Macromolecules 1983, *16*, 291–296

Finally, we discuss the influence of tacticity on $\langle \mu^2 \rangle / x$ and ${}_{\mathrm{m}}K/x$. In Figure 4 we present calculations for the two sets of parameters indicated. The curves for $\langle \mu^2 \rangle / x$ agree with those presented by Cantera et al.[19] and Boyd and Kessner.[22] ${}_{\mathrm{m}}K$ shows a remarkable sensitivity to tacticity, particularly for highly isotactic and syndiotactic PVC chains, which makes this quantity particularly important for characterizing the microstructure of vinyl polymers.

Conclusions

The rotational isomeric state model of Williams, Pickles, and Flory as modified and presented here accounts fairly well for a large number of configurational-dependent properties of PVC and its oligomers. We have shown clearly the importance of second-order interactions, particularly between adjoining Cl atoms in determining the averages of various properties. Cl–Cl repulsive interactions appear to be stronger[27] than previously assumed by Flory and co-workers.[16,17] Also, the first-order interaction parameter E_η, which yields calculated ${}_{\mathrm{m}}K$ and $\langle \mu^2 \rangle$ values in closest agreement with the observed values, is considerably less attractive than the value obtained from epimerization studies. ${}_{\mathrm{m}}K$ appears to be remarkably sensitive to second-order interactions and the tacticity of PVC oligomers and polymers.

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Synthesis and Hydrolysis of Poly(vinyl acetals) Derived from Poly(vinyl alcohol) and 2,6-Dichlorobenzaldehyde[1]

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ABSTRACT: We describe the synthesis and hydrolysis of poly(vinyl acetals) derived from poly(vinyl alcohol) and the pesticide 2,6-dichlorobenzaldehyde. The acetalization reaction under a variety of conditions gave at best a polymer with 68% acetalization. The structure of the polymer, i.e., the ratio of acetal units derived from meso and racemic dyads of poly(vinyl alcohol), was determined by ^{1}H NMR. The acid-catalyzed hydrolysis of this poly(vinyl acetal) in aqueous dioxane at 60 °C was studied in detail. The rate constant for the hydrolysis of the meso and racemic acetal units and the equilibrium constant for meso–racemic intramolecular acetal exchange were determined from these measurements.

Introduction

As part of a general program dealing with controlled-release pesticides, we have prepared a poly(vinyl acetal) from poly(vinyl alcohol) and 2,6-dichlorobenzaldehyde. This aldehyde has been reported[2] to have strong herbicidal and moderate fungicidal activity. In this paper we report the preparation and characterization of the polymer and a detailed study of the kinetics of hydrolysis.

Results and Discussion

Synthesis and Characterization. The acetalization of poly(vinyl alcohol) (PVA) has been studied for a variety of aldehydes.[3] The reaction leads to (1) intramolecular acetalization of primarily 1,3-diol groups, (2) intramolecular acetalization of the occasional 1,2-diol groups, and (3) intermolecular acetalization. Intermolecular acetalization is more a function of reaction conditions and can lead to branched and eventually cross-linked polymer. The latter is easily removed in the purification process. The number of 1,2-diol units in commercial PVA is generally 1–2% and

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Table I
Acetalization of Poly(vinyl alcohol) with 2,6-Dichlorobenzaldehyde[a]

polymer	solvent	DCBA,[b] M	reaction time, h	% Cl	% acetalization
I	$CHCl_3$	0.55	10	11.2	18.5
II	$CHCl_3$	0.55	23	18.9	40
III	$CHCl_3$	0.55	45	22.4	55
IV	$CHCl_3$	0.55	64	23.3	60
V	$CHCl_3$	0.55	64	23.5	61
VI	$CHCl_3$	1.60	72	24.7	68
VII	dioxane	1.60	72	7.9	12
VIII	dioxane	1.60	72	<1	
IX	Me_2SO	0.50	58	20.7	47.5

[a] The reaction is carried out at 40 °C. PVA does not dissolve in the reaction solvent, except for Me_2SO. The reaction was catalyzed by HCl except for polymer VIII, where *p*-toluenesulfonic acid was used instead. [b] PVA = 1.0 M. The catalyst concentration is 4.8×10^{-2} M.

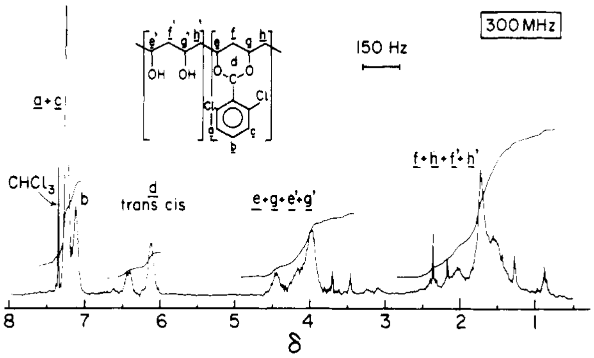
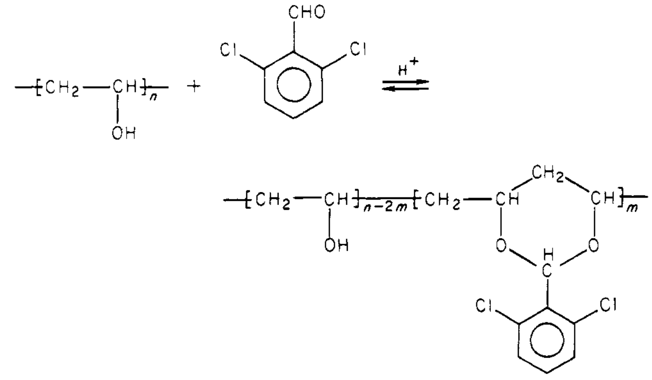


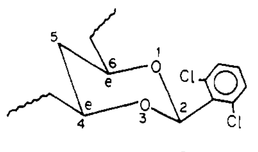
Figure 1. 300-MHz ^{1}H NMR spectrum of PVA–DCBA in $CDCl_3$ at room temperature.

the formation of dioxolanes may be neglected. Normally the acetalization of PVA will lead to the formation of the six-membered-ring acetals, the 1,3-dioxane units. This reaction was used to couple 2,6-dichlorobenzaldehyde (DCBA) to PVA:

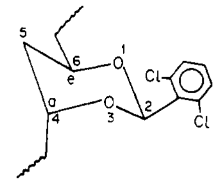


The product was isolated by sequential dissolution and precipitation. The degree of acetalization was determined by chlorine analysis. The reaction conditions and the extent of acetalization are summarized in Table I. The procedure described by Noma et al.,[4] where PVA is suspended in a chloroform solution of aldehyde and catalyst, gave the best results, with a maximum of 68% acetalization (VI).

The products were characterized by UV (λ_{max} = 281 nm, ϵ_{281} = 515 M^{-1} cm^{-1}), IR (diagnostic peaks: $\nu_{C=C}$ = 1579 and 1561, ν_{C-O} = 1011, and ν_{C-Cl} = 780 cm^{-1}), and NMR spectroscopy (Figure 1). Since the commercial PVA we used is atactic, acetalization with DCBA can be expected to lead to two types of structural units.[5]



meso acetal



racemic acetal

Fortunately the two can be distinguished in the NMR according to a study of model compounds prepared from 2,4-pentanediol and the same aldehyde[6] or formaldehyde.[7] Polymer VI was found by NMR analysis to contain 67% and 33% meso and racemic units, respectively. The concentration of dioxolane groups that may have formed from an occasional 1,2-diol unit is too low to be detected by NMR. Titration of the PVA with periodic acid indicates that only 1.5% of 1,2-diol units are present. The polymeric acetal was found to be soluble in chloroform, methylene chloride, benzene, Me_2SO, THF, dioxane, and aqueous dioxane but not in water alone.

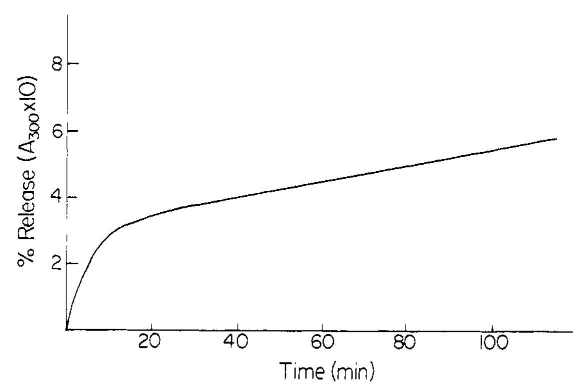


Figure 2. Typical initial hydrolysis curve of PVA–DCBA (68% acetalization) in acidic 29:1 dioxane/water at 60 °C; $[acet]_0 = 6.55 \times 10^{-3}$ M and $[HCl]_0 = 3.3 \times 10^{-2}$ M. The absorbance at 300 nm calculated for complete hydrolysis based on the molar absorptivity of 1550 M^{-1} cm^{-1} is 10.1.

Hydrolysis. We studied the acid-catalyzed hydrolysis of PVA–DCBA in 29:1 dioxane/water solution at 60 °C in order to gain basic information concerning the effect of tacticity on the rate of hydrolysis. The solvent was dictated by the solubility of the polymer. Polymer VI was used for the hydrolysis study.

The liberation of DCBA was monitored spectrophotometrically at 300 nm, where there is little absorbance due to acetal. A typical hydrolysis curve used for initial rate studies is given in Figure 2. The rapid reaction observed during the first 3% of hydrolysis is not an artifact and will be discussed later.

It is well accepted that the rate-determining step in the acid-catalyzed hydrolysis of acetals is the heterolytic cleavage of the carbon–oxonium bond of the protonated acetal.[8] The rate of hydrolysis is equal to the rate of aldehyde formation and can, at any time, be described by eq 1, where k^* is the rate constant for the heterolytic

$$R = \frac{d[\text{aldehyde}]}{dt} = k^*[\text{acetal}{\cdot}\text{H}^+] = k[\text{acetal}][\text{H}^+] \quad (1)$$

$$R_0 = \left(\frac{d[\text{aldehyde}]}{dt}\right)_{3-5\%} = k[\text{acetal}]_0[\text{H}^+]_0 \quad (2)$$

cleavage step, $k = k^*/K_a$, and K_a is the acid dissociation constant of the protonated substrate. The initial rate of hydrolysis, R_0, is given in eq 2. In order to avoid the effect

Table II
Hydrolysis of PVA-DCBA Polymer[a]

expt no.	10^3[acet]$_0$, M	10^3[HCl], M	$10^7 R_0$,[b] M s^{-1}	$10^4 k$,[c] M^{-1} s^{-1}
1	13.11	15.7	0.239	1.16
2	13.11	49.0	0.850	1.32
3	13.11	65.7	0.992	1.15
4	13.11	92.3	1.620	1.34
5	2.03	92.3	0.243	1.30
6	4.06	92.3	0.496	1.32
7	8.29	92.3	1.005	1.31
8	18.54	92.3	2.330	1.36
9	19.65	92.3	2.476	1.36
			av	1.30 ± 0.07

[a] Hydrolysis at 60 °C in 2.9 mL of dioxane solution of polymer (68% acetalization) + 0.1 mL of aqueous HCl. [b] R_0 calculated by dividing the initial slope of A_{300} vs. time (in seconds) by ϵ_{300} of the aldehyde, 1550 M^{-1} cm^{-1}. [c] The rate constant k is calculated by dividing R_0 by [acet]$_0$ and [HCl].

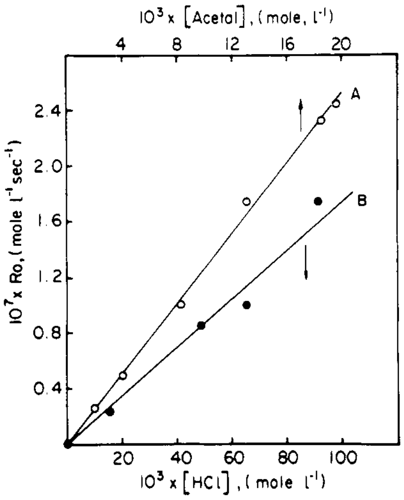


Figure 3. Dependence of the initial rate of hydrolysis of PVA-DCBA in acidic 29:1 dioxane/water at 60 °C on the concentration of acetal and acid.

of the initial rapid reaction, we measured R_0 values at 3-5% conversion. The initial rates, determined for various concentrations of polymeric acetal and hydrochloric acid, are summarized in Table II. A plot of R_0 vs. hydrochloric acid concentration at constant acetal concentration (experiments 1-4) or vs. acetal concentration at constant hydrochloric acid concentration (experiments 4-9), Figure 3, shows a first-order dependence for each of the reactants. Plotting log (R_0/[acetal]$_0$) vs. either log [HCl]$_0$ or H_0, the Hammett acidity constant, gives straight lines with slopes of 1.08 and 0.72, respectively, Figure 4.

The fact that the rate was linear with log [HCl]$_0$ and H_0 does not shed any light on the mechanism of the hydrolysis reaction. This test is usually applied to determine the role of H_2O in the transition state.[9] A linear relationship and a slope of unity for plots of rate vs. log [HCl]$_0$ or H_0 imply the presence or absence, respectively, of H_2O in the rate-determining step. Our results favor the participation of H_2O in the transition state but it is now generally agreed[9] that this test is not informative and, in fact, the concept of H_0 does not strictly apply to an organic/water solvent mixture that contains more than 5% organic solvent.

Each run yields $k = R_0/[\text{acetal}]_0[\text{HCl}]_0$. The average for all runs is (1.30 ± 0.07) × 10^{-4} M^{-1} s^{-1}. This rate constant should be compared to the rate constants for 2-(2,6-dichlorophenyl)-4,6-dimethyl-1,3-dioxane[6] hydrolyzed under identical conditions, which for the meso isomer is (2.14 ± 0.16) × 10^{-4} M^{-1} s^{-1} and for the racemic isomer is (4.31 ± 0.28) × 10^{-3} M^{-1} s^{-1}. There is a similarity in the rate of hydrolysis for the polymer and the meso model compound. This similarity is somewhat surprising since the polymer contains 33% of the more easily hydrolyzed racemic units and it is reasonable to expect that these units would hydrolyze preferentially.

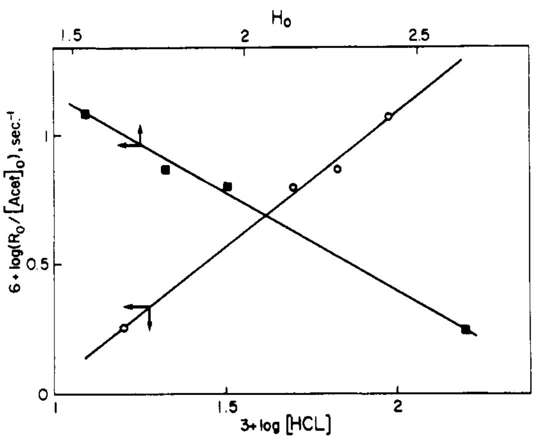
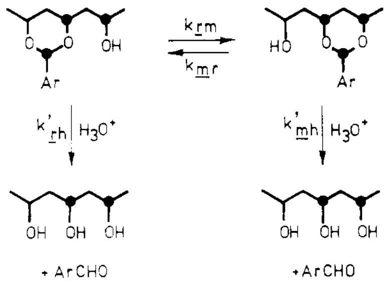


Figure 4. Plot of log (R_0/[acet]$_0$) vs. log [HCl]$_0$ and H_0 for the hydrolysis of PVA-DCBA.

Scheme I



Fujii, Ukida, and Matsumoto[10] in their study of formalized PVA found that the rate of hydrolysis depends on the tacticity of the original PVA—the higher the content of racemic units, the faster the hydrolysis. Shibatani, Fujii, and co-workers[11,12] also studied the formalization of PVA's with varying tacticity as well as the formalization of isomeric diols and triols. This thorough study left no doubt that the meso unit is more easily formed on both kinetic and thermodynamic grounds and that the racemic unit is more easily hydrolyzed. They also demonstrated that these polymeric formals and the triol analogue were subject to intramolecular acetal exchange, racemic acetals being converted to the more stable meso acetals. These same factors were investigated in the hydrolysis of the PVA-DCBA polymer.

The hydrolysis/transacetalization scheme is described in Scheme I. The kinetic analysis of this system is not straightforward. Before exchange can take place, a given acetal oxygen must have a free hydroxyl group as one of its neighbors. The probability (P) of this sequence will depend on the fraction (F) of hydroxyl units converted to acetal units. For $F = 1$, all the hydroxyl pairs are converted to acetals,[13] $P = 0$. As F gets smaller, P approaches unity.

This can be illustrated for a hexamer ($N = 6$), symbolized by six points, with two acetal units, symbolized by two lines connecting adjacent points. The combinations are as follows:

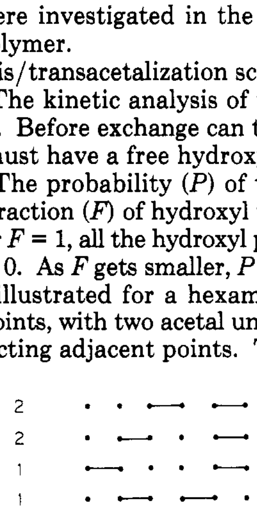


Table III
Large-Scale Hydrolysis and Analysis of PVA-DCBA Polymer[a]

time, h	% acetal $F \times 100$	$10^2[\mathrm{acet_T}]$, M	$10^2[\mathrm{acet_m}]$, M	$10^2[\mathrm{acet_r}]$, M	$[\mathrm{acet_m}]/[\mathrm{acet_r}]$[b]	K[c]
0	68.0	5.33	3.57 (4.02)[d]	1.76 (1.30)[d]	2.03 (3.08)[d]	5.27
1	65.0	5.09	3.77	1.32	2.86	4.59
3	60.0	4.70	3.55	1.15	3.10	4.85
4	57.2	4.48	3.45	1.03	3.35	5.20
5	55.1	4.32	3.30	1.01	3.26	5.05
14.3	40.6	3.18	2.63	0.55	4.81	6.77
27	33.3	2.60	2.41	0.20	12.3	17.3

[a] Hydrolysis of PVA-DCBA (polymer VI) in acidic 29:1 dioxane/water at 60 °C. $[\mathrm{acet_m}]_0 = 3.62 \times 10^{-2}$ M, $[\mathrm{acet_r}]_0 = 1.70 \times 10^{-2}$ M, and $[\mathrm{HCl}] = 9.5 \times 10^{-2}$ M. [b] Measured by NMR. [c] Calculated by eq 5. $K = 5.29 \pm 0.76$ based on first six values. [d] The values in parentheses are based on the polymer that was treated with HCl under anhydrous conditions in order to establish the true equilibrium distribution of meso and racemic acetal units (see text).

For each unsymmetrical arrangement there is its mirror image (not shown). Simple enumeration, for this case where $F = {}^4/_6$, gives $P = {}^{12}/_{24}$. An examination of a large class of oligomers, each at various conversions, leads to the general formula $P = (1 - F)/(1 - F/2)$. The same formula may be derived on the basis of simple statistical arguments. Label any fragment of a long chain, reading left to right, d for a hydroxyl group and l and l' for the beginning and end of an acetal unit. Given l', the probability that this acetal oxygen is followed by a hydroxyl unit is $P = d/(d + l)$ or $(1 - F)/[(1 - F) + F/2]$, which is identical with the equation given above.

Of course, this analysis does not take into consideration stereochemical factors. The same hexamer, assuming a random distribution of configurations, would lead to 32 (2^{N-1}) dyad combinations, one of which is shown in (I). An

● ● ● ○ ● ○ = mmrrr (I)

acetal unit may be represented by m or r. By this convention $F = 0$ when none of the m's or r's are italicized and $F = 1$ when every other m or r is italicized.[14] The transacetalization for one combination of $F = {}^4/_6$ is given by $\mathrm{m}m\mathrm{rr}r \rightleftarrows \mathrm{mm}r\mathrm{r}r$. In this reaction it is implied that the forward reaction requires a $m\mathrm{r}$ triad and the back-reaction a $\mathrm{m}r$ triad, and the equilibrium constant, K, should be expressed in terms of the concentration of these triads.[15] There are theories that describe reactions between adjacent groups on a polymer chain[16] but to our knowledge, there are no theories that apply to our system, which includes reversibility and stereochemical arguments.

An empirical approach to this problem follows. Consider an average chain, N units long with $\mathrm{m_0} + \mathrm{r_0} = N - 1$. The fraction of meso dyads where $F = 0$ is given by $f_\mathrm{m}{}^0 = \mathrm{m_0}/(\mathrm{m_0} + \mathrm{r_0})$ and the fraction of racemic dyads by $f_\mathrm{r}{}^0 = 1 - f_\mathrm{m}{}^0$. For the random polymer, as in this case, $f_\mathrm{m}{}^0 = f_\mathrm{r}{}^0 = 0.5$. The fraction of hydroxyl units converted to acetal units for a long chain ($N \simeq N - 1$) is given by $F = 2([m] + [r]/([\mathrm{m_0}] + [\mathrm{r_0}])$. Under hydrolysis conditions the reaction scheme described above applies and the disappearance of meso and racemic acetals is given by eq 3 and 4, where f_r and f_m are the fractions of racemic and meso

$$-\mathrm{d}[m]/\mathrm{d}t = k_{m\mathrm{h}}[m] + k_{m\mathrm{r}}[m]f_\mathrm{r}P - k_{r\mathrm{m}}[r]f_\mathrm{m}P \tag{3}$$

$$-\mathrm{d}[r]/\mathrm{d}t = k_{r\mathrm{h}}[r] + k_{r\mathrm{m}}[r]f_\mathrm{m}P - k_{m\mathrm{r}}[m]f_\mathrm{r}P \tag{4}$$

dyads, respectively, not linked in acetal formation. If the transacetalization term is large by comparison with the corresponding hydrolysis term, i.e., $k_{m\mathrm{h}} \ll k_{m\mathrm{r}}f_\mathrm{r}P$ and $k_{r\mathrm{h}} \ll k_{r\mathrm{m}}f_\mathrm{m}P$, and equilibrium applies, the equilibrium constant is given by $K = [m]f_\mathrm{r}/[r]f_\mathrm{m}$. This equation breaks down as P approaches zero or F approaches unity.

The equilibrium expression, in order to be useful, must be expressed in terms of the experimental quantities $[m]/[r] = X$ and F. If $f_\mathrm{r} = ([\mathrm{r_0}] - [r])/([\mathrm{r_0}] + [\mathrm{m_0}])$ and $f_\mathrm{m} = ([\mathrm{m_0}] - [m])/([\mathrm{r_0}] + [\mathrm{m_0}])$, the equilibrium constant is given by eq 5. This equation, solved for X, predicts X

$$K = \frac{X^2 + X(1 - F)}{1 + X(1 - F)} \tag{5}$$

$= K$ for $F = 0$ and $X = K^{1/2}$ for $F = 1$ instead of $X = 1$ for $F = 1$ dictated by the fact that $[\mathrm{m_0}] = [\mathrm{r_0}]$.

To sort out the equilibrium and rate constants, it was necessary to measure total hydrolysis or aldehyde formation as well as the ratio of racemic and meso acetal units as a function of time. This was accomplished in a large-scale kinetic run by monitoring aldehyde formation and at various time intervals, removing aliquots and precipitating the polymer for NMR analysis (and subsequent kinetic studies). The results of this experiment are summarized in Table III.

While Table III gives the kinetic results of the large-scale hydrolysis experiment, that is, $[\mathrm{acet_T}]$, $[\mathrm{acet_m}]$, and $[\mathrm{acet_r}]$ as a function of time, the important relationship is between % acetal ($F \times 100$) and $[\mathrm{acet_m}]/[\mathrm{acet_r}]$ of X. By eq 5 the equilibrium constant K is calculated to be 5.29 ± 0.76. The calculation is based on the first six data points and excludes the 27-h point, the point most subject to experimental error. This analysis assumes equilibrium in the transacetalization process. This assumption does not apply to the original polymer ($t = 0$), which was prepared under heterogeneous conditions and does not give the equilibrium distribution of $[\mathrm{acet_m}]$ and $[\mathrm{acet_r}]$. This polymer was equilibrated prior to hydrolysis (see Experimental Section). The corrected $[\mathrm{acet_m}]$ and $[\mathrm{acet_r}]$ and their ratio for the first point are shown in parentheses, and the ratio 3.08 was used in the calculation of K. The other samples were in solution in the presence of acid for 1 h or more and are no doubt completely equilibrated.

The samples isolated from the large-scale hydrolysis studies were the subject of initial rate studies. The results are summarized in Table IV. In the former experiments, Table II, the same polymer was used for each kinetic run and the runs varied by polymer concentrations, e.g., acetal concentration and HCl concentration. In this experiment each set of kinetic runs represents a different polymer, different in the percent acetalization and in the ratio of meso and racemic acetal units. Equation 2, instantaneous rate of aldehyde formation, may be separated into the hydrolysis of the racemic and meso acetals as shown in eq 6. The primed rate constants of the pseudo-first-order

$$R_0 = k_{r\mathrm{h}}'[\mathrm{acet_r}]_0 + k_{m\mathrm{h}}'[\mathrm{acet_m}]_0 \tag{6}$$

reactions are the product of the second-order rate constant and the concentration of the acid catalyst. A plot of $R_0/[\mathrm{acet_r}]_0$ vs. $[\mathrm{acet_m}]_0/[\mathrm{acet_r}]_0$, Figure 5, will give $k_{r\mathrm{h}}'$ as the intercept and $k_{m\mathrm{h}}'$ as the slope. This linear relationship apparently breaks down at low $[\mathrm{acet_T}]$. Based on the

Table IV
Initial Rates of Hydrolysis of PVA-DCBA for Varying Degrees of Acetalization[a]

hours hydrolyzed	% acetalization	$10^3[\text{acet}_T]$, M	$10^7 R_0$, M s^{-1}	$10^3[\text{acet}_r]$, M	$10^4 R_0/[\text{acet}_r]$, s^{-1}	$[\text{acet}_m]/[\text{acet}_r]$
0	68.0	3.90	0.21	1.29	0.16	2.03
		7.69	0.42	2.54	0.17	
		13.59	0.74	4.48	0.17	
3	60.0	4.03	0.20	0.98	0.20	3.10
		6.76	0.39	1.65	0.23	
		12.78	0.69	3.12	0.22	
5	55.1	3.23	0.16	0.76	0.21	3.26
		3.29	0.16	0.77	0.20	
		6.26	0.32	1.47	0.22	
		11.47	0.58	2.70	0.21	
14.3	40.6	2.61	0.13	0.45	0.29	4.81
		5.29	0.27	0.91	0.30	
		10.97	0.53	1.89	0.28	
27	33.3	2.97	0.17	0.21	0.83	12.33
		6.38	0.37	0.48	0.78	

[a] Hydrolysis in 29:1 dioxane/water at 60 °C and [HCl] = 3.33×10^{-2} M.

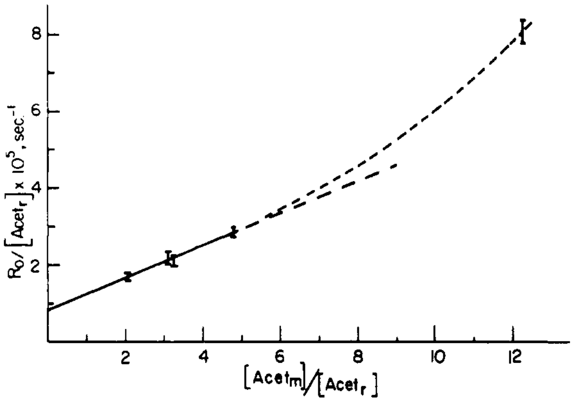


Figure 5. Plot of $R_0/[\text{acet}_r]_0$ vs. $[\text{acet}_m]_0/[\text{acet}_r]_0$ for the hydrolysis of PVA-DCBA of varying degree of acetalization in acidic 29:1 dioxane/water at 60 °C; [HCl] = 3.33×10^{-2} M.

straight-line portion of this curve, $k_{rh}' = 7.37 \times 10^{-6}$ s^{-1} and $k_{mh}' = 4.45 \times 10^{-6}$ s^{-1} with a correlation coefficient of 0.993. The racemic units hydrolyze faster but not much faster than the meso units.

The apparent acceleration in rate for decreasing degree of acetalization, as evidenced in Figure 5, may be a consequence of catalyzed hydrolysis by neighboring hydroxyl groups as they become available, a theory suggested and supported by the hydrolysis studies of Smets and Petit.[17] However, we have insufficient data at low degrees of acetalization to test our system for this neighboring group effect. The kinetic analysis of the reactivity of a functional group and its dependence on the reaction state of its neighbors has been recently reviewed by Platé[16] and by Boucher.[16]

The hydrolysis study is complicated by another process. Returning to Figure 2, we see an initial rapid rate of aldehyde formation by an as-yet defined reaction. It appears that this reaction is fast enough that it precedes and is essentially complete before any other hydrolysis process. Based on this assumption, the burst was treated as a first-order process and gave a rate constant $k' = 1.5 \times 10^{-3}$ s^{-1}. This probably is not the result of hydrolysis of 1,2 acetals because (a) by titration there is only 1.5% 1,2-diol units in the polymer and the initial burst accounts for 3% of the acetal units and (b) according to Kovar et al.,[18] the dioxolanes do not hydrolyze that much faster than the corresponding dioxanes and in some cases they hydrolyze even slower. The burst could come from the hydrolysis of essentially linear acetals formed by hydroxyls far removed from one another along the chain or hydroxyl from separate chains, which would be expected to hydrolyze much faster than the corresponding cyclic acetal (see Table V).

Table V
Rate Constants[a] for the Hydrolysis and Isomerization of PVA-DCBA and Its Model Compounds

polymer hydrolysis	model hydrolysis
$k_{mh} = 1.34 \times 10^{-4}$ M^{-1} s^{-1}	$k_{mh}{}^{b} = 2.14 \times 10^{-4}$ M^{-1} s^{-1}
$k_{rh} = 2.21 \times 10^{-4}$ M^{-1} s^{-1}	$k_{rh}{}^{b} = 4.31 \times 10^{-3}$ M^{-1} s^{-1}
$k^{d} = 4.5 \times 10^{-2}$ M^{-1} s^{-1}	$k^{c} = 8.2$ M^{-1} s^{-1}
$K = 5.29 \pm 0.76$	

[a] Acid-catalyzed hydrolysis in 29:1 dioxane/water at 60 °C. The rate constants were calculated from the respective k's by dividing by [HCl] = 3.33×10^{-2} M. [b] For the hydrolysis of 2-(2,6-dichlorophenyl)-4,6-dimethyl-1,3-dioxane under reaction conditions identical with those of this study. [c] For the hydrolysis of 2,6-dichlorobenzaldehyde di-*tert*-butyl acetal in 20% dioxane/H_2O at 25 °C and $\mu = 0.8$. Anderson, E.; Fife, T. H. *J. Am. Chem. Soc.* **1971**, *93*, 1701. [d] Rate constant for the initial burst treated as a first-order reaction.

Summary

Poly(vinyl acetals) from poly(vinyl alcohol) and 2,6-dichlorobenzaldehyde were prepared under varying conditions. Reaction in chloroform gave at best 68% acetalization. Since the commercial PVA used is atactic, two isomeric types of acetal structures were formed. The hydrolysis studies in 29:1 dioxane/water at 60 °C demonstrated that this reaction is complex but not intractable. The appropriate rate and equilibrium constants are summarized in Table V. These data show that (1) the racemic acetal units hydrolyze faster than the meso units but the difference in the rate of hydrolysis of the isomeric structures was less pronounced in the polymer than was found earlier[6] for model compounds, (2) the racemic acetal and meso acetals are equilibrated by acetal exchange and the ratio will depend on the degree of acetalization and the tacticity of the parent polymer, and (3) a small percentage of the acetal units hydrolyze at a rate that would be expected for linear acetals, suggesting the presence of a small percentage of large cyclic or interchain acetals.

Experimental Section

Materials. Commercial PVA (Mowiol 28-99) was used without purification. 2,6-Dichlorobenzaldehyde (99% pure, Aldrich) was purified by recrystallization from pentane and dried under reduced pressure over phosphorus pentoxide. Chloroform was washed with concentrated sulfuric acid, aqueous sodium bicarbonate, and water. It was dried with calcium hydride and stored under nitrogen in the dark. Dioxane was purified according to the procedure described by Vogel.[19]

Measurements. The chlorine content was determined by the Schöniger combustion method. NMR spectra were recorded on a Varian spectrometer, Type HR-300 (300 MHz). The UV spectra and kinetic studies were performed with a Pye-Unicam 1750-A or a Cary 15 spectrophotometer.

Acetalization of PVA. The procedure that follows is an example of acetalization in chloroform. A 100-mL round-bottom flask, placed in a thermostated bath at 40 °C, was charged with PVA (11 g), DCBA (7.1 g, 40.5 mmol), and 25 mL of chloroform. Concentrated aqueous hydrochloric acid (0.1 mL, 1.2 mmol) was added and the mixture stirred for 3 days. The resulting gel was poured into an excess of methanol. A white precipitate was isolated and further purified by precipitating a dioxane solution of the polymer with methanol. Finally, the reaction product was dried over P_2O_5 under reduced pressure at room temperature and analyzed. Anal. Calcd for $-(C_2H_8O_2)_{32\%}-(C_{11}H_{20}O_2Cl_2)_{68\%}-$: Cl, 24.8. Found: Cl, 24.7. From the NMR integration of the benzylic acetal protons, the ratio of meso/racemic acetal units was calculated to be 67/33. The UV spectrum of a dioxane solution of the polymeric acetal shows maxima at 274 and 281 nm ($\epsilon_{274} = 540$ M^{-1} cm^{-1}, $\epsilon_{281} = 515$ M^{-1} cm^{-1}).

Kinetic Measurements. The hydrolysis of the acetalized PVA (PVA–DCBA) was measured spectrophotometrically by monitoring the formation of DCBA ($\lambda_{max} = 300$ nm, $\epsilon_{max} = 1550$ M^{-1} cm^{-1}) as a function of time. A typical kinetic run follows. A UV cell, fitted with a Teflon stopper and thermostated at 60 °C, was charged with 2.9 mL of a stock solution of the polymer in pure dioxane. After temperature equilibration (ca. 20 min), 0.1 mL of aqueous hydrochloric acid solution was added. The absorption at $\lambda = 300$ nm was recorded continuously as a function of time. From the initial slope of the absorbance vs. time plot (after the burst) and the molar extinction coefficient of DCBA, the initial rate of hydrolysis was determined. For a complete hydrolysis experiment the starting concentration of polyacetal was chosen to be low enough to stay within the absorbance range, even at total hydrolysis.

Hammett Acidity Function. The Hammett acidity function for the reaction medium was determined as described in a previous paper.[6]

Polymer Equilibration. The polymer was prepared under heterogeneous conditions and hydrolyzed under very different but homogeneous conditions. To establish equilibrium under hydrolysis conditions, the original polymer was dissolved in dry dioxane. Dry HCl gas was bubbled through the solution and the reaction tube sealed off. After 1 day at 60 °C the seal was broken and the polymer was precipitated in methanol. By UV analysis no DCBA was liberated in this experiment but by NMR analysis the meso acetal content changed from 67% to 75.5%.

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References and Notes

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(13) This is theoretically possible because acetalization is reversible and not subject to the 86.4% conversion limit calculated by Flory for irreversible reactions: Flory, P. J. *J. Am. Chem. Soc.* **1939**, *61*, 1518.

(14) The sequence where two neighboring dyads are italicized would require one oxygen to be involved in two acetal units.

(15) Another mechanism may apply for low values of F, i.e., $m(\mathrm{m})_a r \rightarrow \mathrm{m}r$ and $r(\mathrm{r})_b\ \mathrm{m} \rightarrow \mathrm{r}m$, where a and b are nonzero integers.

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