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Temperature dependence of crystallization behavior in polyethylene with precisely spaced branches as revealed by time resolved x-ray scattering measurement

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1 Introduction

For the improvement of mechanical properties of linear low density polyethylene (PE), it is important to control the length of short chain branches (SCB) and their intermolecular distribution, i.e., chemical composition distribution, as well as the "intramolecular" distribution of SCBs. Wagener and co-workers have succeeded in synthesizing PEs with precisely spaced branches by acyclic diene metathesis (ADMET) technology [1]. The crystallization behavior of ADMET-PE has been poorly understood. In this work, we observe the crystallization behavior of polyethylene with ethyl branches placed on every 21st carbon (EB21) using synchrotron X-ray scattering measurement [2].

2 Experiment

Combined SAXS and WAXS measurements were performed at BL-15A and BL-6A. The detectors used for data acquisition were PILATUS 300K and 100K (DECTRIS Ltd., Switzerland) for SAXS and WAXS measurement, respectively. Samples were covered by thin mica plates and then were placed in a temperature-controlling stage (Linkam Scientific Instruments Ltd., THMS-600). Samples were initially held at 100 °C for 5 min, and then the temperature was dropped to the isothermal crystallization temperatures at a rate of 100 °C/min.

3 Results and discussion

The changes in SAXS and WAXS pattern during isothermal crystallization of EB21 at 15 ºC and 21 ºC are shown in Figure 1. It is clearly found that the crystallization behaviors in these temperatures are quite different. At 15 ºC, a hexagonal phase of PE was transiently formed at the initial stage of the crystallization, followed by the transformation of the crystal structure (Figure 1(a)). In the SAXS profiles, a single peak (long period) was appeared at the initial stage of the crystallization, and then another peak derived from the initial peak was emerged at lower q after about 100 sec (Figure 1(b)). Combined with the results of TEM observation [2], this indicates that lamellar thickening with an incorporation of one ethyl branch into the lamellae occurs during the crystallization.

On the other hand, at 21 ºC, a triclinic crystal of PE was directly formed from the molten state after an induction period (Figure 1(c)). In the SAXS profiles, only one peak was observed (Figure 1(d)). The lamellar thickness evaluated from the WAXS and SAXS profiles was about 65 Å. This indicates that two ethyl branches are incorporated into the lamellae, since the interval length between neighboring SCBs in the trans zigzag conformation is 25.4 Å. From these results, the degree of ethyl branch inclusion into the lamellae is influenced by the crystallization temperature, which strongly impacts the crystal structure.

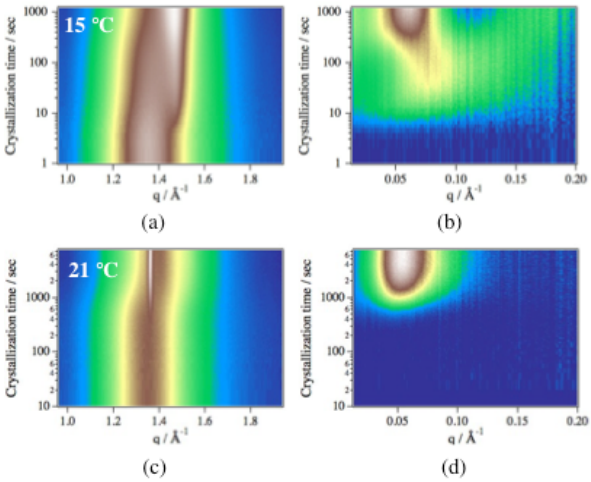

Figure 1 Time evolution of WAXS (a, c) and SAXS (b, d) profiles of EB21 under isothermal crystallization at 15 ºC and 21 ºC. Reprinted with permission from ref 2. Copyright 2013 American Chemical Society.

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References

[1] Smith, J. A et al. *Macromolecules* **2000**, 33, 3781.
[2] Matsui, M et al. *Macromolecules* **2013**, 46, 4438.

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