# Supramolecular Hydrogels

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#### ABSTRACT

In recent years there has been a considerable interest in developing new types of low molecular mass hydrogels because of their potential technological applications. Several classes of *low molecular weight compounds* form stable and efficient gels with aqueous solvents at low concentrations. Gels can be studies by several techniques.

*Keyword*: Supramolecular gel; hydrogels; noncovalent interaction; hydrophobic interaction; entangled network; pH-trigger; morphology; nanometer dimension.

### 1. Introduction

A supramolecular hydrogel is a colloidal material composed of gelator molecules (low molecular weight organic compound) and water molecules. The gelators molecules are arranged in such a way that they form a mesh that traps the water molecules in the interstitial spaces. Such Small organic molecules (low molecular weight) capable of gelling aqueous solvents are called hydrogelators. Gels can be classified as either chemical or physical. Chemical gels form a molecular mesh by covalent bonds, whereas physical gels form as a result of non-covalent interactions. The majority of physical gels are made from polymeric molecules, but non-polymeric molecules can also self-assemble to form aggregates that gelate solvent. Many non-polymeric physical gels have been reported that are capable of forming gels in various organic solvents.<sup>1, 2</sup> Polymeric gels are common but nonpolymeric physical hydrogels are rare.<sup>3,4,5</sup> Studies on supramolecular gels have been of considerable interest in recent years because of the many potential applications like tissue engineering,<sup>6</sup> nanotechnology, used as biomaterials, vehicles for controlled drug release,<sup>7</sup> pollution control etc.<sup>8</sup>. Despite the recent advances, a priori design of a gelator for the gelation of water molecules has remained a challenging task. The aggregation of gelators molecules into fibrous networks is driven by multiple weak interactions such as  $\pi$ -  $\pi$  stacking, H-bonding, van der waals interaction, hydrophobic interactions, salt bridges and transition metal coordination etc..

The *low molecular mass* gelator molecules form a continuous three dimensional entangled network in the solvent, thereby preventing the liquid from flowing via surface tension.<sup>9</sup> The self-assembly process starting from a single

molecule to fibers and ultimately an entangled network structure is thus completely reversible.

A gel can be broken down into a primary, secondary, and tertiary structure like a protein to understand the mechanism of gel formation.<sup>10</sup> The primary structure (angstrom to nanometer scale) is determined by the molecular level recognition. As a result gelator molecules are aggregated in one dimension. There must be a balance between the tendency of the molecules to dissolve or to aggregate for the formation of gel. Hydrophobic interaction becomes most important in the aqueous environments in the formation of hydrogel. The secondary structure (nano- to micrometer scale) is defined as the morphology of the aggregates like micelles, vesicles, fibers, ribbons or sheets. This secondary structure is directly influenced by the molecular structure. Finally the tertiary structure of a gel (micro- to millimeter scale) involves the interaction of individual aggregates and ultimately determines whether a gel is formed or instead, fibers (or other aggregates) precipitated from solution rather than trapped it.<sup>3</sup> The aggregation of gelator molecules occurred through the both branched fibers and entrangled fibers. The long, thin, flexible fibers are better able than shorter fibers to trap the solvent molecules, leading to gelation.<sup>11</sup>

Most gels are formed by techniques similar to crystallization procedures such as heating a solution of gelator molecules to dissolve it and, then allowing the solution to cool. In some cases, gelation is achieved by the use of a cosolvent.

## 2. Techniques

The gel structure and the mechanism of gel formation can be determined by several techniques. The sample preparation for different techniques is most important.

## 2.1 Spectroscopy

Various spectroscopic techniques have been applied to organic hydrogel systems such as NMR, IR, UV, CD and fluorescence spectroscopies. All these techniques can give the information on the molecular organization of the gels. Solution-state NMR spectroscopy gives the information about the formation of hydrogen bonds during gelation. Gel-state NMR spectroscopy has also been used to identify the chemical shift changes from the solution spectrum indicating a change in aggregation. Temperature dependent NMR spectroscopy of gel-state gives the different chemical values of a particular proton at different temperatures.

UV/VIS spectroscopy has been used to detect a change in the hydrophobicity of the surroundings of a particular group which is either part of the gelator molecules or an added probe and identify the charge-transfer interaction,  $\pi$ - $\pi$  stacking, or metal coordination. The presence of H-bond and protonation of amide functionalities can be determined by IR spectroscopy. Chiral gelators with a weak UV/VIS signal will show a significant enhancement of circular dichroism (CD) upon gelation. The helical aggregation of some chiral gelators can be examined by CD spectroscopy. The presence of fluorescent group in gelator has been identified by fluorescence spectroscopy. The fluorescence properties of gelator should be different in solution state and in gel state.

## 2.2 Microscopy

Various Microscopy techniques have been applied to gel systems such as Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM), AFM, STM SPM etc. SEM and TEM images of dried gel provide the valuable information about the morphology of the aggregation. AFM and STM are high resolution microscopic techniques that can be used to study the morphology of gel.

### 2.3 Diffraction

There are two diffraction techniques such as small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS), whose resolution is approximately that of TEM. These diffraction techniques have been applied to hydrogels to investigate the superstructures formed by the fibers. Wide-angle X-ray powder diffraction (XRD) has been used for elucidating the molecular structure of organogels. Crystal structure of gelator provides information about molecular order in the gelled state.

#### 2.4 Rheology

The thermodynamic properties of gel can investigated using differential scanning calorimetry (DSC). The temperature of gelation  $(T_{gel})$  can be measured using "ball drop method" in which a small glass ball is placed on the top of a gel while it is being heated.<sup>12</sup>

### 2.5 Modeling

Higher level energy minimization and molecular dynamics calculations have also been used to model the primary structure of gels.<sup>13</sup> By this modeling, possible modes of aggregation for gelators of both aqueous<sup>14</sup> and organic solvents<sup>15</sup> have been identified.

#### 3. Classes of Hydrogelators

Discoveries of new gelators remain mainly fortuitous. As an aid to defining strategies for the molecular design of new molecular-mass hydrogelators, many of the known ones have been grouped separately accordingly to the subjective view of the authors. There are several distinct classes of small organic hydrogelators characterized by the type and placement of the polar groups. In the following sections, these categories will be discussed.

#### 3.1 Cholesterol based hydrogelators

A novel tripodal cholic acid derivative 1 forms gels in aqueous acid medium at very low concentration.<sup>16</sup> The efficiency of gelator is very high. The gels derived from 1 in acetic acid/water medium are very strong and transparent whereas the gel derived from hydrochloride salt of 1 in water medium is weak and turbid. But the addition of organic cosolvent to the hydrochloride salt of 1 in water led to formation of strong and transparent gel. The gel to sol transition temperature ( $T_{gel}$ ) of the gelator was measure at various concentrations. The values of  $T_{gel}$  decreased at higher acetic acid concentration. The TEM images showed the network structure composed of fibers with submicron dimension.

Tripodal cholamide(1)-based hydrogel has been used as a template to synthesize inorganic nanotubes of metal  $oxide^{17}$  which includes  $SiO_2$ ,  $TiO_2$ ,  $ZrO_2$ , ZnO and WO<sub>3</sub> as well as of metal sulfates such as  $ZnSO_4$  and  $BaSO_4$ . Nanotubes of a desired diameter can easily be made by a suitable choice of the hydrogelator or by slightly modifying the conditions of gelation. Rotational dynamics of polarity sensitive fluorescent dyes (ANS and DHP) in a nonpolymeric aqueous gel derived from tripodal cholamide 1 was studied using ultrafast time-resolved fluorescence technique.<sup>18</sup>

Novel cationic and neutral analogues of bile acids 2 and 3 respectively formed thermoreversible gels in water in presence of sodium chloride (NaCl), whereas neutral 4 formed gels in water in the presence of organic solvents such as ethanol, methanol, DMSO, and DMF. The compound 2 and 3 exhibited different aggregation behaviors. Compound 2 (1% w/v) formed stable thermoreversible gels



Scheme 1. Cholesterol based

in 0-4 M aqueous NaCl solution. It also formed gel 1M aqueous solution of NaBr, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaN<sub>3</sub>, NaNO<sub>3</sub>, KCl, LiCl and BaCl<sub>2</sub>. The thermal stability of the gel derived from **2** (1% w/v of NaCl) increased both the increase in the concentration of **2** and with increased concentrations of NaCl (1% w/v of **2**). The SEM images of xerogel derived from compound **3** and **4** indicate the network structure of submicron dimensions.

#### 3.2 Sugar based hydrogelators

Compounds 5, 6, 7 and 8 are the efficient hydrogels at very low concentrations.<sup>19,20,21,22,23</sup> In these gelators, sugar part helps the molecule for solubility and aromatic group to promote  $\pi$ - $\pi$  aggregation in water. Especially, Compound 5 reveals highly flexible gelation properties. It is capable to gelate a broad variety of organic solvents and water at the same time. Glycosylated amino acid derivative 9 is a potential gelator for aqueous solvent. It was found to have a thermally responsive phase transition.<sup>24,25</sup> This gelator could be useful for the release or capture of drugs or pollutants.<sup>24</sup> A molecule will be either trapped in the gel or



## Scheme 2. Sugar-based

released from the get with heating depending on the chemical properties (hydrophobicity or hydrophilicity). The glycosylated gelator can stabilize myoglobin in its active state for long times without significant leakage into buffer.<sup>25</sup> The Bolaamphiphiles<sup>26</sup> sugar derivatives (**10-16**) forms efficient gel in aqueous solvent.<sup>27, 28</sup> The aggregation properties of sugar derivatives (**10-16**) are different due to presence of different linking chain between the two sugar units. A disaccharide amphiphiles<sup>29</sup> (*Figure 1*) **17** containing one alkyl chain is an efficient hydrogelator in the presence of alcohol cosolvents.<sup>30</sup> Sugar containing fluorocarbons based hydrogel (**18**) have been reported.<sup>31, 32</sup> The fluorocarbons unit has been used for strong hydrophobic force. Xing et al. reported that the

vancomycin-pyrene derivative containing sugar moiety (19) is an efficient gelator for aqueous solvent. This is the first example of an antibiotic hydrogel.<sup>33</sup>

#### 3.3 Amino acid based hydrogelators

Amino acid surfactants with alanine, aspartic acid, glutamic acid as head groups (**20-23**) forms hydrogel at very low concentrations.<sup>34, 35</sup> The formation of gel is pH dependent due to presence of carboxylic acid. The pK<sub>a</sub> values of the acid carboxylic acid can be moderated by varying the length of the alkyl chain. It is found that increase in the chain length, the pK<sub>a</sub> values increases by 2 pH units. The crvo-TEM image indicates the rod like morphology. Lysine derivatives such as compounds 24 and 25 form hydrogel at low concentration. The hydrophobic effects as the major driving force for the formation of hydrogel.<sup>36, 37, 38</sup> Franceschi et al. have been reported the gel-forming amino acid bolaamphiphiles (26-28).<sup>39</sup> They showed that depending on the linker length, micelles, vesicles, or fibers are formed. Lightharvesting hydrogels are formed by two-headed amphipiles (29, 30, 31).<sup>40</sup> The charge-charge interactions and hydrophobic effects are the major driving force for the water gelation. The compound (32) with bulky (phenyl or isopropyl) side chain is effective gelators of both water and organic solvents.<sup>41</sup> In water, the hydrophobic interactions of the side chains promote linear aggregation, and then hydrogen bonding of the adjacent carboxylic acid further strengthens the assembly. Serinebased amphiphiles (33) form hydrogel.<sup>42</sup>

The amino acid derivatives (34, 35) containing terminal carboxylic acid are aggregated in aqueous solution. The aggregation properties are varied with changing pH of the solution.<sup>43,44</sup> The gelation is triggered by photoisomerization of the double bond, going from **37** to **36**<sup>45</sup> Only trans double bond in compound **36**, projects the hydrophobic side chains in an orientation similar to the oxalyl group, thus promoting  $\pi$ -  $\pi$  stacking, fiber formation, and subsequent hydrogelation. The compound (38) is self-assembled through the formation of hydrogel at very low concentration. The formation of gel depends on the pH and ionic strength.<sup>46</sup> It is also found that the molecules form giant vesicles at low pH. The aggregate morphology was also found to depend strongly on the hydrophobicity of the molecule, with lower molecular weight molecules gelling water at lower pH values. In order to get more information about the atomic scale organization, the hydrogel was characterized using crvo-TEM and X-ray diffraction.<sup>47</sup> New L-valine derivatives which have positively charged group formed transparent hydrogels of pure water as well as aqueous solutions containing inorganic acids and salts at 0.2 wt %.<sup>48</sup> In pure water, the hydrgelation abilities significantly depended on he concentrations; **39** has no hydrogelation ability at 70 g/L, while 40 and 41 formed hydrogels of pure water; especially, 41 able to gel pure water at 2 g/L. The hydrogelation ability of **41** was about 15 times better than compound 41. The hydrogelation abilities of 39 and 40 increases in presence of inorganic acids and salts. For 40, the hydrogelation abilities in inorganic salts solution are more than 12 times higher than in pure water. Compared with 40, the thermal stability of **41** is greater. The hydrogels based on **41** and **40**, which contain an inorganic acid and salts have the similar  $T_{gel}$  values, and their MgCl<sub>2</sub> and CaCl<sub>2</sub> hydrogels have good thermal stabilities. The T<sub>gel</sub> of hydrogels based on 41 increases in the presence on inorganic salts. The differences in the thermal stabilities of hydrogelators were measured FT-IR spectra  $D_2O$ . The morphology of the hydrogelators was studies by TEM analysis. Enantiomerically pure, N-alkyllaldonamides (42) is aggregated in water solution due to formation of hydrogel.<sup>49</sup> The recemic mixture did not for gel in water. Different diastereomers forms different morphologies, indicating that the geometry of the head group is for the packing.



Scheme 3. Amino acid based

## 3.4 Nucleotides based hydrogelators

Shimizu and co-workers synthesized various hydrogelators based on nucleotides.<sup>50, 51,52</sup> The molecularorganization of the nucleotide is controlled by

hydrogen bonding of the end groups (43). It is found that solubilizing deoxyribose and phosphodiester groups form hydrogel. The terminal sugar part helps the molecules to aggregate.<sup>50, 51</sup>

#### 3.5 Gemini surfactants based hydrogelators

The surfactant molecule (44) forms hydrogel at very low concentration. It is found that reducing the length of one alkyl chain from 18 methylenes to 10methylenes resulting in the formation of a coaservate (a spongy, water-insoluble mass) rather than gel.<sup>53, 54</sup> For the formation of hydrogel, hydrophobicity palys a determinant role in the structure-function relationship of this molecule. Oda and Hue have reported a family of geminisurfactants with chiral counter ions (45) that form hydrogels.<sup>55,56,57</sup> The morphology of the gels were studies by TEM analysis. The TEM images indicate that the gels are formed from twisted ribbon. From the <sup>1</sup>H NMR spectroscopy, it is found that there is direct interaction of the dications and chiral tartrate anions suggesting that the chiral structure of the aggregate may be induced by the chiral anion.<sup>Error! Bookmark not defined.</sup>



43

Scheme 4. Nucleotide based hydrogelator.



Scheme 5. Gemini surfactants based hydrogels

#### 3.6 Miscellaneous hydrogelators

Roger G. Harrison reported that resorcinarene (46) is an efficient gelator for water.<sup>58</sup> The gelation of this compound is pH-reversible. Aggregation and gelation occur as the pH of the solution is brought bellow 2.5 which corresponds to the pKa value for the protonation of one of the carboxylates at which point the molecule is neutral. The gel can be dissolved by raising pH and reformed again by lowering the pH. The minimum concentration of 46 required for gelation is 7.6 mM or 1.7% by weight. In the presence of divalent cations, in particular Cu<sup>2+</sup>, gelation is inhibited, due to strong interactions of the iminodiacetate ligand and cation. The morphology of the gel was examined by SEM analysis. The SEM images revel that the gel is composed of fibers that form a random network. Muramatsu and co-workers reported that the sodium salts of terpyridine-containing carboxylic acid (47-50) gelate water above CMC, which indicates that the gel is most likely composed of rodlike micelles.<sup>59</sup> Menger and co-workers synthesized various derivatives of aroyl-L-cystines for studies the gelation ability.<sup>60</sup> It is found that the compounds (**51-53**) formed very dilute and thermally stable gels. A large bolaamphiphiles based molecules (54) forms gels in aqueous medium.<sup>61</sup> The large number of hydroxyl head groups of the molecules (54) provides solubility and the hydrophobic core promotes aggregation.



Scheme 6. Miscellaneous hydrogelators.



Figure 1. The division of an amphiphilic structures (a) simple (b) modified.

### 4. Applications of hydrogels

Recently hydrogels are used as scaffolds in tissue engineering.<sup>6</sup> When used as scaffolds, hydrogels may contain human cells in order to repair tissue. Some hydrogels are environmental sensitive. This type of hydrogels have the ability to sense changes of pH, temperature, or the concentration of metabolite and release their load as result of such a change. Hydrogels that are responsive to specific molecules, such as glucose or antigens can be used as biosensors as well as in DDS. Some hydrogels are used in disposable diapers where they capture urine or in sanitary napkins. Silicone hydrogels, polyacrylamides etc. are used in contact lense. Hydrogels composed cross linked polymers such as polyethylene oxide, polyAMPS and polyvinylpyrrolidone are used as medical electrodes. Some hydrogels are used as explosives. Vancomycin-pyrene derivative is used as antibiotic hydrogel.<sup>33</sup> Natural hydrogel materials are being investigated for tissue engineering, these materials include agarose, methylcellulose, hylaronan, and other naturally derived polymers. Some hydrogels are used as dressings for healing of burn or other hard-toheal wounds. Wound gels are excellent for helping to create or maintain a moist environment. Hydrogels are used as drug delivery system particularly ionic drugs. Hydrogels are superabsorbents (they can contain over 99% water) natural or synthetic polymers. Hydrogels may be used as template for material synthesis. Nano particles are synthesized by using the hydrogel networks.

## 5. Conclusion

Non-polymeric physical gels have been reported in many review articles that are capable of forming gels in various organic solvents. But non-polymeric physical gels that form from aqueous solution are uncommon. In this review, several classes of small organic molecules that are capable of forming gels in aqueous solution are reported. Several techniques are reported to studies the hydrogels. The potential applications of hydrogels are also reported here.

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