

# Synthesis of Poly(vinyl butyral)s in Homogeneous Phase and Their Thermal Properties

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**ABSTRACT:** The condensation reaction of butyraldehyde (BA) with poly(vinyl alcohol) (PVA) to give poly(vinyl butyral) (PVB) was studied in detail using *N*-methyl-2-pyrrolidone (NMP) as solvent for PVA and PVBs. PVBs having various degrees of acetalization were obtained. The acetalization reaction under a variety of conditions gave at best a polymer with 97% acetalization. The extent of modification and the structure of the polymer, i.e., the ratio of acetal units from meso and racemic dyads of PVA, were determined by <sup>1</sup>H-NMR. The acetalization degree was reflected in the solubility of PVB; all products were soluble in NMP. PVBs were characterized by IR spectroscopy and <sup>1</sup>H and <sup>13</sup>C-NMR. The glass transition temperatures of PVBs, determined by DSC, increased as vinyl alcohol units increased and displayed a

positive departure from linearity. Thermal degradation of PVBs was studied using differential thermal analysis (DTA) and thermogravimetry (TGA) under dynamic conditions in nitrogen. The content of hydroxyl groups had an effect on the thermal stability of PVBs; the thermal stability of PVBs decreased as vinyl alcohol units increased. The apparent activation energy of the decomposition was determined by the Kissinger and Flynn–Wall methods, which agree well. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5007–5017, 2006

**Key words:** poly(vinyl alcohol); poly(vinyl butyral); *N*-methyl-2-pyrrolidone (NMP); thermal degradation; activation energy

## INTRODUCTION

Poly(vinyl butyral) (PVB) is extensively used in laminated safety glass, paint, adhesives, and binders. It is prepared by reacting poly(vinyl alcohol) (PVA) with butyraldehyde (BA) in the presence of an acid catalyst. The hydroxyl groups of PVA react with BA to form 1,3-dioxane rings (acetal rings) and partial or even almost complete exchange of the original functional group for a new one can occur, and the final product has the character of a copolymer. The balance between residual hydroxyl groups and acetal rings depends on the reaction conditions, and this balance provides distinct properties to the final polymer.

In the acetalization of PVA with aldehydes to produce poly(vinyl acetal)s three different reactions can occur<sup>1</sup>: intramolecular acetalization of the 1,3-glycol group, intermolecular acetalization of the 1,3-glycol group and intramolecular acetalization of the 1,2-glycol group, as shown in Scheme 1. PVA reacts with an aldehyde primarily to form six-membered rings

between adjacent, intramolecular hydroxyl groups, to a lesser extent intermolecular acetals are also formed. This side reaction can lead to branched and eventually crosslinked polymer.<sup>1</sup>

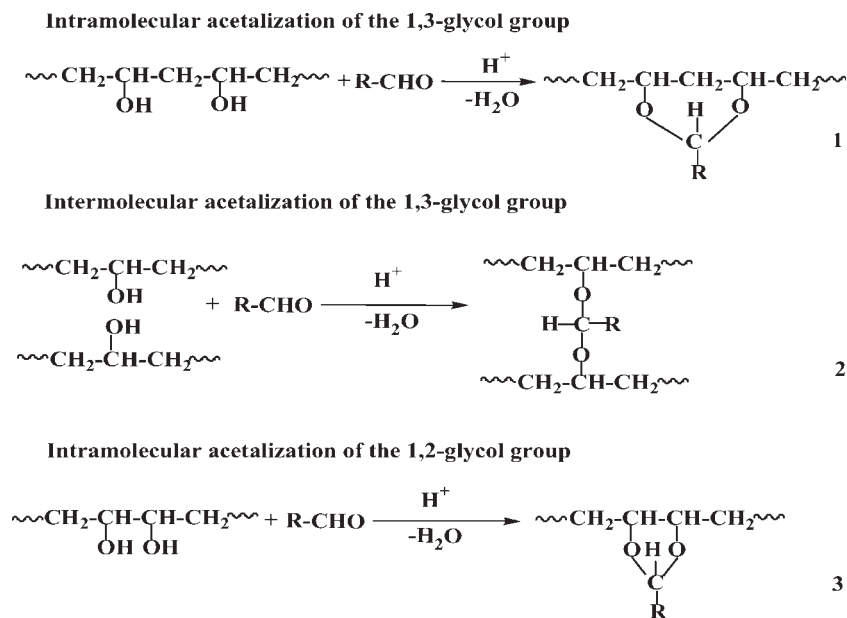
For the preparation of poly(vinyl acetal)s five different processes are known:<sup>2–4</sup>

1. Precipitation. An aqueous solution of PVA reacts with the aldehyde until the homogeneous phase reaction changes to a heterogeneous reaction when the acetal precipitates.
2. Dissolution. PVA powder is suspended in a suitable nonsolvent that dissolves the aldehyde and the final product. The reaction starts out heterogeneously and is completed homogeneously.
3. Homogeneous reaction. The reaction starts in a water solution of PVA. A solvent for the acetal, which can mix with water, is added continuously to prevent precipitation.
4. Heterogeneous reaction. PVA in film or fiber form reacts with the aldehyde.
5. Direct conversion of poly(vinyl acetate) to poly(vinyl acetal). This is also a homogeneous reaction. The poly(vinyl acetate) is dissolved in a suitable solvent and is hydrolyzed by a strong mineral acid and acetalized at the same time.

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Scheme 1

PVA that is used, its degree of hydrolysis, and molecular weight, as well as on the method of preparation.

Homogeneous solution techniques are preferred because of higher degrees of acetalization and a reduction in crosslinking relative to heterogeneous techniques. Using this homogeneous method the distribution of acetal groups is uniform.

Acetalization of PVA under homogeneous conditions demands complete dissolution of PVA and poly(vinyl acetal)s in an appropriate solvent. Because of the strong inter and intramolecular hydrogen bonding PVA can be dissolved only in water or in very polar solvents such as dimethyl sulfoxide (DMSO) or *N*-methyl-2-pyrrolidone (NMP). The acetalization of PVA in homogeneous phase with different aldehydes using DMSO as a solvent has been carried out.<sup>5-10</sup>

A knowledge of thermal degradation of polymers is important in chemical, material, and environmental fields. PVB contains groups which are affected by thermal process, and consequently its physical properties are affected. The thermal degradation of PVB has been studied to analyze its products of decomposition and to obtain kinetic information.<sup>11-15</sup> However, little has been reported in the literature concerning the influence of the degree of substitution of alcohol groups by butyral groups on the thermal degradation of PVB.

The objective of this work was to determine the feasibility of transforming PVA to PVB in homogeneous phase using NMP as a solvent and to study the thermal decomposition of PVB samples using TG and DTA. In this study the effect of reaction conditions on the extent of the reaction has been investigated in detail. The products (PVB) have been characterized

qualitatively and quantitatively using analytical means. The effect of the content of vinyl alcohol units on the thermal stability of resulting polymers has been examined. Also the kinetic analysis of the thermal degradation process has been undertaken under dynamic conditions.

## EXPERIMENTAL

### Materials

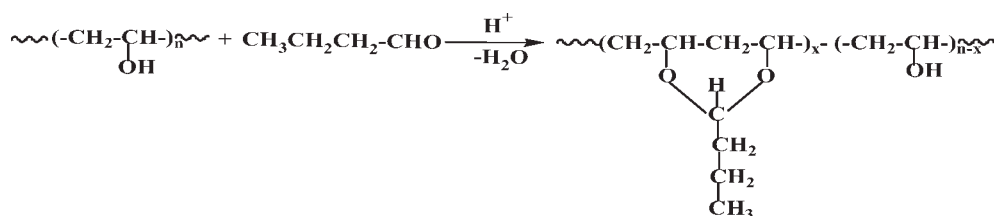
PVA ( $M_w = 108,000$  g/mol, degree of polymerization 1400, degree of hydrolysis 98.8 mol %) supplied by Fluka, was used as received. Butyraldehyde (BA) (Aldrich), *N*-methyl-2-pyrrolidone (NMP) (Fluka), *N,N'*-dimethylpropyleneurea (1,3-dimethyl-3,4,5,6-tetrahydro-2(1H) pyrimidinone) (DMPU) (Fluka) were used without further purification.

### IR and NMR measurements

The IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrophotometer using polymer films on NaCl discs. The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were obtained with a 300 MHz Bruker Avance DPX-300 spectrometer.

### Thermal analysis

DSC measurements were performed on a Polymer Laboratories DSC, connected to a cooling system and calibrated with different standards (indium, tin, lead, and zinc). The scanning rate used was 20°C/min and the glass transition temperature ( $T_g$ ) was taken as the initial onset of the change of the slope in the DSC curve.



Scheme 2

Thermogravimetric analysis (TGA), derivative thermogravimetric analysis (DTG), and differential thermal analysis (DTA) were carried out in nitrogen using a Polymer-Laboratories STA-1000 system (gas flow, 28 mL/min) with 8–12 mg of samples on platinum pans. The weight loss and the rate of weight loss as a function of temperature were recorded at heating rates of 2, 5, 10, and 20°C/min. The following characteristics were determined from the thermogravimetric curves: the initial thermal decomposition temperature ( $T_i$ ), the temperature decomposition for different weight losses ( $T_d$ ), the temperature of maximum rate of the first reaction step ( $T_{\max}^1$ ), the temperature of maximum rate of the second reaction step ( $T_{\max}^2$ ) and the weight loss for the first and the second reaction step ( $W^1, W^2$ ). Differential thermal analysis was carried out using a heating rate of 20°C/min.

### Acetalization of PVA

PVA (0.045 mol based on  $-\text{CH}_2-\text{CHOH}-$  as the repeat unit) was dissolved in NMP at 90°C. Prescribed amounts of hydrochloric acid (35% aqueous) were then added to catalyze the condensation. A definite amount of butyraldehyde was added slowly while stirring at 30°C. The mixture was kept at the prescribed temperature under stirring, and the polymer remained soluble throughout the process. After definite time (between 2 and 72 h) products were isolated by precipitation into water containing a small amount of sodium hydroxide. The polymer was purified by repeated precipitations from the solution in the appropriate solvent (THF or DMSO) into water, and finally dried in vacuum.

### Characterization of poly(vinyl acetal)s

The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of poly(vinyl acetal)s were recorded in  $\text{Me}_2\text{SO}-d_6$  or  $\text{CDCl}_3$  with tetramethylsilane (TMS) as the internal standard.

The degree of acetalization was determined by  $^1\text{H-NMR}$  using the eq. (1):

$$(\text{VB}) = \frac{2}{\left(\frac{3A_{\text{CH}_2}}{A_{\text{CH}_3}}\right) - 6} \quad (1)$$

where (VB) is the mol % of vinyl butyral,  $A_{\text{CH}_2}$  represents the total peak area of methylene protons and  $A_{\text{CH}_3}$  the total peak area of methyl protons.

## RESULTS AND DISCUSSION

### Synthesis of poly(vinyl butyral)

The reaction between PVA and BA leads to the corresponding PVB as shown in Scheme 2.

The reaction shown was carried out with different amounts of BA for a given initial amount of PVA, as indicated in Table I. The acetalization degree increased as the amount of initial BA increased. These results indicate that not all the BA introduced in the reaction medium intervened in the condensation reaction but a yield higher than 90% can be achieved. The acetalization degree is reflected in the solubility of PVB. All products were soluble in NMP, Samples 1 and 2 were soluble in DMSO but not in THF, Products 3–7 were soluble in DMSO and THF, while Samples 8–10 were soluble in THF and  $\text{Cl}_3\text{CH}$  but not in DMSO. It seems most unlikely that with the reaction conditions chosen in this study, intermolecular acetalization could have taken place. If Structure 2 (Scheme 1) is obtained, the resulting polymer should be cross-linked, even if present in modest amounts. Since our

TABLE I  
Effect of Aldehyde Concentration  
on Acetalization Degree

Run	$2[\text{BA}]_0/[\text{OH}]_0$	Acetalization <sup>a</sup> (%)
1	0.500	31
2	0.600	35
3	0.711	44
4	0.800	49
5	0.900	53
6	1.00	57
7	1.20	63
8	1.82	80
9	2.00	88
10	2.60	93

$T = 20^\circ\text{C}$ , Time 3 h,  $[\text{BA}]_0/[\text{HCl}] = 3$ , Solvent: NMP.

<sup>a</sup> Acetalization % =  $100[2\text{VB}/(2\text{VB}+\text{OH})]$ , where VB and OH are the mole fractions of acetal and hydroxyl units, respectively, determined from  $^1\text{H NMR}$ .

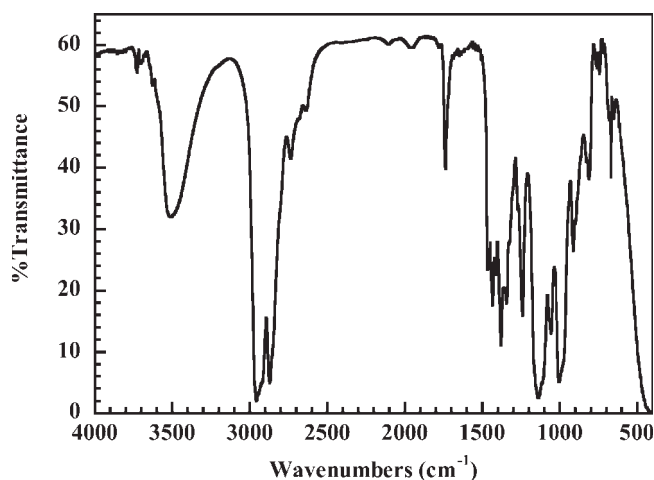


Figure 1 FTIR spectrum of PVB (in thin film on NaCl disc).

products were all entirely soluble in NMP and depending on acetalization degree in DMSO or THF, the occurrence of intermolecular condensation must have been negligible.

The characterization of all these products gave the following information: (1) the FTIR spectra gave typical peaks attributed to PVA, O—H stretching vibration bands at  $3490\text{ cm}^{-1}$ , plus absorptions arising from

the presence of acetalic functions (several peaks in the region between  $1050$  and  $1150\text{ cm}^{-1}$ ). The band at  $1740\text{ cm}^{-1}$  appears because of the acetate group. The IR spectrum of PVB bearing about 85 mol % VB is presented in Figure 1. (2) the  $^1\text{H-NMR}$  spectra allowed confirmation of the expected structures and the quantification of the extent of acetalization. Figure 2 gives a typical example of  $^1\text{H-NMR}$  spectra of PVB bearing 90 mol % VB and PVA. The signals observed between 4.4 and 4.8 are due to the dioxymethine (O—CH—O) proton in the acetal (VB) ring, the signals between 4.4 and 3.6 are due to methine protons in VB and vinyl alcohol (VA) unit and VA hydroxyl protons, the signals between 1.8 and 1.2 are due to the VB and VA methylene protons, and the signal at 0.95 is due to the methyl protons of VB. PVB is formed when butyraldehyde reacts with adjacent hydroxyls on the PVA chain to form butyral rings. The resultant rings are called meso (m) or racemic (r), depending on whether the adjacent hydroxyl groups were at the same (meso) or opposite sides (racemic) of the PVA chain. Figure 3 shows these stereostructures. The dioxymethine protons D and D' could be utilized to determine the fraction of the stereostructure of butyral rings. Values obtained are given in Table II. Shibatani et al.<sup>16</sup> studied the relationship between the stereostructure of

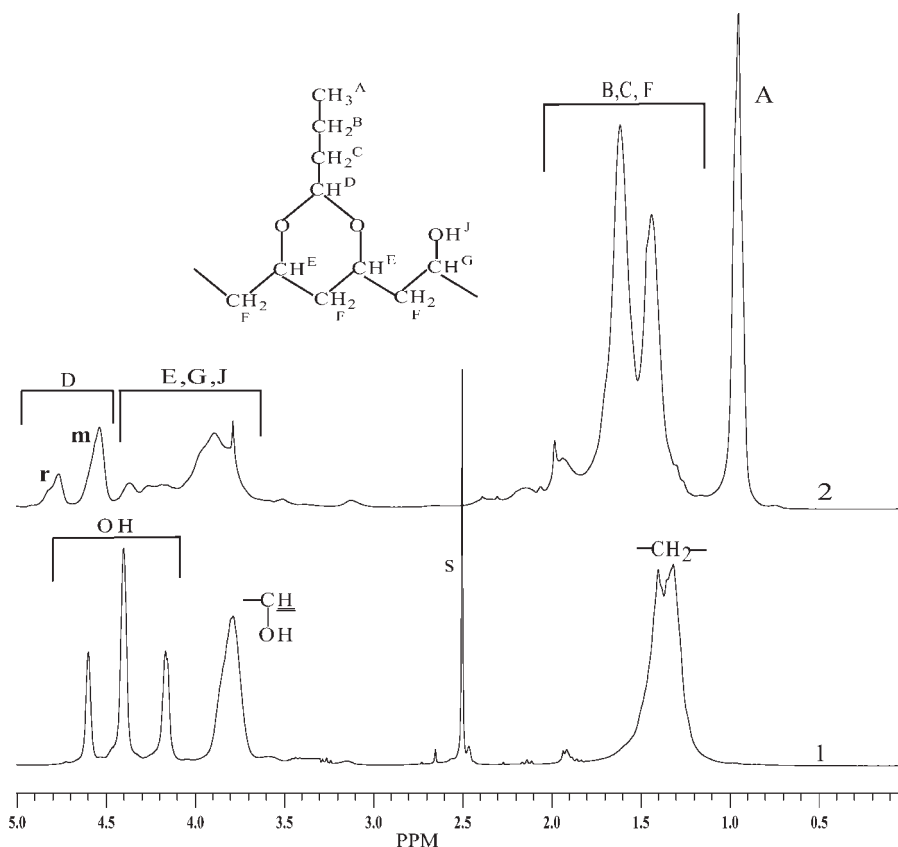
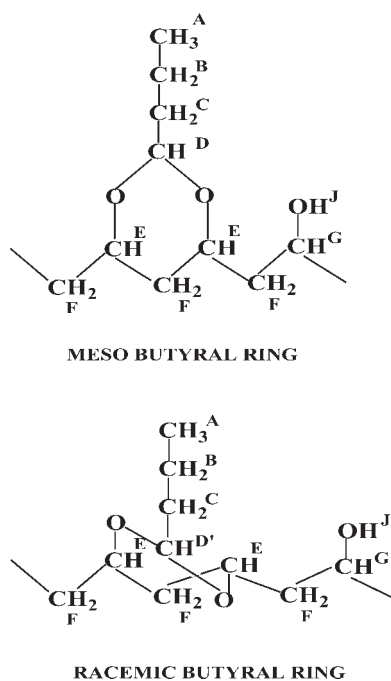


Figure 2  $^1\text{H-NMR}$  spectra of: (1) PVA in  $\text{DMSO-}d_6$ , (2) PVB (90 mol % VB) in  $\text{CDCl}_3$ , m and r refer to the meso and racemic orientation of butyral ring.



**Figure 3** Stereostructures of meso and racemic butyral rings.

PVA and the acetal formation. They found that the formation of mesoacetal is favored kinetically and also thermodynamically.

Figure 4 shows the  $^{13}\text{C}$ -NMR spectrum of PVB and the assignments<sup>17,18</sup> of these lines are indicated on it. The chemical shifts of  $^{13}\text{C}$  resonance lines for PVB are listed in Table III. The higher intensity of the  $\text{C}_{4\text{m}}$  signal with respect to the  $\text{C}_{4\text{r}}$  signal is explained taking into account that mesobutyral ring is more stable than the racemic butyral ring.

Tables IV and V summarize the results obtained with different reaction times. The results show that when the reaction is carried out at  $20^\circ\text{C}$  with  $[\text{BA}]_0/[\text{OH}]_0 = 0.5$ , the acetalization degree increases as reaction time increases up to 48 h, then a plateau is reached (77%). On the other hand, if the temperature is higher,  $60^\circ\text{C}$ , and with a large excess of BA ( $[\text{BA}]_0/[\text{OH}]_0 = 1.3$ ), the influence of reaction time on degree of modification is negligible and a plateau (93–97%) is reached in 3 h. This reaction, carried out using the homogeneous solution method, goes almost to completion with very few unreacted hydroxyl groups remaining. Since neighboring hydroxyl groups from PVA react in pairs, it would be expected that a significant number of isolated hydroxyl groups would remain in the polymer unable to react. According to Flory's theory,<sup>19</sup> the lowest vinyl alcohol content in any poly(vinyl acetal) should be 13%. Flory assumed that the acetalization was irreversible and the random character of the reaction. In this study we have obtained higher experimental yields as reported by other authors<sup>10</sup> using a different solvent. Flory accounted

for conversions exceeding 87% by postulating reversibility of the acetalization. Though such conversions would be possible if the acetalizations were reversible, there is no positive evidence in the literature to suggest reversibility.<sup>20</sup> However, conversions greater than 87% can be explained even for irreversible acetalization, by taking into account the effect of neighboring groups on the reactivity of OH groups. In such a case, acetalization cannot be treated as a random process, but as a nonrandom zipperlike process where the condensation at neighboring hydroxyls is controlled by preexisting acetal groups.<sup>20</sup>

The effect of temperature on acetalization degree is given in Tables VI and VII. For  $[\text{BA}]_0/[\text{OH}]_0 = 0.5$ , the modification extent increases when the reaction temperature increases from  $20$  to  $40^\circ\text{C}$ , beyond this temperature remains constant. If a large excess of BA is used ( $[\text{BA}]_0/[\text{OH}]_0 = 1.3$ ), temperature has no effect on acetalization extent under the used conditions.

Table VIII shows the results obtained when different catalyst concentrations were used. If catalyst (HCl) is absent the acetalization of PVA does not take place, and acetalization degree increases increasing catalyst concentration.

Table IX shows the effect of solvent on modification extent. NMP and DMPU are excellent solvents for PVA, and PVBs display excellent solubility in both of them. DMPU has been previously used to carry out homogeneous esterification of vinyl alcohol copolymers.<sup>21</sup> The same acetalization degree is achieved in both media under the used conditions.

## Thermal analysis

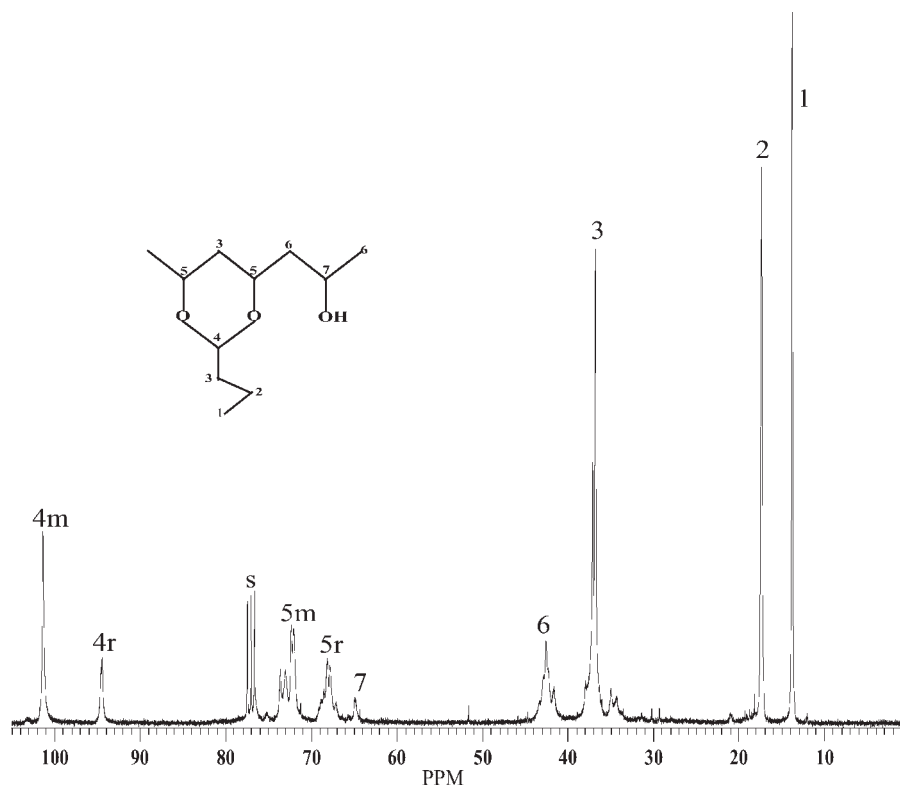
### Calorimetric analysis

The glass transition temperatures of PVBs, as measured from DSC studies, as a function of vinyl alcohol (VA) contents are shown in Figure 5.  $T_g$  increases as VA content increases, this increase displays a positive departure from linearity, which is attributed to higher barriers to main chain mobility than expected from

**TABLE II**  
Degree of Acetalization and Racemic Stereostructure Fraction for PVB, Calculated from  $^1\text{H}$  NMR Spectra

Degree of acetalization (%)	Butyral rings in racemic config (%)
$^1\text{H}$ NMR	
36	7
47	9
55	13
60	18
70	20
82	26
94	29
96	31





**Figure 4**  $^{13}\text{C}$ -NMR spectrum of PVB (90 mol % VB) in  $\text{CDCl}_3$ , m and r refer to the meso and racemic orientation of butyral ring.

simple additivity of the components. Butyral groups have a plasticizing effect, then the substitution of butyral ring units by hydroxyl groups leads to a lower chain mobility. On the other hand, in PVB polymers  $T_g$  values are affected by hydrogen bonding. The increase of the content of hydroxyl groups gives rise to an increase in hydrogen bonding, that leads to an increase of the PVB polymer  $T_g$  above the predicted by additivity. PVBs are not crystalline.

#### Thermal analysis by DTA

The peak temperatures for the various thermal effects observed in the DTA curves of PVBs and PVA are given in Table X.

In the DTA curve of PVA, three endotherms are observed. The first one with its peak minimum at  $231^\circ\text{C}$  that corresponds to the melting temperature of PVA, the second one appears between  $280$  and  $420^\circ\text{C}$ , with its peak minimum at  $347^\circ\text{C}$ , and the third one at a temperature higher than  $420^\circ\text{C}$ . The second endotherm is mainly due to the elimination of side groups and the one at higher temperatures is due to the breakdown of the polymer backbone.<sup>22,23</sup>

In the DTA curves of PVBs (VA content less than 80 mol %) one endotherm, splitted into two peaks, between  $230$  and  $450^\circ\text{C}$  approximately has been observed. If the content of VA units in PVB is 82 mol % two endotherms are observed. PVBs with less than 80 mol % of VA units show higher thermal stability

**TABLE III**  
Chemical Shifts of  $^{13}\text{C}$  Resonance Lines for PVB

$^{13}\text{C}$ chemical shift (ppm)	Carbon
13.7	$\text{CH}_3$ (VB)
17.3	$\text{CH}_2$ (VB)
36.7, 37.1	$\text{CH}_2$ (VB)
41.5, 42.5	$\text{CH}_2$ (VA)
64.8	CH (VA)
67.1, 67.8, 68.1, 68.5	Racemic CH (VB)
72.0, 72.3, 73.0, 73.6	Meso CH (VB)
94.4	Racemic O—CH—O (VB)
101.3	Meso O—CH—O (VB)

VB: vinyl butyral unit; VA: vinyl alcohol unit.

**TABLE IV**  
Effect of Reaction Time on Acetalization Degree

Run	Time (h)	Acetalization (%)
1	2	57
2	3	57
3	7	67
4	24	57
5	48	77
6	72	77

$T = 20^\circ\text{C}$ ,  $2[\text{BA}]_0/[\text{OH}]_0 = 1$ ,  $[\text{BA}]_0/[\text{HCl}] = 3$ , Solvent: NMP.

**TABLE V**  
Effect of Reaction Time on Acetalization Degree

Run	Time (h)	Acetalization (%)
1	3	93
2	7	94
3	24	95
4	48	97
5	72	97
6	96	97
7	120	96
8	144	92

$T = 60^\circ\text{C}$ ,  $2[\text{BA}]_o/[\text{OH}]_o = 2.6$ ,  $[\text{BA}]_o/[\text{HCl}] = 3$ , Solvent: NMP.

than PVA, while PVB with a content of VA units of 82 mol % shows lower thermal stability than does PVA.

#### Thermal analysis by dynamic TG and DTG

Thermogravimetric and differential thermogravimetric curves for PVA and PVBs, obtained at  $20^\circ\text{C}/\text{min}$  in nitrogen, are given in Figures 6 and 7. The TG curves in Figure 6 and DTG curves in Figure 7 show that PVA degrades in two stages, in the first stage water is eliminated, while in the second one the breakdown of the polymer backbone takes place.<sup>22,23</sup> Thermal degradation of PVA starts at about  $280^\circ\text{C}$  and continues up to  $490^\circ\text{C}$  with 90% weight loss.

The decomposition of PVBs takes place in one step (Figs. 6–7) when the content of VA units is less than 80 mol %. The temperature of this step depends lightly on the content of VA units, being between  $280$  and  $480^\circ\text{C}$  approximately. The weight loss is between 80 and 90%. PVB containing 82 mol % of VA units decomposes in two steps, the first one starts at  $230^\circ\text{C}$  with its peak minimum at  $316^\circ\text{C}$  (Fig. 7), and the minimum of the second one appears at  $382^\circ\text{C}$ . The weight loss in the first step is about 40%, and in the second one 50%. It has been postulated<sup>12,13</sup> that the PVB degradation takes place by side-group elimination (alcohol and acetal groups) and main-chain scission. Water and butyraldehyde (butanal) have been identified as the main products of degradation.<sup>12,13</sup> The water arises from the dehydration of PVA. The butyraldehyde is the result of elimination of one of the ace-

**TABLE VI**  
Effect of Temperature on Acetalization Degree

Run	Temperature ( $^\circ\text{C}$ )	Acetalization (%)
1	20	57
2	40	71
3	60	71

Time = 3 h,  $2[\text{BA}]_o/[\text{OH}]_o = 1$ ,  $[\text{BA}]_o/[\text{HCl}] = 3$ , Solvent: NMP.

**TABLE VII**  
Effect of Temperature on Acetalization Degree

Run	Temperature ( $^\circ\text{C}$ )	Acetalization (%)
1	23	93
2	40	97
3	60	93

Time = 3 h,  $2[\text{BA}]_o/[\text{OH}]_o = 2.6$ ,  $[\text{BA}]_o/[\text{HCl}] = 3$ , Solvent: NMP.

tal oxygens (only one oxygen bond on the side group of acetal appears to break in nitrogen environment). In addition of butanal, crotonaldehyde (butenal) and 2,5-dihydrofuran are generated as a result of the main chain scission that takes place after the side group elimination.<sup>13</sup>

From the characteristics of thermal degradation summarized in Table XI and Figure 6, it can be seen that the presence of hydroxyl groups in PVB has effect on thermal stability. These results indicate that the stability of PVBs decreases with increasing the content of VA units in the polymer chain. As shown in Table XII, the incorporation of a small amount of VB in PVA (18 mol %) produces a marked decrease in the  $T_d(T_{10} - T_{80})$  value of the PVB as compared with those values of PVA. However,  $T_d(T_{10} - T_{50})$  values for PVBs with 6–72 mol % VA are higher than those for PVA. The thermal stability of PVA is reduced by the presence of a small content of VB units. All these results indicate that the thermal stability of PVBs is significantly decreased or increased compared with that of PVA depending on the content of VA units. It is deduced that the more stable material is the PVB with the less content of VA units, and the less stable polymers are PVA and the PVB with 82 mol % VA content.

#### Calculation of kinetic parameters

Thermogravimetry is a method widely used for determination of kinetics of degradation of polymers.<sup>24–27</sup> A reaction rate may be defined as the derivative of conversion. For thermogravimetric measurements, conversion may be defined as:

$$\alpha = \frac{(m_0 - m)}{(m_0 - m_f)} \quad (2)$$

**TABLE VIII**  
Effect of Catalyst Concentration on Acetalization Degree

Run	$[\text{HCl}]_o/[\text{BA}]_o$	Acetalization (%)
1	0	0
2	0.068	50
3	0.168	51
4	0.333	57

Time = 3 h,  $T = 20^\circ\text{C}$ ,  $2[\text{BA}]_o/[\text{OH}]_o = 1$ , Solvent: NMP.

TABLE IX  
Effect of Solvent on Acetalization Degree

Run	Solvent	Acetalization (%)
1	NMP	57
2	DMPU	55

Time = 3 h,  $T = 20^\circ\text{C}$ ,  $2[\text{BA}]_0/[\text{OH}]_0 = 1$ ,  $[\text{BA}]_0/[\text{HCl}] = 3$ .

where  $m_0$ ,  $m$ , and  $m_f$  are the initial, actual, and final weights of the sample, respectively. The rate of conversion in a dynamic TGA experiment at constant heating rate can be expressed as:

$$\frac{d\alpha}{dt} = B \frac{d\alpha}{dT} = k(T)f(\alpha) \quad (3)$$

where  $B$  is the heating rate,  $B = dT/dt$ ,  $k(T)$  is the rate constant, and  $f(\alpha)$  is the conversional functional relationship.

For polymer degradation, it is assumed that the rate of conversion is proportional of the concentration of nondegraded material:

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

where  $n$  is the apparent reaction order.

Arrhenius expression, which describes the temperature dependence of the rate constant,  $k(T)$ , may be expressed as:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (5)$$

where  $E$  is the apparent activation energy,  $A$  is the preexponential factor,  $R$  is the gas constant and  $T$  the absolute temperature.

Combining eqs. (1)–(4) the following relation may be derived:

$$\frac{d\alpha}{dt} = B \frac{d\alpha}{dT} = A(1 - \alpha)^n \exp\left(-\frac{E}{RT}\right) \quad (6)$$

The differential eq. (6), is usually manipulated until a straight line can be obtained and the kinetic parameters are predicted from the slope and ordinate values.

In the present study two different nonisothermal methods, the Kissinger<sup>28</sup> and Flynn–Wall<sup>29</sup> methods, are used for the computation of the kinetic parameters. Kissinger method uses the temperature at which the rate of weight loss is at maximum ( $T_{\max}$ ) from which the kinetic parameters are obtained, and assumes that these parameters are independent of  $B$ . Since the maximum rate occurs when  $d(d\alpha/dt)/dt$  is

zero, differentiation of eq. (6) with respect to time and setting the resulting expression equal to zero gives:

$$\frac{BE}{RT_{\max}^2} = An(1 - \alpha_{\max})^{n-1} \exp\left(-\frac{E}{RT_{\max}}\right) \quad (7)$$

where  $\alpha_{\max}$  is the conversion at  $T_{\max}$ .

Kissinger also assumes that the product  $n(1 - \alpha_{\max})^{n-1}$  is not only independent of  $B$ , but is equal or very near to the unity. Substituting this value in eq. (7) and differentiating, neglecting small quantities, then the following expression is obtained:

$$\frac{d\left(\ln\frac{B}{T_{\max}^2}\right)}{d\left(\frac{1}{T_{\max}}\right)} = -\frac{E}{R} \quad (8)$$

Therefore a plot of  $\ln(B/T_{\max}^2)$  versus  $1/T_{\max}$  gives the apparent activation energy for each degradation step.

Flynn and Wall expressed the eq. (6) as:

$$-\frac{d \log B}{d\left(\frac{1}{T_\alpha}\right)} = 0.457 \frac{E}{R} \quad (9)$$

where  $T_\alpha$  is the temperature for an isoconversion level. The apparent activation energy  $E$  can be obtained from the slope of isoconversional plots of  $\log B$  versus  $1/T_\alpha$ . This method provides activation energies as a function of conversion without any assumption about the reaction order. If the determined activation energy is the same for the various values of  $\alpha$ , the existence of a single-step reaction can be concluded with certainty. On the contrary, a change in  $E$  with increasing degree of conversion is an indication of a complex reaction mechanism.

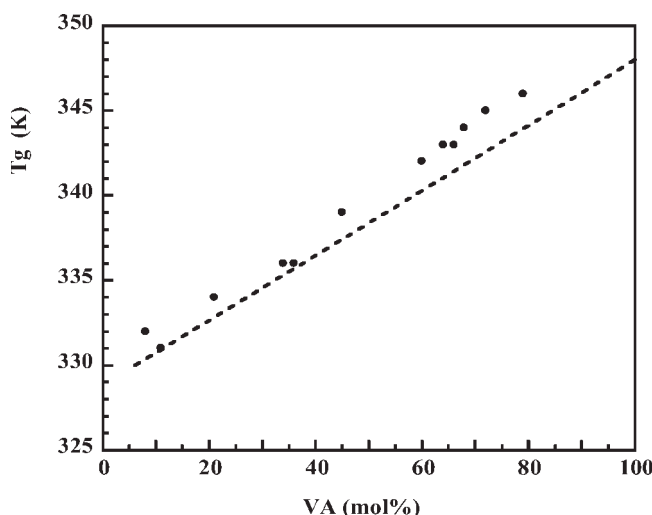


Figure 5 Glass transition temperatures for PVBs.



TABLE X  
Peak Temperatures in DTA Thermograms for PVA and PVBs  
(Heating Rate 20°C/min)

Polymer	VA (mol %)	Endotherm I			Endotherm II		
		$T_i$ (°C)	$T_{max}$ (°C)	$T_f$ (°C)	$T_i$ (°C)	$T_{max}$ (°C)	$T_f$ (°C)
PVA	100	280	347	419	419	450	495
PVB82	82	227	317			360	415
PVB72	72	301	371	439			
			386				
PVB64	64	331	379	442			
			389				
PVB50	50	305	376	437			
			389				
PVB38	38	308	356	455			
			395				
PVB21	21	329	354	458			
			398				
PVB6	6	327	378	460			
			402				

The kinetic parameters were calculated from the TG and DTG curves, using the eqs. (8) and (9). The Kissinger method allows calculation of activation energy from one point (maximum on DTG curve) at several heating rates. The method of Flynn–Wall requires several curves at different heating rates.  $E$  was calculated at various degrees of conversion to test the constancy with respect to conversion.

The values of  $E$  determined by the above-mentioned methods are given in Table XIII, for PVA and PVBs. This parameter has been evaluated using the method of least squares for all the methods. The pre-exponential factor has been calculated at the maximum of reaction rate by eq. (6) for each step of degradation, assuming that  $n(1 - \alpha_{max})^{n-1}$  is equal or very near to the unity.

As can be seen from Table XIII activation energy does not change for conversions of approximately between 0.10 and 0.70 for PVA and PVBs with a content of VA units less than 80 mol %, indicating that the degradation in that region takes place through the cleavage of linkages with similar bond energies. For PVB containing 82 mol % VA two distinct apparent activation energy values can be reported, one value for conversions between 0.05 and 0.40 and another one between 0.50 and 0.70. These results are consistent with the degradation steps reflected in TGA and DTGA curves (Figs. 6–7). The activation energy of the first stage of degradation of PVA is between 137 and 155 kJ/mol. For PVBs with less than 80 mol % VA

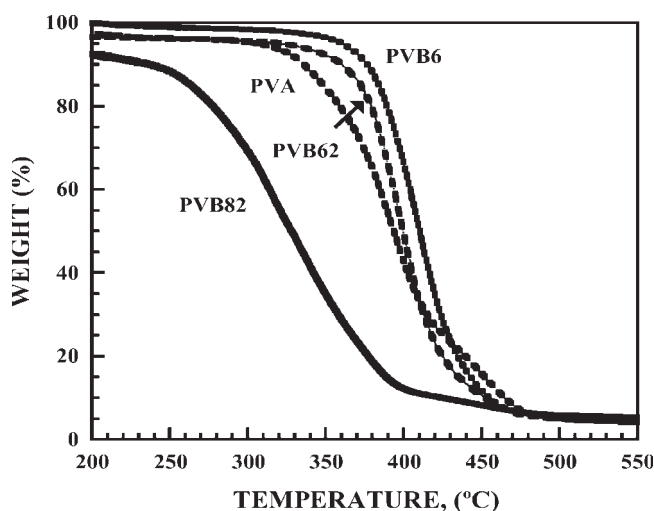


Figure 6 TGA curves for PVA and PVBs. Heating rate 20°C/min.

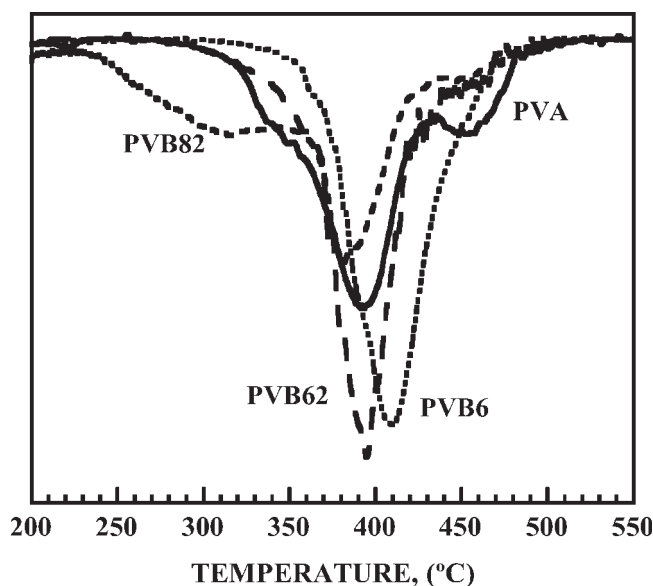


Figure 7 DTG curves for PVA and PVBs. Heating rate 20°C/min.

TABLE XI  
Thermal Analytical Data for PVA and PVBs. (Heating Rate 20°C/min)

Polymer	VA (mol %)	$T_i^1$ (°C)	$T_{max}^1$ (°C)	$W^1$ (%)	$T_i^2$ (°C)	$T_{max}^2$ (°C)	$W^2$ (%)	Residue (%)	Char (%)
PVA	100	279	392	80	–	453	15	5	4
PVB82	82	227	316	35	–	382	50	6	5
PVB72	72	287	392	90	–	–	–	3	3
PVB64	64	308	398	86	–	–	–	5	5
PVB50	50	299	400	83	–	–	–	4	3
PVB38	38	289	402	81	–	–	–	6	6
PVB21	21	303	404	89	–	–	–	7	7
PVB6	6	318	412	93	–	–	–	6	6

TABLE XII  
Temperature of Decomposition at Different Weight Losses of PVA and PVBs. (Heating Rate 20°C/min)

Polymer	VA (mol %)	$T_d$ (°C) at weight loss of							
		10%	20%	30%	40%	50%	60%	70%	80%
PVA	100	336	359	375	385	394	406	415	440
PVB82	82	206	281	308	333	358	376	387	399
PVB72	72	347	370	379	386	392	397	404	417
PVB64	64	359	379	387	393	398	404	411	424
PVB50	50	364	381	388	393	399	405	413	426
PVB38	38	367	384	393	399	405	410	417	429
PVB21	21	357	379	391	398	405	412	420	432
PVB6	6	373	390	398	405	412	417	425	435

units, the activation energy is between 185 and 227 kJ/mol. The activation energy for the first step of degradation of PVB with 82 mol % VA is between 100 and 145 kJ/mol, while that of the second stage obtained by the Kissinger method is 163 kJ/mol, and  $E$  value calculated by the Flynn–Wall method changes with conversion. The lowest activation energy is obtained for PVB82 (18 mol % VB) because for that sample the lowest values of  $T_i$  and  $T_{max}$  are observed.  $E$  value of PVBs containing 6–70 mol %VA does not change greatly with vinyl alcohol content due to the light change in  $T_i$  and  $T_{max}$  observed in these samples. The activation energies obtained indicate that the degrada-

tion is more difficult for PVBs with a content of VA units between 70 and 6 mol % than for PVA and PVB with 82 mol % VA.

## CONCLUSIONS

The acetalization of PVA with butyraldehyde results in a new polymer PVB, which is a copolymer of butyral rings and unreacted vinyl alcohol. NMP is an excellent solvent for PVA and PVBs display excellent solubility in it. In this study an homogeneous reaction medium (NMP) has been used to maintain the poly(vinyl acetal) in solution. PVBs with different degree of acetalization have been synthesized. The reaction goes almost to completion with very few unreacted hydroxyl groups remaining in the polymer. The PVBs with 30–35% acetalization are soluble in DMSO but not in THF, those PVBs with 40–75% acetalization are soluble in DMSO and THF, those products with a degree of acetalization of 80% or higher are soluble in THF and  $Cl_3CH$  but not in DMSO, and all polymers are soluble in NMP. As NMP is the solvent for all PVBs, it is the best reaction medium to carry out the homogeneous acetalization. The fraction of the meso and racemic stereostructures of butyral rings depends on the acetalization degree, being favored the mesoacetal structure. The glass transition temperatures of PVBs increase as vinyl alcohol content increases, and this increase displays a positive departure from line-

TABLE XIII  
Apparent Activation Energies for the Various Stages of Thermal Degradation of PVA and PVBs under Dynamic Conditions

Polymer	VA (mol %)	$\alpha$ (%)	F-W <sup>a</sup>	K <sup>a</sup>	
			$E$ (kJ/mol)	$E$ (kJ/mol)	$\log A$ ( $\text{min}^{-1}$ )
PVA	100	5–70	$151.2 \pm 3.8$	137	11.63
PVB82	82	5–40	$139.3 \pm 6.0$	100	9.88
		50–70		163	14.15
PVB72	72	10–65	$221.2 \pm 5.7$	209	17.64
PVB50	50	15–75	$205.6 \pm 8.2$	184	15.46
PVB6	6	5–80	$213.1 \pm 5.1$	189	15.61

<sup>a</sup> F-W: Flynn–Wall's method; K: Kissinger's method.

arity. The thermal decomposition of PVBs has been examined by dynamic TGA experiments in nitrogen. The results have shown that the thermal stability depends on the content of the hydroxyl groups, increasing with decreasing this content. PVBs with less than 80 mol % VA units are more thermally stable compared with PVA, but PVB with 82 mol % is less stable. The mass loss of PVBs is accomplished in one step, except for the polymer with 82 mol % VA that occurs in two regions. The activation energies estimated by the Kissinger and Flynn–Wall methods are consistent.

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