

McGill University Department of Chemical Engineering

Masters Thesis

Synthesis and use of poly(vinyl alcohol) as a kinetic inhibitor for gas hydrate inhibition

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A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Masters of Engineering *"From time immemorial, man has desired to comprehend the complexity of nature in terms of as few elementary concepts as possible."*

Dr. Abdus Salam, Nobel Laureate

Abstract

Gas hydrates consist of a crystal lattice of water molecules that contain "guest" gas or volatile liquid molecules. The water cage is held together through hydrogen bonding and stabilized by Van der Waals interactions with the guest molecule. Thermodynamic conditions favouring hydrate formation are often found in oil and gas transportation pipelines. This is highly undesirable as the clathrate crystals might agglomerate and plug these pipelines. Kinetic hydrate inhibition is an increasingly attractive approach to minimize hydrate formation that involves the use of low concentrations (<1wt%) of functionalized polymers to interfere with the nucleation and growth processes of hydrate formation under thermodynamically favourable conditions.

This project set out to investigate the inhibition potential of poly(vinyl alcohol) on a methane-water gas hydrate system. Poly(vinyl acetate) (PVAc) was first synthesized using the cobalt mediated radical polymerization process. This process is selected in order to have a good control of the degree of polymerization while maintaining a narrow molecular weight distribution. While the polymer chain length was achieved predictably, high dispersities were observed due to the highly reactive nature of the cobalt complex with oxygen. A more rigorous degassing technique, using freeze-pump-thaw cycles, was implemented in order to achieve an oxygen-free environment to mitigate this observation. Poly(vinyl acetate) was then converted to poly(vinyl alcohol) using a base hydrolysis reaction.

Poly(vinyl alcohol) (PVA) of varying sizes were dissolved in deionized water at a fixed concentration and hydrate growth experiments were conducted to study the effect of size on hydrate growth. The rate of dissolution of methane in to the liquid phase as well as the methane hydrate growth rate was seen to decrease with the addition of the inhibitor. However, no trend was observed for the effect of the size of the polymer on these rates. These rates were also seen

to be lower than when using poly(vinylpyrrolidone) (PVP), a kinetic hydrate inhibitor currently commonly being used in the industry. Although dissolution and growth rates were observed to be larger for PVA than PVP, both of these inhibitors showed much lower rates than pure water.

Résumé

Les hydrates de gaz sont des réseaux cristallins de molécules d'eau contenant des molécules "invité" de gaz ou de liquides volatils. La cage d'eau est maintenue ensemble par des liaisons d'hydrogène et stabilisé par des interactions de Van der Waals avec la molécule hôte. Des conditions thermodynamiques favorables à la formation d'hydrates sont souvent retrouvés à l'intérieure des oléoducs de pétrole. Il n'est pas souhaitable que les cristaux d'hydrate gazeux se forment puisqu'ils peuvent s'agglomérer et former des bouchons dans ces oléoducs. L'inhibition cinétique de ces hydrates est une approche de plus en plus attrayante afin de pouvoir minimiser la formation d'hydrates. Cette technique implique l'utilisation de faibles concentrations (<1% en poids) de polymères fonctionnalisés pour interférer avec le processus de nucléation et le processus de la croissance de la formation des hydrates là ou les conditions d'opérations font en sorte que la formation des hydrates gazeux est thermodynamiquement favorable.

Ce projet vise à étudier le potentiel d'inhibition de l'alcool polyvinylique sur un système d'hydrates, à base du gaz de méthane, dans l'eau. L'acétate de polyvinyle a d'abord été synthétisées en utilisant le procédé de polymérisation radicalaire à médiation par le cobalt. Ce processus est choisi afin d'avoir un bon contrôle sur le poids moléculaire du polymère tout en maintenant un faible degré de dispersion. Bien que la taille des polymères a été synthétisée avec un bon contrôle, de grandes dispersités ont été observés en raison de la nature très réactive à l'oxygène du complexe de cobalt utilisé. Une technique de dégazage plus rigoureux, soit le cycle de congélation-pompe-décongélation, a été mis en œuvre afin d'obtenir un environnement exempt d'oxygène pour atténuer cette observation. L'acétate de polyvinyle a été ensuite converti en alcool polyvinylique en utilisant une réaction d'hydrolyse de base. L'alcool polyvinylique de différentes tailles ont ensuite été dissous dans de l'eau déminéralisée à une concentration fixe. Des expériences de croissance d'hydrate ont ensuite été réalisées afin d'étudier l'effet de la taille sur la croissance des hydrates. Il a été observé que le taux de dissolution du méthane dans la phase liquide ainsi que le taux de croissance d'hydrate de méthane à diminuer avec l'addition de l'inhibiteur. Toutefois, aucune tendance n'a été observée de l'effet de la taille du polymère sur ces taux. Ces taux ont également été observés à être plus faible que lors de l'utilisation de la pyrrolidone polyvinylique, un inhibiteur cinétique des hydrates actuellement couramment utilisé dans l'industrie.

Malgré le fait que les taux de dissolution et de croissance ont été observés à être plus grande pour l'alcool polyvinylique que le pyrrolidone polyvinylique, ces inhibiteurs ont démontré des taux beaucoup plus faible que l'eau pure.

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I. Introduction and Purpose

Although there are instances where the formation of gas hydrate can be beneficial, when appropriate thermodynamic conditions for the formation of gas hydrates are met, the formation of gas hydrates can be problematic depending on their location. In gas pipelines, for example, gas hydrate formation is problematic as they may form plugs that block the flow. These hydrate plugs become damaging to the pipelines themselves and to other equipment downstream.

The prevention of gas hydrate formation becomes increasingly important in these cases. Due to the large costs associated with the thermodynamic inhibition of gas hydrate formation, increasing interest is going towards the development of kinetic inhibitors. These low-dosage hydrate inhibitors delay the onset of nucleation and slow the growth rate of crystals. They require much less quantities within the flow which lowers their operational costs and downstream separation costs.

The purpose of this research is to synthesize and evaluate the methane hydrate inhibition potential of vinyl based polymer surfactants as kinetic hydrate inhibitors. Specifically, this research looks at poly(vinyl acetate/alcohol) as a low cost alternative to other vinyl based kinetic inhibitors currently being used. This research aims to synthesize this polymer and assess its effects on hydrate formation. The effect of the molecular weight of this polymer will also be determined. The potential of hydrate inhibition of the synthesized poly(vinyl alcohol) will also be compared to poly(vinylpyrrolidone), which is a kinetic hydrate inhibitor currently commonly being used by the industry.

II. Background

1. History of gas hydrates

Gas hydrates are crystalline solids consisting of a crystal lattice of water molecules which contain "guest" gas or volatile liquid molecules. The guest molecules are trapped within the cavities while the water cage is held together through hydrogen bonding and stabilized by Van der Waals interactions with the guest molecule. The water lattice, in itself, is thermodynamically unstable and requires the guest molecules to stabilize it via weak van der Waals forces (Sloan & Koh, 2008).

Academic interest

Gas hydrates were discovered by English scientists as early as the 1800s. In 1810, Sir Humphry Davy had observed that aqueous solutions of chlorine solidified more easily than pure water by forming crystalline solids at approximately 9°C (Sloan & Koh, 2008). In 1823, Davy's assistant, Michael Faraday, determined the molecular composition of chlorine hydrates. Many suitable gases (methane, ethane, and carbon dioxide among others) are now known to be capable of forming these non-stoichiometric hydrate compounds under favorable thermodynamic conditions; high pressures and low temperatures. (Englezos P., 1993).

While the interest in hydrates was primarily focused at an academic level on identifying the hydrate-forming compounds and their corresponding thermodynamic conditions, it was joined by a wave of industrial interest in the mid-1930s when it was corroborated that clathrates plugged natural gas pipelines. E.G. Hammerschmidt, from Texas, first reported their presence in natural gas transmission lines, following which they gained industrial interest. He had proven that gas hydrates were the main cause of natural gas pipeline blockage (Hammerschmidt, 1934).

Furthermore, since methane is the main volatile gas composing natural gas (Rojey, 1997), methane hydrates were the principle type of hydrates that research focused upon.

Industrial interest

Following this discovery, significant interest in hydrate research was given by industry in focusing on preventing hydrate formation by either changing the operating conditions or through addition of thermodynamic and kinetic inhibitors (Chatti, 2005). An example of pipeline blockage caused by hydrates is shown in Figure 1 below.



Figure 1: Example of hydrate blockage in natural gas production (Petrobras).

The next milestone in hydrate research began with the discovery of in situ gas hydrates in seafloor sediments along deep continental margins and in permafrost regions by the Russian scientist Yuri Makogon in the 1960s (Makogon, 1966). Both locations are biogenic and thermogenic sources of methane and are capable of supporting the thermodynamic conditions needed to form methane hydrates. Current estimates of the amount of carbon stored in these reserves exceed by a factor of two the amount of carbon stored in all other known fossil fuels combined (Suess & Bohrmann G, 1999). This large volume of naturally occurring gas hydrates is

at the source of the rising interest in its potential use as an alternative energy source (Davidson DW, 1978).

Advantages

Gas hydrate can be used in many other applications as well. Some technologies, for instance, could use gas hydrates for transportation and storage purposes of various gases. The advantage that hydrates present over traditional techniques is the elimination of the reliance on extremely low temperatures and very high pressures while offering comparable storage capacity. Sequestration of carbon dioxide in deep waters with the goal of reducing the concentration of greenhouse gases in the atmosphere is another example of storage capabilities of hydrates (Brewer, 1999) (Chatti, 2005).

Disadvantages

Gas hydrates, despite their numerous technological advantages, can also pose problems to the oil and gas processes by forming plugs in transportation pipelines. One such example is the large oil spill which occurred in the Gulf of Mexico. Plugs of gas hydrates were later found in the pipelines. The oils in the water nearby hindered containment efforts as the risk of hydrate plug formations were high (Crone TJ, 2010). Thermodynamic inhibitors are often added to natural gas mixtures in order to prevent the formation of hydrate plugs. The most common thermodynamic inhibitors are methanol, ethylene glycol, and diethylene glycol (Anderson & Prausnitz, 2004). Despite being sufficient for thermodynamic inhibition, this approach is problematic since the injection of methanol and its additional downstream separation steps dramatically increases process costs. Due to the increase in industrial demand and increase in volumes of transported natural gas, it is more important to develop an environmentally-friendly, cost-effective, and targeted approach to hydrate mitigation.

2. <u>Hydrate Structures</u>

Gas hydrates are commonly referred to as clathrate hydrate compounds. The term "clathrate" describes compounds where one type of molecules forms a lattice which contains another type of molecule. (Englezos P., 1993). In gas hydrates, the lattice structure is formed with water molecules that are linked together by strong hydrogen bonds. The water molecules can be arranged in several different configurations, making it possible to accommodate guest molecules of different sizes in its structural cavities. One cavity, however, can only hold a single guest molecule. One exception to this rule, which only occurs in extreme conditions that seldom happen, is the case of hydrogen clathrates where multiple hydrogen molecules (2 to 4 molecules) have been observed in each cavity (Lokshin, et al., 2004). The guest molecule within the cavities stabilizes the surrounding water cage through weak van der Waals forces (Sloan & Koh, 2008). Only certain molecules can thermodynamically stabilize a specific hydrate structure. Figure 2 below illustrates one type of cavity that forms in the structure I methane hydrate. A methane molecule is positioned in the middle of the cavity while water molecules form a symmetrical polyhedron surrounding it.



Figure 2: Methane molecule enclosed in a water molecule lattice structure. (McGill Hydrate Research Group)

While many hydrate forming gases of different sizes have been identified, there are only three main hydrate structures: structure I, structure II, and structure H. The hydrate crystal lattice of these structures is constructed from different, but specific, arrangements of five basic polyhedral water cavities which allow these three structures to accommodate guest gas molecules of varying sizes. The polyhedron presented in Figure 1 is a 5^{12} -unit cell and is the only polyhedron common to all three structures. The other hydrate cages are classified as $5^{12}6^2$, $5^{12}6^4$, $4^35^66^3$ and $5^{12}6^8$ (Sloan & Koh, 2008). These numbers describe the number and type of polygons forming the polyhedron. A $5^{12}6^2$ polyhedron is formed by 12 pentagons (5 edges) and 2 hexagons (6 edges). Figure 3, below, visualizes the arrangements of the cavities as well the number of polyhedra required to form the unit cells of the three main hydrate structures.



Figure 3: Structure I, structure II, and structure H unit cells and the corresponding polyhedra required to form them (adapted from Koh, 2011).

While each cavity is stabilized by van der Waals forces due to the presence of a guest molecule within, not all cavities are required to be occupied for the entire hydrate structure to be stable. In fact, it has been estimated that small and large cages are only occupied 50% and 95%, respectively (Cláudio, 2008). A perfect crystal is said to be achieved when all cavities are occupied with a guest molecule. The partial occupancy of the clathrate hydrates explains their non-stoichiometric nature.

Types of Structures

Structure I usually forms with guest molecules containing less than 3 carbon atoms (methane and ethane are the most common guest molecules) and is a body-centered cubic (BCC) structure. Naturally occurring structure I hydrates are commonly found in the permafrost regions and ocean floors since these regions contain several large quantities of natural gas deposits (Sloan E., 1998).

The next class of hydrates, structure II, accommodate larger gas molecules and heavier components of natural gases (propane, butane, tetrahydrofuran) or oils. The unit cell of this type of structure is also BCC. Being larger in size, these hydrate structures require more polyhedra and thus, more water molecules. These hydrate structures are usually found in man-made environments (Sloan E., 1998).

The final class of hydrates, structure H, can take up larger molecules (C6+). An important aspect of this structure is that while the other structures can form a single component hydrate, structure H hydrates require the presence of at least two components in order to form. This makes structure H hydrates generally more difficult to form and grow. Structure H hydrates are, however, found in both naturally and man-made environments (Sloan E., 1998).

3. Hydrate Formation Steps

Gas hydrate growth is a crystallization process (Kashchiev & Firoozabadi, 2002) and thus, follows the steps of crystallization which include nucleation, and crystal growth. After the system has cooled, or if the pressure of the system increased, sufficiently to thermodynamically favour hydrate growth, an induction time occurs where the supersaturated system remains in a state of metastability. Following this period, nucleation occurs and the hydrate crystal growth begins after having reached a critical radius.

Nucleation

The nucleation of the hydrate crystal can take place once the appropriate thermodynamic conditions have reached within the mixture of the water and guest molecule. This nucleation process is stochastic and yet to be fully understood. In this process, hydrate cages and clumps of particles grow and decompose until they reach a thermodynamically stable size, known as the critical nucleus (Englezos P. K., 1987). The nucleation process can either be homogeneous or heterogeneous. Heterogeneous nucleation occurs when the crystallization is initiated by an impurity within the solution. Since it is nearly impossible to achieve a pure solution with no impurities, this type of nucleation is the most commonly occurring nucleation process (Sloan & Koh, 2008). After the nucleation step has taken place, the hydrate growth phase proceeds very rapidly.

Crystal Growth

After the hydrate crystal has reached a critical nucleus size, crystal growth can occur. The growth process is generally considered to be a mass limited or a heat transfer limited process (Sun, 2010). There are several valid approaches for measuring and predicting hydrate growth

rates. Different driving forces are usually taken in to account when formulating the mathematical models to predict these growths to account for various different situations.

In a mass transfer limited model, the gas molecules at the solid-liquid interface are incorporated within the water lattice by adsorption and stabilize the structure. In the case where the concentration of the guest molecule is low, the transport process of the guest molecule becomes the rate-liming process (Freer, 2001).

When the crystal growth process is limited by heat-transfer, the heat released by the phase change diffuses into the bulk of the fluid phase and limits subsequent growth. This crystallization process is controlled by the diffusive transfer of the heat and heat transfer rates have a significant impact on hydrate growth (Mori, 2001).

4. Hydrate inhibition

Despite the fact that gas hydrate formation has advantages, they can lead to potential safety hazards. As mentioned earlier, transportation pipeline plugging is a major risk. The inhibition of the formation of these hydrates becomes crucial in these conditions where formation is thermodynamically favourable.

Thermodynamic inhibition

To prevent the formation of hydrates in transportation pipelines, thermodynamic inhibitors are conventionally used. The addition of a third active component shifts the thermodynamic equilibrium. Thermodynamic inhibitors, such as alcohols and electrolytes, are generally added to the water-guest gas molecule mixture at high concentrations (~ 40 wt%), in order to shift this hydrate formation phase boundary away from the operating conditions (Koh, 2002). Figure 4, below, illustrates a hydrate formation phase equilibrium shift. System operation

on line 1 would be thermodynamically favourable for the formation of hydrates until thermodynamic inhibitors are added to shift the line and make that system hydrate free.



Figure 4: Hydrate formation phase equilibrium line shift

Kinetic/anti-agglomerate inhibition

Unlike thermodynamic inhibitors, low dosage hydrate inhibitors do not shift the hydrate formation thermodynamic equilibrium line. They, instead, delay the onset of nucleation by prolonging the induction time of hydrate formation. Anti-agglomerate inhibitors, for their part, slow the growth rate of hydrate crystals that have already formed by preventing the agglomeration of hydrate crystals into large masses (Cha *et al.*, 2013). Kinetic inhibitors, on the other hand, slow the growth phase of hydrate formation. They adsorb onto the growing hydrate crystal surface and reduce the surface area available to other water molecules to adsorb onto the crystal, this inhibiting growth. Both kinetic and anti-agglomerate inhibitors can also modify the hydrate crystal morphology to prevent large hydrate particles from forming. Furthermore, kinetic inhibitors require much smaller concentrations (< 1 wt%) which makes them a growing area of interest in hydrate inhibition (Koh, 2002).

Kinetic inhibition mechanisms

While research is being performed, it has been proven very difficult to understand the exact mechanism of kinetic inhibitions. Some methods for inhibition, however, have been proposed. One of these mechanisms, proposed in 2000 and commonly accepted since then, is the inhibition by adsorption. It was hypothesized that kinetic hydrate inhibitors inhibit hydrate formation by adsorbing onto the growing crystal surface through hydrogen bonds (King et al., 2000). As the kinetic inhibitors adsorb onto the crystal surface, they greatly reduce the surface area available to water to go in to the hydrate phase. They also prevent guest molecule inclusion and render growth unstable in surrounding inhibitor attachment sites. Figure 5 illustrates hydrate formation and growth as well as hydrate inhibitors adsorbing onto the crystal surface to prevent water from going in to the hydrate phase.



Figure 5: Hydrate formation and hydrate inhibitor adsorption onto crystal surface, reducing the surface area of the crystal, to inhibit growth (adapted from Sa et al, 2013).

5. Kinetic Inhibitors

The industry currently favours the use of electrolytes and alcohols as thermodynamic inhibitors rather than kinetic inhibitors due to the fact that kinetic inhibitors are currently not effective enough for general implementation. Their use thus far is very limited. A good understanding of kinetic inhibitions as well as the important properties of kinetic inhibitors which make them more efficient is the key to increasing their inhibition potential. The long chains of monomers of the polymer kinetic inhibitor allow them to adsorb onto a greater surface area, thus limiting further hydrate growth.

Properties of kinetic inhibitors

As mentioned previously, one of the mechanisms of kinetic inhibition, which has been widely accepted, requires the polymer inhibitor to adsorb onto the crystal surface. To allow for greater adsorption, kinetic inhibitors need to, firstly, be very soluble in water in order to be present in sufficient concentration at the hydrate-water front. These polymers need also be able to adsorb well to the polar surface of hydrate crystal made of water molecules (Perrin et al, 1996). Furthermore, the kinetic inhibitors should also have low toxicity to the environment in order for safe use. Due to the small amounts of hydrate inhibitors required, they tend to have low to moderate costs. Water soluble polymers are often functionalized to achieve the abovementioned properties.

vinyl based polymers

Some clues about the types of structures that inhibit ice crystallization have been provided by the nature surrounding us. Natural antifreeze proteins for example, produced by certain plants and fungi, allow them to survive in subzero conditions. Much like kinetic hydrate inhibitors, these antifreeze proteins inhibit the growth of ice by binding to the growing crystals (Goodsell, 2009). The structures of these proteins have certain characteristics such as regular arrays of hydrophilic amino acids which allow them to interact with the surface of the growing crystals (Baardsnes et al, 1999). This has led to the use of certain vinyl based polymers, with functional groups having large tendencies for hydrogen bonding, as good kinetic hydrate inhibitors. In the 1990s, poly(N-vinylpyrrolidone) (PVP) and poly(N-vinylcaprolactam) (PVCap) were both reported to exhibit good hydrate inhibition (Sloan, 1995). While PVP has, since, gone through numerous laboratory and industrial testing and found to be an effective inhibitor (Karaaslan & Parlaktuna, 2002), most of these studies looked at inhibitor sizes obtained from the manufacturer which are often standardized. The molecular structure of PVP and PVCap are presented in Figure 6 below where the similarities of both these polymers can be seen. Both of these structures have the vinyl backbone with a ring structure containing a carbonyl group.



Figure 6: Molecular structure of PVP (left) and PVCap (right).

Since these polymers adsorb onto the crystal surface, one of the characteristics of these polymers that plays a large role in determining the inhibition potential of the polymers is the size of these polymers. Sufficient research has not been done to study the effect of the polymer size on its inhibition potential. The limited research performed has proposed a change in inhibition mechanism with varying polymer sizes. It was proposed that smaller sized kinetic inhibitors favour inhibition by delaying the onset of nucleation while larger polymers favour the inhibition by reducing the crystal growth rate (King et al., 2000).

Polyvinyl alcohol

As mentioned earlier, one of the properties necessary for a kinetic inhibitor is its solubility in water and ability to form hydrogen bonds with water molecules in the hydrate phase in order to adsorb on to the growing hydrate surface. Similar to poly(N-vinylpyrrolidone) and poly(N-vinylcaprolactam) which have an oxygen molecule on the repeating unit allowing them to bond and adsorb on the crystal surface, poly(vinyl alcohol) (,PVA) is a polymer that exhibits good surfactant properties. The oxygen from the hydroxyl group on the repeating unit can readily form hydrogen bonds with water molecules which also makes this polymer soluble in water. As seen in Figure 7 below, the structure of PVA is much less bulkier than PVP and PVCap (Figure 6). Its smaller size allows it to reach water molecules on the growing crystal surface that PVP and PVCap would not be able to reach due to their size.



Figure 7: Molecular structure of PVA

Due to the smaller size of the repeating unit, and thus the polymer, it becomes harder for PVA to cover more surface area on the hydrate crystal surface.

6. Synthesis of KHIs

As mentioned in the previous section, a good control on the structure of the kinetic inhibitor allows us to improve its inhibition potential. In order to study the effect of the size of the polymers on their inhibition properties, for example, the polymers synthesized require being very uniform. Over the years, several controlled radical polymerization methods have been developed in order to meet the demand of highly uniform polymers with the architectures required by the industry for their purpose.

In the early 1900s, the first free radically synthesized polymers were produced (Braun, 2009), and this method rapidly grew in popularity and became very active in the 1930s due to the fact that it does not require severe process conditions and can be used to copolymerize a wide range of monomers (Matyjaszewski et al, 2005). Although conventional free radical polymerization is easy to perform and provide cost-effective, easy industrial methods to produce many products, this polymerization technique has some drawbacks. Due to the fast polymer chain growth of the polymer, they experience problems with uniformity of the polymer chain and free monomer levels. New methods had then been developed in order to control the radical polymerization. Controlled radical polymerization show first order kinetics which makes it easy to obtain exact molecular weights. The uniformity of the polymers synthesized is also much narrower with controlled radical polymerization. The control of radical polymerization can be made in several ways. Among these methods include Radical Addition Fragmentation Chain Transfer (RAFT), Atom Transfer Radical Polymerization (ATRP), Nitroxide Mediated Polymerization (NMP), and Organometallic Mediated Radical Polymerization (OMRP). Similar to all free-radical polymerization reactions, an initiation step is first required to obtain a free radical. This initiation can occur in several different ways such as thermal decomposition,

photolysis, and redox, among others. Once a radical has been formed, it then goes in to a chain propagation step where radical polymerization occurs. The radical initiator attacks the monomer to form a chain with a radical at the active end as seen in Figure 8.



Figure 8: Illustration of a free-radical polymerization propagation step. The initiator with a radical reacts with the monomer to form a chain with the radical at the active end. The chain propagates keeping the free radical at the active end.

The chain then propagates until the monomer is no more available or until the growth is terminated. The termination of the polymerization can occur when two active polymer chain ends combine or when the active chain end combines with the initiator radical (Zumdahl & Zumdahl, 2007). Chain transfer reactions may also occur and terminate the growing polymer chain. None of which are desired as they lead to dead polymer chains with uncontrolled sizes.

Cobalt Mediated Radical Polymerization

As mentioned, there are many ways for the growing chain to stop. We can, however, achieve controlled polymerization by having completely pure reactions such that no inhibition caused by impurities occurs. The polymer chain grows until all the monomer is used. More monomer can be subsequently added to continue growth. Furthermore, if chain termination and chain transfer reactions are completely removed, and the rate of chain initiation is larger than the rate of chain propagation, it is possible to achieve polymer chains that grow at a constant rate and uniformly. These are called "living polymers". These living polymers allow to have good control on size and dispersity on macromolecular levels.

While radical polymerizations are generally very rapid, the inclusion of an organic metal as a mediator slows down this reaction and allows for better control over its size. Various organic metals (Cr(I), Mo(III), Fe(I), V(0), Ti(III), Co(II)) can be used as mediators, however, vinyl based compounds, such as the ones kinetic hydrate inhibitors are made of, have been reported to synthesize best using cobalt (Co(II)) (Semsarzadeh & Amiri, 2011).

While a reaction proceeds via Cobalt Mediated Radical Polymerization (CMRP), three possible reaction mechanisms may be occurring depending upon the choice of initiator, monomers, solvent and operating conditions.

Reversible Termination

The reversible termination mechanism, sometimes called the Persistent Radical Effect (Fischer, 2001), is used to produce polymers with a low PDI and a high molecular weight. A unimolecular initiator, such as an organocobalt complex(R-Co(III)), is used to initiate the reaction. Due to the weak nature of the cobalt-carbon bond, light or heat, under very moderate conditions, can be used to initiate the reaction and create the radical (Debuigne et al., 2005). A cobalt-complex radical (CoII) and a transient organic radical ($R \cdot$) are produced. Propagation occurs as the organic radical reacts with the monomers. The cobalt complex radical (CoII) reversibly reforms a covalent bond with the chain carbon radical since the dormant state is more thermodynamically favoured (Debuigne et al., 2005). Figure 9, below, illustrates these steps.



Figure 9: Reversible Termination Mechanism of CMRP; (1) Weak Cobalt(III)-Carbon bond breaks creating radical, (2) Carbon radical starts polymer chain growth with monomer (3), Cobalt (III) reversibly reforms covalent bond with chain carbon radical (4), Concentration of radicals reduces (5) and minimizes risk of growth termination by combination of two carbon radicals.

The growing polymer chain continuously alters between the active and dormant state due to the reversible nature of the bond. This greatly minimizes the chances for the active chain to terminate its reaction from one of the earlier mentioned termination mechanisms. The downside of this mechanism, however, is that the reaction rate will be much slower and will require much longer reaction times (Caille et al., 2005).

Catalytic Chain Transfer

The Catalytic Chain Transfer mechanism is often used when a very low molecular weight polymer is desired (Debuigne et al., 2005). The main product of a catalytic chain transfer reaction is a short unsaturated chain. In the catalytic chain transfer reaction, instead of the transient radical continuously reacting with the monomer unit, the cobalt complex radical can interfere and take a hydrogen atom from the transient radical and leave an unreactive alkene chain. This is also illustrated in Figure 10 below.

$$M \bullet + \bullet C(CH_3)(X)R \longrightarrow M-C(CH_3)(X)R$$

$$(2) M-H + CH_2 = C(X)R$$

Figure 10: Catalytic chain transfer rection where an unreactive alkene (2) can reversibly form

The kinetic problem with polymerizing vinyl based polymers is the fact that the radicals have such high reactivity that controlling the homopolymerization becomes difficult (Caille et al., 2005). Promising results have been achieved when vinyl acetate was polymerized by using a cobalt complex (Co(acac)₂) as mediator and a conventional radical polymerization initiator, V70, under the reversible termination mechanism (Piette et al., 2012). A dispersity of 1.1-1.2 has been observed (Debuigne et al., 2008), demonstrating very good control of the polymerization until molecular weights of about 20 kg/mol (Maria et al., 2007).

7. Synthesis of PVA

Unlike most other vinyl-based polymers, PVA cannot be synthesized using its monomer. vinyl alcohol is a compound which, under normal conditions, tautomerizes to acetaldehyde. At room temperature, acetaldehyde is more stable than vinyl alcohol. Due to this instability, poly(vinyl alcohol) cannot be synthesized using vinyl alcohol monomer with the cobalt mediated radical polymerization. Instead, PVA is synthesized indirectly by first synthesizing poly(vinyl acetate) and then converting PVAc in to PVA by the hydrolysis of the ester bond.

Figure 11, below, shows the synthesis route for the base hydrolysis reaction for the conversion of PVAc to PVA in methanol.



Figure 11: Synthesis of PVA from hydrolysis of PVAc.

The properties of PVA are dependent on the degree of hydrolysis. Due to the insolubility of PVAc in water, the degree of hydrolysis plays a direct role on the solubility of poly(vinyl acetate/alcohol) in water. In order to obtain a polymer with the most solubility in water, PVAc is allowed to completely hydrolyze to form PVA.

III. Materials and Methods

1. Experimental Setup

Polymerization

The polymerization reaction experiment was setup in such a manner to allow for continuous observations. As illustrated in Figure 12, the polymerization reaction occurs inside of a 50 mL, 24/40, 3 neck, round bottom flask, purchased from DIMA GLASS, placed on top of a heating mantle. The middle opening of the reactor is connected to a condenser column, through which, glycol runs as a coolant at 4°C controlled by a Neslab RTE-740 chiller (not shown in the figure).

The second reactor opening is connected to a nitrogen gas purge line coming from a nitrogen gas tank purchased from MEGS. A thermocouple enters the reactor through the last reactor opening. The temperature signal obtained by the thermocouple is sent to an OMEGAETTE CSC32 temperature controller. The control box reads the signal, converting it to a temperature value displayed on the front interface. The temperature is controlled by a PID controller within the control box which feeds the signal back to the heating mantle, thus controlling the temperature of the solution within the reactor. Adequate mixing is provided by a magnetic stirrer operated by a Thermix® 120M stir plate located below the reactor. The whole setup (besides the gas tank and chiller) is inside of a fume hood for proper safety precautions.



Figure 12: Experimental setup for polymerization reaction. The various components of the setup are indicated on the figure (McGill ChemEng Polymer Science Group).

Freeze-pump-thaw

For the experimental conditions where freeze-pump-thaw cycles were used, a Schlenk line was setup for the removal of air from the solution prior to polymerization. This setup is shown in Figure 13 below. A CHEMGLASS air-free Schlenk tube was held in place by support stands. The vacuum tube of the Schlenk line was connected to a PASCAL 2005SD vacuum pump. The atmospheric tube of the Schlenk line was connected to the nitrogen gas tank purchased from MEGS while the other end of the atmospheric tube of the Schlenk line was connected to a CHEMGLASS air-free 100 mL, 24/40, round bottom flask in which the solution to be degassed would be placed. The flask was mounted on the support stand and a Precision Scientific Company Little Jack® was placed

underneath. The jack was able to lift a PYREX® Brand 3140 dish, containing liquid nitrogen, underneath the round bottom flask for the freezing step.



Figure 13: Freeze-pump-thaw cycle setup where A) Schlenk tube, B) vacuum tube going to a vacuum pump (not shown in the figure), C) nitrogen gas inlet coming from a nitrogen tank (not shown in the figure), D) nitrogen line open to atmosphere, E) Schlenk line connected to an airfree round bottom flask, F) Little Jack ®, G) airfree round bottom flask, and H) PYREX Brand 3140 dish.

Methane Hydrate Growth

The setup used for the study of methane hydrate growth with the synthesized polymer surfactants was a setup previously built by the McGill Hydrate group and used by several previous students. The hydrate experiments were conducted inside of a 316 stainless steel reactor with a capacity of 600 cm³ and a pressure rating of 12MPa. A PPI Dyna/Mag mixer is mounted on top of the reactor to allow for mixing within. Methane gas is supplied to the reactor from a 1000 cm³ reservoir using a control valve set to maintain a constant pressure throughout the

hydrate formation experiment. The reactor and the reservoir are placed inside of a 20% ethylene glycol/water mixture to maintain a constant temperature. The temperature of the cooling bath is controlled using a Neslab RTE-740 chiller in order to maintain the reactor at its operating temperature. The temperature of the reactor is measured using a resistance temperature device probe. The probe used has an accuracy of ± 0.15 K. The pressure of the reactor is monitored using a Rosemount pressure transducer configured to a span on 0-14 MPa with an accuracy of ± 0.065 %. A differential pressure transducer is also used and configured to a span of 0-2 MPa with an accuracy of 0.065%. This allows for an increased accuracy in the results obtained. A National Instruments data acquisition system is also used with LabVIEW in order to record all the readings.

2. <u>Materials and sample preparation</u>

Vinyl acetate was used as a monomer for the polymerization reactions. Liquid vinyl acetate (> 99%) monomer containing 3-20 ppm of hydroquinone as an inhibitor was purchased from Sigma-Aldrich. Powdered 2,2'-Azobis(4-methoxy-2.4-dimethyl valeronitrile) (V70) (chemical structure illustrated in Figure 14) was used as an oil-soluble azo initiator purchased from Wako Pure Chemical Industries.



Figure 14: V70 initiator chemical structure.

The mediator used in the polymerization reactions was cobalt(II) acetylacetonate (Co(acac)₂, illustrated in Figure 15) purchased from Aldrich in powdered solid state.



Figure 15: Cobalt(II) acetylacetonate chemical structure

Finally, poly(vinylpyrrolidone) (PVP) was also obtained from Sigma Aldrich in powder form at an average molecular weight of 10 kg/mol.

The amounts of V-70 initiator, Co(acac)₂ mediator, and vinyl acetate monomer, used for the polymerization reactions were adapted from a published paper by Debuigne (Debuigne , Caille, Detrembleur, et al., 2005) who had observed good size control as well as low dispersities. Table 1, below, summarizes the results obtained by Debuignes.

t , h	Conv., %	$M_{n,SEC}$	M _{n,theor} ,	Ð
		g mol ⁻¹	g mol ⁻¹	
20	11	7 500	5 100	1.25
22	21	12 000	9 800	1.20
25	36	19 500	16 800	1.20
28	51	24 000	23 800	1.20
44	70	30 000	32 700	1.40

 Table 1: Summary of the experimental results obtained by Debuigne , Caille, Detrembleur, et al., 2005)

They had observed low dispersity values (D) for reaction conversion percentages of roughly 20% to 50%. As previously discussed in section I.6, the longer a polymerization reaction runs, the higher the chances of termination reactions occurring is. For this reason, it is neither desired to run the reaction for too long (> 70% conversion) nor too short (< 30% conversion). Since the reactions conducted by Debuigne et al. achieved 100% monomer conversion at around 60 hours, the reactions performed for this thesis research were conducted

for 30 hours in order to achieve a 50% conversion rate. These reactions were performed in bulk at 30° C.

Additionally, it had been observed that the molecular weight depended heavily on the monomer/initiator molar ratio (Debuigne et al., 2012), as is expected in a controlled process.

In order to vary the molecular weights achieved at 50% conversion, the amount of initiator was varied while keeping the amounts of the mediator and initial monomer constant. The total monomer mass of 9.34g (10mL) and $Co(acac)_2$ mass of 17.2 mg was used and remained constant.

The theoretical molecular weight of polymer obtained using radical polymerization can be calculated using the equation:

$$M_{n,th} = MW_m \times \frac{[M]_0 - [M]_t}{[Initiator]_0}$$

Where Mn,p is the number average molecular weight of the obtained polymer, MWm is the molecular weight of the monomer, $[M]_0$ and $[M]_t$ are the initial and final monomer concentration and [initiator]₀ is the initial concentration of the initiator.

 $[M]_0 - [M]_t$ can be simplified to $0.5[M]_0$ since we are aiming for 50% conversion. We then get:

$$M_{n,th} = MW_m \times \frac{0.5[M]_0}{[Initiator]_0}$$

From this equation, we can estimate the initial initiator concentration required in order to have the desired molecular weights.

$$[Initiator]_0 = MW_m \times \frac{0.5[M]_0}{M_{n,th}}$$

Table 2 summarizes the experimental masses of mediator, initiator, and monomer, based

on the theoretical conversion equation, used for each polymerization reactions.

Experiment ID	M _{n,th}	[Co(acac) ₂],	[V70],	[VAc],
	Kg/mol	mg	mg	mg
PVA-10	10	17.2	40.2	9 340.0
PVA-20	20	17.2	20.1	9 340.0
PVA-25	25	17.2	16.1	9 340.0
PVA-30	30	17.2	13.4	9 340.0
PVA-40	40	17.2	10.1	9 340.0

Table 2: Experimental reactant masses used to achieve the theoretical desired molecular weight at 50% conversion.

The masses of the initiator, mediator, and monomer, were measured on an electronic scale and mixed together in a glass vial prior to being added to the reactor. Due to the high reactivity of the cobalt complex with oxygen (from both water molecules and oxygen in the air) (Shirazi et al., 1982), it is crucial to perform these experiments in an oxygen-free environment. The use of a glove box was made in order to achieve an oxygen-free environment during the weighing step of these reactants in order to limit the contact of the cobalt complex with air.

3. Experimental protocol

Freeze-Pump-Thaw cycle

Polymerization experiments were first conducted without using rigorous degassing techniques. However, after seeing high dispersities due to the high reactivity of the cobalt complex to oxygen (discussed in the results section), a more aggressive degassing technique, the freeze-pump-thaw cycle, was implemented before the start of the polymerization reaction in order to further limit the access of the Co(acac)₂ mediator to the oxygen in the environment.

In this technique, the solution mixture of mediator, initiator, and monomer, was first frozen, prior to the reaction, using liquid nitrogen. The air was then pumped out to create a vacuum above the frozen reactant mixture. The reactant solution was then thawed using a warm water bath. As the solution returned to a liquid state, the air that was previously dissolved in the reactants, from the vinyl acetate monomer liquid, was degassed in to the vacuum above. The liquid was then frozen again and vacuum reestablished. This freeze-pump-thaw cycle was repeated multiple times (5-7) in order to remove air from the reactants solution. Following the final vacuum, nitrogen gas was used to bring the pressure back to atmospheric pressure before the solution was thawed for the last time before entering the reactor.

Polymerization reaction

A 50 mL three-neck round bottom flask reactor was placed on the heating mantle on the magnetic stirrer. The reactor was connected by the middle neck to the condenser column through which the cooling liquid was circulating. A small magnetic stir bar was added to the reactor and the remaining two necks of the reactor were shut using a rubber septa. The thermocouple was inserted into the reactor through the septa. A nitrogen gas purge line needle was also inserted in the reactor from the septum of the third neck. The reactor was allowed to purge for several minutes to ensure an oxygen free environment.

Following the completion of the purging cycle, the monomer, initiator, and mediator solution (measured previously and mixed together in a glass vial) were added to the reactor using a syringe. After the addition of the reactant solution, the reactor was allowed to further purge using nitrogen gas to remove any oxygen that might have entered the reactor during the addition of the reactant solution. Following the second purge cycle, the temperature controller and the heating mantle were turned on to increase the temperature to 30° C and allow for the polymerization

reaction to begin. If the temperature of the reactor was observed to be too high, the heating mantle was momentarily removed from underneath and the reactor allowed to cool before the control of the temperature resumed. The reactions were run for a set time duration, in accordance with Table 1, in order to obtain various batches of poly(vinyl acetate) with varying molecular weights.

At the end of the reaction, the product was transferred to a glass vial which was then filled with heptane in order to precipitate the polymer out of solution. The unreacted monomer, initiator, as well as mediator, are soluble in heptane whilst the desired poly(vinyl acetate) polymer product is not. After recovering the precipitated polymer, it was then dissolved in minimal amounts of tetrahydrofuran (THF) to dissolve the polymer and re-precipitated in heptane for purification. This purification cycle was done thrice to obtain a purified polymer and minimize the loss during these cycles. The mass of the recovered polymer was noted for calculating the conversion of the polymer and determining the amount of unreacted monomer. The final purified polymer, still in the heptane solution, was allowed to dry overnight. It was then further dried in a vacuum oven at 55°C for 2 to 4 hours, or longer depending on the dampness of the polymer. After drying, it was stored in a fridge for later use.

The polymer relative molecular weights (MW) and dispersities (D) were determined by gel permeation chromatography (GPC) in a GPC-grade THF solution. Calibration with poly(methyl methacrylate) (PMMA) standards in GPC grade tetrahydrofuran (THF) at 30°C was used to determine the relative molecular weights of poly(vinyl acetate) polymer.

Hydrolysis

In order to perform the hydrolysis reaction on the poly(vinyl acetate) to obtain poly(vinyl alcohol), 2g of PVAc were mixed with 80 mL of ethanol in a 100mL round-bottom flask. The mixture was heated to 40 °C and stirred until the polymer dissolved.

In a separate vial, 2g of sodium hydroxide were dissolved in 20 mL of ethanol. This solution was then added to the PVAc/ethanol solution. The round bottom flask was closed using a Septa and the mixture was left on the heating plate and stirring for 4 hours for the hydrolysis reaction to proceed to completion.

Upon completion, the PVA precipitate was filtered and washed twice using 10mL of ethanol. In order to further purify the polymer, the polymer was dissolved in minimum amounts of deionized water. The polymer was then precipitated out by mixing the solution with 100mL of Acetone. This dissolution and precipitation cycle was repeated three times after which the polymer was filtered and dried overnight.

Hydrate experiments

A 1500mL solution of poly(vinyl alcohol) dissolved in water at 700ppm was prepared for the hydrate experiments. 1.05g of dried, purified, poly(vinyl alcohol) was dissolved in deionized water in a 4L PYREX Glass beaker. The mixture was stirred for 20 minutes to allow complete dissolution. 360 mL of this mixture was then injected in the depressurized hydrate reactor. After injecting the solution, the pressure of the reactor was increased to 500 kPa and the stirring inside the reactor was turned on for 60 seconds. Afterwards, the stirring was stopped and the outlet valve opened to remove the solution to allow rinsing of the reactor. The pressure of the reactor was brought back down to atmospheric pressure and this rinse cycle repeated two more times.

After the last rinse cycle, 300 mL of the polymer solution was injected in the reactor for experiments. After the solution injected, the pressure of the reactor was increased to 1000 kPa and stirring was turned on for 60 seconds to 120 seconds. The stirrer was then turned off and the pressure of the reactor brought down to 100 kPa. This allowed for any air, which might have been introduced inside of the reactor during the loading stage, to go out of the reactor. In order to ensure that all air has been removed from the reactor, this purging cycle was repeat 15 to 20 additional times. This ensured that any air entering the reactor during loading or air dissolved in the deionized water would leave the reactor.

After the completion of the final purge cycle, the pressure of the reactor was brought up to 1000 kPa and left to equilibrate overnight without stirring in order to get the operating temperature of 277.15K inside of the reactor.

After equilibration, the pressure of the reactor was brought up to the operating pressure of 6282 kPa in order to be above the thermodynamic equilibrium line and having a driving force of 2500 kPa favouring the formation of hydrates. The pressure of the reactor reservoir was also increased to at least 400 kPa above the operating pressure of the reactor. This was to ensure that enough methane is available to provide the reactor in order to maintain the operating pressure. As hydrates form, the pressure of the methane gas above the liquid reduces as the methane dissolves in the water. Additional methane is fed to the reactor from the reactor reservoir to maintain a constant pressure.

Once the temperatures and pressures have stabilized at the operating conditions, the control valve, which controls the pressure inside the reactor, is turned on and the LabVIEW program is started in order to begin collecting data. The stirring inside the reactor is then turned on and the experiment begun. Once the beginning of the formation of hydrates is observed, the hydrates are

allowed to grow for 1500 seconds in order to have enough data points for interpolation to determine the growth rate.

After completion of the experiment, the data collected is saved. The control valve is turned off and the pressure of the reactor brought down to 500 kPa. The reactor is then left at that low pressure with stirring on for a sufficient amount of time to allow all hydrates to dissociate. The Treble-Bishnoi equation of state is used to calculate the number of moles consumed at any given time (Trebble and Bishnoi, 1987)

Following this step, three more runs are performed using the same sample in order to have replicates. Once all replicates are completed and the data analyzed, the solution inside the reactor is discarded and a new polymer solution injected in order to rinse the reactor thrice and begin a new set of experiments.

IV. Results and Discussion

1. Polymerization

The results of the polymerization reactions initially performed without using rigorous degassing techniques using the Cobalt Mediated Radical Polymerization method are summarized in Table 3, below. From the results obtained from the gel permeation chromatography, it was observed that a good control on the molecular weight, where the experimental molecular weight was within 5% of the expected molecular weight, was achieved.

Table 3: Experimental results of polymerization reactions without rigorous degassing techniques for the desired number average molecular weights at 50% theoretical conversion.

Experiment ID	$M_{n,th}$ (^{Kg/mol})	Experimental Conversion (%)	Experimental M_n $\binom{\text{Kg}_m}{\text{Mol}}$	Dispersity, Đ
PVA-10	10	49.1	9.93	1.71
PVA-20	20	47.5	19.0	1.92
PVA-25	25	52.8	26.4	1.84
PVA-30	30	51.5	30.9	1.75
PVA-40	40	48.9	39.1	1.66

While the degree of polymerization, with respect to the PMMA standards (in THF at 30° C) of the polymers was achieved within 5% of the expected size, large dispersities were observed. High dispersities indicate that while the average chain length of the polymer obtained may have been 9.93 ^{Kg}/_{mol} (first row of table of results where targeted desired MW is $10^{Kg}/_{mol}$) a significant fraction of chains were of much lower and much larger molecular weights. Using polymers of high dispersities for further hydrate inhibition kinetic studies make the results inconclusive since it cannot be accurately determined the effect of molecular weight on the inhibition process. For example, how entangled is the polymer? This may determine how the polymer chains cover the hydrate surface, etc. One explanation for these high dispersities is that the cobalt complex might have come in contact with oxygen during the experiment. Due to the reactive nature of the cobalt complex with oxygen, it is likely that oxygen was present at different stages of the

polymerization. Some possible routes for air to have come in contact with the cobalt mediator complex include the weighing process. Oxygen coming in contact with the cobalt complex during this process may have inactivated the complex and made it inefficient during the reaction. Since the reactants were measured in a pre-determined ratio for the experiment, the inactivity of some of the mediator would change this ratio and skew the results. In fact, as fewer mediating complexes are active during the reaction, less reversible termination and catalytic chain transfer reactions occur and allow for more termination reactions. The increase in termination reactions also changes the uniformity of the product. Some chains of polymers terminate before others and higher dispersities are observed.

2. Polymerization using rigorous degassing

Following the observation of large D, a more rigorous degassing technique was used to limit the contact of the reactants with oxygen. **Error! Reference source not found.**, below, summarizes the results obtained after implementing the freeze-pump-thaw cycles and using the glove box for measuring reactants. We see in **Error! Reference source not found.** much smaller D achieved in the polymerization reaction indication the presence of a more uniform polymer product.

Experiment ID	$M_{n,th}$ (^{Kg} / _{mol})	Experimental Conversion (%)	Experimental M_n $\binom{\text{Kg}}{\text{mol}}$	Dispersity, Đ
PVA-10	10	51.0	10.2	1.40
PVA-20	20	46.8	18.7	1.43
PVA-25	25	48.8	24.4	1.48
PVA-30	30	50.5	30.3	1.41
PVA-40	40	46.5	37.2	1.47

Table 4: Experimental results of polymerization reactions with rigorous degassing techniques for the desired number average molecular weights at 50% theoretical conversion.

The data obtained from the GPC is compared in Figure 16 below, for the same experimental condition where the desired molecular weight was 20 $^{Kg}/_{mol}$, but where in one case, the glove box was used to weigh the reactants while the other was weighed without the glove box. This figure illustrates a narrower signal (indicative of a lower dispersity) for when the glove box was used.



Figure 16: Comparison of GPC data for the polymerization with and without using the glove box.

The decrease in the D observed when using rigorous degassing techniques strongly suggests that the presence of oxygen during the reaction is disadvantageous and that the use of the glove box and freeze pump thaw cycles mitigated that occurrence.

3. Methane hydrate growth experiments

Figure 17, below, shows the gas consumption curve observed with methane gas in water with 700 ppm of poly(vinyl alcohol) at 10.2 kg/mol. This figure first shows, at the beginning of the experiment, the dissolution stage of the experiment. During this phase, methane gas, at a high pressure above the water/polymer solution, begins to dissolve in the liquid phase. The rate of dissolution is seen to decrease with time as more and more methane is dissolved in the liquid. As the concentration of methane in the liquid phase increases, the driving force for further dissolution decreases, showing a lower rate of dissolution. At t ~ 2000 seconds, the rate of consumption of methane in the gas phase begins to increase again. During this turbidity phase, methane hydrates begin to nucleate. After reaching a critical radius, gas hydrates begin to form.

As methane goes from the liquid phase and in to the hydrate phase, the concentration of methane in liquid decreases. This, in turn, increases the driving force for the dissolution of methane from the gas to the liquid phase in order to maintain a saturated liquid.

This is observed in the figure with an increase of methane consumption indicating methane leaving the liquid phase to go in to the hydrate phase.

We also see in this figure, a linear consumption rate indicating the growth phase of hydrates.



Figure 17: Methane gas consumption curve observed for PVA-10 at 277.15K and 6282 kPa with a molecular weight of 10.2 kg/mol and D 1.40.

Dissolution phase

Figure 18, below, compares the dissolution stage of the experiment with various polymer sizes as well as pure water as a baseline. We see from this figure that the rate of dissolution is lower when the polymer kinetic inhibitor is used in the system. As more components are dissolved in the water, methane has less room to dissolve and the driving force for dissolution is decreased.

While it was observed that the dissolution rate varied with different polymer sizes, no trend was observed for the change of dissolution rate with respect to molecular weight change. This may be due to the fact that the molecular weight changes were not large enough to observe specific trends.



Figure 18: Comparison of the dissolution stage of the experiment of different polymer molecular weights at 277.15K and 6282 kPa. The nomenclature PVA-10 is for poly(vinyl alcohol) at 10 kg/mol desired MW (10.2 kg/mol from experiment from Table 4).

Growth phase

Figure 19, below, shows the results obtained during the growth phase of the experiments. This figure shows the linear trend in the moles consumed as is expected during a crystallization growth phase.

It is seen in this figure, that the growth rate of the hydrates, indicated by the slope of the moles consumed, decreases as the polymers are added. A higher growth rate is observed for pure water where no inhibitors are present. This trend is expected as the addition of the polymers, acting as kinetic hydrate inhibitors, slows the growth rate by adsorbing on to the growing front of the hydrate crystal. As seen previously in section III.4, polymers adsorbing on the hydrate crystal surface reduce the area available for additional water molecules to form hydrates.



Figure 19: Comparison of the growth phase of the experiment of different polymer molecular weights at 277.15K and 6282 kPa. The nomenclature PVA-10 is for poly(vinyl alcohol) at 10 kg/mol desired MW (10.2 kg/mol from experiment from Table 4)

Comparison with PVP

Figure 20, below, compares the growth phase of the experiments of the synthesized poly(vinyl alcohol) at 10.2 kg/mol (PVA-10 in figure) with the growth phase of the experiment using poly(vinylpyrrolidone) (PVP) purchased from Sigma Aldrich. This figure shows that the growth rate of hydrates, while subject to kinetic inhibition using poly(vinyl alcohol), was higher than the growth rate of hydrates inhibited using poly(vinylpyrrolidone).

This may be attributed to the fact that the PVP molecule is much bulkier than PVA due to the larger repeating unit. The larger PVP molecule may be covering more surface area as it adsorbs onto to the crystal front, resulting in a slower growth rate. Additionally, due to the fact that the PVA was synthesized, its molecular weight distribution is higher than the one obtained from Sigma Aldrich. This would have played a role in seeing the increased growth rate as polymer strands of lower and higher molecular weights are also present in the system.



molecular weights of 10.2 kg/mol with poly(vinylpyrrolidone) at 10 kg/mol at 277.15K and 6282 kPa.

Another difference between PVA and PVP is observed when comparing the dissolution phase of the experiment. Figure 21, below, shows a much larger onset of nucleation for PVP as opposed to PVA. This is seen in the figure as methane saturates the liquid but hydrate growth does not begin until much later. In the case of PVA, however, the growth phase begins soon after a high concentration of methane in the liquid phase is achieved (ie. high number of moles consumed by the gas phase in to the liquid phase)



Figure 21: Comparison of the dissolution phase of the experiment of poly(vinyl alcohol) at molecular weights of 10.2 kg/mol with poly(vinylpyrrolidone) at 10 kg/mol at 277.15K and 6282 kPa.

Although dissolution and growth rates were observed to be larger for PVA than PVP, both of these inhibitors showed much lower rates than pure water. This indicates that the poly(vinyl alcohol) synthesized can be used as a kinetic inhibitor. Depending on the situation, poly(vinyl alcohol) can be a substitute to poly(vinylpyrrolidone) considering the much lower costs of production and greater availability of poly(vinyl alcohol).

V. Conclusion

The formation of gas hydrates in gas pipelines is problematic as they may form plugs that block flow. These hydrate plugs become damaging to the pipelines themselves and to downstream equipments such as valves. Due to the high cost of hydrate inhibition using thermodynamic inhibitors, which require large quantities of alcohols or electrolytes (~40 wt%) to thermodynamically disfavor the formation of hydrates, increasing interest is going towards kinetic inhibitors. Kinetic inhibitors are a class of low-dosage hydrate inhibitors that delay the onset of nucleation and slow the growth rate of hydrate crystals. They are generally made of vinyl based polymers which can adsorb onto the crystal surface to inhibit the further formation and growth of these hydrates.

This project set out to determine the effect of the size of poly(vinyl alcohol). Poly(vinyl acetate) was first synthesized using Cobalt Mediated Radical Polymerization and a good control on the size of the polymers was achieved. Polymers of varying molecular weights, from $10^{\text{kg}}/_{\text{mol}}$ to $40^{\text{kg}}/_{\text{mol}}$, were successfully synthesized but high dispersities in the product were observed due to a presumed presence of oxygen. A more aggressive degassing technique, freeze-pump-thaw cycles, was then implemented in order to limit the contact of the reactants with air and further decrease the dispersities.

These polymers, once synthesized, were then converted to poly(vinyl alcohol) using a base hydrolysis reaction in methanol. Poly(vinyl alcohol) with varying sizes, were then dissolved in water at a fixed concentration of 700 ppm in order to undergo hydrate growth experiments.

It was observed that the rate of dissolution of methane in to the liquid phase as well as the methane hydrate growth rate decreased with the addition of the inhibitor. No trend, however, of

the effect of the size of the polymer on these rates was observed. These rates were also seen to be lower than that of poly(vinylpyrrolidone) as a kinetic hydrate inhibitor.

Although dissolution and growth rates were observed to be larger for PVA than PVP, both of these inhibitors showed much lower rates than pure water.

VI. Future Works

As mentioned early, the degree of hydrolysis of poly(vinyl acetate/alcohol) plays a direct role on the solubility of poly(vinyl acetate/alcohol) in water as well as the properties of this polymer. One of the directions that this ongoing research can take is to evaluate the effect of the degree of hydrolysis on the hydrate inhibition potential.

Knowing the properties required in kinetic hydrate inhibitors, polymers can be synthesized to include both hydrophobic and hydrophilic properties in order to increase the inhibition potential of kinetic hydrate inhibitors. PVAc, PVP, and PVCap can be synthesized using the reversible addition-fragmentation chain-transfer (RAFT) polymerization technique. In order to increase the hydrophobicity of these polymers, they can be chain extended with 2-3-4-5-6-pentafluorostyrene to form poly(vinyl acetate/pyrrolidone/caprolactam)-*block*-poly(2-3-4-5-6-pentafluorostyrene). The vinyl end of this polymer can be changed in to its analogous vinyl alcohol to increase its hydrophilicity. By engineering polymers with specific hydrophobic and hydrophilic properties, a great deal of research can be done to examine the effects of those parameters, such as size, hydro(phob/phil)icity, on hydrate inhibition. This can lead to the production of new polymers which may well be efficient enough to compete with thermodynamic inhibitors.

VII. Bibliography

- Anderson, F. E., Prausnitz, J. M. (2004). Inhibition of gas hydrates by methanol, AIChE Journal, Volume 32, Issue 8, pages 1321-1333
- Baardsnes, J.; Jelokhani-Niaraki, M.; Kondejewski, L. H.; et al. (1999). Antifreeze protein from shorthorn sculpin : Identification of the ice-binding surface. Protein Sci. 10(12): 2566-2576
- Braun, D. (2009). Origins and development of initiation of free radical polymerization processes. Int. Jour. Of Polymer Science. Volume 2009, Article ID 893234
- Brewer, P. G. (1999). Direct experiments on the ocean disposal of fossil fuel CO2 . Science , 943-945.
- Caille, J.-R.; Debuigne, A.; Jérôme, R. (2005) Quinone Transfer Radical Polymerization (Qtrp) of Styrene: Catalysis by Different Metal Complexes. Journal of Polymer Science Part A: Polymer Chemistry 43.13 (2005): 2723-33
- Cha, M.; Shin, K.; Seo, Y.; Shin, J.-Y.; Kang, S.-P. (2013). Catastrophic Growth of Gas Hydrates in the Presence of Kinetic Hydrate Inhibitors. Jour. Of Phys. Chem., 117 13988-13995
- Chatti, I. A.-P. (2005). Benefits and drawbacks of clathrate hydrates: a review of their areas of interest. Energy Conversion and Management , 1333-1343.
- Cláudio, P. J. (2008). Modelling of hydrate formation kinetics: State-of-the-art and future directions. Chemical Engineering Science , 2007 2034.
- Crone TJ, T. M. (2010). Magnitude of the 2010 Gulf of Mexico oil leak. Science, 634.
- Davidson DW, E.-D. M. (1978). Natural gas hydrates in northern Canada. 3rd international conference on Permafrost (pp. 938–43). Edmonton: Fuglem MO and AS Judge.
- Debuigne, A., Caille, J.-R.; Detrembleur, C.; Jérome, R. (2005). Effective cobalt mediation of the Radical polymerization of vinyl acetate in suspension. Angewandte Chemie Internation Edition, 44 3439-3442
- Debuigne, A., et al. (2005). Synthesis of Poly(vinyl Acetate) and Poly(vinyl alcohol) Containing Block Copolymers by Combination of Cobalt-Mediated Radical Polymerization and Atrp. Macromolecules 38.23 (2005): 9488-96.
- Debuigne, A.; Warnant, J.; Jérome, R.; et al. (2008) Synthesis of Novel Well-Defined Poly(vinyl Acetate)-B-Poly(Acrylonitrile) and Derivatized Water-Soluble Poly(vinyl alcohol)-B-Poly(Acrylic Acid) Block Copolymers by Cobalt-Mediated Radical Polymerization. Macromolecules 41.7 (2008): 2353-60.

- Englezos, P. K. (1987). Kinetics of formation of methane and ethane gas hydrates. Chemical Engineering Science, 2647–2658.
- Englezos, P. K. (1993). Clathrate Hydrates. Industrial and Engineering Chemistry Research, 1251–1274.
- Fischer, Hanns (2001). The Persistent Radical Effect: A Principle for Selective Radical Reactions and Living Radical Polymerization. Chem. Rev. 101 (12), pp 3581-3610
- Freer, E. M. (2001). Methane hydrate film growth kinetics. Fluid Phase Equilibria , 65–75.
- Goodsell, D. S. (2009). Molecule of the Month: Antifreeze Proteins. Royal Chemistry Society Protein Data Bank. 10.2210/rcsb_pdb/mom_2009_12
- Hammerschmidt, E. G. (1934). Formation of Gas Hydrates in Natural Gas Transmission Lines . Industrial and Engineering Chemistry , 851-855.
- Karaaslam, U. & Parlaktuna, M. (2002). Kinetic inhibition of methane hydrate by polymers. Fuel Chemistry Division Preprints, 47(1), 355-358
- Kashchiev, D., Firoozabadi, A. (2002). Induction time in crystallization of gas hydrates. Jour. Of Cryst. Growth. 250 (2003) 499-515
- King, H.E., Hutter, J.L., Lin, M.Y., Sun, T., (2000). Polymer conformations of gas-hydrate kinetic inhibitors: a small-angle neutron scattering study. Journal of Chemical Physics 112 (5), 2523–2532
- Koh, C. S. (2002). Towards a fundamental understanding of natural gas hydrates. Royal Society of Chemistry, 31 157-167
- Koh, C. S. (2011). Fundamentals and applications of gas hydrates. Annual Review of Chemical and Biomolecular Engineering , 237-257.
- Lokshin, K. A., Y. Zhao, D. He, W. L. Mao, H.-K. Mao, R. J. Hemley et al. (2004). Structure and Dynamics of Hydrogen Molecules in the Novel Clathrate Hydrate by High Pressure Neutron Diffraction. Phys. Rev. Lett. 93 (12): 125503-1
- Makogon, Y. F. (1966). Specialties of Exploration of the Natural Gas Hydrate Fields in Permafrost Conditions. Natural Gas Industry .
- Maria, S.; et al. (2007). Effect of Electron Donors on the Radical Polymerization of vinyl Acetate Mediated by [Co(Acac)2]: Degenerative Transfer Versus Reversible Homolytic Cleavage of an Organocobalt(Iii) Complex. Chemistry A European Journal 13.9 (2007): 2480-92.
- Matyjaszewski, K.; Bombalski, L.; Jakubowski, W.; et al. (2005). Atom Transfer Radical Polymerization in the presence of a reducing agent. WO Patent 2005087819, 96 pp.

- Mori, Y. H. (2001). Estimating the thickness of hydrate films from their lateral growth rates: application of a simplified heat transfer model. The Journal of Crystal Growth, 206–212.
- Perrin, A.; Musa, O. M.; Steed, J. W. (1996). The chemistry of low dosage clathrate hydrate inhibitors. Royal Society of Chemistry, 42 1996-2015
- Piette, Y.; Debuigne, A.; Jérome, C. (2012). Cobalt-mediated radical (co)polymerization of vinyl chloride and vinyl acetate. Polymer Chemistry. 3(10), 2880-2891
- Rojey, A. (1997). Natural Gas: Production, Processing, Transport. New York: Editions OPHRYS.
- Sa, J.-H.; Kwak, G.-H.; Lee, B. R.; Park, D.-H.; Han, K.; Lee, K.-H. (2013). Hydrophobic amino acids as a new class of kinetic inhibitors for gas hydrate formation. Nature, Article Number: 2428
- Semsarzadeh, M. A.; Amiri, S. (2011). Controlled free radical polymerization of vinyl acetate with cobalt acetoacetonate. J. Chem. Sci. Vol 124. No. 2. 521-527
- Shirazi, A.; Goff, H. M. (1982). Carbon-13 and proton NMR spectroscopy of four-and fivecoordinate cobalt(II) porphyrins: analysis of NMR isotropic shift. Inorganic Chemistry, 21(9) 3420-3425
- Sloan, E. D. (1995). Fluid flow of water clathrates within polyvinylpyrrolidone. US Patent 5420370 A
- Sloan, E. D. (1998). Gas Hydrates: Review of Physical/Chemical Properties. Energy & Fuels, 191-196.
- Sloan, E. D., & Koh, C. (2008). Clathrate Hydrates of Natural Gases: Third Edition. New York: Taylor and Francis Group.
- Suess, E., & Bohrmann G, G. J. (1999). Flammable Ice. Scientific American, 76-83.
- Sun, C. Y. (2010). Studies on hydrate film growth. Annual Reports on the Progress of Chemistry, 77–100.
- Wayland, B. B., et al. (1994). Living Radical Polymerization of Acrylates by Organocobalt Porphyrin Complexes. Journal of the American Chemical Society 116.17 (1994): 7943-44.

Zumdahl, S. S.; Zumdahl, S. A. (2007). Chemistry. ISBN-13: 978-0618528448