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Divinylbutyral. II. Polymer Structure

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ABSTRACT

The structure of polydivinylbutyral (PDVB) was found to be very dependent on the temperature of polymerization, according to data from a slow acid hydrolysis in conjunction with spectral analyses. When prepared at high temperatures, PDVB may contain up to 45% of ester and ketal groups. Additional evidence points to a high degree of branching and the presence of large cyclic structures. A short, controlled hydrolysis resulted in an improvement of the physical properties of PDVB.

INTRODUCTION

The polymerization of divinyl acetals and the structure of their polymers has been found to be in agreement with the usual cyclic polymerization mechanism by a number of authors [1]. The formation of polyvinyl alcohol (PVAI) during hydrolysis was advanced as a support for the accepted cyclic mechanism of polymerization. A polarographic analysis of PVAI obtained from

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several polydivinylacetals including polydivinylbutyral (PDVB) indicated a polymeric chain consisting of 72% of 6-membered and 23% of 5-membered (from head-to-head addition) ring structures [2].

In view of this reported structural evidence, it was unexpected when the polymers of highly purified divinylbutyral (DVB) did not yield completely water-soluble PVAI upon hydrolysis. Therefore, the hydrolysis reaction was subjected to a careful investigation. It may be noted that previous investigators [1, 2] studied polymers of rather low molecular weights, sometimes reporting the formation of insoluble by-products during hydrolysis.

RESULTS AND DISCUSSION

When a total hydrolysis of PDVB was attempted with the polymers of this study [3], anomalies in its structure became apparent. A hydrolysis was carried out with two PDVB samples (low and intermediate polymerization temperature) and with Butvar 510. The conditions were identical to those described by Matsuyan [4] and similar to ASTM procedure D1396-58 for determining aldehyde in polyvinyl acetals. Butvar yielded PVAI with expected solubilities. Both PDVB samples formed brown to black resins, part of which were insoluble in all solvents. Water-soluble fractions were found to undergo changes during workup, such as turning methanol soluble. The products obtained by this method were not studied any further.

It was reported [3] that cross-linked PDVB swollen in tetrahydrofuran can be solubilized by short treatment with a few drops of concentrated hydrochloric acid. This proved that cross-links and also branches are linked to the polymer by hydrolyzable groups and not via carbon bonds. Therefore, it was attempted to determine the number and length of branches in noncross-linked PDVB by following the course of a slow hydrolysis at 30°C. The solvent was dioxane, containing 5% by volume of a buffered aqueous hydrochloric acid, after it was established that PDVB is soluble in such a medium. The buffer was adjusted to different acid concentrations, thus keeping the ionic strength constant. The concentration of PDVB was 0.1 mole/liter in acetal groups, which assured a sufficient molar excess (about 25:1) of water available for hydrolysis.

The absolute rate of hydrolysis was established by measuring the increase of carbonyl with UV techniques. To test the validity of this method, a model compound (2-propyl-1,3-dioxolane) was hydrolyzed at first in a 50% water dioxane mixture (upper curve

in Fig. 1). This showed that the data obtained were comparable to those reported in the literature with a similar method [5]. Subsequently, the dioxolane was hydrolyzed in a 5% aqueous dioxane medium which contained the same amount of acid as the 50% mixture did (second highest curve in Fig. 1). It was found that only about one-half of the theoretical carbonyl intensity was recorded,

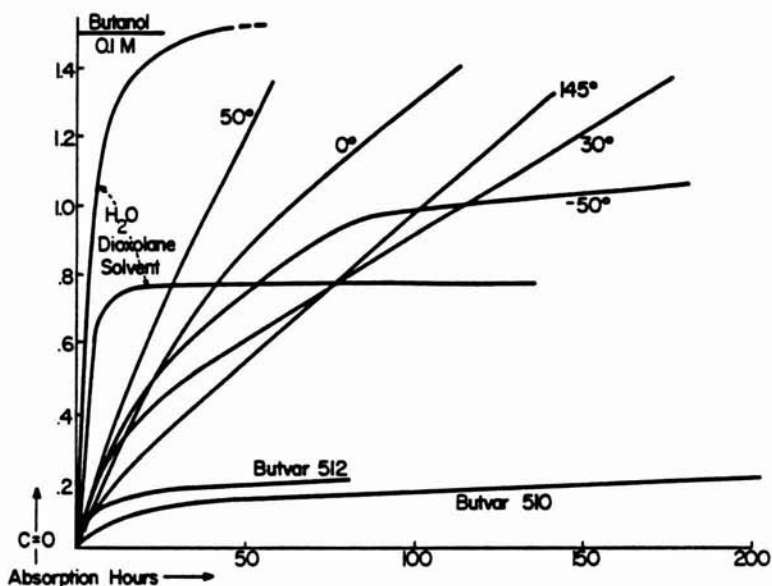


FIG. 1. Hydrolysis of PDVB, Butvar, and 2-propyldioxolane in 95% dioxane at 30°C with 0.02 N HCl. The temperatures of polymerization of DVB are indicated. Absorption at 2.86 (butanal) and 279 μ were measured.

compared to a standard 0.1 M solution of butanal or to data in 50% water-dioxane. It was concluded that in the predominantly organic medium aldol-condensations or hemiacetal formation consumed part of the aldehyde formed. When commercial twice-precipitated Butvar 510 and 512 were subjected to the same conditions, it was surprising to note that the rates were much slower and leveled off at about 25 to 30% of the value for the dioxolane (lowest curves

in Fig. 1). The reason may have been steric hindrance commonly noticed in organic polymer reactions, or stabilization of the acetal by hydrogen bonding from adjacent hydroxyl groups. It is less probable that base-type stabilizers present in commercial Butvar were responsible for its slower hydrolysis since these should have been removed during reprecipitations. Any traces of base left should have been insignificant compared to the amount of HCl present (the solutions were 0.02 N in HCl, i.e., 20% of the "molarity" of Butvar).

The intermediate curves in Fig. 1 are a representative selection of the total number of PDVB samples analyzed. The temperatures of polymerization are indicated on the curves in Fig. 1. It was disappointing to find that there was no correlation between polymerization variables and the absolute rates of hydrolysis, the only exception being an earlier leveling off in carbonyl intensity of samples prepared at -50° . The following conclusions were drawn on the rates of carbonyl formation during hydrolysis:

PDVB is hydrolyzed about three to ten times as fast as Butvar. The latter undergoes only partial (25-30%) hydrolysis under these conditions, while carbonyl produced from PDVB exceeds the amount obtained from a model compound. This indicates that the acetal groups in PDVB are more easily accessible and less stable towards hydrolysis than in Butvar. It also shows that at least part of the carbonyl formed was different from butanal since it did not seem to undergo secondary reactions such as aldol condensations to the same extent. The presence of other carbonyl was confirmed when it was noticed that a second carbonyl peak occurred during the later stages of hydrolysis (at 279 versus 286 $m\mu$). The location of this peak at a lower wavelength suggests a ketone, rather than an aldehyde, or a carbonyl conjugated to unsaturation. For comparison, some carbonyl absorptions of the four-carbon series [6] are listed below:

2-Butenal	312 $m\mu$
3-Butenal	307 $m\mu$
Butanal	282 $m\mu$
2-Butanone	277 $m\mu$
Butyric acid	270 $m\mu$

The second method of exploring the structure of PDVB consisted in following the change in viscosity of hydrolyzing PDVB in the same 95% dioxane medium. Partly hydrolyzed samples were then withdrawn and characterized before the above-noted insolubilization set in.

A similar technique, but using base hydrolysis, has been employed to determine the structure of polyvinyl acetate where branches are linked to the backbone by ester groups. Therefore, the hydrolysis of PDVB was compared with that of polyvinyl acetate and of Butvar (Fig. 2).

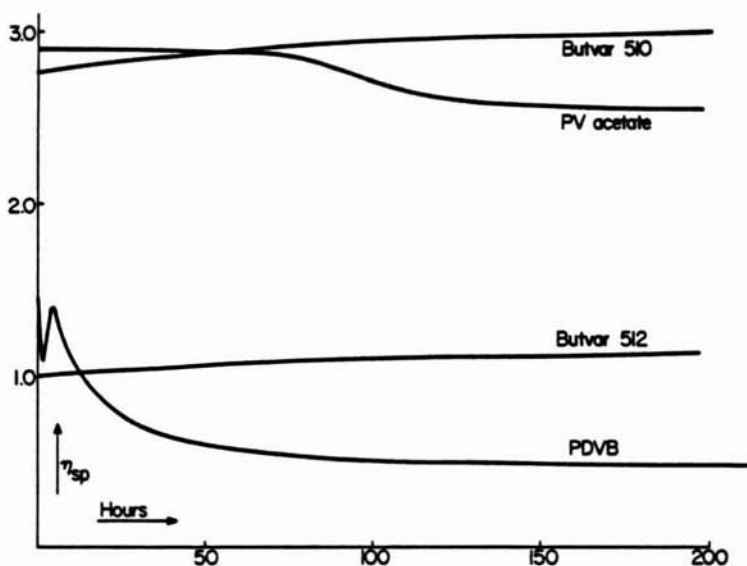


FIG. 2. Changes in specific viscosity of 0.1 M solutions (based on functional groups) of PDVB, Butvar, and polyvinyl acetate in a 0.02 N HCl, 95% dioxane medium at 30°C.

The viscosity of a hydrolyzing solution of Butvar was found to increase slowly with time. This is thought to be due to hydrogen bonding by the newly formed OH-groups. Polyvinyl acetate (PVAc) showed at first a slow, after 80-120 hr a fast, then again a slow decrease in viscosity, probably indicative of the removal of long chain branches. A representative PDVB sample, however, showed a first rapid decrease in viscosity which may be attributed to the cleaving of ketal links. Ketals are known to hydrolyze about 10^4 times faster than acetals [5]. This was followed in most cases by a pronounced, brief increase in viscosity. A tentative explanation

for this increase is the opening of acetal linked large cyclic structures with a corresponding increase in the effective diameter of flowing molecules. The same may account for the initial slowness of the viscosity decrease in PVAc during hydrolysis, except that there is only one type of linkage to be cleaved and the incidence of hydrolyzable links is much lower. While the presence of large rings appears statistically favored in polymers like PVAc and PDVB which cross-link at higher conversion [7], it will be difficult to furnish quantitative proof for this assumption.

Subsequently, the viscosity of hydrolyzing PDVB is seen to decrease to a minimum, supposedly due to cleavage of acetal-linked chain segments or branches which hydrolyze more slowly. Finally, after 10 to 20 days, the viscosity increased and gelation occurred (not included in Figures). Most of the polymer was then insoluble in all solvents, as was experienced also during the rapid, total hydrolysis before. The location and times of the first minima, maxima, and second minima of all samples hydrolyzed at the same acid concentration are listed in Table 1.

Other concentrations of acid shifted the reaction on the time scale and also affected the minimum value (higher η_{sp} at lower acid concentration). A broad spectrum of samples was tested covering the variables temperature and degree of polymerization, degree of conversion, and type of catalyst.

Qualitatively, the course of hydrolysis was identical in all cases. Quantitatively, two relationships were uncovered:

(a) Samples with the highest starting molecular weight (plotted as intrinsic viscosity) showed the sharpest relative decrease in specific viscosity (ratio of viscosity at first minimum over start) as seen in Fig. 3. This was true regardless of other variables except for samples prepared at -50°C . This is in line with the fact that scission of large molecules produces a much larger relative decrease in viscosity than scission of small molecules. More importantly, this observation confirmed the validity of the method by showing that the observed effects were not due to interaction with the medium or to configurational changes, affecting the flow characteristics only, which would have been independent of chain length.

(b) The lowest viscosities in the second minimum showed some relation to the temperature of polymerization (Fig. 4). Between -50° and approximately 30° polymerization temperature, the viscosities of the hydrolysates remained constant, while decreasing

TABLE 1. Changes in Viscosity During Hydrolysis of 0.1 M Solutions (as Acetal) of PDVB Prepared at Different Temperatures of Polymerizations (Medium: 0.02 N HCl, 95% dioxane, 30°)

Polymerization temp (°C)	Initiator	[η]	Start	Specific viscosity		
				1st min (hr)	Max (hr)	2nd min (hr)
-50	BR ₃ -O ₂	0.48	0.64	0.62 (1)	0.66 (6.5)	0.47 (200)
-50	BR ₃ -O ₂	0.32	0.43	0.41 (1)	0.43 (6)	0.37 (80)
0	AIBN	0.49	0.78	0.75 (1)	0.79 (6)	0.44 (200)
0	AIBN	0.79	0.85	0.73 (2)	0.73 (6)	0.41 (80)
30	AIBN	1.10	1.20	1.05 (1)	1.18 (5)	0.48 (200)
50	AIBN	1.00	0.95	0.83 (2)	0.86 (5)	0.42 (210)
50	AIBN	1.05	1.00	0.73 (3)	0.75 (6.5)	0.35 (200)
50	AIBN	0.43	0.42	0.41 (1)	0.41 (15)	0.26 (270)
95	AIBN	0.33	0.47	0.43 (1)	0.45 (6)	0.29 (215)
115	DTBPO	0.10	0.24	0.22 (2)	-	0.18 (200)
145	DTBPO	0.17	0.26	0.25 (1)	-	0.20 (220)

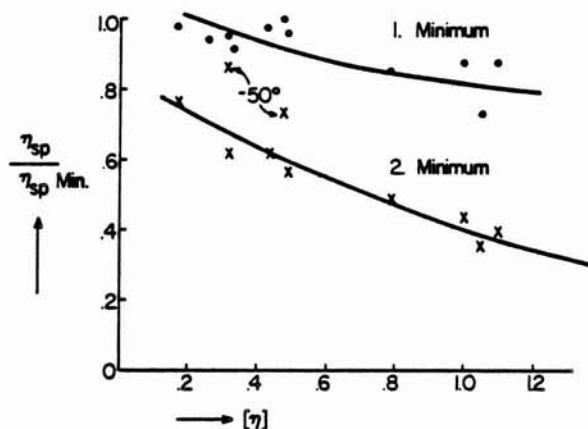


FIG. 3. The dependence of minima in specific viscosity η_{sp} on starting molecular weights (as intrinsic viscosity $[\eta]$) of hydrolyzing PDVB.

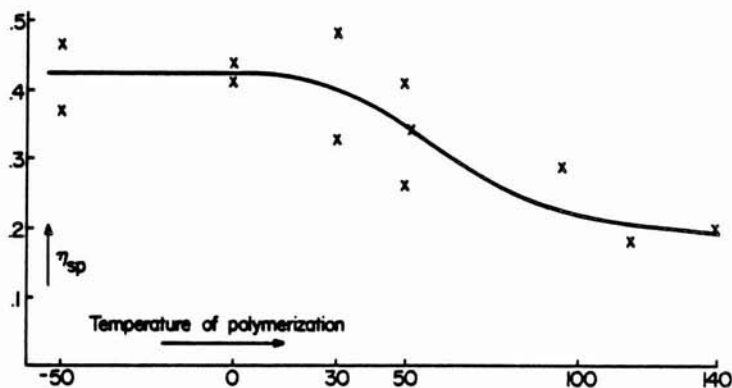


FIG. 4. Effect of temperature of polymerization of DVB on minimum specific viscosity during the hydrolysis of PDVB.

markedly at higher polymerization temperatures. This was confirmed by obtaining osmometric molecular weights on hydrolyzed samples withdrawn at their second minima (Table 2).

TABLE 2

Temp of polymerization (°C)	Nonhydrolyzed $\bar{M}_n \times 10^{-3}$	Hydrolyzed $\bar{M}_n \times 10^{-3}$
-50	32.1	14.8
0	135	14.7
50	110	7.7

It indicated that the nonhydrolyzable chain segments were shortest at higher polymerization temperature, but of equal length when going from about 30° to lower polymerization temperatures, regardless of the starting molecular weights. The actual size of segments and, therefore, the branch density, is thought to be different from the quoted molecular weights. The condensation which eventually leads to gelation of hydrolysates must be going on concurrently with hydrolysis, thus causing continuous aggregation of the segments. This may explain why the minimum viscosities were higher when lower acid concentrations were used, suggesting that the rate of condensation was less acid dependent than that of hydrolysis.

Figure 5 shows the course of hydrolysis of PDVB's prepared at 50° (AIBN), 0° (UV light-AIBN), and at -50° (boron-alkyl-oxygen catalyst) in graphical form. Aliquots were withdrawn at points indicated by arrows. The IR spectra of these partly hydrolyzed, carefully purified polymers showed hydroxyl and two pronounced carbonyl absorptions at 5.55 and 5.80 μ which did not change during several reprecipitations. The spectra were similar to those obtained earlier from thermally degraded PDVB, i.e., in the absence of water. Both carbonyl bands were most intense in samples withdrawn at the first minimum in viscosity and tended to disappear later as the hydroxyl absorptions increased. In Table 3 the intensities of hydroxyl and both carbonyl bands are listed. The intensity of the CH bands at around 3.4 μ was kept constant at 1.0 in the spectra. These qualitative data show that PDVB polymerized at higher temperature developed the least hydroxyl groups at the slowest rate during hydrolysis. Both types of carbonyl were initially of equal intensity, regardless of polymerization temperature. The carbonyl at 5.5 μ disappeared at

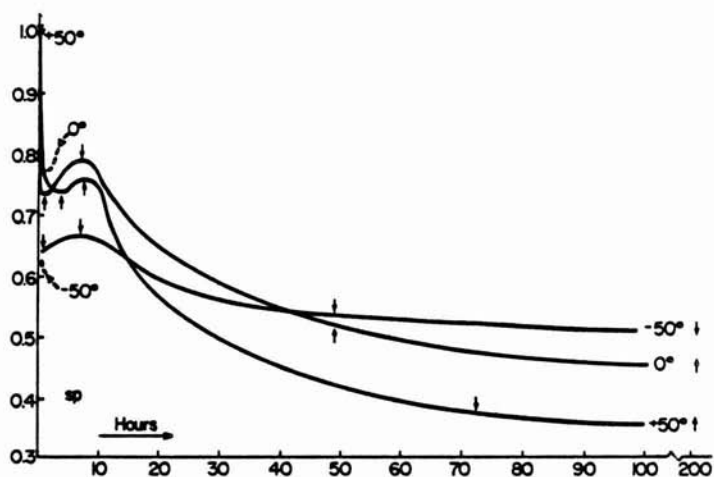


FIG. 5. Changes in specific viscosity during hydrolysis of 0.1 M solutions (based on acetal) of PDVB prepared at different temperatures of polymerization. Medium: 0.02 N HCl, 95% dioxane, 30°C. Arrows indicate points of withdrawal.

TABLE 3. Changes in IR Spectra of PDVB During Hydrolysis

Polymerization temp (°C)	Time (hr), hydrolysis	OH 2.9 μ	CO 5.5 μ	CO 5.8 μ
50	1.5	0.055	0.110	0.240
	7	0.138	0.067	0.150
	72	0.333(?)	0.010	0.090
	200	0.22	0.010	0.090
0	4	0.180	0.090	0.250
	7.5	0.220	0.090	0.260
	49	0.265	0.026	0.135
	200	0.300	0.070(?)	0.190(?)
-50	1	0.180	0.080	0.255
	7	0.240	0.050	0.225
	49	0.400	0.022	0.170
	200	0.470	0.018	0.150

comparable rates from all three polymers. The carbonyl at 5.8μ disappeared fastest from the high temperature and slowest from the low temperature sample. The intensity of the carbonyl bands suggests that approximately 10 to 20 mole-% of acetal units were converted to polymer-attached carbonyls by rough comparison with carbonyl intensities of copolymers of DVB with vinyl acetate.

There were no other changes in the spectra. Curiously, the broad acetal bands at 9 and 10.0μ did not appreciably decrease in intensity. It is believed that the carbonyl at 5.8μ formed during the initial rapid decrease in viscosity is derived from ketal linkages, as suggested above, and which is in line with the UV spectrum. An assignment of the carbonyl band at 5.55μ is difficult since the only carbonyl groups known to absorb in this region (e.g., strained ketons, anhydrides) do not fit easily to the polymer structure deduced from the polymerization mechanism and from other analytical data.

The reason why both carbonyl absorptions decreased in the polymer during extended hydrolysis may have been aldol condensations. This is supported by the fact that at no time during hydrolysis were the polymers fully soluble in water. They were soluble in methanol at the time of the third and fourth withdrawal.

When a 4-hr hydrolysis was repeated with larger amounts of the high (50°) and the low (-50°) temperature samples, it was found that in both cases a significant increase in physical strength had occurred (Table 4). This is thought to be due to removal of irregularities in structure as well as formation of OH groups and the resulting hydrogen bonding.

TABLE 4

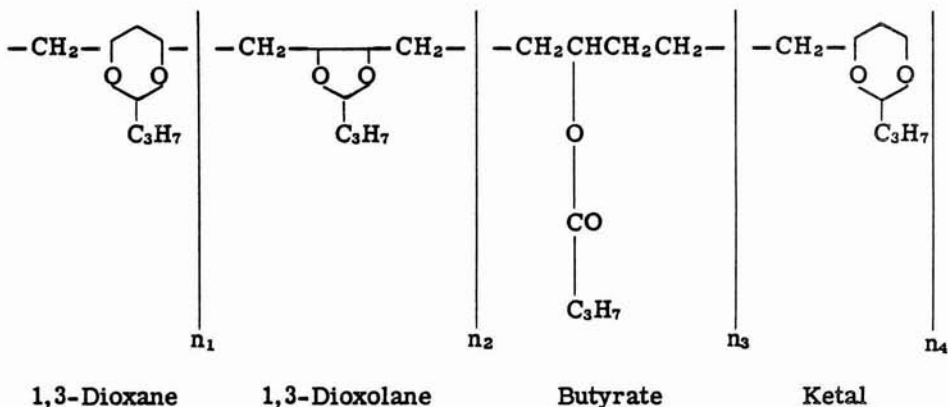
	Polymerization temp ($^\circ\text{C}$)	Tensile strength at		Elongation (%)
		Yield	Break	
Nonhydrolyzed	50	84	361	363
Hydrolyzed		215	480	197
Nonhydrolyzed	-50	2196	1920	71
Hydrolyzed		1100	2604	176

The presence of ketal groups in PDVB is thus considered established. Their amount is thought to range from 5 to 20 mole-%, and to be independent of polymerization temperature. A quantitative determination is complicated by the fact that the ketones during hydrolysis undergo secondary reactions and disappear slowly, while condensation, and eventually gelation, takes place. A mechanism of their formation during the polymerization was suggested in Part I [3].

Furthermore, direct evidence has been presented that branches and cross-links occur at least partially via ketal groups. Other types of hydrolytically weak links are probable but not proven. These would be mainly acetal links and, to a small extent, ester branches of the type found in PVAc. A quantitative determination of their nature, length, and number is subject to the same limitations quoted above for ketal analysis. It is also likely that hydrolyzable links occur not only at branch sites but also within a chain, in accordance with Structures IIIb and IIIc in Ref. 3. Therefore, a quantitative analysis may be impossible.

In analyzing PDVB directly with NMR techniques, it was found that the data were inconclusive. This is evident from Table 5 where there appears to be no correlation of polymerization variables and proton distribution.

The dominant structural elements of PDVB can thus be summarized on the basis of this and the previous [3] study and earlier literature [1], neglecting a number of additional possibilities such as branching from ester:



$$n_1 = 39\text{--}70\%; \quad n_2 = 16\text{--}20\%; \quad n_3 = 2\text{--}25\%; \quad n_4 = 5\text{--}20\%$$

TABLE 5. PDVB-NMR Spectra

No.	CH ₃		(Ether)		Acetal		Total 14	Initiator	Polymerization temp (°C)	Mol. wt.
	3	8	CH ₂ 8	CH 2	CH 1	CH 1				
865416 adjusted	3.00 3.70	6.06 7.46	1.65 2.03	0.65 0.80	11.36 14.0	R ₃ B-O ₂	0-35	48,000		
865436 adjusted	3.00 3.40	6.82 7.72	1.72 1.94	0.85 0.96	12.39 14.0	AIBN	30	73,000		
865445 adjusted	3.00 2.85	8.70 8.28	1.95 1.85	1.07 1.02	14.72 14.0	R ₃ B-O ₂	-50	30,000		
865462 adjusted	3.00 2.96	8.00 7.88	2.15 2.12	1.05 1.03	14.20 14.0	AIBN	25	50,000		
865470	3.00 2.79	9.00 8.36	2.00 1.86	1.05 0.98	15.05 14.0	R ₃ B-O ₂	0	63,000		
865484	3.00 3.02	8.21 8.24	1.81 1.82	0.90 0.91	14.01 14.0	AIBN, UV	30	61,500		
865487	3.00 2.74	9.08 8.28	2.16 1.97	1.10 1.00	15.35 14.0	AIBN	50	41,000		

EXPERIMENTAL

The same analytical instruments were used as in Part I [3].

Materials

Commercial grade Butvar and PVAc were precipitated three times from dioxane into methanol, removing dust particles by filtration.

PDVB prepared according to Ref. 3 was similarly purified. The polymers were dried in a vacuum at 50° until the weights were constant.

Solutions in spectrograde 1,4-dioxane were prepared by volumetric techniques. They were 0.105 M based on calculated 100% acetal units.

Standard 0.1 to 0.8 N aqueous hydrogen chloride solutions of identical ionic strength were prepared with the aid of analytical grade lithium chloride.

Procedure

To 9.50 ml of polymer solution at 30° was added, with magnetic stirring, 0.50 ml of the desired hydrogen chloride solution. The rate of addition was adjusted to permit the dissolving of any precipitate formed at the point of addition. The end of addition was taken as the starting time of hydrolysis. The resulting solutions ranged from 0.005 to 0.02 N HCl at a total ionic strength of 0.04 moles/liter and were 0.0998 M in calculated acetal groups. Higher and lower acid concentrations and different temperatures were found to qualitatively not change the course of hydrolysis.

For monitoring the hydrolysis by UV spectral changes, the solutions were transferred to preheated, tightly stoppered cells which were contained in a thermostated bath at $30 \pm 0.1^\circ$. The solutions were scanned against a nonhydrolyzing reference solution, thus eliminating interference from initially present carbonyl groups. The wavelength of the peaks and the degrees of absorbance were recorded initially every 20 min, later every hour.

Changes in viscosity during hydrolysis were followed initially every 5 min, later every 1 to 10 hr, until gelation occurred. An Ostwald-Fenske viscometer, which gave an initial flow time of

100 to 200 sec, was selected for individual polymer solutions. After charging of the preheated viscometers, the tubes were placed in a Fisher unitized kinematic viscosity bath. The flow times were determined in duplicate with maximum permissible errors of 0.3 sec while the hydrolysis proceeded within the viscometers.

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