Gels

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Gelled Complex Fluids: Combining Unique Structures with Mechanical Stability

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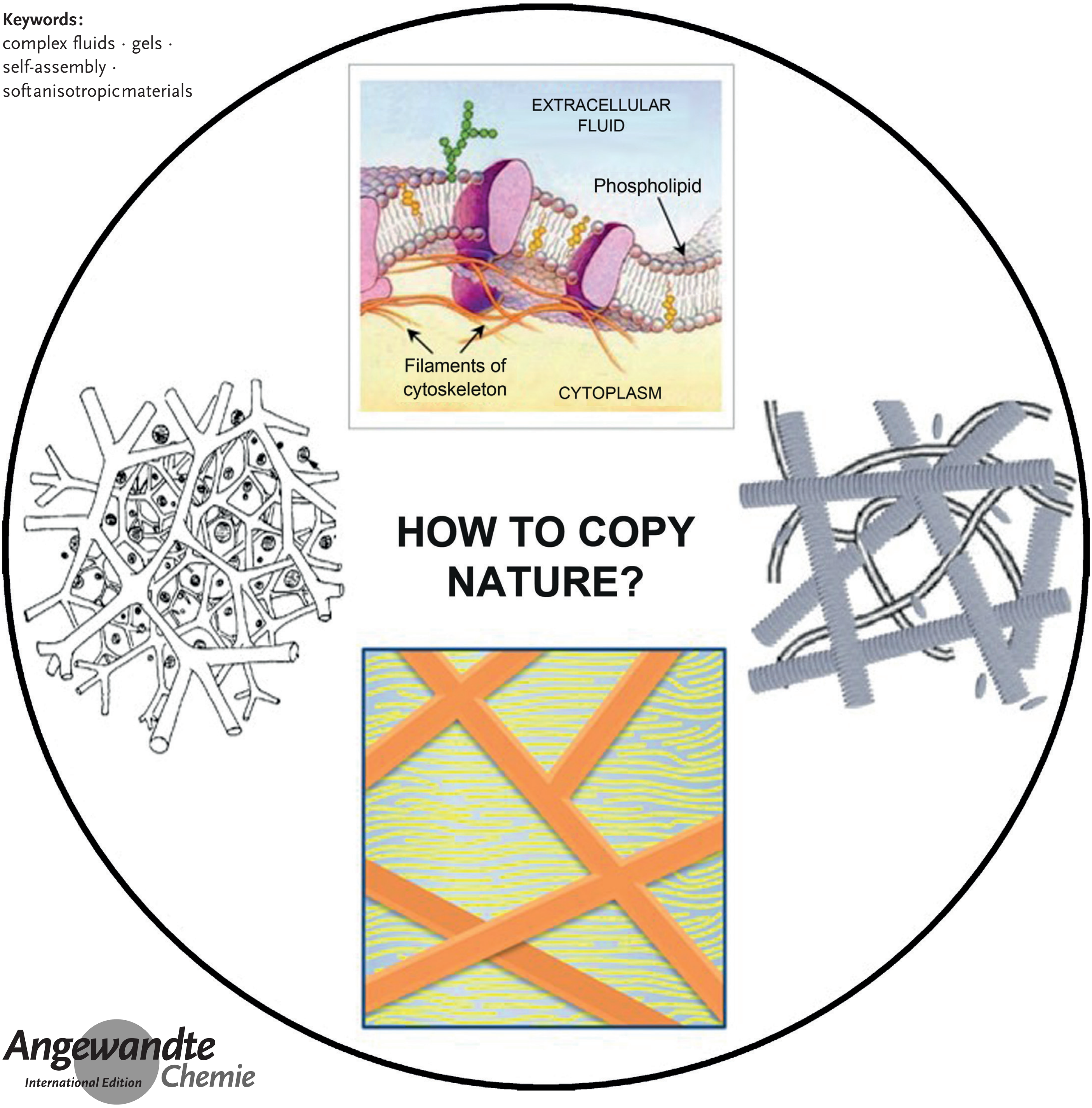

Gelled complex fluids are soft materials in which the microstructure of the complex fluid is combined with the mechanical stability of a gel. To obtain a gelled complex fluid one either adds a gelator to a complex fluid or replaces the solvent in a gel by a complex fluid. The most prominent example of a "natural" gelled complex fluid is the cell. There are various strategies by which one can form a gelled complex fluid; one such strategy is orthogonal self-assembly, that is, the independent but simultaneous formation of two coexisting self-assembled structures within one system. The aim of this Review is to describe the structure and potential applications of various man-made gelled complex fluids and to clarify whether or not the respective system is formed by orthogonal self-assembly.

From the Contents

1. Introduction

Typical examples of complex fluids are micellar solutions, lyotropic liquid crystals, thermotropic liquid crystals, microemulsions, and emulsions. A gel, on the other hand, consists of a gelator and a solvent, and can be defined as a dilute cross-linked system that exhibits no flow in the steady state.[1] The unique selling point of gelled complex fluids is the fact that the two coexisting structures can have two different functions. For example, in transdermal drug delivery, a gel would guarantee a convenient application, while a lyotropic liquid crystal (lyotropic LC) is needed for the effective solubilization of water-insoluble drugs.[2,3] A second example is a membrane-based liquid-crystalline gel, which could incorporate membrane-embedded proteins that are biologically active, thus providing a way in which proteins can be delivered via a stable gel.[4] A third example is related to materials science. Lyotropic LCs are used as templates for the synthesis of highly ordered, nanostructured materials.[5] Gelling these LCs would increase their mechanical stability, which may be helpful for the synthesis. Moreover, it should be possible to "arrest" macroscopically aligned lyotropic LCs, that is, monodomains, by gelling them. These gelled monodomains can be used as templates for macroscopically aligned nanoporous monoliths.[6] Finally, gelled lyotropic LCs might be used as anisotropic electrolyte gels that enable efficient ion migration pathways ("ion channels") for potential applications, for example, in enhanced lithium ion battery systems.[7] Gelled complex fluids are, thus, promising tools for the design of new functional and "smart" materials.

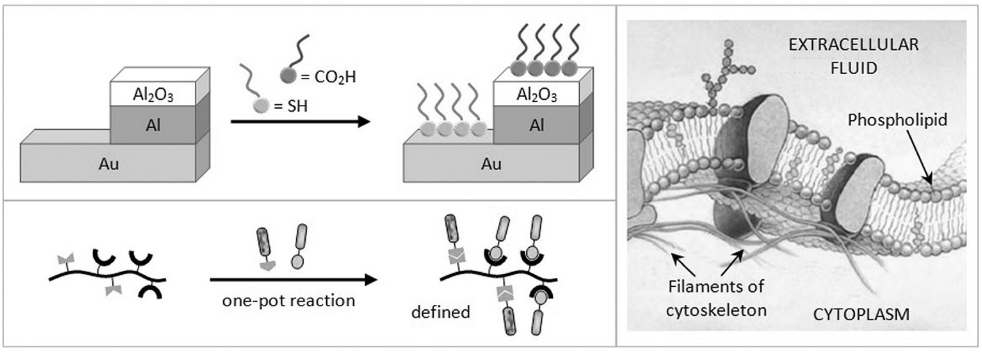

Figure 1. Top left: Orthogonal self-assembled monolayers.[8] Bottom left: Multifunctionalizing a polymer by orthogonal self-assembly.[9] Right: Orthogonal self-assembled structures in a cell[17] (reproduced from Ref. [18], with permission from Springer).

Some gelled complex fluids are orthogonal self-assembled systems. Orthogonal self-assembly is the independent but simultaneous formation of two coexisting self-assembled structures within one system. Laibinis et al. introduced the term "orthogonal self-assembled" in 1989 for monolayers of alkane thiols and alkane carboxylic acids which form at differently treated regions of a surface when exposed to a solution that contains both adsorbates (Figure 1, top left).[8] This behavior is explained by the fact that the noncovalent interactions leading to the two self-assembling processes are selective and non-interfering. However, orthogonal self-assembly is by no means limited to surface chemistry. Hofmeier and Schubert, for example, described how polymers which possess different noncovalent binding sites can be multifunctionalized in single-step reactions as a result of orthogonal self-assembly (Figure 1, bottom left).[9] In both nature and science there are numerous bulk systems that consist of different structures which self-assemble as a result of selective and non-interfering, noncovalent interactions.[10–15] The most prominent example of a "natural" orthogonal self-assembled system is the cell. The cell membrane is a phospholipid bilayer (self-assembled surfactants) which coexists with a variety of other self-assembled architectures such as protein complexes that form scaffolding filaments in the cell, that is, the cytoskeleton (Figure 1, right).[16] The cytoskeleton is a highly sophisticated

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gel, and its combination with the fluid cell membrane leads to a membrane-based liquid-crystalline biogel. The important points of the cell structure are that each self-assembled structure plays a different role and that both self-assembled structures are needed for proper functioning of the cell. In other words, the two structures complement each other, but do not influence one another. This example clearly demonstrates the huge prospects of studying orthogonal self-assembled systems.

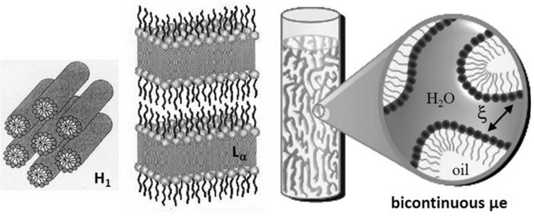

Figure 2. Schematic representations of a lyotropic hexagonal phase (left), a lyotropic lamellar phase (middle), a bicontinuous microemulsion (μe; right); ξ = domain size = 5–50 nm.

2. Complex Fluids and Gels

2.1. Complex Fluids

Complex fluids can be defined as fluids that possess mesoscopic microstructures which determine the characteristic properties of the system.[19] Typical examples of complex fluids are micellar solutions, thermotropic as well as lyotropic liquid crystals, and microemulsions. Binary mixtures of water and surfactant as well as ternary mixtures of water, surfactant, and cosurfactant can form micelles and lyotropic liquid crystals in specific concentration and temperature ranges.[20] Amphiphilic molecules can aggregate into spherical, cylindrical, or discoid micelles, which, in turn, are the building blocks of the lyotropic liquid-crystal phases formed at high volume fractions of micelles. Liquid crystals (LCs) are defined as complex fluids with at least long-range (LR) orientational order of anisometric (e.g. rod- or disklike) molecules (thermotropic LCs) or anisometric micelles (lyotropic LCs), the presence of which give rise to the macroscopic anisotropy of all liquid-crystal phases.[21,22] Long-range orientational order is the only kind of LR ordering existing in the family of nematic phases formed by rod- (N) or disklike (N_d) molecules in the case of thermotropic LCs or formed by cylindrical (N_c) or disklike (N_d) micelles in lyotropic LCs. In addition to LR orientational order, the fluid smectic (SmA, SmC) and columnar (Col) phases of thermotropic LCs as well as the lamellar (L_α) and hexagonal (H_1) phases (Figure 2, left and middle) of lyotropic LCs exhibit quasi-long-range positional order in one or two dimensions. Since the concept of orientational order is meaningless in the case of spherical micelles, the optically isotropic cubic phases are better referred to as plastic crystals rather than as liquid crystals. Since any LR ordering in LCs is not perfect, its quality is measured by certain order parameters, the most important of which are the orientational (nematic) order parameter S and the translational (smectic) order parameter Σ.

Ternary mixtures of water, oil, and surfactant can form thermodynamically stable microemulsions and lyotropic liquid crystals. Microemulsions can form various nanostructures, two typical examples of which are spherical oil droplets dispersed in water or spherical water droplets dispersed in oil. Another prominent structure is the bicontinuous spongelike phase in which both water and oil form continuous phases that are separated by a surfactant monolayer (Figure 2, right). The crucial point is that the curvature of the surfactant monolayer can be changed continuously, thereby leading to a broad variety of structures.[23] The same ternary system that forms microemulsions may be able to also form lyotropic liquid crystals at high surfactant concentrations.[24] The structure of these LC phases is the same as those of the phases formed in binary systems: the hydrophobic domains of the lyotropic liquid crystals are just "swollen" with oil.

2.2. Gels

A gel consists of a gelator and a solvent and can be defined as a dilute cross-linked system which exhibits no flow in the steady state.[1] Its solid-like appearance is caused by the immobilization of solvent molecules in a three-dimensional macroscopic network created by either physical or chemical bonds. At the molecular level, however, the solvent molecules are mobile within the network. Common gel classifications refer to the type of solvent, the type of gelator, or the type of

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cross-links in the network. One such distinction is made between organogels in which an organic solvent is gelled by an "organogelator" and hydrogels in which a hydrophilic solvent is gelled by a "hydrogelator". Another common distinction is made between chemical gels and physical gels. In a chemical gel, the gelator network is built up of cross-linked polymers. The cross-links make these gels robust and tolerant to physical deformation. In contrast to chemical gels, the network structures of physical gels are built from smaller subunits which are held together by noncovalent interactions. Many gels formed by polymers, proteins, and surfactants belong to this class. A distinct class of physical gels is formed by certain low-molecular-weight gelators (LMGs) which self-assemble into gelator fibers. These fibers, in turn, form entangled networks—so-called self-assembled fibrillar networks, SAFINs—which convert the liquid (sol) into a gel. Fiber formation can occur at concentrations below 1 wt%. Moreover, it is reversible and can be triggered by temperature, that is, at high temperatures the system is a liquid sol which gels when the temperature falls below the sol–gel boundary. Our decision to study LMGs was based on two reasons. The first reason is the reversibility of the network formation; the second reason was that only a handful of polymers are biodegradable in vivo. As a consequence, the use of gels has been limited because of concerns regarding cytotoxicity if these polymers are administered into the human body. The discovery of biodegradable LMGs such as fatty acid derivatives, steroid derivatives, and amino acid based LMGs has opened up a new arena, for example, in drug delivery and tissue engineering.[2,25] One prominent example of a biodegradable LMG is 12-hydroxyoctadecanoic acid (12-HOA, Figure 3), which was studied in depth by various groups (see Ref. [26] and references therein). This gelator self-assembles in nonpolar solvents such that the carboxylic acid groups are paired (formation of dimers) and the dimers are held together in the direction of the fiber axis by hydrogen bonds between the hydroxy groups.

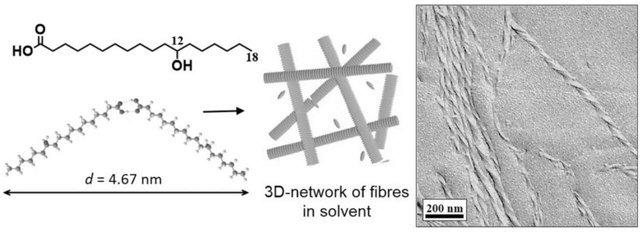

Figure 3. Schematic representation of the gelator 12-HOA, its self-assembly into SAFINs, and a transmission electron microscopy (TEM) picture of the fibers (modified from Ref. [26]).

3. Gelled Complex Fluids

In gelled complex fluids, two structures are combined, namely a complex fluid and a gel network. Different examples of gelled complex fluids are described in the literature. In the following we will describe their structures as well as potential applications. Each example will be discussed with regard to the question of whether the structure is created by orthogonal self-assembly.

3.1. Microemulsion-Based Organogels

Microemulsion-based organogels are gelled water-in-oil droplet microemulsions which are transparent and thermo-reversible.[27] The continuous oil phase is penetrated by a network of gelatin/water rods which are covered by a surfactant monolayer (Figure 4, left). Since a) the gel network forms through self-assembly of gelatin molecules (physical gel), b) the microemulsion forms through self-assembly of surfactants, and c) the size of the water droplets is unaffected by the gel formation, one can call microemulsion-based organogels orthogonal self-assembled systems, even though this expression has never been used in this context. These systems are discussed in relation to transdermal drug delivery: microemulsions are effective drug carrier systems, while gels are renowned for easy handling, directed administration, and enhanced residence times of the drug.[28]

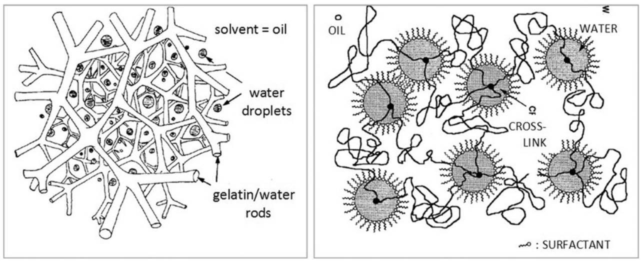

Figure 4. Left: Schematic representation of a microemulsion-based organogel (modified from Ref. [27], with permission from The Royal Society of Chemistry). Right: Microemulsion elastomer cross-linked in water-in-oil microemulsion droplets (modified from Ref. [29], with permission from Springer).

3.2. Microemulsion Elastomers

Microemulsion elastomers are also gelled water-in-oil droplet microemulsions.[29] However, in contrast to the reversibly formed microemulsion-based organogels, microemulsion elastomers are chemical gels with covalently linked junctions in the polymer network (Figure 4, right). Triblock copolymers with hydrophobic middle blocks and hydrophilic, polymerizable end blocks are used for gelation: the two end blocks dissolve in the droplets and are subsequently photopolymerized, that is, chemically cross-linked, within the microemulsion droplets.[30] Thus, the gel network does not form through self-assembly, which is why we cannot talk about an orthogonal self-assembled system.

3.3. Lamellar Hydrogels

Lamellar hydrogels consist of surfactants which self-assemble into a lamellar lyotropic LC, with the bilayers being decorated with short poly(ethylene glycol)-based amphiphilic block copolymers.[4,31] The structure of the gel phase is described as “*highly defected microstructure comprised of a network of connected membrane bilayers with PEG-lipid segregated to the high curvature region*”.[4] Here, the gel properties are not based on a three-dimensional network but on the random orientation of lamellar domains. Again this structure is not compatible with the idea of orthogonal self-assembly. Irrespective of the structure, lamellar hydrogels have great potential for drug delivery and tissue-healing applications.

3.4. Gelled Micellar Solutions

Gelled micellar solutions have been studied intensively in the group of van Esch, who, in 2003, were the first to apply the expression “orthogonal self-assembly” to a gelled complex fluid.[32] They found that low-molecular-weight hydrogelators form a three-dimensional network in aqueous micellar solutions of various surfactants.[32,33] The latter self-assemble to form spherical micelles, worm-like micelles, or vesicles which coexist independently with the gelator network (Figure 5).

3.5. Liquid-Crystalline Physical Gels

Liquid-crystalline physical gels consist of thermotropic liquid crystals and a self-assembled gelator network (SAFIN). In other words, a thermotropic liquid crystal now serves as the solvent for the LMG. The beauty of LC-based systems is the fact that the liquid crystal is anisotropic and exhibits various degrees of internal orientational and translational long-range order. The latter feature can be used to design LC gels with well-aligned fibers (Figure 6). For this purpose, Kato et al. chose systems for which the formation of the LC occurs at temperatures above the sol–gel transition. If a well-ordered liquid crystal forms before the gelator self-assembles into fibers, the resulting fibers are well-aligned when growing in the LC “template”. However, if the gel network is first formed, the fibers are randomly distributed and coexist with LC polydomains. In the latter case, an alignment of the LC gel in an electric field can turn a light-scattering material into a transparent one (switching of a nematic LC gel). Applications in electrooptics, in molecular electronics, and for semiconductors are discussed in detail in Ref. [34]. Note that in these systems two structures coexist, the structural details of which (such as the alignment of the fibers) are influenced by the way the final system is formed. Thus, a gelled thermotropic LC phase is a borderline case between orthogonal self-assembly and soft templating.

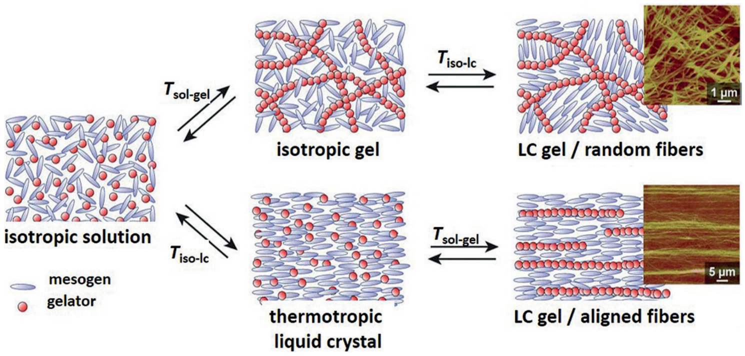

Figure 6. Schematic illustration of two routes by which thermotropic liquid-crystalline physical gels can be formed, and the resulting structures of the LC gels (modified from Ref. [34], with permission from The Royal Society of Chemistry).

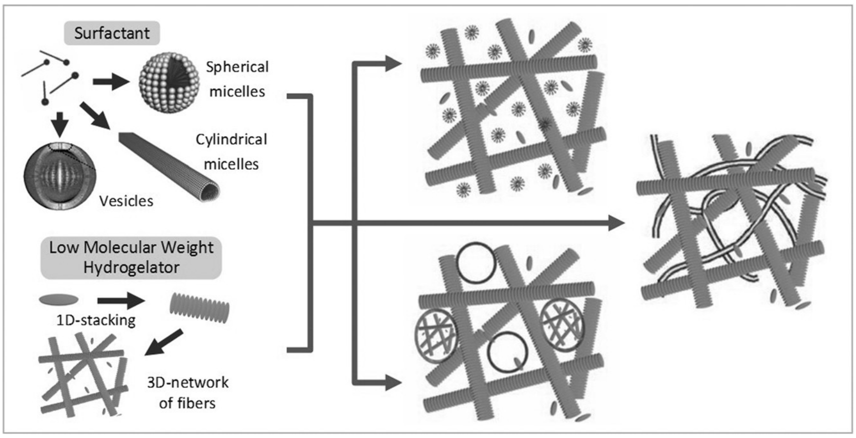

Figure 5. A combination of surfactant assemblies and networks of low-molecular-weight hydrogelators (left) results in gelled solutions of spherical micelles, worm-like micelles, and vesicles (right;[33] reproduced from Ref. [18] with permission from Springer).

3.6. Liquid-Crystalline Chemical Gels

Liquid-crystalline chemical gels, better known as polymer-stabilized liquid crystals, consist of a cross-linked network of polymer chains permeating a continuous thermotropic liquid-crystalline phase.[35] If the polymer network is formed in the liquid-crystalline state, for example, by the in situ polymerization of difunctional monomers in the LC matrix, the polymer chains preferentially grow along the liquid-crystal director, such that the final polymer network mimics the LC director field (Figure 7). In other words, the liquid crystal acts as a soft template for an anisotropic polymer network. Liquid-crystal elastomers (LCEs) formed by the cross-linking of liquid-crystalline side-chain polymers have much in common with LC chemical gels, except that the mesogenic units are covalently linked through flexible alkyl spacers to the polymer network. Weakly cross-linked LCEs, however, behave in many aspects like LC chemical gels.[36] However, they are again not orthogonal self-assembled systems, since the gel network does not form through self-assembly.

A study on the structure and properties of weakly cross-linked LCE particles[37] revealed that flow alignment

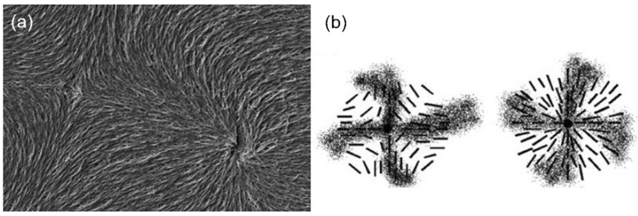

Figure 7. a) SEM image of the polymer network following the director field around a pair of disclination defects (b) in a polymer-stabilized liquid crystal (reproduced from Ref. [35], with permission from The Royal Society of Chemistry).

during the microfluidic synthesis leads to anisotropic LCE particles with a well-defined director field. Since the anisotropy of the polymer chain network is coupled to the anisotropy of the liquid-crystal component, the phase transition from the nematic to the isotropic state leads to a reversible change in the macroscopic shape of the particles (Figure 8). The coupling between LC ordering and macroscopic shape is the general basis for the fascinating application of LCEs as stimuli-responsive actuating materials, among them one-piece micropumps from LCE core–shell particles.[38]

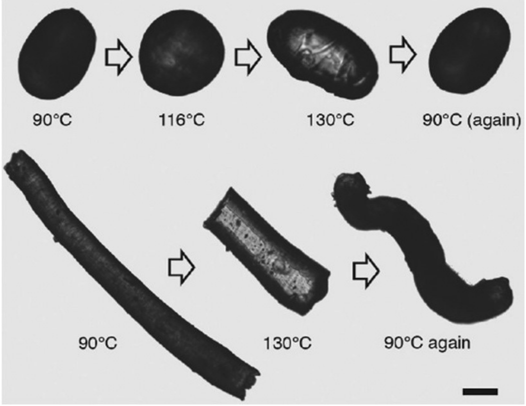

Figure 8. Reversible shape change of LCE particles during the transition between the nematic (90 °C) and the isotropic (130 °C) states; scale bar: 100 μm (reproduced from Ref. [37]).

3.7. Gelled Bicontinuous Microemulsions

Gelled bicontinuous microemulsions can be obtained by adding an appropriate LMG to a bicontinuous microemulsion.[18,39–42] Gelled bicontinuous microemulsions have been clearly identified as one more example of an orthogonal self-assembled system. In gelled microemulsions, the nanostructured microemulsion and the gelator network coexist independently without substantially altering each other's properties (Figure 9). The coexistence of two different self-assembled structures was unambiguously demonstrated by measuring phase diagrams, rheology, small-angle neutron scattering (SANS) curves, and by taking TEM pictures of the model system H_2O–*n*-decane/12-hydroxyoctadecanoic acid (12-HOA)–tetraethylene glycol monodecyl ether ($C_{10}E_4$) at different concentrations of the gelator 12-HOA. Comparing the resulting properties with those of the two base systems, that is, the non-gelled microemulsion H_2O–*n*-decane–$C_{10}E_4$ and the binary organogel *n*-decane/12-HOA, one sees that two independent structures coexist, which self-assemble simultaneously but independently.

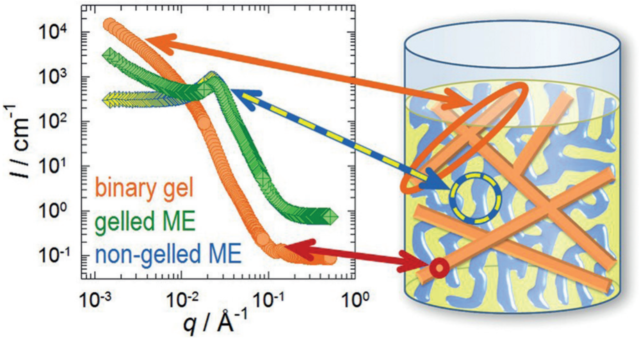

Figure 9. In a gelled bicontinuous microemulsion the two "base" structures, that is, the gel network and the bicontinuous microemulsion, coexist. All coexisting structures, including the crystalline nature of the fibers, are reflected in the respective SANS curve (modified from Ref. [41]).

3.8. Gelled Lyotropic Liquid Crystals

Gelled lyotropic liquid crystals can also be obtained by adding an appropriate LMG to a lyotropic liquid crystal.[43] This study was carried out with the system used for the investigation of the gelled bicontinuous microemulsion since lyotropic liquid crystals were observed at higher surfactant concentrations in this system. The phase boundaries of the non-gelled and the gelled lyotropic LCs were determined visually and by ^{2}H NMR spectroscopy, and it was found that the general pattern of the phase diagram is not altered if one adds the gelator. Further experimental evidence for the idea of gelled lyotropic LC phases being orthogonal self-assembled systems was provided by the rheological properties and by TEM pictures. Based on these measurements, one can conclude that two structures, namely the gel network and a lyotropic LC, self-assemble simultaneously. However, this study does not answer the question of whether these two structures form independently, that is, whether they are exactly the same as the structures observed in the respective parent systems. If this were the case, gelled lyotropic LC phases would be one more type of orthogonal self-assembled systems. However, it could well be that it is also possible to manipulate the final structure experimentally in the same way as reported for the LC-based physical gels mentioned above.[34] For that purpose, the gel network should be formed either before or after the formation of the LC phase. In the first case, Kato et al. observed the formation of random fibers, while in the latter case aligned fibers are formed, that is, the LC phase directs the fiber formation and thus serves as the template.

4. Summary and Outlook

Gelled complex fluids are promising tools for the design of new functional and "smart" materials. The examples presented in this Review range from applications in transdermal drug delivery and tissue healing over batteries, electrooptics, molecular electronics and semiconductors to the synthesis of highly ordered materials. However, irrespective of the potential application of the gelled complex fluids, a characterization of their structures is indispensable. The challenge in studying the structures lies in the fact that complex fluids and gel networks form on different time and length scales as well as at different temperatures. This is especially challenging for those systems that form through orthogonal self-assembly (Table 1). In this case, the choice of gelator and complex fluid allows one to have a system in which the sol–gel transition temperature is above or below the respective formation temperature of the complex fluid, which may have an impact on the final structure, similar to what was reported by Kato et al.

We conclude with the most important questions that should be answered to better understand and finally apply gelled complex fluids:

1) It still needs to be clarified whether the structure of the gel network in a gelled lyotropic liquid crystals depends on the way the sample is gelled, as is the case for the thermotropic liquid crystals mentioned above. Knowing the answer to this question will allow the structure, and thus the properties of the resulting gelled lyotropic LC phase, to be controlled.
2) The fascinating applications of chemically cross-linked liquid-crystalline elastomers as stimuli-responsive actuators crucially depend on the fabrication of macroscopically aligned and cross-linked monodomains, or "liquid single-crystal elastomers" (LSCEs) in the terminology introduced by Küpfer and Finkelmann.[44] It would be interesting to see whether this concept can be transferred to physically cross-linked lyotropic liquid crystals. If this were the case, the macroscopic shape of the new "lyotropic liquid single crystal gels" would respond to external stimuli, such as the vapor pressure of the solvent.
3) Finally, physically cross-linked lyotropic phases might also be advantageous as soft templates in the hydrothermal synthesis of ordered mesoporous silica materials.[45,46] Since their liquid-crystalline order is mechanically stabilized by the gel network, the hydrothermal synthesis might lead to silica materials with higher correlation lengths compared to the non-gelled lyotropic phases. In particular, the templating of cross-linked hexagonal lyotropic monodomains should lead to new catalytic nanopipe reactors formed by macroscopically aligned bundles of nanotubes.[6,47]

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Table 1: Overview of known gelled complex fluids.[a]

Gelled complex fluid	Complex fluid	Gelator	Microstructure	Physical/ chemical gel	Orth. self-assembly
microemulsion-based organogel	microemulsion	gelatin (biopolymer)	water droplets in oil + gelatin network	physical gel	yes
microemulsion elastomer	*microemulsion*	*polymerized ABA block copolymers*	*water droplets in oil or oil droplets in water connected with polymer*	*chemical gel*	*no*
lamellar hydrogels	*lamellar phase*	*PEG-based short block copolymers*	*lamellar bilayers decorated with polymer*	*physical gel*	*no*
gelled micellar solutions	micellar solution	LMG	micelles + gelator network	physical gel	yes
liquid crystalline physical gels	thermotropic liquid crystal	LMG	thermotropic liquid crystal + gelator network	physical gel	borderline case
liquid crystalline chemical gels	***thermotropic liquid crystal***	***cross-linked polymer***	***thermotropic liquid crystal + gelator network***	***chemical gel***	***no***
gelled bicontinuous microemulsions	**microemulsion**	**LMG**	**bicontinuous water and oil domains + gelator network**	**physical gel**	**yes**
gelled lyotropic liquid crystals	**lyotropic liquid crystal**	**LMG**	**lyotropic liquid crystal + gelator network**	**physical gel**	**?**

[a] LMG = low-molecular-weight gelator; italic: not an orthogonal self-assembled system; bold: own work; underlined: borderline case.

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