

Preparation of Poly(vinyl butyral) with High Acetalization Rate

P. CHETRI, N. N. DASS

Department of Chemistry, Dibrugarh University, Dibrugarh 786 004, India

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ABSTRACT: Poly(vinyl alcohol) (PVA) can be dissolved in a nonaqueous medium in the presence of catalytic concentration of ethyl nitrate dimethyl sulfoxide, $C_2H_5ONO_2 \cdot DMSO$ (EN · DMSO). From the PVA solution, poly(vinyl butyral) (PVBu) was prepared by acid-catalyzed homogeneous acetalization of PVA with butyraldehyde. The formation of PVBu was confirmed by IR and 1H -NMR spectra. The degree of acetalization of PVBu was found to be 95 mol %, which was verified by 1H -NMR data and acetylation method. The molecular mass of the polymer was determined by GPC method. 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). The acetal decomposed in three stages. The corresponding initial decomposition temperatures were found to be 285, 390, and above 500°C. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1182–1186, 2001

Key words: poly(vinyl butyral); catalytic concentration; acetalization.

INTRODUCTION

A significant amount of research has been carried out on the synthesis of poly(vinyl acetal),^{1–3} especially poly(vinyl butyral) (PVBu), due to its excellent commercial applications. Minamino⁴ had reported the preparation of PVBu with a degree of acetalization of 80–90.5 mol %. Imai and his co-workers⁵ reported the synthesis of PVBu with degree of acetalization of 7.5 mol % by the Kornblum reaction. The degree of acetalization has an important impact on the properties of the acetals. Generally, the hydrophobic character, the solubility in weakly polar solvents and insulating properties of acetals improve with the increase of degree of acetalization.⁶ The higher the degree of acetalization, the lower is the softening point.

Because acetals are not soluble in water, the acetals of PVA were prepared by the action of aldehydes on PVA in aqueous medium.^{7,8} Because the contact time of the reactants is not very long, the maximum extent of acetalization achieved so far is 86 mol %.⁹ According to Flory,¹⁰ the maximum 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.

Theoretically, 100% acetalization of PVA is possible if the reaction is carried out homogeneously in a nonaqueous solvent. We have already reported the synthesis of poly(vinyl benzal)¹¹ and poly(vinyl formal)¹² with a degree of acetalization about 90–95 mol % in DMF/benzene using a catalytic concentration of EN · DMSO. In this article we are reporting the preparation of PVBu in a nonaqueous medium from PVA and

Correspondence to: N. N. Dass.

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butyraldehyde. The acetal was characterized by IR study, $^1\text{H-NMR}$ 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) was used without further purification. Butyraldehyde (BDH reagent grade), dimethyl formamide (DMF) (BDH reagent grade), 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.¹³ *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.¹⁴ 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 $^1\text{H-NMR}$ techniques.

Methods

The IR of the PVBu was recorded in the region between 4000 and 200 cm^{-1} with a Perkin-Elmer

spectrophotometer using a thin film of the polymer. The thin film of the polymer was made¹⁵ by dissolving PVBu in chloroform and then the concentrated solution (5%) was directly cast on a leveled clean glass plate. The film was dried under vacuum at 50°C for a week. Thickness of the film was about 0.01 cm. The proton NMR was recorded with a WH270 NMR spectrometer. The spectrum was obtained on solution containing 10% (W/V) PVBu in DMSO with tetramethylsilane as an internal reference. The molecular mass of the polymer was determined by the GPC method with a Waters Liquid chromatograph equipped with a GPC-150 C RI detector and μ styragel columns. The columns were 10⁶, 10⁵, 10⁴, 500, and 100A° in series. THF was used as the eluent at a flow rate of 1 mL per min, and the molecular weight calibration was done using polystyrene standards. 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.¹⁶

DSC was traced by Perkin-Elmer DSC-7 kinetic software in air at a scanning rate of 10°/min. Kinetic parameters such as activation energy, order of reaction, and rate constant of melting were evaluated by the method of Freeman and Carroll.¹⁷ TGA and DTG were done by a Perkin-Elmer Thermal Analyzer in air at a heating rate of 10°/min. using 5 ± 1 -mg samples.

RESULTS AND DISCUSSION

Preparation of PVBu

PVA, 4.4 g (0.10 mol, based on $-\text{CH}_2-\text{CHOH}-$ 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 $1 : 1.4 \times 10^{-3}$. Then, butyraldehyde, 7.92 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 90°C. The water produced during the reaction was removed from the reaction medium as it was formed using the Dean and Stark principle.¹⁸ After completion of the reaction, about 200 cc of the solvent was removed by distilling under vacuum. The acetal was precipitated by pouring

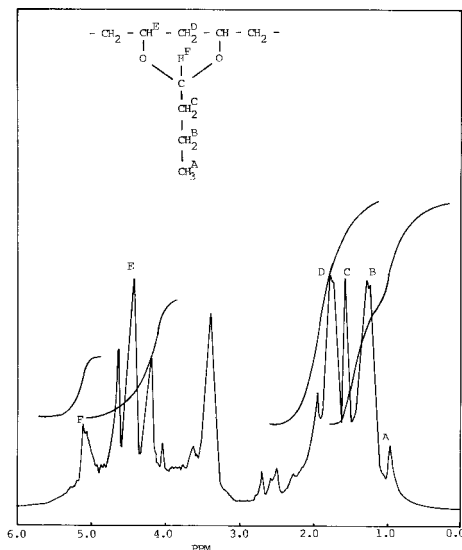


Figure 2 The $^1\text{H-NMR}$ spectrum of the PVBu (in DMSO).

thine (O—CH—O) proton confirmed the formation of the butyral.

The degree of acetalization of the acetal was calculated from the integrals of the various NMR resonances. The comparison of dioxymethine proton (F) at 5.01 ppm and methylene protons (D) at 1.91 ppm yield a ratio of about 1 : 3.8 compared to the expected 1 : 4 value. The ratio of dioxymethine proton (F) to methine proton (E) was found to be 1 : 1.95 compared to the expected 1 : 2 value. So, the extent of the reaction is around 95% from the NMR data. The extent of the acetalization reaction was also calculated by the acetylation method. 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.

From GPC analysis, the weight-average molecular weight (\bar{M}_w) of the acetal was found to be 55,000, 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 PVBu is presented in the Figure 3.

The DSC thermogram for the PVBu is shown in Figure 4. From the DSC studies, the glass tran-

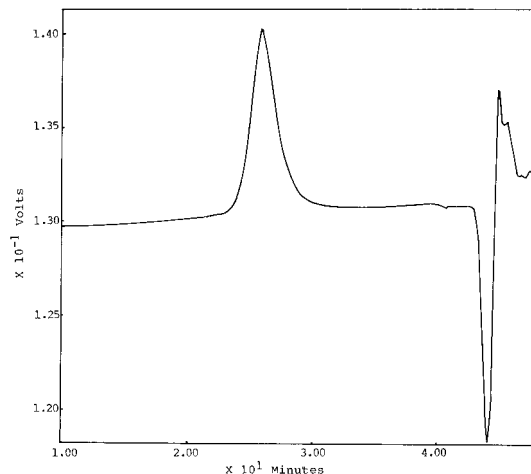


Figure 3 GPC trace of PVBu.

sition temperature, T_g , was found to be 41°C. The activation energy, E , of melting was $38.26 \pm 0.52 \text{ kJ mol}^{-1}$. The order of melting reaction of the acetal was calculated as $n = 1.01 \pm 0.01$. The rate constant, k , was found to be $1.86 \times 10^2 \pm 1.21 \text{ s}^{-1}$. The acetal was soluble in a number of organic solvents like DMF, DMSO, ethanol, methanol, dioxane, tetrahydrofuran, chloroform, glacial acetic acid, cyclohexanone, ethyl acetate, etc. It was insoluble in aliphatic hydrocarbons as well as in drying oils, waxes, and water. So, the extent of crosslinking reaction²³ in acetalization process is practically very small to be neglected in the homogeneous reaction method developed.

The TGA and DTG traces for the PVBu are presented in Figure 5. From the DTG curve it was observed that the acetal decomposed in three stages.²⁴ The decomposition temperatures were determined by the intersection of the tangent to

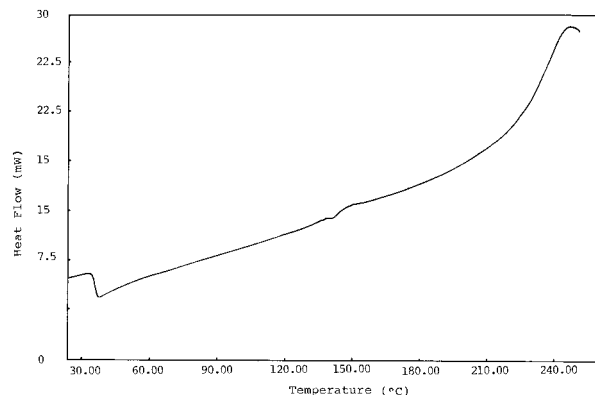


Figure 4 DSC curve of PVBu.

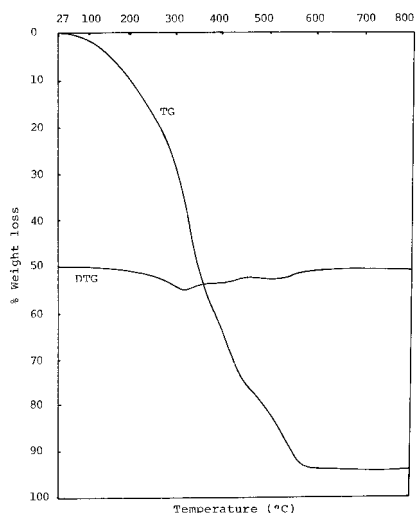


Figure 5 TGA and DTG curves of PVBu in air at heating rate of 10°C/min.

the steepest part of the TGA curve with its baseline. The initial decomposition temperature (IDT_1) for the first stage was found to be at 285°C, and the percentage weight loss at this stage was 20% and maximum decomposition was take place at 320°C. The weight loss at this stage was mainly due to removal of H_2O from the neighbouring pairs of unconverted hydroxyl groups of the acetal.²⁵ The initial decomposition temperature (IDT_2) for the second stage was found to be at 390°C, with a corresponding weight loss of 56% at this stage and maximum decomposition occurs at 460°C. The second stage decomposition was due to the removal of CO , CO_2 , hydrocarbons, etc.^{26,27} from the acetal. The third stage decomposition was due to the production of carbon at temperature above 500°C. Integral procedural decomposition temperature ($IPDT$)²⁸ was found to be 380°C.

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