SYNTHESIS AND CHARACTERIZATION OF GRAFT POLYELECTROLYTES

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ABSTRACT

Water soluble polymers are used as flocculants in wastewater treatment, mineral processing, and pulp and paper production. The work in this thesis focuses on the synthesis of graft polyelectrolytes and the efficiency of the copolymers in flocculation. It was proposed that it would be advantageous to have clusters of high charge that can adsorb strongly to the particle surface, and a long chain of nonionic polymer to bridge the particles together.

Electrolyte copolymers were produced using a high molecular weight polyacrylamide as the backbone polymer and a redox agent, ceric ammonium nitrate, to form a radical site on the polymer. DADMAC monomer was polymerized from these radical sites producing grafts of cationic charge. The copolymers were produced at a range of polymerization conditions including PAM concentration, amount of nitric acid, amount of ceric ion and polymerization temperature. Grafting was successful and homopolymerization of DADMAC was found not to occur. The graft polymers were characterized using NMR, charge titration, viscosity measurements, and gel fraction measurements.

The copolymers were tested for flocculating properties using a model TiO_2 system. The graft copolymers produced performed better than the backbone polyacrylamide, low and high molecular weigh polyDADMAC, and a commercial random copolymer of acrylamide and DADMAC. It was found that both the amount of charge and gel is very important in flocculation performance. However, the testing of the copolymers as a conditioner for a municipal sludge did not show improvement in the drainage rate.

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Chapter 1 Introduction

1.1 Water Soluble Polymers

Water soluble polymers are polymers that are soluble in aqueous media, this solubility is achieved by ionic and nonionic polar functional groups. Polyelectrolytes are polymers with charged functional groups attached along the chain. Most water soluble polymers have at least a small number of charged groups, hence the terms polyelectrolytes and water soluble polymers are usually interchangeable.

Water soluble polymers are classified by charge type: anionic, cationic or nonionic. These polymers can be synthesized from monomers or derived from biological sources such as polysaccharides. Synthetic polymers are produced with specific chemical properties by varying the type of monomer repeat units, a single monomer or a combination of multiple monomers can be used. These monomers can be arranged to give random, alternating, block and graft copolymers.

This primary structure such as bulky side groups, or branches, will affect the configuration of the polymer molecule in solution. Intramolecular effects such as hydrogen bonding and ionic interactions affect the polymer conformation. It is important to note the effect of the charged functional groups on the polymer chain will drastically expand the coil dimensions, but these repulsive forces between the charges are very dependent on the ionic strength of the solution.

1.2 Flocculation

Flocculation is the most important aspect of the separation of solids from an aqueous media. Flocculation is often defined as the gathering together or aggregation of small masses, usually in a liquid media, into larger masses called flocs. Some people use the term flocculation when the aggregation process is via polymers, and the term coagulation when the aggregation is due to a reduction in the charge stabilization of the colloid particles.[1] In this work the terms are not differentiated as such. This act of flocculation allows the now larger particles or flocs to be separated more efficiently. The purpose of flocculation is to allow rapid separation or drainage of the liquid phase from a suspended solid phase while minimizing the amount of solids remaining in the liquid phase and maximizing the amount of solids in the solid phase.

Water soluble polymers, introduced in the 1950's have replaced traditional inorganic flocculants such as aluminum sulfate and ferric chloride. Although polymer flocculants are more expensive they offer many advantages. The flocs formed are typically larger and stronger, salt concentration is not increased and the amount of solids generated is reduced. Sludge dewatered with a polyelectrolyte may typically contain 1% polymer on a dry weight basis, whereas inorganic flocculant concentration may be as high as 20%.[1]

Polymer flocculants are commonly used in industries such as water treatment, paper making, mineral processing and oil recovery.

1.2.1 Water Treatment

The purification of water is the biggest user of water soluble polymers, roughly half the market volume of acrylamide-based polymers is used for water treatment.[2] There are two separation steps in the treatment of water. Polymer flocculants, often in conjunction with traditional inorganics, are used in the initial separation step.[3] This process produces a filtrate that may require additional water treatment, for example if the water will be used as drinking water or it is being released to the environment. The solids stream, often referred to as a sludge, will also need further treatment.

Raw waste water contains 150 mg/L to 400 mg/L of suspended solids and organic matter.[4] Water purification requires the separation of these dissolved and particulate organic and inorganic materials such as humic acids, clays and bacteria. These stable colloidal particles cause turbidity and undesirable colour in the water. They also interfere in the filtration process by blinding the filter media. Flocculants are added to the water to collect these small particulates into larger flocs that will settle or filter easily.

The treatment of industrial waste water or sewage produces a waste stream with a low percentage of solids. Sludge composition, both activated and digested, varies greatly because of the input in the type and concentration of suspended materials and dissolved materials. These sludges can be very difficult to dewater because of varying the microscopic properties. The polymer dosage, and solution conditions may have to be adjusted daily, continuous monitoring is normally necessary.

The solids concentration in the sludge has increased from the original water stream concentration, however it is still very low, normally less than 5.0 wt/vol%.[5] It is necessary to reduce the water content as the transportation and disposal cost are based on the total weight not simply the solids concentrations. Polymer consumption will increase with the percentage of biological solids present.[6] The addition of water soluble cationic polymers produces large strong flocs so that the solids can then be separated more efficiently by mechanical means such as centrifugal force or vacuum filtration. Sludge dewatering is the final solid /liquid step before disposal and generally accounts for a large percentage of the total chemical requirement of a plant.

1.2.2 Pulp and Paper

Pulp and Paper is one of Canada's most valuable industries. In 1988, 25 million tons of newsprint, wood pulp, paper and paperboard were produced, most of which wer exported to more than 40 countries.[7] Pulp fibres are mixed with fillers, pigments and other additives in a dilute slurry. This flows over a wire mesh where the water is rapidly removed. Although the fibres form a filter, the pulp fines and additives can easily pass through the screen.

The process of flocculation is used to retain fillers, pigments, and fibre fines. The flocculants, commonly called retention aids, save money by causing these small particles to stay on the wire and become part of the paper. On a paper machine many different processes occur simultaneously, polymer adsorption, conformational changes, collisions between filler particles and with fibres, and breakage of polymer induced bonds.[8] The flocculation mechanism will be dependent on the type of pulp fibres, type of filler, retention aid utilized, and the paper making process. The most probable mechanism is that the polymer attaches the fillers and fines to the negatively charged pulp fibres. Although some agglomeration of the fines and fillers, may cause larger particles which filter out more easily in the top and centre portions of the sheet.[9] The retention of fines and fillers lowers the amount recycled in the white water and improves the drainage of the paper sheet, improving production costs.

1.2.3 Mineral Processing

In mining operations, slurries of finely divided colloidal mineral and ore particles, known as slimes, are produced during processing. In the past, the mining industry simply dumped these slimes into settling lagoons, treating the slime as a waste, even though valuable minerals remained in the slurry. The cost of extracting the mineral was not profitable. Currently, environmental regulations and increasing awareness of the public have forced the mining industry to look for technologies to separate the solids from the slimes.

Synthetic flocculants such as polyacrylamide are often used to separate the particles from the water. The polymer used must be chosen wisely so that the minerals can then be extracted from the ore. It is not advisable to choose a flocculant that gives very large cohesive flocs, as the minerals are entrapped in the floc.[10]

1.3 Factors Affecting Flocculation

In each of these industrial examples flocculation is a critical process step. Flocculation is a very complicated process, many factors can effect how the particles are destabilized and/or aggregated. There are both system parameters and polymer related variables. Typically the system is defined by the particle charge, particle size, and particle concentration. Polymer related variables are molecular weight, charge density and the polymer dosage. Their effects vary depending on the flocculation mechanism, as will be explained in the section on mechanisms.

1.3.1 System Variables

Particle charge

There are many sources of charge on the particle surface. Insoluble oxides such as TiO2, can become positive by the uptake of H_3O^+ or negative by the uptake of OH^-, while silica changes its surface charge with the gain or lose of a proton There is a pH value where the oxide surface is neutral, the point of zero charge or the isoelectric point (i.e.p). The affinity of the surface for H_3O^+ and OH^- is dependent on the surface chemistry of the oxide. For example the i.e.p. of silica is lower than that of titanium dioxide.

Clay materials have a bulk charge that is not dependent on solution conditions. This charge is due to the isomorphic substitution of Si^{4+} ions in the crystal lattice by Al^{3+} or Ca^{2+}. This crystal structure can give particle with surfaces of different charges.

Colloid particles such as a latex can be produced so that they have functional groups such as carboxyl or sulfate groups that can be ionized at certain solution conditions. It is very important to know how the colloid particle changes with pH and electrolyte concentration as this will also change the interaction of the polymer and particle.

Particle Size

The most important factor that effects settling and filtration is the particle size. Colloidal particles are the cause of turbidity in water because of their small settling velocity. Small particles can easily blind the filter media if they are not effectively flocculated into larger groups. Flocculation is a surface process, hence the consumption of polymer flocculants is directly related to the particle surface area. The surface area to mass ratio increases with a decrease in particle size.

Particle Concentration

Polymer consumption is related to the amount of solids present but a high concentration of particles will improve the probability of collisions between particles.

1.3.2 Polymer Related Parameters

Molecular Weight

Water soluble polymers are more effective than the traditional inorganics because of their macromolecular nature. Molecular weight is a direct measurement of the chain length, thus molecular weight is a very important parameter.

Charge Density

Charge density is often defined as the number of monomeric units with a charge divided by the total number of monomers. Cationic or anionic functional groups on the polymer chain will affect the conformation of the polymer in solution. The repulsive forces of the like charges will cause the polymer chain to be extended, increasing its effective dimension. But more importantly charge groups can interact with the charges on the particle surface allowing for strong adsorption of the polymer to the particles.

Polymer Dosage

There is an optimum amount of polymer that will provide the best flocculation. Too little polymer may produce fragile flocs that are easily destroyed, or simply too few flocs will be formed. An excess of polymer may restabilize the particles. The charge of the particle surface may simply be reversed in the case of polyelectroytes, or the polymer may have completely covered the particle surface, sterically stabilizing the particles.

1.4 Colloid Stability DLVO Theory

Most particles in aqueous media are charged due to the ionization of surface groups or the specific adsorption of ions. In an electrolyte solution the distribution of ions around a charged particle is not uniform, the charge on the particle surface is balanced by an equivalent number of oppositely charged counterions in solution. Thus a double layer of charge is formed around each particle causing an electrical repulsion.

The classical DLVO theory of colloid stability is based on the interactions of van der Waals attraction and this electrical repulsion. This theory assumes that these interaction are additive and independent. It is referred to as the DLVO theory after the four scientists who developed this stability/coagulation theory: Deryaguin and Landau[11], Verwey and Overbeek[12].

1.4.1 Van der Waals Attraction

Van der Waals interaction is the attraction forces between atoms, molecules and macroscopic objects. The interaction between macroscopic bodies arises from spontaneous electric and magnetic polarizations, giving a fluctuating electromagnetic field within the media and in the gap between them.[13] The magnitude of these forces can be calculated knowing the dielectric responses of the interacting media over a very wide frequency range. Unfortunately this data is not always known and the calculations are difficult.

Assuming the pair wise additivity of intermolecular forces, Hamaker developed a simple approach that is normally used to calculate this attractive force[14]. The interaction between two particles is calculated simply by summing the interactions of all the molecules in one particle with all of the molecules in the other. For two spheres, radii a_1 and a_2, separated by a distance d, the interaction energy at close approach , $d<<a$, is given by

$$V_A = -\frac{A_{12}}{6d}\frac{a_1 a_2}{(a_1 + a_2)} \qquad (1.1)$$

A_{12} is the combined Hamaker constant for the media 1 and 2 of which the spheres are composed. This expression simplifies for 2 equal spheres, $a_1 = a_2 = a$, so that the interaction energy between the two spheres becomes:

$$V_A = -\frac{A_{12}a}{12d} \qquad (1.2)$$

Thus Van der Waals attraction forces are inversely proportional to the separation distance. The closer the particles are, the stronger the attractive forces. These expressions are applicable only at close approach, when $d<<a$, but the interactions are usually insignificant at larger distances so these equations are acceptable in most situations.

1.4.2 Electrical Repulsion

The charge on a particle surface is balanced by an equivalent number of oppositely charged counterions in solution. These counter ions are attracted to the particle surface, causing a localization of the counterions close to the particles. However there is also a strong tendency for the ions to diffuse randomly throughout the solution due to their thermal energy. Thus there is a distribution of the counterions away from the particle surface forming an electrical double layer. The Stern layer refers to the layer of hydrated counterions next to the particle surface, and the diffuse layer is the remaining volume of counter ions.

The interaction between charged particles is governed by the overlap of the diffuse layers, thus the potential necessary to calculate the repulsive energy is the potential at the interface of the Stern and diffuse layers. This potential is always less than the particle surface potential. The nature of the electrostatic interaction is influenced by the speed of approach of the two particles, as the double layers may take time to adjust to the changing situation. In an intensively stirred suspension the interaction will occur very rapidly and the double layers will have little time to adjust to the changing situation.[15]

Lyklema has developed an equation for the repulsive interaction energy per unit area for weak overlap of the two spherical particles. Several approximations are necessary to solve the second order differential equation that results from using the Poisson and Boltzman equations, but the resulting equation clearly shows the parameters that are important in colloid stability. [16]

$$\mathrm{V_R} = \frac{64\pi \mathrm{n_S kzT}}{\kappa^2}\frac{(\mathrm{a}+\partial)^2}{\mathrm{H}+2\mathrm{a}}\tanh\left(\frac{ze\zeta_d}{4kT}\right)^2 \exp\left(-\kappa(\mathrm{H}-2\partial)\right) \qquad (1.3)$$

where a = particle radius (nm)

∂ = Stern-layer thickness (nm)

z = valency

k = Boltzman constant 1.38×10^{-23} J/K

T = absolute temperature (K)

n_s = number of salt molecules per unit volume

κ = reciprocal Debye length (nm)

e = elementary charge (C)

H = shortest interaction distance between the two spherical particles (nm)

ζ_d = potential at the diffuse layer (mV)

From this equation we can see that the repulsive forces are dependent on the separation distance as there are two terms in this equation that are proportional to the separation of the particles. The first term is the ratio of the sum of the particle radius and the Stern layer to the sum of the shortest separation distance and the radius of each particle, $(a + \partial)^2/(H + 2a)$. As the separation distance between the two spherical particles increases this term would reduce the repulsive energy. However the last term has a greater influence on the repulsive potential energy. The repulsive forces are also exponentially dependent on the distance between the two outer Helmholtz planes (the outer border of the Stern layer). As the separation distance increases the repulsive energy decreases exponentially, and conversely, as the spherical particles approach each other the repulsive energy increases exponentially.

The electrolyte concentration in solution is also very important. The repulsive energy decreases with increasing electrolyte concentration because of the influence of the Debye-Huckel parameter, κ.

$$\kappa = \left(\frac{e \, \Sigma n_i^\circ z_i^2}{\varepsilon k T} \right)^{1/2}$$

where n_i° = the number of ions of type i per unit volume in the bulk solution far from the particle surface

z_i^2 = valency of ion of type i

ε = electric permittivity of the solvent

Thus κ depends only on the temperature and the bulk electrolyte concentration and valency.

The Van der Waals attractive forces are inversely proportional to the separation distance, eq. (1.1). The closer the particles the stronger the attractive forces, however the electrical repulsion also increases as the particles approach. The total potential energy is the sum of the attractive and repulsive energies, thus the potential energy varies with the distance between the two particles. Typically there is a large primary maximum which stabilizes the colloid system. There can also be a secondary minimum which affects the stability of the colloid system.

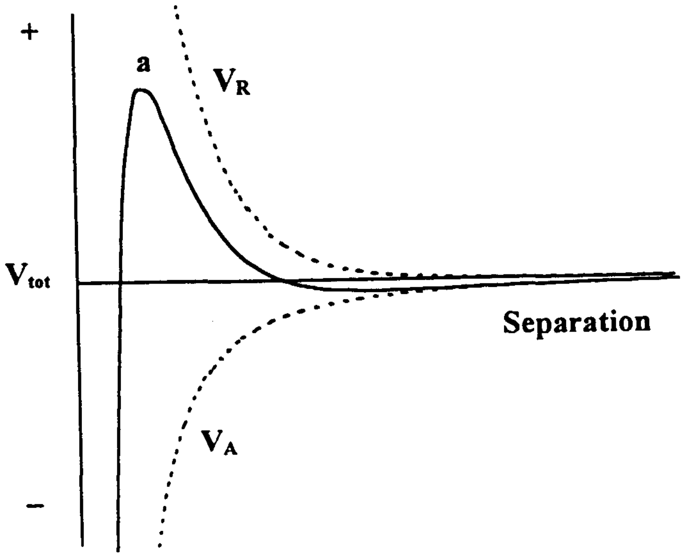

Figure 1.1 DLVO Curve - sum of the attractive and repulsive energies

The Hamaker Constant strongly affects the attraction and the total energy curve, although this is an inherent property of the system, and cannot be altered. The Debye-Huckel parameter, κ, can change the stability curve, in fact an electrically stabilized colloid system can be flocculated simply by adding a large amount of salt. The diffuse layer potential, ζ_d , is a property of the colloidal particle but can be affected by system conditions such as pH, temperature and electrolyte concentration. Thus many factors are important in the stability of suspended colloidal particles. It is very important to understand the system of study.

The addition of polymers to the colloid system changes these equations. The DLVO theory describes the interaction of particles based on the sum of their attractive and repulsive energy. The presence of an adsorbed polymer layer may affect the structure of the electrical double layer and hence modify the electrical repulsion term. The attractive forces between the particles may also be altered because of this polymer layer.[17] The polymer may also sterically stabilize the particles by providing a physical barrier that does not permit the particles to approach each other. However the DLVO equations still give indications of the effect of system interactions, and can predict colloidal stability and/or instability.

1.5 Flocculation Mechanisms

Colloidal stability is very complicated, it is necessary to take all factors into account. In flocculation we want to overcome the stability of these particles and gather them together into larger flocs. This can be done by eliminating the electrical repulsion, adding another force that strongly pulls the particles together, or the addition of a polymer chain that can attach to several particles bridging them together. Thus the stability of the particles can be overcome.

1.5.1 Charge neutralization

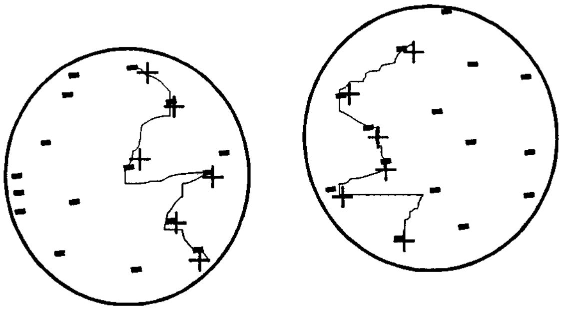

Figure 1.2 The positive charges neutralize the surface

Charge neutralization refers to overcoming the electrical repulsion due to surface charges and allow the attractive Van der Waals forces to override and agglomerate the particles. As previously mentioned this can involve the addition of an excess of salt that surpresses the electrical double layer. Inorganic salts such as hydrolyzed aluminum or iron salts are added to waste water to overcome the repulsive forces and allow the suspended particles to coagulate together. Essentially the electric double layer is being compressed lowering the energy barrier to permit collisions.

Ionic water soluble polymers, polyelectrolytes, can also neutralize the charge and allow the particles to approach each other. For a water soluble polymer to work as a flocculant in a charge neutralization mechanism, the polymer charge has to be opposite to that of the colloid particle. The greater the charge density, that is the amount of charged monomer units, the higher the ability of the polymer to flocculate the particles by neutralizing the particle charge. Typically charged homopolymers are used as they are the most effective. The polymer will have a strong interaction with the colloid surface and the polymer will lie flat on the surface, simply neutralizing the charge. At the optimum flocculation conditions the zeta potential of the system approaches zero, showing complete neutralization.

With an increase of molecular weight, the zeta potential at the optimum polymer concentration becomes larger (more negative in the case of a negative colloid and positive polyelectrolyte). This indicates that no longer is charge neutralization the primary mechanism, perhaps some polymer bridging is involved with increasing molecular weight.[18] The long chain is producing some loops and trains that will stick to other particles and bridge the particles together.

It is difficult to have a polymer system where the mechanism is solely charge neutralization. If one was to examine the configuration of the polymer charges in comparison to the distribution of charges on the particle surface a one to one matching is not possible. In a study by Gregory with a polystyrene latex and cationic polymer, he found that under the conditions in his experiments it would be physically impossible for all of the carboxyl groups to be neutralized individually.[19] This observation has led to the development of the electrostatic patch mechanism developed by both Gregory and Kasper.[20]

1.5.2 Electrostatic Patch Mechanism

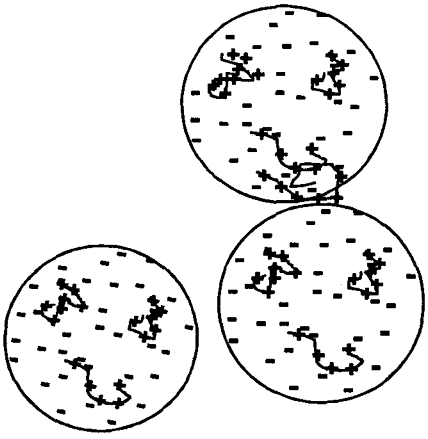

Figure 1.3 Patches of positive charge formed on the negative particles

The electrostatic patch mechanism is an extension of charge neutralization mechanism that accounts for the special nature of polymers. The equilibrium configuration of a highly charged adsorbed polymer on an oppositely charged particle will be very flat, because of the high interaction energy.

The one-to-one matching of charge is difficult because the charge density of the polymer and particle is normally quite different. Polymer adsorption will form clusters of charges on the particle and these domains of different charges will allow for interactions of the particles forming flocs. Aggregates are formed because of strong interaction between the positively and negatively charged areas. There is an additional force pulling the particles together, not simply Van der Waal attraction. As in charge neutralization, the zeta potential of the system is very close to zero.

The flocs formed by this method are small like that of charge neutralization, clusters of particles held together because of opposite charges. These flocs are also easily disrupted by shear forces as there is no physical bond between the particles, only an electrostatic interaction. That is the polymer chains are not bringing the particles together. The charge "mosaic forces" that hold the particles together can easily be sheared, but these electrostatic interactions are also easily re-formed. The damage is not permanent, the interaction forces will pull the particles together again.

Low to medium molecular weight charged homopolymers will be able to adsorb flatly onto the particle surface. If the polymer chain is too long it will not be able to obtain this flat configuration and some loops and trains of the polymer chain may extend into solution promoting the bridging of particles. If too much polymer is added to the system the entire particle surface will be covered with the polymer charge and the particles will now be restabilized by the charged polymer layer.

The time for the polymer to reach its equilibrium configuration is dependent on the number of particles in solution and the rate of agitation. If there is a high concentration of particles, an increase in the probability of collisions, the polymer may still be in its random coil state when another particle "bumps" into it and a polymer bridge could form. The addition of kinetic energy also improves the probability of this collision. Thus the electrostatic patch mechanism explains systems of highly charged, low molecular weight polymers with low particle concentrations.

1.5.3 Bridging

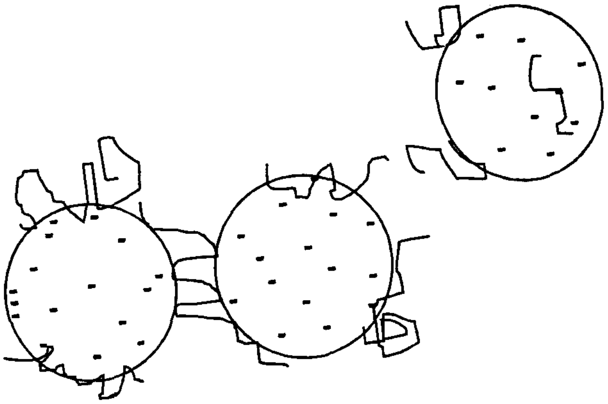

Figure 1.4 Bridges are formed between the particles

The flocculation mechanism that explains most experimental data using polymers is bridging. Most polymeric flocculants are of comparable dimensions to many colloidal particles. A few segments of the polymer chain attach to the particle surface while the rest of the polymer extends into the bulk of the solution forming an adsorbed polymer layer. The attachment of the polymer to the particle surface can be through electrostatic attraction, chemical bonding, hydrogen bonding, hydrophobic association, complex formation, or a number of other means.[21] Strong polymer adsorption occurs on most surfaces because polymers can be in contact with a surface by many monomer segments simultaneously. Only a low bonding energy per segment is adequate so that the polymer adsorption is virtually irreversible.

This process involves the successive adsorption of polymer segments onto the surface, this is often followed by reconformation of the polymer. The reconformation rate decreases with an increase in charge density, but is also dependent on the surface porosity.[22]

The polymer layer spans over the electric double layer of the particle allowing for a point of attachment to another particle. When a single polymer molecule becomes attached to more than one particle these particles are bridged together by the polymer. The polymer chain must be long enough so that one chain can attach to at least one other particle. An increase in molecular weight improves flocculation as this forms longer and/or more loops and tails increasing the collision diameter.[23,24] The molecular weight is only limited by solution properties and ultimately the polymerization capability. Low molecular weight polymers are not effective bridging polymers as the polymer can not span the distance of several particles, a charge neutralization mechanism takes precedence.[25]

A polymer of opposite charge to the colloid particle may have an extra attractive force improving the interaction between them. However if the charge density is too high the adsorption will be too strong and the polymer configuration will be flat on the surface. The lack of trains and loops will prevent effective bridging of particles. This will lead to either a charge neutralization or electrostatic patch mechanism, as shown in a flocculation study of polyethylenimine by Lindquist and Stratton.[26] The polymer charge was altered by pH adjustment. Their tests showed a dependence of the critical flocculation concentration on molecular weight when there was little charge on the polymer. Thus with little or no charge groups the flocculation mechanism was bridging, while with a highly charged polymer the mechanism was electrostatic patch.

Nonionic polymers such as poly(ethylene oxide) are effective flocculants in bridging.[27] Ionic interaction is not necessary as long as a few segments of the polymer are able to approach the particle and attach or adsorb onto the surface. An anionic polymer will often flocculate negatively charged particles better than a neutral polymer. A few segments of the polymer chain are able to overcome the electrical repulsion between the polymer and particle and attach to the particle surface. The improvement in flocculation is due to the configuration of the polymer in solution. The size and shape of polyelectrolytes depend on the ionic strength of the solution and the number of charged groups. Repulsion between the charged segments causes the chain to expand. Thus a charged polymer will be extended in solution producing a larger effective radius then a similar neutral polymer of the same molecular weight. This effect is reduced as the ionic strength of the solution is increased, because the charges are then "screened" by counterions.[28] Thus in the case of low ionic strength solution a charged polymer will have an extended configuration improving the flocculation ability.

Increasing the ionic strength of the solution will reduce the electrical double layer repulsion, allowing the particles to approach closer. This will increase the ability to bridge the particles, although it is also important to account for the effect of electrolyte addition on the polymer. For example with charged polymers the salt may screen the charge groups diminishing their strength or cause contraction of the polymer coils, decreasing the length of the polymer chain. These two effects can reduce the effect of flocculation significantly.

The optimum polymer concentration is directly proportional to the total surface area of the particles. If too much polymer is added to the suspension, the surface of the particles will be completely covered and the polymer chains will not be able to find a vacant site to adsorb onto another particle. The particles will now be both sterically and electrically stabilized and flocculation cannot occur. Thus there is a range of flocculation performance with the addition of polymer. The attractive force between two polymer covered surfaces goes through a maximum with increasing polymer coverage which explains the observation that there is an optimum amount of polymer per particle for efficient flocculation.[29] Maximum flocculation usually occurs when the surface coverage is approximately 50%. Theoretically this is when there is a maximum number of polymer bridges between all of the particles. This optimum dosage will depend on the number of particles in solution and the surface area of these particles. When comparing flocculation results it is important to compare the optimum dosage of each system in order to fairly account for the differences in each system.

An increase in agitation of the system will improve the probability of collisions, increasing the amount of bridging. Similarly the concentration of suspended particles will affect flocculation. An increase in the number of particles will reduce the chance of the polymer chain further adsorbing on the initial colloid particle, as a second particle will be close by to be bridged by the polymer chain.

The flocs formed by the bridging mechanism are very strong because of the strength of the polymer chain bonds. In a study of cationic polyacrylalmides, the flocs formed by lower molecular weight polymers, were smaller and more open, the lower molecular weight polymers do not bind or hold the clay particles as tightly as the polymers of higher molecular weight.[30]

A floc formed by bridging is large and robust to shear forces. However a high shear force can permanently destroy the polymer chain breaking the particle bridges. The polymer chains are then too short for bridging and the remaining polymer is a steric layer preventing the approach of particles. Thus the suspension can become sterically stabilized.

1.6 Flocculation Efficiency

Flocculant manufacturers now offer comprehensive ranges of anionic, cationic and nonionic flocculants that differ from one another in the chemistry of their monomeric building blocks, the nature and size of their ionic charge, and their molecular weight.[31,32] The polymer can be tailored to the colloid system to improve the flocculation efficiency.

For many processes the optimum mechanism is a combination of charge neutralization and bridging. The long polymer chains hold the flocs together and there is strong adsorption because of the ionic bonding. However it is difficult to obtain charged homopolymers of a high molecular weight because of the repulsive forces of the charged monomers. To obtain a suitable molecular weight, the charged monomers are often copolymerized with acrylamide monomer. Acrylamide is very reactive, its rate constant ratio of propagation to termination : $k_P/k_T^{1/2}$ is 4.2 ± 0.2,[33] the highest of all water soluble monomers. Typically a copolymer is produced with the ionic centres randomly distributed along the polymer chain. It is difficult to produce the optimum flocculant in this manner, because the charge groups will not be used efficiently. Many of the charged groups will be in the polymer loops and tails bridging the particles together, not attached to the particle surface. The ionic centres are needed only for improved adsorption at the particle surface. If anything, they could cause a flat configuration of the polymer on the particle surface reducing bridging efficiency.

It would be advantageous to have clusters of high charge that can adsorb strongly to the particle surface, and a long chain of nonionic polymer to bridge the particles together. A graft copolymer of nonionic and charged polymers in a comb structure would provide this. The charge groups would be distributed like fingers that can reach out and adsorb strongly to the oppositely charged particles.

1.7 Research Objectives

Flocculation is a very interesting and dynamic field where the opportunities for improving industrial processes such as wastewater treatment and paper production can be enormous. In 1984, the use of synthetic organic flocculants (calculated as dry mass) in Western Europe was ca. 15,000 t and in the United States ca. 40,000 t, half of this being accounted for by polyacrylamides.[34] The particulates in waste water and paper making are usually negatively charged, hence cationic polymers are used. Poly(dimethyldiallylammonium chloride), PolyDADMAC, is a popular commercial cationic polymer. The positive charge is due to the stable quaternary ammonium group that is not sensitive to pH, hence stable over a wide range of conditions. Although few fundamental studies have been made on cationic polymers due to the difficulty of synthesizing polymers with sufficiently well defined structures, some basic research has been done on DADMAC. The mechanism of polymerization involves an intra-intermolecular cyclization to form a five membered ring.[35]

It has been proposed to produce a graft copolymer of acrylamide and DADMAC. Graft copolymers of polyacrylamide and DADMAC in a comb structure have been formed by Lin and Butler, however the backbone is charged and the grafts are polyacrylamide and no flocculation tests were done. [36,37] A previous thesis has found that a copolymer of PAM and PolyDADMAC to be a very effective flocculant. A high molecular weight PAM was used as the backbone polymer and polyDADMAC was grafted onto PAM using gamma radiation from a nuclear reactor. The graft copolymer produced was a superior flocculant in comparison to the individual polymers subjected to same dose of gamma radiation, and a blend of the two polymers.

However, there were some difficulties with this method. The source of radicals, gamma radiation from a nuclear reactor is very strong and hence not very selective. Radical sites are formed indiscriminately along both polymer chains. A gel or network is easily formed that can limit the solubility and performance of the graft copolymer.

The purpose of this thesis is to produce a graft copolymer of acrylamide and DADMAC with a better defined comb structure using a method that would be commercially viable. We have used a high molecular weight PAM as the backbone polymer and a redox agent, ceric ammonium nitrate (CAN) to produce a radical site on the PAM. DADMAC monomer polymerizes from these radical sites to produce grafts of cationic charge.

The technical objective of this research was to develop a novel class of comb structured graft copolymers with superior flocculation properties in comparison to current commercial products. The scientific objective of this project is to develop a fundamental understanding of the relationship between the molecular configuration of the graft copolymer and its flocculation performance.

1.8 Thesis Outline

Chapter 1 has been a review of water soluble polymers and flocculation. Chapter 2 gives some background on the grafting method using the redox system of ceric ion and nitric acid. The polymerization conditions and characterization of the polymers produced are also given in Chapter 2. These polymers were tested for their effectiveness in flocculating colloidal TiO_2 particles using a Brookhaven disc centrifuge. The results and discussion are given in Chapter 3. In Chapter 4 the polymerization results are confirmed by the production and characterization of two new graft copolymers. In addition, the polymers that performed well in the flocculation tests were analyzed for their ability to dewater sludge from the Burlington Skyway Treatment Plant. The thesis is summarized in Chapter 5.

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Chapter 2 Synthesis and Characterization of Graft Polyelectrolytes

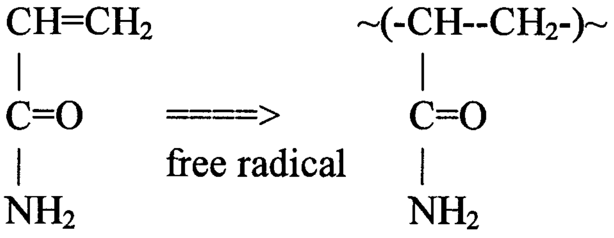
2.1 Introduction

2.1.1 Acrylamide Based Polymers

More than half of all synthetic polymeric flocculants and all of the high and ultrahigh molecular weight water-soluble polymers are copolymers in which the principal monomer is acrylamide.[1] To obtain a cationic polymer, acrylamide is often copolymerized with cationic comonomers. There are many cationic comonomers that are polymerized with acrylamide, the positive charges are due to the quaternary ammonium groups, sulfonium groups or phosphonium groups, although the quaternary ammonium groups are the most common. Common cationic monomers are diallydimethylammonium chloride (DADMAC), diallyldiethylammonium chloride (DADEAC), diethylaminoethyl methacrylate (DEAEMA), dimethylaminoethylmethacrylate (DMAEM) dimethylaminoethylacrylate (DMAEA), 3-(methacrylamido) propyltrimethylammonium chloride (MAPTAC).[2,3] Uniform water soluble copolymers of acrylamide and DMAEM can be synthesized using semi-batch inverse-emulsion polymerization processes.[4] Copolymers of acrylamide with 2-acrylamido-2-methylpropanedimethylammonium chloride have been prepared in aqueous solution as model structures for solution property relationships.[5]

Polyacrylamide can also be chemically modified to produce a high molecular weight cationic polymer via the Mannish reaction. Dimethylamine and formaldehyde are reacted with aqueous polyacrylamide to produce a cationic polymer.[6,7]

In this work the cationic monomer, DADMAC is polymerized from a radical site on the commercially prepared PAM.



$$\begin{array}{ccc} CH{=}CH_2 & & \sim(-CH{-}{-}CH_2-)\sim \\ | & & | \\ C{=}O & \overset{}{\underset{\text{free radical}}{====>}} & C{=}O \\ | & & | \\ NH_2 & & NH_2 \end{array}$$

Figure 2.1 Structure of Acrylamide and Polyacrylamide

Polymerization of diallyldimethylammonium chloride produces a water soluble polymer despite the fact that there are two double bonds in each monomer. Butler and Angelo proposed and confirmed the intra-intermolecular cyclization polymerization mechanism.[8] The five-membered ring structure of polyDADMAC has been confirmed by

C-NMR spectroscopy.[9] PolyDADMAC is the most common quaternary ammonium monomer, and is widely used in industry and research.

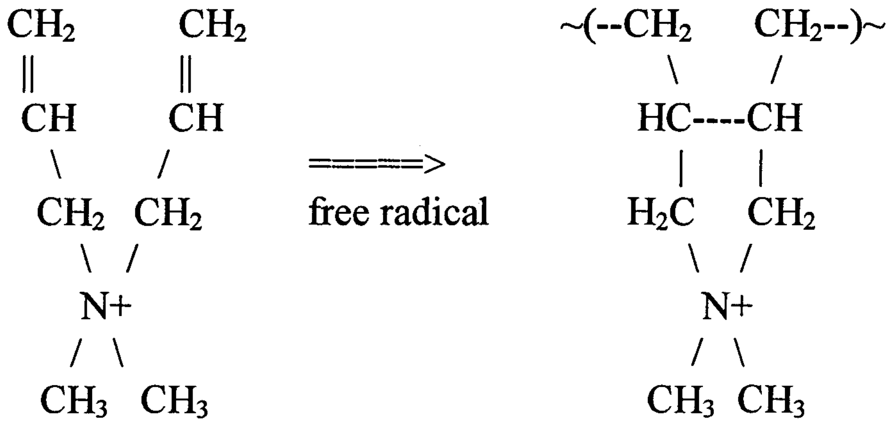


Figure 2.2 Structure of DADMAC and PolyDADMAC

2.1.2 Grafting

Graft copolymers are branched molecular structures where the side chains are composed of monomers that are distinct from the main chain. There are three major methods to synthesize graft copolymers, grafting "from", grafting "onto" and grafting "through".[10]

Grafting "from" refers to the polymerization of a second monomer from the backbone of an existing polymer. The polymer backbone may have initiating sites attached to it, or functional groups capable of generating initiating sites. The sites created on the backbone can be free radical, anionic, cationic, or Ziegler-Natta.

Grafting "onto" refers to the process of pre-formed polymer chains with a reactive site on the chain end reacting with corresponding functional groups along the backbone polymer. The grafts that are produced are well characterized as the polymer side chains are pre-formed and the coupling sites are known. This is a coupling of two polymer chains.

Grafting "through" refers to the polymerization of a monomer in the presence of polymer chains with pendant unsaturations. The side chains are thus incorporated during the polymerization of the backbone.

In each of these grafting mechanisms there exists the possibility of crosslinking. That is if a polymer chain can be coupled to several other polymer chains a three dimensional network of polymer can be produced. This gel is of infinitely large molecular weight, and insoluble in water.

2.1.3 Free Radical Grafting

A radical is defined as an atom or group of atoms with an unpaired electron. Most radicals are electrically neutral, although they are highly reactive because they contain an odd number of electrons (usually seven) in their outer shell rather than a stable inert gas configuration (an octet).[11] Radical addition polymerization refers to the process of the radical adding to the alkene double bond yielding a new radical site at the end of the polymer chain.

Free radical polymerization methods is the oldest and most widely used procedure for the synthesis of graft polymers, because they are relatively simple. However, they usually give heterogeneous materials that are difficult to characterize.[12]

The first step of free radical polymerization is initiation, where a reactive species is formed. The speed of this step is dependent on the chemistry of the initiator. Propagation refers to the successive addition of the monomer to the reactive species. The active centre is always on the end of the polymer chain. The lifetime of a growing polymer molecule may be less than a few seconds.[13] Termination of the polymer chain occurs when the radical centre is destroyed, typically by combination with another radical.

2.1.4 Ceric Ion Initiation

A redox reaction is the process of reduction (electron gain) and oxidation (electron loss). The substance that supplies the electrons is the reducing agent and the substance that removes electrons is the oxidizing agent.[14] Redox initiators involve a single electron transfer generating free radicals that are able to initiate polymerization. The activation energy for radical generation by redox processes is generally lower than that of the thermal homolysis of peroxides, thus are suitable for low temperature polymerization. The major difficulty of redox systems is the rapid disappearance of the redox components, leading to incomplete polymerization.[15]

The ceric ion, Ce^{4+} is a very strong oxidizing agent. It can abstract an electron from the polymer molecule providing a radical site from which the monomer can propagate. The method is applicable for many substrates with labile protons such as alcohols, amides, and urethanes.[16] The use of ceric ion as a redox initiator for grafts and polymerization is well documented. The use of ceric ions to initiate graft polymerization was first discussed by Mino and Kaizerman in 1958.[17]

Acrylamide has been polymerized by the ceric ion in a water solution, although the rate of propagation is substantially increased by the addition of acetoacetanilide. In the presence of acetoacetanilide (N-phenyl-3-oxobutanamide) the rate of polymerization of acrylamide increased 29 times in aqueous solution and 78 times in a water/acetonitrile solution.[18] They also found that a free radical was formed on the acetoacetanilide and this was responsible for the initiation of the polymerization, because they exist as end-groups.

Many other studies have investigated the increased polymerization rate of acrylamide in the presence of reducing agents such as amino acid type chelating agents[19,20], ethylenediamine tetraacetic acid,[21] amino acids,[22] nitrilotriacetic acid,[23] sorbose[24] and azo compounds with methylol.[25] In all of these cases a radical is formed from the decomposition of a complex formed between the ceric ion - reducing agent.

The ceric ion is also extensively used in grafting. Many examples of grafting vinyl monomers to cellulose are discussed in a review article by McDowall, Gupta and Stannett.[26] By grafting various monomers onto cellulose it is possible to attain many different properties including elasticity, sorbancy, ion exchange capabilities, thermal resistance and resistance to microbiological attack.

Acrylamide is a common monomer to form grafts. It has been grafted to many different substrates, such as dextran with a ceric ion and nitric acid initiation system,[27,28] surface modified barium sulfate,[29] and copolymers of N-p-tolyl-2-methyl-acrylamide, N-ptoyl-acrylamide and N-phenyl-2-methylacrylamide with methyl acrylate and MMA.[30] In this last study Qiu found that graft copolymerization of AM onto PMA, PMMA and poly(MA-co-MMA) films did not occur using ceric ion as an initiator, although the method of grafting was not given.

A complex of the ceric ion with functional groups on the polymer chain dissociates forming a radical site on the polymer and the vinyl monomer polymerizes from this site. Acrylamide and many other vinyl monomers have been polymerized using a ceric ion redox system. In this research we have hypothesized that the ceric ion will produce a radical site on the polyacrylamide and the DADMAC monomer will polymerize from this site. The following reaction scheme, modified for the PAM-DADMAC system from the cellulose grafting scheme proposed by Ogiwara et al.[31] shows all possible reactions in our system.

Reaction Scheme:

Initiation

$$\mathrm{Ce(IV)} + \mathrm{PAM\text{-}H} \overset{K}{\Leftrightarrow} \mathrm{COMPLEX} \xrightarrow{k_D} \mathrm{PAM}^{\bullet} + \mathrm{Ce(III)} + \mathrm{H}^{+} \qquad (2.1)$$

$$\mathrm{PAM}^{\bullet} + \mathrm{D} \xrightarrow{k_i} \mathrm{PAM} - \mathrm{D}^{\bullet} \qquad (2.2)$$

$$\mathrm{Ce(IV)} + \mathrm{D} \xrightarrow{k'_P} \mathrm{D}^{\bullet} + \mathrm{Ce(III)} + \mathrm{H}^{+} \qquad (2.3)$$

Propagation

$$\mathrm{PAM}-\mathrm{D}_n^{\bullet}+\mathrm{D}\xrightarrow{k_P}\mathrm{PAM}-\mathrm{D}_{n+1}^{\bullet} \tag{2.4}$$

$$\mathrm{D}_m^{\bullet}+\mathrm{D}\xrightarrow{k_P'}\mathrm{D}_{m+1}^{\bullet} \tag{2.5}$$

Termination

$$\mathrm{PAM}-\mathrm{D}_n^{\bullet}+\mathrm{Ce(IV)}\xrightarrow{k_T}\mathrm{PAM}-\mathrm{D}_n+\mathrm{Ce(III)}+\mathrm{H}^+ \tag{2.6}$$

$$\mathrm{D}_m^{\bullet}+\mathrm{Ce(IV)}\xrightarrow{k_T'}\mathrm{D}_m+\mathrm{Ce(III)}+\mathrm{H}^+ \tag{2.7}$$

$$\mathrm{PAM}-\mathrm{D}_n^{\bullet}+\mathrm{PAM}^{\bullet}\xrightarrow{k_T''}\mathrm{Stabilization} \tag{2.8}$$

$$\mathrm{PAM}^{\bullet}+\mathrm{Ce(IV)}\xrightarrow{k_O}\mathrm{Oxidation\ products}+\mathrm{Ce(III)}+\mathrm{H}^+ \tag{2.9}$$

Initiation with the ceric ion involves the formation of a complex followed by decomposition to yield initiating radicals, eq. (2.1). This step would be the rate limiting step because of the formation of the complex. In the polymerization of acrylonitrile there was a visible induction period, where the start of polymerization was taken as the point of appearance of turbidity in the reaction medium.[32] The initiation of the DADMAC monomer, eq. (2.3) would produce homopolymer instead of graft copolymer and is therefore undesirable. The propagation of the DADMAC monomer would proceed quickly, as in all free radical polymerizations. Termination in a redox system is more complicated. Termination occurs not only by combination of radicals, but the ceric ion also terminates the growing polymer radicals.

2.2 Polymerization

In this study DADMAC is polymerized from a radical site formed by the ceric ammonium nitrate- nitric acid complex on the polyacrylamide backbone.

2.2.1 Polymer Preparation

Polyacrylamide was purchased in granular form from Aldrich Chemical Inc., with a weight average molecular weight of 5×10^6. DADMAC monomer was supplied in solution by Nalco Canada. The solids content of the monomer is 67.8%, determined by drying several samples under vacuum at room temperature. All commercial materials were used without further purification. All water used was deionized and Milli Q filtered.

A set of designed experiments were run to understand the effect of polyacrylamide concentration, the amount of ceric ion, the amount of acid and the polymerization temperature. The conditions of each polymer run are given in Table 2.1. Polymerization took place in 250 mL polyethylene bottles at room temperature, or in a temperature controlled water bath.

Polyacrylamide solutions are extremely viscous at concentrations above 1%. Polymerization can be viscosity limited, thus the PAM content was set less than 0.7% by weight. The amount of ceric ion was used as a ratio in comparison to the amount of PAM present. This way we could understand its effect as the amount of PAM varied. The molar ratio of acrylamide units to ceric ion added was varied from 25 to 75. A low ratio of AM to Ce(IV) represents a high concentration of radical initiator. Nitric acid concentration varied from 1 to 4 mmol/L. DADMAC monomer was constant for all of the runs, at 1 mol/L. A high value was chosen to ensure that monomer would be present throughout the entire reaction, and to limit the possibility of PAM - PAM interactions.

A stock solution of PAM was prepared in advance to ensure complete dissolution of the polymer. The necessary amounts of PAM solution and DADMAC monomer solution were placed into the polyethylene reactor bottle. Immediately prior to the start of polymerization, the nitric acid and water necessary to bring the reaction volume to 200 mL were added. This mixture was then purged with nitrogen gas. In another polyethylene bottle a ceric ammonium nitrate (CAN) solution was purged with nitrogen. After each solution had purged for at least ten minutes, a syringe was used to extract the necessary amount of CAN solution that was then slowly injected into the PAM-DADMAC solution, while still under nitrogen. The reaction mixture was purged with a rapid flow of nitrogen for approximately five minutes. The polyethylene bottle was then sealed with paraffin tape. The bottles were shaken for several minutes to ensure solution homogeneity. Each sample was allowed to react for 24 hours, and the sample was immediately precipitated in acetone to stop the polymerization.

Table 2.1 Polymerization Designed Experiment

Run Number	*Ratio of AM:Ce(IV)*	*PAM conc. g/mL*	*Acid conc. mmol/L*	*Temp ^0C*
1	24.9	0.40%	1.03	25
2	75.5	0.40%	1.03	60
3	25.0	0.70%	1.03	60
4	75.2	0.70%	1.03	25
5	24.8	0.40%	3.97	60
6	75.5	0.40%	3.97	25
7	25.0	0.70%	3.97	25
8	75.2	0.70%	3.97	60
10	52.1	0.55%	2.54	42.5
11	50.2	0.55%	2.54	80
12	50.2	0.20%	2.54	42.5
13	50.3	0.55%	2.57	60
14	49.4	0.20%	2.57	60

2.2.2 NMR Analysis

NMR was used to prove the presence of polyDADMAC, its spectrum is clearly visible, as can be seen in Figures 2.3. The monomer also has distinct peaks at higher ppm, as well much sharper than the broad polymer peaks, shown in Figure 2.4. There are two peaks in the spectra of polyacrylamide as shown in Figure 2.5. Although there is some overlap of one peak of each polyDADMAC and polyacrylamide, the presence of each polymer is apparent in a spectra of the graft copolymer. The height and area of the peaks give an indication of the degree of grafting as shown in Figure 2.6 for graft copolymer run #2 with a low degree of grafting, and Figure 2.7 for graft copolymer run 12 with a high degree of grafting.

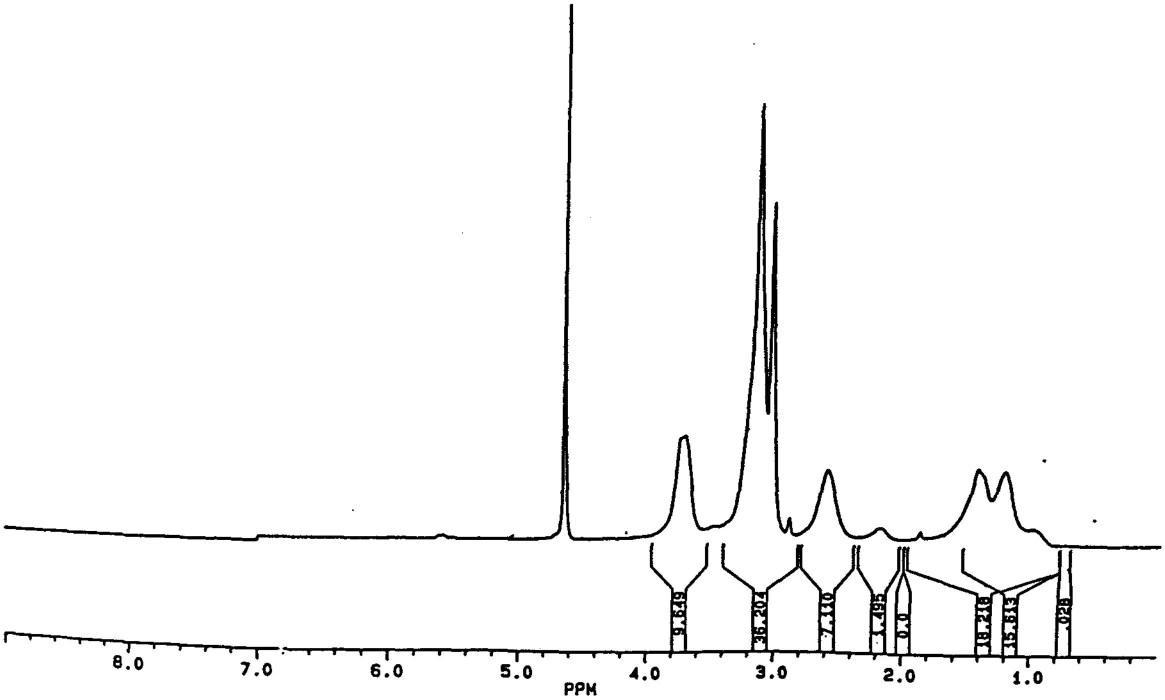


Figure 2.3 Proton NMR spectra of polyDADMAC

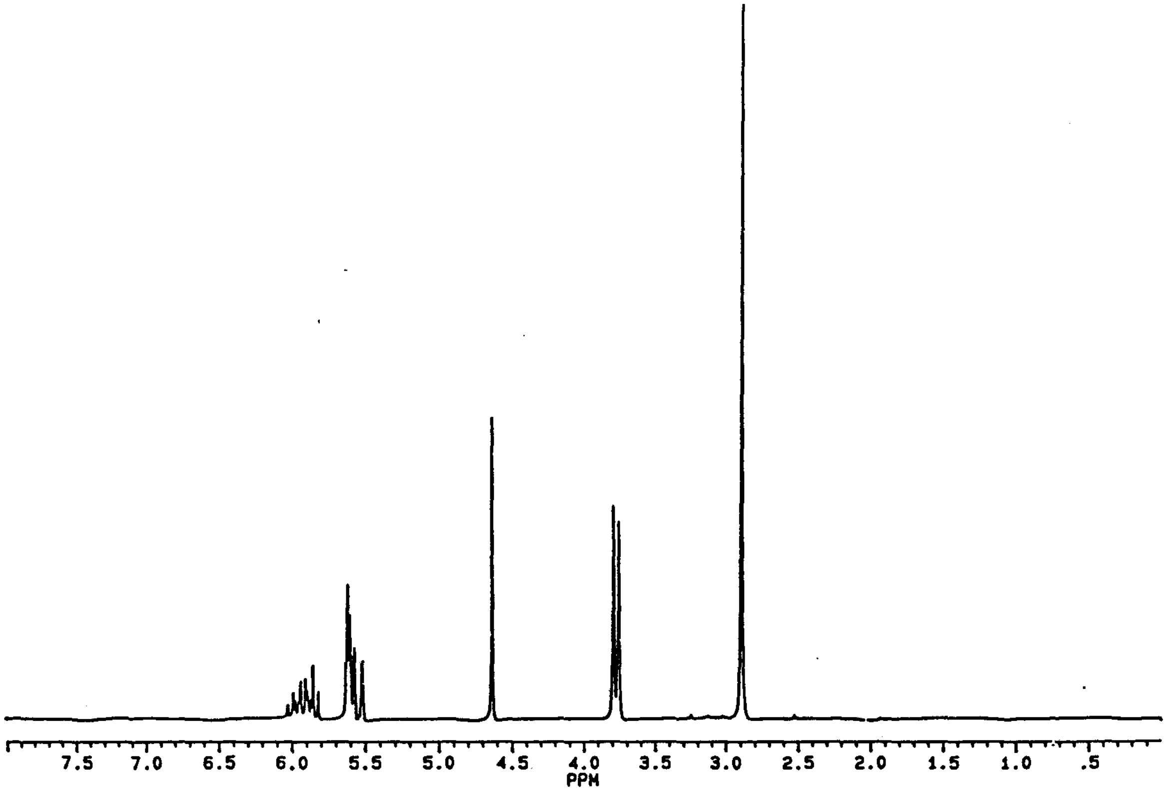


Figure 2.4 Proton NMR spectra of DADMAC monomer

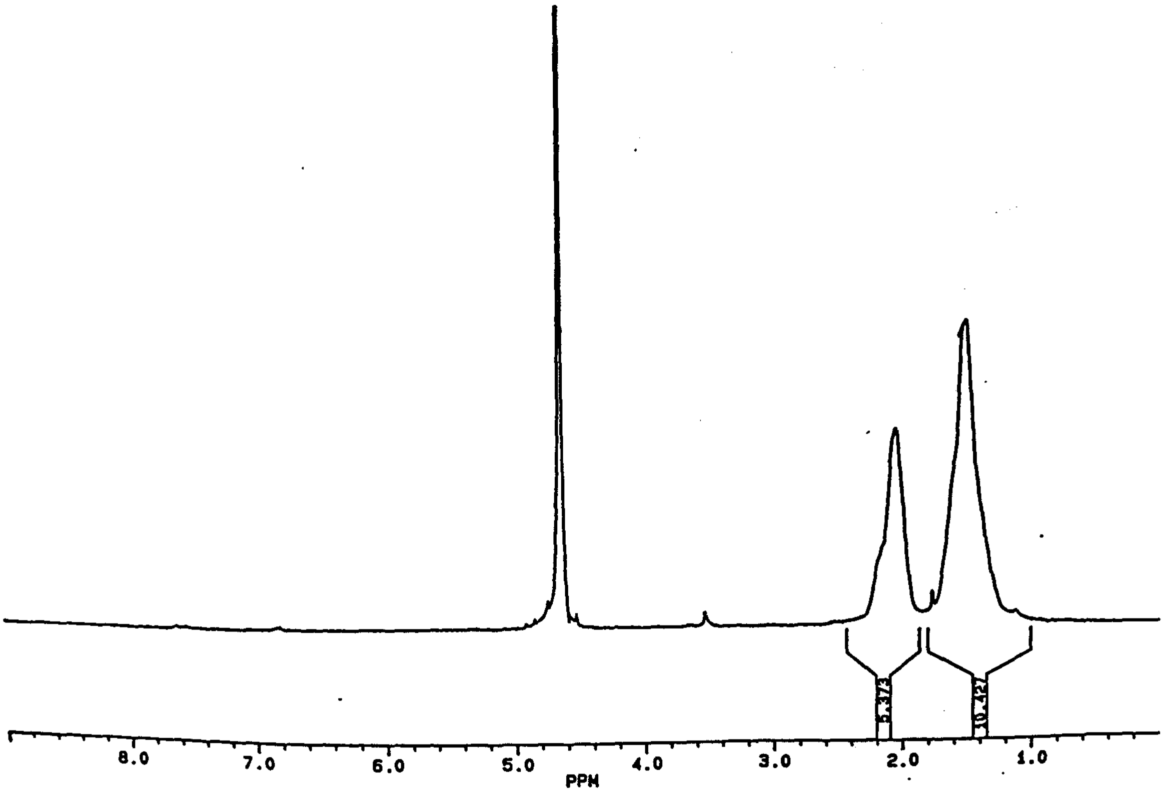


Figure 2.5 Proton NMR spectra of polyacrylamide

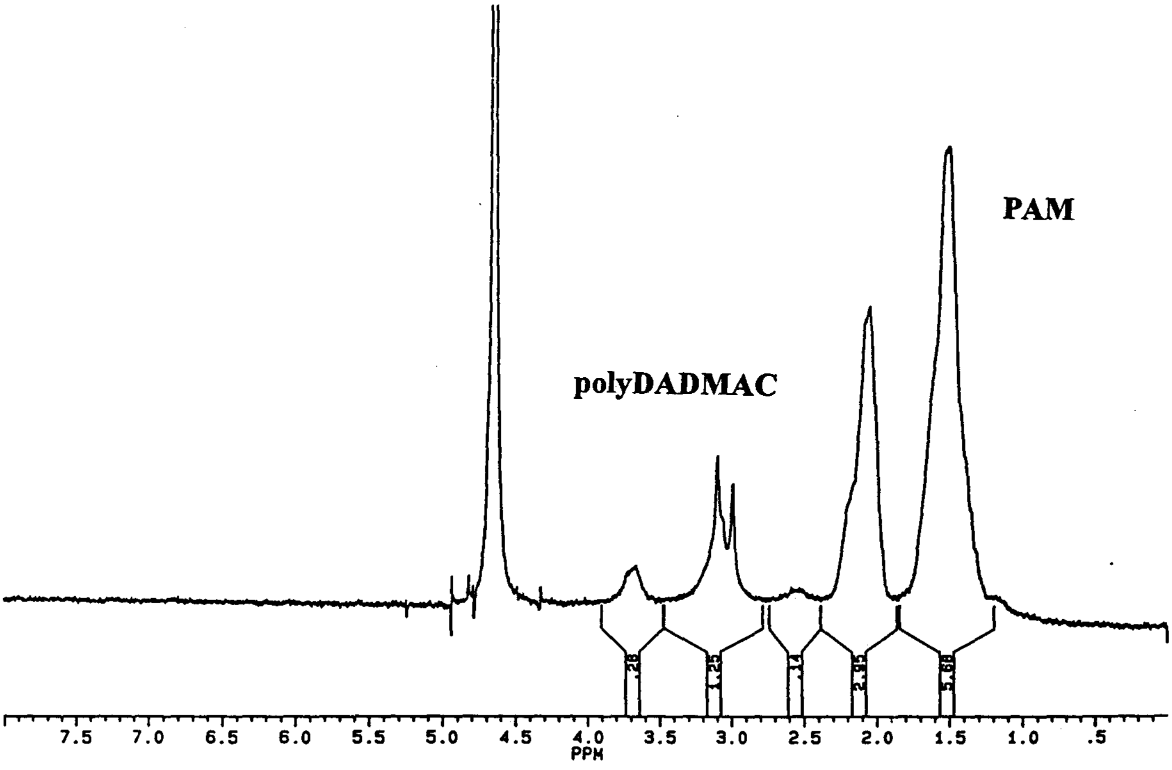


Figure 2.6 Proton NMR spectra of graft copolymer run #2

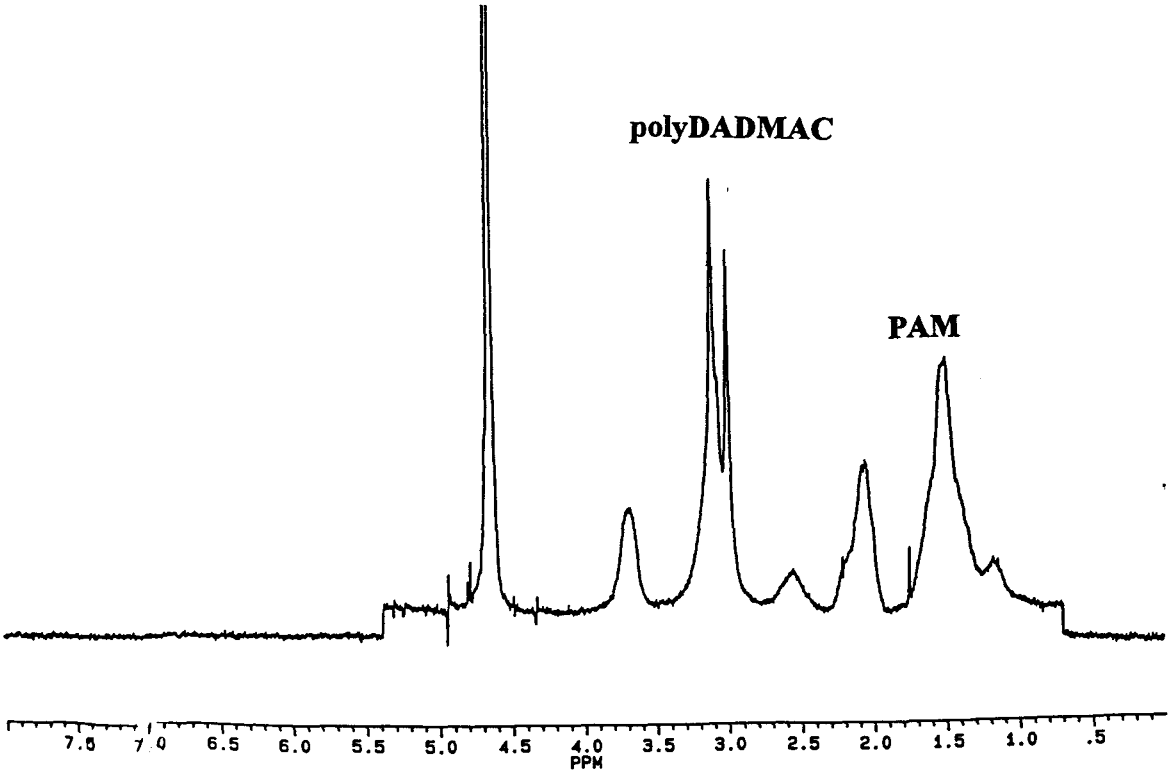


Figure 2.7 Proton NMR spectra of graft copolymer run #12

2.2.3 Copolymer separation and purification

After polymerization the polymer needs to be separated from all residual monomer and ceric ion. Polyacrylamide is insoluble in acetone and methanol, thus either solvent can be used to precipitate PAM out of solution. PolyDADMAC is soluble in methanol, and in acetone it becomes a viscous paste. The DADMAC monomer is soluble in methanol, but not as soluble in acetone. The monomer could easily be trapped in the polymer when precipitating in acetone. This solubility data is summarized in Table 2.2.

Table 2.2 Solubility Data of polymers and monomer

	Acetone	*Methanol*
Polyacrylamide	not soluble	not soluble
PolyDADMAC	not soluble	soluble
DADMAC monomer	somewhat	soluble
PAM g polyDADMAC	not soluble	???

From this information to purify the polymer the copolymer was precipitated out in acetone, then washed it in methanol overnight to remove all DADMAC monomer. Many different conditions were tested and in all of the samples after methanol washing there was no evidence of grafting in the NMR spectra even though qualitatively there was a difference in the appearance of many of the samples, including a darker colour. The degree of grafting could not be measured by an increase in weight because there is a small loss of polymer during the precipitation and filtering of the polymer.

Finally a sample was precipitated from acetone and only half of the polymer washed in methanol. A NMR spectra was taken of each sample, from these spectra it was clear that we were washing away any polyDADMAC that was produced. In the sample that was not washed in methanol, the NMR spectra showed that there was both DADMAC monomer and polyDADMAC present in the sample. The spectra of the same sample that was also washed in methanol did not have peaks of either polyDADMAC or monomer. Thus it is concluded that the solubility of the polyacrylamide changes with the addition of grafts of polyDADMAC, any graft polymer produced was being washed away in the methanol.

To separate the copolymer from the monomer dialysis was used. The copolymer was immediately precipitated in acetone and was left in acetone overnight so that all of the polymer particles would settle to the bottom of the beaker. The acetone/water mixture was siphoned off, new acetone added and the sample filtered. This polymer was then dried under vacuum to remove all residual acetone. A new polymer solution of 1% g/mL of polymer in Milli Q filtered deionized water was prepared. This polymer solution was placed in dialysis tubing with a molecular weight cut-off of 12,000. The water was changed frequently and left for 48 hours. The solutions were placed in plastic beakers and covered to prevent dust from contaminating the samples while evaporating. A thin film of polymer was produced that was broken up and left in the vacuum oven for at least 24 hours to continue to dry.

2.2.4 DADMAC Blank

The purpose of this work was to produce a graft copolymer, not simply a blend of PAM and polyDADMAC. To ensure that the ceric ion did not initiate the homopolymerization of DADMAC, a blank study was done. DADMAC monomer was at a concentration of 1 mol/L, the same as that in the copolymerizations. Ceric ion was 2 mmol/L, an average value used in the designed experiment, nitric acid concentration of 4 mmol/L and the polymerization temperature of 60 ^{0}C. The polymerization time was 24 hours.

Several methods were used to separate the polymer and monomer from water and ceric ion, including evaporation at room temperature and at 50 ^{0}C, and the addition of acetone. In each case there was no sign of polymer in the NMR spectra, only monomer. Thus it is concluded that the DADMAC monomer cannot be polymerized in the presence of ceric ammonium nitrate and nitric Acid. Reaction (2.5), the homopolymerization of DADMAC can not occur, thus we can assume that the polyDADMAC formed is a graft copolymer, not DADMAC homopolymer.

2.3 Characterization of Graft Copolymers

The polymers produced were characterized to determine the effects of the four polymerization factors studied, PAM concentration, ratio of AM unit to ceric ion, concentration of nitric acid and polymerization temperature. The amount of gel, the amount of charge groups, and solution viscosities were measured.

2.3.1 Gel Fraction

During the polymerization, gel is formed. Gel is a three dimensional network that is insoluble in water. Gel is formed easily during free radical polymerization when polymer chains cross link with each other. This gel is undesirable in polymers used for flocculation as polymer bridges can not be formed between the colloid particles with the cross linked gel.

In the previous work on free radical grafting of PAM and polyDADMAC by Min Ma during her Masters thesis,[33] it was found that the gel formed was solely PAM gel. In fact polyDADMAC was found to inhibit the intermolecular crosslinking of gel formation of PAM and DADMAC, because of the repulsion of the quaternary ammonia groups. No gel was formed in solutions of polyDADMAC in the presence of gamma irradiation for five hours. PolyDADMAC gel has been produced although in the presence of *N,N* - methylenebisacrylamide a crosslinking agent.[34]

The gel formed in this reaction would be formed by the combination of polymer radicals, both PAM radicals terminating with PAM radicals, and PAM grafted with DADMAC terminating with either type of polymer radicals. Or simply two types of gel, gel formed solely of PAM or gel containing polyDADMAC.

Experimental

The gel formed in each of the polymerization conditions were small pieces of hard gel. Gel was also formed in the PAM blank reaction. This was a reaction of ceric ion, nitric acid and polyacrylamide without DADMAC monomer. Solutions of known concentration of the graft copolymer were filtered under vacuum using Milli Q filter paper with a pore size of 1.2 μm. The filter paper was weighed prior to filtration, and after vacuum drying. In some cases of high gel, it was extremely difficult to filter the solution. The polymer solution was placed in a plastic centrifugal tubes and the polymer gel collected at the bottom of the centrifugal tube. All of the polymer solution was still filtered although this method reduced the number of filter papers necessary. If the gel was stuck to the side of the centrifugal tube, the tube was dried under vacuum along with the filter papers.

The gel fraction was calculated as:

$$\frac{\text{amount of gel after vacuum dried}}{\text{total amount of polymer in the original solution}}$$

This measurement of gel somewhat exaggerates the gel formation as any soluble polymer coating the gel is not washed off.

Results

Table 2.3 Gel Fraction Results

Run Number	*Ratio of AM:Ce(IV)*	*PAM conc. g/mL*	*Acid conc. mmol/L*	*Temp °C*	*Gel Fraction %*
1	24.9	0.40	1.03	25	69.48
2	75.5	0.40	1.03	60	2.22
3	25.0	0.70	1.03	60	47.75
4	75.2	0.70	1.03	25	20.07
5	24.8	0.40	3.97	60	39.74
6	75.5	0.40	3.97	25	2.98
7	25.0	0.70	3.97	25	60.51
8	75.2	0.70	3.97	60	0.50
10	52.1	0.55	2.54	42.5	13.11
11	50.2	0.55	2.54	80	38.33
12	50.2	0.20	2.54	42.5	18.40
3b	25.0	0.70	1.03	60	51.06
5b	25.1	0.40	3.97	60	42.50
8b	75.2	0.70	4.01	60	10.76
11b	50.0	0.55	2.54	80	19.60
13	50.3	0.55	2.57	60	8.46
14	49.4	0.20	2.57	60	2.09
9-PAA	24.6	0.40%	3.98	60	43.3
PAMblank	24.4	0.40%	3.98	60	41.7

The gel fraction results show that there was a wide spread in the amount of gel produced, samples with none to almost 70% gel. There is an obvious correlation between gel and the ratio of ceric ion that can be seen by simply looking at the data. Runs #1, #3, #5, and #7 have low ratios of AM:Ce(IV), thus a high amount of ceric ion producing gel.

This is also shown in the statistical analysis. The designed experiment data was analyzed using a statistical software program, MODDE. Both the ratio of AM:ceric ion and the concentration of PAM were significant effects at a 95% probability level. The concentration of acid and the polymerization temperature were not significant factors. The acid concentration was dropped from the statistical analysis as it increased the multiple correlation coefficient, R^2. The analysis of variance (ANOVA) table, Table 2.4, shows that the regression fit of the data is significant, and there is no lack of fit. The coefficients are also given in Table 2.5. An increase in the ratio of AM to Ce(IV) lowers the gel fraction, while an increase in PAM concentration increases the gel fraction. These effects can be seen visually by looking at the gel fraction data in Figures 2.8 through 2.11.

Table 2.4 ANOVA results for Gel Fraction

	Degree of Freedom	*Sum of Squares*	*Mean Square*	*F Value*	*Probability*
Total	17	19734	1160.8		
Constant	1	11782.94	11782.9		
Total Corrected	16	7951.058	496.9		
Regression	3	6542.91	2180.9	20.135	3.63E-05
Residual	13	1408.148	108.3		
Lack of Fit (Model Error)	9	1166.53	129.6	2.146	0.24
Pure Error (Replicate Error)	4	241.618	60.4		
	N = 17	Q2 = 0.7113		CondNo = 1.7895	
	DF = 13	R2 = 0.8229		Y-miss = 0	
		R2Adj = 0.782		RSD = 10.4076	
				ConfLev= 0.95	

Table 2.5 Coefficient Data for Gel Fraction

	Coefficient	*Standard Error.*	*Probability*	*Confidence Interval (±)*
Constant	28.908	2.925	2.06E-07	6.319
Ratio	-23.15	3.13	5.22E-06	6.761
PAM conc.	4.99	2.271	0.047	4.906
Temperature	-4.889	2.52	0.074	5.443

As shown in Figure 2.8 there is no statistical effect of acid concentration on the amount of gel produced. There is a wide range of gel fraction values at each concentration, no trends are apparent.

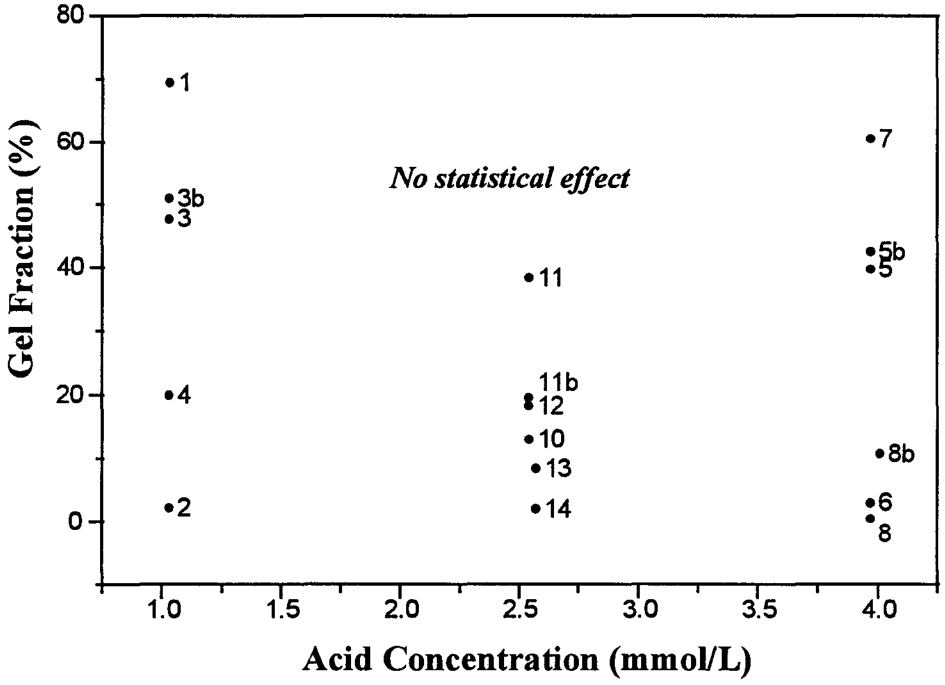


Figure 2.8 Gel fraction data plotted against acid concentration

In Figure 2.9 the trend of increasing gel fraction with an increase in PAM concentration is shown. At a very low concentration of polymer, 0.2 % PAM, little gel was formed, while at higher concentrations of PAM more gel was formed. At each PAM concentration, the acid concentration, ratio of ceric ion and polymerization temperature vary, thus giving the wide range of gel fraction values. The arrow in the figure represents the effect of an increases given by the MODDE software.

The effect of PAM concentration on the gel amount is due to the proximity of the PAM molecules during the polymerization. When a radical is formed on the PAM backbone the probability of another PAM radical being in close proximity will be higher with a higher concentration of PAM. The effect of PAM concentration is not a very strong effect because the increase of viscosity with increasing PAM concentration would limit the diffusion of ceric ion and polymer radicals.

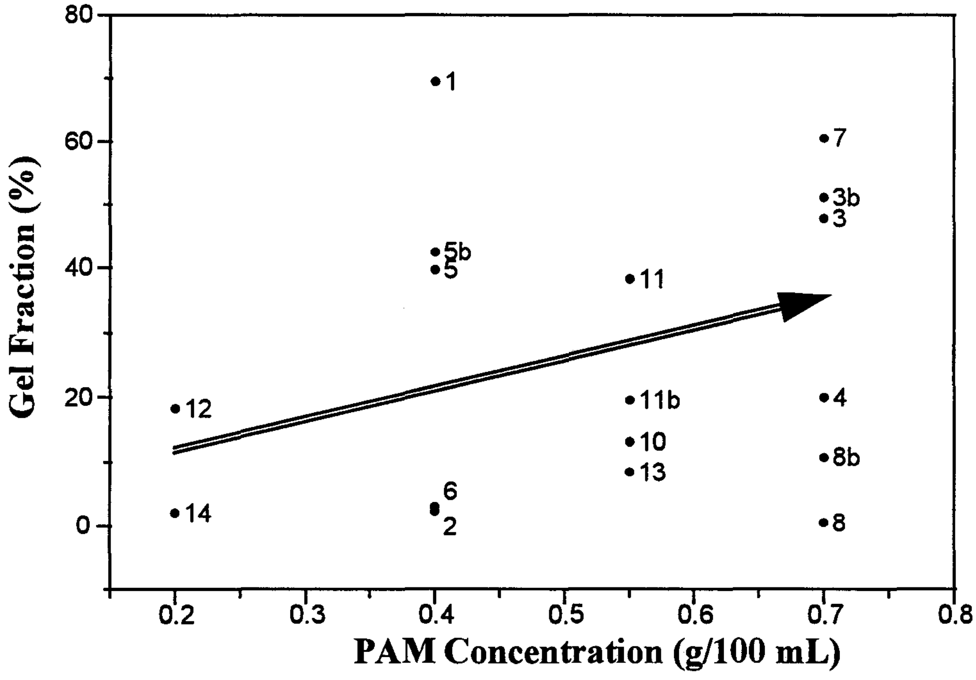


Figure 2.9 Gel fraction data plotted against PAM concentration

In Figure 2.10 the effect of the ratio of AM:Ce(IV) is shown. An increase in the ratio gives a decrease in gel fraction, a lower amount of ceric ion (a higher ratio) produces less gel. At a ratio of 25, there are 25 acrylamide units for every one ceric ion. At a ratio of 75 there are 75 acrylamide units for every one ceric ion, thus a third less ceric ion. An increase in ceric ion will produce more polymer radicals that will be able to crosslink with each other forming a three dimensional network. This is a strong effect.

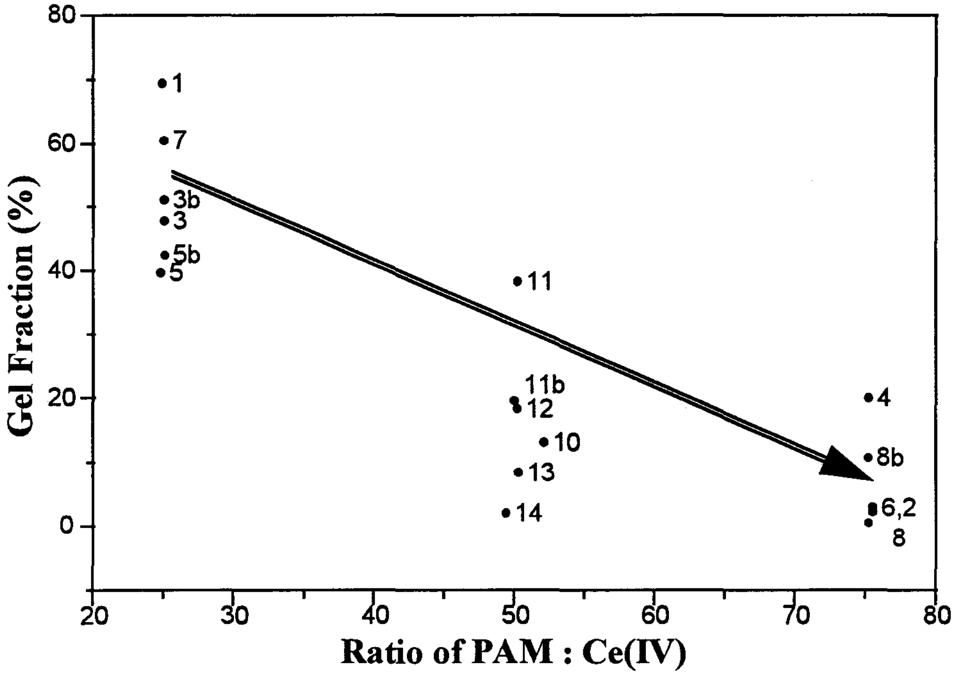


Figure 2.10 Gel fraction data plotted against ceric ion ratio

The gel fraction is plotted against polymerization temperature in Figure 2.11. No statistical effect is apparent. Gel was produced almost immediately as the ceric ion was injected into the PAM-DADMAC mixture, thus polymerization temperature was not a factor. To limit the gel produced, the ceric ion solution was as dilute as possible, and this solution injected very slowly.

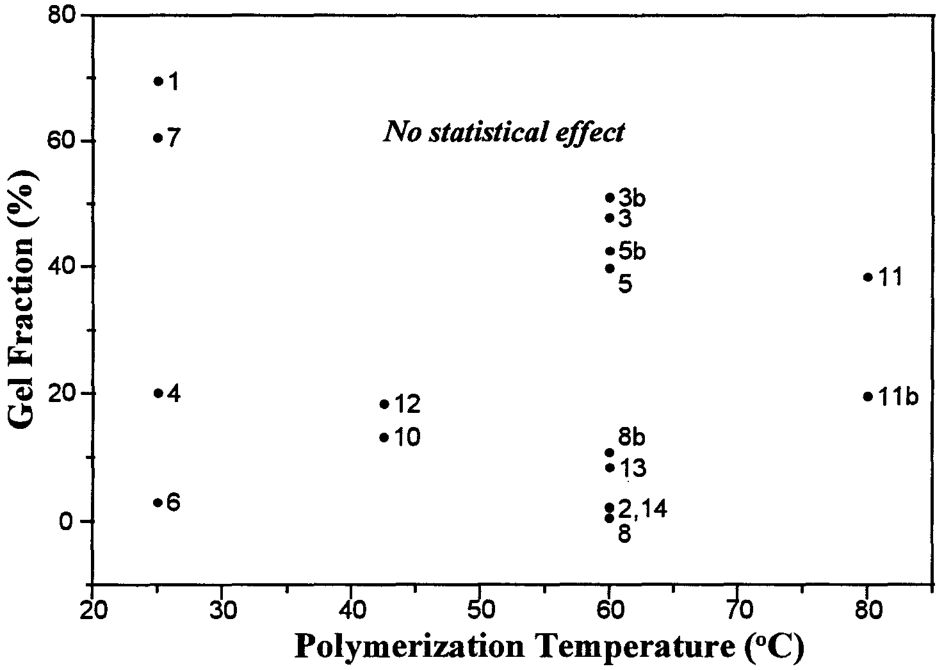


Figure 2.11 Gel fraction data plotted against polymerization temperature

The formation of gel is not wanted in the water soluble polymer industry because of solution properties. These pieces of gel are not soluble and do not act as a flocculant. There is some evidence that a small amount of gel is beneficial, although it is very difficult to control the amount of gel. The formation of gel is exponential and it is thus difficult to limit its formation.

2.3.2 Viscosity Measurements

Theory

Measurements of viscosity of dilute polymer solutions can be used to provide information concerning the effects upon chain dimensions of polymer structure (chemical and skeletal), molecular shape, degree of polymerization (hence molecular weight), and polymer-solvent interactions.[35] The viscosity of polymer solutions is due to the difference in dimensions between the polymer coils and the solvent molecules. The viscosity depends on the nature of solvent, polymer type, polymer molecular weight, polymer concentration, and the temperature.

The viscosity of the polymer solution (η), and that of the solvent (η_0) are measured. The relative viscosity, $\eta_{rel} = \eta/\eta_0$, accounts for the effects of the solvent. The specific viscosity (η_{sp}) is defined as $\eta_{sp} = \eta_{rel} - 1$.

The intrinsic viscosity, $[\eta]$ relates to the intrinsic ability of a polymer to increase the viscosity of a particular solvent in the absence of any intermolecular interactions at a given temperature. The specific viscosity of a solution of concentration c is related to $[\eta]$ by a power series in $[\eta]$c:

$$\eta_{sp} = [\eta]\, c + k_1 [\eta]^2 c^2 + k_2 [\eta]^3 c^3 + \ldots \qquad (2.10)$$

or $$\eta_{sp}/c = [\eta] + k_H [\eta]^2 c \qquad (2.11)$$

This equation is known as the Huggins equation and is valid for $[\eta]c \ll 1$, that is dilute solutions. Also at this condition the following algebraic expansion is valid:

$$\ln(\eta_{rel}) = \ln(\eta_{sp} + 1) \approx \eta_{sp} - \eta_{sp}^2/2 + \ldots \qquad (2.12)$$

Substituting eq. (2.11) into eq. (2.12), and retaining terms in c up to c^2:

$$\ln(\eta_{rel}) = [\eta]c + (k_H - 1/2)[\eta]^2 c^2 \qquad (2.13)$$

which can be rearranged into the form of the Kraemer equation:

$$\ln(\eta_{rel})/c = [\eta] + k_K [\eta]^2 c \qquad (2.14)$$

The Huggins and Kraemer equations are used to evaluate the intrinsic viscosity by plotting the $\ln(\eta_{rel})/c$ and η_{sp}/c against concentration and extrapolating each line to find the intercept at zero concentration, the intrinsic viscosity, $[\eta]$.

The viscosity of dilute polymer solutions are measured using a Ubbelohde capillary viscometer. The fluid inside the capillary tube and measuring bulb is suspended with atmospheric pressure acting both above and below the flowing liquid, thus the pressure head is independent of the total volume in the viscometer. The time that it takes the fluid to pass two etched marks is measured.

Poiseuille's equation is used relate the viscosity, η, to the pressure drop across the capillary:

$$\frac{V}{t} = \frac{\pi r^4 P}{8 \eta L} \tag{2.15}$$

where V = the volume of liquid which flows through the capillary
t = the time that the volume of liquid flowed
r = the radius of the capillary
L = the length of the capillary
η = the viscosity of the fluid
P = the pressure difference across the capillary

During the measurement of flow time, P continuously decreases and is normally given by

$$P = \langle h \rangle \rho g \tag{2.16}$$

where $\langle h \rangle$ = the average pressure head
ρ = the density of the liquid
g = the acceleration due to gravity

Thus Poiseuille's equation, eq. (2.15), can be rearranged to give

$$\eta = \frac{\pi r^4 \langle h \rangle \rho g t}{8 V L} \tag{2.17}$$

or simply $\eta = A\rho t$ where A is a constant for a given viscometer. However absolute measurements of viscosity are not necessary for dilute solutions as we need the viscosity relative to the solvent viscosity. So the relative viscosity becomes:

$$\eta_{rel} = \eta/\eta_0 = \rho\, t/\rho_0 t_0 \qquad (2.18)$$

where ρ and ρ_0 are the densities, and t and t_0 are the flow times of the polymer solution of concentration c and of the pure solvent respectively. Although because dilute solutions are used, we often assume $\rho = \rho_0$, so that eq. (2.18) simply becomes $\eta_{rel} = t / t_0$. By measuring the time for a fixed volume of polymer solution to pass the two etched lines at a series of concentrations , the intrinsic viscosity can be found.

The intrinsic viscosity is often used to find the viscosity averaged molecular weight using the Mark-Houwink equation:

$$[\eta] = KM^a \qquad (2.19)$$

However in this thesis, graft copolymers were produced, and eq. (2.19) is only applicable for linear polymers. But the intrinsic viscosity still is a measure of the configuration of the polymer chain, and we can look at the differences in viscosity to determine differences in structure. The effect of branching is to increase the segment density within the molecular coil. Thus a branched polymer molecule has a smaller hydrodynamic volume and a lower intrinsic viscosity than a linear counterpart of the same molar mass.[35]

The viscosity of polyelectrolyte is highly dependent on electrolyte concentration. A certain amount of the counterions are associated with the charged groups on the polymer chain, while the rest are free in the bulk phase along with any additional ions added. These free ions can act as a shield of the charged groups thus affecting the repulsion of the charge groups. In a study of an acrylamide-DADMAC copolymer the intrinsic viscosity decreases when the concentration of NaCl increases from 0.05 to 0.5 mol/L.[36] Another study of ultrahigh molecular weight hydrolyzed polyacrylamide also shows that the intrinsic viscosity decreases with increasing salt concentration. The effect of the salt also varies with type of salt, for example KCl gave a lower intrinsic viscosity than KI in study by Lee and Lee.[37] The effect of salt is not strong with neutral polyacrylamide, the intrinsic viscosity has been found to increase and/or decrease slightly depending on the study.[38] Thus solution conditions are very important, and it is necessary to be consistent.

Experimental

Viscosity measurements were made in 0.1 M NaCl solution of Milli Q filtered deionized water. Polymer solutions of approximately 0.03% g/mL (0.3 mg/mL) were prepared with previously filtered polymer solutions. The polymer samples were dried for several days under vacuum and stored in a sealed desicator prior to being weighed to make fresh solutions. Polymer solutions were prepared the day before testing in volumetric flasks to ensure complete mixing of the polymer solution, but were not kept for more than 48 hours to prevent degradation of the polymer chains.[39,40] Measurements were taken at 25 ^{0}C, at least three replicates at each concentration.

Results

Table 2.6 Intrinsic viscosity results estimated by Linear Regression

Run Number	*Ratio of AM:Ce(IV)*	*PAM conc. mmol/L*	*Acid conc. mmol/L*	*Temp ° C*	*Intrinsic Viscosity mL/g*
1	24.9	0.40%	1.03	25	150
2	75.5	0.40%	1.03	60	862
3	25.0	0.70%	1.03	60	256
4	75.2	0.70%	1.03	25	560
5	24.8	0.40%	3.97	60	307
6	75.5	0.40%	3.97	25	323
7	25.0	0.70%	3.97	25	345
8	75.2	0.70%	3.97	60	320
10	52.1	0.55%	2.54	42.5	395
11	50.2	0.55%	2.54	80	253
12	50.2	0.20%	2.54	42.5	296
13	50.3	0.55%	2.57	60	629
14	49.4	0.20%	2.57	60	330
8b	75.2	0.70%	4.01	60	583
PAM Blank	24.4	0.40%	3.98	60	150

The viscosity measurements show typical polyelectrolyte behaviour with the curvature of the curves at low polymer concentration. This curvature might have been reduced with a higher salt concentration to shield the quaternary ammonium groups, but we wanted to see this effect. The intrinsic viscosity of the backbone polymer, PAM was found to be 715 mL/g, only one graft copolymer having a higher viscosity than this, run #2. This copolymer was produced with a low amount of ceric ion, low PAM concentration, low acid concentration and a high polymerization temperature. In all other runs the viscosity drops indicating polyelectrolyte branching and/or PAM chain scission. The viscosity of the PAM blank was very low indicating chain scission. The radicals formed on the polymer chain could only react with other polymer radicals or degrade the polymer chain itself. A high content of gel was formed, 42%. In the remaining polymer the chains were degraded because of the radical centres.

The viscosity measurements are of the filtered polymer, the sol. The degree of density measurements given on the viscosity figures are also of the sol. The degree of grafting was calculated using charge titration as described in the next section. The amount of charge would effect the viscosity because of charge repulsions of the quaternary ammonium group of the polyDADMAC.

In Figure 2.12 the viscosity measurements are shown for the ratio of AM:Ceric ion of 25. These copolymers were produced with the highest amount of ceric ion. The viscosity results show a lot of chain scission in these samples. The effects of temperature and PAM concentration are not apparent because of the overwhelming effect of the ceric ion. An increase in ceric ion concentration has also been reported to increase cellulose degradation in a study of PVC being grafted onto cellulose.[41]

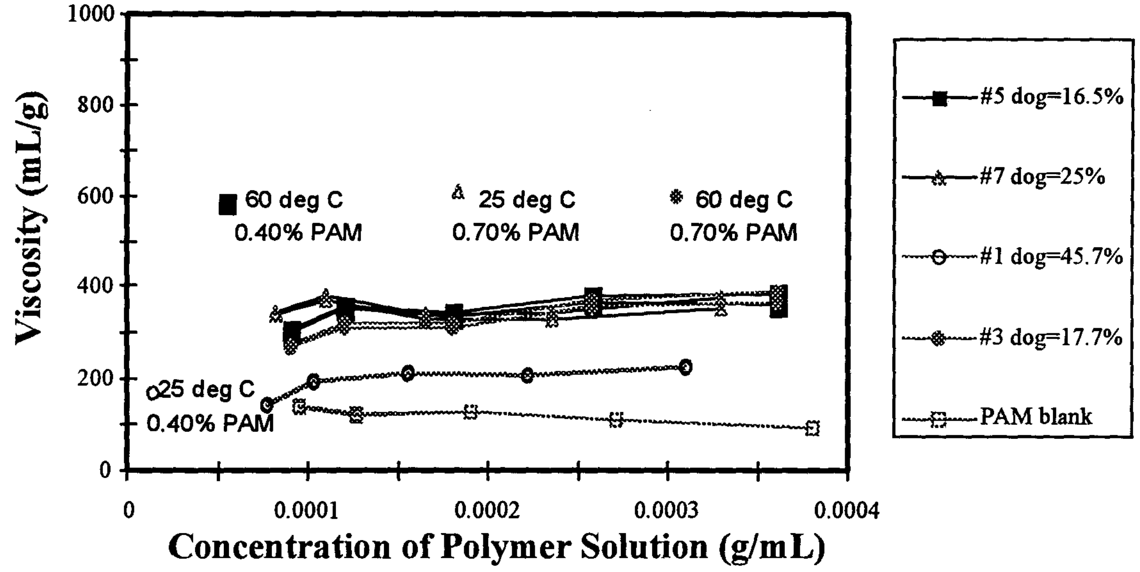


Figure 2.12 Viscosity measurements for polymerization conditions with a ratio of AM unit to ceric ion of 25 - the highest amount of ceric ion

In Figure 2.13 the viscosity measurements are shown of the polymerization runs with the midpoint ceric ion value, a ratio of AM unit to Ce(IV) of 50. A lower viscosity is found for the copolymers produced at a lower PAM concentration of 0.20% and a higher polymerization temperature of 80 ^{0}C. The similarity with these conditions during polymerization is a low viscosity, and thus increased ability of the ceric ion to diffuse through the polymerization mixture. The ceric ion will be able to form radical sites, and also terminate these growing DADMAC grafts. Runs #13 has a higher viscosity than run

#10, when the only polymerization difference is the temperature, run #13 was polymerized at 60 °C, while run #10 was polymerized at 42.5 °C.

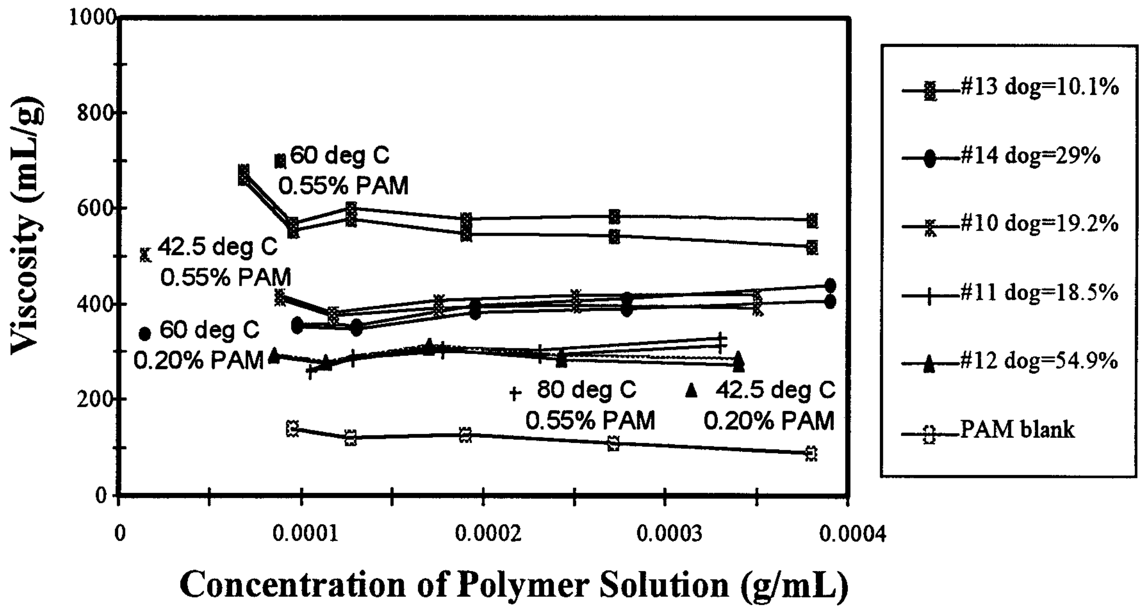


Figure 2.13 Viscosity measurements for polymerization conditions with a ratio of AM unit to ceric ion of 50

In Figure 2.14 the viscosity measurements for the polymerization conditions of AM: ceric ion ratio of 75 are shown. The copolymers produced with a low concentration of ceric ion have a wide of range of viscosity values because of the other polymerization conditions. The copolymer with the highest viscosity was run #2 with a higher polymerization temperature.

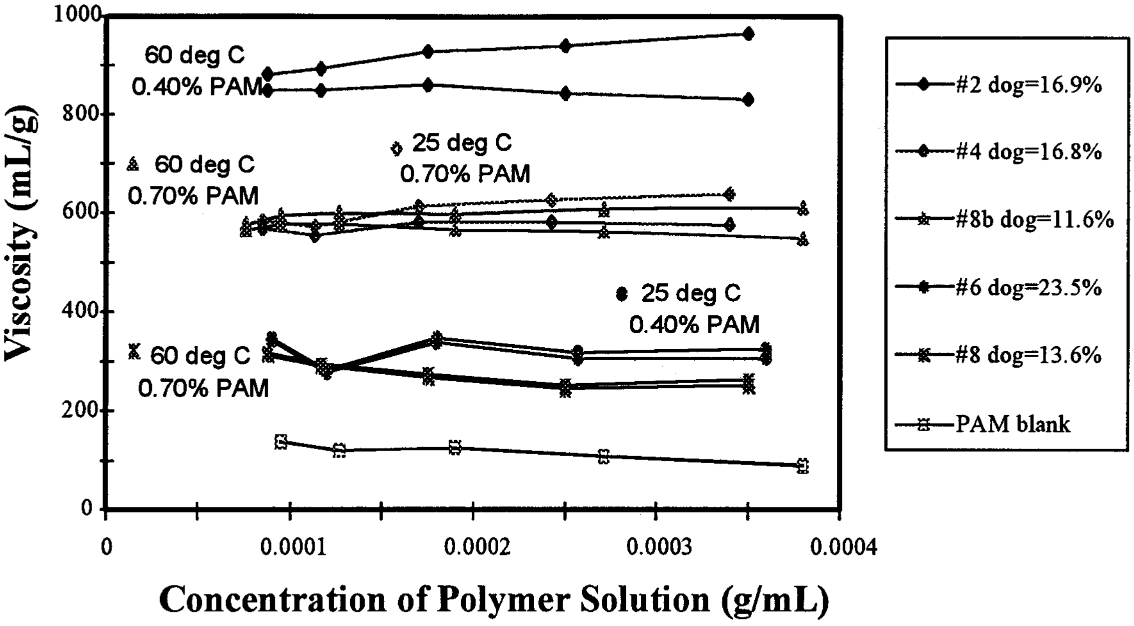


Figure 2.14 Viscosity measurements for polymerization conditions with a ratio of AM unit to ceric ion of 75 - the lowest amount of ceric ion

In order to understand the effect of the polymerization conditions on viscosity, the intrinsic viscosity was plotted against the acid concentration, PAM concentration, ceric ion ratio and polymerization temperature. The statistical analysis on this data was not significant, however the effects of the ceric ion and acid concentration show trends.

In Figure 2.15, an increase in the ratio of AM : Ce(IV) implies an increase in viscosity. Thus an increase in the amount of ceric ion reduces viscosity, via chain scission of the polyacrylamide.

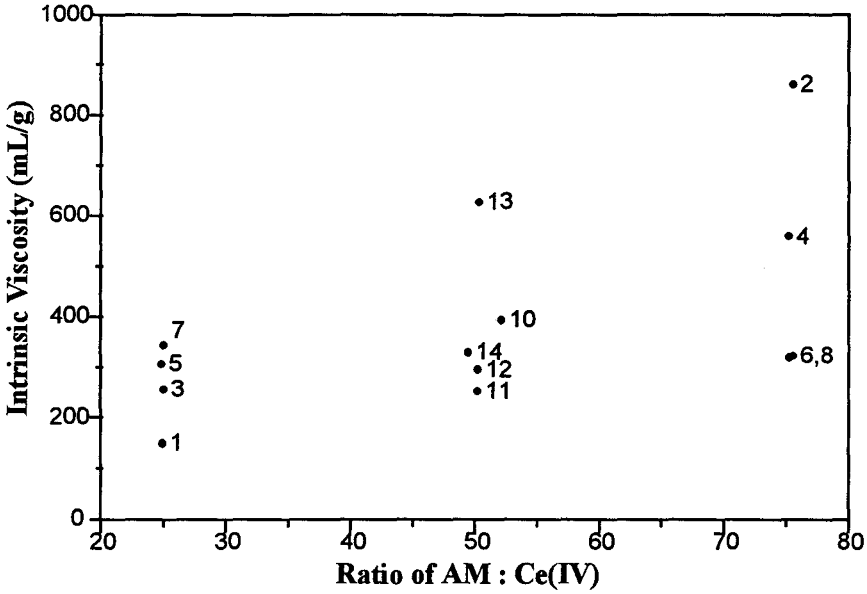


Figure 2.15 Intrinsic viscosity plotted against the ratio of AM : Ce(IV)

In Figure 2.16, the effect of acid concentration may imply a decrease in viscosity with increasing pH, however the effect is probably not significant with respect to the variation in viscosity at each acid concentration level.

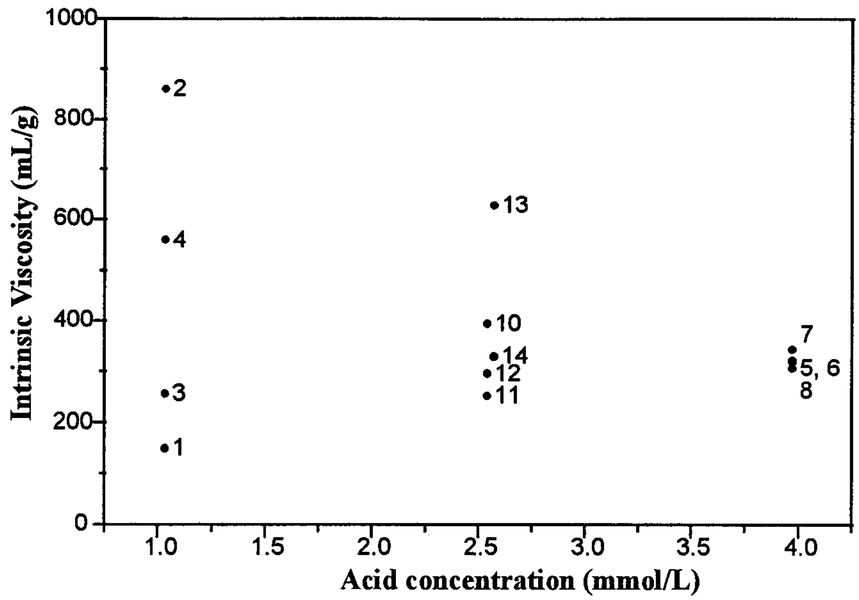


Figure 2.16 Intrisic Viscosity plotted against acid concentration

Figures 2.17 and 2.18 show that there is no consistent effect of PAM concentration and polymerization temperature on the copolymer viscosity.

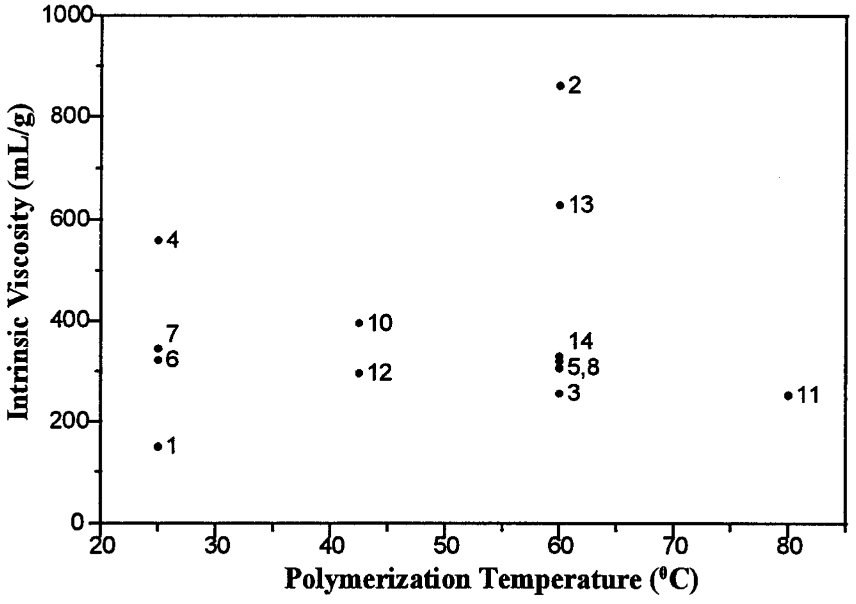


Figure 2.17 Intrisic Viscosity plotted against polymerization temperature

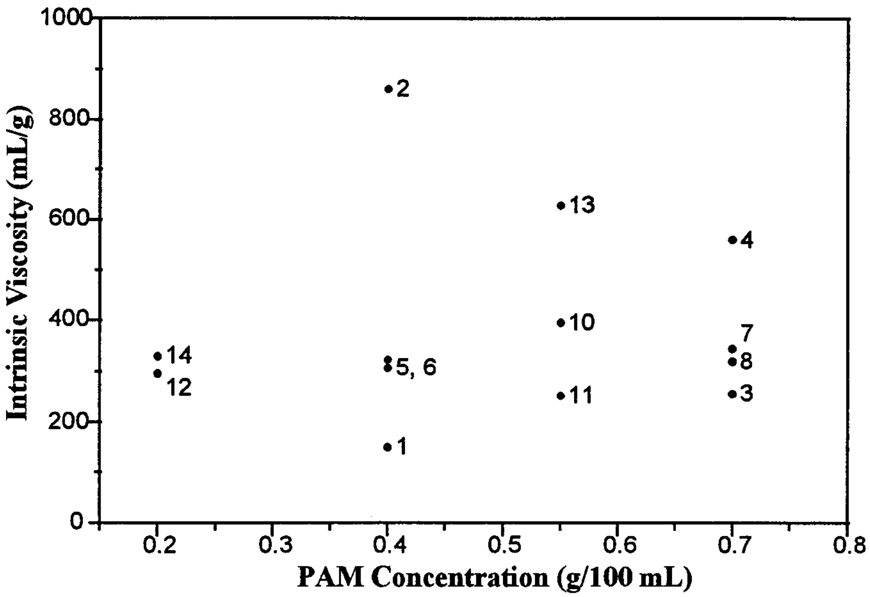
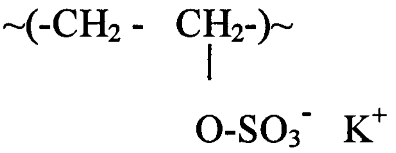


Figure 2.18 Intrisic Viscosity plotted against PAM concentration

2.3.3 Degree of Grafting Measurements

Cationic charge can be determined by polymer titration. The principle of polyelectrolyte titration is that the two polymers form a 1:1 complex in relation to their charge, similar to an acid - base titration. In a polyelectrolyte titration, the charged polymer sample is titrated with a standard anionic or cationic polymer until a point of zero charge is reached as determined by the streaming current cell.[42] Although the end point can also be determined using toluidine blue as an indicator. This method was used to determine the amount of DADMAC in copolymerization studies by Tanaka [43] and Deng and Pelton.[44]

The DADMAC copolymer produced has a cationic charge thus potassium polyvinyl sulfate (PVSK), a standard polymer with anionic charge, was used.



$$\sim(-CH_2-\underset{\displaystyle O\text{-}SO_3^-\ K^+}{\underset{|}{CH_2}}-)\sim$$

Figure 2.19 Chemical structure of PVSK

The charge of the unknown sample is calculated based on charge equivalence of the two polymers at the neutralization point:

$$Vol_A \bullet Charge_A = Vol_B \bullet Charge_B \qquad (2.20)$$

The charge of the standard PVSK was 0.001 N, and the volume of standard polymer solution at the endpoint is given by the titration computer program. A known volume of copolymer solution is titrated, thus the charge is easily calculated. The degree of grafting was calculated assuming that all of the charge was polyDADMAC and every repeat unit of the polyDADMAC polymer has a charge.

Degree of Grafting (DOG)

$$= \frac{(\text{moles of charge of graft copolymer}) \times \text{MW of DADMAC}}{\text{total mass of polymer} - (\text{moles of charge of graft copolymer}) \times \text{MW of DADMAC}}$$

It is assumed that all polyDADMAC is grafted onto PAM based on the fact that the DADMAC monomer could not be polymerized solely in the presence of nitric acid and ceric ion.

Experimental

Charge titrations were done on the Rank Brothers Charge Analyzer II and the Mutek Charge Analyzer at Nalco Canada. The results shown here are averages from runs done at Nalco on the Mutek. The charge titration was made on filtered solutions as any particulate would interfere in the titration therefore the degree of grafting originally calculated is that of the sol. A statistical analysis of these results on the filtered samples was not significant as the varying amount of gel in each sample is not accounted for.

The polymerization conditions produced graft copolymer samples containing both sol and gel. The gel can be solely crosslinked PAM or gel containing both PAM and DADMAC. Based on previous work we assumed that the filtered gel contained only a small amount of polyDADMAC due mainly to residual grafted copolymer caught in the gel. The probability of the graft copolymer forming a gel is low based on repulsion of the positive charges. As well the gel formation occurred immediately upon the addition of the ceric ion solution, before any DADMAC would have been grafted onto the PAM. To confirm this assumption, samples of gel were analyzed by NMR to determine if any polyDADMAC was present. This NMR spectra is difficult to get because the gel is insoluble in water and the particulates make it difficult for the NMR signal to be received. Several samples were attempted, finely ground gel was swollen in water for several weeks and the NMR signal was obtained. This signal, shown in Figure 2.20 was faint, however it is clear only PAM is present, no signals due to polyDADMAC were apparent. From these observations all gel was assumed to be solely PAM, and the degree of grafting was adjusted accordingly:

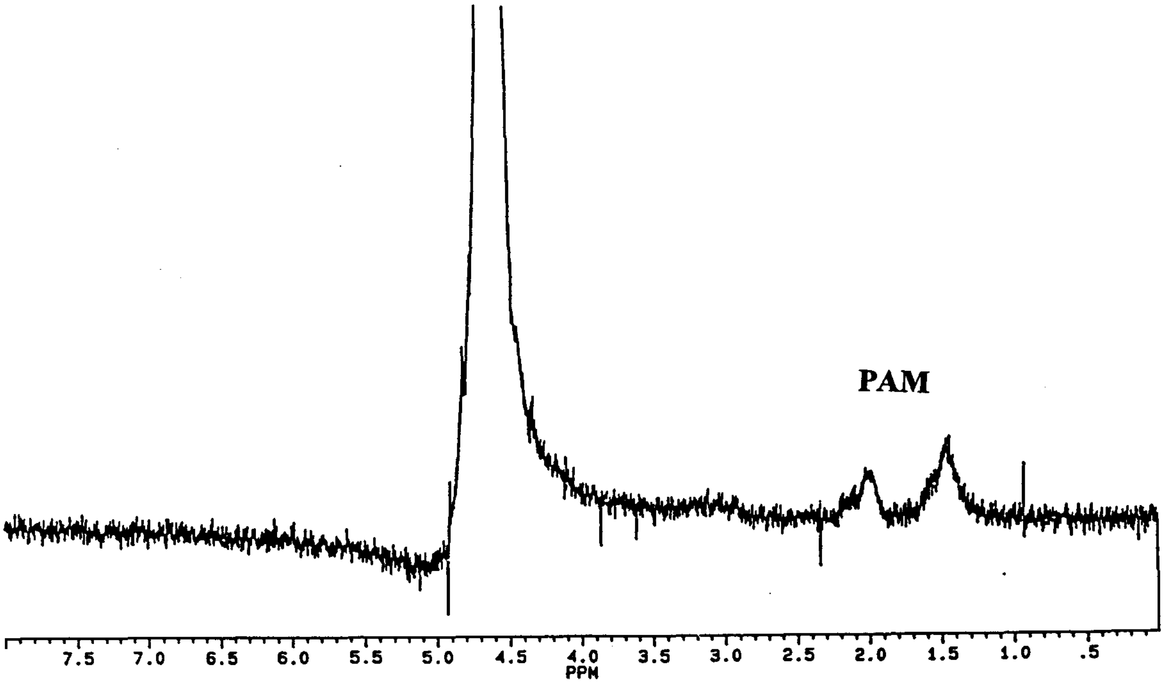


Figure 2.20 Proton NMR spectra of copolymer gel

$$\mathrm{DOG}_{adj}= \frac{\text{(moles of charge of graft copolymer)} \times \text{MW of DADMAC}}{\text{total mass polymer} - \text{(moles of charge of graft copolymer)} \times \text{MW of DADMAC} + \text{mass of gel}}$$

Results

Table 2.7 Degree of Grafting Results

Run Number	*Ratio of AM:Ce*	*PAM conc. g/100 mL*	*Acid conc. mmol/L*	*Temp °C*	*Adjusted DOG %*
1	24.9	0.40	1.03	25	13.82
2	75.5	0.40	1.03	60	16.49
3	25.0	0.70	1.03	60	9.25
4	75.2	0.70	1.03	25	14.03
5	24.8	0.40	3.97	60	11.04
6	75.5	0.40	3.97	25	22.80
7	25.0	0.70	3.97	25	11.76
8	75.2	0.70	3.97	60	13.59
8b	75.2	0.70	4.01	60	10.51
10	52.1	0.55	2.54	42.5	16.68
11	50.2	0.55	2.54	80	11.28
12	50.2	0.20	2.54	42.5	38.24
13	50.3	0.55	2.57	60	9.27
14	49.4	0.20	2.57	60	28.13

The degree of grafting adjusted for the gel content ranged from 9% to 38% as can be seen in Table 2.7. The two runs with the highest amount of DADMAC were the graft polymerizations with a very low concentration of PAM, 0.2%. Thus it is clear that the solution viscosity is very important in the grafting of DADMAC onto PAM. In fact these two runs are outliers in comparison to the rest of the grafting results as can easily been seen in Figure 2.21.

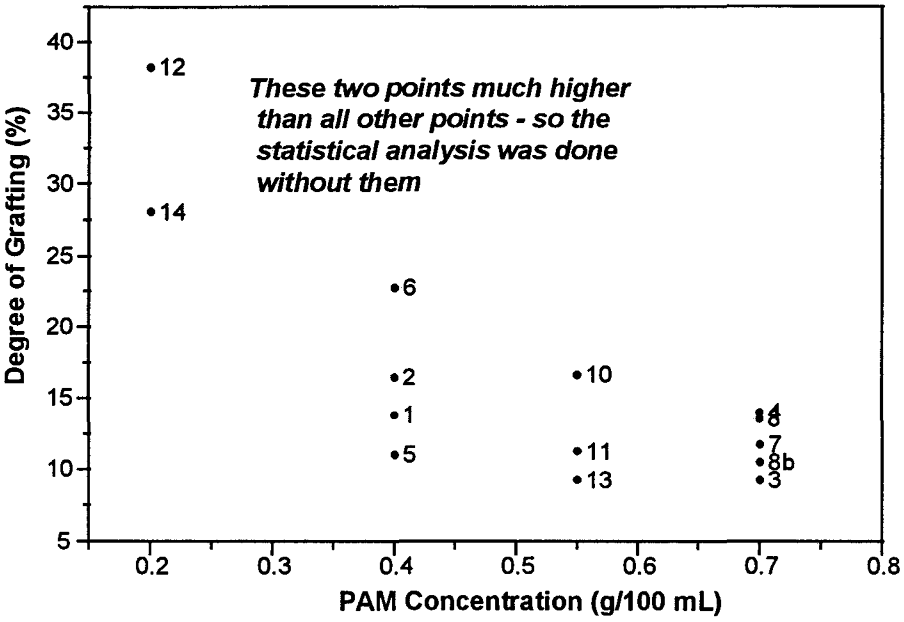


Figure 2.21 Adjusted Degree of Grafting plotted against PAM concentration

The statistical analysis was done on the remaining twelve runs with PAM concentration of 0.40% to 0.70%. From the ANOVA results in Table 2.8, we can see that the regression is significant and there is no lack of fit. Table 2.9 gives the values of the coefficients for the three factors that are significant, the ratio of AM:Ce(IV), PAM concentration and polymerization temperature. The nitric acid concentration did not effect the degree of grafting as can be seen in Figure 2.25 and was therefore dropped from the analysis.

Table 2.8 ANOVA results for Degree of Grafting

	Degree of Freedom	*Sum of Squares*	*Mean Square*	*F Value*	*Probability*
Total	12	2311.9	192.7		
Constant	1	2147.2	2147.2		
Total Corrected	11	164.7	15.0		
Regression	3	126.9	42.285	8.95	0.006
Residual	8	37.8	4.7		
Lack of Fit (Model Error)	7	33.1	4.7	0.996	0.65
Pure Error (Replicate Error)	1	4.7	4.7		
	N = 12 DF = 8	Q2 = 0.4968 R2 = 0.7704 R2Adj = 0.6844		CondNo = 1.5213 Y-miss = 0 RSD = 2.1736 ConfLev= 0.95	

Table 2.9 Coefficient Data for Degree of Grafting

	Coefficient.	*Standard Error.*	*Probability*	*Confidence Interval(±)*
Constant	13.898	0.666	2.92E-08	1.536
Ratio	2.449	0.742	0.011	1.711
PAM conc.	-2.173	0.733	0.018	1.69
Temperature	-1.794	0.601	0.017	1.386

Figures 2.21 and 2.22 show the adjusted degree of grafting plotted against the PAM concentration. The trend of reduced grafting with increasing PAM concentration during polymerization is clear. As previously mentioned this effect is likely due to solution viscosity. The diffusion of ceric ion and DADMAC monomer would be easier with a

lower PAM concentration. The number of ceric ions for each polymer chain is constant at both low and high PAM concentrations, because the AM:Ce(IV) ratio has been controlled. In the polymerization of acrylamide with polymeric azoesters using Ce(IV) the initial molecular weight of the final block polymer was affected by the molar mass of the initial polymeric azoester due to the viscosity of the medium.[45] At low PAM concentration there is more DADMAC monomer for each polymer chain because the total DADMAC concentration was constant at 1 mol/L for each polymerization run. The increase in the amount of DADMAC monomer may effect the degree of grafting, as polymerization rates are usually proportional to the monomer concentration. However in these polymerization runs, the monomer concentration is 10 to 20 times the concentration of PAM, to minimize this effect. The variations in the degree of grafting at each PAM concentration is because the other conditions are also varying and effect the amount of grafting.

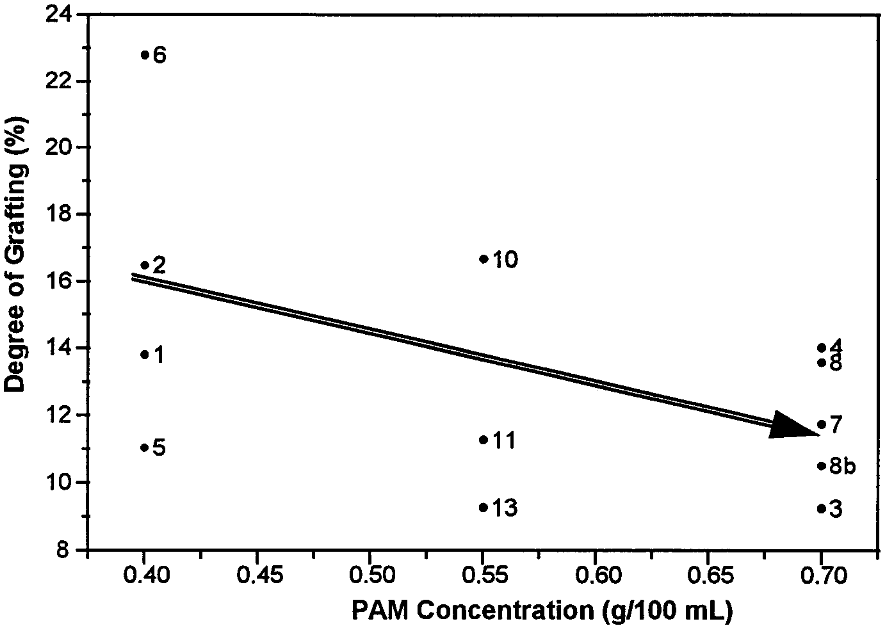


Figure 2.22 Adjusted Degree of Grafting plotted against PAM concentration

Figure 2.23 shows the adjusted degree of grafting plotted against the ratio of AM: ceric ion. This figure shows that the grafting of DADMAC increases with an increase in this ratio. At a ratio of 75 the highest amount of grafting was found. At this ratio for every ceric ion there are 75 acrylamide units, while at a ratio of 25, there are only 25 acrylamide units for every ceric ion, thus there are 3 times as many ceric ions at the low ratio where grafting was limited. This is because the ceric ion not only forms a radical site that initiates grafting it is also the principle method of termination, (eqs (2.6), (2.7), (2.9)). Thus an increase in ceric ion actually reduces the amount of grafting. The termination involves abstraction of a hydrogen atom from a polymeric radical by ceric ion to yield a grafted copolymer chain with a double bond at its end.[46] In the polymerization of acrylonitrile with ceric ion and glycine, the conversion and rate of polymerization consistently decreased with increasing concentration of Ce(IV).[47]

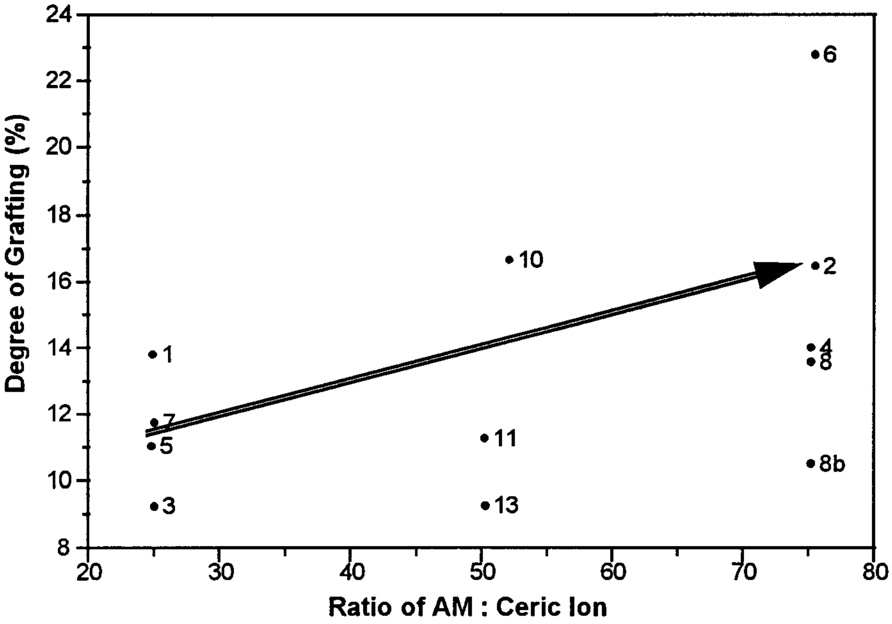


Figure 2.23 Adjusted Degree of Grafting plotted against ratio of AM:Ce(IV)

In Figure 2.24 the effect of polymerization temperature on the degree of grafting is shown. An increase in temperature reduces the amount of DADMAC grafted from the PAM. In free radical polymerization an increase in temperature normally increases the polymerization because of an increase in propagation. In a redox system the initiation of the radical site is slow because of the formation and decomposition of the ceric ion - polymer complex. Temperature will affect diffusion and changes in the rates of initiation, propagation and termination. Hence although propagation may be increased at a higher temperature, the overall polymerization may not increase. At a higher temperature the diffusion of the ceric ion is increased because of a decrease in viscosity and the increase of thermal energy of the ions. This is similar to dead-end polymerization. The rate of initiation is increased significantly, this increase in the number of radicals terminates the growing polymer chains. Thus termination is significantly increased with an increase in temperature.

In a study grafting glycidyl methacrylate from cellulose fibre, as the temperature increased from 30 to 70 ^{0} C, the content of grafting decreased.[48] This decrease in grafting was explained by the oxidation of the alcohol radical to an aldehyde by the elimination of a hydrogen atom. A study on the grafting of methyl methacrylate on cellulose also had a drop in grafting with an increase in temperature from 30 to 50 ^{0} C, although they could not explain this behaviour.[49]

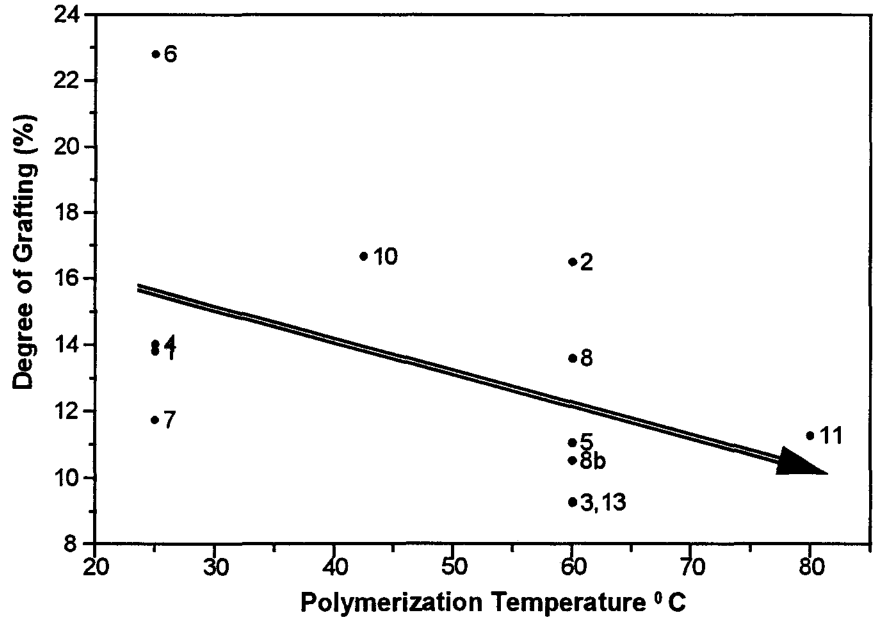


Figure 2.24 Adjusted Degree of Grafting plotted against Polymerization Temperature

In Figure 2.25 it is clear that there was no statistical effect on the amount of DADMAC grafted with acid concentration. This could be that the change in acid concentration is not high enough, or more probable, the competing reactions of termination and initiation reduce any effect. The effect of acid concentration is quite complicated. According to the review of ceric ion grafting of cellulose by McDowall, Gupta, and Stannett [50], the degree of grafting increases with increasing acid concentration, reaches an optimum and then decreases with excess acid. It has been suggested that the initial increase in grafting with increased acid concentration was due to a decrease in the termination rate of the growing polymer chain or an increase in the initiation rate. However, at higher acid concentrations, decreases in grafting were attributed to a corresponding reduction in the ceric-cellulose complex formation as well as an increase in polymer termination rates.

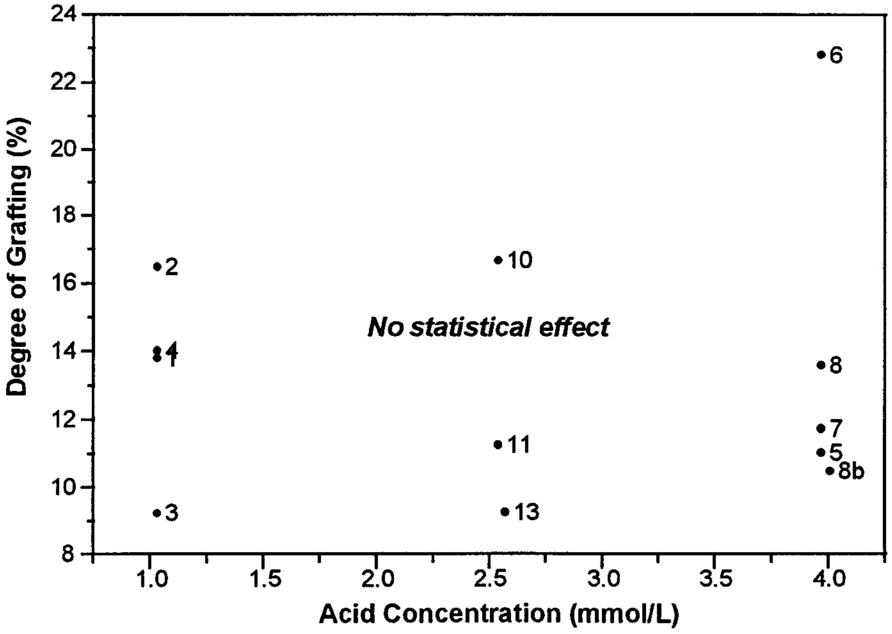


Figure 2.25 Adjusted Degree of Grafting plotted against Acid Concentration

From this study we know that the grafting of DADMAC from the PAM backbone is affected by the PAM concentration in the polymerization mixture, the amount of ceric ion, and the polymerization temperature. The reactivity of DADMAC is much lower than that of acrylamide, Tanaka et al. reported the reactivity ratios of $r_D = 0.58$ and $r_A = 6.7$ for DADMAC and AM respectively.[51]

One factor that was not analyzed was the presence of inorganic salts. In a study by Jaeger et al[52], the rate of polymerization of DADMAC with 2, 2'-azodi-2-methylpropanamidine dihydrochloride and ammonium peroxodisulfate increased in the presence of inorganic salts. The type of counterion also influences the change of the rate. The electrostatic repulsion between the growing polymer cation radicals and monomer cations decreases with increasing ionic strength, thus increasing the propagation rate. In this study, we did not know how the salt would effect the initiation with ceric ion.

2.4 Conclusions

In this chapter we have shown that graft copolymers of polyDADMAC and PAM can be successfully synthesized using the redox agent ceric ammonium nitrate. Homopolymerization of polyDADMAC does not occur, graft copolymers are produced.

We have found that an increase in the amount of ceric ion, increases the amount of gel, and decreases the amount of polyDADMAC grafted from PAM. Increasing the concentration of PAM during polymerization increases the amount of gel produced and decreases the amount of polyDADMAC grafted. Increasing the temperature for polymerization decreased the amount of polyDADMAC grafted, while there was no effect of temperature on the amount of gel produced. There was no statistical effect of the concentration of acid on either the amount of gel or polyDADMAC grafted.

Statistical analysis of the intrinsic viscosity results was inconclusive, there were no consistent changes in viscosity for changes in the four factors studied. The results simply indicated that the ceric ion lowered the viscosity of the copolymers due to chain scission.

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Chapter 3 Flocculation Performance of Graft Copolymers

3.1 Introduction

Water soluble polymers are often used as flocculants. The objective of this chapter is to evaluate the graft copolymers synthesized and characterized in Chapter 2 as flocculants for a TiO_2 model suspension. It is necessary to determine the effects of charge density and gel fraction on flocculation and find the optimum polymerization conditions to produce an effective flocculant.

3.1.1 TiO_2 model suspension

TiO_2 is commonly used as a model suspension for flocculation and adsorption studies.[1,2,3] The charge on the particle surface is controlled by pH adjustment. Inorganic oxides surfaces possess a large number of amphoteric hydroxyl groups that can undergo reaction with either H^+ or OH^- to generate positively or negatively charged sites:[4]

$$MOH + OH^- \rightarrow MO^- + H_2O \qquad (3.1)$$

$$MOH + H^+ \rightarrow MOH_2^+ \qquad (3.2)$$

Thus H^+ and OH^- are the potential determining ions, and the surface charge depends on the relative excess of one type of charged site over the other. The isoelectric point (i.e.p.), the pH when the particle surface charge changes from positive to negative, was previously found to be at a pH of 4.3 as shown in Figure 4.1.[5] The surface charge is constant from pH 7 to 12, therefore in this work the pH of the TiO_2 suspension was adjusted to a pH of 8 using 0.001M NaOH solution (Aldrich Chemical Inc.).

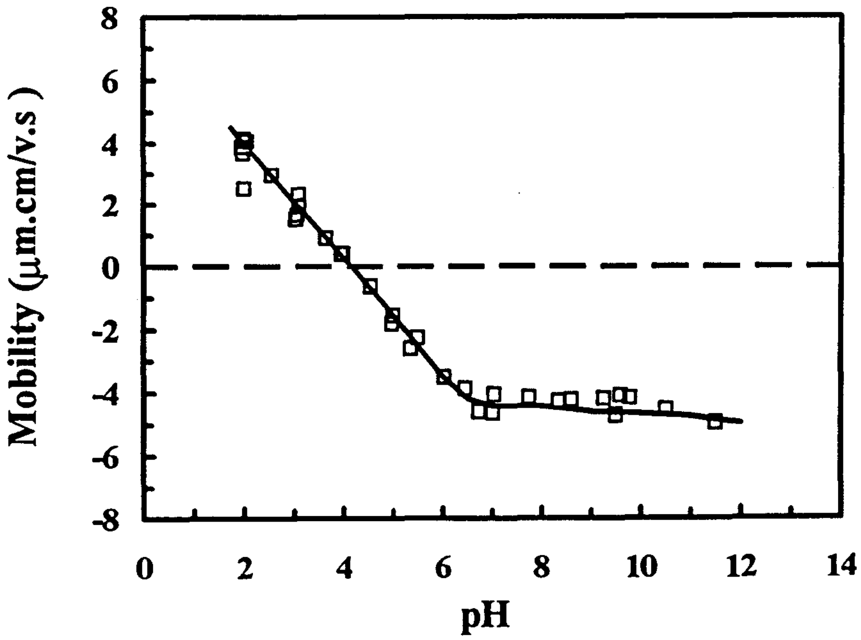

Figure 3.1 Mobility of TiO_2 particles as a function of pH with 10^{-3} M NaCl

The amount and type of any electrolyte in solution is also important. The addition of a salt can flocculate a stable colloid system. The increase in the concentration of the salt leads to a compression of the diffuse double layer of the TiO_2 particle resulting in rapid coagulation of the colloid particles. The salt concentration at which rapid coagulation occurs is called the critical coagulation concentration (c.c.c.). The c.c.c. of a TiO_2 solution is 0.01M NaCl. Thus at a concentration less than this value, the salt will not induce flocculation.

In addition, the salt concentration will effect the charge of the TiO_2 particles. If the salt concentration is raised there are more counterions. As these counterions accumulate near the surface they screen the surface charges. Therefore at a given pH more protons or hydroxide ions can adsorb on the surface, and the double layer capacitance increases. Thus at a pH above the isoelectric point the surface charge becomes more negative with increasing salt concentration at fixed pH.[6] Therefore it is very important to control the salt concentration in flocculation experiments. In this work the salt concentration was 10^{-3} M NaCl. At this level it is low enough not to interfere with the colloid stability.

3.1.2. Particle size distribution measurements

There are many different tests that are used as a measure of flocculation efficiency, such as: the size and strength of the flocs, sedimentation rate, sediment volume, permeability or residual turbidity.[7] In this work we have looked at the number and size of particles before and after flocculation. The increase in the number of large particles indicates the agglomeration of the TiO_2 particles and differences in the performance of the various polymers can be seen. This method has been used to follow the flocculation of colloidal particles, particularly at stages where only a few particles are formed.[8] In this work the TiO_2 particle size distribution is bimodal, most of the particle diameters are less than 0.3 μm, although there are particles up to 1.2 μm in diameter. There are several methods to measure the particle size distribution, in this work we used a disc centrifuge particle sizer to measure the particle size distribution.

3.1.3 Theory of disc centrifuge particle analysis[9]

The Brookhaven BI-DCP Particle Sizer uses centrifugal sedimentation to produce an apparent weight differential particle size distribution directly and rapidly by continuously measuring the attenuation of the light passing through a liquid medium as the particles pass through the light beam. The raw data trace can be converted into a weight, surface area or number distribution. Both the differential and integral (cumulative) forms of the distributions can be calculated.

White light from a tungsten/ halogen lamp is passed through the disc at a distance corresponding to 5 mL of liquid. This fixed position is close to the outer circumference of the cavity. As particles pass through the light beam, the light intensity is extinguished due to scattering and/or adsorption, the transmitted light is measured by a photodiode and recorded by the computer as a function of time.

The time t for a particle to reach the radial position of the detector can be calculated from first principles using Newton's law for centrifugal force:

$$F_c = m_P w^2 r \qquad (3.3)$$

where m_P is the mass of the particle

w is the rotational speed of the disc

r is the radial position with respect to the centre of rotation of the disc

There are two forces which act in opposition to the centrifugal force, the buoyancy and the frictional drag force. The buoyancy is due to the mass of the fluid the particle displaces, m_f

$$F_{buoyancy} = - m_f w^2 r \qquad (3.4)$$

and the frictional drag force is proportional to the radial velocity, dr/dt

$$F_{frictional} = -f\, dr/dt \qquad (3.5)$$

where f, the frictional coefficient depends on the shape and size of the particle as well as the fluid viscosity.

Using Newton's law of motion, F = ma, this gives:

$$m_P \frac{d^2 r}{d^2 t} = \left(m_P - m_R\right) w^2 r - f \frac{dr}{dt} \qquad (3.6)$$

This second order linear differential equation can be solved exactly and it shows that the acceleration is practically zero within milliseconds, therefore the terminal radial velocity is given by:

$$\frac{dr}{dt} = \frac{(m_P - m_R)\,w^2 r}{f} \qquad (3.7)$$

For a spherical particle:

$$f = 3\pi\eta d \qquad (3.8)$$

where η is the viscosity of the spin fluid.

and $m_P = \rho\pi d^3/6$ (3.9)

Substituting eqs. (3.8) and (3.9) into eq. (3.7) and integrating gives:

$$t = \frac{18\eta \ln\left(\frac{R_d}{R_i}\right)}{w^2 d^2 \Delta\rho} \qquad (3.10)$$

where R_i = the initial radius of injected sample at time zero

R_d = the radius of the detector at time t

$\Delta\rho$ = the difference in density between the particle and the spin fluid

Equation (3.10) is the Stokes equation for centrifugal sedimentation. The time that it takes for a particle to reach the detector is inversely proportional to the square of the particle diameter. Thus large particles appear first, the small particles take longer.

3.2 Flocculation Experiments

3.2.1 Sample Preparation

The graft copolymers were prepared as described in Chapter 2. Graft copolymers solutions of 0.5% were prepared and then diluted down to approximately $5\mathrm{x}10^{-5}$ g/mL the day of the experiment. The commercial random cationic polymer, PC-3 was kindly supplied by Nalco Canada. It was prepared by copolymerization of a 50:50 ratio of acrylamide and DADMAC monomers, therefore its charged groups are randomly distributed along the polymer chains.

The titanium dioxide was purchased from Aldrich Chemicals, with a density of 3.9 g/mL. TiO_2 solutions of 50 mg/L were prepared in 0.001M NaCl solutions. The TiO_2 solution was ultrasonicated for three hours to break the self aggregated particles. At room temperature, the pH value of the suspension was adjusted to a pH of 8 by adding 0.001 N NaOH solution. This solution was stable for more than 24 hours, although all flocculation experiments were run within 24 hours. The TiO_2 stock solution remained stirring slowly with a magnetic stirrer for all times.

3.2.2 Flocculation Experiments

Flocculation performance is dependent on both the type and amount of polymer added to the colloid system. Polymer dosage is defined as the mass of polymer per mass of TiO_2. 50 mL of the TiO_2 suspension (2.5 mg) was transferred to a beaker. The polymer dosage tested ranged from 1 to 30 mg of polymer/g TiO_2. The appropriate amount of dilute polymer solution was measured and added by pipette for each polymer dosage. The solution sat for 30 minutes stirring slowly with a magnetic stirrer to allow the particles to flocculate, prior to injection into the centrifugal disk. Experiments were performed at room temperature with the Brookhaven BI-DCP particle sizer in the homogeneous start mode. 15 mL of the flocculated solution was accelerated in the polycarbonate disc at 3000 rpm for 15 minutes. The data collected from each experiment was analyzed using the Brookhaven software version 5.02, using the theory described in section 3.1.3. This gave us the differential and cumulative mass distributions curves plotted against the particle diameter.

3.3 Results and Discussion

3.3.1 Particle Size Distributions

The particle size distributions of several blank TiO_2 solution are shown in Figure 3.2. For each polymer sample at least one blank TiO_2 was analyzed prior to the flocculation experiments. There is a distribution of curves because of the natural distribution of the size of particles in the TiO_2 sample. Replicate runs of the blank TiO_2 were very similar in shape, the differences arise as each 1 L batch of colloidal TiO_2 will vary slightly in particle size.

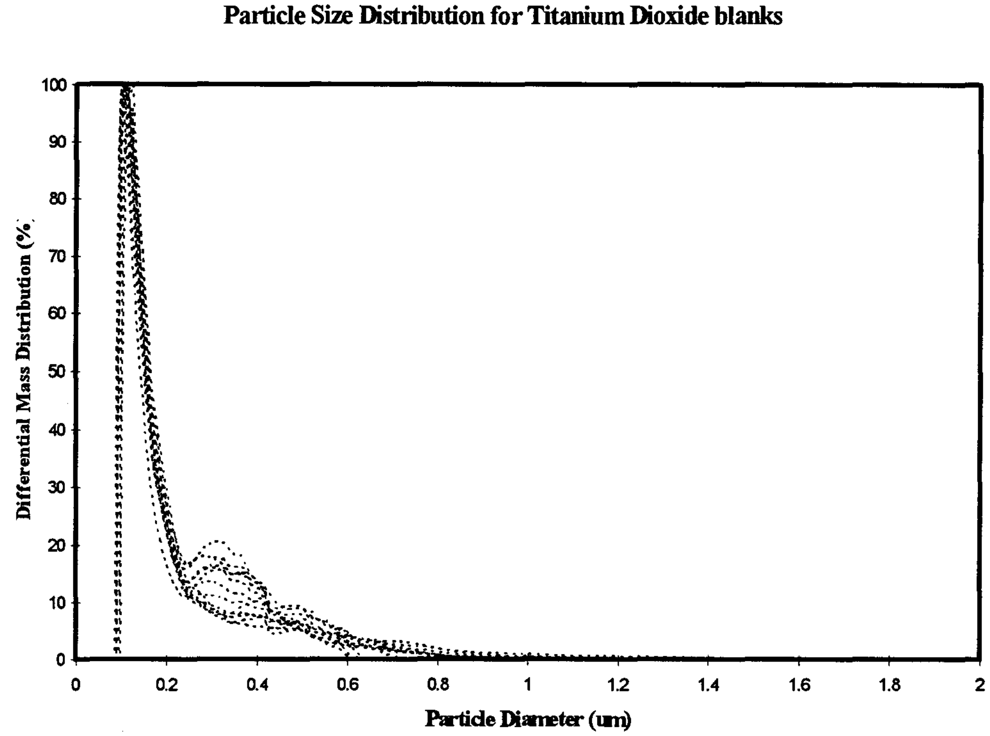

Figure 3.2 Particle size distributions of TiO_2

Figure 3.3 gives an example of the differential mass curve of the flocculated TiO_2 particles for several dosages of graft copolymer run #12. This copolymer was produced at a PAM concentration of 0.2%, a ratio of AM unit : Ce(IV) of 50 and a polymerization temperature of 42.5 ^{0}C. The degree of grafting was the highest of all samples, 38%, and accordingly this sample performed as the best flocculant. The shift of the TiO_2 blank with even a small amount of polymer is clear. That is there is a change in the shape of the distribution, a large increase in the size of the peak representing the larger diameter particles. This indicates that the polymer is flocculating the smaller particles creating larger particles. As the polymer dosage increases the fraction of large particles increases. For copolymer run #12 the largest increase is at a dosage of 6 mg polymer/g of TiO_2. As the dosage increased past this optimum dosage, the size of the particles decreased. The differential mass distribution curves decrease in size, the area of the second peak representing the fraction of large particles decreases. This reduction continues until the flocculation curves begin looking like that of blank.

The reduction of the number of large particles as the polymer dosage increases past an optimum dosage, indicates that the flocculation of the colloidal particles actually decreases. This is referred to as restabilization. The polymer chains have absorbed onto the surface of TiO_2 particle and form a electro-steric barrier that prevents the collision of particles. The particle surface is covered by polymer chains to the extent that there is no free area for a polymer chain that is attached to another particle to form a bridge between the two particles. Thus flocculation is greatly reduced when too much polymer is added. The charge of the polyDADMAC in the graft copolymer may also assist in reducing flocculation. With the adsorption of an excess of the copolymer onto the TiO_2 particle a positive charge barrier repelling the particles may also be formed. Therefore with the addition of excess polymer, flocculation is reduced because of both steric and charge interference.

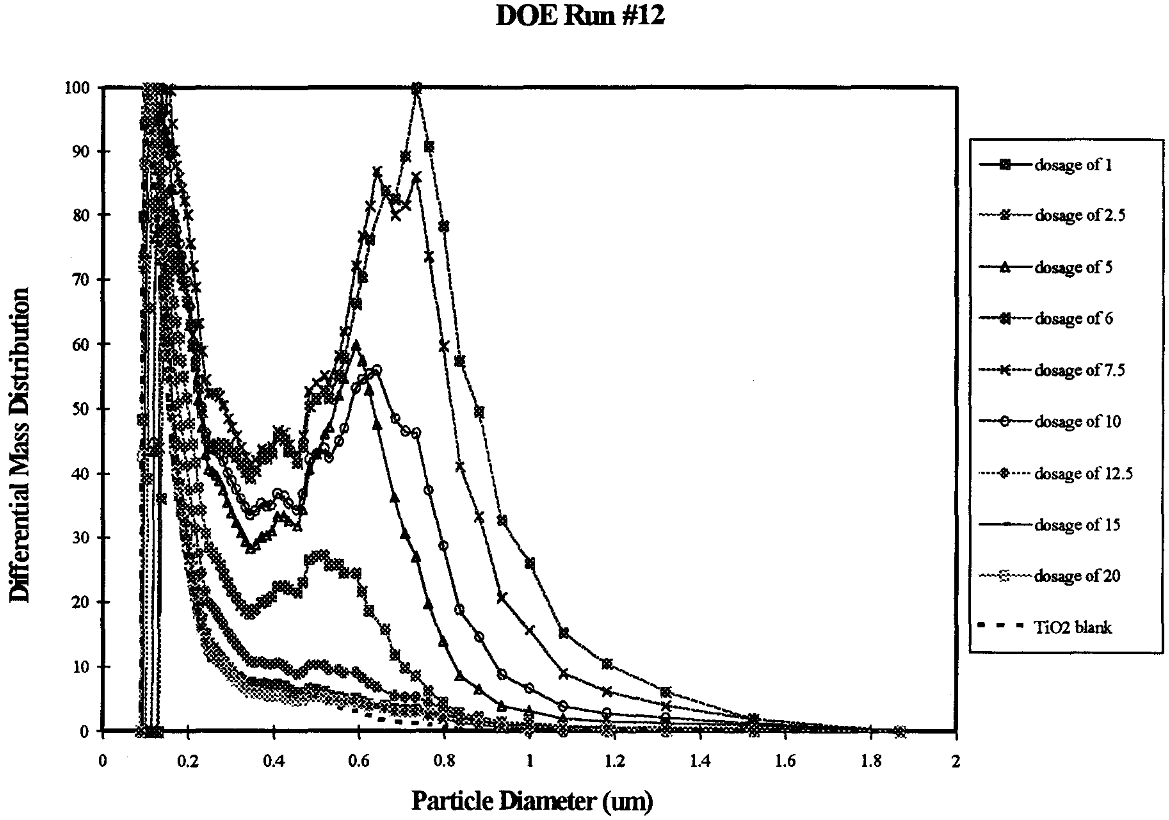

Figure 3.3 **Particle size distributions of TiO_2 flocculated with various polymer dosages of graft copolymer run #12, with degree of grafting of 38%**

These flocculation trends are similar for all of the graft copolymers produced, although the effects are not as drastic. In most cases there is not so great a change in the mass distribution curves. In order to compare the flocculation results for several polymers each mass distribution curve was transformed to a single point, a value defined as the flocculation number. As shown in Figures 3.2 and 3.3, each distribution curve is bimodal, a fraction of small particles and a fraction of large particles. With flocculation, the fraction of large particles increases. This fraction of large particles was found by looking at the cumulative and differential mass distributions in an excel spread sheet. The two curves are separated at the minimum value, and the area of each curve can be calculated using the cumulative distribution. Thus the fraction of large particles can easily be found by subtracting the cumulative distribution value at the minimum point separating the two curves from the final cumulative value as shown in Figure 3.4.

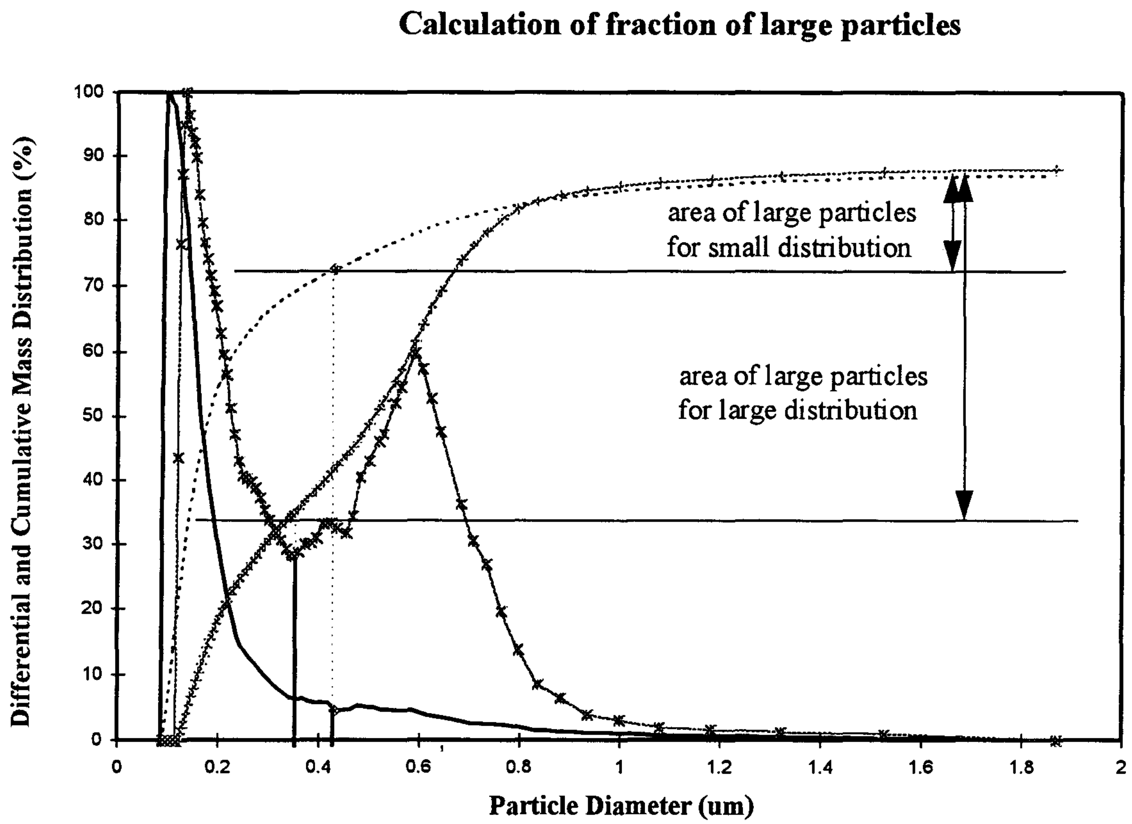
Calculation of fraction of large particles

Figure 3.4 **Differential and cumulative mass distribution of TiO_2 particles and calculation of the fraction of large particles.**

3.3.2 Flocculation Number Results

There is some variation in the TiO_2 blank curves, as was shown in Figure 3.2, thus the fraction of large particles is normalized by the fraction of large particles in the corresponding blank TiO_2 run. This normalization accounts for the growth of particles from the reference distribution, accounting for the variation in colloidal systems.

flocculation number =

$$\frac{\left(\dfrac{\text{final cumulative value} - \text{cumulative at the minimum}}{\text{final cumulative value}}\right)_{polymer}}{\left(\dfrac{\text{final cumulative value} - \text{cumulative at the minimum}}{\text{final cumulative value}}\right)_{TiO_2\ blank}} \tag{3.11}$$

Table 3.1 Flocculation Results for the graft copolymers and reference polymers

Run Number	*Ratio of AM:Ce*	*PAM conc. g/mL*	*Acid conc. mmol/L*	*Temp °C*	*Gel Fraction*	*Adjusted DOG*	*Polymer Dosage*	*Floc Number*
1	24.9	0.40%	1.03	25	69.5%	13.8%	20	5.6
2	75.5	0.40%	1.03	60	2.2%	16.5%	10	2.6
3	25.0	0.70%	1.03	60	47.8%	9.3%	13	2.3
4	75.2	0.70%	1.03	25	20.1%	14.0%	12.5	1.4
5	24.8	0.40%	3.97	60	39.7%	11.0%	20	4.9
6	75.5	0.40%	3.97	25	3.0%	22.8%	10	2.2
7	25.0	0.70%	3.97	25	60.5%	11.8%	15	4.4
8	75.2	0.70%	3.97	60	0.2%	13.6%	12.5	1.5
10	52.1	0.55%	2.54	42.5	13.1%	16.7%	15	2.4
11	50.2	0.55%	2.54	80	38.3%	11.3%	7.5	2.2
12	50.2	0.20%	2.54	42.5	18.4%	38.2%	6	4.4
13	50.3	0.55%	2.57	60	8.5%	9.3%	15	2.4
14	49.4	0.20%	2.57	60	2.1%	28.1%	7.5	2.8
9-PAA	24.6	0.40%	3.98	60	43.3%	24.8%	15	3.9
low MW polyDADMAC					0.0%	100.0%	8	2.9
hi MW polyDADMAC					0.0%	100.0%	6.5	2.1
PC-3					0.0%	50%	6	2.4
Aldrich PAM					0.0%	0.0%	n/a	n/a
PAM Blank					41.7%	0.0%	n/a	n/a

The higher the flocculation number, the greater the degree of flocculation. The flocculation measurements of the graft copolymers and other references are given in Figures 3.5 through 3.9. For each polymer there is a parabolic curve with an optimum flocculation number, at different dosages. On each curve the degree of grafting and the gel fraction are also given. The optimum polymer dosage and the corresponding flocculation number are summarized in Table 3.1. The flocculation results are effected by both the gel fraction and the amount of polyDADMAC.

Figure 3.5 gives the flocculation measurements of the graft copolymers polymerized with a ratio of AM:Ce(IV) of 75, a low value of ceric ion. A flocculation number of 1.0 indicates no flocculation, there is no change in particle size in comparison to the TiO_2 blank solution. Runs number 4 and 8b were both polymerized at a PAM concentration of 0.70%, giving a similar degree of grafting, 14%. The lack of flocculation only means that there was no flocculation within 30 minutes of the addition of polymer, some copolymers take more time for the reconfiguration of the polymer chains. Runs #2 and #6 were polymerized at a PAM concentration of 0.40% and provide more flocculation, although not very great in comparison to some of the other runs. Run # 6 was the run with the highest amount of polyDADMAC not excluding the two runs at a PAM concentration of 0.2%. This copolymer is 22.8 % polyDADMAC by weight, while run #2 is 16.5% polyDADMAC. These two polymers flocculated the colloidal system similarity, as the difference between the two runs is insignificant within the error of the reproducibility of the test.

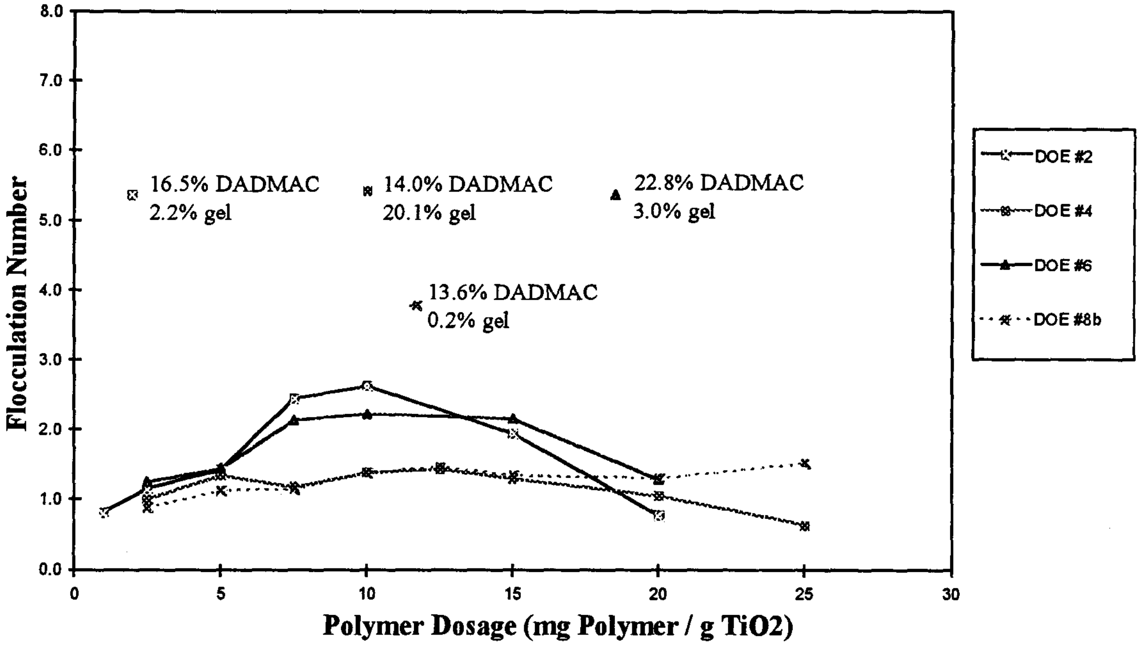

Figure 3.5 Flocculation Measurements for Graft Copolymers with a ratio of AM unit to Ce(IV) of 75

In Figure 3.6 the results for the flocculation of the polymers produced with a ceric ion ratio of 50. In this group run #12 clearly shows its superior performance. With the highest amount of polyDADMAC grafted and the low polymerization concentration of PAM it performs extremely well. Run #14 has the second highest amount of polyDADMAC and the same low polymerization concentration, although it's performance is not as good. Runs #10, #11 and #13 were polymerized at the same conditions except for temperature. Run #10 at 42.5 ^{0}C, #13 at 60 ^{0}C and #11 at 80 ^{0}C. The flocculation numbers are similar for all three runs, with that at 80 ^{0}C being somewhat lower. The difference in the polymer dosages at which the optimum flocculation occurs may be a result of the degree of grafting. Run #10 starts flocculating at a lower dosage and has restabilized the TiO_2 particles before run #13 has started to flocculate. Run #10 has a much higher polyDADMAC content, 16.7%, in comparison to 9.3%, for run #13.

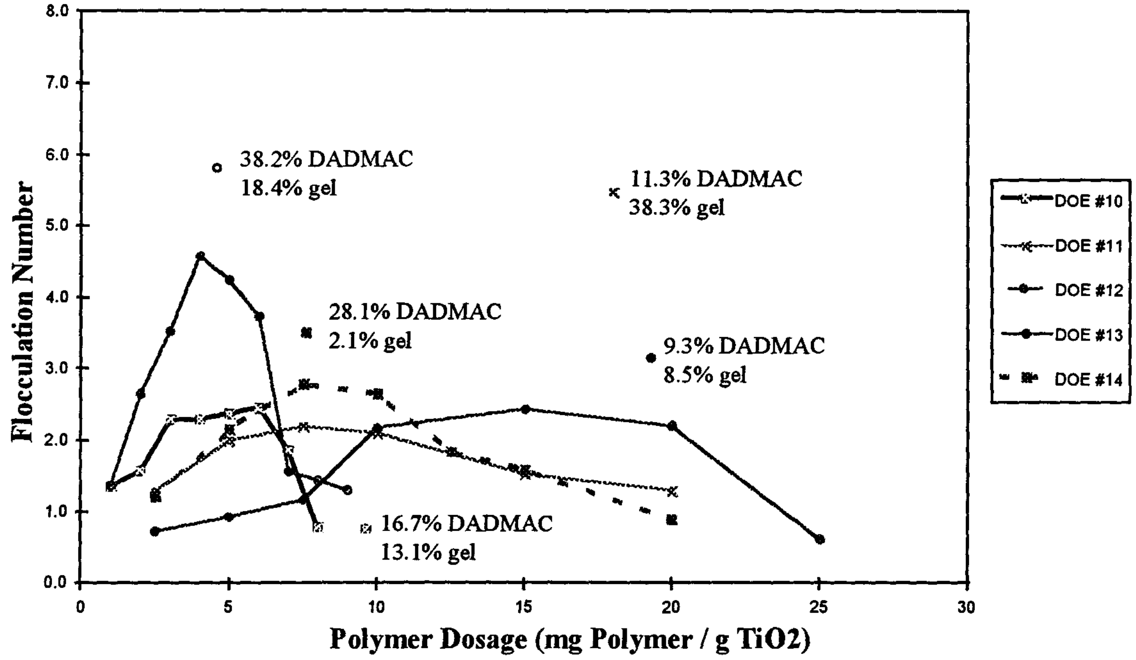

Figure 3.6 **Flocculation Measurements for Graft Copolymers with a ratio of AM unit to Ce(IV) of 50**

In Figure 3.7 the flocculation measurements for the AM to ceric ion ratio of 25 is given. These copolymers were those produced with a high amount of ceric ion and a corresponding high amount of gel. The flocculation numbers are much higher than at the high ceric ion ratio. The range of flocculation is also broader, flocculation occurs at a low dosage and restabilization does not occur until a higher dosage. Runs #3 and #7 were polymerized at 0.7 % PAM concentration, and as in the case of a high ceric ion ratio they were not as good flocculants as those produced at 0.4 %. Runs #5 and #1 were better flocculants. Run #1 with the highest content of polyDADMAC had the highest flocculation number in this group. However the amount of polyDADMAC grafted to the polyacrylamide is only around 10 %, not very much. It is important to note the gel contents in this group are very high. It was proposed that an excessive amount of gel would be detrimental to flocculation, however the results show that gel is necessary for good flocculation.

The gel was found to be only polyacrylamide by NMR, although analysis of gel is difficult. Polyacrylamide is shown in Figure 3.9 not to be an effective flocculant. However at this high content of ceric ion, when a cross linked insoluble polymer is formed there will also be some PAM grafted to PAM, increasing the molecular weight. A soluble network of a microgel has been shown to improve flocculation by trapping the colloidal particles.[10] So although the insoluble polymer gel should not assist in flocculation, the rest of the polymer has been altered to improve flocculation.

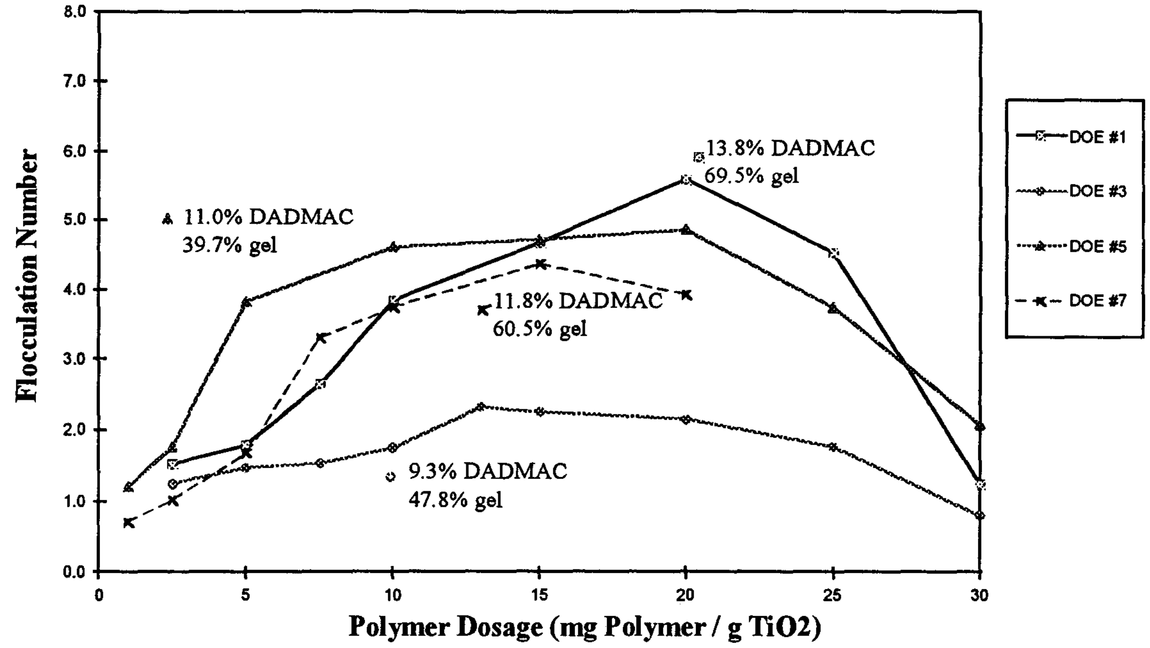

Figure 3.7 Flocculation Measurements for Graft Copolymers with a ratio of AM unit to Ce(IV) of 25

In Figure 3.8 there are flocculation number curves for two different polymers. The top curve is a graft copolymer produced with the backbone polyacrylamide used in all of the other runs. This PAM has a molecular weight of approximately 5 million, with less than 1.5 % acrylic acid groups. In the polymerization of acrylamide some hydrolysis of the amide groups to acrylic acid groups occurs. The other polymer was DADMAC grafted from a polyacrylamide with 10% of the monomer units being acrylic acid. We wanted to see if there would be an increase in grafting with the acid functional group in comparison to the amide group.

In this work we see that the sample made from a polymer with 10% acrylic acid groups has double the amount of grafting. However the molecular weight of this polymer is much lower than that of the original PAM, only 200,000 in comparison to 5,000,000. The effect of viscosity on the diffusion of ceric ion and DADMAC monomer into the polymer matrix is likely the reason for this increase in grafting.

We attempted to use polyacrylic acid in our grafting experiments, but as soon as the DADMAC monomer was added to the polymer solution an insoluble complex was formed. This complex was very stable, it did not degrade upon the addition of excess water or vigorous stirring. The anionic acrylic acid group formed a complex with the cationic quaternary ammonium group on the DADMAC monomer. Therefore polymerization experiments were not done with polyacrylic acid, and we believe that the ceric ion complex is formed with the amide repeat units, not the few acrylic acid groups.

In the flocculation experiments, as shown in Figure 3.8, the polymer produced with the high molecular weight polyacrylamide has superior flocculation properties because of chain length. This polymer is able to bridge the particles better than the shorter backbone of the copolymer produced with a molecular weight of 200,000. Flocculation starts earlier and it takes more polymer to restabilize the TiO_2 particles. So even though there is more than twice as much polyDADMAC in the low molecular weight polymer backbone sample the flocculation is not as great.

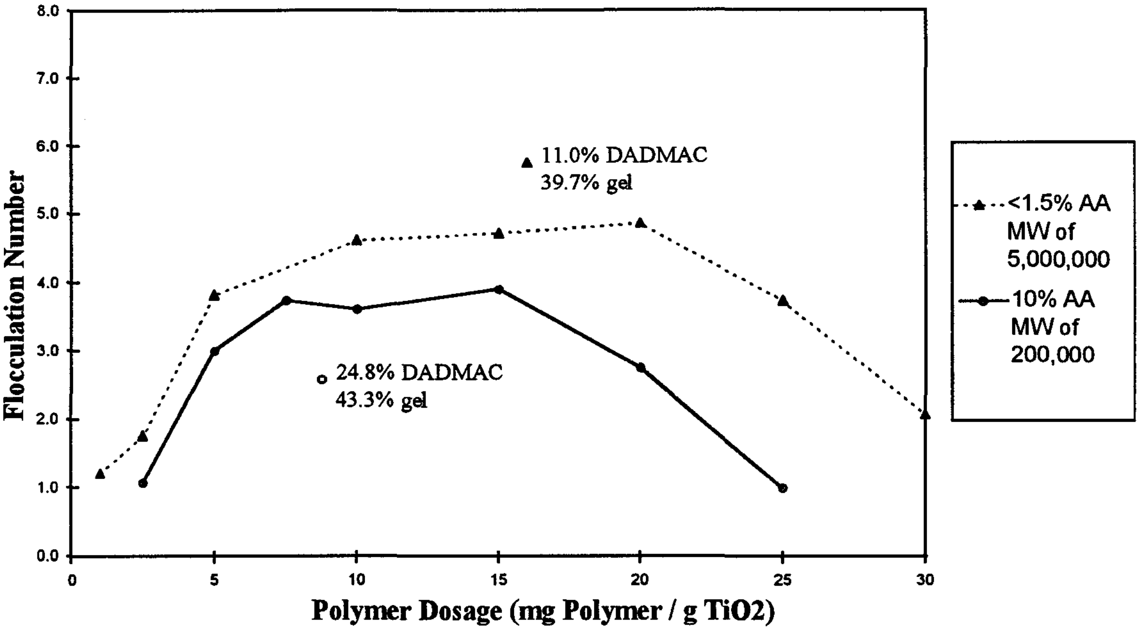

Figure 3.8 **Flocculation Measurements for Graft Copolymers with different polymer backbone**

In Figure 3.9 the flocculation curves of both low and high molecular weight polyDADMAC, the PAM backbone and PAM blank are shown. It is surprising to see that the PAM used as the backbone polymer does not flocculate the colloid system. Usually at such a high molecular weight the nonionic polymer can still bridge the negative particles together, however in this work flocculation is not seen. This behaviour was also seen in the previous study of flocculation of polyacrylamide and polyDADMAC copolymers.[11] The polymer solution was mixed with the TiO2 colloid system for 30 minutes prior to the particle size measurements. Some flocculation was found when the polymer and TiO2 solution mixed for longer periods of time, although the flocculation was still not as good as the performance of the graft copolymers.

The particle size measurements of the PAM blank also show no flocculation. This PAM blank is the same polyacrylamide that has been kept at 60 ^{0}C in the presence of high content of ceric ion and nitric acid. This treatment produced a high content of gel, 42%, and chain scission of the polymer chain as shown by viscosity measurements. As shown in the other flocculation measurements there was improved flocculation with higher gel content, however there is no flocculation with this polymer. The difference is the presence of polyDADMAC. The copolymers with a high gel content also had polyDADMAC grafted to some of the PAM. Therefore although we have assumed that the insoluble gel produced in the graft copolymer is pure polyacrylamide, the remaining copolymer structure must be conducive for flocculation.

There are two flocculation curves for polyDADMAC homopolymer supplied by Nalco Canada. The low molecular weight polymer has a molecular weight of approximately 85,000, while the high molecular weight polymer has a molecular weight of 238,000 found by intrinsic viscosity. The polyDADMAC homopolymers start to flocculate the TiO_2 colloid system at a very low polymer dosage and also stabilize the particles quickly. The flocculation - polymer dosage curves are very sharp for the homopolymer, not broad like most of the copolymers.

The flocculation curve of the random copolymer PC-3 is broader than that of the homopolymers, similar to the curves of the copolymers. The maximum flocculation number is 2.4, not as high as the superior performances by copolymer run # 1, 5, 7. We can see that the flocculation performance of several copolymer samples produced is superior to the random copolymer and pure polyacrylamide and polyDADMAC.

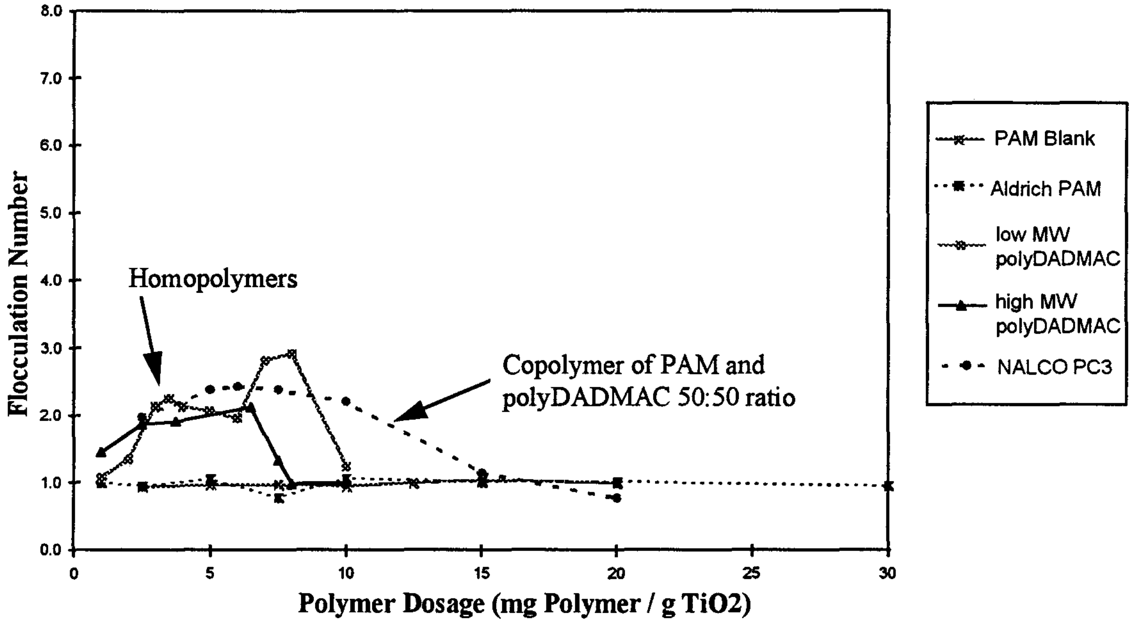

Figure 3.9 Flocculation Measurements of the Reference Polymers

3.3.3 Effect of Gel

The flocculation results have shown that the presence of gel improves the ability of the polymer to flocculate the TiO_2 particles. We have assumed that in the process of the formation of gel the effective molecular weight of the polymer has increased due to crosslinking of several polymer chains. Filtered samples were tested to compare the flocculation results for run # 12 and run #7.

Copolymer run #12 has a high content of cationic charge, 38.2 % polyDADMAC with gel, and 55 % polyDADMAC in the filtered sample, assuming the gel is 100% polyacrylamide. As shown in Figure 3.10 the flocculation curve maximum dropped from 4.4 to 2.6 with the filtered sample. The flocculation curve also broadened. The flocculation curve for run #7 also shows a decrease in flocculation performance for the filtered copolymer.

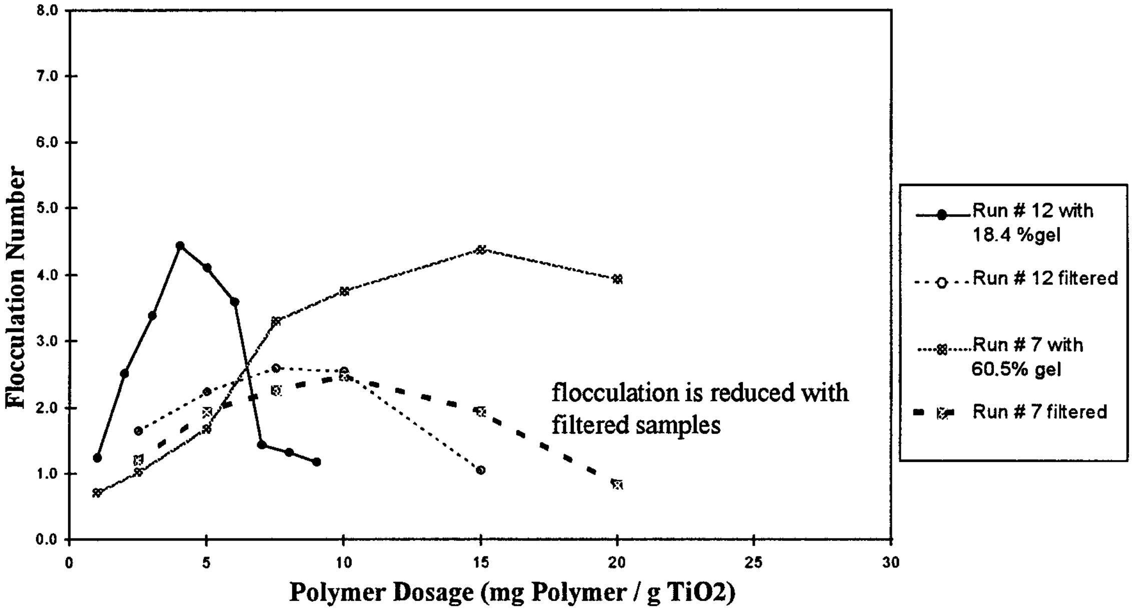

Figure 3.10 Flocculation Measurements of the Filtered Polymers

3.3.4 Statistical Analysis of Flocculation Data

A statistical analysis of the flocculation results, polymer dosage and flocculation number with respect to both gel fraction and adjusted degree of grafting, and the original polymerization factors was done using MODDE software.

Table 3.2 shows the ANOVA results for the statistical analysis of the effect of gel fraction and degree of grafting on the optimum polymer dosage. The regression is significant at a confidence level of 95 %. Runs #11 and #5 were considered replicates by the statistics program as the gel fraction and degree of grafting were within 5% of each other, 39.7 and 38.3 % gel fraction, and 11.0 and 11.3 % by weight polyDADMAC. Even though the performance of these two different polymers was not identical, there is no lack of fit of the model. Although the regression model itself is not good, as shown by the low correlation coefficient. This is also shown in Table 3.3, none of the coefficient values are significant at a 95 % confidence level. Thus we cannot estimate the dosage of polymer at the optimum flocculation point knowing the gel fraction and degree of grafting.

The most significant reason that a model can not be fit to this data, is that the structure of the polymer may be different due to graft polymerization conditions. The polymer configuration was shown to be different in the viscosity measurements. The charge groups may not be arranged the same way, or there may have been significant degradation to the polymer chain.

Table 3.2 ANOVA results for polymer dosage based on the effects of degree of grafting and gel fraction

dosage	*Degree of Freedom*	*Sum of Squares*	*Mean Square*	*F Value*	*Probability*
Total	13	2305	177.3		
Constant	1	2068.9	2068.9		
Total Corrected	12	236.1	19.6		

Regression	2	117.1	58.6	4.926	0.032
Residual	10	118.9	11.8		
Lack of Fit (Model Error)	9	42.9	4.7	0.063	0.997
Pure Error (Replicate Error)	1	76.05	76.05		
	N = 13	Q2 = 0.2374		CondNo = 10.9079	
	DF = 10	R2 = 0.4963		Y-miss = 0	
		R2Adj = 0.3955		RSD = 3.4484	

Table 3.3 Coefficient Data for polymer dosage based on the effects of degree of grafting and gel fraction

dosage	*Coefficient*	*Standard Error.*	*Probability*	*Confidence Interval (±)*
Constant	4.91	4.866	0.337	10.841
degree of grafting	-13.028	6.373	0.068	14.2
gel fraction	2.708	1.96	0.197	4.368

This is also shown in Figures 3.11 and 3.12. The optimum polymer dosage is plotted against the degree of grafting in Figure 3.11. The decrease in the amount of polymer necessary for flocculation when there is an increase in the amount of polyDADMAC grafted to the PAM is clear.

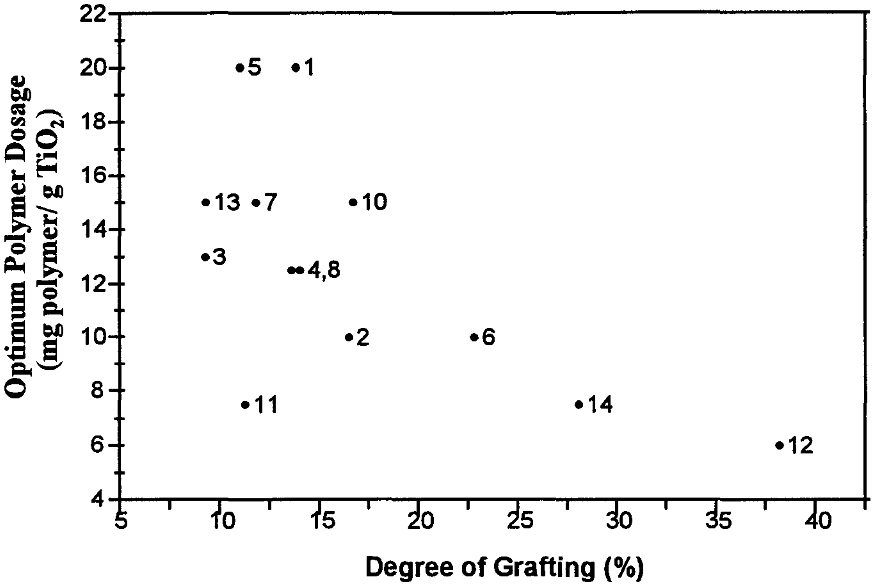

Figure 3.11 Optimum Polymer Dosage plotted against the degree of grafting

The effect of the amount of gel is shown in Figure 3.12. With an increase in gel, the amount of polymer necessary for the optimum flocculation increases, although there is a wide spread in the data. This is why the fit was not significant.

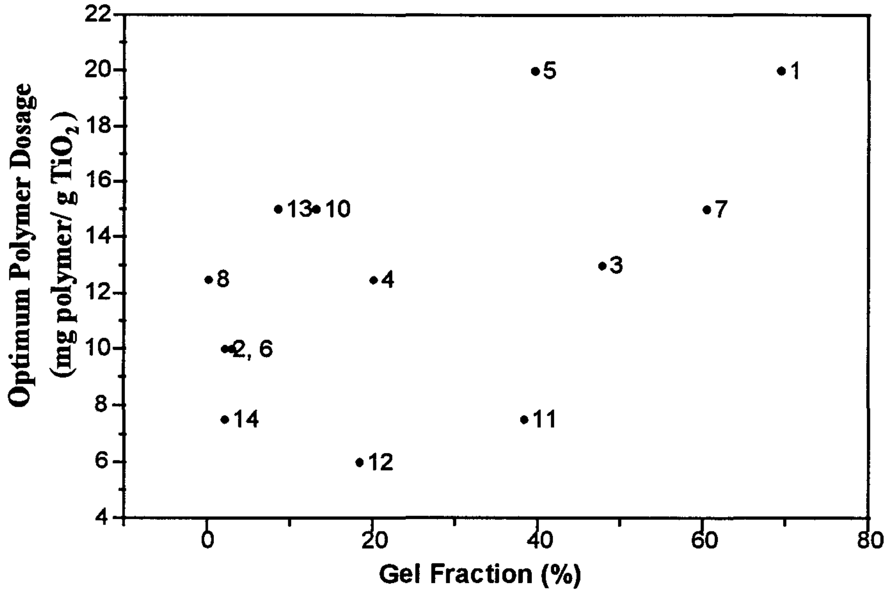

Figure 3.12 Optimum Polymer Dosage plotted against gel fraction

The analysis of variance results for the flocculation number based on the gel fraction and degree of grafting is given in Table 3.4. The regression is significant and there is no lack of fit. The corresponding coefficients are given in Table 3.5. The flocculation number increases with an increase in both the gel fraction and degree of grafting as we saw when analysing the flocculation curves. The statistical analysis is in agreement with our observations.

Table 3.4 ANOVA results for Flocculation Number based on the effects of degree of grafting and gel fraction

flocnum	*Degree of Freedom*	*Sum of Squares*	*Mean Square*	*F Value*	*Probability*
Total	13	139.39	10.722		
Constant	1	117.6	117.601		

Total Corrected	12	21.79	1.82		
Regression	2	13.62	6.8	8.344	0.007
Residual	10	8.164	0.816		
Lack of Fit (Model Error)	9	4.636	0.515	0.146	0.972
Pure Error (Replicate Error)	1	3.528	3.528		
	N = 13	Q2 = 0.4597		CondNo = 10.9079	
	DF = 10	R2 = 0.6253		Y-miss = 0	
		R2Adj = 0.5504		RSD = 0.9036	
				ConfLev= 0.95	

Table 3.5 Coefficient Data for Flocculation Number based on the effects of degree of grafting and gel fraction

flocnum	*Coefficient*	*Standard Error.*	*Probability*	*Confidence Interval (±)*
Constant	6.556	1.275	4.36E-04	2.841
degree of grafting	3.85	1.67	0.044	3.721
gel fraction	2.059	0.514	2.48E-03	1.145

The significance of the effects of degree of grafting and gel fraction are also shown in Figures 3.13 and 3.14. In Figure 3.13 an increase in the flocculation number is shown against an increase in the degree of grafting. Flocculation is improved with an increase in the amount of polyDADMAC grafted from PAM. Two curves could be drawn in this figure, one for the odd numbered runs, #1, 3, 5 and 7 and one for the remaining runs. This splits the data by the amount of ceric ion. Runs #1, 3, 5 and 7, were polymerized at a low ceric ion ratio, and this high amount of ceric ion produced a lot of gel. The curve with the sharper slope, where the degree of grafting is not as much of a factor is the curve of the runs with a lot of gel. Thus the amount of gel is a strong effect.

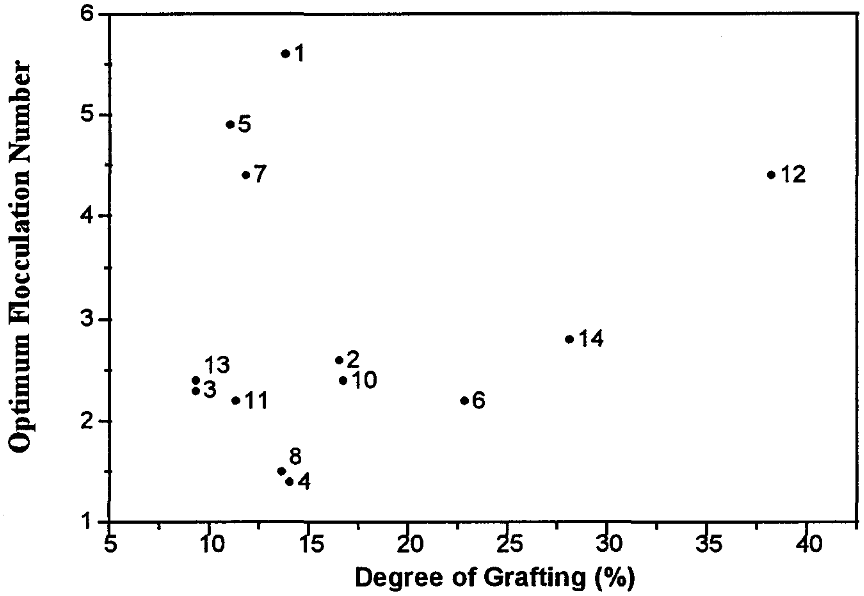

Figure 3.13 Optimum Flocculation Number plotted against the degree of grafting

In Figure 3.14, the effect of gel fraction is shown. An increase in the amount of gel clearly increases the flocculation performance.

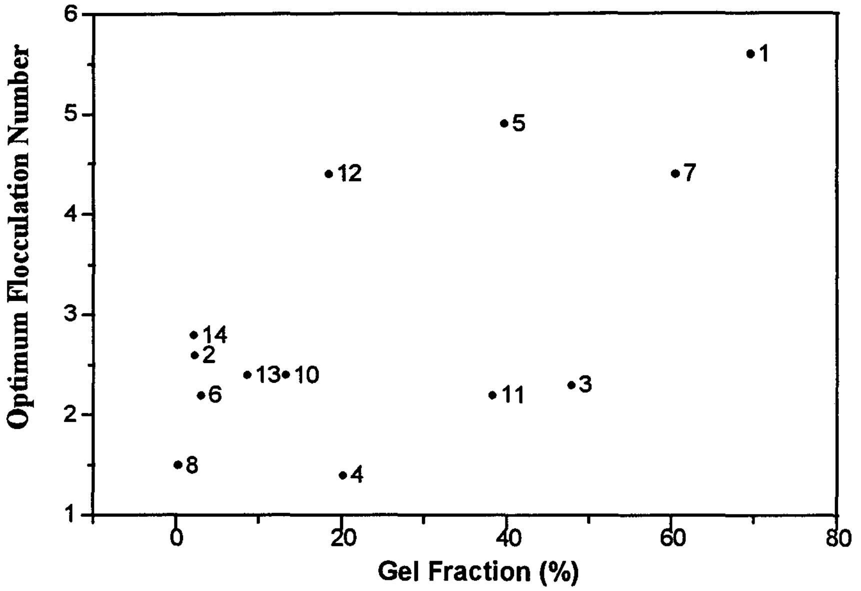

Figure 3.14 Optimum Flocculation Number plotted against gel fraction

In Table 3.6 the analysis of variance results for the regression of the flocculation number with respect to the original polymerization results are shown. The results are as expected, only the ceric ion ratio and PAM concentration effected the gel fraction and degree of grafting, and therefore they were the only significant factors affecting the flocculation number. The regression is a good fit, with a correlation number of 0.65.

Table 3.6 ANOVA results for Flocculation Number based on the effects of PAM concentration and ceric ion ratio

flocnum	*Degree of Freedom*	*Sum of Squares*	*Mean Square*	*F Value*	*Probability*
Total	13	139.39	10.7		
Constant	1	117.601	117.6		
Total Corrected	12	21.789	1.816		
Regression	2	15.45	7.725	12.186	2.08E-03

Residual	10	6.339	0.634	
	N = 13		Q2 = 0.4516	CondNo = 1.624
	DF = 10		R2 = 0.7091	Y-miss = 0
			R2Adj = 0.6509	RSD = 0.7962
				ConfLev= 0.95

As shown in Table 3.7, the coefficient data, an increase in the ratio of AM to ceric ion, causes a decrease in the flocculation number, and an increase in PAM concentration also decreases the flocculating ability of the polymer. Thus a low ratio, indicating a lot of ceric ion will improve flocculation. As shown in Chapter 2, an increase in ceric ion will both increase the amount of gel and decrease the degree of grafting. Hence in the flocculation of the colloidal TiO_2, the amount of ceric ion controlling the gel content is the critical factor affecting the degree of flocculation. In Chapter 2 we found that increase in PAM concentration increased the amount of gel and decreased the amount of polyDADMAC grafted. Because an increase in PAM concentration was found to hinder the flocculation, the effect of PAM concentration is related to the amount of polyDADMAC present.

Table 3.7 Coefficient Data for Flocculation Number based on the effects of PAM concentration and ceric ion ratio

flocnum	*Coefficient*	*Standard Error.*	*Probability*	*Confidence Interval (±)*
Constant	2.845	0.231	2.32E-07	0.515
ratio	-1.177	0.279	1.77E-03	0.622
Pam conc.	-0.487	0.192	0.03	0.428

The effects of PAM concentration and the ratio of ceric ion ratio are shown in Figures 3.15 and 3.16. The increase in PAM concentration causes a decrease in the optimum flocculation number due to a decrease in the amount of polyDADMAC grafted to the PAM backbone.

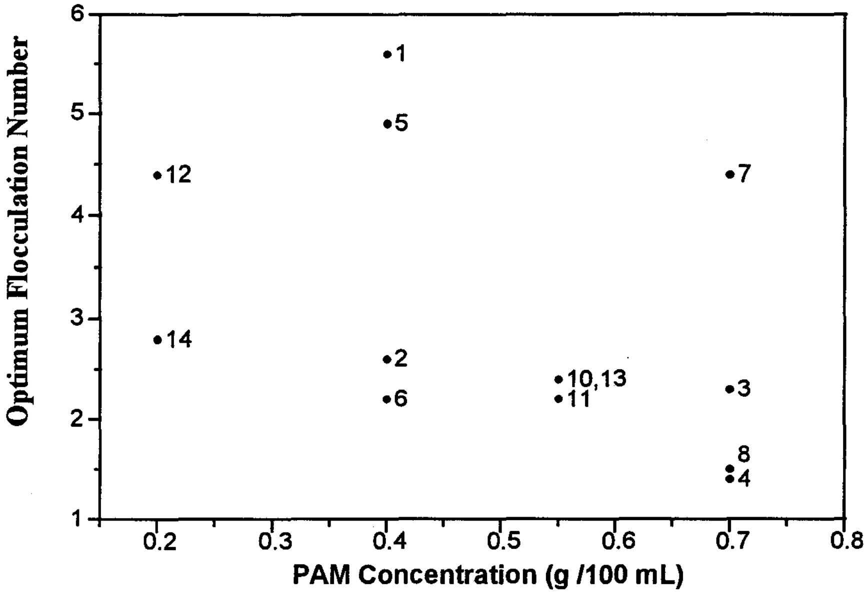

Figure 3.15 Optimum Flocculation Number plotted against PAM concentration

In Figure 3.16, the effect of the ratio of ceric is clear. An increase in the ratio, or a decrease in the amount of ceric ion present decreases the flocculation performance. Thus the presence of gel is very important in these flocculation experiments.

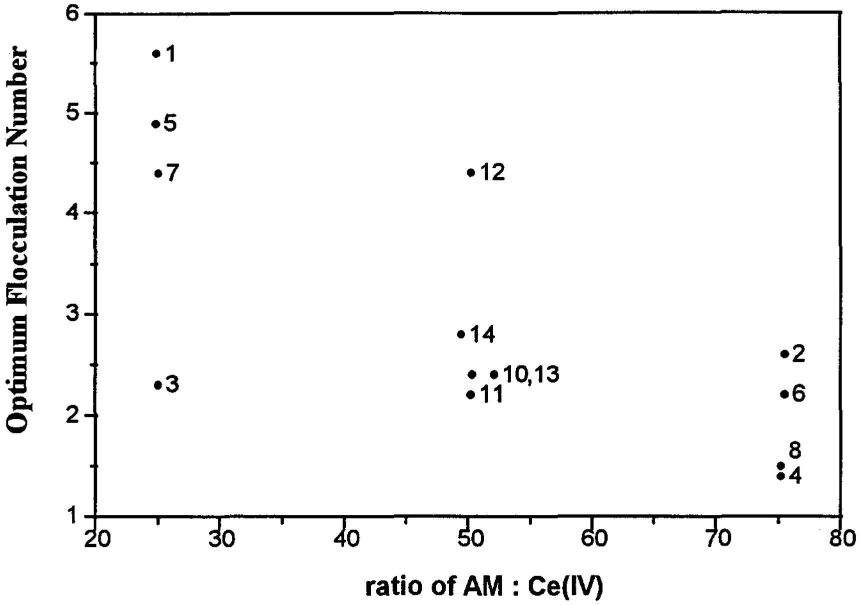

Figure 3.16 Optimum Flocculation Number plotted against the ratio of AM : Ce(IV)

The analysis of variance on the polymer dosage based on the polymerization conditions is given in Table 3.8. There is no significant regression, similar to the polymer dosage based on gel fraction, degree of grafting data. As previously mentioned the configuration of the polymer will also affect the polymer dosage, but as well the lack of accuracy effects this model. The flocculation measurements were done at intervals of polymer dosage ranging from 2 to 5 mg polymer/ g TiO_2, so the actual optimum polymer dosage may not have been found, thus introducing too much error for the regression to overcome. As well the amount of polymer necessary for flocculation is a complicated function of the type of flocculation mechanism. If the polymer is acting in a charge neutralization or electrostatic patch mechanism, the amount of polyDADMAC grafted is very important, however if bridging is dominating the flocculation, the molecular weight, not the amount of charge is important. It is assumed that the flocculation mechanism is a combination of the two, hence the complexity.

Table 3.8 **ANOVA results for polymer dosage based on the effects of PAM concentration and ceric ion ratio**

dosage	*Degree of Freedom*	*Sum of Squares*	*Mean Square*	*F Value*	*Probability*
Total	13	2305	177.31		
Constant	1	2068.9	2068.9		
Total Corrected	12	236.08	19.67		
Regression	2	89.20	44.6	3.037	0.093
Residual	10	146.87	14.69		
	N = 13		Q2 = -0.0469	CondNo = 1.624	
	DF = 10		R2 = 0.3779	Y-miss = 0	
			R2Adj = 0.2534	RSD = 3.8324	
				ConfLev= 0.95	

We cannot see any relationships between the original polymerization conditions and the optimum polymer dosage.

3.4 Conclusions

The flocculation results have shown that the copolymers successfully flocculated the TiO_2 model system. The polymers varied in structure as well as charge density and amount of gel as shown by the variation in flocculation performances. The flocculation curves differed in both optimum polymer dosage and the maximum flocculation number.

The statistical analysis showed that the effect of charge and gel fraction was insignificant on the optimum polymer dosage. However, there was a positive effect for both degree of grafting and gel fraction on the flocculation number, increasing both the amount of charge and amount of gel increases the flocculation number. This was also shown in the flocculation curves.

There is a statistical effect of the original polymerization conditions only on the flocculation number. An increase in ceric ion concentration will produce a lot of gel, increasing the amount of flocculation. An increase in polyacrylamide concentration during the grafting reaction reduces the amount of polyDADMAC grafted and lowers the amount of flocculation.

The graft copolymers had superior performance in flocculating the TiO2 model system in comparison to the reference polymers of polyacrylamide and polyDADMAC. The copolymers also performed better than a commercial random copolymer of polyacrylamide and polyDADMAC with a high molecular weight

The grafting of polyDADMAC from polyacrylamide in a comb structure using ceric ammonium nitrate is successful in producing effect flocculating agents.

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Chapter 4 Test Polymers for Municipal Sludge Dewatering

4.1 Introduction

The purpose of this chapter is to confirm the results obtained in the grafting of polyDADMAC from polyacrylamide, and to test some of the polymers produced in this work for their effectiveness in sludge dewatering. The graft polymers for testing were chosen based on their performance in flocculating the colloidal TiO_2 in the particle size distribution measurements.

4.2 Production of Graft Copolymers

Two fresh batches of graft copolymer samples were produced to optimize the amount of polyDADMAC grafted from the polyacrylamide backbone and confirm the results obtained in Chapters 2 and 3.

4.2.1 Polymer Preparation

These two polymer samples were prepared as described in Chapter 2, although the polymerization took place in 400 mL of solution. The results from Chapter 2 were used to obtain polymerization conditions to optimize both the degree of grafting and gel content. In order to reduce the amount of gel, and obtain the highest amount of grafting, the polymerization took place at 25 ^{0}C, low amount of ceric ion - a ratio of 75, and a low PAM concentration were used. The polymerization conditions are given in Table 4.1.

After 24 hours stirring with a magnetic stirrer, the polymer was precipitated in acetone. Copolymer solutions of 1 wt% were dialyzed for 60 hours in dialysis tubing with a molecular weight cut-off of 12,000. The solutions were then left to evaporate for six days under a rapid air flow. The film of polymer was then placed in a freeze vacuum oven for 24 hours to remove all residual water.

Table 4.1 Polymerization conditions

Sample Number	*Ratio of AM:Ce(IV)*	*PAM conc. g/mL*	*Acid conc. mmol/L*	*Temp ^0C*
1	75	0.40%	2.5	25
2	75	0.20%	2.5	25

4.2.2 Polymer Characterization

The two polymers were produced under similar conditions except for the polymerization concentration of PAM. It was found in Chapter 2 that at a lower PAM concentration the degree of grafting increased.

Gel Fraction and Degree of Grafting

Polymer solutions were filtered and the gel content measured as in Chapter 2. The degree of grafting was measured using the Rank Brothers Charge Analyser. The polymerization conditions were chosen to produce a polymer with a high content of polyDADMAC and a correspondingly low concentration of gel. It was believed that the copolymer produced with a high content of cationic polymer grafted in a comb structure would be an effective flocculant. The results are shown in Table 4.2. The amount of gel is very low as was expected. The predicted values calculated using the models obtained in the regression analysis. The amount of polyDADMAC grafted was much higher than was expected. The model was based on charge titration measurements using the Mutek charge analyzer, while these results were measured with the Rank Brothers charge analyzer. In previous testing the Rank Brothers measurement was higher than those of the Mutek, although not this much higher. This increase in grafting could be due to the stirring during polymerization. This increased the diffusion of both the ceric ion and DADMAC monomer therefore increasing the ability of the monomer to graft to the polyacrylamide.

Table 4.2 Gel Fraction and Charge Titration Results

Sample Number	*Ratio of AM:Ce(IV)*	*PAM conc. g/mL*	*Acid conc. mmol/L*	*Temp ^0C*	*Gel Fraction*	*Degree of Grafting*	*Predicted Gel Fraction*	*Predicted Degree of Grafting*
1	75	0.40%	2.5	25	0.8%	41.7 %	0.76%	20.3%
2	75	0.20%	2.5	25	0.2%	64.8 %	0.0%	23.2%

Viscosity Measurements

Viscosity measurements were made on the two filtered samples in 0.1 M NaCl at 25 ^{0}C as was explained in Chapter 2. The plot is shown in Figure 4.1.

The increase in viscosity with a higher PAM concentration is consistent with the results in Chapter 2. At a low PAM concentration the solution viscosity is decreased and the diffusion of ceric ion is increased. This allows for an increase in the amount of polyDADMAC grafted and chain scission of the polymer chains reducing the viscosity of the copolymer solution.

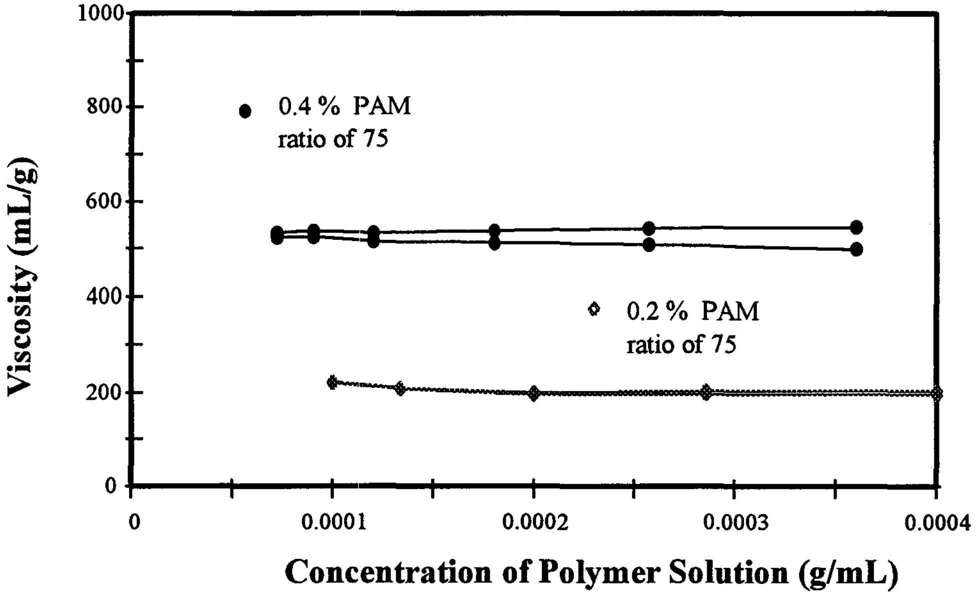

Figure 4.1 **Viscosity Measurements for the samples polymerized at the optimum conditions for grafting**

4.2.3 Flocculation Results

The polymers were tested for flocculation properties of the TiO_2 model suspension using the Brookhaven Disc Centrifuge as in Chapter 3. The flocculation results were not as good as expected (see Figure 4.2). It was believed that the high amount of charge would increase the flocculation results. The flocculation number was not higher than 2 for either polymer, only a doubling in the size of the large fraction. The flocculation - dosage curves are very broad and flat. There is not much of an increase in flocculation number with an increase in polymer dosage.

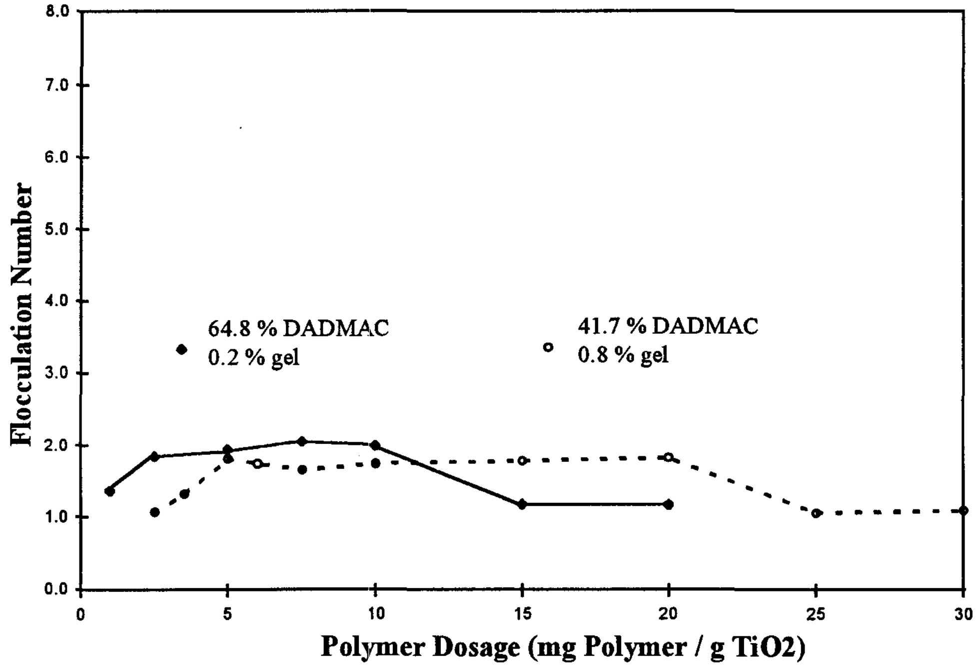

Figure 4.2 **Flocculation measurements for the samples polymerized at the optimum conditions for grafting**

This lack of flocculating ability can be attributed to the lack of gel, which was found to be an indicator of a soluble network, or polymer chains linked together. This increase in effective molecular weight would bridge the particles together. In this case the molecular weight of the polymer is low and the charge is quite high. There is some flocculation but it is not significant in comparison to some of the polymers tested in Chapter 3. The large amount of polyDADMAC is strongly attracted to the negative surface of the TiO_2 particles. This flat configuration would not permit the PAM backbone to bridge the particles.

4.2.4 Summary of Production of Graft Copolymers

Although the new polymers produced were not effective flocculants, the polymerization conditions could be set to obtain predictable results. The grafting of polyDADMAC from PAM is successful and controllable. The comb structure of polyDADMAC grafted onto PAM is not sufficient to effectively flocculate TiO_2 colloidal particles. The polymerization conditions that produce gel also produce polymers of high molecular weight that flocculate the colloidal TiO_2 particles to a greater extent.

This work has shown that it is possible to graft a significant amount of polyDADMAC onto PAM. However, the presence of cationic polymer grafted onto the backbone alone is not enough to produce an effective flocculant. The molecular weight of the polymer must be high enough to bridge the particles together, this is achieved in the presence of gel.

4.3 Sludge Dewatering Testing

Water soluble polymers are used to dewater sludge. Some of the polymers produced in Chapter 2 were tested for their effectiveness as sludge conditioners. Digested sludge was obtained from the city of Burlington Skyway sewage treatment plant.

4.3.1 Introduction

In water treatment the sludge produced contains the solids separated from the waste water concentrated to a level of 1 to 5 % by weight. The sludge from an aerobic digestor contains both organic and inorganic solids with a large variety of particle sizes. There are many methods to separate the solids to a higher concentration including gravity thickening, flotation thickening, and centrifugation.[1] In all cases the separation is improved by conditioning the sludge that thickens the solids into flocs that are strong enough to stand the separation forces.

The objective of sludge conditioning is to alter by physical or chemical means the colloidal properties of the sludge that limit the separation of the water from the particles. Some physical methods include slow freezing and thawing prior to filtration or subjecting the sludge to high levels of heat and pressure.[2] The addition of inorganic materials such as diatomaceous earth or ash can improve the filtration properties, however this also increases the amount of solids to be disposed. Chemical conditioning is more common and involves the addition of inorganic and/or organic chemicals that can alter the surface charge and group the particles into large flocs. Cationic polymers are used due to the net negative charge exhibited by most sewage sludge.

Sludge characteristics are very difficult to control and hence investigating the effectiveness of polyelectrolytes and their interactions with the sludge is very complex. Variation in sludge properties occur even between samples of the same sludge type removed from a given sewage plant at different times. Sludge is also affected by changes in temperature and pH.[3] In this study one sludge sample was used for all of the tests and the test were performed within 6 hours of the sample being taken to prevent degradation of the sludge.

It is important to optimize the addition of chemicals for sludge conditioning from both cost and performance considerations. The relationship between sludge rheology and polymer addition has been used to develop a control system that indicated substantial savings in operational costs.[4,5] In most activated sludge treatment plants, sludge dewatering costs - mostly for polymer - can be the largest part of the plant's operating budget. It is not unusual for an activated sludge plant to require over a half million dollars per year for sludge dewatering chemicals alone.[6] For sludge samples with a solids content less than 1 wt% it was found that the polyelectrolyte dosage for optimal dewatering was independent of the original solids content, but related to the amount of polyelectrolyte required to obtain a zero charge on the anionic colloidal particles in the sludge.[7,8] In a study on biological sludge no relationship between the optimal dosages and electrophoretic mobility was observed. However the electrophoretic mobility is related to surface charge density and not to the total charge, and thus the relationship between dosage and mobility is surface area dependent.[9]

The disposal costs are also reduced with the addition of polyelectrolytes, in a study of polyelectrolyte conditioning of sewage sludge the mean ash content of the presscake was reduced from 50 % to 28 wt%.[10]

4.3.2 Experimental

300 g of sludge was mixed with 50 mL of polymer solution for one minute with gentle stirring using a spatula. The solids content of the sludge measured by oven drying was found to be 2.3 wt% giving a polymer dosage of 0.76 wt% based on solids. The polymer sludge mixture was then poured into the dynamic drainage jar, containing a 40 Mesh screen. The mass of filtrate that passed through the screen into a beaker was monitored and saved in a computer file until the change in weight was found to be sufficiently low.

4.3.3 Results from Sludge Dewatering

The graft copolymers produced using ceric ion were not effective in dewatering this municipal sludge. The only polymer that performed well was the commercial high molecular weight random copolymer from Nalco, PC-3. This polymer has a molecular weight of $2x10^6$, and is much more viscous then the graft copolymers at similar concentrations. The time weight curves are shown in Figure 4.3.

The superior performance of the high molecular weight random copolymer is clear. The dewatering curve for the Nalco polymer, PC-3 is very steep and quickly levels off to a high level. The graft copolymers produced for this thesis do not perform as well for this specific type of sludge. The curves are very similar in shape and height to that of the sludge blanks, samples with no polymer added to the sludge, only 50 mL of water was added to the sludge sample. The difference in performance of the copolymer run #12 is also notable. This is a polymer which performed well in the flocculation of colloidal TiO_2, with a gel fraction of 18.4 wt%, a degree of grafting of 38.2 wt%. This polymer had the highest amount of polyDADMAC grafted in the original set of polymers produced. The dewatering curve shows the slow rate of filtration, with time the mass of filtrate approached that of the sludge blank and other polymers.

The difference in filtrate is also notable. Both the PC-3 sample and run # 12 had very clear filtrates. There was very little particulate in the PC-3 sample, and run #12 had slightly more. The filtrates were placed in polyethylene bottles and allowed to settle. The small amount of particulate in the filtrate of PC-3 and graft copolymer #12 settled immediately, while the other samples remained a black solution over night. After several days the particulate in the remaining solutions also settled, however the volume of black liquid is roughly half of the solution for all samples other than those of run #12 and PC-3, more evidence showing the difference in filtration.

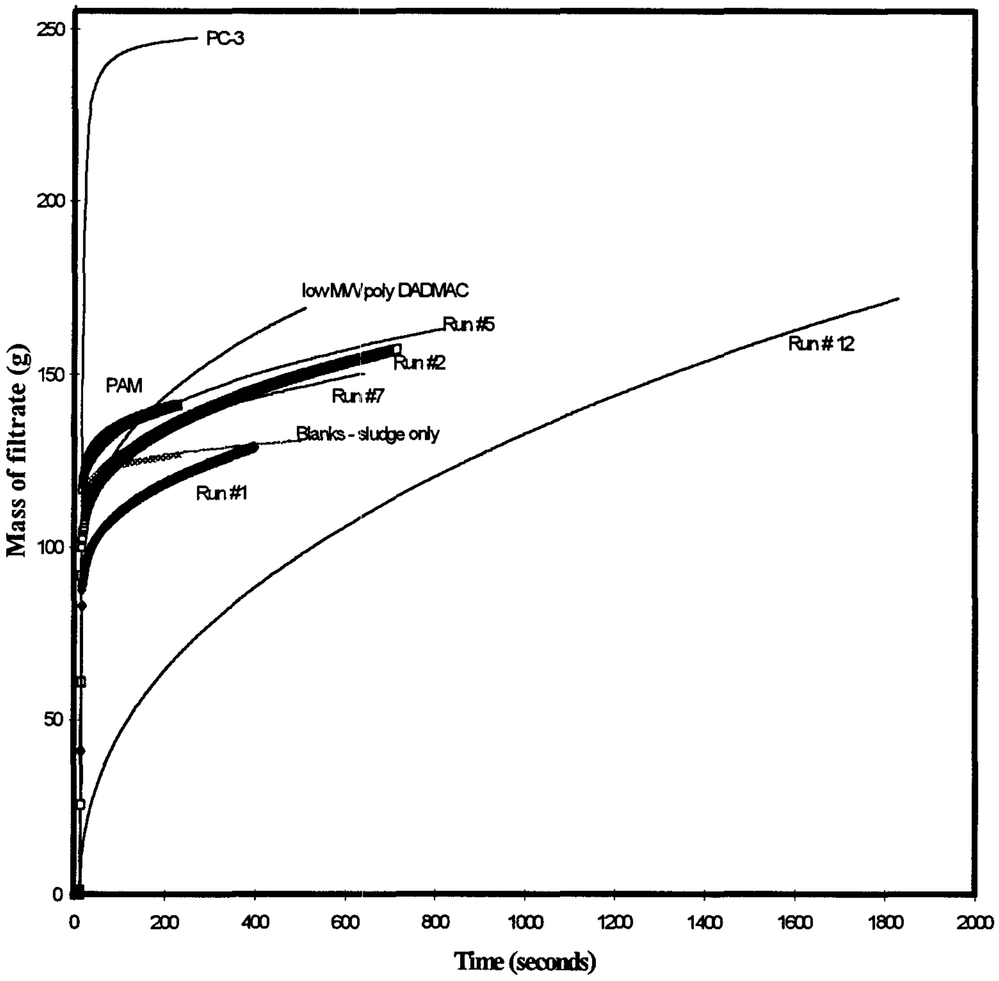

Figure 4.3 Sludge Dewatering Curves for graft copolymers and reference polymers

During filtration the sludge was not stirred thus there was a thick layer of sludge that blocked the filter as shown in the dewatering curves. The curves did not level off because of a slow but steady drip of filtrate passing through the sludge. However with good dewatering this was not a problem as is shown in the curve for the random copolymer, PC-3. Most of the water immediately left the sludge there was little water left in the sludge, that was in the form of large strong flocs. Shear forces have been shown to deteriorate the flocs of sludge causing a increase in polymer dosage necessary to achieve optimum dewatering.[11,12]

In a sludge dewatering study of sewage sludge by Boothe, Flock and Hoover[13], copolymers of DADMAC and Acrylamide similar results were found. Polyacrylamide at all dosages was not effective in dewatering the sludge, and the most effective copolymer was a polymer with a 50:50 ratio of DADMAC to acrylamide. PolyDADMAC performed better than polyacrylamide, but was not as effective as the copolymer, less than 50% of the maximum filtrate volume, with a higher dosage of polymer.

4.3.4 Sludge Dewatering Summary

The copolymers produced using ceric ion to graft the polyDADMAC from the PAM backbone are not effective in dewatering the municipal sludge. The ceric ion forms a radical site that promotes chain scission of the polymer backbone as shown in the viscosity measurements. This degradation of the polymer lowers its effectiveness as a flocculating agent for this particular sludge. The molecular weight of the polymer chain must be high enough to bridge the particles together.

4.4 Conclusions

In this chapter we have shown that the polymerization conditions using ceric ion to graft polyDADMAC from PAM can be set to control the gel fraction and degree of grafting. However we have also found that using the redox agent ceric ammonium nitrate also causes significant chain scission that reduces the effectiveness as the polymers as sludge conditioners, when a high molecular weight polymer is necessary.

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Chapter 5 Conclusions

The purpose of this study was to produce a graft copolymer of acrylamide and DADMAC with a comb structure using a commercially viable method and evaluate it's performance as a flocculant.

5.1 Polymer Synthesis

We used a high molecular weight polyacrylamide as the backbone polymer and a redox agent, ceric ammonium nitrate, to produce a radical site on the polymer. DADMAC monomer polymerized from these radical sites to produce of grafts of cationic charge. The homopolymerization of DADMAC was found not to occur.

We found that increasing the amount of ceric ion, increases the amount of gel produced and decreases the amount of polyDADMAC grafted from the polyacrylamide. The concentration of polyacrylamide also affected the polymerization reaction, increasing the PAM concentration increased the amount of gel produced and decreased the amount of polyDADMAC grafted. The polymerization temperature did not effect the amount of gel produced, however an increase in temperature did decrease the amount of polyDADMAC grafted onto the PAM backbone. A change in the acid concentration did not effect either the amount of gel or polyDADMAC grafted.

5.2 Flocculation Testing

The polymers produced were tested for their flocculating ability using TiO_2 as a model system. The flocculation number, was defined as a measure of the ability of the polymer to increase the number and size of the large particles in the colloidal TiO_2 system. Particle size distribution measurements were made at a range of polymer dosages, to find the flocculation number at optimum polymer dosage.

The backbone polyacrylamide was found to be ineffective in flocculating the colloidal TiO2. The performance of the graft copolymers indicated improved flocculation. Several samples of the graft copolymers had superior flocculation results to that of a high molecular weight random copolymer of acrylamide and DADMAC and polyDADMAC.

There was no statistical significance on the effect of degree of grafting or gel fraction on the polymer dosage, however there was an effect on the flocculation number. An increase in the amount of polyDADMAC in the copolymer was found to increase the flocculation number. The amount of gel also increased the amount of flocculation. The effect of charge confirms our belief that the graft copolymer will be a superior flocculant. The effect of gel fraction is somewhat contradictory, however the presence of gel also indicates the presence of extrememely high molecular weight chains.. This increase in molecular weight improves flocculation.

5.3 Sludge Dewatering

Flocculation testing of the model TiO_2 system shows that the graft copolymers produced using the redox agent, ceric ammonium nitrate, are superior flocculants. In sludge dewatering of a municipal sludge, from the Burlington Skyway sewage treatment plant, the graft copolymers did not show improved performance over a commercial random copolymer.

In sludge dewatering the match of polymer and sludge is critical. Because of the performance of the graft copolymers in flocculating the colloidal TiO2, the copolymers might perform better with sludge from a pulp and paper mill, rather than municipal sludge. Unfortunately, pulp and paper sludge was unavailable.