Crystallization of Lipids
Crystallization of Lipids

Fundamentals and Applications in Food, Cosmetics, and Pharmaceuticals

Edited by Kiyotaka Sato
Hiroshima University, Higashi-Hiroshima, Japan
Contents

Preface  xiii
List of Contributors  xv

1  Introduction: Relationships of Structures, Properties, and Functionality  1
   Kiyotaka Sato
   1.1 Introduction  1
   1.2 Lipid Species  1
   1.2.1 Hydrocarbons  1
   1.2.2 Fatty Acids  2
   1.2.3 Alcohols and Waxes  4
   1.2.4 Acylglycerols  4
   1.3 Physical States and the Functionality of Lipid Products  5
   1.4 Formation Processes of Lipid Crystals  7
   1.5 Polymorphism  9
   1.6 Aging and Deterioration  11
   1.7 Trans-Fat Alternative and Saturated-Fat Reduction Technology  13
   References  15

2  Polymorphism of Lipid Crystals  17
   Kiyotaka Sato
   2.1 Introduction  17
   2.2 Thermal Behavior of Polymorphic Transformations  17
   2.3 Molecular Properties  20
   2.3.1 Subcell and Chain-Length Structures  20
   2.3.2 Conformation of Hydrocarbon Chains  24
   2.3.3 Glycerol Conformations  25
   2.3.4 Polytypism  26
   2.4 Fatty Acids  27
   2.4.1 Saturated Fatty Acids  27
   2.4.2 Unsaturated Fatty Acids  32
   2.5 Monoacylglycerols and Diacylglycerols  37
   2.5.1 Crystal/Molecular Structures  37
   2.5.2 Polymorphic Behavior  39
   2.6 Triacylglycerols (TAGs)  41
   2.6.1 Crystal/Molecular Structures  42
## 3 Molecular Interactions and Mixing Phase Behavior of Lipid Crystals
*Eckhard Floeter, Michaela Haeupler, and Kiyotaka Sato*

### 3.1 Introduction

### 3.2 Thermodynamic Considerations

#### 3.2.1 Framework for Engineering Calculations

#### 3.2.2 Phase Behavior of Co-Crystallizing Components

#### 3.2.3 Governing Principles for Phase Boundaries

### 3.3 Effects of Molecular Structures on the Phase Behavior

#### 3.3.1 Aliphatic Chain-Chain Interactions: n-Alkanes

#### 3.3.2 Mixtures of Fatty Acids

#### 3.3.3 Mixtures of Partial Glyceride Fatty-Acid Esters

#### 3.3.4 Mixtures of TAGs

### 3.4 Mixing Behavior of TAGs in Natural and Interesterified Fats

#### 3.4.1 Cocoa Butter

#### 3.4.2 Palm Oil

#### 3.4.3 Coconut Oil

#### 3.4.4 Milk Fat

#### 3.4.5 Interesterified Fats

### 3.5 Crystallization Properties

### 3.6 Conclusions

## 4 Fundamental Aspects of Crystallization of Lipids
*Hironori Hondoh, Satoru Ueno, and Kiyotaka Sato*

### 4.1 Introduction

### 4.2 Physical and Structural Properties of Lipid Liquids

#### 4.2.1 Preheating Effects

#### 4.2.2 Liquid Phases of Triacylglycerols

### 4.3 Driving Forces for Crystallization

### 4.4 Nucleation

#### 4.4.1 Homogeneous versus Heterogeneous

#### 4.4.2 Polymorph-Dependent Nucleation Kinetics

#### 4.4.3 Secondary Nucleation

#### 4.4.4 Crystal Seeding

### 4.5 Kinetics of Crystal Growth

#### 4.5.1 Mechanism of Crystal Growth

#### 4.5.2 Crystal Growth Rate

#### 4.5.3 Polymorph-Dependent Growth Rate

#### 4.5.4 Spherulite

#### 4.5.5 Epitaxial Growth

#### 4.5.6 Morphology of Crystals

### 4.6 Conclusions

Acknowledgment

References
7  Lipid Crystal Networks Structured under Shear Flow  211
Farnaz Maleky and Gianfranco Mazzanti
7.1  Introduction  211
7.2  Overview of the Formation of Fat Crystals  212
7.3  Temperature Gradients and Optimal Supercooling  213
7.4  Basic Concepts on Shear Flow  214
7.5  Fat Crystallization under Shear  216
7.5.1 Shear Affects Polymorphic Transformations  216
7.5.2 Crystalline Orientation Induced by Shear Flow  219
7.5.3 Shear Affects Fat Structural Properties at the Micro- and Nano-Length Scales  224
7.5.4 Physicochemical Properties of Sheared Fat Matrices  227
7.5.5 Effects of Shear Flow on Mass Transfer Dynamics of Crystallizing and Crystallized Materials  231
7.6  Concluding Remarks  233
References  234

8  Tailoring Lipid Crystal Networks with High-Intensity Ultrasound  241
Yubin Ye, Peter R. Birkin, and Silvana Martini
8.1  Introduction  241
8.2  Fundamentals of Sonication  242
8.2.1 Acoustic Driving Force  242
8.2.2 Acoustic Cell Characteristics  243
8.2.3 Cavitation  244
8.2.4 Experimental Conditions  245
8.3  Tailoring Lipid Crystal Networks  246
8.3.1 Crystallization Kinetics  246
8.3.2 Inferential Mechanism  249
8.3.3 Postsonication Changes  250
8.4  Practical Considerations  255
8.4.1 Oxidation  255
8.4.2 Scale Up  257
8.4.3 Combination with Other Processing Methods  258
8.5  Conclusions and Future Research  258
References  259

9  Effects of Foreign and Indigenous Minor Components  263
Kevin W. Smith and Kiyotaka Sato
9.1  Introduction  263
9.2  Basic Understanding  264
9.3  Effects of Foreign Components  265
9.3.1 Emulsifiers  265
9.3.2 Indigenous Minor Components  276
9.4  Other Additives  276
9.5  Conclusions  278
References  279
10 Crystallization Properties of Milk Fats 283
Christelle Lopez
10.1 Introduction 283
10.2 Milk Fat: A Wide Diversity of Fatty Acids and Triacylglycerols (TAGs) 284
10.3 Crystallization Properties of Bovine Anhydrous Milk Fat (AMF) 285
10.3.1 Thermal Properties 285
10.3.2 Effect of Cooling Rate on AMF Crystals 286
10.3.3 Effect of Shear on AMF Crystals 295
10.3.4 Effect of Minor Lipid Compounds 295
10.4 Crystallization of TAGs in Bovine Milk Fat Globules and Emulsion Droplets 296
10.4.1 Effect of Cooling Rate and Tempering 298
10.4.2 Effect of the Size of Milk Fat Globules and Lipid Droplets 304
10.5 Crystallization Properties of Milk Fat in Dairy Products 306
10.6 TAG Compositions Affecting Crystallization Properties of Milk Fat 308
10.6.1 Technological Process: Dry Fractionation 308
10.6.2 Dietary Manipulations 312
10.6.3 Milk Fat from Various Mammal Species 315
10.7 Liquid TAG Phase 316
10.8 Conclusions 317
References 318

11 Crystallization Behavior of Sunflower Oil–Based Fats for Edible Applications 323
Maria L. Herrera and Silvana Martini
11.1 Introduction 323
11.2 High Stearic High Oleic Sunflower Oil 324
11.2.1 Fractionation of HSHO-SFO 324
11.2.2 Crystallization Behavior 326
11.2.3 Polymorphic Behavior 329
11.3 Blends of Sunflower Oil and Milk Fat 337
11.3.1 Chemical Composition 340
11.3.2 Physical Properties 340
11.3.3 Addition of Palmitic Sucrose Ester 344
11.4 HSHO-Based CBE 347
11.5 Conclusions 348
References 348

12 Physical Properties of Organogels Developed with Selected Low-Molecular-Weight Gelators 353
Jorge F. Toro-Vazquez, Flor Alvarez-Mitre, and Miriam Charó-Alonso
12.1 Introduction 353
12.2 Basic Aspects of LMOGs: From Molecular Architecture to Functional Assemblies 355
12.3 Why Developing Organogels with Vegetable Oils? 356
12.3.1 Vegetable Oils as Solvent in the Development of Organogels with LMOGs 357
12.3.2 Relationship between Molecular Structure of LMOGs and Physical Properties of Organogels 367
12.4 Organogels of Candelilla Wax 373
12.4.1 Rheological Properties of Candelilla Wax Organogels Developed Applying Shear Rate 373
12.4.2 Applications of Candelilla Wax Organogels 377
12.5 Conclusions 377
References 379

13 Formation and Properties of Biopolymer-Based Oleogels 385
Ashok R. Patel

13.1 Introduction 385
13.2 Formation of Polymer-Based Oleogels 386
13.2.1 Polymer Oleogelation through Direct Methods 387
13.2.2 Polymer Oleogelation through Indirect Methods 389
13.3 Properties of Polymer-Based Oleogels 393
13.3.1 Mechanical Properties 393
13.3.2 Temperature Sensitivity 394
13.3.3 Stability in Presence of Water 397
13.4 Potential Applications of Polymer-Based Oleogels 397
13.4.1 Replacement of Beef Fat in Frankfurters 397
13.4.2 Heat-Resistant Chocolates 397
13.4.3 Polymer Oleogels as Alternative to Full-Fat Shortenings 397
13.4.4 Bakery Applications of Ethyl Cellulose Oleogels 398
13.5 Conclusions: Opportunities and Challenges 398
Acknowledgments 401
References 402

14 Lipid Crystallization in Water-in-Oil Emulsions 405
Nicole L. Green and Dérick Rousseau

14.1 Introduction 405
14.2 Basics of Emulsion Properties 406
14.3 Emulsifier Effects on W/O Emulsions 408
14.3.1 Mono- and Diacylglycerols (E471) 409
14.3.2 Sucrose Fatty-Acid Esters (E473) 411
14.3.3 Lecithins (E322) 412
14.3.4 Sorbitan Esters and Polyesters (E491-E496) 413
14.3.5 Polyglycerol Esters (E475 – E476) 415
14.4 Stabilization Modes of W/O Emulsions 415
14.4.1 Pickering Stabilization 416
14.4.2 Network Stabilization 420
14.4.3 Combined Pickering and Network Stabilization 421
14.5 Conclusions 423
References 424
Preface

This text presents new and emerging knowledge, techniques, and applications of lipid crystals, which are major hydrophobic ingredients of semi-solid soft matters—along with liquid oils, water, emulsifiers, and other minor components—used in food, cosmetic, and pharmaceutical industries.

In various semi-solid lipids, the lipid crystals exhibit invaluable physical and chemical properties: solubilization and controlled release of oil-soluble nutrients, drugs and flavoring ingredients, hardness, consistency, melting behavior, spreadability, structuring of liquid oil, water and air cells. This text covers recent advances in the research of polymorphic structures, molecular interactions, nucleation and crystal growth, and crystal network formation of lipid crystals in bulk and emulsion states. Specific efforts have been made to relate two problems of trans-fat alternative and saturated-fat reduction technology to lipid crystallization. Although the latter is still debated in academia and industry, the two problems are the most significant in the edible application of lipids, and one of the key solutions must be present in ideas to improve the crystallization processes of various lipid materials.

In my mind, this text is an evolution of previous publications, Crystallization and Polymorphism of Fats and Fatty Acids and Crystallization Processes of Fats and Lipid Systems, which were published in 1988 and 2001, respectively. During the last decades, three driving forces may have prompted me to publish this text. First, global trends in many lipid-related industries have rapidly changed and developed, and they have pushed us to elucidate knowledge and technology of lipid crystallization. Some of these trends are consumers’ preferences for more natural and healthy lipid materials, ethics and sustainability of raw lipid materials production, and innovation and hybridization of functional end products. Second, driven by these trends, the quantity and quality of the research and technology of lipid crystallization has advanced quickly. Now is the time for a text that can comprehensively review the current studies and foresee the future developments of our research fields. Third, the scientific methods used to analyze the crystallization processes and structures of lipids have also developed (e.g., synchrotron radiation X-ray diffraction and scattering, ultrasonic, laser scattering, near infrared and Raman spectroscopic techniques) and deserve to be reviewed.

The 17 chapters in this text may be categorized in four groups. The first of these begins with Chapter 1, which introduces the readers to the world of lipids, and continues with Chapters 2, 3, and 4 in which the fundamental aspects of lipid crystals and crystallization are further described. In the second group, Chapters 5 through 9, the formation of lipid crystal networks under various external influences of thermal
fluctuation, ultrasound irradiation, shear, and additives is discussed. In the third group, Chapters 10, 11, and 16 review the crystallization properties of lipids in milk fats, sunflower oils, and animal meat tissues, and in Chapters 12 to 15, the lipid crystals in oleogel and emulsion states are discussed. In the final group and chapter, traditional and cutting-edge research tools to analyze lipid crystallization are highlighted.

I hope that this text can be a valuable resource for novel and creative knowledge for R&D technologists in food, cosmetic, and pharmaceutical industries; for professors and graduate students in departments of food science, bioengineering, and life materials science; and all of those who are working with the lipid crystals.

Kiyotaka Sato
List of Contributors

Nuria C. Acevedo
Department of Food Science and Human Nutrition
Iowa State University
Ames, Iowa, United States

Flor Alvarez-Mitre
Facultad de Ciencias Químicas-CIEP
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México

Laura Bayés-García
Facultat de Ciències de la Terra
Universitat de Barcelona
Barcelona, Spain

Peter R. Birkin
Department of Chemistry
University of Southampton
Highfield, Southampton
United Kingdom

Teresa Calvet
Facultat de Ciències de la Terra
Universitat de Barcelona
Barcelona, Spain

Miriam Charó-Alonso
Facultad de Ciencias Químicas-CIEP
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México

John N. Coupland
Department of Food Science
Pennsylvania State University
University Park, Pennsylvania,
United States

Miquel À. Cuevas-Diarte
Facultat de Ciències de la Terra
Universitat de Barcelona
Barcelona, Spain

Eckhard Floeter
Department of Food Technology and Food Chemistry
Technical University of Berlin
Berlin, Germany

Imogen Foubert
Food & Lipids
Katholieke Universiteit Leuven Kulak
Kortrijk, Belgium

Nicole L. Green
Department of Chemistry and Biology
Ryerson University
Toronto, Ontario, Canada

Michaela Haeupler
Department of Food Technology and Food Chemistry
Technical University of Berlin
Berlin, Germany
Maria L. Herrera
Institute of Polymer Technology and
Nanotechnology (ITPN)
National Research Council of Argentina (CONICET)
University of Buenos Aires
Buenos Aires, Argentina

Hironori Hondoh
Graduate School of Biosphere Science
Hiroshima University
Higashi-Hiroshima, Japan

Christelle Lopez
INRA, Science et Technologie du Lait et de l’OEuf
Rennes, France

Farnaz Maleky
College of Food, Agricultural and Environmental Sciences
Department of Food Science and Technology
Ohio State University
Columbus, Ohio, United States

Alejandro G. Marangoni
Department of Food Science
University of Guelph
Ontario, Canada

Silvana Martini
Department of Nutrition Dietetics and Food Sciences
Utah State University
Logan, Utah, United States

Gianfranco Mazzanti
Process Engineering and Applied Science
Dalhousie University
Halifax, Nova Scotia, Canada

Michiyto Motoyama
Institute of Livestock and Grassland Science
National Agriculture and Food Research Organization (NARO)
Tsukuba, Ibaraki, Japan

Ashok R. Patel
International Iberian Nanotechnology Laboratory
Braga, Portugal

Fernanda Peyronel
Department of Food Science
University of Guelph
Ontario, Canada

David A. Pink
Department of Physics
St. Francis Xavier University
Antigonish, Nova Scotia, Canada

Annelien Rigolle
Group Long Term Research and Services Lab (GRS)
Puratos, Groot-Bijgaarden I, Belgium

Dérick Rousseau
Department of Chemistry and Biology
Ryerson University
Toronto, Ontario, Canada

Keisuke Sasaki
Institute of Livestock and Grassland Science
National Agriculture and Food Research Organization (NARO)
Tsukuba, Ibaraki, Japan

Kiyotaka Sato
Hiroshima University
Higashi-Hiroshima, Japan

Kevin W. Smith
Fat Science Consulting Limited
Bedford, United Kingdom

Jorge F. Toro-Vazquez
Facultad de Ciencias Químicas-CIEP
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
Satoru Ueno
Graduate School of Biosphere Science
Hiroshima University
Higashi-Hiroshima, Japan

Koen Van Den Abeele
Wave Propagation and Signal Processing
Department of Physics
Katholieke Universiteit Leuven Kulak
Kortrijk, Belgium

Genya Watanabe
Institute of Livestock and Grassland Science
National Agriculture and Food Research Organization (NARO)
Tsukuba, Ibaraki, Japan

Yubin Ye
Nestlé Development Center
Marysville, Ohio, United States
1

Introduction: Relationships of Structures, Properties, and Functionality

Kiyotaka Sato

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 \( \text{CH}_3-(\text{CH}_2)_n-2-\text{CH}_3 \), in which \( n \) is the...
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 \(-\text{CH}_3\) in \( n \)-hydrocarbons with a carboxyl group (-COOH). In contrast, dicarboxilic acids are formed when both end groups of \(-\text{CH}_3\) in \( n \)-hydrocarbons are replaced with -COOH. There are saturated and unsaturated fatty acids, depending on whether double bonds are included and stereoisomers of \( \text{cis} \) or \( \text{trans} \) unsaturated fatty acids occur.

In nature, a wide variety of fatty acids is present, differing in \( n_c \), the number of double bonds having \( \text{cis} \) or \( \text{trans} \) 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.

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 \( \text{cis} \) double bond at the 9–10 carbon atoms, and elaidic acid is a mono-unsaturated fatty acid having a \( \text{trans} \) 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 \( \text{trans} \) to \( \text{cis} \).
- 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
even-numbered \( n_c - 1 \). For example, \( T_m \) of margaric acid \( n_c = 17 \) (palmitic acid, \( n_c = 16 \)) is 61\(^\circ\) C (63\(^\circ\) 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

<table>
<thead>
<tr>
<th>Systematic</th>
<th>Common</th>
<th>Shorthand</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Saturated</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Octanoic</td>
<td>Caprylic</td>
<td>8.0</td>
<td>Ca</td>
</tr>
<tr>
<td>Decanoic</td>
<td>Capric</td>
<td>10:0</td>
<td>C</td>
</tr>
<tr>
<td>Dodecanoic</td>
<td>Lauric</td>
<td>12:0</td>
<td>L</td>
</tr>
<tr>
<td>Tetradecanoic</td>
<td>Myristic</td>
<td>14:0</td>
<td>M</td>
</tr>
<tr>
<td>Hexadecanoic</td>
<td>Palmitic</td>
<td>16:0</td>
<td>P or PA</td>
</tr>
<tr>
<td>Heptadecanoic</td>
<td>Margaric</td>
<td>17:0</td>
<td>Ma</td>
</tr>
<tr>
<td>Octadecanoic</td>
<td>Stearic</td>
<td>18:0</td>
<td>S or SA</td>
</tr>
<tr>
<td>Nonadecanoic</td>
<td>Nonadecanoic</td>
<td>19:00</td>
<td>No</td>
</tr>
<tr>
<td>Eicosanoic</td>
<td>Arachidic</td>
<td>20:0</td>
<td>A</td>
</tr>
<tr>
<td>Docosanoic</td>
<td>Behenic</td>
<td>22:0</td>
<td>B</td>
</tr>
<tr>
<td><strong>Unsaturated</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c-9-Hexadecenoic</td>
<td>Palmitoleic</td>
<td>16:1, Δ9-ω7</td>
<td>POA</td>
</tr>
<tr>
<td>c-9-Octadecenoic</td>
<td>Oleic</td>
<td>18:1, Δ9-ω9</td>
<td>O or OA</td>
</tr>
<tr>
<td>c-12-Octadecenoic</td>
<td>Petroselinic</td>
<td>18:1, Δ6-ω12</td>
<td>PSA</td>
</tr>
<tr>
<td>t-9-Octadecenoic</td>
<td>Elaidic</td>
<td>18:1, Δ9-ω9</td>
<td>E</td>
</tr>
<tr>
<td>c-11-Octadecenoic</td>
<td>Asclepic</td>
<td>18:1, Δ11-ω7</td>
<td>APA</td>
</tr>
<tr>
<td>12-hydroxy, c-9-Octadecenoic</td>
<td>Ricinoleic</td>
<td>18:1, Δ9-ω9</td>
<td>R</td>
</tr>
<tr>
<td>t-11-Octadecenoic</td>
<td>Vaccenic</td>
<td>18:1, Δ11-ω7</td>
<td>V</td>
</tr>
<tr>
<td>c-9, c-12-Octadeциденои</td>
<td>Linoleic</td>
<td>18:2-ω6, 9</td>
<td>Li</td>
</tr>
<tr>
<td>c-9, c-12- c-15-Octadeциденои</td>
<td>α-Linolenic</td>
<td>18:3-ω3, 6, 9</td>
<td>ALA</td>
</tr>
<tr>
<td>c-6, c-9- c-12-Octadeциденои</td>
<td>γ-Linolenic</td>
<td>18:3-ω6, 9, 12</td>
<td>GLA</td>
</tr>
<tr>
<td>c-11-Eicosanoic</td>
<td>Gondoic</td>
<td>20:1, Δ11-ω9</td>
<td>GOA</td>
</tr>
<tr>
<td>c-5, c-8, c-11, c-14, c-17-Eicosапентанои</td>
<td>Eicosапентанои</td>
<td>20:5, ω3, 6, 9, 12, 15</td>
<td>EPA</td>
</tr>
<tr>
<td>c-13-Docosenoic</td>
<td>Erucic</td>
<td>22:1, Δ13-ω9</td>
<td>Er</td>
</tr>
<tr>
<td>c-4, c-7, c-10, c-13, c-16, c-19-Docosахексанои</td>
<td>DHA</td>
<td>22:6, ω3, 6, 9, 12, 15, 18</td>
<td>DHA</td>
</tr>
</tbody>
</table>

Table 1.1 Systematic, common, and shorthand names of principal fatty acids.
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 lipophilic 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, candelilla 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\(_2\)OH-CHOH-CH\(_2\)OH) 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-glycerol (1-monoacyl-sn-glycerol), β-monoacyl-sn-glycerol (2-monoacyl-sn-glycerol), α, β-diacyl-sn-glycerol (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).
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

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

**Fig. 1.3** Relationships between physical states and functionality of lipid products.
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, \( \alpha \), \( \beta' \), and \( \beta \). In margarines and fat spreads, lipids are first crystallized in the least stable form (\( \alpha \)) by rapid cooling of the molten materials. However, the \( \alpha \) crystals are very short-lived and do not exist in the finished products, in which metastable \( \beta' \) crystals are formed as the most desired polymorphic form. This is because \( \beta' \) crystals are relatively small and can incorporate a large amount of semi-solid oil phases and

![Fig. 1.4](image.png)
water droplets within the crystal network. Thermodynamic stabilization, however, causes the transformation from the metastable $\beta'$ form to the most stable $\beta$ form during storage or other shelf-life conditions. The $\beta$ 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 $\beta$ polymorph (more correctly, Form V of a $\beta$-type polymorph, see Chapter 3) because of its high density and optimal melting point, resulting in the desired sharp melting of chocolate. As $\beta$ crystals crystallize too slowly compared with the $\alpha$ and $\beta'$ 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 ($\Delta T$) 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, $S = X/X_s$. The former refers to crystallization from neat liquid (melt), and the latter to crystallization from solution.
Introduction: Relationships of Structures, Properties, and Functionality

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 \( \alpha \) or \( \beta' \) forms to \( \beta' \) or \( \beta \) 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 point.

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

1.5 Polymorphism
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.