Flow-induced Non-equilibrium Phase Transition in Polyethylene Melt

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Introduction

Understanding phase behaviors of polymers under flow field is potentially important in terms of optimizing material processing. But existing theories describe the flow effect mainly by the way of separating flow-induced rheological properties of chains from structure formation, which is far from real situations where chain deformation and structure formation may proceed simultaneously, especially under strong flow field.

In flow field with chains under orientation or stretching, question arises: how does the phase transition or crystallization proceed in this non-equilibrium condition? In the present study, we performed high time-resolved small-angle x-ray scattering (SAXS) and wide-angle x-ray scattering (WAXS) measurements on the structural development of high density polyethylene (HDPE) melt under step-extension. Some non-equilibrium phase behaviors during and after extension are observed and analyzed.

Experiment and results

Experiment

The sample is HDPE with the number-average (M_n) and weight-average molecular weight (M_w) of 42 kg/mol and 823 kg/mol, respectively. Strain rate and crystallization temperature (T_c) are chosen as experimental variables.

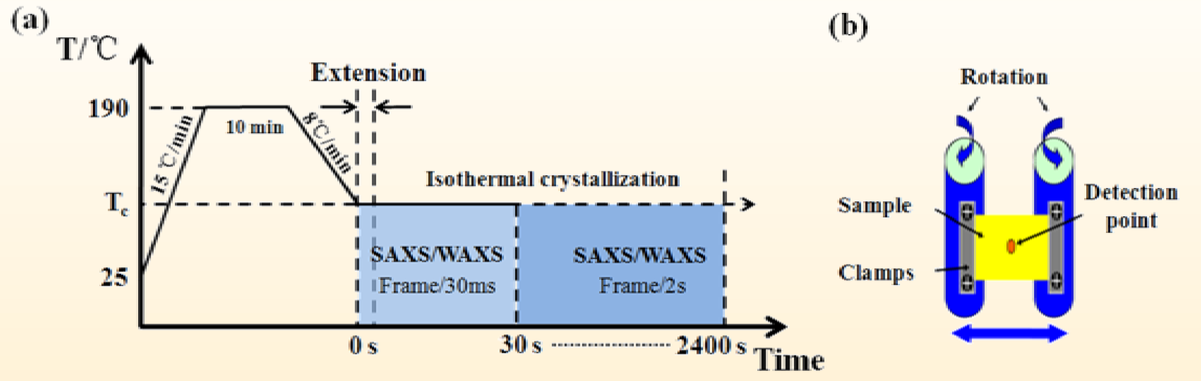


FIG. 1. (a) Experimental procedure. (b) The schematic drawing of homemade two-drum extensional rheometer device used in this *in situ* experiment.

Results

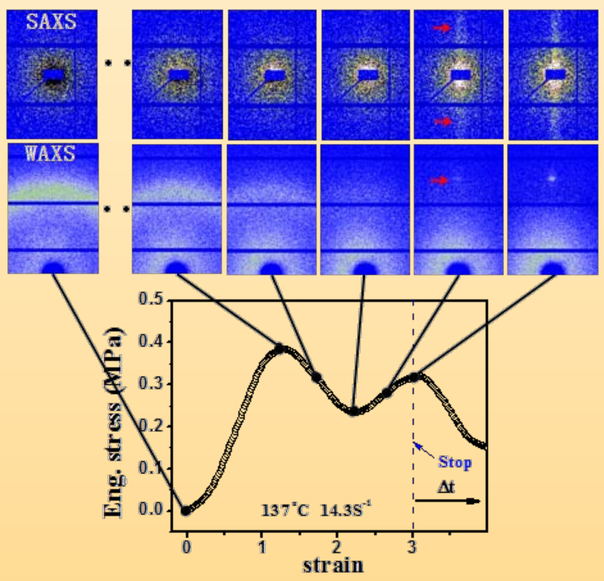


FIG. 2. The engineering stress-strain curve and 2D-SAXS & WAXS patterns collected during extension. Red arrows indicate the streak (SAXS, shish) and crystal scattering (WAXS) signals corresponding to structure formation.

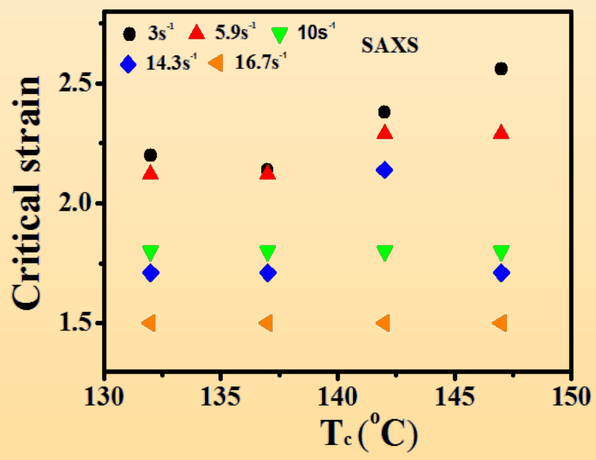


FIG. 3. Critical strain for structure formation extracted from SAXS data at various strain rates and temperatures. At a fixed temperature, the critical strain decreases as strain rate increases. At larger strain rate, the critical strain shows almost no temperature dependence compared with lower strain rate.

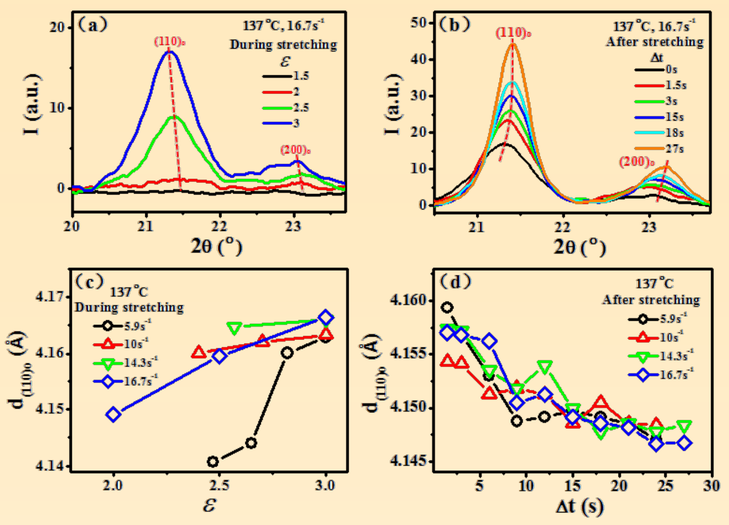


FIG. 4. (a) 1D-WAXS curves at different strains at 137°C during extension. (b) 1D-WAXS curves at different holding times at 137°C after extension. (c), (d) The corresponding interplanar crystal spacing $d_{(110)o}$ during and after extension. It should be noted that only orthorhombic crystal can be formed at 132 and 137°C.

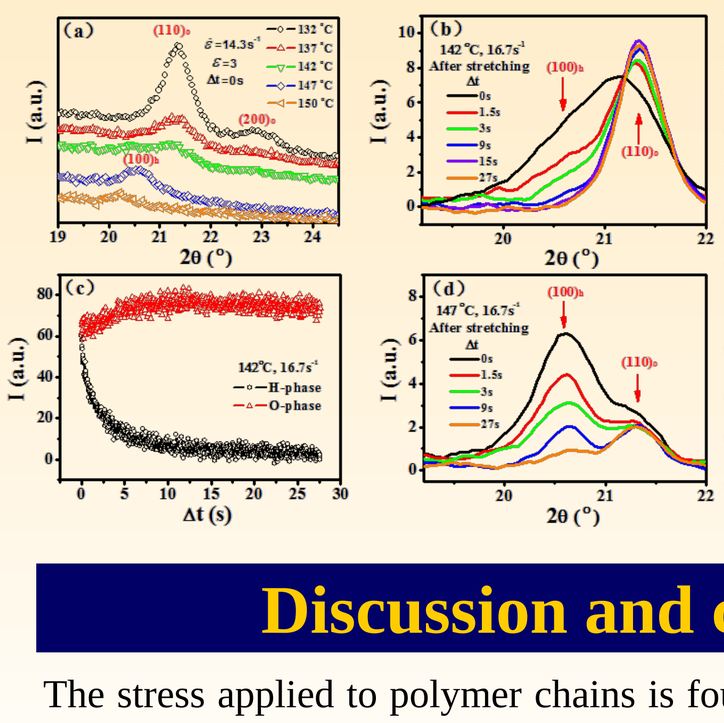


FIG. 5. (a) Orthorhombic and hexagonal crystal can be obtained at low and high temperatures, respectively. (b) 1D-WAXS curves at different holding times at 142°C after extension. (C) Integrated WAXS intensities of H- and O-crystal varying over holding time at 142°C. (d) 1D-WAXS curves at different holding times at 147°C after extension.

Discussion and conclusion

The stress applied to polymer chains is found to play a significant role on providing the system a distinct non-equilibrium nature.

First, the stress will increase the free energy of melt and decrease the energy barrier towards to next phase state. A critical stress is expected to induce phase transition, where the role of temperature (kT) may be buried, as shown in Figure 6.

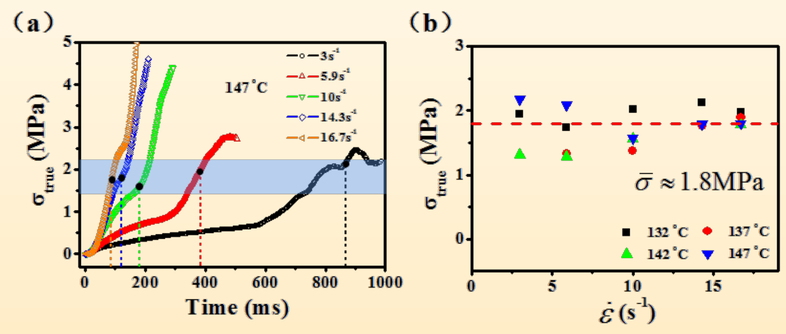
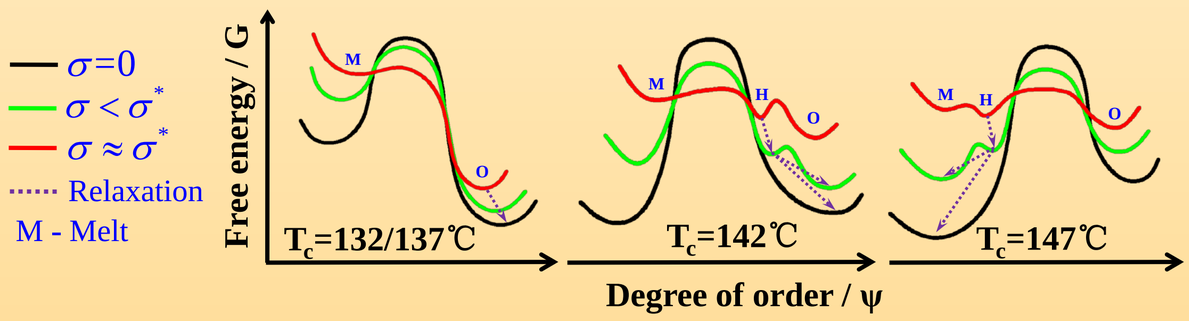


FIG. 6. (a) The true stress-strain curves at 147°C. Black points indicate critical stresses for structure formation. (b) Critical stresses.

Second, a stay on any phase state in principle can be realized. But the stay time is determined by the tress and temperature (kT) together. Evidences are from the detectable shish precursors, different crystal forms and structure relaxation which may depend on temperature or stress.



Above figure shows the possible free energy states of system as a function of degree of order and stress.

Outlook

It is almost impossible to build a non-equilibrium phase diagram as the number of phase states may be infinite. New theories and presentation forms on non-equilibrium phase transition should be developed in future.

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