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Orientation of n-Hexadecane molecules in a single emulsion droplet studied by microbeam two-dimensional SAXS measurement

Tadashi TAKAMIZAWA[1], Yuya SHINOHARA*[1], Satoru UENO[2], and Yoshiyuki AMEMIYA[1]
[1]The University, of Tokyo, Kashiwa, Chiba 277-8561, Japan
[2]Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8528, Japan

Introduction

Recent study on the crystallization of the *n*-Hexadecane (C16) inside oil-in-water (O/W) emulsion droplets using small-angle x-ray scattering (SAXS) and wide-angle x-ray scattering (WAXS) showed that the crystallization behavior inside the emulsion droplets by the surfactant as well as that at the oil-water interface [1,2]. Especially, the appearance of the transient phase [3] has a relationship between the forms of hydrophobic base of the surfactant. These results suggest that the crystallization inside the droplets originates from the interfacial heterogeneous nucleation at the oil-water interface [4]. However, detailed mechanism of crystallization inside a droplet is not clarified, because the SAXS measurement so far was performed over the ensemble of many droplets. In the present study, we used a microbeam x-ray and measured SAXS at various positions in a single emulsion droplet in order to study the local structure of crystals in a droplet.

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. Surfactants were Tween 40 (polyoxyethelene sorbitan monolpalmitate: $C_{62}H_{122}O_{26}$), Tween 80 (polyoxyethelene sorbitan monooleate: $C_{64}H_{124}O_{26}$). 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 32.6 µm. Experiments were performed at BL-4A. The X-ray wavelength was 1.54 Å and the beam size was around 5 µm * 5 µm. A position of the x-ray beam on sample was monitored by an optical microscope. An X-ray CCD detector coupled with an X-ray Image Intensifier [6] was used as the SAXS detector. The sample-to-detector distance was around 650 mm in SAXS.

Results & Discussion

Figure 1 shows the optical microscope image of a crystallized emulsion with Tween 40 and the long axis orientations of C16 obtained by SAXS. Two features are observed; one is that the observed orientation of the long axis is perpendicular to the oil-water interface, and the other is that scattered x-rays are not observed at some parts of emulsion. The former feature is almost the same with the case of the droplets with Tween 80, but the size of region where the long axes (arrows) show the same direction is narrower in Tween 80. Furthermore, the scatterings are observed at all the positions of the droplet with Tween 80. These results suggest that the size of crystals in a droplet with Tween 40 is larger than that with Tween 80. This difference due to the surfactant would be a key for the understanding of crystallization mechanism in a single emulsion droplet.

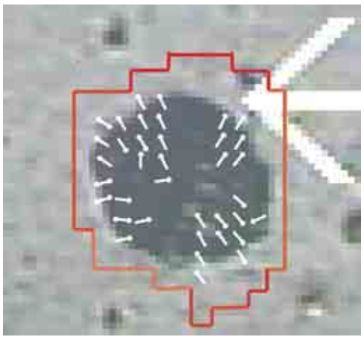

Fig. 1: Optical microscope image of emulsion with Tween 40 and the long axis orientations (represented by white arrow) of C16. The area surrounded by red frame represents the region scanned by a microbeam X-ray. No arrow is drawn in regions where no scattering was observed. The diameter of the droplet is around 50 µm

References

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*shinohara@x-ray.k.u-tokyo.ac.jp