

Effect of surfactants on crystallization of *n*-Hexadecane in emulsion droplet

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Introduction

Crystallization inside a droplet such as an oil-in-water (O/W) emulsion now attracts large attention due to its possibility to control the polymorph inside a droplet. It is suggested that interfacial heterogeneous nucleation has large effects on the process of crystallization in emulsion droplets [1]. Recent study shows that a transient phase of *n*-Hexadecane (C16), so-called rotator phase [2], plays a vital role of crystallization of C16 inside the emulsion droplets and that it has a relationship with the surfactant at the oil-water interface [3,4]. The effect of the interface on the crystallization inside the droplet, however, has not been clarified. In the present study, we performed time-resolved two-dimensional SAXS-WAXS together with Differential Scanning Calorimetry (DSC) during the crystallization of C16 and investigated the effect of surfactant at the oil-water interface on the crystallization inside the droplet.

Experimental

The sample used was *n*-Hexadecane (C16) droplets in an O/W emulsion. Samples of C16 with > 99% purity were purchased from Sigma Chemicals and no further purification steps were taken. Surfactants were Tween 40 (polyoxyethylene sorbitan monopalmitate: C₆₂H₁₂₂O₂₆), Tween 80 (polyoxyethylene sorbitan monooleate: C₆₄H₁₂₄O₂₆). The O/W emulsion droplets were made by microchannel emulsification technique [5], by which we obtained large droplets with nearly monodisperse size distribution. The average diameter of sample was around 32.5 μm.

Time-resolved 2D SAXS-WAXS-DSC experiments were performed at BL-15A. The X-ray wavelength was 1.50 Å. An X-ray CCD detector coupled with a large aperture X-ray Image Intensifier (270 mmφ) [6] was used as a detector. The sample-to-detector distance was around 160 mm. Sample were heated to ~25 °C above the melting temperature and then were cooled to -8 °C with a cooling rate of 2 °C/min.

Results & Discussion

Figure 1 show the result of DSC and time evolution of SAXS intensity from the C16 emulsion during crystallization. The SAXS data are obtained by azimuthally averaging x-ray intensity of SAXS 2nd peak of rotator phase and stable phase. Both the SAXS and DSC data show that the C16 in emulsion droplet with Tween 40 rapidly crystallized into the stable phase via the rotator phase at around 13 °C, while C16 with Tween 80 slowly crystallized into the stable phase. These results suggest that the surfactant at the oil-water interface

strongly influences the crystallization behavior inside emulsion droplets. Further study will reveal the effect of surfactants on crystallization in a single emulsion droplet.

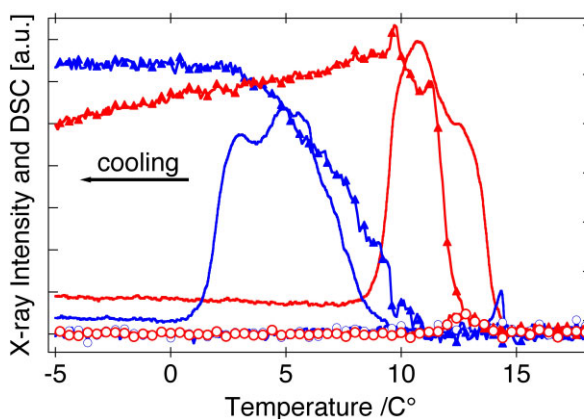


Fig. 1: DSC (line) and time evolution of scattering intensity from the SAXS 2nd peak of the stable phase (shown as triangle), and the SAXS 2nd peak of the rotator phase (shown as circle) during cooling of C16 emulsion droplets. Red and blue lines show the results with Tween 40 and Tween 80, respectively.

References

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