

Characterization of Poly(vinyl Alcohol)

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Synopsis

Molecular weight distributions, long chain branching frequency, and solution viscosities of samples of commercial poly(vinyl alcohol) (PVA) are reported. The PVA was fully reacylated to poly(vinyl acetate) (PVAc) for characterizations by size exclusion chromatography using a low angle light scattering detector. The Mark-Houwink constants for PVAc in toluene were determined to be $K = 0.106 \text{ cm}^3 \text{ g}^{-1}$ and $\alpha = 0.59$, at 25°C. Long chain branching frequency in the commercial PVAs studied was small and was little affected by polymer molecular weight. Some 95% or more of the branches in these species were short. Aqueous solutions at 10% (w/v) of PVA were Newtonian. The polymers examined differed in chemical composition, molecular weight distributions, and mean block lengths of vinyl acetate residues. Variations in a single characteristic, like a solution or intrinsic viscosity, cannot be used to deduce structural differences between PVAs.

INTRODUCTION

The principal characteristics that determine the physical and technological properties of polymers are chemical composition, molecular weight distribution, and branching character. Poly(vinyl acetate) (PVAc) and its derivative poly(vinyl alcohol) (PVA) are not exceptions. Fine differences in PVA microstructure reflect structural variations in the precursor PVAc and in the reaction system used to convert the PVAc to PVA. These differences are often not reflected in the results of commercial quality control tests, but they can be very important in the performance of PVA as a protective colloid in emulsion and suspension polymerizations.

We have earlier¹ reported on the characterization of the molecular architecture of commercial PVAs. Polymer samples were analyzed by ¹³C nuclear magnetic resonance spectroscopy and by differential scanning calorimetry to measure tacticity, chemical composition, branch frequency, and mean run lengths of vinyl acetate and alcohol units.

Further characterization procedures are reported and discussed in this article. Parameters measured here include molecular weight distribution, long chain branching, intrinsic viscosities, and aqueous solution viscosities and unsaturation in the polymer backbone.

Mark-Houwink constants for linear PVAc in toluene are also reported.

This report and its predecessor¹ provide a critical survey of procedures that are thought to give reliable and fairly comprehensive characterizations of the chemical structure of commercial PVAs.

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EXPERIMENTAL

Six commercial partially hydrolyzed PVA samples, referred to as A to F inclusive, were used in this study. These materials have been described earlier.¹

Acetylation Procedure

The following reacetylation procedure was used for all of the six partially hydrolyzed PVA samples under investigation. Five grams of the polymer was placed in a round bottom flask. The flask was purged with nitrogen gas for about 10 mins. Fifty milliliters of a 2:1 pyridine/acetic anhydride solution were added to the reaction vessel, and the contents were heated on a steam bath at 93–94°C, with stirring, under a nitrogen atmosphere. After 4 h, the steam bath was removed, but stirring was continued for another 30 min. The contents of the reaction vessel were then diluted with acetone, and subsequently precipitated out in ice water. The poly(vinyl acetate) produced was collected and dried under vacuum at 60°C for about 20 h.

Gel Permeation Chromatography

Gel permeation chromatographic (GPC) measurements of the poly(vinyl acetate) samples were made in toluene solutions with 500, 10⁴, and 10⁵ Å (nominal porosity) porous polystyrene columns; at a flow rate of 0.5 mL/min using injection volumes of 300–500 μL. Attempts to use silanized porous silica columns were unsuccessful because of adsorption of the poly(vinyl acetate) onto these columns. The polymer samples were analyzed at 25°C, at solution concentrations of about 3.5–4.5 mg/mL, in toluene containing 0.1% (w/v) of 2,6-di-*tert*-butyl-*p*-cresol antioxidant.

The polymer concentration in the eluant was monitored with a differential refractive index detector and KMX-6 (Chromatix) low angle laser light scattering (LALLS) photometer, at a 6–7° angle. The specific refractive index increment (dn/dc) measured with a Chromatix KMX-16 differential refractometer at 25°C in toluene, was found to be –0.027 mL/g for samples A and B, and –0.018 mL/g for the rest. Both the light scattering photometer and differential refractometer employ an He–Ne laser source at 6328 Å wavelength. All solutions were filtered through a 0.5 μm polytetrafluoroethylene filter (FHUP, Millipore Corp.) before analysis.

Intrinsic Viscosities

The intrinsic viscosities of poly(vinyl acetate) solutions were measured in toluene, at 25°C, with an Ubbelohde viscometer that had a pure solvent time of 174.3 s. The intrinsic viscosities were determined by a double extrapolation of Huggins and Kraemer equations. Intrinsic viscosities of the poly(vinyl alcohol)s were measured in dimethylsulfoxide at 23.5°C.

Ultraviolet Spectra

Ultraviolet (UV) spectra of the partially hydrolyzed PVAs were run on a Varian Cary 118 spectrometer, with 1 cm quartz cells (Hellma), in 0.5

(w/v) aqueous solutions. Samples E and F were not characterized because their high acetate content made them effectively insoluble in water.

Rheological Measurements

Rheological measurements were made with a Contraves Rheomat-30 cup-and-bob viscometer, and recorded over a shear range of about 20–662 s⁻¹. The lower shear rate was limited by the instrument response towards the 10% (w/v) aqueous PVA solutions used, while the upper shear rate maximum of 662 s⁻¹ is determined by instrumental design. The sample temperature was held constant at 25 ± 0.1°C.

The procedure for the rheological measurements was essentially that described by Rudin and Baas,² and normally used for characterization of water-based paints. The method measures thixotropy and shear thinning behavior. In the present study all PVA solutions were found to be Newtonian and showed no evidence of thixotropy.

Samples A–D, inclusive, were characterized as 10% (w/v) solutions in water. Samples E and F were not studied because of their low water solubility.

BRANCHING IN PVAc AND PVA

Background

The formation of branches during vinyl acetate polymerization is expected because of the nature of the system. However, the actual detection, and more importantly, the quantitative determination of the amount of branching is not a trivial problem.

Branches in PVAc (which is, of course, the precursor to all commercial PVA) can be long or short and hydrolyzable or nonhydrolyzable. Their nature depends on the following different processes that are responsible for branch formation:

- (i) chain transfer to polymer,³
- (ii) chain transfer to monomer, followed by terminal double-bond copolymerizations,³
- (iii) 1,5-backbiting mechanism,⁴
- (iv) double-backbiting mechanism.⁴

Chain transfer to polymer can occur at both the methine carbon of the main chain, resulting in nonhydrolyzable branches, and at the acetoxy methyl group on the polymer, giving a hydrolyzable branch point.

Chain transfer to monomer at the acetate group results in the formation of a polymer with a terminal double bond, which can copolymerize with monomer to give a hydrolyzable branch point. Chain transfer to monomer at the α - or β -positions, followed by terminal double-bond copolymerization, yields a nonhydrolyzable branch point. This sequence is unlikely, however.³

Nonhydrolyzable branches may occur via a 1,5-backbiting mechanism, followed by chain propagation (similar to ethylene polymerizations⁵), resulting in short branches two monomer units in length. Furthermore, short-

er branches only two carbons (one monomer unit) long could result from a double backbiting mechanism, again by analogy to polyethylene polymerization.⁶

Quantitative determination of branch content in PVAc and PVA has, obviously, important consequences since branching densities can affect physical properties and technological applications of the polymer. For example, short branching may influence protective colloid ability, which can affect the latex viscosity of emulsions polymerized in the presence of PVA,⁷ and crystallinity,^{8,9} which affects tenacity and water resistance of PVA fibres.¹⁰ It is to be expected that the extent of branching in PVA will differ with polymerization conditions¹¹ and reactor type.¹²

McDowell and Kenyon¹³ were among the first to address the problem of branching in PVAc, by experimentally determining the presence of hydrolyzable branches in PVAc. This was done by comparing degrees of polymerization determined by viscosity measurements. Other studies have appeared since, with different approaches to the problem. Most of the earlier work was based on determinations of kinetic rate constants for transfer reactions.¹⁴⁻¹⁶ Nagai and Sagane¹⁷ estimated the amount of short chain branching in PVA by using the infrared absorptions of the 1030 and 1093 cm^{-1} bands in PVA. Graessley and co-workers^{18,19} have shown that broadening of molecular weight distribution, decrease in the intrinsic viscosity, and decrease in molecular weight with saponification and reacylation are attributable to long-chain hydrolyzable branches present in the original PVAc.

A kinetic study of the polymerization of radioactively labelled ^{14}C vinyl acetate, in the presence of a crosslinked PVAc network which can be selectively and quantitatively decrosslinked,²⁰ indicated that chain transfer to the main chain of the polymer was favored over transfer to the acetoxy group,²¹ but that a large number of hydrolyzable branches in PVAc are formed by monomer transfer followed by terminal double bond copolymerization.³

The detection and quantitative determination of short, nonhydrolyzable branches was shown to be possible by using both the ^{13}C NMR spectra of PVA and the ^1H NMR spectra of the acetylated PVA in both commercially available^{1,7} and model compounds.²²⁻²⁴ Estimation of branch content was based on the ratios of the intensities of methine and methylene carbon resonances as well as ratios of the resonance peaks assigned to the β -protons of the β -acetoxyethyl group ($-\text{CH}_2-\underline{\text{CH}_2}-\text{OCOCH}_3$) compared to an internal standard.

In a more recent article,²⁵ the extent of long chain branching in PVAc was measured by gel permeation chromatography. The authors concluded that most of the branching in PVAc occurs through the acetate group, but they also showed the existence of some chain branching in saponified and reacylated polymers.

The general conclusion from these reports seems to be that the original PVAc contains a large concentration of hydrolyzable long chains, while the PVA derived from it contains fewer nonhydrolyzable short branches and only a small amount of long branches.

GPC-LALLS Studies

The amount of branching present in the polymers under investigation has been reported from NMR results.¹ However, the length of these branches was not clear. We have here attempted to determine the frequency of long chain branching by application of GPC-LALLS and the method of Rudin, Grinshpun and O'Driscoll.²⁶

The procedure generates an estimate of the long branches per weight average molecule with specified radius of gyration. The measured values are presented for convenience as number of long branches per 1000 carbon atoms vs. molecular weight. The analysis used is valid only if the number of long branches does not increase with molecular weight.²⁷ This appears generally to be true for low density polyethylene. The present results indicate also that this criterion is valid for the reacetylated PVAs studied in this research.

We note parenthetically that the minimum length for a long branch, as defined by this analysis, lies between 6 and 16 carbon atoms in polyethylenes.²⁶

The procedure used compares the molecular weight of the unknown polymer with that of unbranched species that would elute with the same retention time. That is to say, both the branched and unbranched polymers have the same solvodynamic volumes and presumably the same radii of gyration. The molecular weight of the branched polymer (\bar{M}_w) is measured directly with the LALLS detector, while the molecular weight of the corresponding linear macromolecule is derived from the universal calibration curve. The latter operation in this instance requires information as to the Mark-Houwink constants of unbranched PVAc in toluene.

The Mark-Houwink constants were calculated from the GPC chromatograms and the intrinsic viscosities of two samples of unbranched PVAc in toluene.²⁸ Samples A and D were previously shown to be unbranched from high resolution ¹³C spectroscopy.¹ These polymers were used to establish the constants in the Mark-Houwink equation:

$$[\eta] = K\bar{M}_w^\alpha \quad (1)$$

as $K = 0.106 \text{ cm}^3 \text{ g}^{-1}$ and $\alpha = 0.59$, at 25°C in toluene.

Long chain branching results obtained by GPC-LALLS analyses of the polymer samples are shown in Figure 1. Three polymers (B, E, and F) contained detectable long branches. Samples A, C, and D had no long branches. Samples A and D contained no short branches either, as mentioned, while polymer D was relatively lightly short branched (10 branches per 1000 main chain carbons¹). Sample F, which had the highest total branching, from NMR analyses,¹ also had most long chain branching. Polymers E and B were almost equal in total branching, but E had double the number of long branches. In all cases, the great majority of branches are short. Long branches constitute only 2–3% of the total.

Agarwal and co-workers²⁵ measured long branching in reacetylated PVA by another technique. Their result is consistent with ours, in that the long

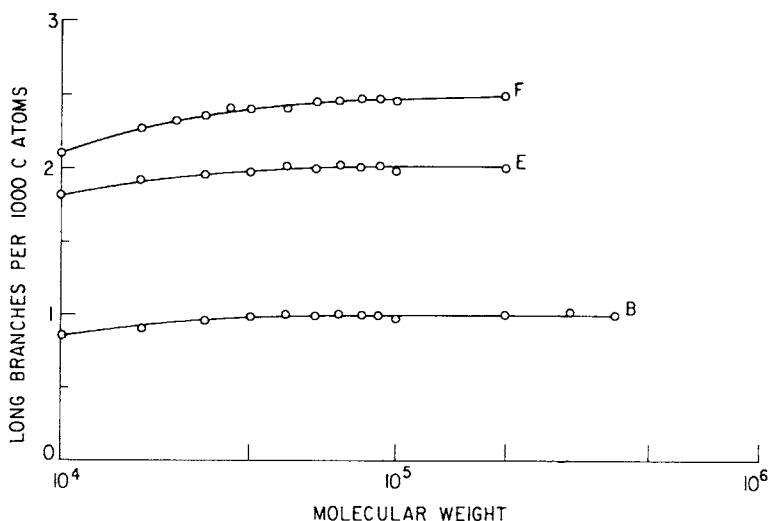


Fig. 1. Long chain branching frequency as a function of molecular weight for samples B, E, and F, in toluene, at 25°C from GPC-LALLS analyses.

chain branch density is small and little affected by molecular weight of the reacylated PVA.

The uniformity in the long chain branching density throughout the molecular weight range shown in Figure 1 is different from long chain branching observed in low density polyethylene (LDPE) by the same technique.²⁶ In LDPE the long chain branching frequency is generally highest at low molecular weights, and decreases continuously with increasing molecular weight.

Variations in the branching distributions may reflect differences in the syntheses of LDPE and PVAc. Commercial PVA is derived from PVAc made by suspension or solution polymerization. In either system most of the polymer is produced under reasonably isothermal conditions. LDPE is made, however, in a nonisothermal reactor with no back mixing. The lower molecular weight polymer is produced at higher temperatures which favor branching reactions and thus long chain branching and molecular weight are inversely correlated.

MOLECULAR WEIGHT

The molecular weight of PVA is believed to be important when this polymer is used as a dispersant and stabilizer. It is reported²⁹ that surface activity increases, i.e., interfacial tension decreases, with decreasing molecular weight, whereas protective colloid ability increases with higher degrees of polymerization. Particle size and latex viscosity are also thought to depend on PVA molecular weight when this polymer is used as a protective colloid in emulsion polymerizations.

The usual control method for molecular size of partially hydrolyzed PVA is by measuring viscosities of 4% aqueous solutions at 20°C. It is obvious, however, that the measured viscosity can also be affected by aggregation in solution, long chain branching, acetate content, and blockiness of residual vinyl acetate units.

Since commercial PVA is a copolymer, its molecular weight distribution cannot be determined at present by GPC unless the material is converted to a homopolymer by complete hydrolysis or by reacetylation. The latter is the more common approach since the product PVAc is soluble in organic solvents and can be analyzed by conventional GPC techniques. This procedure was followed in this work.

Table I lists the different molecular weight averages for the six PVAs under investigation for GPC-LALLS analysis of the reacetylated polymer samples. Also listed are the number average molecular weights of the original, partially hydrolyzed PVAs, as calculated from the number average molecular weight of the reacetylated samples and the degree of hydrolysis determined by NMR analyses.¹

RHEOLOGICAL MEASUREMENTS

It is well known that aqueous solutions of fully hydrolyzed PVA exhibit non-Newtonian behavior,¹⁰ especially for high molecular weight samples at higher concentrations. This is to be expected because of intermolecular interactions resulting from entanglements and hydrogen bonding.

The situation is very different for partly hydrolyzed PVA, however. Hydrophobic residual acetate groups, especially when in blocklike distributions, reduce hydrogen bonding between molecular chains, thus reducing aggregation and increasing water solubility.¹⁰

Rheological measurements of samples A–D inclusive were performed on a cup-and-bob viscometer as described in the Experimental section.

Solutions were measured at 10% concentration rather than the conventional 4% used in quality control procedures in order to fit better into the sensitivity range of the measuring instrument.

All 10% (w/v) aqueous solutions were Newtonian and not thixotropic.

Table II lists the viscosities of the aqueous solutions along with other pertinent characteristics of the polymers. Intrinsic viscosities of the original PVAs are also recorded in Table II.

These polymers differ somewhat in chemical composition, molecular weight distributions, and mean block lengths. Differences in solution viscosity or intrinsic viscosity can be due to variations in any of these parameters. Samples A and B are similar in acetate content and mean block character and the higher viscosities of polymer B solutions presumably reflect the more pronounced high molecular weight tail in the latter sample. Sample C has much lower viscosity in aqueous and DMSO solutions. Its molecular weight parameters are not different enough from those of A and B to account for this behavior. A more likely explanation is the higher acetate content of polymer C.

In any event, it is clear that variations in a single characteristic, like a solution viscosity or intrinsic viscosity, cannot be used to deduce structural differences between PVAs.

The Newtonian behavior of water solutions of these PVAs is consistent with their molecular architecture. We have shown¹ that these polymers have blocklike residual vinyl acetate contents greater than 20 mol% and relatively low crystallinity. These characteristics and the moderate molec-

TABLE I
Molecular Weights of Reactylated PVAs

Sample	\bar{M}_n	\bar{M}_n^a	\bar{M}_w	\bar{M}_z	\bar{M}_w/\bar{M}_n	SD (N) ^b	SD (W) ^b	SKEW (N) ^c	SKEW (W) ^c
A	39,800	24,400	104,600	1,269,000	2.6	50,800	349,000	37.5	26.0
B	44,900	27,800	148,600	4,556,000	3.3	68,300	809,400	93.4	54.9
C	25,000	15,800	90,900	3,078,000	3.6	40,600	521,100	102.5	48.8
D	23,500	14,500	78,200	2,972,000	3.3	35,900	475,700	116.2	51.5
E	11,200	7,900	29,300	478,000	2.6	14,300	114,800	51.5	18.5
F	3,510	2,500	76,400	725,000	21.7	16,000	222,700	46.8	11.3

^a Number average molecular weight of original partially hydrolyzed PVA estimated from \bar{M}_n of reactylated PVA and chemical composition from Ref. 1.

^b Standard deviation of number (N) and weight (W) distributions.³⁰

^c Skewness of number (N) and weight (W) distributions.³⁰

TABLE II
Dynamic and Intrinsic Viscosities of Commercial PVAs

Sample	Composition ¹ vinyl acetate (mol %)	Block ¹ character	Long branches per 1000 C atoms	\bar{M}_w^a	\bar{M}_z^a	Dynamic ^b viscosity (mPa s)	Intrinsic ^c viscosity (mL/g)
A	20.7	0.41	0	104,600	1,269,000	238	117.0
B	21.8	0.41	0	148,600	4,556,000	1019	176.8
C	25.0	0.44	0	90,900	3,078,000	84	63.6
D	21.6	0.46	1.0	78,200	2,972,000	66	69.0
E	40.0	0.72	2.0	29,300	478,000	—	18.8
F	41.9	0.60	2.5	76,400	725,000	—	20.8

^a Molecular weight averages of completely acetylated samples.

^b 10% (w/v) aqueous solutions at 25°C.

^c Dimethyl sulfoxide solutions at 23.5°C.

ular weights of the particular samples minimize intermolecular interactions and result in "well-behaved" solutions even at 10% (w/v) concentration. Aqueous mixtures of PVAs at the concentrations used in emulsion and suspension polymerizations are certainly Newtonian, also.

ULTRAVIOLET SPECTRA

PVA is susceptible to degradation even at temperatures below 100°C, especially in the presence of oxygen and catalytic amounts of acid. The initial decomposition products of partially hydrolyzed PVA are water and acetic acid. Dehydration of the polymer results in the formation of unsaturated ketonic structures, whose presence and concentration can be determined from the ultraviolet spectrum of the polymer sample. Three absorption bands have been observed in the spectra of aqueous PVA solutions, at wavelengths of approximately 225, 280, and 325 nm. These absorption maxima have been attributed to the presence of carbonyl groups conjugated to one, two, and three double bonds, respectively.³¹

It is quite possible that partial degradation during the drying process of PVA could be responsible for the conjugated carbonyl structures, especially in commercial samples. In fact, some commercial samples are not white powders as expected, but may very well be yellow, orange or even brown, reflecting increased amounts of dehydration.

Figure 2 illustrates UV spectra of four of the samples under investigation. Samples A and B (white colored) show the presence of two rather weak absorption maxima at 205 and 270 nm. These two bands correspond to the monoene and diene ketones. Samples C and D (yellow powders from a different manufacturer) differ significantly in their ultraviolet spectra, not only in the presence of an additional band at 320 nm, but obviously in the magnitude of the absorbance for the bands at 280 and 320 nm.

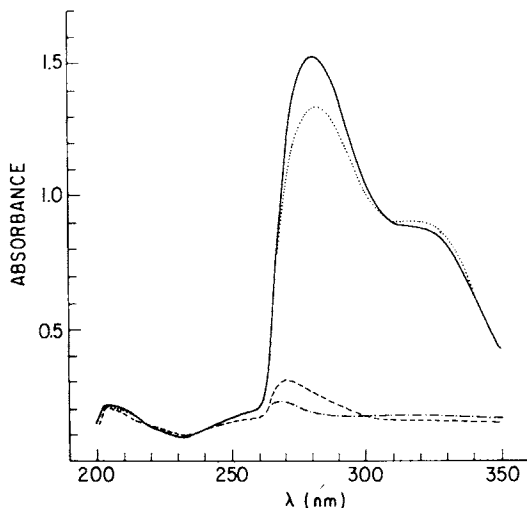


Fig. 2. Ultraviolet spectra of partly hydrolyzed samples in 0.5% (w/v) aqueous solutions: (---)A; (- · - ·)B; (—)C; (···)D.

Differences in the ultraviolet spectra and thus in the concentrations of unsaturated ketonic structures, are significant when we consider the use of PVA as a surfactant and emulsifier. It is known that the presence of these structures retards the rates of polymerization,³² when PVA is used as a protective colloid in emulsion and suspension polymerizations. Also, grafting during free radical polymerization will be facilitated at carbons alpha to unsaturation in the PVA backbone.

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