CHAPTER 5

STUDIES ON FREE RADICAL CROSS-LINKING COPOLYMERIZATION OF ACRYLAMIDE WITH N,N-METHYLENE-BIS-ACRYLAMIDE: SWELLING AND THERMAL BEHAVIOUR OF THE HYDROGEL

5.1 REVIEW OF PREVIOUS WORK

Polymer gels are important materials of both fundamental and technological interests. In recent years, hydrophilic gels called hydrogels have received considerable attention for their use as specific sorbents and as support carriers in biomedical engineering. Hydrogels are of three dimensional cross linked co-polymeric structures, which are able to swell in the aqueous environment. These materials are of great interest due to their promising applications as sensors, separation devices [1,2], actuators [3] and adsorbents. These materials are also used in medicine, in pharmacy as drug delivery systems [4,5] and in solving some ecological and biological problems.

Hydrogels have also been proposed for use in the separation of a range of materials such as macromolecules [6-11], vaccines [12] and yeasts [13] from aqueous solutions. After the adsorption of water, the swollen gel can be heated above T_C (the lower critical swelling temperature) to expel the water and hence regenerate the xerogel for further use [14-16]. Factors determining the feasibility of using hydrogels as separation devices include high swellability, an appropriate T_C and size selectivity. The most widely studied thermosensitive hydrogels are those based on the monomer N-isopropyl acrylamide [17] and its copolymers with comonomers, such as acrylic acid, methacrylic acid, 2-methyl-2-acrylamidopropene sulphonic acid [14,15], trimethylacrylamidopropyl ammonium iodide [18], 3-methyl-1-vinylimidazolium iodide [19], sodium acrylate and sodium methacrylate. However, the application of these materials is limited due to the fact that their swelling is decreased in the presence of salt in solution [7, 19]. This limitation has great importance of thermoreversible hydrogels for concentrating of materials found in electrolyte solution, e.g. biogenic materials such as bacteria or proteins.

Choi and co-workers have synthesized a submicron sized copolymer gels of N-isopropyl acrylamide (NIPA)-N-cyanomethyl acrylamide (NCMA) in which N,N-methylene-bis-acrylamide (Bis) was used as crosslinking agent by precipitation polymerization using ammonium persulphate as *an initiator.*

Nonionic surfactant, Tween 20, which dose not affect the swelling behaviour of nonionic gel, was used to prevent aggregation of gel particles during polymerization [20]. Volume phase transition behaviours of the gel particles with various compositions and crosslinking density were observed by using photon correlation spectroscopy (PCS). The experimental data showed that both the volume transition temperature and the swelling ratio of the copolymer gel particles were varied with the mole ratio of NCMA and NIPA.

Zhuo and co-workers prepared thermally sensitive polymeric gel of N-isopropyl acrylamide using polyethylene glycol as the pore-forming agent and Bis as crosslinker. The copolymerization was carried out at room temperature for 24 hours using ammoniumpersulphate and N,N,N′,N′-tetramethylenediamine as a pair of redox initiators. This poly (N-isopropylacrylamide) gel has significantly large swelling ratio at a temperature below its lower critical solution temperature and exhibits a very fast deswelling rate [21].

Polymeric networks containing ionic and hydrophobic moieties exhibit phase transition in response to external environmental changes, such as solvent composition [22], buffer composition [23], pH [24], temperature [24,25], pressure [26], electronic field [27], electromagnetic radiation [28] and photoelectric stimuli [29], have recently received increasing attention. These hydrogels are generally composed of a thermosensitive component such as N-isopropylacrylamide and a hydrophilic comonomer such as acrylic acid. Yoshioka and co-workers prepared amphiphilic terpolymer xerogels from *N*-isopropylacrylamide, acrylamide, acrylic acid, and *n*-dodecyl acrylamide by both redox initiated polymerization and γ-irradiation polymerization. The swelling equilibrium and swelling kinetics of amphiphilic xerogels prepared by these two polymerization methods were compared and drug release behaviours of the xerogels were also examined using 5-fluorouracil as a model drug [30]. Hsu and Cohen prepared polyacrylamide gels by a standard redox reaction procedure employing ammoniumpersulphate and tetramethylenediamine as a redox initiator. The initial pH of the preparation

was 8.2 and total monomer concentration was kept at 5.133 g/dl where as the amount of the crosslinking agent (Bis) was varied at about 5.32, 2.66 and 1.33% in the initial monomer mixture [31]. Dinarvand and Ansari prepared stimulisensitive copolymers of N-isopropylacrylamide and acrylamide (AM) by ammoniumpersulphate and N,N,N′,N′-tetramethylenediamine redox initiator in which N,N-methylene-bis-acrylamide (Bis) was used as the crosslinking agent. Poly (N-isopropylacrylamide) hydrogels show negative temperature sensitivity and they tend to uptake water and swell at temperature below a phase transition temperature (32°C). But when N-isopropylacrylamide copolymerized with acrylamide in which Bis was used as crosslinking agent, show a higher swelling transition temperature (37°C). For this behaviour this hydrogel has been applied as a functional material for control of drug release rate and for temperature responsive intelligent drug delivery system [32]. Watanabe and co-workers prepared a photoresponsive polymeric hydrogel cantilever of acryloylacetone (AA), AM and Bis that deflects under illumination by two-photon initiated polymerization (TPIP) procedure [33]. In the case of AA-AM-Bis hydrogels, UV excitation at 244 nm leads to a decrease in the absorption peak at about 280 nm (corresponding to the "chelated" enol form) with irradiation time. The changes in the absorption spectra under UV illumination are consistent with those observed previously for poly (acryloylacetone) in solution and films, which have been attributed to a shift in the tautomeric form, the "chelated" enol form to the diketo tautomer [34-37].

Fully neutralized polyacrylate hydrogel exhibits reversible volume changes in solutions containing both monovalent and divalent cations in a concentration range and composition similar to physiological conditions. Sugitani and co-workers synthesized polyacrylic acid gels by free radical crosslinking copolymerization of partially neutralized acrylic acid and Bis in aqueous solutions by ammoniumpersulphate initiator [38]. Recent studies unambiguously indicate that swelling occurs in many physiological systems and plays a crucial role in physiological processes such as nerve excitation, muscle contraction, and cell locomotion. Viewing nerve excitation from a physicochemical standpoint, Tasaki has shown that synthetic polyanionic gels [e.g., poly (methacrylic acid) gels, poly (acrylic acid) gels] can exhibit

discontinuous volume changes by using a biologically plausible mechanism of monovalent-divalent cation exchange [39-43]. Horkay and co-worker prepared fully neutralized sodium polyacrylate hydrogels following the procedure described by Sugitani and the swelling behaviour of the gels were investigated in aqueous solutions of alkali metal (LiCl, NaCl, KCl, CsCl) and alkaline earth metal salts ($CaCl_2$, $SrCl_2$, $BaCl_2$). There are distinct differences between the swelling behaviour of the polyelectrolyte network immersed in solutions of alkali metal and alkaline earth metal salts [44] Some biodegradable polymer such as poly (lactic acid), poly (glycolic acid) and their respective copolymers are already applied in several drug delivery systems [45,46]. Roman and co-workers prepared biodegradable hydrogel by the free radical polymerization of acrylamide and acrylic acid, and some formulations with Bis-acrylamide, in the presence of a corn starch-ethylene-co-vinyl alcohol copolymer blend (SEVA-C) [47]. The hydrogels prepared were characterized by ^1H NMR and FTIR spectroscopies. Swelling studies were performed as a function of pH in different buffer solutions and the authors found that the prepared hydrogels were sensitive to pH in the range from 4 to 9, which is the range similar to physiological conditions. Karadag and Saraydin pepared superadsorbant acrylamide–sodium acrylate hydrogels by free radical polymerization in aqueous solutions in which a multifunctional crosslinker such as trimethylolpropane triacrylate, ethylene glycol dimethacrylate, 1,4-butanediol dimethacrylate or N,N-methylene-bis-acrylamide was employed. They found that acrylamide–sodium acrylate hydrogels were swollen in the range of 860-12,870 % in water, while acrylamide hydrogels swollen in the range 770-1420 %. The equilibrium water content of acrylamide-sodium acrylate hydrogel system was calculated in the range 0.8851-0.9922. [48]. The swellability of poly (N-isopropylacrylamide) (PNIPA) in water is reduced by the presence of salts in the aqueous medium. Poly (NIPA-co-acrylic acid) is more swellable, but its swelling ratio (i.e. mass hydrogel/ mass xerogel) is also reduced by the presence of salts. But chemically crosslinked hydrogels of Zwitterionic monomers exhibits anti-polyelectrolytic behaviour in aqueous salt solution, i.e., swell in salt solution to a grater extent than in pure water [49,50].

With regard to chemically crosslinked thermosensitive Zwitterionic hydrogels, Lee and Yeh [51] reported recently the synthetic process and properties of NIPA-DMAAPS [DMAAPS-N,N-dimethyl (acrylamidopropyl) ammonium propane sulphonate] hydrogel. It was found that the hydrogel exhibits anti-polyelectrolyte behaviour when the content of DMAAPS in the gel was grater than 12 mo l%.

Huglin and co-workers have prepared copolymers of NIPA with Zwitterionic co-monomer, 1-(3-sulphopropyl)2-vinyl-pyridinium-butaine (SPV). The swelling properties were studied in water, aqueous KCl and aqueous KSCN [52]. Swellability of this hydrogel is enhanced at low salt concentration and then reduced at higher ionic strength. In recent studies, the copolymer of acrylamide with diprotic acids were tested as adsorbent in the adsorption of some cationic dyes [53,55], uranyl ions and some heavy metal ions [56,57], the biocompatibility of blood [58], and the adsorption of Bovine Serum Albumin (BSA) [59]. Crosslinked copolymers of acrylamide with 2-hydroxyethyl methacrylate (HEMA) in rod form was prepared by a redox copolymerization method in which Poly (ethylene glycol) (PEG 4000), and Bis were used as a diluent and crosslinking agent respectively [60]. It has been found that the values of equilibrium mass swelling of AM hydrogels ranged from 665% to 1122%, whereas for AM-HEMA hydrogels this values were ranged from 513% to 660%. Therefore, the equilibrium percentage mass swelling of copolymers decreases with increasing HEMA content, which is probably due to the decrease of hydrophilic group number of the copolymers by intermolecular hydrogen bonding between hydroxyl and amide groups and intramolecular hydrogen bonding between amide groups. Recently considerable attention has been paid to a novel class of thermally responsive hydrogel known as interpenetrating polymer network (IPN) [61-65]. Interpenetrating polymer network particles of AM and acrylic acid were prepared using an inverse emulsion polymerization technique by Peppas and co-workers [66]. Macroporous crosslinked polymers are most efficient materials for many separation processes and therefore, they are widely used as starting material for ion exchange resins and as specific sorbents. Such materials are produced by a reaction-induced phase separation technique,

which involves the copolymerization of the monomer-crosslinker mixture in presence of an inert diluent [67-69]. An alternative approach to obtain macroporous polymers with better mechanical performance is the cryogelation technique. Ozmen and co-workers used this technique to prepare macroporous polyacrylamide hydrogels of AM and Bis. The polymerization reactions were carried out in DMSO-water mixture (1:1 by volume) at various temperatures from $-18^{o}C$ to $+22^{o}C$. The formation of the porous structure was observed at or below $0^{o}C$, while large polyhedral pores were formed in the networks at higher temperature [70].

5.2 FREE RADICAL CROSS-LINKING COPOLYMERIZATION OF ACRYLAMIDE WITH N,N-METHYLENE-BIS-ACRYLAMIDE BY Fe(III)-THIOUREA AND Ce(IV)-THIOUREA REDOX INITIATOR SYSTEMS

5.2.1 INTRODUCTION

Hydrogels are hydrophilic type three-dimensional networks, held together by chemical or physical bonds. If enough interstitial space exists within the network, water molecules can become trapped and immobilized, filling the available free volume (71,72). Their utility as biomaterials is well known; it is due to their permeability of small molecules, soft consistency, low interfacial tension, facility for purification and mainly high equilibrium water content which make them similar to the physical properties of living tissues (73,74). Hydrogels can be applied as an interface between bone and an implant (75), as artificial skin (76), as contact lenses (77), as blood contact materials (78) and in-controlled release applications for delivery of enzymes, hormones, contraceptives, anticoagulant etc (79).

Investigations of the swelling behaviour of acrylamide-based hydrogels have been reported repeatedly in the last four decades. In both academic studies and industrial applications acrylamide hydrogels are mostly obtained by the free radical copolymerization of acrylamide (AM) and N,N-methylene-bis-acrylamide (Bis), which is used as a crosslinker. Water is commonly used as reaction medium because of its low cost, low toxicity and the final uses of the gels in aqueous environment. It is well established that properties of acrylamide hydrogels depend upon the monomer concentrations of the initial mixture (80); for example, hydrogels with total higher monomer content will have a tighter network structure and these has been ascribed to the increased interpenetration of polymer chains during network formation (81). Thus swelling behaviour, which depend upon the network structure closely related to the conditions under which the polymer gels are formed (82). No continuous network is formed below a critical concentration of the monomer

(83). As the amount of solvent (water) increases, the network structure becomes increasingly loose. It was also shown experimentally (84-88) and theoretically (89,90) that AM-based hydrogels exhibit inhomogeneous crosslink distribution. Thus the understanding of the formation mechanism of polymer gels is of great interest to predict their physical properties.

In this chapter new results are reported which will enable us to estimate the magnitude of reaction rate of AM-Bis copolymerization in dilute aqueous solutions using Fe(III)-Thiourea and Ce(IV)-thiourea redox initiator systems. For this purpose, a series of experiments with varying amount of the crosslinker were performed at a total monomer concentration of 0.4 (M). Conversions of the monomers were determined by means of gravimetric technique and gel points were measured by viscometric method by allowing a steel sphere of 3mm diameter to fall in the reaction mixture.

5.2.2 EXPERIMENTAL

Materials

The monomer acrylamide (reagent grade, Fluka) was purified by a process as described in section 3.1.2. The cross linker N,N-methylene-bis-acrylamide (Acros Organics, Belgium) was used as received. Ferric chloride (E-Merck) and ceric ammonium sulfate (E-Merck) was used as received. Thiourea (TU) (E-Merck) was recrystallized twice from water and dried under vacuum. The polymerization solvent water was distilled twice before use.

Polymerization Procedure

AM-Bis copolymerizations were carried out in water at 50°C with Fe(III)-TU redox system. Ce(IV)-TU redox initiator system, promotes very fast reaction after the induction period and monitoring of the reaction kinetics gravimetrically was difficult at 50°C . Therefore, the reaction was studied at a lower temperature viz., 40°C. The polymerization reaction was carried out in a

well stopper Pyrex glass bottle in which monomer mixture with requisite amount of TU solution were purged with purified nitrogen gas for 20 minutes to eliminate dissolved oxygen. The purification procedure of nitrogen was same as discussed in the section 3.1.2. In another bottle Fe(III) or Ce(IV) solution were purged with nitrogen for 20 minutes separately. Both the bottles were kept in a constant temperature bath at the experimental temperature to attain equilibrium and finally contents of the two bottles were mixed. After a definite time interval, the polymerization reaction was stopped by lowering the temperature immediately with ice cooled water. The polyacrylamide gels were precipitated out by adding excess of acetone (Merck), washed repeatedly with acetone and dried in vacuum at 50°C for 48 hours. The reproducibility of kinetic data was checked by repeating the experiments at least for two times.

Gel point measurements

Gel point was determined by observing the solubility of the polymer in aqueous medium. For ascertaining the solubility or insolubility of the sample, the polymer was treated with an approximately 50-fold excess of water at room temperature for examination. The formation of insoluble polymer was detected visually from the appearance of gel particles in water. Gel point was also checked by placing a steel sphere of 3mm diameter in the reaction mixture before starting the polymerization reaction. The midpoint between the last time at which sphere moved magnetically and that at which it stopped moving was taken as the gel point. Each gel point was checked by duplicating the experiment under identical condition.

5.2.3 RESULTS AND DISCUSSION

It is well known that in free-radical polymerization, cross-linking enhances the gel effect significantly and the autoacceleration in polymerization rate starts right at zero conversion [91-98]. Figure 5.1-5.5 shows the variation of the % conversion as a function of reaction time in free radical crosslinked polymerization involving Fe(III)-TU redox system up to the start of macrogelation for AM-Bis copolymerization with different crosslinker

contents. The content of the crosslinker was varied from 0 to 14 mol %. The acceleration of the rate of polymerization was observed with increase of the Bis content. No induction period was observed. The macrogelation starts earlier as the Bis content is increased in the monomer mixture. Figure 5.6 - 5.13 represents the variation of the % conversion of the monomer as a function of reaction time in free radical crosslinked polymerization involving Ce(IV)-TU redox system of AM and Bis co-monomer at 40°C. Initial monomer concentration was 0.4 (M) as before. A striking feature of this redox system is that a significant induction period is observed (Figure 5.6-5.13). With the increase of Bis content, induction period is increased and with the rise of temperature induction period is decreased. In the case of Ce(IV)-TU, however, macrogelation occurs within a short period (within ~ 10-20 minute time of starting the polymerization reaction) at 40°C. At 50°C, however, the reaction rate is so fast that kinetic study by gravimetry becomes very difficult to perform. Much like Fe(III)-TU system, macrogelation starts earlier with higher Bis content in Ce(IV)-TU initiating system also. Figure 5.14a shows the macrogelation points in terms of the reaction time as a function of monomer composition. Figure 5.14b records % conversion at the macrogelation point as a function of Bis concentration in the monomer mixture. Both the plots are found to pass through minima. For Fe(III)-TU system this minimum appears at 6 mol % composition of Bis. For Ce(IV)-TU redox system, on the other hand, it occurs in between 4-5 mol % Bis concentration. With increase of Bis concentration in the monomer mixture macrogelation occurs earlier up to a definite Bis % and then with the increase of Bis % macrogelation is delayed (Figure 5.14a, 5.15a, 5.15b, 5.16), this is expected and also predicted by the gelation theories (99). Baselga and co-workers reported similar gelation curves, which showed a minimum at 7 % monomer concentration [101]. Naghash and co-workers also reported 6 mol % critical monomer conversion at the above minima. These authors explained the above feature in terms of low probability for cyclization below 7 %. Figure 5.15a and Figure 5.15b show similar plots for Ce(IV)-TU redox polymerization system at 40°C. Figure 5.16 records macrogelation points in terms of reaction time as a function of Bis content at 50°C. Comparing Figure 5.15b and Figure 5.16 one can say that with the rise of temperature, the gelation time decreases for a fixed monomer percentage.

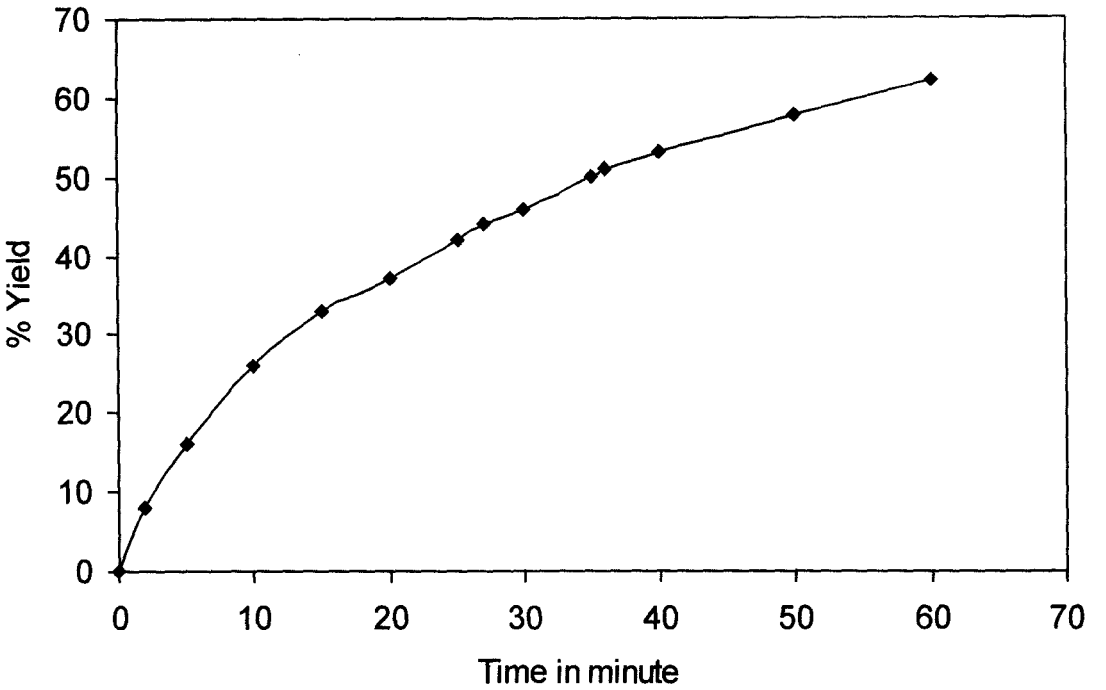


Figure 5.1: Time - conversion plot for aqueous crosslinked polymerization of AM - Bis at 50°C with Fe(III) - TU redox system
Bis = 2 mol%, TU = 0.04 M, $FeCl_3 = 1.5x10^{-3}$ M

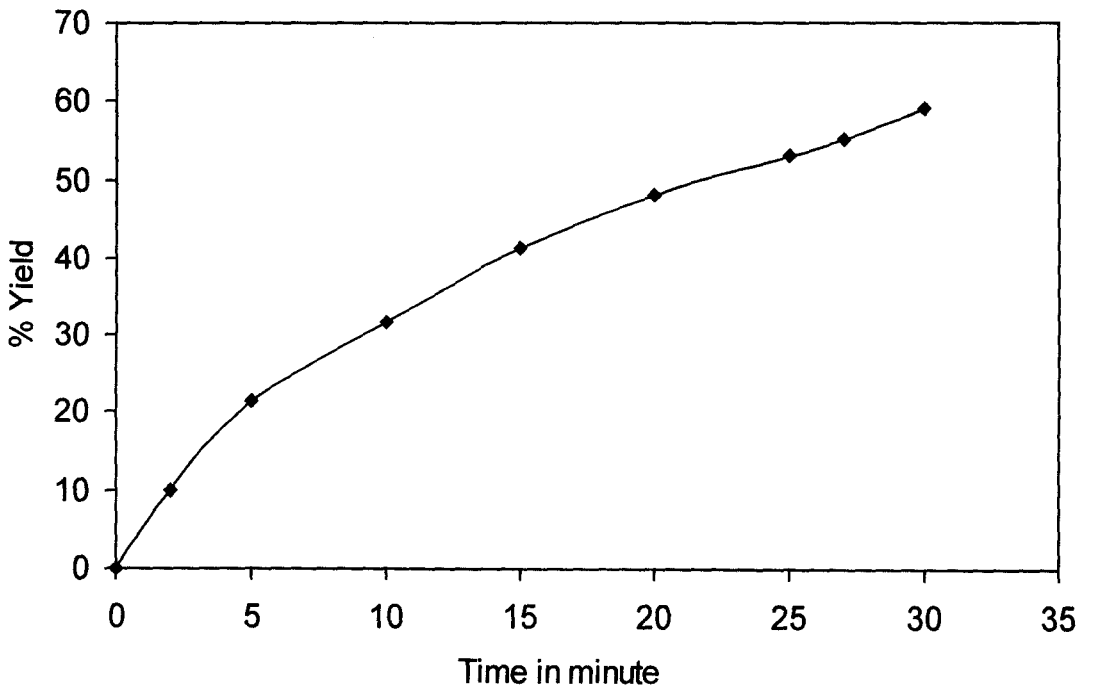


Figure 5.2: Time - conversion plot for aqueous crosslinked polymerization of AM - Bis at 50°C with Fe(III) - TU redox system
Bis = 4 mol%, TU = 0.04 M, $FeCl_3 = 1.5x10^{-3}$ M

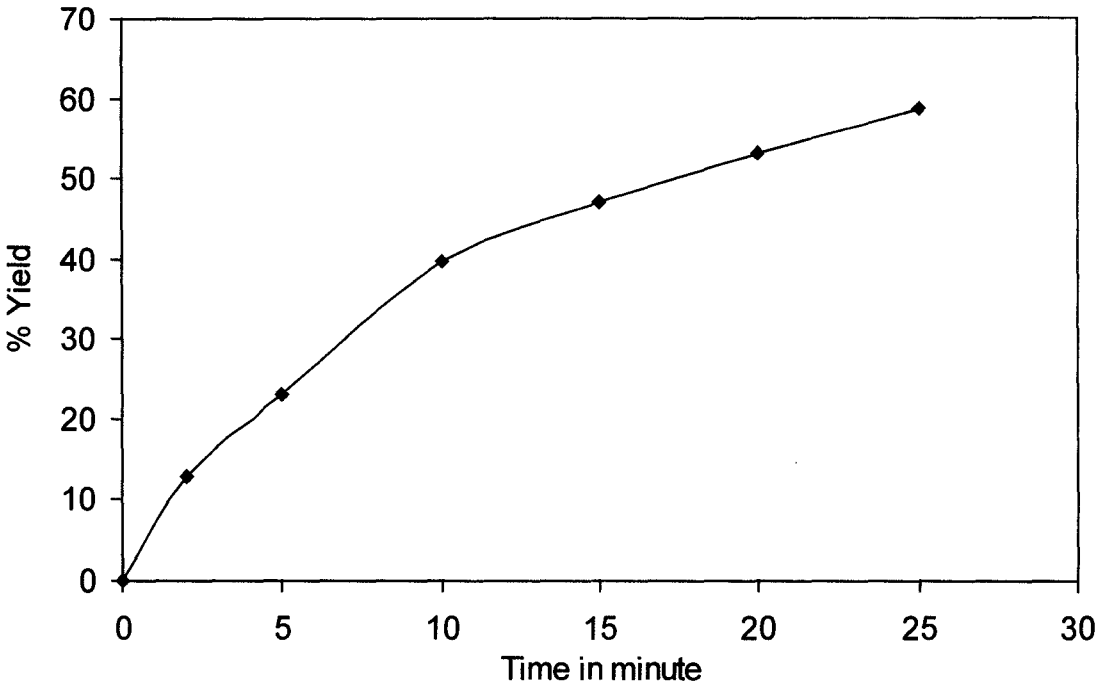


Figure 5.3: Time - conversion plot for aqueous crosslinked polymerization of AM - Bis at 50°C with Fe(III) - TU redox system
Bis = 6 mol%, TU = 0.04 M, $FeCl_3 = 1.5x10^{-3}$ M

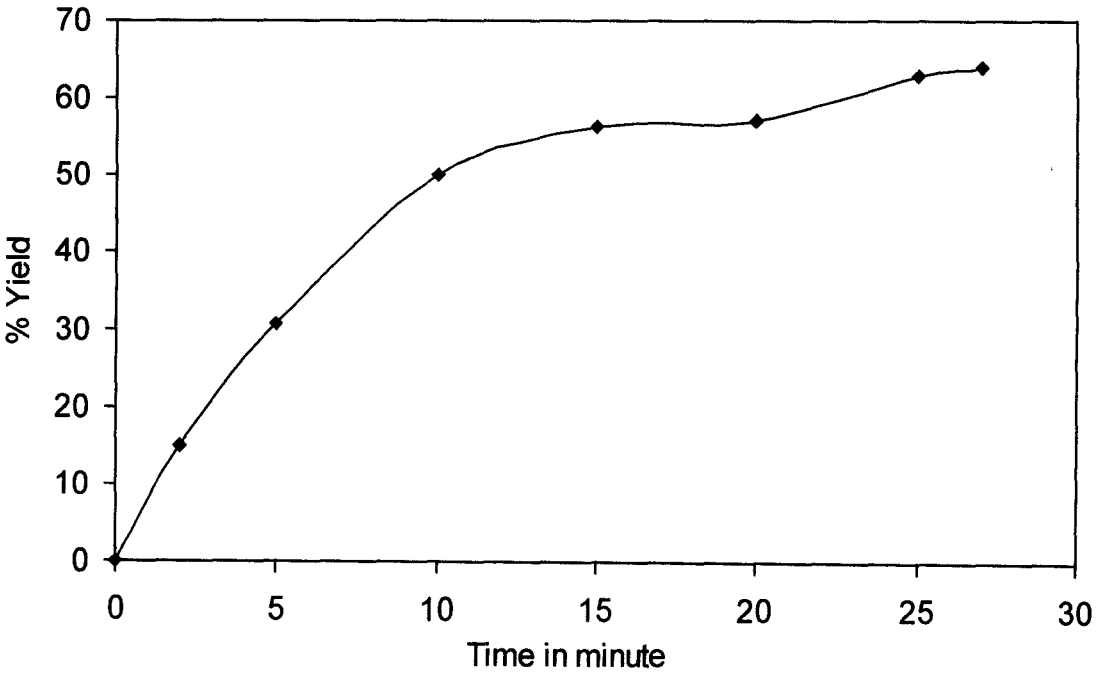


Figure 5.4: Time - conversion plot for aqueous crosslinked polymerization of AM - Bis at 50°C with Fe(III) - TU redox system
Bis = 10 mol%, TU = 0.04M, $FeCl_3 = 1.5x10^{-3}$ M

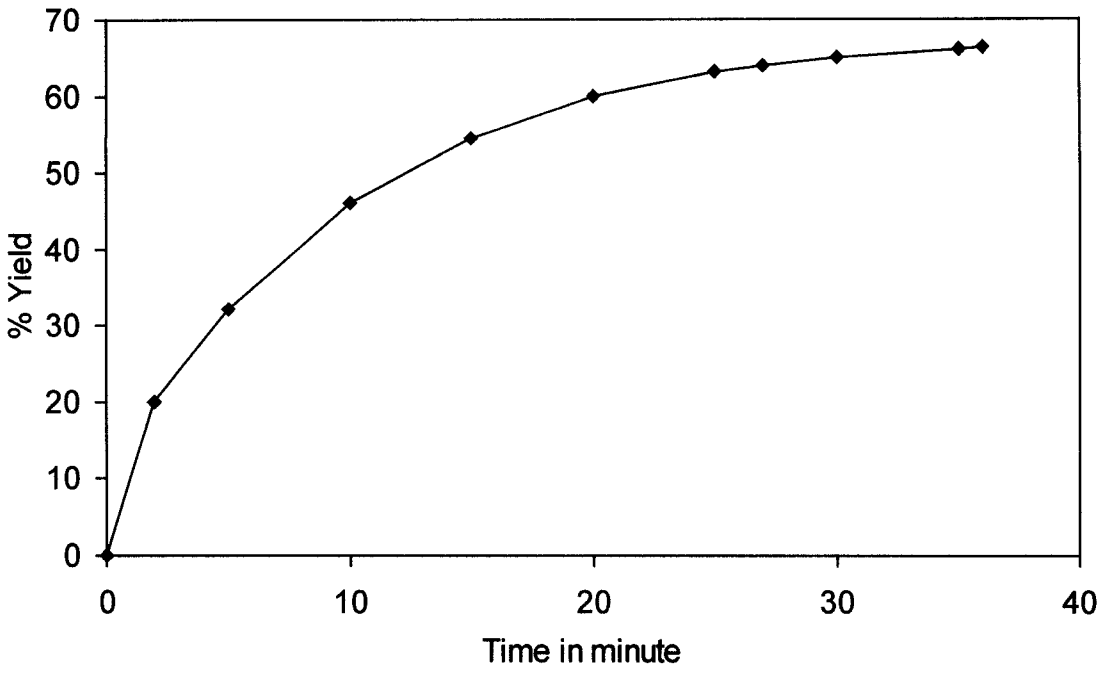


Figure 5.5: Time - conversion plot for aqueous crosslinked polymerization of AM - Bis at 50°C with Fe(III) - TU redox system
Bis = 10 mol%, TU = 0.04M, $FeCl_3 = 1.5x10^{-3}$ M

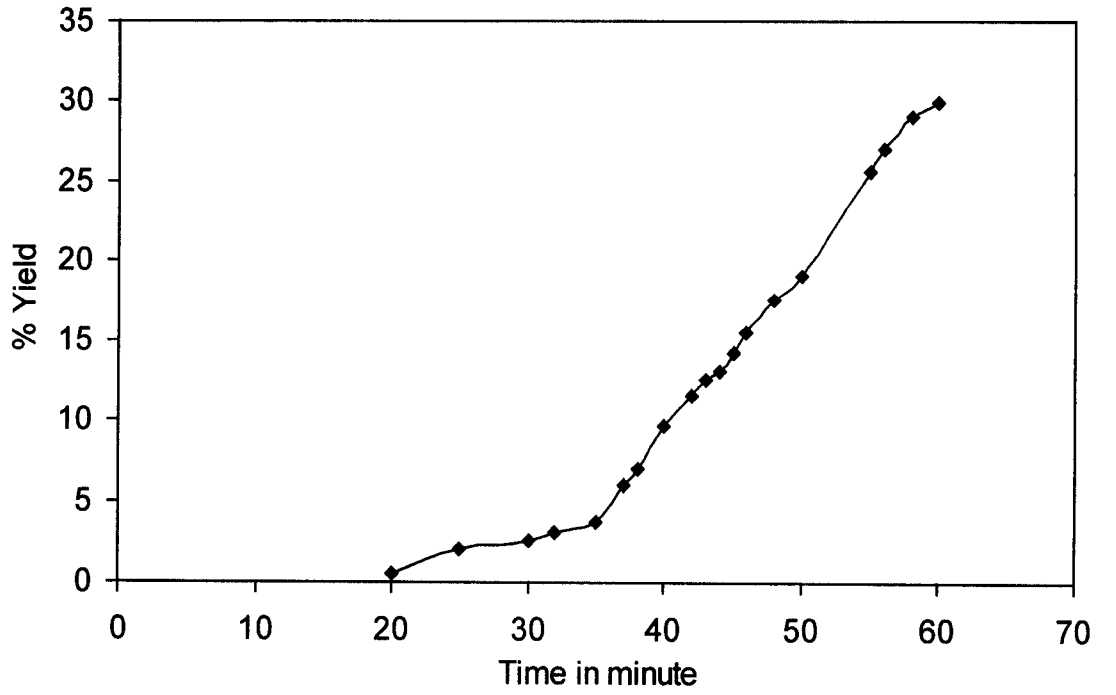


Figure 5.6: Time - conversion plot for aqueous crosslinked polymerization of AM - Bis at 40°C with Ce(IV) - TU redox system
Bis = 0.1 mol%, TU = 0.04 M, Ce(IV) = $1.5x10^{-3}$ M

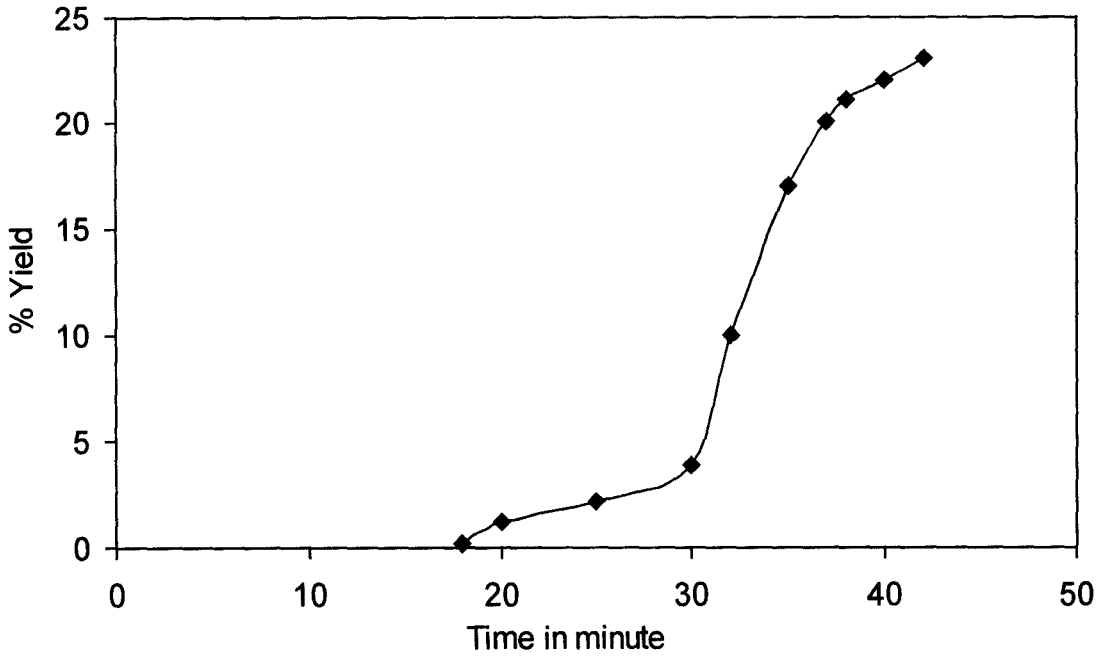


Figure 5.7: Time - conversion plot for aqueous crosslinked polymerization of AM-Bis at 40^0C with Ce(IV) - TU redox system
Bis = 0.3 mol%, TU = 0.04 M, Ce(IV) = $1.5x10^{-3}$ M

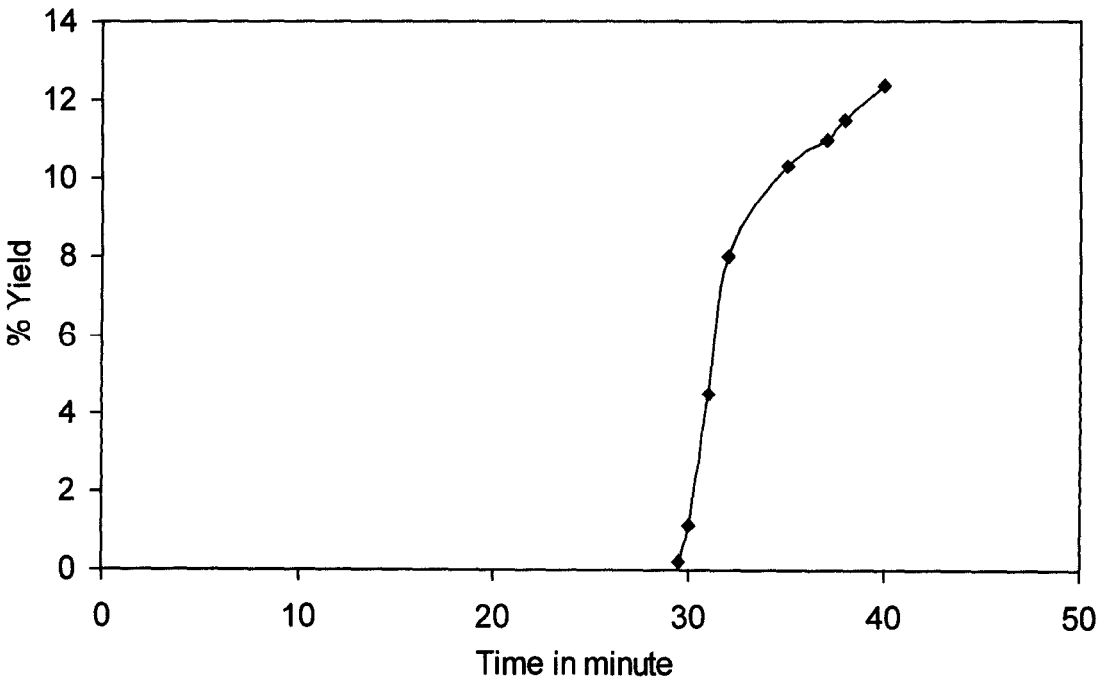


Figure 5.8: Time - conversion plot for aqueous crosslinked polymerization of AM - Bis at 40^0C with Ce(IV) - TU redox system
Bis = 0.5 mol%, TU = 0.04 M, Ce(IV) = $1.5x10^{-3}$ M

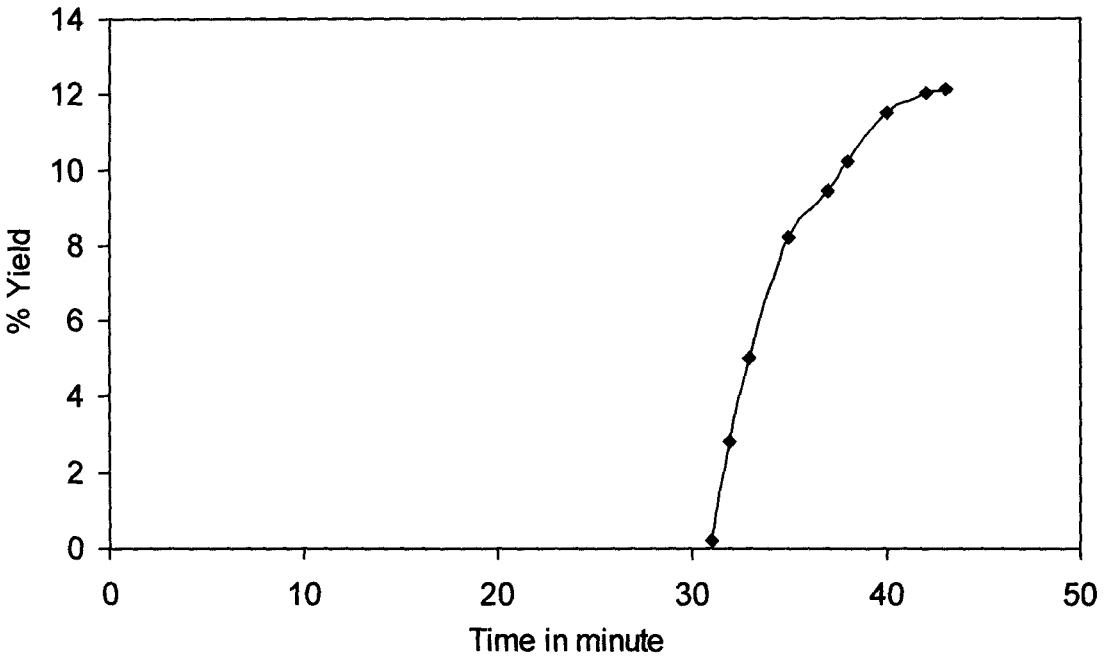


Figure 5.9: Time - conversion plot for aqueous crosslinked polymerization of AM - Bis at 40^0C with Ce(IV) - TU redox system
Bis = 2.0 mol%, TU = 0.04 M, Ce(IV) =$1.5x10^{-3}$ M

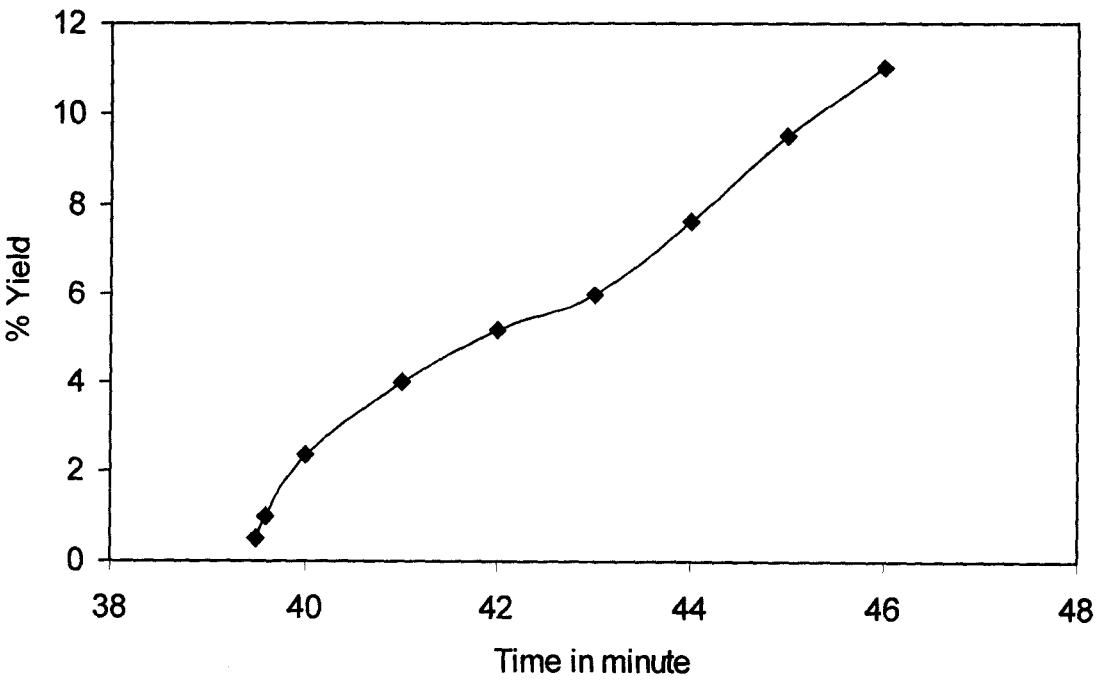


Figure 5.10: Time - conversion plot for aqueous crosslinked polymerization of AM - Bis at 40^0C with Ce(IV) - TU redox system
Bis = 4.0 mol%, TU = 0.04 M, Ce(IV) = $1.5x10^{-3}$ M

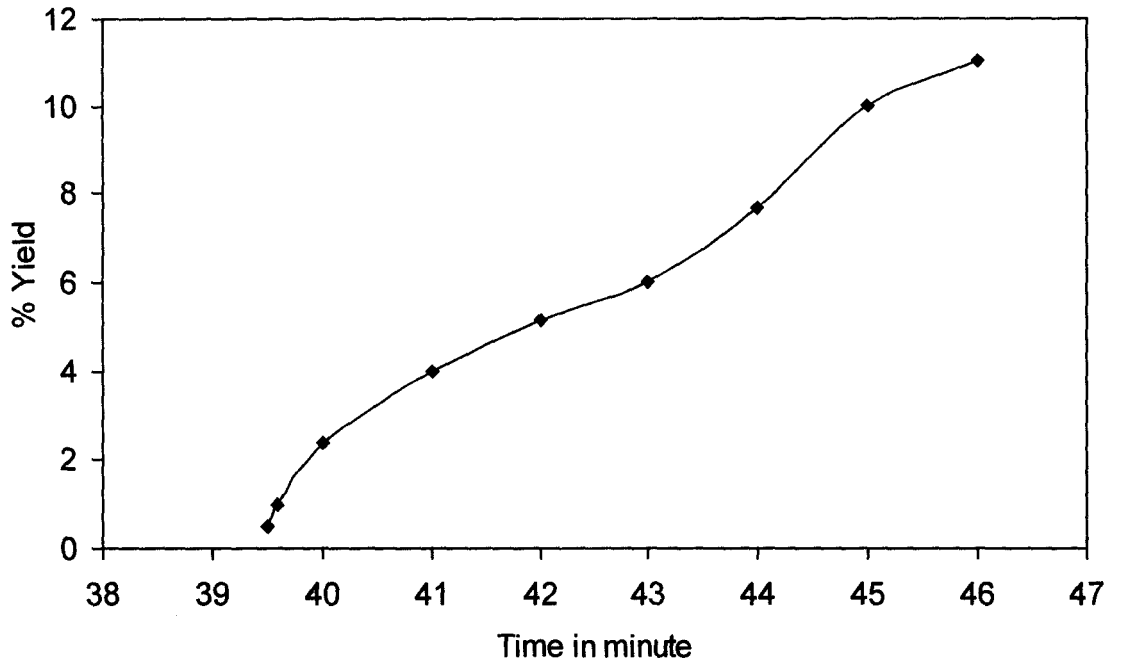


Figure 5.11: Time - conversion plot for aqueous crosslinked polymerization of AM - Bis at 40^0C with Ce(IV) - TU redox system
Bis = 6.0 mol%, TU = 0.04 M, Ce(IV) =$1.5x10^{-3}$ M

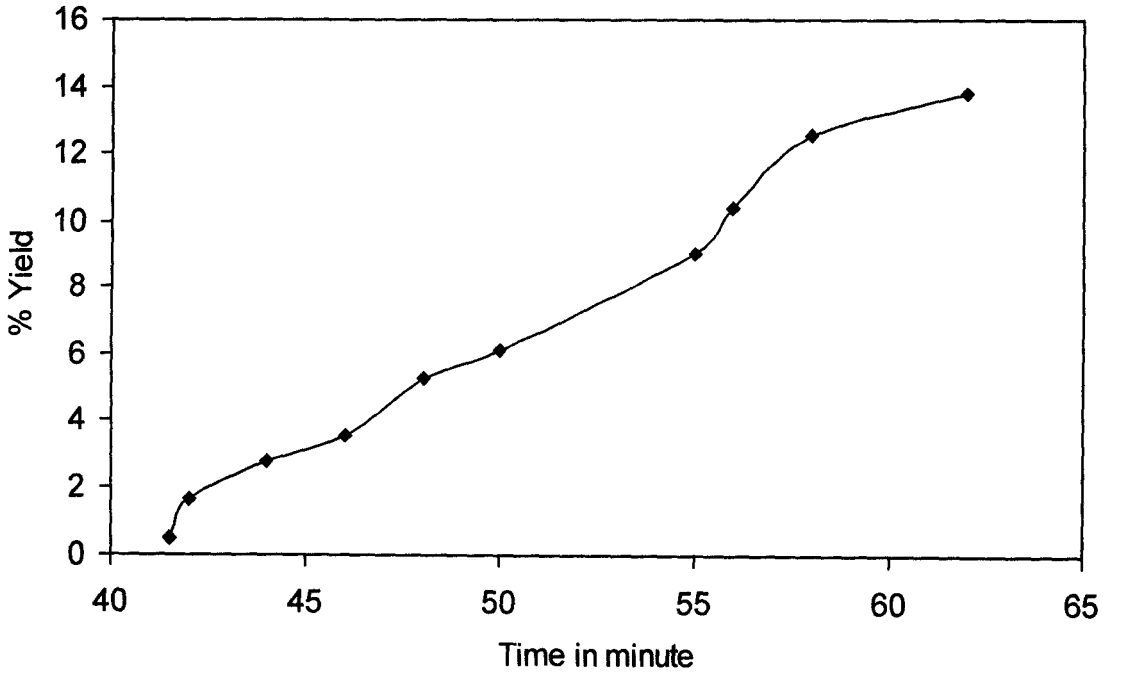


Figure 5.12: Time - conversion plot for aqueous crosslinked polymerization of AM - Bis at 40^0C with Ce(IV) - TU redox system
Bis = 8.0 mol%, TU = 0.04 M, Ce(IV) = $1.5x10^{-3}$ M

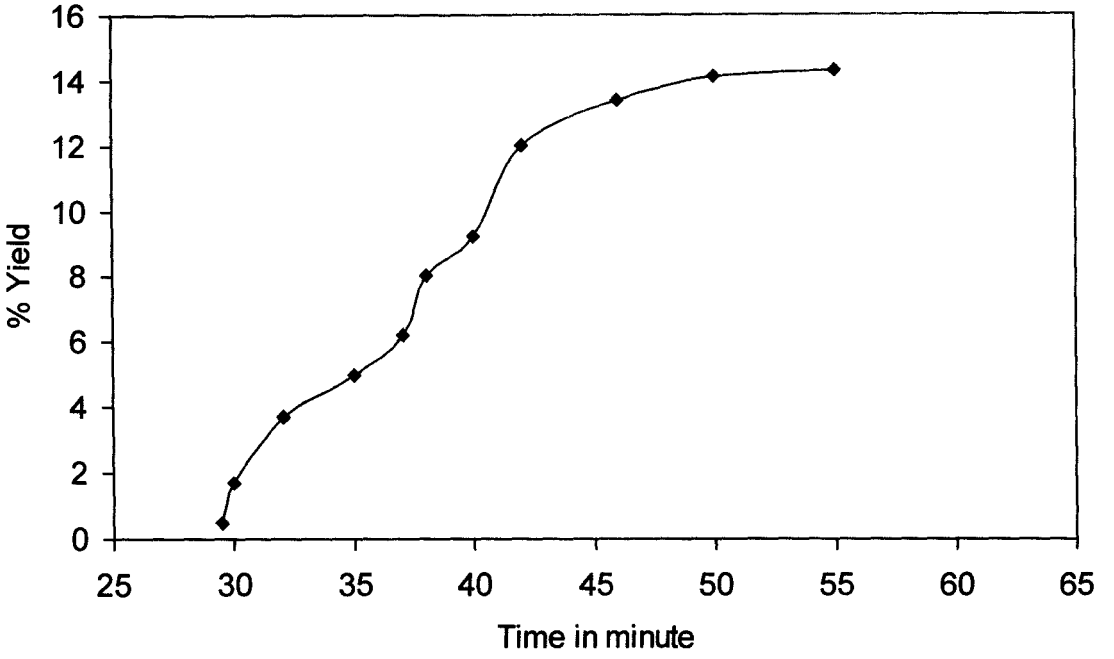


Figure 13: Time - conversion plot for aqueous crosslinked polymerization of AM - Bis at 40^0C with Ce(IV) - TU redox system
Bis = 12 mol%, TU = 0.04 M, Ce(IV) = $1.5x10^{-3}$ M

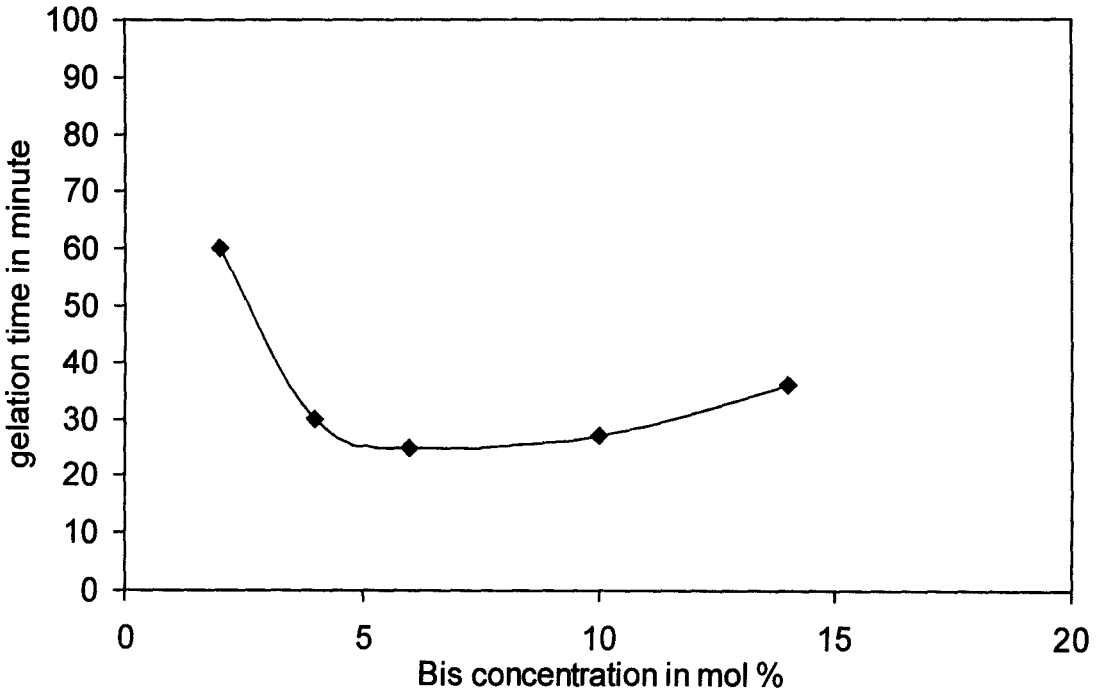


Figure 5.14a: Gelation point in terms of reaction time as a function of Bis concentration for Fe(III) - TU redox initiator system
Polymerization temparature is 50^oC

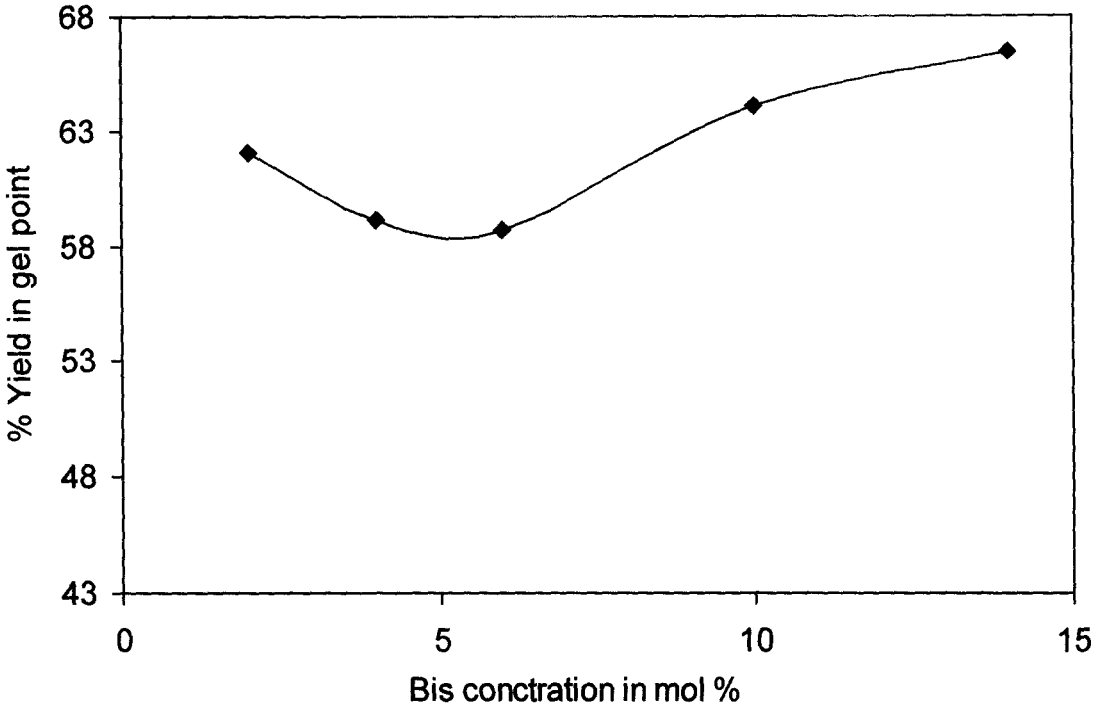


Figure 5.14b: Gelation point in terms of monomer conversion as a function of Bis concentration for Fe(III) - TU redox initiator system Polymerization temparature is 50°C

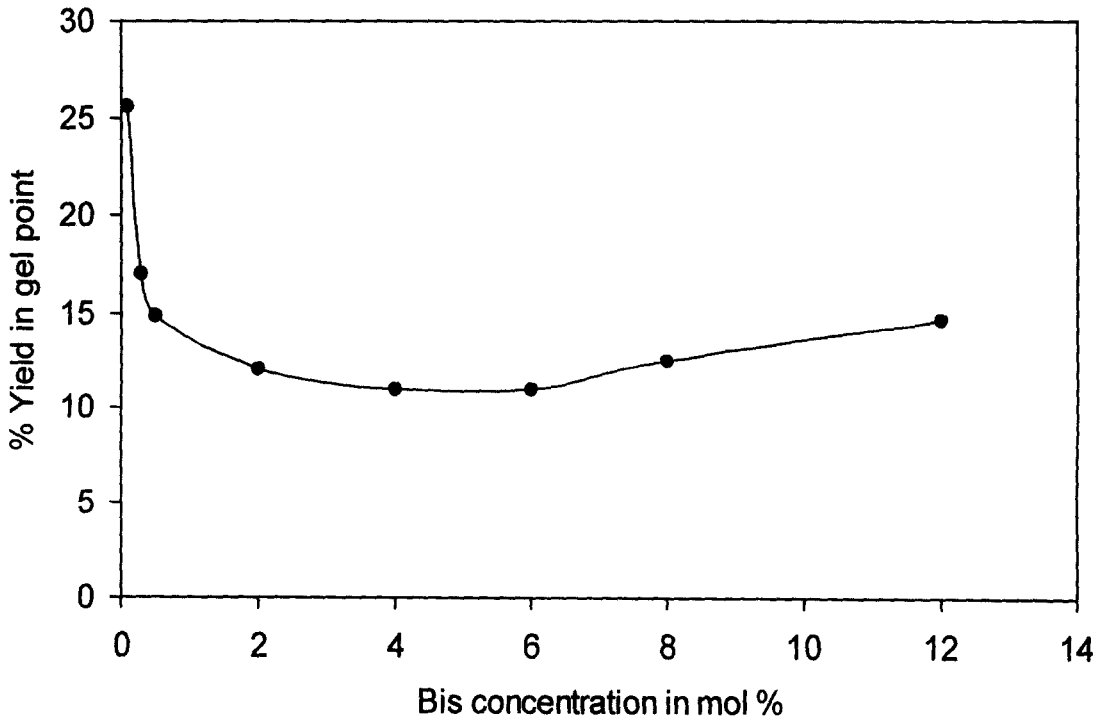


Figure 5.15a: Gelation point in terms of monomer conversion as a function of Bis concentration for Ce(IV) - TU redox initiator system. Polymerization temparature is 40°C

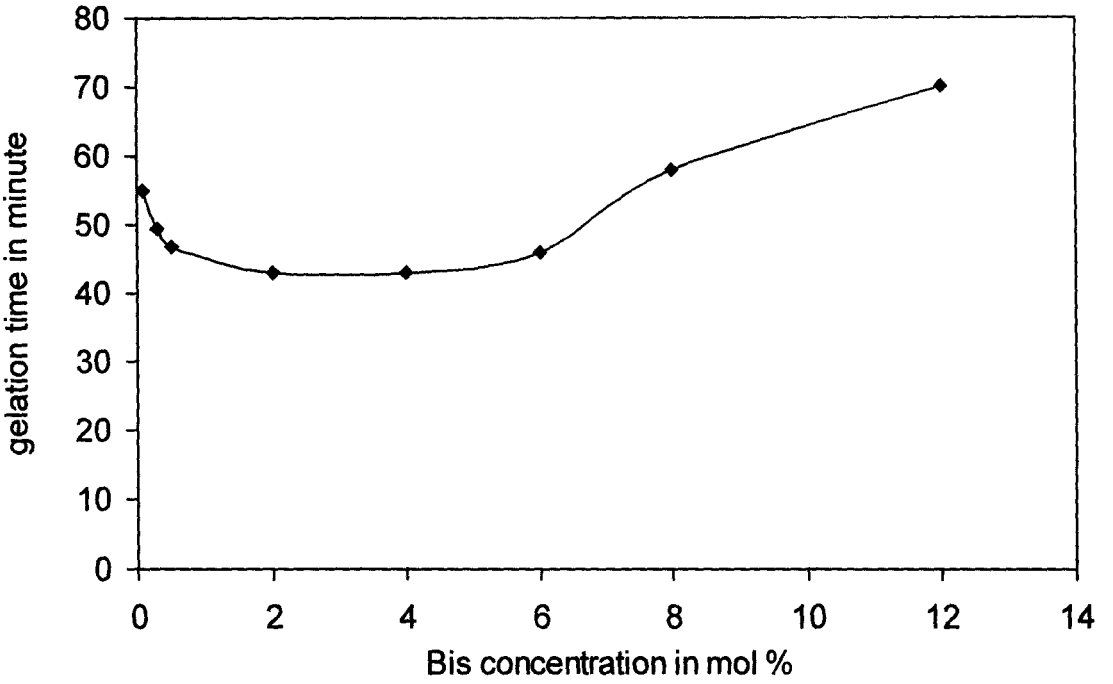


Figure 5.15b: Gelation points in terms of reaction time as a function of Bis concentration for Ce(IV) - TU redox initiator system. Polymerization temparature is 40^0C

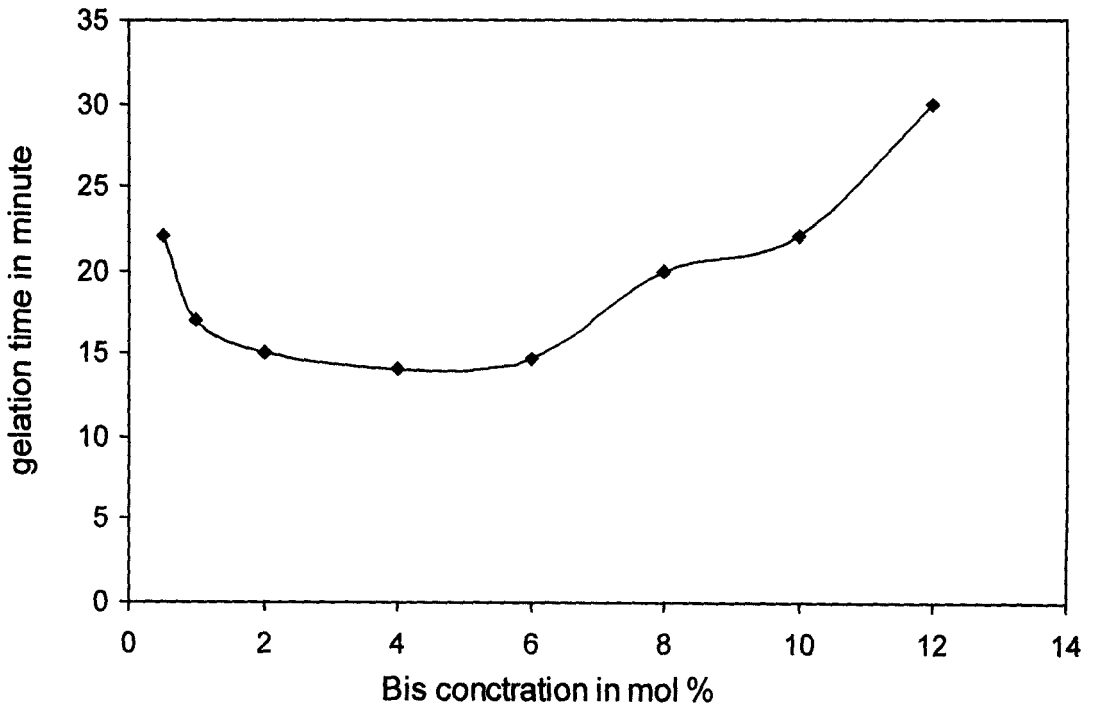


Figure 5.16: Gelation point in terms of monomer conversion as a function of Bis concentration for Ce(IV) - TU redox initiator system Polymerization temparature is 50^0C

5.3 SWELLING AND THERMAL BEHAVIOURS OF HYDROGEL OF ACRYLAMIDE WITH N,N-METHYLENE-BIS-ACRYLAMIDE PREPARED BY Fe(III)-THIOUREA AND Ce(IV)-THIOUREA REDOX INITIATOR SYSTEMS

5.3.1 INTRODUCTION

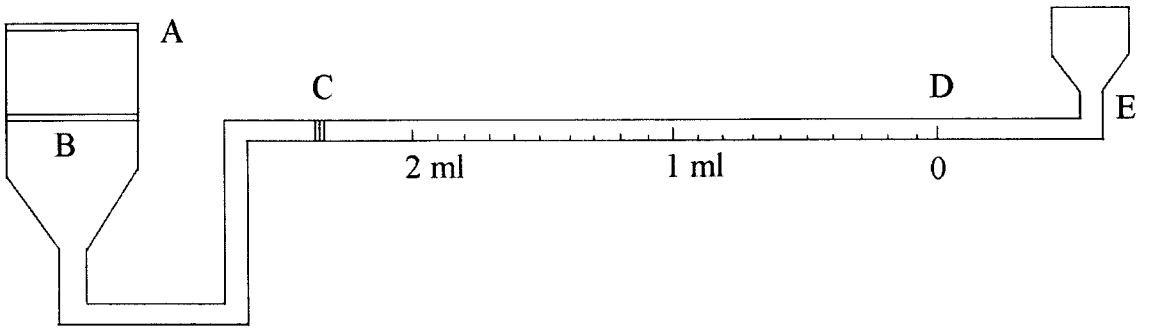
Water-soluble polymers can form hydrogels after crosslinking. The hydrogel is usually insoluble, but can absorb considerable water and swell. The swelling ratio is measured by mass or volume change, which is a macroscopical property. But on the other hand, the swelling ratio strongly depends on the intrinsic properties of corresponding linear polymer, such as solubility and conformation. High solubility and expanded conformation in certain solvents lead to high swelling ratio. Hydrogels, which are hydrophilic natured three-dimensional networks, have been used in bioengineering, biotechnology, medicine, pharmacy, agriculture, food industry, photographic technology and other fields. Swelling properties of acrylamide (AM) hydrogels were very much responsible for its various uses such as controlled release applications for delivery of enzymes, hormones, contraceptives, anticoagulants etc. Recent studies on polyelectrolyte gels unambiguously indicate that swelling occurs in many physiological systems and plays a crucial role in physiological processes such as nerve excitation, muscle contraction, and cell locomotion. The phenomena of gel swelling have been the subject of numerous studies [101-108] in polymer physics. It has been demonstrated that minute changes in the external condition such as temperature [104], solvent composition [106], ionic strength [105-107], and external electric field can induce drastic changes in the state of the swelling network. In particular, it is well known that under certain conditions, polyelectrolyte gels may undergo a discontinuous volume change [104] during swelling. It was found that as a result of coupling between ionization degree and elasticity these systems exhibit a variety of interesting mechanical and scattering properties [109-113].

Therefore, investigations of the swelling behaviour of AM based hydrogels are very much interesting and have been reported during last couple of years. The swelling property, which depends on the network structure, is closely related to the conditions under which the polymer gels are formed [83]. In both academic studies and industrial applications AM hydrogels were obtained by the free radical copolymerization of AM and N,N-methylene-bis-acrylamide (Bis) using various initiator systems. In the section 5.2 new techniques to obtain hydrogels of AM and Bis using Fe(III)-TU and Ce(IV)-TU redox initiator system have been reported. In this section the carefully determined data pertaining to the swelling and thermal properties of the hydrogels prepared, which apparently yielded super absorbent hydrogels at various temperatures are reported.

5.3.2 EXPERIMENTAL

Experiments on swelling

The swelling behaviour of AM-Bis hydrogels was studied in aqueous medium using a purpose built apparatus designed in our laboratory as shown below, in which a graduated horizontal tube of 2 mm diameter (CD) is attached with a 'U' tube by standard joint connector at 'C'. One arm of 'U' tube contains a sintered glass (B) (Borosil$^{(R)}$, Porosity Grade 1, Pore Size 90-150 micron) of 20 mm diameter fitted horizontally in a vertical crucible (A) in the same level of the graduated tube. Other end of the graduated tube is made funnel like (E) in order to help pouring of water for swelling experiment. During running of the experiment, distilled water was filled up in the 'U' tube and the graduated tube up to the zero mark (D). The graduated tube is always kept horizontal and water level in the U tube just touches and wets the sintered glass at the beginning.



The system was maintained at a constant temperature using a water bath keeping the two open ends of the apparatus in air above the water level of the bath. Accurately weighed (~0.5 gm) gel sample in powder form is taken in the sintered glass crucible and immediately water content in the graduated tube starts decreasing due to swelling of the hydrogel. Volume of water absorbed was measured directly after definite time interval and swelling of water per 100 gm. of gel was calculated and plotted as a function of swelling time.

5.3.3 RESULTS AND DISCUSSION

Swelling studies

The swelling property of a polymer in a solvent depends upon the nature of the polymer and the solvent. Percentage swelling (or mass swelling) is the most important parameter in swelling studies. Percentage swelling (% S) was calculated by using the following expression.

$$\% S = [(V_t - V_o)/M_o] \times 100. \quad (55)$$

where V_o is the initial water level (usually zero position of the graduated tube).
V_t is the final water level in the graduated tube after time t.
M_o is the weight of the gel particle in the dry condition.

Effect of crosslinker concentration

The effect of crosslinker concentration on the swelling behaviour of hydrogels is shown in Figures 5.17-5.19. In this experiment crosslinker concentration was varied between 2 mol % to 14 mol %. Total monomer concentration was maintained at 0.4 M. Initially the rate of swelling is increased steadily but ultimately assumes a steady value. However, with the rise of cross linker concentration, swelling decreases. It is well known that as the crosslinker concentration is increased, a decrease in the swelling percentage results because the molecules of the crosslinker occupy positions between the chains of monomers. Thus, as the composition of hydrophilic group decreases, the extent of swelling decreases [60]. Table 5.1 depicts the equilibrium volume swelling [%S(V)] of the hydrogels prepared at different temperatures with different Bis percentages. It is seen from the table that %S(V) is increased for the polymer with lower Bis percentage prepared at higher temperature.

Effect of temperature

To study the effect of temperature on the swelling behaviour of AM hydrogels, hydrogels having variable crosslinker concentration were studied at three different temperatures (i.e. 8°C, 20°C, and 30°C). In all the cases, temperature induces more and more swelling in the hydrogel as is evident from Figure 5.20.

Diffusion of Water

When a glassy hydrogel is brought into contact of water, water diffuses into the hydrogel and the hydrogel swells. Diffusion involves migration of water into pre-existing or dynamically formed spaces between hydrogel chains. Swelling of the hydrogel involves larger scale segmental motion resulting in an increased distance of separation between hydrogel chains. Analysis of the mechanism of water diffusion in swellable polymeric systems has received considerable attention in recent years, because of the important

applications of swellable polymers in the biomedical, pharmaceutical, environmental, and agricultural engineering fields as has already been mentioned.

The following equation is used to determine the type of diffusion of water into hydrogels [114,115].

$$F = (M_t / M_i) = Kt^n \quad (56)$$

Where M_t and M_i represent the amount of solvent diffused into the gel at time t and infinite time, respectively. 'K' is swelling constant related to the structure of the network, and the exponent 'n' is swelling exponent, which is a number to determine the type of diffusion. For cylindrical shapes, if 'n' is the range of 0.45-0.50, diffusion is Fickian, while $0.50 < n < 1.0$ indicates that diffusion is of a non-Fickian type. Above equation is applied to the initial stages of swelling and the plots of ln F versus ln t yield straight lines up to ~60% increase in the mass of hydrogel on water absorption. The n and K values were calculated from the slopes and intercepts of the lines, respectively. Figure 5.21 and 5.22 show the typical curves of swelling kinetics of hydrogel, from which the values of diffusion constants and diffusional exponents of AM-Bis hydrogels were calculated. The values of diffusional exponent range between 0.47 and 0.62 where as the swelling constant, K varies between 5.091×10^{-2} and 11.176×10^{-2}. Therefore, the diffusion of water into hydrogel is considered as non-Fickian type. This behaviour is generally explained as a consequence of a slow relaxation rate of the polymer matrix [115].

Thermogravimetric analysis (TGA)

The thermal stability of copolymers (hydrogel) of AM with Bis (cross linker) prepared under various conditions was analyzed by thermogravimetry (TGA) performed from room temperature to 500°C in air (rate of heating is 5°C per minute). Thermograms of dry hydrogel samples of copolymers of AM and Bis prepared under homogeneous solution conditions (in absence of

vermiculite) by $FeCl_3$-TU initiators are shown in Figure 5.23. In general, the thermograms display multistage weight loss features as a function of temperature. However, the samples are completely decomposed/charred at about 400°C. In almost all the samples, weight loss started at around 200°C. The overall average inflection points (TG_m) obtained from different thermograms as a function of concentration of cross linker (Bis) are shown below (Table 5.2).

The maximum weight loss region lies between 250°C to 400°C except one sample (4 mol % crosslinker), which starts substantial weight loss at 200°C. It is seen that the midpoints of these region (inflection point, TG_m) vary substantially with cross linker concentration. As the concentration of cross linker is increased from 4 mol % (with respect to monomer concentration) to 10 mol %, the thermal stability increases due to increase in the cross linking network. However, it is interesting that 2 mol % of cross linker gives the highest stability. Figure 5.24-5.27 depict the thermograms of dry hydrogel samples prepared by FeV-TU system in presence of 4 mol % cross linker. Table 5.3 shows that the thermal stability in general, is increased dramatically in presence of vermiculite mineral. It is also observed that although thermal stability in general increases with FeV concentration, maximum stability is displayed by an intermediate FeV concentration of 0.005 M. It is also interesting to note that only minor weight loss is observed upto 150°C for all the samples except that prepared in presence of 0.001 M FeV. This particular sample is thermally stable up to 300°C and weight loss starts above this temperature.

If attention is focused on the characteristic features of each thermogram of acrylamide hydrogel, it may be said that the nonstoichiometric loss of water is taken place followed by subsequent loss of ammonia and other gaseous products from the polyacrylonitrile structure formed during decomposition of polyacrylamide and partly from the remaining polyacrylamide in the course of heating [116-118].

Differential Scanning Calorimetric (DSC) study

Differential scanning calorimetry (DSC) was performed by a Perkin-Elmer, (Pyris-6) system (rate of heating 5°C per minute). The DSC profiles (Figure 5.28 - 5.31) show endothermic peaks at 57°C, 70°C and 65°C which indicate the presence of glass transitions for pure copolymers of AM with Bis (dry hydrogel) prepared respectively adding 2 mol %, 6 mol % and 10 mol % crosslinker. The DSC profiles also display the characteristic temperature where softening of the copolymer starts. The onset of softening temperature occurred for the above three samples at 220°C, 215°C and 225°C respectively. Different previous workers have reported different values of glass transition temperature and softening temperature for polyacrylamide homopolymer and copolymer samples [118-126]. Unlike all other samples, the copolymer sample prepared in presence of 4 mol % cross linker (Bis) however, show a DSC profile with a broad endothermic band (centered at 80°C) instead of well-defined peak. However, the softening temperature at 210°C is fairly well defined. Figure 5.32 to 5.39 show DSC profiles of hydrogel samples under moist conditions (gel phase). The endothermic peaks at different temperatures displayed by samples prepared under different conditions may be ascribed to the loss of water. However, interestingly the endothermic peaks displayed by these samples are actually overlap of three closely separated peaks in each case (e.g. Figure no 5.32 & 5.33) indicating three different potential sites for water retention in the acrylamide hydrogel. Water retention characteristics of the hydrogel may be discussed in terms of DSC endothermic peak positions also. Duplicate run were performed (one from upper portion of the sample vessel (low FeV content) and one from lower portion (high FeV content) of an unstirred suspension) for each sample prepared under a definite condition. Endothermic peak temperatures on the DSC profiles clearly manifest the water binding power of the hydrogel samples. For the present hydrogel samples this temperature varies from 110°C (FeV = 2.0×10^{-3} M, cross linker = 4 mol %, TU = 0.04 M, high FeV region) to about 160°C (FeV = 1.5×10^{-3} M, cross linker = 4 mol %, TU = 0.04 M, low FeV region). In Figure 40 endothermic peak temperatures have been plotted as a function of concentration of FeV for both low and high FeV

regions of the vessel. In both the sampling positions, gels prepared in presence of 1.5 x 10^{-3} M FeV (TU = 0.04 M, cross linker = 4 mol %) display highest water removal temperature indicating strongest bond with water molecules. The enthalpy change associated with the endothermic phase change of hydrogels under moist conditions varies from 2398 J/g to 4433 J/g. The enthalpy change for both high and low FeV region samples are plotted as a function of concentration of FeV (Figure 41). Figure 41 shows that the enthalpy-FeV concentration profile pass through a maximum at 1.5 x 10^{-3} M $\overline{\text{Fe(III)}}$. This indicates that the water molecules are strongly bonded with the network structure of the gel that prepared in the presence of 1.5 x 10^{-3} M Fe(III) in the vermiculite mineral (TU = 0.04 M, crosslinker = 4 mol %).

Scanning Electron Microscopy (SEM) image of hydrogel

SEM (LEO S-440, accelerating voltage = 15 Kv, Beam current = 500 pA) images of the water-soluble swellen hydrogel prepared in presence of vermiculite mineral are taken in order to visualize surface morphology of the gel network. Microporasity of gel in presence of the vermiculite mineral is not apparent from SEM picture (Figure 42,43). However, it is seen from the SEM images that vermiculite minerals are heterogenerously scattered in the gel network.

Table 5.I

The production of AM - Bis hydrogels and the value of equilibrium volume swelling [% S(V)] of the same hydrogel

Sample	AM(g)	Bis(g)	Solution (ml)	Bis(mol%)	Temp°C	% S(V)
1	0.696	0.030	25	2	30	2400
2	0.682	0.060	25	4	30	2010
3	0.668	0.092	25	6	30	930
4	0.640	0.154	25	10	30	576
5	0.610	0.216	25	14	30	457
6	0.696	0.030	25	2	20	1982
7	0.682	0.060	25	4	20	1485
8	0.668	0.092	25	6	20	846
9	0.640	0.154	25	10	20	448
10	0.610	0.216	25	14	20	458
11	0.696	0.030	25	2	08	1782
12	0.682	0.060	25	4	08	814
13	0.668	0.092	25	6	08	721
14	0.640	0.154	25	10	08	325
15	0.610	0.216	25	14	08	300

Table 5.2

Cross linker(Bis) conc. in mol % (total monomer conc. 0.4 M)	TG_m/°C
2	335.3
4	264.7
6	288.2
10	305.9

Table 5.3

Conc. of Fe(III) in FeV x 10^3 M	TG_m/°C
0.5	300.0
1.0	382.8
1.5	300.0
2.0	320.7

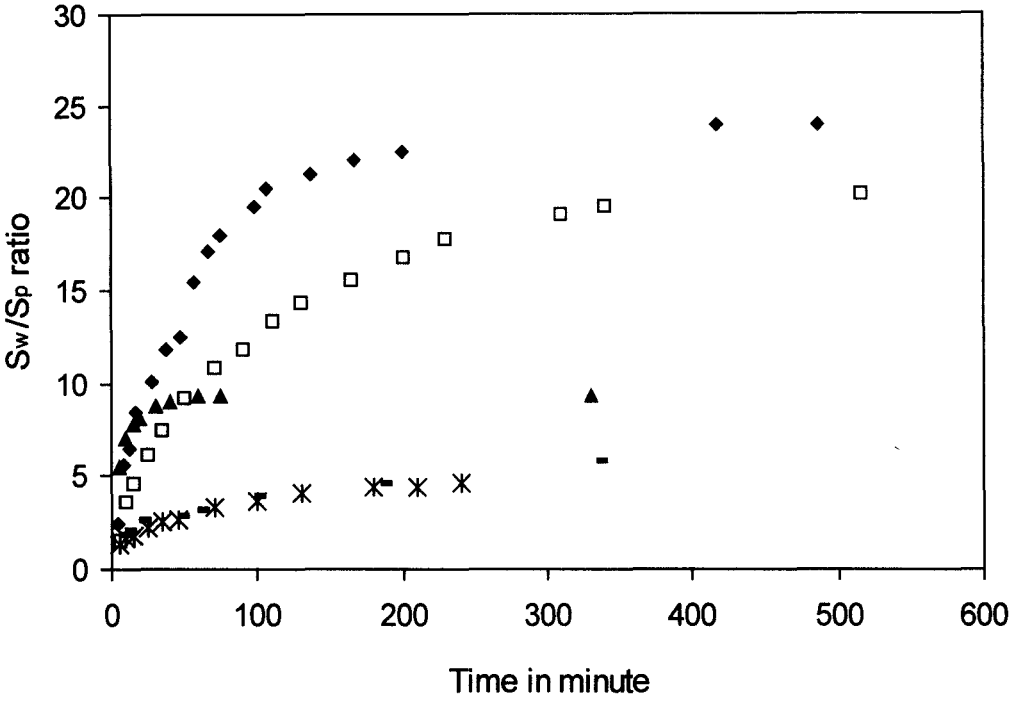


Figure 5.17: Variation of swelling ratio with time of hydyogel of various amount of crosslinker obtained by Fe(III) -TU redox initiator system at 30°C

◆ 2 mol% □ 4 mol% ▲ 6 mol% - 10 mol% ✳ 14 mol%

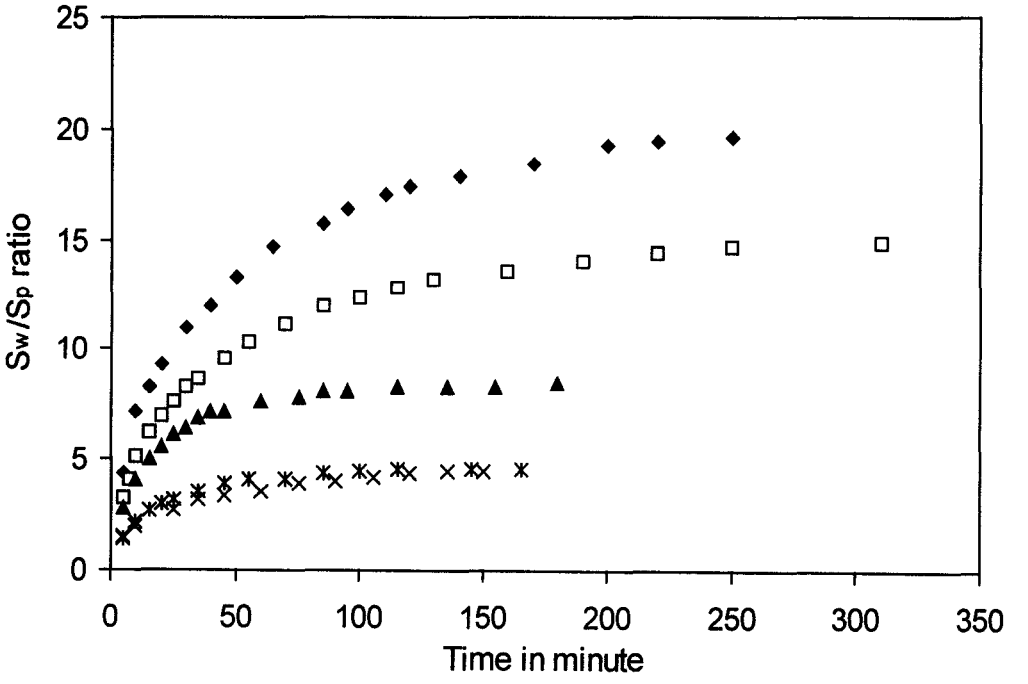


Figure 5.18: Variation of swelling ratio with time of hydyogel of various amount of crosslinker obtained by Fe(III) - TU redox initiator system at 20°C

◆ 2 mol% □ 4 mol% ▲ 6 mol% × 10 mol% ✳ 14 mol%

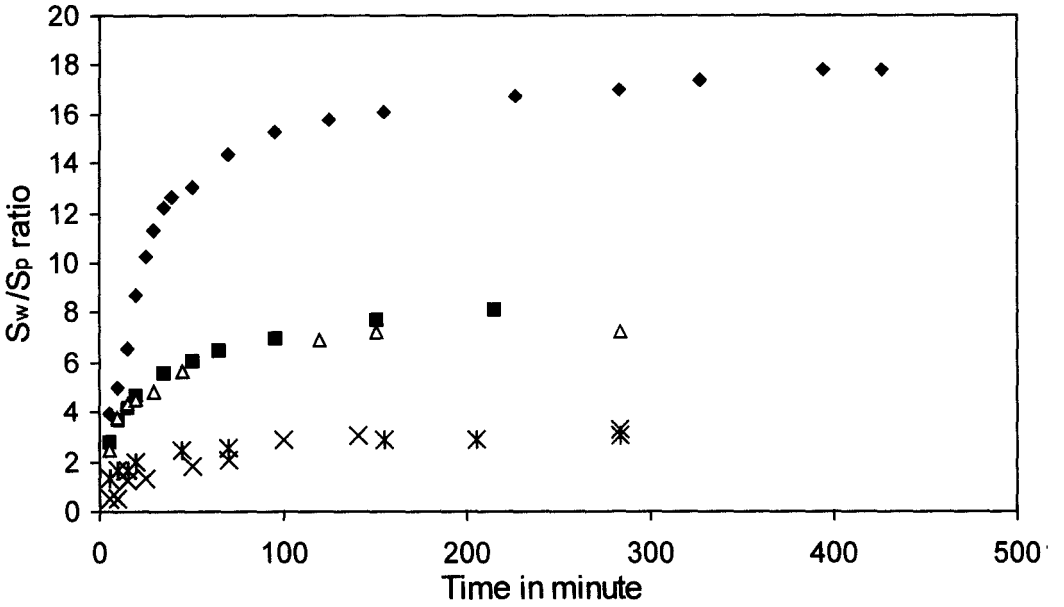


Figure 5.19: Variation of swelling ratio with time of hydyogel of various amount of crosslinker obtained by Fe(III) - TU redox initiator system at 8°C

◆ 2 mol% ■ 4 mol% △ 6 mol% × 10 mol% ✳ 14 mol%

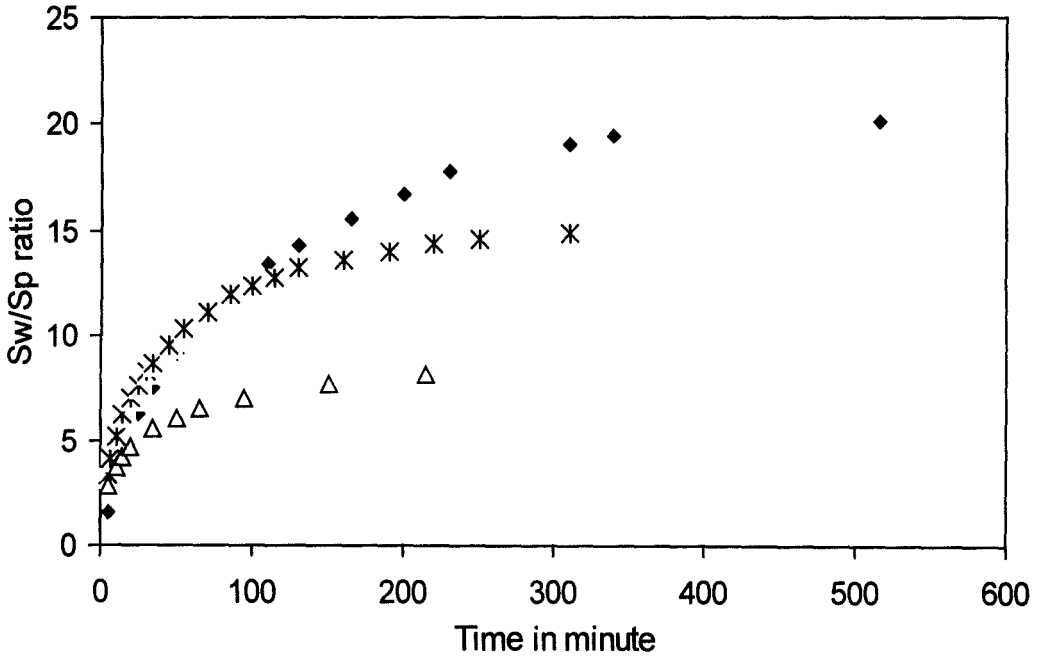


Figure 5.20: Variation of swelling ratio with time of hydyogel of 4 mol% Bis obtained by Fe(III) - TU redox initiator system at different temperature

◆ 30 Degree C ✳ 20 Degree C △ 08 Degree C

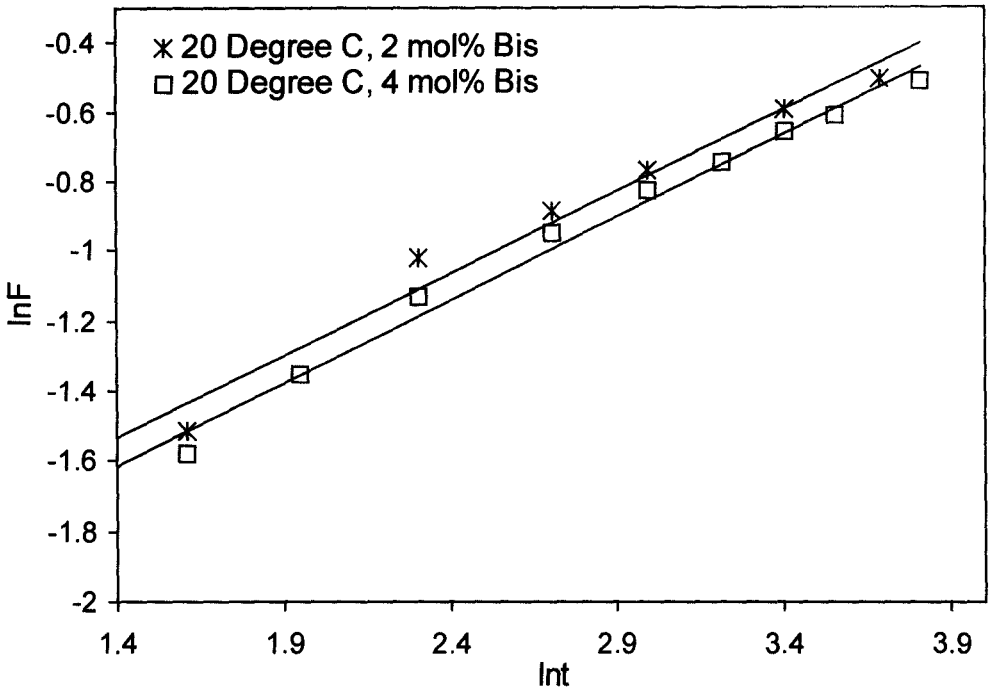


Figure 5.21: The typical curves of swelling kinetics of AM-Bis hydyogel

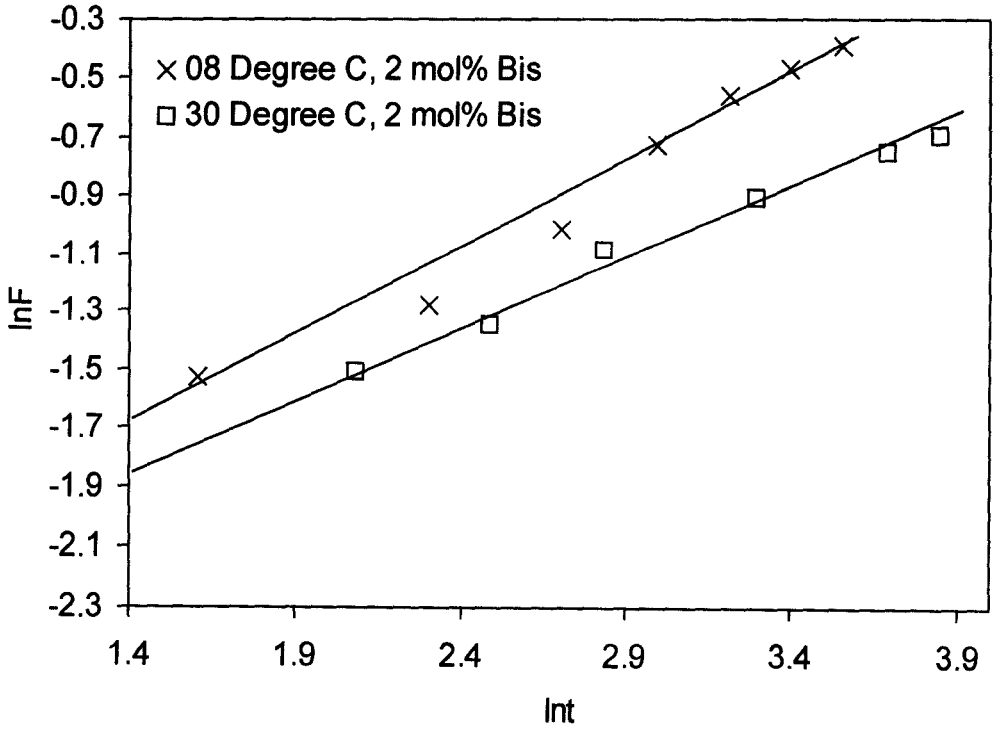


Figure 5.22: The typical curves of swelling kinetics of AM-Bis hydyogel

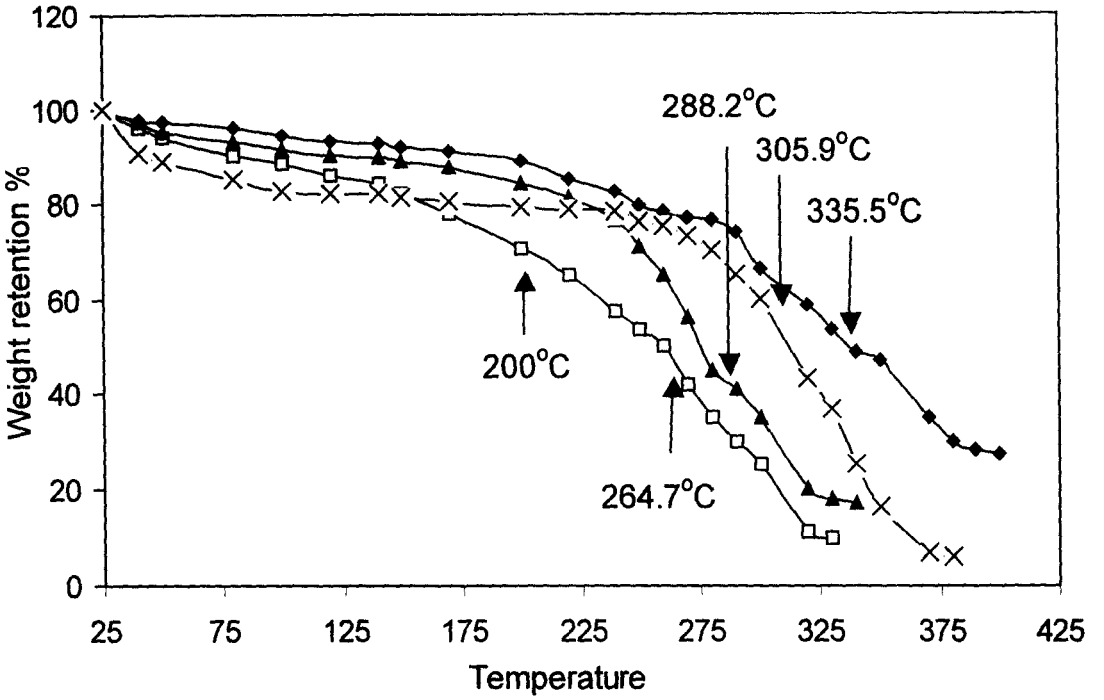


Figure 5.23: Thermal behaviour of dry hydrogels prepared in absence of clay at 50°C using Fe(III)-TU initiating system: $FeCl_3$=1.5 x 10^{-3} M, TU = 0.04 M.
—◆— 2 mo% Bis —□— 4 mol% Bis —▲— 6 mol% Bis —×— 10 mol% Bis

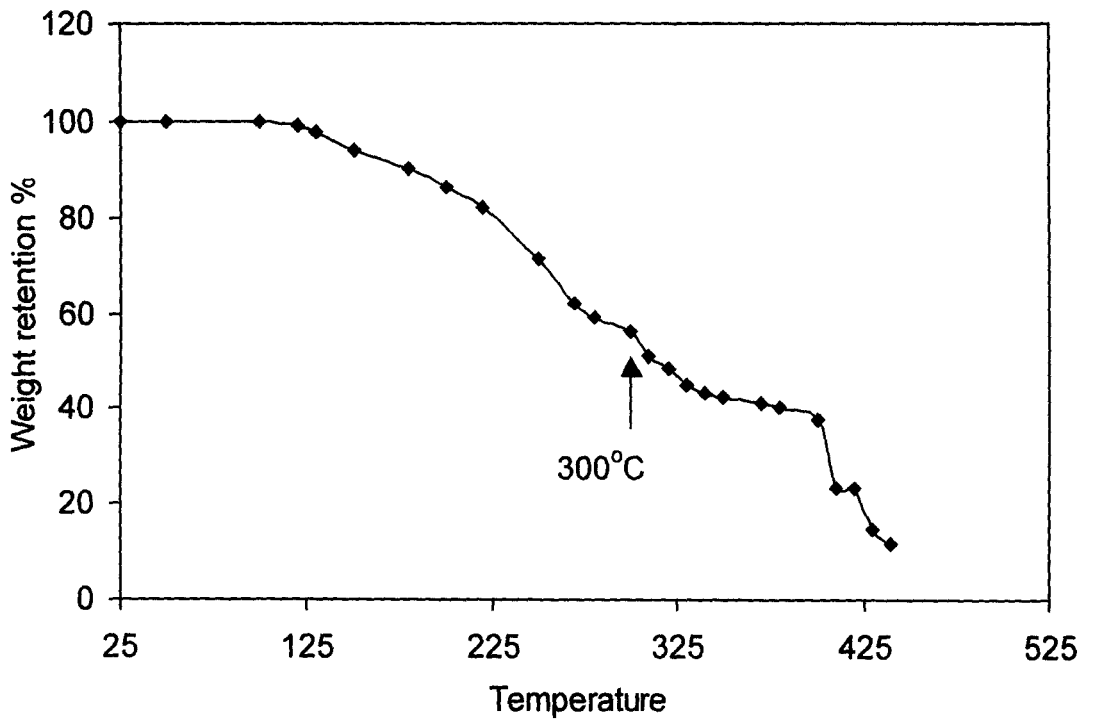


Figure 5.24: Thermal behaviour of dry hydrogel prepared in presence of clay at 50°C using FeV-TU initiating system: Fe(III) ion = 0.5 x 10^{-3} M, Bis = 4 mol %, TU = 0.04 M.

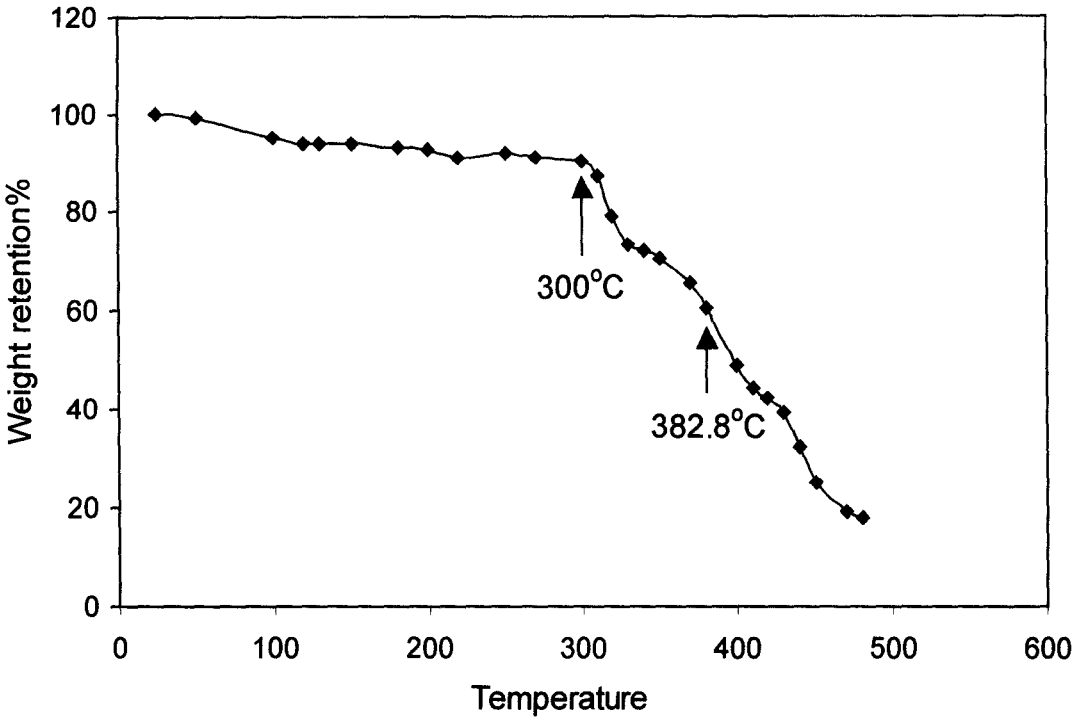


Figure 5.25: Thermal behaviour of dry hydrogel prepared in presence of clay at 50°C using FeV-TU initiating system: Fe(III) ion = 1.0 x 10^{-3} M, Bis = 4 mol %, TU = 0.0 4 M.

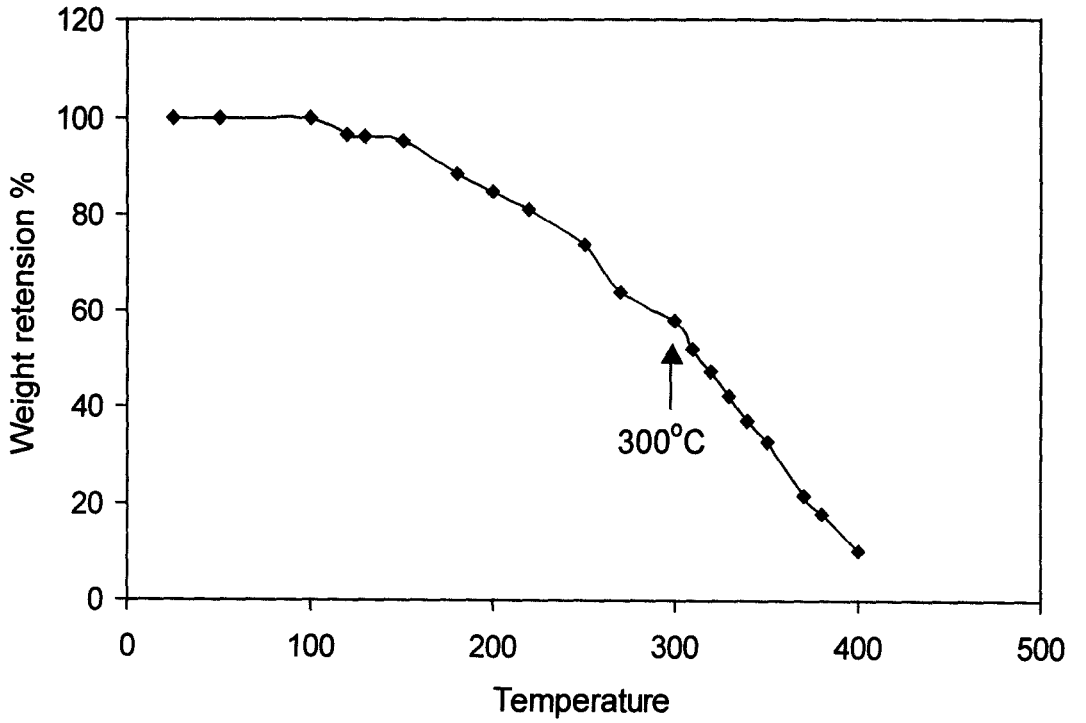


Figure 5.26: Thermal behaviour of dry hydrogel prepared in presence of clay at 50°C using FeV-TU initiating system: Fe(III) ion = 1.5 x 10^{-3} M, Bis = 4mol %, TU = 0.04 M.

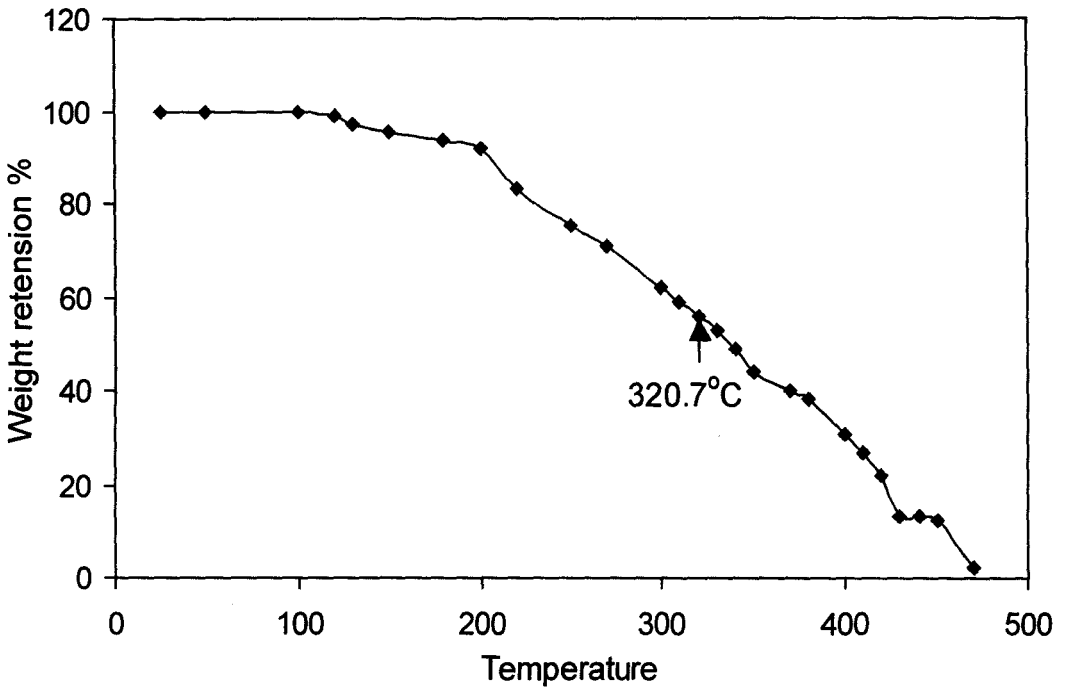


Figure 5.27: Thermal behaviour of dry hydrogel prepared in presence of clay at 50°C using FeV-TU initiating system: Fe(III) ion = 2.0 x 10^{-3} M, Bis = 4 mol %, TU = 0.04 M.

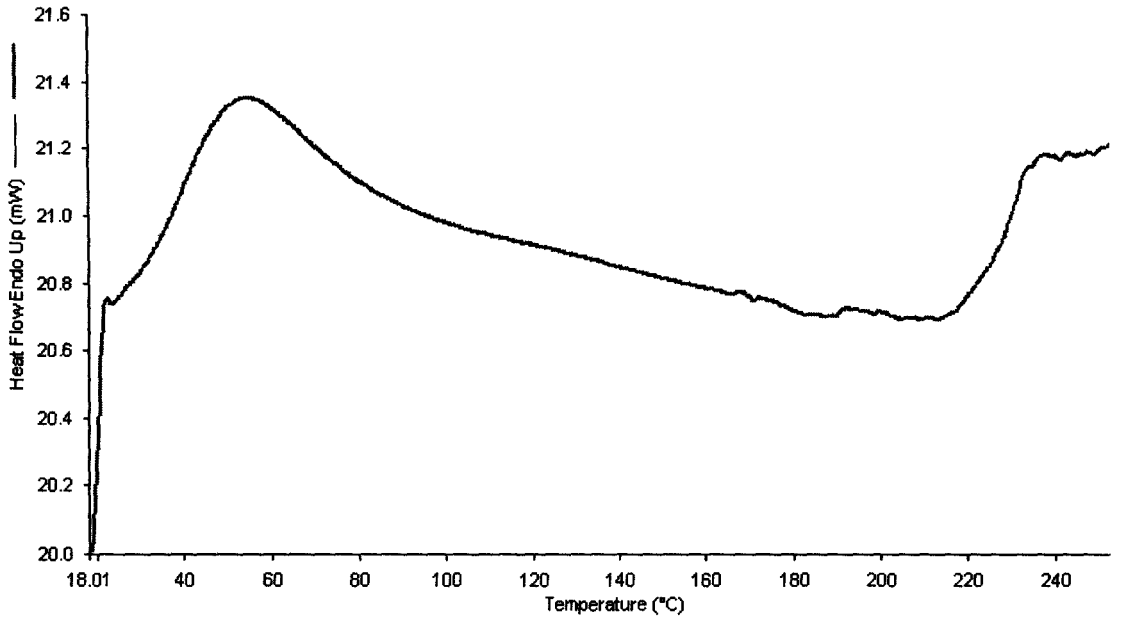


Figure 5.28: DSC curve of dry AM - Bis hydrogel prepared in clay medium: Bis = 2 mol %, Fe(III) in FeV = 1.5 x 10^{-3} M, TU = 0.04 M, Temp= 50°C

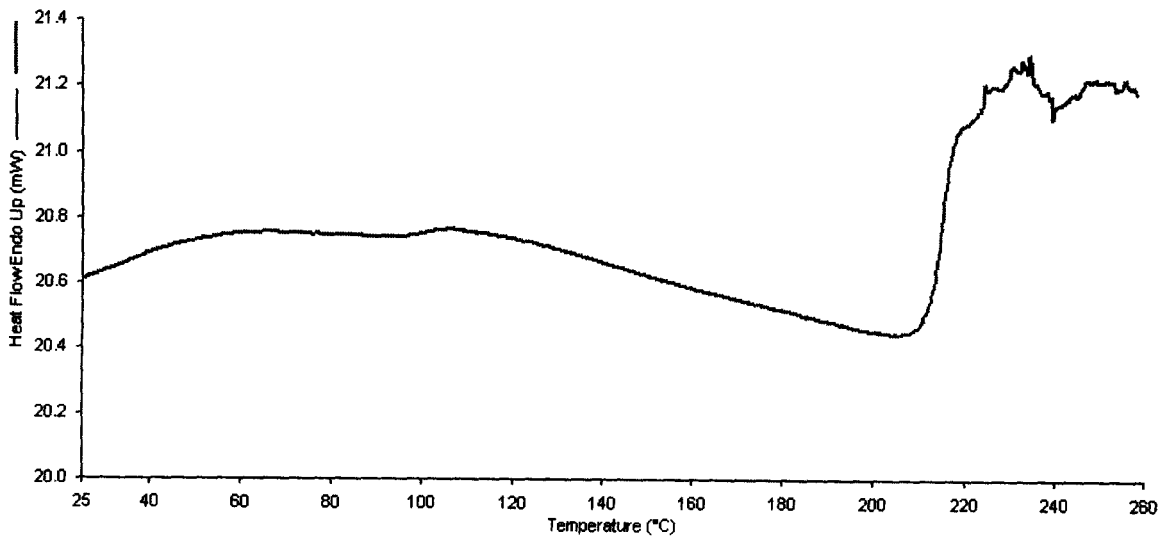


Figure 5.29: DSC curve of dry AM - Bis hydrogel prepared in clay medium: Bis = 4 mol %, Fe(III) in FeV = 1.5 x 10^{-3} M, TU = 0.04 M, Temp = 50°C

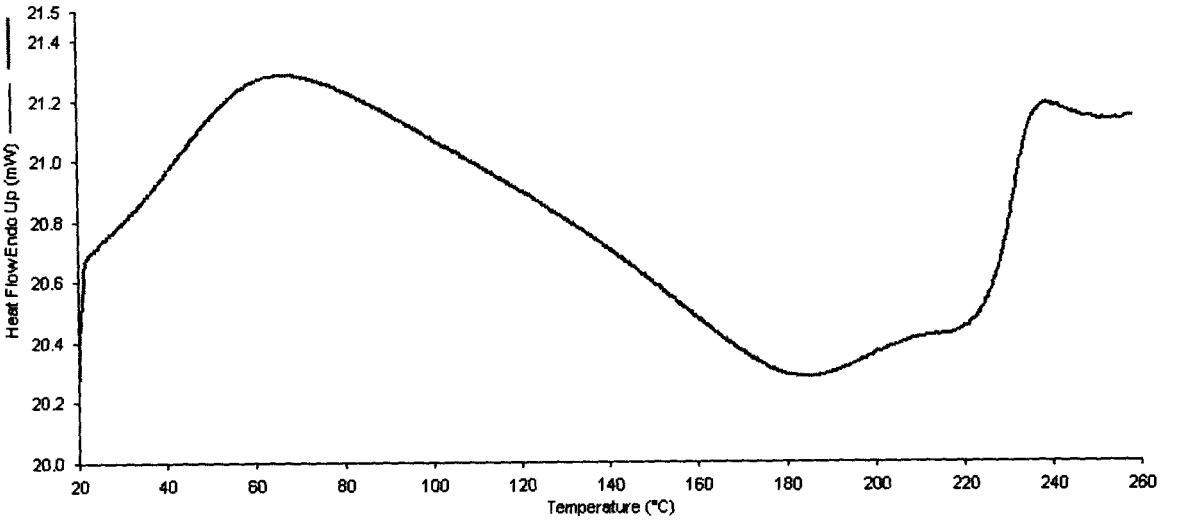


Figure 5.30: DSC curve of dry AM-Bis hydrogel prepared in clay medium: Bis = 6 mol %, Fe(III) in FeV = 1.5 x 10^{-3} M, TU = 0.04 M, Temp= 50°C

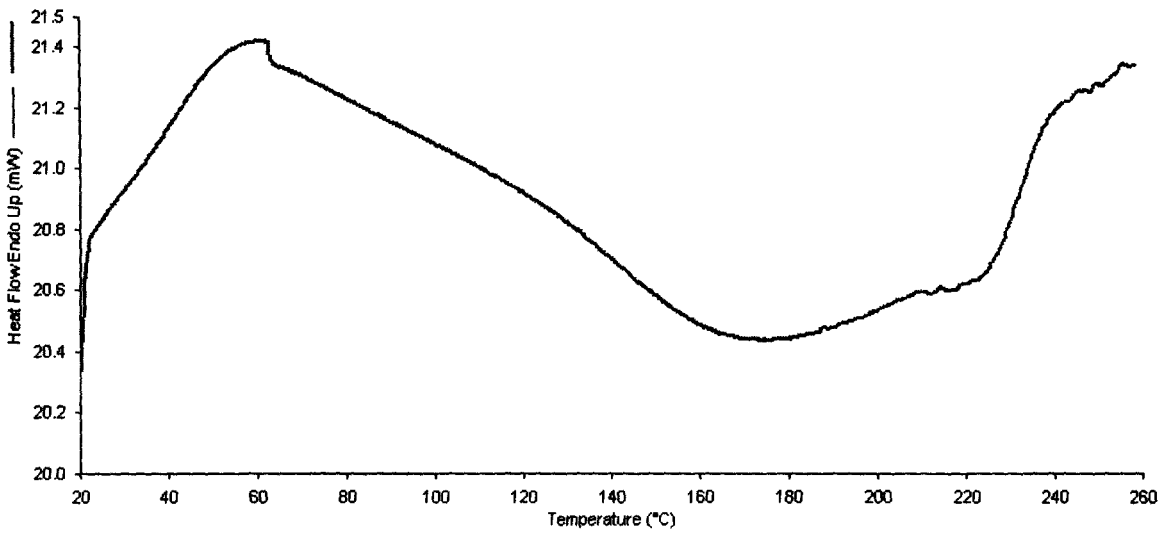


Figure 5.31: DSC curve of dry AM-Bis hydrogel prepared in clay medium: Bis = 10 mol %, Fe(III) in FeV = 1.5 x 10^{-3} M, TU = 0.04 M, Temp = 50°C

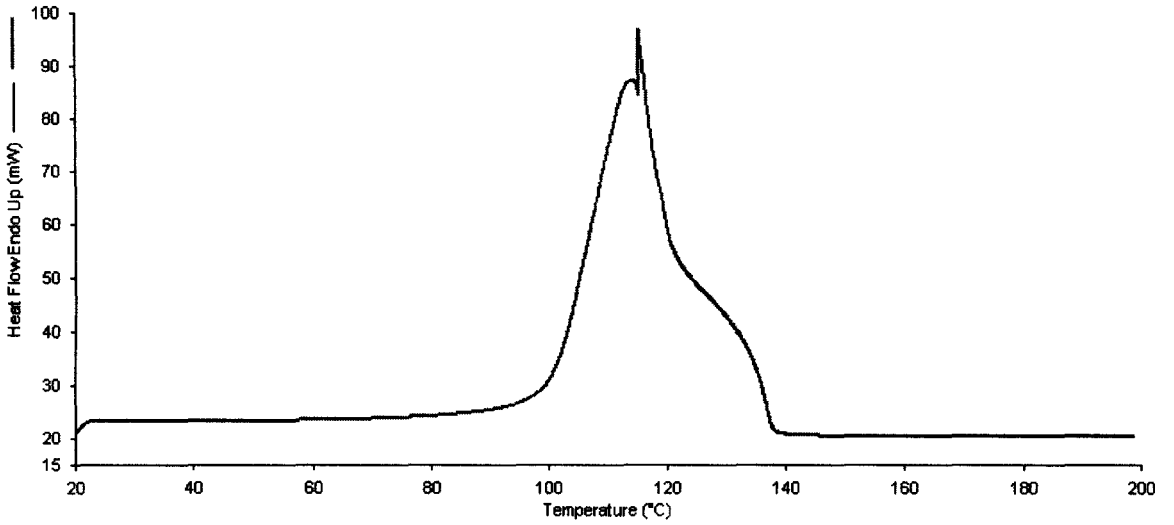


Figure 5.32: DSC curve of moist AM - Bis hydrogel (high FeV content) prepared in clay medium: Bis = 4 mol %, Fe(III) in FeV = $0.5x10^{-3}$ M, TU = 0.04 M, Temp = 50°C

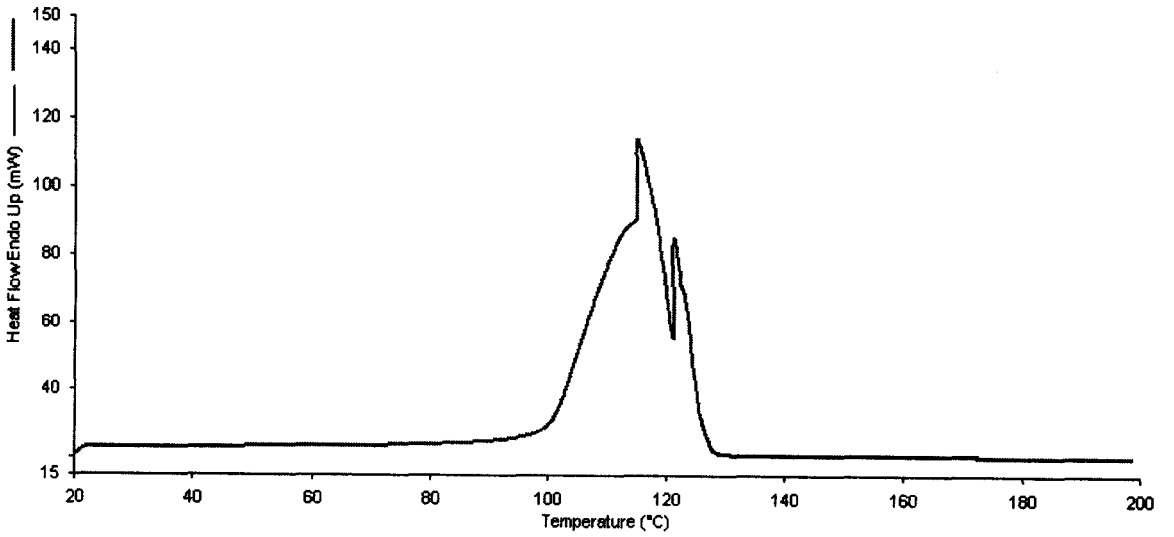


Figure 5.33: DSC curve of moist AM - Bis hydrogel (low FeV content) prepared in clay medium: Bis = 4 mol %, Fe(III) in FeV = $0.5x10^{-3}$ M, TU = 0.04 M, Temp = 50°C

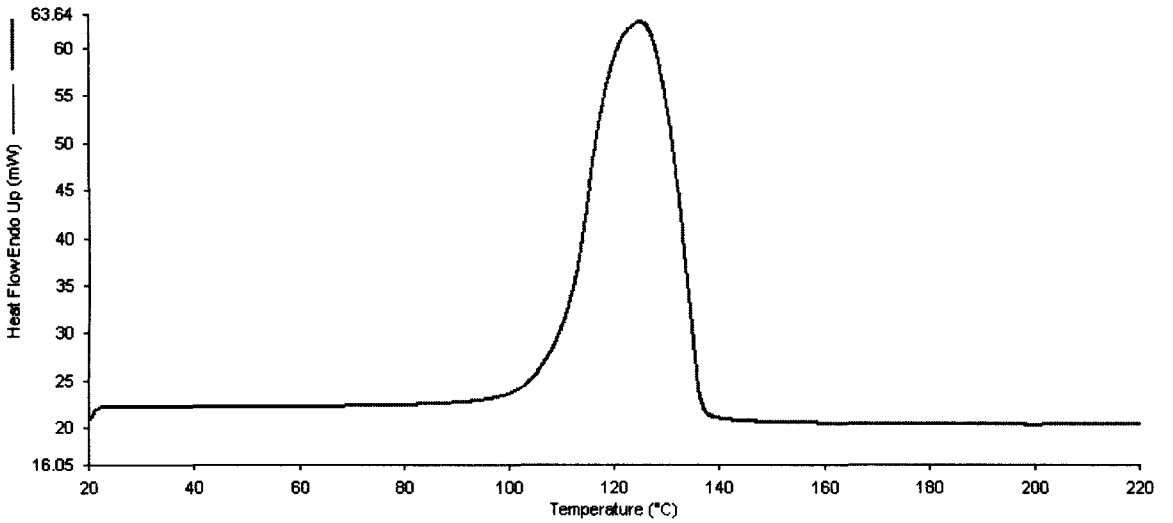


Figure 5.34: DSC curve of moist AM - Bis hydrogel (high FeV content) prepared in clay medium: Bis = 4 mol %, Fe(III) in FeV = $1.0x10^{-3}$ M, TU = 0.04 M, Temp = 50°C

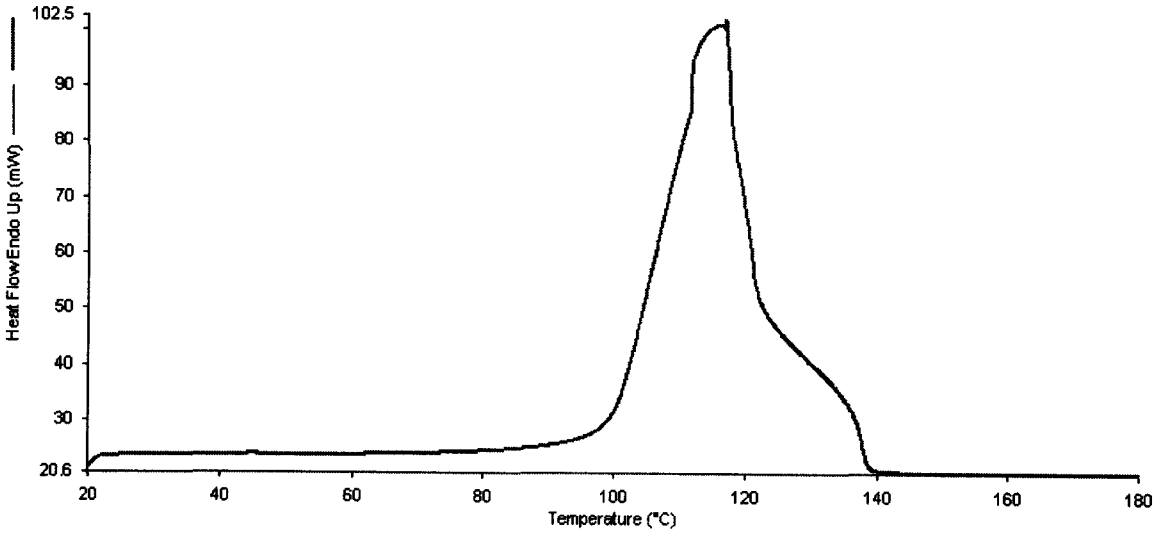


Figure 5.35: DSC curve of moist AM - Bis hydrogel (low FeV content) prepared in clay medium: Bis = 4 mol %, Fe(III) in FeV = $1.0x10^{-3}$ M, TU = 0.04 M, Temp = 50°C

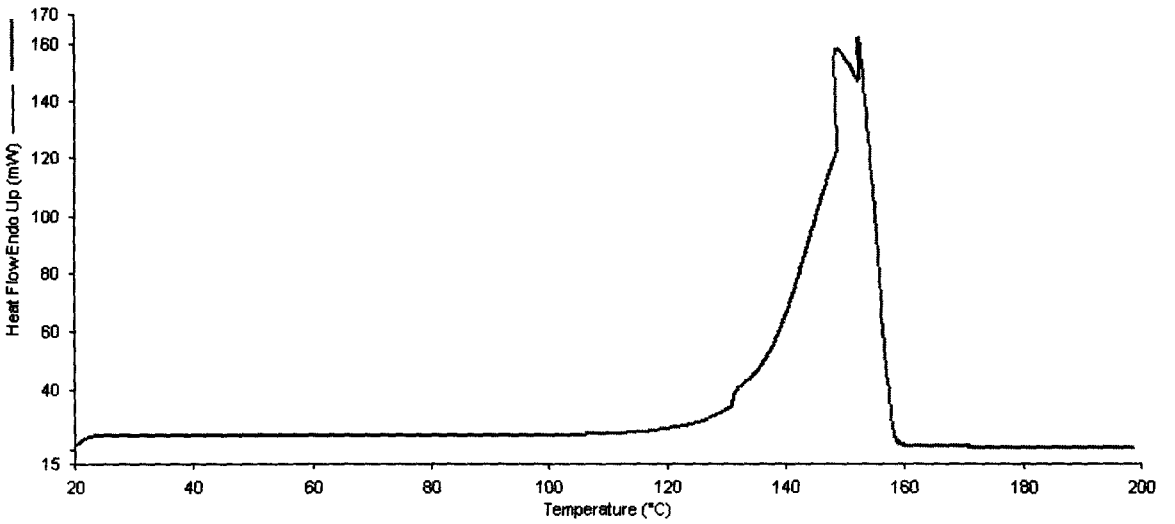


Figure 5.36: DSC curve of moist AM - Bis hydrogel (high FeV content) prepared in clay medium: Bis=4 mol%, Fe(III) in FeV=1.5x10^{-3}M, TU=0.04M, Temp=50°C

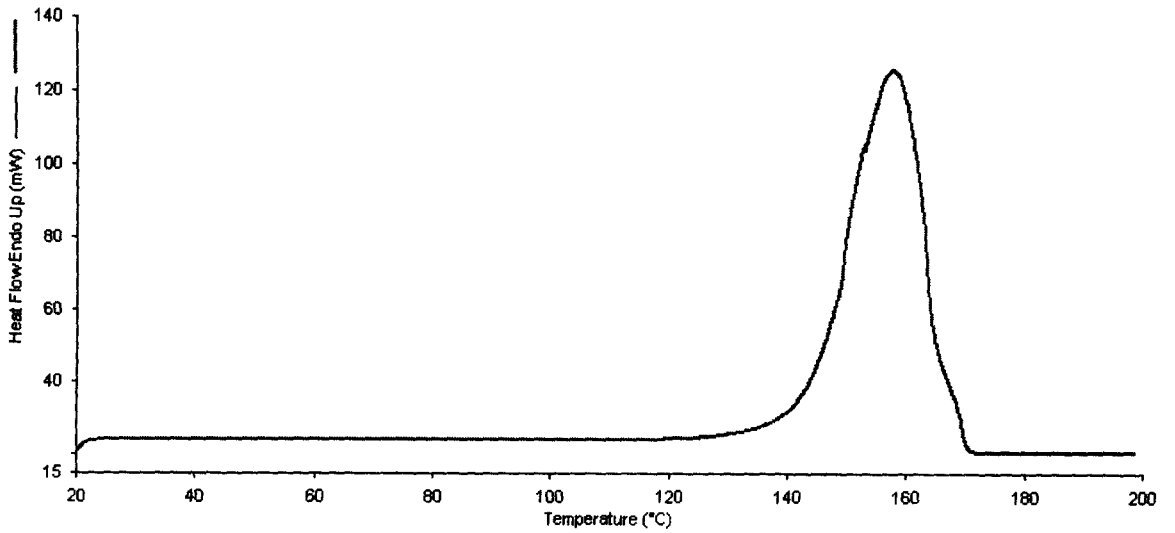


Figure 5.37: DSC curve of moist AM-Bis hydrogel (low FeV content) prepared in clay medium: Bis = 4 mol %, Fe(III) in FeV = 1.5x10^{-3} M, TU = 0.04 M, Temp = 50°C

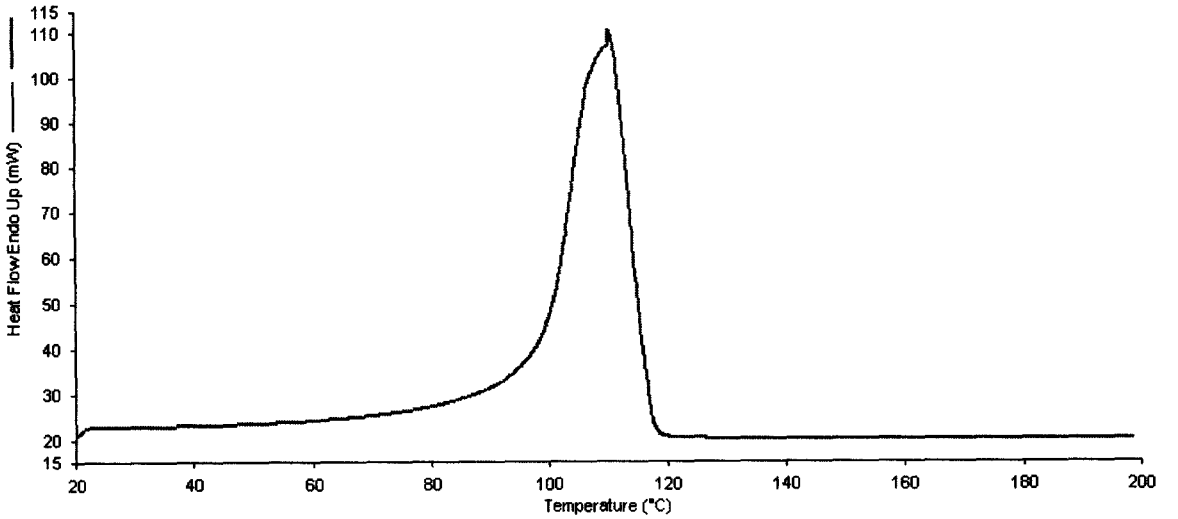


Figure 5.38: DSC curve of moist AM - Bis hydrogel (high FeV content) prepared in clay medium: Bis = 4 mol %, Fe(III) in FeV = 2.0×10^{-3} M, TU = 0.04 M, Temp = 50°C

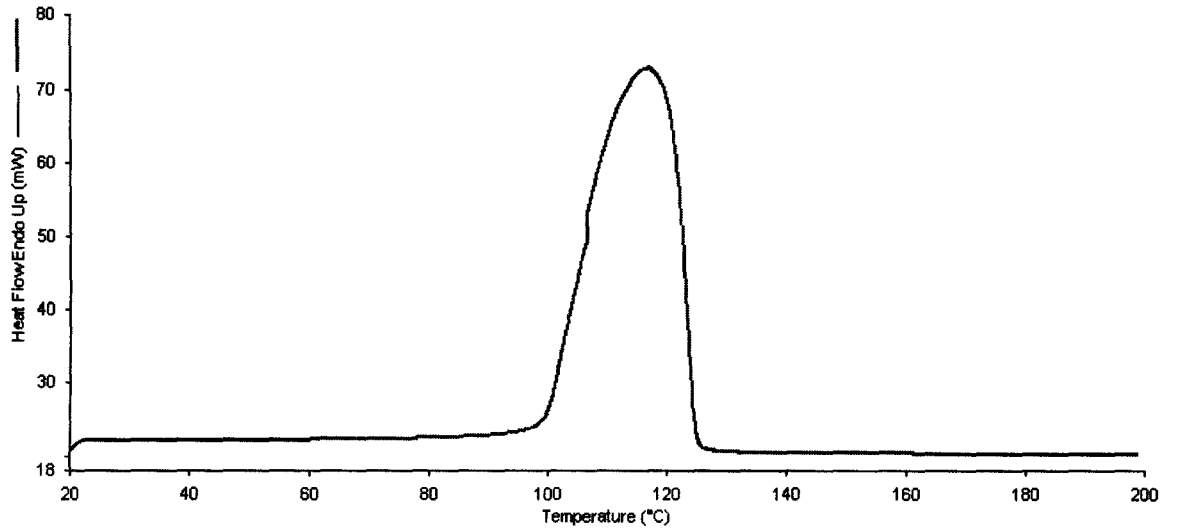


Figure 5.39: DSC curve of moist AM - Bis hydrogel (low FeV content) prepared in clay medium: Bis = 4 mol %, Fe(III) in FeV = 2.0×10^{-3} M, TU = 0.04 M, Temp = 50°C

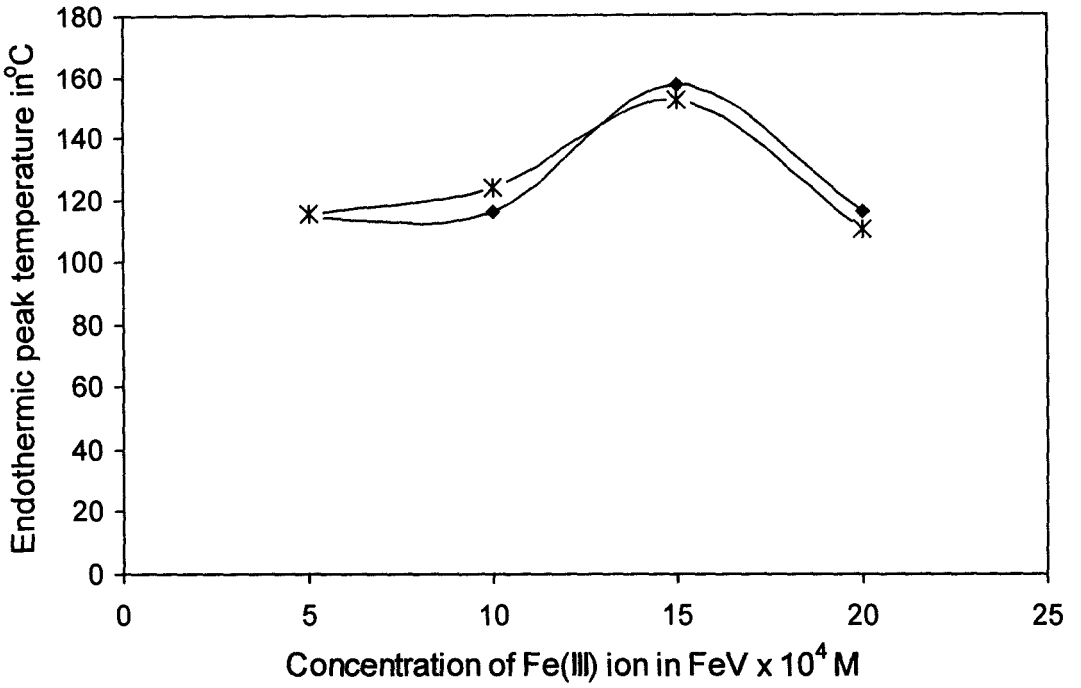


Figure 5.40: Endothermic peak temperature as a function of concentration of Fe(III) ion in FeV

—◆— low FeV region —✳— high FeV region

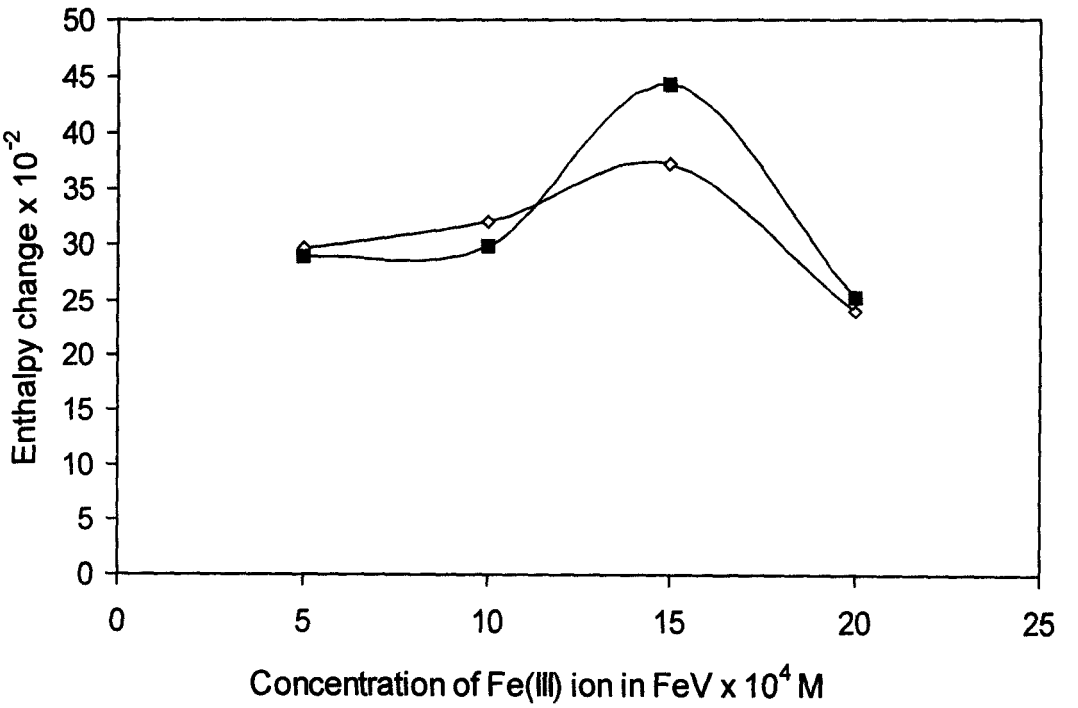


Figure 5.41: Enthalpy change as a function of Fe(III) ion in FeV

—◇— Low FeV region —■— Ligh FeV region

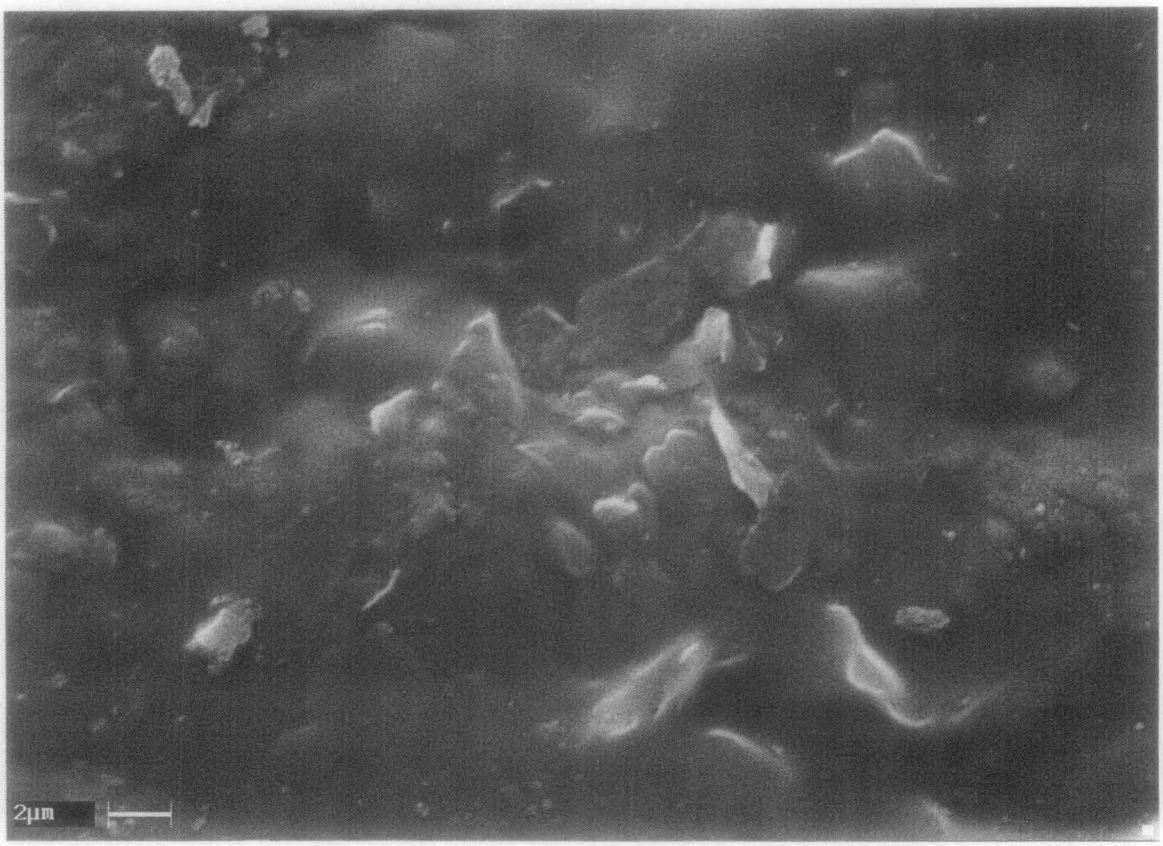


Figure 5.42: SEM image of AM - Bis hydrogel prepared in clay medium: Bis = 4 mol %, Fe(III) in FeV =1.5 x 10^{-3} M, TU = 0.04 M, Temp.= 50°C

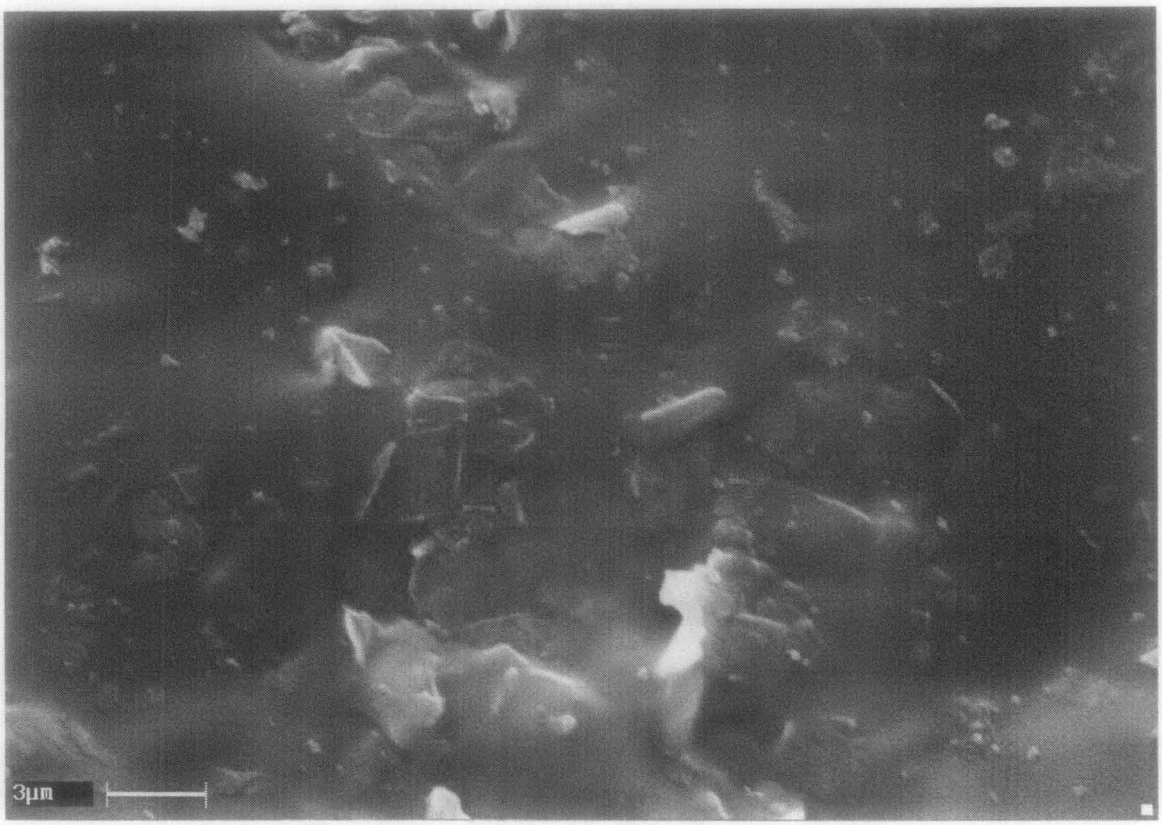


Figure 5.43: SEM image of AM - Bis hydrogel prepared in clay medium: Bis = 4 mol %, Fe(III) in FeV = 2.0 x 10^{-3} M, TU = 0.04 M, Temp.= 50°C

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