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Study on Novel Crystallization Promoters for Fats and Oils by Simultaneous SAXS and WAXS Measurements

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1 Introduction

In order to promote the lipid crystallization, surfactants and materials having long hydrocarbon chains have been used as additives. It is considered that their alkyl chains act as templates for the heterogeneous nucleation by ordering the hydrocarbon-chain moieties of lipids. Recently, it has been clarified that inorganic and organic crystals (i.e., talc, graphite, carbon nanotube, theobromine, terephthalic acid, and ellagic acid dihydrate) remarkably promoted the lipid crystallization to form thermodynamically stable crystals [1, 2]. These additives are sparingly soluble in lipids and possess no long hydrocarbon chains in their molecules, which suggests that the promotional effects are caused by the strong intermolecular interactions between the surfaces of these crystalline materials and lipids.

Although the new crystallization promoters have a great potential in the application to the production and separation processes of oleochemical industry, the crystallization processes induced by them have not been fully studied yet. The crystallization of lipid systems is a complicated process, often involving polymorphic structural changes. Since lipid molecules assemble to form crystals in layered structures having long and short spacings, X-ray scattering measurements in a wide range of scattering angles are required. Taking this into account, we have studied how the promoters affect the lipid crystallization by simultaneous SAXS and WAXS measurements.

2 Experiment

Powder samples of graphite, talc, theobromine and fumaric acid and a thin sheet of highly oriented pyrolytic graphite (HOPG) were used as the promoters. Crystallization of trilaurin(LLL), palm oil and cocoa butter was carried out with and without these promoters. Powder promoters were added at a concentration of 1 wt. % and an HOPG sheet was placed on lipid samples.

A lipid/promoter mixture enclosed with polyimide films into a hole (2 mm ϕ) in an aluminum plate (1.5 mm thickness) was heated at 80°C for 10 min to erase memories of lipid crystals. The mixture was then cooled down to 0°C at a rate of 1°C/min and subsequently heated up to 80°C at a rate of 5°C/min.

Time resolved simultaneous SAXS and WAXS measurements were carried out at BL-10C. The mixture temperature was controlled by using a LINKAM hot/cold stage.

3 Results and Discussion

Figure 1 shows the SAXS and WAXS profile changes during the crystallization of LLL/fumaric acid and LLL/graphite powder mixtures. It turns out that there are remarkable differences in the crystallization process between the two mixtures. For the LLL/fumaric acid mixture showing a weak promotion effect, a reflection appeared at 0.031 $Å^{-1}$ in the SAXS region and its intensity increased as crystallization progressed. The position of the reflection suggests that LLL started to crystallize in the metastable phase β', which is the same result observed for neat LLL. Actually, the WAXS region shows the profile unique to the O⊥ subcell characteristic of the β' phase, such as intense reflections at 0.24 and 0.26 $Å^{-1}$. The stable phase β did not grow during the cooling process of this sample.

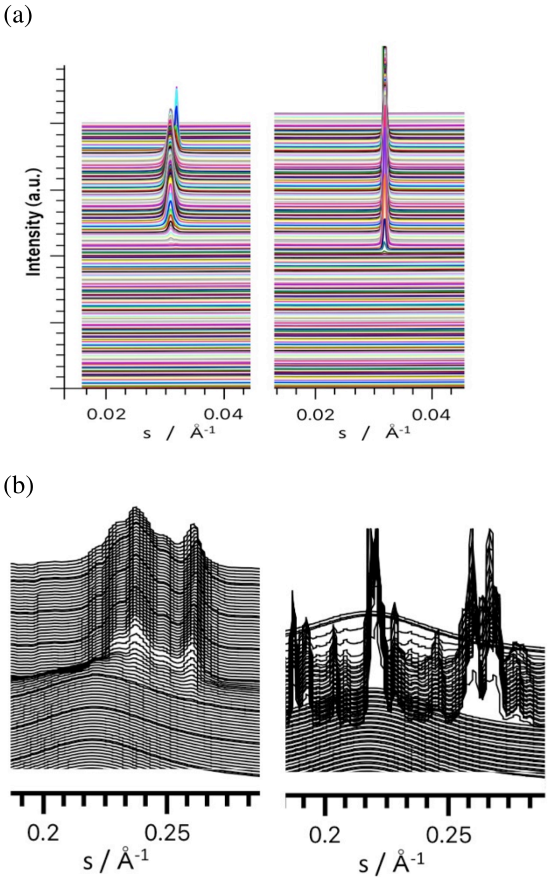

Figure1. X-ray scattering profile changes during the crystallization of LLL/fumaric acid mixture (left) and LLL/graphite powder mixture (right) in the regions of (a) SAXS and (b) WAXS.

On the other hand, the addition of graphite powder having a strong promotion effect induced the crystallization of the β phase. In both the SAXS and WAXS regions, the reflections characteristic of the β phase are observed from the inception of crystallization, such as a long-spacing reflection at 0.032 $Å^{-1}$ and short-spacing reflections due to the T// subcell at 0.22, 0.26 and 0.27 $Å^{-1}$.

The results described above suggest that a strong interaction is exerted between LLL molecules and surfaces of graphite particles, reducing significantly the activation energy for nucleation of the β phase. When a crystal face of this promoter acts as a heterogeneous nucleation site, the generated new nuclei of LLL may have a specific orientation to the crystal face.

In order to clarify the arrangement of LLL molecules in the generated β phase on surfaces of graphite particles, the crystallization of LLL/HOPG system was also investigated. The flat surface of HOPG is covered with the carbon hexagonal network correpondfing to the (001) plane. Figure 2 shows the results of measurements using a sample cell where an HOPG sheet was placed inside one of the polyimide windows to contact LLL and X-rays were applied to the windows perpendicularly. Accordingly, X-rays passed through the hexagonal network of HOPG along its normal.

The striking feature of the LLL/HOPG system is that the peaks appearing in both SAXS and WAXS regions were remarkably weaker than the counterparts in the LLL/graphite powder mixture, though the amount of LLL in the cell was almost the same. This result indicates that the crystalline phase of LLL was highly controlled by the HOPG surface; when crystal nuclei were generated with a specific orientation to the HOPG surface, most lattice planes did not meet the Bragg condition. It can be assumed that the most part of LLL crystals occurred in the LLL/HOPG system grew keeping the specific orientation of their nuclei generated heterogeneously at the surface of HOPG and a small portion of LLL happened to grow with disordered orientations giving the X-ray profile very weak reflections.

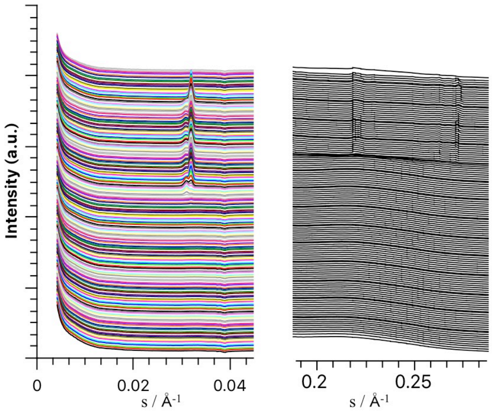

Figure 2. X-ray scattering profile changes during the crystallization of LLL kept in contact with an HOPG sheet.

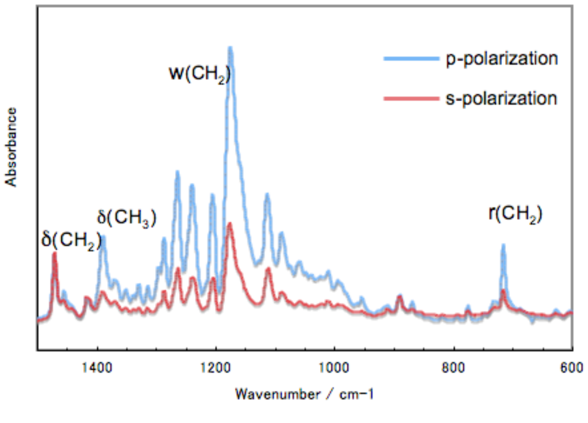

Figure 3. Polarized FTIR–ATR spectra of a crystalline LLL layer grown on a graphite sheet

This assumption is supported by the preliminary obtained FTIR-ATR results on LLL β-form crystals, which formed a thin layer on the surface of a graphite sheet. Figure 3 shows the *p*- and *s*-polarized spectra, emphasizing the vibrational modes whose transition moments are normal and parallel to the sample surface, respectively. The *p*-polarized spectrum shows CH_2 wagging progression bands much more intense than those in the *s*-polarized spectrum. Since the transition moments of the wagging modes of triacylglycerols such as LLL are parallel to their long hydrocarbon chains, the spectral feature indicates that the long axis of LLL molecules preferentially oriented toward the normal of the hexagonal network of graphite. From these results, we now consider that heterogeneous nucleation of LLL β-form crystals at graphite surfaces predominantly takes place to orient their lamellar planes parallel to the hexagonal network.

As shown in Fig. 2, a SAXS peak for the LLL β' phase was observed prior to that for the β phase and the intensity increased at the early stage of crystallization. At the moment, it is not clear wether the β' phase occurred heterogeneously on the surface of HOPG or homogeneously from the bulk of LLL.

Concerning crystal growth mechanisms for other combinations of lipids and promoters, the data analyses are now in progress, which will be presented in the next report.

References

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