

CHAPTER 6

SUMMARY AND CONCLUSION

6. SUMMARIES AND CONCLUSION

In chapter 1, an introduction covering various aspects of the present research scheme on aqueous polymerization of acrylamide is presented. In view of the increasing industrial applications of water-soluble acrylamide polymers in a number of areas including the use of polyacrylamide as water-soluble viscofier in enhanced oil recovery, researches in the field have gained momentum in recent years. Research on the intercalation chemistry of phyllosilicates is increasing rapidly to transform these abundant minerals into new class of selective heterogeneous catalysts. In the present study, attempts have been made to prepare acrylamide polymer having high molecular weight and intrinsic viscosity by polymerizing the monomers on vermiculite surface. A major difficulty of applying redox initiators for polymerization monomers is fast termination by the oxidant of the redox couple. In an attempt to increase the chain length of polyacrylamide, the potential electron acceptors of the redox couple, (e.g., Fe(III) ions of Fe(III)-thiourea initiating system) has been loaded into the interlayer space of vermiculite (phyllosilicate) prior to the reaction. In the introduction part of this chapter, a brief review covering all these aspects viz., homo and copolymers of acrylamide, structure of the mineral clay vermiculite, clay polymer interaction and clay catalyzed polymerization have been presented.

(page 1-25)

Chapter 2 describes the scope and object of the present investigation. 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 application. 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 polymerization process is a simple efficient technique, which yield polymers with high rates. However, as has been just mentioned, one major difficulty of redox technique is the fast

termination process via transfer of electrons to the oxidant of the redox couple resulting in the low molecular weight polymers. If the polymerization is carried out in a constrained space such that the growing polymer chain cannot transfer the electrons efficiently to the oxidant of the redox couple an enhanced chain growth results. A detailed study pertaining to the homopolymerizations of acrylamide in homogenous phase and vermiculite phase by Fe(III)-thiourea are undertaken along with linear copolymerization reaction of acrylamide with diacetone acrylamide. Studies on the solution properties of polyacrylamide have also been undertaken in view of the fact that the role of the hydrodynamic dimensions on different factors which govern the efficiency of their use is important. The study of hydrogels and their response to external environment is of special interest because of their potential use as drug delivery systems, actuators, and separation devices etc. The study also includes reaction kinetics of crosslinking copolymerization of acrylamide with N,N-methylene-bis-acrylamide by Fe(III)-thiourea and Ce(IV)-thiourea redox initiator systems. The hydrogels prepared by the above processes were used to determine swelling characteristic at various temperatures. Thermogravimetric analysis to understand thermal stability and differential scanning calorimetric (DSC) studies in order to know about the phase transitions and nature of interaction in the hydrogel samples were also undertaken.

(page 26-29)

Chapter 3 is concerned with the studies of homopolymerization of acrylamide and copolymerization of acrylamide with diacetoneacrylamide on aqueous vermiculite surface.

(page 30-86)

Section 3.1 deals with the homogeneous polymerization of acrylamide. In the section 3.1.1, a brief introduction and review on this aspect are presented. The experimental techniques for the study of polymerization including the methods of preparation and purification of different vermiculite samples viz., hydrogen vermiculite and ferric vermiculite, method of polymerization process are presented in section 3.1.2. In addition to the

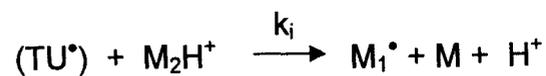
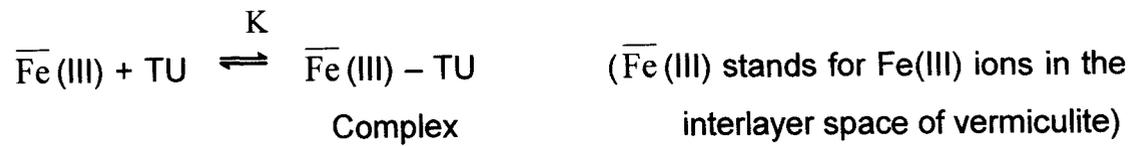
above, different experimental techniques viz., viscometry, potentiometry, conductometric etc are discussed. In the first part of the results and discussion, polymerization results under homogeneous conditions are presented and discussed. The molecular weights of the polymer in this medium were ranged between $(0.3 - 2.3) \times 10^5$ and the initial rates of polymerization were ranged between $(1.2 - 4.2) \times 10^{-5} \text{ mol.L}^{-1}.\text{s}^{-1}$. Use of vermiculite microenvironment affects the polymerization kinetics to a great extent for the same redox reaction in which one of the redox partner viz., Fe(III) is preloaded in the interlayer space of vermiculite prior to the start of polymerization reaction. A detail study concerning the kinetic and mechanistic aspects has been made for the aqueous polymerization of acrylamide with ferric vermiculite-thiourea initiating system. Kinetic, spectroscopic and other analytical data have been taken into consideration to determine the reaction pathways involved. The molecular weights of the polymers initiated in vermiculite interlayer spaces are much higher and ranged from 8.90×10^5 to 2.7×10^6 i.e. approximately 10 times larger than that without the use of any clay mineral. On the other hand, in the presence of vermiculite, R_p values were much higher and a sharp increase of R_p from $5.01 \times 10^{-5} \text{ mol.L}^{-1}.\text{s}^{-1}$ to $14.91 \times 10^{-5} \text{ mol.L}^{-1}.\text{s}^{-1}$ with increase of temperature from 45°C to 60°C at $[\text{TU}] = 0.04 \text{ M}$, $[\text{AM}] = 0.4 \text{ M}$ and $[\text{Fe(III)}] = 3.0 \times 10^{-3} \text{ M}$ was noticed. It is observed that the homogeneous polymerization reaction at 50°C for $[\text{TU}] = 0.04 \text{ M}$, $[\text{Fe(III)}] = 3.0 \times 10^{-3} \text{ M}$, $[\text{AM}] = 0.4 \text{ M}$ yields only 50% conversion after 270 minutes. However, 95% conversion was noticed in the vermiculite phase reaction during that period. The plot of the logarithms of empirical rate constant R_p against the reciprocal of the absolute temperature yields the value of activation energy of the reaction as $9.12 \times 10^3 \text{ cal/mol}$ to $15.0 \times 10^3 \text{ cal/mol}$. The ^{13}C spectra showed methylene, methine and carbonyl carbons of head-to-tail polymer of acrylamide. It seems apparent from the ^{13}C spectra that Bernoulli statistics are followed and stereoregularity has not been observed. However, the polymer trapped inside the interlayer spaces of vermiculite, which could not be extracted by washing with water may have such a possibility of showing stereoregularity. Attempts are being made to extract these polymers in mild condition for further study. The rate of reaction follows the second order kinetics with respect to the monomer concentration, which is

deviated from the homogeneous solution phase reaction condition. The significant changes due to the occurrences of the reaction on the vermiculite surface indicate that mechanism of polymerization is greatly affected by mineral microenvironment. The order of polymerization reaction is found to be 0.5 with respect to metal ion oxidant. The relationship of polymerization rate with thiourea (TU) concentration was obtained from the slope of $\log R_p$ versus $\log [TU]$ plot and from the plot $[TU]$ exponent was found to be nearly 1.0. This value is also different from that of homogeneous polymerization reaction in which second order kinetics with respect to TU is followed. To rationalize the above findings and to predict the possible mechanism of the above polymerization reactions based on the experimental observations, following assumptions are made:

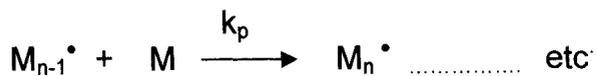
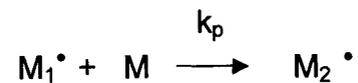
1. Intercalated thiourea reacts fast with Fe(III) ions of the vermiculite layered spaces to form reactive isothiocarbamido primary radical via an intermediate complex. The decomposition of the complex is the rate determining step.
2. In the acidic and metal ion exchanged aqueous vermiculite system, a fraction of the intercalated acrylamide molecules are present near reacting sites as pairs either through hemisalt formation, where two amide molecules share a proton by means of symmetrical hydrogen bond or/and through weak coordination to the exchanged cations.
3. Cage effect is prominent in the vermiculite phase reactions in which the solvent molecules in the constrained space form a potential barrier such that the reactive isothiocarbamido radical cannot diffuse out from the wall of the barrier and favours their recombination.

Various steps of reactions are shown below:

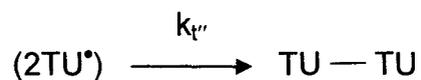
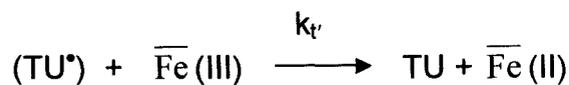
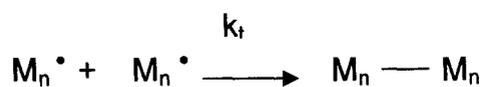
Initiation



Propagation



Termination



Applying steady state conditions for different intermediate species, the rate equation has been found to be

$$R_p = k_p \left(\frac{k_d k_i K K^1}{k_t' k_t''} \right)^{\frac{1}{2}} K_{tu}^a (K_m^a)^2 (L_o^a)^3 [\overline{Fe(III)}]^{\frac{1}{2}} [TU]_s [M]_s^2$$

Where L_o^a , K_m^a , K_{TU}^a are total active sites in unit mass of the mineral and selectivity coefficients of AM and TU for vermiculite respectively.

(page 30-55)

3.2 section of chapter 3 deals with the studies on copolymerization of AM with diacetone-acrylamide (DAAM) using FeV and TU redox initiator system. Copolymer microstructures and reactivity ratios of the copolymers are determined. Observed data indicate that the copolymerization follow the conventional copolymerization kinetics under a prerequisite that the reactivity of a polymer radical is only determined by the terminal monomer unit. Values of r_1 and r_2 have been found to be 0.69 ± 0.03 and 0.75 ± 0.05 respectively for Fineman-Ross method and 0.70 ± 0.08 and 0.65 ± 0.09 for Kelen-Tüdös method. On reversing the indices of the monomer the values of the reactivity ratios changes in Fineman-Ross method to 0.56 ± 0.04 (r_1) and 0.69 ± 0.02 (r_2). The microstructures of the AM-DAAM copolymer are expected to be important in determining the solution properties of the copolymer. For the series of AM-DAAM copolymers, the mean sequence length of acrylamide, μ_{AM} , vary between 29.77 and 2.26 at molar ratio of 95.87/4.13 to 62.66/37.34 respectively. For those molar ratio compositions, the values of mean sequence length of DAAM were 1.006 and 1.144 respectively.

(page 56-70)

In section 3.3 a general discussion of the foregoing study is presented. The experimental results on the adsorption of AM and TU onto vermiculite are also discussed. The adsorption isotherm for Fe(III) ion onto vermiculite exhibits L-type nature, which suggests strong sorbate-sorbent interaction. The maximum saturation corresponds to 1.5 meq/g of the mineral. Two plateau regions indicating two-stage intercalation of amide molecules characterize the isotherm. Unlike AM, TU leads to the single stage adsorption only and the maximum capacity is found to be nearly 2 mmol/g. The first saturation value for AM is nearly 1.0 mmol/g whereas the second one is close to 4.0 mmol/g.

Therefore, it is obvious that if TU forms a monolayer intercalation, AM forms a bilayer at higher concentrations. The bilayers of acrylamide (intake is almost double to that of TU) in the interlayer space of the mineral seems to play pivotal role in affecting the initiation of polymerization and its mechanism in the layered space as compared to the homogeneous polymerization.

(page 71-77)

In chapter 4, the results of the investigation on unperturbed dimension, interaction parameter and related aspects of unhydrolyzed polyacrylamide in water-1,4-dioxane (DO) mixtures have been described. The intrinsic viscosities $[\eta]$ of three different samples of the polymer having different molecular weights were measured in various fractions of solvent composition (ϕ). 1,4-Dioxane is a poor solvent for PAM but water-dioxane mixture acts as a cosolvent in certain proportions. From the relation between $[\eta]$ and M , the unperturbed dimension and molecular expansion factor have been measured. The Huggins constant value in each case was also determined in order to have ideas on the influence of cosolvent system on the aggregation of the polymer. It is observed that there is a maximum in $[\eta]$ vs. ϕ_{DO} plot at the solvent composition $\phi_{DO} = 0.2$ for PAM-type B (medium molecular weight polymer) and type C (low molecular weight polymer) at all the studied temperatures. For type-A PAM (high molecular weight polymer), however, there is no maximum in the plot of $[\eta]$ vs. ϕ_{DO} . It is observed that K_H values are maximum at the solvent composition $\phi_{DO} = 0.3$ for all types of polymers and it increases with an increase in the molecular weight of the polymers indicating higher tendency of intermolecular aggregation for higher molecular weight fractions of the polymers. K_H is smallest and negative at $\phi_{DO} = 0.4$, under this condition DO pulls polymer molecules closer to make polymer side chains twisted around each other. Unperturbed dimensions under non-theta condition were calculated using various equations in different water-DO mixtures. The value of K_θ obtained from three different methods of measurements viz., BSF, I-S-K and Berry agree well with each other except in a few compositions of solvents. It is apparent that at $\phi_{DO} = 0.4$ the polymer has the lowest unperturbed dimension and at $\phi_{DO} = 0.2$ the polymer has the highest

unperturbed dimension. Temperature coefficient of unperturbed dimension, molecular extension factor and coil dimensions of PAM in different water and DO mixtures at various temperatures are determined, The characteristic ratio (C_α), steric factor (σ), volume related parameter (V_E) are also computed in this chapter.

(page 87-111)

In chapter 5 free radical cross-linking copolymerization of acrylamide with N,N-methylene-bis-acrylamide alongwith swelling and thermal behaviours of the hydrogels were studied.

(page 112-137)

In the section 5.1, a brief review on this aspect is presented. In the section 5.2 of this chapter free radical cross-linking copolymerization of acrylamide with n,n-methylene-bis-acrylamide (Bis) by Fe(III)-Thiourea and Ce(IV)-thiourea redox initiator systems were discussed. The polymerization kinetics was studied gravimetrically with varying amount of Bis content. For Fe(III)-thiourea redox initiator system no induction period was observed but for Ce(IV)-thiourea redox initiator system a significant induction period was noticed. Acrylamide-N,N-methylene-bis-acrylamide copolymerizations were carried out in water at 50°C with Fe(III)-thiourea redox system. At 50°C (using Ce(IV)-thiourea redox initiator system) the reaction rate is very fast after the induction period and kinetics was very difficult to study via gravimetric measurements and hence kinetics was studied at lower temperature (i.e., 40°C) only. The onset of macrogelation time and the monomer conversion at that point of time were plotted as a function of Bis concentration in the monomer mixture. Both the plots are found to pass through minima. For Fe(III)-TU system this minimum appears at 6 mol% composition of Bis. For Ce(IV)-TU redox system, on the other hand, it occurs in between 4-5 mol % of Bis concentration.

(page 112-121)

Section 5.3 of this chapter deals with the swelling and thermal behaviour of prepared hydrogels. The swelling experiments were conducted

in aqueous medium by a purpose built apparatus designed in our laboratory. It was observed that with the rise of crosslinker concentration there is a decrease in the swelling percentage because the molecules of the crosslinker are placed between the chains of monomers under this condition. With the rise of temperature, amount of swelling increases for a given crosslinker concentration. The following equation is used to determine the type of diffusion process of water into hydrogels

$$F = (M_t / M_i) = Kt^n$$

Where M_t and M_i represent the amount of solvent diffused into the gel at time t and infinite time, respectively. 'K' is swelling constant related to the structure of the network, and the exponent 'n' is swelling exponent, which is a number to determine the type of diffusion. Above equation is applied to the initial stages of swelling and the plots of $\ln F$ versus $\ln t$ yield straight lines up to ~60% increase in the mass of hydrogel on water absorption. The n and K values were calculated from the slopes and intercepts of the lines, respectively. The values of diffusional exponent range between 0.47 and 0.62 where as the swelling constant, K varies between 5.091×10^{-2} and 11.176×10^{-2} . Therefore, the diffusion of water into hydrogels is considered as a non-Fickian type. This behaviour is generally explained as a consequence of a slow relaxation rate of the polymer matrix.

The thermal stability of the copolymers of AM with Bis prepared under various conditions were analyzed by thermogravimetry (TGA). In general, the thermograms display multistage weight loss features as a function of temperature. However, the samples prepared by Fe(III)-thiourea system are completely decomposed/charred at about 400°C. In almost all the samples, weight loss started at around 200°C. The overall average inflection points vary substantially with crosslinker (i.e., Bis) concentration. The thermal stability of the hydrogel is increased dramatically when prepared in presence of vermiculite mineral. If attention is focused on the characteristic features of each thermogram of acrylamide hydrogel, it may be said that the nonstoichiometric loss of water is taken place followed by subsequent loss of

ammonia and other gaseous products from the polyacrylonitrile structure formed during decomposition of polyacrylamide and partly from the remaining polyacrylamide in the course of heating.

The Differential scanning calorimetric (DSC) profiles show endothermic peaks at 57°C, 70°C and 65°C which indicate the presence of glass transitions for pure copolymers of AM with Bis (dry hydrogel) prepared on adding 2 mol %, 6 mol % and 10 mol % crosslinker respectively. The DSC profiles also display the characteristic temperature where softening of the copolymer starts. The onset of softening temperature occurred for the above three samples at 220°C, 215°C and 225°C respectively. However, interestingly the endothermic peaks displayed by the samples under moist condition are actually the overlap of three closely separated peaks, indicating three different potential sites for water retention in the acrylamide hydrogel. Water retention characteristics of the hydrogel may be discussed in terms of DSC endothermic peak positions also. The enthalpy change associated with the endothermic phase change of hydrogels under moist conditions varies from 2398 J/g to 4433 J/g. Gels prepared in presence of 1.5×10^{-3} M Fe(III) ions in ferric vermiculite (TU = 0.04 M, crosslinker = 4 mol %) display highest water removal temperature indicating strongest bond with water molecules. Scanning electron micrograms are recorded for observing the gel morphology (in presence of vermiculite mineral). Microporosity of gel is not apparent from SEM picture.

(page 122-131)

