TOPICS IN CURRENT CHEMISTRY 256

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Low Molecular Mass Gelators

Design, Self-Assembly, Function

Springer

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Volume Editor: Frédéric Fages

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In references *Topics in Current Chemistry* is abbreviated Top Curr Chem and is cited as a journal.

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Library of Congress Control Number: 2005926237

ISSN 0340-1022
ISBN-10 3-540-25321-1 **Springer Berlin Heidelberg New York**
ISBN-13 978-3-540-25321-1 **Springer Berlin Heidelberg New York**
DOI 10.1007/b105250

Springer is a part of Springer Science+Business Media
springeronline.com

Printed in Germany

Cover design: KünkelLopka GmbH, Heidelberg; *Design & Production* GmbH, Heidelberg
Typesetting and Production: LE-TEX Jelonek, Schmidt & Vöckler GbR, Leipzig

Printed on acid-free paper 02/3141xv – 5 4 3 2 1 0

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Preface

There are certainly plenty of reasons accounting for the fascination exerted during the last several years by low molecular mass gelators (LMGs). At least two of them merit particular attention. On one hand, gelation of organic fluids or water with LMGs represents an extraordinary macroscopic expression of supramolecular self-assembly. It is indeed fascinating to realize how recognition events at the molecular level can lead so efficiently to the generation of three-dimensional continuous networks spanning whole sample volumes. Remarkably, the resulting self-assembled gel-phase materials, obtained at amazingly low concentration of a LMG, are fairly stiff, often at high temperature, and can retain their macroscopic shape, a property characteristic of the solid state of matter. On the other hand, gels are doubtlessly unique materials. They have been known since ancient times – their origin can be traced back to at least Neolithic times – and, ever since, they have played a crucial role in many decisive advances of technology, art and medicine. Gels continue to hold the front page as they not only remain irreplaceable materials in daily life, but are still considered to be one of the most promising materials in the 21th century.

Gels are especially complex systems and, in spite of the huge number of investigations, there is no simple definition of the gel state. It is well known that many polymers, synthetic and natural, form gels. This property largely stems the propensity of long-chain macromolecules to give rise to networks that immobilize the majority liquid component by surface tension. By contrast, LMGs are clearly defined molecular structures and it is their unidirectional self-assembly that serves to build thermoreversible networks of entangled fiber-like aggregates. A major attraction of the supramolecular approach toward gel-phase materials is the possibility to exquisitely control network properties and morphology by precise variations of the LMG chemical structure. As the spectrum of LMGs has considerably enlarged over the last decade, it is thus possible, via rational synthesis, to access a wide diversity of tunable functional materials for applications in separation technologies, medicine, biology, electronics, photonics, templated material synthesis, etc.

This book is intended to provide a comprehensive overview of some of the most exciting chemical and physical aspects in the field of low molecular weight organo- and hydrogelators. The contributions also illustrate the need for a multidisciplinary approach between synthetic, physical and biological chem-

istry, physics and material science. Chapter 1 presents the physical principles of the growth mechanism of fiber and fiber network with LMGs, as treated on the basis of the heterogeneous nucleation model. It also demonstrates that, beside chemical approaches, physical factors can be elegantly exploited to control and manipulate the morphology of self-assembled nanostructures in order to produce materials with desired rheological properties. The systematic synthesis and gelation ability of LMGs containing cholesterol and amide self-assembling motifs, two major classes of versatile gelators, are discussed in Chaps. 2 and 3, respectively. These chapters are intended to outline useful synthetic guidelines for the generation of an ever-increasing variety of molecular architectures within these two families of gelators. Recent developments in the chemistry of nucleobase-containing LMGs are described in Chap. 4. Hydrogen-bonding within these molecular systems involves complementary base pair formation, a process relevant to DNA double-helix formation. As such, their self-assembled gels have emerged recently as a very promising class of soft materials with biomimetic functional features. The self-assembly of chiral organo- or hydrogelators is the subject of Chap. 5. In many cases gelation of water or organic liquids with chiral LMGs is observed to lead to chiral supramolecular aggregates that exhibit a distinct helical or twisted structure, a feature reminiscent of biological systems. Liquid crystalline physical gels that result from the orthogonal self-assembly of liquid crystals and LMGs are presented in Chap. 6. The growth of self-assembled solid fibers in thermotropic liquid crystals leads to the formation of highly anisotropic composite materials with unique potential for the fabrication of optical, electrical, and photofunctional devices. The volume concludes with Chap. 7, a review of the emerging field of dendritic gels. Strictly speaking, dendrimers are not low molecular weight compounds. Yet, in contrast to the case of polymers, they have well-defined structures. In this respect, dendrimer gelators bridge the gap between LMGs and polymers and as such do offer exciting future directions to explore.

Of the many exciting achievements of supramolecular chemistry, it is arguably the control of multiple, specific recognition events at the molecular level that allows the construction of nanoscale architectures of increasing structural or topological complexity. As such, supramolecular synthesis represents a powerful bottom-up fabrication approach that allows one to generate not only novel, beautiful structures, but also uniquely functioning supramolecular devices and highly tunable materials. Clearly the field of low molecular mass organo- and hydrogelators has evolved into a sophisticated science at the frontiers of supramolecular chemistry.

Marseille, January 2005 Frédéric Fages

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Volume Editors: Schalley, Christoph A.; Vögtle, Fritz; Dötz, Karl H.
ISBN: 3-540-22547-1

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Templates in Chemistry II

Volume Editors: Schalley, Christoph A.; Vögtle, Fritz; Dötz, Karl H.
ISBN: 3-540-23087-4

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Top Curr Chem (2005) 256: 1–37
DOI 10.1007/b107170

Published online: 1 July 2005

Gelation with Small Molecules: from Formation Mechanism to Nanostructure Architecture

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Abstract The mechanism of fiber and fiber network formation of small molecular gelling agents is treated on the basis of a generic heterogeneous nucleation model. The formation of a crystallite fiber network can take place via the so-called crystallographic mismatch branching. At very low supersaturations, unbranched fibers form predominantly. As supersaturation increases, small-angle crystallographic mismatch branching occurs at the side face of growth fibers. At very high supersaturations, the so-called wide-angle crystallographic mismatch branching becomes kinetically favorable. Both give rise to the formation of fiber networks, but of different types. Controlling the branching of the nanofibers of small molecular gelatins allows us to achieve the micro/nanostructure architecture of networks having the desired rheological properties. In this regard, the engineering of supramolecular functional materials can be achieved by constructing and manipulating the micro/nanostructure in terms of a "branching creator", or by tuning processing conditions.

Keywords Nanofiber · Nucleation · Branching · Fiber network · Additive

Abbreviations

a	Activity
C	Concentration
D_f	Fractal or Hausdorff–Besicovitch dimension of a pattern
d	Diameter of an object
DIOP	Di-(2-ethylhexyl phthalate) $(C_8H_{17}COO)_2$ (C_6H_4)
EVACP	Ethylene/vinyl acetate copolymer
$f(m)$	Interfacial correlation function
G^*	Complex modulus
G'	Storage modulus
G''	Loss modulus
GP-1	*N*-lauroyl-L-glutamic acid di-*n*-butylamide
ΔG	Gibbs free-energy barrier
h	Height of step of crystal surface
Δh_m	Enthalpy of melting per molecule
ISA	Isostearyl alcohol
L-DHL	Lanosta-8,24-dien-3β-ol:24,25-dihydrolanosterol = 56:44
J	Nucleation rate
k	Boltzmann constant
m	Interfacial matching parameter
N	Number of particles or segments
N_g	Number of crystals per volume
P	Pressure
r_c	Radius of curvature of critical nucleus
R	Radius of gyration of a pattern
R_g	Growth rate of fiber along the axial direction
SA-CMB	Small-angle crystallographic mismatch branching
SEM	Scanning electron microscopy
T	Temperature
t_s	Nucleation induction time
t	Time
WA-CMB	Wide-angle crystallographic mismatch branching
ν_g	Growth rate of bulk crystals
X	Crystallinity of a system
φ	Volume fraction of crystal materials
γ	Interfacial free energy
γ_{step}	Step free energy of crystal surface
μ	Chemical potential
η	Viscosity
θ	Contact angle
Ω	Volume per structural unit
τ	Induction time for the nucleation of new fibers on the host fibers
σ	Supersaturation
ω	Angular frequency
ξ	Branching distance

1 Introduction

Supramolecular functional materials having 3D fibrous network structures formed by, for instance, dilute solutions of polymers, proteins, and inorganic substances like silica or clays in water and organic solvents have been well studied. In recent years there has been rapidly growing interest in such materials, which is motivated by the many potential applications in photographic, cosmetics, food, and petroleum industries, drug delivery, lithography, catalyst supporters, scaffolds for tissue engineering, the novel separation for macromolecules, etc. [1–14]. Supramolecular functional materials with 3D fibrous network structures can be employed as a vehicle for drug delivery and controlled release. The mesh size of 3D fiber networks will determine the rate of drug release.

Macroscopic properties, in particular, the rheological properties of supramolecular functional materials are determined by the micro/nanostructure of fiber networks. These materials have continuous 3D entangled networks in the liquid, thereby preventing the liquid from flowing owing to the capillary force.

Among these materials, those formed from small organic molecules are a special class. In contrast to their macromolecular and inorganic counterparts, it is believed that the network structure formed by low molecular weight organogelators is held together solely by noncovalent forces, including hydrogen bonding, stacking, and solvophobic effects.

Fibrous networks with permanent interconnections will effectively entrap and immobilize liquid in the meshes, and possess both the elastic properties of ideal solids and the viscosity properties of Newtonian liquids. Consequently, self-supporting supramolecular materials will be obtained [8–10, 15–21]. In contrast, systems consisting of nonpermanent/or transient interconnecting (or entangled) fibers or needles can only form weak and viscous paste at low concentrations [6, 7].

Although the formation of supramolecular functional materials from small molecules is an excellent example of a supramolecular self-organization process, most such materials have been found by serendipity rather than design, and many aspects of supramolecular functional materials are still poorly understood. The control of gelation phenomena induced by small molecules and the design of new gelling agents are therefore challenging goals leading to a new area of fascinating organic materials, and it is only recently that a number of successes have been reported.

It was believed [6, 9] that the formation of interconnecting fiber networks, which leads to the formation of supramolecular materials, takes place via molecular self-assembly of nanofibers. Nevertheless, the latest research indicates that the 3D self-organized micro/nanostructure of supramolecular

functional materials is controlled by a so-called crystallographic mismatch branching. This is essentially a special case of heterogeneous nucleation. This implies that even for areas such as supramolecular functional materials where conventionally crystallization was regarded unimportant, knowledge of nucleation is also very crucial.

It is the purpose of this chapter to analyze the kinetics of nucleation under the influence of substrates and additives from the point of view of the solid/fluid structure. On the basis of the knowledge acquired, the principles and strategies for the engineering of micro/nanostructures of various systems, in particular supramolecular functional materials, will be examined.

2 Crystallization of Nanofibers

As can be seen in the following sections, nucleation is the initial step in the formation of crystalline materials. It is also very crucial in determination of the structural synergy between crystals and the substrate. It will be shown that the formation of a fibrous structure of some supramolecular materials is actually controlled by special type of nucleation—crystallographic mismatch nucleation, on the growing tips of fibers. Therefore, a decent understanding of nucleation is very important.

2.1 Thermodynamic Driving Force

Nanofibers which form self-organized fibrous networks in organogels are sometimes found to have a 3D crystalline order [15–18, 21]. The formation of fibers, therefore, takes place in most cases via a crystallization process [15–18, 21], including *nucleation* and *growth* [22–32].

Crystallization is the process that the first-order phase transitions begin with. The driving force for the formation of new phases (e.g., crystals) is $\Delta\mu$, which is defined as the difference between the chemical potentials μ_{mother} and μ_{crystal} of the growth unit in the mother and the crystalline phases [22, 31, 34]:

$$\Delta\mu = \mu_{\text{mother}} - \mu_{\text{crystal}} \cdot \tag{1}$$

When $\Delta\mu > 0$, it is said that the system is supersaturated. This is the thermodynamic precondition for nucleation and growth of the crystalline phase. Conversely, when $\Delta\mu < 0$, the system is undersaturated. Under such conditions, crystals will dissolve. In the case where $\Delta\mu = 0$, the mother phase is in equilibrium with the crystalline phase [20, 29, 32].This implies that under the

given temperature T, pressure P, concentration C, etc., one always has

$$\mu_{\text{mother}}^{\text{eq}} = \mu_{\text{crystal}}, \tag{2}$$

where $\mu_{\text{mother}}^{\text{eq}}$ is the chemical potential of solute molecules in the phase equilibrium (or coexistence) between the mother and the crystalline phases. It follows that for a given condition, μ_{crystal} can be expressed by $\mu_{\text{mother}}^{\text{eq}}$. Therefore, in many cases of practical importance $\Delta\mu$ can be expressed as

$$\Delta\mu = \mu_{\text{mother}} - \mu_{\text{mother}}^{\text{eq}}. \tag{3}$$

For crystallization from solutions, the chemical potential of species i is given by [15, 23, 25]

$$\mu_i = \mu_i^0 + kT \ln a_i \approx \mu_i^0 + kT \ln C_i, \tag{4}$$

where a_i, and C_i denote the activities and concentrations of solute, k is the Boltzmann constant, and T is the absolute temperature. μ_i^0 denotes the standard state ($a_i = 1$) of the solute chemical potential. This then gives rise to the dimensionless thermodynamic driving force:

$$\frac{\Delta\mu}{kT} = \ln \frac{a_i}{a_i^{\text{eq}}} \approx \ln \frac{C_i}{C_i^{\text{eq}}}, \tag{5}$$

where a_{eq} and C_{eq} are, respectively, the equilibrium activities and concentrations of the solute.

Notice that the thermodynamic driving force for crystallization is often expressed in terms of supersaturation. If we define supersaturation as

$$\sigma = \left(a_i - a_i^{\text{eq}}\right)/a_i^{\text{eq}} \approx \left(C_i - C_i^{\text{eq}}\right)/C_i^{\text{eq}} \tag{6}$$

Eq. 5 can then be rewritten as

$$\frac{\Delta\mu}{kT} = \ln(1+\sigma). \tag{7}$$

In the case of $\sigma < 1$, Eq. 7 can be approximated, after the Taylor series expansion, as

$$\Delta\mu/kT = \ln(1+\sigma) \cong \sigma. \tag{8}$$

For crystallization from melts at temperatures not far below the melting or equilibrium temperature, we have the thermodynamic driving force by applying similar thermodynamic principles as [31, 35]

$$\frac{\Delta\mu}{kT} = \Delta h_{\text{m}} \Delta T / kTT_{\text{e}}, \tag{9}$$

$$\Delta T = (T_{\text{e}} - T), \tag{10}$$

where Δh_{m} is the enthalpy of melting per molecule, T_{e} is the equilibrium temperature, and ΔT is supercooling.