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Section 1: Single crystal materials *INVITED*

# CRYSTAL GROWTH OF ORGANIC SOFT MATERIALS IN TEMPLATE-CONTROLLING SYSTEMS

K. Sato, S. Ueno, J. Yano

Faculty of Applied Biological Science, Hiroshima University, Higashi-Hiroshima, 739-8528, Japan

Crystallization phenomena of organic soft materials occurring in template-controlling systems such as emulsions, vesicles, micelles and air-water interfaces have been discussed by reviewing recent work. Long-chain molecular crystals and amino acids were chosen as the model substances of the organic soft materials which are key materials in food, pharmaceutical, nuetraceutical, cosmetic, and other bio-related industry. Three template-accelerated crystallization systems have been examined: template films prepared by physical vapor deposition, template films at the water-in-oil and oil-in-water emulsions. In the all systems examined, it was confirmed that the template films accelerated the heterogeneous nucleation whose kinetic and morphological properties are largely different from batch systems without any template acceleration. In particular, the vapor-deposited template films showed the controlling of polymorphism and molecular orientation of the crystallized materials through specific interface interactions. In the emulsion systems, it was assumed that the heterogeneous nucleation is initiated at the emulsion interface through van der Waals interactions which are minimized in the bulk systems.

*Keywords:* Crystal growth, Organic softmaterials, Oil/water emulsion

## 1. Introduction

Remarkable progress has recently been achieved in the understanding of crystallization phenomena in such complicated systems as emulsions [1, 2], vesicles [3, 4], micelles [5, 6], air-water interfaces [7, 8], ordered substrates [9, 10], etc. The crystallization phenomena observed in these complicated systems are closely related to elementary processes of biological mineralization [11, 12], and crystal engineering processing for the production of advanced materials [13]. It has been understood that one of the most peculiar properties specific to the crystallization processes in the complicated systems is revealed in the nucleation process: active sites present at certain positions play key roles in the nucleation processes, as templates. The template promotes the nucleation of selected materials through specific interactions between the active sites and crystallizing materials [9]. This process may be categorized as interfacial heterogeneous nucleation, which has recently been analyzed more precisely with application of nucleation theories [14, 15].

Classification of the nucleation-activating mechanism has highlighted the critical roles of templates, which were prepared on purpose to promote the nucleation of the selected materials in the growth systems. Fig. 1 depicts four typical template-accelerated growth systems. In Fig. 1(a), the template is an amphiphilic film adsorbed at a substrate, the polar head groups of which catalyze the heterogeneous nucleation of polar crystals in an aqueous solution. In Fig. 1(b), the template is an amphiphilic film constructing water-in-oil (W/O) emulsions, microemulsions or reversed micelles, in which polar crystals are nucleated in the aqueous solution encapsulated in the W/O emulsion. Catalytic interactions between polar groups of the template film and solute molecules may accelerate the heterogeneous nucleation. The nucleation of nonpolar crystals through a planar template and an emulsion interface are shown in Fig. 1(c) and (d), respectively. In the former case, the template is the

amphiphilic film adsorbed at a substrate and the non-polar head groups of the film catalyze the heterogeneous nucleation of non-polar crystals in an organic solution. In Fig. 1(d), the template is the amphiphilic film constructing oil-in-water (O/W) emulsions, microemulsions or micelles, in which non-polar crystals are nucleated in the organic solution encapsulated in the emulsion. Many work for the crystallization of various advanced materials has been made in each template growth system, as reviewed in recent books [12, 13]. Interestingly, well-defined molecular interactions have been unveiled at the heterogeneously nucleating interfaces through specific molecular interactions. Typical cases are electrostatic interactions between polar groups of amphiphilic films and ionic crystals [16], hydrogen bonding between *n*-alcohol films and ice crystals [17], etc.

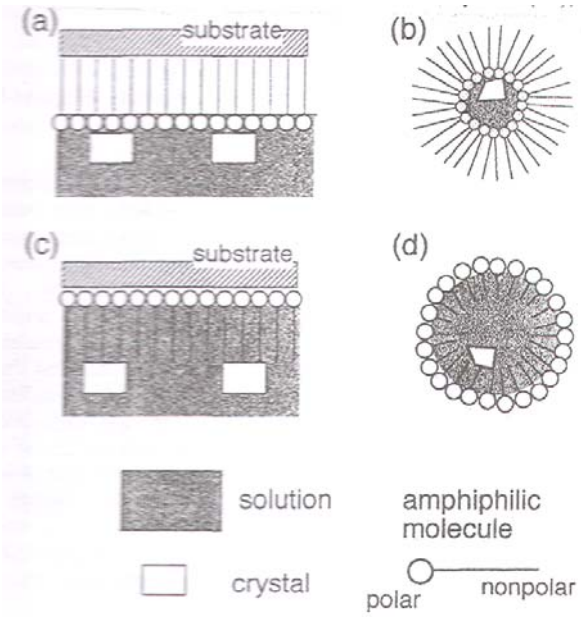


Fig. 1. Four types of template-accelerated crystal growth systems.

It is highly interesting to explore the molecular-level understanding of the template/guest interactions during the heterogeneous nucleation for wider candidates of crystallizing materials and crystallization systems. The template-accelerated crystallization of the type of Fig. 1(a) has been well documented [11-13]. Therefore, this paper discusses recent work of template-accelerated crystallization of organic soft materials examined in the above template systems of Fig. 1(b), (c) and (d), which has been performed by the present authors. Here, the organic soft materials are defined as molecular crystals revealing diversified crystal structures and morphologies to be utilized in pharmaceuticals, cosmetics, foods and other bio-related industry. These materials are crystallized traditionally in batch systems from bulk solutions or liquid. However, fundamental studies of the template-crystallization systems have shown high potential to produce more functional properties compared with the traditional techniques.

## 2. Crystallization of organic crystals in water-in-oil microemulsions

The W/O-type microemulsions are homogeneous, thermodynamically stable systems of nanometers-sized domains of water, as formed in specific ranges of temperature, pressure and compositions of water, oil and emulsifiers. The W/O microemulsions have the ability to solubilize polar crystals and therefore have been used to synthesize microparticles of inorganic crystals, semiconductors, metals as reviewed by Pileni et al. [18]. Crystallization of the organic soft materials in the W/O microemulsions has not been initiated until recently [19]. This is mainly because high

molecular weight values of organic materials result in lower solubility, and stabilization of the W/O emulsions is often disturbed by pH control of aqueous solution which is necessary to increase the solubility of polar organic substances. Therefore, it is necessary to examine, prior to crystallization, the phase stabilization of the W/O microemulsion with the crystallizing materials solubilized in the aqueous medium.

Solubilization and crystallization of an artificial sweetner, aspartame was investigated in W/O(isooctane) microemulsion stabilized with an emulsifier, sodium diisooctylsulfosuccinate (AOT) [19]. Aspartame is a dipeptide made of aspartic acid and phenylalanine. The solubilization measurements showed that the amount of solubilized aspartame depended on the amount of surfactant and temperature; e.g, the maximum AOT/aspartame molar ratio at the W/O interface was 6.2 at 25 ºC. Crystallization of aspartame in the W/O microemulsions thus formed showed that a new polymorphic crystal form was obtained. The new form exhibited unique X-ray diffraction spectra, molecular and thermal properties which are different from previously-known four polymorphs of aspartame. The newly formed aspartame crystals exhibited greatly improved dissolution kinetics, which is valuable for commercial use.

In order to clarify the crystallization mechanisms of organic molecules in the W/O microemulsion, we have studied the crystallization of amino acids, which are key materials in foods and drugs [20]. As a basis to crystallization studies, the solubilization of amino acids (glycine and phenylalanine) in water-in-isooctane microemulsion stabilized by AOT was investigated. The maximum amount of amino acid to be solubilized was determined and the effects of the addition of amino acids in aqueous solution on the size and shape of the microemulsion droplets and their thermal properties were determined with small-angle X-ray scattering (SAXS) and DSC measurements. It was found that the extent of solubilization strongly depended on the hydrophobicity of the amino acid which also determines the location of the guest molecules within the microemulsion. The solubilization of glycine molecules in microemulsions slightly decreased compared with that in bulk water. It decreased with increasing concentrations of AOT and increasing with increasing water content in the microemulsion. In contrast, the solubilization of phenylalanine, which is primarily located at the water/oil interface, increased several times that in the bulk water. The soluble amount of phenylalanine in the microemulsion increased with increasing AOT and water concentrations.

On the basis of the solubilization studies described above, we investigated the crystallization of glycine and phenylalanine from the W/O microemulsions. Crystallization phenomena were strongly affected by the localization of the solubilized molecules within the microemulsion droplets. In the case of glycine, a significant reduction in crystal size was observed in the temperature range investigated (Ti, initial temperature of saturated solution, = 35 ºC, Tc, crystallization temperature, = 5 ºC) (Fig. 2). While the crystals formed in bulk aqueous solution usually grow to mm sizes (Fig. 2a), glycine crystals grown from microemulsions were of the size order of submicron- to micron-meter (Fig. 2b). In addition, polymorphic occurrence was also varied: the γ-form dominantly crystallized from microemulsion particularly from the microemulsion having smaller [water]/[surfactant] molar ratio values, whereas the α-form was the dominant form in the crystallization from the bulk aqueous solution (Fig. 2c).

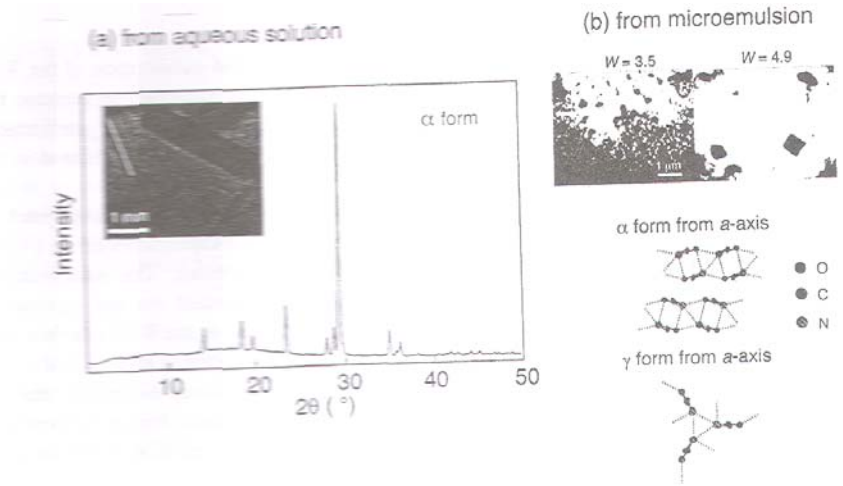


Fig. 2. (a) X-ray diffraction pattern and optical micrographs of glycine crystals obtained from aqueous solution, and (b) electron micrographs of glycine crystals obtained from microemulsions (W, [water]/[emulsifier] molar ratio, = 3.5 (left) and 4.9 (right). (c) α and γ forms of glycine crystals projected from the a-axis. In (c), the dotted lines show hydrogen bonds between molecules.

In the case of phenylalanine, morphology, polymorphism and crystal size were different between the crystals grown from the bulk solution and microemulsion. Phenylalanine crystallizes in two polymorphs from the bulk solution, i.e. the needle-like α-form and plate-like β-form, whereas, in the crystallization from microemulsions, only the β -form occurred (Fig. 3a, b). This difference may be ascribed to the molecular structure of β in which two dimmers make a layered structure (Fig. 3c) [21]. This molecular orientation seems to be easily taken at the W/O interface by inserted into the surfactant layer in the microemulsion. Further clarification is needed for this microscopic mechanisms, which may relate adsorption of solute molecules at the water/oil interfaces to the onset of heterogeneous nucleation primarily occurring at the interface.

The work on the crystallization of amino acids from W/O microemulsions indicates high potentiality to apply this crystallization technique to the other organic soft materials, such as pharmaceuticals and neutraceuticals (the materials related nutrition, drug and healthy problems), with an emphasis to modify the crystal morphology and polymorph of the crystallizing materials.

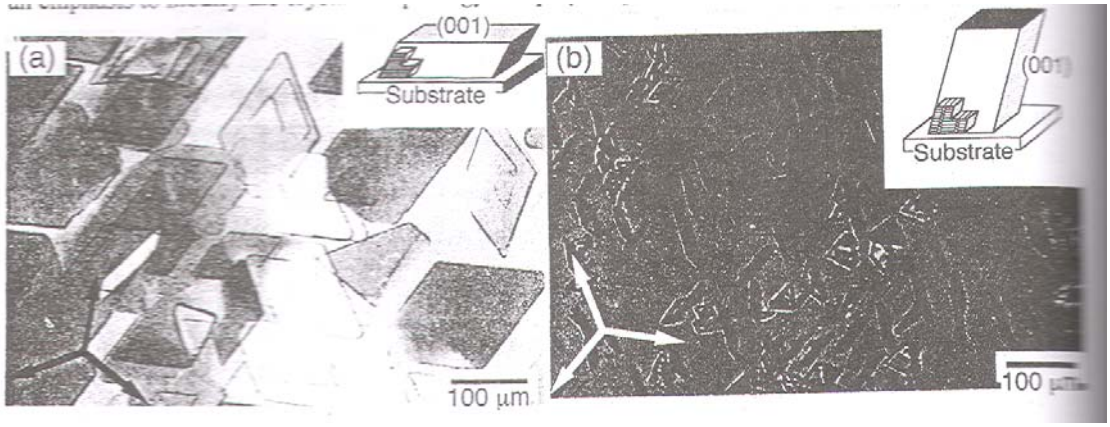


Fig. 3. Optical micrographs of phenylalanine crystals obtained from (a) bulk aqueous, and (b) microemulsion (W=4.9). Crystallization was carried out by cooling the saturated solution at 25 ºC to 5 ºC.

## 3. Template-accelerated crystallization by vapor deposited template films

Organic crystals may interact with the templates through polar and nonpolar forces. Polar forces have the nature of hydrogen bonding and electrostatic interactions, both have a specificity of the molecular interactions. By contrast, nonpolar forces are due to van der Waals interactions which look less specific and much weaker in comparison with the polar interactions. Despite of this, accelerating effects of the template films on the heterogeneous nucleation through van der Waals interactions have been unveiled in recent years, for the template systems depicted in Fig. 1(c) and (d). This section discusses the template-accelerated crystallization of the former type.

Morphological and kinetic observations have been made on heterogeneous nucleation of long-chain *n*-alcohol crystals (herewith referred to guest crystals) from solution, which was accelerated by the presence of vapor-deposited thin films (referred to as templates) of long chain molecules [22, 23]. *n*-Alcohol crystals were chosen as the model material which is representative of fats, lipids, waxes and other long-chain molecules. The host templates were formed by physical vapor deposition [24-26]. The template films were put in slightly supersaturated solution (decane solvent), in which no crystallization occurred over several hours without the template films. The template films accelerated the crystallization within several minutes of induction times. The crystallization behavior was precisely examined by microscopic observation and induction time measurements, with specific attentions to the template-guest relationships in terms of polymorphism, molecular orientation and chain length limitation.

It was confirmed that the host template films accelerated the nucleation of the *n*-alcohol crystals, exhibiting the polymorphic matching, preservation of the molecular orientation and the chain length matching [22]. Fig. 4 shows the influences of the molecular orientation of the template films (monostearoyl-glycerol) on the growth patterns of the guest crystals of behenoyl-alcohol. The template film was vapor-deposited on cleaved mica [23]. In Fig. 4a, the basal plane of the γ form of the guest crystals are almost normal to the template films, e.g., normal to the printed sheet. By contrast, the guest crystals accelerated by the template films, in which the long-chain axes are arranged parallel to the substrate, making an angle about 70° with respect to the substrate, as shown in Fig. 4b. This difference is due to the geometric relations of the host films and guest crystals illustrated in inserted figures. The occurrence of γ form, out of three polymorphs of *n*-alcohol crystal polymorphs, was predominant, because of the matching of β' form of the template film crystal and γ form [23].

Furthermore, a comparison was made for the relative occurrence of the crystallization of three *n*-alcohol crystals ($C_n$-OH, n is the number of carbon atoms) grown under the template-guest combinations, as summarized in Table 1.

Table1. Relative occurrence of guest n-alcohol crystals accelerated by template thin films [22, 23]

| template films | guest crystals | | | |
|---|---|---|---|---|
| | $C_{18}$-OH | $C_{20}$-OH | $C_{22}$-OH | $C_{24}$-OH |
| monoacylglycerols | | | | |
| $C_{16}$-MG | + | +++ | ++ | + |
| $C_{18}$-MG | + | ++ | +++ | + |
| $C_{22}$-MG | + | ++ | ++ | ++ |
| fatty acids 1) | | | | |
| $C_{18}$-acid | +++ | - | - | - |
| $C_{20}$-acid | ++ | +++ | - | - |
| $C_{22}$-acid | - | ++ | +++ | - |
| $C_{24}$-acid | - | - | ++ | +++ |

+++ : most accelerated ++ : very accelerated + : fairly accelerated - : no acceleration

A special attention was paid to the effects of chain length matching, as expressed in n of the guest and template molecules, where two types of template were tested: fatty acid ($C_n$-acid) and monoacylglycerol ($C_n$-MG). The $C_n$-MG templates accelerated the crystallization of $C_n$-OH, even when the n values of the guest crystals were longer than those of the host films by 8. However, the most enhanced acceleration was observed in such a combination that the n value of the template material was smaller than that of the guest material by 4. This makes a clear contrast to the template-guest relations between the combination of $C_n$-acid /$C_n$-OH, in which the acceleration was only observed when the n value of the template films was the same as or longer by 2 than that of the guest crystals.

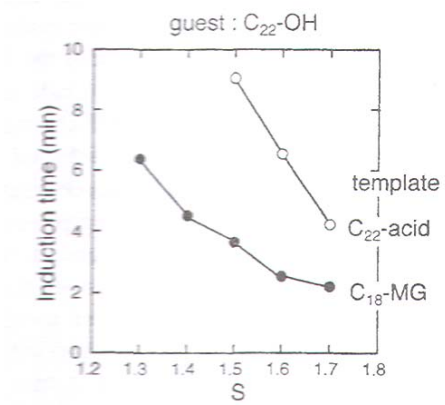


Fig. 4. Induction time values of behenoyl alcohol crystals ($C_{22}$-OH) accelerated by templates of behenic acid ($C_{22}$-acid) and monostearoylglycerol (C18-MG) [23].

The induction time measurements for overall crystallization showed two common properties; (a) the induction time increased with decreasing supersaturation ratio (S) values in the crystallization experiments of the all host-guest combinations examined, and (b) when a particular template film is set, preferred acceleration was observed for the guest crystal which is specific in regard to chain length difference between the host template and guest solute molecules, as revealed in shorter induction times. As an example, Fig. 4 shows the induction time values of the crystallization of the guest material of $C_{22}$-OH with the template films of $C_{22}$- acid and $C_{18}$-MG. The induction time increased with decreasing S values, yet a remarkable difference is seen between the template films of fatty acids and monoacylglycerols, as evidenced in the two sets of experiments. In Fig. 4, the induction time value of 9 minutes with the $C_{22}$- acid film was about 3 times longer than that with the $C_{18}$-MG. As already mentioned, several hours are needed for the nucleation of the guest crystals without the template films at this range of S values. This means that the acceleration effects of the template films became more enhanced with decreasing values of supersaturation, and that the influence of the template-guest molecular interactions is also enhanced with decreasing S values.

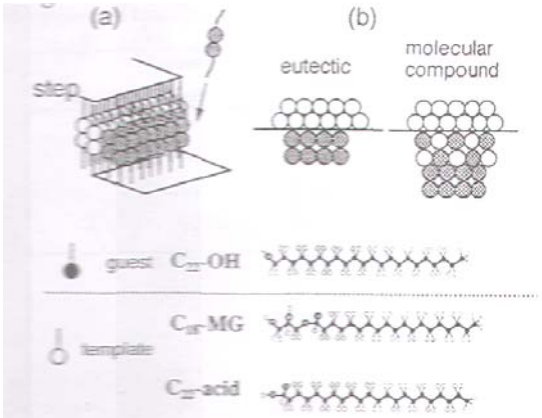


Fig. 5. Model of template-accelerated heterogeneous nucleation [23].

Most of the above results were explained by taking a basic model of the template-assisted nucleation illustrated in Fig. 5 [23]. The model assumes that the heterogeneous nucleation occurs from the steps of the template crystalline films exposing to the solution (Fig. 5a). The van der Waals molecular interactions between the hydrophobic hydrocarbon chains and hydrophilic polar groups of glycerol groups ($C_n$-MG), carboxyl groups ($C_n$- acid) and carbonyl groups ($C_n$-OH) are operative at the steps exposed on the outer surfaces of the template films. Preferential adsorption of the guest molecules, followed by condensation around the steps, may result in the heterogeneous nucleation of the guest crystals. It is reasonably assumed that the attractive forces between the monoacylglycerol and *n*-alcohol molecules are much stronger than those between the fatty acid and alcohol molecules, due to the presence of two OH-groups in the monoacylglycerol templates films. It is also inferred that hydrogen bonding between the monoacylglycerol and alcohol molecules would be operating at the steps. This difference in the template-guest interactions of the two templates is reflected in the phase behavior of the binary mixtures in the bulk state: monoacylglycerols and n-alcohols exhibited molecular compound formation, whereas eutectic phases are formed between fatty acids and n-alcohols (Fig. 5b, [23]).

To conclude, the template-guest interactions are differently operative in the two sets of the thin film templates and the guest materials. By applying this type of the template-accelerated heterogeneous nucleation, one may crystallize the guest crystals with specific molecular orientations and polymorphic forms at reduced rate of nucleation, even when the major molecular interactions are of a nature of van der Waals forces.

## 4. Template-accelerated nucleation in oil-in-water (O/W) emulsions

The crystallization of oil fraction in the O/W emulsion droplets influences stability, rheology and appearance of emulsions, which are employed in cosmetics, foods, pharmaceuticals, etc [27]. Therefore, it is important to analyze the crystallization processes in the emulsions. For this purpose, application of the ultrasonic method to *in-situ* monitor the crystallization processes of the emulsified systems has been conducted for the O/W emulsions by Povey et al. [28-30]. This technique is based on a principle that the crystallization of a liquid oil phase dispersed in a water phase is monitored by the ultrasonic sound velocity which increases by the transformation from liquid to solid phases. In particular, *in-situ* and not-destructive monitoring of crystallization temperature ($T_c$) of the oil phase in the O/W emulsion is facilitated by this technique. Thus, the ultrasonic sound velocity measurements, combined with DSC, electron and optical microscopy, have provided deep insights of the crystallization processes in the O/W emulsions [28-33].

Here discussed are kinetic properties of the crystallization processes, which are remarkably modified by the addition of highly hydrophobic emulsifier molecules forming the template films for nucleation at the oil/water interfaces [31-33]. *n*-Hexadecane (melting pint, 18 ºC) was chosen as an oil phase, and Tween 20 was employed for making the O/W emulsions. The concentration of Tween 20 was 2 wt.% with respect to the oil and water phases. The highly hydrophobic sucrose fatty acid oligoesters (SOEs), palmitic acid (P-170), stearic acid (S-170), oleic acid (O-170) and lauric acid (L-195) moieties, were put in n-hexadecane as the additives (Fig.6a). SOE is a representative food emulsifier [34]. The mean droplet size was 0.8 μm [32, 33].

Fig. 6(b) shows the ultrasonic velocity values of n-hexadecane-in-water emulsions (oil; 20 wt.% and water 80 wt.%) at varying temperature and concentrations of P-170. The following remarks are drawn from Fig. 6(b):

(1) Without the addition of P-170, the emulsification reduced the nucleation rate compared to the bulk systems, e.g., nucleation occurred at 16 ºC in bulk, yet at 3 ºC in the emulsion.

(2) The addition of P-170 accelerated the nucleation in the emulsion system, as revealed in the increases in $T_c$ values with increasing P-170 concentrations. However, no acceleration was revealed in the bulk system.

(3) The acceleration of nucleation occurred through two stages, with increasing concentrations of P-170: e.g., a sharp increase occurred in a low concentration range of P-170 up to about 0.3 wt.%, then a moderate acceleration occurred at P-170 concentrations above 0.6 wt.%.

(4) A separate experiment showed that the rates of crystal growth of n-hexadecane were retarded by the addition of P-170.

Comparative studies with varying SOE additives showed that the addition of P-170 and S-170 remarkably accelerated the nucleation, yet no effect was seen for O-170, and an in-between effect was seen for L-195 (Fig. 6c) [33]. The melting points of P-170 and S-170 are higher than those of O-170 and L-195, because of the fatty acid moiety of each SOE: palmitic (P-170) and stearic acids (S-170) have higher melting points than oleic (O-170) and lauric acids (L-195). Therefore, the acceleration effects of heterogeneous nucleation of the SOEs are dependent on their thermal properties.

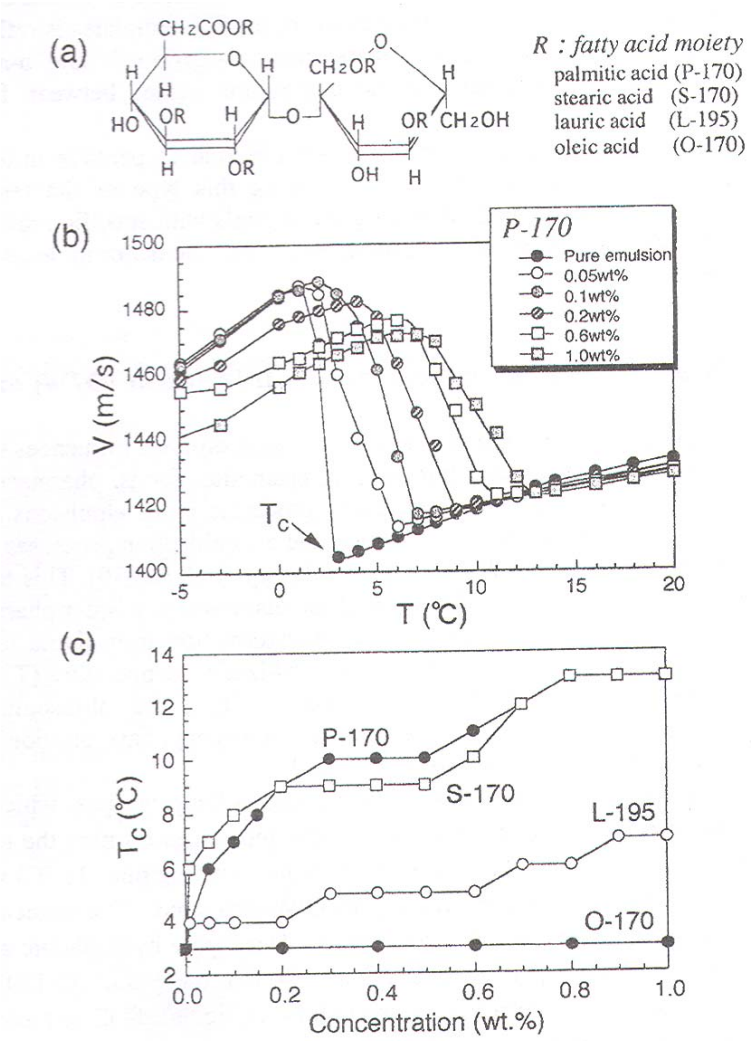


Fig. 6. (a) sucrose oligoester (SOE) molecule model, (b) ultrasonic velocity vales (V) at different temperatures of n-hexadecane - water emulsions with the additive of P-170, (c) Tc variation with additive concentration of four SOEs.

It was assumed that the acceleration of the crystallization is ascribed to heterogeneous nucleation processes caused by the SOE additives. In the present case, the nature of heterogeneity may be ascribed to the adsorption of the hydrophobic SOEs having longer fatty acid chains. Fig. 7 illustrates the template-accelerated heterogeneous nucleation model, which occurs at the oil/water interface for the lower SOE concentrations, and at reversed micelles in the oil phase for the higher SOE concentrations.

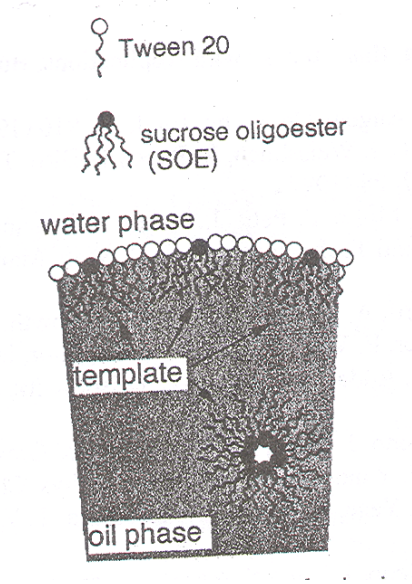


Fig. 7. Model of template-accelerated heterogeneous nucleation in oil/water emulsion with the additive of SOE.

## 5. Conclusion

In general, the roles of templates are critical in chemical reactions, materials production, bio-syntheses, etc. The same is true for the crystallization of inorganic and organic materials, as highlighted above. In the case of the organic soft materials, the templates can be prepared by various ways: physical vapor deposition for the nucleation of non-polar materials, emulsifier films adsorbed at the oil/water emulsions for the nucleation of polar and nonpolar materials. Many phenomenological work has already been accumulated, and further exploration will be made in near future, in particular, along with interests of pharmaceutical and neutraceutical applications. In parallel with these advanced materials research, fundamental work will also be made in such as direct verification of the template film formation in the emulsion systems, precise analysis of heterogeneous nucleation kinetics, etc.

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