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INVESTIGATIONS OF THERMAL ELIMINATION REACTIONS OF POLYMERS BY THERMAL VOLATILIZATION ANALYSIS AND ULTRAVIOLET SPECTROSCOPY*

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Using thermal volatilization analysis with differential condensation of volatile products, with film samples on flat-bottomed silica glass reaction tubes to permit measurements of UV spectra of partly degraded polymer, the thermal stability, the types of volatile products and the development of conjugation in the involatile residue have been compared for poly(vinyl chloride), polychloroprene, poly(vinyl acetate) and vinyl acetate/ethylene copolymers, poly(vinyl formate) and poly(vinyl alcohol). All undergo a side-group elimination reaction at lower temperatures, and polyene breakdown occurs in all the samples between 400 and 500°. The longest polyene sequences are formed by PVC. All the polymers except PVC show some complexity of products in the elimination reaction.

Introduction

The technique of thermal volatilization analysis (TVA) has been fully described, both for the simplest form of the apparatus [1, 2] and for a system with provision for differential condensation of products [3, 4]. The latter modification makes TVA unique among thermoanalytical techniques in providing some information about the types of volatile products evolved from a sample, before any subsequent analysis by spectroscopic or other methods, and by partially separating products may considerably assist these subsequent studies. The use of gas cells for infrared spectroscopic analysis, in conjunction with a TVA system, has been briefly described [4].

Although TVA was developed primarily as a tool for studying degradation of polymers, the technique is applicable to any substance which does not sublime or volatilize under vacuum before decomposition. A number of non-polymeric materials have been examined, and TVA curves for some of them have been published [2].

In investigations of polymer breakdown, interest may centre on one or more of the three main product fractions: the products which are volatile at ambient

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temperature, the products (often waxy or oily) which are volatile only at degradation temperature, and the solid residue of degradation. In the TVA apparatus, these products are conveniently separated as (i) volatile products passing through the vacuum system, which may be further separated by differential condensation, (ii) products which condense out on the limited area of the upper part of the degradation tube which is cooled by a cold water jacket ('cold ring fraction'), and (iii) the solid residue left on the flat base of the degradation tube. Greatest interest is usually focussed on fractions (i) and (iii). The value of TVA in studying (i) has already been well illustrated [1—15], and some further applications are discussed below. Fraction (iii) is less easily studied in many thermal investigations, particularly in cases in which insolubility develops, because of the difficulty of removing it from the degradation vessel.

Most thermobalances use small, frequently cup-shaped, sample holders, often of metal. In the TVA systems already described, however, in order to secure the advantages of thinly-distributed samples, large, flat-based degradation tubes have been employed. These were of Pyrex glass, but silica glass tubes of similar design have now been utilised to permit studies of the ultraviolet spectra of partially-degraded polymers without the need to remove the sample from the tube, since the silica degradation tube, with sample, may be inserted directly into the beam of the spectrometer, with an identical, but empty tube used in the reference beam.

This development of the TVA method now provides a convenient means for simultaneous study of both volatile products and residue of degradation. A number of industrially-important polymers undergo elimination of small molecules leaving a residue which progressively develops increased colour. Poly(vinyl chloride) (PVC), polychloroprene (PC), poly(vinyl acetate) (PVA), poly(vinyl alcohol) (PVAlc) and poly(vinyl formate) (PVF) have now been examined with the particular object of comparing the types of volatile products and the development of conjugation in the polymer backbone.

Experimental

Thermal volatilization analysis

The differential condensation TVA apparatus used was as previously described [4]. For UV spectroscopic measurements, the TVA degradation tubes were constructed of silica glass and were identical in dimensions to the Pyrex tubes already used [1, 2], except that the length was reduced to 11.5 cm to permit the tubes to be accommodated in the beam of the UV spectrometer. All the experiments reported in this paper were carried out at a heating rate of 5° per minute, and degradation temperatures quoted or shown on diagrams are sample temperatures, determined from the recorded oven temperatures using calibration data.

Ultraviolet spectroscopy

A polymer film (between 20 and 100 mg) was cast from 1 ml of solution on the flat base (10 cm^2) of the silica glass degradation tube. Initially, and after various extents of degradation, the spectrum was recorded on a UV spectrometer (Unicam SP 800) with an empty tube in the reference beam. In the work described in this paper, a fresh film was used in each degradation, and the film was heated at 5° per minute to a selected temperature, then cooled rapidly and the spectrum was recorded. A convenient alternative approach, used in experiments on PVC, PC and PVA, not presently reported, utilised isothermal temperatures of 190, 210 and 260°C and single film samples, with interruption of the degradation at suitable times for recording of the UV spectrum.

Thermogravimetry

The Du Pont 950 thermobalance was used in the TG study of PVF. A 5 mg powder sample was heated in a dynamic nitrogen atmosphere.

Materials

Solvents. Cyclohexanone was twice distilled; all other solvents were A.R. grade.

PVC. An additive-free sample (Breon 113, made by British Geon Ltd.) was used. Films were prepared by vacuum evaporation of cyclohexanone solutions.

PC. Butachlor MC 30 (Distillers Co. Ltd.), a mercaptan-modified emulsion polymerized polychloroprene, was reprecipitated twice from toluene into methanol under nitrogen. A sample of PC was also prepared at —40° using a standard low temperature emulsion recipe [16]. Films were prepared by vacuum evaporation of toluene solutions.

PVA. British Drug Houses polymer was used as supplied. Films were prepared by vacuum evaporation of toluene solutions.

Vinyl acetate/ethylene copolymers. Alathon 3130 (12% VA) and Alathon 3185 (33% VA), made by Du Pont, were reprecipitated from warm toluene into petroleum spirit (b. 40—60°). Films were prepared by vacuum evaporation of warm toluene and were opaque due to precipitation occurring before evaporation was complete. Film quality, however, improved when the film was heated.

PVF. Vinyl formate monomer (Koch-Light Laboratories) was twice distilled under vacuum and polymerized under UV irradiation in evacuated sealed dilatometers at 0° in presence of azobisisobutyronitrile. The number-average molecular weight, obtained by calculation [17] from viscosity measurements in acetone at 30° was 170,000.

PVAlc. Gelvatol 060-G (Shawinigan Ltd.) was reprecipitated by methanol from aqueous solution. The manufacturers' specification for the polymer indicated very low residual acetate content ($<0.3\%$) and this was confirmed by the absence of carbonyl absorption in the IR spectrum. Films were prepared by vacuum evaporation of aqueous solutions.

Results and discussion

All these polymers degrade to give volatile products in at least two stages, that at lower temperatures corresponding to the elimination of small molecules formed from side groups present originally. In every case there is a further reaction occurring with maximum rate at a temperature (T_{max}) of 430° or higher, which can be attributed to the breakdown of the residual, essentially hydrocarbon chain. For comparison, it may be noted that polyethylene gives a T_{max} of 440° and polypropylene a value of 430°, at the same heating rate of 5° per minute [2]. All the polymers examined develop visible colour due to unsaturated structures suitable for study by UV spectroscopy. The polymers will be discussed in turn.

PVC

The first peak in the TVA curve (Fig. 1), with maximum at 265°, is for the evolution of hydrogen chloride, which is non-condensable at —100°. The high temperature peak at 458° results from products of which a large proportion are non-condensable at —196°, formed by break up of the unsaturated chains. The UV spectra show maxima and inflections at 235, 267, 279, 290, 312, 327, 342, 366, 390, 414, 440, 464 and 484 mμ (Fig. 2), in agreement with previous observations [18, 19]. The absorption extends to 650 mμ even in the very early stages of reaction. As the reaction proceeds, absorption increases, with the short wavelength peaks growing more rapidly.

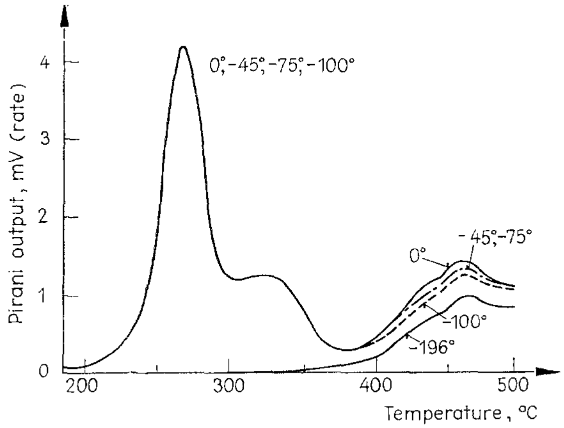

Fig. 1. TVA curves for PVC, 100 mg film sample, 5° per minute

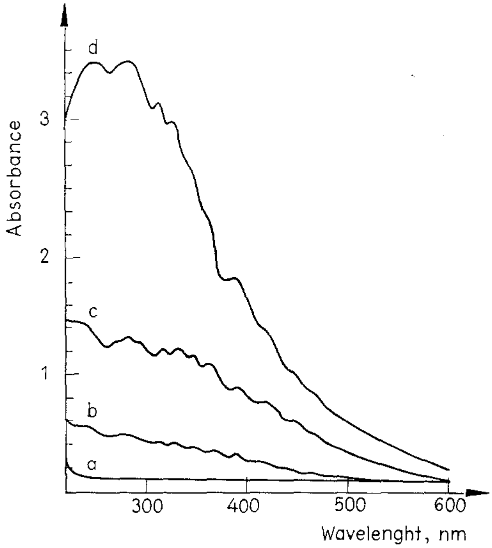

Fig. 2. UV spectra for PVC as 100 mg films initially, (a) undegraded, (b) degraded to 215°, (c) degraded to 227°, (d) degraded to 259°, at 5° per minute

PC

This polymer also degrades by dehydrochlorination and the product distribution pattern is similar to that of PVC. Because the chlorine in PC is vinylic, the polymer shows greater thermal stability than PVC and the dehydrochlorination maximum in the TVA curve (Fig. 3) occurs at 350°. Main chain disintegration becomes extensive at temperatures above 390°.

The UV spectral changes (Fig. 4) are completely different from PVC. The first formed absorption shows maxima at 277 and 288 mμ and inflections at 265 and 300 mμ. Later in the degradation, these peaks become obscured by a featureless

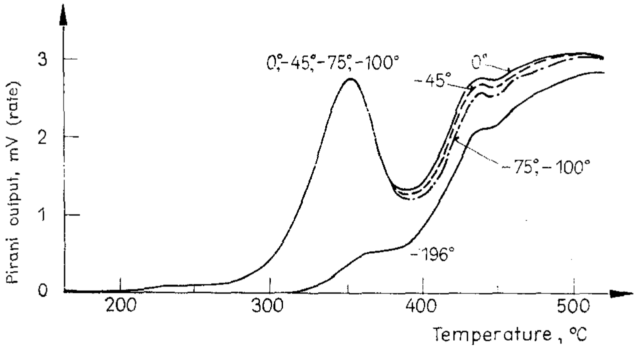

Fig. 3. TVA curves for PC, 100 mg film sample, 5° per minute

absorption extending to 550 mμ. The TVA curve shows only a little dehydrochlorination taking place between 200 and 300°, but the growth of the UV absorption in this temperature range is very striking. In order to determine whether the early part of the degradation is linked to the number of irregularities in the polymer chain, a sample of PC was prepared at —40°. TVA of this polymer indicated that less degradation took place below 300° and this was confirmed by the UV spectroscopic observations.

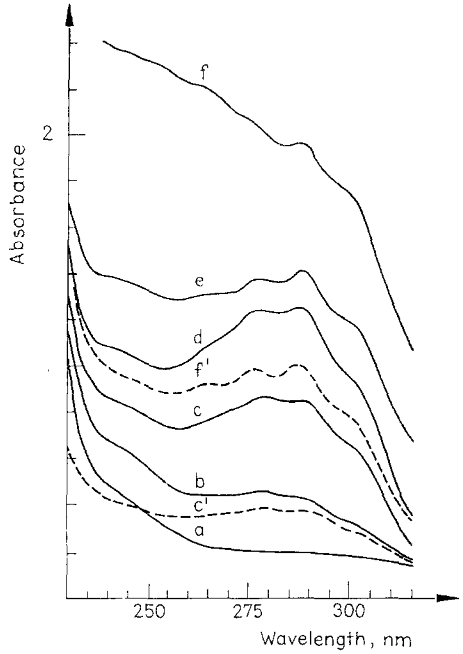

Fig. 4. UV spectra for PC as 20 mg films initially, (a) sample MC 30 undegraded, (b) degraded to 185°, (c) degraded to 210°, (d) degraded to 233°, (e) degraded to 278°, (f) degraded to 295°, (c′) sample prepared at —40° degraded to 233°, (f′) sample prepared at —40° degraded to 295°, all at 5° per minute

The expected conjugated structure from the initial dehydrochlorination of PC is a monochlorotriene, but no reference spectra of compounds containing this group have been found in the literature. Data available on the most closely related compounds [20, 21] suggest that the assignment of the bands below 300 mμ to a monochlorotriene is reasonable.

PVA

This polymer has been shown to eliminate acetic acid [22, 23]. The TVA curve has maxima at 322 and 435°, but during the elimination reaction there are evolved products non-condensable at —75, —100 and —196°, as indicated by the traces shown in Fig. 5. In this diagram, in which the rate scale is non-linear [1, 2], the Pirani gauge after the 0° trap responds to all volatile products, while the gauge following the —196° trap responds only to the non-condensable gases. Infrared spectroscopic analysis of the latter revealed the presence of carbon monoxide and methane. The difference in response in the —75° and —196° curves may be due to the presence amongst the products of water, carbon dioxide and ketene. The last two of these have also been identified by infrared analysis of the gaseous products which are volatile at —75°. Acetic acid is completely trapped at the three lowest temperatures, but at —45° it condenses and distils over to the liquid nitrogen trap at a steady rate, causing the —45° trace to stay at a constant height above the —75° curve. Apart from the effect due to acetic acid, the product distribution at the second peak is similar to that for PVC and PC. Distillation of acetic acid is complete by the time the heating programme reaches 500°, and at this point the —45° curve returns to coincidence with the 0° trace.

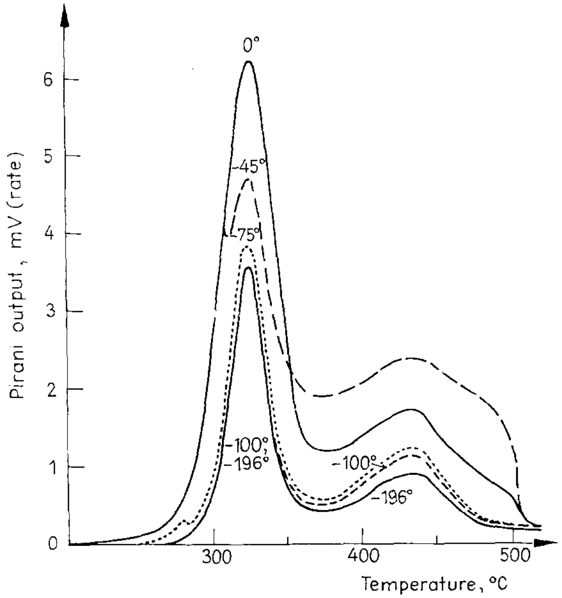

Fig. 5. TVA curves for PVA, 100 mg film sample, 5° per minute

UV spectra of degraded PVA films (Fig. 6) show the growth of polyenes of much shorter length than in PVC. Absorption does not extend beyond 500 mμ, and again the short wavelength absorptions grow more rapidly. Peaks occur at 233, 261, 272, 283, 305, 335, 350 and 380 mμ. The triad centred on 272 mμ is due to the 2,4,6-octatriene chromophore, which has maxima at 252, 263 and 274.5 mμ in solution in hexane and 260, 270 and 279 mμ in chloroform [24]. The more polar of these solvents reproduces the polymer film conditions better and other peaks correspond to maxima in the absorption spectra in chloroform solution of dimethyl polyenes with up to six double bonds in conjugation. Trace quantities of longer polyenes are present, extending the absorption to 500 mμ.

Further evidence for the assignment of the three peaks in the 250—300 mμ region comes from an examination of the spectra (Fig. 7) of degraded films of ethylene/vinyl acetate copolymers. The copolymer with 12% VA can be calculated to contain 18.6% of the VA groups in blocks of two but only 3.7% in blocks of three or more. Absorption is therefore confined to the diene region centred on 235 mμ. The 33% VA copolymer contains 29.6% of the acetate groups in blocks of two, 14.7% in blocks of three and 10.9% in blocks of more than three. Thus absorption beyond the triene region is almost completely absent. The triene peaks observed occur at 261, 272 and 283 mμ in the copolymer, as in PVA.

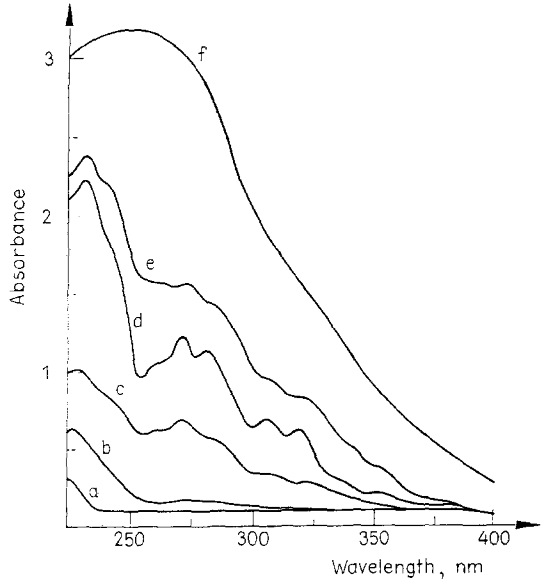

Fig. 6. UV spectra for PVA as 20 mg films initially, (a) undegraded, (b) degraded to 289°, (c) degraded to 301°, (d) degraded to 313°, (e) degraded to 332°, (f) degraded to 381°, at 5° per minute

Degraded films of PVA were examined by Servotte and Desreux [23] by IR spectroscopy but they were unable from their spectra to make a decisive interpretation in favour of the presence of polyenes. The present UV spectroscopic data for PVA show clearly the existence of polyenes in the thermally degraded polymer.

PVF

On degradation this polymer produces spectra which are indistinguishable from those for degraded PVA. PVF is, however, less thermally stable than PVA and the nature of the TVA curve (Fig. 8) is quite different. The elimination reaction shows two peaks, with maxima at 275 and 313°. The reaction begins at about 190°, and at the first peak, the products are almost entirely non-condensable in liquid nitrogen. At the second peak, however, the divergence of the traces shows that condensable material is being formed. Thermogravimetry showed (Fig. 9) a 64% weight loss in a single stage reaction, commencing at about 230° and reaching completion at 375°, with T_{max} at 313°. This weight loss would correspond to quantitative loss of formic acid from the polymer. When formic acid was passed through the TVA apparatus, it was found that it was fully condensed at —75° and lower temperatures, but not condensed at all at 0° or —45°. Heating the degradation tube to 350° while the formic acid was passing through it had no effect on the pattern of condensability. The secondary decomposition in PVF has a maximum rate at 430°.

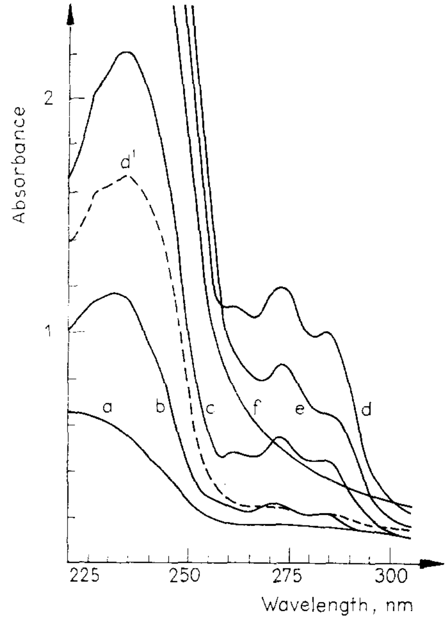

Fig. 7. UV spectra of ethylene/vinyl acetate copolymers as 20 mg film samples initially, (a) 33% copolymer degraded to 301°, (b) degraded to 323°,(c) degraded to 350°, (d) degraded to 356°, (e) degraded to 374°, (f) degraded to 425°, (d') 12% copolymer degraded to 356°, all at 5° per minute

The TVA and TG data for this polymer are in some conflict, and this is possibly an indication that the mode of breakdown of PVF is dependent on the experimental environment — whether in nitrogen or under high vacuum, or whether in the form of thin films or powder sample. It might be argued, for instance, that with thin film samples and vacuum conditions, formyl radicals, which are possible intermediates in the degradation, are able to volatilize, and that these react in the gas phase to give carbon monoxide and hydrogen (both non-condensable), whereas in the case of powder samples at atmospheric pressure such radicals

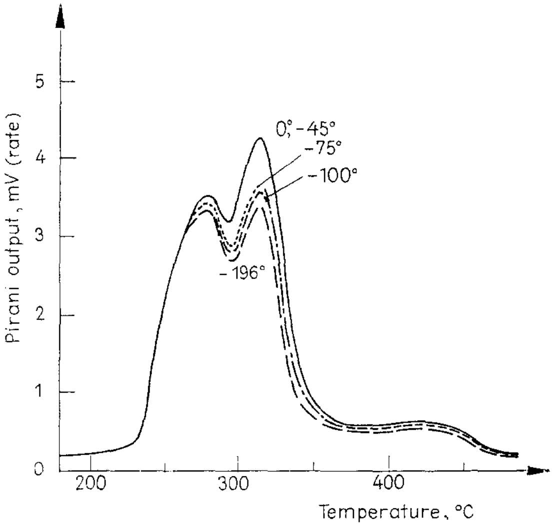

Fig. 8. TVA curves for PVF, 20 mg films sample, 5° per minute

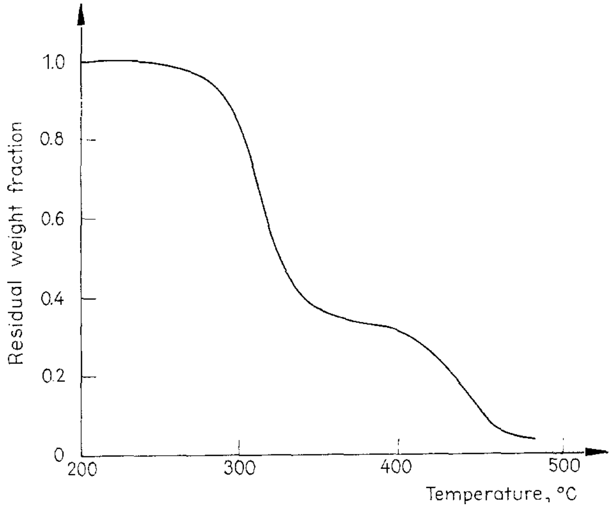

Fig. 9. TG curve for PVF, 5 mg sample, 5° per minute, dynamic nitrogen atmosphere (60 ml/min)

would react with polymer to produce formic acid. A more detailed investigation of the products of degradation of PVF under various conditions is required to clarify the mechanism of breakdown.

PVAlc

The thermal degradation of PVAlc has been studied by several workers [25, 26, 27], and the main products of degradation have been shown to be water from the elimination reaction, and acetaldehyde from depolymerization.

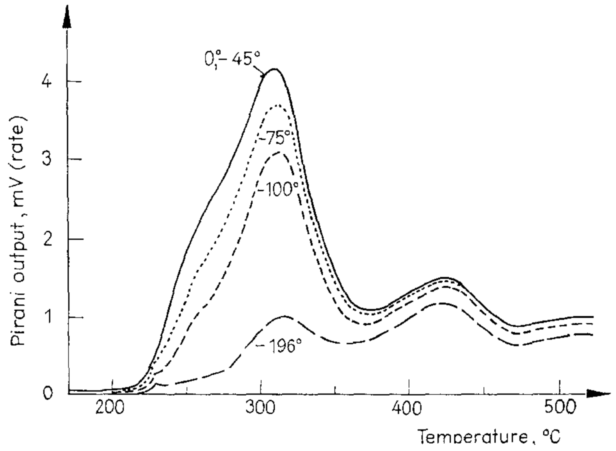

Fig 10. TVA curves for PVAlc, 100 mg film sample, 5° per minute

Four peaks are present in the TVA curve for PVAlc (Fig. 10). The first, low broad peak (not shown in the diagram) has a maximum at 121° and the behaviour in the —75° line is characteristic of water in the TVA system [2]. Because water is used as solvent for the polymer, it is difficult to distinguish between absorbed water volatilizing and water being chemically eliminated. Degradative dehydration of PVAlc has been reported in this temperature range leading to the loss of a variable amount of water. Inter- as well as intramolecular elimination has been suggested [28].

The second TVA peak has a maximum at 310°. Some of the products are trapped at —75°, some at —100° and a very small amount is non-condensable at —196°. The rate maximum in the curves for traps at temperatures lower than —45° occurs at 318°, showing that the product composition changes during this stage of reaction. The Pirani responses at this peak cannot be explained on the basis of water and acetaldehyde alone, and possibly formaldehyde [26] and hydrogen [29], which have also been reported to be formed during the degradation, account for the responses after the —100° and —196° traps.

The remaining two peaks are due mainly to non-condensables and have maxima at 430 and 515°. The existence of *two* high temperature peaks for this polymer may perhaps be due to extensive crosslinking at lower temperatures.

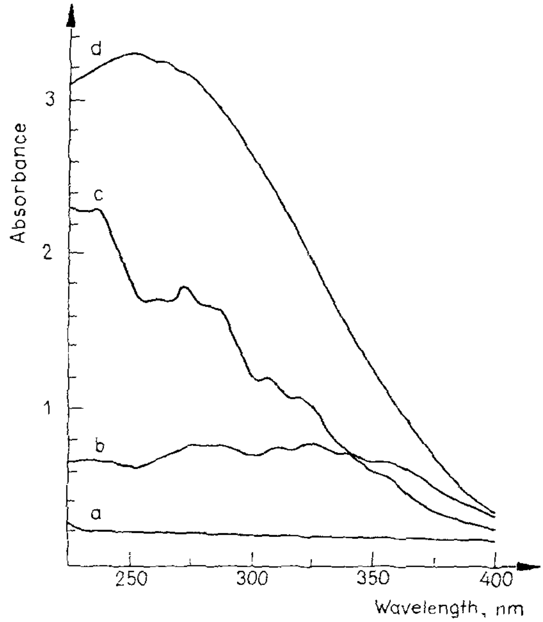

Fig. 11. UV spectra for PVAlc as 100 mg films initially. (a) undegraded; (b) degraded to 221°; (c) degraded to 265°; (d) degraded to 290°; all at 5° per minute

UV spectra of samples of PVAlc frequently contain a peak at 280 mμ which is due to the dienone chromophore [30]. Gelvatol 060-G has no such absorption, and when degraded gave maxima at 235, 263, 273, 283, 307, 322, 335 and 352 mμ (Fig. 11). In the early stages the first four were not as strong as the absorptions at longer wavelengths, but later the pattern became similar to PVA.

Conclusions

All the polymers studied degrade by an elimination reaction which takes place below 400° and produces a residue containing polyenes which undergoes further degradation between 400 and 500° to yield as volatile products mainly substances which are non-condensable. Differential condensation TVA shows that PVC is the only one of the polymers which gives no product other than the expected elimination product in the first stage of breakdown. PC gives hydrogen chloride and a small amount of non-condensables, but PVA, PVF and PVAlc have large

Pirani responses for substances which are less easily condensed than acetic acid, formic acid, water or acetaldehyde.

Elimination occurring at random along the chain would be expected to produce initially short polyenes which became longer as the reaction proceeded. This did not occur in any of the polymers investigated. Apart from PC in which a chlorotriene may be isolable as a first product, elimination in the polymers appears to occur by a chain mechanism involving a number of adjacent units, and both short and longer polyenes are present in the early stages of degradation. The short polyenes increase in concentration as the degradation proceeds. In PVC the number of adjacent units involved is much higher than in the other polymers. Crosslinking could reduce the effective length of conjugation by decreasing the chain mobility and preventing the formation of the planar configuration of the polyene.

More detailed investigations to determine the origin of minor products of degradation of the PVA type of polymer, and a comprehensive study of PC degradation, will be reported subsequently.

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Résumé — L'emploi de la méthode d'analyse par volatilisation thermique avec condensation différentielle des produits volatils, sur des échantillons en film sur tubes de réaction en verre-silice à fond plat permet l'examen des spectres ultraviolets des polymères partiellement dégradés et l'étude de la stabilité thermique, outre l'identification des constituants volatils. On a comparé le développement de la conjugaison dans le résidu non-volatil pour les polychlorure de vinyle, polychloroprène, polyacétate de vinyle et les copolymères acétate de vinyle/éthylène, polyformiate de vinyle et polyalcool vinylique. Dans chaque cas, on a observé une réaction d'élimination du groupe latéral à basse température et rupture du polyène entre 400 et 500°. Les plus longues séquences ont été formées dans le cas du PCV. Tous les polymères, excepté le PCV, montrent une certaine complexité de produits dans la réaction d'élimination.

Zusammenfassung — Die Anwendung der thermischen Verdampfungsanalyse durch Differentialkondensation der flüchtigen Produkte an Filmproben in flachen Quarzglasreaktionsrohren gestattet die Ermittlung der UV-Spektren von teilweise degradierten Polymeren sowie Aussagen über die thermische Stabilität und Types des flüchtigen Produktes. Die Bindungen in dem nichtflüchtigen Rest wurden untersucht und im Falle der Copolymere Poly(vinylchlorid), Polychloropren, Poly(vinylacetat) und Vinylacetat/Äthylen, weiterhin Poly/vinylformat und Poly/vinylalkohol verglichen. Alle erleiden eine Eliminierungsreaktion an der Seitengruppe bei niedrigeren Temperaturen und Polyenabspaltung zwischen 400 und 500°. Die längsten Polyensequenzen werden durch PVC gebildet. Abgesehen vom PVC zeigten alle übrigen Polymere eine gewisse Komplexität in der Eliminierungsreaktion.

Резюме. — Проведены анализы термического испарения полимеров с дифференциальной конденсацией летйчих продуктов. Использовались образцы тонкого слоя (пленка), помещенные в плоскодонную кварцевую трубку, что дало возможность исследовать УФ-спектр частично распавшихся полимеров, термостабильность, состав летучих чподуктов и образование конюгации в нелетучем остатке. Результаты сравнивались для поливинилхлорида, полихлоропрена, поливинилацетат - и винилацетат-этиленовых сополимеров, поливинил — формиата и поливинилового спирта. Каждый из них подвергается реакции отщепления боковых групп при низкой температуре; расщепление полиена происходит во всех образцах в области температур 400—500°. Более длинные ряды полиенов образуются в суйчае ПВЦ. При реакции расщепления все полимеры, кроме ПВЦ, обнаруживают некоторую сложность состава продуктов распада.