

## Crystallization of linear polyethylene bearing pendant carboxyl groups

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## 1 Introduction

Polyethylene (PE) is one of the most widely used commodity plastics with excellent chemical stability, light weight, and mechanical robustness. The chemical stability, however, makes it difficult to be recycled chemically. It has been found recently that PE with pendant carboxyl (-COOH) groups (PE-COOH) could be degraded into small molecules under mild conditions [1]. The degradation could be triggered by blue light irradiation in the presence of a Ce(II) catalyst and worked efficiently even on the polymer in the solid state.

For the practical application of PE-COOH and its degradation scheme, knowledge on the hierarchical crystalline morphology and its formation mechanism is mandatory. In particular, the effects of the pendant -COOH groups need to be clarified. Previous studies on PE-COOH have revealed that relatively bulky -COOH groups were expelled from the PE crystal lattice upon crystallization [2] and that -COOH in the amorphous phase formed hydrogen bonds (H-bonds). Therefore, it is crucial to evaluate the effect of inserting bulky pendant group and the effect of H-bonding interactions between pendant groups separately. However, most of the past works used PE-COOH synthesized by random radical copolymerization, which inevitably introduces alkyl branching, making it difficult to assess the effect of pendant -COOH insertion. In this study, we aimed to elucidate the effects of pendant group insertion and H-bonding on the hierarchical crystalline morphology of PE-COOH by using an alkyl branching-free sample synthesized by recently developed catalytic copolymerization method [3].

## 2 Experiment

PE-COOH was alkyl branching-free and had an  $M_w$  of 15.1 kg/mol and contained 5.7mol% -COOH groups per ethylene repeat unit. As a control polymer without H-bonds, the sample with -COOH groups capped by methylation (PE-COOMe) was synthesized from PE-COOH. Branching-free PE with a similar molecular weight ( $M_w = 28.0$  kg/mol) was also used as a control sample without pendant groups. Small-angle/wide-angle X-ray scattering (SWAXS) measurements were performed using BL-6A and BL-15A2 in KEK-PF.

## 3 Results and Discussion

Differential scanning calorimetry (DSC) studies revealed that both PE-COOH and PE-COOMe had substantially lower crystallization temperature, melting point ( $T_m$ ), and crystallinity ( $X_c$ ) compared to PE, indicating a significant hindering effect of pendant group insertion on crystallization of PE. Comparing PE-COOH

and PE-COOMe, PE-COOH crystallized slower than PE-COOMe. The H-bonding between -COOH groups had an additional hindering effect on the crystallization.

Fig. 1a and b shows the representative in situ SWAXS data during crystallization of PE-COOH. Here, the sample was quenched from 180°C to 100°C and annealed for 1 h. Then the sample was quenched to 25°C and annealed further. In the WAXS profiles, diffractions of PE crystals developed during the first annealing. Interestingly, the diffraction peaks grew further during the second annealing. That is, some components that were unable to crystallize at 100°C could crystallize at a lower temperature (25°C). SAXS showed two broad peaks, suggesting the coexistence of lamellae with larger long period formed at 100°C and those with smaller long period formed at 25°C. Fig. 1c compares the time evolution of  $X_c$  during the two-step annealing process for PE-COOH and PE-COOMe. Interestingly, PE-COOH showed higher crystallinity compared to PE-COOMe at 100°C. This suggests that the H-bonding between -COOH groups facilitated the formation of more crystals at a high temperature.

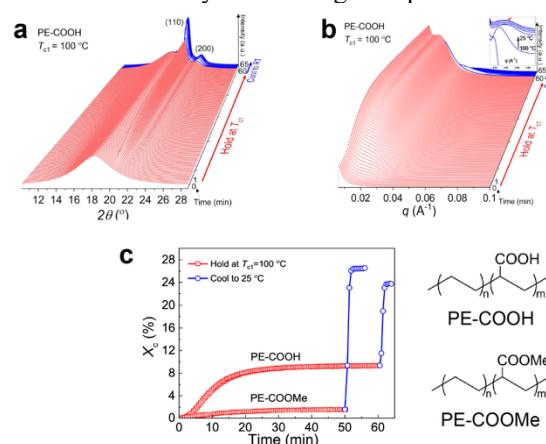


Fig. 1. (a) WAXS and (b) SAXS profiles of PE-COOH during the two-step annealing process. (c) Time evolution of crystallinity obtained from WAXS data.

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## References

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