THESIS

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Ice and hydrate adhesion of Poly(N-vinylcaprolactam)

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1 Abstract

Hydrates are crystalline structures composed of water which contain a high concentration of trapped gas. They form naturally at high pressures (1-10 MPa) and low temperatures (T <0 °C). Hydrates have many different applications such as energy storage, carbon sequestration and energy extraction. However, they can also be problematic, such as in the case of the oil industry where they are known to form under the right conditions in pipelines, resulting in plugging and cessation of production. Hydrate inhibitors have been largely studied and applied as a way to shift the thermodynamic conditions of hydrate formation to even harsher levels, which is a costly solution. Heterogenous nucleation dictates hydrate formation in pipelines. Therefore, a viable alternative is to coat pipeline surfaces with a material that offers little hydrate adhesion. Poly(N-vinylcaprolactam) (pVCap), a hydrate inhibitor, was synthesized by reversible additionfragmentation chain-transfer polymerization (RAFT) polymerization and then tested for its ice and hydrate adhesion. PVCap was successfully synthesized at various different molecular weights. Gel permeation chromatography (GPC) data was difficult to obtain since the polymer was not soluble in the eluent. Nuclear magnetic resonance (NMR) was performed in order to obtain molecular weight data. For a 32.7 kg/mol surface, the adhesion strength was measured as the shear stress required to dislodge the column of ice from the surface which was determined as 508 kPa and 532 kPa for ice and hydrates spun at 2000 rpm respectively. Relation between molecular weight, spin speed, weight % and surface roughness with respect to shear stress was difficult to establish due to large data variations. These were attributed to the ice formation during the procedure which forms random imperfect crystal structures, the bond broken between ice and the surface which was at times an ice-ice break, the point of impact and the freezing time. The outlined results will give a better understanding of the effect of different parameters on polymer surfaces in the quest for an adhesive surface to counteract ice and hydrate adhesion.

2 Résumé

Les hydrates sont des structures cristallines composées d'eau qui contiennent une large partie de gaz piégée. Ils forment naturellement a une haute pression (1-10 MPa) et base température (T< 0° C). Les hydrates ont plusieurs différentes applications tel que le stockage d'énergie et l'extraction d'énergie. Malheureusement, ils peuvent aussi être endommageant comme dans l'industrie pétrolière où ils forment, résultant dans le bouchage du pipeline. Les inhibiteurs d'hydrates ont été largement étudiés et appliqués comme un moyen de changer les conditions thermodynamiques de formation d'hydrates pour les rendre moins favorables. La nucléation hétérogène dicte leur formation dans les pipelines. Donc, une alternative viable est de construire des tuyaux qui ont une surface offrant une bonne résistance contre la formation d'hydrates. Poly(N-vinylcaprolactam) (pVCap), un inhibiteur d'hydrates, a été synthétisé par la polymérisation réversible additionfragmentation chain-transfer polymerization (RAFT) et ensuite testé pour son adhésion vers la glace et les hydrates. PVCap a été synthétisé pour obtenir plusieurs différentes masses moléculaires. Les résultats du gel permeation chromatography (GPC) ont été difficiles à obtenir à cause du polymer qui n était pas dissoluble dans le solvant. La résonance magnétique nucléaire (NMR) a été performée pour obtenir les masses moléculaires. Pour une surface de 32.7 kg/mol la force d'adhésion a été mesurée comme le shear stress pour bouger le bloc de glace de la surface qui était de 508 kPa et 532 kPa pour la glace et les hydrates à 2000 rpm respectivement. La relation entre la masse molaire, la vélocité de rotation, le pourcentage de poids et la rugosité de la surface envers le shear stress été difficile à établir à cause de la variation des résultats. Ceux-ci étaient attribués a la formation de glace qui forme au hasard en une structure de Crystal imparfait, la liaison entre la glace et la surface qui quand brisée était quelque fois entre la glace et non la surface et la glace, le point d'impact et le temps de gel. Les résultats soulignés vont donner une meilleure compréhension de l'effet de différents paramètres sur la surface des polymères dans le but d'obtenir des surfaces adhésives pour contrer la formation de la glace et les hydrates.

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4 Introduction

The dawn of the 21st century has seen many scientific advances that have resulted in the development of diverse sources of energy which are promising alternatives to fossil fuels. While always present, it has always been a challenge to efficiently tap these unlimited resources such as solar, wind and hydro. This is also the case for a resource of great potential, namely gas hydrates, also called gas clathrates. Gas hydrates are crystalline; a form of water that contains large amounts of gas. Water forms a rigid lattice of cages, where most of the cages contain a molecule of natural gas, more commonly methane. The formation of gas hydrates is dictated by a range of high pressures and low temperatures.

It is estimated that more than 10¹⁹g of methane is currently stored in gas hydrates [Kvenvolden, 1993]. Commercial production of just 15% of this gas would provide the world the energy it requires for the next 200 years at the current level of energy consumption [Makogon et al., 2007]. To tap this vast resource, much effort has been expended academically and industrially. Geological surveys have been conducted around the world mapping possible reserves of natural gas hydrates. However, the extraction of this resource is not without risks. Any destabilization during the extraction process could release large amounts of greenhouse gas which could further contribute to global warming.

The discovery of gas-hydrates dates back to 1778 when Priestly bubbled SO_2 through 0°C water at atmospheric pressure [Makogon et al., 2007]. At that time, he did not describe the crystals as hydrates. It was in 1811 that Davy obtained similar crystals of aqueous chlorine clathrates, which he named hydrates of gas[Makogon et al., 2007]. Interest in the field was only ignited more than a century later in the 1930's when Hammerschmidt noticed the plugging of gas pipes during wintertime by the formation of solids. He was able to prove through laboratory testing that the solids consisted not of ice, but of hydrates. Thereafter, extensive research began on the prevention of gas hydrates in pipes. The final spark in the field of hydrates took place in the 1960's when the Markhinskaya well drilled in 1963 in Yakutiya to a depth of 1800m revealed a section of rock at 0°C temperature at the 1450m depth, with permafrost ending at 1200m in depth [Makogon et al., 2007]. After experimental tests, hydrates were experimentally formed in a laboratory in porous media and in real core samples [Makogon, 1966]. These results were conclusive that the natural occurrence of stable gas-hydrates in rock layers was possible.

Since then, much research has been focused on the study of gas hydrates. One of the significant impacts of hydrates is their natural formation in pipelines under the proper conditions, which has resulted in the blockage of many pipelines. Current methods of dealing with hydrate formation is through the addition of chemicals which shift the equilibrium hydrate formation to higher pressures and lower temperatures. Kinetic inhibitors are also added which slow down the formation of hydrates. Moreover, in some cases, studies have been focusing on insulating the pipe or providing heat to the pipeline walls. The costs associated with these methods and with lost oil and gas production due to hydrate plugging can run into billions of dollars(more than \$200 M USD is spent annually on hydrate inhibitors alone) [Smith, 2012]. Due to extensive energy requirements and high costs, research has shifted to the modification of surfaces which can ultimately reduce hydrate adhesion to surfaces. If successful, such a technique can significantly lower the operating costs of pipelines.

5 Background

5.1 Thermodynamics of gas hydrates

A clear understanding of the thermodynamic properties of gas hydrates is critical in all cases such as determining the temperature and pressure that would favour hydrate formation in a pipeline or knowing the necessary conditions required to dissociate a hydrate plug in a pipeline or a natural gas reservoir. Gas hydrate stability depends on temperature, pressure, gas composition, and condensed phase composition [Koh et al., 2011]. Figure 1 demonstrates the range of conditions (T,P) for hydrate stability and the shift of stable region due to the addition of chemical inhibitors such as methanol. Adding 30% methanol shifts the range of hydrate formation to the left, therefore avoiding the possibility of hydrate plugging in pipelines. This method of preventing hydrate formation is also known as gas hydrate avoidance [Koh et al., 2011]. Gas hydrate thermodynamic stability depends on the gas composition. A pure methane gas hydrate would form at a higher pressure than a mix of methane+propane at constant temperature [Koh et al., 2011]. However, due to the high costs related to these time-independent properties, the focus is shifting towards manipulating the time-dependant properties of hydrates instead.



Figure 1 – Methane gas hydrate stability over a range of pressure and temperatures. The addition of distinct amount of methanol shits the hydrate region further to the left, resulting in higher pressures and lower temperatures required for hydrate formation (adapted from [Koh et al., 2011]).

5.2 Hydrate inhibitors

There are 3 classes of hydrate inhibitors. The first and most widely used type of hydrate inhibitors are of the thermodynamic class such as mono-ethylene glycol. They prevent hydrate formation by shifting the hydrate formation curve to even higher pressures and lower temperatures [Akhfash et al.]. Unfortunately, a large concentration of thermodynamic inhibitors are required in order to be effective, up to 50 wt%. For this reason, current research is being focused on low dosage hydrate inhibitors (LDHI's) such as anti-agglomerates which allow hydrates to form but prevent them from clumping together into larger hydrates, or kinetic inhibitors which delay the onset of crystal growth. These species can work at a composition as low as 2 wt%. Even if thermodynamic inhibitors do get replaced by these LDHI's, there will still be an operational cost associated with their use. For further economic cost reduction, the approach that is now being studied is concerned with the enclosing material of the pipe. The reason for this approach is best understood by studying hydrate formation, which occurs through nucleation.

5.3 Nucleation

The classical theory of nucleation is best understood by the water freezing process. When phase change occurs from liquid water to ice, it does not happen instantaneously. Rather, it begins with the formation of numerous small particles of the new phase until it grows and spreads until the transformation has reached its end phase. The transformation of a liquid droplet of water into ice has been largely studied and is described by the term nucleation. There are two types of nucleation, homogenous and heterogenous. By understanding both concepts, one can better understand the nucleation process of hydrates.

5.3.1 Homogenous nucleation

The discussion of homogenous nucleation requires an understanding of the Gibbs free energy. This parameter takes into account the change in internal energy of the system (Δ H) and the change in entropy (Δ S). A transformation will occur spontaneously if Δ G is negative. In order to understand the underlying theory, a simplistic model can be used. Assuming that the liquid is homogenous, nucleation occurs with particles grouping into clusters similar to that of the final phase. Furthermore, these particles can be assumed to be spherical with radius r . From this, two contributions arise to the total free energy change accompanying a solid phase transformation. The first is the energy difference between the solid and the liquid phase, ΔG_{ν} . Its value is negative if the temperature is below the equilibrium solidification temperature and the magnitude of its contribution is the product of ΔG_{ν} and the volume of the spherical nucleus (i.e $\frac{4}{3}\pi r^3$) [Callister and Rethwisch, 2009]. The total free energy is the sum of these terms and comes out to :

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_\nu + 4\pi r^2 \gamma \tag{1}$$

This equation can be plotted in order to gain a better understanding of the theory of nucleation. As seen in figure 2, the sum of the two terms reaches a maximum ΔG before decreasing. This can also be defined as the activation energy required for the formation of a stable nucleus for a radius r^{*}. Expressions for the activation energy and the critical radius can be obtained by differentiating ΔG with respect to r and setting the equation to 0. By doing so, we obtain the following expressions for r^{*} and ΔG^* :

$$r^* = \frac{-2\gamma}{\Delta G_{\nu}} \tag{2}$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_\nu)^2} \tag{3}$$



Figure 2 – Schematic plot of free energy as a function of nucleus radius on which is shown the critical free energy change (ΔG^*) and the critical nucleus radius (r^{*}) (adapted from [Callister and Rethwisch, 2009]).

Where ΔG_{ν} can be defined by the following expression:

$$\Delta G_{\nu} = \frac{\Delta H_f(T_m - T)}{T_m} \tag{4}$$

Replacing ΔG_{ν} back into r^{*} and ΔG^*

$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right) \left(\frac{1}{T_m - T}\right) \tag{5}$$

$$\Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right) \frac{1}{(T_m - T)^2} \tag{6}$$

From equations 5 and 6, it can be noticed that the critical radius and the activation free energy decreases as temperature T decreases. The difference T_m - T is known as the degree of supercooling ΔT . As the temperature T decreases more and more below the equilibrium solidification temperature T_m , nucleation occurs more readily. Thus, an appreciable nucleation rate will only occur after a certain degree of supercooling, and for homogenous systems, this can be on the order of several hundred degrees of Kelvin [Callister and Rethwisch, 2009].

5.3.2 Heterogenous nucleation

Even though the degree of supercooling for nucleation is of the order of several hundreds of degrees, nucleation occurs at just a few degrees of supercooling. This observation is due to the fact that the activation free energy is significantly lowered when particles form on pre-existing surfaces because the surface free energy is reduced. Therefore, it is easier for nucleation to occur on surfaces and due to this difference, it is termed heterogenous nucleation.



Surface or interface

Figure 3 – Nucleation of a solid from a liquid. The solid-surface (γ_{SI}) , solid-liquid (γ_{SL}) , and liquidsurface (γ_{IL}) , interfacial energies are represented by vectors. The wetting angle (θ) is also shown (adapted from [Callister and Rethwisch, 2009]).

The explanation for this comes by considering a water droplet on a surface. It is assumed that this particle spreads out and covers the surface in both phases (liquid and solid), as shown in figure 3. Taking a surface tension balance in the plane of the flat surface leads to:

$$\gamma_{IL} = \gamma_{SI} + \gamma_{SL} \cos\theta \tag{7}$$

From equation 7, r^* and ΔG^* can be derived for heterogenous nucleation as:

$$r^* = -\frac{2\gamma_{SL}}{\Delta G_{\nu}} \tag{8}$$

$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3}{3\Delta G_{\nu}^2}\right) S(\theta) \tag{9}$$



Figure 4 – Schematic of free-energy as a function of nucleus-radius on which are represented curves for both homogenous and heterogenous nucleation. Critical free energies and critical radius are also shown (adapted from [Callister and Rethwisch, 2009]).

The activation free energy between heterogenous and homogenous nucleation can now be compared, as shown in figure 4. Simply due to the availability of surfaces, heterogenous nucleation occurs rather than homogenous nucleation in most cases due to the lower activation free energy required for heterogenous nucleation. Therefore, when considering the nucleation of droplets on surfaces, nucleation will refer to the heterogenous rather than the homogenous process.

5.3.3 Hydrate nucleation

For most industries where hydrate inhibition is preferred, it is important to understand hydrate nucleation since it helps to explain the time associated with hydrate formation and the subsequent growth rate. Hydrate nucleation is a microscopic phenomenon involving tens of thousands of molecules and is difficult to observe experimentally [Mullin, 1993]. Measurements of hydrate nucleation time have indicated that nucleation is a stochastic process [Koh et al., 2011]. Current hypotheses for hydrate nucleation are based upon the better-known phenomena of water freezing [Sloan and Koh, 2008], as previously explained. The first phase of hydrate formation is the induction time. It is the time elapsed until the appearance of a detectable volume of hydrate phase, or equivalently, until a consumption of a detectable number of moles of hydrate gas [Sloan and Koh, 2008]. During the induction period, the temperature and pressure conditions are within the hydrate stable region. However, hydrates do not form within this period because of metastability (i.e. ability of a non-equilibrium state to persist for a longer period of time) [Sloan and Koh, 2008]. The growth period quickly follows the induction phase, where hydrate growth occurs and gas is being concentrated in the hydrate cages. As the water is consumed by hydrate formation, the slope of the gas consumption trace eventually decreases with time. Since hydrate nucleation occurs heterogeneously, surfaces that prevent hydrate adhesion will play a key role in their formation inhibition.

5.4 Hydrophobicity

While heterogenous nucleation is likely to occur under favourable conditions, some surfaces offer a high or low adhesion to water. The ability of a surface to form a high adhesion bond with water is termed hydrophilic whereas a surface that has a tendency to repel water is known as hydrophobic. The focus of this study is inclined towards hydrophobic rather than hydrophilic structures. Hence, the discussion will be elaborated keeping this fact in mind. The concept of hydrophobic structures has been extensively studied by drawing inspiration from various plants found in nature. The most quoted example of a hydrophobic surface that stems from plants is that of the lotus leaf. The lotus leave shows an outstanding water repellency on its upper side which is more robust and less sensitive to mechanical damage due to its combination of micro- and nano-structures with optimized geometry and the unique chemical composition of the epicuticular waxes [Ensikat et al., 2011]. A standard tool for the measurement of water repellency is the measurement of the static contact angle by the 'sessile drop' method. It is the angle θ as depicted in figure 3. The contact angle is an indication of the wetting state of the surface in question. Among hydrophobic surfaces, a special class of superhydrophobic surfaces exist which have a contact angle greater than 150°.

5.4.1 Wetting States

When a small water droplet encounters a solid surface, it forms a sphere of water which forms a discrete angle with the surface. The shape of the droplet is not reproducible and on most surfaces, the contact angle will vary by more than 20 °C [G. McHale et al., 2004]. The droplet can wet the surface either homogeneously (Wenzel state), heterogeneously (Cassie-Baxter state), or anywhere in between the two extremes. The Cassie-Baxter and Wenzel state, as shown in figures 5 and 6, play an important role in the hydrophobicity of the surface. The Cassie-Baxter state allows for air pockets to exist thereby reducing the water-solid interface. On such a rough "low energy" surface, the water gains very little energy through desorption to compensate for any enlargement of its surface. In this situation, spreading does not occur, the water forms a spherical droplet, and the contact angle of the droplet depends almost entirely on the surface tension of the water [Barthlott and Neinhuis, 1996]. This in turn plays an important role in reducing the adhesion strength of the liquid with respect to the surface. Contrary to the Cassie-Baxter state, a Wenzel state occurs when water has occupied all the available space that exists due to surface roughness, allowing for no possibility of an solid-air-water interface. In this case, the adhesion strength between the surface and water is greater, and thus the ability of the surface to repel water is reduced. Naturally, a Cassie-Baxter state is desired for hydrophobic properties over the Wenzel regime.



Figure 5 – The Wenzel regime



Figure 6 – The Cassie-Baxter regime

5.5 Icephobicity

Due to the fact that all three common hydrate structures consist of 85% water on a molecular basis, many of the hydrate mechanical properties resemble those of ice [Sloan and Koh, 2008]. Thus, when tests are conducted in order to determine the adhesion of a surface with respect to hydrates, a good starting point is to test it with respect to ice. Icephobicity is described as the ability of a surface to repel ice or to prevent ice formation due to the structure of the surface. However, the term icephobic is considered broad. Some define icephobicity as a low adhesion strength between ice and a surface. Kulinich and Farzaneh, 2009. More commonly, it is utilized as the reduced shear adhesion stress [Makkonen, 2012]. Some also use reduced normal adhesion strength [Ruan et al., 2013]. There are scholars who define icephobicity as the ability to delay and prevent ice nucleation and formation on surfaces induced by either pouring a supercooled water on the substrate or lowering the substrate temperature after a droplet is placed on the surface [Tourkine et al., 2009]. Such abilities depend on the whether the supercooled water can freeze on the surface and the heterogenous time delay of nucleation associated with the droplet. The ability of a surface to repel or rebound water as it impacts the surface has also been suggested as a characteristic of icephobicity. All these definitions differ with respect to each other, while at the same time being important characteristics of the term icephobic.

The type of surfaces is not the only variable to consider when dealing with icephobicity. The type of snow also plays a role. Different situations result in different forms of snow, such as rime, snow, glaze, frost and ice. The full description of each type of has been compiled in table ??.

Definitions of various water-based solid-phase materials that can be formed from liquid or gaseous water by changes in temperature and/or pressure [Sojoudi et al., 2016].

Type of water phase	Description			
Frost	Spare dendritic crystal structures that nucleate from the vapour phase via			
	desublimation or condensation followed by freezing.			
Glaze	Clear, dense and hard ice; forms from freezing rain of large droplets with			
	diameters ranging from 70um to a few millimetres.			
Rime	White, brittle, and feather-like ice that forms because of freezing of supercooled			
	droplets with diameters in the range of 5 - 70 um originating from clouds or			
	fog.			
Snow	A mixture of ice and water. Snow is 'dry' when the air temperature is blow			
	-1 or -2 °C, but at temperatures closer to freezing point a thin layer of water			
	covers ice, creating wet ice with properties between ice and water.			
Ice	A brittle frozen state of water which can appear transparent or a more or less			
	opaque bluish-white colour depending on the presence of impurities such as			
	particles of soil or bubbles of air.			

Based on the different types of definitions for icephobicity, and the different forms of snow, a great deal of characteristics are required for a surface for it to be truly called icephobic. To compile all the observable characteristics of surfaces and snow types into one icephobic material is a significant challenge, which has not been overcome to date. Therefore, when designing a surface with icephobic characteristics, it is vital to establish beforehand the purpose of the surface in question. For example, an airplane flying at a high altitude is subject to rime which originates from clouds. Once it reaches the ground, it also gets exposed to snow depending on the temperature, or ice if allowed to form. Such a surface must be able to counteract all these different types of water-based solid-phase materials in order to be useful in the industry of aviation. Then, it must also be determined the type of icephobic material desired such as one with a low adhesion strength surface, or one that has a longer delay time of heterogenous nucleation, and so on.

To study all these variables and to form a single surface counteracting all is out of the scope of this project. In terms of icephobicity, the focus will be on a surface which provides low adhesion strength with respect to ice. However, some surfaces exhibit strong adhesion strengths as well. These are also desirable in certain fields and either result is acceptable. Based on the constructed material, different tests can be performed in order to determine the type of water-based solid-phase ice that is counteracted.

5.6 Hydrate inhibitor synthesis

Out of the many different kinetic inhibitors available, one of the most promising ones is Nvinylcaprolactam (VCap) [R. Anderson, 2011, Seo et al., 2017]. Kinetic hydrate inhibitors work by extending the normal induction time of hydrates and are therefore termed nucleation inhibitors. Experimental results have found that pVCap greatly extends the induction time of hydrates with good repeatability, keeping in mind the stochastic nature of hydrate formation [R. Anderson, 2011]. Poly(N-vinylcaprolactam) (pVCap) is a non-ionic water-soluble polymer which has been used as a kinetic hydrate inhibitor [Abay et al.]. It precipitates from solution on heating [Makhaeva et al., 1996] and has a lower critical solution temperature (LCST) of 32°C. Extensive research has been performed on this hydrate inhibitor [Lou et al., 2012, Seo et al., 2017, R. Anderson, 2011, O'Reilly et al., 2011]. However, to the best of our knowledge, no research has been directed towards using it as a surface. One of the challenges with studying this as a polymer surface is the lack of commercial availability. However, it can easily be synthesized via different synthetic pathways. Many research papers are directed towards its synthesis by various means, such as reversible addition-fragmentation chain-transfer polymerization (RAFT) using different chain transfer agents (CTA's) in bulk or using different solvents [Massimo Benaglia[†] and Thang, 2009] [Góis et al., 2016] [Wan et al., 2008] and free radical polymerization [Cortez-Lemus and Licea-Claverie, 2016].

5.7 Reversible addition-fragmentation chain-transfer polymerization (RAFT)

Many different polymerization techniques are available for the synthesis of pVCap. The focus of this thesis will be on RAFT polymerization. Conventional radical polymerization is initiated by a suitable initiator which generates free radicals that adds on to monomer units, thereby growing the chain. The downside of such a technique is the limited control over the chains resulting in a high dispersity, which is a measure of the breadth of the molecular weight distribution. The difference between radical polymerization and RAFT is the addition of a RAFT agent, which adds a reversible mediating step, as seen in figure 7, providing control over the radicals that limits the probability of irreversible chain termination reactions, which causes inactive chain ends and broad molecular weight distributions. CSIRO, the group that invented RAFT polymerizations, has developed a large class of RAFT agents. The several different classes of these are necessary, as not all monomers are compatible with one singular RAFT agent, with there being no such thing as a universal RAFT agent [Massimo Benaglia[†] and Thang, 2009]. The focus of this thesis is on the 2-Cyanopropan-2-yl N-methyl-N-(pyridin-4-yl)carbamodithioate RAFT agent and its effectiveness at controlling N-vinylcaprolactam polymerization reactions. This specific RAFT agent was chosen as it is a carbamodithicate which offers good control over less activated monomers (LAMS) which include monomers with a double bond that bears a saturated carbon atom or is conjugated to a lone pair of oxygen or nitrogen (e.g. NVP) [Stace et al., 2015]. Moreover, to the best of our knowledge, pVCap has not yet been synthesized using this RAFT agent, which is one of the

objectives of this study.

i Initiation Initiator \longrightarrow I^{*} I^{*} + M $\xrightarrow{k_i}$ P^{*}_m

ii Initial equilibrium



iii Reinitiation

$$R^{\cdot} + M \xrightarrow{k_{\text{re-in}}} P_1^{\cdot} \xrightarrow{M} P_n^{\cdot}$$

iv Main equilibrium

$$P_{n}^{*} + \overset{S}{\underset{Z}{\longrightarrow}} P_{m} \xrightarrow{k_{\beta}} P_{n}^{*} \overset{S}{\underset{Z}{\longrightarrow}} P_{m} \xrightarrow{k_{\beta}} P_{n}^{*} \overset{S}{\underset{Z}{\longrightarrow}} P_{m} \xrightarrow{k_{\beta}} P_{n}^{*} \overset{S}{\underset{Z}{\longrightarrow}} P_{m}^{*}$$

v Termination

Figure 7 – General accepted RAFT polymerization reaction mechanism. After the initiation step, which is similar to radical polymerization, the radical reversibly adds on the chain transfer agent (1) to form an intermediate radical (2) which has the ability to fragment and liberate a reinitiating group (3). The new radical can then react with the monomer to reinitiate the reaction. This rapid establishment of addition-fragmentation equilibrium allows control over the molecular weight and molecular weight distribution [Semsarilar and Perrier, 2010].

5.8 Hydrate adhesion

Hydrates can be made by cooling a solution of tetrahydrofuran and water. This combination allows to test the surface for hydrophobicity in a relatively simple manner using the same apparatus as used for ice adhesion. An important factor which can be ignored for ice adhesion is the relative humidity of the room as the solution that will be used to form hydrates is a mixture of THF and water. The relative humidity will have an effect on the concentration of this solution, thereby affecting the hydrate structure.

6 Experimental Section

6.1 Materials

N-vinylcaprolactam (Aldrich, 98%), the RAFT agent 2-Cyanopropan-2-yl-N-methyl-N-(pyridin-4yl)carbamodithioate (Aldrich, HPLC, 97%), and solvents p-xylene (Fischer, \geq 98%), 1,4-dioxane (Fischer, \geq 98%), Tetrahydrofuran(THF, Fischer, \geq 99.9%), chloroform-D (*CDCl*₃, Cambridge Isotopes, 99.8%), toluene (Fischer, \geq 99.5%) were used as received. The initiator 2,2'-Azobis(2methylpropionitrile) (AIBN, Aldrich, 98%) was recrystallized in methanol. Stainless steel 316 12" by 18", 0.03" thick was purchased from McMaster-Carr and cut into 1" by 1.45" pieces to be used as substrate.

6.1.1 Polymer synthesis general procedure

A solution, as described in table 2, containing VCap, RAFT agent, AIBN and solvent was freezepump thawed in order to remove oxygen. This process was carried out three times before the solution was used for the polymer reaction in a setup as shown in figure 8. This synthesis consists of a 25mL 3-neck round bottom flask equipped with a magnetic stir bar, sitting on top of a heating mantle and connected to a condenser capped with a rubber septum which is pierced with a needle to relieve pressure. A chiller provides the necessary cooling water of 50 vol % ethylene glycol/water mixture circulating at 4°C to prevent the evaporation of the monomer and the solvent. A light nitrogen purge was maintained during the entirety of the reaction. The temperature is measured by a temperature well connected to a thermocouple which is inserted in the reactor. The reaction was heated at a rate of 5 - 7 °C min^{-1} and the start of the reaction was recorded when the temperature reached 70 °C. The reaction progress was tracked by taking 0.1 mL of solution at specific time intervals, and the samples were further analyzed by GPC and NMR as described in the subsequent sections. The reaction was terminated when the solution was extremely viscous. It was then purified by pouring it in cold diethyl ether and allowing it to settle after which the liquid was decanted. The remaining polymer was then dried in a vacuum oven at 30°C for 24h.



Figure 8 – Polymerization reactions setup which consists of: (1) Nitrogen inlet, (2) heating mantle, (3) Needle for pressure relief, (4) distillation column, (5) Thermocouple and (6) 3-neck round bottom flask.

6.1.2 Spincoating

The substate which was used for spincoating was stainless steel 316. These were machine-cut into 1" by 1.45" pieces and gently wiped with KIMWIPES (Kimberly-Clark) before being used for spin coating. The purified polymers were dissolved in toluene at specified solid wt% and spin coated onto stainless steel 316 substrates using a WS-400-6NPP-LITE Laurell spin coater at varying

speeds, as specified.

6.2 Measurements

6.2.1 Nuclear Magnetic Resonance (NMR)

¹H NMR was recorded on a Varian Mercury 300 with ATB probe and SMS-100 sample changer at 300 MHz. Deuterated chloroform was used as solvent. The chemical shifts reported are all relative to the residual solvent peak.

6.2.2 Gel Permeation Chromatography (GPC)

The number average molecular weight \overline{M}_n , and dispersity, \overline{D} were measured by GPC (Waters Breeze). The GPC is equipped with differential refractive index (RI 2414) detector as well as a guard column and three Waters Styragel HR columns, which have molecular weight measurement ranges of 0.1 - 5, 0.5 - 20 and 5 - 500 kg mol⁻¹. HPLC grade THF at 40°C was used as the mobile phase with a flow rate of 0.3 mL min⁻¹. The GPC was calibrated using poly(methyl methacrylate) (PMMA) standards in THF at 40 °C.

6.2.3 Ice adhesion apparatus

A custom ice adhesion apparatus was used as depicted in figure 8. The specimens were clamped to an air-cooled thermoelectric Pelter cooling unit (CP-200TT, TE Technology Inc.) whose temperature was controlled by a bidirectional temperature controller (TC-36-25 RS232, TE Technology Inc.). A device driver and graphical user interface allows communication with the temperature controller.Two thermistors (MP-3193, TE Technology Inc.) connected directly to the controller, indicated as TT2 and TT3 in figure 4, monitored the cold and hot sides of the thermoelectric unit, respectively. The temperature of the cold side (TT2) was set to -12 °C for all experiments and the temperature of the mounted specimen was monitored using a 1/16'' T-type thermocouple (TJ36 Series, OMEGA) attached to a reference sample of the same material (copper or stainless steel 314). The thermoelectric unit was placed in a dedicated aluminum frame (80/20 Inc.) and the upper portion of the apparatus was insulated with polystyrene foam insulation (McMaster-Carr) [Ling et al., 2016].

Each experiment was carried out by placing a 2.4 mm thick borosilicate glass tube (Pegasus Industrial Specialties Inc.) with an outer diameter of 15.9 mm and a height of 50 mm was placed on the specimen to be tested. The Pelletier plate was cooled to -12 °C, after which 0.5mL of cooled RO water was pipetted in the glass tube and allowed to freeze. An additional 1.5mL was pipetted over the frozen layer to a total volume of 2.0 mL. Water was poured in stages in order to prevent leakage from the bottom of the glass tube due to hydrostatic pressure. This liquid was allowed to freeze over 30 minutes. The adhesion strength was then evaluated as the shear stress required to dislodge the column of ice in contact with the surface. A remote force tensor (ZPS-DPU-22, Imada Inc.) mounted on a linear translation stage was driven into the ice column at a speed of 5 mm/s. In order to minimize torque, the height of the point of impact was adjusted as to remain no more than 1.5 mm above the sample. The ice adhesion stress, τ_{ice} , was then calculated by taking the measured peak force required to dislodge the ice normalized over the total surface area imposed by the glass tube. Upon completion of the experiment, the sample was brought back to room temperature, dried and replaced by the next sample. A total of twelve samples were used for each data point and the error was computed accordingly.



Figure 9 – Ice adhesion measurement apparatus. (1) Thermoelectric Peltier cooling unit, (2) digital force gauge, (3) motorized linear translation stage, (4) remote force sensor, (5) water/ice column, (6) glass tube, (7) test specimen, (8) aluminum base plate, (9) aluminum clamp, and (10) reference sample for temperature monitoring. TT = temperature transmitter, and PI = proportional-integral controller [Ling et al., 2016]

6.2.4 Surface Roughness

Surface roughness of spincoated polymer surfaces were measured using the Bruker DektakXT profilometer. In order to prevent scratches to the sample, roughness was measured by assuming that the sample is fragile. For each roughness data point, nine roughness measurements on different spin coated surfaces were performed. They were then averaged out to obtain a surface roughness measurement.

7 Results & Discussion

7.1 Reaction mechanics and polymer characterization

The different polymerization runs are summarized in table 2. One of the key differences noticed by using this RAFT agent compared to other attempts at Vcap polymerization is the reaction time. Reactions time for Vcap mediated by xanthate or dithiocarbamate have run from 16 to 48 hours resulting in a yield of 50 % [Wan et al., 2008]. In this case, after 1h to 1h30 minutes time, the reaction mixture became too viscous and subsequent polymerization was not possible which signalled the end of the reaction. There are several different reasons which could explain this difference. The RAFT agent used in this case was different from the one used in previous experiments, which has a different leaving group resulting in a different level of control over the radicals. Moreover, the reaction temperature used in previous experiments was 60 °C whereas in this case 70 °C was used. A lower temperature results in a longer reaction time. The polymerization was also performed in bulk, whereas in this case toluene was used throughout. One of the possible reasons for such a long reaction time that Wan, et al obtained is also linked with the final molecular weight. The previous researchers Mn was to the order of 3-5 kg/mol [Wan et al., 2008] whereby in our case, the molecular weight synthesized was to the order of 10 - 30 kg/mol leading to a significantly more viscous solution which resulted in longer reaction time.

The ratio used in Wan, et al was $[NVCL]_0 : [RAFT] : [AIBN] 150 : 1 : 0.2$ whereas in this case, a much larger amount of NVCL was used compared to the raft agent and initiator, which is 535 : 1: 0.46. This suggests that there is a higher chance of chain propagation and less of a chance for two radicals to react leading to termination which evidently leads to a higher molecular weight.

GPC analysis was performed on all reaction runs. However, there was always an issue with the signal strength of the polymer peaks which was too weak, and thus made it difficult to extract molecular weight and dispersity data. The refractive index of the solvent and solution is important as it is used to determine the concentration which in turn helps to determine the molecular weight of the solution. The refractive index was found to not overlap between the two liquids, hence leading to the fact that the polymer does not dissolve well in THF. For this reason, it was not possible to determine $\overline{M_n}$ or \overline{D} for most of the reactions concerning pVCap. However, determining the number average molecular weight is a required step before proceeding further. Therefore, we turned our attention to NMR.

Run	$[VCap]_0$	$[RAFT agent]_0$	[AIBN] ₀	Solvent	Time	$\overline{M_n}$	Dispersity
	$(mol \ L^{-1})$	$(mol \ L^{-1})$	$(mol \ L^{-1})$		(h)	$(kg \ mol^{-1})$	
1	14.89	2.78×10^{-2}	1.29×10^{-2}	p-xylene	1.5	19.2	1.18
2	7.39	1.39×10^{-2}	$6.51 imes 10^{-3}$	toluene	1	16.4	1.35
3	7.39	2.78×10^{-2}	1.21×10^{-2}	toluene	1.25	17.5	1.48
4	3.59	5.57×10^{-2}	4.87×10^{-3}	toluene	1.5	5.1	-
5^a	7.39	1.59×10^{-2}	1.22×10^{-2}	toluene	1.5	17.0	-
6	7.39	1.59×10^{-2}	1.22×10^{-2}	toluene	1.5	32.7	-
7	7.39	1.43×10^{-2}	1.22×10^{-2}	toluene	1.25	16.0	-

Table 1 – Experimental conditions for homopolymerizations of different monomers using raft agent 2-Cyanopropan-2-yl-N-methyl-N-(pyridin-4-yl)carbamodithioate by RAFT at 70° C

Table 2 - *(a) This run was not freeze-pump thawed before hand. Rather, nitrogen was passed through for 30 minutes before heating the reaction.

In order to use the NMR peaks of the polymer to determine $\overline{M_n}$, it must be analyzed with reference to all that is found in the solution. The RAFT agent was analyzed in its pure form in order to determine its ¹*H* NMR peaks, which can be seen in figure 10.



Figure 10 – Typical ¹*H* NMR spectrum of 2-Cyanopropan-2-yl-N-methyl-N-(pyridin-4-yl)carbamodithioate in chloroform-D. ¹*H* NMR: 1.77 ppm $(6H, -C(CH_3)_2CN)$; 3.65 ppm $(3H, CH_3N)$; 7.31 ppm $(2H, -CH = CNCH_2-)$; 8.83 ppm (2H, -CH = NHCH =).

From this spectrum, we can analyze the resulting spectrum of the polymer shown in figure 11. By the mechanism of the RAFT reaction, it is known that the raft agent attaches itself to one of the ends of polymer. Therefore, if we can determine the intensity of the raft agent with respect to the polymer backbone, we can determine the number of units in the polymer chain, and thereby calculate the number-average molecular weight. This is a well known method described by Izunobi in Polymer Molecular Weight Analysis by 1H NMR Spectroscopy [Izunobi and Higginbotham, 2011]. It is to note that this method assumes that all chain ends are active, which is certainly an ideal case. This however works well for polymers with a molecular weight up to $25kg \ mol^{-1}$ and decreasing in precision with increasing molecular weight. Due to the lower intensity of the raft agent compared to the polymer, there is a possibility of background noise



interfering with the results. In order to decrease this factor, $256 \ ^{1}H$ NMR scans were performed.

Figure $11 - {}^{1}H$ NMR spectrum of poly(N-vinylcaprolactam) in the presence of 2-Cyanopropan-2-yl-N-methyl-N-(pyridin-4-yl)carbamodithioate dissolved in chloroform-D.

By correlating the spectrums of VCap and raft agent with the pVCap spectrum, it can be noticed that at 3.8 ppm 3 hydrogens from the raft agent demonstrate a peak which is not overlapping with any of the other peaks. The polymer peak that can be taken is at 4.4 ppm which corresponds to 1 hydrogen. Thus, the 3.8 ppm peak can be integrated and set to 3, and the corresponding polymer peak can be integrated, which represents the number of units in the polymer chain. This number is then multiplied by the molar mass of VCap, which is 137 $g \mod^{-1}$, giving us the number-average molecular weight $\overline{M_n}$. This was done for polymerization runs 4 to 7. Since the GPC was unreliable, dispersity data for these runs could not be obtained. In figure 11 there is a sharp peak at 2.4 ppm and 7.1 ppm. This corresponds to some remnants of toluene which did not separate properly during the whole purifying process.

It can be noticed that an increase in the RAFT agent decreases the number-average molecular weight, as witnessed through polymerization run 4. The molecular weight was also limited when the reaction was nitrogen purged in the beginning rather than freeze-pump thawed as witnessed by the $\overline{M_n}$ being halved in the case of reaction 5 (17.0kg mol⁻¹) compared to the 6th run (32.7kg mol⁻¹). The main purpose of purifying beforehand is to remove oxygen, which inhibits the reaction. Therefore, it can be clearly established that a freeze-pump thaw is more efficient than a nitrogen purge.

The main objective of performing these polymerization runs (1 to 7) was to obtain different molecular weights and verify their relationship with respect to ice and hydrate adhesion.

7.2 Ice adhesion analysis

Initial results for spincoated samples used for ice adhesion are displayed in figure 12. Four different molecular weights, which were polymerized, were tested. It is important to note that the adhesion is measured by the force required to dislodge the ice from the surface, as previously explained. However, shear stress is always the reported format. Therefore, the force in newtons was converted to shear stress by taking the area over which the ice was frozen, in this case $1.43 \times 10^{-4} m^2$.



Figure 12 – Shear stress as a function of the number average molecular weight for a 5 wt% poly(N-vinylcaprolactam) solution with spin coating speed of 2000 rpm and 95% confidence intervals.

One of the primary concerns with figure 12 is the large confidence intervals. This large variation of shear stress seen across every molecular weight prevents any conclusion from being drawn regarding any possible relation between the two variables. In order to determine the cause of this inconsistency, our attention turned to the mechanics of spin coating.

There are two main parameters which can change during spin coating. These are the thickness of the spin coated sample and its morphology. The thickness of the sample depends on factors such as the spin speed, the viscosity of the solution, the solvent type and the vaporizability rate [Mohajerani et al., 2007]. One of these variables, namely spin coating speed, was tested for different molecular weights in order to ascertain whether thickness truly should not effect adhesion strength, which can be seen in figure 13.

The same variation from figure 12 can be seen across all three molecular weights which were



Figure 13 – Shear stress as a function of spin coating speed for poly (N-vinylcaprolactam) surfaces with a $\overline{M_n}$ of (a)32.7 kg mol⁻¹. (b)5.5 kg mol⁻¹. (c)15.9 kg mol⁻¹ and 95% confidence intervals.

tested in figure 13. The shear stress does seem to be effected by the spin coating speed, and hence the thickness as seen in part (c) of figure 13. However, part (a) and (b) of figure 13 do not reinforce this conclusion. It seems counterintuitive that thickness should have an effect on adhesion strength, as in this case only the surface interactions are important. It is to be expected that morphology should play a more significant role in adhesion strength variability. Therefore, the next step was to identify the morphological changes during spin coating.

Mohajerani, et al reported that the concentration of the solution used for spin coating has a direct effect on the thickness. Moreover, the thickness was found to fluctuate as it increased, also effecting the uniformity of the thickness of the surface [Mohajerani et al., 2007]. If found to be true, then a high concentration could effect the uniformity of the surface, introducing roughness which would effect the adhesion strength. In order to verify the validity of this conclusion, the adhesion strength was also determined by varying the concentration of the solution used for spin coating, as shown in figure 14.



Figure 14 – Shear stress as a function of solution wt% at a spin coating speed of 1000 rpm with 95% confidence intervals for poly(N-vinylcaprolactam).

There is a marginal increase in the shear stress with respect to solution wt%. However, due to the same variability, there seems to be no definitive correlation at 5, 10, 15 wt% of pVCap solution with respect to shear stress. Mohajerani, et al notes that the thickness fluctuation increases with increasing concentration [Mohajerani et al., 2007]. However, such a trend is not noticeable in figure 14. The confidence intervals are similar for 5 and 15 wt%, where a small decrease is seen with 10 wt% but the inconsistent results are cannot be linked to a change of concentration. However, the effect of concentration on the shear stress cannot be ignored either, as it is responsible for thickness fluctuations across the surface which leads to surface non-uniformity. Since it is not the major variable effecting shear stress, our investigation continued with the next step being to determine surface roughness between different molecular weight samples.

7.2.1 Roughness effect



Figure 15 – Surface roughness of 15.9 kg/mol poly(N-vinylcaprolactam) surfaces with respect to the spin coating speed on stainless steel 316 substrates with 95% confidence intervals.

There is not a great variation of roughness between samples spin coated at a different spin speed as seen in figure 15. Verily, spin coating is a procedure which is known to generate thin and uniform surfaces. A slight increase in the average roughness is noticed when the spin speed is increased to 2000 rpm. However, the overall surface roughness is consistent across all spin speeds. In order to ensure that the surface roughness does not change across molecular weights, the roughness on 32.7 kg/mol surfaces was also measured. A comparison of the different molecular weights can be seen in figure 16.



Figure 16 – Surface roughness of stainless steel 316 bare and spin coated with poly(N-vinylcaprolactam) at 1000 rpm and 95% confidence intervals.

An increasing trend of surface roughness is visible in figure 16. Although there is an overlapping of the 15 kg/mol and 32.7 kg/mol surfaces in terms of the possible variation, the results are consistent with the previously mentioned findings that an increased concentration of solution leads to fluctuations in the thickness across the sample, leading to non-uniform thickness [Mohajerani et al., 2007]. This is what seems to be occuring here as the viscosity of the solution increases along with the molecular weight. This increased surface roughness still does not seem to account for the difference in ice adhesion strength. If it were so, then the ice adhesion strength should have changed across molecular weights in a similar fashion. However, the obtained result is that the breaking of the ice does not offer any visible trends which coincide with this increased roughness. In order to prove this fact, these very samples which have been used for figures 15 and 16 were tested for ice adhesion. The results are outlined in figure 17 and figure 18.



Figure 17 – Shear stress of 15.9 kg/mol spin coated poly(N-vinylcaprolactam) at different spin speeds.



Figure 18 – Shear stress of different molecular weights of poly(N-vinylcaprolactam) at 1000 rpm.

As it is evident, there is no clear correlation between surface roughness and shear stress, seen in figures 17 and 18. It is important to note that recent studies have demonstrated that increased surface roughness or the creation of surface patterns lead to increased shear stress which is rationalized by the mechanical interlocking between ice and the texture [Chen et al., 2012]. It can thus only be concluded that the surface is not very rough, and mostly uniform, thereby not significantly affecting ice adhesion.

7.2.2 Shear stress variation hypothesis

The variation in shear stress seen across samples of the same molecular weight and spin speed is apparent. It is important to determine the cause for such a large shear stress change since it impedes the analysis of possible existing correlations between different parameters such as molecular weight vs shear stress and spin speed vs shear stress. It has thus far been established that this inconsistency is present even during the study of different variables such as molecular weight, spin speed, solution weight % and surface roughness. The key to this issue might lie in the way the ice forms. When water is poured into the hollow cylinder and allowed to freeze, it does so without any control other than the temperature. The crystal lattice which forms is therefore truly random. This ice which forms a bond with the surface is then different for each run, which when broken should differ from sample to sample, thus affecting shear stress. Another aspect to consider is the freezing time that water is given. It is well known that ice rearranges itself internally, and the more time it is given, the stronger it becomes. Thus, the question arises whether the amount of time given for the ice to freeze is also significant enough to affect our results. The fact is that over such a short period of time 30 minutes, there should be no significant effect to the ice strength. A fact which was tested by freezing the ice over a period of 6 hours and ending up with similar results to those performed over 30 minutes. However, time is not the only factor at play. There are a few other variables which affect ice strength. These are temperature, strain rate, tested volume and

ice grain size. Each of these variables effect the ice tensile and compressive strength in different orders of magnitude [Petrovic, 2003]. Another important factor is the fracture of the ice-surface bond. In most tests, when the bond between ice and surface was broken, there was always a few ice particles remaining on the surface, which suggest that the adhesion strength being measured is not a bond 100% between ice and the surface, rather also between ice-ice. All these various factors seem to play a significant role in the variable results obtained across all experiments. Thus, it is unlikely that these inconsistencies can be corrected, as they are very difficult to manipulate. The main parameters that should be controlled in order to ensure as consistent results as possible are the freezing time, amount of water used, ascertaining the type of fracture induced (ice-ice or surface-ice) and the point of impact for the force applied.

7.3 Adhesion of hydrates

Hydrate adhesion was determined for poly(N-vinylcaprolactam) surfaces. These results were also compared with previous ice adhesion results, which are demonstrated in figure 19. There is a slight increase between ice shear stress (508 kPa) and hydrate shear stress (532 kPa) spun at 2000 rpm for pVCap. Although, again due to the confidence intervals, these results are not conclusive. It can be said that there is no great difference between the two, knowing that the hydrate tests were performed with a 30 vol% solution of THF in water, whereas ice adhesion tests were simply performed with RO water. It is important to note that these results are affected by the humidity of the room, since it changes the concentration of THF in solution, thereby changing the hydrate structure that is being simulated. This is not the case for ice adhesion, where only water is used. Because hydrate adhesion tests were conducted in lesser quantity than ice adhesion, the humidity is not going to effect the conclusion of these results as it is not varying over the range of the data.



Figure 19 – Ice and hydrate adhesion of poly (N-vinylcaprolactam) for 32.7 kg/mol samples at different spincoating speeds and 95% confidence intervals.

8 Conclusion

The goal of this study was to determine the ice and hydrate adhesion of pVCap. Due to lack of commercial availability, pVCap was successfully synthesized by the RAFT polymerization method. Polymers of molecular weights magnitude 5 kg/mol, 15.9 kg/mol 17 kg/mol and 32.7 kg/mol were synthesized where every run lasted between 1 till 1 h30. The first few runs demonstrated a low dispersity of 1.4. Subsequent runs were difficult to analyze due to the low signal intensity obtained by GPC. NMR was performed to obtain molecular weights data as a workaround.

Ice adhesion tests were performed in order to obtain the shear stress value of pVCap surfaces. The obtained shear stress was found to be 508 kPa for a 32.7 kg/mol sample spun at 2000 rpm, with a large variability. This large deviating of results persisted in subsequent experiments when changing spin speed, molecular weight, solution weight %. This was found not to be caused by the surface roughness of the samples, which was uniform across different molecular weights. This deviation which made it difficult to obtain clear relationships between the several different variables studies, was attributed to the procedure used to determine ice adhesion. The formation of the crystal lattice for ice, the time of formation, the point of impact and the type of break induced between the surface and the ice are some of the different factors suspected to be the cause for this divergence and the resulting large confidence intervals.

The surface roughness obtained for different molecular weights was different in the case of bare stainless steel 316 (0.2 um) compared to the spin coated surfaces of 0.27 um and 0.37 um for 15.9 kg/mol and 32.7 kg/mol respectively. This increase in surface roughness was attributed to the solution wt% of the solution by previous researchers, and found to follow the same trend in this case, where an increased solution wt% resulted in increased surface roughness.

Hydrate adhesion was also performed using the spin coated samples. It was found to be 532 kPa for a 32.7 kg/mol sample spun at 2000 rpm. Comparing this to ice adhesion, there is little difference between the two shear stress values obtained, partially due to the fact that hydrates are mainly composed of water, as in this case were a 35 vol% solution of THF was used. The large discrepancy in results persisted from ice adhesion all the way to hydrate adhesion experimental data.

In conclusion, the primary objective of determine ice and hydrate adhesion was achieved. However, pVCap is far from being the ideal surface to counteract their formation inside pipelines due to the high ice and shear stress. This study gives valuable insight on the different obstacles that lie in the quest for a truly icephobic or hydratephobic surface. Subsequent tests with different polymers will be able to bypass the whole issue of how different parameters effect ice and hydrate adhesion, and focus more on different types of surfaces.

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