

Early Stage Crystallization in Poly (Ethylene-Co-Hexene) by SAXS/WAXD, DSC, OM and AFM

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INTRODUCTION

Recently, there have been intensive studies of exploring the behavior of the early stages of polymer crystallization from solution, glassy state, and molten state. Due to the small volume fraction of the crystals formed in the early stages of crystallization, it makes this investigation difficult because the detection limits of the existing probing techniques are generally low.¹ For example, when single crystals form in dilute solutions, polymer chains may be collapsed into a globular state first.² It is also supported by the molecular simulation work of Liu and Muthukumar.³ However, the experiment is very difficult to carry out.

Simultaneous synchrotron small-angle X-ray scattering (SAXS)/wide-angle X-ray diffraction (WAXD) techniques have been recently used to probe the early stages of crystallization in different polymers such as polyethylene⁴ and polypropylene¹ from the molten states, and poly (ethylene terephthalate)⁵ and poly(aryl ether ketone ketone)⁶ from the quenched glassy state. Even though the experimental results showed that noticeable short-range density fluctuations (10 nm-50 nm) by SAXS are detected prior to the occurrence of three-dimensional crystal formation (< 2 nm) by WAXD, the crystallization process still follows classical nucleation and growth at the early stages.^{1,4} WAXD is proven to have a detection limit of 0.5 to 1 volume percent of three-dimensional ordering crystals, SAXS can provide a lower detection limit (~ 0.1 %) that are more sensitive to the mesoscopic structural changes. By analyzing the time-resolved inter-chain distance in the super-cooling molten state (amorphous) during crystallization may provide further information to understand the crystallization in early stages. In this study, we have focused on the early stage crystallization behavior of a copolymer: poly(ethylene-co-hexene) (PEH with 3 mole % of hexene monomer) in the molten state using the time-resolved SAXS/WAXD techniques. Differential Scanning Calorimetry (DSC) was used to measure the thermal behavior; optical microscope (OM) and atomic force microscopy (AFM) were applied to observe the quenched morphology in real space to compliment the SAXS/WAXD results.

EXPERIMENTAL

Poly(ethylene-co-hexene) (PEH) was supplied by ExxonMobil Chemical Company⁷. It had a weight-average molecular mass, Mw, of 110 K g/mol. The content of hexene in polymer chain was ~3 mole %. The branch density ρ was about 1 branch per 57 backbone carbons. The equilibrium melting temperature of PEH is ~145 °C via thermal analysis.

Time-resolved simultaneous SAXS/WAXD measurement was performed at the beamline X27C in National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). Isothermal crystallization temperatures of 117.8 (± 0.2) °C and 113.5 °C were chosen for this study. The detailed experimental setup of SAXS/WAXD and dual-cell temperature jump apparatus has been described in previous publications.^{1,4,7}

Perkin-Elmer DSC7 was used to follow the isothermal crystallization in PEH. The same thermal condition was also used for the X-ray measurements. The DSC scanning curves were collected at a heating rate of 10 °C /min.

The crystal nucleation and growth process was followed by a Nikon optical microscope equipped with a Kodak Megaplug CCD camera. The crystallization conditions were also similar to the conditions in X-ray and DSC measurements. The quenched samples after crystallization at 114 °C for 30 min and 118 °C for 120 min were characterized by AFM (DimensionTM 3100 from Digital Instruments).

RESULTS AND DISCUSSION

Time evolution profiles of the scattering invariant (from SAXS), Q , the measured crystallinity (from WAXD), X_c , the characteristic inter-chain distance in the amorphous phase (from the WAXD amorphous peak), D-spacing, and the sample temperature were illustrated in Figure 1a for 113.5 °C and Figure 1b for 117.8 °C. Similar to the previous experimental observations, definitive density fluctuations with relatively large scale (30 nm – 40 nm) are seen prior to the measurable three-dimensional ordering formation of crystals (scale < 1 nm). The time lag becomes quite significant at the higher temperature (117.8 °C). There are two features in Figure 1 that need to be discussed. First, the temperature profile at the very initial stage was not exactly “isothermal”, as it takes time for the sample to reach to an equilibrium temperature after the temperature jump. However, it is evident that just before the sample reaches the programmed temperature, the structure of the polymer chains in this “supercooled” state is quite different from that in the original molten state. It is seen that a significant decrease of the inter-chain distance in the amorphous phase occurs. Second, even as the sample reaches the programmed temperature, the D-spacing continuously decreases before the detection of density fluctuations by SAXS. It is thought that the D-spacing decrease in this stage is an indirect evidence that densifications at the very local domains takes places even before the SAXS detection of density fluctuations. We propose that a network-like structure may be formed in the supercooled melt due to the relatively dense cross-linking nuclei, which causes the whole net to contract during cooling process. The crosslinkers may be due to the primary nuclei.

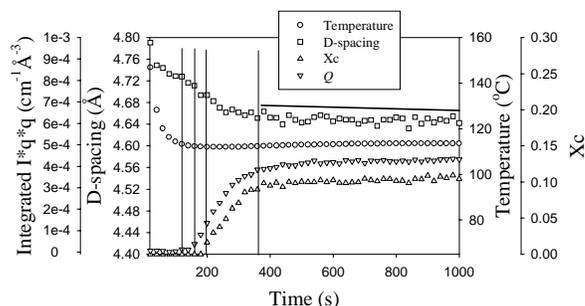


Figure 1a. Time evolution of the scattering invariant, crystallinity, D-spacing and sample temperature (isothermal crystallization temperature is 113.5 °C).

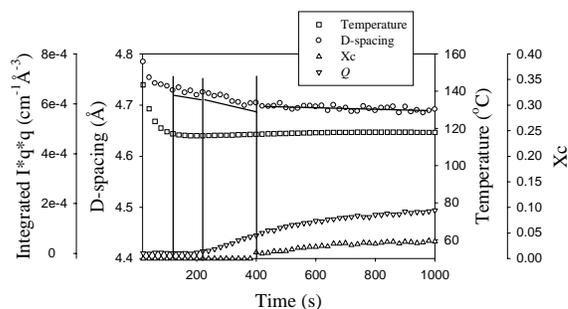


Figure 1b. Conditions are the same as Figure 1a but temperature is set at 117.8 °C (Relative standard deviation: Q (2 %), X_c (1 %), D-spacing (1 %)).

Figure 2 shows that prolonged crystallization at 117.8 °C only

increases the crystallinity from 3 % (1000 s) to 5 % (6200 s) and the D-spacing of the amorphous phase decreases continuously. The subsequent cooling process can cause a rapid decrease in D-spacing and a rapid increase in crystallinity, indicating a large local density change during crystallization.

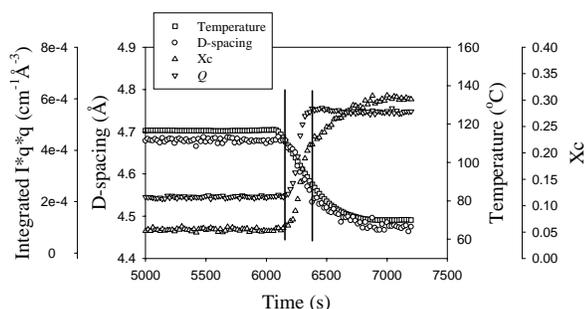


Figure 2. Conditions are the same as Figure 1a but scanned during isothermal and subsequent cooling processes.

DSC curves during melting of PEH are shown in Figure 3, which are obtained from isothermally crystallized samples at 113.5 °C for 2000 s and 117.8 °C for 6200 s. At the higher crystallization temperature, the crystallinity is lower (lower heat flow) but the crystal thickness is larger (higher melting point). These results are also consistent with the lower crystallinity from WAXD and the larger long period from SAXS at high temperatures.

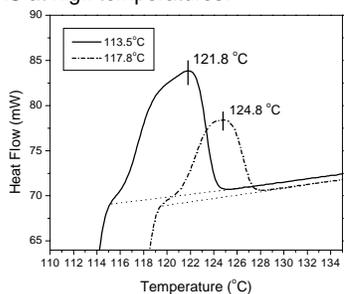


Figure 3. DSC melting thermograms after isothermal crystallization.

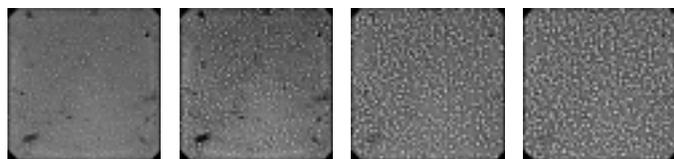
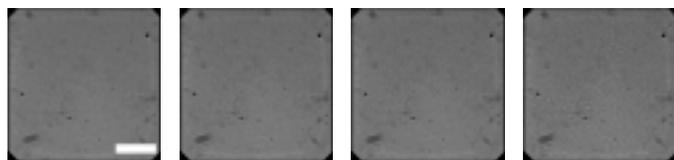


Figure 4. Optical micrographs of PEH isothermally crystallized at 118 °C (top: 0 min; 12 min; 16 min; 24 min. Bottom: 32 min; 40 min; 80 min; 122 min. White bar represents 40 μm).

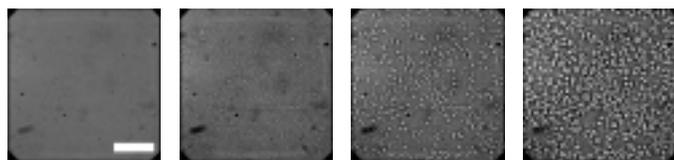


Figure 5. Optical micrographs of PEH isothermally crystallized at 114 °C (5 s; 120 s; 240 s; 480 s. White bar represents 40 μm).

Optical microscope was used to measure the nucleation and growth information of PEH in real space. Figures 4 and 5 shows micrographs of PEH during isothermal crystallization at 118 °C and 114 °C, respectively. The crystals formed are very similar to the central sheaf-like part of a typical spherulite. Within the experimental timeframe, the branching and splaying types was not observed.

Figure 6 shows the average sizes of PEH crystals developed with time by optical microscopy. A linear increase of the size with time is seen in the early stages of crystallization. The growth rates in the early stages of crystallization at 114 °C and 118 °C are calculated as 0.82 (± 0.01) $\mu\text{m}/\text{min}$ and 0.088 (± 0.001) $\mu\text{m}/\text{min}$, respectively. When the growing crystals impinge upon each other, the crystal sizes become almost constant. The final average sizes are 6.5 (± 0.05) μm at 114 °C and 8.0 (± 0.05) μm at 118 °C.

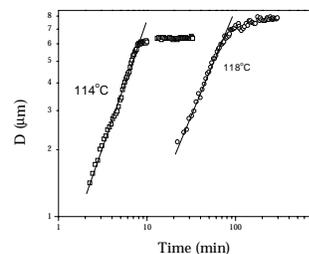


Figure 6. Crystal sizes of PEH with time by OM (Error bar $\sim 2\%$).

AFM micrographs shown in Figure 7 reveal the morphology on the surface of PEH samples quenched after isothermally crystallization at 118 °C (120 min) and 114 °C (30 min). The central sheaf-like part of the spherulites can be clearly identified under both temperatures (more clearly at high temperature). Lamellae form stacks and extend outward from the spherulite center. After quenched by the ice water, the not isolate ring-banded structure can be seen (clearly seen with sample at 114 °C), which surrounds the original spherulitic core.

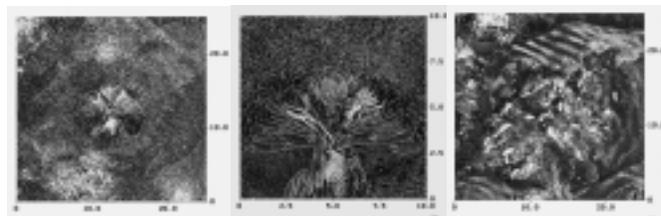


Figure 7. AFM micrographs (phase contrast) (118 °C for 120 min; 118 °C for 120 min at different scale; 114 °C for 30 min).

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