

## Crystallization of polyethylene with precisely spaced branches

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### Introduction

We have investigated the crystallization behavior of polyethylene with precisely spaced branches. The formation of a transient ordered mesophase and subsequent crystallization through packing optimization, quite similar to rotator phase formation in n-alkanes, was observed when EB21 (PE with ethyl branches at every 21<sup>st</sup> backbone carbon) and HB21 (PE with hexyl branches at every 21<sup>st</sup> backbone carbon) were isothermally crystallized at specific crystallization temperatures [1]. The presence of a periodic disturbance in the polymer chains plays an important role in the formation of transient ordered mesophase even in a flexible polymer, and its kinetic pathway is strongly affected by the size of the branch. Furthermore, it has been clarified that the crystalline form of EB21 sensitively depends on its crystallization temperature, while that of HB21 does not show any temperature dependence.

In this study, crystallization of EB21 was observed at various isothermal crystallization temperatures in detail.

### Experimental

#### Sample preparation

EB21 were synthesized by ADMET polymerization technology with ethyl branches precisely spaced on every 21<sup>st</sup> carbon (EB21). The weight-averaged molecular weight ( $M_w$ ) and the distribution ( $M_w/M_n$ ) were  $M_w = 33\ 000$  and  $M_w/M_n = 2.0$ , respectively.

#### Combined SAXS-WAXS measurement

SAXS-WAXS measurement was performed at BL-15A. A CCD coupled with an X-ray image intensifier (Hamamatsu Photonics) and PILATUS (Rigaku) were used for SAXS and WAXS detectors, respectively.

#### Microbeam WAXS measurement

Microbeam WAXS measurement was performed at BL-4A. A CCD coupled with an X-ray image intensifier was used for the detector. The beam size was approximately  $5\ \mu\text{m} \times 5\ \mu\text{m}$ .

### Results

Figure 1 shows WAXS intensity profiles of EB21 at various crystallization temperatures. Below 21 °C, diffraction from hexagonal phase, which was previously observed as a transient phase, was formed while other polymorphs appeared at the temperature above 21 °C. At 21-28 °C, two new polymorphs (here, we call them as form I and form II) were observed. Form I was mainly formed at 21 °C, while form II was mainly formed at 25-

28 °C. At 25 °C, both form I and II coexisted; their spatial distribution was measured by microbeam WAXS as shown in Fig. 2. It has been clarified that the form I exists at the central part of a spherulite while the form II exists at the peripheral region at 25 °C.

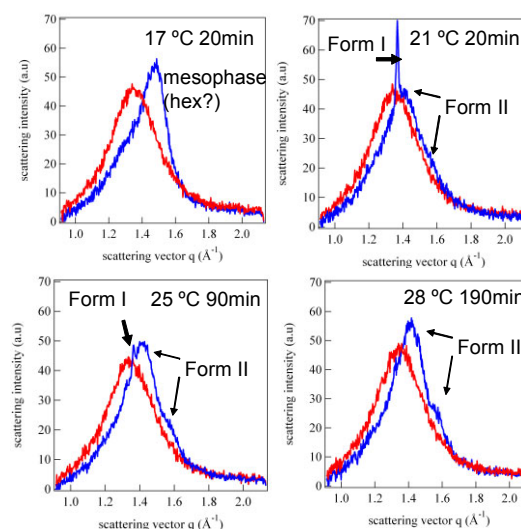


Figure 1: WAXS intensity profiles at various crystallization temperature.

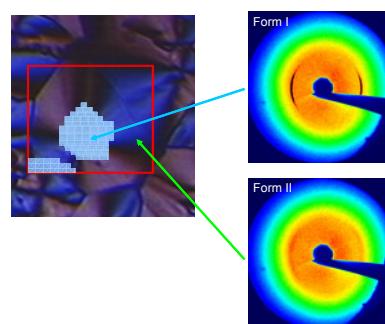


Figure 2: Result of microbeam WAXS. Red squared region is scanned region and form I appeared at light blue filled region.

### Reference

[1] Y. Nozue et al., *Macromolecules* **44**, 4030 (2011).

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