SYNTHESIS AND CHARACTERIZATION OF POLY (BUTYL VINYL ETHER) HOMOPOLYMERS AND COPOLYMERS UTILIZING THE ALUMINUM HYDROGEN SULFATE CATALYST SYSTEM

by

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Thesis submitted to the Faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Chemistry

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February, 1991
Blacksburg, Virginia
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(ABSTRACT)

The synthesis of poly (butyl vinyl ether) and poly (butyl vinyl ether - 2-chloroethyl vinyl ether) random copolymers was accomplished through the use of the aluminum hydrogen sulfate catalyst (AHS). In this system, AHS acts as a heterogeneous catalyst in the cationic polymerization of vinyl alkyl ethers.

Highly isotactic polymers (greater than 70%) have been prepared and characterized by $^1$H and $^{13}$C NMR. DSC characterization of poly(butyl vinyl ether) also reveals that these polymers are semicrystalline. Gel permeation chromatography characterization and intrinsic viscosity data of poly(butyl vinyl ether), and poly(butyl vinyl ether - 2-chloroethyl vinyl ether) homopolymers and copolymers indicate fairly narrow polydispersities, and very high molecular
weights. A study of this copolymerization by $^1$H NMR revealed that the 2-chloroethyl ether monomer was being incorporated along the chain with the greater percentage of the 2-chloroethyl vinyl ether monomer near the chain ends.

Reactions on the pendent chlorine group are currently under investigation in our laboratories. It is anticipated that a range of pendent functional groups can be obtained.
ACKNOWLEDGEMENTS

I would like to acknowledge those who have supported me, offered encouragement, and challenged me to reach my goals in my research at Virginia Tech. I greatly appreciate their patience every time I approached them with '21 questions'. First of all, I would like to acknowledge Dr. Judy Riffle for her support throughout this research. Her enthusiasm and dedication to research provided a solid foundation from which to build upon. My sincere thanks goes to Dr. Gurudas Sinai-Zingde who helped me get started in the laboratory, and provided much needed guidance during my first year of laboratory work. Also, I would like to thank Dr. Akhil Verma for pointing me in the right direction, and for offering valuable advice, discussions, and support throughout my research.

Also, I would like to acknowledge Ms. Qin Liu, and Dr. Babu Jayaraman who have been very helpful in many research discussions. I would also like to thank Allison Goforth, Jeff Mecham, Kathy Johnson, Dr. A. Prasad, Steve McCartney, Tom Glass, and 'everyone' in Dr. Riffle's group for their support and technical assistance in this research.

I wish to acknowledge my advisory committee, Dr. James McGrath, and Dr. Herve Marand for their technical advice and support throughout this research.
Most notably, I would like to thank my parents, John and Diane, my brothers and sisters, Steve, Greg, Chris, Jenny, and Sandy Rose, and my fianceé, Patricia, for their support, encouragement, love, and sincere understanding throughout my research. Lastly, I would like to thank the Virginia Army National Guard for their support, and encouragement during these studies.
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Introduction

Poly (butyl vinyl ether) homopolymers and copolymers have been synthesized previously by living cationic and cationic polymerization methods\textsuperscript{14-18,31}. However, the majority of these initiator-catalyst systems used for the polymerization of poly(alkyl ether)s are homogeneous in solution yielding polymers with their own characteristic properties. In our system, aluminum hydrogen sulfate (AHS) was used in the homopolymerization and copolymerization of butyl vinyl ether as a heterogeneous catalyst. It's inherent effects in polymerizations have also previously been studied by researchers in the 1960's\textsuperscript{1,3-5}.

The aim of this research was to investigate the polymerization of butyl vinyl ether with AHS and to develop controlled, and preferably living synthesis conditions. With the synthetic parameters developed, high molecular weight homopolymers and copolymers can be prepared. Due to their unique morphological characteristics using AHS, the poly (butyl vinyl ether) homopolymers are rubbery, non-tacky materials at room temperature with semicrystalline properties. The semicrystallinity of these materials may be attributed to their tacticity as evidenced by $^1$H and $^{13}$C NMR. Evidence for the high molecular weights are the extremely high intrinsic viscosity values obtained for these materials.
By GPC, fairly narrow polydispersities for both the homopolymer and copolymers have been obtained, revealing that this system may possess possible living polymerization characteristics similar to those obtained by other workers using the homogeneous Hf/ZnI₂ initiator-catalyst system¹⁹-²¹. Additionally, the formation of a random copolymer of butyl vinyl ether and 2-chloroethyl vinyl ether has been studied extensively by ¹H and ¹³C NMR.
Literature Review

Alkyl Vinyl Ethers Polymerized via AHS:

In the cationic polymerization of alkyl vinyl ether monomers, typically, high molecular weight polymers, and/or stereoregular polymers are obtained at low temperatures\(^1\). Synthesis of polymers at higher temperatures often yields irregular structures. With the aluminum hydrogen sulfate (AHS) catalyst, cationic polymerization of alkyl vinyl ethers can be carried out at higher temperatures (e.g. approximately room temperature) to produce high molecular weight materials.\(^1\)\(^-\)\(^5\) These materials are also highly isotactic, and exhibit semi-crystalline properties.

Results for the polymerization of alkyl vinyl ethers using this type of heterogeneous catalyst were first reported by Mosley\(^2\). This initial work encouraged Okamura and coworkers\(^3\) to investigate the cationic polymerization of isobutyl vinyl ether at room temperature using the AHS catalyst. Their work focused on stereospecific aspects of the polymerization, and the relative amount of crystallinity present after fractionation from MEK. To quantify the percent crystallinity of the poly (isobutyl vinyl ether), (PIBVE), the polymer was solubilized in MEK at 30°C, and the weight percent of the insoluble part of the polymer in MEK
was determined. Further evidence for the crystallinity in these polymers was confirmed by X-ray diffraction patterns.

Another study of this heterogeneous catalyst system was performed by Lal and McGrath⁴. Their initial work focused on the polymerization of n-butyl vinyl ether in hexane at 50°C. They showed that, during this polymerization, the rate decreased and became very slow above ≈80% conversion as evidenced by a plot of conversion vs. time. The authors provided no reason for this type of behavior seen with the AHS catalyst. Other vinyl ethers studied included ethyl, isopropyl, and isobutyl vinyl ether. They also considered the nature of the solvent used in the polymerization of vinyl alkyl ethers with AHS to be very important. Polymerization rates were affected by the choice of solvents employed. In either benzene or toluene, the polymerization rates were decreased compared to heptane. However, higher crystalline polymer fractions were obtained using toluene or benzene as the reaction solvent.

The effect of monomer structure on the polymerization rate was also explored. The results revealed that a vinyl ether monomer having a linear alkyl group polymerizes considerably faster than a monomer having a branched alkyl group. It was proposed that the bulkiness of the isobutyl group of the vinyl ether monomer may hinder the approach of the incoming monomer toward the reactive centers of the
heterogeneous catalyst, thereby decreasing its polymerization rate relative to that of the n-butyl alkyl group. These researchers weren't able to elucidate the mechanism for the polymerization of alkyl vinyl ethers with AHS to form crystalline polymers. It was proposed that the steric control using the heterogeneous catalyst may involve by coordination of the ether groups of the polymer with the catalyst centers (scheme 1). Furukawa proposed that this type of complex catalyst, such as the AHS catalyst, should have at least two coordination centers which may be responsible for the formation of the isotactic polymer by the addition of the monomer from the opposite side of the polymer chain.

In 1967, Lal, McGrath, and Trick, reported the effect of temperature and solvents on the stereospecific polymerization of alkyl vinyl ethers catalyzed by AHS. They found that increasing the polymerization temperature from -20°C to 50°C decreased the weight fraction of the MEK insoluble polymer. Using this weight fraction as a measure of stereoregularity, it was concluded that the increase in polymerization temperature reduced the stereoregularity of the polymer of interest. It has been proposed that the increase in the polymerization temperature may decrease the coordination of the ether oxygen atoms of the vinyl ether monomer, and of the growing end of the polymer molecule to
Scheme 14: Proposed mechanism for the polymerization of alkyl vinyl ethers with the AHS catalyst
the metal centers in the heterogeneous counteranion of the metal sulfate complex catalyst. This coordination by the AHS catalyst was proposed to be very important for the formation of isotactic polymers.

The solvent medium used in the polymerization of alkyl vinyl ethers also has an important influence on the properties of these polymers\(^1\). Investigations of the binary solvent systems of carbon disulfide-heptane and carbon disulfide-chlorobenzene for the polymerization of \(n\)-butyl vinyl ether revealed that, as the concentration of carbon disulfide was increased, the fraction of crystalline material increased. With the binary solvent system carbon disulfide-chlorobenzene, the polymerization of vinyl isobutyl ether yielded higher intrinsic viscosity values, and increased crystalline material (MEK insoluble) with greater concentrations of carbon disulfide. However, with the solvent system carbon disulfide-MEK, the polymerization of isobutyl vinyl ether revealed that a solvent ratio of 2:1 gave optimum crystallinity as evidenced by x-ray diffraction patterns. As a result, the authors concluded that the polymers prepared with the AHS catalyst were very sensitive to the exact experimental conditions employed.

Later, Higashimura et al.\(^5\) performed NMR studies on the stereospecific polymerization of methyl vinyl ether with the AHS catalyst system. Methyl vinyl ether was chosen for these
studies because its triad tacticity\(^7\) could be elucidated by NMR spectroscopy\(^8\). These workers also observed that the tacticity of poly (methyl vinyl ether), (PMVE), decreased with an increase in the catalyst concentration over a range of 0.2-1.0g of catalyst per 100 ml of solvent. With an increase in the monomer concentration (5 - 40 vol\%), an increase in the polarity of the reaction medium occurs which decreases the stereoregularity of the PMVE. In a binary solvent system of toluene - hexane, the stereoregularity of PMVE decreased with an increase in the concentration of hexane. However, it should be noted that our results have shown that with a monomer:catalyst concentration of 1000:1 (w/w), P(MVE) was found to be insoluble in toluene.

The copolymerization of methyl vinyl ether with 2-chloroethyl vinyl ether revealed that the methyl vinyl ether polymerized faster. The authors have suggested that the catalyst surface of AHS plays an important role in this polymerization. The AHS catalyst may interact more strongly with methyl vinyl ether than with 2-chloroethyl vinyl ether, which may suggest that the counteranion in the AHS catalyst may not be a simple charged particle. Studies on the tacticity of PMVE by these workers suggest that the orientation of the incoming monomer is only determined by the structure of the end unit, and not by the penultimate unit. They concluded from their results that the penultimate
effect, tested for its validity against the terminal (Bernoulli) effect, doesn't exist for the AHS catalyst system. For a system where the configuration of the monomer relative to the end unit is determined by the catalyst, the enantiomorphically catalyst sites model\textsuperscript{9} showed good agreement with the triad tacticity measured by NMR. Therefore, it was concluded that the steric arrangement of adding monomer in the presence of AHS catalyst is controlled by a catalyst site, where the monomer is absorbed on the catalyst surface before the bond formation of the monomer to a growing chain end occurs.

**Living Cationic Polymerization of Alkyl Vinyl Ethers:**

Cationic polymerization of vinyl compounds yields a propagating species which is an inherently unstable carbocation. This carbocation is extremely susceptible to deactivation by termination and chain transfer\textsuperscript{10}, primarily β proton elimination and transfer to monomer reactions. The possibility of deactivation of the propagating species may occur even without the presence of impurities during polymerization. In general, the criteria for assessing the formation of a living cationic polymer system are as follows\textsuperscript{11}:

a.) increase in polymer molecular weight (M\textsubscript{n}) with increasing amount of consumed monomers;
b.) increase in polymer molecular weight upon addition of a fresh monomer feed to a completely polymerized solution of the same monomer; and

c.) formation of block polymers upon addition of an appropriate second monomer to a completely polymerized solution of the first monomer.

Additionally, the propagating carbocation of the growing chain in living cationic polymerization may be a 'long-lived' species dependent on the appropriate solvent and initiator systems utilized.

In 1979, Higashimura and coworkers\textsuperscript{12,13} reported a long lived propagating species in the cationic polymerization of isobutyl vinyl ether (IBVE) initiated with iodine. Their initial work revealed that with IBVE in toluene, an increase in molecular weight was observed with conversion. Also, with the addition of more monomer, an increase in molecular weight with a narrow molecular weight distribution resulted.

In the search for an initiator with a higher initiation rate relative to propagation for the living cationic polymerization of alkyl vinyl ethers, Higashimura\textsuperscript{14} and others examined the HI/I\textsubscript{2} initiator system. It was observed that in the presence of iodine, HI would initiate polymerization faster than with I\textsubscript{2} alone. It was reasoned that, since HI has a higher dissociation constant than I\textsubscript{2}, it could more easily
provide a positive moeity for initiation. By using HI instead of I₂ to initiate the polymerization, a faster initiation rate relative to the propagation rate occurred. In hexane at -15°C, with an equimolar mixture of HI/I₂, nearly monodisperse poly(IVBE) \( <M_w>/<M_n> \leq 1.1 \) was produced. Similar results were obtained in other solvents such as toluene, and CH₂Cl₂, as well as with other alkyl vinyl ethers\(^{15}\). The effects of the concentration of the monomer, HI, and I₂ on the polymerization of alkyl vinyl ethers have been studied quite extensively\(^{16-18}\). The mechanism for the polymerization of alkyl vinyl ethers using the HI/I₂ system was studied by kinetic characterization, \(^1\)H NMR, \(^{13}\)C NMR and uv-visible spectroscopy\(^{16}\) (scheme 2). It was shown that the hydrogen iodide-alkyl vinyl ether adduct is produced in the initiation step, then the C-I bond is electrophilically activated by the added iodine to propagate the living polymerization. The terminal C-I bond is activated again by I₂ on the resulting living polymer. Overall, the key to the living process is the high stability of the growing chain end where the nucleophilic iodide counteranion can interact strongly with the carbocationic active site.

Since I₂ in the HI/I₂ system serves as an electron acceptor, it may be replaced with other Lewis acids that can electrophilically interact and, in turn, activate the C-I bond of the growing polymer chain. As a result, the use of
Scheme 214: Reaction mechanism for the polymerization of alkyl vinyl ether with the HI/I₂ catalyst system
ZnX₂ or SnX₂ (X = Br, Cl, I), with HI were determined to be efficient initiating systems for the living cationic polymerization of alkyl vinyl ethers¹⁹⁻²¹ (scheme 3). With the HI/ZnI₂ system, these authors were able to obtain well defined living polymers of IBVE and acetoxyethyl vinyl ether above room temperature. Their results showed that the HI/ZnI₂ initiated polymerization occurred much faster than the HI/I₂ reaction. Also, with ZnI₂ alone, no polymerization occurs, whereas with I₂, polymerization does occur even without HI present. Later, further work was reported with the Me₃SiI/ZnI₂ (in acetone) system²² in toluene from 0 to -40°C, with narrow molecular weight distributions obtained. Our work with this system showed that initiation was non-quantitative, and no further work was pursued.

Another class of initiating systems for living vinyl ether polymerizations discovered more recently involves the use of ethyl aluminum dichloride (C₂H₅AlCl₂) in conjunction with an excess amount of inert bases such as carboxylic esters²³,²⁴ and ethers²³,²⁵. Living cationic polymerization of IBVE is achieved using EtAlCl₂ in the presence of ethyl acetate at temperatures up to 70°C in toluene. This research revealed that in the absence of ethyl acetate, a rapid polymerization occurs forming non-living polymers with broad molecular weight distributions. The initiating species in the EtAlCl₂ (20 mM) mediated living polymerization was
Scheme 319-21: Polymerization of alkyl vinyl ethers with the HI/ZnI₂ catalyst system
attributed to adventitious water with the assistance of the organoaluminum, but for more controlled molecular weight, a proctogen such as acetic acid has been added to form the IBVE adduct. It is proposed that the excess ester (10 vol%) stabilizes the propagating species via its interaction with the carbocationic site, thus forming a living end free from chain transfer, termination, and other undesirable reactions\textsuperscript{25} (scheme 4(a)). It has also been proposed that the ester interaction is relatively strong and involves the nucleophilic carbonyl groups which decelerate the polymerization. These researchers have proposed that the acetate anion complexed with EtAlCl\textsubscript{2} is less nucleophilic than the 'neutral' carboxylate esters, which have been added in large excess over EtAlCl\textsubscript{2}. As evidenced from polymerization results, a broad molecular weight distribution results when CH\textsubscript{3}COOH/EtAlCl\textsubscript{2} is utilized in the absence of added base. This accounts for the acetate anion-EtAlCl\textsubscript{2} complex's inability to stabilize the cation without the presence of excess ester. The complex is unstable and poorly nucleophilic since the anionic charge of the acetate anion is delocalized via its complexation with EtAlCl\textsubscript{2}. In the presence of ethers\textsuperscript{25}, the excess amount of ether needed was found to be dependent on its basicity. This was also found to affect the molecular weight distribution of the P(IBVE)'s. The propagating cation in the polymerization of IBVE with EtAlCl\textsubscript{2} (20mM) and ethers
Scheme 4\textsuperscript{25}: Proposed reaction mechanism for the polymerization of alkyl vinyl ethers with the (a) EtAlCl\textsubscript{2} / ester, and the (b) EtAlCl\textsubscript{2} / ether initiating systems
(eg. dioxane (5-10 vol%), or diethyl ether (70 vol%)), revealed that the propagating carbocation may be coordinated to the added ether to form an oxonium ion like species\textsuperscript{25} (scheme 4(b)) that is stable enough to survive during polymerization. No spectroscopic evidence for the proposed oxonium like species was presented. The proposed formation of an oxonium ion species was further studied by forming an IBVE adduct with acetic acid and EtAlCl\textsubscript{2}, with and without excess ethers. Also, it has been proposed that the presence of ether permits the generation of a long lived species, due to possible solvation of the growing carbocation, whereas the counteranion derived from adventitious water/EtAlCl\textsubscript{2} was less nucleophilic, and less likely to stabilize the carbocation on the growing polymer chains.

Quite recently, studies have been performed on the synthesis of amphiphilic block copolymers consisting of hydrophilic and hydrophobic segments\textsuperscript{26-29}. Using the HI/I\textsubscript{2} initiator-catalyst system, controlled structure and molecular weight distribution could be achieved. With this system, the length of the hydrophilic and hydrophobic segments of block copolymers could be controlled. Investigations of 2-hydroxyethyl vinyl ether-alkyl vinyl ether block copolymers\textsuperscript{26} revealed that their surface activity was found to vary in aqueous solutions with different pendent alkyl groups on the vinyl ether. These amphiphilic block copolymers were formed
from either 2-acetoxyethyl vinyl ether or 2-(benzoyloxy)ethyl vinyl ether with alkyl vinyl ethers of varying alkyl group pendent lengths. For efficient copolymerization, 2-acetoxyethyl vinyl ether was polymerized first, followed by an alkyl vinyl ether to ensure 100% blocking efficiency. The ester groups of the block copolymers were hydrolyzed with an acetone/H₂O mixture in the presence of NaOH. Typically, block copolymers with a composition of 90:10(ester:alkyl pendents) and greater were synthesized to obtain minimum surface tension in aqueous solutions. The formation of an amphiphilic block copolymer with pendent amino groups was synthesized by copolymerizing 2-(vinloxy)ethyl phthalimide with an alkyl vinyl ether monomer. Whereas, the formation of an amphiphilic block copolymer with carboxylate groups was synthesized by copolymerizing 2-(vinloxy)ethyl malonate with an alkyl vinyl ether monomer²⁷,²⁸.

Lastly, a number of functionally substituted vinyl ethers are known that carry different pendent groups polymerized by the HI/I₂ and HI/ZnI₂ systems. These polymers of functionalized vinyl ethers are also well defined living polymers. Their functional groups range from saturated esters²⁰,³⁰-³⁴, unsaturated esters³⁵,³⁶, and ethers³⁷ to other substituents³⁸. Their known polymerization kinetics and rates depend on the nature of the substituents on the pendent group of the vinyl ethers.
Cationic Polymerization of Alkyl Vinyl Ethers:

Cationic polymerization of alkyl vinyl ethers is a chain growth reaction where the monomer of interest propagates with a species possessing electrophilic character. In this type of polymerization, the C=C double bond is opened and a catalyst is present to activate the carbocation-counteranion bond to allow the insertion of more monomer. The cationic species present on the propagating chain end must possess electrophilic character and enough stability to survive long enough for insertion of another monomer. The C=C unsaturation combined with an electron donating group enhances the basicity of the π system, which results in a greater tendency for cationic polymerization to occur.

For alkyl vinyl ether polymerizations, cationic initiators in conjunction with Lewis acids are the preferred catalysts for homopolymerization. Friedel-Crafts catalysts can be used for vinyl ether polymerizations. In cationic polymerizations, due to the inherent instability of most cations generated, any impurities in the monomers or solvent may affect the rate of polymerization, the molecular weight, and the propensity for side reactions to occur.

Using certain initiating systems in vinyl ether polymerization, stereoregular polymerization may be induced. It is proposed that significant factors in the steric control
of the cationic chain growth of alkyl vinyl ethers are the degree of association of the growing cation with the counteranion\textsuperscript{40} as well as the nature of the counteranion. The 'tightness' of the growing ion pair and the steric limitations of the monomer approach by side chain substituents control the front or back-side attack of the monomer. Therefore, highly polar solvents that stabilize separated ion pairs favor frontal attack to the growing chain end yielding preferred syndiotactic polymer formation. Nonpolar solvents tend to associate the propagating cation-counteranion pair which leads to back side approach of the incoming monomer and preferred isotactic polymer formation\textsuperscript{40} (figure 1).

The stereochemical configuration of poly(alkyl vinyl ether)s has been studied with \textsuperscript{13}C NMR spectroscopy\textsuperscript{41}. It has been shown that dyad and triad tacticities of vinyl ether polymers are very dependent on the nature of the initiator and the polymerization conditions used. For example, the aluminum sulfate-sulfuric acid catalyst system produces 70% isotactic triads in the stereospecific polymerization of methyl vinyl ether\textsuperscript{5}.

**Stereoregularity of Alkyl Vinyl Ethers:**

The repeat units of poly (alkyl vinyl ether) chains can exist in two opposite stereochemical arrangements (figure
Figure 1: Solvent effects on the stability of ion pairs in chain propagation yielding different stereoregular chain arrangements.
Figure 2\textsuperscript{42}: (a) Possible configurations of alkyl vinyl ether monomers, and (b) stereoconfigurational dyads of alkyl vinyl ethers
2(a)). However, both arrangements are equally likely to form in the polymerization in the absence of a catalyst controlling system. The stereochemical course of the polymerization may be determined by the active site of the polymerizing chain, or by stereospecific catalysts that allow the polymerization to be controlled with respect to the placement of the two configurations in a regular manner. Typically, polymers prepared with the controlled placement of the monomers with regular placement along the chain are crystalline.

The position of the -OR group is determined by the stereochemical configuration of the asymmetric carbon to which it is attached. The asymmetric centers are labelled either $d$ or $l$, where the smallest configurational unit of a polymer chain is the stereoconfigurational dyad$^{42}$ (figure 2(b)). When the stereoconfigurations of two neighboring asymmetric carbon atoms are the same ($dd$ or $ll$), the placement is termed isotactic. When two successive asymmetric atoms have opposite stereoconfigurations ($dl$, $ld$), the placement is termed syndiotactic. When the placement of the -OR units are not consistently isotactic or syndiotactic, the polymer is termed atactic.

Stereoregularity or tacticity along the polymer chains affects its morphology. If the polymer is crystallizable, the monomer units must have configurations that allow them to
occupy equivalent positions along the chain. Through the use of stereospecific catalysts, the stereoconfiguration along polymer chains may be controlled leading to crystalline polymers. The regularity of the monomeric units along a linear polymer chain, either isotactic or syndiotactic, typically lead to crystallinity. Since syndiotactic polymers possess a nearly planar form, this allows for increased packing density of the polymer chains. Isotactic polymers cannot assume a near planar conformation due to the bulkiness of the side chain groups; thus, the packing density is usually decreased. Therefore, the Tm's and Tg's of the polymers should show trends where these values decrease in the order of syndiotactic, isotactic, and heterotactic. It is of importance that the stereoregular forms of these polymers are less soluble than the irregular ones.

Experimental measurements of configurational sequences can now be made for polymers. Through the use of high resolution NMR spectroscopy, one can differentiate between racemic(r) and meso(m) dyads by observing their environment and chemical shifts. Also, one can use NMR spectroscopy to observe isotactic(mm), syndiotactic(rr), and heterotactic(mr) triads (figure 3) on different polymers considering their environments along the chain. With improved NMR techniques, 1H and 13C NMR finer line structures appear as tetrads, pentads, etc., yielding more detailed information about
Dyads:

\[ m \]

\[ r \]

Triads:

\[ mm \]

\[ mr \]

\[ rr \]

Figure 3\textsuperscript{43}: Configurational sequences of polymer chains
stereoregular polymer chains and their mode of polymerization.

The microstructure of polymers exhibiting stereoregularity can be predicted statistically\(^{44}\). For a monomer adding to a growing polymer chain, a conditional probability exists that the monomer will add to produce a meso or racemic dyad at the end of the chain. According to the Bernoulli or terminal model, an incoming monomer adds to the chain end independent of the stereoregularity of the terminal pair on the chain. In the absence of anything fixing the stereochemistry of the incoming monomer, the probability of the monomer adding in the \(d\) or \(l\) form is equal to form either an \((m)\) or \((r)\) dyad. Using the penultimate model, it is assumed that the terminal pair of the growing chain end will influence the stereospecific homopolymerization and follows first order Markov statistics\(^{45}\). Furthermore, the penpenultimate model follows second order Markov statistics and assumes that the terminal pair plus one additional unit influences the stereospecific homopolymerization.

From these models, one can fit the experimental data obtained from the NMR spectrum to the necessary equations and parabolic curves to determine the mode of stereospecific polymerization for the system of interest\(^{45}\). Once the experimental triad values have been determined and fitted to
a particular model, the mechanism governing the propagation may be regarded as terminal, penultimate or higher. This data is tested against calculated theoretical values to determine the internal consistency of the model and agreement with the experiment.

NMR studies on alkyl vinyl ethers have been performed over the past few years to analyze the stereoregularity of polymer chains. Some of the earlier work was focused on the polymerization of methyl vinyl ether (MVE) using homogeneous catalysts such as BF$_3$-OEt$_2$ and SnCl$_4$-CCl$_3$CO$_2$H$^{46,47}$. These authors studied the effects of solvents$^{46}$ with increasing polarity and temperature on the triad tacticity of PMVE, and concluded that the penultimate effect$^{48}$ existed in these polymerizations. Highly stereoregular methyl, iso-butyl, and tert-butyl vinyl ether polymers were formed with the AlF$_3$ catalyst system$^{49}$ and characterization by IR and NMR was performed. $^{13}$C NMR studies on alkyl vinyl ethers revealed the composition of racemic and meso dyads in PMVE$^{50}$. Also, additional $^{13}$C NMR work$^{51}$ showed the relationship between itself and $^1$H NMR for triad tacticities.

Properties of Alkyl Vinyl Ethers:

Poly(alkyl vinyl ether)s may be formed as viscous, sticky, liquid, rubbery, or brittle solids, with waxy properties for the long chain substituents. Exemplary glass
transition temperatures and crystalline melting points are shown in table 1\textsuperscript{52}. The melting points (T\textsubscript{m}'s), and the percent crystallinity of some of these materials may be held suspect due to the thermal degradation behavior of these types of materials. These polymers are typically used as adhesives, surface coatings, lubricants, greases, elastomers, molding compounds, fibers, and in films. Poly(methyl vinyl ether) is used as a nonmigrating plasticizer and tackifier\textsuperscript{53}. It has shown good adhesion to both high and low surface free energy substrates, promotes adhesion of nonadhering materials to glass, metal, and plastic, and is used in pressure sensitive adhesives. Poly(ethyl vinyl ether) is used in moisture permeable non-irritating surgical casts in conjunction with poly(\varepsilon-caprolactone)\textsuperscript{54}. Using copolymers of vinyl ethers with other materials, the applications are numbered, but offer some interesting uses\textsuperscript{55} ranging from binders in aspirin tablets to impact resistant plastics.
Table 1\textsuperscript{2}: Glass transition temperatures and crystalline melting points for poly(alkyl vinyl ether)s

<table>
<thead>
<tr>
<th>Alkyl group</th>
<th>Amorphous, T\textsubscript{g}, °C</th>
<th>Crystalline, mp, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl</td>
<td>-34</td>
<td>144</td>
</tr>
<tr>
<td>ethyl</td>
<td>-42</td>
<td></td>
</tr>
<tr>
<td>isopropyl</td>
<td>-3</td>
<td>191</td>
</tr>
<tr>
<td>n-butyl</td>
<td>-55</td>
<td></td>
</tr>
<tr>
<td>isobutyl</td>
<td>-19</td>
<td>170</td>
</tr>
<tr>
<td>2-ethylhexyl</td>
<td>-66</td>
<td></td>
</tr>
<tr>
<td>n-pentyl</td>
<td>-66</td>
<td></td>
</tr>
<tr>
<td>n-hexyl</td>
<td>-77</td>
<td></td>
</tr>
<tr>
<td>n-octyl</td>
<td>-80</td>
<td></td>
</tr>
<tr>
<td>t-butyl</td>
<td></td>
<td>238</td>
</tr>
</tbody>
</table>
Experimental

Reagents and Monomers (Purification):

Solvents

Toluene. Toluene (Fisher, Certified Grade) (800 ml) was placed in a 1L separatory funnel, washed with cold concentrated $\text{H}_2\text{SO}_4$ (Fisher) twice (60 ml each), and then washed twice with deionized $\text{H}_2\text{O}$ (100 ml each). After the above washings, it was washed with a saturated $\text{NaHCO}_3$ (Fisher) solution (4 x 50 ml) until basic, to remove the remaining acidic impurities. Next, the toluene was added to a 1L erlenmeyer flask, with 2g of anhydrous $\text{MgSO}_4$ (Fisher), and stirred for 2 hours. The toluene was decanted into another 1L erlenmeyer flask, 2g of $\text{P}_2\text{O}_5$ (Aldrich 98+%) was added, and was stirred for 15 minutes to remove any residual water. This was decanted into a 1L round bottom flask (RBF), and Na (Aldrich, 50 wt% dispersion in paraffin) was added. This was refluxed in a distillation still under $\text{N}_2$ (prepurified, 3-5 psi.) until needed.

Monomers

Butyl vinyl ether (BVE). Butyl vinyl ether (Aldrich, 98%) (500 ml) was washed with deionized water (3 x 100 ml) in a 1L separatory funnel, stirred over KOH pellets (Fisher, certified A.C.S.) for 6 hours, and then passed over neutral
alumina to remove any residual $\text{H}_2\text{O}$. The BVE was added to Na (dispersed in paraffin) in a 1L RBF with a stir bar, and stirred for 24 hours with a drying tube (Drierite) attached. The monomer was distilled from Na, then placed via a cannula in an evacuated, flamed dried bottle equipped with a septum.

2-Chloroethyl vinyl ether (CLEVE). 2-Chloroethyl vinyl ether (Monomer-Polymer and Dajac Laboratories) (250 ml) was stirred over CaH$_2$ for 12 hours, and then distilled under N$_2$. The monomer was transferred via cannula to an evacuated, flame dried bottle under N$_2$ equipped with a septum.

Miscellaneous. Chloroform (Fisher, certified grade), chloroform-d (Aldrich, 99.8 atom%), chloroform-d with tetramethylsilane (TMS) (Aldrich, 99.8 atom%) and toluene-d$_8$ (Aldrich, 99+ atom%) were used as received. The deuterated solvents were used in routine NMR spectroscopy analysis.

Reagent Recrystallization Procedure:

Aluminum sulfate octadecahydrate. Aluminum sulfate octadecahydrate (Aldrich, 98+%) (30g) was first dissolved in dilute $\text{H}_2\text{SO}_4$ (1:1 ratio of $\text{H}_2\text{O}:\text{H}_2\text{SO}_4$ (Aldrich, 99.999%)) (200 ml) by stirring in an erlenmeyer flask for 2 hours at 40°C. This material was recrystallized by cooling in an ice bath for 2 hours. The solid material was filtered with a vacuum
filtration funnel, then washed with diethyl ether (6 x 50ml) under N₂ to remove the dilute H₂SO₄. The white powder was dried under vacuum for 24 hours at 40°C.

**Catalyst Preparation (AHS):**

**Aluminum sulfate octadecahydrate.** Recrystallized Al₂(SO₄)₃·18H₂O (12g) was added to 60 ml of concentrated H₂SO₄ (Aldrich, 99.999%) and heated to 90°C for 20 hours with stirring in a RBF equipped with a drying tube (Drierite). This heterogeneous reaction becomes viscous over time. The reaction mixture was filtered under N₂ in an enclosed vacuum filtration apparatus, and washed with diethyl ether to remove any concentrated H₂SO₄. The diethyl ether-H₂SO₄ (milky white color) solution becomes clearer with the removal of H₂SO₄ as the number of ether washings (10 x 25 ml) increases. The catalyst was transferred under N₂ to a RBF, and heated to 40°C under vacuum for 64 hours to remove any residual diethyl ether. After the catalyst (AHS) was dried, it was placed in a glove box to prevent any water uptake, due to its hygroscopic nature. The catalyst particles were further ground using a 'Wig-L-Bug' (Crescent; purchased from Wilmad) particle apparatus. Subsequently, 1.87g of the AHS were transferred to a dried bottle equipped with a stir bar and a septum using a glove box. Approximately 93g of mineral oil (Aldrich) was
added to the bottle with the AHS to form a 2% suspension of the catalyst.

Synthesis of Homopolymers and Copolymers:

Poly (Butyl Vinyl Ether). The polymerization of butyl vinyl ether (BVE) was performed in a 100 ml RBF equipped with a stir bar and sealed with a septum. The apparatus was scrupulously evacuated, flame dried, placed under \( \text{N}_2 \), and flame dried again. Under \( \text{N}_2 \), 0.250g of the 2% AHS suspension in mineral oil (actual: 0.005g AHS) and 65 ml of dried and distilled toluene were added to the reaction flask. The RBF was placed in an isopropanol (Baker) bath with stirring to cool to 10°C, with a Neslab Cryocool immersion cooler (CC-100-II), along with an overhead stirrer to maintain a constant bath temperature. The toluene/AHS solution was cooled a minimum of 30 minutes prior to the addition of BVE.

The BVE was distilled over \([(\text{CH}_3)\_2\text{CHCH}_2\]_3\text{Al} \) (Aldrich, 25 wt.% solution in toluene) with the following procedure. The freeze pump vacuum distillation apparatus was first evacuated, flame dried, placed under \( \text{N}_2 \), and flame dried again. This procedure was repeated three times to remove any moisture or impurities. Then, 10 ml of BVE was added to the distillation apparatus via cannula under \( \text{N}_2 \) with stirring, the BVE was solidified with liquid \( \text{N}_2 \) for 10 minutes, and the apparatus was evacuated for 10 minutes. The vacuum was then
turned off, and the BVE was thawed. This procedure was repeated three times until all of the gases in the apparatus had been removed. The distillation apparatus was again placed under N₂, 0.5 ml of [(CH₃)₂CHCH₂]₃Al was added to the monomer to remove any residual water, and the mixture was stirred for 45 minutes at room temperature. The BVE was again frozen, degassed for 10 minutes, the vacuum was turned off and the BVE re-thawed. This step was performed one to two times to ensure that all of the N₂ had been removed. The receiver flask was placed in an isopropanol/dry ice bath, with the distillation flask in a warm water bath. A slight vacuum was induced to allow the BVE to distill over into the receiver flask. The complete distillation takes approximately 10-15 minutes. The apparatus was placed under N₂, and 6.5 ml of BVE was removed with a syringe. The BVE was added to the reaction flask, which was cooled to 10°C, and placed under a constant N₂ (3 psi.) flow. The reaction flask was covered to prevent exposure to white light. The reaction was terminated with 1 ml of HN(Et)₂ (Aldrich). The viscous reaction mixture was allowed to stir for 1 hour prior to workup. The polymer was diluted with approximately 200 ml of chloroform, then 0.2g of NaHCO₃ was added to neutralize any remaining active AHS and the mixture was stirred for 30 minutes. Gravity filtration (filter paper) was performed on the polymer solution to remove the AHS and NaHCO₃. The
remaining solvents were removed with a rotovap at 50-55°C for 2 hours. The vacuum line was used to remove any residual toluene present in the polymer. The polymer, light orange and rubbery, was obtained with yields ranging from 80-90%.

**Poly (Butyl Vinyl Ether – 2-Chloroethyl Vinyl Ether).** The copolymerization of BVE and CLEVE was performed in a 97:3 mole percent ratio to yield a random copolymer. To a scrupulously evacuated and dried 500 ml RBF under N₂, with a stir bar, 1.28g of a 2% suspension of AHS (actual: 0.025g) and 330 ml of toluene were added. These components were stirred at 10°C for 30 minutes prior to monomer addition. The BVE monomer was vacuum distilled as described above. Then, 32.3 ml of BVE was added to a 50 ml RBF with 0.76 ml (3 mole %) of CLEVE and stirred for 10 min. The monomer mixture was added via a cannula to the reaction RBF under N₂. The reaction flask was placed under 3 psi. N₂ pressure. The copolymer was terminated with 2.0 ml (slight excess) of HN(Et)₂. The workup procedure similiarly follows the P(BVE) homopolymer workup procedure. The copolymer, a light orange and rubbery material, was obtained in 70-80% yields.
Characterization of the Homopolymers, Copolymers and Catalyst:

**$^1$H NMR.** $^1$H NMR measurements were recorded on a Varian Unity 400 MHz Spectrometer with a 5mm multinuclear probe. The instrument was operated at 399.952 MHz with a sweep width of 4500 Hz, and a 54° pulse width of 7.0μs. A total of 16 transients were accumulated and Fourier transformed with an acquisition time of 3.740s each, with no line broadening.

**$^{13}$C NMR.** $^{13}$C NMR measurements were recorded on a Varian Unity 400 MHz Spectrometer with a 5mm multinuclear probe. This instrument operated at 100.577MHz with a sweep width of 25000.0 Hz, and a 90° pulse width of 12.3μs. An acquisition time of 1.1995s, and a line broadening of 1.0 Hz was used. A 90° pulse and a longer relaxation delay were used to obtain quantitative $^{13}$C NMR data. A total of 8000-12000 transients were accumulated. With some of the samples, a relaxation agent, chromium(III) acetylacetonate (Aldrich) was added [10$^{-3}$ mol/L] to shorten the relaxation time, $T_1$, as well as to suppress the NOE$^{57}$.

**$^{27}$Al Solid State (MAS) NMR.** $^{27}$Al Solid State (MAS) NMR measurements were recorded on a Bruker MSL300 Spectrometer with a 4mm rotor. This instrument operated at 78.171MHz with a sweep width of 100,000 Hz, and a 90° pulse width of 4μs. A
total of 300 transients were accumulated for each sample, with a 1.0 molar solution of Al(NO₃)₃ (aq) used as a reference.

¹H Solid State (MAS) NMR. ¹H Solid State (MAS) NMR measurements were recorded on a Bruker MSL300 Spectrometer with a 4mm rotor. This instrument operated at 300MHz with a sweep with of 12,000Hz, and a 90° pulse width of 4µs. A total of 64 transients were accumulated for each sample, with CDCl₃ used as a reference.

Intrinsic Viscosity. Viscosity measurements were made with a Cannon-Ubbelhode size 50 viscometer in CHCl₃ at 25°C, with solution concentrations of 0.02g/dL.

Gel Permeation Chromatography. The apparent molar mass distributions were analyzed by gel permeation chromatography (GPC) for the homopolymers and the copolymers. The instrument used for this analysis was a Waters 150-C ALC/GPC equipped with Ultra Styragel columns of 100, 500, and 1000 Å porosities in CHCl₃. These polymers were analyzed using the UV detector at 254nm in conjunction with the differential refractive index detector, and polystyrene GPC standards. The sample concentrations used were 2 mg/ml with a flow rate of 1 ml/minute.
Electron Spectroscopy for Chemical Analysis (ESCA). This technique was used to investigate the chemical composition of the solid surface of the AHS catalyst. This material was analyzed with the Kratos XSAM-800 at 13KV and 20mA, with 3 scans performed per nucleus of interest. A magnesium anode was used in the analysis of the following elements to determine the atom percentages present in the sample: C$_{1s}$, O$_{1s}$, Al$_{2p}$, and S$_{2p}$.

Elemental Analysis. Elemental analysis was performed on the AHS catalyst by Microlytics (P.O. Box 199 So. Deerfield, MA 01373), and by Galbraith Laboratories Inc. (2323 Sycamore Dr. Knoxville, TN 37921-1750). The analysis was performed to determine the weight percentages of the following elements (C, H, S, Al), and the percent H$_2$O present in the catalyst.

Differential Scanning Calorimetry (DSC). DSC thermograms were obtained for the P(BVE) homopolymer on the Perkin-Elmer DSC 2B. The homopolymer was quenched at -90°C and heated at 10°C/min. on the first heating to observe the T$_g$ and T$_m$. Then the samples were allowed to slow cool at 10°C/min. to observe the crystallization temperature, which was approximately midpoint between the T$_g$ and the T$_m$. 

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Results and Discussion:

Introduction.

The first polymerization of a vinyl ether was reported in 1878 by Winslicenus\textsuperscript{59}. When iodine was added to ethyl vinyl ether, a violent reaction resulted which produced a resinous material. Later, Reppe and his coworkers at I. G. Farbenindustries\textsuperscript{59} developed an acetylene-alcohol reaction for synthesizing alkyl vinyl ether monomers, which launched the extensive use of these monomers. In 1947, Schildknecht et al.\textsuperscript{65} recognized that poly (isobutyl vinyl ether) obtained with BF\textsubscript{3} or BF\textsubscript{3}OEt\textsubscript{2} was either crystalline (non-tacky) or amorphous (tacky) depending on the polymerization conditions. This was the first experimental evidence for the stereoisomerism of the main chain of vinyl polymers.

These monomers are well known to be polymerized by many cationic initiating systems due to their high nucleophilicity. However, low molecular weight polymers have been obtained by free-radical catalysts, UV radiation or heat alone. Anionic initiating systems fail to polymerize alkyl vinyl ethers due to the electron donating nature of the pendent ether substituent.

Stereroregular alkyl vinyl ether polymers may be prepared with the correct choice of reaction conditions. High energy radiation (\(\beta\) or \(\gamma\) rays) creates the formation of syndiotactic polymer chains, and at room temperature
essentially quantitative yields of high molecular weight polymers have been obtained\textsuperscript{60,61}. 
Aluminum Hydrogen Sulfate Catalyst (AHS):

Introduction.

With the aluminum hydrogen sulfate (AHS) catalyst, cationic polymerization of alkyl vinyl ethers can be carried out near room temperature to produce high molecular weight materials. The use of this heterogeneous catalyst in these polymerizations has revealed that the overall reactions are very temperature dependent. Handling of the dried catalyst is performed in a glove box to avoid any moisture uptake. As a result, AHS can be used for alkyl vinyl ether polymerizations as a 2% suspension in mineral oil, and added to the reaction flask by weight assuming a uniform dispersion of the catalyst throughout the mineral oil. Prior to a polymerization, the off-white colored catalyst is easily detectable, but after the polymerization has started, the catalyst isn't noticeably visible. This is also observed once the polymerization is complete, and throughout the workup of the polymer. Consequently, it may be that only the initial stages of the polymerization occurs with the catalyst heterogeneous. Because of the stereospecificity obtained with this catalyst, this heterogeneous versus homogeneous nature warrants further investigation.

The reactivity of the AHS catalyst is very high. Polymerization takes place rapidly using catalyst levels of 0.1 wt. percent at 10°C. Some evidence that elimination
reactions may occur at higher temperatures has been obtained by monitoring the vinyl region in the NMR during polymerizations. The extent of molecular control which can be obtained using this catalyst system, and the number of initiating sites per molecule is currently under investigation. This catalyst may have great importance as an industrial catalytic material due to the ease with which it can be utilized, and due to the fact that it produces semicrystalline, high molecular weight poly (alkyl vinyl ethers) in excess of 300,000 g/mol.

Synthesis of Aluminum Hydrogen Sulfate Catalyst (AHS):

The aluminum hydrogen sulfate catalyst was produced from recrystallized aluminum sulfate octadecahydrate, \( \text{Al}_2(\text{SO}_4)\cdot18\text{H}_2\text{O} \), and concentrated \( \text{H}_2\text{SO}_4 \) with stirring for 20 hours at 90°C. The recrystallized powder is slightly soluble in concentrated \( \text{H}_2\text{SO}_4 \), and as the reaction progresses a slightly viscous, heterogeneous solution evolves. After the reaction is complete, the solution is filtered and washed repeatedly with diethyl ether to remove \( \text{H}_2\text{SO}_4 \). The collected material is dried under vacuum yielding an off-white colored powder (scheme 5).

Due to the hygroscopic nature of the AHS catalyst, it was handled under extremely inert conditions in a glove box. The catalyst was finely ground and a suspension in mineral
\[
\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O} \xrightarrow{\text{CONC. H}_2\text{SO}_4} \text{WHITE PASTE}
\]

\[
90^\circ\text{C} \quad 20\text{h}
\]

\[
\text{WASH WITH ETHER}
\]

\[
\text{DRY (64h, vac., 35^\circ\text{C})}
\]

\[
\downarrow \quad \downarrow
\]

\[
"\text{AWS}"
\]

\[
\rightarrow \text{transfer catalyst to bottle under inert conditions}
\]

\[
\rightarrow \text{prepare 2\% suspension in mineral oil}
\]

Scheme 5: Synthesis of Aluminum Hydrogen Sulfate (AHS) Catalyst
oil was prepared. This suspension can be transferred via syringe to the reaction flask.

**Characterization of the Aluminum Hydrogen Sulfate (AHS) Catalyst:**

$^{27}$Al Solid State (MAS) NMR.

Due to the possible hydration of the catalyst in D$_2$O for a solution NMR sample or a possible resultant structural change, solid state NMR analysis was used instead. This technique is very sensitive to the nature of the aluminum centers present in the AHS catalyst. From $^{27}$Al NMR, certain chemical shift regions can be analyzed which reveal the nature or the coordination number of the Al nuclei. Typically, aluminum carries a coordination number of 3, but it may expand its valence shell up to a coordination number of 6. Also, due to its quadropolar (3/2 spin) nucleus, the relaxation time of the Al atom is short, allowing for an advantageous effect where the nuclear relaxation times are usually very short and spectra may be quickly, and easily obtained$^{12}$.

From $^{27}$Al Solid State (MAS) NMR analysis, the AHS catalyst was analyzed to determine its possible structure. With a 4 mm rotor, the analysis was performed with 1.0 M Al(NO$_3$)$_3$ in deionized H$_2$O used as a reference at 0 ppm. The starting material, Al$_2$(SO$_4$)$_3$·18H$_2$O, produced a sharp, narrow peak at 0 ppm, indicative of a hexacoordinate octahedral
species. To determine if the starting material was different from the AHS catalyst, the catalyst was analyzed using the same reference standards. A single slightly broader symmetrical peak at approximately −20 ppm was observed for this material, indicating that only one type of aluminum species is present in this material (figure 4). Also, it indicates that a fairly symmetrical type of structure may exist for this material. According to Akitt\textsuperscript{63}, the increased substitution of sulfate groups on an aluminum atom will produce an upfield shift of the aluminum peak in an NMR spectrum. A proposed substitution of 6 sulfate groups onto an aluminum atom predicts a peak at approximately −20 ppm in solution referenced to Al(H\textsubscript{2}O)\textsubscript{6}\textsuperscript{3+} at 0 ppm.

\textit{\textsuperscript{1}H Solid State (MAS) NMR.}

The analysis performed on the AHS catalyst by \textit{\textsuperscript{1}H Solid State (MAS) NMR revealed that one type of acidic proton species was present. Relative to CHCl\textsubscript{3}, which was used as a reference at 7.24 ppm, a broad peak at approximately 11 ppm was observed indicative of an acidic type of proton species (figure 5). No quantitative comparison of the ratio of catalyst protons to the CHCl\textsubscript{3} protons was made.

\textit{Electron Spectroscopy for Chemical Analysis (ESCA).}

ESCA is widely used as an analytical technique to investigate the chemical composition of solid surfaces. With
Figure 4: $^{27}\text{Al}$ Solid State (MAS) NMR of $\text{Al}_2(\text{SO}_4)_3\cdot18\text{H}_2\text{O}$ and AHS catalyst
Figure 5: $^1$H Solid State (MAS) NMR of AHS catalyst
the AHS catalyst, we were interested in obtaining the atom percentages of the different elements to aid in the determination of its structure.

The results obtained for this analysis are shown in Table 2. There are approximately 2 sulfur atoms to 1 aluminum atom, 8 oxygen atoms to 1 Al atom, and approximately 3 oxygen atoms per 1 sulfur atom.

**Elemental Analysis.**

This analysis was performed to determine the weight percentages of the different elements present in the catalyst, and to aid in the determination of its structure from a quantitative analysis route (Table 3).

**Proposed Mechanism and Structure of the AHS Catalyst:**

From the results obtained, we have been able to show that the AHS catalyst possesses an octahedral structure, with an acidic proton species present in the structure. The catalyst structure may have some of the sulfate groups coordinated to the aluminum nucleus, while the other surrounding sulfate groups may be covalently bonded to the aluminum nucleus. It is proposed that the structure of the AHS catalyst follows that of a polymeric type of species (figure 6). Analysis performed by ESCA and elemental analysis supports this proposed structure.
Table 2: ESCA analysis results (atom percentages) of the AHS catalyst

<table>
<thead>
<tr>
<th>C_{1s}</th>
<th>O_{1s}</th>
<th>Al_{2p}</th>
<th>S_{2p}</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.01</td>
<td>56.55</td>
<td>7.29</td>
<td>17.14</td>
</tr>
</tbody>
</table>

Table 3: Elemental Analysis results (weight percentages) of the AHS catalyst

<table>
<thead>
<tr>
<th>H(%)</th>
<th>Al(%)</th>
<th>S(%)</th>
<th>H$_2$O(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.97</td>
<td>9.06</td>
<td>26.39</td>
<td>7.25</td>
</tr>
</tbody>
</table>
Figure 6: Proposed Structure of the Aluminum Hydrogen Sulfate (AHS) Catalyst
The protons in the catalyst structure are believed to initiate the polymerization of alkyl vinyl ethers, with their attachment to the sulfate groups that are not bound on both sides by an aluminum nucleus. The counterion believed to stabilize the cation generated on the alkyl vinyl ethers after initiation is the anion of the sulfate group to which the proton was previously attached. The ability of the counterion to covalently bond to the cation should be reduced by the Lewis acidic nature of the electron deficient aluminum nucleus. This atom lowers the nucleophilicity of the sulfate anion that may be generated. Also, the highly stereoregular polymer chains that have been generated with the AHS catalyst suggest that the catalyst itself directs the monomer onto the growing polymer chain end. The aluminum nuclei of the catalyst are believed to coordinate to the pendent ether group of the monomer and to the ether pendent group of the end unit of the growing polymer chain. It is this proposed coordination of the aluminum to the pendent ether groups that may be responsible for the highly isotactic triad sequencing in poly (alkyl vinyl ether) chains obtained with this catalyst (scheme 1).
Synthesis of Butyl Vinyl Ether Homopolymers and Copolymers:

Introduction.

The primary objective of this research was to obtain controlled synthesis conditions for the polymerization of alkyl vinyl ethers via the aluminum hydrogen sulfate (AHS) catalyst system. By utilizing this heterogeneous catalyst, alkyl vinyl ethers undergo cationic polymerization at higher temperatures yielding semicrystalline, high molecular weight materials. The characterization of the homopolymers and copolymers was also deemed very important in order to understand the role of the AHS catalyst system. Moreover, evaluation of these materials was necessary to further use them in a graft copolymerization reaction with 2-alkyloxazolines as blend compatibilizers for the poly(propylene)-Nylon 6 blend systems.

Synthesis of Poly (Butyl Vinyl Ether) Homopolymers:

Synthesis of poly (butyl vinyl ether) homopolymers using the AHS catalyst (2% suspension in mineral oil) was performed at temperatures of 10°C and lower in toluene (scheme 6). Immediately prior to the addition of the butyl vinyl ether monomer to the reaction flask, it was vacuum distilled from Al(iso-Bu). The addition of the catalyst, an off white colored powder, is visible in the reaction flask prior to polymerization, but during and after polymerization, it was undetectable. As the polymerization proceeds, the colorless
Scheme 6: Polymerization of butyl vinyl ether with AHS in toluene at 10°C
solution (1000:1 (w/w) ratio of monomer:catalyst) turns a light yellow-orange color with a noticeable increase in the viscosity of the solution. The polymerization was conveniently monitored by $^1$H NMR to observe the disappearance of the vinylic protons of the monomer. Once the polymerization was complete, the chain ends were terminated with diethylamine. No noticeable color change of the solution is observed upon termination. The resulting material is a light orange-yellow, rubbery material obtained in 75-80% yield.

Polymerization of alkyl vinyl ethers using ARS is believed to occur via initiation of the chains by an acidic proton ($H^+$). The resulting cation is proposed to be stabilized by a counterion complex. The catalyst is proposed to direct the incoming monomer through coordination to the aluminum nucleus onto the growing polymer chain yielding greater than 70% isotactic triad sequencing in the poly (butyl vinyl ether) chains. The polymers obtained are extremely high molecular weight materials. Thus it is assumed that the number of initiating sites present per gram of catalyst must be very small with respect to the amount of monomer added.
Characterization of Poly (Butyl Vinyl Ether) Homopolymers:

$^{1}H$ NMR.

The polymerization of butyl vinyl ether was monitored by $^{1}H$ NMR to observe the disappearance of the vinylic protons in the spectrum of the monomer (figure 7). The samples were run in CDCl$_3$ with 0.03% (v/v) tetramethylsilane (TMS) used as an internal reference. The disappearance of the monomer methine proton at 6.5 ppm, a doublet of doublets, and the disappearance of the methylene protons at 4.1 and 3.9 ppm (doublets) can be easily monitored to observe the progress of the reaction. During the reaction, the peaks present in the spectrum that correspond to the pendent methylene and methyl protons tend to broaden.

$^{13}C$ NMR.

$^{13}C$ NMR analysis was used to confirm that the polymeric material recovered was free of residual monomer (figure 8). The solvent employed was CDCl$_3$ or toluene-d$_6$ for tacticity measurements. The resulting spectrum revealed a clean material with a small percentage of mineral oil present from the catalyst suspension used in the polymerization.

Tacticity Measurements--$^{13}C$ NMR.

The stereoregularity of the homopolymers was obtained by $^{13}C$ NMR. The poly (butyl vinyl ether) homopolymers were solubilized in toluene-d$_6$ with chromium(III) acetylacetonate
Figure 7: $^1$H NMR of butyl vinyl ether (BVE) and poly (butyl vinyl ether)
Figure 8: $^{13}$C NMR of poly (butyl vinyl ether), P(BVE)
added as a relaxation agent to reduce the relaxation times. Previous work revealed that poly (alkyl vinyl ether)s prepared with AHS were highly isotactic materials\(^5\) by \(^1\)H NMR. Poly (butyl vinyl ether) analyzed by \(^1\)H NMR was difficult to interpret due to the slight chemical shift changes of some of the peaks, and the overlap of peaks which were unresolvable for tacticity analysis. However, by \(^13\)C NMR, the analysis of chain stereoregularity was easier due to the larger chemical shift range available to the \(^13\)C nuclei. The nucleus of interest was the methine carbon of the homopolymer. With approximately 8000-12000 scans run for 8-10 hours, the fine splitting of the peaks in the spectrum, due to the environment surrounding the methine carbon were observed. The resulting spectra were expanded, and the peaks of interest were deconvoluted to determine the percent tacticity of this material. According to the literature\(^6\), the methine carbon peak splitting from downfield to upfield indicates the presence of syndiotactic, heterotactic, and isotactic triads, respectively. In the AHS catalyzed polymerization of butyl vinyl ether, approximately 75-80\% isotactic triad content was obtained (figure 9). It has been proposed that the catalyst surface itself plays a major role in these polymerizations\(^1,3-5\). With the homogeneous HI/ZnI\(_2\) catalyst system, a relatively random stereochemical placement of the monomer onto a growing chain end was revealed, yielding a greater percentage of
Figure 9: $^{13}$C NMR for P(BVE) - methine carbon; tacticity determined from deconvolution for HI/ZnI$_2$ and AHS catalyst systems.
syndiotactic triads. The selectivity of this system during a alkyl vinyl ether polymerization is reduced relative to the AHS catalyst system (figure 10).

Gel Permeation Chromatography (GPC).

Analysis of the poly (butyl vinyl ether) homopolymers by GPC revealed that at a monomer to catalyst ratio of 1000:1 (w/w), apparent molecular weights in excess of 300,000 g/mol are achievable. These materials are solubilized in CHCl₃ and analyzed at 30°C using Ultrastyragel columns and poly(styrene) standards. Interestingly, these homopolymers obtained via the AHS catalyst system revealed a fairly narrow polydispersity. The GPC traces obtained for these homopolymers compare well to those obtained from polymers synthesized with the Hf/ZnI₂ catalyst¹¹ (figure 11). Since these traces are narrow, it suggests that this polymerization system may be a 'living' one, and thus, it may be possible to control molecular weight. Polymerizations with lower ratios of monomer to catalyst suggest a similar trend as noted above. However, preliminary studies showed no noticeable apparent molecular weight differences resulting from different monomer:catalyst ratios when the catalyst was used as a suspension in mineral oil. Attempts at controlling the molecular weight through the use of a mineral oil free catalyst are warranted.
Figure 10: $^{13}$C NMR tacticity results of comparison of HI/ZnI$_2$ and AHS catalysts
GEL PERMEATION CHROMATOGRAPHY

- Solvent: CHCl₃
- Temp: 30°C
- Column: Ultrastyragel Polystyrene Standards
- Detector: RI

Poly(Butyl Vinyl Ether)

\[
\frac{M_w}{M_n} = 1.3
\]

\[
M_n = 433900 \text{ (GPC)}
\]

\[
^{25}C \eta_{CHCl_3} = 6.8 \text{ dl/g}
\]

\[
p(BVE) : MW 20,000
\]

\[
\frac{M_w}{M_n} = 1.14
\]

Figure 11: Gel permeation chromatography (GPC) traces of P(BVE) synthesized with HI/ZnI₂ and AHS catalyst systems
Due to the inherent sensitivity and high activity of the AHS catalyst, the proper reaction conditions employed are very important. At higher temperatures of 10°C, a monomer:catalyst concentration of 50:1 and 250:1 yielded broadened polydispersities, while at -35°C, the GPC traces were considerably narrower confirming that the lowered temperature used is important in this system (figure 12). At higher temperatures, in particular at a catalyst concentration of 50:1 at 10°C, the color of the reaction mixture turned black during the polymerization indicating the possible presence of an exotherm during this reaction. From GPC analysis, evidence of tailing (broadening) in these GPC traces at the low molecular weight end confirmed the possibility that early termination may have occurred in some of the growing polymer chains. Earlier work performed on the polymerization of ethyl vinyl ether with the AHS catalyst, as monitored by ¹H NMR, showed evidence of vinylic protons appearing in the spectrum during polymerization which may be due to a β proton elimination reaction.

**Intrinsic Viscosity Measurements [η]:**

The intrinsic viscosity results obtained on the poly (butyl vinyl ether) homopolymers were in excess of 6 dl/g in CHCl₃ at 30°C. These measurements were difficult to obtain due to the high viscosity presented by these high molecular
Poly (Butyl Vinyl Ether)

**Gel Permeation Chromatography (GPC)**

Solvent: CHCl₃  
Column: Ultrastyragel  
Standards: Poly (styrene)  
Temperature: 30°C

**Figure 12:** Gel Permeation Chromatography (GPC) comparison of P(BVE) synthesized with AHS at different reaction temperatures
weight materials. The results of this analysis confirmed qualitatively the apparent molecular weights obtained from GPC, indicating the high molecular weight nature of the materials (figure 11).

**Differential Scanning Calorimetry (DSC).**

These materials have the potential to be semicrystalline due to their highly stereoregular isotactic triad content. These highly stereoregular polymers allow for a more regular placement or packing of the long chain molecules, which is characteristic of semicrystalline materials. Analysis by differential scanning calorimetry (DSC) revealed a $T_g$ of $-55^\circ$C (figure 13) for poly (butyl vinyl ether), which is comparable to that found in the literature$^{52}$. A $T_m$ of 60°C was also obtained for these highly stereoregular materials confirming their semicrystalline nature (figure 14). Upon slow cooling of these polymers at 10°C/minute starting above their $T_m$, a crystallization temperature at 3°C, approximately midpoint between the $T_g$ and $T_m$ was observed (figure 15).

**Synthesis of Poly (Butyl Vinyl Ether-2-Chloroethyl Vinyl Ether) Copolymers:**

The synthesis of poly (butyl vinyl ether-2-chloroethyl vinyl ether) copolymers via the AHS catalyst was prepared with 3-10 mole % of 2-chloroethyl vinyl ether at 10°C in toluene (scheme 7). The low molar percentage of 2-chloroethyl vinyl
Figure 13: Differential Scanning Calorimetry (DSC) results of P(BVE) synthesized with AHS - T$_s$
Figure 14: Differential Scanning Calorimetry (DSC) results of P(BVE) synthesized with AHS - $T_m$
Figure 15: Differential Scanning Calorimetry (DSC) results of P(BVE) synthesized with AHS - $T_x$
\[
\begin{align*}
\text{CH}_2\text{=CH} + \text{CH}_2\text{=CH} & \quad (3-10 \text{ mol \%}) \\
\text{O} & \quad \text{O} \\
(\text{CH}_2)_3 & \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{Cl}
\end{align*}
\]

\[
\text{AHS (0.1 wt \%)} \\
\text{TOLUENE} \\
10^\circ\text{C}
\]

\[
\begin{align*}
\text{O} \quad \text{O} \\
(\text{CH}_2)_3 & \quad \text{CH}_2 \\
\text{CH}_3 & \quad (\text{CH}_2)_3 \\
\text{Cl} & \quad \text{CH}_3
\end{align*}
\]

Scheme 7: Polymerization of butyl vinyl ether and 2-chloroethyl vinyl ether with AHS in toluene at 10°C
ether used in these polymerizations was to allow for adequate spacing between these monomer units where the ethoxyl chloride pendant was to be further utilized in graft copolymerizations.

The butyl vinyl ether monomer was purified as described above for the homopolymer synthesis. Then the two monomers were thoroughly mixed in a flask prior to their addition, via cannula, to the reaction flask with the AHS catalyst and toluene present. The colorless polymerization solution turns to a light yellow-orange color as the reaction proceeds with a notable increase in the viscosity of the solution. The reaction was monitored by $^1$H NMR to observe the disappearance of the vinylic protons of both monomers. The copolymer was terminated with diethylamine. The resulting polymer was a light orange-yellow, rubbery material obtained in 75-80% yield.

**Characterization of Poly (Butyl Vinyl Ether-2-Chloroethyl Vinyl Ether) Copolymers:**

$^1$H NMR.

The polymerization of butyl vinyl ether with 2-chloroethyl vinyl ether was monitored by $^1$H NMR to observe the disappearance of the vinylic protons in the spectrum of the monomers (figure 16). The samples taken during the polymerization were solubilized in CDCl$_3$ with 0.03% (v/v) TMS used as an internal reference.
Figure 16: $^1$H NMR spectrum of comonomers for P(BVE-C1EVE) copolymerization with CHCl$_3$ (internal reference)
An $^1$H NMR study on the polymerization of butyl vinyl ether with 2-chloroethyl vinyl ether was performed to determine if the polymerization yielded a random versus a block copolymer. The AHS catalyst and toluene-$d_8$, which was used as the reaction and lock solvent, and CH$_2$Cl$_2$ (internal reference) were placed in a scrupulously dried and evacuated 10 mm NMR tube with a septum. Then, the contents in the tube were cooled to -78°C with a dry ice/isopropanol bath for 15 minutes. Next, the thoroughly mixed monomers were added to the tube. The 10 mm NMR probe was cooled to 5°C, and equilibrated for 10 minutes prior to insertion of the tube. After the sample tube was placed in the NMR spectrometer, the reaction was monitored from the beginning of the reaction until its completion with scans run at 15 minute intervals. Incorporation of the 2-chloroethyl vinyl ether monomer into the copolymer chain was observed by the disappearance of the methine protons of both monomers with reference to CH$_2$Cl$_2$ (figure 17). From this study, the percent of 2-chloroethyl vinyl ether incorporated into the copolymer relative to the initial feed ratio of 90:10 (butyl vinyl ether: 2-chloroethyl vinyl ether) could be monitored (table 4 and 5). The data obtained revealed that the 2-chloroethyl vinyl ether is 'randomly' incorporated into the copolymer with a tailing of 2-chloroethyl vinyl ether toward the chain ends (figure 18).
Figure 17: $^1$H NMR study of P(BVE-CLEVE) copolymerization - consumption of monomers vs. time
Table 4: Percent conversion as a function of f2 and F2 during the $^1$H NMR copolymerization experiment of butyl vinyl ether : 2-chloroethyl vinyl ether (90:10 mole %)

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>f2</th>
<th>F2</th>
<th>% conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.90</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>0.83</td>
<td>0.96</td>
<td>56.6</td>
</tr>
<tr>
<td>20</td>
<td>0.67</td>
<td>0.95</td>
<td>82.0</td>
</tr>
<tr>
<td>35</td>
<td>0.53</td>
<td>0.95</td>
<td>88.4</td>
</tr>
<tr>
<td>50</td>
<td>0.44</td>
<td>0.94</td>
<td>91.8</td>
</tr>
<tr>
<td>65</td>
<td>0.41</td>
<td>0.94</td>
<td>93.2</td>
</tr>
</tbody>
</table>

f2 = mole fraction in feed (butyl vinyl ether)
F2 = mole fraction in copolymer (butyl vinyl ether)
Table 5: Composition (mole %) of butyl vinyl ether:2-chloroethyl vinyl ether during copolymerization experiment via $^1$H NMR

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>BVE</th>
<th>CLEVE</th>
<th>BVE (copolymer)</th>
<th>CLEVE (copolymer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>88.0</td>
<td>12.0</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>5</td>
<td>35.9</td>
<td>7.5</td>
<td>52.1</td>
<td>4.5</td>
</tr>
<tr>
<td>20</td>
<td>12.1</td>
<td>5.9</td>
<td>75.9</td>
<td>6.1</td>
</tr>
<tr>
<td>35</td>
<td>6.2</td>
<td>5.4</td>
<td>81.8</td>
<td>6.6</td>
</tr>
<tr>
<td>50</td>
<td>3.6</td>
<td>4.6</td>
<td>84.4</td>
<td>7.4</td>
</tr>
<tr>
<td>65</td>
<td>2.8</td>
<td>4.0</td>
<td>85.3</td>
<td>8.1</td>
</tr>
</tbody>
</table>
Figure 18: Plot of $F_1$ (CIEVE-mole fraction in copolymer) vs. percent (%) conversion of $P$(BVE-CIEVE) copolymer
The reactivity of butyl vinyl ether monomer is greater than that of the 2-chloroethyl vinyl ether monomer due to the greater electron donating ability of the butoxy pendent group of the butyl vinyl ether. This pendent group stabilizes the cation generated during polymerization, and also increases the nucleophilicity of this monomer. The ethoxychloride pendent group of the 2-chloroethyl vinyl ether donates electrons less freely to the cation generated during polymerization due to the electron withdrawing effect of the chloride substituent, which also decreases the nucleophilicity of the monomer during polymerization.

\textsuperscript{13}C NMR.

\textsuperscript{13}C NMR was used to determine quantitatively if the 2-chloroethyl vinyl ether monomer was actually incorporated into the copolymer backbone. Approximately 10-15\% (w/v) of the copolymer was solubilized in either CDCl\textsubscript{3} or toluene-d\textsubscript{8} with chromium(III) acetylacetonate used as a relaxation agent. The \textsuperscript{13}C NMR spectra obtained on these copolymers were decoupled eliminating any C-H and H-H coupling. The integrated ratio of the methylene group next to the chlorine of the 2-chloroethyl vinyl ether, and the methyl group of the butyl vinyl ether monomer were compared to determine the ratio of the 2-chloroethyl vinyl ether monomer incorporation into the copolymer (figure 19).
Figure 19: $^{13}$C NMR (quantitative) spectrum of P(BVE-C(EVE)) copolymer relative to P(BVE) homopolymer
Gel Permeation Chromatography.

Analysis by GPC revealed that at a monomer to catalyst ratio of 1000:1, the apparent molecular weights obtained were in excess of 300,000 g/mol. These materials were solubilized in CHCl₃, and analyzed at 30°C using Ultrastyrigel columns and poly (styrene) standards. Fairly narrow molecular weight distributions were found (figure 20).

Intrinsic Viscosity Measurements [η].

The intrinsic viscosity measurements in CHCl₃ at 30°C obtained on the copolymers revealed values of =4.0 d1/g for these materials. These results qualitatively confirm the GPC results, which indicate that the copolymers are high molecular weight materials (figure 20).
GEL PERMEATION CHROMATOGRAPHY

- Solvent: CHCl₃
- Temp: 30°C
- Column: Ultrastyragel Polystyrene Standards
- Detector: RI

Figure 20: Gel Permeation Chromatography (GPC) trace comparison of P(BVE-ClEVE) with P(BVE)
Conclusions

This work has demonstrated that poly (n-butyl vinyl ether) homopolymers and copolymers can be synthesized with a heterogeneous catalyst, AHS, under controlled reaction conditions. These polymerizations produce materials with high molecular weights and relatively narrow polydispersities. This suggests that the AHS catalyst is a heterogeneous catalyst system that may produce a 'living' cationic polymerization in the polymerization of butyl vinyl ether homopolymers and copolymers. This may be the first known cationic heterogeneous catalyst which produces at least quasi-living polymer chains. Additional characterization of the polymers prepared with AHS revealed that these materials were highly isotactic, semicrystalline materials. Further investigations of the living nature of the system are warranted, because this catalyst may offer a route to isotactic block copolymers not obtainable by alternate routes.

Future work with the AHS catalyst system includes determining the extent of molecular weight control without a mineral oil suspension. Studies performed to determine if this catalyst system in the polymerization of butyl vinyl ether is living need to be pursued with a study on the increase in molecular weight versus percent conversion.
Later, a study on the lifetime of the growing chain ends will be performed by the addition of more monomer to active chain ends, and to observe an increase in molecular weight. An analysis to determine the number of active sites per gram of catalyst needs to be investigated, possibly via a titration method, or another form of analysis. Lastly, functionalization of the polymer chains will be pursued once the molecular weight is controllable.
REFERENCES:


Vita

John M. Bronk, son of John and Diane Bronk, was born on February 11, 1965 in Rochester, Minnesota. He graduated from Mazeppa High School in 1983, and joined the Minnesota Army National Guard prior to graduation from high school. He attended the University of Wisconsin-River Falls, and graduated in June of 1988 with a Bachelor of Science Degree in Chemistry. During his undergraduate studies, he worked at 3M (Post-It™ New Products Group) in the area of pressure sensitive adhesives, and new label technologies. He also received his commission as an officer in the Army National Guard in 1987. In the fall of 1988, he entered graduate school in the Department of Chemistry at Virginia Polytechnic Institute and State University, and began his masters research with Dr. Judy S. Riffle. His masters graduate research efforts were focused on obtaining controlled synthesis conditions for the synthesis of poly (alkyl vinyl ether)s with an aluminum hydrogen sulfate catalyst. He will continue in the doctoral research program at VPI & SU.