

# Synthesis and Characterization of Polyvinyl Alkyl Ester and Polyvinyl Alcohol Homopolymers and Blends of Polyvinyl Alkyl Esters

Ronald P. D'Amelia\*, Masashi W. Kimura, Joseph Mancuso

Chemistry Department, Hofstra University, Hempstead, NY

\*Corresponding author: [Ronald.p.damelia@hofstra.edu](mailto:Ronald.p.damelia@hofstra.edu)

Received February 02, 2021; Revised March 05, 2021; Accepted March 14, 2021

**Abstract** Polyvinyl alkyl esters (PVAE) are a family of macromolecules in which the ester side chains (pendant groups) increase in molar mass and hydrophobicity and decrease in structural polarity as the number of carbons in the pendant group increases. These PVAE are commonly used in adhesives, industrial coatings, plasticizers, textile finishes, chewing gum bases, and paint thickeners. The most significant polymer in the family of PVAE is polyvinyl acetate (PVAc), which is the precursor for making polyvinyl alcohol (PVOH), the largest volume water-soluble, non-toxic, biodegradable, and biocompatible polymer in the world used in the manufacture of pharmaceuticals, cosmetics, food industries, laundry detergents, and freshwater sports fishing. In this study, the goal is to synthesize polyvinyl alkyl ester homopolymers of various molecular weights by esterifying polyvinyl alcohol with alkyl anhydrides. The study also includes the synthesis of various polyvinyl alcohol homopolymers from different polyvinyl acetates via hydrolysis. These polymers were studied via gel permeation chromatography (GPC), multi-angle laser light scattering (MALLS), intrinsic viscosity, elemental analysis, Fourier-transform infrared spectroscopy (FT-IR), and nuclear magnetic resonance spectroscopy (NMR). Blends of polyvinyl alkyl ester homopolymers with defined compositions were also studied using quantitative FT-IR.

**Keywords:** elemental analysis, Fourier-transform infrared spectroscopy, gel permeation chromatography, homopolymers, hydrolysis, intrinsic viscosity, multi-angle laser light scattering, nuclear magnetic resonance spectroscopy, polyvinyl acetate, polyvinyl alkyl ester blends, polyvinyl alkyl esters, water-soluble polymers

**Cite This Article:** Ronald P. D'Amelia, Masashi W. Kimura, and Joseph Mancuso, "Synthesis and Characterization of Polyvinyl Alkyl Ester and Polyvinyl Alcohol Homopolymers and Blends of Polyvinyl Alkyl Esters." *Journal of Polymer and Biopolymer Physics Chemistry*, vol. 9, no. 1 (2021): 1-12. doi: 10.12691/jpbpc-9-1-1.

## 1. Introduction

Polyvinyl alkyl esters (PVAE) are a class of macromolecules commonly used for manufacturing adhesives, chewing gum bases, industrial coatings, paint thickeners, plasticizers, and textile finishes. They possess an ester pendant group of variable carbon chain length. As the carbon chain length increases, so too do the molar mass and hydrophobicity while its structural polarity decreases. Figure 1 shows a generic repeat unit for PVAE's, where  $n$  and  $r$  are the number of backbone and methylene ( $-\text{CH}_2-$ ) repeat units, respectively.

Without any methylene units in the side chain, the resulting PVAE is polyvinyl acetate (PVAc), the precursor for synthesizing polyvinyl alcohol (PVOH), the largest volume water-soluble, non-toxic, biodegradable, and biocompatible polymer in the world [1]. To synthesize PVAE's, PVOH of known molecular weight (MW 13,000-23,000) was esterified with a series of acid anhydrides; these products were also made into blends. PVOH was obtained via a saponification/hydrolysis reaction using

PVAc of different molecular weights. Figure 2 shows the general reaction scheme for the synthesis of PVAE from PVAc. The physical properties of these homopolymers were characterized using GPC, MALLS, intrinsic viscosity, elemental analysis, FT-IR, and NMR.

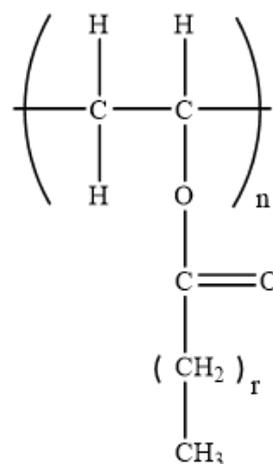


Figure 1. Monomer of PVAE

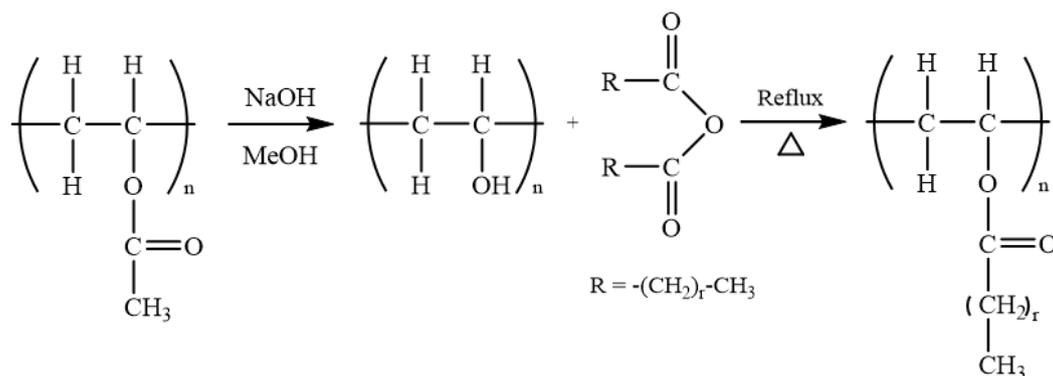


Figure 2. Reaction Scheme of PVAc to PVOH to PVAc

## 2. Materials and Methods

### 2.1. Materials

The PVAc samples were purchased from Union Carbide/DOW Chemical Corp and produced using solution-free radical polymerization; these samples were identified as GB-11, GB-30, GB-50, and GB-75 (numbers representing molecular weights in kDa). These are food-grade gum resins with appearances ranging from a transparent amorphous solid (GB-11) to white pellets (GB-75). The PVOH sample was 98% hydrolyzed with a molecular weight of 13,000-23,000 and was obtained from Sigma-Aldrich. The PVOH sample consisted of small, sand-sized, light-yellow particles. Mallinckrodt's potassium hydroxide (KOH) (87% pure) and anhydrous methanol (MeOH) (99.8% pure) from Spectrum were used for synthesizing PVOH from PVAc. Acetone (99.5% pure) was also supplied by Spectrum. Sigma-Aldrich supplied acetic anhydride (99% pure), propionic anhydride (99% pure), butyric anhydride (98% pure), hexanoic anhydride (97% pure), and sodium tert-butoxide (NaOtBu) (97% pure), which were used in esterifying PVOH into PVAc's. Sigma-Aldrich also supplied polystyrene standards with molecular weights ranging from 2,430-891,000 Da for calibrating the GPC; deuterated chloroform ( $CDCl_3$ ) (>99% deuterated) and deuterated dimethyl sulfoxide (D-DMSO) (>99% deuterated) for NMR analysis; and tetrahydrofuran (THF) ( $\geq 99.9\%$  pure) and toluene (99.8% pure) for dissolving homopolymers for GPC and MALLS analyses.

### 2.2. Methods

#### 2.2.1. Synthesis of PVOH from PVAc

Approximately 3 grams of PVAc (GB-11, -30, -50, or -75) was weighed into a 250-mL round-bottom flask with a condenser, thermometer, and dropping funnel attached. To this, 75-mL of MeOH was added through the dropping funnel and refluxed at approximately (65-70°C) until the PVAc was completely dissolved. Afterward, a solution of approximately 2-grams of KOH dissolved in 25-mL of MeOH was added. After refluxing for an hour, the PVOH precipitated out of the solution and was gathered using Buchner funnel filtration. The PVOH was washed with two 25-mL portions of MeOH and left to dry overnight before weighing.

#### 2.2.2. Synthesis of PVAc from PVOH

Approximately 5 grams of PVOH (MW 13,000-23,000) was weighed into a 250-mL round-bottom flask with a condenser, thermometer, and dropping funnel attached. To this, 25-mL of an acid anhydride (acetic, propionic, butyric, or hexanoic) was added via the dropping funnel. The solution was refluxed for around 3.5-4 hours at different temperatures depending on the anhydride (125°C for acetic, 140°C for propionic, 150°C for butyric, and 250°C for hexanoic). These would yield PVAc homopolymers of PVAc, polyvinyl propionate (PVPr), polyvinyl butyrate (PVBu), and polyvinyl hexanoate (PVHex), respectively. After reflux, the product was precipitated from the solution using 1M KOH until it had a neutral pH. After precipitation, the precipitate was placed in a 1M NaOtBu solution and left alone for several days to neutralize any remaining acid within the product. Afterward, the solution was decanted and the product was placed in a vacuum oven at 50°C for a day. Then, the product was dissolved in acetone and reprecipitated using 200-mL of water to get rid of any remaining acid. Finally, the acetone-water solution was decanted and the product was dried in the vacuum at 50°C for a day. The product was then weighed.

#### 2.2.3. Preparation of PVAc Blends

Blends were prepared using PVAc homopolymers obtained from the esterification of PVOH described above. Four blends of 1-gram total mass were made using PVAc and PVPr in 20- weight percent intervals. Each blend was dissolved in approximately 15-mL of MeOH and mixed thoroughly. The MeOH was first evaporated until a malleable film was left before the solid blends were obtained by placing them in a vacuum oven at low pressure and 50 °C for a day.

#### 2.2.4. Gel Permeation Chromatography (GPC)

A GPC was constructed using the following hardware components: 1-liter solvent bottle, Viscotek DG 700 degasser, Waters 510 HPLC pump, Waters 717Plus autosampler, Waters Styragel gel permeation column HR 3:4:5, Viscotek RALLS detector module 600, Viscotek dual detector – differential refractometer and viscometer model 250, and Viscotek data manager DM 400. The computer software used was Viscotek TriSEC 3.0. Calibration was done using polystyrene samples of varying molecular weights (MW 2,430-891,000). Samples

were dissolved in 4.0 mL of THF and placed in 15x45 mm VWR clear screw vials, capped with polytetrafluoroethylene white Septum and Wheaton black plastic caps with open tops.

### 2.2.5. Multi-Angle Laser Light Scattering (MALLS)

MALLS analyses were done as described previously [2]. For specific refractive index increment (dn/dc) measurements, a Wyatt Optilab model DSP interferometer refractometer was used with a P-10 cell at 35 °C. The dn/dc values were obtained at 690 nm. The instrument was calibrated using aqueous sodium chloride solutions. The data was analyzed from plots of dn vs. concentration using Wyatt DNDC software. The slopes of the dn vs. concentration plots were the dn/dc values for each solution. For light scattering measurements, a Wyatt MALLS photometer model mini-DAWN was used with a K5 cell. Scattering intensities were measured at 45, 90, and 135 degrees at 690 nm and 25 °C. Samples were prepared by dissolving them in THF, acetone, and toluene. Solutions were pumped through Whatman Anotop 25 filter 0.2 μm using a Razel syringe pump set at a flow rate of 6 ccs per hour.

Using the dn/dc values, K and H light scattering constants were calculated using equations 1 and 2, respectively:

$$K = \frac{2\pi^2 n_0^2}{N_0 \lambda^4} \left( \frac{dn}{dc} \right)^2 \quad (1)$$

$$H = \frac{32\pi^2 n_0^2}{N_0 \lambda^4} \left( \frac{dn}{dc} \right)^2 \quad (2)$$

where  $n_0$  is the refractive index of the solvent,  $N_0$  is Avogadro's number, and  $\lambda$  is the wavelength of the incident light. The K and H constants were substituted into the Debye virial equation (Eq. 3) below:

$$\frac{Kc}{R_\theta} = \frac{Hc}{\tau} = \frac{1}{M_w} + 2A_2c + \dots \quad (3)$$

where  $c$  is concentration,  $R_\theta$  is the intensity of light scattering at angle  $\theta$  in degrees,  $\tau$  is the total light scattering (turbidity),  $M_w$  is the weight-average molecular weight, and  $A_2$  is the second virial coefficient.

Zimm plots were obtained by plotting  $Kc/R_\theta$  vs  $\text{Sin}^2\theta/2 + kc$  using Wyatt Aurora software, where  $k$  is the scaling factor of the plot. Double extrapolation of the plot yielded the reciprocal of  $M_w$  as the intercept and  $A_2$  as the slope of the zero-angle line.

### 2.2.6. Intrinsic Viscosity

Intrinsic viscosity measurements were done as described previously [2]. A Cannon-Ubbelohde low shear semi-micro dilution viscometer (size 50) was used. The temperature was kept at approximately  $25.0 \pm 0.1^\circ\text{C}$  using a Cannon Model M-1 Constant Temperature Bath connected to a Haake A81 cooling unit. Approximately 1.5 g of each sample was dissolved in 50 mL of solvent (acetone for PVAc and PVAc's, water for PVOH) and filtered through a Hypo Interchangeable Syringe with a Whatman 25-mm PTFE filter. Each sample at several different concentrations was measured using a stopwatch in triplicates.

Using the measured efflux times of the solution ( $t$ ) and the solvent ( $t_0$ ), the relative viscosities ( $\eta_{rel}$ ) of each sample were calculated using equation 4:

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t\rho}{t_0\rho_0} \approx \frac{t}{t_0} \quad (4)$$

where  $\eta$  and  $\eta_0$  are the viscosities and  $\rho$  and  $\rho_0$  are the densities of the solution and the solvent, respectively. Since the densities of the solution and the solvent are very dilute,  $\eta_r$  is approximately equal to  $t$  divided by  $t_0$ . The specific viscosity of the solution ( $\eta_{sp}$ ) was computed using equation 5:

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_{rel} - 1 = \frac{t}{t_0} - 1 \quad (5)$$

The reduced viscosity ( $\eta_{red}$ ) was calculated using  $\eta_{sp}$  divided by the solute concentration ( $c$ ) in g/dL as expressed in equation 6. Inherent viscosity ( $\eta_{inh}$ ) is also related to concentration and was calculated using equation 7.

$$\eta_{red} = \frac{\eta_{sp}}{c} \quad (6)$$

$$\eta_{inh} = \ln \frac{\eta_{rel}}{c} \quad (7)$$

The intrinsic viscosity  $[\eta]$  was graphically determined by applying both the Huggins (Eq. 8) and Kraemer (Eq. 9) equations and extrapolating them to zero concentration [3,4]. The constants  $k'_H$  and  $k''_H$  are dimensionless and are for a series of polymers of different molecular weights in a given solvent and temperature, and should sum to approximately  $1/2$ . The intercept of the Huggins and Kraemer equations yielded  $[\eta]$ .

$$\eta_{red} = \frac{\eta_{sp}}{c} = [\eta] + k'_H [\eta]^2 c \quad (8)$$

$$\eta_{inh} = \ln \frac{\eta_{rel}}{c} = [\eta] - k''_H [\eta]^2 c \quad (9)$$

The viscosity-average molecular weights ( $M_v$ ) of the homopolymers were calculated from their graphically determined  $[\eta]$  using the logarithmic form of the Mark-Houwink equation (Eq. 10):

$$\log [\eta] = \log K + \alpha \log M_v \quad (10)$$

where  $K$  and  $\alpha$  are constants that vary based on the polymers and solvents. [5] A value of  $\alpha$  that is greater than 0.5 is indicative of a good solvent for the polymer of interest and can be physically interpreted as the flexibility of the polymer in solution. The greater the  $\alpha$  value, the more rigid the polymer is in solution. The  $K$  and  $\alpha$  constants for PVAc in acetone are  $1.8 \cdot 10^{-4}$  dL/g and 0.67, respectively, while those for PVOH in water are  $2.0 \cdot 10^{-4}$  dL/g and 0.76, respectively [2,6].

### 2.2.7. Elemental Analysis

Samples were sent to Galbraith Laboratories in Knoxville, Tennessee, for carbon and hydrogen combustion testing. Percent weight compositions of carbon and hydrogen were obtained, and percent oxygen was calculated by difference.

### 2.2.8. Fourier-Transform Infrared Spectroscopy (FT-IR)

All PVAc, PVOH, and PVAc samples were analyzed using a Bruker Alpha-P FT-IR spectrometer with a Platinum® attenuated total internal reflectance (ATR) quick snap module with a diamond crystal. The Alpha-P unit had a Michelson Interferometer with a SiC globalar as the IR source, the time dependence of the IR intensity was measured with a pyroelectric DTGS detector. The data analyses were done using the Bruker OPUS® software version 7.0.122. Each sample was analyzed by simply pressing the sample between the anvil and diamond crystal, with each measurement represents the average spectrum after 16 scans and at a resolution of four wavenumbers. For quantitative FT-IR measurements, five scans were conducted for each sample and their peak integrations were obtained using the built-in integration feature.

### 2.2.9. Nuclear Magnetic Resonance (NMR)

The proton NMR spectra were obtained using a 400 MHz JEOL model ECS-400 NMR spectrometer. The PVAc's and PVOH's were dissolved in CDCl<sub>3</sub> and D-DMSO, respectively. The JEOL Delta NMR control and process software version 5.0.2 (Windows) was used to analyze each spectrum. Each sample was run as a 16-scan single pulse, 1D proton NMR with a 0.25 Hz resolution and a relaxation time of 5 seconds.

### 2.3. Hazards

KOH and NaOtBu are caustic chemicals that can cause skin burns and eye damage and should be worked with using gloves in a fume hood. Acid anhydrides are flammable, corrosive, and water-sensitive chemicals, and should be handled exclusively in a fume hood. MeOH, THF, toluene, and acetone are flammable and toxic liquids. CDCl<sub>3</sub> is toxic and possibly carcinogenic and should be handled in a fume hood with gloves. D-DMSO is a flammable liquid and should be handled away from heat and electrical sources.

## 3. Results and Discussion

### 3.1. GPC Analysis of PVAc Homopolymers

The molecular weight of polymers is unlike small molecules in that they are frequently represented by a Gaussian distribution. In this Gaussian curve, several key molecular weights can be used to describe any given polymeric material. The  $M_n$  molecular weight represents the number-average molecular weight and it is strictly smaller than the weight-average molecular weight ( $M_w$ ). The molecular weight with the highest probability is referred to as  $M_p$  and is strictly in between  $M_n$  and  $M_w$ . The  $M_p$  represents the weight of the polymer that is at the highest point on the Gaussian curve. Lastly, there is  $M_z$ , which is typically determined via ultracentrifugation and is physically related to the toughness of the material.  $M_z$  is strictly greater than all of the other molecular weights. Taken together, for any given polydisperse polymer, the following relationship holds for  $M_n$ ,  $M_p$ ,  $M_z$ , and  $M_w$ :

$$M_n < M_p < M_w < M_z.$$

Polydispersity is the degree to which the polymer of interest is not uniform and can be calculated by dividing  $M_w$  and  $M_n$ . The various types of molecular weights for GB-11 to 75 are described in Table 1. In each case, the general relationship between the different types of molecular weights holds and the polydispersity index is close to 2.0. This is consistent with the way that PVAc is polymerized because traditional free radical polymerization produces highly polydisperse polymers. The molecular weights of these homopolymers increase from GB-11 to 75 and the  $M_w$  for each homopolymer is incredibly similar to the average molecular weight reported by the manufacturer.

Table 1. Summary of GPC Data of PVAc's

PVAc	Mn (kDa)	Mp (kDa)	Mz (kDa)	Mw (kDa)	Polydispersity Ratio (Mw/Mn)
GB-75	43.6	61.0	172.1	85.8	1.968
GB-50	28.4	47.4	135.5	59.0	2.077
GB-30	20.8	31.8	54.7	35.4	1.702
GB-11	7.85	12.8	20.4	14.0	1.783

### 3.2. MALLS Analysis of PVAc Homopolymers

The dn/dc data (Table 2) was used to construct a Zimm plot that allowed both the light-scattering molecular weight (Table 3) and second virial coefficients (Table 4) to be calculated in THF, acetone, and toluene. An example of a constructed Zimm plot is shown in Figure 3. The average molecular weight determined by MALLS in various solvent systems is consistent with the nominal molecular weight reported by the manufacturer and is consistent with the GPC-determined weight average molecular weight. The second virial coefficients decrease with increasing molecular weight and suggest that PVAc is a good solute in these solvents because the second virial coefficient is strictly greater than zero for all solvent systems [2].

Table 2. Summary of dn/dc (mL/g) Data in Different Solvents

PVAc	THF	Acetone	Toluene	Methanol
GB-75	0.0535	0.1032	0.0135	0.1125
GB-50	0.0525	0.1050	0.0142	0.1197
GB-30	0.0583	0.0971	0.0144	0.1254
GB-11	0.0586	0.1033	0.0189	0.1189

Table 3. Summary of Molecular Weights (kDa) of PVAc's from MALLS Analysis using Different Solvents.

PVAc	THF	Acetone	Toluene	Average
GB-75	80.5	84.3	82.6	82.5
GB-50	57.9	57.1	53.4	56.1
GB-30	30.5	34.5	37.8	34.3
GB-11	10.1	10.3	11.0	10.4

Table 4. Summary of A<sub>2</sub> Values in Different Solvents (mol\*mL/g<sup>2</sup>)

PVAc	THF	Acetone	Toluene
GB-75	9.10E-04	6.20E-04	4.70E-04
GB-50	9.40E-04	7.10E-04	6.10E-04
GB-30	1.30E-03	6.90E-04	1.80E-03
GB-11	1.70E-03	1.10E-03	2.10E-03

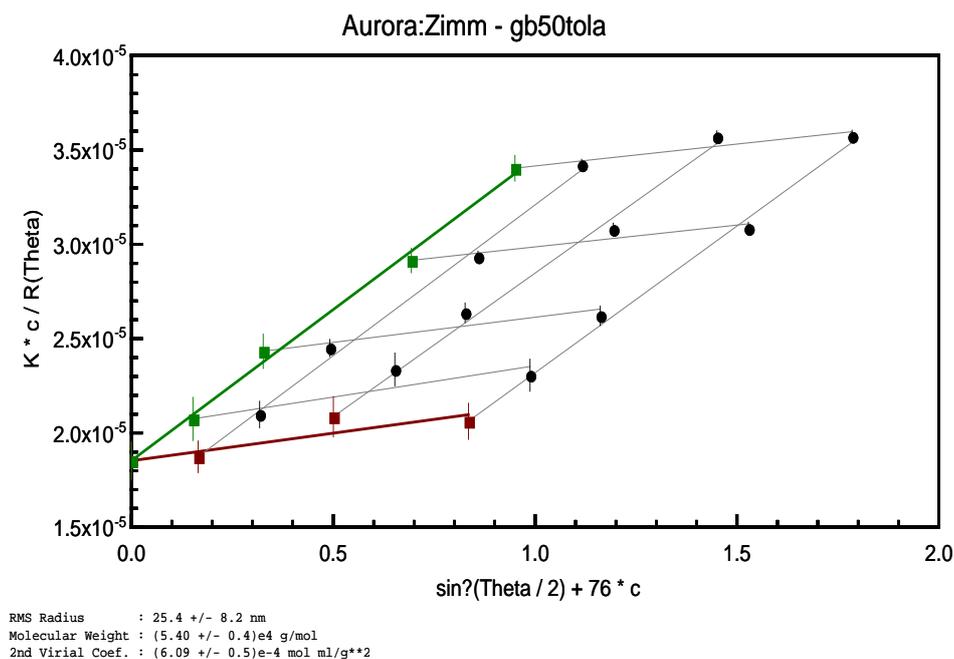


Figure 3. Zimm Plot of PVAc Homopolymer GB-50 in Toluene

### 3.3. Intrinsic Viscosity Analysis of PVAc and PVOH Homopolymers

Table 5. Summary of Intrinsic Viscosities of PVAc's in Acetone

PVAc	Intrinsic Viscosity (Acetone) (cm <sup>3</sup> /g)	M <sub>v</sub> (kDa)
GB-11	0.100	11.275
GB-30	0.172	25.180
GB-50	0.260	46.441
GB-75	0.373	79.268

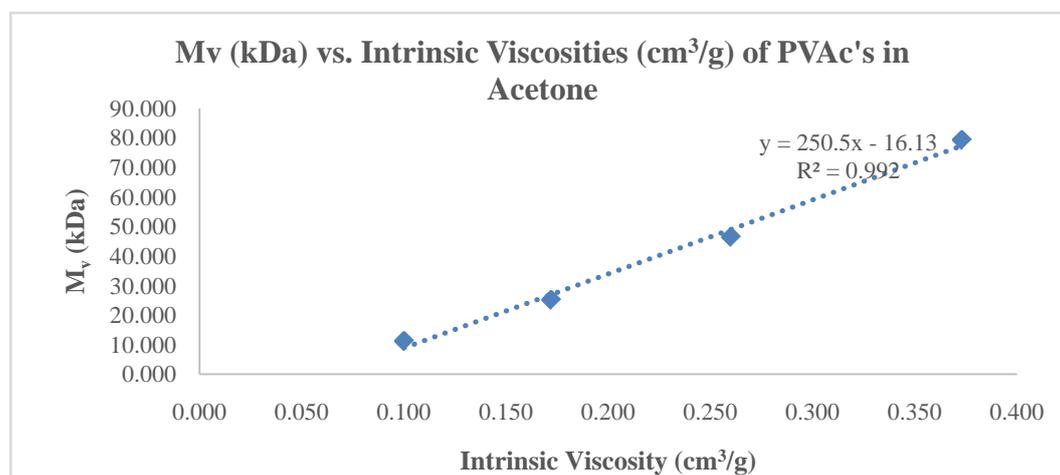
Table 6. Summary of Intrinsic Viscosities of PVOH's in Water

PVOH	Intrinsic Viscosity (Water) (cm <sup>3</sup> /g)	M <sub>v</sub> (kDa)
From GB-11	0.141	5.695
From GB-30	0.229	10.602
From GB-50	0.262	12.657
From GB-75	0.355	18.878
MW 13-23 kDa	0.371	19.973

Table 7. Summary of Intrinsic Viscosities of PVAc's in Acetone

PVAc	Intrinsic Viscosity (Acetone) (cm <sup>3</sup> /g)	M <sub>v</sub> (kDa)
PVAc	0.223	39.039
PVPr	0.230	45.394
PVBu	0.245	51.749
PVHex	---	---

Intrinsic viscosities and molecular weights of the PVAc and PVOH homopolymers in their respective solvents are summarized in Table 5, Table 6, Table 7. Figure 4. demonstrates a linear relationship between increasing intrinsic viscosity and molecular weight of PVAc homopolymers. A similar relationship is shown in Figure 5 using PVOH homopolymers that were synthesized from various PVAc's and with one sample purchased from Sigma-Aldrich. These trends are consistent with the physical significance of viscosity; the longer the polymer chain, the stronger the intermolecular forces between the molecules, and thus the more resistance to flow the bulk material would display.

Figure 4. M<sub>v</sub> (kDa) vs. Intrinsic Viscosities (cm<sup>3</sup>/g) of PVAc's in Acetone

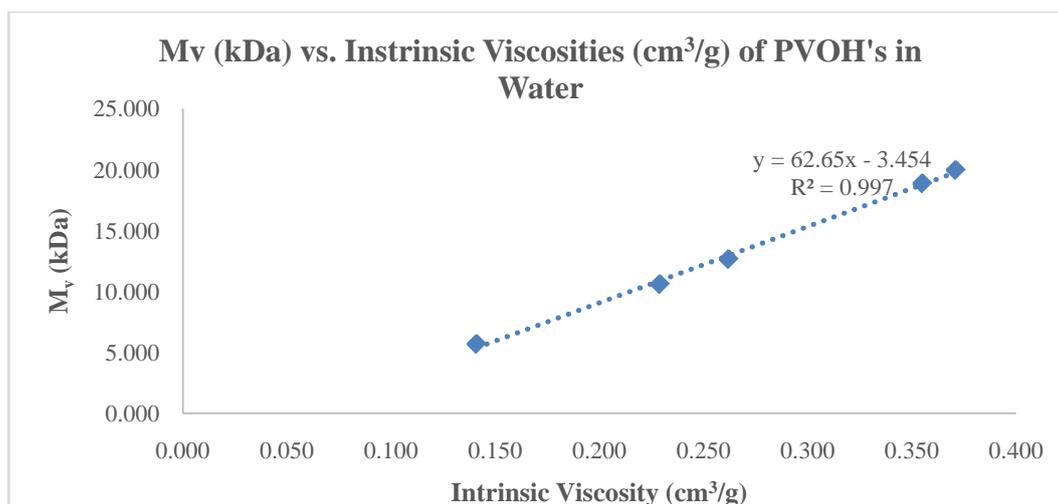


Figure 5.  $M_v$  (kDa) vs. Intrinsic Viscosities ( $\text{cm}^3/\text{g}$ ) of PVOH's in Water

### 3.4. Elemental Analysis of PVAc and PVOH Homopolymers

The elemental analysis results were used to calculate the experimental weight percent oxygen using equation 11:

$$\% O = 100 - \% C - \% H \quad (11)$$

The theoretical weight percent compositions were determined using equation 12 below:

$$\text{Weight \% Composition} = \frac{(MW_E)(n_E)}{(MW_M)} * 100 \quad (12)$$

where  $MW_E$  and  $MW_M$  are the molecular weights of the element and monomer, respectively, and  $n_E$  is the number of atoms of the element in the monomer.

Experimental weight percent compositions of PVAc and PVOH homopolymers agreed with the theoretical weight percentages of carbon, hydrogen, and oxygen. The theoretical weight percent oxygen and experimental weight percent oxygen are plotted in Figure 6. These values show a strong linear relationship and the slope of the line is incredibly close to 1, indicating that percent oxygen that should be there is incredibly close to the experimentally determined percent oxygen. As the number of methylene groups in the pendant chain of the PVAc's increases, the percent carbon and hydrogen should increase and the percent oxygen should decrease. This trend is observed experimentally and is summarized in Table 8.

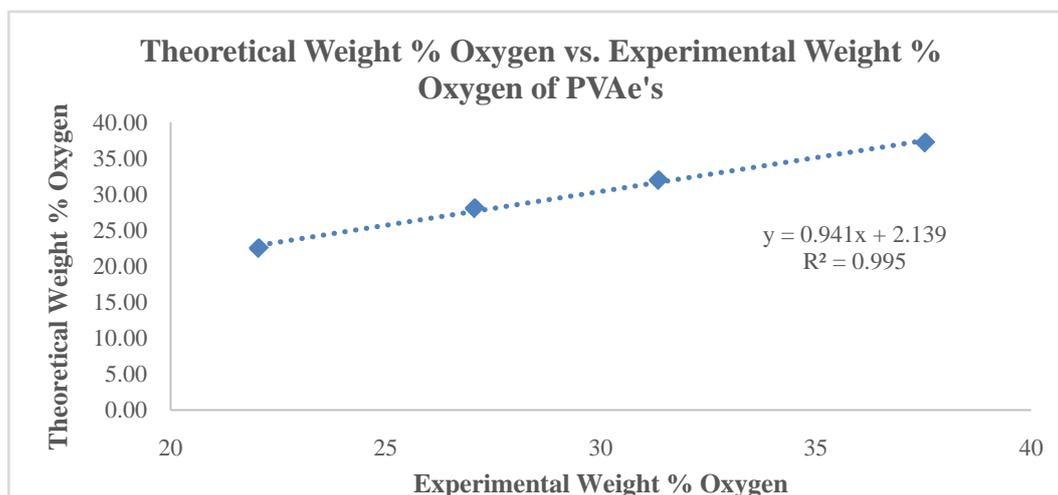


Figure 6. Theoretical Weight % Oxygen Plotted Against Elemental Analysis Determined Weight % Oxygen.

Table 8. Summary of Elemental Analysis Results for PVAc and PVOH Homopolymers

Polymer	Experimental Weight Percent Compositions from Elemental Analysis			Theoretical Weight Percent Compositions		
	% Carbon	% Hydrogen	% Oxygen	% Carbon	% Hydrogen	% Oxygen
PVOH	52.79	9.22	37.99	54.53	9.15	36.32
PVAc	55.57	6.89	37.54	55.81	7.02	37.17
PVPr	59.93	8.73	31.34	59.98	8.05	31.96
PVBu	63.34	9.59	27.07	63.14	8.83	28.03
PVHex	67.53	10.42	22.05	67.57	9.92	22.50

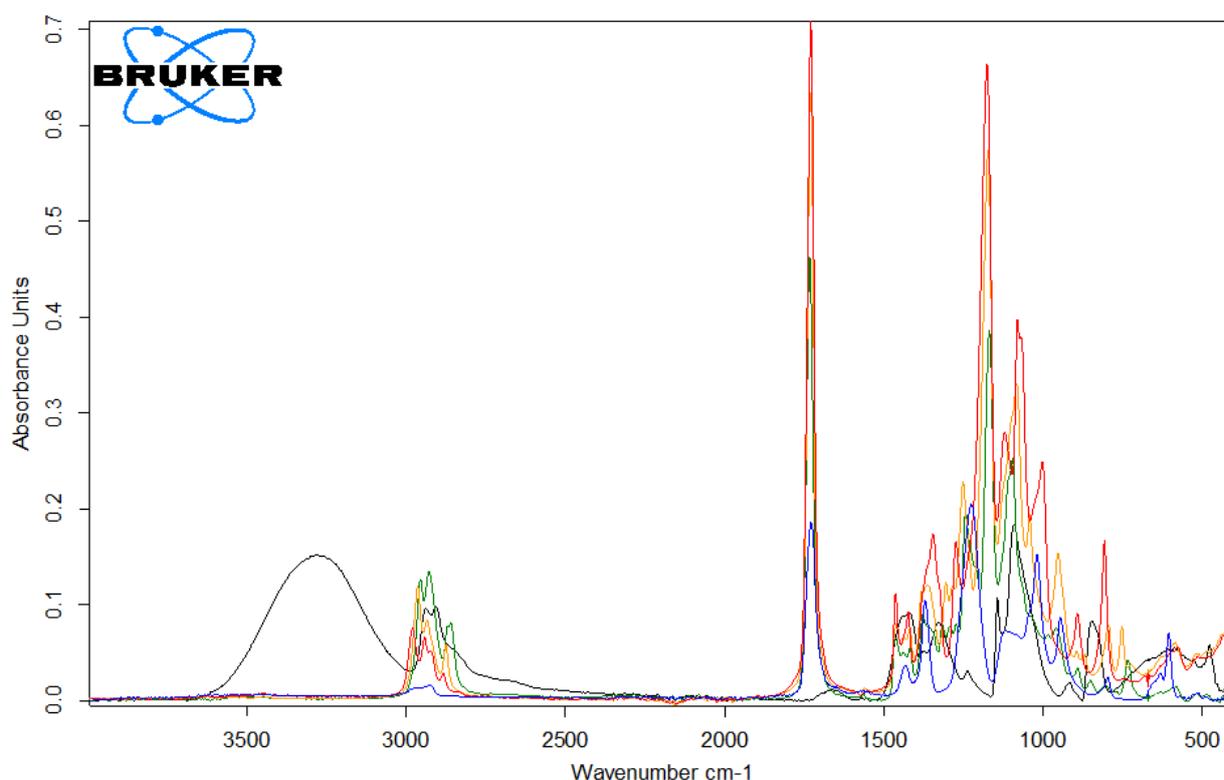
### 3.5. FT-IR Analysis of PVAc and PVOH Homopolymers

All PVAc and PVOH homopolymers were analyzed using FT-IR via absorbance measurements. Table 9 summarizes the IR vibrations for all PVAc and PVOH homopolymers. Stretching and bending vibrations are represented by lowercases nu ( $\nu$ ) and delta ( $\delta$ ), respectively. Figure 7 shows the overlapping spectra of all homopolymers.

PVOH contains a broad peak at approximately  $3300\text{ cm}^{-1}$ , which represents the O-H stretching vibration of the alcohol moiety. There is also a weak peak at approximately  $1660\text{ cm}^{-1}$  due to water absorption [7]. These O-H stretching and bending vibrations are absent among the PVAc homopolymers and each of them contains a peak at approximately  $1730\text{ cm}^{-1}$ , which corresponds to the C=O stretching vibration of an ester group. These data suggest that the alcohol moieties of the PVOH precursors underwent esterification to yield the ester pendant groups of the PVAc homopolymers.

Table 9. Summary of FT-IR Data of PVAc and PVOH Homopolymers Reported in Wavenumbers ( $\text{cm}^{-1}$ ).

Functional Group	Type of Vibration	PVAc	PVPr	PVBu	PVHex	PVOH
Alcohol	$\nu\text{O-H}$	---	---	---	---	3284
Aliphatic	$\nu\text{C-H}$	---	2981	2964	2956	---
Aliphatic	$\nu\text{C-H}$	2925	2943	2935	2930	2939
Aliphatic	$\nu\text{C-H}$	---	2884	2876	2861	2908
Ester	$\nu\text{C=O}$	1728	1729	1730	1732	---
Alcohol (Water)	$\delta\text{O-H}$	---	---	---	---	1660
Aliphatic	$\delta\text{C-H}$	---	1463	1459	1461	---
Aliphatic	$\delta\text{C-H}$	1432	1423	1418	1417	1421
Aliphatic	$\delta\text{C-H}$	1370	1345	1363	1377	1328
Ester/Alcohol	$\nu\text{C-O}$	1224	---	1251	1243	1237
Ester/Alcohol	$\nu\text{C-O}$	---	1174	1172	1168	1142
Ester/Alcohol	$\nu\text{C-O}$	1118	1119	---	---	---
Ester/Alcohol	$\nu\text{C-O}$	---	1079	1081	1095	1090



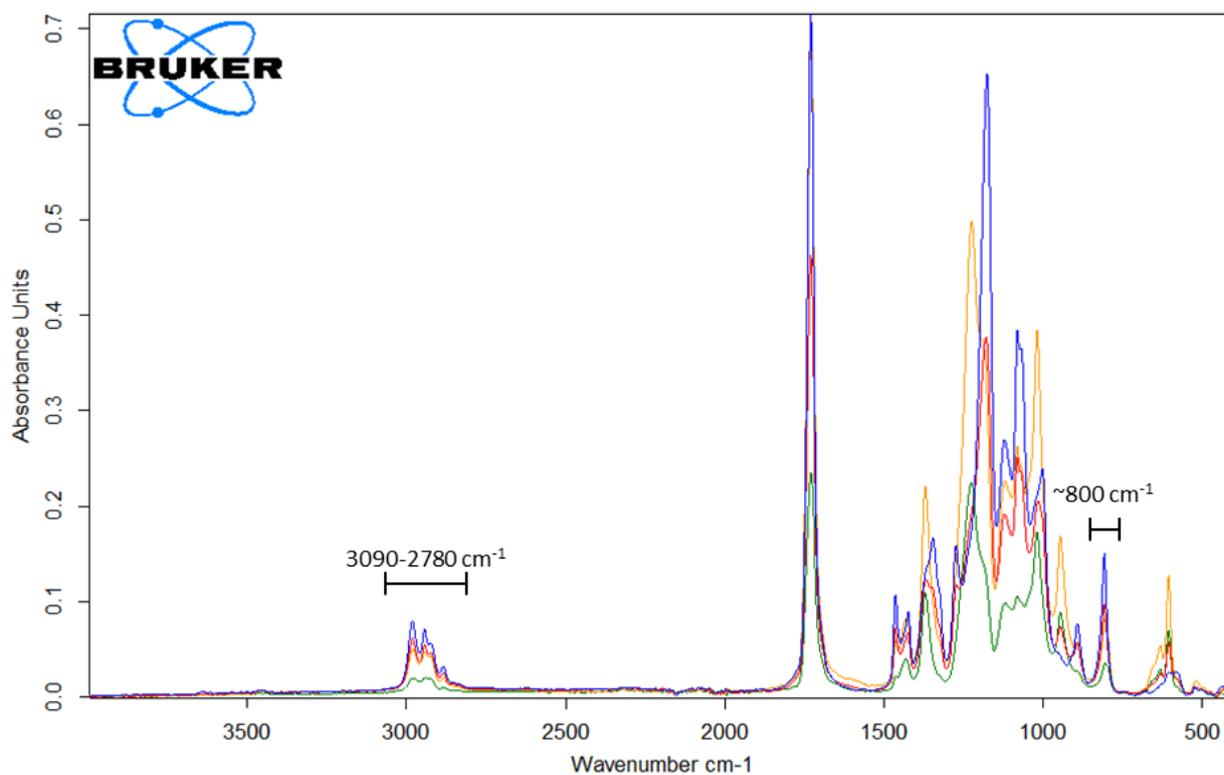
C:\Users\User\Documents\FT-IR\IR Spectra Main Files\Main\MWK-RPD-JNM_PVAc Product from 9-18-19.0	PVAc Product from 9-18-19.1	9/18/2019
C:\Users\User\Documents\FT-IR\IR Spectra Main Files\Main\MWK-RPD-JNM_PVPr Product from 9-18-19.1.0	PVPr Product from 9-18-19.1	9/18/2019
C:\Users\User\Documents\FT-IR\IR Spectra Main Files\Main\MWK-RPD-JNM_PVBu Product from 10-30-19.0	PVBu Crude from 10-30-19	10/30/2019
C:\Users\User\Documents\FT-IR\IR Spectra Main Files\Main\MWK-RPD-JNM_PVHex Product 11-25-2019.0	MK-RPD PVHex Crude 11-25-20	11/25/2019
C:\Users\User\Documents\FT-IR\IR Spectra Main Files\Main\MWK-RPD-JNM_PVOH Product from 7-22-19.0	PVOH Product from 7-22-19	9/9/2019

Figure 7. Overlapped FT-IR Spectra of PVAc and PVOH Homopolymers .Legend above in colors for the specific compounds

### 3.6. FT-IR Analysis of PVAc Blends

Four PVAc-PVPr blends were prepared ranging from 20% to 80% PVPr by weight in 20% intervals and were analyzed quantitatively via FT-IR using absorbance measurements. Figure 8 showcases the overlapping spectra of the PVAc-PVPr blends. Plotted in Figure 9 are

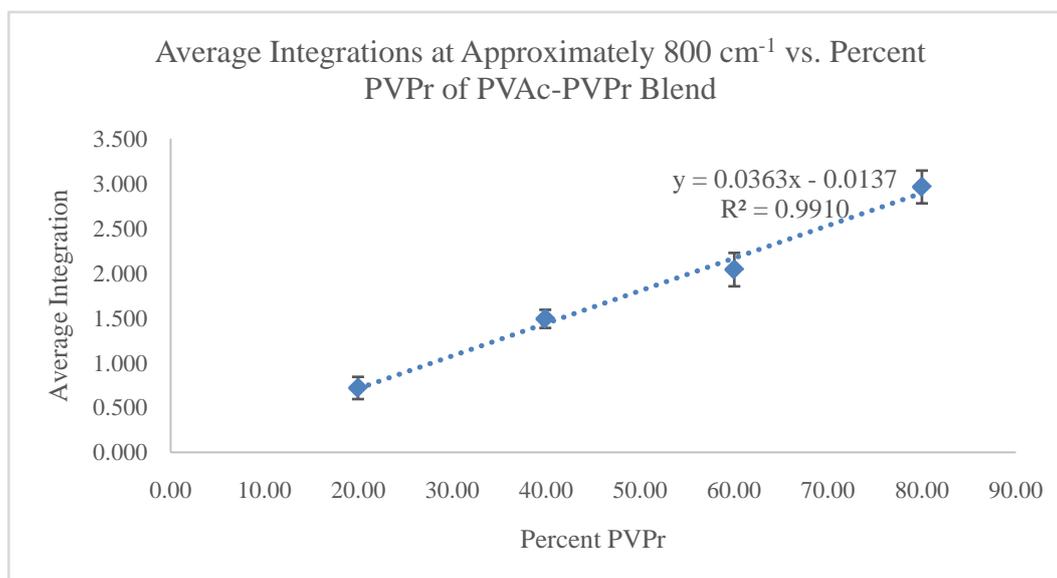
the average integrations of the approximate  $800\text{ cm}^{-1}$  peaks, which represents the C-H rocking vibrations, and demonstrates a linear relationship with increasing peak integration and weight percent PVPr [8]. Figure 10 shows a similar correlation using average peak integrations between  $3090\text{-}2780\text{ cm}^{-1}$ , which consists of the asymmetric and symmetric C-H stretching vibrations.



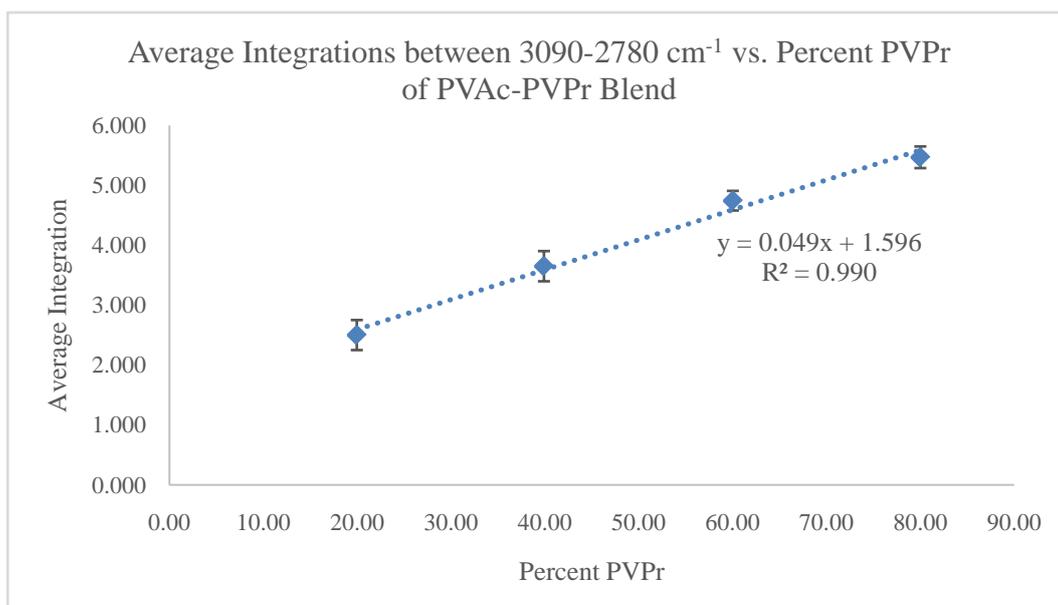
C:\Users\User\Documents\FT-IR\IR Spectra Main Files\Main\PVAc-PVPr Blends\MK-RPD-PVAc-PVP-20.80-Jan6.2020 Scan 2.0	MK-RPD-PV	1/6/2020
C:\Users\User\Documents\FT-IR\IR Spectra Main Files\Main\PVAc-PVPr Blends\MK-RPD-PVAc-PVP-40.60-Jan6.2020 Scan 2.0	MK-RPD-PV	1/6/2020
C:\Users\User\Documents\FT-IR\IR Spectra Main Files\Main\PVAc-PVPr Blends\MK-JM-RPD-PVAc.PVPr-60.40-Scan 2-Jan17.2020.0	MK-JM	1/17/2020
C:\Users\User\Documents\FT-IR\IR Spectra Main Files\Main\PVAc-PVPr Blends\MK-RPD-PVAc-PVP-80.20-Jan6.2020	MK-RPD-PVAc-PVP-	1/6/2020

Page 1/1

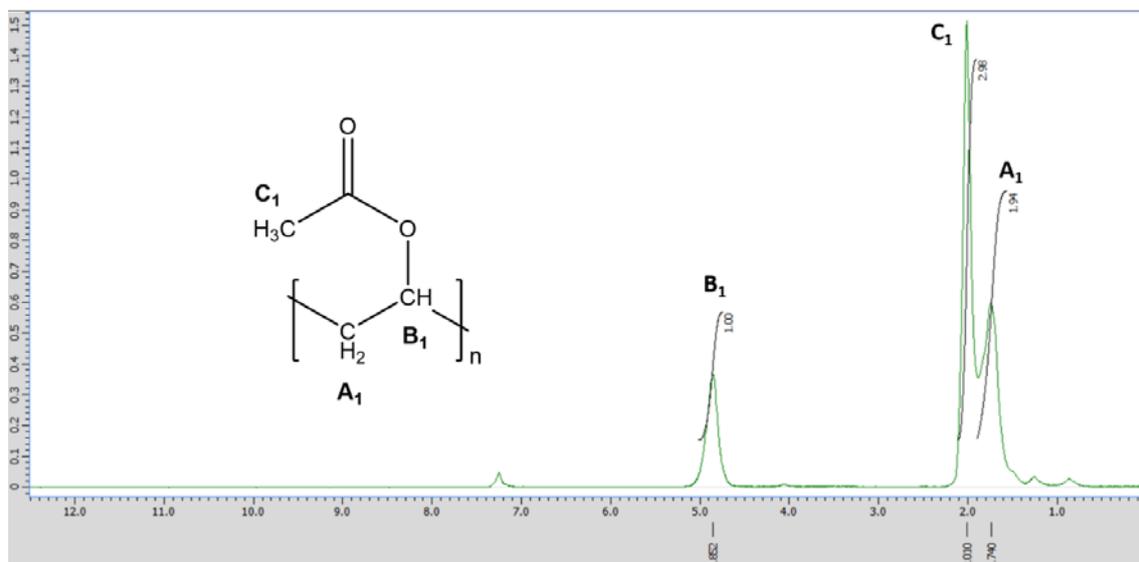
**Figure 8.** Overlapped FT-IR Spectra of PVAc-PVPr Homopolymer Blends. Legend above in colors for the specific blends



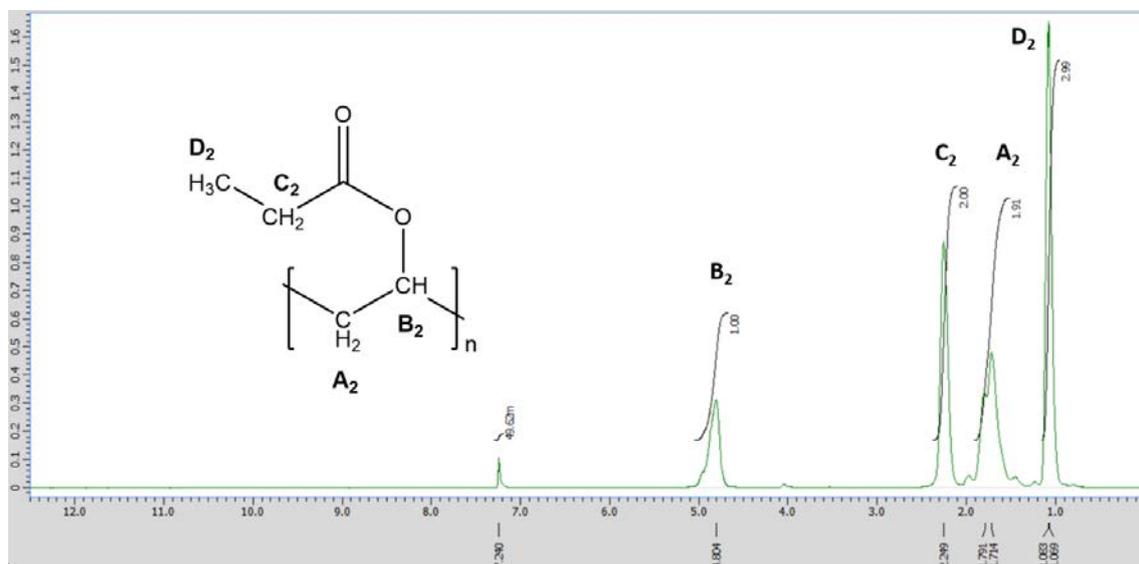
**Figure 9.** Average Peak Integration vs. Percent PVPr of PVAc-PVPr Blend at Approximately  $800\text{ cm}^{-1}$



**Figure 10.** Average Peak Integration vs. Percent PVPr of PVAc-PVPr Blend between 3090-2780  $\text{cm}^{-1}$



**Figure 11.** Proton NMR of PVAc in  $\text{CDCl}_3$



**Figure 12.** Proton NMR of PVPr in  $\text{CDCl}_3$

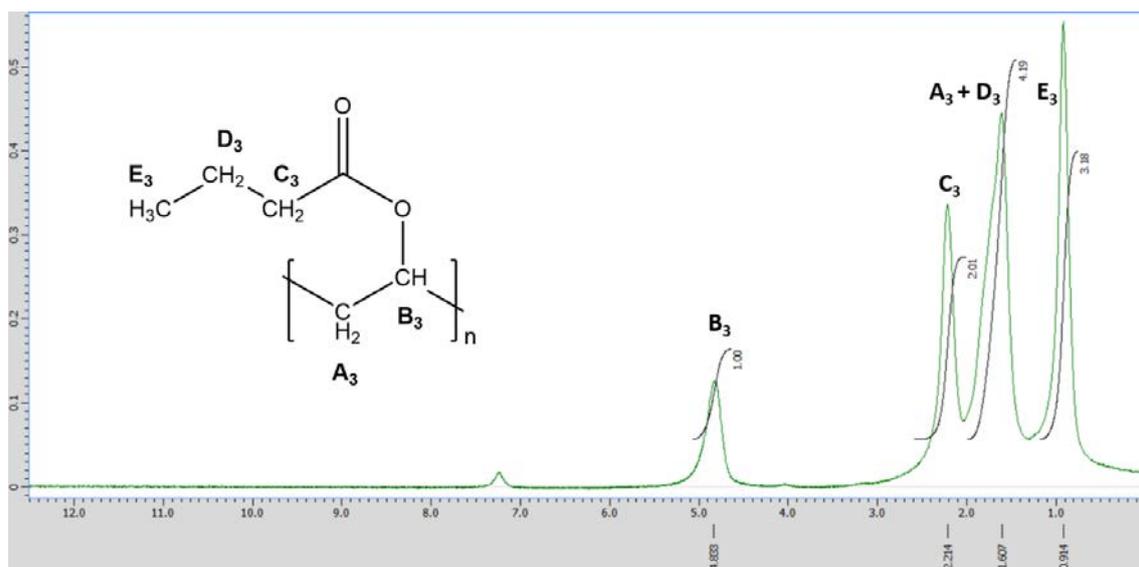
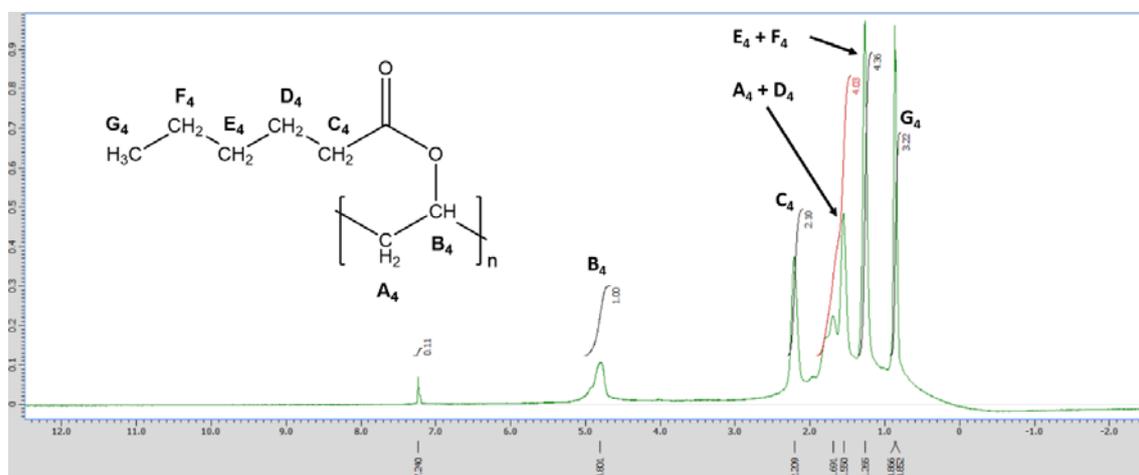
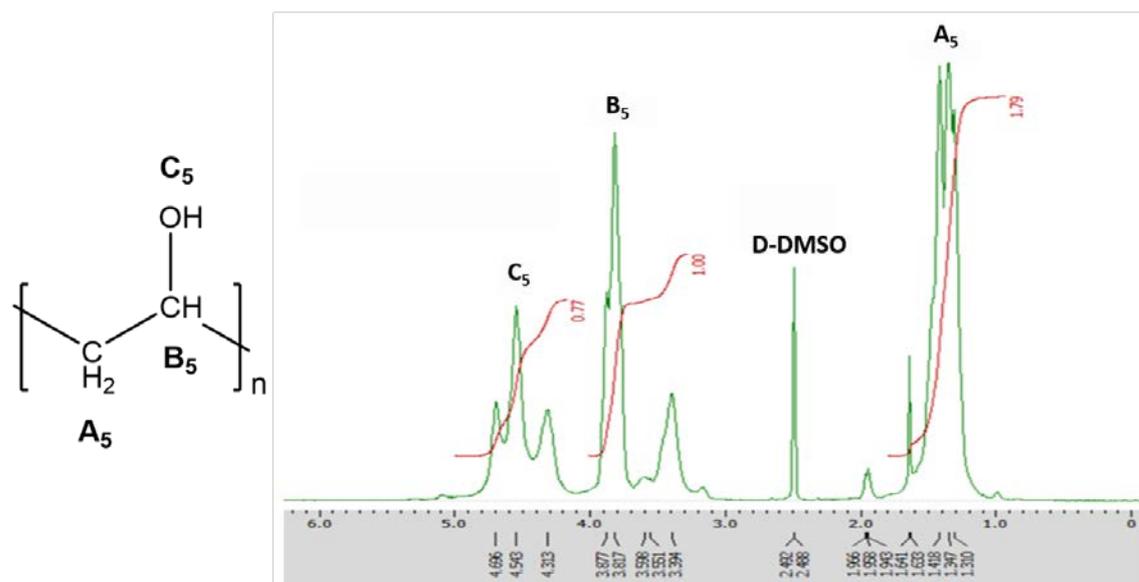
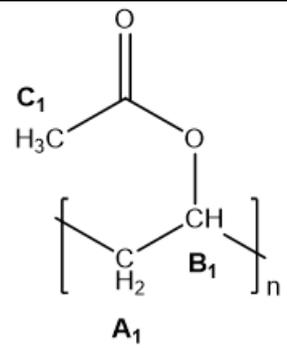
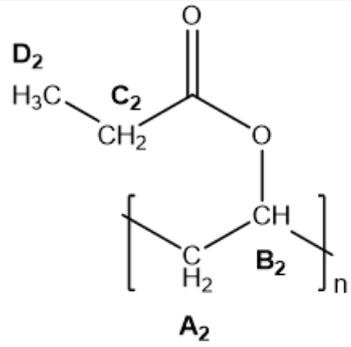
Figure 13. Proton NMR of PVBu in  $\text{CDCl}_3$ Figure 14. Proton NMR of PVHex in  $\text{CDCl}_3$ 

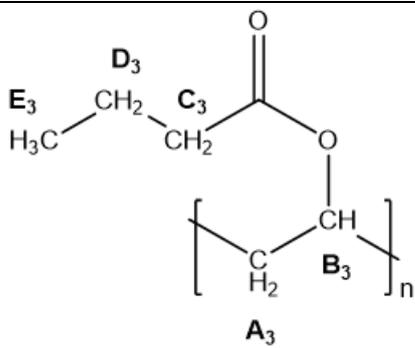
Figure 15. Proton NMR of PVOH in D-DMSO

Table 10. Proton NMR Peak Assignments for PVAc in CDCl<sub>3</sub>


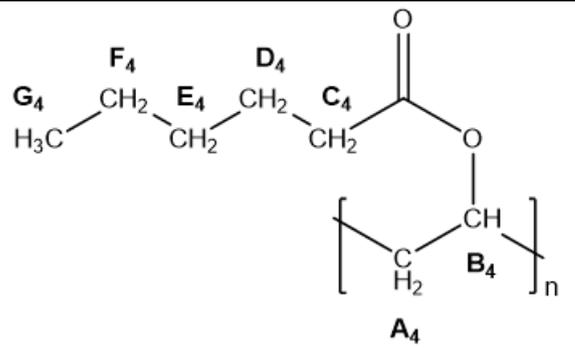
PVAc			
Assignment	Chemical Shift (ppm)	Proton Count	Normalized Integration Value
A <sub>1</sub>	1.740	2	1.94
B <sub>1</sub>	4.852	1	2.98
C <sub>1</sub>	2.010	3	1.00

Table 11. Proton NMR Peak Assignments for PVPr in CDCl<sub>3</sub>


PVPr			
Assignment	Chemical Shift (ppm)	Proton Count	Normalized Integration Value
A <sub>2</sub>	1.714	2	1.91
B <sub>2</sub>	4.804	1	1.00
C <sub>2</sub>	2.249	2	2.00
D <sub>2</sub>	1.069	3	2.99

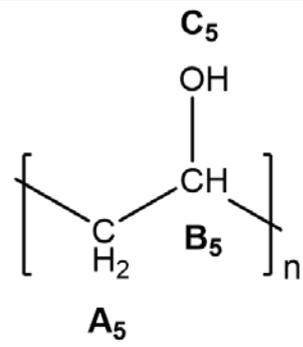
Table 12. Proton NMR Peak Assignments for PVBu in CDCl<sub>3</sub>


PVBu			
Assignment	Chemical Shift (ppm)	Proton Count	Normalized Integration Value
A <sub>3</sub> + D <sub>3</sub>	1.607	4	4.19
B <sub>3</sub>	4.833	1	1.00
C <sub>3</sub>	2.214	2	2.01
E <sub>3</sub>	0.914	3	3.18

Table 13. Proton NMR Peak Assignments for PVHex in CDCl<sub>3</sub>


PVHex			
Assignment	Chemical Shift (ppm)	Proton Count	Normalized Integration Value
A <sub>4</sub> + D <sub>4</sub>	1.550-1.691	4	4.03
B <sub>4</sub>	4.801	1	1.00
C <sub>4</sub>	2.209	2	2.10
E <sub>4</sub> + F <sub>4</sub>	1.265	4	4.36
G <sub>4</sub>	0.852	3	3.22

Table 14. Proton NMR Peak Assignments for PVOH in D-DMSO



PVOH			
Assignment	Chemical Shift (ppm)	Proton Count	Normalized Integration Value
A <sub>5</sub>	1.347	2	1.79
B <sub>5</sub>	3.817	1	1.00
C <sub>5</sub>	4.543	1	0.77

### 3.7. NMR Analysis of PVAe and PVOH Homopolymers

Figure 11 - Figure 14 shows the proton NMR spectra of PVAc, PVPr, PVBu, and PVHex in CDCl<sub>3</sub>, respectively. Figure 15 is the proton NMR spectrum of PVOH in D-DMSO. The peak assignments for each homopolymer are summarized in Table 10 – Table 14. Peaks were assigned based on simulated proton NMR spectra [9,10,11]. The singlet peak at approximately 7.240 ppm is the solvent peak for chloroform for the PVAe's.

## 4. Conclusions

PVAc homopolymers of varying molecular weights can be accurately characterized using GPC to obtain molecular weight information, DNDC to obtain differential refractive index increments, and MALLS to obtain the second virial coefficient in various solvents. The intrinsic viscosity increased as the molecular weight of the PVAc homopolymer increased, which is consistent with intuition,

and the molecular weights obtained via GPC and MALLS analysis were closely mirrored by the viscosity-average molecular weights and those reported by the manufacturer. This strongly suggests that viscosity, MALLS, and GPC-based methods of obtaining molecular weight are highly accurate for polymers in the PVAc family. The second virial coefficient for PVAc's of all molecular weights in toluene, acetone, and THF was all greater than zero, indicating that all of these solvents are "good" for dissolving PVAc because they have favorable solvent-solute interactions. This is consistent with the low structural polarity of the solvent and the PVAc homopolymer.

FT-IR and NMR spectroscopic results and subsequent physical characterization via intrinsic viscosity measurements confirm that a family of polyvinyl alkyl esters can be synthesized via esterification of PVOH homopolymers of various molecular weights. The FT-IR and NMR spectra of all the PVAc lacked O-H stretching vibrations and broad O-H proton peaks, suggesting that the esterification went to near completion. The integration values for the various proton NMR peaks were also consistent with the structure of the PVAc's synthesized. The PVAc increase in intrinsic viscosity and molecular weight as the number of methylene groups increases, which is consistent with chemical intuition, and the elemental analysis results were nearly 1:1 with the expected %CHO.

The weight percent composition of blends of PVAc and PVPr can be accurately obtained via FTIR using the integration values of the peaks at  $800\text{ cm}^{-1}$  and  $3090\text{-}2780\text{ cm}^{-1}$ . This indicates that quantitative FTIR can not only be used to quantify blends of two distinct families of homopolymers, i.e., PVOH and PVAc's, but also can quantify blends of two members of the same polymer family. This greatly extends the utility of quantitative FTIR and strongly suggests that similar analyses can be performed for other polymer families. Further physical characterization of polyvinyl alkyl esters using GPC, MALLS, and DNDC will be reported in due course.

## Acknowledgments

Special thanks to several high school student assistants who worked on this project. Especially Kyle O'Neil and Wayne Simonetti for the GPC work and Lawrence Cheng for the Light Scattering – MALLS data. We also acknowledge the support from Hofstra University HCLAS Faculty Research and Development Grant.

## List of Abbreviations

ATR – Attenuated Total Internal Reflectance  
 c – Concentration  
 CDCl<sub>3</sub> – Deuterated Chloroform  
 D-DMSO – Deuterated Dimethyl Sulfoxide  
 dn/dc – Specific Reflective Index Increment  
 FT-IR – Fourier-Transform Infrared Spectroscopy  
 GPC – Gel Permeation Chromatography  
 IR – Infrared

KOH – Potassium Hydroxide  
 MALLS – Multi-Angle Laser Light Scattering  
 MeOH – Anhydrous Methanol  
 M<sub>n</sub> – Number-Average Molecular Weight  
 M<sub>p</sub> – Molecular Weight at Peak Maximum of a Molecular Weight Distribution Curve  
 M<sub>v</sub> – Viscosity-Average Molecular Weight  
 MW – Molecular Weight  
 M<sub>w</sub> – Weight-Average Molecular Weight  
 M<sub>z</sub> – Molecular Weight Determined by Centrifugation  
 NaOtBu – Sodium tert-Butoxide  
 NMR – Nuclear Magnetic Resonance Spectroscopy  
 PVAc – Polyvinyl Acetate  
 PVAc – Polyvinyl Alkyl Ester  
 PVBu – Polyvinyl Butyrate  
 PVHex – Polyvinyl Hexanoate  
 PVOH – Polyvinyl Alcohol  
 PVPr – Polyvinyl Propionate  
 THF – Tetrahydrofuran  
 δ – IR Bending Vibration  
 ν – IR Stretching Vibration  
 [η] – Intrinsic Viscosity  
 η<sub>inh</sub> – Inherent Viscosity  
 η<sub>red</sub> – Reduced Viscosity  
 η<sub>rel</sub> – Relative Viscosity  
 η<sub>sp</sub> – Specific Viscosity

## References

- [1] Lipsa, R. D.; Tudorachi, N.; Grigoras, A.; Vasile, C.; Gradinariu, P. Study on Poly(Vinyl Alcohol) Copolymers Biodegradation. *Mem. Sci. Sect. Romanian Acad.* 2015, *Tome XXXVIII*, 1-22.
- [2] D'Amelia, R. P.; Tomic, J. C.; Nirode, W. F. The Determination of the Solubility Parameter ( $\delta$ ) and the Mark-Houwink Constants ( $K$  &  $\alpha$ ) of Food Grade Polyvinyl Acetate (PVAc). *J. Polym. Biopolym. Phys. Chem.* 2014, *2* (4), 67-72.
- [3] Huggins, M. L. The Viscosity of Dilute Solutions of Long-Chain Molecules. IV. Dependence on Concentration. *J. Am. Chem. Soc.* 1942, *64* (11), 2716-2718.
- [4] Kraemer, E. O. Molecular Weights of Celluloses and Cellulose Derivates. *Ind. Eng. Chem.* 1938, *30* (10), 1200-1203.
- [5] Masuelli, M. A. Mark-Houwink Parameters for Aqueous-Soluble Polymers and Biopolymers at Various Temperatures. *J. Polym. Biopolym. Phys. Chem.* 2014, *2* (2), 37-43.
- [6] Das, N.; Chakraborty, S.; Biswas, P. K. Novel Polyvinyl Alcohol Based Cr(III)-Sn(IV) Doped In(III) Nitrate Composite Foam: Synthesis, Unit Cell Formulation and Structure. *RSC Adv.* 2012, *2* (24), 9183-9191.
- [7] Jipa, I.; Stoica, A.; Stroescu, M.; Dobre, L.-M.; Dobre, T.; Jinga, S.; Tardei, C. Potassium Sorbate Release from Poly(Vinyl Alcohol)-Bacterial Cellulose Films. *Chem. Pap.* 2012, *66* (2), 138-143.
- [8] Wei, S.; Pintus, V.; Schreiner, M. Photochemical Degradation Study of Polyvinyl Acetate Paints Used in Artworks by Py-GC/MS. *J. Anal. Appl. Pyrolysis* 2012, *97*, 158-163.
- [9] Banfi, D.; Patiny, L. Wwww.Nmrdb.Org: Resurrecting and Processing NMR Spectra On-Line. *Chim. Int. J. Chem.* 2008, *62* (4), 280-281.
- [10] Aires-de-Sousa, J.; Hemmer, M. C.; Gasteiger, J. Prediction of 1H NMR Chemical Shifts Using Neural Networks. *Anal. Chem.* 2002, *74* (1), 80-90.
- [11] Castillo, A. M.; Patiny, L.; Wist, J. Fast and Accurate Algorithm for the Simulation of NMR Spectra of Large Spin Systems. *J. Magn. Reson.* 2011, *209* (2), 123-130.

