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# Preparation of poly(vinyl formal) of high acetalization

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Poly(vinyl alcohol) (PVA) can be dissolved in a non-aqueous medium in the presence of catalytic concentrations of $C_2H_5ONO_2$.DMSO(EN.DMSO). Poly(vinyl formal) (PVF) of 90% acetalization was prepared by acid catalysed homogeneous formalization of PVA of molecular weight 14000 with paraformaldehyde. The formation of the formal was confirmed from the i.r. and $^1H$ n.m.r. spectra. The molecular weight of the polymer was 104000 as determined by g.p.c. The glass transition temperature ($T_g$), activation energy ($E$), order of reaction ($n$) and rate constant of melting ($k$) were computed from d.s.c. thermograms. $T_g$, $E$, $n$ and $k$ were found to be 52°C, $33.29 \pm 0.71\,kJ\,mol^{-1}$, $0.82 \pm 0.01$ and $1.29 \times 10^2 \pm 1.11\,s^{-1}$, respectively. Thermal stabilities were checked by t.g.a. and d.t.g. The formal decomposed in three stages. The corresponding initial decomposition temperatures were found to be 300, 465 and above 500°C. A possible mechanism for the three-step thermal decomposition of PVF is proposed. © 1997 Elsevier Science Ltd.

**(Keywords: poly(vinyl alcohol) (PVA); poly(vinyl formal) (PVF); ethyl nitrate · DMSO (EN · DMSO); paraformaldehyde)**

## INTRODUCTION

The only practical solvent for poly(vinyl alcohol) (PVA) is water. Therefore, the acetals of PVA were generally prepared by the action of PVA with aldehyde in aqueous medium[1-4]. As a result the maximum extent of acetalization achieved up to now has been 86 mol%. Flory[5,6] 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 non-polar solvent when the hydrogen bonding is the least. PVA can be dissolved in an organic solvent in the presence of a catalytic concentration of EN.DMSO. From this solution poly(vinyl formal) (PVF) was prepared by acid catalysed homogeneous acetalization of PVA, with paraformaldehyde. The formal was characterized by i.r., $^1H$ n.m.r., g.p.c., viscometry, t.g.a., d.t.g. and d.s.c. studies and other analytical methods.

## EXPERIMENTAL

### *Materials*

Poly(vinyl alcohol), white crystalline form (CDH reagent grade; viscosity average molecular weight of 14000) contained 1% of residual PVA. Paraformaldehyde (BDH reagent grade) was recrystallized from benzene. Dimethylformamide (DMF) (BDH reagent grade), benzene (BDH reagent grade), dimethyl sulfoxide (DMSO) (BDH reagent grade), were purified by distillation under vacuum. Acrylic acid (BDH reagent grade) was purified according to the procedure adopted by O'Neil[7]. *para*-Toluenesulfonic 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 interaction of acrylic acid with concentrated $HNO_3$ and subsequent decarboxylation with $H_2O_2$ solution. The product was a white crystalline solid[8].

### *Methods*

The i.r. spectrum of the formal 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 was prepared by dissolving PVF in chloroform and then the concentrated solution (5%) was directly cast on a levelled, clean glass plate[9]. The film was dried under vacuum at 60°C for one week. The thickness of the film was 0.01 cm. The $^1H$ n.m.r. spectrum was recorded with a WH-270 n.m.r. spectrometer. The spectrum was obtained in a solution containing 10% (w/v) PVF in DMSO with tetramethylsilane as an internal reference. The molecular weight was determined by g.p.c. using a Waters liquid chromatograph equipped with a GPC 150C RI detector and $\mu$Styragel columns. The columns were $10^6$, $10^5$, $10^4$, 500 and 100 Å in series. Tetrahydrofuran (THF) was used as the eluent at a flow rate of PVAc $1\,ml\,min^{-1}$ and the molecular weight calibration was performed using polystyrene standards. The sample concentration used was 0.2% (w/v) and the injection volume was $50\,\mu l$. The percentage of the unconverted

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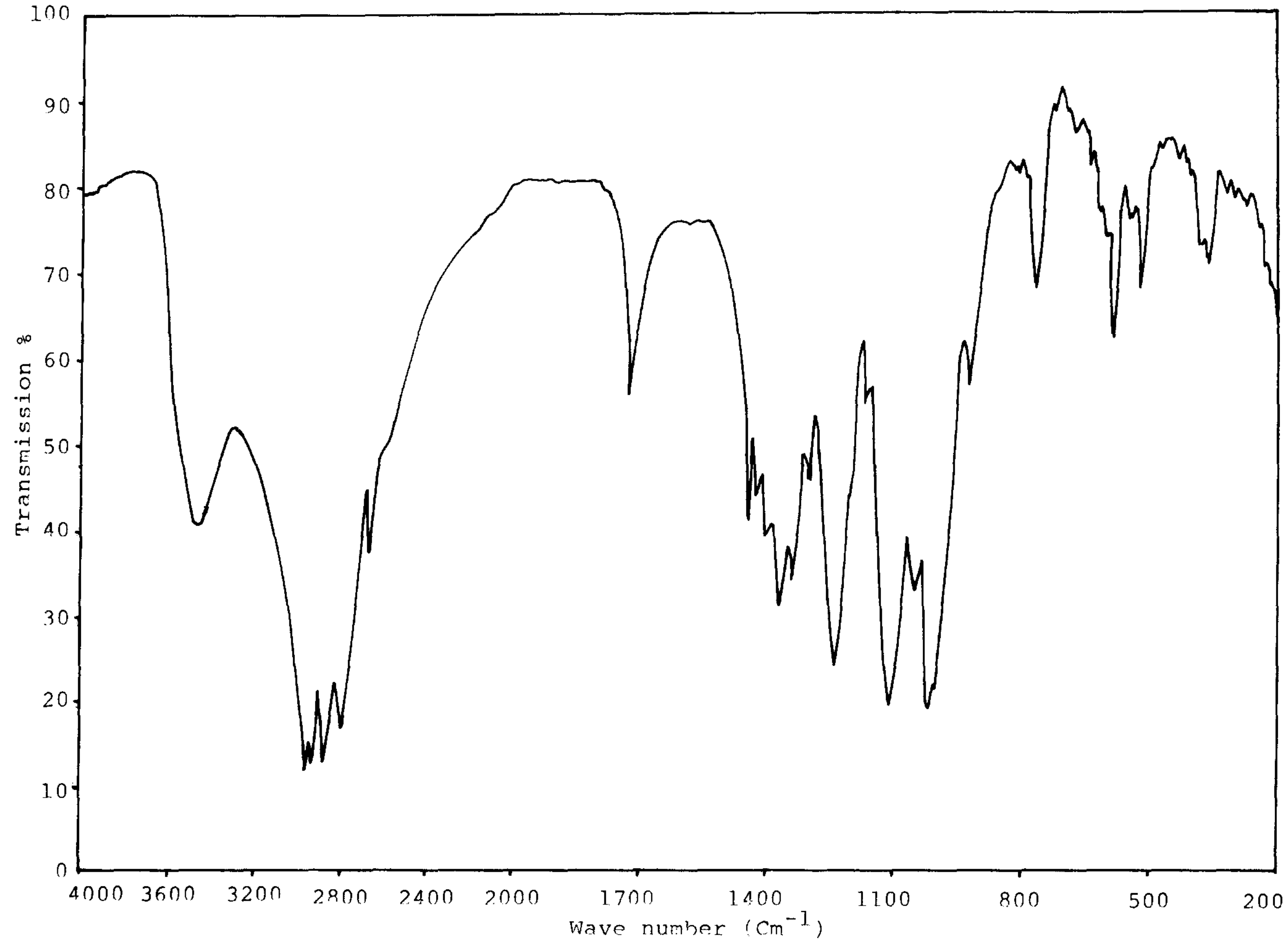


**Figure 1** I.r. spectrum of PVF (in thin film)

hydroxyl groups in the formal was estimated by the acetylation method[10].

The d.s.c. thermogram was traced by Perkin-Elmer DSC-7 kinetic software in air at a scanning rate of 10°C min$^{-1}$. Kinetic parameters such as activation energy, order of reaction and rate constant of melting were evaluated by the method of Freeman and Carroll[11] from the d.s.c. endotherm. The t.g.a. and d.t.g. were carried out by a Perkin-Elmer thermal analyser in air at a heating rate of 10°C min$^{-1}$; 5 ± 1 mg of sample was used.

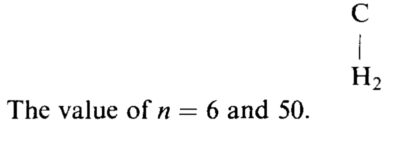
### *Preparation of PVF*

Poly(vinyl alcohol) (4.4 g, 0.10 mol, based on $-CH_2-CHOH-$ as the unit) was dissolved in 150 ml of a solvent mixture of DMF and benzene (4/1, v/v) in the presence of EN.DMSO at 60°C in a round-bottomed flask. The molar ratio of PVA to EN.DMSO was maintained at 1:1.4 × 10$^{-3}$. Paraformaldehyde (3.3 g, 0.11 mol), in 100 ml of DMF, was then 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 the solvent was removed by distilling under vacuum. The formal was precipitated by pouring into a mixed solvent of acetone and petroleum ether (1/2, v/v), four times the volume of the formal solution, with constant stirring. The formal 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, paraformaldehyde, *p*-TSA and EN.DMSO[13]. The acetal was dried at 40°C and stored over anhydrous calcium chloride. The conversion into acetal was nearly 90%.

## RESULTS AND DISCUSSION

It is proposed that the following reactions take place between PVA and paraformaldehyde for the production of PVF[14].

### *Intramolecular acetalization of the 1,3-glycol group*



$$\sim\sim CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2\sim\sim + (CH_2O)_n.H_2O \xrightarrow[-H_2O]{H^+} \sim\sim CH_2-\underset{O-CH_2-O}{\underbrace{CH-CH_2-CH}}-CH_2\sim\sim$$

The value of $n$ = 6 and 50.

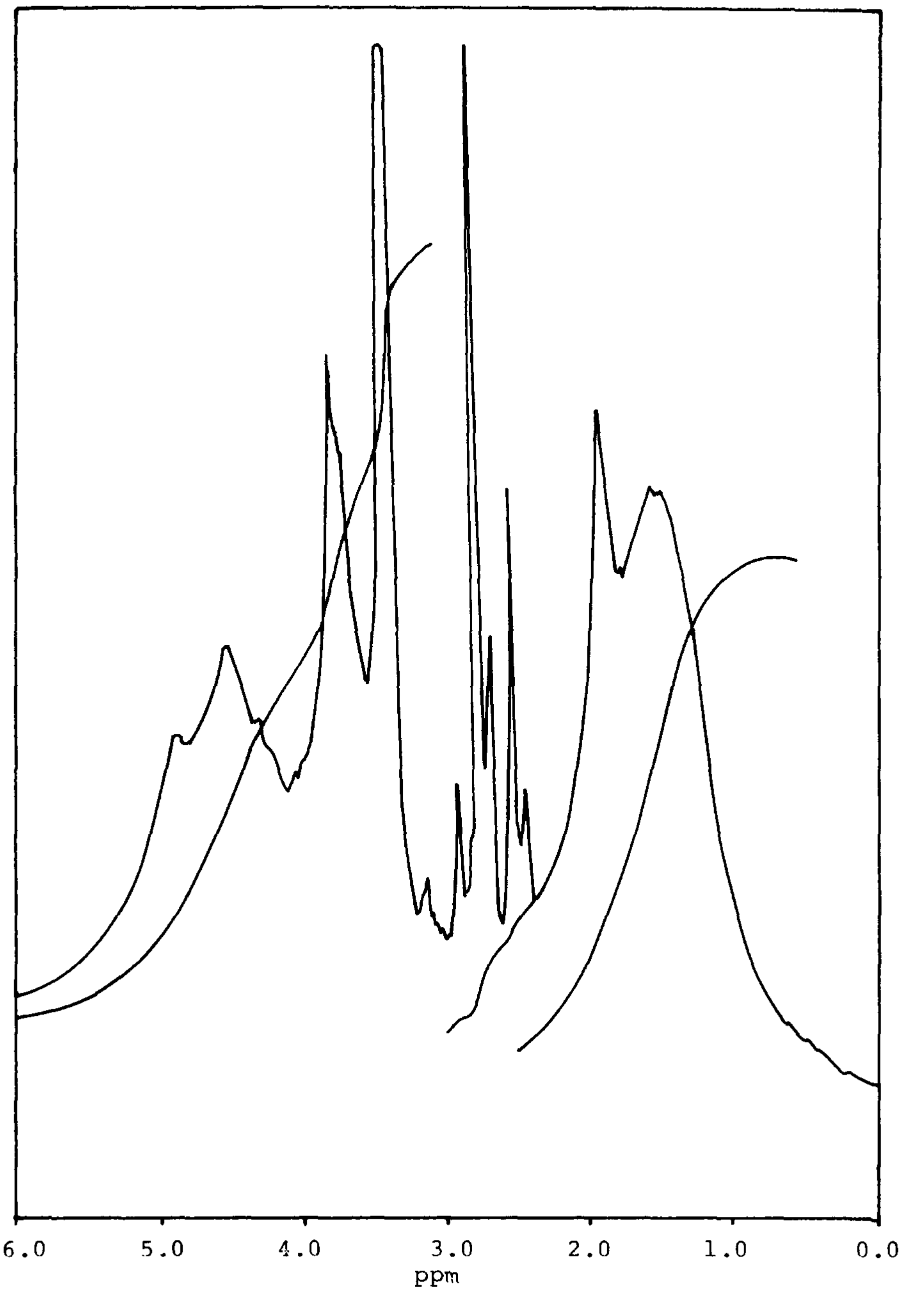
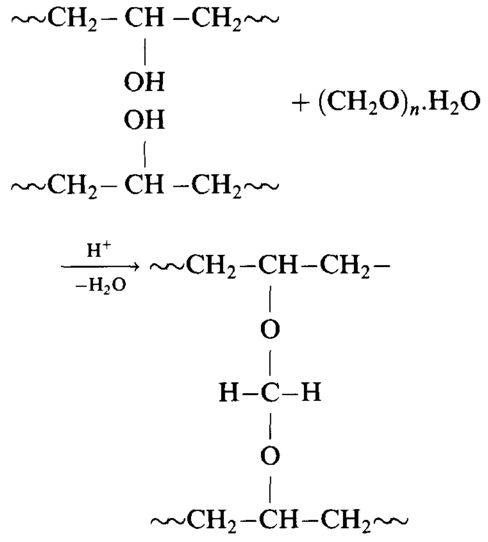


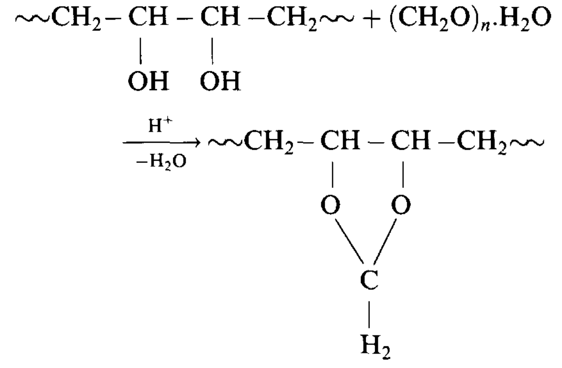
**Figure 2** $^1H$ n.m.r. spectrum of PVF (in DMSO)

*Intermolecular acetalization*



$$\begin{array}{c} \sim\sim CH_2-CH-CH_2\sim\sim \\ | \\ OH \\ OH \\ | \\ \sim\sim CH_2-CH-CH_2\sim\sim \end{array} + (CH_2O)_n.H_2O \xrightarrow[-H_2O]{H^+} \begin{array}{c} \sim\sim CH_2-CH-CH_2- \\ | \\ O \\ | \\ H-C-H \\ | \\ O \\ | \\ \sim\sim CH_2-CH-CH_2\sim\sim \end{array}$$

*Intramolecular acetalization of 1,2-glycol group*



$$\begin{array}{c} \sim\sim CH_2-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_2\sim\sim \end{array} + (CH_2O)_n.H_2O \xrightarrow[-H_2O]{H^+} \sim\sim CH_2-CH-CH-CH_2\sim\sim$$

The i.r. spectrum of PVA[15,16] showed some interesting change when reacted with aldehyde. On formalization, the O–H stretching vibration bands at 3500–3400 cm$^{-1}$ weakened and shifted towards higher frequencies due to cleavage of the polymeric hydrogen bond chain. The i.r. spectrum of PVF is presented in *Figure 1*. The C–H

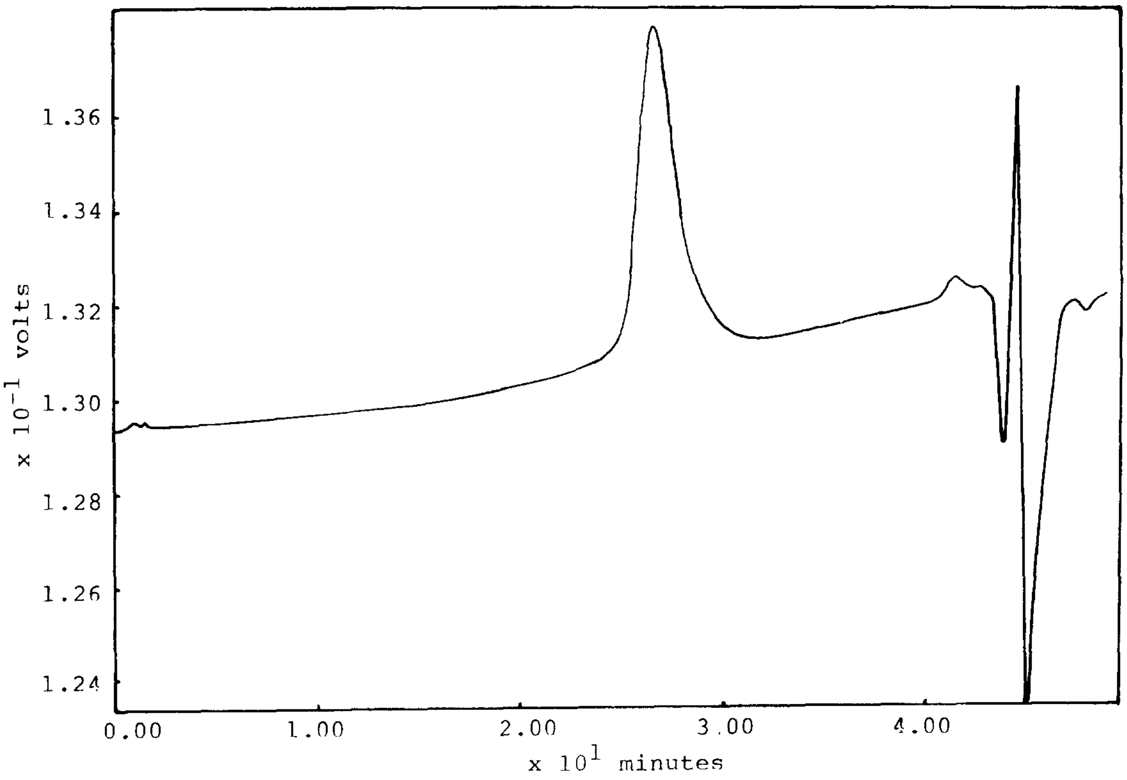


**Figure 3** G.p.c. trace for PVF

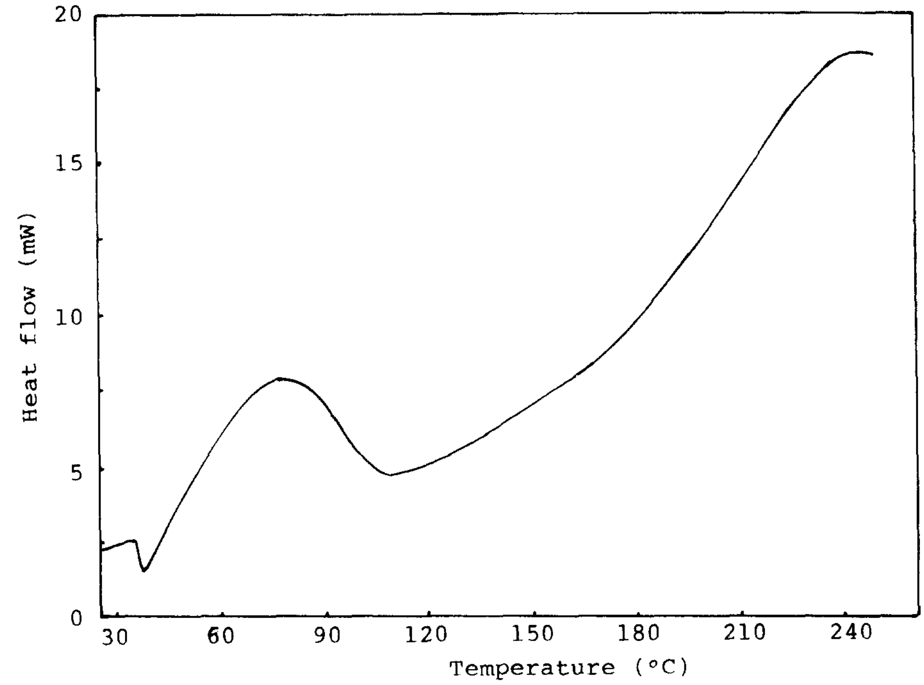


**Figure 4** D.s.c. curve for PVF

stretching bands characteristic of formal appeared at 2960, 2860, 2790 and 2660 cm$^{-1}$. In the region of the C–H bonding vibration, new bands appeared at 1470, 1428, 1400, 1390 and 1360 cm$^{-1}$. The bands at 1180, 1135, 1070 and 1020 cm$^{-1}$ seem to relate to C–O–C–O–C stretching vibrations. These bands confirmed the formation of the formal. The bands at 1735 cm$^{-1}$ appeared to be due to the C=O of the residual acetate group.

A typical $^{1}$H n.m.r. spectrum for PVF is shown in *Figure 2*. The signals observed at 1.3–1.8 and 3.7 ppm are due to methylene (–CH$_2$–) and methine ($-\overset{|}{\mathrm{C}}\mathrm{H}-$) protons, respectively[15–17]. The signals at 4.2–4.8 ppm, due to the dioxymethylene (O–CH$_2$–O) protons, confirmed the formation of the formal.

From g.p.c. analysis (*Figure 3*) the weight-average molecular weight ($\bar{M}_w$) of the formal was found to be 104 000 relative to polystyrene standards of molecular weights 1.8 × 10$^6$, 498 000, 110 000, 20 400, 10 300, 4000 and 2100.

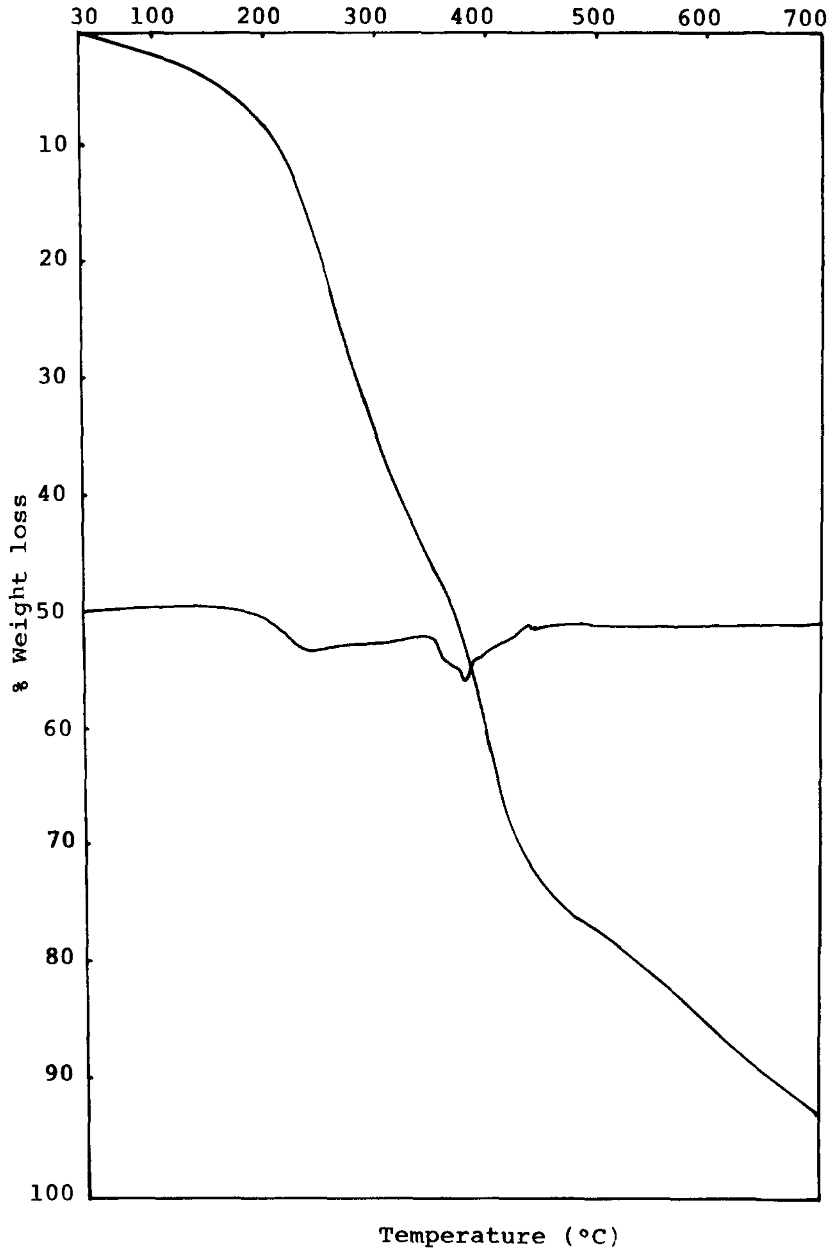


**Figure 5** T.g.a. and d.t.g. curve for PVF in air at heating rate of 10°C min$^{-1}$

The percentage of unconverted hydroxyl groups in the formal was estimated by an acetylation process. The acetylation was performed 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 hydrolysed to acetic acid and was titrated with standard sodium hydroxide solution. Thus, the percentage of unconverted hydroxyl groups can be estimated. The results indicated that 90% of the hydroxyl groups of PVA had been converted into formal groups. The extent of the acetalization reaction was also calculated from the integrals of the various n.m.r. resonances. The relative abundance of each proton calculated from the normalized integrations indicates the extent of reaction in homogeneous acetalization. The comparison of dioxymethylene protons at 4.2–4.8 ppm and methylene protons at 1.3–1.8 ppm yields a ratio of about 1/1.8 compared to the expected 1/2 value. The ratio of dioxymethylene protons to methine protons was found to be 1/1 experimentally, as expected. So the extent of the reaction is 90% from the n.m.r. data.

The acetylation reaction for the formation of PVF from PVA must be very complex as indicated by the polydispersity of PVF, which is as high as 1.73. The specificity of the catalyst coupled with the good solvent properties of formaldehyde helped the extension of the PVA chain, enhancing the probability of intermolecular acetylation with paraformaldehyde. This is indicated by the high $\bar{M}_w$ value of PVF compared to that of poly(vinyl benzal) (PVB) formed from the same PVA. The $\bar{M}_w$ of PVB was only 65 000[13] when formed under the same conditions. This is due to steric hindrance of the phenyl group present in benzaldehyde. Formaldehyde might also enhance the solution property of the organic solvent to dissolve PVA, facilitating interpolymer chain linking between neighbouring hydroxyl groups, affording water elimination.

The acetal was soluble in a number of organic solvents such as DMF, DMSO, THF, ethanol, acetone, chloroform and dioxane.

A typical d.s.c. thermogram for the PVF is shown in *Figure 4*. From the d.s.c. studies the glass transition, $T_g$, was found to be 52°C. The activation energy, $E$, of melting was $33.29 \pm 0.71\,\mathrm{kJ\,mol^{-1}}$. The order of melting reaction of the formal was calculated as $n = 0.82 \pm 0.01$. The rate constant, $k$, was found to be $1.29 \times 10^2 \pm 1.11\,\mathrm{s^{-1}}$.

From t.g.a. and d.t.g. curves (*Figure 5*) it was observed that the formal decomposed in three steps[18]. The decomposition temperatures were determined by the intersection of the tangent to the steepest part of the t.g.a. curve with its strain-line. Thermal oxidation of the PVF began with cleavage of the formal ring[19] and also removal of $H_2O$ from neighbouring pairs of unconverted hydroxyl groups of the formal. The initial decomposition temperature ($IDT_1$) for the first stage was 300°C. The second-stage decomposition was due to the removal of CO, $CO_2$, hydrocarbons[20], etc., from the PVF. The initial decomposition temperature ($IDT_2$) for the second stage was 465°C. The third-stage decomposition was due to the production of carbon at a temperature above 500°C. Also, the integral procedural decomposition temperature[21] was found to be 360°C.

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