duced in all cases by the Clemmensen reduction or Martin's[4] modification of it. Demethylation was accomplished in all cases by refluxing 0.1 mole with a mixture of 130 g. of glacial acetic acid and 50 g. of constant boiling hydrobromic acid.

1,2-Di-*p*-hydroxyphenylethane.—Anisoin was reduced by the Martin modification of the Clemmensen reduction giving 1,2-dianisylethane which on demethylation gave 1,2-di-*p*-hydroxyphenylethane.

1,3-Di-*p*-hydroxyphenylpropane.—*p*-Acetylanisole prepared according to Baranger[5] was condensed with anisaldehyde to give 1-anisyl-2-anisoylethylene. This on reduction and demethylation gave 1,3-di-*p*-hydroxyphenylpropane.

1,4-Di-*p*-hydroxyphenylbutane.—γ-Anisylbutyric acid was prepared by reduction of the *p*-anisoylpropionic acid obtained by condensing succinic anhydride and anisole according to Rosenmund and Shapiro.[6] The acid chloride prepared using thionyl chloride was condensed with anisole and the crude ketone obtained was reduced and demethylated to give 1,4-di-*p*-hydroxyphenylbutane.

1,5-Di-*p*-hydroxyphenylpentane.—Dianisalacetone prepared from anisaldehyde and acetone by the method of Conard and Dolliver[7] was reduced and demethylated to give 1,5-di-*p*-hydroxyphenylpentane, previously prepared by Borsche.[8]

1,6-Di-*p*-hydroxyphenylhexane.—One mole of adipoyl chloride was condensed with two moles of anisole using 2.25 moles of anhydrous aluminum chloride in 500 cc. of carbon disulfide. The diketone was reduced and demethylated to give 1,6-di-*p*-hydroxyphenylhexane. Oxidation of the diketone with alkaline potassium permanganate gave *p*-anisic acid, showing that condensation took place *para* to the methoxyl group.

1,10-Di-*p*-hydroxyphenyldecane.—Sebacoyl chloride and anisole were condensed as in the case of adipoyl chloride, and the diketone reduced and demethylated to give 1,10-di-*p*-hydroxyphenyldecane.

The solubilities in water were determined by the usual method. Solubilities in olive oil were determined by the method of Dunning, Dunning and Reid.[9]

Summary

1. A series of α,ω-di-*p*-hydroxyphenyl alkanes has been prepared having 2, 3, 4, 5, 6 and 10 methylene groups between the benzene rings.

2. The lower members of the series have decided bactericidal properties but are too insoluble in water to prove useful as antiseptics.

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[4] Martin, This Journal, **58**, 1438 (1936).

[5] Baranger, *Bull. soc. chim.*, [4] **49**, 213–222 (1931).

[6] Rosenmund and Shapiro, *Arch. Pharm.*, **272**, 313–323 (1934).

[7] Conard and Dolliver, *Org. Syntheses*, Vol. XII, 1932, p. 22.

[8] Borsche, *Ber.*, **52**, 2079 (1919).

[9] Dunning, Dunning and Reid, This Journal, **58**, 1565 (1936).

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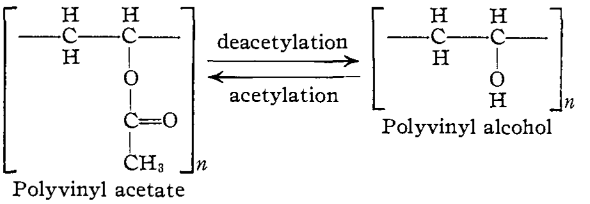
[COMMUNICATION NO. 741 FROM THE KODAK RESEARCH LABORATORIES]

Some Relationships between Polyvinyl Acetates and Polyvinyl Alcohols*

BY W. H. MCDOWELL AND W. O. KENYON

By analogy to the simple organic esters such as ethyl acetate, polyvinyl acetate would be expected to yield the corresponding polyvinyl alcohol by deacetylation and, conversely, polyvinyl acetate would be expected from the acetylation of polyvinyl alcohol as indicated in the formulas:



These reactions have been described by Staudinger and his co-workers,[1,2] by Herrmann and Haehnel[3] and by others.

The present investigations were undertaken to determine whether polyvinyl acetates could be transformed into polyvinyl alcohols and whether the alcohols could be reacetylated to produce polyvinyl acetates which are similar to the original acetates. Because of the polymeric nature of the polyvinyl alcohols and acetates, comparisons are made on the basis of the degree of polymerization as determined by viscosity measurements.

Experimental

Two different series of polyvinyl acetates of various viscosities were used. One series, composed of commercial samples, was used without further purification. The second series was prepared by the following method.

Monomeric vinyl acetate (practical grade) was distilled in an all-glass apparatus and the fraction boiling between 72.2 and 72.8° used for polymerization. Samples of the monomer were placed in all-glass reflux apparatus with the amounts of benzoyl peroxide catalyst (Eastman grade) shown in Table I and heated overnight on steam-baths.

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* Presented before the Paint and Varnish Division of the American Chemical Society at the Boston Meeting, September 11–15, 1939.

[1] Staudinger, *Ber.*, **59**, 3019 (1926).

[2] Staudinger and Schwalbach, *Ann.*, **488**, 8–56 (1931).

[3] Herrmann and Haehnel, *Ber.*, **60**, 1658–1663 (1927).

The polymers obtained were dispersed in acetone, and the dopes were poured into water. The cakes of precipitated resins were steamed to remove excess monomer and decomposition products of the catalyst, cut into small pieces, and dried between 80 and 100° *in vacuo*. The specific viscosities of the polyvinyl acetates obtained are given in Table I.

Table I

Experiment	Benzoyl peroxide, % by weight	Specific viscosity in acetone
I	2	0.050
II	1	.090
III	0.75	.115
IV	.30	.209

The polyvinyl acetates were converted to polyvinyl alcohols by the following method. Samples of resins were dissolved in methanol (about 6 cc. of solvent per gram of resin), and 4% of the theoretical amount of alcoholic potassium hydroxide necessary to react with the acetyl groups was added. On standing overnight at room temperature, a practically colorless, tough gel of polyvinyl alcohol formed. A liquid phase of excess methanol, methyl acetate, potassium acetate, and possibly acetic acid separated by syneresis. This was decanted and the polyvinyl alcohol was dispersed in water. When the aqueous dispersion was stirred into acetone, the white, fibrous polyvinyl alcohol separated. It was soaked in acetone with occasional agitation, separated and freed from acetone *in vacuo*.

The polyvinyl alcohols were reacetylated by the following method. One part of the alcohol was heated on the steam-bath for four hours with ten parts of a 2:1 (vol.) mixture of pyridine and acetic anhydride. The resulting polyvinyl acetate dissolved in the reaction mixture to form a homogeneous dope. The ester was precipitated in water, washed with water, and dried at 80 to 100° *in vacuo*. Acetyl determinations of representative samples indicated that the reacetylated materials possessed acetyl contents equal to those of the original acetates. Specific viscosities were determined in an Ostwald viscometer at 25°, using a solution of 0.1 g. of resin in 100 cc. of solution. Unless otherwise specified, the polyvinyl acetates were measured in acetone and the polyvinyl alcohols in water. The average degrees of polymerization were calculated from the relationship

$$\text{Average degree of polymerization } (D.\ P.) = \frac{\eta_{sp}}{K_m}$$

where η_{sp} is the determined specific viscosity and K_m is the Staudinger constant. The degrees of polymerization of the polyvinyl alcohols and acetates were calculated,[4] using a value of $K_m = 2.6 \times 10^{-4}$.

Average molecular weight polyvinyl alcohol = $D.\ P. \times 44$
Average molecular weight polyvinyl acetate = $D.\ P. \times 86$

In Table II the properties of the various polyvinyl acetates and alcohols are tabulated and compared.

Table II

Expt.	Original polyvinyl acetate Sp. visc.	Original polyvinyl acetate Degree of polym.	Original polyvinyl acetate Mol. wt.	Polyvinyl alcohol by deacetylation Sp. visc.	Polyvinyl alcohol by deacetylation Degree of polym.	Polyvinyl alcohol by deacetylation Mol. wt.	Polyvinyl acetate by reacetylation Sp. visc.	Polyvinyl acetate by reacetylation Degree of polym.	Polyvinyl acetate by reacetylation Mol. wt.
I	0.050	192	16,500	0.043	165	7,250	0.042	162	13,900
II	.090	346	29,800	.056	216	9,500	.056	216	18,600
III	.115	442	38,000	.063	242	10,600	.060	230	19,800
IV	.209	804	69,200	.080	308	13,500	.080	308	26,500
Commerical Samples									
V	0.021	81	6,970	0.027	104	4,580	.015	58	5,000
VI	.048	188	16,200	.048	185	8,140	.026	100	8,600
VII	.069	262	22,500	.063	242	10,600	.033	127	10,900
VIII	.086	330	28,400	.077	296	13,000	.042	161	13,800
IX	.108	415	35,700	.087	335	14,700	.047	181	15,600
X	.126	485	41,700	.090	346	15,200	.049	188	16,200
XI	.223	857	73,700	.322[a]	1240	54,600	.147[b]	565	48,600

[a] Determined in formic acid, 0.1 g. of resin/100 cc. of solution. [b] Determined in benzene, 0.1 g. of resin/100 cc. of solution. The specific viscosities in benzene are comparable with those determined in acetone.

Because of the decrease in molecular weight observed when polyvinyl acetates were deacetylated and reacetylated, a sample of polyvinyl acetate prepared in the laboratory was carried through two of these cycles to ascertain whether or not a further decrease would be observed in the second cycle. The results are shown in Table III.

Table III

Polymer	Specific viscosity	Degree of polymerization	Mol. wt.
(1) Original polyvinyl acetate	0.295	1135	97,600
(2) Polyvinyl alcohol from (1)	.175[a]	672	29,600
(3) Polyvinyl acetate by reacetylation of (2)	.086	330	28,400
(4) Polyvinyl alcohol from (3)	.180[a]	691	30,400
(5) Polyvinyl acetate by reacetylation of (4)	.090	346	29,800

[a] These specific viscosities were determined in formic acid solution, using 0.1 g. of resin per 100 cc. of solution.

The results indicate that a decrease in the degree of polymerization occurred in the first cycle but not in the second, since the values for acetates 3 and 5 are in good agreement. The *D. P.* values

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(4) We wish to thank Dr. Newsome and Mr. Wagner of these Laboratories for these measurements.

for the alcohols 2 and 4 in formic acid corroborate this but are twice as great as expected. The use of a K_m value of 5.2×10^{-4} when calculating the *D. P.* values from measurements in formic acid solution would have given values for the alcohols in agreement with those of the corresponding acetates.

The polyvinyl acetates prepared in the laboratory (I to IV, Table II) underwent degradation during de-esterification to produce polyvinyl alcohols with average chain lengths about one half as great as those of the original acetates. The corresponding acetates produced by reacetylation possessed the same chain lengths, within experimental error, as those of the corresponding alcohols. Experiments with commercial polyvinyl acetates (V to X, Table II) yielded opposite results. The change in the degree of polymerization occurred principally during reacetylation, and the degrees of polymerization of the resulting acetates were about one-half those of the corresponding alcohols. There appeared to be some decrease during deacetylation, especially with the acetates of higher viscosities, though the decrease was slight when compared to that which occurred during reacetylation. The specific viscosity of the polyvinyl alcohol of experiment XI (Table II) was determined in formic acid and cannot be employed in such comparisons.

As indicated by the structural formulas previously given, polyvinyl acetate and polyvinyl alcohol are usually assumed to consist of chains of carbon atoms having hydrogen atoms, acetoxy groups and hydroxyl groups attached. The average chain lengths or degrees of polymerization as calculated from specific viscosity measurements are assumed to be proportional to the number of monomeric units comprising the chains. The conditions of deacetylation and reacetylation are mild and would not be expected to rupture the carbon chains since they do not cause breakage of carbon to carbon linkages of simpler esters. However, if it is assumed that these conditions are sufficient to rupture the carbon chains of high molecular weight compounds, a further rupture might be expected when a reacetylated ester is carried through a second cycle, for the reacetylated compounds still possess large molecular weights (Table II). A sample of polyvinyl acetate prepared in the laboratory was carried through two cycles without decrease of the degree of polymerization during the second cycle (Table III). This suggests that the viscosity decrease is not due to rupture of the carbon chains but is caused by the presence of other, less stable, linkages in the chain which are broken under the experimental conditions. If a limited number of such less stable links are present in the original esters and are broken during the first cycle, no further change would be expected in the second cycle.

While no conclusions concerning the nature of such unstable linkages can be drawn from the present data, we wish to suggest the possibility of oxygen atoms from peroxide catalyst or acetaldehyde from the vinyl acetate entering into the polymer to produce a small number of such linkages. This concept of the inclusion of oxygen in the linear chain of a polymer is not novel. Staudinger and Schwalbach[2] suggest attachment of oxygen to a vinyl acetate molecule to produce an activated addition product from which chain growth proceeds. However, it appears that the effect of such linkages on the properties of the polymers has not been considered previously. An examination of other resins produced by polymerization of ethylenic bonds in the presence of peroxide catalysts might throw additional light on this question.[5]

Summary

1. Polyvinyl acetates of various degrees of polymerization have been deacetylated to polyvinyl alcohols and the latter reacetylated to polyvinyl acetates.

2. The polyvinyl acetates obtained by reacetylation possessed degrees of polymerization, as calculated from specific viscosity measurements, which were less than those of the corresponding original polyvinyl acetates.

3. It is suggested that this decrease of the average chain lengths may be due to rupture of unstable linkages present in the linear molecule.

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[5] The authors wish to thank Mr. L. M. Minsk and Mr. W. T. W. Pepper for certain of the samples of resins used in this work.