

Polymer communication

Early stages of nucleation and growth in melt crystallized polyethylene

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ABSTRACT

Time-resolved synchrotron small angle X-ray scattering (SAXS) was used to investigate the early stages of crystallization in melt crystallized polyethylene. Classic Gibbs nucleation or density fluctuation theory can be used to describe the primary nucleation mechanism. At 110 °C, no signal of crystallization can be detected by SAXS for 30 min. When it is lower than 110 °C, the low q scattering intensity ($0.008 < q < 0.03 \text{ \AA}^{-1}$) begins to upturn, and the primary nucleation process starts. The measured fractal dimension of the critical nuclei is in the vicinity of 3 which is close to the prediction of classic Gibbs nucleation theory. The growth rate of density fluctuations $R(q)$ at different scattering vector q for different temperatures was obtained by analyzing the increase of scattering intensities. The results show that the growth rate of density fluctuation gets much bigger with the decrease of the isothermal crystallization temperature, but there is no signal of spinodal decomposition mechanism, in which there should be a linear relationship between $R(q)/q^2$ and q^2 .

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1. Introduction

Generally speaking, the polymer crystallization process can be divided into three basic regimes; i.e., primary nucleation, secondary nucleation and growth, and secondary crystallization, respectively. If impurities or nuclei agent are not present, it is necessary for primary nucleation to occur first so a crystal can develop. After the formation of crystal nuclei, additional polymer chains will diffuse to the growth front and crystallize further. This regime is usually called secondary nucleation and growth. In polymer systems, the spherulite growth is a macroscopical volume-filling process where crystallization can continue microscopically in the amorphous regions between lamellae, this time regime is usually called secondary crystallization. Lauritzen and Hoffman studied the mechanism of secondary nucleation [1,2], and then lots of other studies have also been focused on this topic [3–9]. Strobl provided some new ideas and experiments in the past twenty years, and proposed that the pathway for the growth of polymer crystallites includes an intermediate metastable phase [10], which suggested a thin layer with mesomorphic structure between the lateral crystal face and the melt. Still, what happens before

secondary nucleation, i.e., the mechanism of primary nucleation is still not understood very well.

Three primary nucleation theories, i.e., classic Gibbs nucleation, spinodal-assisted nucleation, and density fluctuation theory are proposed in the literatures [11–15]. Classic nucleation theory was pioneered by Gibbs, based on the growth of nuclei with final equilibrium composition which are greater than a certain “critical size” determined by the balance between volume transition and interface formation. Theoretical aspects of the evolution of such systems were studied by Langer, Schwartz and others [16,17], and computer simulations revealed the formation and growth of clusters with varying shape and compactness. The spinodal-assisted crystallization was studied by Kaji et al. [12] and Olmsted et al. [13] both experimentally and theoretically. They have studied structural evolution of poly(ethylene terephthalate) (PET) prior to crystal nucleation, and they found a peak in SAXS appearing before there are any signals in DSC, macroscopic density and WAXD. So they suggested that it is the change of chain conformation, i.e., chain conformation fluctuations that induce this spinodal decomposition (SD) type phase separation based on Doi’s dynamic theory for the isotropic-nematic phase transition in liquid crystalline polymers. And Cahn-Hilliard-Cook (CHC) equation was used to analyze their data. However, it is a one-component system, physically it is not possible to take a second derivative of Gibbs free energy with respect to composition to obtain any spinodal point. And the time evolution of Kaji et al.’s SAXS profiles in the low q

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region was not consistent with CHC equation, either. Muthukumar et al. investigated the molecular mechanisms of nucleation and growth, and the accompanying free energy barriers during the very early stages of crystallization. They addressed the question of the growth of density fluctuations in the primordial stage, birth of baby nuclei, which then mature into larger ones, and spontaneous selection of finite equilibrium lamellar thickness. Their results showed that there is no evidence for spinodal decomposition and also explained previous experiments successfully.

In this manuscript, PE homopolymers were used as a model system to investigate the early stages of nucleation and growth.

2. Experimental section

PE was prepared by saturation of mono-dispersed anionically polymerized polybutadiene (PB) with polydispersity index less than 1.1. Polymerizations were initiated with *n*-butyllithium in rigorously purified cyclohexane at 40 °C under purified nitrogen, yielding a PB product with 88% 1,4- and 12% 1,2- units which were determined by ¹H NMR (nuclear magnetic resonance). The weight-average molecular weight of PB is 52 kg/mol (GPC was conducted at room temperature with THF as solvent and polybutadiene as standard). ¹H NMR analysis indicated that the conversion of unsaturated bonds is greater than 99%. After saturation, hot polyethylene solution was precipitated into cold, stirred methanol. Then hydrogen peroxide and hydrochloric acid were added to the solution to remove the Ni catalyst. After washed with hydrogen peroxide and hydrochloric acid three times, residual solvent was removed by drying to constant weight in a vacuum oven at 70 °C. The radius of gyration of PE was estimated to be about 11 nm [18]. The melting point of the polyethylene measured by DSC is 105 °C, and this is consistent with the experimental results of Bates [19]. Synchrotron SAXS was used to study the kinetics of primary nucleation in polyethylene (PE) homopolymer system. The specimens were encased in ring-like copper spacer with capton window on both sides, heated to 130 °C for 10 min, which is well above 110 °C, and quenched to different isothermal crystallization temperature. The SAXS profiles from the temperature quenched melt were then monitored as a function of isothermal crystallization time. We present data obtained from temperature quenched PE melt labeled as PE-108, PE-109 and PE-109.5, in which the number behind PE denotes the isothermal crystallization temperature. For example, PE-108 denotes that the isothermal crystallization temperature is 108 °C.

Time-resolved synchrotron SAXS experiments were conducted at BL16B beam-line on the storage ring of the Shanghai Synchrotron Radiation Facility (SSRF) at Shanghai (China). The incident X-ray wavelength, λ is 1.54 Å. And the sample-detector-distance (SDD) is 505 cm. So the scattering vector, ($q = 4\pi\sin(\theta/2)/\lambda$, where θ is the scattering angle) covers the range between 0.008 and 0.056 Å⁻¹ (Cow tender was used to calibrate the scattering profile). A Mettler hot stage was used to heat the samples wrapped in 50 μm ring-like copper spacer with capton windows on both sides in the X-ray beam. The scattered X-ray intensity was normalized to the primary X-ray beam intensity using the signal of an ionization chamber placed in front of the sample.

3. Results and discussion

Fig. 1 is the SAXS profiles of PE at different temperatures (130 and 110 °C, respectively) and different annealing times (1, 10, 20, 30 min, respectively) taking into account of the effect of incident beam intensity. It shows that the curves almost superimpose for the PE hold at 130 °C and at 110 °C (Corrected intensity at 130 °C is a little larger than that at 110 °C), which means the amplitude of

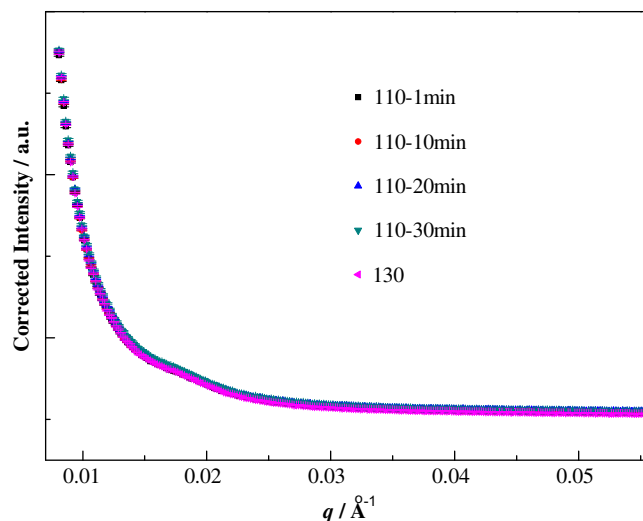


Fig. 1. One dimensional SAXS curves of PE at 130 °C and at 110 °C for different annealing times.

density fluctuation is very small compared with the scattering from amorphous part of PE plus capton window and air. In principle, we can subtract scattering from capton window and air to get the scattering information from both amorphous part and crystal part of PE, but the topic of this manuscript is to study primary nucleation mechanism, the scattered intensity from amorphous part of PE can be considered as background scattering in our system and should be erased. The detailed data reduction procedure is listed in the next section. Fig. 1 clearly demonstrates that the small development of SAXS profile in the first several minutes will be crucial for us to deduce the primary nucleation mechanism when the sample is held at proper isothermal crystallization temperature. Muthukumar et al. simulate the crystallization process in polymer, and found out nuclei or "baby nuclei" was formed by density fluctuation. In his simulation work, the size of "baby nuclei" is just the size of several segments, so the amplitude of density fluctuation in the early stage of primary nucleation should be very weak. What is more, the scattering profiles do not change at all after isothermal crystallization at 110 °C for different times, which means there is no crystallization or this process is so slow that it cannot be observed in our experimental time range. In other words, from the density fluctuation induced primary nucleation model point of view, the energy barrier for the primary nucleation is so large that density fluctuation cannot help the system to overcome it, or from the point view of nucleation and growth model, the bulk free energy of crystal nuclei cannot compensate the interfacial free energy loss.

Fig. 2 is the time evolution of SAXS profiles when isothermal crystallization are conducted at 109.5 °C and at 108 °C, where the corrected scattering intensity I is plotted as a function of the scattering wave vector q . Because $T_{trans} + A_{abs} = 1$, here T_{trans} and A_{abs} are the transmittance and absorptency of the samples, respectively. A_{abs} is determined by the wavelength of the incident X-ray, the thickness, structure and elements in the sample. In the very early stages of primary nucleation, A_{abs} does not change, so T_{trans} can be assumed to be a constant. The corrected scattered X-ray intensity can be obtained through [20]

$$I_{corr}(t, q) = \left[I_{scat}(t, q) - \frac{T_{melt} \cdot I_{inc}(t)}{T_{scat} \cdot I_{inc}(melt)} \cdot I_{melt} \right] \cdot \cos^4 \theta,$$

where $I_{scat}(t, q)$ and $I_{inc}(t)$ are the scattered and incident intensity at time t (min) during isothermal crystallization, while I_{melt} and $I_{inc}(melt)$ are the scattered and incident intensity in the melt state at

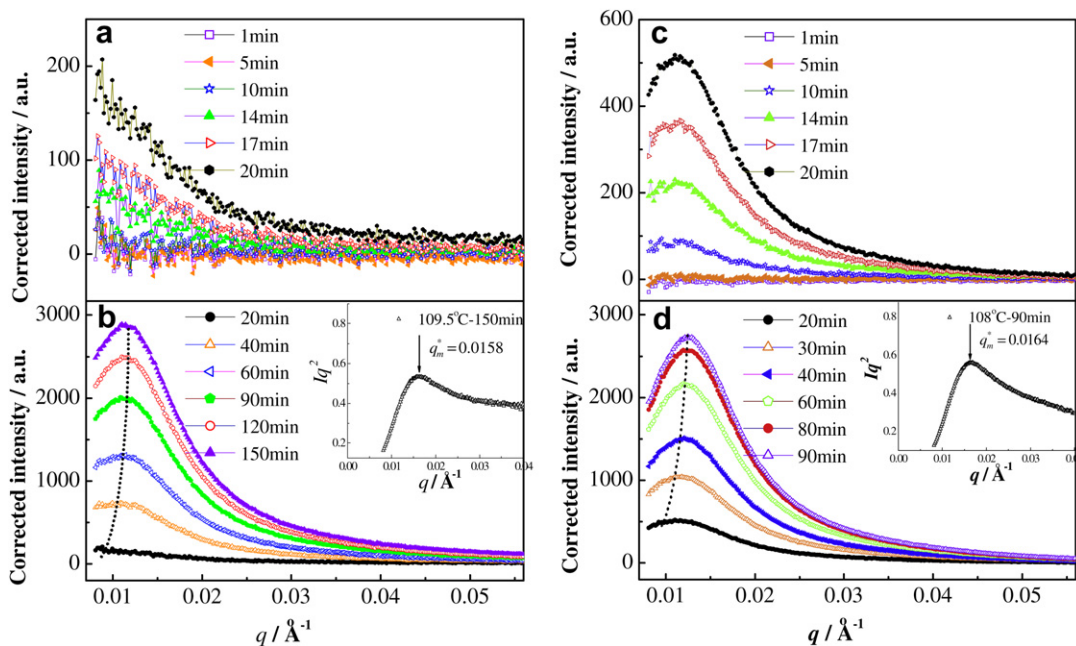


Fig. 2. Corrected intensity SAXS curves of PE after subtraction of the intensity of the melt sample. The sample was isothermal-crystallized at 109.5 °C for (a) 1-to-20min and (b) 40-to-150min, and 108 °C for (c) 1-to-20min and (d) 20-to-90min. The insets in figure (b) and (d) are the Lorentz-corrected SAXS profiles evaluated from 1D-SAXS profiles for the melt-crystallized sample at 109.5 °C for 150 min and 108 °C for 90 min, respectively. q_m^* denotes the scattering vector corresponding to the reciprocal of long period.

110 °C, respectively. T_{melt} and T_{scat} are the transmittance of the sample at 110 °C and at isothermal temperature for different times, which can be considered as constant in the early stages as has been stated before. θ is the scattering angle, and $\cos^4\theta$ is used for solid angle correction. Because I_{melt} contains the scattering information of amorphous part of PE, capton windows and air, and it is subtracted from $I_{scat}(t,q)$, the corrected scattering intensity $I_{corr}(t,q)$ only reflects scattering information from crystallization part of PE samples. Note that I_{melt} at 110 °C is used instead of that at 130 °C because the difference of thermal fluctuation between 110 °C and 130 °C can smear the tiny density fluctuation in the very early stages of primary nucleation. Fig. 2(a) shows that there is no peak in the scattering curves in the very early stages, which clearly demonstrate that the primary nucleation is not a spontaneous process with no energy barrier (the q range between $0.008 < q < 0.056 \text{ \AA}^{-1}$ is used here to be consistent with previous literature [12]), and there is no preferred maximum growth dimension and consequently there is no scattering peak in the q range. When the isothermal crystallization temperature is just held at 109.5 °C, the corrected scattering intensity is almost zero at the very beginning due to energy barrier for primary nucleation and the tiny density fluctuation cannot overcome it. Then the low q scattering intensity begins to upturn which indicates the generation of the critical crystal nuclei. It can be explained by classic Gibbs nucleation or density fluctuation theory. According to the classic Gibbs nucleation theory, the bulk free energy of crystal nuclei larger than a critical size can compensate the surface energy loss and grow in size thereafter; while according to density fluctuation induced primary nucleation theory, "baby nuclei" are formed by density fluctuation, and compete with each other for further growth.

Note there is no scattering peak observed in the early stages, which is not the same as Kaji's work on crystallization of PET who reduced his data by subtracting the scattering intensity at the first minute in the isothermal crystallization process, which may diminish the tiny density fluctuation information in the very early stage of primary nucleation.

After 20 min, the scattering intensity continues to grow and a well defined peak emerges after about 40 min, which means lamella begins to appear, as can be seen from Fig. 2(b). The scattering intensity continues to increase and the peak position gradually shifts to larger q , until a final equilibrium value is obtained. The isothermal crystallization SAXS profiles at 108 °C are very similar to that at 109.5 °C. Fig. 2(c) shows that when the isothermal crystallization temperature decreases to 108 °C, the corrected scattering intensity increases much faster than that at 109.5 °C. In the very early stages, there is no scattering peak in the scattering curves. A well defined peak emerges after only 8 min. Similar to Fig. 2(b), Fig. 2(d) shows that the corrected scattering intensity continues to increase and the peak position gradually shifts to higher q , until the length of the corresponding equilibrium long range order is achieved. The insets in Fig. 2(b) and (d) show that the long period L can be derived from the location of the maximum of the Lorentz-corrected scattering intensity distribution Iq^2 . The values of L are 38 nm at 108 °C and 40 nm at 109.5 °C, respectively. The difference of long period is only 2 nm for 1.5 °C temperature difference, which agrees well with the experimental results of Strobl [21–23].

Fig. 3 is the dependence of growth rate of density fluctuations on the square of scattering vector at 109.5 °C and 108 °C, respectively. The inset in Fig. 3(a) shows that the time evolution of the corrected scattered intensity at $q = 0.0088 \text{ \AA}^{-1}$ give two different regions; in the former stage the corrected scattered intensity increased exponentially, and in the latter stage it leveled off. The exponential increase of corrected scattering intensity at a scattering vector q in the early stage was studied to obtain the relation between the growth rate of density fluctuations and the square of scattering vector q^2 . $I = I_n \exp[R(q)t]$ was used to fit the data in Fig. 2 before the characteristic "spinodal peak" shows up, where I_n and $R(q)$ were two variables. Fig. 2 clearly shows that there is no "spinodal peak" in the early stage of primary nucleation at all. It may be caused by two possible reasons, i.e., there should be no peak at all according to classic Gibbs's nucleation or density fluctuation theory; or there is a peak inside SAXS beam stop. Even if there is

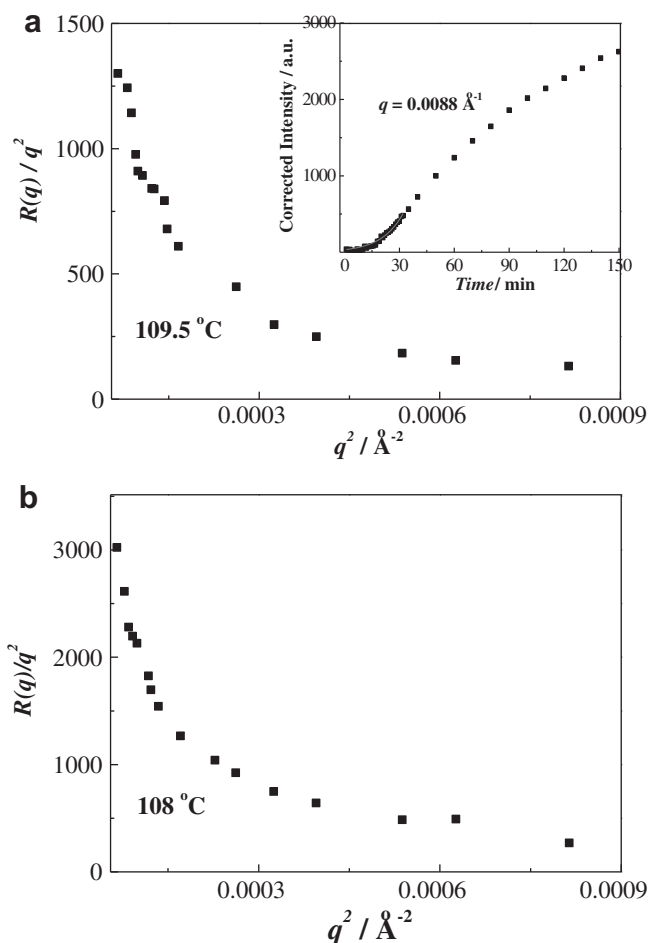


Fig. 3. Dependence of growth rate of density fluctuations $R(q)/q^2$ on the square of scattering vector at (a) 109.5 °C and (b) 108 °C. The inset in figure (a) is the time evolution of scattering intensity at $q = 0.0088 \text{ \AA}^{-1}$, and the solid line denotes best exponential fit in the initial stage.

a "spinodal peak" inside beam stop, it should stay at constant q first and then move to the left (smaller q) to grow bigger in size, but Fig. 2 shows it moves to the right larger q , which is the spherulites filling process instead of spinodal process. According to the spinodal decomposition (SD) mechanism, Cahn-Hilliard plots, $R(q)/q^2$ versus q^2 should be linear. However, as can be seen in Fig. 3(a), when PE was isothermally crystallized at 109.5 °C, there is no simple linear relationship between $R(q)/q^2$ and q^2 . $R(q)/q^2$ decreases monotonically with q^2 , and then levels off. It is similar to Muthukumar's simulation works on the early stage of polymer nucleation and crystallization. When the isothermal temperature decreases to 108 °C, the characteristic of the curves is almost the same, except that the growth rate of density fluctuation is much faster compared with that at 109.5 °C because of the lower energy barrier for primary nucleation at 108 °C. Although all of these phenomena demonstrate that crystal nucleation is a very complicated process, one conclusion can be made: primary nucleation is not a spinodal decomposition mechanism at all.

A close examination of the scaling between nuclei size and its mass is helpful to clarify the primary nucleation mechanism. Chen et al. [24] used SAXS to probe the primary nucleation event. The development of the crystal nuclei size as a function of crystallization time was obtained with the assumption that the primary nuclei of polymers are rod-like. Strobl et al. used time- and temperature-dependent SAXS-experiments to determine the effect of octane and

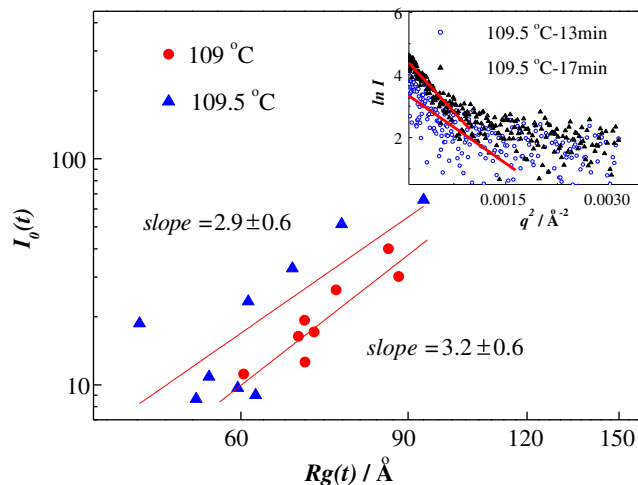


Fig. 4. Log-log plot of R_g at given time versus I_0 at 109 °C and 109.5 °C, respectively, obtained from the Guinier analysis of data in Fig. 2. The inset is the best fit of $\ln I$ versus q^2 when the sample was isothermal crystallized at 109.5 °C for 13 min and 17 min.

butene co-units on the lamellar structure and the melting properties of polyethylene. They got the equations describing lamellar structure parameters and melting points of polyethylene-co-(butene/octene)s [21]. Also they used interface distance distribution function at middle and high q region to get the inter-lamellar thickness [22,23]. In this manuscript, we used the synchrotron SAXS to study the early stage primary nucleation kinetics at low q region before inter-lamellar correlation was formed [21–23]. And Guinier analysis can be used here to investigate the size evolution of critical nuclei in the first several minutes in the isothermal crystallization process when no particle shape can be distinguished [25]. According to this model, the scattered intensity is given by $I_{corr}(t, q) = I_0(t, 0) \exp(-q^2 R_g^2(t)/3)$ when $qR_g < 1$, where $I_0(t, 0)$ and $R_g(t)$ are two variables. $I_0(t, 0)$ is the susceptibility and is proportional to the average mass of the critical nuclei, $R_g(t)$ is the average radius of gyration of the nuclei at time t . Fig. 4 is the log-log plot of $R_g(t)$ versus $I_0(t, 0)$ during the first several minutes in the early stages of isothermal crystallization process, the inset shows best fit of $\ln I$ versus q^2 when the sample was isothermal crystallized at 109.5 °C for 13 min and 17 min. The linear behavior of $\ln I$ versus q^2 is comparatively good as can be seen in the inset. The fractal dimension of the critical nuclei can be obtained from the linear fit of $\log_{10} I_0(t, 0)$ versus $\log_{10} R_g(t)$ in Fig. 4. It can be found that the fractal dimension of critical nuclei is in the vicinity of 3 [11]. The large error bar here partly comes from the limited q range to satisfy $qR_g(t) < 1$ in the Guinier analysis; partly comes from the reason that new nuclei can still be generated and coalesce with pre-formed larger ones. However, at least one conclusion can be made, the crystal nucleation of melt-crystallized polyethylene is not a spinodal decomposition mechanism, and it follows either classic Gibbs nucleation theory, or Muthukumar's density fluctuation model.

4. Conclusions

Synchrotron small angle x-ray scattering was used to study the early stages primary nucleation of crystallization in melt crystallized polyethylene. By analyzing the scattering profiles using Guinier analysis, the susceptibility $I_0(t, 0)$ and size R_g of crystal nuclei at given time can be obtained. The fractal dimension of the crystal nuclei is in the vicinity of 3, which indicates that classical Gibbs nucleation [11] or density fluctuation [14,15] suggested by Muthukumar is responsible for the primary nucleation process.

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