Synthesis of Poly(vinyl benzal) from Poly(vinyl alcohol) in Nonaqueous Medium

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SYNOPSIS

Poly(vinyl alcohol) (PVA) is soluble only in water and so some important derivatives like esters cannot be prepared from PVA. The 100% conversion of PVA to acetal is also elusive as there is strong intermolecular and intramolecular hydrogen bonding. However, PVA can be dissolved in a nonaqueous medium in the presence of a small amount of $C_2H_5NO_3 \cdot DMSO(EN \cdot DMSO)$ and so a maximum extent of conversion may be possible. Here, we report the preparation of poly(vinyl benzal) (PVB) by acid-catalyzed homogeneous acetalization of PVA with benzaldehyde in a nonaqueous medium. The formation of PVB was confirmed by IR and ^{1}H-NMR spectra. The molecular mass of the polymer was determined by the GPC method. The PVB prepared had a degree of acetalization of 95 mol %. The glass transition temperature, T_g, was measured from differential scanning calorimetric (DSC) thermograms. Thermal stabilities were checked by thermogravimetric analysis (TGA) and differential thermogravimetry (DTG). A possible mechanism of three-step thermal decomposition of PVB is proposed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl alcohol) (PVA), unlike many polymers, is soluble in water. Therefore, the acetals of PVA are generally prepared by the action of PVA with aldehyde in aqueous medium.[1-3] The first poly(vinyl acetal)s were prepared by Herrmann and Haehnel[4] by reacting PVA with benzaldehyde. A survey of the literature indicates that the maximum extent of acetalization achieved up to now is 86 mol %,[5] although some patents claim 100 mol % acetalization.[6,7] Commercially available poly(vinyl acetal)s have a degree of acetalization of 70–85 mol %. Flory[8,9] reported that the highest degree of acetalization possible was only 86.46 mol % for 1,3-glycol structures and only 81.60 mol % for 1,2-glycol structures, assuming that only adjacent intramolecular hydroxyl groups were involved in the reaction and that the reaction was not reversible.

The highest degree of acetalization may be achieved if acetalization can be done in homogeneous medium. Theoretically, 100% conversion is possible only if PVA can be dissolved in a nonpolar solvent when hydrogen bonding is the least. PVA can be dissolved in an organic solvent in the presence of a catalytic concentration of $EN \cdot DMSO$. From the solution, poly(vinyl benzal) (PVB) was prepared by acid-catalyzed homogeneous acetalization of PVA, with benzaldehyde. The acetal was characterized by IR study, ^{1}H-NMR study, and GPC, TGA, DTG, and DSC methods.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA), white crystalline form (CDH reagent grade; viscosity-average molecular weight of 14,000; containing 1% of the acetate group), benzaldehyde (BDH reagent grade), dimethylformamide (DMF) (BDH reagent grade),
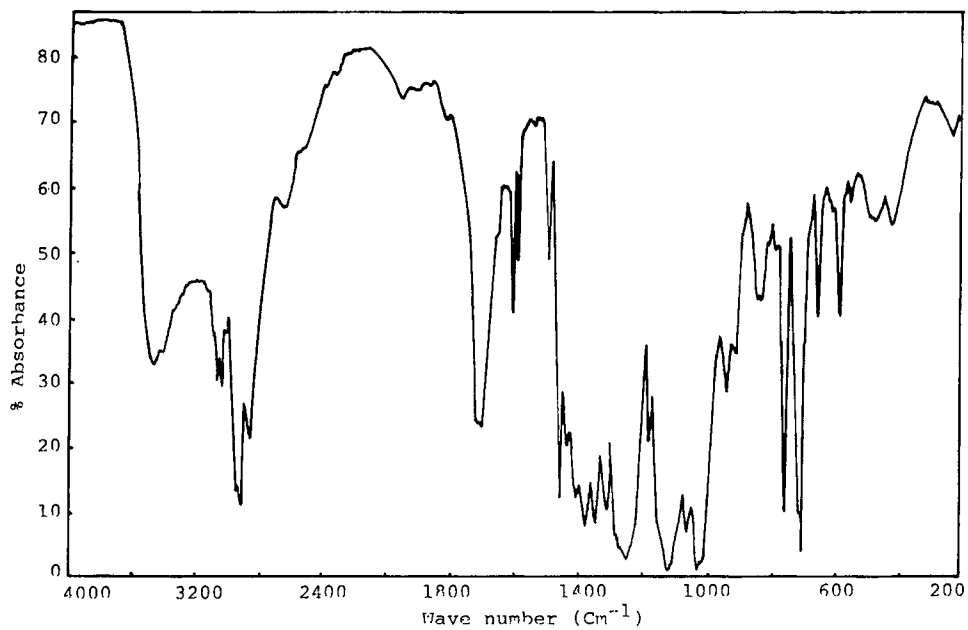
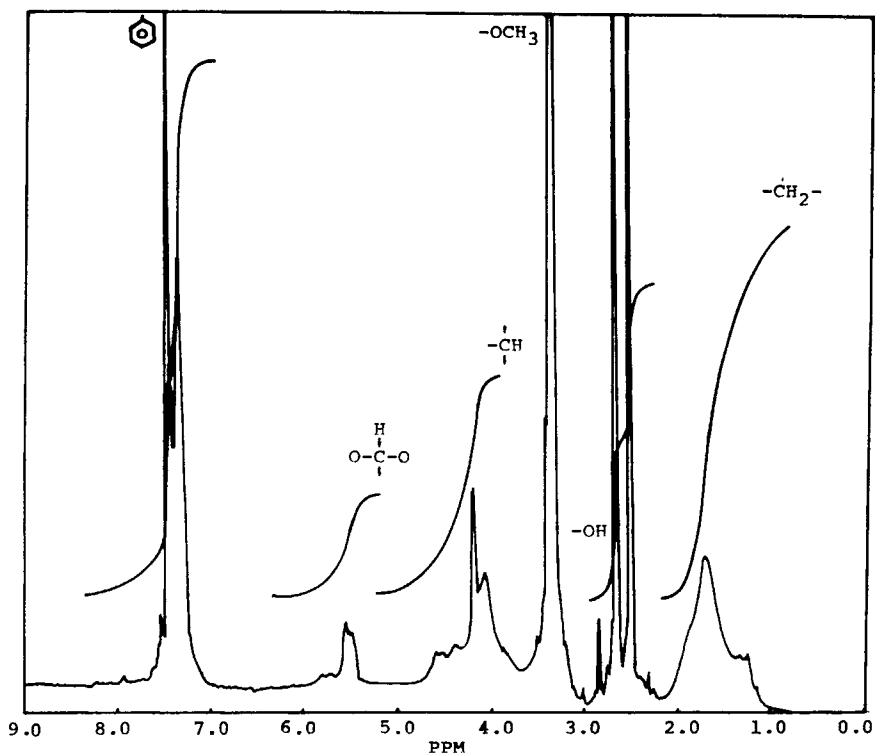**Figure 1**   IR spectra of PVB (in thin film).

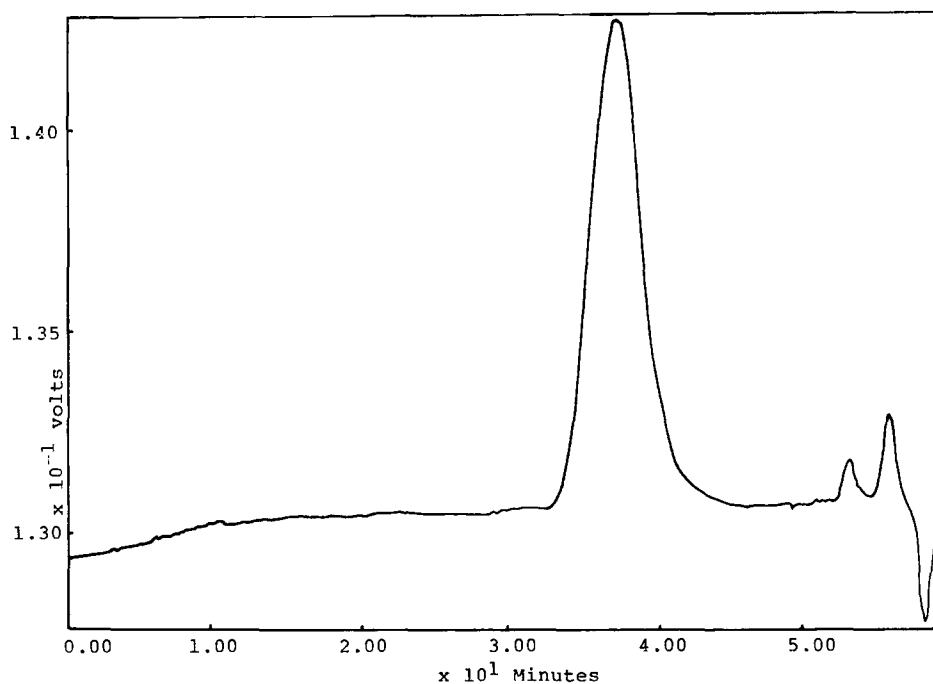**Figure 2**   The ¹H-NMR spectrum of the PVB (in DMSO).

Figure 3 GPC trace of PVB.

benzene (BDH reagent grade), and dimethyl sulfoxide (DMSO) (BDH reagent grade) were purified by distillation under a vacuum. Acrylic acid (BDH reagent grade) was purified according to the procedure adopted by O'Neil.[10] Para-toluene sulfonic acid (P-TSA) (BDH reagent grade) was recrystallized from benzene. Nitric acid (BDH reagent grade) and hydrogen peroxide (E. Merck) were used without further purification. EN·DMSO was prepared by the interaction of acrylic acid with concentrated HNO_3 in DMSO.[11] Purified 7.20 g (0.10 mol) of acrylic acid was mixed with 7.56 g (0.12 mol) of concentrated nitric acid in 100 cc of DMSO. The mixture was then kept at 50°C about 0.5 h. The mixture was cooled to room temperature and then treated with 30% H_2O_2 (v/v) slowly. A brisk evolution of gases took place. One of the gases was CO_2 as analyzed by analytical and IR methods. The mixture was then placed in a bath of ice-cold water for rapid cooling. When turbidity appeared, the mixture was taken out and kept at room temperature (25°C) overnight. A needle-shaped white crystalline product crystallized out. It was purified by recrystallization several times from acetone and stored over anhydrous calcium chloride.

By microanalysis, the elements present in EN·DMSO were found:

ANAL: Calcd: C, 28.40%; H, 6.50%; N, 8.284%; S, 18.93%.

Found: C, 28.39%; H, 6.47%; N, 8.271%; S, 18.91%.

The melting point of the compound was 150°C. The compound was characterized by IR and ^{1}H-NMR techniques.

Methods

The IR of the PVB was recorded in the region between 4000 and 200 cm^{-1} with a Perkin-Elmer spectrophotometer using a thin film of the polymer. The proton NMR was recorded with a WH-270 NMR spectrometer using DMSO as a solvent. The molecular mass of the polymer was determined by the GPC method with a Waters GPC-150C using tetrahydrofuran (THF) as the solvent at 25°C. The chromatograms were recorded using 10^5, 10^4, 10^3, 500, and 100 Å columns in series. The sample was eluted with a flow rate of 1 mL per min. The sample concentration used was 0.2% w/v and the injection volume was 50 μL. The percentage of the unconverted hydroxyl groups in the acetal was estimated by the acetylation method.

DSC was traced by Perkin-Elmer DSC-7 kinetic software in air at a scanning rate of 10°/min. TGA and DTG were done by a Perkin-Elmer thermal an-

Figure 4   DSC curve of PVB.

alyzer in air at a heating rate of 10°/min. Samples of 5 ± 1 mg were used.

RESULTS AND DISCUSSION

Preparation of PVB

PVA, 4.4 g (0.10 mol, based on —CH_2—CHOH— as the unit), was dissolved in 150 cc, of the solvent mixture of DMF and benzene (4 : 1 v/v) in the presence of EN · DMSO at 60°C in a round-bottom flask. The molar ratio of PVA to EN · DMSO was maintained at 1 : 1.4 × 10^{-3}. Then, benzaldehyde, 11.66 g (0.11 mol) taken in 100 cc. DMF, was slowly added to the PVA solution. Homogeneous acetalization was carried out by heating the reaction mixture for about 24 h at a temperature around 80°C. The water produced during the reaction was removed from the reaction medium as it was formed using the Dean and Stark principle.[12] After completion of the reaction, about 200 cc of the solvent was removed by distilling under vacuum. The acetal was precipitated by pouring into a mixed solvent of acetone and petroleum ether (1 : 2 by volume), four times in volume of the acetal solution with constant stirring. The acetal was then dissolved in chloroform and filtered to remove unreacted PVA. Chloroform was

removed by a rotary distillation apparatus. The insoluble white product was filtered off, dissolved in chloroform, and reprecipitated with benzene. This process was repeated several times to ensure the removal of PVA, benzaldehyde, P-TSA, and EN · DMSO. The IR spectrum of the final product was free from sulfonic and nitro groups, indicating the complete removal of P-TSA and EN · DMSO. The acetal was dried at 40°C and stored over anhydrous calcium chloride. The conversion to acetal was nearly 80–90%.

It is proposed that the following reactions take place between PVA and benzaldehyde for the production of PVB[1,13]:

Intramolecular acetalization of the 1,3-glycol group:

Table I   TGA Data of PVB in Air

| IDT$_1$ (°C) | % Wt Loss in 1st Stage | IDT$_2$ (°C) | % Wt Loss in 2nd Stage | IPDT (°C) | Temp at Varying % Wt Loss (°C) | | | | | | | |
					10	20	30	40	50	60	70	80
210	19.8	270	64.2	410	242.2	264.5	278.4	287.1	300	341.3	419.5	492.4

Intermolecular acetalization:
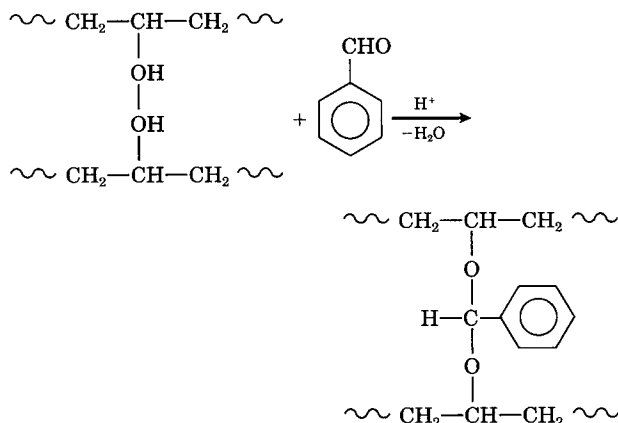
Intramolecular acetalization of the 1,2,-glycol group:
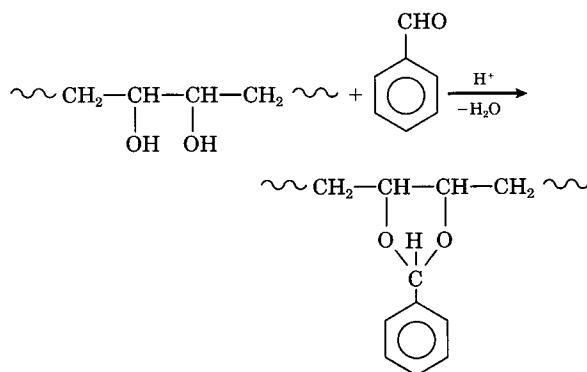
Analysis of PVB

The IR spectrum of PVB is presented in Figure 1. On acetalization, the O—H stretching vibration bands at 3500–3400 cm^{-1} weakened and shifted toward higher frequencies due to the cleavage of a polymeric hydrogen-bond chain.[14,15] The characteristic bands for PVB appeared at 3100, 3080, and 3040 cm^{-1} due to C—H stretching absorption. The peaks at 1600, 1585, 1500, and 1450 cm^{-1} account for C=C stretching and a band between 900 and

700 cm^{-1} accounts for C—H deformation vibrations. These bands confirmed the formation of the acetal. The bands at 1180, 1120, 1060, and 1020 cm^{-1} seem to relate to C—O—C—O—C stretching vibrations.[16] The band at 1735 cm^{-1} appears due to the C=O of the acetate group.

A typical ^{1}H-NMR spectrum for PVB is shown in Figure 2. The signals[16] observed at 1.3–1.9, 4.03, 5.5, and 7.3–7.95 ppm are due to methylene (—CH$_2$—), methine $\left(-\overset{|}{\underset{|}{C}}H-\right)$, dioxymethine $(O-\overset{|}{\underset{|}{C}}H-O)$, and aromatic protons, respectively.

The signals at 2.8 and 3.3 ppm are due to remaining the hydroxyl group (—OH) and methoxy (—OCH$_3$) protons, respectively.[17] The signal at 7.5–7.95 ppm which is due to the aromatic protons confirmed the formation of the acetal.

From GPC analysis, the weight-average molecular weight ($\bar{M}_w$) of the acetal was found to be 65,000, relative to polystyrene standards of molecular weights 1.8 × 10^6, 498,000, 110,000, 20,400, 10,300, 4000, and 2100. The GPC trace of PVB is presented in the Figure 3.

The percentage of unconverted hydroxyl groups in the acetal was estimated by an acetylation process.[18] The acetylation was done with a mixture richer in acetic anhydride (1 vol of acetic anhydride, 3 vol of pyridine) for 10 h at 55–60°C. As a result, the unreacted acetic anhydride was hydrolyzed to acetic acid and was then titrated with standard sodium hydroxide. Thus, the percentage of unconverted hydroxyl groups can be estimated. The results indicated that about 95% of the hydroxyl group of PVA had been converted to acetal groups. The extent of the acetalization reaction was also calculated from the integrals of the various NMR resonances. The relative abundance of each proton calculated from the normalized integrations indicates the extent of the reaction in homogeneous acetalization. The comparison of dioxymethine protons at 5.5 ppm and methylene protons at 1.3–1.9 ppm yields a ratio
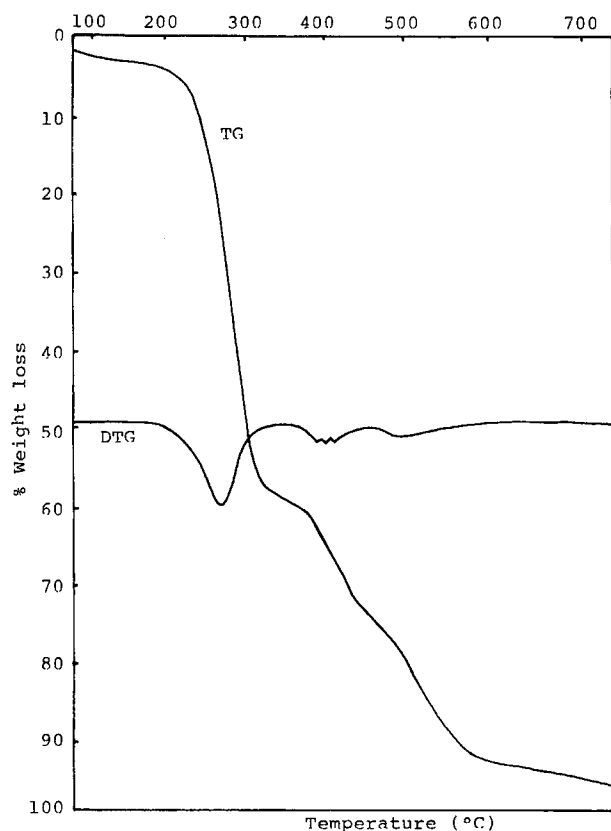
Figure 5 TGA and DTG curve of PVB in air at heating rate of 10°C/min.

To check the thermal stability of the acetal, the TGA and DTG curves were recorded in air. Figure 5 shows typical TGA and DTG curves of PVB. The TGA data are presented in Table I. From DTG curves it was observed that the acetal decomposed in three stages.[20] The decomposition temperatures were determined by the intersection of the tangent to the steepest part of the TGA curve with its baseline. In the first stage degradation. H_2O was removed from neighboring pairs of unconverted hydroxyl groups of the acetal.[21] The initial decomposition temperature (IDT_1) for the first stage of the PVB was 210°C. The second stage decomposition was due to the removal of CO, CO_2, hydrocarbons, etc.[22-24] from the acetal. The initial decomposition temperature (IDT_2) for the second stage of the acetal was 270°C. The third stage of decomposition was due to the production of carbon at temperatures above 500°C. An integral procedural decomposition temperature ($IPDT$)[25] was also found to be 410°C.

The method may lead to the synthesis and development of poly(vinyl esters)[11] if we use an acid in place of aldehyde. However, 100% conversion of all the hydroxyl groups is still elusive.

of about 1 : 3.6 compared to the expected 1 : 4 value. The ratio of dioxymethine proton to aromatic protons from the experimental value is 1 : 5, as expected. The ratio of dioxymethine proton to methine protons was found to be 1 : 2 experimentally, as expected. So, the extent of the reaction is around 90% from the NMR data.

The acetal was soluble in a number of organic solvents like DMF, DMSO, ethanol, acetone, tetrahydrofuran, and chloroform and in solvent mixtures like DMF and benzene, DMF and toluene, DMSO and benzene, and DMSO and toluene. It was observed that the percentage of conversion of hydroxyl groups of PVA to acetal groups reduced the hydrogen bonding and influenced the solubility of the acetal.[19]

A typical DSC thermogram for the PVB is shown in Figure 4. From the DSC studies, the glass transition temperature, T_g, was found to be 70°C. The melting point of PVB was 205°C.

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