The Non-equilibrium Nature of Flow-induced Nucleation in Isotactic Polypropylene

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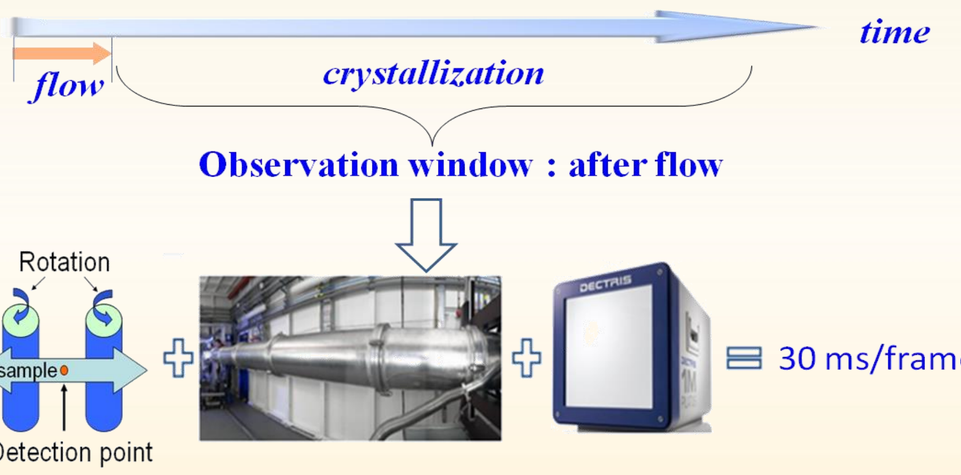
Introduction

As an extremely external driven and kinetics controlled process, flow-induced crystallization (FIC) of polymer is inevitably involved in industrial processing. Over past decades, great efforts have been dedicated to understand the formations of precursor and shish-kebab, the roles of molecular and flow parameters on nucleation. However, the non-equilibrium (NE) nature of FIC is relatively poorly understood.

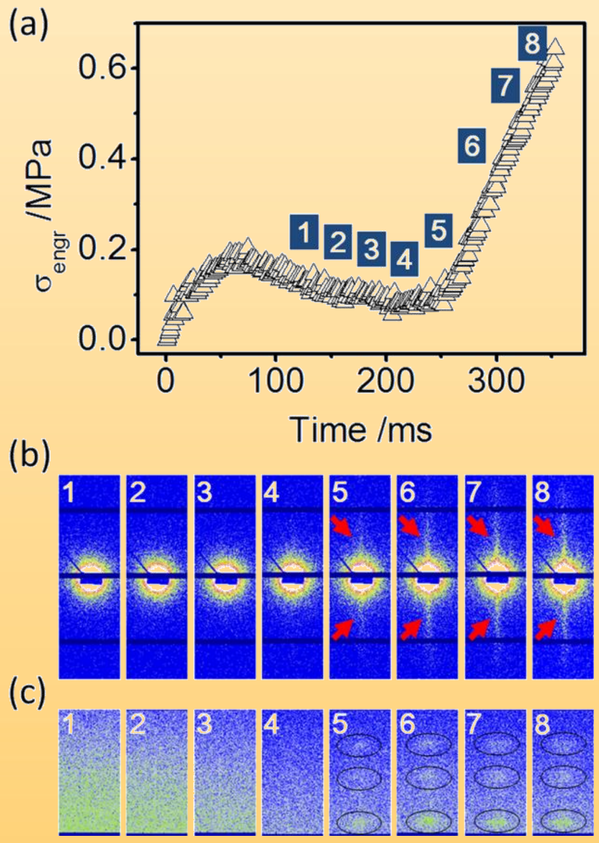
Based on classical nucleation theory, current entropic reduction model (ERM) of FIC treats external work as perturbation on the framework of equilibrium thermodynamics, which, however, obscures the NE nature of FIC. In this work, ultrafast time-resolved investigation under strong flow reveals a constant critical strain or time for nucleation in iPP melt in a wide temperature range. Our discovery contradicts the strain-temperature equivalence predicted by ERM but unveils the non-equilibrium nature of FIC.

Experimental Design and Results



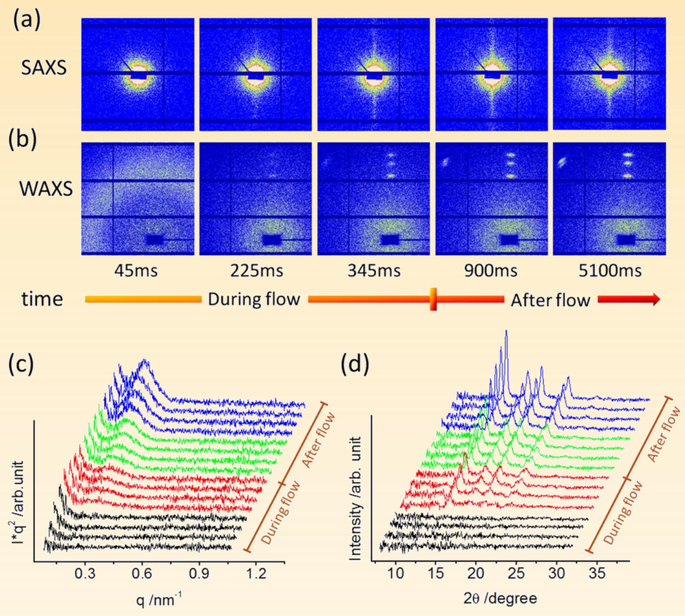
Sample: iPP (SABIC Europe)

A unique homemade extensional rheometer is used to supply well-defined extension flow field as well as to record the rheological information of sample. In all experiments, the strain rate is designed as 12.6 s^{-1} to meet the requirements of both non-equilibrium extension of chain and in-situ measurements during flow. The flow duration is less than 400 ms, during which tens of frames of X-ray scattering patterns are collected. The ultrafast SAXS and WAXS measurements with time resolution of 30 ms are carried out in BSRF.

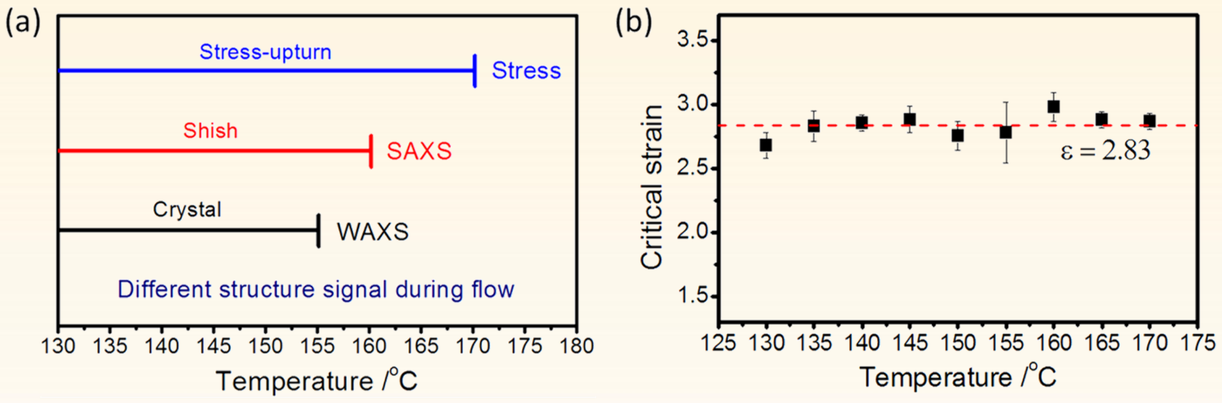


At 140 °C, the onset time for stress-upturn is about 234 ms, which corresponds to a strain of 2.84. The onset strain of stress-upturn is accompanied with the formation of crystalline shish, as evidenced by the simultaneous appearance of the streak signal in 2D SAXS images and the concomitant highly orientated diffraction of monoclinic α-form crystals by WAXS. Here we define the onset strain of SAXS streaks or stress-upturn as the critical strain for nucleation.

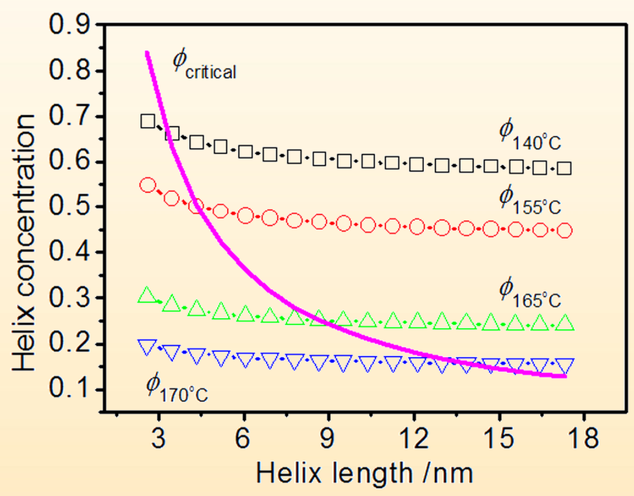
Results and Discussion



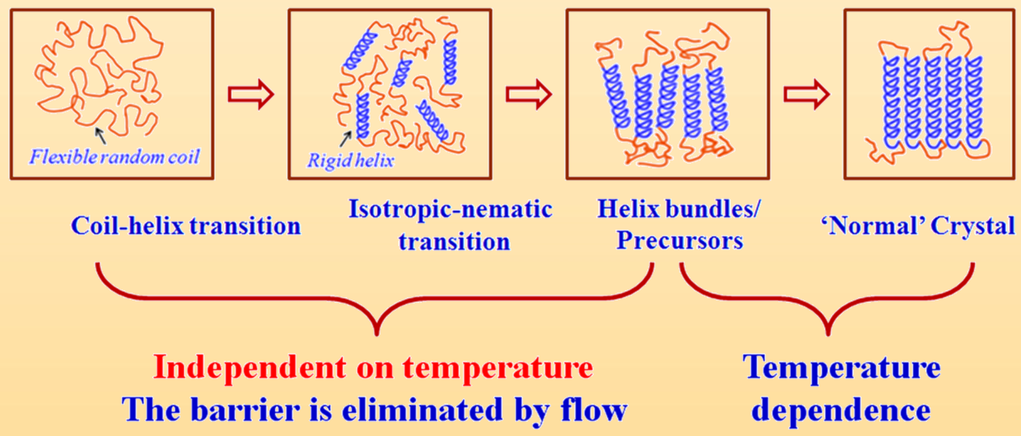
At 130 °C, SAXS images show streak scattering and WAXS images show the monoclinic α -form crystals with a high degree of orientation. Surprisingly, stacks of lamellae were observed during flow, as demonstrated by the appearance of scattering maximum.



Unexpectedly, the critical true strain for nucleation remains almost constant around 2.83. Evidently, the above experimental results demonstrate that ERM for FIC is not valid under strong flow.



The critical strain for nucleation is sufficient to generate both the concentration and compatible alignment of helixes. Coupling between coil–helix transition and orientational ordering drives packs of ordered helix sequences into shish bundles , which further transform into normal crystal.



Our discovery contradicts the strain-temperature equivalence predicted by ERM but unveils the non-equilibrium nature of FIC. In conclusion, a tentative kinetic pathway of nucleation describing stretch-induced hierarchical structural transitions is proposed.

Publication

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