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"Green" Organogelators: Design and Applications

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Review Article

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ABSTRACT

In this review, we survey sustainable approaches, which are encountered in the development of "green" organogelators. These molecules, Low Molecular Weight Organogelators (LMOG), are of increasing interest as precursors of solid-like supra-molecular materials. Nowadays, the development of organogelators is moving towards the rational design of smarter molecules with more functionality. Some of these have been exploited in environmental applications like water purification. Biodegradability and biocompatibility of green gelators have found interest as drug delivery systems like in-situ forming implants. These molecules have often been synthetized from renewable raw materials, using sometimes efficient solvent-free approaches. To the best of our knowledge, there is a lack of synthetic work about organogelators development in the field of the green chemistry. In that sense, we first tried to document the challenging design of green organogelators starting with natural readily available materials, and then illustrate some benign synthetic reactions. Secondly, we highlight the applications of organogelators as biodegradable and eco-friendly materials. Finally, we conclude with a short discussion of the future perspectives and remaining challenges in the development of these gelling molecules as sustainable solutions.

INTRODUCTION

We live in a world facing challenging environmental problems, hence the growing interest in sustainable solutions. In the field of sol-gel science, "green" molecules have been obtained from renewable raw materials, by solvent-free chemistry [1].

Organogelators, low molecular weight organogelators (LMOG), have received considerable attention as molecules capable of self-assembling in organic solvents [2]. A 3-dimensional entangled network entraps the liquid phase by surface tension and capillary forces, leading to a solid-like supramolecular gel. Polymeric gelators assemble by intermolecular covalent cross-linking; whereas LMOG gelation is realized through the formation of weak interactions, like hydrogen bonding, van der Waals, aromatic (π-π) stacking, dipole-dipole forces. The physical gel thus formed is usually thermo-reversible. The gelation is commonly achieved by cooling a solution of LMOG in the solvent below the gel transition temperature Tgel. Through the supersaturation of the solution, the gelation process is based on two essential phases (i) an initial one dimensional nucleation of gelators and (ii) progressively a growth into a 3-dimensional fiber network **(Figure 1)** [3].

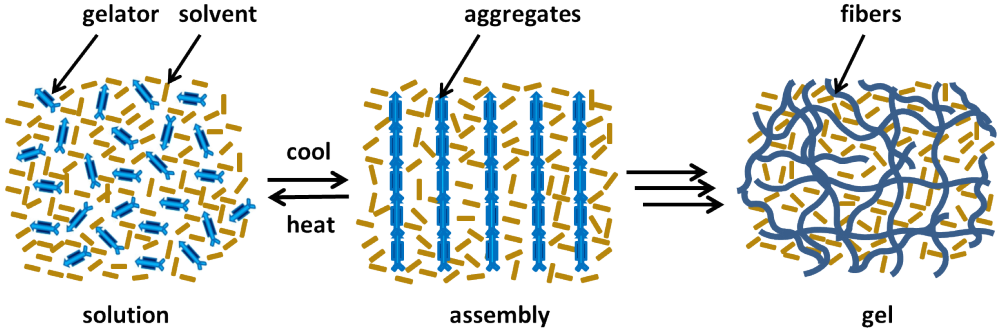

Figure 1. Schematic representation of self-assembly of organogelators in 3-Dimension fiber network [4].

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Although the finding of organogelators has been developed from chance discovery to more rational design, creating molecules that can jellify a selective organic liquid remains challenging. Organogelators have found multiple applications based not only on their fundamental gelation ability, but also on other functionalities like phase selectivity [5], chemosensor property [6], mesogenic behavior [7], photoresponsivity [8], ion and electron conductivity [6], and so on.

In this review, we will focus on organogelators regarded as "green" in light of their synthesis from natural readily available raw materials, by sustainable reactions, their biodegradability and reusable property, and their potential environmental applications such as in water purification.

General Considerations into Organogelator Design

Conception of new gelling molecules and predicting their aggregation behavior in a specific organic solvent is still difficult. Many researches attempt to rationalize the gelation behavior of LMOG [9,10]. It might seem possible after an adequate understanding of various intermolecular interactions; however, no generalizations are so far possible. The rational design starts usually from a model as a known gelator which can be functionalized for extended versatility.

In organic liquids, the major driving forces are hydrogen bonding, van der Waals, π-stacking, and metal-coordination bonds [2]. Long n-alkanes organogelators are rare examples showing gelation by van der Waals forces alone [11]. Adding hydrogen bonding sites to a molecule could be a strategy to probe its gelation behavior, because of the strength and high directionality of their interactions. It exhibits the polarity of the gelator that becomes more solvophobic, and abler to self-assemble.

Strengthen alkyl groups' leads to a better supramolecular gelation by extending van der Waals interactions. A good balance between hydrogen bonding and van der Waals interactions is crucial for efficient organogelation, thereby a large group of gelators is related to relative amphiphiles [12]. Aromatic stacking have shown an important implication in the gelling process, increasing the strength of the structure through π–π interactions [4].

In addition to hydrophilic-hydrophobic balance and specific intermolecular interactions, the spatial conformation of the gelator seems to be important. Although chirality is not necessary for gelling organic solvents, the large majority of supramolecular gelators possess at least one stereogenic center [13]. Molecular chirality is transferred to individual fibers that twist and thus maximize van der Waals interactions forming helical superstructures [2].

"Green" Chemistry Based Design

Creating supramolecular gelators is even more challenging in view of the growing awareness of the ecological problem in link with traditional chemistry. "Green" organogelators have been developed using a renewable feedstock, by a simple one to three steps synthesis, avoiding the utilization of toxic solvents, and minimizing waste [14-16]. Furthermore, some of these ecofriendly materials have found environmental application as phase selective gelators in water purification [17-22].

Organogelators from Renewable Raw Materials

Steroids and their derivatives are very important in the gelators design due to their planar structure. In fact, the polycyclic skeleton defines a one-dimensional plan, which confers rigidity and planarity. Molecules with these properties are capable of establishing van der Waals interactions and consequently they are able to jellify in various organic solvent [23].

Cholesterol Derivatives

Cholesterol is a natural molecule, which plays an important role in the synthesis of LMOG, in light of its self-assembly properties due to its polycyclic structure with a group OH in position C-3. [3]. Many organogelators have been synthetized from cholesterol due to its good potential to be functionalized. Cholesterol can be modified (i) using long-chain alkanes; or (ii) aromatic groups. The cholesterol-polycyclic skeleton allows Van der Waals interaction between two or more molecules, inducing self-assembly and consequently gelation in many organic solvents. Long-chain cholesterol esters and amides are able to jellify in a great variety of organic solvents.

The general structure of cholesterol-based gelators includes a three-block system (ALS): an aromatic group (A), a linker (L) and a steroidal group (S). The aromatic moiety is important in gelation process due to the π–π interactions between two or more moieties [24].

The gelation behavior of cholesterol derivatives has been, even more, optimized by designing dimeric steroidal system A(LS)2 **(Figure 2)**. It was shown that the self-assembly of gelator can be influenced by the length of the linkers (L). It was demonstrated that cholesterol-derivatives, which contain short linker, like few methylene units can jellify easier than cholesterol-derivatives with longer linkers [25] **(Figure 2)**.

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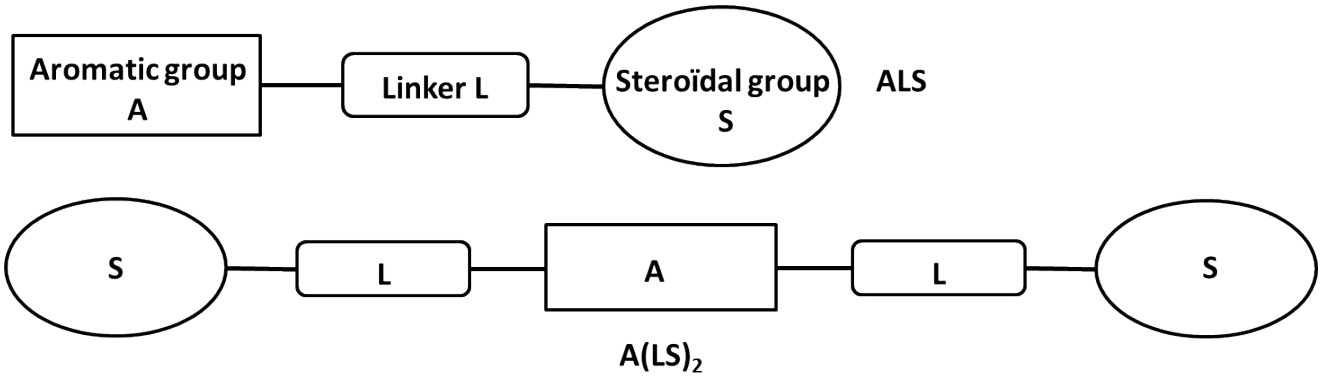

Figure 2. Graphical representation of Cholesterol-based organogelators; (a) ALS system containing aromatic group:linker: Steroidal group in rapport of 1:1:1, (b) A(LS)2 system containing aromatic group:linker:steroidal group in rapport of 1:2:2 [26].

Another possible modification of cholesterol could be the derivatization with one or more chromophores, which contain one or more photoisomerizable moieties. In fact, when these light radiation-sensitive moieties are hit by photons, they transit from an isomer, which is not responsible of gelation to the other isomer, having gelation ability. The sol-gel transition, in this case, is related to light radiations which are a good alternative to temperature-dependent gelation [27].

Fatty Acids Derivatives

Monoglycerides of fatty acids organogelators are, extensively, used as a mixture of glycerol esterified with different C-chain fatty acids, in order to control the gelation process. The particularity of this type of organogelators is their ability to establish interactions, conferring an inverse bilayer. These nanostructures organize into (i) lamellar and planar microstructures, which consequently organize (ii) in a 3-D network [28]. This interesting assembled structure has increased the interest in monoglyceride organogels, especially, for their application in food industry. In fact, these biocompatible products have been used in food production, in order to control the volatile aroma release [29].

Aminoacid Derivatives

Aminoacid-based molecules are, more and more, studied as organogelators due to their high ability of self-assembly in specific solvents [30]. In the last years, it has been investigated the process of hydrophobisation of aminoacids like L-alanine and L-tyrosine; the hydrophobisation allows the gelation of aminoacids derivatives [31]. An important application of L-alanine and L-tyrosine derivatives is the formation of *in-situ* implant after injection [31,32]. The self-assembly mechanism is based (i) on hydrogen bonding in the amide-sites and (ii) on dimerization of the carboxylic groups [30].

L-alanine derivatives are made by aminoacid esterification with fatty acids. The injectable formulation includes ethanol, which has an important role in the gelation process. In fact, ethanol to avoid the gelation before the administration, after the injection it diffuses into the surrounding layers and consequently, the gelators establish interactions, allowing the gelation process [32].

Bastiat et al. investigated the use of L-tyrosine derivatives comparing them with L-alanine derivatives. They noticed that L-tyrosine derivatives have better gelation properties than L-alanine based organogelators. Formulation was prepared using an inhibitor of gelation (i.e. NMP), by this way, the formulation could not jellify at room temperature, but only after injection, the inhibitor diffuses in surrounding tissues and the formulation jellied. The *in-situ* organogel slowly is degraded, releasing the active substance [31].

Another family of aminoacid-type organogelators is based on phenylanine derivative, this family shows high property of gelation at low concentration (1 wt% in organic solvent). Brosse et al. described in 2004 the synthesis route for phenylanine-type organogelators, this reaction is an easy method of preparation based on unexpansive starting materials, methyl ester derivatives.

The different compounds are synthetized in three steps with different R groups; the following gels are obtained by heating in reflux the mixture of organogelator and solvent until complete dissolution. The mixture was then cooled down at 0°C, and they observed the gel formation after few minutes. The authors investigated the relationship between chemical structure and gelation properties; they proved that the polar segment ruled the aggregation due to hydrogen bonds. The hydrophobic portion seems to impact the flexibility and the interactions between fibers in the organogel network.

D-Benzylidene Sorbitol Derivatives

DBS is an inexpensive low molecular weight organogelator. DBS and their derivatives are widespread applied in different domains from pharmaceuticals to cosmetics products [33]. It is a derivative of D-sorbitol, with a butterfly-shaped structure with both hydrophilic and lipophilic groups, which lend self-assembly properties **(Figure 3)**.

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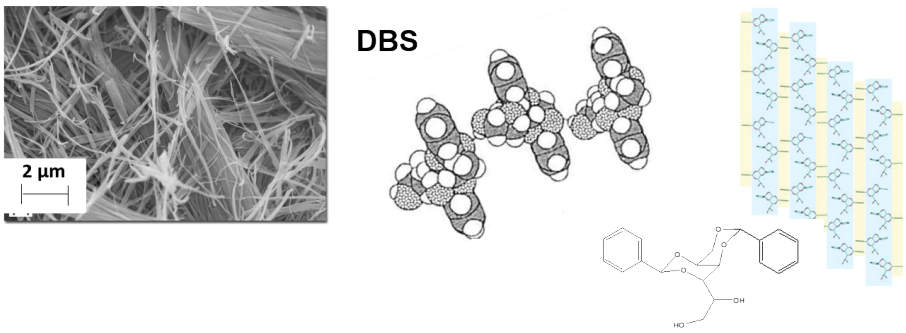

Figure 3. Schematic representation and scanning electron microscopy (SEM) micrographs of DBS (intra- and intermolecular hydrogen bonds, π-π stacking) organization in organic medium.

DBS forms a 3-D network of nanofibrils in different types of matrices, organic solvents and polymers. Meunier as the condensation between D-sorbitol and dimethyl benzaldehyde described the first synthesis in 1891. In 2009, Gupta et al. presented an innovative method for its synthesis in high yield, up to 93%. The patent consists in the reaction between D-sorbitol and dimethyl-benzaldehyde under microwave irradiation and Brønsted acid catalysis **(Figure 4)**.

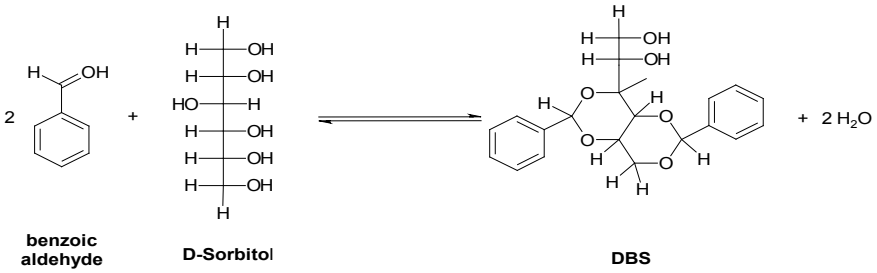

Figure 4. Synthesis of DBS molecules.

Recently, Rum et al. described a synthesis path using microwave technology and natural renewable materials. This innovative method consists in the microwave activation of sorbitol and natural occurring aldehydes in a solvent-free reaction with acid catalysis [34]. The coupling of microwave technology with solvent-free conditions in organic synthesis represents a new and particularly efficient, powerful and attractive strategy. Significant improvements in yields or reaction conditions can be achieved, together with speediness and considerable simplification of work-up and low environmental impact. Starting from sorbitol and naturally occurring aromatic aldehydes, Rum et al. proposed a rapid microwave assisted synthetic procedure in dry media to obtain DBS derivatives using a simple mixture of reagents in the presence of an acidic heterogeneous catalyst [35].

12-Hydroxystearic Acid Derivatives

Despite of 12-hydroxystearic acid (12-HSA) synthesis is not green; it has been employed in the formulation of organogels, which act as scaffolds for cell cultures. In this case, organogels are able to provide a 3-D structure for cells, in order to increase the synthesis of artificial extracellular matrix and consequently to improve cell viability. The organogel formulated contains 12-HSA as organogelators, soybean oil as organic solvent, then it has been leached in order to obtain the scaffold [36] **(Figure 5)**.

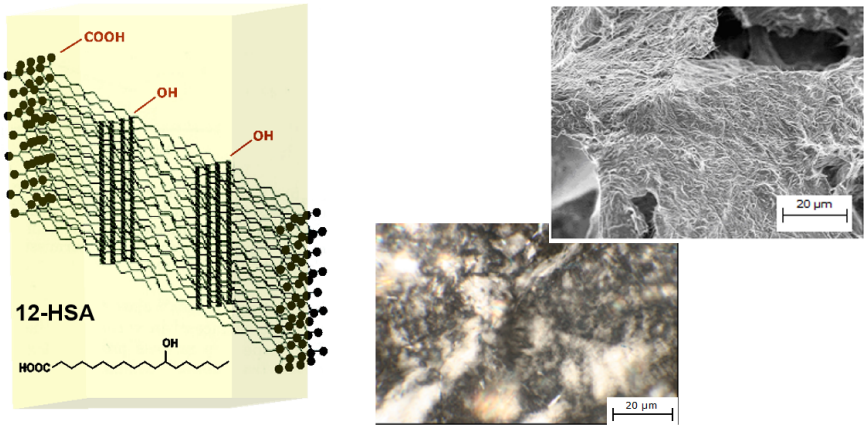

Figure 5. Schematic representation and scanning electron microscopy (SEM) micrographs of HSA (intermolecular hydrogen bonds, Van der Waals interactions).

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In-vitro tests were conducted in order to demonstrate the biodegradability of these products. In fact, pancreatic lipases are added to the organogel and the result is the degradation of the oily phase. This reaction leads to the release of glycerol and fatty acids, which degraded the organogelator [37].

Otherwise, Palomo et al. presented un overview on new colloidal dispersions of Gelled Lipid Nanoparticles (GLN) based on 12-HSA and biocompatible oil phase. They described their concept, formulation methods, techniques used for their characterization and fields of application that these particles could been illustrated **(Figure 6)**.

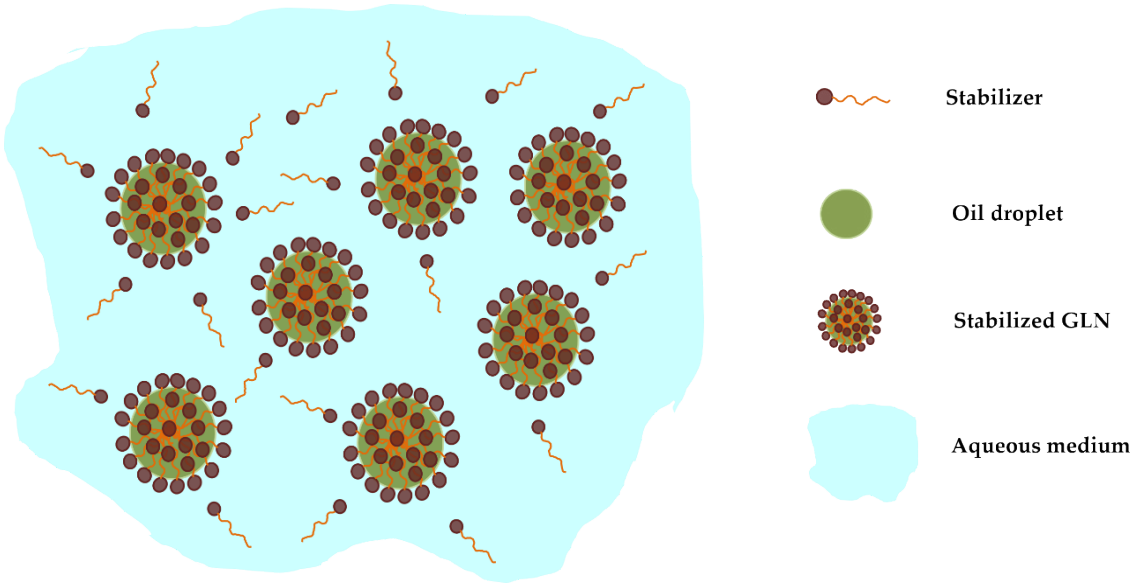

Figure 6. Schematic representation of GLN [38].

Sustainable Reactions

"Click" reaction

"Click" reactions have triggered growing applications in supramolecular chemistry as an efficient solvent-free mechanochemical method for developing organogelators [39-41]. Copper-catalyzed azide-alkyne cycloaddition has been well explored in carbohydrate chemistry. Organogelators have been thus developed from D-glucose and D-glucosamine. The gelation ability of these compounds was investigated in various solvents. The triazole ring showed to be an efficient functional group in the preparation of supramolecular gelators. It was demonstrated that typically carbohydrate derivatives with a good gelation behavior contain a long aliphatic spacer between the triazole ring and the functional group **(Figure 7)** [14,39,40].

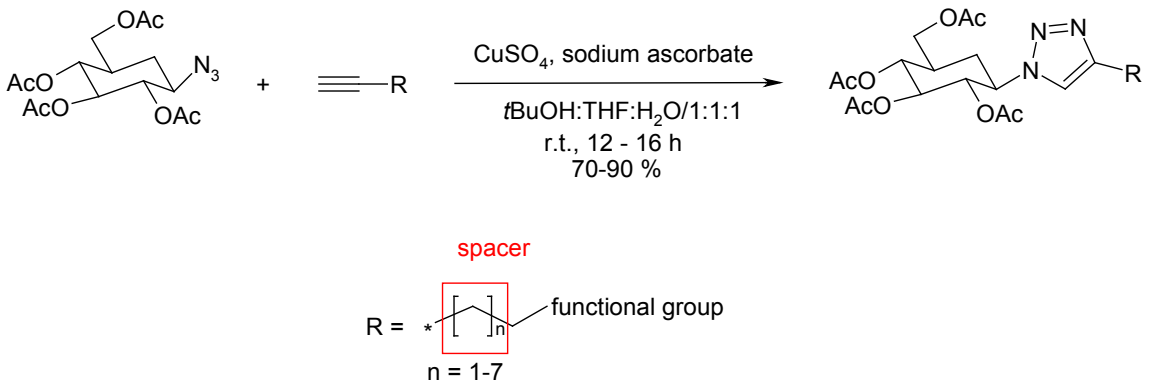

Figure 7. Synthesis of glucosyl triazole by the Copper-catalyzed azide-alkyne reaction [40].

Some of these gelators have shown phase-selective gelation ability from a water-hexane mixture [40] they can be employed in water purification. In fact, such compounds carrying triazole residues can self-assemble through π-π stacking as well as hydrogen bonding interaction.

We also reported organogelation enabled by “click” cross-linking reaction, involving polymeric gelators **(Figure 8)** [41]. Some

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of these molecules showed selective organogelation of dimethyl sulfoxide (DMSO) solvent. When Copper catalysis is used, the alkyne group has to be terminal substituent, but can be internal in case of Ru-catalysis [42] **(Figure 8)**.

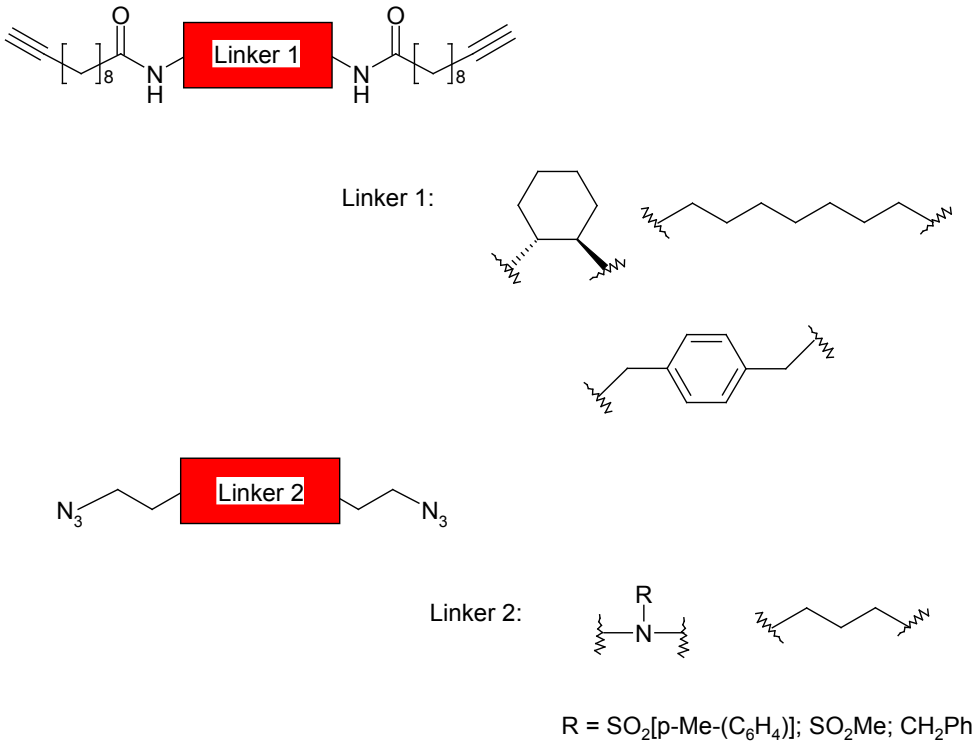

Figure 8. Chemical structures of bis-acetylenes and bis-azides gelators (Díaz et al., 2008).

Azide-alkyne cycloaddition reactions have been patented as method for modulating the properties of organogels [42]. The invention consisted on mixing a modulator molecule with a gelator in solvents to form a reaction mixture. The gelator includes an azide or alkyne functionality. The modulator contains the other function not present in the gelator and a gel property-modifying entity. The product containing a plurality of 1,2,3-triazole rings exhibited various gelation behavior depending upon the reaction conditions.

Michael Addition

Delbecq and co-workers have designed and produced green biodegradable organogelators, using solvent-free Michael addition starting from renewable raw materials. These compounds with sulfide linkage are the precursors of toluene organogels that could be employed as soft-templates for the preparation of various nanoparticles [1] **(Figure 9)**.

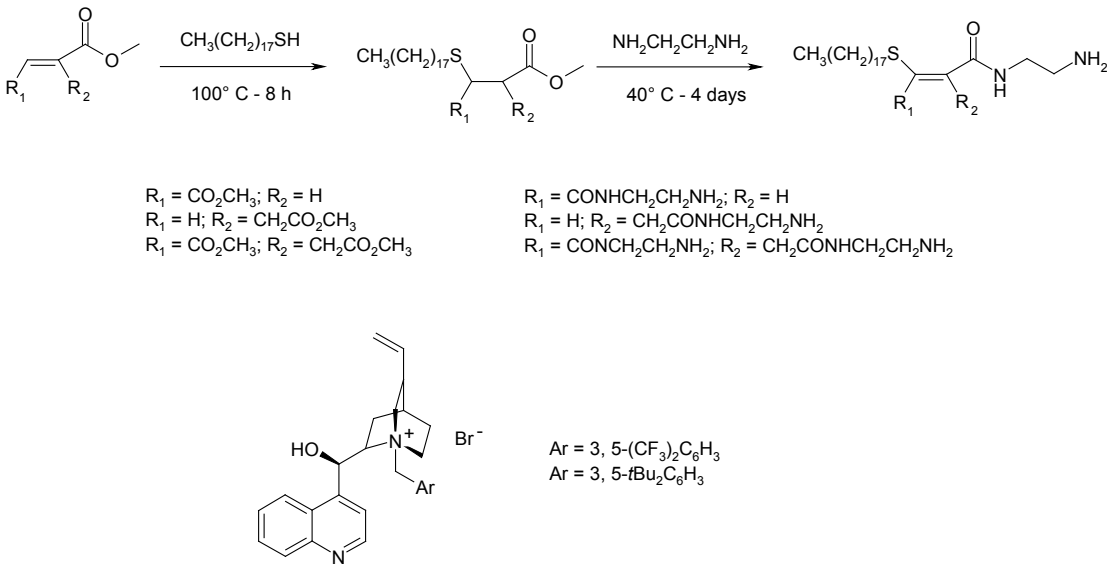

Figure 9. Solvent-free Michael addition for the synthesis of organogelators.

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Enzymatic Catalysis

Enzymatic reactions have been largely used in biorefinery as green chemistry methods to produce organogelators. Biorefinery is a tool, which allows to synthetize chemicals and other materials (i) by converting a biomass, or (ii) using natural sources like sugars, proteins and nucleotides. Due to their regioselectivity and high potential in biological catalysis, enzymes are extensively used in biorefinery to create molecules with controlled self-assembly [7].

An example of biorefinery for the production of amphiphilic gelators based on amygdalin has been reported [43]. The amygdalin is a natural sugar contained in a kernel of many fruits like apricots, peaches and apples. Using a lipase on a peach/apricot biomass, we can synthetize amygdalin/fatty acids-esters derivatives. These esters have amphiphilic properties, which allow using them as organogelators. Due to their natural origin, sugar and fatty acids can be metabolized in smaller metabolic intermediates **(Figure 10)**.

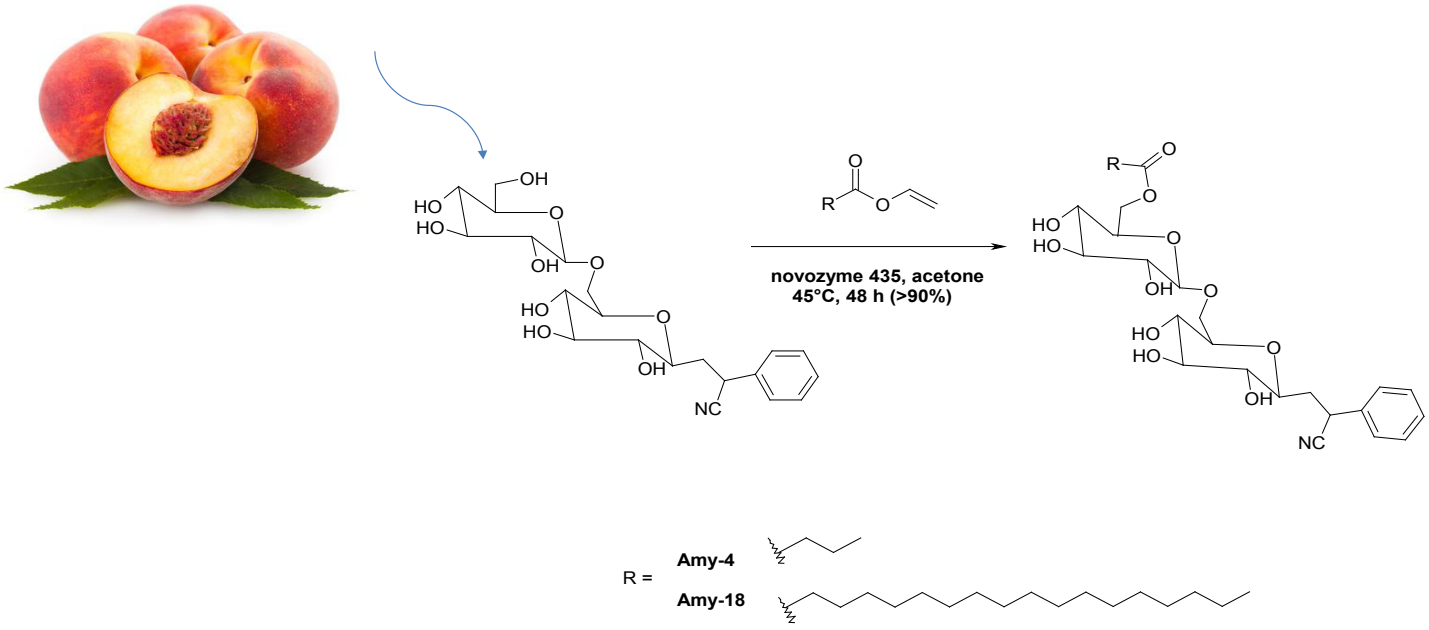

Figure 10. Representation of an enzymatic reaction basing on fruits biomass. Synthesis of amygdalin esters using a Novozyme [7].

The ascorbic acid is a natural molecule that can be extracted from a citrus plant biomass, and it can be used to design organogelators. We can conjugate by green enzymatic reaction, Vitamin C with fatty acids, obtaining ascorbic acid-based amphiphile molecules that can self-assemble in water and in many organic solvents. These organogelators are employed as templates for the formulation of Gold Nano Particles (GNP) due to the reduction potential of Vitamin C. Ascorbic acid- based GNP are embedded with liquid crystals **(Figure 11)**.

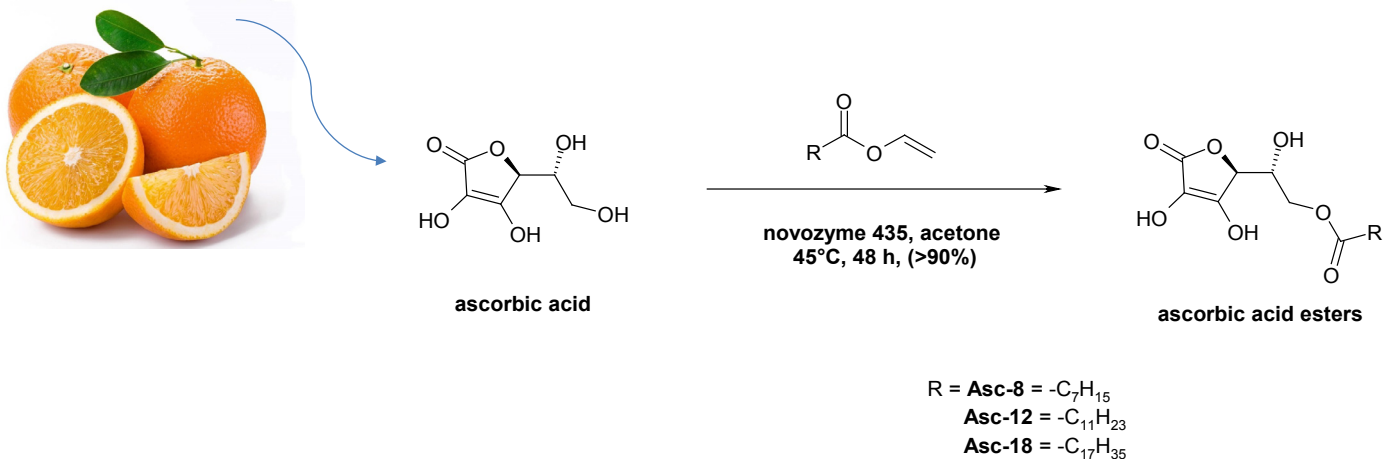

Figure 11. Representation of an enzymatic reaction basing on fruits biomass. Synthesis of ascorbic acid esters using a Novozyme [7].

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Another example of biorefinery application in organogelators production shows the use of enzymatic reaction to transform lipophilic molecules into amphiphilic compounds with better gelation properties. Shell liquids extracted from cashew nuts carried an important role in green and renewable chemistry. Cardanol is represented by a mixture of lipophilic molecules carrying out meta-alkylated phenolic group easily derivatized with a hydrophilic moiety. Amphiphilic molecules thus obtained are good organogelators [7].

External-Stimuli Activated Organogelators

Organogelators self-assemble as a response to (i) temperature changing; (ii) light irradiation; and (iii) pH changing [44-47]. An example of pH-sensitive organogelators is D-glucosamine-based derivatives; it exists two different derivatives (i) urea-derivatives and (ii) amide-derivatives. The gelation properties depending on gelators chemical structures; in fact Goyal et al. demonstrate that the urea derivatives formed a stronger and more elastic gel than amide derivatives [45]. A promising development in supramolecular science is represented by the introduction of photosensitive moieties into the organogelators. These molecules are activated by light irradiation at specific wavelengths. The photon irradiation of these particular organogelators determines a reversible physical structure which induces gelation [8] **(Figure 12)**.

Figure 12. Instantaneous gelation of an organogelator injected in a 37 °C solution [44].

APPLICATIONS

Biodegradable Organogelators

Some organogels have received extensive research interest as biodegradable and biocompatible materials in pharmaceutical and cosmetic manufacturing system. Recently, scientific research focused, even more on the design of organogelators that could be responsive to external stimuli [27]. A real application of external-stimuli activation is the formulation of organogels for *in-situ* implant. This type of formulation consisting in a fluid dosage form containing drug, organogelators and an organic phase; the formulation is then injected subcutaneously **(Figure 13)**. The result of the injection is a biodegradable organogel-implant, which lasts one week. The gelation is assessed when temperature reached 50 °C, after the injection the formulation will be at 37 °C. The temperature decrease allows the gelation [44].

Thermo-sensitive organogelators forming *in-situ* drug release implant have been developed from natural fatty acids with 14-20 carbon atoms of the alkane chains [44]. The gelling system was nontoxic, solvent-free, induced by the body temperature. The increasing of the alkane chain length of fatty acids, enhance the solubility of the organogelator in the vegetable oil, so that the transition temperature increased **(Figure 13)**.

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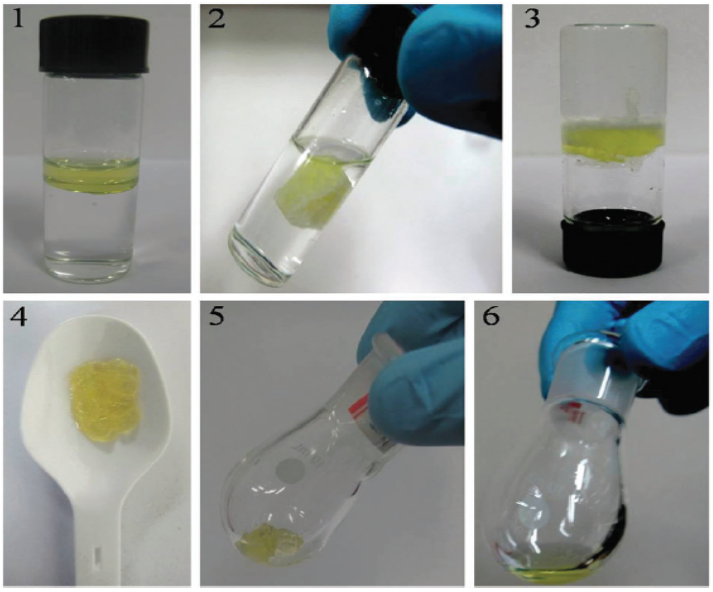

Figure 13. Selective gelation of the organic layer in a water diesel biphasic mixture at room temperature: (1) mixture of 2 ml water and 0.8 ml diesel, (2) gelation of the diesel layer instantaneously after addition of a solution of the gelator, (3) within 45 s the organogel is supporting its entire weight plus the weight of water in the inverted vial, (4) scooped organogel in spoon, (5) collected diesel gel in a round bottom flask, then (6) diesel recovered by distillation.

Water Purification

Among the large number of LMOG, those capable of jelling one solvent preferentially over the other in a given two-phase mixture are termed as phase-selective organogelators (PSOG). It is even more daunting task to achieve the gelation of one solvent from water that competes for the hydrogen bonding sites in the gelator molecule, thereby could disrupt the self-assembled network [5, 18]. This interesting ability has paved the way towards environmental applications in water purification. In this field, the ideal PSG must be efficient to gel the oil phase from water at room temperature, be synthesized with less waste and without toxic agents, with good recovery of the oil from the gel; and be reusable.

DISCUSSION

In 2001, Bhattacharya and Krishnan-Ghosh first reported phase selective gelation from a water-oil mixture, using a simple amphiphilic fatty acid derived amino acid [18]. However, the necessity to heat the system was restraining its potential application in water decontamination from oil-spills. To overcome this practical limitation, organogelators have been designed to induce PSG at room temperature using new approaches such as sonication [5] addition of predissolved gelator in ethanol [46, 47].

It was found that molecules with good selective gelation of oil from water/oil mixture must show H-bonding sites promoting self-assembly, but also lipophilic alkyl chain to exclude water from the supramolecular structure. Such amphiphilic molecules have been developed from naturally occurring materials (e.g., amino acids [5, 19, 46], sugar [15, 47, 40, 47] as efficient, eco-friendly and biodegradable phase-selective gelators.

CONCLUSION AND FUTURE PERSPECTIVES

As precursors of interesting soft-gel materials, organogelators are so attractive in wide industrial fields. Therefore, there is a growing number of studies focusing on the development of these molecules. Nowadays, the majority of research in supramolecular science targets to establish the structure-activity relationship in order to design organogelators with a predicting self-assemble behavior in specific solvents. In that sense, we can imagine the development of a software program as a good perspective. Thus, the rational design could improve the creation of smarter organogelators by significantly saving time and financial support. Environmental and health care applications of biodegradable and biocompatible green gelators present several opportunities going forward.

Many organogelators have been developed until then, but some optimization remains to be considered. For example, biodegradable molecules able to form organogel at body temperature have found interesting applications as *in-situ* forming implants for sustained release drug delivery. However, the need to heat to dissolve the gelling molecule is limiting their use in this field. Thus, the design of organogelators requiring lower, or even no, heating temperature is an oncoming challenge. In addition, the design of biocompatible molecules with sensing properties to specific ions is so attractive in the development of biocaptors.

Technological applications offered by the design of these smart novel molecules promote the replacement of current materials in the not-so-distant future!

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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