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Grafting reactions of vinyl acetate onto poly[(vinyl alcohol)-co- (vinyl acetate)]

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GRAFTING REACTIONS OF VINYL ACETATE ONTO POLY[(VINYL ALCOHOL)-CO-(VINYL ACETATE)]

BY

THOMAS J. MARKLEY

A THESIS
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1994

CERTIFICATE OF APPROVAL

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ABSTRACT

The present research has examined the ability of vinyl acetate (VAc) to preferentially graft onto the methine carbon of poly(vinyl alcohol) (PVOH) over polyvinyl acetate (PVAc) to give highly branched PVOH.

The grafting polymerizations were run in a methanol medium in the presence of poly[(vinyl alcohol)-co-(vinyl acetate)]. Low concentrations of vinyl acetate were added continuously during each reaction in order to favor branching, and the overall conversion of the reaction was determined titrimetrically and gravimetrically.

The effects of varying the concentration of monomer and initiator on the molecular weight of the graft copolymer was studied. The results showed that decreasing the monomer or initiator concentration decreased the molecular weight of the graft copolymer formed. Also, the influence that initiators have on the extent of grafting onto the copolymer was studied. It was determined that of the initiators studied ammonium persulfate led to copolymers with the largest increase in molecular weight.

After polymerization the samples were hydrolyzed and reacetylated in order to determine where grafting occurs along the poly[(vinyl alcohol)-co-(vinyl acetate)] chain. The change in molecular weight of original poly[(vinyl alcohol)-co-(vinyl acetate)] due to the grafting reactions was determined by Gel Permeation Chromatography (GPC) for each polymer (copolymer, fully hydrolyzed or reacetylated) form. ^{13}C NMR was also used to determine the number of grafts that occurred on the main chain methine carbon of the fully hydrolyzed form. The results showed that grafting occurred on the acetate groups of the PVAc units rather than the methine carbon of the PVOH or PVAc units.

1.0 INTRODUCTION

Poly(vinyl alcohol) (PVOH) is a highly crystalline water-soluble polymer. There are many different commercial applications for poly(vinyl alcohol), such as paper sizing, adhesives, and textile sizing. Since many applications for PVOH exist, there is a need for various grades of poly(vinyl alcohol), each with considerably different properties.

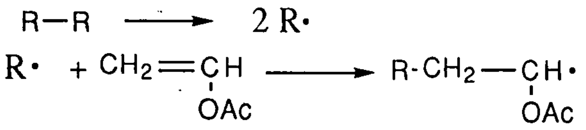
Commercial PVOH normally has only minor branching. PVAc branching is primarily through the acetate side chain, and not the main chain methine or methylene carbon.[1,2] When hydrolyzed to form PVOH, the branches are cleaved, leaving a lower molecular weight, largely linear PVOH.

If PVOH were branched, it could lead to valuable new PVOH properties. Since PVOH is a highly crystalline material, it presently dissolves slowly in hot water. Branched PVOH would be less energy-intensive to dissolve, and might dissolve in cold water. Highly branched PVOH would contain more primary hydroxyl groups (OH). These functional groups could be used for faster, more efficient crosslinking than the secondary OH groups in standard PVOH. Other possible properties of highly branched PVOH include a lower viscosity at high molecular weight, and a lower melting point. This may allow PVOH to be extruded without the use of a plasticizer, or with the use of less plasticizer.

1.1 BACKGROUND THEORY

Relative to other free radical polymerizations to high molecular weight polymers, vinyl acetate polymerization has a high degree of chain transfer.[3] Since the kinetic chain length of vinyl acetate polymerization is partially controlled by chain transfer, the classical scheme of free radical polymerization is reviewed for the reader.

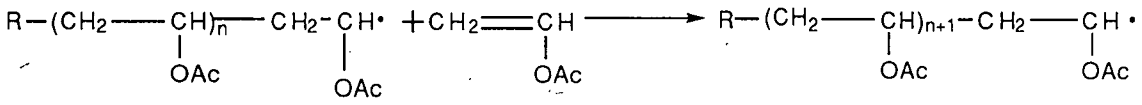
Initiation



$$\mathrm{R-R} \longrightarrow 2\mathrm{R}\cdot$$

$$\mathrm{R}\cdot + \mathrm{CH_2{=}\underset{OAc}{CH}} \longrightarrow \mathrm{R\text{-}CH_2-\underset{OAc}{CH}}\cdot$$

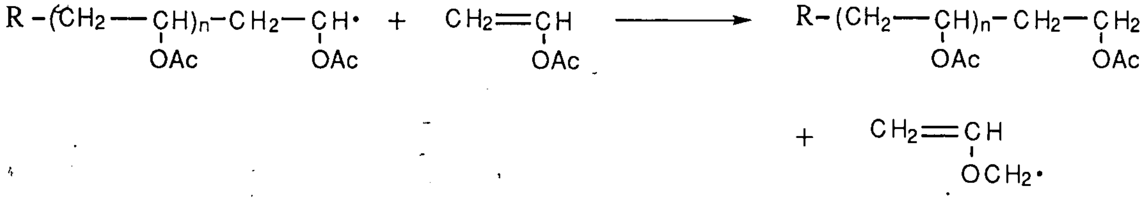
Propagation



$$\mathrm{R-(CH_2-\underset{OAc}{CH})_n-CH_2\text{-}\underset{OAc}{CH}}\cdot + \mathrm{CH_2{=}\underset{OAc}{CH}} \longrightarrow \mathrm{R-(CH_2-\underset{OAc}{CH})_{n+1}-CH_2-\underset{OAc}{CH}}\cdot$$

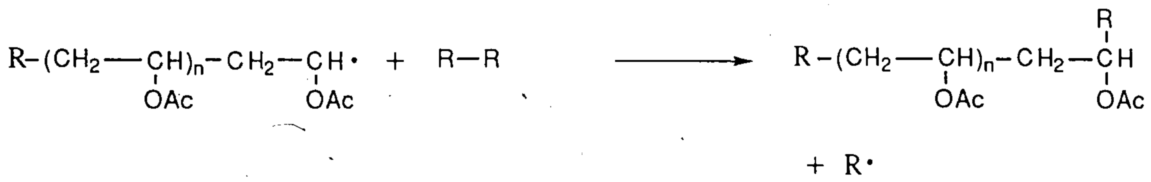
Chain Transfer

A. To Monomer



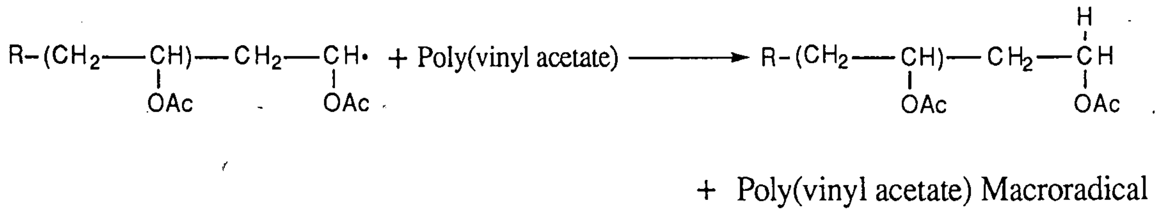
$$\mathrm{R-(CH_2-\underset{OAc}{CH})_n-CH_2-\underset{OAc}{CH}}\cdot + \mathrm{CH_2{=}\underset{OAc}{CH}} \longrightarrow \mathrm{R-(CH_2-\underset{OAc}{CH})_n-CH_2-\underset{OAc}{CH_2}} + \mathrm{CH_2{=}\underset{OCH_2\cdot}{CH}}$$

B. To Initiator



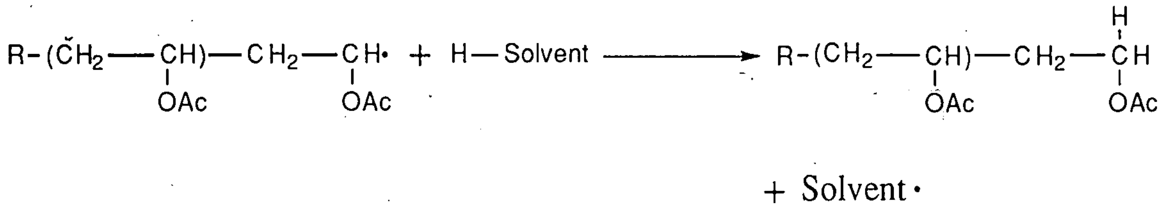
$$\mathrm{R-(CH_2-\underset{OAc}{CH})_n-CH_2-\underset{OAc}{CH}}\cdot + \mathrm{R-R} \longrightarrow \mathrm{R-(CH_2-\underset{OAc}{CH})_n-CH_2-\underset{OAc}{\overset{R}{CH}}} + \mathrm{R}\cdot$$

C. To Polymer



$$R\text{-}(CH_2\text{—}\underset{OAc}{CH})\text{—}CH_2\text{—}\underset{OAc}{CH}\cdot + \text{Poly(vinyl acetate)} \longrightarrow R\text{-}(CH_2\text{—}\underset{OAc}{CH})\text{—}CH_2\text{—}\underset{OAc}{\overset{H}{CH}} + \text{Poly(vinyl acetate) Macroradical}$$

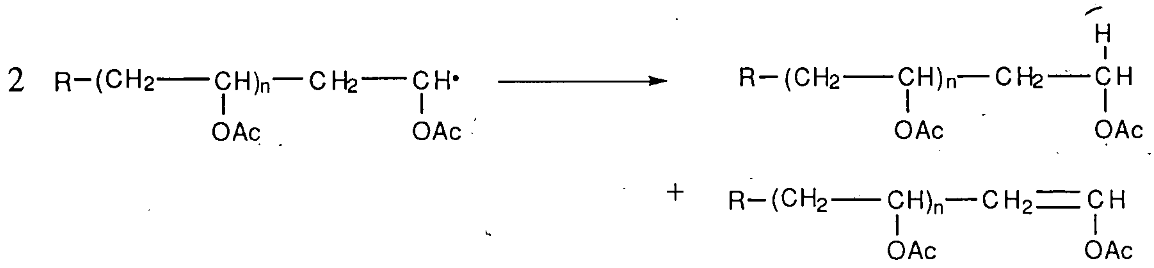
D. To Solvent or Chain Transfer Agent



$$R\text{-}(CH_2\text{—}\underset{OAc}{CH})\text{—}CH_2\text{—}\underset{OAc}{CH}\cdot + H\text{—Solvent} \longrightarrow R\text{-}(CH_2\text{—}\underset{OAc}{CH})\text{—}CH_2\text{—}\underset{OAc}{\overset{H}{CH}} + \text{Solvent}\cdot$$

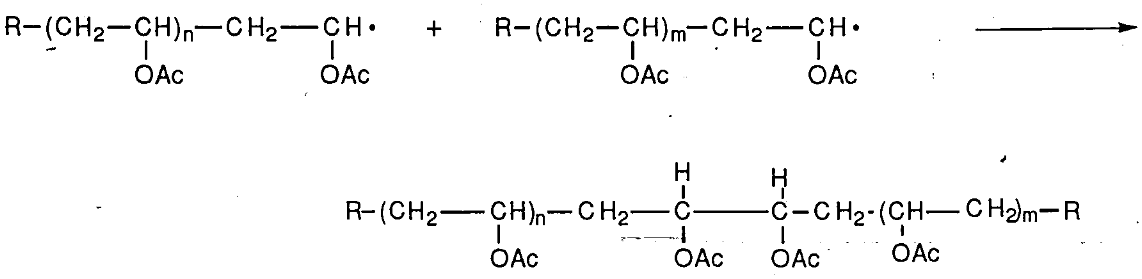
Termination

A. By Disproportionation



$$2\ R\text{-}(CH_2\text{—}\underset{OAc}{CH})_n\text{—}CH_2\text{—}\underset{OAc}{CH}\cdot \longrightarrow R\text{-}(CH_2\text{—}\underset{OAc}{CH})_n\text{—}CH_2\text{—}\underset{OAc}{\overset{H}{CH}} + R\text{-}(CH_2\text{—}\underset{OAc}{CH})_n\text{—}CH_2{=}\underset{OAc}{CH}$$

B. By Coupling



$$R-(CH_2-\underset{OAc}{CH})_n-CH_2-\underset{OAc}{CH}\cdot + R-(CH_2-\underset{OAc}{CH})_m-CH_2-\underset{OAc}{CH}\cdot \longrightarrow R-(CH_2-\underset{OAc}{CH})_n-CH_2-\underset{OAc}{\overset{H}{C}}-\underset{OAc}{\overset{H}{C}}-CH_2-(\underset{OAc}{CH}-CH_2)_m-R$$

Branching which occurs in the polymerization of PVAc

Branching of vinyl acetate occurs by three reactions: chain transfer to monomer(which gives a polymer molecule with a terminal double bond), chain transfer to polymer (which polymerizes with VAc to give a trifunctional branch point in the polymer molecule), and the terminal double bond polymerization in which an entire polymer molecule adds to a growing polymeric radical.[4,5,6,7,8,9,10]

The reaction leading to the formation of graft copolymers in this thesis is the transfer to polymer in which the polymer is poly[(vinyl alcohol)-co-(vinyl acetate)]. The reactions leading to grafting are illustrated below:

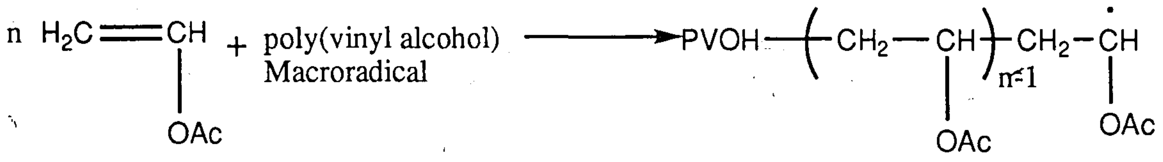
Transfer to PVOH

$$R\cdot + \text{poly(vinyl alcohol)} \longrightarrow RH + \text{poly(vinyl alcohol) Macroradical}$$

Transfer to PVAc

$$R^{\bullet} + \text{poly(vinyl acetate)} \longrightarrow RH + \text{poly(vinyl acetate) Macroradical}$$

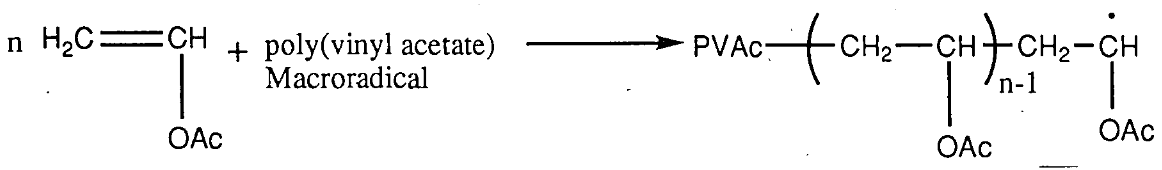
Initiation and Growth of Vinyl Acetate from PVOH Macroradical



$$n\ H_2C{=}CH(OAc) + \text{poly(vinyl alcohol) Macroradical} \longrightarrow PVOH\text{—}\left(CH_2\text{—}CH(OAc)\right)_{n-1}\text{—}CH_2\text{—}\dot{C}H(OAc)$$

Grafted Copolymer

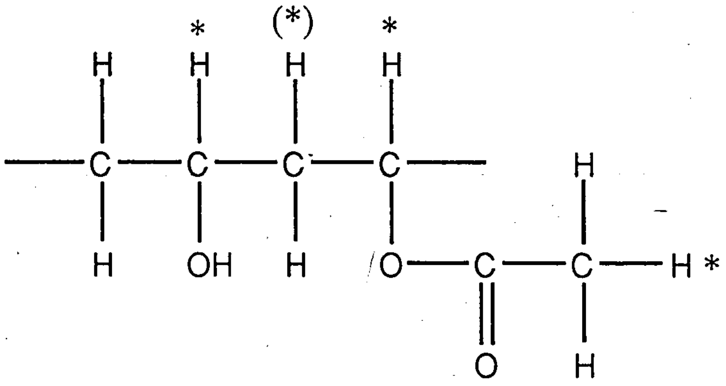
Initiation and Growth of Vinyl Acetate from PVAc Macroradical



$$n\ H_2C{=}CH(OAc) + \text{poly(vinyl acetate) Macroradical} \longrightarrow PVAc\text{—}\left(CH_2\text{—}CH(OAc)\right)_{n-1}\text{—}CH_2\text{—}\dot{C}H(OAc)$$

Grafted Copolymer

The specific sites on the poly((vinyl alcohol)-co -(vinyl acetate)) are:



Although the rate of chain transfer in vinyl acetate polymerization is relatively high, the rate of propagation is still much faster. In PVAc polymerization the k_p (rate of propagation) >> k_{tr} (rate of chain transfer). This leads to a low degree of branching because of the low efficiency of abstracting the methine H as shown in Diagram 1. Diagram 1 also shows that a large number of these branches (grafting on the acetate group leads to the largest number of branches) are hydrolyzable, which leads to linear poly(vinyl alcohol). However, PVOH has a much higher methine abstraction efficiency, as confirmed by published chain transfer constants for the model compounds isopropyl alcohol and isopropyl acetate, as shown in Diagram 2.[3] In all cases the chain transfer constants are relative to k_p where $C = k_{tr}/k_p$.(Abstraction of methylene H's also occurs, but is slower still, and has less effect on final PVOH branching).

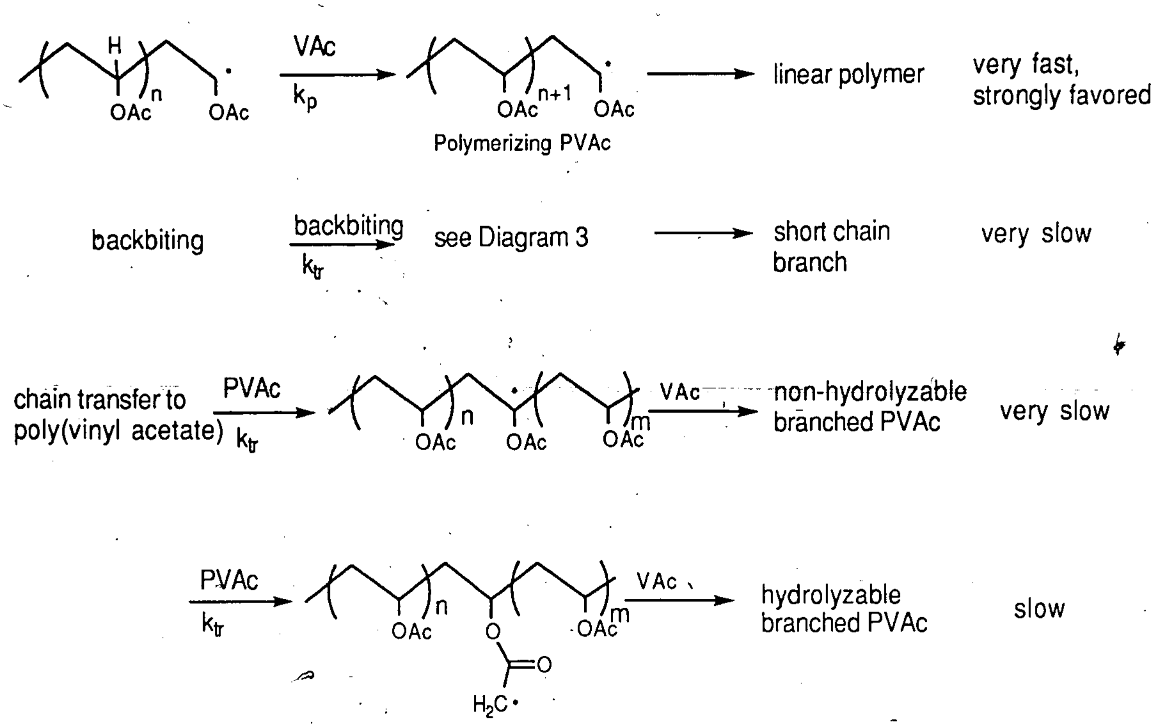


Diagram 1: *Processes of PVAc Polymerization*

isopropyl alcohol: good model for PVOH

isopropyl acetate: good model for PVAc

$C_S = 44.6 \times 10^{-4}$ at 70 °C **5.2 : 1** $C_S = 9.0 \times 10^{-4}$ at 67.5 °C

Ratio for a vinyl acetate radical abstracting a hydrogen from isopropyl alcohol (IPA) compared to isopropyl acetate

isopropyl alcohol

tert-butyl acetate

$C_S = 44.6 \times 10^{-4}$ at 70 °C **7.2 : 1** $C_S = 6.2 \times 10^{-4}$ at 60 °C

Ratio for a vinyl acetate radical abstracting a hydrogen from IPA compared to tert-butyl acetate

Diagram 2: *Chain transfer ratios for model compounds isopropyl alcohol and isopropyl acetate*

The higher methine abstraction efficiency of PVOH was also reported by Okamura and Motoyama who determined the chain transfer constant to PVOH and PVAc to be:[11]

Vinyl acetate chain transfer constant to PVAc: 1.5×10^{-4}

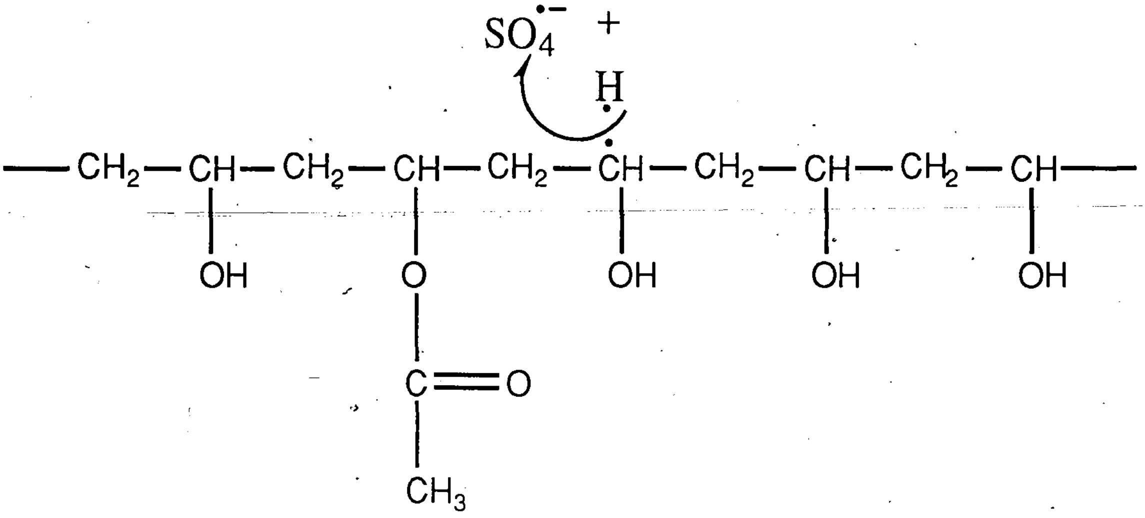
Vinyl acetate chain transfer constant to PVOH: 35.0×10^{-4}

1.2 ROLE OF THE INITIATOR IN GRAFTING REACTIONS

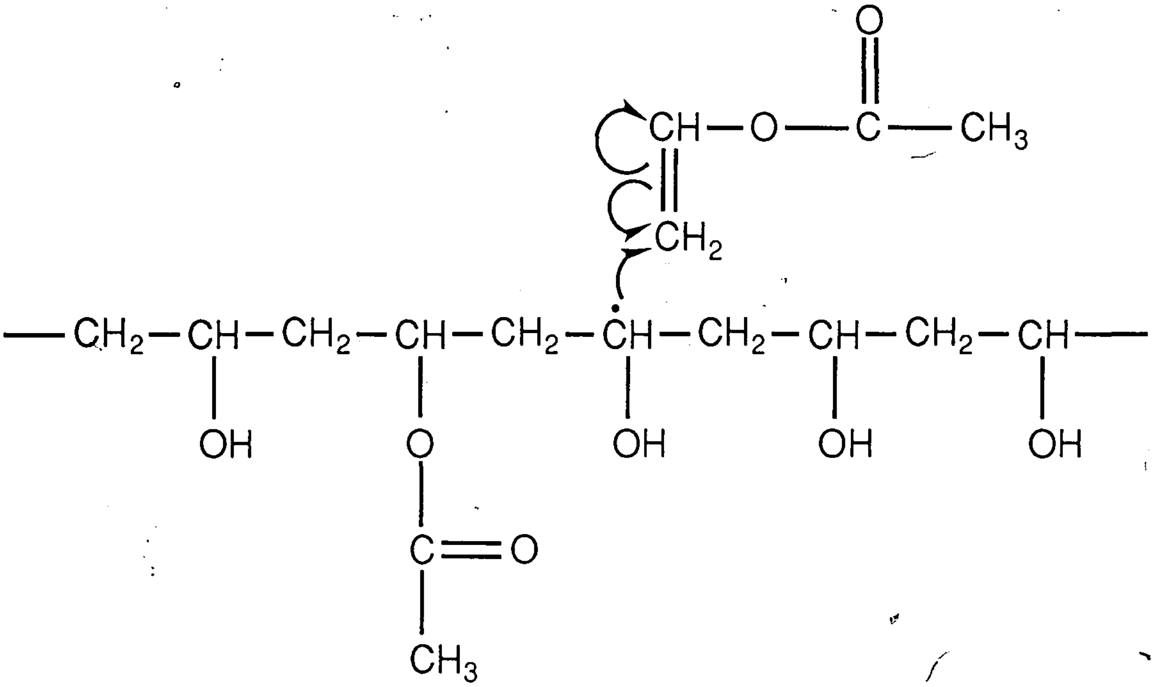
In grafting reactions the amount and type of initiator plays an important role. As the concentration of initiator is increased, the extent of the grafting reaction usually increases. This has been observed when using ammonium or potassium persulfate as the initiator. However, when azobisisobutyronitrile (AIBN) or hydrogen peroxide is used, a low degree of grafting is observed in comparison to persulfate as the initiator. This was observed by Okamura and Motoyama, who found that only 14% of the AIBN reacted with PVOH, while 97% of ammonium persulfate radicals did so.[11]

Heublien and Meissner proposed that the site of grafting of VAc onto the PVOH chains was the methine carbon atom of PVOH and not the acetyl groups of partially hydrolyzed PVOH.[11] Products from model reactions of PVOH and potassium persulfate were studied by ^{13}C NMR ATP experiments. From these experiments Kroener concluded that hydrogen abstraction takes place at both the methine and methylene carbons of the PVOH, but the methine carbon is preferred.[12] From Kroener's findings one would expect the mechanism for the grafting reaction between VAc and PVOH using potassium persulfate as initiator to be as follows:[11]

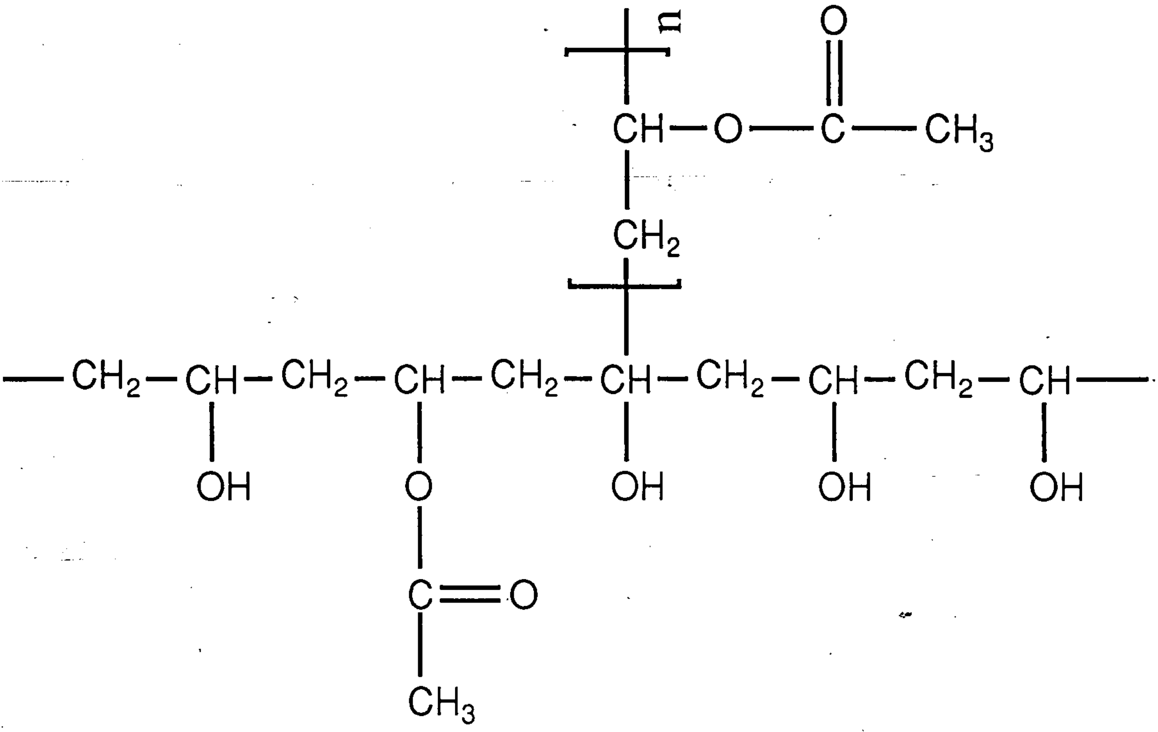
1) Abstraction of the methine hydrogen atom of PVOH by the sulfate ion-radical:



2) Reaction of the free radical of the methine carbon with the vinyl monomer:



3) Formation of poly[(vinyl alcohol)-g-(vinyl acetate)]

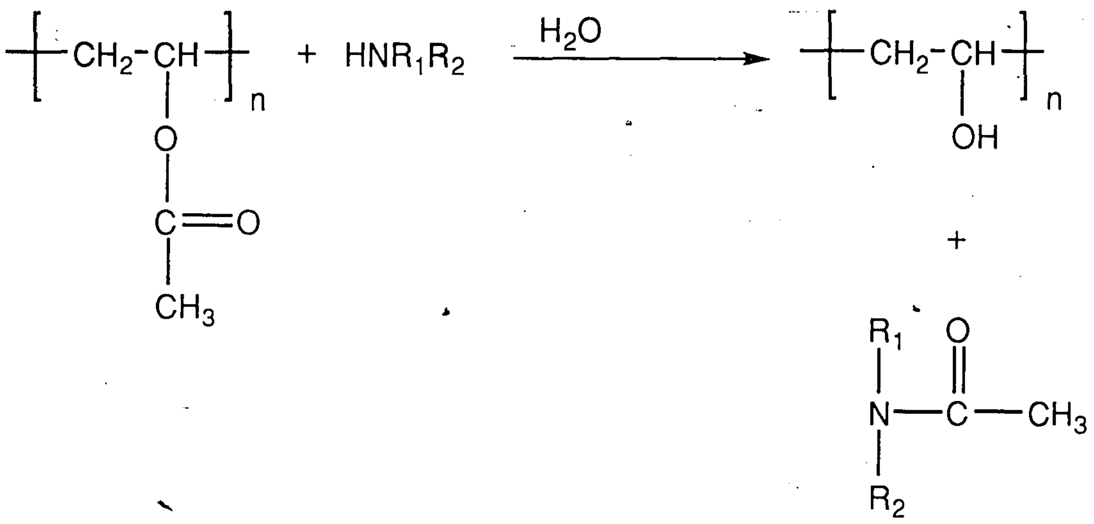


1.3 HYDROLYSIS OF POLY(VINYL ACETATE) TO POLY(VINYL ALCOHOL)

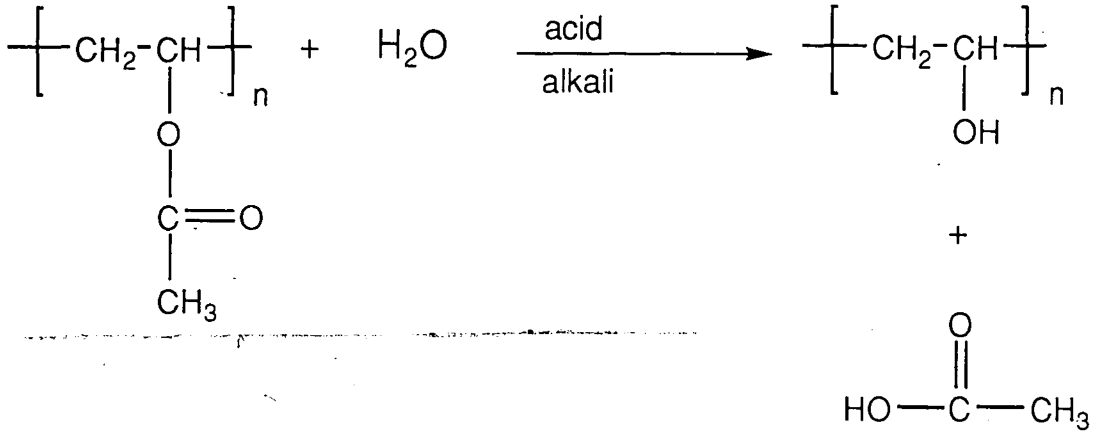
Generally, polymers made by addition polymerization are made from their vinyl monomers; however PVOH cannot be made starting with the monomer vinyl alcohol. The reason for this is that there is a keto-enol equilibrium that lies far to the keto side that converts monomeric vinyl alcohol to acetaldehyde, making polymerization impossible. PVOH is made by the hydrolysis of PVAc and therefore its structural properties are highly dependent upon those of the PVAc.[13]

PVOH was discovered by two German scientists, Haehnel and Herrmann,[14] who in 1924 obtained an ivory-colored PVOH after the addition of alkali, such as NaOH, to an alcoholic solution containing PVAc. There are now several methods used to obtain PVOH. They are grouped into categories such as aminolysis, acid and alkaline hydrolysis, and transesterification using base or acid, with alkaline transesterification in methanol being the most important method industrially. This method is also referred to as saponification. Although the chemical mechanisms are different, the terms hydrolysis and transesterification have been used interchangeably over many years to describe the chemical reaction wherein PVAc is converted to PVOH. This author has fallen into this same habit. The actual chemical reactions for each category are described below:[14]

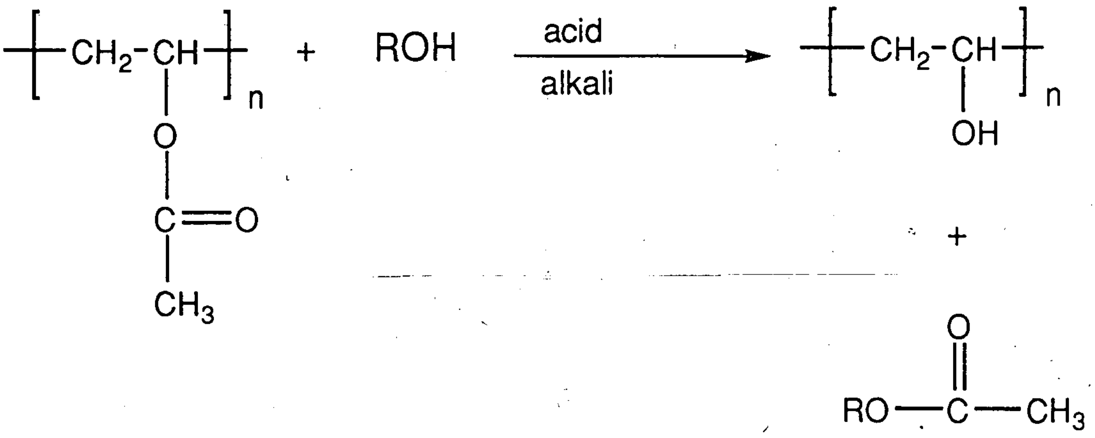
Aminolysis:



Hydrolysis:



Transesterification:



The most widely used catalysts for preparing PVOH via transesterification in methanol are sodium or potassium hydroxides.[15,16,17] The usual amount of alkali metal hydroxide used to give good conversions of PVOH from PVAc range between 0.2 to 4.0 wt% (0.43 to 8.6 mole%) based on PVAc.[15]

When using acid as the catalyst, strong mineral acids such as sulfuric or hydrochloric acid are used. Using acid to partially hydrolyze PVAc to PVOH leads to a more random distribution of acetate groups along the chain than when alkali is used.[14] Also, the rate of hydrolysis is much slower than when using alkali and therefore this process is seldom used industrially unless one is seeking better control in partially hydrolyzing PVAc to a certain percent hydrolysis.

1.4 REMOVAL OF UNREACTED CATALYST BY NEUTRALIZATION

After hydrolysis, PVOH contains unreacted catalyst, such as NaOH. If left in the PVOH, it leads to thermal instability and coloring . The coloring can be avoided, generally by adding acetic acid to lower the effective basicity.[15,17]

1.5 BRANCHING AND HYDROLYSIS OF BRANCHES

Two forms of branching generally occur during the synthesis of PVAc. Short-chain branching occurs because of 1,5 addition and double backbiting.[18,19] Long chain branches occur through the acetoxy group and through the methylene and methine carbons on the main chain.[20] The mechanism leading to short chain branching is illustrated in Diagram 3.[21,22]

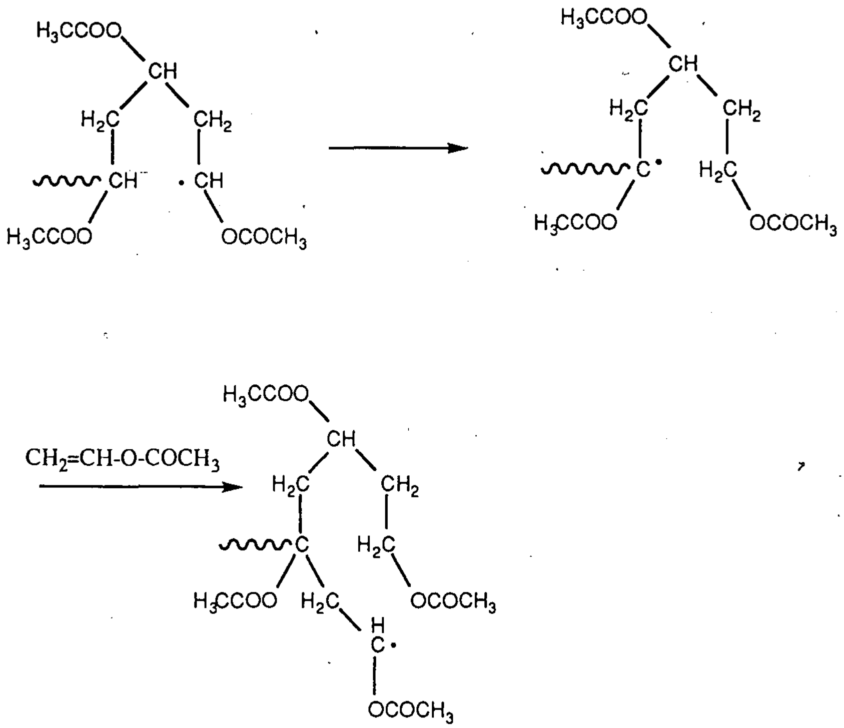


Diagram 3: *Mechanism leading to short-chain branching*

Branches that are formed through the acetoxy groups are hydrolyzable, i.e., cleaved during hydrolysis, whereas branches on the main chain are not cleaved (non-hydrolyzable). Branches on the acetoxy groups thus lead to a lower molecular weight polymer. There are many discrepancies reported in the literature on the mole percent of hydrolyzable branches as a percentage of total branches. These numbers range from 95% to less than 35%.[5,6]

These hydrolyzable branches will leave an alcohol group on the main chain and a methyl ester end group on the branched chain. This is illustrated in Diagram 4.[23]

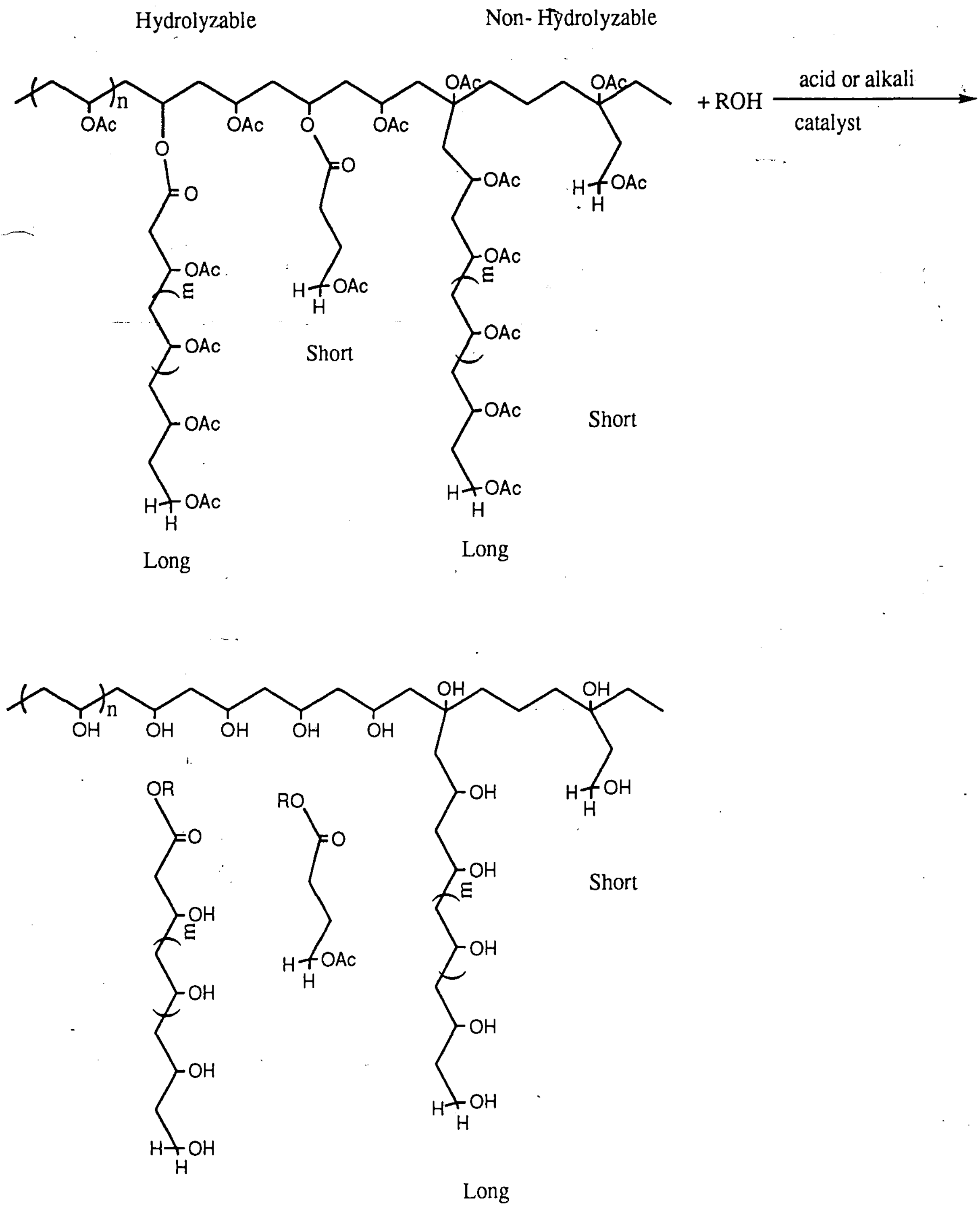
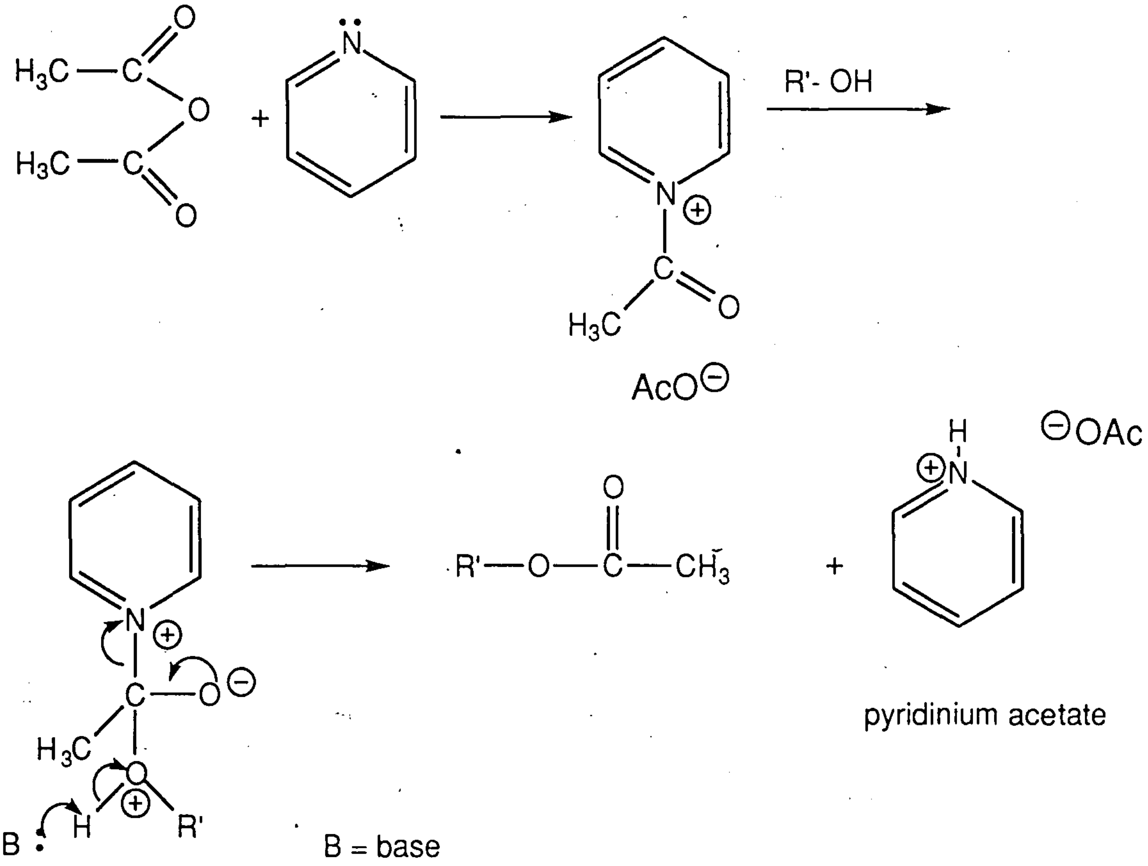


Diagram 4: *Loss of hydrolyzable branches during transesterification*

1.6 ACETYLATION OF POLY(VINYL ALCOHOL) TO POLY(VINYL ACETATE)

On acetylation, PVOH can be converted to PVAc. This is one method used to determine whether grafting onto PVOH occurred on the main chain or on the acetate group. Branching through the acetate group can be detected from changes in molecular weights when a sample is hydrolyzed to PVOH and acetylated back to PVAc. Branches which occur through the main chain methine are not affected by hydrolysis since they are non-hydrolyzable and thus can be detected as an increase in molecular weight which is not lost when a sample is hydrolyzed to PVOH and acetylated back to PVAc.[19,24]

The mechanism for the acetylation of PVOH is known as Nucleophilic Acyl Substitution. This mechanism is shown in Diagram 5.[25]



B = base

Diagram 5: *The mechanism for the acetylation of poly(vinyl alcohol)*

Acetic anhydride can be used as an acylating agent. When acylating alcohols, however, pyridine is used as a catalyst, as it can react with acetic anhydride to form an acyl pyridinium ion. This intermediate is a good acylating agent and reacts more rapidly with the alcohol than does acetic anhydride alone. The end products of this reaction are PVAc and pyridinium acetate. Another nucleophilic catalyst sometimes used is 4-dimethylaminopyridine (DMAP) plus acetic anhydride, which is an even more powerful acylating agent than pyridine plus acetic anhydride.[25,26]

2.0 OBJECTIVE OF RESEARCH:

1. To determine where grafting occurs on the poly[(vinyl alcohol)-co-(vinyl acetate)] chain.
2. To determine whether short branches (1-6 units) or long branches are formed.
3. To use grafting on the poly[(vinyl alcohol)-co-(vinyl acetate)] chain to prepare novel branched PVOH.
4. To study the effect that branching has on the physical properties of PVOH.

3.0 EXPERIMENTAL

3.1 EXPERIMENTAL APPROACH

The following experimental approach was used:

1. Since the rate of propagation is faster than that of transfer reactions in vinyl acetate polymerization, the ratio of polymer to monomer was kept high in order to favor branching.
2. Semi-continuous polymerization was used in order to similulate polymerization at high monomer conversions.
3. High polymerization temperatures were used because the higher the temperature, the greater the extent of branching.

4. Initiators which are noted for their ability to abstract a hydrogen atom were used.
5. A 50/50 copolymer was used which was soluble in methanol. Solubility in methanol is desirable in order to maintain compatibility with the standard process for converting PVAc to PVOH. A problem exists in not being able to separate homopolymer, grafted copolymer, and ungrafted copolymer since all appear soluble in the same solvents. Although this prevented one from determining grafting efficiencies, it did not prevent one from determining the set objectives.
6. The degree of branching was characterized by ^{13}C NMR, Gel Permeation Chromatography (GPC), GPC with on-line Multiple Angle Laser Light-Scattering (MALLS), and GPC with on-line Intrinsic Viscometry. The results are given in Figures 2-6, Tables 4-8 and Appendix 4.

3.2 GRAFT POLYMERIZATION

The polymerizations were carried out in a 1-L reactor kettle equipped with a reflux condenser. All solutions were sparged with N_2 for at least 45 minutes prior to initiator addition. The reactor was heated between 60-80 °C depending on the experiment. The temperature was held relatively constant during the experiments. The monomer was added continously throughout the 4-5 hour reactions, while trying to keep the amount of initiator at a constant concentration. The starting copolymer was poly[(vinyl alcohol)-co-(vinyl acetate)] that had been hydrolyzed to 47% vinyl alcohol; it was obtained from 3-V Corporation as a 35% solids solution in 80% methanol and 20% methyl acetate. This copolymer was determined by GPC to have a M_w of 23,000.

Several polymerization reactions were run in an attempt to find polymerization conditions which favored grafting. The recipes used are given in Table 1. Three different initiators were used: ammonium persulfate, benzoyl peroxide, and tert-butyl peroxyneodecanoate (Trigonox™ 23, Akzo Chemicals, Inc.). All of these initiators are noted for their ability to abstract a hydrogen atom, with persulfate ion being the best.[27] Ascorbic acid was added at the end of all polymerization reactions which used persulfate (except for Polymerization 1), to quench any unreacted initiator.

The unreacted vinyl acetate monomer was removed after each polymerization reaction. The reactor was equipped with a Dean-Stark trap, and the solution was allowed to reflux. Large volumes of methanol were added and stripped off, at the same time removing the unreacted vinyl acetate. Once the vinyl acetate was reduced to ≤ 0.2-0.3% (determined titrimetrically), the reactor was cooled and the sample was removed. The vinyl acetate was removed so that acetaldehyde was not produced during hydrolysis, which leads to discoloration.

Table 1: Recipe for Grafting PVAc onto Poly[(vinyl alcohol)-co-(vinyl acetate)]

Ingredients	Polymerizations 1-3 weight (g)	Polymerizations 4-6 weight (g)
Vinyl Acetate	130	65
Starting Copolymer	130	130
Distilled Deionized Water	0	39
Methanol	363	156
Methyl Acetate	119	0
Ammonium Bicarbonate	0.55 for Poly. 1 only	
Ammonium Persulfate*	3.2	5.6 (Poly. 5), 2 (Poly. 6)
Trigonox 23§	Hold const. at 6.5	Hold const. at 6.5
Benzoyl Peroxide†	10	0
Sodium Acetate	0	5.48 (Poly. 5)
Total Solids	35 %	50 %
Reaction Temperature	60 - 65°C	69 - 73°C

* used for Polymerizations 1,5,6

§ used for Polymerizations 3,4

† used for Polymerization 2 only

3.3 POLYMERIZATIONS 4-6

Based on the results of Polymerizations 1-3, the following changes were made to increase the degree of branching:

1) The methyl acetate present in the commercial copolymer solution was removed to increase the reflux temperature.
2) 20% H_2O was added to the solvent medium to make a more homogeneous solution, while at the same time increasing the reflux temperature.
3) The solids content was increased to 50%.
4) To reduce homopolymerization, 50% monomer (based on copolymer) was added instead of 100%.
5) The monomer addition time was kept the same as in Polymerization 3, to increase the % conversion.

3.4 CONTROL POLYMERIZATION

The conditions used in Polymerization 5 were used in a control polymerization in the absence of poly[(vinyl alcohol)-co-(vinyl acetate)]. To maintain the same concentration of monomer as was used for Polymerization 5, the poly[(vinyl alcohol)-co-(vinyl acetate)] was replaced with an 80/20 methanol/water mixture.

3.5 POLYMERIZATIONS 7-9

A new batch of the 50/50 poly[(vinyl alcohol)-co-(vinyl acetate)] starting copolymer was obtained from 3V Corporation and used for Polymerizations 7-10. Again this batch had been hydrolyzed to 47% vinyl alcohol and came as a 35%

solids solution in 80% methanol and 20% methyl acetate. This copolymer was determined by GPC with on-line Intrinsic Viscometer to have a M_W of 19,500. The amount of initiator was varied from a low concentration in Polymerization 7 to a high concentration in Polymerization 8. A lower concentration of monomer was used in Polymerization 9. The recipes used are given in Table 2.

Table 2: Recipe for Grafting PVAc onto Poly[(vinyl alcohol)-co-(vinyl acetate)]

Ingredients	Polymerization 7 weight (g)	Polymerization 8 weight (g)	Polymerization 9 weight (g)
Vinyl Acetate	65*	65	32.5
Starting Copolymer†	130*	130	130
Distilled Deionized Water	39*	39	32.5
Methanol	156*	156	130
Ammonium Persulfate	3.82*	5.98	5.98
Ammonium Acetate	4.06*	5.16	5.16
Total Solids	50%	50%	50%
Reaction Temperature	68-71.5 °C	67.8-72.5 °C	69.4-70.7 °C

* Normalized to 130g of copolymer

† Poly[(vinyl alcohol-co-vinyl acetate)]; 47% hydrolyzed

3.6 POLYMERIZATION 10

The standard control polymerization conditions and recipe used for Polymerization 5 were also used for another polymerization, but with a redox initiator system: 3.25 g (0.096 mol) of H_2O_2 and 4.8 g (0.027 mol) of L-ascorbic acid were added over the 5 hour reaction period at a reaction temperature of 69-71 °C.

3.7 POLYMERIZATION 11

This polymerization used Airvol 103 (98-99 % hydrolyzed with a M_W of 20,000) as the starting polymer and 90/10 water/t-butanol as the medium. The recipe is given in Table 3.

Table 3: Recipe for Grafting PVAc onto PVOH

Ingredients	Polymerization 11 weight (g)
Vinyl Acetate	50
Airvol 103 (PVOH)	112.5
Distilled Deionized Water	600
t-Butanol	75
Potassium Persulfate	8.41
Sodium Bicarbonate	4.5
Total Solids	20 %
Reaction Temperature	75.9-77.5 °C

The reaction was carried out in a 1-L reactor kettle equipped with a reflux condenser. The PVOH was dissolved in water at 80 °C, and the t-butanol was added. Sodium bicarbonate was added to the reactor to buffer the solution (which remained as one phase). The solution was sparged with N_2 for at least 45 minutes prior to initiator addition. The monomer was added continuously, while the initiator was added at three intervals during the reaction. After the addition of 10-12 mL of VAc, the solution became hazy and bluish. After the addition of 18 mL of VAc, the solution became very hazy. After 1 hour the solution was creamy white, typical of polymer emulsions. This polymer solution was diluted to obtain a 10% solids solution. This solution was slowly added to a beaker containing an excess of acetone. Good mixing was achieved by use of a mechanical stirrer. This solution was stirred for 3 hours, allowed to sit for another

3 hours, and filtered using vacuum filtration to obtain a white solid. This solid was purified by redissolving in water and repeating the process. A small fraction of the solid did not dissolve in water at 90-100 °C for 1 hour. This solid was separated and saved.

3.8 HYDROLYSIS

The standard procedure used for hydrolysis is described below. A fraction of the starting copolymer and the copolymer solutions obtained from Polymerizations 1-5 and 7-10 were hydrolyzed to prepare PVOH. The polymer solutions were added to a jacketed Waring blender and heated to 40-45 °C. These polymers were then hydrolyzed by adding 8-10 mol % NaOH per mole poly(vinyl acetate) (30 mol % NaOH for Polymerizations 4,5, and 7-10 which contained 20% by weight water). Sufficient methanol was added to reduce the NaOH concentration to below 10% by weight. The reagents were mixed in the blender for a short period of time, and then allowed to sit at 40-45 °C for 30 minutes. It should be noted that a gel formed in approximately 5 minutes. This gel was then chopped into fragments and washed with a methanol/acetic acid solution (twice the mol % NaOH used) in a 1-L flask for 1 hour to neutralize any unreacted NaOH. The sample was then centrifuged, and the supernatant layer was decanted; it was then placed in the 1-L flask, and washed with methanol for another hour. The sample was centrifuged again, and the supernatant layer was decanted; it was then dried in a vacuum oven overnight at 60-70 °C.

3.9 REACETYLATION

The standard procedure used for reacetylation of the fully hydrolyzed samples is described below. A fraction of each starting copolymer and the polymers obtained from Polymerizations 4, 5, and 7 were reacetylated to PVAc. The reacetylation consisted of adding 1.50 g of PVOH (3.41×10^{-2} mol), 10.77 g of pyridine (13.62×10^{-2} mol), and 10.43 g of acetic anhydride (10.22×10^{-2}

mol) to a 50-mL round bottom flask equipped with a reflux condenser. The reaction mixture was sparged for 0.5 hours with nitrogen, and then kept under a nitrogen blanket. It was then heated in an oil bath for 2 hours at 100 °C and an additional 2 hours at 90 °C. The products from Polymerizations 4 and 5 both dissolved within 1 hour. In contrast, the solid starting copolymer dissolved slowly, after initially swelling over the first 2 hour period. Over the next hour, the sample dissolved except for a few small gel particles. The sample was filtered to remove the undissolved particles. The solution was slightly yellow. Precipitation in water at room temperature gave a fine precipitate that was difficult to filter, as it became a gummy mass. This was attributed to the low T_g of the PVAc. Therefore, the precipitation process was then modified as described below. Approximately 20 mL of solution was slowly added to an Erlenmeyer flask containing 800 mL of distilled water and diluted to the 1-L mark with ice. The solution was stirred at a moderate rate with a mechanical stirrer. A white fluffy fibrous solid precipitated out of solution, which was filtered and dried. The solid was purified by redissolving in approximately 20 mL of acetone and reprecipitating using the modified process described above. The precipitate was filtered and dried in a vacuum oven at room temperature overnight, then ground with a mortar and pestle. The sample weight varied between 0.85 and 1.56 g.

This procedure is similar to that used for the reacetylation of the fully hydrolyzed samples. However, the copolymers needed to be removed from the methanol medium used during polymerization. The standard procedure used for the reacetylation of the copolymer samples is described below. A fraction of the starting copolymer and the polymers obtained from Polymerizations 4, 5, and 7 were reacetylated to prepare PVAc. These samples were prepared by heating the solutions in a vacuum oven for 4-4.5 hours at 60-70 °C in order to remove the solvent. The samples were then cooled in liquid nitrogen to separate the samples from the pans. Each sample was then ground into a powder. The reacetylation of the starting copolymer consisted of adding 2.50 g of grafted poly[(vinyl alcohol)-co-(vinyl acetate)] which contained no more than 1.20 g of PVOH (2.73×10^{-2} mol), 8.62 g of pyridine (10.89×10^{-2} mol), and 8.34 g of acetic anhydride (8.17×10^{-2} mol) to a 50-mL round-bottom flask equipped with a reflux condenser under a nitrogen atmosphere. For the reacetylation of copolymers from Polymerizations 4, 5, and 7 the amount of pyridine added was increased to 8.8-8.9 g. The amount of acetic anhydride was also increased to 8.5-8.6 g. The reaction mixture was sparged with nitrogen for 0.5 hours and then kept under a blanket of N_2. The solutions gelled before the temperature was increased. The samples were heated in an oil bath for four hours at 100 °C. The solids dissolved in less than 1 hour. The solutions of the starting copolymer and the polymer from Polymerization 4 were slightly yellow. The polymer solutions from Polymerizations 5 and 7 were reddish-yellow. The solids were precipitated from solution using the same process described above. The precipitates were filtered and then purified by redissolving in approximately 20 mL of acetone and reprecipitating. The precipitate was filtered and dried in a vacuum oven at room temperature overnight. The solids were then ground with a mortar and pestle. The sample weight varied between 1.1 and 1.6 g.

3.10 ANALYSIS OF THE GRAFTING POLYMERIZATIONS

3.10.1 DETERMINATION OF MONOMER CONVERSION DURING POLYMERIZATION

The conversion of VAc during polymerization was monitored titrimetrically thoughout each reaction. This involved titrating a known normality of bromide/bromate solution in an acidic methanol/water solution containing the sample to be tested. The bromide/bromate reacts with the acid to form bromine and water; bromine quickly reacts with the double bond in the VAc and is consumed. Once all the VAc is consumed, the bromine formed gives a yellow color, indicating the end of titration.[28]

3.10.2 GEL PERMEATION CHROMATOGRAPHY (GPC) ANALYSIS

3.10.2.1 NON-AQUEOUS GPC ANALYSIS

The poly[(vinyl alcohol)-co-(vinyl acetate)] starting copolymer and the products from Polymerizations 1-6 were characterized for MWD by solvent - based GPC. A Waters 150C GPC was used to determine the molecular weight using a Jordi DVB Linear (50 cm. x 10 mm ID) column. Each sample was dissolved in tetrahydrofuran, (THF, mobile phase) and the molecular weight data were calculated using a non-universal calibration of retention time relative to the retention time of monodisperse poly(styrene) standards. A PE/Nelson Analytical system (SEC (size exclusion chromatography) Report) was used to collect and process data. The SEC Report gives results for the entire sample, and the SEC Peak Molecular Weight Table gives molecular weight information on each peak.

The second batch of the poly[(vinyl alcohol)-co-(vinyl acetate)] starting copolymer, the products from Polymerizations 7-10, and all reacetylated samples were characterized for MWD by solvent-based GPC. A Waters 150C GPC and Viscotek Model 110 Differential Viscometer were used to determine the molecular weight using a Jordi DVB Linear (50 cm x 10 mm ID) column. Each sample was dissolved in 75/25 THF/methanol solution containing 0.01M NaAc (mobile phase), and the molecular weight data were calculated using the universal calibration($[\eta]^*$ M vs. retention volume) relative to the retention volume of monodisperse poly(methyl methacrylate) standards. All non-aqueous GPC studies were performed by the Corporate Research and Services Department of Air Products and Chemicals Inc.

3.10.2.2 AQUEOUS GPC ANALYSIS

All PVOH samples were characterized for molecular weight and molecular weight distribution by aqueous GPC/Multi-Angle Laser Light Scattering (MALLS). Analyses were carried out using the Waters/Millipore 150C GPC with a differential refractive index detector at 35 °C, interfaced to a Wyatt Technology Dawn F MALLS detector (488 nm wavelength) at a flow rate of 1.02 mL/min. A set of six Toyo Soda TSK-PW columns were used for the GPC separations with a mobile phase of aqueous 0.05 N sodium nitrate. Molecular weights were calculated using a value of dn/dc = 0.150, the specific refractive index increment of PVOH. ASTRA and EASI software were used for data processing. The PVOH samples listed in Appendix 4 were characterized for molecular weight and molecular weight distribution by aqueous GPC. Analyses were carried out on a Waters/Millipore 150C GPC (with a differential refractive index detector) at 35 °C. A set of six Toyo Soda TSK-PW columns were used for the GPC separations with a mobile phase of aqueous 0.05 N sodium nitrate at a flow rate of 1.0 mL/min. Column calibration was performed using a series of poly(ethylene oxide) standards from American Polymer Laboratories. Data acquisition and processing were carried out on a PE-Nelson Data Station. All aqueous GPC studies were performed by the Corporate Research and Services Department of Air Products and Chemicals Inc.

3.10.3 NUCLEAR MAGNETIC RESONANCE (NMR) ANALYSIS

3.10.3.1 ^{13}C NMR

^{13}C NMR was used in an attempt to detect branches that occur at a quaternary carbon in both the PVOH and starting poly [(vinyl alcohol)-co-(vinyl acetate)]. For some samples an Attached Proton Test was also run. An Attached Proton Test (APT), also called J-modulated spin-echo, is an NMR experiment in which carbon atoms with odd attached proton multiplicities (CH, CH_3) give either positive or negative peak intensities while carbon atoms with even attached proton multiplicities (C, CH_2) give the opposite peak intensities. This APT experiment can only be used as a qualitative tool and cannot give quantitative results. This technique is described in further detail by Le Cocq et al.[29] and Rabenstein et al.[30]. Also, ^{13}C NMR was used to detect and quantify PVAc in some of the hydrolyzed samples. The experiments were performed at ambient temperature using an IBM SY-200 FT-NMR spectrometer equipped with a 10 mm VSP probe tuned for ^{13}C. The solvents used to dissolve PVOH, D_20, or CD_3OD in the case of poly [(vinyl alcohol)-co-(vinyl acetate)], provided a source for field frequency lock for the ^{13}C NMR experiments. The chemical shift scale was externally referenced. All ^{13}C NMR studies were performed by the Corporate Research and Services Department of Air Products and Chemicals Inc.

3.10.3.2 ^1H NMR

^1H NMR was used to detect and quantify the PVOH in all of the reacetylated samples. In general, these percentages were calculated using the PVAc and PVOH methyl, methylene and methine peak integrals. In PVAc, the methyl peak is centered at 1.9 ppm, the methylene peak is centered at 1.75 ppm and the methine peak occurs between 4.6-5.0 ppm. In PVOH, the methylene peak occurs between 1.2-1.5 ppm and the methine peak between 3.6-4 ppm. The methyl and methylene have more hydrogens than the methine or OH groups; therefore, they have larger integrals, which leads to lower uncertainties in the calculation. However, when overlap due to impurities occurs in these regions, these percentages can be calculated using just the methine peak integrals. Also, ^1H NMR was used to detect and quantify PVAc in some of the hydrolyzed samples. The experiments were performed at ambient temperature using a Bruker ACP-300 FT-NMR spectrometer equipped with a 5 mm Quad probe tuned for ^1H. The solvent used to dissolve PVAc, DMSO-d_6, provided a source for field frequency lock for the ^1H NMR experiments. The chemical shift scale was internally referenced to residual non-deuterated solvent peaks. All ^1H NMR studies were performed by the Corporate Research and Services Department of Air Products and Chemicals Inc.

3.10.4 DETERMINATION OF PERCENT HYDROLYSIS OF POLY(VINYL ALCOHOL) BY TITRATION

The procedure used for the determination of the mol % hydrolysis of poly(vinyl alcohol) is listed in Appendix 1. Four to five grams of each poly(vinyl alcohol) sample were weighed to four decimal places and placed in a 500-mL iodine flask. To each sample, 100 mL of a 75/25 H_20/methanol solution was added along with 5 drops of phenolphthalein indicator. The pH was adjusted by the addition of 0.1N NaOH until a slight pink color was obtained. Then, 10 mL of 0.5N NaOH was added and allowed to reflux for approximately 1 hour. The samples were allowed to cool and then were back-titrated to a slight pink color using 0.1N HCl.

3.10.5 DIFFERENTIAL SCANNING CALORIMETRY (DSC) ANALYSIS

Airvol 103, along with the fully hydrolyzed form of the starting copolymer and the product from Polymerization 5 were characterized for crystallinity by Differential Scanning Calorimetry (DSC). A DuPont DSC, Model 912 was used to determine the glass transition and crystalline melting temperatures. Each sample was heated at a rate of 20 °C/min (with N_2 purging the cell at 50 cc/min) from -50 °C to +250 °C, quench-cooled and reheated. An IBM PC (with a 386 microprocessor by Intel) running on a TA Format System was used to collect the data, which was processed using General Analysis software (TA Instruments).

4.0 RESULTS AND DISCUSSION

4.1 POLYMERIZATIONS 1 & 2

These grafting reactions were unsuccessful, as shown by the low vinyl acetate conversions (Figure 1), and the fact that the molecular weights were the same as those of the starting copolymer (Table 4). The ammonium persulfate used as the initiator was only partially soluble in the methanol/methyl acetate medium which contributed to the low vinyl acetate conversion. Two techniques were used to determine the mol % hydrolysis of the hydrolyzed starting copolymer and the Polymerization 1 product. The first method was titration. The principle behind this method is that the remaining acetate groups are reacted with sodium hydroxide. The amount of sodium hydroxide required is quantified by acid titration. A saponification number is determined, which is directly proportional to the % hydrolysis (see Appendix 1). The second method used was ^{13}C NMR. The equations shown in Appendix 2 were used to determine the mole fraction PVOH and PVAc.[31] The symbols (OH,OH), (OH,OAc) and (OAc, OAc) used in Appendix 2 are shown in Diagram 6.

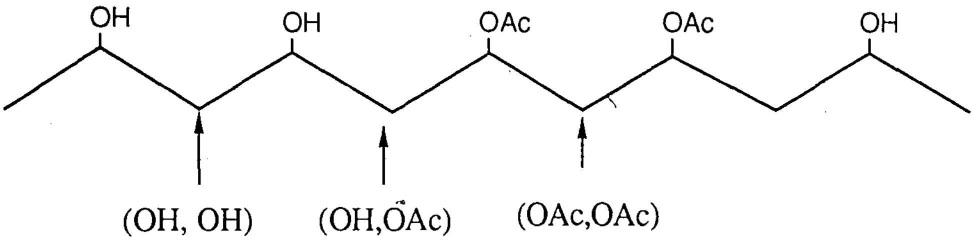


Diagram 6: *Representation of the Methylene Carbons Located between Two Alcohol Groups, One Alcohol Group and One Acetate Group or Two Acetate Groups*

(OH,OH), (OH,OAc) and (OAc, OAc) are the mole fractions of each of the possible triads. These triads are centered in the ^{13}C NMR spectrum, respectively at 44 ppm, 39 ppm, and 37 ppm. These values were calculated from the peak integrals after correcting for the 1,2-glycol content overlapping the (OAc, OAc) methylene peak centered at 37 ppm. The extent of hydrolysis determined by ^{13}C NMR and titration are listed in Table 5. The results by both methods were virtually identical; therefore, the extents of hydrolysis for all of the remaining samples were determined only by ^{13}C NMR, since ^{13}C NMR was run on all hydrolyzed samples for detection of grafting sites. ^{1}H NMR was used where sensitivity limits facilitated a detection of minor components. In Polymerization 2, benzoyl peroxide was used as the initiator. This initiator has a half-life of approximately 35-40 hours at the temperature used. Based on the low monomer conversions shown in Figure 1 and the fact that there was no apparent change in the polymer molecular weight, it appears that the half-life of this initiator was too long. A leak in the reactor during Polymerizations 1 and 2 allowed solvent and monomer to escape, which increased the apparent overall % conversion.

4.2 POLYMERIZATION 3

Trigonox™ 23 peroxyester was used as the initiator. The polymerization proceeded to high conversion (Figure 1), and the molecular weight of the copolymer increased (Table 4). Table 4 shows the molecular weights obtained by GPC for the copolymer samples and the molecular weights obtained by GPC/MALLS for the PVOH samples. However, much homopolymer oligomer was produced, as shown by the bimodal curves in the gel permeation chromatogram (Figure 2). The high molecular weight peak was separated from the low molecular weight peak to give values of M_w, M_n and PDI for each peak. The M_w of the homopolymer oligomer was found to be 4,460.
Why did Polymerization 3 yield oligomer and a low extent of grafting on the main chain? Some possible reasons are listed below.

1) The solution appeared homogenous without any precipitate, however with the use of methanol as the medium, the

hydrophobic Trigonox™ 23 initiator may have given radicals in the hydrophobic VAc-rich region, and fewer radicals in the hydrophilic PVOH-rich region. Adding H_2O may make the solution homogeneous.

2) The rate of hydrogen abstraction by the primary radical is slow compared to the rate of initiation. By changing the initiator, and slowing down the addition of monomer, one may be able to increase the relative rate of hydrogen abstraction.

Table 4 shows the molecular weights obtained by GPC/MALLS for each of the hydrolyzed samples. These data are believed to be invalid however; therefore, they are not discussed in this section See Section 4.10 for details as to why these results were disregarded.

4.3 POLYMERIZATION 4

The polymerization proceeded to high conversion (Figure 1), and the molecular weight of the copolymer was increased (Table 4). The copolymer molecular weight distribution was bimodal; However since less VAc was used, much less oligomer was formed than in Polymerization 3 (Figure 2). The high molecular weight peak was separated from the low molecular weight peak to give values of M_w, M_n and PDI for each peak. There was a 5,800 increase in M_w from the original starting copolymer, which amounted to a 24% overall increase in molecular weight. The M_w of the homopolymer oligomer was 1,500, lower than that formed in Polymerization 3. This was expected since there was less VAc present, and the molecular weight should be directly proportional to the monomer concentration.

A ^{13}C NMR spectrum, and an Attached-Proton-Test (APT) (Figure 3) were run on the hydrolyzed form of this sample. The positive peaks correspond to the methine and methyl carbon atoms, whereas the negative peaks correspond to the methylene and quaternary carbon atoms. A weak downward signal corresponding to the quarternary carbons was observed at 76 ppm. The rest of the signals in this region were due predominately to head-to-head placement and the PVAc backbone methine carbon. These results are in agreement with those of Ovenall[32], who used APT to show that the majority of the peaks in the 70-80 ppm region did indeed correspond to the methine carbon atoms of the head-to-head placements of poly(vinyl alcohol). Jayasuriya[23] observed a weak signal at 78 ppm, which he attributed to the quarternary carbons. The intensity of the quarternary carbon atoms of the poly(vinyl alcohol) sample was much less than that of the corresponding alcohol end groups. This suggests that the end groups were mainly due to the existence of low molecular weight polymer and that the degree of nonhydrolyzable branching was low.[23]

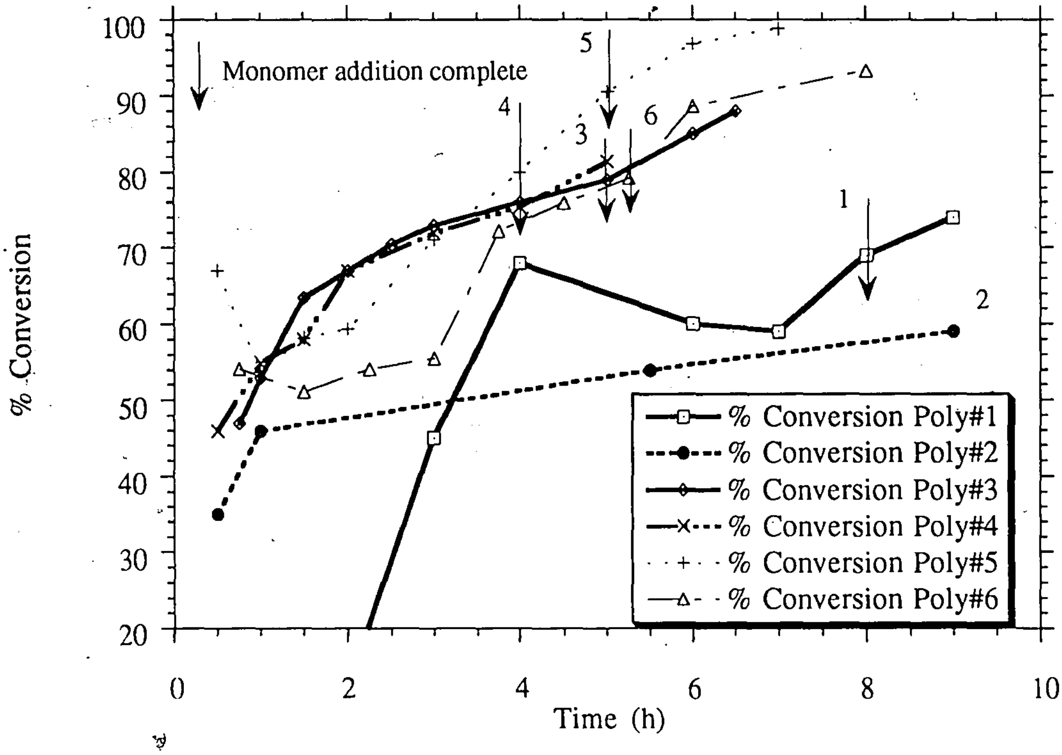
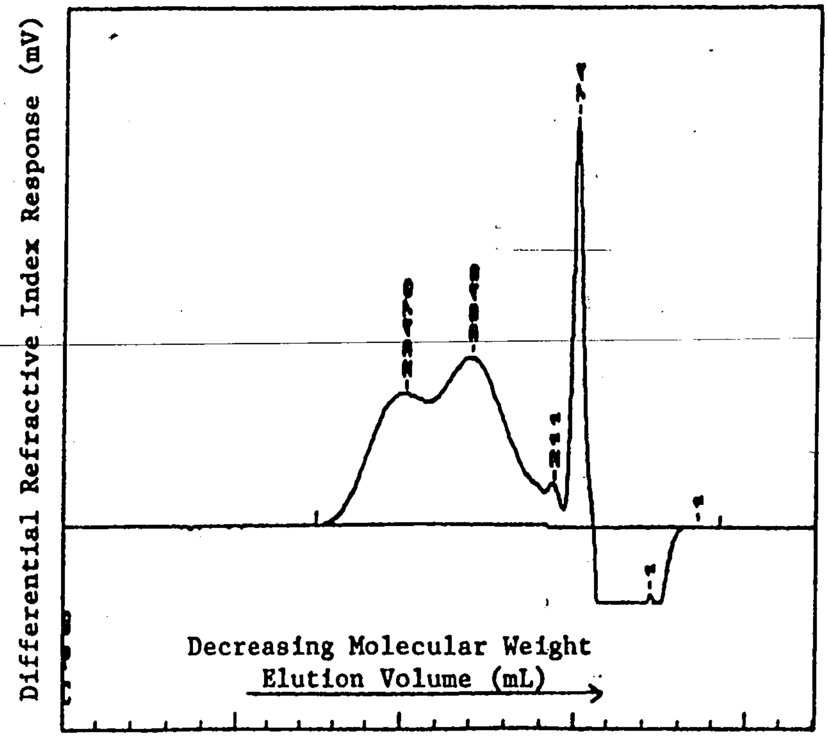
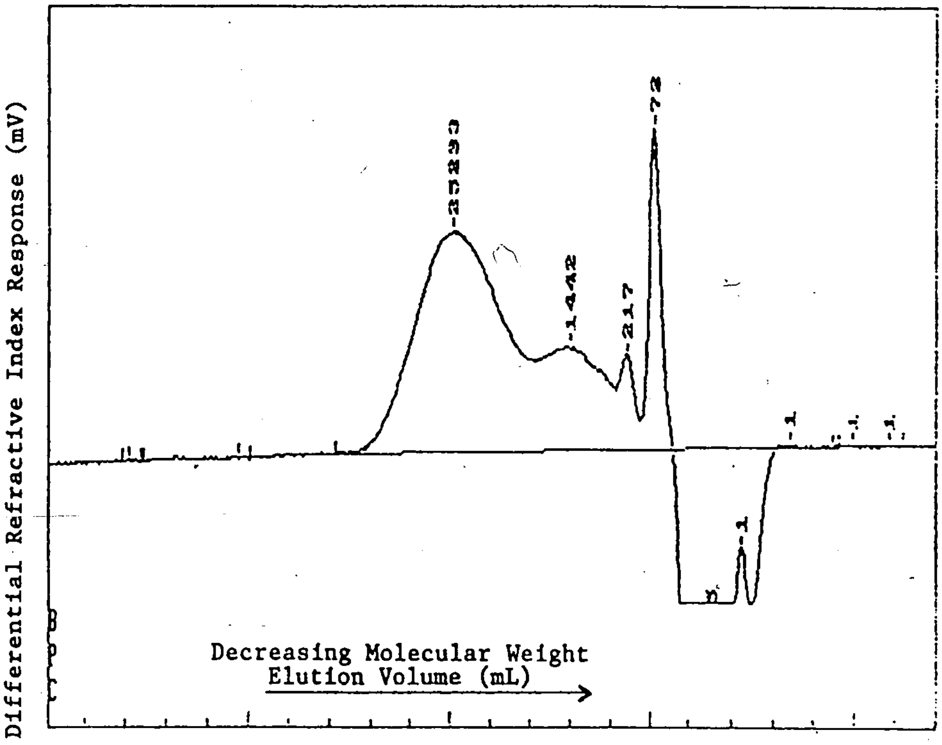


Figure 1: *Conversion of Vinyl Acetate vs. time for the graft polymerization of VAc onto Poly[(vinyl alcohol)- co-(vinyl acetate)] for Polymerizations 1-6 (see text).*



Polymerization 3 chromatogram



Polymerization 4 chromatogram

Figure 2: *Bimodal molecular weight distribution chromatograms of Polymerization 3 and 4*

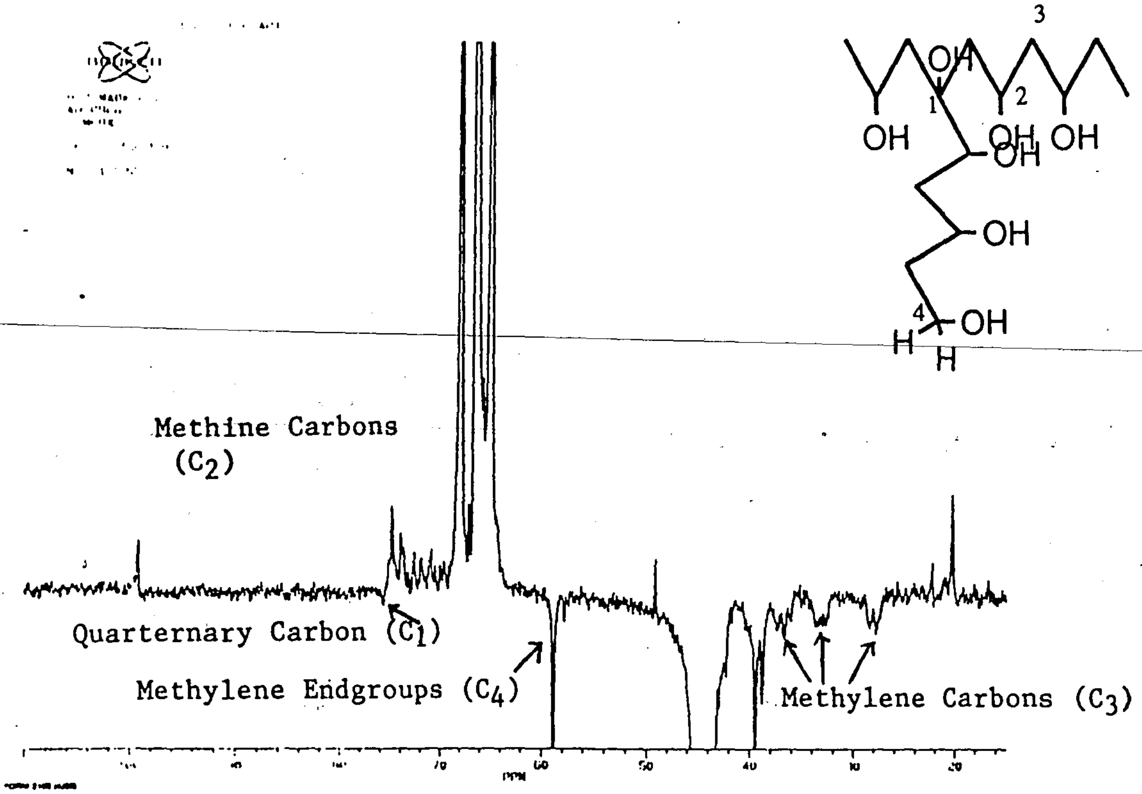


Figure 3: ^{13}C NMR APT spectrum of PVOH 4

4.4 POLYMERIZATIONS 5 & 6

Polymerizations 5 and 6 proceeded to high conversion based on :

a) The high VAc conversions determined titrimetrically (Figure 1).

b) The mass balance, which accounted for 75-91% of the starting copolymer and the VAc, i.e., 25-72 % of the VAc was converted to polymer.

c) The increase in molecular weight (Table 4), which is indicative of grafting onto the copolymer.

The PVAc chains grafted to the starting copolymer should have a length similar to those of the homopolymer. Homopolymer was formed in Polymerizations 3 and 4 (Table 4). Therefore, when 50 g of VAc was polymerized with 100 g of copolymer, the maximum length of the grafted chain should be 18 units, or an increase in M_w of 1500 for each grafted chain.

Ammonium persulfate was used as the initiator, with more initiator being used in Polymerization 5. GPC showed an increase in M_w for each copolymer: There was a 6,500 increase in Mw from the original starting copolymer in Polymerization 5 (28% overall change in molecular weight) and a 4,700 increase in Mw from the original starting copolymer in Polymerization 6 (20% overall change in molecular weight). The smaller overall change in molecular weight for Polymerization 6 was attributed to the use of a smaller concentration of initiator, and lower monomer conversions. Lower concentration of initiator should lead to grafts with longer chain lengths since chain length is inversely proportional to the square root of the initiator concentration. However, the use of a smaller concentration of initiator gave fewer radicals that can abstract a H atom from the starting copolymer to form fewer graft sites.

Figure 4 compares the GPC curves of the starting copolymer with those of Polymerization 5 in which significant grafting occurred, and Polymerization 2 in which little grafting occurred. The conditions used for Polymerization 5 gave a large increase in molecular weight with a unimodal GPC curve and hence were used as the standard conditions for Polymerizations 7-9.

A ^{13}C NMR spectrum and an Attached Proton Test (APT) were run on the hydrolyzed form of Polymerization 5. No carbons that served as grafting sites were detected in the samples; however, unless their concentration was greater than approximately 0.5 molar percent, these sites would not be detected by this technique. The extent of hydrolysis was determined by ^{13}C NMR, and the results are listed in Table 5.

A DSC experiment was run on Airvol 103 along with the fully hydrolyzed form of the starting copolymer and the product of Polymerization 5, to characterize the differences in crystallinity. These experiments were run to see if either long or short-chain branches would change the crystallinity of PVOH.[33] The values of T_m and T_g were similar for all the polymers with T_m being about 220 °C and T_g about 52 °C. At the time of these experiments, it was not known whether the grafting was on the acetate group or the main chain methine carbon. With no grafting on the main chain methine carbon, one would expect no change in crystallinity, as was the case for these experiments.

4.5 CONTROL POLYMERIZATION

The GPC data in Table 4 show an increase in molecular weight in Polymerizations 4, 5, and 6, indicative of grafting onto the copolymer. To verify that grafting onto the copolymer was the reason for this increase in molecular weight and not homopolymerization of VAc, a control polymerization was run in the absence of copolymer. The molecular weight of the homopolymer formed was determined by GPC to be M_W=6,400, M_n=3,000 and a PDI=2.1. These GPC results indicate grafting onto the copolymer must have occurred. Figure 5 compares the GPC curve of the starting copolymer with that of Polymerization 5 in which significant grafting occurred as indicated by the shift in the GPC curve to higher molecular weight. The figure also includes GPC curves from the control polymerization in which the homopolymer that formed was of low molecular weight, much lower than that of the grafted copolymer. One may also speculate from this figure that small concentrations of homopolymer formed during Polymerization 5 lie beneath the molecular weight distribution curve obtained for Polymerization 5. Assuming all grafted chains have similar lengths under constant conditions, the average increase in molecular weight over the starting copolymer is equal to the number of graft chains times the length of graft chains. Based on the molecular weight data obtained by GPC, the predicted number of grafts per polymer molecule in Polymerizations 5, and 8 was one or two. Again, this assumes the length of the graft chain was similar for the control polymerization, and Polymerizations 5 and 8.

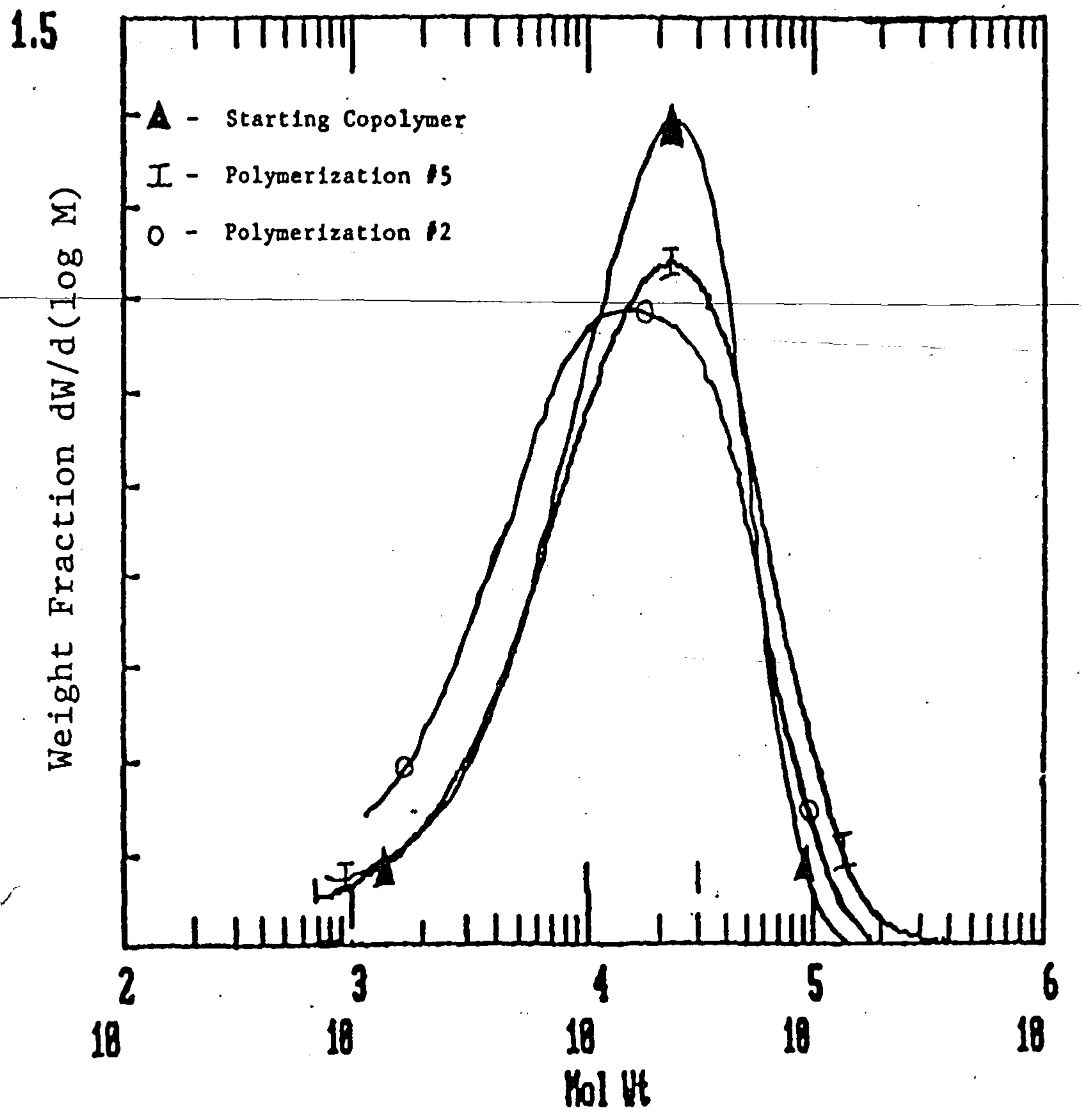


Figure 4: *GPC chromatograms of grafted Poly[(vinyl alcohol)-co-(vinyl acetate)] samples*

Table 4

GPC Results for Polymerizations 1 - 6

	*Copolymer (X)	†PVOH	Copoly(X) minus Copoly(**SC**)	PVOH(X) minus PVOH(**SC**)
Starting Copolymer (SC)	$M_w = 23,300$ $M_n = 9,600$ PDI= 2.4	$M_w = 14,100$ $M_n = 7,900$ PDI= 1.8		
Poly. # 1	M_w = NA M_n=NA PDI=NA	$M_w = 14,200$ $M_n = 8,200$ PDI= 1.7		
Poly. # 2	$M_w = 21,100$ $M_n = 5,100$ PDI=4.1	$M_w = 13,900$ $M_n = 4,600$ PDI= 3.0		$\Delta M_w = -200$ $\Delta M_n = -3,300$
Poly. #3	$M_w = 36,900$ $M_n = 27,000$ PDI=1.4	M_w = NA M_n=NA PDI=NA	$\Delta M_w = 13,600$ $\Delta M_n = 17,400$	
Bimodal	$M_w = 4,500$ $M_n = 2,000$ PDI=2.3			
Poly. #4	$M_w = 29,100$ $M_n = 14,600$ PDI=2.0	$M_w = 19,200$ $M_n = 11,900$ PDI= 1.6	$\Delta M_w = 5,800$ $\Delta M_n = 5,100$	$\Delta M_w = 5,100$ $\Delta M_n = 4,000$
Bimodal	$M_w = 1,500$ $M_n = 1000$ PDI=1.50			
Poly. #5	$M_w = 29,800$ $M_n = 9,700$ PDI=3.0	$M_w = 22,300$ $M_n = 12,100$ PDI= 1.8	$\Delta M_w = 6,500$ $\Delta M_n = 100$	$\Delta M_w = 8,200$ $\Delta M_n = 4,200$
Poly. #6	$M_w = 28,000$ $M_n = 10,200$ PDI= 2.7		$\Delta M_w = 4,700$ $\Delta M_n = 600$	

* molecular weights determined by GPC

† molecular weights determined by GPC/MALLS

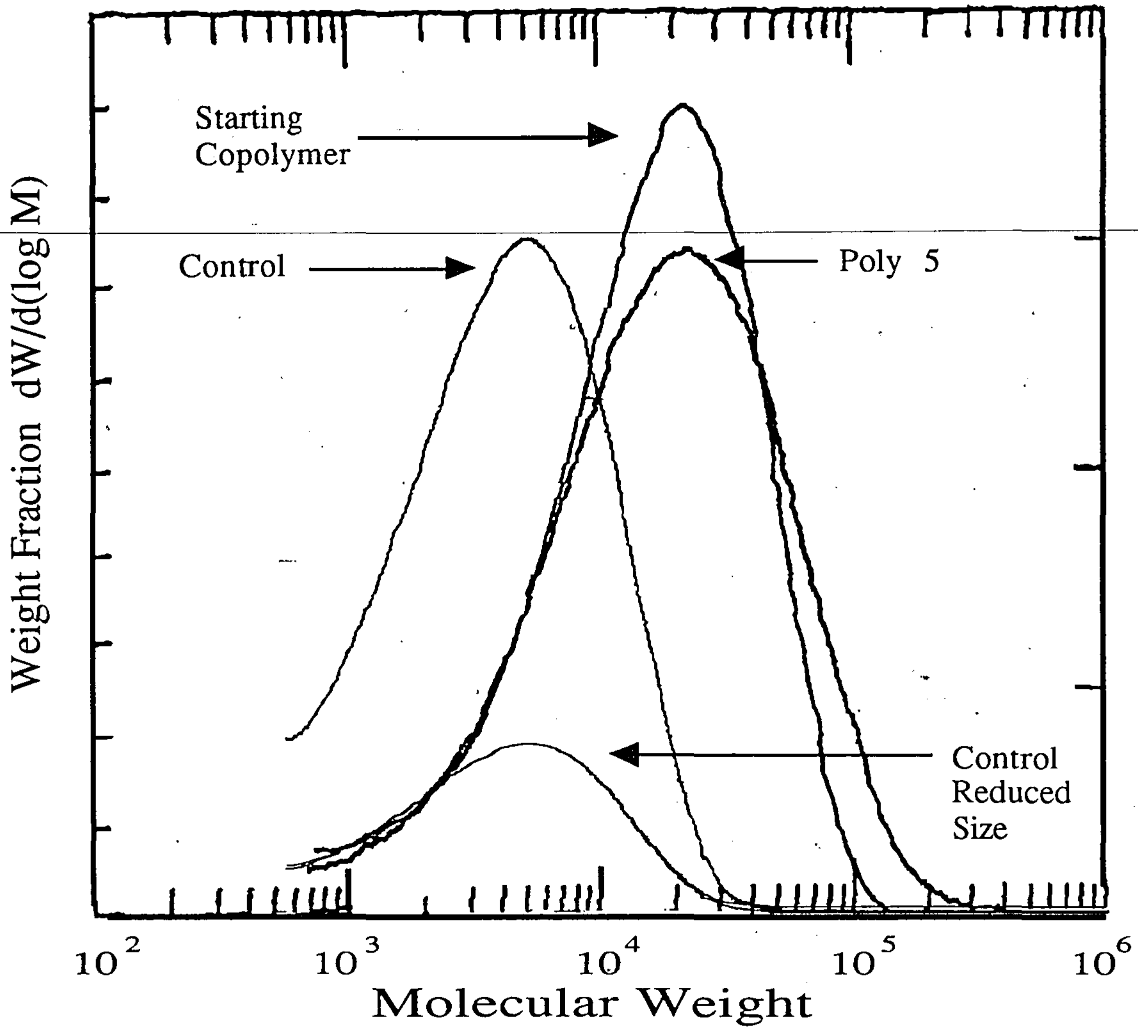


Figure 5: *GPC chromatograms of homopolymer, starting copolymer, and grafted copolymer*

Table 5: Extent of hydrolysis as determined by ^{13}C NMR

Sample	Relative molar percent PVOH	Relative molar percent PVAc
Hydrolyzed SC#1	98.9±0.1,99*	1.1±0.1
PVOH #1	95.2±0.5,96.2*	4.8±0.5
PVOH #2	98.5±0.4	1.5±0.4
PVOH #3	98.6±0.5	1.4±0.5
PVOH #4	100.0	none detected
PVOH #5	98.4 ±0.3	1.6±0.3
Hydrolyzed SC#2	99.5	0.5
PVOH #7	99.5	0.5
PVOH #8	99.5	0.5
PVOH #9	99.5	0.5
PVOH #10	97±1	3±1
PVOH #11	98.6	1.4

* Determined titrimetrically

4.6 POLYMERIZATIONS 7-9

Six polymerizations were run to determine the polymerization conditions that favored grafting. The conditions used in Polymerization 5 gave the largest increase in molecular weight. Those conditions were used as the standard for Polymerizations 7-9.

The conclusion that graft polymerization occurred during Polymerizations 7-9 was based on :

(a) The increase of VAc conversion with time (Figure 6), as determined titrimetrically.

(b) The mass balance, which accounted for 87-90% of the starting copolymer and VAc monomer, i.e., 25-89% of the VAc monomer was converted to polymer.
(c) The GPC data of Table 6, which shows an increase in molecular weight in Polymerizations 7-9, indicative of grafting onto the copolymer.

Ammonium persulfate was used as the initiator, with more initiator being used in Polymerizations 8 and 9. Table 6 shows the molecular weight results determined by GPC/intrinsic viscosity increased for each of the polymer samples: An increase in M_w of 3,400 (17% overall increase) for Polymerization 7 over the original starting copolymer; an increase in M_w of 9,100 (47% overall increase) in Polymerization 8. The smaller overall increase in molecular weight for Polymerization 7 was attributed to the lower concentration of initiator, which gave fewer radicals that can abstract a H atom from the starting copolymer to form fewer graft sites with longer chain lengths. There was an increase of 6,700 in M_w (34% overall increase) over the original starting copolymer in Polymerization 9. The lower concentration of monomer gave a lower overall increase in molecular weight. This was expected since there was less VAc present, and the molecular weight should be directly proportional to the monomer concentration.

A ^{13}C NMR spectrum and an Attached Proton Test (APT) were run on the hydrolyzed form of Polymerization 8. No methine carbons were detected; however, unless their concentration was greater than approximately 0.5 molar percent, they would not be detected. The extents of hydrolysis determined by ^1H NMR are listed in Table 5.

Table 6: GPC Results for Polymerizations 7 - 10

	Copolymer	Difference from Starting Copolymer	Reacetylated Copolymer	Reacetylated PVOH
Starting Copolymer (SC)	M_w = 19,500 M_n= 9,000 PDI= 2.2	NA		
Poly. #7	M_w = 22,900 M_n=11,800 PDI=2.0	M_w = 3,400 M_n=2,800	Mw=25,600 Mn=11,400 PDI=2.25	Mw=27,400 Mn=15,400 PDI=1.78
Poly. #8	M_w = 28,600 M_n=11,800 PDI=2.4	M_w = 9,100 M_n = 2,800		
Poly. #9	M_w = 26,200 M_n=10,600 PDI=2.5	M_w = 6,700 M_n= 1,600		
Poly. #10	M_w = 27,000 M_n=11,400 PDI=2.4	M_w = 7,500 M_n=2,400		

M_w = weight average molecular weight, M_n = number average molecular weight
PDI = polydispersity index

4.7 POLYMERIZATION 10

Figure 6 shows that the conversion of VAc monomer increased with time for Polymeriations 7-10. The GPC data in Table 6 shows there was an increase in M_W of 7,500 (38% overall increase) for Polymerization 10 compared to the original starting copolymer. The redox initiator used in this run should give a steady flux of •OH radicals. The molar concentration of initiator used was also four times that of the persulfate ion used in Polymerization 8; nonetheless, the conversion of vinyl acetate was slightly lower. There was a 7,500 increase in M_W for Polymerization 10, which is slightly lower in comparison to a 9,100 increase in M_W for Polymerization 8. This suggests the product formed in Polymerization 10 had fewer grafted chains or a lower average graft chain length or some combination of the two. Assumption one is consistent with conventional lore[34] which holds that hydroxyl radicals are believed to be not as good at abstracting hydrogen atoms as persulfate radicals and assumption two is consistent of the higher level of initiator. However, since a control polymerization was not run to determine the M_W of the homopolymer using the redox initiator, neither assumption could be confirmed.

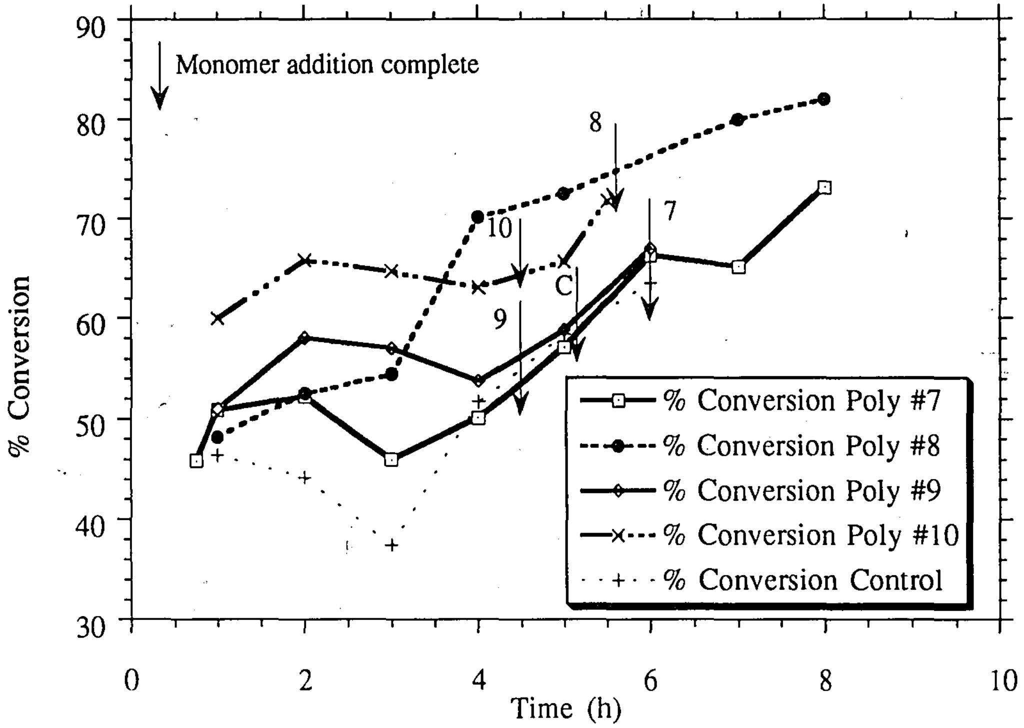


Figure 6: *Conversion of Vinyl Acetate vs. time for the graft polymerization of VAc onto Poly[(vinyl alcohol)-co-(vinyl acetate)] for four polymerization conditions (see text)*

4.8 HYDROLYSIS

A fraction of each starting copolymer, and of the polymers from Polymerizations 1-5 and 7-10, was hydrolyzed to PVOH. The usual concentration of alkali metal hydroxide or alkali metal alcoholates used to give high conversions of PVAc to PVOH in an alcoholic solution range between 0.43 and 8.6 mole%/ mole of PVAc.[15] It was determined that 8-10 mole% NaOH was needed to completely hydrolyze these copolymers in methanol. The amount of NaOH used for each hydrolysis was at the high end of the range generally used. When 1 mole % NaOH was used to hydrolyze the starting copolymer, the sample did not even gel. When 4 mole% NaOH was used to hydrolyze the copolymer of Polymerization 1, the sample was only 96 % hydrolyzed. This was attributed to the fact that the starting poly[(vinyl alcohol)-co-(vinyl acetate)] had already been hydrolyzed to 47 % vinyl alcohol by 3-V Corporation. To obtain a 47 % vinyl alcohol sample, the supplier most likely used an acid hydrolysis, which gives a more random distribution of acetate groups along the chain than when alkali is used. The random distribution of acetate groups is believed to prevent the transesterification reaction from zipping along the backbone, therefore requiring more alkali in order to complete the hydrolysis. Also, the starting copolymer was of low molecular weight, and hydrolysis of low molecular weight PVAc requires more catalyst because of the shorter polymer chain length. Polymerizations 4, 5, and 7-10 were run in methanol solutions containing 20% by weight water. For these solutions, 30 mole% NaOH was used for hydrolysis. The reason for the additional catalyst was the presence of 20 % by weight water. Both transesterification and hydrolysis takes place in this solution. In hydrolysis a stoichiometric amount of NaOH is needed per mole of PVAc, since the reaction forms the sodium salt of acetic acid.

4.9 REACETYLATION OF THE STARTING COPOLYMER AND THE POLYMERS OF POLYMERIZATIONS 4 , 5 AND 7

The extent of grafting onto the main chain can be distinguished from the extent of grafting onto the methyl group of the acetate by hydrolyzing and reacetylating the copolymer. Diagram 7 shows the possibilities of grafting off the main chain methine (graft site (1)) or the methyl group of the acetate (graft site (2)). If grafting occurred at graft site (1), then the molecular weight of the polymer formed by reacetylating, or hydrolyzing followed by reacetylating, should be identical. However, if grafting occurred at graft site (2), the molecular weight of the polymer formed by reacetylating should be higher than that of the polymer formed by hydrolyzing and reacetylating, since the graft site is cleaved during hydrolysis.

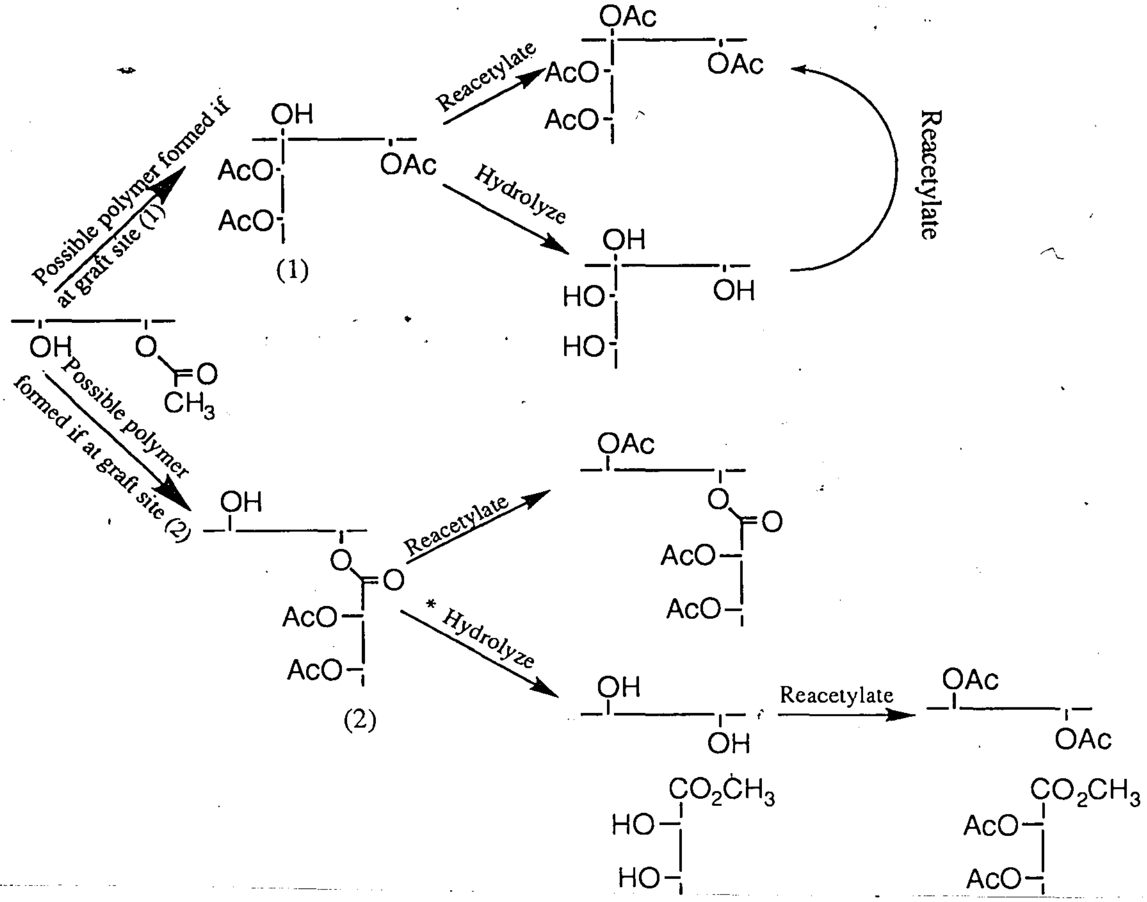


Diagram 7: *Shows how the extent of grafting onto the main chain can be distinguished from the extent of grafting onto the methyl group of the acetate*

The starting copolymer and the copolymers formed in Polymerizations 4, 5 and 7 were reacetylated. The solutions for Polymerizations 5 and 7 were reddish-yellow; this color was possibly due to the ascorbic acid present in high concentrations in these samples; when oxidized by persulfate the ascorbic acid forms ketones, which are good chromophores. This color may also be attributed to pyridine forming a complex with ketone, which has a high charge transfer coefficient.

The fully hydrolyzed forms of the starting copolymer and copolymers formed in Polymerizations 4, 5, and 7 were reacetylated. The extents to which each PVOH and grafted poly[(vinyl alcohol)-co-(vinyl acetate)] were reacetylated are listed in Table 7.

Table 7: Extent Of Reacetylation as determined by ^{1}H NMR

Sample	Relative molar percent PVOH	Relative molar percent PVAc
Reacetylated SC	3.1±0.2	96.9±0.2
Reacetylated Copoly #4	5.5±1.0	94.5±1.0
Reacetylated Copoly #5	2.8±1.0	97.2±1.0
Reacetylated Copoly #7	NA	NA
Reacetylated PVOH SC	2.5±0.2	97.5±0.2
Reacetylated PVOH #4	2.9±0.3	97.1±0.3
Reacetylated PVOH #5	2.8 ±0.1	97.2±0.1

Table 8 lists the molecular weights of the copolymers, reacetylated copolymers and hydrolyzed copolymers determined by GPC. By reacetylating, the amount of grafting onto the main chain vs. the amount of grafting onto the methyl group of the acetate was determined.

Table 8: GPC Results For Polymerizations 4 & 5 After Reacetylation

	Copolymer	Copoly(X) minus Copoly(SC)	Reacetylated Copolymer	Reacetylated PVOH
Starting Copolymer	M_W = 23,300 M_n= 9,600 PDI=2.4	NA	M_W=28,500 M_n=14,800 PDI= 1.9	M_W=29,000 M_n=16,800 PDI= 1.7
Poly. #4	M_W = 29,100 M_n=14,600 PDI=2.0	M_W = 5,800 M_n=5,000	M_W=33,500 M_n=19,600 PDI= 1.7	M_W=29,400 M_n=15,400 PDI= 1.9
Bimodal	M_W = 1,500 M_n=1000 PDI=1.5			
Poly. #5	M_W = 29,800 M_n=9,700 PDI=3.1	M_W = 6,500 M_n= 100	M_W=38,800 M_n=16,900 PDI= 2.3	M_W=32,100 M_n=17,400 PDI= 1.8

Table 8 shows that there was little difference in molecular weight between the reacetylated form of the fully hydrolyzed starting copolymer (SC) and the reacetylated form of the fully hydrolyzed polymers of Polymerizations 4 and 5. However, there was the expected difference in molecular weight between the reacetylated form of the starting copolymer (SC) and the grafted reacetylated form of the copolymers. This meant that grafting occurred mostly at site (2), on the acetate groups and not on the methine carbons of the main chain, as had been expected. Motohashi and Tomita previously reported grafting studies on partially and fully hydrolyzed poly(vinyl alcohol) and speculated that on partially hydrolyzed poly(vinyl alcohol), grafting occurred on the acetate group.[34,35]

4.10 POSSIBLE REASONS FOR GRAFTING ON THE ACETATE VS THE MAIN CHAIN METHINE CARBON:

1. *Steric Effects:*

Using ^{13}C NMR and the equations proposed by Rudin and Bugada[31] (Appendix 1), the Blockiness Index of a polymer can be determined. The Blockiness Index (ß) for the starting copolymer was found to be 0.72, where ß = 0 for blocky, ß = 1 for random, and ß = 2 for alternating copolymers. This indicated that the starting copolymer was more random than blocky. Also, the average sequence lengths of PVOH and PVAc were determined by ^{13}C NMR to be 2.2 and 3.7, respectively. This indicates that the growing polymer radical or VAc monomer molecule may be hindered from entering the PVOH-rich region on the polymer backbone as shown in Diagram 8 by the relatively large acetate groups in the PVAc-rich regions.

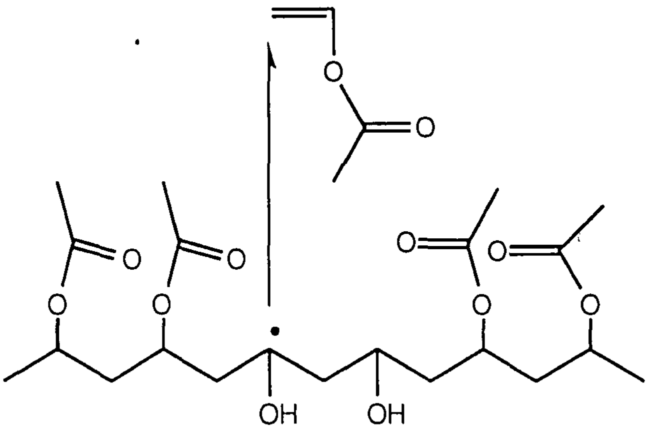


Diagram 8: *Illustration of steric hindrance*

2. *Hydrophobic Effects*

Diagram 9 indicates that the hydrophilic sulfate ion-radical may be hindered from passing through the bulky hydrophobic acetate groups to the PVOH methine carbons because of the randomness of the starting copolymer. Also, the hydrophobic VAc monomer may not reach the hydrophilic PVOH radicals.

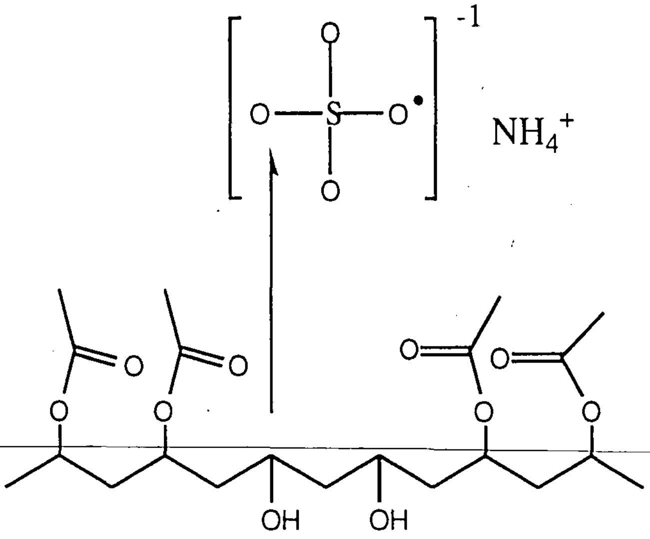


Diagram 9: *Illustration of hydrophobic effects*

3. *Coiling Index:*

The copolymer chain may collapse in a methanol/water medium to form a hydrophobic PVAc outer shell and a hydrophilic PVOH inner core as shown in Diagram 10. If this occurred, the initiator or the monomer may be hindered from reaching the inner core where grafting on the main chain methine carbons could take place.

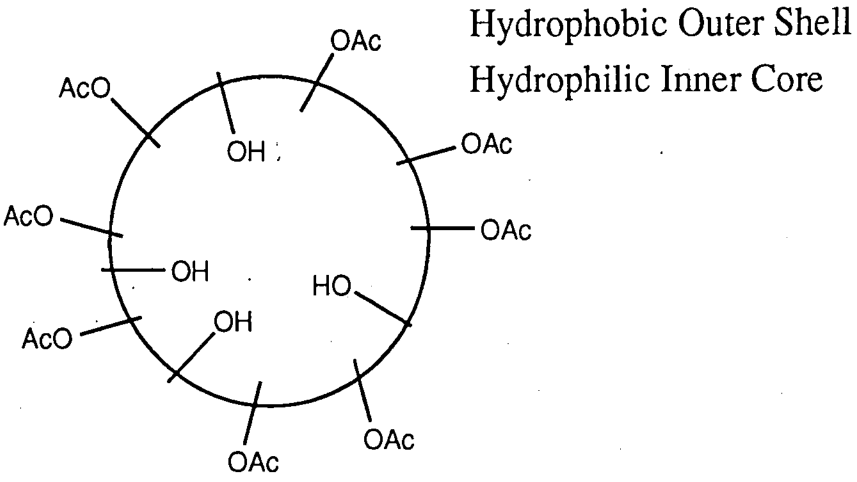
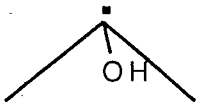


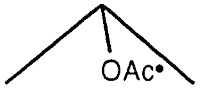
Diagram 10: *Illustration of the copolymer collapsing in the solvent medium to form a hydrophobic PVAc outer shell and a hydrophilic PVOH inner core*

4. Other Possibilities:

The chain transfer constant of PVOH is greater than that of PVAc, but the radical on the main chain methine carbon may add VAc more slowly than the radical on the acetate group. The two types of radicals which form are:



Radical on main chain methine



Radical on the acetate group

The most probable reason why chain transfer would occur on the main chain methine carbon in preference to the acetate group is that a more stable tertiary radical is formed instead of a primary radical. These more stable tertiary radicals on the main chain methine carbon are less reactive than the less stable, more reactive radicals on the acetate group. According to this theory, the rate of addition of VAc to the radicals on the main chain methine carbon (low energy radical) should be slower than the rate of addition of VAc to the radicals on the acetate group (high energy radical). Since the rate of addition of VAc to the radical on the main chain methine carbon is slow, this radical may possibly terminate by reacting with a primary radical or methanol. This hypothesis is supported by the work of Fanta et al.[36], who reported that, during an attempt to graft copolymers onto starch, the molecular weight of the grafted polymer chains did not change greatly when the ratio of methyl acrylate(MA)/VAc was varied from 100:0 and 50:50; however, graft polymerization of pure VAc gave a sharp lowering of the graft molecular weight. Also, Misra et al.[37] reported that, during an attempt to graft copolymers onto PVOH, the molecular weight of the grafted polymer decreased when the MA/VAc ratio was decreased.

4.11 REASONS FOR DISREGARDING THE GPC/MALLS RESULTS

Generally, the results obtained by GPC/MALLS are considered to be more accurate than those obtained by normal GPC techniques. The normal GPC technique is a relative method that requires calibration by an absolute method; a standard of known molecular weight is run; this standard is selected because it has similar chain coiling properties to the polymer being measured. GPC/MALLS is an absolute technique based on Rayleigh light scattering and requires no calibration with standards; it measures an absolute M_w on all increments in the chromatogram.[38,39] MALLS, in combination with GPC, gives the M_n, M_w, M_z and PDI of the polymer.

The GPC/MALLS results obtained in Table 4 for the fully hydrolyzed samples were questioned after the results for the reacetylated samples obtained in Table 8 showed that there was no difference in molecular weight between the fully hydrolyzed starting copolymer and the fully hydrolyzed forms of Polymerizations 4 and 5 after reacetylation. At this stage, a PVOH sample (Airvol 103, 98-98.8 % hydrolyzed), with a M_w of 20,000 was analyzed; the elution time of this sample was compared to that of the fully hydrolyzed form of Polymerization 5 (M_w determined by GPC/MALLS to be 22,300) and the hydrolyzed starting copolymer (M_w determined by GPC/MALLS to be 14,100). The GPC elution time for the fully hydrolyzed form of Polymerization 5 was much closer to the elution time of the hydrolyzed starting copolymer than to that of the Airvol 103 sample indicating very little if any grafts on the fully hydrolyzed Polymer 5.

The chromatograms of the multiple scattering angles exhibited random peak heights, unlike the normal monotonic increase expected as a function of decreasing angle. These light scattering chromatograms are shown in Appendix 3. The normal behavior of the Airvol 103 light scattering chromatograms are also shown in Appendix 3. Wyatt Technology, who markets the MALLS detector, was contacted to help explain this behavior. They pointed out that the sample was exhibiting a secondary effect in addition to the normal light scattering response. Possibly, there was some absorption occurring at the 488 nm wavelength used by the laser. They believe that there was some component in these samples that interfered with the light scattering data. The cause of this interference has not yet been determined. Therefore, the results obtained by GPC/MALLS were considered to be in error. A set of molecular weight data was collected using normal aqueous GPC on the hydrolyzed starting copolymers and the hydrolyzed form of Polymerizations 1,2,4,5,7,8,9, and 10. The molecular weight data for these samples listed in Appendix 4 confirms that there was little or no increase in molecular weight between the hydrolyzed starting copolymers and the hydrolyzed form of Polymerizations 1,2,4,5,7,8,9, and 10.

4.12 POLYMERIZATION 11

All of the previous polymerizations used poly[(vinyl alcohol)-co-(vinyl acetate)] as the grafting substrate in a methanol solution with up to 20 % water. Since the polymerization of VAc in the presence of this copolymer gave grafting on the acetate group, the next step was to polymerize VAc in the presence of completely hydrolyzed PVOH. It has been reported that PVOH serves as a grafting site in the emulsion polymerization of PVAc.[11,12,40] It is well known that PVOH that is incompletely hydrolyzed or grafted with PVAc branches during the early stage of polymerization acts as a good emulsifier and stabilizer for the emulsion polymerization of VAc. Vinyl acetate is partially water soluble (3.5 wt%

at 70 °C), and grafting occurs mostly in the aqueous phase during the early stage of solution polymerization. The length of the growing VAc chain eventually reaches a stage where it is no longer soluble in the water phase, and therefore precipitates from the water phase and forms polymer particles to start the emulsion polymerization. Stabilization of a latex system containing grafted PVOH does not come from electrostatic forces, since grafted PVOH is a nonionic macromolecule. This stabilization comes from the interactions of the polymer chains with the continuous phase, and by the interaction of these polymer chains with those on adjacent particles. This type of stabilization is called steric stabilization.[41]

It is theorized that, if one could increase the solubility of VAc in the aqueous solution, the extent of grafting onto PVOH would be enhanced. In Polymerization 11, t-butanol was added to keep the grafted polymer in solution as long as possible, to increase the degree of branching. Other steps used to increase the extent of grafting were: keeping the concentration of monomer throughout the reaction very low compared to that of the PVOH; running the reaction at high temperature; and using a high concentration of persulfate ion initiator.

The monomer concentration was monitored throughout the reaction by bromate-bromide titration. This concentration was less than 0.4 wt % throughout the reaction, and was lower than in any previous reactions (3-5 wt%). Unfortunately, an emulsion formed early in the reaction, so that the grafting in the aqueous phase was short-lived. The polymer formed during Polymerization 11 was purified (precipitated in acetone, dissolved in boiling water and reprecipitated in acetone), and a ^{13}C NMR spectrum of it showed very little PVAc present, an indication that a normal amount of grafting occurred followed by homopolymerization of PVAc. Also, an Attached Proton Test (APT) showed that no grafted carbon atoms were detected in the sample; however, unless their concentration was greater than 0.5 molar percent, they would not be detected by this technique. The extent of hydrolysis was determined by ^{13}C NMR; the results are listed in Table 5. The small portion of material that precipitated from acetone but did not dissolve in water after 1 hour at 90 °C was believed to be the grafted sample. This sample was dissolved in DMSO-d_6, which is a solvent for both

PVOH and PVAc. A ^{13}C NMR spectrum indicated that 30 mol % PVAc was present in the sample, which would increase the M_w of the sample from 20,000 to 37,100. Also, an Attached Proton Test (APT) showed no grafted carbon atoms in the sample; however, unless their concentration is greater than 0.5 molar percent, they would not be detected by this technique. This means that only one or two long branches were grafted on the backbone of each PVOH molecule.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The present research has investigated the feasibility of using the reported higher efficiency of grafting to the methine carbon of PVOH over that of PVAc to give highly branched PVOH. Vinyl acetate was grafted onto poly[(vinyl alcohol)-co-(vinyl acetate)] with good efficiency (little homopolymer), in good agreement with the observed increase in graft molecular weight vs. the molecular weight of homopolymer formed in the absence of poly[(vinyl alcohol)-co-(vinyl acetate)]. However, solution polymerization of VAc in the presence of poly[(vinyl alcohol)-co-(vinyl acetate)] gave grafting on the acetate group of the PVAc units rather than the expected grafting on the methine carbon of the PVOH or PVAc units. Several hypotheses were proposed to account for these findings. It was determined that the starting copolymer was more random than blocky, with average sequence lengths of PVOH and PVAc of 2.2 units and 3.7 units, respectively. After this discovery the first hypothesis was based on steric hindrance, hydrophobic effects, and the coiling index. The second hypothesis was based on the assumption that the rate of addition of VAc to radicals on the main chain methine carbon (low energy radicals) was slower than the rate of addition of VAc to the radicals on the acetate group (high energy radicals).

The selection of the initiator was found to influence the extent of grafting to the copolymer. Four different initiator systems were studied: persulfate ion, benzoyl peroxide, Trigonox 23, and a hydrogen peroxide/ascorbic acid redox system. Under the given conditions, it was determined that ammonium persulfate gave the highest increase in molecular weight.

The concentration of persulfate ion used in the polymerizations influenced the molecular weight of the grafted copolymer. When the amount of initiator was increased from 3.82 g to 5.98 g, the difference in molecular weight between the grafted copolymer and the original starting copolymer increased from 3,400 to 9,100 g/mol. The smaller overall increase in molecular weight at lower initiator concentrations was attributed to two reasons. Lower concentration of initiator should lead to grafts with longer chain lengths since chain length is inversely proportional to the square root of the initiator concentration. However, the use of a smaller concentration of initiator gave fewer radicals that can abstract a H atom from the starting copolymer to form fewer graft sites. Also, the monomer conversions were lower when a lower concentration of initiator was used.

At constant initiator concentration, the concentration of monomer used in the polymerization influenced the molecular weight of the grafted copolymer. When the amount of monomer was increased from 32.5 g to 65 g, the difference in molecular weight between the grafted copolymer and the original copolymer increased from 6,670 to 9,100 g/mol. It was not determined whether the number of grafts per polymer chain was increased or if more monomer led to longer grafted chains.

It was determined that the amount of NaOH needed for the hydrolysis of a fairly random poly[(vinyl alcohol)-co-(vinyl acetate)] in methanol was at the upper limit of the range generally needed for complete hydrolysis. One to four mole% NaOH was found to be insufficient, whereas 8-10 mol% led to complete hydrolysis.

It was once thought possible to achieve highly branched PVOH using methanol solution polymerization. I believe the formation of highly branched PVOH is still achievable. The work done in this thesis has led me from methanol solution polymerization to aqueous solution polymerization. The aqueous solution polymerization used totally hydrolyzed PVOH, whereas the methanol solution polymerization used a 50/50 PVOH/PVAc copolymer. This should eliminate hydrophobic, steric, and coiling effects that may have prevented grafting from occurring on the methine carbon in the methanol/water solution polymerizations. For success to be achieved, one must find a way to keep the grafted PVOH in solution for a much longer time than was accomplished here. General grafting techniques include: keeping a low monomer concentration compared to that of the PVOH; running the polymerization at high temperature; and the use of high concentrations of initiator. Other ways to accomplish grafting include: finding a chain transfer agent which would give much shorter branches on the main chain, while at the same time producing a radical which either is a good hydrogen abstractor or forms a stable radical which will not induce homopolymerization. If such a chain transfer agent could be found, more branches would be formed on the backbone before it reached the same level of acetate groups which caused the grafted polymer with long branches to precipitate from solution. One must also optimize the ratio of the organic phase to the aqueous phase to where there is just enough aqueous phase to keep the PVOH in solution. Since more organic phase is introduced, the grafted PVAc will stay in solution longer before it becomes insoluble.

Another way to possibly form a highly branched PVOH would be to run the solution polymerization in 1-methyl-2-pyrrolidinone (NMP) (lower chain transfer constant to solvent) or dimethylsulfoxide (DMSO) (higher chain transfer constant to solvent), which are cosolvents for both PVOH and PVAc. As in water these solvents allow one to use completely hydrolyzed PVOH for the graft substrate. However, unlike in water the grafted PVAc on the PVOH backbone will not cause the polymer to precipitate from solution. Again, this would be accomplished by using the following conditions: keeping a low monomer concentration compared to that of the PVOH, running the polymerization at high temperature, and using a high concentrations of initiator. Also, finding a chain transfer agent which would give much shorter branches along the main chain, while at the same time producing a radical which either is a good hydrogen abstractor or which forms a stable radical that would not induce homopolymerization.

One could possibly increase the grafting of VAc on the PVOH by addition of a small amount of monomer that does not require a high energy radical to initiate polymerization, such as dimethyl maleate, maleic anhydride, or methyl acrylate. A chain would start to grow at this graft site, and since only a small amount of this monomer is present, VAc should polymerize to increase the length of the growing chain.

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Appendix 1

PVOH Analytical Methods

Determination of Percent Hydrolysis of Poly(vinyl alcohol)

PROCEDURE

1. Weigh to 0.0001 grams the specified amount of undried poly(vinyl alcohol)

   87-98% hydrolyzed, 1.0-1.5 grams
   98-99% hydrolyzed, 2.0-2.5 grams
   >99% hydrolyzed, 4.0-4.5 grams

2. Transfer the weighed material into a 500 ml iodine flask. Place magnetic stirring bar in the flask.

3. Add 100 ml of 75% H_2O/25% methanol solution. Place flask on a magnetic stirrer and slurry for 5 to 10 minutes.

4. Add 5 drops phenolphthalein indicator. If solution is clear, add 0.1 N NaOH until slightly pink. Then add 0.1 N HCl until solution is clear. If solution is slightly pink initially, add 0.1 n HCl until clear.

5. Add 10.00 ml 0.5 N NaOH to the flask.

6. Connect flask to water-cooled condenser and place on hot plate.

7. Heat the contents of flask to boiling and reflux for 1 hour.

8. Wash condenser walls with 20-30 ml water and remove flask from condenser.

9. Cool flask under cold tap water to room temperature and titrate solution to a colorless endpoint (same endpoint as in Step 4).

10. A blank shall be run whenever a new solution of 75% H_2O/25% methanol is prepared. (Perform Steps 3-9, without sample).

CALCULATIONS

Saponification Number =

$$\frac{(\text{ml HCl Blank} - \text{ml HC1 Sample})\ (\text{N HC1})\ (56.1)}{(\text{Weight sample})\ (\text{Solids as decimal equivalent})}$$

$$\text{Percent Hydrolysis} = 100\left[1 - \left(\frac{44S}{(56100) - 42S}\right)\right]$$

Appendix 2

Formulae Used in Blockiness Calculations

(OH, OH), (OH, OAc) and (OAc, OAc) are the mole fractions of each of the possible triads. These values were calculated from the peak integrals after correcting for the 1,2-glycol content.

$$\text{mole fraction PVOH} = (\text{OH}) = (\text{OH, OH}) + \frac{(\text{OH, OAc})}{2}$$

$$\text{mole fraction PVAc} = (\text{OAc}) = (\text{OAc, OAc}) + \frac{(\text{OH, OAc})}{2}$$

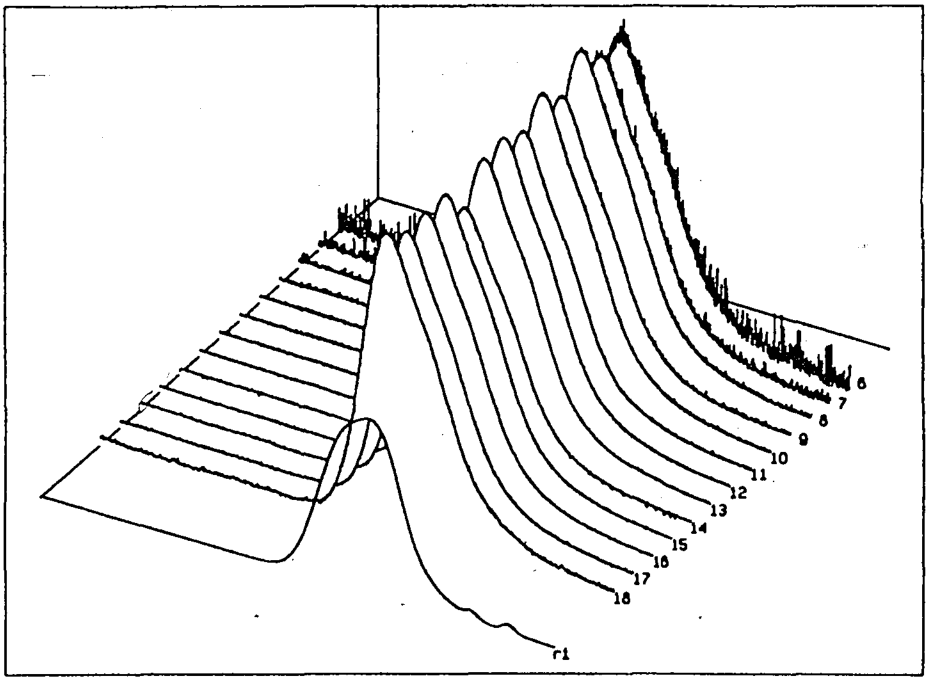
$$\text{Average length of PVOH run} = L_{\text{OH}} = 2\,(\text{OH}) \,/\, (\text{OH, OAc})$$

$$\text{Average length of PVAc run} = L_{\text{OAc}} = 2\,(\text{OAc}) \,/\, (\text{OH, OAc})$$

$$\text{Blockiness index} = n\ (\text{eta}) = \frac{(\text{OH, OAc})}{2\,(\text{OH})(\text{OAc})}$$

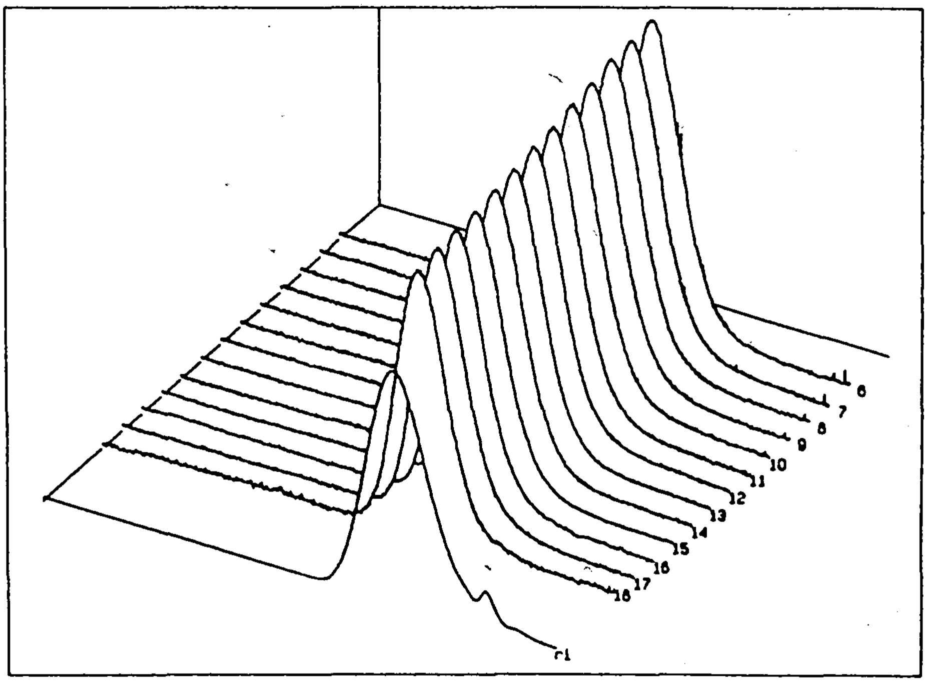
A perfectly blocky copolymer has $n = 0$; an alternating copolymer has $n = 2$.

Appendix 3



MALLS Chromatograms of 13319-31

MALLS Chromatogram of PVOH 7 exhibiting random peak heights



MALLS Chromatograms of Airvol 103 PVOH

MALLS Chromatogram of Airvol 103 exhibiting normal behavior

Appendix 4

	PVOH		PVOH
Starting Material #1	M_w = 10,400 M_n= 4,300 PDI= 2.4	**Starting Material #2**	M_w = 11,300 M_n= 5,400 PDI= 2.1
Poly. # 1	M_w = 12,000 M_n= 5,000 PDI= 2.4	**Poly. # 7**	M_w = 11,100 M_n= 4,600 PDI= 2.4
Poly. # 2	M_w = 10,300 M_n= 3,800 PDI= 2.7	**Poly. # 8**	M_w = 11,300 M_n= 4,600 PDI= 2.4
Poly. #3	M_w = NA M_n=NA PDI=NA	**Poly. #9**	M_w = 11,100 M_n=5,000 PDI=2.2
Poly. #4	M_w = 10,900 M_n= 4,400 PDI= 2.5	**Poly. #10**	M_w = 10,800 M_n= 4,200 PDI= 2.6
Poly. #5	M_w = 12,800 M_n= 5,800 PDI= 2.2		

Vita

Thomas John Markley was born February 16, 1965, in Auburn NY, son of Paul and Diane Markley. He graduated from Moravia High School in 1983. Thomas Markley is married to Christine E. Markley.

Mr. Markley received his A.A.S. in Math/Science in 1985 from Cayuga Community College, Auburn , NY. He then went to SUNY College of Environmental Science & Forestry, Syracuse, NY where he received his B.S. in Chemistry. He graduated with honors in May 1987. In July of 1987 he joined Allied-Signal Inc. and worked as a Research Chemist in Corporate Technology in their polymer laboratory. In April of 1989 he joined Air Products and Chemicals Inc. and continues to work as a Chemist in Corporate Science and Technology Center in their organometallic group.

The author began graduate studies at Lehigh University in 1989 as a part time student. He enrolled in the Masters Program for Chemistry and did his research in polymers.

END

OF

TITLE