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Supramolecular gels: characterization and applications

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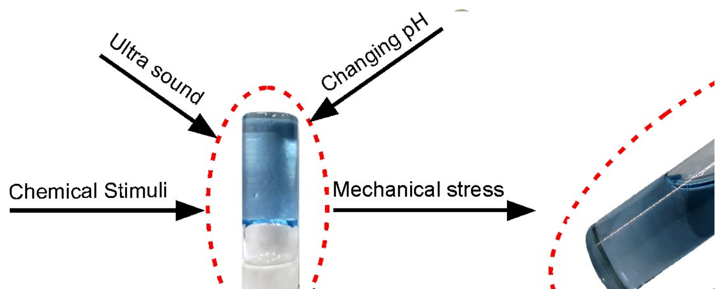
Abstract

Over the last decade the researchers have growing interest towards supramolecular gels not only to know about self assembly process but also for their potential applications in diversified areas. Since gels are sensitive towards several external stimuli like heat, light, pH of medium etc., incorporation of suitable functional groups to these gelators make them fruitful for the use in different fields. In this manuscript, supramolecular gels, their characterization processes such as optical microscopy, scanning electron microscopy, transmission electron microscopy, rheology, dynamic light scattering, X-ray diffraction and FTIR studies have been discussed. Their applications in various field of science and technology such as sensors, template of metal nano particle assembling, drug delivery, dye removal and oil spill recovery have also been discussed.



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1. Introduction

Gel is a soft solid like material which is multi component system and undergoes solid –liquid transition, in which the solvent molecules (major part) trapped into the three dimensional cross-linked network of solid molecules (minor part).[1] Since the 3D network of solid restricts the mobility of liquid so solid part is continuous phase and liquid part is discontinuous phase. The incorporation of liquid into the pores formed by cross-linking of solid prevents collapsing of solid architecture and restricts the flow of liquid.[2] Gels are exhibit properties in wide scale from soft and weak (liquid like) to hard and tough (solid like) due to immobilization of liquid into solid matrix. For this unique nature of gels, are interested from both of scientific community as well as

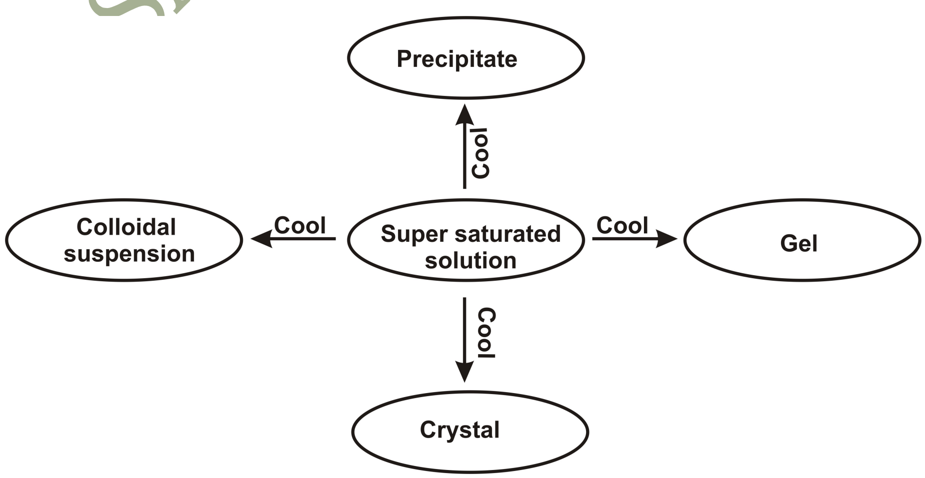

Fig. 1: Schematic representation of aggregation modes

industrial perspective. Gels have tremendous applications in diversified fields like food industry, cosmetics, pharmacology, medicine, biomaterial, electrolyte, sealants, separation techniques etc. The different commercial products derived from polymeric gels are soap, shampoo, jam, jelly, toothpaste, hair gels, contact lenses, gel pens, electronic devices etc which are necessary for our daily life. But in recent years, another kind of gels has drawn more attention, called Low Molecular Weight Supramolecular gels.[3] These gels are produced from small molecules called Low Molecular Weight Organic Gelators (LMOGs) and self-assembly process is responsible for formation of such gels. The supramolecular gels are highly responsive towards solvent change, pH, sonication, and heat-cool cycles etc. because several weak non covalent interactions present among the gelator molecules.[4] The supramolecular gels interested over polymeric gels because LMOGs containing functional group or attachment of molecular receptor to LMOGs are very sensitive to light and chemicals which are useful for the development of photo and chemical sensors.[5] LMOGs in aqueous or organic solvents have tremendous applications in nanomedicine, template synthesis, catalysis, drug delivery, nanoelectronics and sensing.[6] Supramolecular gels are generally made by heating the gelator in appropriate solvents and then cool the saturated solution at room temperature. During cooling of hot saturated solution several types of situations may arise by aggregation of solute molecules (Fig.1). This may be give crystal or precipitation by highly ordered or random assembling of molecules respectively. It may happen that assembled larger particles remain suspended in solvent to form colloidal suspension. Again it may assemble in such a way which produces a strong three dimensional network which can immobilize the solvent and that situation is known as gel.

2. Classification of gels

Gel is viscoelastic solid like substance composed of gelator and solvents. Gels are sub-divided into various categories depending upon different criteria like type of interaction, source, medium and constituents (fig.2).Generally gels are two types based on type of interaction. One is physical gels which are formed through non covalent interaction between gelator molecules as well as solvent molecules and other is chemical gels which are formed by covalent interactions.[7] Due to presence of non covalent interactions like H-bondig, л-л interactions, van der Waals forces, solvophobic interaction etc. into physical gels, they are thermally reversible but chemical gels (poly ester, poly amide) are thermally irreversible for the presence of strong chemical bonds.[8] Depending upon the source gels are classified as natural (naturally occurred macromolecules like starch, collagen, agar etc. forms gel by H-bonding) and artificial or synthetic which is categorized as supramolecular (molecular) and macromolecular (polymer). When the medium is organic solvent it called organo gel. If the medium is water or mixture of water and small amount of organic solvent it called hydrogel and if there was no solvent it is called xerogel. According to Flory gels are mainly four types (a) well-ordered lamellar structures such as phospholipids; (b) disordered covalent polymeric networks like vulcanized rubber ;(c) polymer networks formed through physical aggregation like gelatin; and (d) particulate, disordered structures such as precipitates consisting of highly anisotropic particles or reticular networks of fibres.[9]

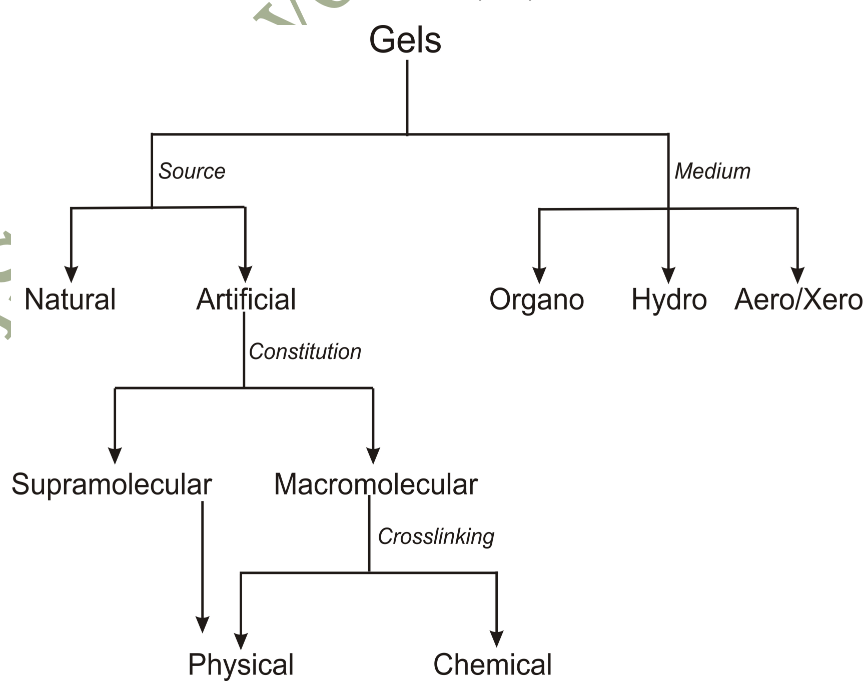

Fig. 2: Classification of gels.

Depending upon the processes of removal of solvent gels are three types (a) aero-gel, (b) xero-gel and (c) cryogel.

3. Supramolecular gel and Low Molecular weight Organogelators

Gels are generated by dissolving a gelator in an appropriate solvent. If the gels are derived from a small organic molecule having low molecular weight (<3000 D) and gel is formed by self-assembly then it is called supramolecular gel and gelator is recognized as low molecular weight organo gelator. Although in past two decades the research in this area has been interested but this type of gelator molecules were discovered in relatively far back and took so much time to recognize their importance.[10] The designing of LMOGs is a great challenge because during gelation only the non covalent interactions are predominant but those should not be so strong to avoid precipitation or crystallization. Again the solubility of such molecules in a solvent should be not high or less. During gelation process the molecules at first dimerize and then polymerized by non covalent interactions. These polymers are held together by virtue of non covalent interaction to afford nano to micro dimensional network structures such as fibers, vesicles, ribbons, sheets, flowers etc. For the reversibility of non covalent interactions these gels are easily breakable and are highly respond towards external stimuli like temperature, pH, solvent, Mechanical stress and light.[11] Due to stimuli responsiveness these have potential applications in material science like bio material,[12] sensors,[13] liquid crystalline material[14]etc. A wide variety of low molecular weighted organo gelator containing structural diversity has been reported like aminoacids,[15] sugars,[16] hydrocarbons,[17] aromatic compounds,[18] halocarbons,[19] fatty acids and esters,[20] steroids,[21] terpenoids[22] etc.

4. Characterization techniques used to study supramolecular gels

Supramolecular gels are made by non covalent interactions among gelator molecules. Due to dynamic nature these gels possessing many fascinating properties but it brings difficulties to characterize the gels. For detailed investigation of supramolecular gels different techniques are used discussed below.

4.1 Spectroscopy study

Different types of spectroscopy studies like NMR (^{1}HNMR, DOSY, NOESY and ROESY), UV, FT-IR, CD, fluorescence spectroscopy are used to identify the type of non covalent interaction present in supramolecular gels.

4.2 Microscopy studies

Various types of optical and electronic microscopes are utilized to identify the morphology formed by the self assembly of gelator molecules such as optical microscope (OM), scanning electron microscope (SEM), field emission scanning electron microscope (FESEM), transmission electron microscope (TEM), atomic force microscope (AFM), polarizing optical microscope (POM) etc. TEM study not only gives the shape of morphology but also can evaluate the thickness of three dimensional superstructures.

4.3 X-ray Techniques

X-ray techniques are crucial to understand the type of intermolecular forces that responsible for the stability of self-assembled structure as well as to determine the diameter of morphologies formed. The various types of x-ray techniques such as single-crystal diffraction, small angle x-ray scattering, wide angle x-ray scattering, small angle neutron scattering are used.

4.4 Computational Technique

Depending upon the behavior of atom or molecules computational approaches helps to investigate the interactions present among gelator molecules along with mechanism of gel formation. High level energy minimization and molecular dynamic calculation used to identify the possible aggregation modes.[23]

4.5 Dynamic Light Scattering

Dynamic light scattering is a very useful technique to determine the size distribution, interactions between particles, stability of suspension etc. It also used to probe the behaviour of complex fluids like concentrated polymer solutions. The aggregation of particles with time led to particles of larger hydrodynamic radius measured by periodic DLS measurement.[24]

4.6 Thermal analysis

Isothermal titration calorimetry (ITC) is a physical method used to determine the non covalent interactions present among gelators where as differential scanning calorimetric (DSC) study is a thermoanalytic process utilized to know the thermal stability of gels.[25]

4.7 Rheology

The study of deformation and flow of a matter under an external pressure is known as rheology. Since the supramolecular gels are behaves solid-like material so rheology is an important factor to calculate the strength and flexibility of gels.[26] The rheology study can investigate the structure of gels from the behavior and magnitude of elastic storage modulus (G') and elastic loss modulus (G'') of gels.[27]

It also investigates the mechanical and self-healing properties of gels.

5. Applications of gel

Gels are important material in day to day life from ancient to modern civilization for their soft but solid like nature which is a unique property. The natural gels of pectin, agar and starch are used in food products from the primitive times. Now a day the applications of gels are found in various fields like cosmetics, food technology, medicine, adhesive, lubricants etc. Especially the gels formed by immobilization of solvent into 3D self assembled network of LMOGs are thermoreversible in nature which is the advantage over the polymeric counterparts are having large area of applications.[28] Some of the applications of gels derived LMOGs are discussed below.

5.1 Supramolecular gels as sensors

The reversible gel to sol transition is inherent property of supramolecular gels which is influenced by heat and makes them for thermosensing applications. Further incorporation of chromophoric group or acid-base sensitive group into LMOGs, gels should have high sensitivity towards physical and chemical stimuli. In presence of photosensitized group, the gel to solution transition of supramolecular gels readily triggered by light due to formation of another isomer or polymerization of gelator. Again the H-bonding present in gels are influenced by acids or bases. This changes in gel structure also affects different properties like color, viscosity, fluoresce, conductivity as well as magnetic susceptibility. These functional supramolecular gelators should be used to fabricate molecular devices like sensors and actuators. Shinanki and co-workers have designed a photoresponsive gel of n-decaylammonium anthracene-9-carboxylate in cyclohexane.[29] The gel transformed into sol at 15^{o}C by irradiating mercury lamp for formation of non gelator dimerized product. Upon warming the solution at 30^{o}C in dark it forms precipitate which reform gel by subsequent heating to solution and then cooling. Pozzo et.al reported a pH responsive gel in acetonitrile of 2,3 di n-alkoxy phenazine derivatives.[30] The protonation of basic sites of phenazine moiety makes them pH responsive. Addition of TFA into gel up to 1 equivalent increases thermal stability but further addition decreases thermal stability. This was explained by the fact that monoprotonation in basic site strengthened the gel but further protonation decreases the solubility of gelator. Ahamed et.al designed 2H chromene derivatives of sodium N-acyl11-amino undecanoa forms organogels which are both light and pH sensitive.[31] The neutral carboxylic acid easily soluble in DMF or DMSO but on addition of NaOH it forms gels. Further, irradiation of 366 nm the gel forms yellow color and started to melt but after switching the light the color faded and eventually forms viscous solution. This is due to photoinduced ring opening colourless cyclic to yellow color acyclic form.

5.2 Supramolecular gels as drug delivery vechile

In recent years gels have drawn more attention in comparison to cream and ointment for their better property and stability. Gels also play the principal role in the field of drug delivery due to their great adaptability in terms of composition and adjustability to different administration routes, from parenteral to non-parenteral ones. Again, for the presence of reversible interactions in biocompatible gel moiety, they can be designed to respond various stimuli like change in pH, ionic strength or action of enzyme to break the gel structure and release the drug to specific target. The bioadhesive or mucoadhesive gels with long residential time in the administration site also help the visualized application. Choi et al. reported a thermo-responsive paclitaxel based hydrogelator containing polymer Pluronic F127 and the mucoadhesive polymer polyethylene oxide.[32] Oral administration of this anti-cancer drug increases local concentration of the drug in the oral mucosa and decrease the systemic side effects caused by the intravenous administration. For better solubility of the drug in water, paclitaxel was incorporated into inclusion complex of dimethyl-β-Cyclodextrin. A (S)-(+) ibuprofen based hydrogelator containing dipeptide linkage was reported by Bhuniya et. al which was hydrolyse in presence of colloidal buffer to release anti-inflamatory drug (S)-(+) ibuprofen.[33] Enzyme also can release the drug from the gelator molecule.

5.3 Supramolecular gels as template for metal nanoparticle assembling

A well ordered organization by assemblies of nanoparticles are more interested for their physical property, that consisting of properties of discrete NPs along with the collective particles which can expand their utilizations in optical and electronic fields.[34] The self-assembled nanofibers produced by supramolecular gels are highly used as a template for assembling of nanoparticles because the gelators can give different types of nano architectures like twisted nanoribbons, nanotubes, coiled nanorods and helical nanofibers.[35] Zhu et al synthesised 3D architectures of CdS nanoparticles using supramolecular gel as template.[36] Li and co-workers synthesized Ag(0) nanochain by photo reduction of a self-assembled Congo Red and Ag(I) nanofibre.[37] Nano composites of different metals like Ag, Au and Pd metals in supramolecular gels are well established. Bhat and Maitra reported that bile acid gelators with thiols can stabilize gold nanoparticles.[38] Majumder et.al synthesized gel-Pd nano tri-hybrid material using arjunolic acid and plant extract.[39]

5.4 Supramolecular gels for dye removal

Water pollution has been a great concern in modern civilization due to contamination of natural water mainly by human activities like toxic dyes based industrial wastes. So to protect water the removal of toxic dyes is mandatory. Several techniques are used to remove the dyes from water like physical, chemical, biological etc. Adsorption is superior to other methods due to its low cost and simple designing.[40] Various efficient adsorbents such as inorganic-organic hybrid materials, porous silica, clay, natural fibers and polymers are utilized for dye adsorption. Recently it is occurred that supramolecular gels are highly effective to remove the dyes from water. Cheng et.al reported that an imidazolium based supramolecular gel can be used to remove toxic dyes.[41] Malik et al. reported that an adenine based bicomponent hydrogel can be applied to remove organic dyes like rhodamine 6G , methylene blue , crystal violet etc.[42]

5.5 Supramolecular gels as a media of reactions

Supramolecular gels have drawn attention for their potential application as medium for chemical reactions. For the presence of limited space in gel the reactants are forced to specific interaction and give specific product. Also in case of chiral gelator the gel network can act as chiral template to carry out asymmetric synthesis. Nguyen et.al reported that diamides containing alkyne and azido groups are self-assembled to give nano tubes and reacted under self-assembled condition in presence of catalyst.[43] Bachl et.al carried out aerobic photooxidation of 1-(4-methoxyphenyl) ethanol in presence of riboflavin tetraacetate-catalyst under blue light in different supramolecular gels.[44] Shinkai et.al have reported the formation of helical inorganic silica utilizing gel network of 1,2-diaminocyclohexane derivatives as chiral template.[45]

5.6 Supramolecular gels as light harvesting systems

It is the time needed for storage of energy for future human beings. Since Solar energy is the easily availed renewable energy resource so conversion and storage of solar energy has gained major importance for the energy revolution. Naturally in photosynthesis process, light harvesting complexes absorb solar energy and transferred to system by conversion. Recently large number of synthetic molecules containing chromophoric group is developed where energy transfer takes place between donor and acceptor chromophores utilizing the gel matrix which is the fundamental requirement of light harvesting systems. Leon et.al synthesized a smart gel composed of1,8-naphthalimide and an acridine derivative in acetonitrile in which both gelators gives fibrillar network by self assembly and produced orthogonal fibrillar morphology and can act as light harvesting system.[46] Toshiaki et.al reported the development of light-harvesting organogel based on tris (phenylisoxazolyl) benzene and pyrene derivative having four phenylisoxazole substituents.[47] In this system photo induced energy transfer does not occur in solution but in the decalin gel, the co-assembled structure exhibited light-harvesting behavior.

6. Conclusion

In this paper we have discussed the driving forces behind the formation of gels, stability gel, mechanical strength, several processes used to characterize the and their morphology and the potential application in several fields of science and technology. Supramolecular gels are must be an important material for development of near future due to their targeted applications.

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