THERMAL DEGRADATION OF COPOLYMERS OF VINYL ALCOHOL AND VINYL BUTYRAL

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A series of copolymers of vinyl alcohol (V-OH) and vinyl butyral (VB) with different degrees of VB substitution were prepared from poly(vinyl alcohol) (PV-OH), and were subjected to thermal degradation under vacuum. The degradation products were then identified. Alcohol rich copolymers showed increased thermal stability, whereas it decreased with the increase in VB contents in the copolymer. No interaction between adjacent V-OH and VB units in the chain was observed. A degradation mechanism is proposed to account for the principal features of the reaction and the products of degradation.

INTRODUCTION

The thermo-oxidative degradation of PV-OH acetals have been studied by various workers [1—7]. The mechanism proposed for the oxidative degradation of acetals by Beachell [1] indicates that there is a substantial difference between the processes of photo and thermal again and it is necessary to consider different mechanisms for the decomposition of acetals of PV-OH in different types of aging. In the present study an effort has been made to contribute to resolution of these problems by investigating the composition of the volatile products from the decomposition of copolymers of V-OH and VB degraded in steps under high vacuum conditions.

EXPERIMENTAL

Materials. The solvents, methanol, conc. H_2SO_4 and *n*-butyraldehyde (C_3H_7CHO) were of A.R. grade. Poly(vinyl alcohol) (PV-OH) (BDH), molecular weight approximately 14,000 was used as supplied. Elemental analysis indicated that residual acetate in the polymer was less than 2%.

Preparation and Purification of Copolymers of V-OH and VB. A homogeneous solution was prepared by warming PV-OH (5g), methanol (4ml), water (41ml) and conc. H_2SO_4 (0.3% of total weight of reaction mixture) in a three necked flask equipped with a mechanical stirrer. A calculated amount of C_3H_7CHO was added with vigorous stirring over a period of 20 mints, while the internal temperature was raised to about 70°. 30 ml hot water at approximately 70° was then added over a period of 15-20 mints. The resulting mixture was agitated for a further 10 mints and a small amount of conc. H_2SO_4 dissolved in 10 ml H_2O added. The reaction mixture was stirred for a further hr and the resultant product filtered and washed repeatedly with water and dilute alkali (NaOH) to remove all traces of acid which could catalyse decomposition.
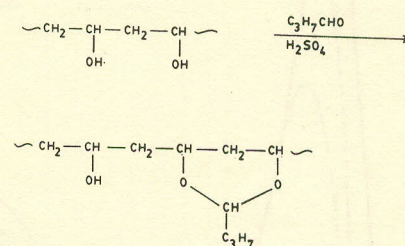
Copolymers were carefully washed with water and dried in a vacuum oven at 80° for several days.

The compositions of copolymers were calculated from elemental analysis using a Perkin Elmer 240 Elemental Analyser.

Thermal Volatilization Analysis (TVA). The TVA method of McNeil was used [8]. 30 mg of each copolymer was used; trap temperatures were 0, −45, −75, −100 and −196° and the heating rate was 10° min⁻¹.

Subambient TVA. The mixture of volatile degradation products obtained by TVA was separated by the subambient TVA technique [9,10]. Briefly, the total condensable products of degradation are collected at −196° and allowed to warm up under conditions of continuous evacuation. The pressure of gases evolved is measured and continuously recorded. Curve of the type shown in Fig.6 is obtained; each peak refers to an individual degradation product which can be collected for analysis and identification.

Thermal Gravimetric Analysis (TGA). TG curves were obtained on a Du Pont 950 thermogravimetric analyser. 10 mg samples were heated under dynamic nitrogen (60 ml min^{-1}) at 10° min^{-1}

The infrared spectra (IR) of copolymers were recorded in KBr pellets on a Perkin Elmer 257 Grating Spectrophotometer.

RESULTS AND DISCUSSION

Thermal Analysis. TVA traces for copolymers containing 4.75%, 8.68%, 24.47% and 50.9% VB are illustrated in Figs.2,3,4,5 respectively. The first low broad peak in the region 90–160° (not indicated in the first threeFigs.)is due to elimination of physically absorbed water. The second peak (much suppressed as compared with PV-OH) appears in the same temperature region as in the case of PV-OH (Fig.1).
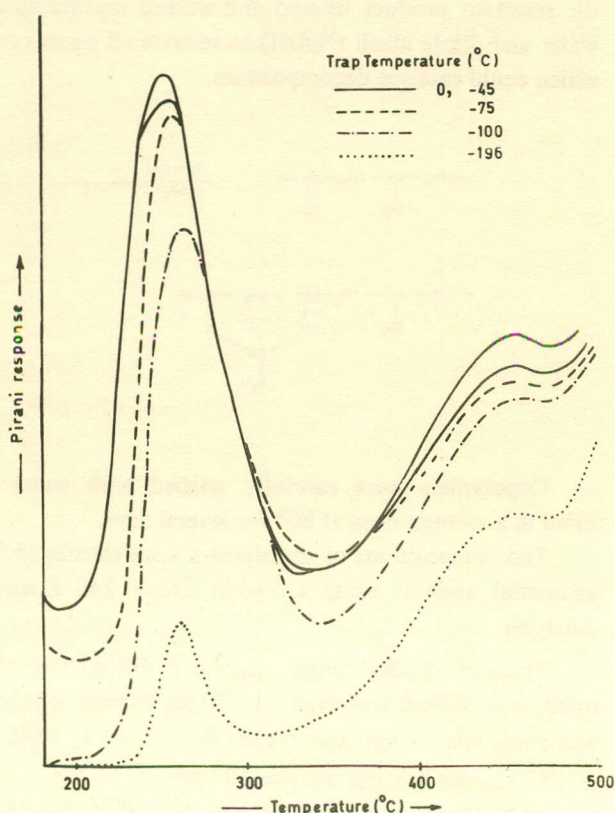

Fig. 1. TVA curve for PV-OH.

Analysis of the degradation products associated with this peak and falling between 200–300° indicates the presence of acetic acid, water, ketene, carbon dioxide and unsaturated hydrocarbons. The main degradation reaction is associated with the third peak. The Pirani responses at this

peak are mainly due to C_3H_7CHO, water and acetaldehyde although some more volatile products are also trapped at −100° and −196°. In alcohol rich polymers (Figs.2,3) water elimination (−75° curve is the characteristic of water)[11] decreases as compared with PV-OH (Fig.1) which may be attributed to the blockage of reaction by VB units thereby meaning a separate initiation step for each V-OH sequence. The water elimination increases with the increasing content of VB units in the chain (Figs. 4, 5). This may be due to electrostatic interaction of butyral groups.
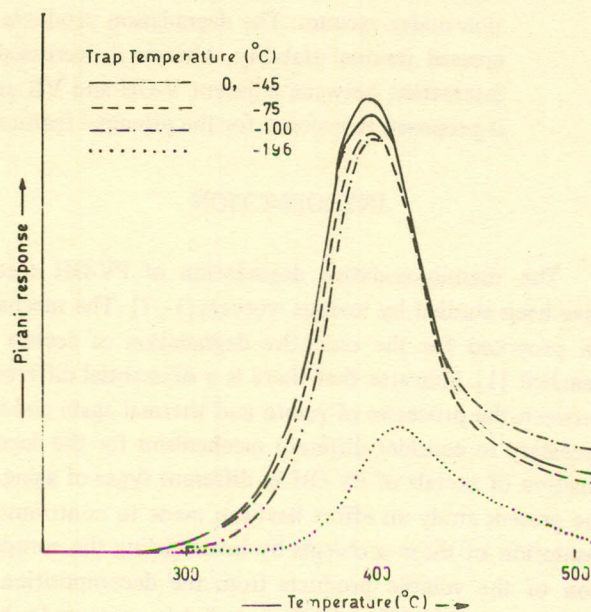

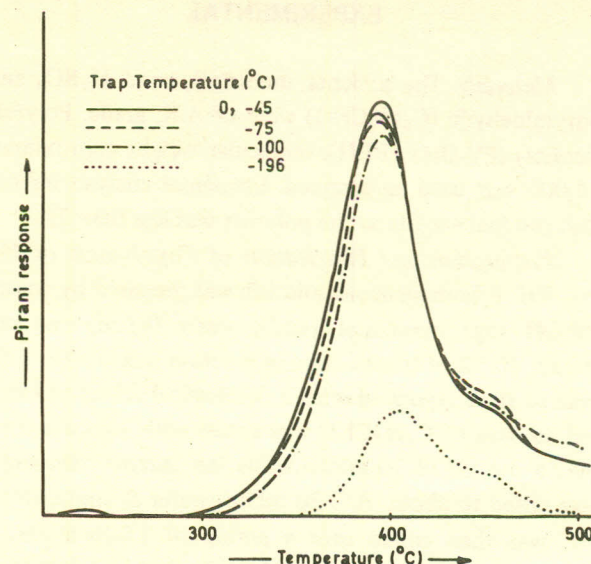Fig. 2. TVA curve for 4.75% V-OH/VB copolymer.

Fig. 3. TVA curve for 8.68% V-OH/VB copolymer.

The vertical broken lines in a subsambient TVA trace (solid line) of 50.9% VB copolymer (Fig.6) indicate the fractions isolated for IR analysis and the dotted line, the temperature of the trap from which the condensable gases are progressively volatilising. The products identified in each stage of the reaction are shown in Table 1.

Figs. 7,8 show TG curves for V-OH/VB copolymers containing 0.35%, 1.66%, 4.75% and 4.75%, 27.47%, 49.20% VB respectively.

There are two distinct regions of weight losses; the first stage is associated with the breakdown of vinyl acetate (V-OAC) and V-OH units, and the second stage is due to the breakdown of butyral units in the chain. Weight loss in alcohol rich polymers at lower temperatures is considered to be resulting from the elimination of physically absorbed water. Fig. 7 shows that the stability compared with PV-OH is increased greatly by small amounts of butyral units. As
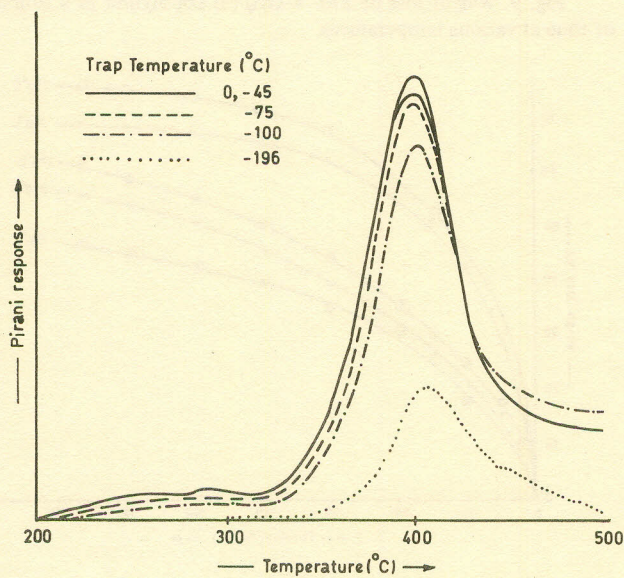
in the case of the TVA data described above this is probably due to the butyral units blocking the progress of water elimination from groups of adjacent alcohol units. It is clear from Fig. 8 that the stability decreases with the in-
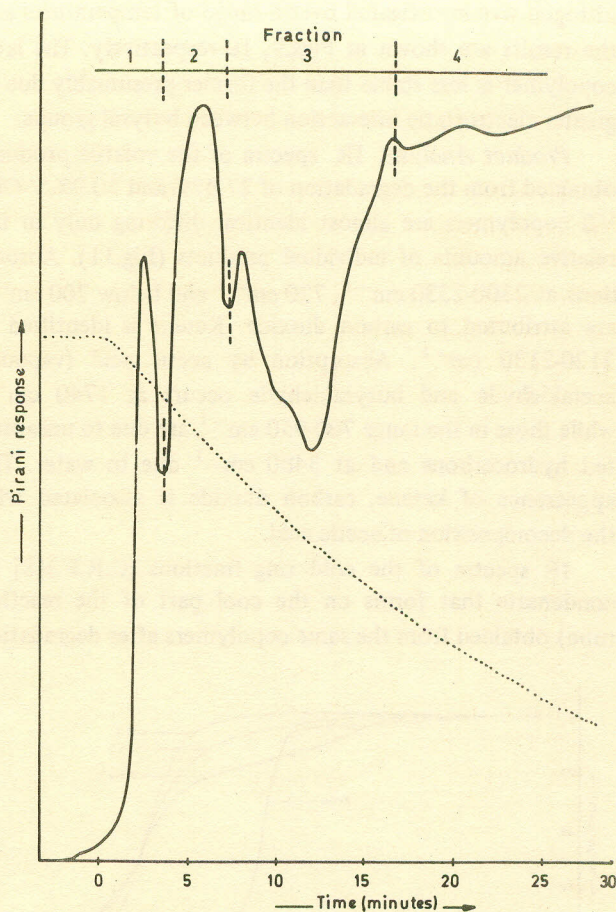

Fig. 6. Sub-ambient TVA of condensable gases from degradation of 50.90% V-OH/VB copolymer.

Fig. 4. TVA curve for 27.47% V-OH/VB copolymer.
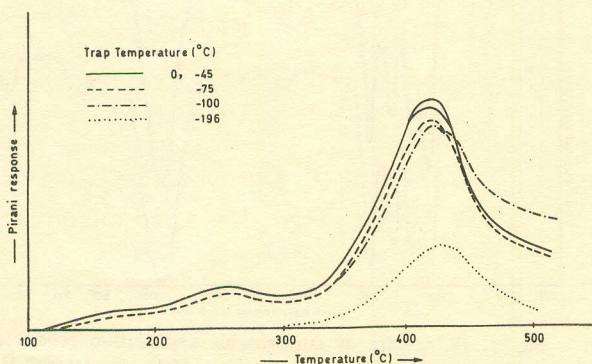
Fig. 5. TVA curve for 50.90% V-OH/VB copolymer.

Table 1. Volatile products of decomposition of 50.9% V-OH/VB copolymer heated to 500°C.

	Fractions		
1	2	3	4
Ethylene	Carbon dioxide	Water	—
Propylene	Ketene	Acetaldehyde	Water
Isobutene	Propylene isobutene	Butyraldehyde	—

crease in the concentration of butyral units probably due to the electrostatic interaction of the butyral units in the chain.

The loss in weight of 27.47% and 50.9% V-OH/VB copolymers which occurs during isothermal heating under nitrogen was investigated over a range of temperatures and the results are shown in Figs.9, 10 respectively. The later copolymer is less stable than the former presumably due to greater electrostatic interaction between butyral groups.

Product Analysis. IR spectra of the volatile products obtained from the degradation of 27.47% and 50.9% V-OH/ VB copolymers are almost identical differing only in the relative amounts of individual products (Fig.11). Absorptions at 2300-2330 cm^{-1}, 720 cm^{-1} and below 700 cm^{-1} are attributed to carbon dioxide. Ketene is identified at 2120-2130 cm^{-1}. Absorption by acetic acid (vapour), acetaldehyde and butyraldehyde occurs at 1740 cm^{-1} while those in the range 700-950 cm^{-1} are due to unsaturated hydrocarbons and at 3480 cm^{-1} due to water. The appearance of ketene, carbon dioxide is associated with the decomposition of acetic acid.

IR spectra of the cold ring fractions (C.R.F.)[8] (a condensate that forms on the cool part of the reaction tube) obtained from the same copolymers after degradation
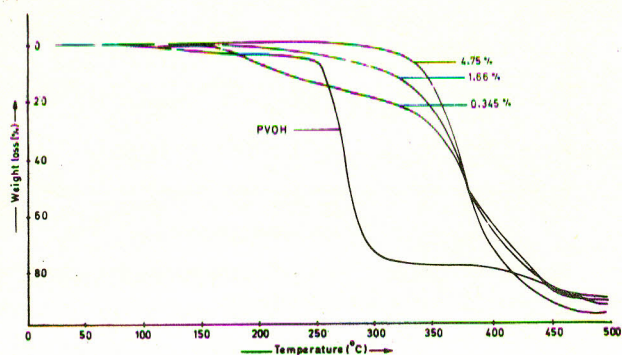

Fig. 9. Weight loss of 27% V-OH/VB copolymer as a function of time at various temperatures.

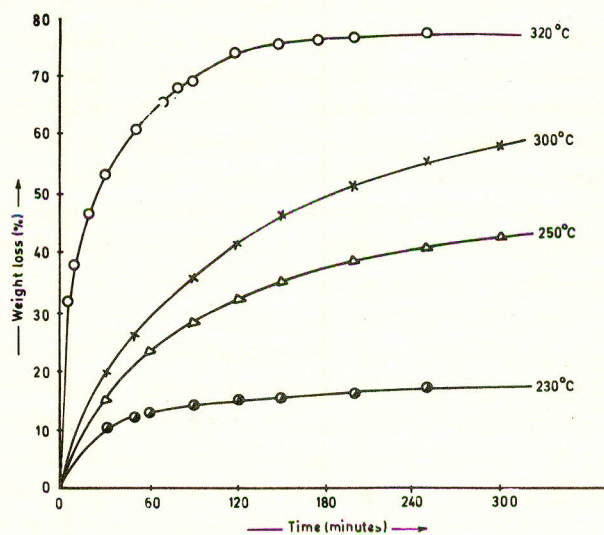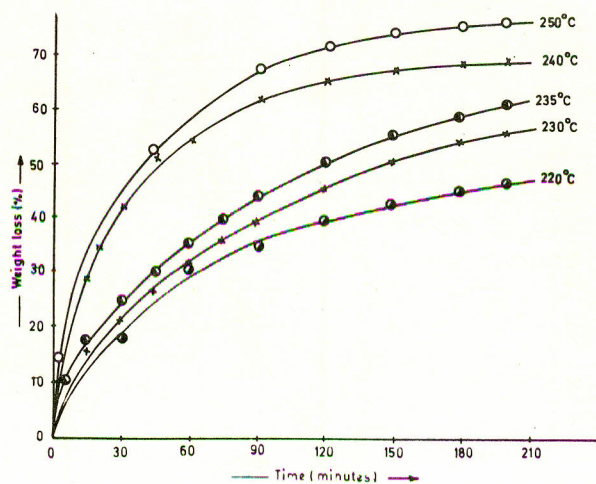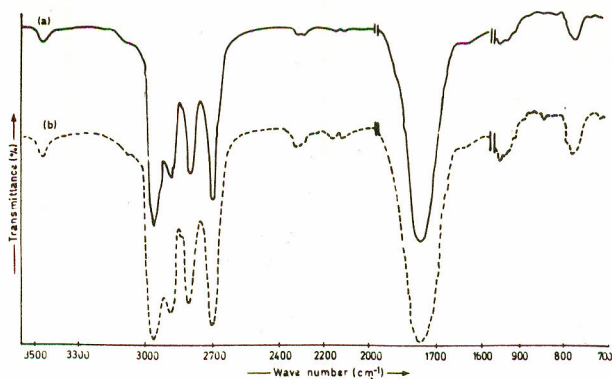Fig.10. Weight loss of 50.90% V-OH/VB copolymer as a function of time at various temperatures.

Fig. 7. TG curves for V-OH/VB copolymers, Dynamic N_2 atmosphere, heating rate 10° min.

Fig. 8. TG curve for V-OH/VB copolymers, Dynamix N_2 atmosphere, heating rate 10° min.

Fig.11. IR spectra of condensable degradation products. (a) 27.47% V-OH/VB copolymer degraded to 500° (b) 50.90% V-OH/ VB copolymer degraded to 500'

to 500° are compared with that of the original undegraded 50.9% V-OH/VB copolymer (Fig. 12). The spectra of the C.R.F.'s run by using the KBr technique are almost identical to that of the undegraded copolymer that accept for the appearance of a few new absorptions. The peak, a little above 300 cm^{-1} and the band in the region 800–900 cm^{-1} arise from conjugation in the degraded copolymer. The carbonyl absorption of the acetate and butyral groups has shifted to lower frequency. There was not sufficient residue for IR investigation.

Structural Changes During Degradation. In order to investigate the structural changes which occur during the degradation of copolymers, 50 mg samples of the copolymers were degraded in steps by programmed heating. The changes which occurred in all the copolymers were qualitatively similar. Hence the description of only 31.66% V-OH/VB copolymer is given.

Fig.13 (a, b, c) shows IR spectra of the undegraded copolymer; the residue of the copolymer was heated to first peak and C.R.F. heated to 500° respectively. No C.R.F. was obtained when the copolymer was heated to first peak. The IR spectrum of the residue (Fig.13 b) differs from that of the undergraded polymer in a slight shift in the carbonyl absorption from 1740 cm^{-1} to 1710 cm^{-1}, the absence of two peaks in the 1200 cm^{-1} and 940 cm^{-1} regions and the appearance of two peaks in the region 800–900 cm^{-1} which are associated with conjugation resulting from the elimination of acetic acid.
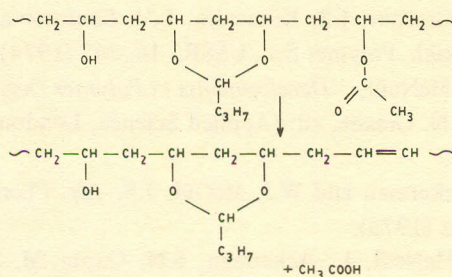
IR spectra of n-butyraldehyde (gas phase), degradation products of the copolymer heated to first and second peaks are shown in Fig. 14 (a, b, c) respectively. The degradation products of the copolymer in the first peak (Fig. 14 b) are acetic acid (1740 cm^{-1}) and water (around 3490–3500 cm^{-1}). Ketene and carbon dioxide were not observed at this stage probably due to the low degradation temperature. The C.R.F. of the copolymer degraded to 500° (Fig. 13 c) shows similar absorptions. Both residue and C.R.F. show residual V-OAC and VB units in the copolymer. Butyraldehyde and water are the main degradation products of the copolymer in the second peak (Fig. 14 c).

Proposed Reaction Mechanism. IR investigations of the degradation products of the copolymers degraded in steps under vacuum have shown that acetic acid and water on the one hand and butyraldehyde on the other are produced in separate steps during degradation suggesting no
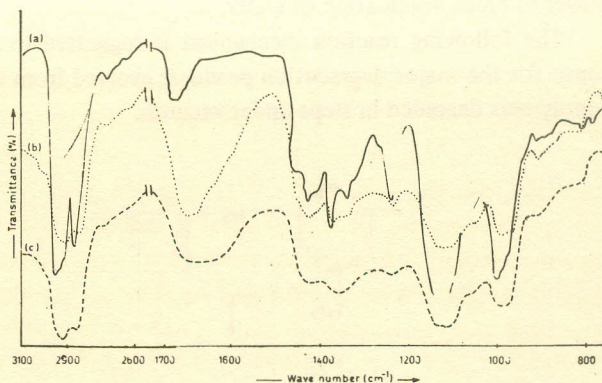
Fig.12. IR spectra of copolymers. (a) undegraded 50.90% V-OH/VB (b) CFR of 27.47% V-OH/VB degraded to 500° (c) CRF of 50.90% V-OH/VB degraded to 500°
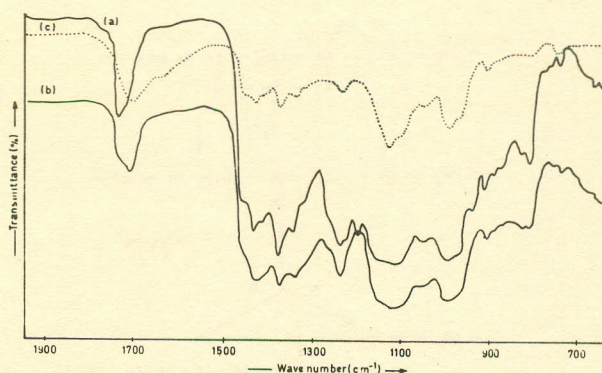
Fig.13. IR spectra of 31.66% V-OH/VB copolymers. (a) CRF of the copolymers (b) Residue of the first peak (c) CRF of the copolymers degraded to 500°.
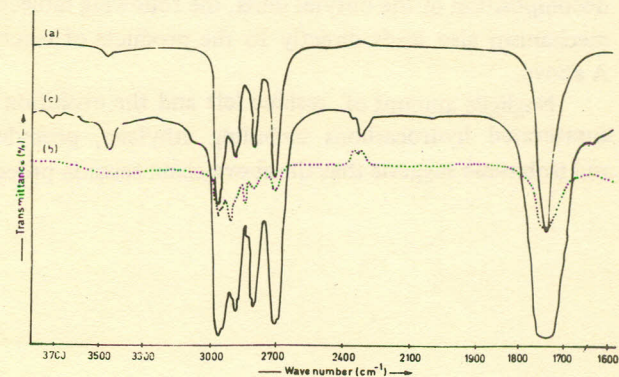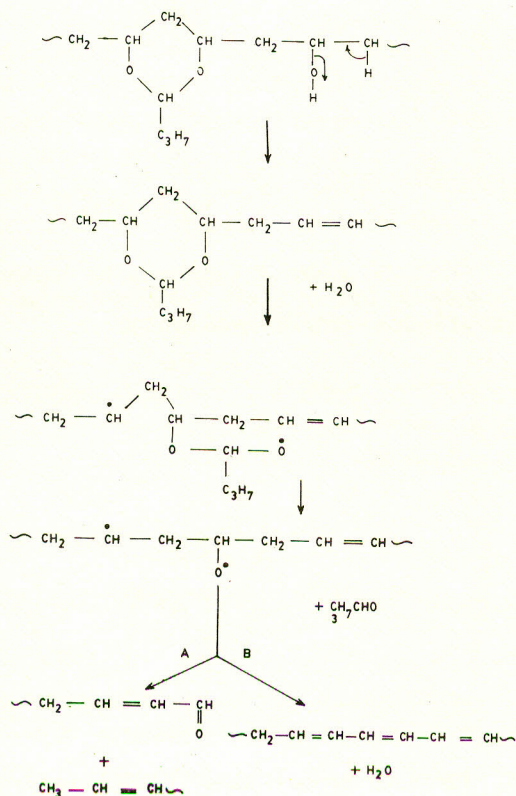
Fig.14. IR spectra of the degradation products of 31.66% V-OH/VB copolymers (a) n-butyraldihyde. (b) copolymer. heated to first peak (c) copolymer heated to second peak.

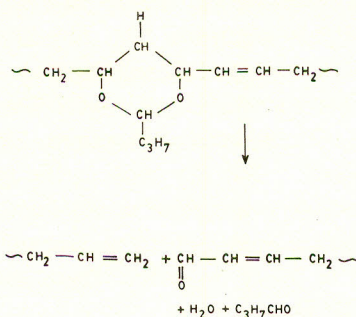interaction between two different groups in the copolymer.

Isothermal study under nitrogen has shown the stability to weight loss of the copolymer as depending upon the concentration of the butyral groups in the chain which may be associated with their electrostatic interaction and their power to block elimination of water.

The following reaction mechanism is suggested to account for the major degradation products evolved from the copolymers degraded in steps under vacuum.

whether radical or molecular, plays an important role in the reaction.

REFERENCES

1. H.C. Beachell, P. Fotis and J.Hucks, J. Polymer Sci., **7**, 353 (1951).
2. Z. Jeolinski and Z. Hippe, Roczniki Chem., **40**, 257 (1966).
3. T. V. Kreitzer, Zh. Prikl, Spektroskopy, **7**, 213 (1967).
4. D. Braun and G. Vorendohre, Farbe u. Lack, **69**, 820 (1963).
5. F. Sadowski and E. Kuhn, Farbe u. Lack, **69**, 267 (1963).
6. O.M. Kilmova, N.I. Duvakina, L.V. Kuzmina, O.S. Romanova and A. S. Golenishcheva, Zhpkh, No. **4**, 902-904 (1967).
7. V.I. Grachev, I.B. Klimenko, L.V. Simirnov and A.F. Gladkikh, Polymer Sci., USSR, **16**, 367 (1974).
8. I.C. McNeill, *Developments in Polymer Degradation* — 1, N. Grassie, ed; (Applied Science, London, 1977), p.43.
9. L. Ackerman and W.J. McGill, J.S. Afr. Chem. Inst., **26**, 82 (1973).
10. I.C. McNeill, L. Ackerman, S.N. Gupta, M. Zulfiqar and S. Zulfiqar, J. Polymer Sci., Polymer Chem. ed., **15**, 2381 (1977).
11. I.C. McNeill and D. Neill, *Thermal Analysis*, (Academic Press, New York 1969), p.353.

As an alternative to the above radical process for the decomposition of the butyral units, the following molecular mechanism also leads directly to the products of reaction A above.

Negligile amount of residue left and the evolution of unsaturated hydrocarbons including ethylene, propylene and isobutene suggests that the above chain scission process,