CHAPTER 2

SCOPE AND OBJECT

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In recent years, scientists and engineers working on environmental and industrial problems have shown interest in water-soluble synthetic polymers because of their very broad range of industrial applications. Important classes of these materials include acrylamide-based polymers, which are widely used as flocculants, adhesives, rheology control agents and also as paper manufacturing, mining, and oil well stimulation etc. During the past few decades, many patents have described the synthesis of homo and copolymers of acrylamide with special properties considering their versatile application in numerous fields in industries. These polymers are also applied as water-soluble viscofiers and displacement fluids in enhanced oil recovery. In the field of soil management, aqueous solutions of acrylamide monomer (AM) together with a redox catalyst are injected into the soil formations. In a predetermined period of time, which may be controlled, the monomers polymerize giving a cross linked rigid gel which prevents the passage of water through the mass and also binds the soil particles together. They are also used to seal off the flow of water into oil wells, drill holes, basements, tunnels, mineshafts, caissons, and dams. Anionic polyelectrolyte such as polyacrylamide-co-sodium acrylate (partially hydrolyzed polyacrylamide) is also used in a variety of water-soluble applications viz., in flocculation and as mobility control agent in enhanced oil recovery. But the critical limitation of polyelectrolyte including those derived from hydrolyzed homo-polyacrylamide is the loss of viscosity in presence of mono and/or multivalent electrolytes. Very high molecular weight polyacrylamide has been found to be exceptionally effective flocculants. Polyacrylamide may be prepared by free radical polymerization of acrylamide using bulk, suspension, emulsion, inverse emulsion and precipitation techniques. Many redox initiator systems involving metal ions as an oxidant viz., Fe(III)-Thiourea, Ce(IV)-EDTA, Ce(IV)-Nitrilotriacetic acid(NTA), $KMnO_4$-glycine, Ce(IV)-Nitrilotripropionic acid(NPA) etc. have been reported to be promising free radical initiators in respect of high reaction rate, small induction period, high percentage yield and low activation energy. Redox initiated polymerization of acrylamide is one of the most common techniques applied for aqueous polymerization because of the simplicity of the technique as well as high yield and reaction rates. However, one difficulty of such a technique is the fast termination by oxidant of the redox couple. Recently a novel technique has been applied in our laboratory to control the linear termination process and to increase the chain growth of acrylamide polymer where the potential electron acceptor (e.g. metal ions) was loaded in the interlayer space of a smectite clay viz, montmorillonite prior to polymerization reaction starts. This ensures the slow termination rate due to inability of a growing polymer chain to transfer to the oxidant trapped inside the layered space. As a result, high molecular weight polymers were formed. The efficiency of the technique lies in the fact that the monomer and the components of redox systems (including the organic activator) could intercalate between the layers of the phyllosilicates, but the growing polymer chain after achieving a certain critical length comes out of the layered space and continue to grow in the bulk solutions. The growing chain is unable to transfer electron to the acceptor (viz, metal ions) placed in the constrained space. Vermiculite is another important smectite of the phyllosilicate group, which may also be efficient in this respect since the basal spacing of vermiculite [d(001) spacing of vermiculite is ~ 1.45 nm] is very close to that of montmorillonite [d(001) spacing of montmorillonite is ~ 1.76 nm]. Further, clay minerals are used industrially as fillers and reinforcers in polymer systems such as elastomers, polyethylene, polyvinyl chloride and other thermoplastics. All things being equal the efficiency of a filler in improving the physico-chemical properties of a polymer system is primarily determined by the degree of its dispersion in the polymer matrix. The most effective way of achieving such compatibility is to graft a suitable polymer on to the filler surface and/or to encapsulate the mineral particles with polymer layer. Indeed, clay minerals, especially those of phyllosilicates (e.g. vermiculite) themselves, are known to catalyze a variety of organic reactions including those lead to polymer formation. Moreover, research on intercalation chemistry of phyllosilicates is gaining momentum rapidly to transform these abundant materials into new classes of selective heterogeneous catalysts. Interestingly, when metallic cations are adsorbed in vermiculite, they are also trapped between interlayer spaces at the negatively charged sites of the minerals like montmorillonite.

Therefore, one of the objectives of the present investigation is to perform the polymerization reaction of acrylamide monomer onto the vermiculite surface by a redox initiators viz., Fe(III)-Thiourea system involving the trapped metal ions with a view to enhance the chain growth of the polymer. Moreover, copolymers of acrylamide have also shown a number of properties lending themselves to a variety of industrial applications. The growing importances of acrylamide copolymers are also related to their use as water-soluble viscofier and displacement fluid in enhanced oil recovery. With a view to prepare copolymers with large hydrodynamic volume and molecular weight, attempts have been made to prepare poly (acrylamide-co-diacetone-acrylamide) on the vermiculite surface.

Many present and possible industrial applications of high molecular weight polymer arise from unusual properties they induce to their solutions. The study of their solution property is a prerequisite for the development of this modern domain. The characterization of very high molecular weight polymers raises a number of problems. Therefore, systematic studies arising from the coupling of different experimental techniques are required for the elucidation of diverse theoretical and experimental aspects. The most important parameters characterizing macromolecular chains in dilute solution are the molecular weight, the mean square radius of gyration and the intrinsic viscosity. Their determination for very high molecular weight polymers opens a large area for discussing, on the basis of different theoretical approximations. The area of discussion includes such subjects as influence of molecular weight and solvent power on concentration domain, theta condition and unperturbed dimensions, chain flexibility in perturbed and unperturbed states, the type of interaction (short range and long range), the conformational characteristics including the transition phenomena influenced by temperature and the solvent.

Highly crosslinked water-soluble polymers, commonly known as hydrogels are widely used as superadsorbent. In order to synthesize the crosslinked water-soluble polymers with desired crosslinking ratio, multifunctional monomers (generally called crosslinking agents) are used. Although its concentration in the formation is low, the chemical and physical nature of the crosslinking agent plays an important role in determining the property profile of the manufactured superadsorbent polymers, N,N-methylene-bis-acrylamide (Bis) is one of the most commonly used di-functional crosslinking agent.

The study of hydrogels and their response to external environment is of special interest because of their potential as drug delivery systems, actuators, and separation devices etc. It is well established that properties of acrylamide hydrogels depend upon the monomer concentrations of the initial mixture as well as the reaction pathway. Thus, the understanding of the formation mechanism of polymer gels is of great interest to predict their physical properties.

The objective of this part of the proposed research is to investigate the reaction kinetics of crosslinking copolymerization of acrylamide (AM) with N,N-methylene-bis-acrylamide with Fe(III)-thiourea and Ce(IV)-thiourea redox initiator system along with the determination of gel points with gravimetric and viscometric techniques. The hydrogels prepared by this process were also used to determine swelling characteristic at various temperatures. The percent gel swelling, equilibrium gel swelling, the effect of crosslinker concentration and the effect of temperature on gel swelling and the diffusion on water into gel are also looked into. Thermogravimetric analysis will be done to understand thermal stability and differential scanning calorimetric (DSC) studies will be undertaken in order to understand about the phase transitions and the nature of interaction in the hydrogel samples.