

Observation of transient rotator phase of *n*-Hexadecane in emulsion droplet by two-dimensional SAXS-WAXS-DSC

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Introduction

Alkanes are among the most basic components of soft materials; nevertheless the precise mechanism of crystallization has not been clarified. Metastable phase of *n*-alkanes (rotator phase) is a key for the understanding of the crystallization. For *n*-Hexadecane (C16), although Sirota and Herhold first observed the transient-rotator phase in bulk samples [1], it was detected in only 9 out of 85 measurements. Recently, the existence of the rotator phase in C16 was experimentally certified [2], while the precise mechanism of crystallization through the rotator phase remains unsolved. In the present study, we have performed 2D-SAXS-WAXS-DSC in order to investigate the structural change at the crystallization.

Experimental

The sample used was C16 droplets in O/W emulsions. Samples of C16 with > 99 % purity were purchased from Sigma Chemicals and no further purification steps were taken. The O/W emulsion droplets were made by microchannel emulsification technique [3], by which we obtained large droplets with nearly monodisperse size distribution. We added 1 wt.% concentration of emulsifier before emulsification. The average diameter of sample was 30 μm .

Experiments were performed at BL-15A. The X-ray wavelength was 1.50 \AA . A large aperture X-ray Image Intensifier (270 mm ϕ) coupled X-ray CCD detector [4] was used as a detector. The sample-to-detector distance was around 160 mm and both SAXS and WAXS were simultaneously measured. We performed time-resolved SAXS-WAXS measurements together with Differential Scanning Calorimetry (DSC). Samples were heated to ~ 10 $^{\circ}\text{C}$ above the melting temperature and the cooled to -8 $^{\circ}\text{C}$ with a cooling rate of 2 $^{\circ}\text{C}/\text{min}$. The exposure time for each image was 1.5 s and an interval between the exposures was 3 s.

Results & Discussion

Figure 1 shows the relationships between the thermal data and SAXS-WAXS intensity from the C16 emulsion during crystallization [2]. These data are obtained by azimuthally averaging SAXS-WAXS intensity. It is shown that both SAXS and WAXS from the rotator phase appear at 14.0 $^{\circ}\text{C}$ and disappears at 10.8 $^{\circ}\text{C}$. The second weak peak of DSC at 10.8 $^{\circ}\text{C}$ corresponds to the sudden increase of scattering intensity from the triclinic phase and the disappearance of scattering from the rotator phase.

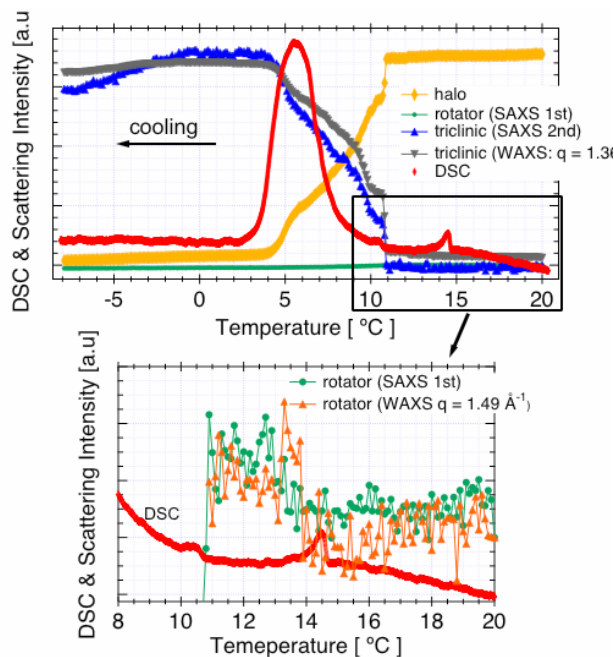


Fig. 1: (upper) DSC and time evolution of scattering intensity profiles from the rotator phase (SAXS 1st), triclinic structure, and halo during cooling of C16 emulsion droplets. (Lower) An expanded view of the marked portion of the upper figure. The scattering intensity profiles from the rotator phase are shown [2].

These results suggest that at this cooling rate, the transition from the rotator phase to the triclinic phase occurs at this temperature and that at the same time the rapid crystallization from the liquid oil into the triclinic phase begins. This situation is very similar to the well-known surface freezing in alkanes and expected as a key for further understanding of the crystallization.

References

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