1

Introduction: Relationships of Structures, Properties, and Functionality

Kiyotaka Sato

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1.1 Introduction

This chapter presents a comprehensive sketch of the lipid species and functionality of lipid crystals present in various end products by outlining different stages of crystallization. In doing so, topics will be highlighted that will be elaborated further in chapters of this book. At the end of this chapter, a particular effort is made to relate *trans*-fat alternative and saturated-fat reduction technology to lipid crystallization because these two issues are the most significant problems in the edible-application technology of lipids and one of the key solutions is lipid crystallization.

1.2 Lipid Species

Lipids are a class of compounds that contain long-chain aliphatic hydrocarbons and their derivatives (O'Keefe 2008). There is a wide variety of lipid materials such as hydrocarbons, fatty acids, acylglycerols, sterols and sterol esters, waxes, phospholipids, plasmalogens, sphingolipids, and so on. Typical lipids whose crystallization properties have critical implications in food and other industries include hydrocarbons, fatty acids, alcohols, waxes, and acylglycerols. Because the lipid species of natural lipids of vegetable or animal resources vary from one to another, the understanding of the crystallization, melting, and physical properties must be based on the effects of major and minor lipid components included in every lipid material.

In this section, we take a brief look at the chemical structures of these typical lipid molecules.

1.2.1 Hydrocarbons

Hydrocarbons comprise a group of the simplest lipid molecules and are composed of hydrogen and carbon atoms. A typical molecular shape of hydrocarbons containing all saturated carbon–carbon bonds is expressed as CH_3-$(CH_2)_{n-2}$-CH_3, in which n is the

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number of carbon atoms. Hereafter, we use n_c as the number of carbon atoms in the all-hydrocarbon chains. In nature, even-numbered and odd-numbered hydrocarbons occur, depending on whether n_c is even or odd.

Molecular interactions operating among the hydrocarbon molecules are van der Waals forces, and these comprise the major molecular interactions among lipid molecules when they contain hydrocarbon chains as hydrophobic moieties. When the number of carbon atoms exceeds four, structural isomers occur (e.g., straight chains or branched chains). The straight-chain hydrocarbons are called *n*-alkanes as illustrated for *n*-octadecane with n_c=18 (Fig. 1.1a).

1.2.2 Fatty Acids

Fatty acids are formed by replacing one end of $-CH_3$ in *n*-hydrocarbons with a carboxyl group (–COOH). In contrast, dicarboxilic acids are formed when both end groups of $-CH_3$ in *n*-hydrocarbons are replaced with –COOH. There are saturated and unsaturated fatty acids, depending on whether double bonds are included and stereoisomers of *cis* or *trans* unsaturated fatty acids occur.

In nature, a wide variety of fatty acids is present, differing in n_c, the number of double bonds having *cis* or *trans* conformations or the positions of the double bonds at the hydrocarbon chains. Similarly to hydrocarbons, even- and odd-numbered fatty acids occur. The principal fatty acids abundantly occurring in nature are summarized in Table 1.1. Although standard (IUPAC) systematic names are given to fatty acids, the common names and abbreviations presented in the table will be used throughout this book.

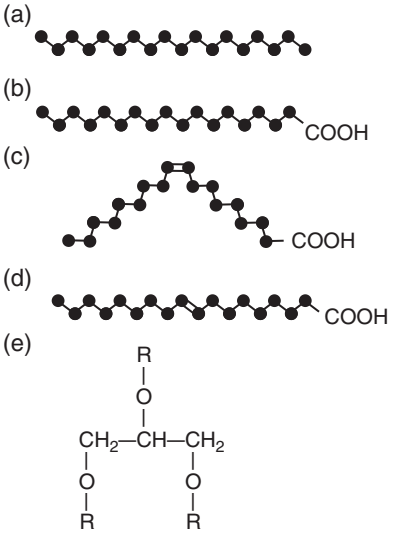


Fig. 1.1 Typical lipid molecules. (a) *n*-Octadecane, (b) stearic acid, (c) oleic acid, (d) elaidic acid, and (e) triacylglycerol. In (a)–(d), carbon atoms are shown except for COOH groups for fatty acids. In (e), R is fatty acid moiety.

As typical fatty acids having n_c=18, stearic acid is a saturated fatty acid, oleic acid is a mono-unsaturated fatty acid having a *cis* double bond at the 9–10 carbon atoms, and elaidic acid is a mono-unsaturated fatty acid having a *trans* double bond at the 9–10 carbon atoms, as seen in Fig. 1.1(b, c, and d). The melting temperatures (T_m) of the three fatty acids in their most stable polymorphic forms are 69° C (stearic acid), 44° C (elaidic acid), and 16.1° C (oleic acid). This typically represents the relationships between T_m and the molecular shapes of the fatty acids in the following aspects.

- At a fixed number of n_c, T_m decreases with increasing numbers of double bonds, and the conformation of the double bonds changes from *trans* to *cis*.
- As for saturated fatty acids, T_m increases with increasing n_c, although the values of T_m for fatty acids with an odd-numbered n_c is a bit lower than those with an

Table 1.1 Systematic, common, and shorthand names of principal fatty acids.

Systematic	Common	Shorthand	Abbreviation
Saturated			
Octanoic	Caprylic	8:0	Ca
Decanoic	Capric	10:0	C
Dodecanoic	Lauric	12:0	L
Tetradecanoic	Myristic	14:0	M
Hexadecanoic	Palmitic	16:0	P or PA
Heptadecanoic	Margaric	17:0	Ma
Octadecanoic	Stearic	18:0	S or SA
Nonadecanoic	Nonadecanoic	19:00	No
Eicosanoic	Arachidic	20:0	A
Docosanoic	Behenic	22:0	B
Unsaturated			
c-9-Hexadecenoic	Palmitoleic	16:1, Δ9-ω7	POA
c-9-Octadecenoic	Oleic	18:1, Δ9-ω9	O or OA
c-12-Octadecenoic	Petroselinic	18:1, Δ6-ω12	PSA
t-9-Octadecenoic	Elaidic	18:1, Δ9-ω9	E
c-11-Octadecenoic	Asclepic	18:1, Δ11-ω7	APA
12-hydroxy, *c*-9-Cctadecenoic	Ricinoleic	18:1, Δ9-ω9	R
t-11-Octadecenoic	Vaccenic	18:1, Δ11-ω7	V
c-9, *c*-12-Octadecadienoic	Linoleic	18:2-ω6, 9	Li
c-9, *c*-12- *c*-15-Octadecatrienoic	α-Linolenic	18:3-ω3, 6, 9	ALA
c-6, *c*-9- *c*-12-Octadecatrienoic	γ-Linolenic	18:3-ω6, 9, 12	GLA
c-11-Eicosanoic	Gondoic	20:1, Δ11-ω9	GOA
c-5, *c*-8, *c*-11, *c*-14, *c*-17-Eicosapentanoic	Eicosapentanoic	20:5, ω3, 6, 9, 12, 15	EPA
c-13-Docosenoic	Erucic	22:1, Δ13-ω9	Er
c-4, *c*-7, *c*-10, *c*-13, *c*-16, *c*-19-Docosahexanoic	DHA	22:6, ω3, 6, 9, 12, 15, 18	DHA

even-numbered n_c–1. For example, T_m of margaric acid n_c=17 (palmitic acid, n_c=16) is 61° C (63° C). This is ascribed to the instability of molecular packing at the lamellar interfaces, where CH_3-CH_3 end groups are stacked against each other, of odd-numbered fatty acids compared to that of even-numbered fatty acids.

These relationships apply to other lipids containing fatty acid chains as their hydrophobic moieties.

The –COOH group is hydrophilic (water soluble), and the hydrocarbon chains are hydrophobic (oil soluble). Therefore, the hydrophobicity or hydrophilicity of a fatty acid molecule as a whole depends on n_c. Fatty acids with $n_c \leq 6$ become water soluble, whereas

they are sparingly water soluble when n_c exceeds 6. Molecules having a hydrophobic moiety in one part and a hydrophilic moiety in another part are called *amphiphilic*, as revealed in other lipids: alcohols, mono- and di-acylglycerols, phospholipids, emulsifiers, and so on.

1.2.3 Alcohols and Waxes

Alcohols are formed by replacing one $-CH_3$ end of *n*-hydrocarbons with –OH. Similarly to fatty acids, the alcohols become liphophilic as n_c increases above 6, and even-numbered and odd-numbered alcohols occur.

There are narrow and broad categories of "waxes." The former refers to the esters of long-chain fatty acids and alcohols. The latter represents "waxy matter" abundantly occurring in nature as epidemic lipids, which include hydrocarbons, ketones, and aldehydes. Here we limit the waxes to the esters of long-chain fatty acids and alcohols. The n_c for constructing naturally occurring waxes vary widely from one wax to another. For example, candellila wax is made of fatty acids with n_c = 16–34 and alcohols with n_c = 22–34, whereas rice bran wax is made of fatty acids with n_c = 16–32 and alcohols with n_c = 24–38.

1.2.4 Acylglycerols

Acylglycerols are formed by esterification of the hydroxyls in glycerol molecules (CH_2OH-$CHOH$-CH_2OH) with fatty acids. Monoacylglycerols (MAGs), diacylglycerols (DAGs), and triacylglycerols (TAGs) are formed when one hydroxyl, two hydroxyls, or three hydroxyls, respectively, are esterified, as summarized in Fig. 1.2.

TAGs (Fig. 1.1 e) are the principal lipids that construct animal adipose tissues, vegetable and edibles fats, and oils. The term used, *fat* or *oil*, depends solely on whether the

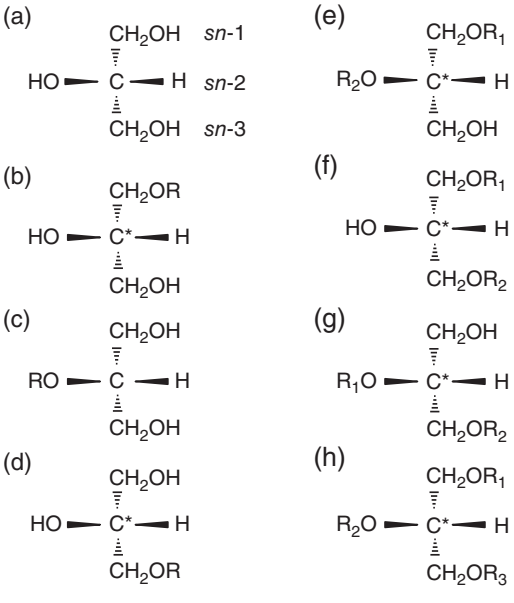


Fig. 1.2 Structure models of acylglycerols. (a) Stereospecific numbering of glycerol, (b) 1-monoacyl-*sn*-glycerol, (c) 2-monoacyl-*sn*-glycerol, (d) 3-monoacyl-*sn*-glycerol, (e) 1,2-diacyl-*sn*-glycerol, (f) 1, 3-diacyl-*sn*-glycerol, (g) 2, 3-diacyl-*sn*-glycerol, and (h) triacylglycerol. C*: chiral carbon; R, a fatty acid moiety; *sn*: stereospecific number.

TAG melts at room temperature (~25° C); at that temperature, fat is in a crystalline state and oil is in a liquid state. MAGs are intermediate products formed during enzymatic decomposition of TAGs during digestion. In addition, MAGs are industrially synthesized and used as emulsifiers because of their strong amphiphilic properties. DAGs are present as relatively minor components in natural oils and fats and are also industrially produced and used as edible fats and oils.

There is no chiral center in a glycerol molecule as seen in Fig. 1.2(a). However, it becomes chiral when for MAGs, a fatty acid is esterified either at the *sn*-1 or at the *sn*-3 positions (Fig. 1.2b and d), for DAGs, two fatty acids are esterified at the *sn*-1 (or *sn*-3) and *sn*-2 positions (Fig. 1.2e and g) or different fatty acid moieties are esterified at the *sn*-1 and *sn*-3 positions (Fig. 1.2f), and for TAGs, the three fatty-acid moieties are all different or different fatty acid moieties are esterified at the *sn*-1 and *sn*-3 positions (Fig. 1.2g). Instead of a numbering method using the *sn*-positions, an alternative description using Greek letters has been employed, as in α-monoacyl-*sn*-glyverol (1-monoacyl-sn-glycerol), β-monoacyl-*sn*-glycerol (2-monoacyl-*sn*-glycerol), α, β-diacyl-*sn*-glyverol (1, 2-diacyl-*sn*-glycerol), α, α'-diacyl-*sn*-glycerol (1, 3-diacyl-*sn*-glycerol), etc.

Optical isomers can occur for chiral acylglycerols, and the mixing-phase behavior of the chiral molecules affects the structural and physical properties in natural lipids when racemic mixtures are present.

TAGs can be simply described by using the abbreviated names of the fatty acids listed in Table 1.1. For example, we have tristearoylglycerol (SSS), 1,3-dipalmitoyl-2-stearoyl-*sn*-glycerol (PSP), and 1,3-distearoyl-2-oleoyl- *sn*-glycerol (SOS). Chiral TAGs can also be described by using the abbreviated names of the fatty-acid moieties. For example *sn*-POS is 1-palmitoyl-2-oleoyl-3-stearoyl-*sn*-glycerol. An equal mixture of both stereoisomers of the chiral TAGs can be described as *rac* (e.g., *rac*-POS), which means that there are equal amounts of *sn*-POS and *sn*-SOP.

Lipid species can be precisely described by highlighting the atomic-level crystal structures in Chapter 2.

1.3 Physical States and the Functionality of Lipid Products

The crystallization and functionality of crystallized lipids are complicatedly influenced by the physical states where the lipids are crystallized, as seen in Fig. 1.3. Before going into the details of the crystallization in various physical states, which will be presented in forthcoming chapters, let us briefly view the relationship between the functionality of lipid products and the physical states presented in the figure.

The liquid state simply refers to an oil phase, as represented by frying oil and biofuel, whose functionality is in heat transfer, viscosity, oxidation stability, and so on. The crystallization process in liquid-state materials may occur as a deterioration of the end product (e.g., the clouding of cooking oils during storage in a refrigerator or precipitation causing an increase in the pouring point for biofuels at chilled temperatures). Therefore, retardation or prohibition of the crystallization of minor-component lipids becomes critical in these products. Lubricants made of vegetable oils also require similar physical properties for optimum functionality.

The crystalline state in a bulk sample signifies that the major portion of the material is composed of lipid crystals, as typically represented in confectionery fat (chocolate).

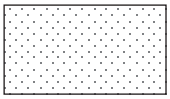
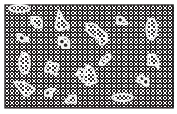
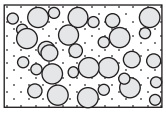
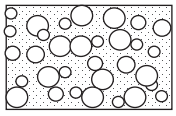
Physical States		Typical Products	Typical Functionality
Liquid		Frying oil Biofuel Lubricant	Heat transfer Viscosity Oxidation stability
Bulk		Chocolate Hard lipstick	Crispy touch Hardness Sharp melting
Gel		Water barrier film Soft lipstick	Hardness/Softness Spreadability Oil-binding property
Emulsion		Cream Mascara Drug carrier	Spreadability Texture Stability
Foam		Whipped cream Ice cream	Dispersibility (air) Stabillity Thermal conductivity

Fig. 1.3 Relationships between physical states and functionality of lipid products.

Fine particles of sugar, cocoa mass, and milk powder are suspended in the continuous phase of cocoa butter crystals, which comprise about 30 wt.% of the total mass of chocolate. Crispy touch, hardness, and sharp melting are typical functionalities of chocolate, which are mostly brought about by the lipid crystals comprising the major matrices of the products. Lipid crystal–based hard lipsticks require the functionalities of hardness, spreadability, gloss, anti-sweating, and anti-blooming of the products. Such properties are also determined by the network of lipid crystals, in which pigments, fragrance materials, and biologically active substances (vitamins, hormones, amino acids, etc.) are dispersed.

The gel state is defined as a two-phase colloidal system consisting of solid components along with water (hydrogels) or oil (oleogels or organogels), in which the solid behavior prevails over the sol state. Oleogels may be defined as lipophilic liquids and solid mixtures in which solid lipid materials (gelators) with lower concentrations can entrap bulk liquid oil by forming a network of gelators in the bulk oil. The gelators can be grouped into two categories: self-assembly systems and crystal-particle systems. Water-barrier films and soft lipsticks are typical products made of oleogels. The morphology, size, density, and crystal networks of lipid crystals are the dominant factors that influence the physical functionalities of the gel state, such as hardness/softness and spreadability.

An emulsion is defined as a two-phase colloidal system consisting of water and oil along with emulsifiers that reduce the water–oil interfacial energy. There are two types of emulsions, water-in-oil (W/O) and oil-in-water (O/W). Butter, margarine, and

spread (W/O) and whipped (O/W) systems are typical emulsion systems consisting of lipid crystals, in which the physical properties of the emulsion, such as the spreadability, texture, and stability, are influenced by the lipid crystals present in the continuous phase of the W/O emulsion or in the dispersed phase of the O/W emulsion. Both the W/O and O/W emulsions are widely employed in the food, cosmetics, and pharmaceutical industries. In particular, nanometer-sized lipid droplets are employed as carrier systems for poorly water-soluble drugs.

Aerated colloidal systems, also known as foams, are widely applied in the cosmetics, food, and porous material production industries. Foams have the significant advantages of shape retention, soft texture, the ability to act as a thermal barrier, and low calorie content. Aqueous foams contain air bubbles in a continuous aqueous phase, like whipped cream and ice cream. Nonaqueous foams are formed by dispersing air bubbles in oil phases and are important for foamed plastics, whipped butter, and confections. In both cases, the dispersibility and stability of air bubbles are major functionalities that are partly governed by the lipid crystals surrounding the air bubbles together with other ingredients such as proteins and starches.

In the lipid crystal–based products displayed in Fig. 1.3, the lipid crystals play critically important roles in revealing the firmness, gloss, melting/crystallization, texture, rheology, and stabilization of water droplets (W/O emulsion) and air cells (foams) by themselves alone or together with emulsifiers, proteins, starch, and so on.

1.4 Formation Processes of Lipid Crystals

The basic principles underlying the formation processes of lipid structures are common to the physical states displayed in Fig. 1.3, including the microscopic and macroscopic features in Fig. 1.4. Polymorphic structures and primary particles of lipid crystals comprise the microscopic features, whereas the formation of flocs and networks of lipid crystals determines the macroscopic features.

The molecular structures of lipids are revealed in polymorphism and primary-particle formation. Polymorphism remarkably influences the macroscopic properties of fat products. For example, there are three polymorphic forms in TAG crystals, α, β', and β. In margarines and fat spreads, lipids are first crystallized in the least stable form (α) by rapid cooling of the molten materials. However, the α crystals are very short-lived and do not exist in the finished products, in which metastable β' crystals are formed as the most desired polymorphic form. This is because β' crystals are relatively small and can incorporate a large amount of semi-solid oil phases and

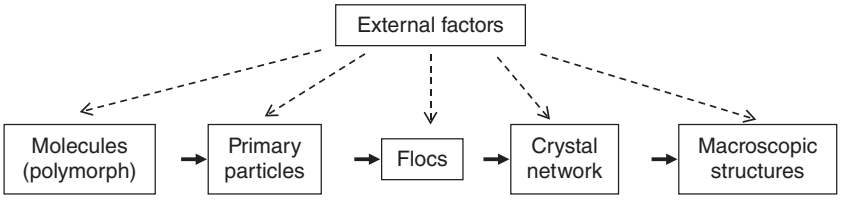


Fig. 1.4 External factors affecting formation processes of lipid crystals.

water droplets within the crystal network. Thermodynamic stabilization, however, causes the transformation from the metastable β' form to the most stable β form during storage or other shelf-life conditions. The β crystals tend to grow into large needle-like agglomerates, which results in a sensation of sandiness in the mouth. In contrast, cocoa butter in chocolate should be crystallized in a β polymorph (more correctly, Form V of a β-type polymorph, see Chapter 3) because of its high density and optimal melting point, resulting in the desired sharp melting of chocolate. As β crystals crystallize too slowly compared with the α and β' forms, the use of a special processing of crystallization called *tempering* is necessary for producing cocoa-butter-based chocolate.

External factors can produce many of the desired microscopic features of lipid crystals, and knowledge of the relationship between their molecular structures, their particle formation along different dimensions, and their spatial networks under internal and external factors gives us optimal ways of designing materials with the desired functionality. Typical factors that have already been applied, or have high potential to be applied, to the actual industrial processing include the following.

a) Internal factors
   - Interesterification (chemical, enzymatic)
   - Fractionation (dry, solvent, detergent)
   - Blending
b) External factors
   - Intentionally varying the temperature
   - Applying shear
   - Applying hydrostatic pressure
   - Adding foreign materials (additives)
   - Applying ultrasound waves
   - Encapsulating of lipids into small droplets (O/W emulsion)

These external factors are thoroughly discussed in this book.

The details of the formation of lipid crystal networks vary from one physical state to another. For example, crystallization in a bulk sample proceeds without the effects of oil–water interfaces, whereas interfacial crystallization in the O/W and W/O emulsion states plays a critical role in creating the lipid crystal network (see Fig. 1.3). The basic streams, however, of the formation of a lipid crystal network can be drawn as in Fig. 1.5, which includes the formation of crystal nuclei (nucleation), the subsequent growth of crystal nuclei (crystal growth), the aggregation of crystal particles, and the formation of a crystal network (network formation). All of these processes should be enabled only when a given set of external conditions (e.g., temperature, pressure, and concentration) provides the driving forces for crystallization as expressed by supercooling or supersaturation. Supercooling (ΔT) is defined as the difference in temperature between the melting point (T_m) and the crystallization temperature (T_c), that is, $\Delta T = T_m - T_c$. Supersaturation (S) is defined as the ratio of the actual solute concentration X in solution to the solubility (X_s) at $T = T_c$, that is, $S = X/Xs$. The former refers to crystallization from neat liquid (melt), and the latter to crystallization from solution.

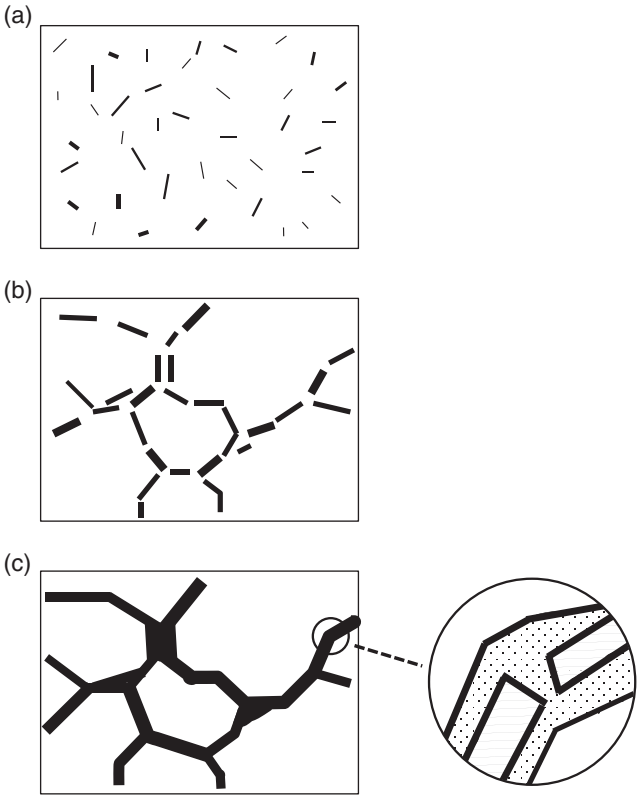


Fig. 1.5 A model of formation processes of lipid crystal network. (a) Nucleation, (b) crystal growth, and (c) network formation.

1.5 Polymorphism

Almost all lipids possess two or more different crystal structures under a given set of thermodynamic conditions. This multiplicity of crystalline structures of the same substance is called *polymorphism*.

The polymorphic behavior of lipid crystals is basically determined by their molecular structure, thermodynamic stability, and phase transformations. The thermodynamic stability of polymorphic forms is illustrated by the relationship of their Gibbs energy values, $G = H - TS$, where H, S, and T are the enthalpy, entropy, and temperature. Polymorphic forms with greater G values are less stable than those with lower ones, which have higher solubility and lower melting points.

Polymorphic transformations occurring during and after crystallization are also quite important. Two types of transformations can occur from less stable forms to more stable polymorphic forms (e.g., from α or β' forms to β' or β forms for TAGs). Solid-state transformation occurs when the metastable form is stored below its melting temperature in the crystalline state. Another type of polymorphic transformation is melt-mediated transformation, which occurs as the temperature rises just above the melting

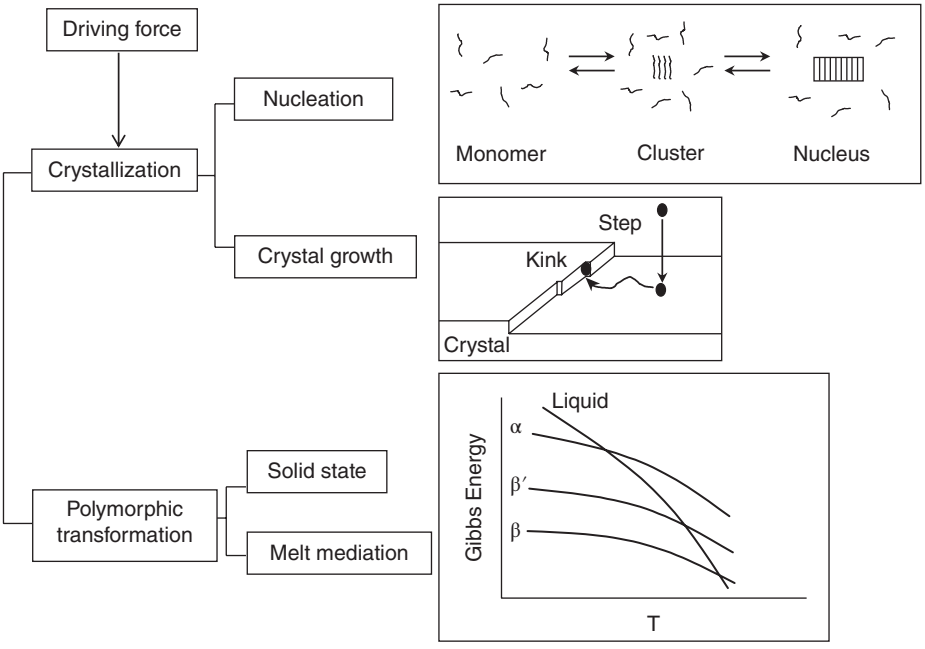


Fig. 1.6 Elementary processes of crystallization of lipids.

point of a metastable form, where melting of the metastable form and successive crystallization of more stable forms occur.

Figure. 1.6 summarizes the elementary processes of the polymorphic crystallization of lipids. We may consider that the nucleation and crystal growth are relatively straightforward in accordance with the theory of nucleation and crystal growth.

Complicated events, however, must occur during the formation of lipid crystal networks in the actual production stages of the lipid products because the methods of distribution and aggregation of the crystal particles differ greatly from those occurring in the initial stages of nucleation and crystal growth. Network formation may be affected by the following processes.

- Nucleation and crystal growth to form primary particles, in which tiny crystals having different sizes and polymorphic forms are present. In addition, the multiple lipid components comprising the lipid products are mixed either in miscible or immiscible phases, depending on the molecular shapes of the lipid components and crystallization.
- Recrystallization of primary crystal particles through Ostwald ripening, polymorphic crystallization, and transformation, as well as variations in the mixing behavior and successive crystallization of different lipid materials.
- Particle–particle interactions including sintering (Fig. 1.5c) may lead to the formation of crystal networks.

One must recall that lipid materials are produced in factory-scale machines under external factors, which particularly affect the nucleation and crystal growth. Recrystallization proceeds during the aging period between factory-scale production and storage in warehouses.

1.6 Aging and Deterioration

The principal flows in the production of lipid materials may be simply drawn as in Fig. 1.7. Raw materials of lipids and water, salts, sugar, protein, starch, and emulsifiers are mixed and then melted or dissolved at elevated temperatures. They are then cooled or evaporated to cause lipid crystallization, which usually is conducted under stirring or shearing conditions for efficiency of heat exchange, emulsification, and aeration. After the dynamic production process has ceased, the lipid materials are kept in storage at optimal temperature ranges over certain periods (days to months) before releasing them into the markets.

Throughout the processes shown in Fig. 1.7, including the commodity circulation of final products at the consumer end, the roles of physical and chemical control may be summarized as follows: sustaining the high value of raw materials, stabilizing the final products, and revealing the functionality of the products.

From the viewpoint of stabilization, it is worthy to note that almost all lipid products are actually in thermodynamically metastable conditions when they retain highly functional properties. In contrast, conversions into thermodynamically stable conditions lead to degradation of the functionality, so this stabilization must be prohibited. The conversion proceeds in accordance with thermodynamic laws, so it is impossible to ultimately shut it off; but practical technology is used to retard the conversion as much as possible by proper methods.

For example, chocolate is in a thermodynamically metastable condition because fine particles of ingredients (e.g., cacao mass, sugar, and others) are dispersed in the crystal networks of cocoa butter and other specialty fats (i.e., suspension). The metastability of chocolate is revealed in many aspects. Specifically, the fine particles of ingredients and fat crystals have sizes ranging from submicrons to several tens of microns, and the fats are not simple components but rather are mixtures of different fat components that differ in melting temperatures. Furthermore, the fat crystals in chocolate are in metastable polymorphic forms (e.g., Form V of cocoa butter and β' of cocoa butter substitute [CBS]). Stabilization may lead to Ostwald ripening, which causes the growth of large particles at the expense of small particles (coarsening) during long-period storage. Different fat fractions can separate when the mixtures of component fats are eutectic. Furthermore, polymorphic transformations from Form V to Form VI of cocoa butter or β' to β of CBS may cause fat blooming. These degradations cause inferior mouth feel, loss of gloss, and so on.

Another example is W/O emulsions like margarine and fat spread, which are in metastable states, as water droplets are forced to disperse in the semi-solid fat phase with the aid of emulsifying reagents by applying a high shear force (emulsification). Also, the fats have multiple components with crystals in metastable β' polymorph form. When the

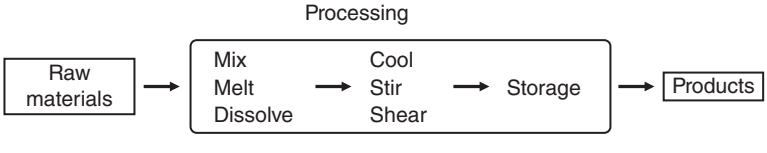


Fig. 1.7 Flows of production of lipid materials.

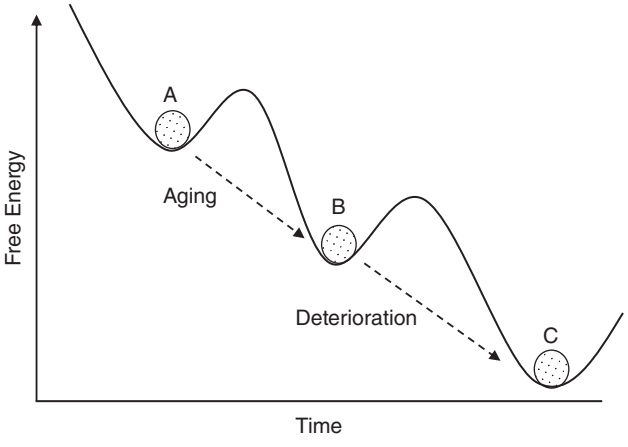


Fig. 1.8 Aging and deterioration of lipid products. A and B are metastable states, C is the most stable state.

measures to sustain such metastable condition are not used, various degradations occur (e.g., coalescence of water droplets, separation of oil and water phase in an extreme case, or granulation of fat crystals, which causes a loss of gloss, decrease in spreadability, etc.).

In any case, metastability and stability during production, commodity circulation, and consumption stages vary from one product to another. However, one may consider the stabilization of lipid products in terms of the diagram of free energy and time given in Fig. 1.8.

There are two stages of a metastable state, A and B. A is the stage between factory production and storage, and B is the stage between storage and circulation in the commodity. Both are metastable, but A is less stable than B. Optimal functionality of the products must be revealed in stage B. However, the most stable state is C, where degradation begins to occur because of stabilization.

We may think that aging is the process of transforming from A to B, and that deterioration corresponds to the transformation from B to C. Technological innovation focuses on how to promote the aging and retard the deterioration. Therefore, the physical properties of lipid crystals affecting the microscopic and macroscopic mechanisms of aging and deterioration in lipid products should be clarified.

In this respect, our particular concerns are focused on the kinetic processes involved in forming lipid crystal networks as revealed in the changes from A to B, which follow nucleation and crystal growth under various external factors noted in Fig. 1.5 (a and b).

To summarize, the crystallization of lipids that occurs in the various production stages is quite dynamic (e.g., the time-size scales differ greatly from one process to another, as shown in Table 1.2). For example, achieving the driving forces for crystallization (e.g. supercooling) may require seconds to minutes, depending on the size of the production system and the rate of cooling. Nucleation begins soon after the driving force is achieved, and the sizes of the crystal nuclei may be on the order of several to several tens of nanometers. Crystals may then grow in several to several tens of minutes. The formation of lipid crystal networks may take longer during aging, typically

Table 1.2 Time-size scales of crystallization processes.

Phenomena	Time	Size
Supercooling	Seconds–minutes	—
Nucleation	Minutes	~50 nm
Crystal growth	Minutes–hours	200 nm–1 μm
Aging	Hours–days	1 μm–10 μm
Deterioration	Weeks–months	20 μm–100 μm

hours to days, and deterioration such as fat bloom formation in chocolate occurs in weeks to months, depending on the temperature and its fluctuations during the distribution and consumption stages.

1.7 *Trans*-Fat Alternative and Saturated-Fat Reduction Technology

Trans-fats can be defined as fats containing *trans*-unsaturated fatty acids, in which the local conformation of hydrocarbon chains at the double bonds is *trans*-type, as illustrated for elaidic acid in Fig. 1.1(d). *Trans*-fats are rather uncommon in nature except for meat and dairy products from ruminants, but they are produced industrially as partially hydrogenated oils (PHOs) from liquid oils containing *cis*-unsaturated fatty-acid moieties. *Trans*-fats have been used in margarine, snack foods, and confections since the 1950s. However, recent nutritional studies have claimed that, depending on the method and quantity of its intake, *trans*-fat can be associated with increased risk of coronary heart disease. Therefore, reduction of *trans*-fat has been a major concern of national and local governments, consumer organizations, and private enterprises (Kodali 2014; Wang et al. 2016). In addition, the intake of saturated fatty acids (SAFAs) and the reduction of SAFAs have also been a critical nutritional concern, although debates about SAFA-related issues are still continuing.

We do not intend to discuss the nutritional issues surrounding *trans*-fat and SAFAs in this chapter, but we do take a closer look into the necessity to cope with the issues around *trans*-fat and SAFAs from the viewpoint of lipid crystallization technology.

There are rational reasons for the long-time use of *trans*-fat: it exhibits such high functionality when employed for edible applications, it is low cost, easily produced, β'-tending and β'-stable crystals, fine crystal network formation, high rates of crystallization, sharp melting behavior, and high oxidation stability. Therefore, so-called "*trans*-fat alternative" technology must satisfy the following requirements.

a) Functionality
   - Maintaining flakiness, firmness, crispiness, melting, and appearance
   - Stabilization of end products (e.g., anti-oxidation)

b) Availability
   - Easily available
   - Smooth processing

c) Economics
   - Not highly expensive

Along these lines, typical examples of *trans*-fat alternative technology are listed.

a) Zero-*trans*-fat resources
   - High-oleic sunflower, high-oleic canola, high-oleic soybean
   - Semi-solid fats (palm, palm kernel, coconuts, fully-hydrogenated fats)
   - Organogels (low-molecular/macromolecular organogelators)
b) Zero-*trans* fat resources + processing
   - Molecular design (esterification)
c) Zero-*trans* fats + processing+ reduced-SAFA
   - Blending of high-oleic soybean/palm/fully-hydrogenated fats
   - Algal oil (high oleic >90%)
   - Fractionation of palm oil, palm kernel oil, coconut oil, high-oleic high-stearic sunflower oil, etc.
   - Esterification (high-oleic soybean + palm fraction, etc.)
d) Efficient uses of additives
   - Emulsifiers

Similarly to *trans*-fat alternative technology, SAFA-reduction technology will have to satisfy the following requirements.

a) Maintaining functionality with reduced SAFA
   - Firmness and gloss
   - Melting and crystallization
   - Texture, rheology, and spreadability
   - Stabilization (water droplets, air cells)
b) Production conditions
   - Availability
   - Economics
   - Minimum changes in processing
c) Limitations
   - Hardness of chocolate
   - Softness of cookies

Along these lines, typical examples of SAFA-reduction technology are as follows.

a) Increasing oleic-acid moiety
   - High-oleic sunflower, canola, and soybean
   - Oleic-rich TAGs (POO, SOO, OPO, OSO, etc.)
b) SAFA-alternative materials
   - Organogels (see above)
   - Fat replacers
   - Increasing starch
c) Modifying crystallization conditions
   - (See above.)

To summarize, we are confident that research on lipid crystallization will play a critically significant role in *trans*-fat alternative and SAFA-reduction technologies. Many chapters of this book share the same aims and desires.

References

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