features can be described as follows. The asymptotic Q^{-2} power law at the low-Q is characteristic for sheet-like 2D structure, and the rapid fall of the intensity for about two orders of magnitude at ca. 0.03 Å^{-1} implies the loss of self-correlation beyond the lamellar thickness. Those are considered the ‘form factor’ of individual sheets with a uniform thickness. Note that Q^{-2} power law associated with random coils occurs at the Q-range higher than ca. 0.1 Å^{-1} because of low molecular weight polymers in this study. On the other hand, the peaks at ca. 0.025, 0.05 and 0.08 Å^{-1} are the first three diffraction orders due to the density correlation among the stacking lamellae, which depict the ‘structure factor’ of lamellar stacks.

Because of the very low noise of the SANS spectra, the spectra of the coil solution (110.0 and 120.0 °C) show clean coil behavior, whereas those of SAXS typically show large excess scattering in the same low-Q region from both the beam-stop spill-over and density fluctuations due to random thermal motions. The cleanness of the SANS spectra of

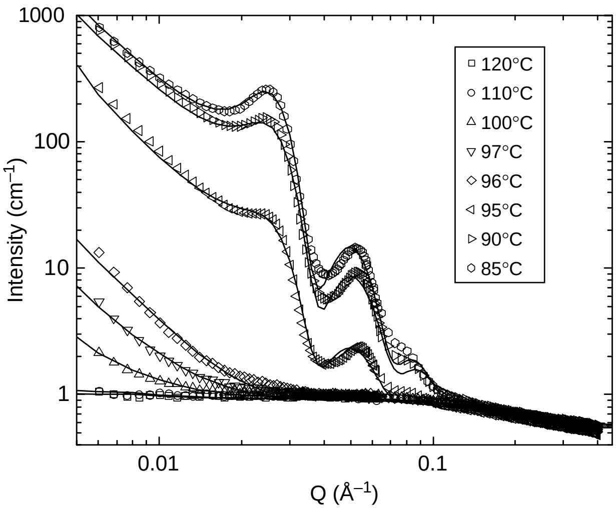

Fig. 1. SANS spectra of the $\phi_0 = 0.24$ solution after cooling from 120.0 °C to various temperatures. The symbols are experimental data and the curves through symbols are the best model fitting. The low temperature (85.0, 90.0 and 95.0 °C) spectra show both the characteristic form and structure factors of stacked lamellae.

homogenous coil solution allows for detecting very slight structural change during the early stages of crystallization.

At temperatures 96.0, 97.0 and 100.0 °C, the scattering intensity arising from the solution background at the low-*Q* indicates the development of new structures from the solution. Because crystallization kinetics is rather slow and crystallinity is low, those SANS spectra represent snapshots of averaged structures at various times during the early stages of crystallization at corresponding temperatures. Those spectra could be emulated by multiplying a constant, 0.05, 0.02, and 0.008 for 96.0, 97.0 and 100.0 °C, respectively, to the lamellar scattering intensities at 95.0 °C, and summing with a relatively invariable coil solution spectrum as that at 120.0 °C. That implies a simple rescaling of the intensity by ϕ_{cry} without invoking a different kinds of structure for the early stage. Furthermore, the high-*Q* cut-off of the scattering signals from nascent crystals at ca. 0.03 $\mathrm{\AA}^{-1}$ implies that the minimum dimension of the crystal in this study is around the extended chain length, which could also be the size of nuclei. The observation of the rapid drop of the form factor intensity is possible only when the background signals (coil scattering in this case) are sufficiently low. On the other hand, at the very early stages, the crystal intensity could drop to below the coil intensity at roughly the *Q*-value corresponding to the lamellar thickness. Beyond this crossover, the scattering from nascent crystals at higher-*Q* is overwhelmed by the coil scattering, resulting in an apparent cut-off.

The detection sensitivity in this study can be estimated. Assuming PE being fully crystallized at 85.0 °C, the ϕ_{cry} of 0.21 (assuming crystal density of 1.0 g/cm^3) is equivalent to the intensity of ca. 10^3 cm^{-1} at 0.006 $\mathrm{\AA}^{-1}$. For the coil solution at 120.0 °C, $\phi_{\mathrm{cry}}=0$, the measured intensity is ca. 1 cm^{-1} with 4% statistical errors. So the detection sensitivity of SANS for the volume fraction crystallinity, ϕ_{det}, is estimated to be ca. 10^{-5} ($4\% \times 1 \div 10^3 \times 0.21 = 8 \times 10^{-6}$), comparable to that of light scattering while more than one decade better than that of SAXS. This is, however, a conservative estimate since the crystallinity at 85.0 °C would be less than ideal, and all crystals are not in perfect lamellar stacks, but the order of magnitude should not be affected.

The detection limit for the amplitude of compositional fluctuations can be estimated from ϕ_{det}. The scattering invariant, which can be experimentally obtained as the integrated total intensity, describes the mean square scattering length density fluctuations, $\Delta\rho^2\phi$, which is independent of the forms of fluctuations. So a small volume fraction of condensed crystal phases with a contrast to the background of 1–0 can yield the same scattering invariant as small amplitude fluctuations throughout the entire sample volume. With $\phi_{\mathrm{det}}=10^{-5}$, the detection limit of the amplitude of composition fluctuations is estimated to be 0.2%. There is no evidence of diverging (or spontaneous, or spinodal-decomposition like) compositional fluctuations during the early stage of crystallization, which would at a point exceed the 0.2% detection limit and be measurable. On the other hand, the possibility of non-diverging (standing-wave like) fluctuations with amplitude $<0.2\%$ still exists.

Based on the scattering features, we can also cast some insights in the SAXS data that led to Kaji et al.'s proposal of the 'spinodal decomposition' mechanism during the early stage of polymer crystallization. As aforementioned, one difference between SAXS and SANS spectra is that the former usually carries large background excess intensities at the low-*Q*. A standard practice to extract the structural signal is by measuring the excess scattering from the melt, and subsequently subtracting that from crystallization spectra. This is illustrated in Fig. 2 using SANS spectra of $\phi_0=0.13$ solution as an example. The filled squares and open circles are experimental data of the solution at 120.0 and 90.0 °C, representing the homogeneous coil solution and the early stage crystallization states, respectively. The *Q*-range in this plot, 0.005–0.05 $\mathrm{\AA}^{-1}$, is also typical of those reported in SAXS studies. The coil solution spectrum shows very clean flat intensity within the range of the plot, indicating neither crystal structures in the sample nor *Q*-dependent background noise in the measurement. The spectrum at 90.0 °C shows intensities in the low-*Q* region due to the crystal formation in the solution. The characteristics of the spectrum are identical to the form factor of nascent lamellar crystals, which shows an intensity cut-off around the *Q*-value corresponding to the lamellar crystal thickness and the asymptotic power-law at the lower-*Q*. The power exponent of −2.2 is slightly higher than that of ideal 2D objects possibly due to both the finite size and fractal surface roughness, whose effect diminishes as crystals grow to large dimension and crystal facets perfect at later times.

To simulate SAXS spectra, we assume the low-*Q* excess intensity (due mainly to the beam-stop spill-over, stray photons, thermal fluctuations, etc.), I_{ex}, as the dotted curve in Fig. 2, which drops rapidly from 100 times the white background at $Q=0.006$ $\mathrm{\AA}^{-1}$ to below the background at ca. 0.02 $\mathrm{\AA}^{-1}$. That is typical in reported SAXS studies [6–10,23].

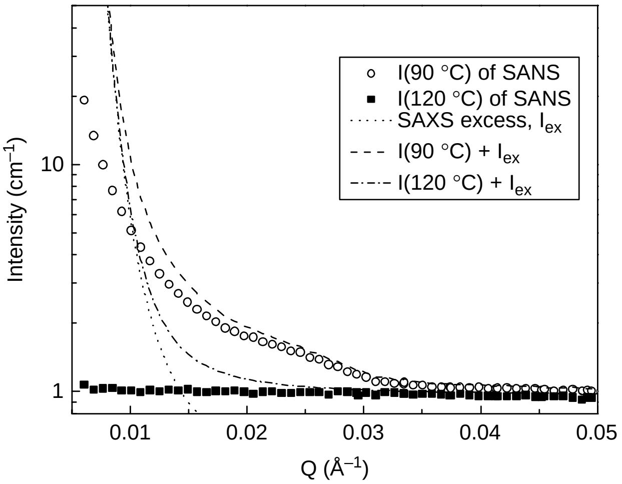

Fig. 2. Illustration of excess signals and simulated spectra for a typical small angle X-ray scattering experiment. The filled squares and open circles are SANS spectra of $\phi_0=0.13$ solution in the coil and the early stage crystallization states, respectively. The dotted curve is assumed SAXS excess intensity at the low-*Q*, and the dash–dotted and dashed curves are simulated SAXS spectra for the melt and the early stage crystals by adding the dotted curve to the corresponding SANS spectra.

The SAXS spectra of the sample are generated by adding the I_{ex} to the corresponding SANS spectra, shown in the same plot as the dash–dotted curve for the coil solution and the dashed curve for the early stage crystals, respectively. It is clear that at the early stage, the Q^{-2} power law is overwhelmed by the much steeper SAXS excess intensity. In principle, true spectrum can be recovered if both spectra with and without crystals are measured accurately and with good statistics. However, in practice obtaining a small difference from two large numbers has always been tricky. For SAXS, it is difficult to measure beam intensity accurately because of the decaying and fluctuating synchrotron light intensity at the ring-exit and the limited accuracy of common intensity monitoring methods. The subtraction could, therefore, be arbitrary. In correcting the background for spectra like the dashed curve in Fig. 2, slight over-subtraction is rather possible, resulting in an apparent peak regarded as the dominant 'spinodal decomposition' wavelength for the early stages of crystallization. As a matter of fact, clean and stand-alone peaks were never reported in SAXS literatures, they all appeared in certain forms of 'shoulder' intensity, similar to that of the dashed curve in Fig. 2. Through comparing the features in SANS and SAXS spectra, we thus speculate that the SAXS peaks for the early stage crystallization are due to the background over-subtraction. The validity of this speculation, however, needs to be examined with further experiments.

As discussed above, features of similar length scales but with higher contrast with the matrix could result in equivalent scattering intensity at a much lower volume fraction. That offers an alternative picture for resolving the difficulties in bridging the length scale gap between the scattering and the optical microscopy: the scattering during the early stage is attributed to isolated individual lamellae, which could be microns apart while giving scattering features similar to features regarded as SD. While this study is carried out on solutions, the speculations on melt crystallization phenomena based on the analog in scattering features need to be tested experimentally.

4. Conclusion

We have learned several things from the current SANS study of polyethylene crystallization from solution. (1) The detection sensitivity of the volume fraction degree of crystallinity is estimated to be 10^{-5}. (2) There is no evidence of diverging or spinodal-decomposition-like density fluctuations in polymer crystallization from solution. (3) By comparing the SANS spectra in this study and the literature SAXS data, it is speculated that the scattering intensity peak in the latter, which is regarded as the signature of the 'spinodal decomposition' mechanism, is a result of the background over-subtraction. The data in this study support the nucleation and growth mechanism for polymer crystallization from solution.

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