

## **CHAPTER 3**

**STUDIES ON HOMOPOLYMERIZATION OF ACRYLAMIDE  
AND COPOLYMERIZATION OF ACRYLAMIDE WITH  
DIACETONE ACRYLAMIDE ON AQUEOUS VERMICULITE  
SURFACE**

### **3.1 AQUEOUS POLYMERIZATION OF ACRYLAMIDE BY Fe(III)-THIOUREA REDOX COUPLE ON VERMICULITE SURFACE**

#### **3.1.1 INTRODUCTION AND REVIEW OF PREVIOUS WORK**

Water-soluble polymers are polymers that can either dissolve or swell in water to form either solution or hydrogel. The water-soluble polymers are commonly synthesized from water-soluble monomers, like: acrylic acid and its sodium salt, acrylamide, hydroxyethyl-methacrylate, hydroxyethyl-acrylate, vinylpyrrolidone, quaternary ammonium salt, like dimethyldiallyl ammonium chloride etc. Among all the water-soluble polymers polyacrylamide and poly acrylic acid based water-soluble polymers are used in the wide range of products because of their high performance and low cost. In view of increasing industrial applications of water soluble acrylamide polymers, clay minerals, and there combinations in various fields including the use of polyacrylamide as water soluble viscofiuers in enhanced oil recovery present scheme of study is undertaken [1]. High molecular weight polyacrylamide has such other applications as effective flocculants and chemical grouts. The synthesis is commercially implemented by various processes including solution polymerization, inverse suspension polymerization, inverse emulsion polymerization,  $\gamma$ -ray initiation polymerization, ultrasonic wave and photo polymerization. They generally follow the free radical polymerization mechanism. The solvent allows easier stirring, since the viscosity of the reaction mixture is decreased. On the other hand, the presence of solvent may create new difficulties; chain transfer to solvent and/or to the solute may occur. There are some advantages by using water as solvent over organic solvents because water is cheep, clean and environmental friendly and chain transfer to the solvent is not possible. However, for homogeneous polymerization process it is limited to only water-soluble polymers and monomers. Each of the above processes has its associated disadvantages, however, which limits its practical use in the manufacturing of the water-soluble polymers. Over the last 20 years, the use of thiourea (TU) and N-substituted thiourea as redox components for the initiation of aqueous vinyl

polymerization has been examined [2]. These experiments applied various oxidants, viz., metallic salts, organic and inorganic peroxides, persulphate, permanganate, and bromate to name a few. A number of articles have also appeared in the literature on graft polymerization of various monomers using the above initiators [2,3]. The special features of these systems are a very short induction period, a relatively low energy of activation and the low temperature required.

Polymerization of acrylamide (AM) in aqueous solution with different free radical initiators have been reported by several workers [4-31]. Dainton and co-workers made detailed study of the polymerization kinetics in aqueous solution using x-rays and  $\gamma$ -rays for initiation [32]. They also studied the photosensitized initiation by hydrogen peroxide and ferric ion [33]. Redox polymerization of acrylamide (AM) include the initiation systems such as chlorate-sulfite [34], persulphate-metabisulphate [35], Ce(III)-3-chloro-1-propanol [36], and ferric ion-bisulfite [37]. Polyacrylamide was also prepared within the temperature range 30°C to 50°C dilatometrically, initiated by potassium persulfate in water at pH range 3.20 to 4.08. The polymerization rates were half order with respect to initiator and 1.25-order with respect to the monomer [38]. Mandal and co-workers reported the polymerization of methyl methacrylate initiated by a redox system composed of ferric perchlorate and thiourea [39-41]. Narita and co-workers prepared polymethylmethacrylate initiated by ferric salts and thiourea in dimethyl sulfoxide solution. With increase in the concentration of TU, a decrease in the degree of polymerization as well as an increase in the conversion was observed. With increasing concentration of the ferric ion the degree of polymerization decreases, although the conversion is independent of the ferric ion concentration [42,43]. Sugimura and co-workers reported the polymerization of acrylonitrile in aqueous solution with hydrogen peroxide ( $H_2O_2$ ) and TU redox initiator and they observed the rate of polymerization of 0.5 order with respect to  $H_2O_2$  and TU and first order to monomer concentration [44]. Ghanasundaram and co-workers observed that for the initiator, bis[2-[(2-hydroxy-ethyl)amido] ethoxide] copper(II) at pH 1.8, the

polymerization rate was first order with respect to AM monomer and 0.5-order with respect to catalyst [45]. Faster polymerization rate and high molecular weight polymers were obtained in presence of 2,2'-azobis[2-(N,N'-ethylenamidino)] propane initiator than those obtain using  $K_2S_2O_8$ -Mohr's salt initiating system [7]. The rate of polymerization ( $R_p$ ) of AM by peroxydiphosphate in  $H_2S_2O_4$  was decreased when the temperature was raised from 30°C to 50°C but increased above that temperature range and the rate was independent of pH [46]. The aqueous polymerization of acrylic acid and AM initiated by peroxydiphosphate-sodium thiosulfate redox system was investigated within the temperature range of 25-35°C by Lenka and co-workers. They observed first order kinetics with respect to both the monomers and 0.5 order with respect to peroxydiphosphate [47]. Kinetics of polymerization in aqueous acetic acid (ACOH) using  $Pb(OAC)_4$  as initiator was studied by Balakrishnan who found that polymerization rate was first order with respect to AM [13]. The propagation and termination reactions of the  $K_2S_2O_8$  initiated polymerization of AM in water were not influenced by the anionic emulsifier Dowfax-2-Al [14]. The induction of polymerization was affected by manganous salts while the polymerization rate and polymer molecular weight were not affected to a detectable degree, as was observed by Xuanchi [15]. Using trigol and polyethylene glucol initiators, it was found that the yield and the molecular weight of the polymer decreased with increasing chain length of substituted AM [17]. Cvetkovska and co-workers explained the kinetic model by the formation of a monomer-initiator complex and inhibiting effect of the Mn(II)acetylacetonate formed by the reduction of Mn(II) acetylacetonate [18]. The polymerization rate of AM in  $H_2SO_4$  or ACOH by Co(III) system showed similar mechanism as that of  $Pb(OAC)_4$  initiator in ACOH [19]. Vaskova and co-workers found that in mixtures of water and aliphatic alcohols, in the presence and absence of inhibitor, the rate of polymerization and molecular weight were reduced depending upon the length and character of the aliphatic chain [20]. Liu and co-workers observed that the polymerization rate depends on catalytic concentration, and pH of the solution [21,23]. Takahashi and co-workers found that the average molecular weight of polymer was  $(1-7) \times 10^4$  when (2,2'-bipyridine) cobult(II) complex was used as inhibitor [25]. Bhanu and co-workers observed that co-ordinately

unsaturated Co(II) complexes significantly inhibit the thermal polymerization of AM but they imparted a significant induction period during AIBN (azobisisobutyronitrile) initiated polymerization of AM [28]. High molecular weight polyacrylamide could be obtained by using heptane as the organic phase,  $K_2S_2O_8$  as catalyst and sorbital-s-20 system as the emulsifier [30]. The author also reported that the polymer molecular weight was increased with the increase in concentration of AM and emulsifier, but decreased with the increase in the catalyst concentration. Redox catalyst systems were frequently employed for polymerization at comparatively lower temperatures. Bajpai and co-workers investigated the polymerization of AM initiated by  $KMnO_4$ -various amino acids and unsaturated acids redox couples [48-59]. A value of  $KMnO_4$  catalyst exponent of unity in the rate equation confirmed a unimolecular chain termination process by the redox system [48,53]. However, a bimolecular chain termination was observed for other redox systems [50,52-57]. The same result was observed in the case of  $KMnO_4$ -glyceric acid in  $H_2O$ -DMF also [59]. The rate of polymerization was first order with respect to the monomer in all the above systems. Bajpai and co-workers suggested that polymer-molecular weight was directly proportional to the initial monomer concentration and inversely proportional to the rate of initiation. With the increase of temperature, the molecular weight of polymer was decreased in most of the cases. The effect of various additives (alcohols, natural salts, complexing agents) on the polymerization rate was also investigated. Polymerization was initiated by radicals generated in the decomposition of the oxidant-reductant complex. A numbers of workers studied the mechanism and kinetics of aqueous polymerization of AM in acidic medium initiated by Ce(IV)-reductant couples [60-76]. The rate of polymerization was first order for the monomer and half order with respect to Ce(IV) ion in cases where the initiator was either Ce(IV)-thioglycolic acid or Ce(IV)-L-cysteine [63,64]. In the polymerization of AM initiated by Ce(IV)-thiourea in water, the polymerization rate is governed by the relation  $R_p = k_p[AM]^{1.20}[Ce(IV)]^{0.5}[TU]^{0.5}$ . Presence of alkyl phenyl carbonate increased the polymerization rate of AM initiated by Ce(IV) in  $H_2O$ -MeCN and  $H_2O$ -HCONH<sub>2</sub> and decreased the activation energy of polymerization compared to the system where Ce(IV) was used alone [74]. The rate of polymerization was

derived as  $R_p = k[AM]^{1.5}[Ce]^{0.39}[\text{alkyl phenylcarbonate}]$ . The overall rate of polymerization was faster and activation energy was lower with Ce(IV)-p-acetotoluidide system compared to Mn(III)-p-acetotoluidide system [73]. Different workers studied the effects of various aliphatic diamines on vinyl polymerization using persulfate as initiator [77-78]. They suggested that the promoting activities of diamines on vinyl polymerization were of the order: t-diamine > s-diamine > p-diamine. In a reversible redox initiating system involving metals and porphyrin, the aqueous polymerization rate depended on the types of metal viz., [Fe(III), Cu(II), Ce(IV), Ti(IV), Mn(II)] in the porphyrin complex, polymerization temperature and concentration of AM [79]. Cheng and co-workers observed that, amino acid type chelating agents such as nitrilotriacetic acid (NTA), nitrilotripropionic acid (NPA), iminodiacetic acid (IDA), and ethylenediamine tetraacetic acid (EDTA) were used in combination with Ce(IV) as the redox initiators for the aqueous polymerization of AM and the NTA-Ce(IV) initiator showed the most promising polymerization rate and conversion [80]. Carboxylic acids promoted and enhanced the polymerization rate of AM initiated by Mn(OAc)<sub>4</sub> [81]. The kinetics and mechanism of aqueous polymerization of AM initiated by the persulphate catalyst in the presence of different activators were studied by several workers [82-87]. Kurenkov and co-workers observed that, higher molecular weight polymers could be obtained with higher conversions using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> redox system during adiabatic polymerization of AM in comparison to the K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>-CuSO<sub>4</sub> system [82-84]. Molecular weight of the polymer was increased with increasing monomer concentration but decreased with the increase of catalyst concentration. Akopyan and co-workers obtained polymers having molecular weight of  $8.0 \times 10^5$  at 25°C by three component catalyst system comprising of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, triethanolamine and amino acetic acid [86]. The overall polymerization rate was increased in the presence of Cu(II) ions for the polymerization initiated by persulfate-(dimethylamido) ethylmethacrylate-Cu(II) catalyst [85]. The polymerization kinetics, mechanism, polymer molecular weight and effect of additive were examined by several workers for various redox polymerization involving chelate complexes [88-105]. For a radical polymerization of AM initiated by Mn(III)-

acetylacetonate in aqueous solution of pH 2.0, Cvetkovska explained the deviation of the kinetics from the conventional kinetic model via the formation of a monomer-initiator complex [89]. Smith obtained polymers having molecular weight as high as  $4.0 \times 10^6$  by Fe(II)-hydroperoxide redox initiator at the temperature range between  $-20^\circ\text{C}$  and  $+40^\circ\text{C}$  [90]. Wu and He obtained polyacrylamide having average molecular weight of  $10^7$  at room temperature by  $\text{NaHSO}_3\text{-O-MnSO}_4$  catalyst [91]. They also pointed out that the presence of  $\text{MnSO}_4$  would only affect the catalytic activity of the system but it did not involve in chain propagation or termination. Electrochemical study of the redox initiator systems, Ce(IV)-EDTA /  $\text{N}_2\text{H}_4\text{-H}_2\text{O}_2$  and Ce(IV)-EDTA /  $\text{NH}_2\text{OH-H}_2\text{O}_2$ , in alkaline aqueous medium (pH 9-11) showed that the former redox system was more effective than the later [94]. Lenka and co-workers observed that the polymer rate was decreased with increasing thiosulfate concentration and was first order with respect to AM during aqueous polymerization of AM initiated by potassium peroxydiphosphate / Na-thiosulfate redox system [47]. Namasivayan and Natarajan examined the kinetics of the thermal polymerization of AM in the presence of  $\text{CCl}_4$  and a bis-amino acid chelate of Cu(II) with glutamic acid, serine or valine [97]. The activation energy of polymerization reaction decreased from 18.7 to 4.5 kcal/mol on addition of 1.0 ppm Fe during the polymerization by  $\text{H}_2\text{O}_2\text{-NH}_2\text{OH.HCl}$  redox couple [98]. From the observation, it was concluded that the predominant reaction appeared to be Fe-catalyzed decomposition of the peroxide in presence of small amount of  $\text{NH}_2\text{OH.HCl}$ . Sur and Choi found that the reaction rate in presence of  $\text{CoCl}_2$  and N,N-dimethylaniline was proportional to  $[\text{AM}]^{1.08}$  and  $[\text{Co(II)}]^{0.53}$  indicating bimolecular termination process to be involved [102,105]. The rate of polymerization and the maximum yield decreased when the temperature was raised above  $40^\circ\text{C}$ . Chshmarityan and Beileryan observed that the polymerization of AM in aqueous solution initiated by  $\text{K}_2\text{S}_2\text{O}_8\text{-Ag}$  (aminoacetate) chelate system was first order in monomer and 0.5 order in initiator [106].

Some researchers investigated a series of sulfur-containing compounds as electron donors in photo induced free-radical (e.g. ethionine, methionine, methioninemethyl ester etc) polymerization, in conjugation with 4-

carboxybenzophenone (CB) as sensitizer [107]. The results were compared with that of the non-sulfur-containing compounds, alanine and triethanolamine. The best initiation yields are observed for the system CB (phenylthio) acetic acid. The kinetic and mechanistic features of potassium ditelluratoargentate(III) (DTA) initiated aqueous polymerization of AM have been investigated in an alkaline medium by Yanghai and co-workers [108]. The polymerization behaviour as functions of [AM], [DTA], pH as well as temperature, have been studied. The overall rates of polymerization have been determined from gravimetry. The rates were found to bear 1.68 and 0.76 dependence on AM and DTA concentrations respectively. The overall activation energy of AM polymerization is measured as 33.6 kJ/mol. Recently large number of monomers with only a few exceptions have been successfully polymerized by atom transfer radical polymerization (ATRP) process, yielding polymers of predetermined chain length, low polydispersity, and well defined chain ends in which a catalytic amount of a transition metal complex is required. Atom transfer radical polymerization (ATRP) of acrylamide has been carried out by Mandal and co-workers in water or in glycerol-water (1:1 v/v) medium at 130°C using water-soluble initiators, viz. 2-chloropropionamide or 2-bromopropionamide and CuX (X=Cl, Br) bipyridine complex as catalyst. Extraneous addition of CuX<sub>2</sub> (20 mol % of CuX) and/or excess X<sup>-</sup> ions (1 M alkali halide) in the reaction mixture helps to reduce molecular weight polydispersity [109]. Huang and Wirth obtained polyacrylamide (PAM) with a polydispersity index value of 1.11 when ATRP of acrylamide was carried out in DMF at 130°C using benzyl chloride initiator and CuCl/bipyridine catalyst [110]. Fichri studied suspension polymerization of AM in mixtures of methanol-water system by potassium persulphate initiator [111]. It has been shown recently that polyacrylamide can be prepared in aqueous media electrochemically using an activated iridium electrode [112], and in non-aqueous media using a platinum electrode [113]. The flow of high current densities through aqueous solution of AM and NaNO<sub>3</sub> from platinum electrodes promotes the generation of polyacrylamide in which polymerization rate is proportional to  $[AM]^{1/2}[NaNO_3]^{-3/4}$  [114].

Ability of clay minerals to intercalate various molecules and their catalytic properties are long known. The clay polymer interaction has found wide and varied applications [115]. Montmorillonite, smectite clay has been shown to catalyze the polymerization of some unsaturated organic compounds such as styrene and hydroxyethylmethacrylate and yet to inhibit polymer formation from other structurally related monomers such as methyl methacrylate [116]. This behaviour is believed to be due to electron accepting or electron donating sites on the clay minerals. However, it has been shown that montmorillonite can be used in conjugation with organic substances, viz., alcohols, thiourea etc. to polymerize methyl methacrylate in aqueous medium [116,117]. In this system, the lattice substituted Fe(III) of the mineral is probably involved in forming initiating radicals in presence of TU [118]. In view of the use of AM in various applications including that as displacement fluid in secondary oil recovery, high molecular weight polyacrylamide with large hydrodynamic volume is essential. Recently it has been shown that linear termination process is controlled in aqueous polymerization of AM, by loading metal ions of Fe(III)-TU systems in the interlayer space of montmorillonite and thereby high molecular weight polymer is formed. Vermiculite, being a smectite clay like montmorillonite may also provide potential microenvironment for aqueous AM polymerization to high degree. In this section of the present chapter, attempts have therefore been made to examine the catalytic activity of clay mineral (viz., vermiculite) in the aqueous polymerization process of water-soluble polymers and also to prepare polymers having high molecular weight and degree of polymerization. Vermiculite microenvironment seems to have a dramatic effect on the polymerization of AM by Fe(III)-TU combination in aqueous medium. A detail study concerning the kinetics and mechanistic aspects has been made for the aqueous polymerization of AM with ferric vermiculite (FeV)-TU initiating system. Spectroscopy and other analytical data are taken into consideration to determine the pathways involved in the reaction. Another objective of the present study is to prepare high molecular weight polymers for subsequent studies on solution properties in aqueous and aqueous- organic mixtures, which is included in chapter 4 of the thesis.

### 3.1.2 EXPERIMENTAL

#### Materials and purification

Acrylamide (AM, reagent grade, Fluka) was purified by recrystallization from methanol (two times) and dried in vacuum at 45°C for two day. Thiourea (TU, E.Marck) (m.p.180°C) used after recrystallization three times from distilled water. Vermiculite mineral (Aldrich, USA) was grinded in a ball mill under moist condition for two days in order to reduce the particle size. An aqueous suspension of 25 liter of the grinded vermiculite was prepared adjusting a suitable pH (~8) in double distilled water. After every 24 hours, 10 cm layer of the suspension (from the top) was siphoned out to get particles of size less than 2  $\mu\text{m}$  and each time the original volume was restored maintaining the same pH by adding water and dilute alkali solution. The clay mineral was then collected after acidification with HCl to pH ~ 4 and allowing to settle at the bottom of the container or by centrifugation (REMI-24). The coagulated clay was washed repeatedly with double distilled water and centrifuged. This process gives acid free clay sample having particle size less than 2  $\mu\text{m}$ . Free iron oxide was removed by dithionite-citrate method [119]. Organic matters were removed by gently heating at 80°C with 30%(v/v) H<sub>2</sub>O<sub>2</sub> (Merck) (2 ml per 3 lit clay suspension). H<sup>+</sup>- vermiculite (HV) was prepared by shaking the stock of the mineral (3% w/v) in presence of 0.2 M HCl for about 6 hrs followed by repeated centrifugation (20,000 rpm) and washing with double distilled water. The HV suspension thus obtained was stored at 5-10°C. The cation exchange capacity (CEC) of vermiculite was determined by potentiometric titration with standard KOH solution under nitrogen atmosphere and found to be 1.50 meq.g<sup>-1</sup>. Fe(III)-vermiculite (FeV) was prepared by shaking HV suspension (3%w/v) in presence of 0.3 (M) FeCl<sub>3</sub> (reagent grade) at pH 2.5 for 6 h. followed by purification, by repeated centrifugation and washing with doubled distilled water until the test of Fe(III) ion in the supernatant was negative. Separate adsorption experiments of Fe(III) ions on HV showed that maximum exchange of Fe(III) ion on to the mineral was same or slightly exceeded the CEC (i.e.1.50 meq.g<sup>-1</sup>). The colloid content of clay

minerals in each stock was determined by evaporating a known volume to complete dryness. The FeV suspension thus obtained was stored at 5-10°C.

The commercial grade nitrogen was passed through a series of bubblers containing Fiesser's solution [120]. The oxygen free nitrogen was dried by passing through two bubblers containing conc. H<sub>2</sub>SO<sub>4</sub> before use.

## **Polymerization**

Measured quantities of AM were taken in well-stoppered Pyrex glass bottles, which were made black to stop the possible photo-initiated polymerization. Requisite amount of TU solution was added to the bottles and the mixtures were purged with purified nitrogen for 30 minutes for removing dissolved oxygen at the experimental temperature, keeping on a constant temperature water bath. Dilute HCl solution was added dropwise to maintain pH. FeV suspension and FeCl<sub>3</sub> solution were deaerated with purified nitrogen for 30 minutes. For homogeneous polymerization, the reaction was started by adding deaerated FeCl<sub>3</sub> solution to the monomer solution and to start in clay medium FeV suspension was added. To determine the degree of conversion as a function of polymerization time the reaction were stopped at different time interval by chilling the mixture by placing the vessels immediately on ice bath. The polymer solution was centrifuged to remove FeV clay suspension. The polyacrylamide was precipitated out by adding excess of acetone (Merck), purified by washing repeatedly with acetone and dried in vacuum at 40°C for 48 hours. The dry samples of polymer as well as the mineral were weighted to determine the polymer yield and non-extractable polymers in the clay minerals respectively.

## **Determination of the Molecular Weight by Viscosity Measurements**

The molecular weight of the synthesized polymers were determined using a suspended level Ubbelohde Viscometer placed in thermostated water bath at appropriate temperature (accuracy, ±0.1°C) and a digital stopwatch

with accuracy  $\pm 0.1$  sec measured the flow time. A series of PAM solutions of different concentrations in aqueous 0.1 M NaCl solutions were prepared and the times of flow of the solutions were measured. Specific viscosity ( $\eta_{sp}$ ) was calculated from the time of flow of polymer solution and that of water. The intrinsic viscosity ( $[\eta]$ ) value was obtained from the intercept of the plot of  $\eta_{sp}/C$  versus  $C$ , following the relation.

$$[\eta] = \eta_{sp}/C, \text{ Lim } C \rightarrow 0$$

Where  $C$  stands for concentration of polymer solution. The molecular weight of the synthesized polymer was finally calculated using the Mark-Houwink relationship [121,122]

$$[\eta] = 9.33 \times 10^{-3} M^{0.75} \text{ cm}^3 / \text{g}.$$

### Potentiometric and Conductometric Measurements

The redox behaviour of Fe(III)-TU and FeV-TU systems were examined by potentiometric titration of either  $\text{FeCl}_3$  solution or FeV suspension with TU. The electrochemical cells were simple, as shown below:

- i. Pt/Fe(III),Fe(II) || KCl,HgCl<sub>2</sub>,Hg/Pt
- ii. Pt/Fe(III)V, Fe(II)V || KCl,HgCl<sub>2</sub>,Hg/Pt

A stoppered Pyrex beaker fitted with nitrogen gas inlet-outlet tubes, Pt-electrode, salt bridge and mechanical stirring arrangements was placed in a thermostat at 50°C. 20 ml  $\text{FeCl}_3$  solution or FeM suspension was then titrated at pH 2.0 with standard thiourea solution under nitrogen atmosphere.

Measurements of pH were made using Systronics (pH system 361, India) pH-mV meter. The meter was standardized using two-point calibration method. Conductance measurements were carried out on Systronics conductivity meter-306 using a dip type cell with a cell constant of  $1.15 \text{ cm}^{-1}$ .

The cell was calibrated by standard KCl solutions. The measurements were made in a container maintained at desired temperature.

### 3.1.3 RESULTS AND DISCUSSION

For homogeneous polymerization of AM using Fe(III)-TU redox couple initiator, the initial rate of polymerization, polymer yield after a definite time interval and the molecular weights were determined and results are shown in Table 3.1. The molecular weights of the polymer were ranged between  $(0.3 - 2.3) \times 10^5$  and the initial rates were ranged between  $(1.2 - 4.2) \times 10^{-5} \text{ mol.L}^{-1}.\text{s}^{-1}$ .

The influences of vermiculite microenvironment on aqueous polymerization of acrylamide using Fe(III)-TU redox initiator was studied and a dramatic change of polymerization kinetics and mechanism were observed. Tables 3.2-3.4 show data pertaining to the initial rate of polymerization ( $R_p$ ), polymer yield ( $X_L$ ), intrinsic viscosity ( $\eta$ ), as well as the molecular weight ( $M_V$ ) which depend upon the concentration of TU, AM, Fe(III) ion concentration as well as temperature. Amount of non-extractable polymer is also shown. Molecular weight values measured from the intrinsic viscosities are ranged from  $8.90 \times 10^5$  to  $2.7 \times 10^6$  i.e. approximately 10 times larger than that of the polymer formed in absence of clay mineral.

For conducting the polymerization reaction in clay environment, Fe(III) ion was initially loaded in the interlayer space of vermiculite and polymerization reaction was performed in the constrained space of clay such that the growing polymer chain can not transfer electrons to the metal ion oxidant and terminate the propagation of the reaction as has already been mentioned. Table 3.2 shows that with increase of FeV concentration from 0.06 % to 0.20% in the reaction mixture at a fixed AM and TU concentration the initial rate of polymerization increases from  $2.02 \times 10^{-5}$  to  $7.94 \times 10^{-5} \text{ mol.L}^{-1}.\text{s}^{-1}$  and yield after 4.5 hrs also increases up to 90 %. On increasing the concentration of catalyst more thiourea is oxidized to generate relatively more isothiocarbamido radicals and hence the initial rate of polymerization is increased. However, at FeV concentration above 0.20 %, both the initial rates

of polymerization as well as yield are decreased. At a fixed TU and Fe(III) concentration (in moles of interlayer Fe(III) ion per 1000 ml of reaction mixture) all the parameters viz.,  $R_p$ ,  $X_L$ ,  $[\eta]$ , and  $M_v$  are increased with the AM concentration as shown in the Table 3.3. With the increase of AM concentration (from 0.3 to 0.6 M), the reactive species isothiocarbamido radicals can experience a greater number of collision with the intercalated monomer molecules and the chain propagation continue to proceed and the intrinsic viscosity increases from 172 ml.g<sup>-1</sup> to 628 ml.g<sup>-1</sup>. At a AM concentration lower than 0.3 M, no significant reaction takes place due to very few number of collisions. On the other hand the  $R_p$  increases from  $2.23 \times 10^{-5}$  to  $7.78 \times 10^{-5}$  mol.L<sup>-1</sup>.s<sup>-1</sup> as the concentration of TU is increased from 0.03 to 0.08 M. At TU concentration below 0.03 M the concentration of the initiating species is too small to initiate polymerization reaction as observed from the Table 3.4.

**Table 3.1**

Polymerization of acrylamide with Fe(III) - TU redox initiator in absence of clay Mineral at 50°C (pH=1.98)

Fe(III) mmol.L <sup>-1</sup>	[TU] mol.L <sup>-1</sup>	[AM] mol.L <sup>-1</sup>	$R_p^a \times 10^5$ mol.L <sup>-1</sup> .s <sup>-1</sup>	$X_L^b$ %	$[\eta]^c$ ml.g <sup>-1</sup>	$M_v \times 10^{-5}$
1.5	0.04	0.4	4.21	70	72	1.52
3.0	0.04	0.4	6.40	51	65	1.33
4.0	0.04	0.4	1.22	47	50	0.93
8.0	0.04	0.4	2.10	27	57	1.12
1.5	0.04	0.3	4.20	57	78	1.69
1.5	0.04	0.6	11.1	69	98	2.30
1.5	0.01	0.4	1.88	45	22	0.31

<sup>a</sup>Initial polymerization rate, <sup>b</sup>Yield after 4.5 hrs. <sup>c</sup>Intrinsic viscosity

**Table 3.2**

Polymerization of AM (0.4 M) in aqueous medium (25 ml) in presence of 0.04 M TU and at various concentrations of FeV at 50°C (pH 1.98)

[FeV] in %	Fe(III) mmol.L <sup>-1</sup>	R <sub>p</sub> x10 <sup>5</sup> mol.L <sup>-1</sup> .s <sup>-1</sup>	X <sub>L</sub> in %	[η] ml.g <sup>-1</sup>	M <sub>v</sub> x10 <sup>-5</sup>	Non-extractable PAM(wt%)
.06	0.90	2.02	64	376	13.81	0.081
.08	1.20	5.33	79	318	11.05	0.090
.10	1.50	5.75	84	404	15.20	0.125
.20	3.0	7.94	90	395	14.75	0.123
.30	4.5	5.20	74	271	8.90	0.268
.40	6.0	4.12	49	352	12.65	0.315

**Table 3.3**

Polymerization of AM in aqueous medium (25 ml) in presence of 0.04 M TU and 0.1 % FeV at 50°C and at various concentrations of monomer (pH 1.98)

[AM] mol.L <sup>-1</sup>	R <sub>p</sub> x10 <sup>5</sup> mol.L <sup>-1</sup> .s <sup>-1</sup>	X <sub>L</sub> in %	[η] ml.g <sup>-1</sup>	M <sub>v</sub> x10 <sup>-5</sup>	Non-extractable PAM(wt%)
0.3	3.16	62	172	04.87	0.051
0.4	5.75	84	404	15.20	0.125
0.5	9.73	70	530	21.83	0.133
0.6	13.01	85	628	27.38	0.162

**Table 3.4**

Polymerization of AM (0.4 M) in aqueous medium (25 ml) in presence 0.1 % FeV at 50°C and at various concentrations of thiourea (pH 1.98)

[TU] mol.L <sup>-1</sup>	R <sub>p</sub> x10 <sup>5</sup> mol.L <sup>-1</sup> .s <sup>-1</sup>	X <sub>L</sub> in %	[η] ml.g <sup>-1</sup>	M <sub>v</sub> x10 <sup>-5</sup>	Non- extractable PAM(wt%)
.03	2.23	37	366	13.33	0.117
.04	5.75	84	404	15.20	0.125
.06	6.44	85	326	11.4	0.134
.08	7.78	93	430	16.5	0.175

Figure 3.1 shows the polymerization kinetics with and without the use of vermiculite clay. The figure shows that the kinetics of polymerization depends upon the temperature. Presence of clay mineral enhances R<sub>p</sub> and X<sub>L</sub> to a great extent. It is observed that the homogeneous polymerization reaction at 50°C (for [TU] = 0.04 M, [Fe(III)] = 3.0 × 10<sup>-3</sup> M, [AM] = 0.4 M) yields only 50% conversion after 270 minutes. While, 95% conversion was noticed for the same concentration of Fe(III) ion if it is preloaded in the vermiculite layers. For homogeneous reaction, the initial rate of polymerization, R<sub>p</sub>, increases from 1.2 × 10<sup>-5</sup> mol.L<sup>-1</sup>.s<sup>-1</sup> to 2.1 × 10<sup>-5</sup> mol.L<sup>-1</sup>.s<sup>-1</sup> for the increase in temperature from 45°C to 60°C at [Fe (III)] = 3.0 × 10<sup>-3</sup> M, [TU] = 0.04 M and [AM] = 0.4 M. The increase of rate with temperature is not very high. On the other hand in the presence of vermiculite, R<sub>p</sub> is much higher and it is sharply increased from 5.01 × 10<sup>-5</sup> mol.L<sup>-1</sup>.s<sup>-1</sup> to 14.91 × 10<sup>-5</sup> mol.L<sup>-1</sup>.s<sup>-1</sup> for the rise in temperature from 45°C to 60°C at [TU] = 0.04 M, [AM] = 0.4 M and [Fe(III)] = 3.0 × 10<sup>-3</sup> M. However, at lower concentrations of Fe(III) in homogeneous medium (~ 1.5×10<sup>-3</sup> M), the initial rate of polymerization at 50°C is close to that of heterogeneous medium reaction, but the intrinsic viscosity of the polymer is significantly much higher. Figure 3.2 and 3.3 show the extent of conversion as a function of polymerization time at various FeV concentrations. The figures

show that with the increase of FeV from 0.06 % to 0.2% the initial rate of polymerization increases, but at higher concentrations of FeV the initial rate of polymerization decreases. Figure 3.4 depicts the rate of polymerization as a function of TU concentration under constant monomer concentration of 0.4 M at pH 1.98. Metal ion concentration was kept fixed at  $1.5 \times 10^{-3}$  M. The influence of AM concentration on the polymerization rate was studied over a concentration range (0.30 M to 0.60 M) (TU and Fe(III) in FeV concentrations were kept at a constant value of 0.04 M and  $1.5 \times 10^{-3}$  M respectively; the temperature was 50°C, and the pH was  $2 \pm 0.1$ ). Figure 3.5 shows the extent of conversion as a function of polymerization time with the variation of monomer concentration. All the curves in this figure show similar trend with respect to conversion efficiency as a function of time except that at  $[AM] = 0.3$  M. Under this condition the reaction rate is substantially slow. At a AM concentration lower than 0.3 M, no significant yield results, which is due to either very few collisions per second or secondary recombination of isothiocarbamido radicals. In general, the monomer conversion rate was very fast at earlier stage of polymerization.

### Effect of Temperature

The effect of temperature on the rate of polymerization, polymer yield and molecular weight were investigated over a temperature range of 45°C to 60°C and the data are shown in the Tables 3.5 to 3.7.  $R_p$  as well as  $X_L$  increase with increasing polymerization temperature as shown in the Figure 3.6. The variation of molecular weight of the polymer as a function of AM, TU and FeV concentrations at different temperatures are shown in Figures 3.7-3.9 while the molecular weight of the polymer clearly increases with AM concentration (Figure 3.7), its variation as a function of TU and Fe(III) concentrations are rather complex (Figure 3.8 and 3.9). The plot of the logarithm of empirical rate constant  $R_p$  against the reciprocal of the absolute temperature yields the activation energy value of  $9.12 \times 10^3$  cal/mol to  $15 \times 10^3$  cal/mol (Figure 3.10 and 3.11).

**Table 3.5**

Polymerization of AM in aqueous medium (25 ml) in presence of 0.04 M TU  
and 0.1 % FeV and varying AM concentrations  
at different temperatures (pH 1.98)

[AM] mol.L <sup>-1</sup>	Temp. in °C	R <sub>p</sub> x10 <sup>5</sup> mol.L <sup>-1</sup> .s <sup>-1</sup>	X <sub>L</sub> in %	[η] ml.g <sup>-1</sup>	M <sub>v</sub> x10 <sup>-5</sup>	Non- extractable PAM(wt%)
.30	60	6.170	78	200	5.960	0.042
.40		10.67	82	343	12.22	0.124
.50		15.66	84	400	15.00	0.105
.60		8.110	78	410	15.50	0.157
.30	50	3.160	62	172	04.87	0.050
.40		5.750	84	404	15.20	0.125
.50		9.730	70	530	21.83	0.133
.60		13.01	85	628	27.38	0.162
.40	45	4.200	25	200	5.960	0.051
.50		6.400	76	519	21.25	0.124
.60		8.910	75	532	21.92	0.155

**Table 3.6**

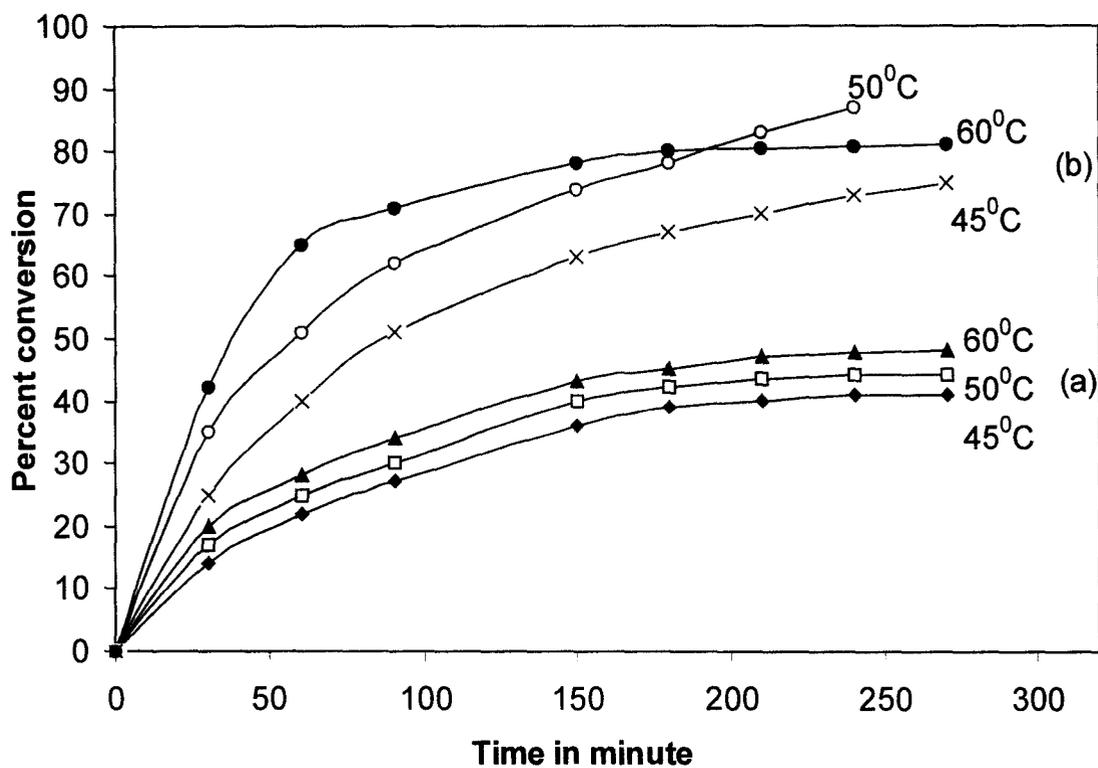
Polymerization of AM (0.04 M) in aqueous medium (25 ml) in presence of 0.1 % FeV and varying TU concentrations at different temperatures (pH 1.98)

[TU] mol.L <sup>-1</sup>	Temp. in °C	R <sub>p</sub> x10 <sup>5</sup> mol.L <sup>-1</sup> .s <sup>-1</sup>	X <sub>L</sub> in %	[η] ml.g <sup>-1</sup>	M <sub>v</sub> x10 <sup>-5</sup>	Non- extractable PAM(wt%)
.03	60	6.670	79	272	8.970	0.112
.04		10.67	82	343	12.22	0.124
.06		8.890	64	510	20.75	0.121
.08		18.46	87	261	8.490	0.118
.03	50	2.230	37	366	13.33	0.117
.04		5.750	84	404	15.20	0.125
.06		6.440	85	326	11.40	0.134
.08		7.780	93	430	16.50	0.175
.03	45	2.230	34	520	22.39	0.085
.04		4.200	25	200	5.960	0.051
.05		4.470	68	542	22.50	0.124
.08		5.490	71	555	23.22	0.115

**Table 3.7**

Polymerization of 0.5 M AM in aqueous medium (25 ml) in presence of 0.04 M TU and varying amounts of FeV at different temperatures (pH 1.98)

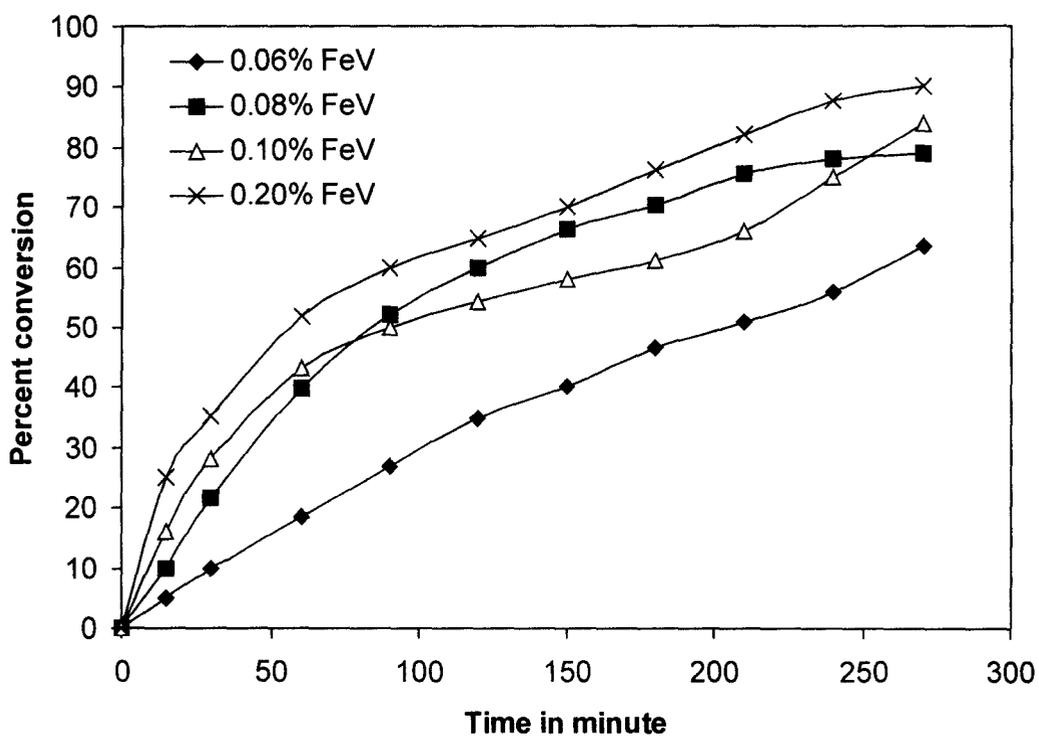
[FeV] in %	Fe(III) in FeV mmol.L <sup>-1</sup>	Temp. in °C	R <sub>p</sub> <sup>a</sup> x10 <sup>5</sup> mol.L <sup>-1</sup> .s <sup>-1</sup>	X <sub>L</sub> in %	[η] ml.g <sup>-1</sup>	M <sub>v</sub> x10 <sup>-5</sup>	Non- extractable PAM(wt%)
.05	0.75	60	20.0	94	210	06.35	0.045
.10	01.5		10.6	87	254	08.18	0.124
.20	03.0		14.9	79	282	09.41	0.128
.30	04.5		17.8	95	204	06.11	0.210
.70	10.5		13.3	66	201	05.99	0.204
.06	0.90	50	2.02	64	376	13.81	0.081
.08	1.20		5.33	79	318	11.05	0.090
.10	1.50		5.75	84	404	15.20	0.125
.20	03.0		7.94	90	395	14.75	0.123
.30	04.5		5.20	74	270	08.90	0.268
.40	06.0		4.12	49	352	12.65	0.315
.05	0.75	45	2.23	63	514	20.96	.0215
.10	01.5		4.20	74	342	12.17	0.051
.20	03.0		5.01	75	278	09.25	0.124
.30	04.5		6.30	88	216	06.60	.2151



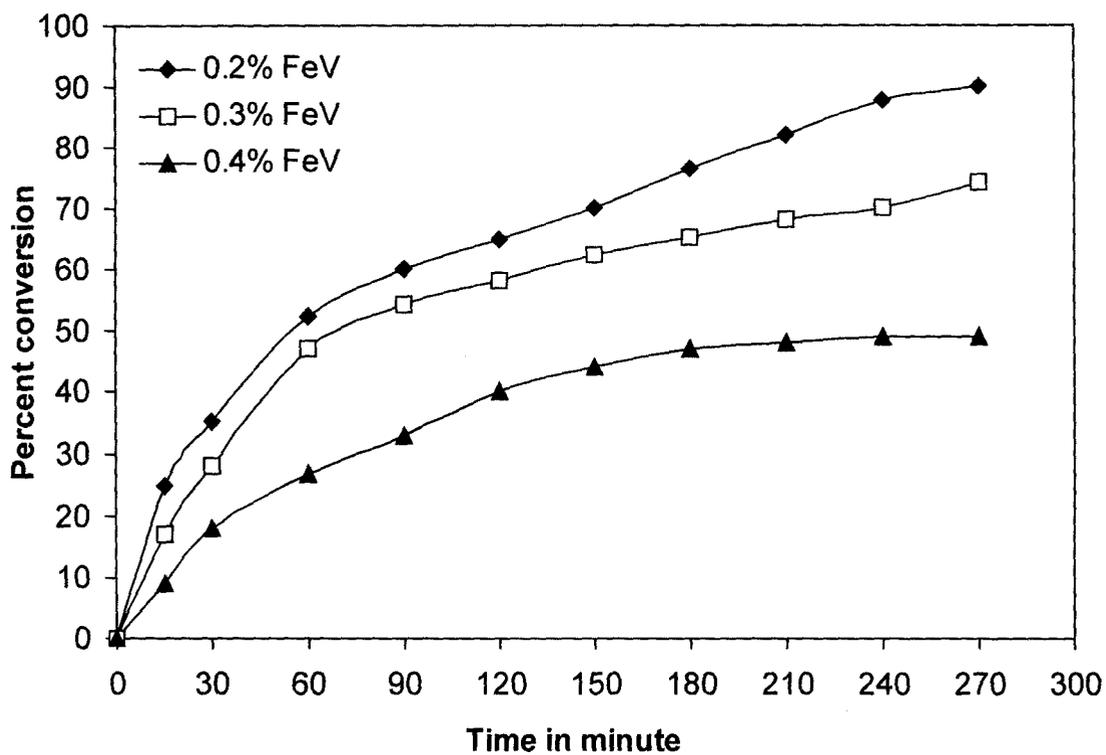
**Figure 3.1:** The effect of vermiculite on the course of polymerization

(a)  $[\text{Fe(III)}] = 3 \times 10^{-3} \text{ M}$ ,  $\text{FeV} = 0$ ,  $[\text{AM}] = 0.4 \text{ M}$ ,  $[\text{TU}] = .04 \text{ M}$ ,  $\text{pH} = 2.01$

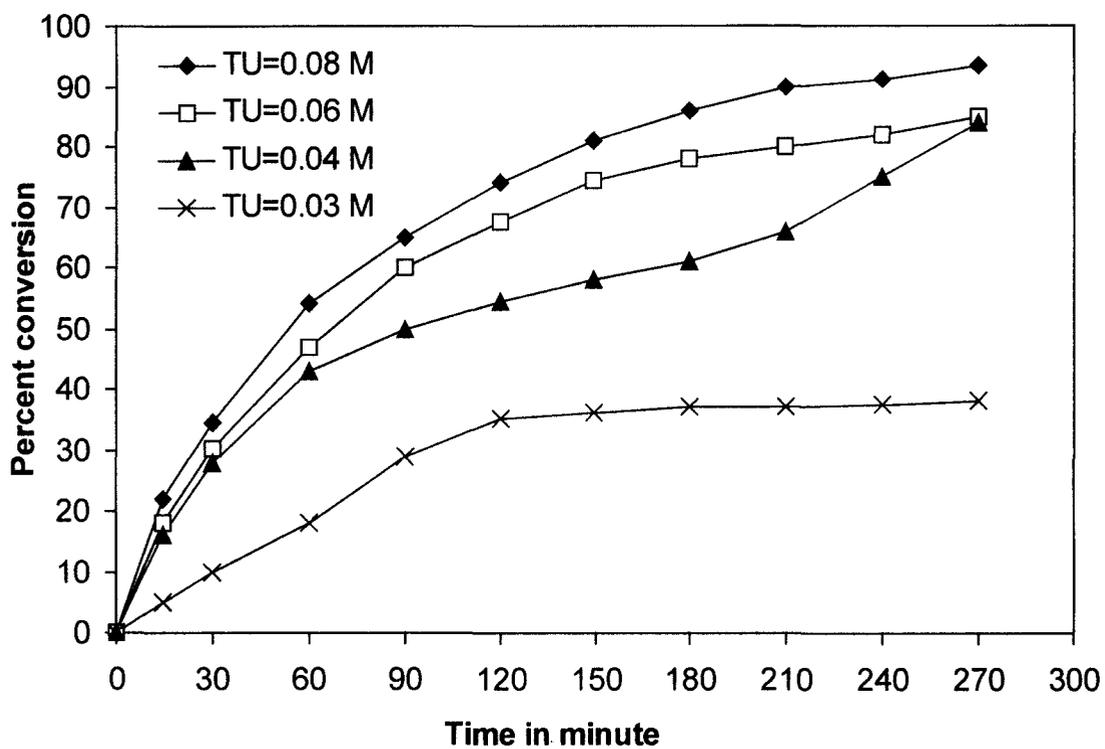
(b)  $[\text{Fe(III)}] = 3 \times 10^{-3} \text{ M}$ ,  $\text{FeV} = 0.2\%$ ,  $[\text{AM}] = 0.4 \text{ M}$ ,  $[\text{TU}] = .04 \text{ M}$ ,  $\text{pH} = 1.98$



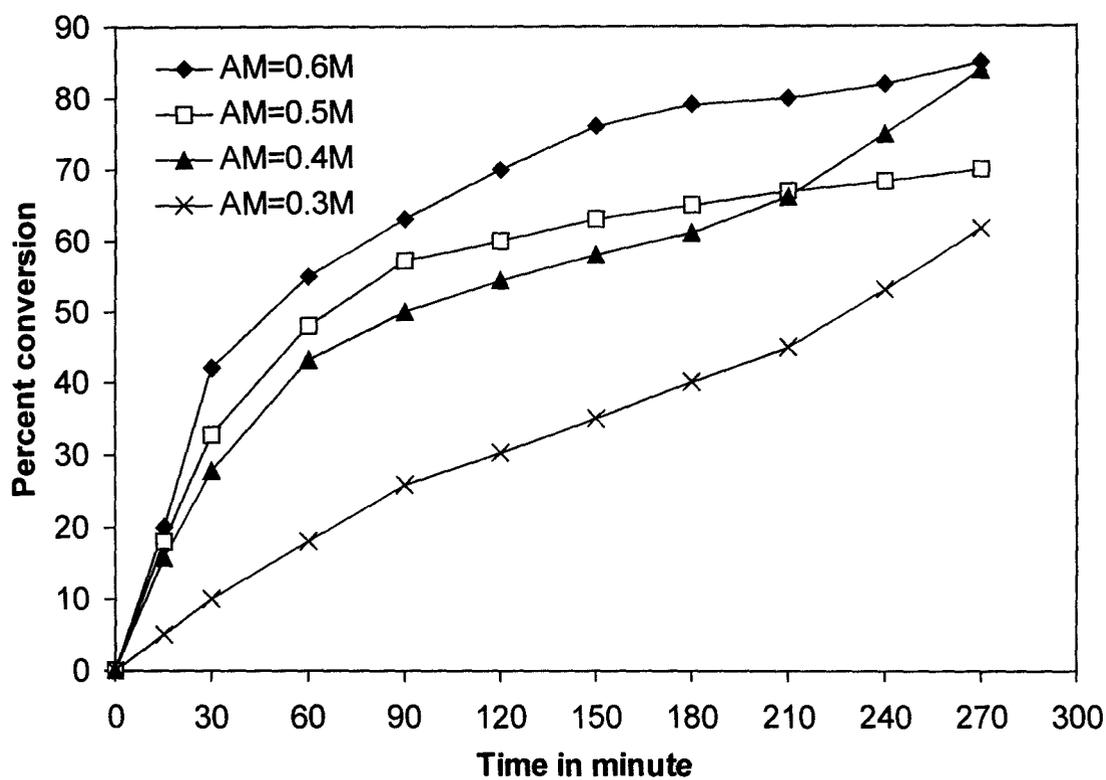
**Figure 3.2:** Time-conversion plots for the aqueous polymerization of AM with varied amount of FeV at 50°C: [AM] = 0.4 M, [TU] = 0.04 M



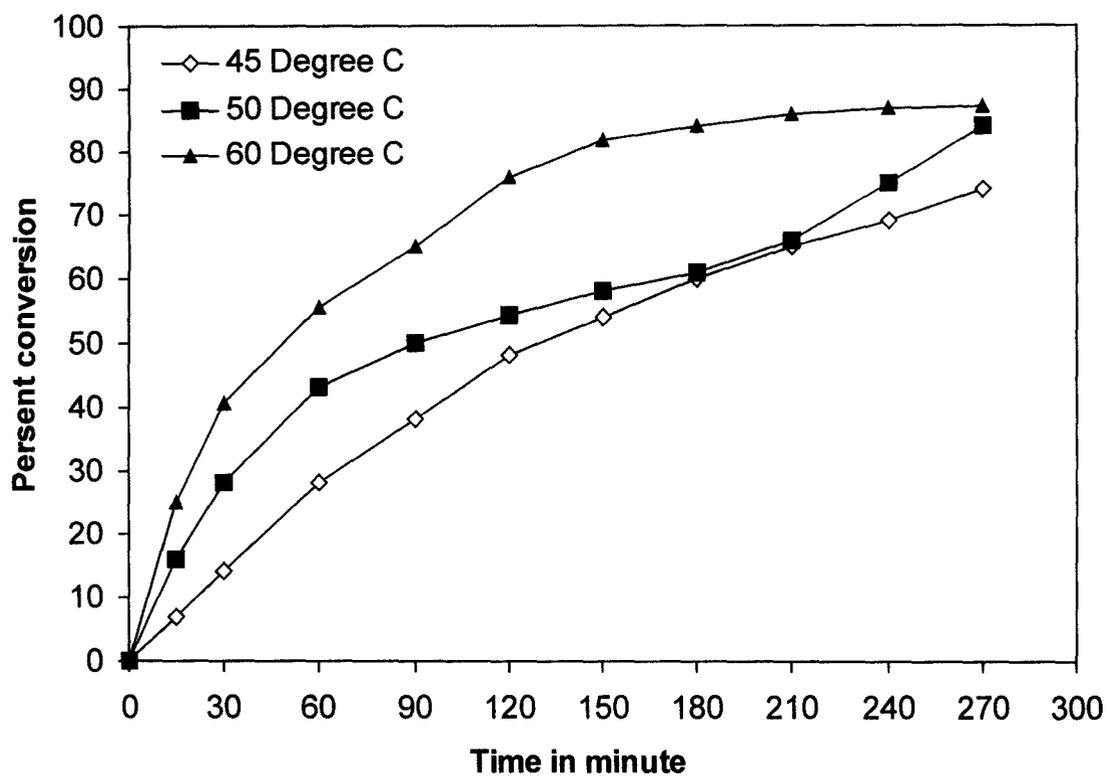
**Figure 3.3:** Time-conversion plots for the aqueous polymerization of AM with varied amount of FeV at 50°C: [AM] = 0.4 M, [TU] = 0.04 M



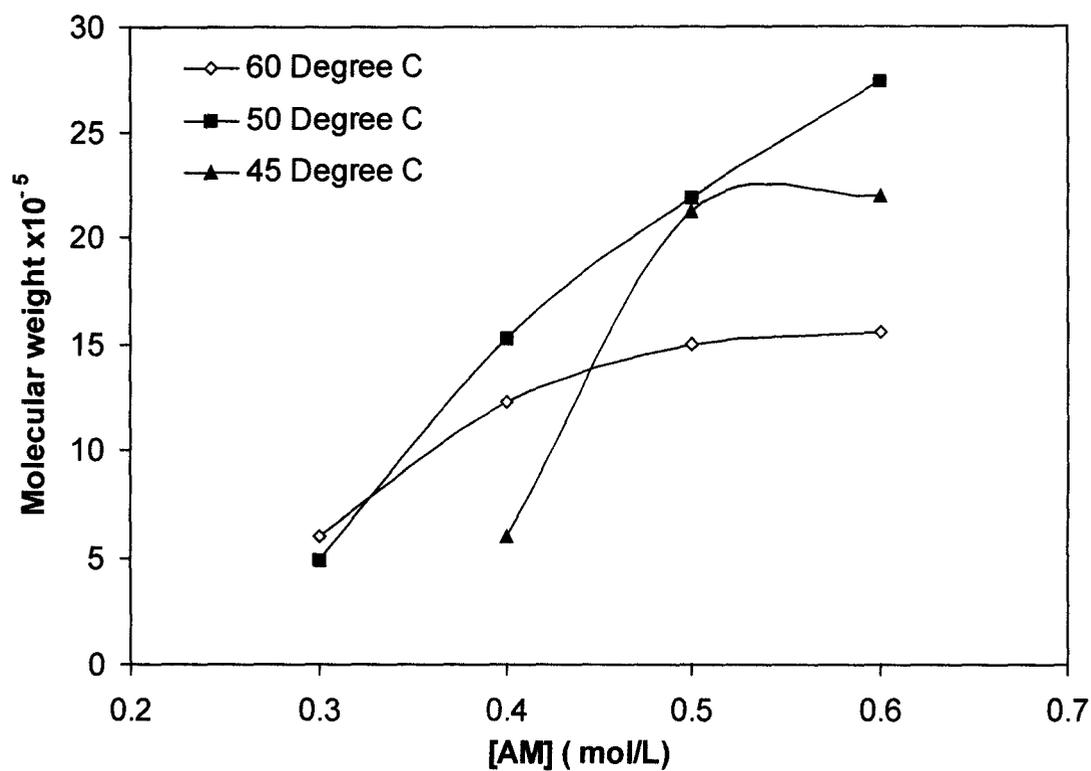
**Figure 3.4:** Time-conversion plots for the aqueous polymerization of AM with varied amount of TU at 50°C: [AM] = 0.4 M, [FeV] = 0.1%



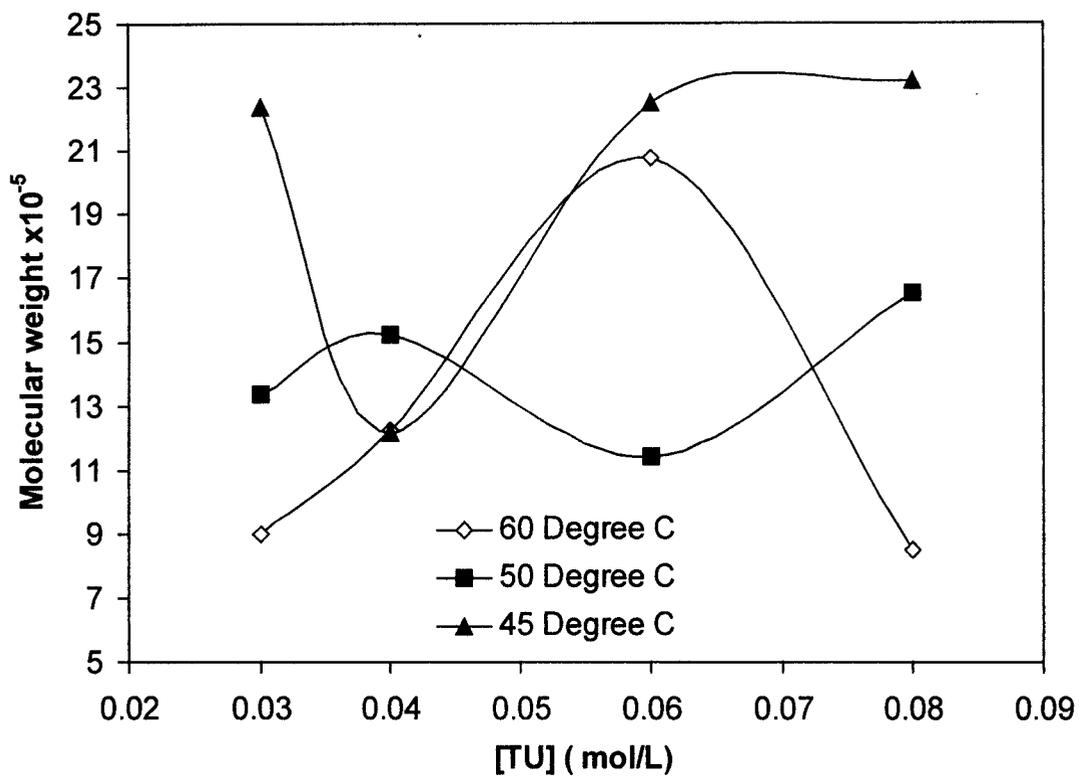
**Figure 3.5:** Time-conversion plots for the aqueous polymerization of AM with varied amount of AM at 50°C: [TU] = 0.04 M, [FeV] = 0.1%



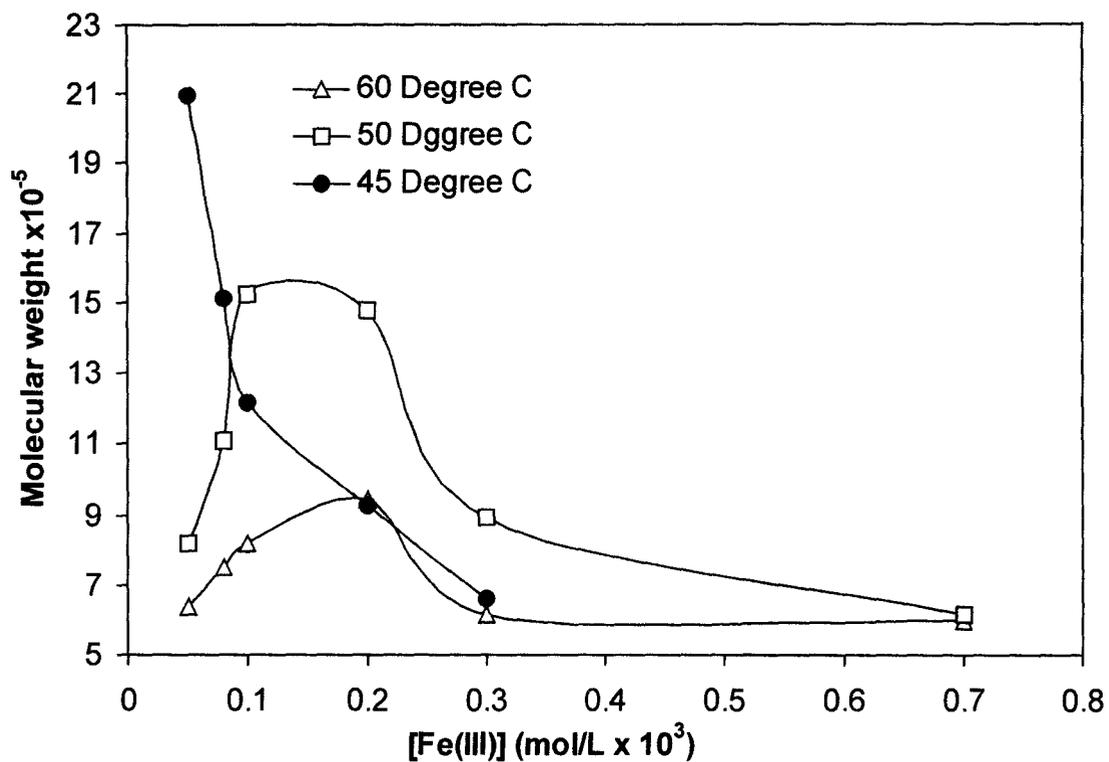
**Figure 3.6:** Time-conversion plots for the aqueous polymerization of AM with different temperature:  $[AM] = 0.4 \text{ M}$ ,  $[TU] = 0.04 \text{ M}$ ,  $[FeV] = 0.1\%$



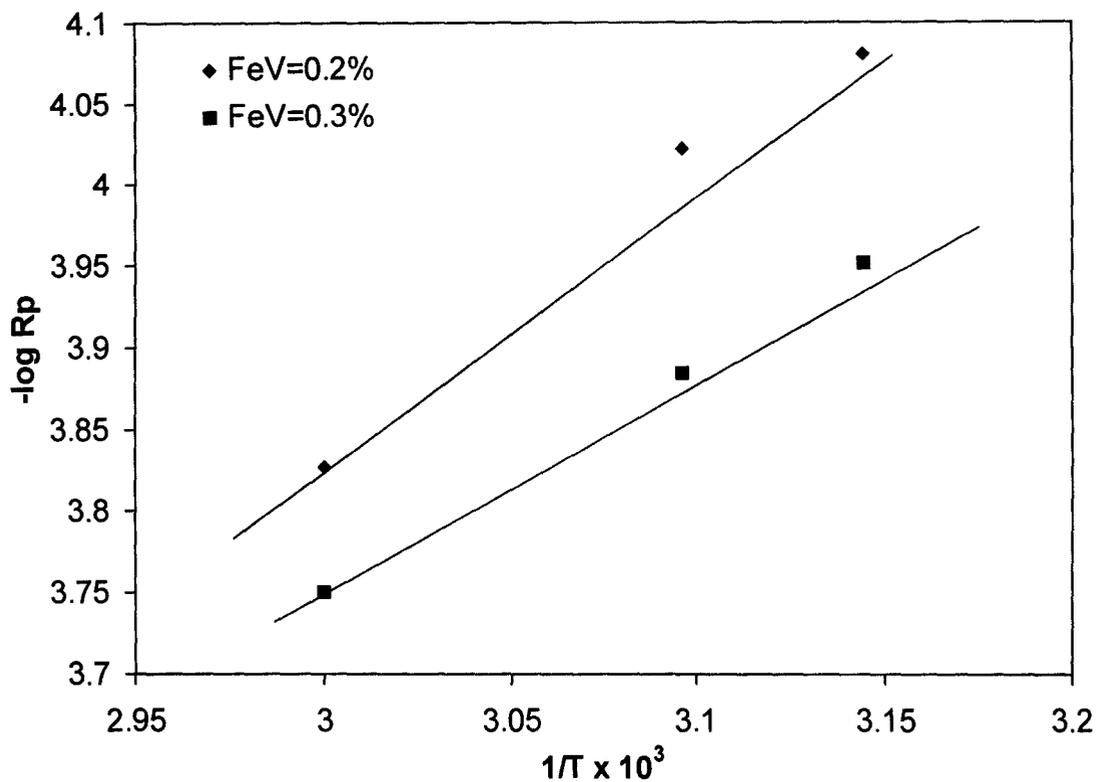
**Figure 3.7:** Plots of Molecular weight versus [AM] for polymerization of AM at different temperature, FeV = 0.1%, [TU] = 0.04 M



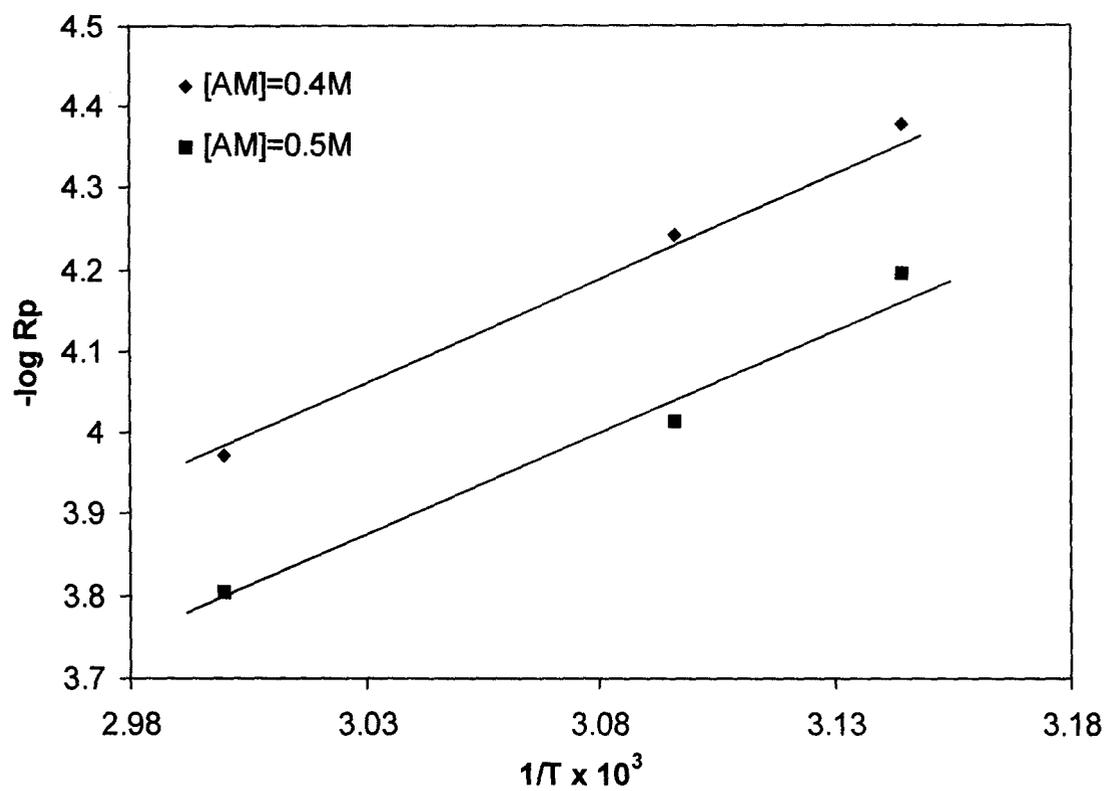
**Figure 3.8:** Plots of Molecular weight versus [TU] for polymerization of AM at different temperature, FeV=0.1%, [AM]=0.4M



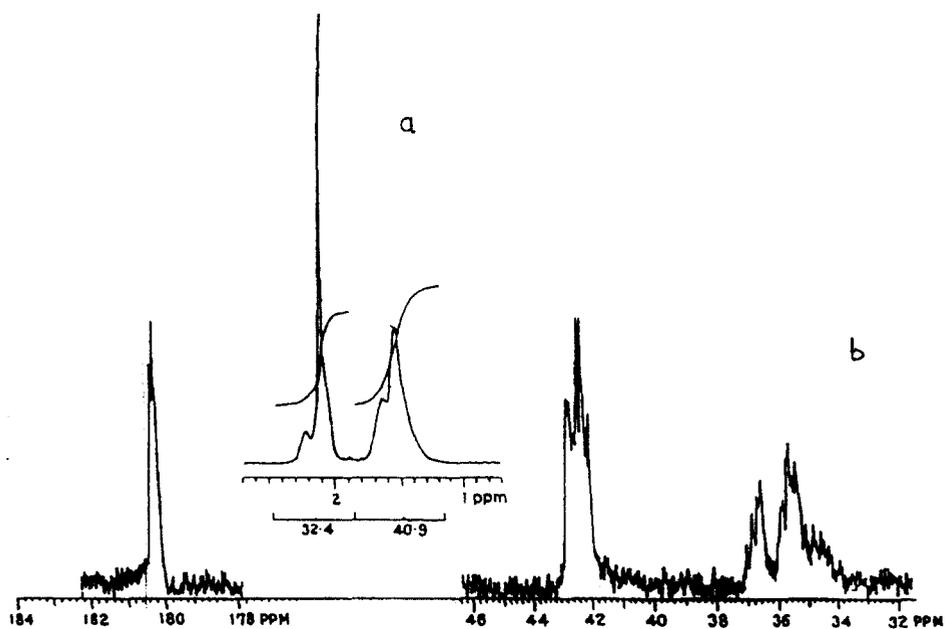
**Figure 3.9:** Plots of Molecular weight versus Fe(III) ion concentration in FeV for polymerization of AM at different temperature, [TU] = .04 M, [AM] = 0.4 M



**Figure 3.10:** Plots of  $-\log R_p$  versus  $1/T$  with different concentrations of  $\text{Fe(III)}$  ion in FeV for polymerization of AM,  $[\text{TU}] = .04 \text{ M}$ ,  $[\text{AM}] = 0.4 \text{ M}$



**Figure 3.11:** Plots of  $-\log R_p$  versus  $1/T$  with different concentrations of AM for polymerization of AM,  $FeV = 0.1\%$ ,  $[TU] = .04 M$



**Figure 3.12:**  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra of thiourea terminated polyacrylamide on vermiculite surface, (a)  $^1\text{H}$  nmr spectrum, (b)  $^{13}\text{C}$  nmr spectrum.

## **$^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of PAM**

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of polyacrylamide samples obtained from the polymerization on vermiculite surface by FeV-TU initiator are shown in Figure 3.12.  $^1\text{H}$  spectrum of polyacrylamide is not usually a well resolved spectrum and no special feature is apparent in the present spectrum except that of overlapping of a sharp line with chemical shift of 2.357 ppm near the  $-\text{CHCONH}_2$  position. This line in all probability represents the hydrogen from the isothiocarbamido end group of thiourea terminated PAM. The expanded  $^{13}\text{C}$  spectra showed methylene, methane and carbonyl carbons of head-to-tail polymer of acrylamide. The carbonyl carbon (181.8 ppm) splitting was small. The methine resonance (43.78 – 44.45) is a triplet, which further split, showing pentad sensitivity. The low field and high field triplet peaks may be assigned to rr (syndiotactic) and mm (isotactic) sequences respectively. The central peak corresponds to heterotactic sequences (mr+rm). The methylene carbon lines (36.37 – 38.43) also fall into three well-separated groups with 20 lines required by hexad sensitivity resolved. It seems apparent from the  $^{13}\text{C}$  spectra that Bernoulli statistics is followed and stereoregularity has not been observed. Both  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra of polyacrylamide are similar to those obtained in presence of montmorillonite microenvironment. However, the polymer trapped inside the interlayer spaces of vermiculite, which could not be extracted by washing with water may have such possibility of showing stereoregularity. Attempts are being made to extract these polymers in mild condition for further study.

## **Kinetics and Mechanism**

Polymerization mechanism and kinetics both are affected to a great extent due to the occurrence of the reaction in the mineral microenvironment resulting in the significant increase in the molecular weights and intrinsic viscosities of the polymers. The variation of the initial rate of polymerization as a function of monomer concentration in the presence of vermiculite is shown (double logarithm plot) in Figure 3.13 and also indicates that probably a

second order kinetics with respect to monomer is followed. A rate dependence of second order and above on monomer concentration was also observed earlier in heterogeneous and precipitation polymerization of acrylamide and various interpretations, including 'cage effect' [123] and 'complex theory' [124] were proposed to account for the significant departure from first order kinetics. The 'cage effect' suggests that when an initiator decomposes into two radicals, there is a formation of a potential barrier by the surrounding solvent molecules, which prevent their immediate diffusion and favours their destruction by mutual recombination. The 'complex theory' is based on the formation of a complex between the initiator and the monomer, the rate of initiation then being determined by the rate of decomposition of the complex. The 'cage effect' seems to be a good conceptual starting point in explaining the high monomer exponent, which has been observed in the present system. Figure 3.14 shows that with the increase of FeV concentration the initial rate of polymerization increases linearly at three different temperatures (i.e. 45°C, 50°C, 60°C). The slope of the plot of  $\log R_p$  vs  $\log[\text{Fe(III)}]$  is almost 0.50, which indicates that the rate of polymerization is approximately 0.5 order with respect to metal ion oxidant. Not all the points fall on the same line (in the logarithm plot) because of the heterogeneous reaction mixtures. Figure 3.15 shows the rate of polymerization as a function of variation of TU under constant monomer concentration of 0.4 M at pH = 1.98. Metal ion concentration remains fixed at  $1.5 \times 10^{-3}$  M. The relationship of polymerization rate with TU concentration was obtained from the slope of the plot of  $\log R_p$  versus  $\log [\text{TU}]$ , which yielded a order of 1.0 with respect to [TU]. At three different temperatures, viz., 45°C, 50°C and 60°C, the slope remains almost identical indicating first order kinetics throughout. This value is, however, different from that of homogeneous reaction for which an order of 2.0 was reported to follow [125].

To rationalize the experimental results and to predict a possible mechanism for the seemingly complex polymerization reaction occurring in the mineral microenvironment, the following assumptions are made [126].

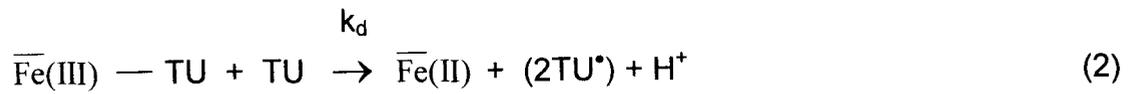
1. Intercalated TU reacts fast with Fe(III) ions of the vermiculite layered spaces to form reactive Isothiocarbamido primary radical via an intermediate complex. The decomposition of the complex is the rate-determining step [79,127].
2. In the acidic and metal ion exchanged aqueous vermiculite system, 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 [128]. The protonated as well as the complexed amide pairs are at first equilibrium with unprotonated and free amide molecules, respectively, which are defined by a protonation constant or a formation constant. In view of high monomer exponent, it is certain that it must have resulted in part from the involvement of monomer in the initiation step, where such monomer pairs are entailed.
3. Since the reactive TU radicals are formed as pairs, assumption of the 'Cage effect' seems to be conceptually appropriate. The initiation step involves collision of the 'amide pairs' with caged TU radicals at the wall of the cage and random diffusion of the radicals from the cage and their secondary recombination are less significant in comparison to the rate of dimerization of charged radicals or their reaction with acrylamide.

Various steps of reactions are shown below:

Initiation



[ $\overline{\text{Fe(III)}}$  stands for Fe(III) ions in the interlayer space of vermiculite]



Propagation



Termination



(Caged species are enclosed in brackets)

Using the equation (1) and (2) the consumption rate of Fe(III) concentration is given below.

$$-\frac{d}{dt}[\overline{\text{Fe}}(\text{III})] = \frac{k_d K [\overline{\text{Fe}}(\text{III})][\text{TU}]^2}{1 + K[\text{TU}]} \quad (9)$$

Now, assuming that the rate of formation of TU radicals is exactly equal to the rate of disappearing intercalated  $\overline{\text{Fe}}(\text{III})$  ions, we obtain, (considering the steady state of TU radical).

$$\frac{k_d K [\overline{\text{Fe}}(\text{III})][\text{TU}]^2}{1 + K[\text{TU}]} = k_i K^1 [\text{TU}^\bullet][\text{M}]^2 + \frac{k'_t [\text{TU}^\bullet][\overline{\text{Fe}}(\text{III})]}{1 + K[\text{TU}]} + k''_t [\text{TU}^\bullet] \quad (10)$$

( $K^1 = [\text{M}_2\text{H}^+]/[\text{M}]^2$ ) is the apparent protonation constant at a fixed pH (or a formation constant)

$$[\text{TU}^\bullet] = \frac{k_d K [\overline{\text{Fe}}(\text{III})][\text{TU}]^2}{\left( k_i K^1 [\text{M}]^2 + \frac{k'_t [\overline{\text{Fe}}(\text{III})] + k''_t}{1 + K[\text{TU}]} \right) (1 + K[\text{TU}])} \quad (11)$$

Again considering the steady state of  $\text{M}_n^\bullet$  radical

$$k_i K^1 [\text{TU}^\bullet][\text{M}]^2 = k_t [\text{M}_n^\bullet]^2 \quad (12)$$

$$[\text{TU}^\bullet] = (k_t [\text{M}_n^\bullet]^2) / (k_i K^1 [\text{M}]^2) \quad (13)$$

Equating RHS of equation (11) and (13)

$$[\text{M}_n^\bullet]^2 = \frac{k_i K^1 K k_d [\overline{\text{Fe}}(\text{III})][\text{TU}]^2 [\text{M}]^2}{k_t \left( k_i K^1 [\text{M}]^2 + k_i K^1 K [\text{M}]^2 [\text{TU}] + k'_t [\overline{\text{Fe}}(\text{III})] + k''_t (1 + K[\text{TU}]) \right)} \quad (14)$$

$$[M_n^*] = \frac{(k_i K^1 K k_d)^{\frac{1}{2}} [\overline{\text{Fe(III)}}]^{\frac{1}{2}} [\text{TU}][\text{M}]}{k_t^{\frac{1}{2}} (k_i K^1 [\text{M}]^2 + k_i K^1 K [\text{M}]^2 [\text{TU}] + k_t' [\overline{\text{Fe(III)}}] + k_t'' (1 + K [\text{TU}]))^{\frac{1}{2}}} \quad (15)$$

$$R_p = k_p [M_n^*] [\text{M}]$$

$$R_p = \frac{k_p (k_i K^1 K k_d)^{\frac{1}{2}} [\overline{\text{Fe(III)}}]^{\frac{1}{2}} [\text{TU}][\text{M}]^2}{k_t^{\frac{1}{2}} (k_i K^1 [\text{M}]^2 + k_i K^1 K [\text{M}]^2 [\text{TU}] + k_t' [\overline{\text{Fe(III)}}] + k_t'' (1 + K [\text{TU}]))^{\frac{1}{2}}} \quad (16)$$

If the oxidative termination (step 7) is assumed to be insignificant in comparison with the dimerization rate of caged radicals, equation (16) reduces to:

$$R_p = \frac{k_p (k_i K^1 K k_d)^{\frac{1}{2}} [\overline{\text{Fe(III)}}]^{\frac{1}{2}} [\text{TU}][\text{M}]^2}{k_t^{\frac{1}{2}} (k_i K^1 [\text{M}]^2 + k_i K^1 K [\text{M}]^2 [\text{TU}] + k_t'' (1 + K [\text{TU}]))^{\frac{1}{2}}} \quad (17)$$

The interpretation of high kinetic order of the monomer finally hinges on the dominance of a reaction between caged radicals and those of monomers with the radical at the cage wall. Although the concentration of the monomer and TU in solution phase were fixed mostly at 0.40 mol. L<sup>-1</sup> and 0.04 mol. L<sup>-1</sup> respectively, the concentration of intercalated species must be much lower, specially due to the presence of water molecules in the interlayer spaces. Thus, the concentrations, [M] and [TU], in the vermiculite gel phase should be

$$[\text{M}] = L_o^a \theta_m = \frac{L_o^a K_m^a [\text{M}]_s}{1 + K_{tu}^a [\text{TU}]_s + K_m^a [\text{M}]_s} \quad (18)$$

$$[\text{TU}] = L_o^a \theta_m = \frac{L_o^a K_{tu}^a [\text{TU}]_s}{1 + K_{tu}^a [\text{TU}]_s + K_m^a [\text{M}]_s} \quad (19)$$

(subscript s denotes solution)

( $L_o^a$  and  $\theta$  are the total active sites in unit mass of vermiculite and the fraction of total sites occupied by such species respectively;  $K_m^a$  and  $K_{TU}^a$  are the selectivity coefficients).

The denominators of equations (18) and (19) are nearly unity. By appropriate substitution of  $[M]$  and  $[TU]$  in equation (17) and considering the dominance of the last term of the denominator over others, the equation becomes

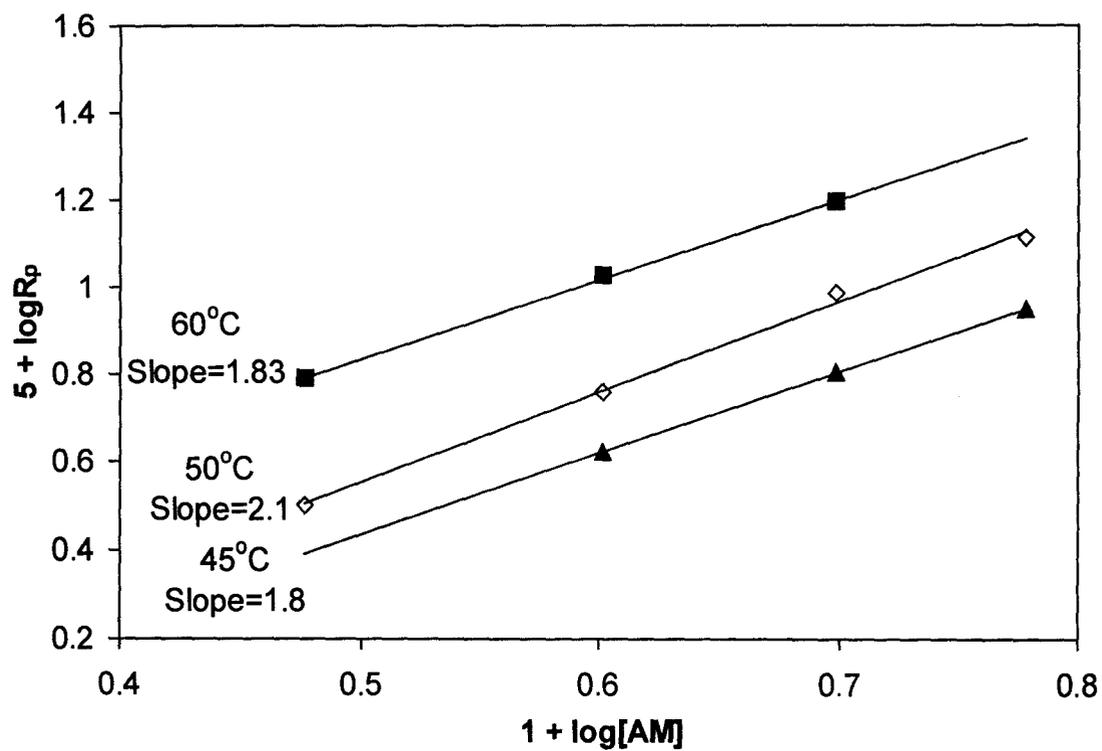
$$R_p = \frac{k_p \left( \frac{k_d k_i K K^1}{k_t' k_t''} \right)^{\frac{1}{2}} K_{tu}^a (K_m^a)^2 (L_o^a)^3 [\overline{Fe(III)}]^{\frac{1}{2}} [TU]_s [M]_s^2}{\left( 1 + K L_o^a K_{tu}^a [TU]_s \right)^{\frac{1}{2}}} \quad (20)$$

(Values of  $K_m^a$  (or  $K_{TU}^a$ ),  $L_o^a$  and  $K$  are of the order of  $10^{-2}$ ,  $2 \text{ mmol.g}^{-1}$  and  $2 \text{ L.mol}^{-1}$  respectively [126]. Small values of above parameters including that of  $K^1$  ensure that terms involving quadratic and higher concentration terms are very small in the present conditions [129,130].

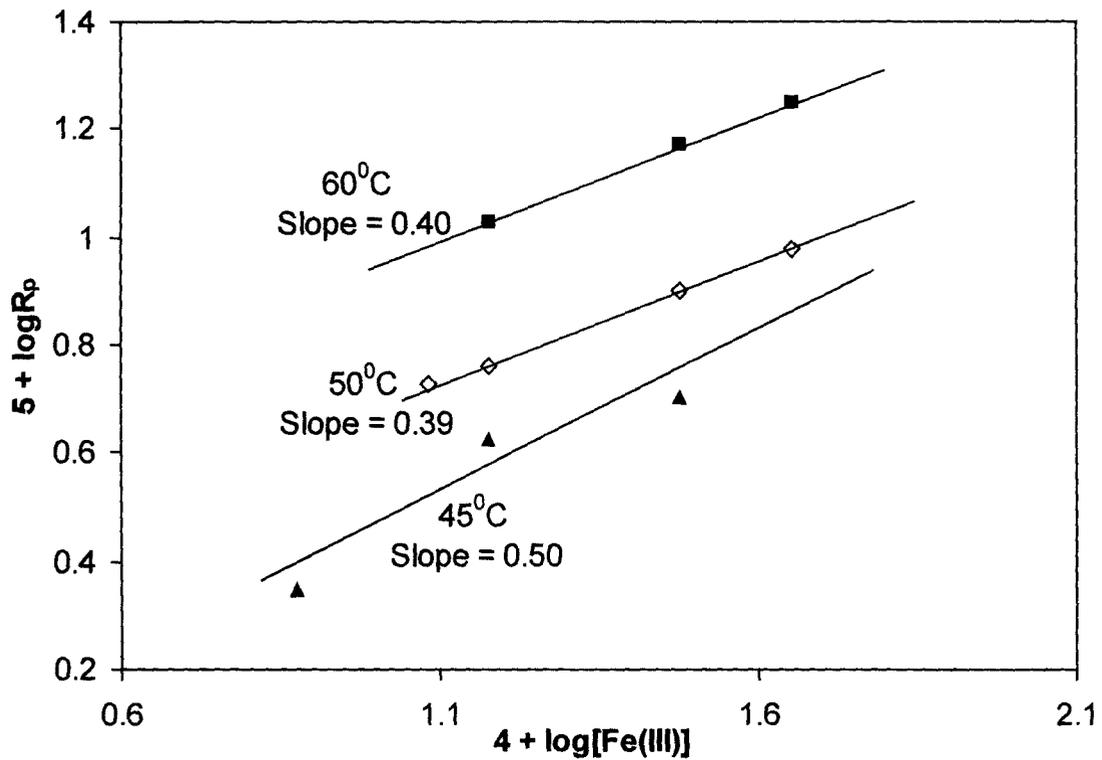
Further inspection of equation (20) shows that the value of  $K L_o^a K_{TU}^a [TU]_s$  in the denominator varies from  $10^{-5}$  to  $10^{-6}$  for the variation of aqueous TU concentration from 0.05 to 0.005  $\text{mol.L}^{-1}$ . This implies that the rate equation under the present condition is reduced to

$$R_p = k_p \left( \frac{k_d k_i K K^1}{k_t' k_t''} \right)^{\frac{1}{2}} K_{tu}^a (K_m^a)^2 (L_o^a)^3 [\overline{Fe(III)}]^{\frac{1}{2}} [TU]_s [M]_s^2 \quad (21)$$

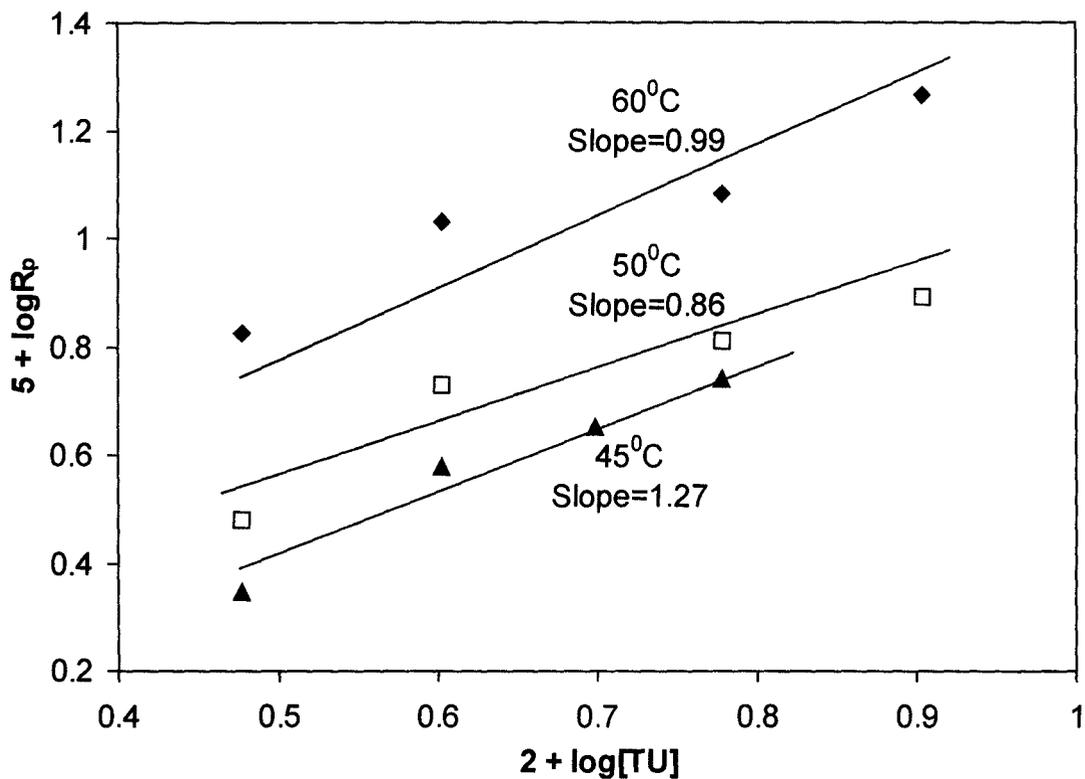
Reviewing the above result, it is found that equation (21) could satisfactorily account for the present behavior of the Fe(III)-TU initiated acrylamide polymerization exhibited in the aqueous vermiculite layered spaces.



**Figure 3.13:** Logarithm plot of  $R_p$  versus  $\log [AM]$ ,  
 $[Fe(III)] = 1.5 \times 10^{-3} M$ ,  $[TU] = 0.04 M$ ,  $FeV = 0.1\%$



**Figure 3.14:** Logarithmic plot of  $\log [\text{Fe(III)}]$  versus  $\log R_p$ ,  $[\text{TU}] = 0.04 \text{ M}$ ,  $[\text{AM}] = 0.4 \text{ M}$ : (  $[\text{Fe(III)}]$  represents moles of ferric ions in the vermiculite gel phase )



**Figure 3.15:** Logarithmic plot of  $R_p$  versus  $\log [TU]$ ,  
 $Fe(III) = 1.5 \times 10^{-3} M$ ,  $[AM] = 0.4 M$ ,  $FeV = 0.1\%$

## **3.2 COPOLYMERIZATION OF ACRYLAMIDE WITH DIACETONE ACRYLAMIDE BY Fe(III)-THIOUREA REDOX COUPLE ON VERMICULITE SURFACE**

### **3.2.1 INTRODUCTION AND REVIEW OF PREVIOUS WORK**

The current level of development in the manufacture of synthetic copolymers has been derived from the prior knowledge and understanding of the chemistry of natural copolymers, such as polysaccharides formed from pentose and hexose sugars, proteins as condensation products of different amino acids, and DNA and RNA formed by the reaction of purine and pyrimidine bases with inorganic phosphate. These natural copolymers play significant roles in the structure and functions of various plant and animal tissues.

The main goal on copolymer production is to obtain polymers with improved physico-mechanical properties (e.g. processibility, elastic modulus, thermal and electrical conductivity, etc) [131]. Copolymers of acrylamide have shown a number of properties lending themselves to a variety of industrial applications. Of growing importances are those related to use as water-soluble viscofiers and displacement fluids in enhanced oil recovery [132-137].

Two of the critical limitations of polyelectrolytes are, however, loss of viscosity in the presence of mono or multivalent electrolytes (viz. NaCl, CaCl<sub>2</sub> etc.) and ion binding to the porous reservoir rock substrates. Copolymers of acrylamide and acrylates can be synthesized by several methods including those of solution [138-149] and emulsion [150-153] polymerizations. The physical properties of the copolymers in some cases, are dependent on the method of preparation. The copolymers of AM with sodium acrylate in aqueous ammonium persulphate solution was conducted at 70°C for 60 min. producing a honeylike copolymer which had molecular weight  $1.25 \times 10^6$  as reported by Soltez and co-workers [138]. Cationic free radical copolymers of acrylamide with dimethylaminoethyl methacrylate and dimethylaminoethyl

acrylate had been prepared by Baade and Hunkeler [139] with azocyano valeric acid and  $K_2S_2O_8$  at 45°C–60°C. Lafuma and Durand have found that during random copolymer formation of AM and a quaternary ammonium acrylate monomer, the cleavage of the ester function occurred in mild alkaline medium with a simultaneous inter-chain reaction resulting in imide group formation [140]. Lavrov and co-workers have reported that copolymerization of 2-hydroxyethyl methacrylate with AM in aqueous solution in the presence of  $(NH_4)_2S_2O_8$ -ascorbic acid redox catalyst preceded without the gel effect characteristic of bulk polymerization [141]. The reactivity ratio of the dimethylamidoethyl methacrylate methyl chloride salt with AM at 54°C were 1.54 and 0.30 respectively when the redox azo-compounds were used as catalyst [142]. The molecular weight of copolymers of auxin-containing monomers with AM was determined to be in the range of  $5.5 - 18.0 \times 10^4$  when a 4-pyrrolidinopyridine and dichloro-hexyl-carbodiimide [143] catalysts were used. For AM-Na-acrylate copolymer, prepared in aqueous solution at room temperature and at pH 7.4 - 12.1, the reactivity ratios were 0.9-1.18 and 0.32-0.48 respectively [144]. McCormick and Salazar have reported that the increasing randomness in the copolymers of acrylamide with Na-3-acrylamido-3-methylbutanoate is observed if prepared in NaCl solution rather than in distilled water [146]. The polyelectrolytes had inherent hydrogen bonding capacity and pseudo plasticity and exhibited large dimension in aqueous solution [147]. In inverse microemulsion copolymerization of AM with methylacrylate initiated with AIBN was a typical "dead-end" polymerization [150]. In inverse emulsion polymerization method, incorporation of high hydrophile-lyophile balance coemulsifier in addition to the water-in-oil type main emulsifier increased the rate of polymerization significantly. Free radical copolymerization of AM with butylacrylamide or isopropyl methacrylate in the presence of AIBN in DMF at 60°C was investigated by Srinivasula, Rao and co-workers [151,152]. The chemical structures of random copolymers of AM with Na-2-sulfoethylmethacrylate in dextran were determined by McCormick in order to gain a more complete understanding of the structure–property relations and performance under simulated field conditions encountered in enhanced oil recovery [153]. Homo and copolymer of AM and acrylic acid (AAc) were synthesized by Rakshit and co-workers by free radical solution

polymerization technique in which hydrogen peroxide, potassium persulphate and benzoylperoxide were used as initiators [154]. The reactivity ratios of AM ( $r_1$ ) and AAc ( $r_2$ ) were determined as 0.427 and 0.947 respectively by Kelen-Tüdös method and 0.463 and 1.092 respectively by Fineman-Ross method. Feed ratios of the monomers were 85:15 (w/w), 65:35 (w/w), and 50:50 (w/w), of AM and AAc respectively for the synthesis of copolymers. Water-soluble copolymers of AM with methacrylamide were prepared by Hocking and co-workers using  $K_2S_2O_8$  as the initiator [155]. These polymers were characterized by traditional fourier transform photoacoustic infrared,  $^{13}C$  NMR, and chemical analysis technologies. These give a good qualitative picture of the effect of the introduction of the backbone methyl group on the hydrodynamic volumes of the copolymer products. Candau and co-workers prepared copolymers of AM and sodium acrylate of various compositions by free radical polymerization initiated at 20°C by irradiation from a source of ultra violet light in microemulsions stabilized by a nonionic emulsifier [156]. McCormick and co-workers prepared copolymers of acrylamide with 6-(2-acrylamido-2-methylpropyldimethylammonio) hexanoate (AMPDAH) in an aqueous NaBr solution in which feed ratios of AM and AMPDAH were varied from 98.5:2.5 to 0:100 mol %. The polymerizations were carried out to 20-30 % conversion and copolymer compositions were determined with  $^{13}C$  NMR. The reactivity ratios determined from the nonlinear least-square method gave values of  $r_1 = 0.98$  and  $r_2 = 0.85$ , indicating random incorporation of the comonomers into the final copolymer [157].

The synthesis and characterization of copolymers of AM with N-alkylacrylamide were investigated by McCormick and co-workers in aqueous solution utilizing Na-dodecyl sulphate as a surfactant and  $K_2S_2O_8$  as the initiator [158]. A remarkable increase in apparent viscosity was observed at low mol fractions of N-alkylacrylamide in the copolymer at a critical concentration, which is a function of alkyl chain length in the monomer and copolymer molecular weight. The viscosity behaviour is interpreted in terms of a concentration dependent model involving interchain hydrophobic association in aqueous solution [158]. The copolymer microstructures and reactivity ratios of copolymers of AM with N-(1,1-dimethyl-3-oxo-butyl)

acrylamide were studied by McCormick and Blackmon and the value of  $r_1r_2$  determined to be 2.20 [159]. The copolymer of AM with N-(1,1-dimethyl-3-oxo-butyl)acrylamide yielded a  $r_1r_2$  value of 0.75 and the copolymer of AM with N,N-dimethyl acrylamide provided  $r_1r_2$  value of 0.86 as reported by McCormick and Chen [1]. Monoazeotropic and non ideal copolymers were formed during copolymerization of methylmethacrylate with AM, N-methylacrylamide and N,N-dimethylacrylamide in 1,4-Dioxane solution at 65°C in presence of AIBN as initiator [160]. Low molecular weight water-soluble copolymers of AM with itaconic acid, methacrylic acid and acrylic acid were prepared in the presence of  $K_2S_2O_8$  and thioglycerine by Sumi and co-workers [161]. Granular copolymers of ethylacrylate (EAC) and acrylonitrile (ACN) were prepared by Thomas with dispersed bentonite when EAC and ACN were dissolved in ethanol and heated under reflux condition with benzoyl peroxide for 6 hours [162]. The copolymerization of methyl methacrylate with acrylonitrile and methacrylonitrile were studied by Bhattacharya in the presence of hydrogen-montmorillonite(HM)-thiourea redox couple [163]. Simionescu and co-workers prepared high molecular weight AM-co-2-acrylamido-2-methyl propane sulfonic acid (AMPS) copolymers by plasma-initiated copolymerization in water solutions [164]. The reactivity ratios determined by Kelen-Tüdös method, were shown to be  $r_1=1.04$  and  $r_2= 0.41$ . Some microstructural aspects of the copolymers are also presented by the authors. More recently McCormick and Chen synthesized random copolymers of AM with Sodium-2-sulphoethyl methacrylate and with sodium-2-acrylamido-2-methylpropene sulphonate in aqueous solutions utilizing persulphate as initiator. Copolymer compositions were determined by elemental analysis and by infrared spectroscopic method. Monomer reactivity ratios were calculated using Fineman-Ross, Kelen-Tüdös, and/or Mayo-Lewis techniques. The copolymer microstructures, including mean square length distributions, were calculated from reactivity ratio values [165].

Ktritskaya and Ponomarev studied the possibility for initiating AM and acrylic acid polymerization in acidic solutions in contact with metal surfaces of Mg and Al [166]. They observed the maximum rate of polymerization to be 2 wt% per minute and established the occurrence of quadratic termination of

growing chains. Ebril and Uyan synthesized copolymers of itaconic acid and acrylamide [167]. Homopolymers of itaconic acid (IA) and its copolymers with acrylamide (IA-AM) were synthesized using either ceric ammonium nitrate  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  in combination with nitrilotriacetic acid (NTA) or potassium persulphate at pH 1 as initiators. The chain structures of the resulting products have been studied by FTIR spectroscopy. It is concluded from a comparison of spectroscopic results with gravimetric and viscometric data that the depression of yields and viscosity numbers in the case of Ce(IV)-NTA redox pair result from interactions between the constituents of the redox initiator and IA. The graft copolymerization of methylmethacrylate (MMA) onto starch with potassium ditelluratocuprate(III)-starch redox system as initiator was studied in alkaline medium by Yinghai and co-workers [168]. The grafting parameters have been determined as a function of temperature, ratio of monomer to starch, initiator concentration, and the pH. The structure of the graft copolymers was confirmed by FTIR, X-ray diffraction, and scanning electron microscope (SEM). Kurenkov and co-workers studied the kinetics of copolymerization of acrylamide with magnesium, calcium, and strontium-2-acrylamido-2-methylpropanesulfonates in aqueous solutions in the presence of potassium persulphate-sodium hydrosulfite redox initiating system at pH 9 at 50°C [169]. Importance of the study lies in the fact that at least one of the above copolymers has already shown some promises by not losing its solution viscosities in the presence of added electrolytes [170]. Block copolymers are macromolecules comprising of chemically dissimilar and terminally connected segments. Novel block copolymers of poly (ethylene glycol)(PEG) with various vinyl monomers namely acrylonitrile, acrylamide, methyl methacrylate and methacrylic acid were synthesized using Ce(IV)-PEG and Mn(III)-PEG redox system in aqueous acidic medium [171].

In the present work attempts have been made to prepare water soluble copolymers of AM with N-(1,1-dimethyl-3-oxybutyl) acrylamide (commonly referred to as diacetone acrylamide, DAAM) on the vermiculite surface by interlayer trapped Fe(III) ions in the presence of TU. Objective of the present study is two fold. (1) To examine whether the copolymerization reaction could be initiated in the interlayer space of vermiculite with a redox initiator (viz.,

Fe(III)-TU) system. (2) To prepare copolymers with high molecular weight and large hydrodynamic volume. The success in copolymerization would result in relatively pure copolymer without subsequent solvent extractions. Moreover, the microenvironment of the clay mineral may control the structure and physico-chemical property of the copolymer. Present part of this chapter deals with the studies on copolymerization of AM with DAAM. The microstructures and reactivity ratios of the copolymers are reported.

### **3.2.2 EXPERIMENTAL**

#### **Materials and purification**

The purification techniques of acrylamide (AM) (reagent grade, Fluka) and thiourea (Merck) were discussed in previous section (3.1.2). Method of preparation and characteristics of Fe(III)-vermiculite (FeV) were similar to those as already mentioned in section (3.1.2). N-(1,1-dimethyl-3-oxybutyl)acrylamide commonly known as diacetone acrylamide (DAAM) (reagent grade, Fluka) was used as received.

#### **Polymerization**

The copolymerization (in absence of crosslinker) of AM with DAAM was conducted in aqueous solution at 50°C at pH ~2 using 0.1%(w/v) of FeV and 0.04 M of thiourea as the initiator. Table 3.9 lists reaction parameters for five series of reactions in which the ratio of the monomers in the feed and reaction times were varied. A specified amount of DAAM dissolved in distilled water was added to the mixtures of AM and thiourea solutions of known concentrations in 100 ml stoppered pyrex bottles under nitrogen. In another set of bottles, known amounts of aqueous FeV suspensions were degassed and finally added to the former bottles under nitrogen atmosphere. The pH of the final mixture was adjusted to  $2.0 \pm 0.1$  by drop-wise addition of 0.01M HCl solution, well shaken and immediately placed in thermostatic bath of appropriate temperature. pH adjustment was necessary to ensure the formation of adequate amount of the amino-sulfenyl primary radicals to initiate

the copolymerization reaction [172]. After the specific time intervals, the copolymerization reactions were stopped by chilling the mixture by placing the vessels immediately on ice bath. FeV suspension was separated by centrifugation ( $1.5 \times 10^4$  rpm). AM-DAAM copolymers were precipitated out by the addition of excess of acetone. The copolymers and FeV were washed separately by acetone and water respectively. The copolymers and FeV were then dried at  $60^\circ\text{C}$  under vacuum for 48 hrs. Copolymer yields were determined gravimetrically.

### **Elemental analysis**

Elemental analyses of carbon and nitrogen for the AM-DAAM copolymers were conducted by Central Drug Research Institute (CDRI), Lucknow, India. The copolymer compositions were calculated based on C/N weight % ratios because of the variability of absolute values due to the hygroscopic nature of the polymers. Elemental analyses were conducted at polymer conversion levels, low and high, to assess drift in the copolymer composition.

### **Viscosity measurements**

A series of copolymer solutions of different concentrations in aqueous 0.1(M) NaCl were prepared from the 0.5% stock solution. Details of intrinsic viscosity measurement technique have already been mentioned in section 3.1.2.

## **3.2.3 RESULTS AND DISCUSSION**

High molecular weight water soluble copolymers of AM with DAAM are formed on the vermiculite surface by a redox initiating system involving trapped Fe(III) and TU in the interlayer space of the mineral. Intrinsic viscosities of copolymers are ranged from 154.9 to  $369.8 \text{ ml.g}^{-1}$ . The study of copolymerization involves the calculation of reactivity ratios of the monomers. Present investigation involves the copolymer of AM with DAAM, which have

been chosen because (1) the groups attached to the vinyl groups are electron withdrawing and (2) the position occupied by the methyl group in the monomer (DAAM) is similar with respect to the vinyl carbon atom. It is evident from the Table 3.8 that AM copolymerized with DAAM from high monomer composition ratio (i.e., 40:1) to low monomer composition ratio (i.e., 1.33:1). It has been found that the same monomer pair can not polymerize at lower than 4:1 monomer composition ratios in the interlayer spaces of montmorillonite using the same Fe(III)-TU redox system [126] . The reactions were also conducted in the presence of surfactant, Triton X-100(R). With increase in the concentration of the surfactant from 0.01 to 0.02 mol.L<sup>-1</sup> the monomer conversion decreases for a given AM:DAAM ratio. On the other hand, for a given surfactant concentration, monomer conversion increases with decrease in the AM:DAAM ratio.

**Table 3.8**

Copolymerization of AM in aqueous medium (25 ml) with DAAM in presence of 0.04M TU and 0.1 % (w/v) FeV at 50°C (pH=1.98) in presence of varying amounts of DAAM

[AM] mol.L <sup>-1</sup>	[DAAM] mol.L <sup>-1</sup>	[AM] / [DAAM]	Triton X-100(R) Mol.L <sup>-1</sup>	Conversion (%) after 4.5 hrs.
0.40	0.02	20.0	0.01	20.0
0.40	0.04	10.0	0.01	67.1
0.40	0.06	6.66	0.01	46.1
0.40	0.08	05.0	0.01	78.2
0.40	0.02	20.0	0.02	-
0.40	0.04	10.0	0.02	32.3
0.40	0.06	6.66	0.02	45.2
0.40	0.08	05.0	0.02	62.0
0.40	0.01	40.0	-	66.5
0.40	0.02	20.0	-	31.6
0.40	0.04	10.0	-	36.3
0.40	0.06	6.66	-	35.8
0.40	0.08	05.0	-	64.5
0.40	0.15	2.66	-	81.0
0.40	0.20	02.0	-	75.0
0.40	0.25	01.6	-	48.0
0.40	0.30	1.33	-	30.6

**Table 3.9**

Reaction parameters for the copolymerization of AM with DAAM at 50°C in distilled water in vermiculite microenvironment  
(Total monomer concentration 0.42 M)

Sample number	Monomer concentration in the feed			Reaction time (min)	Conversion (%)	Elemental analysis (Wt %)		Mol% of DAAM in copolymer	[ $\eta$ ] ml g <sup>-1</sup>
	[AM]	[DAAM]	$\frac{[AM]}{[DAAM]}$			C	N		
DAAM-10-1	0.41	0.01	41.0	90	21.0	43.51	15.63	4.130 ± 0.01	
DAAM-10-2	0.41	0.01	41.0	150	34.2	43.08	15.72	3.270 ± 0.02	369.8
DAAM-10-3	0.41	0.01	41.0	210	41.5	44.38	15.65	5.140 ± 0.05	
DAAM-20-1	0.40	0.02	20.0	90	16.0	44.06	14.98	7.190 ± 0.02	
DAAM-20-2	0.40	0.02	20.0	150	70.0	42.95	13.70	10.96 ± 0.07	319.1
DAAM-20-3	0.40	0.02	20.0	210	73.6	44.03	14.43	9.330 ± 0.06	
DAAM-30-1	0.38	0.04	9.50	90	22.0	45.55	13.76	14.36 ± 0.09	
DAAM-30-2	0.38	0.04	9.50	150	39.4	45.50	14.29	11.91 ± 0.08	292.2
DAAM-30-3	0.38	0.04	9.50	210	82.9	46.69	12.63	21.88 ± 0.10	
DAAM-40-1	0.34	0.08	4.25	90	21.0	48.05	13.12	21.21 ± 0.09	
DAAM-40-2	0.34	0.08	4.25	150	36.0	47.39	13.42	18.66 ± 0.12	250.3
DAAM-40-3	0.34	0.08	4.25	210	59.6	46.57	13.30	18.08 ± 0.20	
DAAM-50-1	0.27	0.15	1.80	90	22.5	53.45	11.90	37.34 ± 0.24	
DAAM-50-2	0.27	0.15	1.80	150	26.0	73.54	16.27	37.89 ± 0.27	154.9
DAAM-50-3	0.27	0.15	1.80	210	28.0	53.44	11.60	39.58 ± 0.21	

## Reactivity ratios

The variation in feed ratios and the resultant copolymer compositions as determined from elemental analyses were used to calculate the reactivity ratios for the AM-DAAM copolymer system (Table 3.9). The Fineman-Ross method [173] and Kelen-Tüdös method [174] were employed to determine the monomer reactivity ratios at low conversion. Figure 3.16 is the Fineman-Ross plot for the copolymer of acrylamide ( $M_1$ ) and diacetone acrylamide ( $M_2$ ).

The reactivity ratios  $r_1$  and  $r_2$  for the monomer pair  $M_1$  and  $M_2$  can be determined by

$$F \frac{(f-1)}{f} = r_1 \left( \frac{F^2}{f} \right) - r_2 \quad (22)$$

Where  $f = d[M_1] / d[M_2]$ ,  $F = [M_1] / [M_2]$ ,

i.e., ' $f$ ' is the molar concentration ratio in the copolymer and ' $F$ ' is the molar concentration ratio in the feed.

The reactivity ratios  $r_1$  was determined to be 0.69 from the slope and  $r_2 = 0.75$  from the intercept in the Fineman-Ross plot. However, it is well known that in Fineman-Ross analysis, values of reactivity ratio are dependent on the indexing of the monomers. On reversing the indexes of the monomer (i.e. assuming DAAM as  $M_1$  and AM as  $M_2$ ), the values of reactivity ratios are changes to  $0.56 \pm 0.04$  and  $0.69 \pm 0.02$  respectively.

The Kelen-Tüdös approach was used to determine the reactivity ratios for the same monomer pair according to equation 23:

$$\gamma = r_1 \xi - r_2 (1 - \xi) / \alpha \quad (23)$$

Where  $\gamma = G / (\alpha + H)$  and  $\xi = H / (\alpha + H)$

The transformed variable G and H given by

$$G = \frac{\{[M_1] / [M_2]\} \{d [M_1] / (d [M_2] - 1)\}}{d [M_1] / (d [M_2])} \quad (24)$$

$$H = \frac{\{[M_1] / [M_2]\}^2}{d [M_1] / (d [M_2])} \quad (25)$$

The parameter  $\alpha$  is calculated by taking square root of the product of the lowest and highest values of H for the copolymerization series. A plot of the data according to the Kelen-Tüdös method is shown in Figure 3.17. Reactivity ratios were determined for AM, DAAM monomer pair as  $r_1 = 0.70$  and  $r_2 = 0.65$  respectively. The observed data in the Kelen-Tüdös plot are linear, an indication that this copolymerization follow the conventional copolymerization kinetics under a prerequisite that the reactivity of a polymer radical is only determined by the terminal monomer unit [175]. The values of  $r_1$ ,  $r_2$  obtained from Fineman-Ross and Kelen-Tüdös treatment for the polymerization of AM with DAAM on vermiculite surface are listed in Table 3.10.

**Table 3.10**

Reactivity ratios for co-polymerization of AM ( $r_1$ ) with DAAM ( $r_2$ )

Method	$r_1$	$r_2$
Fineman-Ross <sup>a</sup>	$0.69 \pm 0.03$	$0.75 \pm 0.05$
Fineman-Ross <sup>b</sup>	$0.56 \pm 0.04$	$0.69 \pm 0.02$
Kelen-Tüdös	$0.70 \pm 0.08$	$0.65 \pm 0.09$

<sup>a</sup> $M_1 = \text{AM}, M_2 = \text{DAAM}.$

<sup>b</sup> $M_1 = \text{DAAM}, M_2 = \text{AM}.$

Figure 3.18 shows the changes of co-polymer composition as a function of feed composition in which co-polymer compositions were determined from the experimentally determined reactivity ratios. Experimental points on the figures are, however, restricted up to 64 mol % of AM in the feed for AM-DAAM copolymers because no copolymers were formed below that value.

### Copolymer Microstructure

The microstructures of the AM-DAAM copolymers are expected to be important in determining the solution properties of copolymers. As mentioned earlier, observed data follow the conventional copolymerization equation and the adherence of the data to this equation is an important point in establishing the validity of the statistical microstructure analyses. The statistical distribution of monomer sequences,  $M_1-M_1$ ,  $M_2-M_2$ , and  $M_1-M_2$  may be calculated utilizing equation 26 to 28 [176-178]

$$X = \phi_1 - 2\phi_1(1-\phi_1) / \{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1(1-\phi_1)]\}^{1/2} \quad (26)$$

$$Y = (1-\phi_1) - 2\phi_1(1-\phi_1) / \{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1(1-\phi_1)]\}^{1/2} \quad (27)$$

$$Z = 4\phi_1(1-\phi_1) / \{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1(1-\phi_1)]\}^{1/2} \quad (28)$$

The mole fractions of  $M_1-M_1$ ,  $M_2-M_2$ , and  $M_1-M_2$  sequences in the copolymer are designated by X, Y and Z respectively.  $\phi_1$  represents the mole fraction of  $M_1$  in the copolymer, and  $r_1$  and  $r_2$  are the reactivity ratios, for the respective monomer pairs. Mean square lengths,  $\mu_1$  and  $\mu_2$  can be calculated utilizing equation (29) and (30) [168].

$$\mu_1 = 1 + r_1 [M_1] / [M_2] \quad (29)$$

$$\mu_2 = 1 + r_2 [M_2] / [M_1] \quad (30)$$

The intermolecular linkage and mean sequence length distributions for the AM-DAAM copolymers are listed in Table 3.11. The Kelen-Tüdös values of reactivity ratios were used for sequence distribution calculation. For the series of AM-DAAM co-polymers, the mean sequences length of acrylamide,  $\mu_{AM}$ , varied from 29.77 at a 95.87/4.13 molar ratio of AM-DAAM in the copolymer to 2.26 with a 62.66/37.34 mole ratio. For those compositions, values of  $\mu_{DAAM}$  were 1.006 and 1.144 respectively.

### **Effect of feed composition**

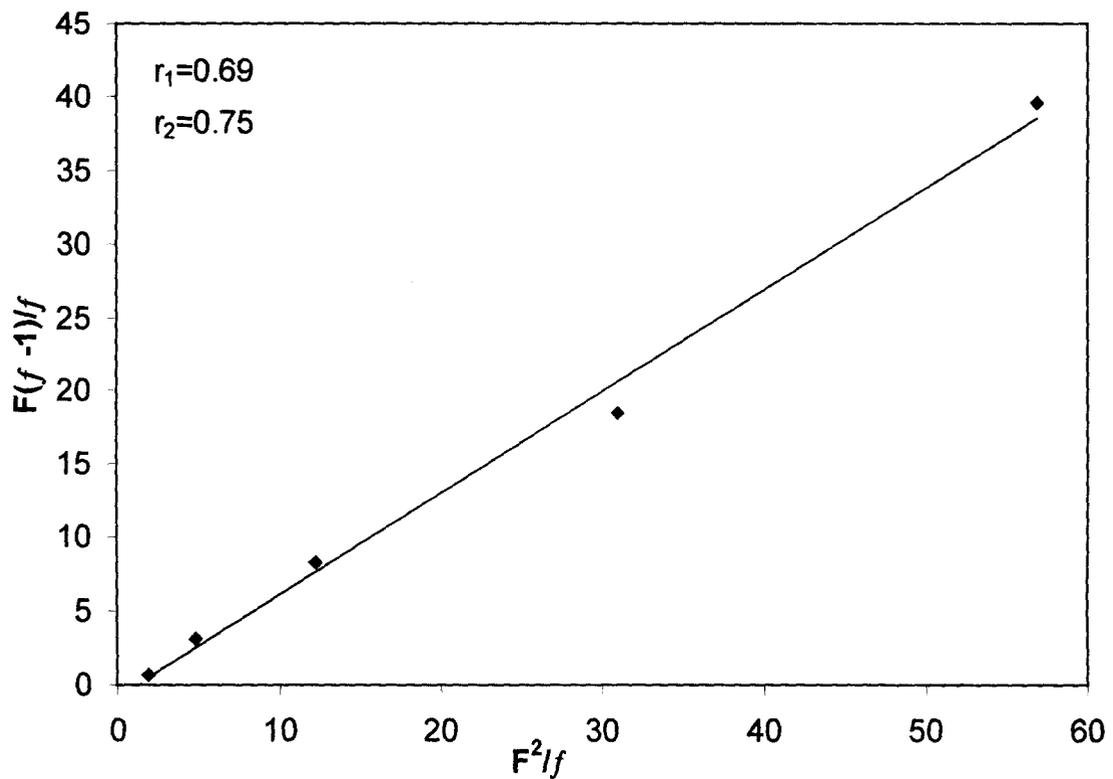
The effect of feed composition on intrinsic viscosity of AM-DAAM copolymers synthesized at high conversions are shown in Table 3.9. Figure 3.19 illustrates the effect of feed composition on the intrinsic viscosity of copolymer. It is interesting to note that in a copolymerization involving acrylamide, the molecular weight gradually decreases with increasing monomer content and this may be explained by the increased cross-termination rates in copolymerization as compared to the very slow rate of termination observed for homopolyacrylamide [179,180].

**Table 3.11**

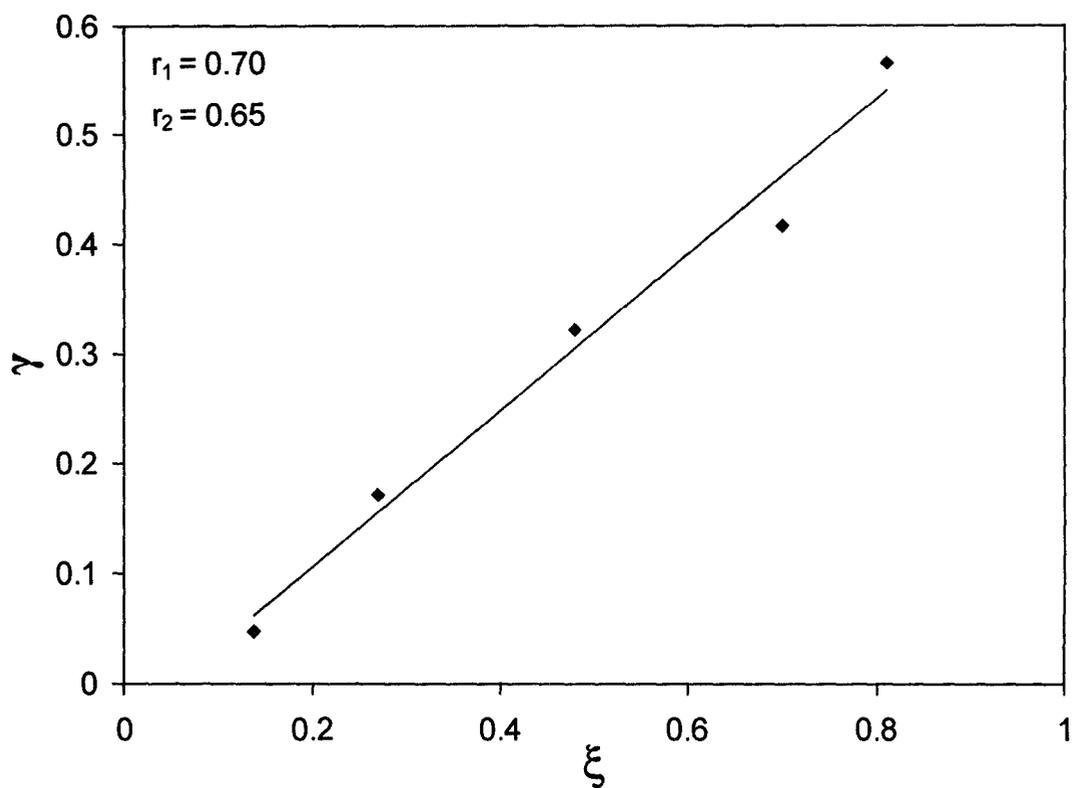
Structural data for the co-polymers of AM with DAAM

Sample number	Composition <sup>a</sup>		Blockiness <sup>b</sup>		Alternation <sup>b</sup>	Mean sequence length		$\frac{\mu_{AM}}{\mu_{DAAM}}$
	(mole %)		(mole %)		(mole %)			
	AM	DAAM	AM-AM	DAAM-DAAM	AM-DAAM	$\mu_{AM}$	$\mu_{DAAM}$	
DAAM-10-1	95.87	4.130	91.77	0.030	08.18	29.77	1.006	29.59
DAAM-20-2	92.81	7.190	85.72	0.120	14.16	15.04	1.013	14.85
DAAM-30-3	85.64	14.36	71.76	0.500	27.74	7.670	1.027	7.470
DAAM-40-4	78.79	21.21	58.81	1.240	39.95	3.980	1.061	3.750
DAAM-50-5	62.66	37.34	42.48	17.17	40.35	2.260	1.144	1.980
DAAM-10-1	96.73	3.270	93.48	0.030	06.49	29.77	1.006	29.59
DAAM-20-2	89.04	10.96	78.34	0.270	21.39	15.04	1.013	14.85
DAAM-30-3	88.09	11.91	76.49	0.330	23.18	7.670	1.027	7.470
DAAM-40-4	81.34	18.66	63.58	0.900	35.52	3.980	1.061	3.750
DAAM-50-5	62.11	37.89	30.29	6.070	63.64	2.263	1.144	1.980
DAAM-10-1	94.86	5.140	89.77	0.060	10.17	29.77	1.006	29.59
DAAM-20-2	90.67	9.330	81.53	0.190	18.28	15.04	1.013	14.85
DAAM-30-3	78.12	21.88	57.57	1.340	41.09	7.670	1.027	7.470
DAAM-40-4	81.92	18.08	64.67	0.840	34.49	3.980	1.061	3.750
DAAM-50-5	60.42	39.58	27.79	6.960	65.25	2.263	1.144	1.980

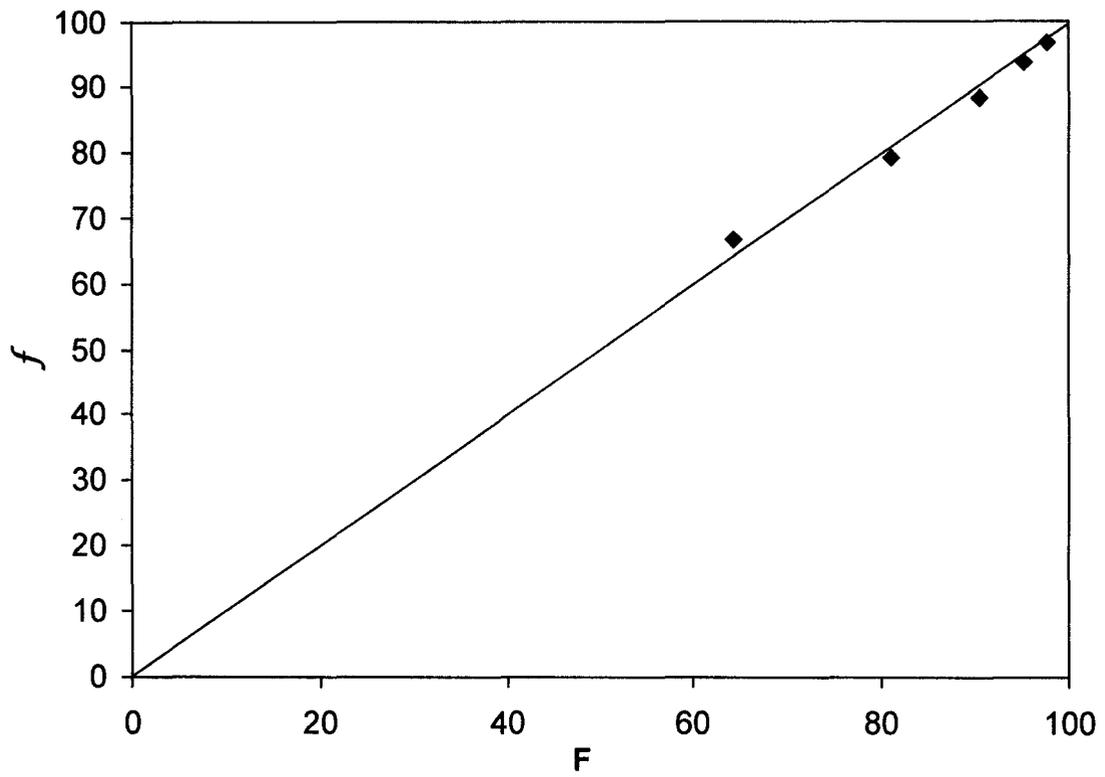
<sup>a</sup> Calculated from elemental analysis<sup>b</sup> Statistically calculated from the reactivity ratios



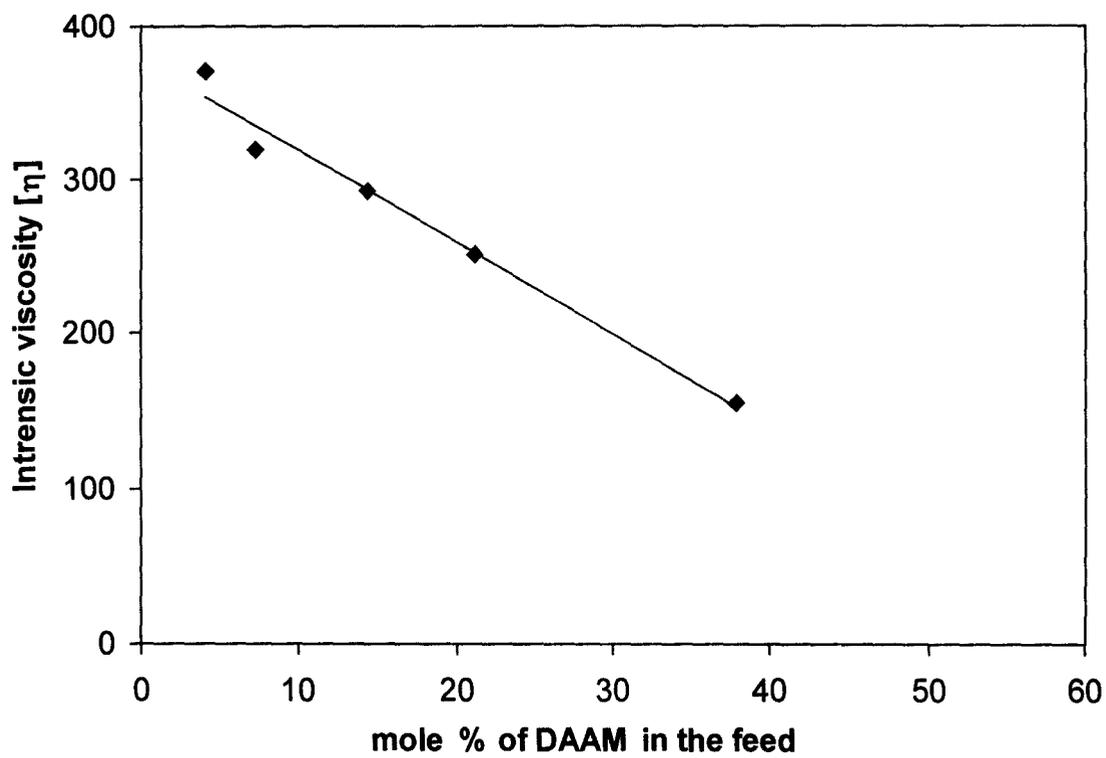
**Figure 3.16:** Determination of reactivity ratios for copolymerization of AM ( $M_1$ ) with DAAM ( $M_2$ ) by Fineman-Ross method



**Figure 3.17:** Determination of reactivity ratio for copolymerization of AM with DAAM by Kelen-Tüdös method



**Figure 3.18:** Copolymer composition as a function of feed composition for the copolymerization of AM with DAAM

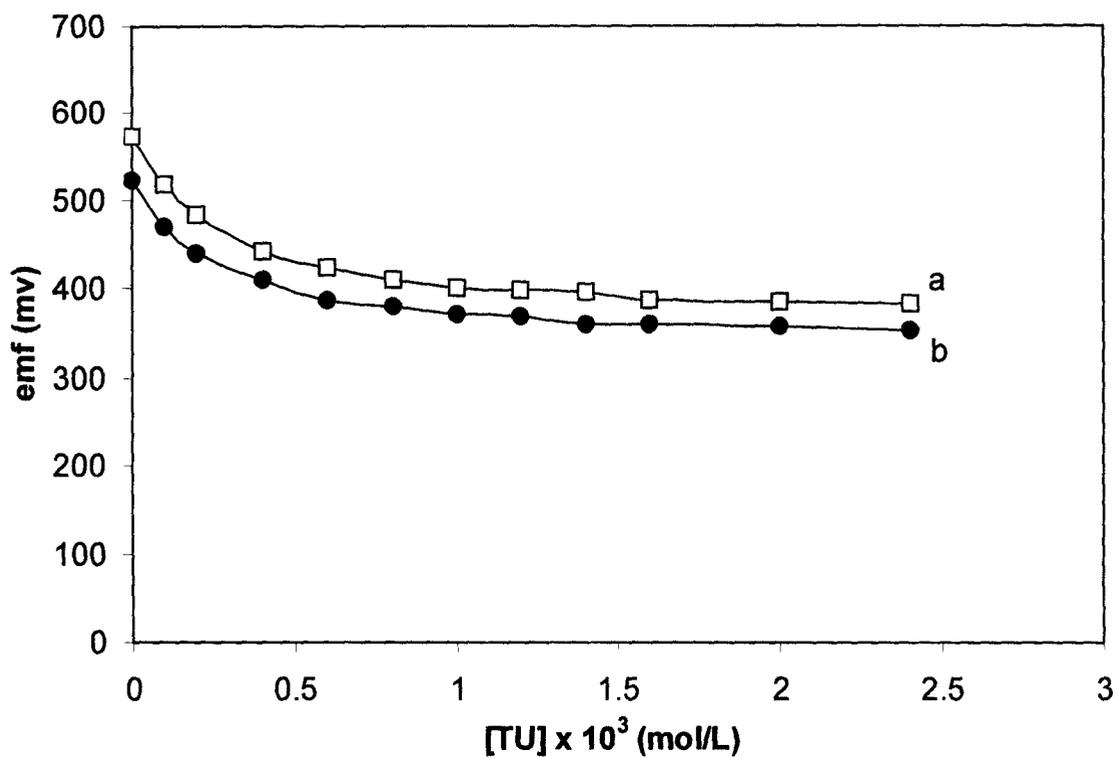


**Figure 3.19:** Effect of feed composition on the intrinsic viscosity of AM-DAAM

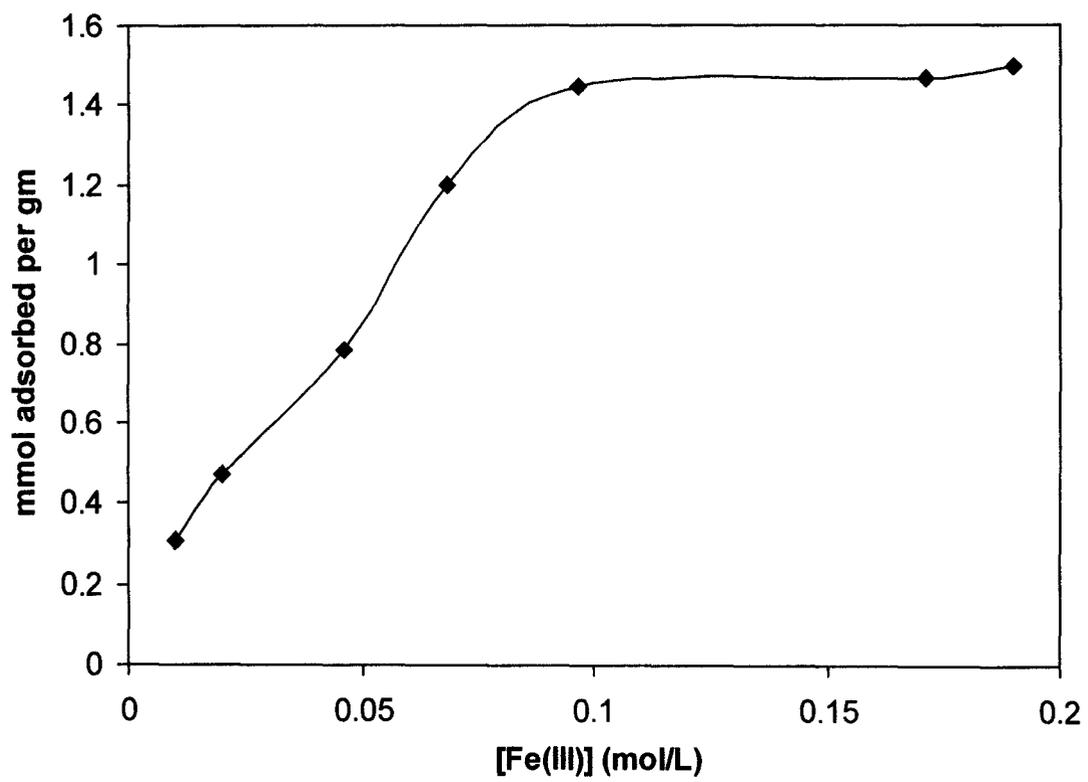
### 3.3 GENERAL DISCUSSION

Some redox systems with TU as reductant have been found to be quite effective in initiating vinyl polymerization in aqueous media. Polymers obtained in the process have all been found to contain amino endgroups as determined by the application of dye interaction [181] and dye partition [182] techniques [183]. Previous studies showed that polymerization of various water insoluble vinyl monomers by redox couples involving TU as the reductant, involves isothiocarbamido primary free radicals in aqueous acid solutions [184]. Owing to high 'g' anisotropy and a very short relaxation time, detection of this radical by ESR spectroscopy was not possible until recently, when ESR study of spin adducts of the radical was reported [172]. The redox characteristics of Fe(III) ions towards TU in solution phase as well as that in the interlayer space of vermiculite are almost identical. This is evident from the data of potentiometric titration of Fe(III) ( $1.5 \times 10^{-3}$  M) in FeV interlayer or FeCl<sub>3</sub> solution ( $1.5 \times 10^{-3}$  M) with TU (Figure 3.20). It is believed that same initiating radicals are also involved when Fe(III) ions are trapped inside the layer space of vermiculite.

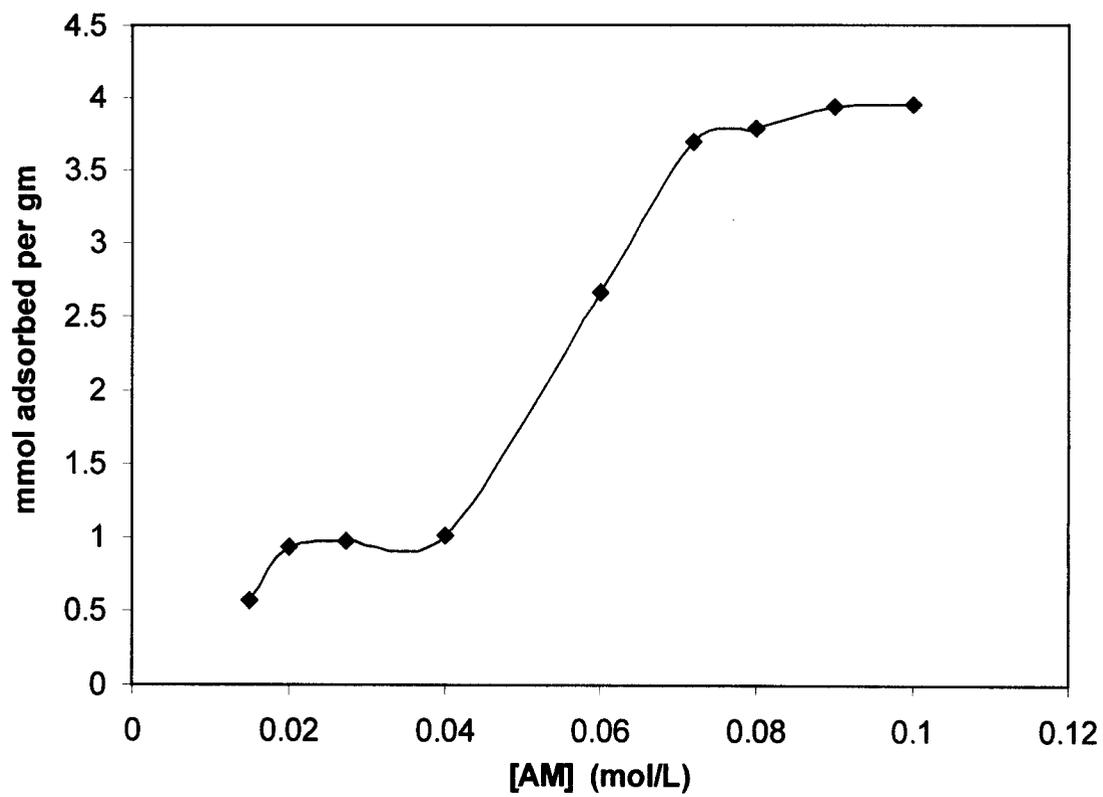
The adsorption isotherm for Fe(III) ion onto vermiculite exhibit L-type nature as shown in the Figure 3.21, which suggests strong sorbate-sorbent interaction. The maximum saturation corresponds to 1.5 meq/g of the mineral. Figure 3.22 shows that the AM molecules are readily adsorbed from the aqueous solution onto the surface 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 (adsorption isotherm shown in Figure 3.23) only and the maximum adsorption capacity is found to be nearly 2 mmol/g. Figure 3.22 shows that 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



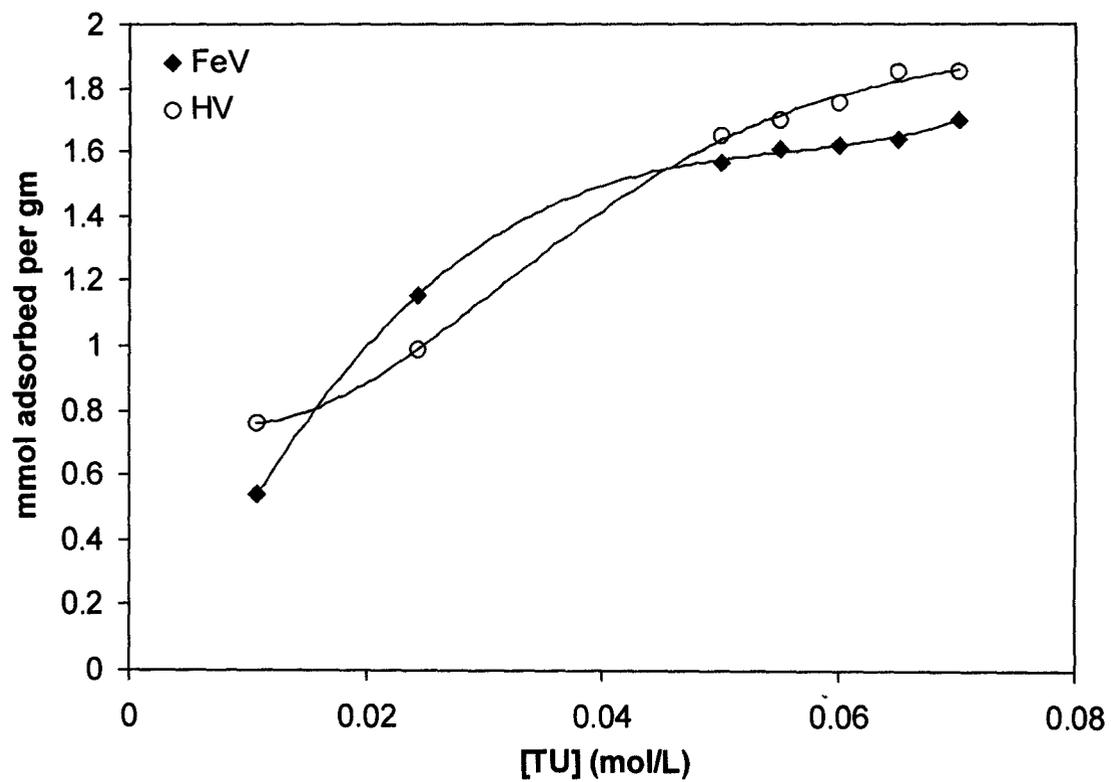
**Figure 3.20:** Potentiometric titrations of (a) FeV ( $1.5 \times 10^{-3}$  M in terms of exchanged Fe(III) per 1000 ml of suspension) versus TU, (b) FeCl<sub>3</sub> ( $1.5 \times 10^{-3}$  M) versus TU



**Figure 3.21:** Adsorption isotherm of Fe(III) ion on HV



**Figure 3.22:** Adsorption isotherm of AM on FeV



**Figure 3.23:** Adsorption isotherm of TU on FeV

the layered space as compared to the homogeneous polymerization. However, the reason behind first break at 1.0 mmol/g is not certain. Tables 3.12-3.14 give an idea about the strength of intercalation of AM, TU molecules and Fe(III) ions in both FeV and HV interlayer spaces respectively. The distribution coefficient ( $K_D$ ) values are low and of the order of  $10^{-1}$  in the concentration range of AM and TU used for polymerization experiments. The distribution coefficients have been calculated according to the relation:

$$K_D = m_{i(s)} / m_{i(l)} \quad (31)$$

Where  $m_{i(s)}$  and  $m_{i(l)}$  are the concentrations of the species in the solid and liquid phase respectively.

**Table 3.12**

Intercalation of acrylamide molecules in ferric vermiculite interlayer spaces

Mineral %	Conc of added AM (mol.L <sup>-1</sup> ) x 10 <sup>-2</sup>	Conc of free AM (mol.L <sup>-1</sup> ) x 10 <sup>-2</sup>	Conc of adsorbed AM (mol.L <sup>-1</sup> ) x 10 <sup>-3</sup>	Distribution coefficient ( $K_D$ )
FeV 0.32	10.0	8.89	11.0	0.12
	9.00	7.49	15.0	0.20
	8.00	6.79	12.8	0.19
	7.20	5.38	18.1	0.33
	6.00	5.03	09.6	0.19
	4.00	3.70	02.9	0.08
	2.80	2.51	02.9	0.12
	2.00	1.70	03.0	0.17

**Table 3.13**

Intercalation of thiourea molecules in ferric vermiculite and hydrogen vermiculite interlayer spaces

Mineral %	Conc of added TU (mol.L <sup>-1</sup> ) x 10 <sup>-2</sup>	Conc of free TU (mol.L <sup>-1</sup> ) x 10 <sup>-2</sup>	Conc of adsorbed TU (mol.L <sup>-1</sup> ) x 10 <sup>-3</sup>	Distribution coefficient (K <sub>D</sub> )
FeV 0.32	7.00	6.47	5.30	0.08
	6.50	5.85	6.50	0.11
	6.00	5.60	4.00	0.07
	5.50	5.02	4.80	0.09
	5.00	4.53	4.70	0.10
	4.00	3.30	7.00	0.21
	3.00	2.56	4.40	0.17
HV 0.32	7.00	6.37	6.30	0.10
	6.50	6.10	4.00	0.06
	6.00	5.42	5.80	0.10
	5.50	4.78	7.20	0.15
	5.00	4.48	5.20	0.12
	4.00	3.46	5.40	0.16
	3.00	2.69	3.10	0.11

**Table 3.14**

Intercalation of Fe(III) ion in hydrogen vermiculite interlayer spaces

Mineral %	Conc of added Fe(III) ion (mol.L <sup>-1</sup> ) x 10 <sup>-2</sup>	Conc of free Fe(III) ion (mol.L <sup>-1</sup> ) x 10 <sup>-2</sup>	Conc of adsorbed Fe(III) ion (mol.L <sup>-1</sup> ) x 10 <sup>-2</sup>	Distribution coefficient (K <sub>D</sub> )
HV 0.388	2.29	1.08	1.20	1.11
	3.82	2.00	1.82	0.91
	7.64	4.60	3.04	0.66
	11.4	6.80	4.66	.685
	15.3	9.65	5.63	.583
	22.8	17.1	5.69	.332
	24.8	19.0	5.82	.306

Low charge vermiculite may have interlayer expansion characteristic, which bear closer resemblance to those of high charge montmorillonite. Moreover, its ability to form complexes with organic compounds bears a striking resemblance to that of montmorillonite. Basal spacing measurement from X-ray diffractogram of unoriented powder sample of hydrogen-montmorillonite, TU treated Fe(III)-montmorillonite and Fe(III)-montmorillonite-PAM adduct before and after glycerol treatment show the existence of intercalated PAM in the layered spaces of the mineral. However, intercalation of TU and Fe(III) does not result in the expansion of the basal spacing of the mineral [126]. Using infrared spectroscopy, Tahaun and Morland have confirmed that amides predominantly protonate on the oxygen atom in the acidic clay system [185]. Comparing the results of adsorption on the surfaces of montmorillonite and vermiculite minerals it may be argued that like montmorillonite phase reaction, the bilayer adsorption of acrylamide in the internal surface of the vermiculite also play a pivotal role in affecting the initiation of polymerization and its mechanism as compared to the homogeneous polymerization reaction. In acidic medium, amides may apriori

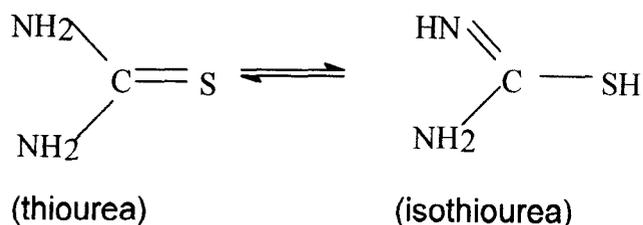
accept a proton on either the oxygen or the nitrogen atom. Spectroscopic as well as solution studies, however, support the possibility of coming about of the former alternative [128].

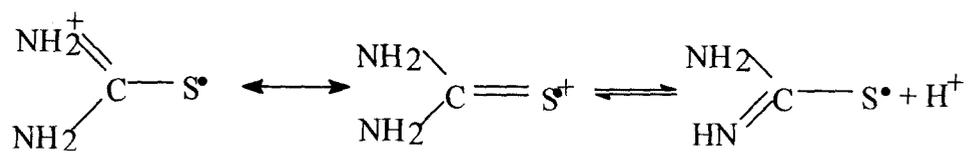
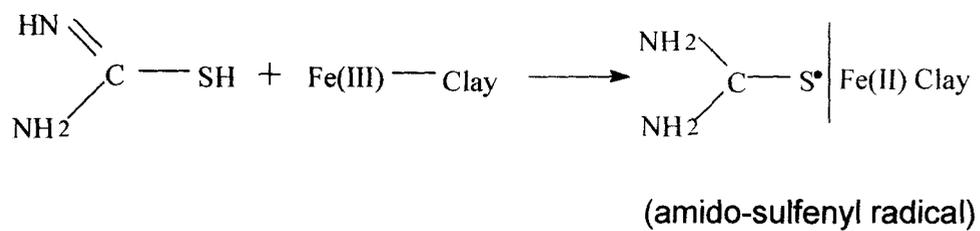
Linear termination of aqueous acrylamide polymerization by metal ions was observed long back [186]. While the linear termination by metal ions is a very common phenomenon in solution phase reaction, it is not possible in presence of clay mineral and transfer to Fe(III) ion is almost controlled in the case of reaction in the layered spaces. Aqueous polymerization of AM by Fe(III)-TU redox couple shows kinetic behaviour and mechanism similar to those of other redox initiated polymerizations of AM. On the other hand, polymerization initiated by the same redox couple but by loading Fe(III) ions in the interlayer spaces of vermiculite influences the kinetics as well as the mechanism to a great extent. The latter technique increases the degree of polymerization and the intrinsic viscosity of the polymers dramatically by decreasing the rate of linear termination process. The method was demonstrated to be a promising technique of achieving high molecular weight polymers for redox initiated reactions, where low molecular weight polymers are often displayed. The maximum  $M_v$  were found to be  $2.3 \times 10^5$  and  $2.7 \times 10^6$  in the absence and presence of vermiculite respectively, while  $[\eta]$  values increased from 98 to 628 ml g<sup>-1</sup> due to the presence of the mineral under identical condition. The polymers, characterized by <sup>1</sup>H and <sup>13</sup>C nmr., where mostly thiourea terminated head-to-tail polymers with mixed tacticities were formed and Bernoulli statistics were followed. The kinetic study showed the monomer, TU and metal ion exponents to be 2.0, 1.0 and 0.5 respectively where as in homogeneous aqueous medium polymerization these values are 1.0, 2.0 and 0.5 respectively. Thus it is evident that the modification achieved with respect to kinetics and mechanism of the acrylamide polymerization in the vermiculite phase stems from a number of factors viz.,

1. Instead of collision between a monomer molecule and an initiating radical, a monomer pair is involved in the initiating step.

2. 'Cage effect' is prominent in vermiculite phase reaction where a pair of TU radicals forms a potential barrier to hinder diffusion of the radicals and favours their recombination.
3. Rate of linear termination process decreases significantly because transfer to Fe(III) ions is highly restricted for the latter's location in the layered spaces of the mineral and diffusion of the living radical through vermiculite gel is rather slow. In general, loading of the oxidant, i.e. metal ions, of the redox couple in the interlayer space of clay minerals offers a potential method of achieving very high degree of polymerization for a redox initiating acrylamide polymerization reaction.

Aqueous polymerization of AM is also dependent significantly on the pH of the solution. Previous report showed that low-moisture content clay minerals promote the spontaneous cationic polymerization of styrene but interfere with the free radical polymerization. Both Brönsted and Lewis acidity have been involved in the cationic polymerization initiated by dry clay minerals. The acidity of the clay increases on drying [41,187,188]. In the present study, the reaction is carried out in aqueous medium and the surface acidity is less as compared to the dry mineral. Above pH 2.10, no significant polymerization takes place. The metal ion, Fe(III), in the interlayer space of vermiculite reacts with isothiurea, the tautomeric form of thiourea, generating amido-sulfenyl radical to initiate polymerization. At low pH, the tautomeric equilibrium of TU in aqueous solution is shifted towards isothiocarbamido form facilitating the formation of primary radical. Moreover, the protonated form of the amido-sulfenyl radical at low pH is more stable than the radical itself and consequently the dimerization process is less favourable [189].





isothiocarbamido free radical

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