# Design, Synthesis, Characterization of a new pH-Responsive Copolymer and its Application in Oil Sands Tailings Treatment

by

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# Abstract

This research aims at treating mature fine tailings (MFT) with a novel pH-responsive copolymer poly (N,N-dimethylaminoethyl methacrylate-co-acrylamide-co-acrylic acid) p(DMAEMA-co-AM-co-AA). Compared with conventional polyacrylamide (PAM), the conformation and property of this novel copolymer can be switched by pH variation, enhancing the compaction of settled/flocculated tailings furthermore. The copolymer was synthesized with 16, 20 and 24 hours respectively. The characterization, by mass spectrometry, Fourier Transform Infrared spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR), turbidity and viscosity measurements, of this novel copolymer were conducted. Mechanism of conformational change by pH-switching was proposed.

The flocculation of this copolymer was investigated to determine the optimal dosage. Moreover, the compaction of settled/flocculated tailings was achieved by changing the pH due to the change of conformation. Initial settling rate, supernatant turbidity, solid content, yield stress and water drainage of the sediment were examined to study the optimal condition of pH-responsive flocculant for treating MFT. QCM-D was used to study the adsorption of this copolymer on the silica surface and the copolymer’s conformational change at varied pHs.

# Preface

Some of the research conducted for this thesis forms part of a paper to be submitted. All the experiments were conducted by me with help from Chao Han in Magnetic Resonance (NMR), Lan Liu in Mass Spectrometry (MS), Jeremiah Bryksa in Elemental Analysis and Adriana Brionse in Fourier Transform Infrared spectroscopy (FTIR). The coauthors, Dr. Zifu Li, Dr. Yunhui Li, Professor Zhenghe Xu and Professor Qingxia Liu at the University of Alberta, helped me by discussing and suggesting on my work. The content in chapters 3 and 4 partially comes from the paper I wrote.

# Acknowledgement

I would love to present my sincere thanks and gratitude to Prof. Zhenghe Xu, Prof. Qingxia Liu and Dr. Harbottle for their kind guidance and belief in my project. They helped me find the matching project and taught me all the pertinent knowledge and information. I have to thank Dr. Zifu Li and Dr. Yunhui Li, who Prof. Xu assigned to guide me into this specific area of research and transit from my curriculum study stage to research life. I have worked with both of them and produced a large amount of valuable results.

I also have my gratitude towards Chen Wang, Ian Osborn and Colin Klein for their helpful discussion about tailings flocculation process. Chao Han, Lan Liu, Jeremiah Bryksa and Adriana Brionse have also helped me a lot in the Nuclear Magnetic Resonance (NMR), Mass Spectrometry (MS), Elemental Analysis and Fourier Transform Infrared spectroscopy (FTIR) measurements. Without their assistance, I could not have obtained all the results. Besides, with help from every other individual from the group, I could sincerely feel the kindness and friendship people showed me and I could never forget the help people provided me when I was in need. Moreover, I am very thankful to Mr. James Skwarok, Ms. Jie Ru and Ms. Lisa Carreiro for their diligent work to maintain our great labs and manage my accounts and profiles. I would not have achieved those research accomplishments without their efforts.

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# Chapter 1 Introduction

## 1.1 Fundamentals of oil sands

Oil sands in Canada are a special kind of resource, containing a naturally occurring mixture of sand, water, clay and bitumen, which can be extracted to crude oil. 20% of the bitumen is located within 70 meters from the surface but the majority (80%) is found much deeper underground [1]. Canadian oil sands are mainly located in three deposits, mainly in the Athabasca region, with the rest in Peace River and Cold Lake [2]. Thanks to Alberta's rich heavy oil resources, Canada has a potential to be the contributor with secure supply of crude oil worldwide for over 200 years. Oil sands have helped supply growing global energy needs. Being proven to have 173 billion barrels of oil, which can be recovered economically with current technology, Alberta is the third-largest oil reserve in the world by now [3]. In 2013, about 3.4 million barrels of crude oil, of which 1.9 million from oil sands, are produced daily in Canada. It is expected that 4.8 million barrels from oil sands will be produced daily in 2030 [1].

## 1.2 Oil sands extraction processes

Currently, there are two main industrial processes for bitumen extraction for oil sands: the Steam-Assisted Gravity-Drainage (SAGD) and the Clark Hot Water Extraction (CHWE). CHWE is mostly used as the standard extraction process for open pit mining when the bitumen is not buried deep underground, less than 70 meters. SAGD is the most commonly used in in-situ operations for extracting bitumen 75 meters below the ground surface [4]. There are also some other extraction processes available, such as the Cyclic Steam Stimulation (CSS) used mainly in Cold Lake area [5] [6].

### 1.2.1 SAGD and other extraction processes

Realizing that around 80% of the oil sands resource is located underground in depths that cannot be extracted by open pit mining, Roger Butler and his colleagues at Imperial Oil developed the Steam-Assisted Gravity-Drainage (SAGD) for bitumen recovery in the late 1970s [3]. In SAGD, a pair of wells, with a separation space between each other, runs parallel from the surface into the oil sands formation horizontally as illustrated in Fig. 1.

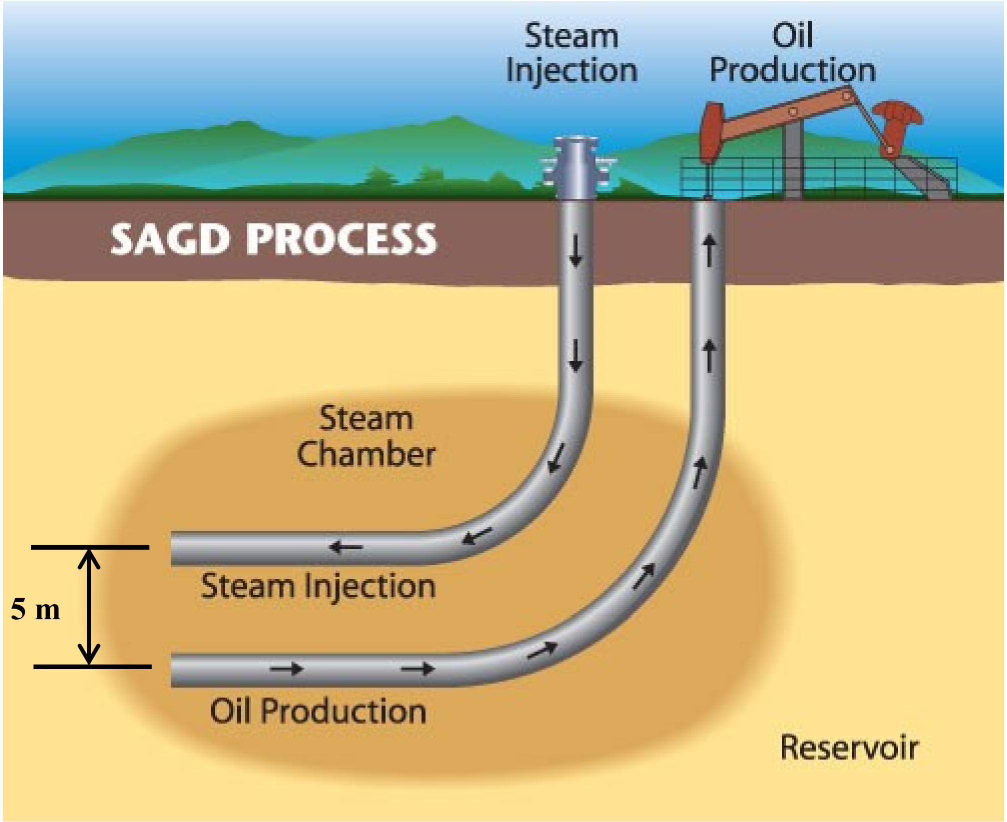

Figure 1 Schematic diagram of SAGD process [7].

Cyclic Steam Stimulation (CSS), Vapour Extraction Process (VAPEX), Toe to Heel Air Injection (THAI) and Supercritical Fluid Extraction (SFE) are also available extraction methods for in-situ oil sands extraction [8] [9].

### 1.2.2 Clark hot water extraction (CHWE)

The Clark Hot Water Extraction (CHWE) was developed and implemented by Dr. Karl Clark with Alberta Research Council in the 1920s. The concept is to mix hot water with open-pit mined oil sands, and the bitumen is able to float with air bubbles to the top of the system [3].

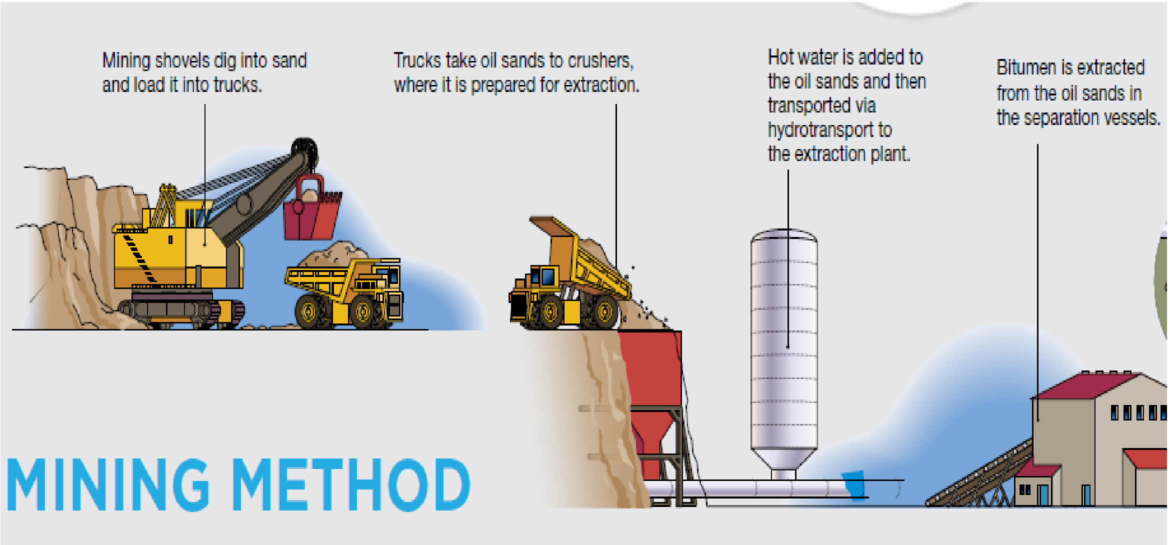

**Figure 2 Schematic flowchart of open-pit mining process [1].**

Fig. 2 shows a typical flowchart of bitumen production from surface mining [1]. Oil sands which are mined using shovels and transported by trucks are crushed into smaller pieces.

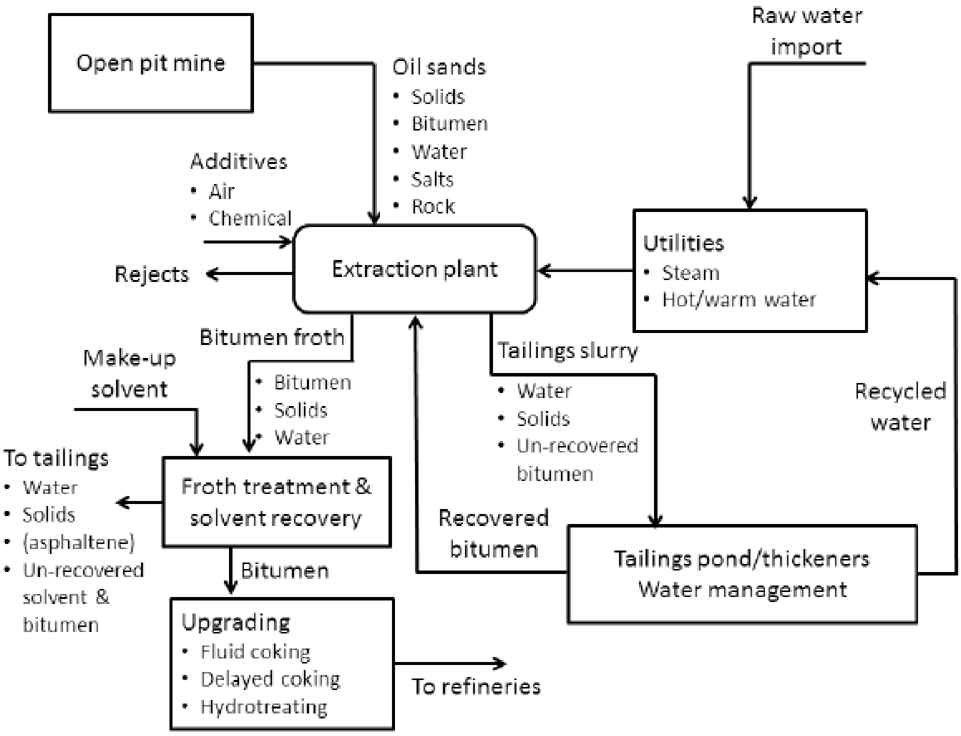

**Figure 3 Hot water bitumen extraction process [3].**

Fig. 3 shows a flow diagram of CHWE process from mining to upgrading. After mining and crushing, water and additives are added into the slurry preparation equipment to reduce the size of the crushed oil sands lumps. Then the oil sands are fed into hydrotransport pipelines with warm recycled process water and air. The slurry at the exit of the pipeline is diluted with water and delivered into gravity separation vessels within the extraction plant. The aerated bitumen aggregates are less dense than the slurry and able to float to the top as froth. The bitumen froth is then sent to the froth treatment plant to remove the solids and residual water, while the heavier solids settle to the bottom as tailings. In some cases, the tailings from gravity separation vessels are reprocessed with middlings to maximize the bitumen productivity [3] [10]. Mostly, the tailings waste goes to tailings pond or thickeners for further water management [3]. As the Clark Hot Water Extraction is an operationally complex and capital intensive process which has been commercially used for 45 years, many other extraction methods based on CHWE are developed for bitumen production [11] [12] [13].

Along with the increased productivity and stimulated economy, the development of oil sands industry is limited by the environmental issues. The greenhouse gas (GHG) emission, the usage of clean water, and the tailings are the three most important environmental concerns to be addressed [1]. A large number of organizations, including the Alberta Environment, the Energy Resources Conservation Board and the Alberta Sustainable Resource Development, have been established to be responsible for various aspects of oil and gas regulation, and to assure the environmental impacts are controlled and the development of oil sands resources is efficient and safe [14] [15].

## 1.3 Current technologies and challenges in tailings treatment

### 1.3.1 Tailings issues

Tailings are by-products of all mining operations. The oil sands tailings slurry is an alkaline aqueous suspension which contains residual bitumen, sands, fine solids and clays [3] [16] [17]. Tailings are discharged and contained in large structures above ground, known as tailings ponds, or in former mine pits awaiting reclamation [18]. The larger sand particles in the tailings settle to form a stable deposit very quickly, while the finer clay particles take years or centuries to settle. These solids remain suspended in the form of sludge, which contains 30% fines and 70% water by total mass. This material is regarded as mature fine tailings (MFT), as illustrated in Fig. 4 [3]. The mean particle size of MFT is around 7 μm. The average solids content of MFT is about 33%. The viscosity of tailings varies from 0 to 5000 cP and it increases with time after it is deposited. MFT shear stress is typically much less than 1 kPa, which is why MFT is fluid-like [19].

There are two major issues on MFT management currently. First, a huge amount of tailings is being produced from open-pit mining process every day.

Approximately 3.3 $m^3$ of tailings sludge is produced from one barrel bitumen. It is estimated that Suncor will have 800 million $m^3$ of fine tailings accumulated by 2033, if the production proceeds as planned. A total area of more than 130 $km^2$ has been occupied for storing tailings. The operation to maintain the tailings ponds costs a large amount of energy and money. The impact on the environment and ecology is also inevitable. Second, as the fresh water intake is limited by strict legislation, the tailings need treatment, by which the tailings ponds can be reclaimed and the water reused. At Canadian Natural Resources, Suncor and Syncrude, the extraction plant receives most of the water from the clarified tailings. However, natural settling is not fast enough for water recycle. Additional physical and chemical treatments are needed to accelerate the settling process [3].

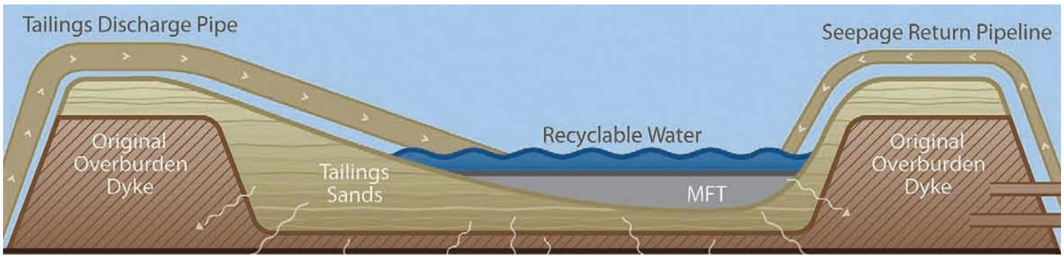

**Figure 4 Schematic diagram of a tailings pond [3].**

Various attempts were made in the past decades to increase the settling velocity of the tailings for efficient water recycling and to compact the tailings sediment, thus reducing volume of tailings ponds [3]. For better understanding and engineering the current tailings treatment technologies, it is beneficial to review the fundamental knowledge in colloidal stability in the next chapter.

### 1.3.2 Physical treatment of oil sands tailings

Several physical tailings treatments are utilized to produce self-supportive dry stackable deposits, which allows for a large amount of warm water recycled for extraction process and immediate land reclamation in mined pit.

Freeze-Thaw process makes the water trapped in tailings form ice crystals in winter. In summer, the water is released from the reticulate ice, leading to a significant reduction in deposit volume. Natural drying makes use of sunlight to evaporate the water in MFT for optimal deposition. In centrifugation, the tailings are sent into a horizontal decanter centrifuge. An enhanced gravity force is applied on the tailings by fast rotation of the centrifuge, which squeezes out the water in the tailings. Filtration is another alternative for tailings treatment. In filtration process, the tailings are forced to flow through interstitial voids of a formed filter cake via pressure or vacuum. The water can flow though the filter cake, while the solids are blocked in the filter [3].

In addition to the physical treatments, there are two main chemical tailings treatments available as well, which are respectively consolidated tailings technology and thickened tailings technology.

### 1.3.3 Consolidated tailings technology (CT)

Treatment of matured fine tailings with calcium sulphate (gypsum) is called consolidated tailings as shown in Fig. 5 [20]. Syncrude and Suncor both have a long-term consolidated fine tailings program which mixes gypsum with tailings to form an inert landfill material. ‘Inert’ means that the material is chemically inactive [21]. The added calcium ions from gypsum destabilize the fine particles in the tailings suspension and lead to a very high settling velocity [22]. However, the recycled water contains a considerable amount of calcium ions which are harmful to the extraction process [23].

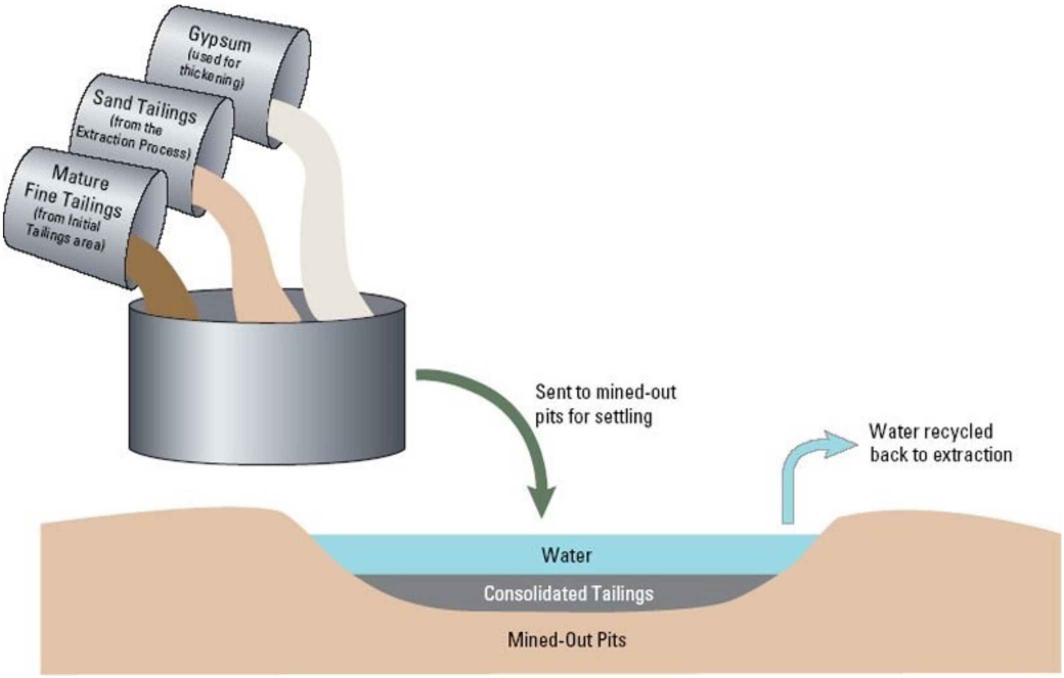

**Figure 5 Schematic diagram of CT technology [20].**

### 1.3.4 Thickened tailings technology (TT)

Some companies, like Albian Sands, use mechanical thickeners to mix tailings with polymer to recover water and heat prior to settling which speeds up the settling process as illustrated in Fig. 6 [18].

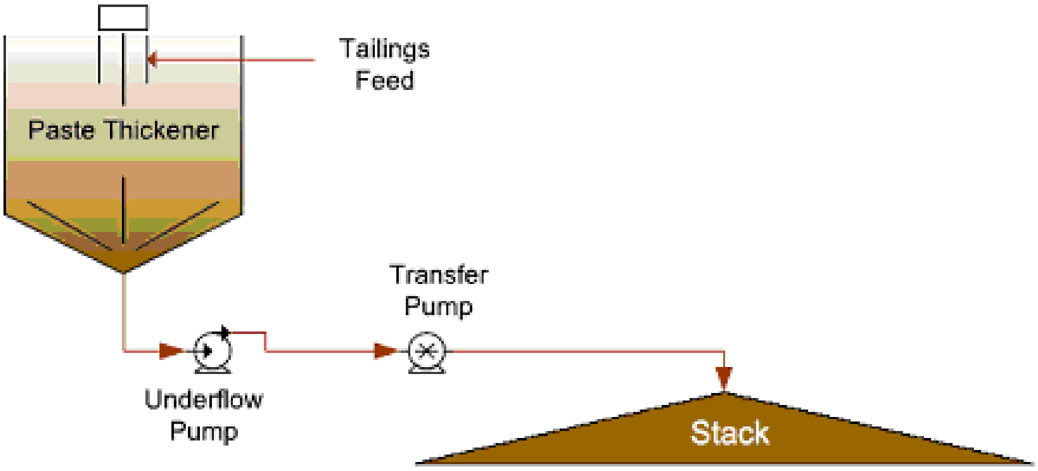

**Figure 6 Schematic diagram of TT technology [24].**

TT technology has been a dramatically step-forward for fresh fluid fine tailings treatment [24] [25]. More energy saving is achieved by more recycled warm water from thickener overflow [26]. Besides, compared with CT using gypsum, polymer flocculants have fewer side effects on the quality and chemistry property of released water for recycle. However, the ability of dewatering, turbidity of supernatant water and stability of the sediments obtained from the polymer flocculants treatment still need improving.

Temperature or pH-responsive polymer flocculants have drawn increased attention for tailings treatment since 1996 [27]. Due to the conformational change of the flocculants with variation in process condition (temperature and pH), the flocs formed after flocculation process can be further compacted, leading to faster water drainage out of the sediment and higher sediment strength. This responsive property makes it possible to control the conformation of flocculant molecules by adjusting the environmental condition. The conformational change of the flocculant molecules can be used to compact the tailings sediment, which is a significant advantage over normal polymer flocculant. For instance, poly(NIPAM), a temperature-responsive polymer, has been utilized to enhance tailings flocculation and compaction. The polymer was added into the tailings at its extended state for flocculation [28]. In this early study, the temperature was increased to the value higher than its lower critical solution temperature (LCST) for compaction. The results show that settling at higher temperature than its LCST results in significantly smaller sediment volume. This observation indicates that the polymer molecules changed from a stretched and extended conformation to a coil-like conformation with increasing temperature. It is the change in conformation of flocculant molecules that induces more compacted flocs, resulting in smaller sediment volume.

### 1.4 Objectives and organization of this thesis

This research is aimed at utilizing a pH-responsive polymer flocculant that switches its conformation when pH in the environment is adjusted accordingly to develop a novel and effective way of tailings treatment by accelerating the settling velocity, maximizing the release water for recycle, and compacting the sediment for reclamation.

Objectives of this work include:

1. Design, preparation and characterization of a pH-responsive copolymer which can provide good flocculation at high pH and compaction at lower pH.

2. Study the pH-responsive mechanism of zwitterionic copolymers in aqueous solution.

3. Explore the flocculation and compaction performance of the synthesized pH-responsive polymer flocculant on tailings.

The thesis comprises of six chapters.

Chapter 1 gives an introduction on background information of oil sands, bitumen extraction processes, oil sands tailings issues and treatment technologies, and available polymer flocculants for current utilization. Chapter 2 presents an overview of the fundamentals of colloid dispersion and surface chemistry, and reviews the literature on pH-responsive polymer flocculants relevant to the present work. Chapter 3 introduces how this pH-responsive copolymer is designed, synthesized and characterized in details. Chapter 4 illustrates the dual pH-responsive mechanism of random zwitterionic copolymer in aqueous solution. Chapter 5 presents the results and discussion on the effect of the pH-responsive polymer flocculant on flocculation and compaction of kaolinite suspensions. Conclusions are drawn in Chapter 6. The future work is recommended in Chapter 7.

# Chapter 2 Literature review on colloidal stability

## 2.1 Basics on colloid dispersion and surface chemistry

It is one of the principal considerations in tailings treatment that most of the colloidal particles in recycled water should be removed so that the bitumen extraction would not be affected by using this recycled water. The water chemistry is a key physicochemical property on extraction process. This removal process needs to be done within a very short time. So it is essential to recall the basic science related to optimizing the physicochemical conditions of the tailings system and have a better understanding of the colloidal behaviors of fine solids in tailings water [3].

### 2.1.1 Electrical double layer

There are various kinds of interactions between particles in a colloidal system. The stability of the colloidal dispersion is influenced by the surface property of particles in clay-aqueous system. A charged colloidal particle in an electrolyte solution is surrounded by ionic cloud which is named electrical double layer to remain a dispersed state [29]. In such a system, the surface with one type of ions attracts the opposite type of ions in the solution, and the electrical double layer contains both types of ions close to the charged surface [30]. Stern et al used the Stern model to describe the profile of electrical potential distribution near the charged surface as shown in Fig. 7 [31] [32].

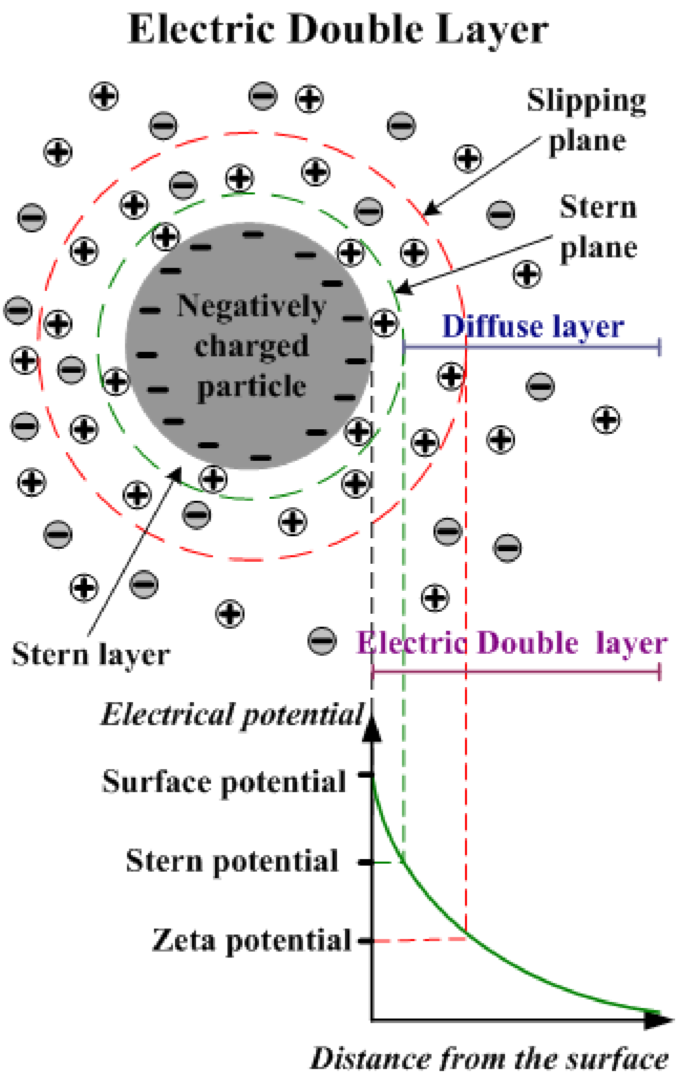

**Figure 7 Schematic illustration of the electrical double layer [31].**

Stern layer is the space between the charged particle surface and the Stern plane. The ions in the Stern layer are believed to be bounded to the particle surface [33]. The potential at the Stern plane is called the Stern potential ($\psi_s$). The slipping plane is deemed to contain the ions and the solution that move around the particle surface, and the potential at the slipping plane is known as the zeta potential ($\zeta$) which depends on the type of electrolytes and their concentrations [32].

As reported, zeta potential for tailings pastes at a water content of 34.4% varied from -28.18 mV to -30.49 mV (tailings paste: pH ≈ 7.5) [34] [35]. It can reach around -40 mV when the pH of tailings water is above 8.0. As the process water for oil sands extraction usually has a pH of 8.2, zeta potential on the surface of the fine particles in tailings paste is so negative that those particles would stabilize due to the high repulsive force to each other and barely settle [36].

### 2.1.2 DLVO theory

DLVO is named after scientists Derjaguin, Landau, Verwey and Overbreek in 1941. The stability of the colloidal system depends on the net interaction resulting from the attraction and repulsion between the particles, as presented in Fig. 8 [3].

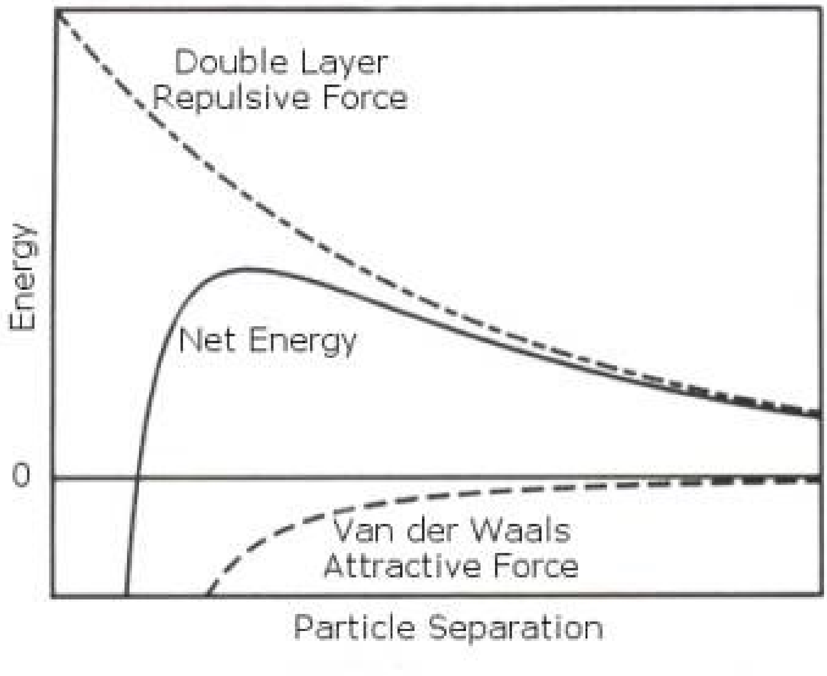

**Figure 8 General illustration of DLVO theory [3].**

If the net interaction between the particles is repulsive, the system is stable. Conversely, if it is attractive, the particles destabilize and agglomerate. Usually in oil sands tailings treatment, compressing the electrical double layer by adding coagulant or flocculant can increase the overall attraction between clay particles, leading to sedimentation of the tailings.

## 2.2 Coagulation and flocculation theory

As mentioned above, the oil sands tailings colloidal system is stable, with dispersed fine solids that cannot settle due to the net repulsive interaction between those charged particles as illustrated in Fig. 9. However, it is feasible that colloidal particles can be removed from dispersions by addition of chemicals [37]. Presently, there are two important ways to settle those colloidal particles, coagulation and flocculation.

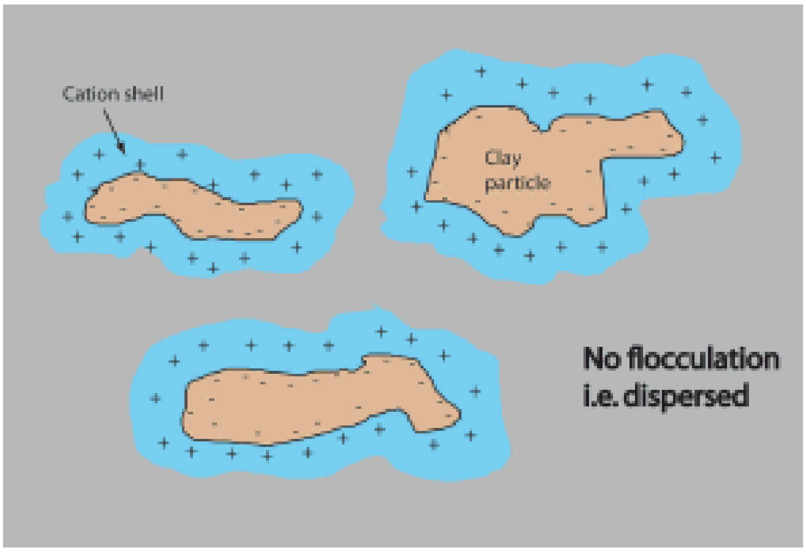

**Figure 9 General illustration of suspended clay particles in tailings water [3].**

In the process of coagulation, the charges on particles are neutralized and reduced by adding inorganic multivalent cations or cationic organic polyelectrolyte known as coagulant. The repulsive forces will be decreased or eliminated when the attractive van der Waals forces outweighs the repulsive forces (see Fig. 10 (a) and (b)). Particles can be therefore brought together and form flocs [38]. The coagulants can be inorganic salts such as aluminum sulphate ($Al(SO_4)_3 \cdot 14H_2O$), potassium alum ($KAl(SO_4)_2 \cdot 12H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), lime (80% Calcium hydroxide), sulfuric acid, fly ash and carbon dioxide [39]. The cationic polyelectrolyte (cationic polymer) can also coagulate particles by charge neutralization. There are varieties of cationic polyelectrolyte available, as has been reviewed in detail [40]. Usually, but not always, they possess quaternary ammonium groups that have a formal positive charge irrespective of pH. As shown in Fig. 10 (b), the cationic polyelectrolyte adsorbs onto the surface of the oppositely charged particles and attracts other particles, which is called ‘electrostatic patch’.

Flocculation process refers to the macroscopic aggregation of suspended particles into loosely packed flocs by addition of polymeric flocculant. Flocculants are usually organic polyelectrolytes [41] [42]. Polymer bridging has been currently the most recognized mechanism to explain the flocculation process of long-chain polymer flocculants since the 1950s [43]. Long-chain polymers adsorbed on particles can have loops and tails extending some way into solution. This gives the possibility of attachment of these dangling polymer segments to other particles, thus bridging particles together. Such a mechanism is considered extremely important in practice. A schematic diagram of particles bridged by adsorbed polymer flocculant is given in Fig. 10 (c). One important thing about the polymer bridging is the optimal dosage. Because there should be sufficient unoccupied surface on a particle so that the segments of polymer chains can have space to get adsorbed on those particles, the adsorbed amount should not be too high to have enough space for bridging. Of course, the adsorbed amount should not be too low as the available segments of polymer chains for bridging will be insufficient. It is usually believed that, in the bridging system, polymers with higher molecular weight have stronger affinity to attach and bridge more particles, forming larger aggregates or flocs [40] [44].

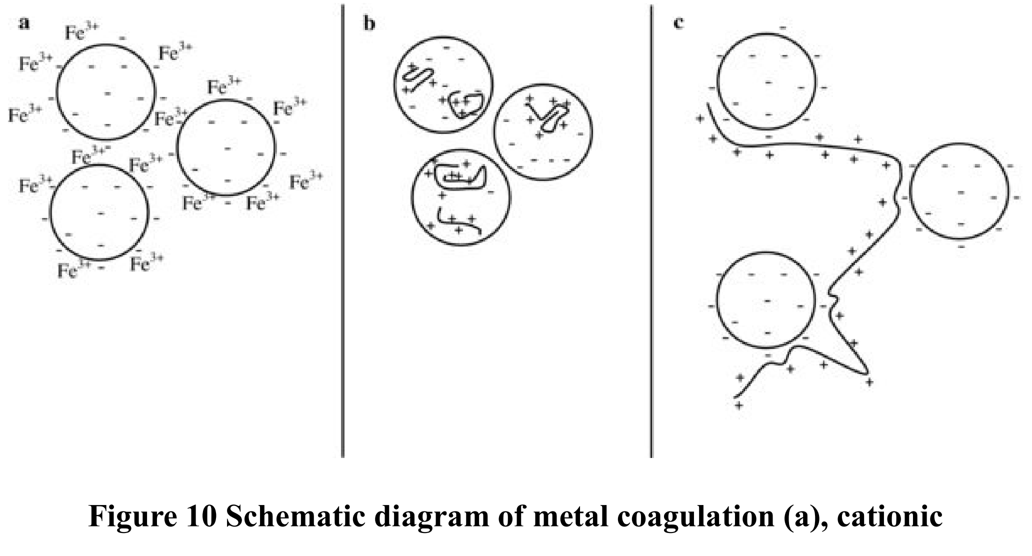

**Figure 10 Schematic diagram of metal coagulation (a), cationic polyelectrolyte coagulation (b) and flocculation (c) [45].**

Cationic polymer with a large molecular weight usually acts as both coagulant and flocculant. The positive charges on the polymer can act as the anchor to reduce the repulsive force between the particles which will form flocs. The long-chain structure of the polymer then makes it possible to stretch out and grab those flocs to become larger fluffy flocs. However, the flocs are loose, porous and easy to segregate.

## 2.3 Temperature and pH-responsive flocculants

As mentioned in Chapter 1, thickened tailings technology utilizing polymeric flocculant for tailings treatment has some limitations, including the sediment of low solids content and turbid supernatant. In order to overcome the limitations of the tailings treatments using traditional polymer flocculant, an innovative method of flocculation resulting in both rapid sedimentation and low sediment moisture was proposed by George V. Franks. It relies on changing the inter-particle forces by controlling a stimulus such as pH or temperature [46]. The novel responsive polymers and copolymers have been brought into this application to realize higher settling rate and better sediment quality in terms of higher strength and lower water content of the sediment [47] [48].

Temperature-responsive polymers have either upper critical solution temperature (UCST) or lower critical solution temperature (LCST), and switch its conformation by either cooling below the UCST or heating above the LCST. The most typical temperature-responsive polymer, PNIPAM, is hydrophilic and soluble in water when the temperature is below its LCST, but exhibits a phase transition with increasing the temperature [49] [50]. PAA and PDMAEMA are typical pH-responsive polymers whose solubility, volume, and chain conformation can be manipulated by changes in pH due to the change of charge on the polymer chains [51] [52]. The temperature and pH-responsive monomers can also be copolymerized together and change its conformation by adjusting both pH and temperature [53] [54]. The molecular weight plays a very important role in stimulus-responsive polymers. Higher molecular weight polymers result in more effective flocculation and sediment compaction, which is the same with normal polymer flocculant such as polyacrylamide [55] [56]. Therefore, it is expected to make the polymeric flocculant with larger molecular weight so that there will be enough segments on the polymer chains for bridging. Based on all these new findings, an innovative methodology for tailings treatment will be proposed and a novel zwitterionic pH-responsive copolymer flocculant will be utilized in this work.

# Chapter 3 Design, synthesis and characterization of the pH-responsive copolymer

## 3.1 Design of the pH-responsive copolymer

As mentioned in the last chapter, though the commercial polyacrylamide based polymers result in relatively rapid settling, they are incompetent in achieving the clear supernatant water, desired sediment properties such as high sediment shear yield stress and fast water drainage from the sediment. In order to obtain both high settling velocity and better sediment quality with high yield stress and low water content after drainage, this work is focused on design and synthesis of a novel zwitterionic pH-responsive copolymer that exhibits two different states of conformation, depending on solution pH. The hypothesis for tailings treatment using this copolymer is that this copolymer can be applied for flocculation and compaction of oil sands tailings separately by switching the solution pH, as proposed in Fig. 11.

It is expected to add the copolymer flocculant at its extended state into the tailings water with large amounts of suspended fine particles. At this point, the long-chain polymer is very well soluble in the water phase and is able to bridge with those particles by adsorption. This process is regarded as flocculation of the fines to achieve rapid settling, followed by collapsed state due to the pH switching from pH a to pH b (which is called compaction), when the fluffy flocs are brought together to produce denser flocs. The formation of more compacted flocs makes more trapped water released from the sediment and increases the strength of the compacted sediment.

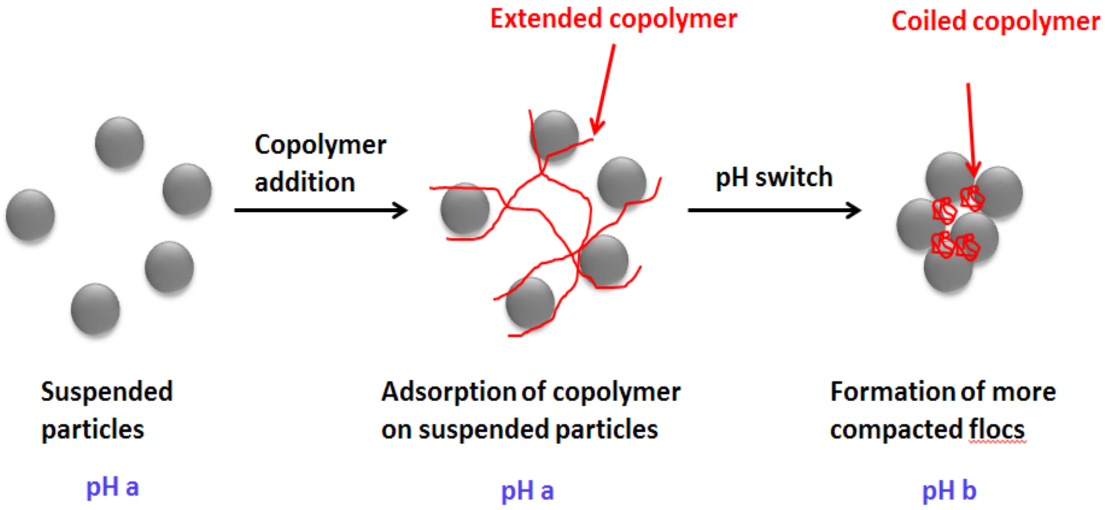

**Figure 11 Scheme of enhancing consolidation of flocs by switching polymer conformation.**

To justify the feasibility of this innovative method, a typical random zwitterionic pH-responsive copolymer, poly(DMAEMA-co-AM-co-AA), was designed to achieve the goal. As the warm water bitumen extraction process is operated in the pH range from 8.5 to 9.0 and $H^+$ can be used to lower tailings water pH from basic to close neutral, the pH-responsive polymer allows us to fine-tune its properties in tailings water, achieving the desired switching functionality. Compared with the temperature-responsive polymer which requires more energy input for conformation control, the pH-responsive polymer is more practical and environmentally safe for this application. As illustrated in Fig. 12, the chemical structure of the zwitterionic pH-responsive copolymer was designed to have three components in total.

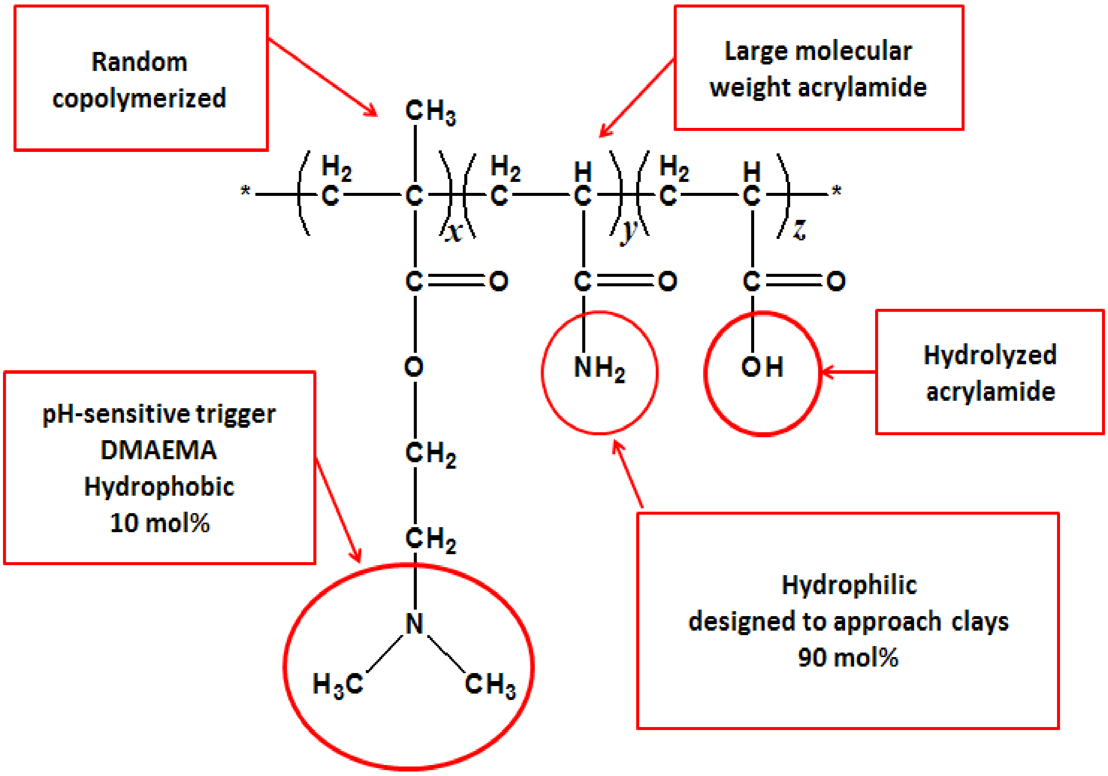

**Figure 12 Design of the chemical structure of poly(DMAEMA-co-AM-co-AA).**

It was recently reported that poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) is a pH-responsive polymer [57] [58]. PDMAEMA contains hydrophobic side chains with tertiary amine groups, which can be protonated in the solution by reacting with $H^+$ to become hydrophilic. So the charge on DMAEMA in solution can be reversibly controlled by pH adjustment. Therefore, DMAEMA was brought into this copolymer as a pH-sensitive trigger. DMAEMA was incorporated with non pH-responsive, large molecular weight polyacrylamide.

The acrylamide segment which was responsible for the water soluble property of the copolymer was introduced to make the copolymer inclined to adsorb onto the fine particles in the tailings water. Plus, acrylamide was desired to have very large molecular weight of the resulting copolymer because of its high propensity to be polymerized in the solution. The third component was acrylic acid, which originated from basic hydrolysis during the synthesis and acted as the pH-sensitive trigger as well. The carboxylic group was deprotonated under alkaline condition. It is expected that whether the pH was higher or lower than the switching pH, the polymer could be extended in water phase due to the existence of charge on either DMAEMA or AA. It could switch to collapsed state when the pH reaches the switching point. The copolymer was obtained by random copolymerization method, which is usually used for producing large molecular weight polymer desired for this application. This synthesis can be performed at room temperature, requiring little energy input, and be easy to scale up.

## 3.2 Synthesis of poly(DMAEMA-co-AM-co-AA)

### 3.2.1 Materials

Acrylamide, N,N-dimethylaminoethyl methacrylate (DMAEMA) (98%), ammonium persulfate (APS) (98%), and N,N,N',N'-tetramethylethylenediamine (TMEDA) were purchased from Sigma-Aldrich. Poly(2-(dimethylamino)ethyl methacrylate) was purchased from Polymer Source Inc. with a molecular weight of 90200 g/mol. Poly(acrylamide–co–acrylic acid), partial sodium salt with 20 wt% of acrylamide was purchased from Aldrich and the molecular weight is 200,000 g/mol. Deuterium oxide ($D_2O$) was purchased from Acros Organics with D-enrichment > 99.75% and nitrogen flushed. Sodium Hydroxide (NaOH) reagent pellets was purchased from Acros. All these materials were used as received without further purification.

### 3.2.2 Synthesis route of poly(DMAEMA–co–AM–co–AA)

As shown in Fig. 13, the desired copolymer was synthesized using solution polymerization technique with ammonium persulphate (APS) as the initiator and tetramethylethylenediamine (TMEDA) as the accelerator. The polymerization proceeded at room temperature based on free radical polymerization mechanism. Two monomers, DMAEMA and acrylamide, were used for this synthesis. Acrylic acid came from the basic hydrolysis during the synthesis. The hydrolysis possibly occurred on acrylamide and DMAEMA units in the polymer during the reaction process [59] [60] [61].

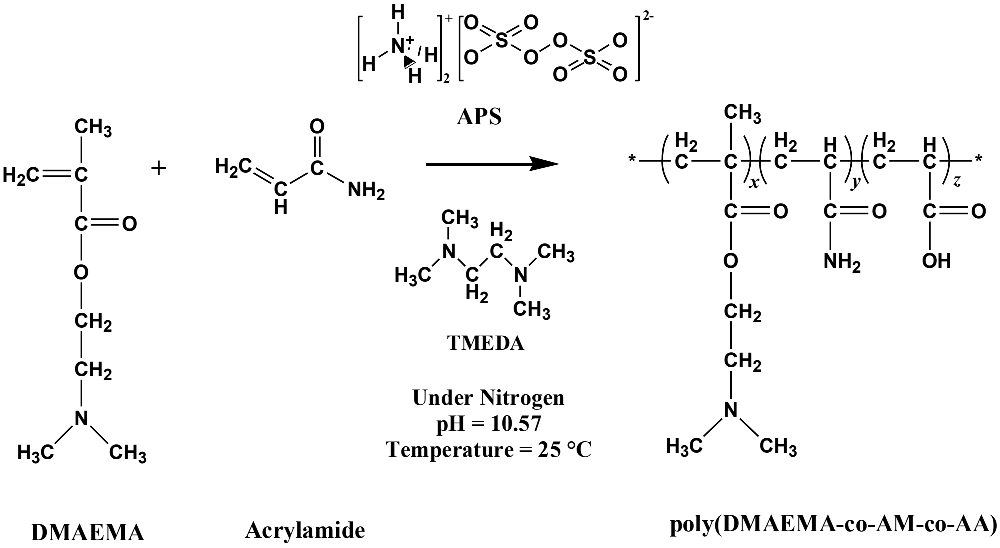

**Figure 13 Synthesis route of poly(DMAEMA-co-AM-co-AA).**

The mixture of DMAEMA (0.0157 mol, 2.4603 g) and acrylamide (0.1409 mol, 10.0116 g) in 100 mL DI water was purged by nitrogen gas for two hours until the oxygen was removed from the reaction system. Then APS (0. 04382 mmol, 0.001 g) and TMEDA (1 μL) were added sequentially by injection into the mixture, and the reaction was conducted under nitrogen atmosphere for 16 hours. Fig. 14 shows the apparatus for synthesis. The polymerization reaction was initiated by APS and accelerated by TMEDA under protection of nitrogen gas. The pH and temperature of the reaction were maintained at 10.6 and 25 °C respectively. The monomer concentration in the solution was controlled to be 1.6 mol/L. The synthesized polymer product was washed with acetone with a volume ratio of 15 (acetone): 1 (polymer solution), then dried in a vacuum oven for 6 hours [62]. The polymer solution used for characterization and application was prepared by dissolving the polymer powder into DI water and shaking for 24 hours. Synthesis of poly(DMAEMA–co–AM–co–AA) for 16 hours was repeated three times to confirm the reproducibility of the synthesis. The copolymers from three different batches all have an average molecular weight of 2.35 million g/mol, measured by Ubbelohde viscometer. The yield was approximately 0.25. The polymer flocculant was used in the form of an aqueous solution of 1000 ppm concentration.

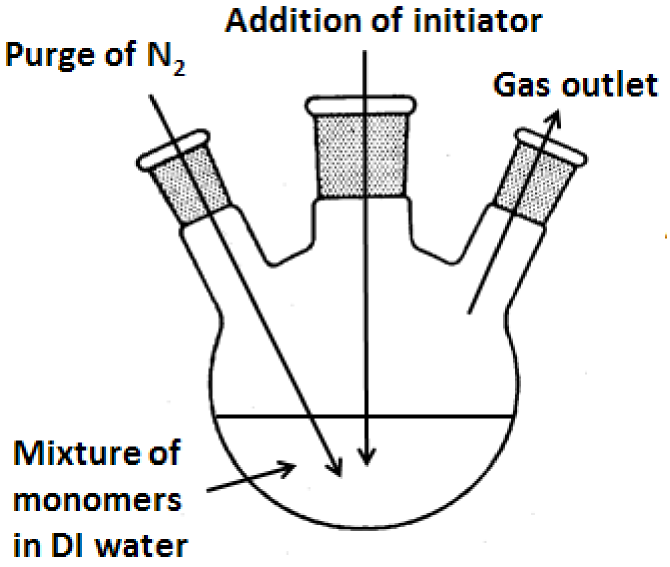

**Figure 14 Apparatus used for polymerization reaction.**

Compared with the atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer polymerization (RAFT), which are mostly used for synthesizing well-defined block copolymers, the random solution copolymerization utilized in this study is more easily conducted. Our objective is to produce the random copolymer, which is easier to scale up if necessary. For the synthesis of zwitterionic block copolymers, the procedure is more complex due to the strict requirement on the reaction environment and the difficulty to remove the catalyst in the final product [63]. In the copolymer synthesized using random copolymerization, the two monomer units are randomly connected to each other, unlike the block copolymer which has two to three blocks of homopolymer chains connecting end-to-end. As the block copolymer is synthesized by obtaining each block separately in sequence, this well-defined structure of the block copolymer makes it more simplified to manipulate the monomer composition as needed, while the random distribution of monomer units in random copolymerized zwitterionic copolymer makes characterization of the copolymer difficult, and led to challenges in understanding the mechanism for its pH-responsive behavior.

## 3.3 Characterization of poly(DMAEMA-co-AM-co-AA)

### 3.3.1 Molecular weight measurement

Viscosity measurement of copolymer poly(DMAEMA–co–AM–co–AA) in water solution was conducted by an Ubbelohde type viscometer at 22°C. The flow time was recorded to an accuracy of ± 0.2 s. Extrapolation procedure from data obtained for 5 concentrations of solutions was used to evaluate [η] from Huggins equation, $\eta_{sp}/c = [\eta] + k_h[\eta]^2c$ ($k_h$ is the Huggins parameter) [64]. The average molecular weight was calculated based on the Mark–Houwink (M–H) equation shown below.

$$[\eta] = KM^{\alpha}$$

The synthesized polymer products from 16 hours reaction was dissolved in DI water to make solutions of 5 different concentrations (1.000 g/L, 0.875 g/L, 0.700 g/L, 0.538 g/L and 0.412 g/L). Before measurement, the flow time of DI water in the viscometer was obtained as the standard baseline. Then the flow time of 5 polymer solutions with different concentrations were measured at pH of 8.7. The relationship between concentration of the polymer solution (x axis) and corresponding $\eta_{sp}/c$ [L/g] (y axis) was plotted as shown in Fig. 15. The intrinsic viscosity $[\eta]$ could be obtained by extrapolation to the y axis. The intercept was $[\eta]$. The average molecular weight could be calculated by using Mark–Houwink equation $[\eta] = KM^{\alpha}$, equaling to $2.35 \times 10^6$ g/mol. In our case, the K value of 0.0063 and the $\alpha$ value of 0.8 was used in calculation of the molecular weight of the copolymer with acrylamide and monomers with amine group [65]. Thus the resulting molecular weight of the synthesized copolymer was an estimated value. Because the copolymer was synthesized by random copolymerization, there was a wide distribution of the molecular weight in this copolymer. So the molecular weight obtained here was just an average number of the wide distribution of molecular weight.

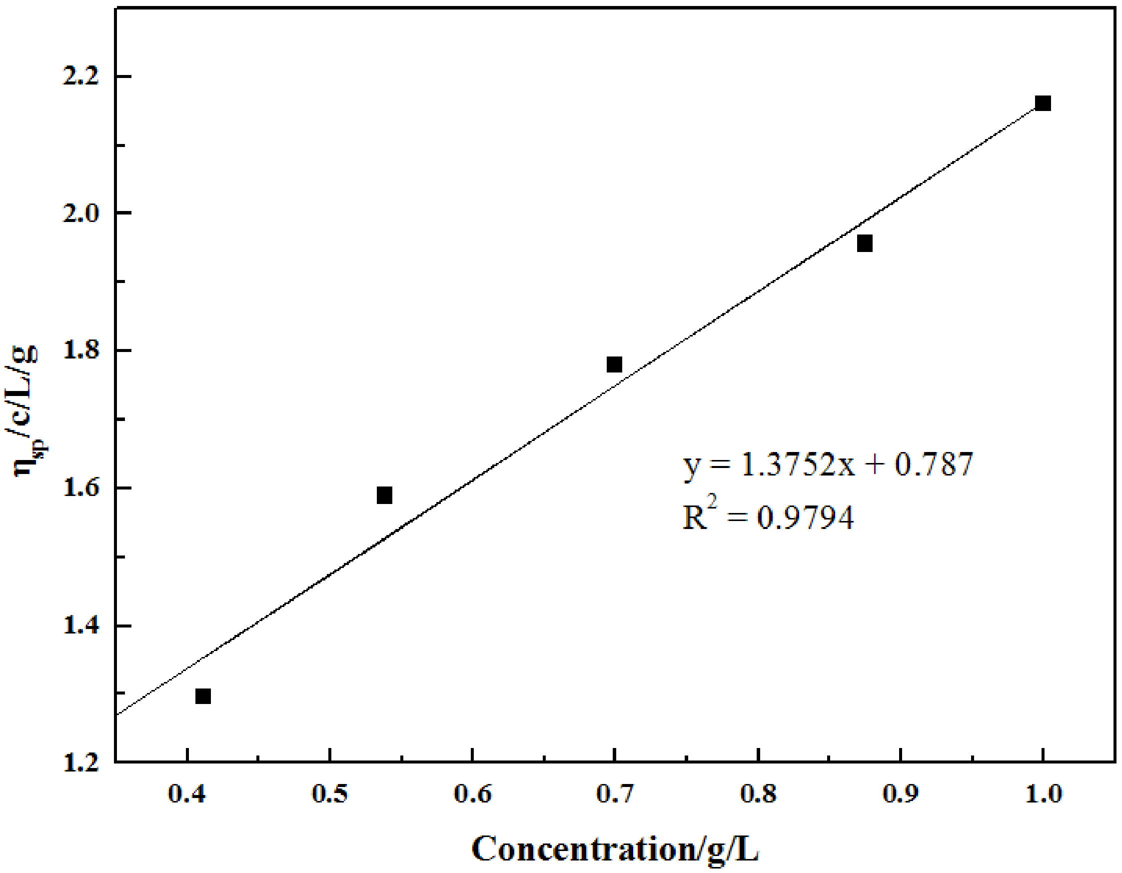

**Figure 15 Plot for calculating intrinsic viscosity [η].**

### 3.3.2 Mass spectrometry

Mass spectrometry was utilized to confirm the existence of acrylic acid in the copolymer. It was performed on a QTrap 4000 mass spectrometer (Applied Biosystems, Foster City, USA) equipped with a Turbo VTM ion source in the negative mode to determine the existence of the negative charged chemical group, anionic acrylic acid in the synthesis system. Before measurement, the polymer solution after synthesis and precipitation was dried out in the vacuum oven for two days until it became solid. A small proportion of the solid was dissolved into methanol. Then the solution was introduced into mass spectrometer by a syringe pump (Harvard Apparatus) at 10μL/min. The mass spectrometer was operated in the negative mode with Q1 MS scan mode (m/z 60 - 1000 Da) at a rate of 1000 $Da\cdot s^{-1}$. In the negative mode, the acrylic acid fractures became ionized and carried negative charge, which can be detected in the electric field. The Data was collected and analyzed by Analyst 1.6 software (Applied Biosystems).

While the polymer solution was sprayed into the instrument, the acrylic acid group became ionized and carried negative charge. However, the acrylamide group with a similar mass to acrylic acid would not be negatively charged. This excluded the influence from the neutral acrylamide with a similar m/z of 71. It is clearly found in Fig. 16 that there is a peak at 71 in the spectrum corresponding to the negatively charged acrylic acid group in the copolymer. Thus, the existence of acrylic acid in the copolymer is determined.

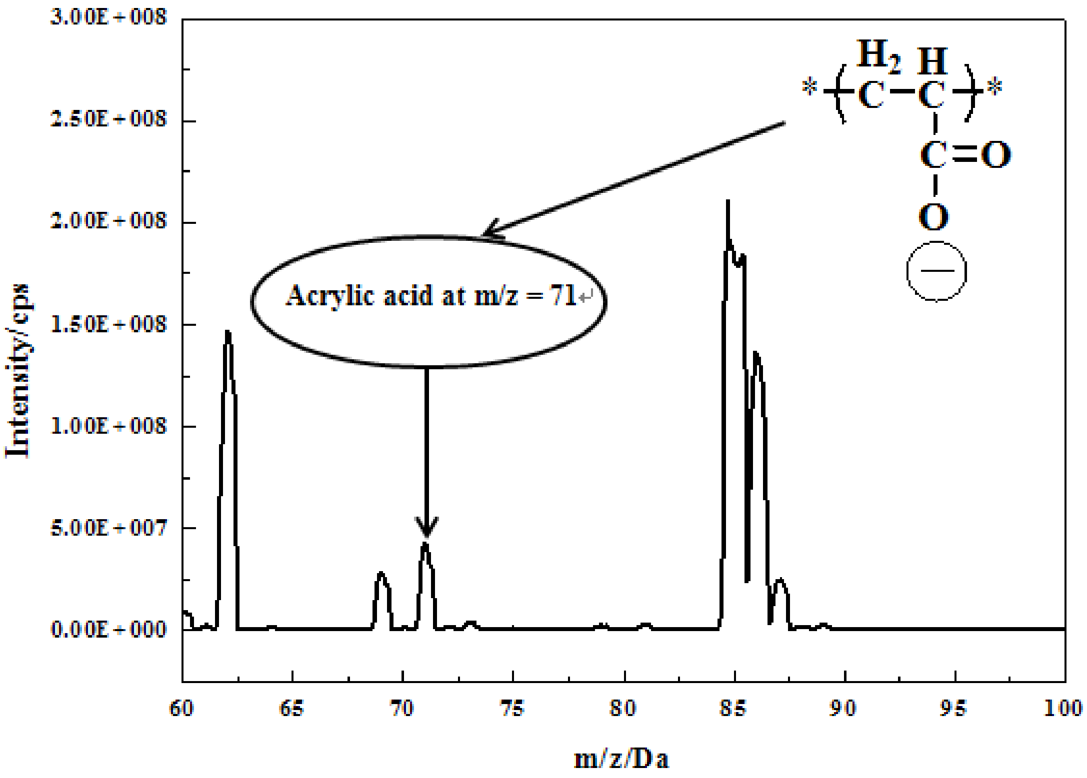

**Figure 16 MS spectrum of synthesized copolymer (16 hours reaction).**

### 3.3.3 Fourier transform infrared spectroscopy (FTIR)

The FTIR further confirmed the presence of both acrylic acid and acrylamide groups in the copolymer. It was used with a diffuse reflectance accessory to run the solid samples. Then the polymer sample was prepared with KBr which were both grinded in a mortar with pestle for 3 minutes. A mixture of 0.02 g KBr and 1.5 mg polymer powder was used for each test. After the center burst signal was checked (The reading should be 4 - 8 volts for KBr only), the background was also checked using KBr. Then the polymer sample with KBr was examined. Within the range from 500 to 4000 cm$^{-1}$, the peaks corresponding to the stretching and vibration of hydroxide, carbonyl and amide groups can be observed in the spectrum.

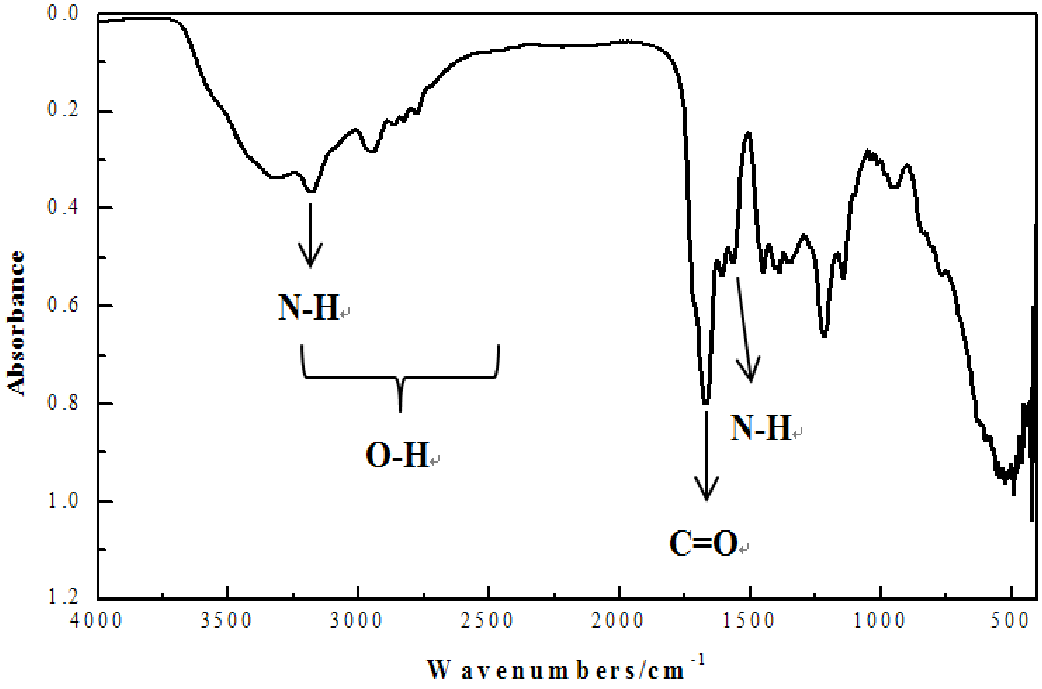

**Figure 17 FTIR spectrum of poly(DMAEMA-co-AM-co-AA).**

As shown in Fig. 17, the very typical wide peak at from 2500 to 3300 cm$^{-1}$ in the spectrum corresponds to the stretching of hydroxide group in acrylic acid. The peak for stretching carbonyl group in acrylic acid is found at 1700 cm$^{-1}$. As for the acrylamide, the two peaks respectively corresponding to the stretching and bending of amide group in acrylamide are found at 3300 and 1600 cm$^{-1}$.

### 3.3.4 Nuclear Magnetic Resonance (NMR)

The existence of DMAEMA was verified by 1H NMR. The spectrum was obtained with an Agilent/Varian 500 MHz spectrometer using $D_2O$ as solvent. The NMR tube for the measurement was 5 mm in diameter and 15 cm long. Before the test, the NMR tube was washed by DI water and acetone for 6 times. Around 10 mg polymer powder was put into the tube, and 0.5 mL $D_2O$ solvent was injected to dissolve the polymer powder. The tube was then placed in the magnet entry port. The spectrum showed the peaks corresponding to the hydrogen atoms at different positions in the polymer and their intensity.

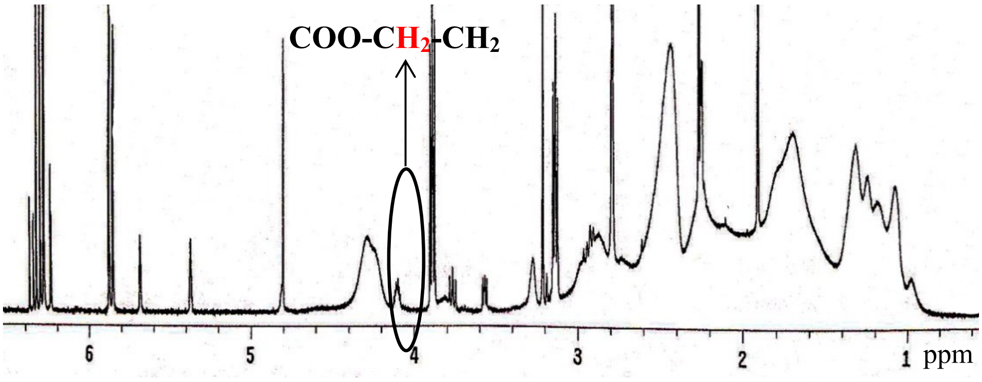

**Figure 18 NMR spectrum of poly(DMAEMA-co-AM-co-AA).**

As shown in Fig. 18, as DMAEMA has a typical methylene proton neighboring to the ester bond, there is a peak attributable to this specific proton which is located at 4.1 ppm in the NMR spectrum. As all the other hydrogen atoms in the copolymer lie in the range from 1 - 3 ppm, the NMR spectrum does not allow for confirmation of other chemical groups in the copolymer. Together these three different characterizations clearly indicate that poly(DMAEMA-co-AM-co-AA), as seen in figure 13, has been successfully prepared.

### 3.3.5 Solution property of poly(DMAEMA-co-AM-co-AA)

The copolymer synthesized for 16 hours shows a turbidity transition from low to very high in the aqueous solution at various pHs. Turbidity of the polymer solution for the titration experiments was measured using a Micro100 Laboratory Turbidimeter from HF Scientific. The polymer solution was obtained by dissolving the polymer powder into DI water one day before use. The sample of polymer solution (10 mL) was stirred by a magnetic stirrer, and small aliquots of 0.01 M HCl solution was added by a microsyringe. An electrode immersed in the solution was used to determine the pH value at which the turbidity changed. Values were recorded when the measurements were performed at least twice and were reproducible.

The pH of the original polymer aqueous solution is around pH=8.7. As shown in Fig. 19, at higher or lower pH, the turbidity of the solution is low and the solution is clear. The turbidity of the polymer solution increases sharply when the pH of the solution goes towards the medium switching pH by titration, until the turbidity reaches the maximum value. The pH where the turbidity of the solution starts to get cloudy is named higher critical solution pH (HCSpH) if the pH changes from basic condition and lower critical solution pH (LCSpH) if the pH changes from the acidic condition. These two terms are similar to upper critical solution temperature (UCST) and lower critical solution temperature (LCST) in thermal-responsive polymer, which are the temperature when the polymer solution becomes cloudy. The result shows a dual sharp transition from two sides in the state of the copolymer from highly extended to collapsed state over a very narrow pH range. Both acid and base titrations were conducted to confirm that the dual switching was reversible.

The pH-switching property of the copolymer from three different batches is quite identical to each other. Therefore, the switching pH as well as the LSCpH and HSCpH of the copolymer from 16 hours reaction time are confirmed to accurate.

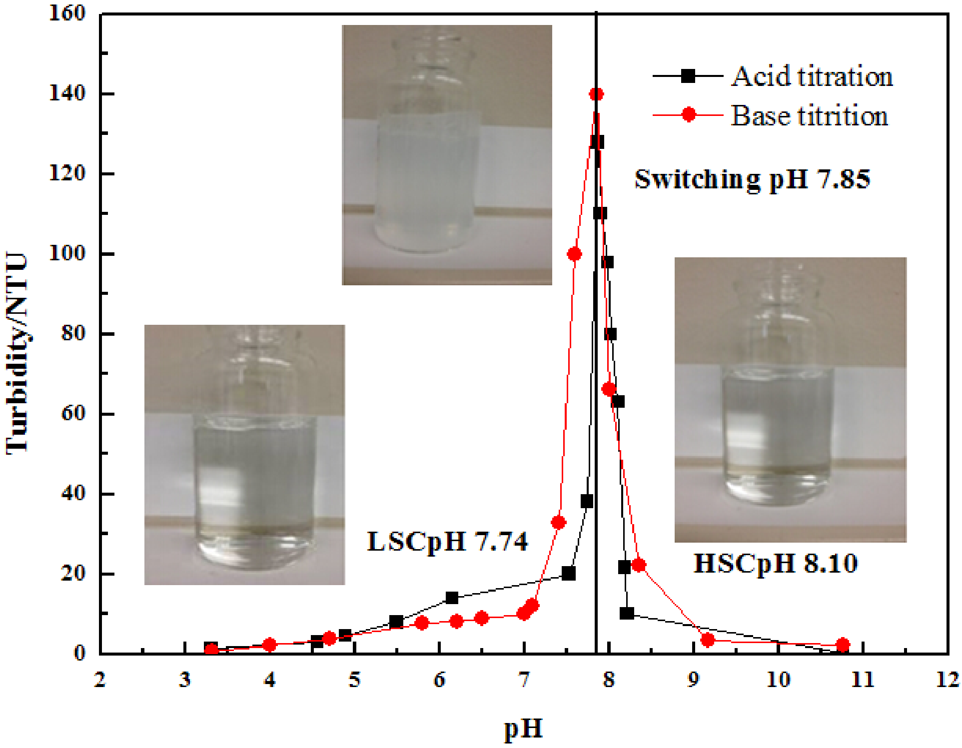

**Figure 19 Titration of synthesized polymer solution (16 hours reaction).**

# Chapter 4 Understanding the dual pH-responsive mechanism of random zwitterionic copolymers in aqueous solution

## 4.1 pH-responsive mechanism of diblock copolymer in aqueous solution

Zwitterionic pH-responsive copolymers have been receiving increased attention in the past few years, as these polymers can adopt different conformations at various pH conditions. Zwitterionic pH-responsive copolymers with tailored structures are playing an important role in a wide range of applications, including drug release systems [66] [67], gene delivery devices [68], bio-sensing and imaging [69] [70], anti-biofouling films and coatings [71-79], protein resistance [80], smart emulsion and foam stabilization, and flocculation for waste water treatment [81] [82]. Functionality of the copolymer can be well manipulated by controlling the structure [83]. Well-defined zwitterionic pH-responsive block copolymers have been widely studied for reduction of biofouling. Poly([2-(acryloyloxy)ethyl] trimethyl ammonium chloride (TMA)-b-2-carboxy ethyl acrylate (CAA)) is one such polymer, bearing positively charged quaternary amine groups and negatively charged carboxylic acid groups that can switch from bacteria-adhesive to bacteria-resistant depending on the pH in the environment. The tunable conformation of the copolymer also makes it capable of collecting and releasing bio contaminants [84]. The other example in protein separation is a zwitterionic triblock copolymer, poly((dimethylamino)ethyl methacrylate (DMAEMA)-b-methyl methacrylate (MMA)-b-methacrylic acid (MAA)), which forms micelles of different sizes and sequence when the pH varies. This copolymer has been utilized for the separation of charged biomolecules such as proteins in ion-exchange displacement chromatography. As it precipitates out of the solution at the isoelectric point of pH, the copolymer displacer can be easily recycled after use [85] [86]. Very recently, poly(4-vinylbenzoic acid (VBA)-b-(diethylamino)ethyl methacrylate (DEA)) diblock zwitterionic copolymer carrying positive charges at lower pH and negative charges at higher pH has been synthesized by atom transfer radical polymerization (ATRP) [87]. This polymer formed micelles in an aqueous solution due to either protonation of DEA or ionization of VBA, but became insoluble at its isoelectric point of pH 7.4 [88]. Based on the structure of p(VBA-b-DEA), similar zwitterionic copolymers have been obtained for research, such as p(DMAEMA-b-AA) [89], p(DMAEMA-b-MAA) [90], p(DEA-b-MAA) [91] *etc*. The whole categories of zwitterionic diblock copolymers possess a particular pH-responsive solution property. At pH values close to the isoelectric point, the copolymer precipitates out of the aqueous solution. The copolymer then becomes soluble when the pH is adjusted away from the isoelectric point [92]. The isoelectric point of pH is defined as the pH where the turbidity of the polymer solution reaches a maximum [90]. This phenomenon is attributed to the conformational change of the copolymer, which occurs as the pH is altered [93].

Insolubility of the copolymer over a range of pH is theoretically due to the attractive electrostatic interactions between the polymer chains of opposite charge [94].

### 4.2 Mechanism study on random zwitterionic pH-responsive copolymer

Unlike the block zwitterionic copolymer with a well-defined structure, the random zwitterionic copolymer has randomly arrayed cationic and anionic units in the structure [95]. The random zwitterionic copolymer also plays an exceptionally important role in the biotechnology field [96], as well as waste water processing in the oil industry [97-102]. Poly(diallyldimethylammonium chloride (DADMAC)-co-acrylamide (AM)-co-acrylic acid (AA)) is one of such zwitterionic random copolymers which can be utilized as surface stickiness mitigator in soil agglomeration. The adherent character of soil agglomerator can be controlled by this kind of copolymer to improve the agglomeration property and efficiency. It is believed that the copolymer helps prevent hydroxide-mediated precipitation of the soil agglomerator, and additionally helps it to remain anchored to the soil body [97]. The other example is poly(acrylamide (AM)-co-4-vinylpyridine propylsulfobetaine (VPPS)) which has both positive charge and negative charge. Due to the possession of two kinds of charge, it is an effective flocculant for both negative charged kaolin and positive charged hematite suspensions, and its flocculation performance outweighs the pure polyacrylamide

(PAM) [100]. Nevertheless, the behavior of random zwitterionic copolymer in response to pH change is not well defined. In other words, the mechanism to account for the pH-responsive phenomenon of random zwitterionic copolymer remains to be understood.

### 4.2.1 Solution property of copolymer from different reaction times

In different applications, we need the copolymer to change its conformation within different pH ranges. It is assumed that the change in the polymer composition may change the switching pH. To figure out if we could tune the composition of the polymer with reaction time varied, poly(DMAEMA–co–AM–co–AA) was synthesized for 16, 20 and 24 hours, which changes the degree of hydrolysis of DMAEMA and AM. As shown in Fig. 20, the switching pH, as well as the HSCpH and LSCpH of the polymer solution decrease when the reaction time increases. For the following discussions, we will use switching pH to represent the dual turbidity transition range between HSCpH and LSCpH..

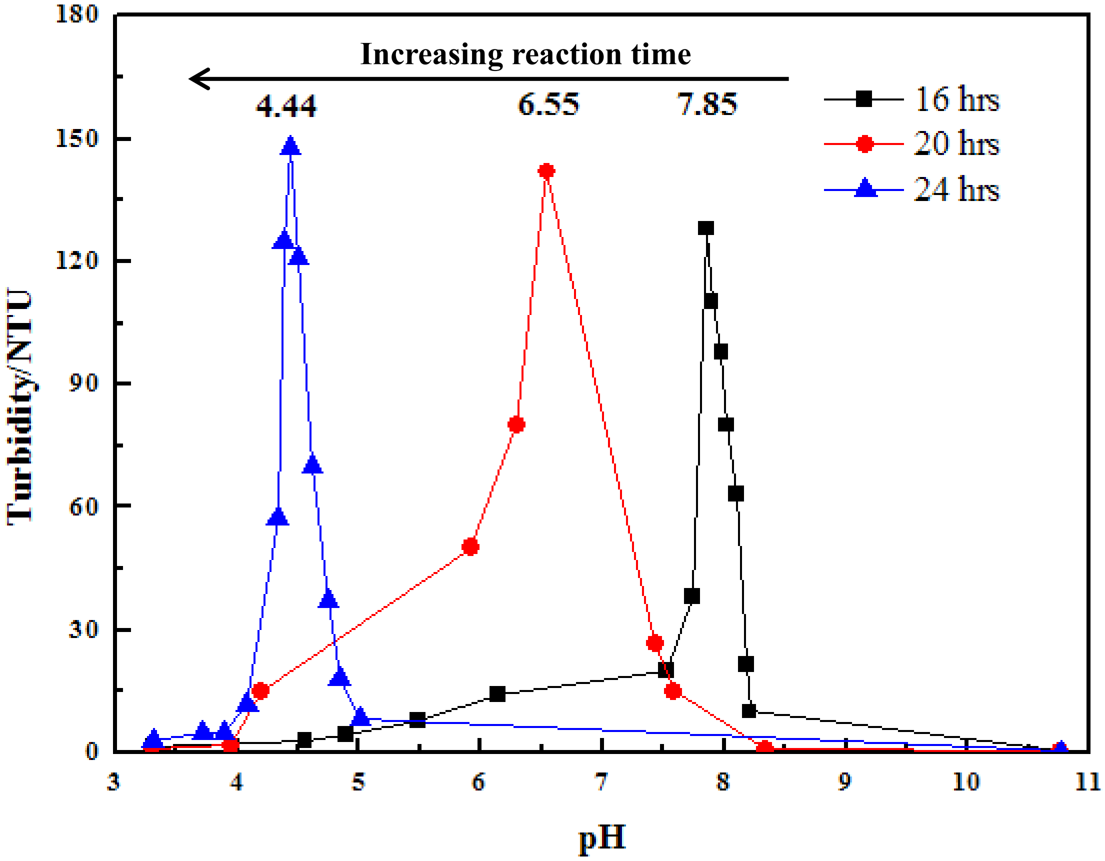

**Figure 20 Influence of reaction time on the pH-switching property of copolymer.**

### 4.2.2 Elemental analysis of polymers from different reaction times

To understand the correlation between the reaction time and the switching pH, Ubbelohde viscometer was used to calculate the average molecular weight of the copolymer synthesized for 16, 20 and 24 hours. The molecular weight of the copolymer was increased from 2.35 to 6.63 and to 11.94 million g/mol.

Elemental analysis was also used to show the ratio of the monomer components in the copolymer. Elemental analysis was performed on the Thermo Scientific Flash

2000 CHNSO - organic elemental analyzer. Carbon, hydrogen, nitrogen and oxygen elements were measured in the furnace where the combustion occurred. Carrier and reference gas were both helium. The polymer sample of around 10 mg was wrapped in a tin foil, and then put into the furnace for combustion. The weight percentage of each element in the polymer sample was obtained by the calculation of the instrument through the amount of $CO_2$ and $H_2O$ that were produced from the combustion. Each test was repeated three times, and the average number was utilized for further calculation.

Table 1 shows the weight percentage of carbon, nitrogen in the copolymer and their on standard deviations from different reaction time directly obtained from elemental analysis repeated three times. Having known the weight percentage of carbon and nitrogen, we calculated the weight percentage of three monomers in the copolymer by setting a three element linear equation group. In this group, we had X, Y, and Z respectively representing the weight percentage of DMAEMA, acrylamide and acrylic acid. As we knew the structure of each monomer, we added the weight of carbon and nitrogen from each monomer, and the sum equaled to the weight of carbon and nitrogen obtained from the elemental analysis measurements. After solving the equation group, we obtained the weight percentage of the three monomers in the copolymer respectively, as indicated in Table 2. We found out that more acrylic acid was formed from hydrolysis with longer reaction time. The molecular weight and the ratio of AA to DMAEMA in the copolymer increase with increasing reaction time. So additional measurement is needed to verify which one of them dominates the switching pH.

| **Reaction Time(hours)** | **Carbon(wt%)** | **Nitrogen(wt%)** |
|---|---|---|
| **16** | **53.4±0.01** | **12.8±0.02** |
| **20** | **52.5±0.01** | **12.8±0.02** |
| **24** | **52.0±0.01** | **13.0±0.02** |

**Table 1 Amount of carbon and nitrogen in synthesized copolymers from different reaction times.**

$$X + Y + Z = 100$$

$$0.089X + 0.197Y = \text{Nitrogen (wt\%)}$$

$$0.611X + 0.507Y + 0.5Z = \text{Carbon (wt\%)}$$

| **Reaction time (hours)** | **16** | **20** | **24** |
|---|---|---|---|
| ***X*-DMAEMA (wt%)** | **27.3** | **19.0** | **14.3** |
| ***Y*-Acrylamide (wt%)** | **52.6** | **56.4** | **59.5** |
| ***Z*-Acrylic acid (wt%)** | **20.1** | **24.6** | **26.2** |
| **AA:DMAEMA (wt:wt)** | **0.74** | **1.29** | **1.83** |
| **Molecular Weight (Million Dalton)** | **2.35** | **6.63** | **11.94** |
| **LCSpH** | **7.74** | **6.30** | **4.33** |
| **HCSpH** | **8.10** | **7.43** | **4.84** |
| **Switching pH** | **7.85** | **6.55** | **4.44** |

**Table 2 Summary of the synthesized copolymers.**

### 4.2.3 Titration of model copolymers

To differentiate whether it is the ratio of AA to DMAEMA or the molecular weight that determines the switching pH of the synthesized polymer solution, the commercial model copolymers were used as a model system for titration experiments. They are poly(AM-co-AA) and pDMAEMA, which both have much smaller molecular weight than the synthesized copolymers. The two kinds of commercial polymers were mixed together and prepared as solution with a concentration of 1000 ppm. The ratio of AA to DMAEMA was controlled by controlling the weight percentage of the two kinds of commercial polymers in the solution. Commercial model copolymer solutions with various ratios of AA to DMAEMA from 0.7 to 2.8 were titrated in the same manner as the synthesized polymer solutions. As observed in Fig. 21 (A), the same pH switching phenomenon as synthesized polymer solutions is achieved. Besides, the switching pH of the model copolymer solutions also decreases when the ratio of AA to DMAEMA increases even though the molecular weights of the model copolymers are much smaller than the synthesized ones. As seen from Fig. 21 (B), there is a good agreement of pH-switching phenomenon between the model copolymers and synthesized copolymers as long as they have the same ratio of AA to DMAEMA. This indicates that the ratio of AA to DMAEMA in the copolymer that dominates the pH switching behavior instead of the molecular weight. Thus, a solid relationship between the ratio of AA to DMAEMA and the switching pH of the copolymer is established. We could conclude that the switching pH of the copolymer is controlled by the ratio of AA to DMAEMA but not the molecular weight.

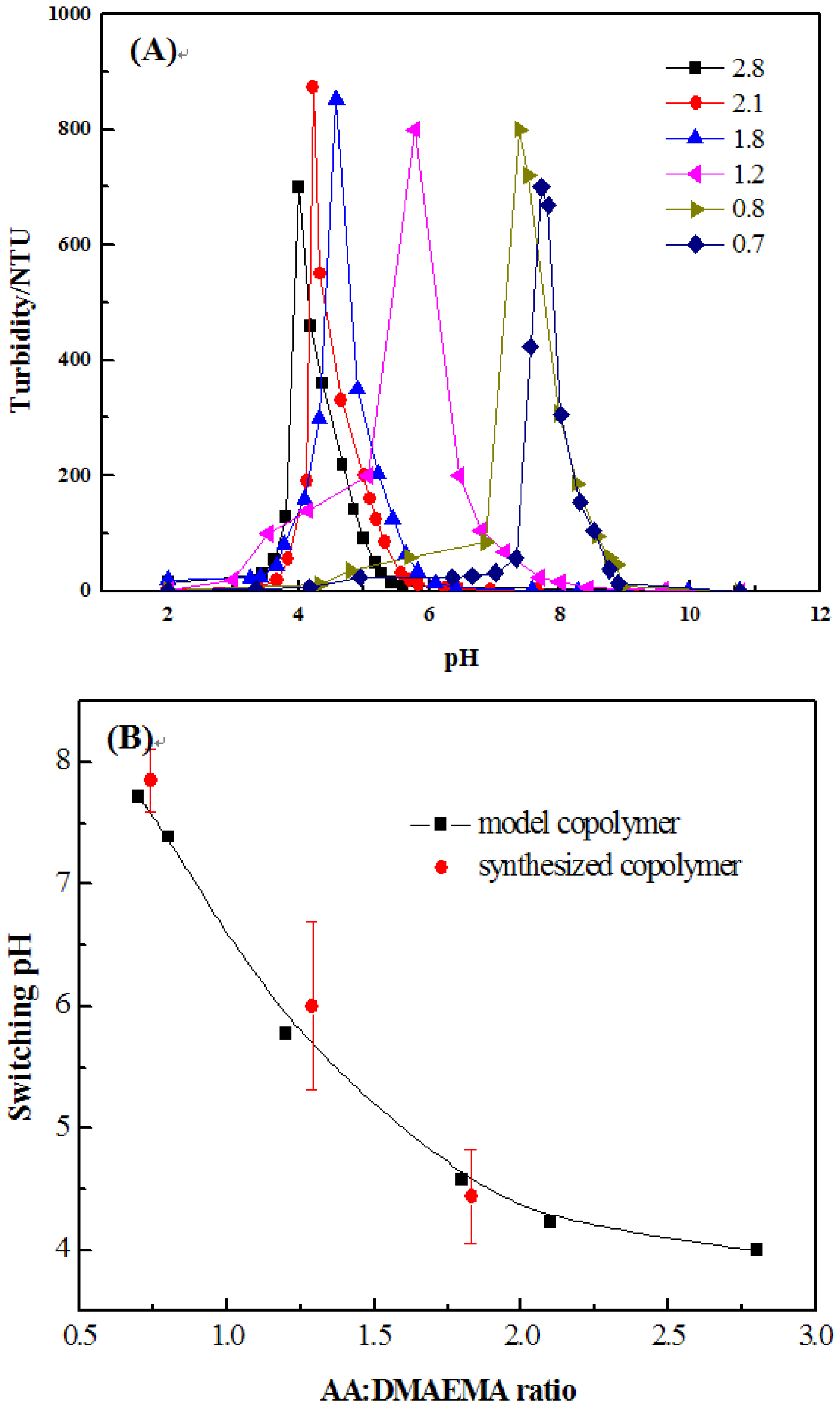

Figure 21 Titration of model copolymers with different AA to DMAEMA ratios (A), comparison between model and synthesized copolymers (B).

### 4.2.4 Proposed pH-switching mechanism of zwitterionic copolymer

Based on the confirmative results, we proposed that a mechanism for the pH-response of the random zwitterionic copolymer in aqueous solution is the same with block zwitterionic copolymer, even though the charged groups in random copolymer are not arranged in a specific sequence. While the random zwitterionic copolymer has a much larger molecular weight than the block copolymer, the switching pH is not affected as long as the ratio of two oppositely charged units remains the same. Fig. 22 clearly shows how the pH influences the interaction between the negatively charged groups and positively charged groups in the aqueous solution, and further influences the solution turbidity. When the pH is high, the acrylic acid groups are deprotonated and carry negative charge. The copolymer is well dissolved and extended in aqueous solution, which makes the solution appear clear. When the pH value is low, the DMAEMA groups are protonated and carry positive charge. Within this range, the copolymer is also at its extended state in aqueous solution and the solution is clear. However, when the pH is medium, both the acrylic acid and DMAEMA groups carry charges. The electrostatic interaction between the positive charge on DMAEMA groups and negative charge on AA groups dominates the copolymer switching from extended to collapsed state. This electrostatic interaction is possibly an intermolecular force between different polymer chains. Increasing the ratio of AA to DMAEMA reduces the pH for the switching. This trend is in accordance with block copolymers. For the synthesized copolymers, by adjusting the reaction time and thus the extent of hydrolysis, we can precisely tune the dual pH-responsive turbidity transition of random zwitterionic copolymer solution to specific range for a variety of applications.

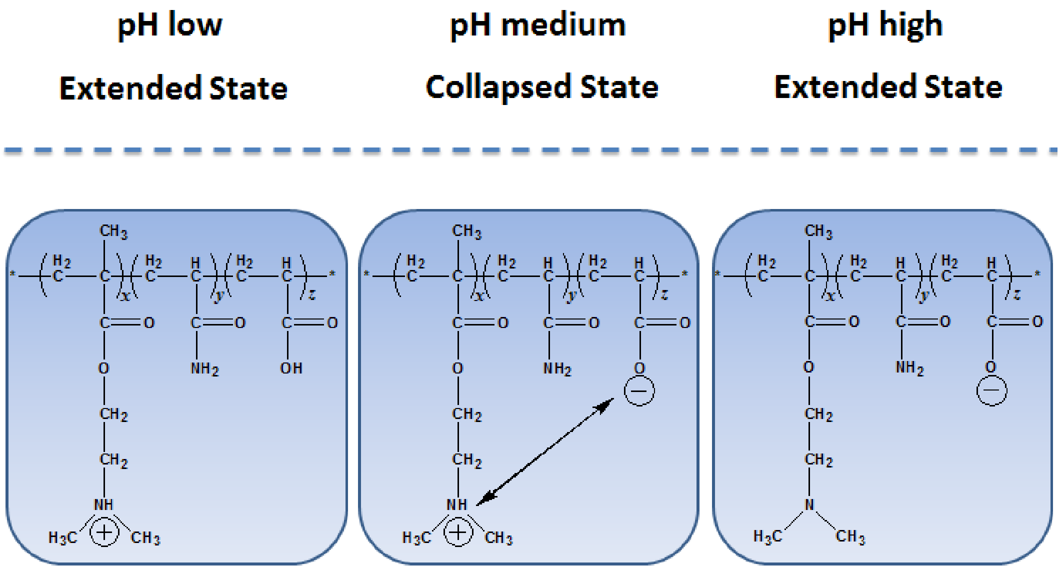

**Figure 22 Proposed pH-response mechanism of zwitterionic copolymers.**

# Chapter 5 Application of pH-switchable copolymer in flocculation and compaction of tailings

In Alberta, the majority of the clays in tailings are kaolinite (69%). A small amount of montmorillonite and smectite clays may be present [3]. Therefore, kaolinite suspension was used for investigating the effectiveness of the pH-responsive polymer flocculant in flocculating and compacting tailings. In our work, flocculation refers to the process wherein colloidal particles of kaolinite suspension are aggregated to form flocs or flakes due to the addition of polymer flocculant. Compaction means the further treatment to the sediment formed after flocculation in order to increase the solid content and sediment strength. As for the flocculation, different dosages of polymeric flocculant were tested to obtain the optimal one, which was followed by pH change in the sediment. Initial settling rate, supernatant water turbidity, sediment yield stress, solid content and dynamic water drainage were used to determine its flocculation and compaction performance.

## 5.1 Flocculation tests

### 5.1.1 Materials and procedures

The kaolinite suspension was prepared by adding kaolinite particles into DI water. The kaolinite particles with an average diameter of 1 μm used for experiments were ground from the dry crude kaolin directly from the mine site. The crude kaolin has 90% solids, and it was purchased from Thiele Kaolin Company. The average zeta potential of the kaolinite particles in aqueous solution is -34.36 mV measured by Zeta PALS. 5 wt% of kaolinite particle suspension in DI water was used for all the flocculation tests. The temperature of the tests was controlled to be 22°C. And pH for the flocculation was maintained to be 8.2. The copolymer for the flocculation tests was synthesized for 20 hours. The average molecular weight equals to $6.63 \times 10^6$ g/mol. The reason for choosing this reaction time for flocculation experiments is that the switching pH is around 6.5 very close to neutral. So it is convenient and feasible to adjust the solution pH around this point in industry applications.

The dry polymer flocculants were stored in sealed glass bottles kept out of light. To prevent significant decay of polymeric molecules, flocculant stock solutions of 1000 ppm were prepared with DI water one day prior to their use. The polymer solution was prepared and shaken overnight before the flocculation tests.

Before each flocculation test, the kaolinite suspension was stirred to make it homogeneous and the samples taken have the same composition. Fig. 23 shows the impeller and mechanical stirrer used to mix the kaolinite suspension in the beaker with a baffle in it. The baffle could avoid the formation of big lumps during the stirring. The stirring rate was controlled to be 350 rpm so that fewer solids settled onto the bottom, and the time was set usually about 1 hour, which was enough to make the suspension homogeneous. Paraffin film was used to cover the beaker to avoid water evaporation.

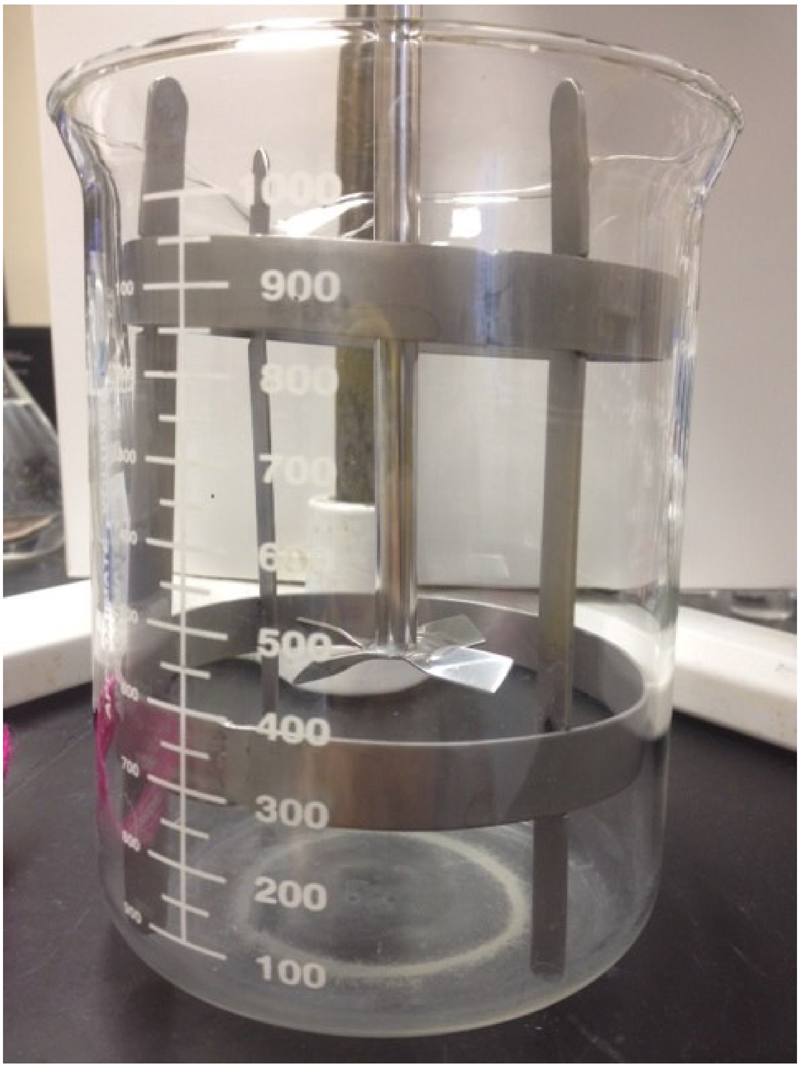

**Figure 23 Home-made baffle and customized impeller mixing.**

After the kaolinite suspension became homogeneous, the pH of kaolinite suspension was adjusted to 8.3 by adding diluted sodium hydroxide solution to assure the pH condition was close to practical process. Then the polymer solution of a stock concentration of 1000 ppm was injected into the beaker slowly, while the mixing rate was lowered to 300 rpm in case of breaking the flocs formed during the addition of flocculant. The amount of polymer solution needed for each test was controlled according to the dosage. Different dosages were applied so as to find the optimal dosage.

The mixing was stopped right after the addition of polymer solution. The flocculated suspension was transferred into a 100 mL graduated cylinder. After inverting the cylinder for 5 times, it was placed on a bench. The suspension mud-line was recorded with time during the settling period as shown in Fig. 24. The height of the mud-line for every 5 seconds of settling was recorded to calculate the settling rate. Initial settling rate (ISR) could be gained through calculating the slope of the steep curve of normalized mudline height as a function of settling time. The supernatant clarity was obtained by measuring the turbidity of the water syphoned out of the cylinder after 5 minutes of settling.

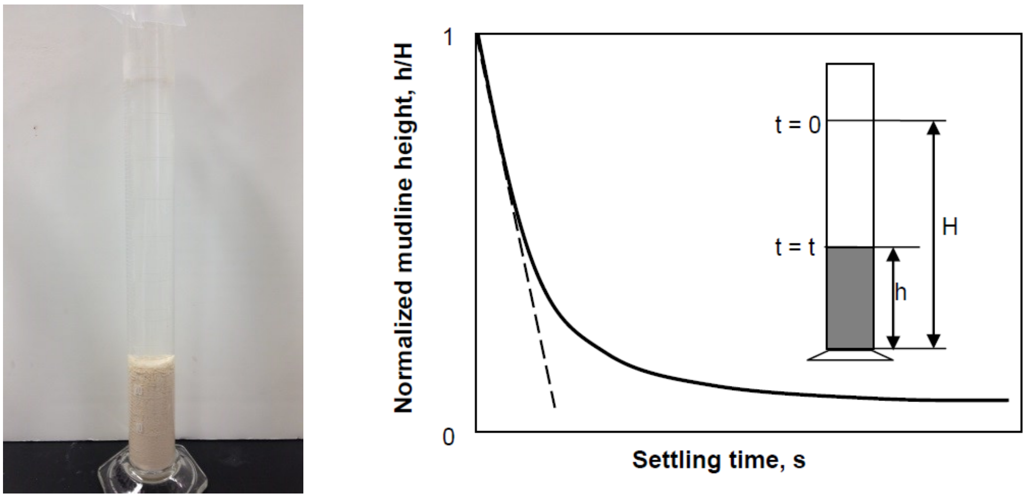

Figure 24 Flocculation test setup and a typical settling curve.

### 5.1.2 Results of flocculation tests

The dosage chosen for the flocculation tests varied from 0.2 kg/ton to 5.0 kg/ton. Kg/ton refers to the amount of polymer flocculant (in kilograms) that was used per ton of kaolinite particles in the system. From the results shown in Fig. 25, without any addition of polymer flocculant, the mud-line of the kaolinite suspension in the cylinder barely moves within the first 5 minutes, while the addition of polymer flocculant for other flocculation tests dramatically accelerates the settling rate. Besides, increasing the dosage of polymer flocculant improves the settling rate.

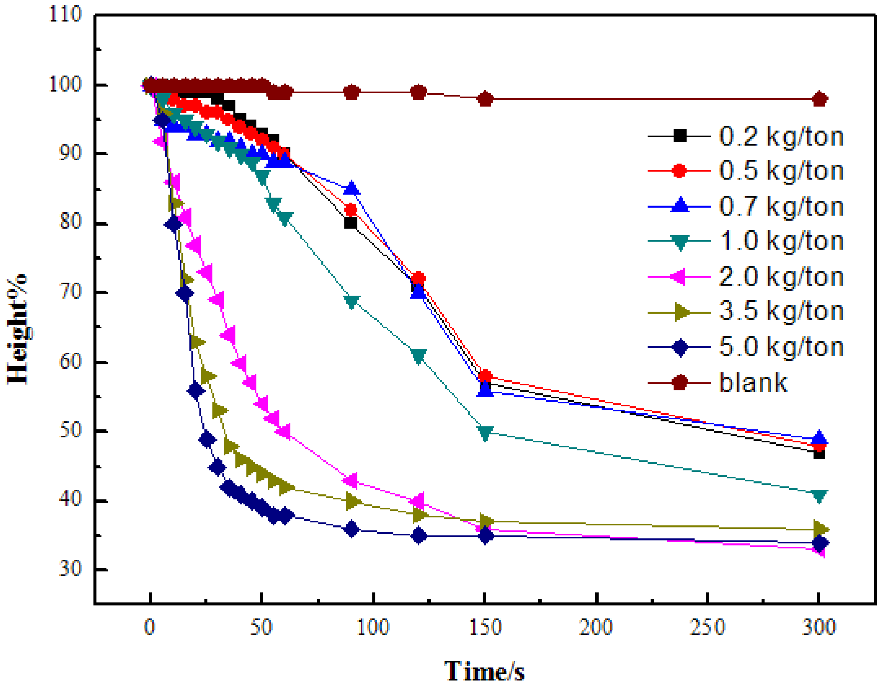

**Figure 25 Settling curves from different dosages of polymer flocculant for flocculation tests.**

Based on the results from the settling curve, the initial settling rate for each dosage was calculated and exhibited in Fig. 26. The supernatant water after 5 minutes settling was syphoned, and the turbidity was measured as well. The turbidity of supernatant water from each settling test could also be found in Fig. 26.

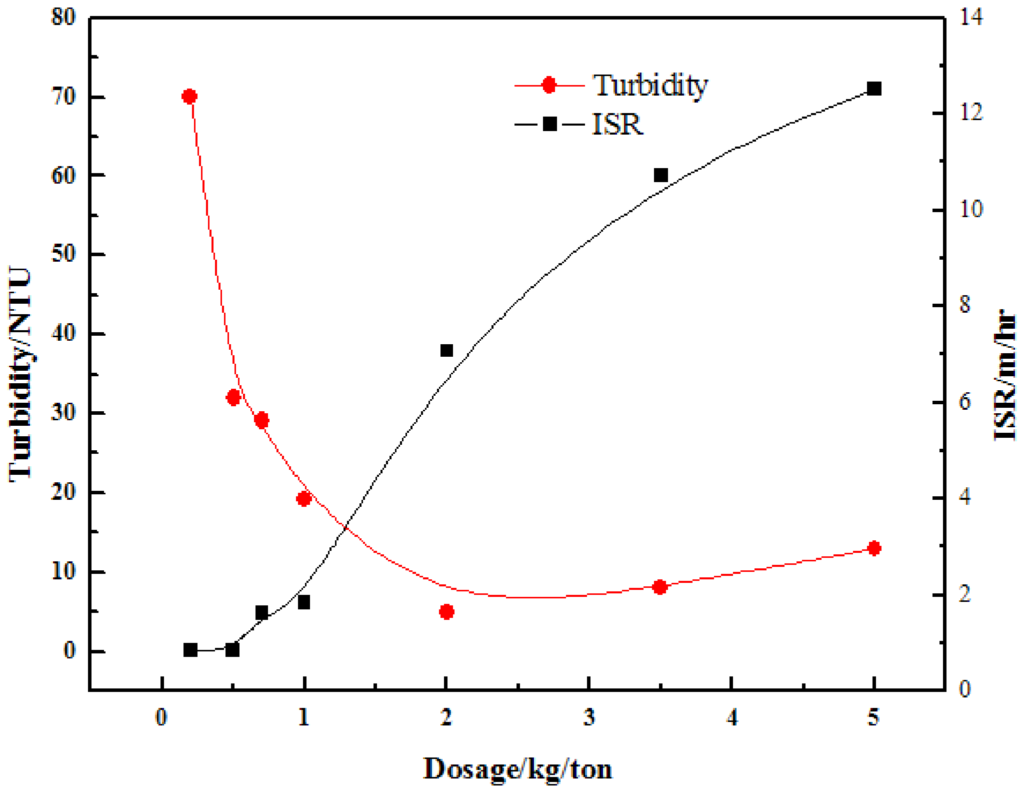

**Figure 26 Influence of polymer dosage on initial settling rate and supernatant water turbidity.**

It is obvious that the higher dosage of polymer flocculant results in faster settling, indicating that there is no local overdose of using this polymer flocculant. Usually excessive amount of polymer flocculant leads to worse flocculation performance due to local overdose. It has been suggested that optimum flocculation occurs when half the surface area of solid particles is covered with polyelectrolytes. At higher concentration the flocculation performance is detained and the surface is thoroughly covered by the absorbed polymer flocculant layer [40]. However, in our case, the settling rate is not reduced when the dosage is extremely high, so another parameter, supernatant turbidity, should be taken into consideration for choosing the optimal dosage for further compaction experiments.

As one of the aims of flocculation process is to purify turbid water, the optimum condition could be evaluated in terms of minimum supernatant turbidity after sedimentation of flocs. Therefore, 2 kg/ton among various dosages was selected to be the optimal dosage for compaction test, because the initial settling rate is relatively high and the supernatant turbidity is the lowest.

## 5.2 Compaction tests

### 5.2.1 Materials and procedures

Now that the optimal dosage for compaction was determined to be 2 kg/ton, the compaction test was conducted under this optimum condition. However, the yield stress and solid content of the sediment were needed to confirm the effect of the pH-responsive polymer, the cylinder for compaction was switched to the large-scale and removable one as shown in Fig. 27.

Figure 27 Experiments set-up for compaction tests.

After the flocculation using 2 kg/ton as the dosage was completed for 1 hour, the yield stress and solid content were measured respectively. Then the cylinder was placed on the bench for 24 hour before the yield stress and solid content were measured again to check the effect of polymer switching on the sediment. Within 24 hours, the pH of kaolinite suspension has already automatically decreased to 6.8, where the polymer in the sediment should have switched to collapsed state [103].

For settled tailings pastes, the rheology highly depends on water content. Compaction of the tailings pastes is a process of dewatering that changes the rheological properties and increases the stability of the tailings pastes. Yield stress is one of the most relevant operational parameters to understand the rheological properties of the tailings pastes after compaction process [104]. Vane viscometer has been successfully used by several researchers in the determination of the yield stress of materials [105] [106].

The yield stress was measured by a Haake VT 550 vane viscometer with a FL – 100 type of vane, as shown in Fig. 28. It is designed with a rotational speed preset and measures the flow resistance of a sample. The torque maintaining the set speed is proportional to the viscosity, so all final information on the viscosity, shear stress and the shear rate is calculated from the torque required, the set speed and the geometry factors of the applied sensor.

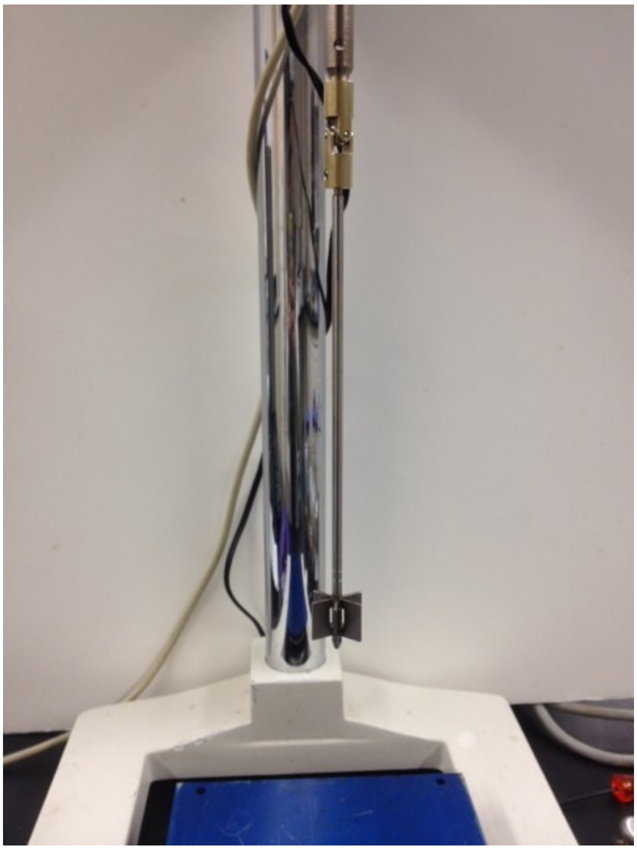

**Figure 28 Instrument for measuring yield stress.**

The test procedure involved a gentle immersion of the four-bladed vane spindle into the tailings pastes in the large cylindrical container as shown in Fig. 27. The vane was then rotated very slowly at a constant rotational speed of 0.01397 $s^{-1}$. The resulting stress was monitored with time. A stress - time profile was obtained after 10 minutes. Initially, the stress increased linearly with time, which was the elastic deformation regime. The stress reached a peak, and then decreased and reached an equilibrium state (residual shear stress). The yield stress, $\tau_y$, was calculated from the maximum torque, $M_o$, and the vane dimensions, according to the following formula:

$\tau_y = M_o/[(H/D + 1/3)(\pi D^3/2)]$

H and D are the height and diameter of the vane, respectively [107].

### 5.2.2 Results of compaction tests

The yield stress and solid content before and after pH change were obtained. There is a 140% increase of yield stress and 43% increase of solid content after pH change from 8.2 to 6.8 as illustrated in Fig. 29 and 30. The change of the yield stress and solid content implies the rheological properties of the flocculated sediment are influenced by the pH variation. Based on the conclusion we have drawn in chapter 4, that the pH change makes the copolymer switch from extended to collapsed state due to intra-molecular electrostatic interaction, we can deduct that this copolymer state transition produces denser flocs in the sediment. And this process releases the trapped water and strengthens the sediment. The results also confirm the hypothesis proposed in chapter 3, that rapid settling rate can be achieved when the copolymer is added at its extended state, followed by collapsed state to compact flocs upon pH change of sediment environments.

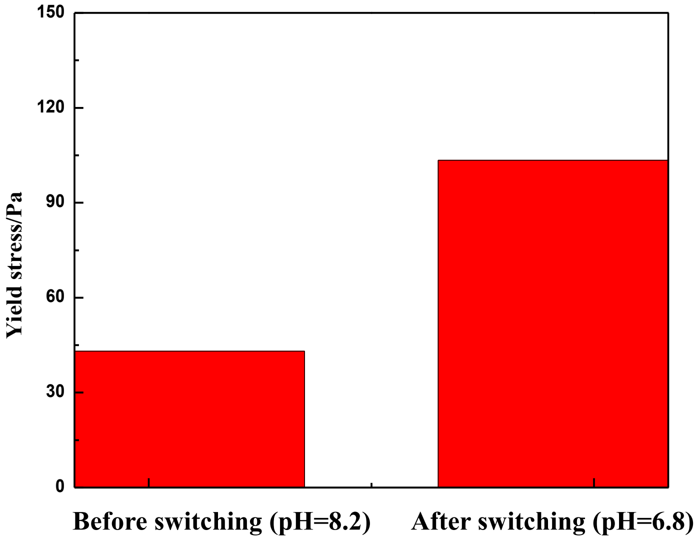

**Figure 29 Influence of pH change on sediment yield stress.**

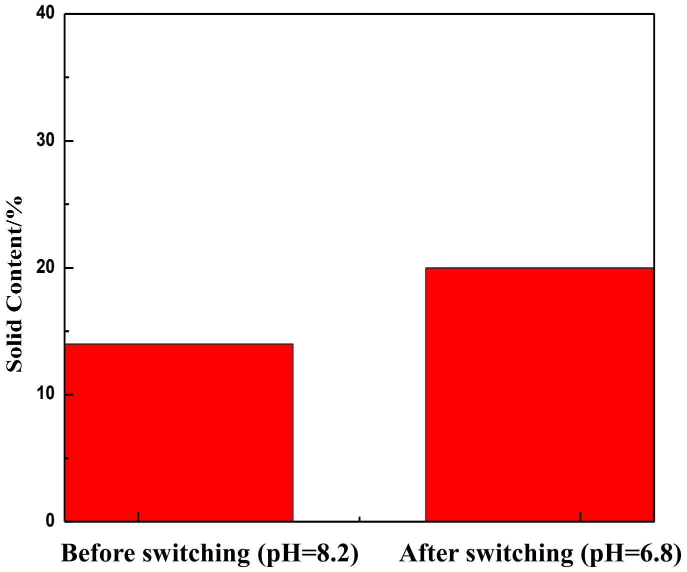

**Figure 30 Influence of pH change on sediment solid content.**

Water drainage process was examined to evaluate the water releasing velocity after the compaction of flocs. After overnight placement (pH decreased from 8.2

to 6.8) for compaction, the supernatant water was syphoned out of the cylinder, and the sediment pastes were placed upon a metal filter sieve. A beaker was put underneath to catch the water released from the sediment pastes. The water drainage process was monitored for 1 hour until there was nearly no more water released, and the weight of drained water was measured every 2 minutes as shown in Fig. 31. Both the sediment pastes treated in the same process by the synthesized copolymer and commercial polymer HPAM were tested. The comparison of drainage velocity between these two kinds of polymers shows that the pH change in the sediment made the entrapped water release more quickly when the pH-responsive polymer flocculant is applied. The sediment drained for overnight became a really dry stack and easy to move without breaking apart as shown in the picture in Fig. 31. The fast water drainage from sediment compaction further proves that switching the copolymer from extended to collapsed state can compact the sediment by releasing more entrapped water.

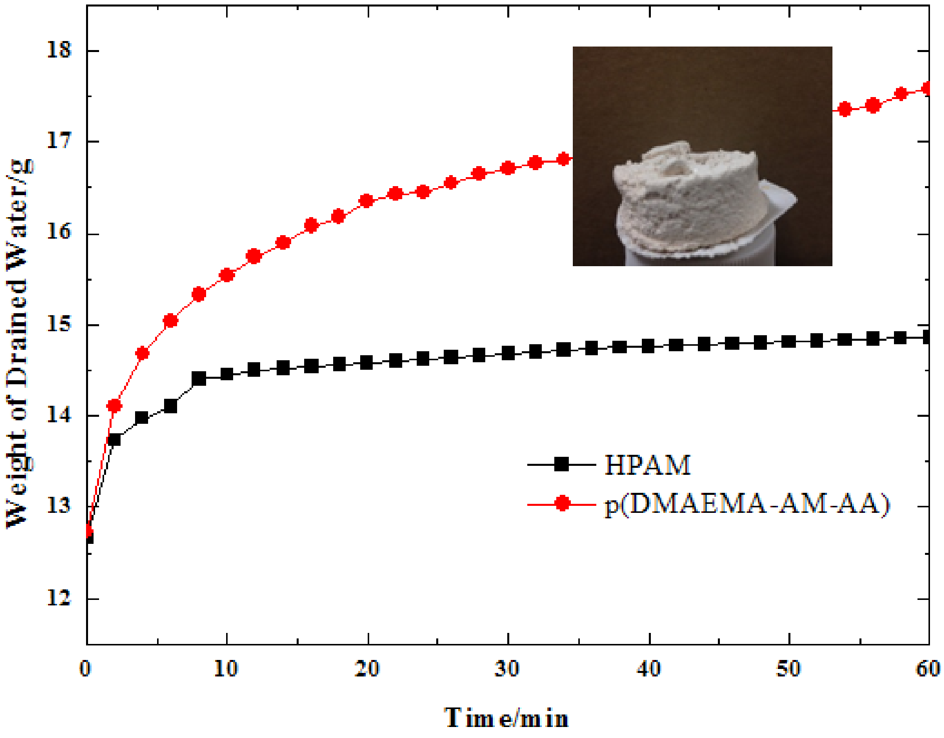

**Figure 31 Comparison of water drainage between synthesized copolymer and HPAM.**

### 5.3 QCM-D measurements

To understand the adsorption process of the synthesized copolymer and verify the occurrence of the conformational change when pH varies on kaolinite particles, silica sensor was used to simulate the kaolinite surface, which is mainly composed of silica atoms. Adsorption kinetics of the 20 hours synthesized copolymer on silica sensor was studied by a Q-Sense E4 quartz crystal microbalance with dissipation (QCM-D). The adsorption behavior of the copolymer on silica and the polymer conformational change at varying solution pH was investigated. QCM-D is a powerful technique to study the adsorption behavior of polymers on solid surfaces. It can determine not only the adsorbed mass of the polymers by measuring the changes in resonance frequency (Δf) of quartz crystal sensors, but also the structural (viscoelastic) properties of the adsorbed layers by measuring the dissipation (D) [108]. When the frequency decreases, it means the adsorbed mass of the polymer increases. Dissipation represents the stiffness of the polymer adsorbed on the silica surface. Lower dissipation value means more rigid structure of the polymer; higher dissipation value means the polymer is more stretched [109]. By taking advantage of this technique, the adsorption characteristics of the synthesized copolymer on silica surface and the polymer conformational change at varying pH were studied.

### 5.3.1 QCM-D experiment procedure

Before the experiment, the polymer (20 hours reaction) solution with a stock concentration of 1000 ppm was prepared by dissolving polymer powder into DI water with shaking overnight. DI water with pH 4.5, 6.5 and 8.7 were prepared as the rinsing liquid to create backgrounds with different pH for the adsorbed copolymer on silica sensor. The temperature was controlled to be 22°C. The silica sensor was treated by UV ozone for 10 minutes and immersed in sodium dodecyl sulfate (SDS) 2 wt% solution for 30 minutes. Then it was rinsed with DI water, dried with nitrogen and placed in UV ozone for another 10 minutes. All the modules and plastic tubes were sonicated for 1 hour and dried with nitrogen prior to use. After all the accessories were cleaned properly, the sensor was inserted into the module and they were connected to the polymer solution by the tubes through a peristaltic pump. The solution flow rate was maintained at 0.15 mL/min. At the beginning, DI water (pH = 8.7) was pumped into the flow module to establish a stable baseline. The polymer solution was then introduced into the flow module at the same flow rate until a new equilibrium was achieved. After the adsorption equilibrium was established, DI water (pH = 8.7) was pumped in again to wash out the copolymers that were not strongly adsorbed on the silica sensor. Then DI water (pH = 6.5) was introduced to change the pH of the solution as well as the mass and conformation of the polymer until a new equilibrium occurred. Eventually, DI water of pH 8.7, 4.5 and 8.7 was sequentially introduced to check the corresponding mass and conformational change of the adsorbed copolymer on the silica sensor.

### 5.3.2 QCM-D results

The resonance frequency and dissipation of the experiment are both shown in Fig. 32. There is a distinct drop in frequency and rise in dissipation starting from introducing the polymer solution, indicating there is a large amount of copolymer adsorbed on the silica sensor. Introduction of DI water (pH = 8.7) increases the frequency and decreases the dissipation to a small extent, suggesting that a small amount of copolymer not strongly adsorbed on the silica surface is washed away.

Then DI water (pH = 6.5) is introduced to lower the solution pH. As a result, the frequency decreases, which indicates that the polymer changes from extended to collapsed state and some dangling segments of the polymer in the aqueous solution collapse onto the silica surface. The decrease of dissipation indicates that the collapsed state also makes the polymer layers more rigid. Similar observation can be found in the study by Plunkett et al. They made the temperature-responsive polymer adsorbed on a golden surface and adjusted the temperature above the low critical solution temperature (LCST), where the dissolved polymer became insoluble and deposited onto the surface, leading to a sudden frequency decrease (indicating a mass increase). The collapse of the polymer with increasing temperature above LCST also resulted in a steady decrease in the dissipation, the same as our observation [110]. When the solution pH is adjusted back to 8.7, both the frequency and dissipation increase accordingly. However, when the solution pH drops directly to 4.5, the frequency decreases and the dissipation increases dramatically. This is attributed to the protonation of the DMAEMA groups that makes the polymer carry much positive charge attracted to the negative charge on silica surface by electrostatic interaction, but the polymer also becomes extended which leads to a higher dissipation. Thus, the corresponding conformational change of the copolymer at varied pH is verified.

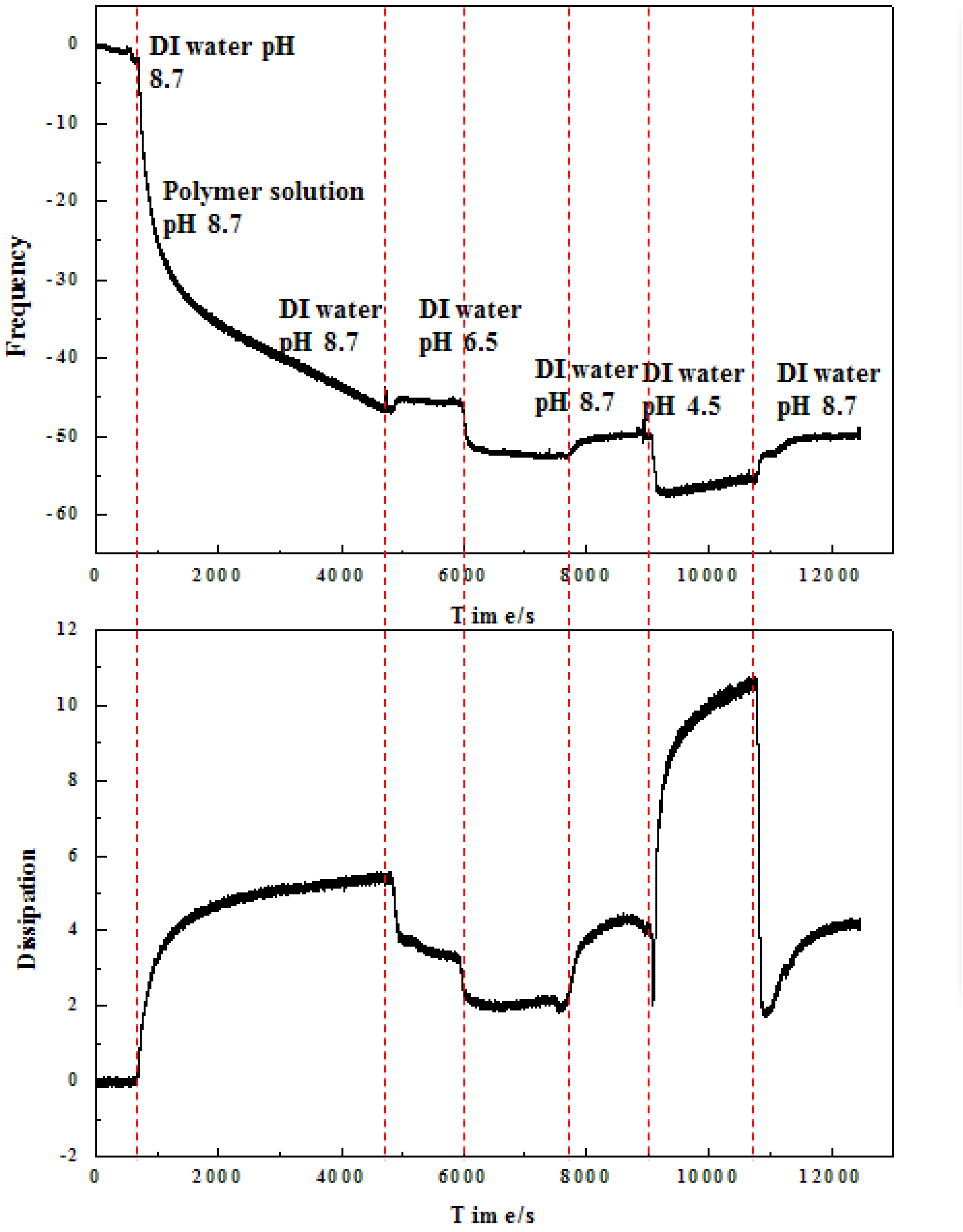

**Figure 32 Adsorption characteristics of the synthesized copolymer (20 hours reaction) on silica surface based on QCM-D measurement**

### 5.4 Flocculation study of the copolymer on MFT

To understand the process of floc formation after adding the polymer solution into MFT, Focused beam reflectance measurement (FBRM) was conducted to measure the size of flocs formed during the flocculation process. The polymer solution was injected into MFT until the mean size of the flocs becomes stable. The maximum dosage was 5 kg/ton.

In FBRM technology, a particle-track probe is immersed into MFT slury with no dilution. A focused laser scans the surface of the probe window and tracks individual chord lengths - measurements of particle size, shape and count. This real-time measurement is presented as a distribution and statistics which are trended over time.

As shown in Fig. 33, the mean chord length of the floc particles formed during the flocculation process of MFT increases from 20 μm to 550 μm when the dosage of the polymer flocculant increases to 5 kg/ton. Then the flocs become stable and the mean chord length remains the same under high-speed agitation. Compared with two commercial polymer flocculants, AF 246 and polyDADMAC, the synthesized copolymer leads to larger size of flocs in flocculation process, while AF 246 produces much smaller flocs, which breaks up under further agitation, and polyDADMAC barely flocculates the particles in MFT.

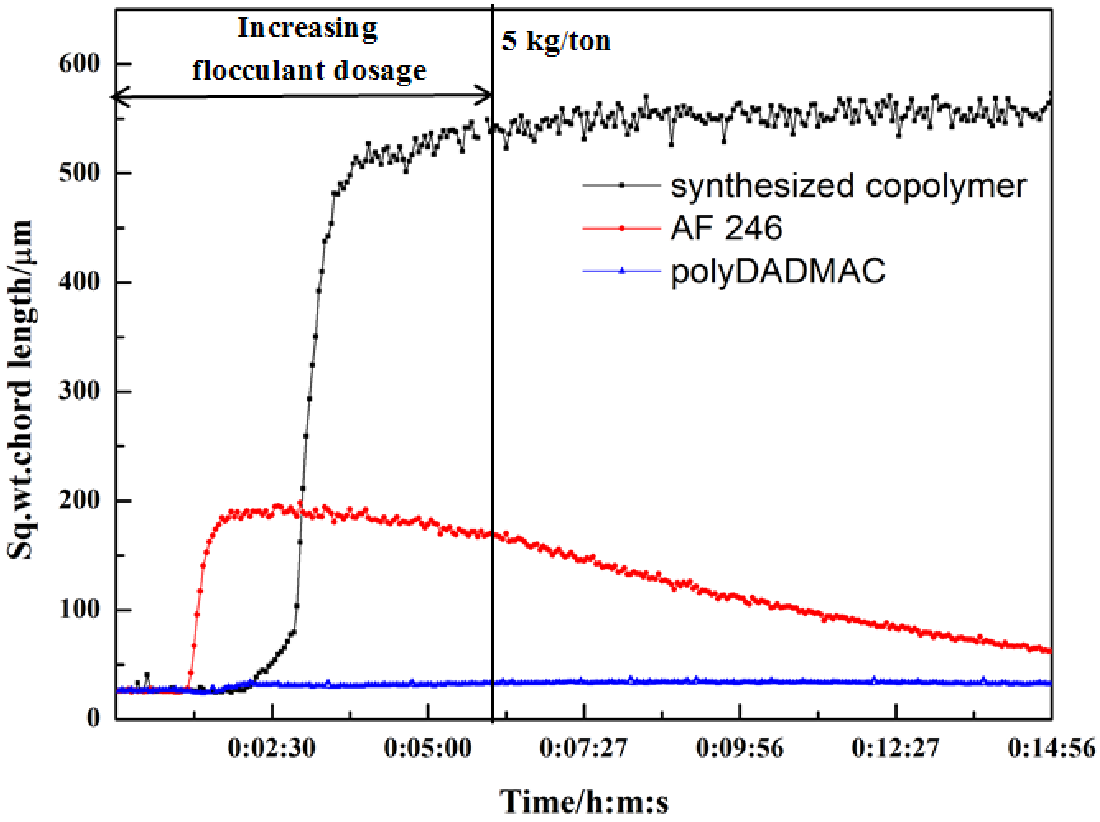

**Figure 33 Flocculation of MFT with increasing dosage of copolymer solution**

It indicates that the copolymer flocculant can also gave an outstanding performance in particles aggregation and floc formation in real MFT. The effect is much better than two commercial polymer flocculants, AF 246 and polyDADMAC.

# Chapter 6 Conclusions

Random copolymerization has been utilized to synthesize an innovative pH-responsive zwitterionic copolymer, poly(2-(dimethylamino)ethyl methacrylate–co–acrylamide–co–acrylic acid). Mass Spectrometry, FTIR and NMR were used to confirm the existence of AA, AM and DMAEMA in the copolymer.

The copolymer synthesized for 24 hours has a lower switching pH than those of 16 and 20 hours. Elemental analysis was conducted to determine that the ratio of AA to DMAEMA in the copolymer from 24 hours was larger than those of 16 and 20 hours. The relationship between the ratio of AA to DMAEMA and the switching pH of the copolymer was further verified by introducing commercial model copolymer compounds with different ratios (0.7 – 2.8) of AA to DMAEMA for titration. A solid relationship between the ratio of AA to DMAEMA and switching pH of the polymer solution was obtained, which indicated the increasing ratio of AA to DMAEMA in the copolymer lowered the switching pH. Moreover, the switching pH of the polymer solution was independent of copolymer molecular weight. A mechanism for the conformational change at the switching pH was therefore proposed. The electrostatic force between the positive charge on DMAEMA groups and negative charge on AA groups dominates the polymer conformational change from extended to collapsed state, which leads to the solution turbidity transition.

The copolymer can be used as flocculants for model tailings, kaolinite suspension. Excellent flocculation performance with high initial settling rate and super clear supernatant water was obtained by utilizing the copolymer flocculant with the optimal dosage (2kg/ton) of the polymer solution. Furthermore, more compacted sediment was formed by taking advantage of pH-responsive property of the copolymer flocculant. The decrease in pH of the sediment after overnight placement led to higher sediment yield stress and more water release. The water could be drained quickly and efficiently. QCM-D measurements furthermore verified the adsorption of the copolymer on silica surface and its conformational change at varied pH conditions.

To summarize, the response to pH and tunability of the switching pH give this copolymer exceptional advantages in the design of tailings treatment process. The copolymer can be directly added into the tailings at pH above 8.0 for flocculation. $CO_2$ can be used as natural source of $H^+$ to adjust the pH in the tailngs for compaction. The distinct clean supernatant water is able to be recycled without many further treatments. The fast water drainage makes the sediment after compaction easy for reclamation. Therefore, this copolymer can be an effective alternative for oil sands tailings treatments. Besides, the copolymer can also be utilized in other applications which require different pH-switching ranges.

# Chapter 7 Future work

AFM measurements can be utilized to detect different interactions by stretching these polymer chains on silica and alumina surface at varied pH in aqueous solution.

Application of this copolymer to real oil sands MFT has been tried at the initial stage. However, other parameters still need to be considered to evaluate the copolymer's performance in flocculation of MFT. More experiments should be conducted to confirm its effectiveness on MFT.

# Chapter 8 Contribution to original knowledge

In chapter 2, the literature was reviewed and the relevant research was summarized. In this study, a conceptually novel process based on a pH-responsive polymer flocculant was designed for oil sands mature fine tailings treatment. The flocculant was added into the tailings at its extended state to bridge the fine particles for flocculation. Then the solution pH was adjusted to the switching point where the polymer molecules become collapsed for compacting the flocs from the flocculation process. This innovative copolymer was designed, prepared and characterized. A mechanism to account for the dual pH-responsive property of this pH-responsive polymer flocculant was proposed. New methodologies, including elemental analysis and commercial polymers titration, were used to obtain the proposed mechanism. The switching pH of the copolymer was also tunable to various ranges with different weight ratios of AA to DMAEMA. The pH-responsive polymer flocculant was applied to MFT treatment, and thus the feasibility of this novel process was confirmed.

# References

[1] "Upstream Dialogue - The facts on oil sands, " The Canadian Association of Petroleum Producers, 2014.

[2] "Oil sands 2014 Quarter Report," Business in Alberta, 2014.

[3] J. Masliyah, J, Czarnecki and Z. Xu, Chapter 1, 2 in *Handbook on Theory and Practice of Bitumen Recovery from Athabasca Oil Sands Volume I: Theoretical Basis,* Edmonton, Kingsley Knowledge Publishing, 2011, pp. 1-125.

[4] K. Kisman and K. Yeung, "Numerical study of the SAGD process in the Burnt Lake oil sands lease," in *International heavy oil symposium,* 1995, pp. 275-286.

[5] J. J. Sheng, "Cyclic Steam Stimulation," *Enhanced Oil Recovery Field Case Studies,* p. 389, 2013.

[6] C. Beattie, T. Boberg, and G. McNab, "Reservoir simulation of cyclic steam stimulation in the Cold Lake oil sands," *SPE Reservoir Engineering,* vol. 6, pp. 200-206, 1991.

[7] The Oil Sands Developers Group. (2009). Steam Assisted Gravity Drainage (SAGD)[Online]available: http://www.oilsandsdevelopers.ca/index.php/oil-sands-technologies/in-situ/the-process-2/steam-assisted-gravity-drainage-sagd/

[8] R. Butler and I. Mokrys, "Closed-loop Extraction Method for the Recovery of Heavy Oils and Bitumens Underlain by Aquifiers: The Vapex Process," *Journal of Canadian Petroleum Technology,* vol. 37, pp. 41-50, 1998.

[9] B. Yadali Jamaloei, R. Kharrat, and F. Torabi, "Analysis and correlations of

viscous fingering in low-tension polymer flooding in heavy oil reservoirs," *Energy & Fuels,* vol. 24, pp. 6384-6392, 2010.

[10] Q. Dai and K. H. Chung, "Hot water extraction process mechanism using model oil sands," *Fuel,* vol. 75, pp. 220-226, 1996.

[11] T. P. Clarke, "Oil sands hot water extraction process," ed: Google Patents, 1980.

[12] R. D. Humphreys, "Tar sands extraction process," ed: Google Patents, 1999.

[13] J. S. Rendall, "Hot water bitumen extraction process," ed: Google Patents, 1989.

[14] "Enhancing Assurance - The First 90 Days," Government of Alberta, 2010.

[15] "Investing in our Future: Responding to the Rapid Growth of Oil Sands Development. Section 5," Government of Alberta, 2006.

[16] C. Wang, D. Harbottle, Q. Liu, and Z. Xu, "Current state of fine mineral tailings treatment: A critical review on theory and practice," *Minerals Engineering,* vol. 58, pp. 113-131, 2014.

[17] R. J. Chalaturnyk, J. Don Scott, and B. Özüm, "Management of oil sands tailings," *Petroleum Science and Technology,* vol. 20, pp. 1025-1046, 2002.

[18] "Facts about Alberta’s oil sands - Tailings Management," Government of Alberta, 2014.

[19] "Oil sands tailings technology review," BGC Engineering Inc., 2010.

[20] "Tailings Management," Syncrude website. www.syncrude.ca.

[21] "Facts about Alberta's oil sands and its industry," Oil Sands Discovery Centre, 2014.

[22] D. L. Caughill, N. Morgenstern, and J. Scott, "Geotechnics of nonsegregating oil sand tailings," *Canadian Geotechnical Journal,* vol. 30, pp. 801-811, 1993.

[23] S. Renault, C. Lait, J. Zwiazek, and M. MacKinnon, "Effect of high salinity tailings waters produced from gypsum treatment of oil sands tailings on plants of the boreal forest," *Environmental Pollution,* vol. 102, pp. 177-184, 1998.

[24] Y. Xu, H. Hamza and J. Matthews, "Enlargement of fine particles in the oil sands industry - flocculation and thickening," in *Proceedings of the UBC-McGill Biennial International Symposium on Fundamentals of Mineral Processing,* 2004.

[25] H. Li, J. Long, Z. Xu, and J. H. Masliyah, "Synergetic Role of Polymer Flocculant in Low-Temperature Bitumen Extraction and Tailings Treatment," *Energy & Fuels,* vol. 19, pp. 936-943, 2005.

[26] N. Beier, W. Wilson, A. Dunmola, and D. Sego, "Impact of flocculation-based dewatering on the shear strength of oil sands fine tailings," *Canadian Geotechnical Journal,* vol. 50, pp. 1001-1007, 2013.

[27] Y. Deng, H. Xiao, and R. Pelton, "Temperature-sensitive flocculants based on poly (N-isopropylacrylamide-co-diallyldimethylammonium chloride)," *Journal of colloid and interface science,* vol. 179, pp. 188-193, 1996.

[28] H. Li, J. Long, Z. Xu, and J. H. Masliyah, "Flocculation of kaolinite clay suspensions using a temperature-sensitive polymer," *AIChE journal,* vol. 53, pp.

479-488, 2007.

[29] H. Ohshima and K. Furusawa, *Electrical Phenomena at Interfaces: Fundamentals: Measurements, and Applications* vol. 76: CRC Press, 1998.

[30] D. Fuerstenau, M. Fuerstenau, V. Lovell, R. King, S. Allison and P. Harris, "Principles of Flotation," *South African Institute of Mining and Metallurgy, Chapter 2,* 1982.

[31] R. Parsons, "The electrical double layer: recent experimental and theoretical developments," *Chemical Reviews,* vol. 90, pp. 813-826, 1990.

[32] J. H. Masliyah and S. Bhattacharjee, *Electrokinetic and colloid transport phenomena*: John Wiley & Sons, 2006.

[33] D. Henderson, "Recent progress in the theory of the electric double layer," *Progress in Surface Science,* vol. 13, pp. 197-224, 1983.

[34] R. Ifill and T. Etsell, "Enhanced settling of fine silica by direct AC electrocoagulation," *Mineral Processing and Extractive Metallurgy (Trans. Inst. Min. Metall. C),* vol. 122, pp. 137-145, 2013.

[35] M. Kwak, D. F. James, and K. A. Klein, "Flow behaviour of tailings paste for surface disposal," *International journal of mineral processing,* vol. 77, pp. 139-153, 2005.

[36] R. Zhu, Q. Liu, Z. Xu, J. H. Masliyah, and A. Khan, "Role of dissolving carbon dioxide in densification of oil sands tailings," *Energy & Fuels,* vol. 25, pp. 2049-2057, 2011.

[37] J. R. Bratby, "Coagulation and flocculation: with an emphasis on water and wastewater treatment," in *Coagulation and flocculation: with an emphasis on water and wastewater treatment*, ed: Uplands Press, 1980.

[38] V. O. Aseyev, H. Tenhu, and F. M. Winnik, "Temperature dependence of the colloidal stability of neutral amphiphilic polymers in water," in *Conformation-Dependent Design of Sequences in Copolymers II*, ed: Springer, 2006, pp. 1-85.

[39] J. C. Crittenden, R. R. Trussell, D. W. Hand, K. J. Howe, and G. Tchobanoglous, *MWH's Water Treatment: Principles and Design*: Wiley, 2012.

[40] B. Bolto and J. Gregory, "Organic polyelectrolytes in water treatment," *Water research,* vol. 41, pp. 2301-2324, 2007.

[41] J. Gregory and C. R. O'Melia, "Fundamentals of flocculation," *Critical Reviews in Environmental Science and Technology,* vol. 19, pp. 185-230, 1989.

[42] V. Aseyev, H. Tenhu, and F. M. Winnik, "Non-ionic thermo-responsive polymers in water," in *Self Organized Nanostructures of Amphiphilic Block Copolymers II*, ed: Springer, 2011, pp. 29-89.

[43] R. Ruehrwein and D. Ward, "Mechanism of clay aggregation by polyelectrolytes," *Soil Science,* vol. 73, pp. 485-492, 1952.

[44] M. Nasser and A. James, "The effect of polyacrylamide charge density and molecular weight on the flocculation and sedimentation behavior of kaolinite suspensions," *Separation and purification technology,* vol. 52, pp. 241-252, 2006.

[45] M. Hjorth, K. V. Christensen, M. L. Christensen, and S. G. Sommer, "Solid–liquid separation of animal slurry in theory and practice. A review," *Agronomy for sustainable development,* vol. 30, pp. 153-180, 2010.

[46] G. V. Franks, "Stimulant sensitive flocculation and consolidation for improved solid/liquid separation," *Journal of colloid and interface science,* vol. 292, pp. 598-603, 2005.

[47] D.-C. Wu, Y. Liu, and C.-B. He, "Thermal- and pH-responsive degradable polymers," *Macromolecules,* vol. 41, pp. 18-20, 2008.

[48] S. Y. Kim, S. M. Cho, Y. M. Lee, and S. J. Kim, "Thermo- and pH-responsive behaviors of graft copolymer and blend based on chitosan and N-isopropylacrylamide," *Journal of Applied Polymer Science,* vol. 78, pp. 1381-1391, 2000.

[49] H. Li, J. Long, Z. Xu, and J. H. Masliyah, "Flocculation of kaolinite clay suspensions using a temperature-sensitive polymer," *AIChE journal,* vol. 53, pp. 479-488, 2007.

[50] J. Long, H. Li, Z. Xu, and J. H. Masliyah, "Improving oil sands processability using a temperature-sensitive polymer," *Energy & Fuels,* vol. 25, pp. 701-707, 2011.

[51] S. Dai, P. Ravi, and K. C. Tam, "pH-Responsive polymers: synthesis, properties and applications," *Soft Matter,* vol. 4, pp. 435-449, 2008.

[52] G. V. Franks, C. V. Sepulveda, and G. J. Jameson, "pH-sensitive flocculation:

Settling rates and sediment densities," *AIChE journal,* vol. 52, pp. 2774-2782, 2006.

[53] J.-P. O'Shea, G. G. Qiao, and G. V. Franks, "Temperature-responsive solid-liquid separations with charged block-copolymers of poly (N-isopropyl acryamide)," *Langmuir,* vol. 28, pp. 905-913, 2011.

[54] T. Mori, J. Tsubaki, J.-P. O'Shea, and G. V. Franks, "Hydrostatic pressure measurement for evaluation of particle dispersion and flocculation in slurries containing temperature-responsive polymers," *Chemical Engineering Science,* vol. 85, pp. 38-45, 2013.

[55] H. Li, J. P. O'Shea, and G. V. Franks, "Effect of molecular weight of poly (N-isopropyl acrylamide) temperature-sensitive flocculants on dewatering," *AIChE journal,* vol. 55, pp. 2070-2080, 2009.

[56] J.-P. O'Shea, G. G. Qiao, and G. V. Franks, "Solid–liquid separations with a temperature-responsive polymeric flocculant: effect of temperature and molecular weight on polymer adsorption and deposition," *Journal of colloid and interface science,* vol. 348, pp. 9-23, 2010.

[57] N. Orakdogen, "pH-responsive swelling behavior, elasticity and molecular characteristics of poly (N, N-dimethylaminoethyl methacrylate) gels at various initial monomer concentrations," *Polymer bulletin,* vol. 67, pp. 1347-1366, 2011.

[58] D. Han, X. Tong, O. Boissière, and Y. Zhao, "General strategy for making $CO_2$-switchable polymers," *ACS Macro Letters,* vol. 1, pp. 57-61, 2011.

[59] P. van de Wetering, N. J. Zuidam, M. J. van Steenbergen, O. A. G. J. van der Houwen, W. J. M. Underberg, and W. E. Hennink, "A Mechanistic Study of the Hydrolytic Stability of Poly(2-(dimethylamino)ethyl methacrylate)," *Macromolecules*, vol. 31, pp. 8063-8068, 1998.

[60] K. Yasuda, K. Okajima, and K. Kamide, "Study on Alkaline Hydrolysis of Polyacrylamide by 13C NMR," *Polymer journal*, vol. 20, pp. 1101-1107, 1988.

[61] K. C. Taylor and H. A. Nasr-El-Din, "Acrylamide copolymers: A review of methods for the determination of concentration and degree of hydrolysis," *Journal of Petroleum Science and Engineering*, vol. 12, pp. 9-23, 1994.

[62] S. Sakohara and K. Nishikawa, "Flocculation and compaction of highly concentrated suspension by using thermo-sensitive polymers," *Kagaku Kogaku Ronbunshu,* vol. 26, pp. 298-304, 2000.

[63] S. McDonald and S. P. Rannard, "Room temperature waterborne ATRP of n-butyl methacrylate in homogeneous alcoholic media," *Macromolecules,* vol. 34, pp. 8600-8602, 2001.

[64] R. J. Young and P. A. Lovell, *Introduction to polymers* vol. 2: Chapman & Hall London, 1991.

[65] G. Robinson, S. B. Ross-Murphy, and E. R. Morris, "Viscosity-molecular weight relationships, intrinsic chain flexibility, and dynamic solution properties of guar galactomannan," *Carbohydrate Research,* vol. 107, pp. 17-32, 1982.

[66] C. Giacomelli, L. Le Men, R. Borsali, J. Lai-Kee-Him, A. Brisson, S. P.

Armes, "Phosphorylcholine-based pH-responsive diblock copolymer micelles as drug delivery vehicles: light scattering, electron microscopy, and fluorescence experiments," *Biomacromolecules,* vol. 7, pp. 817-828, 2006.

[67] W. Lin, Z. Wang, and S. Chen, "Zwitterionic polymers for targeted drug delivery," *Functional Polymers for Nanomedicine,* pp. 227, 2013.

[68] Y.-J. Shih, C.-W. Tsai, L. L. Tayo, and Y. Chang, "Zwitterionic nanocarriers for gene delivery," in *Intracellular Delivery II*, ed: Springer, pp. 35-53, 2014.

[69] M. Bernards and Y. He, "Polyampholyte polymers as a versatile zwitterionic biomaterial platform," *Journal of Biomaterials Science, Polymer Edition,* vol. 25, pp. 1479-1488, 2014.

[70] J. Hu and S. Liu, "Responsive polymers for detection and sensing applications: current status and future developments," *Macromolecules,* vol. 43, pp. 8315-8330, 2010.

[71] S. Chen, S. Chen, S. Jiang, M. Xiong, J. Luo, J. Tang*, et al.*, "Environmentally friendly antibacterial cotton textiles finished with siloxane sulfopropylbetaine," *ACS Applied Materials & Interfaces,* vol. 3, pp. 1154-1162, 2011.

[72] F. Cao, L. Tan, L. Xiang, S. Liu, and Y. Wang, "Application of the copolymers containing sulfobetaine methacrylate in protein separation by capillary electrophoresis," *Journal of Biomaterials Science, Polymer Edition,* vol. 24, pp. 2058-2070, 2013.

[73] T. Bai, F. Sun, L. Zhang, A. Sinclair, S. Liu, J. R. Ella-Menye*, et al.*, "Restraint of the differentiation of mesenchymal stem cells by a nonfouling zwitterionic hydrogel," *Angewandte Chemie,* 2014.

[74] H. Yu, Y. Cao, G. Kang, J. Liu, M. Li, and Q. Yuan, "Enhancing antifouling property of polysulfone ultrafiltration membrane by grafting zwitterionic copolymer via UV-initiated polymerization," *Journal of Membrane Science,* vol. 342, pp. 6-13, 2009.

[75] Y. Chang, W. Yandi, W.-Y. Chen, Y.-J. Shih, C.-C. Yang, Y. Chang*, et al.*, "Tunable bioadhesive copolymer hydrogels of thermo-responsive poly(N-isopropyl acrylamide) containing zwitterionic polysulfobetaine," *Biomacromolecules,* vol. 11, pp. 1101-1110, 2010.

[76] Q. Shi, Y. Su, W. Zhao, C. Li, Y. Hu, Z. Jiang*, et al.*, "Zwitterionic polyethersulfone ultrafiltration membrane with superior antifouling property," *Journal of Membrane Science,* vol. 319, pp. 271-278, 2008.

[77] B. Cao, Q. Tang, L. Li, C.-J. Lee, H. Wang, Y. Zhang*, et al.*, "Integrated zwitterionic conjugated poly (carboxybetaine thiophene) as a new biomaterial platform," *Chem. Sci.,* 2014.

[78] S. Chen, S. Chen, S. Jiang, Y. Mo, J. Luo, J. Tang*, et al.*, "Study of zwitterionic sulfopropylbetaine containing reactive siloxanes for application in antibacterial materials," *Colloids and Surfaces B: Biointerfaces,* vol. 85, pp. 323-329, 2011.

[79] Q. Zhou, X.-P. Lei, J.-H. Li, B.-F. Yan, and Q.-Q. Zhang, "Antifouling, adsorption and reversible flux properties of zwitterionic grafted PVDF membrane prepared via physisorbed free radical polymerization," *Desalination,* vol. 337, pp. 6-15, 2014.

[80] Y. Chang, S. Chen, Z. Zhang, and S. Jiang, "Highly protein-resistant coatings from well-defined diblock copolymers containing sulfobetaines," *Langmuir,* vol. 22, pp. 2222-2226, 2006.

[81] O. J. Cayre, N. Chagneux, and S. Biggs, "Stimulus responsive core-shell nanoparticles: synthesis and applications of polymer based aqueous systems," *Soft Matter,* vol. 7, pp. 2211-2234, 2011.

[82] F. Xuan and J. Liu, "Preparation, characterization and application of zwitterionic polymers and membranes: current developments and perspective," *Polymer International,* vol. 58, pp. 1350-1361, 2009.

[83] M. A. C. Stuart, W. T. Huck, J. Genzer, M. Müller, C. Ober, M. Stamm*, et al.*, "Emerging applications of stimuli-responsive polymer materials," *Nature materials,* vol. 9, pp. 101-113, 2010.

[84] L. Mi, M. T. Bernards, G. Cheng, Q. Yu, and S. Jiang, "pH-responsive properties of non-fouling mixed-charge polymer brushes based on quaternary amine and carboxylic acid monomers," *Biomaterials,* vol. 31, pp. 2919-2925, 2010.

[85] C. S. Patrickios, L. R. Sharma, S. P. Armes, and N. C. Billingham,

"Precipitation of a water-soluble ABC triblock methacrylic polyampholyte: effects of time, pH, polymer concentration, salt type and concentration, and presence of a protein," *Langmuir,* vol. 15, pp. 1613-1620, 1999.

[86] C. Patrickios, S. Gadam, S. Cramer, W. Hertler, and T. Hatton, "Block methacrylic polyampholytes as protein displacers in ion-exchange chromatography," *Biotechnology progress,* vol. 11, pp. 33-38, 1995.

[87] V. Bütün, S. Liu, J. Weaver, X. Bories-Azeau, Y. Cai, and S. Armes, "A brief review of ‘schizophrenic’ block copolymers," *Reactive and Functional Polymers,* vol. 66, pp. 157-165, 2006.

[88] S. Liu and S. P. Armes, "Polymeric surfactants for the new millennium: A pH-responsive, zwitterionic, schizophrenic diblock copolymer," *Angewandte Chemie International Edition,* vol. 41, pp. 1413-1416, 2002.

[89] Z. Xiong, B. Peng, X. Han, C. Peng, H. Liu, and Y. Hu, "Dual-stimuli responsive behaviors of diblock polyampholyte PDMAEMA-b-PAA in aqueous solution," *Journal of colloid and interface science,* vol. 356, pp. 557-565, 2011.

[90] B. Mao, L. Gan, Y. Gan, K. Tam, and O. Tan, "Controlled one-pot synthesis of pH-sensitive self-assembled diblock copolymers and their aggregation behavior," *Polymer,* vol. 46, pp. 10045-10055, 2005.

[91] S. Dai, P. Ravi, K. C. Tam, B. Mao, and L. Gan, "Novel pH-responsive amphiphilic diblock copolymers with reversible micellization properties," *Langmuir,* vol. 19, pp. 5175-5177, 2003.

[92] A. B Lowe and S. P Armes, "Synthesis and aqueous solution properties of novel zwitterionic block copolymers," *Chemical Communications,* pp. 1035-1036, 1997.

[93] X. Han, X. Zhang, H. Zhu, Q. Yin, H. Liu, and Y. Hu, "Effect of composition of PDMAEMA-b-PAA block copolymers on their pH- and temperature-responsive behaviors," *Langmuir,* vol. 29, pp. 1024-1034, 2013.

[94] X. D. Tang, Y. Chen, F. Q. Yu, and M. S. Pei, "Novel pH-responsive triply hydrophilic block copolymer with reversible micellization property," *Solid State Phenomena,* vol. 181, pp. 88-91, 2012.

[95] T. A. Wielema and J. B. Engberts, "An ESR spin label study of the dynamics of a zwitterionic polymer, a polyelectrolyte, poly (methacrylic acid) and poly (acrylic acid) in aqueous solution," *European polymer journal,* vol. 24, pp. 647-650, 1988.

[96] P. Busch, K. Giede, H. Hoeffkes, L. Schieferstein, and K. Seidel, "Zwitterionic polymers and their use in hair treatment preparations," ed: Google Patents, 1989.

[97] A. E. Sherry, "Use and application of defined zwitterionic copolymer," ed: Google Patents, 2013.

[98] J. Liu, Y. Ma, T. Xu, and G. Shao, "Preparation of zwitterionic hybrid polymer and its application for the removal of heavy metal ions from water," *Journal of hazardous materials,* vol. 178, pp. 1021-1029, 2010.

[99] M. Balastre, R. Crooks, and C.-T. Vuong, "Copolymer containing zwitterionic units and other units, composition comprising the copolymer, and use," ed: Google Patents, 2014.

[100] Z. Gui, J. Qian, Q. An, H. Xu, and Q. Zhao, "Synthesis, characterization and flocculation performance of zwitterionic copolymer of acrylamide and 4-vinylpyridine propylsulfobetaine," *European Polymer Journal,* vol. 45, pp. 1403-1411, 2009.

[101] H. Chen, Z. M. Wang, Z. B. Ye, and L. J. Han, "The solution behavior of hydrophobically associating zwitterionic polymer in salt water," *Journal of Applied Polymer Science,* vol. 131, 2014.

[102] H. Zheng, Y. Sun, J. Guo, F. Li, W. Fan, Y. Liao*, et al.*, "Characterization and evaluation of dewatering properties of PADB, a highly efficient cationic flocculant," *Industrial & Engineering Chemistry Research,* vol. 53, pp. 2572-2582, 2014.

[103] Y. Phadungchewit, "The role of pH and soil buffer capacity in heavy metal retention in clay soils," *Doctoral Dissertation,* McGill University, 1990.

[104] M. Kwak, D. F. James, and K. A. Klein, "Flow behaviour of tailings paste for surface disposal," *International journal of mineral processing,* vol. 77, pp. 139-153, 2005.

[105] N. Q. Dzuy and D. Boger, "Direct yield stress measurement with the vane method," *Journal of Rheology (1978-present),* vol. 29, pp. 335-347, 1985.

[106] H. A. Barnes and Q. D. Nguyen, "Rotating vane rheometry—a review," *Journal of Non-Newtonian Fluid Mechanics,* vol. 98, pp. 1-14, 2001.

[107] S. K. Gawu and A. Fourie, "Assessment of the modified slump test as a measure of the yield stress of high-density thickened tailings," *Canadian geotechnical journal,* vol. 41, pp. 39-47, 2004.

[108] L. Alagha, S. Wang, Z. Xu, and J. Masliyah, "Adsorption kinetics of a novel organic–inorganic hybrid polymer on silica and alumina studied by quartz crystal microbalance," *The Journal of Physical Chemistry C,* vol. 115, pp. 15390-15402, 2011.

[109] L. Alagha, S. Wang, L. Yan, Z. Xu, and J. Masliyah, "Probing adsorption of polyacrylamide-based polymers on anisotropic basal planes of kaolinite using quartz crystal microbalance," *Langmuir,* vol. 29, pp. 3989-3998, 2013.

[110] M. A. Plunkett, Z. Wang, M. W. Rutland, and D. Johannsmann, "Adsorption of pNIPAM layers on hydrophobic gold surfaces, measured in situ by QCM and SPR," *Langmuir,* vol. 19, pp. 6837-6844, 2003.