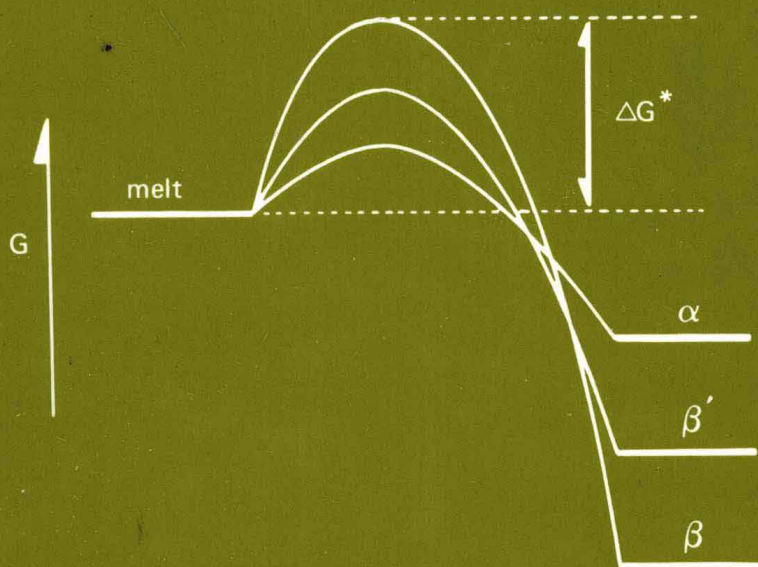


surfactant science series

volume **31**

CRYSTALLIZATION AND POLYMORPHISM OF FATS AND FATTY ACIDS



edited by
Nissim Garti
Kiyotaka Sato

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Marcel Dekker, Inc.

New York and Basel

Library of Congress Cataloging-in-Publication Data

**Crystallization and Polymorphism of fats and fatty acids / edited by
Nissim Garti, Kiyotaka Sato.**

p. cm. — (Surfactant science series ; v. 31)

Includes index.

ISBN 0-8247-7875-8

1. Acids, Fatty. 2. Oils and fats. I. Garti, Nissim.

II. Sato, Kiyotaka. III. Series.

QD305.A2C975 1989

547.7'7—dc19

88-23380

CIP

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MARCEL DEKKER, INC.

270 Madison Avenue, New York, New York 10016

Current printing (last digit):

10 9 8 7 6 5 4 3

PRINTED IN THE UNITED STATES OF AMERICA

CRYSTALLIZATION AND POLYMORPHISM OF FATS AND FATTY ACIDS

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Preface

This book is written for those who are investigating the physical and chemical characteristics of fats and fatty acids. These fatty species have increasingly attracted great interest in material sciences and industry (foods, cosmetics, pharmaceuticals, etc.). Current research is directed toward an understanding of the critical roles of fatty species in organized biosystems. In all of these research efforts, polymorphism is the most essential phenomenon among the physical and chemical properties of fats and fatty acids; it so far has not been covered in a monograph. Hence, this book will be a handy reference on the basic concepts and techniques concerning the physical behaviors related to the crystallization and phase transformations of polymorphic fats and fatty acids.

To date, there have been two different approaches to the study of polymorphic phenomena: (1) microscopic analyses of the polymorphic structures and their phase transformations and (2) technical control of the production conditions using macroscopic, for example, morphological or rheological, data. Now there is an increasing necessity to better support and correlate the foregoing two approaches and, furthermore, to give a sound basis for their future development, in accordance with recent advances in research.

For this reason, we decided to compile a text containing up-to-date knowledge of polymorphism and crystallization. The reader will learn how different polymorphs can be obtained with and characterized by modern techniques, and how polymorphic behaviors can be sensitively influenced by varying internal and external factors. The crystallization processes are discussed from the viewpoints of thermodynamics and kinetics of nucleation and crystal growth. Recent topics in the practical problems of highly advanced production technologies are reviewed as well.

Divergent aspects of the relevant problems are divided into two parts according to the main considerations: fundamentals, which are covered in Part I, and applications, to which Part II is devoted.

In "Fundamentals," the thermal properties, structural information, and crystallization processes of fatty acids and acylglycerides are discussed. Chapter 1 provides the conceptual background for the phenomena of the polymorphism and phase transformation. Chapters 2-4 discuss the thermal behaviors and crystal and molecular structures of the polymorphic modifications of the acylglycerides and fatty acids. Reporting most of the thermal data of the last 50 years, Chapter 2 also gives a historical review of the polymorphism of glycerides. Quite new findings on the polymorphism of some principal unsaturated fatty acids are described in Chapters 4 and 6. The fundamental theories of nucleation and crystal growth are presented in Chapter 5, with an emphasis on specified characteristics of long-chain compounds. Chapter 6 discusses the crystallization behaviors of both saturated and unsaturated fatty acids and glycerides. Chapters 5 and 6 also review the combined factors of thermodynamics and kinetics that lead to the crystallization and transformation of polymorphic forms.

"Applications" consists of five chapters, all of which are closely related to the practical use of fatty species. The role of surfactants in the crystallization and phase transformation of polymorphic fats and fatty acids is discussed from fairly microscopic points of view in Chapter 7. Chapter 8 deals with the fat crystal structures in cream and butter, exhibiting visualized information obtained with varying microscopic techniques. The polymorphism of cocoa butter is reviewed in Chapter 9, since it is critically related to the physical deterioration of chocolate and confectionery fats. Chapter 10 relates other topics in the area of confectionery fats to the crystallization behaviors of hard butter and addresses the possibility of replacing natural cocoa butter with suitable fats. Finally, the solidification problems encountered during the preparation of fatty species from raw materials are discussed in Chapter 11.

We would like to express sincere thanks to all our coauthors for their hard work and patience. A hearty acknowledgment is also given to Professor M. Okada, Hiroshima University, who encouraged us throughout this entire project. Many researchers and publishers have kindly given their permission to reproduce their results in this book.

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I

FUNDAMENTALS

1

Crystallization and Polymorphic Transformation: An Introduction

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I. INTRODUCTION

The aim of this book is to review and elucidate the phenomena of crystallization and polymorphic transformations of fats and fatty acids. The polymorphism of fatty species is closely related to phase changes and structural modifications of solid compounds. This phenomenon significantly affects the physical properties of end products, such as edible solid fats, confectionery fats, and cosmetics, and has critical implications in understanding the biological behavior of various lipid systems.

Studies in this area are relevant from both the scientific and technological points of view, and in this book we take both views. In this chapter we give a brief conceptual introduction so that readers will be able to share a common understanding of some terminology and physical background underlying the relevant phenomena.

II. DEFINITION OF POLYMORPHISM AND POLYTYPISM

Almost all fats and fatty acids possess two or more solid phases under a given set of thermodynamical conditions. These solid phases can be divided into two categories: polymorphism and polytypism [1], as illustrated in Figure 1.

Polymorphism may be defined as the ability to reveal different unit cell structures in crystal, originating from a variety of molecular conformations and molecular packings [2]. It is quite reasonable to believe that the long-chain fatty species may have divergent possibilities of constructing polymorphic structures because of different types of molecular interactions via, for example, methyl end groups, polar head groups, or bulky aliphatic chains. One may see this even in a simple example of stearic acid: four polymorphs at room temperature. It should also be true for many fats having more complicated molecular structures (see the following chapters).

Polytypism can be defined as one-dimensional polymorphism, since it is caused solely by a different stacking sequence of the long-chain lamellae in a particular direction. The two-dimensional arrangements of the unit cell are the same, while the third, most commonly along the long-chain axis, is a variable integral multiple of a common unit. If the lamella-lamella interaction energy is rather weak, as usually revealed via methyl end groups of fatty species, one polymorph can reveal a few different polytypes under suitable conditions. For example, stearic acid B polymorph has two basic polytypes (see Chapters 4 and 6).

So far, studies in this area have paid more attention to polymorphism. However, polytypism may also have an important influence on the structural changes in fatty species, even in complicated systems.

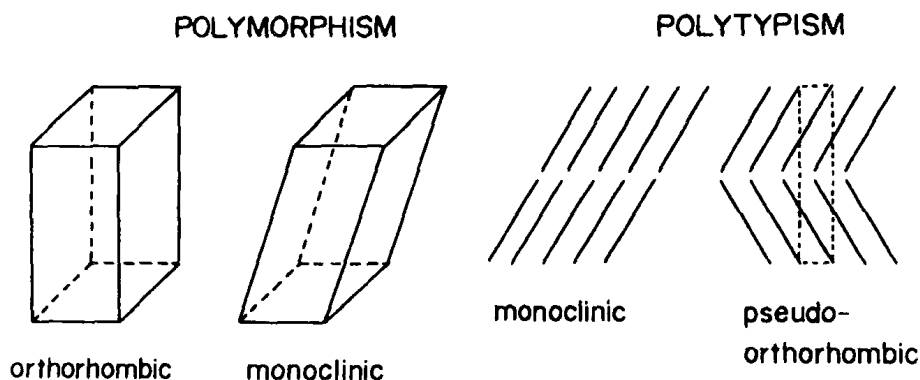


FIG. 1. Illustrations of polymorphic and polytypic modifications.

III. DIFFERENTIATION OF CRYSTALLIZATION AND TRANSFORMATION PROCESSES

The crystallization and transformation of the structural modifications discussed above are controlled by their thermodynamic stability and by external conditions. The thermodynamic stability is determined by a relationship involving the Gibbs energy, $G = H - TS$, where H , S , and T are enthalpy, entropy, and temperature, respectively. The Gibbs energy relationship can be evaluated by experimentally measuring the solubility of each modification in combination with a determination of the melting and phase transformation behaviors. It should be noted that modifications having larger Gibbs energies reveal higher solubilities and lower melting points.

Since almost all transformations of fats and fatty acids, of both melting/solidification and solid-state transformations, are of first order, there is a thermal hysteresis phenomenon characterized by supercooling for the appearance of the more stable forms. In addition, irreversibility of the transformation is of considerable importance, being associated particularly with solid-state transformation. This irreversibility is attributed to the fact that some of the thermal activation processes necessary to the transformation are kinetically blocked due to steric hindrance. The possible steric hindrance may be via molecular reconfiguration of the bulky aliphatic chains, rearrangement of the methyl end groups at the lamella-lamella interface, and so on [3].

Being based on the elementary features noted above, Figure 2 depicts three typical cases of crystallization and transformation processes, in which the former two are of *enantiotropic* polymorphism, and the third is *monotropic*. Two forms, A and B, are exemplified.

Case 1. When the Gibbs energies of A and B, $G(A)$ and $G(B)$, cross at T_0 and a reversible solid-state transformation occurs, an exclusive crystallization of the more stable forms is caused at all the temperatures.

Case 2. When $G(A)$ and $G(B)$ cross at T_0 but irreversible solid-state transformations from both A to B ($T > T_0$) and B to A ($T < T_0$) are kinetically hindered, simultaneous occurrence of both forms is possible at temperatures where metastability for unstable forms is attained. In this case the melt crystallization is affected by whether or not the solid-state transformation from A to B occurs below the melting point of B. If it occurs, B solidifies. If not, A or B can appear. Usually, A converts to B at T'_0 below the melting point of B. Therefore, the high-temperature form usually occurs from the melt phase. In contrast to melt crystallization, the occurrence of both A and B below T'_0 is possible from solution, being sensitively affected by temperature, concentration, solvent, and so on. In this regard, another kind of transformation must be introduced here—