CHAPTER 2

SCOPE AND OBJECT

SCOPE AND OBJECT OF THE PRESENT WORK

In recent years, scientists and engineers working on environmental and industrial problems have renewed their interest in water-soluble synthetic polymers because of their very broad range of applications. Important classes of these materials are the acrylamide-based polymers, which are widely used as flocculants, adhesives, rheology control agents, paper manufacturing, mining, and oil well stimulation etc. During the past decades, many patents have described the synthesis of homo and copolymers of acrylamide with special properties considering its versatile application in numerous fields in industries and also as water-soluble viscofier and displacement fluids in enhanced oil recovery. Anionic polyelectrolyte such as poly acrylamide-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 polyelectrolytes 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. Redox initiated polymerization of acrylamide is one of the most common technique 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 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 polymer was 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) embedded 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 is even less than that of montmorillonite. Further, industrially clay minerals are used 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, specially 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 (Detail discussion is in Chapter 1).

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., Ce (IV)/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 leading themselves to a variety of industrial applications and the growing importance are 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-N-tert-butyl acrylamide) on the vermiculite surface. In an attempt to examine the scope of the technique, another redox couple viz., Fe (III)/ TU system will also be tested. However, one important objective of the above study is also to prepare polymers of desired molecular weight by selective application of the technique in order to carry on further studies on solution properties of polymers as mentioned below.

According to hydrodynamics, the specific viscosity of a Newtonian liquid containing a small amount of dissolved material should depend in the first approximation only upon the volume concentration and the shapes of the suspended particles. The unperturbed dimension (UD) of a given polymer in a solvent does not depend on the nature of the solvent, as long as the solvent has no influence on the rotation of the chain segments. This is true in many cases, especially for nonpolar polymer-solvent pairs, but in the cases of polar polymer - polar solvents systems, the unperturbed dimension vary considerably with the nature of the solvent. Most of the polymeric materials are soluble only in a limited number of primary solvents, but they could be made soluble in all proportions in mixtures consisting of two or more solvents, which may be individually poor solvent for the polymers. Several mixtures of nonsolvents are also known which produce good solvent systems or at least increase the solvency power of primary solvents. 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 state, the type of interaction (short range and long range), the conformational characteristics including the transition phenomena influenced by temperature and solvent.

Polyelectrolyte finds a widening field of applications based on their specific properties. In recent years the study of polyelectrolytes has been stimulated by the use of newly available experimental techniques and the introduction of new theoretical concepts. Solutions of polyelectrolyte exhibit a behavior that may differ considerably from that of either uncharged macromolecules or low-molar-mass electrolytes. The origin of this specificity lies in the combination of properties derived from those of long-chain molecules with properties that results from charge-charge interactions. Physical properties of polyelectrolyte solutions have been studied for long time, but several of them have not yet found a satisfactory theoretical explanation. In many cases a qualitative understanding is available but a quantitative interpretation is still lacking. Such a study is of interest from both industrial as well as academic points of view. Recently the interest is mainly focused on the relationship between the structure/charge density and the state of conformation. Although the solution behaviour of the polyelectrolyte homopolymers has been well studied the structure property relationship in charged co and ter polymers is yet to be fully investigated. The development of the dual charge on the same chain is expected to produce interesting effects on the final state of its conformation. Polyelectrolyte solution has been much more extensively studied in aqueous solution than in nonaqueous solution and in aqueous-organic mixtures.

In view of the above a detail study of solution properties of nonionic (unhydrolyzed) and anionic (hydrolyzed) polyacrylamide in water and water-organic (N, N dimethyl formamide) mixtures has been carried out. It is well established that the introduction of ionic groups in a polymer results in its expansion in aqueous solution. The use of aqueous polymer solutions in secondary oil recovery has been the subject of great interest as has already been mentioned. It is reported that (G. Muller, J.P. Laine, J.C. Fenyo, J. Pol. Sc., Polymer Chem. Ed.,17,1979,659) more oil is recoverable by the addition of only small quantity of polymers to injection water. The choice of polymer to be added to injection water must take into consideration a number of parameters, viz., the pH of the reservoir and the nature and concentration of salts. The effectiveness of the polymers is related to their molecular weight, the absence of branched chains and solubility in water. The enhanced recovery seems to be a consequence of molecular expansion that results from electrostatic repulsion between the charges carried by the polymer chains. To understand the role of charged groups on factors that govern the efficiency of PAM in the above use especially in the salt rich waters, complete molecular characterization is required. In the case of charged PAM the relative dissociation of the ionic groups and the distribution and alignment of the charged dipoles along the chain are expected to play a decisive role on the final state of conformation of the polymer chain. In addition, the synergism in properties of surfactants and polymers in aqueous solutions has been the focus of intensive fundamental applied research. Attention to this area of research is driven by numerous industrial applications of water borne fluids incorporating mixtures of both polymers and surfactants. These include detergents, cosmetics, paints and coating, photographic films, food and pharmaceutical products. The surfactant provides emulsion property and the polymers impart colloidal and special rheological features. When surfactants are employed in practice they are almost without exception mixed with various substances either unintentionally or for improving their performances. This is also true for polymers in solution. When a surfactant and a polymer are mixed together in aqueous solutions, often significant changes in properties of the individual species appear. These may arise because both the polymer and the surfactant belong to the group of substances whose solution property shows marked deviation from regularities. Thus polymer surfactant interactions are not only a diverse industrial interest but also stimulate academic investigations. The practical importance of polymer-surfactant systems has led to a significant experimental effort to study their behaviour.

Keeping the above in view the behaviour and properties of hydrolyzed PAM as a function of the factors which are known to effect the expansion of polyelectrolyte molecules i.e., the degree of ionization, polymer concentration and the concentration of added salt have been investigated. PAM is of interest because it is possible to obtain high molecular weight samples that are easily soluble in water. Moreover, the controlled hydrolysis of PAM samples yield polymers of various charge densities. Because its effectiveness is related to the state of extension of dissolved chains, hydrolysis is a powerful means of increasing viscosities and because the electrostatic repulsion that govern the extension are sensitive to the added salt, hydrolysis is an important chemical variable. The object of the work, therefore, is two fold (1) to study ionomeric and polyelectrolytic characteristics of weakly and strongly hydrolyzed PAM in aqueous solution in terms of their solution properties and (2) effect of the charges on polymer chain vis-à-vis screening by added electrolyte and to show how the polyelectrolyte behaves like a neutral polymer in presence of sufficient amount of salt.