

ABSTRACT

STEGALL, THOMAS ADAM. Analysis, Characterization and Optimization of Polyvinylacrylamide Conversion into Polyvinylamine via the Hofmann Rearrangement. (Under the direction of Dr. Samuel Hudson.)

The optimization of synthesizing polyvinyl amide (PVAm) from polyvinyl acrylamide (PVAA) was investigated. The polymer samples were characterized via Fourier transform infrared spectroscopy, acid-base titration, differential scanning calorimetry (DSC), and dilute solution viscometry. FTIR Attenuated Total Reflectance (ATR) spectroscopy was applied to compare the relative quantities of NH_2 and acrylamide $\text{C}=\text{O}$ groups by measuring absorption peak heights and drawing a calibration curve based on direct measurement via acid-base titration. DSC was performed to illustrate changes in polymer glass transition temperature (T_g) and melting point (T_m) during polymer conversion, and demonstrated that significant changes in chemical and physical structure occurred. Dilute solution viscometry was used to demonstrate that the produced polymer showed polyelectrolyte properties, which indicated formation of carboxylic acid functional groups via acrylamide hydrolysis side reactions. Viscometry was used also to indicate that degradation occurred across all samples examined, however no clear trend emerged relating reaction conditions to sample degradation and loss of molecular weight.

The Hofmann rearrangement was evaluated for separate reaction mixtures containing 30-50% NaOH base concentration. Each sample of a given NaOH concentration was divided into room temperature 25°C and chilled -10°C samples to evaluate the effects of temperature on the reaction. Finally, quantities of polymer were removed from samples after 1 and 2 hours, in order to investigate the effects of time on the polymer samples. In total, 12 samples were produced and evaluated.

Based primarily on the combined FTIR and titration data, the optimum reaction conditions for maximal conversion (52.6% amine) of PVAA into PVAm were identified as 25⁰C, under the highest base concentration (50%), having been reacted for the longest time, 2 hours. Conversion minimum (31.0-33.8% amine) was demonstrated under the coldest temperatures at lowest base concentration (30%); however the reaction time variable showed little influence under these conditions. DSC indicated that a complex terpolymer or more complex structure had been formed.

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Analysis, Characterization and Optimization of Polyvinylacrylamide Conversion into
Polyvinylamine via the Hofmann Rearrangement

by
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DEDICATION

This work is dedicated to all the important people in my life who have helped me on the long road to higher education. My sincerest thanks go to Dr. Samuel Hudson, who always listened to my ideas, helped sculpt them into a focused and insightful thesis, and always tried to be available whenever I had concerns and questions. I also want to thank Ms. Birget Andersen and the people of the College of Textiles Analytical Instrumentation and Services Lab, who trained me on the FTIR instrumentation that allowed me to collect my most important data, and whose data recovery efforts on my behalf were greatly appreciated. I am also deeply thankful to Mr. Charles Domingo, whose advice helped guide me through some of the ups and downs of preparing this thesis. Finally, I am eternally grateful for the unwavering support of my parents, who did everything in their power to ensure that I had a chance to reach my goals.

BIOGRAPHY

Thomas Stegall was born in Charlotte, North Carolina in 1988. He was homeschooled for much of his early academic life, later attending the North Carolina School of Science and Mathematics in Durham, North Carolina for his junior and senior year of high school, graduating in 2007. He began his undergraduate studies immediately thereafter, attending North Carolina State University and earning a B.S in Polymer and Color Chemistry in May of 2011. Continuing his academic goals, his graduate work at NCSU commenced in the fall of 2011.

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CHAPTER ONE

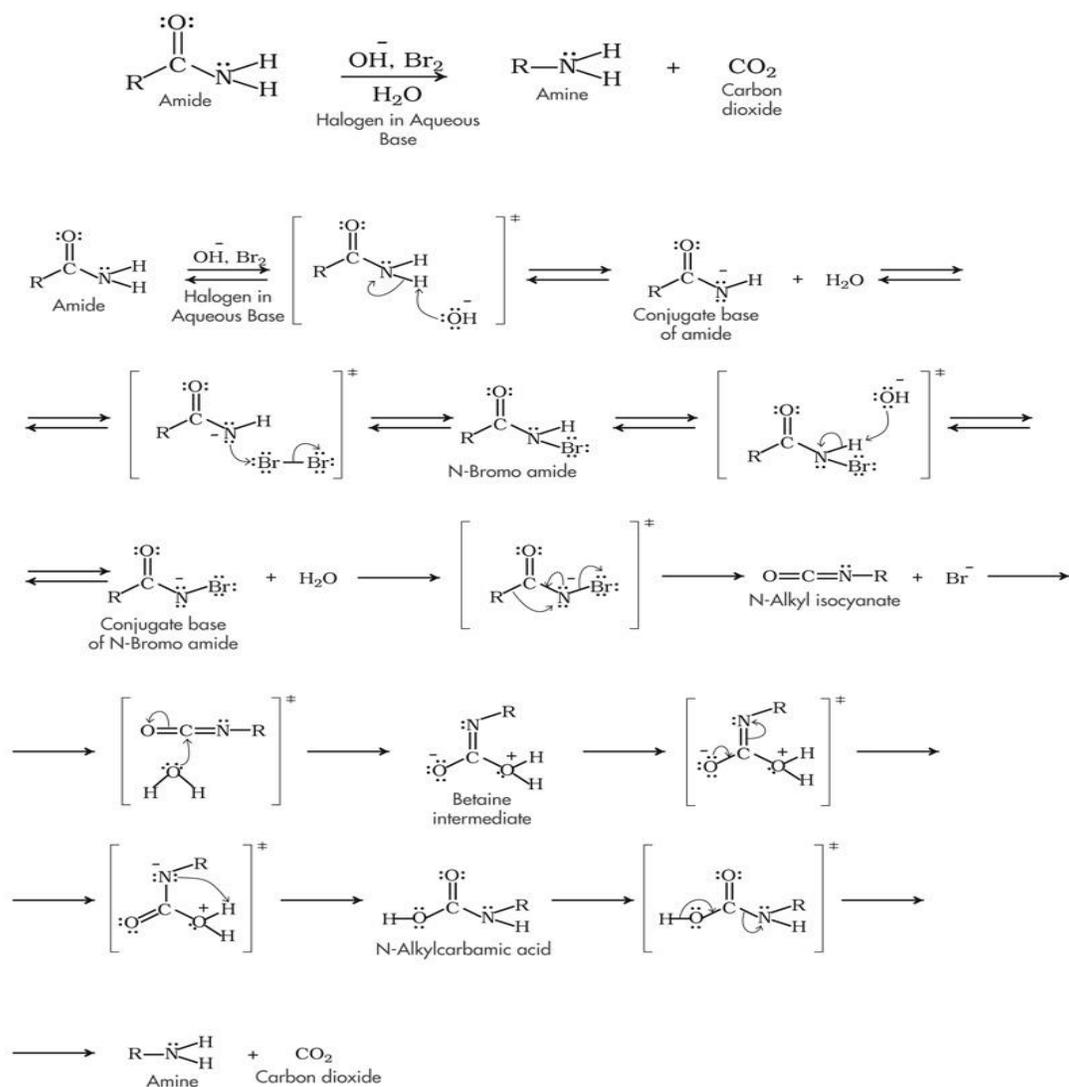
Polyvinylamine (PVAm) is an extremely interesting polymer because it offers a significant density of reactive amine functional groups on a structurally simplistic polymer. However, certain species of polymer cannot be synthesized via common production methods such as free radical polymerization, including PVAm. When synthesizing polyvinyl amine from the vinylamine monomer, tautomerization restructures the monomer before polymerization reactions can begin. The vinylamine monomer changes bond configuration, moving its carbon-carbon double bond to the carbon-nitrogen bond and becoming a stable, nonreactive primary imine [1]. However, a completed polymer chain with primary amide functional groups might instead be converted into PVAm directly, producing the desired PVAm product without risking tautomerization.

The research interest is to investigate conversion of polymeric acrylamide functional groups into polymeric amine functional groups, synthesizing PVAm without requiring the unstable vinyl amine monomer. The Hoffman rearrangement, developed by August Wilhelm von Hoffman in 1881 [2], offers a useful technique for direct conversion of polyvinyl acrylamide functional groups into PVAm vinyl amines. Previous studies have had mixed results in successfully utilizing the Hofmann rearrangement, and further examination of the details of the reaction is crucial for evaluating the potential feasibility of this conversion process.

Scheme 1.1 illustrates the traditional Hoffman rearrangement uses a strong base to strip a single hydrogen from the amine group, forming a negatively charged conjugate base.

This conjugate base reacts with either dissolved diatomic bromine or chlorine in solution, creating a halogenated amine. Continued deprotonation of this new halogen-amide molecule leads to further acid-base reactions, losing the second hydrogen and forming the conjugate base of the halogenated amide. The conjugate base undergoes electron rearrangement to form an alkyl isocyanate, which is extremely unstable in the presence of water. The isocyanate functional group immediately hydrolyzes to form the desired amine and a single molecule of carbon dioxide which leaves the reaction system in gaseous form.

Scheme 1.1. Hofmann Reaction Mechanism [3]



The Hoffman rearrangement essentially takes the C=O group in the acrylamide functional group and removes it from the group via this series of intermediates, which leaves the NH₂ group attached directly to the carbons which form the backbone of the polymer chain. By performing this reaction on a fully functionalized polyvinyl acrylamide chain, it is

theoretically possible to create polyvinyl amine at high functional group density, bypassing the need for the unstable vinyl amine monomer.

For the purposes of this experiment, polyvinyl acrylamide (PVAA), which has many acrylamide groups along its backbone, offers a superior starting material for full or partial conversion into PVAm. PVAA is an inexpensive, easily obtainable stock product, and widely used industrially as a flocculant in wastewater treatment and paper making to force dispersed particles to agglomerate into larger, more easily filtered solids [4].

Historically, polyvinyl amine has been virtually uninvestigated in the scientific literature, primarily due to its synthesis difficulties. The few existing scientific studies of PVAm have primarily focused on the polymer's ability to greatly strengthen recycled pulp and paper products which have undergone fiber degradation, but not on categorizing the pure PVAm material [5]. Recycling pulp and paper relies heavily on starching the end product to enhance the strength and degradation resistance of the recycled material. However, in an effort to conserve water during the recycling process, closed loop recycling systems are typically employed, which add salts to the pulp mix over multiple recirculations of the water cycle. Eventually, starch loses its ability to stabilize the pulp mixture at high salt concentrations [5]. Polyvinyl amine is more stable under high salt concentrations, and is well known for its utility in extending the maximum recyclability of paper products.

Polyvinyl amine may have other highly significant properties beyond stabilizing recycled paper, particularly the strong chelating characteristic of the many NH₂ groups along its chain backbone. Chelation of metals is a complex process in which a single positively charged metal ion forms two or more separate coordination bonds between a polydentate

ligand and the central metal atom [6]. The large structures formed by this process can have a wide variety of physical properties which are not always easily predictable based on the coordination complex's structure. Amine groups are often used in the chelation process because their strongly electronegative characteristics provide ideal coordination sites for positive metal ions. In theory, polyvinyl amine is an exceptional chelating agent because a long chain polymer contains many amine functional groups to bind large numbers of metal ions. The flexibility of the carbon-carbon polymer backbone would also enable free rotation, permitting the amine groups to position themselves into more stable bond geometries. By increasing the coordination complex stability, the chelated metal ion is better entrapped, improving ion storage duration. At the most basic level, using polyvinyl amine as a chelating agent offers the possibility for creating extremely specific filters for metal filled water, such as toxic mine runoff. The positive environmental impact of filtering dangerous mine waste is potentially significant to the health of many communities and ecosystems. Examining the physical properties of highly chelated polymer chains is beyond the scope of this investigation, but the possibilities are of great interest for future research.

The purpose of this study is to optimize conversion of polyvinyl acrylamide into polyvinyl amine via the hydroxide/hypochlorite based Hofmann rearrangement. To obtain the necessary data, the effects of varying length of reaction time, reaction temperature, and concentration of base on the post-reaction polymer chain length, degree of functional group conversion, and physical properties of the final polymer product will be examined.

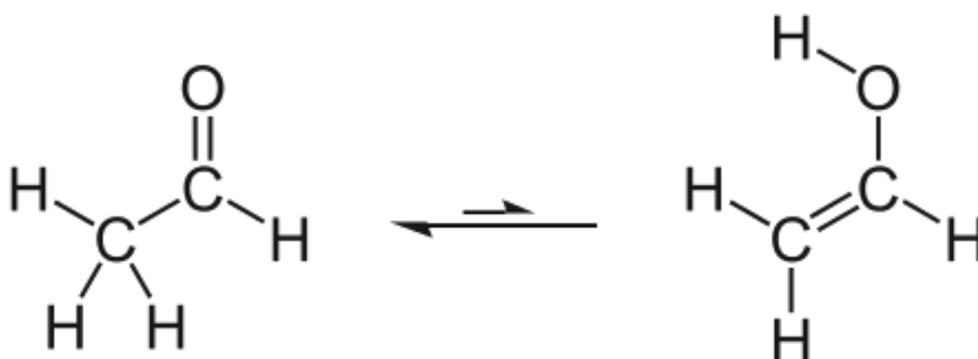
Differential Scanning Calorimetry (DSC), Fourier Transform Infrared spectroscopy

(FTIR), acid-base titration and intrinsic viscosity testing will be performed to produce a broad range of data for comparative examination.

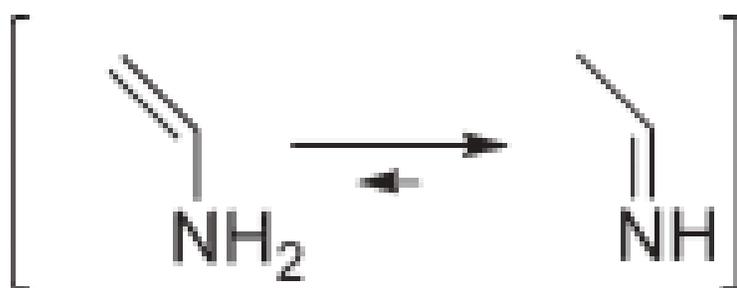
CHAPTER TWO

Polyvinylamine (PVAm) is virtually impossible to synthesize from the vinylamine monomer due to tautomerization into a stable, nonreactive imine form. This reaction is analogous to that of vinyl alcohol, which tautomerizes into acetaldehyde [7]. Schemes 2.1 and 2.2 below indicate the more stable chemical form of each potential vinyl monomer.

Scheme 2.1. Tautomerization of Vinyl Alcohol into Acetaldehyde [8]



Scheme 2.2. Tautomerization of Vinylamine into imine [7]



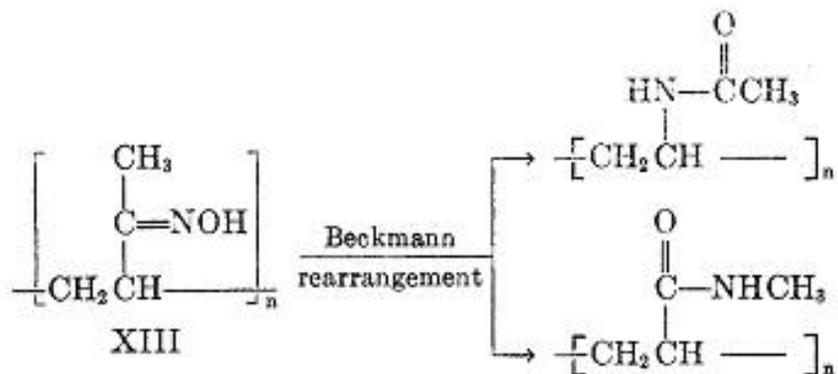
Vinylamine

To circumvent this inability to synthesize polyvinylamine via more standard reaction mechanisms, chemists have investigated utilizing polymers with functional groups that can be chemically altered into the desired vinyl amine form. If possible, converting a premade polymer from its original chemical structure into polyvinylamine would bypass the issue with tautomerization of the vinyl amine monomer into an imine compound which cannot be polymerized [7].

Because of its potential applications in chemistry, researchers have investigated safe, economical, and efficient means by which to create PVAm for many years. An early attempt to synthesize PVAm was performed by Jones, Zomlefer and Hawkins in 1944, seeking to capitalize on PVAm's high chemical reactivity. The researchers employed various techniques to synthesize the polymer, including the Beckmann rearrangement of polyvinyl methyl ketoxime and the hydrazine hydrolysis of polyvinyl phthalimide [9].

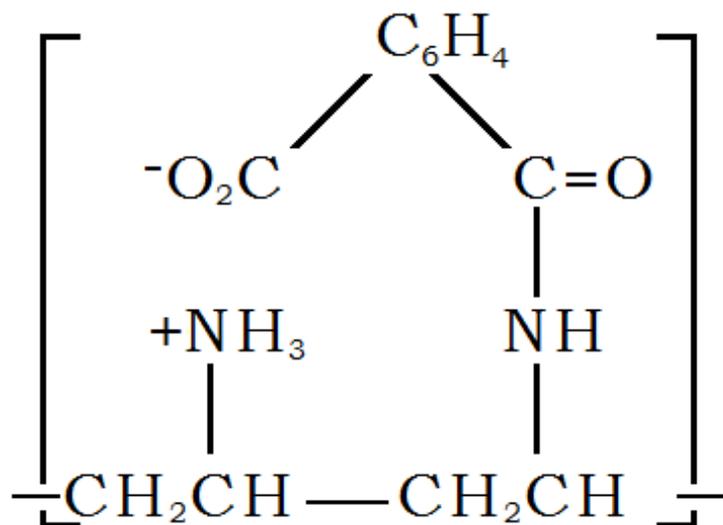
Unfortunately, the polyvinyl methyl ketoxime needed for the Beckmann rearrangement proved unsuitable, and the researchers suspected that the reaction conditions had been improperly chosen, though they did not offer speculation regarding what conditions might be superior. Nevertheless, their synthesis procedure was reported and the authors hoped that in the future, this reaction and the reasons for its lack of success might be further investigated. Scheme (2.3) illustrates the results of the Beckmann rearrangement of polyvinyl methyl ketoxime, producing very different compounds than the hoped-for polyvinylamine.

Scheme 2.3. Beckmann Rearrangement products [9]



The hydrazine hydrolysis was then shown to form a copolymer with only partial amine functionality and a long pendant group, neither PVAm nor polyphthalmic acid as had been expected. [9]. Scheme 2.4 illustrates this partially amine-functionalized copolymer.

Scheme 2.4. Partially aminated polymer following hydrazine hydrolysis [9]



It appeared that this copolymer, despite having some amine functionality, would not show any of the desired properties of polyvinyl amide, due in part to the ringlike structure formed by the negatively charged $-O_2C$ group being attracted to the positively charged $+NH_2$ group. The close proximity and steric hindrance of the long chain renders this copolymer highly dissimilar to the desired properties of isolated polyvinylamine. Possible reasons why alternate structures might have formed were not discussed as part of their work. However, experiments later performed by Reynolds and Keaton [10] succeeded using very similar methods, but it is unclear why Jones' group did not meet with success. Based on the degree of similarity between the successful and unsuccessful experimental methods, it is possible that further hydrolysis would have obtained the expected PVAm.

One of the first truly successful methods for synthesizing PVAm recorded in the scientific literature was described by Reynolds and Kenyon in 1947. This experiment expanded on hydrazine techniques previously utilized by others. Prior to their groundbreaking work, no PVAm polymer had been prepared, in pure NH_2 functionality or in salt form. The researchers proposed a modified method based on the hydrazine hydrolysis of polyvinylphthalimide as described earlier in 1944. This method is illustrated in Scheme 2.5.

representing 85% of a theoretical maximum nitrogen content for pure PVAm of 32.25.

Titration indicated that via this methodology, PVAm was produced such that up to 95.8% of the nitrogen was free amino groups, with 4.2% present as incomplete hydrolysis products such as imides. Source: [10].

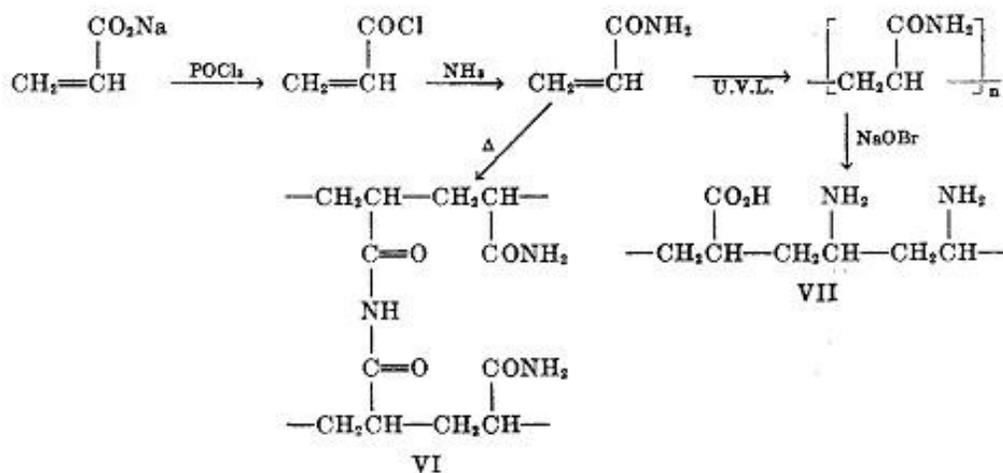
The phthalimide based reaction pathways, though successful on the small scale, were not well suited for industrial scale synthesis of PVAm. Hydrazine in particular is flammable, unstable, and toxic and the chemicals are too expensive for economical polymer production. An alternate method to the hydrazine process was necessary, and a reaction developed in 1881 by Hofmann was re-examined for its potential to radically streamline the process of PVAm synthesis. The Hofmann rearrangement utilizes aqueous bromine under strongly basic conditions to form hypobromite, which will react with a primary amide and form an isocyanate intermediate. This intermediate rapidly hydrolyzes in the presence of water to form a primary amine, giving off only carbon dioxide as a byproduct [2].

As part of their work in 1944, Jones, Zomlefer, and Hawkins also examined the Hofmann rearrangement and sought to use it to convert polyvinylacrylamide into PVAm [9]. Their first synthesis process used for forming the polyacrylamide starting material was flawed, forming a crosslinked product composed primarily of imide functionality. However, by choosing to utilize ultraviolet light and benzoyl peroxide to initiate polymerization, the polyacrylamide was successfully obtained.

Using hypobromite degradation in the manner of the Hofmann rearrangement, the polyacrylamide was observed to form a partially aminated polymer. Calculations showed that the polymer produced was of lowered nitrogen value, ranging from 9.7% to 15%, a far cry

from the theoretical maximum of 32.5% [9], [12]. Because the polymer lost so much nitrogen, the desired PVAm was not obtained and the reaction was deemed unsuccessful. In Scheme 2.6, the crosslinked imine formed by thermal polymerization is labeled compound VI, and the partially aminated polymer after bromination is marked as compound VII.

Scheme 2.6. Bromine-based synthesis of PVAm/PVAA copolymer [9]



Based on information gained from more modern literature, it is likely that a possible culprit in the poor amine functionalization was the 80⁰C temperature at which the Hofmann rearrangement was warmed immediately after adding all reaction mixture components. Tanaka [11] later indicated that performing these halogenation rearrangements under continuously cold conditions, much greater amination could be obtained.

To further understand the Hofmann rearrangement and its potential in producing PVAm, additional studies were undertaken by Arcus in 1951 to examine the reaction of a different starting polymer, polymethacrylamide, with hypochlorite and hypobromite in

aqueous solution via the Hofmann rearrangement, and ascertain the process' effectiveness converting methacrylamide into the desired amide groups. The methacrylamide was successfully converted into multiple different functional groups, but less than 5.5% amine functional group content was obtained. Unfortunately, most of the converted product was primarily carboxyl and alkylacylurea units produced in undesirable side reactions. Importantly, the rate of Hofmann reaction with hypobromite was very slow, sometimes requiring months to reach completion, and the active hypobromite was still present upon conclusion of many experimental trials. Consequently, more aggressive hypochlorite was used for further experimentation. Because the hypobromite delayed the reaction so significantly, most future research involving the Hofmann rearrangement adopted hypochlorite over hypobromite as their primary halogenated reagent. Additionally, permitting the reaction mixture to stand for three to four days was proven to favor the production of alkylacylurea groups, but did not increase conversion to amine groups. Finally, after adding excessive amounts of base under warm conditions to guarantee maximum hydrolysis of amine to carboxyl groups, intrinsic viscosity changed very little, even after intense hydrolysis. This data indicated that the decrease of intrinsic viscosity during the reaction was due to degradation and chain scission rather than hydrolysis [12]. From this observation, it can be concluded that excess base will not significantly harm the converted polymer. Having too much base is preferable to having too little base, which could impede the reaction's completion.

Further optimization of the halogenated Hofmann rearrangement method for producing PVAm was performed in 1956 by Schiller and Suen, who utilized the simpler

polyvinylacrylamide (PVAc) rather than polymethylacrylamide as in Arcus' work. In order to reduce the potential for hydrolysis which would destroy the desired amine groups on the converted PVAm polymer, Schiller and Suen chose to perform their experimentation at room temperature in order to alter the reaction kinetics. The theoretical nitrogen content of PVAc and PVAm were calculated to be 19.7% and 32.5% respectively, and the room temperature reaction method produced total nitrogen percentages of between 21.4% and 21.7%, indicating that a reasonable percentage of nitrogen was retained on the polymer. Source: [13]. Using the Van Slyke analysis technique indicated that perhaps 60% of that nitrogen was bound as amine groups, assuming no nitrogen loss during reaction. The Van Slyke technique utilizes the reaction of an aliphatic amine with nitrous acid to evolve free nitrogen in gaseous form according to the mechanism $\text{RNH}_2 + \text{HNO}_2 = \text{ROH} + \text{H}_2\text{O} + \text{N}_2$ [14]. By evaluating the volume of gas produced, calculating the moles of nitrogen gas present, and assuming that only aliphatic amines were consumed in the reaction, the moles of amine may be calculated to a reasonable degree of accuracy. Even if some nitrogen was lost due to side reactions or procedural error, 60% of the 21.4% nitrogen remaining on the synthesized polymer (12.8% amino groups) still indicated that Schiller and Suen's room temperature process improved amine yield significantly over the Arcus technique's 5.5% amino groups.

Polyvinyl acrylamide (PVAA) was reexamined as a potential precursor polymer to PVAm in the 1970s in light of the Hofmann rearrangement's ability to convert amide functional groups into amines quickly and cheaply. Because PVAA can be produced to a high degree of repeat unit amide functionality and molecular purity, researcher Tanaka proposed to use PVAA as a starting material and examine an alternate set of reaction

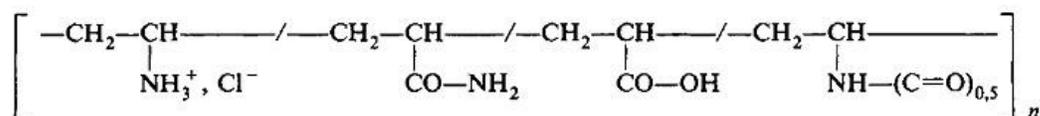
conditions which could dramatically improve percent conversion of acrylamide into amine functional groups. It was definitively demonstrated that very high concentrations of NaOH base were conducive to producing the highest percentage of amine conversion, with peak concentrations of 6 mole/kg providing greater than 90% amine functional groups on the converted polymer. Excess amounts of hypochlorite degraded the polymer end product significantly, and the viscosity decreased most drastically when the molar ratio of hypochlorite to acrylamide groups exceeded one. It was concluded that residual NaOCl was primarily responsible for observed chain scission. Finally, by performing the reaction at very cold temperatures, either at -10 degrees C or 0 degrees C, the amount of free chlorine decreased much more quickly than at temperatures above 10 degrees C. It was further observed that roughly 80% of the available chlorine was removed from solution after 30 minutes, indicating that the reaction was mostly completed within that time period. Adjusting the temperature either up or down after that point had little effect on the final amine percentage. If the reaction was permitted to occur at 10 degrees C or greater from the very beginning, the temperature of the reaction continued to rise and a very sharp decrease in viscosity was observed, providing strong evidence that performing the Hofmann rearrangement under warm or room temperature conditions was suboptimal for amine production. Ultimately, Tanaka's work outlined certain conditions that pointed towards an efficient and comprehensive technique for obtaining PVAm, which are worthy of further examination [11].

After Tanaka's work in establishing conditions favorable to polyvinylamine's production from polyvinylacrylamide, research was undertaken to further characterize the

synthesis methodology. Lamenting the fact that less than 10 papers describing different attempts to optimize the PVAm production technique existed prior to their research in 1992, Achari, Coqueret, Lablache-Combiere, and Loucheux reopened the investigation into PVAm and sought to examine a broader range of initial reaction conditions. Source: [15]. As had others before them, the Achari group noted the potentially exceptional reactivity and simplicity of PVAm as a prime motivator for their research. This piece of literature indicated that Tanaka's exceptional work had gone largely ignored since its publication in 1979, and that a method involving polymerizing tert-butyl N-vinylcarbamate monomer followed by deprotection of amino groups was the preferred method for creating PVAm. This method was deemed superior to the Hofmann hypobromite synthesis technique using polyvinylacrylamide as a starting material because it was claimed to cause too much chain scission and polymer degradation [16]. To present a counterargument to the prevailing PVAm synthesis theory, Achari's research group examined the Tanaka synthesis by carefully separating the different phases of the Hofmann rearrangement of the polyvinylacrylamide using hypochlorite and categorizing the compounds observed. In particular, the nature of potential side reactions and the experimental conditions which might favor specific products were investigated, in order to more accurately quantify the physical and chemical properties of PVAm produced by the Tanaka technique. Beginning with a moderate quantity of base and varying quantities of active hypochlorite agent, it was discovered that the chlorination phase (Curtius rearrangement) [17] of the reaction progressed virtually to 100% completion after 45 minutes to an hour, whereupon only trace amounts of active oxidation agent remained. After this phase, primarily isocyanates were expected to be present, and another

large quantity of base was added to stabilize the isocyanates so that they could hydrolyze into amine groups. Ultimately, the Achari group concluded that with lowered concentrations of hypochlorite, the primary side reaction consisted of hydrolysis of unreacted acrylamide NH₂ groups to carboxylic acid. With excessive amounts of hypochlorite, urea bridges formed instead, but only to a small extent, 1-5% molar functionality relative to starting acrylamide. Scheme 2.7 depicts a composite scheme representing the various side groups present in the hypothetical PVAm copolymer, with amine, acrylamide, carboxylic and urea groups present.

Scheme 2.7. Complex copolymer produced via Hofmann rearrangement [15]



With the understanding provided by this research, examining PVAm spectra produced by the Tanaka methodology may become significantly easier by anticipating what functional groups may be present. Additionally, by controlling the initial reaction conditions, the molecular structure of the final product may be manipulated and controlled.

Ultimately, the story of synthesizing PVAm is a long tale, told in widely dispersed fits and starts. Since the first serious attempts at producing this intriguing polymer more than half a century ago, few chemists have investigated the various possible synthesis reactions, and fewer still have tried to optimize what their predecessors have published. What is known is that PVAm can be effectively produced using the Hofmann degradation of polyvinyl acrylamide, and that chlorine rather than bromine is the most efficient reagent in that

reaction. Excessive hypochlorite remaining in solution will lead to heavy chain scission. High quantities of base will stabilize the reaction intermediates best and permit the excess hypochlorite to react, removing itself from the reaction mixture. Performing the Hofmann reaction at elevated temperatures has been shown to be conducive to reaction failure via chain scission. Chilling the reaction mixture can prevent some of the chain scission, but the primary source of polymer degradation remains the hypochlorite active reagent. More research is needed to investigate the details of the Hofmann-based production of PVAm, both to verify the historical methodology and results, and to continue to understand and optimize this synthesis technique.

CHAPTER THREE

3.1 Hofmann Reaction Setup and Procedures

The Hofmann rearrangement reaction of concentrated NaOCl bleach under strongly basic conditions with dissolved polyvinyl acrylamide (PVAA) was systematically investigated under a broad range of reaction conditions as described in Table 3.1. The proposed mechanism involves the deprotonation of an amide by the base, which forms a temporary anion. This anion then attacks the halogen, forming a halo-amide. Repeated deprotonation creates another anion, which can then rearrange to form an isocyanate, which is partially stabilized under basic conditions. Isocyanates in the presence of water will undergo proton transfer, creating a pair of carboxylate and ammonium anions. The carboxylate anion will then release CO₂ as gaseous product, and the ammonium anion will become stabilized as the desired primary amine product. Based on the limited literature available, reaction time, reaction temperature, and concentration of NaOH base present in the reaction are the variables pertaining most to the percent conversion into amine potential. As given in Table 3.1, the concentration of base was varied from 30 to 50 percent, the temperature was controlled at two different temperatures, 25⁰C and 0⁰C, and half of each sample was removed from solution for methanol rinsing and analysis after 1 and 2 hours, respectively.

Table 3.1. Optimization spectrum of Hofmann Rearrangement

Hofmann Rearrangement Reaction Conditions					
Sample Designations	NaOH (%)	Temperature (Celsius)	Reaction Time (Hrs)	NaOCl (mL)	
W-30-1H	30	25	1	10	
W-30-2H	30	25	2	10	
W-40-1H	40	25	1	10	
W-40-2H	40	25	2	10	
W-50-1H	50	25	1	10	
W-50-2H	50	25	2	10	
C-30-1H	30	-10	1	10	
C-30-2H	30	-10	2	10	
C-40-1H	40	-10	1	10	
C-40-2H	40	-10	2	10	
C-50-1H	50	-10	1	10	
C-50-2H	50	-10	2	10	

3.2 Reaction Preparation Techniques

Polyvinylacrylamide (PVAA) was purchased from Carolina Biological Supply Company. This polymer was known to be 100% pure; however the exact molecular weight was not printed on the label. The PVAA was placed into solution, but the polymer chips simply absorbed all the water and swelled up to become large lumps of gelatinous material. A blender was used to break up the gelled material, and the shredded gel was diluted into water until a suitably liquid material was obtained. The ratio of polymer to water was approximately 20 grams of polymer gel per liter. All materials requiring weighing in this set of thesis experiments were measured using a Mettler-Toledo AB104-S type enclosed scale. 97% pure for ACS analysis sodium hydroxide pellets produced by Acros Organics were used to create two different stock solutions of concentrated base. Two separate one liter solutions were prepared by addition of hydroxide pellets, making 11M and a 15M solutions. Following the procedure outlined in Tanaka's paper [11], the PVAA solution was chilled to 0 degrees C using a Fisher Scientific Isotemp Refrigerated Coolant Model 910, and 10 mL of chilled 2M NaOCl bleach was added, followed by the addition of 2mL of chilled 15M NaOH. The solution was cooled further to -10 degrees C, whereupon an additional 65 mL of chilled 11M NaOH was added. The solutions were allowed to stand for 24 hours, remaining chilled.

After the polymer solution was finished reacting, the polymer was removed from solution via precipitation with 99.8% pure methanol, purchased from Sigma-Aldrich. A white solid was successfully formed, however very little total mass was recovered, less than half a gram. Using this procedure, it was judged that the dilution factor necessary to counteract the

gelation of the PVAA was too extreme, and that too little polymer mass was actually present in solution. Without enough material to perform the requisite analysis, this polymer was discarded and another stock material was procured.

A second raw material, produced by Aldrich Chemistry, was later used. This new pre-dissolved stock solution was 50% polyacrylamide by weight, and its average Mw was known to equal 10,000, much smaller than the original stock polymer.

Again following the Tanaka procedure, a solution was prepared using 5 grams of 50% polymer solution, chilled to 0 degrees C, and the two base solutions were added sequentially as before, following an identical procedure.

In an effort to improve polymer recovery, the solution was centrifuged at 2,500 RPM for 60 seconds using an IEC HN-SII 15,000 RPM centrifuge. With the majority of the polymer at the bottom of the test tube, the solution was decanted to remove the majority of the base/bleach solution. The remainder of the polymer solution was rinsed three times with methanol to precipitate the solid material and remove any lingering active reaction agents in order to halt continued reaction.

After rinsing was complete, the solidified polymer was placed into a small glass vial and inserted into a desiccator for 24 hours in order to evaporate all lingering methanol. The polymer produced in this way was sealed and stored for future examination. This process was repeated several more times to gain competence in decanting and preparing solid polymer. Having established the viability of the Tanaka procedure for producing polyvinyl amine and gained experience in its use, the procedure was tested under new conditions in the hope that a more streamlined process could be identified.

Based on the literature surrounding this polymerization reaction, it was hypothesized that the long standing time for the reaction might be unnecessary, as the reaction should proceed to completion within about an hour. Examination of differing levels of base concentration and its effects on the final product was also performed. Finally, a comparative analysis of reaction temperature was performed, reacting a sample at warmer room temperatures of 25 degrees C for every sample reacted at chilled temperatures.

Another set of reactions were performed using a larger 25 g of polymer solution in order to ensure that a sufficient mass of solid polymer could be obtained. 6 samples were prepared, 3 to be reacted at 0 degrees C and three to be reacted at 25 degrees C room temperature. Each set of three was exposed to different concentrations of base, 30% (7.5M), 40% (10M), and 50% (12.5M), in order to examine the effects of varying base concentration. The two sets of warm and cold samples were exposed to a modified condensed reaction. To the cold reactions, 65 mL of chilled 30%, 40%, and 50% base were added, respectively. 10 mL of chilled NaOCl bleach was added to each sample. Likewise, to the three warm reactions, 65 mL of room temperature 30%, 40%, and 50% base were added, respectively. 10 mL of room temperature NaOCl bleach was also added to each room temperature sample. For the larger samples of polymer, roughly half the volume of polymer was withdrawn from the reaction vessel after one hour, centrifuged at 2,500 RPM for 60 seconds, and decanted.

Each 1-hour sample was rinsed with methanol three times and desiccated for 24 hours, then was sealed into a glass vial for storage. The same process was repeated after two hours to remove the rest of the sample from solution, clean it, and store it. Removing part of

each sample at 1 and 2 hour intervals permitted examination of the time variable in this process.

3.3 Analysis of Products

3.3.1 Intrinsic Viscosity Measurement

Following the production of samples with sufficient mass, an Ubbelohde Cannon type 1C E396 viscometer was used to examine the flow rate of each polymer sample. This viscometer proved to have an excessively large capillary and passed samples through much too quickly for useful data to be obtained. A second viscometer was tested, this time a Cannon type 25 121, which proved to have very long effluent times. To find an appropriate middle ground, a third Cannon OB viscometer was used which gave values in a more reasonable time frame.

For the viscometry experimentation, 1 gram of polymer was dissolved in 200 mL of distilled water to produce a .5% solution of polymer. 20 mL of this solution was added to the viscometer and eluted three times. Each time, the elution time was recorded and then the average of the three values was calculated. Next, 10 mL of .5% solution was diluted with 10 mL of water to produce a .25% solution. The same procedure was followed, eluting three times, recording the travel time for each measurement, and averaging the three values. Finally, a solution of 5 mL .5% solution was diluted with 15 mL of water to produce a .125% solution. This solution was examined via the same viscometry methods described above.

The viscometry data was plotted on Excel 2007 in the form of Huggins and Kraemer plots, and the slope and k values were obtained by plotting linear regression lines [20]. The value η is defined as the relative viscosity and η_0 is defined as the solvent viscosity. Both of these values were obtained through direct viscometry measurements as previously described. When neutral polymers are in solution, the calculated Huggins and Kraemer plots will have

slopes which intersect at a single value, known as the intrinsic viscosity. This value indicates how tightly coiled a given polymer is in a given solvent, and ranges from about .5 of tightly coiled polymers to a maximum of 2 for fully extended rigid rods. If the solvent type is held constant, but different samples of a polymer produce different values for the intrinsic viscosity, then those samples likely have different molecular weights, all else being held equal. If given the calculated intrinsic viscosity η and K-A values obtained from literature, the Mark-Houwink equation $[\eta] = K M^a$ may be used to calculate M, the polymer's molecular weight.

3.3.2 Acid-Base Titration of Amine Functional Groups

Acid-base titration was performed in order to quantify the amount of amine functional groups on the copolymer produced by experimentation. To prepare for the titration, 1 liter of .5 molar NaOH base solution was prepared. This base solution was standardized using KHP. 1 gram of KHP was dissolved into 200 mL of distilled water. 3 drops of phenolphthalein indicator were added to the solution of KHP, and the pH was recorded using a clean, calibrated pH electrode. A 50 mL buret was filled with NaOH solution, and the meniscus was zeroed. The KHP solution was titrated incrementally, and the pH was recorded at each increment along with the volume of base used. When the endpoint was near, smaller increments were used. A curve was plotted for the standardization titration and was used to determine the true standardized molarity of the NaOH solution according to Equations 3.1 and 3.2.

$$\frac{(1 \text{ g KHP in solution})}{(\text{Molar weight of KHP (204 g/mol)})} = .0049 \text{ mol KHP in solution} \quad (3.1)$$

$$\frac{(.0049 \text{ mol KHP})}{(.01975 \text{ L titrated NaOH})} = \text{Standardized Molarity of NaOH} = .248\text{M} \quad (3.2)$$

Before titrating the polymer, 1 gram of material was dissolved in 50 mL of .1 M HCl to ensure a small excess of acid. A pH electrode was inserted into the acid solution and the initial pH was recorded. The 50 mL buret was charged with 50 mL of standardized NaOH base and leveled to the meniscus. This base was then added incrementally to the acid/polymer solution and the pH at each increment was recorded. After the inflection point

was passed and the solution became basic instead of acidic, more base was added until the pH exceeded 10, to ensure that the titration was complete.

3.3.3 Fourier Transform Infrared Spectroscopy

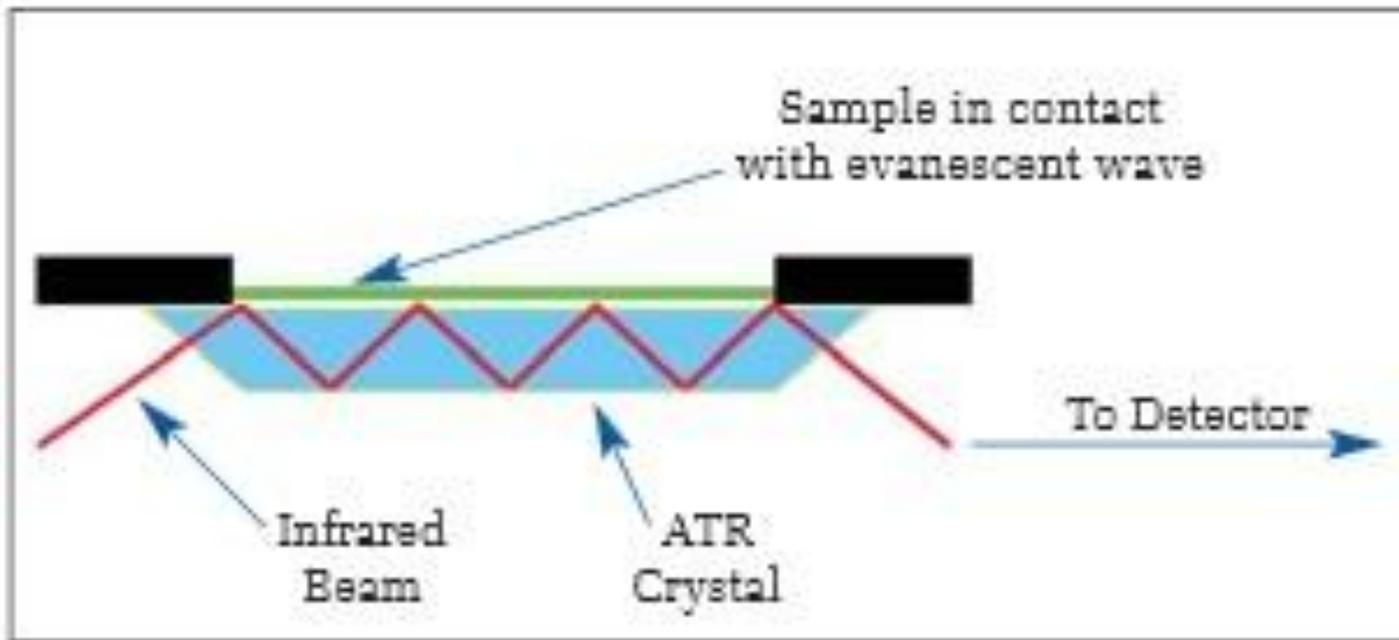
Fourier Transform Infrared (FTIR) spectroscopic analysis was performed using a Nexus 470 FT-IR ESP instrument with 10 micron viewing area manufactured by Nicolet. The parameters of the analysis set the number of scans to 64, resolution at 4, correction to ATR, and interferogram gain set to 2 for optimum spectral readability. Background was collected every 30 minutes to ensure minimal moisture and CO₂ peaks observed in samples and to aid in sample data consistency over time. If excessive noise was noticed in the spectra, the background was recalibrated early. NH₂ is known to produce a strong, distinctive FTIR signal at around 1560 cm⁻¹, and amide groups produce a strong signal at approximately 1650 cm⁻¹, and these peaks were of primary interest to the examination.

NH₂ and CH₂ characteristic peaks were identified for each polymer sample and their absorption peak heights were calculated using Image J software. The path length for the samples was not known because some samples were gelatinous whereas others were solid. To obtain relevant data, the CH₂ absorption peak height at roughly 2950 cm⁻¹ was measured and used as a normalization yardstick because the Hofmann rearrangement did not interact with the amount of CH₂ present in the polymer chain, and therefore the total amount of CH₂ would remain constant between individual samples of closely similar mass.

Attenuated Total Reflectance (ATR) spectroscopy offered an enhancement to traditional FTIR analysis if liquid or gelatinous samples. Normally, liquids and gels must be cast into a thin film cell or compressed into a difficult to produce and maintain KBr powder matrix. The FTIR-ATR instrument instead utilized a crystal with very high internal refractive index values which redirected the infrared beam to strike the sample multiple times,

collecting data with each pass. This process is illustrated in Scheme 3.1. Using ATR instruments permitted the sample to simply be compressed onto the ATR crystal by using a pressure arm, obviating the need for pellets or thin films [18]. ATR was considered an ideal methodology for this research because of the varying crystallinity and physical structure of the polymer samples produced. Because some samples formed hard plastic chips and others remained gelatinous and semi-liquid, multiple sample preparation techniques were needed for standard FTIR. ATR enabled a single instrument to analyze all samples as they were following Hofmann rearrangement. Without varying sample preparation techniques, instrumental and operator error were greatly minimized, and reduced sampling times immensely.

Scheme 3.1. Schematic of ATR analysis process [18]



By dividing the acrylamide C=O absorption peak heights by the CH₂ peak height, Equation 3.3, the relative amount of C=O in each sample was calculated.

$$\frac{(\text{Abs C=O (1650 cm}^{-1}\text{)})}{(\text{Abs CH (2950 cm}^{-1}\text{)})} \quad (3.3)$$

These values were related to percent conversion of acrylamide groups into amine groups by multiplying the volume of NaOH solution titrated by the calculated molarity of the standardized base, .248 M. As shown in Equation 3.4 this calculation provided the moles of amine in each 1 gram sample of reacted polymer.

$$\text{Vol NaOH (mL)} \times \text{NaOH Molarity (M)} = \text{Moles of Amine/gram} \quad (3.4)$$

Dividing the known polymer sample weight by the calculated number of moles of amine gives the molecular weight of the overall structure carrying the amine group, presented in Equation 3.5.

$$\text{Vol NaOH (mL)} \times \text{NaOH Molarity (M)} = \text{Moles of Amine/gram} \quad (3.5)$$

From this value, the 43 g/mol molecular weight of the vinyl amine group was subtracted to leave only the molecular weight of acrylamide groups. The remainder was

divided by the 71 g/mol formula weight of acrylamide in Equation 3.6, which indicated the multiples of acrylamide groups present in the overall structure.

$$(\text{Sample Weight (g)})/(\text{Amine (mol)})=\text{Structure Molecular Weight} \quad (3.6)$$

Taking the number obtained from Equation (3.6), the percent conversion was calculated using Equation (3.7), and all 4 samples were evaluated using this methodology.

$$(\text{Structure Molecular Weight (g)}- 43 \text{ g/mol})/(71 \text{ g/mol})=\text{X acrylamide groups} \quad (3.7)$$

3.3.4 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was utilized to examine the glass transition temperature and melting point of the stock polyvinyl acrylamide polymer and selected samples of the copolymer produced in the laboratory. A Perkins Elmer Diamond DSC with Intracooler was used, running a program to heat the sample from -50 degrees C to 200 degrees C at a rate of 30 degrees C per minute. Graphs of the heating curve were obtained and glass transition temperatures were extrapolated based on observed inflection points. Melting points were calculated based on observed maximum peak heights. Qualitative comparisons of the different heating curves were obtained.

CHAPTER FOUR

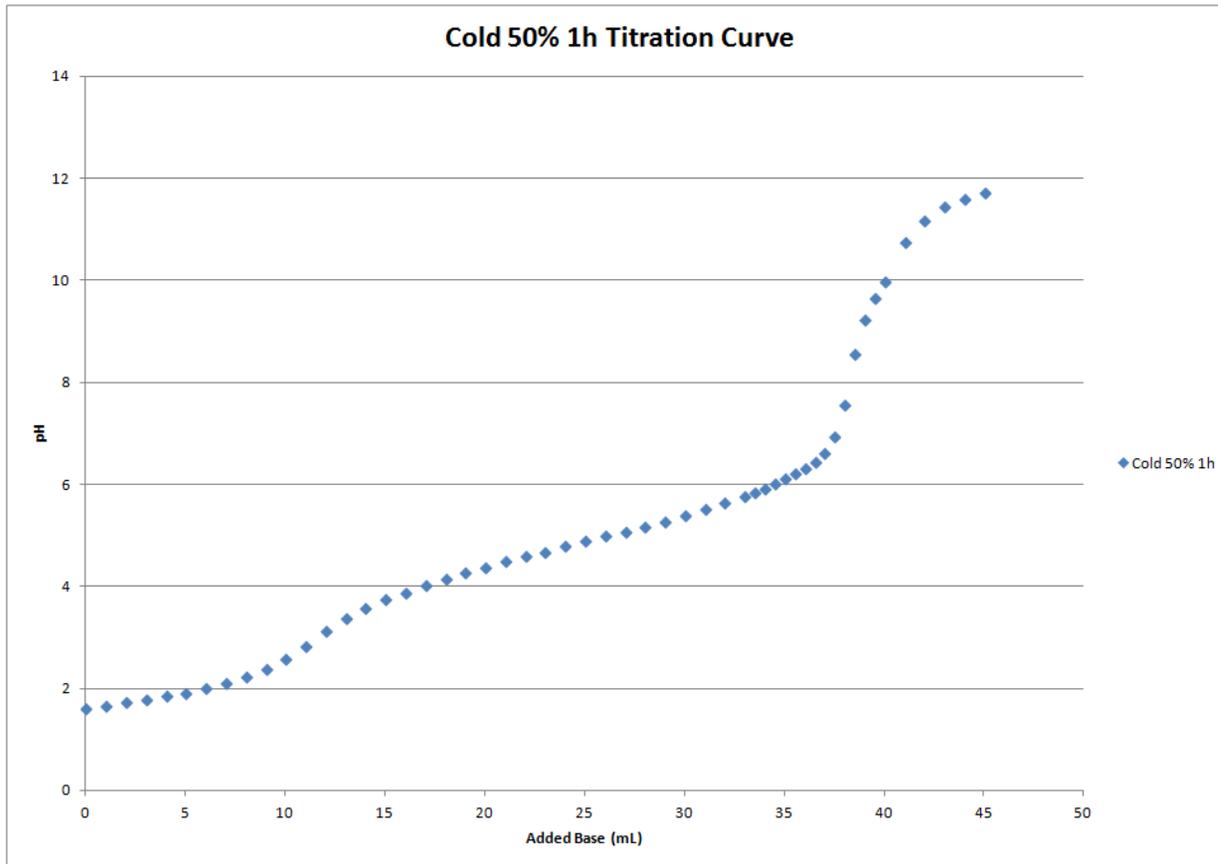
4.1 Titration of Acidified Amine Functional Groups

Direct measurement of the amine content of four polymer samples was performed using acid-base titration. By adding excess HCl to a dissolved polymer solution, each NH_2 amine group became protonated to the NH_3^+ acidified form. Every unit of NaOH base added to the acidified polymer solution introduced a single OH^- ion, which restored the protonated amine groups to charge neutrality by removing a hydrogen atom. Because each NaOH molecule neutralized a single unit of acidified amine, the molar amount of NaOH base added was therefore directly equal to the molar amount of NH_2 amine present on the polymer in a 1:1 ratio.

The converted copolymer produced was a weak base, and two inflection points in the titration curve were observed, as shown in the example Scheme 4.1. Further titration curves are located in Appendix A. The volume of base added was calculated by estimating the midpoint of each inflection point, and subtracting the larger volume from the smaller volume. The moles of base titrated into the acidified solution were calculated by multiplying the volume of NaOH solution titrated by the calculated molarity of the standardized base, .248 M. Equation 4.1 provided the moles of amine in each 1 gram sample of reacted polymer.

$$\text{Vol NaOH (L)} \times \text{NaOH Molarity (M)} = \text{Moles of Amine/gram} \quad (4.1)$$

Scheme 4.1. Titration curve of PVAm copolymer showing 2 inflection points



4.2 FTIR Spectroscopy and Relative Peak Heights

The FTIR spectra obtained for the various polymer samples showed the strongest indication that the Hofmann rearrangement reaction had indeed succeeded in converting acrylamide functional groups to amide functional groups. Scheme 4.2 shows the original, unreacted PVAA stock polymer. The most notable peak on this absorption spectrum for the purposes of this research was the strong C=O peak visible at approximately 1650 cm^{-1} , a distinctive signature of the acrylamide functional group.

Comparatively, at the extreme ends of the reaction conditions, very different spectra were obtained. As evidenced by Scheme 4.3, sample C-30-1H shows an extremely prominent absorption peak at 1558 cm^{-1} , clearly indicating the presence of primary amines. This peak is totally absent in the stock PVAA spectrum, confirming that no amine was present on the stock polymer, and therefore must have come from the Hofmann rearrangement reaction. Theoretically, sample C-30-1H had the least total conversion to amine functional groups, because colder reaction conditions slow the reaction progress, and removing product after only one hour of reaction might have interrupted conversion. Additionally, reducing the concentration of base favored preventing polymer degradation but impeding functional group conversion. The observed peak heights of C=O groups from stock PVAA and the NH_2 peak from converted PVAm segments of the copolymer were relatively equal, which indicated large sections of remaining unreacted PVAA.

Scheme 4.4 shows the spectrum of sample W-50-2H at the other extreme of Hofmann optimization experimental conditions, with maximum base concentration, maximum reaction time, and maximum theoretical rate of reaction under warm kinetic conditions. Under these

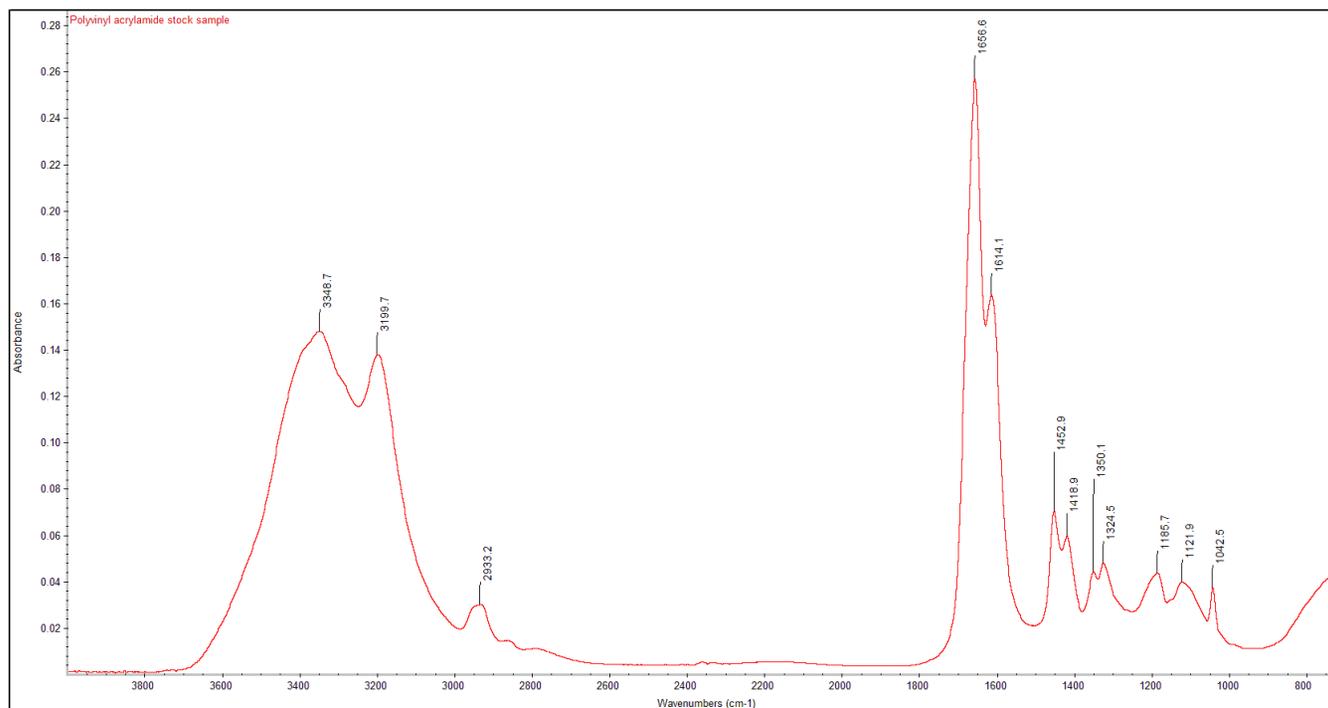
reaction conditions, it became clear that the relative NH_2 and $\text{C}=\text{O}$ peak heights, and therefore relative quantities of functional groups, were significantly imbalanced in favor of the amine product in comparison to the same two peak heights in sample C-30-1H. This qualitatively signified that the warm sample's conversion was significantly higher.

In total, 13 FTIR spectra were created, one for each reacted sample and the unreacted stock PVAA polymer. Plotting these spectra aligned with one another on the same axes permitted a comparison of relative heights of the important functional group absorbance peaks. Scheme 4.5 illustrates the varying shapes observed in each polymer spectra, indicating various changes in molecular structure from sample to sample. Further FTIR spectra are presented in Appendix B.

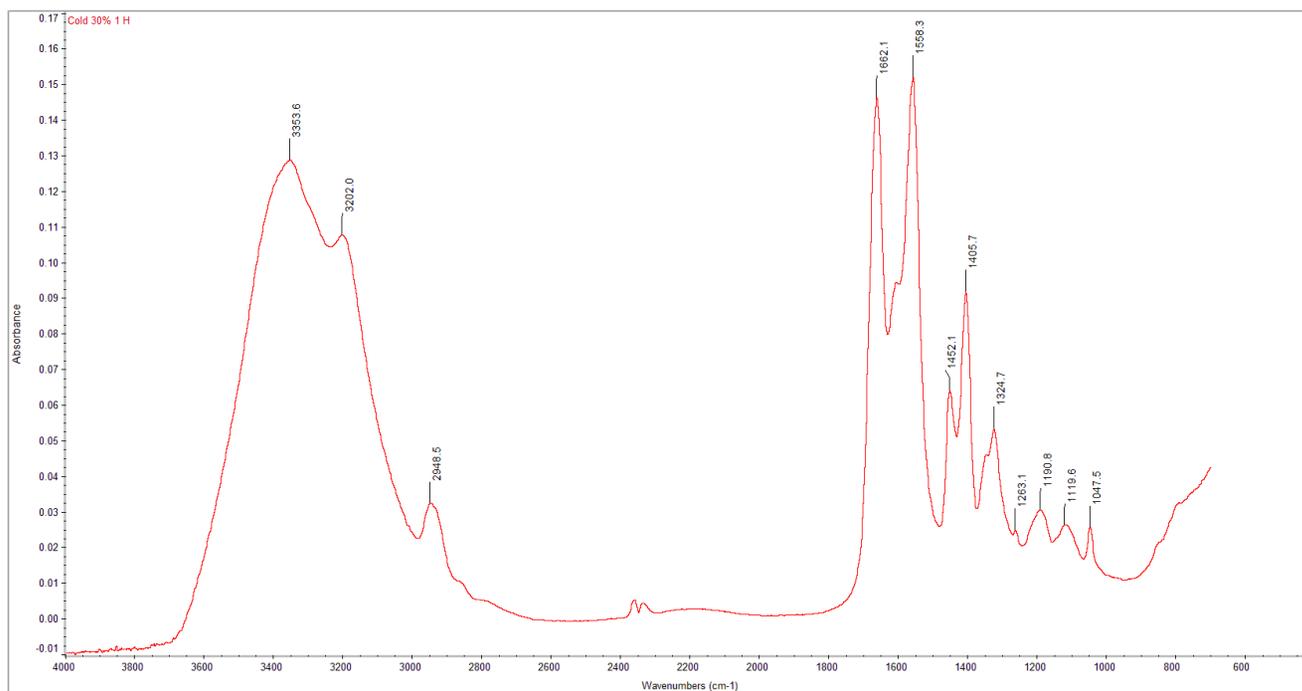
Assigning the titrated values of molar NH_2 present in selected polymer samples to the measured NH_2 functional group absorption spectra peak heights obtained via FTIR enabled production of a calibration curve relating peak height to amine content. From this calibration curve based on the equations outlined in chapter 3, a regression line was drawn and extrapolation of amine content for all samples was performed.

Scheme 4.6 illustrates the regression line and equation drawn using the titrationally measured amine quantities and the corresponding spectral peak heights.

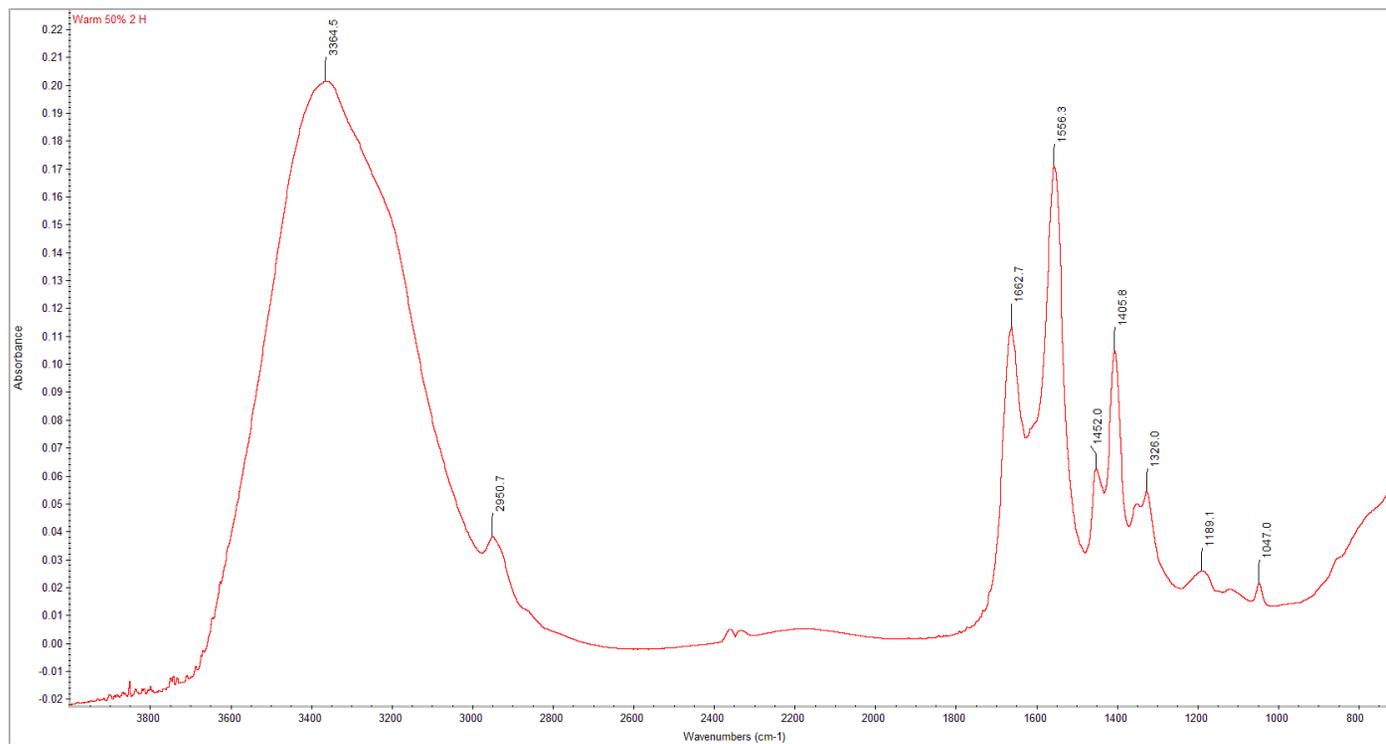
Scheme 4.2. PVAA stock polymer FTIR spectra before Hofmann rearrangement



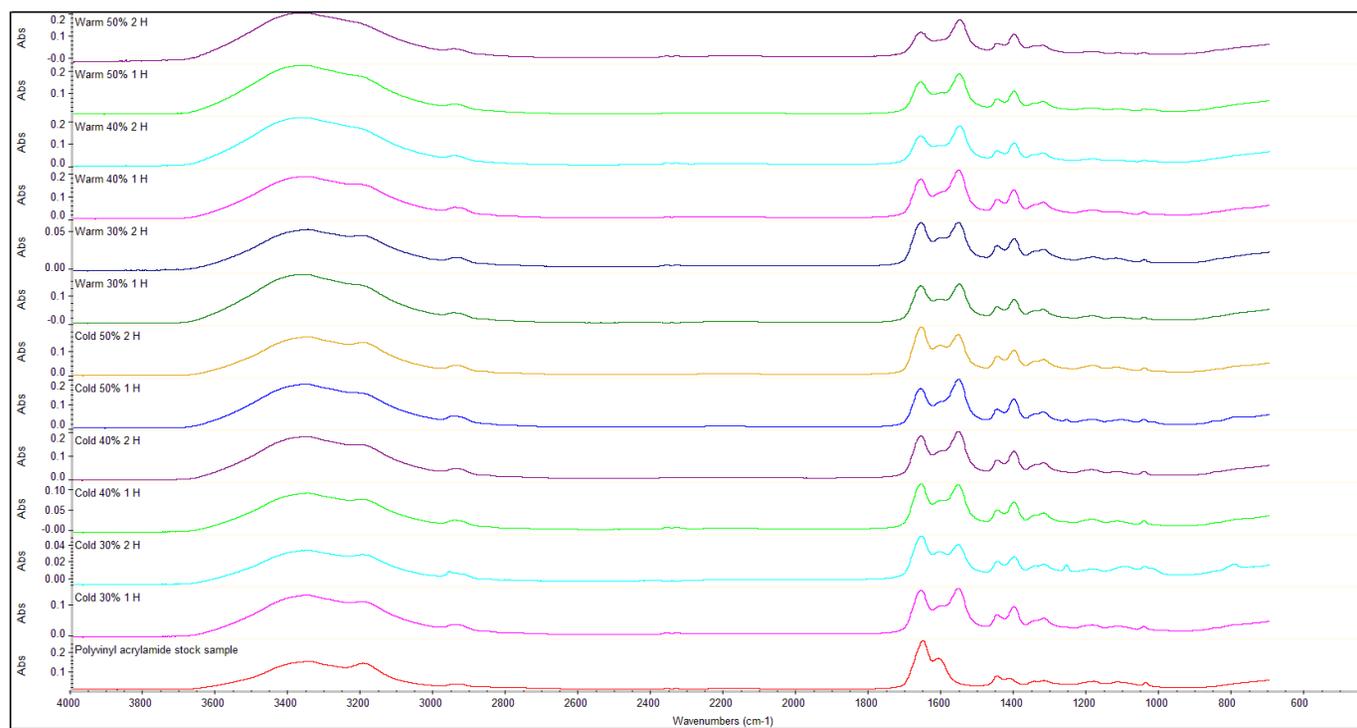
Scheme 4.3. C-30-1H FTIR spectra showing presence of amine peak at 1558 cm⁻¹



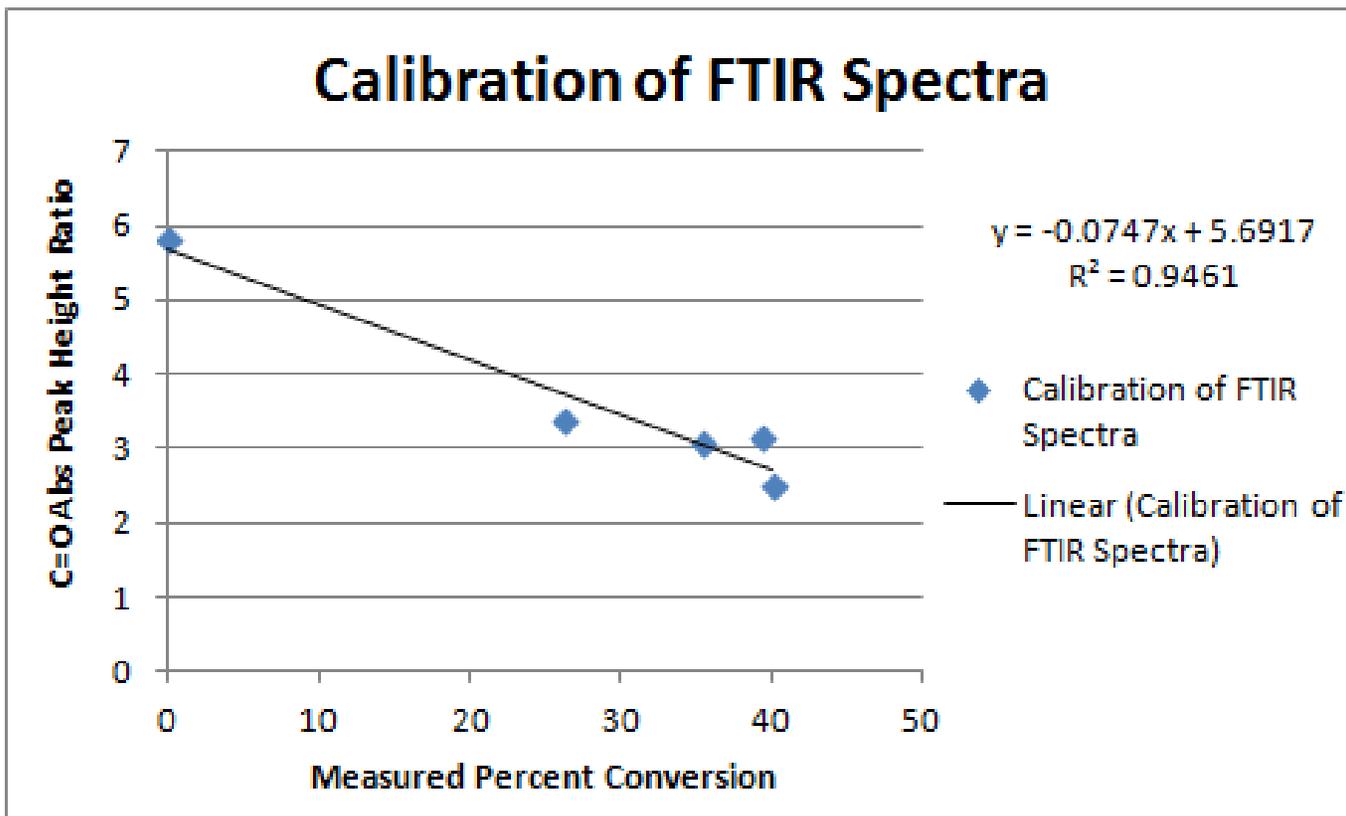
Scheme 4.4. W-50-2H FTIR spectra showing 1558 cm⁻¹ and 1650 cm⁻¹ peaks



Scheme 4.5. All FTIR spectra side by side illustrating overall differences



Scheme 4.6. Calibration using data from titration and peak height data from FTIR



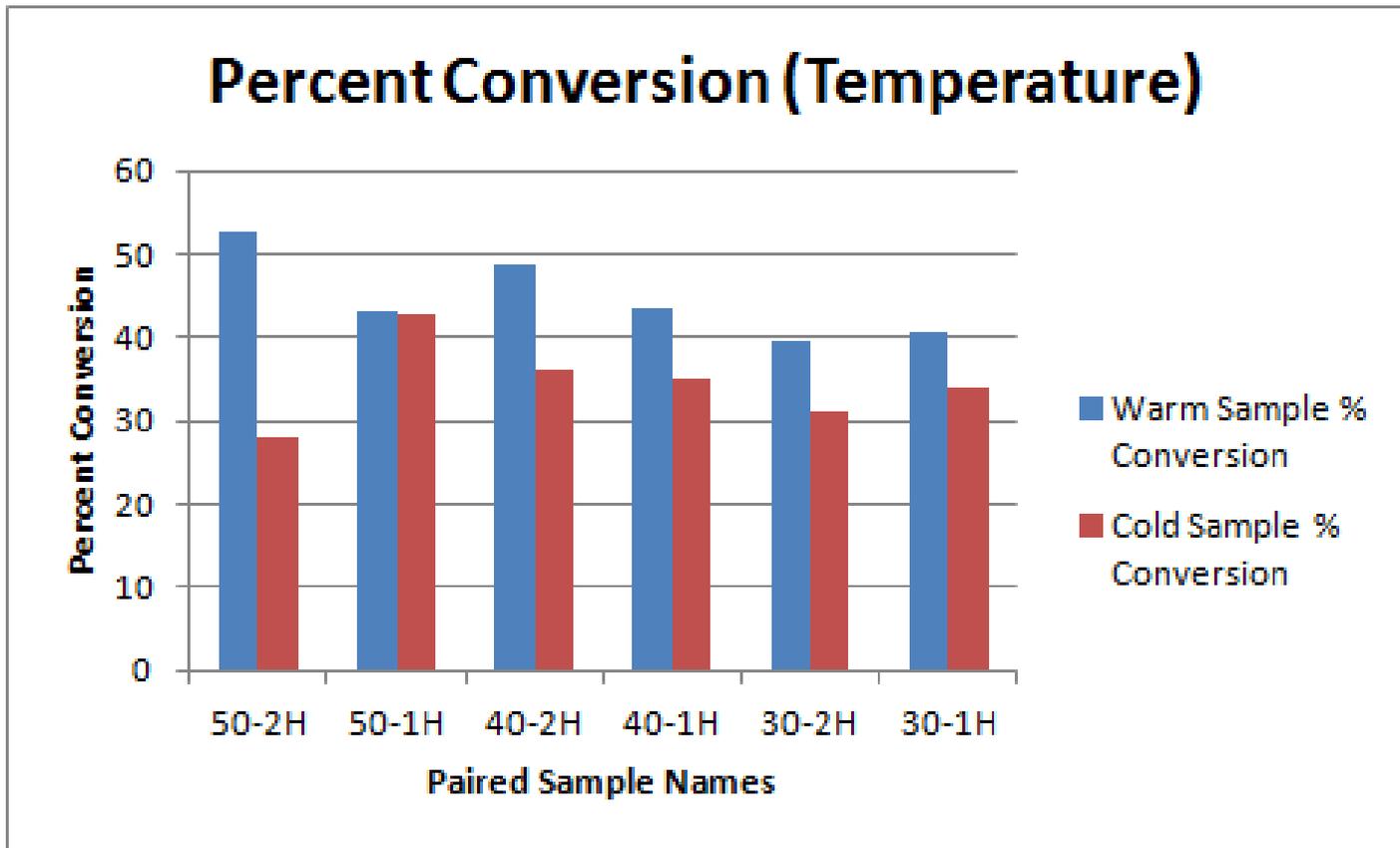
Scheme 4.7 compares the relative percent conversion for the samples created under room temperature conditions versus the samples created under cold conditions. It is clear from the collected data that in general, the room temperature polymer samples showed much higher percent conversion relative to the chilled samples. Though the relative difference was very small in the case of both warm and cold 50-1H samples, the trend was consistent across all samples examined. These findings were unexpected, because the literature indicated that cold reactions should have higher percent conversion than warm samples. One possibility is that the chilled reactions proceeded more slowly than expected due to altered reaction kinetics, and the reaction was not completed after two hours.

Analysis of the Hofmann rearrangement optimization with respect to NaOH concentration, displayed in Scheme 4.8, display strong correlation between increased base concentration and increased percent conversion. This matched well with predictions derived from the available literature, with the exception of the cold 2H polymer samples. Cold 1H samples followed the expected trend of increasing conversion with greater concentration of base, but after another hour had passed, it appeared that increasing NaOH concentration had little effect on the percent conversion to amine. In the case of cold 30% and cold 50% 2H samples, percent conversion actually decreased.

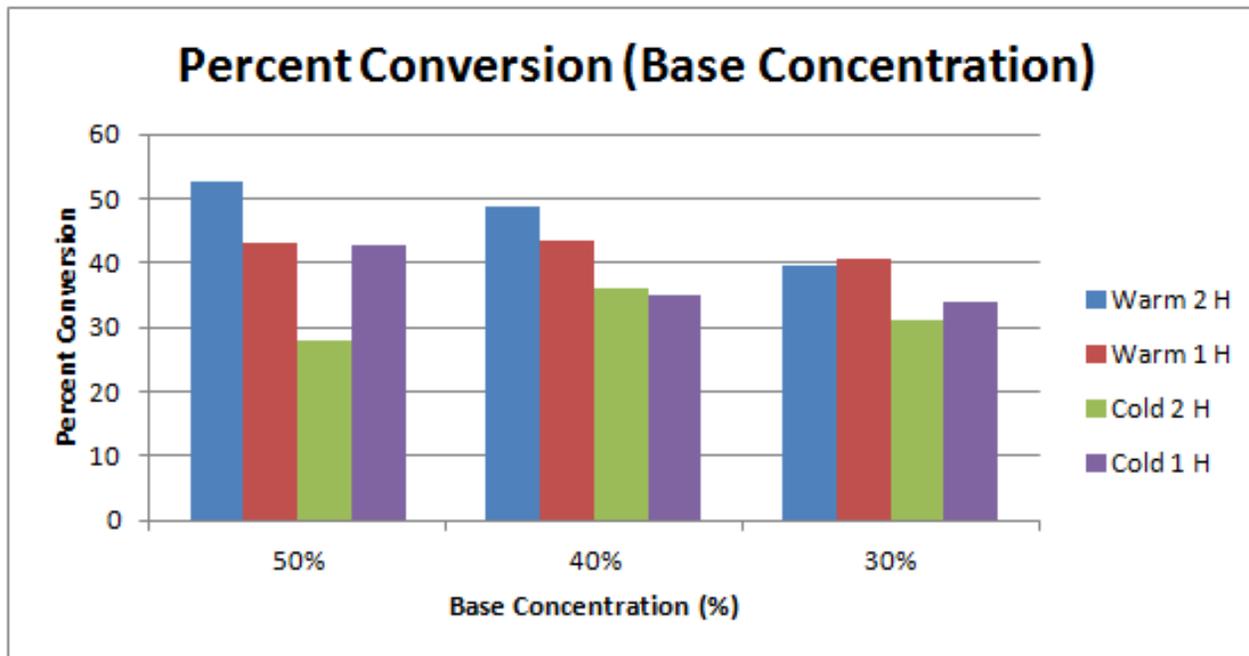
Most of the percent conversions after 1 hour were concentrated near each other, but after two hours, the variance between the highest and the lowest conversion became much greater, as illustrated in Scheme 4.9. This trend indicated that time does not have an easily interpretable relationship with percent conversion. Some samples continued to increase in percent conversion over time, while others actually lost amide functionality.

A likely culprit for decreasing amide functionality with increasing time was the possibility of acrylamide groups hydrolyzing into carboxylic acid which did not participate in the Hofmann rearrangement. By undergoing this hydrolysis process, illustrated in Scheme 4.10, nitrogen functionality was potentially lost during the reaction in the form of free NH_3 ammonia gas. It was therefore likely that hydrolysis of acrylamide groups was the primary competing reaction against the Hofmann rearrangement, consuming a portion of the initial acrylamide. Supporting this conclusion was the qualitative observation that every synthesized polymer sample emitted a strong smell of ammonia after Hofmann reaction completion.

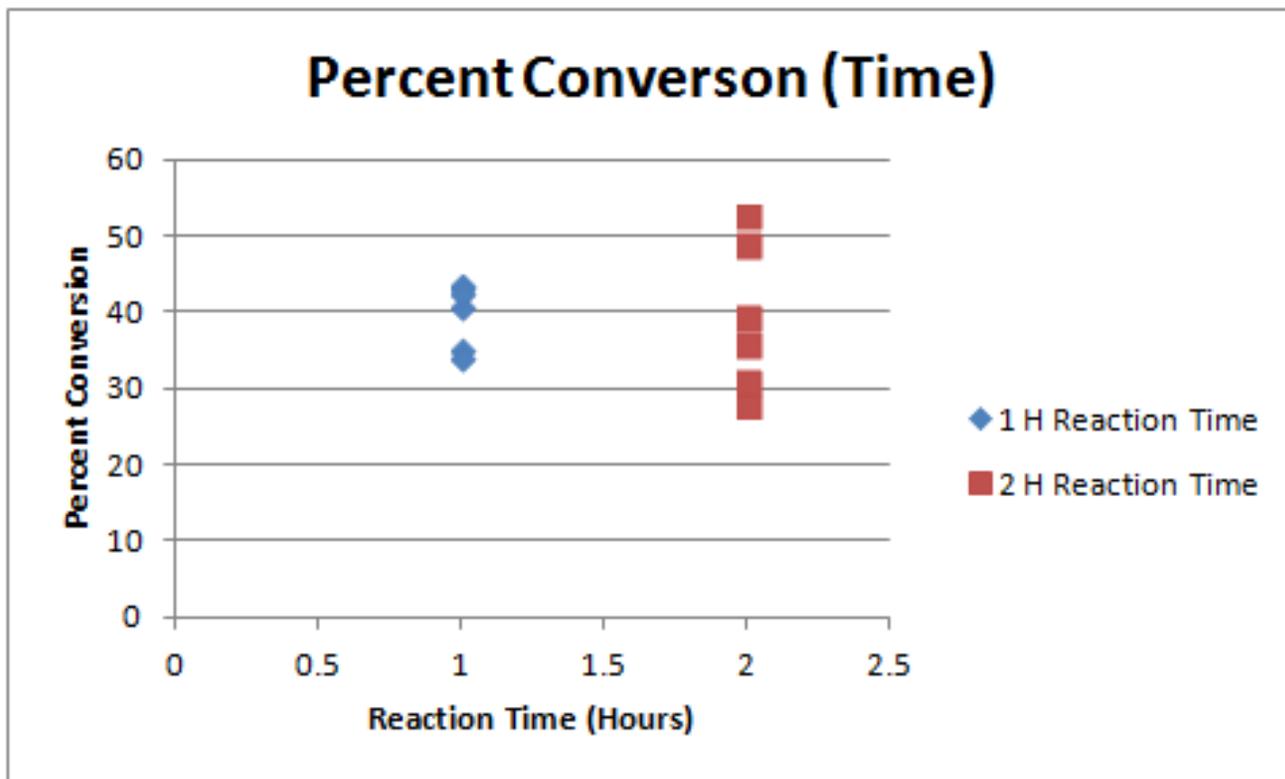
Scheme 4.7. Relative conversion with respect to temperature



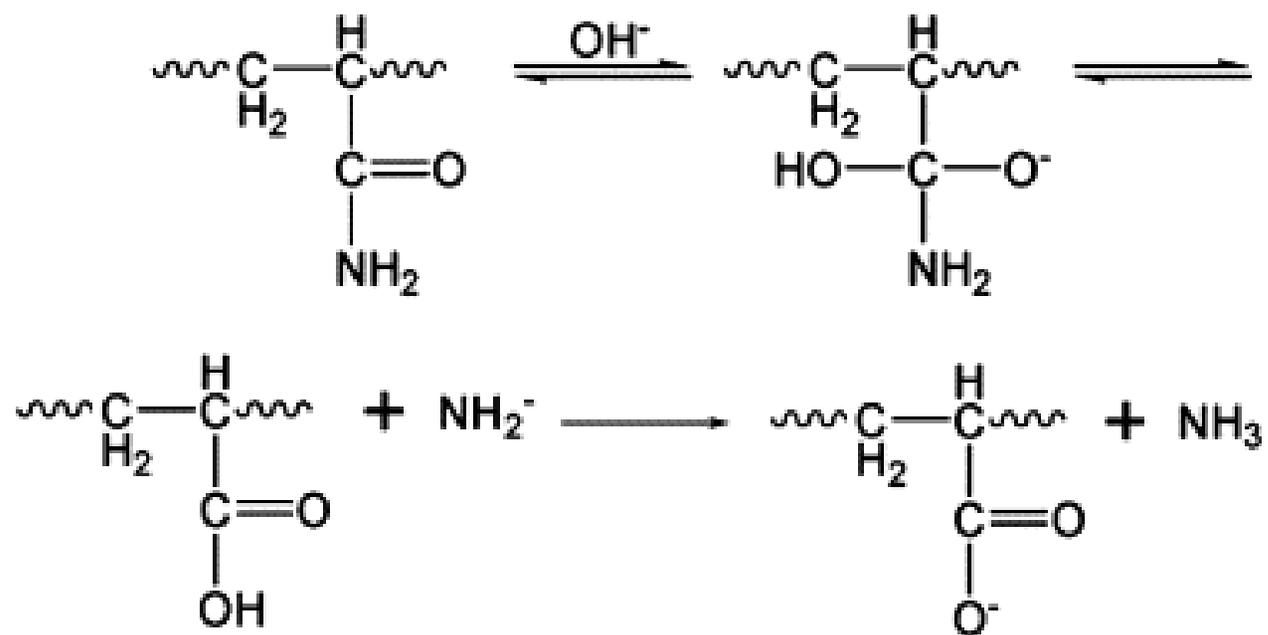
Scheme 4.8. Relative conversion with respect to base concentration



Scheme 4.9. Relative conversion with respect to time



Scheme 4.10. Hydrolysis of acrylamide to carboxylic acid [19]



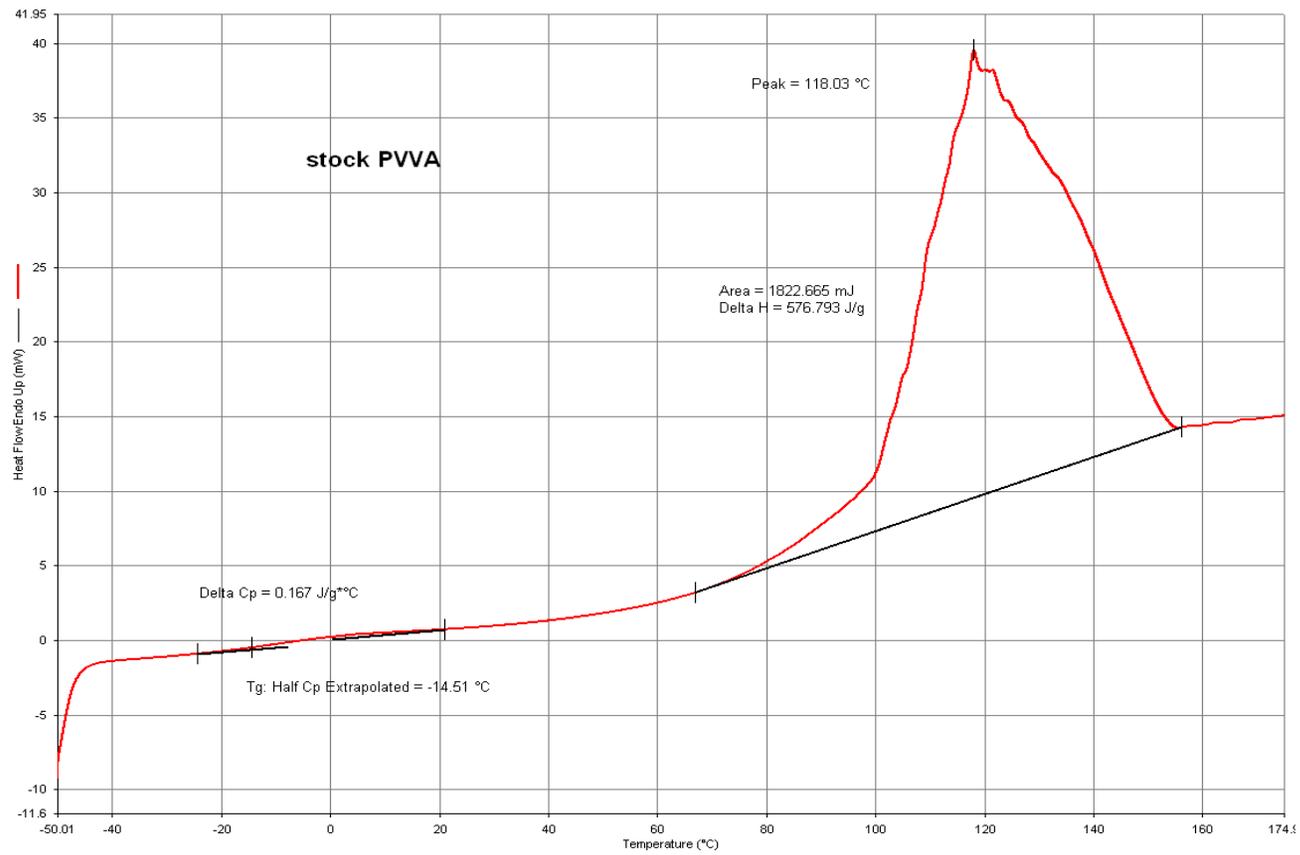
4.3 Differential Scanning Calorimetry

Thermal characterization of both PVAA and PVAm was almost entirely unreported in the available scientific literature. Categorizing the melting point (T_m) and glass transition point (T_g) of the polymer samples was therefore performed using DSC in order to provide preliminary findings. These results may prove extremely useful for future continuation of this work or categorization experimentation performed by other research groups. In Scheme 4.11, the melting point for the stock PVAA was calculated to be approximately 118°C , as evidenced by the single large peak visible in the figure. Comparing this graph to Scheme 4.12, a dramatically different picture was seen. That sample showed a slightly lowered glass transition temperature (T_g) and a significantly lowered melting temperature, (T_m). Similar results were observed in Scheme 4.13, with the notable addition of a second, scalloped T_m peak. In addition, Scheme 4.13 showed an increase in T_g of approximately 7°C . The drop in T_g indicated that the C-30-2H sample became less mobile, possibly as a consequence of losing bulky, flexible acrylamide groups and gaining small, inflexible amine groups. The scalloped peak in Scheme 4.13 likely signified that multiple polymer segments were present in the sample, including remaining PVAA, converted PVAm, carboxylic acid groups, and any other possible side products. Each copolymer segment theoretically produced a small melting peak of its own, but without established literature data for comparison, more in-depth analysis of the scalloped section was not possible.

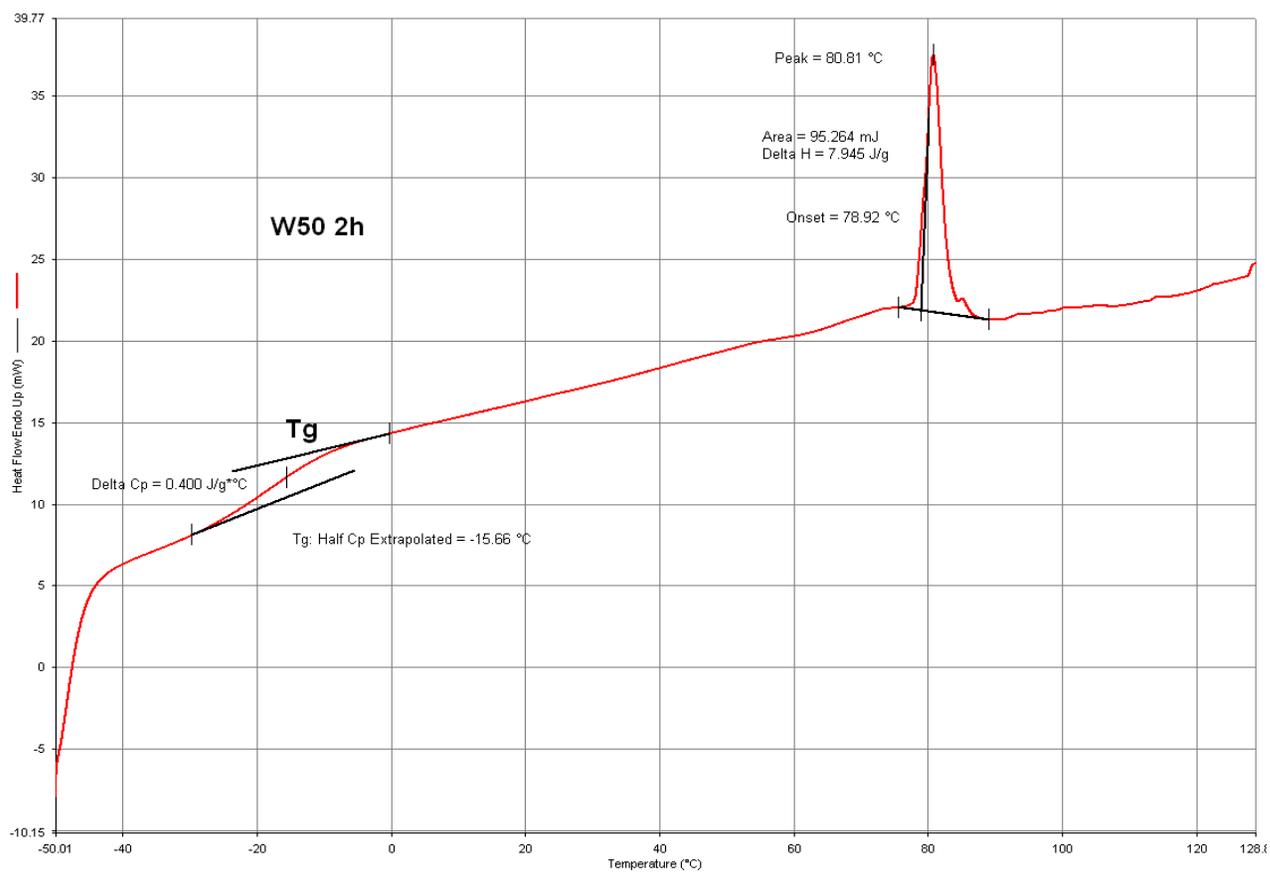
Ultimately, quantitative comparisons to literature data regarding the expected glass and melting transitions of these polymer samples could not be made, but the general trends are evident from the experimentally obtained heating graphs. It is possible that these are

among the first examples of pure PVAA and copolymers of PVAm copolymers whose transition temperatures have been investigated using DSC.

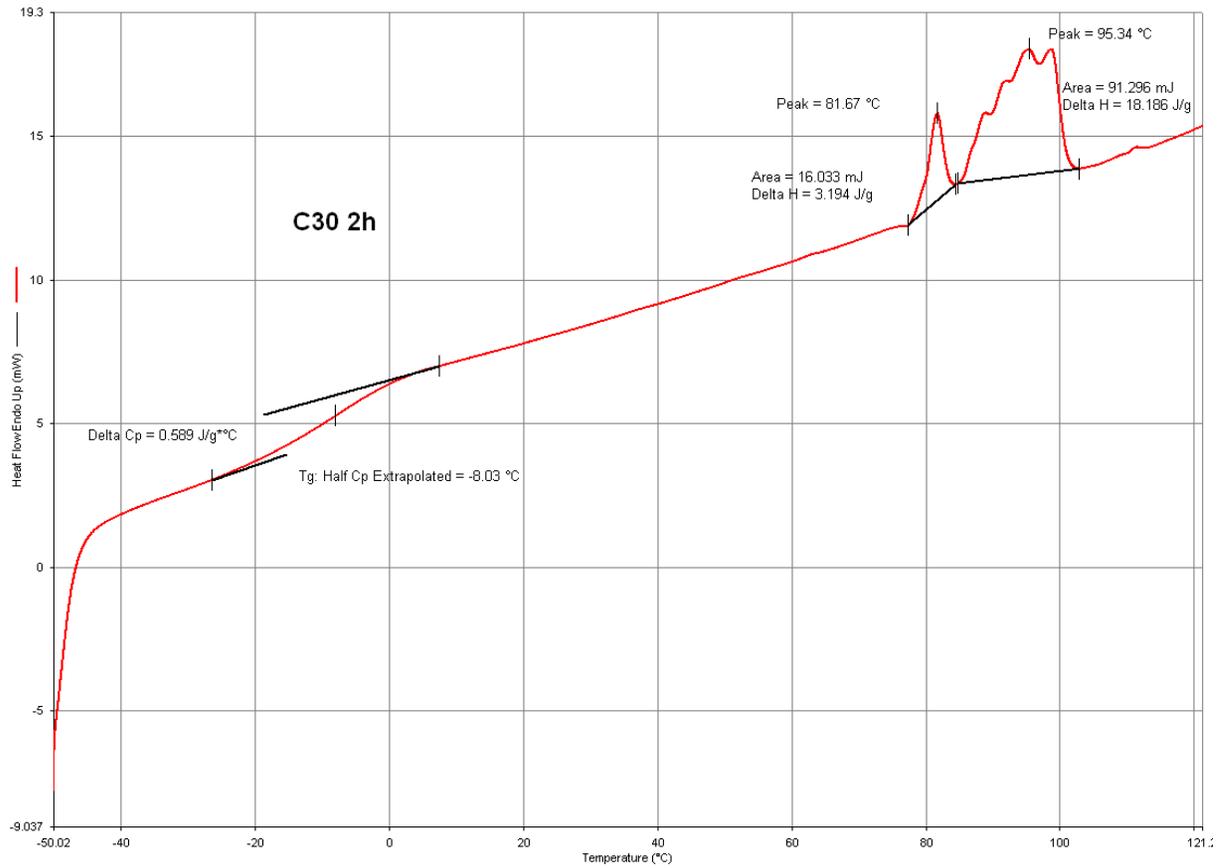
Scheme 4.11. Stock PVVA DSC data



Scheme 4.12. W-50-2H DSC data showing altered T_g and T_m



Scheme 4.13. C-30-2H DSC data with unusual scalloped secondary Tm peak



4.4 Viscometric Characterization of PVAm Copolymers

After performing dilute solution viscometry on the stock PVAA and converted polymer samples, the Huggins and Kraemer plots were calculated via linear regression based on the elution times through the viscometer for each sample. Because the literature did not provide established values for the Mark-Houwink equation relevant to PVAm, only relative measurements were obtained.

Producing the Kraemer plots required calculation of the inherent viscosity, $\ln(h / h_0)$ vs. concentration, and the Huggins plot required calculating the reduced viscosity h_{red} , which is equal to h_{sp} , the specific viscosity of the polymer, divided by the concentration of the solution. The copolymer of PVAA and polyvinyl amide (PVAm) was a polyelectrolyte in solution, and the Huggins plot had a negative slope rather than a positive slope as is typical for neutral polymers.

At low concentrations, polyelectrolytes have very similar looking Huggins and Kraemer plots, with similar slopes, and the difference becomes asymptotic as concentration approaches zero. While the Kraemer plot behaves as expected, having linear, negative slope, the Huggins plot changes behavior dramatically, with values for reduced specific viscosity approaching extremely large values at concentration = 0. An example is illustrated in Scheme 4.15. Greater concentrations of polymer at the beginning of dilution showed greater divergent tendencies. The two lines did not intersect at the y-axis, and because of this unusual polyelectrolyte property, a Mark-Houwink equation could not be calculated. The y-intercept of the Kraemer plot was used to estimate a relative value for the intrinsic viscosity of the PVAA/PVAm copolymers.

A clear trend did not develop with regard to molecular weight and polymer chain degradation during the Hofmann rearrangement. Almost all polymer samples showed some degree of degradation. Some samples showed an increase in relative molecular weight, which was interpreted to indicate possible formation of urea side groups which then crosslinked in solution, artificially increasing the mass of some polymer chains. However, the stock PVAA Huggins intercept was lower than most of the reacted samples' Huggins intercepts, indicating that its intrinsic viscosity, and therefore molecular weight, was higher. These relative values are given in Table 4.1. Decreases in molecular weight were attributed primarily to chain scission during Hofmann rearrangement, and some conversion of heavier acrylamide groups to lighter amine groups.

Scheme 4.14. Example viscometric plot of Huggins equation with polyelectrolytes. [21].

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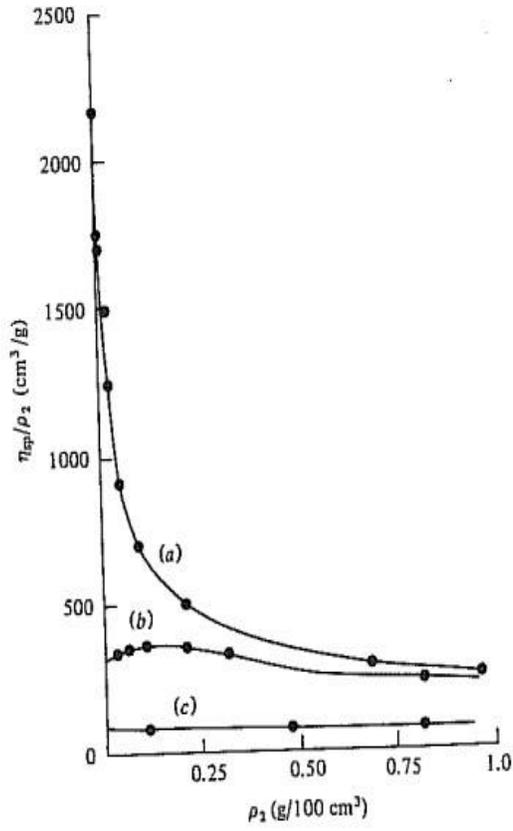


Table 4.1. Polymer samples with Huggins and Kraemer intercepts.

		Reaction Conditions versus Intercepts			
Sample		Huggins Intercept		Kraemer Intercept	
Stock Polymer		0.2806		0.285	
C-40-1H		0.5432		0.555	
C-40-2H		0.5028		0.5135	
C-50-1H		0.2424		0.2435	
C-50-2H		0.4436		0.4525	
W-30-1H		0.3553		0.36	
W-30-2H		0.4782		0.49	
W-40-1H		0.12		0.1195	
W-40-2H		0.22		0.2177	
W-50-1H		0.6589		0.68	
W-50-2H		0.4313		0.44	

CHAPTER FIVE

5.1 Summary

Polyvinyl acrylamide (PVAA) successfully reacted with NaOCl bleach active reagent under highly basic conditions to form a complex copolymer with structural units of vinyl amine, acrylamide, and acrylic acid. The reaction conditions for the Hofmann rearrangement were examined using aqueous solutions of concentrated bleach at constant concentration and varying concentrations of strong base, varying reaction temperatures, and varying permitted reaction times. The replacement of acrylamide functional groups via the Hofmann rearrangement directly influenced the chemical characteristics of the final copolymer, and had noticeable effects on the polymer's physical properties. Copolymer viscosity in solution decreased indicating that some chain degradation occurred, glass transition temperature and melting points generally decreased, indicating loss of crystalline regions. The reaction product structure was investigated via Fourier Transform Infrared (FTIR) spectroscopy and acid-base titrations primarily, and supporting examinations were performed using Differential Scanning Calorimetry (DSC) and dilute solution viscometry.

FTIR displayed a new absorption band at approximately 1560 cm^{-1} in all samples post-Hofmann rearrangement, which represented the increased quantity of NH_2 present in the final copolymers. The strong band representative of the amide remaining from stock PVAA at 1650 cm^{-1} remained present through all samples as well, but the relative quantity of amide to amine was demonstrated to shift in favor of the amine under warm conditions with high

base after the longest reaction times. This unexpected trend was identified consistently across most samples with only a few outliers.

Acid-base titration was exceptionally successful in relating the molar quantity of NaOH base titrated into acidic solution to the amine quantity of each polymer sample. By obtaining this quantitative data and associating amine content with amine FTIR peak height, titration enabled the use of FTIR spectra analysis in a quantitative rather than a qualitative fashion.

Viscometry measurements indicated qualitatively that the polymer presented signs of degradation under most reaction conditions. In general, higher quantities of base predominantly have the expected negative effects on chain length, but enough variance was present in the data that no clear trends emerged.

Differential Scanning Calorimetry indicated that complex reaction chemistry took place in the solution beyond the relatively simple primary Hofmann rearrangement. The scalloped appearance of the heating curve for the C-30-1H sample may indicate a terpolymer or even more intricate copolymer being systematically produced.

5.2 Future Research

Ultimately, the Hofmann rearrangement was successfully optimized under a wide range of conditions. For future research, more information is needed regarding identification of side reactions that may have occurred, as well as quantitative data obtained through further investigative methods like nuclear magnetic resonance. Viscometric measurements illustrated a more complex Huggins plot than was anticipated in the case of polyelectrolytes. Adding salt and dilute acid to the solution may counteract the charged nature of the polymer and enable a more standard Huggins plot to be obtained during future studies. Performing gel permeation chromatography and associating that data with a Huggins-Kraemer intersection point obtained through viscometry would enable identification of k - a values for PVAm copolymers which were unreported in the scientific literature.

Broadening the reaction conditions will be of great use in further quantifying this reaction. Increasing concentration of base may continue to improve percent conversion, and in the case of Hofmann rearrangements at cold temperatures, the run length of each reaction would be extended in order to ensure that the reaction proceeded to completion. Additionally, a superior method for removing the polymer from storage was needed. The glue-like nature of many samples made weighing and manipulating the polymers extremely difficult, contributing to a large quantity of sample mass loss as residue. Reducing this mass loss would permit reactions on a smaller, more efficient scale.

An extremely unusual result was obtained through experimentation which was totally unexpected. Both the stock PVAA polymer and the samples reacted at warm temperatures were a similar pale off-white color. However, many of the cold samples became extremely

deep blue, indicating the presence of unanticipated reaction chemistry. The scope of this research did not permit the investigation of this coloration, but it was hypothesized that the blue color may have derived from copper that was accidentally introduced into the cold samples. Where this hypothetical copper came from was definitely uncertain, because multiple experimental runs of cold samples all developed the same coloration, even using different glassware and different experimental locations.

Nevertheless, one of PVAm's most intriguing theoretical properties is a high affinity for chelating metals of all kinds, and future research should incorporate Atomic Absorption spectroscopy in order to confirm or deny the presence of copper on the post-Hofmann rearrangement polymers. Obtaining N₂ elemental analysis will also permit greater understanding of the unwanted side reactions of amide hydrolysis.

As described earlier in this thesis, acid-base titration experimentally determines the amine present, but N₂ analysis gives the nitrogen lost in the form of NH₃. Finally, experimentation to further understand the unusual polyelectrolyte nature of the PVAm copolymers, which possess both basic NH₂ groups and acidic acrylic acid groups, especially their interactions when dissolved into aqueous solution, may prove highly illuminating.

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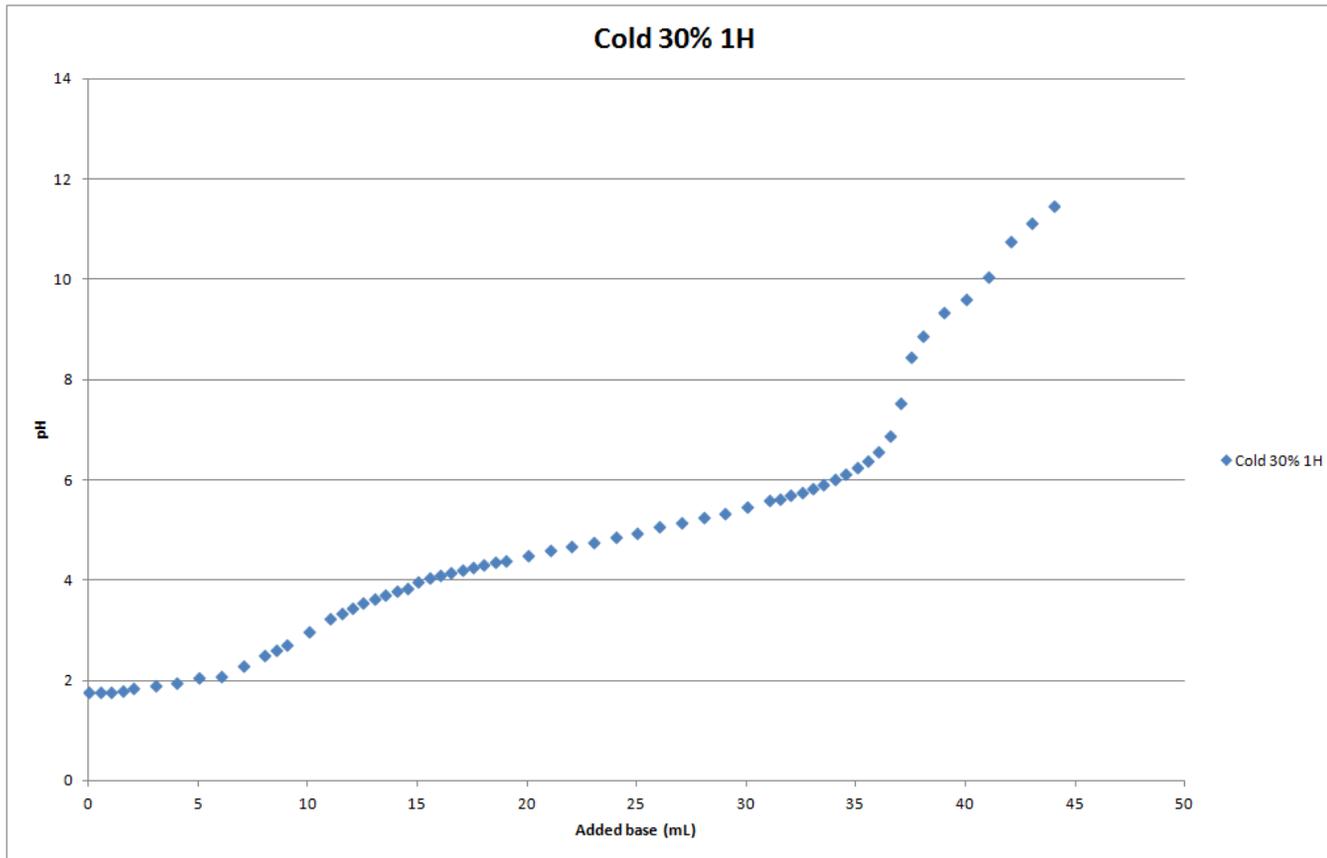
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APPENDICES

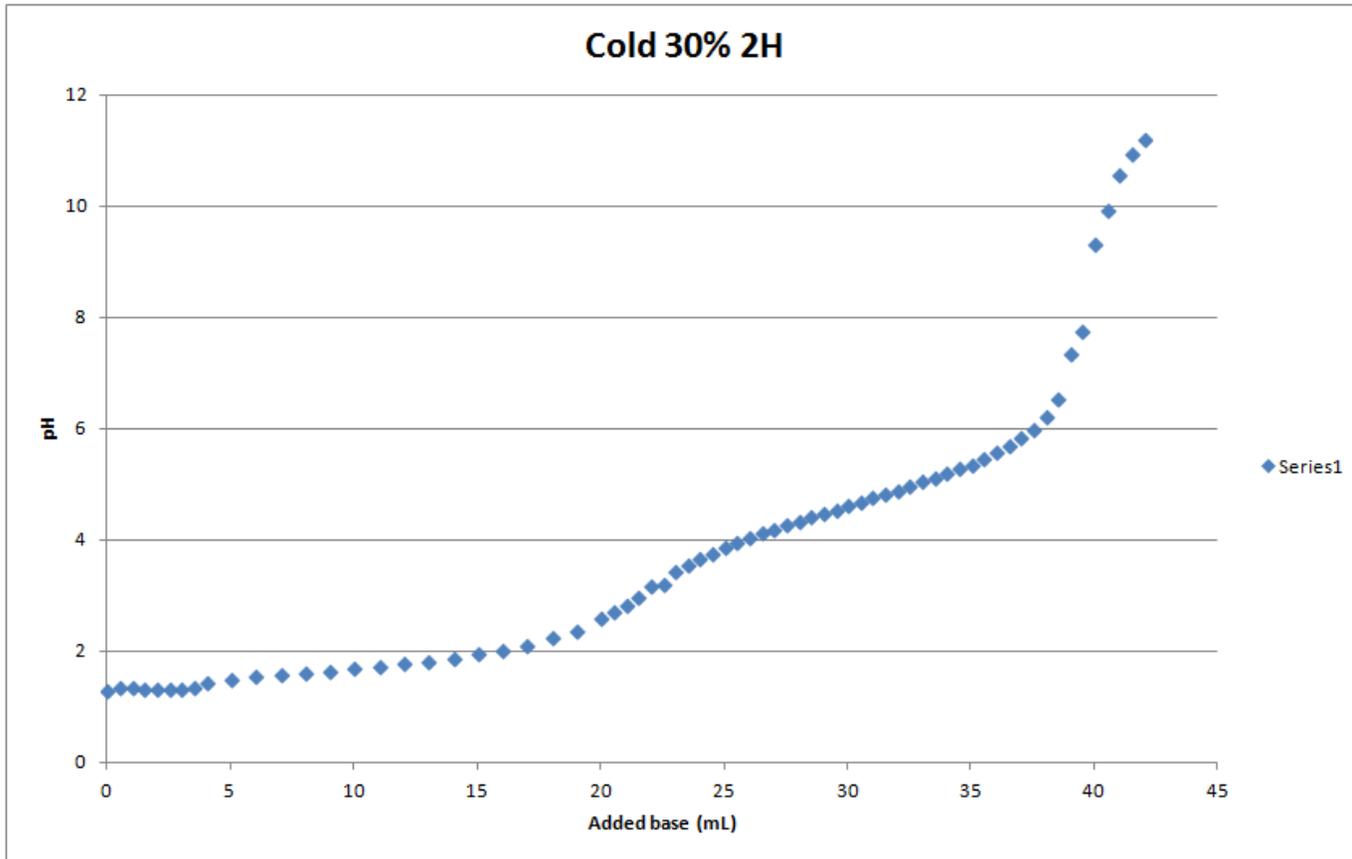
APPENDIX A

This appendix contains the supplementary titrations curves used to create the calibration regression for calculating percent amine on polymer samples.

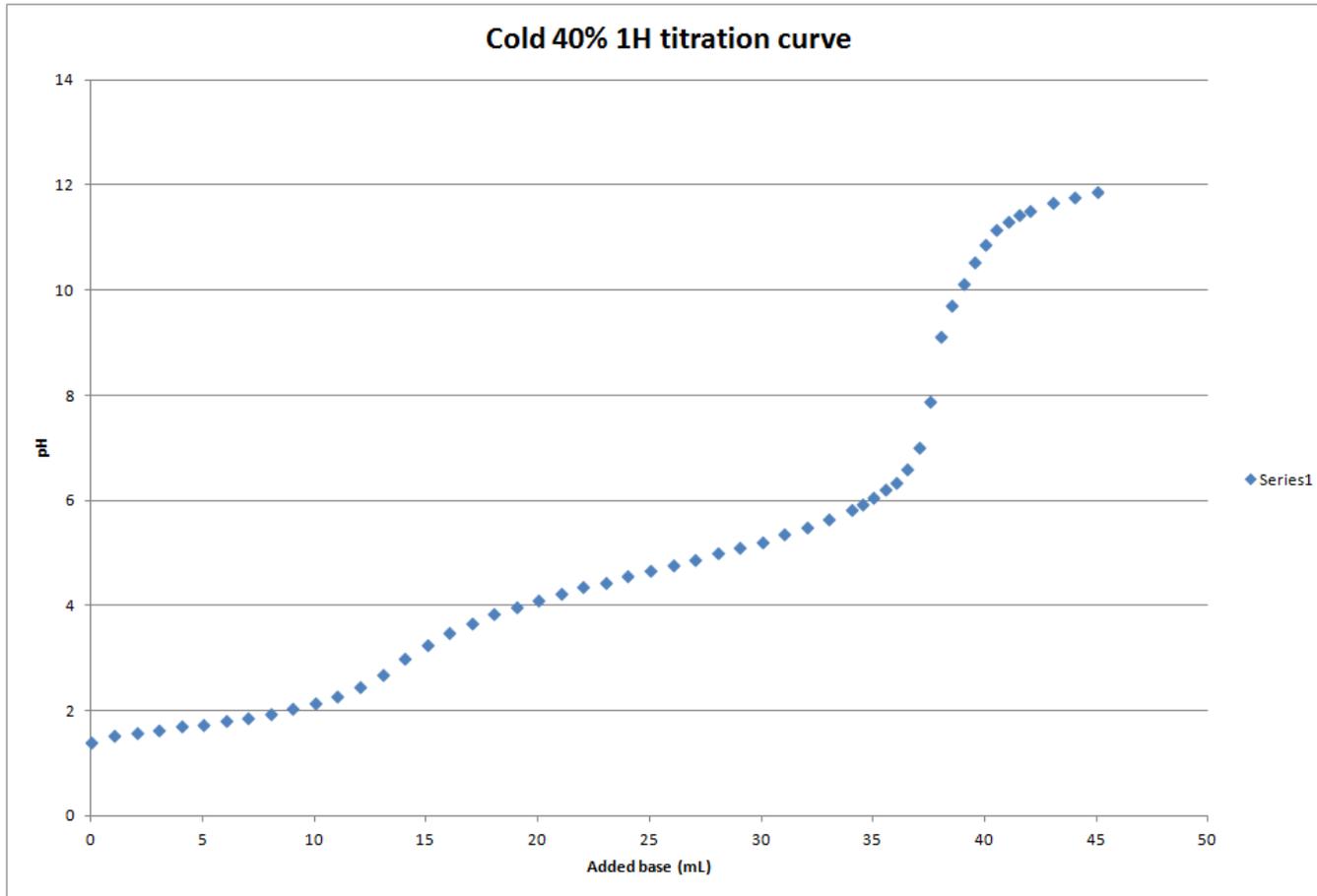
Scheme A.1. C-30-1H titration curve



Scheme A.2. C-30-2H titration curve



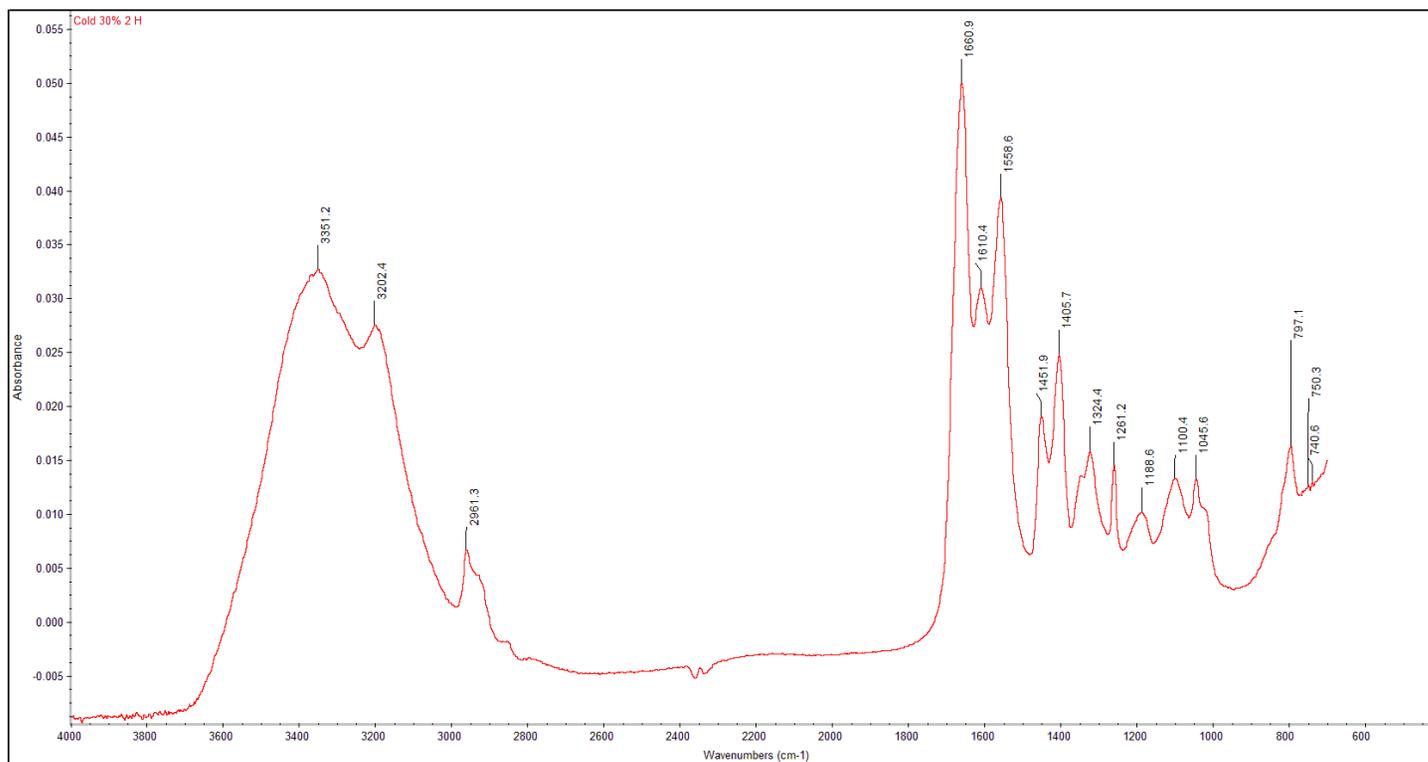
Scheme A.3. C-40-1H titration curve



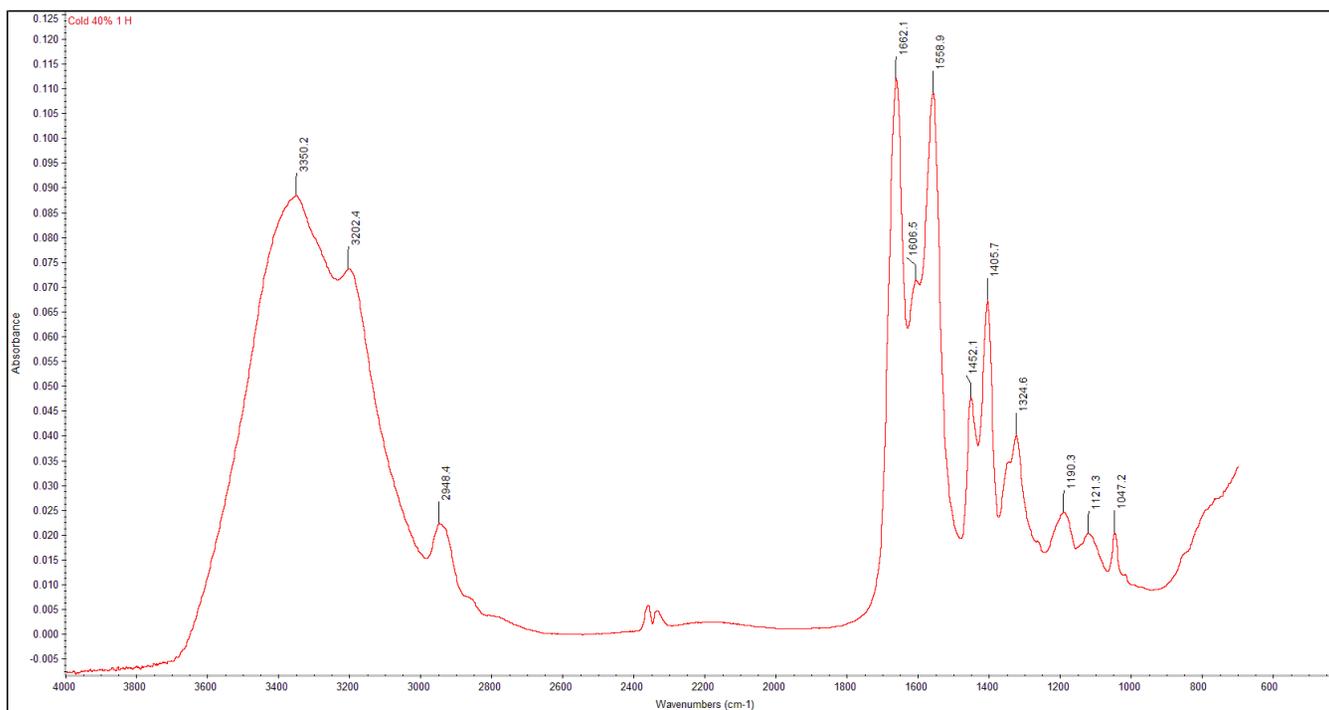
APPENDIX B

This appendix contains the supplementary FTIR spectra derived from analysis of PVAm copolymers.

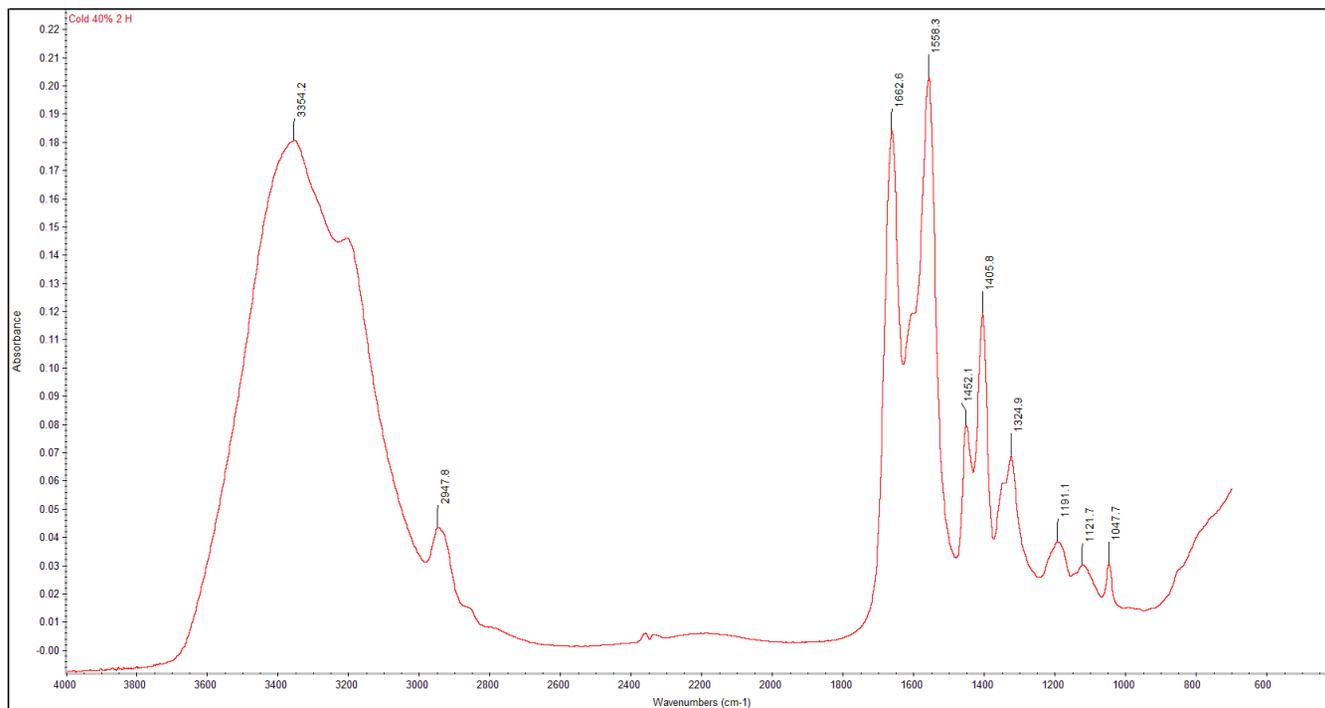
Scheme B.1. C-30-2H spectra



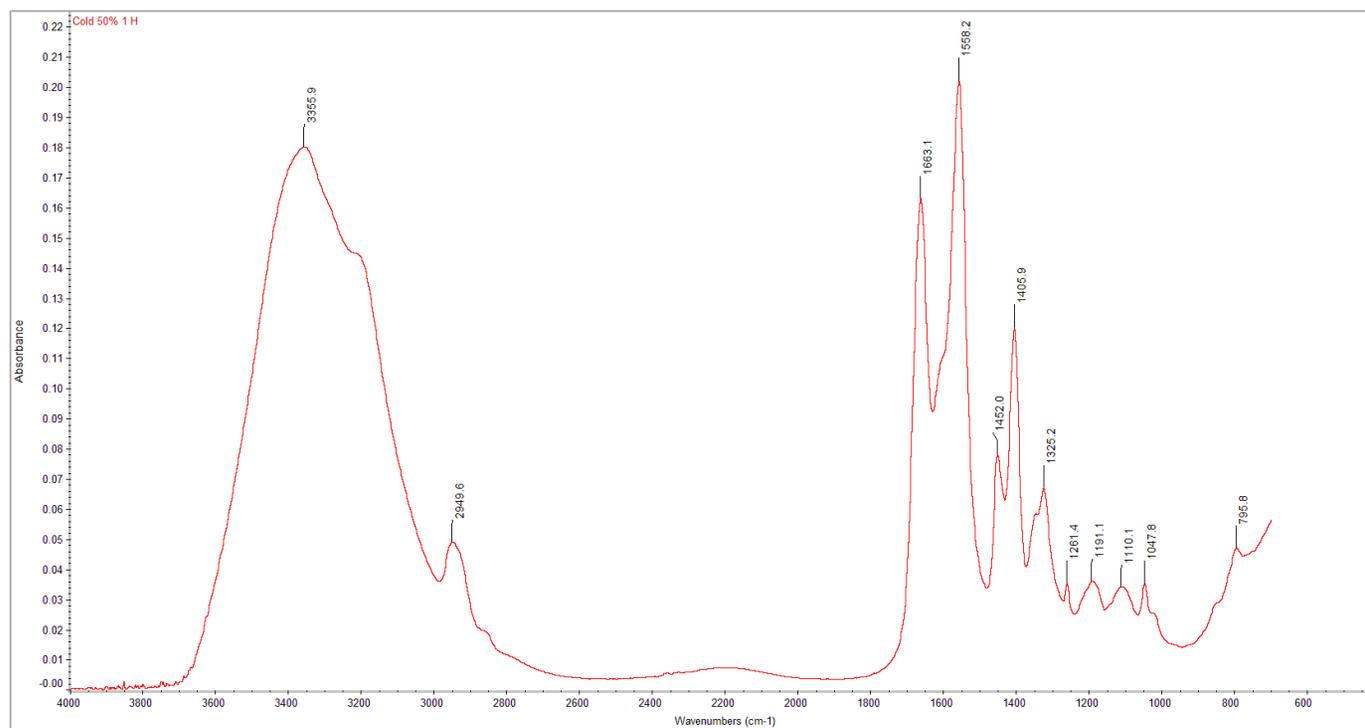
Scheme B.2. C-40-1H spectra



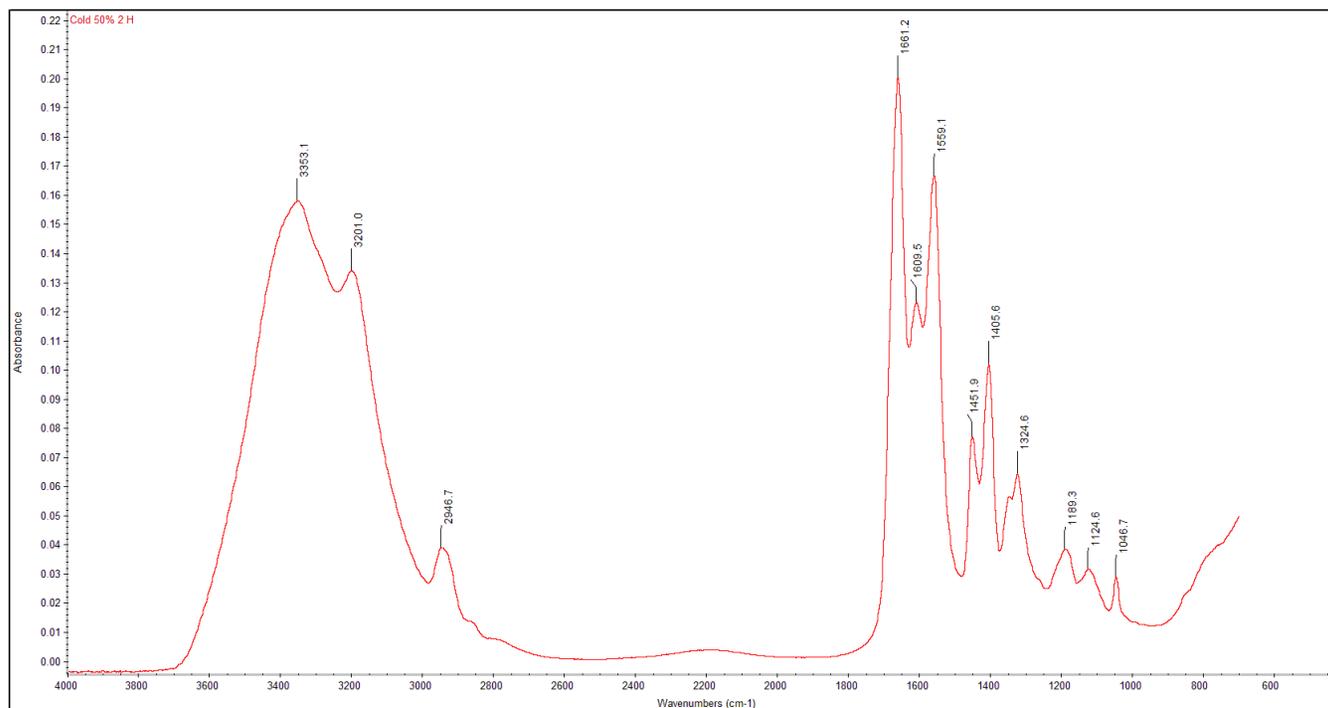
Scheme B.3. C-40-2H spectra



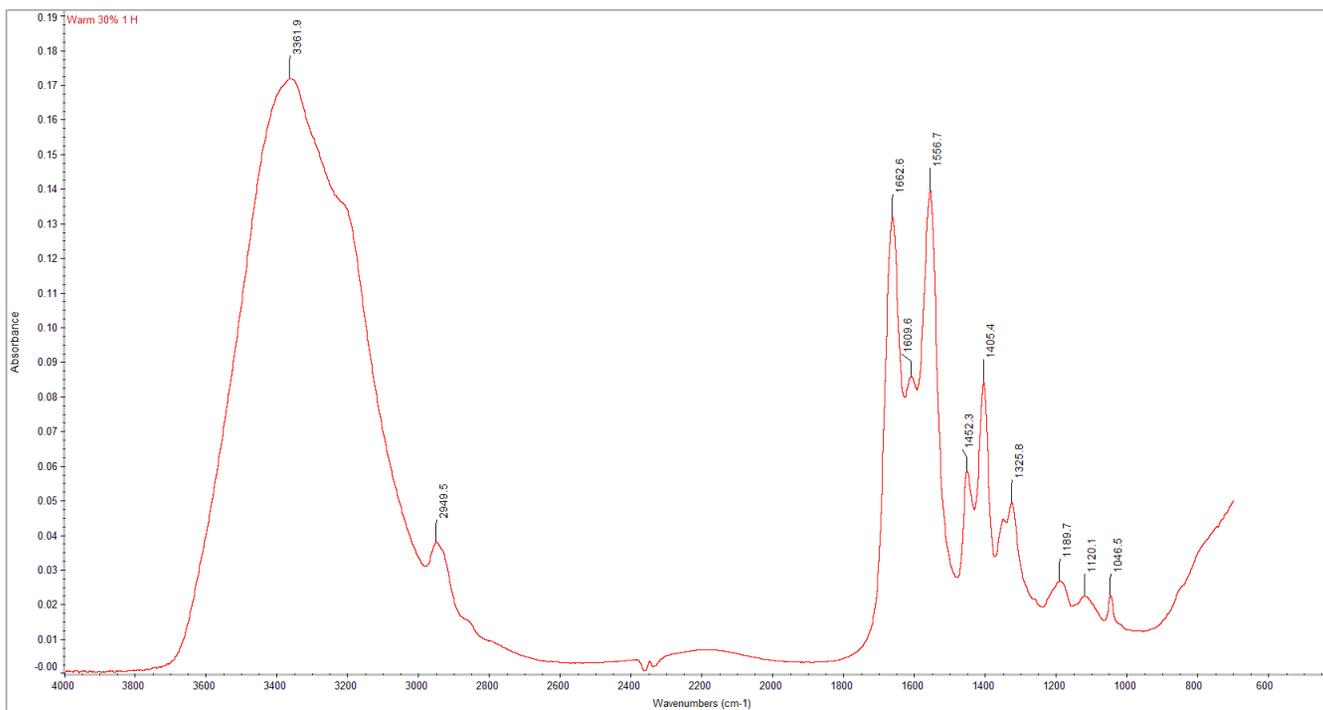
Scheme B.4. C-50-1H spectra



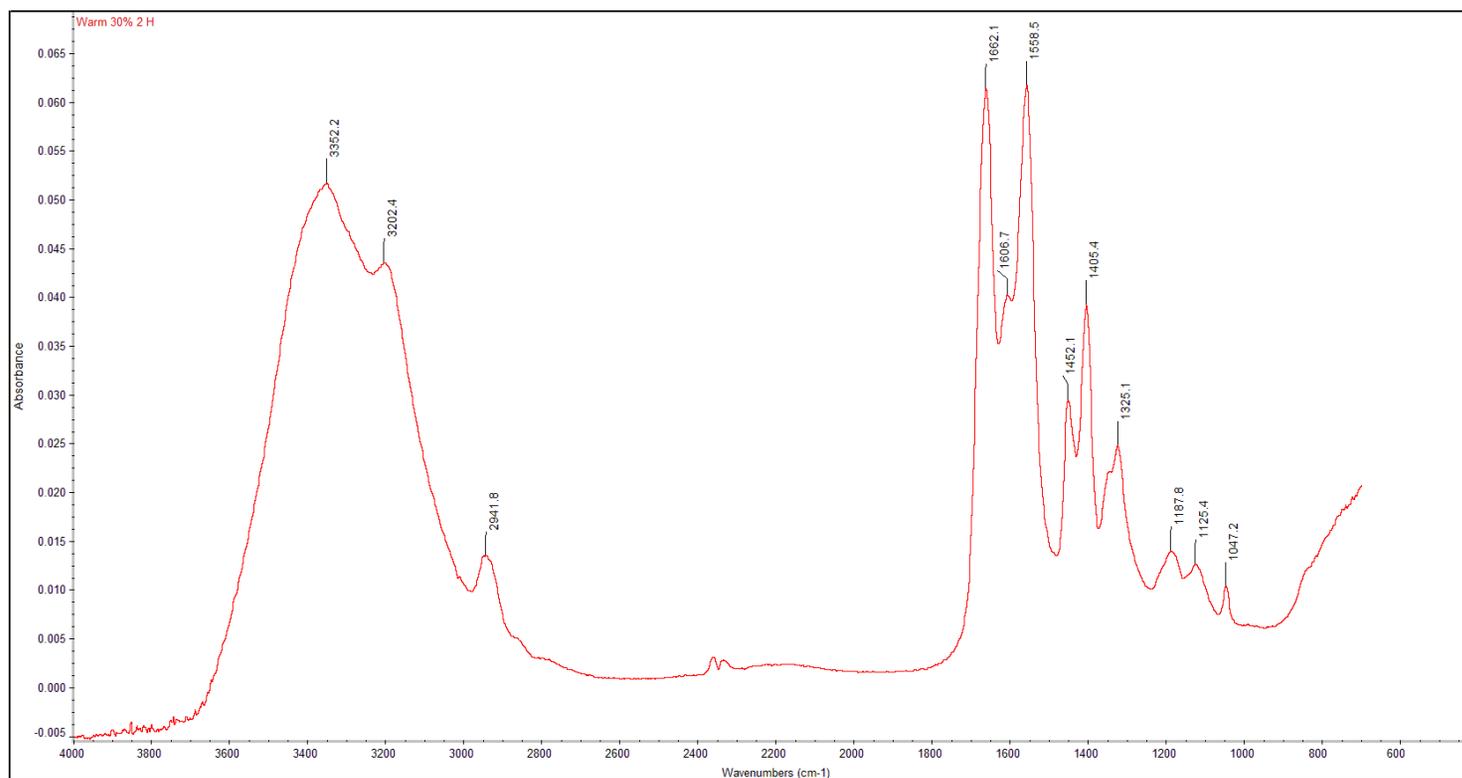
Scheme B.5. C-50-2H spectra



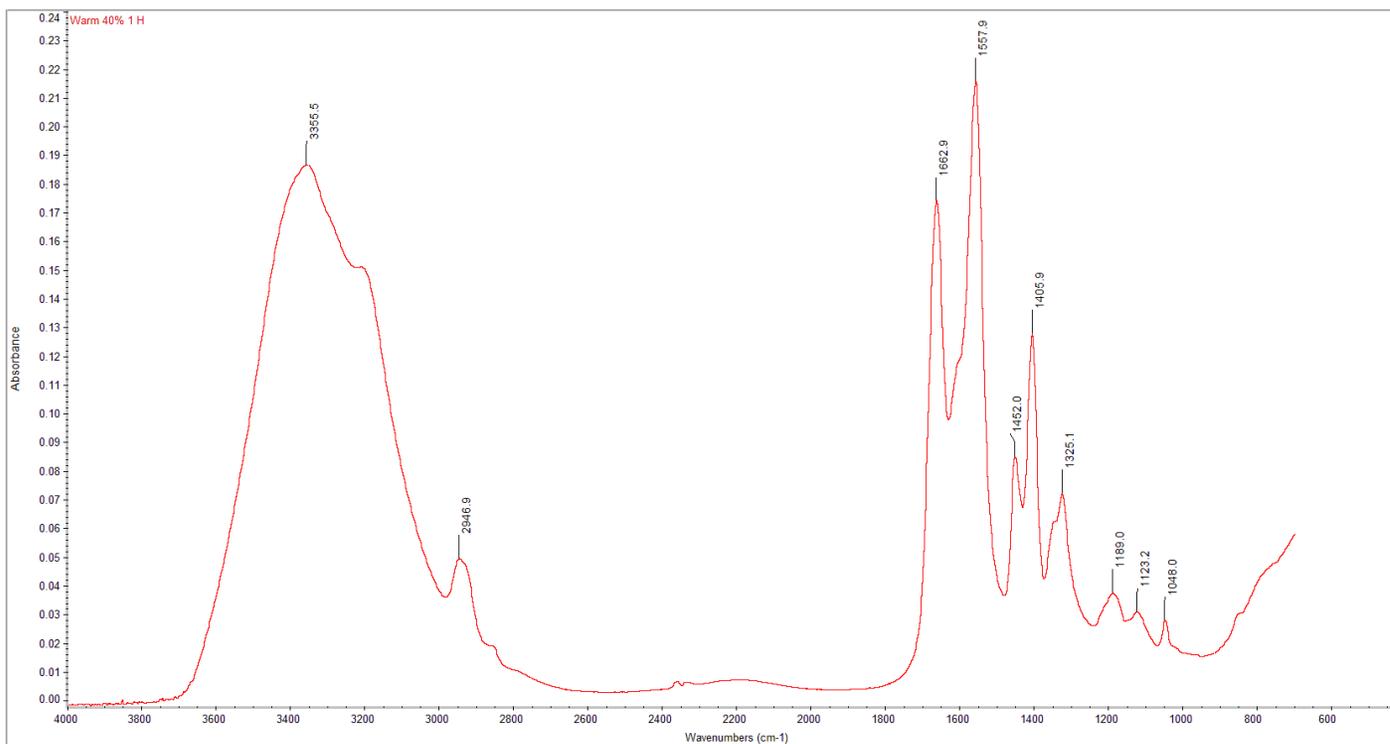
Scheme B.6. W-30-1H spectra



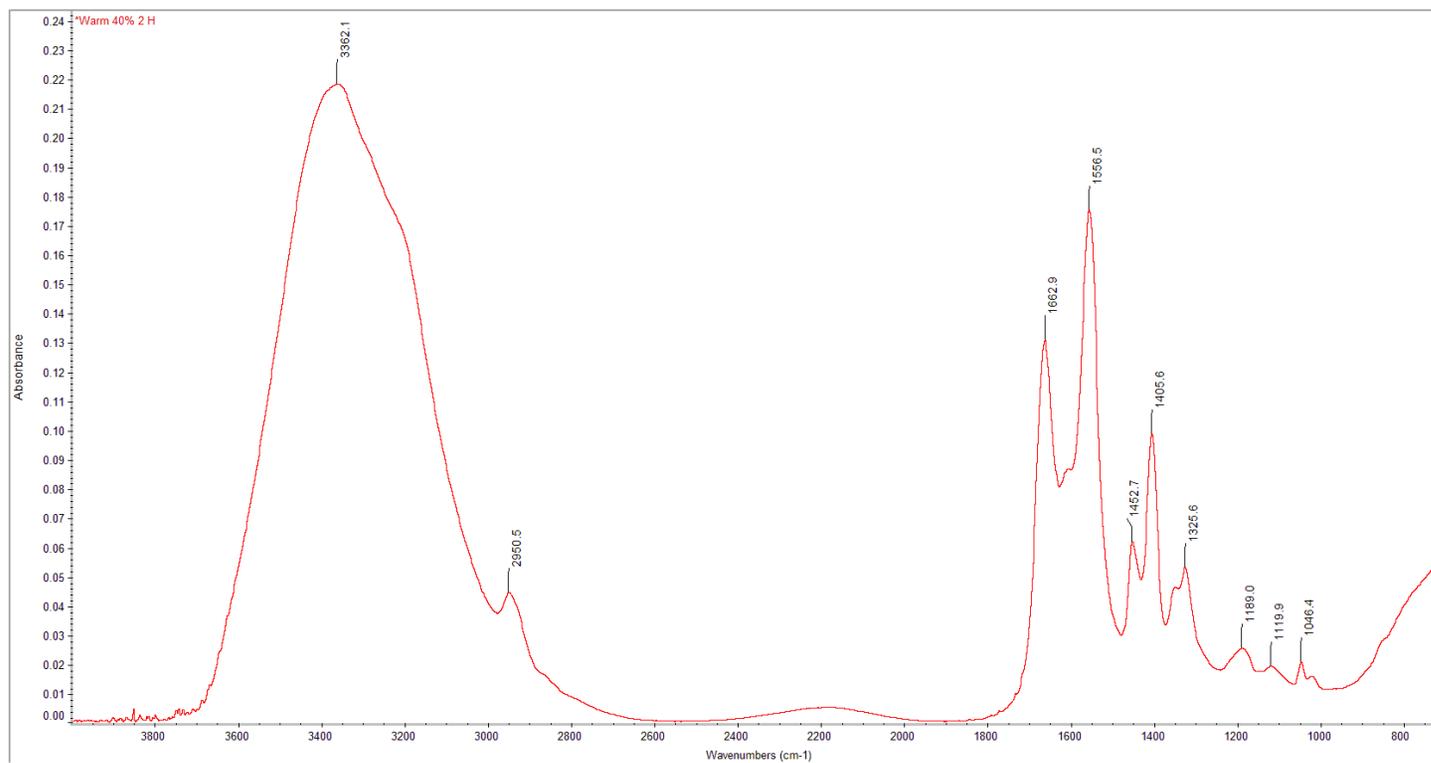
Scheme B.7. W-30-2H spectra



Scheme B.8. W-40-1H spectra



Scheme B.9. W-40-2H spectra



Scheme B.10. W-50-1H spectra

