THE THERMAL DEGRADATION OF POLY(METHYL VINYL KETONE) AND POLY(METHYL *ISO*PROPENYL KETONE)

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Abstract—The degradations have been studied by thermal volatilization analysis and thermogravimetry, with infrared and ultraviolet spectroscopic investigations of products. Under temperature-programmed heating conditions, PMVK first splits out water from adjacent side groups by a random process, giving a fused ring system as the first formed product. As the temperature is raised, chain scission occurs, leading eventually to a total weight loss as great as 90 per cent. This scission process appears to involve fission of bonds between adjacent ring structures, rather than breakdown of the rings themselves; it is accompanied by the production of small amounts of methane and carbon monoxide. The residue remaining above 500° is stable to temperatures greater than 800°, and is presumably a form of carbon.

The thermal decomposition of PMIK, under the same conditions, is superficially similar, although some differences in behaviour are also apparent. Monomer production occurs in PMIK, proceeding concurrently with the early stages of the coloration reaction. The yield of monomer is prevented from attaining 100 per cent by the cyclisation process, since the formation of the six membered rings greatly reduces the kinetic chain length of depolymerization. The large amount of methane and carbon monoxide evolved in the later stages of the decomposition of PMIK can be taken as an indication that cyclisation in this polymer is less efficient than in PMVK. A steric interpretation for this factor has been advanced.

INTRODUCTION

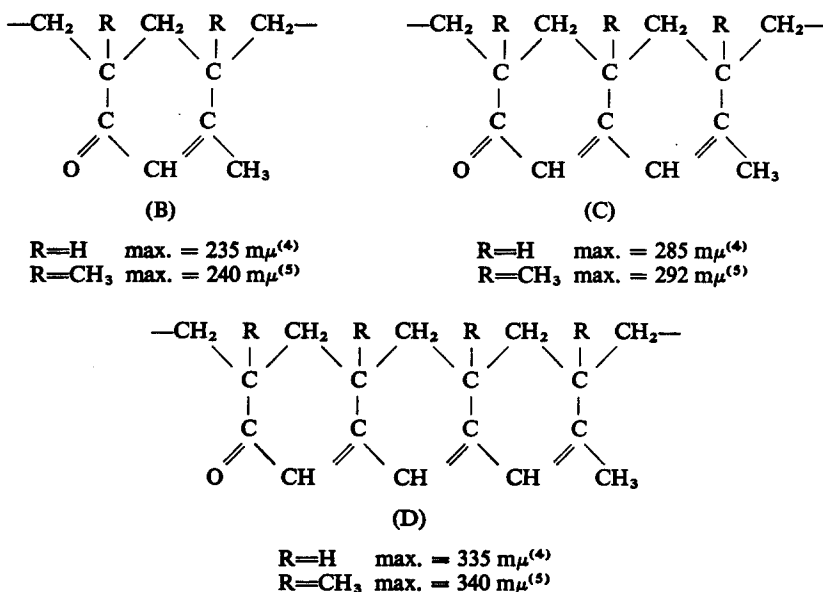Poly(methyl vinyl ketone) PMVK, and poly(methyl *iso*propenyl ketone) PMIK, have the following structures:
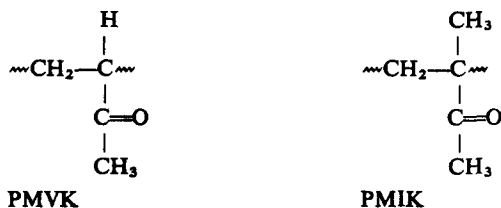
Some interest has already been taken in the degradation of these polymers, the earliest work being that of Marvel and co-workers[1,2] who showed that the polymers had a "head to tail" arrangement of monomer units, yielding water and a cyclohexenone ring system (A) on heating:
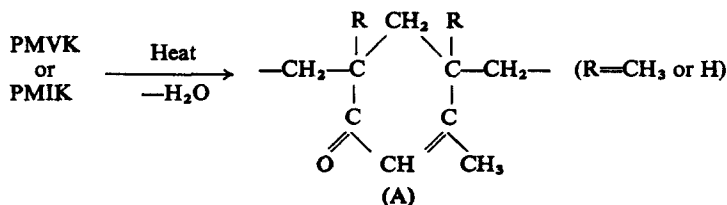

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Grassie and Hay,[3,4] and Matzuzaki[5] confirmed the earlier findings and by study of the C:H:O ratio in the residue,[4,5] and by i.r.[3,5] and u.v. absorption spectroscopy,[4,5] showed that the residue was converted on heating to structures of the type B, C and D:

(B)

R=H   max. = 235 mμ[4]
R=CH$_3$ max. = 240 mμ[5]

(C)

R=H   max. = 285 mμ[4]
R=CH$_3$ max. = 292 mμ[5]

(D)

R=H   max. = 335 mμ[4]
R=CH$_3$ max. = 340 mμ[5]

The yellow coloration of the residue was believed to be due to structures of these types. Wall[6] and Hay[4] have pointed out that, by contrast with polyacrylonitrile,[7,8] the random nature of the cyclization process in PMVK and PMIK means that not all the oxygen can be eliminated from the polymer as water. This is due to the formation of "incompatible" structures, such as (E) and (F), shown below, which prevent the cyclization process from proceeding along the entire length of the molecule:

(E)

(F)
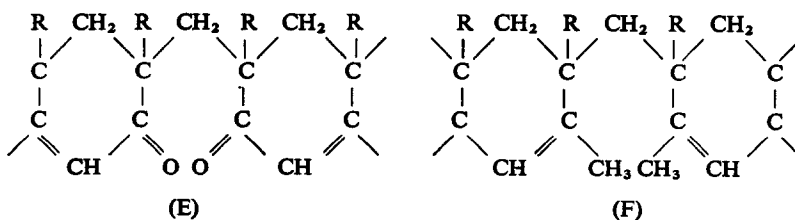
The work reviewed above clearly established the following points:

(a) The polymers have a "head to tail" structure.
(b) Both polymers on heating undergo an intramolecular condensation of adjacent pendant groups, eliminating water by a mechanism which is probably analogous to that of the "aldol" condensation.[3]
(c) This reaction is random in nature so that side chains react in "clusters" rather than the cyclization passing through the length of the molecule. As a consequence, 79 to 85 per cent of the oxygen is lost as water from PMVK, and 63 per cent of the oxygen is eliminated from PMIK, under suitable conditions.[2]

Some aspects of the thermal degradation of these polymers, however, have not been fully elucidated.

Unzipping of the PMIK chain to monomer might be expected by analogy with other 1:1 disubstituted polymers. For example, both polyacrylonitrile and polymethacrylonitrile undergo coloration reactions. In the case of the latter, however, monomer yields of up to 100 per cent have been reported when the polymer prepared was free of methacrylic acid units.[9] Similarly, poly(methyl methacrylate) decomposes quantitatively to monomer, while monomer yields from poly(methyl acrylate) are negligible.[10]

Monomer was detected by Marvel[2] in the pyrolysis products of PMIK. It was not established, however, whether it was a major product.

It was not clearly shown in what way the additional methyl group in PMIK affected the rate or extent of cyclisation in the two polymers.

The thermal stability of the condensed ring system, formed by water elimination, was not examined. It is of interest to observe whether or not cyclization leads to the formation of a stable residue akin to that formed in the pyrolysis of polyacrylonitrile. It was hoped that study of the polymers using thermal volatilization analysis (TVA) might help to clarify these points.

EXPERIMENTAL

Methyl vinyl ketone and methyl *iso*propenyl ketone (Bisol Ltd.) were purified by washing first with alkali to remove inhibitor and then several times with distilled water; they were dried over anhydrous magnesium sulphate. Before polymerization, each monomer was distilled three times under vacuum, only the middle fractions being used. It was checked that the i.r. spectra of the purified monomers agreed with those of reference spectra.[11]

PMVK (1) was prepared by bulk polymerization of MVK at 60° with 0·1 % w/v azobis*iso*butyronitrile, PMVK (2) at 40° with 0·1 % initiator and PMVK (3) at 40° with 1 % initiator.

PMIK (4) was prepared by bulk polymerization of MIK at 40° with 1 % initiator and PMIK (5) at 60° with the same initiator concentration. PMIK (6) was prepared by allowing the monomer to polymerize at ambient temperature, in air, without initiator.

Both polymers were isolated by precipitation in methanol and purified by reprecipitation from acetone. The PMVK samples were rubbery, clear and soft, whereas the PMIK samples were white powders. Both polymers were soluble in ketonic solvents but not in toluene or benzene.

The number-average molecular weights of the six polymers, in the order listed above, determined osmotically in methyl ethyl ketone solution using a Mechrolab Model 501 osmometer with 300 grade Sylvania cellophane membrane, were as follows: (1) 132,000, (2) 401,000, (3) 362,000, (4) 70,500, (5) 59,100, (6) 220,000.

Thermogravimetry (TG) was carried out using 10 mg samples on the Du Pont model 950 TG instrument, for which the platinum sample holder measured 1 cm long × 0·5 cm wide × 0·25 cm deep. Temperature measurement was by a chromel–alumel thermocouple placed 1 mm from the sample holder. The heating rate was 10°/min and a dynamic nitrogen atmosphere (80 ml/min) was used.

Thermal volatilization analysis (TVA) was carried out using a system providing for differential condensation of products in four parallel lines in which Pirani gauges were preceded by initial cold traps at 0°, −45°, −75° and −100°, respectively, and followed by a trap at −196°. The apparatus, and the interpretation of the TVA curves obtained, has been fully described[12] Samples of 50 mg size were used, in the form of powder for PMIK and thin slices for PMVK. The Pyrex glass degradation tube had a base area of 10 cm.^{2} The heating rate was 10°/min. Temperatures quoted are sample temperatures determined from continuously-recorded oven temperatures by calibration experiments, as discussed previously.[13]

THERMAL STABILITY OF THE POLYMERS

TG curves for PMVK and PMIK samples are shown in Fig. 1. The other samples of PMVK and PMIK behaved similarly. Clearly, PMIK is less stable than PMVK,

although both polymers degrade to approximately the same final percentage residue. The residue of both polymers was found to be stable in the range 500–800°.

Figures 2 and 3 show TVA curves obtained using the differential condensation apparatus.[12] Comparison of these reveals a number of features. No monomer is evolved in the thermal decomposition of PMVK. In the main degradation peak, the trace for the Pirani placed beyond the −75° trap shows the typical behaviour of water in the system, the slow distillation of water from the −75° trap to the liquid nitrogen trap showing as an output of 0·2 to 0·3 mv on the Pirani. If monomer had been a major product, it would have appeared on the −75° trace, since it is not condensed in the evacuated system at this temperature. This is in agreement with the conclusions reached by Hay[14] who showed that water was the only product at 250° in isothermal experiments.
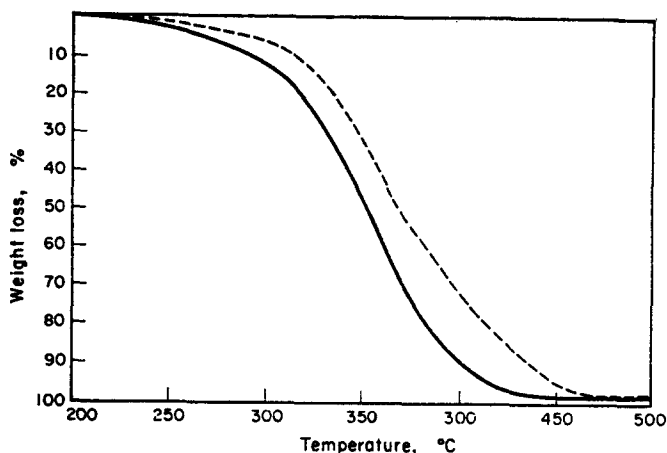

FIG. 1. Thermogravimetric curves (10°/min, N₂) for PMIK (continuous line) and PMVK (dotted line).

In PMIK, however, a major part of the first peak is due to material which is not condensed at −75°. Although no data is available on the behaviour of methyl iso-propenyl ketone in the differential condensation TVA apparatus, product analysis (described below) shows this material to be monomer.

Beyond the first peak of the TVA curve, the decomposition of both polymers is accompanied by the production of material which is not condensed at −100°. For the same initial weight of material, it is apparent that a greater amount of non-condensable material is evolved from PMIK than from PMVK.

At the end of an experiment, it was found that the upper portion of the degradation tube was covered with a brown ring, the nature of which is discussed below. Interruption of the degradation at various temperatures established that in both polymers this fraction began to appear just after the maximum of the first degradation peak had been passed.

It was also observed that both polymers had yellowed noticeably at temperatures as low as 220°, i.e. before the onset of the main degradation peak.
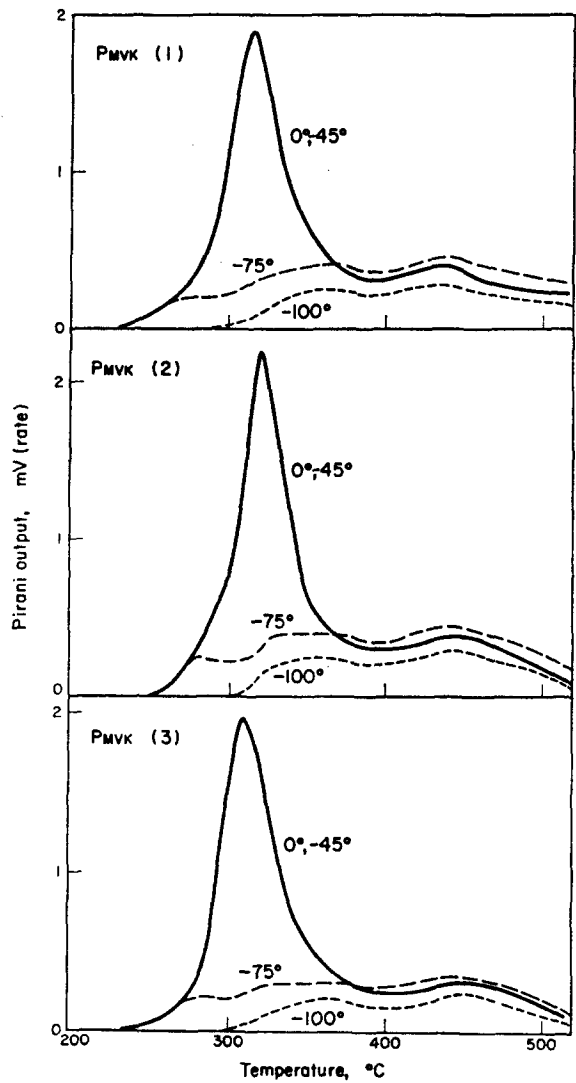
FIG. 2. Differential condensation TVA curves for three PMVK samples (10°/min).
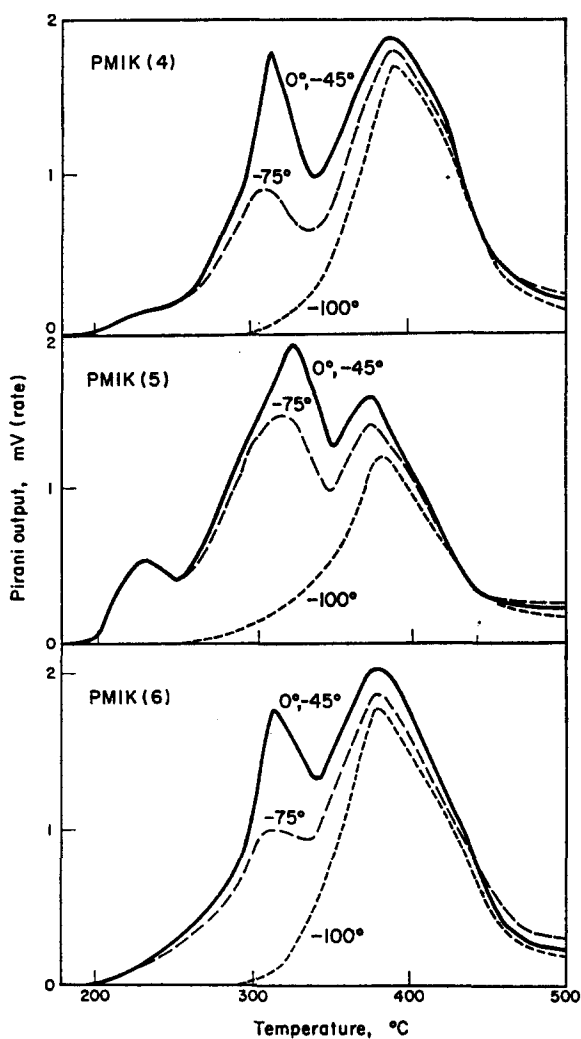
FIG. 3. Differential condensation TVA curves for three PMIK samples (10°/min).

PRODUCT IDENTIFICATION

The degradation products from PMVK and PMIK can be classified into fractions:

(a) The involatile residue, comprising products involatile at 500° under vacuum.

(b) The "cold-ring fraction", collected on the water-cooled upper part of the TVA degradation tube, which consists of products volatile at degradation temperatures but involatile at room temperature, under vacuum.

(c) Products condensable at −100°.

(d) Products not condensed at −100°.

Fraction (a)

The structural changes occurring in the residue as a result of the intramolecular cyclization reaction have been thoroughly investigated[4,5] and have been discussed

above. The structure of the residue remaining at 500° was examined, in the case of PMIK by i.r. spectroscopy. The broad spectrum indicated that all carbonyl groups had been eliminated from the polymer, and suggested that the residue was probably an impure form of carbon. Presumably the residue from PMVK degradation is similar, although it was not possible to isolate a suitable sample for i.r. analysis.

Fraction (b)

The cold-ring fraction was examined by i.r. and u.v. spectroscopy. The upper portion of the degradation tube was wiped with a tissue moistened with the appropriate solvent (A.R. carbon tetrachloride for i.r., "Spectrosol" hexane for u.v.) and the tissue then extracted with a further portion of the same solvent, and a spectrum taken of the extract. The corresponding spectra for PMVK were almost identical. Ultra-violet peaks at 230 and 280 mμ suggest that groupings of type B and C (see above) are present in this fraction. Slight absorption in the region 330–335 mμ may be attributable to D type ring formations. The i.r. spectrum was consistent with the presence in the sample of unsaturated six-membered ketone rings.

Fraction (c)

The products from the pyrolysis of PMIK which were condensable at −100° were trapped out at this temperature and distilled into a capillary tube reservoir. On thawing out, the products separated into two layers of approximately equal volumes. When the reservoir was opened, a strong smell of monomer was detected. The lower liquid layer was water miscible, while the upper layer was organic. Since water was evidently present, it was removed by shaking the products with "Analar" carbon tetrachloride containing anhydrous magnesium sulphate, before an i.r. spectrum was taken. In a similar fashion, the liquid was dried before taking a u.v. spectrum in hexane.

The i.r. spectrum was identical to that for methyl *iso*propenyl ketone[11] while the λ_{max} value of the u.v. absorption is in good agreement with the literature value for this compound.[15]

The material not condensed at −75° in the TVA thermogram of PMIK is thus clearly established as monomer.

By contrast, the liquid products from PMVK degradation were not found to contain monomer.

Fraction (d)

The identity of the product which was not condensed at −100° was established for each polymer, using the closed degradation system shown in Fig. 4. Two-hundred milligrams of the polymer was placed in tube T, and the system was then evacuated through the 5 mm stopcock C, taps A and B being open. All the taps were then closed, and the system was clamped in position so that the lower portion of tube T was in the TVA oven. A cold-trap at −100° was placed around the cold finger D, and the sample was heated at 10°/min to 500°, and then allowed to cool. Taps A and B were then opened and L was immersed in a liquid nitrogen bath. After 5 min A was closed, the cold-trap was removed, the gas cell disconnected from the system, and a spectrum was taken. The characteristic peaks of methane and carbon monoxide were clearly
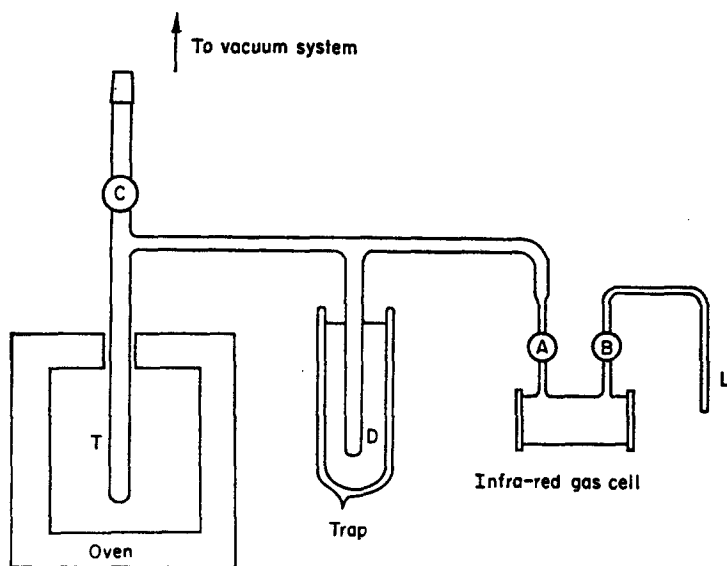
FIG. 4. Apparatus for infrared analysis of volatile degradation products. (A, B, C: stopcocks, D, L: cold fingers, T: sample tube.)

evident. The PMVK spectrum differed only in that the intensities of the peaks were somewhat reduced.

Monomer production in PMIK

The production of monomer forms an important part of the thermal decomposition behaviour of PMIK. Up to 50 per cent of the liquid products are methyl *iso*propenyl ketone.
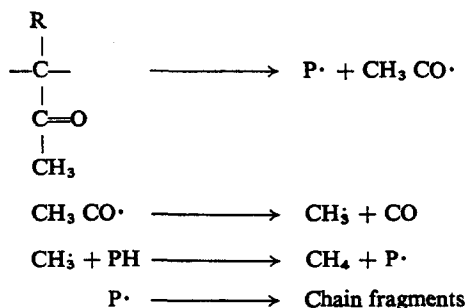
By analogy with polymers of other 1:1 disubstituted monomers, the production of monomer from PMIK is not unexpected. Indeed the TVA curves suggest that in the early stages of decomposition monomer is the major product (the 0°, —45° and —75° Pirani traces are, at this stage, coincident). Gradually, however, the —75° trace falls below the others, indicating the increasing rate of water elimination. The T_{max} for monomer production comes before that of the 0° and —45° traces, indicating that monomer production is a separate process from the cyclization of pendant groups.

Depolymerization is presumably prevented from going to completion by the formation of structures such as (B), (C) and (D) (see Introduction) which do not permit the unzipping reaction to pass through them. It is apparent from Fig. 3 that monomer production occurs to a much greater extent for PMIK (5), the lowest molecular weight sample, but the effect of initial mol. wt. has not been studied in detail.

Formation of methane and carbon monoxide

Above 350°, the production of carbon monoxide and methane from PMIK is clearly a major process, and is indicated in the TVA curves by the rise in the trace for material which is not condensed at —100°. This process is less important in PMVK.

A possible mechanism for the production of these compounds is shown on page 123: where PH and P· denote a polymer molecule and polymer radical, respectively.

$$\begin{array}{c} R \\ | \\ -C- \\ | \\ C{=}O \\ | \\ CH_3 \end{array} \qquad \longrightarrow \qquad P\cdot + CH_3CO\cdot$$

$$CH_3CO\cdot \longrightarrow CH_3^{\cdot} + CO$$

$$CH_3^{\cdot} + PH \longrightarrow CH_4 + P\cdot$$

$$P\cdot \longrightarrow \text{Chain fragments}$$

Obviously, only pendant $CH_3CO—$ groups which have not participated in a cyclization reaction can split off in this manner. If this mechanism is correct, the TVA evidence suggests that there are a greater number of such unreacted groups in PMIK than remain in PMVK, and therefore that the cyclization process goes to a smaller extent of conversion in PMIK than in PMVK.

The origin of the "cold-ring fraction"

The formation of the cold-ring fraction roughly parallels the production of non-condensable material in both polymers, suggesting that a fragmentation of the chain may follow the elimination of pendant groups, as indicated in the above reaction scheme.

TG shows that the polymeric residue resulting from water elimination is unstable in the case of both polymers, weight loss extending to approximately 95 per cent in each case. It has already been suggested that unreacted pendant groups are a possible source of this instability. However, another site of chain scission may be the bridging methylene group between "incompatible" ring formations such as (E) and (F). This process can be visualized as involving the breaking of the bond between the methylene group and the adjacent ring structure, possibly accompanied by hydrogen transfer. Scission of this bond would lead to the formation of the cold-ring fraction, without concurrent production of non-condensable material:
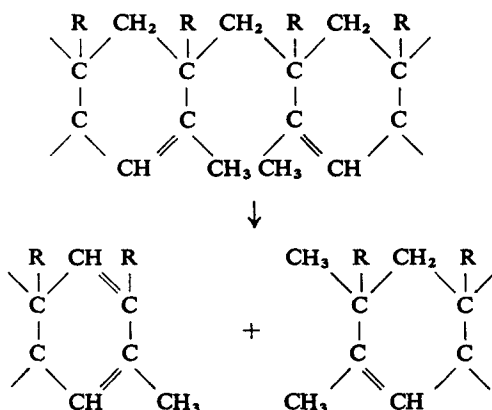
Presumably, this is the more important mode of chain scission in PMVK.

Comparison of the TG and TVA traces for PMVK reveals an interesting feature. Approximately 50 per cent of the total weight loss from PMVK samples occurs above

370°, yet above this temperature the Pirani traces suggest that volatilization is almost complete. Cold-ring fraction is being produced, however, and the formation of this product fraction registers as a weight loss in the TG curves, but does not appear as a Pirani output, owing to the cold-ring fraction being involatile at room temperature.

*Relative extents of cyclization in PMVK and PMIK*

Evidence exists to suggest that the cyclization reaction in PMIK goes to a lower conversion than in PMVK:

(a) As mentioned previously, Marvel[2] showed that the percentage of the original oxygen content eliminated as water from PMIK was less than that evolved from PMVK, under similar conditions.

(b) The greater amount of carbon monoxide and methane evolved from PMIK than from the same weight of PMVK can be interpreted as being due to the presence of a greater number of unreacted pendant groups in PMIK than in PMVK.

(c) Cooper and Catterall[16] have observed that, in the presence of base, PMIK colours (as a result of base catalysed cyclization) more slowly than PMVK.

A possible explanation of these points can be made in terms of the well established principles of conformational analysis.[17]

It has been established that cyclohexane ring systems will adopt that conformation which minimizes unfavourable steric interactions between substituents attached to the six-membered ring. In particular, where bulky substituents occupy positions 1–3 relative to one another on the ring, the conformation adopted will be such as to minimize "diaxial" interactions. Thus, in the scheme below, conformation (I) will be of higher energy than (II). The energy separation between the alternative conformations will be a function of the size of the groups X and Y.

The ring closure reactions in PMVK and PMIK probably proceed via the 2-hydroxy cyclohexanone (IV), which eliminates water, giving the cyclohexene-one, (V).[3]
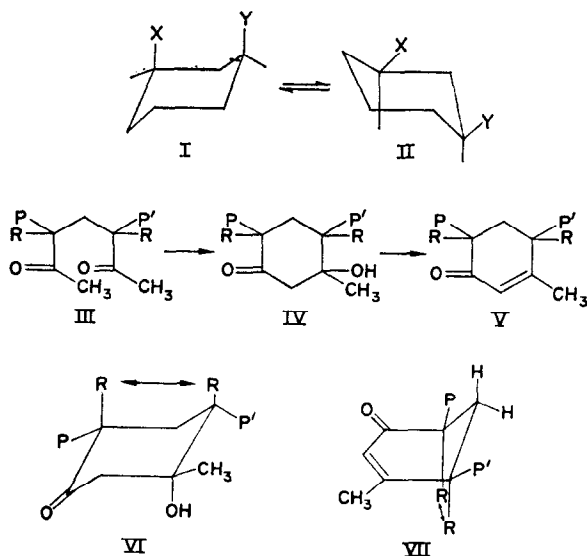
The conformation adopted by (IV) is probably (VI). P and P′, being portions of the polymer chain, are extremely bulky, and are therefore forced to adopt the equatorial-equatorial positions shown. This forces the two R groups into 1–3 diaxial positions. Clearly, where R = CH_3 (in PMIK) the interaction between the groups will be greater than for R = H (in PMVK). Thus the formation of the cyclohexanol is sterically hindered in PMIK. Similarly, there is interaction between the groups R in the cyclohexenone (V), as indicated in (VII). We would thus predict that the larger was group R, the slower would be the coloration reaction. The results of Cooper and Catterall[16] suggest that the reactivity towards base follows this prediction.

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Résumé—Les dégradations ont été étudiées par volatilisation thermique et thermogravimétrie, en analysant les produits par spectroscopie infra-rouge et ultra violette. Dans des conditions d'élévation programmée de la température, la poly(MVC) dégage d'abord de l'eau de ses groupements latéraux adjacents selon un processus statistique, en donnant comme premier produit un système cyclique. Quand on élève la température, il se produit des ruptures de chaînes, ce qui peut éventuellement conduire à une perte totale de poids atteignant 95 pour cent. Ce processus de rupture semble provenir de la rupture de liaisons entre des structures cycliques adjacentes, plutôt que de la destruction des cycles eux-mêmes; il est accompagné par la production de petites quantités de méthane et d'oxyde de carbone. Le résidu qui reste au-dessus de 500° est stable jusqu'à des températures supérieures à 800°: il s'agit vraisemblablement d'une forme de carbone.

La décomposition thermique de la poly(MIC) est globalement semblable dans les mêmes conditions, bien que quelques différences de comportement apparaissent également. Il y a formation du monomère à partir de la poly(MIC) en même temps que débute la réaction de coloration. Le rendement en monomère ne peut pas atteindre 100 pour cent à cause du processus de cyclisation, puisque la formation de cycles à six atomes, réduit considérablement la longueur de la chaîne cinétique de dépolymérisation. Les grandes quantités de méthane et d'oxyde de carbone produites dans les derniers stades de la décomposition de la poly(MIC) peuvent être considérées comme une indication de ce que la cyclisation est moins efficace dans ce polymère que dans la poly(MVC). Ce résultat est interprété par un effet stérique.

Sommario—Si è studiata la degradazione di tali polimeri a mezzo di analisi a volatilizzazione termica e termogravimetrica, con investigazione dei prodotti mediante analisi spettroscopica ultravioletto. In condizioni di riscaldamento programmato, dal PMVK fuoriesce dapprima acqua proveniente da gruppi laterali, con processo irregolare, e si ha un sistema anulare fuso come prodotto di prima formazione. Man mano che la temperatura cresce, si verificano scissioni di catena, che conducono infine ad una perdita totale di peso maggiore del 90%. Sembra che tale scissioni interessi legami tra

strutture anulari adiacenti, piuttosto che essere una rottura degli anelli stessi. La scissione è accompagnata dalla produzione di piccoli quantitativi di metano e ossido di carbonio. Il residuo che resta ad oltre 500° è stabile a temperature maggiori di 800° ed è probabilmente una forma di carbonio.

Nelle medesime condizioni, la decomposizione termica del PMIK è simile in prima analisi, sebbene siano evidenti alcune differenze di comportamento. Con il PMIK si ha la produzione di monomeri, che avviene contemporaneamente ai primi stadi della reazione di colorazione. La resa di monomero non arriva al 100% per via della ciclizzazione, dato che la formazione degli anelli a sei membri riduce fortemente la lunghezza cinetica di catena di depolimerizzazione. La grande quantità di metano e ossido di carbonio che si sviluppa negli stadi finali della decomposizione del PMIK è indice che la ciclizzazione in questo polimero è meno efficiente che nel PMVK. Si è formulata un'interpretazione sterica di questo fatto.

Zusammenfassung—Die Untersuchung des Abbaus wurde verfolgt durch thermische Verdampfungsanalyse und Thermogravimetrie, mit Infrarot- und Ultraviolett-spektroskopischen Bestimmungen der Produkte. Unter Temperatur-programmierten Erhitzungsbedingungen spaltet PMVK in einem statistischen Prozess zunächst aus den benachbarten Seitengruppen Wasser ab, so daß sich als erstes Reaktionsprodukt ein geschlossenes Ringsystem bildet. Mit Erhöhung der Temperatur tritt Kettenspaltung ein, was schließlich zu einem gesamten Gewichtsverlust bis zu 95 Prozent führt. Dieser Prozess scheint auf die Spaltung von Bindungen zwischen benachbarten Ringstrukturen zurückzuführen zu sein und nicht auf einen Abbau der Ringe selbst; gleichzeitig entstehen geringe Mengen von Methan und Kohlenmonoxid. Der über 500° verbleibende Rückstand ist stabil gegenüber Temperaturen über 800° und ist vermutlich eine Form von Kohlenstoff.

Die thermische Zersetzung von PMIK unter denselben Bedingungen ist in mancher Beziehung ähnlich, obwohl einige Unterschiede im Verhalten auffallen. Bei PMIK findet eine Bildung von Monomerem statt, die gleichzeitig mit den ersten Stufen der Verfärbungstreaktion fortschreitet. Die Ausbeute an Monomerem führt durch den Cyclisierungsprozess nicht bis zu 100 Prozent, da die Bildung der sechsgliedrigen Ringe die kinetische Kettenlänge für den Abbau zu stark reduziert. Die große Menge von Methan und Kohlenstoffmonoxid, die im späteren Verlauf der Zersetzung von PMIK freigesetzt wird, kann als Hinweis dafür genommen werden, daß bei diesem Polymeren die Cyclisierung weniger ausgeprägt ist als bei PMVK. Für diese Tatsache wird eine sterische Erklärung vorgeschlagen.