CHAPTER -2

SCOPE AND OBJECT

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Water soluble synthetic polymers are extensively used in the industry in numerous products and processes from adhesives to cosmetics, from explosives to medical products and from oil technology to paper technology. Among the water soluble synthetic polymers, polyacrylamide is one which is a very effective flocculant for finely divided solids in aqueous suspensions. These polymers are used in acid, neutral or alkaline systems even in the presence of high concentration of electrolytes. They have found wide applications in the treatment of ores, particularly acid-leached uranium ore, minerals and metal particles, sewage, industrial waste and chemical precipitants as already mentioned. Extremely high molecular weight polyacrylamide have been found to be exceptionally effective flocculants. Aqueous solutions of acrylamide monomer together with a redox catalyst are injected into 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.

In view of the above, redox polymerization technique for the acrylamide polymerization is of great importance. However, usually redox polymerization of acrylamide in aqueous medium yields polymers having not so high molecular weight primarily because of fast termination process via transfer to the oxidant of the redox couple (e.g., metal ions at the higher oxidation states). Many potential redox catalysts involving metal ions as the oxidants viz., Fe(III)/Thiourea (TU), Ce(IV)/EDTA, Ce(IV)/Nitriloacetic acid etc. have been shown to be very promising free radical initiators in respect of high reaction rate, small induction period, low activation energy and above all their simple experimental procedures. Even these systems yield polymers having low molecular weights only, due to the fast termination process as mentioned above. An appropriate redox polymerization technique which yields very high molecular weight polyacrylamide would, therefore, be an ideal procedure for many purposes.

Industrially, clay minerals are used as fillers and reinforcers in polymer systems such as elastomers, polyethylene, polyvinylchloride 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 specially those of phyllosilicates (e.g., montmorillonite) themselves are known to catalyse a variety of organic reactions including those which lead to polymer formation. Moreover, research on the intercalation chemistry of phyllosilicates is gaining momentum rapidly to transform these abundant minerals into new classes of selective heterogeneous catalysts. These aspects have already been mentioned in the introduction. Interestingly, when metallic cations are adsorbed by montmorillonite, they are trapped between the interlayer spaces at the negatively charged sites of the minerals. If polymerization reaction could be initiated in the interlayer spaces of the mineral by redox couples involving the trapped metal ions, one may expect a controlled linear termination process because the growing polymer chain may not be able to transfer to these metals in the constrained spaces. This technique may also be proved useful for acrylamide polymerization in view of previous claim of stereoregular polymerization of acrylonitrile and acrylic acid monomers on smectite clays.

Therefore, one major objective of the present investigation is to perform the polymerization reaction of acrylamide monomer on the montmorillonite surfaces by redox initiators (Fe(III)/Thiourea) involving the trapped metal ions with a view to enhance the chain growth of the polymer. A detail solution phase reaction will also be performed involving the same redox couple ($FeCl_3$ /

Thiourea) in order to check what modifications pertaining to kinetics and mechanism have been achieved by the mineral phase reaction. A detail aspect of kinetics and mechanism of the reaction of both the procedures will be looked into. The technique of interlayer polymerization will be applied to other redox systems (viz., Ce(IV)/EDTA) to examine the scope of the proposed technique of controlling the termination process.

In addition, copolymers of acrylamide have shown a number of properties leading themselves to a variety of industrial applications. Of growing importances are those related to use as water soluble viscofiers and displacement fluid in enhanced oil recovery. Two of the critical limitations of polyelectrolytes including those derived from hydrolysing homopolyacrylamide, are the loss of viscosity in the presence of mono and multivalent electrolytes (NaCl, $CaCl_2$ etc.) and ion binding to the porous reservoir rock substrate. Some attempts have been made including that of preparing copolymers of acrylamide with diacetone acrylamide (N (1, 1 - Dimethyl - 3 - oxylbutyl) acrylamide) having large hydrodynamic dimensions in electrolyte solutions. Another objective of the present investigation is, therefore, to attempt to prepare this (viz., poly (acrylamide - co - N - (1,1 - Dimethyl - 3 - oxylbutyl) acrylamide)) and other copolymers (viz., poly (acrylamide - co - N - tert - butyl acrylamide)) on the montmorillonite surface with a view to have copolymers with higher molecular weights and intrinsic viscosities. Composition of copolymers, reactivity ratios of monomers and also the microstructure of copolymers would be examined.

In view of the use of polyacrylamide for preparing highly viscous solution in the secondary oil recovery process, the understanding of the role of charged groups on different factors which govern the efficiency in their use is important. A complete molecular characterization including the knowledge of their unperturbed dimensions is also necessary. A detail study of solution properties of polyacrylamide in water and water-organic solvent will be carried out for this purpose.