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Synthesis And Characterization Of Poly(Vinyl Propional) With High Acetalization Rate

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ABSTRACT

In this paper an attempt has been made to dissolve poly(vinyl alcohol) (PVA) in non-aqueous medium in the presence of catalytic concentration of $C_2H_5ONO_2 \cdot DMSO$ (EN-DMSO). Poly (vinyl propional) (PVPL) was prepared by acid catalysed homogeneous acetalization of PVA of molecular weight 14,000 with propanaldehyde. The formation of the acetal was confirmed by IR and 1H -NMR spectroscopy. The PVPL prepared had a degree of acetalization of 92 mol%. The molecular mass of the acetal was determined by gel permeation chromatography (GPC). The glass transition temperature, T_g and other kinetic parameters were measured from differential scanning calorimetric (DSC) thermograms. Thermal stabilities were checked by thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) method. The acetal decomposed in three stages. The corresponding initial decomposition temperatures were found to be 280, 410 and above 500°C. © 2007 Trade Science Inc. - INDIA

KEYWORDS

Ethyl nitrate dimethyl
sulfoxide;
Poly (vinyl alcohol);
Propanaldehyde;
Poly (vinyl propional);
Acetalization.

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]. A survey of the literature indicates that the maximum extent of acetalization

achieved up to now has been 86 mol%, although some patents claimed 100 mol% acetalization^[4,5]. Commercially available poly (vinyl acetal)s have a degree of acetalization of 70-85 mol%. Flory^[6] postulated 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

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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 non-polar solvent when a hydrogen bonding is the least. PVA can be dissolved in a solvent mixture of DMF and benzene(4:1 v/v) in the presence of catalytic concentration of ethyl nitrate dimethyl sulfoxide, $C_2H_5ONO_2 \cdot DMSO$ (EN \times DMSO). From this solution poly(vinyl-propional) (PVPL) was prepared by acid-catalysed homogeneous acetalization of PVA, with propionaldehyde. The acetal was characterized by IR study, 1H -NMR study, GPC, TGA, DTG and DSC methods.

EXPERIMENTAL

Materials

PVA, white crystalline form (CDH reagent grade; viscosity average molecular weight of 14,000; containing 1% of residual acetate group) was used without further purification. Propionaldehyde (BDH reagent grade), dimethyl formamide, DMF (Merck, reagent grade), benzene (Ranbaxy, reagent grade), Dimethyl sulfoxide, DMSO (Merck reagent grade), were purified by distillation under vacuum. Acrylic acid (Merck, reagent grade) was purified according to the procedure adopted by O'Neil^[7]. Para toluene sulfonic acid, PTSA (BDH reagent grade) was recrystallized from benzene. Nitric acid (Ranbaxy, reagent grade) and hydrogen peroxide were of analytical grade and were used without further purification.

EN \times DMSO was prepared as before^[8] by interaction of acrylic acid with conc. HNO_3 in DMSO. The compound was characterized by analytical and spectral data.

Preparation of PVPL

PVA (4.4g, 0.10 mol based on $-CH_2-CHOH-$ as the repeat unit) was dissolved in 150 ml of a solvent mixture of DMF and benzene(4:1, v/v) in presence of EN \cdot DMSO at 60°C in a round-bottom flask. The molar ratio of PVA to EN \cdot DMSO was maintained^[9] at $1:1.4 \times 10^{-3}$. Propionaldehyde 6.38g (0.11 mol) taken in 100 ml DMF, was then added slowly to the PVA solution. Homogeneous acetalization was carried out

by heating the reaction mixture for about 24h 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^[10]. After completion of the reaction 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 v/v), 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 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 complete removal of unreacted PVA, propionaldehyde, PTSA and EN \cdot DMSO. The acetal was dried at 40°C and stored over anhydrous calcium chloride.

Methods

The IR of the acetal was recorded in the region between 4000 cm^{-1} and 200 cm^{-1} with a Perkin-Elmer spectrophotometer using thin film of the polymer. The proton NMR was recorded with a WH 270 NMR spectrometer. The spectrum was obtained on solution containing 10%(w/v) PVAL, in DMSO with tetramethylsilane as an internal reference. Molecular weight was determined by gel permeation chromatography (GPC) method using THF as the solvent. The percentage of the unconverted hydroxyl group in the acetal was estimated by acetylation method^[11].

DSC was traced by Perkin-Elmer DSC-7 kinetic software in air at a scanning rate of 10°C/min. Kinetic parameters such as activation energy, order of reaction, and rate constant of melting were evaluated by the method Freeman and Carroll^[12]. TGA and DTG were performed using a Shimadzu, DT-30B thermal analyzer in air at a heating rate of 10°C/min using 5 ± 1 mg samples.

RESULTS AND DISCUSSION

It is proposed that the following reaction may take place between PVA and propionaldehyde for the production of PVPL^[13].

The IR spectrum of PVA showed some interesting change when reacted with aldehyde. On acetalization, the O-H stretching vibration bands at 3500-

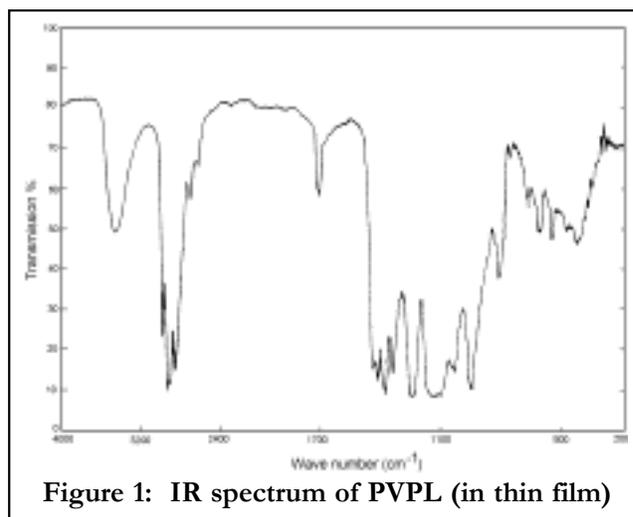
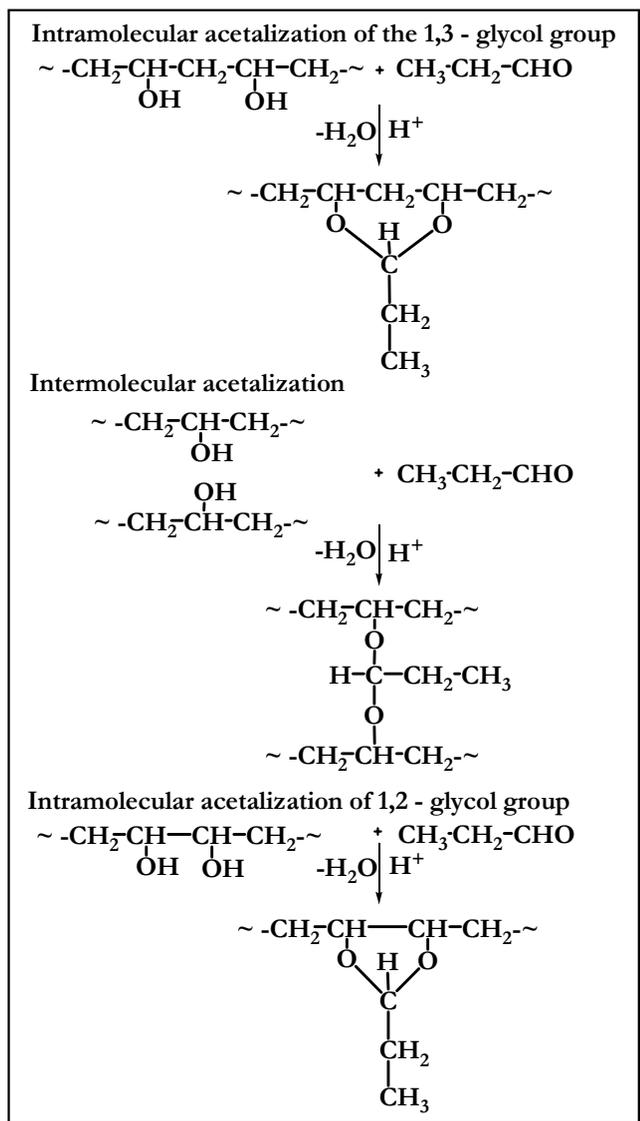
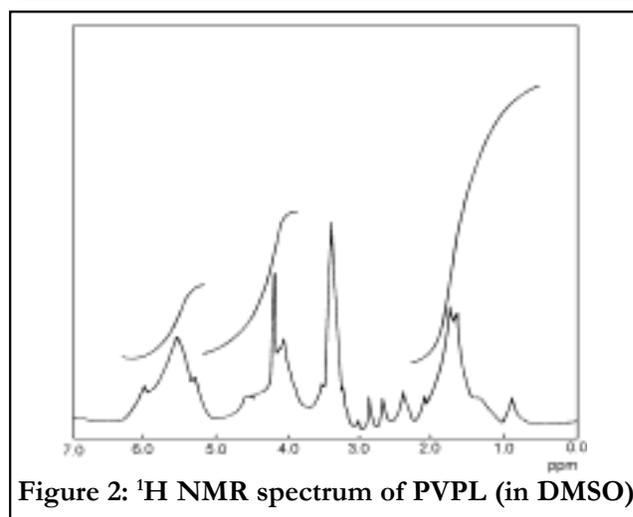


Figure 1: IR spectrum of PVPL (in thin film)

Figure 2: ¹H NMR spectrum of PVPL (in DMSO)

3400cm^{-1} weakened and shifted towards higher frequencies due to cleavage of the polymeric hydrogen bond chain^[14]. The IR spectrum of PVPL is presented in figure 1. In the region of C-H bonding vibration, the characteristic bonds^[15] for PVPL, appeared at 1355 , 1252 and 966cm^{-1} . The bands at 1180 , 1136 , 1098 and 1020cm^{-1} seem to relate to C-O-C-O-C stretching vibrations. These bands confirmed the formation of the acetal. The band at 1735cm^{-1} appeared to be due to the C=O of the residual acetate group.

A typical ¹H-NMR spectrum for PVPL is shown in figure 2. The signals observed at 0.92, 1.3-1.9 and 4.1 ppm are due to methyl (-CH₃), methylene (-CH₂-) and methine (-CH-) protons respectively^[16]. The signals at 5.01 ppm appears due to the dioxymethine (O-CH-O) proton^[17] confirmed the formation of the acetal.

From GPC analysis the weight average molecu-

lar weight (\bar{M}_w) of the acetal was found to be 20,000 to relative polystyrene standards of molecular weights 1.8×10^6 , 498000, 110000, 20400, 10300, 4000 and 2100.

The percentage of unconverted hydroxyl groups in the acetal was estimated by acetylation process. The acetylation was done with a mixture richer in acetic anhydride (1 vol. of acetic anhydride, 3 vol. of pyridine) for ten hours at 60°C . As a result, the unreacted acetic anhydride was hydrolyzed to acetic acid and was titrated with standard sodium hydroxide. Thus the percentage of unconverted hydroxyl groups can be estimated. The results indicated that 92% of the hydroxyl group of PVA had been converted to acetal groups.

The acetal was soluble in a number of organic solvents like DMF, DMSO, dioxane, ethanol, chloroform, glacial acetic acid, tetrahydrofuran, ethyl acetate, glycol, acetone etc.

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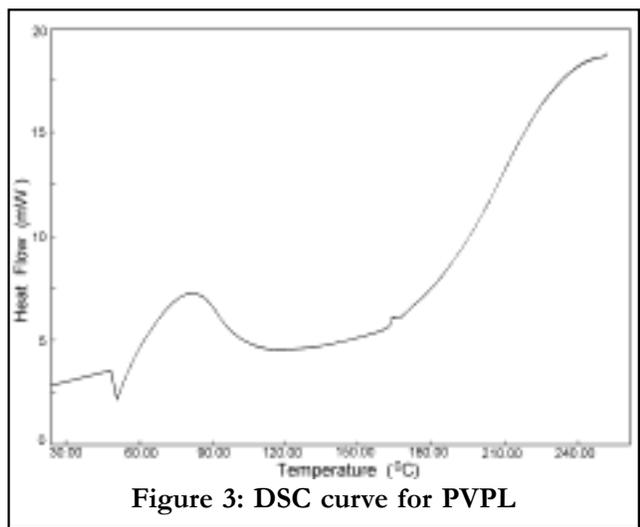


Figure 3: DSC curve for PVPL

A typical DSC thermogram for PVPL is shown in figure 3. From the DSC studies the glass transition temperature, T_g , was found to be 50°C. The activation energy, E , of melting was 34.26±0.51 kJmol⁻¹. The order of melting reaction of the acetal was calculated as $n=1.01±0.02$. The rate constant, k , was found to be $1.22 \times 10^2 \pm 1.32 \text{ s}^{-1}$.

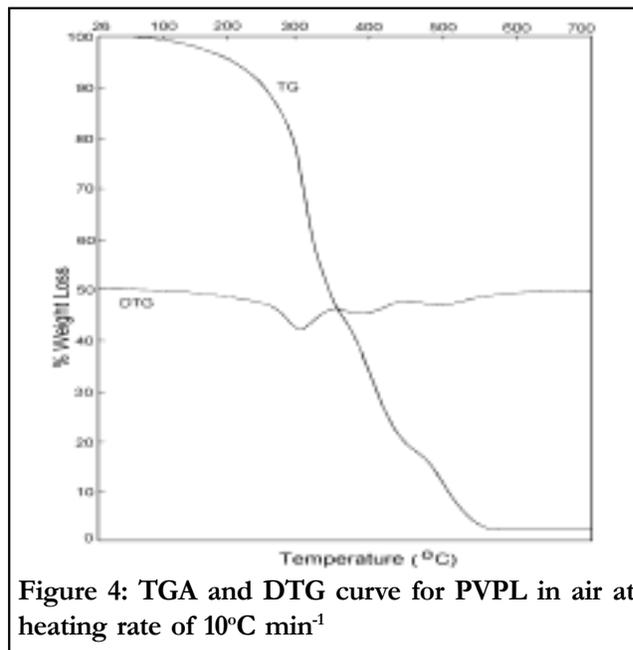
From TGA and DTG curves (Figure 4) it was observed that the acetal decomposed in three steps^[18]. The decomposition temperatures were determined by the intersection of the tangent to the steepest part of the TGA curve with its baseline. Thermal oxidation of the PVPL began with cleavage of the acetal ring^[19-20] and also removal of H₂O from neighboring pairs of unconverted hydroxyl groups of the acetal. The initial decomposition temperature (IDT₁) for the first stage was 280°C. The second stage decomposition was due to the removal of CO, CO₂, hydrocarbons^[21,22] etc., from the PVPL. The initial decomposition temperature (IDT₂) for the second stage was 410°C. The third stage decomposition was due to the production of carbon at a temperature above 500°C. Also, the integral procedural decomposition temperature^[23] (IPDT) was found to be 375°C.

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Figure 4: TGA and DTG curve for PVPL in air at heating rate of 10°C min⁻¹

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