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Review Article

Nanogels: Multifunctional Platforms in Biomedical Science – A Review

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ABSTRACT

Nanogels are one of the techniques in nanotechnology which has been most prevalent in successful medication delivery inside the body and in addition topical treatment. Nanogels based materials have high drug loading capacity, biocompatibility, and biodegradability which are the key points to design a drug delivery system effectively. A few crosslinking techniques have been utilized as a part of the best approach to frame the hydrogel network structures, which can be characterized in two noteworthy gatherings of artificially and physically-instigated crosslinking. The pursuit of this review article is to concisely describe the recent development of nanogel drug delivery system in terms of drug loading and swelling of drug from nanogels. Recently different types of nanogel along with the synthetic procedure, mechanism of drug release from nanogel carrier and applications are mainly focused.

INTRODUCTION

Nanotechnology, a relatively novel technique, offers a broad scope for a smart drug delivery and drug manufacturing (nanomedicine) approach involving the design, synthesis and characterization of materials or molecules and devices that have effective function at nanometer scale. Development of novel nano-sized particulate drug delivery systems (DDS) have shown the profound impact on disease prevention, diagnosis, and treatment as reported after the researches in academic laboratories and pharmaceutical companies all over the world[1]. Nanogels are polymer-based, crosslinked hydrogel particles with nanometer-scale dimensions, typically ranging from 20 to 200 nm. The term 'nanogels' defined as the nanosized particles formed by physically or chemically crosslinked polymer networks that is swell in a good solvent. The term "nanogel" was first introduced to define cross-linked bifunctional networks of a polyion and a nonionic polymer for delivery of polynucleotides[2]. Nanogels are swollen in nano-sized networks composed of hydrophilic oramphiphilic polymer chains, which can be ionic

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or non-ionic. Not, only for drug delivery the nanogels is investigated from a longer period of time for making miscellaneous agents like quantum dots, dyes and other diagnostic agents[3]. Nanogels are a type of flexible and versatile biomaterials with nanoscale dimensions. Nanogels can be made up of natural polymers, synthetic polymers, or a mixture of natural and synthetic polymers. Commonly used natural polymers mainly include proteins and polysaccharides.

ADVANTAGES OF NANOGELS

1. The particle size and surface properties can be manipulated to avoid rapid clearance by Phagocytic cells, allowing both passive and active drug targeting. .
2. Can incorporate both hydrophilic and hydrophobic drugs and charged solutes.
3. High drug loading capacity.
4. Better permeation via biological membranes due to extremely small size.
5. Easily escape entrapment by reticuloendothelial system.
6. Controlled and sustained drug release at the target site, improving the therapeutic efficacy and reducing side effects. Drug loading is relatively high and may be achieved without chemical reactions; this is an important factor for preserving the drug activity.
7. Highly biocompatible and biodegradable.
8. Ability to reach the smallest capillary vessels, due to their tiny volume, and to penetrate the tissues either through the paracellular or the transcellular pathways.
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10. Excellent transport characteristics.

ROUTE OF ADMINISTRATION OF NANOGELS

Nanogels are versatile drug delivery systems that can be administered through various routes, each offering distinct advantages for targeted and controlled therapy. These routes are

- Oral
- Intranasal
- Topical
- Parenteral
- Ocular
- Pulmonary

PROPERTIES OF NANOGELS

Biocompatibility and Degradability

Nanogel based drug delivery system is highly biocompatible and biodegradable due to this characteristic it is highly promising field now a days.

Swelling Property in Aqueous Media

The most beneficial feature of nanogels is their rapid swelling/de-swelling characteristics. Nanogels are soft nanomaterials[2]. Swelling of nanogels in aqueous environment is controlled by both nanogel structure chemical nature of polymer chains, degree of cross-linking, charge density for polyelectrolyte gels and environmental parameters for polyelectrolyte gels - pH, ionic strength and chemical nature of low molecular mass ions for thermo-responsive gels – temperature. It is well recognized that a balance between the osmotic pressure and the polymer elasticity determines physical dimensions of a hydrogel particle[4].

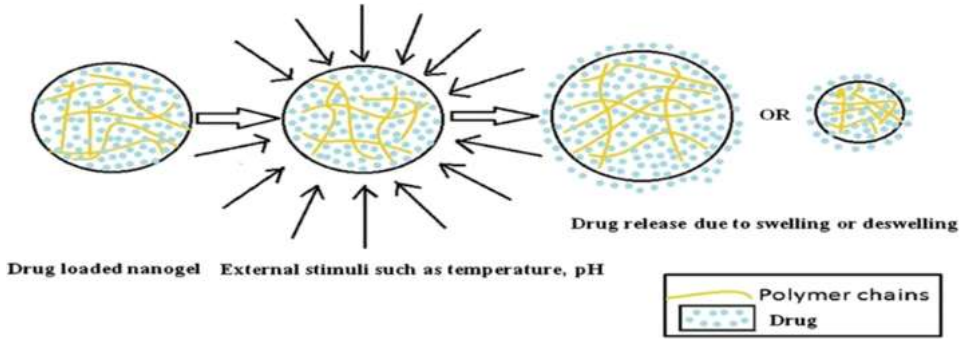

Fig. 1: Drug release model from nanogel.

Solubility

Nanogels are able to solubilize hydrophobic drugs and diagnostic agents in their core or networks of gel [2]. In addition hydrophobic molecules can be solubilized into hydrophobic domains presented in some nanogels. Notably, in most cases loading due to hydrophobic interactions alone results in relatively low loading capacities[3].

Electromobility

Nanogels could be prepared without employing energy or harsh conditions such as sonication or homogenization, which is critical for encapsulating biomacromolecules.

Higher Drug Loading Capacity

The properties of higher drug loading capacity of nanogels depend on the functional group present in the polymeric unit[5]. These functional groups have a tremendous effect on drug carrying and drug-releasing properties, and some functional groups have the potential to conjugate with drugs/antibodies for targeting applications. These pendent functional groups of polymeric chains contribute toward establishing hydrogen bonding or vander Waals forces of interactions within the gel network and thus facilitate the drug-carrying efficiency[6].

Particle Size

Nanogels typically range in size of 10-100 nm in and hence are effective in avoiding the rapid renal exclusion but are small enough to avoid the uptake by the reticuloendothelial system[7]. Size is a key factor in the biodistribution of long-circulating nanoparticles on the basis of physiological parameters such as hepatic filtration, tissue extravasation, tissue diffusion, and kidney excretion[8].

Colloidal Stability

Nanogels or polymeric micellar nanogel systems have better stability over the surfactant micelles and exhibit lower critical micelle concentrations, slower rates of dissociation, and longer retention of loaded drugs[9].

Non-immunologic

Response this type of drug delivery system usually does not produce any immunological responses.

Others

Both type of drugs (hydrophilic and hydrophobic drugs and charged solutes) can be given through nanogel. Such properties of nanogel are significantly influenced by temperature, presence of hydrophilic/hydrophobic groups in the polymeric networks, the cross-linking density of the gels, surfactant concentration, and type of cross-links present in the polymer networks.

CLASSIFICATION OF NANOGELS

Nanogels are more commonly classified into two major ways. The first classification is based on their responsive behaviour, which can be either stimuli-responsive or non-responsive. In the case of non-responsive microgels, they simply swell as a result of absorbing water.

1. Stimuli-responsive nanogels swell or deswell upon exposure to environmental changes such as temperature, pH, magnetic field, and ionic strength.
2. Multi-responsive nanogels are responsive to more than one environmental stimulus. The second classification is based on the type of linkages present in the network chains of gel structure; polymeric gels (including nanogel) are subdivided into two main categories.

Physically Cross-Linked Nanogels

Hybrid Nanogels

Hybrid nanogels are defined as a composite of nanogel particles dispersed in organic or inorganic matrices[10]. Group of studies have demonstrated nanogel formation in an aqueous medium by self assembly or aggregation of polymer amphiphiles, such as pullulan-poly(N-isopropylacrylamid) (PNIPAM), hydrophobized polysaccharides, and hydrophobized pullulan[12]. Pullulan is extensively used in food, cosmetic and pharmaceutical industries because it is easily modifiable chemically, non-toxic, non-immunogenic, non-mutagenic, and non-carcinogenic[12]. The merits of pullulan are that it is biocompatible, biodegradable, blood compatible and non-immunogenic[13]. It can be chemically modified to various derivatives to endow amphiphilic property. These nanogels have the ability to form complexes with various proteins, drugs, and DNA; and it is even possible to coat surfaces of liposomes, particles, and solid surfaces including Cells. These hybrid nanogels are also capable of delivering insulin and anticancer drugs more effectively. CHP is composed of pullulan backbone and cholesterol branches. The CHP molecules self aggregate to form mono-dispersed stable nanogels through the association of hydrophobic groups that provide physical crosslinking points[14,15].

Micellar Nanogels

Polymeric micelles are nanosized particles with a typical core–shell structure where the core can solubilise the hydrophobic drug and the corona stabilizes the interface between the core and the outside medium[17,18]. Polymer micellar nanogels can be obtained by the supramolecular self-assembly of amphiphilic block or graft copolymers in aqueous solutions[19]. Since the use of block polymer micelles as drug-carrying vehicles was proposed in 1980s, micellar drug delivery systems (DDSs), which are aimed to deliver drugs at predetermined rates and predefined periods of time, have attracted increasing research attention[20]. They possess unique core-shell morphological structures, where a hydrophobic block segment in the form of a core is surrounded by hydrophilic polymer blocks as a shell (corona) that stabilizes the entire micelle. The core of micelles provides enough space for accommodating various drug or biomacromolecules by physical entrapment. Furthermore, the hydrophilic blocks may form hydrogen bonds with the aqueous media that lead to a perfect shell formation around the core of micelle.

Liposome Modified Nanogels

Liposomes are simple microscopic vesicles in which lipid bilayer structure is present with an aqueous volume entirely enclosed by a membrane, composed of lipid molecules. There are number of components present in liposomes, with phospholipid and cholesterol being the main ingredients[21]. In particular, liposomes have been used as carriers for many kinds of molecules such as anticancer, anti-bacterial, anti-fungal and anti-viral agents, and bioactive macromolecules[22].

Chemically Cross-Linked Gels

Chemical gels are comprised of permanent chemical linkages (covalent bonds) throughout the gel networks. The properties of cross-linked gel system depend on the chemical linkages and functional groups present in the gel networks[18]. Chemically crosslinked hydrogels are synthesized by chain growth polymerization, addition and condensation polymerization and gamma and electronbeam polymerization. Chain-growth polymerization includes free radical polymerization, controlled free radical polymerization, anionic and cationic polymerization[22]. It is done by three process viz., initiation, propagation, and termination. After initiation, a free radical active site is generated which adds monomers in a chain link-like fashion[23]. The crosslinking agent is explained by the e.g. by using the disulfide cross linking in the preparation of nanogel (20 – 200 nm) the pendant thiol groups are achieved "environmentally friendly chemistry".

Synthesis Techniques of Nanogel

Current approaches used for the preparation of nanogels can be classified into following categories:

1. Novel pullulan chemistry modification, [24].
2. Novel photochemical approach, [25].
3. Novel free radical polymerization process with inverse miniemulsion technique, [26].
4. Addition fragmentation transfer (RAFT) process, [27].
5. Emulsion photopolymerisation process, [28].
6. Chemical modifications[29].

Drug Loading Techniques in Nanogel

Nanogels are widely used as carriers of therapeutic agents. A successful nanodelivery system should have a high drug-loading capacity, thereby reducing the required amount of carrier. Drugs can be incorporated in nanogels by

Covalent Conjugation

Covalent conjugation of biological agents can be achieved using preformed nanogels or during nanogel synthesis . For e.g. Acrylic groups are modified with enzymes and copolymerized with acrylamide either in inverse microemulsion or dilute aqueous solution to obtain nanosized hydrogel[5].

Physical Entrapment

In cholesterol – modified pullulan nanogels proteins was incorporated by physical entrapment SiRNA in HA nanogels. In nonpolar domains by addition of hydrophobic molecules formed a hydrophobic chain which is present in selected Nanogels[5]. Physical entrapment is mainly determined by the sizes of nanocarrier pores and enzyme molecules. Other approaches are based on the functional groups on the surfaces of enzymes and nanocarriers[30].

Self-Assembly

Biological self-assembly provides illustrations of thermodynamically stable supramolecular arrays that not only have regular architectures but also have intelligen functions[31]. The self-assembly phenomenon has been defined as the autonomous, spontaneous, and reversible organization of molecular units into structurally stable and well-defined aggregates in which defects are energetically rejected. It has many beneficial features such as –

- It is cost-effective,
- Versatile and facile,
- The process occurs towards the system's thermodynamic minima, resulting in stable and robust structures.

Self-assembly occurs toward the system's thermodynamic minima and through a balance of attractive and repulsive interactions, which are generally weak and non covalent, such as electrostatic, vander waals, and coulomb interactions, hydrophobic forces, and hydrogen bonds[32]. Many molecules are self–assembly is characterized by diffusion followed by specific association of molecules through non–covalent interaction, hydrophobic associations or including electrostatics. Individually, such interactions are weak, but dominate the structural and conformational behaviour of the assembly due to the large number of interactions involved [33]. While oppositely charged polysaccharides associates readily as a result of electrostatic attractions[34]. Interactions with neutral polysachharides lead to be weaker or non – existent, by the modification with chemical it is able to trigger assembly being necessary. The polysaccharides which are highly water soluble, inducing the formation of nanoparticles via hydrophobic interactions. This kind of amphiphilic polymer can be used by three methods.

- Hydrophilic chains grafted to a hydrophobic backbone (grafted polymer).
- Hydrophobic chains grafted to a hydrophilic backbone.

Upon contact with an aqueous environment, amphiphilic polymers spontaneously form self-aggregated nanoparticles, via intra- or intermolecular associations between the hydrophobic moieties, primarily to minimize the interfacial free energy. The important feature, from the physicochemical point of view is that the molecule is able to orient itself to expose the hydrophilic regions to the polar environment (normally the aqueous medium) and the hydrophobic segments aggregates in the internal core of the material. The concentration above which the polymeric chains aggregate is called the critical micelle concentration or the critical aggregate concentration[2].

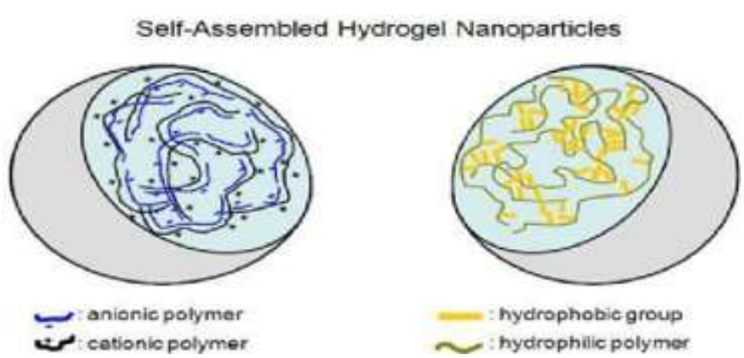

Fig 2. Schematic representation of intermolecular interactions driving self-assembly processes that includes (an electrostatic interactions and (b) hydrophobic association.

Mechanism of Drug Release from Nanogels

Diffusion Mechanism

Example: The diffusional release of doxorubicin from stable hydrogel nanoparticles based on pluronic block copolymer[2]. Various nanomedicine are follows this mechanism & simple procedure, such as polymeric micelles that have already reached a clinical stage[5].

Nanogel Degradation

The degradation of these nanogels was shown to trigger the release of encapsulated molecules including rhodamine 6G, a fluorescent dye, and Doxorubicin, an anticancer drug, as well as facilitate the removal of empty vehicles[2]. Significant mesh size alteration has been seen in dietylaminoethyl methyacrylate cationic nanogel for release of medium size molecules by virtue of pH sensitivity[35].

Displacement by Ions Present in the Environment

There is an increased interest in developing nanogels that can release biological agents in response to environmental cues at the targeted site of action. For example: disulfide cross-linked POEOMA nanogels biodegraded into water-soluble polymers in the presence of a glutathione tripeptide, which is commonly found in cells[36]. Cell membrane-triggered release of negatively charged drugs from complexes with cationic nanogels was also proposed to explain cellular accumulation of an NTPs drug delivered with nanogels [2].

pH Responsive Mechanism

In the acidic skin pH the reactive oxygen species scavenging the on & off 8catalytic activity by the platinum nanoparticles containing nanogel and for the reason of protonation of crosslinked poly (2 – (N, N – diethylamino) methacrylate) core and PEG [37]. When there is exit low PH the polymers methacrylic acid – ethyl acrylate are insoluble 3D structures, again by increasing the PH ranges acidic groups ionizes due to the polymeric chains repulsions begins and lead to a particular release profile of procaine hydrochloride[38]. The control the release kinetics mechanism shown by the drug temozolidine due to swelling action of pH sensitive polyacryrlic acid chains[39].

Photochemical Internalization and Photoisomerisation

Excitation of photosensitizers loaded nanogels leads to production of singlet oxygen and reactive oxygen species. which cause oxidation of cellular compartment walls such as endosomal barrier walls which effects release of therapeutics into cytoplasm[4]. Polyelectrolyte hydrogels that incorporate biological agents via electrostatic bonds allow for release of biological agents in response to environmental changes. Cis-trans isomerisation of azobenbenzene by photoregulation in azo-dextran nanogel loaded with aspirin as model drug exhibited that E-configuration of azo group lead to better release profile of drug than z-configuration at 365 nm radiation[40].

Application of Nanogels

Nanogels have been transforming the field of curative medicines. In the short duration since the appearance of the concept, these non-conventional drug delivery systems have served as potential candidates for wide spectrum of applications.

Anticancer Therapy

Many polymeric nanogels have been employed for cancer therapy. Incorporating chemotherapeutic drugs into the nanogel not only increases the bioavailability but also enhanced permeability and retention. Nanogel are being used to deliver drugs more effectively in cancer chemotherapy. One of the polymeric nanogels for use in patients with breast cancer, which has received FDA approval also, is Genexol-PM [41].

Autoimmune Disease

A study conducted designed and tested a novel nanogel drug delivery vehicle for the immunosuppressant mycophenolic acid (MPA). The results of this study concluded that there is a better efficacy of nanogel based local drug delivery for lupus erythematosus as it targets antigen-presenting cells. This new drug delivery system increases the longevity of the patient and delays, the onset of kidney damage, a common complication of lupus[42].

For Local Anaesthesia

Pain control is one of the top priorities in therapeutics in dental treatment. Improvement of regional administration of local anaesthetics could be achieved by incorporating them into drug delivery systems[43]. In a study conducted to develop and evaluate thermoreversible in situ gelling drug delivery system for periodontal anaesthesia. It was found that Pluronic gel proved to be a promising carrier for effective release of Mepivacaine hydrochloride throughout the dental procedure[43]. Nanogels are probably one of the better candidates due to the lesser pain during injection and longer blood circulation time [44].

Stopping Bleeding

A protein molecule which is in solutions & been used for formation of nanogel has been used to stop bleeding, even in severe gashes. The proteins have mechanism of self – assemble on the nanoscale in to a biodegradable gel[45].

Ocular Problems

Polyvinyl pyrrolidone – poly (acrylic acid) (PVP/PAAc) nanogel is pH sensitive and prepared by γ – radiation – induced polymerization. It is used to encapsulate pilocarpine in order to maintain an adequate concentration of the pilocarpine at the site of action for prolonged of time[46].

Neurodegenerative Diseases

Nanogel is a promising system for delivery of oligonucleotides (ODN) to the brain. For treatment of neurodegenerative disorders systemic delivery of oligonucleotides (ODN) to the central nervous system is needed. Macromolecules injected in blood are poorly transported across the blood-brain barrier (BBB) and rapidly cleared from circulation. Nanogels bound or encapsulated with spontaneously negatively charged ODN results in formation of stable aqueous dispersion of polyelectrolyte complex with particle sizes less than 100 nm which can effectively transported across the BBB. The transport efficacy is further increased when the surface of the nanogel is modified with transferrin or insulin[47].

Diabetics

"An Injectable Nano-Network that Responds to Glucose and Releases Insulin" has been developed. It contains a mixture of oppositely charged nanoparticles that attract each other. This keeps the gel together and stops the nanoparticles drifting away once in the body. In vivo experiments conducted in diabetic rats in 2012 revealed that insulin-loaded nanogels decreased the blood glucose levels by 51% from the baseline level for almost 2 hours. Significantly, when compared with free insulin the insulin-loaded nanogels could keep blood glucose levels stable and avoided blood sugar variations[48].

Nasal Drug Delivery

Nanogel drug delivery systems hold great potential to overcome some of the barriers in delivery. Nanogels are efficiently taken up by nasal mucosa and therefore, may possibly be used as efficient transport and delivery systems for therapeutics through nasal mucosa. The use of nanogels for vaccine delivery via nasal route is a new approach to control the disease progression. Nanogels are high-viscosity systems containing nanoparticulates (NPs, microcapsules, NEs, etc.) in a polymer network[49]. The advantages of nanogel takeaccount of reduced mucociliary clearance due to elevated viscosity, reduction in taste impact due to reduced postnasal drip towards nasopharynx, reduced irritation due to soothing/emollient excipients and target delivery to mucosa for better absorption[50]. In situ gelling agents are incorporated in the formulation of nanogel. These systems are appears as liquids in storage conditions but converted to gels at the site of application. This conversion is triggered by the pH, temperature, presence of any other ionic or biological component etc[51].

FUTURE PROSPECTS.

Advanced Stimuli-Responsive Drug Delivery

Nanogels can be finely tuned to respond to pH, temperature, redox, or light—enabling precise, on-demand drug release at disease sites like tumors or inflamed tissues

- Researchers are experimenting with dual- or multi-stimuli systems (e.g., pH + temperature or NIR light triggers) to improve targeting and control delivery even further.

Targeted Applications in Medicine

- **Cancer therapy:** Capable of selective uptake, delivering chemo drugs like doxorubicin or cisplatin with improved tumor targeting and reduced side effects .
- **Wound healing & infection control:** Formulations with silver, antibiotics, or growth factors help heal wounds and penetrate bacterial biofilms resistant to conventional treatments
- **Neurological, ophthalmic, and anti-viral uses:** Early research shows promise in crossing the blood–brain barrier and enabling sustained drug release in eye and viral therapies .
- **Biosensing & imaging:** Nanogels encapsulate sensors or imaging agents (MRI, CT, optical), offering better retention and multimodal diagnostic capabilities

Expanding into Environmental, Agricultural, and Cosmetic Uses

- As smart carriers in agriculture, nanogels could slowly release fertilizers or pesticides and conserve soil moisture In environmental clean-up, they could help capture heavy metals or pollutants in water.
- In cosmetics, their ability to hydrate, retain active ingredients, and control release makes them ideal for skincare and novel formulations.
- Additionally, emerging applications in anti-biofilm therapies, agriculture, environmental remediation, and smart materials are poised to broaden the impact of nanogels beyond biomedicine.

CONCLUSION

Nanogels are promising, innovative and smart drug delivery system that can play a vital role by addressing the problems associated with traditional and modern therapeutics such as nonspecific effects and poor stability. Every new research entails to discovery of new polymeric systems and novel mechanistic approaches with promising role in therapies and new innovation on fabrication of nanogel design. Recent developments in nanogel and nanotechnology have provided a bright insight into the applications of nanogel in the management of ocular problems, nasal drug delivery, vaginal drug delivery etc.

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