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# Synthesis of Integrated Polymers for Soil Stabilization

Dissertação para obtenção do Grau de Mestre em Engenharia Química e Bioquímica

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**"Be so good they can't ignore you"**

**Steve Martin**

**À memória da minha avó!**

**Ao meu pai e à minha mãe!**

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## Abstract

In this work, the synthesis of vinylpyrrolidone- (VP), vinyl acetate- (VA) and acrylamide- (AM) based polymers and copolymers was developed with a view to their application as drilling fluids. P(VP-co-VA), P(AM-co-VA) and P(AM-co-VP) were synthesized with different monomer ratio (87-13%, 75-25% and 50-50%) in water with the aim of obtaining a copolymer which is: (1) water soluble in a ratio of 1 g per liter of water (2) and able to exhibit a viscosity value ≥ 55 s/quart. The material fulfilling these requirements may be applied as (i) a main compound or as (ii) an additive for drilling fluids. All viscosity measurements were performed in a Marsh funnel as preliminary tests to select which was the best candidate polymer for the previous objectives. The chemical composition of all polymers and copolymers was investigated by FTIR-ATR or/and solid state $^{13}C$ NMR to ensure the success of polymerization. Polymers and copolymers which achieved the previously mentioned requisites (1) and (2) were characterized by scanning electron microscopy (SEM), zeta potential and their molecular weight was determined in an Ubbelohde type I Capillar viscometer. Partially hydrolyzed P(AM-co-VA) with a weight monomer ratio of 75-25% of acrylamide and VP, respectively, and partially hydrolyzed P(AM-co-VP) with a weight monomer ratio of 87-13% of acrylamide and VP, respectively, showed a viscosity of 56 s/quart in water, gathering all needed conditions to be evaluated according to suspension and settling tests with soil. These suspension and settling tests were performed with clay in distilled-deionized and tap water.

P(AM-co-VA) were not able to suspend clay neither as main viscosifier nor as additive. P(AM-co-VP) did not reveal suspending clay capacity as main viscosifier, but when 1g of copolymer is added to one liter of PolyMud® solution (1 g/L) comprising distilled-deionized water, 100% of soil suspension was reached over a period of 24 hours. When tap water was used, P(AM-co-VP) exhibited the best performance by keeping in suspension 90% of the total clay present in solution over 24 hours.

In addition, PVP was successfully used as additive to a PolyMud® solution (1 g/L), comprising distilled-deionized water, exhibiting in suspension capacity of 90% of the total clay during 24 hours.

**Keywords:** vinylpyrrolidone; acrylamide; vinyl acetate; polymerization; suspension; soil stabilization;

## Resumo

Neste trabalho desenvolveram-se polímeros e copolímeros com base nos monómeros de vinilpirrolidona (VP), acetato de vinila (VA) e acrilamida (AM) com vista à sua aplicação em perfuração de solos. Estudaram-se as sínteses dos polímeros de vinilpirrolidona (PVP), de poliacetato de vinila (PVA) e dos copolímeros P(VP-co-VA), P(AM-co-VA) e P(AM-co-VP) com diferentes rácios de monómeros (87-13%, 75-25% e 50-50%) em meio aquoso, com o objetivo de se obter um material com as seguintes características: (1) solúvel em água num rácio de 1 grama por litro de água e (2) passível de atingir uma viscosidade superior a 55 s/quart nesse mesmo rácio. Uma vez atingidas estas propriedades, o material pode ser usado como: (i) agente viscosificante principal, ou (i) como agente aditivo. Todas as medições de viscosidade foram efetuadas num funil de Marsh como medida preliminar para a seleção do melhor candidato a preencher todos os referidos objetivos. A composição química dos os polímeros e copolímeros foi estudada por FTIR-ATR e/ou $^{13}$C NMR no estado sólido. Os polímeros e copolímeros que completaram os requisitos (1) e (2) mencionados, foram também caracterizados por microscopia eletrónica de varrimento (SEM), potencial zeta e determinação de peso molecular por um viscosímetro capilar Ubbelohde do tipo I. O P(AM-co-VA) com a composição 75% de AM e 25% de VA, parcialmente hidrolisado, e o P(AM-co-VP) com a composição 87% de AM e 13% de VP, parcialmente hidrolisado, apresentaram uma viscosidade de 56 s/quart em água, reunindo assim todas as condições necessárias para que pudessem ser testados com solo, por forma a avaliar as suas capacidades de suspensão ou decantação em água destilada e desionizada ou em água da torneira.

O copolímero P(AM-co-VA) não conseguiu suspender argilas como agente viscosificante principal nem como aditivo. O copolímero P(AM-co-VP) não revelou capacidade em suspender argilas como agente viscosificante principal, no entanto, quando 1 g deste composto é adicionado a uma solução de PolyMud® em água destilada e desionizada com uma concentração de 1 g/L conseguiu reter toda a argila em suspensão durante 24 horas. Contudo, quando água da torneira é utilizada, o copolímero P(AM-co-VA) consegue suspender cerca de 90% da quantidade total de argila durante 24 horas, quando usado como aditivo nas mesmas condições.

Adicionalmente, o PVP foi utilizado com sucesso como aditivo para uma solução PolyMud® em água destilada e desionizada (1 g/L), conseguindo manter em suspensão 90% da quantidade de argila inicial durante 24 horas.

**Palavras-chave:** vinilpirrolidona; acrilamida; vinil acetato; polimerização; suspensão; estabilização de solos.

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**Abbreviations**

AM – acrylamide

AIBN – 2,2’-azobisisobutyro-nitrile

CaO – calcium oxide

$CaSO_4$ – calcium sulfate

cP – centipoises

CPC – critical polymer concentration

$CO_2$ – carbon dioxide

dd_water – distilled-deionized water

FTIR-ATR – attenuated total reflectance Fourier transform infrared spectroscopy

$g/m^3$ – gram per cubic meter

h - hour

HD – hydrolysis degree

HPAM – partially hydrolyzed polyacrylamide

KCl – potassium chloride

kJ/mol – Kilojoule per mole

KOH – potassium hydroxide

M – mol/L (number of moles in one liter, molar concentration)

$MgSO_4$ – magnesium sulfate

$Na^+$ - sodium cation

NaHLS – sodium hydroxymethyl lignosulfate

NaLS – sodium lignosulfonate

$n_{NaOH}/n_{AM}$ –molar quantity of NaOH to molar quantity of acrylamide ratio

$n_{NaOH}/n_{VA}$ –molar quantity of NaOH to molar quantity of vinyl acetate ratio

$n_{NaOH}/n_{VP}$ –molar quantity of NaOH to molar quantity of vinylpyrrolidone ratio

NaOH – sodium hydroxide

NaPS – sodium persulfate

NMR – nuclear magnetic resonance

$OH^-$ - hydroxide anion

P(AM-co-VA) – poly(acrylamide-co-vinyl acetate)

P(AM-co-VP) – poly(acrylamide-co-vinylpyrrolidone)

P(VP-co-VA) – poly(vinylpyrrolidone-co-vinyl acetate)

PAM – polyacrylamide

PEI – polyethyleneimine

PolyGMAc – glycerol polymonoacrylate

PolyGMMA – glycerol polymethacrylate

PVA – poly(vinyl alcohol)

PVAc – poly(vinyl acetate)

PVP – polyvinylpyrrolidone

rpm – rotations per minute

s/quart – second per quart

scCO$_2$ – supercritical carbon dioxide

SEM – scanning electron microscopy

$t_{1/2}$ – half-life time

Tg – glass transition temperature

v/v – volume to volume ratio, % percentage by volume

VA – vinyl acetate

VP – vinylpyrrolidone

$w_{init}/w_{mon}$ – weight of initiator to weight of monomer ratio

w/w – weight to weight ratio, % percentage by weight

WBFs – water-based fluids

# Chapter 1.

## 1. Introduction

The social and urban development that we have witnessed in recent decades is leading to huge architectural and structural challenges all over the world. However, for enormous constructions, deep and larger foundations must be constructed, otherwise integrity may be compromised and catastrophic situations arise. Therefore, it is paramount to provide adequate soil stabilization during execution of any foundation element. On the other hand, social and urban development requires an increase in energetic needs and consequently an increase in fossil fuels. Then, deep holes must be opened on the earth's surface in increasingly harshest sites. Herein, the main focus is the soil stabilization under slurry during and after boring, drilling or excavating conditions for foundation constructions and for oil recovery.

## 1.1. General concepts about soil stabilization

Soil stabilization is a method used to improve soil strength, bearing capacity and durability under adverse moisture and stress conditions [1]. This stabilization can be performed by mechanical or chemical methods, to create an improved soil material with the desired properties. Soil stabilization can be applied in a wide range of fields, such as agriculture [2], roads [3], construction of foundations [4], and oil drilling [5][6].

Soil stabilization methods can be characterized by the type or procedure of fluid used to improve the physical properties of soil. The common changes are related to strength, permeability and stability of soil [5]. In detail, these methods can be divided in three main groups: granular, thermal and electro kinetic, and chemical stabilization.

### 1.1.1. Soil stabilization for foundations

Great foundations can be accomplished with an efficient foundation or borehole with excellent walls stability. Foundation or borehole stability is a critical factor in improving drilling efficiency while minimizing problem costs associated with well construction and foundation [7][8]. Hole stability can be defined by the conditions under which the soil surrounding the hole will start to flop [8][9]. Shear strength is a property that enables a material to stay in equilibrium when its surface is not horizontal. The shear strength is the maximum resistance that a soil or rock can take against shear stress. This property differs in each soil or rock type. For soils this is not a constant value and can vary with: (i) water and air content, (ii) depth below the surface, and (iii) methods used for stabilization. These methods are used for stabilization since provide supporting ability and bearing capacity, and allow walls to be stable and cohesive [10]. Nevertheless, foundation and borehole stability is not only related to mechanical or economic issues, since the interaction between soil and drilling fluid is a crucial factor [10].

Interactions between soil, water and admixtures agents are of great importance of study. A soil with a low water percentage will be coherent and dense. Thus, increasing the water content, its consistency may change from solid to plastic and even to liquid which cause swelling, loss of strength and cohesion of the soil. For example, the cohesion of some clays depends on the affinity of the mineral surfaces to water and their interaction with it. Thus, when this affinity is compromised, it may result in the destruction of the desirable soil cohesion, which lead to the need of soil conditioners addition. The diffuse double-layer thickness of the clay particles, the concentration and size of particles, valence of ions near particle surface, and the position of water molecules in soil structure, may affect the behavior of cohesive soils. [11][12]

Thus, it is fundamental to use a drilling fluid in order to keep controlled the interactions of soil particles and water, and consequently, all soil particles.

### 1.1.2. Drilling Fluids

A drilling fluid is an aqueous solution of soil conditioners. Drilling fluids or drilling muds, are used in the drilling of wells for the recovery of oil, gas, water or in foundations. The drilling fluids represent 15 to 18% of the total cost of petroleum well drilling [13]. For decades these fluids were clay based usually including a mixture of water, clay, weighting material and a few other chemicals. Nowadays, the composition strays form allow the inclusion of many synthetic forms that are compatible with the environment. As an example, some desirable properties, such as density, may be provided to a fluid by replacing the water with oil, or alternatively adding oil to the water [14].

The chemical and mechanical properties of soil can be highly changed after contacting with the drilling fluid.

Rotary drilling requires a method of fluid circulation to clear cuttings from the borehole. This method is classified by the type of drilling fluid used and/or the way the fluid is circulated through the borehole. The two most common methods are: (1) direct circulation, which consists in recirculate the fluid down through a hollow drill pipe, across the face of the drill bit, and upward through the drill hole, the water absorption increases and the diffusion layer of rock particles will thicken, which will increase hydration leading to an increase of volume, producing swelling stress [10]. In reverse circulation, the fluid flows from the mud pit down the borehole outside the drill rods and passes upward through the bit. Cuttings are carried into the drill rods and discharged back into the mud pit [15]. Also in drilling of pile foundations, a drilling fluid is needed to support the walls of the bored pile. However, the action of soil around the bored pile in sands and clays are different [16]. Thus, several types of drilling fluids can be used to modify some properties of each type of soil such as water sensitivity, volume change, strength, stiffness, compressibility, permeability, swelling or workability [11].

The drilling fluid also serves to cool and lubricate the drill bit, to raise the cuttings to the surface for disposal and to deal the sides of the well to prevent loss of the drilling fluid into the formation surrounding the drill hole. The drilling fluid must have both proper viscosity (6% of a high-quality bentonite (w/w) gives around 85 s/quart of viscosity in a Marsh Funnel [17]) and some degree of gelation to carry the drilled solids to the surface, over a screen to remove the large chips, and to remove sands in the settling basin [18]. In cases in which high gas pressure is encountered, it is often necessary to add a material which increase the specific gravity of the drilling mud in order to increase its weight and hold down the gas pressure. In case sandy or slough formation are encountered, it is necessary to use a material with a high colloidal dispersion to produce a viscous mud which, by filtration through the walls of the drilled hole, will provide a waterproof or substantially waterproof coating along the walls of the drilled holes. This will prevent the loss of drilling mud to the surrounding formations hence the migration of water or slough the surrounding formations into the hole, avoiding collapses [19].

As already mentioned during drilling operations, the walls of the rock, in particular of water-sensitive argillaceous rocks, have a tendency to swell. The swelling can interfere with the flow of the fluid or the passage of the drilling tool, disintegrating the drilled hole. When argillaceous material is disintegrated and is released into the fluid, problems related to the control of drilling fluid viscosity may appear. Furthermore, cleared argillaceous rocks may aggregate together in the drilling mud, affecting the fluids circulation and mechanically block the drilling head [20]. Swelling can only be overcome by using non water-based fluids or by treating the mud with chemicals which will reduce the ability of the water in the mud to hydrate the clays in the construction (inhibitors). These fluids are known as inhibited fluids (ex: salts or products based salts) [21][22]. Clark *et al*. 1976 [23] developed a mud for drilling water sensitive shale's containing a high molecular-weight, partially hydrolyzed polyacrylamide and potassium chloride, as a inhibited fluid.

The possible combinations to accomplish a drilling fluid can be endless. Each drilling fluid is different from another, and it is desirable to have a drilling fluid able to meet as many properties as possible, such as viscosifiers and pH control agents, in order to fill all needs in soil stabilization processes.

### 1.1.3. Type of drilling fluids

#### 1.1.3.1. Water-based fluids

Water-based fluids (WBFs) are the most widely used systems, and are considered less expensive than oil-based fluids or synthetic-based fluids (synthetic means that these fluids come from industrial processes rather than being found in nature. An example of this is related to paraffin's synthesized by Fischer-Tropsch reaction [14][24]. The oil- or synthetic-based fluids, also known as invert-emulsion systems, have an oil or synthetic base as the continuous phase and brine as the internal phase. Invert-emulsion systems have a higher cost per unit than most water-based fluids because of solvent cost, so they often are selected when wall conditions call for reliable shale inhibition or excellent lubricity. Water-based systems and invert-emulsion systems can be formulated to tolerate relatively high drill temperatures (above 60 °C) [25]. WBFs are used to drill approximately 80% of all wells [26]. The base fluid may be fresh water, seawater, brine or saturated brine. The type of fluid selected depends on anticipated well conditions or on the specific interval of the well being drilled.

WBFs fall into two broad categories and two subcategories: non-dispersed and dispersed systems using or not material able of clay inhibition

- Dispersed fluids – Contain chemical thinners or dispersants to effect flow control.
- Non-dispersed fluids – Do not contain any chemical thinner or dispersant in their composition.
- Inhibited fluids – These kind of fluids can contain high salt concentration in their composition [23][27] or other kind of material competent to inhibit clay swelling in shale formations [21][22]
- Non-inhibited fluids – Do not contain any material capable of inhibit clay swelling.

#### 1.1.3.2. Oil-based fluids

Oil-based fluids were developed and introduced to help address several drilling problems as the formation of clays that react, swell or slough after exposure to water-based fluids or contaminants. Nowadays, oil-based fluids are formulated with diesel, mineral oil, or low-toxicity linear olefin and cyclic paraffin [14][28]. The electrical stability of the water phase is monitored to ensure that the strength of the emulsion is maintained at or near a specific value [14]. For example, in oil-based systems, barite is used to increase system density, and specially-treated organophilic bentonite is the primary viscosifier. The ratio of the oil percentage to the water percentage in the liquid phase of an oil-based system ranges from 65/35 to 95/5 [14][29][30].

Oil-based fluids are being replaced by low-toxicity linear olefins and cyclic paraffin (synthetic-based fluids) [28] and high low-toxicity performance water-based fluids with inhibited clay swelling properties [14].

### 1.1.4. Weighing/Densifiers materials

Weighing materials or densifiers are compounds that are dissolved or suspended in drilling fluids to: (i) equilibrate physical forces and pressure inside wells and, (ii) to decrease the effect of sloughing or heaving shale that may be found in stressed areas. Any material that is denser than water or oil and does not adversely affect any other property of the drilling fluid, can be used.

There are several types of materials that can be applied in this purpose.

#### 1.1.4.1. Barite and Galena

Barite (Figure 1.1) is a barium sulphate mineral with a density from 4.2 to 4.5 g/cm$^3$ and have been used to increase the density of drilling fluids since 1922 [31]. Galena (Figure 1.2) is a lead sulphite mineral with a high density approximately 7.5 g/cm$^3$.

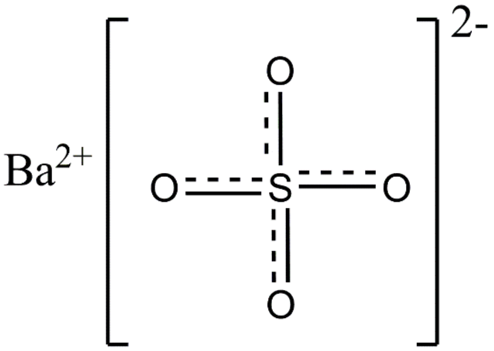

Figure 1.1 - Schematic representation of Barite

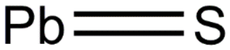

Figure 1.2- Schematic representation of Galena

J. Earley 1959 [32] developed a barite and galena weighing material for oil-based systems, with a particle size which 99% will preferably pass at least a 200 mesh screen. In order to carry all the barite in the emulsion phase, these particles of barite should have at least about 50% of its surface coated with an adsorbed layer of an organic material from the group of compounds represented by the general formulae $[RN^+H_2\ (CH_2)_3NH_3^+]\ [X^-]_2$ wherein R is selected from alkyl and alkene radical having about 12 to 18 carbon atoms, and X is an anion of an week organic acid and $[H_3N^+R]\ X^-$ wherein R is selected from an alkyl radical having about 8 to 15 carbon atoms and X is an anion of a weak organic acid. G. Miller *et al*. 1975 [33] developed an aqueous drilling fluid with weighing agents such as barite or galena. Both minerals are used in drilling fluids to increase their specific gravity [34]. Also, other authors refer Barite or Galena as preferred weighting agents to drilling fluids [30][35][36][37][38]. Later, Dhiman *et al*. 2012 [39] concluded that an increase of percentage of barite in a drilling fluid tends to increase the rheological properties of the fluid, such as, the correlation between flow behavior of the material and its internal structure. Barite and Galena are minerals used in water based drilling fluids or can also be treated and employed in oil based drilling fluids [33][37]. Nowadays, barite is still widely used as the standard weighting agent in the drilling fluid industry [40][41], and a proof of this, is the HALLIBURTON company that sell BAROID 41®, a product which contains barium sulfate that allow the increase mud density up to 2516 $Kg/m^3$ [42]. M-I BAR is another company that sell a barite weighing agent through a product named by CrisOil [43].

MESSINA INCORPORATED have a weighing material called HI-WATE® comprising an extreme density galena with a specific gravity between 7.0 and 7.5 [44].

#### 1.1.4.2. Iron Oxides

Stinson *et al*. 1942 [27] developed a new iron oxide weighting material with capacity to increase specific gravity of drilling muds. The process of producing iron oxide weighting materials involves:

(i) calcining pyrite cinder at a temperature of at least 982 °C, and (ii) in the presence of an alkali metal salt accelerating agent, reduce its sulfide and sulfate content to less than 5%, and water soluble compounds to less than 0.2%. This material possesses a high density, from 4 to 5 g/cm$^3$, fine particle size and cellular surface structure. Drilling muds containing iron oxides keep the most advantageous viscosity and do not allow rapid segregation of coarser fractions, packing or hard settling while maintain the drilling mud free of impurities with a pH slightly greater than 7. Later, Miller *et al*. 1975 [33] developed a substantially acid soluble aqueous sea water drilling fluid comprising calcium and magnesium compounds with a weighting agent such as iron oxide to adjust the mud weight. Recently, Todd 2002 [41] developed a drilling fluid comprising improved bridging agents to help remove the filter cake. This fluid can contain weighting material such as iron oxides. Also, some other authors refer to iron oxides as one of the preferably weighting agents to use in water based drilling fluids [20][30][37][38][39]

#### 1.1.4.2.1. Ilmenite and Hematite

Ilmenite and Hematite, with a repeating unit of $FeTiO_3$ and $\alpha\text{-}Fe_2O_3$ respectively, are specific iron oxide minerals. When compared to barite, these materials have relatively higher values of hardness[3], which can give some problems in drilling equipment [40][45]. However, they carry a greater specific gravity which reduce the amount needed to accomplish some density to the drilling fluids [40][46]. In detail, Bizanti *et al*. 1988 [46] shows that itabirite, a type of hematite mineral, needs lower solids content to obtain a desired weight when compared to barite. Moreover, itabirite exhibited better rheological properties, like the correlation between the flow behavior of material and its internal structure. However, worse filtration properties and abrasive problems in equipment can occur when this mineral is used [40]. These problems can be overcome with the addition of some filtration control agents like carboxymethyl cellulose [22] or using coating agents [40].

Later, Saasen *et al*. 2001 [47] and more recently, Tehrani *et al*. 2014 [40] affirmed that the use of Ilmenite is environmental safer than barite. The possibility of reduce solids content in drilling fluids decrease the impact of the weight material on fluid rheology. Also Dhiman *et al*. 2012 [39] tested two samples of a mud comprising 10% by weight of barite and hematite. Hematite mud showed an increase of 7% in density, 19% in plastic viscosity, 57% in yield point and 77% in gel strength compared to barite mud. This statement was also emphasized by other authors that refer Ilmenite and Hematite as possible weighing agents [30][40][48]

Commercially, iron oxide weighting agent, based on hematite, is sold by CrisOil company through the product FER OX® (with a specific gravity of at least 5) [43].

Hi-Dense® No.5 is a weigh additive comprising Ilmenite with approximately 80% of the particles are 325 mesh or smaller. This product is sold by HALLIBURTON [42].

#### 1.1.4.2.2. Dolomite

Dolomite, with a repeating unit of $CaMg(CO_3)_2$, is a mineral based on a calcium or magnesium carbonates with a density between 2.8 and 2.9 g/cm$^3$. Miller *et al*. 1975 [33] claims a water drilling fluid with about 190 to about 665 Kg/m$^3$ of solids content comprising 30 to 70 percent by weight of dolomite with about 20 to 60 percent by weight of magnesium sulfate and small amounts of calcium or magnesium oxide in a brine solution capable of being weighted to 1440 to 2400 Kg/m$^3$. As an example, a sea water drilling fluid comprising 190 Kg/m$^3$ of dolomite, 190 Kg/m$^3$ of MgSO4, 19 Kg/m$^3$ of CaSO4 and 19 Kg/m$^3$ of CaO, can reach an apparent viscosity of 20 centipoises (cP) and a plastic viscosity of 15 cP after hot rolling. This drilling fluid didn’t settle after aging. Lee *et al*. 2001[35] developed a glycol based aqueous drilling fluid with tuning density capacity by adding dolomite or any other conventional weighing agent. Dolomite as a weighing agent is not used as much as barite or other iron oxides like hematite but Cebo Holland B.V. report the use of this mineral as a weighing agent in their drilling fluids [48].

### 1.1.5. pH-control agents

Additives are used to optimize pH in water based drilling fluids. In almost all cases, it is important to maintain an alkaline pH in order to control many drilling fluids system properties. The pH also affects the solubility of many viscosifiers, some divalent ions such as calcium, and promote the dispersion or flocculation of clays (avoiding clay swelling). [49][50] An alkaline medium have a higher concentration of $OH^-$ groups in solution, deprotonating the OH groups of many viscosifiers.

#### 1.1.5.1. Caustic Soda

Caustic soda is the commercial name for sodium hydroxide (NaOH). It is a strong base which is largely soluble in water and dissociates into sodium ($Na^+$) and hydroxyl ion ($OH^-$) in solution. It is used in water-base muds as a source of hydroxyl ions to basify the solution. Cannon *et al*. 1935 [51] settled a drilling fluid for combating heaving shale with high alkaline level by means of caustic soda. Later, Scheuerman 1973 [23] developed a drilling process using a shale protective polymer drilling fluid system keeping the pH between 9.5 and 10.0 with addition of NaOH to the drilling fluid. Alaskari *et al*. 2007 [49] also tested drilling fluids behavior including carboxymethyl cellulose with pH variations between 8.96 and 12.58. The author used caustic soda to reach the optimum pH (12.58) to this drilling fluid.

### 1.1.6. Flocculating/deflocculating materials

These materials are one of the most important during drilling operations. Flocculation materials generally change the rheological properties of the fluid but their main function is to allow solids coagulation for further precipitation. On the other hand, deflocculating or dispersant materials hold up solid suspension.[52]

Dispersed systems are treated with chemical dispersants designed to deflocculate clay particles to improve the rheology control in higher density muds. Commonly used dispersed muds include lime and other cationic systems. A solids-laden dispersed system can decrease the rate of penetration significantly and contribute for the drilling hole erosion. [14]

Simple gel-and-water systems used for top hole drilling are non-disperse, as are many of the advanced polymer systems that contain little or no bentonite. A properly designed solids-control system can be used to remove fine solids from the mud system and help maintain drilling efficiency. The low-solids, non-disperse polymer systems rely on high and low molecular weight long chain polymers to provide viscosity and fluid-loss control. Low-colloidal solids are encapsulated and flocculated for more efficient removal at the surface, which in turn decreases dilution requirements.[49][52]

### 1.1.6.1. Modified Lignosulfonate

Various methods for the modification of lignosulfonates have been proposed. Reintjes *et al*.1988 [53] developed a modified lignosulfonate material capable of being used to preparing drilling fluid dispersant products with significantly improved performance and thermal properties. It could also be prepared from sulfonation of purified lignosulfonates by reaction with sulfite-bisulfite salts. Years later, Martyanova *et al*. 1997 described a method for the modification of lignosulfates by condensation with formaldehyde. Later, Ibragimov *et al*. 1998 founded a new method of lignosulfonate modification with iron salts. Therefore, chromium-modified lignosulfates are highly effective as dispersants and useful in controlling the viscosity of drilling fluids. However, because chromium is potentially toxic, less toxic substitutes are being developed by combining tin or cerium sulfate with an aqueous solution of calcium lignosulfonate (Figure 1.3), producing tin or cerium sulfonate and a solid calcium sulfate [48]. Later, Zhang *et al*. 2011 [54] prepared a sodium hydroxymethyl lignosulfate (NaHLS) by hydroxymethylation of sodium lignosulfonate (NaLS) to improve the performance as drilling fluid additive. Drilling fluids with NaLS as additive can achieve better rheology behavior, filtration loss reducer and clay inhibition ability. However, at 30°C, NaHLS can improve NaLS apparent viscosity in 31%, fluid loss control in 20% and reducing the thickness of mud cake in 60%.

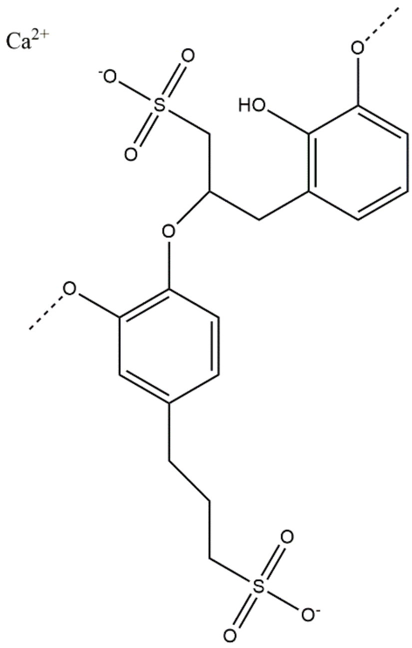

*Figure 1.3- A representative example of a calcium lignosulfate*

An example of this application is a commercial Chrome Lignosulfonate used as deflocculant and fluid loss control agent for water based mud systems. [55]

#### 1.1.6.2. Polyethyleneimine

The use of polymers to control the stability of clay dispersions and their flocculation, is of great technological importance. The system of drilling muds can be stabilized by the adsorption of polymers onto the surfaces of clay particles by rheology influence. Polyethyleneimine (PEI) (Figure 1.4) is a cationic polymer used as a stabilizer of industrial suspensions. PEI can be adsorbed on silicon dioxide, silicon carbide, iron oxide and zirconium dioxide. The PEI molecules are strongly adsorbed on the surface of clay minerals causing flocculation.

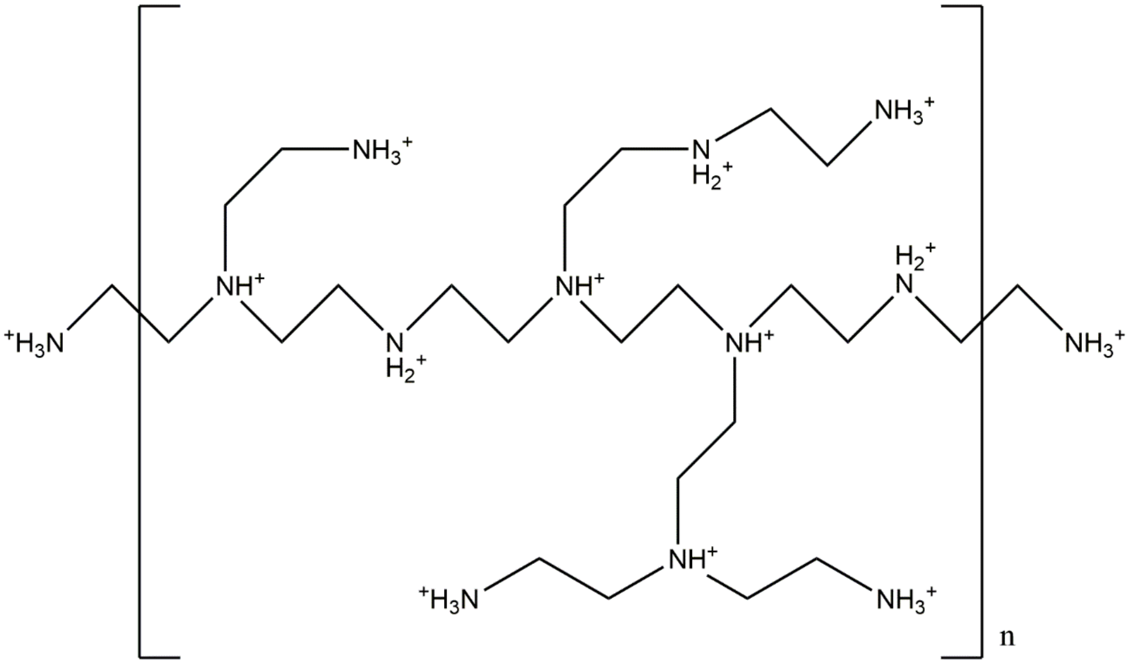

*Figure 1.4- Schematic structure of Polyethyleneimine*

Alemdar *et al*. 2005 [56] studied the influence of the cationic polymer, PEI on the flow behavior of bentonite suspensions (2% w/w). The suspension flocculates by the addition of PEI up to a concentration of 1 g/L and deflocculates at about PEI concentration of 4.5 g/L.

#### 1.1.6.3. Deflocculant agent

In the process of drilling a hole in the ground, as already said, one of the most common drilling fluid additive used is bentonite. During the drilling processes, there is a propensity for solids to stay suspended by drilling fluid. However, at the end of drilling it is needed to settle these solids before cementing. Bostyn *et al*. 2010 [57] presented an alternative method to separate undesirable contaminants from drilling fluids by adding a dispersing agent to cause contaminating solids and/or the bentonite or polymer particles to settle. As example of this application, from 50g to 2Kg of oligomer, polymer or copolymer should be added to 1 $m^3$ of slurry of bentonite particles having a specific weight from 1.01 to 1.40 $g/cm^3$ submitted to a settling/separation step for a period from 5 to 60 minutes, to let separate contaminating solids from said bentonite slurry.

### 1.1.7. Clay inhibitor material

Clay-inhibition materials should be used in clay drilling in order to inhibit clay swelling and avoid the collapse of drilled hole walls.

#### 1.1.7.1. Potassium Chloride

Clark *et al*. 1976 [58] developed a potassium-based polymer mud that has been successful controlling problems associated with drilling of water-sensitive shales. Polyacrylamide/potassium chloride system mud provides a superior and efficient protection to the clays when compared with other systems containing sodium chloride as salt or polynomic cellulose, polysaccharide, modified starch, polyethylene oxide or vinyl ether – vinylpyrrolidone copolymer in their compositions.

Years later, Anderson *et al*. 1979 [59] invented a drilling fluid comprising carboxymethyl-cellulose or similar as viscosifier, flaxseed gum and a salt of either potassium of ammonium with the intention of study the effect of various salts on the drilling of shale formations. The tests were made by submitting samples of shales to 16 hours of mechanical agitation, followed by filtering and weighting to determine the amount of shale remaining. After, the remainder was agitated for 2 hours and followed the same procedure of filtering and weighting as mentioned. The percentage of shale recovered demonstrates the effect stability of salt in the drilling mud. The results, for potassium chloride was 73.4% in the first step and 69.8% in the second step, higher than any other salt mentioned in this experiment. The concentration was 57 g/L of salt used.

Joel *et al*. 2012 [60] studied the effect of potassium chloride on rheological properties of a water based drilling fluid contaminated by various shale concentrations and reported that the use of potassium chloride in a 0.2%, 0.4%, 1%, 2% and 4% of concentration in a drilling fluid with 1%, 2%, 4%, 7% and 10% of shale respectively, resulted in a percentage reduction of viscosity of 0%, 36%, 60%, 94% and 181% relatively compared to results without KCl.

#### 1.1.7.2. Glycol and glycol derivatives

Twynam *et al*. 1994 [61] referred that an improvement of shale inhibition can be obtained by (i) choosing glycol or a glycol derivate (Figure 1.5) and, (ii) its concentration to meet such needs, but there isn't much information available. Years later, Lee *et al*. 2001 [35] developed an improved glycol based aqueous drilling fluid with demonstrated utility in controlling and reducing swelling clay formations. Author showed that a superior inhibition of bentonite clay swelling could be obtained at 70% or higher concentrations of diethylene glycol in water.78 inexpensive

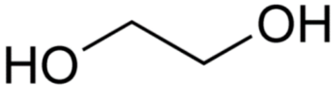

*Figure 1.5- Structural schematic of ethylene glycol*

### 1.1.7.3. Polyoxyalkyleneamine

Polyoxyalkyleneamines (Figure 1.6) are a general class of low-toxicity compounds that contain primary amino groups covalently connected to a polyether backbone.

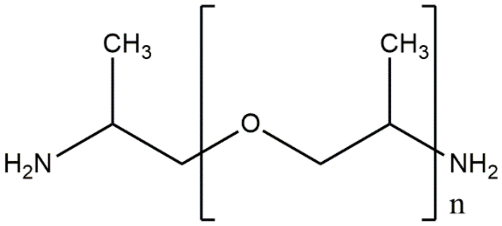

*Figure 1.6- Generic schematic structure of a Polyoxyalkyleneamine.*

Patel *et al*. 2002 [62] invented a drilling fluid comprising a swelling clay inhibitor, preferably a polyoxyalkyleneamine and monoamines. The quantity of shale hydration inhibition agent should be from 7 to 45 g/L of drilling fluid. The demonstration of the performance of the drilling fluid was given by various extensive tests, such as rheology measurement, yield point or plastic viscosity. Years later, Patel *et al*. 2007 [34] developed another water-based fluid for use in drilling wells where shale clays swells in the presence of water. The shale swelling inhibition agent in this fluid is the reaction product of a polyoxyalkylenediamine with an alkylene oxide. Full tests are also presented in the patent.

Qu *et al*. 2009 [21] tested and investigated the inhibitive property of polyoxyalkyleneamine in a sodium montmorillonite (bentonite) fluid and the test indicated that a 2 %(w/w) polyoxyalkyleneamine could supress the swelling of shales effectively in several water-based drilling fluids. Toxicity and compatibility tests of polyoxyalkyleneamine showed that this polymer was environmental-friendly and compatible with other drilling fluid additives.

### 1.1.8. Viscosifiers

### 1.1.8.1. Inorganic systems

### 1.1.8.1.1. Bentonite

Bentonite is an aluminum phyllosilicate clay absorbent consisting mostly in montmorillonite. There are a few types of bentonites depending on the dominant elements, such as K, Na, Ca and Al [63]. Montmorillonite is an agglomerate of lamellar platelets. Each platelet have three layers comprising a central octahedral alumina ($Al_2O_3$) layer, and two tetrahedral silica ($SiO_2$) layers. Each platelet can have its silicon and aluminum ion substituted by lower valence metals, such as magnesium and iron. To compensate this unbalance charges, calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$) and Sodium ($Na^+$) ions can stand outside the reticular structure with water molecules. This is the main cause of hydration in the crystal grid [64].

Bentonite has been the most widely used thickening agent. The solids content of a typical water based drilling fluid is 5-7% bentonite while the remain quantity are chemical additives and drilled solids [18]. Bentonite is able to generate high viscosity solutions with a small percentage in water, a relatively thin, but substantially waterproof, coating along the walls of the drilled hole which effectively walls off the surrounding formation and prevents loss of drilling mud to the surrounding formation. This consequently prevents infiltration or sloughing from the formation into the drill hole. Since bentonite is a colloidal material, it exhibits relatively low mechanical strength. Although it serves admirably the function of controlling the viscosity of the muds and of preventing the settling and segregation of cuttings in the hole, the protective coating on the walls of the hole formed by bentonite alone is not sufficiently dense in all instances to meet the practical conditions encountered, and occasionally leads to difficulties. This material is relatively expensive for this purpose, but the amount of bentonite employed in the drilling processes must assure the mechanical strength of the hole coating normally called cake or must be adjusted using other additives [19]. Clem 1978 [18] claimed a polymer obtained from the reaction of polyacrylic acid with 3-10 mole % calcium chloride to form a partially calcium salt of polyacrylic acid and/or a partial calcium salt of sodium polyacrylate. The resulted mixture was polymerized with soluble persulfate and/or a calcium chloride using 1-15% of the molar amount necessary to full neutralize the acrylic acid. The authors declare that the polymer obtained can be added to the drilling fluid in about 7-50% of the total weight of bentonite (the solids content of a water based drilling fluid of the present invention is in the range of about 5-7% bentonite) to achieve an excellent ultra-low solids drilling fluid. This allowed for a lower filtrate loss as low as drilling fluids with five times much solids. An addition of 0.907 Kg of polyacrylic acid to a ton of bentonite in 38 Kg/m$^3$ of Wyoming Bentonite can be reached 23.5 cP of apparent viscosity. Later, Lee *et al*. 2001 [35] reported that when 50g of bentonite are added to 350mL of a 50/50 mixture of diethylene glycol and water is possible to achieve an apparent viscosity of 77 cP. At commercial level, QUIK-GEL® Viscosifier is an efficient product composed by high-yielding Wyoming sodium bentonite sold by Halliburton [65].

#### 1.1.8.1.2. Attapulgite

Attapulgite is a non-swelling magnesium aluminum silicate mineral with a three-dimensional crystal structure with unique colloidal properties, especially resistance to high concentration of electrolytes [66]. Attapulgite can be used in drilling fluids with the primary function of removing bit cuttings from the drilling hole. In addition, this clay mineral lubricates the bit, prevents hole sloughing, forms impervious filter cake on the walls of the drilled hole, preventing fluid loss to porous material on the walls. The most important characteristic of this clay is the ability to build up a suitable viscosity at relatively low solid content without any loss of viscosity during the drilling of the well. In comparison to bentonite, it does not require any additional chemical treatment in areas where salts such as calcium sulfate or magnesium sulfate are encountered because these contaminants prevent bentonite swelling thus it is ineffective in yielding or maintaining viscosity in their presence. Attapulgite does not depend on swelling to build up viscosity and remains quite stable in the presence of these contaminants. Great stability can be also achieved under high temperature conditions [67][68].

Horton *et al*. 1968 [69] developed an improved gel-forming grade of attapulgite clay with a very low grit content (which passes through 60 or 150 mesh). This attapulgite improvement results in a viscosity at 25°C of 66 cP with a load of 95 g/L in water. Later, Shannon *et al*. 1969 [70] developed a drilling fluid containing asbestos and carboxymethylcellulose having a degree of substitution of at least 0.9 (ratio of carboxyl groups per anhydroglucose unit), both as viscosifiers and lost circulation agents. This drilling fluid can reach a viscosity of 46 cP with a 3.5% by weight of attapulgite in water with a presence of 19 g/L of Coalinga asbestos.

### 1.1.8.1.3. Sodium Silicates

Sodium Silicate (Figure 1.7) belongs to a group of chemicals used in industry as adhesives, cements, cleaning compounds, deflocculants and protective coatings. They are produced at various ratios of $Na_2O:Si_2$ (Sodium oxide and silica ratio).

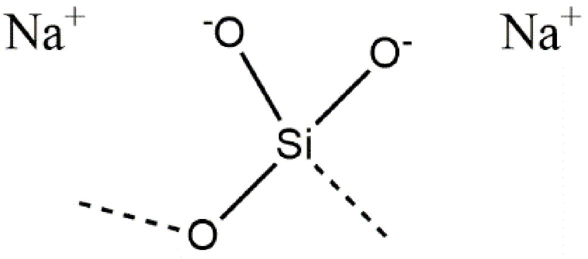

*Figure 1.7-Sodium silicate structure, where each Silica atom is joined to four oxygen atoms which two of them are electronically stabilized by two sodium ions.*

Sodium silicate and metasilicate reduce the mobility of water in cement. When they dissolve, the ions react with calcium salts in water solutions and form an insoluble gel of calcium silicates. Sodium silicate promotes dissolution of silicates from soil particle surfaces with a pH increase, contributing to the reaction of cementation [71]. Sodium silicate stabilization seems to work well with silica sands, however, with high activity clays [72]. Sodium metasilicate can function as a cement accelerator. Flushing the hole with an aqueous solution of a multivalent cation salt followed by a concentrated solution of sodium silicate can strengthen both the drilled hole surface and the cement/formation bond. [73]

Sodium silicate drilling fluids can be used to drill intact shales and chalks. In addition, these inorganic systems are environmentally friendly, inexpensive [74], and can dewater shale, resulting in a less porous and permeable wellbore. These type of drilling fluids present a high level of shale inhibition and an improved bonding at the wellbore interface. [74] 2-3% sodium silicate has a similar yield as 10% bentonite providing higher strength in comparison to other extended cements [75].

Wayne *et al*. 1951 [76] prepared a solution with sodium silicate compounds to form a degelling action on drilling fluids comprising water, a viscosifier like bentonite, a weighing agent like iron oxide or similar. Wayne *et al*. mentioned the need to reduce the viscosity of drilling fluids initially to control the viscosity of fluids which are compounded in situ. As example, a drilling mud with 8 percent weight of bentonite can reach 34 cP, but when 0.2 g/L of sodium metasilicate or sodium orthosilicate is added, this viscosity decreases to 23 cP.

Later, Hill 1972 [77] – developed a silicate compatible drilling fluid comprising sodium or potassium silicate or a mixture of sodium silicate and potassium chloride. This fluid is capable of stabilizing the shale, preventing it from swell, disperse or sloughing. However, Khodja *et al.* 2010 [13] tested some typical drilling fluids containing xanthan gum as viscosifier (with or without bentonite), polyanionic cellulose as fluid loss reducer and some swelling inhibitors such as partially hydrolyzed polyacrylamide, sodium silicate and polyalkyleneglycols to improve shale stability. The partially hydrolyzed polyacrylamide and polyalkyleneglycols present similar properties, though the silicate system exhibits the best viscosity, filtrate and gel results as shown by authors.

#### 1.1.8.2. Polymeric systems

In the last decades, polymers started to be a target of high attention as soil conditioners [78]. Polymeric soil conditioners should be distinguished as either natural or synthetic [79]. Natural polymers that act as soil conditioners are polyuronic acids, alginic acids, polysaccharides, and humus [80]. However, in the 1950's extensive research was conducted on synthetic polymers as soil conditioners in order to create customized solutions according the soils' needs and properties [79][81]. Polymers are organic colloids composed of monomers, linked together either in straight or branched chains to form macromolecules. A single polymer may contain thousands of monomers. The number of monomers in a polymer determines its molecular weight and is usually called degree of polymerization [82].

Nowadays, polymers are developed and used to overcome some drilling problems such as drilled hole wall's instability, stuck pipe, fill the bottom of the hole and solids build up in drilling fluid, where conventional drilling fluids are not satisfactory enough. Basically, they are the most attractive materials to use since they are non-toxic, do not cause serious environmental problems and exhibit proprieties that avoid less fluid loss, and formation of thinner filtration cake, depending on their composition and concentration [83].

Polymer drilling fluids are used to drill reactive formations where the requirement for shale and clay inhibition is significant. Shale and clay inhibitors frequently used are salts, glycols and amines, and all are compatible with the use of bentonite. High molecular weight polymers create a film that coats and delays the hydration of clays, therefore delaying reactivity of clay material inhibiting disintegration or dispersion [84].

By varying the degree of polymerization, polymers are synthesized to suit various purposes. A high degree of polymerization in water results in a high viscosity in solution and in an increased resistance to solubilized salts. In detail, a polymer with huge molecular chains, will be less affected by salts since these salts can be attached at the end of chains. Thus, the linearity of chains will not be compromised and consequently, the viscosity will not be affected. Each polymer is characterized by the critical polymer concentration (CPC), which refers to the polymer concentration at which the polymer fluid properties changed dramatically [83]. For example, the critical concentration of polyvinylpyrrolidone (PVP) in water at 25°C is 44.1 g/L [85].

#### 1.1.8.2.1. Polyelectrolytes

Polymers that carry electrostatic charges are called polyelectrolytes. Rabiee *et al*. [86] used the term polyelectrolyte to denote polymers which contain more than 15% of ionic groups.

Anionic polymers may interact with particles in aqueous dispersions in several ways resulting in the stability or instability of the dispersions. Mortimer *et al*. [87] mentioned that particles in solid-liquid phases can be destabilized by polymer bridging, charge neutralization or polymer adsorption (Figure 1.8) and can be stabilized by electrostatic and steric repulsive forces. Negatively charged polymers, called anionic polyelectrolytes, are widely used as flocculants on clays, rheology control agents and adhesives[86][87].

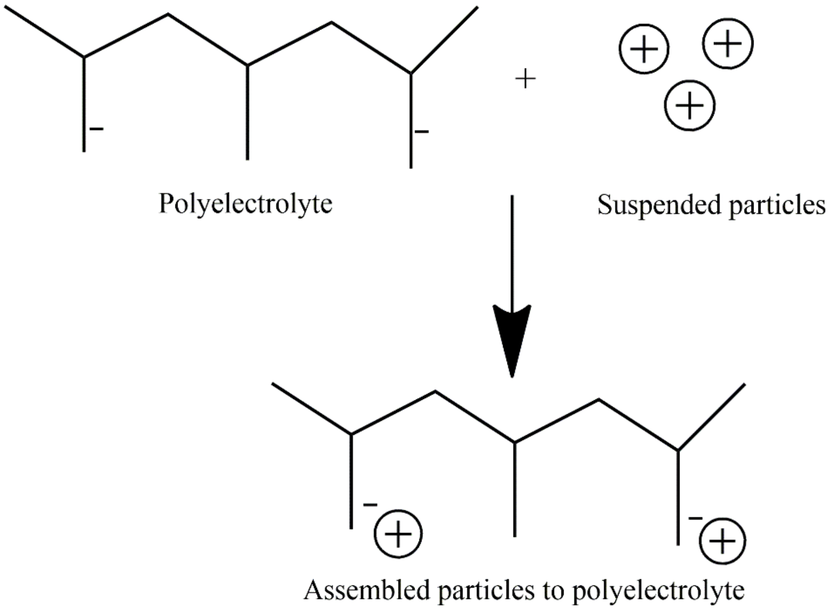

*Figure 1.8- Schematic representation of flocculation effect of a polyelectrolyte to suspended particles with opposite charges. These particles join the polymer chain in suspension.*

Most particles suspended in an aqueous solution have a negative surface charge caused by: (1) an asymmetric distribution of constituent ion on the particle surface, (2) ionization of surface groups caused by pH effect, and (3) substitution of silicon atoms by aluminum atoms in inorganic clays [87]. This phenomena causes an electrical layer around each particle and means that small colloidal particles will not settle because the inter-particle interactions will repulse each other at close distances. The function of a polyelectrolyte in a solid-aqueous liquid separation process is to overcome the electro kinetic repulsive forces among suspended particles inducing a coagulation effect by direct reduction of the surface charge on the particles or, by the adsorption of the polyelectrolyte molecule in solution onto the surface of some suspended particles joining them together into a network [87]. This network acts like a huge particle which has a smaller contact area per weight leading to deposition of particles (Figure 1.9) [88]. This occurs when gravity force becomes higher than drag force [89].

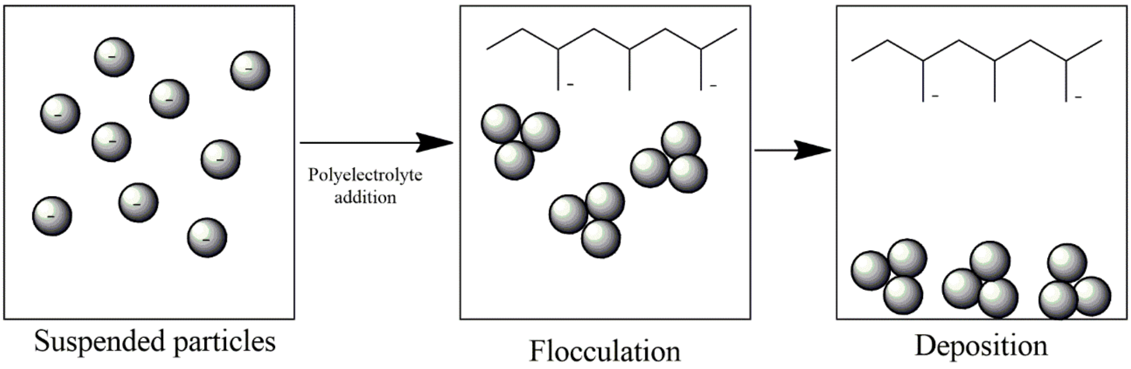

*Figure 1.9- Schematic representation of flocculation and deposition processes of a polyelectrolyte with the same anionic character as particles.*

Some low charge density polyelectrolytes with a very high molecular weight, which can be obtained tuning the hydrolysis degree for lower values (below 20%) like partially hydrolyzed polyacrylamide, can be used as flocculants because of their ability to bridge a lot of small particles settling them in a very short time compared to low/mid molecular weight polyelectrolytes [87][90][91][92].

#### 1.1.8.2.2. Polyacrylamide

The rheological properties of an aqueous polymeric solution are affected by the polymer hydrolysis degree and it is an important factor to maintain the fluid viscosity. Durst *et al*. 1986 [93] studied the influence of hydrolysis degree on pressure drop, and he found out that a higher viscosity was associated to higher hydrolysis ratios. Therefore, four different partially hydrolyzed polyacrylamides (HPAM) with a molecular weight ranging between $9.7\times10^6$ and $9.9\times10^6$ g/mol and 3.4%, 11.4%, 30.5% and 47.5% molar hydrolysis, respectively, were studied. The viscosity in a low-shear Zimm-Crothers viscometer with 500 ppm of HPAM were 3000, 4300, 6500 and 8800 $cm^3/g$, respectively.

Masao Hasegawa *et al*. 1976 [94] developed a partially hydrolyzed polyacrylamide (Figure 1.10) which has a high molecular weight and high water solubility which is suitable to use as a flocculant. This acrylamide can be polymerized in aqueous solution in the presence of an alkali metal hydroxide such as sodium hydroxide and boric acid, whereby a partial hydrolysis of the polymer formed can be occurred at the same time that polymerization step.

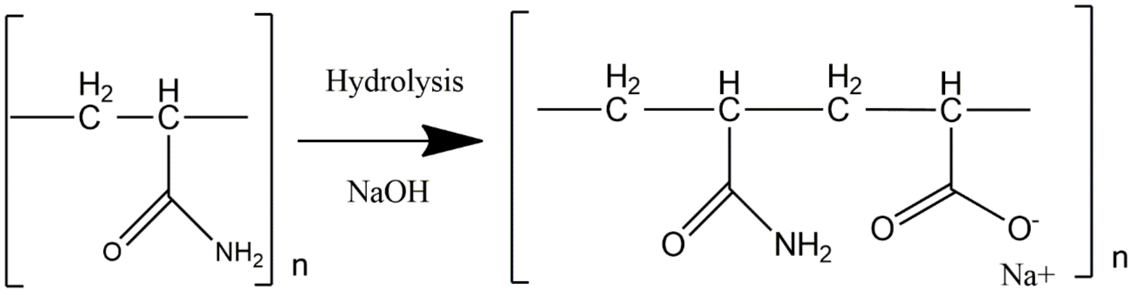

*Figure 1.10- Representation of hydrolysis with sodium hydroxide of a polyacrylamide to a copolymer containing acrylamide and sodium acrylate units*

Goodhue *et al*. 1995 [12] developed a acrylamide based polymer for a soil stabilization fluid able: to control fluid loss control, to stabilize the formation being excavated, to improve loading and removal of soil by excavating tools and to allow the development of high concrete-to-formation friction coefficients. This fluid can be used in well drilling in a vertical, angled, or horizontal drilled hole, tunnels, trenches, or other excavation type, and at high concentration (10% (w/w)) to low concentration (0,1% (w/w)) able to reach, with a Marsh Funnel, viscosity between 55 and 100 s/quart. Higher viscosities can be attainable by a polymer with high molecular weight. In addition, the author also mentions that an acrylamide copolymer with a molecular weight higher than 10 million can be used. The anionicity of the copolymer can be obtained through the hydrolysis of acrylamide during the polymerization or by copolymerization of acrylamide with other anionic monomers comprising acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, vinyl or, styrene sulfonic acid and water soluble salts [95][12][96]. The molar percentage of the monomers in the polymer should be preferably between 35 and 65%. The composition of each polymer and the hydrolysis degree should be optimized for the particular soil formation and water conditions [12][23][86][90][92][97].

Later, A. Rabiee *et al*. 2010 [86] mentioned that partially hydrolyzed polyacrylamide is a linear copolymer with high molecular weight with two different monomers acrylamide and acrylate which gives negative charges to the polymer allowing it to be applied as an additive to drilling muds. These negatively charged polymers are widely used as flocculants, rheology control agents and adhesives. They are employed in drilling operations as viscosity control agents for enhanced drilled hole stability, lesser degree in engineering fluids used for lubrication, for effluent reclaiming. The author also refers that the amide group of this copolymer can cause adsorption of particles. The polar amide groups can bind with silica and alumina and the nonpolar segment can cause adsorption of non-polar particles. The copolymer can adsorb on negatively charged surfaces some di- or trivalent ions such as calcium, magnesium and aluminum. This adsorption can result in a bridging between carboxylate groups on polyacrylamide chain and anionic surface sites causing a flocculation effect. It is also referred that a polyelectrolyte adsorption decreases with increasing salt concentration by mean of an important electrostatic attraction role. Rabiee [86] also mentioned that a high-molecular-weight partially hydrolyzed polyacrylamide can be used as a shale-control additive to drilling fluids because this copolymer can seal micro fractures and coat shale surfaces with a film capable of retarding dispersion and disintegration. Recently, Pomerleau

2015 [98] reported a drilling fluid with desired viscosifying properties by dissolving hydrolyzed polyacrylamide to an solution of glycerol/water with ratios between 95/5 to 20:80 in volume. Potassium chloride, as will forward mentioned, can also be used as a shale inhibitor in most partially hydrolyzed polyacrylamide muds. HPAM can also be used as suspending and dispersing agent.

### 1.1.8.2.3. Glycerol polymonoacrylate and glycerol polymonomethacrylate

To solve the problems of clay swelling and wall disintegration, Karagianni *et al*. 2012 [20] developed a drilling fluid comprising a polymer with at least 65% to 95% by weight of hydroxylated units comprising an –OH group. This polymers can be made of glycerol polymonoacrylate (polyGMAc) (Figure 1.11a) or glycerol polymonomethacrylate (polyGMMA) (Figure 1.11b)

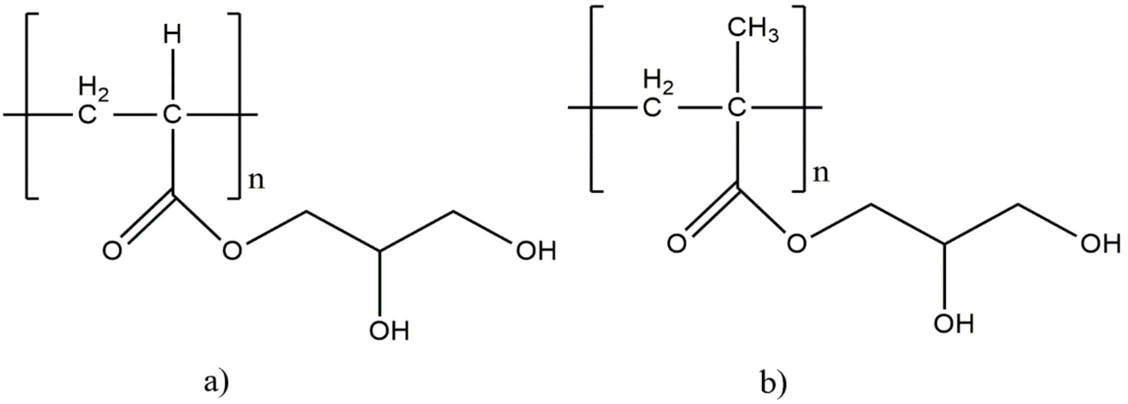

*Figure 1.11- Representative structure of: a) glycerol polymonoacrylate (polyGMAc) and b) glycerol polymethacrylate (polyGMMA)*

The weigh-average molar mass of the polymer can preferably be between 2000 and 4000000 g/mol. The polymer content on the drilling fluid is advantageously between 1% and 3% by weight. The liquid vehicle can be water or a silicate based fluid which is a water mud comprising silicates. These drilling fluids should operate at high pH (approximately 12). Silicates protect water-sensitive clays from invasion by water through two mechanisms: (1) by gelling - when silicate oligomers are in a high pH solution, they polymerize and form three-dimensional networks; (2) by precipitation - the fluid around the clays comprises $Ca^{2+}$ and $Mg^{2+}$ cations which react with silicates to form insoluble precipitates. These polymers can be used as a wellbore consolidation agent, filtrate-reducing agents, lubricating agents and accretion-inhibiting agents. An example of a drilling fluid comprising a polymer of this type, could be a silicate-based drilling mud with the following percentages by weight: 5% of dry silicates, 20% Brine, 0.1% of antifoaming agent, 0.5% xanthan gum, 1% of glycerol polymonomethacylate homopolymer with a weight-average molecular weight of approximately 5600 g/mol, and NaOH or KOH in order to adjust the pH to 12.

#### 1.1.8.2.4. Carboxymethyl cellulose (CMC)

Carboxymethyl-cellulose (CMC) (Figure 1.12) is a high absorbent polyelectrolyte derived from natural materials. A wide range of properties such as biodegradability, low density, relatively low cost, non-toxic material and availability from renewable resources have contributed to an increased interest in this material. [99]

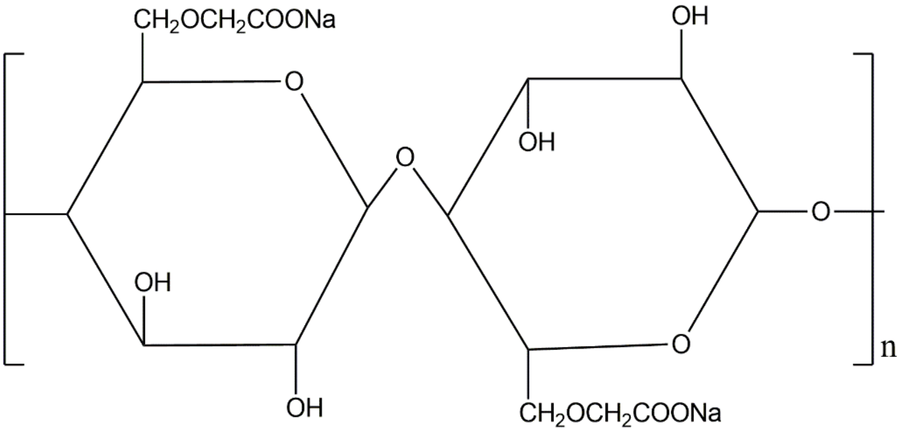

*Figure 1.12- Representative structure of sodium carboxymethyl-cellulose (CMC)*

Anderson *et al*. 1979 [59] developed a process and a composition of a drilling fluid with capacity to stabilize the shale in an effective way. This fluid contain a non-clay based viscosifier such as carboxymethyl cellulose to obtain a desired viscosity, and potassium or ammonium salt to provide cations to the system and prevent swelling of shale. CMC should be used in a typical concentration of 3.8 g/L. Anderson *et al*. made some shale rolling tests to determine the degree of mechanical stability. These tests were performed using a mechanical agitation with soil during 16 hours followed by a filtration and a weighing. The remaining soil was agitated with a fresh water for about 2 hours and filtered again. The remaining soil was weighed to determine how much soil was recovered. For a cellulose based polymer, it was possible to recover about 65% of initial soil in the first step and 55% of the remaining soil in the second step. Jain *et al*. 2015 [100] synthesized a carboxymethyl-graft-polyacrylamide copolymer by free radical polymerization method able to be used as a drilling fluid additive to improve rheological and filtration properties. A drilling fluid comprising this copolymer may be used for the drilling of water sensitive shale formations. The author compared a drilling fluid containing CMC homopolymer, xanthan gum (0.3% by weight), polyanionic cellulose (0.8% by weight) and KCl (5% by weight) with another drilling fluid with the same composition but comprising the graft polymer aforementioned instead of the CMC homopolymer, and reported an improvement on apparent viscosity. This improvement depends on polymer concentration. For an addition of 0.3%, 0.6 and 0.8% by weight of copolymer comparing with the addition of the same amount of homopolymer, the viscosity increased from 19 to 21 cP, 23.5 to 32 cP, and 28.5 to 39 cP, respectively.

CMC can also be used as a fluid-loss reducing in freshwater and seawater muds. CMC effect is drastically reduced in brine and high concentrate saltwater. Wagner in 1944 [22] developed a water based drilling mud containing water soluble alkali metal carboxymethyl cellulose capable of

forming a filter cake on the walls of the well preventing fluid loss in a range of 99.57% to 99.97%, tested with an “A.P.I. (American Petroleum Institute) low pressure wall building tester filter press” with a pressure of 70 ton/m$^2$ applied for 30 minutes. Wagner found that sodium carboxymethyl-cellulose can give a satisfactory and economical mixture with 15 g/L. Author also gives an example to demonstrate the value of water soluble alkali metal carboxymethyl-cellulose in drilling muds where the weight was 40.0 g/L and the viscosity measured in a Stormer viscometer 1931 model, made by Arthur H. Thomas Company was, about 33 cP.
At commercial level, GRINDSTED® CMC is an efficient product in salted and salt-saturated water sold by Danisco Textural Ingredients Co., Ltd. [101]

#### 1.1.8.2.5. Hydroxyethyl Cellulose (HEC)

Dupre *et al*. 1981 [102] developed a drilling fluid combining acid-containing polymers and polysaccharides which exhibited an effective behavior in small amounts (2.8 - 5.7 Kg/m$^3$ of polymer vs 71 - 100 Kg/m$^3$ of clay) to provide inhibition of clay swelling, great viscosity, and fast drilling. Dupre *et al*. also reported a Brookfield viscosity at 22°C of about 3000 to 200000 cP in an alkaline system using 2 percent by weight of hydroxyethyl-cellulose (Figure 1.13) in distilled water. This drilling fluid is composed by a mixture of this «macromolecular polysaccharide and an ethylenically unsaturated carboxylic acid copolymer with a molecular weight from about 250000 to 5000000 g/mol. The quantity of this two compounds can vary from 0.38 to 19 g/L in the drilling fluid. Reddy *et al*. 2014 [103] reported that an aqueous drilling fluid comprising between 1% and 2% by weight of hydroxyethyl cellulose like Natrasol Plus®, available from Hercules, Inc. can reach 270 to 3800 cP.

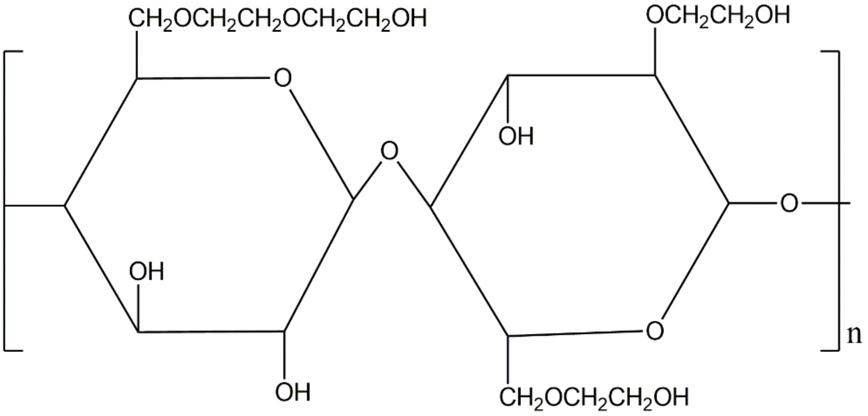

*Figure 1.13 - Representative structure of hydroxyethyl-cellulose (HEC).*

#### 1.1.8.2.6. Sulfobetaine Units

The betaines are a class of zwitterions [104]. These materials contain positive and negative charges separated by alkyl groups. Some of them are water soluble, but all of them are soluble in salt solutions.

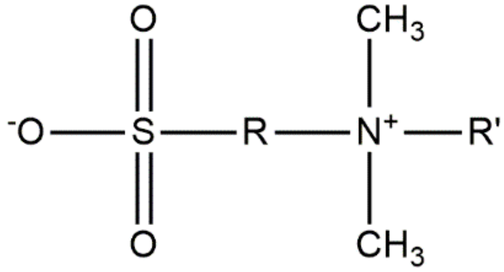

*Figure 1.14- Schematic representation of a sulfobetaine unit, where R represents an alkali and R' represents any hydrocarbonet*

Water soluble polymers like hydrolyzed acrylamide, vinylpyrrolidone, and copolymers of the previous ones are water viscosifiers, which are achieved through a combination of high molecular weight and the presence of ionic groups along the polymer chain, or the presence of hydrogen bonds. However, these polymers are salt-sensitive which affects the rheological properties of the solution in water. Schulz *et al*. 1986 [104] developed betaine copolymers that can be used to change the rheological properties of water and brine. These polymers are copolymers of N-vinylpyrrolidone and pyridine-based betaine monomers. Such polymers contain both positive and negative charges and their rheological properties remain unaffected or can be improved in the presence of some salts. Fenchl *et al*. 2002 [105] developed terpolymers (composed by three distinct monomers) based on sulfobetaines (Figure 1.14) for use as thickeners for aqueous salt solutions. These polymers are composed by methacrylamide (Figure 1.15a), hydroxyalkyl methacrylate (Figure 1.15b) and sultobetaine monomers.

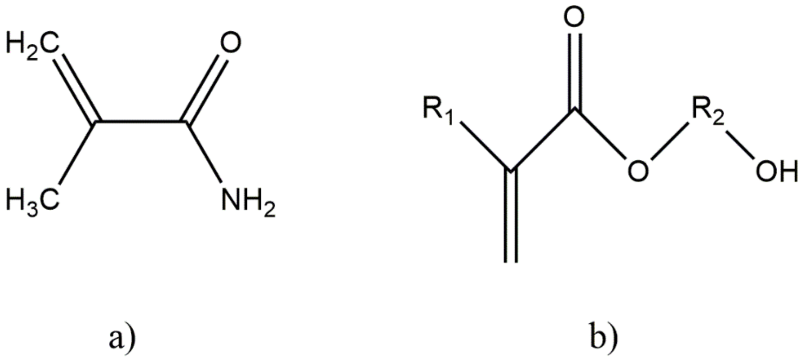

*Figure 1.15- Schematic structure of: a) methacrylamide and b) hydroxyalkyl-methacrylate.*

An example of a terpolymer mentioned by this patent could be prepared in water with N-3(3-sulfopropyl)-N-methacryloyloxyethyl-N, N-dimethylammonium betaine, hydroxyethyl methacrylate and dimethylacrylamide using 2,2’-azobis(N,N-dimethyleneisobutyamidine) dihydrochloride as initiator. This solution have a solids content of 8% by weight and a Brookfield viscosity (20rpm, spindle No.1) of 750 cP at 20°C. These polymers contain positive and negative charges separated by alkyl groups, showing an antipoly-electrolytic behavior in salt solutions, swelling up instead of contracting. Later, Monin *et al*. 2014 [106] developed a drilling fluid able to be used in oil or gas extraction and in civil engineering applications, in particular for excavation and/or digging operations to increase the viscosity of saline aqueous compositions. This drilling fluid comprises a copolymer including a hydrophobic or amphiphilic units, such as sulfobetaine or phosphobetaine or carboxybetaine units, and any hydrophilic units able to polymerize a linear macromolecular chain. An example, could be a copolymerization of Poly(sulfopropyldimethylammoniopropylmethacrylamide/acrylamide/lauryl methacrylate) in a molar ratio of 29.5/67.5/3. A drilling fluid with 1% concentration of the aforesaid terpolymer can achieve a viscosity of 119 cP in a NaBr brine (44.6%), 304 cP in a $CaCl_2$ (23%) and $CaBr_2$ (33%) brine, and 998 cP in a $CaBr_2$ (23%) and $ZnBr_2$ (53%) brine. Furthermore, the aforesaid terpolymer was mixed in a $CaCl_2$ (23%) and $CaBr_2$ (33%) brine with 20% by volume of sand particles. For a terpolymer concentration of 0.13%, 0.48%, 0.81% and 1%, sand sedimentation can be reduced in 24%, 66%, 91% and 99%, respectively.

Since the aim of this thesis is the development of new polymeric systems to be applied in soil stabilization, in order to give an answer to the needs associated to this topic, it is crucial to understand what kind of polymers can be synthesized and evaluated as possible candidates for this purpose.

## 1.2. Polymers

The evolution of society demands the constant search for new and improved materials able to meet special requirements in order to fill gaps and needs.

Nowadays, polymers have been a key class of materials for the development of a huge variety of products in different areas, such as, bioengineering [107], drilling fluids for oil drilling and foundations [108][109], plastics [110], rubbers [111], resins [112], adhesives [113], coatings [114], flocculants [115], clothing [116], paintings [117], food industry [118] among others.

Since new challenges, motivated by economical or environmental issues, are coming up every day, new polymeric materials have been designed and prepared. Therefore, it is urgent to keep investigating the polymer's world in order to improve the ones already established, and create new ones to cover all needs and go further with outstanding products to solve technological issues raised by the industry.

### 1.2.1. Polymerization mechanisms

The term polymer become from Greek roots that means many parts and designates a molecule made up by repetition of some simpler units [119]. The oldest reference of polymers remount to 1833, when Berzelius used the terminology polymer for the first time to describe the relation between compounds having the same empirical formula but different molecular weight [120][121]. Years later, vinyl polymers had been discovered, first poly(vinyl chloride) in 1835 [122], actually used as window frames, bottles, wallcoverings, among others [123], and polystyrene in 1839 [124], extensively used in packaging applications and thermal insulation [125]. In 1860, Laurenço reported a synthesis of poly(ethylene glycol) [126], essentially used in biotechnical and biomedical applications [127]. Decades later, in 1900s, Leo Baekeland announced the synthesis of phenol formaldehyde resin [128]. But only in 1920, Hermann Staudinger proposed an idea of “macromolecules” and reported a structure of polymers as long-chain molecules [129]. W. H. Carothers developed nylon synthesis in 1939 [130]. More than 20 years later, Ziegler-Natta developed stereoregular polymerization (1963) [131] and Paul Flory defined polymer solution property (1974) [132]. Since that date, many advances have been accomplished in polymers.

Nowadays, there are two main mechanisms, where all polymers can fit: (1) step-grow polymerization and (2) chain-growth polymerization.

On one hand, step-grow polymerization requests higher temperatures (an example is given by the temperature of polymerization of 3,5-bis(hydroxymethyl)-1-propargyloxybenzene-based polyurethanes which can reach 300°C) than chain growth polymerization and don’t need any addition of initiator. The repetitive unit has not the same amount of atoms as the reagent (exception made to polyurethanes) [133]. The polymerization reaction occurs between two complementary reagents with functional groups. Several polymers could be obtained by this type of polymerization: (1) low molecular weight polymers obtained by polymerization of monomers with only one functional group, (2) linear polymers obtained by polymerization of monomers with two functional groups, and (3) branched polymers obtained by polymerization of monomers with more than two functional groups. Usually, this type of polymerization needs a specific catalyst that control the polymer structure. The most well-known step-growth polymers are Nylon [134], Teflon [135] and polyurethanes [136].

On the other hand, chain growth polymerization can be: (1) radical, (2) ionic, or (3) coordination. All monomers may have unsaturations in their structure, normally double or triple bond between carbon atoms and they grow by chain polyaddition [119].

- Radical polymerization is initiated by adding to a radical produced from a suitable initiator a molecule of monomer [119]. After the initiation step, the radical reacts with a free monomer to break one bound to form a radical in the monomer that will react with another monomer and so on, but its nature, or the nature of the initiator, does not influence the propagation rate constant, the selectivity, or the stereochemistry of the ensuing propagation [137]. All these assets of radical propagation are determined by the nature of the polymerized monomer and by the conditions under which reaction develops, such as temperature, pressure, and the nature of the solvent. The list of monomers that can be polymerized by radical mechanism is limited to the vinyl, vinylidene, and diene types, whereas additional monomers, e.g., aldehydes, ketones, numerous heterocyclics, and so forth, not polymerizable by the radical technique, are polymerizes by ionic procedures [138][139].
- Ionic polymerization starts with a reaction of a monomer with a species capable of forming am electrically charged or highly polar active group on the added monomer molecule. Ionic polymerization is referred to as cationic or anionic when the active terminal group is positively or negatively charged. The polymerization mode and rate depend on the composition of the reacting mixture which is affected by temperature and the nature of

the solvent. Aldehydes, ketones, numerous heterocyclics and other monomers not polimerizable by radical technique, are polymerizable by ionic procedures [139][140].

- Coordination polymerization originated when Ziegler discovered ethylene polymerization with $TiCl_4/Et_3Al$ catalyst system. Coordination polymerization starts with a reaction of a monomer with a growing macromolecule through an organometallic active center [141].

Chain growth polymerization has been used specially in production of polyacrylonitrile [142], polyacrylamide [143], polystyrene [144] or polyethylene [145].

Further details about polymerization mechanisms can be found in literature [146][139] [133]. However much attention will be done to free radical polymerization mechanism.

### 1.2.2. Polymerization methods

#### 1.2.2.1. Conventional polymerization methods

Conventional free-radical polymerizations can follow a few different processes that require different polymerization conditions. Every monomer can be successful polymerized in one or more than one method [119]. Generally free-radical polymerizations are carried out in: (1) bulk polymerization, (2) solution polymerization, (3) suspension polymerization, and (4) emulsion polymerization.

Bulk polymerization – This type of polymerization is carried out with no solvent where the initiator is mixed in the bulk with the monomer [147]. This process results in a clear polymer with a minimum contamination but it is difficult to control heat dissipation due to radical chain polymerization highly exothermic nature, high activation temperature and gel effect caused by polymer formation. This heat dissipation control problem can lead to an auto acceleration polymerization causing thermal degradation, development of chain unsaturation and a production of an inferior quality product. In extreme cases, bulk explosions can occur [138]. Bulk polymerization is more common used for step polymerization, however, this method is used to the polymerization of ethylene, styrene and methyl methacrylate [119].

Solution polymerization – is carried out in a solvent where initiator and monomer are soluble. This type of mechanism can avoid almost the disadvantages of bulk polymerization because the solvent acting as a diluent decreasing the medium viscosity improving heat transfer and heat dissipation. However, this method requires removal or recovery of the polymerization solvent in order to isolate the polymer. Still, solution polymerization can be of enormous advantage if the polymer formed is to be applied in solution. This method, usually only gives low molecular weight polymers.

Suspension polymerization – This method is a combination of the two already mentioned ones. Suspension polymerization occurs in the presence of a continuous phase in which the monomer is insoluble but the initiator is monomer-soluble. The monomer is suspended by agitation in the mixture. The main advantages of this type of polymerization are; (1) a great heat and viscosity control, and (2) no need of solvent remove. The final product have a spherical bead form.

However, it often needs the addition of a stabilizer able to maintain the suspension of the monomer and polymer in solution causing a contaminated final product [119][148][149]. The most common suspension polymerizations are carried out with styrene, methyl methacrylate, vinyl chloride, and vinyl acetate monomers.

Emulsion polymerization – This kind of polymerization is very similar to suspension polymerization, where polymerization reactions are easier to control in both these methods. Than in bulk polymerization type. Water works like a bath sink making heat transfer and heat dissipation easier. However, emulsion polymerization differs from suspension polymerization mainly because of initiator type used. The initiator, in emulsion polymerization, is solvent soluble. Also, this polymerization method differs from any other by its mechanism and reaction characteristics where smaller size particles are in suspension by an additive action. Some of advantages of this method are: (1) reduced thermal and viscosity problems when compared to bulk polymerization method, (2) final product can be directly used without further separation, and (3) polymer molecular weight and polymerization rate can be increased simultaneously. However, some disadvantages can be listed: (1) the monomer should be nearly insoluble in water and the polymer soluble in its own monomer, (2) contaminated final product could be obtained by the use of additives to help maintain small particles in suspension during polymerization [119][150]. This kind of mechanism is largely used for polymerizing or copolymerizing vinyl monomers such as styrene, vinyl chloride, vinyl acetate, acrylates or methacrylate [119].

### 1.2.2.2. Non-conventional polymerization methods

Non-conventional polymerization methods are investigated to achieve new structures and functionalities for old materials. As alternatives to conventional technologies, non-conventional mechanisms have been developed recently. These methods resort to the smart use of properties inherent to the materials in order to achieve a control on the surface characteristics [151]. In one hand, the used technique can be non-conventional such polymer material processing include moulding, writing and printing, laser scanning, self-organization and surface instabilities utilizations [152]. In the other hand, a non-conventional polymerization can use a non-conventional solvent in polymerization process, such as ionic liquids [153][154] or supercritical carbon dioxide[146][155][156][157].

Polymerization in supercritical $CO_2$ was reviewed in some literature [155][156]. Supercritical $CO_2$ while a good solvent for many monomers is a very poor solvent for almost all polymers with the exception of fluoropolymers and polymerizations taken to very low conversions. Most of polymerizations in supercritical $CO_2$ are precipitation, dispersion or emulsion polymerizations. Supercritical fluids have the best of two domains: they can have gas-like diffusivities (which can have important implications for reaction kinetics) and liquid-like densities that allow the solvation of many compounds and they exhibit changes in solvent density with small changes in temperature or pressure. [155]

### 1.2.3. Initiator

The initiation of a polymerization is usually a direct consequence of highly active species formed by dissociation or degradation of some monomer molecules (step-growth polymerization) by heat or radiation or by dissociation or decomposition of some chemical structures known as initiators (chain growth polymerization). This reactive species may be a free radical, cation, or anion which can react with the monomer molecule by breaking bonds and forming another reactive center in the monomer to resume the polymerization.

An initiator is different from a catalyst. A catalyst and a substrate form a transition complex which is decomposed and the catalyst is regenerated. An initiator is incorporated in the chain and usually do not regenerate again [137].

A diversity of initiator structures can be used and radicals can be formed by a variety of thermal, photochemical, and redox methods [158][159][160]. However, more importance will be done to thermal decomposition of initiators.

The thermal decomposition of a compound is the most common way to stimulate radical formation to start the polymerization. The list of compounds that can be used as thermal initiators are very limited. To choose an initiator, the bond dissociation energy of the compound should be such that the dissociation is not made too slowly or too quickly. Compounds with a bond dissociation energy from 100 – 170 kJ/mol are usually suitable.

The most common free radical initiators are: azonitriles and azo-derivatives, alkyl and acyl peroxides, hydro and ketone peroxides, peresters and peroxy carbonates. However, the main type of initiators with bond dissociation in this range contain a O-O (peroxide) bond such as diacyl peroxides, dialkyl peroxides, peroxy esters, azo compounds [119], and others. It is important to select an initiator which concentration will not reduce significantly during the polymerization reaction. From previous studies, it looks that an initiator with a $t_{1/2}$ of about 10h at a given reaction temperature is a worthy choice [119].

The decomposition of most organic free radical initiators tracks first order kinetics by the follow reaction:

*Equation 1.1- First order decomposition of a initiator I*

$$\frac{d[I]}{dt} = k_d \times [I]$$

Where [I] is the initiator concentration (mol/L), t is the time (s) and $k_d$ is the decomposition rate ($s^{-1}$).

Two different types of radical initiators were used in this thesis: (1) a azo compounds, by far the most important compound of this type, 2,2'-azobisisobutyro-nitrile (AIBN) and (2) an alkali persulfate, sodium persulfate (NaPS).

The mechanism of these initiators starts with the formation of radicals:

(1) AIBN:

*Equation 1.2- Thermal decomposition of AIBN in to two free radicals*

$$C_6N_4H_{12} + heat \rightarrow N_2 + 2C_3NH_6^{\bullet}$$

(2) NaPS:

*Equation 1.3- Dissociation of NaPS ions in sodium and persulfate*

$$Na_2S_2O_8 \rightarrow 2Na^+ + S_2O_8^{-2}$$

*Equation 1.4- Thermal decomposition of persulfate ion in to two free radicals*

$$S_2O_8^{-2} + heat \rightarrow 2SO_4^{-\bullet}$$

After the initiation step, the radical reacts with a free monomer to break *C=C* bond to form a radical in the monomer that will react with another monomer and so on.

A wide range of initiators are reported by Dixon at Polymer Handbook [158] with decomposition rates for some solvents at a given temperature.

### 1.2.4. Monomers

Polymers can have one or more kind of monomers. When a monomer is polymerized alone, it is called homopolymerization, but when two or more different monomers are polymerized together, it is called copolymerization [124].

*Equation 1.5- General representation of monomer combination of a random copolymer*

$$XM_1 + YM_2 \rightarrow M_1M_2M_2M_1M_1M_1M_2M_1 \ldots$$

The relative quantity and reactivity of two or more monomers enter into the copolymer determine the distribution of the monomers along the chain. Every copolymerization follows a statistical law. For example, a copolymerization that follows a Bernoullian process have a completely random distribution along the chain and, according to IUPAC terminology, are referred to as random copolymers [119][161]. Statistical copolymers are influenced by each monomer reactivity [162]. As said, copolymerization could be specified by special attributes being into count the frequency of entry of various monomers into the chains [124]:

- Random – As mentioned before, random copolymers don't have any specific order to be crafted [163]. The order by which the monomers react are independent from their type and follows a zero order Markov [119].

The monomer reactivity (k) signifies that the rate of reaction of the growing chain radicals towards each of the monomers is the same:

*Equation 1.6- Ratio of monomer reactivities*

$$r_1 = \frac{k_{11}}{k_{12}} = r_2 = \frac{k_{22}}{k_{21}} = 1$$

Namely, the monomer 1, have the same capacity to bond with itself and with monomer 2.

- Alternating – In this kind of copolymerization, both monomers have a reactivity ratio (r) of almost 0, in other words, the monomers are incapable of undergoing homopolymerization and each radical monomer prefers to add exclusively the other monomers leading to alternation between each monomer units along copolymer chain [119][124][164].

*Equation 1.7- Rate of reaction of an alternate copolymer*

$$r_1 = r_2 = 0$$

- Block – As opposed to alternating copolymerization, block polymers are composed by sequences of same type of monomers [165]. The reactivity ratio of both monomers are higher than 1, in other words, the monomers have more capacity to bind with the same type than with the other type, producing blocks of the same kind of monomers in the polymer chain [119].

*Equation 1.8- Rate of reactions and monomer reactivities of a block copolymer*

$$r_1 = \frac{k_{11}}{k_{12}} > 1\ ;\ r_2 = \frac{k_{22}}{k_{21}} > 1$$
$$k_{11} > k_{21}\ ;\ k_{22} > k_{12}$$

- Graft – A Graft copolymer isn’t a linear polymer, it is instead a sequence of one kind of monomer with some ramifications of the second sort. Usually, this kind of polymerization is performed in two steps, a homopolymerization followed by a reaction of homopolymer in solution with an initiator and monomers of a second type to produce a crafted copolymer [166][167][168]. An example of a copolymer formed by this method ih high-impact polystyrene, made by polymerizing styrene in the presence of poly(1,3-butadiene), and ABS, made by copolymerizing styrene/acrylonitrile in the presence of poly(1,3-butadiene) [119].

### 1.2.5. Type of polymers

#### 1.2.5.1. Vinyl polymers

Vinyl polymers are products of the polymerization of monomers comprising vinyl groups. Vinyl polymers are always polymerized by chain growth polymerization with radicals. Vinyl polymers can be of many types, such as acrylics, polyamines, polystyrene among others [169]. The first article reporting the synthesis of vinyl polymers was published in 1835 with the synthesis of poly(vinyl chloride) [122] and the synthesis of polystyrene in 1839 [124]. The most well-known and important commercial polymers nowadays are polyethylene, polypropylene, polyvinyl acetate, polyacrylonitrile, polyvinyl alcohol, polyacrylamide, and the previously mentioned polystyrene and poly(vinyl chloride) [170].

#### 1.2.5.2. Acrylic

Acrylics are esters of acrylic acids (Figure 1.16), they are products formed by the reaction of an acrylic acid and alcohol. These esters polymerize really quickly to form exceptionally clear polymers. These polymers are widely used in applications that require clear and lasting surfaces, such as aircraft and automobile industries. Acrylics are used in a wide range of applications such as adhesives, textile industry, paint industry, paper coatings and cement modifiers. Acrylics have specific properties such as gloss, hardness, adhesion and flexibility, and all those properties could be modified by changing the composition of the monomer mixture used in the polymerization process or by modifying the polymerization parameters, such as polymerization temperature, initiator, hydrolysis or solvent [124].

The principal monomers in this class are:

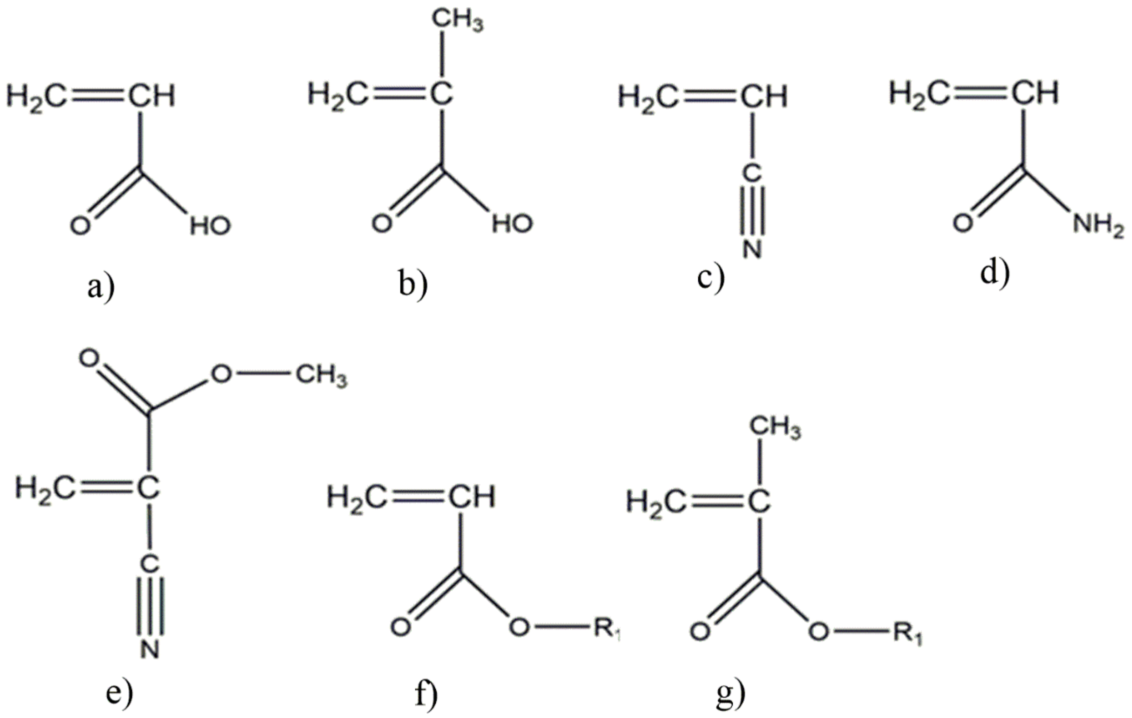

Figure 1.16- Chemical structures of different types of monomers: a) Acrylic acid; b) Methacrylic acid; c) Acrylonitrile; d) Acrylamide; e) Cyanoacrylates; f) and g) Esters of acrylic acid and methacrylic acid, respectively.

These monomers may be polymerized by emulsion or solution polymerization (Figure 1.16). The molecular weight of polymer and the degree of polymerization will be higher by emulsion polymerization rather than solution polymerization [171]. However, most of these monomers are water soluble and polymerize giving water soluble polymers what makes emulsion polymerization in water impossible. Thus, to polymerize water soluble monomers by emulsion polymerization requires the use of another solvent, usually a less “*green”* one what makes the entire process less clean [172][173]. On the other hand, bulk polymerization is not practical because of the difficulty to control the high rate and heat of polymerization of acrylates and acrylic polymers tends to precipitation when polymerized in suspension [124].

Most of the references for polymerization of acrylic polymers were from 1940’s. Some references can be found, as example, Arnold 1949 [174] developed a new method to polymerize and copolymerize acrylonitrile and other nitriles with acrylate monomers in the presence of ammonium perdisulfate as initiator. Later, Lincoln 1954 [175] advanced a new method for production and use of solutions of polyacrylonitrile and copolymers comprising 85% or more of acrylonitrile and 15% or less of vinyl chloride, or 60% or more of acrylonitrile and 40% or less of methacrylonitrile to be used as shaped articles such as filaments, films and foils. In the 60’s, Goode *et al*. 1960 [176] studied the mechanisms of organolithium and organomagnesium compounds initiators of stereospecific anionic polymerization of acrylates and methacrylates. Since the 40’s, numerous new developments have been accomplished, new methods to produce acrylic polymers and novel applications have been discovered to them. Lane *et al*. 1973 [177] developed a low-temperature flexibility and oil-resistant core-shell acrylic elastomer polymer to be used in gaskets, seals, O-rings, belting, wire coatings and hydraulic hose. These elastomers can also be useful as bonding agents for textiles and paper. These acrylic elastomers contain at least two polymers that are chemically and/or physically bound together. The elastomer has on its composition a first-stage polymer comprising at least 50% of an alkyl acrylate and a second-stage polymer having at least 60% of an alkyl acrylate or a mixture of alkyl acrylates and 0 to 40% of comonomers, such as acrylonitrile. Both stages have been polymerized with diisopropyl benzene hydroperoxide as initiator and the preferably polymerization mechanism to both stages is emulsion polymerization although suspension polymerization mechanism could be also used. Later, preparation of polymers with selective memory for a substrate around which a polymeric structure has been formed aroused considerable interest. Norrlöw *et al.* 1984 [178] revealed a new method for preparing an acrylic polymer containing recognition sites obtained by imprinting microparticulate porous silica carrying acrylate groups in bulk polymerization.

However, acrylic polymers have vast applications, such as: (1) coatings; Antonelli *et al*. 1986 [179] and Nickle *et al*. 1994 [180] both developed coatings compositions to be used as colored or pigmented finish to be applied to automobile and truck bodies. (2) absorbents; Nagasuna *et al.* 1990 [181] developed a water absorbent resin comprising an acrylic polymer with one or more anionic character monomers such as acrylic acid, methacrylic acid, and others. (3) flocculants and thickeners; Shioji *et al*. 2007 [182] advanced a new process to the production of methacrylic polymers to be used as flocculants and thickeners. (4) catalysts; Díaz-Díaz *et al*. 2012 [183] used hemo-acrylic polymers as catalysts in the oxidative dehalogenation of 2,4,6-trichlorophenol. (5) adhesives; Liu *et al*. 2014 [184] developed a cationic UV-crosslinkable acrylic polymers comprising functional groups for pressure sensitive adhesives.

Over time, new forms of acrylic polymers synthesis have been developed. These polymers have been synthesized by bulk, solution, suspension and emulsion mechanisms as homopolymers or copolymers with different initiators. However, as said before, new solvents are being developed such as carbon dioxide [185][186]. Examples of this method could be given by Romack *et al*. 1995 [185] in a precipitation polymerization of acrylic acid in supercritical carbon dioxide using AIBN as a free radical initiator, Canelas *et al*. 1996 [186] in a dispersion polymerization of styrene also in supercritical carbon dioxide, or Barroso *et al*. 2009 [157] in the development of pH-responsive poly(methylmethacrylate-co-methacrylic acid) membranes using $scCO_2$ technology.

As seen, the list is almost unlimited, new methods and procedures are developed every moment for acrylic polymers.

#### 1.2.5.3. Poly(N-vinyl lactams):

Poly(N-vinyl lactams) are condensation products that contain amide groups. Since this kind of polymers have a hydrogen bounding to water molecules, many of these polymers exhibit a great solubility in water. N-vinyl compounds became commercially available by Reppe vinylation of lactams [122]. One of the most investigated n-vinyl lactam monomers is N-vinylpyrrolidone.

N-vinylpyrrolidone is a water soluble monomer that is usually polymerized in aqueous solution. Commercial grades of PVP have an average molecular weight from about 10000 to 360000 g/mol. N-vinylpyrrolidone can be polymerized either in bulk, solution, or in suspension. Cationic polymerization with $BF_3$ only leads to oligomers. Radical polymerization of N-vinylpyrrolidone can lead to degrees of polymerization from 10 to 100000 corresponding to molecular weights from 1000 to 10 million [187]. PVP is actually mostly used in cosmetic formulations, especially hair lacquers, as binder in pharmaceutical tablets [188][189]. An interesting application of PVP is in aqueous solution as a blood plasma substitute [190]. However, PVP have a lot of other applications like as hydrogel in UV-curing technique synthesis [191], ocular implants [192], as absorbent for chromatographic separation [193], as stabilizer in dispersion polymerization of styrene in polar solvents [194], as protective media for colloids in photochemical formation [195] and electrochemical synthesis [196] of silver nanoparticles, as incorporate agents of silver nanoparticles in other polymers such as polymer nanofibers [197], or as stabilizer in pulsed sonoelectrochemical synthesis of copper nanoparticles [198].

However, all started around 1941, when Reppe *et al*. [199], developed the first polymerization of an N-vinyl lactam in water solution in the presence of alkali sulphites in an inert atmosphere. Later, Schuster *et al*. 1943 [200] patented a process to polymerize N-vinyl lactams using bulk polymerization processes comprising N-vinyl-alpha-pyrrolidone and hydrogen peroxide, or potassium persulfate, or benzoyl peroxide as initiators at temperatures between 40 and 150°C. Although, other authors improved these processes, using new conditions or initiators, such as Beller 1954 [190], Breitenbach 1957 [201], Fried *et al*. 1975 [202] and Haaf *et al.* 1985 [187]. Some different initiators could be used, such as hydrogen peroxide [200][190][187] or AIBN [201][202]. However, when hydrogen peroxide is used a chain with a low molecular weight is obtained [202] and higher the concentration of initiator, the lower the molecular weight of PVP produced [187]. Breitenbach 1957 [201] reported that using AIBN as initiator in a ratio of $5 \times 10^{-4}$ mole AIBN / mole N-vinylpyrrolidone at 20°C can obtain a rate of polymerization of 0.4 %/hour, however, Fried *et al.* 1975 [202] developed a process for copolymerization of N-vinylpyrrolidone utilizing a catalyst suspension of AIBN mixed with a sample of the polymer or copolymer to be synthesized in water. Then, water, monomers, and ammonia are stirred in a vessel at temperature from 60°C to 120°C. Suspension catalyst is added gradually during the reaction to obtain a copolymer within 6 hours with a viscosity from 9000 to 60000 cP (20 percent by weight of copolymer in water).

The viscosity of polyvinylpyrrolidone in water depends on the average molecular weight and the degree of polymerization, which can be described by its K-value. Swei *et al*. 2002 [203] reported the viscosity of PVP solutions with a K-value between 92.1 and 95.4 obtained a viscosity between 12 a 14 cP respectively for a 2% of PVP weight percent in water and between 23 and 29 cP respectively for a 3% of PVP weight percent in water.

#### 1.2.5.4. Other vinyl polymers of interest

Poly(vinyl acetate) (PVAc) is also a vinyl polymer. PVAc is soluble in acetone, chlorobenzene, chloroform, dioxane, methanol, and toluene [204]. However, it is not soluble in water [205]. It is used in industry as an adhesive material [206], a paint, and a gum base for chewing gum because of his relative low glass transition temperature (Tg ~ 30°C) [169]. PVAc can be hydrolyzed to poly(vinyl alcohol) (PVA), and PVA is a water-soluble synthetic polymer and can be categorized by: (i) the degree of hydrolysis, (ii) the viscosity of an aqueous solution, and (iii) the average molecular weight. Low-viscosity grades tend to have a low number of monomer units with average molecular weights ranging from 45000 to 50000 g/mol. However, high viscosity grades, with fully-hydrolyzed monomers can reach an average molecular weight from 200000 to 225000 g/mol which affects some PVA properties such as compatibility, rheology and water solubility. Fully hydrolyzed PVA with long chains may be only soluble in hot water. However, PVA of 88 percent hydrolysis should be soluble in both cold and hot water [207]. PVA can’t be prepared by polymerization of the corresponding monomer, unlike other vinyl polymers, the only way to obtain this polymer is by polymerization of vinyl acetate to PVAc followed by hydrolysis [189]. In 1924, W. O. Herrmann and W. Haehnel were the first to prepare PVA by saponification of poly(vinyl esters) with sodium hydroxide (without hydrolyze). However, just in 1932, W. O. Herrmann, W. Haehnel, and H. Berg discovered that PVA could also be prepared from transesterification of poly(vinyl esters) with alcohol and alkali catalyst [189]. PVA is used in textile industry in the sizing of stable fiber yarns and filaments [208], as an aqueous solution, alone or in combination for packaging and cigar adhesives [209], in paper industry in the production of coated papers with specific barrier properties. It is also used as carrier to optical brighteners [210]. PVA can also be used for bonding nonwoven fabrics of all kinds, in temporary bonding agents for ceramics or as a release agent for cast resin moldings, in the production of highly absorbent sponges [189]. PVAc can be polymerized in water following an emulsion polymerization technique using PVA as stabilizer [211][212]. Dunne *et al*. 1965 [213] and González *et al*. 1996 [214] reported an emulsion polymerization of PVAc using potassium persulfate as initiator and sodium bicarbonate as buffer. This polymerization is possible because vinyl acetate reacts with PVA to form graft polymers. When the PVA chain is too long, it becomes insoluble and precipitates from the water phase. However, some authors reported the polymerization of vinyl acetate in an aqueous medium without the use of an emulsifier or stabilizing agent [215][216].

## Chapter 2.

### 2. Objectives

The goals of this thesis comprise the development of new polymers that were not synthesized yet to the purpose of soil stabilization. These polymers may be employed as main compounds or additives of drilling fluids.

These new polymers must:

1. Exhibit a viscosity ≥ 55 s when dissolved in water considering a ratio of 1:1 (1 g of polymer in 1 L of water)
2. Be able to suspend 100% of soil during 24 h.
3. Be able to settle soil in 2 h, when the soil is 100% suspended.

## Chapter 3.

## 3. Materials and Protocols

### 3.1. Materials

N-vinylpyrrolidone (VP, ≥98% purity, purchased from Merck KGaA), vinyl acetate (VAc, purity ≥99% with 3-20ppm hydroquinone as inhibitor) was purchased from Aldrich, sodium bicarbonate, acrylamide (AM, purity ≥98%) was purchased from Fluka Analytical, 2,2_-azobis(isobutyronitrile) (AIBN) was purchased from Xilong Chemical Co., Ltd, sodium perfsulfate (≥98% purity, purchased from Xilong Chemical Co., Ltd.), ammonia (25%, purchased from Labchem), poly(vinyl alcohol) (PVOH with 85-89% hydrolysis and 72000 g/mol) was purchased from Biochemica, clay (was purchased from Terracota do Algarve), sand (from Costa da Caparica beach), polymer A (PolyMUD®), additive A (Alfa-Bond®), sodium chloride (NaCl, was purchased from Sobeltec Fine Chemicals), and distilled-deionized water ($H_2O$). Argon (Ar) was supplied by Praxair with 99.998% purity. Sodium hydroxide (96% purity, purchased from Xilong Chemical Co., Ltd.) and acid boric was purchased from LabChem. Acetone (p.a.). All reagents were used without any further purification.

### 3.2. Polyvinylpyrrolidone (PVP)

The synthesis of PVP was adapted from the procedure described by Haaf *et al*. [187] and Fried *et al*. [202]. The polymerization reactions were performed in a 250 mL reaction vessel with 3 tubular openings equipped with a condenser and a stirring rod with Teflon blade. The reaction vessel was immersed in a thermostated oil bath with ±3 ºC of stability. Temperature control was performed by a probe contacting the oil connected to a Scilogex *MS7-H550-Pro* heating plate. The internal agitation is assured by the stirring rod with Teflon blade connected to an IKA Eurostar 20 motor. The vessel was charged with VP monomer, ammonia (20 µL), and distilled-deionized water (40 mL). The inertization was performed using Argon (Ar) during a period of 15 minutes through one of the openings of the reaction vessel. The initiator was introduced after inertization in a quantity ranging from 0.026% to 1% of monomer concentration. The reactions were performed at a temperature of 80 ºC under stirring (100 rpm) during 8 h.

The hydrolysis of PVP was carried immediately after polymerization in the same reaction vessel immersed in the same oil bath. The vessel was charged with 50 mL of a water solution containing 1.07 g of sodium hydroxide and 1.66 g of boric acid. The hydrolysis reactions were performed at temperatures between 95 and 110 ºC under stirring at 250 rpm during 7 h.

### 3.3. Poly(vinyl acetate) (PVAc) and Poly(vinyl alcohol) (PVA)

The synthesis of PVAc was adapted from the procedure described by González *et al*. [214]. The polymerization reactions were performed in a 250 mL reaction vessel with 3 tubular openings equipped with a condenser and a stirring rod with Teflon blade. The reaction vessel was immersed in a thermostated oil bath with ±3 ºC of stability. Temperature control was performed by a probe contacting the oil connected to a Scilogex *MS7-H550-Pro* heating plate. The internal agitation is assured by the stirring rod with Teflon blade connected to an IKA Eurostar 20 motor. The vessel was charged with 44mL of distilled-deionized water and 1.55 g of poly(vinyl alcohol). The mixture was stirred at 95 ºC during 0.5 h to assure the complete dissolution of the polymer. The mixture was cooled to room temperature and heated again to 60 ºC. The inertization was performed using Argon (Ar) during a period of 15 minutes through one of the openings of the reaction vessel. Once the polymerization temperature was attained, 5mg of sodium bicarbonate and 3.638 g of vinyl acetate. After 15 minutes, 1 mg of initiator (sodium persulfate) was introduced. The reactions were performed at 60 ºC under stirring (250 rpm) during 4 h.

The hydrolysis of PVAc to PVA was carried out immediately after polymerization in the same reaction vessel immersed in the same oil bath. The vessel was charged with 50 mL of sodium hydroxide solution containing from 0.42 g to 4.2 g of solids content. The hydrolysis reactions were performed at 100 ºC and 250 rpm during 1.5 – 4 h.

### 3.4. Poly(vinylpyrrolidone-co-vinyl acetate) (P(VP-co-VA))

The synthesis of P(VP-co-VA) was adapted from the procedure described by Fried *et al*. [202]. The polymerization reactions were performed in a 250 mL reaction vessel with 3 tubular openings equipped with a condenser and a stirring rod with Teflon blade. The reaction vessel was immersed in a thermostated oil bath with ±3 ºC of stability. The vessel was charged with VP and VAc monomers (typically 10 g of feed monomer mixture), in composition ratios ranging from 50 to 75 % (w/w) of VP and 25 to 50% of VAc, ammonia (typically 20 µL), distilled-deionized water (40 mL). Temperature control was performed by a probe contacting the oil connected to a Scilogex *MS7-H550-Pro* heating plate. The internal agitation is assured by the stirring rod with Teflon blade connected to an IKA Eurostar 20 motor. The inertization was performed using Argon (Ar) during a period of 15 minutes through one of the openings of the reaction vessel. The initiator was introduced after inertization in a quantity ranging from 0.07 to 0.53% of monomer concentration. The reactions were performed at 80 ºC and 100 rpm during 8 h.

### 3.5. Poly(acrylamide-co-vinyl acetate) (P(AM-co-VA))

The synthesis of P(AM-co-VA) was adapted from the procedure described by Fried *et al*. [202]. The polymerization reactions were performed in a 250 mL reaction vessel with 3 tubular openings equipped with a condenser and a stirring rod with Teflon blade. The reaction vessel was immersed in a thermostated oil bath with ±3 ºC of stability. Temperature control was performed by a probe contacting the oil connected to a Scilogex *MS7-H550-Pro* heating plate. The internal agitation is assured by the stirring rod with Teflon blade connected to an IKA Eurostar 20 motor. The vessel was charged with AM and VA monomers (10 g of feed monomer mixture), in composition ratios ranging from 25 to 75% (w/w) of AM and 25 to 75% (w/w) of VA, with a concentration of monomers to water of 25% in a total volume of 40 mL of distilled-deionized water. The inertization was performed using Argon (Ar) during a period of 15 minutes through one of the openings of the reaction vessel. The initiator was introduced after inertization in a quantity ranging from 0.035% (NaPS) to 0.33% (AIBN) of monomer concentration. The reactions were conducted in a temperature of 80 ºC, at 100rpm during 2 h.

The hydrolysis of P(AM-co-VA) was carried immediately after polymerization in the same reaction vessel immersed in the same oil bath. The vessel was charged with 50 mL of water solution containing sodium hydroxide and boric acid enough to hydrolyze the acrylamide units in a molar percentage from 15 to 55%. The hydrolysis reactions were executed at 90 ºC and 250 rpm during 7 h.

### 3.6. Poly(acrylamide-co-vinylpyrrolidone) (P(AM-co-VP)) synthesis

The synthesis of P(AM-co-VP) was adapted from the procedure described by Fried *et al*. [202]. The polymerization reactions were performed in a 250 mL reaction vessel with 3 tubular openings equipped with a condenser and a stirring rod with Teflon blade. The reaction vessel was immersed in a thermostated oil bath with ±3 ºC of stability. Temperature control was performed by a probe contacting the oil connected to a Scilogex *MS7-H550-Pro* heating plate. The internal agitation is assured by the stirring rod with Teflon blade connected to an IKA Eurostar 20 motor. The vessel was loaded with AM and VP monomers (typically 10 g of feed monomer mixture), in composition ratios ranging from 25 to 87% (w/w) of AM and 13 to 75% of VP, and distilled-deionized water (typically 40mL). The inertization was performed using Argon (Ar) during a period of 15 minutes through one of the openings of the reaction vessel. The initiator was introduced after inertization in a quantity ranging from 0.005 to 0.34% of monomer concentration. The reactions were performed at a temperature range between 60 ºC and 80 ºC, at 100 rpm during 2 h.

The hydrolysis of P(AM-co-VP) was carried immediately after polymerization in the same reaction vessel immersed in the same oil bath. The vessel was loaded with 50 mL of water solution containing sodium hydroxide and boric acid enough to hydrolyze the acrylamide units in a molar percentage from 25 to 55 %. The hydrolysis reactions were performed at 90 ºC and 250 rpm during 7 h.

*Figure 3.1- Synthesis assemblage*

### 3.7. Polymers isolation and drying

The polymers solutions obtained after polymerization or hydrolysis were drained into a 500mL beaker containing 400 mL of acetone. The beakers were keep at permanent agitation in a shaker for 16 hours.

The acetone was drained from the beaker and the polymers were cut into small pieces. The polymers were put in a hoven for 24 hours.

### 3.8. Scanning electron microscopy (SEM)

The morphology of scaffolds was investigated using SEM in Hitachi S-2400 equipment, with an accelerating voltage set to 15 kV. Scaffolds samples were frozen and fractured in liquid nitrogen for cross-section analysis. All samples were gold coated before analysis.

### 3.9. Viscosity measurements

The measurement of viscosity was performed after dissolve 2 g of each polymer in 2 L of water. The mixtures were stirred with a magnetic agitator during at least 2 hours to assure an efficient polymer dissolution. After complete dissolution, the viscosity was measured in a Marsh funnel by observing the time that a certain volume of the polymeric solution takes to flow between the cone and the cup of the Marsh funnel.

*Figure 3.2- Marsh Funnel*

### 3.10. Attenuated Total Reflectance Fourier Transform Infrared spectroscopy analysis (FTIR-ATR)

The FTIR-ATR accessory (from Bruker) containing a platinum diamond crystal at a nominal incident angle 45º, yielding about 12 internal reflections at the sample surface. All spectra (100 scans at 4.0 cm$^{-1}$ resolution and rationed to the appropriate background spectra) were recorded at approximately 25ºC. The samples were about 0.02 g.

*Figure 3.3- FTIR-ATR apparatus*

### 3.11. Nuclear Magnetic Ressonance measurements (NMR)

Solid-state 13C MAS NMR spectra were acquired with a 7T (300 MHz) AVANCE III Bruker spectrometer operating at 75 MHz (13C), equipped with a BBO probehead. The samples were spun at the magic angle at a frequency of 10 kHz in 4 mm-diameter rotors at room temperature. The 13C MAS NMR experiments were acquired with proton cross polarization (CPMAS) with a contact time of 1.2 ms, and the recycle delay was 2.0 s.

### 3.12. Molecular weight determination

The molecular weight determinations were perfomed in an Ubbelohde type I Capillar viscometer with a bath at 25ºC, using water as solvent for each polymer. Seven solution were prepared to each polymer: (1) 20 mL of 0.2 mol/L NaCl solution; (2) 18 mL of 0.2 mol/L NaCl solution and 2 mL of 0.05 g/dL polymer solution; (3) 16 mL of 0.2 mol/L NaCl solution and 4 mL of 0.05 g/dL polymer solution, (4) 12 mL of 0.2 mol/L NaCl solution and 8 mL of 0.05 g/dL polymer solution, (5) 8 mL of 0.2 mol/L NaCl solution and 12 mL of 0.05 g/dL polymer solution, (6) 4 mL of 0.2 mol/L NaCl solution and 16 mL of 0.05 g/dL polymer solution, and (7) 20 mL of 0.05 g/dL polymer solution. The viscometer was loaded with one solution at time. The time the fluid takes to travel from one determined point to another is registered. The experiment is repeated 3 times to all solutions. Polymer molecular weight is obtained from solvent viscosity and solution of polymer viscosity.

### 3.13. Zeta potential determination

Zeta potential determinations were performed in a JS94H Microelectrophoresis Aparatus equipped with a quartz cell. The zeta cell was filled with about 1.5 mL of polymeric solution at different pH. The cell was exposed to an electrical current and the particle movement were registered. A zeta potential graphic at different pH can be obtained with all values recorded.

*Figure 3.4- JS94H Microelectrophoresis Apparatus*

### 3.14. Suspension tests

Suspension tests were performed in a 5L beaker. The internal agitation was assured by the stirring rod with Teflon blade. The beaker was charged with 2L of distilled-deionized water or tap water , with or without 10 mL of a 2M sodium hydroxide solution to reach pH=12, and with a polymer or copolymer selected among all the ones polymerized in this thesis or a commercial one (polymer A). The mixtures were stirred during 1hour to achieve all polymer dissolution. After this time, solutions viscosity were measured. Soil (clay of sand) was added to the mixtures (typically 400g) and the mixtures were stirred for 2 more hours to accomplish the swell of soil and a sample was taken. Solutions viscosity and density were determined and an additive was added. The additive varied according to the polymer or copolymer in study. The mixtures were stirred for one more hour and a sample was taken every hour. All samples were evaluated after 10, 20, 30 minutes, 1, 2 and 24 hours after being collected, in order to monitor soil suspension or soil precipitation. After take 3 or 4, the stirring was switched off and 24 hours later, solutions viscosity and density were measured again.

*Figure 3.5- Suspension tests apparatus*

# Chapter 4.

## 4. Results and discussion

The synthesis of polymers under study were performed using different methodologies to find out which one conducted to a dry final product which: (1) is water soluble in a ratio of 1:1 (1 g of dry polymer in 1 liter of water) (2) and has a viscosity value higher than 55 s/quart in the said ratio. The polymer that fulfilled the previous requisites, was selected for further studies in order to understand its performance when applied (1) as a main compound or (2) as an additive for drilling fluids. Its suspension and settling capacities were also evaluated.

### 4.1. Polymer Synthesis

Different polymer synthesis were performed. However, for all the experiments, the polymer isolation and purification were executed following the same procedures as described in Chapter 3. In detail, at the end of each syntheses, final polymers were removed from reaction vessel to a beaker filled with acetone in order to precipitate and isolate the polymer from the reaction medium. The beaker containing the polymer was submitted to a permanent agitation during 16 hours to remove water from polymer to acetone (phase inversion method). After this process, the polymer was dried in an oven and powdered. The powder was then solubilized in a concentration of 1 g/L in distilled and deionized water (dd_water) to evaluate the water solubility and viscosity. The viscosities of previous solutions were evaluated in a Marsh funnel. The viscosity measurement followed by polymer drying, came up as a measure control to decide which the polymers were near of the goals of this work, for further and detailed characterization. Viscosity of a polymeric solution increases with polymeric molecular weight and chain linearity. Molecular weight determinations were performed in an Ubbelohde capillary viscometer for some of the polymers that exhibited viscosities values with interest. Other characterization methods were also performed such as SEM, FTIR-ATR, NMR, and zeta potential.

In order to trying to accomplish the objective of this thesis, a strategy based on copolymer synthesis was investigated. In detail, three different copolymers were synthetized with the combination of the two previous mentioned monomers (VP and VA) and acrylamide.

The acrylamide was chosen because from the GEO company knowledge, acrylamide based polymers are easy to generate polymers with high molecular weight and consequently high viscosities (above 50 s/quart).

#### 4.1.1. Polyvinylpyrrolidone

For the PVP polymerization, the variables under study were: (1) type and concentration of the initiator, (2) presence of ammonia, (3) agitation type, (4) volume of reactor, and (5) hydrolysis degree (HD) and temperature. Reaction conditions were kept constant such as mentioned in Chapter 3.

In order to study the influence of the initiator, the reactions were performed with (1) an organic initiator (AIBN), and (2) a persulfate (sodium persulfate (NaPS)) using different concentrations. All reactions were performed with a magnetic stirrer without the hydrolysis step.

*Table 4.1- Initiator conditions and viscosity variations with the use of two different initiators of PVP polymerization.*

| **Run** | **Initiator** | **Inititator concentration %($w_{init}/w_{mon}$)** | **Polymer mass formed (g)** [a] | **Viscosity (s/quart)** [b] |
|---|---|---|---|---|
| Run 1 | AIBN | 0.240% | 3.2 | 27 ± 2 |
| Run 2 | NaPS | 0.240% | 2.1 | 28 ± 2 |
| Run 3 | AIBN | 0.042% | 3.8 | 28± 2 |
| Run 4 | NaPS | 0.042% | 1.1 | n.a. |

[n.a.] – Not available
[a] Polymer mass formed with 4.2g of monomer.
[b] Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

All runs revealed the same viscosity suggesting that the concentration and type of initiator used, had no effect on the viscosity generated by the final product. Nevertheless, the results show that lower yield was achieved for the reaction with 0.042% NaPS. The analysis of data collected in Table 4.1 indicates that AIBN was the initiator with better performance for VP polymerization.
In a concordance with the literature [217][202], PVP can be produced either using NaPS or AIBN as initiators, but as higher product yields were obtained in the assays with AIBN, this initiator was selected for further studies.

*Initiator concentration*

In order to evaluate in detail the impact of initiator concentration in PVP polymerization different experiments were performed varying the AIBN concentration. All reactions were performed with a magnetic stirrer without the hydrolysis step.

*Table 4.2- Polymer viscosity variations in function of initiator concentration used during the VP polymerization.*

| **Run** | **Initiator concentration %($w_{init}/w_{mon}$)** | **Polymer mass formed (g) [a)]** | **Viscosity (s/quart) [b)]** |
|---|---|---|---|
| Run 5 | 1% | 2.6 | 26 ± 2 |
| Run 6 | 0.348% | 2.5 | 28 ± 2 |
| Run 1 | 0.240% | 3.2 | 27 ± 2 |
| Run 3 | 0.125% | 3.8 | 27 ± 2 |
| Run 7 | 0.067% | 3.7 | 27 ± 2 |
| Run 8 | 0.042% | 3.4 | 29 ± 2 |
| Run 9 | 0.026% | n.a. | n.a. |

N.a. – Not available
a) Polymer mass formed with 4.2 g of monomer.
b) Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

The results suggest that PVP can be formed with a concentration ratio of initiator between 0.042% and 1% ($w_{init}/w_{mon}$). For the assay with 0.026% ($w_{init}/w_{mon}$) no product could be recovered. Comparing the results obtained, the viscosity shows to slightly increase for lower initiator concentrations (29 s/quart), however, this value is still far away from the goal of this work (≥ 55 s/quart). Higher viscosity obtained in Run 8, is related with greater amount of polymer formed. This trend is in agreement with previous reported results showing that the increase of initiator content tends to decrease the molecular weight of the final polymer and thus a decrease of the viscosity [187].

All runs revealed the same range of viscosity, within its uncertainty, which suggest that when the concentration of initiator vary within 0.042 % and 1 %($w_{init}/w_{mon}$), it does not influence the viscosity of the final polymer, at least for the conditions herein studied

*Ammonia content*

In order to evaluate the influence of ammonia content in PVP polymerization, different experiments were performed using AIBN as initiator, and with the two different concentrations that led to the best mass yields (a ratio of 0.90 and 0.88 g of polymer per monomer gram were obtained). All reactions were performed with a magnetic stirrer without the hydrolysis step.

*Table 4.3- Polymer viscosity in function of ammonia addition during PVP polymerization.*

| **Run** | **Initiator concentration %($w_{init}/w_{mon}$)** | **Ammonia (addition of 20 µL)** | **Polymer mass formed (g) a)** | **Viscosity (s/quart) b)** |
|---|---|---|---|---|
| Run 3 | 0.125% | Yes | 3.8 | 27± 2 |
| Run 10 | 0.125% | No | 3.6 | 27 ± 2 |
| Run 7 | 0.067% | Yes | 3.7 | 27 ± 2 |
| Run 11 | 0.067% | No | 3.6 | 27 ± 2 |

a) Polymer mass formed with 4.2 g of monomer.
b) Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

The addition of ammonia can activate the polymerization of VP in solution [190], however, in this work the addition of ammonia did not influence the final viscosity obtained in the two experiments with different initiator concentrations. Nevertheless, in run 3 and run 7 the polymerization reaction was faster and the polymer was formed earlier (the bulk viscosity was observed earlier in runs 3 and 7), although the relatively constant mass yield registered.

In accordance with the literature [190], ammonia activated the polymerization, the polymerizations started earlier when ammonia was added.

*Hydrolysis*

In order to evaluate the impact of hydrolysis in the viscosity of the final product, run 3 was tested with and without hydrolysis. The hydrolysis step was performed after the polymerization step. The objective of hydrolysis is to generate more hydrophilic groups in the polymer chains in order to increase hydrogen bonding between polymer chains and simultaneously improve the water uptake capacity of the polymer and consequently, increase its viscosity. Hydrolysis reactions were performed for 30 % of molar monomers quantity of VP at 90 ºC and 105 ºC. These experimental conditions were based on hydrolysis of polyacrylamide presented in literature [94]. The final products presented approximately the same viscosity (28 ± 2 s/quart), at both temperatures.

In a marked contrast with the data reported in literature [93], the results obtained in this work suggest that PVP does not work the same way than acrylamide. No viscosity influence was observed in PVP after the hydrolysis step, which suggest that PVP hydrolysis was not achieved at any tested temperature. This fact may be related to the presence of the rings in VP units which can somehow hamper the hydrolysis process. In the literature [218], this effect can be overcome by a raise in hydrolysis temperature. Besides that, PVP chain have a helicoidally spatial conformation which reduce chain length and viscosifier capacity what can result in a polymer with capacity to reach high viscosity values in very dilute solution.

*Agitation type*

In order to evaluate the influence of agitation type in the reaction output, two different equipment for stirring were tested, (1) magnetic and (2) cutting blades stirrer. All reactions were performed without the hydrolysis step.

*Table 4.4- Viscosity variations in function of agitator type used during PVP polymerization*

| **Run** | **Agitator type** | **Polymer mass formed (g)** [a)] | **Viscosity (s/quart)** [b)] |
|---|---|---|---|
| Run 8 | Magnetic stirrer | 3.7 | 29 ± 2 |
| Run 12 | Cutting blades | 4.1 | 29 ± 2 |

[a)] Polymer mass formed with 4.2 g of monomer.
[b)] Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

No viscosity influence was observed, however when the cutting blades stirrer was used the bulk viscosity appeared earlier. This observation suggests that the cutting blades stirrer promoted the interaction of all reactants and consequently the polymerization started faster and earlier. A proof of this is that run 12 led to more 11% of polymer mass than run 8 (the one that was synthesized under a magnetic stirrer) to the same amount of VP. This observation emphasizes that using agitation with cutting blades a more extensive reaction with a higher mass yield was achieved. However, the obtained viscosity value is still far away from the target of this work.

*Reactor capacity*

In order to evaluate the impact of the reaction volume in polymerization progress two volumes, 14 and 40 mL were tested. The idea of this study was to investigate if the increase of volume reaction could increase the mobility of growing polymer chains and consequently promote efficiently the progress of polymerization reaction. All reactions were performed with a magnetic stirrer without the hydrolysis step. Comparative results are presented in the Table 4.5.

*Table 4.5- Viscosity variations in function of total reaction volume used during PVP polymerization*

| **Run** | **Total volume (mL)** | **Polymer mass formed (g) / monomer mass (g)** | **Viscosity (s/quart)** [a)] |
|---|---|---|---|
| Run 6 | 14 | 0.88 | 28.5 ± 2 |
| Run 13 | 40 | 0.91 | 28 ± 2 |

[a)] Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

The results suggest that an increase in reaction volume does not influence the viscosity of the final product but better mass yields were obtained (instead of 0.88 g, 0.91 g of polymer were formed per grams of monomer used). However, higher volumes should be tested to evaluate more thoroughly the impact of volume reaction. Heat dissipation is increasingly hindered with bigger reaction volumes [219].

Summing up, the preferable reaction conditions to PVP polymerization were achieved in a 250 mL reaction vessel without hydrolysis with a concentration of monomer to water of 30%, with a concentration of initiator to monomer of 0.042%, in a total water volume of 40 mL, at the absence of ammonia, at 80ºC and 100 rpm. The elected initiator for VP polymerization was AIBN. Results discussed before revealed that it is possible to produce water soluble PVP. However, the objective of achieving a viscosity of 55 s/quart with a polymeric aqueous solution containing 1g of polymer per liter of water was not possible to accomplish. This can be explained to the helicoidal predisposition that polymer tends to acquire in solution caused by the semi-flexible ring connected to the polymer backbone in every monomer.

Further studies must be performed regarding PVP. One approach could be the VP polymerization through another mechanism such as bulk polymerization. Another one should go through a copolymerization of VP with another monomers.

#### 4.1.2. Poly(vinyl alcohol)

PVA was another polymer investigated in this thesis to accomplish the goal.

In order to obtain PVA as final product or partially hydrolyzed poly(vinyl acetate) (PVAc) comprising vinyl acetate (VA) and vinyl alcohol units, a poly(vinyl acetate) (PVAc) synthesis was performed before hydrolysis. The synthesis of PVAc was adapted from the procedure described by González *et al*. [214]. For the PVA formation, the variables in study were: (1) hydrolysis degree (HD), and (2) hydrolysis reaction time. Reaction conditions were kept constant such as mentioned in Chapter 3.

*Hydrolysis*

In order to evaluate how HD influences the final polymer, three different HD to PVAc were performed during 1.5 hours.

*Table 4.6- Viscosity variations in function of PVA HD.*

| **Run** | **Hydrolysis percentage %($n_{NaOH}/n_{VA}$)** | **Viscosity (s/quart)** $^{a)}$ |
|---|---|---|
| Run 14 | 250% | 27 |
| Run 15 | 50% | n.a |
| Run 16 | 25% | n.a |

$^{N.a}$. – Not available
$^{a)}$ Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

The hydrolysis performed with a molar ratio of 250 % ($n_{NaOH}/n_{VA}$) led to a yellowish and hard polymer. This polymer was not soluble in water at room temperature. However, it was soluble in hot water at 90 ºC and once cooled down again, it did not precipitate. This obtained polymer registered a viscosity of 27 s/quart when dissolved in water at a quantity of 1 g/L. The hydrolysis performed with molar ratios of 50 % and 25 % ($n_{NaOH}/n_{VA}$) a beige and soft polymers were formed. These polymers cannot be dissolved in cool or hot water, consequently, the viscosity was not possible to be measured.

In order to evaluate the impact of hydrolysis duration in the final polymer, two different hydrolysis reaction times, 1.5 and 4 hours, were tested with the objective to obtain a water soluble polymer with a viscosity within the objectives. A hydrolysis of 50 % was chosen to be fixed while its time were varied. However, the final products of both experiments results in water insoluble polymers.

Summing up, PVAc can be successfully hydrolyzed to PVA with a molar ratio of 250 % ($n_{NaOH}/n_{VA}$). However, the objective to reach a viscosity of 55 s/quart with a polymeric aqueous solution containing 1 g of polymer for each water liter was not possible to accomplish. In order to meet the proposed objectives, VA must be polymerized with another mechanism of polymerization such as bulk polymerization, as it was previous mention for VP. Another approach should go through a copolymerization of VA with another monomers.

### 4.1.3. Poly(vinylpyrrolidone-co-vinyl acetate)

The synthesis of P(VP-co-VA) was adapted from the procedure described by Fried *et al*. [202]. The variables under study were: (1) the monomers ratio, and (2) initiator concentration. Reaction conditions were kept constant such as mentioned in Chapter 3.

*Monomer ratio*

In order to evaluate how monomers ratio affects P(VP-co-VA) viscosity, two experiments were performed with AIBN concentration of 0.280% ($w_{init}/w_{mon}$). The copolymerization was performed with two different ratios of VP and VA (75:25 and 50:50, run 17 and 18, respectively). At the end of assays, no polymers were isolated. Furthermore, no visible bulk viscosity was achieved which suggest that no polymerization or a very low ratio of polymerization occurred.

*Initiator concentration*

Different initiator concentrations were tested to compare with previous experiments.

*Table 4.7- List of performed experiments with different initiator concentrations and monomer ratios to synthesize P(VP-co-VA).*

| **Run** | **Monomer ratio (VP%:VA%)** | **Initiator concentration %($w_{init}/w_{mon}$)** |
|---|---|---|
| Run 17 | 75:25 | 0,280% |
| Run 19 | 75:25 | 0,080% |
| Run 18 | 50:50 | 0,280% |
| Run 20 | 50:50 | 0,560% |

The results suggest that a copolymer comprising vinylpyrrolidone and vinyl acetate cannot be isolated for reactions performed with VP ratios from 75 % to 50 % ($w_{mon}/w_{poly}$) and with an initiator concentration varying from 0.08 % to 0.56 % ($w_{init}/w_{mon}$). Furthermore, no visible bulk viscosity was achieved which suggest that no polymerization or a very low ratio of polymerization was performed.

In order to obtain a copolymer able to reach the target viscosity value of 55 s/quart with a polymeric aqueous solution containing 1g of polymer, other synthetic procedure and initiator type should be investigated.

### 4.1.4. Poly(acrylamide-co-vinyl acetate)

For the P(AM-co-VA) copolymerizations, the variables under study were: (1) the monomers ratio, (2) initiator type, (3) the use of surfactant, and (4) hydrolysis degree (HD). AIBN was used as reaction initiator [202]. NaPS was also investigated as initiator in an attempt to reply the initiator used in the literature for acrylamide polymerization [93]. Reaction conditions were kept constant such as mentioned in Chapter 3.

*Initiator type and monomers ratio*

P(AM-co-VA) copolymerizations were prepared with three different monomer ratios using AIBN and NaPS as initiators without hydrolysis. The results are presented in Table 4.8.

*Table 4.8- Viscosity evaluation of P(AM-co-VA) solutions according to initiators and monomers ratios used.*

| **Run** | **Monomer ratio (AM%:VA%)** | **Initiator** | **Initiator concentration %($w_{init}/w_{mon}$)** | **Polymer mass formed (g)** [a)] | **Viscosity (s/quart)** [b)] |
|---|---|---|---|---|---|
| Run 21 | 75:25 | AIBN | 0.33% | 1.6 | n.a. |
| Run 22 | 75:25 | NaPS | 0.035% | 5.9 | 28 ± 2 |
| Run 23 | 50:50 | AIBN | 0.33% | 1.3 | n.a. |
| Run 24 | 50:50 | NaPS | 0.035% | 3.2 | 28 ± 2 |
| Run 25 | 25:75 | AIBN | 0.33% | n.a. | n.a. |
| Run 26 | 25:75 | NaPS | 0.035% | n.a. | n.a. |

[n.a]. – Not available
[a)] Polymer mass formed with 10 g of monomers.
[b)] Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

For reactions performed with 25 % weight content of acrylamide and AIBN, no polymers were isolated, however, when acetone was added to the polymerization media, solutions with a milky aspect were formed but no polymer could still be isolated. When acrylamide content is increased to 50 % or 75 %, the isolation of the copolymers was successfully achieved. For a copolymer final product comprising from 75 or 50 %(w/w) of acrylamide, the use of AIBN as initiator results in a low mass yield when compared to the use of NaPS. In the case of a copolymer containing 75 % (w/w) of acrylamide, the yield of reaction using AIBN decreased to a quarter of the yield obtained with NaPS. Thus, due to monomer economy, no viscosity evaluation was performed for copolymerizations with yields below 20 %. The best result corresponds to the copolymer formed with 75% of acrylamide weight content synthesized with NaPS as initiator.

*Surfactant use*

As aforementioned, PVAc is not soluble in water and when it is polymerized in aqueous media, can lead to short chains that precipitate quickly while growing up. Consequently, the use of a surfactant on PVA polymerization can delay this phenomenon, allowing the growing of polymer chains [214]. Therefore, a surfactant was tested in the copolymerization of P(AM-co-VA) to evaluate polymer chain growth and, consequently, the viscosity. NaPS was used in concentration of 0.035% ($w_{init}/w_{mon}$).

A solution containing 50% of acrylamide and 50% of vinyl acetate by weight content was copolymerized in the presence of PVA as surfactant. This monomer ratio was chosen because of its lower mass yield reported in the previous chapter.

When PVA is used as surfactant to the copolymerization of P(AM-co-VA), no viscosity changes were observed, since the viscosity was kept at 27 ± 2 s/quart. However, no further conclusions can be done to the copolymer chain length.

*Hydrolysis degree*

As evaluated previously studied for homopolymeric systems, the influence of HD was also investigated for the copolymeric systems. From the literature point of view, viscosity of polyacrylamide solutions can be enhanced with hydrolysis [93]. Based on this, the HD for polyacrylamide-based copolymers was examined. NaPS was used in concentration of 0.035% ($w_{init}/w_{mon}$).

*Table 4.9- Viscosity evaluation of hydrolyzed P(AM-co-VA) solutions with different HDs.*

| **Run** | **HD %** | **Polymer mass formed (g)** [a)] | **Viscosity (s/quart)** [b)] |
|---|---|---|---|
| Run 22 | 0% | 7.7 | 28 ± 2 |
| Run 27 | 15% | 8.2 | 42 ± 2 |
| Run 28 | 25% | 8.5 | 50 ± 2 |
| Run 29 | 30% | 7.3 | 50 ± 2 |
| Run 30 | 35% | 8.7 | 46 ± 2 |
| Run 31 | 40% | 8.0 | 56 ± 2 |
| Run 32 | 55% | 9.8 | 43 ± 2 |

[a)] Polymer mass formed with 10 g of monomers.
[b)] Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

The results suggest that HD can highly influence the viscosity of this copolymer. For a copolymer containing 40% of hydrolyzed monomer groups (run 31), a viscosity of 56 s/quart can be reached. However, when a lower hydrolysis ratio was applied, the viscosity is under that value. This fact can be justified by a low charge density in polymeric chains what reduces inter-chain interaction. A lower value of viscosity is also presented to a copolymer with 55% of HD. This fact can be explained by an excess of charge density which led to a copolymer structure reorganization, translated in a loss of copolymer chain linearity and consequently in a decrease of viscosity. The result of run 31, with the viscosity value of 56 ± 2 s/quart, the main objective of this work (1g of polymer in 1 L of water generates a viscosity ≥ 55 s/quart) was achieved.

Further work should be performed to investigate how it could be possible to reach higher viscosity values for 1:1 ratio of polymer in water. Playing with solvent addition or monomer and initiator quantities could also be pushed in order to figure out if better polymer performances could be achieved. Polymerization volume should also be investigated to understand how the reaction volume can impact reaction medium, as it was evaluated for the polymeric systems previously discussed.

### 4.1.5. Poly(acrylamide-co-vinylpyrrolidone)

The synthesis of P(AM-co-VP) was also investigated as a function of the following variables: (1) concentration and type of initiator, (2) HD, (3) monomer concentration, (4) addition of monomers, initiator and water during reaction, and (5) reaction vessel volume. Reaction conditions were kept constant such as mentioned in Chapter 3.

*Initiator*

In an attempt to study initiator type influence on copolymerization of AM and VP, two different initiator types where used: (1) AIBN, an organic compound, indicated by literature [202] adapted for this copolymerization, and (2) NaPS, a persulfate, in an attempt to reply the initiator used in the literature for acrylamide polymerization [93].

*Table 4.10- Viscosity evaluation of P(AM-co-VP) solutions synthesized with two distinct initiators.*

| Run | Monomer ratio (AM%:VP%) | Initiator | Initiator concentration %($w_{init}/w_{mon}$) | Polymer mass formed (g) [a)] | Viscosity (s/quart) [b)] |
|---|---|---|---|---|---|
| Run 33 | 87:13 | AIBN | 0.33% | 7.0 | 28 ± 2 |
| Run 34 | 87:13 | NaPS | 0.035% | 9.4 | 28 ± 2 |
| Run 35 | 50:50 | AIBN | 0.33% | 4.1 | 28 ± 2 |
| Run 36 | 50:50 | NaPS | 0.035% | 7.1 | 28 ± 2 |

[a)] Polymer mass formed with 10 g of monomers.
[b)] Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

Table 4.10 compiles the results obtained. It is. The bulk viscosity and the mass of final product obtained allow us to conclude that P(AM-co-VP) copolymerizations can be initiated by both initiators with both monomer ratios but it was not possible to evaluate the effect of initiator and monomer ratios in this copolymerization. However, for a constant amount of monomer (10 g), when the reactions were initiated by NaPS, a higher quantity of polymers (9.4 g and 7.1 g) were formed when compared to reactions initiated by AIBN (7.0 g and 4.1 g, respectively). Furthermore, when an 87:13 ratio is used a higher mass yield is achieved using any of the two studied initiators. In the next experiments only NaPS was used as initiator due to the higher quantity of polymer formed.

*Hydrolysis degree*

As aforementioned, polyacrylamide solutions viscosity can be enhanced with hydrolysis [93]. Various HDs were studied to each monomer ratio using NaPS as initiator in a concentration of 0.035% ($w_{init}/w_{mon}$). The first set of experiments was performed for a monomer ratio of 50% by weight of AM and 50% by weight of VP.

*Table 4.11- Viscosity evaluation of P(AM-co-VP) solutions containing the same amount of each monomer with and without hydrolysis.*

| **Run** | **HD %** | **Polymer mass formed (g)** [a)] | **Viscosity (s/quart)** [b)] |
|---|---|---|---|
| Run 36 | 0% | 7.1 | 28 ± 2 |
| Run 37 | 30% | 7.6 | 34.5 ± 2 |
| Run 38 | 40% | 9.4 | 33 ± 2 |

[a)] Polymer mass formed with 10 g of monomers.
[b)] Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

The results suggest that a slightly increase on copolymer viscosity can be achieved with a HD of 30 %. However, when HD is increased to 40 %, the polymer presents the same viscosity when it is hydrolyzed with 30 %. In accordance to the literature [93][176][12], P(AM-co-VP) hydrolysis can improve the solution viscosity of polymers with this monomer composition ratio. Nevertheless, it was not sufficient to achieve the desired viscosity value (≥ 55 s/quart).

A second set of experiments was performed for a monomer ratio of 87 % by weight of AM and 13 % by weight of VP.

*Table 4.12- Viscosity evaluation of P(AM-co-VP) solutions containing 87% by weight of acrylamide and 13% of VP with and without hydrolysis.*

| **Run** | **HD %** | **Polymer mass formed (g)** [a)] | **Viscosity (s/quart)** [b)] |
|---|---|---|---|
| Run 34 | 0% | 9.4 | 28 ± 2 |
| Run 39 | 25% | 9.2 | 47 ± 2 |
| Run 40 | 30% | 9.9 | 49 ± 2 |
| Run 41 | 35% | 8.7 | 48 ± 2 |
| Run 42 | 40% | 9.0 | 44 ± 2 |

[a)] Polymer mass formed with 10 g of monomers.
[b)] Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

The increase of acrylamide content combined with hydrolysis allowed an increase of solution viscosity of 15 s/quart (run 40), comparatively with run 37 presented in

Table 4.11. This observation is in agreement with previous reported work [93][176][12]. Herein, a higher viscosity value was achieved with a hydrolysis of 30% while with 40% HD, the copolymer viscosity decreased. This fact can be explained by chain winding caused by excess charges, which reduce chain linearity [220].

*Initiator concentration*

In order to go further in viscosity target of the obtained copolymers, the aforementioned experiment containing 87% by weight of acrylamide hydrolyzed at a ratio of 30% by acrylamide weight was tested with two different concentrations of initiator. In the next set of experiments, HDs of the copolymers were kept at 30% of hydrolysis acrylamide content. NaPS was used as initiator

*Table 4.13- Viscosity evaluation of hydrolyzed P(AM-co-VP) solutions with different monomer compositions containing different initiator concentrations.*

| **Run** | **Monomer ratio (AM%:VP%)** | **Initiator concentration %($w_{init}/w_{mon}$)** | **Polymer mass formed (g)** [a)] | **Viscosity (s/quart)** [b)] |
|---|---|---|---|---|
| Run 40 | 87:13 | 0.035% | 9.9 | 49 ± 2 |
| Run 43 | 87:13 | 0.027% | 9.4 | 49 ± 2 |

a) Polymer mass formed with 10 g of monomers.
b) Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

In contrast with the literature [221], no viscosity improvement was registered with the decrease of concentration of the initiator. However, the reduction was only of 25% of the starting point and could be insufficient to register a boost on the viscosity.

*Monomer concentration*

In order to investigate all variables to improve viscosity of the obtained copolymers, a couple of experiments were performed to the two monomer ratios studied. In addition to the variables already mentioned as kept constants, in the next set of experiments, HDs were kept at 30% hydrolysis acrylamide content in the copolymer.

The previous experiments performed showed that an initiator content of 0.027% ($w_{init}/w_{mon}$) was the best initiator concentration to be used in both monomers ratios. In the next experiments an initiator content of 0.027% ($w_{init}/w_{mon}$) was used.

The results suggest that a decrease in monomer concentration also decreases viscosity of both copolymers. However, when a concentration of monomer in solution of 50% is used, no viscosity alterations were registered (.

*Type vs moment addition*

In order to improve polymer synthesis, and consequently copolymer viscosity, a series of tests were performed to study how the addition of solvent, monomer and initiator could influence the reaction mechanism. The addition of these compounds can be performed either at the start of reaction or during the polymerization in order to tune the properties of the polymer. These compounds can be added by two means: (1) added manually, as a shot, with all volume being added once, and (2) added with the help of a peristaltic pump, with a constant flow. In addition to the variables already mentioned as kept constants, in the next set of experiments only a mixture of monomers with 87 % (w/w) of AM and 13 % (w/w) of VP. HDs were kept at 30 % ($n_{NaOH}/n_{AM}$).

Regarding water addition, a set of tests were performed in order to study how the addition of water to the growing polymer mixture can affect the viscosity of the final product. Water can be added by the aforementioned ways at room or reaction temperatures. The addition of water as shots to the reaction mixture influenced negatively the viscosity of the growing polymer chain. Worst viscosity results were achieved to the polymerizations to which cold water was added (35 ± 2 s/quart). A decrease from 8 to 16 s/quart in final polymers was registered with the shot adding method. The addition of water to the reaction mixture with the help of a peristaltic pump in a constant flow can influence the viscosity of the final polymer in two different ways: (1) negatively by decreasing solution viscosity in 6 ± 2 s/quart when the starting mixture contains a monomers to water concentration of 25 % (43 ± 2 s/quart) and (2) positively, by increasing solution viscosity in 4 ± 2 s/quart when the starting mixture contains a monomers to water concentration of 50% (53 ± 2 s/quart.). The total weight of monomers was 10 g and the total volume of water was 20 mL. The addition of water after the start of the polymerization was performed in a constant flow rate of 4 mL/min during 5 minutes. The hydrolysis of this copolymer was performed by 30 % of the total amount of acrylamide content. The solution viscosity of the produced copolymer was 53 ± 2 s/quart. (Appendix 1)

This can be explained by an increase of the copolymer molecular weight. When water is added in a controlled way, it dissolves the polymer and the unreacted monomers contributing to the extension of the reaction between the unfinished polymer and the unreacted monomers.

Regarding monomers addition a set of tests was performed. Monomers were added in solution with a concentration in water of 25 % by the aforementioned ways at both room and reaction temperatures. The addition of the monomer solution as shots to the reaction mixture results in no significant viscosity impact to the growing polymer chain. However, best results can be obtained with a starting mixture containing 87 % (w/w) of acrylamide and 13 % (w/w) of VP. The addition of monomer solution after the start of the polymerization was performed in a constant flow rate of 4 mL/min during 5 minutes. The composition of the monomer solution was the same as the starting solution with the same monomers ratio. The hydrolysis of this copolymer was performed by 30 % of the total amount of acrylamide content. The solution viscosity of the produced copolymer was 51 ± 2 s/quart. (Appendix 2)

In order to study how the addition of initiator can change the way which a polymer chain grows, an experiment was performed with slow addition of a solution of initiator during three minutes. The addition of the solution of initiator was performed with the help of a peristaltic pump with a constant flow. The addition of initiator solution was performed in a constant flow rate of 6.67 mL/min during 3 minutes. The composition of the solution of initiator was 3 mg of NaPS in 20 mL of water. The hydrolysis of this copolymer was performed by 30 % ($n_{NaOH}/n_{AM}$). The solution viscosity of the final copolymer was 49 ± 2 s/quart with 10.9 g of polymer being produced.

Further experiments should be performed to investigate how a slowly addition of a solution of initiator can influence the viscosity of the copolymers. (Appendix 3)

To evaluate the addition of initiator solution with different monomers ratio and times of addition, a set of experiments was carried out.

In a first step, acrylamide was polymerized without VP in the presence of different amounts of initiator, and then, VP was added with another variable portion of initiator. The total amount of initiator added to the copolymerization was 3 mg. The starting mixture contained only 8.7 g of acrylamide and 40 mL of water in all experiments. A first quantity of initiator was introduced to start acrylamide polymerization. VP and the remaining initiator were added in a single shot, 3 minutes after the start of the reaction (this is the necessary time to synthesize polyacrylamide with the necessary degree of polymerization to develop some initial bulk viscosity). The results are presented in the Table 4.14.

*Table 4.14- Viscosity evaluation of hydrolyzed P(AM-co-VP) solutions with a delay on VP addition to the reaction varying the initiator concentration added on start and during reaction progress.*

| **Run** | **Initial water content (mL)** | **Initial VP:AM content (g:g)** | **First Initiator addition (mg)** | **VP:AM addition after initiator (g:g)** | **Second initiator addition (mg)** | **Polymer mass formed (g) [a)]** | **Viscosity (s/quart) [b)]** |
|---|---|---|---|---|---|---|---|
| Run 43 | 40 | 1.3 : 8.7 | 3 | 0 | 0 | 9.4 | 49 ± 2 |
| Run 57 | 40 | 0 : 8.7 | 3 | 1.3 : 0 | 0 | 5.2 | 47 ± 2 |
| Run 58 | 40 | 0 : 8.7 | 2.61 | 1.3 : 0 | 0.39 | 12.77 | 54 ± 2 |
| Run 59 | 40 | 0 : 8.7 | 2 | 1.3 : 0 | 1 | 12.13 | 50 ± 2 |
| Run 60 | 40 | 0 : 8.7 | 1.5 | 1.3 : 0 | 1.5 | 11.3 | 50 ± 2 |
| Run 61 | 40 | 0 : 8.7 | 1 | 1.3 : 0 | 2 | 11.6 | 49 ± 2 |

N.a. – Not available
a) Polymer mass formed with 10 g of monomers.
b) Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

In the Table 4.14, it is possible to observe that this process of adding the VP monomer 3 minutes after the start of the reaction can influence the properties of the final polymer in two different ways: (1) negatively by decreasing the quantity of the final product in 45% when the initiator is added in its full quantity to the acrylamide at the beginning of the reaction (5.2 g) and (2) positively, by increasing solution viscosity in 5 ± 2 s/quart and by increasing mass yield in 30% when the starting mixture contains only 87% of the solution of initiator with the rest being added with VP after 3 minutes the reaction starting. Best results were obtained with a starting mixture containing 8.7 g of acrylamide, 40 mL of water and 2.61 mg of initiator and the adding as a shot of 1.3 g of VP and 0.39 mg of initiator 3 minutes after the starting of the reaction. The hydrolysis of this copolymer was performed by 30 % ($n_{NaOH}/n_{AM}$). The solution viscosity of the produced copolymer was 54 ± 2 s/quart. This method of polymerization give rise to block copolymers. This viscosity increase can be explained by long chain portions of acrylamide and acrylic acid monomers (obtained after hydrolysis step) which may establish strong inter-chain interactions.

In a second step, VP was polymerized without AM in the presence of different amounts of initiator, and then, an acrylamide solution was added with another variable portion of initiator. The total amount of initiator added to the copolymerization was 3 mg. The starting mixture contained only 1.3 g of VP and 20 mL of water in all experiments. A first quantity of initiator was introduced to start VP polymerization. The addition of AM and the remaining initiator was performed in a single shot 3 minutes after the start of the reaction (this is the necessary time to let VP monomers to form enough long polymer chains to develop some initial bulk viscosity). This adding is performed with 20 mL of water. However, the process of adding the AM monomer 3 minutes after the start of the reaction influence in a negative way the properties of the final polymer by decreasing solution viscosity in 13 ± 2 s/quart and mass yield in 6% to 35% when the starting mixture contains from 13% to 50% of the solution of initiator with the rest being added with AM after 3 minutes of the start of the reaction.

To summarize, the addition of the VP monomer after the start of the AM polymerization can result in an increase of 5 ± 2 s/quart in a solution of the obtained copolymer and an increase in mass yield of about 30%. However, when VP is used as starting monomer, a decrease of 13 ± 2 s/quart in a solution of the obtained copolymer was registered.
Further work should be performed in order to investigate how the addition of these monomers in combination with initiator can improve viscosity of the copolymer.

*Total reaction volume*

In order to study how the total volume of the reaction can influence the mass yield and the polymer viscosity, a reaction with a fourfold total volume was carried out. In addition to the variables already mentioned as kept constants, HD were kept at 40% ($n_{NaOH}/n_{AM}$).

*Table 4.15- Viscosity evaluation of hydrolyzed P(AM-co-VP) solutions with different reactor volumes and water volume.*

| **Run** | **Reactor volume (mL)** | **Total water volume (synthesis) (mL)** | **Total water volume (hydrolysis) (mL)** | **Polymer mass formed (g) / monomer mass (g)** | **Viscosity (s/quart) [a)]** |
|---|---|---|---|---|---|
| Run 42 | 250 | 40 | 50 | 0.9 | 44 ± 2 |
| Run 66 | 1000 | 160 | 200 | 1.32 | 56 ± 2 |

a) Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

In the Table 4.15, it is observed that an increase in the reaction volume can lead to an increase of 7 ± 2 s/quart in solution of the obtained copolymer (56 ± 2 s/quart).

The proposed objective may be successfully achieved if P(AM-co-VP)) is copolymerized with a mass ratio of 87 %(w/w) of acrylamide content and 13 %(w/w) of VP content, using NaPS as initiator 0.027% $wt_{init}/wt_{mon}$, in 160 mL of water. Finally, the copolymer should be hydrolyzed in 40% ($n_{NaOH}/n_{AM}$). This copolymer can reach a viscosity of 56 s/quart with a concentration of 1 g in one liter of dd_water.

Further work should be performed in order to optimize the solution viscosity and mass yield by varying different parameters such as: water addition, monomer and initiator content, water volume. The agitation method should be also improved to assure a faster medium homogeneity.

To summarize, two copolymers – (1), a copolymer with a mass ratio of 75 %(w/w) of acrylamide content and 25 %(w/w) of VA content with an HD of 40 %($n_{NaOH}/n_{AM}$); (2), another copolymer with a mass ratio of 87 %(w/w) of acrylamide content and 13 %(w/w) of VP content with an HD of 40% ($n_{NaOH}/n_{AM}$) - were synthesized fulfilling the first objective of this work thesis: to reach a viscosity of 56 s/quart with 1g of the copolymer in one liter of dd_water.

Both copolymers, the ones that fit the first objective of this thesis, were further characterized and then evaluated to find out their suitability to be used as components of drilling fluids.

## 4.2. Polymer characterization

PVP, PVAc, P(AM-co-VA) and P(AM-co-VP) were chemically and morphologically characterized using different techniques.

### 4.2.1. SEM

In order to evaluate polymers and copolymers morphology and to understand how the different monomers influence the spatial conformations and rearrangements, analysis of scanning electron microscopy was performed.

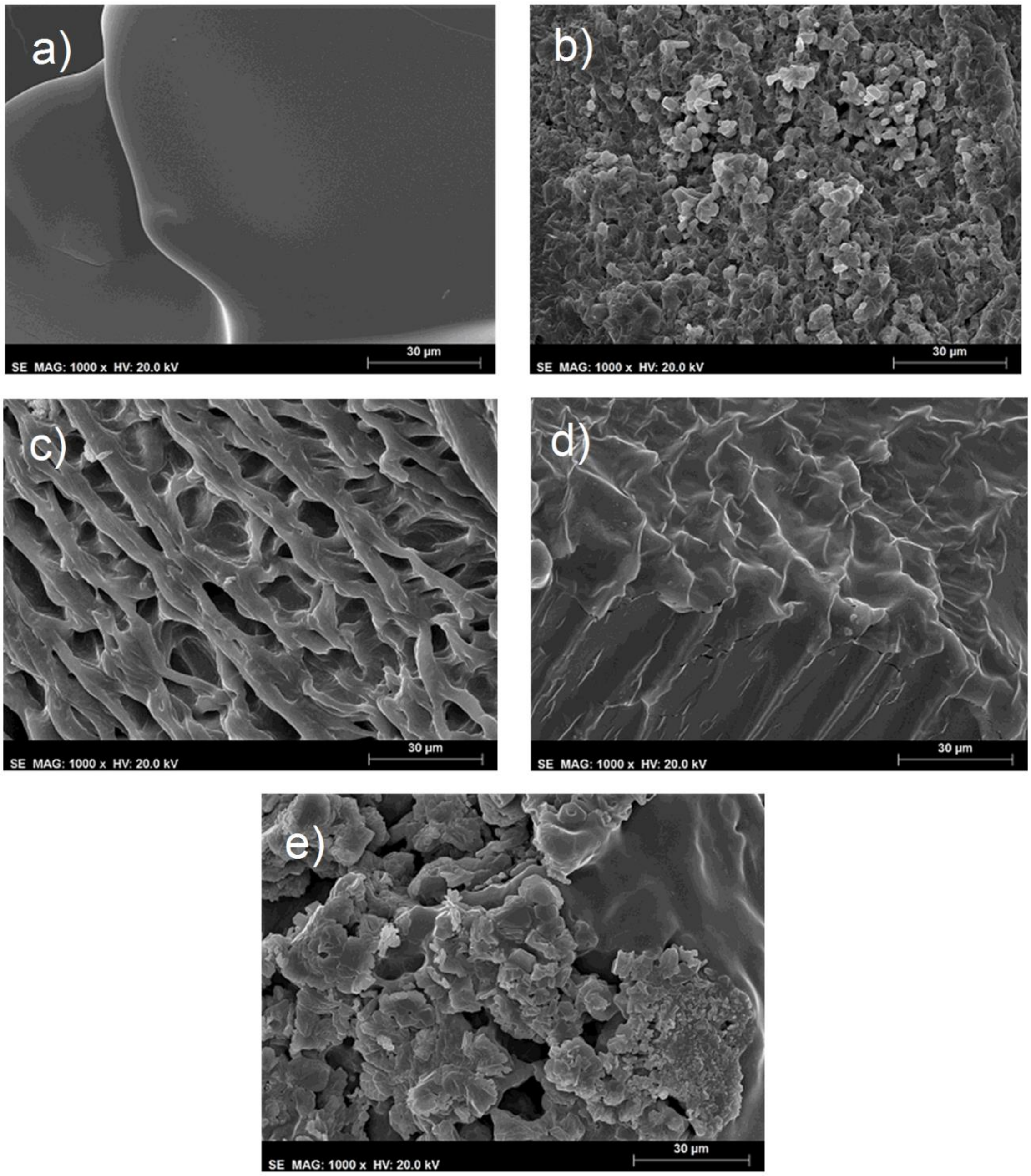

*Figure 4.1- SEM of VP- and VA-based polymers and copolymers with an enlargement of 1000x. a) PVP with no hydrolysis. b) PVAc with 250% HD. c) P(AM-co-VP) comprising 87% of AM and 13% of VP with 25% (nNaOH/nAM). d) P(AM-co-VP) comprising 87% of AM and 13% of VP with 40% ($n_{NaOH}/n_{AM}$). e) P(AM-co-VA) comprising 75% of AM and 25% of VA with 40% ($n_{NaOH}/n_{AM}$).*

The Figure 4.1 represents the SEM images of PVP (Figure 4.1 a)), PVA (Figure 4.1 b)), P(AM-co-VP) with 25% of hydrolysis (Figure 4.1 c)), P(AM-co-VP) with 40% of hydrolysis (Figure 4.1 d)), and P(AM-co-VA) (Figure 4.1 e)). In Figure 4.1 a) and b) the PVP and the PVAc non-hydrolyzed are represented. Both polymers present themselves differently, while PVP shows large and isolated particles, PVAc exhibits small and agglomerated particles.

In Figure 4.1 c) and d) P(AM-co-VP) 25% and 40% hydrolyzed, respectively, are represented. Through these images it is clear that the increase of hydrolysis degree highly affects the morphological structure of copolymers. In detail, the increase of hydrolysis content turns the homogeneous and spherical pores of particles more elongated like channels. In the Figure 4.1 e) it is represented the P(AM-co-VA) structure with 40% of hydrolysis It can be observed that the copolymer have an irregular structure with very small particles agglomerated.

### 4.2.2. FTIR-ATR

FTIR-ATR analyses were performed in order to validate the chemical structures of polymers and copolymers herein synthesized as well as to understand the impact of reaction conditions in the features of final products.

Figure 4.2 shows the FTIR-ATR spectra of two PVP polymers with and without hydrolysis. The HD of the experiment represented in this spectrum was tuned to 30%. The results show the principal chemical groups of PVP polymers.

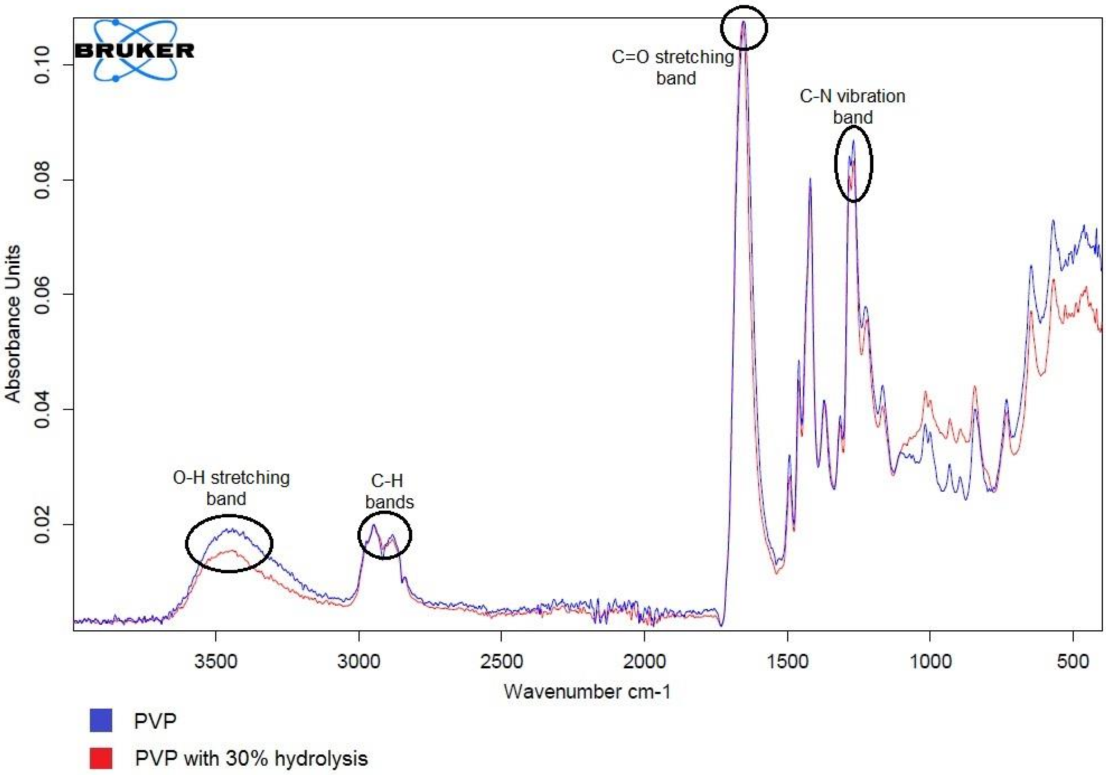

*Figure 4.2- FTIR-ATR spectra of a PVP and PVP with 30% hydrolysis.*

Chemical structures of PVP and partially hydrolyzed PVP are very similar, which is in agreement with the literature [218]. For the represented partially hydrolyzed PVP the aim was to possess 30% of its monomers hydrolyzed, however, no notable differences in carbonyl stretching bands were registered between both spectrums which suggests that the hydrolysis method used was not efficient.

In Figure 4.2 it is possible to observe the carbonyl stretching bands (C=O) of VP units associated in PVP polymer at 1661 cm$^{-1}$, the hydroxyl stretching bands (O-H) at 3434 cm$^{-1}$, the asymmetric carbon-hydrogen bond (C-H) at 2955 cm$^{-1}$, and the vibrations of C-N bonds at 1291 and 1018 cm$^{-1}$. This is in agreement with the literature [222], which proves the success of the PVP synthesis herein presented.

Figure 4.3 shows the FTIR-ATR spectra of two PVAc polymers with different HD. The principal chemical groups of partially and fully hydrolyzed PVAc polymers are clearly depicted.

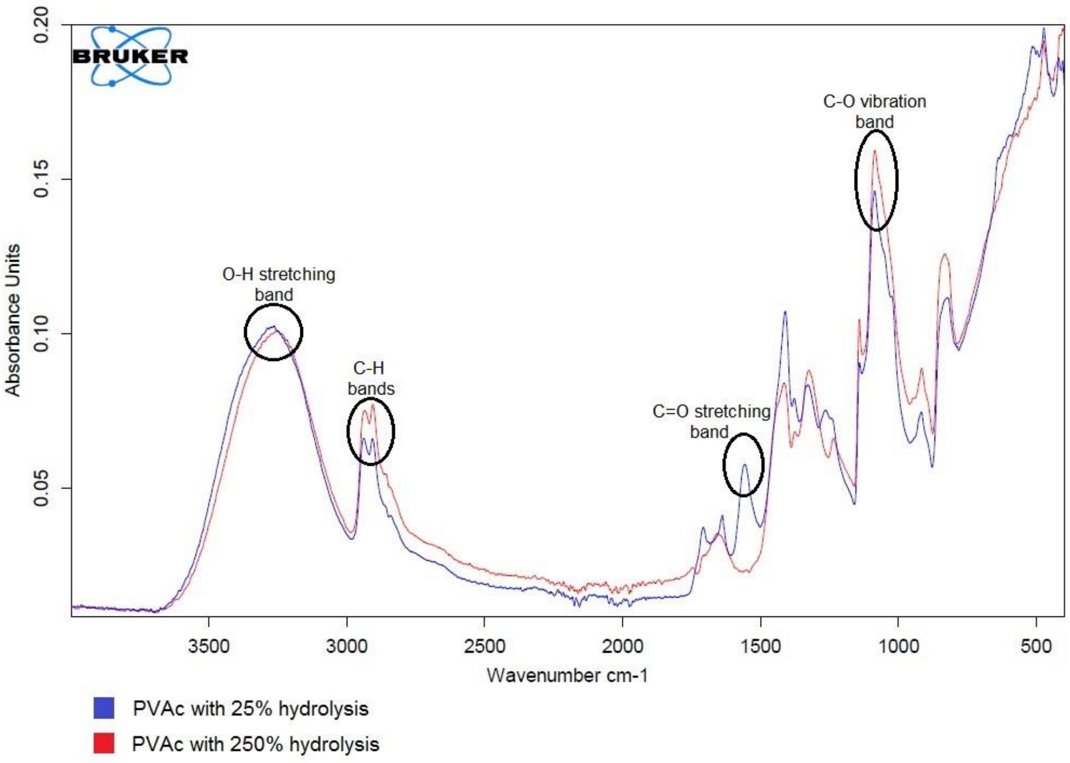

*Figure 4.3- FTIR-ATR spectra of PVAc with HD of 25% and 250%*

Chemical structures of PVAc and fully hydrolyzed PVAc (PVA) are distinct. In accordance with the literature [223][224], PVAc FTIR-ATR spectra do not present hydroxyl stretching bands (O-H) when compared with PVA. However, PVAc FTIR-ATR spectra present notorious carbonyl stretching bands (C=O). PVAc hydrolysis tends to turn C=O bonds into C-O which may justify the FTIR-ATR spectra difference.

In Figure 4.3 it is possible to observe the carbon-hydrogen bonds at 2900-3000 cm$^{-1}$, and the vibrations of C-O bonds present a strong peak around 1100 cm-1. The hydroxyl stretching band is presented at 3200-3400 cm$^{-1}$ in both spectra which suggests that a high PVAc hydrolysis was performed, however, in PVAc with only 25% of hydrolyzed groups, a minor band is observed around 1600 cm$^{-1}$ which suggests that some non-hydrolyzed C=O bonds are present. This is in agreement with the literature [223][224], demonstrating the success of the PVAc synthesis and hydrolysis herein presented.

Figure 4.4 shows the FTIR-ATR spectra of P(AM-co-VA) copolymers with different HDs. The HD of each experiment is represented in the figure. Results show the principal chemical groups of not only partially hydrolyzed P(AM-co-VA) polymers but also of a non-hydrolyzed P(AM-co-VA) polymer.

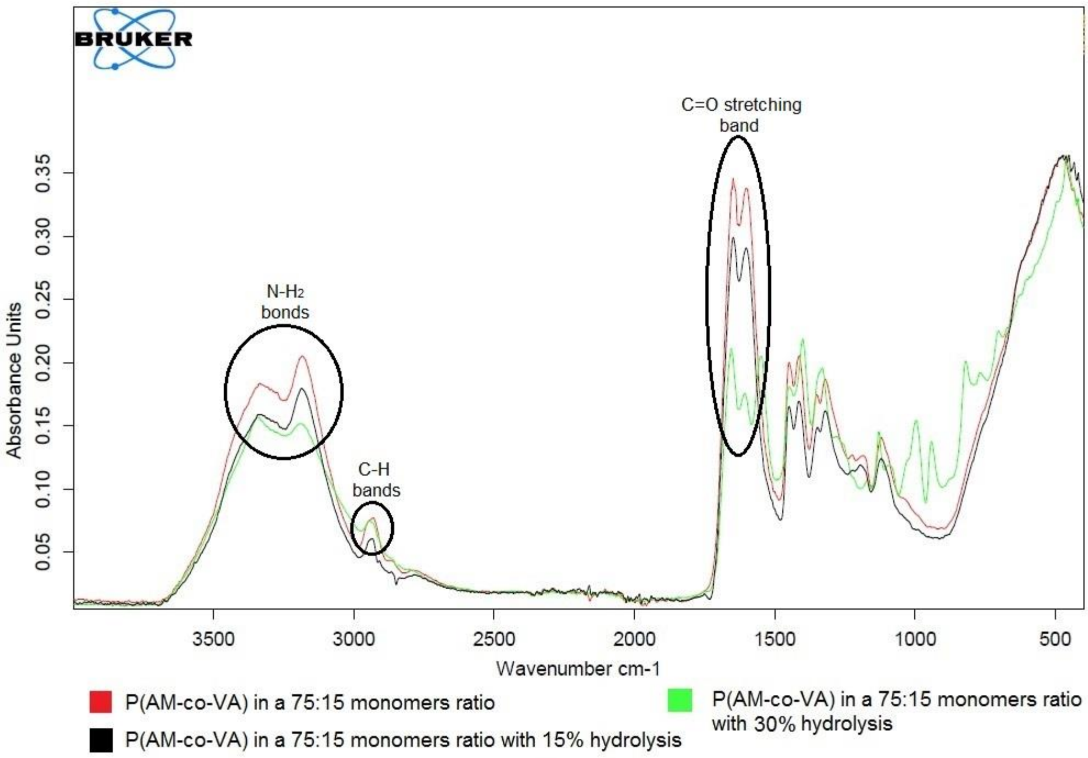

*Figure 4.4- FTIR-ATR spectra of P(AM-co-VA) with HD of 0%, 15% and 30%.*

Chemical structures of P(AM-co-VA) copolymers depend on HD. Acrylamide and vinyl acetate monomers presented in the copolymers are hydrolyzed to acrylic acid and vinyl alcohol, respectively.

In Figure 4.4 it is possible to observe the characteristic peaks of acrylamide and hydrolyzed vinyl acetate units in all spectra. The amine bonds (N-H$_2$) peaks are represented by two bands between 3200 and 3450 cm$^{-1}$, a double band appears between 1550 and 1650 cm$^{-1}$ corresponding to the carbonyl stretching bands, moreover the intensity of these peaks is dependent of the HD, which suggest that a copolymer with a higher HD should have a less intense peak, this is in accordance with the FTIR-ATR spectra presented. Another difference between hydrolyzed and non-hydrolyzed copolymers with acrylamide content is the ability to lose amine groups when hydrolyzed. A copolymer with a higher HD presents a less intense peak between 3200 and 3450 cm$^{-1}$ which is in agreement with the results. The carboxylate groups are also represented in the spectra by a band of medium intensity around 1550 cm$^{-1}$ which is only visible in P(AM-co-VA) with 40% acrylamide HD. This is in agreement with the literature [223][224][225], which proves the success of the P(AM-co-VA) synthesis and hydrolysis herein presented.

Figure 4.5 shows the FTIR-ATR spectra of P(AM-co-VP) copolymers with different HD. The HD of each experiment is represented in the figure. Results show the principal chemical groups of not only partially hydrolyzed P(AM-co-VP) polymers but also of non-hydrolyzed P(AM-co-VP) polymer.

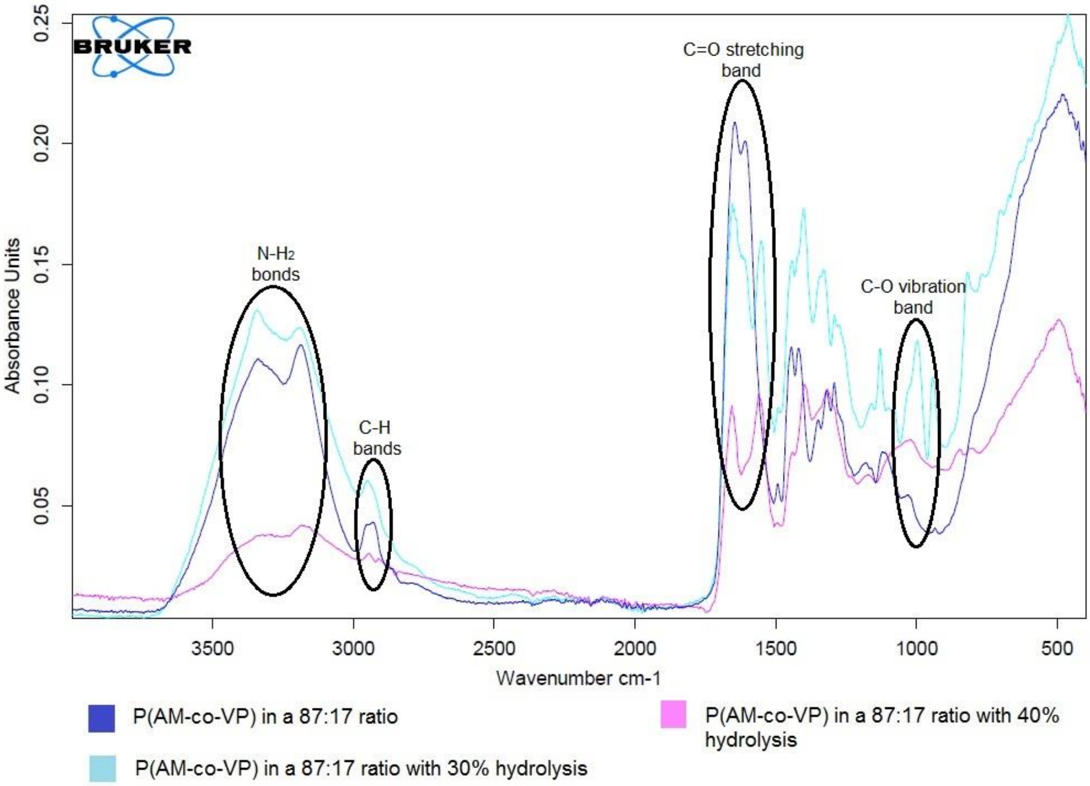

*Figure 4.5- FTIR-ATR spectra of P(AM-co-VP) with HD of 0%, 30% and 40%*

Chemical structures of P(AM-co-VP) copolymers depend on HD. Acrylamide monomers presented in the copolymers are hydrolyzed to acrylic acid. As mentioned before, vinylpyrrolidone are not able to be hydrolyzed at 90ºC in a significant quantity.

In Figure 4.5, it is possible to observe the characteristic peaks of acrylamide and vinylpyrrolidone units in all spectra. The amine bonds (N-H$_2$) peaks are represented by two peaks between 3200 and 3450 cm$^{-1}$, a double peak appears between 1550 and 1650 cm$^{-1}$ corresponding to the vibrations of C=O bonds, moreover the intensity of these peaks is dependent of the HD, which suggest that a copolymer with a higher HD should have a less intense peak, this is in accordance with the FTIR-ATR spectra presented. Another difference between hydrolyzed and non-hydrolyzed copolymers with acrylamide content is the ability to lose amine groups when hydrolyzed. A copolymer with a higher HD present a less intense peak between 3200 and 3450 cm$^{-1}$ which is in agreement with the results. The carboxylate groups are also represented in the spectra by a band of medium intensity around 1550 cm$^{-1}$ which is only visible in P(AM-co-VP) with 40% acrylamide HD. This is in agreement with the literature [222][225], which profs the success of the P(AM-co-VP) synthesis and hydrolysis herein presented.

### 4.2.3. NMR

In order to validate the polymer structures and chemical groups of P(AM-co-VA) and P(AM-co-VP) copolymers, solid state $^{13}$C Nuclear Magnetic Resonance (13C NMR) measurements were performed. Solid state $^{13}$C NMR retrieves large bands which can overshadow some peaks. Only P(AM-co-VA) and P(AM-co-VP) copolymers were submitted to this analysis since they were the ones that filled the first main goal of this thesis (best candidates for the purpose of this thesis).

No calibration was performed to the equipment when NMR tests were performed. However, in further discussion with the NMR operator it was concluded that all results have a positive dislocation phase of 65 ppm.

Figure 4.6 shows the NMR spectrum of partially hydrolyzed P(AM-co-VP) copolymer comprising 87% by weight of acrylamide content. The HD was 30% of molar acrylamide content.

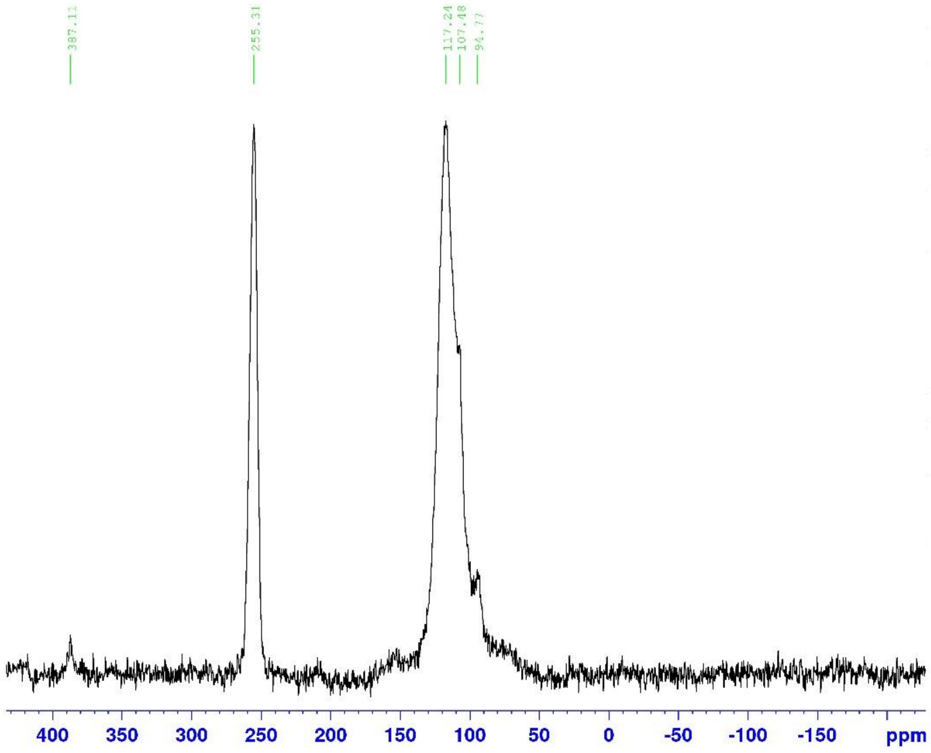

*Figure 4.6- NMR spectrum of a partially hydrolyzed P(AM-co-VP) copolymer comprising 87% by weight of acrylamide content. The HD was 30% of molar acrylamide content.*

In the Figure 4.6 and after adding the positive dislocation of 65 ppm to each theoretical peak, it is possible to observe the characteristic peaks of acrylamide and vinylpyrrolidone units in the spectrum. The C-C and C-C(O) peaks of the vinylpyrrolidone ring are visible at 94 and 107 cm$^{-1}$ respectively. The C-H2 and C-N peak of both monomers are overshadowed at 117 cm$^{-1}$. The

C=O peak of both monomers are also overshadow at 255 $cm^{-1}$. This is in agreement with the literature [226][227][228] and confirms the success of the P(AM-co-VP) synthesis and hydrolysis herein presented.

Figure 4.7 shows the NMR spectrum of partially hydrolyzed P(AM-co-VA) copolymer comprising 75% by weight of acrylamide content. The HD was 30% of molar acrylamide content.

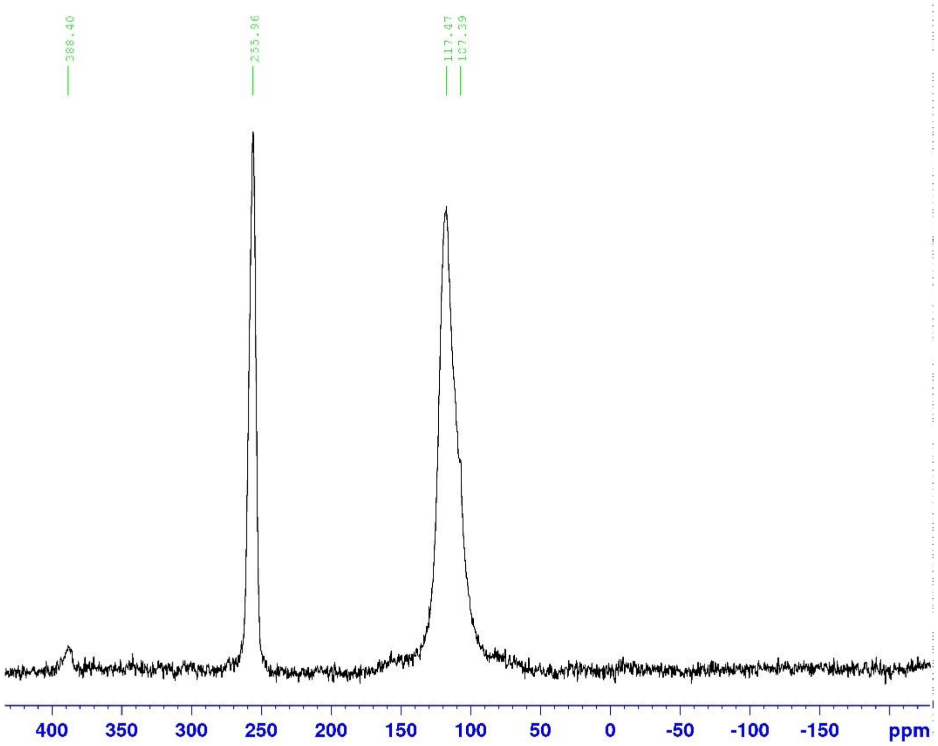

*Figure 4.7- NMR spectrum of partially hydrolyzed P(AM-co-VA) copolymer comprising 75% by weight of acrylamide content. The HD was 30% of molar acrylamide content.*

In the Figure 4.7 and after adding the positive dislocation of 65 ppm to each theoretical peak, it is possible to observe the characteristic peaks of acrylamide and vinyl acetate units in the spectrum. The C-C(O) peaks of the vinyl acetate is visible at 107 $cm^{-1}$, the C-H2 of both monomers are overshadow at 117 $cm^{-1}$, and the C=O peak of both monomers are also overshadowed at 255 $cm^{-1}$. This is in agreement with the literature [228] and proves the success of the P(AM-co-VA) synthesis and hydrolysis herein presented.

To summarize, NMR spectrum give an extra confirmation about the synthesis and hydrolysis of the P(AM-co-VA) and P(AM-co-VP) copolymers.

### 4.2.4. Molecular weight determination

In order to estimate the molecular weight of P(AM-co-VA) and P(AM-co-VP) copolymers a capillary (Ubbelohde) viscometer was used. This viscometer is used to calculate specific and intrinsic viscosity by determining experimentally the viscosity of very dilute polymer solutions. This intrinsic viscosity can be used to determine the molecular weight by using Mark-Houwink empirical correlation. PVP and PVAc polymers are not able to be characterized by this method because of its nonlinear chain and low viscosity in dilute solutions.

The Table 4.16 presents the copolymers synthesis characteristics to calculate their molecular weight for each experiment.

*Table 4.16-List of experiments of the copolymers synthesis characteristics to calculate their molecular weight*

| **Experiment** | **Copolymer** | **Composition** | **Hydrolysis[a)]** | **Observations** |
|---|---|---|---|---|
| P1 | P(AM-co-VP) | 87% AM / 13% VP | 30% | Followed the protocol |
| P2 | P(AM-co-VA) | 75% AM / 25% VA | 30% | Followed the protocol |
| P3 | P(AM-co-VP) | 87% AM / 13% VP | 40% | Followed the protocol |
| P4 | P(AM-co-VA) | 75% AM / 25% VA | 40% | Followed the protocol |
| P5 | P(AM-co-VP) | 87% AM / 13% VP | 30% | Monomers present in a 15% concentration to water |
| P6 | P(AM-co-VP) | 87% AM / 13% VP | 30% | Monomers present in a 50% concentration to water |
| P7 | P(AM-co-VP) | 50% AM / 50% VP | 30% | Monomers present in a 50% concentration to water |
| P8 | P(AM-co-VP) | 87% AM / 13% VP | 40% | Polymerization starts only with AM |
| P9 | P(AM-co-VP) | 87% AM / 13% VP | 40% | Polymerization starts only with VP |

[a)] Hydrolysis percentage performed to the total acrylamide content

Table 4.17 presents the intrinsic viscosity and the calculated molecular weight of some synthetized copolymers.

*Table 4.17 – Intrinsic viscosity and the calculated molecular weight of synthetized copolymers*

| **Experiment** | **Viscosity (s/quart)[a)]** | **Intrinsic viscosity (dL/g)** | **Molecular weight (g/mol)** |
|---|---|---|---|
| P1 | 49 | 5.1 | $1.7 \times 10^6$ |
| P2 | 50 | 5.4 | $1.8 \times 10^6$ |
| P3 | 56 | 7.2 | $2.7 \times 10^6$ |
| P4 | 56 | 6.8 | $2.5 \times 10^6$ |
| P5 | 36 | 3.8 | $1.2 \times 10^6$ |
| P6 | 51 | 8.2 | $3.2 \times 10^6$ |
| P7 | 33 | 3.4 | $1.0 \times 10^6$ |
| P8 | 53 | 6.5 | $2.3 \times 10^6$ |
| P9 | 36 | 4.3 | $1.4 \times 10^6$ |

[a)] Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

In Table 4.17, it is possible to observe that the molecular weight of each copolymer varies with: (1) the type of copolymer, (2) HD, (3) monomers ratio and concentration, and (4) sequence in monomer addition to the polymerization reactor.

The type of copolymer influences the molecular weight, however, no comparison can be performed between different types of copolymers. Different monomers influence the chains growth differently with distinct spatial conformations and rearrangements. Nevertheless, results from P1 to P4 suggest that both copolymeric systems with the same HD have a similar molecular weight.

The results of the experiments P1, P5 and P6 suggest that the monomer concentration in water influences molecular weight of the growing polymer. A variation in concentration of monomer to water from 25% to 15% reduced molecular weight of the growing polymer in 30% (from $1.7 \times 10^6$ g/mol to $1.2 \times 10^6$ g/mol). This molecular weight reduction had a negative impact on copolymer solution viscosity (in a concentration of 1g/L) of 13 s/quart. However, when the concentration of monomer in water was changed from 25% to 50% it resulted in an increase of about 50% in the molecular weight of the copolymer (from $1.7 \times 10^6$ g/mol to $3.2 \times 10^6$ g/mol).). This increase in molecular weight showed a positive impact on copolymer solution viscosity (in a concentration of 1g/L) of 7 s/quart.

The comparison of the experiments P1 and P7 suggests that a reduction in the content ratio of acrylamide in copolymer reduces its molecular weight. A reduction from 87% to 50% of acrylamide ratio in copolymer resulted in a decrease of the molecular weight of 40% (from $1.7 \times 10^6$ g/mol to $1.0 \times 10^6$ g/mol). This reduction in molecular weight had a negative impact on copolymer solution viscosity (in a concentration of 1g/L) of 16 s/quart.

Finally, a comparison of the experiments P1, P8 and P9 suggests that a copolymerization starting only with VP decreases the molecular weight of the growing polymer by 18% (from 1.7 x $10^6$ g/mol to 1.4 x $10^6$ g/mol), which results in a decrease of 13 s/quart on the viscosity of the copolymer solution (1 g/L). On the other hand, a copolymerization starting only with AM increases the molecular weight of the growing polymer by 35% (from 1.7 x $10^6$ g/mol to 2.3 x $10^6$ g/mol), which results in no viscosity changes of the copolymer solution (1 g/L) and an increase of 27% in intrinsic viscosity.

Thus, the molecular weight of the mentioned copolymers can be maximized by polymerization of acrylamide with VP in a molar ratio of 87:13, respectively, with further hydrolysis of 30% of the acrylamide content. In a marked contrast, the best viscosity properties in solution can be achieved with: (1) a copolymer containing acrylamide and VP in a molar ratio of 87:13, respectively, with hydrolysis of 40% ($n_{NaOH}/n_{AM}$) (2) a copolymer containing acrylamide and VA in a molar ratio of 75:25 respectively with hydrolysis of 40% of the acrylamide content.

### 4.2.5. Zeta potential

In drilling applications, clay hydration is promoted at high pH values. Thus, it is fundamental to evaluate the polymers behavior under different pH conditions. Therefore, zeta potential studies were performed to P(AM-co-VA) and P(AM-co-VP) copolymers, since these were the ones that accomplished the first goal of this thesis. This study was performed in order to evaluate the copolymers behavior at various pH conditions.

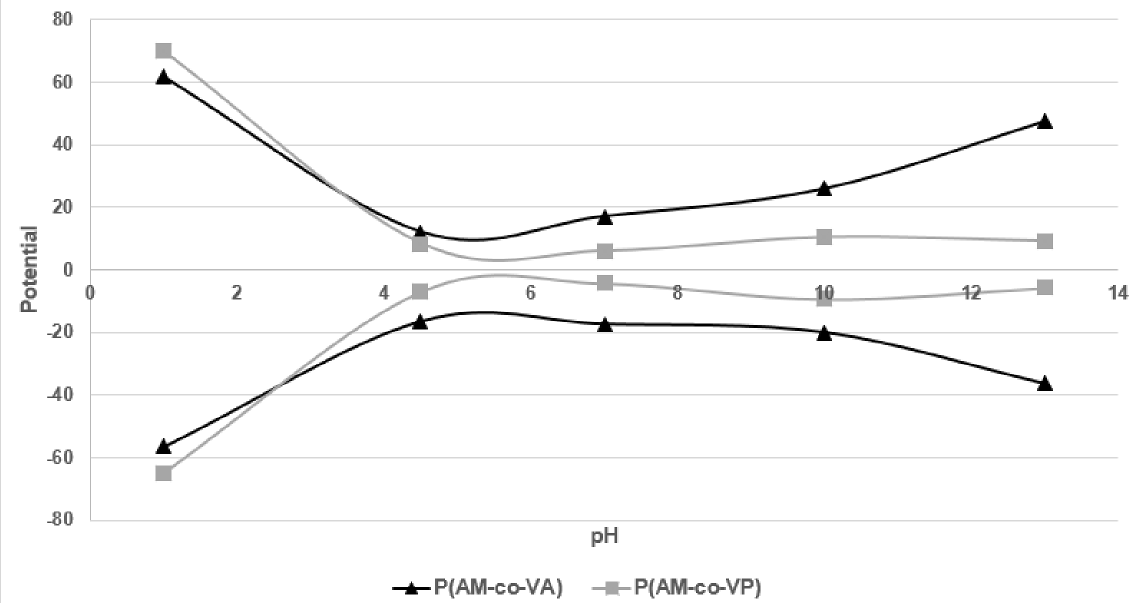

*Figure 4.8- Graphic representation of zeta potential in function of pH of two copolymers: (1) P(AM-co-VA) comprising 75% by weight of acrylamide and 25% of vinyl acetate with a hydrolysis molar ratio of 30% of total acrylamide content and (2) P(AM-co-VP) copolymer comprising 87% by weight of acrylamide and 13% of vinylpyrrolidone with a hydrolysis molar ratio of 30% of total acrylamide content.*

In Figure 4.8, it is possible to observe the electric response of the two copolymeric systems at different pH. An excess of $H^+$ ions are present at low pH values which suggests a protonation of amide group of acrylamide units and consequently, additional charges to the copolymers system making them more responsive to electric field. However, when pH is raised to 4.5, the amide group of acrylamide units is deprotonated and the chains stay stable with electric charges due to the diminution of charges along the polymer chain. From pH 10 to 13, acrylamide hydrolyzed groups tends to lose a proton due to the lower concentration of $H^+$ ions in the solution. The loss of these protons retrieves a negative charge to the copolymers. This loss is more prominent in P(AM-co-VA) hydrolyzed copolymers due to the additional loss of protons of the hydrolyzed vinyl acetate unit.

### 4.3. Evaluation of suspension vs precipitation capacity

In order to accomplish the last goal of this thesis (evaluate the capacity of selected polymers for clay suspension or settling), some experiments involving only clay were performed.

The final result should be one of the following events: (1) a fully suspended clay in the drilling fluid after 24 hours of gravity action (more than 90% of clay suspended, in comparison with the starting point) and (2) a fully precipitated clay in the bottom of the beaker after 24 hours (almost 0% of clay suspended in comparison with the starting point). Furthermore, after clay addition, the polymer viscosity should be maintained above 55 s/quart.

The suspension or precipitation capacity was evaluated for the polymers mentioned in Table 4.18, under different operational conditions.

Table 4.18 Designation of polymers and copolymers used for the followed tests.

*Table 4.18- List of polymers and copolymers used in the evaluation of suspension and precipitation capacity*

| Polymer / Copolymer | Composition | Hydrolysis[a)] | Viscosity (s/quart)[b)] |
|---|---|---|---|
| P(AM-co-VP) | 87% AM / 13% VP | 30% | 49 |
| P(AM-co-VA) | 75% AM / 25% VA | 30% | 50 |
| PVP | 100% VP | 0% | 28 |
| PolyMud® | Acrylamide based | - | 78 |

[a)] Hydrolysis percentage performed to the total acrylamide content

[b)] Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.

Suspension/precipitation tests were performed in a 5L beaker. The internal agitation was assured by the stirring rod with a Teflon blade. The beaker was charged with 2 L of dd_water or tap water, depending on the test, with or without 10 mL of a 2 M sodium hydroxide solution to reach pH=12, and with a polymer or copolymer selected from Table 4.18. The mixtures were stirred during 1hour to achieve all polymer hydration. Then, solutions viscosity was measured. Clay was added to the mixtures in a quantity of 400 g and the mixtures were stirred for 2 hours more to complete soil hydration. Once soil hydration completed, a control sample was taken to measure viscosity and density. The next samples were taken hour by hour, and evaluated after 10, 20, 30 minutes, 1, 2 and 24 hours after being collected, in order to monitor clay suspension or clay precipitation. After taking 3 or 4 samples, the stirring was switched off and 24 hours later, the viscosity and density of solutions were measured again.

### 4.3.1. P(AM-co-VP) and P(AM-co-VA) as main viscosifiers of drilling fluids

In a first approach, P(AM-co-VP) and P(AM-co-VA) copolymers were used as main viscosifiers and compared with the PolyMud®, which worked here as a control. The results are shown in Table 4.19.

*Table 4.19- Sedimentation, density and viscosity values of polymers and copolymers tested as main viscosifiers in a concentration of 2 g of polymers for 2 liter of water at pH = 12 without any further additive.*

| | | **Viscosity (s/quart)** [a] | | | **Density** | | **Sedimentation** [b] | |
|---|---|---|---|---|---|---|---|---|
| **Compound** | **Water type** | **Before clay addition** | **After 2 hours** | **After 24 hours** | **Start point** | **After 24 hours** | **After 10 minutes (%)** | **After 24 hours (%)** |
| PolyMud® | Tap | 61 | 69 | 66 | 1.110 | 1.035 | No visible | 68% |
| PolyMud® | Distilled-deionized | 77 | 75 | 73 | 1.100 | 1.075 | No visible | 25% |
| P(AM-co-VP) | Distilled-deionized | 35 | 37 | 33 | 1.100 | 1.000 | 100% | 100% |
| P(AM-co-VA) | Distilled-deionized | 41 | 33 | 35 | 1.100 | 1.000 | 100% | 100% |

[a] Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.
[b] Sedimentation percentage of the total suspended quantity after 2 hours of clay addition.

In Table 4.19, it is possible to observe that the application of the mentioned polymers at pH 12 were not effective at suspending or precipitating the clay. P(AM-co-VP) and P(AM-co-VA)

copolymers lose between 10 to 15 s/quart when pH is adjusted to 12 and all clay precipitated after 10 minutes by gravity. On the other hand, PolyMud® solutions did not lose any viscosity after pH adjustment or clay addition. However, when tap water is used to PolyMud®, a loss of 16 s/quart is tracked. This can be explained by the presence of salts in tap water.
PolyMud® can attach 25% of clay precipitated after 24 hours when dd_water was used and, 68% with tap water.

In order to improve the viscosity and clay suspension of polymers and copolymers, tests involving the use of a commercial additive, Alfa-bond® were performed. The tests were similar to the previous ones, but with the Alfa-bond® addition (0.5% v/v) after clay hydration. The incorporation of Alfa-bond® in the system created jelly foam due to air incorporation. This effect allowed clay suspension, however the density was impossible to be measured. This occurred for PolyMud® and copolymers.
These experiments suggest that the copolymers synthesized in this thesis did not demonstrated better suspension or settling capacity compared to PolyMud®.

### 4.3.2. P(AM-co-VA), P(AM-co-VP) and PVP as additives for drilling fluids

As second approach, P(AM-co-VA), P(AM-co-VP) and PVP were tested as additives to a PolyMud® based solution.
Table 4.20 presents the tests conditions of the P(AM-co-VA) copolymer applied as an additive to a total volume of 2 L of a polymeric solution of PolyMud® in a concentration of 1 g/L in dd_water at pH = 12.

*Table 4.20 - Sedimentation, density and viscosity values of P(AM-co-VA) copolymer tested as an additive to a PolyMud® system with a concentration of 2 g of PolyMud® for 2 liter of dd_water at pH = 12 without any further additive.*

| P(AM-co-VA) quantity | Viscosity (s/quart) [a)] | | | Density | | Sedimentation [b)] | |
|---|---|---|---|---|---|---|---|
| | Before clay addition | After 2 hours | After 24 hours | Start point | After 24 hours | After 10 minutes (%) | After 24 hours (%) |
| 0.1 g | 78 | 65 | 66 | 1.100 | 1.070 | No visible | 30% |
| 0.2 g | 74 | 67 | 75 | 1.100 | 1.075 | No visible | 25% |

[a)] Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.
[b)] Sedimentation percentage of the total suspended quantity after 2 hours of clay addition.

In the Table 4.20, it is possible to observe that the application of the P(AM-co-VA) as an additive to a PolyMud® solution is not effective (30% of the total amount of clay deposited after 24 hours) when compared with the application of the PolyMud® with no additives (25% of the total amount of clay deposited after 24 hours of rest). Further work should be performed with the increase of P(AM-co-VA) content as an additive.

*Table 4.21- Sedimentation, density and viscosity values of P(AM-co-VP) copolymer tested as an additive to a PolyMud® system with a concentration of 2 g of PolyMud® for 2 liter water at pH = 12 without any further additive.*

| **P(AM-co-VP) quantity** | **Water type** | **Viscosity (s/quart) [a)]** | | | **Density** | | **Sedimentation [b)]** | |
|---|---|---|---|---|---|---|---|---|
| | | **Before clay addition** | **After 2 hours** | **After 24 hours** | **Start point** | **After 24 hours** | **After 10 minutes (%)** | **After 24 hours (%)** |
| 0.1 g | Distilled-deionized | 78 | 65 | 53 | 1,100 | 1,090 | No visible | 10% |
| 0.2 g | Distilled-deionized | 74 | 70 | 73 | 1,100 | 1,080 | No visible | 20% |
| 1 g | Distilled-deionized | 74 | 69 | 82 | 1,100 | 1,090 | No visible | 10% |
| 2 g | Distilled-deionized | 75 | 68 | 89 | 1,100 | 1,100 | No visible | 0% |
| 0.1 g | Tap | 76 | 68 | 79 | 1,100 | 1,040 | No visible | 60% |
| 0.2 g | Tap | 75 | 68 | 77 | 1,100 | 1,045 | No visible | 60% |
| 1 g | Tap | 76 | 64 | 81 | 1,100 | 1,070 | No visible | 25% |
| 2 g | Tap | 76 | 64 | 93 | 1,100 | 1,075 | No visible | 25% |

[a)] Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.
[b)] Sedimentation percentage of the total suspended quantity after 2 hours of clay addition.

In the Table 4.21, it is noticed that the application of the P(AM-co-VP) as an additive to a PolyMud® solution is effective (no deposits after 24 hours of rest) when compared with the application of the PolyMud® with no additives (25% of the total amount of clay deposited after 24 hours of rest). When suspension tests were performed in dd_water better performances were achieved. Best performance (100% of suspension after 24h) was achieved when 2 g of P(AM-co-VP) were used as “additive” to the PolyMud® solution with a concentration of 1 g/L. Also when tap water is used the best results were achieved with 2 g of P(AM-co-VP) as “additive” (an improvement from 68% of deposit to only 25% of the total amount of clay deposited after 24 hours). This quantity, 2 g of P(AM-co-VP), can reach 75% of suspension of the total clay present in the solution after 24 hours.

P(AM-co-VP) demonstrated the best results in dd_water and tap water. It is composed with the same main monomer than P(AM-co-VA), however, very distinct results were achieved. Since VP presence in the copolymer is the key difference between the mentioned copolymers, a PVP polymer was tested as additive.

*Table 4.22 - Sedimentation, density and viscosity values of PVP polymer tested as an additive to a PolyMud® system with a concentration of 2 g of PolyMud® for 2 liter water at pH = 12 without any further additive.*

| PVP quantity | Water type | Viscosity (s/quart)[a)] | | | Density | | Sedimentation [b)] | |
|---|---|---|---|---|---|---|---|---|
| | | Before clay addition | After 2 hours | After 24 hours | Start point | After 24 hours | After 10 minutes (%) | After 24 hours (%) |
| 0.5 g | Distilled-deionized | 73 | 65 | 78 | 1,100 | 1,055 | No visible | 45% |
| 1 g | Distilled-deionized | 74 | 65 | 71 | 1,100 | 1,090 | No visible | 10% |
| 0.5 g | Tap | 76 | 66 | 76 | 1,100 | 1,025 | No visible | 75% |
| 1 g | Tap | 76 | 66 | 82 | 1,100 | 1,045 | No visible | 55% |
| 2 g | Tap | 76 | 67 | 70 | 1,100 | 1,050 | No visible | 50% |

[a)] Viscosity evaluation of 1 gram of polymer in 1 liter of dd_water measured by a Marsh funnel at 25ºC.
[b)] Sedimentation percentage of the total suspended quantity after 2 hours of clay addition.

In Table 4.22, it is possible to observe that the application of the PVP as an additive to a PolyMud® solution is effective when compared with the application of the PolyMud® with no additives. When suspension tests were performed in dd_water, better performances were achieved. The best performance was achieved when 1 g of PVP was used as additive to the PolyMud® solution with a concentration of 1 g/L. This quantity can reach a 90% suspension of the total clay present in solution after 24 hours. When 2 g of PVP was used the suspension capacity did not improve (only 50% of suspension after 24h)

To summarize, when dd_water was used as solvent to the solution of PolyMud® in a concentration of 1 g/L, P(AM-co-VP) exhibited the best performance as additive, by keeping the total clay amount in suspension after 24 hours. PVP also exhibited a good performance by keeping in suspension 90% of the total clay presented in solution after 24 hours. When tap water was used, P(AM-co-VP) as an additive (0.5 g/L), exhibited the best performance by keeping in suspension 90% of the total clay present in solution after 24 hours.

## 5. Conclusions

The major breakthrough of this work was the synthesis of VP, VAc and AM copolymers able to exhibit viscosity values over 55 s/quart, when dissolved in a ratio of 1:1 in water, for application in drilling fluids.

PVP, PVAc, P(AM-co-VA) and P(AM-co-VP) copolymers were successfully synthesized in aqueous media after optimization of a huge number of variables during the synthesis process. However, it was P(AM-co-VP) copolymer with 87% of acrylamide and 13% of VP content and hydrolyzed in 40% that fulfilled the required properties for the envisaged application since it displayed a viscosity of 56 ± 2 s/quart at a concentration of 1 g/L. Moreover, NMR combined with FTIR-ATR results, strongly suggested the success of the copolymer synthesis. Molecular weight determination performed by a capillary (Ubbelohde) viscometer retrieved a P(AM-co-VP) molecular weight of $2.7 \times 10^6$ g/mol, which is in agreement with the viscosity value obtained for this copolymer. Regarding the soil suspension and settling tests, P(AM-co-VP) exhibited the best performance as an additive to a PolyMud® solution of 1 g/L of distilled water, since it was able to suspend 100% of the clay amount with a concentration of 1 g/L during 24 hours, and 90% with a concentration of 0.5 g/L of tap water under 24 hours.

Also as an additive, PVP came up as a good alternative since it was able to suspend 90% of the total clay in a solution during 24 hours when it is used with a concentration of 0.5g/L, however, only when distilled-deionized water was used.

Also P(AM-co-VA) copolymer comprising 75% by weight of acrylamide, 25% of VP and 40% of hydrolysis degree, was able to reached 56 ± 2 s/quart with a concentration of 1 g/L of water. NMR combined with FTIR-ATR results, strongly suggested the success of copolymer synthesis. Molecular weight determination performed by a capillary (Ubbelohde) viscometer retrieved a P(AM-co-VA) molecular weight of $2.5 \times 10^6$ g/mol, which is in agreement with the obtained viscosity value. Considering the soil suspension and settling tests, P(AM-co-VA) did not reveal the capacity to act as main viscosifier neither as an additive.

These preliminary results allowed the achievement of the two first goals of this thesis. The data herein reported point out for a good starting point in the development of new promising polymers to be employed in drilling fluids applications. However, further work must be performed in order to improve copolymer viscosities and the performances of these materials when acting as drilling fluids for suspending clays and other types of soil, as sands. Furthermore, the settling capacity of polymers for different types of soil should be examined deeply, since this objective was less investigated. Studies of economic viability should also be considered in order to reach attractive alternatives from scientific and commercial perspectives.

## 6. **References**

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## 7. Appendix Section

*Appendix 1 –Viscosity evaluation of P(AM-co-VP) with 30% HD with a delay on water addition to the reaction varying the way and the duration of the addition after the start of the reaction.*

| **Run** | **Initial water content (mL)** | **Water addition after initiator (mL)** | **Duration (min)** | **Obs** | **Polymer mass formed (g)** [a)] | **Viscosity (s/quart)** [b)] |
|---|---|---|---|---|---|---|
| **Run 44** | 40 | 0 | n.a. | No water was added after initiator | 9.4 | 49 ± 2 |
| **Run 47** | 40 | 40 | 15 | A shot every 5min | 6.8 | 35 ± 2 |
| **Run 48** | 40 | 40 | 5 | A single shot after 5min | 7.0 | 42 ± 2 |
| **Run 49** | 40 | 40 | 5 | Continous pumping | 8.3 | 44 ± 2 |
| **Run 50** | 20 | 20 | 15 | A shot every 5min | 7.1 | 33 ± 2 |
| **Run 51** | 20 | 20 | 5 | Continous pumping | 8.3 | 53 ± 2 |

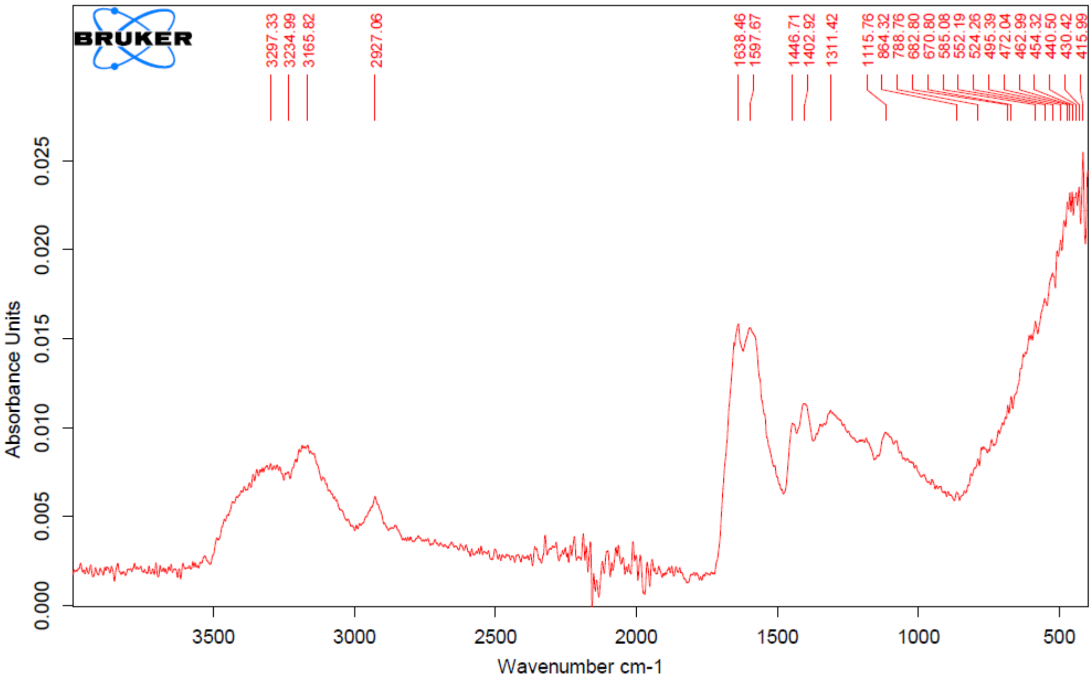
*Appendix 2 - Viscosity evaluation of P(AM-co-VP) with 30% HD with a delay on water and monomer addition to the reaction varying the way and the duration of the addition after the start of the reaction.*

| **Run** | **Initial water content (mL)** | **Initital AM:VP content (g:g)** | **Water addition after initiator (mL)** | **AM:VP addition after initiator (g:g)** | **Duration (min)** | **Obs** | **Polymer mass formed (g) / monomer mass (g)** | **Viscosity (s/quart)** [a)] |
|---|---|---|---|---|---|---|---|---|
| Run 44 | 40 | 1.3 : 8.7 | 0 | 0 | n.a. | Nothing was added after initiator | 0.94 | 49 ± 2 |
| Run 52 | 40 | 1.3 : 8.7 | 40 | 1.3 : 8.7 | 5 | A single shot | 0.81 | 47 ± 2 |
| Run 53 | 40 | 1.3 : 8.7 | 40 | 1.3 : 8.7 | 12 | Continous pumping | 0.66 | 50 ± 2 |
| Run 54 | 40 | 1.3 : 8.7 | 40 | 1.3 : 8.7 | 5 | Continous pumping | 1.17 | 46 ± 2 |
| Run 55 | 40 | 1.3 : 8.7 | 40 | 1.3 : 8.7 | 5 | Continous pumping | 0.69 | 51 ± 2 |

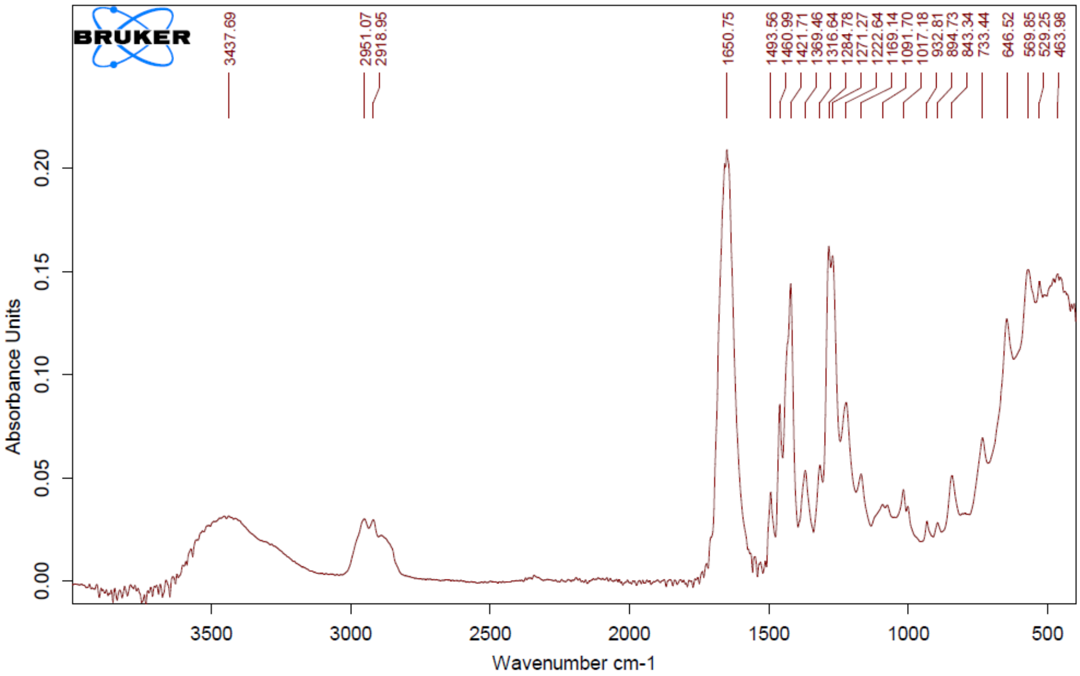
*Appendix 3 - Viscosity evaluation of P(AM-co-VP) with 30% HD with a controlled initiator addition*

| **Run** | **Initial water content (mL)** | **Initital AM:VP content (g:g)** | **Water addition with initiator (mL)** | **Initiator (mg)** | **Duration (min)** | **Obs** | **Polymer mass formed (g)** [a)] | **Viscosity (s/quart)** [b)] |
|---|---|---|---|---|---|---|---|---|
| **Run 44** | 40 | 1.3 : 8.7 | 0 | 3 | n.a. | A single shot | 9.4 | 49 ± 2 |
| **Run 56** | 20 | 1.3 : 8.7 | 20 | 3 | 3 | Continuous pumping | 10.9 | 49 ± 2 |

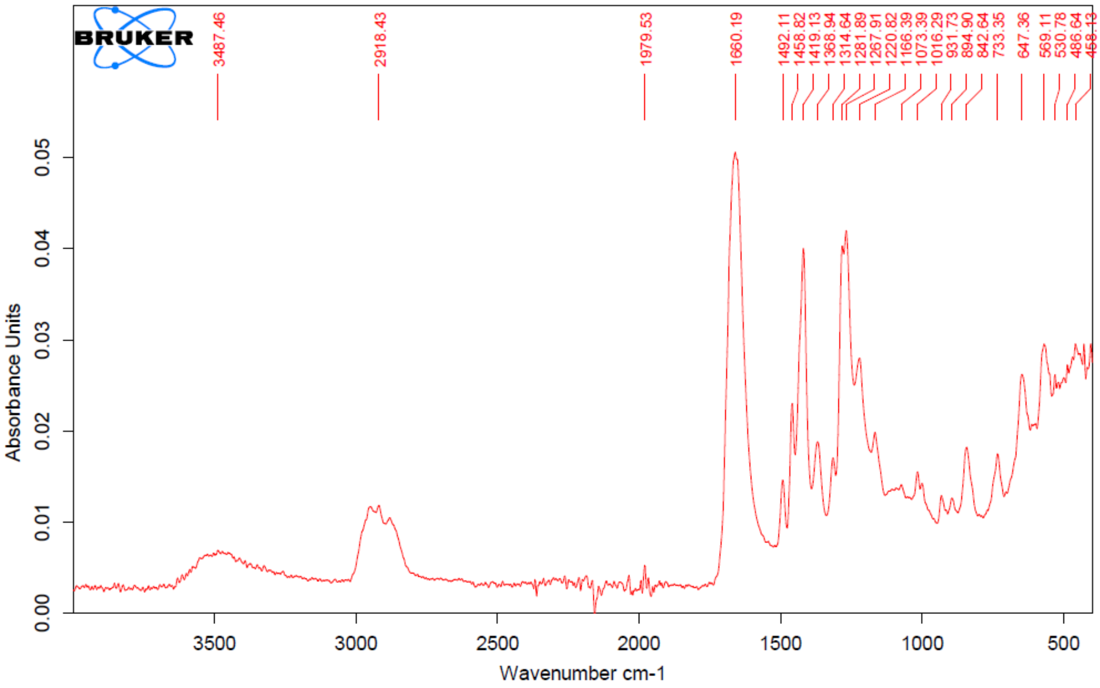
*Appendix 4- FTIR-ATR of Run 1*



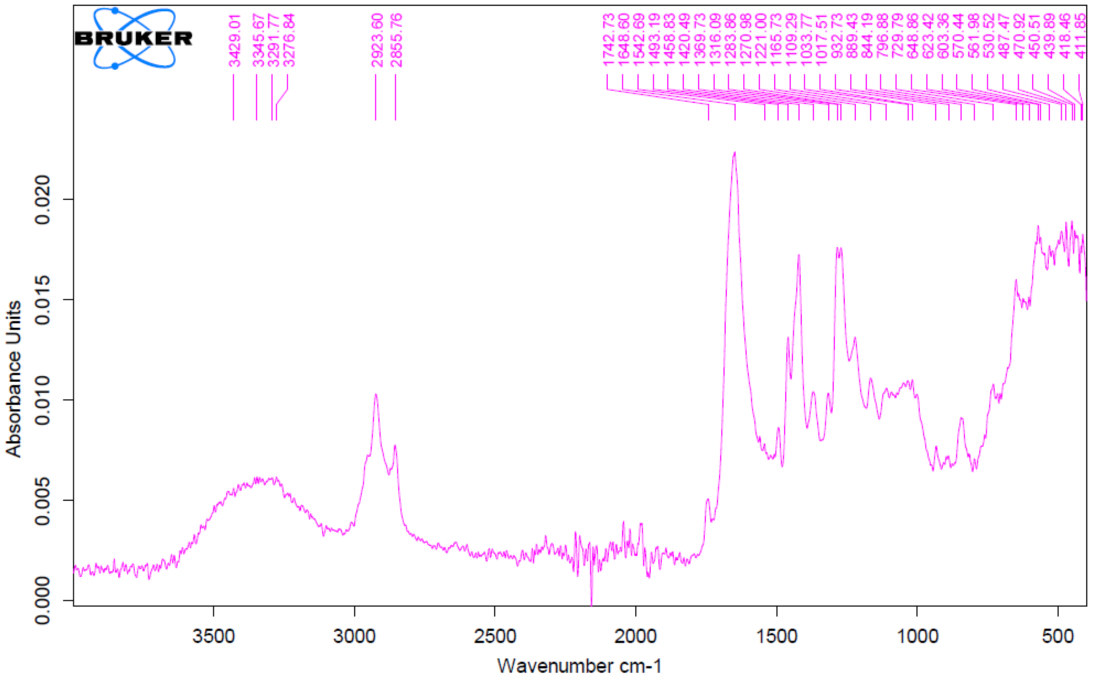
*Appendix 5- FTIR-ATR of Run 3*



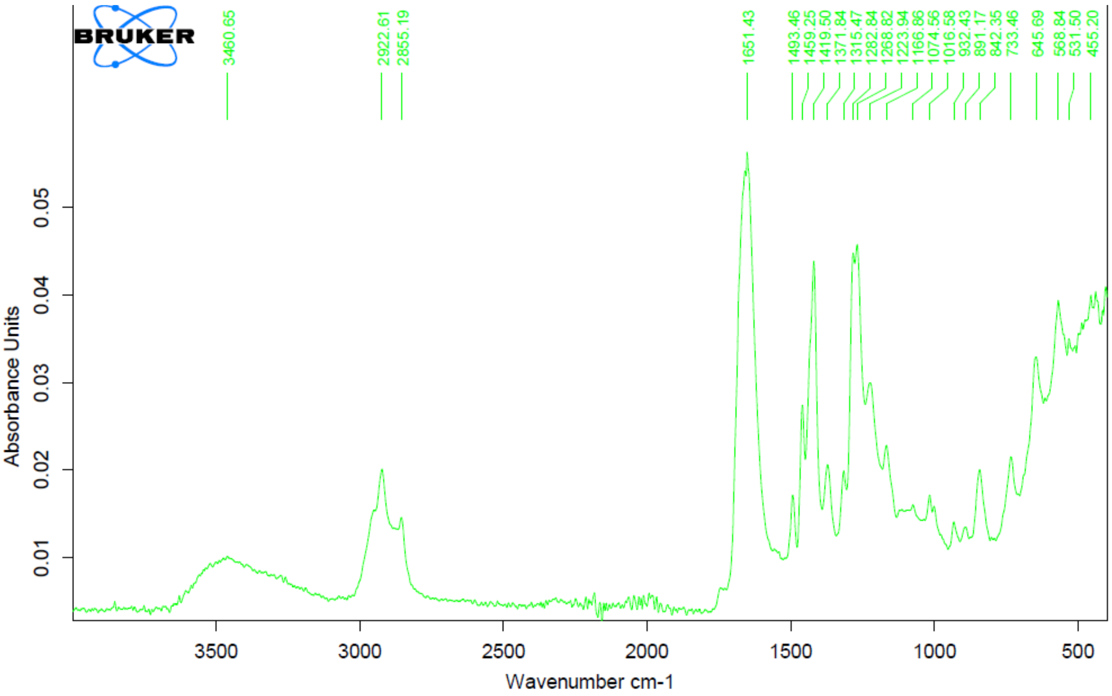
*Appendix 7- FTIR-ATR of Run 6*



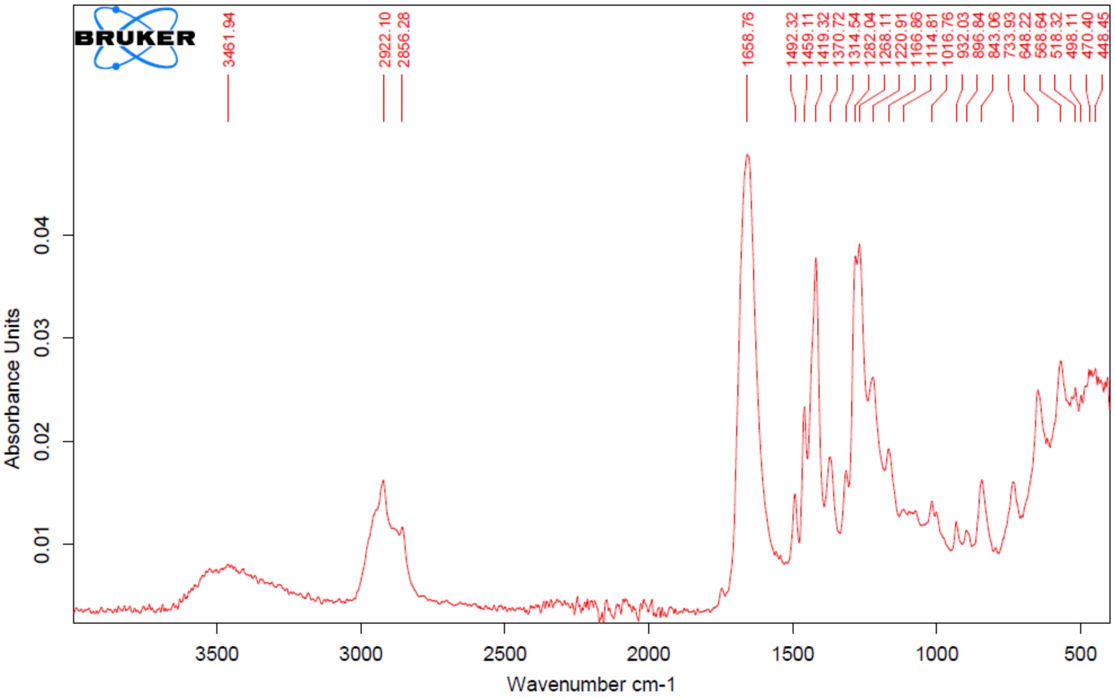
*Appendix 6- FTIR-ATR of Run 8*



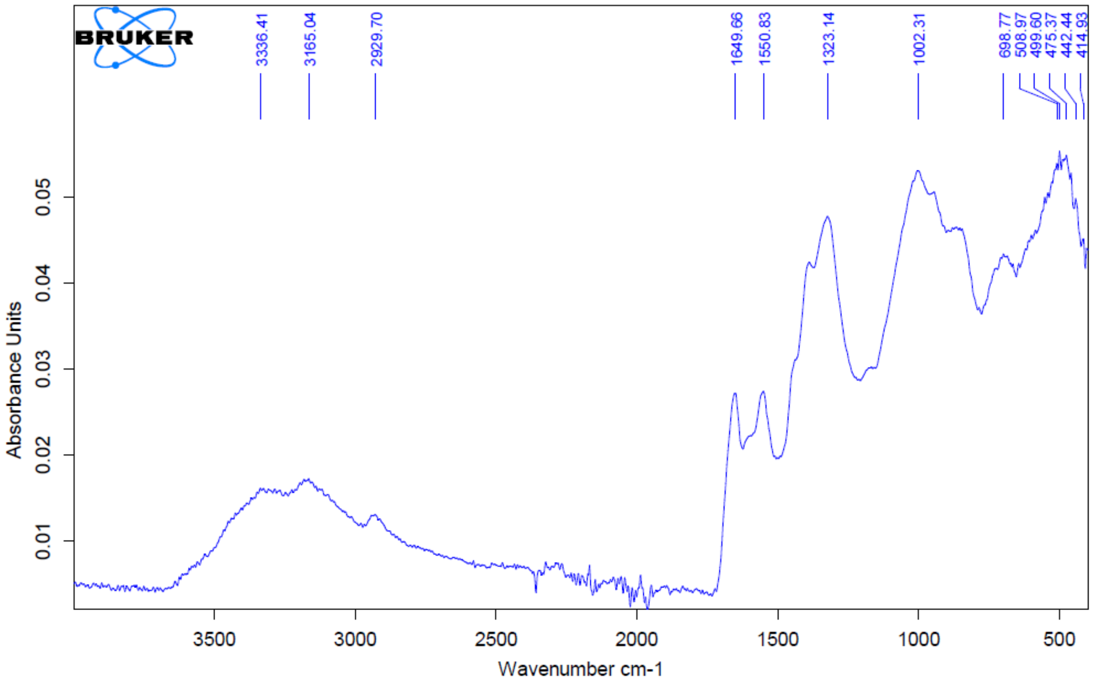
*Appendix 9- FTIR-ATR of Run 10*



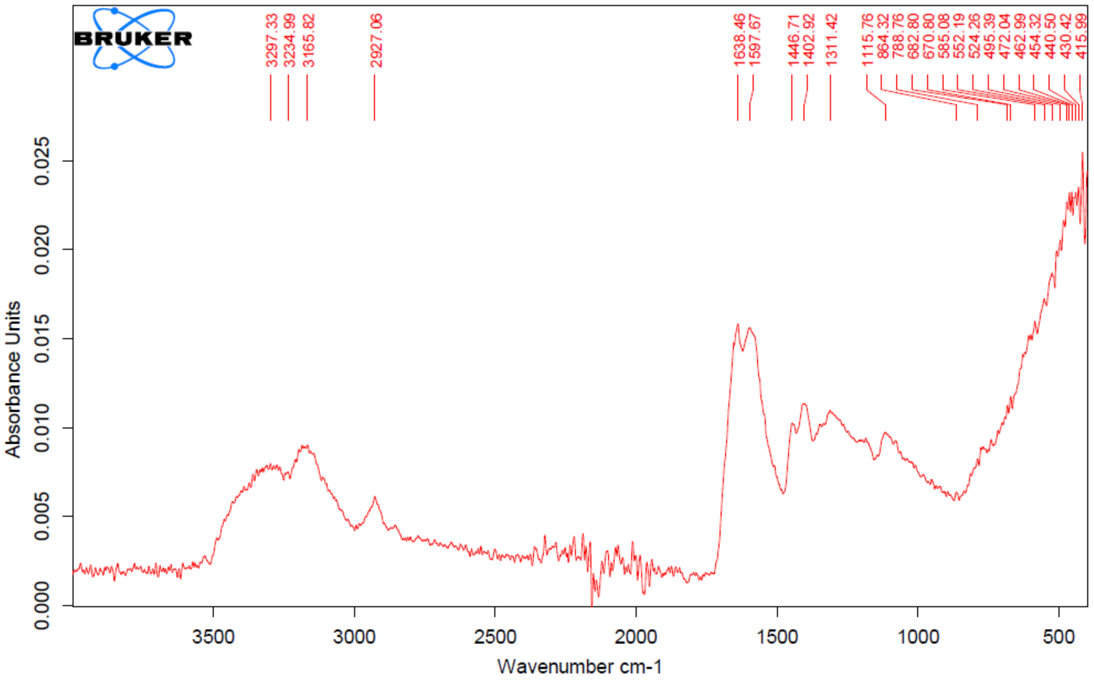
*Appendix 8- FTIR-ATR of Run 11*



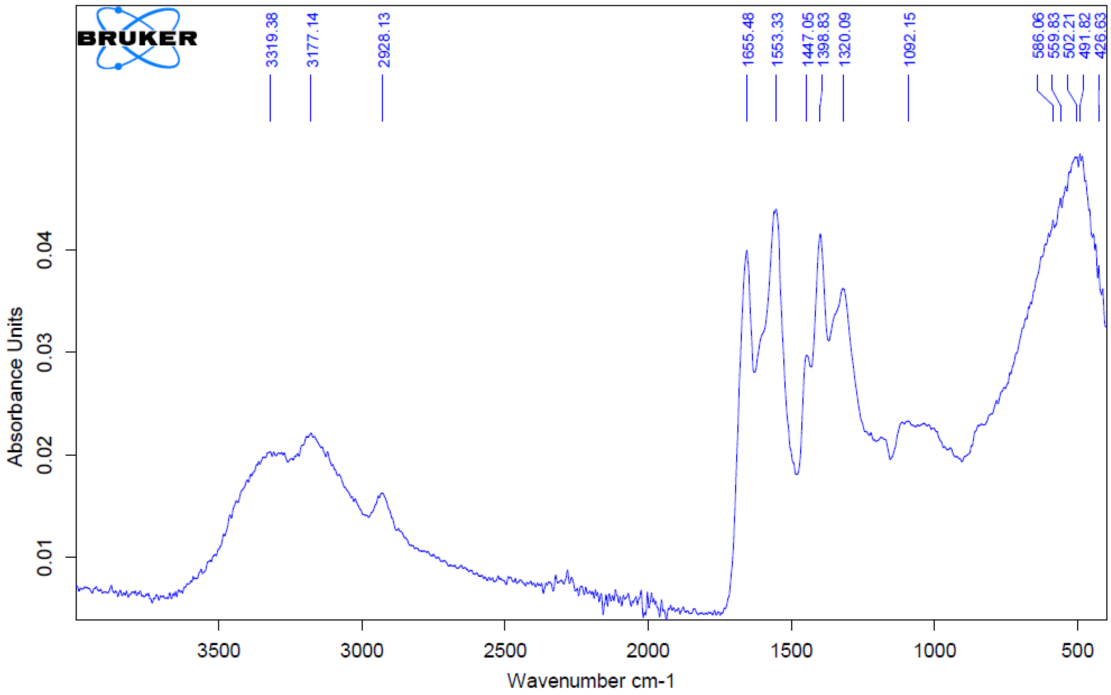
*Appendix 10- FTIR-ATR of Run 22*



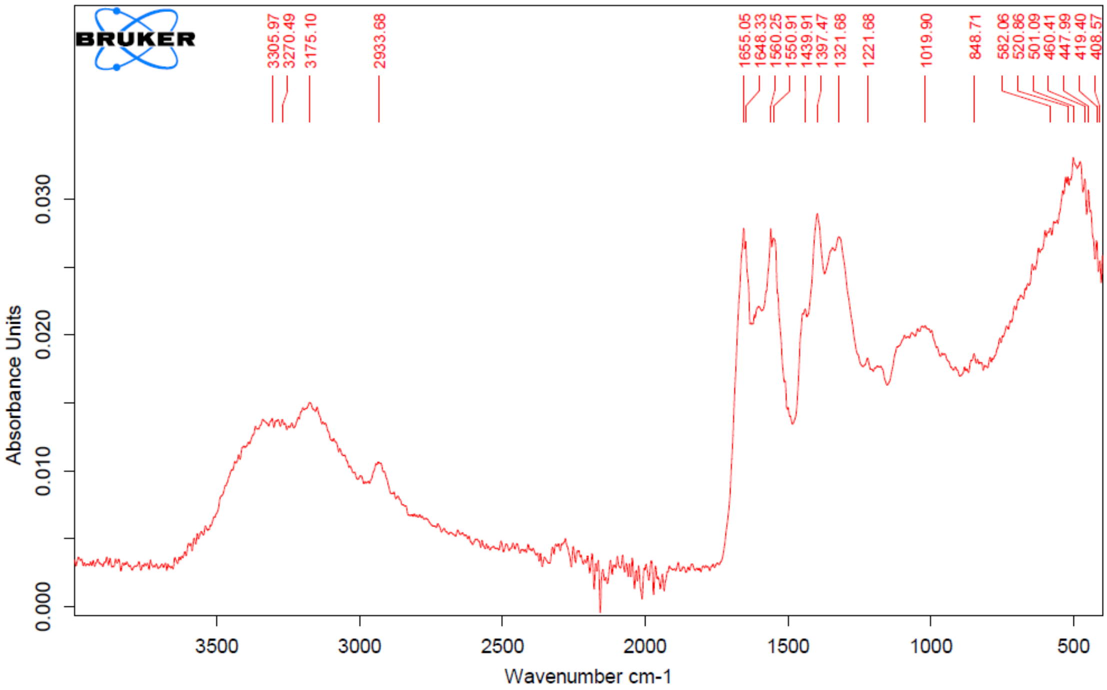
*Appendix 11- FTIR-ATR of Run 24*



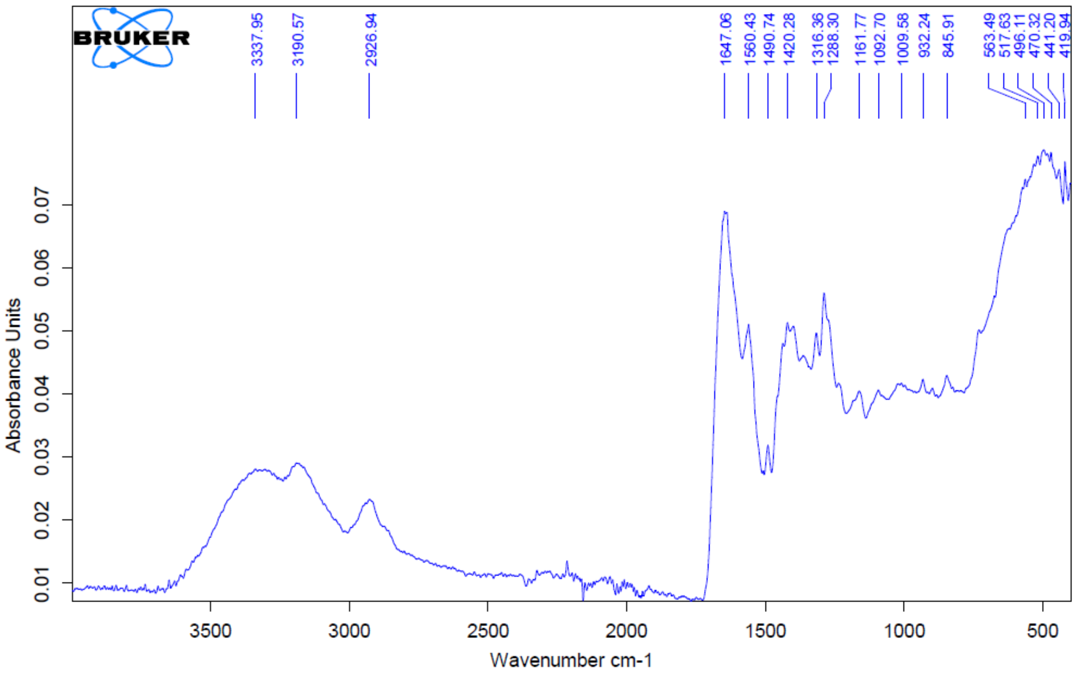
*Appendix 12- FTIR-ATR of Run 29*



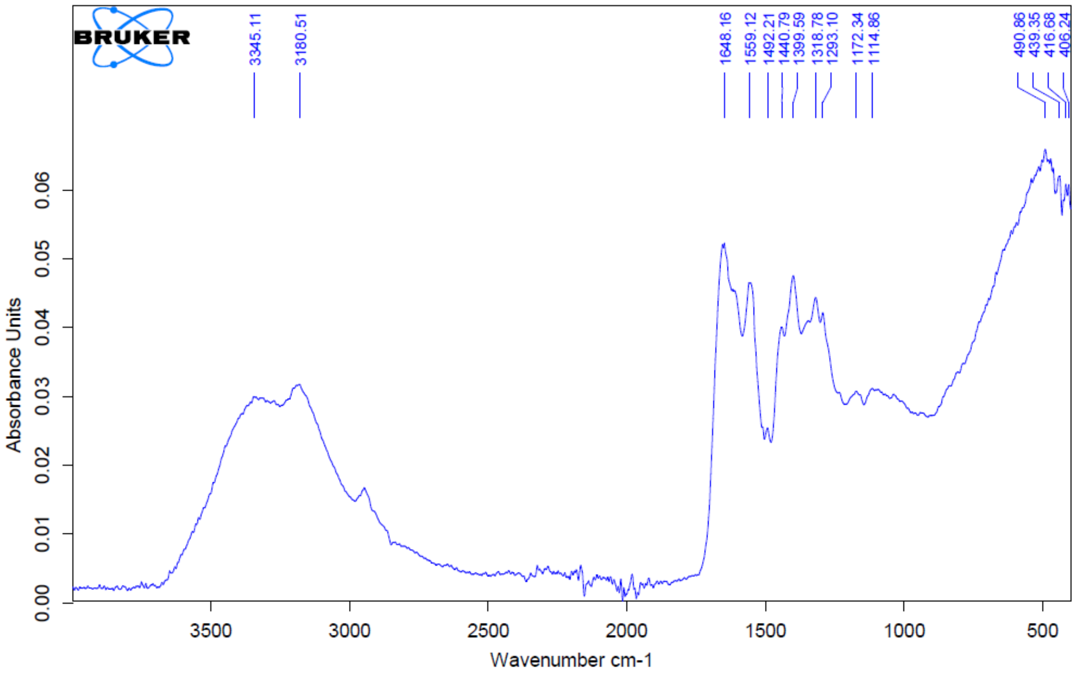
*Appendix 13- FTIR-ATR of Run 32*



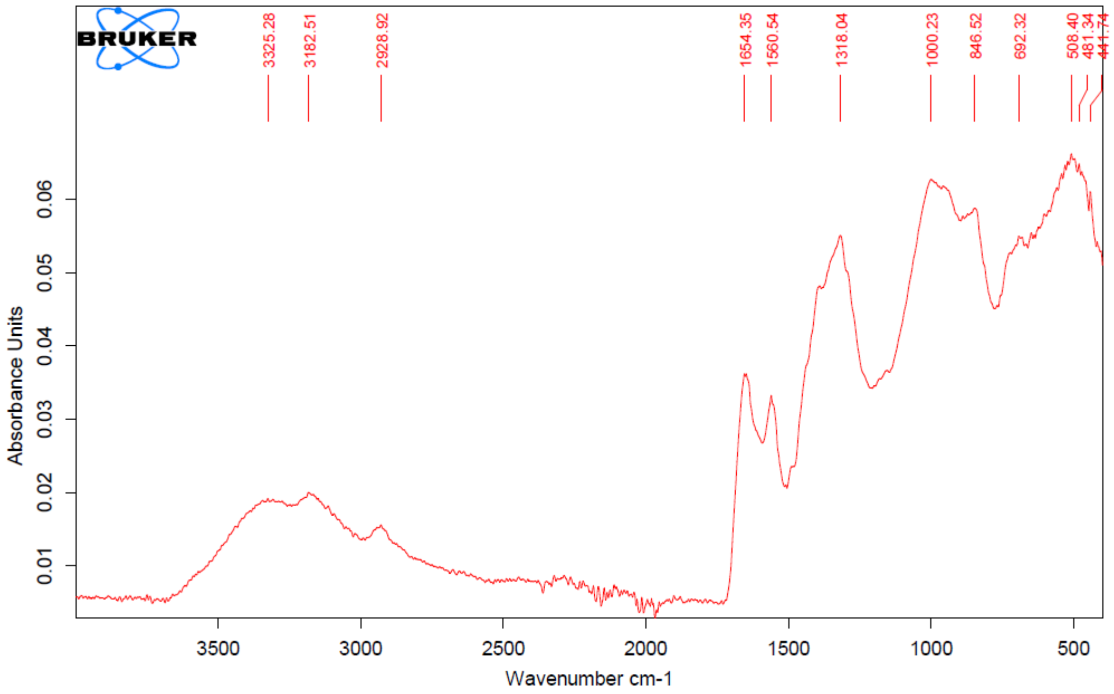
*Appendix 14- FTIR-ATR of Run 36*



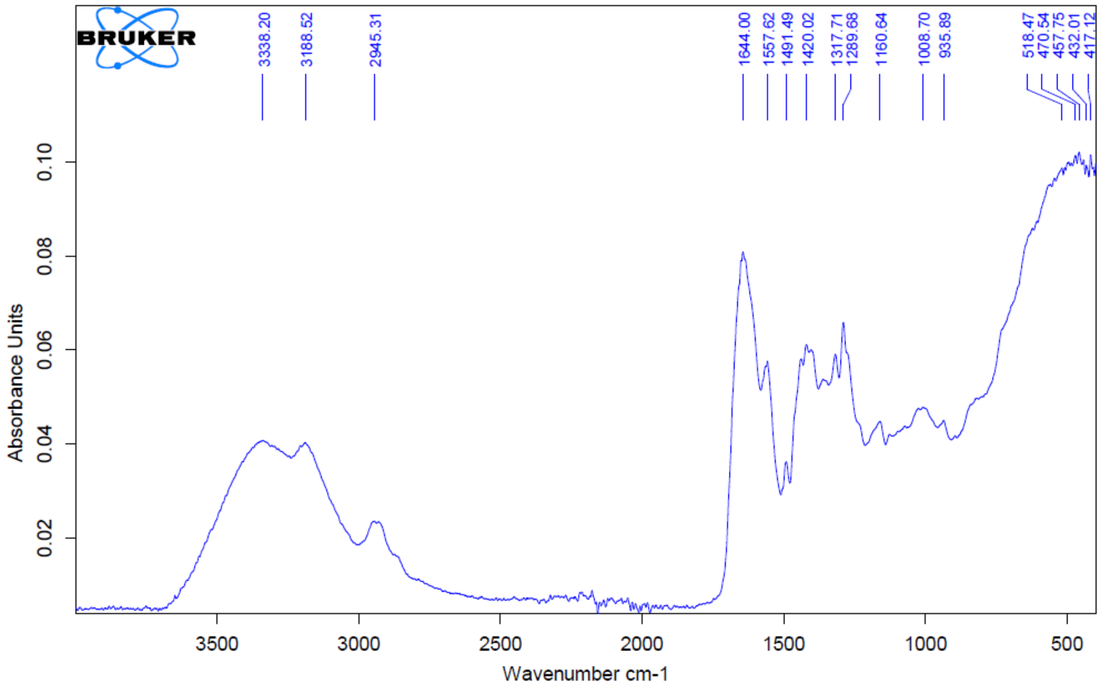
*Appendix 15- FTIR-ATR of Run 34*



*Appendix 17- FTIR-ATR of Run 38*



*Appendix 16- FTIR-ATR of Run 43*



*Appendix 18- FTIR-ATR of Run 66*