CHAPTER-1

Introduction
1.1 Nanogels

1.1.1 Introduction

The research field in the domain of nanoscience and nanotechnology has attracted much attention in the recent years. The great interest lies in the fact that selective reactivity of macromolecules controlled over nanoscale dimensions is providing the means to prepare unique nanomaterials (nanogels / microgels) for fundamental and applied studies in nanoscience and nanotechnology. Polymeric nanogels as soft nanomaterials have attracted much attention as subject of study in basic science and as components of materials for cosmetics, biotechnology, and medicine [1-2]. Polymeric nanogels can be defined in detail on the basis of their size / and structure. The nanogels are compact, globular, internally cross-linked macromolecule with particles of polymer gel (two component-system consisting of a permanent three-dimensional network of linked polymer chains with molecules of solvent filling the pores of this network) having the dimensions in the order of nanometer range. This approach is based on the fact that nanogel is an individual entity or part of one macromolecule on account of linkage of all its chain segments. Also, such entities can be synthesized by polymerization process and

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in the absence of crosslinking it would lead to the formation of a single linear polymer chain. Nanogels possess tunable chemical composition and three-dimensional physical structure which enables control over water content, mechanical properties, and biocompatibility [3-4]. Moreover, nanogels offer significant opportunities for targeted applications as a consequence of their tunable size (nm range), interior network [5] (enabling incorporation of bio-molecules such as drugs, proteins, and DNA) and a large surface area for multivalent bioconjugation [6-7].

Very important and perhaps the most studied so far are nanogels composed of hydrophilic polymers which are capable of swelling in water. Such gels, irrespective of their dimensions, form a large group of compounds named hydrogels. Oh et al. [8] defined nanogels as crosslinked polymeric particles, which can be considered as hydrogels if they are composed of water soluble / swellable polymer chains. Typical hydrogel forming polymers are those containing hydrophilic groups as -OH, -COOH, -NH₂, -CONH₂, -CONH, -SO₃H or ether linkages. Generally, all water-soluble polymers, including those of natural origin can be transformed into hydrogels. Thus, hydrogels have ordered three dimensional networks, crosslinked together either physically (entanglements, crystallites), or chemically (tie-points, junctions), with well-defined physicochemical properties and easily reproducible drug release profiles.

1.1.2 Methods of Preparation

Polymerization or crosslinking is usually carried out in colloidal dispersions to ensure formation of nano size species. Various synthetic strategies for nanogels preparation have been reported by Oh et al. [8]. Typically, nanogels can be synthesized by radical heterogeneous polymerization in an inverse mini- or microemulsion [9-10].
1.1.2.1 Cross-Linking Polymerization

In first technique, monomers or their mixtures are the starting materials and is based on polymerization and cross-linking, also called “cross-linking polymerization”. Emulsion polymerization is certainly the most widely used process to prepare polymer colloids. Emulsions are heterogeneous colloidal and opaque systems with droplet size ranging from 100 to 1000 nm. It is a kinetically stable system and requires mechanical work against colloidal instability. The mechanism and kinetics of the emulsion polymerization reaction have been extensively studied since 1930 [11].

In macroemulsion process, each micelle may serve as a separate microreactor, protected from the contact with other micelles by the stabilizing action of surfactant. Thus in such a confined space the polymerization and cross-linking reactions can be carried out to a high degree of monomer conversion.

In a classical free-radical emulsion polymerization, the system initially consists of monomer molecules that are dispersed in the liquid phase in the form of micelles (a few nm) and monomer droplets (0.1-1 mm). Such a microheterogenous system is stabilized by the presence of surfactants. The radicals are generated in the liquid phase. In some systems, initiation and first propagation steps also take place in the solution. As the growing chain has the tendency to become phase separated, surfactant protected polymer-monomer particles are being formed, where the further polymerization and cross-linking steps take place. During the chain growth, monomer molecules diffuse from the droplets and any inactive micelles to the active particles containing growing chain(s). After these outer monomer sources are used up then only the rest of the monomers inside the active particles react, these particles do not grow longer (or may even contract due to internal
cross-linking when multifunctional monomers are present) and, upon nearly complete consumption of the monomer, the process is finally terminated.

Miniemulsion is classically defined as aqueous dispersions of relatively stable oil droplets within a size range of 50–500 nm prepared by shearing a system containing oil, water, a surfactant, and a so-called "co surfactant" [12]. Polymerization of the oil droplets of such miniemulsion turned out to be very promising and extends the possibilities of classical emulsion polymerization [13]. Polymerization in carefully prepared miniemulsion results in latex particles which have about the same size as the initial droplets [14].

In a monomer-containing emulsion, with increasing surfactant concentration the amount of monomer stored in the droplets decreases while more monomer molecules form micelles. When a critical value of emulsifier concentration is reached, no monomer droplets are left, with all the monomer being present in micelles. Such a transparent micellar solution is a starting point for the polymerization in microemulsion. In such a system the polymerization in monomer droplets is avoided. In the absence of this side effect known from the macroemulsion technique, nearly monodisperse nanogels can be synthesized. The notation 'microemulsion' is used for all dispersions of two separated and well defined phases stabilized by interfacial surfactant layers, where the droplet size is a thermodynamically controlled equilibrium property.

In contrast to emulsions which are white, opaque, unstable and contain 1-10 μm droplets, microemulsions are transparent. The colloidal particles spontaneously formed in microemulsion are typically up to nanometric-scale, globular droplets of the minor solvent, each one is surrounded by a surfactant monolayer and thus dispersed in the
bulk solvent. Once the conditions are favorable, microemulsion formed spontaneously and little mechanical work (such as ultrasonic or vigorous agitation) is required. The nanoscale compartmentalization in microemulsion can be used as a reaction medium for the controlled formation of colloids.

Microemulsion polymerization has been an important synthetic route to nanosize polymer materials. In most cases, the nanogels in the range of 10-60 nm are available. Microemulsion covers oil/water (O/W), bicontinuous (intermediate phase where O/W emulsion transfers to the W/O emulsion) and water/oil (W/O i.e. inverse type). These three types of microemulsion are formed corresponding to the relative amounts of oil phase, water phase and emulsifier as shown in Figure 1.1.

In order to highly stabilize monomer-solubilized micelles and extend the region of microemulsion, medium chain alcohols (e.g., pentanol) are often used as a co-surfactant, besides a large amount of emulsifier is also used. Medium chain alcohol is localized in the interface between the monomer-swollen micelles and the continuous phase to decrease interfacial energy. Thus, both hydrophobic and hydrophilic nanogels can be obtained by carrying out the polymerization in O/W [15-16] and W/O [17-18] using hydrophobic and hydrophilic monomers respectively. Usually hydrophilic and hydrophobic initiators can be used in O/W or W/O microemulsion polymerization. Antonietti et al. [19] reviewed the literature of polymerization in microemulsion, mainly on the synthetic aspect of this technique such as the particle size control, analysis of the diversity of surfactants to obtain polymerizable microemulsions and kinetic aspect of polymerization in microemulsion. The kinetics of free-radical polymerization of acrylamide (AM) initiated by dibenzoyl peroxide in non-percolating and percolating
inverse microemulsion (toluene/AOT/water/AM) and the properties of polyacrylamide (PAM) particles formed from these inverse microemulsion were investigated by Barton et al. [20].

Fig. 1.1 Relationship between microemulsion type (W/O, Bicontinuous, O/W) and relative amounts of oil phase and water phase

The nucleation mechanism of emulsion polymerization can be applied to microemulsion polymerization after some modifications. It is considered that the monomer-swollen micelles capture the radicals / oligomeric radicals from the continuous phase, where the initiator decomposes to radicals and they grow to oligomeric radicals with monomers dissolved in the continuous phase, to polymerize monomers inside micelles to form nuclei. Because the monomer droplet is not present, the growing particle is provided with
a monomer by other un-nucleated micelles to form nuclei through the diffusion process (i.e. diffusion of monomer through the continuous phase) or collision (i.e. coalescence with neighboring micelles) [21]. Both mechanisms are feasible in oil-continuous microemulsion where droplet stability is attained by steric stabilization. Therefore, not all of the micelles convert to polymer particles. After the polymerization, a part of the micelles will remain in the continuous phase. Being different from conventional emulsion polymerization, it was found that the number of particles increased continuously until the polymerization was completed. Therefore, it is considered that the possibility of initiating free radicals in the continuous phase being captured by un-nucleated micelles, rather than by polymer-containing nuclei is very high throughout the polymerization. The final particle was composed of only one single-polymer molecule. Thus once a micelle captured a radical and polymerized the monomer therein forms a nucleus, this nucleus no longer captured another radical. The newly decomposed radicals were likely to be captured by un-nucleated micelles. This was a very special case. Many authors found that the final particles consisted of 2-10 polymer molecules. It has been demonstrated by electron microscopy that the particles grow rapidly until a certain diameter is reached. The diameter of each particle then remains constant while the number of particles grow steadily during the course of the reaction. Evidently, the system undergoes new particle nucleation during the entire polymerization process. This is contrary to conventional emulsion polymerization where the first nucleation stage is followed by a particle growth at constant particle number [22].

At the start of microemulsion polymerization, the number of monomer swollen micelles is very large, typically of the order of $10^{21}$ per litre. After polymerization, the inverse
microemulsion contains water swollen polymer particles as the dispersed phase [23]. On completion of reaction, the number of nanogels is about three orders of magnitude smaller. Consequently, only a small fraction of the surfactant molecules is needed to stabilize the nanogels. This means that after reaction there is an excess of surfactant which forms small micelles which coexist with the nanogels. Furthermore, it was found by Candau et al. [24] that addition of AM into aqueous phase extends the microemulsion region steadily with isoparaaffinic oil (Isopar M) as solvent. Here, AM behaved like a co-surfactant and located in the interface between the microemulsion and the oil phase.

Chen et al. [25] explained mechanism, kinetics, influences of the kind of solvent, kind and concentration of emulsifier, monomer content, agitation speed on the rate of process and product properties of AM microgel formation through inverse emulsion polymerization.

Inverse miniemulsion polymerization is a heterogeneous W/O polymerization process that can be applied to the synthesis of water-soluble polymeric particles. This process involves aqueous droplets (including water-soluble monomers), stably dispersed with the aid of oil-soluble surfactants in a continuous organic media by sonification [26]. Polymerization occurs within the aqueous droplets producing stable colloidal particles upon the addition of radical initiators. Recent reports have demonstrated the synthesis of water-soluble particles of poly(2-hydroxyethyl methacrylate), PAM and polyacrylic acid [27-29] as well as temperature sensitive hollow microspheres of poly(N-isopropylacrylamide) (PNIPAM) [30].
Neyret and Vincent [31] co-polymerized in inverse microemulsion N,N'-methylenebisacrylamide (N MBA) with equimolar or nonequimolar amounts of cationic [2-(methacryloxy)ethyl]trimethylammonium chloride and anionic sodium 2-acrylamido-2-methylpropanesulfonate and obtained polyampholyte microgels of very interesting swelling and flocculation properties.

1.1.2.2 Intramolecular Cross-Linking of Polymer Chains

In second technique the starting material is not a monomer, but a polymer and is based on intramolecular cross-linking of macromolecules. This is of great importance when the product is intended for biomedical use, where even small quantities of residual monomer may be potentially harmful and thus unacceptable. It can be carried out through chemical intramolecular cross-linking or radiation-induced cross-linking.

Among all the synthesis techniques mentioned above, microemulsion is used for this work to synthesize AM based nanogels and nano size composites. This is because on account of its unique properties such as spontaneous formation (easy to prepare), low viscosity (easy to transport and mix), molecularly ordered interfaces (easy to control diffusivity as membrane), large interfacial area (accelerates surface reactions), low interfacial tension (flexible high penetrating power), mutual solubilization of water and oil (thus possessing both hydrophilic and hydrophobic characteristics). Such promising features make microemulsion an attractive medium for polymerization. Microemulsion polymerization is a particularly suitable, albeit special, technique. Also, the optical transparency and thermodynamic stability of microemulsions are advantageous for chemical, photochemical or high energy radiation techniques [32].
Many attractive advantages of microemulsion polymerization have been recognized. The primary goal of polymerization in microemulsion is to control the structural properties, small particle size, narrow distribution of particles, spherical morphologies, high molecular weight (10^6-10^7 g/mol) and high reaction rate makes this method attractive for the preparation of nanogels [33-36]. Due to the large interfacial area between the oil and aqueous phases the microemulsion-dispersed droplet phase provides a unique microenvironment for polymerization reactions. It has also been reported that polymerization reaction carried out in nanostructured media like micelles or microemulsions allows the synthesis of smart polymeric nanogels with controlled architectures and well defined characteristics [34, 37].

The polymer latexes produced by emulsion process contain particles of bigger size and hence look opaque and their storage requires addition of stabilizers to prevent phase separation, whereas nanogels obtained through microemulsion route exhibit good stability over longer periods. Advantage of this method is the biocompatibility of synthesized nanogels as biocompatibility is useful in novel applications like microencapsulation or drug delivery. It has also been of particular interest to prepare stable and uniform inverse nanogels via inverse microemulsion polymerization, since the classical inverse emulsion technique is known to produce unstable latexes with broad particle size distribution. Because the nanogels obtained by the microemulsion are very small, the film cast from such small nanogels shows high transparency and brightness; the novel size feature can also be used as drug carrier in venous injection of the drug delivery system. Besides, other promising features of microemulsion involve the
possibility to fix permanently the labile structure of these systems and to secure therein tightly solubilized molecules.

1.1.3 Properties

Dimensions and molecular weight of swollen nanogels are often similar to macromolecules in solution. But the presence of internal bonds results in different physicochemical properties such as fixed shape, different rheological behavior, higher resistance to degradation and the ability to trap other molecules within their structure.

Nanogels have gained considerable attention in recent years owing to their unique characteristics of a hydrogel system (e.g., hydrophilicity and extremely high water content) with a nanoparticle (e.g., very small size). In an aqueous environment hydrogel can absorb water and swell isotropically to maintain its original shape [38-39]. Swollen hydrogels maintain their shape without dissolving even in abundant water because of the presence of chemical or physical crosslinking of polymer chains. The shape, stability and water insolubility of hydrogels are the results of the presence of three-dimensional linkages.

Because of the presence of high water content, rubbery property, elasticity and reversible swelling - hydrogels have been frequently compared with the natural tissues or soft tissues. Due to their fair to excellent biocompatibility, hydrogels are usually well tolerated as implants. It is important for hydrogels, to be biocompatible and non-toxic in order to be a useful biomedical nanogel. Most polymers used for biomedical applications must pass a cytotoxicity and in-vivo toxicity tests. Most toxicity problems associated with hydrogels arise due to unreacted monomers, oligomers and initiators that leach out
during application. Steps are taken to eliminate contaminants from hydrogels by repeated washing and treatment.

Nanogels possess high loading capacity which is greatly employed for pharmaceutical nanocarriers. Unloaded nanogels in a swollen state contain considerable amount of water. Loading of biological agents is often achieved through self-assembly mechanism involving electrostatic, vander waals, and/or hydrophobic interactions between the agent and the polymer matrix. Water-soluble drug molecules including anticancer drugs and bioactive molecules (e.g., protein) can be incorporated into the nanogel network, rendering the nanogel potential as drug carrier for biomedical applications [40-42]. Ideal nanogels as nanocarrier for drug delivery should be efficient and convenient for loading drug molecules.

For non biodegradable applications, it is essential that the nanogel matrix maintains physical and mechanical integrity. Mechanical stability of the nanogel is, therefore, an important consideration when designing a therapeutic system. For example, drugs and other biomolecules must be protected from the harmful environments in the body such as, extreme pH environment before it is released at the required site. The strength of the material can be increased by incorporating crosslinking agents, co-monomers, and increasing degree of crosslinking. There is however, an optimum degree of crosslinking, as a higher degree of crosslinking also leads to brittleness and less elasticity. Elasticity of the nanogel is important to give flexibility to the crosslinked chains, to facilitate movement of incorporated bioactive agent. Thus a compromise between mechanical strength and flexibility is necessary for appropriate use of these materials.
1.1.4 Applications

The hydrogels have attained the stage of commercial applications such as soft contact lenses, drug delivery systems and wound dressings. Medical applications of hydrogels have been reviewed by Kamath and Park [43], Byrne et al. [44], Hoffman [45], Graham [46] etc.

Very recently, Raemdonck et al. [47] have highlighted the recent advances in the interface between biology and nanomedicine with the emphasis on nanogels as carriers for controlled drug delivery. Oh et al. [8] has reviewed the recent developments of nanogel particles as drug delivery carriers for biological and biomedical applications. Nanogels are widely used for biopharmaceuticals in cells as well as for drug delivery across cellular barriers. There has been interest in applying nanogels to drug delivery systems, such as protein delivery, scaffold for bone growth factor [48-49] etc. De and Hoffman [50] synthesized lightly crosslinked polyacrylic acid nanoparticles through reverse microemulsion polymerization for mucosal drug delivery. The drug timolol maleate was loaded into the nanoparticles from aqueous drug solutions and, when the drug-loaded particles were dispersed in a phosphate buffer solution, the drug slowly released from the nanoparticles.

These nanogels also find applications as binders in textile products, adhesives, paints, additives, rheological modifiers and biomedical compounds. They are also used as size calibration standards for fundamental research.
1.2 Polyacrylamide based Nanogels

1.2.1 Introduction

AM monomer is of hydrophilic and water soluble type. Usually it is soluble in a large variety of organic solvents. Since it is amide, its solution may be expected to have considerable compatibility or solvency for a variety of materials such as inorganic salts. PAM, even when of high molecular weight is also readily dissolved in water. So PAM is termed as water-soluble polymer. The water-soluble polymers and copolymers of AM have extensive applications in many fields. This water-soluble polymer can be transformed to a water-swellable polymer by using a cross-linker during polymerization process. Now the crosslinked polymer of PAM is termed as superabsorbents i.e. cross-linked networks of hydrophilic polymers with a high capacity of water-uptake and they can retain water after being heated for several hours or being under pressure [51]. The literature reports several different works attributed to PAM, covering variety of aspects such as synthesis, properties and applications. This shows the active interest in this monomer in the broad domain of hydrophilic monomers on account of unique properties of the corresponding polymer. However, the same interest can be tilted a bit towards micro and nanometer range as such PAM can be applied further for various advanced applications to improve the lifestyle of mankind [52-53].

Gao et al. [54] briefly reported in his paper about the peculiar traits of ultrafine PAM nanoparticles as an example of one of the many interesting materials used for drug delivery in-vivo. Furthermore, PAM can easily copolymerize with other monomers to introduce functional groups; thus, targeting tags can be incorporated to guide drug delivery. All this suggests that PAM nanoparticles may be used as a novel class of safe
nanosize drug carriers for the in vivo delivery of a variety of therapeutic moieties. PAM nanogels can be easily modified through chemical routes to make them cationic / anionic / amphoteric / hydrophobic / more hydrophilic in nature. Thus features of PAM nanogels can be summarized as a type of water dispersible, crosslinked polymeric nanoparticles. Because of their small size, porous structure, swelling behavior in different environment and ability to be functionalized, they are potential carriers for drugs and other molecules in biological system.

1.2.2 Preparation and Properties

The preparation of PAM nanogels specifically can be achieved through mass, solution, suspension, emulsion, inverse emulsion, inverse miniemulsion, microemulsion or photoinitiated polymerization [55-56].

The synthesis of hydrogels is typically accomplished by free radical polymerization (although step polymerization has also been used) or by modification or functionalization of existing polymers [57]. Doherty et al. [58] developed sparsely cross-linked “nanogels” via inverse emulsion (W/O) copolymerization of AM and a low percentage of N MBA. Less attention was devoted to the inverse emulsion polymerization, the first study devoted to inverse miniemulsion polymerization was published by Landfester et al. [59]. Relatively small and narrow distributed latexes in a size between 50-200 nm were made of AM and acrylic acid.

Schiilemans et al. [60] prepared bilayer-coated PAM hydrogel nanoparticles by photoinitiated polymerization of AM and N MBA in the inner compartment of liposomes. Sun et al. [61] developed core-shell PAM magnetic nanogels with controllable particle
size produced via a photochemical method in an emulsion-free aqueous system. However, in contrast to all synthesis processes, W/O microemulsion polymerization process is well known [62].

Leong and Candau [63] studied the polymerization of AM in W/O microemulsion (i.e., reverse micelle solution) from then onwards a series of studies on polymerizations of AM and its copolymerization in W/O microemulsion were made by Candau and coworkers [64-65]. Free radical polymerization of water-soluble monomers in inverse microemulsion was studied in many papers [66]. This was shown for water-soluble monomers and more particularly for AM [67]. Very few studies have been carried out on polymerizations of a water soluble monomer in cationic microemulsion. Yan et al. [68] polymerized AM in an W/O microemulsion with cetyl trimethyl ammonium bromide (CTAB) and hexanol as the surfactant and co-surfactant, respectively. Shi et al. [67] studied the solubilization of AM in CTAB/butanol/octane/water W/O microemulsion with $^{13}$C NMR method and reported that AM was mainly solubilized in the stern layer of droplets at low AM content and transfers to palisade layer and distributes along the hydrocarbon chain of the surfactant.

Given below is the detailed mechanism of homopolymerization of AM in inverse microemulsion by Barton and Juranicova [69]-

In the case of AM monomer and ammonium persulphate (APS) as initiator, both initiation and propagation loci are in the dispersed water phase (inverse micelles). Two mechanisms for the formation of polymer particles can be proposed. The first mechanism supposes the formation of initiating monomer radicals in inverse micelles and
propagation reactions with monomer in the same micelles. Thermal decomposition of APS initiator in water pools of inverse micelles yields a pair of sulfate anion radicals which, besides cage recombination, escape from the cage and undergo addition reactions with AM. AM (oligomer) radicals then have three possibilities to react: mutual termination which leads to the loss of radical centres and to the formation of low molecular weight products; propagation reaction with AM (formation of AM oligomers and high molecular weight AM polymer); or they may exit from the water pools of inverse micelles through the phase boundary into the oil phase and initiate radical reactions there. It is important to recognize that the formation of growing PAM chains of high molecular weight is possible only if the termination of monomer and oligomer radicals is suppressed and propagation of the said radicals is favored. Simple tools for favoring the propagation reactions of monomer radicals with monomer at the expense of mutual termination reactions of monomer radicals in the water pools of inverse micelles are either decreasing of the rate of initiation (by decreasing the concentration of initiator or reaction temperature) and/or increasing the concentration of the reactive monomer in the water pools of inverse micelles. The alternative mechanism for initiation and propagation reactions in inverse micelles supposes first the exit of AM radicals from the water pools of inverse micelles into the oil phase. Next, the entry of an AM monomer radical from the oil phase into the water pool of another (non-polymerizing, dormant) inverse micelle initiates AM polymerization in an inverse micelle. Such a mechanism needs the transportation of monomer radicals through the two phase boundaries (water/oil and oil/water). Both mechanisms for polymer particle formation in inverse
microemulsion include the transportation of water pool components (e.g., AM and/or AM radicals) among individual micelles also during inelastic collisions of micelles.

Poly(methyl methacrylate) nanosize particles, made by microemulsion polymerization, were dispersed in an AM aqueous solution, which was polymerized in the presence of a cross-linking agent to yield microstructure hydrogels by Nuno-Donlucas et al. [70]. These microstructure hydrogels exhibit higher equilibrium swelling and larger young modulus than conventional PAM hydrogels. The results of Meyer and Richtering [71] demonstrates that a semibatch reaction (reactants are added gradually over a certain time) gives more homogeneous morphology of PNIPAM than a simple batch reaction (all the reactants are added at the start). Fernandez et al. [72] investigated swelling and de-swelling kinetics, volume phase transition temperatures and mechanical properties at the equilibrium swelling states and found that nanostructured hydrogels exhibit larger equilibrium water uptake, faster swelling and de-swelling rates and similar volume phase transition temperature than those of conventional hydrogels.

1.2.3 Applications

PAM family of polymer finds their applications in numerous fields including flocculants for waste water treatment, paper-strengthening agents, oil recovery, soil conditioning, agriculture, biomedical applications etc. [73-78]. PAM hydrogels are also widely used in agriculture, horticulture and private hygiene products [79-83] on account of their peculiar property to absorb large amounts of water without dissolving while maintaining their shape [84-85]. A family of PAM particularly 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) is considered to be suitable as polymers for cosmetic thickeners due to its
However, their nanosize counterparts prove themselves to be more efficient, productive in advance applications of above mentioned field.

Nanogels of PAM have found uses in paper making industry, as contrast agents for molecular imaging in magnetic resonance imaging [87-88]. Fluorescent ionophore can be covalently reacted with PAM matrix and can be used as nanosensors for intracellular chemical analysis, as a center for the photochemical production of singlet oxygen for treatment of cancer cells [89-90]. Gao et al. [91] successfully encapsulated the hydrophobic meta-tetra(hydroxyphenyl)chlorin (photosensitizer) into hydrophilic PAM nanoparticles. Their ultra-small size help the nanoparticles to evade the reticuloendothelial system and produce singlet oxygen more efficiently that diffuse out of the nanoparticles so as to kill living tumor cells. Sun et al. [92] developed phosphate sensors by embedding proteins in PAM nanoparticles. This nanoparticle embedding method provides a novel promising tool for in-vivo metabolite studies. It also demonstrates a universal method for embedding different fragile bioactive elements, such as antibodies, genes, enzymes, and other functional proteins, in nanoparticles for sensing, biological catalysis, and gene delivery.

Proteins and dyes could also be encapsulated by radical polymerization in inverse microemulsion by Poulsen et al. [93]. Deng et al. [94] presented a new approach for the preparation of hydrophilic magnetic nanogels (less than 100 nm) through inverse microemulsion polymerization which can be used in drug delivery for hydrophilic anti-cancer drugs (e.g., Adriamycin). Sun et al. [30] developed core-shell PAM magnetic nanogels for potential applications in targeted radiopharmaceutical carriers for cancer therapy and in biological and medical studies as well.
Doherty et al. [95] developed covalently linked, linear PAM chains, as novel DNA sequencing matrices for capillary electrophoresis. The presence of covalent cross-links affords nanogel matrices with enhanced network stability relative to standard linear PAM and thus improving the separation of large DNA fragments.

1.3 Copolymeric Nanogels

1.3.1 Introduction

It has been discussed (Section 1.1 and 1.2) in detail about the nanogels and PAM based nanogels along with their properties and significance in various fields. Such nanogels can be modified further by either incorporation of auxiliary monomer to pre-formed polymeric nanogels (with crosslinker) during polymerization process, or copolymerization of two different monomers simultaneously (with crosslinker). This will lead towards formation of copolymer nanogels with inheritance of certain unique features / properties, based upon the type of requirement of copolymer nanogels. In this way, copolymer nanogels with multitude of features such as increase swelling capacity for obtaining superabsorbents, smart nanogels (giving response to environment triggers such as temp, pH, ionic strength), presence of important functional groups (hydroxyl, carboxylic, sulfonic etc.) [96], improved thermal and mechanical stability and other such features can be easily obtained. For many applications, nanogels with large water absorption capacity and favorable thermo-mechanical stability in the swollen state are required [97-98]. These properties can be usually obtained by incorporation of functional polymers in the polymer chains. In this way it can be expected to obtain functional / multifunctional groups bearing nanogels with desired features.
In recent years attention has been directed to stimuli responsive (temperature, pH, solvent, ionic strength and electric field) hydrogels. Most of the hydrogels operating in aqueous medium are based on PNIPAM, Poly(N-vinyl-caprolactam), or other water soluble polymers such as poly(acrylic) acid, poly(methacrylic acid) or poly(2-(diethylamino)ethyl methacrylate) [99-103]. The special interest in PNIPAM is dedicated to their temperature-sensitivity which enables fabrication of “smart” or “switchable” or “stimuli-responsive” materials. The temperature sensitivity of hydrogels could also be combined with pH sensitivity by copolymerization of AM/NIPAM monomer with ionic monomers such as AMPSA, acrylic acid, vinylimidazole, 4-vinylpyridine, 2-hydroxyethylmethacrylate etc. Introduction of ionic structures into polymeric materials alters the polymer morphology, and consequently has a profound effect on the physical and chemical properties [104], such as solution viscosity and mechanical behavior. Thus functionalized smart hydrogels or stimuli-responsive with defined size and enhanced colloidal stability have been achieved. Thus copolymers bearing functional groups can be used for inclusion of drugs or other bioactive agents.

Copolymerization of AM with sodium acrylate forms an ionic polymer at normal pH. Copolymerization of AM with ionic (sulfonated) monomer such as AMPSA represents functionality that is useful for yielding a wide variety of products. Several sulfonic acid copolymers have been studied to synthesize superabsorbent polymers on account of its utility in pharmaceutical, agriculture, and other industries. Moreover, AMPSA offers hydrogen-bonding capability and polyelectrolyte behavior in aqueous solution which is characteristic of special interest in enhanced oil recovery [105]. Also for enhanced oil recovery, polymer with thermal stability, shear resistance, retention of higher solution
viscosity is required [106]. These features can be easily obtained with copolymers of AM and AMPSA.

1.3.2 Preparation and Properties

The preparation and properties of both crosslinked nanogels as well as water-soluble gels based on copolymers of AM/NIPAM and/or AMPSA are mentioned below. Though certain copolymer gels/hydrogels are not of nanosize, but their mode/technique of synthesis as well as specific properties are taken into consideration here.

Monodisperse hydrophilic polymer microspheres with various functional groups such as amide, pyrrolidone and carboxylic acid, with spherical shape and smooth surface in the size range 120-600 nm were prepared by distillation precipitation copolymerization of functional comonomers including NIPAM, N-vinylpyrrolidone, methacrylic acid with NMBA as a crosslinker by Liu et al. [107]. Monodisperse nanogels were synthesized by free-radical precipitation polymerization with either NIPAM or N-isopropylmethacrylamide as the main monomer, with acrylic acid or 4-acrylamido fluorescein as a comonomer and NMBA as a cross-linker by Blackburn and Lyon [108]. Durmaz and Okay [109] prepared AM-AMPSA based hydrogels by free radical copolymerization at 40 °C in presence of NMBA as the crosslinker to study the formation mechanism and swelling behavior of hydrogels. Liu et al. [51] prepared cross-linked copolymer of AM with AMPSA by solution polymerization. Poly(acrylamide-co-2-acrylamido-2-methyl-1-propane sulfonic acid) were also synthesized by using gamma radiation and copolymerization as well as crosslinking was observed by viscosity measurement on reaction mixture subjected to varying
radiation doses. The copolymer gels were characterized by Differential scanning calorimeter, X-ray diffraction, Scanning electron microscope, Fourier transform infrared spectrophotometer and elemental analysis. Besides crosslinked gels, certain water-soluble gels were also prepared with AM and AMPSA [110]. Travas-Sejdic and Easteal [111] studied free-radical copolymerization of AM with AMPSA at 25 °C and 80 °C. Dispersion polymerization was also employed to synthesize copolymers of AM and AMPSA by Wu et al. [112]. The recent progress in the field is towards the synthesis of copolymer microgels based on sulfonic acid and AM by microemulsion polymerization. The copolymerization of AM, AMPSA and styrene was carried out by Gao et al. [113] in a microemulsion medium and ternary water soluble copolymers based on PAM which contained both strong anion groups (-SO3Na) and hydrophobic blocks (polystyrene) were obtained. The structure and composition of copolymers were characterized by Fourier transform infrared, ultraviolet and elemental analysis. Kaneda et al. [114] prepared poly(dimethylacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid) minute-sized microgels by inverse microemulsion polymerization.

The detailed microstructure and compositional heterogeneity of copolymers is of great importance in considering copolymer properties. Copolymers of AM with sulfonated (ionic) comonomers, particularly AMPSA offers high stability in solution due to stronger hydrogen bonding capability thus altering the polymer morphology and introducing polyelectrolyte behavior in aqueous solution [111]. AMPSA is a relatively strong acid, has strongly ionizable sulfonate group; dissociates completely in the overall pH range and is known for its hydrolytic stability, high tolerance towards
divalent cations [109, 115-116]. Moreover, $-\text{SO}_3^-$ group imparts greater hydrophilic character, causes more swelling of nanogel in water, provide anionic character at wide range of pH [117]. The geminal dimethyl group and the sulfomethyl group combine to sterically hinder the amide functionality and provide both hydrolytic and thermal stabilities to AMPSA-containing polymers [118-120].

Garcia-Salinas et al. [121] measured the electrophoretic mobility and hydrodynamic diameter of PNIPAM microgel particles copolymerized with AMPSA as a function of pH and electrolyte concentration. Anionic hydrogels of AMPSA were prepared with different amount of cross-linker dose and used for in-situ preparation of magnetic and metal particles by Sahiner [122]. Four different copolymers of AM and acrylic acid; AM and AMPSA; N,N'-dimethylacrylamide and acrylic acid; N,N'-dimethylacrylamide and AMPSA were prepared by Sabhapondit et al. [106] and it was found that copolymers bearing sulfonate group were more brine compatible polymers and thermally stable. For copolymers to be useful for enhanced oil recovery, they must possess good thermal stability, resistance to biological degradation which can be easily obtained with copolymers of AM and AMPSA [123].

1.3.3 Applications

The applications of crosslinked nanogels as well as water-soluble gels based on copolymers of AM/NIPAM and /or AMPSA are mentioned below.

The multifunctionality of copolymer nanogels results in some interesting applications such as preparation of hollow thermosensitive microgel capsules, colloidal crystals, microlens arrays, specific targeting of cancer cells and drug delivery [124-126].
Brueggemeier et al. [127] reported the development, characterization and use of protein-AM copolymer hydrogels for measuring protein concentration and activity. NIPAM based copolymer microgels also find application in metal ion binding, example includes binding of Pb\(^{2+}\) cations by poly(N-isopropylacrylamide-co-sodium acrylate) [128]. Ravindra et al. [129] developed surfactant modified poly(AM-co-AMPSA) hydrogels and observed the drug release behavior.

Being a strong acid, AMPSA has a wide variety of applications (as itself / its salt / as a commonomer), including packaging films, foams stabilizers, photographic materials, and water absorbents [130-132]. Hydrogels based on AMPSA have been used in biochemistry, for skin contact electrodes, to adhere medical devices to the skin or for drug delivery applications such as iontophoresis [133-135]. Besides, AMPSA is also used in personal care products and cosmetics. Simionescu and Chelaru [123] synthesized acrylamide-co-sodium-2-acrylamido-2-methyl propane sulfonic acid copolymers while Subhapondit et al. [106] prepared and characterize four different copolymers, i.e., poly(acrylamide-co-sodium acrylate), poly(acrylamide-co-sodium-2-acrylamido-2-methyl propane sulfonate), poly(N,N-dimethylacrylamide-co-sodium acrylate) and poly(N,N-dimethylacrylamide-co-sodium-2-acrylamido-2-methyl propane sulfonate) for enhanced oil recovery purpose. The properties of gels and hence their applications in their respective fields are expected to show better performance at nanometer level. No doubt the nano counterparts of above mentioned gels will prove themselves to be smarter, efficient and effective when they take over the field of biochemistry, enhanced oil recovery, as water absorbents, cosmetics etc.
1.4 Composite Nanogels

1.4.1 Introduction

The need for materials which possess unique properties that cannot be attained by conventional polymer composites or even its individuals has focused the light on a new class of materials so called nano-size composites. It involves the study of multiphase materials with different compositions where at least one of the constituent phases has dimensions less than 100 nm. The promise of nanosize composite lies in their multifunctionality, the possibility of realizing unique combination of properties unachievable with traditional materials. The challenges in reaching promise are tremendous. They include control over the distribution in size, uniform dispersion and reduced agglomeration of the nanosize constituents in the organic matrix, tailoring and understanding the role of interfaces between structurally or chemically dissimilar phases on bulk properties. A variety of morphological composites (organic/inorganic) have been developed depending on the formation mechanism, surface chemistry and the size of inorganic particles [136]. Nanosize composites combine the advantages of the inorganic material (e.g., rigidity, thermal stability) and the polymer (e.g. processability, flexibility, ductility, dielectric). Moreover, they usually also contain special properties of nanofillers leading to materials with improved mechanical, thermal, electrical and optical properties as compared to their macro- and micro-counterparts.

A prominent feature of nanosize composite is that the nano size filler leads to a dramatic increase in interfacial area as compared with traditional composites. This interfacial area creates a significant volume fraction of interfacial polymer with properties different from the bulk polymer (interaction zone) even at small filler dose [137-138]. Thus nano-fillers facilitates in providing miscibility with the polymer matrix and exploiting the unique
synergism of the nanosize composites to create revolutionary materials. Such composites have shown improvement in properties including toughness, thermal stability etc. Significant effort has been devoted in both academia and industry in last few years to develop this new class of materials. Nanosize composites have attracted a great deal of interest from material scientists since their applications have dramatically improved material properties in engineering plastics, coatings and adhesives [139-141].

1.4.2 Silica Composites

The commonly used ultrafine particles for embedment purposes are: three-dimensional nanoparticles (e.g., carbon black, silicon dioxide, titanium dioxide, aluminium oxide), two-dimensional nanofibers (e.g. nanotube, whisker), or one-dimensional disc like nanoparticles (e.g. clay platelets) and so forth. However, versatility of three-dimensional nanoparticles makes them promising for their wide use in the preparation of composites. Among which silica is viewed as being very important as it has extremely large surface area and smooth nonporous surface, which could promote strong physical contact between the filler and the polymer matrix [142]. Such nanoparticles offer enormous advantages over traditional macro- or micro-particles (e.g., talc, glass, carbon fibers) due to improved adhesion between nanoparticle and polymer and lower amount of loading to achieve equivalent properties. Consequently, silica composites have attracted substantial academic and industrial interest. In fact, among the numerous inorganic/organic composites, silica composites are the most commonly reported in the literature and are widely used in many fields of colloid and material science because they exhibit special properties that are substantially different from those of bulk material. Considerable efforts have been devoted to the design and controlled fabrication of silica composite particles with tailored morphologies. Owing to many uses of
different methods for the synthesis of polymer-silica particles have been reported. The preparation, characterization, properties and applications of polymer/silica nano size composites have become a quickly expanding field of research [146-151].

1.4.3 Preparation and Properties

As pointed out by Hajji et al. [152], nanocomposites system can be prepared by various synthesis routes on account of ability to combine different ways to introduce each phase. The organic component can be introduced as (i) a precursor (monomer / oligomer), (ii) a preformed linear polymer (in molten, solution or emulsion states) or (iii) a polymer network physically or chemically crosslinked. The mineral part can be introduced as (i) a precursor (e.g. tetraethylxosilane - TEOS) or (ii) preformed nanoparticles. Organic or inorganic polymerization generally becomes necessary if at least one of the starting moieties is a precursor. This leads to three general methods for the preparation of polymer/silica nanocomposites according to starting material and processing techniques: blending, sol-gel and in-situ polymerization (Figure 1.2).

![Diagram of the three general approaches to prepare polymer/silica nanocomposites](image)

Fig. 1.2 The three general approaches to prepare polymer/silica nanocomposites.
Blending is generally just mixing of the silica nanoparticles into the polymer; a sol-gel process can be done in in-situ in the presence of preformed organic polymer or simultaneously during the polymerization of the monomer(s); the method of in-situ polymerization involves the dispersion of nanosilica in the monomer(s) and then polymerization is carried out. However, silica nanoparticles are generally introduced directly in the blending and in-situ polymerization methods, whereas silica precursors are used in the sol-gel process, among which the most widely used ones are silicon alkoxides, TEOS, tetramethoxysilane (TMOS), alkoxy silane-containing polymers etc.

In recent years, considerable effort has been spent on the elaboration of particulate or colloidal polymer-silica composites with defined morphologies and properties. These materials represent a new category of composites which can exhibit remarkable properties (mechanical, electrical, optical, chemical, rheological etc.) by an appropriate combination and structuration of the organic and inorganic components inside the nanoparticles. It can be divided into systems with a polymer core and a silica shell or vice versa [153]. Various methods have been developed for their preparation such as sol-gel process (resulting in coating of polymer colloids with silica), in-situ heterophase polymerization (resulting in polymer encapsulation of silica nanoparticles).

1.4.3.1 Sol-Gel Process

A polymer-inorganic oxide composite with uniformly distributed particles of nano-dimensions could only be made possible after the sol-gel process came into existence in 1980s when several silica-polymer hybrids were developed [154]. The sol-gel process under mild conditions offers an efficient and convenient approach to the synthesis of organic-inorganic composite material which is nanoscale in domain size [155-157]. The
Pulkovits et al. [164] performed in situ generation of bulk nanocomposites of SiO₂/PMMA using reverse (W/O) microemulsion. TEOS was hydrolyzed in the reverse micelles containing aqueous ammonia. During the hydrolysis of TEOS, polymerization of the continuous methyl methacrylate (MMA) phase was initiated and after thermal polymerization, solid blocks of poly(methyl methacrylate) (PMMA) were obtained in which nanometer-sized silica particles were trapped in the solid polymer matrix. The reverse micelle-mediated approach produced composites of high transparency comparable with that of pure PMMA.

14.3.2 In-situ Polymerization

In this method, the polymer/silica nanocomposite particles are prepared via heterophase polymerization which includes emulsion polymerization, emulsifier-free emulsion polymerization, miniemulsion polymerization, dispersion polymerization etc [165-168].

Emulsion polymerization is normally referred to as seeded emulsion polymerization since silica nanoparticles are generally used as seeds and are encapsulated by polymer. Espiard et al. [169] reported results on the encapsulation of silica particles through emulsion polymerization using coupling agent. The silane molecule allowed the grafting of a significant amount of polymer from the early stages of polymerization. Thus silane provided reactive double bonds for covalent attachment of the growing polymer chains on the silica surface.

The emulsifier free systems are often not truly free of an emulsifier. The monomer or comonomers usually contains a part that resembles the structure of an emulsifier at one end of the molecular chain. Such a monomer or comonomers can play the role of an
emulsifier while polymerizing. In 1999, Barthet et al. [170] reported the synthesis of colloidal dispersions of polymer/silica nanocomposite particles in high yield by homopolymerizing 4-vinylpyridine in the presence of an ultrafine silica sol using free-radical initiator in aqueous media.

Recently, miniemulsion polymerization has turned out to be an attractive way to obtain nanocomposites particles, especially when the synthesis of more complex particles is involved. In 2001, Tiarks et al. [171] first reported the preparation of polymer/silica nanocomposites by using miniemulsion polymerization. The size and morphology control of the nanocomposite particles by miniemulsion polymerization was studied by Zhang et al. [172].

An aqueous dispersion polymerization route to colloidal polymer nanocomposites via the free radical copolymerization of 2-hydroxypropyl methacrylate and 4-vinylpyridine in the presence of an ultrafine silica sol was reported by Percy et al. [168].

Among other polymerization method, in-situ microemulsion polymerization for the preparation of polymer/silica nanocomposites is rarely reported [173-175]. Depending on the composition of the oil, water and surfactant, the nanostructure of microemulsion may be described as water droplets dispersed in oil medium or vice-versa. By choosing the right concentrations, both the oil and water phases can be a continuum, thus forming a bicontinuous microemulsion. Chow and Gan [174] presented a simple and convenient method for the preparation of silica/polymer nanocomposites with a polymerizable bicontinuous microemulsion as a template for directing nanoparticles of silica to disperse uniformly in the polymerized microemulsion system.
There are several advantages of using the in situ-polymerization method. These include ease of handling, the speed of the process and better performance of the final products [176]. It is obvious that the most important factors that affect the properties of composites are the dispersion and the adhesion at the polymer and filler interfaces. Zheng et al. [177] studied the effects of nanoparticles of SiO₂ on the performance of nanocomposites. Uniform dispersion of nanoparticles was critical to the morphological structure and impact strength of the nanocomposites.

Among different synthesis routes discussed above, microemulsion polymerization is selected for the preparation of composites with controlled compositions, sizes, shapes and surface properties. The surface coating of inorganic nanoparticles with polymer via microemulsion polymerization is regarded as an effective method to increase dispersing ability and interfacial adhesion simultaneously [178-179]. In order to avoid agglomeration of fillers, nano size composites are synthesized by in-situ polymerization. In-situ polymerization is a method where at first inorganic fillers or reinforcements are dispersed in the monomer or monomer solution, and then this mixture is polymerized using as usual polymerization techniques. It has also been found that AMPSA helps in compatibilizing clay and polymer matrix and hence better dispersing the clay platelets in the polymer matrix in order to render nano size composites [180]. It was also possible to improve the thermal, mechanical and morphological properties by controlling the processing conditions. The properties of nano size composites strongly depend on their composition, size of the particles, interfacial interaction etc. [181]. The interfacial interaction between polymer and silica (which depends on preparative method) strongly affects the size, thermal and other properties of the nanocomposites. The internal surfaces
(interfaces) are critical in determining the properties of nanofilled materials, since silica nanoparticles have high surface area-to-volume ratio, particularly when the size decreases below 100 nm. This high surface area-to-volume ratio means that for the same particle loading, nano size composites will have a much greater interfacial area, much more extensive interaction zone and thus it can have significant impact on properties [182].

Depending on the composition and the microstructure, the effects of different nanoparticles on the properties of polymers are different. In recent years polymer-silica composites are widely used in many fields of colloid and material science because they exhibit special properties that are substantially different from those of bulk material. Modification of colloidal suspensions based on the combination of organic and inorganic components, such materials can be designed with a variety of morphologies. It has been found that after the introduction of filler, polymer properties such as toughness, stiffness, dimension stability, flammability are significantly improved. The incorporation of inorganic materials on the nanoscale can enhance fire retardancy and mechanical strength of organic polymers and coatings [183-184]. The significant impact on other properties such as thermal, mechanical, morphological, flame retardancy, optical, gas transport, rheological and electrical are also evident [185-191]. Chen et al. [192] prepared various environmentally friendly hybrid materials with the desired properties such as abrasion-resistant, UV shielding, reactive, catalytic, optical, electrical etc. Liu et al. [193] reported robust colloidal stability of PNIPAM grafted colloidal silica. Amide polymers such as PAM have been found to be most suitable for the preparation of polymer composites with silica due to the −NHCO-groups in the polymer chains, which very easily form hydrogen bonds with silanol groups. FTIR spectroscopy showed that substantial hydrogen bonding occurred in the
nanocomposites of PAM and silica [194]. Park and Lee [195] compared FTIR spectra of composites with silica and concluded that abundant silica existed on the surface which was expected to improve the water resistance and abrasion resistance properties. Jain et al. [196] investigated the crystallization behavior of nanocomposites through wide-angle X-ray diffraction pattern and concluded that silica nanoparticles induced the formation of crystals. One of the primary reasons for adding inorganic fillers (silica) to polymers is to improve their mechanical properties. Generally, the incorporation of nanometer-sized inorganic particles can enhance thermal stability by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition.

1.4.4 Applications

Silica-polymer nano size composites are a promising new class of materials that have many possible applications in aerospace materials, structural materials, electronics, sensors and other areas [197-200]. Since the polymer/silica nanocomposites not only can improve the physical properties such as the mechanical and thermal properties but can also exhibit some unique properties, they have attracted strong interest in many industries. Also, many other potential and practical applications composites have been reported such as in coatings [201], proton exchange membrane [202], encapsulation of organic light-emitting devices [203], chemosensors [204], metal uptake [205] etc. Ravi et al. [206] designed, synthesized, and evaluated hydrogel nanocomposite (PAM/silica) for use as an auto-focusing intra-ocular lens. Shin et al. [207] developed a hybrid nanogel based on interpenetrating networks of thermosensitive PNIPAM gels and tailored nanoporous silica. A sustainable positive thermo-responsive drug release profile is obtained. When the temperature rises, the polymer gel shrinks, squeezing the drug into the porous channels, and at the same time, opening the pores
the outside media. Thus the drug slowly diffuses out of the porous channels. To improve oil recovery Yang-Chuan et al. [208] prepared nanocomposites of AM-styrene-AMPSA copolymers with monodisperse silica particles.

1.5 Aim

Synthesis and characterization of acrylamide based nanosize hydrogels and silica composites through W/O microemulsion polymerization.

1.6 Objectives

Since several decades there has been remarkable growth in the widespread usage of PAM, the exclusive properties of PAM/PNIPAM/PAMPSA group provides a stark differentiation and promotes interest to proceed for interesting studies in this family for synthesis and characterization of nanogels, ionic copolymer nanogels, nano size composites.

- To study the phase stability of different types of microemulsions with variation of anionic and non-ionic surfactants concentration and to determine the size of reverse micelles.
- To study the composition effect of AM/AMPSA monomers on phase stability of microemulsion and to determine the size of nanodroplets containing aqueous solution of monomers.
- Preparation of polyacrylamide nanogels through W/O microemulsion polymerization.
- To synthesize poly(acrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid) nanogels and to investigate the effect of copolymer composition on size, equilibrium swelling and pH sensitivity of copolymer nanogels.
To synthesize polyacrylamide/silica nanocomposites and to study the dose effect of filler on size of composites.

To study the copolymer composition effect on interaction, thermal stability, and morphology of nanosize poly(acrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid)/silica composites without surface treatment of silica.

In the present study, AM monomer is exclusively selected for preparation of nanogels. Besides another hydrophilic and acidic-monomer, AMPSA from the same family is also selected for copolymer synthesis. The abovementioned features of AMPSA monomer, the availability and relative cheapness of AM monomer facilitates to combine the advantages of these hydrophilic monomers through microemulsion polymerization process. Further, nanosize composites of AM with filler as well as functionalized composites of AM, AMPSA with filler have also been prepared through same route. So, on the basis of microemulsion stability, PAM nanogels, poly(acrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid) [poly(AM-co-AMPSA)] copolymer nanogels, PAM/Silica (PAM/SiO₂) nano size composites and poly(acrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid)/silica [poly(AM-co-AMPSA)/SiO₂] composite nanogels have been synthesized by W/O microemulsion process, in which water/toluene inverse emulsion was used to make the product a fine powder. These nanostructures have been characterized by Dynamic light scattering, Fourier transform infrared spectrophotometer, ¹H-Nuclear magnetic resonance spectrometer, Elemental analysis, Thermogravimetry analyzer, Differential scanning calorimeter, Scanning electron microscope and Transmission electron microscope to determine their size, polydispersity, presence of functional groups, polymer chain composition, thermal stability, morphology and shape.