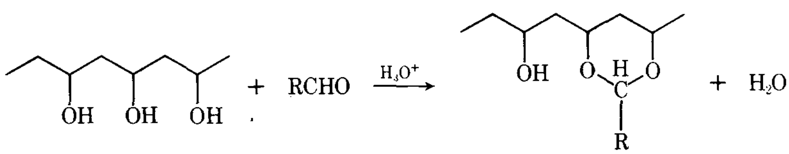
The Synthesis of Acetals of Poly(vinyl Alcohol) which Show Lower Consolute Temperature Behavior in Water

We have had occasion to study the preparation and properties of partial acetals of poly(vinyl alcohol) as part of a project aimed at preparing polymers which have solubilities in water which decrease as the temperature is raised.[1] We found that acetals of low substitution indeed have this property and are prepared simply by the direct reaction of the aldehyde in water in the presence of acid. We found that for certain aldehydes, the reaction takes place in quantitative fashion in water solution with very dilute mineral acid, up to 50% substitution. Normally, one does not use such mild conditions for acetal formation, but usually concentrated sulfuric (10*N*) or hydrochloric acid is used.[2,3] Preparations under these latter conditions necessitate the precipitation and isolation of the polymer. Our process for acetals starts with a PVA solution in 0.01*N* acid to which are added small amounts of aldehyde. The resulting solutions may be neutralized with a pinch of base and coated directly to yield films without any isolation or purification steps. Acetal formation under such mild conditions has been also noted for pentaerythritol.[4]

We find that with regard to acetal formation, those aldehydes which form weak hydrates most readily enter into acetal formation, e.g., acetaldehyde, propionaldehyde, and butyraldehyde.[5,6] Those which form stronger hydrates do not react under such mild conditions but require stronger acid catalysis, e.g., chloral or formaldehyde. With the more hydrophobic aldehydes, the water solubility property is obtained over a very narrow range of low substitutions. The acetals such as those derived from acetaldehyde have the property of temperature-inverse solubility in water over a wide range of temperatures and degree of substitutions, the cloud point decreasing with increasing D.S. We have found that the cloud point is also a simple and accurate measurement of the D.S. after a master curve is constructed relating the cloud point to the per cent substitution (D.S.).



EXPERIMENTAL

The acetal experiments were conducted on a solution of PVA (Elvanol 72-60, du Pont) to which the aldehyde and 0.5 ml of 18 *N* sulfuric acid were added. The amounts of reactants were chosen to give the desired substitution with a final concentration of poly(vinyl acetal) of 7.5%. The final degree of substitution was usually obtained within a 19-hr period. When no acid was employed, no reaction occurred as expected; however, with acetic acid the reaction took three weeks to complete. In this manner, we obtained the data plotted in Figure 1. The reaction rate and D.S. was determined by cloud point and also by the hydroxyl analysis using the pyridine–acetic anhydride method,[7] or by the direct aldehyde determination using hydroxylamine hydrochloride.[8] Chloral and formaldehyde failed to react under these conditions, but did when 10 ml sulfuric acid was used.

A typical synthetic procedure follows: Into a 2-liter, three-necked flask fitted with stirrer and condenser, containing 1 liter distilled water, is added 88 g (2 moles) PVA (Elvanol 72-60, du-Pont). The slurry is heated to 90° on a steam cone. After solution is complete, the contents are cooled to 20°, and 8.8 g (0.2 mol) acetaldehyde is added followed by 1 ml concentrated reagent sulfuric acid. The mixture is stirred for 7 hr and neutralized with dilute potassium bicarbonate. *The cloud point of the above preparation is 60–65° with precipitation, which is also a good analytical check for 20% substitution.*

Films of the above material and other similar compositions tend to have temperature latitude towards diffusing species. At elevated temperatures, the film becomes less permeable although the diffusion rate of the particular species wants to increase. In the cold, the acetal is less hydro-

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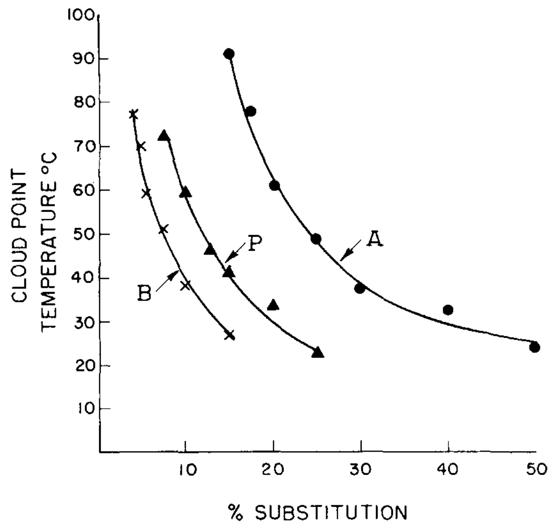

Fig. 1. Dependence of cloud point of 7.5% aqueous solutions of the partial acetals of poly(vinyl alcohol) on degree of substitution. Curve A, acetaldehyde acetal; curve P, propionaldehyde acetal; curve B, butyraldehyde acetal.

gen bonded and more permeable (soluble) although the diffusion rate tends to be slower in the cold. Hence, these films are temperature compensating.

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